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

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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.

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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 $MoO_3$ catalyst has been found to be the most active and selective for oxygenates production.[5] It is conceivable that the large surface ($> 1000$ $m^2$ $g^{-1}$) 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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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 $H_2O$/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/$SiO_2$) were prepared by impregnation method by using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ 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.

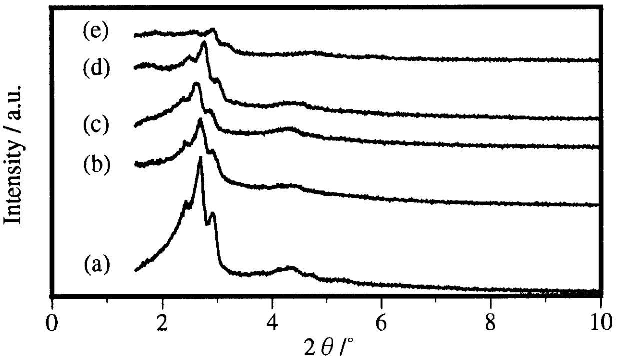

Fig. 1. XRD patterns for the calcined samples of (a) siliceous SBA-1, (b) Mo-SBA-1(Mo = 4.8 wt%), (c) Mo-SBA-1(Mo = 7.3 wt%), (d) Mo-SBA-1(Mo = 8.8 wt%) and (e) Mo/SBA-1(Mo = 9.0 wt%).

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/$SiO_2$ 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 $MoCl_5$ (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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to the gel with the following mole ratios: 1 TEOS/0.13 CTEABr/(5–10) HCl/125 $H_2O$/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 ($Mo^{5+}$ cation/$Mo_7O_{24}{}^{6-}$ 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 |

[a] The starting gel with the compositions of 1TEOS/0.13CTEABr/xHCl/125 $H_2O$/yMo. [b] x = 10, y = 0. [c] x = 5, y = 0.2. [d] x = 8, y = 0.2. [e] x = 10, y = 0.2. [f] Impregnation of SBA-1 with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. [g] Impregnation of $SiO_2$ with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

Mo-SBA-1 series samples possess characteristics of a mesoporous material, i.e., a BET surface area over 1000 m$^2$ 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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. $Mo/SiO_2$ sample only had a considerably small BET surface area below 100 m$^2$ g$^{-1}$ and a small pore volume of 0.12 cm$^3$ g$^{-1}$.

Figure 2 shows the Raman spectra of crystalline $MoO_3$, $Mo/SiO_2$, 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 $MoO_3$ and $Mo/SiO_2$) corresponding to bulk $MoO_3$[7] in the spectrum of Mo-SBA-1 sample (Figure 2d) indicates that no free $MoO_3$ 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 $MoO_3$ (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 >> $Mo/SiO_2$. This order is in agreement with the expectation by the BET results as shown in Table 1.

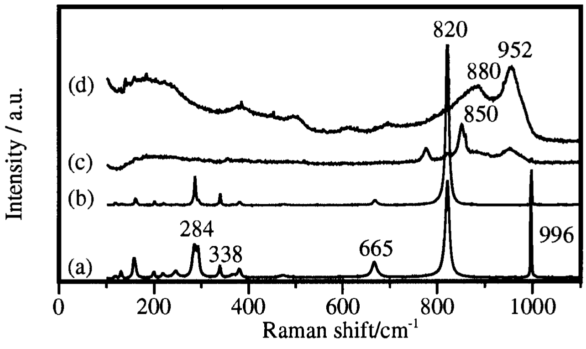

Fig. 2. Laser-Raman spectra of (a) crystalline $MoO_3$, (b) $Mo/SiO_2$ (Mo = 9.0 wt%), (c) Mo/SBA-1(Mo = 9.0 wt%) and (d) Mo-SBA-1 (Mo = 8.8 wt%).

As shown in Table 2, both Mo-SBA-1 and Mo/SBA-1 catalysts exhibited much higher $CH_4$ conversion and selectivity to HCHO than those of amorphous $Mo/SiO_2$. 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 $CH_4$ conversion. These results are consistent with the observation by Faraldos et al.,[8] who reported that $CH_4$ 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 /% HCHO | CO | $CO_2$ | $C_2$[c] | Yield of HCHO/% |
|---|---|---|---|---|---|---|
| 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 |

[a] Reaction conditions: catalyst = 0.5 (g), T = 953 K, $CH_4/O_2$/He = 90/20/20 (ml/min), time on stream = 0.5 h. [b] The number in parentheses represents Mo amount (wt%). [c] $C_2H_4 + C_2H_6$. [d] T = 963 K. [e] T = 958 K.

It is also clear from Table 2 that the Mo-SBA-1 prepared by direct synthesis showed a slightly higher $CH_4$ 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 ($Mo/SiO_2$) catalysts, due to the presence of high dispersion and isolation of Mo in the SBA-1 framework.

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