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Co-Condensation Assisted Preparation of Mo^{VI} Schiff Base Modified Mesoporous Silica Catalyst for Enhanced Epoxidation of Olefins

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An organic–inorganic catalyst was prepared by the reaction of *p*-salicylidine aminobenzoic acid with mesoporous silica modified with 3-chloropropyl groups. The hydrolysis and co-condensation of tetraethylorthosilicate (TEOS) and 3-chloropropyltrimethoxysilane (CPTES) took place during the preparation process. $MoO_2(acac)_2$ was then introduced into the mesoporous silica functionalized with a Schiff base ligand. The structural properties of the prepared catalysts were investigated by a series of techniques, such as elemental analysis, X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectra, scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ adsorption/ desorption curves, and thermogravimetric analysis (TGA). The results demonstrated that the Mo^{VI} Schiff base complex was successfully tethered on the silica support, and the hexagonally ordered mesoporous structure of the SBA-15-type silica was well retained after the anchoring reaction. The heterogeneous catalyst showed good catalytic activities in the liquid-phase epoxidation of olefins with *t*-BuOOH as the oxygen source in 1,2-dichloroethane solvent at 80°C. Several important factors, including oxidant-to-substrate ratio, solvent, and catalyst reusability, were investigated. Under the optimum reaction conditions, using this heterogeneous catalyst for the cyclohexene epoxidation reaction, a high conversion of 97.20% and selectivity of >99% was achieved after 4 h, while the catalytic activity nearly remained unchanged over four runs.

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Introduction

Epoxides are important organic intermediates for the organic synthesis of fine chemicals.^[1] Olefin epoxidation in the liquid phase is one of the most important industrial reactions for epoxide production. During these epoxidation reactions, the catalyst plays a crucial role and dominates the whole reaction. Finding an efficient catalyst for the epoxidation of olefins has been a hot research field. To date, heterogeneous complexes have been used as alternative structures to not only combine the advantages (rich active sites and good compatibility with reaction species) but also remedy the disadvantages (poor recyclability and residues in products) of homogeneous complexes in catalytic epoxidation. Several organic-inorganic heterogeneous catalytic systems with transition metal (Mn, V, Mo, Ti, Co, etc.) Schiff base complexes have been used to oxidize olefins to epoxides.^[2] As a typical heterogeneous complex, a mesoporous silica supported Mo^{VI} Schiff base has been widely applied in olefin epoxidation due to its high catalytic activity.^[3]

On the basis of these reported results, it is well acknowledged that the surface properties of functionalized mesoporous silica are crucial for their catalytic performances, which are largely

dependent on the preparation procedures. In general, postsynthetic grafting and co-condensation methods are used to functionalize morphous silica materials, both of which involve the co-condensation of siloxane and organosiloxane precursors to produce hybrid organic-inorganic networks. The postsynthetic grafting method typically results in serious nonhomogeneous surface coverage and an uneven distribution of organic species throughout the material.^[4] At the same time, the low reactivity of the surface silanols in the post-synthetic grafting process limits the extend of surface functionalization.^[5] Alternately, the co-condensation method minimizes the number of processing steps and produces mesoporous materials with a relatively uniform distribution of the organic functionalities in addition to high loadings of organic groups without blocking the entrance of the pores.^[6] The well dispersed catalytic sites partially integrated on the wall of these materials offer reduced resistance to the diffusion of molecules within the mesochannels and are more resistant to leaching than if they were grafted onto the ordered mesoporous silica.^[7] This high loading of organic groups imparts poor wettability during the epoxidation reaction leading to favourable contact with reactive species.^[8] In addition to the



Scheme 1. Preparation of ordered Mo-SB-Cl-SiO₂.

enhanced loading of functional groups, the particle size and shape of the resulting mesoporous silicas could be controlled by the co-condensation method.^[9] It can be thus deduced that this co-condensation approach provides a new synthetic route for functional mesoporous silica heterogeneous catalysts potentially with enhanced catalytic activity in olefin epoxidation.^[10]

In this work the co-condensation assisted method was employed for the synthesis of a novel mesoporous organosilica bearing a high density of Mo^{VI} Schiff base complexes (Scheme 1). The obtained materials were characterised by using elemental analysis, X-ray diffraction (XRD), FT-IR spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ adsorption/desorption analysis, and thermogravimetric analysis (TGA). The hybrid catalysts were used for the epoxidation of olefins. The effects of different reaction variables were investigated in the epoxidation reaction. Furthermore, the stability and reusability of the organic–inorganic catalyst were evaluated.

Experimental

Materials

Analytical reagent grade olefins (Aladdin, China), Pluronic P123 triblock copolymer ($M_n = 5800$) (Sigma–Aldrich, China), 3-chloropropyltriethoxysilane (CPTES), and tetraethylorthosilicate (TEOS) (Sinopharm Chemical Reagent Co., Ltd) were used as obtained. MoO₂(acac)₂, SBA-15 (a mesoporous silica material), *p*-salicylidine aminobenzoic acid (abbreviated as H₂SB), and Mo-SB (Mo complexed to *p*-salicylidine aminobenzoic acid) were prepared according to the reported methods.^[11] Details of synthetic procedures are given in the Supplementary Material. Other chemicals and solvents of analytical reagent grade were used without purification.

*Synthesis of Mo-SB-Cl-SiO*₂ *Material* (Co-Condensation Method)

The sequence of events in the functionalization of $Cl-SiO_2$ with H_2SB and $MoO_2(acac)_2$ is depicted in Scheme 1.

Preparation of Cl-SiO₂

The material was prepared by a co-condensation method. In a typical synthesis, 1.0 g of Pluronic P123 was thoroughly dissolved in 35 mL of water and 5 mL of concentrated hydrochloric acid. The solution was heated to 40°C and 2.08 g (2.3 mL) of TEOS was added. After 1 h of TEOS prehydrolysis, CPTES (0.5 mL) was added into the aqueous dispersion using a syringe over 10 min. The resultant mixture was stirred at 40°C for 24 h, followed by hydrothermal treatment at 100°C for another 24 h under static conditions. Finally, the solid was filtered off and was then subjected to Soxhlet extraction with dry methanol for 72 h. The white solid (Cl-SiO₂) was dried at 80°C under vacuum for 8 h.

Preparation of SB-Cl-SiO₂

The preparation of SB-Cl-SiO₂ was adapted from a similar procedure.^[12] The previously synthesized Cl-SiO₂ (1.0 g) and DMF (10 mL) were placed in a flask equipped with a magnetic stirrer and a reflux condenser. The mixture was stirred for 10 min, and afterwards a solution of 0.5 g H₂SB in 10 mL of DMF was added, followed by the addition of 10 mL of ethylacetate with 2.25 g of triethylamine. The reaction mixture was heated to 90°C and kept for 10 h under stirring. After cooling to room temperature, the pale yellow solid power was separated by filtration, washed with hot DMF (3 × 50 mL), and ethanol several times. After drying at 80°C, SB-Cl-SiO₂ was obtained.

Preparation of Mo-SB-Cl-SiO₂

The preparation of Mo-SB-Cl-SiO₂ was as follows: SB-Cl-SiO₂ (1 g) was added to 10 mL of methanol, and the mixture was heated to 85° C. A hot ethanolic solution (35 mL) of 0.75 g of MoO₂(acac)₂ was then added dropwise under stirring. The colour of the solution gradually changed to deep blue. After stirring for 24 h, the product was filtered, washed by Soxhlet extraction with ethanol to remove the unreacted MoO₂(acac)₂, and dried at 80°C. The acquired solid was labelled Mo-SB-Cl-SiO₂.

Synthesis of Mo-SB-Cl-SBA-15 Material (Post-Grafting Method)

For comparison, a counterpart material was prepared via the same grafting method except Cl-SBA-15 was replaced by Cl-SiO₂. The preparation of Cl-SBA-15 was in accordance with our previous work.^[2a] The grafted hybrid was denoted as Mo-SB-Cl-SBA-15.

Epoxidation Procedures

The performance of the catalysts was investigated in the epoxidation of a model cyclohexene substrate. In a typical procedure, cyclohexene (2.5 mmol), oxidant (5.0 mmol), *tert*-butyl hydroperoxide (TBHP, 65 wt.-% in water solution), and catalyst (25 mg) were added to 1,2-dichloroethane (1,2-DCE, 10 mL) in a 25 mL two-neck round bottom flask and the reaction was carried out under reflux for an appropriate duration at 80°C. After finishing the reaction, the reaction mixture was centrifuged and analysed using a gas chromatograph (GC, SP-6890A) equipped with an FID detector and a capillary column (SE-54 30 m × 0.32 mm × 0.25 µm). The identity of the products was confirmed using gas chromatography–mass spectrometry (GC-MS, Perkin-Elmer, Clarus 500).

Materials Characterization

TGA of the as-fabricated materials was performed using Thermo Gravimetric System Mettler Toledo at a temperature ramping rate of 10 °C min⁻¹ under air. FT-IR spectra were recorded on a NICOLET 6700 FT-IR Thermoscientific spectrometer using a KBr pellet technique in the $500-4000 \text{ cm}^{-1}$ region. Adsorption and desorption isotherms for nitrogen were obtained at -196°C using a Micromeritics ASAP 2010. The materials were outgassed at 95°C and 0.1 Pa for 6 h before the measurement. XRD patterns were recorded by a Bruker diffractometer (D8) using a curved detector from 0.8 to 10 (2 θ) with a resolution of 0.02 at 40 kV, 40 mA, with Cu Ka radiation $(\lambda 1.54056 \text{ A})$. SEM and energy-dispersive X-ray spectroscopy (EDS) mapping were carried out using a Hitachi S-4800 equipped with a field-emission gun with an accelerating voltage at 2 kV and an Oxford Instruments 80 mm² silicon drifted detector with an accelerating voltage of 15 kV and current of 15 mA. TEM was performed on a JEOL JEM-2100F with an acceleration voltage of 200 kV. All materials were prepared by finely dispersing the materials in ethanol using sonication and were deposited uniformly on a 400 mesh copper grid coated with a perforated carbon film and dried in air. The content of molybdenum in the host materials and leaching of molybdenum into the solution were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin-Elmer AA-300 spectrophotometer.

Results and Discussion

Textural Characterisation

TGA and Element Analysis

The TGA curve of Cl-SiO₂ (Fig. 1c) exhibited a 3–4 wt-% weight loss in the region of 25–120°C which was assigned to the removal of physically adsorbed water and solvent inside the pores.^[13] A further ~2 wt-% of weight loss in the region of 150–300°C was attributed to desorption of the chemisorbed water on the silica surface.^[14] A major weight loss (~13 wt-%) between 300 and 700°C was attributed to the decomposition of the 3-chloropropyl groups. In comparison with Cl-SiO₂, SB-Cl-SiO₂



Fig. 1. TGA curves of (a) Mo-SB-Cl-SBA-15, (b) SB-Cl-SiO₂, (c) Cl-SiO₂, and (d) Mo-SB-Cl-SiO₂.



Fig. 2. IR spectra of (a) Cl-SiO₂, (b) SB-Cl-SiO₂, (c) Mo-SB-Cl-SiO₂, and (d) Mo-SB-Cl-SBA-15.

(Fig. 1b) had a lower weight loss below 300°C. When the temperature increased to 700°C, SB-Cl-SiO₂ underwent an ~ 17 wt-% weight loss (higher than that in Cl-SiO₂) certifying the successful immobilization of the Schiff base ligand on the organic-inorganic silica matrix. As for Mo-SB-Cl-SiO₂ (Fig. 1d), its TGA curve also showed a weight loss between 25 to 300°C. Furthermore, a \sim 20 wt-% loss for Mo-SB-Cl-SiO₂ was observed from 300 to \sim 700°C, which indicated the decomposition of the Mo^{VI} Schiff base ligand complex.^[15] Comparing the weight losses between SB-Cl-SiO₂ and Mo-SB-Cl-SiO₂, it was found that the difference was \sim 3.3 wt-%, which suggests the possible formation of MoO₃ and grafting of the Mo^{VI} Schiff base complex into the organic-inorganic silica matrix.^[16] From Fig. 1a, it is clearly seen that the mass loss of Mo-SB-Cl-SBA-15 is lower than that of Mo-SB-Cl-SiO₂. The result indicates a lower amount of functional groups bonded to the surface through the post-grafting method compared with the co-condensation method. According to the ICP-AES results, the Mo contents were determined to be 0.2366 and $0.085 \text{ mmol g}^{-1}$ for Mo-SB-Cl-SiO₂ and Mo-SB-Cl-SBA-15, respectively. Mo-SB-Cl-SiO₂ showed a higher amount of Mo than Mo-SB-Cl-SBA-15, which is in good agreement with the TGA results.

FT-IR Spectroscopy

FT-IR spectra provided further evidence for the successful immobilization of the Mo^{VI} Schiff base on the mesoporous material and the results are shown in Fig. 2. The characteristic absorption peaks at 3450 and 1634 cm⁻¹ for Cl-SiO₂, SB-Cl-SiO₂, Mo-SB-Cl-SiO₂, and Mo-SB-Cl-SBA-15 are assigned to



Fig. 3. (a) X-Ray diffraction patterns of (i) Cl-SiO₂, (ii) SB-Cl-SiO₂, (iii) Mo-SB-Cl-SiO₂, and (iv) Mo-SB-Cl-SBA-15; (b) partly enlarged view.

an O-H stretching vibration and deformation vibration of phyisorbed water and potential surface hydroxy groups. The bands at 2983 and 2927 cm⁻¹ are attributed to the CH₂ asymmetric and symmetric stretching vibrations of the propyl chain, respectively. The broad peak between 1000 and $1250 \,\mathrm{cm}^{-1}$ corresponds to Si–O–Si asymmetric vibrations, a slight peak at 800 cm^{-1} to a Si–O–Si symmetric vibration, and the peak at 960 cm⁻¹ to the Si-O stretching of Si-OH.^[17] Compared with Cl-SiO₂, SB-Cl- SiO_2 showed weaker absorption bands at 1634 and 960 cm⁻¹ due to the introduction of the Schiff base ligand into the organic silica matrix. For SB-Cl-SiO₂, the C=N stretching vibration peak was not clearly apparent because it was overlapped with the O-H deformation vibration peak.^[18] After treatment with ⁻¹ are MoO₂(acac)₂, two new adjacent bands at 908 and 871 cm⁻ observed (Fig. 2c) and they are characteristic peaks of a cis-MoO $_2$ group.^[19] This is powerful evidence for the formation of Mo-SB-Cl-SiO₂. The expected symmetric (Mo=O) band is not observed due to the overlap with a broad band with medium intensity at 960 cm⁻¹ for Si-O vibrations in silanols.^[20] For the FT-IR spectrum of Mo-SB-Cl-SBA-15 (Fig. 2d), due to the lower ligand content, the characteristic C=N stretching vibration at 1643 cm⁻ is weakened and the characteristic Mo=O stretching vibration is not clearly apparent at 908 cm^{-1} .

XRD Analysis

Fig. 3a displays the XRD patterns of Cl-SiO₂, SB-Cl-SiO₂, Mo-SB-Cl-SiO₂, and Mo-SB-Cl-SBA-15. Cl-SiO₂ showed a characteristic diffraction peak at $2\theta = 0.8-1.2$ corresponding to the (100) reflection of SBA-15-type materials.^[21] This confirms the formation of a mesoporous structure. For SB-Cl-SiO₂ and Mo-SB-Cl-SiO₂, the intense (100) reflections suggest that the mesoporous organosilica maintained its structural integrity after anchoring of the Mo^{VI} Schiff base complex. Compared with Cl-SiO₂, the XRD pattern of the SB-Cl-SiO₂ and Mo-SB-Cl-SiO₂ (Fig. 3b, curve i) showed the (110) and (200) reflections with a lower intensity due to the decreased mesoscopic order of the materials and the contrast matching between the silicate framework and organic moieties located inside the Cl-SiO₂ channels. It can also be seen from Fig. 3b, comparing Cl-SiO₂, SB-Cl-SiO₂, and Mo-SB-SiO₂, that the position of this reflection for Mo-SB-SiO₂ is shifted to a lower angle (or higher d-value) which is caused by the incorporation of the Schiff base ligands and the coordination with $MoO_2(acac)_2$ in the pores of Cl-SiO₂ leading to expansion of the unit cell parameter.^[5a] In

comparison with Mo-SB-Cl-SBA-15, Mo-SB-Cl-SiO₂ showed diffraction peaks with lower intensity and higher position. This might be due to loss of regularity and enlargement of the pore in the 2D hexagonal structure of mesoporous silica by a co-condensation assisted method.

N₂ Adsorption/Desorption

Nitrogen adsorption/desorption experiments were performed on the Cl-SiO₂, SB-Cl-SiO₂, Mo-SB-Cl-SiO₂, and Mo-SB-Cl-SBA-15 materials to compare their surface areas and pore size distributions (Fig. 4a, b, Table 1). Cl-SiO₂, SB-Cl-SiO₂, and Mo-SB-Cl-SiO₂ revealed type IV isotherms with a H2-type hysteresis loop. The steep adsorption step around $P/P_0 = 0.40-$ 0.70 demonstrated the formation of well structured mesoporous materials with narrow pore size distributions, as it was derived from the Barrett-Joyner-Halenda (BJH) analysis shown in Fig. 4a. The total pore volume decreased when loading of the organic ligand increased. In addition, the mean pore size is slightly shifted to lower values for the same reasons discussed above. Cl-SiO₂, SB-Cl-SiO₂, and Mo-SB-Cl-SiO₂ show a sharp peak (Fig. 4b) that indicates the uniform pore size distributions of the materials. Their pore diameters were 3.82, 3.66, and 3.60 nm, respectively, as summarised in Table 1. The Brunauer-Emmett-Teller (BET) surface area and pore volume of the Mo-SB-Cl-SiO₂ catalyst were lower than those of SB-Cl-SiO₂ confirming the successful immobilization of MoO₂(acac)₂ in the organosilane framework. Mo-SB-Cl-SBA-15 displayed a type IV isotherm with H1-type hysteresis loop, which indicates a typical mesoporous material with high regularity. Mo-SB-Cl-SBA-15 had a larger pore diameter and pore volume and a lower BET surface area than Mo-SB-Cl-SiO₂. This is a result of the greater number of organic ligands and metallic active sites in Mo-SB-Cl-SiO₂ prepared by the co-condensation assisted method, which is consistent with TGA and ICP-AES analyses.

SEM, TEM, and EDS

SEM images of Cl-SiO₂ and Mo-SB-Cl-SiO₂ were recorded and the results are shown in Fig. 5a, d. The results show that both Cl-SiO₂ and Mo-SB-Cl-SiO₂ had a wormlike structure with high regularity. However, Mo-SB-Cl-SiO₂ became slightly coarse. Loading Mo-SB-Cl-SiO₂ with the Mo^{VI} Schiff base affected the surface morphology of the mesostructure. In addition, more detailed structural information of the Cl-SiO₂ and Mo-SB-Cl-SiO₂ nanocomposite was determined by TEM. The TEM image



Fig. 4. (a) Nitrogen adsorption isotherms and (b) pore size distribution profiles of the initial material (i) Cl-SiO₂, (ii) SB-Cl-SiO₂, (iii) Mo-SB-Cl-SiO₂, and (iv) Mo-SB-Cl-SBA-15.

Table 1. Characteristics of support and catalysts, specific surface area S_{BET} : specific surface area; V_{BJH} : pore volume; D_{BJH} : pore diameter

Sample	Mo content [mmol g^{-1}]	$\frac{S_{\rm BET}}{[\rm m^2 g^{-1}]}$	$\frac{V_{\rm BJH}}{\rm [cm^3 g^{-1}]}$	D _{ВJH} [nm]	
Cl-SiO ₂	_	681.58	0.62	3.82	
SB-Cl-SiO ₂	_	523.09	0.50	3.66	
Mo-SB-Cl-SiO ₂	0.2366	486.59	0.44	3.60	
Mo-SB-Cl-SBA-15	0.0850	476.88	0.62	5.24	

of the Mo-SB-Cl-SiO₂ material shows a well ordered rodlike structure of the channels (Fig. 5e) from the side view and a typical honeycomb structure with SBA-15-type mesostructured materials from the profile view (Fig. 5f). Loading of the Mo^{VI} Schiff base did not destroy the mesoporous structure of the support. This observation is in good agreement with the nitrogen adsoption/desorption results. The mesoscopic order was further confirmed by TEM images (Fig. 5b, c, e, f) as definitive evidence of the structure ordering achieved. EDS mapping was employed to probe the presence of Si, O, C, N, and Mo elements and to corroborate the distribution throughout the Mo-SB-Cl-SiO₂ material (Fig. 5h–l). The existence of Si, O, C, N, and Mo elements and their uniform distribution was clearly demonstrated, which further confirms that the Mo^{VI} Schiff base had been successfully chelated into the mesoporous silica.

Catalytic Epoxidation Activity

The reaction conditions for the catalytic epoxidation were: cyclohexene (2.5 mmol), *n*-octane (1.25 mmol, internal standard), 1,2-DCE (10 mL), TBHP (5 mmol), 80°C, and catalyst (25 mg, homogeneous catalyst Mo-SB with the same amount of Mo^{VI} as heterogeneous catalyst Mo-SB-Cl-SiO₂). As determined by GC-MS, the product is cyclohexene epoxide, and the by-products are 2-cyclohexene-1-ol, 1,2-cyclohexenediol, and 2-cyclohexene-1-one.

The catalytic activity of Mo-SB, Mo-SB-Cl-SiO₂, and Mo-SB-Cl-SBA-15 was investigated and the results are given in Fig. 6. For Mo-SB-Cl-SiO₂, \sim 80.46 % cyclohexene conversion was obtained during the initial 0.5 h. When the reaction time increased to 4 h, the conversion reached 97.20 % which is slightly lower than that for the highly active homogeneous Mo-SB catalyst. These results indicate that the Mo-SB-Cl-SiO₂ is an

effective heterogeneous epoxidation catalyst. In comparison with Mo-SB-Cl-SBA-15, the Mo-SB-Cl-SiO₂ showed a higher conversion for the epoxidation under the same conditions. On the one hand, the Mo-SB-Cl-SiO₂ catalyst exhibited a higher density of Mo^{V1} active sites leading to its higher catalytic epoxidation efficiency.^[7b,22] On the other, most of the –OH groups on the surface of the silica mesoporous precursor were replaced by 3-chloropropyl groups through the co-condensation method, which could improve the hydrophobicity of Mo-SB-Cl-SiO₂ and have a beneficial effect on the epoxidation reaction.^[23]

Effects of Different Oxidant/Olefin Molar Ratios

To study the effect of oxidant amount on epoxidation, four different molar ratios of aqueous TBHP to cyclohexene (0.5:1, 1:1, 2:1 and 3:1) were investigated. As shown in Fig. 7, when the TBHP-to-cyclohexene molar ratio increased to 2:1, the highest conversion (97.20%) was obtained during 4 h and the selectivity was over 99%. With a further increase of TBHP-to-cyclohexene molar ratio to 3:1, the conversion slightly decreased to 91.56%. The excess TBHP probably led to the generation of *tert*-butyl alcohol, which has been reported to act as a competitive inhibitor for the attack of TBHP at a molybdenum(vI) centre and restrain the epoxidation process.^[24] In addition, the corresponding increase in water upon use of excessive TBHP is adverse for the epoxidation of olefins.

Effects of Different Solvents

To evaluate the influence of various solvents on the epoxidation, the epoxidation experiments for Mo-SB-Cl-SiO2 were performed in CHCl₃, CH₂Cl₂, 1,2-DCE, C₂H₅OH, t-BuOOH, EtOAc, and CH₃CN and the results are summarised in Table 2. When using 1,2-DCE and CH₃Cl as solvents, the substrate and oxidant could be easily transferred to the surface of Mo-SB-Cl-SiO₂ causing the good dispersion of the product and by-product. Thus, 1,2-DCE and CH₃Cl mediated reactions showed the best conversions and epoxide yields. It is worth mentioning that CH₂Cl₂ gave a low conversion largely due to the lower boiling point of the solvent. In the case of C2H5OH, EtOAc, and CH₃CN, all of which contain donor atoms (O or N), these solvents tended to coordinate strongly with the Mo^{VI} centre. Table 2 shows the turnover frequency (TOF) defined as the ratio of produced epoxide to the number of Mo moieties in Mo-SB-Cl-SiO₂. The activity order of $C_2H_5OH > EtOAc > CH_3CN$ (TOF: 74.32 > 41.54 > 22.68) can be explained by the increasing coordination ability of $CH_3CN > C_2H_5OH > EtOAc$ and their competition with the oxygen molecule to occupy the coordination sites of the catalyst. The by-product *t*-BuOOH was

also employed as the solvent and a lower conversion and selectivity were obtained in this case, which indicated that *t*-BuOOH may inhibit the reaction by competing with the oxidant for coordination to the metal centre. The results indicate



Fig. 5. SEM and TEM images at different magnifications. (a, d) SEM of Cl-SiO₂ and Mo-SB-Cl-SiO₂, respectively; (b, c) TEM of Cl-SiO₂; and (e, f) TEM of Mo-SB-Cl-SiO₂. (h–l) EDS elemental mapping images of Si, O, C, N, and Mo, respectively.



Fig. 6. Testing of different catalyst in the conversion of cyclohexene.



Fig. 7. Epoxidation of cyclohexene with different molar ratios of oxidant/ olefin catalyzed by Mo-SB-Cl-SiO₂. Reaction conditions: cyclohexene (2.5 mmol), oxidant (appropriate molar amount), 1,2-DCE (10 mL), *n*-octane (1.25 mmol) as internal standard, catalyst (25 mg), and reaction temperature (80°C). Determined by GC-MS, the product is cyclohexene epoxide, and the by-products are 2-cyclohexene-1-ol, 1,2-cyclohexenediol, and 2-cyclohexene-1-one.

that the solvent, on the one hand, potentially influences the adsorption of reagents and the diffusion of products during the epoxidation. On the other, it possibly causes polarization and inductive effects affecting the activity and stability of the metal

Table 2. Screening of solvents and reaction conditions in the oxidation of cyclohexene

Reaction conditions: cyclohexene (2.5 mmol), *n*-octane (1.25 mmol) as internal standard, *t*-BuOOH (5 mmol), solvent (10 mL). Reactions were performed under reflux at 80°C in an oil bath. GC conversion based on starting olefin. Determined by GC-MS, the product is cyclohexene epoxide, and the by-products are

²⁻cyclohexene-1-ol, 1,2-cyclohexenediol, and 2-cyclohexene-1-one

Entry	Solvent	Time [h]	Conversion [%]	Selectivity [%]	$TOF^{A}[h^{-1}]$
1	CH ₂ Cl ₂	8	72.54	> 99	38.32
2	CHCl ₃	1	80.07	> 99	338.42
3	1,2-DCE	1	85.14	> 99	359.85
4	CH ₃ CN	12	64.40	76.76	22.68
5	EtOAc	8	78.62	98.94	41.54
6	t-BuOH	4	65.24	98.01	68.93
7	$\rm C_2H_5OH$	4	70.34	96.12	74.32

^ATurnover frequency (TOF) was calculated by the expression, $TOF = (mmol of epoxide)/(mmol of Mo^{VI} \times reaction time (h)).$

Effects of Different Olefin Substrates

In order to assess the general applicability of the method, various olefins were subjected to the oxidation protocol over Mo-SB-Cl-SiO₂ under the optimized reaction condition and the results are given in Table 3. As shown, the order of increasing reactivities based on TOFs correspond to cyclooctene > cyclohexene > cyclopentene > 1-pentene > 1-hexene > 1-octene. Branched and cyclic olefins with double bonds attached to secondary carbons were found to be better active substrates than linear 1-olefins. To explain this trend, two determining factors involving electronic effects and steric effects should be taken into consideration.^[25] The higher electronic density of the double bond tended to exhibit more epoxidation reactivity. Cyclooctene was more reactive than cyclohexene or cyclopentene due to the existence of more electron donating $(CH_2)_6$ cyclic bridges connected to the double bond. In contrast, under the same reaction conditions, the catalytic activities for the

Entry	Substrate	Structure	Time [h]	Conversion [%]	Selectivity [%]	$TOF^{B}[h^{-1}]$
1	cyclopentene		1	63.54	98.43	268.55
2	cyclohexene	\bigcirc	1	85.14	> 99	359.85
3	cyclooctene		1	87.10	> 99	368.13
4	1-phenyl-1-cyclohexene		4	50.42	78.84	53.28
5	4-methyl-1-cyclohexene	CH ₃	1	73.59	98.73	311.03
6	1-octene	$\wedge \wedge \wedge / /$	8	61.53	> 99	32.51
7	1-hexene		8	74.50	98.41	39.36
8	1-pentene		4	82.08	> 99	86.73
9	2-vinylnaphthalene		4	64.73	61.74	68.40
10	trans-stilbene		12	45.34	56.45	15.97

^AReactions were performed in 1,2-DCE (10 mL) with catalyst (25 mg), substrate (2.5 mmol), TBHP (5.0 mmol), *n*-octane (1.25 mmol) as internal standard. The reactions were performed at 80°C.

^BTOF was calculated by the expression: TOF = (mmol of epoxide)/(mmol of Mo^{VI} × reaction time(h)).

epoxidation of the linear olefins increased with the decreasing chain length of the olefins. The effect of epoxidation of 1-octene was stronger than 1-hexene or 1-pentene, which could be attributed to the larger hexyl group connected to the double bond sterically hindering the approach to the catalyst metal centre with respect to 1-hexene and 1-pentene with a smaller group. These results clearly indicate that, in addition to the intrinsic reactivity of the double bond, olefin length and accessibility to the active sites of the catalyst were the major limiting factors of the catalytic reaction.^[25] Not only cyclohexene but also linear olefins were catalytically oxygenated with high selectivity to epoxide products. The selectivity for 1-epoxypentene, 1-epoxyhexane, and 1epoxyoctane were > 99, 98.41, and > 99% in the reaction time of 4, 8, and 8 h, respectively. The other cycloolefin compounds bearing electron-donating groups, for example 4-methyl-1cyclohexene, gave excellent conversion of epoxidation products. However, olefins bearing electron-withdrawing groups, such as 1-phenyl-1-cyclohexene, afforded lower conversion of the corresponding coupling adducts. The conversion of 1-phenyl-1cyclohexene and 4-methyl-1-cyclohexene seemed to proceed in a similar way. The lower catalytic activity of 1-phenyl-1-cyclohexene compared with 4-methyl-1-cyclohexene was probably because of its increased steric hindrance.^[26] The electronic effects and steric effects can also be used to explain the catalytic activity of 1-phenyl-1-cyclohexene and 4-methyl-1-cyclohexene. Olefins having double bonds with one or two electron-withdrawing groups at the both ends were also investigated in this study. As a typical olefin with an electron poor terminal, 2-vinylnaphthalene exhibited medium conversion of 64.73 % and a selectivity of 61.74 % over 8 h because its epoxide was prone to further unwanted ringopening reactions in the epoxidation reaction. The sterically demanding substrate trans-stilbene lead to a 45.34% conversion and a 56.45% selectivity for a longer reaction time of 12h. The formation of side products took place because of ring-opening during the epoxidation of trans-stilbene. Furthermore, the epoxide of *trans*-stilbene was unstable and apt to ring-opening at high temperature.



Fig. 8. Evaluation of the recyclability of Mo-SB-Cl-SiO₂ towards the cyclohexene epoxidation reaction. Catalytic activity for the 1st, 2nd, 3rd, and 4th run. Conditions: catalyst (25 mg), 1,2-DCE (10 mL), cyclohexene (2.5 mmol), TBHP (5 mmol), *n*-octane (1.25 mmol) as internal standard, and temperature 80° C. Determined by GC-MS, the product is cyclohexene epoxide, and the by-products are 2-cyclohexene-1-ol, 1,2-cyclohexenediol, and 2-cyclohexene-1-one.

Recovery and Stability

The reusability of the catalyst is an important factor for heterogeneous catalysts in the epoxidation of olefins. Recycling experiments were carried out under the optimized reaction conditions. For this purpose, after the first run of the epoxidation reaction, the used catalyst was filtered, washed with ethanol, and then employed for the next epoxidation reaction. In the recycling study, the epoxidation conditions were the same as that in the first run. It was observed that conversion with cyclohexene decreased slightly after the second run (Fig. 8). The above procedure was repeated for another two cycles. It was determined that the cyclohexene conversions were 100, 99.35, 98.84, and 97.75 % over 8 h in the first, second, third, and fourth cycle, respectively. We did not observe any substantial loss in the catalytic activity of the immobilized catalyst. The results indicate that the Mo^{VI} Schiff base complex is strongly bonded to organic-inorganic silica matrix. In addition, in order to understand the change of catalyst Mo-SB-Cl-SiO2 in the cycle test, FT-IR (Fig. S1, Supplementary Material), XRD (Fig. S2, Supplementary Material), and CHN measurements were performed during the recycling experiments. There were no obvious changes in the FT-IR spectra and XRD patterns of the fresh and recycled catalyst, indicating the unchanged structure of Mo-SB-Cl-SiO₂ in the epoxidation reaction. Accordingly, the prepared Mo-SB-Cl-SiO₂ hybrid could act as a stable heterogeneous catalyst for epoxidation reaction.

In order to further confirm the stability of Mo-SB-Cl-SiO₂, we carried out comparative epoxidation reactions to evaluate the effect of possible leaching of the metal complex from the immobilized catalyst into the reaction medium and the results are shown in Fig. 9. After 2 h of reaction, the organic phase and the solid phase were separated. The epoxidation reaction was afterwards performed at 80°C in the organic phase for another 8 h with the same amount of reagents. In this case, there was nearly no generation of epoxide. Moreover, the ICP-AES analysis result showed a negligible molybdenum loss of 0.14 mol.-% for Mo-SB-Cl-SiO₂.



Fig. 9. The plot of time against conversion for the epoxidation of cyclohexene. Reaction conditions: cyclohexene (2.5 mmol), 1,2-DCE (10 mL), *n*-octane (1.25 mmol), catalyst (25 mg), and temperature 80° C. Determined by GC-MS, the product is cyclohexene epoxide, and the by-products are 2-cyclohexene-1-ol, 1,2-cyclohexenediol, and 2-cyclohexene-1-one.

Conclusion

In conclusion, the Mo-SB-Cl-SiO₂ was prepared by a cocondensation assisted method, and exhibited an enhanced catalytic epoxidation activity that can compare with a homogeneous counterpart. Mo-SB-Cl-SiO₂ displayed a 2D-hexagonal mesoporous framework. In comparison with Mo-SB-Cl-SBA-15 prepared by a post-grafting assisted method, the Mo-SB-Cl-SiO₂ showed a higher catalytic activity towards epoxidation reactions, mostly due to the higher density of Mo^{VI} active sites. Among the experiments on the effects of different substrates, Mo-SB-Cl-SiO₂ showed an increasing activity in the order: cyclooctene > cyclohexene > cyclopentene > 1-pentene > 1-hexene > 1-octene, which was determined by both electronic effects and steric effects. The Mo-SB-Cl-SiO2 was a highly stable catalyst in the epoxidation of olefins. This work potentially provides an insight into a novel strategy for preparing organicinorganic epoxidation catalyst with enhanced activity.

Supplementary Material

The preparation process of SBA-15, $MoO_2(acac)_2$, *p*-salicylidine aminobenzoic acid, and Mo-SB as well as the Fourier transform infrared spectrum and small-angle XRD pattern of the catalyst before and after reusing are available on the Journal's website.

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