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# Synthesis of a $\text{Fe}_3\text{O}_4@P4VP@$ metal–organic framework core–shell structure and studies of its aerobic oxidation reactivity†

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A novel core–shell magnetic  $\text{Fe}_3\text{O}_4@P4VP(\text{poly}(4\text{-vinylpyridine}))@MIL-100(\text{Fe})$  composite material has been successfully synthesized. The  $\text{Fe}_3\text{O}_4@P4VP$  core was initially prepared *via* polymerization of P4VP on the surface of pre-made  $\text{Fe}_3\text{O}_4$  microspheres. The MIL-100(Fe) (MIL, Matériel Institut Lavoisier) metal–organic framework shell was then introduced through a layer by layer strategy. The obtained  $\text{Fe}_3\text{O}_4@P4VP@MIL-100(\text{Fe})$  catalyst was applied in the selective oxidation of alcohols using molecular oxygen as the oxidant, and a variety of substrates were tolerated. The initial activity of the  $\text{Fe}_3\text{O}_4@P4VP@MIL-100(\text{Fe})$  core–shell catalyst was maintained after ten reuses.

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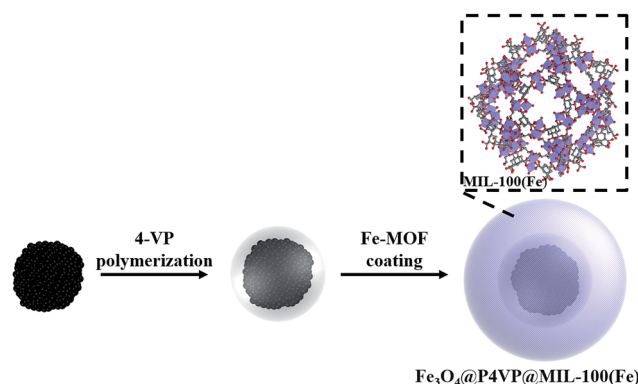
## 1. Introduction

Catalytic oxidations, such as conversions of alcohols to their corresponding carbonyl compounds, are of considerable importance in fine and industrial organic chemistry.<sup>1</sup> Recently, aerobic transition metal-promoted selective oxidations have received increasing attention because of the inexpensiveness and environmental friendliness of molecular oxygen.<sup>2</sup> Studies about homogenous catalysts are abundant in the literature.<sup>3</sup> However, homogeneous catalysts are inherently difficult to recover from the reaction mixture, causing industrial wastes and additional costs.<sup>4</sup> For this reason, heterogeneous catalysts are preferable for organic transformations, as they display several advantages during the purification and recovery steps of products and catalysts.<sup>5</sup>

As a result, numerous heterogeneous catalysts, such as molecular sieve,<sup>6</sup> polymer supported<sup>7</sup> and inorganic microspheres supported ones, have been developed in recent years.<sup>8</sup> Among these solid catalysts, core–shell structured ones have been considered the most ideal ones, thanks to their unique physicochemical and multi-functional properties.<sup>9</sup> Core–shell structures bearing magnetic functionality are of particular interest as an effective separation method because of their easy and quick response in an external magnetic field.<sup>10</sup> A variety of magnetic core–shell composites have been developed utilizing different coatings, such as silica, carbon, polymer and porous materials on a  $\text{Fe}_3\text{O}_4$  core.<sup>11</sup> Several hybrid magnetic core–shell

nanocatalysts have been utilized in a variety of catalytic reactions including reductions, oxidations, epoxidations, coupling reactions and photocatalysis.<sup>12</sup> Many studies have reported immobilization of transition metal salts into core–shell structures.<sup>13</sup> On the other hand, significant metal leaching and poor catalyst recyclability have been recurring issues in these metal immobilized systems. It is difficult to address such limitations because of the low molecular interactions present in the coordination bonds between the metal and the core–shell structure (Scheme 1).<sup>14</sup>

Metal–organic frameworks (MOFs)<sup>15</sup> have gained increasing focus in catalysis, as a kind of porous materials with extremely large surface area, a high number of active sites and good stability.<sup>16</sup> Therefore, fabrication of MOFs coated magnetic core–shell catalysts could address the problem of catalyst leaching and the need for recyclability.<sup>17</sup> In this work, we wish to report a core–shell–shell structured  $\text{Fe}_3\text{O}_4@P4VP@MIL-100(\text{Fe})$



Scheme 1 Schematic illustration of the synthesis of  $\text{Fe}_3\text{O}_4@P4VP@MIL-100(\text{Fe})$ .

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catalyst, which was assembled by coating MIL-100(Fe) on the surface of  $\text{Fe}_3\text{O}_4$ @P4VP microspheres.<sup>18</sup> The inner shell of the P4VP polymer layer played an important role in the absorption of  $\text{Fe}^{3+}$  ions for the formation of the MIL-100(Fe) shell, as well as in protecting the magnetic core from destruction and aggregation during the oxidation process. The synthesized  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) was characterized by TEM, field-emission SEM (FESEM), powder X-ray diffraction (PXRD), nitrogen adsorption/desorption analysis, FTIR spectroscopy, thermogravimetric analysis (TGA) and vibrating sample magnetometry (VSM). The aerobic oxidation of alcohols was investigated using our synthesized  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) catalyst and great yields were achieved. A variety of alcohols was compatible with our oxidation system and the core-shell catalyst could be rapidly separated by an externally applied magnetic field.

## 2. Experimental section

### 2.1 Materials

Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), polyvinyl pyrrolidone (PVP;  $M_w = 58\,000$ ), 4-vinyl pyridine (4-VP, 96%), divinylbenzene (DVB, 80%), 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ), potassium persulfate (KPS, 99%), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), trimethylacetaldehyde, benzyl alcohol, substituted benzyl alcohols, 2-pyridinemethanol, cinnamic alcohol, 3-methyl-2-buten-1-ol, 3-methyl-2-buten-1-ol, 1-octyl alcohol, 1-phenyl-ethanol, 2-cyclohexen-1-ol, cyclopentanol, cyclooctene, cyclohexene, cyclododecene, norbornene and  $\alpha$ -pinene were purchased from Alfa Aesar. Poly(acrylic acid) (PAA;  $M_w = 1800$ ) was obtained from Sigma-Aldrich. Anhydrous ethanol, ethylene glycol (EG), sodium acetate and potassium nitrite were purchased from Beijing Chemical Reagents Company (China). 4-Vinyl pyridine was purified by distillation under reduced pressure to remove inhibitor hydroquinone before use.

### 2.2 Synthesis of $\text{Fe}_3\text{O}_4$ nanoparticles with PAA

The  $\text{Fe}_3\text{O}_4$  nanoparticles modified on the surface with poly(acrylic acid) (PAA) were synthesized by solvothermal method according to reported literature. Firstly,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (1.08 g) and PAA (0.108 g) were dissolved in ethylene glycol (40 mL) under magnetic stirring at 60 °C, followed by adding sodium acetate (9 g) under vigorous stirring to form a uniform solution. Then, the solution was decanted to a stainless-steel autoclave with Teflon-lining (50 mL) and maintained at 200 °C for 12 h. After the autoclave was cooled to room temperature, the black product was collected using a magnet. The  $\text{Fe}_3\text{O}_4$  nanoparticles modified with PAA were washed with deionized water and ethanol several times, collected and dried under vacuum.

### 2.3 Preparation of core-shell $\text{Fe}_3\text{O}_4$ @P4VP microspheres

The core-shell  $\text{Fe}_3\text{O}_4$ @P4VP microspheres were prepared by coating P4VP shell on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles through radical initiated polymerization.  $\text{Fe}_3\text{O}_4$  nanoparticles modified with PAA (0.1 g) were dispersed in 100 mL of a 0.15 wt% PVP aqueous solution under ultrasonication. The uniform solution was mixed with emulsion of 4-VP (0.125 g) and DVB

(0.125 g) in aqueous solution (20 mL) that contains PVP (0.05 g). Then it was emulsified by ultrasonic after placed in a 250 mL four-necked flask. The liquid was mechanically stirred for 4 hours under a flow of nitrogen and then polymerization of 4-VP was initiated by KPS (10 mg); at this point, the solution was heated to 70 °C. Core-shell  $\text{Fe}_3\text{O}_4$ @P4VP microspheres were obtained after 4 h, washed with deionized water and ethanol three times and dried under vacuum.

### 2.4 Synthesis of core-shell-shell $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) microspheres

The core-shell-shell  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) microspheres were synthesized by a step-by-step strategy. Typically, 0.05 g of  $\text{Fe}_3\text{O}_4$ @P4VP microspheres were dispersed in 10 mL of a 4.0 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  ethanol solution for 15 minutes and collected with a magnet. Then the microspheres were dispersed in a  $\text{H}_3\text{BTC}$  ethanol solution (4 mL, 10 mM) and stirred at 70 °C for 30 minutes. The product was washed with ethanol and vacuum dried after twenty cycles.

### 2.5 Typical catalytic procedure for aerobic oxidation of alcohol

Alcohol (1.0 mmol),  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) catalyst (5 mol%) were mixed in acetonitrile (5 mL); TEMPO (0.5 equiv.) and  $\text{KNO}_2$  (0.2 equiv.) were added in a 25 mL flask equipped with a condenser. The catalytic reaction was stirred at 75 °C under 1 atm of  $\text{O}_2$ . After the reaction, the  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) catalyst was recovered by applying an external magnetic field and the yield of product was determined by GC-MS.

### 2.6 Leaching test and catalyst recycling

The hot filtration test for the aerobic oxidation of benzyl alcohol was performed on a sample taken from the mixture after letting the reaction run for 4 hours. The catalyst was separated by a magnet and the supernatant solution was transferred into a new flask letting the reaction continue in absence of the catalyst. After certain reaction time, the reaction solution was analyzed by GC-MS. The recyclability of the heterogeneous catalyst was tested for the oxidation of alcohols and epoxidation of olefins. The reaction run with a batch of recycled catalyst was performed under the conditions described above.

## 3. Results and discussion

The  $\text{Fe}_3\text{O}_4$  microspheres modified with PAA were synthesized by a solvothermal method reported in literature.<sup>19</sup> These microspheres were composed of tiny  $\text{Fe}_3\text{O}_4$  nanocrystals within 10 nm (Fig. 1a). The P4VP shell was successfully grafted on  $\text{Fe}_3\text{O}_4$  to form core-shell composite microspheres held together by hydrogen bonds between carboxyl groups of PAA chains and pyridine. The diameters of the magnetic core and polymer shell were about 200 and 38 nm, respectively (Fig. 1b).  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) core-shell-shell catalysts were prepared by a layer-by-layer method with 5 to 20 assembling cycles (Fig. 1c-f). The  $\text{Fe}^{3+}$  ions were adsorbed on the surface of P4VP through



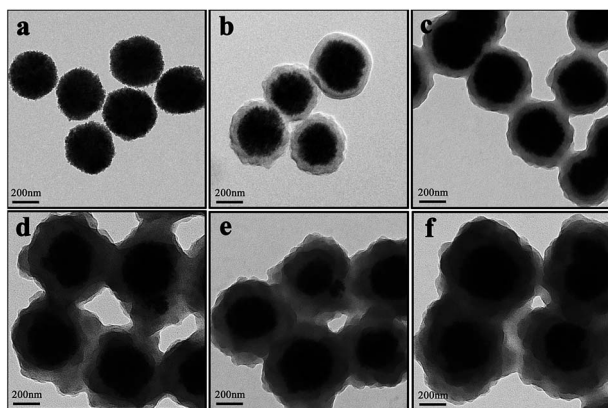


Fig. 1 HRTEM images of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) core-shell after (c) 5, (d) 10, (e) 15, (f) 20 assembling cycles.

pyridine coordination, followed by reacting with 1,3,5-benzenetricarboxylic acid to complete each assembling cycle. The thickness of the MIL-100(Fe) shell was controlled by adjusting the assembling cycle. The MOF shells could be increased significantly to achieve a thickness ranging between 15 and 90 nm.

To further confirm the crystalline structures of the  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) microspheres, powder XRD were performed and the patterns are shown in Fig. 2. The diffraction peaks of  $\text{Fe}_3\text{O}_4$  (Fig. 2a) agree with standard JCPDS 75-1609.39 indicating a face-centered cubic lattice. After coating with P4VP, the peaks of the core-shell  $\text{Fe}_3\text{O}_4$ @P4VP microspheres are almost the same as those for  $\text{Fe}_3\text{O}_4$ , because of the low-crystalline nature of the polymeric shell (Fig. 2b). However, after the introduction of the MIL-100(Fe) layer, several new peaks appeared on the XRD pattern (Fig. 2c). These new peak match the peaks present in the simulated MIL-100(Fe) pattern (Fig. S1†), which indicates that the formation of MIL-100(Fe) was successful.

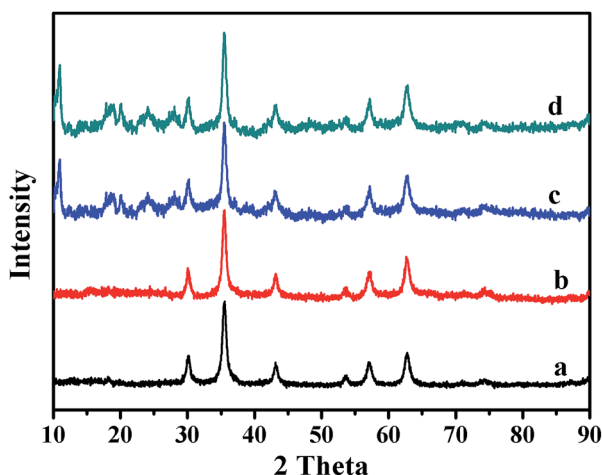


Fig. 2 XRD patterns of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4$ @P4VP, (c)  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) and (d) recycled  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe).

The EDX elemental maps further support the successfulness of the synthesis of  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe), and that the iron MOF was well grafted on the surface of  $\text{Fe}_3\text{O}_4$ @P4VP (Fig. 3). The iron elemental maps of the  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) also showed an excellent distribution of iron content on the surface. The existence of iron in the  $\text{Fe}_3\text{O}_4$  core structure was also observed, as shown in Fig. 3.

The FTIR spectrum of the product is shown in Fig. 4. The relatively high intensity of the band at  $592\text{ cm}^{-1}$  is characteristic of Fe–O vibrations. The characteristic absorption bands at 1707, 1250, and  $1165\text{ cm}^{-1}$  correspond to the C=O stretching of the carboxylic group, to the in-plane bending of C–O–H, and to the  $-(\text{C}-\text{O})\text{H}$  stretching, proving the existence of rich  $-\text{COOH}$  functional groups on the surface of the  $\text{Fe}_3\text{O}_4$  particles. As for the  $\text{Fe}_3\text{O}_4$ @P(4-VP-DVB) microspheres, the characteristic absorptions at 1603, 1562, and  $1417\text{ cm}^{-1}$  are attributed to the vibrational modes of the pyridine ring. The band at  $1603\text{ cm}^{-1}$  corresponds to the stretching vibration absorption of the C–N bond, and the bands at around 1562 and  $1417\text{ cm}^{-1}$  are attributed to the stretching vibration absorption of the C=C bond; this further proves the encapsulation of P4VP on the surface of the  $\text{Fe}_3\text{O}_4$  particles. The peaks at 1435 and  $1575\text{ cm}^{-1}$  are due to the stretching vibrations of the C–C bonds of the benzene ring, while the peaks at 1376 and  $1618\text{ cm}^{-1}$  are

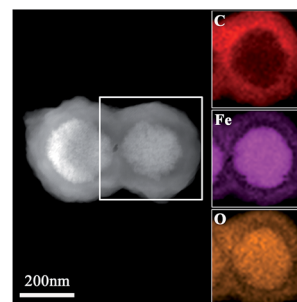


Fig. 3 The TEM images of the  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) and EDX elemental maps of Fe, O and C, respectively.

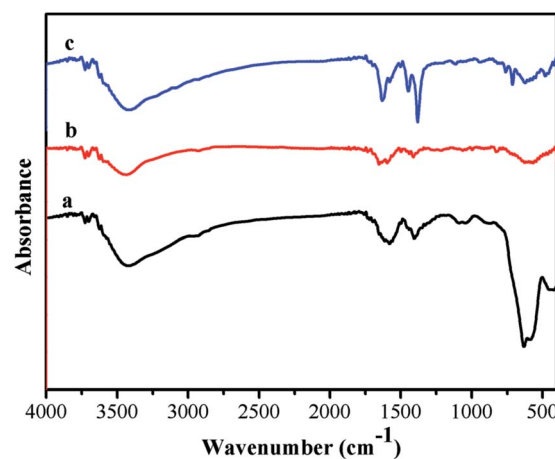


Fig. 4 FTIR spectra of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4$ @P4VP and (c)  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe).



attributed to the C–O stretching vibrations of the carboxylic moiety, suggesting that MIL-100 (Fe) shell has been successfully grafted on the surface of  $\text{Fe}_3\text{O}_4$ @P4VP.

Surface area and pore size distribution were characterized by nitrogen adsorption/desorption experiment. The  $\text{N}_2$  adsorption/desorption isotherms are shown in Fig. 5 and the curves are formed by the type I isotherms (Fig. 5). In addition, the isotherms are of type II at the range of high  $P/P_0$ . The surface area and pore volume of  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) were calculated by the BET model and the values were determined to be 346.2 and  $2.31 \text{ m}^3 \text{ g}^{-1}$ , respectively. The surface area is significantly improved, when compared to its  $\text{Fe}_3\text{O}_4$ @P4VP precursor, which has a surface area of  $31.1 \text{ m}^2 \text{ g}^{-1}$ .

TGA curves of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) are shown in Fig. 6. For PAA modified  $\text{Fe}_3\text{O}_4$  microspheres, the weight loss was about 17 wt% over two steps, attributed to the desorption of adsorbed water and PAA chains in  $\text{Fe}_3\text{O}_4$  microspheres (Fig. 6a). The TGA curves of the  $\text{Fe}_3\text{O}_4$ @P4VP microspheres exhibited three steps of weight loss with 52 wt% of the initial weight remaining. Elimination of water, decomposition of the oligomeric structure and the desorption of P4VP shell correspond to the three weight losses (Fig. 6b). As expected, the mass loss of  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) was lower than that of  $\text{Fe}_3\text{O}_4$ @P4VP, likely due to the formation of iron oxide through calcination (Fig. 6c).

The magnetic properties of  $\text{Fe}_3\text{O}_4$  (PAA),  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) were measured by vibrating sample magnetometry (VSM). All three samples exhibited superparamagnetism, presenting no remanence or coercive forces (Fig. 7). The resultant magnetization saturation values of  $\text{Fe}_3\text{O}_4$  (PAA),  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) were 73.90, 47.35 and  $28.21 \text{ emu g}^{-1}$ , respectively, indicating strong magnetic response by the materials. The saturation magnetic moment of  $\text{Fe}_3\text{O}_4$ @P4VP and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) are lower than that of  $\text{Fe}_3\text{O}_4$  because the P4VP and MOF shells are non-magnetic materials. Moreover, the saturation magnetic moment shows linear dependence on the content of magnetite. Therefore, the amount of P4VP and MIL-100(Fe) calculated

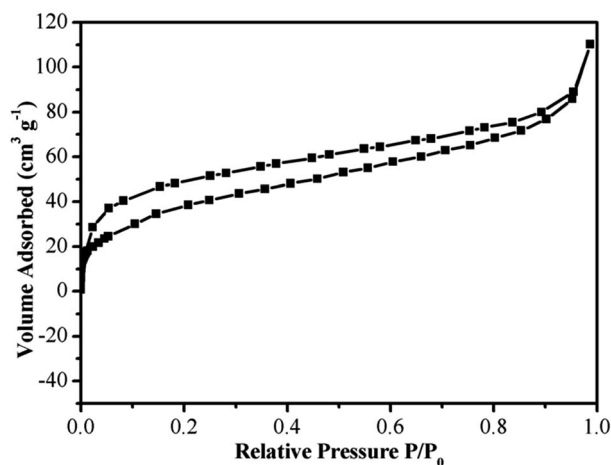


Fig. 5  $\text{N}_2$  adsorption–desorption isotherms of the  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) catalyst.

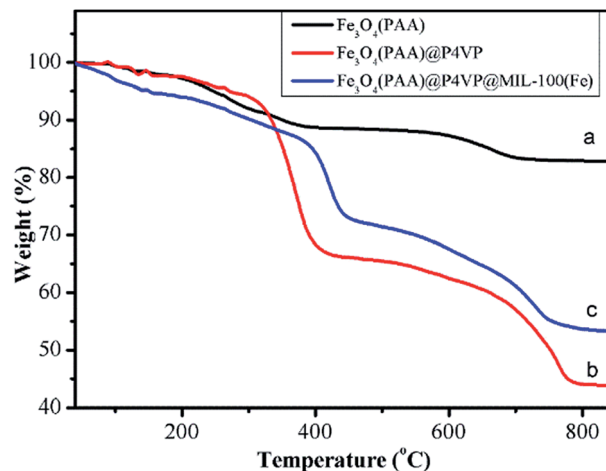


Fig. 6 TGA curves of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4$ @P4VP and (c)  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe).

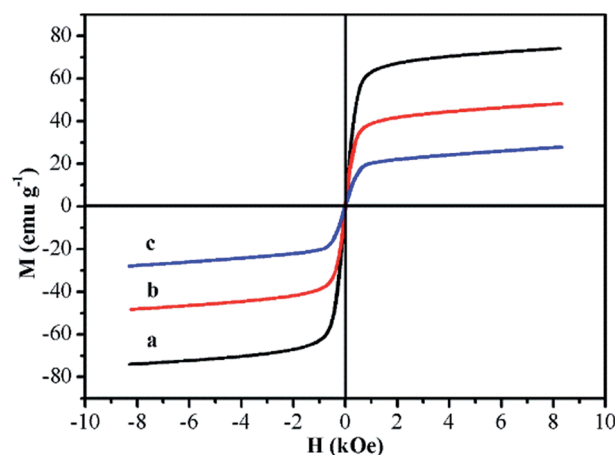


Fig. 7 Room-temperature magnetic hysteresis loops of (a)  $\text{Fe}_3\text{O}_4$ , (b)  $\text{Fe}_3\text{O}_4$ @P4VP and (c)  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe).

according to the VSM results were 21.41 wt% and 40.42 wt%, respectively.

The catalytic activity of the synthesized  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) toward the aerobic oxidation reaction was evaluated employing alcohol substrates, and using TEMPO as the radical initiator. No benzaldehyde was detected in the absence of the catalyst under our reaction conditions (Table 1, entry 1). Also, the employment of  $\text{Fe}_3\text{O}_4$ @P4VP as the catalyst failed to oxidize any benzyl alcohol to its corresponding aldehyde (Table 1, entry 2). Homogeneous iron catalysts were evaluated and almost quantitative conversion was observed. However, slightly lowered selectivity was observed due to the formation of benzoic acid (Table 1, entries 3 and 4). 82% conversion and 99% selectivity were achieved using MIL-100(Fe) MOF catalyst at 5 mol% catalyst loading (Table 1, entry 5). The amounts of MIL-100(Fe) and  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) added in this reaction were 5 mol%, based on the same iron loading (Table 1, entries 5 and 6). The  $\text{Fe}_3\text{O}_4$ @P4VP@MIL-100(Fe) catalyst gave an excellent conversion and yield due to the efficient utilization of the





Table 1 Optimization of the aerobic oxidation reaction conditions<sup>a</sup>

Entry	Catalyst	Solvent	Conv. <sup>b</sup>	Sel. <sup>b</sup>
1	—	CH <sub>3</sub> CN	<5%	—
2	Fe <sub>3</sub> O <sub>4</sub> @P4VP	CH <sub>3</sub> CN	<5%	—
3	FeCl <sub>3</sub>	CH <sub>3</sub> CN	99%	92%
4	Fe(NO <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN	99%	93%
5	MIL-100(Fe)	CH <sub>3</sub> CN	86%	99%
6	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	CH <sub>3</sub> CN	99%	99%
7 <sup>c</sup>	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	CH <sub>3</sub> CN	36%	99%
8 <sup>d</sup>	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	CH <sub>3</sub> CN	62%	99%
9	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	PhCH <sub>3</sub>	82%	99%
10	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	THF	67%	99%
11	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe)	EtOH	25%	99%

<sup>a</sup> Reaction conditions: 1.0 mmol of benzyl alcohol, 5 mol% of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst, 5.0 mL of solvent, 0.2 mmol of TEMPO, and 0.2 mmol of KNO<sub>2</sub>; 60 °C, 12 h under 1 atm O<sub>2</sub>.

<sup>b</sup> Conversions and selectivities were calculated by GC-MS using nitrobenzene as the internal standard. <sup>c</sup> H<sub>2</sub>O<sub>2</sub> was used as the oxidant. <sup>d</sup> Air was used as the oxidant.

porous MOF structure, which was coated as a nanolayer on the magnetic core. Hydrogen peroxide has been utilized as the oxidant, only low yield was obtained (Table 1, entry 7). Our reaction condition is not compatible with aqueous hydrogen peroxide oxidant. Furthermore, air was also tested as the low concentration form of oxygen and moderate yield was obtained (Table 1, entry 8). Further solvent screenings showed that CH<sub>3</sub>CN is the most suitable solvent for the benzyl alcohol oxidation (Table 1, entries 6, 9–11). Aromatic solvents such as toluene gave slightly compromised yields, presumably due to their lower polarity (Table 1, entry 9). Moreover, oxygen containing solvents, such as THF and ethanol, were not suitable oxidation reaction solvent due to possible metal coordination (Table 1, entries 10 and 11).

Conversion was monitored over time employing various catalyst loadings of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe); the results are summarized in Fig. 8. Relatively low conversion was observed at 1–3 mol% of catalyst loading, indicating the crucial role of the Fe-derived catalyst. However, conversion and yield were not satisfying until the catalyst loading was increased to 5 mol%. As a result, 5 mol% loading of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) was chosen to be the optimal reaction condition for future studies.

With the optimal reaction conditions in hand, several alcohol substrates were chosen to study the aerobic oxidation catalytic performance of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe). Benzyl alcohol was transformed to the corresponding benzaldehyde in 99% yield after 12 h (Table 2, entry 1). For the aerobic oxidation of benzyl alcohol in presence of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) as the catalyst, the turnover number (TON) was calculated to be 20. Electron-rich benzyl alcohols, such as *p*-methyl benzyl alcohol and *p*-methoxy benzyl alcohol were reactive under the optimal reaction conditions, affording 99% and 92% yield, respectively

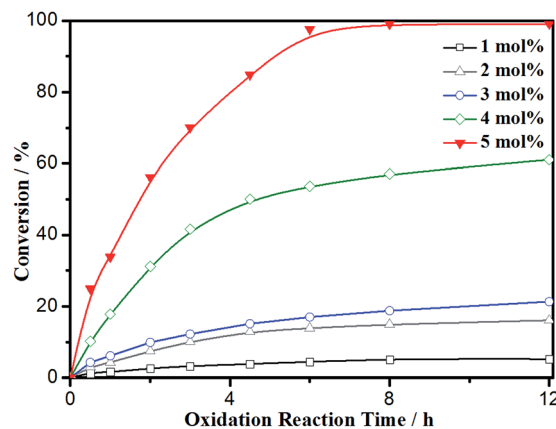


Fig. 8 Conversion vs. time at various core-shell catalyst loading.

Table 2 Aerobic oxidation of a variety of alcohols<sup>a</sup>

Alcohol Substrate	Reaction Conditions	Conv.	Sel.
Benzyl alcohol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	99%	99%
<i>p</i> -Methyl benzyl alcohol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	99%	99%
<i>p</i> -Methoxy benzyl alcohol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	99%	99%
<i>p</i> -Fluoro benzyl alcohol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	93%	99%
2-Pyridylmethanol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	99%	99%
Cinnamyl alcohol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	94%	99%
1-Phenylethanol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	35%	99%
Cyclohexanol	Fe <sub>3</sub> O <sub>4</sub> @P4VP@MIL-100(Fe), CH <sub>3</sub> CN, TEMPO, KNO <sub>2</sub> , O <sub>2</sub>	22%	99%

<sup>a</sup> Reaction conditions: 1.0 mmol of alcohol, 5 mol% of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst, 5.0 mL of solvent, 0.5 mmol of TEMPO, and 0.2 mmol of KNO<sub>2</sub>; stirred at 60 °C for 12 h under 1 atm O<sub>2</sub>.

(Table 2, entries 2 and 3). Alcohol substrates bearing electron-withdrawing functional groups were also tolerated; although a slightly lowered yield was observed for *p*-fluoro benzyl alcohols (Table 2, entry 4). The heterocyclic alcohol pyridin-2-ylmethanol was converted smoothly to its corresponding aldehyde in the presence of the Fe derived core-shell catalyst (Table 2, entry 5). Cinnamyl alcohol was also evaluated as an example of allylic alcohol; cinnamaldehyde was formed as the only product in 92% yield (Table 2, entry 6). In order to test the transformation of secondary alcohols to ketones, 1-phenylethanol and cyclohexanol were both tested; unfortunately, only low conversions were observed (Table 2, entries 7 and 8).



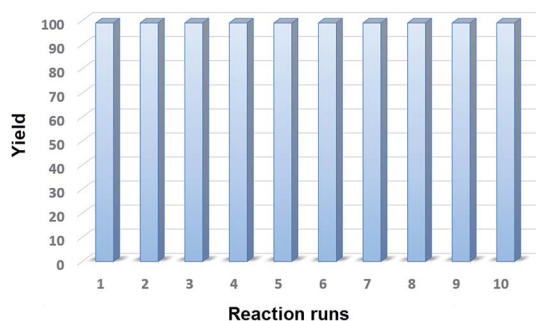


Fig. 9 Core-shell Fe-MOF catalyst recyclability test.

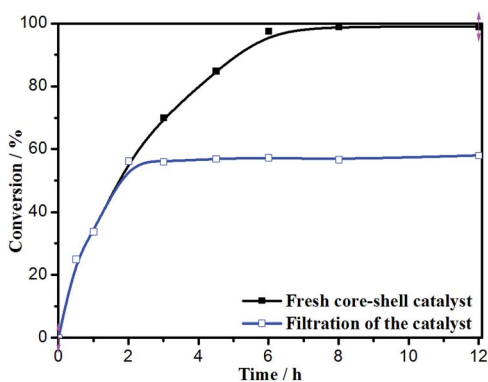


Fig. 10 Hot filtration test of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe).

The recyclability of the catalyst was studied applying the optimal reaction conditions and utilizing 5 mol% of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst in acetonitrile (Fig. 9). The same batch of the Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst was reused over ten reaction cycles; conversion and selectivity were retained at 99%, and the yield of benzaldehyde was compromised only slightly after ten cycles (Fig. 6). The retaining of high conversions and selectivities after ten cycles indicates that the core-shell MOF heterogeneous catalyst is highly stable. FT-IR and XRD spectra showed no significant difference between fresh Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) and the batch analyzed after being used ten times (Fig. S2 and S3<sup>†</sup>).

The hot filtration test was conducted to confirm the heterogeneous nature of the catalytic aerobic oxidation (Fig. 10). The Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst was isolated through magnet after 2 h of reaction and the mixture was stirred for another 10 h. Conversion to product stopped after the catalyst was removed. This result indicates that the strong covalent bond ensures the stability of Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) material during the oxidation process. And that there is almost no Fe<sup>3+</sup> leaching into the reaction solution, as also confirmed by ICP-AAS analysis.

## 4. Conclusions

During this study a novel magnetic core-shell Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst was designed, prepared and fully

characterized. The composite microspheres were composed by a magnetic Fe<sub>3</sub>O<sub>4</sub>(PAA) core, a P4VP middle layer, and a MIL-100(Fe) MOF shell. Taking advantage of their porous Fe-derived layer, the magnetic composite microspheres were utilized as an efficient catalyst for the selective aerobic oxidation of alcohols. A variety of alcohol substrates were tolerated under our optimized conditions. The initial catalytic activity of the Fe<sub>3</sub>O<sub>4</sub>@P4VP@MIL-100(Fe) catalyst was retained after at least ten consecutive reaction cycles. A hot filtration test suggested extremely low leaching of iron into the solution. Further applications of the prepared core-shell MOF catalyst are currently under investigation.

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