Effects of Water Vapor upon Partial Oxidation of Methane over Highly-dispersed MoO_3/SiO_2

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Effects of water vapor upon the partial oxidation of methane on silica-supported molybdenum oxide catalyst strongly depend upon the dispersion states of Mo ions, and highly dispersed Mo ions depress the production of CO_2 by an addition of water vapor into the feed gas.

Direct conversion of methane into methanol has been of significant interest in the field of chemical engineering and catalysis.[1] There have been, at least, two problems in this attractive research program; one is the design of a reactor which is effective for the depression of methanol combustion and the other is the development of a catalyst which selectively produces methanol from methane and oxygen. A key point in the first problem is the residence time of methanol yielded on catalysts.[2] Since catalysts employed for the reaction can work at the temperatures higher than 823 K, methanol still remained on the catalyst surface is sequentially oxidized into formaldehyde, CO and, finally, CO_2.[3] While for the latter problem the properties of active sites generated on the catalyst surfaces should be defined, since it was reported that methane adsorbed on one sites preferentially produced CO_2 and methane on the other sites yielded methanol and formaldehyde.[4] In this paper we will discuss about the relationship between the dispersion states of MoO_3 and the selectivity into methanol and formaldehyde in the partial oxidation of methane on MoO_3/SiO_2 catalyst under an excess amount of water vapor.

MoO_3/SiO_2 catalysts were prepared by two different methods; a conventional impregnation method using an aqueous solution of $(NH_4)_6Mo_7O_{24}4H_2O$, and an alkoxide method using $(NH_4)_6Mo_7O_{24}4H_2O$ dissolved in ethylene glycol at 333 K and ethylsilicate.[5] Both catalysts were dried at 383 K for 24 h, followed by calcination at 873 K for 3 h. Amounts of MoO_3 loaded on the supports were all settled to be 2 wt% of the supports.

X-ray diffraction of the calcined catalysts prepared by the impregnation showed several peaks, assigned to MoO_3 crystallites sized about 270 A estimated from the half-width of (020) reflection. No diffraction peaks are, however, detected for the catalyst by alkoxide method. In order to study the local structure around Mo ions in the alkoxide catalyst, the catalyst was subjected to EXAFS measurements. The details of the measurements and analysis of EXAFS have been described elsewhere.[6] Figure 1 shows a Fourier transform of the catalyst together with the those of the impregnated catalyst and MoO_3 powder, and 5 wt% catalysts were used, here, for EXAFS measurements. Although the structure of the impregnated catalyst resembles that of bulk MoO_3, only one peak due to Mo-O is observed in the alkoxide catalyst. It is thus concluded that Mo ions in the alkoxide catalyst are in a very different environment from those in the impregnated catalyst, and might be in atomic dispersion in silica forming Mo-O-Si network.

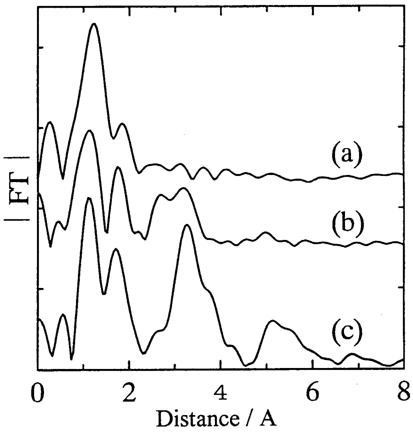

Figure 1. Fourier transforms of EXAFS spectra of 5% MoO_3/SiO_2; (a) alk., (b) imp., and (c) MoO_3 crystallite.

Partial oxidation of methane into methanol and formaldehyde was carried out at 773~923 K using a flow type reactor where 1.5 g of the catalyst powder was placed. Gases consisting of helium, methane, oxygen and water vapor with a volume ratio of 50/22/3/25 were supplied into the reactor with a space velocity of 2800 h^{-1}, and the products were analyzed by a gas chromatography using columns packed with Carbosieve S-II for methane, oxygen, CO and CO_2, and with APS-201 for methanol, formaldehyde and water vapor, respectively. Note that water vapor was supplied by a syringe into a pre-heater, heated at 523 K, where methane and oxygen were mixed with water vapor to be introduced into the reactor.

Conversion of methane and selectivities of methanol, formaldehyde, CO and CO_2 are given in Table 1. Since the amount of methanol produced was too small, the total amount of methanol and formaldehyde was noted as an amount of oxygenated products. At the right-hand side of the Table, yield of oxygenated products are given. It was found that the alkoxide catalyst showed 10 times higher yield than the impregnated catalyst at any reaction temperatures employed. This is attributed to the difference in the dispersion states of Mo ions in silica support.

Table 1. Partial oxidation of methane on MoO_3/SiO_2

Catalyst	Reaction Temperature(°C)	%CH_4 Conversion	Selectivity (%) HCHO	CH_3OH	CO	CO_2	Yield(%) HCHO+CH_3OH
MoO_3/SiO_2 (imp)	500	0.58	32	2	25	41	0.20
	550	1.2	13	1	35	51	0.17
	600	4.0	12	1	33	54	0.52
	650	6.6	1	0	18	81	0.07
MoO_3/SiO_2 (alk)	500	1.0	73	13	0	14	0.86
	550	2.9	52	8	10	30	1.7
	600	8.2	35	11	17	37	3.8
	650	12	11	4	23	62	1.8

Since it is well known that water vapor is inevitable for the partial oxidation of methane over MoO_3/SiO_2 catalyst,[7] effects of the additional water vapor upon the catalysis of Mo ions in both catalysts were studied. The reaction was carried out under the same conditions employed above except the absence of diluting helium. Thus, the gases introduced into the catalyst bed, heated at 873 K, consisted of methane, oxygen and water vapor with a space velocity of 2800 h^{-1}. The methane/oxygen volume ratio was settled to be 9 in all the experimental runs, and the amount of water vapor in the feed gases changed from 5 to 95 vol%. Results obtained on the impregnated catalyst are shown in Figure 2 and those on the alkoxide catalyst are in Figure 3. The reaction on the impregnated catalyst was depressed by the addition of water vapor, but less depression was detected for the alkoxide catalyst. Significant difference was observed in the selectivities of oxygenated compounds and CO_2. On the impregnated catalyst the selectivity of oxygenated compounds decreased, while that of CO_2 increased as the amount of water vapor in the feed increased. Opposite results were obtained on the alkoxide catalyst, i.e., the selectivity of oxygenated compounds increased and that of CO_2 decreased, as more water vapor was added. This suggests that the active sites favored for the production of CO_2 from methane were generated on the impregnated catalyst by the additional water vapor, but those on the alkoxide catalyst were strongly suppressed. The difference in the effects of water vapor upon the active sites may be ascribed to the difference in the dispersion states of Mo ions in the catalyst. One of the possible precursors of methanol is surface methoxides; $CH_3O(ad)$, which are considered to react with surface OH groups to produce methanol. These OH groups are supplied from water vapor and are activated to react with the surface methoxides. Accordingly, well-dispersed MoO_3 crystallites may enhance the activation of the surface OH groups.

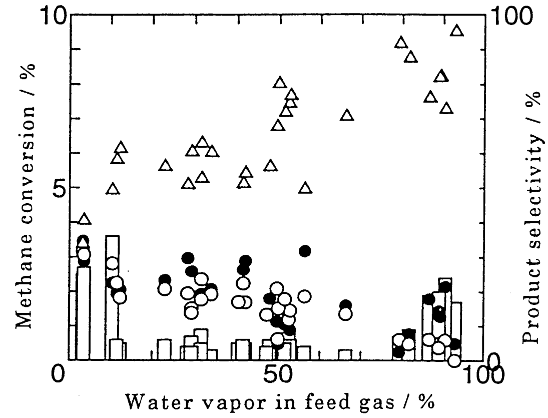

Figure 2. Effects of water vapor upon the partial oxidation of methane over impregnated MoO_3/SiO_2 catalyst; amounts of CH_4 and O_2 in the feed gas were constant in all run (□; CH_4 conversion, ○: CO, △: CO_2, ●: CH_3OH+HCHO).

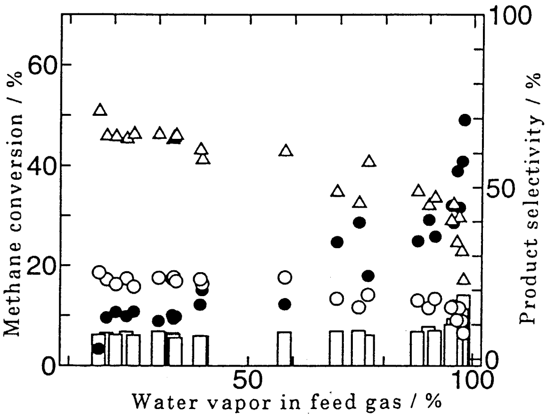

Figure 3. Effects of water vapor upon the partial oxidation of methane over alkoxide MoO_3/SiO_2 catalyst; amounts of CH_4 and O_2 in the feed gas were constant in all run (□; CH_4 conversion, ○: CO, △: CO_2, ●: CH_3OH+HCHO).

References and Notes

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