

Dimethyl Ether (DME): A Clean Fuel of the 21st Century and Catalysts for It

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Abstract: Dimethyl ether (DME) is a substitute of LNG and light oil. DME burns without particulate matters and SO_x, so DME is a clean fuel. DME is a storage and carrier of hydrogen. For these usages, useful catalysts such as DME steam reforming catalysts and DME synthesis catalysts should be developed. I have developed those new effective Cu-Zn/Al₂O₃ catalysts. The catalysts prepared by a sol-gel method produce DME faster than usual mixed catalysts of methanol synthesis catalysts and methanol dehydration catalysts. The sol-gel Cu-Zn/Al₂O₃ catalysts also produce hydrogen faster than usual mixed catalysts of DME hydrolysis catalysts and methanol steam reforming catalysts. It is the reason why that alumina sites (working for dehydration and hydrolysis) and copper sites (working for methanol synthesis and methanol steam reforming) are co-existing and distributing well on the surfaces of the catalysts prepared by the sol-gel method. Therefore, the consecutive reactions (methanol synthesis, methanol dehydration, and water-gas shift reactions; or DME hydrolysis and methanol steam reforming reactions) smoothly occur, and DME and hydrogen is produced fast, respectively. These catalysts will be very effective for production of DME and hydrogen, and new energy system. The systems using these catalysts lead the hydrogen and DME society well.

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

1 Introduction

Dimethyl ether (DME) is the smallest ether, and its chemical formula is CH₃OCH₃. DME usually exists as gas, but it is easy to liquefy by cooling at -25°C at atmospheric pressure and by pressurizing under 5 atm at room temperature. Therefore, DME is easy to handle like liquefied petroleum gas (LPG). DME will be used as fuel of substitute of LPG. In China, DME is mixed into LPG and used as a domestic fuel. Cetane number of DME is 55-60, so DME will be used as a diesel fuel. In Japan, China, Sweden and so on, DME buses and trucks are testing on public roads. DME does not contain poisonous substances, and it burns with no particulate matters (PM), no sulphur oxides (SO_x), and less nitrogen oxides (NO_x). Therefore, DME is expected as a clean fuel for the 21st century [1]. DME is able to replace light oil and LPG, and its physical properties are similar to those of LPG. It is possible that DME infrastructures will be settled more rapidly than hydrogen, because existing LPG infrastructures can be used for DME.

On the other hand, it is expected that fuel cell is one of the methods to restrain the global green effect. Steam reforming of methane, LPG, gasoline, and methanol is actively researched and developed as hydrogen supply methods for the fuel cells. Methanol steam reforming is easy to perform at around 250-300°C. However, the toxicity of methanol is high, and its infrastructure is not well developed. The infrastructures for natural gas, LPG, and gasoline are well established, but those steam reforming are difficult even at high temperatures around 800°C, and they contain sulphur resulting in catalyst poisoning. DME is expected as excellent hydrogen carrier and hydrogen storage, because DME will be easy to reform into hydrogen if there will be excellent catalysts of DME steam reforming. Therefore, I have been studying on DME steam reforming for hydrogen production, and researching on catalysts for DME steam reforming and DME synthesis [2, 3].

2 Experimentals

2.1 Catalyst preparation

Most catalysts were prepared by the sol-gel method. For example, γ - Al_2O_3 was obtained by aluminium isopropoxide (AIP) hydrolysis. AIP (Wako Pure Chemical Industries, Ltd.) 50 g was crushed using a mortar, and then dissolved in hot water (app. 70°C, app. 500 ml). HNO_3 (Wako) was added until the pH of the mixture decreased to 1–2, and a clear-sol of boehmite was formed. Water in the sol was evaporated under reduced pressure, and the gel was obtained. The obtained gel was dried at 170°C for a day. The dried gels were ground using an agate mortar until the diameter of each grain of powder was less than 150 μm . The powder was calcined at 500°C for 5 h, and app. 12 g alumina was obtained. The calcined powder was found to be mainly γ -alumina by measured X-ray diffraction analysis. Other catalysts, such as SiO_2 , $\text{Cu}/\text{Al}_2\text{O}_3$, Cu/SiO_2 , Cu/ZrO_2 , 1wt.% $\text{Ru}/\text{Al}_2\text{O}_3$ were prepared by tetraethyl orthosilicate (TEOS) (Wako), zirconium tetra-n-propoxide (ZTP) (Mitsuwa's Pure Chemicals, Inc.), ethylene glycol (EG) (Wako), copper (II) nitrate trihydrate (Wako), zinc (II) nitrate hexahydrate (Wako), ruthenium (III) acetylacetonate (Strem Chemicals, Inc.). Some metal precursors, EG, and water were mixed with AIP, TEOS, or ZTP, and each mixture was hydrolyzed, dried, and calcined as described above. For comparison, CuO-ZnO (1:1) (N211) (Nikki Chemical Co., Ltd.) was used as one sample of commercial catalysts and as one sample of methanol steam reforming catalysts. N211 was ground using an agate mortar until the diameter of each grain of powder was less than 150 μm , and then calcined at 500°C for 5 h before use for steam reforming. $\text{Cu-Zn}(25\text{-}25\text{wt.}\%)/\text{Al}_2\text{O}_3$ was used as one sample of catalysts prepared by impregnation method and as one sample of methanol steam reforming catalysts. $\text{Cu-Zn}(25\text{-}25\text{wt.}\%)/\text{Al}_2\text{O}_3$ was prepared by immersing alumina (BK-103) (Sumitomo Chemical Co., Ltd.) in an aqueous solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, followed by stirring and heating. The dried catalyst was ground using an agate mortar until the diameter of each grain of powder was less than 150 μm , and then calcined at 500°C for 5 h. BK-103 was calcined at 500°C for 5 h before use as the catalyst support. All of the catalysts were calcined in air at 500°C for 5 h as described above, and reduced in H_2 flow (10 ml/min) at 450°C for 10 h. These treatments may sinter the metals of catalysts and the catalysts themselves, and lead to a deterioration of activity. However, we consider that the sintering

before steam reforming is smaller trouble for a comparison of catalyst activity than sintering while steam reforming. Instead of duration test of the catalysts, the catalysts after this severe pretreatment were compared on the activity, selectivity and so on.

2.2 Apparatus and steam reforming of DME

DME steam reforming was performed in a flow reactor (7.6mm i.d. Pyrex tube) using 0.10 g of catalyst (particle size, ground < 150 μm) in the temperature range from 200 to 500°C at atmospheric pressure. The reaction gas, a mixture of DME (2 mmol $\text{g}_{\text{-cat}}^{-1} \text{h}^{-1}$) and water (6 mmol $\text{g}_{\text{-cat}}^{-1} \text{h}^{-1}$), was supplied to the catalyst layer. Reactant flow with Ar carrier gas was adjusted using two mass flow controllers (Brooks 580E). For the analysis of reactants and products, two gas chromatographs (GCs) were used. One was a Shimadzu GC-6AM equipped with a thermal conductivity detector (TCD), a methanalyzer (for CO analysis), and a flame ionization detector (FID). The GC 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), methane, and CO were quantitatively analyzed. The other was a Shimadzu GC-4C with TCD and FID, and equipped with a Porapak Q stainless column (60–80 mesh, 1m long, i.d. 3 mm) and a Porapak R stainless column (80–100 mesh, 0.5m long, i.d. 3 mm) in series. Its carrier gas was helium. Methane, CO_2 , H_2O , DME, methanol, and some hydrocarbons were quantitatively analyzed.

2.3 Apparatus and direct DME synthesis

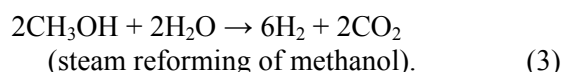
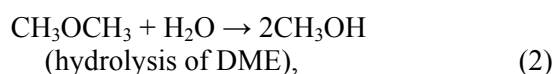
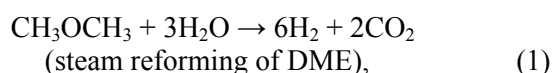
For hydrogenation of carbon monoxide, $\text{Cu-Zn}(36\text{-}4 \text{wt.}\%)/\text{Al}_2\text{O}_3$ catalyst prepared by the sol-gel method was used in single, not mixed with other catalysts such as alumina. As the comparison, a mixed catalyst with a commercial catalyst CuO-ZnO (N211) and alumina (BK-103) was used. This mixed catalyst is similar catalysts for patent catalysts for DME direct synthesis [4]. The all catalysts were calcined at 500°C for 5 h and were reduced by flowing H_2 at 450°C for 10 h. 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 $\text{H}_2/\text{CO}/\text{Ar} = 7.5/7.5/1.5 \text{ ml min}^{-1}$. Argon gas was an internal standard for gas chromatography. The reaction gas and products were analyzed by gas chromatographs (TCD and FID). Scanning Electron Microscope & Energy Dispersive X-ray spectrometer (SEM-EDS; JEOL JSM-6060LA

(JED□2300)) analysis was performed for the surface characterization.

3 Results and discussion

3.1 Steam reforming of DME

The results for steam reforming at 300°C with the main catalysts are shown in Table 1. The alumina catalysts prepared by the sol-gel method mainly produce hydrogen, and in the case of Al₂O₃ (Sol) without metal methanol is formed. On the other hand, the silica catalysts produce no hydrogen, and there is no activity for steam reforming of DME (SRDME). The CuO-ZnO (N211) and the impregnated catalysts, Cu(10wt.%)/ZrO₂ and Cu-Zn(25-25wt.%)/Al₂O₃, also have less activity for SRDME. Cu(10wt.%)/SiO₂ catalysts have excellent activity for steam reforming of methanol (SRM); however, there is no hydrogen produced on the SRDME. The temperature dependence of SRDME over the Al₂O₃ was determined. DME was hydrolyzed into methanol from 200°C, and that conversion of DME becomes 100% from 450°C. These results suggest that Al₂O₃, especially on Lewis acid sites, is excellent for hydrolyzing DME into methanol. The produced methanol reforms to H₂ and CO₂ when steam is passed over an active metal, such as Cu. H₂ production with SRDME consists of two steps: the first is DME hydrolysis, and the second is SRM. The chemical equation of SRDME (Eq. (1)) is separated for that of DME hydrolysis (Eq. (2)) and that of SRM (Eq. (3)), as follows:



The Cu/SiO₂ and CuO-ZnO catalysts are excellent catalysts for SRM [10]: however, DME is not hydrolyzed into methanol, and H₂ is not produced. Cu/ZrO₂ also produces less hydrogen for the same reason. Cu-Zn(25-25wt.%)/Al₂O₃ prepared by the impregnation method is also an excellent catalyst for SRM, and the catalyst support is alumina; however, less H₂ is produced. It is speculated that Al₂O₃ and Lewis acid sites are

covered with Cu and Zn; therefore, there is a smaller number of active sites for DME hydrolysis. Thus methanol is not produced well, and SRM does not occur. CuO-ZnO (N211) and Cu-Zn(25-25wt.%)/Al₂O₃ were physically mixed in 1/1 (weight ratio) with γ-Al₂O₃ prepared by the sol-gel method, respectively. However, both rates of H₂ production are smaller than that of Cu(10wt.%)/Al₂O₃ prepared by the sol-gel method. In these results, the Cu(10 wt.%)/Al₂O₃ catalysts prepared by the sol-gel method are excellent catalysts for H₂ production with SRDME. The reason is speculated to be that the Lewis acid sites on γ-Al₂O₃ for the hydrolysis of DME and active sites for SRM such as copper are coexistent and distributed well on the surfaces of the catalysts. Therefore, the two reactions occur well and H₂ is produced in large quantities. Ru(1wt.%)/Al₂O₃ prepared by the sol-gel method also produces H₂ and CO in large quantities. It is speculated that decomposition of methanol occurs instead of SRM, Eq. (3) [5]. For PEFC, CO concentration in H₂ gas must be reduced. Therefore, Cu is the best metal for CO reduction and production of H₂, as with SRM [6-8]. Cu(10 wt.%)/Al₂O₃ prepared by the sol-gel method is one of the best catalysts for H₂ production with SRDME.

Further experiments for catalyst optimization lead that the Cu-Zn(29-1wt.%)/Al₂O₃ catalyst shows the excellent activity of SRDME; the DME conversion is 95%, H₂ yield is 95%, and CO concentration was 0.8 mol.% (Cf. Fig. 1). I have developed new catalysts for H₂ production from DME, and the catalysts give us a great potential for H₂ supply from DME.

3.2 Direct DME synthesis

The single type catalyst and the mixed catalyst were carried out for CO hydrogenation. The part of the results is shown in Fig. 2. 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-103) at 310°C of the higher reaction temperature. Dependency of H₂/(H₂+CO) ratio was investigated on Cu-Zn(36-4wt.%)/Al₂O₃ catalyst prepared by the sol-gel method. DME is produced with the fastest production rate at the ratio of H₂/(H₂+CO) = 0.5 (Cf. Fig. 3). 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,



Pressure dependency was determined. The part of the results are shown in Fig. 4. DME production rate is increasing with increase of the reaction pressure, and selectivity for DME is approaching to 100%. In other experiments, even if the reaction gases contain some oxygen, the sol-gel Cu-Zn/Al₂O₃ catalysts produce DME effectively with long durability. This means that DME will be produced from syngas contaminated by O₂, and DME will be synthesized without O₂ removal process for gasification gases of biomass, coal, and so on. DME will be produced economically by these catalysts.

3.3 Catalyst surface for DME reactions

Cu-Zn/Al₂O₃ catalysts prepared by the sol-gel method in single use produce hydrogen more effectively at lower reaction temperature than physically mixed catalysts with DME hydrolysis catalysts and methanol steam reforming catalysts. It is probably the reason why Al₂O₃ for DME hydrolysis into methanol and Cu for methanol steam reforming into H₂ and CO₂ are co-existing closely and well-dispersed on the catalyst surface. In the case of the mixed catalysts there are longer distances between the DME hydrolysis catalysts and methanol steam reforming catalysts than those of the two sites on the Cu-Zn/Al₂O₃ catalyst prepared by the sol-gel method. In order to confirm this speculation, SEM-EDS analysis was performed on the surface of the Cu-Zn/Al₂O₃ catalysts. SEM-EDS analysis has confirmed that copper sites and alumina sites are co-existing and the both sites are dispersed well on the surface of Cu-Zn/Al₂O₃ catalyst prepared by the sol-gel method. Al (alumina) exists on the whole in the catalyst surface. Cu is dotted in it. If Al₂O₃ is compared to sea water, it is observed that Cu is exposed from sea level (Al₂O₃ surface) like an iceberg and is dotted in the surface of sea. Al₂O₃ and Cu are co-existing and are distributing with sufficient balance as guessed. It is considered that DME hydrolysis into methanol occurs on the Al₂O₃ and steam reforming of the methanol into H₂ and CO₂ immediately performs on Cu very near the Al₂O₃. In case of mixed catalysts there are some distances between DME hydrolysis catalysts and

methanol steam reforming catalysts, so it is difficult to carry out these two reactions immediately. It is concluded that the Cu-Zn/Al₂O₃ catalyst prepared by the sol-gel method with a single use has these two reactions occur sequentially efficiently and a quick hydrogen production rate is obtained by the Cu-Zn/Al₂O₃ catalyst.

In the case of direct DME synthesis, the sol-gel catalysts, single type catalysts that have copper sites for methanol synthesis (and water gas shift reaction) 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 DME direct synthesis. 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.

4 Conclusion

I have developed the appropriate and excellent catalysts for DME steam reforming (catalysts for hydrogen production) and direct DME synthesis (catalysts for hydrogen storage catalysts). These catalysts, Cu-Zn/Al₂O₃ catalysts prepared by the sol-gel method, produce hydrogen at around 300°C in case of DME steam reforming, and produce DME with higher activity and higher selectivity under lower or milder reaction temperature and pressure in case of direct DME synthesis. Even if the reaction gases contain some oxygen, the sol-gel Cu-Zn/Al₂O₃ catalysts produce DME with long durability. Therefore, DME will be produced economically with O₂ removal process of such as biomass gasification gases. These catalysts play significant role in new hydrogen and DME society (Fig. 5) [9].

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Table 1 Steam reforming of dimethyl ether over some catalysts at 300°C

Catalyst (g _{-cat} ⁻¹ h ⁻¹)	Rate of production (mmol g _{-cat} ⁻¹ h ⁻¹)			
	H ₂	CO ₂	CO	MeOH
γ-Al ₂ O ₃ (Sol) 0.78		0.16	0.026	0.14
SiO ₂ (Sol) 0.000		0.000	0.004	0.000
Cu (10%) / Al ₂ O ₃ (Sol) 0.000	9.7	3.4	0.061	0.061
Cu (10%) / SiO ₂ (Sol) 0.000	0.000	0.048	0.000	0.000
Cu-Zn (9-1%) / SiO ₂ (Sol) 0.000	0.000	0.003	0.000	0.000
Cu (10%) / ZrO ₂ (Sol) 0.000	0.009	0.036	0.000	0.000
Ru (1%) / Al ₂ O ₃ (Sol) 0.21	6.7	0.22	2.5	2.5
Zn (10%) / Al ₂ O ₃ (Sol) 0.69	0.36	0.24	0.012	0.012
CuO-ZnO (50-50%) (N211) 0.000	0.000	0.000	0.000	0.000
CuO-ZnO + Al ₂ O ₃ (Sol) (Mix) 0.000	2.9	1.1	0.006	0.006
Cu-Zn (25-25%) / Al ₂ O ₃ (Imp) 0.000	0.048	0.040	0.000	0.000
Cu-Zn / Al ₂ O ₃ (I) + Al ₂ O ₃ (S) (M) 0.000	7.6	2.7	0.042	0.042

* Catalyst: 0.1g, reaction gas: DME-water = 2-6 mmol g_{-cat}⁻¹ h⁻¹.

Sol, S: catalyst prepared by a sol-gel method, **Imp, I:** catalyst prepared by an impregnation method, **Mix, M:** catalyst physically mixed two catalysts.

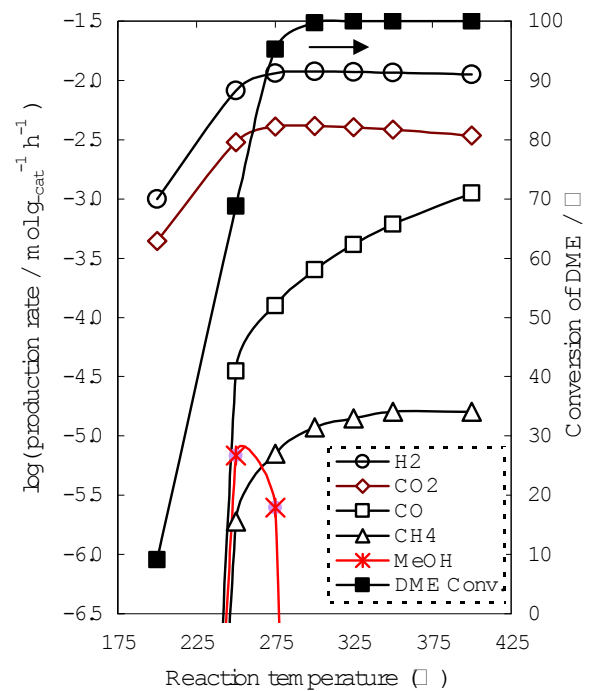


Fig. 1 Steam reforming of DME over Cu-Zn(29-1wt.)/Al₂O₃ catalyst prepared by the sol-gel method.

Catalyst weight; 0.1 g, DME-H₂O = 2-6 mmol g_{-cat}⁻¹ h⁻¹.

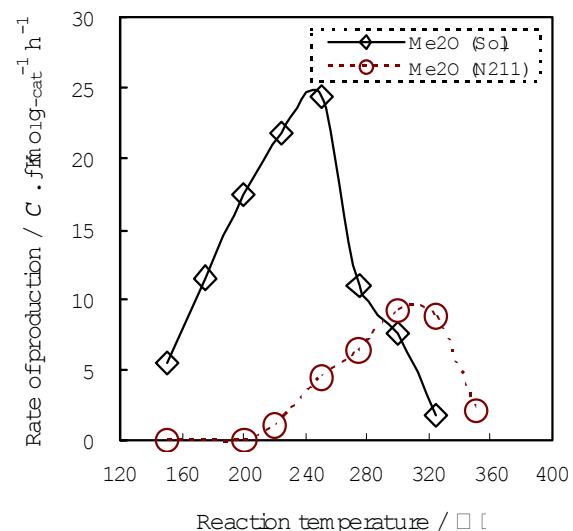


Fig. 2. Activity of CO hydrogenation over Cu-Zn(36-4wt.)/Al₂O₃ prepared by the sol-gel method (*sol*) and a catalyst (*N211*) physically

mixed CuO-ZnO (1:1) and Al₂O₃. Catalyst weight: 0.5 g, H₂/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

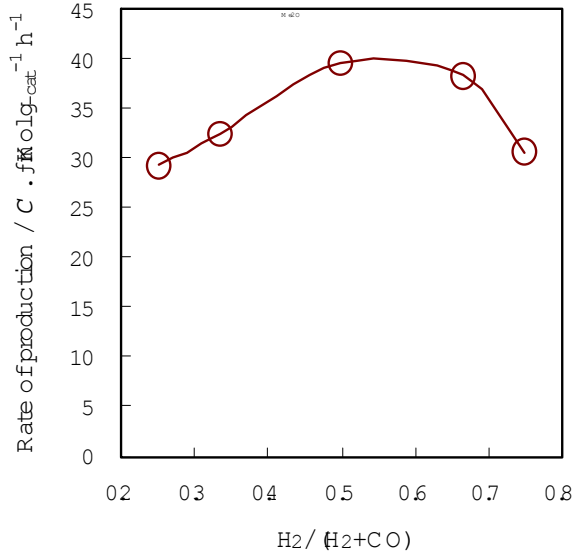


Fig. 3. H₂/(H₂+CO) and activity of DME production on CO hydrogenation over Cu-Zn(36-4wt.)/Al₂O₃ catalyst at 220°C. Catalyst weight: 0.5g, (H₂+CO)/Ar = 15/1.5 ml min⁻¹.

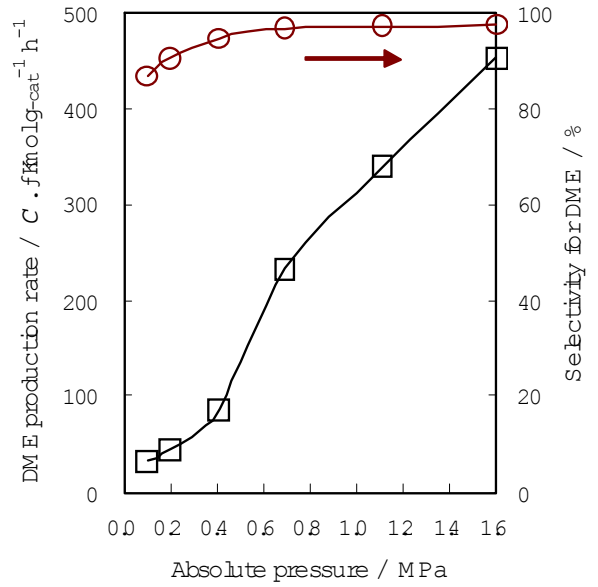


Fig. 4. Effect of pressure to DME production rate and selectivity on CO hydrogenation over Cu-Zn (36-4wt.)/Al₂O₃ catalyst at 220°C. Catalyst weight: 0.5 g, H₂/CO/Ar = 7.5/7.5/1.5 ml min⁻¹.

