

5.5 Methanol Chemistry

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5.5.1 Why Methanol?

One major problem of regenerative energy from wind and solar power is its naturally fluctuating abundance, which does not necessarily match the current energy demand (see chapter 1). A very powerful and versatile energy storage strategy is to store excess energy as bond energy in products of a chemical reaction. These products can be sustainable synthetic fuels in the transportation sector, and be available to compensate in times of low wind or sunlight irradiation in the energy sector. Moreover, the products can be used as a carbon source for the chemical industry. Methanol is a very promising candidate for such an energy storage molecule.

Methanol, CH_3OH , is the smallest alcohol and liquid at ambient temperature. Currently existing gasoline distribution and storage infrastructure like pipelines, road tankers and filling stations would require little modification to operate with methanol [1-2]. Methanol is a versatile fuel as it can be used directly in combustion engines or as feed for fuel cells (see chapter 3.4), either for a direct methanol fuel cells (DMFCs), or as on-board hydrogen storage for downstream proton exchange membrane fuel cells (PEMFCs). In the latter case, hydrogen has to be liberated from methanol. This is possible at relatively mild conditions by steam reforming of methanol (see section 5.5.7). Direct combustion of methanol in motor engines is attractive due to its good combustion properties. Methanol has a high octane number (RON=133), comparable to currently available gasoline blends. The emissions of NO_x and hydrocarbons (not of CO and formaldehyde) are lower compared to gasoline, while the thermal efficiency and the motor power are higher by ca. 15 and 10%, respectively [3]. It has to be noted, however, that the energy density of methanol is only ca. 50% of that of gasoline, leading to an increased volume-based consumption. Today, up to 3% methanol is used as a blend in gasoline (M3). Pure methanol (M100) or mixtures of methanol and gasoline (e.g. M85, 85% methanol, 15% gasoline) have been proved feasible in large-scale practical studies [1-2, 4-5] with several hundred cars in the USA and Germany. In the 1960s, gasoline has been completely replaced by methanol in the Indy Car Racing circuit in the USA for safety reasons; in contrast to gasoline methanol fires can be extinguished with water. Methanol-containing fuels (MW50, 50% methanol, 50% water) have also been used as a synthetic fuel for temporarily increased performance of aircrafts during the Second World War.

Methanol is particularly interesting, because it can be produced by hydrogenation of the greenhouse gas CO_2 (see section 5.5.5). Thus, anthropogenic CO_2 , e.g. from industrial exhaust or coal power plants, could be used for its manufacture. The amount of CO_2 emitted upon methanol combustion is then equal to the amount consumed during its production. Such CO_2 recycling via methanol has been proposed by Olah et al. [2] as a carbon-neutral “methanol economy”.

Another promising aspect of the use of methanol in energy applications is that its synthesis already is a large-scale industrial process (see section 5.5.3). Thus, regarding a further up-scaling of methanol production, which is necessary for energy-related application, a mature technology and long-lasting experience already exist. This is an important advantage compared to completely new approaches that have to be developed from scratch like renewable hydrogen or biofuels. Today, methanol is an important platform molecule in chemical industry. It is further upgraded into other chemical intermediates like formaldehyde or acetic acid. Zeolite catalyzed methanol to olefins (MTO) and methanol to gasoline (MTG) processes, developed by Mobil, open a pathway for direct conversion of methanol into fuels and chemicals currently derived exclusively from petroleum. However, these are only expected

to become economically viable in the case of high petroleum prices. Among the direct products of methanol conversion methyl-tert-butyl-ether (MTBE) and dimethylether (DME) are of relevance for the energy applications. MTBE is used as an octane-booster to improve the anti-knocking properties of gasoline, but recently has been banned by some states due to environmental concerns. DME has been proposed as a potential substitute for Diesel fuel.

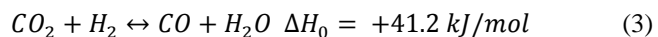
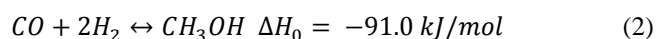
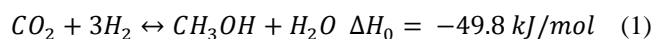
Methanol production today is not a sustainable process, but is part of a petrochemical route for conversion of fossil carbon into chemicals and fuels (see section 5.5.3). It has to be emphasized that a one-to-one up-scaling of existing industrial methanol synthesis capacities for fuel production is not useful. This is mainly because the current industrial process has not been developed and optimized under the boundary conditions of conversion of anthropogenic CO₂, but rather for synthesis gas feeds derived from fossil sources such as natural gas or coal. The switch to an efficient large-scale methanol synthesis with a neutral CO₂-footprint is still a major scientific and engineering challenge and further research and catalyst and process optimization is urgently needed to realize the idea of a sustainable “methanol economy”.

Obviously, the other reactant for methanol production by CO₂ hydrogenation is hydrogen. Thus, all considerations on the use of methanol as sustainable fuel are only useful, if a regenerative source of hydrogen is available. The electrolysis of water (see chapter 3) through renewably derived electricity such as hydro- or wind power, or alternatively gasification of biomass (see chapter 2) may serve as such a source [2]. Hence, the primary chemical energy storage has to happen in form of hydrogen production. The further conversion of hydrogen into methanol is associated with a gain in volumetric and a loss in gravimetric energy density, but also with a much easier handling of the energy carrier. This does not only imply distribution and storage without pressurized or cryogenic containers, but also safety issues. However, it should not be concealed that methanol itself is toxic and flammable, with risks and safety measures for every-day use, that are comparable to those of gasoline [2].

This chapter focuses on the catalytic aspects of methanol chemistry and covers thermodynamic, kinetic, chemical engineering and materials science aspects. It provides brief introductions into these topics with the aim of establishing an overview of the state-of-the-art of methanol chemistry with only a snapshot of the relevant literature. It highlights what the authors think are the most relevant aspects and future challenges for energy-related catalytic reactions of methanol. It is not meant to provide a complete literature overview on methanol synthesis and reforming.

5.5.2 Introduction to methanol synthesis and steam reforming

The current primary feed stock for industrial methanol synthesis is synthesis gas – a mixture of CO, CO₂ and hydrogen derived from the reforming of natural gas or other hydrocarbons [2]. The inter-conversion of carbon oxides and methanol, central to methanol synthesis and steam reforming, is defined by three equilibrium equations below.



Methanol synthesis from CO₂ (equation 1) and CO (equation 2) is mildly exothermic and results in volumetric contraction. Methanol steam reforming (MSR) refers to the inverse of reaction 1 and the inverse of reaction 2 is conventionally referred to as methanol decomposition – an undesired side reaction to MSR. The slightly endothermic reverse water-gas shift (rWGS) reaction (equation 3) occurs as a side reaction to methanol synthesis and MSR. According to Le Chatelier’s principle, high pressures and low temperatures would favor methanol synthesis; whereas the opposite set of conditions would favor MSR and methanol decomposition. It should be noted

that any two of the three reactions are linearly independent and therefore sufficient in describing the compositions of equilibrated mixtures.

A precise quantitative description of the methanol synthesis equilibrium must account for the non-ideal behaviors of the gas species, in particular those of water and methanol. Skrzypek *et al.* show that the Soave-Redlich-Kwong equation gives good agreement with experiment [6]. Although non-idealities lead to higher methanol yields compared to those expected from ideal gas behavior [7], non-corrected equilibrium calculations suffice in qualitatively illustrating the equilibrium behavior as a function of conditions. Figure 1 A. and B. shows the ideal gas methanol and CO yields respectively for a 3:1 H₂:CO₂ feed mixture. The methanol yield displays a positive dependence on pressure and an inverse dependence on temperature, whereas the rWGS yield shows weak pressure dependence and increase with increasing temperature. The addition of CO to the feed mixture has a positive effect on the equilibrium yield of methanol, as will be discussed in detail in section 5.5.5.

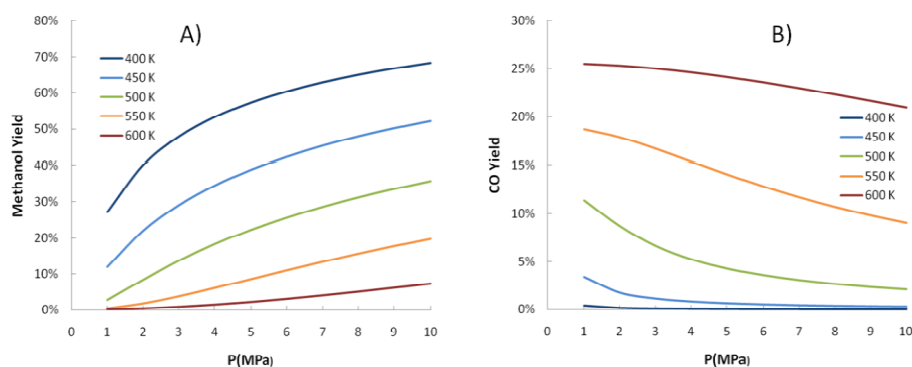


Figure 1. Equilibrium Methanol and CO yields from 3:1 H₂:CO₂ mixture

The current “low pressure” synthesis process (see section 5.5.3) yields methanol with greater than 99% selectivity on a CO free basis. The equilibrium constants (per CO₂ molecule reacted) for the formation of common byproducts at 250°C are shown in Figure 2. The high methanol selectivity is fairly astonishing, considering that the formation of ethers, ketones, and alkane impurities found in industrial methanol is more thermodynamically favored than is the formation of methanol. Similarly, coke – another thermodynamically favored product and common cause of catalyst deactivation is never observed [8]. This observation unambiguously states that the aforementioned products are kinetically inaccessible on the used Cu/ZnO-based catalyst that will be described in more detail in section 5.5.5. From these thermodynamic considerations the need for more active CO₂ hydrogenation catalyst becomes apparent. Even at temperatures associated with the low pressure process, K₂ lies between 10⁻⁵ and 10⁻⁶ allowing for a single pass methanol yield of 15-25% and thus necessitating the implementation of costly recycling loops.

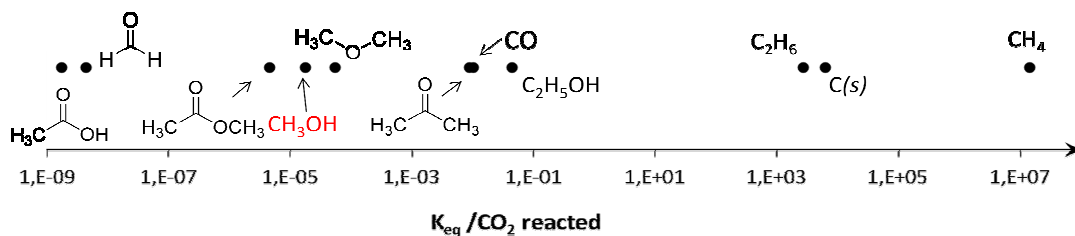


Figure 2. The equilibrium constant of formation methanol synthesis byproducts from 3:1 H₂:CO₂ mixtures at 250°C

MSR is also carried out on active methanol synthesis catalysts at similar temperatures (see section 5.5.7), but unlike methanol synthesis, it is not subject to thermodynamic constraints. Thermodynamic considerations play a lesser role in MSR, as the inverse of reactions 1 and 2 can be considered irreversible at atmospheric pressure. However, lower temperature operation would thermodynamically hinder CO formation via methanol decomposition and rWGS. A low CO content is desired for MSR-PEMFC combinations (see section 5.5.7). To that end, the development of catalysts active at lower temperatures still remains the central goal of methanol catalysis research.

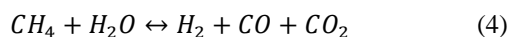
5.5.3 Today's industrial methanol synthesis

As mentioned in section 5.5.1, unlike hydrogen and other potentially renewable fuels, methanol would be a mature starting point for portable energy applications. The first internal combustion engines relied exclusively on alcohol, namely bio-derived ethanol, as a fuel [2]. The advent of economically competitive petroleum distillates in half 20th century lead to the nearly complete replacement of alcohol fuels, but rising petroleum prices have spurred new interest in alcohols as fuels [9]. However, economically feasible production of bio-ethanol (see chapter 2) remains relegated to regions with sufficient agricultural capacity and it may interfere with food production. In contrast to ethanol, methanol can be obtained economically from diverse feedstocks, including the reforming of natural gas and coal as well as agricultural residues and municipal waste [2, 5].

In 2009 worldwide production of methanol was around 40 million metric tons. Although this amount represents only 0.01 % of the worldwide gasoline production, it is nearly equivalent to the total biodiesel and bioethanol production [10]. From this number it is clear that a large-scale replacement of gasoline by methanol as fuel requires an enormous increase of the world-wide methanol synthesis capacities. Today, chemical intermediates dominate methanol consumption. Formaldehyde – a platform molecule for the synthesis of polymer resins is responsible for nearly half of the total demand. Acetic acid, MTBE and methyl methacrylate (MMA) – a monomer, constitute another 25% [7, 11]. Direct fuel and additive usage accounts for 15% of demand, but is expected to rise.

Until the commercialization of the first heterogeneous catalytic process for methanol synthesis by BASF in the 1920's, methanol was produced exclusively from the dry distillation of wood. The BASF process utilized sulfur-containing coal or coke derived synthesis gas and ZnO/Cr₂O₃ catalyst operating at 300-450 °C [12]. High pressures (100- 300 bar) were required to counteract these thermodynamically unfavorable temperatures. Although the superior activity of Cu-based methanol synthesis catalysts was reported shortly thereafter [13], only the advent of natural-gas derived sulfur free synthesis gas allowed for feasible industrial application. The commercialization of more active Cu/ZnO/Al₂O₃ based catalysts (see section 5.5.5) by ICI in the 1960's lead to the application of milder reaction conditions; 240-260°C and 50-100 bar – in a “low pressure” process [14]. Since its inception, this process has been optimized to yield methanol with a >99% selectivity and 75% energy efficiency, and has thus become the exclusive means of methanol production [2]. Catalysts based on supported palladium and other noble metals have also been shown to yield methanol at current process conditions, but due to their price, these materials remain only of academic interest.

Methanol synthesis plants utilizing the low pressure process currently operate at capacities of 2×10⁵ to 2×10⁶ metric tons per year [14]. Such installations are comprised of a synthesis gas production unit, the actual methanol synthesis reactor, and a separation and purification section. The production and purification of synthesis gas accounts for 50-80% of the total cost of methanol production, with the remaining cost associated with the actual synthesis and purification of methanol [2, 7]. Although a variety of carbonaceous feedstocks can be transformed into synthesis gas, the steam reforming of natural gas (equation 4) is by far the most common option, especially for large plants [2, 14-15].



Gas mixtures with a modulus value M (equation 5) around 2 satisfy the stoichiometric requirements.

Countries with large domestic coal reserves, such as China and South Africa rely primarily on coal gasification to produce synthesis gas. This synthesis gas is hydrogen deficient ($M < 2$) and must undergo a further water-gas shift step to yield a CO_2 rich mixture [2]. Methanol synthesis from CO_2 and CO_2 -rich mixtures provides special catalyst and reactor design challenges, which will be further discussed in more detail.

Industrial methanol synthesis is carried out in fixed bed flow reactors, which are designed to achieve effective removal or dissipation of the heat generated during this exothermic reaction. The original adiabatic quench reactor developed by ICI consists of a single catalyst bed, with cold syngas injected at several points along the axial direction of the bed. The Kellogg and Haldor-Topsøe reactor designs consist of a series of catalyst beds with inter-stage cooling of the products. A quasi-isothermal reactor developed by LURGI consists of several tubular catalyst beds surrounded by an outer shell of boiling water [7]. The pressure in the shell is used to control the reaction temperature. The ICI and LURGI configurations account for approximately 60% and 30% of global methanol production respectively. Crude methanol leaving the reactor contains volatile impurities such as dissolved gases, light hydrocarbons, esters and ketones (Figure 2), that are removed in an initial stripping step. Less volatile impurities such as water and heavier alkanes (C_{8+}) are removed as bottoms in subsequent distillation steps [2, 7, 14]. A simplified schematic of a methanol synthesis plant is shown in Figure 3.

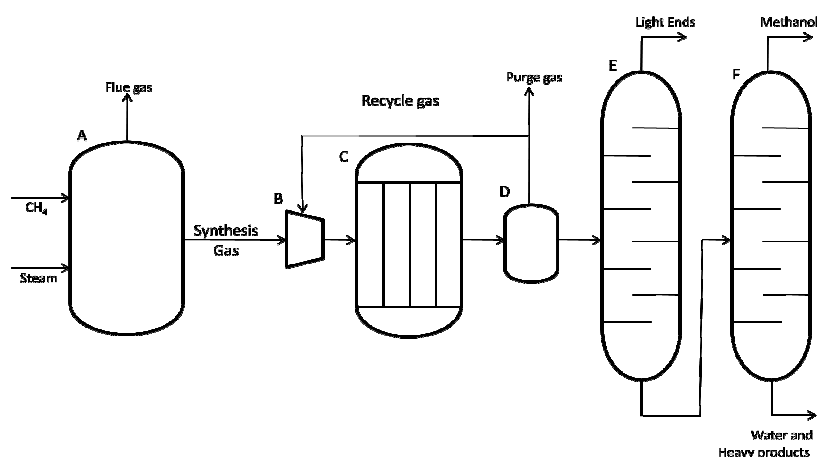


Figure 3. A simplified schematic of a methanol synthesis plant. A) Gasifier B) Compressor C) Methanol Reactor D) Flash drum E) Light-Ends column F) Methanol column

Low pressure methanol synthesis relies almost exclusively on catalysts based on copper, zinc oxide and alumina. The catalysts are produced by ICI (now Johnson Matthey), Südchemie, Haldor Topsøe, BASF and other chemical enterprises and contain 50-70 atomic % CuO , 20-50% ZnO and 5-20% Al_2O_3 . Instead of alumina, also Chromium oxide and rare earth oxides have also been used. The mixed oxide catalysts are usually shipped as 4-6 mm cylindrical pellets with BET surface area of 60-100 m^2/g . The catalysts are activated in situ with dilute hydrogen, often derived from off-gases from synthesis gas production. The activation procedure takes place at 190-230°C, completely reducing copper oxide to metallic crystallites interspersed by a $\text{ZnO-Al}_2\text{O}_3$ matrix. More details on the preparation and properties of Cu/ZnO -based methanol synthesis catalysts will be given in a section 5.5.6.

Typical $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst life times are about 2 years, with one third of the total activity loss occurring during the first 1000 hours of operation. The loss of activity with time is compensated by increasing the reaction temperature. Deactivation occurs through loss of copper dispersion during particle growth or poisoning by impurities. High partial pressures of water, associated with CO_2 rich gas mixtures, have also been shown to accelerate particle growth. However, the complete removal of CO_2 leads to an even faster deactivation by dispersion

loss [16]. Sulfur is a potent poison for Cu catalysts, however sulfur poisoning is seldom a problem as syngas feeds are desulfurized to less than 0.5 ppm. The ZnO catalyst component provides some protection against sulfur poisoning by scavenging sulfur irreversibly as ZnS, and thereby preserving a large fraction of catalyst activity even at sulfur loading of a several percent [7, 16].

5.5.4 The reaction mechanism of methanol synthesis

Gas feeds for industrial methanol synthesis usually contain both CO and CO₂. Which carbon oxide serves as the primary source for methanol formation, has been arguably the most important question pertaining to the reaction mechanism. Early work by Klier and co-workers assumed that CO was the primary source, and that the active site consisted of Cu⁺ species dissolved in ZnO. However, Klier's model predicted a zero rate of methanol production in the absence of CO₂, and it was assumed that CO₂ and water prevented over-reduction of Cu and thus helped maintain a population of active Cu⁺ species [17-18]. In the 1980's experiments conducted by Razovskii and later by Chinchin *et al.* involving the use of ¹⁴CO or ¹⁴CO₂ tracers in methanol synthesis from CO₂/CO/H₂ mixtures over commercial catalysts proved conclusively that CO₂ was the primary methanol source [19-20]. Chinchin *et al.* measured the radioactivity of reaction products at the outlet of a reactor operating with a ¹⁴CO₂/¹²CO feed. As shown in Figure 4, at lower space velocities, scrambling of carbon isotopes between CO and CO₂ through WGS resulted in the incorporation of both isotopes into methanol. At high space velocities, where the rate of scrambling is negligible and conversion is low, methanol retained the specific radioactivity of the ¹⁴CO₂, indicating that only carbon from CO₂ was incorporated. Chinchin *et al.* showed that even when present at very low concentrations (100 ppm), CO₂ was the primary carbon source for methanol.

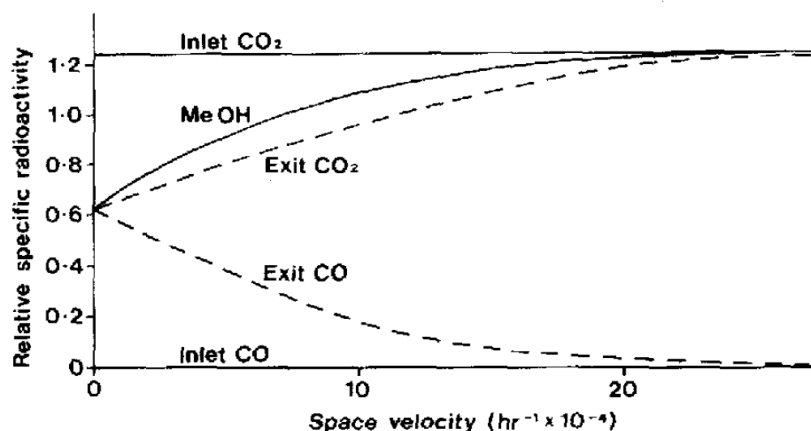


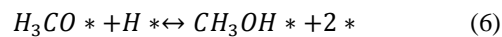
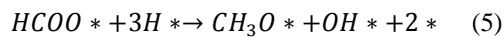
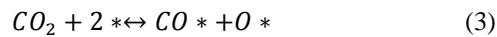
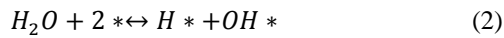
Figure 4. Effect of Space velocity on ¹⁴C distribution in Methanol synthesis products from [19]

In situ spectroscopic studies have identified a variety of species such as formate, dioxymethylene, carbonate and methoxide to co-exist under methanol synthesis conditions on Cu/ZnO-based catalysts [21-22]. FTIR studies of Cu Zn based catalysts under H₂/CO₂ identified the presence of formate bound to both Cu and ZnO, whereas methoxyl was found on ZnO only. Carbonates were found to form via CO₂ adsorption on ZnO [23] and partially oxidized Cu [22], and were quickly converted into formate via Cu activated hydrogen. Upon exposure to CO mixtures, only zinc-bound formate was observed [21]. The hydrogenation of these formates to methoxyl is thought to be rate determining in methanol synthesis. However, this hydrogenation may not be direct, as – even in the presence of hydrogen – the rate of methanol synthesis on Cu/SiO₂ from formate was negligible compared to the rates of formate decomposition into CO₂ and H₂ [24]. The presence of water and/or hydroxyl groups was found to be critical for methanol formation [25]. However, the absence of direct coverage by reducible oxygen species, (and therefore of Cu⁺) was confirmed by CO pulse experiments on catalysts in the working state [26].

Surface science studies on Cu single crystals also identify formate as an abundant surface species, but report a wide range of activities for methanol synthesis. The intrinsic reaction rates reported by Szanyi and Goodman for the hydrogenation of CO/CO₂ mixtures on Cu(100) were four orders of magnitude below those reported for high surface area Cu Zn catalysts [27-28]. Rasmussen *et al.* report rates 2-3 orders of magnitude higher than those reported by Szanyi and Goodman for Cu(100), but using CO₂/H₂ mixtures. Yoshihara *et al.* report rates comparable to those on high surface area catalysts on polycrystalline copper [29], and even three times higher rates on the more open Cu(110) surface [30]. Yoshihara and Rasmussen both confirm the absence of oxygen on the Cu surface, assume metallic Cu to be the active phase [30-31]. Furthermore, ZnO is assumed to maintain metallic Cu in a form that more closely resembles an open surface, thereby acting as a promoter [30]. Direct deposition of up to 0.19 ML of Zn on a polycrystalline Cu surface has been shown to increase CO₂ hydrogenation activity by a factor of six, thus suggesting a more direct role for ZnO [32].

The structure sensitivity of the rWGS reaction, that accompanies methanol synthesis, was even more pronounced, with Cu(110) being an order of magnitude more active than polycrystalline Cu. Furthermore, kinetic studies of CO₂ hydrogenation on Cu/ZnO catalysts yielded a temperature-dependent non-zero CO selectivity at the limit of zero CO₂ conversion [21, 30, 33]. These findings suggest that both reactions do not share a common intermediate. Whereas methanol formation is associated with formate hydrogenation, the rate of the rWGS reaction is controlled by direct dissociation of CO₂, a direct “redox” process that is more favorable on open surfaces [30].

Theoretical studies confirm the importance of formate as a surface intermediate, and its sequential hydrogenation as being rate determining. A highly simplified version of the mechanism proposed by Askgaard *et al.* for methanol synthesis from CO₂ on Cu(111) is given below [34], where step 3-6 may each represent a series of reaction events. The formation of formate from CO₂ with hydrogen is a fast process, and CO₂ is thought to bind directly to adsorbed hydrogen in an Eley-Rideal step [35], instead of forming carbonate by binding to surface oxygen species [36]. Askgaard *et al.* propose that the hydrogenation of H₂COO* is rate limiting, whereas Yang *et al.*, Hu *et al.* and Grabow and Mavrikakis, identify the hydrogenation of HCOO* and CH₃O* respectively as rate determining [35-37]. The presence of adsorbed Zn may promote methanol synthesis on Cu(111) by stabilizing formate and associated transition states [38]. Zhao *et al.* show that methanol cannot be formed directly through formate hydrogenation on Cu(111), but is instead formed by a hydrogen transfer reaction requiring the presence of water [39]. According to Grabow and Mavrikakis, the main role of CO in promoting the hydrogenation of CO₂ is the removal of site-blocking OH species via rWGS, although the direct hydrogenation of CO is said to account for 1/3 of the methanol produced under industrial conditions [36].



5.5.5 Methanol synthesis from CO₂ – Thermodynamic and kinetic considerations

Methanol synthesis from waste CO₂ streams has potential to contribute to the limitation of worldwide CO₂ emissions, and to serve as an alternative carbon source to fossil fuels, if a renewable source of hydrogen is available (see section 5.5.1). The main obstacle to methanol synthesis from CO₂ rich streams is thermodynamics. The

equilibrium yield of methanol from 25% CO/CO₂ rest H₂ mixtures of varying CO/CO₂ ratio is shown in Figure 7. For pure CO, a one-pass methanol yield of nearly 55% can be obtained at 525 K, while pure CO₂ would only yield 18%. Besides the addition of CO, this equilibrium limitation can be overcome by operating at lower temperatures- an option that requires more active catalysts, or by implementing higher recycle ratios, or product extraction- an option that requires higher capital investment [7].

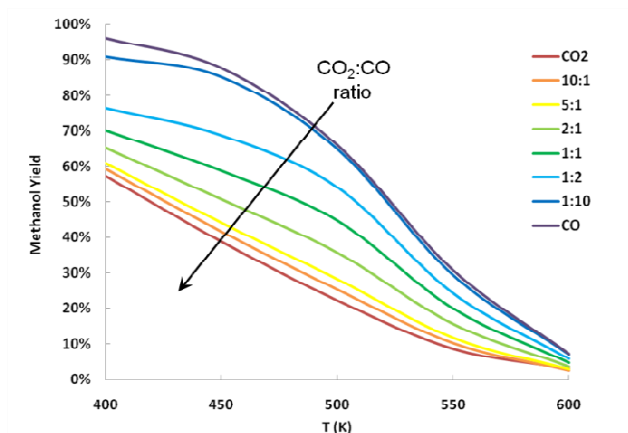


Figure 7. Equilibrium yield of methanol at 50 bar from 3:1 CO₂/H₂ mixtures as a function of CO₂/CO ratio

The feasibility of methanol synthesis from CO₂ can be achieved by circumventing the thermodynamic limitations through innovative reactor design. These design considerations involve efficient product removal without excessive recycling of feed gases. One strategy involves a liquid phase reactor using a high-boiling hydrocarbon oil solvent. The methanol and water can be separated from the solvent upon cooling, whereby the solvent is recycled back into the reactor. The use of alkane and alcohol solvents under supercritical conditions has also been proposed. Liquid phase methanol synthesis has the advantage of higher capacities and better temperature control. However diffusion limitations may be encountered with solvent present in the pores of the catalyst. Furthermore, catalysts that are stable in the solvent environment must be developed. Other strategies involve a series of gas-phase reactors with inter-stage absorption of methanol and water by a polar liquid solvent, or a in-situ desorption with a solid such as alumina [7, 40].

Although CO₂ has been shown to undergo hydrogenation faster than CO, kinetic limitations would arise in a process operating at high conversions, as in industrial applications. Several investigators have shown that a maximum in methanol production with CO₂/CO ratio occurs at CO₂ concentrations of 2-5 mol% of total carbon [18, 33, 41]. Klier *et al.* ascribed this behavior to active Cu⁺ sites being created by oxidation at low CO₂ concentrations, and surface poisoning by strongly bound CO₂ at higher concentrations, thus resulting in an activity maximum [18]. Further investigations have shown that such a maximum in the synthesis rate is only exhibited at high reactant conversions, thus indicating that product inhibition plays an important role [33, 41-43]. Shibzada *et al.* have studied the effect of methanol synthesis rate versus CO₂/CO ratio in an integral internal recycle reactor compared to a differentially operated down flow micro reactor. Their results (Figure 8) show that a maximum exists at 2% CO₂ in the integral reactor, while in the differential reactor (operated at < 0.3% methanol yield) at almost linear relationship between the methanol synthesis rate and CO₂ concentration was observed. These investigators have correlated the methanol synthesis rate at integral conditions with the concentration of water in the product stream during CO₂ hydrogenation. Furthermore, they have shown that co-feeding of water to a differential reactor in concentrations similar to those formed during integral operation results a 10-fold decrease of the methanol synthesis rate [33]. These results show conclusively that water acts to inhibit methanol synthesis from CO₂, and that the promotional effects of CO at integral conversion arises from its ability to “scavenge” excess water via WGS [22, 44].

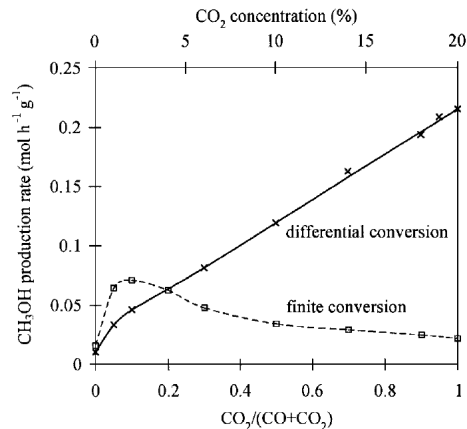


Figure 8. Methanol synthesis at differential and integral conditions at 250°C and 50 bar from [33]

Indirect evidence for the inhibitory role of water in methanol synthesis can be drawn from a simple experiment involving the variation of space velocities. In Figure 9A, the methanol synthesis and rWGS rates as a function of space velocity for two Cu/ZnO based catalysts are shown. The more active catalyst is derived from a zincian malachite (MA) precursor [45] (see section 5.5.6) and promoted with Al_2O_3 . It possesses a Cu surface area of $30 \text{ m}^2/\text{g}$, while the less active catalyst is derived from a hydrotalcite (HT) precursor [46] and possesses a smaller Cu surface area ($7 \text{ m}^2/\text{g}$). In both catalysts the rate of rWGS shows little variation with increasing space velocity, whereas the rate of methanol synthesis increases dramatically. The concentration of the reactants does not vary significantly throughout this space velocity range as the maximum CO_2 conversion is not higher than 14% for the MA catalyst. However the concentrations of water and methanol decrease by a factor of 3 when increasing the space velocity from 10 to $80 \text{ mmol}/\text{g}_{\text{cat}}\text{min}$, as a result of product dilution. In the absence of external mass transport limitations these results imply product inhibition of methanol synthesis. The rWGS reaction does not seem to be product inhibited. Furthermore the rWGS rate seems to remain constant even as the concentration of methanol decreases at higher space velocities, also due to product dilution. The lack of correlation between methanol partial pressure and CO production rate implies that CO does not form from methanol. Although methanol decomposition ($K = 200$ at 230°C) is more thermodynamically favorable than rWGS ($K = 0.01$ at 230°C) at these conditions, the former has been shown to be kinetically unfavorable on Cu [47].

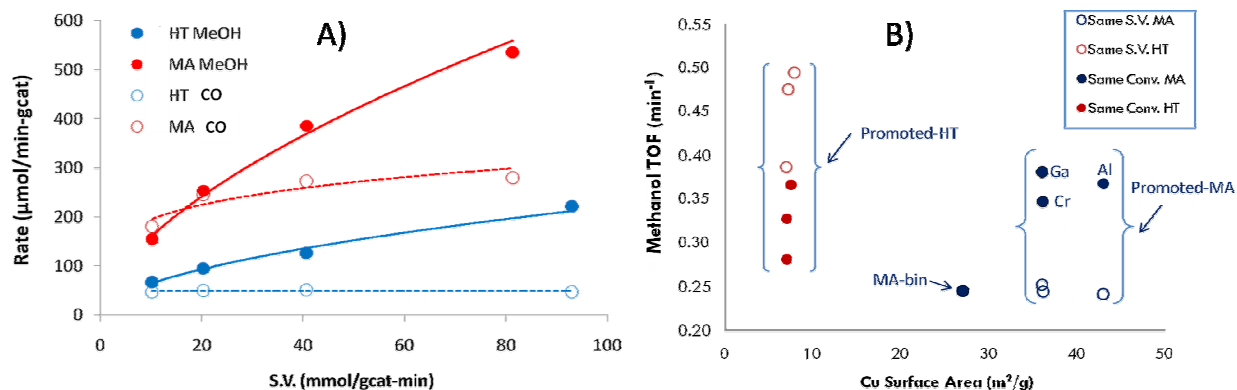


Figure 9. The variation of CO and methanol production rates with space velocity (A) and methanol synthesis rates on promoted CuZn based catalysts derived from hydrotalcite and Malachite precursors (B). Reaction conditions: 200 mg catalyst 30 bar, 230°C K 3:1 $\text{H}_2:\text{CO}_2$

When comparing the intrinsic methanol synthesis activity of both catalysts (TOF per surface Cu site measured with N₂O-RFC) at the space velocity of 20 mol/g_{cat}min, the HT catalysts (0.54 min⁻¹) appears twice as active as the MA catalyst (0.24 min⁻¹). Although both catalysts are exposed to nearly the same reactant concentration, the MA catalyst operates at 11% CO₂ conversion and is exposed to 3.5 times as much reaction-inhibiting water as the HT catalyst (X = 3.3%). If both catalysts are tested at the same CO₂ conversion (5-6%), they show a similar intrinsic activity (TOF ca. 0.35 min⁻¹). These results suggest that the interpretation of catalytic activity data for the hydrogenation of CO₂ is a strong function of the measurement conditions, and therefore great caution must be taken when comparing and interpreting reactivity data for different materials. It is noted that for methanol synthesis from CO-containing feed gases, these considerations less important, as water is scavenged by CO.

The selectivity to methanol is another important consideration in CO₂ hydrogenation. Methanol synthesis and rWGS are independent reaction channels on Cu-based catalysts (see sections 5.5.2, 5.5.4). On Cu based catalysts the apparent activation energies are reported around 120 kJ/mol and 70 kJ/mol for rWGS and methanol synthesis respectively [24, 48-49]. As a result of this difference, selectivity towards methanol decreases with increasing temperature. The selectivity to methanol also increases with total reaction pressure, as the total pressure increases the rate of methanol synthesis, but does only weakly affect the rate of rWGS [50] (Figure 1B). How the properties of Cu/ZnO-based catalysts can be tailored in order to favor methanol synthesis over rWGS is a key question for catalyst development for CO₂ hydrogenation. Recently Liao *et al.* showed that methanol selectivity can be controlled by the shape of ZnO crystallites in catalysts consisting of physical mixtures of Cu and ZnO crystallites [51]. They suggest that a stronger Cu-ZnO interaction observed for plate-like crystallites showing the polar (002) face as opposed to non polar rod-like crystallites is responsible for higher methanol selectivity. These results suggest that tuning the so-called synergy between Cu and ZnO (see section 5.5.6) is a promising approach to improve the selectivity of Cu towards methanol synthesis. The undesired rWGS is known to be more structure sensitive than methanol synthesis on copper. Therefore, another selectivity control strategy may involve controlling Cu particle size and shape [27]. Another approach is the use of promoters. Arena *et al.* have suggested that adding promoters such as ZrO₂ which increase the hydrophobicity of the catalyst surface would lead to better activity in CO₂ hydrogenation [48, 52] due to less product inhibition by water. Oxides such as Al₂O₃, Cr₂O₃, Ga₂O₃ or ZrO₂ are known to promote methanol synthesis [53]. They may improve Cu dispersion and stability [8], but also the intrinsic catalytic properties of the exposed Cu surface [54]. The latter is probably related to an adjustment of the properties of the ZnO crystallites and related to modified interactions between Cu and ZnO. A clear picture of the nature of the promoting effect of different oxides and their influence on the selectivity in CO₂ hydrogenation is still lacking.

When studying the effect of promoters on the methanol synthesis activity of differently promoted catalysts, again great caution is needed for a reliable comparison of performance data. An example is shown in Figure 9B. The intrinsic methanol synthesis activities for a series of MA derived catalysts and a series of HT derived catalysts with difference promoters are plotted as a function of Cu surface area and compared to an unpromoted binary MA derived catalyst (MA-bin). The activity was measured at the either the same space velocity or the same CO₂ conversion. When considering activities measured at the same space velocity, all HT based catalysts appear intrinsically more active than the MA derived ones. All promoted MA-based catalysts show the same intrinsic activity as MA-bin under these conditions. One might thus presume that the promoting effect is limited to improvement of the Cu dispersion within this series of samples. However, isoconversion activities of both promoted series fall in the same range (0.3-0.35 min⁻¹) and are significantly greater than that of the unpromoted sample (0.25 min⁻¹), showing clearly that the presence of the promoters also improves the intrinsic activities of the MA-derived catalysts.

5.5.6 Cu/ZnO-based methanol synthesis catalysts¹

Commercial Cu/ZnO/Al₂O₃ methanol synthesis catalysts are often mistaken as supported systems, but neither ZnO nor Al₂O₃ represent classical extended oxidic supports. This is apparent, when considering the typical composition of modern Cu/ZnO/(Al₂O₃) catalysts, which is characterized by a molar Cu:Zn ratio close to 70:30, while the amount of Al₂O₃ typically is significantly lower than that of ZnO. This Cu-rich composition manifests itself in a peculiar microstructure of the industrial Cu/ZnO/Al₂O₃ catalyst (Figure 5) [56], which is composed of spherical Cu nanoparticles of a size of ca. 10 nm (Figure 5B,C) and often even smaller ZnO nanoparticles arranged in an alternating fashion. Thus, porous aggregates are formed (Figure 5A) in which the oxide particles act as spacers between Cu particles (Figure 5B [56]). The presence of inter-particle pores as seen in the HRTEM image (Figure 5B) allows some access to the “inner surface” of larger Cu/ZnO aggregates (Figure 5A).

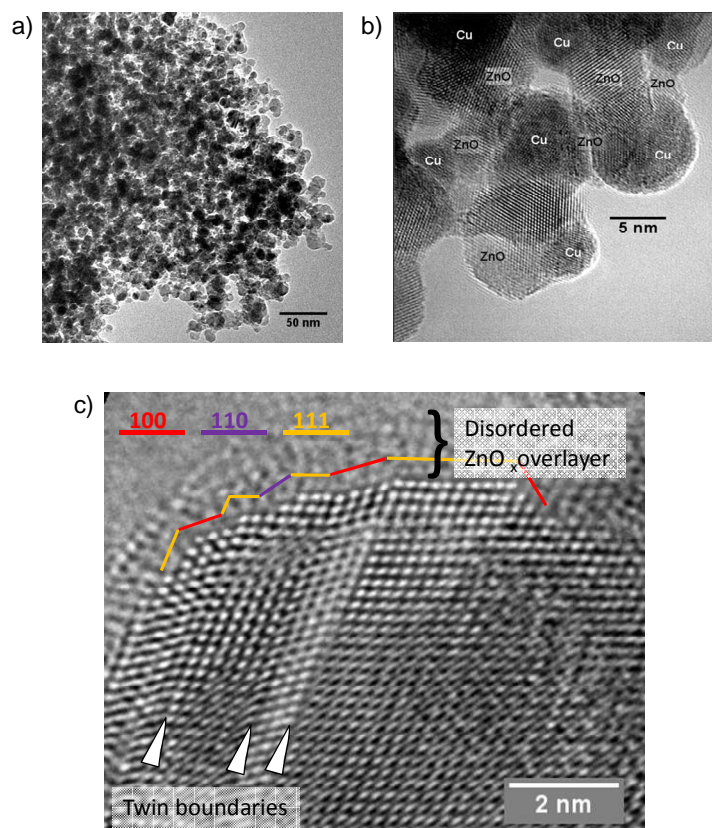


Figure 5: (High resolution) TEM images of a Cu/ZnO/Al₂O₃ methanol synthesis catalyst consisting of porous aggregates (A) of metallic Cu and ZnO nanoparticles (B [56]) showing details of the surface faceting, decoration and defect structure (C [57]), which is discussed in detail in the text.

This unique microstructure can be described as an intermediate stage between a supported catalyst and a bulk metallic sponge or skeletal Raney-type catalyst. It enables a reasonably high dispersion of Cu and exposure of many Cu-ZnO interfaces at a high total Cu content. The specific Cu surface area (SA_{Cu}) of methanol catalysts can be determined by reactive N₂O titration [58-59], which causes surface oxidation of the Cu particles and allows calculation of SA_{Cu} from the amount of evolved N₂. The SA_{Cu} of state-of-the-art methanol synthesis catalysts measured by this method amounts to 25-35 m²g⁻¹. If reliable data of the average Cu particle size are available, e.g. by sufficient TEM observations [56], the degree of oxide coverage of the Cu particles, i.e. the average ratio of interface area to surface area, can be calculated [60]. For industrial Cu/ZnO/Al₂O₃ catalysts, this value is around

¹ Part of this section is based on work previously published in ref. [55].

35%. The favorable microstructure and the proper balance of Cu dispersion and loading in this type of Cu/ZnO/(Al₂O₃) catalysts leads to a large SA_{Cu}, which is probably the most important property of a methanol synthesis catalyst.

The SA_{Cu} has been observed to scale linearly with the activity for sample families with a similar preparation history [54]. However, between these families considerably different intrinsic activities, i.e. activities normalized by SA_{Cu}, can be found [60]. Thus, in agreement with the structure sensitivity of methanol synthesis over Cu [30], different “qualities” of Cu surfaces can be prepared, which vary in the activity of their active sites and/or in the concentration of these sites. Differences in intrinsic activity of the exposed SA_{Cu} can be related to defects and disorder in the Cu nanoparticles and to the role of ZnO. Clearly, one role of ZnO that is apparent from Figure 2B is to act as spacer and stabilizer avoiding direct contact of the Cu particles and preventing them from sintering [61]. But it is generally agreed that the role of ZnO in Cu-based methanol synthesis catalysts exceeds the function of a mere physical stabilizer. In addition to this geometrical function, a so-called Cu-ZnO synergy is described in literature for methanol synthesis [7, 62-63]. The nature of this synergy and the contribution of ZnO to the active site of methanol synthesis are strongly debated and several models have been proposed, e.g., Cu⁺ ions in the ZnO matrix [64], ZnO segregated on Cu⁺ [65], electron-rich Cu at the Cu-ZnO heterojunction [66], CuZn surface alloy formation [67] or Cu metal supported on ZnO [22]. Strong metal-oxide-interactions (SMSI) between Cu and ZnO were observed at highly reducing conditions [68-69] and it was suggested that partially reduced ZnO_x migrates onto the surface of the Cu particles under methanol synthesis conditions [70]. On a supported Cu/ZnO model catalyst, reversible wetting/de-wetting was observed as the reduction potential of the gas phase was varied [71], an observation not made on Cu/SiO₂.

Another contribution to variations of intrinsic activity is the different amount of defects and disorder in the metallic Cu phase. This disorder can manifest itself in form of lattice strain detectable, e.g., by line profile analysis of XRD peaks [72], ⁶³Cu-NMR lines [73], or as an increased disorder parameter (Debye-Waller-factor) derived from extended X-ray absorption fine structure (EXAFS) spectroscopy [74]. Strained copper has been shown theoretically [75] and experimentally [76] to have different adsorptive properties compared to unstrained surfaces. Strain, *i.e.* local variation in the lattice parameter, is known to shift the centre of the d-band and alter the interactions of metal surface and adsorbate [77]. The origin of strain and defects in Cu/ZnO is probably related to the crystallization of kinetically trapped non-ideal Cu in close interfacial contact to the oxide during catalyst activation at mild conditions. A correlation of the concentration of planar defects in the Cu particles with the catalytic activity in methanol synthesis was observed in a series of industrial Cu/ZnO/Al₂O₃ catalysts by Kasatkin *et al.* [56]. Planar defects like stacking faults and twin boundaries can also be observed by HRTEM and are marked with arrows in Figure 5C [57].

Recently, experimental and theoretical evidence for a model of the active site of industrial methanol synthesis that combines the role of ZnO and defects in Cu has been presented [57]. Planar defects have been shown to lead to changes in surface faceting of the Cu nanoparticles (Figure 5C) associated with formation of steps and kinks that were assumed to represent high energy surface sites of special catalytic activity. For a series of Cu/ZnO-based catalyst a linear correlation of the defect concentration with the intrinsic activity of the exposed Cu surface was observed. In addition, (partial) surface decoration of Cu with ZnO_x by SMSI have been confirmed by HRTEM (Figure 5C) and in-situ XPS. The high catalytic activity of surface steps containing Zn was supported by DFT calculations. Thus the active site of industrial methanol synthesis could be identified as a complex surface ensemble requiring a high energy site due to defects in Cu and the presence of Zn in the close vicinity due to in-situ adjustment of Zn surface decoration. It is noted again that a successful methanol synthesis catalyst also requires large total SA_{Cu}; the aforementioned results may offer new options for a knowledge-based fine-tuning of the intrinsic activity of the Cu surface in Cu/ZnO materials with already optimized Cu dispersion.

In the technical catalyst, these three requirements – large SA_{Cu}, defective Cu nanoparticles and many reactive interfaces to ZnO – are elegantly realized by the nanoparticulate and porous Cu/ZnO arrangement shown in Figure 5. Preparation of this microstructure requires a homogeneous and maximized intermixing of the Cu and Zn species

in order to stabilize the alternating arrangement of small Cu and ZnO nanoparticles. Thus, the main goal of catalyst synthesis is to carry over and maintain the perfectly homogeneous cation distribution in the starting mixed solutions to a maximum extent to the final catalyst [78]. Different methods of Cu/ZnO catalyst preparation can be found in literature [79], but this preparation is most successfully achieved by co-precipitation, which is by far the most important and technically applied technique. Figure 6A gives a schematic overview of the multistep synthesis route of Cu/ZnO catalysts introduced by ICI in the 1960s [61, 80]. It comprises co-precipitation [78] and ageing [73, 81] of a mixed Cu,Zn,(Al) hydroxy-carbonate precursor material, thermal decomposition yielding an intimate mixture of the oxides and finally activation of the catalyst by reduction of the Cu component [82]. The synthesis parameters of this route have been studied in many academic and industrial groups and a high degree of optimization could be achieved over the last decades by mostly empirical fine-tuning of the conditions [78, 83-85]. The delicate nanoparticulate and porous microstructure of the industrial methanol synthesis catalyst (see above) can only be obtained if the optimized parameters are strictly obeyed during synthesis. Especially the synthesis conditions during the early co-precipitation and ageing steps turned out to be crucial for the catalytic properties of the resulting methanol synthesis catalyst. This phenomenon, sometimes termed the “chemical memory” of the Cu/ZnO system [86], indicates the critical role of the preparation history of this catalyst system [72, 84, 87]. Baltes *et al.* [84] elaborated a quantitative basis of the chemical memory in a systematic study and reported dramatic difference in SA_{Cu} and catalytic activity for Cu/ZnO/Al₂O₃ catalysts of the same composition as pH or temperature of the co-precipitation step was varied (Figure 6B).

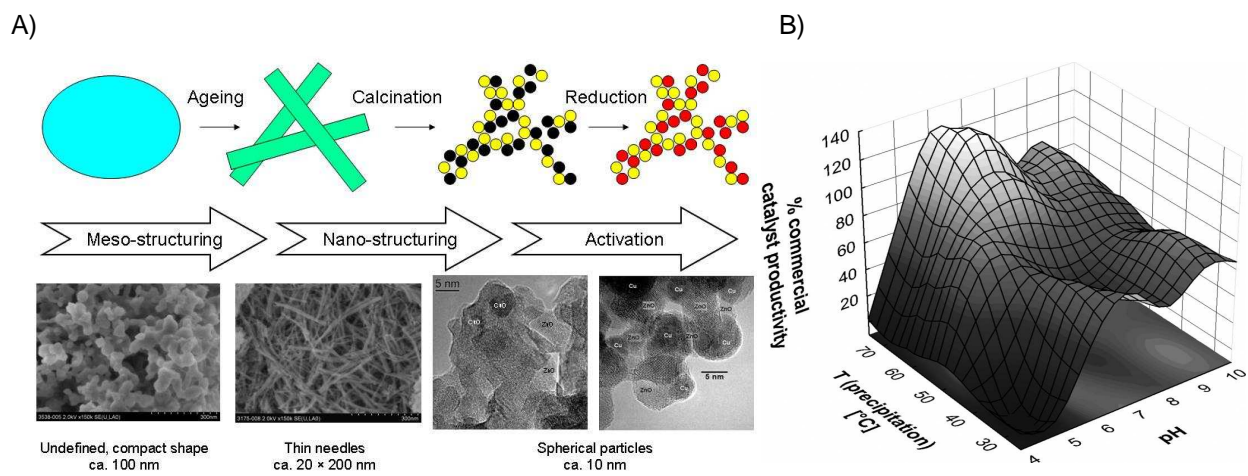


Figure 6: A) Simplified geometrical model [45, 88] for the preparation of industrial Cu/ZnO catalysts comprising subsequent meso- and nano-structuring of the material from [55]. In a first microstructure directing step (meso-structuring) the Cu,Zn co-precipitate crystallizes in form of thin needles of the zincian malachite precursor, $(Cu,Zn)_2(OH)CO_3$. In a second step, the individual needles are decomposed and de-mix into CuO and ZnO. The effectiveness of this nano-structuring step depends critically on a high Zn-content in the precursor, which in zincian malachite is limited to Cu:Zn ca. 70:30 due to solid state chemical constraints [74]. Finally, inter-dispersed CuO/ZnO is reduced to yield active Cu/ZnO. B) Chemical memory: Dependence of catalytic activity in methanol synthesis on the conditions of the co-precipitation and ageing steps from [84].

5.5.7 Methanol steam reforming (MSR)²

Methanol is a promising candidate for a hydrogen storage molecule to be used for decentralized (on-board) hydrogen generation in combination with downstream PEMFCs. It has a high H:C ratio of 4:1 and no C-C bond, which has to be broken. MSR is the preferred way to liberate hydrogen from methanol as it generates a high hydrogen concentration in the product stream, runs at relatively low temperatures of 200 – 300 °C, and unlike methanol decomposition does not directly produce CO, which acts as a poison for the downstream PEMFC anode catalyst. MSR was first described in 1921 by Christiansen [89] and research on its application for hydrogen

² This section is based on the work previously published in ref. [55].

production has a long history [90]. The recently renewed interest was triggered by the development of fuel cell technology requiring clean and preferably renewable hydrogen. A number of general overview articles and reviews are available addressing the role of MSR in this context [11, 90-95]. In areas, where steam reforming of natural gas is not an option, MSR is also applied in the methanol-to-hydrogen (MTH) process to produce hydrogen in relatively small-sized units.

MSR is an endothermic reaction (see section 5.5.2) and requires external heating. It is sometimes used in combination with exothermic partial oxidation of methanol (autothermal reforming or oxidative steam reforming) [96-97] or combustion of methanol [93] in order to generate the necessary heat. The endothermicity of MSR is much weaker compared to steam reforming of other hydrocarbons or higher alcohols [93] and reformer units can be relatively small enabling the onboard combination with PEMFCs. A comparison between methanol and other molecules as reactants for onboard hydrogen production can be found in the comprehensive review by Palo *et al.* [11]. The detrimental role of CO in the effluent for the downstream PEMFC is to be emphasized. CO chemisorbs irreversibly on Pt-based fuel cell catalysts and causes irreversible site blocking. Its concentration has to be below ca. 20 ppm in order to prevent poisoning, which is usually not achieved in the reformer outlet gas. Thus, in technical applications, a gas purification step has to be introduced between reformer and fuel cell. The CO concentration in the gas stream can be lowered by means of WGS reaction, preferential oxidation (PROX) or using Pd membranes, which in all cases complicates the setup and generates costs [98]. Generally, a low selectivity to CO – in addition to high activity and stability – is, thus, a major and particular requirement for a successful MSR catalyst to be used for onboard hydrogen production. Methanol reforming catalysts should be particularly stable towards abrupt changes of the conditions of reforming, *i.e.* work reliably in transient situations like on-off operations as well as in steady state to produce sufficient amounts of hydrogen on demand.

Commercial industrial Cu/ZnO-based catalyst for methanol synthesis (see section 5.5.6) or WGS are also active in MSR. Cu/ZnO/Al₂O₃ catalysts or the unpromoted binary Cu/ZnO model system were thus employed in many studies of MSR [55]. While preparation and composition of the industrial Cu/ZnO/Al₂O₃ catalysts have been adjusted for application of methanol synthesis and WGS, modifications of the Cu/ZnO/X system turned out to improve the properties for use in MSR. In particular, choosing another second oxide phase X like rare earths [99] or ZrO₂ [100-104], or employing new catalyst precursors like layered double hydroxides [105-108], or even changing to ZnO-free samples and using ZrO₂ and/or CeO₂ [109-113] for preparation of Cu-based catalysts was reported to lead to interesting MSR performance.

Several studies are available addressing the mechanism and kinetics of the MSR reaction over Cu based catalysts [114-120]. There is agreement nowadays that CO₂ is a direct product of the MSR reaction and not of a sequence of methanol decomposition and WGS reactions. The main source of CO is the rWGS reaction taking place as a secondary reaction after MSR. Frank *et al.* [120] presented a comprehensive microkinetic analysis of the MSR reaction based on the work of Peppley *et al.* [116]. They investigated several Cu-based catalysts with various oxide components showing considerably different activities. Similar activation energies support the idea that the surface chemistry is independent of the oxide material (with the exception of Cu/Cr₂O₃/Fe₂O₃, which behaved differently). Dehydrogenation of methoxy groups is the rate limiting step and by means of DRIFTS experiments methoxy and formate species were found as the dominating species at the surface. Two distinct kinds of active sites were considered, one for the adsorption and desorption of oxygenates and one for hydrogen. Two reaction pathways of the methoxyl intermediate are discussed via dioxomethylene/formate, intermediates of the reverse methanol synthesis reaction, or methyl formate. Recent theoretical studies favor the former pathway [121-122].

There are many similarities between methanol synthesis and MSR [117]. This is often accounted for by the concept of microscopic reversibility, as MSR formally is the reverse reaction of methanol synthesis from CO₂ (see section 5.5.2). It has to be considered, however, that the different reactant gas mixtures used for MSR and methanol synthesis will affect the surface state of the catalyst, which consequently will be different under highly reducing methanol synthesis conditions compared to the less reducing MSR feed. Thus, unlike forward and reverse reactions

at equilibrium, methanol synthesis and MSR probably may take place over practically different catalytic surfaces. This general limit of the application of the concept of microscopic reversibility has been pointed out by Spencer for WGS and rWGS [123] and is valid accordingly also for methanol synthesis and MSR [8]. One may conclude that an optimized methanol synthesis catalyst, for which the fine tuning of preparation and operation conditions is far more advanced, will also be active in MSR due to its generally large SA_{Cu} and represents a powerful reference system, but it does not necessarily represent the optimal catalyst for this reaction [8]. Finding Cu/ZnO/X systems with a composition and microstructure optimized for the MSR reaction is thus the major current challenge in development of a MSR catalyst for energy applications. In this context it is interesting to note that the Cu-ZnO synergy (see section 5.5.6) does not seem to be as critical factor in case of MSR compared to methanol synthesis [124] or this synergistic effect is not as strictly limited to ZnO. Highly active Cu-based MSR catalysts can also be prepared in absence of ZnO, e.g. as Cu/ZrO₂.

The question to what is the active site of Cu-based catalysts in MSR is still unclear and debated in literature. Similar to the methanol synthesis reaction, either metallic Cu⁰ sites, oxidized Cu⁺ sites dispersed on the oxide component or at the Cu-oxide interface or a combination of both kinds of sites are discussed to contribute to the active ensembles at the Cu surface. Furthermore, the oxidic surface of the refractory component may take part in the catalytic reaction and provide adsorption sites for the oxygenate-bonded species [125], whereas hydrogen is probably adsorbed at the metallic Cu surface. Similar to methanol synthesis, factors intrinsic to the Cu phase also contribute to the MSR activity in addition to SA_{Cu} . There are two major views discussed in literature relating these intrinsic factors either to the variable oxidation state of Cu, in particular to the *in situ* adjustment of the Cu⁰/Cu⁺ ratio at the catalyst's surface [101, 106, 126-132], or to the defect structure and varying amount of disorder in metallic Cu depending on the microstructure and preparation history of the catalyst [73-74, 133-134].

Drawbacks of Cu-based MSR catalysts are related to its pyrophoricity and low stability with time on stream and against changing conditions like redox- or heating cycles. In methanol synthesis, which is operated at a similar temperature like MSR, modern Cu/ZnO/Al₂O₃ catalysts can deliver stable performance over years on stream. The same catalyst may tend to deactivate more rapidly under MSR conditions suggesting a critical role of the gas phase composition on the deactivation behavior, most probably of water in the feed. In addition to thermal sintering induced by mobility of Cu, steam-induced segregation or re-crystallization of the ZnO component will have a detrimental effect on the porosity of the Cu/ZnO aggregates and cause a loss of SA_{Cu} . Löffler *et al.* [135] investigated the stability of several commercial WGS catalysts in the MSR reaction and fitted their data using a sintering model. Cu/ZnO/Al₂O₃ formulations were found to be most active compared to other catalyst compositions, but were also most prone to deactivation by sintering. In their analysis of catalyst deactivation of a commercial Cu/ZnO/Al₂O₃ catalyst during MSR, Thurgood *et al.* [136] revealed in addition to the loss of surface area, a decrease in intrinsic activity with time on stream. The other major problem of Cu-based MSR catalysts is the formation of CO during MSR, typically in the low %-range. Agrell *et al.* [137] reported that the problem of CO formation over Cu/ZnO/Al₂O₃ catalysts can be attenuated by increasing the steam-to-methanol ratio or by the addition of oxygen or air (oxidative MSR). Also decreasing the contact time and lowering of the reaction temperature leads to lower CO selectivity, but has a negative effect on the overall efficiency. Thus, probably the best way to make a Cu-based MSR catalyst less selective to CO is to make it more active at lower temperatures.

Pt- and Pd-based intermetallic catalysts have been suggested as an alternative for Cu [55, 138]. In particular the ordered compound PdZn shows interesting MSR activity and CO₂ selectivity, which are higher compared to non-alloyed pure Pd – a methanol decomposition catalyst. This observation has triggered a lot of research activity in the recent years [139-142]. With regard to application, these and other new catalysts have to prove their competitiveness in comparison with the traditional Cu/ZnO system. Unfortunately, firm comparisons with Cu-based catalysts and studies of pyrophoricity and stability against changes in operating conditions are not always available. In general, all on-board MSR applications always have to compete with the alternatives of more mature methanol combustion engines and technically simpler DMFCs.

5.5.8 Challenges and perspectives in catalyst and process development for energy-related application of methanol

The thermodynamics of methanol synthesis and MSR necessitate process operation at lower temperatures. Therefore, the development of catalysts that function at low temperatures will remain the goal of methanol catalysis research for the foreseeable future. Although most researchers agree that copper-based catalysts will remain the industry standard, numerous possibilities exist for the improvement of the activity, selectivity and stability of these materials through the incorporation of promoters, more efficient exploitation of the Cu-ZnO synergy and implementation of new synthesis strategies. Therefore, a deeper understanding of the active sites for methanol synthesis, MSR and rWGS on Cu-based catalysts is desirable and essential to further knowledge-based catalyst development. Here, combined effort from the fields of theory, material science, model catalysis and reaction kinetics is needed. Several studies have exhaustively characterized model systems, whose structure does not represent the unique interspersed structure of industrial CuZnO catalysts. Although these studies shed some light on the general nature of the Cu-Zn interaction, they cannot provide sufficient insight into what makes the current state of the industry catalyst active, and how it could be improved. With that in mind, complementary *in situ* structural and surface studies on working industrial catalysts would be beneficial to validate the conclusions drawn from model studies and promise further progress in the understanding and optimization of methanol catalysts.

In contrast to traditional methanol synthesis, where selectivity to CO formation is not a major issue, diminishing the rate of rWGS is critical to the efficient methanol synthesis from CO₂ as well as MSR. In that respect properties such as particle size, interaction with oxide matrix, and identity of exposed Cu crystal planes should be investigated in more detail with respect to CO selectivity. Furthermore, targeted synthesis strategies can be developed to take these factors into account and in the end allow for tailoring the CO₂ and CO reaction channels on Cu surfaces. Due to the relatively harsh reaction conditions that hinder application of some *in situ* techniques and the entangled reaction network of relevant C1 conversions, the contribution from theory to mechanistic understanding is critical. Because such studies should be consolidated with experimental data carefully determined under relevant conditions, also here a stronger focus on the “real” multi-component functional catalyst is needed. Although it has been conclusively established that CO₂ is the source of methanol on CuZnO, a very recent detailed theoretical study on Cu surfaces suggest that CO may not only promote CO₂ hydrogenation but also directly contribute to methanol formation [36]. Since this study does not take into account Zn promotion, it is difficult to extrapolate their conclusions to the industrial system. One solution to this discrepancy would be to construct models based on input from characterization studies of industrial materials. As a second option, experimentalists could approach the current models and validate them by determining the methanol carbon source on Cu particles dispersed on inert supports (irreducible Carbon, Silica, Alumina). Both approaches would yield significant insight into the role of ZnO, Cu as well as the respective synthesis gas components in the H₂/CO₂/CO/CH₃OH/H₂O reaction network.

Future wide-spread use of anthropogenic CO₂ in combination with renewable hydrogen as well as the implementation of coal, biomass and other non-conventional sources of synthesis gas will lead to sub-optimal synthesis gas compositions. Efficient incorporation of these synthesis gas mixtures into the current methanol synthesis infrastructure will necessitate the re-development of catalysts to perform stably under high concentrations of CO₂, water and impurities. To that end, advanced characterization methods must be implemented to discriminate between surface area loss by sintering, loss of active sites by defect annealing and poisoning by impurities. The freely available data basis of Cu/ZnO catalyst deactivation is still relatively sparse and more investigations are needed to draw firm conclusions on the role of different deactivation mechanisms. Additionally, current high-throughput testing methods for methanol synthesis catalysts would need to be modified to take product inhibition from water into account. Deeper understanding of the performance of a catalyst at industrially relevant integral conditions can be gained through activity measurements at differential conditions in the presence and absence of water, as performed by Sahibzada *et al.* [33]. In this manner the catalyst’s intrinsic activity can be de-convoluted from its susceptibility to inhibition, thus allowing both properties to be optimized independently.

In summary, as one among other energy storage strategies, methanol has great potential as a sustainable synthetic fuel and seems particularly promising for the transportation sector. The industrial methanol synthesis process with Cu/ZnO-based catalysts represents a good starting point for implementation of methanol chemistry in a future energy scenario. However, the thermodynamic constraints of CO₂ hydrogenation require further research. The key remains the development of catalysts with better low temperature activity. Despite the long-lasting experience with the industrial processes, methanol chemistry is scientifically not yet mature. Elaboration of a firm scientific basis for effective catalyst design by resolving the open questions to the mechanism and nature of the active sites of the relevant reactions is a major challenge for the future.

1. Moffat, S.M., *Methanol Powered Science*, 1991. **251**: p. 515-515.
2. Olah, G.A., A. Goepfert, and G.K.S. Prakash, *Beyond oil and gas : the methanol economy*. 2006, Weinheim an der Bergstrasse, Germany: Wiley-VCH. xiv, 290 p.
3. Aldrich, B., *ABC's of AFV's: A Guide to Alternative Fuel Vehicles*. 1995: Diane Pub.
4. *Methanol: the clear alternative for transportation*. 2011, www.methanol.org.
5. Reed, T.B. and R.M. Lerner, *Methanol - Versatile Fuel for Immediate Use*. Science, 1973. **182**(4119): p. 1299-1304.
6. Skrzypek, J., et al., *Thermodynamics and kinetics of low pressure methanol synthesis*. The Chemical Engineering Journal, 1995. **58**: p. 101-108.
7. Hansen, J.B. and P.E.H. Nielsen, *Methanol Synthesis*, in *Handbook of Heterogenous Catalysis*, Ert, et al., Editors. 2008, Wiley-VCH
8. Twigg, M.V. and M.S. Spencer, *Deactivation of copper metal catalysts for methanol decomposition, methanol steam reforming and methanol synthesis*. Topics in Catalysis, 2003. **22**(3-4): p. 191-203.
9. Bernton, H., W. Kovarik, and S. Sklar, *A History of Power Alcohol*. 2010, Lincoln, NE: Bison Press. xiv, 290 p.
10. *Statistical Review of World Energy*, B. Global, Editor. 2011.
11. Palo, D.R., R.A. Dagle, and J.D. Holladay, *Methanol steam reforming for hydrogen production*. Chemical Reviews, 2007. **107**(10): p. 3992-4021.
12. Stiles, A., *Methanol, Past, Present, and Speculation on the Future*. AIChE Journal, 1977. **23**(3): p. 362-275.
13. Lewis, W.K. and P.K. Frolich, *Synthesis of Methanol from Carbon Monoxide and Hydrogen*. Industrial and Engineering Chemistry, 1928. **20**(285).
14. Weissermel, K. and H.-J. Arpe, *Industrial organic chemistry*. 4th completely rev. ed. 2003, Weinheim: Wiley-VCH. xix, 491 p., 20 folded leaves of plates.
15. Fiedler, E., et al., *Methanol in Ullmann's Encyclopedia of Industrial Chemistry*. 2011, Wiley-VCH Weinheim.
16. Kung, H.H., *Deactivation of Methanol Synthesis Catalysts - a Review*. Catalysis Today, 1992. **11**(4): p. 443-453.
17. Kung, H.H., *Methanol Synthesis*. Catalysis Reviews, 1980. **22**(2): p. 235-259.
18. Klier, K., et al., *Catalytic Synthesis of Methanol from CO/H₂ iV. The Effect of Carbon Dioxide*. Journal of Catalysis, 1981. **74**: p. 343-360.
19. Chinchin, G.C., et al., *Mechanism of Methanol Synthesis from Co₂/Co/H₂ Mixtures over Copper/Zinc Oxide/Alumina Catalysts - Use of C-14-Labeled Reactants*. Applied Catalysis, 1987. **30**(2): p. 333-338.
20. Rozovskii, A.Y., *Kinetika i Kataliz*, 1980. **21**: p. 87.
21. Fujita, S., et al., *Mechanism of the Formation of Precursors for the Cu/Zno Methanol Synthesis Catalysts by a Coprecipitation Method*. Catalysis Letters, 1995. **34**(1-2): p. 85-92.
22. Waugh, K.C., *Methanol Synthesis*. Catalysis Today, 1992. **15**(1): p. 51-75.
23. Saussey, J., J.C. Lavalley, and C.J. Bovet, *Chem. Soc. Faraday Trans.*, 1982. **87**: p. 1457.
24. Yang, Y., et al., *Isotope effects in methanol synthesis and the reactivity of copper formates on a Cu/SiO(2) catalyst*. Catalysis Letters, 2008. **125**(3-4): p. 201-208.
25. Yang, Y., et al., *(Non)formation of Methanol by Direct Hydrogenation of Formate on Copper Catalysts*. Journal of Physical Chemistry C, 2010. **114**(40): p. 17205-17211.
26. Muhler, M., et al., *On the Role of Adsorbed Atomic Oxygen and Co₂ in Copper-Based Methanol Synthesis Catalysts*. Catalysis Letters, 1994. **25**(1-2): p. 1-10.
27. Nakamura, J., J.M. Campbell, and C.T. Campbell, *Kinetics and Mechanism of the Water-Gas Shift Reaction Catalyzed by the Clean and Cs-Promoted Cu(110) Surface - a Comparison with Cu(111)*. Journal of the Chemical Society-Faraday Transactions, 1990. **86**(15): p. 2725-2734.
28. Szanyi, J. and D.W. Goodman, *Methanol Synthesis on a Cu(100) Catalyst*. Catalysis Letters, 1991. **10**(5-6): p. 383-390.
29. Yoshihara, J., et al., *Methanol Synthesis and Reverse Water-Gas Shift Kinetics over Clean Polycrystalline Copper*. Catalysis Letters, 1995. **31**(4): p. 313-324.
30. Yoshihara, J. and C.T. Campbell, *Methanol synthesis and reverse water-gas shift kinetics over Cu(110) model catalysts: Structural sensitivity*. Journal of Catalysis, 1996. **161**(2): p. 776-782.
31. Rasmussen, P.B., et al., *Methanol Synthesis on Cu(100) from a Binary Gas-Mixture of Co₂ and H₂*. Catalysis Letters, 1994. **26**(3-4): p. 373-381.
32. Nakamura, J., et al., *Methanol Synthesis over a Zn-Deposited Copper Model Catalyst*. Catalysis Letters, 1995. **31**(4): p. 325-331.
33. Sahibzada, M., I.S. Metcalfe, and D. Chadwick, *Methanol synthesis from CO/CO₂/H₂ over Cu/ZnO/Al₂O₃ at differential and finite conversions*. Journal of Catalysis, 1998. **174**(2): p. 111-118.
34. Askgaard, T.S., et al., *A Kinetic-Model of Methanol Synthesis*. Journal of Catalysis, 1995. **156**(2): p. 229-242.
35. Yang, Y.X., et al., *Fundamental studies of methanol synthesis from CO(2) hydrogenation on Cu(111), Cu clusters, and Cu/ZnO(000)(1 over-bar)*. Physical Chemistry Chemical Physics, 2010. **12**(33): p. 9909-9917.
36. Grabow, L.C. and M. Mavrikakis, *Mechanism of Methanol Synthesis on Cu through CO(2) and CO Hydrogenation*. ACS Catalysis, 2011. **1**(4): p. 365-384.

37. Hu, Z.M., K. Takahashi, and H. Nakatsuji, *Mechanism of the hydrogenation of CO(2) to methanol on a Cu(100) surface: dipped adcluster model study*. Surface Science, 1999. **442**(1): p. 90-106.
38. Morikawa, Y., K. Iwata, and K. Terakura, *Theoretical study of hydrogenation process of formate on clean and Zn deposited Cu(1 1 1) surfaces*. Applied Surface Science, 2001. **170**: p. 11-15.
39. Zhao, Y.F., et al., *Insight into methanol synthesis from CO(2) hydrogenation on Cu(111): Complex reaction network and the effects of H(2)O*. Journal of Catalysis, 2011. **281**(2): p. 199-211.
40. Saito, M., *R&D activities in Japan on methanol synthesis from CO2 and H2*. Catalysis Surveys from Japan, 1998. **2**: p. 175-184.
41. Lee, J.S., et al., *A Comparative-Study of Methanol Synthesis from Co2/H-2 and Co/H-2 over a Cu/ZnO/Al2O3 Catalyst*. Journal of Catalysis, 1993. **144**(2): p. 414-424.
42. Chanchlani, K.G., R.R. Hudgins, and P.L. Silveston, *Methanol Synthesis from H-2, Co, and Co2 over Cu/ZnO Catalysts*. Journal of Catalysis, 1992. **136**(1): p. 59-75.
43. Liu, G., et al., *The Rate of Methanol Production on a Copper-Zinc Oxide Catalyst - the Dependence on the Feed Composition*. Journal of Catalysis, 1984. **90**(1): p. 139-146.
44. Bart, J.C. and R.P.A. Sneed, *Catalysis Today*, 1987. **2**: p. 1.
45. Behrens, M., *Meso- and nano-structuring of industrial Cu/ZnO/(Al(2)O(3)) catalysts*. Journal of Catalysis, 2009. **267**(1): p. 24-29.
46. Behrens, M., et al., *Phase-Pure Cu,Zn,Al Hydroxalcite-like Materials as Precursors for Copper rich Cu/ZnO/Al2O3 Catalysts*. Chemistry of Materials, 2009. **22**(2): p. 386-397.
47. Greeley, J. and M. Mavrikakis, *Methanol decomposition on Cu(111): A DFT study*. Journal of Catalysis, 2002. **208**(2): p. 291-300.
48. Arena, F., et al., *Solid-state interactions, adsorption sites and functionality of Cu-ZnO/ZrO2 catalysts in the CO2 hydrogenation to CH3OH*. Applied Catalysis A., 2008. **350**: p. 16-23.
49. Stoczynski, J., et al., *Effect of metal oxide additives on the activity and stability of Cu/ZnO/ZrO2 catalysts in the synthesis of methanol from CO2 and H2*. Applied Catalysis A., 2006. **310**: p. 127-137.
50. An, X., et al., *Methanol Synthesis from CO2 Hydrogenation with a Cu/Zn/Al/Zr Fibrous Catalyst**. Chinese Journal of Chemical Engineering., 2009. **17**(1): p. 88-94.
51. Liao, F., et al., *Morphology-Dependent Interactions of ZnO with Cu Nanoparticles at the Materials Interface in Selective Hydrogenation of CO2 to CH3OH*. Angewandte Chemie International Edition, 2011. **50**: p. 2162-2165.
52. Arena, F., et al., *Synthesis, characterization and activity pattern of Cu-ZnO/ZrO2 catalysts in the hydrogenation of carbon dioxide to methanol*. Journal of Catalysis, 2007. **249**(2): p. 185-194.
53. Saito, M., et al., *Development of copper/zinc oxide-based multicomponent catalysts for methanol synthesis from carbon dioxide and hydrogen*. Applied Catalysis a-General, 1996. **138**(2): p. 311-318.
54. Kurtz, M., et al., *New synthetic routes to more active Cu/ZnO catalysts used for methanol synthesis*. Catalysis Letters, 2004. **92**(1-2): p. 49-52.
55. Behrens, M., *Methanol Steam Reforming*, in *Catalysis for alternative energy generation (eds: L. Gucci, A. Erdohelyi), M. Armbruster, Editor*. 2012, Springer.
56. Kasatkina, I., et al., *Role of lattice strain and defects in copper particles on the activity of Cu/ZnO/Al2O3 catalysts for methanol synthesis*. Angewandte Chemie-International Edition, 2007. **46**(38): p. 7324-7327.
57. Behrens, M., et al., *Methanol Synthesis over Cu/ZnO/Al2O3: The Active Site in Industrial Catalysis*. Science.
58. Chinchin, G.C., et al., *The Measurement of Copper Surface-Areas by Reactive Frontal Chromatography*. Journal of Catalysis, 1987. **103**(1): p. 79-86.
59. Hinrichsen, O., T. Genger, and M. Muhler, *Chemisorption of N2O and H-2 for the surface determination of copper catalysts*. Chemical Engineering & Technology, 2000. **23**(11): p. 956-959.
60. Behrens, M., et al., *The Potential of Microstructural Optimization in Metal/Oxide Catalysts: Higher Intrinsic Activity of Copper by Partial Embedding of Copper Nanoparticles*. Chemcatchem, 2010. **2**(7): p. 816-818.
61. Spencer, M.S., *The role of zinc oxide in Cu ZnO catalysts for methanol synthesis and the water-gas shift reaction*. Topics in Catalysis, 1999. **8**(3-4): p. 259-266.
62. Burch, R., R.J. Chappell, and S.E. Golunski, *Synergy between Copper and Zinc-Oxide during Methanol Synthesis - Transfer of Activating Species*. Journal of the Chemical Society-Faraday Transactions I, 1989. **85**: p. 3569-3578.
63. Kanai, Y., et al., *The synergy between Cu and ZnO in methanol synthesis catalysts*. Catalysis Letters, 1996. **38**(3-4): p. 157-163.
64. Klier, K., *Methanol Synthesis*. Advances in Catalysis, 1982. **31**: p. 243-313.
65. Jansen, W.P.A., et al., *Dynamic behavior of the surface structure of Cu/ZnO/SiO2 catalysis*. Journal of Catalysis, 2002. **210**(1): p. 229-236.
66. Frost, J.C., *Junction Effect Interactions in Methanol Synthesis Catalysts*. Nature, 1988. **334**(6183): p. 577-580.
67. Nakamura, J., Y. Choi, and T. Fujitani, *On the issue of the active site and the role of ZnO in Cu/ZnO methanol synthesis catalysts*. Topics in Catalysis, 2003. **22**(3-4): p. 277-285.
68. Topsøe, N.Y. and H. Topsøe, *On the nature of surface structural changes in Cu ZnO methanol synthesis catalysts*. Topics in Catalysis, 1999. **8**(3-4): p. 267-270.
69. d'Alnoncourt, R.N., et al., *The influence of strongly reducing conditions on strong metal-support interactions in Cu/ZnO catalysts used for methanol synthesis*. Physical Chemistry Chemical Physics, 2006. **8**(13): p. 1525-1538.
70. Grunwaldt, J.D., et al., *In situ investigations of structural changes in Cu/ZnO catalysts*. Journal of Catalysis, 2000. **194**(2): p. 452-460.
71. Hansen, P.L., et al., *Atom-resolved imaging of dynamic shape changes in supported copper nanocrystals*. Science, 2002. **295**(5562): p. 2053-2055.
72. Kurr, P., et al., *Microstructural characterization of Cu/ZnO/Al2O3 catalysts for methanol steam reforming - A comparative study*. Applied Catalysis a-General, 2008. **348**(2): p. 153-164.
73. Knipf, B.L., et al., *Rational design of nanostructured copper-zinc oxide catalysts for the steam reforming of methanol*. Angewandte Chemie-International Edition, 2004. **43**(1): p. 112-115.
74. Gunter, M.M., et al., *Redox behavior of copper oxide/zinc oxide catalysts in the steam reforming of methanol studied by in situ X-ray diffraction and absorption spectroscopy*. Journal of Catalysis, 2001. **203**(1): p. 133-149.
75. Sakong, S. and A. Gross, *Dissociative adsorption of hydrogen on strained Cu surfaces*. Surface Science, 2003. **525**(1-3): p. 107-118.
76. Girgsdies, F., et al., *Strained thin copper films as model catalysts in the materials gap*. Catalysis Letters, 2005. **102**(1-2): p. 91-97.

77. Hammer, B. and J.K. Nørskov, *Electronic factors determining the reactivity of metal surfaces*. Surface Science, 1995. **343**(3): p. 211-220.
78. Behrens, M., et al., *Understanding the complexity of a catalyst synthesis: Co-precipitation of mixed Cu,Zn,Al hydroxycarbonate precursors for Cu/ZnO/Al(2)O(3) catalysts investigated by titration experiments*. Applied Catalysis a-General, 2011. **392**(1-2): p. 93-102.
79. Schimpf, S., *Methanol Catalysts*, in *Synthesis of Solid Catalysts* (ed: de Jong, K. P.), M. Muhler, Editor. 2009, Wiley VCH: Weinheim. p. 329.
80. Waller, D., et al., *Copper-zinc oxide catalysts. Activity in relation to precursor structure and morphology*. Faraday Discussions of the Chemical Society, 1989. **87**: p. 107-120.
81. Whittle, D.M., et al., *Co-precipitated copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation: effect of precipitate ageing on catalyst activity*. Physical Chemistry Chemical Physics, 2002. **4**(23): p. 5915-5920.
82. Fierro, G., et al., *Study of the reducibility of copper in CuO-ZnO catalysts by temperature-programmed reduction*. Applied Catalysis a-General, 1996. **137**(2): p. 327-348.
83. Gunter, M.M., et al., *Implication of the microstructure of binary Cu/ZnO catalysts for their catalytic activity in methanol synthesis*. Catalysis Letters, 2001. **71**(1-2): p. 37-44.
84. Baltes, C., S. Vukojevic, and F. Schuth, *Correlations between synthesis, precursor, and catalyst structure and activity of a large set of CuO/ZnO/Al₂O₃ catalysts for methanol synthesis*. Journal of Catalysis, 2008. **258**(2): p. 334-344.
85. Li, J.L. and T. Inui, *Characterization of precursors of methanol synthesis catalysts, copper zinc aluminum oxides, precipitated at different pHs and temperatures*. Applied Catalysis a-General, 1996. **137**(1): p. 105-117.
86. Bems, B., et al., *Relations between synthesis and microstructural properties of copper/zinc hydroxycarbonates*. Chemistry-a European Journal, 2003. **9**(9): p. 2039-2052.
87. Shen, G.C., S.I. Fujita, and N. Takezawa, *Preparation of Precursors for the Cu/ZnO Methanol Synthesis Catalysts by Coprecipitation Methods - Effects of the Preparation Conditions Upon the Structures of the Precursors*. Journal of Catalysis, 1992. **138**(2): p. 754-758.
88. Behrens, M., et al., *Knowledge-based development of a nitrate-free synthesis route for Cu/ZnO methanol synthesis catalysts via formate precursors*. Chemical Communications, 2011. **47**(6): p. 1701-1703.
89. Christiansen, J.A., *A reaction between methyl alcohol and water and some related reactions*. Journal of the American Chemical Society, 1921. **43**: p. 1670-1672.
90. Prigent, M., *On board hydrogen generation for fuel cell powered electric cars - A review of various available techniques*. Revue De L Institut Francais Du Petrole, 1997. **52**(3): p. 349-360.
91. Navarro, R.M., M.A. Pena, and J.L.G. Fierro, *Hydrogen production reactions from carbon feedstocks: Fossils fuels and biomass*. Chemical Reviews, 2007. **107**(10): p. 3952-3991.
92. Sa, S., et al., *Catalysis for methanol steam reforming-A review*. Applied Catalysis B-Environmental, 2010. **99**(1-2): p. 43-57.
93. de Wild, P.J. and M.J.F.M. Verhaak, *Catalytic production of hydrogen from methanol*. Catalysis Today, 2000. **60**(1-2): p. 3-10.
94. Joensen, F. and J.R. Rostrup-Nielsen, *Conversion of hydrocarbons and alcohols for fuel cells*. Journal of Power Sources, 2002. **105**(2): p. 195-201.
95. Cheekatamarla, P.K. and C.M. Finnerty, *Reforming catalysts for hydrogen generation in fuel cell applications*. Journal of Power Sources, 2006. **160**(1): p. 490-499.
96. Velu, S., K. Suzuki, and T. Osaki, *Oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts; a new and efficient method for the production of CO-free hydrogen for fuel cells*. Chemical Communications, 1999(23): p. 2341-2342.
97. Lattner, J.R. and M.P. Harold, *Autothermal reforming of methanol: Experiments and modeling*. Catalysis Today, 2007. **120**(1): p. 78-89.
98. Park, E.D., D. Lee, and H.C. Lee, *Recent progress in selective CO removal in a H(2)-rich stream*. Catalysis Today, 2009. **139**(4): p. 280-290.
99. Tsai, M.C., et al., *Promotion of a copper-zinc catalyst with rare earth for the steam reforming of methanol at low temperatures*. Journal of Catalysis, 2011. **279**(2): p. 241-245.
100. Breen, J.P. and J.R.H. Ross, *Methanol reforming for fuel-cell applications: development of zirconia-containing Cu-Zn-Al catalysts*. Catalysis Today, 1999. **51**(3-4): p. 521-533.
101. Agrell, J., et al., *Production of hydrogen from methanol over Cu/ZnO catalysts promoted by ZrO₂ and Al₂O₃*. Journal of Catalysis, 2003. **219**(2): p. 389-403.
102. Matsumura, Y. and H. Ishibe, *High temperature steam reforming of methanol over Cu/ZnO/ZrO(2) catalysts*. Applied Catalysis B-Environmental, 2009. **91**(1-2): p. 524-532.
103. Jones, S.D. and H.E. Hagelin-Weaver, *Steam reforming of methanol over CeO(2)- and ZrO(2)-promoted Cu-ZnO catalysts supported on nanoparticle Al(2)O(3)*. Applied Catalysis B-Environmental, 2009. **90**(1-2): p. 195-204.
104. Velu, S. and K. Suzuki, *Selective production of hydrogen for fuel cells via oxidative steam reforming of methanol over CuZnAl oxide catalysts: effect of substitution of zirconium and cerium on the catalytic performance*. Topics in Catalysis, 2003. **22**(3-4): p. 235-244.
105. Velu, S., et al., *Oxidative steam reforming of methanol over CuZnAl(Zr)-oxide catalysts for the selective production of hydrogen for fuel cells: Catalyst characterization and performance evaluation*. Journal of Catalysis, 2000. **194**(2): p. 373-384.
106. Costantino, U., et al., *Cu-Zn-Al hydrotalcites as precursors of catalysts for the production of hydrogen from methanol*. Solid State Ionics, 2005. **176**(39-40): p. 2917-2922.
107. Turco, M., et al., *Production of hydrogen from oxidative steam reforming of methanol - I. Preparation and characterization of Cu/ZnO/Al₂O₃ catalysts from a hydrotalcite-like LDH precursor*. Journal of Catalysis, 2004. **228**(1): p. 43-55.
108. Turco, M., et al., *Production of hydrogen from oxidative steam reforming of methanol - II. Catalytic activity and reaction mechanism on Cu/ZnO/Al₂O₃ hydrotalcite-derived catalysts*. Journal of Catalysis, 2004. **228**(1): p. 56-65.
109. Ritzkopf, I., et al., *Decreased CO production in methanol steam reforming over Cu/ZrO₂ catalysts prepared by the microemulsion technique*. Applied Catalysis a-General, 2006. **302**(2): p. 215-223.
110. Purnama, H., et al., *Activity and selectivity of a nanostructured CuO/ZrO₂ catalyst in the steam reforming of methanol*. Catalysis Letters, 2004. **94**(1-2): p. 61-68.
111. Liu, Y.Y., et al., *Highly active copper/ceria catalysts for steam reforming of methanol*. Applied Catalysis a-General, 2002. **223**(1-2): p. 137-145.

112. Szyzbalski, A., et al., *In situ investigations of structure-activity relationships of a Cu/ZrO₂ catalyst for the steam reforming of methanol*. Journal of Catalysis, 2005. **233**(2): p. 297-307.
113. Mastalir, A., et al., *Steam reforming of methanol over Cu/ZrO₂/CeO₂ catalysts: a kinetic study*. Journal of Catalysis, 2005. **230**(2): p. 464-475.
114. Jiang, C.J., et al., *Kinetic Mechanism for the Reaction between Methanol and Water over a Cu-ZnO-Al₂O₃ Catalyst*. Applied Catalysis a-General, 1993. **97**(2): p. 145-158.
115. Takezawa, N. and N. Iwasa, *Steam reforming and dehydrogenation of methanol: Difference in the catalytic functions of copper and group VIII metals*. Catalysis Today, 1997. **36**(1): p. 45-56.
116. Peppley, B.A., et al., *Methanol-steam reforming on Cu/ZnO/Al₂O₃ catalysts. Part 2. A comprehensive kinetic model*. Applied Catalysis a-General, 1999. **179**(1-2): p. 31-49.
117. Rozovskii, A.Y. and G.I. Lin, *Fundamentals of methanol synthesis and decomposition*. Topics in Catalysis, 2003. **22**(3-4): p. 137-150.
118. Lee, J.K., J.B. Ko, and D.H. Kim, *Methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst: kinetics and effectiveness factor*. Applied Catalysis a-General, 2004. **278**(1): p. 25-35.
119. Peppley, B.A., et al., *Methanol-steam reforming on Cu/ZnO/Al₂O₃. Part 1: The reaction network*. Applied Catalysis a-General, 1999. **179**(1-2): p. 21-29.
120. Frank, B., et al., *Steam reforming of methanol over copper-containing catalysts: Influence of support material on microkinetics*. Journal of Catalysis, 2007. **246**(1): p. 177-192.
121. Lin, S., et al., *Pathways for methanol steam reforming involving adsorbed formaldehyde and hydroxyl intermediates on Cu(111): density functional theory studies*. Physical Chemistry Chemical Physics, 2011. **13**(20): p. 9622-9631.
122. Lin, S., D.Q. Xie, and H. Guo, *Methyl Formate Pathway in Methanol Steam Reforming on Copper: Density Functional Calculations*. ACS Catalysis, 2011. **1**(10): p. 1263-1271.
123. Spencer, M.S., *On the Activation-Energies of the Forward and Reverse Water-Gas Shift Reaction*. Catalysis Letters, 1995. **32**(1-2): p. 9-13.
124. Saito, M., et al., *Effects of ZnO contained in supported Cu-based catalysts on their activities for several reactions*. Catalysis Letters, 2002. **83**(1-2): p. 1-4.
125. Noei, H., et al., *The identification of hydroxyl groups on ZnO nanoparticles by infrared spectroscopy*. Physical Chemistry Chemical Physics, 2008. **10**(47): p. 7092-7097.
126. Goodby, B.E. and J.E. Pemberton, *Xps Characterization of a Commercial Cu/ZnO/Al₂O₃ Catalyst - Effects of Oxidation, Reduction, and the Steam Reformation of Methanol*. Applied Spectroscopy, 1988. **42**(5): p. 754-760.
127. Raimondi, F., et al., *Structural changes of model Cu/ZnO catalysts during exposure to methanol reforming conditions*. Surface Science, 2003. **532**: p. 383-389.
128. Raimondi, F., J. Wambach, and A. Wokaun, *Structural properties of Cu/ZnO/Si methanol reforming catalysts: Influence of the composition of the reactant mixture and of the Cu island size*. Physical Chemistry Chemical Physics, 2003. **5**(18): p. 4015-4024.
129. Reitz, T.L., et al., *Time-resolved XANES investigation of CuO/ZnO in the oxidative methanol reforming reaction*. Journal of Catalysis, 2001. **199**(2): p. 193-201.
130. Busca, G., et al., *Methanol steam reforming over ex-hydrotalcite Cu-Zn-Al catalysts*. Applied Catalysis a-General, 2006. **310**: p. 70-78.
131. Busca, G., et al., *Hydrogen from alcohols: IR and flow reactor studies*. Catalysis Today, 2009. **143**(1-2): p. 2-8.
132. Vargas, M.A.L., et al., *An IR study of methanol steam reforming over ex-hydrotalcite Cu-Zn-Al catalysts*. Journal of Molecular Catalysis a-Chemical, 2007. **266**(1-2): p. 188-197.
133. Zhang, X.R., et al., *A unique microwave effect on the microstructural modification of Cu/ZnO/Al₂O₃ catalysts for steam reforming of methanol*. Chemical Communications, 2005(32): p. 4104-4106.
134. Wang, L.C., et al., *Production of hydrogen by steam reforming of methanol over Cu/ZnO catalysts prepared via a practical soft reactive grinding route based on dry oxalate-precursor synthesis*. Journal of Catalysis, 2007. **246**(1): p. 193-204.
135. Loffler, D.G., S.D. McDermott, and C.N. Renn, *Activity and durability of water-gas shift catalysts used for the steam reforming of methanol*. Journal of Power Sources, 2003. **114**(1): p. 15-20.
136. Thurgood, C.P., et al., *Deactivation of Cu/ZnO/Al₂O₃ catalyst: evolution of site concentrations with time*. Topics in Catalysis, 2003. **22**(3-4): p. 253-259.
137. Agrell, J., H. Birgersson, and M. Boutonnet, *Steam reforming of methanol over a Cu/ZnO/Al₂O₃ catalyst: a kinetic analysis and strategies for suppression of CO formation*. Journal of Power Sources, 2002. **106**(1-2): p. 249-257.
138. Iwasa, N., S. Masuda, and N. Takezawa, *Steam Reforming of Methanol over Ni, Co, Pd and Pt Supported on ZnO*. Reaction Kinetics and Catalysis Letters, 1995. **55**(2): p. 349-353.
139. Penner, S., et al., *Growth and structural stability of well-ordered PdZn alloy nanoparticles*. Journal of Catalysis, 2006. **241**(1): p. 14-19.
140. Karim, A., T. Conant, and A. Datye, *The role of PdZn alloy formation and particle size on the selectivity for steam reforming of methanol*. Journal of Catalysis, 2006. **243**(2): p. 420-427.
141. Liu, S.T., et al., *Hydrogen production by oxidative methanol reforming on Pd/ZnO: Catalyst preparation and supporting materials*. Catalysis Today, 2007. **129**(3-4): p. 287-292.
142. Föttinger, K., et al., *Dynamic Structure of a Working Methanol Steam Reforming Catalyst: In Situ Quick-EXAFS on Pd/ZnO Nanoparticles*. Journal of Physical Chemistry Letters, 2011. **2**(5): p. 428-433.
143. Grunwaldt, J.D., et al., *In Situ Investigations of Structural Changes in Cu/ZnO Catalysts*. Journal of Catalysis, 2000. **194**: p. 452-460.