Development of Cu/ZnO/Al₂O₃ Catalyst for Dimethyl Ether Synthesis from CO–CO₂–H₂ Mixture

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The objective of this study is to develop a catalyst for direct synthesis of dimethyl ether ((CH₃)₂O, DME) from a CO–CO₂–H₂ mixture such as blast furnace gas. For this purpose, precipitated Cu–ZnO–X (X=Al₂O₃, Cr₂O₃, ZrO₂ or Ga₂O₃) were systematically prepared by changing chemical composition and their catalytic activity was measured. For Cu–ZnO–Al₂O₃ catalyst, compositional research was on two parameters, namely Cu/ZnO ratio (3/7–5/5) and content of Al₂O₃ (0–33.0 mol%). The influence of each parameter was estimated by DME and MeOH yields for the same catalyst mass. Some Cu–ZnO–Al₂O₃ catalysts synthesized DME more than MeOH, in which the DME activity was related to specific surface area and existence of broadened ZnO peaks in XRD patterns. In contrast, three other Cu–ZnO catalysts including another oxide (Cr₂O₃, ZrO₂ or Ga₂O₃) synthesized only MeOH without DME. Content of Al₂O₃ was more influential on DME synthesis than Cu/ZnO ratio. In conclusion, the most active composition of Cu–ZnO–Al₂O₃ catalyst for DME synthesis was Cu/ZnO=4/6 with 14.3 mol% Al₂O₃ and interestingly this composition was included within the range of usual MeOH synthesis catalysts.

KEY WORDS: dimethyl ether; Cu–ZnO–Al₂O₃; catalyst; blast furnace; energy; industrial waste gas; CO–CO₂–H₂.

1. Introduction

As a method of reducing CO₂ discharge from a blast furnace (BF), catalytic synthesis of methanol (CH₃OH, MeOH) has been reported in previous papers.^{1–4)} MeOH is attracting worldwide attention, because it is not only an important industrial raw material for chemicals such as formaldehyde,⁵⁾ but is also a clean fuel which burns without emission of NO_x and SO_x. For the same reason, dimethyl ether ((CH₃)₂O, DME) is also expected to be a clean energy source with large calorific value and easy transportation properties, the same as LPG.⁶⁾ In addition, DME synthesis is more advantageous than MeOH,⁵⁾ from a thermodynamics viewpoint, because its equilibrium yield is much larger. For this reason, we should pay much more attention to DME synthesis. DME can also easily be reformed to MeOH by hydrolysis, if necessary.

However, DME catalysis from CO₂-containing synthesis gas has been rarely published in spite of its significance. Industrially, DME is generally produced from MeOH by using catalysts such as Al₂O₃. Thus, major attention^{8–12)} has been directed to develop a catalyst with the function of dehydration. For synthesizing DME directly from CO–CO₂–H₂ mixtures, not MeOH, we showed in previous studies^{4,7)} that a hybrid catalyst of

Cu–ZnO–Ga₂O₃ and γ-Al₂O₃ is relatively effective, in which the two are physically mixed. This new catalyst appealed to the possibility of direct DME synthesis from industrial waste gas containing much CO₂, such as BF offgas. However, it is not easy to uniformly mix different density catalysts in a packed bed reactor and to determine the optimum mixing ratio of the hybrid catalyst. The hybrid catalyst causes another problem for application in a state-of-the-art slurry reactor, because mixture of the two catalysts is difficult in liquid due to their density difference. Thus a single catalyst for DME synthesis from a CO–CO₂–H₂ mixture is very attractive from not only an academic but also an industrial viewpoint.

The aim of this study is to develop catalysts for synthesizing DME from CO–CO₂–H₂ mixtures such as BF offgas and, particularly, to determine an optimum composition of Cu, ZnO and Al₂O₃ for high yield of oxygenates (MeOH + DME), in which Cr₂O₃, ZrO₂ or Ga₂O₃ were also examined instead of Al₂O₃.

2. Materials

For synthesizing DME from CO–CO₂–H₂ mixtures such as BF gas, we prepared catalysts of Cu–ZnO–X (X=Al₂O₃, Cr₂O₃, ZrO₂, Ga₂O₃) by the precipitation

Table 1. Chemical composition of fifteen catalysts used.
Cu/ZnO/Al₂O₃ system

Cu/ZnO	Al ₂ O ₃ mol%	Composition, mol%
3/7	0.0	30.0/70.0/ 0.0
	6.7	28.0/65.3/ 6.7
	14.3	25.7/60.0/14.3
	23.1	23.1/53.8/23.1
	33.0	20.0/47.0/33.0
4/6	0.0	40.0/60.0/ 0.0
	6.7	37.3/56.0/ 6.7
	14.3	34.3/51.4/14.3
	23.1	30.8/46.1/23.1
5/5	6.7	46.7/46.7/ 6.7
	14.3	42.9/42.9/14.3
	23.1	38.5/38.5/23.1

Cu/ZnO/Oxide (Cr ₂ O ₃ , ZrO ₂ , Ga ₂ O ₃) system		
Cu/ZnO	Oxide mol%	Composition, mol%
3/7	14.3	25.7/60.0/14.3

method. Chemical composition of the catalysts prepared is given in **Table 1**. Twelve catalysts of the Cu–ZnO–Al₂O₃ system were prepared, in which additive content of alumina was systematically changed under three different ratios of Cu/ZnO. In addition, three catalysts with different oxides (Cr₂O₃, ZrO₂, Ga₂O₃) instead of alumina were also prepared for comparison. The preparation procedure of the catalysts was reported in detail elsewhere.^{2,4,5)} For the Cu–ZnO–Al₂O₃ catalyst, the procedure framework is as follows;

(1) Three commercial chemicals of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O are first dissolved in distilled water at room temperature, to obtain aqueous solutions of 1 mol/dm³ with the desired molecular ratio of the metallic elements.

(2) The obtained solution and 0.7 mol/dm³ sodium carbonate (Na₂CO₃·10H₂O) solution are mixed at 353 K all at once, to precipitate the carbonates of Cu, Zn and Al. The precipitate, recovered by filtration, is sintered at 673 K after sufficient drying at 393 K.

(3) Next, the sinter is crushed in a mortar and particles of size 0.35–0.84 mm are separated by sieving for packing into a reaction tube.

(4) The packed catalyst is finally reduced by pure hydrogen at 653 K just before the experiments.

3. Method

Figure 1 shows a schematic diagram of an experimental system for DME synthesis, consisting of three parts: gas supplier, fixed-bed reactor and gas analyzer. The molar ratio of feed gas excluding nitrogen, CO/CO₂/H₂=4/4/1 (molar basis), corresponds to operating data¹⁾ of a BF with natural gas injection of 50 Nm³ per ton-hot-metal. Nitrogen was added to the feed gas to avoid CO₂ liquification in the cylinder so the composition of the actual feedgas is CO/CO₂/H₂/N₂=35/35/8.7/21.3. After the feedgas was introduced, outlet gas from the fixed-bed reactor was analyzed by two kinds of gas chromatography: FID (Flame Ionization Detector) for DME,

Fig. 1. Experimental apparatus for dimethyl ether and methanol synthesis.

FID: Flame Ionization Detector
TCD: Thermal Conductivity Detector

Fig. 2. Schematic representation of catalytic fixed bed reactor.

MeOH and hydrocarbon(HC, mainly methane), and TCD (Thermal Conductivity Detector) for CO, CO₂, H₂ and N₂.

An enlargement of the reactor is shown in **Fig. 2**. The reactor employed was made of SUS316 stainless steel tube with 10mm outer diameter and 8mm inner diameter. The prepared catalyst was fixed at the middle position of the uniform temperature zone, on which glass beads were placed for preheating the feed gas and for obtaining radially-uniform flow. To measure temperature changes of the catalyst during the experiment, we introduced a CA type thermocouple, 1mm in outer diameter, into the bed. The experimental conditions of this study were 523 K, 1.0 MPa inlet pressure and

Fig. 3. Measured yields of methanol and dimethyl ether for all catalysts.

1.0×10^{-6} m³/sec (STP) flowrate of the feed gas. These were determined based on our previous studies.^{2,3)} The measurements were continued until outlet gas composition reached a steady state.

4. Results and Discussion

All monitored components of the outlet gas (CO, CO₂, H₂, MeOH, DME, HC, N₂) reached constant values with negligible further temperature changes after approximately 6 h. The obtained concentrations of MeOH and DME for each catalyst were then defined as their final yields. Figure 3 shows bar graphs of evaluated yields of DME and MeOH, for all of the catalysts prepared. Here, Cu/ZnO ratio in the catalysts in the horizontal direction of the graph is constant and the three rows of the graph are for different Cu/ZnO ratios: 3/7, 4/6 and 5/5. The bar height indicates the DME and MeOH yields. Obviously, some catalysts of Cu–ZnO–Al₂O₃ gave good yields of DME with little MeOH synthesis although only MeOH is normally synthesized from CO–H₂ gas as mentioned later. The results suggest significant influence of Al₂O₃ content on DME yields, in comparison to Cu/ZnO ratio. The highest yield of DME+MeOH was given by the catalyst of 14.3% Al₂O₃ with Cu/ZnO=4/6. Performance of this catalyst ($0.159 + 0.024 = 0.183$ C mol%/g-cat.) is the same level as the hybrid catalyst ($0.160 + 0.018 = 0.178$ * C-mol%/g-cat.). In contrast, addition of oxides of Cr₂O₃, ZrO₂ and Ga₂O₃ instead of Al₂O₃ did not cause DME generation, although Cu–ZnO–Ga₂O₃ showed the highest yield of MeOH among all of the catalysts.

To make clear the effects of Al₂O₃ content and Cu/ZnO ratio in the Cu–ZnO–Al₂O₃ system, we redrew data in the following two figures. Figure 4 shows the effect of Al₂O₃ content on DME and MeOH yields with Cu/ZnO=3/7. The sharp rise in DME yield indicates strong sensitivity to Al₂O₃ content, in comparison to the MeOH yield. Both peaks of DME and MeOH curves were inter-

Fig. 4. Effect of alumina content on dimethyl ether and methanol yields over catalysts of Cu/ZnO=3/7, together with other oxides.

estingly identically located at 14.3 mol% Al₂O₃. Similar tendencies were also observed for the other Cu/ZnO ratios of 4/6 and 5/5. This is explained well by the concept⁷⁾ that DME is produced by a series reaction *via* MeOH synthesis (BF gas → MeOH → DME).

Figure 5 shows the effect of Cu/ZnO ratio on yields of DME and MeOH. Peaks of DME curves were observed at Cu/ZnO=4/6, with weak dependence on Cu/ZnO ratio. Strangely, Cu–ZnO catalysts without Al₂O₃ showed little activity for DME and MeOH syntheses, in spite of experimental reports⁸⁾ claiming that Cu–ZnO is effective for synthesizing MeOH from mixtures of CO, H₂ and a little CO₂. In addition, they claimed no effect of Cu–ZnO–Al₂O₃ catalyst on DME synthesis at all, although the chemical composition of industrial catalysts (Cu: 12–66 mol%, ZnO: 17–62 mol%, Al₂O₃: 4–38 mol%) covers this study's best catalyst (34.3/51.4/14.3). This is mainly due to syngas composition (CO–CO₂–H₂). Regarding the relationship between syngas

* This value was estimated from Ref. 7) by unifying a unit.

Fig. 5. Effect of Cu/ZnO ratio on yields of dimethyl ether and methanol.

Fig. 6. Effect of Al₂O₃ content and oxides on specific surface area of catalysts with molar ratio of Cu/ZnO = 3/7.

composition and catalyst composition, a noteworthy result was recently reported by Fujita and coworkers.¹²⁾ They examined the catalyst mechanism of Cu–ZnO under CO–H₂ and CO₂–H₂ by means of diffuse reflectance FT-IR spectroscopy. The result demonstrated that Cu promotes CO₂ conversion to MeOH and ZnO promotes CO conversion. This suggests that the CO/CO₂ ratio of syngas would have significant influence on the optimum catalyst composition in the Cu/ZnO system. Therefore a similar study should be extended to CO–CO₂–H₂ mixtures for constructing an advanced catalyst theory.

Figure 6 shows measured surface area of the catalysts of Cu/ZnO = 3/7. The measured specific surface area showed strong Al₂O₃-content dependence. Interestingly, this result can explain well the catalyst property of the Cu–ZnO–Al₂O₃ system (see Fig. 3). That is, we can conclude that the catalysts with large surface area cause

Fig. 7. SEM photographs of 14.3 mol% Al₂O₃ catalysts with Cu/ZnO = 4/6. (Top: ×20 k, Bottom: ×50 k)

high yields of DME. The surface area of 14.3 and 23.1 mol% Al₂O₃ catalysts (approximately 33 m²/g) were more three times higher in comparison to the catalyst without Al₂O₃. Judging from scanning electron microscopy (SEM) observations (Fig. 7), this difference of surface area is induced by the surface structure of the obtained catalysts, because the 14.3 mol% Al₂O₃ catalyst has a rough skin with fine particles. Conversely speaking, control of nucleus generation in catalyst preparation for increasing the effective surface area of the catalyst is crucial. Similarly, the 14.3 mol% Ga₂O₃ catalyst showed large surface area and good catalyst properties. However, this applied to only MeOH synthesis, not DME synthesis.

Figure 8 shows XRD (X-ray diffraction) patterns of the Cu–ZnO–Al₂O₃ catalysts used, in which three substances of Cu, ZnO and ZnAl₂O₄ were detected as main peaks. Peaks of Al or Al₂O₃ never appeared in spite of our expectation. With increasing Al₂O₃ from 0 to 14.3 mol%, peaks of Cu and ZnO were broadened and their heights became smaller. In this range, the catalysts became more active for DME and MeOH synthesis with increasing Al₂O₃ (see Fig. 4). In contrast, 23.1 and 33.0 mol% Al₂O₃ catalysts showed ZnAl₂O₄ peaks instead of ZnO peaks, however its peak width was very broad. In addition, the Cu peaks of the 33.0 mol% catalyst became very weak. According to these results, we can expect that the optimum composition of the catalyst would range between 14.3 and 23.1 mol% Al₂O₃. As for the mechanism of DME direct synthesis

Fig. 8. XRD patterns of catalysts with molar ratio of Cu/ZnO=3/7.

from CO-CO₂-H₂, Al₂O₃ micro-structure must be a key point as mentioned above. Microscopic research of catalyst structure is also needed in the future.

5. Conclusion

Fifteen kinds of Cu-ZnO-Al₂O₃ and Cu-ZnO-Oxide (Cr₂O₃, ZrO₂, Ga₂O₃) catalysts were systematically studied for direct synthesis of DME from CO-CO₂-H₂ mixture. The experimental conditions were 523 K, 1.0 MPa pressure and 2.0 g catalyst weight. The following conclusions were drawn:

(1) The most noteworthy finding is the significant

catalytic activity of Cu-ZnO-Al₂O₃ in DME synthesis, not MeOH, from CO-CO₂-H₂ mixture. The catalyst of 34.3Cu-51.4ZnO-14.3Al₂O₃ (Cu/ZnO=4/6 (mole basis)) showed the best activity for DME synthesis.

(2) Addition of oxides other than Al₂O₃ to the Cu-ZnO system was not effective for DME synthesis at all, although Cu-ZnO-Ga₂O₃ catalyst showed the best activity for MeOH synthesis.

(3) The catalytic mechanism of the system of Cu-ZnO-Al₂O₃ is still not well explained. However, catalysts showed strong relationship between DME activity and surface area, and XRD peaks of ZnO in active catalysts tend to be broadened without Zn and ZnAl₂O₄ peaks.

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