Catalysis Communications 64 (2015) 91–95

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Aluminum metal–organic framework as a new host for preparation of encapsulated metal complex catalysts

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ARTICLE INFO

Article history:
Received 27 December 2014
Received in revised form 6 February 2015
Accepted 7 February 2015
Available online 10 February 2015

Keywords:
Metal–organic frameworks
Cyclohexane oxidation
MIL-100(Al)
Encapsulation
Metal complexes

ABSTRACT

A facile strategy for encapsulation of metal complex guests into MOFs was proposed. This strategy involves pre-adsorbing metal salt on MOF, and then coordinating the metal ions with the organic ligand, as exemplified by encapsulation of tris(1,10-phenanthroline) Cu(II) complexes (CuPhen) in MIL-100(Al) (denoted as CuPhen/MIL). CuPhen encapsulated in MIL-100(Al) showed higher catalytic activity than the neat CuPhen and CuPhen encapsulated in zeolite-Y. The prepared CuPhen/MIL catalyst was stable and could be reused at least three times without significant loss in activity. This work is beneficial for the host–guest chemistry study and the development of new heterogeneous catalysts.

1. Introduction

Metal complexes as homogeneous catalysts have widespread applications in many catalytic reactions. However, the difficulties in recovery and recycling of the catalysts limit their reuse [1–4]. Therefore, many efforts have been devoted to solve these problems, in which immobilization of metal complexes on solid matrices is a promising approach [5–7]. In the various immobilized catalysts, it has been established that zeolite encapsulated organometallic compounds and transition metal complexes ("ship-in-a-bottle" hybrids) can be highly selective and efficient catalysts [7–10]. The steric constrain imposed by the walls of the zeolite plays a vital role in modifying the properties, namely, magnetic, electronic, and redox behaviors of the encapsulated complexes [7,11–13]. These changes in the properties of the transition metal complexes upon encapsulation have led various researchers to develop newer heterogeneous catalysts and apply them in various organic transformations [9,11,14–16]. Nevertheless, for zeolite encapsulated metal complex hybrids, the commonly used zeolite host is zeolite-Y due to its unique structural properties, that is, large supercages (for accommodating metal complexes) and small pore size (for preventing the leaching of the encapsulated guests). While other zeolites, due to their structural limitation, cannot be used as the hosts for "ship-in-a-bottle" hybrids. The small selected range for hosts, to some extent, limits the development of the new encapsulated hybrids.

Metal–organic frameworks (MOFs), owing to their high porosity, large surface area and chemical tenability, have become highly promising functional hybrid materials [17–20]. Compared with the traditional porous materials, such as zeolite and mesoporous materials, MOFs have more topologies and tunable and functionalizable nanospaces [20–23], which provide an excellent platform to accommodate guest species and to prepare new host–guest materials. MIL-100(Al) ($Al_3O(OH)(H_2O)_2[BTC]_2 \cdot nH_2O$, BTC = benzene-1,3,5-tricarboxylate) is one of the mesoporous metal(III) trimesate MIL-100. The porosity of MIL-100(Al) originates from both 25 Å and 29 Å mesopores, which are accessible via 5.5 Å and 8.7 Å windows, respectively [24,25]. The structural properties of MIL-100(Al) make it a potential and promising host for preparation of "ship-in-a-bottle" catalysts since its two distinctly different polyhedral cages can accommodate large metal complexes and the small pore size can effectively limit the escape of the encapsulated guests. At present, the application of MIL-100(Al) as the host matrix for encapsulation of metal complexes has been rarely reported.

In this work, tris(1,10-phenanthroline) Cu(II) complexes (CuPhen), being able to efficiently catalyze cyclohexane oxidation, were encapsulated into MIL-100(Al) by pre-adsorption of Cu(II) salt into the MIL-100(Al) followed by coordination of Cu(II) ions with 1,10-phenanthroline ligand. The prepared hybrids showed much higher catalytic activity than the neat CuPhen and CuPhen encapsulated in zeolite-Y in cycloalkane oxidation with H_2O_2.

2. Experimental

2.1. Catalyst preparation

MIL-100(Al) was hydrothermally synthesized and purified according to a previously published procedure [26]. MIL-100(Al) encapsulated

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http://dx.doi.org/10.1016/j.catcom.2015.02.011

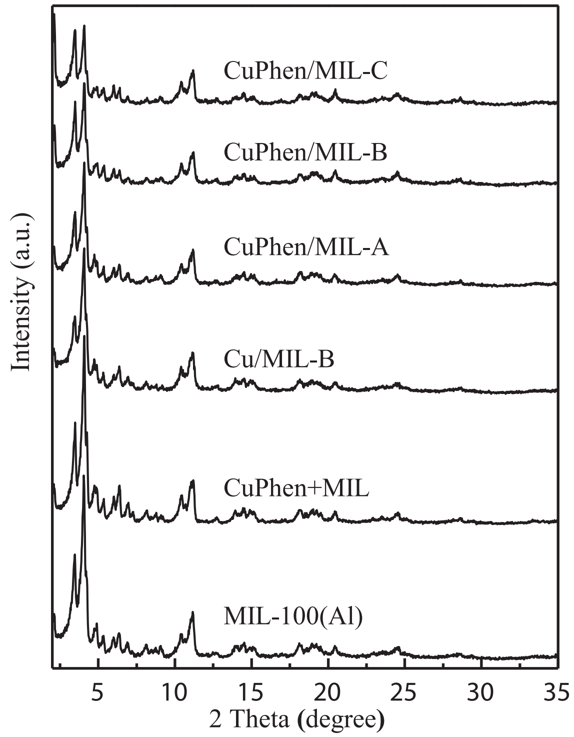


Fig. 1. XRD patterns of the different samples.

Table 1
Cu content and the textural properties of the different samples.

Samples	Cu (wt.%)	N (wt.%)	S_{BET} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)
MIL-100(Al)	–	–	1512	0.685
Cu/MIL-A	0.50	–	1497	0.685
Cu/MIL-B	1.00	–	1486	0.684
Cu/MIL-C	3.00	–	1460	0.680
CuPhen/MIL-A	0.28	0.35	1265	0.570
CuPhen/MIL-B	0.55	0.76	1201	0.561
CuPhen/MIL-C	0.65	0.81	1140	0.559

Cu complexes (denoted as CuPhen/MIL) were prepared by the following strategies. First, 0.027 g of $CuCl_2 \cdot 2H_2O$ was dissolved in 20 mL of water, and then 1.0 g of MIL-100(Al) was added. After the mixture was stirred at room temperature for 24 h, the solid was filtrated and dried at room temperature. The obtained sample was denoted as Cu/MIL-B. Second, 1.0 g of Cu/MIL-B was added into 20 mL ethanol solution containing 0.16 g of 1,10-phenanthroline and then the mixture was stirred at room temperature for 24 h. After filtration, Soxhelt extraction with ethanol and acetone and drying were done, the final sample was obtained and denoted as CuPhen/MIL-B. After adjusting the amount of $CuCl_2 \cdot 2H_2O$ in the first step, CuPhen/MIL samples with different CuPhen loadings were prepared.

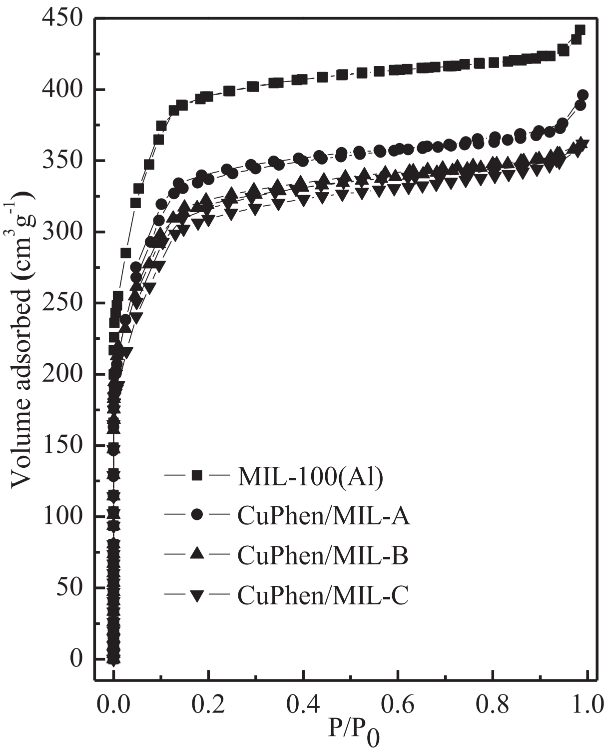


Fig. 2. N_2 adsorption/desorption isotherms of MIL-100(Al) and the different CuPhen/MIL samples.

The tris(1,10-phenanthroline) Cu(II) complexes were synthesized based on the procedure described by Detoni et al. [4]. Zeolite-Y encapsulated CuPhen (CuPhen/Y) were prepared according to the method reported in the literature [8]. The Cu content was 0.72 wt.%.

2.2. Characterization

The Cu contents in the samples were measured by ICP analysis. The N contents in the samples were measured by a verioELcube elemental analyzer. The XRD patterns were recorded on a Shimadzu XRD-6000 Diffractometer with Cu Kα radiation. Diffuse reflectance UV–vis (DR UV–vis) was measured by a Cary-300 Absorption Spectrometer. Nitrogen adsorption isotherms were measured at −196 °C on a Quantachrome Autosorb analyzer. Before the measurement, the sample was evacuated at 150 °C for 3 h. The BET surface area was calculated according to desorption branch, while the pore volume was estimated at a relative pressure of 0.99. Solid state ^{13}C CP-MAS NMR spectra were recorded on a Bruker Avance III 600 MHz Wide Pore spectrometer.

2.3. Catalytic reaction

The liquid-phase oxidation of cycloalkane with H_2O_2 (30% in aqueous solution) was carried out under a stirring condition in a sealed autoclave. A typical reaction mixture is as follows: 0.05 g catalyst, 10 mL solvent, 9.5 mmol substrate, and 38 mmol H_2O_2 (30% in aqueous solution). Unless otherwise stated, the reaction temperature is 70 °C and time is 3 h. After reaction, the liquid product was separated by centrifugation and analyzed by a GC-7890F gas chromatograph equipped with a polyethylene glycol packed column and a flame ionization detector with benzyl chloride as an internal standard.

3. Results and discussion

3.1. Characterization of MIL-100(Al) and CuPhen/MIL samples

The XRD patterns of the different samples (Fig. 1) confirmed that MIL-100(Al) was successfully synthesized [26] and adsorption of Cu salt had little influence on the structure of the host. After encapsulation of CuPhen, the CuPhen/MIL samples still preserved the framework of the host MIL-100(Al) but $2\theta = 4.0$ Bragg intensity gradually decreased with increasing CuPhen loadings. The large guests located inside the cages of the host generally strongly bound to the internal surface of the cage and crystallographically belong to the structure and symmetry of MIL-100 and therefore influencing the structure factors of the Bragg peaks [27]. Thus, the variation of the relative intensities might confirm the existence of CuPhen within the cages of the host. In order to further prove this, we measured the XRD pattern of CuPhen + MIL (CuPhen impregnated MIL-100(Al)) and also gave the result in Fig. 1. CuPhen with

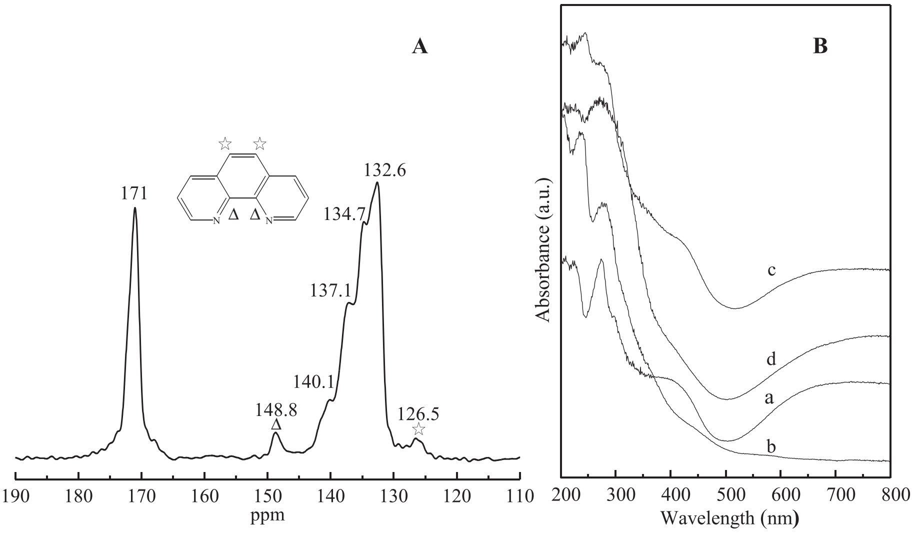


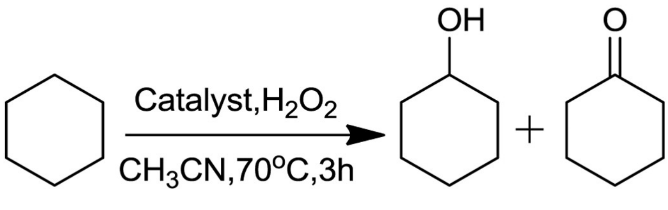
Fig. 3. (A) ^{13}C CP-MAS NMR spectrum of CuPhen/MIL-B. (B) DR UV–vis spectra of the different samples ((a): CuPhen, (b): MIL-100(Al), (c): CuPhen/MIL-B, (d): CuPhen/Y).

large size (~13 Å) cannot enter into the cavities of MIL-100(Al) through its relative big window (8.7 Å), hence, they can only locate on the external surface of MIL-100(Al) host. As expected, no such change was observed.

As shown in Fig. 2, the N_2 adsorption/desorption isotherms of MIL-100(Al) and CuPhen/MIL samples showed a mixture of type I and IV curves. The textural parameters listed in Table 1 showed that after pre-adsorbing Cu salt, the surface areas and pore volumes of the obtained Cu/MIL samples nearly kept the same as those of their MIL-100(Al) precursor, while a significant decrease in the surface area and pore volume was observed over CuPhen/MIL samples. Moreover, the decreasing extent tended to increase gradually with increasing CuPhen loading. The changes in the specific surface areas and total volumes (Table 1) clearly indicated that a part of the CuPhen was located within the porous structure of the host MIL-100(Al). The CuPhen guests laying on the surface of grains do not contribute to the textural properties.

ICP measurement (Table 1) showed that the Cu contents in the encapsulated systems were much less compared to the corresponding Cu/MIL samples. The decrease in the Cu content could be attributed to the removal of CuPhen formed on the external surface of MIL-100(Al) and the un-coordinated Cu ions in the extraction treatment. Moreover, it was worthy of noting that there was no obvious increase in the encapsulation amount of CuPhen as the pre-adsorbed Cu content was beyond 3%. In addition, according to the N content in the sample, the ligand-to-metal ratio in each CuPhen/MIL sample was close to 3:1, suggesting octahedral coordination around the central Cu cations [8].

Successful formation of CuPhen in MIL-100(Al) can be further confirmed by ^{13}C CP-MAS NMR spectrum and DR UV–vis spectra (Fig. 3). Fig. 3(A) is the ^{13}C CP-MAS NMR spectrum of the prepared CuPhen/MIL-B. It revealed typical ^{13}C spectra of MIL-100(Al) host and CuPhen complex. The overlapped signals in the chemical shift range of 132–140 ppm are assigned to the aromatic carbons from MIL-100(Al) host or the Phen ligand and the signal at 171 ppm is assigned to the carboxylate groups of framework trimesate BTC [26,28,29]. The two weak signals at 126.5 and 148.8 ppm are assigned to the chemical shifts in the Phen ligand [30,31]. Fig. 3(B) is the DR UV–vis spectra of the different samples. All the samples showed two intense bands at about 240 and 278 nm. These bands are assigned to the organic linkers of MIL-100(Al) host or the Phen ligand. Compared with MIL-100(Al) host, two additional bands, a weak shoulder band at about 440 nm and a broad band at about 670 nm, were observed in the spectrum of CuPhen/MIL-B. The band at 440 nm can be assigned to the ligand-to-metal charge transition, while the band at 670 nm can be ascribed to d–d electron transition. These provide effective evidences for the encapsulation of CuPhen in the cavities of MIL-100(Al). Moreover, compared with pure CuPhen, no significant red or blue shift related to the distortion of CuPhen was observed, which was different from that observed over zeolite-Y encapsulated CuPhen. The metal complexes encapsulated in zeolite-Y usually undergo a distortion under the steric constraint imposed by the zeolite matrix, due to the small size of the supercages in zeolite [8]. In contrast, the size of the cavity in MIL-100(Al) is much larger than that of the supercage in zeolite-Y, thus, the CuPhen encapsulated in MIL-100(Al) matrix do not undergo such a distortion.



Scheme 1. The reaction path for cyclohexane oxidation.

3.2. Catalytic properties of the prepared samples

The catalytic performances of the prepared catalysts were tested in the cyclohexane oxidation and cyclohexanol and cyclohexanone are the major products (Scheme 1). As shown in Table 2, no cyclohexane conversion was observed over MIL-100(Al) demonstrating that MIL-100(Al) host was not responsible for the oxidation activity. Cu/MIL-B showed catalytic activity in cyclohexane oxidation with H_2O_2, but its catalytic activity was much lower than that of the corresponding CuPhen/MIL-B. This result not only indicates that the CuPhen is more reactive than the Cu^{2+}, but also, from another aspect, demonstrates that

Table 2
Catalytic results obtained over the different samples.

Samples	TON	Conversion (%)	Selectivity (%)	
			-one	-ol
MIL-100(Al)	–	–	–	–
CuPhen [a]	71	12.3	75	25
Cu/MIL-B	93	7.9	67	33
CuPhen/Y	195	11.9	73	27
CuPhen/MIL-A	467	11.1	71	29
CuPhen/MIL-B	458	21.4	69	31
CuPhen/MIL-C	384	21.2	66	34

[a] 0.005 g catalyst.

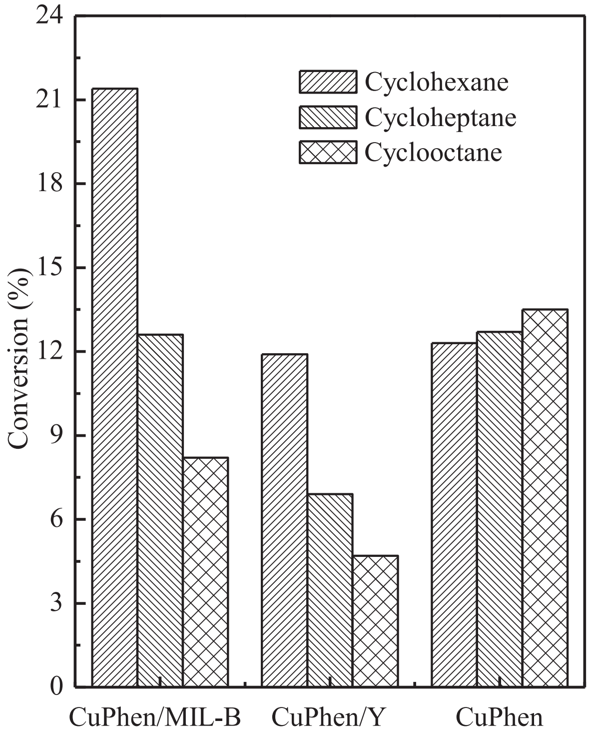


Fig. 4. Catalytic results of cycloalkane oxidation over different catalysts.

the Cu^{2+} ions in MIL-100(Al) are successfully coordinated with the Phen ligand. In addition, CuPhen/MIL gave a catalytic activity higher than the CuPhen/Y and pure CuPhen catalysts, indicating that the properties of the hosts have great influence on the encapsulated CuPhen. The higher activities obtained over encapsulated CuPhen than over neat CuPhen are due to the site isolation, which may inhibit the degradation of the metal complex in the presence of H_2O_2 [32,33]. The differences in catalytic activities obtained over CuPhen/MIL and CuPhen/Y may be a consequence of the different structural properties of the two hosts. MIL-100(Al) host has a larger supercage (25 Å and 29 Å) and window (one of the window size is 8.7 Å) than zeolite Y host (13 Å for supercage and 7.4 Å for window), which are favorable for the diffusion of the substrates and the generation of active transition-states [34]. Therefore, CuPhen encapsulated in MIL-100(Al) gave higher activity than that in zeolite Y.

The catalytic results on the substrates with different sizes are shown in Fig. 4. The main products are cycloalkanone (-one) and cycloalkanol (-ol) and the ratios of -one to -ol obtained over the different samples are nearly 7/3. From Fig. 4, it can be seen that the catalytic activity obtained over the two catalysts decreased with the increase of the substrate size, even if CuPhen/MIL-B was more active than CuPhen/Y. In contrast, pure CuPhen gave higher activity in cycloheptane or cyclooctane oxidation than in cyclohexane oxidation. These results further confirmed that CuPhen in the two catalysts were encapsulated in the cavities of the hosts, and the uniformed pore size of the hosts endowed the shape-selectivity of the prepared hybrids.

Table 3
Catalytic results obtained over CuPhen/MIL-B under the different reaction conditions.

Reaction temperature (°C)	Reaction time (h)	Conversion (%)	Selectivity (%)	
			-one	-ol
30	3	–	–	–
40	3	2.6	74	26
50	3	5.5	74	26
60	3	12.5	68	32
70	3	21.4	68	32
80	3	12.5	64	36
70	0.5	4.6	77	23
70	1	7.1	73	27
70	2	18.2	69	31
70	4	21.8	67	33
70	5	22.1	67	33

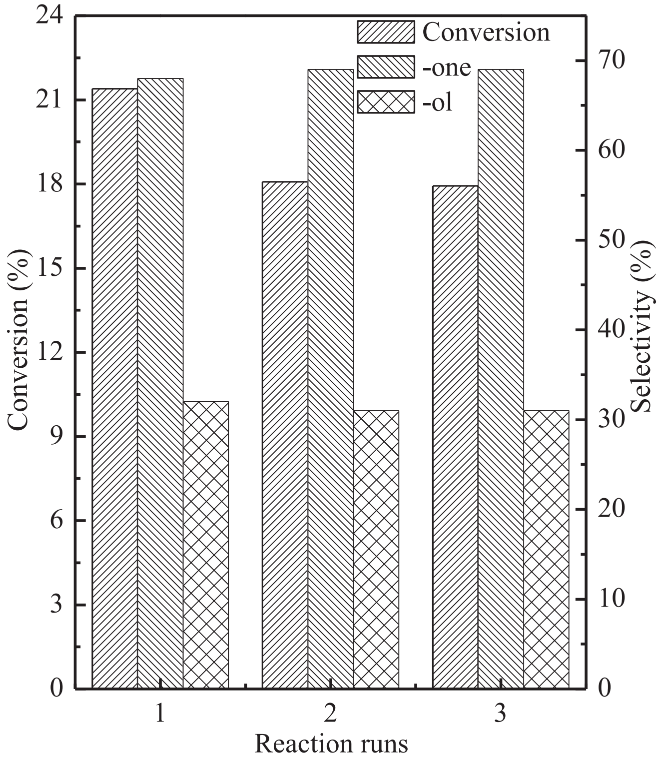


Fig. 5. Cyclohexane conversion and selectivity obtained over CuPhen/MIL-B within three repeated reaction runs.

The effects of reaction temperature and time on cyclohexane conversion were investigated over CuPhen/MIL-B and illustrated in Table 3. As expected, cyclohexane conversion increased with reaction temperature although no conversion was detected when the reaction temperature was below 30 °C. However, when the temperature was above 70 °C, the conversion decreased gradually which might be owing to the quicker decomposition of H_2O_2 under higher temperature. The cyclohexane conversion increased with the increase in the reaction up to 3 h. An attempt to further increase the cyclohexane conversion by prolonging the reaction time failed, probably due to that most of the added H_2O_2 was consumed when the reaction was carried out for 3 h [14].

The stability of the prepared catalyst was investigated with CuPhen/MIL-B as an example. After one reaction run, the catalyst was recovered by centrifugation and then used for the next run under the same reaction conditions. Fig. 5 depicts the catalytic results of three successive recycles. It could be seen that the reused catalyst still retained at 87% of its original activity after the third run. The loss in activity could be due to the loss of the very fine catalyst particles in the recycle and the degradation of the CuPhen under the employed reaction conditions. To check the contribution of homogeneous reactions, the following experiment was carried out. When the reaction was performed for 1 h, the catalyst was separated from the reaction mixture, and left the reaction for another 2 h. It was found that the cyclohexane conversion was only increased to 8.5% from 7.1%. In contrast, if the catalyst was not separated, the cyclohexane conversion reached 21.4%. This proves that encapsulation of CuPhen in MIL-100(Al) can lead to the formation of a reusable, and therefore, an environmentally benign heterogeneous catalyst.

4. Conclusions

In conclusion, tris(1,10-phenanthroline) Cu(II) complexes were successfully encapsulated in MIL-100(Al) by pre-absorption of metal salts and then coordination of absorbed metal ions with the ligand. The prepared CuPhen/MIL catalyst showed much higher activity in the oxidation of cycloalkanes than the corresponding neat CuPhen and CuPhen/Y. Besides, the catalyst was reusable and no significant activity loss was observed after three runs. This work provides a facile and efficient strategy for encapsulation of metal complex guests into MOFs, and is beneficial for host–guest chemistry studies and the development of new heterogeneous catalysts.

Acknowledgment

This work is supported by the National Natural Science Foundation of China (No. 20971095) and Research Project supported by Shanxi Scholarship Council of China (2013-047).

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