

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

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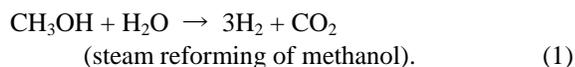
Abstract— Cu/SiO₂, Cu/Al₂O₃, and Cu/ZrO₂ catalysts were prepared by using sol-gel methods. Cu-Zn/Al₂O₃ catalyst was prepared by impregnation method. These catalysts and commercial CuO-ZnO catalyst were used for hydrogen production by methanol steam reforming. Catalysts prepared using the sol-gel method 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/SiO₂ 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.

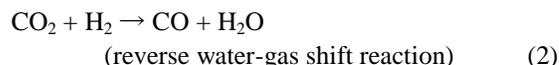


Methanol can be reformed by steam at very lower reaction temperature than gasoline, LPG, methane, and other hydrocarbons. CO affects Pt electrodes of polymer electrolyte

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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 H₂ 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/SiO₂, Cu/Al₂O₃, and Cu/ZrO₂ catalysts were prepared by sol-gel methods [17-19]. Cu/SiO₂ catalysts were obtained by hydrolysis of mixed solution with tetraethyl orthosilicate (TEOS), Cu(NO₃)₂, ethanol, water, and small amount of ethylene glycol (EG). Cu/Al₂O₃ was gotten by hydrolysis of

mixed solution with aluminium isopropoxide (AIP), $\text{Cu}(\text{NO}_3)_2$, water, and small amount of EG. Cu/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 Cu/SiO_2 catalysts, TEOS, ethanol, water, and EG were mixed, stirred, and heated at $\sim 80^\circ\text{C}$ for ~ 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 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 ~ 5 h. In the way of the 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°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 μm . The powder was calcined at 500°C for 5 h. Before steam reforming of methanol, the catalysts were reduced by flowing H_2 (99.99%, 10ml min^{-1}) at 450°C for 10 h, and were evacuated at 300°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, 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°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 N_2 gas at -196°C . After the evacuation of 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°C . After

the evacuation of CO gas at 300°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. H_2 , Ar (as internal standard for GC analysis), 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. CH_4 , CO_2 , H_2O , 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, 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 Cu/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 H_2 amount (%) of the five catalysts are in Fig. 1. The $\text{Cu}/\text{Al}_2\text{O}_3$ and Cu/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 Cu/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 ~ 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 ^a (%)	Percentage of surface metal ^a (%)	Average metal diameter ^a (nm)
Cu(10 wt.)/SiO ₂ (sol)	527	84	5.4	6.5	16
Cu(10 wt.)/Al ₂ O ₃ (sol)	199	104	6.6	21	13
Cu(10 wt.)/ZrO ₂ (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 ₂ O ₃ (imp.)	36	59	0.77	68	1.3 × 100

^a 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.

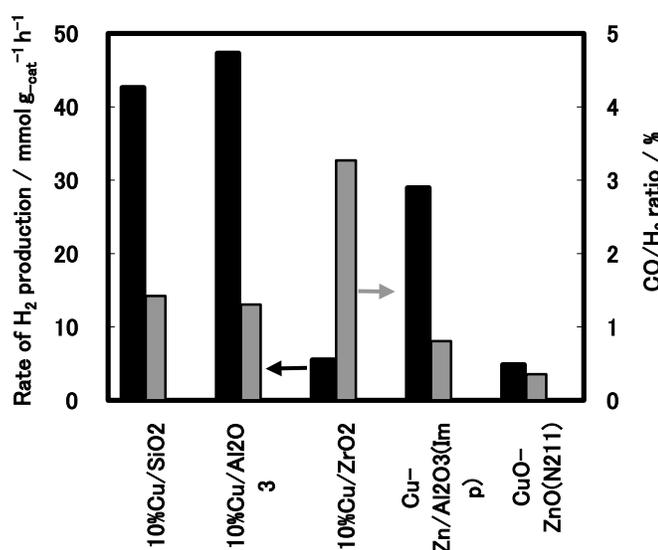


Fig. 1 Steam reforming of methanol over some catalysts. (Reaction temperature: 300 °C, catalyst weight: 0.1 g, CH₃OH-H₂O = 16-16 mmol g_{cat}⁻¹ h⁻¹.)

excellent for the methanol steam reforming catalysts.

The Cu/Al₂O₃ and Cu/SiO₂ 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 H₂ 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/Al₂O₃ catalyst prepared using the sol-gel method, methanol conversion leached almost 100% from 300 °C, on the other hand the Cu/SiO₂ catalyst shows more the 87% methanol conversion from 300 °C. However, both of the Cu/Al₂O₃ and Cu/SiO₂ catalysts give fast H₂ production rate more than 38 mmol g_{cat}⁻¹ h⁻¹ from 250 °C. In the case of Cu/Al₂O₃ catalyst, H₂ production rate is slightly

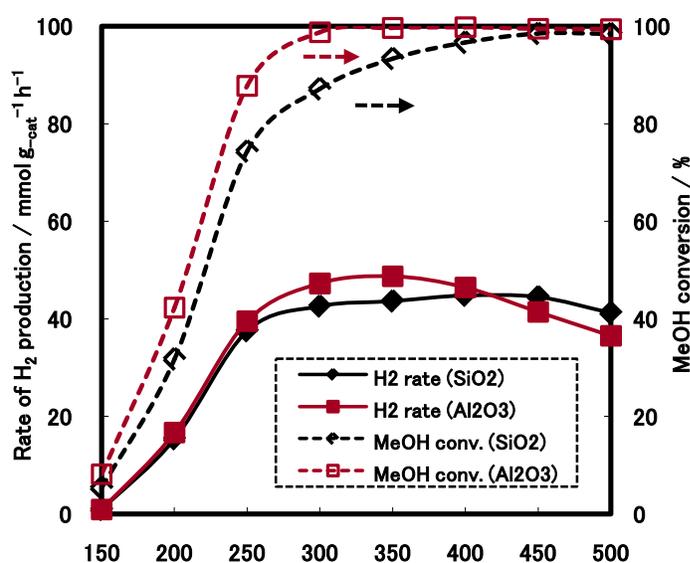


Fig. 2 Temperature dependence of H₂ production rate and methanol conversion over Cu(10 wt.)/SiO₂ and Cu(10 wt.)/Al₂O₃ catalysts prepared by using the sol-gel method. (Catalyst weight: 0.1g, CH₃OH-H₂O = 16-16 mmol g_{cat}⁻¹ h⁻¹.)

decreased from 400 °C to 500 °C.

The temperature dependence of the selectivity for products by carbon base over Cu/Al₂O₃ catalyst is plotted in Fig. 3. CO selectivity increases while CO₂ selectivity decreases depending on temperature increasing. Reverse water-gas shift reaction occurs at the higher reaction temperature. By this reaction H₂ 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/Al₂O₃ catalyst. From 150 °C to 500 °C, there was no temperature when CO₂ selectivity is higher than 95% in the case of Cu/Al₂O₃ catalyst prepared using the sol-gel method.

The temperature dependence of the carbon base selectivity

for products over the Cu/SiO₂ 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/Al₂O₃ catalyst. By-product is only HCOOCH₃ and selectivity for it is only 3%. Therefore, methanol steam reforming by Cu/SiO₂ is very good hydrogen supply way for PEFC, because fewer amounts of by-products, except of H₂ and CO₂, are produced.

IV. CONCLUSIONS

We have developed excellent catalysts for hydrogen production by methanol steam reforming. Cu(10 wt.)/SiO₂ 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/SiO₂ 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.)/Al₂O₃ catalysts prepared using the sol-gel method also excellent catalysts for hydrogen production by methanol steam reforming. Hydrogen production rate of Cu/Al₂O₃ catalyst is faster than that of Cu/SiO₂ catalyst at ~350 °C. Bad things of the Cu/Al₂O₃ catalyst are high CO selectivity and production of much amount of by-products, such as CO, DME, and CH₄. However, Cu/Al₂O₃ methanol steam reforming system will be good for solid oxide fuel cells (SOFC), because CO, DME, and CH₄ can be fuel for SOFC.

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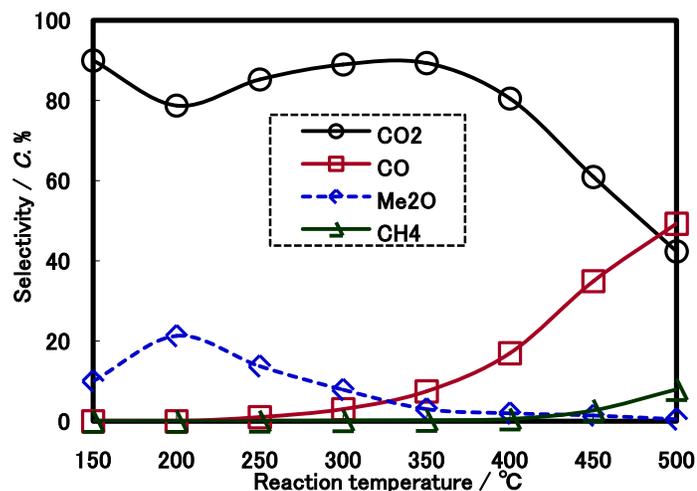


Fig. 3 Selectivity for carbon products over Cu(10 wt.)/Al₂O₃ catalyst prepared by using the sol-gel method. (Catalyst weight: 0.1g, CH₃OH-H₂O = 16-16 mmol g_{cat}⁻¹ h⁻¹.)

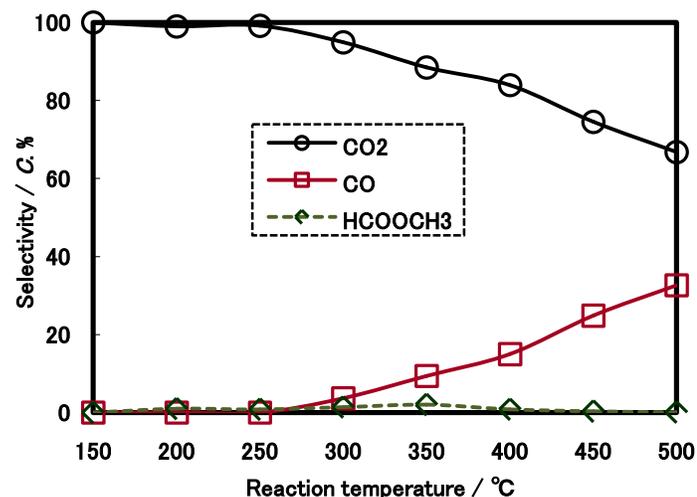


Fig. 4 Selectivity for carbon products over Cu(10 wt.)/SiO₂ catalyst prepared by the sol-gel method. (Catalyst weight: 0.1g, CH₃OH-H₂O = 16-16 mmol g_{cat}⁻¹ h⁻¹.)