Synthesis of novel immobilized tridentate Schiff base dioxomolybdenum(VI) complexes as efficient and reusable catalysts for epoxidation of unfunctionalized olefins

Yuedong Li, Xiangkai Fu*, Biwei Gong, Xiaochuan Zou, Xiaobo Tu, Junxian Chen

College of Chemistry and Chemical Engineering, Research Institute of Applied Chemistry Southwest University, The Key Laboratory of Applied Chemistry of Chongqing Municipality, Key Laboratory of Eco-environments in Three Gorges Reservoir Region (Ministry of Education), Chongqing 400715, PR China

ABSTRACT

A series of tridentate Schiff base dioxomolybdenum(VI) complexes have been immobilized onto modified synergistic organic–inorganic hybrid support chloromethyl-ZPS-PVPA [zirconium poly (styrene-phenylvinylphosphonate)-phosphate] to prepare a new type of heterogeneous catalyst. The as-synthesized catalysts exhibited good to excellent catalytic efficiency in epoxidation of unfunctionalized olefins, using *tert*-butyl hydroperoxide (TBHP) as oxidant. Surprisingly, up to 99% ee values were obtained when α-methylstyrene was chosen as substrate in this oxidant system with these heterogeneous catalysts. Furthermore, the immobilized catalyst showed a stable catalytic activity in manifold reuses.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic epoxidation of alkenes is a powerful strategy for the synthesis of various chiral intermediates in the pharmaceutical as well as in the agrochemical industries, and various methods have been employed to fulfill this particular reaction. While the Schiff base dioxomolybdenum(VI) catalysts are the most promising candidates for the epoxidation of unfunctionalized olefins by organic hydroperoxides [1]. TBHP is environment-friendly, and the by-product of the reaction, *tert*-butyl alcohol, can be conveniently separated and recycled or used in other industrial processes [1,2]. Besides, the nature of the hydroperoxide also has an effect on the enantiomeric excess of asymmetric epoxidation [3]. Hence, these unique properties of TBHP can be exploited in organocatalyzed epoxidation of olefins as oxygen source.

During the past several decades, many classic transition metal complexes with Schiff base ligands have been employed in homogeneous catalysis [4–6]. These catalysts usually display higher activities for the catalytic reactions. However, the separation and recycling of the expensive catalysts, as well as leaching of the active metal into the solvent and the insufficient stability of the catalysts are still problematic in homogeneous phase. Another disadvantage

in homogeneous system is that the formation of μ-oxo dimmers and other polymeric species will lead to irreversible catalyst deactivation [7].

Compared with the homogeneous catalysts, the heterogeneous catalysts have the inherent advantages, including convenient separation of catalysts from reaction mixture and facility of purifying products. Thus, in recent years, many groups have devoted to utilizing solid support in the heterogenization of some transition metal catalysts in an attempt to tailor-made catalysts for desired performance. They have immobilized the homogeneous catalysts onto inorganic solids [8–12] and organic polymers [13–16]. However, the heterogeneous catalysts generally lead to partial loss of activity, only few of them exhibit higher catalytic activity than their corresponding homogeneous counterparts [17,18].

In comparison with the vast number of inorganic materials and organic polymers which are employed so far for the immobilization of homogeneous catalysts, the organic–inorganic hybrid materials as very promising support hold unique position. They have both the advantages of organic materials such as light weight, flexibility, and inorganic materials such as high strength, heat stability and chemical resistance [19]. This finding will provide precious knowledge about synthesis of organic–inorganic hybrid materials, especially for inorganics that do not have active groups on their surface [20,21]. Synergistic organic–inorganic hybrid material combining of zirconium phosphate and polystyrene was rarely

---

reported. If combined, modified or modulated with each other, they could learn from other's strong points to offset one's weakness and mutual support of relative advantages, which could get a new type of organic–inorganic hybrid material with special new characteristic and brand-new use. Organic–inorganic hybrid material as support and a series of heterogeneous catalysts have been explored in our group [22–29]. In previous work, we have reported the chiral salen Mn (III) complex axially immobilized onto diamine- or polyamine-modified ZPS-PVPA and their use in catalytic epoxidation [26]. Especially, the conversion and enantiometric excess could exceed 99% in the epoxidation of α-methylstyrene. The chiral salen Mn (III) complex axially immobilized onto phenoxyl-modified ZSP-PVPA was also reported, and showed comparable or even higher conversions and enantioselectivities than the relevant literature in the asymmetric epoxidation of unfunctionalized olefins [29]. It is worth mentioning that the heterogeneous catalysts afforded remarkable increases of conversion and ee values in the absence of expensive O-coordinating axial bases for the asymmetric epoxidation of α-methylstyrene for the first time, which may overcome the last obstacle for wide application in organic synthesis as well as in industry of chiral Jacobsen's catalyst.

Taking into account aforementioned factors, our continuing interest in the field of the support led us to regard the organic–inorganic hybrid material as a potential tool. We herein report the preparation, characterization, and investigation of catalytic activities of the immobilized tridentate Schiff base dioxomolybdenum(VI) complexes as heterogeneous catalysts in the epoxidation of olefins. The effect of various oxidants, solvent nature and reaction temperature on the activity and selectivity were also studied. Recycling experiments further demonstrated that efficient catalysts were highly reusable without noticeable loss of activity even after repeated use for ten times in the epoxidation reactions.

2. Experimental

2.1. Materials

Cyclooctene, styrene, α-methylstyrene and n-nonane were purchased by Alfa Aesar. $MoO_2(acac)_2$ was prepared according to the literature method [30]. Other commercially available chemicals were laboratory-grade reagents from local suppliers.

2.2. Physical measurements

FT-IR spectra were recorded from KBr pellets using a Bruker RFS100/S spectrophotometer (USA), and diffuse reflectance UV–vis spectra of the solid samples were recorded in the spectrophotometer with an integrating sphere using $BaSO_4$ as standard. The Mo content of the catalyst was determined by a TAS-986G (Pgeneral, China) atomic absorption spectroscopy. X-ray photoelectron spectroscopy (XPS) was performed on a KRTO-SXSAM800 spectrometer. TG analyses were performed on a SBTQ600 Thermal Analyzer (USA) with the heating rate of $20\,°C\,min^{-1}$ from 25 to $1000\,°C$ under flowing N_2 ($100\,ml\,min^{-1}$). SEM were performed on KYKY-EM 3200 (KYKY, China) microscopy. TEM were obtained on a TEC-NAI10 (PHILIPS, Holand) apparatus. Nitrogen adsorption isotherms were measured at 77 K on a 3H-2000I (Huihaihong, China) volumetric adsorption analyzer with BET method. The conversions (with n-nonane as internal standard) and the ee values were analyzed by gas chromatography (GC) with a Shimadzu GC2010 (Japan) instrument equipped using a chiral column (HP19 091G-B213, 30 m × 30 m × 0.32 mm × 0.25 μm) and FID detector, injector 230 °C, detector 230 °C.

2.3. Synthesis of diaminomethyl-zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZAMPS-PVPA)

The synthesis and characterization of ZPS-PVPA and ZCMPS-PVPA have been reported earlier [26] (Scheme 1). To a suspension of ZCMPS-PVPA (5.0 g) that had been pre-swelled in toluene (10 ml) for 30 min was added proper amount of 1,2-diaminocyclohexane or 1,2-diaminobenzene (the molar ratio of amines to chlorine element in ZCMPS-PVPA is 10:1), and the mixture was kept at 80 °C for 12 h. After the reaction, the product was filtered, washed with ethanol to remove superfluous amine, then dried in vacuo to yield 5.6 g of the product as yellow solid. The products were abbreviated as 1a, 1b in turn.

2.4. Synthesis of the immobilized Schiff base ligands

A series of the immobilized Schiff base ligands were synthesized according to the standard method [31–36] with minor modifications (Scheme 2). In a typical procedure, a mixture of ZAMPS-PVPA (1.0 g) in absolute ethanol (20 ml) was added activated silica gel and the substituted aldehydes or ketones (2 mmol, benzoin, salicylaldehyde, acetylacetone, 3,5-di-tert-butyl-2-hydroxy-benzaldehyde). The mixture was refluxed for 20 h under dry argon atmosphere to afford the immobilized Schiff base ligands, and abbreviated as 2a–2h in turn. These solids were filtered, washed with ethanol to remove superfluous aldehydes or ketones and dried in vacuo to yield 1.1 g of the product.

2.5. Synthesis of the immobilized Schiff base molybdenum catalysts 3a–3h

All the immobilized Schiff base dioxomolybdenum(VI) complexes were synthesized using a ligand exchange procedure (Scheme 2). A solution of $MoO_2(acac)_2$ (0.30 g) in absolute ethanol (30 ml) was added the immobilized Schiff base ligand (0.60 g) and heated at 60 °C for 24 h [33–36]. The immobilized molybdenum catalyst was separated by filtration, and soxhlet extracted with a mixture of dichloromethane and ethanol (1:1) to remove the unreacted $MoO_2(acac)_2$, then dried in vacuo at 80 °C.

2.6. Procedure for catalytic epoxidation

In a typical reaction [33,36], to a mixture of catalyst (2.0 mmol%, the amount was calculated via the active centers of metal), n-nonane (1.0 mmol) as an internal standard and olefin (1.0 mmol) in 1,2-dichloroethane (3.0 ml) was added TBHP (0.30 ml, 2.0 mmol, 75% in di-tertiary butyl peroxide) under stirring. The mixture was kept at 75 °C for the appropriate time. The catalyst was precipitated from the reaction mixture by adding the equal volume of hexane, then the organic phase was separated and purified on a silica-gel plates or a silica-gel column, and then analyzed by GC to determine the reactant conversion and the product selectivity. Blank experiment in the presence of oxidant and in the absence of catalyst was also performed under the same experimental conditions.

3. Results and discussion

3.1. Preparation of the catalyst

The first step is a substitution reaction of ZCMPS-PVPA chloro groups with excess of 1,2-diaminocyclohexane or 1,2-diaminobenzene to produce substituted monoamine (ZAMPS-PVPA). Correspondingly, the sharp C–Cl peak at $706\,cm^{-1}$ in the ZAMPS-PVPA practically disappeared or was seen as a weak band after introduction of amines. The reaction solution was added activated silica gel in the second step, which could remove yielding
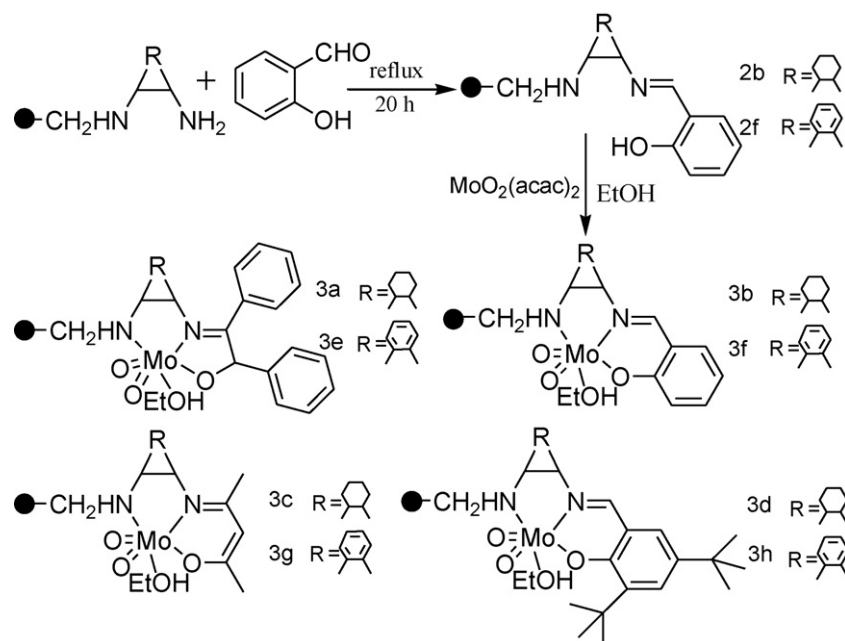
Scheme 1. Synthesis of the support.
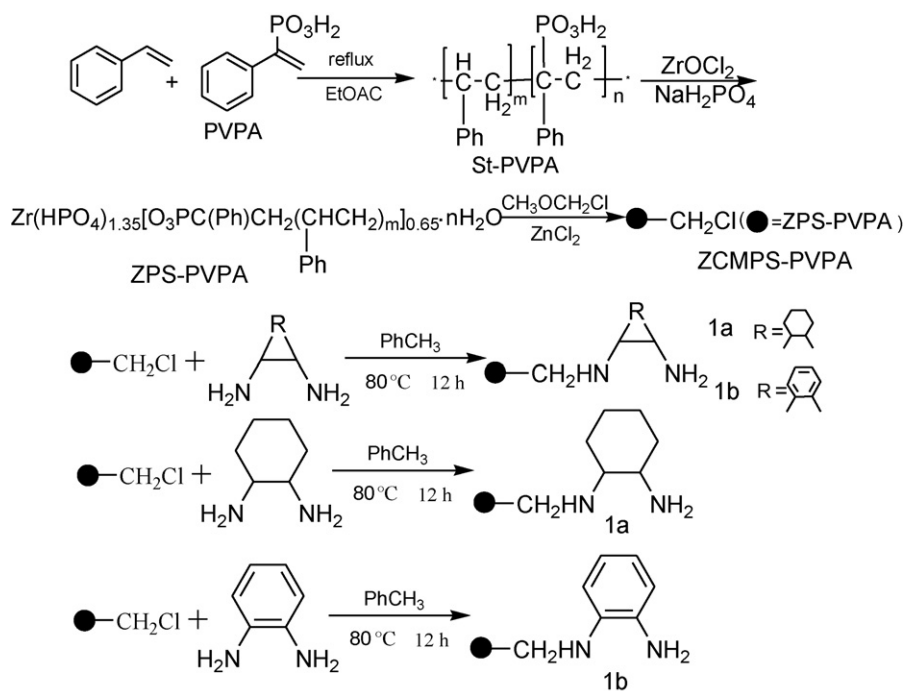
water during the reaction process. Finally, the coordination reaction of Schiff base ligands with excess of $MoO_2(acac)_2$ to afford the immobilized dioxomolybdenum(VI) catalysts. To reduce or eliminate any negative effects caused by $MoO_2(acac)_2$, soxhlet extraction of the product was carried out to remove superfluous $MoO_2(acac)_2$ from the catalysts.

3.2. Characterizations of the immobilized molybdenum catalysts

3.2.1. Spectral analysis

As shown in Fig. 1, the main characteristic bands in the IR spectra of the heterogeneous catalysts (3b and 3c) were similar

to the immobilized Schiff base ligands. Comparing the IR spectra of the ZAMPS-PVPA (1a) with the immobilized ligands (2b and 2c), it is found that the IR bond of the immobilized Schiff base ligands at $1628\,cm^{-1}$ can be assigned to the characteristic stretching vibration of C=N imine bond. In addition, all Mo(VI) complexes show a characteristic IR absorption in the ranges of $930–940\,cm^{-1}$ (ν_s) and $910–895\,cm^{-1}$ (ν_{as}), which were assigned to the cis-MoO_2 fragment. Solvated complexes of the general formula $[MoO_2(L)(ML)]$ have very similar IR spectral data. The differences occur in the bands of the coordinated solvents [37]. Therefore, the spectra of $[MoO_2(L)(EtOH)]$ shows a broad band in the range of $3400–3200\,cm^{-1}$ which is due to the $\nu(O–H)$ stretch, and they also

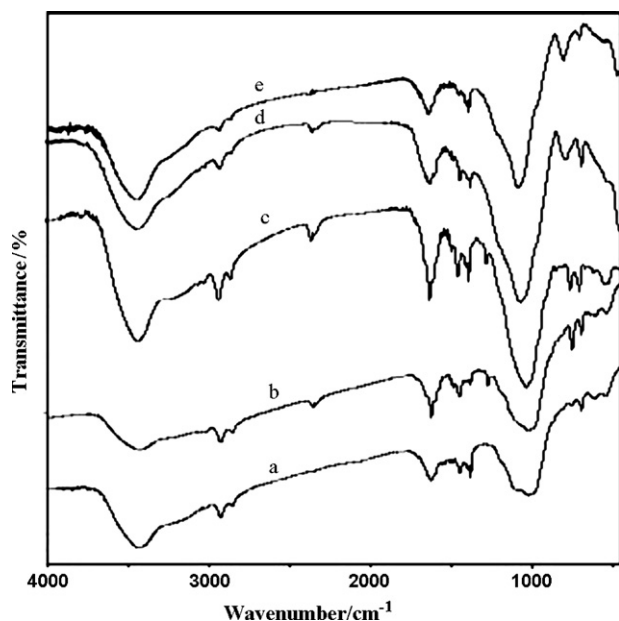**Scheme 2.** Synthetic route of the immobilized Schiff base dioxomolybdenum(VI) catalysts.

Fig. 1. FT-IR spectra of (a) 1a; (b) 2b; (c) 3b; (d) 2c; (e) 3c.

show a similar band 1030 cm^{-1} which corresponds to the ν(C–O) stretch of alcohol. The range of 1600–1500 cm^{-1} corresponds to the ν(C=C) and ν(C=N) stretch of aromatic rings. The ν(C$_{ar}$–O) is at 1550 cm^{-1} and for ligand L it is at 1500 cm^{-1}, which suggests the coordination of deprotonated phenoxy group of the ligand. It can be clearly concluded that MoO$_2$(acac)$_2$ is successfully coordinated with the Schiff base ligands to afford the immobilized tridentate Schiff base molybdenum complexes.

Diffuse reflectance UV–vis spectra (Fig. 2) also gave obvious evidence for the successful coordination. The ZAPS-PVPA (a) and the Schiff base ligand (b) presented only the bond of phenyl and C=N imine groups of 200–400 nm in UV–vis spectra. All the characteristic bands appeared in their spectra but the coordinated catalyst (c) exhibited a blue shift from MoO$_2$(acac)$_2$ (d) 253, 366 and 500 nm to 253, 328 and 400 nm, which indicated that an interaction existed between MoO$_2$(acac)$_2$ and the Schiff base ligands [25,26,28].
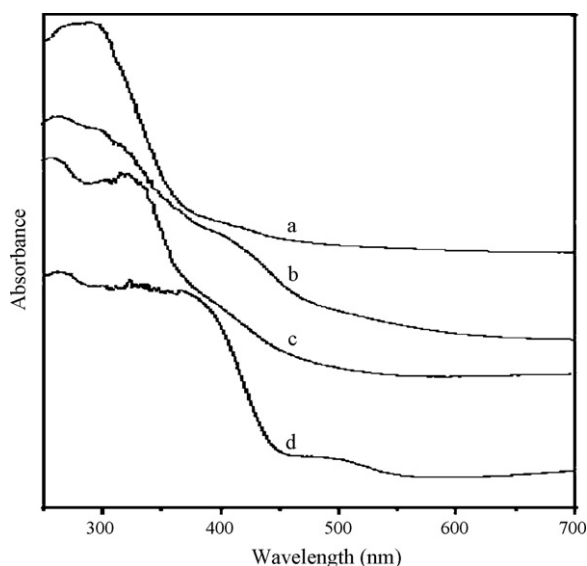

Fig. 2. UV–vis spectra of (a) 1a, (b) 2b, (c) 3b and (d) MoO$_2$(acac)$_2$.
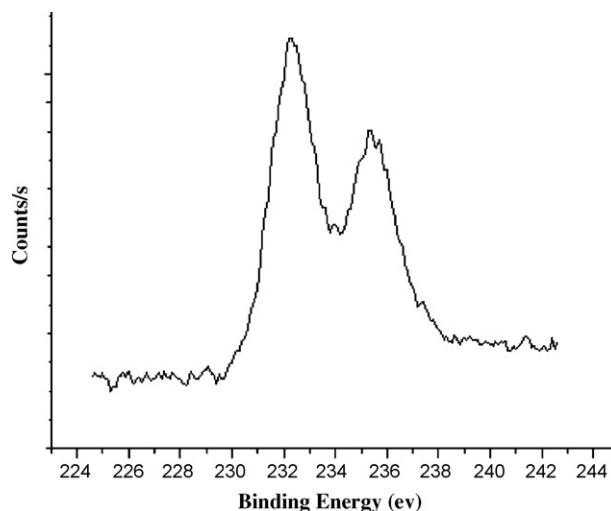

Fig. 3. XPS spectrum of catalyst 3b.

3.2.2. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful technique to investigate the electronic properties of the species formed on the surface. Fig. 3 showed the Mo 3d XPS spectra of MoO$_2$(acac)$_2$ coordinated on the immobilized Schiff base ligands. The major peaks around 232.1 and 235.3 eV were attributed to Mo 3d$_{5/2}$ and Mo 3d$_{3/2}$, respectively, which indicated Mo atoms with an oxidation state of 6+ for the catalyst 3b [38].

3.2.3. Nitrogen sorption studies and Mo content of the immobilized molybdenum catalysts

The specific surface area of the materials and Mo content of the immobilized molybdenum catalysts were shown in Table 1. The amount of the immobilized molybdenum catalysts based on the Mo element for 3b, 3c, 3f and 3g calculated by atomic absorption spectroscopy were 0.36–0.48 mmol/g. It is well known that the introduction of homogeneous catalysts or metal complexes onto supports leads to a decrease in the specific surface area of the supporting material [25,26]. Compared with ZAMPS-PVPA (1a, 1b), the immobilized Schiff base molybdenum catalysts exhibited decreased BET surface area. It can be clearly concluded that MoO$_2$(acac)$_2$ was successfully located on the Schiff base ligands surface.

3.2.4. Analysis of surface morphology

Scanning electron micrograph (SEM) was recorded to understand morphology of the surface of the support and catalyst. The SEM of the heterogeneous catalyst 3b is shown in Fig. 4(a), which indicated that the diameter of the particles of the heterogeneous catalyst 3b was in submicron. Also, it showed that the catalyst was loose, and had various caves, holes and porous. The TEM photograph of the catalyst 3b was shown in Fig. 4(b). Actually, many

Table 1
Nitrogen sorption studies and Mo content of the immobilized molybdenum catalysts.

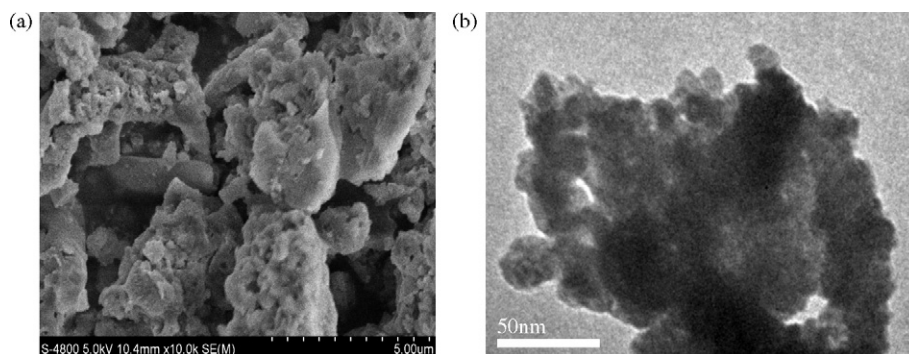| Supports and the immobilized Schiff base catalysts	BET surface area (m^2/g)	Content of Mo (mmol/g)
ZPS-PVPA	186	–
1a	92	–
1b	105	–
3b	79	0.36
3c	83	0.43
3f	98	0.40
3g	91	0.48

(a) (b)

Fig. 4. (a) SEM photograph of the catalyst 3b and (b) TEM photograph of the catalyst 3b.

holes and cavums were showed in gray and black, respectively. And many channels could be discerned clearly, which showed blank in Fig. 4(b). These micropores and secondary channels will increase the surface area of the catalysts and provide enough space for substrates to access to the catalytic active sites [25,26,28,29]. The catalyst was an aggregation of many small particles to some extent. Generally, one of the advantages of the layered zirconium phosphate is that all the organic groups are located on the surfaces, interlamellar regions and interlayer surfaces no matter whether they are crystalline semi-crystalline or amorphous, which results from their self-assembled layered structure on the nanometer scale [39].

3.2.5. Thermal analysis

The behavior of 3b's thermo-stability over a broad temperature range of 25–1000 °C was shown in Fig. 5. The initial 12.94% weight loss was observed from 20 to 150 °C, corresponding to the loss of crystallization water weakly bound to the material. Due to the fragmentation of the appended organic groups, the second peak with weight loss 41.25% in the temperature range of 150–650 °C is followed by decomposition of the immobilized Schiff base dioxomolybdenum complex. In the temperature range of 650–1000 °C the losses were attributed to the dehydrolysis of $Zr(HPO_4)_2$ to ZrP_2O_7. These indicate that the catalyst is thermally stable up to 150 °C [23,24,27].

3.3. Catalytic epoxidation

Under optimized conditions, the catalytic activities of the catalysts were explored for the epoxidation of different substrates
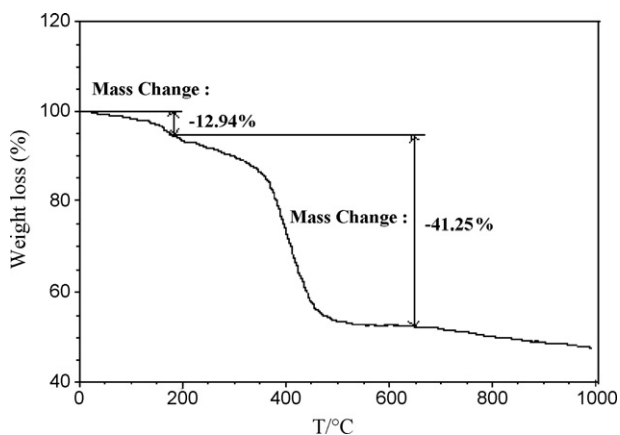

Fig. 5. TG curves for catalyst 3b.

using TBHP as the oxidant. It is worth pointing out that all catalytic reactions proceeded smoothly with good to excellent results (Table 2).

On the basis of reported epoxidation mechanism earlier [33,35,40,41], higher electron donating ability of olefin double bond is expected to promote the reaction rate. The order of increasing reactivities are as cyclooctene > α-methylstyrene > styrene. Electronic and steric effects should be taken into consideration to explain the trend. Therefore, more electron-rich cyclic olefin cyclooctene has more activities than the conjugated α-methylstyrene and styrene due to the presence of more electrons donating $(CH_2)_6$ cyclic bridges connected to the double bond. Especially, cyclooctene can be almost quantitatively converted into the corresponding epoxides. A similar increase in yield for cyclooctene was also reported for the Schiff base molybdenum complexes immobilized on MCM-41 [33]. As the same reason, compared with styrene, α-methylstyrene has the same change tendency with cyclooctene. The results demonstrated that catalyst structures and olefins should be taken into consideration, which affected the catalytic activity. The heterogeneous catalysts showed good catalytic activity for aromatic alkenes, like α-methylstyrene (Conv%: 90%; Sele%: 75%). These positive data suggested that the substrates have easily access to the immobilized active sites on the ZPS-PVPA, and that the active sites retaining structures that are similar to that of the free catalyst $MoO_2(acac)_2$. Interestingly, α-methylstyrene was epoxidized with TBHP as an oxidant in blank experiment, which exhibited excellent enantioselectivities up to 99%. Asymmetric epoxidation of olefins by using a combination of achiral metal complex and chiral ligand was reported [42–44]. Chiral epoxides were obtained for α-methylstyrene, though the heterogeneous catalysts are achiral. One possible explanation is that the TBHP as an oxidant also plays the role of chiral inducement in the epoxidation of α-methylstyrene in 1,2-dichloroethane, meanwhile, these catalysts can only effectively promote the process of catalytic reactions [45]. The observed novel catalytic behavior is currently in progress.

The higher activity for the epoxidation of olefins obtained in the catalytic reactor system can be attributed to the three beneficial effects of support ZAPS-PVPA: (i) the well-ordered and unconstrained pore and cavities structure of the surface makes all active catalyst sites easily available to the reactant; (ii) short catalyst contact time allows more turnovers while retaining high selectivity and minimizing over-oxidation [25–29,46]; (iii) the microenvironment effects originating from polystyrene parts which are hydrophobic and the hybrid zirconium phosphate-phosphonate parts which are hydrophilic and having self-assembled layered structure with nanometer scale were responsible for the results obtained in the epoxidation of olefins. Numbers of active sites of the catalysts would be favorable to create ideal microenvironment with adequate flexibility and rigidity for the contact of catalytic active

Table 2
The epoxidation of cyclooctene, styrene and α-methylstyrene catalyzed by the immobilized Schiff base Mo(VI) catalysts (3a–3h) with *tert*-BuOOH as oxidant systems[a].

Entry	Substrate[b]	Catalyst	Time (h)	Conversion (%)	Selectivity (%)	Ee[c] (%)	TOF[d] × 10^{-4} (s^{-1})
1	A	3a	8	100	97	–	16.8
2		3b	8	100	99	–	17.2
3		3c	8	100	>99	–	17.4
4		3d	8	100	>99	–	17.4
5		3e	8	95	97	–	16.0
6		3f	8	98	96	–	16.3
7		3g	8	98	97	–	16.5
8		3h	8	98	97	–	16.5
9	B[e]	3a	12	46	38	–	2.02
10		3b	12	57	50	–	3.30
11		3c	12	60	50	–	3.47
12		3d	12	62	33	–	2.37
13		3e	12	21	63	–	1.53
14		3f	12	47	54	–	2.94
15		3g	12	47	47	–	2.56
16		3h	12	50	55	–	3.18
17	C[e]	3a	12	78	56	>99	5.06
18		3b	12	90	60	>99	6.25
19		3c	12	90	62	>99	6.46
20		3d	12	92	67	>99	7.13
21		3e	12	43	64	>99	3.19
22		3f	12	45	69	>99	3.59
23		3g	12	59	72	99	4.92
24		3h	12	71	75	99	6.16
25[f]	A	–	8	10	36	–	–
26[f]	B	–	12	9	26	–	–
27[f]	C	–	12	6	43	>97	–

[a] Reactions were performed in 1,2-dichloroethane (3 ml) with catalyst (2 mmol%), substrate (1 mmol), n-nonane (internal standard, 1 mmol), and TBHP (2 mmol) at 75 °C.
[b] A = cyclooctene, B = styrene, C = α-methylstyrene.
[c] (S)-form [45].
[d] Turnover frequency (TOF) = [mol of product]/[mol of catalyst] × time (s^{-1}).
[e] Selectivity toward the formation of epoxide [45].
[f] Reaction was carried out without catalyst.

centers and reactants [25,29,47].

The catalysts prepared from 1,2-diaminocyclohexane ligands represented higher activities than the catalysts from 1,2-diaminobenzene ligands (3a–3d vs 3e–3h). The order can be explained with consideration of the following three factors. Firstly, the amino groups in catalysts 3e–3h possess conjugated lone pair electrons which are connected with a benzene ring while the amino groups in catalysts 3a–3d possess free lone pair electrons which are connected with a six-member cycloalkyl ring. Secondly, the complexation trend is enhanced by increasing the π-accepting character of the tridentate Schiff base ligands. Thus, the higher π-accepting character of 1,2-diaminobenzene ligands in 3e–3h explains the decreased activity [36]. In addition, the higher π-accepting character of the tridentate Schiff base ligands deriving from functionalized aldehydes or ketones can enhance the competitive coordination of *tert*-BuOH (instead of TBHP) to the metal center and make the catalyst be less reactive [33]. At last, the rigidity of 1,2-diaminobenzene ligands in 3e–3h also affect their activities and selectivities. Thus, the catalysts prepared from 1,2-diaminobenzene ligands showed higher selectivities than the catalysts from 1,2-diaminocyclohexane ligands (3e–3h vs 3a–3d) for the epoxidation of α-methylstyrene and styrene.

3.4. The recycling of the immobilized the Schiff base dioxomolybdenum catalyst

To assess the long-term stability and reusability of the heterogeneous catalysts and the leaching of Mo from the immobilized catalysts during the epoxidation of olefins, cyclooctene was used as a mode substrate. Recycling experiments were carried out with the catalyst 3d. In a typical recycle experiment, the catalyst was precipitated from the solution by adding the equal volume of hexane after each experiment. Then the organic phase was separated, and the catalyst was washed with hexane to remove *tert*-BuOH, and dried in vacuo at 80 °C. The recovered catalyst was weighed and reused in the next run. In every run the same ratio of the substrate-to-catalyst and solvent-to-catalyst was kept.

The data in Table 3 showed only a slightly decrease in activity and selectivity for the first six runs. The filtrate showed no trace of the metal complex on leaching of Mo by AAS after the first run, which indicated that the $MoO_2(acac)_2$ was strongly coordinated with the immobilized Schiff base ligands. Further recycles of the heterogeneous catalyst resulted in the continuously decrease of conversion and selectivity for the second six runs (Conv%: from

Table 3
The recycles of catalyst 3d in the epoxidation of cyclooctene[a].

Run	Time	Conversion (%)	Selectivity (%)[b]	TOF[c] × 10^{-3} (s^{-1})
1	8	100	>99	1.74
2	8	99	>99	1.72
3	8	99	>99	1.72
4	8	98	>98	1.68
5	8	99	>98	1.70
6	8	98	97	1.65
7	8	98	97	1.65
8	8	96	95	1.58
9	8	95	95	1.57
10	8	95	92	1.52
11	8	93	90	1.45
12	8	92	89	1.42

[a] The reaction conditions are the same as in Table 2 entries 1–8.
[b] Selectivity toward the formation of epoxide.
[c] Same as in Table 2.

Table 4

The results of the epoxidation of cyclooctene catalyzed by the catalyst 3b in different solvents[a].

Solvent	Time	Conversion (%)	Selectivity (%)[b]	TOF[c] $\times 10^{-3}$ (s^{-1})
Toluene	8	80	99	1.38
n-Hexane	8	96	99	1.65
1,2-Dichloroethane	8	100	99	1.72
Ethyl acetate	8	40	96	0.67
Ethanol	8	62	96	1.03
Acetonitrile	8	68	97	1.15

[a] The reaction conditions are the same as in Table 2 entries 1–8, and n-hexane at 68 °C.

[b] Same as in Table 3.

[c] Same as in Table 3.

Table 5

The results of the epoxidation of cyclooctene catalyzed by the catalyst 3b in different oxidants[a].

Solvent[b]	Oxidant	Time (h)	Conversion (%)	Selectivity (%)[c]
1,2-DCE	–	8	–	–
	UHP	8	–	–
	H_2O_2	8	53	96
	TBHP	8	100	99
CH$_3$CN/H$_2$O	H_2O_2	8	12	96
	NaIO$_4$	8	8	95
1,2-DCE/H$_2$O	NaIO$_4$[d]	8	–	–
	KHSO$_5$[d]	8	–	–

[a] The reaction conditions are the same as in Table 2 entries 1–8.

[b] A 3:1 mixture of organic solvent:water was used.

[c] Same as in Table 3.

[d] Tetrabutylammonium bromide (0.01 g) was used.

98% to 92%; Sele%: from 97% to 89%). The decrease in the activity for more cycles might be caused by a physical loss during the recovery process and/or by a gradual degradation of catalysts under the epoxidation condition. In addition, because the micropores and secondary channels were partly plugged after several recycle epoxidation, it can induce the decrease of the conversion [25,26,28,29].

3.5. Effect of solvent

To gain a better understanding of this unique catalytic system, the catalyst 3b was selected as the typical catalyst to investigate the effects of various solvents on the conversion and selectivity epoxidation of cyclooctene (Table 4). The difference among these solvents is that the catalyst 3b is more readily dissolvable in 1,2-dichloroethane than polar solvent. In particular, only 62% conversion was obtained in ethanol. This possibly indicated that the solvent containing oxygen atoms with a lone electron pair can induce coordination with the metal center of the Schiff base dioxomolybdenum(VI) catalysts [33,48] or the formation of μ-oxo dimers and other polymeric species which lead to irreversible catalyst deactivation [7]. Therefore, 1,2-dichloroethane was chosen as reaction media for the epoxidation of cyclooctene.

3.6. Effect of reaction temperature

When the reaction temperature droped below 50 °C, it showed a very low conversion. However, a significant growth in the product yield is observed at a higher temperature. An increase in the reaction temperature from 55 to 80 °C leads to the increase of the epoxide conversion from 35% to 98%. However, an increase in temperature causes additional thermal TBHP decomposition and consequently leads to lower selectivity to epoxide formation. These might have been the result of epoxide ring opening reactions induced by TBHP present in reaction [33]. Hence, 75 °C was chosen as reaction temperature.

3.7. Effect of oxidant and time

The efficacy of the different oxidants like TBHP, H_2O_2, UHP, NaIO$_4$ and KHSO$_5$ in the oxidation of cyclooctene was also studied (as shown in Table 5). Comparatively, TBHP was the best oxidant in catalytic epoxidation reaction. The results indicated that other oxidants have poor ability to oxidize the cyclooctene, the amount of cyclooctene oxide after 8 h was only 7.6%. Also, no cyclooctene
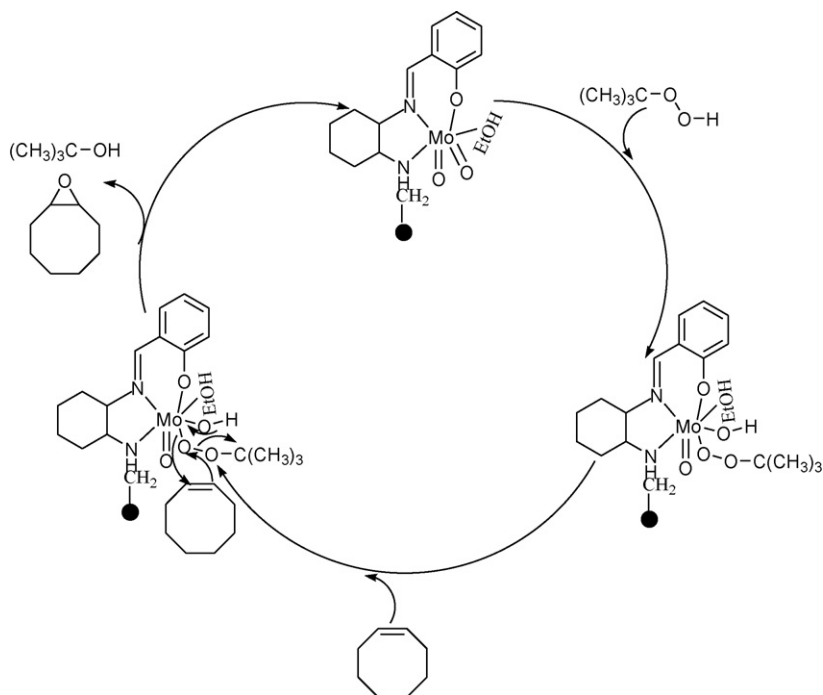
Scheme 3. Probable mechanism of epoxidation of cyclooctene with TBHP in presence of catalysts 3a–3h.

oxide was detected in the absence of oxidant in the reaction mixture. In the case of cyclooctene epoxidation with the Schiff base dioxomolybdenum(VI) catalysts, the increase of reaction time from 5 to 10 h led to an increase of epoxide yield while the TBHP conversion also increased in accordance with the epoxide formation [35]. However, selectivity toward the formation of epoxides has slightly decreased. These might have been the result of epoxide ring opening reactions induced by adding a further sustained reaction [33].

3.8. Probable mechanistic route for cyclooctene oxidation

Epoxidation of olefins using the immobilized Schiff base dioxomolybdenum(VI) catalysts gave their epoxides. On the basis of Sobczak's ideas [40], the experimental and theoretical studies [49–51] reported, a probable mechanism for the epoxidation of cyclooctene is presented in Scheme 3. The reaction rates displayed first order depending on catalyst and substrate concentrations. There are the crucial stages of the process. When epoxidation of some olefins in the presence of the heterogeneous catalyst, the catalytic cycle involves transferring of a TBHP proton to one of the terminal oxygen atoms of MoO_2 group and coordinating of t-BuOO$^-$ anion to the Lewis acidic molybdenum center to the olefin that lead to the formation of the peroxo oxygen bonded intermediate in the first step [33,36]. Therefore, reaction of an olefin as a nucleophile with oxygen as an electrophile easily explains the observation that electron-rich olefins react faster than electron-poor olefins. Then formation of epoxide and conversion of TBHP into t-BuOH, which remains in the coordination sphere restricts the reaction rate. They are in good agreement with the experimental results that ethanol is not advantageous for the epoxidation of olefins.

4. Conclusions

In summary, a series of tridentate Schiff base dioxomolybdenum(VI) complexes were successfully immobilized onto a promising organic–inorganic hybrid ZPS-PVPA via covalent bond. The prepared heterogeneous catalysts are found to be highly reactive in the epoxidation of unfunctionalized olefins. Moreover, these catalysts are of higher stability and reusability in the oxidation reactions and can be reused ten times without noticeable loss of activity. Excellent enantiomeric excess was obtained for the epoxidation of α-methylstyrene in this oxidant system, which do not involved any costly chiral ligand or additives, while the catalysts only effectively promote the process of catalytic reactions. The above mentioned principles and extensible designs, which will have the potential to open a new avenue and definitely exert a profound influence on the practical catalytic asymmetric epoxidation as well as in industry of achiral immobilized Schiff base dioxomolybdenum(VI) catalyst. Further studies on this approach are underway in our laboratory.

References

[1] K.A. Jorgensen, Chem. Rev. 89 (1989) 431–458.
[2] J.M. Brégeault, J. Chem. Soc., Dalton Trans. (2003) 3289–3302.
[3] S.S. Woodard, M.G. Finn, K.B. Sharpless, J. Am. Chem. Soc. 113 (1991) 106–113.
[4] R.H. Holm, J.M. Berg, Acc. Chem. Res. 19 (1986) 363–370.
[5] S.F. Gheller, B.E. Schultz, M.J. Scott, R.H. Holm, J. Am. Chem. Soc. 114 (1992) 6934–6935.
[6] R. Dinda, P. Sengupta, S. Ghosh, W.S. Sheldrick, Eur. J. Inorg. Chem. (2003) 363–369.
[7] X.L. Wang, G.D. Wu, J.P. Li, N. Zhao, W. Wei, Y.H. Sun, J. Mol. Catal. A: Chem. 276 (2007) 86–94.
[8] C. Baleizao, B. Gigante, H. Garcia, A. Corma, J. Catal. 215 (2003) 199–207.
[9] A.R. Silva, J. Vital, J.L. Figueiredo, C. Freire, B.D. Castro, New J. Chem. 27 (2003) 1511–1517.
[10] D.P. Serrano, J. Aguado, R.A. García, C. Vargas, Stud. Surf. Sci. Catal. 158 (2005) 1493–1500.
[11] H.D. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209–1211.
[12] R.I. Kureshy, I. Ahmad, N.H. Khan, S.H.R. Abdi, K. Pathak, R.V. Jasra, J. Catal. 238 (2006) 134–141.
[13] D.A. Annis, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 4147–4154.
[14] N.T.S. Phan, D.H. Brown, P. Styring, Tetrahedron Lett. 45 (2004) 7915–7919.
[15] Y.-S. Kim, G. In, C.-W. Han, J.-M. Choi, Microchem. J. 80 (2005) 151–157.
[16] B. Bahramian, V. Mirkhani, M. Moghadam, S. Tangestaninejad, Appl. Catal. A: Gen. 301 (2006) 169–175.
[17] Y. Song, X. Yao, H. Chen, G. Pan, X. Hu, Z. Zheng, J. Chem. Soc., Perkin Trans. 1 (2002) 870–873.
[18] B.M. Choudary, T. Ramani, H. Maheswaran, L. Prashant, K.V.S. Ranganath, K.V. Kumar, Adv. Synth. Catal. 348 (2006) 493–498.
[19] J. Gong, X.D. Li, B. Ding, D.R. Lee, H.Y. Kim, J. Appl. Polym. Sci. 89 (2003) 1573–1582.
[20] T. Shichi, K. Takagi, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 113–130.
[21] M. Czka, K. Cholewa-Kowalska, M. Kogut, J. Non-Cryst. Solids 287 (2001) 10–14.
[22] Y. Sui, X.K. Fu, X.B. Ma, J.R. Chen, R.Q. Zeng, React. Funct. Polym. 64 (2005) 55–62.
[23] R.F. Bai, X.K. Fu, H.B. Bao, W.S. Ren, Catal. Commun. 9 (2008) 1588–1594.
[24] Y. Sui, X.K. Fu, J.R. Chen, L.Y. Yin, Catal. Commun. 9 (2008) 2616–2619.
[25] W.S. Ren, X.K. Fu, H.B. Bao, R.F. Bai, P.P. Ding, B.L. Sui, Catal. Commun. 10 (2009) 788–793.
[26] B.W. Gong, X.K. Fu, J.X. Chen, Y.D. Li, X.C. Zou, X.B. Tu, P.P. Ding, L.P. Ma, J. Catal. 262 (2009) 9–17.
[27] H.S. Shen, X.K. Fu, H.B. Bao, J.X. Chen, B.W. Gong, Polym. Adv. Technol. 20 (2009) 77–83.
[28] W.S. Ren, X.K. Fu, J. Mol. Catal. A: Chem. 312 (2009) 40–47.
[29] X.C. Zou, X.K. Fu, Y.D. Li, X.B. Tu, S.D. Fu, Y.F. Luo, X.J. Wu, Adv. Synth. Catal. 352 (2010) 163–170.
[30] G.J. Chen, J.W.M. Donald, W.E. Newton, Inorg. Chem. 15 (1976) 2612–2615.
[31] J.H. Clark, D.J. Macquarrie, E.B. Mubofu, Green. Chem. 2 (2000) 53–56.
[32] C.D. Nunes, M. Pillinger, A.A. Valente, J. Rocha, A.D. Lopes, I.S. Gonçalves, Eur. J. Inorg. Chem. (2003) 3870–3877.
[33] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 248 (2006) 53–60.
[34] T. Luts, W. Suprun, D. Hofmannb, O. Klepel, H. Papp, J. Mol. Catal. A: Chem. 261 (2007) 16–23.
[35] T. Luts, R. Frank, W. Suprun, S. Fritzsche, E. Hey-Hawkins, H. Papp, J. Mol. Catal. A: Chem. 273 (2007) 250–258.
[36] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, Catal. Commun. 8 (2007) 6–10.
[37] Z.D. Tomić, A. Kapor, A. Žmirić, V.M. Leovac, D. Zobel, S.D. Zarić, Inorg. Chim. Acta 360 (2007) 2197–2206.
[38] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of XPS, Perkin Elmer Corporation, Eden Prairie, MN, 1992.
[39] X.J. Wu, X.B. Ma, Y.L. Ji, Q. Wang, X. Jia, X.K. Fu, J. Mol. Catal. A: Chem. 265 (2007) 316–322.
[40] J. Sobczak, J.J. Ziolkowski, J. Mol. Catal. A: Chem. 13 (1981) 11–42.
[41] Y. Sui, X.R. Zeng, X.N. Fang, X.K. Fu, Y.A. Xiao, L. Chen, M.H. Li, S. Cheng, J. Mol. Catal. A: Chem. 270 (2007) 61–67.
[42] T. Hashihayata, T. Ito, T. Katsuki, Tetrahedron 53 (1997) 9541–9552.
[43] B.M. Choudary, U. Pal, M.L. Kantam, K.V. Shiva Ranganath, B. Sreedharb, Adv. Synth. Catal. 348 (2006) 1038–1042.
[44] Y. Wang, Z.Q. Wu, Z.K. Li, X.-G. Zhou, Tetrahedron Lett. 50 (2009) 2509–2511.
[45] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801–2803.
[46] S.H. Cho, N.D. Walther, S.T. Nguyen, J.T. Hupp, Chem. Commun. (2005) 5331–5333.
[47] N.A. Caplan, F.E. Hancock, P.P.C. Bulman, G.J. Hutchings, Angew. Chem. Int. Ed. 43 (2004) 1685–1688.
[48] M. Minelli, J.H. Enemark, R.T.C. Brownlee, M.J. O'Connor, A.G. Wedd, Coord. Chem. Rev. 68 (1985) 169–278.
[49] C.D. Nunes, A.A. Valente, M. Pillinger, J. Rocha, I.S. Gonçalves, Chem. Eur. J. 9 (2003) 4380–4390.
[50] R.A. Sheldon, J.A.V. Doorn, J. Catal. 31 (1973) 427–437.
[51] S. Mukherjee, S. Samanta, B.C. Roy, A. Bhaumik, Appl. Catal. A: Gen. 301 (2006) 79–88.