

Synthesis of a new polystyrene@Fe₃O₄ magnetic microspheres

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In this article, the synthesis process of magnetic polystyrene@Fe₃O₄ was investigated, which are suitable for the application in magnetically stabilized fluidized-bed reactors. The magnetic polystyrene@Fe₃O₄ coated with Fe₃O₄ were prepared by suspension polymerization. In the reaction, triethoxy(vinyl)silane, styrene, divinylbenzene, liquid paraffin, gelatin, benzoyl peroxides (BPO) were used as the surfactant, monomers, the crosslinking agent, a porogenic agent, a dispersant, an initiator, respectively. Simultaneously, the chemical composition, morphologies, particle sizes, the amount of Fe₃O₄ coated were analyzed. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (FTIR), vibrating sample magnetometer (VSM) analysis and thermo gravimetric analysis (TGA). The results showed that the new type of magnetic polystyrene@Fe₃O₄ microspheres were porous, spherical in shape with a narrow particle size distribution in the range of 150–200 μm. The amount of Fe₃O₄ coating reached to 12.39%, and the maximum saturation magnetization was 51.71 A·m²·kg⁻¹ at room temperature. In addition, the results also showed that polystyrene@Fe₃O₄ magnetic microspheres have good acid resistance and good suspendability.

Keywords: suspension polymerization, microspheres, Fe₃O₄, surface modification, coating.

Introduction

Magnetic polymer microspheres are a special type of magnetic and surface-functionalized microspheres, prepared by the combination of an organic polymer and an inorganic magnetic material [1-4]. They have a great potential in chemical engineering, biological, medical and environmental sciences. However, these magnetic polymer microspheres are easily to reunite due to their large specific surface areas and high surface energies. Therefore, surface modification by silane-based inorganic molecules and polyethylene glycol have often been used to prevent molecular reunion [5-7].

In recent years, more and more attention has been focused on the core-shell magnetic composites with Fe₃O₄ nanoparticles as core and the polymer as shell [8]. For example, Denkbass et al. prepared magnetic chitosan nanoparticles by suspension crosslinking technology with the particle size of 100–200 μm [9]. Chen. et al. prepared magnetic polymethyl methacrylate nanoparticles by spray suspension polymerization, which were used hydrophobic Fe₃O₄ magnetofluid as the magnetic substance [10]. Especially, the cerium ion-chelated magnetic

silica microspheres were also synthesized, with an excellent performance [11].

According to a large amount of literature, there were little reports about polymer composite materials, which the polymer as the core and Fe₃O₄ nanoparticles as the shell. These materials not only have higher magnetism, but also were applied in more and more fields, such as chemical catalysis, environmental engineering, medicine and biological engineering [12]. For example, in order to solve the problem of difficult separation and recovery of nano-catalysts, nano-scale catalysts were immobilized on the magnetic microspheres, which caused to be separated [13]. In addition, these magnetic microspheres were used to analyze and detect the hydrazine content in waste water [14].

It can be inferred that these magnetic materials will be a kind of new and multifunctional materials. So in this article, a new type of magnetic polymer material was prepared through the suspension polymerization, which used polymer as the core of, iron oxide as the shell of. The magnetic materials will be applied in magnetically stabilized fluidized-bed reactors in the following work [15].

Experimental

Materials

Fe₃O₄ (AR), triethoxy(vinyl)silane (SG-151, CP), poly-

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styrene (AR), divinylbenzene (AR), benzoyl peroxides (BPO, CP), paraffin (CP), gelatin (CP), Mg_2SO_4 (AR), Na_2CO_3 (AR) and other materials were purchased from Sinopharm Chemical Reagent Co. Ltd.

Characterization

D8 ADVANCE X-ray powder diffractometer was used for analyzing the crystal structure of the samples. JSM-6700F Scanning Electron Microscope was used to detect the morphologies and microstructures of samples. Vibrating sample magnetometer was used to test the magnetic properties of the samples. Thermo gravimetric analysis was used to determine the amount of the Fe_3O_4 coated on the samples.

Surface modification of Fe_3O_4 nanoparticles

6.0 g of Fe_3O_4 nano-magnetic powder and 7.5 g triethoxy(vinyl)silane were transferred into a 500 mL three-necked flask, followed by addition of 175 mL absolute ethanol and 175 mL of distilled water. Subsequently, the above suspending solutions was shaking at 40 °C for 16 h under nitrogen atmosphere with stirring speed of 600 rpm. Finally, the solid obtained was washed by ethanol and deionized water repeatedly, and dried under vacuum at 60°C for 48 h.

Preparation of magnetic polystyrene@ Fe_3O_4 microspheres

0.22 g of gelatin was taken in a 500 mL 3-necked round-bottomed flask and then 80 mL of distilled water was added and the mixture was allowed to soak for 12 h. The flask was then placed in a 35 °C water heating and the mixture was stirred at 600 rpm for 1 h, followed by sequential addition of 0.2 g of BPO, 7 mL divinylbenzene, 24 mL of styrene, and 11 mL liquid wax. This reaction was stirred for 30 min and heated up to 45 °C at a heating rate of 0.5 °C/min. 0.63 g of anhydrous sodium carbonate and 1.25 g of anhydrous

magnesium sulfate were added, and raised temperature to 80 °C, lasted for 10 min, then 2.0 g of SG-151 modified Fe_3O_4 magnetic powder was added and reacted for 4 h. Increase the temperature to 95°C again and maintained for 2 h. Finally, waiting for the reaction dropped to 80 °C, washed and filtered with the deionized water of 60 °C, and then dried under vacuum for 24 h.

Results and Discussion

SEM analysis

Fig. 1 represents the SEM images of microsphere samples. S_1 ~ S_2 represent polystyrene microsphere and S_3 ~ S_4 stand for magnetic polystyrene@ Fe_3O_4 microsphere. It can be obviously seen from Fig. 1 that the polystyrene microspheres had smooth surfaces with the sizes of 150 ~200 μm , which were sphere and better dispersion. At the same time, it can also be seen in the SEM images of S_3 ~ S_4 , the sizes of the polystyrene@ Fe_3O_4 microspheres prepared were in the range of 150~250 μm , but the surface is uneven and black. Therefore, it can be said that the sizes of magnetic polystyrene@ Fe_3O_4 microspheres were slightly larger than the polystyrene microspheres, and covered with small amounts of Fe_3O_4 nanoparticles.

X-ray diffraction analysis (XRD)

Fig. 2(a, b and c) represent the X-ray diffraction-patterns of polystyrene @ Fe_3O_4 magnetic microspheres, Fe_3O_4 nanoparticles and polystyrene microspheres, respectively. It can be clearly seen from Fig. 2(a) and (b), both of the Fe_3O_4 nanoparticles and the synthesized polystyrene magnetic microspheres were showed the same diffraction peaks at 18.3°, 30.2°, 35.5°, 43.1°, 53.6°, 57.0°, and 62.8°. This result is consistent with the XRD patterns of Fe_3O_4 reported previously [12]. In additionally, it can be seen from Fig. 2(a) and (c) that there was a large dispersed diffraction peak at 20°, which is the typical diffraction peak for amorphous polystyrene. These results showed that Fe_3O_4 was not

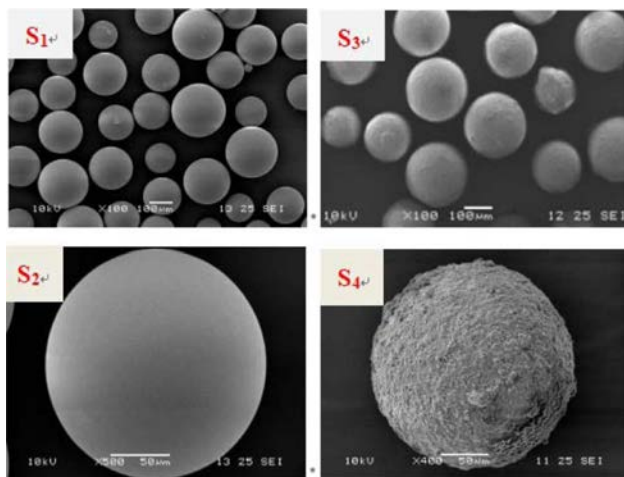


Fig. 1. SEM images of samples, S_1 ~ S_2 polystyrene microsphere; S_3 ~ S_4 magnetic polystyrene@ Fe_3O_4 microsphere.

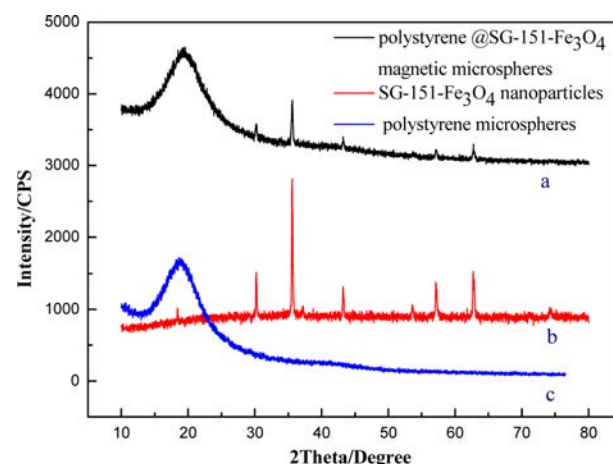


Fig. 2. XRD patterns of polystyrene microspheres Fe_3O_4 nanoparticles and polystyrene@ Fe_3O_4 magnetic microspheres.

only coated on the surface of polystyrene, but also the crystal structures of Fe₃O₄ and polystyrene unchanged in the reaction.

FTIR diffraction analysis (FTIR)

From Fig. 3, the absorption peaks are obviously seen at 3,439 cm⁻¹ and 3,081 cm⁻¹, they were the stretching peak of O-H adsorbed on the surface of microspheres. And while, the absorption peaks at 3,081 cm⁻¹, 3,059 cm⁻¹ and 3,025 cm⁻¹, which were aromatic hydrogen on aromatic rings and the bending vibration of C-H; The absorption peaks at 2,922 cm⁻¹ and 2,851 cm⁻¹ represented the C-H on polystyrene main chain; The serial absorption peaks at 1,630 cm⁻¹~1,452 cm⁻¹ were the C=C on benzene; The absorption peaks at 697 cm⁻¹ and 757 cm⁻¹ showed that it was a monosubstituted benzene. Especially, the absorption peaks at 537 cm⁻¹ was the Fe-O of Fe₃O₄. All of these showed that the prepared magnetic microspheres contained polystyrene and Fe₃O₄. This results further illustrated that Fe₃O₄ had been coated on the surface of polystyrene.

Thermogravimetric analysis (TGA)

Fig. 4 represents the thermo gravimetric curves of magnetic polystyrene@Fe₃O₄ at a nitrogen atmosphere with a heating rate of 2 °C/min. It can be seen from Fig. 4 that the weight of magnetic polystyrene@Fe₃O₄ microspheres decreased for the reason of water and residual inorganics removed at below 200 °C. Moreover, it was found that the prepared polystyrene magnetic microspheres coated the higher amount of Fe₃O₄, which reached to 12.39%. However, in the reaction, if added the unmodified Fe₃O₄, the amount of Fe₃O₄ was only 7.35%. This result illustrated that Fe₃O₄ modified by surfactant (SG-151) was easier to be coated on the surface of polystyrene. It may be ascribed to the double bonds formed on the surface of the Fe₃O₄ in the during of the modified reaction, which could be better coated

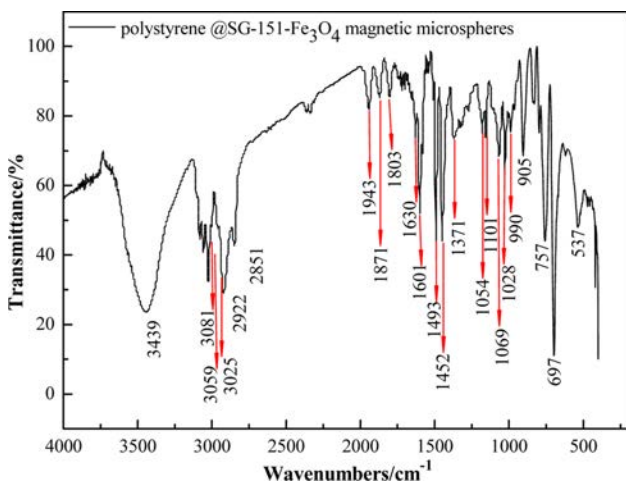


Fig. 3. FTIR curves of the magnetic polystyrene@Fe₃O₄ microspheres.

on the surface of polystyrene.

Analysis of magnetic properties (VSM)

Seen from the Fig. 5, the VSM diagram of the polystyrene@SG-151-Fe₃O₄ magnetic microspheres was analyzed, used the modified Fe₃O₄ magnetic microspheres and polystyrene microspheres as the Controlled experiments. As can be obviously seen from Fig. 5, the saturated magnetic intensities of the prepared magnetic polystyrene@SG-151-Fe₃O₄ microspheres was reached to 51.71 A·m²·kg⁻¹, which used the modified Fe₃O₄ in the reaction. But if used the unmodified Fe₃O₄, the saturated magnetic intensities was only 20.90 A·m²·kg⁻¹. It can be seen that, the prepared magnetic polymeric materials in this study show higher magnetism and better superparamagnetism, if used the modified Fe₃O₄ during the preparation of magnetic polystyrene@Fe₃O₄ microspheres. Obviously, the saturated magnetic intensities of the polystyrene microspheres and the SG-151 modified Fe₃O₄ nano-magnetic were 1.59 A·m²·kg⁻¹ and 71.97 A·m²·kg⁻¹, respectively. This result showed that the magnetism of magnetic polystyrene microspheres

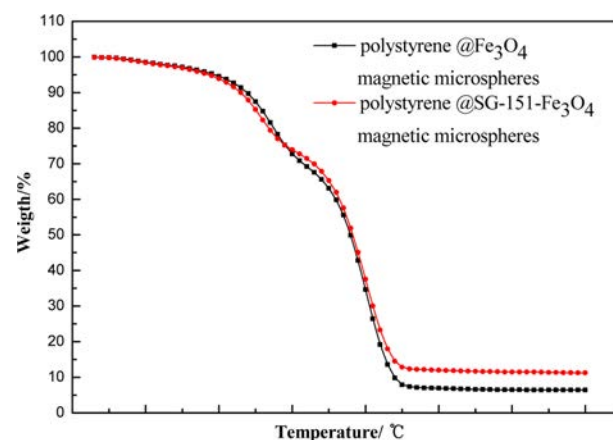


Fig. 4. TGA curves of the magnetic polystyrene@Fe₃O₄ microspheres

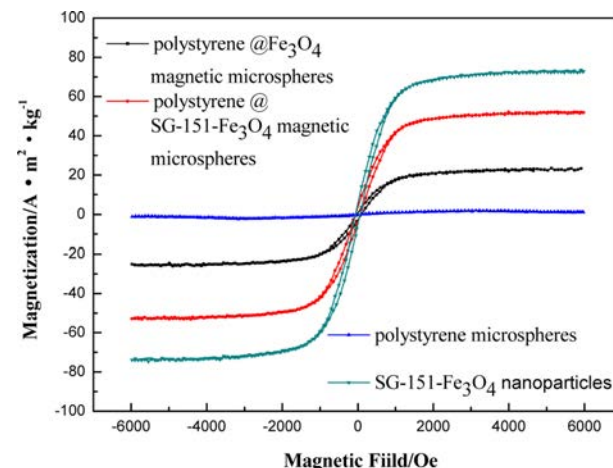


Fig. 5. The VSM diagrams of the magnetic polystyrene microspheres.

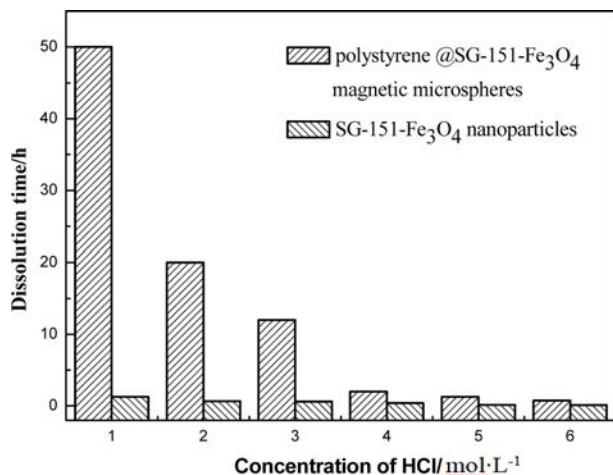


Fig. 6. The acid resistance of the magnetic polystyrene microspheres.

significantly increased, if added SG-151 modified Fe₃O₄ nano-magnetic in the process of preparation. The saturated magnetic intensities of the prepared magnetic polystyrene@ SG-151-Fe₃O₄ microspheres was 32.52 times higher than the polystyrene microspheres, 2.47 times of the prepared magnetic polystyrene@Fe₃O₄ microspheres, approximately 80% of the SG-151 modified Fe₃O₄. It may be owed to the increased amount of Fe₃O₄ coating on the surface of polystyrene microspheres, resulting in the higher magnetic.

Acid resistance of magnetic microspheres

Fig. 6 represents the dissolution time of the prepared magnetic polystyrene@SG-151-Fe₃O₄ microspheres and SG-151 modified Fe₃O₄ nano-magnetic at different concentration of HCl. In the experiments, added 0.2 g magnetic polystyrene@SG-151-Fe₃O₄ microspheres and SG-151-Fe₃O₄ nanoparticles into different beakers contained 10 mL different concentration hydrochloric acid solution. After reacted for some time, all of the solution could be changed yellow, but the colour of the solutions (1mol/L⁻¹HCl) were changed mostly slow. Seen from the figure 6, the solutions (1 mol/L⁻¹HCl) changed to be yellow for 50 min and 1.27 min of the polystyrene@SG-151-Fe₃O₄ microspheres and SG-151-Fe₃O₄ nanoparticles, Respectively. It can be obviously seen that the acid resistance of the magnetic polystyrene microspheres more better than the SG-151-Fe₃O₄ nanoparticles. In especial, when the concentration of HCl is less than 3 mol·L⁻¹, the magnetic polystyrene microspheres have better acid resistance. So, it has more extensive application value.

Applications of magnetic microspheres

A certain amount of polystyrene magnetic microspheres was weighed and introduced into a magnetically stabilized fluidized bed. The bed was then vented and a U-shaped differential pressure gauge was used to determine the pressure drop of the bed. Meanwhile, the

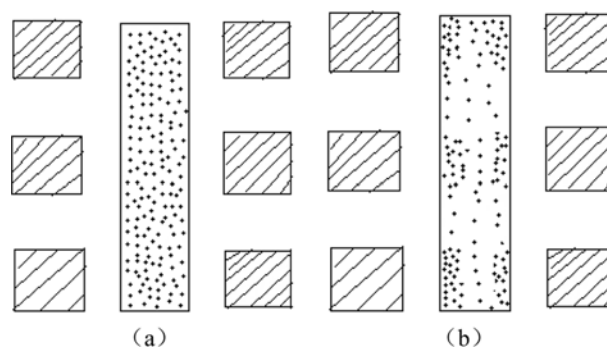


Fig. 7. Suspension of polystyrene@Fe₃O₄ magnetic microspheres in a magnetically stabilized fluidized bed reactor.

flow state of the bed layer was reflected by the changes in the pressure drops. The average of the gas phase holdup was measured by the changes in the liquid level of the bed [15, 16]. The suspension performances of polystyrene@ SG-151-Fe₃O₄ magnetic microspheres in magnetically stabilized fluidized bed reactor, before and after applying the magnetic field, are shown in Fig. 7.

Fig. 7(a) shows the suspension state of particles in magnetically stabilized fluidized bed at the absence of magnetic field. From the Fig. 7(a), we can see that uniformly dispersed magnetic polystyrene microspheres in the in the stabilized fluidized bed reactor. Fig. 7(b) shows the suspension of polystyrene@ SG-151-Fe₃O₄ magnetic microspheres, when a magnetic field formed in the fluidized bed with a voltage of 200 V. When the intensity of magnetic field reached to 2000 Oe, the polystyrene@ SG-151-Fe₃O₄ magnetic microspheres fast moved to the magnetic field zone in the magnetically stabilized fluidized bed reactor. According to the Fig. 7(a) and (b), it can be accounted that the polystyrene@ SG-151-Fe₃O₄ magnetic microspheres had better suspendability in the stabilized fluidized bed reactor without magnetic field, once under the magnetic field, the polystyrene magnetic microspheres shown better magnetism again. So, the prepared magnetic polystyrene @SG-151-Fe₃O₄ microspheres could be expected to be applied to the magnetic catalysis field [16, 17].

Conclusions

In this paper, a new type of magnetic polymer material was prepared by suspension polymerization with Fe₃O₄ nanoparticles as the shell and polystyrene as the core. The experimental results showed that double bonds were present on the surfaces of Fe₃O₄ nanoparticles after modification by surfactant SG-151 leading to a better coating of these nanoparticles on the polymer material. The polystyrene@SG-151-Fe₃O₄ magnetic materials was spherical with uneven and black surface of the sizes 150~200 μm, and the better superparamagnetism. The amount of Fe₃O₄ coated on

the magnetic polymer material reached 12.39%, and the highest saturation magnetization was 51.71 A·m²·kg⁻¹. Meanwhile, polystyrene@Fe₃O₄ magnetic microspheres have good acid resistance and good suspendability. In the future, a reactor system suitable for the magnetically stabilized fluidized bed will be presented, for the mathematical modeling and a suitable reaction system will be simulated and established using the magnetic polystyrene microspheres as the catalyst [14].

Acknowledgments

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