Synthesis and applications of polystyrene@Fe_3O_4 magnetic microspheres

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Abstract

The method for synthesis of magnetic polystyrene microspheres coated with Fe_3O_4 nanoparticles, for applications in magnetically stabilized fluidized-bed reactors, was investigated. The microspheres were prepared by suspension polymerization using triethoxy(vinyl)silane as the surfactant, modified Fe_3O_4 nanoparticles, styrene as monomers, divinylbenzene as the crosslinking agent, liquid paraffin as a porogenic agent, gelatin as a dispersant, and BPO as an initiator. Chemical composition, morphologies, particle sizes, magnetic properties of the magnetic polystyrene microspheres, and amount of Fe_3O_4 coated were investigated by scanning electron microscopy (SEM), infrared spectroscopy, X-ray diffraction (XRD) analysis, magnetic property using vibrating sample magnetometer and thermogravimetric analysis. The results showed that the new type of synthesized polystyrene@Fe_3O_4 magnetic microspheres were porous, spherical in shape with a narrow particle size distribution in the range of 250~300μm. The amount of Fe_3O_4 coating reached 7.81％, and the maximum saturation magnetization was 3.97 emu/ g.

Keywords

suspension polymerization, Fe_3O_4 magnetic nanoparticles, surface modification, coating, magnetic polystyrene microspheres.

1. Introduction

Magnetic polymer microspheres are a special type of magnetic and surface functional microspheres, prepared by the combination of an organic polymer and an inorganic magnetic material[1-2]. They have broad range of applications and good prospects for use in various fields like chemical engineering, medical, and environmental sciences. In recent years, they have attracted tremendous attention of scholars, both at home and abroad. For example, Lenz et al. synthesized a type of magnetostrictive fiber material, which generates axial stress on optical fibers under the effect of a magnetic field[3].

In this paper, a new type of magnetic polymer material was prepared by suspension polymerization with the polymer as a core and magnetic material as the shell, which was then applied to magnetically stabilized fluidized-bed reactors [4].

2. Methodol

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 ^{0}C water bath and the mixture was stirred at 600 rpm for 1 h, followed by sequential addition of 0.2 g of benzoyl peroxide, 7 mL divinylbenzene, 24 mL of styrene, 6 mL of acrylic acid, and 11 mL liquid wax. This reaction mixture was stirred for further 30 min and heated up to 45^{0}Cat a heating rate of 5^{0}C/ 10 min. 0.63 g of anhydrous sodium carbonate and 1.25 g of anhydrous magnesium sulfate were then added and the temperature was raised to 80^{0}C gradually and allowed to react at this temperature for 10 min. 2.0 g of SG-151 modified Fe_3O_4 magnetic powder was then added followed by stirring at 80^{0}C for 4 h. Then the reaction mixture was heated to 95^{0}C and left at this temperature for 2h. Finally the reaction mixture was cooled to 80^{0}C, washed and the solution filtered while it cooled down to 60 ^{0}C and then dried under vacuum for 24 h.

3. Results and discussion

3.1 SEM analysis

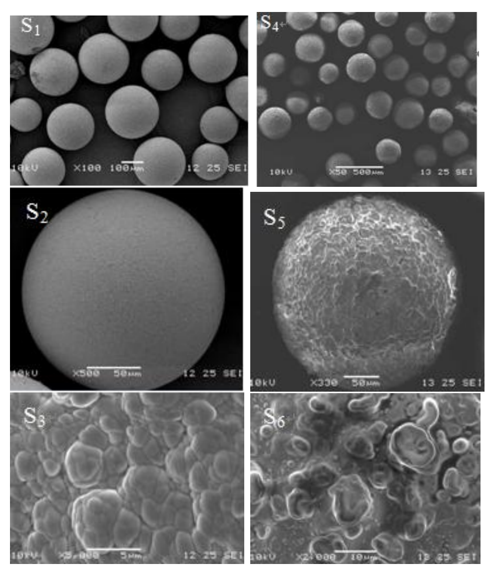

Fig. 1 SEM images of samples- S1~S6

It can be seen in the micrographs of S1~S3 that the polystyrene microspheres had smooth surfaces with particle sizes of 150~200μm. They were spherical in shape and possessed good dispersibility. It can be seen in the micrographs of S4~S6 that the particle sizes of the magnetic polystyrene spherical microspheres prepared by

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the surface-modification with Fe_3O_4, were in the range of 250~300μm, with good dispersibility and obviously had rough surfaces.

3.2 Thermogravimetric analysis (TGA)

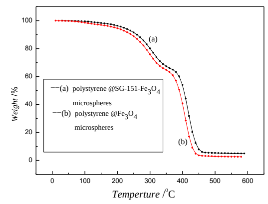

Fig. 2 TGA curves of the polystyrene@Fe_3O_4 magnetic microspheres

It can be seen from Fig.3 that under a nitrogen atmosphere at a heating rate of 2^0C/ min, the polystyrene magnetic microspheres lost water and residual inorganics below 200 ^{0}C. At a temperature above 450 ^{0}C, the weight of the sample hardly underwent any change, indicating that the polystyrene microspheres in the magnetic polystyrene microsphere samples had been completely decomposed. The amount of Fe_3O_4 that covered the microspheres could be determined. By analyzing the two thermogravimetric curves in Fig.4, it was found that the polystyrene magnetic microspheres prepared using SG-151 modified Fe_3O_4, had the highest amount of Fe_3O_4 coating, which was 7.81%.

3.3 Analysis of magnetic properties (VSM)

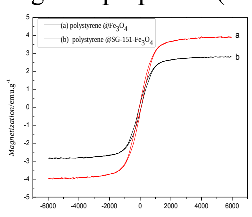

Fig.3 The VSM diagrams of the magnetic polystyrene microspheres prepared by SG-151 modified with and unmodified Fe_3O_4

As can be seen from Fig.4, the saturated magnetic intensities of the magnetic polystyrene microspheres obtained before and after the modification of Fe_3O_4 nano-magnetic powder were 3.00emu/g and 3.97emu/g, respectively. This indicated an enhancement in the magnetic properties of polymeric materials after coating and it also showed relatively good superparamagnetism.

3.4 Applications of Magnetic Microspheres

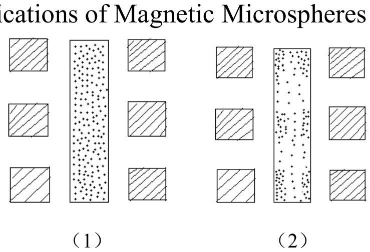

Fig.4 Suspension of polystyrene@Fe_3O_4 magnetic microspheres in a magnetically stabilized fluidized bed reactor

Fig. 4(1) shows a magnetically stabilized fluidized bed, which in the absence of magnetic field shows uniformly dispersed magnetic polystyrene microspheres in the visual cylinder. Fig. 4 (2) shows the schematic diagram of the suspended magnetic polystyrene microspheres, when a magnetic field was applied to the fluidized bed, which was connected to a voltage of 200 V, and vented with air, water and polystyrene microspheres at 500 mL/ min to form a three-phase system. When the intensity of magnetic field reached 2000 Oe, the polystyrene magnetic microspheres moved partially towards the magnetic field in the magnetically stabilized fluidized bed, whereas in the case of the fluidized bed region without applied magnetic field, microspheres were seen suspended in it. The polystyrene magnetic microspheres filled the entire magnetic fluidized bed pipeline, indicating that the prepared magnetic microspheres had good suspendability, which can be applied at high magnetic field intensities.

3. Conclusions

In this paper, a new type of magnetic polymer material was prepared by suspension polymerization with Fe_3O_4 nanoparticles as the shell and polystyrene as the core. The experimental results showed that after modification by surfactant SG-151, double bonds were present on the surfaces of Fe_3O_4 nanoparticles, leading to a better coating of these nanoparticles on the polymer material. The experimentally obtained new polystyrene@Fe_3O_4 magnetic materials were spherical microspheres with particle sizes of 250~300μm and possessed relatively good superparamagnetism. The amount of Fe_3O_4 coated on the magnetic polymer material reached 7.81%, and the highest saturation magnetization was 3.97emu/ g. In 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 [4].

Acknowledgments

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