Novel Catalytic Performance of SnO_2 for the Steam Reforming of Methanol

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Steam reforming of methanol took place over SnO_2 catalyst, not forming carbon monoxide appreciably. The reaction was suggested to proceed through the steam reforming of formaldehyde formed by the dehydrogenation of methanol.

Methanol is often considered as a promising hydrogen source for a fuel cell and an alternative energy source for automotives.[1–3] Hydrogen can be produced from methanol through two different processes, namely, steam reforming ($CH_3OH + H_2O \rightarrow CO_2 + 3H_2$) and partial oxidation ($CH_3OH + 1/2O_2 \rightarrow CO_2 + 2H_2$).[4–6] For the purpose of supply to a fuel cell, the minimization of CO formation occurring in both processes as a side reaction is required, because CO acts as a poison to the electrode of fuel cell.

Steam reforming of methanol has been performed on group VIII metals[4,5] or Cu-containing[7–9] catalysts. The activity of Cu/ZnO catalyst has investigated extensively in relation to the dispersion of Cu particle[8] or Cu/Zn ratios[9] and the high performance of $Cu/ZnO/ZrO_2/Al_2O_3$[6] and Cu/CeO_2[10] catalysts has been also reported. The problems on these catalysts are their activities for methanol decomposition and water-gas shift reaction. CO formed by the methanol decomposition reacts with water present in the reaction system but remains in some extent because of the equilibrium of water-gas shift reaction. CO formation by the reverse water-gas shift reaction of steam reforming products is also a matter for consideration. We reported novel activity of SnO_2 for the methanol conversion (eq 1)[11] which formed equal amounts of CO_2 and CH_4 and very recently have found that the catalyst promotes the methanol steam reforming unaccompanied by the water-gas shift reaction.

$$2CH_3OH \rightarrow CO_2 + CH_4 + 2H_2 \qquad (1)$$

SnO_2 catalyst used in this study was obtained from Kanto Chemical Co., and was calcined at 723 K for 2 h in nitrogen prior to the reaction. The catalytic reaction was carried out with a fixed bed flow type reactor at an atmospheric pressure. The typical reaction conditions were; temperature, 623 K; $N_2/CH_3OH/H_2O$ feed ratio, 2/1/1; total flow rate, 37.5 $cm^3\ min^{-1}$; and catalyst amount, 0.97 g. The products in the effluent stream were analyzed by on-line gas chromatograph equipped with a thermal conductivity detector and a flame ionization detector. The catalysts before or after the reaction were characterized by X-ray powder diffraction (XRD).

Figure 1 shows the effect of reaction temperature on the steam reforming over SnO_2 catalyst. The reaction was conducted 3 hours at every temperature and activity change was not observed appreciably during the reaction. A substantial amount of hydrogen was detected in the effluent gas but was not analyzed for every run quantitatively. The main product was CO_2, suggesting that the steam reforming of methanol proceeded predominantly. The selectivity was as high as 80% independently of the reaction temperature. CH_4 was formed at ca. 10% selectivity. As reported previously, SnO_2 catalyzes selectively the methanol conversion into CO_2, CH_4, and hydrogen. The present result indicates that the methanol conversion was suppressed by the presence of water vapor. Small amounts of HCHO, CO, and dimethyl ether (not shown) were also produced. The selectivity of HCHO decreased slightly with increasing reaction temperature. It is to be noted that the selectivity of CO is very low and decreases from 1.4% at 623 K to 0.8% at 698 K. Assuming that CO_2 and CO are formed via water-gas shift reaction, the selectivity of CO is calculated thermodynamically to be 1.6% at 623 K and 17.0% at 698 K. It is likely that water-gas shift reaction does not take place under this reaction condition and CO_2 is formed through direct reaction between water and methanol or methanol-derived species adsorbed on SnO_2 surface. The catalyst was inspected by XRD after the steam reforming at 698 K. The XRD pattern did not change from that observed with the fresh catalyst and showed the presence of only SnO_2 phase. However, diffraction lines assigned to metallic Sn phase were observed with the catalyst exposed to the mixture of nitrogen and methanol at the same temperature (698 K). The facts show that the reduction of SnO_2 into Sn metal is inhibited by the presence of water.

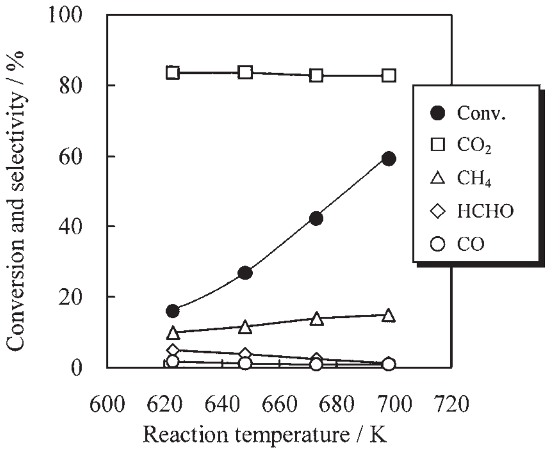

Figure 1. Effect of temperature on the steam reforming of methanol over SnO_2. Catalyst, 0.97 g; total flow rate, 37.5 $cm^3\ min^{-1}$; $N_2/CH_3OH/H_2O$, 2/1/1.

Figure 2 shows the effect of contact time (*W*/*F*) on the steam reforming at 698 K. *W* and *F* represent the amount of catalyst and the total flow rate, respectively. The data were collected by varying the amount of catalyst and by fixing the total flow rate of the feed. As seen in the figure, the conversion of methanol and CO_2 selectivity increased with increasing *W*/*F*, while HCHO selectivity decreased. The increase in CO_2 selectivity corresponds well to the decrease in HCHO selectivity, suggesting that HCHO is an intermediate of this particular steam reforming.

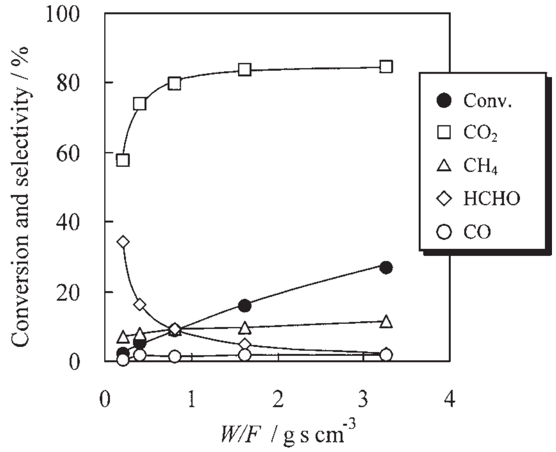

Figure 2. Effect of contact time on the steam reforming of methanol over SnO_2. Reaction temperature, 623 K; catalyst, 0.123–1.94 g; total flow rate, 37.5 cm^3 min^{-1}; $N_2/CH_3OH/H_2O$, 2/1/1.

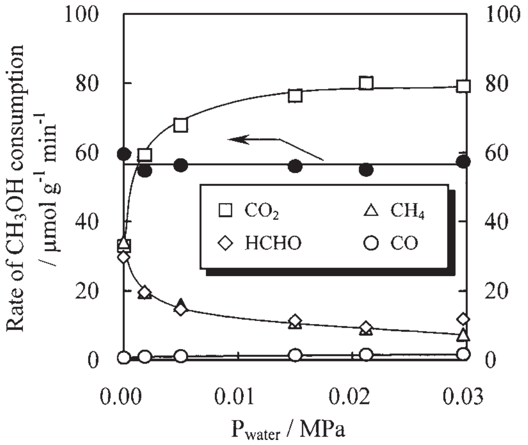

Figure 3. Effect of partial pressure of water on the steam reforming of methanol over SnO_2. Reaction temperature, 623 K; catalyst, 0.49 g; total flow rate, 35.5–55.9 cm^3 min^{-1}; $N_2/CH_3OH/H_2O$, 4/1/0–2.7/1/1.3.

The steam reforming was carried out at 623 K by varying the partial pressure of water. The mixture of methanol and water was fed at various molar ratios and the partial pressure of methanol was maintained at 0.02 MPa by adjusting the flow rate of nitrogen. Accordingly, the total flow rate changed from 35.5 to 55.9 cm^3 min^{-1}, but the values of methanol conversion fell in the range of 6.2–9.4%. Figure 3 shows the rate of methanol consumption and the selectivity of each product as a function of partial pressure of water. In the absence of water, the selectivity of CH_4 was approximately equal to that of CO_2, as reported previously.[11] The rate of methanol consumption was not affected largely by the presence of water vapor regardless of its partial pressure. The fact suggests that the rates of methanol conversion (eq 1) and steam reforming are controlled by the same elementary step, probably the dehydrogenation of methanol to HCHO. The selectivity of HCHO and CH_4 decreased with increasing the partial pressure of water while the selectivity of CO_2 increased. At higher partial pressure of water, HCHO formed seems to react with water preferentially to form CO_2 and H_2 through an intermediate like formic acid or formate species, and with methanol to some extent to form $HCOOCH_3$ which readily decomposes to CO_2 and CH_4. The selectivity of CO was very low at the whole range of water partial pressure.

Although the reaction mechanism is still under investigation, this steam reforming of methanol over SnO_2 is considered to proceed through the steam reforming of HCHO formed by the dehydrogenation of methanol and not to be accompanied by the water-gas shift reaction.

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