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Boron, Phosphorus, and Alkaline Earth-Metal Mixed Oxides as Active Catalysts in Partial Oxidation of Methane into Formaldehyde

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Alkaline earth element-added boron and phosphorus mixed oxides supported on Cab-O-Sil showed high catalytic activity in partial oxidation of methane to HCHO at <773 K. The results of the experiment using $^{18}O_2$ suggested that the lattice oxygen atoms of the catalyst are responsible for the oxidation.

Partial oxidation of CH_4 into HCHO remains one of the major challenges in the chemistry and processes for direct CH_4 conversion. Clearly a direct conversion of CH_4 into HCHO would be highly attractive compared to the current process that requires steam reforming of CH_4, CH_3OH synthesis from syngas, and oxidation of CH_3OH to HCHO. Many attempts have been made to convert CH_4 into C_1 oxygenates (CH_3OH and HCHO).1-7) The prospective catalysts for this reaction reported so far are molybdenum oxide based catalysts,1,3,6) metal phosphates,2) or boron oxide based catalysts.4,5) However, the catalytic activity and selectivity to C_1 oxygenates are still far from satisfactory. Therefore, the purpose of this work is to explore a better catalyst based on the mixed oxides of boron and phosphorus (denoted as BP-O hereafter). BP-O are active and selective for partial oxidations of C_2H_6 and C_3H_8 into corresponding oxygenates.8,9)

We have suggested previously that the mixed oxides of B_2O_3 with moderate basic compounds such as CaO, MgO, and BeO could be an active and selective catalyst for HCHO synthesis.4) The use of Cab-O-Sil as a carrier improved the catalytic function of the mixed oxides.4) Thus, various metal-added BP-O on Cab-O-Sil are tested for this reaction.

All the catalysts were prepared by immersing Cab-O-Sil to an aqueous solution of metal(M) nitrates, H_3BO_3 and H_3PO_4 (M:B:P=1:1:1 mol ratio). After the water was evaporated from the solution at 373 K, the residue was

Table 1. Active Catalysts for Partial Oxidation of CH_4 to HCHO[a)]

Catalyst	% CH_4 Conversion	% HCHO Selectivity	% HCHO Yield
MgBP-O/Cab-O-Sil	8.1	22.0	1.8
BeBP-O/Cab-O-Sil	6.1	28.4	1.7
CaBP-O/Cab-O-Sil[b)]	5.0	26.3	1.3

a) Reaction conditions: T=773 K, Catalyst weight=1.0 g, $P(CH_4)=P(O_2)=33.8$ kPa, Flow rate=180 $ml\cdot min^{-1}$. b) Flow rate=60 $ml\cdot min^{-1}$.

calcined in air at 623 K for 2 h and subsequently at 923 K for 2 h. The content of each element was adjusted to be 2.0×10^{-3} $mol\cdot g^{-1}$.

The catalytic tests were carried out using a fixed-bed flow reactor (quartz) at the same partial pressure of CH_4 and O_2 (34 kPa). The total pressure was balanced to atmospheric pressure by He. The products were analyzed by gas-chromatography using columns packed with Gaskuropack 54 and TSR-1(10%)/Flusin T. The oxygen isotope distribution in the products during oxidation of CH_4 with $^{18}O_2$ was measured by a quadrupole mass spectrometer. The conversion of CH_4, the product selectivities, and the yields of products were calculated on the basis of the CH_4 reacted.

Table 1 shows the results of alkali metal-added BP-O that are active at the temperatures lower than 773 K. The products were HCHO, CO, H_2O and a trace of CO_2. CH_3OH and C_2 compounds (C_2H_4 and C_2H_6) were not formed. Therefore, the selectivity to CO in Table 1 was roughly calculated by subtracting the HCHO-selectivity from 100%. In general, the catalytic partial oxidation of CH_4 at ≤ 1 bar requires higher temperatures than 823 K.[1-7)] Thus, the catalysts in Table 1 are quite active for the formation of HCHO compared to the catalysts reported previously. Addition of Sr and Ba to BP-O/Cab-O-Sil did not induce any catalytic activity at low temperatures (< 823 K). The results in Table 1 show that MgBP-O/Cab-O-Sil is most active among the catalysts tested in this work. Al_2O_3, $SiO_2\cdot Al_2O_3$, TiO_2, Nb_2O_3, and $AlPO_4$ were used as carriers for MgBP-O instead of Cab-O-Sil. None of these carriers improved the catalytic activity better than MgBP-O/Cab-O-Sil.

The catalytic test for MgBP-O/Cab-O-Sil with different ratios of Mg and B (where B/P ratio was fixed to one) has indicated that one to one ratio gives the highest catalytic activity. Moreover, the best loading for each element on Cab-O-Sil was found to be 1.5 to 2.0×10^{-3} $mol\cdot g^{-1}$. The X-ray diffraction analysis of this sample confirmed the existence of a poorly crystallized B_2O_3, but no compound oxide formation was observed.

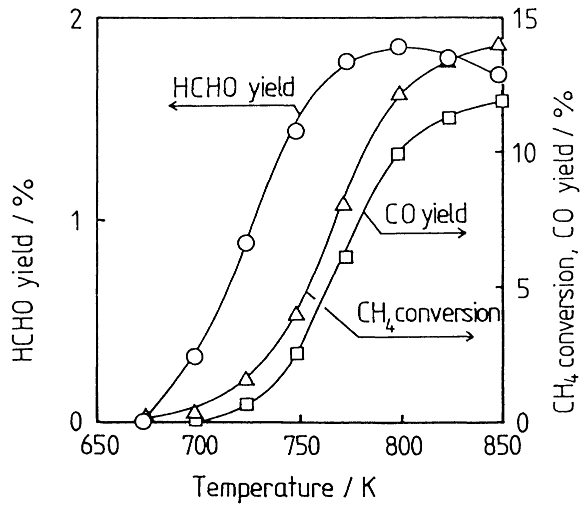

Fig. 1. Oxidation of CH_4 on MgBP-O/Cab-O-Sil as functions of temperature. $P(CH_4)=P(O_2)=34$ kPa, F=180 $ml\cdot min^{-1}$, W=1.0 g.

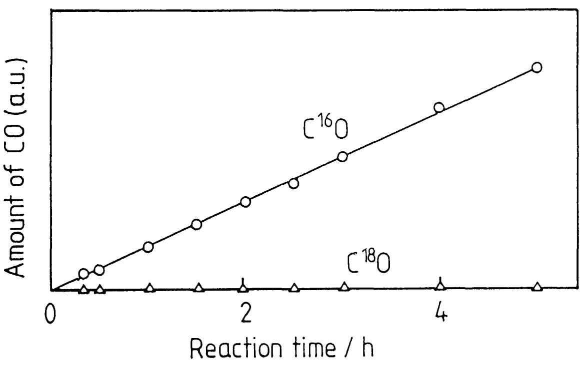

Fig. 2. Distribution of oxygen isotopes in CO. T=773 K, Initial pressure; $P(CH_4)=P(^{18}O_2)=1.3$ kPa.

The temperature effects on the conversion of CH_4 and on the yields of products observed for MgBP-O/Cab-O-Sil are shown in Fig. 1. The results in Fig. 1 show that the reaction occurs at >673 K with high HCHO selectivity. The HCHO yield increased sharply with a rise in temperature up to 773 K, but the HCHO selectivity decreased considerably at >750 K. The decrease in the HCHO selectivity was always accompanied with the corresponding increase in the CO selectivity. However, CO_2 was not observed at least at the temperatures lower than 773 K. These observations show that the primary product is HCHO and CO is formed from HCHO. The corresponding changes in the selectivities of HCHO and CO were also observed as increasing the contact time. This result also supported the above conclusion.

Since the activation of CH_4 over solid catalysts is usually required high temperatures (> 873 K), the importance of gas phase chain reactions has been recognized by many researchers.[10] A catalyst might just be an initiator of the gas phase chain reactions. Thus, the product distributions may be determined wholly in the gas phase. If this is the case for the catalytic oxidation of CH_4 with MgBP-O/Cab-O-Sil, most of the products should come from the gas phase chain reactions. This question can be answered by the experiment using a gas mixture of $^{18}O_2$ and CH_4. Figure 2 shows the distribution of oxygen isotopes in the CO formed during the oxidation of CH_4 with $^{18}O_2$ over MgBP-O/Cab-O-Sil (0.50 g). The experiment was carried out using a closed gas-circulation system. The HCHO, H_2O and CO_2 formed were always collected in a cold trap at 77 K during the reaction. The results in Fig. 2 clearly show that the $^{18}O_2$ in the gas phase is not introduced to CO. The analysis of the collected products confirmed that $^{18}O_2$ was not transferred into HCHO either. The exchange reaction between $^{18}O_2(g)$ and $^{16}O(bulk)$ took place slowly compared with the oxidation of CH_4. Thus, the $^{18}O_2$ in the gas phase was not diluted appreciably with $^{18}O^{16}O$ and $^{16}O_2$. These observations strongly suggest that the lattice oxygen atoms of the catalyst is responsible for the formation of HCHO. In other words, the addition of oxygen to methane occurs on the surface. The contribution of gas phase oxidation can be neglected under the reaction conditions in this work. However, the gas phase reaction must become important at higher pressures (> 1 bar).

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