Novel Activity of SnO_2 for Methanol Conversion: Formation of Methane, Carbon Dioxide, and Hydrogen

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SnO_2 catalyzed methanol conversion to form methane, carbon dioxide and hydrogen selectively. It was suggested that formaldehyde was an intermediate to give methyl formate that readily decomposed into methane and carbon dioxide.

Methanol is one of the important feedstocks in chemical industries. Methanol is decomposed into carbon monoxide and hydrogen over metal catalysts,[1] dehydrogenated into formaldehyde or methyl formate over Zn- or Cu-containing catalysts,[2,3] and dehydrated into dimethyl ether and successively to hydrocarbons over acid catalysts.[4] Shido et al.[5] reported that Mo dimer oxycarbide species in NaY supercages catalyzed a conversion of methanol into methane, carbon dioxide and hydrogen (eq 1). However, the catalyst also promoted dehydration of methanol to form dimethyl ether.

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

Recently, we found that SnO_2 promoted the reaction (1) selectively. The results are reported here.

Three kinds of SnO_2 were employed as catalysts. SnO_2-A was prepared by decomposition of tin hydroxide. $SnCl_4 \cdot 5H_2O$ was dissolved in distilled water and an Na_2CO_3 solution was added until pH value attained 4. The resultant precipitate was washed until no Cl^- ions were detected, dried overnight at 110 °C, and then calcined at 450 °C in air for 2 h. SnO_2-B and SnO_2-C were purchased from Kanto Chemical Co. and Soekawa Chemicals, respectively. MgO, ZnO, ZrO_2, La_2O_3, and CeO_2 were obtained by decomposition of magnesium carbonate, zinc carbonate, zirconium hydroxide, lanthanum hydroxide, and cerium hydroxide, respectively, in an N_2 stream at 450 °C for 2 h. The BET surface area of metal oxide was measured by N_2 adsorption at liquid nitrogen temperature using a conventional flow-type adsorption apparatus. Powder X-ray diffraction (XRD) patterns of fresh and used catalyst were recorded with Rigaku RAD-1VB.

The reaction of methanol was carried out in a conventional flow-type reaction system with a Pyrex glass reactor under atmospheric pressure. The feed gas consisted of 25 vol% of methanol and N_2 balance. The total flow rate was 40 $cm^3\,min^{-1}$. The catalysts were pretreated in an N_2 stream at 450 °C for 2 h prior to the reaction. The feed and effluent gases were analyzed with an on-line gas chromatograph (Shimadzu GC-7A) equipped with a thermal conductivity detector and a flame ionization detector using Porapak-T and Molecular Sieve 13X columns.

Table 1 summarizes the activities of various metal oxide catalysts. The reactions over three SnO_2 catalysts were not different substantially and yielded methane, carbon dioxide, and formaldehyde. Methane and carbon dioxide were formed in approximately equal amount and their total selectivity was higher than 80%. Small amounts of carbon monoxide and dimethyl ether and a detectable amount of methyl formate were also formed. The product distribution indicates that the reaction (1) takes place on SnO_2 selectively. The specific rates of methanol conversion were 4.65, 4.12, and 5.31 $\mu mol\,min^{-1}\,m^{-2}$ for SnO_2-A, -B, and -C, respectively, suggesting that the catalytic activity was independent on the surface structure. The other oxides of metal neighboring on a periodic table, PbO, Sb_2O_3, and Bi_2O_3, were also tested for the reaction (not shown). However, these oxides were reduced to metallic state during the reaction yielding carbon dioxide and water at even relatively low temperature of 350 °C, and did not show any catalytic activity.

MgO and ZnO catalyzed the decomposition of methanol into carbon monoxide and hydrogen. The major products over CeO_2 were carbon monoxide and methane. The amount of carbon monoxide was twice or more higher than that of methane. The result suggests that carbon monoxide was formed by the decomposition of methanol and a reverse water gas shift reaction between carbon dioxide and hydrogen formed by the reaction (1). La_2O_3 is known to have both acidic and basic properties,[6] and gave the decomposition and the dehydration products, carbon monoxide and dimethyl ether. ZrO_2 is relatively more acidic than

Table 1. Catalytic reaction of methanol over various metal oxides at 375 °C

Catalyst	Surface area $/m^2g^{-1}$	Catalyst weight /g	Conversion /%	Selectivity/% CH_4	CO_2	CH_2O	CO	MF	DME
SnO_2-A	50	0.3	15.6	39.3	39.8	17.4	0.7	0	2.8
SnO_2-B	32	1.0	29.2	43.4	45.6	7.8	0.9	tr.	2.3
SnO_2-C	12	1.0	13.8	38.9	40.4	18.2	0.8	tr.	1.7
MgO	252	1.0	9.2	0	1.9	0.4	94.1	0	3.5
ZnO	37	0.2	35.0	0.5	10.9	5.0	76.9	0	0.2
CeO_2	94	1.0	14.9	30.2	1.8	0.3	65.6	0	2.1
La_2O_3	51	1.0	14.4	0	3.7	2.8	60.5	0	36.9
ZrO_2	141	1.0	46.4	tr.	0	8.0	0.3	0	91.6

MF, methyl formate and DME, dimethyl ether.

above oxides and catalyzed the dehydration into dimethyl ether preferentially.

Figure 1 shows the results of the reaction over SnO_2-A at various temperatures. The catalytic activity did not change appreciably throughout the reaction and no difference was observed between the XRD patterns of fresh and used catalysts. The values of selectivity to methane and carbon dioxide increased with increasing reaction temperature, while the selectivity to formaldehyde decreased from 24.7% at 350 °C to 11.1% at 400 °C.

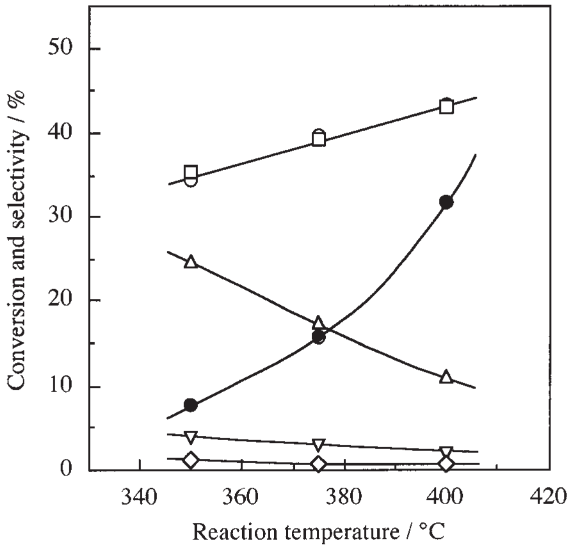

Figure 1. Reaction of methanol over SnO_2-A at various temperatures; conversion of methanol (●) and selectivities to methane (◯), carbon dioxide (□), formaldehyde (△), carbon monoxide (◇), and dimethly ether (▽). The amount of catalyst was 0.3 g.

Figure 2 shows the effect of contact time (W/F) on the conversion and selectivity in the reaction over SnO_2-B at 375 °C. The conversion increased up to 50% with W/F linearly. Formation of methane and carbon monoxide in an equal amount was observed again at any conversion level and increased with W/F, while the selectivity to formaldehyde decreased. The results indicate that the reaction (1) takes place over the SnO_2 catalyst through the dehydrogenation of methanol to formaldehyde and subsequent reaction to form methane and carbon dioxide.

Scheme 1 summarizes the reaction pathway deduced from the results mentioned above. Since methane and carbon dioxide are formed in the same amount by the reaction, they seem to be formed via decomposition of methyl formate species adsorbed on SnO_2 catalyst. Methanol is dehydrogenated to formaldehyde over SnO_2 catalyst and formaldehyde reacts subsequently with methanol to form methyl formate, as proposed for the dehydrogenation of methanol over Cu catalyst.[7] Methyl formate was formed in very small amounts as seen in Table 1. It is assumed that the methyl formate species formed on SnO_2 is unstable under the reaction conditions and is readily decomposed into methane and carbon dioxide.

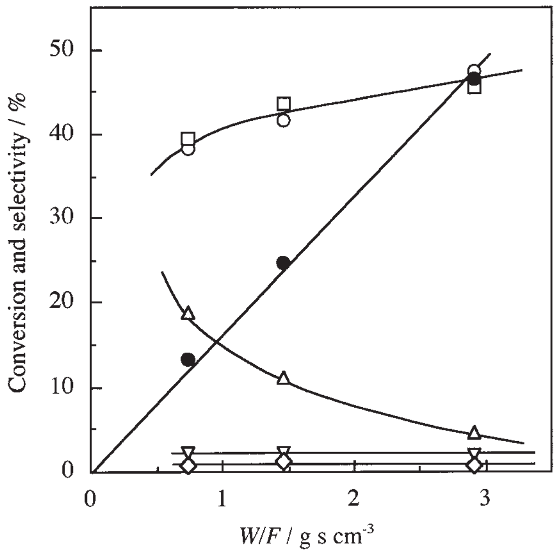

Figure 2. Change in conversion and product selectivity as a function of W/F in the reaction of methanol over SnO_2-B at 375 °C; conversion of methanol (●), and selectivities to methane (◯), carbon dioxide (□), formaldehyde (△), carbon monoxide (◇), and dimethyl ether (▽).

$$2\ CH_3OH$$
$$\downarrow$$
$$CH_2O\ +\ CH_3OH\ +\ H_2$$
$$\downarrow$$
$$[HCOOCH_3]\ +\ 2\ H_2$$
$$\downarrow$$
$$CH_4\ +\ CO_2\ +\ 2\ H_2$$

Scheme 1.

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