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Short communication

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

Yanfeng Chen [a], Binbin Fan [a,*], Ningyue Lu [a], Ruifeng Li [b,*]

[a] Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, PR China
[b] Key Laboratory of Coal Science and Technology MOE, Taiyuan University of Technology, Taiyuan 030024, PR China

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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.

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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

* Corresponding authors.
E-mail addresses: fanbinbin@tyut.edu.cn (B. Fan), rfli@tyut.edu.cn (R. Li).

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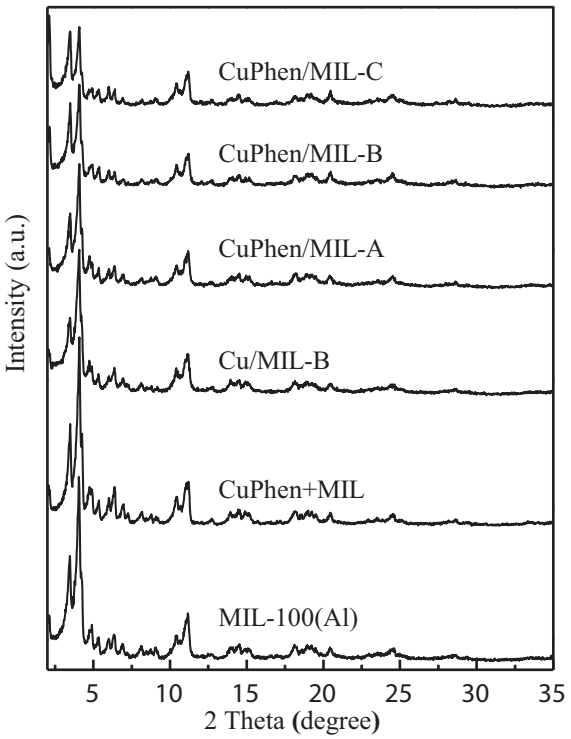

Fig. 1. XRD patterns of the different samples.

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,

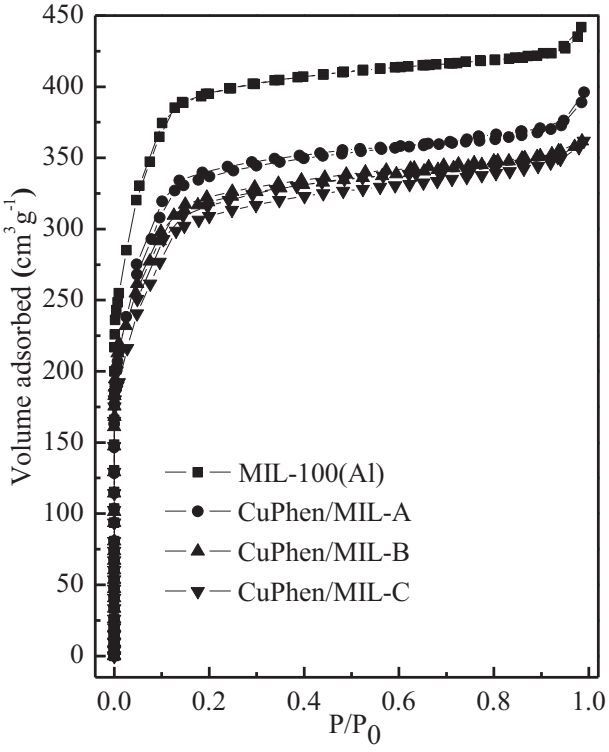

Fig. 2. N_2 adsorption/desorption isotherms of MIL-100(Al) and the different CuPhen/MIL samples.

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

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.

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

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