Direct Synthesis of Dimethyl Ether (DME) from Syngas
Kaoru TAKEISHI, and Yoshimi AKAIKE
Department of Materials Science and Chemical Engineering
Shizuoka University
3-5-1, Jouhoku, Naka-ku, Hamamatsu-shi, Shizuoka-ken, 432-8561
JAPAN
tcktake@ipc.shizuoka.ac.jp

Abstract: We have developed appropriate and excellent catalysts for direct DME synthesis. The catalysts, Cu-Zn/Al2O3 catalysts prepared by the sol-gel method, produce DME with high DME activity and high DME selectivity under milder reaction temperature and pressure compared with the usual direct DME synthesis catalysts (mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts). It will be the reason why the methanol synthesis active sites (copper) and the methanol dehydration active sites (alumina) on the sol-gel Cu/Al2O3 catalysts exist closer than those of the mixed catalysts.

Key-Words: Dimethyl ether, DME, hydrogen, clean fuel, catalyst, sol-gel method, alumina, copper, direct synthesis, syngas.

1 Introduction
Dimethyl ether (DME) is slightly expensive chemical now, because DME is manufactured by dehydration process of methanol. However, DME is expected as a clean fuel for the 21st century, from the reasons that DME does not contain poisonous substances, and DME burns without particulate matters (PM) [1]. DME will be used as substitutes of liquefied petroleum gas (LPG) and diesel oil, and will be used for hydrogen carrier. Therefore, demand of DME will increase rapidly, and it is necessary to mass-produce DME economically. There is a method, direct synthesis of DME, that DME is synthesized directly from syngas (hydrogen and carbon monoxide), not synthesized by dehydration of methanol. Excellent catalysts for the direct synthesis are necessary. In this study, copper alumina catalysts prepared by the sol-gel method that is appropriate for DME steam reforming [2, 3] are applied for direct DME synthesis (3H2 + 3CO → CH3OCH3 + 2CO2) that is similar reaction of DME steam reforming (CH3OCH3 + 3H2O → 3H2 + 2CO2).

2 Experiments
For hydrogenation of carbon monoxide, Cu-Zn (36-4wt.%)/Al2O3 catalyst prepared by the sol-gel method was used in single, not mixed with other catalysts such as alumina. As the comparison, a mixed catalyst with a commercial catalyst CuO-ZnO (50-50wt.%) (N211, Nikki Chemical Co., Ltd.) and alumina (BK-105, Sumitomo Chemical Co., Ltd.) was used. This mixed catalyst is similar catalysts for patent catalysts for direct DME synthesis [4]. The all catalysts were calcined at 500 °C for 5 h and were reduced by flowing H2 at 450 °C for 10 h. This severe pretreatment was particularly performed for reactive comparison to avoid the catalytic deterioration with sintering of the catalysts by the reaction heat on continuous experiments with the same catalysts. A flow reactor was used for CO hydrogenation. The used weight of catalysts was 0.5 g, and the supply of the reaction gas flow was mainly H2/CO/Ar = 7.5/7.5/1.5 ml min⁻¹. Argon gas was an internal standard for gas chromatography. The reaction gas and products were analyzed by gas chromatographs (TCD and FID). Scanning electron microscopy - energy dispersion X-ray spectrometry (SEM-EDS) analysis was performed for the surface characterization.

3 Results and discussion
3.1 CO hydrogenation
The single type catalyst and the mixed catalyst were carried out for CO hydrogenation. The part of the results is shown in Fig. 1. Much amount of DME was produced over Cu-Zn(36-4wt.%)/Al2O3 catalyst prepared by the sol-gel method at 250 °C of the lower reaction temperature. The less amount of DME was produced over the mixed catalyst of the methanol synthesis catalyst (N211) and the methanol dehydration catalyst (BK-105) at 310 °C of the higher reaction temperature. In other experiments, even if the reaction gases contain some oxygen, the sol-gel
Cu-Zn/Al₂O₃ catalysts produce DME effectively with long durability. The single type catalysts that have copper sites for methanol synthesis and alumina sites for methanol dehydration on the surface are more appropriate and more excellent for direct DME synthesis than the mixed catalysts that are one of the patent catalysts for direct DME synthesis.

3.2 Hydrogen ratio for direct DME synthesis
Dependency of H₂/(H₂+CO) ratio was investigated on Cu-Zn(36-4wt.%)/Al₂O₃ catalyst prepared by the sol-gel method. Fig. 2 shows the part of the results. DME is produced with the fastest production rate at the ratio of H₂/(H₂+CO) = 0.5. It is suggested that DME is produced over Cu-Zn/Al₂O₃ catalyst prepared by the sol-gel method, with the reaction of the chemical equation, 3H₂ + 3CO → CH₃OCH₃ + CO₂.

3.3 Surface analysis of the catalysts
SEM-EDS analysis confirmed that copper sites for methanol synthesis (and water gas shift reaction) and alumina sites for methanol dehydration are co-existing and the both sites are dispersed well on the surface of Cu-Zn/Al₂O₃ catalyst prepared by the sol-gel method. The distances of the sites for each reaction (methanol synthesis, methanol dehydration, and water gas shift reaction) are shorter than those of the mixed catalyst, so the reactions are more sequentially and systematically occurred, and the DME production rate will be faster.

3.4 Pressure effect for direct DME synthesis
Dependency of pressure for CO hydrogenation was investigated on Cu-Zn(36-4wt.%)/Al₂O₃ catalyst prepared by the sol-gel method. Fig. 3 and Fig. 4 show the part of the results. Rate of DME production is linearly increased with increasing of the reaction absolute pressure. Production rate of methanol also increases with increasing the pressure. Methane production rate is almost stable. (Cf. Fig. 3) From these phenomena, selectivity for DME is increased to 100% depending on the increase of the reaction pressure. The DME selectivity is 98% under the pressure of 1.6 MPa. (Cf. Fig. 4) This value is very high compared with some companies’ data and the reaction condition is milder than those of the companies’ (Cf. Table 1 [5]).

3.5 Durability test of the catalyst for direct DME synthesis
Durability test for direct DME synthesis, catalyst life-time test was carried out. Fig. 5 and Fig. 6 show the part of the results. In case of DME production rate, there was a decrease of about 100 µmol g⁻¹ cat⁻¹ h⁻¹ from the first biggest rate. However, the DME rate production is almost constant after this decrease. Rate production of methane and methanol also slightly decreased. However, there is no obvious big deactivation such as less production. The further development is still need, but the catalysts are stable and they have enough capability for practical use.

4 Conclusion
We have developed the appropriate and excellent catalyst for direct DME synthesis. The catalysts, Cu-Zn/Al₂O₃ catalysts prepared by the sol-gel method, produce DME with high activity and high selectivity under the mild reaction temperature and pressure.

References:
Fig. 1. Activity of CO hydrogenation over Cu-Zn(36-4wt.%)/Al₂O₃ (Sol), and a catalyst (N211) physically mixed CuO-ZnO(50-50wt.% and Al₂O₃). Catalyst: 0.5 g, H₂/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

Fig. 2. H₂/(H₂+CO) and activity of CO hydrogenation over Cu-Zn(36-4wt.%)/Al₂O₃ at 220 °C. Catalyst: 0.5 g, (H₂+CO)/Ar = (Total 15 ml min⁻¹)/1.5 ml min⁻¹.

Fig. 3. Effect of pressure on activity of CO hydrogenation over Cu-Zn(36-4wt.%)/Al₂O₃ catalyst at 220 °C. Catalyst: 0.5g, H₂/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

Fig. 4. Effect of pressure on selectivity of CO hydrogenation over Cu-Zn(36-4wt.%)/Al₂O₃ catalyst at 220 °C. Catalyst: 0.5g, H₂/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.
Fig. 5. Time course of activity on CO hydrogenation over Cu-Zn(36-4wt.%)Al2O3 catalyst at 220 °C under 1.1 MPa. Catalyst: 0.5g, H2/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

Fig. 6. Time course of selectivity on CO hydrogenation over Cu-Zn(36-4wt.%)Al2O3 catalyst at 220 °C under 1.1 MPa. Catalyst: 0.5g, H2/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

Table 1  Comparison of reaction results on direct DME synthesis between our single-type catalyst and some mixed catalysts developed by some companies [5]

<table>
<thead>
<tr>
<th>Catalyst type</th>
<th>Single type</th>
<th>Mixed type</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cu-Zn/Al2O3 prepared using sol-gel method)</td>
<td>(Methanol-synthesis, dehydration condensation, and water-gas shift reaction catalysts)</td>
<td></td>
</tr>
<tr>
<td>Developer</td>
<td>Shizuoka Univ.</td>
<td>JFE (NKK)</td>
</tr>
<tr>
<td>H2/CO Ratio</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Reactor type</td>
<td>Fixed bed reactor</td>
<td>Slurry reactor</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
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<td>250-280</td>
</tr>
<tr>
<td>Reaction pressure (MPa)</td>
<td>1.6</td>
<td>5-6</td>
</tr>
<tr>
<td>One-pass conversion (%)</td>
<td>5-15</td>
<td>55-60</td>
</tr>
<tr>
<td>DME/(DME+Methanol)(%)</td>
<td>98</td>
<td>90</td>
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