Direct synthesis of dimethyl ether from carbon dioxide and from mixture of carbon dioxide and carbon monoxide over copper alumina catalysts prepared by using the sol-gel method

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Abstract— Cu-Zn/Al_2O_3 catalyst and Cu-Ga/Al_2O_3 catalyst were prepared by using consecutive sol-gel method. These catalysts were used for direct synthesis of dimethyl ether (DME) from carbon dioxide, and from mixture of carbon dioxide and carbon monoxide. For comparison, a mixed catalyst of methanol synthesis catalyst and methanol dehydration catalyst was prepared according to a patent. The catalysts prepared by the sol-gel method are more effective for DME and methanol synthesis from CO_2. Cu-Ga/Al_2O_3 catalyst is more effective for higher DME selectivity than Cu-Zn/Al_2O_3 catalyst. These significant catalysts were also tested for direct DME synthesis from mixture of CO_2 and CO. The Cu-Zn/Al_2O_3 catalyst is more effective than the Cu-Ga/Al_2O_3 catalyst in this case.

Keywords— Dimethyl ether (DME), direct synthesis, carbon dioxide, carbon monoxide.

I. INTRODUCTION

DIMETHYL ether (DME) is expected as one of clean fuels and energy for the 21st century [1, 2], because DME burns with emission of no particulate matter (PM), no SOx, and less NOx. The cetane number of DME is 55-60, and DME is attractive as a clean fuel for diesel engines. Physical properties are similar to those of liquefied petroleum gas (LPG). DME is easily liquefied at -25 °C under atmospheric pressure, and under 0.6 MPa at ambient temperature. DME is easily handled like LPG. DME will be produced from coal, natural gas from small and medium-size gas field, biomass, and so forth. In China, there are many DME plants with more than 10,000 tons/year capacity. The produced DME is mixed with LPG, and the mixed DME/LPG is used for cooking and heating as domestic fuel. DME has also recently become a potential fuel for hydrogen production to be used in fuel cells. There is possibility that DME infrastructures will be settled more rapidly than those of hydrogen, because LPG infrastructures existing are able to use for DME. The syngas is produced from natural gas, coal, coal bed methane, biomass, and so on. Therefore, DME is a multi-use and multi-source fuel.

DME is mainly produced by dehydration of methanol and is a byproduct of the methanol manufacturing process. However, DME and new technologies for DME production have recently drawn attention as contributors to creating a stable energy supply and demand in the future. They also have environmental benefits because DME is produced through syngas from multiple sources. There are two methods of industrialized and demonstrated new technologies for DME production: indirect DME synthesis (a two-step process) and direct DME synthesis (a one-step process).

For the indirect-synthesis method, methanol is produced from syngas and the produced methanol is dehydrated to DME; these two processes are carried out in different reactors. For methanol dehydration, solid catalysts such as γ-alumina, zeolite and sulfuric acid are used. Therefore, costs for development are also reduced. The rationalized industrial plant can be installed promptly. However, the system will be complicated because the products are a mixture of DME, methanol and water, and thus distillation, purification and recycling processes will be needed. The price of DME depends on the price of methanol, with the DME price usually approximately twice that of methanol. This is a big problem for this method. There are some disadvantages, as discussed previously, but all industrial DME plants in the world use this indirect DME-synthesis method.

In the direct-synthesis method, DME is produced from syngas directly in a reactor. The merit of the direct synthesis method is that the manufacturing process is economical because the methanol synthesis and dehydration processes are performed in one reactor. The equilibrium conversion of syngas is much higher compared with the conversion of the methanol synthesis, and it is possible to reduce the unreacted gas ratio so that it is very low. The reaction equation of the direct synthesis method is shown in Equation 1; copper-based catalysts are used for this method as they are very effective in the water–gas shift reaction. Therefore, this method is more suitable to use with CO-rich gas than methanol synthesis and indirect DME synthesis [3, 4].

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \qquad (1)$$

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This method is known as the one-step process, but actually consists of three reaction steps: methanol synthesis (Equation 2), methanol dehydration (Equation 3) and the water–gas shift reaction (Equation 4). For methanol synthesis, copper-based catalysts are usually used. The copper-based catalysts work for the water–gas shift reaction, which occurs by H_2O produced from the methanol dehydration and CO in the same reactor.

$$CO + 2H_2 \rightarrow CH_3OH \qquad (2)$$

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (3)$$

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (4)$$

From this reaction mechanism, a mixture of the methanol-synthesis catalysts, methanol-dehydration catalysts and water–gas shift reaction catalysts is used. Slurry reactors and fixed-bed reactors have been developed for this process by some companies [5-12].

We have developed the excellent direct DME synthesis catalysts by using the sol-gel method. The Cu-Zn/Al_2O_3 catalysts prepared using the sol-gel method have higher activity and selectivity for direct DME synthesis from syngas (mixed gas of H_2 and CO) than usual direct DME synthesis catalysts, mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts [2,13-15]. This time, these sol-gel catalysts are applied for direct DME synthesis from carbon oxides; mixture of CO, CO_2, and H_2. The chemical equation of the direct DME synthesis from CO_2 will be as follows:

$$6H_2 + 2CO_2 \rightarrow CH_3OCH_3 + 3H_2O \qquad (5).$$

This reaction works for utilization of CO_2 and reduces of CO_2 which is one of the major components of green house gases. If excellent catalysts will be developed and be used widely, the problem of global warming and problem of environment such as air pollution will be solved. If hydrogen will be produced using sustainable energies such as sun light power, window power, hydropower, and so on, the produced DME works as hydrogen carrier and energy carrier.

II. EXPERIMENTAL

A. *Catalyst preparation*

In this research, Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst and Cu-Ga(24-6 wt.%)/Al_2O_3 catalyst were used. All catalysts used for this research were prepared by using consecutive sol-gel methods. Cu-Zn/Al_2O_3 and Cu-Ga/Al_2O_3 was obtained by hydrolysis of aluminium isopropoxide (AIP) and ethylene glycol (EG), and mixing of aqueous solution with $Cu(NO_3)_2$, $Zn(NO_3)_2$, or $Ga(NO_3)_2$,respectively. Each amount of $Cu(NO_3)_2$, $Zn(NO_3)_2$, or $Ga(NO_3)_2$ for the catalyst preparation depended on the loading metal amount of the needed catalysts. AIP (purity: 95%), EG, $Cu(NO_3)_2$-$3H_2O$ (purity: 99%), $Zn(NO_3)_2$-$9H_2O$ (purity: 99%) were manufactured by Wako Pure Chemical Industries, Ltd. (Wako). $Ga(NO_3)_2$-nH_2O (Ga content: 19.04%) was purchased from Mitsuwa's Pure Chemicals. For example, Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst was prepared by using consecutive sol-gel method as follows. AIP (29.5 g) was crushed using a mortar, and then dissolved in hot water (~70 ^oC). A small amount of EG (e.g. ~5% of the all solution amount) was added as a sort of a surfactant into the mixed hot water. This mixture was stirred and heated at ~70 ^oC for ~30 min. Then, diluted HNO_3 (Wako) aqueous solution was added every 15 min in several times, and pH of the mixture was lowered with the several addition until the pH decreased to 1-2. Usually all this process took ~5 h. In the way of the HNO_3 addition, a clear-sol of boehmite was formed. A mixed aqueous solution of $Cu(NO_3)_2$-$3H_2O$ (5.76 g) and $Zn(NO_3)_2$-$9H_2O$ (6.89 g) was added into the clear-sol. This mixture was stirred and heated at ~70 ^oC till its volume decreased to less than 200 ml for putting into a egg-plant shaped flask. The condensed mixture and its washing solution were evaporated under reduced pressure using a rotary evaporator for taking out water, and then the gel was obtained. The obtained gel was dried at 170 ^oC for a night. The dried gel was ground using an agate mortar until the diameter of each grain of powder was less than 150 μm. The powder was calcined at 500 ^oC for 5 h, and usually ~10.0-g Cu-Zn(15-15 wt.%)/Al_2O_3 was obtained. Before reaction, 1.0-g Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst was reduced by flowing H_2 (99.99%, 10ml min^{-1}) at 450 ^oC for 10 h. These treatments may be sever condition for copper catalysts, and sinter the metals of the catalysts and the catalysts themselves, and lead to a deterioration of activity. However, we consider that the sintering before reaction is smaller trouble for a comparison of catalyst activity than sintering while reaction. Instead of duration test of the catalysts, the catalysts after this sever pretreatment were compared on the activity, selectivity, and so forth.

Cu-Ga(24-6 wt.%)/Al_2O_3 catalyst was also prepared by the consecutive sol-gel method and pre-treated in the almost same way of the above-mentioned Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst preparation procedure and pre-treatment.

Each catalyst prepared using the sol-gel method was used in single without mixing of an acid catalyst such as alumina.

Patent catalyst developed by Kansai Electric Power Co. (KEPCO) & Mitsubishi Heavy Industries (MHI); one of the mixed catalyst of methanol synthesis catalyst and methanol dehydration catalyst; CuO-ZnO-Al_2O_3-Ga_2O_3-MgO (100:25:15:5:1) & Al_2O_3-ZrO_2 (100:10) was prepared depending on the patent [16].

The reactions were carried out with pressurized fixed bed reactor, and the usual reaction pressure was 0.9 MPaG (absolute pressure 1.0 MPa). Reactant gas flow was $H_2/(CO_2+CO)/Ar = 15.0/5.0/2.0$ ml min^{-1}, and catalyst weight was 0.5 g. Each gas flow was adjusted using four mass flow controllers (Brooks 580E). Online two gas chromatographs were used. The one was for analysis of gas phase and was a Shimadzu GC-14 equipped with a conductivity detector (TCD), a methanizer (for CO analysis), and a flame ionization detector (FID) in series, and had an MS-5A stainless column (60–80 mesh, 5m long, i.d. 3 mm) and its carrier gas was nitrogen. H_2, Ar (as internal standard for GC analysis), CH_4, and CO were quantitatively analyzed. The other GC was for analysis of liquid phase and was a Shimadzu GC-14 equipped with a TCD, and an FID in series, and had a Porapak T stainless column (60–80 mesh, 2m long, i.d. 3 mm) and its carrier gas was helium. CH_4, CO_2, DME, H_2O, methanol, and some hydrocarbons were quantitatively analyzed.

III. RESULTS AND DISCUSSION

The Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst and the patent catalyst were tested for CO_2 hydrogenation, respectively. The results are shown in Fig. 1 and Fig. 2. The Cu-Zn(15-15 wt%)/Al_2O_3 catalyst produced DME fastest among the all Cu-Zn/Al_2O_3 catalysts. The maximum of DME selectivity is 14 *C*.%. However, under the reaction temperature of 160 ^{o}C, CO production was reduced and DME selectivity became larger, and the biggest value was 65.8 *C*.% by the Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst. On the other hand, the DME production rate became slower with 15 μmol $g_{\text{-cat}}^{-1}$ h^{-1}, and its rate was less than 1/3 of the DME production rate under 180 ^{o}C, 200 ^{o}C, and 220 ^{o}C. However, these data are much better than those by the patent catalysts developed by KEPCO & MHI [16]. For better DME selectivity, it is clarified that lower reaction temperature makes DME selectivity higher; however, the DME production rate becomes lower, so other compositions of Cu-Zn-Al_2O_3 should be developed. After many catalysts were prepared and the catalysts were tested for direct DME synthesis from CO_2, we have developed more excellent catalysts, Cu-Ga/Al_2O_3. At present, the Cu-Ga(24-6 wt%)/Al_2O_3 catalyst prepared using the consecutive sol-gel method is the best catalyst for direct DME synthesis from CO_2. The results of the Cu-Ga/Al_2O_3 catalyst are shown in Fig. 3. The DME selectivity increased to about 30 *C*.%, and DME production rate improved to 63 μmol $g_{\text{-cat}}^{-1}$ h^{-1}.

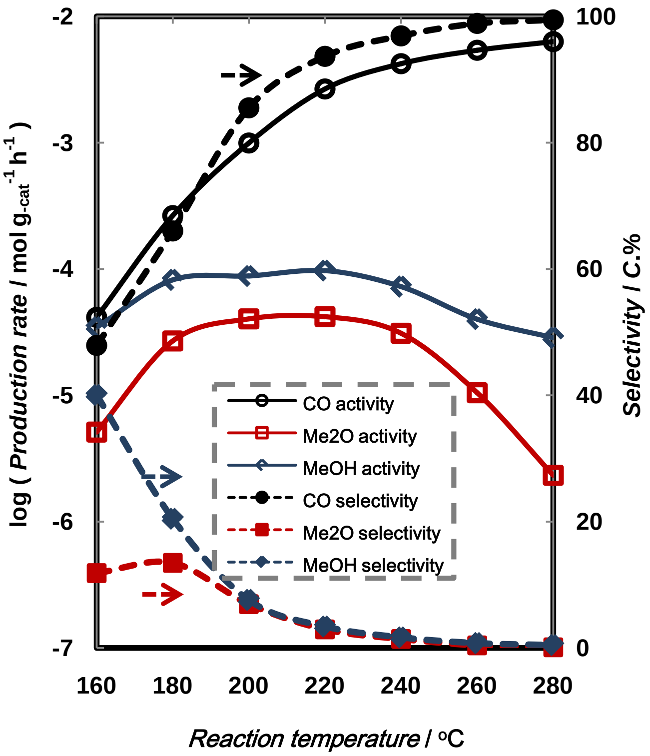

Fig. 1. CO_2 hydrogenation over the Cu-Zn(15-15 wt.%)/Al_2O_3 catalysts prepared using the sol-gel method. Catalyst weight: 0.5 g; reaction gas: $H_2/CO_2/Ar$ = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

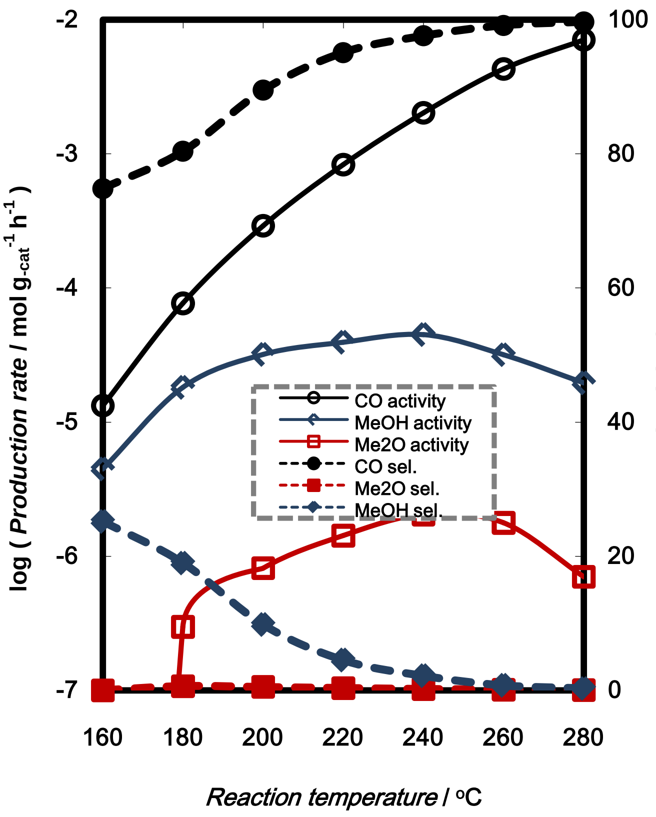

Fig. 2. CO_2 hydrogenation over the patented catalyst by KEPCO & MHI, (CuO-ZnO-Al_2O_3-Ga_2O_3-MgO(100:25:15:5:1) & Al_2O_3-ZrO_2 (100:10)). Catalyst weight: 0.5 g; reaction gas: $H_2/CO_2/Ar$ = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

This Cu-Ga/Al_2O_3 catalyst was compared with the patent catalyst developed by KEPCO and MHI, a mixed catalyst of methanol synthesis catalysts and methanol dehydration catalysts. These results are in Fig. 4. The production rate of DME and methanol are much faster than those of the patent catalyst even if the optimal reaction temperature for the sol-gel catalyst is lower than that for the patent catalyst.

Then, the Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst and Cu-Ga(24-6 wt.%)/Al_2O_3 catalyst prepared using the sol-gel method were tried for hydrogenation of various ratio mixture of CO_2 and CO for direct DME synthesis, respectively. Figure 5 shows a part of the results of the DME production and methanol production at 220 ^{o}C, 240 ^{o}C, and 260 ^{o}C of the reaction temperature over Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst. In the case of the Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst (Fig. 5), the DME production rate is increased with the increasing of the ratio of CO/(CO+CO_2). Figure 6 shows a part of the results of the DME production and methanol production at 220 ^{o}C, 240 ^{o}C, and 260 ^{o}C of the reaction temperature over Cu-Ga(24-6 wt.%)/Al_2O_3 catalyst. In the case of the Cu-Ga/Al_2O_3 catalyst,

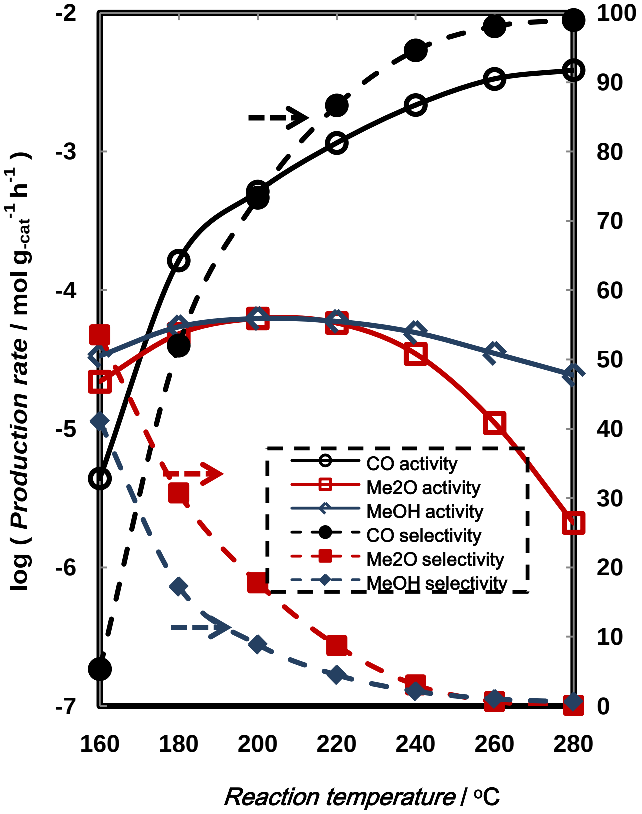

Fig. 3. CO_2 hydrogenation over the Cu-Ga(24-6 wt.%)/Al_2O_3 catalysts prepared using the sol-gel method. Catalyst weight: 0.5 g; reaction gas: $H_2/CO_2/Ar$ = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

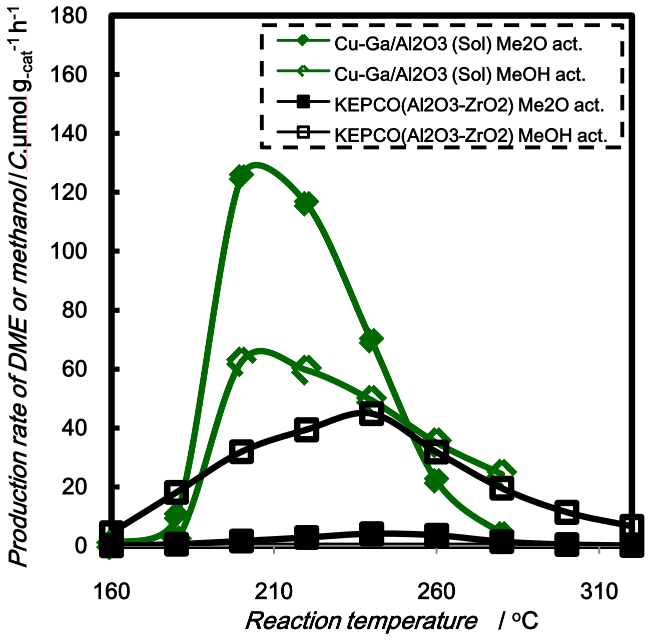

Fig. 4. Production rate of DME or methanol on CO_2 hydrogenation over the Cu-Ga (24-6wt.%)/Al_2O_3 catalysts prepared using the sol-gel method and over KEPCO & MHI catalyst (CuO-ZnO-Al_2O_3-Ga_2O_3-MgO(100:25:15:5:1) & Al_2O_3-ZrO_2(100:10)). Catalyst weight: 0.5 g; reaction gas: $H_2/CO_2/Ar$ = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

there is an optimal ratio around 0.8, but the DME production rate was much slower than the rate by Cu-Zn(15-15 wt.%)/Al_2O_3. Ga is one of rare-metals and very expensive, therefore the Cu-Zn(15-15 wt.%)/Al_2O_3 catalyst is useful as practical catalysts.

From these results, CO_2 should be reacted with H_2 into DME and CO, and these DME and CO will be separated, then the separated CO should be hydrogenated to DME. It becomes a two-step DME synthesis from CO_2, but it would be practical for the industrial. It is not really a direct DME synthesis method, but I have developed the significant catalysts using the sol-gel method for direct DME synthesis from CO_2 and CO compared with the mixed catalysts such as the patent catalysts of KEPCO & MHI.

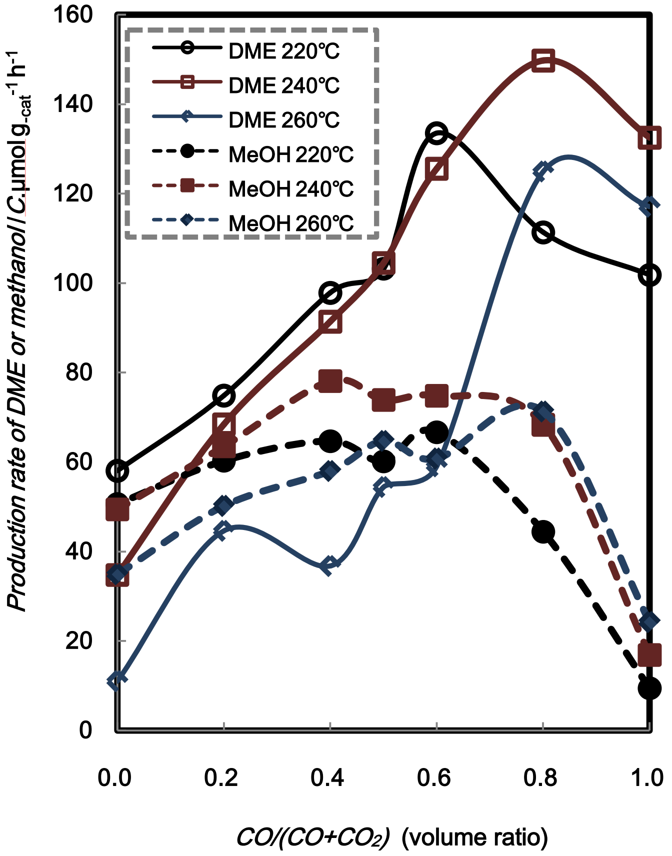

Fig. 5. Hydrogenation of CO_2+CO mixture over Cu-Ga(24-6wt%)/Al_2O_3 catalyst prepared using the consecutive sol-gel method. Catalys weight: 0.5 g; reaction gas: $H_2/(CO_2+CO)/Ar$ = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

IV. CONCLUSIONS

1) We have developed excellent direct DME synthesis catalyst. Cu/Al_2O_3 catalysts prepared using the sol-gel method are more effective for direct DME synthesis from CO_2 than the mixed catalysts.
2) By hydrogenation of CO_2, main product is CO. Reverse water-gas shift reaction is mainly occurs.

3) In the case of the Cu-Ga/Al_2O_3 sol-gel catalyst for DME synthesis by CO_2 hydrogenation: the DME production rate is 62 μmol g_{-cat}^{-1} h^{-1}, and the DME selectivity is 19 *C*.%, higher activity and selectivity than those by mixed catalysts.

4) For the practical use, mixed CO_2+CO gas such as biomass gasification gas will be hydrogenated for DME synthesis. The inexpensive catalyst, Cu-Zn/Al_2O_3 catalysts are very effective for the DME synthesis.

5) It may be better that DME synthesis is carried out over the Cu-Zn/Al_2O_3 catalysts, and the produced DME and CO will be separated, and the CO will be used for DME synthesis over the Cu-Zn/Al_2O_3 again.

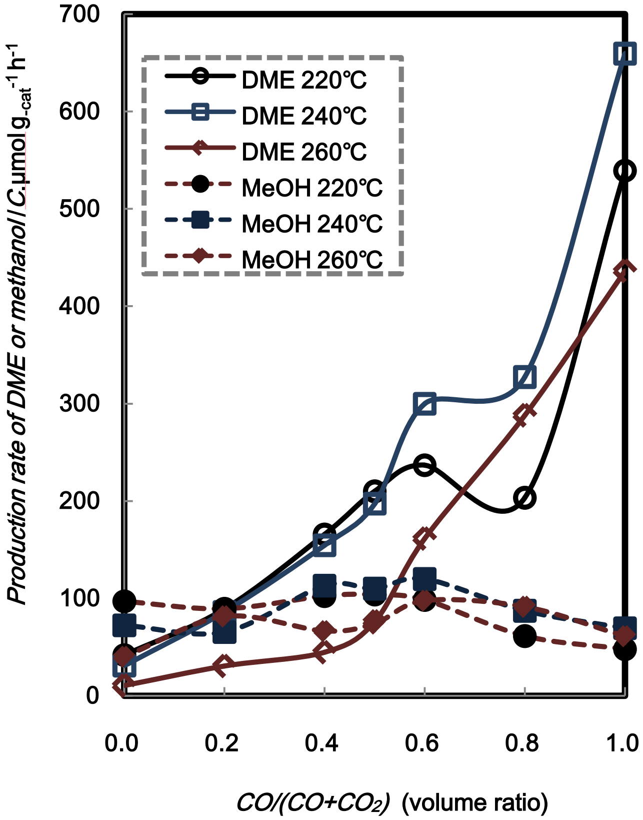

Fig. 5. Hydrogenation of CO_2＋CO mixture over Cu-Zn(15-15 wt.%) /Al_2O_3 catalyst prepared using the consecutive sol-gel method. Catalys weight: 0.5 g; reaction gas: H_2/(CO_2＋CO)/Ar = 15.0/5.0/2.0 ml min^{-1}; reaction pressure: 0.9 MPaG.

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