

Direct dimethyl ether synthesis from synthesis gas: The influence of methanol dehydration on methanol synthesis reaction

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Abstract

Direct dimethyl ether (DME) synthesis from synthesis gas is studied with regard to potential effects of methanol dehydration on methanol formation and copper-based catalyst performance. For this, the influence of the operating conditions (space velocity, temperature, pressure, time-on-stream and syngas composition) on activity, selectivity and stability of the catalyst was studied and compared for methanol synthesis and direct DME synthesis. The advantage of the direct over the two-step DME synthesis is apparent at conditions where syngas conversion to methanol is thermodynamically limited. However, under the applied operating conditions, results suggest that combining methanol synthesis and dehydration has a negative effect on the methanol formation kinetics. The origin of the observed phenomena is investigated by varying dehydration catalyst and by introducing dehydration products (DME and water) into the methanol synthesis feed. Choice of the solid acid catalyst does not seem to affect methanol formation, and DME is also found to be practically inert over the methanol synthesis catalysts. Water injection, on the other hand, led to a significant decrease in the methanol synthesis rate. Thus, formation of an additional amount of water through methanol dehydration might be an explanation for the lower methanol formation rate in the direct DME synthesis.

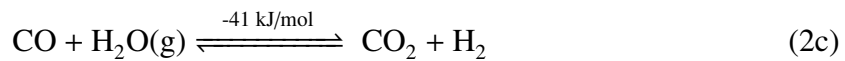
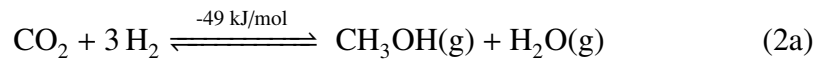
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Keywords: Methanol synthesis, Methanol dehydration, Direct DME synthesis, Dimethyl ether, Effect of water

1. Introduction

Prior to 1990, dimethyl ether (DME) had a limited commercial application, mainly as a propellant in aerosol spray cans. Over the past few decades, DME usage has grown remarkably by its introduction as an LPG substitute/blendstock for household applications [1]. The pioneering collaborative research efforts by Hal-dor Topsøe, Amoco and Navistar International Corp. in the 1990s [2, 3], drew a lot of attention to DME as a promising alternative fuel for compression ignition engines, due to the high cetane number and low particulate matter emissions, which in turn enable achieving somewhat lower NO_x emissions [4, 5]. The conventional DME production route, i.e. methanol dehydration (Equation 1), has the drawback of being highly dependent on the price of methanol. In addition, methanol production from synthesis gas (Equation 2) is limited by thermodynamic constraints, and to ensure an acceptable overall conversion a high pressure and a large recycle stream to the reactor is required.



Alternatively, DME can be synthesized directly from synthesis gas using a dual-functional catalyst system that permits both methanol synthesis (over a Cu-based catalyst) and dehydration (over an acidic catalyst) in a single reactor. While syngas conversion to methanol is significantly limited by equilibrium, further conversion of methanol to DME shifts the equilibrium toward more methanol formation and allows higher single-pass conversion. Hence, the direct DME synthesis is thermodynamically and economically more favorable than the two-step process[4, 6, 7].

In addition to this well-known synergistic effect of methanol synthesis and methanol dehydration, the interactions between the methanol synthesis and dehydration functions of the direct DME synthesis catalyst have been studied by several research groups. García-Trenco et al. reported detrimental interactions between Cu/ZnO/Al₂O₃ and HZSM-5 in the hybrid catalysts prepared by slurry or grinding methods, leading to a dramatic loss of the available Brønsted acid sites through partial exchange of zeolite protons by Cu²⁺ and Zn²⁺, and blockage of the zeolite micropores by metallic catalyst particles [8]. The same group also found a correlation between the amount of the extra framework aluminum (EFAL) species on the external surface of the zeolite and the deactivation of the Cu-based methanol synthesis catalyst during the direct DME synthesis over the hybrid catalyst prepared by grinding [9, 10]. They hypothesized that EFAL species may migrate onto the Cu-based catalyst through a water assisted surface diffusion mechanism and modify the interaction between ZnO_x and Cu, causing progressive deactivation of the active copper sites [9]. Ordonsky et al. reported that, in a hybrid catalyst prepared by kneading, the hydroxyl groups on the zeolite outer surface assist copper sintering and migration into the zeolite pores, followed by Cu ion exchange with the zeolite protons leading to deactivation of both the metallic and the acid functions of the catalyst [11]. Peng et al. attributed the catalyst deactivation during slurry-phase direct DME synthesis to a detrimental interaction between the methanol synthesis catalyst and γ -alumina and hypothesized the migration of Cu- and Zn-containing species onto the acid catalyst as the likely mechanism [12]. Such adverse interactions between the metallic and the acid functions of the hybrid catalysts require an intimate solid-state contact between the two components, and hence, are highly dependent on the preparation method of the hybrid [8, 9, 12, 13]. There have been several efforts to minimize these detrimental interactions in the hybrid catalysts with a high degree of interdispersion between their two components [11, 14].

Another aspect of the interactions between the methanol synthesis and the methanol dehydration during the direct DME synthesis is the possible effect of each step's (by)products on the other step. For one thing, partial pressure of water might be different during the direct DME synthesis compared to its pressure during independent methanol synthesis and independent methanol dehydration under comparable operating conditions. Water introduces diverse effects on both functions of the hybrid catalyst. For instance, high content of water caused by hydrogenation of a CO₂-rich syngas over the metallic component of the hybrid catalyst enhances the deactivation of the Lewis sites of the acid component through strong water adsorption [15]. On the other hand, extra amount of water formed

through methanol dehydration over the acid component of the hybrid, enhances the deactivation of the metallic component by assisting morphological changes and hydrothermal leaching of Zn and Al [11, 16]. At the same time, water is known to attenuate coke formation and deposition over both functions of the hybrid catalysts [16, 17]. Furthermore, formation of hydrocarbons in parallel with methanol synthesis [18, 19] or methanol dehydration [20] can eventually lead to carbon compounds deposition and deactivation of both functions of the hybrid catalyst.

Combining methanol synthesis and dehydration in a single step may also pose some effect on the kinetics of the reactions. Such interactions are less discussed in the literature, although limited learnings exist from the literature concerning each of the two steps. Most experimental work regarding the direct DME synthesis has been performed under conditions, at which the independent methanol formation in absence of dehydration would be thermodynamically limited and/or the methanol dehydration influences the overall reaction rate. Hence, the assessment of any potential effects from methanol dehydration on methanol synthesis kinetics is not straightforward. The objective of this work is to provide a better understanding of the effects that combining methanol synthesis and methanol dehydration in a single reactor can have on the performance of the methanol synthesis catalyst. In order to do this, the influence of operating conditions (space velocity, temperature, pressure, time on stream and syngas composition) on activity, selectivity and stability of the methanol synthesis catalyst was compared for the direct DME synthesis and the methanol synthesis alone under comparable conditions, at which, methanol formation is controlling the overall kinetics and the interference of thermodynamics on the syngas conversion is minimized.

2. Materials and methods

Methanol synthesis was conducted over either a commercial Cu/ZnO-based or a homemade Cu/ZnO/Al₂O₃ catalyst, referred to as CZA for simplicity. The homemade CZA catalyst was prepared by co-precipitation of a solution of the metal nitrate salts, i.e. Cu(NO₃)₂, Zn(NO₃)₂ and Al(NO₃)₃, with sodium carbonate in a sodium acetate solution at 50°C and pH 7.0. Precipitates were then filtered, washed thoroughly with deionized water, dried overnight and calcined at 400°C for 2 h [21]. The resulting homemade catalyst has Cu/Zn/Al molar ratio of 22/57/21 as determined by ICP. Prior to syngas introduction, the catalyst was reduced in situ in a diluted H₂ flow (3% H₂ in N₂) over a 9 h-long stepwise temperature increase, followed by an 8 h treatment at 250°C. Three different solid

acid catalysts were used for methanol dehydration to DME; γ -alumina from Sasol Germany (PURALOX 5/200), ZSM-5 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 80 from Zeolyst International (CBV 8014) and NaHZSM-5 prepared from the commercial zeolite. The zeolite was received in ammonium form and calcined in air at 600°C to produce HZSM-5. An aliquot of the HZSM-5 was treated with a suitable amount of NaNO_3 solution at 75°C and calcined in air at 600°C to produce NaHZSM-5. Elemental analysis with ICP-MS confirmed a successful sodium exchange ($\text{Na}/\text{Al}=12$ mol.%) and NH_3 -TPD showed 10% reduction in the zeolite acidity upon ion-exchange. Hybrid catalysts for the direct DME synthesis from syngas were made by physically mixing the pre-pelletized metallic and acidic catalysts with mass ratio of 8:1 (ZSM-5 as acid function) or 1:4 (γ -alumina as acid function). The catalysts were packed into the reactor as powders in the particle size range 80-125 μm .

Experiments were conducted in a stainless steel micro packed bed reactor-heat exchanger, fabricated at the Institute of Micro Process Engineering (IMVT), Karlsruhe Institute of Technology. The reactor consists of a 6 cm long reaction slit with rectangular cross section of 8.8×1.5 mm^2 , sandwiched between cross flow channels for circulation of a heat transfer oil. Such reactors have been studied earlier under similar operating conditions for the methanol [21–23] and the direct DME [24–26] syntheses, and established as practically isothermal, isobaric, free from mass transfer limitations, and with a narrow residence time distribution.

Premixed synthesis gas with H_2 to CO molar ratio of either 1 (Syngas-1) or 2 (Syngas-2) was used as feed. Composition of both gas mixtures is given in Table 1. Feed flow rates and reactor pressure were controlled using digital mass flow controllers and a digital back pressure controller (Bronkhorst). Introduction of water to the reaction environment was done by evaporating the pressurized deionized water into the feed stream using a Controlled Evaporator Mixer (Bronkhorst). The reaction temperature was monitored by measuring the reactor skin temperature using thermocouples inserted into the holes in the reactor housing which provide a proximity to the reaction slit on top of its centerline [24]. The tubing was heated to avoid condensation of water, methanol and other possible liquid products. Products were analyzed online using an Agilent 7890 gas chromatograph equipped with a thermal conductivity detector and a flame ionization detector. Assessment of the carbon balance across the system gives an error that is typically below 2%, and never higher than 5%. The experiments were conducted at temperatures, pressures and space velocities of $210\text{--}270^\circ\text{C}$, 10-50 bar and $150\text{--}800$ $\text{Ncm}^3/\text{min}/\text{g}$ catalyst, respectively.

Syngas conversion, X_c , product yield, Y_P , and overall methanol formation rate,

Table 1: Composition (mol%) of the applied premixed synthesis gases.

	H ₂	CO	CO ₂	CH ₄	N ₂
Syngas-1	42	42	5	6	5
Syngas-2	56	28	5	6	5

r_{MeOH} , are calculated on a carbon basis as follows:

$$X_c = \left(1 - \frac{(n_{CO} + n_{CO_2})_p}{(n_{CO} + n_{CO_2})_f} \right) \times 100, \quad (3)$$

$$Y_P = \frac{n_{MeOH} + 2n_{DME}}{(n_{CO} + n_{CO_2})_f} \times 100, \quad (4)$$

$$r_{MeOH} = \frac{n_{MeOH} + 2n_{DME}}{w_{CZA \text{ cat.}}}, \quad (5)$$

where n_i is the molar flow rate of component i in either the feed (f) or the product (p) stream and $w_{CZA \text{ cat.}}$ is the mass of the methanol synthesis catalyst. Equilibrium data was estimated from the Gibbs free energy of the compounds using the Aspen HYSYS V8.0 software.

3. Results and discussion

Figure 1 compares methanol yield over the commercial CZA catalyst with the overall methanol and DME yield (carbon basis) in the direct DME synthesis under identical operating conditions. The direct DME synthesis was performed using a mixture of the pre-pelletized commercial CZA catalyst with an excess amount of HZSM-5 (mass ratio 8:1). Therefore, the overall direct DME synthesis was controlled by methanol formation, i.e. practically all the methanol formed was converted further to DME. Accordingly, the flow rate was adjusted to obtain an identical space velocity based on the CZA catalyst mass for both experiments.

Syngas conversion to methanol is thermodynamically limited. As expected from an exothermic reaction that proceeds with reduction in number of moles, equilibrium syngas conversion decreases by temperature and increases by pressure (Le Chatelier's principle). The equilibrium product yields in the methanol and the direct DME syntheses are indicated in Figure 1. The main advantage of the direct DME synthesis is evident as lifted thermodynamic constraints and a

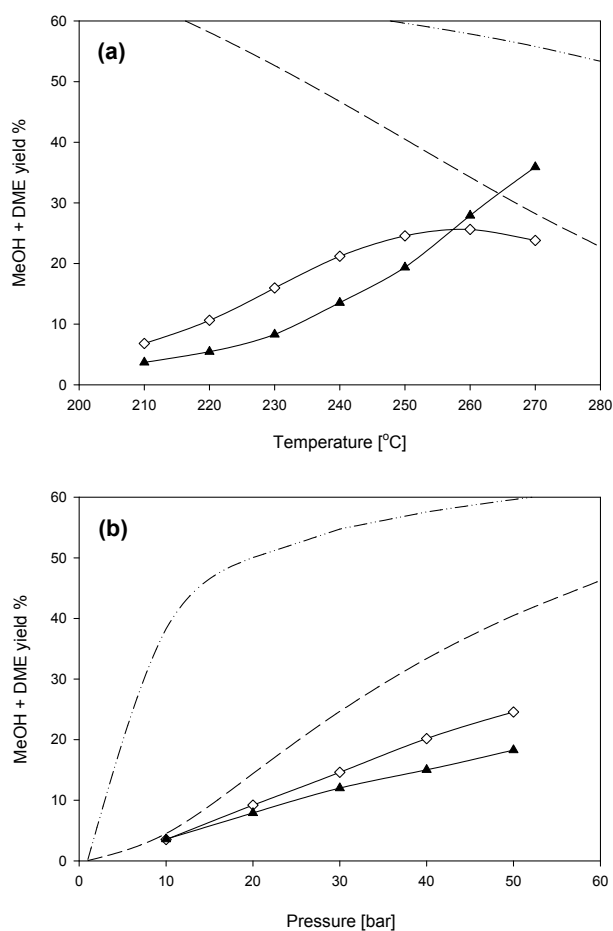


Figure 1: Product yields against (a), reaction temperature at P=50 bar, and (b), pressure at T=250°C, for methanol synthesis (◇) and direct DME synthesis (▲) from Syngas-2 under an identical space velocity based on CZA catalyst mass. The equilibrium product yields of the methanol and the direct DME syntheses are denoted by dash and dash-dot lines, respectively.

higher possible yield in the direct DME synthesis. Under the applied conditions and at higher temperatures, methanol yield is limited thermodynamically in the methanol synthesis experiment, while under the same conditions, conversion and yield continue their increase with temperature in the direct DME synthesis. Apart from this synergistic effect, however, the results suggest that combining methanol synthesis and dehydration in a single reactor impairs the methanol formation kinetics. This can be observed as a lower product yield (lower methanol formation rate) in the direct DME experiment at lower temperatures and higher pressures

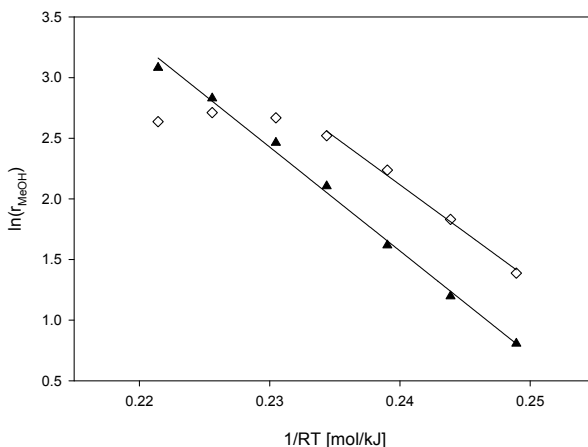


Figure 2: Arrhenius plots for the methanol synthesis (\diamond) and the direct DME synthesis (\blacktriangle) from Syngas-2 at P=50 bar.

where the influence of the equilibrium on the methanol synthesis is smaller. Such a negative effect can also be seen from the experimental results reported by at least one other research group [18], although it is not discussed specifically by them.

Arrhenius plots for both experiments are presented in Figure 2. The apparent activation energy for methanol formation seem to be similar in both the methanol and the direct DME syntheses experiments in the kinetic regime. As methanol synthesis is under the influence of equilibrium at higher temperatures, linear regression was performed for the data at lower temperatures only. From the plot, the apparent activation energy is estimated to be around 85 kJ/mol, consistent with values reported in literature. Yoshihara et al. obtained an activation energy of 77 ± 10 kJ/mol over clean polycrystalline copper [27]. Bøgild-Hansen and Højlund-Nielsen also reported activation energies in the range of 75-100 kJ/mol for methanol formation in their comprehensive literature review including several models and experimental results [28].

3.1. Effect of the dehydration catalyst

ZSM-5 possesses strong Brønsted acidity capable of catalyzing methanol and DME dehydration to hydrocarbons. However, in comparison with methanol dehydration to DME, such reactions are known to take place at relatively higher temperatures and substantially higher contact times [29]. Having this in mind, similar sets of experiments were repeated with different catalyst systems to investigate any possible effect from by-products or catalyst interactions. The results are

plotted in Figure 3 as a comparison between product yield for methanol synthesis and direct DME synthesis. Analogous to the previous experiment, the direct DME synthesis experiments are controlled by methanol formation. The graph includes results from both commercial and homemade CZA catalysts, between which the former is significantly more active. Differences in acidity are represented by applying HZSM-5 with strong Brønsted and weaker Lewis acid sites, NaHZSM-5 with similar type of acid sites but lower acidity, and γ -Al₂O₃ with moderate to weak Lewis acidity. In spite of the differences in acidity and the possible by-product formation over the different dehydration catalysts, the same negative effect of dehydration on methanol formation kinetics is evident in all the experiments. Moreover, the activation energy for methanol formation obtained from either methanol or direct DME experiments is the same within the experimental error, irrespective of the choice of catalyst. The average of the calculated activation energies are 85 kJ/mol (standard deviation 4 kJ/mol) and 88 kJ/mol (standard deviation 2 kJ/mol), obtained respectively from the methanol synthesis experiments and the direct DME synthesis experiments.

The conclusion drawn above regarding the adverse effect of dehydration on methanol synthesis kinetics regardless of the choice of the catalysts, is supported by the data obtained by varying pressure or space velocity under otherwise constant operating conditions (not presented here). In short, at higher space velocities (lower conversions) and at higher pressures, where the effect of equilibrium on methanol synthesis is smaller, the methanol formation rate during methanol synthesis surpasses the methanol formation rate during direct DME synthesis under identical operating conditions. This is also valid for both synthesis gas mixtures used, having varying H₂ to CO ratio and identical CO₂ mole fraction of 5 mol% (see Figure 3c).

3.2. Catalyst deactivation

Catalyst deactivation was monitored, not only to make sure that the results are credible, but also to investigate any possible effect of the methanol dehydration on the CZA catalyst stability. Deactivation curves for the CZA catalyst and its hybrids with the three solid acid catalysts are presented in Figure 4. Activity loss was monitored as a decline in the product yield at 250°C and 50 bar, and normalized with respect to the yield at the same conditions at time on stream (TOS) of 10 h. The deactivation during methanol synthesis experiment was monitored at a higher space velocity (initial methanol yield 10%) to exclude the effect of equilibrium. Considering that the overall synthesis kinetics is controlled by the methanol formation in all the experiments, loss of activity during the direct DME

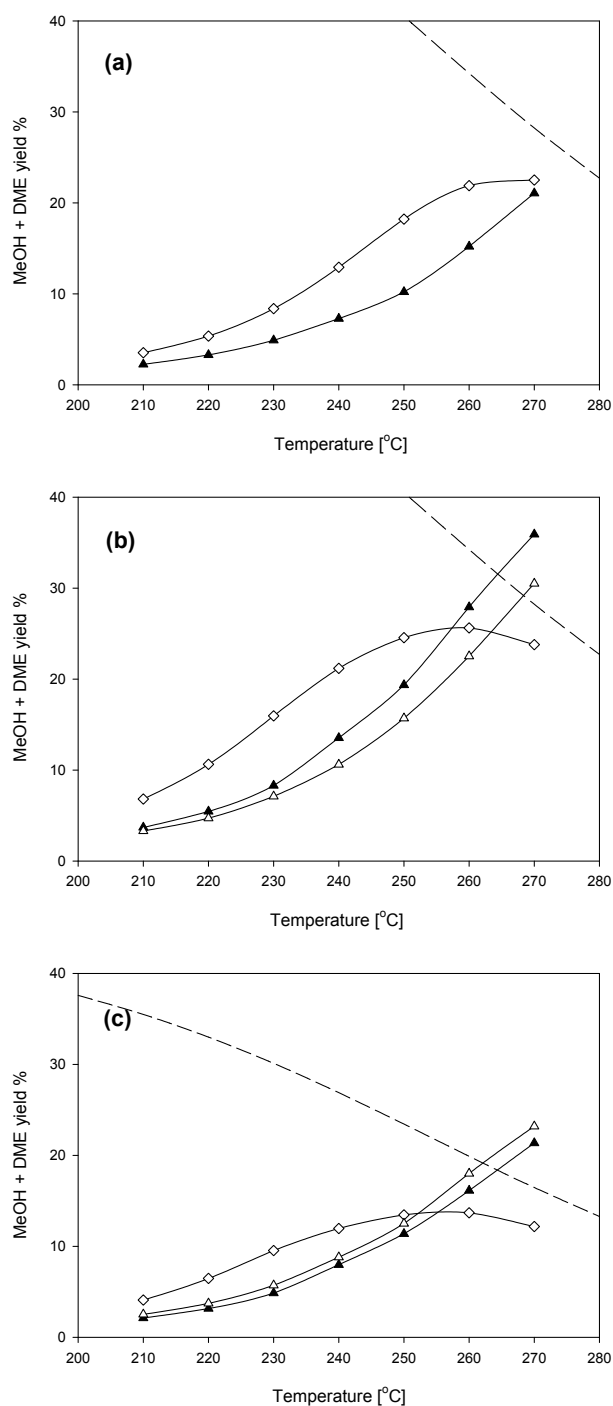


Figure 3: Product yields against reaction temperature for methanol synthesis and direct DME synthesis under an identical space velocity (based on CZA catalyst mass) and P=50 bar; (a) Syngas-2 over the homemade CZA catalyst (◇) and its hybrid with HZSM-5 (▲), (b) Syngas-2 over the commercial CZA catalyst (◇) and its hybrid with HZSM-5 (▲) or γ -Al₂O₃ (△), (c) Syngas-1 over the commercial CZA catalyst (◇) and its hybrid with HZSM-5 (▲) or NaHZSM-5 (△). The dashed lines represent the methanol synthesis equilibrium.

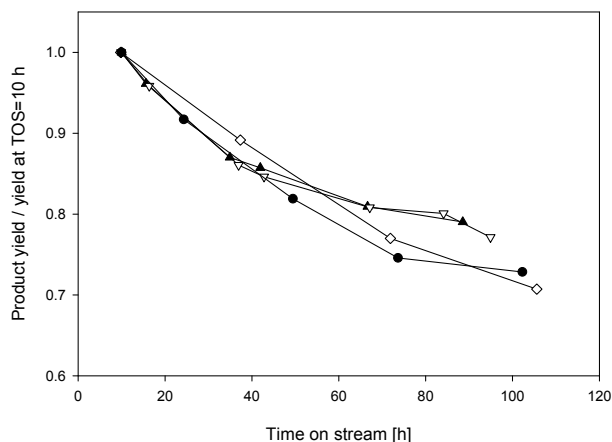


Figure 4: Apparent activity loss of the CZA catalyst during methanol synthesis (\diamond) and direct DME synthesis in a hybrid with HZSM-5 (\blacktriangle), γ -Al₂O₃ (∇) and NaHZSM-5 (\bullet). Product yield at T=250°C and P=50 bar is normalized against the yield at TOS=10 h.

syntheses is correlated to the deactivation of the CZA catalyst. Excess of the acid component of the hybrid catalysts was sufficient so that a probable deactivation of the acid catalysts during the direct DME experiments (increase over TOS of the product stream's methanol content) was not observable. Between the data points presented in Figure 4, catalysts in all the experiments went through a series of changes in space velocity, temperature (210-270°C) and pressure (10-50 bar). However, the applied changes were comparable with regards to the extent, the sequence, and their corresponding TOS, and hence, is not expected to affect the relative differences of the presented curves.

Bøgild-Hansen and Højlund-Nielsen reviewed the deactivation causes of Cu/ZnO-based methanol synthesis catalysts and identified copper sintering and poisons, most commonly S, Cl and As-containing compounds and Fe and Ni carbonyls, as the main causes of activity loss [28]. There are also claims that coke formation in parallel with methanol synthesis can deactivate the metallic function of the hybrid catalysts [18, 19, 30]. However, such deactivation was associated with a considerable Fischer-Tropsch activity and paraffin formation, which is not common for typical Cu-based methanol synthesis catalysts. In addition, as mentioned earlier, detrimental interactions between metallic and acid components of the hybrid catalyst [9–12] as well as methanol dehydration (by)products (water [16] and hydrocarbons [31]) are reported to be influential on methanol synthesis catalyst deactivation during the direct DME synthesis.

The catalysts deactivated in all the experiments and apparent activity loss over the course of 100 h was between 20 and 30%. Moreover, the deactivation of the methanol synthesis catalysts does not follow any particular trend and no evident effect from the dehydration catalysts or the dehydration (by)products on stability of the CZA catalysts can be confirmed from our results. This is valid for both metallic catalysts and their physical mixtures with all the three solid acid catalysts under the applied operating conditions. This is in agreement with the experimental results showing that interactions between the two components of the catalyst requires a proximity [12] which is not met in the hybrids prepared by physically mixing the pre-pelletized components [8, 9, 13]. In the absence of poisons from the applied ultra-pure premixed synthesis gases, as well as the absence of iron and nickel carbonyl formation [28] within the tubings and the reactor (as confirmed by XPS analysis of the spent catalysts, not shown), and the lack of any meaningful differences among the stabilities of the CZA, alone and in the hybrid catalysts, sintering of copper crystallites is probably the main cause of the catalyst deactivation.

With regards to influence of the deactivation on validity of the comparison made between the data presented earlier in this work, it is worth mentioning that catalysts in all the experiments went through a similar sequence of changes in operating conditions and deactivation was monitored closely. To minimize the effects of the activity loss on the result, the data points forming each curve were obtained in a relatively short time span (24 h), and the curves that have been compared to each other were obtained at virtually similar TOS. Hence, despite the slight differences in catalyst deactivation during different experiments, the conclusion drawn earlier regarding the adverse effect of dehydration on methanol synthesis kinetics can be held credible. By ruling out the role of dehydration catalyst or by-products on this adverse effect, it is logical to explore the influence of methanol dehydration products, i.e. DME and water, on the CZA catalyst performance.

3.3. *Effect of DME*

DME forms from methanol in the presence of an acid catalyst. To examine the potential effect of DME on the CZA catalyst, a premixed syngas containing 2.5 mol.% DME, with otherwise identical molar ratios between the reactants as in Syngas-2, was used as the methanol synthesis feed. The flow rate of the reactants was kept identical to the one applied in the methanol synthesis experiments without DME application, and the total pressure was increased accordingly to maintain the same partial pressures of the reactants. The DME content of the new

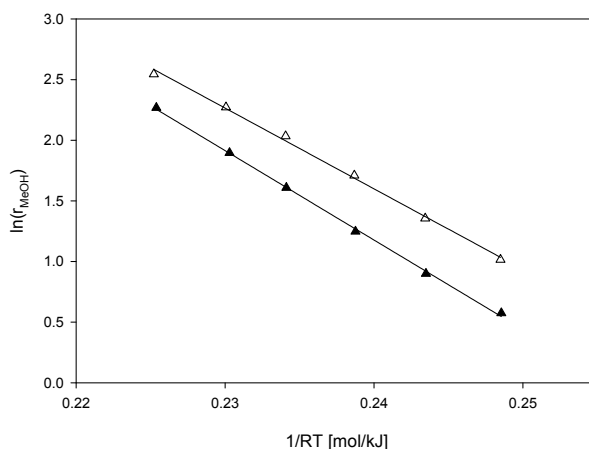


Figure 5: Arrhenius plots for methanol syntheses with (Δ) and without (\blacktriangle) presence of DME in the feed, at $P_{\text{total}}=41$ and 40 bar, respectively.

feed was sufficient to create a DME partial pressure in the same range as if all the formed methanol converts to DME. Figure 5 compares the Arrhenius plots of the methanol synthesis from the feed with and without DME. The experiments were performed at a relatively high space velocity where the effect of the methanol synthesis equilibrium is negligible (initial methanol yield at 250°C and 50 bar was 12%). According to the results, addition of DME to the methanol synthesis feed does not affect the methanol formation kinetics. The differences in the methanol formation rate are due to the catalyst deactivation, but regardless of the presence of DME in the feed, the apparent activation energy is estimated to be the same within the experimental error.

3.4. Effect of Water

Additional water formation from methanol dehydration to DME (Equation 1) can potentially affect the methanol synthesis kinetics. Water can not be detected by the applied GC and its mole fraction in the product stream of both the methanol and the DME syntheses is too small to be determined from the oxygen mole balance within the experimental error. However, a considerable CO_2 formation in the direct DME synthesis, as opposed to the net CO_2 consumption in the methanol synthesis, is an indication of a higher water partial pressure over the bifunctional catalyst. Analogous to the previous experiment with DME, the potential effect of water on methanol synthesis kinetics was studied by injecting water into the methanol synthesis feed and comparing the result with the one from the dry standard syngas (Syngas-2). Pressure was increased upon introduction of water to

compensate for dilution of the syngas and to keep the partial pressures of the reactants unchanged. Unlike DME, water is involved in the methanol synthesis through the WGS (Equation 2c), and the CO₂ hydrogenation (Equation 2a) reactions. Figure 6 presents the observed CO₂ conversion (formation) and selectivity at different reaction temperatures from Syngas-2, with and without addition of water. Water was added at two different mole fractions of 6.6% and 9.4% in the feed, giving partial pressures of 3.5 and 5.2 bar, respectively. In absence of water from the feed, CO₂ is consumed overall during the synthesis, i.e. CO₂ conversion to methanol is higher or equal to its formation through the WGS reaction. The CO₂ partial pressure in the product stream closely follows the equilibrium prediction throughout the whole temperature range.

With water in the feed, CO₂ formation via the WGS reaction by far exceeds the CO₂ conversion via hydrogenation, as represented by the negative overall conversion values in Figure 6. Water injection boosts CO conversion, although the main part of the CO ends up as CO₂ in the effluent stream. Under such conditions, the methanol formation is virtually zero below 240°C and at higher temperatures the formation rate is still considerably lower in comparison to the synthesis rate from the dry syngas. At higher temperatures, the selectivity towards methanol starts to increase while the CO₂ formation approaches its equilibrium. The Arrhenius plot for the methanol synthesis before and after the water injection is presented in Figure 7. The activation energy for methanol formation increases notably from ~85 kJ/mol to ~140 kJ/mol upon injection of water. Apart from the differences caused by the catalyst deactivation, no significant changes were observed in the methanol formation rate or the activation energy by increasing the partial pressure of water from 3.5 to 5.2 bar.

The effect of water on the methanol synthesis has been studied by several researchers. Vedage et al. observed that an optimum amount of water in a H₂:CO mixture increases the methanol formation rate dramatically, while a water content outside a narrow window around this optimum, leads to a considerably lower rate [32]. They also showed that while the methanol formation rate is very sensitive to the water content and temperature, the WGS activity remains high irrespective of the conditions, thus giving a low water content in the exit gas even for high water partial pressures in the feed. Klier et al. demonstrated a similar influence on the methanol formation by gradual substitution of CO with CO₂ in a mixture of H₂ and CO [33]. Figure 8, presenting a selection of the results from these two studies, clearly shows the analogy between the effects of water and CO₂ on the methanol synthesis. This effect from CO₂ on methanol synthesis kinetics is backed up by other experimental investigations for both gas phase [34–36] and

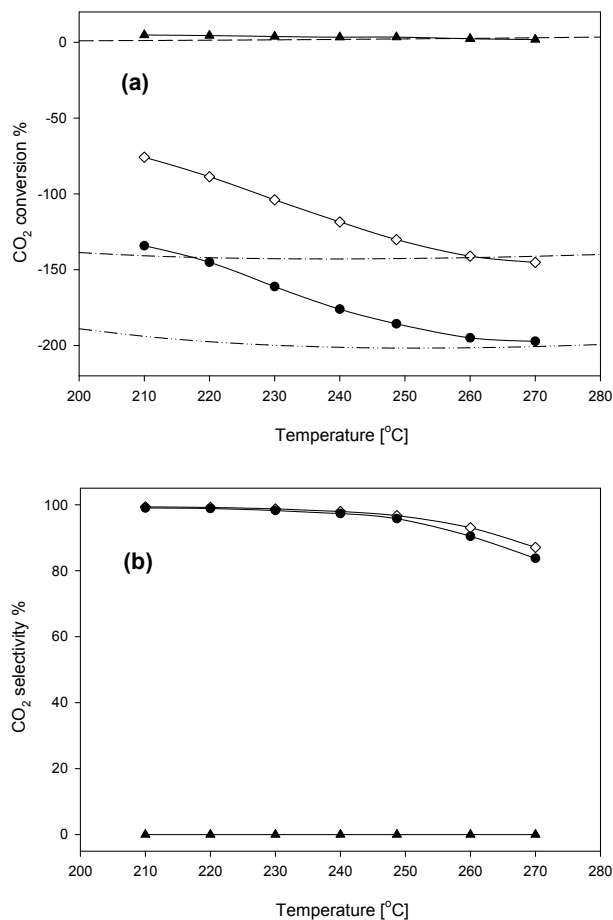


Figure 6: (a), conversion (formation) of CO₂, and (b), C selectivity toward CO₂, against reaction temperature in methanol synthesis from Syngas-2; (▲) dry feed at P=50 bar and SV=650 Ncm³/min/g, (◇) 6.6 mol% water in Syngas-2 at P=53.6 bar and SV=800 Ncm³/min/g, and (●) 9.4 mol% water in Syngas-2 at P=55.2 bar and SV=650 Ncm³/min/g. The respective equilibrium CO₂ conversion is depicted by the dash lines.

liquid phase [37] methanol synthesis, while some other studies suggest such effect might be dependent on the operating conditions. The work of Chanchlani et al. demonstrated a positive effect of CO₂ addition, however existence of an optimum is only confirmed at higher temperatures (T>250°C, P=24 bar) [38]. Similarly, Liu et al. observed only a continuous increase in the methanol formation rate by increasing the CO₂ partial pressure (P=17 atm, T<225°C), but observed a strong inhibitory effect from water [39]. They reported that, for instance, presence of as

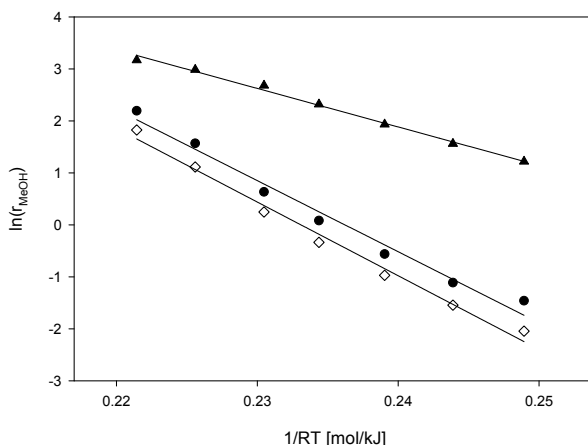


Figure 7: Arrhenius plots for methanol syntheses with and without presence of water in the feed. (▲) dry Syngas-2 at P=50 bar, (◇) 6.6 mol% water in Syngas-2 at P=53.6 bar, and (●) 9.4 mol% water in Syngas-2 at P=55.2 bar.

low as 0.82 mol.% water in a syngas comparable to our Syngas-2, led to a 78% reduction in the methanol synthesis rate.

All in all, literature seems to be consistent regarding the fact that a small amount of either water or CO₂ in a H₂:CO mixture considerably enhances the methanol formation rate. However, the effect of high CO₂ partial pressures is in question and the inconsistency regarding that may come from the differences in the applied operating conditions or the applied Cu/ZnO-based catalysts. On the contrary, there is a fair agreement on the inhibitory effect of water at higher mole fractions (>5 mol.%) or in the presence of a considerable amount of CO₂ in the syngas. Klier et al. attributed the promoting effect of CO₂ in low concentrations, to its ability to partially oxidize Cu⁰ to a more active Cu⁺, and the inhibitory effect of CO₂ in higher concentrations, to its strong adsorption [33]. However, Bøggild-Hansen and Højlund-Nielsen believe a more correct explanation of the CO₂ effects is, at low concentrations, the availability of the necessary CO₂ reactant (they conclusively identified hydrogenation of CO₂ as the main synthesis route, and not CO), and at high concentrations, site blockage through water formation [28].

Under the standard methanol synthesis conditions, water forms through CO₂ hydrogenation and is consumed via the WGS reaction. Formation of an additional amount of water via methanol dehydration in the direct DME synthesis may lead to a higher partial pressure of water and eventually a reduction in the methanol synthesis rate, especially considering that the synthesis gases used in this study

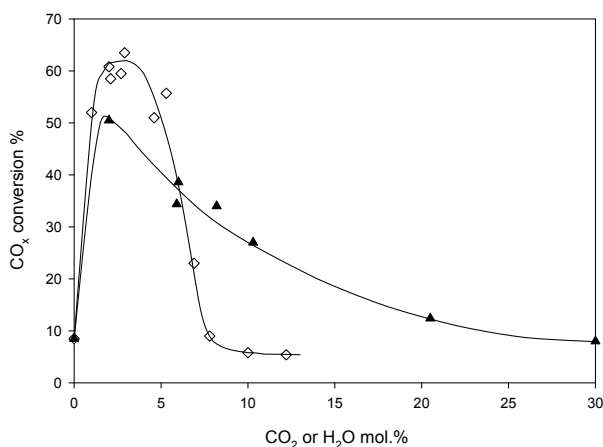


Figure 8: Effect of water addition (\diamond) and CO substitution with CO_2 (\blacktriangle) on methanol synthesis from a syngas with H_2 to C ratio of 70/30 at 235°C and 75 atm, adopted from Ref 32 and 33 respectively.

already contained a considerable amount of CO_2 . Such an adverse effect from the methanol dehydration on the methanol synthesis kinetics may vary in the extent or even be the opposite by using a synthesis gas with a different CO_2 content or at operating conditions outside the range of what have been studied here.

3.5. Mass Transfer limitations

Due to a laminar flow in the microchannel reactor (Reynolds number ~ 1), diffusion plays an important role in transferring the reactants to the catalyst surface and removing the products from it. The methanol and DME syntheses from the standard synthesis gases applied, are considered free from mass transfer limitations based on our previous studies [21, 24]. However, changes in gas composition and pressure, alter the diffusivities of the components in a gas mixture. Thus, a dramatic decline in the reactants' diffusivities upon dilution of the feed with DME or water and the corresponding pressure increase can reduce the mass transfer rate to the extent that affects the reaction rate. To evaluate the significance of the changes, the diffusivities of CO and CO_2 in the reactor feed are calculated and compared for the different feed compositions. CO_2 has the lowest diffusivity but its mole fraction is small in the feed, while CO is more abundant and is expected to be the main source of carbon in the products, either via direct hydrogenation or via CO_2 .

The multi-component molecular diffusion coefficient for component i , with mole fraction of x_i in a mixture of n gases can be calculated using Equation (6)

proposed by Wilke [40]. The equation is derived with the assumption that other components in the mixture are stagnant. Although this condition is not met, for the sake of simplicity we choose to use the equation for evaluating the changes in diffusivity.

$$D_{im} = (1 - x_i) \left(\sum_{\substack{j=1 \\ j \neq i}}^n \frac{x_j}{D_{ij}} \right)^{-1} \quad (6)$$

D_{ij} is the binary diffusivity coefficient (cm²/s) that can be calculated from the Fuller-Schettler-Giddings [41] equation, given as follows:

$$D_{ij} = \frac{1.00 \times 10^{-3} T^{1.75}}{P \left[(\sum_i v)^{\frac{1}{3}} + (\sum_j v)^{\frac{1}{3}} \right]^2} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}} \quad (7)$$

There, T is temperature (K), M_i and M_j are molecular masses of component i and j , P is the total pressure (atm) and, $\sum_i v$ and $\sum_j v$ are the summation of the special diffusion volume coefficients for component i and j , the value of which is given by Fuller et al. for simple molecules or can be calculated using the method presented by them [42]. The estimated values for CO diffusivity in the feed, before and after injection of DME or water, are presented in Figure 9. The diffusivity of CO is reduced 13% by addition of DME, and 12 and 18% by injection of water.

Manipulation of the reactants' diffusivities by syngas dilution with He or Ar was performed earlier in our group [21, 24] to demonstrate that both methanol and direct DME syntheses in similar microchannel reactors and under an identical range of operating conditions are free from mass transfer limitations. A summary of the results is also presented in Figure 9. As can be seen, the CO diffusivity in Syngas-2, even after addition of water or DME, is in the same range as the ones that have already been established (in Ref. 24 and 21) as sufficiently high to keep the synthesis rate intact from the external mass transfer limitations. Considering that the CO conversion level in the present study is lower compared to the ones in Ref. 24 and 21, similar or somehow larger diffusivities ensure that the diffusion rates surpass reaction kinetics. The same is valid for the CO₂ diffusivity. All in all, the synthesis rate can be claimed to be independent of the external mass transfer, and in the methanol synthesis experiments, deviations of the Arrhenius plots from a straight line at higher temperatures is likely the effect of the reverse reactions on the synthesis kinetics.

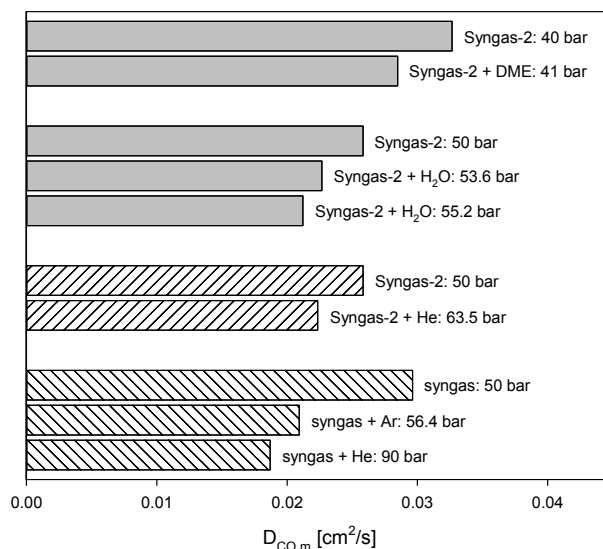


Figure 9: Estimated CO diffusivities in undiluted and diluted syngas at 250°C. Bars patterned with upward and downward diagonal lines correspond to the values calculated based on the data from Ref. 24 and 21, respectively. In the former, the gas composition is identical to Syngas-2, and in the later, syngas is a mixture of $H_2:CO:CO_2:N_2 = 65:25:5:5$ mol.%.

4. Conclusions

A series of methanol synthesis and direct DME synthesis (controlled by methanol formation) were performed under identical operating conditions, and the results as a function of temperature, space velocity, pressure and time on stream were compared. At high syngas conversions where methanol synthesis is affected by the equilibrium, the methanol formation rate in the direct DME synthesis surpasses the rate in the methanol synthesis. Apart from this well-known effect of circumventing thermodynamic limitations, the result suggests that combining methanol synthesis and dehydration impairs the methanol formation kinetics under the operating conditions applied. At lower conversion, where the reverse reactions are insignificant, the methanol formation rate is strikingly lower in the direct DME synthesis. To better understand the origin of this effect, three different solid acid catalysts with different acidities were used. No effect from the dehydration catalysts (or their potential byproducts) on the CZA catalyst performance can be confirmed, and the negative effect of the dehydration on the methanol synthesis kinetics is common for all the three dehydration catalysts. The potential effect of the methanol dehydration products (DME and water) was also studied by ad-

dition to the methanol synthesis feed. DME is found to be practically inert over the CZA catalyst. Addition of water, on the other hand, dramatically reduces the methanol formation rate, while boosting CO conversion to CO₂ via the WGS reaction. Presence of water in the feed also causes an increase in the apparent activation energy for methanol synthesis. Literature suggests that addition of CO₂ or water into a H₂:CO mixture enhances the methanol formation rate up to an optimum mole fraction, above which the rate decreases dramatically. Formation of water via methanol dehydration in the direct DME synthesis is expected to create the same effect on the methanol synthesis as the addition of water or CO₂ to the feed. The synthesis gases used in this study already contained a considerable amount of CO₂, which might be close to or above the optimum mole fraction. Hence, the additional water formation in the direct DME synthesis, is sufficient to lead to a strong reduction in the methanol synthesis rate.

Acknowledgment

The financial support from the Research Council of Norway (contract No. 208351/E30) is gratefully acknowledged.

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