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The Catalysts for the Synthesis of Formaldehyde by Partial Oxidation of Methane

In the current chemical industry, methane is converted to formaldehyde through a three-step process involving steam reforming at high temperatures, methanol synthesis, and partial oxidation of methanol to formaldehyde. The steam reforming process requires a lot of energy as well as complicated engineering steps. Unlike this multistage process, the direct conversion of methane to formaldehyde by partial oxidation does not require energy input. Moreover, a one-step conversion would be the most simple and rational way for synthesizing formaldehyde.

The catalytic partial oxidation of methane to CH_3OH and HCHO using N_2O as an oxidant has been studied extensively for MoO_3/SiO_2 (*1, 2*) and V_2O_5/SiO_2 (*3*). However, when replacing N_2O with O_2 as the oxygen source, only a few attempts were successful at getting CH_3OH or HCHO (*4, 5*). The purpose of this work is to look for the metal oxides which are active and selective for synthesizing HCHO by partial oxidation of methane using oxygen as the oxidant. The factors determining the catalytic activity and selectivity will be discussed.

All the catalysts were prepared by immersing silica gel (Davison, 28-200 mesh) to an aqueous solution of metal salts ((Ca-, Mg-, La-, Ce-, Pr-, Sm-, Y-, Fe-, Al-, Ga-, and Bi-nitrates), $ZrO(NO_3)_2$, H_3BO_3, H_3PO_4, H_3AsO_4, $(NH_4)_{10}W_{12}O_{41}$, $SbCl_3$, $SnCl_2$, Nb_2O_5-$x$$H_2O$, and $Ba(OH)_2$) and then evaporating the water at 100°C. For some experiments Cab-O-Sil was used as a support. The silica gel or the Cab-O-Sil impregnated with the metal salts was calcined in air at 573 K for 2 h and subsequently at 923 K for 2 h. The contents of the metal oxides were adjusted to be 9.1 wt% assuming that the metal oxides on the silica gel or on the Cab-O-Sil were in the oxidation states which are shown in Fig. 1. The catalytic experiments were carried out using a conventional fixed-bed flow reactor at atmospheric pressure. The reactor was made of quartz tube. The internal diameter of the reactor at the catalyst bed was 12 mm, but after that the catalyst bed was decreased to 3 mm in order to pass out the products rapidly from the hot zone of the reactor because formaldehyde is susceptible to decompose at high temperatures. The mixture of CH_4 and O_2 diluted with He was fed to the catalyst bed. The effluent gas at time on stream of 60 min was analyzed by gas chromatography. The conversion of CH_4, the selectivities, and yields of products were calculated on the basis of carbon numbers of the methane reacted.

Catalytic activities and selectivities for the partial oxidation of methane have been tested for various metal oxides supported on silica gel. The experiments were carried out under the conditions as follows unless otherwise stated: $T = 873$–1023 K, $P(CH_4) = 50.7$ kPa, $P(O_2) = 10.1$ kPa, and $W/F(=$ weight of catalyst/flow rate$) = 0.17$ g h liter^{-1}. The products observed were HCHO, CO_2, CO, C_2H_6, C_2H_4, H_2O, and a trace of CH_3OH. The selectivity for each product depended, of course, on the catalysts and temperatures. In general, the selectivities to C_2-compounds (C_2H_6 + C_2H_4) increased above 973 K, but that to HCHO decreased sharply above 923 K.

The conversion of CH_4 observed for various metal oxides/SiO_2 at 923 K are plotted

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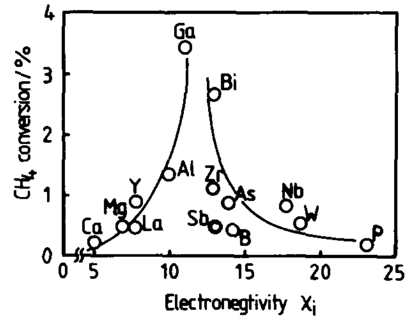

FIG. 1. Conversion of CH_4 versus electronegativities of the metal cations of the oxides. The elements indicate the metal oxides as follows: Ca(CaO), Mg(MgO), Y(Y_2O_3), La(La_2O_3), Ga(Ga_2O_3), Al(Al_2O_3), Bi(Bi_2O_3), Zr(ZrO_2), Sb(Sb_2O_3), As(As_2O_3), B(B_2O_3), Nb(Nb_2O_5), W(WO_3), P(P_2O_5).

against the electronegativities of the metal cations of the oxides determined by Tanaka and Ozaki (*6*) in Fig. 1. The results in Fig. 1 suggest that the most active oxides for activation of methane are the ones of which cations have intermediate electronegativities among the metal oxides tested. The selectivities to HCHO observed for the metal oxides in Fig. 1 are plotted as a function of the electronegativity in Fig. 2. The results in Fig. 2 indicate that the selectivity to HCHO increases as a rise in the electronegativity of the cations of the metal oxides.

It is generally believed that partial oxidation of methane is initiated by abstraction of hydrogen from methane (*1*, *5*) (step 1 in Scheme 1 below).

$$CH_4 \xrightarrow[1]{\text{H-abstraction}} CH_{4-x} \xrightarrow[2]{\text{O-addition}}$$

$$HCHO \xrightarrow[3]{\text{H-abstraction}} CO,\ CO_2$$

SCHEME 1

Here, let us hypothesize that the dehydrogenated intermediate species CH_{4-x} (x = 1 or 2) would undergo subsequent conversions through steps 2 and 3 in Scheme 1. Addition of oxygen to the CH_{4-x} results in the formation of HCHO in step 2. The hydrogen of HCHO is further abstracted in step 3 and finally oxidized to CO and CO_2. The selectivity to HCHO is determined by the relative rate of step 2 compared to that of step 3. It is believed that the oxygen possessing more negative charge would be more reactive for oxidative abstraction of hydrogen from hydrocarbons. On the contrary, when the negative charge on oxygen is decreased, approaching to neutral oxygen, the electrophilic addition of oxygen becomes more feasible (*7–9*). We can expect that the quantity of the negative charge on the oxygen adsorbed on metal oxides would change depending on the electronegativity of the cations of the oxides, i.e., the more electronegative the cations the more electrophilic the oxygen adsorbed. The rate of conversion of CH_4 is determined by the rate of step 1 or 2. The volcano shape correlation between the conversion of CH_4 and electronegativities observed in Fig. 1 can be explained as follows. For the metal oxides of smaller electronegativity (basic oxides), the rate of conversion of CH_4 is controlled by step 2. For the oxides on the left side in Fig. 1, the rate of conversion increases with the rise in the electronegativity of the cations because the rate of step 2 increases with the rise in electrophilicity of the oxygen adsorbed on the metal oxides. However, the ability of the oxygen to abstract hydrogen from CH_4 (step 1) must decrease with the increasing electrophilicity of the oxygen adsorbed. For the cations of greater electronegativity,

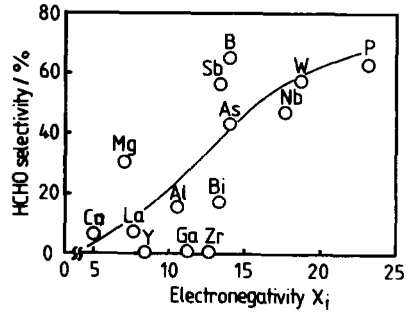

FIG. 2. Selectivity to HCHO versus electronegativities of metal cations of the oxides.

the rate-determining step shifts to step 1. Thus the rate of conversion of CH_4 decreases with a rise in electrophilicity of the oxygen adsorbed on the oxides on the right side (acidic oxides) in Fig. 1. Moreover, we can explain the observation that the metal oxides with large electronegativities showed higher selectivity to HCHO (Fig. 1), because the rate of step 2 in Scheme 1 becomes faster than that of step 3 with the increasing electrophilicity of the oxygen adsorbed on the cations.

Although acidic metal oxides are selective catalysts for the synthesis of HCHO as described above, they cannot be active for the activation of methane in step 1 (H-abstraction). In fact, the yields of HCHO observed for the oxides of Sb, As, B, Nb, W, and P were less than 0.5%.

The selectivity to HCHO was the highest for the B_2O_3/SiO_2 as shown in Fig. 2. However, the conversion of methane was as low as 0.25%. Therefore, various metal oxides were added to B_2O_3/SiO_2 in order to improve the conversion of methane. The additives tested were the oxides of the metal cations of lower electronegativity (basic or amphoteric metal oxides) to improve the rate of step 1. The content of the metal oxides (M_xO_y) added was 8.3 wt% ($M_xO_y : B_2O_3 : SiO_2 = 1 : 1 : 10$). The silica gel was impregnated with aqueous solutions of H_3BO_3 and the salts of M. The salts on the silica gel were converted to the oxides as described earlier. Figure 3 shows the conversion of CH_4 and the yield of HCHO observed for various mixed oxides at 823 K. Most of the mixed oxides tested showed higher CH_4-conversion and HCHO-yield than the catalyst without additives (* indicates B_2O_3/SiO_2 without additives). The effects of basic oxides such as MgO, CaO, Pr_2O_3, and Sm_2O_3 on the HCHO-yield were high. This can be ascribed to the improvement in the rate of step 1 in Scheme 1.

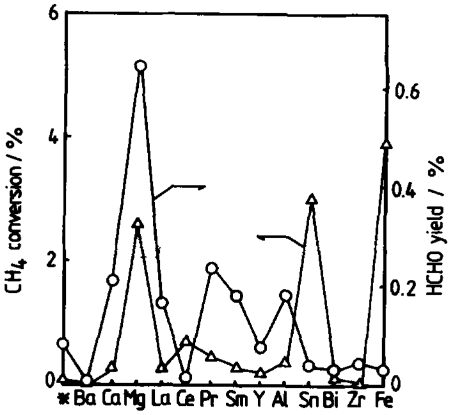

FIG. 3. Effect of metal oxide additives to the B_2O_3/SiO_2 catalyst on the conversion of CH_4 and yield of HCHO. *, B_2O_3/SiO_2 only; the metal oxides added, Ba(BaO), Ca(CaO), Mg(MgO), La(La_2O_3), Ce(CeO_2), Pr(Pr_2O_3), Sm(Sm_2O_3), Y(Y_2O_3), Al(Al_2O_3), Sn(SnO_2), Bi(Bi_2O_3), Zr(ZrO_2), Fe(Fe_2O_3).

Since the enhancing effect of MgO on the yield of HCHO was particularly high, the most favorable composition of the mixed oxides of MgO and B_2O_3 was examined. In conclusion, the mixed oxide of the one to one atomic ratio of Mg and B was the most active catalyst for the production of HCHO. X-ray diffraction analysis for the mixture of MgO and B_2O_3 (1 : 1 atomic ratio) calcined at 973 K in air showed the formation of compound oxides $Mg_2B_2O_5$. Therefore, this compound oxide may work bifunctionally to convert CH_4 into HCHO.

The effects of the oxides of alkaline earth metals were shown in Fig. 4. Here, the mixed oxides were supported on Cab-O-Sil. The catalysts were prepared by means of the similar method described earlier. The atomic ratio of alkaline earth metal and boron for the mixed oxides was adjusted to unity. The content of the mixed oxide on Cab-O-Sil was 10 wt%. The experimental conditions for Fig. 4 were different than those for Fig. 3. As can be seen in Fig. 4, the HCHO-yield and CH_4-conversion increased with the decreasing atomic number of alkaline earth elements in the periodic table. Strong base oxides such as SrO and BaO did not enhance but decreased the yield of HCHO compared with the yield for B_2O_3/SiO_2. The strong base oxides might

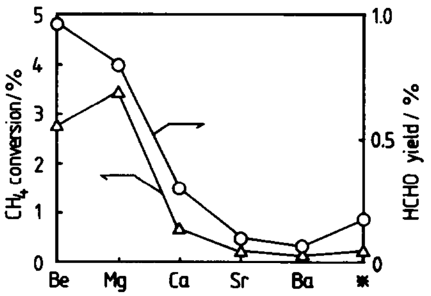

FIG. 4. Effect of alkaline earth oxides to B_2O_3/Cab-O-Sil catalyst on the conversion of CH_4 and yield of HCHO. *, B_2O_3/Cab-O-Sil only. Experimental conditions: $T = 873$ K, $P(CH_4) = 38.0$ kPa, $P(O_2) = 12.7$ kPa, $W/F = 0.42$ g h liter^{-1}.

poison the active sites on B_2O_3 which is a weak acid oxide. This unfavorable effect must be negligible for moderate base oxides such as BeO and MgO. In conclusion, the results in Fig. 4 suggest that the mixed oxides of B_2O_3 with moderate basic compounds are better catalysts for the high production of HCHO.

As described earlier, Scheme 1 indicates that both hydrogen abstraction (step 1) and oxygen addition (step 2) are required to produce HCHO by partial oxidation of methane. Thus, acid–base bifunctional catalysts must give a better HCHO-yield. However, the nature of the catalysts and detailed reaction mechanism are not known at the moment. Further studies are needed to clarify these points.

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