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Synthesis of Fe₃O₄@P4VP@ZIF-8 Core-shell Microspheres and their **Application in a Knoevenagel Condensation Reaction**

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Abstract: In this work, a core-shell magnetic composite Fe₃O₄@P4VP@ZIF-8 microspheres were successfully designed and synthesized. A polymerization approach on the surface of pre-made Fe₃O₄ microspheres was employed for the synthesis of Fe₃O₄@P4VP. The zinc-derived Zeolite Imidazolate Framework (ZIF) shell was introduced through a layer-by-layer strategy. The obtained Fe₃O₄@P4VP@ZIF-8 core-shell structure was employed as an efficient Knoevenagel condensation catalyst for a variety of aldehydes. Furthermore, the inner P4VP layer also served as a basic additive in the condensation reaction process, while much less homogeneous basic

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additive was used . High catalytic reaction efficiency was achieved when the P4VP layer was utilized in combination with a Lewis acidity bearing ZIF-8 layer. The $Fe_3O_4@P4VP@ZIF-8$ catalyst was tested for recyclability and no drop in the catalytic activity was observed after more than five cycles.



Keyboards:

Metal-organic Framework; Core-shell; Knoevenagel Reaction; Heterogeneous Catalysis; Polymer

Introduction

The Knoevenagel condensation reaction is widely used in industrial synthetic organic processes, as simple starting materials can be facilely transformed to densely functionalized products.[1] No wastes or by-products are generated during the condensation process. Various homogeneous bases, such as pyridine and piperidine, have been commonly used as the catalyst for the Knoevenagel condensation reaction.[2] However, homogeneous catalysts bear implicit limitations in their recycling and can cause severe equipment corrosion.[3] As a result, heterogeneous catalysts are preferable alternatives.[4]

Core-shell structured materials are considered ideal heterogeneous catalysts and gained increased interests due to their unique physicochemical and multi-functional properties.[5] Magnetic core-shell structures are of particular interest because of their ease of recovery through the application of an external magnetic field.[6] Hence, numerous magnetic core-shell nanocatalysts were developed for immobilization of the transition metals.[7] However, there are still several drawbacks associated with immobilized magnetic core-shell nanocatalysts.[8] The amount of the active sites is limited due to the small surface area and metal leaching may occur during the catalytic process.[9]

Recently, metal–organic frameworks (MOFs) attracted lots of attention as porous materials with an extremely large surface area, numerous active sites and good stability.[10] They have been often investigated as heterogeneous catalysts for their high surface areas, unique topology and tunable properties.[11] The strong covalent bonds in the MOFs structure ensures the stability of the active metal centers, addressing the issue of metal leaching and deactivation.[12] The introduction of metal-organic framework structural layer as the Lewis acidic shell promotes the organic reaction efficiently and protects the inner material core, furnishing a chemically stable heterogeneous catalyst.[13] For example, $Fe_3O_4@MOF$ nanocomposites were synthesized as a magnetically recoverable catalyst[14] or UO_2^{2+} adsorption reagent.[15]

In this work, we wish to report a novel core-shell-shell structured catalyst, $Fe_3O_4@P4VP(poly(4-vinylpyridine))@ZIF-8(Zeolitic Imidazolate Framework-8),$ involving a coated MOFs layer (Scheme 1).[16] The zinc derived ZIF-8 was grafted onto the surface of the $Fe_3O_4@P4VP$ microspheres through layer-by-layer assembly.[17] The inner shell of P4VP plays an important role in the rapid coordination with zinc ion, forming a ZIF-8 layer for the protection of the magnetic core structure. This core-shell-shell offers more functionality and higher stability than $Fe_3O_4@MOF$ nanocomposites. Furthermore, the P4VP shell can also serve as a basic catalyst for the Knoevenagel condensation.[18] In the meanwhile, the coated MOF

layer functions as a Lewis acid co-catalyst to facilitate the reaction.[19] During this study, the efficient Knoevenagel condensation reaction of a variety of aldehydes was achieved using the $Fe_3O_4@P4VP@ZIF-8$ multifunctional catalyst.[20]



Scheme 1. Schematic illustration for the preparation of Fe₃O₄@P4VP@ZIF-8.

Experimental section

Synthesis of core-shell-shell Fe₃O₄@P4VP@ZIF-8 microspheres

The core-shell-shell Fe₃O₄@P4VP@ZIF-8 microspheres were synthesized by step-by-step strategy. In general, 0.05 g of Fe₃O₄@P4VP were dispersed in 5 mL (10 mM) Zn(NO₃)₂·6H₂O methanol solution for 15 minutes. Then the microspheres were dispersed in 2-methylimidazole (2-MeIM) methanol solution (4 mL, 10 mM) for 30 minutes. After twenty cycles, the Fe₃O₄@P4VP@ZIF-8 nanoparticles were separated, washed with absolute ethanol, and dried under vacuum at 80 °C for 6 h.

Typical catalytic procedure for Knoevenagel condensation reaction

In a typical reaction, to a 5-mL reaction vessel, 1.0 mmol of benzaldehyde and 1.5 mmol of malononitrile were dissolved in 2.0 mL of toluene. To the reaction 1.0 mol% of Fe₃O₄@P4VP@ZIF-8 catalyst was then added. The heterogeneous solution was stirred at room temperature (23 °C) for 2 h. The final yield and selectivity of the Knoevenagel condensation product were measured by GC-MS using *n*-dodecane as the internal standard.

Results and Discussion

The Fe₃O₄@PAA microspheres were synthesized according to a literature reported solvothermal method;[19] the microspheres were composed of Fe₃O₄ nanocrystals of diameter not greater than 10 nm (Fig. 1a). The Fe₃O₄ nanoparticles were successfully coated with P4VP to form core-shell composite microspheres, taking advantage of the hydrogen bond between carboxyl groups of PAA chains and pyridine. The diameters of the magnetic core (central black sphere) and polymer shell (outer gray shell) were about 200 nm and 38 nm, respectively, as shown in Fig. 1b.



Fig. 1 HRTEM images of (a) Fe₃O₄, (b) Fe₃O₄@P4VP, (c) Fe₃O₄@P4VP@ZIF-8 and (d) recycled Fe₃O₄@P4VP@ZIF-8.

The Fe₃O₄@P4VP@ZIF-8 core-shell-shell catalyst was prepared by layer-by-layer method with 20 assembly cycles (Fig. 1c). The Zn²⁺ ions were adsorbed on P4VP initially through pyridine coordination, and then reacted with 2-methylimidazole to complete the assemble procedure. This process was repeated twenty times to achieve the core-shell-shell structure. The introduction of a zinc salt has no impact on the sphere morphology of core-shell material according to HRTEM characterization. The SEM image of Fe₃O₄@P4VP@ZIF-8 shows microspheres with a diameter of 400 nm.



Fig. 2 EDX mapping of Fe₃O₄@P4VP@ZIF-8.

The EDX elemental maps verified the successful synthesis of core-shell structured $Fe_3O_4@P4VP@ZIF-8$. The EDX map in Fig. 2 clearly shows that zinc derived ZIF-8 was coated on the surface of $Fe_3O_4@P4VP$.



Fig. 3 XRD patterns of (a) Fe_3O_4 , (b) $Fe_3O_4@P4VP$, (c) $Fe_3O_4@P4VP@ZIF-8$ and (d) recycled $Fe_3O_4@P4VP@ZIF-8$

To further confirm the crystalline structures of Fe_3O_4 , $Fe_3O_4@P4VP$ and $Fe_3O_4@P4VP@ZIF-8$ microspheres, powder XRD was performed and the patterns are shown in Fig. 3. The diffraction peaks of Fe_3O_4 (Fig. 3a) agree with standard JCPDS 75-1609.39 indicating the face-centered cubic lattice. After P4VP coating, the XRD pattern of core-shell $Fe_3O_4@P4VP$ microspheres was almost identical to the pattern of Fe_3O_4 , as layer of polymeric shell is not crystalline (Fig. 3b). Several peaks of ZIF-8 were observed on the XRD pattern for the $Fe_3O_4@P4VP@ZIF-8$ core-shell-shell structure. The new ZIF-8 peak is in agreement with previously published literature. In addition, these peaks also match our simulated ZIF-8 XRD peaks (Fig. S1).



Fig. 4 FTIR spectra of a) Fe₃O₄ (PAA), b) Fe₃O₄@P4VP and c) Fe₃O₄@P4VP@ZIF-8.

The FTIR spectra of the synthesized microspheres are shown in Fig. 4. The high intensity of the band at 592 cm⁻¹ is the characteristic peak of the Fe-O vibrations. In addition, absorption bands at 1707, 1250, and 1165 cm⁻¹ correspond to the C=O stretching of the carboxylic acid group and to in-plane deformations of C-O-H, and -(C-O)H stretching. This observation suggested that -COOH functional groups derived from PAA are located on the surface of Fe₃O₄ particles. In the FTIR spectrum

of Fe₃O₄@P4VP microspheres, the characteristic absorptions at 1603, 1562, and 1417 cm⁻¹ are attributed to the vibration of the pyridine ring (Fig. 4b). After the introduction of ZIF-8 layer, a major new peak appears at 1683 cm⁻¹, indicating the large amount of carboxylate groups (Fig. 4c).



Fig. 5 N₂ adsorption/desorption isotherms of Fe₃O₄@P4VP@ZIF-8.

The surface area of our synthesized Fe₃O₄@P4VP@ZIF-8 was calculated by measuring the N₂ adsorption/desorption isotherms and the value was determined to be 410.3 m²g⁻¹. The isotherms shown in Fig. 5 are a combination of type I and IV isotherms, which suggested a mixture of microporous and mesoporous structures (Fig. 3). It is a significant improvement when compared with its non-porous Fe₃O₄@P4VP precursor, which only has a BET surface area of 14.8 m²g⁻¹. The highly porous shell strongly facilitates the catalytic process, which takes advantage of the newly introduced MOF layer.



Fig. 6 TGA curves of a) Fe₃O₄ (PAA), b) Fe₃O₄@P4VP and c) Fe₃O₄@P4VP@ZIF-8.

TGA analysis of Fe₃O₄@P4VP@ZIF-8 and its precursors were measured and shown in Fig. 6. PAA coated Fe₃O₄ microspheres are relatively stable with a weight loss of 17 wt%, which we attributed to the desorption of solvent and to the decomposition of PAA chains. The TGA curve of Fe₃O₄@P4VP microspheres showed three steps of weight loss with 52 wt% remaining. The loss of water, decomposition of oligomer, and the desorption of P4VP shell respectively account for the three weight losses. As expected, there is less mass loss between 300 to 400 °C for Fe₃O₄@P4VP@ZIF-8 in comparison to its precursor, due to the zinc oxide formed by calcination.



Fig. 7 Magnetic hysteresis loops of a) Fe₃O₄, b) Fe₃O₄@P4VP and c) Fe₃O₄@P4VP@ZIF-8.

Vibrating sample magnetometry (VSM) was utilized to measure the magnetic properties of Fe_3O_4 , $Fe_3O_4@P4VP$ and $Fe_3O_4@P4VP@ZIF-8$ (Fig. 7). According to the VSM results, the magnetization saturation values of Fe_3O_4 , $Fe_3O_4@P4VP$ and $Fe_3O_4@P4VP@ZIF-8$ were 74.2, 48.4 and 27.7 emu g⁻¹, respectively; these values indicate a material which is superparamegantic. The saturation magnetic momentum of Fe_3O_4 , $Fe_3O_4@P4VP$ and $Fe_3O_4@P4VP@ZIF-8$ are lower than that of Fe_3O_4 due to the additional P4VP and MOF shells layers. Moreover, the saturation magnetic momentum shows linear dependence on the content of magnetite.



Table 1. Reaction condition optimization.^a

^a Reaction conditions: To 1.0 mmol benzaldehyde and 1.5 mmol malononitrile in 2 mL of solvent 1 mol% of catalyst (based on active catalytic site) was added. The

reaction solution was stirred at 23 °C for 2 h. ^b The yield was measured by GC-MS using *n*-dodecane as the internal standard.

Several reaction factors were evaluated during the optimization of the Knoevenagel condensation reaction (Table 1). Firstly, a control experiment was performed to study the background rate of the reaction. The result indicated that there was no reactivity in the absence of the catalyst (Table 1, entry 1). Pyridine functioned as a decent homogeneous base catalyst and a yield of 91% was achieved (Table 1, entry 2). Fe₃O₄ microspheres showed no catalytic activity under our reaction conditions in presence of benzaldehyde and malononitrile (Table 1, entry 3). After coating with P4VP, Fe₃O₄@P4VP provided a moderate yield of 2-benzylidenemalononitrile taking advantage of basic functionality of P4VP layer (Table 1, entry 4). ZIF-8 can also promote the Knoevenagel condensation reaction as a Lewis acid although in low yields (Table 1, entry 5). The combination of Fe₃O₄@P4VP and ZIF-8 significantly increased the yield in 2-benzylidenemalononitrile product (Table 1, entry 6). The existence of both Lewis basicity and Lewis acidity strongly facilitates the Knoevenagel condensation reaction of benzaldehyde. In light of this, the synthesized Fe₃O₄@P4VP@ZIF-8 catalyst was tested and it gave its optimal yield at 1 mol% catalyst loading (based on the number of zinc equivalents) when stirred at room temperature for 2 h (Table 1, entry 7). The amount of Fe₃O₄@P4VP and ZIF-8 in Fe₃O₄@P4VP@ZIF-8 catalyst were consistent with the one used in entry 6, for parallel comparison. The outer MOF layer allows the free entry and exit of the organic molecule and it also serves as a good Lewis acid for aldehyde activation. The basic functionality of P4VP ensures the deprotonation of the adduct intermediate and its dehydration, which leads to the benzylidenemalononitrile product. The synthesized Fe₃O₄@P4VP@ZIF-8 catalyst showed significantly improved turnover number (TON) and turnover frequency (TOF) than several other MOF promoted Knoevenagel condensation reaction (Table S1).

Further evaluation indicated that toluene is the most suitable reaction solvent for further Knoevenagel catalytic studies (Table 1, entries 7-11). Dichloromethane and

acetonitrile gave comparable, but slightly compromised yields of the desired product using $Fe_3O_4@P4VP@ZIF-8$ catalyst (Table 2, entries 8 and 9). Oxygen atom containing solvents, such as ethanol and THF, gave only decent yields of the desired benzylidenemalononitrile product (Table 2, entries 10 and 11).

Table 2. Knoevenagel condensation reaction promoted by Fe₃O₄@P4VP@ZIF-8.^a

SCÍ



^aReaction conditions: 1.0 mmol of benzaldehyde, 1.5 mmol of malononitrile and 1 mol% of Fe₃O₄@P4VP@ZIF-8 were dissolved in 2 mL of solvent. The reaction solution was stirred at 23 °C for 2 h. The yield was measured by GC-MS using *n*-dodecane as the internal standard. ^b 6 h of reaction time.

A variety of aldehydes were evaluated employing the $Fe_3O_4@P4VP@ZIF-8$ catalyst using malononitrile as the nucleophile (Table 2). Non-substituted and methyl substituted aromatic aldehydes were compatible with the optimized reaction conditions, which gave yields of 99% in the desired benzylidenemalononitrile product (Table 2, entries 1 and 2). The *tert*-Butyl substituted benzaldehyde showed a slightly compromised yield (Table 2, entry 3). It is postulated that the small pore size of the ZIF-8 support limits the catalytic activity towards the Knoevenagel condensation of large aromatic aldehydes. Electron-rich aldehyde, such as 4-methoxybenzaldehyde, is compatible with $Fe_3O_4@P4VP@ZIF-8$ catalyst under the optimal reaction condition

(Table 2, entry 4). Aldehydes bearing a 4-fluoro electron-withdrawing group were suitable substrates due to their electron-deficient nature (Table 2, entry 5). Furthermore, the heteroaromatic aldehyde reacted smoothly with malononitrile in the presence of Fe₃O₄@P4VP@ZIF-8 catalyst (Table 2, entry 6). Lastly, an alkyl aldehyde such as cyclohexane carbaldehyde was also compatible with the malononitrile nucleophile employing 1 mol% of catalyst. However, extended reaction time was required to achieve an almost quantitative yield (Table 3, entry 7).



Fig. 8 Hot filtration test for the Knoevenagel condensation reaction.

A hot filtration test was conducted to confirm the heterogeneous nature of the aerobic oxidation catalysis (Fig. 8). The Fe₃O₄@P4VP@ZIF-8 catalyst was removed using an external magnet and isolated after 40 min and the aldehyde/malononitrile mixture was stirred for additional 80 min at room temperature. After the separation of the Fe₃O₄@P4VP@ZIF-8 catalyst, no further conversion of benzaldehyde was observed; the yield in benzylidenemalononitrile was determined to be only 57%. This result indicates that the carboxylate ligand bonded to the Zn⁺ species are highly stable and strongly attached to the surface of Fe₃O₄@P4VP. The ICP-AAS of the reaction solution showed that the concentration of Zn was 5.4 ppm, which suggests extremely low leakage of Zn²⁺ ion.



Fig. 9 Fe₃O₄@P4VP@ZIF-8 catalyst recycling test.

Finally, the recyclability of Fe_3O_4 @P4VP@ZIF-8 was studied using benzaldehyde as the model reaction at room temperature. The same batch of catalyst was reused six times and the conversion and selectivity of the product remained at 99% levels (Fig. 9). The high yield and selectivity of the product after six cycles indicated the high stability of the core-shell heterogeneous catalyst and an extremely low leakage of zinc ion. The 6-time reused Fe_3O_4 @P4VP@ZIF-8 catalyst was characterized by SEM, XRD and FTIR. showing no structure alternation on the ZIF-8 framework (Fig. 1d, 3d and S2). As we expected, Fe_3O_4 @P4VP@ZIF-8 is stable under the Knoevenagel reaction conditions.

Conclusions

In conclusion, a novel magnetic core-shell Fe₃O₄@P4VP@ZIF-8 material was developed as efficient catalyst for the Knoevenagel condensation reaction. The microspherical nanoparticles were composed of a magnetic Fe₃O₄(PAA) core, of a P4VP middle layer, as well as of a zinc derived ZIF-8 shell layer. The magnetic composite microspheres were utilized as an efficient catalyst taking advantage of basicity of both P4VP and ZIF-8. High reaction efficiency were achieved utilizing the newly developed Fe₃O₄@P4VP@ZIF-8 catalyst. A variety of aldehyde substrates were converted to the corresponding benzylidenemalononitrile products in good

yields under the optimized reaction conditions. Furthermore, the conversion and selectivity of benzaldehyde using $Fe_3O_4@P4VP@ZIF-8$ as a catalyst was maintained after at least six consecutive reaction cycles. A hot filtration test also suggested the extremely low leakage of zinc ions during the catalytic reaction.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version.

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Highlights

1. A newly designed Fe₃O₄@P4VP@ZIF-8 core-shell catalyst is reported.

2. Layer-by-layer strategy was utilized to achieve core-shell structure at 400 nm.

3. The $Fe_3O_4@P4VP@ZIF-8$ core-shell material can be applied in an efficient Knoevenagel reaction.

4. Rapid catalyst recycling through external magnetic field.