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Article

Fe₃O₄@UiO-66-NH₂ core-shell nanohybrid as stable heterogeneous catalyst for Knoevenagel condensation

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ABSTRACT

Magnetic separation is an attractive alternative to filtration or centrifugation for separating solid catalysts from a liquid phase. Here, core-shell Fe₃O₄@UiO-66-NH₂ nanohybrids with well-defined structures were constructed by dispersing magnets in a dimethylformamide (DMF) solution containing two metal-organic framework (MOF) precursors, namely ZrCl₄ and 2-aminobenzenetricarboxylic acid. This method is simpler and more efficient than previously reported step-by-step method in which magnets were consecutively dispersed in DMF solutions each containing one MOF precursor, and the obtained Fe₃O₄@UiO-66-NH₂ with three assembly cycles has a higher degree of crystallinity and porosity. The core-shell Fe₃O₄@UiO-66-NH₂ is highly active and selective in Knoevenagel condensations because of the bifunctionality of UiO-66-NH₂ and better mass transfer in the nano-sized shells. It also has good recycling stability, and can be recovered magnetically and reused at least four times without significant loss of catalytic activity and framework integrity. The effects of substitution on the reactivity of benzaldehyde and of substrate size were also investigated.

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1. Introduction

Metal-organic frameworks (MOFs) are crystalline porous materials. They have attracted much attention because of their characteristics such as well-defined porosities, high surface areas, and chemical stabilities [1,2]. MOFs are promising materials for various technological applications, including gas storage [3], separation [4], drug delivery [5], and chemical sensing [6]. In recent years, MOFs have been shown to have potential applications as heterogeneous catalysts [7–9].

The efficient separation and recycling of catalysts is a major objective of sustainable and green chemistry. Heterogeneous catalysts have a number of significant advantages over homo-

geneous ones because they are easily recoverable, reusable, and waste is minimized. Filtration or centrifugation are widely used to separate solid catalysts from the liquid phase, but these methods are cumbersome, especially when the catalyst particle sizes are in the sub-micrometer to micrometer range; these are more active than bulk catalysts because mass transfer is less limited [10]. Magnetic separation of catalysts is an attractive alternative to filtration or centrifugation.

Recently, many attempts have been made to integrate MOFs with magnets to facilitate their separation using an external magnetic field [11–16]. Ke et al. [12,14] reported the preparation of a novel type of porous core-shell microspheres with a magnetic core and a designable MOF shell using a versatile

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step-by-step assembly strategy; the porous $\text{Fe}_3\text{O}_4@\text{MIL-100}$ had good catalytic activity and recyclability in Claisen–Schmidt condensations. Although considerable progress has been made in the synthesis of such magnetic nanohybrids, their use as heterogeneous catalysts still needs to be explored. Recently, Zhang et al. [15,16] reported the preparations of $\text{Fe}_3\text{O}_4@\text{IRMOF-3}$ and $\text{Fe}_3\text{O}_4@\text{Cu}_3(\text{BTC})_2\text{-NH}_2$ core-shell nanohybrids and their catalytic performances in Knoevenagel condensations. These nanohybrids were active and selective, but their structures were damaged during recovery after the reaction. It is therefore necessary to select stable MOFs as the shell. Numerous MOFs have been reported to date; of these, UiO-66 and its amino-substituted analogue UiO-66- NH_2 , synthesized using ZrCl_4 as the metal source, are highly stable [17–20]. The synergistic action of the Lewis sites and base groups in UiO-66- NH_2 is needed to achieve optimum performance in Knoevenagel condensation and cross-aldol reactions [20,21].

Recently, $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2$ was prepared using a step-by-step method by dispersing Fe_3O_4 consecutively in dimethylformamide (DMF) solutions of ZrCl_4 or 2-aminobenzenetricarboxylic [22]. However, the powder X-ray diffraction (PXRD) patterns of the resulting $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2$ showed only a broad peak between 5° and 10° because of the poor degree of crystallinity of UiO-66- NH_2 . Activity loss was observed during recycling experiments because of partial destruction of its porosity.

In this study, $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2$ core-shell nanohybrids were prepared using a simpler and more efficient method and were evaluated as heterogeneous catalysts for Knoevenagel condensations. A schematic diagram of the procedure is shown in Scheme 1. The core-shell nanohybrids were highly active and selective in Knoevenagel condensations because UiO-66- NH_2 is bifunctional and mass transfer in the shell is less limited. The core-shell hybrid material $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2\text{-3}$ prepared using three assembly cycles with well-defined structure and high porosity showed good recycling stability. It was recovered magnetically and reused at least four times without significant loss of catalytic activity and framework integrity.

2. Experimental

2.1. Preparation of $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2$ core-shell nanohybrid material

As shown in Scheme 1, the magnetic nanohybrid was prepared using a step-by-step assembly method. The first step involved modification of Fe_3O_4 nanospheres with polyacrylate

sodium salt (PASS), and the second step was assembly of $\text{Fe}_3\text{O}_4@\text{PASS}$ nanospheres and MOF precursors. The Fe_3O_4 nanospheres were synthesized using a previously reported solvothermal method [16]. In a typical synthesis, the prepared Fe_3O_4 (1 g) was added to an aqueous solution of PASS ($M_r = 3000$, 1.6%, 60 mL) and the mixture was shaken for 24 h. The solid product (denoted by $\text{Fe}_3\text{O}_4@\text{PASS}$) was collected using a magnet and washed with distilled water and DMF. $\text{Fe}_3\text{O}_4@\text{PASS}$ (0.35 g) was dispersed in a DMF solution (80 mL) containing ZrCl_4 (20 mmol) and 2-aminobenzenetricarboxylic acid (20 mmol). The solid was collected magnetically after stirring for 4 h at 120°C and then redispersed in a fresh solution containing the two reagents in the concentrations indicated above. After one to three assembly cycles, the samples were collected magnetically, washed with ethanol, and dried under vacuum at 100°C . The resultant nanohybrid materials were denoted by $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2\text{-}n$, where n is the number of assembly cycles.

2.2. Characterization

PXRD patterns were recorded using a Bruker D4 Endeavour with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405\text{ nm}$) at 40 kV and 40 mA. Infrared (IR) spectra were recorded using a Thermo Nicolet Nexus 470 Fourier-transform IR spectrometer. Scanning electronic microscopy (SEM) was performed using a Quanta 3D FEG instrument. Transmission electron microscopy (TEM) was performed using a Tecnai G2 F20 instrument at an accelerating voltage of 200 kV with a LaB6 filament; samples were prepared by placing a drop of a colloidal solution on a carbon-coated copper grid and evaporating the solvent in air at room temperature. Nitrogen sorption isotherms were recorded at -196°C using an ASAP 2000 system in static mode. The samples were out-gassed at 120°C for 3 h prior to the measurements.

2.3. Knoevenagel condensation

Knoevenagel reactions were performed in a 25-mL round-bottomed flask equipped with a magnetic stirrer. In a typical experiment, a desired amount of catalyst (0 or 3% $-\text{NH}_2$) and benzaldehyde (8 mmol) were mixed in DMF (5 mL). The flask was placed in an oil bath that had been preheated to 80°C . The reaction was started by adding ethyl cyanoacetate (7 mmol) to the flask. The reaction was monitored using a gas chromatograph (GC-2010 plus, Shimadzu) equipped with an Rxi@-1 capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.5\text{ }\mu\text{m}$) and a flame ionization detector. The temperature program for gas chromatography was as follows: 50°C for 5 min, $10^\circ\text{C}/\text{min}$ to 250°C , and 5 min at 250°C .

Scheme 1. Preparation of $\text{Fe}_3\text{O}_4@\text{UiO-66-NH}_2$ composite.

graphic analysis was set as follows: the temperature was held at 150 °C for 5 min, then raised to 180 °C at 30 °C/min and held for 15 min. The inlet and detector temperatures were 280 °C. The analysis was performed directly after sampling to avoid any additional conversion. In the recycling experiments, the catalyst was recovered magnetically when the reaction was finished, washed with DMF (3 × 5 mL), and reused directly without further purification for the next run with fresh benzaldehyde and ethyl cyanoacetate. The catalyst was used for four consecutive runs.

3. Results and discussion

3.1. Synthesis and characterization

Magnetic nanohybrids were prepared using a self-assembly method by dispersing magnets in a DMF solution containing two MOF precursors, i.e., ZrCl_4 and 2-aminobenzenetricarboxylic acid. Polyacrylate sodium chains in this composite acted as a bridge, connecting the internal Fe_3O_4 and external UiO-66- NH_2 layer. The crystallinities and compositions of the synthesized materials were investigated using PXRD; the results are shown in Fig. 1. The Fe_3O_4 @PASS pattern had intense reflections at $2\theta = 30.1^\circ$, 35.5° , 43.1° , 53.4° , and 57.0° ; these are typical of Fe_3O_4 (JCPDS 19-0629) and correspond to the (220), (311), (400), (422), and (511) planes, respectively [12,22]. Fe_3O_4 @UiO-66- NH_2 prepared using two or three cycles had additional intense reflections at 2θ between 5° – 60° , which are typical of UiO-66- NH_2 and confirm the formation of highly crystalline UiO-66- NH_2 on the magnetic nanoparticles [17,18]. However, in our previous work, only a broad peak between 5° and 10° was observed in the PXRD pattern of Fe_3O_4 @UiO-66- NH_2 prepared by dispersing magnets consecutively in DMF solutions each containing only one of the MOF precursors [22].

The PXRD results showed that the nanohybrids consisted of Fe_3O_4 nanoparticles and UiO-66- NH_2 , but we needed to determine whether the nanohybrids were Fe_3O_4 @UiO-66- NH_2

Fig. 3. N_2 adsorption-desorption isotherms of Fe_3O_4 @PASS (1), Fe_3O_4 @UiO-66-NH₂-1 (2), Fe_3O_4 @UiO-66-NH₂-2 (3), and Fe_3O_4 @UiO-66-NH₂-3 (4).

Table 2
Textural properties of materials.

Material	Shell thickness (nm)	BET surface area (m ² /g)	Total pore volume (mL/g)
Fe_3O_4	0	129	0.28
Fe_3O_4 @UiO-66-NH ₂ -1	< 50	44	0.11
Fe_3O_4 @UiO-66-NH ₂ -2	100	128	0.20
Fe_3O_4 @UiO-66-NH ₂ -3	150–200	342	0.31
Fe_3O_4 @UiO-66-NH ₂ -3*	150–200	356	0.29

* Recovered Fe_3O_4 @UiO-66-NH₂-3 after the Knoevenagel condensations in DMF.

creasing number of assembly cycles. The BET surface area increased from 44 to 342 m²/g, and the total pore volume increased from 0.11 to 0.31 mL/g. For comparison, a composite was also prepared using the step-by-step method described by Ke et al. [12,22], in which the two components of UiO-66-NH₂ were added separately. The BET surface area of the composite was only 121 m²/g, and the total pore volume was 0.11 mL/g, even after 10 steps. The method in which the two components of UiO-66-NH₂ are added together is clearly more efficient for core-shell nanocomposite production.

3.2. Catalyst activity

The catalytic activities were tested by performing liquid-phase Knoevenagel condensations of benzaldehyde and ethyl cyanoacetate in the presence of Fe_3O_4 @UiO-66-NH₂ or nano-sized UiO-66-NH₂. The results are summarized in Table 3. All the Fe_3O_4 @UiO-66-NH₂ samples had high activities in this reaction. In blank experiments, yields less than 22% were obtained in 2 h (Table 3, entries 1 and 2). When nano-sized UiO-66-NH₂ (particle size less than 100 nm) was used, 80.3% of yield was achieved in 1 h, with a turnover frequency (TOF) of 26.8 h^{−1}. The activities of Fe_3O_4 @UiO-66-NH₂ and nano-sized UiO-66-NH₂ (with equivalent amounts of UiO-66-NH₂) were compared under identical conditions. The TOFs and selectivities of all the core-shell magnetic MOFs were comparable to or higher than those of nano-sized UiO-66-NH₂.

Fig. 4 shows the time courses of product formation using

Table 3
Knoevenagel condensation results.

Catalyst	<i>t</i> (h)	Yield (%)	TOF (h ^{−1})	Selectivity (%)
No	2	20.7	—	52.7
Fe_3O_4 (55.8 mg)	2	21.4	—	50.8
UiO-66 (58.3 mg)	1	42.3	—	86.4
UiO-66-NH ₂ (61.5 mg)	1	80.3	26.8	98.7
Fe_3O_4 @UiO-66-NH ₂ -1 (437.4 mg)	1	86.6	28.9	98.3
Fe_3O_4 @UiO-66-NH ₂ -2 (117.3 mg)	1	84.8	28.3	99.1
Fe_3O_4 @UiO-66-NH ₂ -3 (76.9 mg)	1	73.2	24.4	97.9

Reaction conditions: 8 mmol benzaldehyde, 7 mmol ethyl cyanoacetate, and desired amount of catalysts (0 or 0.21 mmol −NH₂, 0 or 3%) in 5 mL of DMF at 80 °C.

various Fe_3O_4 @UiO-66-NH₂-*n* nanohybrids. The shell thickness is clearly one of the crucial parameters that affect the specific activities. Fe_3O_4 @UiO-66-NH₂-1, which has a thin shell (< 50 nm), had the best activity (TOF = 28.9 h^{−1}) under identical conditions. The activity decreased with increasing shell thickness and Fe_3O_4 @UiO-66-NH₂-3, with the thickest shell (150–200 nm), had the lowest activity (TOF = 24.4 h^{−1}); this is because the diffusion efficiency in the porous material was lower in a thick shell. The data in Table 3 show that although UiO-66 was much less active than UiO-66-NH₂, the yield achieved using the NH₂-free MOF was higher (42.3% after 1 h) than that achieved in the blank non-catalytic reaction. This suggests that the Knoevenagel reaction can be promoted by Zr(IV) centers (Lewis acid sites). Yang et al. [20] recently suggested that UiO-66-NH₂ was bi-functional. The high catalytic performance of the core-shell nanohybrid in the Knoevenagel condensation is probably a result of the bi-functional character of UiO-66-NH₂ and better mass transfer in the shells.

Once we had established that Fe_3O_4 @UiO-66-NH₂ was a good catalyst for the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate, we extended the study to the condensations of various aromatic aldehydes with cyanoacetate. The results are listed in Table 4. The activity of Fe_3O_4 @UiO-66-NH₂-3 in the reaction with 4-methylbenzaldehyde

Fig. 4. Time-dependent yields for reactions between benzaldehyde and ethyl cyanoacetate in DMF at 80 °C using Fe_3O_4 @UiO-66-NH₂-1 (1), Fe_3O_4 @UiO-66-NH₂-2 (2), Fe_3O_4 @UiO-66-NH₂-3 (3), and UiO-66-NH₂ (4) as catalysts.

Table 4

Fe₃O₄@UiO-66-NH₂-3 catalyzed Knoevenagel condensations of various substrates.

Entry	Aldehyde	<i>t</i> (h)	Yield (%)
1		1.0	73.2
		2.0	98.0
2		2.0	96.2
3		0.08	64.1
		0.16	98.2
4		0.08	66.9
		0.16	97.6
5		0.08	70.6
		0.16	99.3
6		2.0	52.2
		4.0	97.4
7		2.0	32.4
		4.0	79.1

Reaction conditions: 8 mmol aromatic aldehydes, 7 mmol ethyl cyanoacetate, and 79.9 mg Fe₃O₄@UiO-66-NH₂-3 (corresponding to 0.21 mmol -NH₂, 3%) in 5 mL of DMF at 80 °C.

(Table 4, entry 2) was similar to that in the reaction with the unsubstituted benzaldehyde (Table 4, entry 1). The activities in the reactions with nitro-substituted benzaldehydes were much higher than that with benzaldehyde; $\geq 97\%$ yields were achieved in only 10 min (Table 4, entries 3–5). This reflects the accelerating effect of the strongly electron-withdrawing nitro group in reactions involving nucleophilic attack at a carbonyl group. The catalyzed reactions of the three nitro-substituted benzaldehydes proceeded readily to give $\geq 97\%$ yields in 10 min, but the initial reaction rates of these substrates were different. The initial reaction rate with 4-nitrobenzaldehyde was lower than those with the 2- and 3-isomers; the 3-isomer gave the highest reaction rate. The effect of substitution on the reactivity of benzaldehyde is similar to that observed for the Knoevenagel condensation catalyzed by UiO-66-NH₂ [20].

The catalyst was also active in the Knoevenagel reactions of larger aromatic aldehydes (1-naphthaldehyde and 9-anthraldehyde) with cyanoacetate, although the yields were lower for bulky aldehyde substrates (Table 4, entries 1, 6, and 7). The decreased yields indicate size effects. Table 4, entries 1, 6, and 7 show that the yield from the reaction of 9-anthraldehyde with ethyl cyanoacetate (2 h, 32.4%) was much lower than that for 1-naphthaldehyde (2 h, 52.2%), which was much lower than that for benzaldehyde (2 h, 98.0%). The order of the activities is benzaldehyde ($\sim 6.0 \times 4.3 \text{ \AA}^2$) > 1-naphthaldehyde ($\sim 6.0 \times 7.2 \text{ \AA}^2$) > 9-anthraldehyde ($\sim 5.9 \times 9.2 \text{ \AA}^2$). These results show that the probability of bulky substrates forming transition-state

Fig. 5. Recycling experiments using Fe₃O₄@UiO-66-NH₂-3. Reaction conditions: 24 mmol benzaldehyde, 21 mmol ethyl cyanoacetate, and 240 mg Fe₃O₄@UiO-66-NH₂-3 (0.21 mmol -NH₂, 3%) in 15 mL of DMF at 80 °C.

complexes is significantly decreased by the limited space in the porous catalyst.

In addition to catalytic activity and selectivity, long-term stability is important for solid catalysts. Although Fe₃O₄@UiO-66-NH₂-1 had the highest activity, Fe₃O₄@UiO-66-NH₂-3, with a higher amino loading, was used in recycling experiments for the Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate in DMF. After each cycle, the solid was magnetically separated, washed with DMF, and then reused in the next cycle. Fig. 5 shows that the yields and selectivities in four consecutive runs were almost the same. However, in our previous work, activity loss was clearly observed when Fe₃O₄@UiO-66-NH₂ prepared by dispersing magnets consecutively in DMF solutions each containing one of the MOF precursors was used [22]. This new synthetic method clearly improves the recycling stability. We used PXRD and nitrogen adsorption-desorption isotherm measurements to verify the high stability. After four consecutive cycles, the peak positions and shapes of the PXRD patterns (Fig. 6) had not changed sig-

Fig. 6. PXRD patterns of fresh Fe₃O₄@UiO-66-NH₂-3 (1) and Fe₃O₄@UiO-66-NH₂-3 recovered from reaction in DMSO (2) and DMF (3).

Fig. 7. Nitrogen adsorption-desorption isotherms of fresh $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2-3$ (1) and $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2-3$ recovered from reaction in DMF (2).

nificantly, confirming that $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2-3$ is a stable heterogeneous catalyst and the framework porous structures were unchanged during the reaction. The nitrogen adsorption-desorption isotherms (Fig. 7) show that the textural properties of the catalyst were unchanged by the reaction. SEM and TEM images (Fig. 8) showed no obvious differences between the sizes and morphologies of the catalyst before and after the reaction, again proving that the catalyst is stable during the reaction. A hot-filtration experiment was also performed to confirm the heterogeneous nature of the catalytic reaction (Fig. 9). The solid catalyst was removed, using a magnet, from the hot solution 0.5 h after initiating the catalytic test. The reaction of the filtrate was then monitored for another 2 h. No significant catalytic conversion was observed, indicating that no active sites leached from the solid.

Fig. 8. SEM (a,b) and TEM (c,d) images of fresh (a,c) and recovered (b,d) $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2-3$ from reaction in DMF.

Fig. 9. Hot filtration experiment. Normal reaction process in DMF (1); $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2-3$ was removed from the reaction mixture after 0.5 h (2).

4. Conclusions

$\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2$ with a well-defined structure was synthesized by dispersing magnets in a DMF solution containing two MOF precursors, i.e., ZrCl_4 and 2-aminobenzenetricarboxylic acid. Its core-shell structure was confirmed using TEM, its composition was determined using SEM-EDS, and the presence of amino groups was confirmed using IR spectroscopy. The sharp and intense diffraction peaks in the PXRD pattern of the shell of $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2$ prepared using three assembly cycles of the new method showed that the crystallinity of its shell was higher than that of $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2$ prepared by dispersing magnets consecutively in DMF solutions each containing one of the MOF precursors. The new material also had a higher surface area and pore volume. The new core-shell $\text{Fe}_3\text{O}_4@\text{UiO}-66-\text{NH}_2$ nanohybrid is an ideal recyclable catalyst for Knoevenagel condensations because of the bifunctionality of UiO-66-NH₂ and better mass transfer in the nano-sized shell. It is worth noting that the activities of the magnetic UiO-66-NH₂ materials were comparable to or higher than that of nano-sized UiO-66-NH₂. The recycling stability of the new material was improved by its high degree of crystallinity and high porosity. It was magnetically separated using an external magnet and was stable in terms of activity and structure when recycled at least four times in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate in DMF. The effect of substitution on the reactivity of benzaldehyde and size effects of substrates were similar to those observed for the Knoevenagel condensation catalyzed by UiO-66-NH₂. These MOF-based core-shell magnetic catalysts, which can be prepared simply, are expected to have large-scale industrial applications, in which separation and recycling are important to reduce costs and waste production.

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Graphical Abstract

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Fe₃O₄@UiO-66-NH₂ core-shell nanohybrid as stable heterogeneous catalyst for Knoevenagel condensationYanmei Zhang*, Tianlin Dai, Fan Zhang, Jing Zhang, Gang Chu, Chunshan Quan
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Core-shell magnetic metal-organic framework (Fe₃O₄@UiO-66-NH₂) with well-defined structure was constructed by dispersing magnets in a DMF solution containing two MOF precursors, i.e., ZrCl₄ and 2-aminobenzenetricarboxylic acid. It is an active and stable heterogeneous base catalyst for Knoevenagel condensation.

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核壳结构Fe₃O₄@UiO-66-NH₂磁性纳米复合材料的合成及其催化Knoevenagel缩合反应性能

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摘要: 金属有机骨架(MOF)材料是由过渡金属离子与有机配体通过配位键连接构成的高度有序的超分子化合物。这类材料比表面积大, 孔隙率高, 热稳定性好, 而且具有规整可调的孔结构、易于功能化的骨架金属离子和有机配体, 在多相催

化领域具有潜在应用前景. 将纳米尺寸的MOF材料等多孔材料作为催化剂, 可以提高反应传质效率, 从而提高催化反应活性, 但纳米MOF催化剂的分离和回收困难. 将磁性纳米粒子和MOF材料组装成核壳结构的磁性MOF材料, 不仅可简化催化剂的分离回收, 而且通过控制壳层材料的厚度可以实现催化剂的高活性和高选择性.

我们曾将磁核 Fe_3O_4 纳米粒子交替放入含有一种MOF材料前体的DMF溶液中, 采用层层组装法制备了磁性 $\text{Fe}_3\text{O}_4@\text{UiO}-66\text{-NH}_2$ 纳米复合材料. 经过十步组装后的材料的透射电镜(TEM)结果证实为核壳结构. 但未出现明显的 $\text{UiO}-66\text{-NH}_2$ 的X射线衍射(XRD)特征峰, 说明壳层材料 $\text{UiO}-66\text{-NH}_2$ 的结晶度较低; 同时由于其孔结构的破坏或堵塞, 在反应中出现明显失活.

本文进一步改进自组装方法制备了核壳结构的磁性 $\text{Fe}_3\text{O}_4@\text{UiO}-66\text{-NH}_2$ 纳米复合材料, 用XRD、傅里叶变换红外光谱(FT-IR)、TEM、扫描电镜(SEM)和氮气吸附等方法对材料的组成和结构进行了表征, 并考察了其在Knoevenagel缩合反应中的催化性能. 结果表明, 所制材料是以 Fe_3O_4 为核, 以 $\text{UiO}-66\text{-NH}_2$ 为壳的核-壳结构材料. 经三次组装后出现了一系列 $\text{UiO}-66\text{-NH}_2$ 的XRD特征峰, 说明采用新方法制备的复合材料中壳层材料 $\text{UiO}-66\text{-NH}_2$ 结晶度高, 晶体结构规整. N_2 吸附-脱附结果表明, 材料具有较高的比表面积和孔容.

该复合材料在Knoevenagel缩合反应中表现出与纳米 $\text{UiO}-66\text{-NH}_2$ 相当或更好的催化活性和选择性, 而且因壳层材料的孔道限阈效应而对底物表现出尺寸选择性. 由于材料结晶度和晶体结构规整度的提高, 催化剂稳定性更好, 通过简单磁性分离即可分离和回收催化剂, 循环使用4次而未出现明显失活. 相对于本课题组之前报道的 $\text{Fe}_3\text{O}_4@\text{CuBTC-NH}_2$, $\text{Fe}_3\text{O}_4@\text{IRMOF}-3$ 和 $\text{Fe}_3\text{O}_4@\text{UiO}-66\text{-NH}_2$ 材料, 本文所制的 $\text{Fe}_3\text{O}_4@\text{UiO}-66\text{-NH}_2$ 是一类结构更加稳定的高效固体碱催化剂.

关键词: 金属有机骨架材料; $\text{UiO}-66\text{-NH}_2$; 四氧化三铁; 多相催化剂; Knoevenagel缩合反应; 磁性分离

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