Structural Regulation of Magnetic Polymer Microsphere@Ionic Liquids with an Intermediate Protective Layer and Application as Core–Shell–Shell Catalysts with High Stability and Activity

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ABSTRACT: A novel ionic liquid immobilized on a magnetic polymer microsphere catalyst is reported in this paper. The obtained core−shell−shell catalyst consisted of magnetic nanoparticles (MNPs) as the core, catalytic inert St-co-DVB as the intermediate protective layer, and cross-linked polyaryl imidazole ionic liquids as the active catalytic layer located at the outermost \[\text{Im[OH]}/\text{MNPs@P(St-DVB)@P(VBC-DVB)}\]. This catalyst exhibited a high ion-exchange rate (64.65%), high saturation magnetic strength, and excellent acid and alkali corrosion resistance. In the catalyzed Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, the conversion of benzaldehyde maintained at 92.1% during six times reuse. Optimizing the materials of the protective layer and regulating the thickness of the inert protective layer decreased the corrosion ratio of MNPs in acidic media from 44.82 to 0.44%. Adjusting the thickness of the catalytic layer realized excellent catalytic activity (97%) and high magnetic response performance. In summary, introducing an inert protective layer to the structure of ionic liquids immobilized on the magnetic polymer microsphere catalyst, regulating its thickness, and optimizing its structure achieved a catalyst with high activity, excellent stability, and easy magnetic separation.

1. INTRODUCTION

As a new type of composite functional material, magnetic polymer microspheres have magnetic response, multifunction, easy biodegradation, and biocompatibility and nontoxicity properties and can be easily modified through supplementary means.4−6 Owing to these unique physical and chemical properties, magnetic polymer microspheres have wide applications in biomedicine,7−9 targeted drugs,10 separation engineering,11 cancer therapy,12 and water treatment,13 especially in the field of catalysis,14−16 such as asymmetric Michael and aldol reactions,17 substitution,18 Suzuki−Miyaura coupling reaction,19−21 and so on. Ionic liquids (ILs) exhibit excellent physical and chemical properties and high catalytic activity.22−26 A large number of studies have revealed that catalysis field is a suitable and promising application area for ILs. Compared with traditional catalysts, ILs show better activity, selectivity, and stability in Suzuki−Miyaura coupling reaction, Mizoroki−Heck reaction, and Knoevenagel condensation.27−34 Recently, great efforts have been made to integrate magnetic polymer microspheres with ILs to develop a catalyst with extremely high efficiency, good stability, and excellent recyclability for various advanced applications.35−37 Ali et al. adopted a functionalized poly (ILs)-coated magnetic nanoparticle to efficiently catalyze the synthesis of 1,1-diacetyl from aldehydes.38 Magnetic nanoparticles (MNPs) coated by polymeric sulfonic acid-functionalized imidazolium showed excellent catalytic performance and outstanding paramagnetism in selective oxidation of benzyl alcohol.39 In our previous work, magnetic CoFe2O4 nanoparticle-supported basic poly(IL) catalysts had been successfully applied in transesterification and Knoevenagel condensation with excellent conversion of 93 and 97%, respectively.37

However, great challenges remain to maintain the stability of ILs immobilized on a magnetic polymer microsphere catalyst in a changeable working environment and harsh reaction conditions. In acidic environment, H+ will enter the interior of the core−shell−shell catalyst to corrode MNPs.39,40 On the other hand, O−Si bond between the MNPs and the polymer is easily broken at high pH.41 High-temperature, high-humidity environment will also lead to the destruction of the core−
shell catalyst. Low stability is a stumbling block for large-scale applications of magnetic polymer microsphere-supported IL catalysts. Zhen et al. found that quick destruction of the [BsAlm][OTf]/SCF catalyst leads to remarkable slash in its activity of esterification of oleic acid and straight-chain alcohols. Ren et al. applied a three-layered structure to improve the activity and stability of N-propyl imidazole alkaline ion liquid@MNP catalysts. Obviuously, many improvements have been achieved in promoting their catalyst activity, but the methods to improve the stability of magnetic polymer microsphere supported IL catalysts are rare.

It is reasonable to introduce an inactive copolymer layer as the protective layer between the MNPs and the active catalytic layer to avoid corrosion and leakage of MNPs. Herein, for the first time, a novel catalyst for a core−inactive protective layer−active catalytic layer structure was proposed. An alkaline IL catalyst supported on poly(p-chloromethylstyrene)/3-mercaptopropyltrimethoxysilane-functionalized MNP composite microspheres with polystyrene layer (Im[OH]/MNPs@P(St-DVB-VBC)) was successfully synthesized (Scheme 1). The core of Im[OH]/MNPs@P(St-DVB-VBC) was MNPs modified by the silane coupling agent. The inactive protective layer was an interconnected network shell formed by the inert copolymer of styrene (St) and divinylbenzene (DVB). The active catalytic layer was cross-linked polyaryl imidazole IL obtained by copolymerization of vinyl benzyl chloride (VBC) with DVB, quaternionization reaction with N-propyl imidazole, and alkaline ion exchange. Compared with ILs immobilized on the magnetic polymer microsphere catalyst without the intermediate protective layer (Im[OH]/MNPs@P(VBC-DVB) or Im[OH]/MNPs@P(VBC-St-DVB-VBC)), Im[OH]/MNPs@P(St-DVB-VBC) exhibited better stability, more alkali loading, and higher catalytic conversion. The quantitative relationship between the thickness of the organic layer and the magnetism intensity, catalytic activity, and structural stability of the magnetic polymer microsphere-supported IL catalyst has been rarely studied. Therefore, it is necessary to investigate the effects of the thickness of the protective layer and catalytic layer on the stability, catalytic activity, alkali loading, and recovery of Im[OH]/MNPs@P(St-DVB-VBC) catalysts.

2. RESULTS AND DISCUSSION

2.1. Structural Characteristics and Properties of Catalysts with Different Structures. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images showed that all catalysts were spherical core−shell structures with a diameter of 200−300 nm. The dark core section was magnetic microspheres, and the bright outer section was the organic polymer and IL layer (Figure 1A). The core−shell−shell Im[OH]/MNPs@P(St-DVB-VBC) catalyst showed less agglomeration than core−shell Im[OH]/MNPs@P(VBC-DVB) and Im[OH]/MNPs@P-
VBC-St-DVB) catalysts. Better dispersion was beneficial to catalytic applications. The peaks of Fourier transform infrared (FTIR) spectroscopy (Figure S5c) at 1724 cm$^{-1}$ (C=O) and 1094 cm$^{-1}$ (Si−O−Si) were ascribed to MNP functional groups. The characteristic peaks of the benzene ring around 1452, 1510, and 1601 cm$^{-1}$ were clearly observed, and the peaks at 677 and 1274 cm$^{-1}$ were attributed to C−Cl and Cl−C−H, respectively. Therefore, it indicated that MNPs@P(St-DVB). Im[OH]/MNPs@P(VBC-DVB), (b) Im[OH]/MNPs@P(VBC-St-DVB), and (c) Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) were successfully prepared. The magnetic property of the catalyst is of crucial importance to its application. The magnetic properties of Im[Cl]/MNPs@P(VBC-St-DVB), Im[Cl]/MNPs@P(VBC-St-DVB), and Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) were investigated by a vibrating sample magnetometer (VSM) (Figure 2A). The magnetization of samples could be completely saturated at high fields of up to 30,000 Oe. The saturated magnetic intensities of Im[OH]/MNPs@P(VBC-DVB), Im[OH]/MNPs@P(VBC-St-DVB), and Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) were 0.90, 1.09, and 2.17 emu/g, respectively. Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) showed the highest saturation magnetic strength, which meant its excellent separation property. The stability of the magnetic polymer microsphere support is important for the recycling characteristics of the catalyst. The decompose of supports consists of two aspects: one is the corrosion of MNPs in the acidic environment and the other one is fracture of Si−O−Si structure between the MNPs and polymer in the alkali environment. Therefore, the stability of Im[Cl]/MNPs@P(VBC-DVB), Im[Cl]/MNPs@P(VBC-St-DVB), and Im[Cl]/MNPs@P(St-DVB)@P(VBC-DVB) catalysts in acid and alkali media was investigated. Figure 3 shows the TEM images of the samples corroded by hydrochloric acid. The TEM images showed that the morphology of Im[Cl]/MNPs@P(VBC-DVB) microspheres was obviously deformed, and no obvious MNPs were found. The shell layer of Im[Cl]/MNPs@P(VBC-St-DVB) was relatively intact, and only a part of MNPs was contained in the microspheres. In contrast, the shell layer of Im[Cl]/MNPs@P(St-DVB)@P(VBC-DVB) was complete, and there was no deformation after corrosion. The core of MNPs basically maintained the same. This result was attributed to the introduction of intermediate polystyrene (PS) protect layer that gave more protection to MNPs and made the organic layer more stable. Meanwhile, a catalytic layer was placed on the outermost layer to form a stable core−shell structure to hinder the H$^+$ access to the magnetic core. The low polarity of the PS protective layer was beneficial to the inhibited H$^+$ from diffusing into the interior of the microspheres, which achieved more protection of the internal MNPs. Furthermore, the mass loss of MNPs in the supernatant was quantitatively calculated after acid corrosion (Figure 2B). The loss of MNPs of Im[Cl]/MNPs@P(VBC-DVB)@P(VBC-DVB) was much lower than those of of Im[Cl]/MNPs@P(VBC-DVB) and Im[Cl]/MNPs@P(St-DVB). That meant the low polarity of the PS protect layer showed strong hydrophobicity and...
hindered H⁺ to enter the core of the catalyst to corrode the MNPs. The stabilities of the prepared three catalysts in an alkaline environment were investigated (Figure 2B). No absorption peaks of the iron ion complex occurred after the three different catalysts were corroded in the aqueous solution of NaOH, which indicated that the MNPs in the catalyst did not leak into the solvent. Such a phenomenon could be attributed to the following reasons. For one thing, the outer layers of the three structural catalysts had a protective polymer that prevented OH⁻ permeating into the interior of the catalyst. For another, the cross-link structure of the copolymer prevented the leakage of the MNPs from the network structure.

In summary, the intermediate low polarity PS protect layer gave more protection to MNPs, made outer organic layer more stable by bonding with the magnetic core, and led to the excellent stability of the core—inactive protective layer—active catalytic layer catalyst in acid and alkali media. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate was used to evaluate the catalysts. Catalysts were recycled from the reaction mixture by external magnetic field separation. After being washed with methanol, the recovered catalysts were directly used for subsequent experiments. The conversion of benzaldehyde catalyzed by Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) maintained 92.1% during six times reuse, much higher than those of Im[OH]/MNPs@P(VBC-St-DVB) (88.3%) and Im[OH]/MNPs@P(VBC-DVB) (85.7%) (Figure 2C). The core—inactive protective layer—active catalytic layer catalyst exhibited excellent stability and reusability.

2.2. Structural Regulation of Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB).

Based on the above discussion, the catalyst Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) with core—inactive protective layer—active catalytic layer structure showed perfect stability, excellent catalytic performance, and suitable magnetic response characteristics. It is well known that a thicker protective layer has more improvement in stability and a thicker catalytic layer has more increase in catalytic active site loading. However, more thickness of the organic layer on the surface of the magnetic nanoparticle will decrease the magnetic responsiveness of the catalyst, which affects the recovery performance of the catalyst. The quantitative relationship between the thickness of the inactive protective layer and the magnetism intensity, catalytic activity, and structural stability of the magnetic polymer microsphere-supported IL catalyst was investigated for the first time. Similarly, the same research was done for the thickness of the active catalytic layer, catalytic activity, and magnetic properties.

In this study, the thickness of the inactive protective layer was regulated by changing the amounts of St and DVB added (details are in Supporting Information 1.2, Figure S2, Table S1). SEM images (Figure 4A) revealed that the diameters of the obtained microspheres gradually increased from 200 to about 300 nm with the increase of the St amount. Dynamic light scattering (DLS) showed the same trend of diameter change (Figure S6, Table S1). The stability of Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) with different thicknesses of the inactive protective layer in acid was studied by erosion in acidic solutions. As can
be seen from Figure 4B, with the increase in the amount of St added, the color of erosion solution was lighter, which indicated that less amount of CoFe₂O₄ MNPs corroded. With the increase of the thickness of the inactive protective layer, the loss of CoFe₂O₄ MNPs of Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) by acid corrosion decreased from 44.82 to 0.44% (Figures 4B and S4, Table S1). To obtain proper stability of the catalyst, the value of \( \frac{n_{St}}{n_{VBC}} \) should be no less than 0.5:1. At this point, Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) exhibited excellent stability in an acidic solution.

The magnetic properties of catalysts with different thicknesses of the inactive protective layer were investigated. With the increase in the value of \( \frac{n_{St}}{n_{VBC}} \) from 0.5 to 5, the magnetization saturation value decreased from 2.78 to 0.208 emu/g (Figures 4B and S4, Table S1). To obtain proper stability of the catalyst, the value of \( \frac{n_{St}}{n_{VBC}} \) should be no less than 0.5:1. At this point, Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) exhibited excellent stability in an acidic solution. The magnetic properties of catalysts with different thicknesses of the inactive protective layer were investigated. With the increase in the value of \( \frac{n_{St}}{n_{VBC}} \) from 0.5 to 5, the magnetization saturation value decreased from 2.78 to 0.208 emu/g (Figure 4C, Table S1). According to the observation of experimental phenomena (Figure 4C), when the saturation magnetic intensity of the sample was equal to or less than 1 emu/g, the magnetic separation performance of the catalyst was too weak to realize rapid separation from the reaction system. It meant that, only when the value of \( \frac{n_{St}}{n_{VBC}} \) was equal to or less than 1, the catalyst could be readily magnetized and manipulated by an applied magnetic field to realize rapid separation from the reaction system in a magnetic field of 300 mT.

Briefly, the inactive protective layer could be quantitatively regulated by the amount of St added. The quantitative relationship among the thickness of the inactive protective layer, stability, and the magnetic properties was revealed. To obtain proper stability and magnetic property, the proper range of \( \frac{n_{St}}{n_{VBC}} \) was from 0.95 to 1.70 (Figure 4D).

Active catalytic layer is where chemical reactions take place. Proper thickness of the active catalytic layer is of great importance in the practical application. To regulate the thickness of the catalytic layer, a series of samples with different amounts of VBC were prepared (details are in Supporting Information 1.3, Figure S3). The obtained catalysts with different thicknesses of the catalytic layer were characterized by SEM (Figure 5A) and DLS (Figure S7, Table S2). With the increase in the amount of VBC, the particle sizes of the catalysts increased, indicating that the thickness of the catalytic layer could be regulated by the amount of VBC.

The catalytic performance of the catalysts with different thicknesses of the catalytic layer for Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate was investigated. As could be seen (Figure 5B, Table S2), with the increase in the amount of VBC added, the conversion of benzaldehyde showed a trend of increase at the first stage followed by a decrease. This is attributed to the increase of the local active center, which promoted an increase in conversion. Then, the increase in the thickness of the catalytic layer directly led to the increase in mass-transfer resistance, which in turn caused a certain degree of reduction in conversion, especially in the reaction systems with the same amount of the active center. Therefore, the proper value of \( \frac{n_{St}}{n_{VBC}} \) added in the reaction mixture was from 1/3:1 to 1:1.

Magnetic properties are of great importance to the separation and recycle of the catalyst. The increase of the thickness of the catalytic layer for Knoevenagel condensation between benzaldehyde and ethyl cyanoacetate was investigated. As could be seen (Figure 5B, Table S2), with the increase in the amount of VBC added, the conversion of benzaldehyde showed a trend of increase at the first stage followed by a decrease. This is attributed to the increase of the local active center, which promoted an increase in conversion. Then, the increase in the thickness of the catalytic layer directly led to the increase in mass-transfer resistance, which in turn caused a certain degree of reduction in conversion, especially in the reaction systems with the same amount of the active center. Therefore, the proper value of \( \frac{n_{St}}{n_{VBC}} \) added in the reaction mixture was from 1/3:1 to 1:1.

Magnetic properties are of great importance to the separation and recycle of the catalyst. The increase of the thickness of the catalytic layer sharply weaken the magnetic response intensity of catalysts in the magnetic field. With the molar ratio of \( n_{St} \) and \( n_{VBC} \) ranging from 2 to 1/3, the saturation magnetic strength ranged from 4.949 to 0.156 emu/g (Figure 5C, Table S2). In the polymerization reaction, only when the value of \( \frac{n_{St}}{n_{VBC}} \) was equal to or less than 1 the catalysts could be easily magnetized and separated from the reaction system in a magnetic field of 300 mT.
Briefly, the catalytic layer could be quantitatively regulated by the amount of VBC. To obtain a proper catalytic and magnetic property, the proper range of $n_{\text{St}}/n_{\text{VBC}}$ was from 0.65 to 1.26 (Figure 5D).

The catalyst obtained in the range of 0.95–1.70 of $n_{\text{St}}$ and $n_{\text{VBC}}$ showed excellent stability and recyclability, and the catalyst obtained in the range of 0.65–1.26 of $n_{\text{St}}$ and $n_{\text{VBC}}$ exhibited high catalytic ability and recyclability.

3. CONCLUSIONS

In summary, a novel concept of inert protective layer as the intermediate protective structure of magnetic polymer-supported ILs was proposed in this study. A core–shell–shell catalyst with CoFe$_2$O$_4$, MNPs as the core, S–co-DVB inactive protective layer as the intermediate shell, and cross-linked polyaryl imidazole IL active catalytic layer as the outermost shell and possessing high activity, excellent stability, and easy magnetic separation was designed and synthesized. This Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB) catalyst exhibited high ion-exchange rate (64.65%) and excellent acid and alkali corrosion resistance (the corrosion ratio of MNPs in acidic media decreases from 44.82 to 0.44%). In the catalyzed Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, the conversion of benzaldehyde maintained at 92.1% during six times reuse, which was much higher than those of Im[OH]/MNPs@P(VBC-St-DVB) (88.3%) and Im[OH]/MNPs@P(VBC-DVB) (85.7%). The quantitative relationship between the thickness of the organic layer and the magnetism intensity, catalytic activity, and structural stability of the magnetic polymer microsphere-supported IL catalyst has been innovatively revealed. The thickness of the S–co-DVB protective layer and the polyaryl imidazoles IL catalytic layer could be accurately controlled by the amounts of St and VBC. To obtain a catalyst with excellent stability and recyclability, the optimum value of $n_{\text{St}}/n_{\text{VBC}}$ was 0.95 to 1.70. To obtain a catalyst with high catalytic ability and recyclability, the optimum value of $n_{\text{St}}/n_{\text{VBC}}$ was 0.65 to 1.26. The quantitative correlation between the thickness of the protective and catalytic layer and the stability, activity, and magnetic properties of the catalyst can be used to optimize the design of good stability, high activity, and easy separation of ILs immobilized on the magnetic polymer microsphere catalyst.

4. EXPERIMENTAL SECTION

4.1. Materials. VBC (95%), St (> 98%), DVB (95%), and N-propyl imidazole were obtained from J&K Scientific Ltd (Beijing, China). Methylbenzene, sodium hydroxide (NaOH), methanol, 2,2-azobisobutyronitrile (AIBN), and other chemicals were purchased from Beijing Chemical Works (Beijing, China). γ-Methacryloxypropyltrimethoxysilane-modified CoFe$_2$O$_4$ nanoparticles (MNPs) were synthesized according to a published literature.

4.2. Preparation of Catalysts. Three kinds of catalysts were prepared by three steps, which are solution polymerization, quaternization, and ion-exchange reaction. The synthesis procedures are described in Scheme 1.

4.2.1. Preparation of Magnetic Polymer Microspheres. Magnetic polymer microspheres were all prepared by solution polymerization.

For the preparation of MNPs@P(VBC-DVB), MNPs (0.1 g) were dispersed in acetonitrile (40.0 mL) and sonicated for 10 min followed by addition of 2.5 mL of VBC and 0.625 g of DVB. The obtained mixture was placed in a four-necked flask, heated to 70 °C under N$_2$ protection, and added to AIBN to react for 4 h. The obtained solid product was magnetically separated, washed three times with ethanol, and placed in a vacuum oven at 60 °C for 12 h to obtain MNPs@P(VBC-DVB).

For the preparation of MNPs@P(VBC-St-DVB), MNPs (0.1 g) were dispersed in acetonitrile (40.0 mL) and sonicated for 10 min followed by addition of 1.25 mL of VBC, 1.25 mL of St, and 0.625 g of DVB. The obtained mixture was placed in a four-necked flask, heated to 70 °C under N$_2$ protection, and added to AIBN to react for 4 h. The obtained solid product was magnetically separated, washed three times with ethanol, and placed in a vacuum oven at 60 °C for 12 h to obtain MNPs@P(VBC-St-DVB).

For the preparation of MNPs@P(St-DVB)@P(VBC-DVB), MNPs (0.1 g) were sonicated for 10 min in acetonitrile (40.0 mL) to form a uniform mixture, followed by the addition of a certain amount of St and DVB. The obtained mixture was introduced into a four-necked flask under a N$_2$ atmosphere and heated to 70 °C. AIBN (2 wt.% to St) was added, and the reaction was continued for 2 h. Thereafter, a certain amount of VBC and DVB was added, and the reaction was continued for 3 h at 70 °C with the same amount of AIBN as in the first step. Finally, the obtained product was magnetically separated, washed three times with toluene and ethanol, and placed in a vacuum oven at 60 °C for 12 h to obtain a brown product [MNPs@P(St-DVB)@P(VBC-DVB)].

4.2.2. Preparation of Alkaline ILs Immobilized on Copolymer-Coated Magnetic Nanoparticles. The procedures to prepare three kinds of alkaline ILs immobilized on copolymer-coated MNPs are the same. Magnetic polymer microspheres (0.3 g) and N-propyl imidazole (4.4 g) were poured into a toluene/methanol (30.0/10.0 mL) mixture at 90 °C. The resultant product was purified by methanol and then annealed in a vacuum oven at 150 °C for 3 h. After that, the obtained product (0.2 g) was dispersed in a mixture of NaOH, toluene, and ethanol (0.2 g/15 mL/5 mL) and stirred for 10 h. The obtained magnetic microspheres @ alkaline IL-immobilized polymers [Im[OH]/MNPs@P(VBC-DVB), Im[OH]/MNPs@P(VBC-St-DVB), or Im[OH]/MNPs@P(St-DVB)@P(VBC-DVB)] were separated by an external magnet and washed with ethanol until neutral.

4.3. Characterizations. SEM images were obtained with a JSM-7500F scanning electron microscope. TEM images were conducted on a JEOL 2010F microscope at 200 kV. FTIR spectroscopy was conducted via a Shimadzu IR A-1 spectrophotometer. Thermal gravimetric analyses were performed in air with a heating rate of 10 °C/min on a WCT-1D thermogravimetric and differential thermal analyzer. The size distribution of samples was calculated from a Malvinic Mastersizer 2000 analyzer. The magnetic properties of the samples were measured with a VSM. The UV–visible spectrophotometer used for spectra acquisition was from Shimadzu (UV-2450, Tokyo, Japan). The content of OH$^-$ was determined by back titration. The stability of catalysts in acid and alkali media and catalytic performances were determined in the same way as in the reported literature.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02777.

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Notes
The authors declare no competing financial interest.

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