Reusable super-paramagnetic metal oxides/SiO_2/zeolite nano-composites

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Metal oxides/SiO_2/zeolite (MSZ) is being developed to treat radioactive wastewater at the Fukushima Daiichi Nuclear Power Plant. XRD and Raman spectroscopy showed Fe_3O_4 was not damaged while MSZ synthesis. Its adsorption capacity was almost same as plain zeolite, suggesting most of zeolite is present on the surface of MSZ.

Keywords: Zeolite; Fe_3O_4; $CoFe_2O_4$; Silica coated metal oxide nanoparticles; Adsorption

1. Introduction

A massive amount of radioactive wastewater has been generated after the Fukushima Daiichi Nuclear Power Plant accident. For the treatment of wastewater, zeolite has been practically used in situ. Since zeolite possesses high adsorption capacity, modified zeolites have been also developed to seek more efficient treatment of the wastewater. One of the modified zeolites is magnetically modified zeolite (MMZ). Nano-sized Fe_3O_4 and $CoFe_2O_4$ are widely used for the MMZ because of their superparamagnetic properties. However, they might be damaged while the treatment process or reusing the MMZ. Therefore, we have studied MMZ having silica coated metal oxides (MSZ) to protect the metal oxides.

2. Experimental details

Fe_3O_4 and $CoFe_2O_4$ were synthesized by Solvothermal method under a nitrogen atmosphere. These metal oxides were coated with SiO_2 by Stöber method: Fe_3O_4 or $CoFe_2O_4$ were dispersed in ethanol solution (the ratio of ethanol to water was 4 to 1); pH was adjusted by ammonia solution to about pH 10.5. The mixture was sonicated at 30 °C for 2 hr. Finally, MSZ was made by mixing metal oxides/SiO_2 with the seeds, and the mixture was heated in the same way as making the zeolite.

X-ray diffraction (XRD), X-ray fluorescence (XRF) and Transmission Electron Microscope (TEM) were used to characterise the metal oxides, metal oxides/SiO_2 and MSZ. Their magnetic properties were characterized by Vibration Sample Measurement (VSM) or Magnetic Property Measurement System (MPMS). The adsorption capacity of MSZ toward SR was measured by batch experiment, where concentration of Sr was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

3. Results and Discussion

MSZ has kept its superparamagnetic property including that Fe_3O_4 was not damaged while MSZ synthesis. To distinguish between Fe_3O_4 and γ-Fe_2O_3 (Their XRD peaks are in the almost same petitions), Raman spectrum was also used, and it had a high Raman peak around 670 cm^{-1}. The calculated particle sizes of Fe_3O_4 and $CoFe_2O_4$ from XRD peaks (8 to 30 nm) were bigger than observed by TEM (4.5 to 9.5 nm). The magnetizations of Fe_3O_4 and $CoFe_2O_4$ were 55.7 emu/g and 45 emu/g at 20 kOe at room temperature. After silica coating, these values decreased depends on the thickness of silica layer. When the silica thickness was around 2 nm, the magnetization was almost same as the metal oxides. The magnetizations of MSZ was dramatically decreased to less than 9 emu/g at 20 kOe due to the zeolite, but MSZ could be attracted by a neodymium magnet in solution. The adsorption capacity of MSZ was almost same as plain zeolite, suggesting most of zeolite is present on the surface of MSZ.