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Partial oxidation of methane over silica supported molybdenum oxide catalysts

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Two kinds of MoO_3/SiO_2 catalysts, MoO_3-I and MoO_3-S, were prepared by impregnation and sol–gel method, respectively. When MoO_3 loading was increased, formation of MoO_3 crystals was observed to begin at a MoO_3 loading of 8 and 16 wt% with MoO_3-I and MoO_3-S, respectively. The highest yield of formaldehyde from methane oxidation was attained also at those critical values of MoO_3 loading of 8 and 16 wt% over MoO_3-I and MoO_3-S, respectively. It is suggested that the active species for formaldehyde formation is well dispersed molybdenum oxide clusters on SiO_2 support: the optimum dispersion of the clusters affords the highest activity for formaldehyde formation.

Keywords: molybdenum oxide; silica support; sol–gel; impregnation; partial oxidation; methane

1. Introduction

The catalytic oxidation reactions of methane into more valuable materials such as ethane, ethylene, formaldehyde and methanol are very important from both the industrial and fundamental points of view due to the existence of large natural gas reserves, and have been studied intensively in recent years [1–5]. Most work has been focused on oxidative coupling of methane, and relatively few studies have been carried out on the conversion reaction to oxygenated compounds [6–8]. It has been shown that supported molybdenum oxide is an active catalyst for the partial oxidation of methanol [9] and propene [10] due to its mild oxidation capability; its activity and selectivity are strongly related to the preparation method.

The heterogeneous oxidation of methane generally occurs at relatively high temperatures ($>500°C$) due to the high stability of the C–H bond in the methane mole-

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cule. In these conditions, it seems that selective production of C_1 oxygenates is very difficult to attain as the result of subsequent oxidation of the products. When oxygen was used as an oxidant, formaldehyde was obtained as the partial oxidation product over the silica-supported MoO_3 catalysts [11,12].

We have found that the dispersion of molybdenum oxide is one of the controlling factors for formaldehyde production [13]. However, the details of the catalysts are not yet clear. In the present paper, molybdenum oxides supported on silica were prepared with different methods in order to investigate the effect of the preparation method on their physicochemical properties and catalytic activity.

2. Experimental

The molybdenum oxide catalysts were prepared by two methods: impregnation method and sol–gel method. The first series of samples, denoted MoO_3-I-x, where x means MoO_3 content (wt%), were prepared by the impregnation method, as follows: the calculated amount of aqueous ammonium heptamolybdate (81^+ wt% as MoO_3, Wako) solution was added into a suspension of fumed silica (Aerosil 380) in distilled water. The solution was then evaporated to dryness at 100°C in a rotary evaporator. The solid obtained was dried at 120°C overnight and then calcined at 650°C for 5 h in air. The second ones denoted MoO_3-S-x were prepared by the sol–gel method. The calculated amount of ammonium heptamolybdate was dissolved in ethylene glycol (99^+%, Tokyo Kasei), in which orthoethyl silicate (95^+%, Wako) was then added. The resultant solution was aged with stirring at ca. 80°C for 5 h. Water and a small amount of nitric acid were poured to the solution and kept at 80°C with continuous stirring until it became gel. The gel was then evacuated at 100°C for 5 h with a rotary evaporator. The resulting powder was calcined at 650°C for 5 h in air.

The catalytic oxidation of methane was carried out in a conventional fixed-bed flow reactor at ambient pressure. The U-shaped quartz reactor was mounted vertically in a tubular furnace. The inlet diameter was 7 mm and outlet was 4 mm for rapid removal of the product from the reactor. Both ends of the catalyst bed were plugged with quartz wool. The temperature was measured by a thermocouple placed in the center of the catalyst bed. Most of the experiments were carried out with 0.3 g of the supported catalysts. The mixture of methane (14.5 ml/min) and air (8.0 ml/min) diluted with nitrogen (36 ml/min) was fed to the catalyst bed unless noted otherwise. The product gases were analyzed by gas chromatography using molecular sieve 13X and Porapak Q columns. Before reaction, the catalysts were activated in an air flow at 550°C for 1 h.

The conversion of methane was calculated from the methane in the products and that introduced in the feed. The selectivities were calculated from the conversion of methane to each product on carbon base. Each reaction was followed from the initial stage to the attainment of steady state with the periodic analyses. Blank experiments performed on empty reactor packed with quartz wool indicated that initiation of partial oxidation of methane did not occur at 550–750°C in the absence of catalysts.

Specific surface area was measured with an Omnisorp 100 by BET method. Powder X-ray diffraction patterns were recorded on a MAC Science Model MXP-18 diffractometer using Cu Kα radiation.

Scanning electron microscope (SEM) images were obtained by using a Hitachi S800 machine with Kevex3600 electron probe X-ray microanalyzer (EPMA). The samples were mounted on an aluminum holder and coated with a thin platinum film. X-ray photoelectron spectra (XPS) were obtained with a PHI-5000 spectrometer employing Mg Kα radiation (1254 eV) and an electron flood gun to provide charge neutralization of the non-conducting samples. Binding energies (BE) were determined from the difference from the Si 2p peak (103.4 eV).

3. Results and discussion

The blank test with silica (Aerosil 380) was carried out in the temperature range from 550 to 750°C with CH_4/O_2 ratio of 9.1. Conversion of methane was very low at temperatures below 650°C with formation of traces of COx. At above 650°C, conversion of methane increased up to 0.5% but only COx and a trace of formaldehyde were produced.

The main products of the reaction over the MoO_3/SiO_2 catalysts were CO, CO_2 and HCHO. A considerable amount of H_2O was produced. Excellent carbon mass balances (100 ± 3%) were obtained for the reaction. Traces of C_2 hydrocarbons were observed at the higher reaction temperature. By contrast, a trace of methanol was observed at the lower reaction temperature. Reproducibility of ±10% for the conversion of methane and the product selectivities was obtained.

The conversion of methane and the yield of formaldehyde over MoO_3-I and MoO_3-S catalysts at 575°C are shown in figs. 1 and 2, respectively. It is obvious that the yield of formaldehyde strongly depended on MoO_3 loading: it increased, reached maximum and then decreased with the increase in MoO_3 loading. A similar trend was observed for the conversion of methane. The optimum MoO_3 loadings were the same for both the yield of formaldehyde and the conversion of methane in each series of catalysts, and were 8 and 16 wt% in the MoO_3-I and the MoO_3-S, respectively.

The conversion of methane increased with reaction temperature, however, the selectivity to formaldehyde decreased associated with an increase in the selectivity to COx. Changes in the yield of formaldehyde over MoO_3-I-1, 8 and 16 and MoO_3-S-1, 16 and 32 with the reaction temperature are shown in figs. 3 and 4, respectively. The yield of formaldehyde increased at first, reached maximum and then decreased over both series of catalysts with reaction temperature. The reaction temperature at which the yield of formaldehyde took the highest value

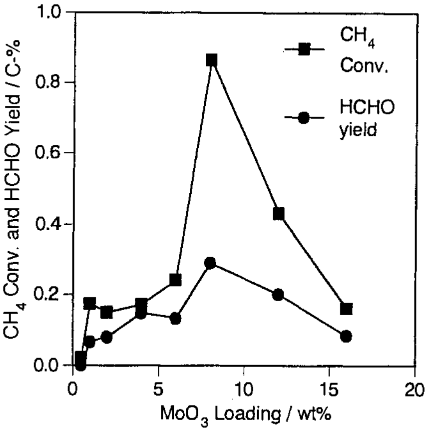

Fig. 1. Changes in CH_4 conversion and HCHO yield with MoO_3 loading at 575°C over MoO_3/SiO_2 catalysts prepared by the impregnation method.

(denoted T_f hereinafter) differed with loading of MoO_3. It is clear that the catalyst with higher T_f showed the lower maximum yield of formaldehyde. The temperature range affording formaldehyde was broader over the catalysts with low MoO_3 loading that those with high MoO_3 loading.

Figs. 5 and 6 summarize the effect of MoO_3 loading on maximum yield of formaldehyde and the T_f value over the MoO_3-I and the MoO_3-S series, respectively. The catalyst with the lower T_f afforded clearly the higher yield of formaldehyde over both series of catalysts. It is obvious that the optimum MoO_3 loadings for the production of formaldehyde were ca. 6 and 16 wt% in the MoO_3-I and the MoO_3-S catalysts, respectively.

The flow rate of feed gas (F/W) showed a significant effect on the product distri-

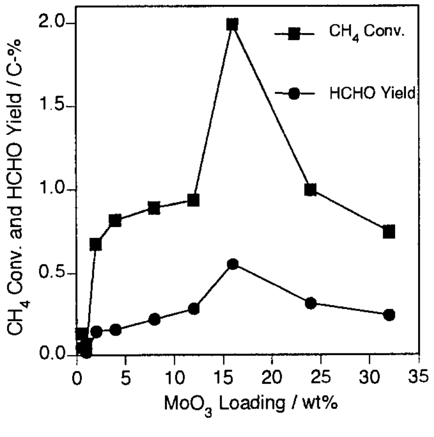

Fig. 2. Changes in CH_4 conversion and HCHO yield with MoO_3 loading at 575°C over MoO_3/SiO_2 catalysts prepared by the sol–gel method.

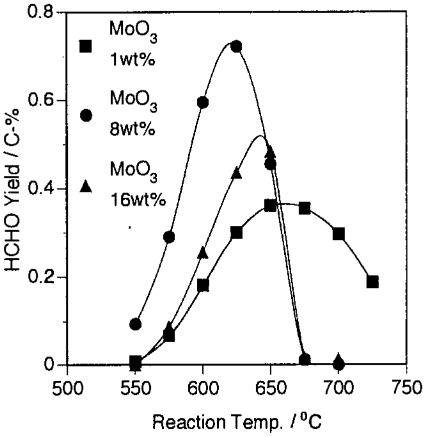

Fig. 3. Effect of MoO_3 loading on HCHO yield over MoO_3/SiO_2 catalysts prepared by the impregnation method.

bution. Table 1 summarizes this effect of F/W on the oxidation over the MoO_3-S-8 catalyst. When F/W increased from 0.171 to 0.682 g h/ℓ under a constant CH_4/O_2 ratio close to 9.1, the conversion of methane decreased from 3.68 to 1.37%. The selectivity to formaldehyde increased from 5 to 28.7% with the subsequent decreases in the selectivity to CO and the selectivity to CO_2. A large amount of CO was observed at the low F/W. These suggest that the longer residence time increases the CO formation via the decomposition of formaldehyde. It is likely that the high flow rate is favorable for formaldehyde formation as observed by Spencer et al. [14].

The influence of CH_4/O_2 molar ratio on the conversion of methane and selectiv-

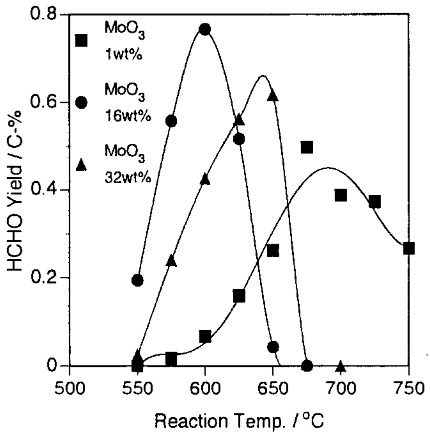

Fig. 4. Effect of MoO_3 loading on HCHO yield over MoO_3/SiO_2 catalysts prepared by the sol–gel method.

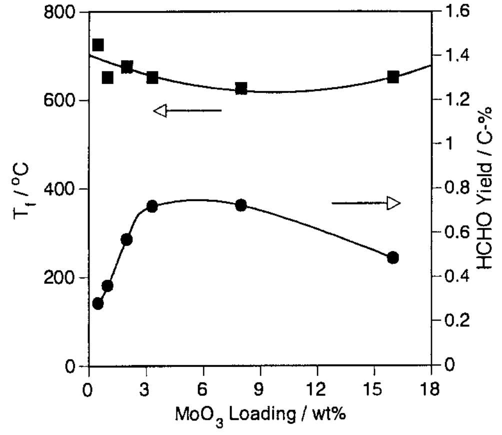

Fig. 5. Maximum HCHO yield and T_f over MoO_3/SiO_2 catalysts prepared by the impregnation method.

ity to formaldehyde was tested at 625°C over the MoO_3-S-8 catalyst (table 2). The CH_4/O_2 ratio was changed from 2 to 18 under constant values of partial pressure and flow rate of methane. The selectivity to CO was almost constant, while the conversion of methane decreased with an increase in the CH_4/O_2 molar ratio. The selectivities to formaldehyde and CO_2 increased and decreased with the increase in CH_4/O_2 molar ratio, respectively.

The intensity of X-ray diffraction peak ($d = 0.326$ nm) of the catalysts is plotted in fig. 7. This peak is attributed to a (021) peak of the orthorhombic MoO_3. For the samples with much lower MoO_3 loading, an undefined amorphous phase seems to exist, but at higher loading diffraction peaks due to MoO_3 were observed on both series of catalysts. However, formation of MoO_3 crystals on the MoO_3-I

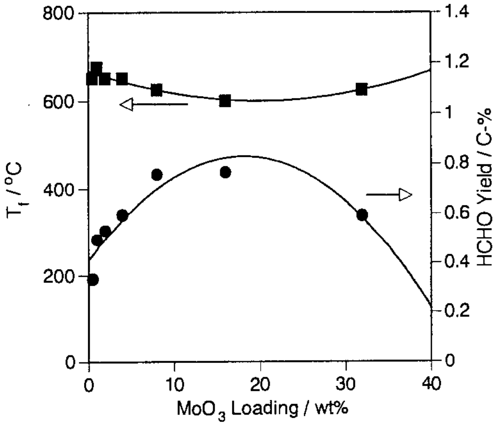

Fig. 6. Maximum HCHO yield and T_f over MoO_3/SiO_2 catalysts prepared by the sol–gel method.

Table 1
Effect of flow rate of the feed gas on the catalytic performance of Mo-S-8 in the methane oxidation. Catalyst: 0.3 g; feed (molar ratio, $CH_4 : O_2 : N_2 = 9.1 : 1 : 26.5$); reaction temperature: 625°C

F/W (g h/ℓ)	CH_4 conv. (%)	Selectivity (C%)		
		HCHO	CO	CO_2
0.171	3.68	6.0	78.0	16.0
0.341	3.62	21.0	67.0	12.0
0.512	1.82	23.7	65.3	11.0
0.682	1.37	28.7	60.5	10.8

occurred at lower MoO_3 loading compared with the MoO_3-S. While at high MoO_3 loading (>20 wt%), the peak intensity of the MoO_3-S is stronger than that of the MoO_3-I at the same MoO_3 loading. The peak width in the XRD patterns decreased with the MoO_3 loading. It is therefore likely that a good dispersion of MoO_3 can be achieved when the MoO_3 loading is below 8 and 16 wt% with the MoO_3-I and the MoO_3-S, respectively.

The BET surface area of the catalysts is shown in fig. 8. The specific surface area decreased with an increase in MoO_3 loading on both series of catalysts. Large decrease in the surface area occurred up to the loadings of ca. 8 and 16 wt% in the MoO_3-I and the MoO_3-S, respectively. Each of these values coincided well with the value at which MoO_3 crystals began to grow up in the MoO_3-I and the MoO_3-S, respectively (fig. 7). Further increase in MoO_3 loading resulted in almost constant surface area (ca. 100 m^2/g). Thus it is considered that the MoO_3 moiety plugged the mesopores of the SiO_2 support, resulting in the decrease in the BET surface area.

The SEM photographs of the typical catalysts are shown in fig. 9. At low MoO_3 loading large aggregates of the small spherical particles were observed like in fig. 9a. The distributions of Mo and Si were homogeneous through the aggregates from the EPMA data. The formation of long thin blades was observed at the

Table 2
Effect of CH_4/O_2 ratio in the feed gas on the catalytic performance of Mo-S-8 in the methane oxidation. Catalyst: 0.3 g; feed 58.5 ml/min (CH_4 14.5 ml/min, air 4.0–36.3 ml/min, N_2 remainder); reaction temperature: 625°C

CH_4/O_2	CH_4 conv. (%)	Selectivity (C%)		
		HCHO	CO	CO_2
2.0	4.43	19.6	66.2	14.2
3.0	4.21	21.2	66.0	12.8
4.5	4.01	20.7	66.4	12.9
9.1	3.62	21.0	67.0	12.0
18.0	2.18	23.3	65.1	11.6

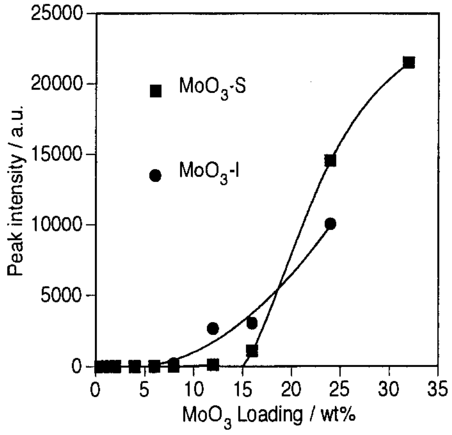

Fig. 7. Change in the X-ray diffraction peak intensity of MoO_3 with MoO_3 loading.

MoO_3 loading of no less than 8 and 16 wt% with Mo-I and Mo-S series like in fig. 9b, respectively. They were assigned to pure MoO_3 crystals from their crystal habit and the elemental analysis by EPMA. On the other hand, the distribution of Mo and Si over the aggregates was homogeneous. The proportion of pure MoO_3 blades to the aggregates (silica-supported MoO_3) increased with MoO_3 loading. These observations were in good agreement with the results of XRD; Mo is distributed homogeneously up to MoO_3 loadings of 8 and 16 wt% in the Mo-I and Mo-S series, respectively.

The photoelectron spectra showed the characteristic Mo 3d doublet. The binding energy of the Mo $3d_{2/5}$ peaks became higher with an increase in the MoO_3 loading, ranging from 231.5 to 232.9 eV, as is shown in table 3. These values were somewhat below those reported for large MoO_3 crystals [15]. At low Mo content

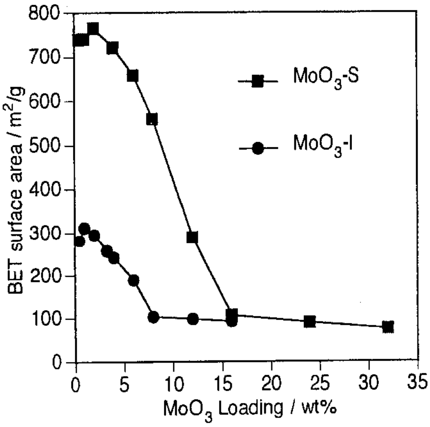

Fig. 8. Effect of MoO_3 loading on BET surface.

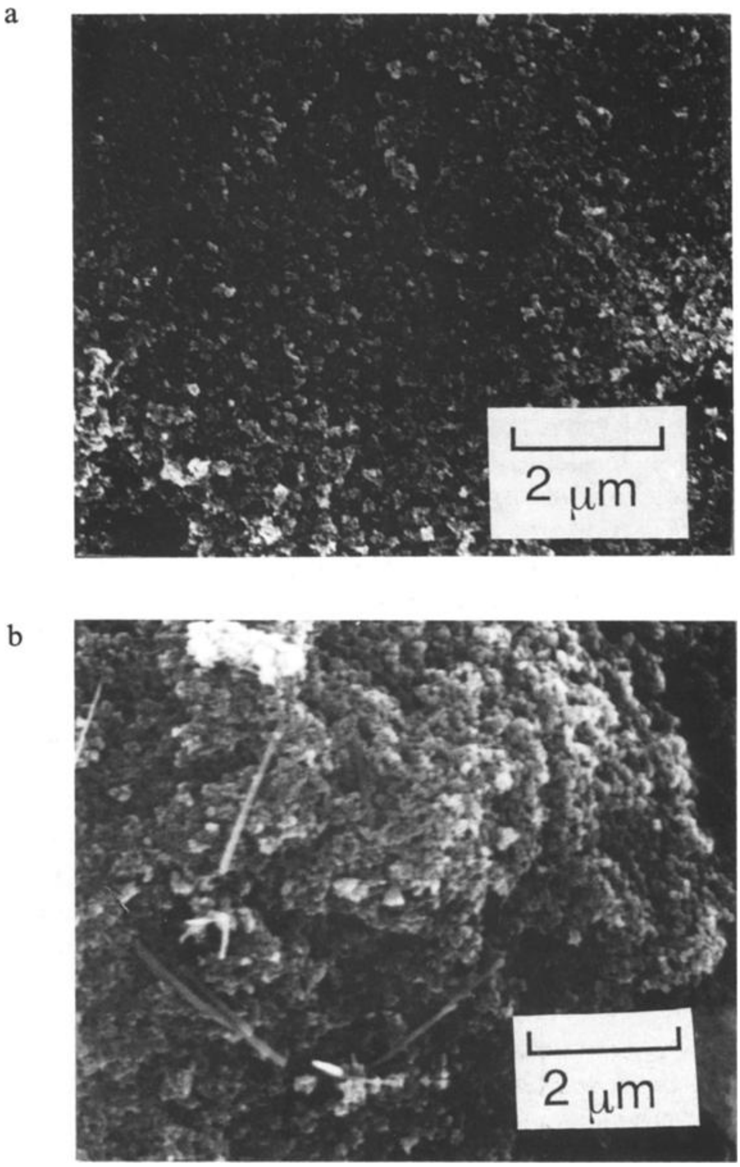

Fig. 9. Scanning electron photomicrographs of Mo-S-8 (a) and Mo-S-16 (b).

broad peaks were observed. As the MoO_3 loading increased the width of the peaks decreased and the separation of the doublet peaks became better. The Mo/Si intensity ratios were derived from the XPS data, and were also summarized in table 3. The Mo/Si intensity ratio increased linearly in the low MoO_3 loading region, suggesting the high dispersion of MoO_3 over SiO_2. On the other hand, the slow increase of this ratio for high Mo loading indicates formation of MoO_3 clusters.

Table 3
XPS relative intensities and binding energies of Mo $3d_{5/2}$ of Mo/SiO_2 catalysts prepared by the sol–gel method

Mo loading (wt%)	Mo/Si [a] (a.u.)	BE of Mo $3d_{5/2}$ (eV)
1	0.62	231.5
2	1.15	231.4
4	1.85	232.2
8	2.38	232.3
16	3.06	232.9
32	3.23	232.7

[a] Peak intensity ratio of Mo 3d to Si 2p.

These results suggested that the chemical state of the Mo atoms changed with MoO_3 loading. It is considered that, at low MoO_3 loading, Mo atoms interact strongly with SiO_2 and might form a certain specific compound on SiO_2 [16,17], such as silicomolybdic acid at very low MoO_3 loading [16].

As described above, the catalytic behaviors largely depended on the MoO_3 loading. The absence of XRD peaks of MoO_3 at low MoO_3 loading and elemental analyses by EPMA suggest a uniform distribution of molybdenum oxides in good agreement with the results reported by Barbaux et al. [18]. Ozkan et al. proposed that terminal oxygen (Mo=O) located on the side planes of MoO_3 crystals promotes the formaldehyde production, while bridging oxygen (Mo–O–Mo) located on the basal planes accelerates the deep oxidation of methane [19]. It is thus considered that small clusters of molybdenum oxide are the active species for the selective production of formaldehyde from methane. The results shown in figs. 3, 4, 7, 8 and 9, suggest the following: at low MoO_3 loading, highly dispersed molybdenum oxide does not aggregate at relatively low temperatures so much, but gradually aggregates at the medium temperatures to form small clusters of molybdenum oxide, which are active for the selective production of formaldehyde. On the other hand, formation of large MoO_3 crystals occurs at relatively low temperature over the catalysts with high MoO_3 loading, which catalyzes the deep oxidation of methane.

In conclusion, well dispersed molybdenum oxide clusters on SiO_2 support are considered to be active species for the selective production of formaldehyde from methane. MoO_3/SiO_2 catalyst prepared by the sol–gel method gave well dispersed molybdenum oxide even at the MoO_3 loading of 16 wt%. By contrast, the maximum MoO_3 loading to get well dispersed molybdenum oxide was 8 wt% over the catalysts prepared by impregnation method. Hence, the sol–gel method is considered to be superior to the impregnation method for preparing well dispersed MoO_2/SiO_2 catalysts.

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