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Article

Fabrication of amino-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ for heterogeneous Knoevenagel condensation

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ABSTRACT

Metal organic frameworks (MOFs) are an important platform for heterogeneous catalysts. Although MOFs with a smaller particle size exhibit better catalytic performance because of less diffusion limitations, their separation and recycling after catalytic reactions are difficult. The integration of MOFs with magnetic nanoparticles could facilitate their recovery and separation. Especially, the shell thickness of the core-shell structured composites is controllable. In this study, amino-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ was fabricated by a stepwise assembly method and its catalytic performance in Knoevenagel condensation was investigated. The results demonstrated that the magnetic hybrid material exhibited a core-shell structure, with a shell thickness of about 200 nm. Furthermore, it not only exhibited high catalytic activity, but remarkably, it could also be easily recovered magnetically and recycled without obvious loss of catalytic efficiency after three cycles.

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1. Introduction

Knoevenagel condensation between a C=O group and an activated methylene group is one of the most useful carbon-carbon bond coupling reactions used to prepare several important chemical intermediates for the pharmaceutical industry. In general, organic bases or Lewis acid catalysts in a homogeneous system effectively catalyze this reaction. However, it is difficult to reuse homogeneous catalysts and their utilization leads to a number of environmental problems. The utilization of a heterogeneous catalyst instead of the homogeneous counterpart is a promising way to overcome these problems. Some important advantages of heterogeneous systems over homogeneous counterparts are their easier handling, sim-

ple workup and recyclability [1]. For this reason, several alternative heterogeneous catalysts have been successfully applied in Knoevenagel condensation, such as zeolites [1,2], nitrogen containing carbons [3], organically functionalized mesoporous silica [4] and metal organic frameworks [5].

In the last decade, metal organic frameworks (MOFs) have attracted considerable attention for heterogeneous catalysis because of the ability to tailor the pore size and chemical functionality over a wide range [6,7]. Although it has been well proven that nanosized porous materials exhibit better catalytic efficiency because of less diffusion limitations, their complete separation from the reaction mixture is not easy. Magnetic separation based on magnetic nanoparticles has received considerable attention and has been used in a variety of fields,

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mainly because of easy separation and locations. The integration of MOFs with magnetic nanoparticles could facilitate their recovery and separation. Attempts to use this strategy have been published very recently [8–13]. Fe₃O₄ cored Cu₃(BTC)₂ magnetic microspheres have been prepared using a versatile step-by-step assembly strategy [8]. Zhang *et al.* [13] prepared Fe₃O₄ cored IRMOF-3 magnetic microspheres and tested their catalytic activities in Knoevenagel condensation reactions. The specific activity of IRMOF-3 in the microspheres was higher than the pure IRMOF-3, which having larger particles, probably because of lower diffusion of the reactants in the nanosized shell [13]. Although the Fe₃O₄ cored MOFs magnetic microspheres are promising alternatives for heterogeneous catalysts, reports on their preparations and applications are still limited.

The copper-based MOF Cu₃(BTC)₂ (HKUST-1) is a typical MOF with the above mentioned exceptional properties and has been intensively studied. This material forms face-centered cubic crystals that contain a three dimensional square-shaped channel system (1.0 nm × 1.0 nm) and accessible nanocavities. Moreover, coordinative vacancies on the Cu²⁺ species could be obtained by sample dehydration, which provides not only potential catalytic activity but also novel functionalized materials by surface decoration with electron rich functional groups [9,14–17]. In our initial attempt, Fe₃O₄ cored Cu₃(BTC)₂ magnetic microspheres were prepared and tested in the Knoevenagel condensation. Although it could promote the Knoevenagel condensation using the Lewis acid sites (unsaturated Cu²⁺ sites) and be recovered magnetically, an effort is still required to functionalize the porous frameworks with specific sites for higher efficiency. As reported, the coordinatively unsaturated Cu²⁺ sites could be surface decorated with electron rich functional groups to develop novel functionalized materials [9]. Recently, we published our original work on the surface modification of pure Cu₃(BTC)₂ with an amino-containing ligand. Although, as expected, its catalytic activity in Knoevenagel condensation as a heterogeneous catalyst was enhanced greatly, its separation from the reaction mixture through filtration was cumbersome [19]. Therefore, as schematically shown in Scheme 1, an amino-functionalized magnetic Cu₃(BTC)₂ with a core-shell structure was prepared and used as a magnetically separable heterogeneous catalyst for Knoevenagel condensations between benzaldehyde and ethyl cyanoacetate or ethyl acetoacetate. Importantly, this amino-containing magnetic Fe₃O₄@Cu₃(BTC)₂ not only showed high efficiency toward the Knoevenagel condensation, but could also be recovered magnetically and reused three times without obvious loss of its catalytic properties.

2. Experimental

2.1. Characterization

The powder X-ray diffraction (PXRD) patterns were recorded on Bruker D4 Endeavour with Cu K α (λ = 0.15405 nm) radiation at 40 kV and 40 mA at a scanning rate of 4°/min. Fourier transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm^{−1} on a Thermo Nicolet Nexus 470 Fou-

rier transform infrared spectrometer. Scanning electron microscopy (SEM) studies were carried out with a Quanta 3D FEG instrument. Transmission electron microscopy (TEM) studies were carried out with a Tecnai G2 F20 equipped with an LaB₆ filament at an acceleration voltage of 200 kV. A carbon-coated copper grid was used to prepare the samples. The Brunauer-Emmett-Teller (BET) surface area and pore volume were calculated from the nitrogen sorption isotherms measured at −196 °C on an ASAP 2000 system in the static measurement mode. The samples were outgassed at 120 °C for 3 h prior to the measurement.

2.2. Preparation of Fe₃O₄@[Cu₃(BTC)₂]_n

The Fe₃O₄ nanospheres were synthesized by a solvothermal method as reported previously [20]. In a typical preparation, a solution containing FeCl₃·6H₂O (2.7 g, 10 mmol), NaAc (5.7 g, 70 mmol) and 50 mL of ethylene glycol was stirred for 1 h at 50 °C, and then the mixture was placed in an autoclave and heated to 200 °C for 8 h. After cooling, the black magnetic microspheres were magnetically collected, followed by washing with ethanol. The solid was dried at 60 °C in an oven and denoted as Fe₃O₄.

Then, 3 g of as-prepared Fe₃O₄ was dispersed into 240 mL of an ethanol solution of mercaptoacetic acid (1.74 mmol/L). The product was magnetically collected and washed with distilled water and ethanol. The obtained solid (denoted as MAA-Fe₃O₄) was re-dispersed in ethanol. The process for the preparation of Fe₃O₄@[Cu₃(BTC)₂]_n is schematically shown in Scheme 1. First, 3.0 g of MAA-Fe₃O₄ was dispersed in 240 mL of Cu(CH₃COO)₂·H₂O ethanol solution (10 mmol/L). After stirring for 30 min at 70 °C, the solid was magnetically separated from the solution and re-dispersed in 240 mL of benzenetricarboxylic acid (H₃BTC) ethanol solution (10 mmol/L). The solid was magnetically collected again after stirring for 1 h at 70 °C. After a given number of cycles, the samples were washed with ethanol and dried under vacuum at 100 °C. The resulting composite materials were abbreviated as Fe₃O₄@[Cu₃(BTC)₂]_n according to their cycle numbers.

2.3. Surface modification of Fe₃O₄@[Cu₃(BTC)₂]₂₅ with 3-aminopropyltriethoxysilane

Amino-functionalized Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂ was prepared by surface grafting using 3-aminopropyltriethoxysilane (APS) as the modifier. As illustrated in Scheme 1, typically, 0.1 g of Fe₃O₄@[Cu₃(BTC)₂]₂₅ was dehydrated at 120 °C under vac-

Scheme 1. Preparation procedure for Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂ composite material.

uum for 4 h and then 1 mL of APS in dry toluene (50 mL) was added. The resultant mixture was heated to reflux under N₂ for 24 h, during which the amino groups were grafted onto the supports. After being cooled, magnetically separated and washed thoroughly with toluene and ethanol, the solid was dried under vacuum at 60 °C overnight to give Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂.

2.4. Knoevenagel condensation

The reaction was performed in a 25-mL round bottom flask with a magnetic stirrer. Typically, an amount of catalyst (0.21 mmol -NH₂, 3%) and 8 mmol of benzaldehyde were mixed in 5 mL of solvent. After temperature adjustment under nitrogen, the reaction was started by adding 7 mmol of ethyl cyanoacetate. The conversion of ethyl cyanoacetate was periodically analyzed by gas chromatography (GC-2010 plus, Shimadzu) equipped with Rxi@-1 capillary column (30 m × 0.25 mm × 0.5 μm) and flame ionization detector (FID).

The reusability of the magnetic catalysts was tested. The catalyst was magnetically recovered and washed with ethanol (3 × 5 mL). Then it was reused directly without further purification for the next run with fresh benzaldehyde and ethyl cyanoacetate. It was used for three consecutive runs.

To test whether the reaction is a heterogeneous process, a hot filtration test was carried out. The reaction was conducted and monitored as described above, but the catalyst was magnetically removed after 30 min.

3. Results and discussion

Magnetic Fe₃O₄ nanoparticles were first prepared from FeCl₃·H₂O with ethylene glycol as reducing agent and sodium acetate (NaAc) as stabilizer in a solvothermal reaction [20]. Fe₃O₄@Cu₃(BTC)₂ composites were synthesized using a step-wise assembly strategy described by Ke et al. [8]. The crystal nature and composition of the as-synthesized materials were first characterized by PXRD and the results are summarized in Fig. 1. The PXRD patterns of naked (Fig. 1(1)) and parceled (Fig. 1(2)–(5)) Fe₃O₄ nanoparticles all present characteristic peaks at 2θ = 30.1°, 35.5°, 43.1°, 53.4°, 57.0° and 62.6°, corresponding to the (220), (311), (400), (422), (511) and (440) planes, respectively. This indicates that the particles were pure Fe₃O₄ with a spinel structure and its crystal phase remained intact during the parceling process. In particular, as shown in Fig. 1(2)–(5), the Fe₃O₄@[Cu₃(BTC)₂]_n exhibit both characteristic peaks of Fe₃O₄ and Cu₃(BTC)₂, revealing the co-existence of Fe₃O₄ and Cu₃(BTC)₂ in the composite materials. It can also be observed that the peak intensities indexed to Cu₃(BTC)₂ increase with the wrapping steps. Furthermore, the weak and broad diffraction peaks of Cu₃(BTC)₂ confirmed the formation of nanosized Cu₃(BTC)₂ crystals on the surface of the magnetic particles, and the size was estimated to be approximately 26 nm by applying the Scherrer formula on the diffraction peaks of Cu₃(BTC)₂. Post-modification of Fe₃O₄@[Cu₃(BTC)₂]₂₅ with APS under mild condition was done to widen its catalytic applications. As expected, their XRD pat-

Fig. 1. PXRD patterns of Fe₃O₄@[Cu₃(BTC)₂]_n and Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂ materials. (1) Fe₃O₄; (2) Fe₃O₄@[Cu₃(BTC)₂]₅; (3) Fe₃O₄@[Cu₃(BTC)₂]₁₅; (4) Fe₃O₄@[Cu₃(BTC)₂]₂₅; (5) Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂.

terns (Fig. 1(4) and (5)) were very similar before and after modification, indicating the structure of Fe₃O₄@[Cu₃(BTC)₂]₂₅ remained intact.

Although PXRD results demonstrated that the nanocomposites were composed of Fe₃O₄ nanoparticles and Cu₃(BTC)₂, it did not confirm if the nanocomposite is a real Fe₃O₄@[Cu₃(BTC)₂]_n nanocomposite or just a physical mixture of two separate phases of Fe₃O₄ and Cu₃(BTC)₂. To gain further insight into the microstructure of the as-synthesized Fe₃O₄@Cu₃(BTC)₂ nanocomposites, the materials were further characterized by SEM and TEM techniques. Representative SEM (Fig. 2(a)) and TEM (Fig. 2(d)) images reveal that the prepared Fe₃O₄ nanoparticles were spherical in shape and had a diameter distribution of around 100–600 nm. As expected and shown in Fig. 2(e), the TEM image of the formed nanocomposites clearly show core-shell structures with Fe₃O₄ as the core and Cu₃(BTC)₂ as the shell. The thickness of the shell is about 200 nm after 25 assembly cycles. No obvious structural change was observed after surface modification when comparing their SEM and TEM images (Fig. 2(b)–(c) and 2(e)–(f)). The amino-group content in Fe₃O₄@Cu₃(BTC)₂-NH₂ calculated from SEM-EDS results is approximately 2.1 mmol/g (Fig. 3). It can be concluded that Cu₃(BTC)₂ was successfully wrapped on the

Fig. 2. SEM (a–c) and TEM (d–f) images of different materials. (a, d) Fe₃O₄; (b, e) Fe₃O₄@[Cu₃(BTC)₂]₂₅; (c, f) Fe₃O₄@[Cu₃(BTC)₂]₂₅-NH₂.

Fig. 3. SEM-EDS image of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$.

surface of the Fe_3O_4 nanoparticles and the amount of $\text{Cu}_3(\text{BTC})_2$ could be controlled by the number of wrapping cycles.

Fig. 4 shows the FT-IR spectra of the bare Fe_3O_4 and $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$, as well as the amino-functionalized sample. Typical peaks at 580 cm^{-1} for naked Fe_3O_4 originated from the symmetric stretching of Fe-O-Fe . Features at 1620 , 1560 and 1720 cm^{-1} are ascribed to the benzene skeleton vibration and the stretching vibration of the C=O of the ligands in $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$. After the introduction of amino groups, typical peaks at 3440 and 3490 cm^{-1} corresponding to the symmetric and asymmetric stretching of primary amines as well as typical peaks at 2920 and 2845 cm^{-1} associated with C-H vibrations were observed. This results confirm the introduction of amino-containing ligands onto $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$. The amino group should be attached to the $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$ through a coordination mode. Both amino and methoxy groups in the APS molecule competitively play a role as possible coordination sites to the coordinatively unsaturated Cu^{2+} sites.

The N_2 adsorption-desorption experiments were used to verify the porous structure of the hybrid materials as well as to calculate their surface area and pore volumes. As shown in Fig. 5, the completely reversible isotherm of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$ exhibited Type-I behavior, typical for microporous materials.

Fig. 4. FT-IR spectra of different materials. (1) Fe_3O_4 ; (2) $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$; (3) $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$.

Fig. 5. N_2 adsorption-desorption isotherms of different materials measured at $-196\text{ }^\circ\text{C}$. (1) Fe_3O_4 ; (2) $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$; (3) $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$.

For comparison, the BET surface area and pore volumes are summarized in Table 1. The BET surface area of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$ is $462\text{ m}^2/\text{g}$ and the total pore volume is $0.38\text{ cm}^3/\text{g}$, which were comparable to those reported by Ke et al. [8]. The amino-modified sample $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ exhibited a significant decrease in both surface area and pore volume. The BET surface area decreased significantly from $462\text{ m}^2/\text{g}$ to $129\text{ m}^2/\text{g}$, and the total pore volume decreased from $0.38\text{ cm}^3/\text{g}$ to $0.16\text{ cm}^3/\text{g}$, after amino-ligand grafting. Obviously, the decreases are caused by the inclusion of APS into the nanocages. Similar results were also observed for the surface modification of pure $\text{Cu}_3(\text{BTC})_2$ in our original work [19].

Knoevenagel condensation has been employed as a classic test reaction to analyze the activity of a variety of solid base catalysts. Therefore, the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate was selected as a model reaction to evaluate the catalytic activity of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$. Solvent polarity has strong effects on the catalytic Knoevenagel reactions [18,21–24]. To establish the solvent effects for $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$, the reaction was carried out in a variety of organic solvents and the results are summarized in Table 2. The highest activity of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ was found in DMSO, which had the highest dielectric constant ($\epsilon = 48.9$). Conversion of ethyl cyanoacetate in dimethyl sulfoxide (DMSO) was 97% after 1 h (Table 2, Run 6). Ethanol (a protic solvent, $\epsilon = 24.3$) was also found to be a good medium and the conversion of ethyl cyanoacetate was 84% after 1 h (Table 2, Run 7) under the same

Table 1
Textural properties of different materials.

Material	BET surface area (m^2/g)	Total pore volume (cm^3/g)
Fe_3O_4	129	0.28
$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$	462	0.38
$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$	129	0.16
$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2^a$	53	0.07
$\text{Cu}_3(\text{BTC})_2$	1088	0.70
$\text{Cu}_3(\text{BTC})_2\text{-NH}_2^b$	139	0.15

^a Recovered materials from the reaction mixture.

^b Prepared according to Ref. [18].

conditions. By contrast, much lower activities were found in tetrahydrofuran (THF) ($\epsilon = 7.5$), toluene ($\epsilon = 2.4$) and hexane ($\epsilon = 1.9$), indicating that the aprotic and less polar solvents are not good media for this reaction. For example, conversion of ethyl cyanoacetate was only 8% after 1 h in the presence of hexane (Table 2, Run 8). The results above are consistent with the reported conclusions that the polarity of the media has a strong effect on the reaction route and reaction rate of the Knoevenagel condensation reaction [18,21–24]. As reported, the reaction rate for the IRMOF-3 catalyzed Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate was much higher in polar solvents than in nonpolar solvents [18]. A similar effect was also observed for the amino-containing silica catalyzed reaction [4]. The strong difference in activity is probably because of the polarity and amphiprotic properties of the solvents. The polar solvents could stabilize the carbanion intermediate and their amphiprotic properties could favor the electrophilic polarization of the carbonyl group in benzaldehyde [22]. All results above demonstrated that amino-tagged MOFs performed better in highly polar solvents or protic solvents.

As reported, the Knoevenagel condensation is a modification of an aldol condensation and the mechanisms depend on the nature of the catalysts used [22–28]. As shown in Table 2, conversions of ethyl cyanoacetate in the absence of solid or in the presence of Fe_3O_4 were only 33% and 31% after 2 h, respectively (Table 2, Run 1–2). Conversion of ethyl cyanoacetate in the presence of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]$ was 56% after 2 h (Entry 5) because of the Cu(II) centers (Lewis acid sites). As expected, conversion of ethyl cyanoacetate in the presence of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ was 92% after 2 h (Table 2, Run 6). Similarly, $\text{Cu}_3(\text{BTC})_2\text{-NH}_2$ was also much more active than $\text{Cu}_3(\text{BTC})_2$ (Run 3–4) observed in our original work [19]. Obviously, the introduction of amino groups into the materials leads

Table 2

Results of Knoevenagel reactions in different organic solvents.

Run	Material	Solvent (Dielectric constant)	<i>t</i> (h)	<i>X</i> ^c (%)
1	Blank	Ethanol (24.3)	2	33
2	Fe_3O_4	Ethanol (24.3)	2	31
3	$\text{Cu}_3(\text{BTC})_2$	Ethanol (24.3)	2	56
4	$\text{Cu}_3(\text{BTC})_2\text{-NH}_2^a$	Ethanol (24.3)	2	90
5	$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}$	Ethanol (24.3)	2	57
6	$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$	DMSO ^b (48.9)	1	97
7		Ethanol (24.3)	2 (1)	92 (84)
8		Hexane (1.9)	1	8
9		THF (7.5)	1	52
10		Toluene (2.4)	1	6
11	APS	Ethanol	1	77
12	Blank	DMSO (48.9)	1	23

Reaction conditions: 8 mmol benzaldehyde, 7 mmol ethyl cyanoacetate, and the desired amount of catalyst (0.21 mmol -NH_2 , 3% or 0%) in 5 mL of solvent at 80 °C. ^a $\text{Cu}_3(\text{BTC})_2\text{-NH}_2$ was prepared according to Ref. [18]. ^b 20 mg of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ (0.04 mmol -NH_2 , 0.6%). ^c Conversion of ethyl cyanoacetate.

to an appreciable increase of their activity for the Knoevenagel condensation. Previous studies have shown that the reaction proceeds via aldimine intermediates for amino-based catalysts [4,26,27]. As illustrated in Scheme 2, two nucleophilic addition-elimination processes are involved in the presence of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$. First, an aldimine intermediate at the catalyst surface formed from the amino group and the aldehyde. The formation is facilitated by the Cu(II) because the C=O bond is polarized by the Lewis acid site [26]. Subsequently, the product is formed from the second addition-elimination processes between the methylene and aldimine group. The bifunctional character could be used to explain the high activity of $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ for the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate. Actually, compared to the homogeneous system using APS as the catalyst (Table 2, Run 11), the magnetically separable heterogeneous catalyst $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ had better catalytic performance (Table 2, Run 7) in the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate, probably because of the cooperative effect between the Lewis acid site (Cu^{2+}) and the amino group (-NH_2). Similarly, IRMOF-3 was also reported to yield higher conversion rates than the homogeneous analogue aniline in the Knoevenagel condensation [18].

When a solid catalyst is used for liquid-phase reactions, an issue of great concern is whether the catalytic process is heterogeneous or homogeneous. In the latter case, species that have leached into the liquid phase are partially or fully responsible for the observed catalytic activity. This is practically undesirable. To show that the reaction is catalyzed heterogeneously by the MOF itself rather than soluble components leached from the materials, a hot filtration experiment was carried out. After the reaction proceeded at 80 °C for 30 min, the catalyst was removed magnetically. The filtrate was further heated at the same temperature and the composition was monitored at given time intervals. The results are showed in Fig. 6 together with those obtained for the reaction under the same conditions but without the filtering step. Clearly, no appreciable reaction took place after removal of the catalyst. The above experimental results distinctly showed that no active species leached into the liquid phase and provides direct evidence for the heterogeneity

Scheme 2. Generalized mechanism for the Knoevenagel condensation reaction of benzaldehyde and ethyl cyanoacetate catalyzed by $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$.

Fig. 6. Hot filtration reactions. (1) Normal reaction process in ethanol; (2) $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ was removed from the reaction mixture after 0.5 h.

of the present catalyst system.

Apart from good catalytic activity and selectivity, long-term stability is an important criterion for solid catalysts. As mentioned above, the best activity was found in DMSO. Therefore, to check the stability for $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$, the catalyst was recycled for the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate in DMSO (Table 3). After each cycle, the solid was magnetically separated, washed with DMSO and then reused in the next cycle. The conversion in the second run (Table 3, Run 2) was much lower than the first run (Table 3, Run 1), and the PXRD patterns (Fig. 7(3)) of the recovered catalyst demonstrate that its crystal structure was completely destroyed by the reaction process, with only a broad peak evident between 5° – 30° . Its SEM image (Fig. 8(b)) also confirms the disappearance of the shell, probably resulting from metal–DMSO coordination. Ethanol was chosen as an alternative solvent for recyclability (Table 3, Run 3–5). It is noteworthy that, as we expected, the catalyst activity is stable during the recycle reaction, and the stability of the structure was further confirmed by PXRD (Fig. 7(2)), SEM (Fig. 8(c)) and TEM (Fig. 8(d)). The catalyst could be recovered magnetically from the reaction medium and recycled three times without obvious loss of the activity and selectivity. The minor loss of the activity is probably owing to the loss of solid during the separation, rather than from the leaching of the amino groups from the support. Thus, a sacrificial balance between activity and recyclability needs to be made.

Table 3

Recycle results of Knoevenagel reaction by $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ in DMSO and ethanol.

Run	Catalyst	Cycle	Solvent	t (h)	X^c (%)
1	$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2^a$	1st	DMSO	1	97
2		2nd		1	62
3	$\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2^b$	1st	Ethanol	2	92
4		2nd		2	88
5		3rd		2	80

Reaction conditions: ^a 0.02 g $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ (0.04 mmol -NH_2 , 0.6%); ^b 0.1 g $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ (0.21 mmol -NH_2 , 3%), 8 mmol benzaldehyde and 7 mmol ethyl cyanoacetate in 5 mL of DMSO or ethanol, 80°C . ^c conversion of ethyl cyanoacetate.

Fig. 7. PXRD patterns of fresh and recovered $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$. (1) Fresh; (2) Recovered from reaction in ethanol; (3) Recovered from reaction in DMSO.

4. Conclusions

In this work, a novel core-shell structured $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ material was successfully fabricated as active solid base catalysts for Knoevenagel condensation. Core-shell structure was confirmed by PXRD and TEM techniques, its composition was confirmed by SEM-EDS and the amine functionality was confirmed using FT-IR spectroscopy. The core-shell $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$ material is ideal recyclable catalysts for Knoevenagel condensation by combining a superparamagnetic core for efficient magnetic separation and a porous MOF shell for high catalytic activity. The remarkable activity for Knoevenagel condensation reactions is ascribed to the presence of amino groups as well as Lewis acid copper ions in $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$. Obvious solvent effects on the conversion and stability were observed and ethanol was selected as a good medium providing a balance between activity

Fig. 8. SEM (a–c) and TEM (d) images for fresh and recovered $\text{Fe}_3\text{O}_4@[\text{Cu}_3(\text{BTC})_2]_{25}\text{-NH}_2$. (a) Fresh; (b) Recovered from reaction in DMSO; (c, d) Recovered from reaction in ethanol.

Graphical Abstract

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Fabrication of amino-functionalized $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ for heterogeneous Knoevenagel condensation

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Amino-functionalized magnetic metal organic frameworks ($\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2\text{-NH}_2$) were fabricated through a stepwise assembly method and used as an effective heterogeneous base catalyst in Knoevenagel condensation.

and recyclability. The catalyst could be easily separated from the reaction mixture and reused without significant change in the catalytic activity after three reaction cycles.

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氨基化磁性 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 材料的合成及其在 Knoevenagel 缩合中的催化性能

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摘要: 金属有机骨架材料具有大比表面积、高孔隙率、热稳定性好、规整且可调控的孔结构、易于功能化的骨架金属离子和有机配体等优点, 是制备多相催化剂的重要材料之一。虽然减小金属有机骨架材料等多孔材料的粒径可以提高反应物的传质效率, 从而提高其催化活性; 但是, 纳米尺寸催化剂的分离和回收困难。将磁性纳米粒子和金属有机骨架材料结合制备具有核-壳结构的磁性金属有机骨架材料是解决上述问题的有效方法。此类材料兼具磁性材料和金属有机骨架材料

的双重优势,既可以磁性分离,又具有金属有机骨架材料的催化活性.而且,厚度可控的壳层材料表现出与纳米催化剂相当甚至更好的催化活性.我们采用逐层自组装方法制备了核-壳结构的磁性 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 复合材料,并对材料进行氨基化修饰,制备了基于金属有机骨架材料的磁性多相碱催化剂.采用粉末X射线衍射(XRD)、傅里叶变换红外光谱(FT-IR)、透射电镜(TEM)、扫描电镜(SEM)、氮气吸附等方法对材料的组成和结构进行了表征,并考察了材料在Knoevenagel缩合反应中的催化性能.

首先采用粉末XRD表征材料的晶体结构.在复合材料 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 的XRD谱中,同时出现了 Fe_3O_4 和 $\text{Cu}_3(\text{BTC})_2$ 的特征衍射峰.采用氨基配体修饰后,材料的XRD谱没有明显变化,说明修饰后的材料保持了 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 的晶体结构.透射电镜结果表明,包裹25次得到的磁性复合材料 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 是以 Fe_3O_4 为核心,以 $\text{Cu}_3(\text{BTC})_2$ 为壳的核-壳结构,壳层厚度大约为200 nm.氨基修饰后,材料的透射电镜图相对修饰前无明显变化.扫描电镜结果表明,合成的 Fe_3O_4 为球形结构,粒径为100–600 nm.采用 $\text{Cu}_3(\text{BTC})_2$ 进行包裹后,在 Fe_3O_4 表面生长了由 $\text{Cu}_3(\text{BTC})_2$ 纳米颗粒组成的壳层.采用氨基配体修饰后,材料的形貌无明显改变.进一步采用氮气吸附表征材料的孔结构并测定材料的比表面积和孔体积.结果表明,由于大比表面的 $\text{Cu}_3(\text{BTC})_2$ 的引入,复合材料 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 的比表面积增大为 $462 \text{ m}^2/\text{g}$,孔体积为 $0.38 \text{ cm}^3/\text{g}$.氨基修饰后,材料的比表面积和孔体积都有较大程度的降低,说明配体分子占据了壳层材料 $\text{Cu}_3(\text{BTC})_2$ 中的纳米孔道.

采用苯甲醛和氰基乙酸乙酯的Knoevenagel缩合反应作为模型,考察了材料的催化活性.研究发现, Fe_3O_4 对此反应几乎没有活性, $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 给出了中等的催化活性.在材料上引入氨基后,由于氨基和 $\text{Cu}_3(\text{BTC})_2$ 上的Lewis酸性位点的协同效应,在很大程度上提高了材料的催化活性.溶剂效应实验结果表明,反应溶剂对材料的活性和选择性具有较大影响,极性或质子性溶剂有利于反应的进行.多相催化剂的循环稳定性是其重要评价指标之一.热过滤实验结果表明,滤液中无催化活性,反应中的催化活性来源于固体材料,此催化反应为多相催化.随后考察了材料的循环稳定性.虽然氨基化 $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2$ 材料在溶剂DMSO中表现出最高的催化活性,但XRD和电镜表征结果表明,材料在DMSO中结构遭到破坏,因此循环过程中催化剂的活性损失严重.然后考察了氨基化材料在乙醇中的循环稳定性,发现材料在乙醇中表现出较好的循环稳定性.通过简单磁性分离进行催化剂的分离和回收,催化剂循环使用3次而没有明显的活力损失.而且,XRD和电镜表征结果显示,催化剂的结构在反应过程中没有遭到明显破坏.

关键词: 四氧化三铁; 金属有机骨架材料; 多相催化剂; Knoevenagel缩合反应; 磁性分离

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