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## Introduction

Olefin epoxidation has attained extensive consideration because the epoxide product is versatile and indispensable intermediate in the manufacture of both fine chemicals and pharmaceuticals.<sup>1-3</sup> During the past decade, considerable effort has been paid to develop inexpensive, recyclable, high active and selective metal-based catalysts to realize large-scale production.4-6 Despite homogenous transition metal complexes exhibit high catalytic activity and selectivity in the epoxidation reactions, many inherent drawbacks hamper their industrial application: (a) difficulty in the catalyst regeneration and product separation, (b) deactivation of the catalysts by formation of dimeric peroxo- and  $\mu$ -oxo species and (c) increasing the negative influence on environment and reducing industrial interest.<sup>7-9</sup> With the rapid development of catalyst separation and preparation technology, encapsulation various transition metal Schiff complexes on insoluble solid supports to realize

# Different transition metal (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> or VO<sup>2+</sup>) Schiff complexes immobilized onto threedimensional mesoporous silica KIT-6 for the epoxidation of styrene<sup>†</sup>

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Highly ordered three-dimensional *la3d* mesoporous silica KIT-6 was functionalized with 3aminopropyltriethoxysilane (3-APTES), following by post-grafting of various transition metal ( $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  or  $VO^{2+}$ ) Schiff complexes onto amino-functionalized KIT-6. The surface functionalized materials were analyzed by a series of characterization techniques such as XRD, X-ray photoelectron spectroscopy (XPS),  $N_2$  adsorption-desorption, IR spectroscopy, inductively coupled plasma (ICP), scanning electron microscopy (SEM), and thermal gravimetric analyses (TGA), *etc.* The characterization results demonstrated structural intact of the mesoporous hosts throughout the grafting procedures and successfully anchoring of transition metal Schiff complexes on the modified KIT-6. The obtained organic–inorganic hybrid materials were subsequently employed as catalysts for the epoxidation of styrene under optimized reaction conditions. It was indicated that Cu-NH<sub>2</sub>-KIT-6 showed very high substrate conversion (98.6%) and excellent epoxide selectivity (97.8%) when using *tert*-butyl hydroperoxide (TBHP) as the oxidant at 80 °C after 6 h. It was also observed that the catalyst could be recycled three times without obvious loss in catalytic activity and selectivity.

heterogenization of homogeneous catalysis has become a universal means to solve the above questions.

Periodically mesoporous silica materials, such as SBA-15,10,11 MCM-41,12 MCM-48 13 and hexagonal mesoporous silica (HMS),<sup>14</sup> have been widely used as catalyst support. Therein, the cubic phase MCM-48 with a highly branched and interpenetrating bicontinuous of network channels exhibits particular promise for advanced functionality. However, MCM-48 is fabricated under restrictive synthesis conditions because it is an intermediate during the transformation from a hexagonal phase to a lamellar phase. Additionally, the weak hydrothermal stability of MCM-48 in boiling water might induce structural collapse due to the rapid hydrolysis of the silica in the amorphous atomic scale of the network pores, which severely restricts its practical application.15,16 Recently, Kleitz et al. have synthesized a novel type of mesoporous silica with threedimensional cubic Ia3d symmetry called KIT-6.17 The material exhibits excellent textural parameters such as high surface area, large pore volume, high chemical stability for recyclability, tunable pore diameter simply by altering the aging temperature. The pore structure of KIT-6 is similar to that of MCM-48 but its pore diameter is much larger than the later.18 The unique structure of KIT-6 is superior to other solid support because its three-dimensional interpenetrating bicontinuous networks of chiral channel offer more active sites and resistance to



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agglomeration, thus allowing more reactant molecules and precursor solution diffusion through the pore channels.<sup>19</sup>

Various transition metal (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup> or VO<sup>2+</sup>) Schiff complexes modified ordered mesoporous silica have been reported as active heterogeneous catalyst for styrene epoxidation with TBHP as oxidant, which lead to a high conversion and epoxide selectivity because the catalysts possess both Lewis acid and weak oxidant.20 Koner et al. reported that copper(II) Schiff modified 2D-hexagonal phase MCM-41 material gave 97% conversion of styrene and 86% epoxide selectivity after 24 h with TBHP as oxidant.<sup>21</sup> Tang et al. reported metal (Co<sup>2+</sup>, Cu<sup>2+</sup> or Mn<sup>2+</sup>) Schiff modified mesoporous silica nanoparticles (MSN) with ca. 99% styrene conversion and over 63% epoxide selectivity after 24 h with TBHP as oxidant.<sup>22</sup> However, as far as we are aware, hitherto, no report on the covalent anchoring of transition metal ( $Fe^{2+}$ , Co2+, Ni2+, Cu2+ or VO2+) Schiff complexes on three dimensional mesoporous silica KIT-6 and the application in the epoxidation of styrene.

In the present work, we attempt to synthesize a novel recyclable heterogeneous catalyst Cu-NH<sub>2</sub>-KIT-6 by post-grafting method for the epoxidation of styrene. The influence of catalyst amount, molar ratios of oxidant to styrene, reaction temperature and time on catalytic performance has also been investigated. Compared with other congeneric transition metal (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> or VO<sup>2+</sup>) Schiff complexes grafted on KIT-6, the catalytic investigation clearly reveals that Cu-NH<sub>2</sub>-KIT-6 is a real efficient heterogeneous catalyst for the epoxidation of styrene.

## Experimental

#### Materials and methods

P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) (Aldrich), 3-aminopropyltriethoxysilane (3-APTES) (Aldrich), tetraethoxysilane (TEOS 99%), 1-butanol (99%), hydrochloric acid (HCl 37%), styrene (98%), salicylalde-hyde (99%), *tert*-butyl hydroperoxide (TBHP 70%), Cu(CH<sub>3</sub>COO)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, VOSO<sub>4</sub>, Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and all organic solvents are A.R. grade. Na/diphenylketone ketyl was used to dry toluene, and then the toluene is distilled under N<sub>2</sub> atmosphere.

Small angle powder XRD patterns were collected with a Riguku D/MAX2550 diffractometer with Cu-K $\alpha$  radiation ( $\lambda$  = 1.5418 Å) at 50 kV and 200 mA. The diffractions were recorded in the  $2\theta$  range of 0.6–5° and in steps of 2° min<sup>-1</sup>. The morphology of the samples was obtained with JEOS JSM 6700F filed-emission scanning electron microscope. The metal content of the catalysts was measured by inductively coupled plasma atomic emission analyses (Perkin-Elmer Optima 3300 DV). The infrared spectra of the materials were conducted on a Nicolet 6700 instrument in the range of 400–4000 cm<sup>-1</sup> using KBr pellet technique. The N2 adsorption-desorption isotherms were recorded at -196 °C on an adsorption analyzer (Micromeritics ASAP 2010). Prior to this measurement, each sample was degassed at 150 °C for 12 h. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) equation and pore size distribution was calculated using Barrett-JoynerHalenda (BJH) algorithm. Thermogravimetric analyses of the samples were performed on a Netzch Sta 449c thermal analyzer with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub> atmosphere. X-ray photoelectron spectroscopy (XPS) was measured on Scienta ESCA200 spectrometer using Al-K $\alpha$  radiation.

#### Preparation of the support

The synthesis of pure silica KIT-6 was using P123 as a structuredirecting agent and 1-butanol as a co-solvent under mild acidic conditions. The molar gel composition of the reaction mixture is TEOS : P123 : HCl : H<sub>2</sub>O : BuOH = 1 : 0.017 : 1.83 : 195 : 1.31.<sup>23</sup> In a typical synthesis, P123 (6 g) was dissolved in the mixture of distilled water (216 ml) and 37% HCl (9.8 ml). Stirring at 35 °C for 4 h to make the template completely dissolution and then 1butanol (6 g) was added at once with continuous stirring for another 1 h. Following TEOS (12.8 g) was dropped into the mixture was carried out in a closed polypropylene bottle and aged at 100 °C for 24 h under static hydrothermal condition. The obtained product was filtered without washing and dried at 60 °C for 12 h. Finally the resultant white powder was calcined at 550 °C for 6 h in a flowing air for surfactant removal.

#### Preparation of amino-functionalized KIT-6

Amino-functionalized KIT-6 was synthesis according to the following procedure described in our previous work.<sup>24,25</sup> 3-APTES (0.54 ml) was added to a suspension of KIT-6 (1 g) in dry toluene (30 ml) under N<sub>2</sub> atmosphere and refluxed at 110 °C for 12 h. Afterwards, the sample was filtered, washed with dry toluene and anhydrous ethanol for several times, and then dried under vacuum overnight. The resulting material was denoted as NH<sub>2</sub>-KIT-6.

#### Synthesis of heterogeneous catalyst Cu-NH<sub>2</sub>-KIT-6

Covalent attachment of copper( $\pi$ )–Schiff complex onto aminofunctionalized KIT-6 by a post-grafting method. NH<sub>2</sub>-KIT-6 (1 g) was refluxed with salicylaldehyde (2.3 mmol) in absolute methanol (30 ml) under N<sub>2</sub> atmosphere at 60 °C for 5 h. The resultant yellowish product was filtrated, washed with methanol and dried under vacuum. The sample was denoted as S-NH<sub>2</sub>-KIT-6. Finally, the Cu-NH<sub>2</sub>-KIT-6 was prepared by addition of Cu(CH<sub>3</sub>COO)<sub>2</sub> (1.15 mmol, 0.21 g) to the above yellowish solid in anhydrous methanol (30 ml) stirring at room temperature for 24 h. Then the mixture was filtered, washed repeatedly with water, ethanol and extracted with dichloromethane using a Soxhlet for 24 h. The product was dried under vacuum overnight (Scheme 1A). The content of Cu loaded onto KIT-6 was determined by ICP-AES which is 0.22 mmol g<sup>-1</sup>.

For comparison, Fe-NH<sub>2</sub>-KIT-6, Co-NH<sub>2</sub>-KIT-6, VO-NH<sub>2</sub>-KIT-6 and Ni-NH<sub>2</sub>-KIT-6 were also synthesized through a similar synthesized process with Cu-NH<sub>2</sub>-KIT-6. The metal content of the synthesized congeneric transition metal (Fe<sup>2+</sup>, Co<sup>2+</sup>, VO<sup>2+</sup>, Ni<sup>2+</sup>) Schiff complex onto KIT-6 is 0.12 mmol g<sup>-1</sup>, 0.14 mmol g<sup>-1</sup>, 0.21 mmol g<sup>-1</sup>, and 0.14 mmol g<sup>-1</sup>, respectively.



Scheme 1 (A) Preparation of heterogeneous catalyst Cu-NH<sub>2</sub>-KIT-6, and (B) Preparation of homogeneous catalyst Cu-Salen.

#### Synthesis of homogeneous Cu-Salen complex

The Cu-Salen complex was synthesized by the established procedure.26,27 An equimolar amount of 3-APTES (2.3 mmol) was mixed with salicylaldehyde (2.3 mmol) in anhydrous ethanol. The resultant mixture was refluxed for 3 h under protection of nitrogen. Removal of the solvent under reduced pressure yields a yellow semi-viscous liquid. The structure of Salen ligand could be confirmed by IR spectroscopy (ESI Fig. S1<sup>†</sup>). Then Cu(CH<sub>3</sub>- $COO_{2}$  (1 mmol) was dissolved in ethanol, followed by addition of appropriate Salen ligand in 1:2 molar ratio of Cu: Salen. The mixture was refluxed for 12 h, evaporation of ethanol and cool to room temperature, washed with cold ethanol and dried vacuum to obtain a green solid Cu-Salen (Scheme 1B). The structure of Cu-Salen was determined by IR spectroscopy (ESI Fig. S1<sup>†</sup>). The  $\nu$ (C=N) band in Salen ligand appears at 1633 cm<sup>-1</sup> and shifts to lower wavenumber for Cu-Salen complex due to coordination of azomethine nitrogen with copper.

#### Catalytic reaction

Styrene epoxidation reactions were performed in a 10 ml round bottom flask equipped with a magnetic stirrer and reflux condenser. Styrene (2 mmol), catalyst (10 mg) and appropriate amount of TBHP were added into 2 ml of acetonitrile. Then the mixture was stirred continuously at a desired temperature in an oil bath. At the end of the reaction, the solid catalyst was filtered, washed with acetonitrile and dichloromethane, dried at vacuum and reused without further purification. The products of epoxidation reaction were quantified and monitored *via* gas chromatography (Shimadzu, GC-8A) equipped with a HP-5 capillary column and a FID detector.

### **Results and discussion**

#### Spectroscopic characterization

Fig. 1 shows the IR spectra. In all case, the typical Si–O–Si bands are observed nearly at 1080, 802, 464 cm<sup>-1</sup> due to the formation of KIT-6 silica framework. The bands around 3430 and 1630 cm<sup>-1</sup> are mainly aroused by the bend vibration of O–H and physical adsorption of water molecular.<sup>28</sup> After functionalization of 3-APTES for KIT-6, the intensity of the O–H stretching bands markedly weakens which was caused by the interaction between the surface Si–OH and 3-APTES. The presence of C–H and N–H bending vibration nearly at 2950 and 687 cm<sup>-1</sup>, respectively can demonstrate that 3-APTES has been successfully anchored onto KIT-6.<sup>29</sup> In addition, a serious of aromatic



Fig. 1 FT-IR spectra of (a) KIT-6, (b) NH<sub>2</sub>-KIT-6, (c) S-NH<sub>2</sub>-KIT-6, (d) Cu-NH<sub>2</sub>-KIT-6, (e) Fe-NH<sub>2</sub>-KIT-6, (f) Co-NH<sub>2</sub>-KIT-6, (g) Ni-NH<sub>2</sub>-KIT-6 and (h) VO-NH<sub>2</sub>-KIT-6.



Fig. 2 Small-angle XRD patterns of (a) KIT-6 (b) NH $_2$ -KIT-6 and (c) Cu-NH $_2$ -KIT-6.

ring in the range of 1350-1600 cm<sup>-1</sup> and C=N stretching vibration at around 1645 cm<sup>-1</sup> are presented in S-NH<sub>2</sub>-KIT-6, indicating the grafting of salicylaldehyde precursor onto NH2-KIT-6. In addition, the peaks of IR spectra in Fig. 1d-h, the C=N stretching vibration slightly shifts to the region of 1643-1629 cm<sup>-1</sup> due to the coordination of the nitrogen with metal. Thus, the FT-IR results suggest the immobilization of metal Schiff complex onto KIT-6.

#### **XRD** studies

The low angle powder XRD patterns of KIT-6, NH<sub>2</sub>-KIT-6 and Cu-NH<sub>2</sub>-KIT-6 are depicted in Fig. 2. The pure KIT-6 sample shows a sharp intense peak around  $2\theta$  of 0.88 corresponding to the (211) plane, several hump ordered reflections for the (220) and (420) planes, indicating that the material is a highly ordered mesoporous structure with the cubic Ia3d symmetry.30,31 After organic-functionalization and encapsulation of metal complex, there is a slight decline in the intensity of the diffraction peaks, thereby conforming that the Cu-Schiff should successfully



Fig. 3  $N_2$  adsorption-desorption isotherms and pore diameter distributions of (a) KIT-6 and (b) Cu-NH<sub>2</sub>-KIT-6.



Fig. 4 SEM images of (a) KIT-6, (b) NH<sub>2</sub>-KIT-6 and (c) Cu-NH<sub>2</sub>-KIT-6. Fig. 6 XPS spectra of (a) Cu(CH<sub>3</sub>COO)<sub>2</sub> and (b) Cu-NH<sub>2</sub>-KIT-6.

anchor onto the surface of KIT-6 and the cubic Ia3d symmetry of the support is synchronously preserved.

#### Nitrogen adsorption-desorption measurements

The nitrogen adsorption-desorption isotherms and pore size distributions of KIT-6 and Cu-NH<sub>2</sub>-KIT-6 are showed in Fig. 3. Both of the samples display type IV isotherms with a pronounced capillary condensation step and H1 hysteresis loop at high relative pressure, indicating the presence of uniform mesoporous structure with narrow pore size distribution and large channel.32 However, after functionalization, a sharp reduction in the specific surface area from 887 m<sup>2</sup> g<sup>-1</sup> to 512 m<sup>2</sup>  $g^{-1}$  and a slight decrease in pore diameter from 6.14 nm to 5.75 nm have been found, implying that the organometallic groups have been successfully anchored onto KIT-6.

#### SEM studies

The morphologies of KIT-6, NH<sub>2</sub>-KIT-6 and Cu-NH<sub>2</sub>-KIT-6 are presented in Fig. 4. All of the samples are agglomeration of small random particles without explicit shape on the border.33 Even though KIT-6 experienced a multistep post treatment,



Fig. 5 TG profiles of (a) KIT-6 and (b) Cu-NH<sub>2</sub>-KIT-6.



virtually no tremendous variation has been found compared with the parental morphology.

#### Thermal analyses

To estimate the amount of covalently anchored complex on KIT-6 and its thermal stability, thermogravimetric analysis was employed and the relevant thermograms are presented in Fig. 5. The weight lose below 250 °C is ascribed to physically absorbed water molecules.34 A slight mass loss of 2.1% is observed in calcined KIT-6 between 250 °C and 800 °C, which is attributed to the loss of condensation of hydroxyl groups. For Cu-NH<sub>2</sub>-KIT-6, 3.9% mass loss in the region of 250 °C to 450 °C due to decomposition of aminopropyl groups, suggesting the immobilization of 3-APTES on KIT-6. Thermograms of Cu-NH<sub>2</sub>-KIT-6 also appears a relatively large weight loss of 8.7% in the range from 450 to 700 °C, which is mainly related to the decomposition of Cu-Schiff ligand.35 It can be approximately calculated that the loading of Schiff base groups is 0.47 mmol  $g^{-1}$  on account of the weight loss, which is nearly in agreement with the Cu content of 0.22 mmol  $g^{-1}$  estimated by ICP. The molar

ratio of ligand/metal is close to the nominal value of 2 : 1. All these results indicate that Cu–Schiff complex has been anchored onto KIT-6.

#### **XPS** measurements

Fig. 6 displays the Cu 2p XPS spectra of  $Cu(CH_3COO)_2$  and Cu-NH<sub>2</sub>-KIT-6. The binding energies of Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  in Cu(CH<sub>3</sub>COO)<sub>2</sub> appear at 934.8 and 954.8 eV, respectively. For the Cu-NH<sub>2</sub>-KIT-6, the Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  peaks respectively shift to lower values of 934.3 and 954.0 eV, which can be explained through the coordination of copper atoms with azomethine nitrogen of anchored Salen resulting in the increase of the electronic density around copper atoms.<sup>34</sup> Thus we can conclude that copper( $\pi$ ) complex was successfully covalently anchored onto KIT-6 by post-grafting method.

#### **Catalytic properties**

The catalytic performance of Cu-NH<sub>2</sub>-KIT-6 was carried out in the epoxidation of styrene with TBHP as oxidant. In order to get

Table 1	Epoxidation	of styrene	under	various	reaction	conditions

						Product selectivity <sup>c</sup> (mol%)	
(mg)	Temperature (°C)	Molar ratio of styrene/TBHP	Time (h)	Conversation <sup><i>a</i></sup> (%)	$\operatorname{TOF}^{b}\left(\mathrm{h}^{-1} ight)$	So <sup>c</sup>	Others
10	80	1:1	6	40.6	61.5	92.4	7.6
10	80	1:2	6	85.1	128.8	100	0
10	80	1:3	6	98.6	149.4	97.8	2.2
_	80	1:3	6	—	_	—	_
30	80	1:3	6	96.2	48.6	89.3	10.7
10	80	1:3	3	79.6	241.2	90.4	9.6
10	80	1:3	4	92.4	210	96.6	3.4
10	80	1:3	5	96.6	175.6	96.4	3.6
10	80	1:3	8	99.1	112.6	91.3	8.7
10	25	1:3	6	6.8	10.3	6.9	93.1
10	40	1:3	6	14.3	21.6	19.9	80.1
10	60	1:3	6	58.4	88.5	77	23

<sup>*a*</sup> *Reaction conditions*: styrene (2 ml); acetonitrile (2 ml). <sup>*b*</sup> TOF, h<sup>-1</sup>: (turnover frequency) moles of substrate converted per mole metal ion per hour. <sup>*c*</sup> So: styrene epoxide. Others: benzaldehyde, benzoic acid.

Catalyst	Conversation (%)	Epoxide selectivity (%)	TOF $(h^{-1})$	Time (h)	Reference		
KIT-6		_	_	6	This study		
Cu–Salen	89.7	84.9	20.2	6	This study		
Cu-NH <sub>2</sub> -KIT-6	98.6	97.8	149.4	6	This study		
Ni-NH <sub>2</sub> -KIT-6	12.7	88.7	30.2	6	This study		
Fe-NH <sub>2</sub> -KIT-6	14.8	88.1	41.1	6	This study		
Co-NH <sub>2</sub> -KIT-6	37	89.3	88.1	6	This study		
VO-NH <sub>2</sub> -KIT-6	36.8	90.4	55.8	6	This study		
Cu-NH <sub>2</sub> -MCM-41	97	86	124	24	21		
Cu-NH <sub>2</sub> -MSN	99	79	103	24	22		
Cu-NH <sub>2</sub> -MS <sup>a</sup>	86.3	95	64.2	24	37		
Cu-Y <sup>b</sup>	21	6		24	38		

 Table 2
 Epoxidation of styrene with TBHP catalyzed by a variety of catalysts

<sup>*a*</sup> Cu-NH<sub>2</sub>-MS: copper(II) Schiff anchored onto amino-functioned 2D-hexagonal mesoporous silica. <sup>*b*</sup> Cu-Y: copper(II) phthalocyanine encapsulated in zeolite Y.

the optimal reaction conditions, different parameters such as catalyst amount, substrate/oxidant molar ration, reaction time and temperature were investigated. From the results of different styrene/TBHP molar rations in Table 1, it can be seen that the conversion of styrene remarkably improves from 40.6% to 98.6% after 6 h by increasing the styrene/TBHP molar ratio from 1 : 1 to 1 : 3. It is also found that the epoxide selectivity does not change much by increasing the styrene/TBHP molar ration. Above results indicate that TBHP plays a crucial role in the epoxidation of styrene and the styrene/TBHP molar ratio of 1 : 3 is optimal for running the epoxidation reaction.

The influence of catalyst amount on the catalytic performance was performed by varying the catalyst amount from 10 to 30 mg and the results are showed in Table 1. It is interesting to note that without catalyst exhibited negligible catalytic activity attributed to no active sites. However, a sharp increase in the styrene conversion (98.6%) and epoxide selectivity (97.8%) was attained by using 10 mg Cu-NH<sub>2</sub>-KIT-6 as catalyst, which suggest Cu–Schiff complex successfully covalently anchored onto KIT-6 and the presence of active sites. Nevertheless, when increasing catalyst amount up to 30 mg, epoxide selectivity reduces to 89.3% and the styrene conversion also slightly decreases to 96.2%. Increasing the catalyst amount could provide more active sites, but inevitably results in further oxidation of the product styrene oxide. Thus, the catalyst amount (10 mg) is sufficient for the good conversion of styrene.

The reaction time has some influence on the catalytic behavior. As can be seen from Table 1, the epoxide selectivity gradually increased from 90.4% to 97.8% by prolonging the reaction from 3 h to 6 h, while further prolonging reaction time has no significant influence on the styrene conversion but results in the decrease of epoxide selectivity.

The temperature has great influence on the catalytic performance. As shown in Table 1, low temperature causes very low styrene conversion and epoxide selectivity. For example, only 6.8% of styrene conversion and 6.9% of epoxide selectivity can be achieved at 25 °C. Increasing reaction temperature could synchronously raise the catalytic activity.

Compared with a series of copper based heterogeneous catalyst conducted by previous reports (Table 2), it is obvious that Cu-NH<sub>2</sub>-KIT-6 possesses the highest conversation, epoxide selectivity and turnover frequency. Most importantly, our reaction was carried out only needing 6 h, while the reported catalysts needed 24 h for the epoxidation of styrene. The excellent catalytic performance of Cu-NH<sub>2</sub>-KIT-6 can attribute to the three dimensional mesoporous structures to avoid pore blockage and facilitate reactants diffusion into the pores. However, it should be noted that the other congeneric transition metal ( $Fe^{2+}$ ,  $Co^{2+}$ , VO<sup>2+</sup>, Ni<sup>2+</sup>) Schiff complexes grafted on KIT-6 have not so good catalytic performance. For example, only 12.7% conversion of styrene and 88.7% selectivity to epoxide can be obtained over Ni-NH<sub>2</sub>-KIT-6. This result may means that the synergistic effect between Cu(II) Schiff complex and KIT-6 support are superior to the others. In addition, the pure KIT-6 showed negligible catalytic performance since no active sites. The homogeneous Cu-Salen complex exhibited lower catalytic activity than its heterogeneous catalyst, which is probably due to the anchoring Cu–Salen onto three dimensional mesoporous silica KIT-6 efficiently avoiding the dimerization of active sites.<sup>36</sup>

We have investigated the recyclability and stability of the modified material for styrene epoxidation with TBHP as oxidant. The solid catalyst was easily recovered by filtration after each reaction cycle, washed thoroughly with acetonitrile and



Fig. 7 Reuse of the Cu-NH<sub>2</sub>-KIT-6 catalyst.



Scheme 2 Proposed mechanism for epoxidation of styrene with TBHP over copper(III) catalyst.

dichloromethane, dried in the vacuum at 60 °C for 12 h and reused for the subsequent cycles. The reused catalyst exhibited a negligible decrease in the catalytic activity and epoxide selectivity in three consecutive runs (shown in Fig. 7). To test if copper is leaching out of the catalyst in liquid phase reaction; the reaction mixture was hot filtered out at the end of the reaction and subjected to inductively coupled plasma analysis techniques. The result suggested almost no detectable copper metal ions in the filtrate solution.

Based on our experimental results and other related literature.<sup>39,40</sup> A reasonable reaction mechanism for epoxidation of styrene with TBHP over Cu-NH<sub>2</sub>-KIT-6 catalyst (LCu<sup>II</sup>) has been postulated in Scheme 2. In the first step, LCu<sup>II</sup> was coordinated with TBHP to form an active copper(III)-peroxo species I. Then, the activated oxygen of I consecutively interacted with C=C of styrene molecule to form cyclic intermediate III. Finally, III subsequently released to the epoxide, simultaneously accompanied with the regeneration of copper(II) catalyst. The formation of benzaldehyde and benzoic acid may be caused by deep oxidation of TBHP.

## Conclusions

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Novel heterogeneous catalysts have been synthesized by covalently anchored various transition metal (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> or VO<sup>2+</sup>) Schiff complexes onto amine functionalized KIT-6. The characterization results demonstrate that the pore structure of KIT-6 remain intact after multiple synthetic procedures. In addition, a detail research was carried out to optimize the reaction conditions of styrene epoxidation over Cu-NH<sub>2</sub>-KIT-6. Compared with copper(n) complex grafted onto other supports (*e.g.* zeolite Y, MCM-41, MSN and MS) and different metal (*e.g.* Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, or VO<sup>2+</sup>) Schiff complexes grafted onto KIT-6, Cu-NH<sub>2</sub>-KIT-6 exhibits excellent catalytic performance such as high conversion, excellent epoxide selectivity, high TOF and good recyclability due to its unique pore structure of KIT-6 and efficient synergistic effect between Cu(n) Schiff and the KIT-6 support.

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