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

Kaoru TAKEISHI and Hiromitsu SUZUKI

***Abstract*—** We have already reported that Cu(10 wt.%)/SiO_2 catalyst prepared by using the sol-gel method is excellent catalyst for hydrogen production by methanol steam reforming. Zn, Pd, Au, Pt, Ir, Re, Rh, Ru, Ag, Cr, Mn, Fe, Co, Ni, Mo, Sn were added to the Cu/SiO_2 catalyst on the way of its sol-gel preparation process and Cu-M(9-1 wt.%)/SiO_2 catalysts were prepared using the sol-gel method, respectively. These catalysts were tested for hydrogen production by methanol steam reforming, respectively. Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared using the sol-gel method is the most excellent catalyst for hydrogen production by methanol steam reforming at 350 ^{o}C. On the other hand, low temperature methanol steam reforming system is needed for waste heat recovery around 200 ^{o}C. For this purpose, Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared using the sol-gel method is most excellent among the catalysts, while the Cu-Zn(9-1 wt.%)/SiO_2 catalyst produces 1/10 amount of H_2 that of hydrogen produced at 350 ^{o}C.

***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 crucial for C1 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.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H^{0}_{298\,K} = -49.7 \text{ kJ mol}^{-1}$$
(steam reforming of methanol). (1)

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 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

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H^{0}_{298\,K} = +41.2 \text{ kJ mol}^{-1}$$
(reverse water-gas shift reaction) (2)

compared by the high 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].

Heat of combustion of 1 mol methanol is 726 kJ (higher heating value, HHV). On the other hand, heat of combustion of 3 mol hydrogen is 286 x 3 = 858 kJ (HHV). These mean, if 1mol methanol is steam-reformed to 3 mol hydrogen, combustion heat will increase 132 kJ. If this methanol steam reforming is carried by waste heat, it becomes waste heat recovery using methanol steam reforming. There are lots of waste heats in plants of steel, chemicals, power generation, and so on and such waste heat temperature is around 200 ^{o}C or higher than 200 ^{o}C. For this purpose, effective methanol steam reforming catalysts at lower reaction temperature around 200 ^{o}C are needed.

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_2 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

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distribution becomes sharp and the metal particles are difficult to sinter or coagulate between each other [10-16].

We have already reported that Cu(10 wt.%)/SiO_2 catalysts prepared using the sol-gel method are excellent catalyst for hydrogen production by methanol steam reforming. In this research, effects of metal addition to the Cu(10 wt.%)/SiO_2 catalysts are investigated. There are lots of waste heat more than 200 °C in steel plants, chemical plants, power generation plants, and so on. Waste heat recovery is very important for restraint of global warming. Therefore, effective catalysts for hydrogen production by methanol steam reforming at low temperature are also needed. Methanol steam reforming at low reaction temperature is also tested by these catalysts.

II. EXPERIMENTAL

A. Catalyst preparation

Cu(10 wt.%)/SiO_2, Cu(10 wt.%)/Al_2O_3, and Cu-M(9-1 wt.%)/SiO_2 catalysts were prepared by using sol-gel methods [17-19]. "M" means a metal, and in this research it is one metal from Zn, Pd, Au, Pt, Ir, Re, Rh, Ru, Ag, Cr, Mn, Fe, Co, Ni, Mo, and Sn. It is written "M", and such as Zn, Mn, Co, and Sn are existing oxides in the catalysts, but for ease and form the base of the preparation process it is written Cu-M/SiO_2 or Cu-Zn/SiO_2.

For example, Cu-Zn/SiO_2 catalyst was obtained by hydrolysis of mixed solution with tetraethyl orthosilicate (TEOS), $Cu(NO_3)_2$, $Zn(NO_3)_2$, ethanol, water, and small amount of ethylene glycol (EG). Cu/Al_2O_3 catalyst was gotten by hydrolysis of mixed solution with aluminium isopropoxide (AIP), $Cu(NO_3)_2$, water, and small amount of EG.

In the case of Cu-Zn(9-1 wt.%)/SiO_2 catalyst, TEOS, ethanol, water, and EG were mixed, stirred, and heated at ~80 °C for ~30 min. Amount of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ for the catalyst preparation depended on the loading metal amount of the needed catalysts will be added to the mixture. This time, mixed aqueous solution of $Cu(NO_3)_2$ and $Zn(NO_3)_2$ for 9 wt.% Cu and 1 wt.% Zn, was added to the TEOS 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 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 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 sever pretreatment were compared on the activity, selectivity, and so forth.

For the metal precursur, mainly nitrates were used, details are as follows; $Cu(NO_3)_2$-$3H_2O$, $Zn(NO_3)_2$-$6H_2O$, $Pd(NO_3)_2$, $HAuCl_4$-$4H_2O$, $[Pt(C_5H_7O_2)_2]$, $IrCl_3$, ReO_2, $Rh(NO_3)_3$, $[Ru(C_5H_7O_2)_3]$, $AgNO_3$, $Cr(NO_3)_3$-nH_2O, $Mn(NO_3)_2$-$6H_2O$, $Fe(NO_3)_3$-$9H_2O$, $Co(NO_3)_2$-$6H_2O$, $Ni(NO_3)_2$-$6H_2O$, $(NH_4)_6Mo_7O_{24}$-$4H_2O$, SnC_2O_4. Each metal precursor is added on the way of sol-gel preparation process of Cu-M/SiO_2 catalysts, respectively.

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 mmol g_{-cat}^{-1} h^{-1}) and water (16 mmol g_{-cat}^{-1} 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 that 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 Cu(10 wt.%)/SiO_2, Cu(10 wt.%)/ Al_2O_3, Cu-Zn(9-1 wt.%)/SiO_2, Cu-Pd(9-1 wt.%)/SiO_2, Cu-Au (9-1 wt.%)/SiO_2, Cu-Pt(9-1 wt.%)/SiO_2, Cu-Ir(9-1 wt.%)/SiO_2, Cu-Re(9-1 wt.%)/SiO_2, Cu-Rh(9-1 wt.%)/SiO_2, Cu-Ru(9-1 wt.%)/SiO_2, Cu-Ag(9-1 wt.%)/SiO_2, Cu-Cr(9-1 wt.%)/SiO_2, Cu-Mn(9-1 wt.%)/SiO_2, Cu-Fe(9-1 wt.%)/SiO_2, Cu-Co(9-1 wt.%)/SiO_2, Cu-Ni(9-1 wt.%)/SiO_2, Cu-Mo(9-1 wt.%)/SiO_2, Cu-Sn(9-1 wt.%)/SiO_2 catalysts prepared by using the sol-gel method were in Table 1. The Cu-Au(9-1 wt.%)/SiO_2 catalyst using the sol-gel method has the biggest surface area, 660 m^2 g^{-1}, among the catalysts. The Cu(10 wt.%)/Al_2O_3 catalyst prepared busing the sol-gel method has the smallest surface area, 199 m^2 g^{-1}, among the catalysts. The Cu-Ni(9-1wt.%)/SiO_2 catalyst prepared using the sol-gel method has the most dispersed metal on the surface of the catalyst. The Cu-Au(9-1wt.%)/SiO_2 catalyst prepared by the sol-gel method has the least dispersed metal on the surface of the catalyst. The Cu-Ni(9-1wt.%)/SiO_2 catalyst has also the smallest metal particles. The Cu-Au(9-1wt.%)/SiO_2 catalyst has also the biggest metal particles.

Table 1 Characterization of some catalysts

Catalyst	BET specific surface area (m^2 g^{-1})	Metal dispersion (%) [a]	Average metal particle size (nm) [a]
Cu(10wt.%)/SiO_2	527	5.4	16
Cu(10wt.%)/Al_2O_3	199	6.6	13
Cu-Zn(9-1wt.%)/SiO_2	501	3.7	24
Cu-Pd(9-1wt.%)/SiO_2	573	3.9	23
Cu-Au(9-1wt.%)/SiO_2	625	2.8	33
Cu-Pt(9-1wt.%)/SiO_2	536	3.7	25
Cu-Ir(9-1wt.%)/SiO_2	533	3.8	24
Cu-Re(9-1wt.%)/SiO_2	452	4.6	20
Cu-Rh(9-1wt.%)/SiO_2	462	5.1	17
Cu-Ru(9-1wt.%)/SiO_2	660	4.5	19
Cu-Ag(9-1wt.%)/SiO_2	467	4.8	18
Cu-Cr(9-1wt.%)/SiO_2	502	4.7	19
Cu-Mn(9-1wt.%)/SiO_2	517	4.8	18
Cu-Fe(9-1wt.%)/SiO_2	483	6.7	13
Cu-Co(9-1wt.%)/SiO_2	503	6.2	14
Cu-Ni(9-1wt.%)/SiO_2	405	7.8	11
Cu-Zr(9-1wt.%)/SiO_2	272	3.5	26
Cu-Mo(9-1wt.%)/SiO_2	574	5.7	16
Cu-Sn(9-1wt.%)/SiO_2	560	4.1	22

[a] Metal dispersion and average metal particle size of catalysts were estimated by each amount of CO adsorbed and metal loading amount. 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.

These catalysts were used for methanol steam reforming. Hydrogen production rate and CO/H_2 production ratio by each catalyst at 350 °C reaction temperature are shown in Fig. 1. Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared using the sol-gel method produce hydrogen fastest, 54 mmol g_{-cat}^{-1} h^{-1} with the lowest CO/H_2 ratio, 1.4%. That hydrogen yield is almost 100%. Therefore, the Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared by using the sol-gel method is very excellent catalyst for hydrogen production by methanol steam reforming.

Addition of Zn promotes hydrogen production from methanol and inhibits CO production. On the other hand, there are no metal that can promote hydrogen production and can inhibit CO production except Zn. Therefore, Zn is an excellent promoter for methanol steam reforming over the Cu/SiO_2 catalyst prepared using the sol-gel method. Probably, other metals deactivated methanol steam reforming and/or activated methanol decomposition.

$$CH_3OH \rightarrow 2H_2 + CO \quad \Delta H^0_{298\,K} = +90.2 \text{ kJ mol}^{-1} \quad \text{(methanol decomposition)} \qquad (3)$$

Therefore, CO/H_2 ratio or CO production were increased and H_2 production was decreased. Physical properties above-mentioned are not so effective for hydrogen production by methanol steam reforming this time.

Considering waste heat recovery, those catalysts were used for methanol steam reforming at 200 °C reaction temperature. Part of the results, hydrogen production rate and CO/H_2 production ratio by each catalyst are shown in Fig. 2. In this case, Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared by the sol-gel method produced hydrogen not so much compared with Cu(10 wt.%)/Al_2O_3 catalyst and Cu(10 wt.%)/Al_2O_3 catalyst prepared using sol-gel method. There are no metal that can promote hydrogen production from the Cu(10 wt.%)/SiO_2 catalyst prepared using the sol-gel method, except Pd. Pd promotes hydrogen production with ~1.7 times faster compared with that of the Cu(10 wt.%)/SiO_2 catalyst. Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared by using sol-gel method is very excellent catalyst for low temperature methanol steam reforming and will be used for waste heat recovery around 200 °C.

The Cu-Zn(9-1 wt.%)/SiO_2 catalyst and the Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared by using the sol-gel method are compared by reaction temperature dependence of hydrogen production. Parts of the results are in Fig. 3. From 200 °C to ~270 °C hydrogen production rate by Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared using sol-gel method is faster than that by Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared by sol-gel method. However, hydrogen production rate by the Cu-Zn(9-1 wt.%)/SiO_2 catalyst is much faster than that by the Cu-Pd(9-1 wt.%)/SiO_2 catalyst. These catalysts are very excellent catalyst for hydrogen production by methanol steam reforming. These catalysts optimum reaction temperature are different, so the Cu-Zn(9-1 wt.%)/SiO_2 catalyst and the Cu-Pd(9-1 wt.%)/SiO_2 catalyst should be used at each optimum reaction temperature, ~350 °C and ~250 °C, respectively.

IV. CONCLUSIONS

We have developed excellent catalysts for hydrogen production by methanol steam reforming. Cu-Zn(9-1 wt.%)/SiO_2 catalyst prepared by using sol-gel method is very excellent for hydrogen production, hydrogen production rate is 54 mmol g_{-cat}^{-1} h^{-1} with the low CO/H_2 ratio, 1.4%, at 350 °C reaction temperature. That hydrogen yield is almost 100%. On the other hand, hydrogen production rate 350 °C is 41 mmol g_{-cat}^{-1} h^{-1} by Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared using the sol-gel method. However, H_2 production rate at 200 °C by the Cu-Pd(9-1 wt.%)/SiO_2 catalyst is much faster than that by the Cu-Zn(9-1 wt.%)/SiO_2 catalyst. Considering waste heat recovery by using methanol reforming at ~200 °C, Cu-Pd(9-1 wt.%)/SiO_2 prepared by the sol-gel method is an excellent catalyst. These catalysts optimum reaction temperature are different, so the Cu-Zn(9-1 wt.%)/SiO_2 catalyst and the Cu-Pd(9-1 wt.%)/SiO_2 catalyst should be used at each optimum reaction temperature, ~350 °C and ~250 °C, respectively.

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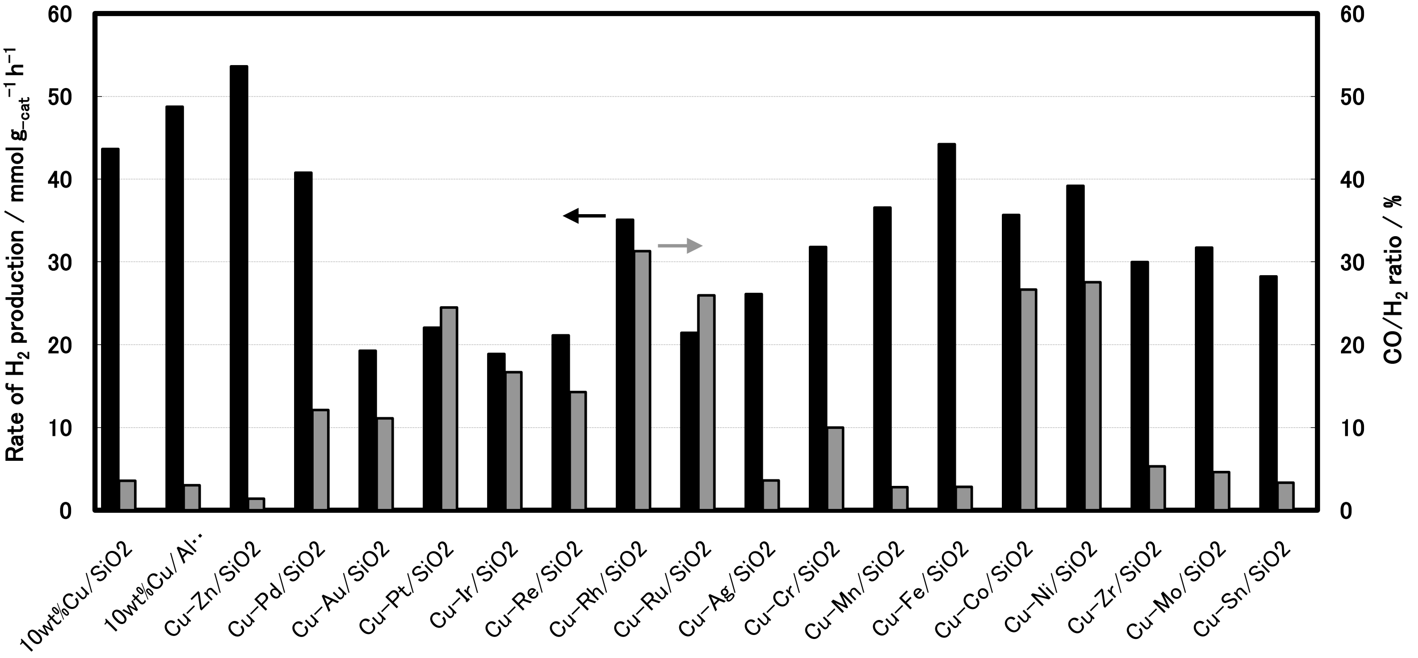

Fig. 1 Rate of H_2 production and CO/H_2 ratio in products of methanol-steam reforming over some Cu/SiO_2 catalysts prepared by using the sol-gel method at 350 °C. Catalyst weight: 0.1 g, CH_3OH-H_2O = 16-16 mmol g_{-cat}^{-1} h^{-1}.

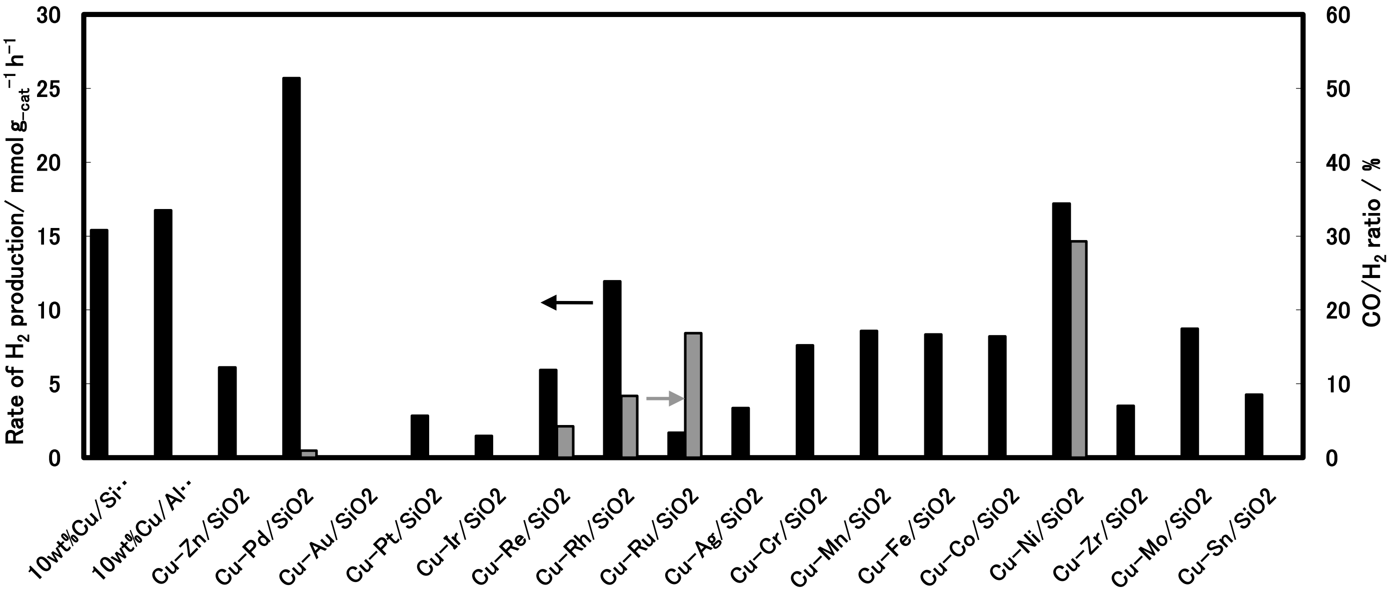

Fig. 2 Rate of H_2 production and CO/H_2 ratio in products of methanol-steam reforming over some Cu/SiO_2 catalysts prepared by using the sol-gel method at 200 °C. Catalyst weight: 0.1 g, CH_3OH-H_2O = 16-16 mmol g_{-cat}^{-1} h^{-1}.

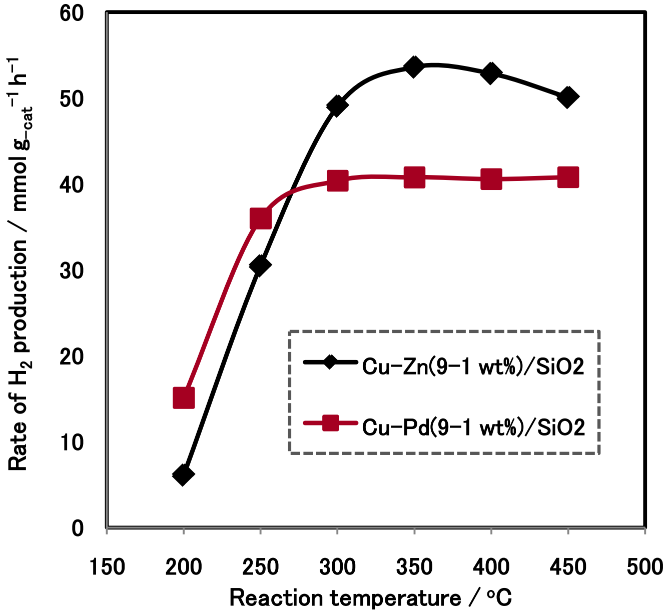

Fig. 3 Reaction temperature dependence of H_2 production rate of methanol steam reforming over Cu-Zn(9-1 wt.%)/SiO_2 catalyst and Cu-Pd(9-1 wt.%)/SiO_2 catalyst prepared by using sol-gel method. Catalyst weight: 0.1 g, CH_3OH-H_2O = 16-16 mmol g_{-cat}^{-1} h^{-1}.