Simultaneous Production of Methanol and Dimethylether from Synthesis Gas

DOCTORAL THESIS

Submitted to the Department of Chemical Engineering of the University of Patras

by

Siranush Akarmazyan

In Partial Fulfilment of the Requirements
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DEDICATED

To my Mother
ΤΑΥΤΟΧΡΟΝΗ ΠΑΡΑΓΩΓΗ ΜΕΘΑΝΟΛΗΣ ΚΑΙ ΔΙΜΕΘΥΛΑΙΘΕΡΑ ΑΠΟ ΑΕΡΙΟ ΣΥΝΘΕΣΗΣ

ΥΠΟ

της SIRANUSH AKARMAZIAN

Τμήμα Χημικών Μηχανικών
Πολυτεχνική Σχολή, Πανεπιστήμιο Πατρών

ΕΞΕΤΑΣΤΙΚΗ ΕΠΙΤΡΟΠΗ

Δ. ΚΟΝΤΑΡΙΔΗΣ, Αναπληρωτής Καθηγητής
Τμ. Χημικών Μηχανικών, Πανεπιστήμιο Πατρών
Πρόεδρος της εξεταστικής επιτροπής

Σ. ΒΕΡΥΚΙΟΣ, Καθηγητής
Τμ. Χημικών Μηχανικών, Πανεπιστήμιο Πατρών

Χ. ΠΑΠΑΔΟΠΟΥΛΟΥ, Επικουρός Καθηγήτρια
Τμ. Χημείας, Πανεπιστήμιο Πατρών

Σ. ΜΠΟΓΟΣΙΑΝ, Καθηγητής
Τμ. Χημικών Μηχανικών, Πανεπιστήμιο Πατρών

Σ. ΜΠΕΜΠΕΛΗΣ, Αναπληρωτής Καθηγητής
Τμ. Χημικών Μηχανικών, Πανεπιστήμιο Πατρών

Χ. ΚΟΡΔΟΥΛΗΣ, Καθηγητής
Τμ. Χημείας, Πανεπιστήμιο Πατρών

Κ. ΤΡΙΑΝΤΑΦΥΛΛΙΔΗΣ, Αναπληρωτής Καθηγητής
Τμ. Χημείας, Αριστοτέλειο Πανεπιστήμιο Θεσσαλονίκης
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SIRANUSH AKARMAZYAN

EXAMINATION COMMITTEE

D. KONDARIDES, Associate Professor
Dep. Chemical Engineering, University of Patras
President of the examination committee

X. VERYKIOS, Professor
Dep. Chemical Engineering, University of Patras

Ch. PAPADOPoulos, Assistant Professor
Dep. Chemistry University of Patras

S. BOGOSIAN, Professor
Dep. Chemical Engineering, University of Patras

S. BEBELIS, Associate Professor
Dep. Chemical Engineering, University of Patras

Ch. KORDULIS, Professor
Dep. Chemistry, University of Patras

K. TRIANTAFYLLIDIS, Associate Professor
Dep. Chemistry, Aristotle University of Thessaloniki
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ABSTRACT

Dimethylether is a non-toxic liquefied gas, which is projected to become one of the fundamental chemical feedstock in the future. Dimethylether can be produced from syngas via a two-step (indirect) process that involves synthesis of methanol by hydrogenation of CO/CO$_2$ over a copper based catalyst and subsequent dehydration of methanol to DME over an acidic catalyst. Alternatively, DME can be produced in an one-step (direct) process using a hybrid (bifunctional) catalyst system that permits both methanol synthesis and dehydration in a single process unit. In the present research work the production of DME has been studied by applying both the indirect and direct processes. Firstly, the methanol synthesis and methanol dehydration reactions involved in the indirect process have been studied separately. Afterwards, these two reactions have been combined in the direct DME production process by using a hybrid catalyst comprising a methanol synthesis and a methanol dehydration component.

The methanol synthesis by CO$_2$ hydrogenation has been investigated over commercial and home-made CuO/ZnO/Al$_2$O$_3$ catalysts with the aim to identify optimal experimental conditions (CO$_2$:H$_2$ ratio, flow rate, temperature) that could be then used in the direct conversion of CO$_2$/H$_2$ mixtures into methanol/DME. Obtained results reveal that the conversion of CO$_2$ and the yields of reaction products (CH$_3$OH and CO) increase when the concentration of H$_2$ in the feed and the reaction contact time are increased. It was found that both Cu$^+$/Cu$^0$ species are important for the conversion of CO$_2$/H$_2$, although the presence of Cu$^0$ seems to be more important for selectivity/yield of methanol. The stability of the CuO/ZnO/Al$_2$O$_3$ catalyst has been also investigated. It was observed that the main reason for the deactivation of catalyst is the water produced via the methanol synthesis and reverse water gas shift reactions. However, the catalytic activity and products selectivity were recovered slowly to their original levels after applying a regeneration procedure, indicating that deactivation by water is reversible.

The dehydration of methanol to dimethylether (DME) has been investigated over a range of catalysts including alumina, silica-alumina and zeolites with different physicochemical characteristics. The effects of temperature and the presence of water vapour in the feed on catalytic performance have been studied in detail. The reactivity of catalysts has been evaluated by determining the reaction rates per gram of catalyst per acid site (total: Brönsted+Lewis) and per Brönsted/Lewis mole ratio. In addition, the reaction mechanism has been
investigated over a selected catalyst, with the use of transient-MS and in situ DRIFTS techniques.

Results obtained for alumina catalysts show that the catalytic activity and selectivity are determined to a large extent by the textural properties, degree of crystallinity and total amount of acid sites of catalysts. In particular, the methanol conversion curve shifts toward lower reaction temperatures with an increase of specific surface area. However, the enhanced catalytic activity of high-SSA samples cannot be attributed solely to the higher amount of surface acid sites, implying that the reaction rate is determined to a large extent from other parameters, such as textural properties and degree of crystallinity. Results of mechanistic studies indicate that interaction of methanol with the Al₂O₃ surface results in the formation of two kinds of methoxy groups of different adsorption strength. Evidence is provided that DME evolution is associated with methoxy species that are weakly adsorbed on the Al₂O₃ surface, whereas more strongly held species decompose to yield surface formate and, eventually, CH₄ and CO in the gas phase.

Results obtained over zeolite catalysts show that catalytic performance depends on the topology of zeolites due to differences in micropore structure and Si/Al ratio as well as on the number, strength and nature of active acid sites. The activity of zeolite catalysts for the methanol dehydration to DME follows the order ZSM-5 > Ferrierite > Mordenite ~ Beta ~ USY > H-Y. The strong Brönsted acid sites of ZSM-5 zeolites with relatively high Si/Al ratio represent the most active sites in methanol dehydration to DME reaction. However, the overall reactivity of the ZSM-5 zeolites is also affected by the balance of the Brönsted to Lewis acid sites. The activity of Beta and USY zeolites is determined by both Lewis and Brönsted acid sites. The moderate/low reactivity of Ferrierite, Mordenite and H-Y zeolite are determined by the abundant Brönsted acid sites of relatively weak/moderate strength.

The direct CO₂ hydrogenation to methanol/DME has been investigated using admixed catalysts comprising a methanol synthesis (commercial copper based catalyst: CZA1) and a methanol dehydration component (different alumina/zeolite catalysts: γ-Al₂O₃, ZSM-5, W/γ-Al₂O₃, USY(6), Ferrierite(10)). It has been revealed that the conversion of CO₂ is always lower than the corresponding equilibrium values predicted by thermodynamics, indicating operation in the kinetic regime. The nature of the methanol dehydration component of the admixed catalysts was found to be important for both CO₂ conversion and methanol dehydration. In particular, DME selectivity/yield, depends strongly on the nature of acid sites (both Lewis and
Brønsted) as well as the textural (meso/macro porosity) and topological properties of methanol dehydration component of the admixed catalysts. The yield of DME obtained at a temperature of 250°C decreases following the order CZA1/ZSM-5, CZA1/USY(6) > CZA1/Ferrierite(10) > CZA1/W/γ-Al₂O₃ >> CZA1/γ-Al₂O₃. The long-term stability experiments conducted over selected bifunctional catalytic systems revealed that the catalysts deactivate with time-on-stream, mainly due to water produced via methanol synthesis, methanol dehydration and reverse water gas shift reactions. In case of the CZA1/ZSM-5 admixed catalyst the catalytic activity and products selectivity were almost recovered after regeneration indicating that deactivation by water is reversible.
Curriculum Vitae

Name/Surname: Siranush Akarmazyan
Address: Solonos 25 Rio-Patras, Greece,
Email: akarmazyan@chemeng.upatras.gr,
Date of Birth: 16.03.1985

EDUCATION

2001-2006 Chemical Engineer of Chemical Technology of Organic Materials at the State Engineering University of Armenia (Polytechnic) in the Department of Chemical Technologies and Environmental Engineering, with honors degree.


2009-2013 PhD candidate at the Laboratory of Heterogeneous Catalysis of the Department of Chemical Engineering, University of Patras, Greece.

2013-2014 Part work of PhD has been carried out in the Chemistry Department of the same university. The subject of the thesis is “Simultaneous production of methanol/dimethyl ether from synthesis gas, (Supervisor Associate Professor D. Kondarides).

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CONFERENCES


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1.1 Introduction

The energy generation, distribution, and consumption must be closely balanced for an ideal energy infrastructure. However, the world energy consumption is steadily increasing for a variety of reasons, which include enhancement in quality of life, population increase, industrialization, rapid economic growth of developing countries, increased transportation of people and goods, etc. There are many types of fuel available worldwide, the demand for which strongly depends on application and use, location and regional resources, cost, purity and environmental impact factors, global and regional policies, etc. [1]

The use of fossil fuels such as coal, oil or natural gas (i.e., hydrocarbons) is essential for modern life. However, when fossil fuels are burnt they produce carbon dioxide (CO$_2$) and water (H$_2$O) as combustion products. It is a great challenge to reverse this process and produce hydrocarbon fuels from CO$_2$. Nature, in its process of photosynthesis, recycles CO$_2$ and water into new plant life using the Sun’s energy. Fermentation and other processes can convert plant life into biofuels and other products. However, natural formation of new fossil fuels takes a very long time, making them non-renewable on the human timescale [2].

As we continue to burn hydrocarbon reserves (oil, natural gas, coal) and generate energy at an alarming rate, diminishing resources and sharp increase of prices will inevitably lead to supplement or replacement of fossil fuels by feasible alternatives [1, 2]. Thus, it is crucial for mankind of our time to elaborate new efficient approaches to liberate itself from its dependency on fossil fuel resources, to develop alternative fuel sources and, concomitantly, to mitigate global warming caused by the emissions of carbon dioxide.

Alternative eco-friendly fuels (synthetic natural gas, alcohols, esters, ethers, hydrogen, Fischer-Tropsch fuels, biofuels) have attracted significant attention in
recent years due to their good properties such as being renewable, sustainable and environmentally friendly. However, each selected fuel candidate must be evaluated according to their different economic, technological, environmental and versatility aspects. Among these, dimethyl ether (DME) is considered as a promising eco-friendly fuel and is projected to become one of the fundamental chemical feedstock in the 21st century.

1.2 DME: Properties

In 1995, extensive collaborative research efforts among Amoco, Haldor Topsoe and Navistar International Corp showed that DME could be a novel, low-emissions alternative fuel for diesel engines and could be manufactured at large-scale from methanol with a simple dehydration technology [3]. DME, with a chemical formula CH$_3$-O-CH$_3$ (Fig. 1.1), is the simplest of all ethers. It is a colorless, non-toxic, non-corrosive, non-carcinogenic and environmentally friendly chemical which is mainly used as an aerosol propellant in various spray cans, replacing banned CFC gases. The degradation of DME in the atmosphere takes place very easily and it shows a low tropospheric ozone-forming potential.

As a secondary fuel, DME can be derived from a variety of feedstocks such as natural gas, crude oil, propane, residual oil, coal and bio-mass waste products. Since DME’s properties are very similar to those of liquefied petroleum gas (LPG), the LPG infrastructure can be easily applied for DME. Under standard atmospheric conditions, DME is in gaseous phase and condenses to liquid phase above 0.5 MPa pressure. The flammability range of DME is 3.4 to 27% by volume in air [4]. Unlike methanol, it is non-toxic (or its toxicity is extremely low) which explains its use as a propellant. It burns with a visible blue flame like natural gas, and does not cause any greenhouse effect.

1.3 DME: Perspectives

1.3.1 DME as an alternative transportation fuel

DME fuel differs significantly from other fuels because of its unique physical and combustion and emission characteristics. The most important physical and chemical properties of DME are summarized in Table 1.1, in comparison with other
fuels. A detailed presentation of DME properties is given below, together with an evaluation of its advantages and disadvantages as an alternative transportation fuel.

**Table 1.1:** Properties of DME and other fuels.

<table>
<thead>
<tr>
<th>Property</th>
<th>Methane CH₄</th>
<th>DME CH₃OCH₃</th>
<th>MeOH CH₃OH</th>
<th>EtOH C₂H₅OH</th>
<th>Diesel -</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar weight (g mol⁻¹)</td>
<td>16.04</td>
<td>46.07</td>
<td>32.04</td>
<td>46.07</td>
<td>198.4</td>
<td>[5]</td>
</tr>
<tr>
<td>Carbon content (wt. %)</td>
<td>73.3</td>
<td>52.2</td>
<td>37.5</td>
<td>52.2</td>
<td>87</td>
<td>[5]</td>
</tr>
<tr>
<td>Hydrogen content (wt. %)</td>
<td>23.9</td>
<td>13.0</td>
<td>12.5</td>
<td>13.0</td>
<td>13</td>
<td>[6]</td>
</tr>
<tr>
<td>Oxygen content (wt. %)</td>
<td>0</td>
<td>34.8</td>
<td>50</td>
<td>34.8</td>
<td>0</td>
<td>[6]</td>
</tr>
<tr>
<td>Sulfur content (ppm)</td>
<td>7-25</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>~250</td>
<td>[5]</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-162</td>
<td>-24.9</td>
<td>64</td>
<td>78</td>
<td>125-400</td>
<td>[5]</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.00072</td>
<td>0.661</td>
<td>0.792</td>
<td>0.785</td>
<td>0.856</td>
<td>[5]</td>
</tr>
<tr>
<td>Air/fuel ratio</td>
<td>17.2</td>
<td>9.0</td>
<td>6.5</td>
<td>9.0</td>
<td>14.7</td>
<td>[6]</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>540-560</td>
<td>235</td>
<td>350</td>
<td>420</td>
<td>250</td>
<td>[7, 8]</td>
</tr>
<tr>
<td>Heat of vaporization (kJ/kg)</td>
<td>509</td>
<td>460</td>
<td>1103</td>
<td>900</td>
<td>600</td>
<td>[6, 8]</td>
</tr>
<tr>
<td>Cetane number</td>
<td>-</td>
<td>&gt;55</td>
<td>5</td>
<td>&lt;15</td>
<td>40-55</td>
<td>[6]</td>
</tr>
<tr>
<td>Octane number</td>
<td>120</td>
<td>-</td>
<td>108</td>
<td>111</td>
<td>-</td>
<td>[8]</td>
</tr>
<tr>
<td>Heating value (MJ/kg)</td>
<td>49</td>
<td>28.8</td>
<td>21.3</td>
<td>26.8</td>
<td>42.5</td>
<td>[6, 9]</td>
</tr>
</tbody>
</table>

*Cetane number:* This number indicates the ignition quality of a fuel, and it is a measure of the ignition delay between the starts of injection and combustion of the fuel. It can be determined by engine tests using two hydrocarbon reference fuel blends of known cetane number. Generally, a higher cetane number results in easier ignition, more complete combustion and cleaner exhaust. High cetane number provides performance benefits related to improved cold starting, reduced smoke emission during warm-up, reduced noise, reduced fuel consumption and exhaust emission [10]. In contrast, a fuel with low cetane number increases the ignition delay and the auto-ignition temperature, it produces higher emissions and results in higher consumption. In Table 1.1 are presented the cetane numbers for
natural gas, alcohols (methanol, ethanol), diesel fuels and DME. Among these, natural gas and alcohols possess very low cetane numbers (and high octane numbers) and therefore are not suitable for compression-ignition (CI) engines. The cetane number of DME is even higher than that of diesel fuel, owing to the fact that the C-O bond breaking energy is lower than that of C-C and C-H bond that are present in conventional fuels [11]. This feature of DME provides mild engine operations with much lower noise and reduced pollutant levels [11-14].

Latent heat of Vaporization: Generally, latent heat of vaporization is a measure of the heat amount which is needed for the evaporation of a liquid. In the case of fuels, the higher the heat of vaporization the larger the amount of heat required for vaporization, which results in smaller amount of heat remaining for combustion process. The latent heat of vaporization of alcohols (particularly methanol) is much higher than that of DME and, therefore, it results in reduction of the heat amount, which is necessary for increasing of the gas temperature. Apart from this, it causes slower evaporation, poor fuel-air mixing, poor cold starting and warm-up performance [10, 15]. It is generally known that nitrogen oxides production significantly depends on temperature. The latent heat of DME is higher than that of diesel fuel (Table 1.1) which is beneficial for reducing the air-fuel mixture temperature before initiation of combustion and, thus, the NOx emissions are found to be lower for DME fuel compared to diesel [11, 14].

Volutility: An important feature of a fuel is its boiling point. Generally, fuels with low boiling point can be evaporated faster, resulting in easier cold starting and thus much better combustion. The volatility influences many other properties, including density, flash point, auto-ignition temperature, viscosity and cetane number. High volatility could cause vapor lock and lowering of the flash point [10]. Regarding DME, it evaporates rapidly due to its low boiling point (-25 °C) which allows relatively low fuel injection pressures of <300 bar, compared to 2000 bar for modern diesel engines [16]. In addition, it has a beneficial influence when a liquid-phase DME spray is injected into the diesel engine cylinder, resulting in immediate evaporation [3, 8].

Oxygen content: Oxygen content of a fuel has a strong influence on its combustion properties. Many research groups focus their studies on the addition of different oxygenated compounds to diesel [15, 17] and gasoline fuels [18, 19], aiming to improve the combustion process. An improved combustion can help to reduce the pollutant emissions (CO, NOx, unburned hydrocarbons (HC) and soot) without major modifications of the engine design. DME is an oxygenated compound
(about 34.8% of oxygen) and does not have any carbon-carbon (C-C) bonds. These two factors play an important role when DME is used in combustion processes. It is well known that the C-O bond energy is lower than that of the C-H bond which means that the C-O bond splits easier than the C-H bond. This characteristic lowers DME auto-ignition compared to conventional fuels. In DME combustion process, the presence of intra-molecular oxygen provides soot oxidation whereas the absence of C-C bond leads in the reduction of particulate matter (PM) emission [7, 11].

Similar to alcohols, DME has a comparably lower heating value and lower combustion enthalpy (energy content) owing to the oxygen content. As a result, a higher amount of fuel is needed in order to produce the same amount of energy. For DME, about 48% more mass of fuel should be injected in order to deliver the same amount of energy that is provided by diesel fuel [20, 21]. In the engine injection equipment, lubricity is an important quality characteristic in the boundary lubrication regime. When it has a low value, it reduces the injection pump durability due to extensive wear. Viscosity is a dominant property in the hydrodynamic regime, which diminishes hydrodynamic or elastohydrodynamic film formation capacity and, when it is low, it may cause leakage [22]. The currently available fuel-injection systems have reduced lifetime and therefore must be modified when the engine is fuelled with DME. This is because DME (like alcohols) possesses poor viscosity (thus poor tension) and lubricity. Furthermore, DME has the ability to dissolve organic compounds and, therefore, it is not compatible with elastomers and plastic materials. In order to prevent the detrimental effect on the engine life, additives for enhancing the lubricity must be implied and a careful selection of sealing materials (based on high-tension components) is required [7, 11, 22]. Another disadvantage of DME is its low bulk modulus, which affects the compressibility properties of DME possessing four or six times higher values than that of diesel [7, 11].

1.3.2 DME as a fuel for gas turbines

The gas turbine is a continuous-flow engine which develops steady flame during combustion and allows the use of various fuels [23, 24]. Although natural gas is the main fuel that is used in gas turbines for power generation, a number of studies have dealt with the use of DME for thermal power generation [9, 25]. The results obtained show that DME can be a clean and efficient fuel for this purpose provided that appropriate modifications of the combustor, fuel nozzle and burner are made [23, 26].
1.3.3 DME as a fuel for indoor uses

Serious adverse consequences for health and environment can be caused by the combustion of solid fuels (biomass and coal) in household cooking, especially when energy conversion technologies are not clean and/or unproductive. Inefficient biomass combustion creates high amounts of indoor health-damaging air pollutants such as carbon monoxide, nitrogen oxides, volatile organic carbons, black carbon, polycyclic aromatic hydrocarbons, and other health damaging gases. According to the World Health Organization “Fuel for Life” publication, this “kitchen killer” turn out to be responsible for 1.6 million deaths and 2.7% of the global burden of disease [27]. Generally, it is known that cooking with liquid or gas fuels is much cleaner and more energy-efficient than with solid fuels. The liquefied petroleum gas (LPG) consisting of propane and butanes, stored either separately or together, is a widely used fuel for domestic purposes due to its superior combustion characteristics. However, the production of LPG is strongly correlated to the production of oil and gas, which means that the price of LPG follows the price of oil and natural gas [28]. LPG is considered as an expensive energy source for poor households and, due to market growth, a further increase of the LPG price is expected in the future.

The physical characteristics (e.g., boiling point and vapour pressure) of DME are very similar to those of LPG, so it can be stored and handled in a similar manner [3, 29-31]. Thus, DME can be used as substitute/alternative of LPG for domestic cooking and heating without modifying equipment.

It may be noted that, in China, DME started to be used as a substitute for LPG in 2003. Most of the DME currently produced in China is indeed used as a mixture with LPG (nearly 90% in 2007), mainly for heating and cooking purposes [2, 32]. Marchionna et al. [33] confirmed that the use of 15-20 vol. % of DME in LPG/DME blends would not require any modification of existing distribution and users’ appliances.

1.3.4 DME as an alternative aerosol propellant

Chlorofluorocarbons (CFCs) are incombustible, chemically stable, and easily liquefied substances invented in 1928. These compounds have been recognized as ideal gases to be used as aerosols, refrigerants, cleaning, drying, blowing agents, etc. In 1974 M. Molina and F. Rowland described in their publication the harmful effects of CFCs to the stratospheric ozone layer. They found that these chemically inert compounds may remain in the atmosphere for a very long time and by
reaching to upper stratosphere may produce a vast amount of free chlorine atoms. These free chlorine atoms react with ozone molecules and lead to the destruction of stratospheric ozone [34, 35]. The first global environmental treaty, known as the Montral Protocol, was signed on September 1987 to set policies that would eliminate the production and consumption of CFCs [36].

It has been reported that DME as well as other low-molecular-weight hydrocarbons, such as butane and propane, can be used as a green aerosol propellant in the cosmetics industry (aerosol-based products like hair spray, shaving cream, personal care mousse, antiperspirants, and air freshers) and can effectively replace chloro-fluoro-carbons (CFC) because of its environmentally benign properties [37].

1.3.5 DME as a hydrogen source and carrier

Hydrogen is a very clean and carbon-free energy carrier which has attracted significant attention in recent years, mainly due to its potential use in fuel cell applications. At present, most of the world’s hydrogen is produced from natural gas (~97 % CH₄). The primary ways in which methane is converted to hydrogen involve reaction with either steam (steam reforming), oxygen (partial oxidation), or both in sequence (autothermal reforming) [38]. Steam reforming of fuels has attracted much attention as an efficient technology for hydrogen production because it provides a higher reformate quality (e.g. higher hydrogen production yield, lower rate of side reactions and by-products) in comparison to partial oxidation or autothermal reforming processes [39, 40]. To achieve the benefits of the hydrogen economy, it is necessary to produce hydrogen from non-fossil resources, such as water and biomass-derived methanol or ethanol [38]. Recently, many researchers have directed their attention to hydrogen production from methanol/ethanol [41]. Methanol is one of the promising candidate-sources of hydrogen due to its high volumetric energy density, easy storage and transportation [42, 43]. However, the infrastructure of methanol is not well developed and the toxicity of methanol is high [44]. In this respect, an increasing interest has been observed towards DME as an efficient, suitable hydrogen source in past several years [45-50]. The relatively low reforming temperature of DME (200–350 °C), its large hydrogen content, and its non-corrosive and non-toxic nature play a crucial role for this purpose [51, 52].

1.3.6 Direct DME Fuel cells (DDMEFCs)

Fuel cells are considered to be the most promising energy conversion devices,
which directly convert chemical energy into electricity, with very high efficiency (>40%). Advantages of FCs include the fact that their efficiency is independent of the Carnot cycle for thermal machines and that they can be designed for both mobile and stationary applications. These devices produce only water as byproduct when hydrogen is used as fuel, without undesired residual emissions and, consequently, has no impact on the greenhouse effect [38]. During the past decades, hydrogen was the most commonly applied fuel for fuel cells because of its high electrochemical oxidation rate over fuel cell anode with zero emission. On the other hand, many chemical fuels such as hydrocarbons and oxygenated-hydrocarbons are believed to be more practical fuels for fuel cells than hydrogen for the near future application [53]. Direct methanol fuel cells, direct ethanol fuel cells and proton exchange membrane fuel cells are widely studied in this field [54, 55]. DME is also considered as a promising fuel for the direct type fuel cell (DDFC) owing to its advantages for this application. Contrary to methanol and ethanol, DME decreases the crossover effect, owing to its low dipolar moment (1.3D) [56]. Since 1 mole of DME can produce 12 electrons by complete oxidation while 1 mol methanol can produce 6 electrons, the fuel cells that operate with DME can result in more efficient fuel management [57]. Conversely to ethanol, DME does not have C-C bonds, which allows the oxidation process to proceed completely. Unlike methanol, DME has low toxicity and relatively low flammability and explosive limit [56, 58].

1.3.7 DME as a chemical intermediate

DME can serve as an important chemical intermediate for the production of chemicals such as dimethoxymethane (DMM), methyl acetate (MA), formaldehyde, dimethyl sulphate and ethanol. Below are summarized the most known processes where DME is used as a chemical intermediate.

Production of dimethoxymethane: At present there are several DMM synthesis routes, including direct oxidation of DME. Several research groups have been working on this subject under different reaction conditions by applying various catalysts. It has reported by Liu et al. [59] that there is 56.8% DMM selectivity in oxidation reaction of DME when H₅PV₂Mo₁₀O₄₀ is used as a catalyst. Qingde et al. [60] studied the reaction over MnCl₂⁻, SnCl₄⁻, CuCl₂⁻ modified H₄SiW₁₂O₄₀/SiO₂ catalysts in a continuous flow fixed-bed reactor. They concluded that modification with MnCl₂ promotes the activity of the catalyst and increases the DMM selectivity.

Production of methyl acetate: Today, more than 50% of industrially manufactured acetic acid is produced from methanol carbonylation reaction over a
rhodium/iodide homogeneous system, which was discovered in 1966 by Monsanto [61-63]. Considerable attempts have been made to develop a heterogeneous system for the methanol or ether carbonylation process [64]. It has been shown that the carbonylation of DME with carbon monoxide exhibits unpredictable activity and selectivity over H-MOR zeolite [63, 65, 66].

**Production of formaldehyde:** DME can be used to synthesize formaldehyde (HCHO), which is an important intermediate for the synthesis of other chemicals. Iglesia and co-workers [67] investigated the synthesis of formaldehyde from DME oxidation on MoOx and VOx domains supported on SnO2, CeO2 or Fe2O3. Results of their exploratory studies showed that MoOx/Al2O3 is a highly selective catalyst and that an increase of HCHO selectivity is achieved by increasing MoOx loading on Al2O3.

**Production of ethanol:** Traditionally, ethanol is produced from fermentation of corn or food based feedstock. Considering the growing concerns about worldwide food shortage, it is strongly required to develop a novel and environmentally friendly ethanol synthesis method. In this respect, a new route for the synthesis of ethanol from DME and syngas has been proposed using an indirect route that does not involve any agricultural feedstock [68]. In this process, DME and CO are first converted to methyl acetate over a zeolite catalyst, which is then hydrogenated to methanol and ethanol. The process has the additional advantage of recycling the formed methanol to DME and water.

1.4 DME: Demand, manufacturing plants and production costs

The global DME demand is expected to rise to over 7 million metric tons/year by 2015 while the global capacity ranges between 10 and 12 million metric tons/year. China is the main country where nearly all of the commercial DME plants have been built for fuel applications. During 2011, there were 60 DME producers in 18 provinces, of which 17 have capacities of at least 200,000 metric tons per year [3]. DME commercialization and projects’ development activity are taking place also in Iran, Egypt, Russian, South Korea, Sweden, Brazil, Taiwan, Turkey and Trinidad. There are plans for significant DME capacity additions in Uzbekistan 100,000 tons/year for 2013 and 800,000 tons /year in Indonesia. Other projects are planned in Egypt (200,000 tons /year) and India (265,000 tons /year). In China another 600,000 tons /year is under construction and a further 20m tons /year is planned by 2020 [69].

DME cost estimation is difficult to determine, because it strongly depends on
the plant capacity and the raw material and transportation costs. NKK Corporation in Japan has estimated the price of DME production from natural gas. At a natural gas price of $1.50US/MMBTU with a transportation distance of 6000km the estimated DME price was $6.0US/MMBTU for a DME plant capacity 2500 tons/day.

1.5 DME: Environment and safety issues

Global warming and climate change refer to an increase in average global temperature and in today’s scenario it is threat to the survival of mankind. Natural events and human activities are believed to be contributing to an increase in average global temperature, caused primarily by the increase of the concentration of the “greenhouse” gases in the atmosphere [70]. Several of the major greenhouse gases occur naturally but increases in their atmospheric concentrations over the last 250 years are largely due to human activities. Long-lived greenhouse gases for example, CO₂, methane (CH₄) and nitrous oxide (N₂O), are chemically stable and persist in the atmosphere over time scales of a decade to centuries or longer, so that their emission has a long-term influence on climate. Because these gases are long lived, they become well mixed throughout the atmosphere much faster than they are removed and their global concentrations can be accurately estimated from data at few locations [71].

In order to measure the warming effects on the troposphere generated from the emission of different gases, it has been proposed to use the Global Warming Potential (GWP) evaluation index. The GWP is used to measure the greenhouse gas effect of a gas based on its radiative properties relative to CO₂ over a given time frame. A gas with a higher GWP indicates that it has more impact on the environment [72]. In Table 1.2 are listed the global warming potentials of some greenhouse gases in comparison with that of DME. The calculated GWP index data for DME shows that it is friendly compound for the atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>GWP index</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20 years</td>
<td>100 years</td>
<td>500 years</td>
<td>Ref.</td>
</tr>
<tr>
<td>DME</td>
<td>1.2</td>
<td>0.3</td>
<td>0.1</td>
<td>[73]</td>
</tr>
<tr>
<td>CO₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>[74]</td>
</tr>
<tr>
<td>CH₄</td>
<td>62</td>
<td>21</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>275</td>
<td>310</td>
<td>156</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.2: Global warming potentials of DME, CO₂, CH₄ and N₂O.
Unlike conventional diesel fuel, DME is a gas at ambient temperature. Thus, the widespread use of DME may require additional investment in infrastructure associated with fuel distribution and delivery. In addition, DME is an ether and therefore can react with molecular oxygen at ambient temperatures to form hydroperoxides. Thus, it is possible that prolonged exposure in air may induce autoxidation of DME to produce explosive organic peroxides during transportation and storage [75]. Naito et al. [75] have studied the oxygen/DME reactivity and the autoxidation rate and assess of DME safety by means of ARC and oven storage tests. They concluded that under oxygen-rich conditions there is a capability for DME autoxidation, but the rate is lower than that of diisopropyl ether (DIPE) and diethyl ether (DEE).

1.6 DME production

Traditionally, dimethyl ether is produced in a two-step process from synthesis gas (CO/H\textsubscript{2}/CO\textsubscript{2}) originating from natural gas, coal or biomass. The process involves synthesis of methanol by hydrogenation of CO/CO\textsubscript{2} over a copper based catalyst [76-79] and subsequent dehydration of methanol to DME over an acidic catalyst [80, 81].

The reactions of methanol formation via hydrogenation of CO (reaction 1.1) or CO\textsubscript{2} (reaction 1.2) are exothermic and they both result in a stoichiometric decrease of the total number of molecules on their right side. Therefore, reactions (1.1 and 1.2) are thermodynamically limited and are favoured at low temperatures and high pressures.

\[
\begin{align*}
\text{CO} + 2\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} & \Delta H &= -90.4 \text{ kJ mol}^{-1} & 1.1 \\
\text{CO}_2 + 3\text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} & \Delta H &= -49.2 \text{ kJ mol}^{-1} & 1.2 \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 & \Delta H &= -41.2 \text{ kJ mol}^{-1} & 1.3 \\
2\text{CH}_3\text{OH} & \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} & \Delta H &= -24.0 \text{ kJ mol}^{-1} & 1.4
\end{align*}
\]

For many years, methanol has been produced from synthesis gas, consisting mainly of CO, H\textsubscript{2} and small amount CO\textsubscript{2}, at high pressures (150-250 bar) and at high temperatures (573-633 K). After 40 years of development, a new catalytic system introduced by ICI (Imperial Chemical Industries) has considerably mitigated the operation conditions of the reaction.

First activities for DME production were based on dehydration of methanol. For this two-step technology there are several licensors including Haldor Torspe,

11
Linde/Lurgi, Toyo Engineering, Uhde, MGC (Mitsubishi Gas Chemical Company), China Southwestern Research Institute of Chemical Industry and China Energy [3]. In 2012, the global methanol demand for use in DME production was estimated to be approximately 3.7 million tonne. The methanol dehydration reaction is a gas-phase exothermic reaction, which is not favored thermodynamically at high temperatures (detailed thermodynamic study in Chapter 2). The reaction takes place over solid acid catalysts and, therefore, several such materials have been investigated including Al$_2$O$_3$ [82-84], zeolites [85-87] and mixed metal oxides [87-89]. Among these, the most extensively studied materials are based on Al$_2$O$_3$. This is because Al$_2$O$_3$ is characterized by high surface area, excellent thermal stability, high mechanical resistance and suitable acidity for the reaction that yields good performance in terms of methanol conversion and DME selectivity, the latter being almost 100%.

Alternatively, DME can be produced from synthesis gas in a one-step (direct) process [90-93] using a hybrid (bifunctional) catalytic system that permits both methanol synthesis and dehydration in a single process unit. The catalyst used for the one-step process, should efficiently catalyze both methanol and DME synthesis reactions. Generally, it consists of two types of active sites: one that catalyzes methanol synthesis from syngas (reactions 1.1, 1.2), which is typically composed of CuO-ZnO based catalysts [94, 95], and another that promotes dehydration of methanol to DME, which is based on an acidic material.

The direct method of DME production is more economical than the indirect method because of two reasons. First, the thermodynamic limitation in indirect method is higher than in the direct method. Thermodynamic limitations imply that methanol synthesis from CO (reaction 1.1) or CO$_2$ (reaction 1.2) is favoured at low temperatures and high pressures. These constraints can be reduced by co-production of DME because the equilibrium constant of the methanol dehydration reaction is much higher than that of methanol synthesis [96]. Water formed by methanol dehydration (reaction 1.4) can be removed from the system by the water gas shift (WGS) reaction (reaction 1.3), which also results in a shift of the equilibrium composition toward the desired direction [97, 98]. Second, in the two-step process, the purification, transportation of methanol and subsequent methanol dehydration to DME in a separate unit are costly. In the one-step process these steps can be eliminated because production of methanol and DME take place simultaneously in the same reactor.
1.6.1 Methanol synthesis from CO₂/CO hydrogenation

Methanol is one of the most versatile compounds and one of the top ten chemicals produced in the chemical industry. The methanol industry spans the entire globe, with production in Asia, North and South America, Europe, Africa and the Middle East. Worldwide, over 90 methanol plants have a combined production capacity of about 100 million metric tons (almost 33 billion gallons or 90 billion liters), and each day more than 100,000 tons of methanol are used as a chemical feedstock or as a transportation fuel (60 million gallons or 225 million liters). Methanol is also a truly global commodity, and each day more than 80,000 metric tons of methanol are shipped from one continent to another [99].

![Figure 1.2: Future methanol demand](image)

The largest consumer of methanol worldwide is formaldehyde production accounting for almost 25% by 2016 and with Gasoline/Fuel applications becoming the largest demand sector, totalling 41% (Fig. 1.2). Acetic acid/anhydride and MTBE each share almost 10% of methanol market volume. Methanol to Olefins (MTO) and methanol to propylene (MTP) demand is anticipated to become a high growth sector, rising to 22% by 2016 (Fig. 1.2), the vast majority of which is forecast to take place in China. Other uses of methanol include wastewater denitrification, hydrogen carrier for fuel cells, transesterification of vegetable oils for biodiesel production and electricity generation [100].

The first large scale methanol synthesis plant was developed by BASF (“Badische Anilin und Soda Fabrik” a German company) in 1923, using ZnO/Cr₂O₃ catalyst at temperatures of 573-633 K and pressures of 150-250 bars. In 1966 ICI developed a ternary CuO/ZnO/Al₂O₃ catalyst and replaced the commercial high
pressure temperature technology with a new low pressure and low temperature process by changing the feedstock from coal to natural gas [101, 102]. Indeed, development of such a system operating under milder reaction conditions, enhances significantly the methanol production profitability. Today, this process is considered as the most commonly employed process for methanol production from synthesis gas [103].

There are three reactions that are involved in the synthesis of methanol: methanol production from carbon dioxide (Eq. 1.1), methanol production from carbon monoxide (Eq. 1.2) and the water-gas-shift reaction (WGS) (Eq. 1.3). It should be mentioned that, regardless the choice of the carbon oxide, water gas shift reaction (forward or reverse) always exists in the reaction process as the copper based catalysts are excellent catalysts also for WGS and reverse WGS reactions.

Although this technology has been developed for almost 100 years, there are still several key questions concerning to mechanism and C source which remain contradictory. Discussions are being continued also about the kinetic model of the reaction, the role of catalyst’s components, the duration of catalysts life and the effect of the WGS reaction.

A typical industrial plant for methanol synthesis operates with H₂-rich gas inlets (typical reactant gas mixture -10%CO/10%CO₂/80%H₂/ or 5%CO/5%CO₂/90%H₂) [104, 105]. Thus, it is not clear which carbon oxide is the source for methanol synthesis. The question about the actual carbon source in methanol synthesis appeared in 1962 when the activating effect of CO₂ in the synthesis gas was discovered [106]. It has been reported that the reaction is ~ 100 times slower when CO₂ is absent in feed composition. The presence of CO₂, enhances the durability and the life time of the catalyst [107].

Until the beginning of the eighties, the synthesis of methanol was assumed to occur only via hydrogenation of carbon monoxide and the kinetics expressions for the methanol synthesis reaction rate were expressed only in terms of CO and H₂ partial pressures, even in mixtures containing CO, CO₂ and H₂ [108]. Two mechanisms have been suggested to explain the formation of methanol from CO. The first one assumed that adsorbed CO reacts on active copper centers with dissociatively adsorbed hydrogen in a series of successive hydrogenation steps until MeOH is formed (Scheme 1.1 A). According to the second mechanism, CO reacts with OH to give formate species, and subsequent hydrogenation and dehydration steps result in the formation of surface methoxyl species and methanol (Scheme 1.1 B) [109].
**Scheme 1.1:** The proposed reaction path for methanol synthesis through CO hydrogenation.

Further mechanistic investigations revealed that the reaction proceeds via CO₂ conversion to a surface formate species which is then reduced to form methoxy species that is hydrogenated to methanol (**Scheme 1.2**) [109, 110].

**Scheme 1.2:** The proposed reaction path for methanol synthesis through CO₂ hydrogenation.

\[
\begin{align*}
H_2(g) + 2^* & \leftrightarrow 2H^* \\
CO_2(g) + H^* & \leftrightarrow HCOO^* \\
HCOO^* + H^* & \leftrightarrow HCOOH^* + ^* \\
HCOOH^* + H^* & \leftrightarrow H_2COOH^* + ^* \\
H_2COOH^* + ^* & \leftrightarrow H_2CO^* + OH^* \\
H_2CO^* + H^* & \leftrightarrow H_3CO^* + ^* \\
H_3CO^* + H^* & \leftrightarrow CH_3OH(g) + 2^* \\
OH^* + H^* & \leftrightarrow H_2O(g) + 2^*
\end{align*}
\]
The role of CO is to remove surface oxygen by keeping the metal surface in a highly reduced state \[107\]. Later on, a Russian group conducted isotope-labelling studies and proved that methanol is produced over copper-containing catalysts mainly from CO\(_2\) and not CO \[111\]. In the last decade, attention has been focused on the role of CO\(_2\) in the synthesis of methanol \[112\]. Today, a mechanism starting from CO\(_2\) is mostly accepted although a recent work by Yang and co-workers \[113\] revealed that the preferred carbon source for the reaction changes from CO\(_2\) to CO as the temperature is lowered.

1.6.1.1 Cu/Zn/Al\(_2\)O\(_3\) catalyst: The role of each component

Copper-zinc-alumina (Cu/Zn/Al\(_2\)O\(_3\)) remains the most commonly used industrial methanol synthesis catalyst. Copper is the main component of this catalyst, whereas zinc and alumina are used as promoters. The co-precipitation method is commonly applied for the preparation of ternary copper based catalyst \[114\]. Carbonates, hydroxycarbonates or hydroxides of alkali metals serve as precipitating agents. The process is difficult to control; it is essential to keep the solution homogeneous to allow the two components to precipitate simultaneously, and variations of pH throughout the solution should be avoided.

The role of each component of a typical copper-zinc-alumina methanol synthesis catalyst is still under debate. It has been reported by many researchers that copper is the main active catalyst component \[107, 115, 116\] although when used alone it is not an efficient catalyst \[117\]. The activity of Cu/Al\(_2\)O\(_3\), Cu/ZnO and Cu/ZnO/Al\(_2\)O\(_3\) catalysts has been examined by Kurtz \textit{et al.} \[118\]. They found that the surface area of copper metal plays an important role on methanol synthesis reaction and there is an almost linear relationship between catalytic activity and metallic copper surface area. The authors concluded that catalytic activity increases in the order of Cu/Al\(_2\)O\(_3\) < Cu/ZnO < Cu/ZnO/Al\(_2\)O\(_3\).

The higher activity of Cu/ZnO, compared to Cu/Al\(_2\)O\(_3\), suggests that there is a synergy between Cu-Zn oxides. A possible explanation for this synergy has been proposed by Burch \textit{et al.} \[119\] and involves the reverse H\(_2\) spillover effect. In particular, it has been reported that hydrogen initially dissociated on metallic Cu, spills over onto ZnO and copper and accelerates the hydrogenation of surface intermediates. It has been also reported that Zn can efficiently prevent sintering of copper crystallites into larger crystallites by keeping the copper surface highly dispersed. Zinc oxide also protects the copper surface from poisons (sulfur and chlorides) \[104, 107\]. However, it was found that zinc oxide is not so stable under
reaction conditions and, for this reason, another refractory oxide (typically Al$_2$O$_3$) is commonly used as a stabilizer of zinc oxide. Al$_2$O$_3$ inhibits thermal sintering and poisoning of the catalyst, and provides additional thermal and catalytic stability as well as higher intrinsic activity [120, 121]. Other promoters like zirconia silica, gallia and chromia are also able to beneficially affect Cu dispersion, stability, activity and selectivity of the catalyst [115].

1.6.1.2 Reduction of Cu/Zn/Al$_2$O$_3$ catalyst

In order to activate the Cu/Zn/Al$_2$O$_3$ catalyst, the initially present copper (II) oxide has to be reduced to metallic copper. In general, the reduction of copper oxide is carried out with H$_2$ (pure or diluted with N$_2$) at elevated temperatures (>470 K) and involves two steps. In the first step, metal nuclei are formed. In the second step, nuclei accumulate to form metal crystallites. The rates of both processes depend on temperature and on the nature of the substrate. Reduction at lower temperatures (<570 K) provides a narrow distribution of small metal crystallites. Reduction at higher temperatures (>670 K) gives a broader distribution and larger metal crystallites [122]. The importance of valence state (Cu$^0$ or Cu$^{+1}$) of Cu has been a subject of controversy for many researchers. It has been reported that CuO undergoes complete reduction, and metallic copper (Cu$^0$) is the real active phase [123]. However Wang and et al. reported that both Cu metal and Cu$_2$O are required for an active catalyst and appropriate specific Cu$^+/Cu^0$ ratio is crucial for optimal catalytic performance of methanol synthesis from synthesis gas [124].

1.6.1.3 Deactivation of copper-based catalyst

Many factors can cause deactivation of copper catalysts. Sintering of copper crystallites is the most important reason for this, and can cause fast deactivation of industrial methanol synthesis catalysts. When sintering occurs (Fig. 1.3), the agglomeration of small metal crystallites results in reduction of copper surface area. The rate of sintering increases with increasing temperature, thus the influence of sintering can be suppressed by decreasing the reaction temperature. However, low reaction temperature inhibits the catalytic performance and decreases the rate of the methanol formation reaction. Another parameter that accelerates the sintering process is the presence of steam. A fast catalytic deactivation is expected, when a CO$_2$-rich feed composition is used for methanol synthesis. This is because of the presence a high amount of water, which is produced during the methanol synthesis and reverse water gas shift reactions.
Poisoning by sulphur, chlorine or other compounds is another possible reason for deactivation of copper-based catalysts. However, in normal plant operation, the effect of these compounds is negligible, because they are removed during the earlier stages of generation of synthesis gas. Carbon deposition (coking) on commercial copper catalysts is generally not important because these materials are not acidic, and they operate under mild conditions [125].

1.6.1.4 Operational conditions, CO\textsubscript{2} conversion and MeOH yield

In Table 1.3 are listed different catalysts and reaction conditions used for CO\textsubscript{2} hydrogenation to MeOH together with representative results obtained in catalytic performance tests. It can be seen that the reaction has been studied under different operational conditions: the temperatures ranging from 220 to 270 °C and the pressure from 1.25 to 8 MPa. A very important issue of methanol synthesis from CO\textsubscript{2} hydrogenation is the low CO\textsubscript{2} conversion. Results presented in Table 1.3 show that the conversion of CO\textsubscript{2} is rather low, ranging from 2 to 20 % depending on temperature, pressure and catalyst applied. It has been found that methanol formation through CO\textsubscript{2} hydrogenation exhibits about 3-10 times lower productivity than that of CO hydrogenation. This can be due to the presence of excess water formed through CO\textsubscript{2} hydrogenation, and the reverse water gas shift (RWGS) reaction. The presence of high amounts of water decreases the methanol synthesis reaction rate [115, 126].

The continuous presence of (RWGS) reaction is a problematic issue for CO\textsubscript{2} hydrogenation to methanol. Copper-based catalysts, the most popularly studied catalytic systems for the WGS reaction, have also been applied to the RWGS
Table 1.3: Catalysts and reaction conditions used in CO₂ hydrogenation to methanol reaction [117].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction conditions</th>
<th>Reaction results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure (MPa)</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>Cu–Zn/SiO₂</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu–Zn–Ga/SiO₂</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu–Ga/ZnO</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu/ZnO</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu–Ga/ZnO</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu–Zn–Ga/SiO₂</td>
<td>2</td>
<td>270</td>
</tr>
<tr>
<td>Cu–V/γ-Al₂O₃</td>
<td>3</td>
<td>240</td>
</tr>
<tr>
<td>Cu/ZnO</td>
<td>5</td>
<td>250</td>
</tr>
<tr>
<td>Cu/SiO₂</td>
<td>1.25</td>
<td>250</td>
</tr>
<tr>
<td>(Zn)Cu/SiO₂</td>
<td>1.25</td>
<td>250</td>
</tr>
<tr>
<td>Ag/ZnO/ZrO</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Au/ZnO/ZrO₂</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂Ga₂O₃</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂MnO</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂B₂O₃</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂In₂O₃</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂Gd₂O₃</td>
<td>8</td>
<td>220</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO₂Y₂O₃</td>
<td>8</td>
<td>220</td>
</tr>
</tbody>
</table>

The latter is an endothermic reaction, and thus high temperatures would facilitate the formation of CO and water.

A commercial Cu/Zn/Al catalyst (G66A, Sud Chemie AG) has been examined by Arena et al. [127] for the title reaction. They reported that the poor catalytic performance of commercial Cu/Zn/Al catalyst is due to the negative effect of water on the rate of methanol formation (at 240°C, 30bar $X_{CO2} = 15.9\%$, $Y_{MeOH} = 7.7\%$). In recent years, the copper catalysts promoted with Zr have attracted attention for their better catalytic activity and stability [78, 128]. It is believed that the strong hydrophilic character of alumina carrier promotes the poisoning effect of water on active sites and thus depresses the functionality of conventional copper-based catalysts [105].

Ban et al. have investigated the effects of temperature and space velocity on the performance of modified Cu/Zn/Zr catalysts [129]. They found that the conversion of CO₂ reaches a maximum at 230 °C and that methanol selectivity
decreases with increasing temperature. The authors concluded that the controlling factor of the reaction shifts from kinetics to thermodynamics. The Ce-doped Cu/Zn/Zr was found to be the most active catalyst (at 230°C, 30bar $X_{\text{CO}_2}=22.8\%$, $Y_{\text{MeOH}}=12.1\%)$. The catalytic activity and stability tests over Cn/Zn/Al (CZA), Cu/Zn/Zr (CZZ) and Cu/Zn/Zr/Al (CZZA) catalysts have been studied by another research group [78]. Results obtained showed that the conversion of CO$_2$ and the yield of methanol were a little higher on CZZA compared to CZA and CZZ (at 230°C $X_{\text{CO}_2}=23.2\%$, $Y_{\text{MeOH}}=13.9\%)$. Thus, Al$_2$O$_3$-ZrO$_2$-promoted catalysts were found to exhibit better catalytic properties and stability compared to catalysts supported on either Al$_2$O$_3$ or ZrO$_2$ alone. Other copper-based catalysts promoted with different elements like Si, Ga, Mn, Mg, La, Ce, Y, Gd- have been also investigated and tested for methanol synthesis reaction (Table 1.3).

### 1.6.2 DME synthesis from methanol dehydration

Dehydration of methanol to DME is a typical acid catalyzed reaction. The process has been studied extensively under different operational conditions. Depending on the catalyst employed, the reaction temperature varies in the range 110-370 °C and the pressure from 1 to 20 bar (Table 1.4).

<table>
<thead>
<tr>
<th>Feed composition</th>
<th>Catalyst</th>
<th>Temp. (°C)</th>
<th>Pressure (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH-water</td>
<td>γ-alumina</td>
<td>270-370</td>
<td>16</td>
</tr>
<tr>
<td>MeOH-N$_2$</td>
<td>Clinoptilolite-zeolite</td>
<td>310-350</td>
<td>1</td>
</tr>
<tr>
<td>MeOH-water-N$_2$</td>
<td>m-ZSM-5</td>
<td>220-320</td>
<td>10</td>
</tr>
<tr>
<td>MeOH-water</td>
<td>Sulphonic acid ion exchange resin</td>
<td>118-150</td>
<td>20</td>
</tr>
<tr>
<td>MeOH-water</td>
<td>Amberlyst-35</td>
<td>110-135</td>
<td>9</td>
</tr>
<tr>
<td>MeOH-He</td>
<td>Y and ZSM-5</td>
<td>180-310</td>
<td>1</td>
</tr>
<tr>
<td>MeOH-N$_2$</td>
<td>H-mordenite</td>
<td>200-300</td>
<td>1</td>
</tr>
<tr>
<td>MeOH-N$_2$</td>
<td>γ-alumina</td>
<td>140-230</td>
<td>10</td>
</tr>
<tr>
<td>MeOH-water</td>
<td>γ-alumina</td>
<td>290-360</td>
<td>2.1</td>
</tr>
<tr>
<td>MeOH</td>
<td>γ-alumina and HZSM-5</td>
<td>150-400</td>
<td>1</td>
</tr>
</tbody>
</table>

Fixed bed reactor is the most convenient reactor that has been used for the title reaction. However, other reactors like slurry, fluidized bed, and tubular flow reactors have also been used [131].

Depending on the catalyst and the reaction temperature applied, the dehydration of methanol can lead to the formation of DME, olefins, or
aromatic/paraffinic hydrocarbons. The stronger the acidity of the catalyst, whether Bronsted or Lewis, the greater tendency of the material to form olefins and hydrocarbons. These consecutive reactions are accelerated at the expense of DME at temperatures greater than about 300°C. The general reaction scheme is given in Scheme 1.3 [132]

**Scheme 1.3:** The consecutive reactions occurring during methanol dehydration process.

\[
2\text{CH}_3\text{OH} \xrightarrow{-\text{H}_2\text{O}} (\text{CH}_3)_2\text{O} \xrightarrow{-\text{H}_2\text{O}} \text{C}_2\text{--C}_5 \text{ olefins} \\
\downarrow \\
\text{paraffins} \\
\text{aromatics} \\
\text{cycloparaffins} \\
\text{C}_6^+ \text{ olefins}
\]

Catalysts that have been investigated include Al$_2$O$_3$, zeolites and mixed metal oxides [82-84, 86-89]. Among these, the most extensively studied materials are based on Al$_2$O$_3$ and HZSM-5.

Generally, alumina has a wide range of applications in heterogeneous catalysis due to its high surface area, acid-base properties, thermal stability and mechanical strength. Regarding the title reaction, alumina has an additional advantage: it does not catalyse the consecutive reactions to hydrocarbons because of its less strong acid sites. The main drawback of alumina is deactivation in the presence of water. During the reaction, methanol and water compete with each other for the same sites on alumina. The catalytic activity of alumina reduces due to the fact that it has a stronger tendency to water than to methanol.

With the purpose to enhance the catalytic activity of these materials, different kind of modifications have been made. Silica, phosphorous-modified catalysts seem to show improved catalytic activity, compared to pure alumina. Yaripour et al. [133] have studied the reaction over silica-modified γ-alumina catalysts. They concluded that increase of silica loading results in higher surface areas and higher surface acidity and, thus, the modified alumina exhibits better catalytic performance, compared to the unmodified one. The same group investigated the methanol dehydration reaction over phosphorous-modified alumina [134]. They showed that phosphorus-modified catalysts exhibit a better performance than the untreated γ-
Another important conclusion was that the DME formation is mainly related to sites with weak and medium acidity.

Mixed metal oxides have also been used as catalysts for the methanol dehydration reaction. Sun et al. [135] have synthesized and tested amorphous Nb$_2$O$_5$ and NbOPO$_4$ samples and compared their results with previously reported results obtained for γ-Al$_2$O$_3$ and H-ZSM-5 catalysts. They concluded that the above catalysts exhibit the same activity as γ-Al$_2$O$_3$ but lower than that of H-ZSM-5. Interestingly, the Nb$_2$O$_5$ and NbOPO$_4$ samples were found to be 100% selective for DME production. In the work reported by Jun et al. [136] B$_2$O$_3$/γ-Al$_2$O$_3$, ZrO$_2$/γ-Al$_2$O$_3$ catalysts together with SiO$_2$/γ-Al$_2$O$_3$ were synthesized and used in catalytic performance tests. Results obtained indicated that among the modified γ-Al$_2$O$_3$ catalysts only SiO$_2$/γ-Al$_2$O$_3$ exhibited improved catalytic performance. Ladera et al. reported on the catalytic activity of NbO$_x$/TiO$_2$ catalysts and concluded that the increase of Nb surface density leads in an increase of dimethyl ether selectivity. The improved catalytic activity observed with increase of Nb content was attributed to the higher strength of acid sites and the formation of Brønsted acid sites [88].

The mechanisms that have been proposed for the methanol dehydration reaction can be divided into two major groups: Langmuire Hinshelwood and Eley-Rideal [137]. The Langmuire Hinshelwood-type mechanism, originally developed by Jain and Pillai in 1967 [132], assumes the presence of both acidic and basic sites on the catalyst surface. Two molecules of methanol adsorbed on two neighboring acidic and basic sites interact to produce one molecule of DME and one molecule of water (Scheme 1.4).

**Scheme 1.4**: Bimolecular mechanism of methanol dehydration on an acid-base pair [132].

The Eley Rideal mechanism assumes interaction of methanol molecules with acidic sites only. The acid site on the catalyst attacks the nucleophilic oxygen of the methanol molecule. The surface species then react either together or with a gas-phase methanol molecule leading to DME formation [137, 138].
Zeolites are another widely studied type of solid-acid catalysts used for methanol dehydration to DME. Among these, the medium-pore ZSM-5 zeolite is of particular interest [80, 139-141]. Generally, the HZSM-5 catalyst possesses higher activity than γ-Al₂O₃ catalyst. In addition, HZSM-5 is more active at low temperatures [130, 142, 143]. However, unlike alumina, this zeolite accelerates the consecutive reaction to hydrocarbons at high reaction temperatures (Scheme 1.3). These differences between zeolite and alumina are explained mainly by the different acidity of these two materials. The γ-alumina exhibits only Lewis acidity, whereas HZSM-5 has both Lewis (due to the extra-framework aluminum) and Brønsted acid sites (aluminum located in the framework of the zeolite). It is believed that dehydration of methanol may take place over both Lewis acid–base pair and Brønsted acid–Lewis base pair sites [130]. The nature and strength of the surface acid sites and the interaction of methanol with these sites determine the reaction path, yield and selectivity [137]. However, which acid sites catalyze the methanol dehydration to sole DME is not clear. Some authors have proposed that Brønsted acidity exhibits higher activity than Lewis acidity [87]. However, other investigators did not find a direct relationship between the methanol dehydration rate and the nature of acid sites on HZSM-5 zeolites [144]. Takeguchi et al. [97] studied silica-alumina catalysts together with H-ZSM5 zeolite and found that water and NH₃ are competitively adsorbed on Lewis acid sites (silica-alumina catalysts), whereas adsorption of NH₃ on Brønsted acid sites (H-ZSM-5) was not much affected by the presence of water. They concluded that Lewis acid–base pairs are the major active sites for methanol dehydration at atmospheric pressure, where the partial pressure of water formed is low and thus water adsorbed on acid sites is negligible. In this case, the methanol dehydration rate on Brønsted acid sites seems to be much slower than that on Lewis acid sites. However, under the synthesis gas to DME (STD) reaction conditions, the partial pressure of the water formed by the dehydration of methanol is quite high and, as a result, the activity of Lewis acid sites was found to be suppressed by adsorbed water at lower temperatures. Under these conditions the Brønsted acid–Lewis base pair sites are the major active sites for the methanol dehydration reaction.

In addition to the strong acidity of HZSM-5 zeolite, another factor that might effect the production of DME and may cause rapid catalyst deactivation is the narrow and slender microporous structure of HZSM-5 zeolite. This may hinder the fast DME diffusion from the narrow channels of catalyst [86, 145].
Other zeolitic materials have been also investigated for methanol dehydration reaction. Khandan et al. [146] studied the performance of five different types of zeolites, namely Y, Mordenite, Beta, ZSM-5 and Ferrierite in a slurry reactor. The authors found that among these materials, the H+-form of Mordenite zeolite showed the highest conversion ($X_{\text{MeOH}}=96.4\%$) and DME selectivity ($Y_{\text{DME}}=65.7\%$). They also concluded that the methanol conversion is directly related to the acidity of catalyst, while selectivity and stability are strongly correlated to the strength of acidic sites. Another group [147] has investigated methanol dehydration over different commercial H, Na-form mordenite catalysts at 300 °C and atmospheric pressure in a fixed bed reactor. Results showed that the H-form mordenite, with the best catalytic activity, exhibits $X_{\text{MeOH}}=84\%$ and $Y_{\text{DME}}=84\%$. Its higher activity has been attributed to the higher dispersion of active sites (higher surface area), whereas its selectivity and long term stability corresponds to the medium acid strength due to higher Si/Al ratio. In agreement with Khandan et al. [146] the authors concluded that the H-form mordenite samples are much more active compared to the Na-form mordenite catalysts.

Various modifications and treatments have been applied for zeolites in order to impart better activity and selectivity to DME and to limit/inhibit the consecutive reactions in methanol dehydration process. Treatment with steam for framework dealumination and different modification are generally adopted methods for acidity modification of ZSM-5 [148]. Lee et al. [148] showed that phosphorus-loaded ZSM-5 zeolites exhibit improved catalytic properties compared to the phosphorus-free ZSM-5 sample. Results of another work [146] indicates that the low selectivity and stability of H+-form Mordenate can be improved by modification with various metals such as Na, Al, Zr, Mg, Cu, Zn and Ni.

Dealumination, i.e. dislodgement of framework Al, is commonly used to enhance the (hydro)thermal stability of the zeolite, to modify its acidic properties by increasing its lattice Si/Al ratio and to introduce intracrystalline mesoporosity which can improve the diffusion limitations within zeolite [149-151]. It has been reported that, the severe steaming of zeolite decreases the acidity of HZSM-5 and lowers the rate of conversion of formed DME to other hydrocarbons and coke [151].

Regarding the reaction pathway, two possible routes have been proposed for DME formation over zeolites: Stepwise and concerted, as shown in Scheme1.5 (a) and (b) respectively. The first one includes the formation of a methoxy group followed by its interaction with another methanol molecule, which leads to DME and the regeneration of the Brønsted acid site. The second pathway involves the
simultaneous adsorption and subsequent reaction of two methanol molecules to give DME [152].

**Scheme 1.5:** Mechanism proposed for DME formation (a) stepwise and (b) concerted.

![Scheme 1.5 Mechanism proposed for DME formation](image)

1.6.3 Direct Methanol/DME synthesis from CO₂

The principle of direct DME production from CO/CO₂ is the combination of methanol synthesis and dehydration process in a single reactor unit. As mentioned in Section 1.6, the direct process allows higher CO/CO₂ conversions and a simple reactor design that results in much lower DME production costs [153]. Considerable attention has been given to this process in order to develop a catalytic system that can be applicable for industry. However, in spite of these efforts, the low CO₂ conversion and the low selectivities and yields of desired products achieved so far are not acceptable for industrial applications.

In Table 1.5 are listed catalytic materials that have been used for direct DME production by CO₂ hydrogenation. It can be observed that in most cases Cu/Zn or Cu/Zr are the main components of these materials. Modifications of the metal based component by addition of promoters (Ga, Mn, La, Ce, Y, Si, Ti, V, Pd) have also been implemented aiming to improve the catalytic activity. Zhang *et al.* investigated V-modified CuO–ZnO–ZrO₂/HZSM-5 catalysts and reported that V-modification can efficiently enhance the catalytic performance [154]. In particular, the CO₂ conversion and DME selectivity over CZZV₀.₅H increase compared to the unmodified CZZV₀HZSM-5 catalyst. Interesting results have been obtained by Wengui [155], who tried to modify the CuO-ZnO-Al₂O₃ catalyst by different La loadings. The addition of La to the CuO-ZnO-Al₂O₃/HZSM-5 catalyst was found to
increase the dispersion of copper particles and thus enhanced the catalytic activity. The authors reported that with the addition of La, the conversion of CO\textsubscript{2} increased from 11.7\% to 25.1\%–43.8\% and the DME selectivity from 16.0 \% to 71.2 \%. More catalytic systems used for the title reaction are presented in Table 1.5. The reaction has been studied under different operational conditions: the temperatures ranging from 200 to 275 °C and pressure from 2.0 to 5.0 MPa. Erena et al. [156] found that the optimum temperature of the reaction is 275 °C. The investigators concluded that at this temperature the production of DME is maximized and CuO site sintering is not significant. Another research group [157] suggested that the maximum reaction temperature should be 250 °C because the catalyst can be deactivated at higher temperatures due to sintering.

**Table 1.5:** Catalysts and operating conditions for DME production by CO\textsubscript{2} hydrogenation.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>T (°C)</th>
<th>P (MPa)</th>
<th>X\textsubscript{CO2} (%)</th>
<th>Y\textsubscript{DME} (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–ZnO–Al\textsubscript{2}O\textsubscript{3}+HZSM-5</td>
<td>250</td>
<td>3.0</td>
<td>-</td>
<td>12.5</td>
<td>[158]</td>
</tr>
<tr>
<td>CuO-ZnO-Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}+HZSM-5</td>
<td>260</td>
<td>3.0</td>
<td>25.2</td>
<td>5.8</td>
<td>[159]</td>
</tr>
<tr>
<td>Cu/ZnO/ZrO\textsubscript{2}+H-Ga-Silicalite</td>
<td>250</td>
<td>3.0</td>
<td>19.0</td>
<td>8.6</td>
<td>[160]</td>
</tr>
<tr>
<td>CuO–TiO\textsubscript{2}-ZrO\textsubscript{2}+HZSM-5</td>
<td>250</td>
<td>3.0</td>
<td>15.6</td>
<td>7.4</td>
<td>[161]</td>
</tr>
<tr>
<td>V modified CuO-ZnO-ZrO\textsubscript{2} + HZSM5</td>
<td>270</td>
<td>3.0</td>
<td>32.5</td>
<td>19.1</td>
<td>[154]</td>
</tr>
<tr>
<td>Pd-CNT promoted Cu/ZrO\textsubscript{2}+HZSM5</td>
<td>250</td>
<td>5.0</td>
<td>12.5</td>
<td>6.475</td>
<td>[161]</td>
</tr>
<tr>
<td>CuO-ZnO-Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}+HZSM-5</td>
<td>250</td>
<td>5.0</td>
<td>30.9</td>
<td>21.2</td>
<td>[157]</td>
</tr>
<tr>
<td>CuO-ZnO-Al\textsubscript{2}O\textsubscript{3} + NaHZSM-5</td>
<td>275</td>
<td>3.0</td>
<td>43.8</td>
<td>26</td>
<td>[162]</td>
</tr>
<tr>
<td>La-modified CuO-ZnO-Al\textsubscript{2}O\textsubscript{3}+HZSM-5</td>
<td>250</td>
<td>3.0</td>
<td>43.8</td>
<td>30</td>
<td>[155]</td>
</tr>
<tr>
<td>Cu/Mo + HZSM-5</td>
<td>240</td>
<td>12.3</td>
<td>9.5</td>
<td>18.8</td>
<td>[163]</td>
</tr>
<tr>
<td>Pd-modified CuO-ZnO-Al\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2}+HZSM-5</td>
<td>200</td>
<td>3.0</td>
<td>18.6</td>
<td>13.7</td>
<td>[164]</td>
</tr>
<tr>
<td>multi-walled carbon nanotubes on CuO-ZnO-Al\textsubscript{2}O\textsubscript{3} + HZSM-5</td>
<td>262</td>
<td>3.0</td>
<td>46.2</td>
<td>20.9</td>
<td>[165]</td>
</tr>
<tr>
<td>CuO-ZnO-Al\textsubscript{2}O\textsubscript{3} + HZSM5</td>
<td>260</td>
<td>5.0</td>
<td>29</td>
<td>18.8</td>
<td>[166]</td>
</tr>
</tbody>
</table>

Zha et al. [165] investigated the direct DME production from CO\textsubscript{2} reaction by varying the reaction temperature in the range 232-302 °C. Results obtained showed that the DME selectivity at 262°C takes a value of 45\% while further increase of temperature results in reduction of DME selectivity to 31 \% due to Cu sintering. Pressure is another important parameter for this reaction and, according to thermodynamics, it plays a beneficial role for DME production from CO\textsubscript{2}
hydrogenation. The pressure used by different research groups varies from 2.0 MPa to 5.0 MPa (Table 1.5). Some authors have studied the effects of pressure on catalytic activity and product selectivity. Erena and co workers [156] reported that the optimum pressure is 4.0 MPa. The authors concluded that under this operating pressure the conversion and also the yields of organic compounds are much higher than those obtained at lower pressures. On the contrary, other investigators reported that the CO₂ conversion and DME selectivity decreased when the pressure was increased from 3.0 MPa to 4.0 MPa [165].

In CO₂ hydrogenation reaction, an important parameter which affects the reactor efficiency is the space velocity. An et al. [157] reported that increase of the space velocity from 1000 to 10000 mL/(g cat·h) results in a decrease of the conversion as well as the yield of DME over Cu/Zn/Al/Zr/HZSM5 catalyst. They also found that the DME yield decreases faster than the methanol yield. This has been explained by considering that the reaction on HZSM-5 component is affected more strongly by the space velocity than the reaction on the Cu- based component. The values of CO₂ hydrogenation and DME yield listed in Table 1.5 were obtained under optimal experimental conditions. It can be observed that the conversion of CO₂ takes value from 12.5% to 46.2% and DME yield from 0.45 to 30% depending on the catalyst applied and experimental conditions used.

Considerable attention has been given in the literature regarding the method of development of an effective catalyst for the direct process. Generally, two different methods of combining a methanol synthesis function and a solid acid function can be applied. In the first one, the methanol synthesis and the methanol dehydration catalyst components exist together as a single entity (hybrid catalysts) [167]. These catalysts are generally prepared by co-precipitation, impregnation, combined co-precipitation or ultrasound-assisted methods [161, 167-169]. In the second method, the powders of separately prepared functions are just mechanically blended (mixed catalysts) [170, 171]. Another widely applied method for preparing the hybrid catalysts is by grinding the components in their powder form and then pelletizing the homogenous solid mixture to the desired particle size [172].

It has been reported by many authors that the catalysts prepared by physical mixing have better catalytic activity than the catalysts prepared by other methods [169, 173, 174]. Bonura et al. [169] have applied four different methods for the combination of Cu–ZnO–ZrO₂ and H-ZSM5 catalysts (Fig. 1.4 A-D). The authors concluded that the bifunctional (d) sample, prepared by physical mixing exhibits
a superior performance compared to the other investigated samples, mainly when a zeolite loading of 50 wt.% is used.

![Figure 1.4](image)

**Figure 1.4**: Different procedures for the combination of Cu–ZnO–ZrO$_2$ and H-ZSM5 catalysts: catalyst (a) obtained by applying a reverse co-precipitation method under ultrasound irradiation, (b) is obtained by loading dual-bed of same size Cu–ZnO–ZrO$_2$ (first bed) and HZSM-5 catalyst (second bed), (c) homogeneous solid mixture and (d) homogeneous physical mixture of Cu–ZnO–ZrO$_2$ and H-ZSM5 catalysts [169].

The catalytic performance of these two functional catalysts depends strongly on the metal-oxide to acid surface sites ratio. Sierra *et al.* [175] reported that the rate limiting step of DME direct synthesis is determined by the methanol synthesis reaction thus they used 2:1 as metal-oxide to acid surface ratio. Kim *et al.* [170] have also found that the overall DME direct synthesis can be determined by the methanol synthesis rate on the mixed catalyst. However, other authors [167, 176] reported that the rate limiting step is determined by the acid properties of the dehydrating catalyst, i.e., its acid strength and number of acid sites.

### 1.7 Aim and motivation of the present study

The principal aim of the present work is the development of an efficient catalytic system for the simultaneous production of methanol/dimethyl ether from CO$_2$ hydrogenation at relatively low pressure (30 bar).

Currently, on a large industrial scale, methanol is mainly produced by CO/CO$_2$/H$_2$ mixtures originating from fossil fuel sources. The replacement of CO with CO$_2$ in methanol synthesis is believed to be one of the most attractive route for CO$_2$ utilization. The use of CO$_2$ as chemical feedstock solves not only the problems
related to the global climate changes arisen due to the “greenhouse effect”, but also offers a feasible way to mitigate the humankind dependence on fossil fuel resources.

The H₂ reactant required for this process can be produced from excess electricity of wind turbines or photovoltaics via water electrolysis. In this respect, the process has the additional advantage of providing a means of storing renewable energy. In addition, the production of H₂, by means of certain modern electrolysers, takes place under a pressure of ~30 bar. This means that the produced H₂ can directly be used in CO₂ hydrogenation to methanol reaction at the same pressure.

Thermodynamically, the methanol synthesis from CO₂ is favoured at low temperatures and high pressures. In this respect, the simultaneous conversion of methanol into dimethylether provides a means of shifting the equilibrium toward the desired direction.

The whole concept of methanol/DME production from CO₂ and renewable resources is shown schematically in Fig. 1.5.

![Figure 1.5](image_url)

**Figure 1.5:** Schematic representation of the synthesis of methanol/dimethyl ether from CO₂ and renewable resources.

### 1.8 Main issues and tasks of the present study

The challenges for transforming CO₂ into value added chemicals including methanol/DME are various. A considerable amount of contributions have been undertaken by many researchers to improve the chemical reactions converting the CO₂ to useful chemicals over both homogeneous and heterogeneous catalysts. The CO₂ is a very stable and chemically inert compound and it is not easy to break the C–O bond and make new C–H bond. In order to activate the CO₂ molecule, high
reaction temperatures are required. However, thermodynamically, the methanol synthesis is not favorable at high reaction temperatures. In addition, the catalyst deactivation is highly possible at high temperatures. Hence, one of the key issues is the development of an efficient catalyst with high stability and activity for CO$_2$ hydrogenation at relatively low reaction temperatures.

The second important issue in this process is the low productivity of methanol/DME. There is a strong competition between the methanol synthesis and the reverse-water-gas shift (RWGS) reaction that take place during CO$_2$ hydrogenation reaction. Thus, in bi-functional catalysts, the metallic part should exhibit high selectivity to methanol and simultaneously low selectivity to CO formed through the RWGS reaction.

The next problematic part of the process is the excess of water present under conditions of simultaneous production of methanol/DME from CO$_2$ hydrogenation. The presence of water is not evitable in methanol production from CO$_2$, methanol dehydration to DME and RWGS reactions. Hence, both methanol synthesis and methanol dehydration components in the bi-functional catalyst must be stable under these reaction conditions.

By taking into account all issues mentioned above, the present research work addresses the following major tasks.

- A detailed thermodynamic analysis of the title reaction with a purpose to find the optimum conditions for running the catalytic experiments (Chapter 2).
- Investigation of the methanol dehydration to dimethyl ether reaction over materials with different physicochemical characteristics (aluminas and zeolites) with the purpose to develop a suitable acid catalyst that could be then combined with a methanol synthesis catalyst and used for the direct conversion of CO$_2$/H$_2$ into methanol/dimethyl ether (Chapter 4 and 5).
- Investigation of CO$_2$ hydrogenation to methanol reaction over copper based catalysts. Optimization of experimental conditions (temperature, pressure, space velocity, CO$_2$/H$_2$ ratio) (Chapter 6).
- Development of bi-functional catalysts by combining a methanol synthesis and a methanol dehydration catalyst for the direct conversion of CO$_2$/H$_2$ to methanol/dimethyl ether (Chapter 6).
1.9 References

CHAPTER 2

THERMODYNAMIC ANALYSIS

2.1 Introduction

In this chapter, a thermodynamic analysis is made for the CO$_2$ hydrogenation to methanol/dimethyl ether reaction. The overall process involves the following chemical reactions:

\[
\begin{align*}
\text{CO}_2 + 3\text{H}_2 &= \text{CH}_3\text{OH} + \text{H}_2\text{O} & \text{(2.1)} \\
\text{CO} + 2\text{H}_2 &= \text{CH}_3\text{OH} & \text{(2.2)} \\
\text{CO} + \text{H}_2\text{O} &= \text{CO}_2 + \text{H}_2 & \text{(2.3)} \\
2\text{CH}_3\text{OH} &= \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} & \text{(2.4)}
\end{align*}
\]

By considering CO$_2$ as the carbon source, the overall reaction will be

\[
2\text{CO}_2 + 6\text{H}_2 = \text{CH}_3\text{OCH}_3 + 3\text{H}_2\text{O} \quad \text{(2.5)}
\]

The thermodynamic analysis of the above reactions (2.1-2.5) has been carried out using the Outokumpu HSC Chemistry program [1]. The program was used to calculate the heat capacity, enthalpy, entropy and Gibbs energy values of the reactions as well as the equilibrium compositions. Results were then used to calculate the equilibrium conversion of reactants and equilibrium selectivities of products for each reaction. For comparison purposes, the enthalpy, entropy and Gibbs energy values have been also calculated manually by using the equations presented in Section 2.2. In addition to these, the effects of temperature, pressure and reactant’s
molar ratio on the conversion and selectivities of products for each reaction have been studied separately.

2.2 Thermodynamic evaluation of chemical equilibrium

Thermodynamics enables us to predict with confidence the equilibrium pressures or concentrations of reaction mixtures. Calculations may start from the following equation, which allows determination of heat of reaction, $\Delta H_{r,T}^{\circ}$, at any temperature, $T$, by applying the Kirchhoff’s law [2-6].

\[
\Delta H_{r,T}^{\circ} = \Delta H_{r,T_o}^{\circ} + \int_{T_o}^{T} \sum \nu_i C_{p,i}^o dT \frac{J}{mol}
\]  

For $T_o=298$ K, 2.2.1 equation will be

\[
\Delta H_{r,T}^{\circ} = \Delta H_{r,298}^{\circ} + \sum \nu_i C_{p,i}^o dT
\]  

where $\Delta H_{r,298}^{\circ}$ and $\Delta H_{r,T}^{\circ}$ are the standard enthalpies of reaction at temperatures of 298 K and $T$, respectively, $\nu_i$ is the stoichiometric coefficient of reactants and products and $C_{p,i}^o$ are the standard heat capacities of compounds involved in the reaction. Thus, the enthalpy of reaction at any temperature, $T$, can be calculated when the heat capacities of compounds are known. Experimental heat capacity data are often presented as polynomial functions of temperature of the form:

\[
C_{p}^o = a + bT + cT^2 \frac{J}{mol \cdot K}
\]  

where $a$, $b$, $c$ are constants in ideal-gas heat-capacity equation. The values of these constants for all compounds of interest are listed in Table 2.1. By using the proper $a$, $b$ and $c$ values, $\Delta a$, $\Delta b$, $\Delta c$ can be calculated for any given reaction with the use of the following equations.

\[
\Delta a = \sum \nu_i \cdot a_i \frac{J}{mol \cdot K}
\]
\[ \Delta b = \sum_{i} v_i \cdot b_i \frac{J}{mol \cdot K^2} \]  \hspace{1cm} 2.2.5

\[ \Delta c = \sum_{i} v_i \cdot c_i \frac{J}{mol \cdot K^3} \]  \hspace{1cm} 2.2.6

The values of the standard enthalpy, \( \Delta H^0_{r,298} \), and the standard Gibbs energy, \( \Delta G^0_{r,298} \), of the reaction at a temperature of 298 K and pressure of 1 atm, can be calculated with the use of equations 2.2.7 and 2.2.8, respectively.

\[ \Delta H^0_{r,298} = \sum_{Pr} v_i \Delta H^0_{f,298K} - \sum_{Re} v_i \Delta H^0_{f,298K} \frac{J}{mol} \]  \hspace{1cm} 2.2.7

\[ \Delta G^0_{r,298} = \sum_{Pr} v_i \Delta G^0_{f,298K} - \sum_{Re} v_i \Delta G^0_{f,298K} \frac{J}{mol} \]  \hspace{1cm} 2.2.8

where \( \Delta H^0_{f,298K} \) and \( \Delta G^0_{f,298K} \) are the standard enthalpies and standard Gibbs energies of formations in their reference state (298 K, 1 atm) and are listed in Table 2.1 for all compounds of interest.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( A ) J/mol K</th>
<th>( B \times 10^3 ) J/mol K</th>
<th>( C \times 10^5 ) J/mol K</th>
<th>Temp. range (K)</th>
<th>( \Delta G^0_{f,298K} ) (kJ/mol)</th>
<th>( \Delta H^0_{f,298K} ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)</td>
<td>27.095</td>
<td>11.274</td>
<td>12.488</td>
<td>50-1000</td>
<td>-394.38</td>
<td>-393.51</td>
</tr>
<tr>
<td>H(_2)</td>
<td>23.969</td>
<td>30.604</td>
<td>-6.418</td>
<td>50-1000</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>36.540</td>
<td>-34.802</td>
<td>11.681</td>
<td>50-1000</td>
<td>-228.42</td>
<td>-241.81</td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>39.192</td>
<td>-58.082</td>
<td>35.010</td>
<td>50-1000</td>
<td>-162.24</td>
<td>-200.94</td>
</tr>
<tr>
<td>CO</td>
<td>32.524</td>
<td>-32.533</td>
<td>9.827</td>
<td>50-1000</td>
<td>-137.16</td>
<td>-110.53</td>
</tr>
<tr>
<td>CH(_3)OCH(_3)</td>
<td>36.257</td>
<td>50.466</td>
<td>24.102</td>
<td>100-1000</td>
<td>-112.92</td>
<td>-184.11</td>
</tr>
</tbody>
</table>

With the help of values obtained for \( \Delta a, \Delta b, \Delta c \) the enthalpy of the reaction can be calculated according to:
\[
\Delta H^\circ_{R,T} = \Delta H^\circ_{R,298} + \Delta a \cdot (T - 298) + \frac{1}{2} (\Delta b) \cdot (T - 298)^2 + \frac{1}{3} (\Delta c) \cdot (T - 298)^3
\]

2.2.8

For \(T= 0\) K, equation 2.2.8 is given by

\[
\Delta H^\circ_{R,T} = \Delta H^\circ_o + \Delta a \cdot T + \frac{1}{2} (\Delta b) \cdot T^2 + \frac{1}{3} (\Delta c) \cdot T^3 \cdot \frac{J}{mol}
\]

2.2.9

where \(\Delta H_o\) is a constant which indicates the heat of reaction at temperature of \(0^\circ K\) [8]. At \(T=298\) K from equation 2.2.9, \(\Delta H_o\) can be calculated as follows

\[
\Delta H_o = \Delta H^\circ_{R,298} - \Delta a \cdot 298 - \frac{1}{2} (\Delta b) \cdot 298^2 - \frac{1}{3} (\Delta c) \cdot 298^3 \cdot \frac{J}{mol}
\]

2.2.10

The standard Gibbs free-energy change, \(\Delta G^\circ_{R,T}\), at any temperature can be estimated using the Van’t Hoff equation (2.2.11)

\[
\Delta H^\circ_R = -RT \frac{d(\Delta G^\circ_R / RT)}{dT}
\]

2.2.11

where \(R=8.314\) \(J/mol\) \(K\) is the universal gas constant. Equation 2.2.11 can be rearranged as follows.

\[
\Delta G^\circ_{R,T} = \Delta H_o - \Delta a \cdot T \cdot \ln T - \frac{\Delta b \cdot T^2}{2} - \frac{\Delta c \cdot T^3}{6} - \frac{IR \cdot T \cdot J}{mol}
\]

2.2.12

where \(I\) is an integration constant. At \(T=298 K\), the value of \(IR\) can be calculated from equation 2.2.12

\[
IR = \frac{\Delta H_o}{T} - \Delta a \cdot \ln T - \frac{\Delta b \cdot T^2}{2} - \frac{\Delta c \cdot T^3}{6} - \frac{\Delta G^\circ_{R,T}}{T} \cdot \frac{J}{mol \cdot K}
\]

2.2.13
\( \Delta G_{RT}^0 \) at any other temperature may then be calculated from equation 2.2.12, and \( \Delta S_{RT} \) at any temperature can be calculated from equation 2.2.14

\[
\Delta G = \Delta H - \Delta S \cdot T \Rightarrow \Delta S = \frac{\Delta H}{T} - \frac{\Delta G}{T} \quad J \text{ mol}^{-1} \text{ K}
\]

Finally, the equilibrium constant can be calculated with the use of the following equation

\[
-RT \ln K_p = \Delta G^o \Rightarrow K_p = \exp \left( -\frac{\Delta G_{RT}^0}{R \cdot T} \right)
\]

In the following sections (2.3-2.7), all necessary thermodynamic parameters of reactions (2.1-2.5) have been calculated with the use of equations 2.2.1 to 2.2.15.

**2.3 \( \text{CO}_2 \) hydrogenation to methanol**

\[
\text{CO}_2 + 3\text{H}_2 = \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (2.1)
\]

By taking the values of \( a, b, c, \Delta G_{f,298}^o, \Delta H_{f,298}^o \) for \( \text{CO}_2, \text{H}_2, \text{CH}_3\text{OH}, \text{H}_2\text{O} \) from Table 2.1 and by using the equations 2.2.4 to 2.2.8, the following values have been calculated:

\[
\Delta a = -23.27 \frac{J}{\text{mol} \cdot \text{K}}
\]
\[
\Delta b = -195.97 \cdot 10^{-3} \frac{J}{\text{mol} \cdot \text{K}}
\]
\[
\Delta c = 53.457 \cdot 10^{-5} \frac{J}{\text{mol} \cdot \text{K}}
\]
\[
\Delta G_{RT}^0 = 3720 \frac{J}{\text{mol}}
\]
\[
\Delta H_{RT}^0 = -49240 \frac{J}{\text{mol}}
\]

By inserting the values of \( \Delta a, \Delta b, \Delta c \) and \( \Delta H_{RT}^0 \) in equation 2.2.10, the enthalpy of reaction at temperature of 0°K will be

\[
\Delta H_o = -38319.6 \frac{J}{\text{mol}}
\]
By using the values of $\Delta a, \Delta b, \Delta c, \Delta H_o$ and $\Delta G_{R298}^o$ the IR constant can be calculated according to equation 2.2.13

$$\text{IR} = 12.7865 \frac{J}{\text{mol} \cdot K}$$

According to equation 2.2.9, the dependence of reaction enthalpy on temperature can be expressed as follows:

$$\Delta H_{R,T} = -38319.6 - 23.27 \cdot T - 97.985 \cdot 10^{-3} \cdot T^2 + 17.819 \cdot 10^{-5} \cdot T^3$$

From equation 2.2.12 standard Gibbs free-energy change at any given temperature can be calculated as follows:

$$\Delta G_{R,T} = -38319.6 + 23.27 \cdot T \cdot \ln(T) + 97.985 \cdot 10^{-3} \cdot T^2 - 8.9095 \cdot 10^{-5} \cdot T^3 - 12.786 \cdot T$$

The equilibrium constant of the reaction derived from equation 2.2.15 is given as follows:

$$K_p = \exp \left( \frac{-38319.6 + 23.27 \cdot T \cdot \ln(T) + 97.985 \cdot T^2 \cdot 10^{-3} - 8.9095 \cdot T^3 \cdot 10^{-5} - 12.786 \cdot T}{8.314 \cdot T} \right)$$

Representative results are shown in Figures 2.1, 2.2, 2.3, 2.4 where the changes of Gibbs free–energy ($\Delta G_{R,T}^o$), enthalpy ($\Delta H_{R,T}^o$) and entropy ($\Delta S_{R,T}^o$) of the reaction as well as the equilibrium constant are plotted as functions of reaction temperature.

![Figure 2.1: $\Delta G_{R,T}^o$ dependence on temperature in CO$_2$ hydrogenation to methanol reaction.](image1)

![Figure 2.2: $\Delta H_{R,T}^o$ dependence on temperature in CO$_2$ hydrogenation to methanol reaction.](image2)
Results presented in Fig. 2.2 show that the reaction is exothermic at temperatures up to 923 K, where $\Delta H^0_{R,T}$ becomes positive. $\Delta G^0_{R,T}$ takes positive values and increases with increasing reaction temperature (Fig. 2.1) thus the temperature increase is not favorable for the reaction. In Figure 2.5 is shown the equilibrium conversion of carbon dioxide as a function of reaction temperature and pressures in the range of 1 to 100 bar. It is observed that the reaction is favored at low temperatures and high pressures.
According to reaction 2.1, the stoichiometric H₂:CO₂ ratio is equal to 3:1. However, the H₂/(CO+CO₂) ratio used in industry is quite high. Thus, it is essential to study the effect of CO₂:H₂ ratio on the conversion of CO₂ to methanol/DME. In this study, CO₂ was chosen to be the only carbon source for both methanol synthesis and simultaneous production of methanol/dimethyl ether. The effects of CO₂:H₂ ratio on CO₂ conversion, methanol selectivity and CO selectivity, calculated for \( P=30 \) bar and \( T=180-240 \, ^\circ\text{C} \), are presented in Figures 2.6, 2.7 and 2.8 respectively. It is observed that increase of the H₂:CO₂ ratio results in a monotonic increase of the conversion of CO₂ and the methanol selectivity. Thus, thermodynamics imply that when the H₂ content is increased, the hydrogenation of CO₂ to methanol is enhanced.

**Figure 2.6:** Effect of CO₂:H₂ ratio on CO₂ conversion in CO₂ hydrogenation to methanol reaction. \( P=30\text{bar}, \, T=160-280 \, ^\circ\text{C} \).

**Figure 2.7:** Effect of CO₂:H₂ ratio on CH₃OH selectivity in CO₂ hydrogenation to methanol reaction. \( P=30\text{bar}, \, T=160-280 \, ^\circ\text{C} \).

**Figure 2.8:** Effect of CO₂:H₂ ratio on CO selectivity in CO₂ hydrogenation to methanol reaction. \( P=30\text{bar}, \, T=160-280 \, ^\circ\text{C} \).
2.4 CO hydrogenation to methanol

\[ \text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH} \] (2.2)

The calculated values of \( \Delta a, \Delta b, \Delta c, \Delta G_{R,298}^0 \) and \( \Delta H_{R,298}^0 \) obtained with the use of the data listed in Table 2.1 and equations 2.2.4 to 2.2.8 (section 2.2) are listed below:

\[
\begin{align*}
\Delta a &= -41.270 \frac{J}{\text{mol} \cdot K} \\
\Delta b &= -86.757 \cdot 10^{-3} \frac{J}{\text{mol} \cdot K} \\
\Delta c &= 38.019 \cdot 10^{-5} \frac{J}{\text{mol} \cdot K} \\
\Delta G_{R,298}^0 &= -25080 \frac{J}{\text{mol}} \\
\Delta H_{R,298}^0 &= -90410 \frac{J}{\text{mol}}
\end{align*}
\]

From equation 2.2.10 the enthalpy of reaction at temperature of \( 0^\circ \text{K} \) is

\[
\Delta H^0 = -77613.087 \frac{J}{\text{mol}}
\]

By using the values of \( \Delta a, \Delta b, \Delta c, \Delta H_o \) and \( \Delta G_{R,298}^0 \) the IR constant can be calculated according to equation 2.2.13

\[
\text{IR} = 66.133 \frac{J}{\text{mol} \cdot K}
\]

According to equation 2.2.9, the enthalpy of the title reaction as a function of temperature is given by the following equation:

\[
\Delta H_{R,T} = -77613.087 - 41.270 \cdot T - 43.379 \cdot 10^{-3} \cdot T^2 + 12.673 \cdot 10^{-5} \cdot T^3
\]

From equations 2.2.12 and 2.2.15 the standard Gibbs free-energy change and the equilibrium constant can be calculated as follows:

\[
\Delta G_{R,T} = -77613.087 + 41.270 \cdot T \cdot \ln T + 43.379 \cdot 10^{-3} \cdot T^2 - 6.336 \cdot 10^{-5} \cdot T^3 - 66.133 \cdot T
\]

\[
K_p = \exp \left( -\left[ -77613.087 + 41.270 \cdot T \cdot \ln T + 43.379 \cdot 10^{-3} \cdot T^2 - 6.336 \cdot 10^{-5} \cdot T^3 - 66.133 \cdot T \right] / 8.314 \cdot T \right)
\]

Representative results are shown in Figures 2.9, 2.10, 2.11, 2.12 where the changes of Gibbs free-energy (\( \Delta G_r^0 \)), enthalpy (\( \Delta H_r^0 \)) and entropy (\( \Delta S_r^0 \)) of the title
reaction also the equilibrium constant are plotted as functions of reaction temperature.

\[ \Delta G^o_T \] depends on temperature in CO hydrogenation to methanol reaction.

\[ \Delta H^o_T \] depends on temperature in CO hydrogenation to methanol reaction.

\[ \Delta S^o_T \] dependence on temperature in CO hydrogenation to methanol reaction.

\[ \ln(K_p) \] depends on equilibrium constant of CO hydrogenation to methanol reaction.

In Figure 2.13 the equilibrium conversion of carbon monoxide is plotted as a function of reaction temperature and pressure.
As a conclusion the reaction is exothermic as $\Delta H^0_{R,T}$ takes negative values with increasing the temperature in the range 273-1023 K (Fig. 2.10). $\Delta G^0_{R,T}$ takes positive values at temperatures higher than 398 K (Fig. 2.9) thus the temperature increase is not favorable for the reaction. From Fig. 2.13 it is evident that the equilibrium conversion of CO increases with increasing pressure. Because of the decrease of number of moles in the right side of reaction 2.2 the increase of pressure results in a shift of the reaction to the right according to the Le Chatelier’s principle.

### 2.5 The water gas shift reaction

$$\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \quad (2.3)$$

The values of $\Delta a, \Delta b, \Delta c, \Delta G^0_{R,298}$ and $\Delta H^0_{R,298}$ presented below have been calculated by taking the data of $a, b, c, \Delta G^0_{f,298K}, \Delta H^0_{f,298K}$ for CO$_2$, H$_2$, CH$_3$OH and H$_2$O compounds from Table 2.1 and by using the equations 2.2.4 to 2.2.8.

\[
\Delta a = -18 \frac{J}{\text{mol} \cdot \text{K}}
\]

\[
\Delta b = 109.213 \cdot 10^{-3} \frac{J}{\text{mol} \cdot \text{K}}
\]

\[
\Delta c = -15.438 \cdot 10^{-5} \frac{J}{\text{mol} \cdot \text{K}}
\]
\[ \Delta G_{R298}^0 = -28800 \frac{J}{mol} \]
\[ \Delta H_{R298}^0 = -41170 \frac{J}{mol} \]

From equation 2.2.10 the enthalpy of reaction at temperature of 0°C is
\[ \Delta H_o = -3923459 \frac{J}{mol} \]

By using the values of \( \Delta a, \Delta b, \Delta c, \Delta H_o \) and \( \Delta G_{R298}^0 \) the IR constant can be calculated according to equation 2.2.13
\[ \text{IR} = 53.347 \frac{J}{mol \cdot K} \]

From equation 2.2.9 the enthalpy of the reaction can be determined at any temperature by the following equation:
\[ \Delta H_{R,T} = -39293.459 - 18 \cdot T + 54.607 \cdot 10^{-3} \cdot T^2 - 5.146 \cdot 10^{-5} \cdot T^3 \]

According to equations 2.2.12 and 2.2.15 the standard Gibbs free-energy change and the equilibrium constant can be calculated as follows:
\[ \Delta G_{R,T} = -39293.459 + 18 \cdot T \cdot \ln T - 54.607 \cdot 10^{-3} \cdot T^2 + 2.573 \cdot 10^{-5} \cdot T^3 - 53.347 \cdot T \]
\[ K_p = \exp\left(\frac{-39293.459 + 18 \cdot T \cdot \ln T - 54.607 \cdot 10^{-3} \cdot T^2 + 2.573 \cdot 10^{-5} \cdot T^3 - 53.347 \cdot T}{8.314 \cdot T} \right) \]

Representative results are shown in Figures 2.14, 2.15, 2.16, 2.17, 2.18 where the changes of Gibbs free-energy (\( \Delta G_T^0 \)), enthalpy (\( \Delta H_T^0 \)), entropy (\( \Delta S_T^0 \)), equilibrium constant of the reaction as well as the equilibrium conversion of CO are plotted as functions of reaction temperature. The results obtained show that Gibbs free energy of the reaction increases with increasing temperature and becomes positive at temperatures higher than 950 K. The reaction is exothermic, with \( \Delta H_{R,T}^0 \) and \( \Delta S_{R,T}^0 \) decreasing from -41.15 to -55.6 and from -42.1 to -59.02, respectively, with increasing the temperature from 273 to 1023K.
**Figure 2.14:** $\Delta G^0_T$ dependence on temperature in water gas shift reaction.

**Figure 2.15:** $\Delta H^0_T$ dependence on temperature in water gas shift reaction.

**Figure 2.16:** $\Delta S^0_T$ dependence on temperature in water gas shift reaction.

**Figure 2.17:** Effect of temperature on equilibrium constant of water gas shift reaction.

**Figure 2.18:** Effect of temperature on CO conversion in water gas shift reaction.
2.6 Methanol dehydration to DME

\[ 2\text{CH}_3\text{OH} = \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (2.4) \]

From the data listed in Table 2.1 \((a, b, c, \Delta G_{f,298K}^0, \Delta H_{f,298K}^0)\) for \(\text{CH}_3\text{OH}, \ \text{CH}_3\text{OCH}_3\) and \(\text{H}_2\text{O}\) and the use of equations 2.2.4 to 2.2.8 the values of \(\Delta a, \Delta b, \Delta c, \Delta G_{R,298}^0\) and \(\Delta H_{R,298}^0\) have been calculated as follows:

\[
\Delta a = -5.587 \frac{J}{\text{mol} \cdot K} \\
\Delta b = -131.828 \cdot 10^{-3} \frac{J}{\text{mol} \cdot K} \\
\Delta c = -34.237 \cdot 10^{-5} \frac{J}{\text{mol} \cdot K} \\
\Delta G_{R,298}^0 = -16860 \frac{J}{\text{mol}} \\
\Delta H_{R,298}^0 = -24040 \frac{J}{\text{mol}}
\]

From equations 2.2.10 and 2.2.13 the enthalpy of reaction at temperature of 0\(^\circ\)K and the IR constant for this reaction take the following values:

\[
\Delta H_o = -25208388 \frac{J}{\text{mol}} \\
\text{IR} = -10.758 \frac{J}{\text{mol} \cdot K}
\]

According to equations 2.2.9, 2.2.12 and 2.2.15 the enthalpy, Gibbs free-energy change and the equilibrium constant of the title reaction can be calculated as follows

\[
\Delta H_{R,T} = -25208.388 - 5.587 \cdot T + 65.914 \cdot 10^{-3} \cdot T^2 - 11.412 \cdot 10^{-5} \cdot T^3 \\
\Delta G_{R,T} = -25208.388 + 5.587 \cdot T \cdot \ln T - 65.914 \cdot 10^{-3} \cdot T^2 + 5.706 \cdot 10^{-5} \cdot T^3 + 10.758 \cdot T \\
K_p = \exp\left( -\left(-25208.388 + 5.587 \cdot T \cdot \ln T - 65.914 \cdot 10^{-3} \cdot T^2 + 5.706 \cdot 10^{-5} \cdot T^3 + 10.758 \cdot T \right) / 8.314 \cdot T \right)
\]

In Figures 2.19, 2.20, 2.21, 2.22 are plotted the changes of Gibbs free-energy \((\Delta G^0_T)\), enthalpy \((\Delta H^0_T)\), entropy \((\Delta S^0_T)\), as well as equilibrium constant of the methanol dehydration to dimethyl ether reaction as functions of temperature. It is observed that the reaction is exothermic, with \(\Delta H^0_T\) and \(\Delta S^0_T\) decreasing from -23.7 to -83.7 kJ mol\(^{-1}\)
and from -23.9 to -98.9 kJ K\(^{-1}\), respectively, with increasing temperature in the range of 0-750 °C. The reaction is not favored thermodynamically at temperatures higher than 525 °C, where \(\Delta G^\circ_T\) takes positive values.

**Figure 2.19**: \(\Delta G^\circ_{R,T}\) dependence on temperature in methanol dehydration to DME reaction.

**Figure 2.20**: \(\Delta H^\circ_{R,T}\) dependence on temperature in methanol dehydration to DME reaction.

**Figure 2.21**: \(\Delta S^\circ_{R,T}\) dependence on temperature in methanol dehydration to DME reaction.

**Figure 2.22**: Effect of temperature on equilibrium constant of methanol dehydration to DME reaction.
When methanol is produced via hydrogenation of CO\textsubscript{2}, the gas mixture contains considerable amounts of water steam. Thus it is important to study the effect of water presence in the feed composition for the methanol dehydration to dimethyl ether reaction. Figure 2.23 shows the equilibrium conversion of methanol as a function of reaction temperature in (a) the absence and (b) in the presence of 10\% H\textsubscript{2}O in the initial reactants composition. It is observed that the equilibrium conversion decreases from 94\% to 79\% by increasing temperature from 150 to 500 oC. Addition of 10\% water results in a slight decrease of equilibrium conversion values. For example, at 150 oC the conversion of methanol is 92 \% and at 500 oC is 73 \%. Thus, as expected, when water is added in the feed, dehydration of methanol to dimethyl ether is inhibited.

The calculated values for selectivity to dimethyl ether in the temperature range of 150 to 500 oC were found to be constant at 100\% both in the absence and in the presence of water in the feed.

Figure 2.23: Equilibrium conversion of methanol as a function of temperature in (a) the absence and (b) in the presence of 10\% H\textsubscript{2}O in the feed. P=1\textit{bar}, T=150-500 oC

2.7 One step hydrogenation of CO\textsubscript{2} to Methanol/DME

\textit{2CO}_2 + 6\textit{H}_2 = \textit{CH}_3\textit{OCH}_3 + 3\textit{H}_2\textit{O} (2.5)

From the data listed in Table 2.1 (\(a, \ b, \ c, \ \Delta G^0_{298K}, \ \Delta H^0_{298K}\)) for CO\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{3}OCH\textsubscript{3}, H\textsubscript{2}O and the use of equations 2.2.4 to 2.2.8, the values of \(\Delta a, \Delta b, \Delta c, \Delta G^0_{R,298}\) and \(\Delta H^0_{R,298}\) have been calculated:
\[ \Delta a = -52.127 \frac{J}{mol \cdot K} \quad \Delta b = -260.112 \cdot 10^{-3} \frac{J}{mol \cdot K} \quad \Delta c = 72.677 \cdot 10^{-5} \frac{J}{mol \cdot K} \]

\[ \Delta G_{R298}^{0} = -9420 \frac{J}{mol} \quad \Delta H_{R298}^{0} = -122520 \frac{J}{mol} \]

According to equations 2.2.10 and 2.2.13 the enthalpy of reaction at temperature of 0°K and the IR constant for the title reaction take the following values

\[ \Delta H_{o} = -101847642 \frac{J}{mol} \quad \text{IR}=14.812 \frac{J}{mol \cdot K} \]

From equations 2.2.9, 2.2.12 and 2.2.15 the enthalpy, Gibbs free-energy change and the equilibrium constant of the title reaction are determined as follows:

\[ \Delta H_{R,T} = -101847.642 - 52.127 \cdot T - 130.056 \cdot 10^{-3} \cdot T^2 + 24.226 \cdot 10^{-5} \cdot T^3 \]

\[ \Delta G_{R,T} = -101847.642 + 52.127 \cdot T \cdot \ln T + 130.056 \cdot 10^{-3} \cdot T^2 - 12.113 \cdot 10^{-5} \cdot T^3 - 14.812 \cdot T \]

\[ K_p = \exp\left(-\left[-101847642 + 52.127 \cdot T \cdot \ln T + 130.056 \cdot 10^{-3} \cdot T^2 - 12.113 \cdot 10^{-5} \cdot T^3 - 14.812 \cdot T\right] \right) \]

Results of the thermodynamic study for the changes of Gibbs free-energy (\(\Delta G_T^0\)), enthalpy (\(\Delta H_T^0\)), entropy (\(\Delta S_T^0\)) and the equilibrium constant of the reaction are shown in Figures 2.24, 2.25, 2.26, 2.27. In Figure 2.28 the equilibrium conversion of carbon dioxide is plotted as function of reaction temperature and pressure.

**Figure 2.24:** \(\Delta G_T^0\) dependence on temperature in CO\(_2\) hydrogenation to methanol/DME reaction.

**Figure 2.25:** \(\Delta H_T^0\) dependence on temperature in CO\(_2\) hydrogenation to methanol/DME reaction.
Figures 2.29, 2.30, 2.31 and 2.32 represent the effect of CO$_2$:H$_2$ molar ratio on CO$_2$ conversion and selectivities towards methanol, DME and CO respectively. As shown in Fig. 2.29, the CO$_2$ equilibrium conversion curve shifts upwards with increasing the H$_2$ content. A slight variation of methanol selectivity is predicted by thermodynamic calculation (11-15%) when the CO$_2$:H$_2$ ratio is 1:3.
When the H₂ content in the feed increases, a small increase of methanol selectivity is observed at high temperatures (Fig. 2.30). A similar behavior is observed for selectivity to dimethyl ether (Fig. 2.31). On the contrary, the CO selectivity
decreases in the presence of excess of H₂ (Fig. 2.32).

**Fig. 2.33** shows the equilibrium conversion of CO₂ for the methanol synthesis (reaction 2.1) and the methanol/dimethyl ether synthesis (reaction 2.5). The beneficial effect of the simultaneous methanol/dimethyl ether production is obvious. At a temperature of 200 °C and pressure of 30 bar the CO₂ conversion to methanol/dimethyl ether is 37%, while CO₂ conversion to methanol alone is only 24%. In **Fig. 2.34** are plotted the selectivity toward methanol (trace a) and methanol/dimethyl ether (trace b) as a function of reaction temperature. It is worth to say that the selectivity of desired products can be kept at almost 100% through the one step process (reaction 2.5) at relatively low temperatures (up to 220 °C). Thus, from the thermodynamic point of view, the methanol/dimethyl ether synthesis via the one-step CO₂ hydrogenation reaction (reaction 2.5) is more favorable compared to that of methanol synthesis alone (reaction 2.1).

![Graph](image1.png)

**Figure 2.33**: Equilibrium conversion of CO₂ as a function of temperature in (a) methanol synthesis and (b) methanol/DME synthesis. $P=30$ bar, $CO₂:H₂=1:3$, $T=160-280°C$.

![Graph](image2.png)

**Figure 2.34**: Selectivities to reaction products as functions of temperature in (a) methanol synthesis and (b) methanol/DME synthesis. $P=30$ bar, $CO₂:H₂=1:3$, $T=160-280°C$.  

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2.8 Conclusions

A detailed thermodynamic analysis has been performed for the CO$_2$ hydrogenation to methanol/dimethyl ether reaction. The effects of temperature, pressure and feed composition on the equilibrium conversion of reactants and selectivities to the main products have been investigated. The general conclusions of this study are summarized below:

The methanol synthesis both from CO and CO$_2$ is thermodynamically restricted being favorable at low temperatures and high pressures. This thermodynamic restriction represents a major challenge in commercial methanol synthesis. An efficient way to by-pass it, is the continuous removal of methanol from the reaction system, either physically or by transforming to another product.

The results of thermodynamic calculations elucidate, that the co-production of DME during CO$_2$ hydrogenation permits higher CO$_2$ conversion and higher selectivity toward oxygenates (methanol/DME mixture) compared to those obtained over methanol synthesis alone. In other words, when methanol synthesis and methanol dehydration reactions are employed in tandem, the thermodynamics is forced to shift toward the desired direction. The mitigation of thermodynamic restriction in this way enables also to apply lower reaction pressures than those required for methanol synthesis alone. Thus, from the thermodynamic point of view, the simultaneous production of methanol/DME via hydrogenation of CO$_2$ is an interesting and efficient way to overcome the limitations of methanol synthesis and represents a promising process for industrial applications.

Results of thermodynamic analysis for direct CO$_2$ hydrogenation to methanol/DME reaction indicate also that the reaction is very exothermic thus the reaction temperature must be controlled. In addition, the excess of H$_2$ content results in increase of CO$_2$ conversion, selectivities to oxygenates and decrease of selectivity to CO.
2.9 References


This chapter describes the experimental setups and techniques that have been employed for the characterization of catalytic materials. These include the methods used to determine the textural properties (B.E.T and B.J.H. methods), crystallinity, phase composition, morphology (XRD, ICP-AES, TEM, and HTEM methods), and acidity (TPD of ammonia and pyridine) of materials and the equipment used to evaluate the catalytic performance.

### 3.1 Textural properties of materials (B.E.T and B.J.H Methods)

Gas adsorption methods are extensively used for the characterization of porous solids. Of particular importance is the application of physical adsorption for the determination of the specific surface area and pore size distribution of catalysts with the use of methods such as BET and BJH.

Gas adsorption (particularly physical adsorption) occurs whenever a gas (the adsorptive) interacts with the surface of a solid (the adsorbent) and forms the adsorbate (Figure 3.1). As gas adsorption proceeds, molecules are attracted to the pore surface of the solid (Figure 3.2 A). The specific surface area can be evaluated at the stage where the first monolayer forms (Figure 3.2 B).

**Figure 3.1:** Physical adsorption scheme.
3.1.1 Determination of specific surface area by the B.E.T method

The specific surface area (SSA) is undoubtedly one of the most important characteristics of solids. The SSA can be determined by the BET method, which is based on the adsorption of probe gases to the surface of solids. The main idea of BET analysis is that, at low relative pressures, gas molecules of known size adsorb on the surface of solid to form a monolayer (Figure 3.2 B). Adsorption isotherms can be obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at a constant temperature (77 K when nitrogen is used as adsorptive). In order to cover entirely the surface of solids and to have measurable amounts of adsorption, the surface must be cooled [2, 3]. Once the amount of adsorbate required to form a monolayer is known, the surface area of the material can be determined by using the average cross-sectional area of the adsorbate molecule [4].

Nitrogen is the most commonly used gas for such measurements because of its favourable characteristics. These include its relatively strong interaction with solid surfaces and the well-known cross-sectional area of adsorbed nitrogen molecules. In addition, the value of constant “C” in the BET equation (see below, eq. 3.1) is sufficiently small to prevent localized adsorption and yet adequately large to prevent the adsorbed layer from behaving as a two dimensional gas. Furthermore, nitrogen is a good coolant and it is available in high purity.

The BET theory has been developed and published in 1938 by S. Brunauer, H. P. Emmett and E. Teller [5], who extended Langmuir’s kinetic theory of multilayer adsorption. The BET theory assumes that when the surface is covered with only one layer of adsorbate, an equilibrium is established between that layer and the vapor, and where two layers are adsorbed, the upper layer is in equilibrium with the vapor, and so forth. Since the equilibrium is dynamic, the actual location of the surface sites covered by one, two or more layers may vary but the number of
molecules in each layer remains constant [2].

By using the Langmuir theory and equation as a starting point Brunauer, Emmett and Teller expressed the BET equation as follows

\[
\frac{1}{V \cdot \left(\frac{P_0}{P} - 1\right)} = \frac{1}{V_m \cdot C} + \frac{(C - 1) \cdot P}{V_m \cdot C \cdot P_0}
\]

where \( P \): is the equilibrium pressure of the adsorbate
\( P_0 \): is the saturation pressure of adsorbate
\( V \): is the quantity of adsorbed gas
\( V_m \): is the quantity of monolayer adsorbed gas
\( C \): is the BET constant, which is expressed by the following equation

\[
C = \frac{\exp(Q_1 - Q_2)}{RT}
\]

where \( Q_1 \): is the heat of adsorption for the first layer
\( Q_2 \): is the heat of adsorption for the second layer.

In Figure 3.3 is depicted a plot of \( \frac{P}{V(P_0 - P)} \) as a function of \( \frac{P}{P_0} \) which is known as BET plot. The slope \( A \) and the intercept \( B \) of the BET plot are

\[
A = \frac{C - 1}{V_m C}, \quad B = \frac{1}{V_m C}
\]

From these two equations the values of \( V_m \) and \( C \) can be calculated

\[
V_m = \frac{1}{A + B}, \quad C = 1 + \frac{A}{B}
\]

Figure 3.3: BET plot.
With the use of $V_m$, the total surface area can be calculated by the following equation

$$S_t = \frac{V_m \cdot N \cdot A}{M_v}$$

where

- $N$ : is the Avogadro’s number
- $A$ : is the cross sectional area of the adsorbate. For nitrogen, $A$ is equal to 0.162 nm$^2$
- $M_v$ : is the molar volume and equals 22400 ml

Finally, the specific surface area can be calculated by dividing the $S_t$ to the sample weight

$$S_{BET} = \frac{S_t}{m} \left[ \frac{\text{m}^2}{\text{g}} \right]$$

3.1.2 Characterization of porous materials

The extension of the physical sorption process described in Section 3.1 (Figure. 3.2) results in the formation of multilayers on the pore surface. As the pressure increases the gas initially adsorbs in pores with the smallest sizes (Figure 3.4 A). Further extension of this process results to saturation, when all pores are completely filled (Figure 3.4 B). Adsorption isotherms can be obtained across this wide range of relative pressure and by studying the adsorption/desorption branches of the recorded isotherms and hysteresis loops the characterization of pore features (pore size, shape, volume) can be obtained.

![Figure 3.4:](image)

**Figure 3.4:** (A) Gas adsorption process, and (B) formation of multilayers [1].

3.1.2.1 Adsorption isotherms

In 1985, the IUPAC proposed the final classification of the physisorption isotherms which consist of six types of isotherms as shown in Figure 3.5. Type I
isotherms (the Langmuire isotherm) are obtained for microporous adsorbents which are characterized by relatively small external surfaces. The exposed surface resides within the micropores and leaves little or no external surface for additional adsorption. **Type II** isotherms are most commonly observed with non porous adsorbents with strong fluid wall attractive forces. The knee of the isotherms indicates the monolayer coverage. Further increase of the relative pressure results in multilayer adsorption. **Type III** isotherms are characteristic of processes where the heats of adsorption are lower than the adsorbate heat of liquefaction. Thus, as adsorption proceeds, additional adsorption is facilitated because the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface. **Type IV** isotherms are mainly encountered with mesoporous adsorbents and present the monolayer-multilayer adsorption isotherms similar to **Type II**. The knee of the isotherm corresponds to the completion of the first monolayer which occurs at low pressures. At higher pressures, a progressive filling of the pores occurs by capillary condensation processes. **Type V** isotherm is not very common, but can be observed with certain porous adsorbents. It is related to weak adsorbate-adsorbent interaction similar to the Type III isotherms. Both Type IV and V isotherms exhibit hysteresis loops. **Type VI** isotherm occurs for some non-porous materials and represents a stepwise multilayer adsorption [2, 6-8].

![IUPAC classification of adsorption isotherms](image)

**Figure 3.5:** IUPAC classification of adsorption isotherms.

### 3.1.2.2 Capillary condensation and hysteresis loops

The sorption behaviour in mesopores depends on the fluid-wall attraction and the attractive interactions between the fluid molecules. This leads to the
occurrence of multilayer adsorption and capillary (pore) condensation (at $P/P_0 \approx 0.2$). The pore walls are covered by a multilayer adsorbed film at the onset of pore condensation [3]. In this process, gas molecules condense into a liquid-like phase in the pores at pressures lower than the saturation pressure. Capillary condensation is very often accompanied by hysteresis, which makes the pore size analysis more complicated. Adsorption hysteresis occurs when there are differences between adsorption and desorption curves of the isotherms. According to the IUPAC classification the adsorption desorption hysteresis loops are categorized into four types, denoted as H1, H2, H3, and H4, which are shown in Figure 3.6. Type H1 is characteristic of porous material possessing cylindrical pores open at both ends. The adsorption and desorption branches are almost vertical and parallel to each other. Type H2 hysteresis loop is associated with complex pore networks and is more difficult to interpret. The pore structure commonly consists of pores with ill-defined shape and wide pore size distribution.

Figure 3.6: IUPAC classification of hysteresis loops.

Type H3 hysteresis loop does not exhibit any limiting adsorption at high relative pressures, and is observed for aggregates of plate-like particles which give rise to slit-shaped pores. Finally, Type H4 is characteristic of complex structures containing both micropores and mesopores and is often associated with narrow slit-like pores [3, 4]

3.1.2.3 Porosity

Porous materials are important in numerous applications, including photovoltaics, catalysis, sensing, filtration, sorption, thermal insulation, fabrication of lightweight structures, and regenerative medicine [9]. Pores can be classified according to their orientation in the material, availability to an external fluid, width (size) and shape, and dimensional structure. Generally, pores can be of two main
kinds: open and closed. In Figure 3.7 is shown a schematic picture of a porous material. Closed pores are active in macroscopic properties but inactive in fluid flow or gas adsorption processes. As shown in Figure 3.7 region a they are completely isolated from neighbours, without any contact with the external surface. In Figure 3.7 b, c, d, e and f regions are open pores because they are connected with the material surface. These pores are used for separation, catalysis and sensing applications [10]. Pores which are open only in one end are named as blind pores (b, f regions) while pores with two open ends are called through pores (e region). Speaking about the open pores one should make a distinction between pores and surface roughness.

![Figure 3.7: Schematic cross-section of a porous material [7].](image)

Surface roughness is commonly found at the external surface, it is larger and more diffused on the surface than deeper in the material (Figure 3.7 g).

The pore width is defined as the diameter in case of a cylindrical pore and as the distance between opposite walls in case of a slit pore [3]. According to the International Union of Pure and Applied Chemistry (IUPAC 1972) pore sizes are classified as follows: macro- (>50 nm), meso- (2–50 nm) and micro- (<2 nm). Pores may also be classified according to their shape. They may be cylindrical, slit-shape, cone-shape and ink bottle (Figure 3.8).

![Figure 3.8: Types of pores according to the pore shape: (a) cylindrical, (b) slit-shape, (c) cone-shape and (d) ink bottle [11].](image)
To make a quick distinction between different porous systems, it is convenient to use the parameter “porosity” (denoted $\varnothing$) which is a measure of the void spaces in a material and is defined as the ratio of pore volume to total volume (bulk volume):

$$\varnothing = \frac{\text{pore volume}}{\text{total volume}}$$  \hspace{1cm} 3.5

Porous materials can be separated also into three types according to their porosity: low porosity (below 1-10%), medium porosity (10–70%) and high porosity (more than 70%) [12].

3.1.2.4 Pore size distribution (PSD)

The pore size distribution (PSD) is one of the important attributes that is used for characterization of porous materials, and is defined as the distribution of pore volume with respect to pore size. It is an important factor which controls the diffusion of reactants and products in the porous catalyst and thus an essential property for catalyst characterization [13]. In catalytic systems a deactivation of catalysts can occur through the pore blockage. The study of pore volume and size distribution can be used to control such processes by comparing the used catalyst with the fresh one.

Numerous methods and theories exist for the estimation of pores characteristics. Dubinin-Radushkevich approach, Horvath and Kawazoe (HK) methods are used for micropore size materials but are not suitable for mesopore materials. For macroporous and some mesoporous materials the Kelvin equation (e.g. BJH-method) is commonly applicable [14].

The Kelvin equation (3.6) is used to interpret type IV isotherms, which are the general isotherms for adsorption on mesoporous materials

$$\frac{\ln P}{P_0} = -\frac{2\gamma V}{rRT}$$  \hspace{1cm} 3.6

where $P_0$: is the saturated vapor pressure at absolute temperature $T$
$\gamma$: is the surface tension
$V$: is the molar volume of the liquid
$r$: is the radius of the cylindrical pore
$R$: is the gas constant
This equation applies to the range of the isotherm that corresponds to capillary condensation, that is, the section of the isotherm above the first “knee”. Using the Kelvin equation, one can calculate the value of the pore radius for any point on the isotherm. According to the capillary condensation hypothesis, all the pores with radii smaller than that size become filled at that pressure. Consequently one can obtain the cumulative pore volume as a function of pressure. The pore size distribution is then obtained by taking the derivative of the cumulative pore volume as a function of pore radius [15].

3.1.3 Apparatus and experimental procedures

A Micromeritics TriStar 3000 apparatus has been used for the determination of the specific surface area of the catalysts using N\textsubscript{2} adsorption at the temperature of liquid nitrogen (-196 °C) by applying the BET method. The TriStar 3000 is an automated gas adsorption analyzer which contains three ports, allowing to analyze up to three samples simultaneously. It consists of the TriStar analyzer, a FlowPrep degasser for preparing samples, a vacuum pump, and a control module for analysis and report options. The FlowPrep is a degassing unit which is used to remove adsorbed contaminants from the surface and pores of a sample before analysis [16].

It is important to know the true sample mass, because results are expressed in units of surface area per gram of sample. For this reason, prior to the analysis, the weight of the empty tube and then of the same tube containing the sample (~100 mg) was measured. After the sample has been weighted the moisture and other substances adsorbed on the surface of the sample, were removed \textit{in situ} by heating at 573 K for 1 h under a stream of nitrogen with a use of Flowprep 060 degasser. When the degassing procedure was completed, the sample weight was measured once again to record the sample mass after degassing. Afterwards the sample was transferred to an analysis port where the measurement was accomplished.

SSAs were calculated following the standard B.E.T. method for nitrogen relative pressures in the range 0.06 < \( P/P_0 \) < 0.20. Together with SSA, the pore size and volume have been also determined. Pore size distribution of the samples was determined following the Barret–Joyner–Halenda (BJH) method at liquid nitrogen temperature (-196 °C) using the apparatus software.
3.2 X-ray diffraction (XRD)

Generally, solid materials may be amorphous or crystalline. An amorphous material does not have any regular arrangement of atoms. In contrast, a crystalline material can be represented by a regular unit cell, which is considered as the smallest building block of atoms in space. The arrangement of these unit cells in three dimensions builds a crystal lattice [17-19]. The dimensions of the unit cell in a crystalline material can be described by three axes namely: a, b, c and the angles between the axis are α, β, γ [17]. A schematic diagram of a unit cell is given in Figure 3.9. X-ray diffraction (XRD) is a nondestructive spectroscopic technique used for elucidation the structural properties of crystalline materials. It is an essential method for characterization of solid catalytic systems, because most of these materials (about 95%) are crystalline.

![Figure 3.9: A unit cell from a three dimensional lattice](image)

Determination of crystal structures are possible when x-rays, electrons or neutrons are allowed to diffract from crystals. Since the diffracted beams appear at characteristic diffraction angles and intensities determined by crystal structure, the beam positions and intensities in the diffraction patterns can be used to determine the crystal structure of materials [18]. XRD is the most powerful technique which gives information from phase composition to crystallite size and from lattice strain to crystallographic orientation [17]. It is also the most common method used by scientists due to the following reasons: (a) only a very small amount of sample is required, (b) the specimen preparation is very easy and (c) the investment in capital equipment required for obtaining diffraction patterns is relatively small [18].
3.2.1 X-rays: Properties and Production

X-rays were discovered in 1895 by the German physicist Roentgen and were so named because their nature was unknown at that time. X-rays are electromagnetic radiation of the same nature as light but of much shorter wavelength. X-rays used in diffraction experiments have wavelengths lying approximately in the range 0.5-2.5 Å, whereas the wavelength of visible light is of the order of 6000 Å. X-rays therefore occupy the region between gamma and ultraviolet rays in the complete electromagnetic spectrum (Fig. 3.10) [19].

![Figure 3.10: X-ray region as part of electromagnetic spectrum.](image)

X-rays are produced when fast-moving electrons are suddenly stopped by a metal target. This is achieved in an X-ray tube consisting of two metal electrodes enclosed in a vacuum chamber. Electrons are produced by heating a tungsten filament cathode, maintained at a high negative potential (30-50kV). The electrons produced are accelerated toward the anode (the metal tungsten is a typical example). The high energy electrons lose their energy by collision with a water-cooled anode and this loss of energy is manifested as x-rays (Figure 3.11). Actually, less than 1 % of the electrons energy is converted to x-rays and the rest is dissipated as heat [18].

![Figure 3.11: Schematic diagram of an X-ray tube.](image)
3.2.2 X-ray diffraction and Bragg’s equation

In order to describe the phenomena of diffraction by atoms of a crystal, one should introduce two important terms: scattering and interference. When x-rays of a given frequency incident an atom, they interact with its electrons, causing them to oscillate with the frequency of the x-ray beam. Since electrons become vibrating electrical charges, they reradiate the x-rays with no change in frequency. These reflected rays come off the atoms in any direction [20]. In other words, a general scattering occurs. Scattering is a process when the incident radiation is absorbed and then reemitted in different directions. If scattering takes place from many atoms, the scattered waves from the different atoms can interfere. Interference is the superposition of two or more of these scattered waves producing a resultant wave that is the sum of the overlapping wave contributions. There are two main types of interferences: constructive and destructive. If the waves are in phase, with the same wavelength but different amplitude then constructive interference occurs (Fig. 3.12 A). If the waves are 180° out of phase, with exactly the same wavelength and amplitude then the destructive interference occurs (Fig. 3.12B). Finally, a diffraction may be defined as constructive interference of more than one scattered wave [18, 21].

![Figure 3.12: (A) Constructive and (B) Destructive interferences between two waves.](image)

The main target of x-ray diffraction by crystals is to know the highly restricted conditions in which the scattered x-rays from atoms and the incident x-rays are completely in phase and reinforce each other to produce a detectable diffraction beam. The law that governs the latter case is known as Bragg’s law, which relates the wavelength of the x-rays to the spacing of the atomic planes, d, in a crystal in a very simple equation [18, 20, 22]. The equation, known as Bragg equation, can be easily derived from basic principle of scattering. The derivation of the Bragg equation can be easily done by using the Figure 3.13 in the following
way: Let us assume that x-rays beam ray $a_1$ and $a_2$ impinge at an angle $\theta$ onto a set of parallel planes (hkl), A and B (Fig. 3.13). The line oA$_i$ is drawn perpendicular to the incident rays and is therefore a wave front. Points o and m, which lie on this wave front, must be in phase. The line oA$_r$ is drawn perpendicular to the reflected rays $a_1$ and $a_2$, and the condition for oA$_i$ to be a wave front is that the reflected rays must be in phase at points o and n. This condition can only be satisfied if the distance mpn equals a multiple of a complete wavelength; that is, it must equal $\lambda$ or $2\lambda$ or $3\lambda$ or $n\lambda$, where $\lambda$ is the wavelength of X-rays and n is an arbitrary integer [20].

![Figure 3.13: Schematic figure used to derive the Bragg equation [20].](image)

An examination of Fig. 3.13 shows that both the distances mp and pn equal $d \sin \theta$. The distance mpn is, accordingly, $2d \sin \theta$. If this quantity is equated to $n\lambda$, the Bragg’s equation is obtained (eq. 3.7)

$$n\lambda=2d \sin \theta$$

where

- $n$: (an integer) is the "order" of reflection,
- $\lambda$: is the wavelength of the incident X-rays, nm
- $d$: is the interplanar spacing of the crystal, nm
- $\theta$: is the angle of incidence.

In the Bragg equation, the values of $\lambda$ and $\theta$ are known and, therefore, the d spacing can be calculated. The characteristic set of d-spacings and theirs intensity generated in a typical X-ray scan provides a unique "fingerprint" of the phases present in the sample.

Every crystalline material has its unique x-ray pattern (x-ray intensity versus with scattering angle) and a certain compound has only one unique pattern. Based on this pattern it is possible to characterize the crystalline structure of each material. By this method it is also possible to identify the crystalline phases and
orientations, lattice parameters strain and grain size and atomic arrangements. About 50,000 inorganic and 25,000 organic single components, crystalline phases, diffraction patterns have been collected as standards. The main use of powder diffraction is to identify components in a sample by a search/match procedure. Furthermore, the areas under the peaks are related to the amount of each phase present in the sample.

3.2.3 Experimental

In the present study, the x-ray diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer equipped with a Ni-filtered Cu radiation (Kα1 = 0.15418 nm) and a LynxEye detector, operated at 40 kV and 40 mA. The diffraction patterns were recorded in the range 2° < 2θ < 85° with a step size 0.015° and a scan speed of 0.3 s/step. The phase identification was based on JCPDF data files. The average size of crystallites was assessed using the Scherrer equation (eq 3.8) [19]

\[
d = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta}
\]

where

- d: is the average crystal size
- \(\lambda\): is the X-ray wavelength
- \(\beta\): is the value of line-broadening
- \(\theta\): is the Bragg angle

3.3 Electron microscopy (EM)

Electron microscopy (EM) is a key technique that uses a beam of highly energetic electrons to examine the materials in very fine scale. EM was developed when limitations of Light Microscopes (in the early 1930's) were reached. In that period it was an essential scientific desire to analyze fine materials, which was not possible using Light Microscopes. EM uses a focused beam of electrons to image the sample, while Light Microscopy uses photons. Usually, electrons are more useful than photons for imaging because the electron beam in EM has a much smaller wavelength than light used in light microscopy so it achieves better resolution. EM involves the interaction of accelerated electron source with the sample to be analyzed under vacuum conditions. The resulting interactions cause the emission of various particles or radiation. Collection of these emissions or
radiation using different detectors enables the combination of different types of signals with the purpose of characterizing the materials. As these detected signals result from different mechanisms of formation, they provide additional information for characterization [23].

3.3.1 Electron-matter interaction

Electrons are one type of ionizing radiation, which is the general term given to radiation that is capable of removing the tightly bound, inner-shell electrons from the attractive field of the nucleus by transferring some of its energy to individual atoms in the specimen. One of the advantages of using ionizing radiation is, that once an electron interacts with specimen, it produces a wide range of secondary signals from the specimen, some of which are summarized in Figure 3.14 [24]. Among these, it is essential to understand the electron scattering because it is fundamental to all electron microscopies. As an electron travels through the specimen interaction volume, two types of scattering events occur: elastic and inelastic scattering. In case of elastic scattering no energy interchange occurs. These signals are mainly exploited in TEM and electron diffraction methods. When inelastic scattering occurs, electrons lose their energy while passing through the specimen. In this case several processes may take place and the following signals can be generated: secondary electrons, Auger electrons, characteristic and continuum x-rays, long-wavelength radiation in the visible, IR and UV spectral range (cathodoluminescence), lattice vibrations or phonons, and electron oscillations or plasmons [23-25].

![Figure 3.14: Electron-specimen interaction [24].](image)
3.3.2 Transmission electron microscopy (TEM)

The Transmission Electron Microscope (TEM) was developed by Max Knoll and Ernst Ruska in 1931 Germany. As the name suggests the electrons are transmitted through the specimen in this microscope. TEM is ideal for investigating thin nanomaterials (maximum thickness ~300 nm), as very high resolution is possible (better than ~0.5 nm) using it. Electrons of very high energy (typically >50 keV) are used which pass through a series of magnetic lenses, as in an optical or SEM microscopy [26].

The basic components of TEM are the electron source, condenser lens, specimen, objective lens, diffraction lens, intermediate lens, projector lens and a fluorescent screen in the given order. There may be some additional lenses in different microscopes in order to improve the image quality and resolution. The focal lengths of these electromagnetic lenses are varied to obtain optimized images rather than moving the lenses themselves as is done in an optical microscope. The components of a TEM have to be housed in a chamber under high vacuum (~10^-3 to ~10^-4 Pa) for its proper functioning. As illustrated in Fig. 3.15, TEM has the advantage that one can not only obtain the images of the specimen but also diffraction patterns, which enable to understand the detailed crystal structure of the sample. Using diffraction analysis one can obtain size-dependent changes in the lattice parameters as well as defects in the sample.

![Figure 3.15: Schematic illustration of basic components of TEM](image-url)
The operation of TEM can be described as follows: A stream of electrons formed by an electron gun is directed to the condenser lenses, which focus them onto the specimen so as to illuminate only the area being analyzed. Then the electron beam passes through the condenser aperture and “hits” the surface of the sample. An image is formed in the image plane of the objective lens. The role of this lens is important because this lens generates the first intermediate image. With the selector aperture one can select one area of the image which is then magnified by the magnifying system. The magnifying system consists of intermediate and projector lenses. An intermediate image is formed in the image plane of the intermediate lens. The final image forms by the projector lens on a fluorescent screen or a recording device.

In the present study, TEM and HRTEM images were obtained using a JEM-2100 transmittance electron microscope operating at 200kV. The sample was suspended in water in an ultrasonic bath and then a small droplet was deposited onto a TEM copper grid coated with carbon film.

3.4 Inductive coupled plasma-atomic emission spectroscopy (ICP-AES)

Atomic emission spectroscopy (AES) is one of the oldest spectroscopy techniques. As the name implies, these techniques involve electromagnetic radiation (light) that is absorbed and/or emitted from atoms of a sample. In AES, the atomic emission spectrum of a sample is used for the determination of its qualitative or quantitative elemental composition. Because of its high detection power and the increasing variety of excitation sources available (flames, furnaces, electrical discharges, plasmas), AES is the most universally used method for multi-element analysis [27, 28]. More recently, plasmas have been introduced in AES techniques as atomization/excitation sources. The Inductive Coupled Plasma (ICP) is a well-established AES technique that utilizes plasma as an atomization/excitation source. ICP-AES has proved to be a versatile analysis technique of wide scope and coverage. It allows the direct analysis of liquids, thus including either aqueous or organic solutions, and the method is intrinsically suited for simultaneous multi-element analysis [29].

3.4.1 Absorption of electromagnetic radiation

The phenomena of absorption and emission of electromagnetic radiation can be more easily described once the nature of atomic and ionic spectra is understood. In Figure 3.16 is shown the Bohr model of an atom that comprises a nucleus
surrounded by electrons traveling around the nucleus in discrete orbitals. Every atom has a number of orbitals where the electrons travel. Each of these electron orbitals has an energy level associated with it. When a certain amount of energy is added to the atom it may be excited to a higher energy level. An excited atom is less stable and thus in a very short time it decays back to a lower energy level by losing energy through a collision with another particle or by emission of electromagnetic radiation. As a result the electron returns to an orbital closer to the nucleus [27, 28].

Figure 3.16: Bohr model of an atom. As energy is absorbed by an atom, an electron jumps to an orbital with a higher energy level. The atom may decay to a lower energy state by emitting a photon of energy hv [28].

Figure 3.17 illustrates the excitation, ionization and emission processes schematically, where horizontal lines represent the energy levels of an atom and the vertical arrows represent energy transitions.

Figure 3.17: Energy level diagram depicting energy transitions where (a) and (b) represent excitation, (c) is ionization, (d) is ionization/excitation, (e) is ion emission, and (f), (g) and (h) are atom emission [28].

The difference in energy between the upper and lower energy levels (E) can be expressed by Plank’s equation [27]:

\[ E = h\nu \]  

where
\[ h: \text{is the Planck's constant (} h = 6.626 \times 10^{-34} \text{ J s}) \]
\[ \nu: \text{is the frequency of emitted radiation} \]

Since frequency (\( \nu \)) and wavelength (\( \lambda \)) are related by the equation
\[ \lambda = \frac{c}{\nu} \quad 3.10 \]
where \( c \): is the light speed (\( c = 2.997 \times 10^8 \text{ m s}^{-1} \))

The combination of the 3.9 and 3.10 equations gives
\[ E = \frac{hc}{\lambda} \quad 3.11 \]

The derived equation (3.11) shows the energy-wavelength relation. Every element has its own characteristic set of energy levels and thus its own set of absorption and emission wavelengths. This is the main property that makes atomic spectrometry useful for element-specific analytical techniques.

3.4.2 ICP-AES: Operation and sources

The role of the excitation sources in AES technique is of fundamental importance. An excitation source must be able to remove the water (or other solvent) from a liquid sample (desolvation), break the sample particles into molecules (dissociation), break the molecules into atoms (atomization) and add energy to the atoms (excitation) [27]. In Figure 3.18 are presented the steps involved in determining the elemental content of an aqueous phase sample by ICP-AES.

Generally, there are many types of sources used in analytical atomic spectroscopy to dissociate sample molecules into free atoms: flames, furnaces and electrical discharges, high-power lasers. More recently, other types namely plasmas, have been proposed as atomization/excitation sources for atomic spectroscopy analysis [28, 30]. A plasma is an electrically neutral, highly ionized gas with sufficiently high temperature to atomize, ionize and excite most of the elements of the Periodic Table. Although there have been many attempts to generate plasma with different gases such as oxygen, hydrogen and carbon dioxide, most analytical plasmas operate with pure argon or helium [30, 31]. This is because these gases can be obtained in a relatively pure form also they have good characteristics for atomization, ionization and excitation of the analyte, and are readily available. Plasmas are characterized by their temperature, as well as their electron and ion densities [30, 32].
1. Sample Preparation: Some samples require special preparation steps including dissolution (solid samples) treatment with acids, heating, microwave digestion.

2. Nebulization: Liquid converted to aerosol.

3. Desolvation/Volatization: Water is driven off, and remaining solid and liquid portions are converted to gases.

4. Atomization: Gas phase bonds are broken, and only atoms are present. Plasma temperature and inert chemical environment are important at this stage.

5. Excitation/Emission: Atoms gain energy from collisions and emit light of a characteristic wavelength.


**Figure 3.18:** General steps involved in the analysis of aqueous samples by ICP-AES [32].

In **Figure 3.19** is shown a schematic illustration of an assembly of three concentric glass tubes (named as “torch”), used for generating an ICP. The ICP is generated by coupling the energy from a radio frequency (RF) generator into a suitable gas via a magnetic field which is induced through two- or three-turn, water-cooled copper coil. The plasma has a ‘weak spot’ at the centre of its base, through
which the inner gas flow, containing the sample, is introduced. The spark, a source of ‘seed’ electrons, causes ionization of the argon carrier gas. Subsequent collisions with other gaseous atoms cause further ionization so that the plasma becomes self-sustaining. This occurs almost instantaneously [30, 32-34]

![Figure 3.19: The scheme of an ICP torch [32].](image)

In this study a Plasma 400 (Perkin Elmer) spectrometer, equipped with Cetac6000AT+ ultrasonic nebulizer has been used to determine the chemical composition (wt. % of Al and Na) of the investigated zeolitic and silica-alumina catalysts.

### 3.5 Infrared spectroscopy (FTIR)

The infrared spectroscopy is considered as an essential characterization technique to investigate the molecules structure and bonding. This technique plays an important role in the characterization of heterogeneous catalysts, because it permits direct monitoring of the surface interaction between the adsorbed molecules and the catalysts [35]. As is shown in Figure 3.20, the infrared region is one small part of the electromagnetic spectrum which is located between the visible and microwave regions and it is usually divided in NIR-IR, mid-IR and far-IR
regions. The first region (NIR-IR) allows the study of overtones and harmonic or combination vibrations. The mid-IR region is used to study the fundamental vibrations and the rotation-vibration structure of small molecules, whereas the far-IR region is employed for the low heavy atom vibrations (metal-ligand or the lattice vibrations) [36].

![Image of electromagnetic radiation spectrum](image)

**Figure 3.20**: IR region as a part of electromagnetic radiation spectrum [37].

The infrared spectroscopy is one of the oldest and more versatile experimental techniques which has been commercially available since 1940s. However, the most significant advances in infrared spectroscopy were reached after the introduction of Fourier-transform infrared (FTIR) spectrometers. FTIR spectroscopy has improved dramatically the quality of infrared spectra and minimized the time required to obtain data [38].

3.5.1 *Infrared absorption*

The absorption of infrared radiation by molecules is similar to other absorption processes (Fig. 3.17): molecules are excited to a higher energy state when they absorb infrared radiation. In this absorption process, those frequencies of infrared radiation which match the natural vibrational frequencies of the molecule in question are absorbed and the energy absorbed serves to increase the amplitude of the vibrational motions of the bonds in the molecule. However, not all bonds in a molecule are capable of absorbing infrared energy, even if the frequency of the radiation exactly matches that of the bond motion [39]. The fundamental requirement for infrared activity is that the dipole moment of the molecule or the functional group must change during the vibration (Fig. 3.21). A bond must
present an electrical dipole that is changing at the same frequency as the incoming radiation in order for energy to be transferred. Since every type of bond has a different natural frequency of vibration, and since two of the same type of bond in two different compounds is in two slightly different environments, no two molecules of different structure have exactly the same infrared spectrum. The larger the dipole moment change, the more intense is the absorption band [36, 38, 39].

![Dipole Moment Change](image)

**Figure 3.21**: Change in dipole moment of a heteronuclear diatomic molecule [38].

### 3.5.2 Molecular vibration

All the atoms in molecules are in continuous vibration with respect to each other. Molecular vibrations can range from the simple coupled motion of the two atoms of a diatomic molecule to the much more complex motion of each atom in a large polyfunctional molecule [40]. It is known that a molecule has three independent degrees of freedom of motion. Molecules with N atoms have 3N degrees of freedom, three of which represent translational motion in the x, y, and z axes and three represent rotational motion in x, y, and z axes (two for linear molecules). The remaining 3N-6 (for nonlinear molecules) and 3N-5 (for linear molecules) degrees of freedom give the number of ways that the atoms in nonlinear/linear molecules can vibrate (i.e., fundamental vibrations or normal vibrational modes) [36, 37, 40]. For example, the linear molecule H-Cl has only one vibration along the H-Cl axis as (3x2)-5=1, whereas the non linear molecule H₂O has three vibrational modes as (3x3)-6=3. The two vibrations are along the chemical bonds O-H symmetrical ($\nu_s$) and asymmetrical ($\nu_{as}$) O-H bonds and one bending vibration ($\delta$) which is the angle change of the two bonds in H-O-H [36].

Vibrations can involve either a change in bond length (stretching) or bond angle (bending). When there is a change in bond length it results to symmetric (the
bond length increase or decrease symmetrically) and asymmetric (the bond length increase or decrease asymmetrically) stretching vibration (Fig. 3.22). When there is change in angle between two bonds it results in bending vibrations. There are four types of bending vibrations: scissoring, rocking, wagging, and twisting (Figure 3.22). These two vibrational modes can be analyzed in the mid-IR range because the absorption bands associated with the stretching and bending vibrations in molecules, typically occur in the wavenumber range $\sim500–4000$ cm$^{-1}$ [37].

![Different types of vibrational modes](image)

**Figure 3.22:** Different types of vibrational modes [37].

Three types of instruments for IR absorption measurements are commonly available: (1) dispersive spectrophotometers with a grating monochromator; (2) Fourier-transform (FT) spectrometers, which employ an interferometer and (3) non-dispersive photometers using a filter or an absorbing gas, which are applied for analysis of atmospheric gases at specific wavelengths. Until the 1980s, the most widely used instruments for IR measurements were dispersive spectrophotometers. Today, for mid- and far-IR measurements, this type of instruments has been largely displaced by Fourier-transform spectrometers because of their speed, reliability, improved signal to noise ratio and convenience [41].

Commercially available FTIR-instruments are based on the Michelson interferometer with a movable mirror to acquire an interferogram. The Michelson
The interferometer was invented by Albert Abraham Michelson in the famous Michelson–Morley experiment. The Michelson interferometer is a device that can divide a beam of radiation into two paths and then recombine the two beams after a path difference has been introduced. A condition is thereby created under which interference between the beams can occur. The variation of intensity of the beam emerging from the interferometer is measured as a function of path difference by a detector. The simplest form of the Michelson interferometer is shown in Figure 3.23. It consists of two mutually perpendicular plane mirrors, one of which can move along an axis that is perpendicular to its plane. Bisecting the fixed mirror and the movable mirror is a beamsplitter, where a collimated beam of radiation from an external source can be partially reflected to the fixed mirror (at point F for the median ray) and partially transmitted to the movable mirror (at point M). When the beams return to the beamsplitter, they interfere and are again partially reflected and partially transmitted. Because of the effect of interference, the intensity of each beam passing to the detector and returning to the source depends on the difference in path of the beams in the two arms of the interferometer. The variation in the intensity of the beams passing to the detector and returning to the source as a function of the path difference ultimately yields the spectral information in a Fourier transform spectrometer [40].

Figure 3.23: Optical diagram of a Michelson interferometer [40].
3.5.3 Experimental  
3.5.3.1 In situ DRIFT Spectra  

In situ infrared spectra of the studied catalysts were obtained with the use of a Nicolet 6700 spectrometer equipped with a diffuse reflectance (DRIFT) cell (Spectra Tech), an MCT detector and a KBr beam splitter. The spectrometer consists of following four parts (Figure 3.24)  

- Source  
- Michelson interferometer  
- Sample chamber  
- Detector  

The infrared light from the broadband Source A, is directed into the interferometer and impinges on the IR beamsplitter B (a thin layer of KBr), which splits the incoming beam into two separate beams of approximately the same intensity. One of the beams is reflected off the beamsplitter and is directed onto the fixed mirror C. The second beam is transmitted through the beamsplitter and directed to the moving mirror D.  

![Figure 3.24: Nicolet 6700 optical layout](image)

Afterwards the beams reflect off the surfaces of the two mirrors and recombine at the beamsplitter. Here constructive and destructive interference occurs, depending on the position of the moving mirror relative to the fixed mirror.
The resulting beam passes through the sample chamber where selective absorption takes place and then continues on to the detector [42].

In the sample chamber is placed a Diffuse Reflectance Accessory specially designed for FTIR spectrophotometer (Figure 3.25), which comprises four flat and two ellipsoidal mirrors (M₃ and M₄). Light from the interferometer is reflected by the flat mirrors, M₁ and M₂, onto an ellipsoidal mirror, M₃. This ellipsoidal mirror collects and focuses the light onto the Diffuse Reflectance cell, where the sample is placed (Figure 3.25). The light is diffusely reflected from the sample, and a portion of the reflected light is collected by the second ellipsoidal mirror, M₄. The light is refocused on the flat mirrors, M₅ and M₆, and then onto the detector. Water vapor and carbon dioxide present in the environment can interfere with the sample spectrum because water absorbs around 4000-3500 cm⁻¹ and 2000-1300 cm⁻¹, while carbon dioxide absorbs at 2350 and 688 cm⁻¹. These absorbances may often mask weak features that are of interest. For this reason, dry air is used to purge the sample chamber of water and carbon dioxide.

Figure 3.25: Optical layout of the Diffuse Reflection Accessory (DRIFT) [40].

In Figure 3.26 is illustrated the Diffuse Reflectance cell, which consists of a dome with ZnSe windows and a cylindrical ceramic oven where the sample is placed. The access to the sample is from the top of the attachment of DRIFT accessory (Fig. 3.25), by sliding the ellipsoidal mirrors (M₃ and M₄) out of the way. The dome is sealed properly in order to isolate the ceramic oven and allows the control of the gas phase around the sample. The sample, in the form of very fine powder, is placed in the cylindrical oven. The surface must be as flat as possible, to
increase the intensity of the reflected infrared radiation. The temperature measurement at the catalyst bed is made with the use of a thermocouple positioned in the middle of the bed. A continuous circulation of water around the dome makes possible to obtain spectra at temperatures up to 800°C.

**Figure 3.26:** Diffuse Reflectance cell.

The gas inlet of the cell is directly connected to a flow system equipped with mass flow controllers, two temperature-controlled saturators containing methanol and water, respectively, and a set of valves which allowed selection and control of the feed gas composition. The He streams, which pass through the saturators, are mixed with another He stream to give the desired feed composition.

In a typical experiment, the catalyst powder was first treated at 450°C under He flow for 10 min and subsequently cooled down to room temperature (RT) under He flow. During the cooling stage, background spectra were collected at temperatures of interest. In situ TPD-DRIFTS experiments were performed following interaction of the pretreated sample with a flowing gas mixture consisting of either 1.5%H₂O (in He) or 0.5%CH₃OH (in He) at 25°C for 30 min, purging with He for 30 min, and subsequent stepwise heating (with 50°C increments) under He
flow up to 450 °C. The same procedure was followed to investigate the reactivity of methanol in the presence and in the absence of water in the feed (TPSR-DRIFTS experiments), with the exception that interaction of the catalyst with 0.5%CH₃OH (in He) or 1.5% H₂O + 0.5% CH₃OH (in He) at 25°C for 30 min was followed by heating under a flow of the same reaction mixture. Spectra were recorded after reaching the desired temperature at a resolution of 4 cm⁻¹. In all experiments, the total flow rate through the DRIFT cell was 30 cm³min⁻¹.

3.5.3.2 FT-IR spectroscopy combined with in-situ pyridine adsorption

A range of experiments have been conducted in order to determine the amount and strength of Brönsted and Lewis acid sites of catalysts (alumina, silica-alumina and zeolites). These experiments were performed by means of Fourier transform–infrared (FT-IR) spectroscopy combined with in situ adsorption of pyridine. The FT-IR spectra were recorded on a Nicolet 5700 FTIR spectrometer (resolution 4 cm⁻¹) using the OMNIC software and a specially designed heated, high-vacuum IR cell with CaF₂ windows. Data processing was carried out by the GRAMS software. All samples were finely ground in a mortar and pressed in self-supported wafers (15 mg cm⁻²). The wafers were outgassed in situ at 450 °C for 1 h under high vacuum (10⁻⁶ mbar) and a background spectrum was recorded at 150 °C. Adsorption/equilibration with pyridine vapours was then conducted at 150 °C, by adding pulses of pyridine for 1 h at a total cell pressure of 1 mbar. Spectra were recorded at 150 °C, after equilibration with pyridine at that temperature and after outgassing for 30 min at higher temperatures, i.e. 250, 350 and 450 °C, in order to evaluate the strength of the acid sites. The bands at 1545 cm⁻¹ (pyridinium ions) and 1450 cm⁻¹ (coordinated pyridine) were used to identify and quantify the Brönsted and Lewis acid sites, respectively, by adopting the molar extinction coefficients provided by [43].

3.6 Temperature-programmed experiments (TPD and TPR) coupled with mass spectrometry

Temperature-programmed desorption (TPD) of probe molecules is a widely used method for analyzing the adsorption/desorption properties of solid catalysts. TPD gives information about the energy required for each respective molecule to desorb and for the relative coverage of the desorbing species.

The main idea of this technique is that the probe molecules interact with the catalyst surface and adsorb onto it to a fixed coverage θ at a temperature T₀ for
which desorption is impossible. Subsequently, the surface temperature is ramped up linearly with time $t$ according to
\[ T = T_0 + \beta t \]  
where
\[ \beta \] is the heating rate

As the temperature increases, energy is provided to the adsorbed species which results to their desorption. The desorption rate goes through a maximum at a peak temperature of $T_p$. The desorption rate in general exhibits an Arrhenius type behavior and is expressed by the Polanyi-Wigner equation [44, 45].

\[ \frac{dN}{dt} = -\frac{1}{\beta} v_n N^n \exp\left( -\frac{E_{\text{des}}}{RT} \right) \]  
where
\[ N \] is the concentration of the adsorbed gas
\[ n \] is the order of desorption
\[ E_{\text{des}} \] is the activation energy
\[ R \] is the universal constant

Compared to other analytical techniques, TPD is an inexpensive and simple experimental method to set up and run, and may provide information closely related to the catalytic properties and the reactions in question. With the proper choice of probe molecule, it is frequently possible to relate TPD curves to the catalytic activity and selectivity of a particular catalyst and to determine the probable state of the catalyst under working conditions [46].

3.6.1 Experimental

Temperature-programmed experiments were conducted by using an experimental system depicted in **Figure 3.27**, which consists of a gas flow system, a reactor and an analysis system. The gas flow system consists of a pressure regulator, mass flow meters and valves which regulate, measure and control the inlet gases. The reactor consists of a quartz tube of length 30 cm and outer diameter of 6 mm. In the central part of the tube with a diameter of 8 mm, is placed the catalytic bed. The reactor is placed in the oven the temperature of which is controlled using a K-type thermocouple located between the reactor and the oven walls. The temperature of the sample is measured in the middle of the catalyst bed through a second K-type thermocouple which is placed in a quartz tube of 3 mm
diameter that runs through the catalyst bed. The oven is connected to a programmable temperature controller (Omega CN 2010) that permits linear temperature rise. The device is equipped with appropriate valves (electric actuators) which allow the abrupt change of the reactor feed from one gas mixture another. By appropriate adjustment of valves it is possible to avoid pressure drop in the reactor during such a change. The analysis system consists of mass spectrometer (Omnistar/Pfeiffer Vacuum), which is connected to a computer for recording and analyzing results.

**Figure 3.27:** Schematic representation of the system used for the temperature programmed experiments.

In the present study, temperature-programmed experiments have been used for the investigation of the adsorption/desorption properties of catalysts toward methanol. In addition, the total acidity of samples was measured by temperature-programmed desorption of ammonia (NH$_3$-TPD).

**3.6.1.1 TPD-MS and TPSR-MS of methanol**

In a typical experiment, a pre-weighed amount of catalyst (100 mg) was placed in a quartz microreactor, heated under He flow at 450 °C for 15 minutes to remove adsorbed species from the catalyst surface and subsequently cooled down to room temperature. The feed was then switched to a 0.5% CH$_3$OH (in He) mixture
(30 cm³ min⁻¹) for 30 min, by controlling the flow of two independent He lines, one of which passed through a saturator containing liquid methanol. For TPD-MS experiments the system was then purged with He flow (30 cm³ min⁻¹) for 10 min and temperature was increased linearly (β=15 °C min⁻¹) up to 500 °C. TPSR-MS experiments were performed in a similar manner, with the exception that linear heating was performed under flowing 0.5% CH₃OH (in He) mixture.

An Omnistar/Pfeiffer Vacuum mass spectrometer (MS) was used for on-line monitoring of effluent gas composition. The transient-MS signals at m/z= 2 (H₂), 15 (CH₄), 18 (H₂O), 28 (CO), 31 (CH₃OH), 45 (CH₃OCH₃) and 44 (CO₂) were continuously recorded. Responses of the mass spectrometer were calibrated against standard mixtures of accurately known composition.

3.6.1.2 TPD-MS of ammonia

In a typical experiment, an appropriate amount of catalyst to result in a common SSA of ca. 30 m² for all samples was placed in a quartz reactor and heated at 450 °C under flowing He for 15 min to remove adsorbed species from the catalyst surface, treated with 20% O₂ (in He) at 300 °C for 30 min, purged with He at 450 °C for 15 min and subsequently cooled down to room temperature under flowing He. The flow was then switched to 0.5% NH₃ (in He) for 30 min. Finally, the system was purged with flowing He (30 cm³ min⁻¹ ) for 15 minutes to remove gas-phase and weakly adsorbed ammonia, and the temperature was increased linearly from 25 to 500 °C with a heating rate of 30 °C min⁻¹. The desorption process was monitored by a mass spectrometer (Omnistar/Pfeiffer Vacuum) connected on line with the reactor outlet.

3.7 Experimental setup for methanol dehydration reaction

Catalytic performance tests for methanol dehydration to DME have been carried out using the experimental setup shown in Figure 3.28. The system consists of a flow measuring and control system, the reactor and an on line analysis system. The flow system is equipped with a mass-flow controller (MKS) to control the flow of the inlet gas He, a syringe pump (Brantree Scientific Inc.), which is used for feeding methanol, and a set of valves, which allows selection of gas feed composition and introduction of the gas mixture to the reactor or to a by-pass loop stream. Methanol is pumped into a vaporizer where it is vaporized and heated to 170 °C and mixed with the He stream coming from the mass-flow controller. The
resulting gas mixture is then fed to the reactor through stainless steel tubing maintained at 150 °C by means of heating tapes.

Figure 3.28: Schematic representation of the experimental setup used for the catalytic performance tests for methanol dehydroation reaction.

In Figure 3.29 is presented the schematic diagram of the reactor used for the catalytic performance tests. It consists of a 25-cm long quartz tube (6 mm O.D.) with an expanded 1-cm long section in the middle (8 mm I.D.), in which the catalyst sample is placed. Reaction temperature is measured in the middle of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well, which runs through the cell. The reactor is placed in an electric furnace, the temperature of which is controlled using a second K-type thermocouple placed between the reactor and the walls of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed.

The analysis system consists of a gas chromatograph (Shimadzu) interfaced to a personal computer. The chromatograph is equipped with two packed columns (Porapak-Q, Carbowax) and a TCD detector and operates with He as the carrier gas. The injection of the gas mixture to the desired column is achieved by means of six-
port and four port valves heated at 150 °C.

![Diagram of fixed bed reactor](image)

**Figure 3.29**: Schematic illustration of the fixed bed reactor.

Determination of the response factors of the detectors for methanol, dimethyl ether, CH₄, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ has been achieved with the use of gas streams of known composition. Helium gas (He) is supplied from high-pressure gas cylinder (Messer Griesheim GMBH) and are of ultra-high purity.

In a typical experiment, an amount of 400 mg (for alumina) or 100mg (for zeolites) of fresh catalyst (0.18<d<0.25 mm) was placed in the reactor, heated at 450 °C under He flow and left at that temperature for 1 hour. The flow was then switched to the reaction mixture, which consisted of 30% CH₃OH in He the catalyst was conditioned under reaction conditions at 400 °C for 30 min, and the concentrations of reactants and products at the reactor effluent were determined using the analysis system described above. The conversion of methanol and selectivity to reaction product i (S) were calculated using the following expressions:

\[
X_{\text{MeOH}} = \frac{C_{\text{MeOH}}^{\text{in}} - C_{\text{MeOH}}^{\text{out}}}{C_{\text{MeOH}}^{\text{in}}} \times 100\%
\]

3.14
\[
S_i = \frac{v_i (\text{mol of product } i)}{(C_{\text{MeOH}}^{\text{in}} - C_{\text{MeOH}}^{\text{out}})} \times 100\%
\]

where

\(v_i\): is the number of carbon atoms in molecule \(i\) (e.g., 1 for \(\text{CH}_4\), 2 for \(\text{DME}\) and 3 for \(\text{C}_3\text{H}_8\))

\(C_{\text{MeOH}}^{\text{in}}\): is the inlet concentration of methanol

\(C_{\text{MeOH}}^{\text{out}}\): is the outlet concentration of methanol

Under certain experimental conditions (e.g., reaction over ZSM-5 catalysts at temperatures higher than ca. 300 °C) several reaction products with more than three carbon atoms were formed, which were not quantified separately. Selectivity toward these higher hydrocarbons (HC) has been estimated indirectly using the following expression:

\[
S_{(HC)}(\%) = 100 - \sum_i S_i
\]

where

\(i\) - denotes \(\text{DME, CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{C}_3\text{H}_6\) and \(\text{C}_3\text{H}_8\).

Similar measurements are obtained following a stepwise lowering of temperature, until conversion of \(\text{CH}_3\text{OH}\) drops close to zero. A few more measurements are then obtained by stepwise increasing temperature to check for possible catalyst deactivation. In all cases, data points are averages of at least three measurements. All experiments were performed at near atmospheric pressure.

Kinetic measurements were performed in separate experiments where the conversion of methanol was kept below 15% so that differential reaction conditions could be assumed, with negligible heat and mass transfer effects. Reaction rates were calculated using the following expression:

\[
r_{\text{MeOH}} = \frac{(C_{\text{MeOH}}^{\text{in}} - C_{\text{MeOH}}^{\text{out}}) \cdot F}{W}
\]

where

\(r_{\text{MeOH}}\): is the conversion rate of methanol (mol \(\cdot s^{-1} \cdot g_{\text{cat}}^{-1}\)),

\(F\): is the total flow rate (mol \(s^{-1}\))

\(W\): is the mass of catalyst (g)
3.8 Experimental setup for CO$_2$ hydrogenation to methanol/DME

A home-made reactor system was designed and constructed in order to investigate the catalytic performance of the prepared materials for CO$_2$ hydrogenation to methanol or methanol/dimethyl ether.

The set up consists of three main parts: a flow measuring and controlling system, the reactor and an on line analysis system (Figure 3.30). The flow system is equipped with four mass-flow controllers (Brooks model 5850) and a flow read-out apparatus (Brooks model 0154), which allow to set and control the flow of each gas. Various valves allow the selection of the gas or the gas mixture to be fed into the reactor or to be analyzed by the gas chromatograph. It is also possible to introduce methanol and DME for the calibration of the chromatograph signal.

The reactor assembly consists of two pressure indicators (PI) (for pressures up to 100 bars). One is placed in the reactor inlet line and the other one at the reactor feed effluent line in order to check the pressure before and after the catalytic bed. There are also two pressure relief valves for safety reasons; the valves automatically open to release the gas in case pressure exceeds a certain limit, being 60 bar in the present case.

The catalytic performance tests were carried out in a downflow reactor consisting of a 36-cm long stainless steel tube (12 mm O.D.) with an expanded 4-mm long section in the middle (16 mm I.D.), where a stainless steel porous disk (particles diameter >90μm, Mott Corporation) is placed. This disk holds the catalyst in a fixed position and creates a fixed bed catalytic reactor. The reactor is heated in an electric furnace. The temperature is controlled using a K-type thermocouple placed near to the catalyst bed. The pressure is controlled via a back pressure regulator (BPR) valve which can create pressures up to 70 bars. The reactor effluent is conducted to the analysis section via stainless steel tubing maintained at 180 °C by means of heating tapes to avoid condensation of the products. The chromatograph is equipped with a TCD detector and two packed columns (Porapak-Q, Carbowax) connected in series. Helium (He), of ultra-high purity, is used as carrier gas. The injection of the gas mixture to the columns is achieved by means of two six-port valves and a sampling loop, heated at 160 °C. The response factors for each compound have been determined by using gas streams of known composition.
Figure 3.30: Schematic representation of the experimental setup used for catalytic performance tests for CO₂ hydrogenation to methanol/dimethyl ether reaction.

In a typical experiment, 0.5 g of fresh catalyst for methanol synthesis reaction or 1g for methanol/DME direct synthesis reaction (0.125<d<0.18 mm) was placed in the reactor. Prior to the activity test, the catalyst was reduced in situ with pure H₂, (100ml/min) under atmospheric pressure at 300 °C (temperature increase rate 2 °C/min) for 1 hour. After reduction, the reactor was cooled down to 100 °C. At this temperature the gas mixture was introduced and the pressure was increased. The activity measurements were performed at 3.0 MPa, at temperatures 180-250 °C where the CH₃OH, CO, dimethyl ether and water were the only products formed.
The concentrations of reactants and products at the reactor effluent were analyzed at steady state, using the analysis system described above. The data were collected for 12 h or longer, after the introduction of the reactants and when the steady state conditions are achieved. Methane was used as an internal standard. The CO\textsubscript{2} conversion as well as the selectivity and yields toward CH\textsubscript{3}OH, dimethyl ether, CO and oxygenates were calculated using the following equations:

\[
X_{\text{CO}_2} = 1 - \left[ \left( \frac{\text{CO}_2^{\text{out}}}{\text{CO}_2^{\text{in}}} \right) \times \left( \frac{\text{CH}_4^{\text{in}}}{\text{CH}_4^{\text{out}}} \right) \right] \times 100\%  
\]

\[
S_i(\%) = \frac{v_i \cdot \text{(mol of product i)}}{C_{\text{CO}_2^{\text{in}}} - C_{\text{CO}_2^{\text{out}}}} \times \left( \frac{\text{CH}_4^{\text{in}}}{\text{CH}_4^{\text{out}}} \right) \times 100  
\]

\[
S_{\text{oxygenates}} (\%) = \frac{(2 \times C_{\text{DME}} + C_{\text{MeOH}})}{C_{\text{CO}_2^{\text{in}}} - C_{\text{CO}_2^{\text{out}}}} \times \left( \frac{\text{CH}_4^{\text{in}}}{\text{CH}_4^{\text{out}}} \right) \times 100  
\]

\[
Y_i(\%) = \frac{S_i \times X_{\text{CO}_2}}{100}  
\]

where
- \(C_{\text{CO}_2^{\text{in}}}, C_{\text{CO}_2^{\text{out}}}\) are the inlet and outlet concentrations of carbon dioxide
- \(C_{\text{CH}_4^{\text{in}}}, C_{\text{CH}_4^{\text{out}}}\) are the inlet and outlet concentrations of methane
- \(C_{\text{DME}}, C_{\text{MeOH}}\) are the concentrations of DME and MeOH
- \(S_{\text{oxygenates}}\) is the selectivity to (MeOH + DME)
- \(i\) denotes DME, CH\textsubscript{3}OH and CO
3.9 References

CHAPTER 4

METHANOL DEHYDRATION TO DIMETHYL ETHER OVER AL₂O₃ CATALYSTS

In this chapter, dehydration of methanol to dimethyl ether (DME) is investigated over a set of eight commercial and self-prepared Al₂O₃ catalysts with different physicochemical characteristics. The effects of temperature and the presence of water vapour in the feed on catalytic performance are studied. A detailed characterization of catalysts has been carried out with respect to their textural properties (B.E.T. and B.J.H. methods), acidity (TPD of ammonia), crystallinity, phase composition and morphology (XRD, TEM). Catalytic activity and selectivity have been evaluated in the temperature range of 150-400 °C, at atmospheric pressure, in the absence and in the presence of water in the feed. The adsorption/desorption properties of catalysts toward methanol and water as well as the reaction mechanism have been investigated with the use of transient-MS and in situ DRIFTS techniques.

4.1 Preparation of Al₂O₃ catalysts

A variety of commercial and self-prepared Al₂O₃ catalysts in powder form were used to study the effects of physicochemical characteristics on catalytic performance for the title reaction. Commercial catalysts investigated (see Table 4.1 for suppliers and notations) include an α-Al₂O₃ sample (denoted as Al1) and five different γ-Al₂O₃ samples (Al2 to Al6). All materials were used as received, with the exception of Al6 (AKZO), which was first treated with tri-distilled water for 24 hours at 50 °C under continuous stirring, filtrated and dried at 120 °C overnight. It was then suspended in a slightly acidic solution at pH 5-6 (adjusted with HNO₃, 1M) for 1 hour and then in a
basic solution at pH 9 (adjusted with NH₃, 1M) for 1 hour. Finally, the sample was filtrated, dried at 90 ºC overnight and then calcined at 550 ºC for 4h.

Self-prepared Al₂O₃ samples were synthesized employing two different sol-gel methods (SG1, SG2). The SG1 catalyst was synthesized following a preparation procedure similar to that described by Keshavarz et al. [1]. Aluminium isopropoxide Al(OC₃H₇)₃ (Fluka, purum >97%) and hexadecyl-trimethyl-ammonium bromide C₁₉H₄₂BrN (Merck, for synthesis), denoted as Al.iso and CTAB respectively, were dissolved in an appropriate amount of isopropanol. The molar ratio CTAB/(Al.iso) was 0.8. The hydrolysis step was carried out at 70 ºC by a by dropwise addition of a water-isopropanol solution (H₂O/Al.iso molar ratio =90) under vigorous stirring. The mixture was peptized under stirring by adjustment of the pH to 5.5, using HNO₃ 10 wt %. Afterwards it was left to age at ambient temperature for 2 h. The sample was finally dried at 110 ºC overnight and calcined at 450 ºC (temperature ramp 5 ºC /min from ambient to 450 ºC) for 5 h and then at 600 ºC (20 ºC /min) for 30 min for the complete removal of the organic precursor. For the synthesis of the SG2 catalyst, an aqueous solution of ethanol was first prepared and its pH was adjusted at 2 with the use of HNO₃. The mixture was then added into an ethanol solution of Al(OC₃H₇)₃ (Alfa Products) under vigorous stirring and a gel was formed. The gel was left at 25 ºC under stirring for 24 hours until nearly all the liquid was evaporated. The solid residue was dried at 120 ºC for 12 hours, calcined in air at 600 ºC for 3 h and stored in a sealed vial. Sample powders were pelletized without binder in a hydraulic press and then crashed and sieved to the required mesh size (0.18<d<0.25 mm).

Results and discussion

4.2 Physicochemical characterisation of catalysts

The analyses of the textural properties show that the textural characteristics of the fresh catalysts vary significantly from one sample to another. In Table 4.1 is shown the specific surface area (SSA) of the fresh and used catalysts and the pore volume and pore size of the used catalysts. The textural analysis of the used catalysts showed that exposure to the reaction conditions did not result in appreciable changes of SSA of commercial catalysts (samples A1 to Al6), but was more important for self-prepared materials, namely SG1 and SG2 (Table 4.1).
Table 4.1: Specific surface area (SSA), pore volume and pore size of the studied catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>SSA (m² g⁻¹)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fresh catalyst</td>
<td>Used catalyst</td>
<td>Used</td>
</tr>
<tr>
<td>α-Al₂O₃ Alfa Products</td>
<td>Al1</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>-</td>
</tr>
<tr>
<td>γ-Al₂O₃ Alfa Products</td>
<td>Al2</td>
<td>94</td>
<td>91</td>
<td>0.25</td>
</tr>
<tr>
<td>γ-Al₂O₃ Houdry</td>
<td>Al3</td>
<td>139</td>
<td>132</td>
<td>0.30</td>
</tr>
<tr>
<td>γ-Al₂O₃ Engelhard</td>
<td>Al4</td>
<td>202</td>
<td>200</td>
<td>0.78</td>
</tr>
<tr>
<td>γ-Al₂O₃ Sasol Puralox</td>
<td>Al5</td>
<td>196</td>
<td>193</td>
<td>0.58</td>
</tr>
<tr>
<td>γ-Al₂O₃ Akzo, treated</td>
<td>Al6</td>
<td>232</td>
<td>224</td>
<td>0.65</td>
</tr>
<tr>
<td>Al₂O₃ (home made) Sol-gel, method 1</td>
<td>SG1</td>
<td>346</td>
<td>304</td>
<td>2.13</td>
</tr>
<tr>
<td>Al₂O₃ (home made) Sol-gel, method 2</td>
<td>SG2</td>
<td>160</td>
<td>139</td>
<td>0.16</td>
</tr>
</tbody>
</table>

The specific surface areas (SSA) range from less than 0.5 m² g⁻¹ for α-Al₂O₃ (Al1) to 346 m² g⁻¹ for Al₂O₃ prepared by sol-gel method (SG1). It is observed that SG1 has the highest specific surface area, the highest pore volume and the highest average pore diameter, compared to other samples investigated. Although its SSA is comparable to that reported by Keshavarz et al. [1], for a material prepared following a similar method, the pore volume and the average pore diameter are significantly higher. The SSA for Al2 and Al3 samples are 94 and 139 m² g⁻¹ respectively and they have almost the same pore volume and pore diameter. Although Al4 and Al5 samples show almost the same SSA which is 202 m² g⁻¹ for Al4 and 196 m² g⁻¹ for Al5 the Al4 shows a little bit higher pore volume and average pore diameter. Finally, the textural properties for SG1 and SG2 differ remarkably indicating the important influence of the preparation method.
The nitrogen adsorption/desorption isotherms of all used samples are similar to those of the fresh catalysts and are shown in Figure 4.1. It is observed that the investigated materials differ substantially regarding their porosity and can be classified into three main groups. For Al4, Al5 and Al6 samples, the classical type IV isotherm (according to the IUPAC classification) can be observed, typical for mesoporous solids (Figure 4.1A). The type H1 hysteresis loop, occurring at the relative pressure range \( P/P_0 = 0.7-0.9 \), indicates broad pore size distribution with uniform cylindrical shape \([2, 3]\).

The Al2 and Al3 samples exhibit quite different \( \text{N}_2 \) adsorption/desorption isotherms having two inflection points, which implies non uniform pores’ shape and lower porosity (Figure 4.1B). The calculated mean diameter of the pores is also smaller for these two aluminas (Table 4.1). The BJH analysis indicates that Al1 is a non porous material, as expected for a \( \alpha \)-\( \text{Al}_2\text{O}_3 \) sample (not shown).

The two home-made aluminas are very different from one another but also very different from all the other aluminas investigated here. The analysis of the textural properties of SG2 shows a type IV isotherm and H2 hysteresis, attributed to nonuniform size and/or ink bottle shape (Figure 4.1B) \([2, 3]\). SG2 has much lower porosity and pores (Table 4.1).

On the contrary, the \( \text{N}_2 \) adsorption/desorption isotherm for SG1 (Figure 4.1C) resembles to a type II with almost no plateau at high \( P/P_0 \) values, which is usually observed for materials with macropores or interparticular mesoporosity \([4]\). This type of isotherms, characteristic of clay minerals, suggests \( \text{N}_2 \) physisorption between aggregates of platelet particles giving rise to slit-shaped pores \([5]\). The hysteresis loop that appears at higher relative pressure compared to the other aluminas, indicates the presence of larger mesopores. Thus, from this \( \text{N}_2 \) adsorption/desorption isotherm (Figure 4.1C) high porosity, large pores with uniform size and shape is expected for SG1.
Figure 4.1: The N\textsubscript{2} adsorption/desorption isotherms of the studied Al\textsubscript{2}O\textsubscript{3} samples. The hollow and solid symbols denote N\textsubscript{2} adsorption and desorption isotherms, respectively.
In **Figure 4.2** is shown the pore size distribution of the catalysts. Results indicate that catalysts maintained their mesoporous structure after the catalytic performance tests and that the pore size distribution curves possess almost the same shape for the fresh and used catalysts.

Results presented in **Figure 4.2 A** confirm the mesoporous structure of Al4, Al5 and Al6 samples with an average pore width of about 10 nm, while larger pores of about 17.3 nm are also measured for Al4. This observation confirms the calculated average pore size given in **Table 4.1**. The pore size distribution for the SG1 sample (**Figure 4.2A**) elucidates the existence of pores that are much larger than those of any other material studied here, with an average pore diameter 22.7 nm and total porosity of 2.13 cm$^3$g$^{-1}$. On the contrary, the pore size distribution of the samples Al2, Al3 and SG2 (**Figure 4.2 B**) indicates much lower porosity and small pores with an average pore diameter less than 10 nm. Additionally, for the SG2 sample the pore size distribution curve shows the existence of micropores.

![Figure 4.2: Pore size distribution of the studied Al$_2$O$_3$ catalysts.](image)

In **Figure 4.3** are shown the XRD patterns of the fresh catalysts. It is observed that the materials consist mainly of $\gamma$-alumina. However, the width of the peaks varies, indicating differences in crystallinity. Sample Al3 exhibits sharp peaks and signifying larger crystallite size while samples prepared by the sol-gel methods give very broad
diffraction bands due to the poor crystallization of the alumina. For sample Al2, multiple peaks are clearly observed, e.g. besides of the peak at $2\theta = 45.91^\circ$, corresponding to the (400) plane of $\gamma$-Al$_2$O$_3$, there is another peak located at 46.75$^\circ$. This implies that other crystallographic phases besides of $\gamma$-Al$_2$O$_3$ are also present, probably $\delta$-Al$_2$O$_3$ and $\chi$-Al$_2$O$_3$. Synthesis conditions and thermal treatment define the extent of hydroxyls incorporation and structural rearrangements resulting in the formation of various transition aluminas [6]. The detection of $\chi$-Al$_2$O$_3$ indicates that gibbsite was present in the precursor oxyhydroxide, while the presence of $\delta$-Al$_2$O$_3$ is due to heating above 750 °C.

![X-ray diffraction (XRD) patterns obtained over the indicated Al$_2$O$_3$ catalysts. Symbols correspond to the following JPCS data: ▲ 10-0425 $\gamma$-Al$_2$O$_3$, ● 04-0877 $\delta$-Al$_2$O$_3$, + 04-0880 $\chi$-Al$_2$O$_3$ ○ 21-1307 AlO(OH).](image)

**Figure 4.3:** X-ray diffraction (XRD) patterns obtained over the indicated Al$_2$O$_3$ catalysts. Symbols correspond to the following JPCS data: ▲ 10-0425 $\gamma$-Al$_2$O$_3$, ● 04-0877 $\delta$-Al$_2$O$_3$, + 04-0880 $\chi$-Al$_2$O$_3$ ○ 21-1307 AlO(OH).

It is worth noting that slight shifts of the diffraction peaks are observed for the other samples, which indicate differences in the lattice parameters and/or the presence of other transition aluminas, especially in the case of SG1. In the XRD
pattern of the fresh Al5, the presence of aluminum oxide hydroxide (AlO(OH), JPCS 21-1307) was also detected, with most intense peaks located at 14.5° (not shown) and 28.2°. This phase is absent after catalytic tests, indicating that water is removed under reaction conditions. For the other aluminas there are not any remarkable changes observed after catalytic tests (XRD patterns not shown). The degree of crystallization, expressed by the average crystallites size, has been calculated from the XRD patterns using the Scherrer equation and results obtained are summarized in Table 4.2. It is observed that the average particles size varies, being smaller for the home made SG materials. In accordance, the samples with smaller crystallites exhibit higher SSAs. No increase of the particles’ size is observed for the used catalysts, confirming the stability of the materials under reaction conditions.

Table 4.2: The average particle size of fresh and used catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
</tr>
<tr>
<td>Al1</td>
<td>-</td>
</tr>
<tr>
<td>Al2</td>
<td>7.1 ± 0.1</td>
</tr>
<tr>
<td>Al3</td>
<td>8.3 ± 0.1</td>
</tr>
<tr>
<td>Al4</td>
<td>5.2 ± 0.1</td>
</tr>
</tbody>
</table>

The TEM images of Al4, Al5, Al6 and SG1 samples are shown in Figure 4.4. It is observed that Al4 consists of small uniform aggregates of almost spherical shape. Al5 presents elongated aggregates of about 20-40 nm. In Al6, the particles have needle-like shape morphology. SG1 seems similar to Al6 with shorter and thinner needles. However, the two materials are quite different. Al6 is well crystallized as it can be seen in the HRTEM images (Figure 4.5a).
On the contrary, a large part of SG1 is amorphous (Figure 4.5b). Al5 also presents amorphous areas but to a much lower degree. These results are in accordance with the XRD analysis that shows the lower crystallinity of the SG1 as compared to the commercial aluminas.

Generally, the rate of reactions occurring through heterogeneous acid catalysis is determined by the characteristics of the acid sites (number, strength and density). It has been reported that the rate of methanol dehydration reaction depends strongly on the acidity of catalyst employed.

Figure 4.4: TEM images obtained over (a) Al4, (b) Al5, (c) Al6 and (d) SG1 samples.

Figure 4.5: HRTEM images of (a) Al6 and (b) SG1 samples.
The acidity of aluminas was measured with temperature programmed desorption of ammonia. The choice of base probe material is important in obtaining TPD measurements. With solid acid catalysts, a small base molecule such as ammonia is typically used. Ammonia is a suitable probe molecule for this purpose because of its strong basicity, its ability to adsorb selectively on sites of different strengths and its small kinetic diameter (0.26 nm), which allows detection of acidic sites located into very narrow pores [7, 8]. By using this method, it is possible to gather information related to the concentration and strength of acid sites.

In Figure 4.6 are shown typical NH$_3$-TPD patterns obtained for Al2, Al4, SG1 and SG2 catalysts. It is observed that, in all cases, TPD patterns are characterized by an intense desorption peak located at ca. 105 ºC and a broad asymmetric decaying “tail” which extends up to ca. 500 ºC. Qualitatively similar NH$_3$-TPD profiles are typically observed for different crystalline phases of Al$_2$O$_3$ [9-11]. It should be noted that no other products, such as H$_2$ or N$_2$, were detected during adsorption/desorption experiments, indicating that adsorption and desorption of ammonia on the present materials take place molecularly. The total amounts of NH$_3$ desorbed per gram of catalyst are listed in Table 4.3.

**Table 4.3:** The ammonia uptake of the studied catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Al2</th>
<th>Al3</th>
<th>Al4</th>
<th>Al5</th>
<th>Al6</th>
<th>SG1</th>
<th>SG2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ uptake (µmol g$^{-1}$)</td>
<td>227</td>
<td>293</td>
<td>443</td>
<td>486</td>
<td>608</td>
<td>886</td>
<td>438</td>
</tr>
</tbody>
</table>

The NH$_3$-TPD patterns of Figure 4.6 show that ammonia is adsorbed on the surface of Al$_2$O$_3$ catalysts with different strengths. Since the catalytic activity of solid acids for methanol dehydration depends on both the number and strength of acid sites, an attempt has been made to elucidate the type of acid sites present on each sample. For this, the NH$_3$-TPD profiles were deconvoluted into Gauss functions, on the assumption of a normal distribution of the desorption activation energies arising from a corresponding heterogeneity sites distribution [7]. The fitting procedure showed that all experimental curves may be deconvoluted into (at least) four peaks with their maxima located at 104±4 ºC (peak I), 135±14 ºC (peak II), 205±32 ºC (Peak III) and
$322\pm36\,^{\circ}\text{C}$ (peak IV) (Figure 4.6). Peaks I and II may be attributed to desorption of NH$_3$ from weak acid sites, whereas peaks III and IV correspond to medium and strong acid sites, respectively [7, 8, 12-15].

Figure 4.6: NH$_3$-TPD profiles obtained over the indicated Al$_2$O$_3$ catalysts.

The exact nature of the adsorption sites (Brönsted or Lewis) corresponding to the four TPD peaks cannot be concluded from the present results. It has been
proposed that the peak at 105 °C may be attributed to Brönsted acid sites and the peaks at higher temperature to Lewis sites [8].

It is also observed that the NH$_3$ uptake per gram of catalyst depends strongly on specific surface area of the sample, and increases linearly with increase of SSA (Figure 4.7). If the same data are expressed per unit surface area, the density of surface acid sites is approximately the same for all samples, taking an average value of 2.45 μmol m$^{-2}$ (Figure 4.7).

![Graph showing NH$_3$ uptake vs. specific surface area]

**Figure 4.7:** Amount of ammonia desorbed in NH$_3$-TPD experiments as a function of the specific surface area of Al$_2$O$_3$ catalysts.

### 4.3 Catalytic performance tests

Results of catalytic performance tests obtained over the studied catalysts with the use of a feed composition consisting of 30% CH$_3$OH (in He) are summarized in Figure 4.8 where the conversion of methanol ($X_{\text{MeOH}}$) is plotted as a function of reaction temperature. The equilibrium conversion curve for methanol dehydration to DME is also shown, (dashed line) for comparison. As observed in Figure 4.8A, the Al1 catalyst is, practically, inactive in the temperature range of interest. This should be expected, because of the very low SSA of α-Al$_2$O$_3$ (Table 4.1). Samples Al2 and Al3, with SSAs of ca. 90 and 130 m$^2$ g$^{-1}$, respectively, exhibit measurable methanol
conversion at temperatures higher than 200 °C, reach equilibrium conversion at around 350°C. The methanol conversion curve shifts toward significantly lower temperatures over samples Al4 and Al5 with SSAs around 190 m² g⁻¹, exhibiting significant activity at temperatures lower than 200 °C and reaching equilibrium conversions at temperatures around 230 °C for the Al4 (Figure 4.8A).

![Conversion curves](image)

**Figure 4.8:** Conversion of methanol as a function of reaction temperature obtained over (A) commercial Al1, Al2, Al3, Al4, Al5 and (B) Al6, SG1, SG2 catalysts.
In Figure 4.8B are shown similar results obtained over the pretreated commercial alumina sample (Al6) and the self-prepared catalysts synthesized with the use of sol-gel method (SG1, SG2). It is observed that, although Al6 and SG1 are characterized by relatively large SSAs (Table 4.1), their catalytic activity is inferior, compared to that of the best performing Al4 sample.

Regarding selectivity to reaction products, typical results obtained over the Al4 sample are shown in Figure 4.9, where selectivities to DME ($S_{\text{DME}}$), carbon monoxide ($S_{\text{CO}}$) and methane ($S_{\text{CH}_4}$) are plotted as functions of reaction temperature. It is observed that the catalyst is 100% selective toward DME in the temperature range of 150 to ca. 325 °C. At higher temperatures, small amounts of CO and trace amounts of CH$_4$ appear in the gas phase. Selectivity toward these species increases progressively with increase of temperature to 400 °C at the expense to that of DME. Similar results were obtained for all Al$_2$O$_3$ catalysts investigated.

![Selectivities to reaction products as functions of reaction temperature obtained over the Al4 sample.](image)

It may be noted that the occurrence of side reactions responsible for the evolution of CO and CH$_4$ above ca. 325 °C explains the reason why conversion of methanol exceeded the equilibrium values predicted by thermodynamics for this reaction in this temperature range (Figure 4.9).
4.4 Kinetic measurements

Results of kinetic measurements obtained with the use of a feed composition consisting of 30% CH₃OH (in He) are summarized in the Arrhenius plots of Figure 4.10A, where the reaction rate is expressed per gram of catalyst. The apparent activation energy \( E_a \) of the methanol dehydration reaction was calculated from the slope of the fitted lines and results obtained are summarized in Table 4.4. It is observed that \( E_a \) is, practically, the same for all studied catalysts taking an average value of 24±4 kcal mol\(^{-1}\), in agreement with literature results [16].

<table>
<thead>
<tr>
<th>catalyst</th>
<th>Al1</th>
<th>Al2</th>
<th>Al3</th>
<th>Al4</th>
<th>Al5</th>
<th>Al6</th>
<th>SG1</th>
<th>SG2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_a ) (kcal mol(^{-1}))</td>
<td>18.5</td>
<td>25.1</td>
<td>26.2</td>
<td>27.0</td>
<td>29.8</td>
<td>21.4</td>
<td>24.1</td>
<td>19.5</td>
</tr>
</tbody>
</table>

Results of Figure 4.10A show that the rate of methanol conversion per gram of catalyst depends strongly on the nature of the Al\(_2\)O\(_3\) sample employed.

Figure 4.10: Arrhenius plots of specific reaction rates obtained over the studied Al\(_2\)O\(_3\) samples under differential reaction conditions, expressed (A) per gram of catalyst and (B) per mol of surface acid sites.

In particular, the rate at temperatures around 200 °C is more than two orders of magnitude (ca. 200 times) higher for samples Al4 and Al5, compared to that of Al2 and
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Al3, with other catalysts exhibiting intermediate activity. These differences cannot be explained solely by taking into account differences of the SSA or of the total number of acid sites (determined by NH3-TPD) of the catalysts, which vary only by a factor of 3 for the studied samples (Table 4.3). This is clearly evidenced in the Arrhenius plots of Fig. 4.10B, where the reaction rates are divided with the moles of ammonia desorbed per unit mass of catalyst. If the reaction rate was directly proportional to the total number of acidic sites, all data points should fall on the same Arrhenius line, which, obviously, is not the case. Thus, although some authors reported that catalytic activity correlated well with the number of acidic sites of γ-Al2O3 [14], no such correlation could be obtained in the present study, in agreement with results of other investigators [9].

Results of Fig 4.10 imply that physicochemical characteristics other than SSA or total number of surface acid sites (estimated by NH3-TPD) determine to a large extent the activity of Al2O3 catalysts for the title reaction. It has been reported, for example, that alumina samples with the highest proportion of weak/moderate acid sites exhibit the best catalytic performance and stability for the synthesis of dimethyl ether, and that the variation in activity of Al2O3 catalysts is a result of different acidities and ratios of weak to strong acidic sites [1, 12, 16, 17]. This explains the reason why catalytic activity can be varied by addition of promoters or by controlling the acidic properties of alumina or zeolites [18, 19]. Based on these arguments, an attempt has been made to correlate catalytic activity of the studied samples with the number of weak, medium or strong acid sites estimated by deconvolution of the NH3-TPD patterns (Fig. 4.6). Results of this analysis (not shown for brevity) did not show a direct correlation between the amount of acid sites of different strengths with catalytic activity. This may be, at least in part, due to the absence of clearly resolved peaks in the NH3-TPD patterns (Fig. 4.6), which does not allow accurate determination of the surface concentration of acid sites of various strength. It should be noted that the NH3-TPD method does not provide information related to the types of acidic sites (e.g., Brønsted or Lewis sites) present on the catalyst surface [9], which have been reported to have different activities [18].

The assessment of the textural properties showed that, in addition to SSA, the aluminas differ also in their porosity and average pore diameter. The importance of the pores’ structure for dehydration reactions has been reported for materials
characterized by microporosity such as zeolites and pillared clays [20-23]. Methanol dehydration, considered as a bimolecular reaction between two methoxy species or between a methoxy species and an undissociated methanol adsorbed on adjacent surface sites, would require the close proximity of two acid sites with adequate acidity but also pores having size large enough to permit this type of reactions. Even larger pores would be needed if one considers a single dehydration site for the formation of a methoxy species that would react with a methanol molecule in the gas phase. On the other hand, ammonia is an excellent probe molecule for testing the acidic properties of solid catalysts due to its strong basicity and small molecular size that allow for detection of acidic sites located also into very narrow pores [7]. Thus, acids sites in narrow pores, although titrated by ammonia, may be ineffective for DME formation due to stereochemical inhibition.

Raimondo et al. [22] have studied the acidity/porosity relationships on oxide-pillared materials and concluded that dehydration is favoured in large pores. Even though the above restrictions should not apply in the case of mesoporous materials such as aluminas, results of the present study indicate that the aluminas having cylindrical pores of an average width of about 9-10 nm and total porosity 0.60-0.80 cm$^3$g$^{-1}$ exhibit higher methanol conversion, compared to those with lower porosity. Further increase of porosity (SG1) does not induce additional activity enhancement. Comparable results have also been reported in other studies, with the use of similar materials for the title reaction [24].

Another parameter that can affect catalytic behaviour is the degree of crystallinity of the materials. The XRD patterns (Fig. 4.3) and the TEM images (Figs. 4.4 and 4.5) revealed differences in the crystallinity of the alumina samples. Having in mind that smaller crystallites signify higher number of defects and therefore higher number of methanol adsorption sites, the decrease of the crystallite size should be accompanied by an analogous increase in methanol conversion. This is true when the crystallites’ size decrease from 7.0-8.0 nm (Al2 and Al3) to about 5.0-5.5 nm (Al4, Al5, Al6). Further decrease of crystallites size, as in the case of SG1, does not result in further increase of the activity. It should be noted, however, that this material is highly amorphous.

Based on the above discussion, it may be concluded that the textural properties, degree of crystallinity and total amount of acid sites determine to a large extent the
catalytic behaviour of the studied alumina catalysts for the dehydration of methanol to dimethyl ether.

4.5 Effects of the presence of water vapour in the feed

It is known that in methanol dehydration reaction the catalytic activity and stability may be affected by the presence of water, which is an inevitable product under the reaction conditions. It is believed that water blocks the active sites of catalyst through competitive adsorption with methanol on the catalyst surface. Yuchuan Fu et al. [25] showed that water adsorbs on the Lewis acid sites and poisons the strong Lewis acid sites. Under realistic reaction conditions, where methanol is produced via hydrogenation of CO₂, the gas mixture contains considerable amounts of water steam, which may influence the activity and stability of both methanol synthesis and methanol dehydration catalysts. In order to address this issue, the effects of the presence of 10% water vapour in the feed on catalytic performance have been investigated over the Al⁴ sample and results are shown in Figure 4.11.

**Figure 4.11:** (A) Conversion of methanol as a function of reaction temperature obtained over Al₂O₃ catalyst (Al⁴ sample) (a) in the absence and (b) in the presence of 10% H₂O in the feed. (B) Effect of addition of 10% H₂O in the feed on the conversion of methanol at T= 215°C.

It is observed that the presence of water decreases substantially the catalytic activity, which is evidenced by a shift of the methanol conversion curve toward higher
temperatures by ca. 50 °C (Fig. 4.11A). This is accompanied by an increase of the apparent activation energy of the reaction from 27 to 37 kcal mol⁻¹, in good agreement with previous studies [16]. Interestingly, the presence of water in the feed does not influence selectivity to reaction products (Fig. 4.9).

In Fig. 4.11B is shown the variation of the conversion of methanol ($X_{\text{MeOH}}$) with time-on-stream obtained over the Al4 sample at a constant temperature of 215 °C, in the absence and in the presence of water in the feed. It is observed that, when a 30%CH₃OH (in He) mixture is fed to the reactor, the catalyst exhibits a very stable performance with the conversion of methanol acquiring values around 60%. Addition of 10% H₂O in the feed results in a substantial decrease of methanol conversion. However, catalytic activity is restored when water is removed from the feed and $X_{\text{MeOH}}$ returns to its initial value. This clearly shows that the effect of water on catalytic performance is reversible.

Results of Fig. 4.11 show that Al4 deactivates in the presence of water. This behaviour, which is typically observed for solid acid catalysts [12, 16], is believed to be due to blocking of the active sites for methanol conversion via competitive adsorption of water on the catalyst surface [12, 16, 26, 27]. These issues are discussed in more detail in the following section.

It should be noted that the presence of water in the feed shifts equilibrium of the methanol dehydration reaction to the left and, therefore, part of the observed decrease of methanol conversion is due to thermodynamic reasons (see, for example, dashed lines in Fig. 4.11A). Thus, when water is present in the reaction mixture, a higher reaction temperature is always required to achieve the same level of conversion. In practice, the negative effect of water can be suppressed if the one-step syngas-to-DME hybrid catalyst contains a component, which is active to the water-gas shift (WGS) reaction, in which case excess water may be removed efficiently [16].

4.6 Mechanistic studies

The nature, relative population, thermal stability and reactivity of species formed on the catalyst surface under reaction conditions have been investigated with the use of in situ DRIFTS and transient-MS techniques, following interaction of Al₂O₃ (Al4) with either (a) 1.5% H₂O (in He) or (b) 0.5% CH₃OH (in He) or (c) 1.5% H₂O+0.5% CH₃OH (in He) mixtures.
4.6.1 Adsorption/desorption characteristics of water

In Figure 4.12 are shown DRIFT spectra obtained following exposure of the Al₂O₃ catalyst to a 1.5% H₂O (in He) mixture at 25 °C for 30 min, switch to He flow for 30 min (trace a) and subsequent stepwise heating at 450 °C under He flow (traces b-i).

**Figure 4.12:** DRIFT spectra obtained over the Al₂O₃ (Al4) catalyst following interaction with 1.5%H₂O at 25 °C for 30 minutes and subsequent stepwise heating at the indicated temperatures under He flow.
It is observed that the spectrum obtained at 25 °C (trace a) is characterized by two absorption bands located at 1645 and 1390 cm\(^{-1}\), a broad feature in the 3500-2800 cm\(^{-1}\) region and several overlapping, negative peaks in the 3800-3500 cm\(^{-1}\) region. The intense band at 1645 cm\(^{-1}\) can be assigned to the \(\delta\)(HOH) bending vibrations of weakly (physically) adsorbed water, and the weak band at 1390 cm\(^{-1}\) can be attributed to the same vibration of water molecules adsorbed on coordinatively unsaturated aluminium ions \[28, 29\].

The latter adsorption sites could have been formed during pretreatment of the sample at 450 °C under He flow, which is known to result in partial dehydroxylation of the \(\text{Al}_2\text{O}_3\) surface \[28, 30\].

The broad band in the 3500-2800 cm\(^{-1}\) region contains contributions of \(\nu\)(OH) stretching vibrations originating from various species, including weakly adsorbed water molecules, hydrogen-bonded hydroxyl groups, and shifted \(\nu\)(OH) vibrations of alumina surface caused by interaction with adsorbed water \[31\].

Regarding the “negative” bands observed in the range of 3800-3500 cm\(^{-1}\), they appear in the region where the \(\nu\)(OH) stretching vibrations of various configurations of hydroxyl groups of alumina are expected to occur \[28, 30\]. The loss of intensity observed in this region upon exposure to water vapour indicates that hydroxyl groups initially present on the \(\text{Al}_2\text{O}_3\) surface interact with adsorbed water molecules \[29, 31\] and that this interaction results in a shift of absorption toward lower wavenumbers (increased intensity in the 3500-2800 cm\(^{-1}\) region). It may be noted that, according to the analysis of Knozinger and Ratnasamy \[30\], a maximum of five different OH configurations are expected to be present on the surface of aluminas, their actual occurrence and relative concentration depending on the relative contributions of the different crystal phases. These configurations may be tentatively correlated to the five (negative) spectral features located at ca. 3765, 3745, 3725, ~3670 and ~3585 cm\(^{-1}\) (Fig. 13A, traces a-c).

Stepwise increase of temperature under He flow results in a progressive decrease of the intensities of the bands located at 1645, 1390 and 3500-2800 cm\(^{-1}\) (traces b-i). These spectral features disappear at temperatures higher than ca. 250 °C, indicating desorption of physically adsorbed and coodrivate bonded water molecules \[29\]. This is accompanied by the progressive disappearance of the negative
bands in the 3800-3500 cm⁻¹ region and the restoration of the coverage of hydroxyl groups on the alumina surface.

4.6.2 Temperature programmed desorption of methanol

The TPD pattern obtained following interaction of Al₂O₃ (Al4) with 0.5% CH₃OH (in He) at 25 °C is shown in Fig. 4.13A. It is observed that desorption of methanol starts at room temperature and goes through a maximum at 105 °C. This indicates that a substantial amount of methanol is weakly held on the catalyst surface and desorbs in the gas phase according to:

\[ \text{CH}_3\text{OH}_{(ad)} \leftrightarrow \text{CH}_3\text{OH}_{(g)} \]  

Dimethyl ether (DME) starts to evolve at temperatures around 150 °C, goes through a maximum at ca 210 °C and is present at the reactor effluent at temperatures as high as 400 °C. At temperatures higher than 325 °C, CO, H₂ and CH₄ start to evolve in the gas phase and their concentrations reach a maximum at around 420 °C. Desorption of all products is completed below 550 °C.

**Figure 4.13A:** TPD pattern obtained over the Al₂O₃ (Al4) catalyst following interaction with 0.5% CH₃OH (in He) at 25 °C for 30 min and subsequent linear heating (\( \beta = 15 \, \text{oC min}^{-1} \)) under He flow.
Results of Fig. 13A show that Al₂O₃ (Al4) is able to selectively dehydrate methanol toward DME at temperatures lower than ca. 350 °C, in agreement with results presented in Fig. 4.1. At higher temperatures, adsorbed species are decomposed toward almost equal amounts of CH₄, H₂ and CO (Fig. 4.13A). This indicates that the overall reaction that takes place at temperatures above 350 °C may be described as decomposition of DME:

\[
\text{CH}_3\text{OCH}_3(\text{ad}) \leftrightarrow \text{CH}_4 + \text{CO} + \text{H}_2
\]

A similar experiment was conducted with the use of DRIFTS in order to investigate the nature and reactivity of species formed on the catalyst surface. Results of this DRIFTS-TPD experiment are presented in Fig. 4.13B which shows spectra obtained following interaction of Al₂O₃ with 0.5% CH₃OH (in He) at 25 °C for 30 min, purging with He for 30 min (trace a), and subsequent stepwise heating (with 50 °C increments) at 450 °C under He flow (traces b-i).

It is observed that the (background-subtracted) spectrum recorded at 25 °C (trace a) is characterized by negative bands in the \( \nu(\text{OH}) \) region (3800-3500 cm\(^{-1} \)) as well as by several bands in the C-H stretching frequency region (3100-2700 cm\(^{-1} \)) and in the C-H deformation and C-O stretching regions (1600-1050 cm\(^{-1} \)). Two weak, broad bands can be also discerned at ca. 3200 and 2600 cm\(^{-1} \).

As discussed above, the negative bands located at ca. 3765, 3730 and 3675 cm\(^{-1} \) can be attributed to losses of \( \nu(\text{OH}) \) intensity of (at least) three different types of free hydroxyl groups initially present on the Al₂O₃ surface. These groups are known to hydrogen-bond to adsorbed methanol and methoxy (CH₃O-) species, thereby resulting in the appearance of “negative” bands in the \( \nu(\text{OH}) \) region [32-37] :

\[
\text{CH}_3\text{OH}^{(g)} + \text{OH}^{(a)} \leftrightarrow \text{CH}_3\text{HO}⋯\text{HO}^{(a)} \quad 4.3 \\
\text{CH}_3\text{OH}^{(g)} + \text{OH}^{(a)} \leftrightarrow \text{CH}_3\text{O}⋯\text{H}_2\text{O}^{(a)} \quad 4.4
\]

Based on literature results [38], the “negative” spectral features observed in the \( \nu(\text{OH}) \) region can be assigned to medium-strong (3765 cm\(^{-1} \)), medium-weak (3730 cm\(^{-1} \)) and weak (3675 cm\(^{-1} \)) Lewis acid sites of Al₂O₃.
The variety of bands observed below 3200 cm\(^{-1}\) (trace a) can be attributed to adsorbed methanol and/or methoxy groups as follows: The intense peaks in the \(\nu(C-H)\) region, located at 2938 and 2822 cm\(^{-1}\), can be assigned to the \(\nu_{as}(CH_3)\) and \(\nu_s(CH_3)\) modes, respectively, of adsorbed methanol/methoxy species [39, 40]. A second pair of peaks, located at ca. 2950 and 2845 cm\(^{-1}\), which appear as shoulders at low temperatures (traces a-c) but are clearly resolved at higher temperatures (e.g., traces

**Figure 4.13B:** DRIFT spectra obtained over the Al\(_2\)O\(_3\) (Al4) catalyst following interaction with 0.5\% CH\(_3\)OH (in He) at 25 °C for 30 minutes and subsequent stepwise heating at the indicated temperatures under He flow.
d-i), can be attributed to similar species bonded more strongly on the Al₂O₃ surface [34]. The broad band observed between 1550 and 1400 cm⁻¹ is due to antisymmetric and symmetric δ(CH₃) modes (peaks at 1480 and 1445 cm⁻¹) [35, 41] and may contain a contribution from δ(OH) deformation mode [34]. The peaks located at 1190 and 1115 cm⁻¹ can be assigned to γ(CH₃) rocking modes [36, 37, 41] and the peak at 1090 cm⁻¹ to ν₉₉₆(CO) antisymmetric stretching [37, 41] of adsorbed methanol and/or methoxy species. The broad band located at ca. 2600 cm⁻¹ can be assigned to a combination band of the methyl rock (1115 cm⁻¹) and methyl deformation (1480 cm⁻¹) modes of adsorbed methoxy species [35, 36]. Finally, the broad band centered at ca. 3200 cm⁻¹ can be attributed to the O-H stretching frequency of molecularly adsorbed methanol [34, 37].

It should be noted that all vibrational frequencies of adsorbed methanol lie, in general, very close to those of their methoxy counterparts [33-37, 39-43] and also to those of adsorbed dimethyl ether [37, 41, 44]. Thus, it is difficult to determine from the spectra of Fig. 4.13B the extent to which methanol is adsorbed molecularly or in the form of methoxy groups. However, the presence of undissociatively adsorbed methanol is verified by the broad feature located at ca. 3200 cm⁻¹, which is uniquely associated with the O-H stretching frequency of methanol [35-37]. This band is discernible in the spectra recorded in the temperature range of 25 to 150 °C (traces a-c) and disappears at higher temperatures. This is in agreement with results of TPD experiments of Fig. 14A, which show that weakly held methanol desorbs molecularly from the Al₂O₃ surface in this temperature range.

As shown in the TPD pattern of Fig. 4.13A, evolution of small amounts of methanol in the gas phase continues at temperatures higher than 150 °C, where molecularly adsorbed methanol is not present on the catalyst surface (Fig. 4.13B). This indicates that gas-phase methanol may be also formed by combination of surface species according to [32, 42]:

\[
\begin{align*}
\text{CH}_3\text{O} \quad (\text{a}) + \text{OH} \quad (\text{a}) & \leftrightarrow \text{CH}_3\text{OH} \quad (\text{g}) + \text{O} \quad (\text{surf}) & 4.5 \\
\text{CH}_3\text{O} \quad (\text{a}) + \text{H}_2\text{O} \quad (\text{a}) & \leftrightarrow \text{CH}_3\text{OH} \quad (\text{g}) + \text{OH} \quad (\text{a}) & 4.6
\end{align*}
\]

This argument is supported by the observation that heating at 200 °C (Fig. 4.13B, trace d), which induces desorption of weakly adsorbed methanol, leads in a substantial decrease of the intensity of the negative bands in the ν(OH) region.
As mentioned above, vibrational frequencies of adsorbed dimethyl ether lie very close to those of adsorbed methoxy species [41]. This may explain the reason why no significant differences are observed in the position of IR bands in the $\nu$(C-H) region upon heating the sample at 150-250 °C (Fig. 14B, traces c-e), where evolution of DME occurs in the gas phase (Fig. 14A). It may be noted, however, that the pair of peaks at 2938/2822 cm$^{-1}$ decreases in intensity in this temperature range and that this results in the resolution of the pair of peaks at ca. 2950/2845 cm$^{-1}$. It may then be suggested that formation of DME involves weakly adsorbed methoxy species (doublet at 2938/2822 cm$^{-1}$) and not methoxy species that are bonded more strongly on the Al$_2$O$_3$ surface (doublet at 2950/2845 cm$^{-1}$).

Regarding the mechanism of DME formation, it has been proposed that dehydration of methanol over Al$_2$O$_3$ catalysts, may occur via two possible routes: The first one involves interaction of adsorbed methoxy species with undissociated methanol (4.7) [42], and the second involves reaction between two adsorbed methoxy species adjacent to a hydroxyl group (4.8) [35, 37, 45].

\[
\begin{align*}
\text{CH}_3\text{OH} \text{ (ad)} + \text{CH}_3\text{O} \text{ (ad)} & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{OH} \text{ (ad)} \quad 4.7 \\
2\text{CH}_3\text{O} \text{ (ad)} & \leftrightarrow \text{CH}_3\text{OCH}_3 + \text{O} \text{ (surf)} \quad 4.8 \\
2\text{OH} \text{ (a)} & \rightarrow \text{H}_2\text{O} \text{ (g)} + \text{O} \text{ (a)} \quad 4.9
\end{align*}
\]

The present results support the second reaction pathway, because DME evolution is observed at temperatures above 150 °C, where only methoxy species, and not molecularly adsorbed methanol, are present on the catalyst surface (Fig. 4.13B). In addition, evidence is provided that DME production is associated with methoxy species that are weakly adsorbed on the Al$_2$O$_3$ surface.

Increase of temperature above 150 °C results in a progressive decrease of the intensities of all bands associated to methoxy/DME species (Fig. 4.13B, traces d-i). This is accompanied by the development of new bands located at 2905, 1593, 1395 and 1372 cm$^{-1}$, which can be attributed to $\nu$(CH), $\nu_{as}$(COO), $\delta$(CH) and $\nu_{s}$(COO) modes, respectively, of surface formate species [35, 37, 40, 46]. These species may be produced by oxidation of methoxy groups with intermediate formation of dioxomethylene species [32, 33, 46] or by decomposition of surface methoxy species residing on strong Lewis acid sites [35]. The bands attributed to surface formate
species progressively increase in intensity with increasing temperature from 150 to 450 °C (traces c-i) and then disappear upon heating at higher temperatures (spectra not shown for clarity). When methoxy species are completely removed from the catalyst surface, the negative bands in the $\nu$(OH) region return to base line levels, indicating that all O-H bands have been gradually restored to their original shape and intensity.

Comparison of the DRIFT spectra presented in Fig. 4.13B with the TPD pattern of Fig. 4.13A shows that conversion of methoxy to formate species occurs at temperatures where DME production is, practically, diminished and CH$_4$, H$_2$ and CO start to evolve in the gas phase. This is in agreement with results of previous studies, which reported that conversion of methoxy into formate species is accompanied by evolution of CH$_4$ and H$_2$ [35], whereas decomposition of formates yields CO and H$_2$O [44]. Careful inspection of the DRIFT spectra of Fig. 4.13B shows that development of bands attributed to formate species takes place at the expense of those corresponding to the strongly held methoxy species (doublet at 2950/2845 cm$^{-1}$). Thus, it may be argued that weakly adsorbed methoxy species are converted to DME whereas more strongly held methoxy species are converted to surface formates and, eventually, to CH$_4$, H$_2$ and CO in the gas phase.

4.6.3 TPSR of methanol in the absence and in the presence of water

The effects of reaction temperature and feed composition on catalytic activity and selectivity have been investigated with the use of the temperature-programmed surface reaction (TPSR) technique. Results obtained following interaction of the Al$_2$O$_3$ catalyst with 0.5%CH$_3$OH (in He) at 25 °C for 30 min and subsequent linear heating ($\beta$=15 °C min$^{-1}$) at 650 °C under the same flow are shown in Fig. 4.14A, where the MS responses of methanol, DME, CH$_4$, CO, CO$_2$ and H$_2$ are plotted as functions of temperature.

It is observed that the TPSR pattern is qualitatively similar to that obtained for TPD of methanol (Fig. 4.13A). In particular, increase of temperature results in desorption of a substantial amount of weakly adsorbed methanol, which peaks at ca 90 °C and then decreases abruptly at temperatures higher than ca 150 °C. This is accompanied by evolution of DME, which is the only reaction product formed in the temperature range of 150 to 350 °C, in agreement with results of Fig. 4.9. Further
increase of temperature results in the evolution of CH₄, CO and H₂, in accordance to the decomposition reactions discussed above. Formation of CO₂ and additional amounts of H₂ at temperatures above 500 °C can be attributed to the occurrence of the water-gas shift (WGS) reaction.

![Figure 4.14A: TPSR pattern obtained over the Al₂O₃ (Al4) catalyst following interaction with 1.5% CH₃OH (in He) at 25 °C for 30 min and subsequent linear heating (β= 15 °C min⁻¹) under the same gas mixture flow.](image)

A similar experiment was conducted employing DRIFTS in order to study the nature and population of species present on the catalyst surface under reaction conditions as a function of reaction temperature. Results obtained are summarized in Fig. 4.14B, which shows spectra obtained following exposure of the catalyst to 0.5 % CH₃OH (in He) for 30 min (trace a) and subsequent stepwise heating at 450 °C (traces b-i) under the same reaction mixture.

It is observed that spectra obtained in the TPSR experiment of Fig. 4.14B, i.e., under flowing methanol (in He), are qualitatively similar to those obtained in the TPD experiment of Fig. 4.13B, i.e., under flowing He. The main difference is that, in the former case (Fig. 4.14B), absorption peaks attributed to surface formates (located at
Figure 4.14: DRIFT spectra obtained over the Al₂O₃ (Al4) catalyst following interaction with (B) 0.5% CH₃OH (in He) or (C) 0.5% CH₃OH+1.5%H₂O (in He) at 25 °C for 30 min and subsequent stepwise heating at the indicated temperatures under the same reaction mixture flow.
ca. 2900, 1593, 1392 and 1370 cm\(^{-1}\)) appear at lower temperatures, and their relative intensities are much higher, compared to those obtained under He flow (Fig. 4.13B). Regarding methoxy species, they behave in a way similar to that discussed in Section 4.5.2. In particular, at temperatures up to ca. 150 \(^\circ\)C (traces a-c) the surface is populated mainly by the weakly adsorbed methoxy groups characterized by a pair of peaks at 2940/2827 cm\(^{-1}\). At higher temperatures, where production of DME takes place in the gas phase (Fig. 4.14B), the relative population of this species decreases, providing additional evidence that it is related to DME formation.

Finally, at temperatures higher than 400 \(^\circ\)C (traces h-i) the catalyst surface is covered mainly by strongly adsorbed methoxy groups (2946/2842 cm\(^{-1}\)) and formate species that, as discussed above, are responsible for the evolution of \(\text{CH}_4\), \(\text{H}_2\) and \(\text{CO}\) in the gas phase.

The effect of addition of water in the feed has been investigated by DRTIFS-TPSR using a 0.5\%CH\(_3\)OH+1.5\%H\(_2\)O (in He) mixture and spectra obtained are presented in Fig. 4.14C.

It is observed that the spectrum recorded at 25 \(^\circ\)C (trace a) is characterized mainly by bands attributed to adsorbed water (compare with Fig. 4.12). The appearance of two weak bands at 2953 and 2835 cm\(^{-1}\) indicates that only small amounts of adsorbed methanol/methoxy species are present on the catalyst surface and shows clearly that adsorption of methanol at room temperature is suppressed significantly in the presence of water. Stepwise increase of temperature results in a progressive decrease of the amount of adsorbed water, which diminishes at 200-250 \(^\circ\)C (traces d-e), and to a concomitant increase of the coverage of methoxy species, which reaches a maximum in the same temperature range. This is accompanied by the appearance of bands attributed to surface formate species, the intensity of which increases significantly upon further increase of temperature (traces e-i).

It is of interest to note that a couple of new bands located at 1454 and 1575 cm\(^{-1}\) are resolved at 200 \(^\circ\)C (trace d) and increase progressively in intensity upon increasing temperature to 450 \(^\circ\)C (traces e-i). These bands, which were not observed in TPD (Fig. 4.13B) and TPSR (Fig. 4.14B) of methanol, can be attributed to carbonate-carboxylate species [47, 48]. These structures are not intermediate compounds in the dehydration of methanol but may be responsible for the occurrence of side reactions that lead to the appearance of \(\text{H}_2\) and \(\text{CO}\) in the gas phase.
4.7 Conclusions

The activity and selectivity of Al$_2$O$_3$ catalysts for the dehydration of methanol to dimethyl ether have been investigated over a number of alumina samples of variable physicochemical characteristics. Results show that catalytic behaviour is determined by the textural properties, degree of crystallinity and total amount of acid sites of Al$_2$O$_3$. Below are summarized the general conclusions of the obtained results.

- Increase of specific surface area results in a shift of the methanol conversion curve toward lower reaction temperatures.
- Enhanced catalytic activity of high-SSA samples cannot be attributed solely to the higher amount of surface acid sites (estimated by NH$_3$-TPD) implying that the reaction rate is determined to a large extent from other parameters, such as textural properties and degree of crystallinity.
- Conversion of methanol at a given temperature is generally higher for materials with cylindrical pores of an average width of about 9-10 nm, total porosity of 0.60-0.80 cm$^3$g$^{-1}$ and crystallite size of ca 7-9 nm. Materials with higher porosity and/or smaller crystallite size are less active, most probably due to their highly amorphous nature.
- The apparent activation energy of the reaction is, practically, the same for all studied catalysts taking an average value of 24±4 kcal mol$^{-1}$.
- Addition of water vapour in the feed does not influence selectivity to reaction products but results in an increase of the apparent activation energy and in a (reversible) shift of methanol conversion curve toward higher temperatures.
- Results of mechanistic studies indicate that interaction of methanol with the Al$_2$O$_3$ surface results in the formation of two kinds of methoxy groups of different adsorption strength. Evidence is provided that DME evolution is associated with methoxy species that are weakly adsorbed on the Al$_2$O$_3$ surface, whereas more strongly held species decompose to yield surface formate and, eventually CH$_4$ and CO in the gas phase.
4.8 References

In the present chapter, dehydration of methanol to DME is investigated over a set of thirteen zeolite catalysts, including MFI (ZSM-5 and silicalite), faujasite (Y and USY), Beta, Mordenite and Ferrierite zeolites. For comparison purposes, one γ-Al₂O₃ and two amorphous silica-alumina (ASA) catalysts are also tested. The chapter starts with a short introduction part related to the properties of zeolites with emphasis given on the characteristics of the materials investigated in the present study.

The materials have been characterized with respect to their textural properties (B.E.T. and B.J.H. methods), acidity (TPD of ammonia and FTIR spectroscopy coupled with in situ sorption of pyridine), chemical composition (ICP-AES), crystallinity and morphology (XRD). Catalytic activity and selectivity for the title reaction have been evaluated in the temperature range of 130-400°C, at atmospheric pressure, in the absence and in the presence of water in the feed at a total flow rate of 30 cm³ min⁻¹ (W/F=0.003 g/cm³ min⁻¹). Kinetic measurements were performed in separate experiments under differential reaction conditions.

5.1 Introduction
About 250 years ago a new family of minerals have been discovered and named as zeolites from the Greek words "zeo" (to boil) and "lithos" (stone). Approximately 40 zeolite minerals are found in nature and, currently, 600 zeolite materials are known and new ones are discovered every year. Each zeolitic structure is denoted with the use of a three-letter code. For example FAU stands for faujasites, MFI for ZSM-5 and
MOR for mordenite. Within a given structure there can still be many different zeolites, as the composition may vary [1-3]. Zeolites are extensively used in many important industrial applications, including purification and gas mixtures separation processes where they are applied as adsorbents. Furthermore, zeolites are used as ion exchangers for water softening processes in detergent industry, where they are used to replace calcium and magnesium cations with sodium cation. In addition, zeolites are used in catalytic industry mainly in the petroleum refining area (catalytic cracking/hydrocracking processes), in synfuel production (well-known Methanol-To-Gasoline process) and petrochemical processes like production of ethylbenzene by alkylation of benzene, xylene isomerisation, toluene disproportionation [1, 2, 4].

5.1.1 Zeolites Structure, Composition and General Properties

Zeolites are crystalline, microporous materials consisting of AlO$_4$ and SiO$_4$ tetrahedra connected via oxygen atom bridges. The AlO$_4$ tetrahedra induce the negative charge of the lattice while extraframework cation (usually proton, NH$_4^+$, and metal cations) compensates it, so that the overall framework is kept neutral (Fig. 5.1).

$$\text{M}^{m+}_{n/m} \cdot [\text{Si}_1\text{Al}_n\text{O}_2] \cdot n\text{H}_2\text{O}$$

extraframework cations \quad framework \quad sorbed phase

**Figure 5.1:** The three components usually presented in zeolite composition.

The framework composition depends on the synthesis conditions. Zeolites are made by hydrothermal synthesis under pressure in autoclaves, in the presence of template molecules such as tetramethylammonium, which act as structure directing agents [3]. Post-synthesis modifications are also used to insert Si or Al into the framework. Generally, the amount of Al within the framework can vary over a wide range, with Si/Al ratio ranging from $=1$ to $\infty$. As the Si/Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity of zeolites increases. Typically, in as-synthesized zeolites, water present during synthesis occupies the internal voids of the zeolite (Fig. 5.1). The sorbed phase and organic non-framework cations can be removed by thermal treatment/oxidation, making the intracrystalline space available. The fact that zeolites retain their structural integrity upon loss of water makes them different from other porous hydrates [1].
Generally, the structure of zeolites can be one, two or three dimensional and may comprise channels (interconnected or separated) or cages. Some of the structures can have two sets of cages, the largest one named as supercage. The micropore of zeolites is typically constructed from 12-, 10- and 8-rings, and sizes of the pores are roughly 0.7 nm (large), 0.55 nm (medium), and 0.4 nm (small) respectively [2]. Figure 5.2 shows the pore sizes and framework structures of typical zeolites. The sizes of the intracrystalline pores and nanospaces, depending on the type of zeolite framework, are close to the molecular diameters of light hydrocarbons [5].

![Diagram of pore sizes and framework structures of typical zeolites](image)

**Figure 5.2:** The porous structure of zeolitic materials and the molecular diameter of some hydrocarbons [5].

Functions of the zeolites as catalytic materials are based mainly on the shape selectivity and strong acidity. Shape selectivity is a unique property of the zeolites [2]. These materials with a microporous and uniform pore size structure have the ability to control the pore openings and so they efficiently act as “molecular sieves”. The shape selectivity is classified into three types: reactant, product and reaction selectivity (Figure 5.3). In the first case, one of the reactants is excluded because it cannot enter the zeolite pores. In the second case, species A reacts to give two produces, B and C, but C is too large to leave the pore. In the third case, the onward reaction of B to C is prohibited, e.g. because the transition state for this step does not fit [3]. This means that the selectivity of the catalytic reaction depends on the pore diameter and by efficiently controlling the pore openings it is possible to have fine shape selectivity. Chemical vapor deposition of silica on the external surface of zeolites is one of the methods that can be used to effectively control the pore-opening size without affecting the internal solid acidity. Furthermore, it is also possible to adjust the porous structure of zeolites.
Figure 5.3: Classification of zeolite shape selectivity [3].

It is known that the catalytic activity of zeolites is often suppressed due to diffusion limitations caused by slow mass transfer in the zeolite micropores. It has been shown that the modification of zeolite from micro- to meso- porosity can effectively improve the mass transfer phenomena and may reduce the residence time of molecules in the micropores by shortening their diffusional length. There are many ways to generate mesoporous zeolites: steaming (dealumination) at temperatures above 500°C, acid/base leaching [6-8] and zeolite synthesis [9].

5.1.2 Acidity: The role of Si/Al ratio

In several catalytic reactions the catalyst acidity is considered one of the key parameters for controlling the catalytic process. The acidity of zeolites and zeotypes is a complex issue. Acidity may refer to the type of acid site, the density and distribution of these sites, as well as the acid strength of each individual acid site. These properties are interdependent and play an essential role in the activity and selectivity in catalytic reactions. A zeolite framework constructed only by silicon and oxygen atoms is neutral, but replacing a tetravalent Si atom with a trivalent Al atom creates a negative charge on the framework, which must be neutralised by an ion-exchangable cation such as K⁺, Na⁺,NH₄⁺ etc. that resides inside the zeolites pores. If these cations are ion
exchanged with protons, strong Brønsted acidic sites are formed within the zeolite framework, as illustrated in Scheme 5.1 [10]. In zeolites both Brønsted (proton donor) and Lewis (electron-pair acceptor) acid sites coexist. Brønsted sites in zeolites must be able to transfer a proton to the base adsorbed molecule. These acid sites are related to protons belonging to the structural OH-groups of the zeolites associated with the Al-O-Si binding group. Lewis acid sites are associated to incompletely coordinated Al-O species (Scheme 5.2).

**Scheme 5.1:** (A) Basic unit of neutral zeolite (only silicon/oxygen atoms) and (B) Basic unit of strong acidic zeolite (alumina/silicon/oxygen atoms ion exchanged with proton)

![Scheme 5.1](image)

**Scheme 5.2:** Basic units of Brønsted and Lewis acid sites.

![Scheme 5.2](image)

Under high temperature conditions, water escapes from the zeolite structure and, as a result, from two Brønsted acid sites coordinatively unsaturated Al$^{3+}$ ions are formed, which are known as Lewis acid sites (Figure 5.4).
An ideal (defect-free) zeolite in the acid form should not have Lewis acid sites, but these can be introduced by ion exchange or by steaming to create defect sites associated with extra-framework aluminium [12]. There are many methods for characterization of the acidity properties of zeolites. A very common one is the temperature-programmed desorption (TPD) of a basic probe molecule, which exploits the fact that more thermal energy is required to detach a base from stronger acid sites than weaker acidic sites. Typical bases used are NH$_3$ or pyridine. However, this method cannot distinguish Brønsted from Lewis sites. In order to do so, infrared spectroscopy is the method of choice. For example, pyridine can be adsorbed as pyridinium ion on a Brønsted site whereas it is coordinatively bonded to a Lewis acid site. The vibrational frequencies are distinct, with the Lewis-bound sites giving rise to bands located at 1450 and 1600 cm$^{-1}$, and the Brønsted-bound site at 1520 and 1620 cm$^{-1}$ [1].

The zeolite framework composition is usually described by the silicon to aluminum (Si/Al) ratio or the silica to alumina (SiO$_2$/Al$_2$O$_3$) ratio. These quantities are inversely proportional to acid site density [12]. The acidity, which depends on the amount of framework aluminum, can be adjusted either during the synthesis or during the post synthesis treatments of the zeolite, such as dealumination, ion-exchange, etc. [13]. The framework Al content controls also the hydrophilic-hydrophobic nature of zeolite. The zeolites with high concentrations of H$^+$ (high content of Al) are hydrophilic, having strong affinities for polar molecules small enough to enter the pores. The highly siliceous zeolites are inherently hydrophobic, taking up organic compounds from water-organic mixtures; the transition occurs at a Si/Al ratio near 10 [11]. The stability of the zeolite framework also depends on Si/Al ratio. The stability of the crystal lattice increases with increasing Si/Al ratio. Thermal stability of...
zeolites varies over a large temperature range and the decomposition temperature ranges from 700 to 1300°C [11]. For example, for low-silica zeolites the decomposition temperature is 700°C, whereas completely siliceous zeolites, such as silicalite, are stable up to 1300°C [1].

5.2 Zeolitic materials used in this study

The methanol dehydration to DME reaction has been studied over thirteen different zeolitic materials with various physicochemical characteristics. Below is given a brief description of these materials which are separated into four zeolite-type groups.

5.2.1 Zeolites ZSM-5

ZSM-5 zeolite belongs to the MFI structure, which is one of the most important and extensively studied zeolite framework. ZSM-5 is a medium pore size material with straight and sinusoidal channels. The straight channel has a diameter of 5.3-5.6 Å, whereas the sinusoidal channels have diameters of 5.1-5.5 Å (Fig. 5.5). In the MFI framework, the Si/Al ratio can range from 10 to infinity and when the framework is Al-free the zeolite is denoted as silicalite.

![Figure 5.5](image)

**Figure 5.5:** (A) Primitive unit cell of siliceous MFI; 12 T sites: yellow: Si or Al atoms, red: O atoms. (B) Schematic representation of the ZSM-5 “pipe system” viewed along the (010) direction. Straight channels composed of 10MR parallel to the b axis and intersecting sinusoidal channels parallel to the a axis [14]
Having 10-membered rings, ZSM-5 zeolite is an intermediate between classical shape-selective zeolites (such as ferrierite, erionite, chabazite) and large pore zeolites (such as faujasite, mordenite and fault-free offretite) [1, 2, 4, 11].

The catalytic performance of this material relies mainly on acidity (the acid strength and acid type). H-ZSM-5 zeolites have two different types of acid sites: Brønsted and Lewis acid sites. Brønsted acid sites are related to aluminum located in the framework of the zeolites whereas Lewis acid sites are related to the extra-framework aluminum (EFAL) or distorted aluminum in the framework. The acidic density and strength in zeolites increases with decreasing Si/Al ratio since acid sites are associated with Al presented in the structure. The strongest Brønsted acid sites can be obtained for completely isolated Al in the framework due to the higher electronegativity of Si compared to Al. The acidity depends also on cation type. It is known that the H-forms of zeolites are strong acidic materials. The H-form zeolites are obtained very easily by thermal treatment of the NH$_4$-form zeolites. The formation of H-form zeolite takes place at ca. 500 $^\circ$C when almost all NH$_3$ molecules are removed from NH$_4$-formed zeolite. In spite of the acidity, ZSM-5 zeolites have also strong coke resistance. The coke formation is a shape-selective process and ZSM-5 due to its medium size pore structure does not favour the production of heavy, large size coke molecules.

H-ZSM-5 zeolites are the most extensively studied catalysts for the methanol dehydration reaction and [15-17] is one of the best catalysts for this reaction (100% selectivity to DME) at relatively low temperatures. At high reaction temperatures, HZSM-5 favours the production of undesirable by-products (high hydrocarbons even coke) due to presence of strong acid site. This results in deactivation of the catalyst because the by-products hinder the access to the acid sites and plug the zeolite pores. Several attempts have been made in order to correlate the methanol dehydration rate with acid density, nature or strength of different catalysts including HZSM-5 zeolite. Ramos et al.[18] tried to correlate the rate with both total and more acidic Brønsted acid sites (obtained from the amount of pyridine sorbed at 250 $^\circ$C) in different solid acids including HZSM-5. They found that the methanol dehydration rate is correlated with the density of more acidic Brønsted acid sites. Trenco et al.[19-21] showed that the best linear correlation is obtained when the initial dehydration rate is plotted against the amount of strong Brønsted acid sites (those retaining pyridine at
400°C). They also reported that no such linear correlation is obtained when the initial rates are plotted against the total (Brønsted + Lewis) amount of acid sites (estimated from the NH₃ uptakes) or the density of Brønsted acid sites measured by FTIR-pyridine after desorbing the base at 250°C [20]. The authors stated that, the methanol dehydration activity (in the absence of deactivation phenomena) in the studied zeolites is dictated by the density of strong Brønsted acid sites rather than by the pore topology [20]. Kim et al. [22] concluded that the solid acid catalysts with high acid strength show the highest activity for methanol dehydration and that the γ-sites (peak observed at 500°C in NH₃-TPD spectra) in ZSM-5 catalysts are responsible for this reaction. On the contrary the relatively weak acid sites appearing below 450°C in the NH₃-TPD spectra are not important for dehydration of methanol to DME. On the other hand, based on the pyridine adsorption IR results, Mao et al.[23] concluded that there is no direct relationship between the activity for methanol dehydration and the nature of acid sites on HZSM-5 zeolites. Similarly, Laugel et al. [15] could not establish any clear relationship between the concentration of Brønsted acid sites and the catalytic activity of the different catalysts. In spite of the above findings, most researchers have claimed that the reaction takes place on all kinds of acid sites. The acid sites with weak or intermediate strength are responsible for the selective DME formation, whereas, the strong acid sites may further convert DME to light olefins that finally cause coke deposition and deactivation of catalyst [24-26].

In this study three ZSM-5 zeolites with different Si/Al ratio (provided by Zeolyst) were tested: CBV 2314 (Si/Al = 11.5), CBV 5524G (Si/Al = 25), CBV 8014 (Si/Al = 40). All the commercial samples were provided in ammonium form and were converted to proton form via calcination at 500°C for 2 hrs in air flow. A Silicalite zeolite (provide by Union Carbide) with Si/Al > 1000 was also used.

5.2.2 Zeolites Y

Zeolite Y (also zeolite X) exhibits the FAU (faujasite) structure and it is one of the most widely used catalyst in industrial processes (isomerisation, cracking, hydrocracking of petroleum products) [13]. In 1962, these zeolites were for the first time used as catalysts and the results obtained brought a huge revolution in petrochemical industry due to significant improvement of the existing processes [27].
The thermal stability of zeolite Y in these industrial processes is an important parameter as the temperature can range from 700 to 900 °C. In 1967, in addition to already investigated methods for stabilization of these zeolites, a new route has been reported for the synthesis of thermally stable Y(FAU) zeolite by McDaniel and Maher. The new highly stable form of Y was named “ultrastable Y (USY)” [4]. As shown in Figure 5.6 the FAU framework structure consists of a double 6 ring (D6R hexagonal prism), cages (inside diameter 7 Å) adjacent to hexagonal prism and supercages (inside diameter 13 Å) placed among the cages [1, 11].

![Figure 5.6](image)

**Figure 5.6:** (A) Primitive unit cell of FAU zeolite. Due to the high symmetry only one T site (yellow, T = Si or Al) and four inequivalent oxygen atoms (red, O). The ball and stick model highlights the hexagonal prism and (B) Schematic representation of the Faujasite structure FAU zeolite The corners denote the position of T sites (T = Si or Al) and the lines the bridging oxygen atoms. Different cation positions are indicated by Roman numerals whereas oxygen positions are indicated by Arabic numerals. Four different positions of the protons covalently bound to the oxygen around an Al atom [14].

The FAU structure resembles the diamond structure if we consider that the sodalite cages are the carbon atoms and the double 6-rings are C-C bonds [28, 29]. This group of zeolites has the biggest channels and supercages, which permit access to quite large molecules, making this structure applicable in catalytic processes.
The synthesis of DME via methanol dehydration over different Y zeolites has been studied by several authors, who investigated the resistance of these materials to water and the effects of the Si/Al ratio and acidity on catalytic performance [15, 16, 30]. The reaction has been also investigated over various modified zeolite Y catalysts (La, Ce, Pr, Nd, Sm via ion-exchange) and further applied for direct DME synthesis from hydrogenation of synthesis gas [24, 31]. Fei et al. [24] reported that methanol dehydration proceeds easily on the surface of HY and metal-modified HY zeolites. The stability of these materials was found to depend strongly on their acidity strength. The latter parameter should be depressed in order to prevent carbon deposition. Similarly, Jin et al.[31] concluded that Y zeolites with high proportion of moderate strength acid sites are more stable for methanol dehydration to DME.

In the present study, the following materials of this family have been investigated: NH₄NaY zeolite (CBV 300) with Si/Al = 2.55, USY (CBV 712) with Si/Al = 6, USY (CBV 780) with Si/Al = 40 and NaY (CBV 100,) with Si/Al = 2.55. All four samples has been provided by Zeolyst. The NH₄NaY (CBV 300) and USY (CBV 712) zeolites have been converted to their proton form by calcination at 450°C for 3 hrs or at 500°C for 2 hrs in air flow, respectively. The other two materials were already in proton form.

5.2.3 Zeolites Beta

Zeolite Beta can be described as three-dimensional, large pore zeolite with 12-ring structure. As can be seen in Figure 5.7 the framework structure of this zeolite contains three intersecting channels. The structure consists of straight 12-membered rings channels of a free aperture of 6.6·6.7 Å viewed along axis [1 0 0] and zigzag 12-membered rings channels of 5.6·5.6 Å viewed along axis [0 0 1].

Due to their large-pore system, large available micropore volume and good hydrothermal stability, Beta type zeolites have been used in several catalytic reactions. Additionally possessing a high-silica framework they have good thermal stability and consider as hydrophobic materials. Similar to zeolite Y, zeolite Beta has been used in the Fluid Catalytic Cracking (FCC) process of gas oil in the petroleum refinery.

Methanol dehydration to DME and other hydrocarbons has been investigated over different Beta type zeolites [32-35]. Dimitrova et al.[33] have studied the reaction over Beta zeolites with variable Si/Al ratio prepared by applying different methods.
They found that the porous structure as well as acidity of catalysts varies depending on the preparation method employed. All catalysts were found to possess activity in methanol conversion to DME reaction, although the catalyst with strong Brønsted sites facilitated the formation of (C2–C4) hydrocarbons.

Figure 5.7: Stereographic drawings and perspectives views of zeolite Beta viewed along the [1 0 0] and [0 0 1] axes. The 12-membered ring free pore apertures of straight and zig-zag channels are also shown for a good visualization of its structure. In the stereographic drawings the spheres represent the oxygen atoms and the tetrahedrally coordinated Si/Al atoms. Perspective views show the pore network of zeolite Beta containing straight and zigzag channels. The cylinders represent the channels of the zeolite Beta [36].

In this study three Beta zeolites with different Si/Al ratio (provided by Zeolyst) were used: CP 814E (Si/Al = 12.5), CP 811E (Si/Al = 37.5), CP 811C (Si/Al = 150). CP 814E and CP 811E were received in the ammonium form and were converted to the proton form by calcination at 500°C for 2 hrs in air flow; CP 811C was already in proton form.
5.2.4. Mordenite and Ferrierite Zeolites

Mordenite (framework code MOR) is considered as large pore zeolite and consists of 12-ring pore channels (0.65 x 7.0 Å) in [001] direction interconnected by 8-ring (3.4 x 4.8 Å) side pockets in [010] direction. Mordenite zeolite is widely used in industry, particularly for alkylation and isomerization reactions [37-39]. Because the 8-MR channels are too small for most molecules, the transport of molecules within this zeolite occurs only along the c axis. This is a crucial characteristic with several important implications. First, diffusion in one dimension is an inherently slower process than diffusion in two or three dimensions especially, when molecules are of the same size as the pore diameter, a case that forces molecules to move in “single file” because of steric constrains. Single-file diffusion is a very slow process. It implies that under typical reaction conditions, only a small fraction of the pore volume is actually accessible to the reacting molecules, i.e., the fraction of the pores that is very close to the pore mouths. Second, one-dimensional pore zeolites are highly prone to pore blockage because it is easy to completely block access to micropores by blocking the pores near their entrances [1]. Different strategies have been applied to overcome these drawbacks including the creation of intracrystal mesopores [37, 38] and the synthesis of nanometer-sized mordenite [40].

Figure 5.8: (A) Primitive unit cell (dashed frame) and conventional orthorhombic cell (solid frame) on the (0 0 1) projection of siliceous mordenite. Four inequivalent T sites (yellow, T = Si or Al) and ten inequivalent oxygen atoms (red, O). (B) Schematic representation of the mordenite “pipe system” [14].
Ferrierite (FER) is a medium-pore zeolite, possessing a two-dimensional network consisting of 10-ring channels (4.3×5.5 Å) in the [0 0 1] direction perpendicularly intersected with 8-MR channels (3.4×5.5 Å) in the [0 1 0] direction [2, 13]. In Figure 5.9 is shown the structure of this zeolite in two directions. Due to its excellent stability toward thermal, hydrothermal as well as chemical treatments this material attracted significant attention in industrial applications.

MOR zeolite has been used for the methanol conversion to DME reaction [41, 42] more frequently than FER zeolite. On the other hand, FER zeolite has been used in direct DME production from synthesis gas [43-45]. A range of different MOR catalysts have been investigated for methanol dehydration to DME [46]. Results obtained showed that catalysts with high surface area and medium acid strength (high Si/Al ratio) exhibit highest catalytic activity, selectivity and long term stability. N. Khadan et al. [41] have investigated the methanol conversion to DME over five different types of zeolites (Y, Mordenite, Beta, ZSM-5, Ferrierite). They concluded that methanol conversion and selectivity toward DME are reduced as the Si/Al ratio is increased. The methanol conversion depends on the amount of catalyst acidity whereas DME selectivity and catalyst stability depend on the strength of acidic sites.

Figure 5.9: Structure of ferrierite in the [0 0 1] and [0 1 0] directions. The openings of the 10-MR and 8-MR pores are colored [47].
In this study the Mordenite (CBV 21A) and Ferrierite (CP 914C) both with Si/Al=10 ratio has been provided by Zeolyst. They were both in ammonium form, and were thus converted to proton form via calcination at 500°C for 2 hrs in air flow.

A commercial γ-Al₂O₃ catalyst (Engelhard, Al-3992), a commercial silica-alumina (ASA-0.5, Harshaw) catalyst with Si/Al= 0.5 and a laboratory synthesized silica-alumina catalyst (ASA-35) with Si/Al= 35 [48] were also tested for comparison purposes.

Results and Discussion

5.3 Physicochemical characterization of catalysts

The physicochemical characteristics of all materials investigated in this Chapter are summarized in Tables 5.1 to 5.4. It is observed that the chemical composition (Al, Na content) and textural/structural properties of the studied catalysts vary significantly from one sample to another, as discussed in detail below.

Results obtained for the four Y and ultra-stable Y zeolites are presented in Table 5.1. It is observed that the Si/Al ratio ranges from 2.55 for CBV100 (NaY) to 40 for CBV780 (USY). Regarding chemical composition, the highest Al, Na content is observed for NaY zeolite (Al -9.35 wt.% and Na-8.01 wt.%) and the lowest for USY40 zeolite (Al-0.85 wt.% and Na-0.01 wt.% ). The pore size (pore opening) is 7.4 Å, while the internal pore space which corresponds to the internal pore size of cages for Y zeolite is 11.24 Å [49]. As described in section 5.2.2, the Y-zeolite exhibits FAU type framework with 12-membered rings and 3 dimensional structure. The HY (2.55) and NaY(2.55) zeolites exhibit relatively high specific surface areas of 918 m²/g and 893 m²/g, respectively, and their meso/micro surface is almost negligible. The other two samples exhibit measurable values of meso/macro surface, i.e. 154 m²/g for USY (6) and 160 m²/g for USY (40). The specific surface area of these samples is high (761-776 m²/g) most of it corresponding to micropore area.
**Table 5.1:** Chemical, textural, topological characteristics of Y-zeolites.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>Chemical composition (wt. %)</th>
<th>Surface area $^b$ (m²/g)</th>
<th>Pore size $^c$ (Å)</th>
<th>Int. pore space (Å) $^d$</th>
<th>Frame. type pore dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV 100 Zeolyst</td>
<td>NaY (2.55)</td>
<td>9.35 8.01</td>
<td>893 863 30</td>
<td></td>
<td></td>
<td>FAU, 12M-rings, 3-Dimen.</td>
</tr>
<tr>
<td>CBV 300 Zeolyst</td>
<td>H-Y (2.55)</td>
<td>9.68 2.10</td>
<td>918 882 36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBV 712 Zeolyst</td>
<td>USY (6)</td>
<td>5.90 0.03</td>
<td>761 607 154</td>
<td></td>
<td>7.4×7.4</td>
<td></td>
</tr>
<tr>
<td>CBV 780, Zeolyst</td>
<td>USY (40)</td>
<td>0.85 0.01</td>
<td>776 616 160</td>
<td></td>
<td>11.24</td>
<td></td>
</tr>
</tbody>
</table>

$^a$: Numbers refer to atomic Si/Al provided by the zeolite/silica-alumina manufacturer.

$^b$: Total surface area was determined by multi-point BET analysis, micropore area by V-t plot analysis and meso/macropore area by difference.

$^c$: International Zeolite Association, Structure Commission [50]

$^d$: Maximum included sphere diameter (calculation from packing of the spheres into rigid zeolite frameworks) [49]

These $^a$; $^b$; $^c$; $^d$ are referred also for Tables 5.2–5.4

In **Table 5.2** are summarized the physicochemical properties of zeolite ZSM-5 samples. The surface area varies from 390 m²/g for Silicalite to 454 m²/g for ZSM-5 (25). Similar to zeolite-Y samples, ZSM5 zeolites exhibit mostly microporous surface area. Interestingly, ZSM-5(40) and Silicalite samples display similar meso/macro surface areas of about 105 m²/g, which indicates a similar amount of mesopores in these samples. Results of chemical composition measurements show that all ZSM-5 samples are almost Na-free (**Table 5.2**). It is also observed that increase of Si/Al ratio from 11.5 to 40 results in a decrease of Al content from 3.20 to 0.91. As expected, the Al content is almost negligible for the Silicalite sample (Si/Al >1000).

The physicochemical characteristics of Beta (12.5), Beta (37.5), Beta (150), Mordenite and Ferrierite Zeolites are listed in **Table 5.3**.
**Table 5.2:** Chemical, textural, topological characteristics of ZSM-5 zeolites.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>Chemical composition (wt. %)</th>
<th>Surface area ( \text{b} ) (m²/g)</th>
<th>Pore size ( c ) (Å)</th>
<th>Int. pore space ( d ) (Å)</th>
<th>Frame. type pore dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBV 2314 Zeolyst</td>
<td>ZSM-5 11.5</td>
<td>3.20 0.06 418 362 56</td>
<td></td>
<td></td>
<td>5.1x5.5  5.3x5.6</td>
<td>MFI, 10-mem. rings, 3-Dimen</td>
</tr>
<tr>
<td>CBV 5524G Zeolyst</td>
<td>ZSM-5 25</td>
<td>1.50 0.03 454 360 94</td>
<td></td>
<td></td>
<td>6.36</td>
<td></td>
</tr>
<tr>
<td>CBV 8014 Zeolyst</td>
<td>ZSM-5 40</td>
<td>0.91 0.03 437 332 105</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicalite Un. Carbide</td>
<td>Silicalite</td>
<td>0.26 ~0 390 284 106</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 5.3:** Chemical, textural characteristics of Beta, Mordenite and Ferrierite zeolites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>Chemical composition (wt. %)</th>
<th>Surface area ( \text{b} ) (m²/g)</th>
<th>Pore size ( c ) (Å)</th>
<th>Int. pore space ( d ) (Å)</th>
<th>Framework type pore dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP 814E, Zeolyst</td>
<td>Beta 12.5</td>
<td>2.90 0.01 671 452 219</td>
<td></td>
<td></td>
<td>6.6x6.7  5.6x5.6</td>
<td>BEA, 12-mem. rings, 3-Dimen</td>
</tr>
<tr>
<td>CP 811E, Zeolyst</td>
<td>Beta 37.5</td>
<td>0.76 0.03 599 386 213</td>
<td></td>
<td></td>
<td>6.68</td>
<td></td>
</tr>
<tr>
<td>CP 811C, Zeolyst</td>
<td>Beta 150</td>
<td>0.27 0.01 624 441 183</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBV 21A, Zeolyst</td>
<td>MOR 10</td>
<td>3.63 0.02 528 491 37</td>
<td>6.5x7.02, 6x 5.7</td>
<td></td>
<td>6.70</td>
<td>MOR,12; 8-mem. rings, 1-Dimen</td>
</tr>
<tr>
<td>CBV 914C, Zeolyst</td>
<td>FER 10</td>
<td>3.72 0.06 368 336 32</td>
<td>4.2x5.4, 3.5x4.8</td>
<td></td>
<td>6.31</td>
<td>FER, 10; 8-mem. rings, 2-Dimen</td>
</tr>
</tbody>
</table>
It is observed that the Al content of Beta zeolites decreases by increasing the Si/Al ratio. The Beta (12.5) zeolite exhibits the highest surface area (671 m²/g) among these catalysts, which are all characterized by the existence of significant amount of meso/macroporosity.

The Mordenite (10) and Ferrierite (10) zeolites have almost the same Al content (ca. 3.6 wt.%) and negligible Na content. The surface area of Mordenite (10) is much higher than that of Ferrierite (10) however they both exhibit mostly micro porosity. These zeolites differ also according to their framework type and pore dimensions. As shown in Table 5.3 the Mordenite (10) exhibits MOR type framework 12 and 8 membered rings while the Ferrierite has FER type framework 10- and 8- membered rings.

In Table 5.4 are listed the results of physicochemical characterization of alumina and silica alumina catalysts. It is observed that these materials differ significantly from zeolites with respect to their textural and structural properties. The specific surface area varies from 195 m²/g for γ-Al₂O₃ to 470 m²/g for ASA (35). These samples exhibit mainly mesoporous structure and their pore size varies from 60-150 Å.

Table 5.4: Chemical, textural, topological characteristics of alumina and silica-alumina catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>Chemical composition (wt. %)</th>
<th>Surface area b (m²/g)</th>
<th>Pore size c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
<td>Na</td>
<td>Total</td>
</tr>
<tr>
<td>Al-3992 Englehard</td>
<td>γ-Al₂O₃</td>
<td>-</td>
<td>-</td>
<td>195</td>
</tr>
<tr>
<td>ASA -0.5 Harshaw</td>
<td>ASA (05)</td>
<td>27.5</td>
<td>0.09</td>
<td>208</td>
</tr>
<tr>
<td>ASA-35 Home made</td>
<td>ASA (35)</td>
<td>1.60</td>
<td>0.12</td>
<td>470</td>
</tr>
</tbody>
</table>

Representative XRD patterns of the studied zeolites are shown in Figure 5.10. It is observed that all samples are highly crystalline and they all exhibit the characteristic diffraction pattern of the respective zeolite structure [50]. The sharp and intense peaks in the XRD pattern of the ultra-stable Y (USY) zeolite verify that the greater part of this material is still highly crystalline despite the NH₄-exchange,
calcination and hydrothermal treatment steps that it has been subjected during its preparation. The two USY variants (CBV 712, Si/Al = 6 and CBV 780, Si/Al = 40) exhibit similar patterns (only the pattern of CBV 712 is shown in Fig. 5.10), while the unit cell size for the two zeolites is 24.35 Å and 24.24 Å, respectively (data provided by Zeolyst). This indicates that USY (40)/CBV 780 has been subjected to more intense framework dealumination and the remaining crystalline zeolitic framework has higher Si/Al ratio and thus smaller unit cell size due to the replacement of aluminum atoms by silicon atoms which have smaller atomic radius [51]. The relatively broader XRD peaks of zeolite Beta shown in Figure 5.10, compared to those of the rest of the zeolites, is in accordance with the small nano-crystal morphology.

![Figure 5.10: Representative XRD patterns of zeolite samples.](image)

The nitrogen adsorption-desorption isotherms (at -196°C) of the various zeolites are shown in Figure 5.11. It is observed that the adsorption isotherms of the parent (H+ or NH4+-exchanged) Y, Mordenite, Ferrierite and ZSM-5 zeolite samples are typical for microporous materials (type I in the IUPAC classification, exhibiting the characteristic plateau over the whole \( P/P_0 \) range, after the formation of the nitrogen monolayer within the micropores at very low \( P/P_0 \) (i.e. ≤ 0.01). In the case of Beta
zeolite the isotherm shows a continuous increase of adsorbed nitrogen over the whole
$P/P_0$ range (combination of type I and II isotherms) with a relatively steep pronounced
increase at $P/P_0 \geq 0.85$, which corresponds to meso/macropore sizes of ~35-60 nm (as
determined by Barret-Joyner-Halenda -BJH- pore size distribution analysis). This type
of meso/macroporosity can be attributed to inter-particle voids that are formed by the
aggregation of nano-sized primary crystals/particles, as has been discussed above.

**Figure 5.11:** Representative N$_2$ adsorption-desorption isotherms of samples.

The adsorption isotherm of USY (CBV 712, Si/Al = 6) zeolite exhibits also
combined characteristics of type I and II isotherms (mainly type I), with a gradual
increase of nitrogen uptake at $P/P_0 > 0.4$. This indicates the presence of secondary
mesopores and macropores that have been generated by the partial framework
dealumination and breakdown of the crystalline structure due to the hydrothermal
treatment of this zeolite [51]. The commercial γ-Al$_2$O$_3$ and amorphous silica-alumina
(ASA) catalysts exhibit nitrogen adsorption-desorption isotherms of similar shape
(representative isotherms of catalyst ASA, Si/Al = 0.5 are shown in Figure 5.11), which are characteristic of mesoporous materials with relatively disordered mesostructure and broad pore size distribution (average pore size of 15 nm).

In Table 5.5 are listed the total number of acid sites (expressed as mmol NH₃ per gram of catalyst determined by TPD-NH₃) and the molar ratio of Brønsted to Lewis acid sites (B/L ratio determined by FT-IR measurements coupled with in situ sorption of pyridine) of these catalysts.

**Table 5.5: Acidity of investigated catalysts.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total acid sites a (mmol NH₃/g)</th>
<th>Type of acid sites b (B/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaY (2.55)</td>
<td>0.10</td>
<td>0.1</td>
</tr>
<tr>
<td>H-Y (2.55)</td>
<td>3.32</td>
<td>15.1</td>
</tr>
<tr>
<td>USY (6)</td>
<td>0.68</td>
<td>1.6</td>
</tr>
<tr>
<td>USY (40)</td>
<td>0.07</td>
<td>2.5</td>
</tr>
<tr>
<td>ZSM-5 (11.5)</td>
<td>1.09</td>
<td>3.8</td>
</tr>
<tr>
<td>ZSM-5 (25)</td>
<td>0.55</td>
<td>3.9</td>
</tr>
<tr>
<td>ZSM-5 (40)</td>
<td>0.27</td>
<td>6.6</td>
</tr>
<tr>
<td>Silicalite</td>
<td>0.12</td>
<td>1.7</td>
</tr>
<tr>
<td>Beta (12.5)</td>
<td>0.59</td>
<td>1.9</td>
</tr>
<tr>
<td>Beta (37.5)</td>
<td>0.34</td>
<td>2.1</td>
</tr>
<tr>
<td>Beta (150)</td>
<td>0.08</td>
<td>1.8</td>
</tr>
<tr>
<td>Mordenite (10)</td>
<td>0.97</td>
<td>13.7</td>
</tr>
<tr>
<td>Ferrierite (10)</td>
<td>0.72</td>
<td>9.3</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>0.28</td>
<td>only Lewis</td>
</tr>
<tr>
<td>ASA (35)</td>
<td>0.29</td>
<td>0.6</td>
</tr>
<tr>
<td>ASA (0.5)</td>
<td>0.20</td>
<td>only Lewis</td>
</tr>
</tbody>
</table>

* Determined from TPD-NH₃

* Mole ratio of Brønsted to Lewis acid sites determined from FT-IR experiments with in situ pyridine adsorption.
The number of Brönsted and Lewis acid sites of all catalytic materials, as determined by pyridine adsorption/equilibration at different temperatures (i.e. 150, 250, 350 and 450°C), are shown in Figures 5.12 and 5.13.

**Figure 5.12:** Amount of Brönsted acid sites of (A) ZSM-5, Beta, Mordenite and Ferrierite zeolites and (B) Zeolite- Y, γ-Al₂O₃ and silica-alumina catalysts as determined by FT-IR measurements of *in situ* sorbed pyridine at increasing temperature.
Ammonia is a relatively small and very basic molecule and is being used as probe molecule for the determination of the total number of acid sites of zeolites and other aluminosilicate materials [51-55]. Ideally, the NH$_3$ molecules should "titrate"
quantitatively the Brönsted acid sites (bridging hydroxyls) that originate from the aluminum atoms possessing tetrahedral coordination in the crystalline zeolitic framework. In such a case the ammonia (acid sites) to aluminum mole ratio should be equal to 1, assuming that the content of Na⁺ is negligible. From the data listed in Table 5.5, the value of this ratio has been calculated to be 0.8-1.0 for the parent Y and ZSM-5 zeolites, with most of the acid sites being of the Brönsted type. This is evidenced by the FT-IR/pyridine results shown in Figure 5.12 and the relatively high values of the B/L mole ratio (i.e., 4-15) listed in Table 5.5.

The NH₃/aluminum mole ratio for the Beta zeolites is also high (0.8-1.2) and close to unity. On the other hand, for the Beta zeolite with low Si/Al ratio (12.5), as well as for the Mordenite and Ferrierite zeolites with low Si/Al ratios (10), the value of the ratio drops to 0.5-0.7. This indicates that part of aluminum is not tetrahedrally coordinated in the zeolitic framework and cannot generate acidic bridging hydroxyls. The presence of extra-framework aluminum (or silicon-aluminum) oxyhydroxide species in the parent H⁺-exchanged zeolites can be attributed either to incomplete crystallization of the synthesis gel or to the various post-synthesis treatment steps (calcination to remove the organic template, ion-exchange of the sodium cations with ammonium ions, and final calcination to produce the H⁺-form) that are applied in order to prepare the acidic H⁺-zeolites. These extra-framework Al (EFAL) species can function as Lewis acid sites, which in the case of Beta zeolite are relatively increased compared to the rest of zeolites (except the USY zeolites), as can be seen from the data in Table 5.5 (the B/L ratio for the Beta zeolites is relatively low, ~2).

Similar to the case of USY zeolite production, the hydrothermal treatment of zeolites leads to the formation of significant amounts of EFAL species [51, 52], which result in lower values for the NH₃/aluminum mole ratio, i.e., (0.3 for USY (6) and 0.2 for USY(40)). This is a strong indication that the EFAL species have limited capability of adsorbing NH₃ (compared to the bridging hydroxyls), while on the other hand, can induce Lewis acidity (as also observed for the parent calcined Beta zeolites). Indeed, the ratio of B/L acid sites for USY (6) is 1.6 (compared to 15 of the parent HY (2.55) zeolite). Removal of a significant part of EFAL via post-synthesis treatment of USY zeolites results in higher bulk Si/Al (as is the case of CBV (40) and eventually to somehow improved ratio of B/L acid sites, i.e., 2.5 (Table 5.5).
Although the presence of EFAL species in the zeolite can result in lower NH$_3$/aluminium ratio than that expected if all aluminum was within the zeolite framework, it may not be the sole reason, especially for the small pore zeolites. As mentioned above, the NH$_3$/aluminium ratio for Mordenite zeolite is 0.7 and for Ferrierite is 0.5 thus being in accordance with the decreasing micropore size of these two zeolites, especially compared to Y and Beta zeolites. The kinetic diameter of the ammonia molecule is ~2.6 Å (critical diameter ~3.6 Å) and that of pyridine is ~5.9 Å, being similar (or even larger in the case of pyridine) with the pore size of these two zeolites. This possible effect of the size of probe molecule can be also identified in the curves of Figure 5.12A, where it can be seen that despite the similar Si/Al ratios of the ZSM-5(11.5), Beta(12.5), Mordenite (10) and Ferrierite (10) zeolite samples, the two latter zeolites adsorb a considerably lower amount of pyridine on their Brönsted acid sites.

As far as the acidity strength is concerned, it is well-known that the higher amount of isolated framework Al atoms (higher framework Si/Al ratio) induce Brönsted acid sites (attributed to bridging framework hydroxyls) of higher strength, as is for example the case of ZSM-5 zeolite compared to Y zeolite [51, 52, 56, 57]. The data and curves of Figures 5.12 and 5.13, which show the relative ability of the zeolites to retain pyridine adsorbed on Brönsted and Lewis acid at various equilibration temperatures (i.e. 150, 250, 350 and 450 °C), provide a qualitative evaluation of the relative acidity strength of the zeolites. The higher the relative amount of acid sites (i.e., the amount of sorbed pyridine) at higher equilibration temperatures, the higher the acid strength of the catalyst. For ZSM-5 zeolites (Si/Al = 11.5, 25, 40) ~60-85% of the pyridine sorbed on Brönsted acid sites at 150 °C remains sorbed at 450 °C, indicating the relatively high acid strength of ZSM-5 zeolite (especially of that with the higher Si/Al of 40). Interestingly, this value was 70% for Silicalite, verifying the presence of Al traces in tetrahedral framework sites, which act as strong Brönsted acid sites. In the case of Beta zeolites (Si/Al= 12.5, 37.5, 150) the percentage is lower, i.e., 35-65%, as is for the parent Y zeolite (50%), the two USY zeolites (65% for CBV 712 and 40% for CBV 780), and Mordenite zeolite (60%). On the other hand, almost all pyridine remained sorbed on Ferrierite zeolite up to 450 °C, but this can be misleading since, as discussed above, pyridine cannot be considered as a "safe" probe molecule for measuring the acidity of this small pore zeolite. In contrast to
the Brønsted acid sites, the Lewis sites of all zeolites exhibit relatively high strength, since the same amount of pyridine remains sorbed on the samples over the whole equilibration temperature range, i.e., 150-450°C (Figure 5.13).

With regard to the amorphous silica-alumina (ASA) and γ-Al₂O₃ catalysts, the high aluminum content ASA sample (Si/Al = 0.5) and the γ-Al₂O₃ catalysts possess only Lewis acid sites, while the ASA catalyst with low aluminum content (Si/Al= 35) contains both Brønsted and Lewis acid sites, with B/L ratio of 0.6 (Table 5.5). The Brønsted acid sites of ASA(35) as well as Lewis acid sites of ASA(0.5) and γ-Al₂O₃, are of low strength, as can be revealed by the steep decline of the respective curves in Fig. 12B and Fig. 5.13B. Contrarily, the Lewis sites of ASA(35) Fig. 5.13B exhibit higher strength.

5.4 Catalytic performance tests and kinetic studies

5.4.1 Zeolites ZSM-5 and silicalite

5.4.1.1 Catalytic performance in the absence of H₂O in the feed

The catalytic performance tests in the absence of water in the feed were carried out under following experimental conditions: feed composition: 30% CH₃OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm³ min⁻¹.

Results of catalytic performance tests obtained over the three ZSM-5 and the Silicalite catalysts are shown in Figure 5.14 (A-D) where the conversion of methanol (X_MeOH) and selectivities to reaction products (S) are plotted for each sample as functions of reaction temperature. The equilibrium conversion curve for methanol dehydration to DME is also shown (dashed line), for comparison. Regarding the ZSM-5(11.5) catalyst, it is observed that it exhibits measurable MeOH conversion at temperatures lower than 150 °C and reaches equilibrium at ca. 290 °C (Fig. 5.14 A). Under these conditions, the catalyst is 100% selective to DME. Increase of reaction temperature above 300 °C results in an abrupt decrease of S_DME and in the formation of CH₄, C₂H₄, C₃H₆, C₃H₈ and higher hydrocarbons (HC). This is accompanied by an increase of methanol conversion, which takes values higher than those corresponding to equilibrium conversion of MeOH to DME (Fig. 5.14 A). This is a typical behavior of ZSM-5 zeolite in the methanol-to-hydrocarbons (i.e to light olefins and/or aromatics) reaction owing to its strong Brønsted acid sites and its medium-size channel-like micropore morphology [10, 58-61]. In the MTH process, the formation of DME has
been identified as the intermediate step towards the formation of hydrocarbons with ≥ 2 carbons atoms. Qualitatively similar results were obtained for ZSM-5(25), ZSM-5(40) and Silicalite catalysts (Fig. 5.14 B-D).

**Figure 5.14**: Conversion of methanol ($X_{\text{MeOH}}$) and selectivities to reaction products ($S$) as functions of reaction temperature obtained over (A) ZSM-5(11.5), (B) ZSM-5 (25), (C) ZSM-5(40) and (D) Silicalite zeolites. Experimental conditions: feed composition: 30% CH$_3$OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

The methanol conversion curves and selectivities to DME obtained over the ZSM-5 and the Silicalite catalysts are compared in Fig. 5.15A and Fig. 5.15B,
respectively. It is observed that increase of the Si/Al ratio from 11.5 to 25 results in a shift of the $X_{\text{MeOH}}$ curve to lower temperatures whereas further increase of Si/Al ratio to 40 has the opposite effect. The methanol conversion curve is shifted toward significantly higher temperatures for the Silicalite catalyst, which is characterized by a very low aluminum content (Si/Al>1000) (Fig. 5.15A).

![Graph A](image)

**Figure 5.15**: (A) Conversion of methanol, (B) selectivity to DME, (C) reaction rates expressed per gram of catalyst and (D) reaction rate expressed per total acid sites of catalysts obtained over the ZSM-5 and silicalite catalysts. Experimental conditions: feed composition: 30% CH$_3$OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$. 
It may be noted that the three ZSM-5 catalysts investigated reach equilibrium conversion to DME practically at the same temperature (290-300 °C), which is ca. 40 °C lower compared to that of the Silicalite sample. Interestingly, selectivity to DME seems to depend strongly on conversion of methanol. In particular, all four samples are 100% selective toward DME under conditions where methanol conversion is lower than that corresponding to equilibrium, and decreases sharply when $X_{\text{MeOH}}$ exceeds these values (Fig. 5.15B). This provides evidence that DME is the primary reaction product.

Results of kinetic measurements obtained for this set of catalysts are summarized in the Arrhenius plot of Fig. 5.15C, where the reaction rates are expressed per gram of catalyst. It is observed that catalytic activity follows the order of ZSM-5(25)>ZSM-5(40)>ZSM-5(11.5)>>Silicalite, i.e., it is similar to that obtained for methanol conversion (Fig. 5.15A). However, the activity of the three ZSM-5 catalysts (per gram of catalyst) does not vary significantly with Si/Al ratio. The apparent activation energy ($E_a$) of the methanol dehydration reaction was calculated from the slope of the fitted lines shown in Fig. 5.15C. Results show that $E_a$ is, practically, the same for the three ZSM-5 catalyst (54±5.5 kJ/mol) and similar to that obtained for the Silicalite sample (68±2.5 kJ/mol). This implies that the same reaction mechanism is operable for this set of catalysts under the present experimental conditions.

In order to evaluate the intrinsic reactivity of the acid sites of the catalysts, the reaction rates were also expressed per total number of acid sites (from TPD-NH$_3$) and the respective Arrhenius plots are shown in Fig. 5.15D. It is clear that the above order of the catalytic activity changes to ZSM-5(40)>Silicalite>ZSM-5(25)>>ZSM-5(11.5), i.e. the acid sites of ZSM-5(40) exhibit the highest reactivity followed by that of silicalite and ZSM-5(25), all three being significantly more reactive than those of ZSM-5(11.5). This could be attributed to the slightly stronger Brönsted sites of ZSM-5(40) compared to those of ZSM-5(25) and the significantly weaker Brönsted sites of ZSM-5(11.5) (Fig. 5.12A). Another possible explanation could be the higher Brönsted to Lewis (B/L) sites molar ratio of ZSM-5(40) compared to the other two ZSM-5 zeolites (Table 5.5), as discussed below. The surprisingly high specific reactivity of the silicalite zeolite, which contains very low amount of aluminum atoms, may be attributed to the presence of few but strong Brönsted acid sites (see section 5.3). Similar conclusions have been obtained in other studies on different catalytic reactions [52, 62].
Although the presence of more and/or stronger Brønsted acid sites seems to be the dominating factor in determining the reactivity of the ZSM-5 zeolites, still however the contribution from the Lewis acid sites is important. This can be realized by comparing the rates expressed per total acid site (Fig. 5.15D) with those expressed per total Brønsted or Lewis acid site (Fig. 5.16 A and B). If the Brønsted acid sites were the only active sites in DME formation, then the silicalite zeolite would have been the more reactive catalyst (Fig. 5.16 A), which however is not the case.

**Figure 5.16**: Arrhenius plots of reaction rates obtained over the ZSM-5 and silicalite catalysts (A) expressed per total Brønsted acid sites and (B) expressed per total Lewis acid sites. Experimental conditions: feed composition: 30% CH$_3$OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

5.4.1.2 Effects of the presence of H$_2$O in the feed

Under realistic reaction conditions, where methanol is produced via hydrogenation of CO$_2$, the gas mixture contains considerable amounts of water steam, which may influence the activity and stability of the methanol dehydration catalyst. In order to address this issue, the effects of the presence of 10% water vapour in the feed on catalytic performance have been investigated over the ZSM-5 and Silicalite samples, and results obtained are summarized in **Figure 5.17**. Similar to what was observed in the absence of H$_2$O in the feed (Fig. 5.14), the ZSM-5 zeolite catalysts exhibit
measurable activity at temperatures around 150 °C, and $X_{\text{MeOH}}$ increases progressively with increase of reaction temperature.

**Figure 5.17:** Conversion of methanol ($X_{\text{MeOH}}$) and selectivities to reaction products (S) as functions of reaction temperature obtained over (A) ZSM-5(11.5), (B) ZSM-5 (25), (C) ZSM-5(40) and (D) Silicalite zeolites in the presence of water vapor in the feed. Experimental conditions: feed composition: 30% CH$_3$OH + 10% H$_2$O (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

The methanol conversion curves and selectivities to DME obtained over the ZSM-5 and the Silicalite catalysts in the presence and in the absence of water in the feed are compared in **Figure 5.18**. It is observed that addition of H$_2$O results in a shift of the methanol conversion curves toward higher temperatures, which is more pronounced for the Silicalite sample.
Figure 5.18: Conversion of methanol ($X_{\text{MeOH}}$) and selectivity to DME as function of reaction temperature obtained over (A) ZSM-5(11.5), (B) ZSM-5(25), (C) ZSM-5(40) and (D) silicalite zeolites, in the absence (closed symbols, solid lines) and in the presence (open symbols, dashed lines) of 10% H$_2$O in the feed. The equilibrium conversion curves for methanol dehydration to DME are shown, for comparison. Experimental conditions: mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

Comparison of the methanol conversion curves obtained in the presence of H$_2$O (Fig. 5.19A) shows that the three ZSM-5 catalysts exhibit similar performance and reach equilibrium at temperatures around 300 °C, i.e., similar to those obtained in the absence of water. In contrast, the conversion curve of Silicalite is affected more
strongly by the presence of water and is shifted significantly toward higher temperatures.

The inhibiting effect of water can be attributed to the competition between water and methanol molecules for the same active acid sites, in agreement with results of

**Figure 5.19:** (A) Conversion of methanol, (B) selectivity to DME, and (C) reaction rates expressed per gram of catalyst and (D) reaction rate expressed per total acid sites of catalysts obtained over the ZSM-5 and silicalite catalysts. Experimental conditions: feed composition: 30% CH$_3$OH + 10% H$_2$O (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.
previous studies [63]. This implies that higher reaction temperatures are required to compensate this loss and achieve similar rates with those obtained with the dry feed.

Regarding selectivity to reaction products, all samples are 100% selective toward DME at temperatures lower than ca. 250 °C, and \( S_{\text{DME}} \) decreases rapidly at temperatures where \( X_{\text{MeOH}} \) exceeds equilibrium for DME formation (Fig. 5.19B). It is of interest to note that, under these conditions, selectivity toward higher hydrocarbons (\( S_{\text{HC}} \)) is generally higher in the presence of \( \text{H}_2\text{O} \) (Fig. 5.17) compared to the dry feed (Fig. 5.14).

The results of reaction rate measurements are summarized in the Arrhenius plots of Fig. 5.19C, where the rates are expressed per gram of catalyst. Similar to what was observed in the absence of water vapour (Fig. 5.15C) the three ZSM-5 catalysts exhibit practically the same activity, which is significantly higher compared to that of the silicalite zeolite. In all cases, reaction rates are lower in the presence of steam (compare results of Fig. 5.15C and Fig. 5.19C). Addition of \( \text{H}_2\text{O} \) affects also the apparent activation energy of the reaction which, in the case of ZSM-5 catalysts, increases from 54±5.5 kJ/mol to 74±5.6 kJ/mol. The situation is again different when the rates are expressed per total acid sites of the catalysts (Fig. 5.19D). The ZSM-5(40) zeolite appears to have the more active acid sites, as in the dry feed experiments, while the reactivity of ZSM-5(11.5) seems to be less affected by the addition of water compared to those of the rest of the catalysts (compare results of Fig. 5.15D and Fig. 5.19D).

In Figure 5.20 are compared the rates expressed per total Brönsted and Lewis acid sites over this set of catalysts when water is present in the feed. It is observed that the rates obtained for all catalysts fall almost on the same line (Fig. 5.20A). This indicates that the activity of these samples for methanol dehydration reaction in the presence of water is determined by the number of Brönsted sites present on the catalyst surface. It is worth to mention that no such correlation was found in the absence of water in the feed composition over these catalysts.
Figure 5.20: Arrhenius plots of reaction rates obtained over the ZSM-5 and silicalite catalysts (A) expressed per total Brönsted acid sites and (B) expressed per total Lewis acid sites. Experimental conditions: feed composition: 30% CH$_3$OH +10% H$_2$O (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

5.4.1.3 Long-term stability tests

The variation of the conversion of methanol with time-on-stream obtained over the ZSM-5 and Silicalite catalysts at a constant temperature for a period of about 40 hours is shown in Fig. 5.21. Dashed vertical lines indicate shutting down of the system overnight, where the catalyst was kept at room temperature under He flow. It should be noted that the reaction temperature was different in each case and was chosen so as to result in approximately the same initial methanol conversion of ca. 80%. In all cases, the reactor was initially fed with a 30%CH$_3$OH (in He) mixture for a period of ca. 20 hours. Then, water vapour (10% H$_2$O) was added in the feed for a period of ca. 15 hours and, after that, the feed was switched back to the dry mixture. Under these conditions, all catalysts were 100% selective toward DME. After ~15 hrs under dry feed conditions, the conversion of methanol over the ZSM-5(11.5) and silicalite zeolites was relatively stable, compared to the slight deactivation observed for the ZSM-5(25) and ZSM-5(40) samples, despite the considerably higher temperatures at which the former zeolites were tested (Fig. 5.21). Addition of 10% H$_2$O in the feed was found to result in a decrease of methanol conversion, which was not recovered when water was removed from the feed. This effect was less significant for the ZSM-5(11.5) zeolite and more pronounced for the most active ZSM-5(25) catalyst (Fig. 5.21).
Figure 5.21: Conversion of methanol ($X_{\text{MeOH}}$) as a function of time-on-stream in the absence and in the presence of water vapor in the feed over ZSM-5 and silicalite zeolites. Experimental conditions: feed composition: 30% CH$_3$OH (+ 10% H$_2$O) in He; mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$. Dashed vertical lines indicate shutting down of the system overnight, where the catalyst was kept at room temperature under He flow.

Results presented in Fig. 5.21 show that that the presence of water in the feed results in an irreversible deactivation of all ZSM-5 and Silicalite catalysts investigated here, in a manner that depends on the Si/Al ratio of MFI zeolite and, probably, on the reaction temperature employed. It has to be noted that, at the reaction temperatures selected to perform the stability tests, the formation of hydrocarbons is negligible under wet feed conditions as can been seen in Fig. 5.17. Thus, a possible reason for
this irreversible deactivation could be the framework dealumination of zeolites, even under these mild hydrothermal conditions, which may lead to changes in their acidic properties, i.e. decrease of the Brønsted acid sites associated with the framework Si(OH)Al bridging hydroxyls.

5.4.2 Zeolites Y

5.4.2.1 Catalytic performance in the absence of H₂O in the feed

Results of catalytic performance tests obtained over the four Y zeolites investigated are presented in Fig. 5.22, where the conversion of methanol (Fig. 5.22A) and selectivity toward DME (Fig. 5.22B) are plotted as functions of reaction temperature. It is observed that the NaY(2.55) zeolite is practically inactive in the temperature range of interest, with \( X_{\text{MeOH}} \) reaching a value of only 30% at 445 °C (Fig. 5.22A). The low activity of this sample can be related to its low acidity (Table 5.1).

This is supported by the fact that the more acidic HY(2.55) catalyst, which has the same Si/Al ratio, and has resulted from the Na-Y zeolite by ion-exchange, is significantly more active. This sample exhibits measurable activity at temperatures lower than 200 °C and reaches equilibrium conversion at ca. 380 °C. A similar conversion curve, with higher conversions at intermediate temperatures, was obtained for the ultra-stable USY(6) catalyst. Interestingly, an increase of the bulk Si/Al ratio of the USY zeolites from 6 to 40 results in a significant decrease of catalytic activity. This is evidenced by the shift of the MeOH conversion curve obtained for USY(40) to higher temperatures by more than 60 °C, compared to USY(6) (Fig. 5.22A).

Regarding selectivity to reaction products, results presented in Fig. 5.22B show that the H-Y zeolite is 100% selective towards DME at temperatures up to ca. 270-280 °C, where conversion of methanol is relatively low (~30%). These values are significantly lower, compared to the ~100% selectivity and 80-90% conversion obtained over the ZSM-5 zeolites at the same temperature. However, high conversion-selectivity levels were obtained over the USY(6) zeolite at higher temperatures (~345 °C), while the USY(40) catalyst exhibited a lower conversion of ca. 60% for maximum selectivity of 100% at ~380 °C.

Results of kinetic measurements obtained over Y zeolite catalysts are summarized in the Arrhenius plot of Fig. 5.22C, where reaction rates are expressed per gram of catalyst. It is observed that the HY(2.55) and USY(6) catalysts have similar
activity, which is about one order of magnitude higher compared to that of USY(40) and more than two orders of magnitude higher than that of NaY(2.55). Similar to what was observed for the ZSM-5 zeolites, when the reaction rates are expressed per total acid site (Brønsted+Lewis) the reactivity profile of the catalysts changes and the zeolites USY(6) and USY(40) appear as the most reactive ones followed by H-Y and Na-Y zeolites (Fig. 5.22D). The higher reactivity of the USY zeolites can be related to the fact that they contain both Brønsted and Lewis acid sites, which are stronger than those present on the parent H-Y zeolite (Fig. 5.12B and Fig. 5.13B).

Figure 5.22: (A) Conversion of methanol, (B) selectivity to DME, and reaction rates expressed (C) per gram of catalyst and (D) per total acid site over the Y and USY catalysts. Experimental conditions: feed composition: 30% CH₃OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm³ min⁻¹.
5.4.2.2 Effects of the presence of water in the feed and long-term stability tests

The effects of the presence of water in the feed on catalytic activity and stability have been investigated over the best performing USY(6) catalyst and results obtained are presented in Fig. 5.23.

**Figure 5.23:** Results of catalytic performance tests, kinetic measurements and long-term stability tests obtained over the USY(6) zeolite catalyst. (A) Effects of the presence of H$_2$O in the feed on the conversion of methanol and selectivity to DME. (B) Arrhenius plot of reaction rates (expressed per gram of catalyst) in the absence and in the presence of water vapour in the feed. (C) Conversion of methanol as a function of time-on-stream in the absence and in the presence of water vapor in the feed. Dashed vertical lines in (C) indicate shutting down of the system overnight. Experimental conditions: feed composition: 30% CH$_3$OH (+ 10% H$_2$O) in He; mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.
It is observed that, the addition of water results in a substantial decrease of methanol conversion (Fig. 5.23A) and the reaction rate (Fig. 5.23B), which is accompanied by an increase of the apparent activation energy of the reaction (Fig. 5.23B). Selectivity to DME is slightly affected, remaining ~100% for the whole temperature range up to equilibrium conversion (Fig. 5.23A).

As shown in Fig. 5.23C, the USY(6) catalyst is very stable in the absence of water in the feed for a period of ~ 20 hrs at 280°C with a methanol conversion of ~50%. Addition of 10% H$_2$O results in a decrease of $X_{\text{MeOH}}$, which is partially restored when the feed is changed again to the dry mixture. This could be related to the relatively high stability of the zeolitic framework of these materials (named ultra-stable zeolites). This stability originates from their preparation protocol, which includes various hydrothermal treatment steps at ca. 500-700°C starting from NH$_4$-exchanged Y zeolite. Thus, the framework dealumination of the USY zeolites under the milder hydrothermal conditions of the reaction is relatively small compared to that of the fresh Y or ZSM-5 zeolites. Therefore, the framework Brønsted acid sites are slightly affected under the present reaction conditions, leading to recovery of activity upon removal/desorption of water.

5.4.3 Zeolites Beta

5.4.3.1 Catalytic performance in the absence of H$_2$O in the feed

The catalytic performance of Beta zeolite catalysts has been investigated over three samples of different Si/Al ratio, and results obtained in the absence of H$_2$O in the feed are shown in Fig. 5.24.
Figure 5.24: Conversion of methanol ($X_{\text{MeOH}}$) and selectivities to reaction products ($S$) as functions of reaction temperature obtained over Beta zeolite catalysts: (A) Beta (12.5); (B) Beta(37.5) and (C) Beta (150). The equilibrium conversion curve for methanol dehydration to DME is shown with dashed line. Experimental conditions: feed composition: 30% CH$_3$OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

The three samples show measurable methanol conversion at temperatures lower than 200 °C, and $X_{\text{MeOH}}$ reaches equilibrium in the temperature range of 350 to 400 °C. Interestingly, and in spite of the different acidity of these materials (Table 5.5 and Figs. 5.12A and 5.13A), the methanol conversion curves obtained over Beta(12.5), Beta(37.5) and Beta(150) catalysts are similar to each other (Fig. 5.25A).
Experimental conditions: feed composition: 30% CH$_3$OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$.

In contrast, selectivity to reaction products depends strongly on the type of the Beta zeolite employed (Fig. 5.25). As shown in Fig. 5.25B, the Beta(12.5) catalyst is 100% selective toward DME in the whole temperature range investigated whereas $S_{DME}$ decreases abruptly over the Beta(37.5) sample at temperatures above 350 °C, i.e. before reaching equilibrium conversion to DME. At 400°C the Beta(37.5) zeolite showed high selectivity toward higher hydrocarbons. Regarding to Beta (150) catalyst, selectivity to DME starts to decrease at substantially lower temperatures, i.e., above 250 °C (Fig. 5.25B).

Results of kinetic measurements obtained over the three Beta zeolite catalysts are shown in the Arrhenius plot of Fig. 5.25C. It is observed that these materials exhibit practically the same activity per gram of catalyst, and have the same apparent activation energy for the reaction ($E_a$=64±2.1 kJ/mol). However, when the rates are expressed per total acid sites, the Beta(150) appears to possess the most reactive sites (Fig. 5.25D).
5.4.3.2 Effects of the presence of water in the feed and long-term stability tests

The effects of addition of 10% H\textsubscript{2}O in the feed on catalytic performance have been investigated over the Beta(37.5) catalyst and results obtained are summarized in Fig. 5.26.

**Figure 5.26:** (A) Effects of the presence of H\textsubscript{2}O in the feed on the conversion of methanol and selectivity to DME obtained over the Beta (37.5) zeolite. (B) Arrhenius plot of reaction rates obtained in the absence and in the presence of H\textsubscript{2}O. Experimental conditions: feed composition: 30% CH\textsubscript{3}OH (+ 10% H\textsubscript{2}O) in He; mass of catalyst: 100 mg; total flow rate: 30 cm\textsuperscript{3} min\textsuperscript{-1}.

In contrast to what was observed for ZSM-5 and HY zeolites, the presence of water vapor does not affect significantly the conversion of methanol at low temperatures (Fig. 5.26A). It is of interest to note that the specific reaction rates and the apparent activation energy are, practically, the same in the absence and in the presence of steam (Fig. 5.26B). In addition, selectivity toward DME remains above 90% at high temperatures in the presence of steam. This latter observation may indicate the significant deactivation of the zeolitic Brönsted acid sites that lead to the formation of higher hydrocarbons and the predominant role of the existing or even newly formed Lewis acid sites.

Results of the long-term stability tests performed with the use of the Beta samples at 230 °C are shown in Fig. 5.27.
A decrease of conversion was observed over the Beta(12.5) catalyst upon addition of water, which was however fully reversible after returning back to the dry feed (Fig. 5.27). Regarding the Beta (37.5) sample, it is observed that $X_{\text{MeOH}}$ decreases progressively with time-on-stream but does not seem to be affected by addition of H$_2$O in the feed. Stabilization of conversion is finally attained after a period of ca. 25 hrs-on-stream. Similar results were obtained for the Beta(150) zeolite catalyst. The conversion of methanol over this catalyst tends to stabilize after ca. 10 hours-on-stream and slightly increases following addition of H$_2$O in the feed. This behavior could be related to the resistance to hydrothermal deactivation of the active Lewis acid sites present in this zeolite compared to the framework Brönsted acid sites of ZSM-5.

Figure 5.27: Conversion of methanol ($X_{\text{MeOH}}$) as a function of time-on-stream in the absence and in the presence of water vapor in the feed over Beta zeolite catalysts at $T=230 \, ^\circ\text{C}$. Experimental conditions: feed composition: 30% CH$_3$OH (+ 10% H$_2$O) in He; mass of catalyst: 100 mg; total flow rate: 30 cm$^3$ min$^{-1}$. Dashed vertical lines indicate shutting down of the system overnight, where the catalyst was kept at room temperature under He flow.
zeolites. An additional possible explanation for this behavior can be the ability of the high-Si/Al Beta zeolites of not being affected by the addition of water at relatively low reaction temperatures (Fig. 5.26A).

5.4.4 Zeolites Mordenite and Ferrierite

Results of catalytic performance tests and kinetic measurements obtained with the use of the dry feed over the Mordenite(10) and Ferrierite(10) zeolites are summarized in Fig. 5.28.

**Figure 5.28:** (A) Conversion of methanol, (B) selectivity to DME and (C) reaction rates obtained over the Mordenite(10) and Ferrierite(10) zeolite catalysts. Experimental conditions: Feed composition: 30% CH₃OH (in He), mass of catalyst: 100 mg; total flow rate: 30 cm³ min⁻¹.
It is observed that the methanol conversion curve of Mordenite(10) is shifted toward higher temperatures by ca. 30-40 °C, compared to that of Ferrierite(10), whereas \( X_{\text{MeOH}} \) reaches equilibrium at ca. 400 °C for both samples (Fig. 5.28A). Under the present experimental conditions, these materials are 100% selective toward DME in the whole temperature range investigated (Fig. 5.28B).

Results of kinetic measurements show that the apparent activation energy of the reaction is similar over these two samples. However, the reaction rate is about 5 times higher for Ferrierite(10) compared to Mordenite(10) zeolite (Fig. 5.28C).

5.4.5 Alumina and silica-alumina (ASA) catalysts

In Fig. 5.29 are compared the results of catalytic performance tests and kinetic measurements obtained over \( \gamma\)-Al\(_2\)O\(_3\), ASA(0.5) and ASA(0.35) catalysts in the absence of water vapor in the feed.
In agreement with results of the Chapter 4, it is observed that $\gamma$-Al$_2$O$_3$ is a relatively active catalyst, which shows measurable activity at temperatures around 170 °C and reaches equilibrium conversion at ca. 290 °C (Fig. 5.29A). It is of interest to note that, in contrast to what was observed for other active materials, such as ZSM-5 zeolites (Fig. 5.14), further increase of temperature does not result in methanol conversions higher than those of equilibrium conversion of MeOH to DME. The Lewis acid sites (of weak/moderate strength) of the $\gamma$-Al$_2$O$_3$ are highly active for the total conversion of methanol, with 100% selectivity to DME. A qualitatively similar behavior is observed for the ASA(0.5) catalyst (with low Si/Al of 0.5), the conversion curve of which is shifted to higher temperatures by ca. 30 °C and reaches equilibrium at around 310 °C. The ASA(35) catalyst with Si/Al of 35 is much less active compared to the other two materials and $X_{\text{MeOH}}$ reaches equilibrium at temperatures around 400 °C. These results indicate that increase of Si/Al ratio of the amorphous silica-alumina catalysts has a negative effect on catalytic performance. However, all three materials are 100% selective towards DME with the exception of $\gamma$-Al$_2$O$_3$, for which $S_{\text{DME}}$ decreases slightly at temperatures higher than 350 °C (Fig. 5.29B).

Results of kinetic measurements obtained for this set of catalysts are presented in the Arrhenius plot of Fig. 5.29C. It is observed that, in the temperature range investigated, the reaction rates per gram of catalyst are 2-3 times higher for $\gamma$-Al$_2$O$_3$ compared to ASA(0.5) and more than one order of magnitude higher compared to ASA(35). The apparent activation energy determined for $\gamma$-Al$_2$O$_3$ (103±4.1 kJ/mol) is the highest among those of other catalysts investigated in this study. A similar value ($E_a = 93±4.7$ kJ/mol) was obtained for ASA(0.5) and a much smaller one ($E_a = 72±4.0$ kJ/mol) for the ASA(35) catalyst with the highest Si/Al ratio.

From the results presented above it becomes apparent that insertion of Si in the structure of alumina reduces the activity of "pure" $\gamma$-Al$_2$O$_3$ which contains only Lewis acid sites of relatively low/medium strength (Fig. 5.13B). The activity of ASA(0.5) is
lower than that of $\gamma$-$\text{Al}_2\text{O}_3$ despite that this catalyst contains also only Lewis acid sites of similar strength with those of $\gamma$-$\text{Al}_2\text{O}_3$. However, when the reaction rates are expressed per total number of acid sites (Fig. 5.29D), the two catalysts appear to have almost similar reactivity. The generation of Brönsted acid sites of relatively weak/moderate strength in ASA(35) and probably the different nature of the remaining Lewis sites have a pronounced negative effect on activity, despite the almost double surface area of this catalyst compared to $\gamma$-$\text{Al}_2\text{O}_3$ and ASA(0.5).

Regarding to the effect of water addition in the feed, results presented in Chapter 4 [64], show that $\gamma$-$\text{Al}_2\text{O}_3$ exhibits a reversible decrease of activity in the presence of $\text{H}_2\text{O}$, whereas the selectivity to DME remains unaffected (Chapter 4 Fig. 4.10 and 4.12B).

### 5.5 Comparison of various zeolitic catalysts

Results of catalytic performance tests and kinetic measurements obtained over representative zeolitic catalysts are summarized and compared in Fig. 5.30. It is observed that the conversion of methanol follows the order ZSM-5(40) > ZSM-5(11.5) > Ferrierite(10) > Mordenite(10) ~ Beta(12.5) ~ USY(6) > HY(2.5). The ZSM-5 zeolite is clearly the most active zeolitic catalyst, regardless its Si/Al ratio. Amongst the ZSM-5 variants, those of relatively high Si/Al ratio, such as ZSM-5(40) and ZSM-5(25), contain stronger Brönsted acid sites and exhibit the highest activity. Up to a certain reaction temperature of ca. 270-290°C, which coincides with the temperature for equilibrium conversion of methanol to DME, the ZSM-5 zeolites are also 100% selective toward the formation of DME (up to ~85% conversion). Above this temperature, the conversion increases further reaching 100%. This indicates the onset of other reactions that are favoured under these conditions, which lead to the formation of light and higher hydrocarbons via oligomerization, alkylation, cracking, isomerization, hydrogen transfer and aromatization reactions [58, 60, 61]. As the rest of the zeolites are less active, compared to ZSM-5, they reach equilibrium conversion at much higher temperatures, of ca. 350-400°C, still being ~100% selective toward DME, except in the case of H-Y zeolite whose selectivity decreases substantially at temperatures much lower than those corresponding to equilibrium conversion. As a result, slightly lower yields of DME can be obtained by the less active zeolites, since as the reaction
temperature increases the equilibrium conversion of methanol to DME drops from ca. 90% at 250°C to 85% at 400°C.

Figure 5.30: (A) Conversion of methanol, (B) selectivity to DME, (C) reaction rates expressed per gram of catalysts and (D) reaction rates expressed per total acid sites obtained over the zeolites ZSM-5(40), ZSM-5 (11.5), Ferrierite(10), Mordenite(10), Beta(12.5), USY(6) and HY(2.55). Experimental conditions: feed composition: 30% CH₃OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm³ min⁻¹.

The activity variation of the various zeolitic catalysts can be also revealed by comparing the Arrhenius plots of reaction rates when expressed per gram of catalyst
Despite the clear differences in reactivity amongst the various zeolites, the apparent activation energies ($E_a$) are not significantly different, thus indicating the similar nature of active sites for the reaction under study. These sites could be either Brönsted acid sites on the bridging hydroxyls of the zeolitic framework or extra-framework Si or Si-Al oxy(hydro)oxide species acting as Lewis acid sites. The somehow lower activation energy obtained over the ZSM-5 zeolites can be indicative that the relatively stronger Brönsted acid sites of this type of zeolites are the most appropriate for the dehydration of methanol to DME. An additional factor could be related with favourable confinement effects induced within the ZSM-5 channel-like micropores of $\sim$0.55 nm that may enhance diffusion and adsorption of methanol.

When the rates are expressed per total acid site (Fig. 5.30D), the reactivity of the acid sites of the various zeolites can be qualitatively evaluated. It becomes clear that the acid sites of ZSM-5(40) are the most reactive ones, even when compared to those of ZSM-5(11.5), as discussed in the respective ZSM-5 section above. On the other hand, the acid sites of H-Y and Mordenite zeolites appear to be the least reactive. A direct comparison of the different microporous structures of the MFI, Beta, Mordenite and Ferrierite zeolites, even for the catalyst samples with more or less similar Si/Al ratio of ca. 10-12.5, would not be safe due to significant variations in the acidic properties of these zeolites, i.e. number, strength and type (Brönsted or Lewis) of acid sites.

5.5.1 Correlation of reaction rates with acidity

The direct correlation of methanol dehydration reaction rates (expressed per gram of catalyst) with the number of total acid sites of all the catalysts tested (including γ-Al$_2$O$_3$ and ASA) is schematically depicted in Fig. 5.31. The rates are compared at the standard temperature of 260°C at which all catalysts are $\sim$ 100% selective towards DME. In the same figure, the correlation of the reaction rates with the Brönsted to Lewis acid sites ratio (B/L) is also shown. This latter correlation presents the combined effect of Brönsted and Lewis acid sites on the reactivity of the catalysts. It can be observed that the rate for ZSM-5 zeolites decreases with increasing total acid sites, while it increases with increasing B/L ratio (Fig. 5.31 A and C). This is an additional indication, in accordance with the discussion above, that the strong Brönsted acid sites of ZSM-5 zeolites with relatively high Si/Al ratio (ca. 40) favour the dehydration of methanol to DME, at least at the moderate temperature of 260°C.
Figure 5.31: Reaction rates expressed per gram of catalysts versus (A, B) total number of acid sites and (C, D) Brönsted to Lewis acid sites mole ratio (B/L) for all catalysts tests at 260°C. Experimental conditions: feed composition: 30% CH₃OH (in He); mass of catalyst: 100 mg; total flow rate: 30 cm³ min⁻¹.

In contrast to ZSM-5 zeolites, the increase of the total acid sites of Beta and USY zeolites leads to higher reaction rates, which cannot be associated with a change in the B/L ratio, as this remains almost the same for all the catalysts (Fig. 5.31 A and C). Thus, it can be suggested that both Brönsted and Lewis acid sites contribute equally importance to the activity of these zeolites. Furthermore, this increase of reaction rate cannot be associated with increased strength of Brönsted acid sites as the most active
Beta(12.5) zeolite possesses sites of lower strength compared to those of Beta(37.5) (Fig. 5.12A).

As far as the Mordenite(10), Ferrierite(10) and H-Y(2.5) zeolites are concerned, they exhibit very high B/L ratio (Table 5.5) and their moderate catalytic activity is mainly associated with their Brønsted acid sites of relatively moderate strength (Fig. 5.12 A and B). In contrast, the relatively weak Lewis acid sites of γ-Al₂O₃ or low-silicon ASA(0.5) appear to be more reactive than the weak/moderate zeolitic Brønsted acid sites in the dehydration of methanol to DME reaction.
5.6 Conclusions

The activity and selectivity of zeolite catalysts for the dehydration of methanol to dimethyl ether have been investigated over a number of zeolites together with alumina, silica-alumina catalysts. Results show that catalytic behaviour depends on the topology of zeolites due to differences in zeolite micropore structure and Si/Al ratio as well as on the number, strength and nature of active acid sites. Below are summarized the general conclusions of this investigation:

- The activity of zeolite catalysts for the methanol dehydration to DME follows the order ZSM-5 > Ferrierite > Mordenite ~ Beta ~ USY > H-Y. Under the experimental conditions employed here, the selectivity to DME is ~100% at reaction temperatures of 280-300°C, where equilibrium conversion of methanol to DME (ca. 80-85%) is achieved for all catalysts, with the exception of the H-Y zeolite that is less selective at lower temperatures and conversions. At temperatures above ca. 300 °C, the high reactivity of the ZSM-5 zeolites leads to conversion values higher than those corresponding to the equilibrium conversion of methanol to DME, because of the onset of side reactions which lead to the formation of higher hydrocarbons. As a result, conversion of methanol reaches 100% $T \leq 400°C$, which is accompanied by a significant decrease of DME selectivity and increased formation of light as well as higher hydrocarbons.

- The reactivity of the zeolite catalysts was evaluated by determining the reaction rates per gram of catalyst, per acid site (total: Bronsted+Lewis) and per B/L mole ratio. By combining these kinetic results with the acidic properties of the zeolites (number, type and strength of acid sites) the following conclusions have been extracted:
  - The strong Brönsted acid sites of ZSM-5 zeolites with relatively high Si/Al ratio (ca. 40) represent the most active sites in methanol dehydration to DME reaction. However, the overall reactivity of the ZSM-5 zeolites is also affected by the balance of the Brönsted to Lewis acid sites (B/L ratio).
  - The activity of Beta and USY zeolites is determined by both Lewis and Brönsted acid sites.
  - The moderate/low reactivity of Ferrierite, Mordenite and H-Y zeolite with Si/Al ratios of 10, 10 and 2.5, respectively, are determined by the abundant Brönsted acid sites of relatively weak/moderate strength.
Results obtained over γ-Al₂O₃, ASA (0.5) and ASA (35) samples reveal that, γ-alumina and ASA (0.5) with weak Lewis acid sites exhibit qualitatively similar behavior, whereas ASA (35) with relatively weak/moderate strength of Brönsted acid sites possess much less catalytic activity.

Long-term stability tests have been performed under dry and wet feed compositions for most zeolitic materials. Results obtained showed that:

- The ZSM-5 and USY zeolites are relatively stable under dry feed conditions. The hydrothermally stabilized framework of USY zeolites offers better resistance in the presence of water in the feed compared to the ZSM-5 zeolites, which showed a permanent deactivation.

- Beta zeolites showed a progressive loss of their activity in long-term tests (ca. 15-20 hrs) under dry feed conditions. Interestingly, the catalytic activities of Beta (37.5) and Beta(150) zeolites do not seem to be affected by the addition of H₂O vapor in the feed. The catalytic activity of Beta(12.5) was affected by the addition of 10% water in the feed but this effect was found to be reversible.

Based on the results of catalytic activity and long-term stability tests of the various zeolites, the ZSM-5 and USY zeolites as well as γ-Al₂O₃ can be considered as the most promising methanol dehydration catalysts that could be used in the one step CO₂ hydrogenation to methanol/DME process.
5.7 References


In this chapter, the methanol synthesis reaction from CO$_2$-H$_2$ mixtures is investigated over commercial and home-made CuO/ZnO/Al$_2$O$_3$ catalysts. Catalytic activity, selectivities and yields of reaction products have been evaluated at 30 bar pressure, in the temperature range of 170-250 °C, using different feed compositions (CO$_2$:H$_2$= 1:3, 1:6, 1:9) and flow rates. The aim is to identify optimal experimental conditions that could be then used in the study of the direct conversion of CO$_2$/H$_2$ mixtures into methanol/DME. The chapter involves also the investigation of the direct CO$_2$ hydrogenation to methanol/DME reaction over a set of bifunctional catalysts comprising a methanol synthesis and a methanol dehydration component. The latter experiments have been carried out at 30 bar pressure, in the temperature range of 180-250 °C, using a feed composition of CO$_2$:H$_2$=1:6, and 30ml/min flow rate.

### 6.1 CO$_2$ hydrogenation to methanol over copper-based catalysts

#### 6.1.1 Preparation of copper-based catalysts

Two different commercial and home-made CuO/ZnO/Al$_2$O$_3$ catalysts have been investigated for the methanol synthesis reaction (Table 6.1). The commercial copper based catalyst, denoted as CZA1, was provided by Alfa Aesar (45776). The home-made copper based catalyst, denoted as CZA2, was synthesized by co-precipitation, following the method described by Baltes et al. [1]. The solutions of the precursor salts (Cu(NO$_3$)$_2$·3H$_2$O, (0.3 mol/L), Zn(NO$_3$)$_2$·6H$_2$O (0.15 mol/L), Al(NO$_3$)$_3$·9H$_2$O (0.05 mol/L)) and the solution of the precipitant (Na$_2$CO$_3$ (1 mol/L)) were added dropwise (6ml/min) in 200 mL of distilled water kept at 65 °C under vigorous stirring. The precipitation was performed at pH 6.2±0.1. During precipitation and aging the temperature and pH were kept constant. After aging for 1 h, the precipitate was filtered and washed thoroughly with distilled water to
remove Na	extsuperscript{+} ions, dried at 80 °C for 8h and finally calcined. The calcination was performed by heating from room temperature to 300 °C, with a heating ramp of 2 °C/min, and then keeping at 300°C for 3h.

**Table 6.1:** Copper based catalysts studied for the methanol synthesis reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition (%)</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CuO</td>
<td>ZnO</td>
</tr>
<tr>
<td>CuO/ZnO/Al	extsubscript{2}O	extsubscript{3}, Alfa Aesar, 45776</td>
<td>63.5</td>
<td>24.7</td>
</tr>
<tr>
<td>CuO/ZnO/Al	extsubscript{2}O	extsubscript{3}, Home made</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

**Results and discussion**

6.1.2 Physicochemical characterization of catalysts

Results of catalyst characterization are summarized in **Table 6.2**, which shows the specific surface area (SSA), pore volume and average pore size of fresh, reduced and used catalysts. It is observed that the SSA of the fresh CZA1 catalyst (102 m	extsuperscript{2} g	extsuperscript{-1}) is relatively higher than that of the fresh CZA2 catalyst (86 m	extsuperscript{2} g	extsuperscript{-1}).

**Table 6.2:** Specific surface area (SSA), pore volume, pore size and particle size of fresh, reduced and used CZA1 and CZA2 catalysts.

<table>
<thead>
<tr>
<th>Cat.</th>
<th>SSA (m	extsuperscript{2} g	extsuperscript{-1})</th>
<th>Pore volume (cm	extsuperscript{3} g	extsuperscript{-1})</th>
<th>Average pore size (nm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh</td>
<td>Red.</td>
<td>Used</td>
<td>Fresh</td>
</tr>
<tr>
<td>CZA1</td>
<td>102</td>
<td>72</td>
<td>79</td>
<td>0.2</td>
</tr>
<tr>
<td>CZA2</td>
<td>86</td>
<td>56</td>
<td>54</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The nitrogen adsorption/desorption isotherms of CZA1 and CZA2 samples are shown in **Figure 6.1**. As it can be seen, the catalysts differ substantially regarding their porosity. CZA1 presents the classical type IV isotherm (according to the IUPAC classification), which is typical for mesoporous solids. The type H1 hysteresis loop, which occurs at the relative pressure range P/P	extsubscript{0}=0.6-0.9, indicates a broad pore size distribution with cylindrical shape [2, 3]. Indeed, pores with size in the range 2-8 nm (shown in **Figure 6.2**) were measured for fresh CZA1, the average pore width being 7.8 nm (**Table 6.2**).
Figure 6.1: The \( \text{N}_2 \) adsorption/desorption isotherms of fresh, reduced and used CZA1 and CZA2 catalysts.

Figure 6.2: Pore size distribution of fresh, reduced and used catalysts.

The \( \text{N}_2 \) adsorption/desorption isotherm for CZA2 (Figure 6.1), resembles a type II isotherm with almost no plateau at high \( P/P_0 \) values, which is usually observed for materials with macropores or interparticular mesoporosity [4]. The hysteresis loop appearing at higher relative pressures indicates larger mesopores. Thus, high porosity and large pores are expected for CZA2. A large pore size distribution can be observed (Figure 6.2): a small contribution of pores around 3 nm and the main porosity being due to pores in the range 10-30 nm. The average pore diameter for this catalyst has been calculated to be 23 nm and the total porosity 0.6 \( \text{cm}^3\text{g}^{-1} \), which are much higher than that of CZA1 (Table 6.2).
Exposure of the catalysts to reduction and reaction conditions results in a substantial deterioration of the texture, which is more pronounced for the home-made material (Figures 6.1, 6.2 and Table 6.2). In the case of the used CZA1 catalyst, the smaller pores are destroyed to a higher extent and larger pores are formed (Figure 6.2). The average pore size increases to 10.6 nm but the total pore volume remains the same (Table 6.2). Although there is no important change in the pore size distribution of the used CZA2 (Figure 6.2 and Table 6.2), the number of pores decreases considerably after reduction and catalytic tests, resulting in much lower total pore volume as compared with the fresh catalyst. Summarizing, the two catalysts have different textural properties and CZA1 exhibits higher resistance to sintering.

The XRD patterns of the fresh, reduced and used CZA catalysts are shown in Figure 6.3. Results obtained confirm the presence of CuO monoclinic phase at $2\theta = 35.6^\circ, 38.8^\circ, 66.1^\circ$ for both the home-made (CZA2) and the commercial (CZA1) catalysts [5, 6]. The peaks observed at $31.8^\circ, 36.3^\circ, 47.5^\circ, 56.7^\circ, 61.63^\circ, 62.9^\circ$ and $68.08^\circ$ can be assigned to ZnO [6-9]. However, the presence of the intense peak located at $2\theta = 35.8^\circ$ for CZA1 and at $2\theta = 35.9^\circ$ for CZA2, which is situated between the peaks at $2\theta = 35.6^\circ$ corresponding to CuO and $2\theta = 36.3^\circ$ corresponding to ZnO, indicates the presence of a common Cu-Zn-O phase. Reflections due to Al$_2$O$_3$ could not be observed, indicating that the Al$_2$O$_3$ phase is in the amorphous state [10]. In the XRD pattern of the CZA1 catalyst, the presence of magnesium oxide (MgO(OH), JPCS 27-0759) was also detected at $2\theta = 26.5^\circ$, while other reflection peaks of MgO are covered by those of ZnO.

After reduction the two catalysts exhibit more important differences in their XRD patterns. For CZA1 catalyst, peaks due to CuO decrease in intensity (although not completely disappearing) and one new sharp peak appears at $43.3^\circ$ which is accompanied by two other peaks located at $50.4^\circ$ and $74.1^\circ$. All of these new peaks are attributed to metallic Cu [8]. In the case of used CZA2, the CuO diffraction peaks become more intense and narrower whereas the peaks attributed to Cu$^0$ are just discernible. The peaks corresponding to ZnO remain almost intact. The peak at $2\theta = 36.3^\circ$ corresponding to ZnO is more clearly observed. In the case of CZA2, after reduction the CuO diffraction peaks become more intense and narrower and the peaks attributed to Cu$^0$ are just discernible. Two peaks are clearly observable at $2\theta = 35.6^\circ$ and $2\theta = 36.4^\circ$, showing the decomposition of the common Cu-Zn-O phase. The peaks corresponding to ZnO remain almost intact. The XRD pattern of CZA2 indicates that the catalyst is not fully reduced.
After catalytic tests the peak corresponding to ZnO for CZA1 is sharper and the peak of metallic copper decreases in intensity. In the case of the used CZA2 catalyst, CuO diffraction peaks become more intense and narrower, whereas peaks corresponding to Cu$_2$O are also detected (Figure 6.3). It is also observed that the peak of ZnO at $2\theta=36.3^\circ$ and that of CuO at $2\theta=35.6^\circ$ overlap. A similar behavior has been observed by other authors [6]. It is worth mentioning that the peak located at $2\theta=43.3^\circ$ is intense in the XRD pattern of the used CZA1 catalyst while it is hardly seen for the used CZA2 catalyst. The other 2 peaks attributed to metallic Cu ($50.4^\circ$ and $74.1^\circ$) are observed only in the XRD pattern of the used CZA1 catalyst.

![Figure 6.3: X-ray diffraction (XRD) patterns obtained for CZA1 catalyst: a) fresh, b) reduced, c) used, and for CZA2 catalyst: d) fresh, e) reduced, e) used.](image-url)

Summarizing, the differences in the XRD patterns of the two catalysts show that under the same reduction and reaction conditions CZA1 is reduced to a higher degree than CZA2. Peaks corresponding to ZnO are more intense for CZA2, compared to the CZA1 catalyst. This is due to the different composition and the preparation method used for these catalysts.
6.1.3 Catalytic performance tests and kinetic measurements

Results of catalytic performance tests obtained over the CZA1 and CZA2 catalysts are summarized in Figure 6.4, where the conversion of CO2 ($X_{CO2}$), selectivities ($S_{MeOH}, S_{CO}$) and yields ($Y_{MeOH}, Y_{CO}$) of reaction products are plotted as functions of reaction temperature. The equilibrium conversion-selectivity-yield curves are also shown for comparison. It should be noted that methanol and CO were the only carbon-containing products detected under the present reaction conditions.

As observed in Figure 6.4A, the CO2 conversion increases with increasing the reaction temperature. The selectivity to methanol is favoured at low temperatures whereas $S_{CO}$ increases with increasing the reaction temperature. Arena *et al.* [11-14] have extensively studied the methanol synthesis via CO2 hydrogenation. Their results published in [11] showed that the CO2 conversion and methanol selectivity curves were always beyond the equilibrium levels when Cu/Zn/Al or Cu/Zn/Ce are used as catalysts, indicating operation in the kinetic regime. The experimental conditions used in the present study are different than those used in [11]. However, as observed in Fig. 6.4A, the reaction over CZA1 and CZA2 catalysts is far from thermodynamic equilibrium. The CO2 conversion curve is lower than that expected by thermodynamics indicating that the system is controlled by kinetics for the whole temperature range.

The methanol selectivity curve is near to that at equilibrium, as predicted by thermodynamics, only at temperatures lower than 180°C. However increase of temperature cases a rapid decrease of the methanol selectivity curve. The representative curves of CO yield obtained over the CZA1 and CZA2 catalysts (Fig. 6.2 C,D) show well coincidence with the CO equilibrium yield curve at temperatures up to ca. 200°C. At higher temperature the yield of CO takes higher values than those predicted by thermodynamics. This indicates that the formation of CO is not only due to the RWGS reaction. Arena *et al.* [11] have found that CO forms via both parallel (RWGS) and consecutive methanol decomposition paths at temperatures higher than 200°C. Thus, although the present catalytic results indicate that higher temperatures (T>250°C) are needed in order to reach equilibrium conversion, there are two negative aspects: the observed methanol decomposition and the possible deactivation of the Cu-based catalyst due to sintering [15]. Methanol synthesis reaction over the Cu/Zn/Zr and CZZX (X = La, Ce, Nd and Pr) catalysts was studied by Ban *et al.* [5] in the temperature range from 210 to 250 °C. The authors concluded that the maximum conversion is
obtained at 230 °C. Taking the above mentioned factors into account, the CO₂ hydrogenation to methanol/DME has been examined in this study at temperatures up to 250°C.

**Figure 6.4**: Conversion of carbon dioxide (X_CO₂), selectivities and yields of CO and methanol as functions of reaction temperature obtained over CZA1 catalyst (A), (C) and CZA2 catalyst (B), (D). Experimental conditions: feed composition: CO₂:H₂=1:6; flow rate 60ml/min; P=30bar; W/F=0.0083 g/ml min⁻¹; T=170-240°C.

Up to now the state of active sites (Cu₀ or Cu⁺) of copper based catalysts is not clear. Some authors consider that Cu₀ are the active sites [16], whereas others claim that Cu⁺ species are important for methanol synthesis reaction [17]. More recent studies confirm that both Cu⁺ and Cu₀ species are involved in the methanol synthesis reaction [12, 18, 19]. Results of the present study show that both species
are present on the reduced CZA1 and CZA2 catalysts (Fig. 6.3). However, the relative amount of the metallic phase on the reduced CZA1 catalyst is higher than that of the reduced CZA2 catalyst. If only metallic species were active for the title reaction then CZA2 catalyst should not exhibit almost the same catalytic activity as CZA1. Results presented in Fig. 6.4 show that conversion of CO$_2$ is, practically, the same for the CZA1 and CZA2 catalysts. However the selectivity as well as the yield of methanol is a little higher over the CZA1 sample. It might be possible that the Cu$^+$ species facilitate the CO formation via RWGS reaction [20]. For exhibiting better methanol selectivity, the CZA1 has been chosen as methanol synthesis component of the bifunctional catalytic system for the direct CO$_2$ conversion to methanol/DME reaction.

Results of kinetic measurements obtained over the CZA catalysts are summarized in the Arrhenius plot of Figure 6.5, where the reaction rates are expressed per gram of catalyst.

![Figure 6.5](image)

**Figure 6.5:** Arrhenius plots of specific reaction rates obtained over the studied CZA samples under differential reaction conditions.

As it can be seen the activity of these catalysts (per gram of catalyst) does not vary significantly. The apparent activation energy ($E_a$) of the methanol synthesis reaction was calculated from the slope of the fitted lines. It is observed that $E_a$ is, practically, the same for these two catalysts taking a value of 10.4 kcal mol$^{-1}$ for CZA1 and 13.4 kcal mol$^{-1}$ for CZA2.
6.1.4 Effects of feed composition and flow rate on catalytic performance

In direct production of methanol/DME through CO₂ hydrogenation the evaluation of optimal reaction conditions is an important step for maximizing the methanol/DME production, for shifting the CO₂ conversion toward methanol and also to minimizing catalyst deactivation. For this reason the effects of feed composition and flow rate on catalytic performance have been studied over the CZA1 sample. Results showing the effects of CO₂:H₂ ratio in the feed on the conversion of CO₂ and the selectivities to reaction products are presented in Figure 6.6. Reaction stoichiometry demands a CO₂:H₂ molar ratio 1:3. With this ratio, a 3% CO₂ conversion is achieved at 180 °C, which increases to 14% at 240 °C. However, as temperature increases, selectivity to CO augments at the expense of methanol. These results indicate that a competition exists between methanol synthesis, methanol decomposition and reverse water gas shift reactions: methanol synthesis is favored at lower temperatures and the other two reactions at higher temperatures.

Increasing the hydrogen content in the feed (changing the CO₂:H₂ molar ratio to 1:6), enhances both CO₂ conversion and methanol production over the entire temperature range investigated (Fig. 6.6). Further increase of hydrogen content in the feed, CO₂:H₂ molar ratio to 1:9, has no considerable effect on CO₂ conversion up to 220 °C, provoking an increment of CO₂ conversion at higher temperatures. However, for this CO₂:H₂ ratio, CO production is promoted for the whole temperature range. Taking all the above into account, it may be concluded that CO₂ hydrogenation to methanol is favoured in the presence of excess of H₂ in the feed, in agreement with literature results [21]. The CO₂:H₂ = 1:6 molar ratio seems adequate for methanol synthesis and has been chosen as the feed composition for further investigations.
Figure 6.6: The effects of feed composition on (A) conversion of carbon dioxide \( \left( X_{CO_2} \right) \), (B) selectivity to methanol \( \left( S_{MeOH} \right) \) and (C) selectivity to CO \( \left( S_{CO} \right) \) obtained over CZA1 catalyst. Experimental conditions: flow rate 60ml/min; \( W/F=0.0083 \) g min/ml; \( P=30 \) bar; \( T=180\text{-}240^\circ C \).

Two different flow rates have been chosen in order to investigate the influence of the space velocity on the catalytic activity and products selectivities over the CZA1 catalyst. Results obtained are summarized in Figure 6.7, which shows the effects of space velocity on CO\(_2\) conversion (A), methanol yield (B) and CO yield (C) in the temperature range of 180-250 °C.
Figure 6.7: The effects of reaction flow rate on (A) conversion of carbon dioxide ($X_{\text{CO}_2}$), (B) selectivity to methanol ($S_{\text{MeOH}}$), (C) yield of methanol ($Y_{\text{MeOH}}$), (D) selectivity to CO ($S_{\text{CO}}$) and (E) yield of CO ($Y_{\text{CO}}$) obtained over CZA1 catalyst. Experimental conditions: feed composition $\text{CO}_2: \text{H}_2=1:6$, $P=30\text{bar}$, catalyst amount-0.5g, $T=180-250^\circ\text{C}$. 
It is observed that the decrease of flow rate (increase of contact time) results in an increase of both the CO₂ conversion and the yields of both reaction products in agreement with literature results [5, 7, 11]. Zhang et al. [22] reported that with the increase of space velocity, the conversion of CO₂ decreases and CH₃OH selectivity increases. However, no such conclusion can be extracted based on the present results. In this work flow rate of 30ml/min is chosen as an optimal reaction rate for the methanol synthesis reaction. Representative results obtained for this flow rate are summarized in Figure 6.8, which shows the CO₂ conversion, selectivities to products and yields of products in the temperature range of 180-250 °C.

**Figure 6.8**: (A) Conversion of carbon dioxide (X_{CO₂}), selectivities to CO, methanol and (B) conversion of carbon dioxide (X_{CO₂}) and yields of CO and methanol as functions of reaction temperature obtained over CZA1 catalyst. Experimental conditions: feed composition CO₂:H₂=1:6, flow rate 30ml/min, P=30bar, W/F=0.016 g/ml min⁻¹, T=180-240°C.

The stability of the methanol synthesis catalyst was also investigated. In Figure 6.9 are presented the CO₂ conversion and the yields of products obtained over the CZA1 sample at a constant temperature of 250 °C, after 1, 9, 25 and 46 hours on stream. It is observed that the conversion of CO₂ as well as the yields of methanol and carbon monoxide gradually decrease with time-on-stream. However, catalytic activity and products yields are restored after the catalyst is regenerated under H₂ flow (100ml/min) at 200 °C for 1 hour at atmospheric pressure (the values are presented after the dashed vertical line in Fig. 6.9). The formation of carbonaceous deposits (coking) and crystal growth of Cu crystallites (sintering) are
considered as the main reasons for the deactivation of methanol synthesis catalysts [23, 24].

**Figure 6.9:** The conversion of carbon dioxide ($X_{CO2}$) and yields of CO and methanol ($Y_{CO}$, $Y_{MeOH}$) obtained after 1, 9, 25, 46 hours on stream and regeneration (after dashed line) over the CZA1 catalyst. Experimental conditions: flow rate 30ml/min, feed composition CO$_2$:H$_2$=1:6, W/F=0.016 g min/ml, P=30bar, T=250$^\circ$C. Regeneration conditions: 100ml/min H$_2$ flow, at 200$^\circ$C, for 1 hour, at atmospheric pressure.

The presence of water under reaction conditions may suppress coking but causes additional problems such as the temporary poisoning of the active sites [7], the formation of new copper and zinc phases that are not active for the reaction and/or permanent loss of activity due to metal loss caused by hydrothermal leaching [24]. The synthesis of methanol from CO$_2$ hydrogenation involves the formation of 1 mol of water per mol of methanol (CO$_2$ + 3H$_2$ → CH$_3$OH + H$_2$O). During the combined synthesis of methanol/DME more water is formed from methanol dehydration (2CH$_3$OH → CH$_3$OCH$_3$ + H$_2$O). Wang et al. [24] reported the formation of Cu$_2$(OH)$_2$CO$_3$ and Zn$_5$(OH)$_6$(CO$_3$)$_2$ phases due to higher partial pressure of water in DME synthesis, resulting in the decrease of the number of active sites of the Cu-based catalyst and the weakening of the synergistic effect between Cu and ZnO. Cu$^{0}$ crystal growth and metal loss of Zn and Al (hydrothermal leaching) may also be enhanced due to the presence of water [24]. Consequently, deactivation during the combined methanol/DME synthesis over a bifunctional catalytic system is more rapid for the methanol synthesis component than for the methanol dehydration [24]. Li et al. [7] have observed that water addition in the feed during
CO₂ hydrogenation to methanol, results in the immediate decline of CO₂ conversion, the decrease depending on the amount of water. Conversion has been found to recover slowly to the original level when the water was removed from the feed. These results suggested that poisoning of the active sites due to water is reversible [7]. Taking into account that in the present case catalytic activity can be easily restored under H₂ flow at 200°C for 1 hour, it seems reasonable to assume that under these reaction conditions (e.g. 30 bar and 250°C), the main reason for deactivations is water strongly adsorbed on the active sites. This inhibits the CO₂ hydrogenation reaction and leads in temporary catalyst deactivation, in accordance with the conclusion of Li et al. [7].

6.2 CO₂ hydrogenation to methanol/DME over hybrid catalysts

6.2.1 Preparation of copper-based catalyst admixed with alumina and W/alumina catalysts

The catalysts used in this section have been made by admixing CZA1, a metal based catalyst for methanol synthesis, and γ-Al₂O₃ (Engelhard, denoted as Al4 see Chapter 4 Table 4.1), an acid component for methanol dehydration. The selection of Al4 catalyst as an acid component is based on the results obtained during the investigation of methanol dehydration reaction over different alumina catalysts (Chapter 4). Briefly, the Al4 with SSAs around 190 m² g⁻¹, possessing mainly mesoporous structure, was found to exhibit significant activity in methanol dehydration reaction and was able to reach equilibrium conversions at temperatures around 230 °C under atmospheric pressure. As an acidic catalyst, Al4 possesses only Lewis acid sites with a weak to medium acidic strength.

One more catalyst has been made by admixing CZA1 with a separately prepared W/Al₂O₃ catalyst. The supported WO₃ catalyst has been used as alcohols dehydration catalyst by many researchers [25-27]. In this work the W/Al₂O₃ has been synthesized by wet-impregnation [28] of aqueous ammonium (para) tungstate, (NH₄)₁₀H₂(W₂O₇)₆ (Sigma-Aldrich, 322385) onto Al₂O₃ (Engelhard, Al4) support. An aqueous solution of ammonium tungstate was first prepared. The Al4 was added to above solution. Afterwards the mixture was placed in a water bath and the evaporation of water takes place at vacuum under 50°C. The resulting slurry was dried at 100°C for 2 hours and then calcined at 450°C for 4 hours.

Prior to admixing the metallic and acidic components, they were dried, crashed and sieved to the required mesh size (0.125<d<0.18mm). Subsequently, they were mixed in a solution of methanol and the resulting slurry mixture was left
to dry at room temperature under stirring. In Table 6.3 are listed the investigated admixed catalysts used in this section for CO$_2$ hydrogenation to MeOH/DME reaction.

**Table 6.3:** Copper based catalyst admixed with γ-alumina and WO$_3$-γ-alumina catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass ratio of metal/acid functions</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comm. copper based catalyst + γ-Al$_2$O$_3$ Engelhard</td>
<td>1:1</td>
<td>CZA1/Al4</td>
</tr>
<tr>
<td>Comm. copper based catalyst + γ-Al$_2$O$_3$ Engelhard</td>
<td>1:2</td>
<td>CZA1/Al4</td>
</tr>
<tr>
<td>Comm. copper based catalyst + WO$_3$/γ-Al$_2$O$_3$ Engelhard</td>
<td>1:1</td>
<td>CZA1/WAl4</td>
</tr>
</tbody>
</table>

**Results and discussion**

6.2.2 *Catalytic performance tests over CZA1/Al4 and CZA1/WAl4 catalysts*

6.2.2.1 *CZA1/Al4 admixed catalyst (1:1 and 1:2 ratios)*

Results of catalytic performance tests, obtained over the CZA1/Al4 (ratio 1:1) catalyst with the use of CO$_2$:H$_2$=1:6 feed composition, are summarized in Figure 6.10, where the conversion of carbon dioxide, selectivities and yields of products are plotted as functions of reaction temperature. The equilibrium conversion-selectivity-yield curves are also shown for comparison. Results obtained indicate that the admixed catalyst exhibits very low activity. The CO$_2$ conversion at 240 °C is 21.1%. It is observed that the CO$_2$ conversion is far from equilibrium, especially at low temperatures, and that the selectivity and yield of CO are much higher than those at equilibrium. Frusteri *et al.* [29], studied multifunctional Cu–ZnO–ZrO$_2$/H-ZSM5 catalysts prepared by various methods and reported that methanol-to-CO decomposition or RWGS reactions are more favoured than the CO$_2$ hydrogenation reaction at high temperature (>200 °C). It is observed also that the selectivity to methanol is higher than that of equilibrium, whereas the selectivity to DME is only 1.18% at 240 °C. The presence of high concentrations of methanol (Y$_{MeOH}$=7 % at 240 °C) at the reactor effluent indicates that the amount of acid sites is insufficient to convert the formed methanol to DME under these reaction conditions.
γ-Al₂O₃ has been studied extensively as acidic component for direct DME synthesis from CO/H₂ mixtures [10, 30-33] but not so often for direct DME synthesis from CO₂/H₂ mixtures [23]. The main reason is probably related to the excess of water formed via three different reactions during CO₂/H₂ conversion, contrary to CO/H₂ conversion where water is formed only via methanol dehydration reaction. Results presented in Fig. 6.10 indicate that water produced through the methanol synthesis, RWGS and methanol dehydration reaction has blocked all the active sites for methanol consumption through competitive adsorption with methanol on the alumina surface. Xu et al. [34] studied the methanol dehydration to DME reaction over γ-alumina by introducing different amounts of water. They found that the gradual increase of water partial pressure results in the progressive increase of activation energy of the reaction. They attributed the increase in Ea to the heat of water adsorption on the surface of γ-Al₂O₃ at high water coverage [34].

Another factor which may be responsible for the observed dramatic deactivation of Al4 alumina catalyst is the high pressure of the reaction. Under these conditions, the reaction temperature must be higher than 230°C (under
30 bar pressure water evaporates at 230°C) to prevent the water condensation on the catalyst surface.

An attempt has been made to study the methanol dehydration reaction over bare Al₄γ-alumina under high pressure. In Figure 6.11 are presented the results of catalytic performance tests obtained over Al₄ under 1 and 10 bar pressure together with the equilibrium conversion curve (dashed line). It is observed that the methanol dehydration reaction is effected by increase of pressure at low reaction temperatures. Zhang et al. [35, 36] have examined methanol dehydration to DME reaction by ranging the pressure from 0.1 to 1.0MPa at two different temperatures (280 and 320°C) and concluded that the methanol conversion is unaltered by pressure. As can be seen in Figure 6.11, at temperatures higher than 300 °C the methanol conversion curve at 0.1 MPa and 1.0MPa pressure coincides and follows the equilibrium conversion curve.

![Figure 6.11](image)

**Figure 6.11**: (A) Conversion of methanol as a function of reaction temperature under 1 bar and 10 bar pressure. Experimental conditions: flow rate 183 ml/min, amount of catalyst: 2g, T=150-400°C.

The acidic nature (only Lewis acid sites) of Al₄ alumina may also be a possible reason of this catalytic behaviour. Takeguchi et al. [37] reported that during the syngas to DME reaction the pressure of water formed by the dehydration of methanol is quite high, and activity of Lewis acid sites is suppressed by adsorbed water at lower temperatures. In this case, the Brønsted acid–Lewis base pair sites become the major active sites for the dehydration of methanol in the STD process. Mao et al. [31] investigated the direct synthesis of DME from
synthesis gas over different hybrid catalysts. They have also concluded that the dehydration reaction becomes the rate-determining step when γ-Al₂O₃ is used as acid component, because the acidity of γ-Al₂O₃ is not strong enough to convert effectively the produced methanol to DME. This conclusion is in line with the results presented in Figure 6.10: over a catalyst configuration having a metal:acid ratio of 1:1, the methanol dehydration step is the rate determining step.

By changing the ratio of the hybrid catalyst components, the DME/MeOH ratio in the product mixture can be controlled. If the same amount of methanol formation catalyst is used, reaction systems with higher loading of the methanol dehydration catalyst would lead to higher DME yield at the expense of methanol yield. In an attempt to increase the production of DME through methanol dehydration, the amount of acid component in the CZA1/Al4 bifunctional system has been raised to CZA1/Al4 (ratio 1:2). The results of catalytic activity tests obtained of using a CO₂:H₂=1:6 feed composition are presented in Figure 6.12.

It is observed that increase of the amount of the acid component in the mixed catalyst results in a small increase in the yield of DME (Y_{DME}=2.1% at 250°C). However, the largest part of produced methanol still remains unconverted. Abu-Dahrieh et al. [10] have also explored the effect of the acid fraction in the admixed catalyst for the direct conversion of CO/H₂ using a homemade methanol synthesis catalyst and a commercial alumina catalyst. The authors reported that the increase of the amount of the acid component results in a small increase of the DME yield but there is no significant difference between 0.33 and 0.5 acid fraction.
Figure 6.12: (A) Conversion of carbon dioxide \(X_{\text{CO}_2}\), selectivities to CO \(S_{\text{CO}}\), methanol \(S_{\text{MeOH}}\), DME \(S_{\text{DME}}\) and oxygenates \(S_{\text{MeOH}+\text{DME}}\); (B) yields of CO \(Y_{\text{CO}}\), methanol \(Y_{\text{MeOH}}\), DME \(Y_{\text{DME}}\) and oxygenates \(Y_{\text{MeOH}+\text{DME}}\) as functions of reaction temperature obtained over the CZA1/Al4 (ratio=1:2) catalyst. Experimental conditions: flow rate 60ml/min, \(W/F=0.0083\ g\ \text{min/ml}\) (based on the amount of CZA1 catalyst), \(\text{CO}_2:\text{H}_2=1:6\), \(P=30\)bar, \(T=170-250^\circ\text{C}\).

6.2.2.2 Effect of flow rate

Results presented in Figure 6.13 show the effects of flow rate on the conversion of \(\text{CO}_2\) and the yields of reaction products obtained over the CZA1/Al4 (1:2) catalyst with a use of \(\text{CO}_2:\text{H}_2=1:6\) ratio in the feed.

Results obtained show that decrease of the reaction flow rate from 60 ml/min to 30ml/min results in a significant increase of the conversion of \(\text{CO}_2\) and the yields of products. Allahyari et al. [38, 39], who investigated the direct DME production from syngas hydrogenation, have also observed a significant decrease in DME yield by increasing GHSV. They concluded that longer contact time favours the reaction of methanol dehydration to DME. The effect of space velocity for the title reaction has been studied also by An et al. [15]. The authors observed a decrease of the conversion of \(\text{CO}_2\), the yields of DME and methanol with increase of space velocity. The faster decrease of DME yield has been explained by considering that the methanol dehydration reaction is more affected by space velocity than the methanol synthesis reaction [15]. This indicates that, longer contact time is beneficial not only for the \(\text{CO}_2\) hydrogenation to methanol (Fig. 6.7) but also for the methanol dehydration reaction and, thus, for the direct \(\text{CO}_2\) hydrogenation to methanol/DME (Fig. 6.13).
Figure 6.13: The effects of reaction flow rate on (A) conversion of carbon dioxide ($X_{\text{CO}_2}$), (B) yield of methanol ($Y_{\text{MeOH}}$), (C) yield of DME ($Y_{\text{DME}}$) and (D) yield of CO ($Y_{\text{CO}}$) obtained over the CZA1/Al4 catalyst. Experimental conditions: feed composition CO$_2$:H$_2$=1:6, P=30bar, T=180-250°C.

In the subsequent experiments, a flow rate of 30ml/min has been chosen to study the direct CO$_2$ hydrogenation to methanol/DME. Results obtained over the CZA1/Al4 catalyst (ratio=1:2) with a flow rate of 30 ml/min and a CO$_2$: H$_2$ ratio of 1:6 are summarized in Figure 6.14, where the conversion of CO$_2$, the selectivities and the yields of reaction products are plotted as functions of reaction temperature.
Figure 6.14: (A) Conversion of carbon dioxide ($X_{CO2}$), selectivities to CO ($S_{CO}$), methanol ($S_{MeOH}$), DME ($S_{DME}$) and (B) yields of CO ($Y_{CO}$), methanol ($Y_{MeOH}$), DME ($Y_{DME}$) as functions of reaction temperature obtained over CZA1/Al4 (ratio=1:2) catalyst. Reaction conditions: Flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst), CO$_2$:H$_2$=1:6, P=30bar, T=220-250°C.

6.2.2.3 CZA1/WAl4 admixed catalyst (1:1 ratio)

Results of catalytic performance tests obtained over the CZA1/WAl4 (1:1) catalyst with a CO$_2$:H$_2$=1:6 ratio in the feed and a flow rate of 30ml/min, are presented in Figure 6.15, where the conversion of CO$_2$, the selectivities and yields of products are plotted as functions of reaction temperature. It is observed that the CO$_2$ conversion increases with increase of temperature from 180 to 250 °C and reaches a value of ca. 28% at 250 °C. The CO yield also increases monotonically in this temperature range with reaction temperature and reaches a value of 15.1% at 250 °C, indicating the occurrence of the endothermic RWGS reaction. The selectivity to methanol gradually decreases whereas DME selectivity increases with increasing the reaction temperature. Regarding the yields of reaction products, $Y_{DME}$ increases with increase temperature and takes a value of 6.1% at 250 °C whereas $Y_{MeOH}$ does not change appreciably (4.5-6.68 %) in this temperature range. Thus, the total yield of organic compounds formed increases considerably (12 % at 250 °C), being higher than that achieved in the case where a CZA1/Al4 (1:2) catalyst is used (Figure 6.14).
Figure 6.15: (A) Conversion of carbon dioxide ($X_{\text{CO}_2}$), selectivities to CO ($S_{\text{CO}}$), methanol ($S_{\text{MeOH}}$), DME ($S_{\text{DME}}$) and oxygenates ($S_{\text{MeOH+DME}}$); (B) yields of CO ($Y_{\text{CO}}$), methanol ($Y_{\text{MeOH}}$), DME ($Y_{\text{DME}}$) and oxygenates ($Y_{\text{MeOH+DME}}$) as functions of reaction temperature obtained over CZA1/WAl4 (1:1) catalyst. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst), $\text{CO}_2$:H$_2$=1:6, P=30bar, T=180-250°C.

6.2.3 Catalytic performance tests over copper based catalyst admixed with different types of zeolite catalysts

In the literature the use of HZSM-5 zeolite as acidic component in bifunctional catalyst for direct $\text{CO}_2$/H$_2$ conversion to methanol/DME is relatively well established [15, 29, 40-42]. Other zeolitic materials have been investigated however for DME production from synthesis gas [43-46]. DME production by $\text{CO}_2$ conversion over -zeolites other than HZSM-5 has rarely been examined [47]. Taking this into account, a set of bifunctional catalysts have been investigated, where the acidic component was one of four different zeolitic materials possessing different framework structures and thus different physicochemical characteristics. The catalysts used in this section together with the mass ratio of the metallic and acidic functions are listed in Table 6.4. The admixed catalysts have been prepared following the procedure described in section 6.2.1. The Table 6.5 presents the main physicochemical characteristics of these four zeolites.
Table 6.4: List of copper-based catalyst admixed with zeolitic materials.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass ratio of metal /acid functions</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comm. copper based catalyst + Ferrerite(10)</td>
<td>1:1</td>
<td>CZA1/FER(10)</td>
</tr>
<tr>
<td>Comm. copper based catalyst + USY(6)</td>
<td>1:1</td>
<td>CZA1/USY(6)</td>
</tr>
<tr>
<td>Comm. copper based catalyst + HZSM-5 (11.5)</td>
<td>1:1</td>
<td>CZA1/HZSM-5(11.5)</td>
</tr>
<tr>
<td>Comm. copper based catalyst + HZSM-5(25)</td>
<td>1:1</td>
<td>CZA1/HZSM-5(25)</td>
</tr>
<tr>
<td>Comm. copper based catalyst + HZSM-5 (11.5)</td>
<td>2:1</td>
<td>CZA1/HZSM-5(11.5)</td>
</tr>
</tbody>
</table>

Table 6.5: Textural characteristics and acidity of the zeolite catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Notation</th>
<th>SSA (m$^2$ g$^{-1}$)[a]</th>
<th>Total acid sites (b) (mmolNH$_3$ g$^{-1}$)</th>
<th>Type of acid sites (B/L)[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FER (Si/Al=10) CP914C</td>
<td>FER(10)</td>
<td>368 336 32 0.72</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>USY (Si/Al=6) CBV 712</td>
<td>USY(6)</td>
<td>761 607 154 0.68</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>ZSM5 (Si/Al=11.5) CBV2314</td>
<td>HZSM-5 (11.5)</td>
<td>418 362 56 1.09</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>ZSM5 (Si/Al=25) CBV 5524G)</td>
<td>HZSM-5 (25)</td>
<td>454 360 94 0.55</td>
<td>3.9</td>
<td></td>
</tr>
</tbody>
</table>

[a]: Total surface area was determined by multi-point BET analysis, micropore area by V-t plot analysis and meso/macropore area by difference

[b]: Determined from TPD-NH$_3$

[c]: Mole ratio of Brønsted to Lewis acid sites determined from FT-IR experiments with in situ pyridine adsorption.

The ZSM-5 (Si/Al=11.5, CBV 2314), ZSM-5 (Si/Al=25, CBV 5524G), FER (Si/Al=10, CP 914C) and USY (Si/Al=6, CBV 712) zeolites provided by Zeolyst, were converted to their proton form via calcination at 500°C for 2 hrs in air flow. The selection of these zeolites was based on the results of catalytic performance tests obtained in the study of the methanol dehydration to DME reaction (Chapter 5). Briefly, it has been found that the catalytic activity of these materials decreases in
the order of HZSM-5(25)/HZSM-5(11.5)<FER(10)<USY(6). The selectivity to DME is ~100% at reaction temperatures of 270-290°C, where equilibrium conversion of methanol to DME is ca. 80-85%. These materials exhibit different physicochemical characteristics, including micro/meso/macroporous structure, Si/Al ratio, acidic properties (total number, nature and strength of acid sites) and hydrothermal stability.

6.2.3.1 CZA1/FER(10) admixed catalyst (1:1 ratio)

Results of catalytic performance tests obtained over the CZA1/FER(10) (1:1) catalyst with the use of feed a composition of CO₂:H₂ =1:6 and a flow rate of 30ml/min are shown in Figure 6.16.

**Figure 6.16:** (A) Conversion of carbon dioxide (X_{CO₂}), selectivity to CO (S_{CO}), methanol (S_{MeOH}), DME (S_{DME}) and oxygenates (S_{MeOH+DME}); (B) yield of CO (Y_{CO}), methanol (Y_{MeOH}), DME (Y_{DME}) and oxygenates (Y_{MeOH+DME}) as functions of reaction temperature obtained over CZA1/FER(10) (1:1) admixed catalyst. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst), CO₂:H₂=1:6, P=30bar, T=180-250°C.

Representative equilibrium curves of conversion-selectivities–yields are also depicted for comparison. It is observed that the conversion of CO₂ increases gradually with the increase of temperature and reaches a value of 28.5% at 250°C. The selectivities to CO and DME increase also with increase of temperature at the expense of methanol selectivity. It is worth to mention that selectivity to oxygenates (S_{MeOH+DME}) takes a value of 48% at 250°C which is significantly
higher, compared to that obtained over bare CZA1 catalyst in methanol synthesis reaction at the same reaction conditions ($S_{\text{MeOH}}=37.2\%$ see Figure 6.7B). The yield of methanol shows a rather constant value of 2.6-4 % over the whole temperature range investigated (Fig. 6.9B). The yield of DME increases with increase of reaction temperature and takes a value of 9.5% at 250 °C.

6.2.3.2 CZA1/USY(6) admixed catalyst (1:1 ratio)

Results of catalytic performance tests obtained over the CZA1/USY(6) (1:1) catalyst with the use of a feed composition of CO$_2$:H$_2$ =1:6 and a flow rate of 30ml/min, are presented in Figure 6.17.

![Figure 6.17](image)

**Figure 6.17:** (A) Conversion of carbon dioxide ($X_{\text{CO}_2}$), selectivity to CO ($S_{\text{CO}}$), methanol ($S_{\text{MeOH}}$), DME ($S_{\text{DME}}$), oxygenates ($S_{\text{MeOH+DME}}$) and (B) yield of CO ($Y_{\text{CO}}$), methanol ($Y_{\text{MeOH}}$), DME ($Y_{\text{DME}}$) and oxygenates ($Y_{\text{MeOH+DME}}$) as functions of reaction temperature obtained over CZA1/USY(6) (1:1) admixed catalyst. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst) CO$_2$:H$_2$=1:6, P=30bar, T=180-250°C.

In this figure, the conversion of CO$_2$, selectivities and yields of reaction products are plotted as functions of reaction temperature and are compared to the corresponding equilibrium curves. It is observed that the CO$_2$ conversion increases with increasing the reaction temperature from 180 to 250 °C and reaches a value of 29.2% at 250 °C. At 180 °C, selectivity to DME takes a value of 43.3% value ($Y_{\text{DME}}=1.28\%$) and selectivity of methanol a value of 38.4% ($Y_{\text{MeOH}}=1.13\%$). At temperature higher than 220°C the methanol selectivity curve practically coincides
with that corresponding to equilibrium. Further increase of temperature results in a significant increase of the yield of DME, which takes a value of 11.8% at 250 °C. Methanol yield remains almost constant over the whole temperature range investigated, increasing from 1.1% at 180 °C to 3.5% at 250 °C. This indicates that, under the present conditions, almost all of the MeOH formed is converted to DME. In this case, the MeOH synthesis reaction seems to be the rate limiting step. CO yield also increases with increasing the reaction temperature and reaches a value of 13.9% at 250 °C. However, it is observed that at this temperature the yield of oxygenates (S_{MeOH+DME}=15.3%) is higher than the yield of CO.

In Figure 6.18 are presented the values of CO₂ conversion and products yields obtained over the CZA1/USY(6) (1:1) sample at a constant temperature of 250 °C, after 1, 9, 25 hours on stream.

![Figure 6.18](image)

**Figure 6.18**: Conversion of carbon dioxide (X_{CO₂}) and yields of products (Y_{CO}, Y_{MeOH}, Y_{DME}, Y_{oxygenates}) obtained after 1, 9 or 25 hours on stream, and after regeneration (data presented after the dashed line) of the CZA1/USY(6) (1:1) catalyst. Reaction conditions: flow rate 30ml/min, CO₂:H₂=1:6, P=30bar, T=250°C. Regeneration conditions: 100ml/min H₂ flow, at 200 °C, for 1 hour, at atmospheric pressure.

It is observed that both the conversion of CO₂ and the yields of products remain almost unchanged after 9 hours on stream. However, catalytic performance decreases significantly after 25 hours-on-stream. Subsequent in situ treatment of the catalyst under H₂ flow at 200 °C for 1 hour at atmospheric pressure was found to restore partially the catalytic activity (these values are presented after the dashed line).

6.2.3.3 CZA1/HZSM-5 (11.5) and CZA1/HZSM-5 (25) admixed catalysts (1:1ratio)

Results of catalytic performance tests obtained over the CZA1/HZSM-5 (11.5) (1:1) and the CZA1/HZSM-5 (25) (1:1) catalysts are shown in Figure 6.19 where the conversion of carbon dioxide (X_{CO₂}), selectivities and yields to reaction products (S_i and Y_i) are plotted for each sample as functions of reaction temperature.
Figure 6.19: (A) Conversion of carbon dioxide ($X_{\text{CO}_2}$) and selectivities to reaction products ($S_i$) as functions of reaction temperature obtained over (A) CZA1/HZSM-5(11.5) and (B) CZA1/HZSM-5 (25) catalysts; yields of reaction products ($Y_i$) as functions of reaction temperature obtained over (C) CZA1/HZSM-5 (11.5) and (D) CZA1/HZSM-5 (25) catalysts. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst, $\text{CO}_2$:$\text{H}_2$=1:6, P=30bar, T=180-250°C.

It is observed that the conversion of $\text{CO}_2$ at temperature of 180 °C is similar for the two catalysts (3.8% and 2.9%, respectively). However, there are differences in the selectivities to reaction products. In particular, selectivity to DME takes a value of 34.8% over CZA1/HZSM-5 (11.5)) and 47.9 % over CZA1/HZSM-5 (25) at 180°C. On the contrary, the selectivity to MeOH at 180°C is higher for
CZA1/HZSM-5 (11.5) (45.9%) compared to CZA1/HZSM-5 (25) (29%). This indicates that under the present experimental conditions, the HZSM-5 (25) component of the hybrid catalyst exhibits better methanol dehydration activity than that of the HZSM-5 (11.5) catalyst. These results are in well agreement with those obtained over the same catalysts under conditions of methanol dehydration to DME reaction (Chapter 5 Figure 5.15A). Increase of reaction temperature results in an increase of CO₂ conversion, which reaches almost the same value (X_{CO₂}=28%) for both samples.

The overall selectivity to oxygenates takes, practically, the same value over these two catalysts (S_{MeOH+DME}=80% over CZA1/HZSM-5 (11.5) and S_{MeOH+DME}=77% over CZA1/HZSM-5 (25)). Regarding the yields of reaction products, it is observed that the yield of methanol is almost constant over the whole temperature range examined taking values around 1-3% for both CZA1/HZSM-5 catalysts (Figure 6.19C and D). The low amount of methanol indicates that almost all methanol produced is converted to DME. As expected, the CO yield also increases with increasing temperature and at 250 °C it reaches to a value of 14.8% over CZA1/HZSM-5 (11.5) and 13.5 % over CZA1/HZSM-5 (25). Finally, the yields of oxygenates take almost the same value of Y_{MeOH+DME}=14 % for both catalysts tested.

In Figure 6.20 are presented the values of CO₂ conversion and of products yields obtained over the CZA1/HZSM-5 (11.5) and CZA1/HZSM-5 (25) samples at a constant temperature of 250 °C, after 1, 9 or 25 hours on stream. It is observed that the conversion of CO₂ as well as the yields of oxygenates obtained over both catalysts decrease gradually with time-on-stream. The yield of CO remains almost unchanged after 25 hours on stream for both samples, although over the CZA1/HZSM-5 (11.5) catalyst it seems a little higher. A possible change of the metallic Cu valence state may occur during the experiments conducted under long time-on-stream conditions, by forming a Cu⁺ species, which are probably more favourable for CO formation [29]. Subsequent in situ treatment of the catalyst under H₂ flow at 200 °C for 1 hour results in restoration of the initial catalytic activity. A probable reason for the observed reversible catalyst deactivation is the significant amount of water produced during the reaction which can affect the functionalities of both the metallic and acidic components of the catalysts.
Figure 6.20: Conversion of carbon dioxide ($X_{CO2}$) and yields of products ($Y_{CO}$, $Y_{MeOH}$, $Y_{DME}$, $Y_{oxygenates}$) obtained after 1, 9 or 25 hours on stream and after regeneration (data presented after the dashed lines) over A) CZA1/HZSM-5 (11.5) and B) CZA1/HZSM-5 (25) (1:1) catalysts. Experimental conditions: flow rate 30ml/min, feed composition CO$_2$:H$_2$=1:6, P=30bar, T=250°C. Regeneration conditions: 100ml/min H$_2$ flow, at 200°C, for 1 hour, at atmospheric pressure.

6.2.3.4 CZA1/HZSM-5 (11.5) (2:1 ratio)

Results obtained over CZA/HZSM-5(11.5), CZA/HZSM-5(25) and CZA1/USY(6) catalysts indicate that the overall DME synthesis reaction is controlled by the methanol synthesis reaction, because methanol is almost completely converted to DME. In an attempt to facilitate the methanol production from CO$_2$ hydrogenation the fraction of the methanol synthesis catalyst in the hybrid catalyst has been increased. In Figure 6.21 are illustrated results of the catalytic performance tests obtained over CZA1/HZSM-5(11.5) (2:1) catalyst with the use of a CO$_2$:H$_2$ =1:6 ratio in the feed and a flow rate of 30ml/min. It is observed that the conversion of CO$_2$ increases gradually with the increase of temperature and reaches a value of 29.8 % at 250°C.
Figure 6.21: (A) Conversion of carbon dioxide ($X_{CO_2}$), selectivity to CO ($S_{CO}$), methanol ($S_{MeOH}$), DME ($S_{DME}$), oxygenates ($S_{MeOH+DME}$) and (B) yield of CO ($Y_{CO}$), methanol ($Y_{MeOH}$), DME ($Y_{DME}$) and oxygenates ($Y_{MeOH+DME}$) as functions of reaction temperature obtained over CZA1/HZSM-5(11.5) (2:1) hybrid catalyst. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst, CO$_2$:H$_2$=1:6, P=30bar, T=180-250°C.

The use of a larger amount of copper-based component in the hybrid catalyst results in a small increase of methanol selectivity ($S_{MeOH}$=13.5%) and yield ($Y_{MeOH}$=4%) at 250°C but decreases the DME selectivity ($S_{DME}$=35.6%) and yield ($Y_{DME}$=10.6%) at 250°C. Thus, the overall selectivity/yield of oxygenates remains, practically, the same and does not vary significantly with the increase of the CZA1/HZSM-5(11.5) catalyst ratio from 1:1 to 2:1.

In Figure 6.22 are shown the conversion of CO$_2$, selectivities and yields of products obtained over the CZA1/HZSM-5(11.5) (2:1) sample at a constant temperature of 250 °C, after 1 or 9 hours on stream and after treatment in the presence of H$_2$. A significant decrease of CO$_2$ conversion as well as of the selectivities and yields of oxygenates is observed after 9 hours-on-stream. The procedure of regeneration restores only the yield of methanol.
Figure 6.22: Conversion of carbon dioxide ($X_{\text{CO}_2}$) and yields of products ($Y_{\text{CO}}$, $Y_{\text{MeOH}}$, $Y_{\text{DME}}$, $Y_{\text{oxygenates}}$) obtained after 1 or 9 hours on stream and after regeneration (data presented after the dashed line) over the CZA1/HZSM-5(11.5) (2:1) catalyst. Experimental conditions: flow rate 30ml/min, feed composition CO$_2$:H$_2$=1:6, P=30bar, T=250°C. Regeneration conditions: 100ml/min H$_2$ flow, at 200°C, for 1 hour, at atmospheric pressure.

6.4 Comparison of various admixed catalysts

The conversion of CO$_2$ and yields of reaction products as functions of reaction temperature obtained over all admixed catalyst investigated are illustrated in Figure 6.23. The equilibrium curves of CO$_2$ conversion and yields of carbon monoxide, methanol, DME and oxygenates are also presented for comparison (dashed line). It is easy to notice that regardless of the catalyst used, the reaction occurs under the kinetic regime with CO$_2$ conversion curve being lower than that predicted by thermodynamics over the whole temperature range investigated. The yield of CO takes higher values than those thermodynamics allow (Fig. 6.23E). This increase of CO yield over all catalysts investigated indicates the occurrence of the RWGS reaction in full kinetic regime. No significant difference in CO$_2$ conversion is observed, although at low temperatures (180-200°C) the activity of the CZA1/WAl4 is somewhat higher. However, noticeable differences exist between the yields of reaction products over the various catalysts investigated (Figures 6.23 B-E). In particular, the CZA1/Al4 (ratio 1:2) catalyst exhibits the lowest selectivity to DME. The next catalyst which exhibits low activity to DME is CZA1/WAl4.
Figure 6.23: (A) Conversion of carbon dioxide ($X_{CO_2}$), (B) yield of methanol ($Y_{MeOH}$), (C) DME ($Y_{DME}$), (D) oxygenates ($Y_{MeOH+DME}$) and (E) CO ($Y_{CO}$) as functions of reaction temperature obtained over CZA1/HZSM-5 (11.5), CZA1/HZSM-5 (25), CZA1/FER (10), CZA1/USY (6), CZA1/WAl4 (ratio 1:1) and CZA1/Al4 (ratio 1:2) admixed catalysts. Experimental conditions: flow rate 30ml/min, W/F=0.016 (based on the amount of CZA1 catalyst), $CO_2:H_2$=1:6, $P$=30bar, $T$=180-250°C.
From Figure 6.23 B it can be seen that these two catalysts give higher methanol yield, indicating that methanol produced is not consumed for the production of DME. This behaviour may be due to the poor acidity of these samples or the fast deactivation of acid sites by the adsorption of water formed.

Generally, the activity of these types of bifunctional catalytic systems is affected by acidity. It has been reported that the selectivity to DME depends on the acid intensity of strong acid sites [48]. However, by comparing the values of DME yields obtained over CZA1/WAl4 and CZA1/Al4 catalysts it is easy to notice that CZA1/WAl4 exhibits higher activity towards DME production than that of over CZA1/Al4 catalyst. The acidity of γ-Al2O3 (commercial Engelhard), WO3/Al2O3 (prepared by wet impregnation) and USY zeolite has been compared by Soled et al. [49]. They observed that the addition of WO3 to γ-Al2O3 increases the Brönsted site density (per m²) at the expense of Lewis sites while maintaining the density of total sites constant. Thus, the enhanced catalytic activity of CZA1/WAl4 in the present study may be explained by the modification of the nature of acid sites, equilibrating Lewis and Brönsted acid sites. However, taking into account that the methanol dehydration component in the case of CZA1/Al4 (1:2) is two times higher than that in CZA1/WAl4, the presence of tungsten seems to also increase the density of total sites. The CZA1/WAl4 catalyst is the most efficient of all catalytic configurations tested for the methanol and DME production at low temperatures (180−200°C).

The methanol yields obtained over CZA1 mixed with different zeolitic materials are lower than those obtained over the alumina based-catalysts and also lower than those expected by thermodynamic calculations. These results indicate that almost all of the produced methanol is consumed via the methanol dehydration reaction. The amounts of produced DME are far from those predicted by thermodynamics, especially at low temperatures and approach equilibrium values at relatively high temperatures. By comparing the results in terms of yields of DME obtained over these admixed catalysts, it can be seen that the activity of the zeolites decreases in the order of HZSM-5(25)=HZSM-5(11.5)>USY(6)>FER(10). Interestingly, enhanced catalytic activity has been observed over USY (6) for methanol dehydration to DME. This catalyst exhibits almost the same activity and product selectivity as HZSM-5 (25) or HZSM-5 (11.5). It is worth to mention that the catalytic activity of USY(6) for this reaction at atmospheric pressure was lower than that of FER (10) and much lower than that of HZSM-5 (25) or HZSM5 (11.5) catalysts (Fig. 5.30 A).
Indeed, the reaction environment of direct DME formation through \( \text{CO}_2 \) hydrogenation is different than that of DME formation via methanol dehydration. In the former case, the presence of reactants (\( \text{CO}_2 \) and \( \text{H}_2 \)) or significant amount of produced CO can influence the acidic properties of methanol dehydration component of the admixed catalyst. Generally, \( \text{CO}/\text{H}_2 \) serve as weak base probe molecules for characterization of the acidity of zeolitic materials [50-53]. Furthermore, carbon monoxide is a small probe molecule, which may interact only with strong acid sites in zeolites as can be observed by infrared spectroscopy [54]. Dondue et al. [50] have studied the acid sites of ZSM-5 and Y zeolites by using various probe molecules, including CO. They observed the TPD spectra of CO only at high temperature (620-690°C) which indicates that CO molecules interact with the very strong acid sites. The authors concluded that the unusual strong adsorption of CO seems to be an important finding for the recognition of the strongest Brönsted acid sites of zeolites. Regarding the \( \text{H}_2 \)-zeolite interaction, it has been shown that the adsorption of \( \text{H}_2 \) in MFI zeolite is very low compared to that of \( \text{CO}_2 \) or CO [51]. Thus it is possible, that these compounds may interact with strong Brönsted acid sites of zeolitic materials and decrease the concentration and/or the strength of these acid sites.

The acidic properties of zeolitic materials used in admixed catalysts are summarized in Table 6.5. It can be seen that the USY (6) catalyst possess the lowest number of total acid sites (0.68 mmol \( \text{NH}_3/g \)) and the HZSM-5 (11.5) the highest (1.09 mmol \( \text{NH}_3/g \)). In both ZSM-5 zeolites, most of acid sites are of the Brönsted type, as evidenced from the relatively high values of the \( B/L \) mole ratio (~4) given in Table 6.5. The FER (10) zeolite exhibits very high \( B/L \) molar ratio (9.3). On the contrary to these, the \( B/L \) mole ratio of USY (6) zeolite is rather low (1.6) due to presence of extra-framework aluminium species, which induce Lewis acidity. In addition, ZSM-5 zeolites are characterized by relatively high acid strength. This is conclude by the fact that ~85% of pyridine sorbed on Brönsted acid sites at 150°C remains sorbed at 450°C, whereas this percentage is only ~65% for USY (6) zeolite. Thus, the relatively low catalytic activity of ZSM-5 (11.5), ZSM-5 (25) and FER(10) catalysts for the direct formation of DME can be attributed to the possible interaction between the reaction intermediate species and the strong Brönsted acid sites of these zeolites. This interaction may result in reduction of strong acidity of zeolites.

In addition to the reaction environment, the partial deactivation of the catalysts may be due to the interaction between the two catalytic components of
the admixed CZA1/ZSM-5 catalysts. In particular, the acid properties of the methanol dehydration component can be altered by the presence of oxide mixtures (CuO–ZnO) [55, 56]. The contact between these components depends mainly on the preparation method, which can result in an increase or a decrease of zeolite acidity in bifunctional catalyst [56-60]. It has been reported that, in addition to coke deposition, Cu sintering and presence of high amounts of water, the interaction of ion-exchange copper/zinc with protons of the zeolite can also cause deactivation of catalyst [45, 56, 57, 61-63]. It has been reported that isolated Cu$^{2+}$ cations occupy exchange positions in HZSM-5 zeolite, which results in a decrease of its Brönsted acidity [56]. As a consequence, the catalyst activity decreases due to the reduced zeolite activity for the methanol dehydration reaction. Thus, the decreased catalytic performance of the two CZA1/ZSM-5 and the CZA1/FER (10) catalysts may be explained also by the possible detrimental interaction between metal-acid components, which results in reduction of Brönsted acidity of zeolite. On the other hand, the USY (6) zeolite, which has the lowest B/L mole ratio, does not seem to be affected from these interactions, exhibiting almost similar activity as the ZSM-5 zeolites.

Another factor which may also influence the catalytic activity is the different microporous structure of these zeolites. Generally, it is known that the diffusion of DME is hindered in the narrow microporous channels of ZSM-5 zeolites, where DME does not diffuse quickly enough [64-67]. When DME production occurs via CO$_2$ hydrogenation at high pressures in the presence of bifunctional catalysts, the mass transfer limitations might be stronger than those of DME production through methanol dehydration at atmospheric pressure. Comparison of the textural properties of these three zeolites shows that USY (6) exhibits a significant amount of meso/macroporous porosity (meso/macroporous surface area is 154 m$^2$/g), whereas HZSM-5 (25) and FER zeolites have almost microporous structure ($S_{\text{meso/macroporous}}=94$ m$^2$/g for HZSM-5 (25) and $S_{\text{meso/macroporous}}=32$ m$^2$/g for FER (10)). Thus, the existence of mesoporous structure in USY(6) zeolite might also have a beneficial role in terms of DME yield in direct CO$_2$ conversion to methanol/DME. However, the direct comparison of the structures of ZSM-5, Ferrierite(10) and USY(6) is not safe, as the acidic properties of these zeolites, i.e. number and strength of Brönsted/Lewis acid may differ significantly from each other.
6.5 Conclusions

The catalytic performance of commercial and home-made CuO/ZnO/Al$_2$O$_3$ catalysts for the direct conversion of CO$_2$/H$_2$ mixtures into methanol/DME have been investigated, focusing on the optimization of operating conditions. Below are summarized the general conclusions of this work.

- Both Cu$^{+}$/Cu$^0$ species are important for the conversion of CO$_2$/H$_2$, although the presence of Cu$^0$ seems to be more important for selectivity/yield of methanol.
- The conversion of CO$_2$ and the yields of reaction products steadily increase when the concentration of H$_2$ in the feed is increased.
- Higher contact times result in an increase of the CO$_2$ conversion and the yields of reaction products.
- The calculated apparent activation energy for methanol synthesis is 10.4 kcal mol$^{-1}$ for the catalyst in which copper is completely reduced (CZA1) and 13.4 kcal mol$^{-1}$ for the catalyst in which Cu$^0$, Cu$_2$O and CuO can be detected after reduction and after catalytic tests (CZA2).
- The main reason for the deactivation of copper based-catalysts is the presence of water, which is strongly adsorbed on the active sites, inhibiting the CO$_2$ hydrogenation reaction. When water is removed from the feed, the catalytic activity and products selectivity are recovered slowly to their original levels indicating that deactivation by water is reversible.

The direct CO$_2$ hydrogenation to methanol/DME has also been investigated using admixed catalysts comprising a methanol synthesis and a methanol dehydration component. The general conclusions of this part of the study are summarized as follows:

- The conversion of CO$_2$ and the yields of products increase with increase of contact time.
- Under the experimental conditions employed, the measured values of the conversion of CO$_2$ were always found to be lower than the corresponding equilibrium values predicted by thermodynamics, indicating operation in the kinetic regime. On the contrary, the values of CO yields were always higher than those expected by thermodynamics.
- The nature of the methanol dehydration component of the admixed catalysts is important for both CO$_2$ conversion and methanol dehydration.
- The conversion of CO$_2$ at 250$^\circ$C is almost the same for all samples consisting of CZA1 admixed with the four different zeolites catalysts investigated.
The CO₂ conversion obtained over CZA1 admixed with W/γ-Al₂O₃ and γ-Al₂O₃ is lower than that obtained using zeolites as methanol dehydration component.

✓ DME selectivity/yield, depends strongly on the nature of acid sites (both Lewis and Brønsted) as well as the textural (meso/macro porosity) and topological properties of methanol dehydration component of the admixed catalysts. The yield of DME obtained at a temperature of 250°C decreases following the order CZA1/ZSM-5, CZA1/USY(6) > CZA1/FER (10) > CZA1/ WAl4 >> CZA1/Al4.

✓ The best catalytic performance was obtained for the CZA1/ZSM-5 bifunctional system. Increase of the mass ratio of the methanol synthesis component from 1:1 to 2:1 over this catalyst had no significant effect on the yield of oxygenates.

✓ The bifunctional catalytic system deactivated with time-on-stream. Deactivation is mainly due to water and it is reversible to a great extent. In the case of CZA1/ZSM-5 (1:1) admixed catalysts, the catalytic activity and products selectivity are almost recovered after regeneration of the used catalysts with H₂ flow at 200 °C for 1 hour.
6.6 References

CHAPTER 7

GENERAL CONCLUSIONS

SUGGESTIONS FOR FUTURE WORK

In the present thesis the production of DME from CO$_2$/H$_2$ mixtures has been investigated by considering both the indirect (two-step) and the direct (one-step) catalytic processes. In the case of the indirect process, the CO$_2$ hydrogenation to methanol has been investigated over commercial and home-made copper-based catalysts. The methanol dehydration to DME, i.e., the second step of the indirect process, has been investigated over a range of acidic materials including γ-alumina, silica-alumina and zeolite catalysts. The aim of studying these two reactions was to identify the optimal experimental conditions as well as to develop efficient, selective and stable metal-based and acid catalysts that could be combined and used for the direct conversion of CO$_2$/H$_2$ mixtures into methanol/DME (one-step process). The general conclusions of this work are summarized below.

7.1 Methanol dehydration to DME over Al$_2$O$_3$ catalysts

The methanol dehydration to DME reaction has been studied over eight different alumina catalysts with various physicochemical characteristics. Results obtained show that catalytic activity and selectivity to DME are determined by the textural properties, degree of crystallinity and total amount of surface acid sites of Al$_2$O$_3$. The following conclusions have been extracted based on the results of catalyst characterization and catalytic performance tests:

- Increase of specific surface area results in a shift of the methanol conversion curve toward lower reaction temperatures.
- Enhanced catalytic activity of high-specific surface area (SSA) samples cannot be attributed solely to the higher amount of surface acid sites (estimated by
implying that the reaction rate is determined to a large extent from other
parameters, such as textural properties and degree of crystallinity.

Conversion of methanol at a given temperature is generally higher for
materials with cylindrical pores of an average width of about 9-10 nm, total
porosity of 0.60-0.80 cm$^3$g$^{-1}$ and crystallite size of ca 7-9 nm. Materials with higher
porosity and/or smaller crystallite size are less active, most probably due to their
highly amorphous nature.

The apparent activation energy of the reaction is, practically, the same for
all studied Al$_2$O$_3$ catalysts taking an average value of 24±4 kcal mol$^{-1}$.

Addition of water vapour in the feed does not influence selectivity to reaction
products but results in an increase of the apparent activation energy and in a
(reversible) shift of methanol conversion curve toward higher temperatures.

Results of mechanistic studies indicate that interaction of methanol with the
Al$_2$O$_3$ surface results in the formation of two kinds of methoxy groups of different
adsorption strength. Evidence is provided that DME evolution is associated with
methoxy species that are weakly adsorbed on the Al$_2$O$_3$ surface, whereas more
strongly held species decompose to yield surface formate and, eventually CH$_4$ and
CO in the gas phase.

7.2 Methanol dehydration to DME over zeolite catalysts

The methanol dehydration to DME reaction has been studied also over
thirteen different zeolitic materials and their catalytic performance was compared
to that of alumina and silica-alumina catalysts. The catalytic activity and selectivity
of zeolites was found to depend on the topology of these materials, related to
differences in zeolite micropore structure and Si/Al ratio, as well as on the number,
strength and nature of active acid sites. The following conclusions have been
extracted:

The activity of zeolite catalysts for the methanol dehydration to DME follows
the order ZSM-5 > Ferrierite > Mordenite ~ Beta ~ USY > H-Y. Under the
experimental conditions employed here, the selectivity to DME is ~100% at reaction
temperatures of 280-300°C, where equilibrium conversion of methanol to DME (ca.
80-85%) is achieved for all catalysts, with the exception of the H-Y zeolite that is
less selective at lower temperatures and conversions. At temperatures above ca.
300 °C, the high reactivity of the ZSM-5 zeolites leads to conversion values higher
than those corresponding to the equilibrium conversion of methanol to DME,
because of the onset of side reactions which lead to the formation of higher
hydrocarbons. As a result, conversion of methanol reaches 100% at \( T \leq 400^\circ C \), which is accompanied by a significant decrease of DME selectivity and increased formation of light as well as higher hydrocarbons.

The reactivity of the zeolite catalysts has been evaluated by determining the reaction rates per gram of catalyst, per acid site (total: Bronsted+Lewis) and per B/L mole ratio. By combining these kinetic results with the acidic properties of the zeolites (number, type and strength of acid sites) the following conclusions have been extracted:

- The strong Brönsted acid sites of ZSM-5 zeolites with relatively high Si/Al ratio (ca. 40) represent the most active sites for the methanol dehydration to DME reaction. However, the overall reactivity of the ZSM-5 zeolites is also affected by the balance of the Brönsted to Lewis acid sites (B/L ratio).
- The activity of Beta and USY zeolites is determined by both Lewis and Brönsted acid sites.
- The moderate/low reactivity of Ferrierite, Mordenite and H-Y zeolite with Si/Al ratios of 10, 10 and 2.5, respectively, is determined by the abundant Brönsted acid sites of relatively weak/moderate strength.
- Results obtained over \( \gamma \)-Al\(_2\)O\(_3\), ASA (0.5) and ASA (35) samples reveal that \( \gamma \)-alumina and ASA (0.5) with weak Lewis acid sites exhibit qualitatively similar behavior, whereas ASA (35) with relatively weak/moderate strength of Brönsted acid sites possess much less catalytic activity.

Long-term stability tests have been performed under dry and wet feed compositions for most zeolitic materials. Results obtained showed that:

- The ZSM-5 and USY zeolites are relatively stable under dry feed conditions. The hydrothermally stabilized framework of USY zeolites offers better resistance in the presence of water in the feed compared to the ZSM-5 zeolites, which showed a permanent deactivation.
- Beta zeolites showed a progressive loss of their activity in long-term stability tests (ca. 15-20 hrs) under dry feed conditions. Interestingly, the catalytic activities of Beta (37.5) and Beta(150) zeolites do not seem to be affected by the addition of H\(_2\)O vapor in the feed. The catalytic activity of Beta(12.5) was affected by the addition of 10% water in the feed but this effect was found to be reversible.
7.3 CO₂ hydrogenation to methanol

The methanol synthesis reaction from CO₂-H₂ mixtures has been studied over commercial (CZA1) and home-made (CZA2) CuO/ZnO/Al₂O₃ catalysts. Below are summarized the general conclusions of this investigation:

✓ Both Cu⁺/Cu⁰ species are important for the conversion of CO₂/H₂, although the presence of Cu⁰ seems to be more important for selectivity/yield of methanol.
✓ The conversion of CO₂ and the yields of reaction products steadily increase when the concentration of H₂ in the feed is increased.
✓ Higher contact times result in an increase of the CO₂ conversion and the yields of reaction products.
✓ The apparent activation energy for methanol synthesis is 10.4 kcal mol⁻¹ for the catalyst in which copper is completely reduced (CZA1) and 13.4 kcal mol⁻¹ for the catalyst in which Cu⁰, Cu₂O and CuO can be detected after reduction and after catalytic tests (CZA2).
✓ The main reason for the deactivation of copper based-catalysts is the presence of water, which is strongly adsorbed on the active sites, thus inhibiting the CO₂ hydrogenation reaction. When water is removed from the feed, the catalytic activity and products’ selectivity are recovered slowly to their original levels, indicating that deactivation by water is reversible.

7.4 Direct CO₂ hydrogenation to methanol/DME

The direct CO₂ hydrogenation to methanol/DME has been investigated using admixed catalysts comprising a methanol synthesis and a methanol dehydration component. The general conclusions of this part of the study are summarized as follows:

✓ The conversion of CO₂ and the yields of products increase with increase of contact time.
✓ Under the experimental conditions employed, the measured values of the conversion of CO₂ were always found to be lower than the corresponding equilibrium values predicted by thermodynamics, indicating operation in the kinetic regime. On the contrary, the values of CO yields were always higher than those expected by thermodynamics.
✓ The nature of the methanol dehydration component of the admixed catalysts is important for both CO₂ conversion and methanol dehydration.
✓ The conversion of CO₂ at 250°C is almost the same for all samples consisting of CZA1 admixed with the four different zeolites catalysts investigated. The CO₂
conversion obtained over CZA1 admixed with W/γ-Al₂O₃ and γ-Al₂O₃ is lower than that obtained using zeolites as methanol dehydration component.

✓ DME selectivity/yield, depends strongly on the nature of acid sites (both Lewis and Brönsted) as well as the textural (meso/macro porosity) and topological properties of the methanol dehydration component of the admixed catalysts. The yield of DME obtained at a temperature of 250°C decreases following the order CZA1/ZSM-5, CZA1/USY(6) > CZA1/FER (10) > CZA1/ WAl4 >> CZA1/Al4.

✓ The best catalytic performance was obtained for the CZA1/ZSM-5 bifunctional system. Increase of the mass ratio of the methanol synthesis component from 1:1 to 2:1 over this catalyst had no significant effect on the yield of oxygenates.

✓ The bifunctional catalytic system deactivates with time-on-stream. Deactivation is mainly due to the presence of water and it is reversible to a great extent. In the case of CZA1/ZSM-5 (1:1) admixed catalysts, the catalytic activity and selectivity are almost recovered after regeneration of the used catalysts with H₂ flow at 200 °C for 1 hour.

7.5 Suggestions for future work

The future work could focus on the following aspects:

✓ Further investigation of the methanol dehydration reaction over zeolite catalysts at high pressure conditions.

✓ Synthesis and testing of other metal-based catalysts for methanol synthesis reaction.

✓ Synthesis and testing of other bifunctional catalytic systems for CO₂ hydrogenation to methanol/dimethyl ether reaction, by applying various preparation methods.

✓ Detailed investigation of the CO₂ hydrogenation to methanol/dimethylether reaction mechanism with the use of in-situ FTIR and transient-MS techniques.