Mo-functionalized MCF meso-material and its catalytic performance for epoxidation of propylene by cumene hydroperoxide

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A B S T R A C T
The Mo-containing MCF (Mo-MCF) material was synthesized hydrothermally and used to catalyze the epoxidation of propylene with cumene hydroperoxide (CHP). The structure properties of the catalyst and the structure of surface molybdenum species were characterized by BET, TEM, XRD, Raman and UV–vis spectroscopies. It has been shown that, the Mo-MCF material has the meso-structure of silica MCF after introduction of molybdenum, and there are three molybdenum species of the isolated molybdenum species, polymolybdate species and little crystalline MoO3 of <5 nm existed in the MCF support, among which isolated and poly-molybdenum species are responsible for an increase of the epoxidation selectivity. The distribution of the molybdenum species is obviously affected by the preparation process. On the MoO3/MCF catalyst prepared by an impregnation, more polymolybdate species would congregate into dense MoO3, resulting in a decrease of the epoxidation selectivity. Comparatively, HMS, SBA-15 and SiO2 support were used to study the effect of the textural properties on the catalytic performance of Mo-containing catalyst. The results show that the structure character of support is another important factor to influence the catalytic performance of the catalyst, and the Mo-MCF material having the structure that is favorable for CHP molecules to access the active Mo sites, would restrain the decomposition of CHP and help to increase the epoxidation selectivity.

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1. Introduction

Molybdenum complexes are one of the versatile catalysts for the olefin epoxidation with alkyl hydroperoxide or hydrogen peroxide, and have been widely studied in the synthesis, cleaving ligand and catalytic efficiency [1–7]. For a difficult separation of the homogeneous catalysts from the reaction system, the considerable attentions have been paid on the heterogenization of these homogeneous catalysts on the inorganic supporting materials [8–10], hybrid materials [11], polymers [12–14] or ionic liquids [15] by covalently grafting homogeneous molybdenum catalysts. However, all these methods suffer the same drawback that synthesis of the molybdenum complexes is difficult and uneconomical. The direct synthesis of heterogeneous molybdenum catalysts can overcome this drawback. Mo-MCM-41 synthesized by an o xo-peroxo route has a high dispersion of the Mo species and used in the epoxidation of cyclohexene with tert-butyl hydroperoxide (TBHP) [16]. Mo-SBA-15 has also been synthesized by using the mixed surfactants [17] or non-ionic surfactants [18] and used as the catalyst for an epoxidation of 1-octene with TBHP. It should be noticed that, in the studies of these molybdenum-containing meso-silica catalysts, the model reaction used is commonly the epoxidation of liquid olefins, such as cyclohexene, octane and so on, which are easier to react with alkyl hydroperoxide. To the best of our knowledge, few papers have been reported about the molybdenum-containing meso-silica catalyst for an epoxidation of propylene, although the soluble molybdenum naphthenate catalyst has been successfully used in the Halcon process to produce propylene oxide (PO) by an epoxidation of propylene with tert-butyl hydroperoxide (TBHP) [19].

Recently, the hydroperoxide routes including propylene oxide/styrene monomer (POSM) and propylene oxide/tert-butyl alcohol (POTBA) are the most important processes to produce PO. However, the hydroperoxide routes need to commercialize or recycle the alcohol co-product in a fixed amount, and the profit of enterprise is restricted by the co-product market. In 2003, Sumitomo Chemical has commercialized the process of producing PO with cumene hydroperoxide (CHP) as an oxygen donor [20]. The advantages of this process are that, cumene is oxidized more easily to hydroperoxidate than styrene, and no co-product is produced.

In this paper, the molybdenum-containing meso-silica materials were synthesized and used to catalyze the epoxidation of propylene with CHP. Considering the larger molecule size of CHP, silica meso-cellular foam (MCF) was used as the support, which is an outstanding catalyst support for the large molecule reactions because of its open system of large pores (about 30 nm of diameter) with wide windows and highly hydrothermal stability [21]. For
example,WO3-containing MCF was used to catalyze an o-heterocyclization of cycloocta-1,5-diene with aqueous H2O2 [22], showing high catalytic activity and selectivity. The Mo-functionalized MCF mesoporous material was synthesized hydrothermally, and as a comparison, the MoO3/MCF catalyst synthesized by an impregnation method, Mo-containing SBA-15 and HMS were synthesized hydrothermally, and MoO3/SiO2 was synthesized by the sol–gel method, by which the effects of preparation method and the support structure on the catalytic performance of the Mo-containing silica were studied. And a relation between the molybdenum species and their catalytic performance has been studied and discussed.

2. Experimental

2.1. Preparation of catalyst

The Mo-MCF catalysts were synthesized as follows: 2 g Pluronic P123 triblock copolymer (EO10PO70EO10, Mv = 5800, Aldrich) was added to 75 mL of HCl (1.6 M) and stirred for 4 h at 40 °C, and 2 g 1,3,5-trimethylbenzene (TMB) was added to this solution and stirred for 2 h. Then 4.4 g Si(OCH2CH3)4 (TEOS) was added to the above solution and stirred for 15 min, and ammonium heptamolybdate ((NH4)6Mo7O24·4H2O, 0.2 mol/L) aqueous solution was added to obtain the synthesis solution. After being aged at 40 °C under moderate stirring for 24 h, this synthesis solution was crystallized at 100 °C for 1 day. The solid product was filtered and dried at room temperature, and finally it was calcined at 550 °C in air for 5 h to obtain the Mo-MCF catalyst. Based on the mole ratio (n) of Si/Mo in the synthesis solution, the catalyst was denoted as Mo-MCF(n). If ammonium heptamolybdate aqueous solution was not added to the synthesis solution, the pure silica MCF material was obtained.

The MoO3/MCF catalyst was synthesized by the impregnation method as follows: the pure silica MCF material was immerged in the ammonium heptamolybdate aqueous solution for 24 h. Then the excessive water was completely evaporated at 60 °C, and the catalyst was finally obtained after being calcined at 550 °C in air for 5 h.

Mo-HMS(13) and Mo-SBA-15(13) were synthesized according to the method described in the references [23,24]. 4%MoO3/SiO2 was synthesized by the sol–gel method [25].

2.2. Characterization of catalyst

The specific surface areas, the pore volumes and the mean pore diameters of the catalysts were measured on a Quantachrome NovaWin2 apparatus, and calculated by the BET method. Transmission electron micrographs (TEM) of the samples were obtained on a Joel JEM 2010 scan–transmission electron microscope, and the samples to be measured were supported on the carbon–coated copper grids for the testing. The molybdenum content in the catalyst was determined by an inductively coupled argon plasma (ICP, TJA IRIS 1000) after the sample was solved in the solution of HF–HCl. The XRD patterns of catalysts were performed on a Rigaku D/max-2550VB/PC diffractometer with CuKα radiation at 40 kV and 100 mA. The laser Raman spectra of samples were obtained on a Renishaw Raman spectrometer at ambient condition and the 514 nm line of a Spectra Physics Ar+ laser was used for an excitation. The UV–vis spectra were recorded on a Varian Cary 500 spectrophotometer using the diffuse reflectance technique in the range of 200–800 nm, and BaSO4 was used as the reference.

2.3. Catalytic epoxidation of propylene

The epoxidation reaction of propylene was carried out in an autoclave (100 ml) placed in a temperature equilibrated oil bath. In a typical experiment, the mixture of 20 ml tert-butyl alcohol, 10 ml cumene hydroperoxide (48%, industrial) and 0.2 g catalyst was placed into autoclave, and propylene was charged to 0.5 MPa at 6 °C. Then this reaction mixture was heated to 80 °C under magnetic stirring and kept at 80 °C for 4 h, in which the pressure increased from 0.5 MPa at 6 °C to 2.2 MPa at 80 °C.

The propylene oxide was analyzed by Clarus 500 GC (PerkinElmer) equipped with a FID detector and AE.PEG-20 M separation column (30 m×0.32 mm), and toluene was used as an internal standard. The conversion of CHP was determined by an iodometric analysis. The conversion of CHP (XCHP), the selectivity to PO (SCHP) for CHP and the yield of PO (YP0) are calculated as follows:

\[
X_{CHP}(\%) = \frac{n_{CHP} - n_{nPO}}{n_{nCHP}} \times 100\% ,
\]

\[
SCHP(\%) = \frac{n_{nPO}}{n_{nCHP}} \times 100\% ,
\]

\[
YP0(\%) = \left( \frac{SCHP \times X_{CHP}}{100} \right) \times 100\% ,
\]

wherein, \( n_{CHP} \) and \( n_{nPO} \) are the initial and terminal mole number of CHP in the reaction mixture, respectively; \( n_{nPO} \) is the mole number of PO produced.

3. Results and discussion

3.1. Textural and structure properties of Mo-silica mesoporous materials

Nitrogen physisorption was used to determine the physical parameters of the synthesized mesoporous materials. The results show that all the samples have the similar absorption/desorption isotherms, a type-IV isotherm with a typical hysteresis loop of mesoporous materials, which indicates that the introduction of Mo species does not destroy the meso-structure of MCF. Fig. 1 are the N2 absorption/desorption isotherms and BJH window-size distribution curves of pure silica MCF and Mo-MCF(13). Compared with pure silica MCF, the amount of adsorbed nitrogen on Mo-MCF(13) decreases significantly, which is associated with its smaller specific surface area. The window size of Mo-MCF becomes bigger and its distribution is only slightly broader after introduction of molybdenum species in MCF. The windows interconnecting the cells in the MCFs come from the contact areas between the composite droplets of TMB/P123 [21]. After an introduction of molybdenum species, the droplets become bigger by the complexation of molybdenum species with P123 which makes the Mo species locate in the corona area of the structure directing agent micelles [18]. The smaller droplet curvatures provide a large contact area between touching spheres, resulting in the bigger windows.

The window sizes of the samples were calculated from the desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) model, and the specific surface areas of the samples were calculated by the Barrett–Emmett–Teller (BET) equation. The textural parameters of the mesoporous materials with different MoO3 loadings are listed in Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m2/g)</th>
<th>Pore volume (cm3/g)</th>
<th>Average window diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-MCF(13)</td>
<td>1000</td>
<td>0.15</td>
<td>3.5</td>
</tr>
<tr>
<td>Mo-MCF(9)</td>
<td>1050</td>
<td>0.18</td>
<td>4.5</td>
</tr>
<tr>
<td>Mo-MCF(6)</td>
<td>1100</td>
<td>0.20</td>
<td>5.5</td>
</tr>
<tr>
<td>Mo-MCF(3)</td>
<td>1150</td>
<td>0.23</td>
<td>6.5</td>
</tr>
<tr>
<td>Pure silica MCF</td>
<td>1200</td>
<td>0.25</td>
<td>7.5</td>
</tr>
</tbody>
</table>

The BET surface area, pore volume and average window diameter of pure silica MCF is 800 m2/g, 1.6 cm3/g, and 8.1 nm, respectively. The presence of molybdenum species leads to a decrease of BET surface area of MCF, such as that of Mo-MCF(57) is only 661 m2/g, and with an increase in the MoO3 loading (fall of Si/ Mo = n) its BET surface area decreases continuously, except for Mo-MCF(9). The pore volume of the Mo-MCF sample has the same changing trend as the same as its surface area with the MoO3 amount. However, the window diameter of Mo-MCF increases with an increase in the MoO3 amount. The data of window diameters suggest that molybdenum species has entered or embedded into the inner walls of MCF and does not congregate.
in the pores, because the window diameter of MCF will decrease after an impregnation of metal ions, such as the window diameter of 4% MoO\textsubscript{3}/MCF has only 7.8 nm. The Mo-MCF(9) sample has higher surface area and larger pore volume than other Mo-doped MCF samples, indicating that the higher concentration of molybdenum ions may vary the synthesis mechanism of the Mo-MCF meso-materials.

Compared with Mo-MCF(13), the Mo-SBA-15(13) and Mo-HMS(13) samples possess the higher surface area, but smaller pore volume and window/pore diameter. The order of BET surface area is Mo-MCF(13) < Mo-SBA-15(13) < Mo-HMS(13); the order of pore volume and window/pore diameter is Mo-MCF(13) > Mo-SBA-15(13) > Mo-HMS(13).

The results in Table 1 show also that, the ratio of Si/Mo in the solid determined by ICP–AES is much higher than the ratio of Si/Mo in the synthesis gel, that is to say, only a small part of molybdenum species in the gel can enter into the meso-materials. An introduction of molybdenum species with a low content into the MCF and SBA-15 is caused by the strong acid environment of H\textsuperscript+/Mo > 90 in the synthesis of Mo-MCF and Mo-SBA-15. As it is reported, the acid condition does not favor the formation of Si–O–metal bonds and destroys them once being formed [26]. But on the other hand, when the H\textsuperscript+/Mo ratio is above 2 the heptamolybdate species can be depolymerized to form monomeric molybdenum species [27], which can help molybdenum species to enter into the meso-material more easily. As Mo-HMS was synthesized at about neutral condition, the heptamolybdate species that do not favor Mo entering into the meso-material exist in the synthesis solution, so Si/Mo ratio in Mo-HMS(13) is highest and reaches 123.

Table 1
Physico-chemical parameters of the synthesized mesoporous materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Mo\textsuperscript{a} (mol/mol)</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
<th>Pore volume (cm\textsuperscript{3}/g)</th>
<th>Average window diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCF</td>
<td>∞</td>
<td>800</td>
<td>1.6</td>
<td>8.1</td>
</tr>
<tr>
<td>Mo-MCF(57)\textsuperscript{b}</td>
<td>264.1</td>
<td>661</td>
<td>1.5</td>
<td>8.9</td>
</tr>
<tr>
<td>Mo-MCF(27)</td>
<td>77.6</td>
<td>579</td>
<td>1.4</td>
<td>9.7</td>
</tr>
<tr>
<td>Mo-MCF(13)</td>
<td>61.5</td>
<td>560</td>
<td>1.4</td>
<td>10.3</td>
</tr>
<tr>
<td>Mo-MCF(9)</td>
<td>67.1</td>
<td>741</td>
<td>2.3</td>
<td>12.4</td>
</tr>
<tr>
<td>4%MoO\textsubscript{3}/MCF</td>
<td>59.2</td>
<td>419</td>
<td>1.1</td>
<td>7.8</td>
</tr>
<tr>
<td>Mo-SBA-15(13)</td>
<td>70.6</td>
<td>718</td>
<td>1.2</td>
<td>6.6</td>
</tr>
<tr>
<td>Mo-HMS(13)</td>
<td>123</td>
<td>871</td>
<td>0.7</td>
<td>3.6</td>
</tr>
<tr>
<td>4%MoO\textsubscript{3}/SiO\textsubscript{2}</td>
<td>58.6</td>
<td>410</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The mole ratio of Si/Mo in the solid determined by ICP.
\textsuperscript{b} The mole ratio of Si/Mo in the synthesis solution.

\[ \text{Fig. 1. Nitrogen absorption/desorption isotherms and BJH pore size distribution curves of MCF and Mo-MCF(13).} \]

\[ \text{Fig. 2. TEM photograph of Mo-MCF(13) material.} \]

silica MCF. Besides, no crystalline MoO\textsubscript{3} particles could be observed, illustrating that the MoO\textsubscript{3} species have been well dispersed in the mesoporous silica.

3.2. Molybdenum species characterization

\[ \text{Fig. 3 shows that the XRD patterns of Mo-MCF and 4%MoO\textsubscript{3}/SiO\textsubscript{2}. For all the samples, the diffraction peaks of crystalline MoO\textsubscript{3} at 2\theta (°) = 12.7, 23.3, 25.6, 27.2 and 38.9 have not been observed, indicating that molybdenum species are well dispersed on silica support or the MoO\textsubscript{3} crystallites are too small to be detected by XRD.} \]
Raman spectroscopy is one of the effective methods to probe crystalline and amorphous nanoscale oxides [28]. In the Raman spectra of supported molybdenum species, the bands at about 994, 820 and 666 cm\(^{-1}\) can be attributed to the electron transitions in the Mo\(=\)O groups and vibration mode of the Mo–O–Mo bridges in crystalline MoO\(_3\); the bands at 875 and 950 cm\(^{-1}\) may be ascribed to the antisymmetric stretching of Mo–O–Mo and Mo\(=\)O stretching of surface poly-molybdenum species, respectively [29]. The Raman spectra of Mo-MCF(13), Mo-MCF(9) and 4\%MoO\(_3\)/SiO\(_2\) are shown in Fig. 4. For the three samples, a broad band between 940 and 1000 cm\(^{-1}\) is observed, indicating that the polymolybdate species and little crystalline MoO\(_3\) species coexist on silica.

Further an investigation of molybdenum species was performed by a UV–vis spectroscopy, and the results are shown in Fig. 5. All the samples have three bands located at 215, 240 and 320 nm, which can be attributed to the electron transitions in the Mo=O bonds of isolated molybdenum species, Mo–O–Mo bonds of oligomerized molybdate species and dense phase MoO\(_3\), respectively [18]. However, the shares of each molybdenum species are different for different catalysts. For the Mo-MCF(13), Mo-SBA-15(13) and Mo-HMS(13) samples, there is a similar distribution of molybdenum species. Comparing with Mo-MCF(13) synthesized in one-pot, 4\%MoO\(_3\)/MCF synthesized by an impregnation method has more dense phase MoO\(_3\) but much less poly-molybdenum species. The bigger peak at 320 nm in the UV–vis spectrum of 4\%MoO\(_3\)/SiO\(_2\) shows that, there are more crystalline MoO\(_3\) on 4\%MoO\(_3\)/SiO\(_2\) than other catalysts because of a conglomeration of molybdenum species.

Based on the spectra of UV–vis, XRD and Raman of Mo-functionalized samples, it can be concluded that in the silica matrix there are three molybdenum species of isolated molybdenum species, polymolybdate species and little crystalline MoO\(_3\) of <5 nm that can not be detected by XRD.

### 3.3. Catalytic performance of Mo-MCF for the epoxidation of propylene

The Mo-MCF mesoporous materials were used as the catalyst in the epoxidation of propylene with CHP, and the results are shown in Table 2. The MCF support is inactive for the epoxidation of propylene, and the molybdenum species embedded in/on the silica support are the active sites. With an increase in the molybdenum amount, both the conversion of CHP and the selectivity of PO increase when the ratio of Si/Mo (in the synthesis gel) is higher than 13, because of an increase of the surface concentration of active sites. Over the Mo-MCF(13) catalyst the conversion of CHP and the selectivity of PO are 80.3% and 92.3%, respectively. When the ratio of Si/Mo (in the synthesis gel) is reduced from 13 to 9, the conversion of CHP and selectivity to PO over the Mo-MCF(9) catalyst decrease from 80.3 to 78.5% and 92.3 to 80%, respectively, which is caused by the actual decrease of Mo content in Mo-MCF(9) (see Table 1). In the catalytic epoxidation of propylene with CHP, there are mainly three reactions, one objective reaction (the epoxidation of propylene) and two competition side-reactions of consecutive reaction (the ring-open of PO to propylene glycol) and parallel reaction (the decomposition of CHP). As no propylene glycol was detected in the reaction solution, a decrease of PO selectivity was caused by the decomposition of CHP. If there were not enough surface concentration of active sites, the catalytic epoxidation of propylene would slow down and the decomposition reaction of CHP would dominate in the competition side-reactions, leading to the decrease in the selectivity to PO.

The results in Table 2 show that, using Mo-MCF(13) catalyst the higher selectivity of PO can be obtained than using 4\%MoO\(_3\)/MCF catalyst, the former is 92.3% and the latter is 75.5%, which indicates that the hydrothermal synthesis method is more suitable to achieve an effective catalyst than the impregnation method for the Mo-containing MCF catalyst used in an epoxidation of propylene with CHP. In the preparation of Mo-MCF(13), although Mo atom cannot be incorporated into a silica framework replacing a silicon atom because that the atom geometry of Mo does not allow isomorphic substitution of silicon atom [18], it can be embedded into the MCF structure under the action of surfactant. By the combustion of surfactant during calcinations, the interaction between the active species and support can be strengthened [22], preventing from the congregation of poly-molybdenum species to crystalline MoO\(_3\) in Mo-MCF. As shown in Fig. 5, there are less dense phase MoO\(_3\) on Mo-MCF(13) than on 4\%MoO\(_3\)/MCF. The results above show that the isolated and poly-molybdenum species in MCF help to an increase of the PO selectivity. Although the window size of 4\%MoO\(_3\)/MCF is less than that of Mo-MCF(13), the windows size of ~8 nm of 4\%MoO\(_3\)/MCF has a little influence on the diffusion of the reactant molecules.

The textural property of the support is also an important factor to influence the catalytic performance of Mo-containing catalyst. For the Mo-SBA-15(13), Mo-HMS(13) and Mo-MCF(13) mesostructure materials, although their distributions of the molybdenum species are similar, as shown in Fig. 5, their catalytic performances are quite different for the epoxidation of propylene with CHP. The orders of their catalytic activities are as follows: Mo-MCF(13) ≈ Mo-SBA-15(13) ≈ Mo-HMS(13) for the conversion of CHP; and Mo-MCF(13) > Mo-HMS(13) ≈ Mo-SBA-15(13) for the selectivity to PO. The difference in the activities can be explained by the difference in active molybdenum sites, and the difference in the selectivity to PO may be due to the unique textural properties of supports. The MCF material possesses a high porosity and aerogel-like, three-dimensional, continuous, ultra-large mesopores with wide windows [21]. This open system of large pores is very
convenient for the CHP molecules to access the active Mo sites, restricting the decomposition of CHP and increasing the selectivity to product. The SBA-15 material possesses uniform tubular channels [24] and the CHP molecules would diffuse into and out of the tube pores to access the active Mo sites; however the pore is of tube with less size (6.6 nm) than the window size (~10 nm) of MCF, a part of CHP can be decomposed in the zone without or with less active Mo sites, which leads to some decline of the selectivity to PO comparing with the selectivity to PO on Mo-MCF. For the HMS material, although its mesopores with shorter channels and large textual porosity [30,31] can provide transport channels for the reactants to access the active centers, but the mass transfers of the reactants and product inside Mo-HMS(13) are not so easy comparing with the Mo-MCF(13) because that the pore domain size of Mo-HMS(13) is only 3.6 nm, resulting in the lower selectivity (85.5%) to PO than the selectivity (92.3%) of Mo-MCF(13) to PO. Moreover its molybdenum content is lower, the ratio of Si/Mo is 123 (Table 1), resulting in the lower conversion of propylene (57.9%).

The 4%MoO₃/SiO₂ sample displays the best activity for the title reaction with the conversion of 83.6% and worst selectivity of 69.8%. The high activity is due to its actual highest molybdenum contents. However, its lower specific surface area leads to a lower dispersion of molybdenum species on SiO₂, just as Fig. 5 shows, 4%MoO₃/SiO₂ possesses a large amount of dense MoO₃, resulting in the decrease of the selectivity.

The results above mentioned show that, the distribution of molybdenum species and the structure character of support are the two main factors influencing the catalytic performances of Mo-functionalized silica materials for the epoxidation of propylene with CHP. The isolated and poly-molybdenum species with an enough amount is the key to increase the selectivity of PO. Besides, the structure of the support which is convenient for the mass transfer of the reactants and products helps to improve the performance of the catalyst, such as the Mo-MCF(13) catalyst possesses an open system of large pores and good molybdenum distribution, and has the excellent catalytic performance for the epoxidation of propylene with CHP.

4. Conclusions

In conclusion, MoO₃ can be successfully introduced into silica MCF by the hydrothermal method, in which the meso-structures of MCF are not destroyed. There are three molybdenum species of the isolated molybdenum species, polymolybdate species and crystalline MoO₃ of <5 nm existed in the Mo-containing MCF material, and their subsistent state is remarkably influenced by the preparation method and directly related to the catalytic perfor-

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>XCHP (%)</th>
<th>SPO (%)</th>
<th>YPO (%)</th>
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<tbody>
<tr>
<td>MCF</td>
<td>3.0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mo-MCF(57)</td>
<td>32.8</td>
<td>72.9</td>
<td>23.9</td>
</tr>
<tr>
<td>Mo-MCF(27)</td>
<td>76.5</td>
<td>88.9</td>
<td>68.0</td>
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<tr>
<td>Mo-MCF(13)</td>
<td>80.3</td>
<td>92.3</td>
<td>74.1</td>
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<tr>
<td>Mo-MCF(9)</td>
<td>78.5</td>
<td>80.0</td>
<td>62.8</td>
</tr>
<tr>
<td>4%MoO₃/MCF</td>
<td>79.5</td>
<td>73.5</td>
<td>60.0</td>
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<tr>
<td>Mo-SBA-15(13)</td>
<td>79.4</td>
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<td>Mo-HMS(13)</td>
<td>57.9</td>
<td>85.5</td>
<td>49.5</td>
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<td>4%MoO₃/SiO₂</td>
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<td>58.4</td>
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<tr>
<td>MoO₃</td>
<td>16.0</td>
<td>3.8</td>
<td>0.6</td>
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</tbody>
</table>

Table 2
The catalytic performances of Mo-containing materials.
mance of the catalyst. The isolated and poly-molybdenum species are responsible for the high selectivity to PO in the epoxidation of propylene with CHP. The structure character of support is another important factor to influence the catalytic performance of the catalyst. The catalyst with the structure that is convenient for a mass transfer of CHP can restrain the decomposition of CHP and improve the selectivity to PO. For the Mo-MCF(13) catalyst synthesized hydrothermally, the good distribution of molybdenum species (more isolated and poly-molybdenum species) on the support and the open system of large pores are in favor of improving its catalytic property.

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