1. Introduction

Production of methanol from CO\textsubscript{2} by hydrogenation is a potential method for decreasing CO\textsubscript{2} emissions\textsuperscript{1)}~\textsuperscript{3}). Dehydration of the methanol can form dimethyl ether (DME, CH\textsubscript{3}OCH\textsubscript{3}), a source of clean energy. DME does not emit particulate matter (PM) since it contains no C-C bond. The chemical properties are very similar to those of liquefied petroleum gas (LPG)\textsuperscript{3,4}). Therefore, DME is a promising fuel that can be synthesized from CO\textsubscript{2} emissions.

Scheme 1 shows the overall DME synthesis from CO\textsubscript{2} and H\textsubscript{2} via methanol, which involves methanol synthesis (1) and methanol dehydration (2), whereas reverse water gas shift (RWGS) (3) and methanol decomposition (4) are undesirable side reactions resulting in CO formation.

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (1)
\]
\[
2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (2)
\]
\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3)
\]
\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad (4)
\]

Cu-Zn catalysts are widely utilized for methanol synthesis via CO\textsubscript{2} hydrogenation (1)\textsuperscript{5)~7}). In addition, In\textsubscript{2}O\textsubscript{3} catalysts\textsuperscript{8,9)} and TiO\textsubscript{2}-based catalysts\textsuperscript{10,11)} have been reported as a catalyst for methanol synthesis in recent years. Solid acid catalysts, such as zeolite, are widely utilized for methanol dehydration (2), whereas reverse water gas shift (RWGS) (3) and methanol decomposition (4) are undesirable side reactions resulting in CO formation.

\[
\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad (1)
\]
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2\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad (2)
\]
\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad (3)
\]
\[
\text{CH}_3\text{OH} \rightarrow \text{CO} + 2\text{H}_2 \quad (4)
\]
reverse water gas shift (3) and methanol decomposition (4). By-product water can cause deactivation of the Cu-Zn and zeolite catalysts\(^{16}\). Therefore, direct synthesis of DME from a CO\(_2\)-H\(_2\) mixture requires high methanol selectivity.

DME synthesis from a mixture of CO\(_2\) and H\(_2\) using a tandem reactor has been extensively investigated to improve the process efficiency by omitting the dehydration step. A catalyst specific for DME synthesis was prepared by mixing a methanol synthesis catalyst with a methanol dehydration catalyst\(^{17\text{-}21}\). DME synthesis rarely uses methanol synthesis catalysts other than Cu-Zn catalysts\(^{22,23}\). Cu-Zn catalysts are optimized for CO hydrogenation (a current methanol synthesis process), but are not sufficient active for CO\(_2\) hydroge-
nation\(^{24}\). Cu-Zn catalysts are not suitable for DME synthesis in the tandem reactor because of the significant poisoning by water. Therefore, new cata-
lysts must be developed that are specific for CO\(_2\) hydrogenation.

Recently, we reported the use of copper nanoparticles supported on amorphous ZrO\(_2\) (Cu/a-ZrO\(_2\); denoted as CZ) as an active catalyst for CO\(_2\) hydrogenation\(^{25\text{-}27}\). The most significant feature of the CZ catalyst is the high selectivity for methanol compared to the Cu-Zn catalyst because methanol decomposition (4) is suppressed\(^{26}\). Furthermore, the CZ catalyst is presumably more resistant to water than the Cu-Zn catalyst because the a-ZrO\(_2\) support has a large number of hydroxyl groups on the surface. In contrast, DME formation via methanol dehydration (2) depends on the acidity of the solid acid catalyst. Acidic zeolites (FER, MFI, and CHA) and a-Al\(_2\)O\(_3\) are employed for DME formation due to their satisfactory catalytic performances\(^{19\text{-}21}\). FER has the highest activity because of the strong acid sites\(^{20}\). Therefore, the CZ catalyst, in combination with a solid acid catalyst, is a potential catalyst for DME synthesis from the CO\(_2\)-H\(_2\) mixture.

The present study investigated DME synthesis from a mixture of CO\(_2\) and H\(_2\) using a mixture of CZ catalyst with FER-type zeolite. For comparison of catalytic activity, we also prepared a Cu/ZnO/Al\(_2\)O\(_3\) catalyst mixed with FER-type zeolite. Evaluation of the catalytic performances revealed the advantage of the CZ catalyst for one pass DME synthesis from a CO\(_2\)-H\(_2\) mixture.

2. Experimental

2.1. Catalyst Preparation

The CZ catalyst was prepared by an incipient wetness impregnation method using amorphous ZrO\(_2\) (NND supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd.) and copper nitrite monohydrate (Cu(NO\(_3\))\(_2\); Kanto Chemical Co., Inc.). a-ZrO\(_2\) was impregnated with an aqueous solution of Cu(NO\(_3\))\(_2\). The gel was dried at 110 °C overnight and calcined at 350 °C for 5 h in an electric furnace. According to our previous research\(^{25\text{-}27}\), copper cations in the catalyst were doped into the amorphous ZrO\(_2\). Cu/ZnO/Al\(_2\)O\(_3\) (MDC-7 supplied by Clariant K.K.; denoted as MDC) was used as a Cu-Zn catalyst in this experiment.

FER-type zeolite (HSZ-720KOA supplied by Tosoh Corp.) was protonated with ammonium nitrate solution and then calcined at 500 °C in air prior to use. The protonated sample was named FER.

For the activity test, the copper-based catalyst and the FER-type zeolite were physically mixed in an agate mortar for 10 min with the same copper content. Therefore, the amount of the mixed catalyst used for the activity test was as follows: (i) 500 mg of CZ, (ii) 500 mg of CZ and 100 mg of FER (denoted as CZ + FER), (iii) 100 mg of MDC, and (iv) 100 mg of MDC and 100 mg of FER (denoted as MDC + FER).

2.2. Characterization

The specific surface areas (SSAs) of the copper based catalyzed FER zeolite were measured by N\(_2\) adsorption at 77 K (BELSORP-mini II, MicrotracBEL Corp.) after a heat treatment to remove surface moisture. The copper content of the CZ and the MDC, and SiO\(_2\)/Al\(_2\)O\(_3\) molar ratio of FER, were measured by X-ray fluorescence (XRF, Epsilon I, Malvern PANalytical). Transmission electron microscopy (TEM) images of the mixed catalysts of CZ + FER and MDC + FER were collected using a JEM-2100F (JEOL Ltd.) operated at 200 kV. The exposed surface areas of metallic copper of the CZ and the MDC were measured by an N\(_2\)O titration technique, according to our previous study\(^{27}\). We previously reported that the interaction between copper and a-ZrO\(_2\) prevents N\(_2\)O molecules from oxidizing the metallic copper surface, which hinders the accurate measurement of the surface area of metallic copper\(^{27}\). Therefore, the space velocity and catalytic activity for the reaction test were normalized by the copper amount rather than by the copper surface area. Furthermore, the amount of acid site on FER was evaluated by NH\(_3\)-temperature-programmed desorption (TPD) measurement after removing moisture adsorbed on the surface at 500 °C. H\(_2\)O titration and NH\(_3\)-TPD were measured using a BELCAT (MicrotracBEL Corp.).

2.3. Activity Test

Catalytic activity tests were conducted using a high-pressure fixed-bed flow tubular reactor (PID Eng&Tech, Microactivity Effi reactor). The catalyst was charged into the reactor with 5.0 g of quartz sand as a diluent. After H\(_2\) reduction (H\(_2\)/N\(_2\) = 10/50 mL min\(^{-1}\)) at 300 °C for 2 h, stabilizing treatment was conducted at 270 °C for 12 h to evaluate the stable activity. The feed gas was supplied at 42 mL\(_{STP}\) min\(^{-1}\) with composition of CO\(_2\)/H\(_2\)/N\(_2\) = 1/3/1. Thus, the feed gas volume per unit time per unit weight (denoted as F/W) was ca. 70 L\(_{STP}\) h\(^{-1}\) g\(_{Cu}\)^{-1}. The reaction temperature and pressure were 180-230 °C and 1.0 MPa, respectively. The
products were analyzed using gas chromatographs equipped with a flame ionization detector (FID, for the detection of CH₃OH and DME) and a thermal conductivity detector (TCD, for the detection of N₂, CO, and CO₂). The conversion and selectivity were calculated based on the carbon products.

3. Results and Discussion

3.1. Catalyst Properties

The SSAs of the CZ and MDC catalysts were 221 m² g⁻¹ and 61 m² g⁻¹, respectively, as shown in Table 1. The SSA of the CZ catalyst was larger than that of the MDC catalyst due to the amorphous support. The copper contents of the CZ and MDC catalysts were 7 wt% and 38 wt%, respectively (Table 1). The copper content of the MDC catalyst was five-fold higher than that of the CZ catalyst. The exposed surface areas of metallic copper of the CZ and MDC catalysts were 7.8 μmol g⁻¹ and 118 μmol g⁻¹, respectively (Table 1). The metal surface area for the MDC catalyst was larger than that for the CZ catalyst. Therefore, the amount of surface copper acting as the active sites of the CZ catalyst was much smaller than that of the MDC catalyst, although the CZ catalyst had a larger SSA. The SiO₂/Al₂O₃ molar ratio, SSA, and amount of acid sites of the FER catalyst were 18.1, 384 m² g⁻¹, and 0.25 mmol-NH₃ g⁻¹, respectively.

Figure 1 shows the TEM images of the mixed catalysts of CZ + FER and MDC + FER. The FER particles of 400-500 nm size were partially covered with copper-based catalyst particles of <50 nm size. The particle sizes were almost the same in the copper-based and FER catalysts, and contact between these catalysts was confirmed.

3.2. Comparison with Cu–Zn Catalyst

First, the activities of the CZ, CZ + FER, MDC, and MDC + FER catalysts were compared. Figure 2 presents the formation rates of DME, CH₃OH, and CO in DME synthesis from CO₂-H₂ mixture over these catalysts at 230 °C, and the carbon-based selectivity based on the total of CH₃OH and DME. Since neither CZ nor MDC produced any DME, the presence of FER was essential for methanol dehydration to form DME (2). CO₂ conversions over CZ, CZ + FER, MDC, and MDC + FER catalysts were 2.4, 3.0, 4.3, and 1.9 %, respectively. Since the formation rate of CO via the sequential reaction (4) is substantially dependent on CO₂ conversion, the CO formation rate over the CZ + FER catalyst was higher than that over the CZ catalyst, indicating that the sequential reaction (4) proceeded over both CZ and FER catalysts. The methanol yield of CZ (9 mmol h⁻¹ g Cu⁻¹) was higher than that of MDC (7 mmol h⁻¹ g Cu⁻¹), and the methanol selectivity of CZ

| Table 1 Properties of the Catalysts |
|---|---|---|---|
| Catalyst | SSA [m² g⁻¹] | Cu content [wt%] | N₂O conc. [μmol g⁻¹] |
| CZ | 221 | 7 | 7.8 |
| MDC | 61 | 38 | 118 |
| FER | 384 | - | - |

Percentages in the figure correspond to the CH₃OH + DME selectivity. F/W: ca. 70 LSTP h⁻¹ g Cu⁻¹.

Fig. 2 Catalytic Activity of the Prepared Catalysts for Conversion of the CO₂ and H₂ Mixture at 230 °C and 1.0 MPa

J. Jpn. Petrol. Inst., Vol. 63, No. 6, 2020
(64.0 %) was higher than that of MDC (29.6 %). Therefore, CZ catalyst was more specific for CO2-to-methanol hydrogenation than MDC, consistent with our previous report. The formation rates of CH3OH and DME over CZ + FER (6 mmol h\(^{-1}\) g\(_{\text{Cu}}\)\(^{-1}\)) were approximately three-fold higher than those over MDC + FER (2 mmol h\(^{-1}\) g\(_{\text{Cu}}\)\(^{-1}\)) despite the same F/W (ca. 70 L\(_{\text{STP}}\) h\(^{-1}\) g\(_{\text{Cu}}\)\(^{-1}\)). Such improvement may be significant for the manufacturing processes of chemical products from CO2-H2 mixture.

Next, the relationship between CO2 conversion and product selectivity over CZ + FER and MDC + FER catalysts was investigated (Fig. 3). CO2 conversion was controlled by changing the F/W: CO2 conversion increased with lower F/W from 20 to 120 L\(_{\text{STP}}\) h\(^{-1}\) g\(_{\text{Cu}}\)\(^{-1}\). CO selectivity increased with higher CO2 conversion, whereas methanol and DME selectivity simultaneously decreased. Therefore, methanol decomposition (4) is inevitable at high CO2 conversion over both catalysts. This study focused on the trendline between CO2 conversion and CO selectivity. The trendline for the CZ + FER catalyst was below 60 C-%, whereas that of MDC + FER is above 60 C-%. CZ catalyst shows relatively low activity for the undesirable methanol decomposition (4), leading to high selectivity for DME and methanol. Therefore, the catalytic activity of DME formation over the mixture of Cu-based catalyst and FER-type zeolite could be increased by changing the CuZnO/Al2O3 catalyst to the CZ catalyst.

### 3.3. Performance of CZ Catalyst

**Figure 4** shows the effect of the amount of zeolite addition on the activity of CZ + FER catalyst. CO2 conversion was almost the same due to the introduction of the same amount of CZ catalyst into the catalyst bed, which converts CO2 to methanol. The CZ + FER catalyst showed sufficient DME synthesis activity: DME selectivity was ca. 30 % with 500 mg of CZ mixed with a small amount of FER (25 mg). However, further increase in the amount of FER from 25 to 500 mg did not affect the DME selectivity, probably due to the extent of the equilibrium between CH3OH and DME (2).

**Figure 5** shows the temperature dependence of CO2 conversion and DME selectivity over the CZ + FER and MDC + FER catalysts. The CZ + FER catalyst showed higher activity than the MDC + FER catalyst at all temperatures. In particular, the difference in catalytic activity was remarkable at high temperatures at which large amounts of water were produced. Therefore, the catalytic activity of CZ + FER was superior for DME synthesis from CO2-H2 mixture.

The high DME yield over our CZ + FER system probably results from the superior catalytic perfor-
formance of the CZ catalyst for CO$_2$-to-methanol hydroge- 
nation. This study used the CZ catalyst (7 wt% Cu/a- 
ZrO$_2$), which showed the best performance for metha-
olan production among a series of Cu/a-ZrO$_2$ catalysts$^{25}$. 
The CZ catalyst produced more methanol than the 
MDC catalyst even with F/W of ca. 8 LSTP h$^{-1}$ g-cat$^{-1}$ $^{27}$ 
(contact time normalized by catalyst weight) and ca. 70 
LSTP h$^{-1}$ g-Cu$^{-1}$ (contact time normalized by Cu load-
ing, present Fig. 2). However, the low conversion of 
CO$_2$ is one of the drawbacks of the CZ + FER system 
for industrial applications, due to the catalytic perfor-
ance limitations of the CZ catalyst. In the future, we 
intend to further improve the activity of the CZ catalyst 
for DME formation.

4. Conclusion

The CZ + FER catalyst has potential for DME syn-
thesis from CO$_2$-H$_2$ mixture at 230 °C. The CZ can 
convert CO$_2$ selectively to methanol and suppress unde-
sirable CO formation. The present study revealed that 
using a catalyst with high methanol selectivity from 
CO$_2$-H$_2$ mixture, such as the Cu/a-ZrO$_2$ catalyst, 
compared to the Cu-Zn catalyst, can directly synthesize 
chemicals such as DME.

Acknowledgment

We are grateful to Dr. Takashi Toyao and Mr. Ting 
Kah Wei, Hokkaido University, for their kind help with 
the TEM measurements. This research was supported 
by the Cooperative Research Program of Institute for 
Catalysis, Hokkaido University (Grant, 19B1012), 
Japan, and Unexplored Challenge 2050, New Energy 
and Industrial Technology Development Organization 
(NEDO), Japan.
要   旨
非晶質ジルコニア担持銅触媒と FER 型ゼオライト複合触媒上の CO₂-H₂混合ガスからのジメチルエーテル合成

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CO₂と H₂の混合ガスから一段でのジメチルエーテル（DME）合成を目的として、Cu 系触媒とゼオライトの混合触媒の触媒性能を評価した。非晶質ジルコニアを担体とした担持銅触媒（Cu/a-ZrO₂）と FER 型ゼオライトの混合触媒は、CO₂水素化に用いられる Cu/ZnO/Al₂O₃と FER 型ゼオライトの混合触媒よりも高い DME 収率を示した。非晶質ジルコニアを担体とすることで、副反応である CO 生産が抑制されるため、高い DME 収率を示したと考えられる。また、FER 型ゼオライトはメタノール脱水に有効な触媒を有しており、これらの混合が CO₂から一段での DME 合成に有効であることが示された。反応圧力 1.0 MPa、反応温度 230 ℃の条件での DME 選択率は、その条件での平衡組成である 40 % に近い値を示しており、Cu/ZnO/Al₂O₃との混合触媒よりも約 2 倍の DME 生成量を達成した。