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This is a Final draft version of a publication published by Elsevier in Journal of CO2 Utilization

DOI: 10.1016/j.jcou.2018.01.002

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Please cite the publication as follows:

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Alcohol promoted methanol synthesis enhanced by adsorption of water and dual catalysts

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Abstract

Alcohol-promoted methanol synthesis uses heterogeneous methanol synthesis catalysts in alcoholic solvents where the alcohols act as a co-catalyst. In the presence of alcohol, the reaction proceeds through alcohol formate ester as an intermediate, allowing methanol synthesis at lower temperatures than conventional gas-phase synthesis. In the present work, alcohol-promoted CO₂ hydrogenation to methanol was studied experimentally using a Cu/ZnO catalyst with 1-butanol and 2-butanol as solvents. As water is known to inhibit methanol synthesis on Cu/ZnO catalysts, the alcohol-promoted process was further developed by in-situ adsorption of water using a 3Å molecular sieve. The methanol productivity significantly improved as a result of the lowered concentration of water.

The concentration of water was thus identified as a key factor affecting the overall methanol productivity. As the alcohol-promoted methanol synthesis process is characterized by two separate reaction steps, the use of separate catalysts optimized for each step offers an interesting approach for the development of this process. Such a dual-catalysis concept was tested using a copper chromite catalyst together with Cu/ZnO. Promising results were obtained, as methanol productivity increased with the addition of copper chromite. Catalyst characterization was carried out using XRD and SEM-EDS and potential effects of observed changes in catalyst structure during reaction are discussed.

Keywords

CO₂ hydrogenation, methanol synthesis, Cu/ZnO, liquid-phase, alcohol promoted, dual catalysis, copper chromite, molecular sieve

Conflicts of interest: none
1. Introduction

Development of efficient and flexible energy storage methods is critical for a global shift from a fossil fuels based economy to a renewable energy based economy [1]. The use of surplus peak electricity generated from fluctuating renewable energy sources, such as wind and solar energy, for the production of chemical compounds would enable energy storage in a highly transportable form at high energy density. Generation of hydrogen by electrolysis of water is the common starting point in chemical energy storage strategies [2]. However, due to the difficulties and hazards associated with large-scale storage and transportation of gaseous hydrogen, further utilization of hydrogen for production of carbon-containing liquid fuels and chemical compounds might be preferable.

Methanol is an example of such a potential liquid-phase chemical energy carrier [3]. Methanol is an important and versatile industrial chemical that can also be used as a fuel in power generation and in internal combustion engines and fuel cells [4]. Additionally, methanol is a versatile raw material for synthesis of a variety of chemical products. For instance, methanol can be transformed into gasoline in the methanol-to-gasoline process (MTG) [5] or into olefins in the methanol-to-olefins process (MTO) [6].

Current production of methanol is based on catalytic conversion of synthesis gas generated from fossil sources, commonly natural gas. The syngas is mainly composed of mixtures of hydrogen, carbon monoxide and carbon dioxide. In conventional methanol synthesis, copper and zinc oxide (Cu/ZnO) catalysts are generally employed at reaction temperatures of 200-300 °C and pressures of 50-100 bar [7].

The methanol synthesis process can be described by the following three equilibrium reactions:

\[
\begin{align*}
\text{CO}_2 + 3 \text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H^0 = -49.8 \text{kJ/mol} \\
\text{CO} + 2 \text{H}_2 & \rightleftharpoons \text{CH}_3\text{OH} \quad \Delta H^0 = -91.0 \text{kJ/mol} \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H^0 = 41.2 \text{kJ/mol}
\end{align*}
\]

The exothermic reactions (1) and (2) represent, respectively, the hydrogenation of CO\(_2\) and CO to methanol. Reaction (3), the water-gas shift (WGS) reaction, is relevant to methanol synthesis as the reaction is also activated by the copper-based methanol synthesis catalysts [8]. As methanol synthesis is exothermic and results in a reduction of molar volume, methanol synthesis is favored by low temperatures and high pressures. However,
temperatures above 200 °C are required for sufficiently high reaction rates, and thus the thermodynamic equilibrium limits the methanol synthesis to low conversion levels. Hydrogenation of pure CO₂ to methanol is also possible but the equilibrium conversions are even lower than for CO. Figure 1 shows the calculated equilibrium conversion of stoichiometric CO and CO₂ feeds at different temperatures and pressure. The conversions are modelled by Soave-Redlich-Kwong equations of state, which have been shown to accurately predict experimental results in methanol synthesis [9]. However, the hydrogenation of CO₂ on Cu/ZnO catalysts is highly selective to methanol, with other thermodynamically more favorable products such as methane, ethers and ketones formed only in negligible amounts [10].

Figure 1. Effect of temperature and pressure on the equilibrium carbon conversion from stoichiometric CO₂:H₂ (1:3) and CO:H₂ (1:2) mixtures. Calculated with the predictive Soave-Redlich-Kwong (PSRK) [11] equation of state in Aspen Plus.

To overcome the thermodynamic limitations in the gas-phase methanol process, liquid-phase synthesis processes have been proposed as an alternative approach to enable lower reaction temperatures in syngas reactions. Early developments utilized highly basic catalyst systems such as alkali alkoxides in combination with copper chromite [12, 13, 14] or nickel-based catalysts [15, 16, 17]. Methanol synthesis from CO/H₂ at temperatures as low as 100 °C and pressures between 30 and 65 bar were reported [18]. However, the basic catalysts are incompatible with
CO₂ or water, the presence of which, even at trace amounts, leads to rapid catalyst deactivation [17]. A method proposed by the Brookhaven National Laboratory (BNL) also utilized a highly basic system for the conversion of CO to methanol at significantly low temperature and pressure [19]. Furthermore, liquid-phase methanol synthesis from CO₂-containing synthesis gas in inert hydrocarbon solvent has been demonstrated in the LPMeOH process [20].

CO₂ has been identified as the main carbon source in methanol synthesis from syngas [21]. Hence, it may be expected that methanol can also be produced by hydrogenation of pure CO₂. Hydrogenation of CO₂, captured from point sources or even directly from the atmosphere, would then provide a sustainable source of carbon-based fuels and chemicals while helping to reduce the atmospheric concentration of CO₂ [22]. Some pilot-scale methanol processes that can use CO₂ as the starting material have been developed. These include the CAMERE process [23], which combines the reverse water-gas-shift reaction and methanol synthesis from syngas, and the Matsui Chemicals process [24], which directly converts CO₂ to methanol. Additionally, Carbon Recycling International established commercial methanol production from CO₂ in 2011, and the Svartsengi plant is presently operating at a capacity of above 5 million liters per year [25]. The process utilizes geothermal energy readily available in Iceland.

One possible way to influence the reaction kinetics and conditions is to change the reaction route that leads to the formation of methanol. A novel alcohol-promoted liquid-phase methanol synthesis process first proposed by Fan et al. [26] is based on the combination of a conventional Cu/ZnO catalyst and alcohol as a catalytic solvent. The alcohol promotes methanol synthesis by altering the reaction route, allowing operation at lower temperatures. In the presence of the alcohol, the reaction proceeds through the formate ester of the corresponding alcohol as an intermediate. As a result, methanol can be produced from syngas at temperatures starting from 170 °C and pressures in the range of 30 to 50 bar [27]. Importantly, the process does not employ basic catalysts sensitive to deactivation by CO₂, allowing direct conversion of CO₂. The following reaction steps have been proposed for this process [28], supported by subsequent in-situ IR observations [29]:

1. Hydrogenation of carbon dioxide into formic acid

\[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH} \]  \hspace{1cm} (4)
2. Reaction of formic acid with ethanol, forming ethyl formate

\[ \text{HCOOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{HCOOC}_2\text{H}_5 + \text{H}_2\text{O} \]  

(5)

3. Hydrogenation of ethyl formate, forming methanol and ethanol

\[ \text{HCOOC}_2\text{H}_5 + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{C}_2\text{H}_5\text{OH} \]  

(6)

The net reaction is the hydrogenation of carbon dioxide to methanol (Eq. 1) with a standard reaction enthalpy of -49.8 kJ/mol. Different alcohols have been shown to possess different promoting effect for methanol synthesis. Tsubaki et al. [30] found linear alcohols to be more effective compared to their branched counterparts, with n-butanol showing the best results. Zeng et al. [31] reported that the yield of both methanol and the corresponding ester decreased with increasing carbon number of the 1-alcohols from ethanol to 1-hexanol. For alcohols with the same carbon number but different structure, 2-alcohols were found to have higher activity, which was explained by a combination of spatial and electronic effects. As a result, 2-propanol showed the highest promotional effect. Later, 2-butanol was reported as the most effective solvent for the continuous methanol synthesis in a semibatch reactor [32].

As the alcohol-promoted methanol synthesis process is characterized by two separate reaction steps, the utilization of separate catalysts optimized for each reaction could be beneficial. Such dual- or cascade catalytic systems have been considered previously for methanol synthesis. Huff and Sanford [33] reported effective CO₂ conversion to methanol at 135 °C using a combination of homogeneous catalysts. Chen et al. [34] used heterogeneous catalysts in 1,4-dioxane solvent: copper chromite for the hydrogenation of CO₂ to formate and Cu/Mo₂C for the formate hydrogenolysis to methanol. This system was capable of methanol production at rates comparable to conventional gas-phase synthesis at 135 °C and exhibited methanol selectivity above 75%. The methanol synthesis was promoted by the addition of ethanol, with the reaction proceeding through ethyl formate, as reported in the alcohol-promoted process. On the other hand, copper chromite is known to catalyze the hydrogenolysis of esters to alcohols, i.e. the latter stage in the alcohol-promoted reaction route [35]. As such, copper chromite appears an interesting component of a dual catalytic system for alcohol-promoted methanol synthesis.
In comparison to CO-containing syngas feed, CO$_2$ hydrogenation to methanol is further complicated by the increased formation rate of water. Water is formed as a byproduct in methanol synthesis, and in the absence of CO, the water-gas shift reaction proceeds in the reverse direction, producing more water. The negative effect of water on methanol synthesis on Cu/ZnO-based catalysts has been well documented [36]. This effect has been explained as a combination of kinetic inhibition effects and structural catalyst deactivation. Water-derived hydroxyl species can block the active sites on the catalyst, resulting in kinetic inhibition. The presence of water can also accelerate the sintering of copper particles [37], resulting in decreased copper dispersion and catalyst deactivation. Removal of methanol and water using membrane reactors [38, 39] and by condensation at high pressures [40] or low temperatures [41] has been previously described for gas-phase methanol synthesis. Reactive distillation [42] provides a further possible approach for continuous product removal, particularly in liquid-phase processes, and has been proposed in literature for the methanol synthesis process [43] and for the Fischer-Tropsch process [44] operating at similar conditions. In addition, selective removal of water by adsorption on zeolite molecular sieves has also been suggested in sorption-enhanced methanol [45] and related dimethyl ether [46] synthesis operated in the gas-phase.

In the present work, alcohol-promoted methanol synthesis was investigated experimentally using a commercial Cu/ZnO-based methanol synthesis catalyst with 1-butanol and 2-butanol as the solvents. 2-butanol was selected because of the previously reported high activity for methanol synthesis, and 1-butanol was considered interesting because of the potentially simplified product separation due to the higher boiling point of the alcohol. As novel developments, enhancement of the alcohol-promoted methanol synthesis by \textit{in-situ} adsorption of water and by the use of dual catalysts were studied. Water adsorption was carried out using a molecular sieve. Methanol synthesis combined with water removal has previously been modelled based on 4Å molecular sieves [45], and the use of 4Å molecular sieves has been modelled for a related dimethyl ether (DME) synthesis [46]. However, experimental work of methanol synthesis promoted by water adsorption has not been published earlier to our knowledge. A dual catalyst system comprising of a combination of Cu/ZnO and copper chromite catalysts was tested with the aim of improving methanol productivity by influencing separately the formate formation and hydrogenolysis reaction steps.
2. Materials and methods

A Parr 4520 autoclave reactor with an inner volume of 450 ml was used for the reaction experiments. The reactor was connected to a Parr 4848 control unit used to control the reaction temperature and mixing speed. A mixing speed of 600 rpm was used in all experiments. Liquid samples from the reaction mixture were collected using a water-cooled sample collection vessel, in which any vapors present in the sample were condensed prior to collecting the sample.

Analysis grade 1-butanol and 2-butanol, were used as solvents. A commercial Cu/ZnO-based methanol synthesis catalyst (Alfa Aesar, 65.5 % CuO, 24.7% ZnO, 10.1% Al₂O₃, 1.3% MgO) was used. The catalyst was ground and sieved to 150-500 µm for each experiment. The 3Å molecular sieve (UOP, beads with diameter of 2 mm), was also ground and sieved to 150-500 µm. An initial experiment with the unground molecular sieve was also performed. The molecular sieve was activated by heating to 250 °C for at least 8 hours under air and subsequent cooling to ambient temperature inside a desiccator prior to use. Powdered copper chromite (Sigma-Aldrich) was used in the dual catalyst experiments. A mixed gas containing 75% hydrogen and 25% carbon dioxide was used as the reaction feed gas, and a mixed gas containing 5% hydrogen in nitrogen was used for activation of the catalysts. A diagram of the experimental setup is presented in Figure 2.
The ground Cu/ZnO catalyst and the copper chromite catalyst were activated *in-situ* in the reactor vessel. Catalyst activation was performed under 5 bar of the 5% H\textsubscript{2}/N\textsubscript{2} mixed gas, with the gas inside the reactor replaced every 30 minutes. The temperature was 200 °C during the activation. Following catalyst activation, the reactor was cooled and the catalysts were kept under the activation gas until the reaction experiment was executed. 200 ml of the alcohol was quickly poured into the reactor, minimizing the contact time of the catalysts with air. The reactor was purged with nitrogen and heated to the reaction temperature under N\textsubscript{2}. At the reaction temperature, an initial liquid sample was collected and the reactor was pressurized with the feed gas (CO\textsubscript{2}:H\textsubscript{2} = 1:3) to the set reaction pressure, which was 60 bar unless otherwise noted. Constant pressure was maintained during the experiments by replacing the consumed reaction gas with fresh gas. The total reaction time was 6 hours and liquid samples were collected every 2 hours.

An Agilent Technologies 6890N gas chromatograph with a thermal conductivity detector was used for analysis of the liquid samples. A polar Zebron ZB-WAXplus column was used for the 2-butanol samples. An isothermal method with the column temperature at 70 °C and helium (1.1 ml/min) as a carrier gas was used. For the 1-butanol samples, a non-polar HP-1ms column was used due to insufficient separation of butanal and methanol in the ZB-WAXplus.
column. A temperature program with an initial temperature of 50 °C (3 minute hold) followed by a 25 °C/min ramp to 100 °C (3 minute hold) was used. Helium (0.7 ml/min) was used as the carrier gas. In the ZB-WAXplus column, the retention times were 2.9 min for methanol, 3.0 min for 2-butanone, 3.8 min for 2-butanol, and 3.9 min for water. In the HP-1ms column, the retention times were 2.7 min for water, 2.9 min for methanol, 4.7 min for butanal, and 5.8 min for 1-butanol. Sample concentrations were calculated by the external standard method.

Analysis uncertainty was estimated by repeated measurements and by estimation of the uncertainty related to the preparation and analysis of the calibration standards. The total uncertainty is expressed as the relative standard deviation for each product compound in 1-butanol and 2-butanol, which is presented as error bars in the relevant figures. In 1-butanol, the relative standard uncertainty is 8% for methanol, 11% for water and 12% for butanal. In 2-butanol, the relative standard uncertainty is 8% for methanol and 11% for water. The uncertainty related to the experimental procedure was estimated as relatively insignificant.

Characterization of the Cu/ZnO catalyst by XRD and SEM-EDS was performed in order to observe any structural changes in the catalyst during the reaction. The catalyst used in methanol synthesis in 1-butanol at 180 °C was analyzed before the reaction (in calcined form) following grinding, and also after the experiment. A separate batch of ground catalyst was characterized by XRD following reduction by the method described above.

XRD analysis was performed on a Bruker D8 Advance system with Cu-Kα radiation at 2θ of 20° to 90° at 0.02° increment, with fixed sample illumination and LYNXEYE 1D detector. For analysis, a layer of the ground catalyst in the 150-500 µm particle size range was placed on the plastic powder specimen holder, which was rotated at 10 rpm during analysis. Phase analysis was performed in DIFFRAC.SUITE EVA software based on the PDF 4+ 2018 database. SEM micrographs and EDS element analyses were obtained using a Hitachi SU3500 Scanning Electron Microscope with SE detector and Thermo Fisher Scientific UltraDry SDD EDS. The acceleration voltage was varied between 10 and 20 kV. The samples were introduced as 150-500 µm particles on a two-sided carbon tape, without coating.

3. Results and discussion

3.1 Detected reaction products
In addition to methanol and water, significant quantities of alcohol dehydrogenation products were found in the reaction mixture. Alcohol dehydrogenation is known to be catalyzed by copper catalysts [47] with the reaction yielding corresponding aldehydes or ketones and hydrogen as products [48]. For instance, the dehydrogenation of 1-butanol yields butanal, while 2-butanol is dehydrogenated to 2-butaneone. These reactions have also been identified in other published studies on alcohol-promoted methanol synthesis [49].

Figure 3 depicts a typical concentration profile of the observed reaction products in 1-butanol during 6 hours of reaction time. The temperature was 180 °C and pressure 60 bar for the experiment depicted. Similar concentration curves were observed for all reaction conditions and alcohols used.

![Graph showing concentration profiles of Butanal, Methanol, and Water against Reaction time, h]

**Figure 3.** Typical concentration profile of the detected reaction products in 1-butanol. 20 g of Cu/ZnO catalyst in 200 ml of alcohol, temperature 180 °C, feed gas CO$_2$:H$_2$ = 1:3, total pressure 60 bar.

The highest concentration of dehydrogenation products was found after heating of the reaction mixture prior to introducing the reaction feed gas. A corresponding increase in the reactor pressure was noticed during the heating process. The pressure increase was presumably caused by the hydrogen formed in the alcohol dehydrogenation reaction. The peak concentration of the dehydrogenation products varied depending on the temperature and the alcohol used but always remained below 10% of the total solution on a mass fraction basis. However, the concentration of the aldehyde or ketone significantly decreased under the reaction gas atmosphere with increasing reaction time. The dehydrogenation reactions appear to reverse direction under increased hydrogen pressure,
returning the original alcohols to the solution. Due to the relatively minor conversion of the alcohols and the apparent reversibility of these reactions, alcohol dehydrogenation is not considered harmful for the overall process.

The concentration of methanol continuously increases over the 6 hours of reaction time. Thus, equilibrium conversion is not reached during this time, and more methanol would likely form if the reaction time were increased. The higher total concentrations of methanol and water found in the molecular sieve experiments (Section 3.3 Water removal by molecular sieve are further evidence that the equilibrium product concentration is not reached. However, in many of the experiments, the methanol production rate decreases after 4 hours of reaction time, as evidenced by the declining slope of the methanol concentration curve in Figure 3. As the thermodynamic equilibrium is not reached at this point, the methanol synthesis rate appears to be limited by kinetic effects, most likely by inhibition caused by the by-product water.

The concentration of water also increases during the reaction as water is formed both as the by-product of CO₂ hydrogenation to methanol and also in the RWGS reaction. The amount of water formed is significantly higher than the amount of methanol. In 1-butanol at 180 °C, the end concentration of water is almost 7 times the end concentration of methanol (Figure 3). A similar result is found at higher reaction temperatures. Figure 4 presents the concentrations of methanol and water in 1-butanol at reaction temperatures of 180, 200 and 220 °C.

If water is only formed as the by-product of methanol synthesis, the molar amounts of methanol and water formed should be equal. The much higher concentrations of water compared to methanol suggest that a significant majority of the water is formed in reactions other than methanol synthesis. On the Cu/ZnO catalyst, the RWGS reaction is most likely the source of the excess water. The high molar ratios of water to methanol formed would suggest that the RWGS reaction is the main reaction in this system and the total selectivity to methanol is rather low. In 1-butanol (Figure 4), the molar ratio of water to methanol ranges approximately from 7 to 10, which implies methanol selectivity in the range of 10-20 %. Some water is also present at the start of the reaction, most likely formed during the reduction of the catalyst. This amount of water is significant in some of the experiments, for example, in 1-butanol at 220 °C (Figure 4), constituting a potential disadvantage of the in-situ catalyst activation method.

Although hydrogenation of the esters is considered to be the rate-determining step in this process [26], alkyl formates, the intermediate products of alcohol-promoted methanol synthesis, were not detected in
the reaction mixture, neither in 1-butanol nor in 2-butanol. The formate esters appear to be rapidly hydrogenated into methanol and alcohol (reaction 9) and their concentrations remain below the detection limit of the analysis method. As the intermediates were not detected, it was not possible to confirm that the reactions proceed through the suggested reaction route. However, the overall promoting effect of the alcohols was convincingly confirmed by a blank experiment in hexane at 180 °C, in which no methanol was formed.

Figure 4. Overall effect of temperature on the formation of methanol and water in alcohol promoted methanol synthesis with 1-butanol as solvent. 20 g of Cu/ZnO catalyst. Feed gas CO₂:H₂ = 1:3. Total pressure 60 bar. Error bars for the concentration of water at 180 and 200 °C are omitted for clarity.

3.2 Effect of reaction temperature and pressure

Reactions in 1-butanol were carried out using a constant overall pressure at different temperatures. Figure 5 shows the combined effect of the reaction temperature and the partial pressure of the reaction gas on methanol productivity with constant total pressure at 180, 200 and 220 °C. The methanol productivity is measured as grams of methanol produced per kg of catalyst per hour. The concentrations of the reaction products in these experiments are shown in Figure 4. Methanol productivity is found to decrease with increasing temperature at the temperature range studied. This result can be explained by the decreased partial pressure of the reaction gas due to increased vapor
pressure of 1-butanol at constant total pressure. The partial pressures, shown also in Figure 5, are calculated by subtracting the alcohol vapor pressure from the total reaction pressure.

![Diagram](image.png)

**Figure 5.** Effect of temperature on methanol productivity with 20 g of Cu/ZnO catalyst in 200 ml of 1-butanol. Reaction time 6 hours, feed gas CO\(_2\):H\(_2\) = 1:3, total pressure 60 bar.

As the concentration of water did not markedly change when the reaction temperature was varied (Figure 4), it can be concluded that the effect of the RWGS reaction does not explain the lowered methanol productivity at increased temperature.

In theory, the reduced methanol synthesis rate at increased temperatures could also be explained by increased selectivity to CO. Increased CO formation by the RWGS reaction should also lead to increased production of water, as water is also formed in the RWGS reaction. The increased concentrations of water would further inhibit the rate of methanol synthesis. However, the concentration of water did not markedly change when the reaction temperature was varied (Figure 4). Thus, it is concluded that the RWGS reaction does not explain the lowered methanol productivity at increased temperature.

The reactions in 2-butanol were carried out using a constant reaction gas partial pressure at different temperatures and a constant temperature at different reaction gas partial pressures. The effect of the feed gas partial pressure on methanol productivity can be clearly seen in Figure 6, which presents methanol productivity at different reaction
temperatures with CO$_2$+H$_2$ partial pressure fixed to 40 bar by varying the total reaction pressure. A significant increase in the methanol production rate with increasing reaction temperature is observed.

Figure 7 presents the methanol productivity at a fixed reaction temperature of 180 °C with the feed gas partial pressure varied from 30 to 50 bar. The productivity clearly increases with the increased partial pressure. The obtained productivities in 2-butanol seem to be higher than in 1-butanol. It should however be noted that the higher productivity values in 2-butanol might be explained by the lower amount (10 g) of catalyst used. The specific productivity of the catalyst appears to decrease as a result of increased water formation due to the RWGS reaction when larger amounts of catalysts are used. This effect is discussed further in Section 3.3.

Figure 6. Effect of temperature on methanol productivity with 10 g of Cu/ZnO catalyst in 200 ml of 2-butanol. Feed gas (CO$_2$:H$_2$ = 1:3), partial pressure 40 bar, reaction time 6 h.
Figure 7. Effect of reaction gas partial pressure on methanol productivity with 10 g of Cu/ZnO catalyst in 2-butanol at 180 °C. Feed gas (CO$_2$:H$_2$ = 1:3), reaction time 6 h.

3.3 Water removal by molecular sieve

Continuous removal of water from the reaction mixture was tested by addition of a zeolite molecular sieve. Molecular sieves with a pore diameter of 3 Å can be used for the dehydration of alcohols because of their selective adsorption of water [50]. The selective adsorption is based on size exclusion of molecules larger than water in the inner microporous structure of the zeolite.

The limiting effect of water on the alcohol-promoted methanol synthesis process was first confirmed by performing an experiment with approximately 1.4 mol/dm$^3$ of water added to 2-butanol. This concentration is slightly above the maximum concentration range of water found in the experiments (Figure 4). At 180 °C and 60 bar of total pressure, the methanol production rate was approximately 74% lower than in the base experiment with no water added. The concentration of water did not significantly increase during this experiment but rather remained relatively constant at the apparent equilibrium level.

Next, the effect of in-situ adsorption of water by the addition of a 3Å molecular sieve was tested. The relative amounts of the catalyst and the molecular sieve were varied, maintaining a total solids mass of 50 g. The results of these experiments are presented in Figure 8. A base experiment with 20 g of catalyst and no molecular sieve is also presented for comparison.
Figure 8. Effect of catalyst and molecular sieve mass on methanol and water formation in 2-butanol. Temperature 180 °C, feed gas CO\textsubscript{2}:H\textsubscript{2} = 1:3, total pressure 60 bar.

Compared to the base case with 20 g of Cu/ZnO catalyst and no molecular sieve, the addition of the unground molecular sieve increased the methanol productivity from 8.2 g/kg/h to 11.2 g/kg/h. A more significant improvement was found with the molecular sieve ground into 150-300 µm particle size range. Due to the clear effect of the particle size, the adsorption of water appears to be significantly diffusion-limited for the unground molecular sieve. With 20 g of catalyst, the addition of 30 g of the ground molecular sieve increases the methanol productivity to 33.6 g/kg/h, an increase of over 300% over the Cu/ZnO catalyst used without a molecular sieve. Keeping the total amount of solids (catalyst + molecular sieve) at 50 g, the methanol productivity increased with increasing amounts of molecular sieve. For instance, the productivity increased to 54.4 g/kg/h using 10 g of the catalyst and 40 g of the molecular sieve. These results clearly show that the catalyst is most effectively utilized for methanol synthesis when larger relative amounts of the molecular sieve to the catalyst are used. This observation can be explained by the increased water adsorption capacity of the larger amount of the molecular sieve, leading to decreased concentrations of water, as shown in Figure 8.
3.4 Dual catalysts

To test the dual catalysis concept for alcohol-promoted methanol synthesis, copper chromite (CuCr) was used in combination with the Cu/ZnO catalyst. The ratios of the two catalysts were varied: 20 g of the Cu/ZnO catalyst was used with 10 g of CuCr, and vice versa. The experiments were carried out in 2-butanol at 180 °C and 60 bar of total pressure, corresponding to a CO₂ + H₂ partial pressure of 50.1 bar. The results of these experiments are presented in Figure 9. A base experiment with 20 g of Cu/ZnO catalyst and no copper chromite is also presented for comparison.

![Figure 9](image)

Figure 9. Effect of different amounts of Cu/ZnO and copper chromite (CuCr) catalysts on the formation of methanol and water in 2-butanol. Reaction time 6 hours. Temperature 180 °C, feed gas CO₂:H₂ = 1:3, total pressure 60. An experiment with 20 g of Cu/ZnO catalyst and no copper chromite is included for comparison.

The addition of the copper chromite catalyst clearly increases the methanol productivity. Both the absolute methanol production rate, as measured by the methanol end concentration, and the specific productivity of the catalyst increase with addition of copper chromite. The increased productivity can be explained either by a synergistic effect between the two catalysts or by higher methanol synthesis activity of CuCr compared to Cu/ZnO. However, a higher intrinsic activity of copper chromite appears unlikely, as the activity of Cu/ZnO for methanol synthesis is well-known.
and industrially applied. Fan et al. [26] also reported higher methanol yield and selectivity of Cu/ZnO compared to CuCr in alcohol promoted methanol synthesis. Fan et al. also found similar CO selectivity, or RWGS activity, for both of the catalysts. This is supported by the present results, as the concentration of water was not significantly affected by the changed ratio of Cu/ZnO and CuCr (Figure 9, columns 2 and 3), supporting similar RWGS activity of the two catalysts. The overall methanol selectivity appears to be higher with the combined catalysts, as the ratio of methanol to water produced is increased compared to Cu/ZnO used alone.

3.5 Characterization of Cu/ZnO catalyst before and after reaction

The structural features of the Cu/ZnO catalyst before and after reaction were investigated by the means of XRD and SEM-EDS in order to assess the catalyst stability. Figure 10 presents the X-ray diffractograms of the catalyst as supplied in the calcined form, following reduction in 5% hydrogen, and following use in alcohol-promoted methanol synthesis in 1-butanol at 180 °C. It is noted that the same batch of catalyst was analyzed prior to reduction and following the reaction, while the reduced catalyst was prepared and analyzed separately.

Figure 10. X-ray diffractograms of the unused Cu/ZnO catalyst (A), the reduced catalyst (B), and the catalyst following methanol synthesis from CO₂ and H₂ (1:3) in 1-butanol at 180 °C (C).
The calcined catalyst is largely amorphous, showing a minor pattern corresponding to copper(II)oxide (CuO) typical to Cu/ZnO catalysts [51]. The patterns are identified based on the PDF 4+ 2018 crystallography database. The reduced catalyst presents with a clearly defined pattern consistent with crystalline, copper(I)oxide (Cu$_2$O), and metallic copper. Weak crystalline features of zinc oxide are also evident, consistent with previous studies [52]. As the reduction of copper proceeds stepwise from CuO to Cu via Cu$_2$O [53], the presence of Cu$_2$O may imply incomplete reduction, possibly due to insufficient reduction time or temperature. However, as the reduced catalyst sample was transferred and analyzed in contact with air, re-oxidation of copper crystallites during this process cannot be ruled out.

Only metallic copper and zinc oxide is found present in the used catalyst. Cu/ZnO catalysts are known to show dynamic structural changes depending on the oxidation potential of the gas phase [54, 55] and ongoing reduction of the catalyst at the reaction conditions is possible. As the reduced and used catalyst analyzed here are not from the same batch of ground and prepared catalyst, batch-to-batch variation cannot be eliminated as a cause of the observed structural differences.

The peaks corresponding to zinc oxide are more clearly defined compared to the reduced catalyst, potentially indicating continuing crystallization of ZnO at the reaction conditions. Lunkenbein et al. [56] identified zinc oxide as the more dynamic phase compared to metallic copper under reaction conditions, and found that crystallization of ZnO and the resulting loss of reactive Cu-ZnO interfaces is the main mechanism of initial catalyst deactivation. The SEM-EDS elemental maps of copper and zinc presented in Figure 11 indicate that such a process may have initiated in the catalyst used here. The unused (calcined) catalyst shows a relatively homogeneous distribution of both copper and zinc. However, a degree of segregation of these elements can be observed in the used catalyst, with the elemental map showing distinct areas with high content of zinc (oxide) that are relatively poor in copper.
Further insight is provided by the SEM images presented in Figure 12. Distinct crystals in the micrometer dimension can be observed, identified as zinc oxide by the EDS analysis. No such features were found in the unused catalyst. It is concluded that agglomeration and crystallization of zinc oxide during reaction has occurred, acting as a potential deactivation mechanism for the catalyst. However, as long-term stability tests were not performed here, the actual effect of these structural changes on the activity of the catalyst cannot be discussed.

These observations can be compared to other findings discussed in literature. Previously, the stability of Cu/ZnO catalyst in alcohol promoted methanol synthesis has been explored by Reubroycharoen et al. [32] who found the performance stable during 40 hours of continuous methanol synthesis (at 170 °C), and by Jeong et al. [57] who found no decline in activity during 60 hours of reaction (150 °C). In contrast to our results, Jeong et al. found no changes in the XRD profile of the catalyst before and after reaction. Other than the lower reaction temperature, the differing findings might be explained by different feed gas composition, as a CO-rich syngas was used in these studies opposed to the CO₂:H₂
mixture used here. Therefore, it is possible that the detected differences might be caused by the large amount of water present in the reaction system in the present study.

Figure 12. SEM micrographs of the Cu/ZnO catalyst following methanol synthesis from CO₂ and H₂ (1:3) in 1-butanol at 180 °C. Zinc oxide crystals are highlighted.

4. Conclusions

Methanol synthesis from CO₂ was studied in an alcohol-promoted liquid-phase process using conventional Cu/ZnO and copper chromite as catalysts. 1-butanol and 2-butanol were found to act as catalytic solvents, allowing methanol synthesis at lower temperatures than conventional gas-phase processes. Although it was not possible to determine the exact reaction route, it is expected that the promoting effect of the alcohols is based on a reaction route proceeding through the intermediate of formate ester of the alcohol.

The effect of continuous water removal using molecular sieve adsorption was explored. The addition of a 3Å molecular sieve significantly enhanced methanol productivity. Grinding of the molecular sieve resulted in improved results due to the shorter diffusion path compared to the granular material. The maximum methanol productivity of
54.4 g/kg/h was found when the maximum relative amount of the molecular sieve (40 g) to the catalyst (10 g) was used. The final methanol concentration after 6 hours of reaction time reached 0.5 mol/dm³. The catalyst was most effectively used for methanol synthesis when the amount of molecular sieve was maximized, which minimized the concentration of water. The water concentration was found to significantly affect the rate of methanol synthesis. The overall methanol production rate in this process appears to be limited by the concentration of water and its effects on the catalyst surface. To prevent the negative effects of water, continuous water removal or development of more water resistant catalysts is vital for further development of this process. Based on the results, the use of a 3Å molecular sieve for water removal appears a promising approach.

The methanol productivity obtained in the current research can be compared to results reported in other studies. Yang et al. [49] found an even higher methanol productivity of up to 167 g/kg/h for alcohol-promoted methanol synthesis at 170 °C and 50 bar using an optimized Cu/ZnO catalyst composition. The difference to the results presented here can be explained mainly by the different feed gas composition in their experiments (CO/CO₂/H₂/Ar = 32.4/5.1/59.5/3.9). For gas-phase CO₂ hydrogenation to methanol, productivity values even up to 1200 g/kg/h have been achieved [58]. However, these results were obtained at a relatively high temperature of 240 °C and at high space velocities giving relatively low CO₂ conversions.

Dual catalysis by the combination of Cu/ZnO with copper chromite was also studied in this work. A remarkable increase in catalytic activity was found for the dual catalyst. When 20 g of copper chromite and 10 g of Cu/ZnO was used, the productivity increased by 80% compared to the use of 20 g of the Cu/ZnO catalyst alone. A synergistic effect between the two catalysts is suggested, which is possibly based on an increased formation rate of the formate ester intermediate by the copper chromite catalyst. The two catalysts appeared to have similar reverse water-gas shift activity, as the concentration of water did not change when the relative amounts of Cu/ZnO and copper chromite were varied.

Structural changes in the catalyst during alcohol-promoted methanol synthesis were found by the means of XRD and SEM-EDS investigations. EDS elemental analysis showed that segregation of copper and zinc oxide had taken place, and both XRD analysis and SEM imaging provided evidence that crystallization of zinc oxide occurred. Such phenomena has previously been identified as cause of catalyst deactivation due to the loss of reactive Cu-ZnO interfaces [56]. However, comprehensive catalyst stability tests were not performed in the current study, and thus
the effect of the observed changes on catalytic activity cannot be determined conclusively. It is clear that stability
tests at different reaction temperatures and, importantly, at different feed gas compositions are necessary to further
classify the alcohol-promoted methanol synthesis process.

Acknowledgements

The Authors are grateful for Finnish Academy of Science for "Micro- and millistructured reactors for catalytic
oxidation reactions" MICATOX project funding, number: 269896. Funding provided by the Lappeenranta
University of Technology Doctoral School is also gratefully acknowledged.
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