Fe-containing Y as a host for the preparation of a ship-in-a-bottle catalyst

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Abstract

Encapsulation of Fe(phen)$_3$ in zeolite Y via directly complexing hydrothermally synthesized FeY with phenanthroline (abbreviated as phen) was first tried. The as-prepared materials have been characterized with XRD, FTIR, diffuse reflectance UV-vis spectroscopy (DRS), TG/DTA and ICP techniques. Further, their catalytic performance was also explored with cyclohexane oxidation and styrene oxidation as model reactions. It has been shown that Fe(phen)$_3$ is stably immobilized on zeolite Y, as proved by its basically unchanged catalytic property within three reaction recycles for the oxidation of cyclohexane. The as-prepared Fe(phen)$_3$/Y exhibits much stronger oxidation ability than FeY and Fe(phen)$_3$/Y prepared by the conventional flexible ligand method where Fe ions were introduced into the host by ion-exchanging Na$^+$ cations.
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Keywords: FeY; Fe(phen)$_3$; Encapsulation; Ship-in-a-bottle material; Cyclohexane oxidation

1. Introduction

Encapsulation of redox transition metal complexes in zeolites and related materials is one of the subjects of current catalysis research due to their potentiality as biomimetic heterogeneous catalysts for the oxidation of alkanes, alkenes and alcohols [1–14]. The as-prepared hybrid organic–inorganic material not only has heterogeneous catalysis characteristics, but also retains high catalytic efficiency originating in homogeneous catalysis due to the site-isolated effect. In addition, the steric constraints imposed on the transition metal complex by zeolite channels, the negative charge of the zeolite framework and distribution of the positive charge of the cations as well as surface properties of the zeolite can also lead to specific interactions, inducing structural and functional modification, as compared to pure complexes [15]. In this respect, encapsulation of Fe complex has been attracting much attention [4,5,13,14]. Herron et al. reported that upon encapsulation inside zeolites NaX and NaY, iron phthalocyanine was a highly selective catalyst for the formation of alcohols and ketones in oxidation of alkanes by iodosobenzene [13]. Kimura et al. found that the NaY-encapsulated Fe phthalocyanine was slightly distorted from the original planar structure due to intrazeolitic constraints, and gave a higher *trans*/*cis* ratio of 2-butene in hydrogenation of butadiene than it was on the external surface of NaY [14].

So far several approaches have been taken for the inclusion of transition metal complexes in zeolites [1–3]. The choice of a specific method is dictated by the size of the ligand relative to the free diameter of the

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zeolite channels. Among them, the flexible ligand method may be most extensively studied, as it is a straightforward and simple strategy. The flexible ligand method is based on the principle that the free ligand guests can easily enter into the cavities of the zeolite host material because they are flexible enough to pass through the restricting windows giving access to the larger cages. However, once the ligand has entered in the zeolite cage and chelated with the previously exchanged transition metal ions, the formed complex is unable to escape from the zeolite host matrix due to its much larger size than zeolite pore diameter [16].

Incorporation of transition metals in microporous and mesoporous materials has drawn considerable interests since this process gives rise to materials with acid and/or redox property [17–20]. However, a serious problem, namely leaching of the active component of metal ions, happened to these redox molecular sieves in the process of liquid-phase oxidation reactions [19]. This problem shortens the catalyst life. Effective prevention of metal leaching from redox molecular sieves during the liquid-phase oxidation of alkanes, alkenes and alcohols with H_2O_2 as an oxidant is a challenge in heterogeneous catalysis. This is the goal of our work, and we made it possible by directly complexing hydrothermally synthesized FeY with phenanthroline (phen). Further, the catalytic performance of the as-prepared materials was investigated for cyclohexane and styrene oxidation as model reactions.

2. Experimental

FeY was synthesized with aluminum sulfate, water glass ($[SiO_2] = 7.0$ mol/l, $[OH] = 4.07$ mol/l), NaOH, $FeCl_3$, and deionized water. A typical preparation procedure is as follows: 5 ml of water glass was first diluted with 8.7 ml of deionized water (solution A), and then, solution B consisted of 5 ml of NaOH aqueous solution (5 mol/l) and 2 ml of structure-directing agent was mixed with solution A under stirring condition. After 10 min, solution C prepared with 4.66 g of aluminum sulfate, a certain amount of $FeCl_3$ and 24 ml of water was slowly added to the above mixture, and the resulting mixture was stirred for about 30 min. The resultant gel was sealed into a stainless

steel autoclave and statically crystallized at 90 °C for 27 h. The product was filtered, washed with water, dried at 90 °C overnight and calcined at 300 °C for 5 h. To prepare Fe(phen)$_3$/Y, FeY was first treated with hydroxylamine hydrochloride (NH$_3$OHCl). Then, a certain amount of phen ligand, equal to 4.5 times of Fe amount in the samples, was dissolved in 15 ml of ethanol in an inert atmosphere, followed by addition of 1.5 g of the treated FeY. A large excess of phen was introduced so that as many Fe ions can be complexed as possible. This mixture was further stirred at 90 °C for 24 h. Finally, the solid fraction was Soxhlet-extracted for 24 h with ethanol to remove the residual phen and complexes present on the external surface.

Oxidation of cyclohexane and styrene was carried out in a self-made reactor (50 ml), which contains 2 mmol of cyclohexane or styrene as substrate, 2 mmol of H_2O_2 as oxidant, 10 ml of acetone as solvent and 0.1 g of Fe(phen)$_3$/Y as catalyst. The product was analyzed by a GC-9A gas chromatograph with a flame ionization detector.

X-ray diffraction (XRD) patterns of the samples were recorded on a Rigaku Dmax/γA X-ray diffractometer with Cu Kα radiation. Diffuse reflectance UV-vis spectroscopy (DRS) were measured with a PE Bio λ-40 spectrophotometer equipped with an integration sphere. FTIR spectra were recorded on a Fourier transform infrared spectrometer (PE 1760) using the conventional KBr pellet technique. The metal contents in the products were determined by an inductively coupled plasma spectrometer (LABTAM 8410). TG/DTA curves were obtained on a Rigaku CN8076E1 apparatus. Samples were heated from room temperature up to 800 °C at a ramping rate of 10 °C/min under flowing air using alumina sample holders.

3. Results and discussion

3.1. Characterization of samples

Powder X-ray diffraction (XRD) patterns of FeY-1.12 and the as-prepared Fe(phen)$_3$/Y-0.85 are shown as examples in Fig. 1. Those of other samples are similar to them. The sample notations are presented in Table 1. Fig. 1 shows that FeY samples have the FAU topological structure with high
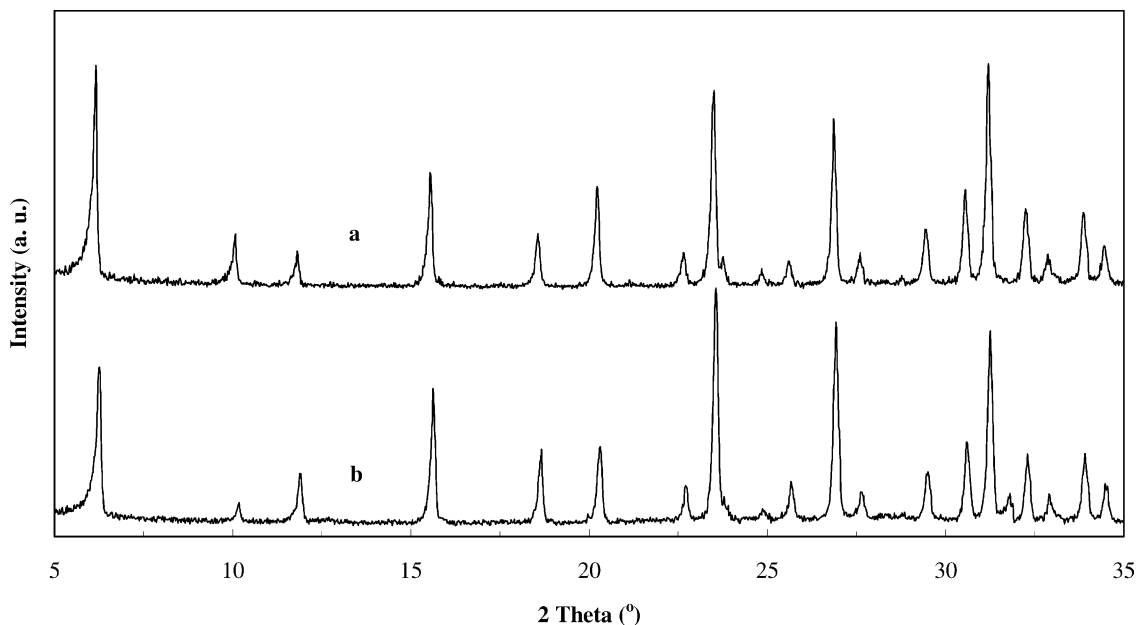
Fig. 1. XRD patterns of the as-synthesized FeY (a) and Fe(phen)$_3$/Y (b).

crystallinity. Upon complexing Fe ions with phen ligand and further Soxhlet-extracting, the FAU structure basically remains unchanged. This indicates that complexing and extraction processes do not have so strong influence on the structure of the parent FeY materials. Nevertheless, slight modification occurs, as confirmed by the alteration of the relative intensity of the peaks at 2 2 0 and 3 1 1 reflections (2θ of about 10 and 12°, respectively). For FeY, I_{220} is higher than I_{311}, whereas after being coordinated to phen, I_{220} becomes lower than I_{311}. This is typical for the

formation of large transition metal complex ion in the supercage of zeolite Y [8], indicating that at least part of Fe ions in the hydrothermally synthesized FeY samples, like the NaY samples ion-exchanged with Fe cations, can be complexed with phen and the formed Fe complex is encapsulated in the supercages of Y. This can also be verified by FTIR and the UV-vis spectroscopy.

The FTIR spectra of the extracted Fe(phen)$_3$/Y and FeY are given in Fig. 2. It clearly shows that no absorption band is observed between 1300 and 1500 cm^{-1} in the spectrum of FeY, while some bands appear in the spectrum of the extracted Fe(phen)$_3$/Y. These bands are attributed to the vibrations of C=C and C=N [5,6], proving the presence of phen. Since the Fe(phen)$_3$/Y sample underwent a thorough extraction, it is not possible for free phen to be embedded in FeY because uncomplexed phen with a much smaller kinetic diameter than the pore opening of zeolite Y can be easily removed during the process of extraction. Fig. 3 shows that FeY has no absorption band in the UV-vis region except for a weak broad band around 600 nm due to the forbidden d–d transition, whereas a strong broad band at about 520 nm is present in the DRS spectrum of Fe(phen)$_3$/Y besides the above weak band.

Table 1
Catalytic results of FeY, Fe(phen)$_3$/Y and Fe(phen)$_3$/Y(FL) for the oxidation of cyclohexane[a]

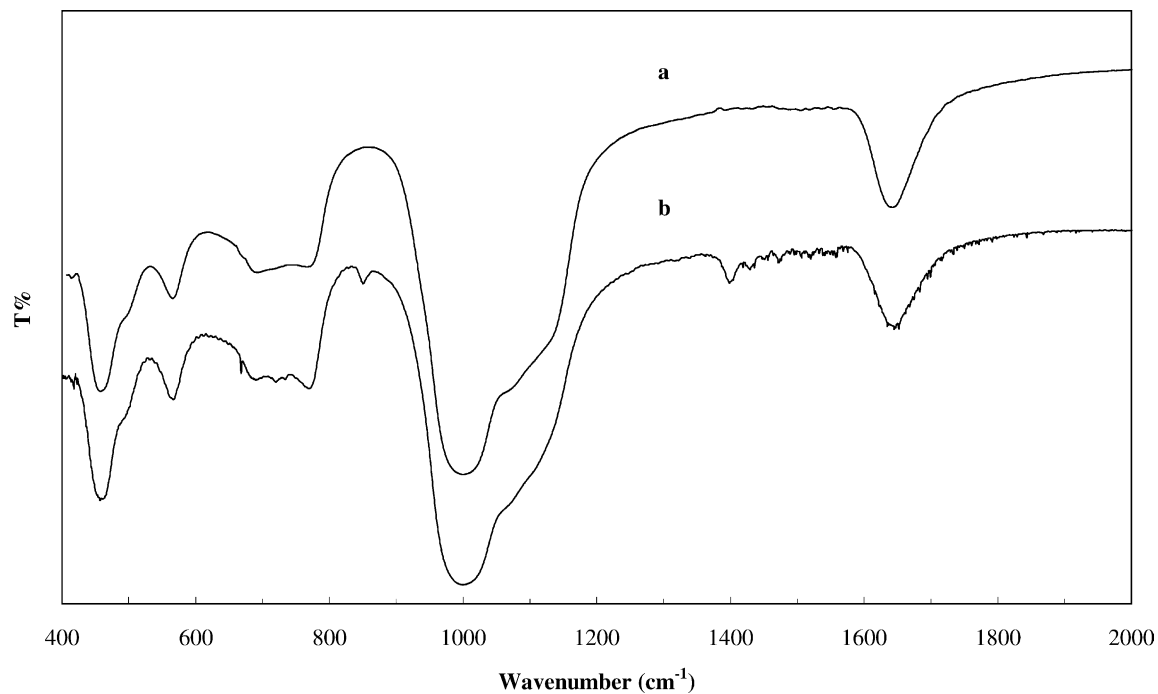| Catalyst	Metal content (%)	Conversion (%)
FeY-0.74	0.74	0.4
FeY-2.04	2.04	0.6
Fe(phen)$_3$/Y-0.69	0.69	2.80
Fe(phen)$_3$/Y-0.85	0.85	3.81
Fe(phen)$_3$/Y-2.00	2.00	6.84
Fe(phen)$_3$/Y(FL)-0.50	0.50	1.38
Fe(phen)$_3$/Y(FL)-1.00	1.00	1.52
Fe(phen)$_3$/Y(FL)-1.50	1.50	2.87

[a] Reaction temperature: 55 °C.

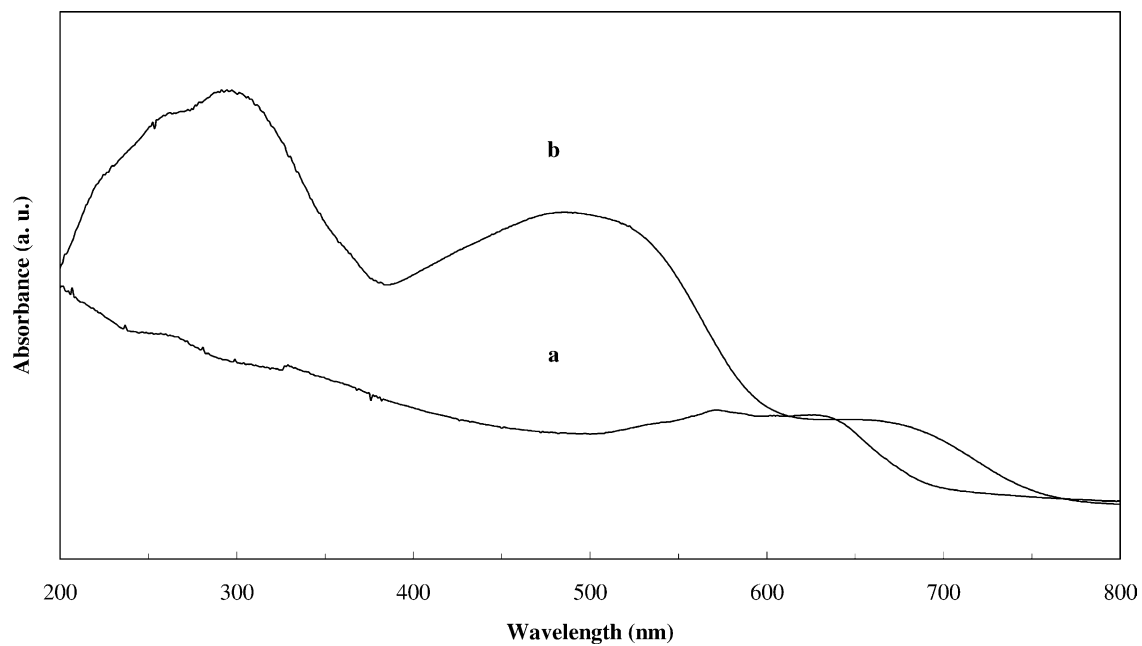Fig. 2. FTIR spectra of the as-synthesized FeY (a) and the extracted Fe(phen)$_3$/Y (b).

Fig. 3. DRS spectra of the as-synthesized FeY (a) and the extracted Fe(phen)$_3$/Y (b).
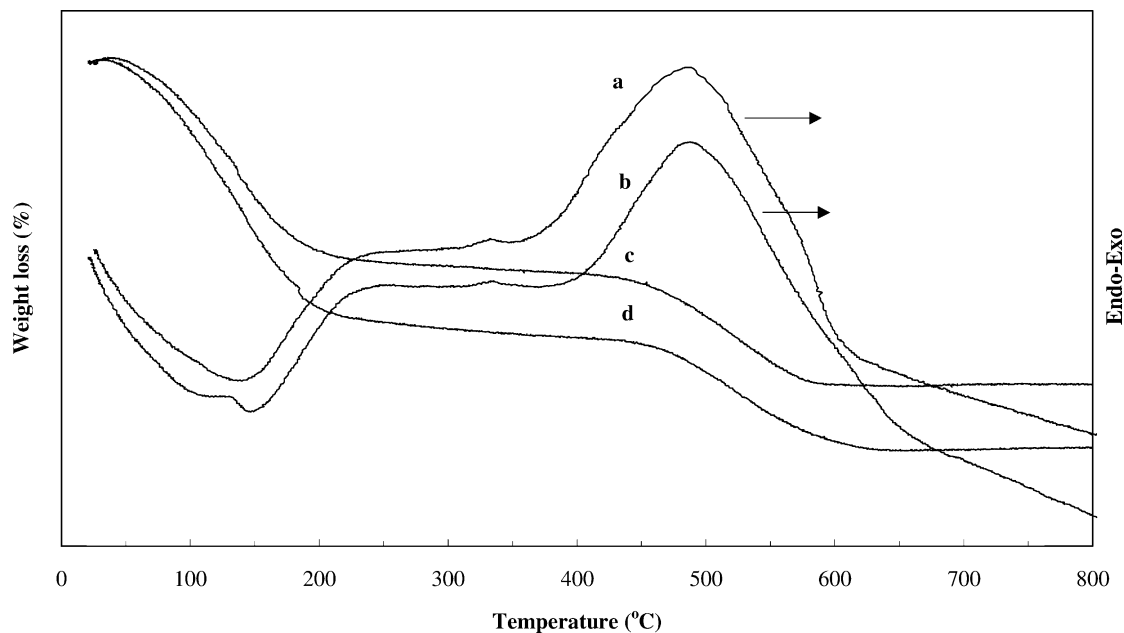
Fig. 4. TG/DTA curves of the extracted Fe(phen)$_3$/Y (a and c) and Fe(phen)$_3$/Y(FL) (b and d).

This strong band is attributed to the metal-to-ligand charge-transfer transitions (MLCT), and consequently indicative of the immobilization of Fe(phen)$_3$ complex on zeolite Y. ICP analysis and the weight loss above 300 °C (Fig. 4) show that the mole ratio of phen to Fe ions is close to 3. This reveals that the formed Fe complex in FeY is indeed Fe(phen)$_3$. In addition, as can be also seen in Fig. 4 the thermal behavior of the as-prepared Fe(phen)$_3$/Y is comparable with that of Fe(phen)$_3$/Y made by using the conventional flexible ligand method (designated as Fe(phen)$_3$/Y(FL)). The endothermic peak observed at temperature below 250 °C in the DTA curve is due to the desorption of physically adsorbed and/or occluded water, whereas the exothermic peak around 520 °C is ascribed to the combustion of Fe(phen)$_3$ complex encaged in the host. This implies that encapsulation of the metal complex in zeolite by different methods has no significant effect on the thermal stability of the immobilized metal complex if it is located in the same position in the host. As compared to Fe(phen)$_3$ impregnated on the external surface of NaY, which decomposes and burns at about 446 °C [5], the thermal stability was greatly enhanced. This gives another piece of strong evidence for the inclusion of Fe(phen)$_3$ in FeY.

3.2. Catalytic performance of Fe(phen)$_3$/Y for the oxidation of cyclohexane and styrene

Table 1 summarizes the catalytic results of FeY-*m* (*m* designates the iron content (wt.%)), Fe(phen)$_3$/Y-*m* and Fe(phen)$_3$/Y(FL)-*m* for the oxidation of cyclohexane at 55 °C. It can be seen that FeY exhibits very low catalytic activity, but upon complexing with phen, its catalytic oxidation ability is drastically enhanced, and with increasing Fe content, the conversion increases without lowering TOF. Compared with Fe(phen)$_3$/Y(FL), the catalytic activity is doubled. This is further confirmed by the catalytic results of Fe(phen)$_3$/Y-0.69 and Fe(phen)$_3$/Y(FL)-0.5 for the oxidation of styrene with H$_2$O$_2$ at room temperature using acetone as a solvent (Fig. 5). It is clear that Fe(phen)$_3$/Y-0.69 is much more active than Fe(phen)$_3$/Y(FL)-0.5. This is accounted for by the site-isolation of Fe(phen)$_3$ in the host and the absence of complex and/or phen ligand in the channel of the former sample. Such high dispersion is very difficult to be realized by using the classical flexible ligand method when more metal complex molecules were supported [6,21]. The conversion of cyclohexane on Fe(phen)$_3$/Y-0.85 in its oxidation is plotted against the

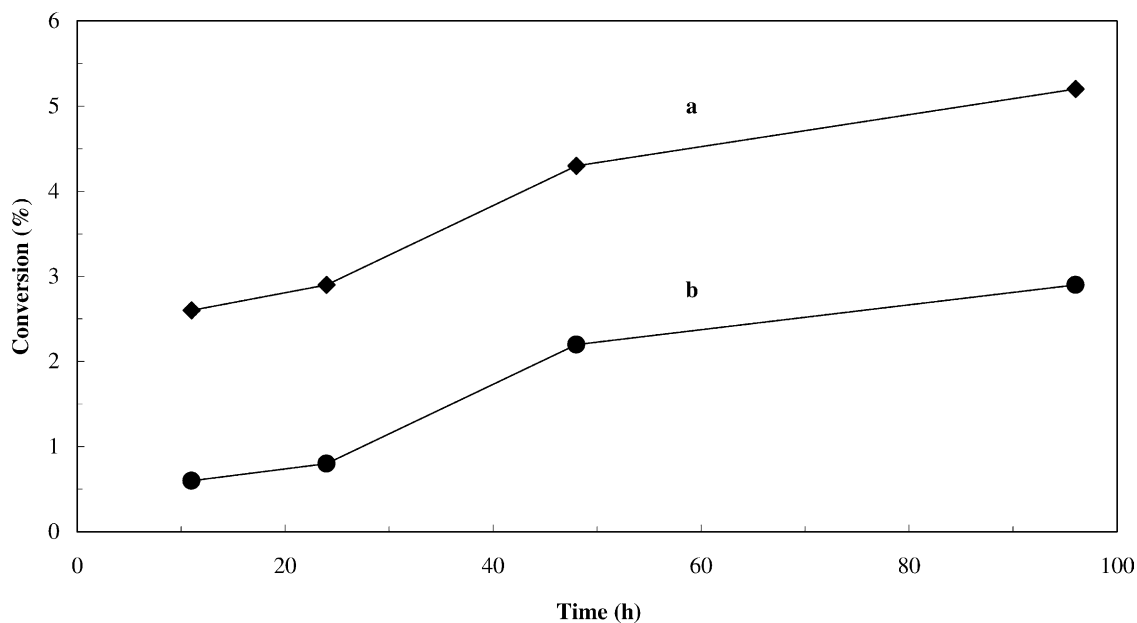Fig. 5. The catalytic results of (a) Fe(phen)$_3$/Y-0.69 and (b) Fe(phen)$_3$/Y(FL)-0.5 for the oxidation of styrene.

reaction time in Fig. 6. As expected, the conversion almost linearly increases with the time, and it reaches about 17% when the reaction proceeds for 65 h. For comparison, the result with Fe(phen)$_3$/Y(FL) with a iron content of 1.0% was also included in Fig. 6, which shows that the oxidation ability of the latter is much lower than that of the former, and as the reaction goes on, the difference between the two samples
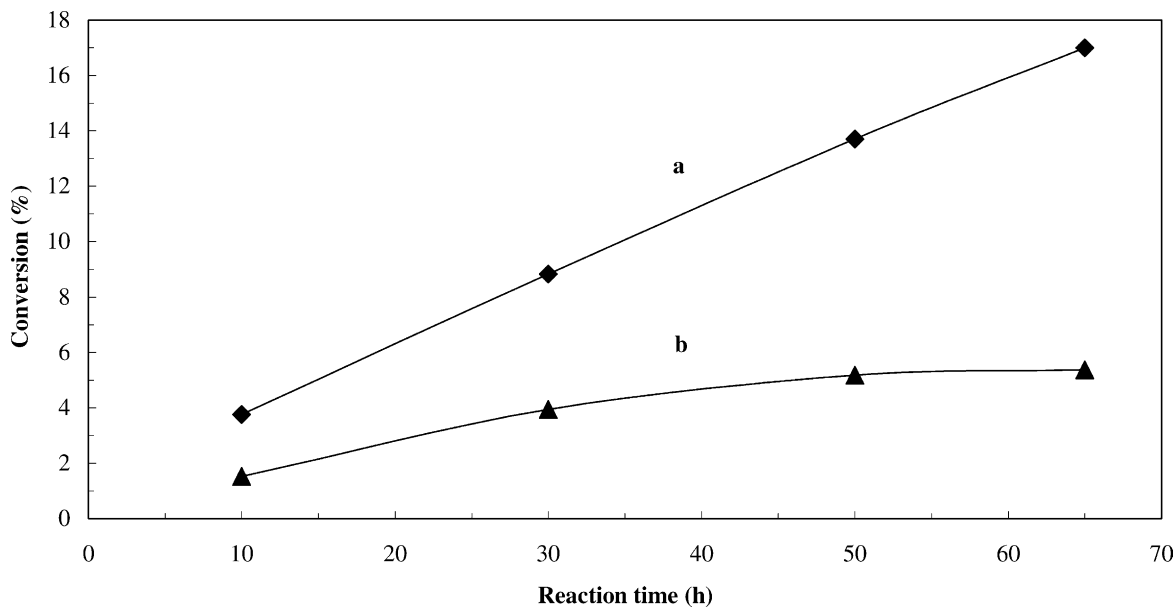

Fig. 6. The conversion of cyclohexane as a function of the reaction time over Fe(phen)$_3$/Y-0.85 (a) and Fe(phen)$_3$/Y(FL)-1.0 (b).

Table 2
Catalytic results of Fe(phen)$_3$/Y-0.69 for the oxidation of cyclohexane within three recycles[a]

Recycles	Conversion (%)	Selectivity (%)		
		Cyclohexanone	Cyclohexanol	Others
1	4.38	67.7	26.9	5.4
2	5.79	65.2	26.2	8.6
3	5.95	68.0	27.2	4.8

[a] Reaction temperature: 60 °C.

becomes marked. Despite of this, a similar trend was found for the selectivity (not shown here) of both samples that cyclohexanone and cyclohexandiol gradually increase with the time at the expense of cyclohexanol. The catalytic stability of Fe(phen)$_3$/Y-0.69 was further investigated since a good catalyst should have a long life. As shown in Table 2, the activity of Fe(phen)$_3$/Y-0.69 (after the first reaction, it was washed with acetone for three times and continued for the subsequent run, and thus, repeated for the third run.) does not decrease during three runs. The lower conversion in the first run is probably due to the presence of a small part of uncomplexed Fe ions, which were mostly leached during the process of the first reaction. Afterwards, the catalytic performance remains stable, as proved by the similar conversion of cyclohexane and product selectivity for the second and third runs. This shows that Fe(phen)$_3$/Y is a highly active, selective and stable biomimetic heterogeneous catalyst for the oxidation of alkanes and alkenes.

4. Conclusions

This work developed a new method for the encapsulation of Fe(phen)$_3$ in zeolite Y, viz. directly complexing hydrothermally synthesized FeY with phenanthroline. XRD, FTIR, DRS and TG/DTA characterization showed that phen could coordinate Fe ion in FeY to form Fe(phen)$_3$ complex, which was encaged in zeolite Y. This is evidenced by the changes of the relative intensity of the 2 2 0 and 3 1 1 reflections of the XRD patterns, presence of absorption bands in the region of 1200–1500 cm^{-1} in the FTIR spectrum, appearance of a strong broad band around 520 nm in the DRS spectrum and comparable thermal stability with Fe(phen)$_3$/Y(FL). The as-prepared Fe(phen)$_3$/Y as a catalyst exhibits much higher activity than Fe(phen)$_3$/Y(FL) for the oxidation of cyclohexane and styrene, and its catalytic performance remains stable at least within three reaction cycles. This substantiates that our developed method is practicable, not only providing a new way for the preparation of ship-in-a-bottle materials with good catalytic property, but also effectively hindering metal ions leaching from the transition metal-containing molecular sieves in liquid-phase oxidation reactions.

Acknowledgements

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