

# Hydrogen production by steam reforming of methanol over copper catalysts prepared by using the sol-gel method

Kaoru TAKEISHI and Hiromitsu SUZUKI

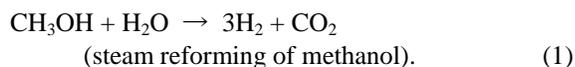
**Abstract**— Cu/SiO<sub>2</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, and Cu/ZrO<sub>2</sub> catalysts were prepared by using sol-gel methods. Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation method. These catalysts and commercial CuO-ZnO catalyst were used for hydrogen production by methanol steam reforming. Catalysts prepared using the sol-gel method have bigger specific surface area, more highly dispersed copper metal particles on the catalyst surface, and higher durability for heat. These excellent physical properties work for faster hydrogen production rate and higher methanol conversion at wide range reaction temperature from 150 °C to 500°C. Especially, the Cu/SiO<sub>2</sub> catalyst prepared using the sol-gel method is the most excellent catalyst for hydrogen production for fuel cells, because amount of by-product is smallest among the catalysts.

**Keywords**— Copper catalyst, hydrogen, methanol steam reforming, sol-gel method.

## I. INTRODUCTION

METHANOL is one of the very important basic chemical raw materials. Methanol is easy to decompose to carbon monoxide and hydrogen. Therefore, it is possible to consider that methanol is a liquefied syngas (mixed gas of carbon monoxide and hydrogen). Methanol is important for CI chemistry. Methanol also can be used as fuel for engines, fuel cell, and so on. Nowadays, methanol is expected as a clean fuel and energy, because fuel cells have excellent energy efficiency for restraint of global warming, environmental problem, air pollution, and so on.

Hydrogen production by steam reforming of methanol occurs at around 300 °C (Eq. 1), on the other hand those of gasoline, liquefied petroleum gas (LPG), methane, and other hydrocarbons occur at around 800 °C.

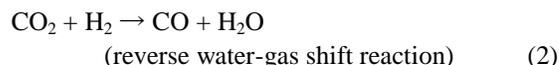


Methanol can be reformed by steam at very lower reaction temperature than gasoline, LPG, methane, and other hydrocarbons. CO affects Pt electrodes of polymer electrolyte

Kaoru TAKEISHI (Corresponding author); Course of Applied Chemistry and Biochemical Engineering, Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, 3-5-1, Jyohoku, Hamamatsu-shi, Shizuoka-ken, 432-8561, Japan (e-mail: takeishi.kaoru@shizuoka.ac.jp).

Hiromitsu SUZUKI; Department of Materials Science and Engineering, Faculty of Engineering, Shizuoka University,

fuel cell (PEFC) badly. The amount of produced CO is very smaller than those of gasoline, and other hydrocarbons. It is because that methanol reforming temperature is very low and reverse water gas shift reaction does not occur so much



compared by the temperature for the hydrocarbons. Therefore, CO reducing system become smaller and hydrogen production system by methanol can be smaller than those by hydrocarbons. Casio Computer Co., Ltd. has developed a coin-size methanol reformer [1].

N. Takezawa et al. have reported that copper catalysts are very excellent for hydrogen production by methanol steam reforming [2-8]. However, copper catalysts have a problem that the catalysts are deactivated at more than 350 °C easily. On the other hand, VIII group metals such as Pt and Pd have strong durability for high temperature, but they produce much amount of CO with H<sub>2</sub> production [7, 9].

The sol-gel method that is one of the ceramics preparation methods is used for the manufacture of the optical fiber and the functional film and so on, in addition that used as the low-temperature glass synthesis method. The catalyst preparation method by using the sol-gel method passes through the liquid-phase at the starting point, and then metallic particle solidifies in the form that is storing into the network structure of the gel support. Therefore, the sol-gel preparation method can produce catalysts with higher surface area and higher metal dispersion than impregnation method. Also, the particle size distribution becomes sharp and the metal particles are difficult to sinter or coagulate between each other [10-16].

In this research, copper catalysts are prepared by using the sol-gel method, and the sol-gel catalysts are compared with the commercial catalyst and the impregnation catalyst.

## II. EXPERIMENTAL

### A. Catalyst preparation

Cu/SiO<sub>2</sub>, Cu/Al<sub>2</sub>O<sub>3</sub>, and Cu/ZrO<sub>2</sub> catalysts were prepared by sol-gel methods [17-19]. Cu/SiO<sub>2</sub> catalysts were obtained by hydrolysis of mixed solution with tetraethyl orthosilicate (TEOS), Cu(NO<sub>3</sub>)<sub>2</sub>, ethanol, water, and small amount of ethylene glycol (EG). Cu/Al<sub>2</sub>O<sub>3</sub> was gotten by hydrolysis of

mixed solution with aluminium isopropoxide (AIP),  $\text{Cu}(\text{NO}_3)_2$ , water, and small amount of EG.  $\text{Cu}/\text{ZrO}_2$  was obtained by hydrolysis of mixed solution with zirconium(IV) tetrapropoxide (TPZ), propanol,  $\text{Cu}(\text{NO}_3)_2$ , ethylene glycol, and water.

In the case of  $\text{Cu}/\text{SiO}_2$  catalysts, TEOS, ethanol, water, and EG were mixed, stirred, and heated at  $\sim 80^\circ\text{C}$  for  $\sim 30$  min. Amount of  $\text{Cu}(\text{NO}_3)_2$  for the catalyst preparation depended on the loading metal amount of the needed catalysts, this time 10 wt.% Cu, was added to the mixture. After 1 h stirring and heating, diluted  $\text{HNO}_3$  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  $\sim 5$  h. In the way of the  $\text{HNO}_3$  addition, a clear-sol of silica was formed. Water in this sol was evaporated and taken out under reduced pressure using a rotary evaporator, and the gel was obtained. The obtained gel was dried at  $170^\circ\text{C}$  for a night. The dried gel was ground using an agate mortar until the diameter of each grain of powder was less than 150  $\mu\text{m}$ . The powder was calcined at  $500^\circ\text{C}$  for 5 h. Before steam reforming of methanol, the catalysts were reduced by flowing  $\text{H}_2$  (99.99%,  $10\text{ml min}^{-1}$ ) at  $450^\circ\text{C}$  for 10 h, and were evacuated at  $300^\circ\text{C}$  for 1 h, respectively. These treatments may be severe 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 methanol steam reforming is smaller trouble for a comparison of catalyst activity than sintering while the steam reforming. Instead of duration test of the catalysts, the catalysts after this severe pretreatment were compared on the activity, selectivity, and so forth.

$\text{Cu}(10\text{ wt.}\%)/\text{Al}_2\text{O}_3$  and  $\text{Cu}(10\text{ wt.}\%)/\text{ZrO}_2$  were prepared similarly by the above-mentioned procedure using AIP and TPZ, respectively.

As one of the reference catalysts, a commercial catalyst,  $\text{CuO-ZnO}$  catalyst (N211,  $\text{CuO}/\text{ZnO} = 1$  (weight ratio), Nikki Chemical) was used.  $\text{Cu-Zn}(25-25\text{ wt.}\%)/\text{Al}_2\text{O}_3$  catalyst was prepared by impregnation method using  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ , and  $\gamma\text{-Al}_2\text{O}_3$  (BK-105, Sumitomo Chemical) for another reference catalyst.

### B. Apparatus and steam reforming of methanol

Methanol steam reforming was performed in a flow reactor (7.6 mm i.d. Pyrex glass tube) using 0.10 g of catalyst in the temperature range from 150 to  $500^\circ\text{C}$  at atmospheric pressure. The reaction gas, a mixture of methanol ( $16\text{ mmol g}_{\text{cat}}^{-1}\text{h}^{-1}$ ) and water ( $16\text{ mmol g}_{\text{cat}}^{-1}\text{h}^{-1}$ ), was supplied to the catalyst layer. Reactant flow with Ar carrier gas was adjusted using two mass flow controllers (Brooks 580E). The reactor was part of a closed circulation system. After the above-mentioned reduction and evacuation, and before the reaction, the BET specific surface area of the catalyst in the reactor without the exposure to the air was measured using  $\text{N}_2$  gas at  $-196^\circ\text{C}$ . After the evacuation of  $\text{N}_2$  gas at room temperature for 30 min, the amount of CO it adsorbed in the same reactor without the exposure of the air was analyzed using CO gas at  $0^\circ\text{C}$ . After

the evacuation of CO gas at  $300^\circ\text{C}$  for 1 h, steam reforming of methanol over the same catalyst was performed in the same reactor without the exposure of the air.

For the analysis of reactant and products, two gas chromatographs (GCs) were used. One was a Shimadzu GC-6AM equipped with a thermal conductivity detector (TCD), a methanizer (for CO analysis), and a flame ionization detector (FID). The GC had an MS-5A stainless column (80-100 mesh, 5 m long, i.d. 3mm) and its carrier gas was nitrogen.  $\text{H}_2$ , Ar (as internal standard for GC analysis),  $\text{CH}_4$ , and CO were quantitatively analyzed. The other was a Shimadzu GC-4C with TCD and FID, and equipped with a Porapak Q stainless column (80-100 mesh, 1m long, i.d. 3 mm) and a Porapak R stainless column (80-100 mesh, 0.5 m long, i.d. 3 mm) in series. Its carrier gas was helium.  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , methanol, dimethyl ether (DME), methyl formate and some hydrocarbons were quantitatively analyzed.

## III. RESULTS AND DISCUSSION

Physical properties of  $\text{Cu}(10\text{ wt.}\%)/\text{SiO}_2$ ,  $\text{Cu}(10\text{ wt.}\%)/\text{Al}_2\text{O}_3$ ,  $\text{Cu}(10\text{ wt.}\%)/\text{ZrO}_2$  catalysts prepared by using sol-gel methods,  $\text{CuO-ZnO}$  catalyst in commercial, and  $\text{Cu-Zn}(25-25\text{ wt.}\%)/\text{Al}_2\text{O}_3$  catalyst prepared by impregnation method are in Table 1. The  $\text{Cu}/\text{SiO}_2$  prepared by the sol-gel method has the biggest surface area,  $525\text{ m}^2\text{ g}^{-1}$ , among the catalysts. The  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst prepared using the sol-gel method has the biggest amount of CO adsorbed,  $104\text{ }\mu\text{mol g}^{-1}$ , among the catalysts. From amount of CO adsorbed, Cu metal dispersion and Cu metal particle size are estimated, and the data of each catalyst are also in Table 1.  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst prepared by the sol-gel method has the biggest metal dispersion among the catalysts.  $\text{Cu}(10\text{ wt.}\%)/\text{ZrO}_2$  catalyst prepared using sol-gel method has the biggest percentage of surface metal among the catalysts. Sol-gel method gives better physical properties to catalysts than impregnation method and the commercial catalyst.

These catalysts were used for methanol steam reforming. The hydrogen production rate ( $\text{mmol g}_{\text{cat}}\text{h}^{-1}$ ) and the ratio of produced CO and  $\text{H}_2$  amount (%) of the five catalysts are in Fig. 1. The  $\text{Cu}/\text{Al}_2\text{O}_3$  and  $\text{Cu}/\text{SiO}_2$  catalysts prepared by the sol-gel methods produce hydrogen much faster than  $\text{Cu-Zn}/\text{Al}_2\text{O}_3$  catalyst prepared by the impregnation method, commercial catalyst, and  $\text{Cu}/\text{ZrO}_2$ . Production of hydrogen is related to the amount of CO adsorbed to catalyst for the Table 1 and Fig. 1. It is speculated that the copper amount of the catalyst surface is related to the hydrogen production. The sol-gel method makes copper well dispersed on the catalyst surface and amount of copper on the surface of the catalyst bigger. These copper sites work to methanol steam reforming and hydrogen production. More amounts of copper produce more hydrogen with faster rate than the catalyst prepared by impregnation method and commercial catalyst, even if their Cu loading percent, 10 wt.% is lower than other loading percents, 25 wt.% and  $\sim 50$  wt.%. For better hydrogen production from methanol, copper should be well dispersed on the catalyst and the sol-gel method is very

Table 1 Characterization of catalysts

Catalyst	BET specific surface area ( $\text{m}^2 \text{g}^{-1}$ )	Amount of CO adsorbed ( $\mu\text{mol g}^{-1}$ )	Metal dispersion <sup>a</sup> (%)	Percentage of surface metal <sup>a</sup> (%)	Average metal diameter <sup>a</sup> (nm)
Cu(10 wt.)/SiO <sub>2</sub> (sol)	527	84	5.4	6.5	16
Cu(10 wt.)/Al <sub>2</sub> O <sub>3</sub> (sol)	199	104	6.6	21	13
Cu(10 wt.)/ZrO <sub>2</sub> (sol)	15	16	1.0	44	84
CuO–ZnO(50–50 wt.%) (N211)	11	5.8	0.038	21	26 × 100
Cu–Zn(25–25 wt.)/Al <sub>2</sub> O <sub>3</sub> (imp.)	36	59	0.77	68	1.3 × 100

<sup>a</sup> Metal dispersion, percentage of surface metal, and average metal diameter of catalysts were estimated by each amount of CO adsorbed. This method could have some errors of real metal particle size and metal dispersion; however, we adopted it for ease of use and for measurability *in situ* before methanol steam reforming.

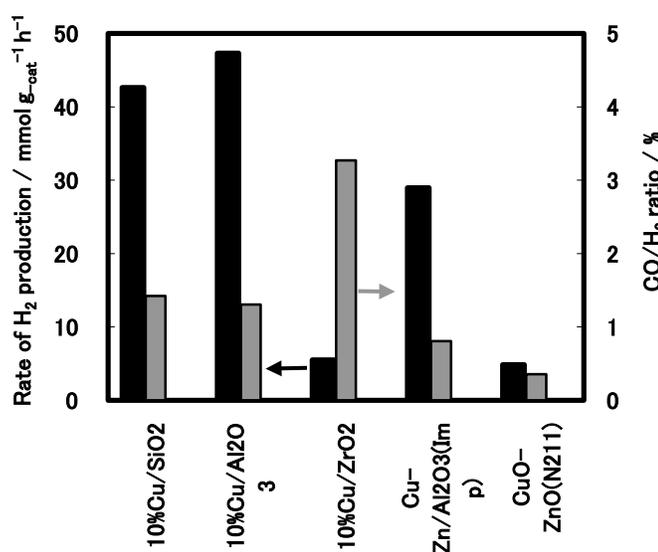


Fig. 1 Steam reforming of methanol over some catalysts. (Reaction temperature: 300 °C, catalyst weight: 0.1 g, CH<sub>3</sub>OH-H<sub>2</sub>O = 16-16 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.)

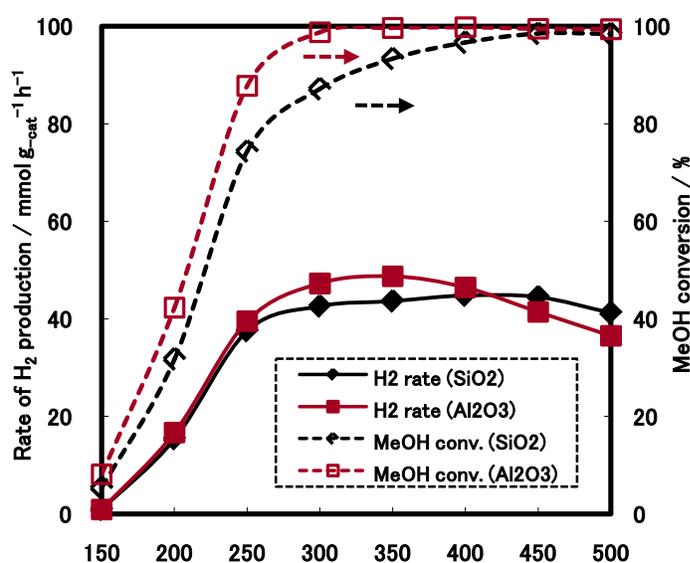


Fig. 2 Temperature dependence of H<sub>2</sub> production rate and methanol conversion over Cu(10 wt.)/SiO<sub>2</sub> and Cu(10 wt.)/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by using the sol-gel method. (Catalyst weight: 0.1g, CH<sub>3</sub>OH-H<sub>2</sub>O = 16-16 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.)

excellent for the methanol steam reforming catalysts.

The Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/SiO<sub>2</sub> catalysts, these two excellent catalysts for hydrogen production were tested for methanol steam reforming at wide range reaction temperature from 150 °C to 500 °C. Temperature dependence for hydrogen production and methanol conversion of methanol steam reforming over the two catalysts are in Fig. 2. From 250 °C to 500 °C both catalysts give high methanol conversion and high H<sub>2</sub> production rate even if 500 °C. Therefore, sol-gel preparation methods also give us excellent methanol steam reforming catalysts with high durability for high reaction temperature. In the case of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst prepared using the sol-gel method, methanol conversion leached almost 100% from 300 °C, on the other hand the Cu/SiO<sub>2</sub> catalyst shows more the 87% methanol conversion from 300 °C. However, both of the Cu/Al<sub>2</sub>O<sub>3</sub> and Cu/SiO<sub>2</sub> catalysts give fast H<sub>2</sub> production rate more than 38 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> from 250 °C. In the case of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst, H<sub>2</sub> production rate is slightly

decreased from 400 °C to 500 °C.

The temperature dependence of the selectivity for products by carbon base over Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is plotted in Fig. 3. CO selectivity increases while CO<sub>2</sub> selectivity decreases depending on temperature increasing. Reverse water-gas shift reaction occurs at the higher reaction temperature. By this reaction H<sub>2</sub> amount decreases at the higher reaction temperature. Small amount of methane also produces at higher temperature, more than 400 °C. At the lower reaction temperature, at ~200 °C, DME is produced by methanol dehydration reaction over the acid sites of the alumina of the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. From 150 °C to 500 °C, there was no temperature when CO<sub>2</sub> selectivity is higher than 95% in the case of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst prepared using the sol-gel method.

The temperature dependence of the carbon base selectivity

for products over the Cu/SiO<sub>2</sub> catalyst is plotted in Fig. 4. Reverse water-gas shift reaction occurs at the higher reaction temperature. However, the CO increasing rate is not so rapid compared with that by Cu/Al<sub>2</sub>O<sub>3</sub> catalyst. By-product is only HCOOCH<sub>3</sub> and selectivity for it is only 3%. Therefore, methanol steam reforming by Cu/SiO<sub>2</sub> is very good hydrogen supply way for PEFC, because fewer amounts of by-products, except of H<sub>2</sub> and CO<sub>2</sub>, are produced.

#### IV. CONCLUSIONS

We have developed excellent catalysts for hydrogen production by methanol steam reforming. Cu(10 wt.)/SiO<sub>2</sub> catalysts prepared by using the sol-gel method produce hydrogen very well and methanol conversion is almost 100% at 300 °C and higher temperature. By-product is only CO and methyl formate. Cu/SiO<sub>2</sub> has high durability for high temperature, even if 5000 °C.

Sol-gel preparation methods give us excellent catalysts. The catalysts prepared using the sol-gel method have bigger surface area, higher metal dispersion, and higher durability for heat than impregnation method catalysts and commercial catalysts. Cu(10 wt.)/Al<sub>2</sub>O<sub>3</sub> catalysts prepared using the sol-gel method also excellent catalysts for hydrogen production by methanol steam reforming. Hydrogen production rate of Cu/Al<sub>2</sub>O<sub>3</sub> catalyst is faster than that of Cu/SiO<sub>2</sub> catalyst at ~350 °C. Bad things of the Cu/Al<sub>2</sub>O<sub>3</sub> catalyst are high CO selectivity and production of much amount of by-products, such as CO, DME, and CH<sub>4</sub>. However, Cu/Al<sub>2</sub>O<sub>3</sub> methanol steam reforming system will be good for solid oxide fuel cells (SOFC), because CO, DME, and CH<sub>4</sub> can be fuel for SOFC.

#### REFERENCES

- [1] Y. Kawamura, N. Ogura, T. Yamamoto, A. Igarashi, *Chemical Engineering Science*, **61** (2006) 10092-10101.
- [2] H. Kobayashi, N. Takezawa, C. Minochi, *Chemistry Letters*, **(12)** (1976), 1347-1350.
- [3] C. Minochi, H. Kobayashi, N. Takezawa, *Chemistry Letters*, **(5)** (1979), 507-510.
- [4] H. Kobayashi, N. Takezawa, C. Minochi, K. Takahashi, *Chemistry Letters*, **(10)** (1980), 1197-1200.
- [5] N. Takezawa, H. Kobayashi, *Hyomen*, **20** (1982), 555-562.
- [6] M. Shimokawabe, N. Takezawa, H. Kobayashi, Haruo, *Bulletin of the Chemical Society of Japan*, **56** (1983), 1337-1340.
- [7] K. Takahashi, H. Kobayashi, N. Takezawa, *Chemistry Letters*, **(6)** (1985), 759-762.
- [8] K. Miyao, H. Onodera, N. Takezawa, *Reaction Kinetics and Catalysis Letters*, **53** (1994), 379-383.
- [9] S. Kasaoka, T. Shiraga, *Nenryo Kyokaiishi*, **59(633)** (1980), 40-47.
- [10] M. Machida, K. Eguchi, H. Arai, *Journal of Catalysis*, **103** (1987), 385-393.
- [11] M. Machida, K. Eguchi, H. Arai, *Bulletin of the Chemical Society of Japan*, **61** (1988), 3659-3665.
- [12] M. Machida, K. Eguchi, H. Arai, *Journal of the American Ceramic Society*, **71** (1988), 1142-1147.
- [13] T. Lopez, P. Bosch, M. Asomoza, R. Gomez, *Journal of Catalysis*, **133** (1992), 247-259.
- [14] T. Lopez, L. Herrera, R. Gomez, W. Zou, K. Robinson, R. D. Gonzalez, *Journal of Catalysis*, **136** (1992), 621-625.
- [15] E. Romero-Pascual, A. Larrea, M. Asomoza, R. D. Gonzalez, *Journal of Solid State Chemistry*, **168** (2002), 343-353.
- [16] M. Azomoza, T. Lopez, R. Gomez, R. D. Gonzalez, *Catalysis Today*, **15** (1992), 547-54.
- [17] K. Takeishi, H. Suzuki, *Applied Catalysis A: General*, **260** (2004) 111-117.
- [18] K. Takeishi, *Biofuels*, **1** (2010) 217-226.
- [19] K. Takeishi, Y. Akaike, *Applied Catalysis A: General*, **510** (2016) 20-26.

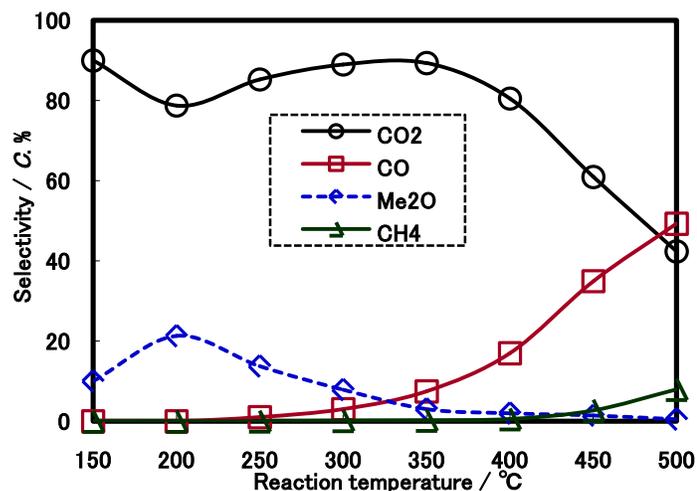


Fig. 3 Selectivity for carbon products over Cu(10 wt.)/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by using the sol-gel method. (Catalyst weight: 0.1g, CH<sub>3</sub>OH-H<sub>2</sub>O = 16-16 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.)

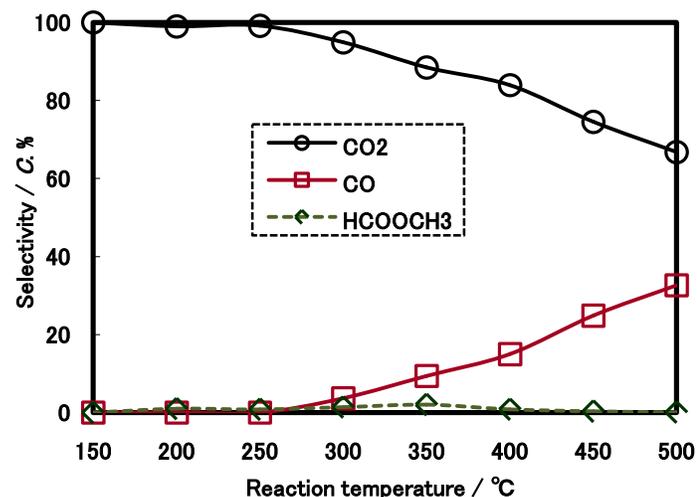


Fig. 4 Selectivity for carbon products over Cu(10 wt.)/SiO<sub>2</sub> catalyst prepared by the sol-gel method. (Catalyst weight: 0.1g, CH<sub>3</sub>OH-H<sub>2</sub>O = 16-16 mmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>.)