



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 3 Å 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.

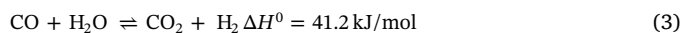
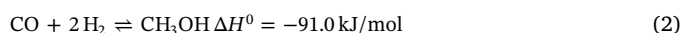
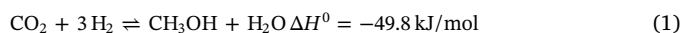
1. Introduction

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:



The exothermic reactions (1) and (2) represent, respectively, the hydrogenation of CO₂ 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

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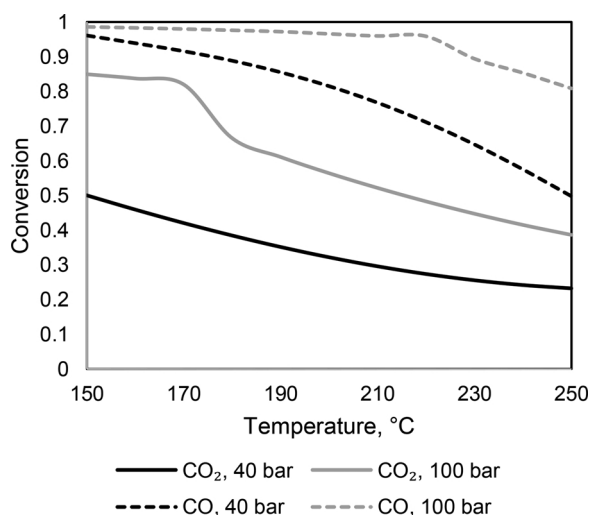


Fig. 1. Effect of temperature and pressure on the equilibrium carbon conversion from stoichiometric CO₂:H₂ (1:3) and CO:H₂ (1:2) mixtures. Calculated with the predictive Soave-Redlich-Kwong (PSRK) [58] equation of state in Aspen Plus.

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. Fig. 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].

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 [11,12,13] or nickel-based catalysts [14,15,16]. Methanol synthesis from CO/H₂ at temperatures as low as 100 °C and pressures between 30 and 65 bar were reported [17]. However, the basic catalysts are incompatible with CO₂ or water, the presence of which, even at trace amounts, leads to rapid catalyst deactivation [16]. 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 [18]. Furthermore, liquid-phase methanol synthesis from CO₂-containing synthesis gas in inert hydrocarbon solvent has been demonstrated in the LPMeOH process [19].

CO₂ has been identified as the main carbon source in methanol synthesis from syngas [20]. 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 [21]. Some pilot-scale methanol processes that can use CO₂ as the starting material have been developed. These include the CAMERE process [22], which combines the reverse water-gas-shift reaction and methanol synthesis from syngas, and the Matsui Chemicals process [23], 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 [24]. The process utilizes geothermal energy readily available in Iceland.

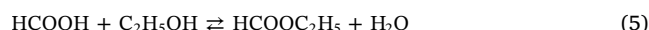
One possible way to influence the reaction kinetics and conditions is to change the reaction route that leads to the formation of methanol. A novel alcohol-promoted liquid-phase methanol synthesis process first

proposed by Fan et al. [25] 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 [26]. 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 [27], supported by subsequent *in-situ* IR observations [28]:

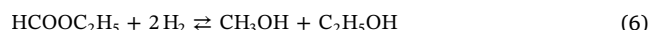
1 Hydrogenation of carbon dioxide into formic acid



2 Reaction of formic acid with ethanol, forming ethyl formate



3 Hydrogenation of ethyl formate, forming methanol and ethanol



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. [29] found linear alcohols to be more effective compared to their branched counterparts, with n-butanol showing the best results. Zeng et al. [30] 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 [31].

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 [32] reported effective CO₂ conversion to methanol at 135 °C using a combination of homogeneous catalysts. Chen et al. [33] 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 [34]. 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, CO₂ 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 [35]. 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

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