Synthesis and character investigation of magnetic alumina microspheres

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Abstract.Magnetic alumina microspheres with Fe_3O_4 core/Al_2O_3 shell structure were synthesized by the oil column method. Fe_3O_4/SiO_2/Al_2O_3 particles showed to be fit for applications as a magnetic carrier due to their magnetic properties and pore structure. The specific surface area and pore volume of the Fe_3O_4/SiO_2/Al_2O_3 composite microspheres calcined at 500°C were 200 m^2/g and 0.77 cm^3/g, respectively.

1. Introduction

In recent years, magnetically stabilized bed(MSB) has been widely used in various fields, such as petrochemicals, biochemicals, and environmental chemicals. The most important feature of MSB is that there is a uniformly stable magnetic field in the axial direction, so the magnetic catalyst particles are in arrange of uniform, stable and order[1-7]. MSB has the advantages of both fixed and fluidized beds, such as low bed pressure, low abrasion, and high mass-transfer rate.

In order to meet the requirements of MSB for the magnetic properties of catalyst, it is very important to prepare carriers with high specific saturation magnetization. Magnetic alumina carrier with $NiFe_2O_4$ as magnetic core has been widely investigated [8-11]. Although the magnetic properties of the spheres with $NiFe_2O_4$ can fit for the magnetic stabilized bed, the magnetic properties of the balls are narrowly adjusted.

The magnetic properties of the carrier is determined by the magnetic core in the magnetic carrier, so the magnetic core is very important. Fe_3O_4 magnetic powder is a kind of typical magnetic recording material, which has higher specific saturation magnetization and lower coercion force than $Ni_{0.8}Co_{0.2}Fe_2O_4$ spinal phase[12-13]. In the work, magnetic alumina spheres were prepared by oil column method with Fe_3O_4 magnetic powder as the magnetic core.

Specifically, the Fe_3O_4 magnetic powder, acidic alumina sol, and hexamethylenetetramine solution are mixed evenly below 10°C and drip the mixture into hot oil. With the partial decomposition of hexamethylenetetramine, alumina spheres was aged at higher temperatures and to remove hexamethylenetetramine completely. Finally, alumina spheres were washed, dried and calcined at high temperature[14]. The purpose of the work is to synthesize magnetic alumina spheres, and investigate the structure and magnetic properties of the synthesized magnetic samples.

2. Experimental

2.1 Experimental materials

Sphere-type Fe_3O_4 was purchased from Shanghai Material Corp., China; alumina sol contains 11% aluminum from Beijing technology Co., Ltd. China; hexamethylenetetramine (HMT), tetraethyl orthosilicate (TEOS) and ammonia solution (28 wt%) were from Shanghai ChemicalCorp., China

2.2 Preparation of core-shell Fe_3O_4/SiO_2 composites

Fe_3O_4/SiO_2 composites were prepared according to the reported method[15]. Briefly, 2.5g Fe_3O_4 was put into hydrochloric acid of 2000mL(0.1mol L^{-1}) with ultrasonic treatment for 15 minutes and then washed by sub-water. Then spread it evenly in solution of ethanol (1440 mL), water (360mL)and ammonia (20mL of 28wt%). After stirring for 0.5h, the reaction was continued after adding tetraethyl orthosilicate of 5g at room temperature and stirred for 6h to obtain sample Fe_3O_4/SiO_2. Then the samples were washed by ethanol and deionized water, and dried at room temperature, respectively.

2.3 Preparation of Magnetic Alumina spheres

A certain amount of Fe_3O_4/SiO_2 was ultrasonically dispersed into 50g aluminum sol below 10°C.Subsequently, a certain amount of hexamethylene solution with a concentration of 40 wt%(less than 10°C) was added dropwise to the above prepared

   Then stirring vigorously to obtain a homogeneous mixture. The sol mixture prepared was dispersed into vacuum pump oil column(100°C) by a droplet distributor. Lastly, a spherical drop was formed according to the interfacial tension between sol droplets and vacuum pump oil phase. The samples were put in the autoclave with the vacuum pump oil at a pressure of 0.5 ~ 0.6 MPa, then aged at 140°Cfor 6 hours. At last, the samples was washed with deionized water. Subsequently, the washed sample was dried at 120°Cand calcined at 500°C.

2.4 Analysis and characterization

The X-ray powder diffraction (XRD) were in a Panalytical X'Pert Pro MPD diffract meter. The magnetic properties were using a Lake Shore vibrating sample magnetometer(VSM). Elemental analysis was using a Shimadzu ICPS-75000.A Hitachi S-4800 scanning electron microscope (SEM) and JEM-2100UHR Transmission electron microscope (TEM) was used.

3. Results and discussion

3.1 Characterization of needle Fe_3O_4 and Fe_3O_4/SiO_2

The properties of needle Fe_3O_4 magnetic sample before and after coating SiO_2 film was characterized. Then the results of the morphology, crystal structure, and magnetic properties of needle Fe_3O_4 and Fe_3O_4/SiO_2 were shown in Figure 1 to 4.
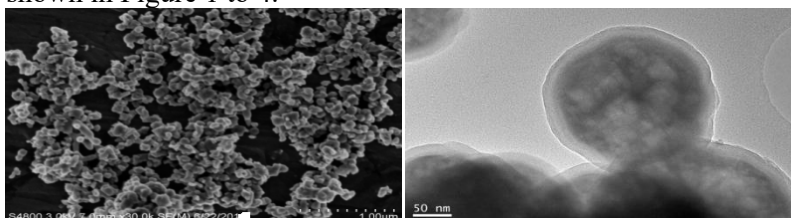

Figure 1 SEM micrographs of Fe_3O_4/SiO_2 Figure 2 TEM micrographs of Fe_3O_4/SiO_2

   Figure 1 shows the SEM image of Fe_3O_4/SiO_2. It can be seen that the primary particle size of Fe_3O_4/SiO_2 is around 100nm, and the surface is smooth and uniform. Figure 2 shows TEM image of Fe_3O_4/SiO_2. It can be showed that the sample has a core-shell structure. The SiO_2 coating is relatively uniform and dense with a thickness of approximately 15 nm.
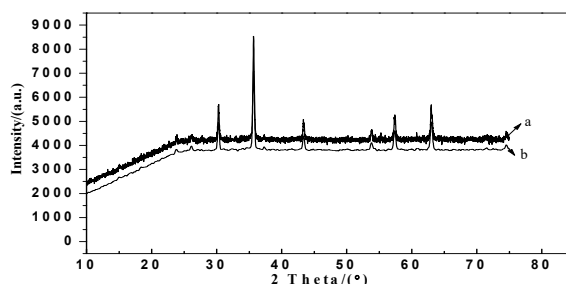
Figure 3 XRD patterns Fe_3O_4 and Fe_3O_4 /SiO_2

The XRD diffraction patterns of Fe_3O_4 and Fe_3O_4/SiO_2 are shown in Figure 3. It shows feature peak with typical cubic of Fe_3O_4(PDF Card No. 65-3107)corresponding to the diffraction angle (2θ). These are 30.3°, 35.7°, 43.3°, 57.3°, and 63.0°, respectively.

The diffraction planes are (220), (311), (400), (511) and(440), the corresponding crystal plane spacing is 0.295nm,0.252 nm, 0.209 nm, 0.170 nm, 0.161 nm, and 0.148 nm, respectively, belonging to the peak of the Fe_3O_4 crystal phase and Fe_3O_4/SiO_2 complex.The characteristic diffraction peak of the composite material is similar to that of Fe_3O_4, and there are no new ones. The crystal phase shows that Fe_3O_4 and silica are two phase. No new crystal phase was generated due to the amorphous nature of SiO_2.
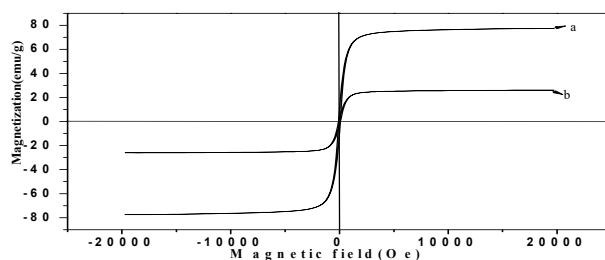

Figure 4 Magnetization hysteresis loops of Fe_3O_4 and Fe_3O_4 /SiO_2

Magnetic analysis was performed on a Lakeshore 7407 instrument. Figure 4 shows the magnetic properties of Fe_3O_4 and Fe_3O_4/SiO_2 measured at 300K. As can be seen from the figure, the magnetic properties of both samples are ferromagnetic with a hysteresis loop. The specific saturation magnetization of Fe_3O_4/SiO_2 is lower (25 emu/g) corresponding to the Fe_3O_4 (74 emu/g). The coercivity force of Fe_3O_4/SiO_2(390 Oe) is slightly smaller than the corresponding Fe_3O_4 (400 Oe). Elemental analysis shows that the weight of Fe_3O_4 in Fe_3O_4/SiO_2 sample is 62.8 wt% , which is according to theoretical value of 63 wt% .

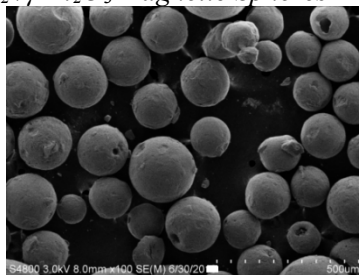*3.2. Characterization of Fe_3O_4 /SiO_2 /γ-Al_2O_3 Magnetic Spheres*

Figure 5 SEM micrographs of magnetic Al_2O_3 microspheres

The samples were prepared by oil column method.The results is shown in Figure 5.As can be seen from Figure 5, magnetic alumina spheres were prepared by a rapid dropping method. The magnetic

$Fe_3O_4/SiO_2/\gamma-Al_2O_3$ microspheres have uniform particle size, most of which is in the range of 100~200 μm.

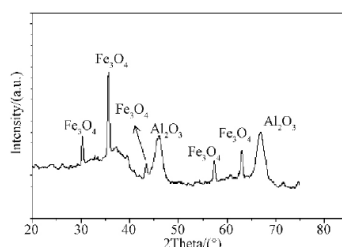Figure 6 XRD patterns of Fe_3O_4 /SiO_2 /Al_2O_3 microspheres

Figure 6 shows the XRD spectrum of the magnetic $Fe_3O_4/SiO_2/Al_2O_3$ balls. From the spectrum it can be seen that the characteristic diffraction peaks $\gamma-Al_2O_3$ and Fe_3O_4 appear according to the standard card (JCPDS No. 10-0425), and the diffraction angle (2θ) is 46. 9° and 66. 6° of the two relatively strong $\gamma-Al_2O_3$ characteristic peaks, assigned to crystal planes for (400) and (440). The corresponding lattice spacings are 197nm and 0.140nm.

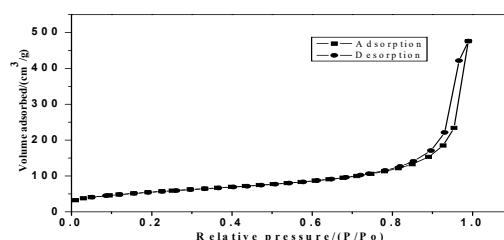Figure 7 N_2 adsorption-desorption isotherms of Fe_3O_4 /SiO_2 /$\gamma-Al_2O_3$microspheres

Figures 7 are adsorption-desorption isotherms and pore size distribution curves of magnetic $Fe_3O_4/SiO_2/\gamma-Al_2O_3$ spheres. According to the IUPAC standard, magnetic adsorption-desorption isotherms are Type IV, which has a significant hysteresis loop at $P/P_0 = 0. 85$ shows due to the capillary condensation phenomenon of the mesopore in the higher pressure . The hysteresis loop is H1 type and H3 superposition.
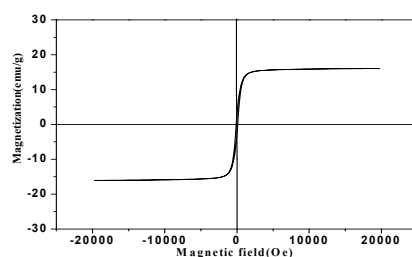

Figure 8 Magnetization hysteresis loops of Fe_3O_4 /SiO_2 /$\gamma-Al_2O_3$

Figure 8 shows the magnetic hysteresis of magnetic $Fe_3O_4/SiO_2/\gamma-Al_2O_3$ balls. It still has ferromagnetic properties. The saturation magnetization (Ms) and residual magnetism (Mr) of sample is 15.1emu/g, 2.4emu/g, respectively.

4. Conclusions

Alumina micro-spheres with magnetic Fe_3O_4 cores were successfully synthesized. The $Fe_3O_4/SiO_2/\gamma-Al_2O_3$ microspheres have a high value of specific saturation magnetization of 15.1 emu/g and low values of coercivity and remanence, and they have well-formed spheres with smooth surfaces and a particle size distribution in the rangeof 100~200 μm. Their average specific surface area and total pore volume are 16.8 nm, 200m²/g and 0.77 cm³/g,respectively. Therefore, the $Fe_3O_4/SiO_2/\gamma-Al_2O_3$ microspheres prepared in this work could be utilization in the magnetically stabilized bed technology.

Acknowledgements

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