

Mo-Containing SBA-1 Mesoporous Molecular Sieves as Catalysts for Partial Oxidation of Methane

Lian-Xin Dai,* Yong-Hong Teng, Kenji Tabata, Eiji Suzuki, and Takashi Tatsumi[†]

Research Institute of Innovative Technology for the Earth (RITE), 9-2 Kizugawadai, Kizu-cho, Soraku-gun, Kyoto 619-0292

[†]Division of Materials Science and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501

(Received April 14, 2000; CL-000358)

Mo-Containing SBA-1 mesoporous molecular sieves synthesized under strongly acidic conditions exhibited catalytic performance, superior to that of Mo-impregnated pure silica SBA-1 or silica gel, for the partial oxidation of methane with oxygen as an oxidant.

Since the discovery of ordered mesoporous molecular sieves with uniform pore sizes larger than 20 Å, much research work has been devoted to this new class of mesoporous materials, denoted M41S.^{1,2} Recently, Huo et al. reported the synthesis of a novel mesoporous molecular sieve denoted SBA-1 (*Pm3n* cubic) under strongly acidic synthesis conditions.^{3,4} From the point of view of catalytic application, the synthesis of three-dimensional mesoporous materials such as SBA-1 containing transition-metal has been collecting much attention.

The direct partial oxidation of methane to oxygenates has been focused in connection with the chemical utilization of natural gas. Among the oxidation catalysts, silica-supported MoO₃ catalyst has been found to be the most active and selective for oxygenates production.⁵ It is conceivable that the large surface (> 1000 m² g⁻¹) of cubic mesoporous materials makes it possible to create highly dispersed, i.e., much more active catalytic sites by incorporating transition-metal ion Mo into its silica-based frameworks. The large pore (> 20 Å) with a 3-D channel system makes it easy to discharge the produced oxygenates to the outside of pore, preventing the deep oxidation. In the present study Mo-containing SBA-1 with cubic structure is synthesized and used as a catalyst for the partial oxidation of methane.

Mo-Containing mesoporous materials, Mo-SBA-1, were synthesized under acidic conditions using cetyltriethylammonium bromide (CTEABr) as a surfactant, TEOS as a silica source, and (NH₄)₆Mo₇O₂₄·4H₂O as a Mo source in an aqueous solution of HCl. The surfactant CTEABr was synthesized by the reaction of cetyl bromide with an equimolar amount of triethylamine in acetone solution under reflux conditions. A typical synthesis was conducted as follows: CTEABr, HCl (35%) and distilled water were combined to obtain a homogeneous solution, which was stirred for 30 min and cooled at 273 K. TEOS and Mo precursor solution, which were precooled to 273 K, were added to the above mixture under vigorous stirring. After stirred for 5 min, the mixture was allowed to react at 273 K under static condition for 6 h. The molar composition of the gel was as follows: 1 TEOS/0.13 CTEABr/(5–10) HCl/125 H₂O/0.2 Mo. The precipitate was filtered, dried (without washing) at 393 K overnight and then calcined in air at 903 K for 4 h. Siliceous SBA-1 was synthesized with the same procedure (HCl/TEOS = 10) except that no Mo was added. Supported Mo catalysts on SBA-1 (Mo/SBA-1) and amorphous silica (Mo/SiO₂) were prepared by impregna-

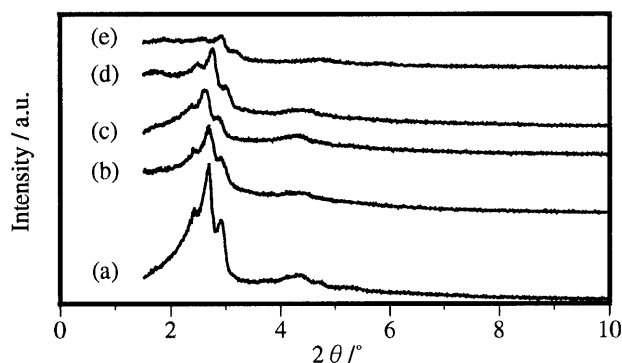


Fig. 1. XRD patterns for the calcined samples of (a) siliceous SBA-1, (b) Mo-SBA-1 (Mo = 4.8 wt%), (c) Mo-SBA-1 (Mo = 7.3 wt%), (d) Mo-SBA-1 (Mo = 8.8 wt%) and (e) Mo/SBA-1 (Mo = 9.0 wt%).

tion method by using (NH₄)₆Mo₇O₂₄·4H₂O as the Mo source, then dried at 393 K overnight and calcined at 903 K for 4 h. The partial oxidation of methane was carried out using a fixed-bed quartz reactor. The products were analyzed by an on-line gas chromatograph connected to a methanator.

Figure 1 illustrates the XRD patterns of various samples prepared by different methods. Table 1 summarizes the preparation conditions and physical properties of the Mo-containing SBA-1 mesoporous materials, together with the data of Mo/SiO₂ for comparison. As displayed in Figure 1, all the samples showed the typical characteristic XRD patterns of the SBA-1 cubic phase which can be indexed to the *Pm3n* space group.^{3,4} Morey et al.⁶ reported the incorporation of Mo into SBA-1 using MoCl₅ (aq) as the metal atom source with the Si/Mo ratio of 16 in the starting gel. They found that only 0.4 at.% Mo was incorporated due to the high solubility of Mo species under strongly acidic conditions. In our study, however, a significantly large amount of Mo was successfully substituted into the SBA-1 by adding (NH₄)₆Mo₇O₂₄·4H₂O to the gel with the following mole ratios: 1 TEOS/0.13 CTEABr/(5–10) HCl/125 H₂O/0.2 Mo. Interestingly, although the Mo species would be easily soluble in the concentrated aqueous solution of HCl, Mo incorporation increased monotonously with the concentration of HCl in the starting gel (HCl/TEOS = 5 → 10) (Table 1), whereas no significant change in the structural regularity of Mo-SBA-1 was observed (Figure 1b–d). For HCl/TEOS = 10, the Mo-SBA-1 containing up to 8.8 wt% Mo (Si/Mo = 16) was formed while maintaining a fairly well-ordered cubic structure (Figure 1d). Therefore, the different Mo precursors (Mo⁵⁺ cation/Mo₇O₂₄⁶⁻ anion) resulted in a remarkable difference in the amount of Mo incorporation; the anionic Mo species favored the incorporation of Mo into the SBA-1 framework according to the S⁺ X⁻ I⁺ synthesis route.^{3,4}

It can be seen from Table 1, both siliceous SBA-1 and

Table 1. Synthesis Conditions and Physical Properties of Calcined Various Samples

Sample ^a	Mo /wt%	S _{BET} /m ² g ⁻¹	Pore diameter /Å	Pore volume /cm ³ g ⁻¹
SBA-1 ^b	0.0	1511	22	0.82
Mo-SBA-1 ^c	4.8	1438	21	0.74
Mo-SBA-1 ^d	7.3	1271	20	0.65
Mo-SBA-1 ^e	8.8	1071	20	0.55
Mo/SBA-1 ^f	9.0	718	23	0.42
Mo/SiO ₂ ^g	9.0	81	62	0.12

^aThe starting gel with the compositions of 1TEOS/0.13CTEABr/xHCl/125 H₂O/Mo. ^bx = 10, y = 0. ^cx = 5, y = 0.2. ^dx = 8, y = 0.2. ^ex = 10, y = 0.2. ^fImpregnation of SBA-1 with (NH₄)₆Mo₇O₂₄·4H₂O. ^gImpregnation of SiO₂ with (NH₄)₆Mo₇O₂₄·4H₂O.

Mo-SBA-1 series samples possess characteristics of a mesoporous material, i.e., a BET surface area over 1000 m² g⁻¹ and a uniform pore size of ca. 20 Å. A considerable decrease in the surface area for the impregnated sample Mo/SBA-1 should be attributed to the loss of crystallinity seen in the XRD pattern (Figure 1e), indicating that the cubic structure of SBA-1 was partly destroyed during the impregnation of SBA-1 with an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O. Mo/SiO₂ sample only had a considerably small BET surface area below 100 m² g⁻¹ and a small pore volume of 0.12 cm³ g⁻¹.

Figure 2 shows the Raman spectra of crystalline MoO₃, Mo/SiO₂, Mo/SBA-1 and Mo-SBA-1 samples. The absence of sharp peaks at ca. 996, 820, 665 cm⁻¹ and several others below 400 cm⁻¹ (seen in MoO₃ and Mo/SiO₂) corresponding to bulk MoO₃⁷ in the spectrum of Mo-SBA-1 sample (Figure 2d) indicates that no free MoO₃ phase was presented and the Mo was highly dispersed in the silica-based SBA-1 catalyst. For the Mo-SBA-1 sample, the Mo species might consist of an octahedral polymolybdate (O_h-Mo) at 952 cm⁻¹ and a tetrahedral molybdate (T_d-Mo) at 880 cm⁻¹.⁷ In the case of Mo/SBA-1 prepared by impregnation method, besides of O_h-Mo (952 cm⁻¹) and T_d-Mo (shifted to 850 cm⁻¹) species, a trace amount of MoO₃ (996 and 820 cm⁻¹) was also detected. Thus, the degree of Mo dispersion on the catalysts could be arranged in the order Mo-SBA-1 > Mo/SBA-1 >> Mo/SiO₂. This order is in agreement with the expectation by the BET results as shown in Table 1.

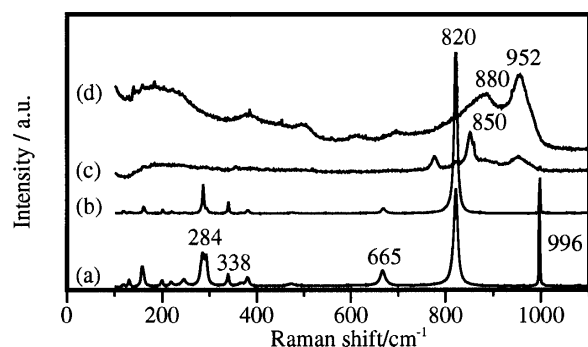


Fig. 2. Laser-Raman spectra of (a) crystalline MoO₃, (b) Mo/SiO₂ (Mo = 9.0 wt%), (c) Mo/SBA-1 (Mo = 9.0 wt%) and (d) Mo-SBA-1 (Mo = 8.8 wt%).

As shown in Table 2, both Mo-SBA-1 and Mo/SBA-1 catalysts exhibited much higher CH₄ conversion and selectivity to HCHO than those of amorphous Mo/SiO₂. The high selectivity

to HCHO on the former could be related to their highly dispersed Mo on the large surface of SBA-1 as described above. For the Mo-SBA-1 series catalysts synthesized under different acidic conditions (HCl/TEOS = 5 → 10), the selectivity and yield for the formation of HCHO linearly increased with increasing Mo content on the catalyst compared at the similar CH₄ conversion. These results are consistent with the observation by Faraldos et al.,⁸ who reported that CH₄ conversion and HCHO selectivity are dependent on the metal loading and the dispersion of the surface species.

Table 2. Partial Oxidation of Methane over Various Mo-Containing Catalysts^a

Catalyst ^b	Conv. /%	Selectivity /%				Yield of HCHO /%
		HCHO	CO	CO ₂	C ₂ ^c	
Mo-SBA-1(4.8) ^d	8.0	11.0	65.0	22.7	1.3	0.88
Mo-SBA-1(7.3) ^e	8.1	13.7	58.7	27.1	0.5	1.11
Mo-SBA-1(8.8)	8.1	15.5	59.6	23.8	1.1	1.25
Mo/SBA-1(9.0)	7.7	13.8	55.4	27.7	3.1	1.06
Mo/SiO ₂ (9.0)	1.5	8.9	53.4	20.0	17.6	0.14

^aReaction conditions: catalyst = 0.5 (g), T = 953 K, CH₄/O₂/He = 90/20/20 (ml/min), time on stream = 0.5 h. ^bThe number in parentheses represents Mo amount (wt%). ^cC₂H₄ + C₂H₆. ^dT = 963 K. ^eT = 958 K.

It is also clear from Table 2 that the Mo-SBA-1 prepared by direct synthesis showed a slightly higher CH₄ conversion and HCHO selectivity in comparison with the Mo/SBA-1 sample prepared by the impregnation method. Higher dispersion and isolation of the active sites Mo incorporated into the SBA-1 phase can be attributed for the enhanced catalytic performance in the partial oxidation of methane.

The present study demonstrates that a considerably large amount of Mo can be effectively incorporated into the cubic SBA-1 mesophase under strongly acidic conditions. The Mo-SBA-1 synthesized by direct synthesis method exhibits higher activity and selectivity for HCHO formation than the Mo-impregnated siliceous SBA-1 (Mo/SBA-1) and amorphous silica (Mo/SiO₂) catalysts, due to the presence of high dispersion and isolation of Mo in the SBA-1 framework.

We acknowledge financial support of New Energy and Industrial Technology Development Organization (NEDO). L.-X. Dai and Y.-H. Teng were supported by a fellowship from NEDO.

References and Notes

- C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
- K. A. Koyano and T. Tatsumi, *J. Chem. Soc., Chem. Commun.*, **1996**, 145.
- Q. Huo, D. I. Margolese, U. Ciesla, D. G. Demuth, P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schuth, and G. D. Stucky, *Chem. Mater.*, **6**, 1176 (1994).
- Q. Huo, D. I. Margolese, and G. D. Stucky, *Chem. Mater.*, **8**, 1147 (1996).
- R. G. Herman, Q. Sun, C. Shi, K. Klier, C.-B. Wang, H. Hu, I. E. Wachs, and M. M. Bhasin, *Catal. Today*, **37**, 1 (1997).
- M. S. Morey, A. Davidson, and G. D. Stucky, *J. Porous Mater.*, **5**, 195 (1998).
- C. C. Williams and J. G. Ekerdt, *J. Phys. Chem.*, **95**, 8781 (1991) and references cited therein.
- M. Faraldos, M. A. Banares, J. A. Anderson, H. Hangchun, I. E. Wachs, and J. L. G. Fierro, *J. Catal.*, **160**, 214 (1996).