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Effect of Water on Liquid Phase DME Synthesis from Syngas over Hybrid Catalysts Composed of $Cu/ZnO/Al_2O_3$ and γ-Al_2O_3

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Abstract−DME synthesis from syngas via methanol has been carried out in a single-stage liquid phase reactor. $Cu/ZnO/Al_2O_3$ and γ-Al_2O_3 were used together as methanol synthesis catalyst and dehydration catalyst, respectively. The influence of water on the catalytic system was investigated mainly. Water affected the activity of methanol dehydration catalyst as well as methanol synthesis catalyst. Thus, removal of water from the reaction system, by adding a dehydrating agent or controlling methanol formation rate by the reaction parameters, was efficient in maintaining the high catalytic activity and stability.

Key words: Dimethyl Ether Synthesis, Methanol Synthesis, Water Gas Shift Reaction, Synthesis Gas, Solid Acid Catalyst, Dehydration, LPDME^{TM}

INTRODUCTION

Air pollution is one of the most serious environmental problems all over the world. Since diesel engines of buses and trucks exhaust a huge amount of NO_x and particulates, a clean alternative fuel is highly demanded. The use of oxygenated hydrocarbons, such as alcohols and ethers, as substitutes for petroleum-derived fuels has been the subject of attention in recent years [Brown et al., 1991]. Oxygenates are attractive as fuels and fuel additives in a broad range of combustion applications because of their clean-burning characteristics, which lead to reduced emissions of pollutants such as carbon monoxide, reactive hydrocarbons and nitrogen oxides.

An alternative starting point could be the synthesis of dimethyl ether (DME) from syngas via methanol. Three reversible, exothermic and thermodynamically equilibrium limited chemical reactions are involved. These are methanol synthesis,

$$CO+2H_2 \leftrightarrow CH_3OH\ (\Delta H=-21.6\ \mathrm{kcal/mol}) \qquad (1)$$

methanol dehydration for the production of DME,

$$2CH_3OH \leftrightarrow CH_3OCH_3+H_2O\ (\Delta H=-5.6\ \mathrm{kcal/mol}) \qquad (2)$$

and water gas shift reaction (WGSR),

$$CO+H_2O \leftrightarrow CO_2+H_2\ (\Delta H=-21.6\ \mathrm{kcal/mol}) \qquad (3)$$

Since methanol formed by reaction (1) is removed by methanol dehydration [reaction (2)], equilibrium conversion of DME synthesis reaction becomes higher than that of the methanol synthesis. Since water formed by methanol dehydration is also removed from the reaction system by the WGSR, equilibrium shifts toward the right hand side of reaction (2). Hydrogen produced from the WGSR promotes the formation of methanol in reaction (1). Therefore, from the thermodynamic point of view, DME synthesis process from syngas is more favorable than methanol synthesis [Chadwick et al., 1999; Choi et al., 2000]. Equilibrium conversions of the reactions mentioned above are presented in Fig. 1.

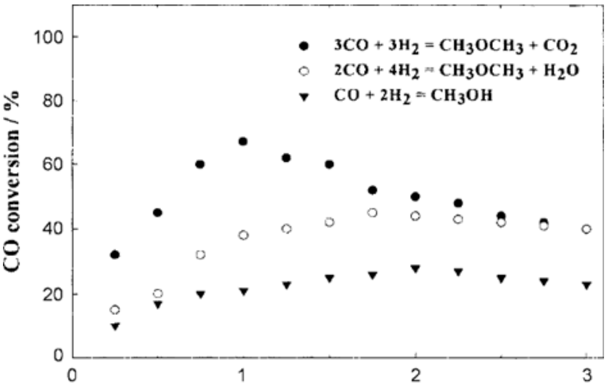

Fig. 1. Equilibrium conversions of the involved reactions in DME synthesis from syngas at 30 atm and 280 °C [Fujimoto et al., 1998].

As shown above, the reactions involved for the synthesis of DME are highly exothermic. Although a gas phase single-step syngas-to-DME process would provide the advantage of greater production rates, the process is most likely to be still subject to the limitation in heat removal, which is preventing effective realization of the system. For efficient heat removal and fine temperature control, Liquid Phase Dimethyl Ether Process (LPDME^{TM}) was proposed and developed by Air Products [Brown et al., 1991; Peng et al., 1995, 1997, 1999] with the support of the US Department of Energy (DOE). In this process, syngas is converted into DME in a single, slurry phase reactor using a physical mixture of methanol synthesis catalyst and a solid acid dehydration catalyst, dispersed in a mineral oil.

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The effect of water on the synthesis of DME has been investigated partly by several groups. Takeguchi et al. studied the effect of water on the catalytic activity for the synthesis of DME from methanol dehydration in a fixed bed reactor [Takeguchi et al., 2000]. The addition of water to the feed decreased methanol conversion while increasing selectivity to CO_2. When H_2 was used as a balance gas, methanol conversions both to DME and CO_2 decreased. In the presence of H_2, the reverse WGSR took place to shift the equilibrium composition to $CO+H_2O$ side, and then the formed water suppressed the DME synthesis. These results clearly showed that equilibrium of the WGSR influenced the conversion of methanol as well as the selectivity of the products. Brown et al. investigated the effect of water as a substitute reagent for H_2 in the liquid phase DME synthesis process from low H_2/CO ratio coal derived syngas [Brown et al., 1991]. WGSR catalyst was loaded with methanol synthesis and dehydration catalyst. Co-fed water was shifted to H_2 by WGSR. At the lower feeding rate of steam, both methanol and DME productivities increased to levels comparable with high H_2/CO ratio syngas. Further increase of the feeding rate of steam did not increase methanol productivity, but did cause sharp decrease in DME productivity. This decrease could be explained by the decrease in the activity of the acid catalyst with increasing H_2O partial pressure.

From the results of the literature, we could conclude that water produced during the reaction might affect the catalytic activity and the productivity of DME due to the equilibrium composition limitation. But these effects were not systematically investigated to date for the direct synthesis of DME from syngas using methanol synthesis catalyst and dehydration catalyst.

Therefore, in this study, we have focused on the effect of water to the performance of the liquid phase direct synthesis of DME from syngas. We could finally find out that water affected both the activity of the methanol synthesis catalyst and the dehydration catalyst. By controlling the formation rate of methanol and the removal of water from the reaction system, however, high catalytic activity and stability could be obtained.

EXPERIMENTAL

The Cu/ZnO/Al_2O_3 catalyst for the methanol synthesis was prepared by the co-precipitation method [Inui et al., 1996]. Nitrates of copper, zinc, and aluminum were dissolved in water and mixed together, and the precipitates were obtained by dropwise adding sodium carbonate solution into the nitrates solutions. The precipitates were filtered, washed, dried at 120 °C overnight and calcined at 250 °C for 4 h. The thus-formed Cu/ZnO/Al_2O_3 catalyst had the composition of Cu/Zn/Al=46.7/37.6/15.7 on weight basis (ICP). For the dehydration catalyst, γ-Al_2O_3 manufactured by Sumitomo Chemicals was used. The hybrid catalysts were prepared by physically mixing the methanol synthesis catalyst, Cu/ZnO/Al_2O_3 with the dehydration catalyst, γ-Al_2O_3.

The catalysts were reduced prior to the reaction by in-situ method with flowing H_2 at 100 mL/min [Lee et al., 1999]. The reaction was carried out in a slurry reactor (Autoclave Engineers) with a capacity of 100 mL. Syn gas having a H_2/CO ratio of 1 (total flow rate: 100 mL/min) was allowed to react on the catalyst suspended in a liquid medium (mineral oil, 50 mL). The reaction was carried out at 30 atm and 250 °C. The composition of products and the CO conversion were determined by means of gas chromatography.

Table 1. Reaction conditions for the investigation of the effect of water for DME synthesis from syngas

Type	Reaction	Cu/ZnO/Al_2O_3	γ-Al_2O_3
A	Methanol synthesis	Water adsorbed	Not used
B	DME synthesis	Water adsorbed	Used
C	DME synthesis	Used	Water adsorbed
D	DME synthesis	Water adsorbed	Water adsorbed

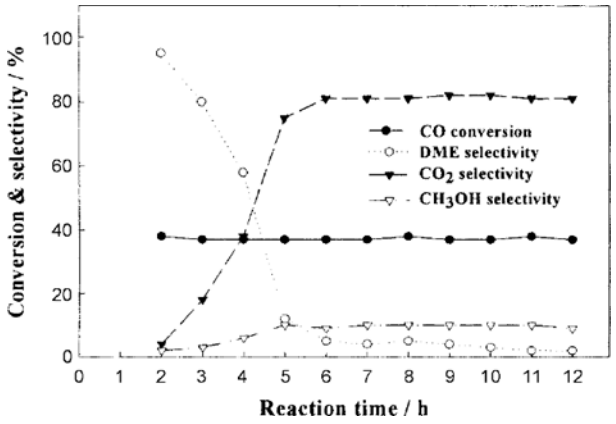

Fig. 2. CO conversion and product selectivity in DME synthesis from syngas (Cu/ZnO/Al_2O_3 1.5 g+γ-Al_2O_3 0.3 g).

To investigate the effect of water on the catalytic activity, reactions described in Table 1 were carried out. For these reactions, water vapor was adsorbed on the catalysts at 100 °C with N_2 as carrier at flow rate of 100 mL/min. The adsorbed amount of water was measured by the magnetic suspension balance.

RESULTS AND DISCUSSION

The reaction results in the standard conditions are shown in Fig. 2. CO conversion was about 40%, which was far below the equilibrium conversion. Furthermore, after 6 h on stream, DME selectivity decreased to 5%, while CO_2 selectivity increased to 80%. This seems to be caused by the WGSR due to H_2O formed by the dehydration of methanol. The formed H_2O suppressed the formation of DME, as well. Methanol was, however, continually formed during 12 h. The CO_2 and H_2 formed by the WGSR could react to form methanol and H_2O ($CO_2+3H_2 \leftrightarrow CH_3OH+H_2O$) [Lee et al., 1995, 2000]. Therefore, methanol was thought to be continually formed by the hydrogenation of CO_2. The H_2O formed by the hydrogenation of CO_2 shifted the equilibrium [reaction (2)] to the left hand side, which suppressed the formation of DME further. These results indicate that the reactions mentioned above are linked together and the equilibriums are influenced by the presence of water.

Therefore, in order to increase the equilibrium conversion and the selectivity to DME, the reactions involved should be controlled and optimized toward the reaction conditions containing as small amount of water as possible.

To investigate the effect of water on the catalytic activities more precisely, catalysts were pretreated by water before the reaction and the activities were tested. The amounts of water adsorbed on Cu/

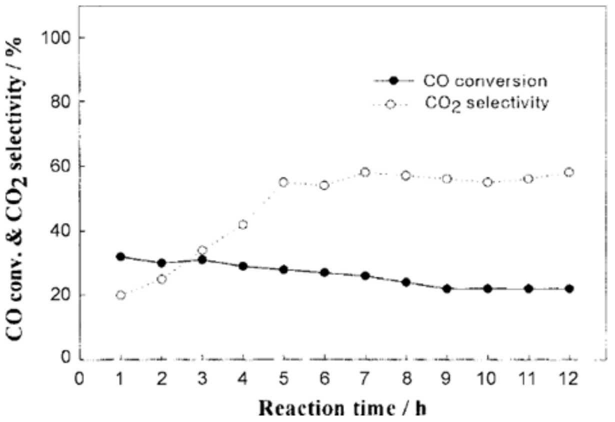

Fig. 3. Methanol synthesis reaction over Cu/ZnO/Al_2O_3 (1.5 g) pretreated by water.

ZnO/Al_2O_3 and γ-Al_2O_3 were 14.7 wt% and 17.6 wt%, respectively. As shown in Fig. 3, when the reaction was carried out over only the methanol synthesis catalyst pretreated by water (Type A in Table 1), CO conversion was almost same as the standard reaction of DME synthesis (Fig. 2) at the beginning, but decreased gradually from 36% to 22% with time on stream. Contrary to this, CO_2 selectivity increased from 20% to 55%. Cu/ZnO/Al_2O_3 is known to catalyze both the methanol synthesis and the WGSR. When the amount of H_2O in the reaction system was negligible, H_2 could be easily adsorbed on the surface of the catalyst, thus methanol formation proceeded. On the other hand, when H_2O was adsorbed on the catalyst, H_2 could not be easily adsorbed on the catalyst surface, so methanol formation was depressed. In other words, WGSR proceeded with the adsorbed H_2O allowing an increase of CO_2 formation. Therefore, we could conclude that H_2O formed during the reaction could suppress the methanol formation.

The effect of adsorbed water on DME synthesis over Cu/ZnO/Al_2O_3 and γ-Al_2O_3 is shown in Fig. 4. When water was adsorbed on the methanol synthesis catalyst only, CO conversion decreased from 70% to 23%, while DME selectivity reached 95%, which indicates that once methanol formed it could be easily converted to DME on the surface of γ-Al_2O_3. So in this case, the formation of DME was limited by the formation of methanol.

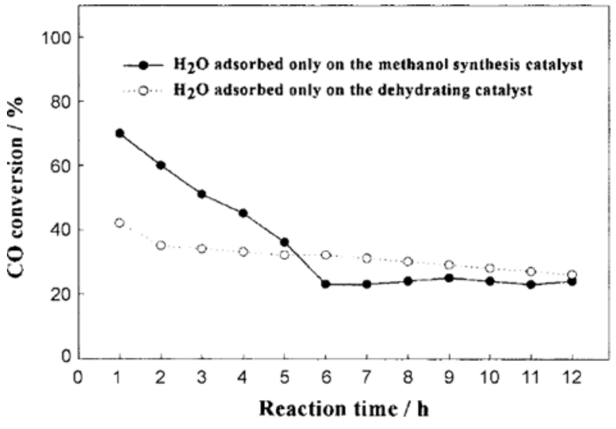

Fig. 4. DME synthesis reaction over Cu/ZnO/Al_2O_3 (1.5 g)+γ-Al_2O_3 (0.3 g), where the only one catalyst was pretreated by water.

When water was adsorbed only on the dehydration catalyst (γ-Al_2O_3), only methanol was formed with a decrease of the formation rate. This means that water affected the catalytic activity of the dehydration catalyst, which has been reported in several studies [Inui et al., 1996; Takeguchi et al., 2000; Sofianos et al., 1991]. And finally, when water was adsorbed on both the methanol synthesis catalyst and the dehydrating catalyst, no reaction occurred.

From the experiments for the effects of water on the catalytic activities, it was verified that water formed during the reaction would influence the activity of the dehydration catalyst as well as the methanol synthesis catalyst. Therefore, the removal of water was a key factor to increase the conversion of CO to the level of the equilibrium conversion.

As a direct method to remove water formed during the reaction, $MgSO_4$ was employed as dehydrating agent with the catalysts. The reaction result is represented in Fig. 5. When the dehydrating agent was loaded, CO conversion was very high at the beginning but decreased quickly to the level of the standard condition (Fig. 2). Since the amount of water formed during the reaction was larger than the capability of the dehydrating agent, the ability of dehydrating agent suddenly decreased when saturated by water. However, it should be noted that CO conversion could be increased by removing water.

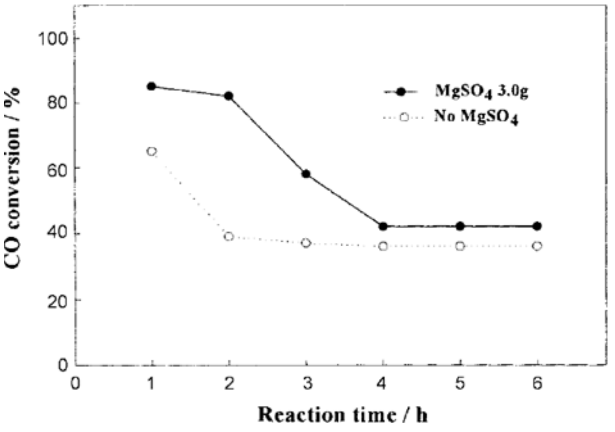

Fig. 5. DME synthesis from syngas with the dehydrating agent (Cu/ZnO/Al_2O_3 1.5 g+γ-Al_2O_3 0.3 g).

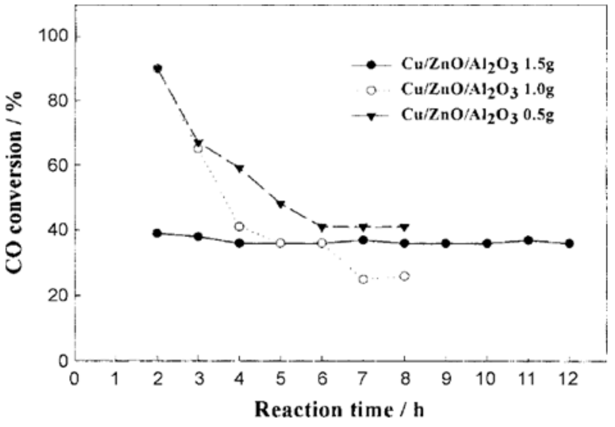

Fig. 6. Effect of amount of the methanol synthesis catalyst in DME synthesis from syngas (γ-Al_2O_3, 0.3 g; feed flow rate, 100 ml/min).

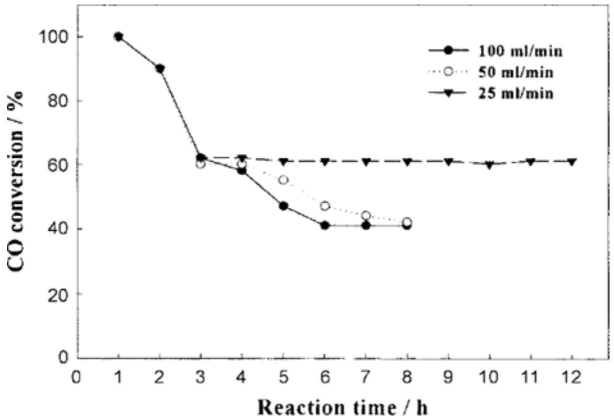

Fig. 7. Effect of feed flow rate in DME synthesis from syngas (Cu/ZnO/Al$_2$O$_3$ 0.5 g+γ-Al$_2$O$_3$ 0.3 g).

The effect of amount of the methanol synthesis catalyst was investigated. The amount of the dehydration catalyst was kept constant at 0.3 g while the amount of the methanol synthesis catalyst was varied from 0.5 g to 1.5 g. As shown in Fig. 6, when the amount of the methanol synthesis catalyst was diminished to 0.5 g, the CO conversion increased. Some induction period was observed in this case, but the steady state conversion was clearly higher than that of the standard condition. The higher catalytic activity with smaller amount of methanol synthesis catalyst can be explained as follows. Methanol formation rate via CO$_2$ hydrogenation was controlled by diminishing the amount of the methanol synthesis catalyst, which decreased the amount of water produced, and finally allowed higher conversion to DME.

With considering this aspect, the effect of feed flow rate was investigated. The result is shown in Fig. 7. When the feed flow rate decreased, CO conversion was improved. At the flow rate of 25 ml/min, steady-state CO conversion almost reached the equilibrium conversion. Methanol formation rate might be controlled to suppress the formation of water by decreasing the feed flow rate. Mass transfer of water formed might be influenced by decreasing the feed flow rate, as well.

CONCLUSIONS

For DME synthesis reaction from syngas in a single-stage liquid phase reactor, water produced during the reaction affected both the activity of the methanol synthesis catalyst and the dehydration catalyst. Employing a dehydrating agent was effective for an instant to remove water, but it could not be continued for long due to the limited capacity. By diminishing the amount of methanol synthesis catalyst and the feed flow rate, methanol formation rate could be controlled and the formation of water was suppressed, which increased the steady-state CO conversion nearly to the equilibrium conversion.

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