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Direct conversion of methane into methanol over MoO_3/SiO_2 catalyst in an excess amount of water vapor

K. Aoki[a,*], M. Ohmae[a], T. Nanba[a], K. Takeishi[a], N. Azuma[a],
A. Ueno[a], H. Ohfune[b], H. Hayashi[b], Y. Udagawa[b]

[a]*Department of Materials Science, Shizuoka University, Hamamatsu 432, Japan*
[b]*Research Institute for Scientific Measurements, Tohoku University, Sendai 980, Japan*

Abstract

Well-dispersed MoO_3 on SiO_2 showed a high activity for partial oxidation of methane (mixed with oxygen in a molar ratio of 9:1) into methanol and formaldehyde at 873 K in an excess amount of water vapor, which is attributed to the formation of silicomolybdic acid (SMA) on the catalyst surface during reaction. One of the roles of SMA for the partial oxidation of methane is proved to depress the successive oxidation of methanol and formaldehyde into carbon oxides. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

One of the most attractive studies in the field of chemical engineering and catalysis is the direct conversion of methane into methanol. Atroschenko was the first to investigated the various metal oxides as a catalyst for the partial oxidation of methane, and reported that MoO_3 was one of the best catalysts at elevated temperatures and pressures [1]. Later, successive oxidation of methanol formed was revealed to be a troublesome problem, and a reactor equipped with a rapid quenching system was devised to avoid the successive oxidation [2]. Dowden studied the mechanism of methanol formation from methane and oxygen on MoO_3/SiO_2 catalyst, and proposed three elemental steps; dehydrogenation of methane, insertion of oxygen to form methoxide, and hydrolysis of the methoxide into methanol [3]. A small amount of water vapor had been found to be inevitable for the partial oxidation of methane on MoO_3 catalyst, and the role of water vapor was thus elucidated. Liu et al. [4] also reported that the catalytic activity of MoO_3/SiO_2 for the partial oxidation of methane by N_2O was significantly enhanced when a small amount of water vapor was added to a feed gas.

Recently, structural changes of MoO_3 have been studied by infrared and Raman spectroscopy. Moffat et al. [5] reported the formation of SMA($H_4SiMo_{12}O_{40}$) by interactions of SiO_2 and MoO_3 in an aqueous solution, and studied the catalysis of SMA for the partial oxidation of methane. SMA was, however, not stable at the temperatures higher than 573 K and decomposed into SiO_2 and MoO_3 crystallites, hence the catalytic activity of SMA for partial oxidation of

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*Corresponding author.

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methane was almost the same as that of MoO_3/SiO_2 catalyst [6]. Deltcheff et al. [7] has also reported the easy formation of SMA, when well-dispersed MoO_3/SiO_2 catalysts were conducted into water. Thermal stability of SMA seems, however, to strongly depend upon the partial pressure of water vapor in the atmosphere, and the present authors are curious if SMA is stable or not in an excess amount of water vapor at elevated temperatures. Consequently, well-dispersed MoO_3/SiO_2 was prepared, and was subjected to the partial oxidation of methane in an excess amount of water vapor.

2. Experimental

MoO_3/SiO_2 catalysts were prepared by two different methods; impregnation and sol/gel methods. Impregnation was carried out using an aqueous solution of $(NH_4)_6Mo_7O_{24}4H_2O$ and silica powder prepared by hydrolysis of ethylsilicate. In the sol/gel method, $(NH_4)_6Mo_7O_{24}4H_2O$ dissolved in ethylene glycol was added into ethylsilicate to be hydrolyzed into gels. Both catalysts were dried at 383 K for 24 h, followed by calcination at 873 K for 3 h. Amounts of MoO_3 loaded were all settled to be 2 wt% of the catalyst. Since no diffraction peaks were detected for the catalysts prepared by sol/gel method, EXAFS was employed to reveal the structures around Mo ions in the catalysts. EXAFS measurements and analyses were the same as those mentioned in the previous paper [8]. EXAFS was also employed to discuss the structures around Mo ions during the partial oxidation of methane. The reaction was carried out at 773–923 K using a flow reactor with 1.5 g of the catalyst.

Gases, generally consisting of helium as a diluent, 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}. Products were analyzed by a gas chromatography using columns packed with Carbosieve S-II for methane, oxygen, CO and CO_2, and packed 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 well mixed with water vapor to be conducted into the reactor. In the latter part of this work no diluent was added into the feed, and the amount of water vapor supplied was varied up to 90 vol% of the feed to clarify the effects of water vapor upon the catalysis of Mo ions. Methanol combustion on both catalysts was also studied in an excess amount of water vapor at 623 K. In this case, methanol was mixed with water in proper proportions and supplied to the reactor through syringe. The molar ratio of oxygen/methanol was settled to be 2 in all the experimental runs.

3. Results

EXAFS Fourier patterns of both catalysts calcined at 873 K for 3 h are shown in Fig. 1, together with that of standard MoO_3 crystallites. Only one peak assigned to be Mo–O bonding was observed for the calcined sol/gel catalyst, although molybdenum oxides in the impregnated catalysts were found to be MoO_3 crystallites. The catalytic activities for the partial oxidation of methane are given in Table 1, with the gases consisting of $He/CH_4/O_2$/water vapor with a volume ratio of 50/22/3/50. Assuming the first order reaction with respect to methane, apparent activation energies on both catalysts were calculated to be 26.0 kcal/mol

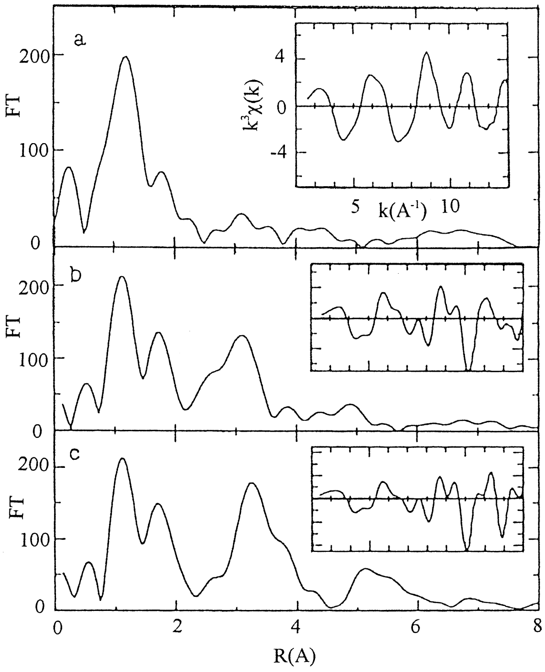


Fig. 1. EXAFS Fourier patterns of: (a) sol/gel, (b) impregnation and (c) standard MoO_3.

Table 1
Comparison of the activities of the impregnated and sol/gel catalysts

Catalyst	Reaction temperature (°C)	CH_4 conversion (%)	Selectivity (%)				Yield (%) HCHO+CH_3OH
			HCHO	CH_3OH	CO	CO_2	
MoO_3/SiO_2 (imp)	500	0.58	32	2	25	41	0.20
	550	1.2	13	1	35	51	0.17
	600	40	12	1	33	54	0.52
	650	6.6	1	0	18	81	0.07
MoO_3/SiO_2 (sol/gel)	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

on impregnated catalyst and 28.2 kcal/mol on sol/gel catalyst. This result suggests a similar reaction mechanism on both catalysts.

Effects of water vapor upon the partial oxidation of methane over the catalysts were studied using gases consisting of CH_4/O_2/water vapor with a volume ratio of 22/3/x, where x was varied from 2.8 to 225, corresponding to the fraction of water vapor varying from 10 to 90 vol% of the feed gas. The reaction was carried out at 873 K, and the results obtained for impregnated catalysts are shown in Fig. 2(a), and those for sol/gel catalysts in Fig. 2(b), respectively. The selectivity of oxygenates, including both methanol and formaldehyde, on impregnated catalysts gradually decreased with an increase in the fraction of water vapor, but that on sol/gel catalysts was enhanced when the fraction of water vapor was higher than 60 vol%. The reaction was quenched when it reached to the stationary state, and the catalysts (sol/gel) were promptly removed from the reactor to be submitted to EXAFS measurements. EXAFS Fourier pattern result is shown in Fig. 3(a), with the Fourier pattern of the standard SMA crystallites in Fig. 3(b).

In order to discuss the successive oxidation of methanol produced, the combustion of methanol on both catalysts was carried out in an excess amount of water vapor. Since at higher temperatures most of the methanol were completely fired into carbon dioxide, the experiments were carried out at 623 K using 1.5 g of the catalysts. Mixture of water and methanol was first conducted into pre-heater, heated at 573 K, and then introduced into the reactor with flowing O_2/He. The products were CO, CO_2 and formaldehyde analyzed by gas chromatography, and the results obtained are depicted in Fig. 4.

4. Discussion

In the first part of the discussion, we will think about the dispersion states of Mo ions both in the impreg-

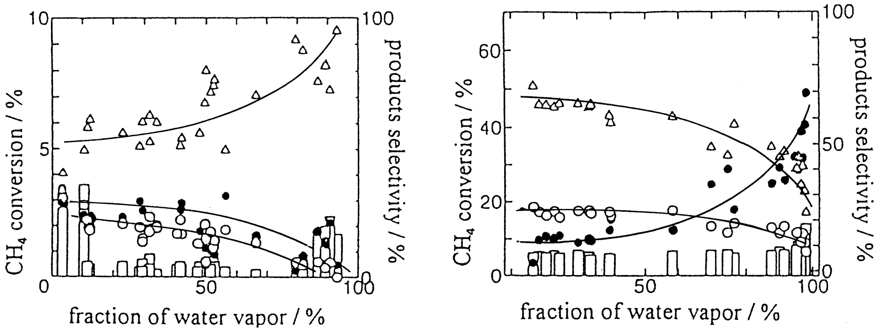


Fig. 2. (a) Effects of water vapor upon the partial oxidation of methane on the impregnated catalyst at 873 K. (b) Effects of water vapor upon the partial oxidation of methane on the sol/gel catalyst at 873 K. ((□) CH_4 conversion, (○) CO, (△) CO_2 and (●) CH_3OH+HCHO).

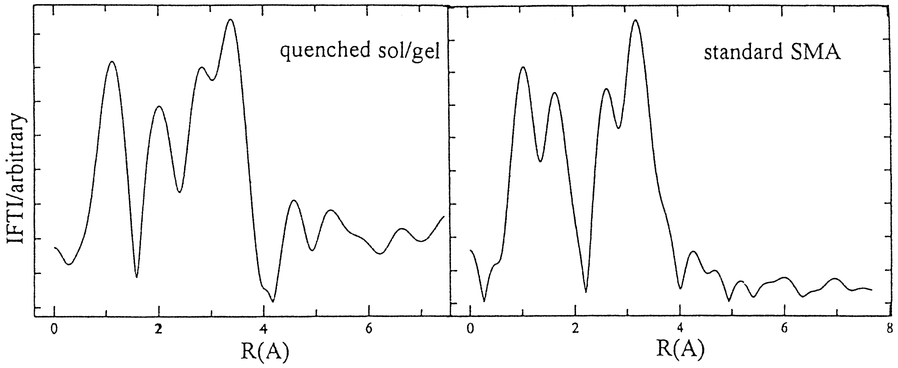


Fig. 3. (a) EXAFS Fourier pattern of the quenched sol/gel catalyst and (b) EXAFS Fourier pattern of the standard SMA crystallites.

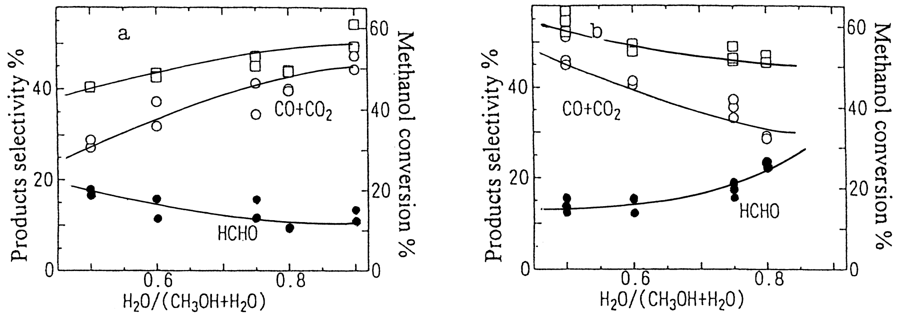
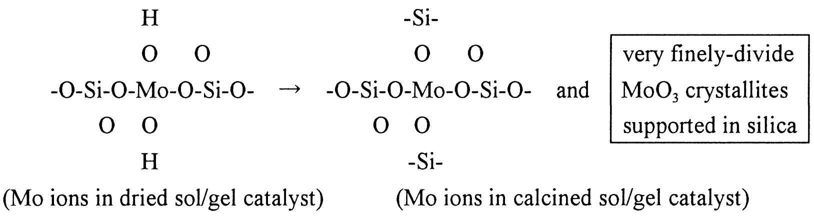


Fig. 4. Effects of water vapor upon methanol combustion on (a) impregnated and (b) sol/gel catalyst at 623 K. ((□) CH_4 conversion, (○) $CO+CO_2$, (●) HCHO).

nated and sol/gel catalysts. XRD of the impregnated catalyst showed several peaks assigned to MoO_3 crystallites sized around 200 A, estimated from the half-width of (0 2 0) reflection. No diffraction peals were, however, detected for the sol/gel catalysts, and the catalysts were subjected to EXAFS measurements. As given in Fig. 1, only one peak due to Mo–O bonding was observed for the calcined sol/gel catalyst, suggesting that Mo ions in the sol/gel catalyst were in a different environments from those in the impregnated catalyst. Since EXAFS and FTIR measurements for the dried sol/gel catalysts have made clear of the local structures around Mo ions, which will be published in the near future, we concluded the following structures for Mo ions in the dried and calcined sol/gel catalysts. In the calcined catalyst, we believe that a part of Mo ions are coagulated to form tiny MoO_3 crystallites, but most of the Mo ions are still atomically dispersed in –Si–O–Si– network.



$$\begin{array}{ccccc} \text{H} & & \text{-Si-} & & \\ \text{O O} & & \text{O O} & & \\ \text{-O-Si-O-Mo-O-Si-O-} & \rightarrow & \text{-O-Si-O-Mo-O-Si-O-} & \text{and} & \boxed{\begin{array}{c}\text{very finely-divide}\\ \text{MoO}_3\text{ crystallites}\\ \text{supported in silica}\end{array}} \\ \text{O O} & & \text{O O} & & \\ \text{H} & & \text{-Si-} & & \end{array}$$

(Mo ions in dried sol/gel catalyst) (Mo ions in calcined sol/gel catalyst)

Table 1 showed an excellent activity and selectivity of sol/gel catalyst, in comparison with impregnated catalyst, for the partial oxidation of methane into oxygenates at 873 K in an excess amount of water vapor. Most of the papers have reported only the formation of formaldehyde caused by the successive oxidation of methanol. Around a third of the oxygenates produced on the sol/gel catalysts was methanol, indicating the depression of the successive oxidation of methanol on finely divided MoO_3 catalysts in an excess amount of water vapor. While on the impregnated catalyst, trace amounts of methanol were observed at any temperatures studied even in an excess amount of water vapor. Effects of the water vapor upon the combustion of methanol on Mo ions are given in Fig. 4, where the volume ratio of water vapor to methanol was modified in a wide range. Though the combustion temperature was 623 K (lower than the temperature for partial oxidation of methane), it was clear that the combustion of methanol into CO and CO_2 was deterred on the sol/gel catalyst by addition of the water vapor, but not on the impregnated catalyst. Accordingly, finely divided MoO_3 catalyst and an excess amount of water vapor in the feed are concluded to be the important conditions for the depression of successive oxidation of methanol. Conclusion above was reflected on the selectivity of oxygenates in the partial oxidation of methane on the sol/gel catalyst at 873 K, as shown in Fig. 2(a) and (b). The selectivity of oxygenates on the sol/gel catalyst rapidly increased when the fraction of water vapor was higher than 60 vol%, which is due to the depression of the successive oxidation of oxygenates by addition of an excess amount of water vapor (higher than 60 vol%).

In order to see what happened on the sol/gel catalyst in an excess amount of water vapor at higher temperatures, suddenly quenched catalysts (not dried) were submitted to the EXAFS measurements, as shown in Fig. 3(a). EXAFS Fourier pattern obtained showed four clear peaks, and was quite different from the patterns of dried sol/gel catalyst and MoO_3 crystallites, given in Fig. 1(a) and (c). It rather resembles, but not complete, to the EXAFS Fourier pattern of the standard SMA crystallites. Thus, we tentatively conclude that finely dispersed SMA-like structures might remain on the sol/gel catalyst, in an excess amount of water vapor, through an equilibrium between the formation and decomposition of SMA from and into finely divided MoO_3 and SiO_2 as follows:

$$\begin{array}{c}\text{an excess amount of water vapor}\\ \downarrow\\ \text{finely divided MoO}_3\text{ crystallites} + \text{SiO}_2 \rightleftharpoons \text{finely dispersed SMA-like structures.}\end{array}$$

The formation of these SMA like structures seem to depress the successive oxidation of methanol, and to increase the yields of oxygenates during partial oxidation of methane.

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