



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

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### ABSTRACT

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  $\text{MoO}_3$  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  $\text{MoO}_3/\text{MCF}$  catalyst prepared by an impregnation, more polymolybdate species would congregate into dense  $\text{MoO}_3$ , resulting in a decrease of the epoxidation selectivity. Comparatively, HMS, SBA-15 and  $\text{SiO}_2$  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, chelating 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 oxo-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

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example,  $\text{WO}_3$ -containing MCF was used to catalyze an *o*-heterocyclization of cycloocta-1,5-diene with aqueous  $\text{H}_2\text{O}_2$  [22], showing high catalytic activity and selectivity. The Mo-functionalized MCF mesoporous material was synthesized hydrothermally, and as a comparison, the  $\text{MoO}_3/\text{MCF}$  catalyst synthesized by an impregnation method, Mo-containing SBA-15 and HMS were synthesized hydrothermally, and  $\text{MoO}_3/\text{SiO}_2$  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 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ ,  $M_{\text{av}} = 5800$ , Aldrich) was added to 75 mL 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  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (TEOS) was added to the above solution and stirred for 15 min, and ammonium heptamolybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ , 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  $\text{MoO}_3/\text{MCF}$  catalyst was synthesized by the impregnation method as follows: the pure silica MCF material was immersed 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% $\text{MoO}_3/\text{SiO}_2$  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  $\text{CuK}\alpha$  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  $\text{Ar}^+$  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  $\text{BaSO}_4$  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 magnetical 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 ( $X_{\text{CHP}}$ ), the selectivity to PO ( $S_{\text{CHP}}$ ) for CHP and the yield of PO ( $Y_{\text{PO}}$ ) are calculated as follows:

$$X_{\text{CHP}}(\%) = \frac{n_{\text{CHP}}^i - n_{\text{CHP}}^t}{n_{\text{CHP}}^i} \times 100\%$$

$$S_{\text{CHP}}(\%) = \frac{n_{\text{PO}}}{n_{\text{CHP}}^i - n_{\text{CHP}}^t} \times 100\%$$

$$Y_{\text{PO}}(\%) = (S_{\text{CHP}} \times X_{\text{CHP}}) \times 100\%$$

wherein,  $n_{\text{CHP}}^i$  and  $n_{\text{CHP}}^t$  are the initial and terminal mole number of CHP in the reaction mixture, respectively;  $n_{\text{PO}}$  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  $\text{N}_2$  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  $\text{MoO}_3$  loadings are listed in Table 1.

The BET surface area, pore volume and average window diameter of pure silica MCF is  $800 \text{ m}^2 \text{ g}^{-1}$ ,  $1.6 \text{ cm}^3 \text{ g}^{-1}$ , 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  $661 \text{ m}^2 \text{ g}^{-1}$ , and with an increase in the  $\text{MoO}_3$  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  $\text{MoO}_3$  amount. However, the window diameter of Mo-MCF increases with an increase in the  $\text{MoO}_3$  amount. The data of window diameters suggest that molybdenum species has entered or embedded into the inner walls of MCF and does not congregate

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