Preparation of Magnetic BEA-type Zeolite via Dry-Gel Conversion Method

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ABSTRACT

Removal of harmful substance from industrial wastewater is important to realize a sustainable and ecofriendly development. Crystalline microporous aluminosilicates, so called zeolites, are suitable adsorbents for such application. Nowadays, composites of zeolite and magnetic particles (i.e. magnetic zeolites) have been found to ensure rapid and reliable separation from waste medium through magnetic separation. Hydrothermal treatments in the liquid phase have hitherto been applied to prepare magnetic zeolites; however, the incorporation of magnetic particles by this method is difficult to control since it depends greatly on whether the zeolite nucleates in the vicinity of the magnetic particle or not. Here, magnetic zeolites were synthesized using a different route, the dry-gel conversion method, for the first time to overcome this problem. A precursor gel containing magnetite as the magnetic particle was prepared in advance to ensure magnetite incorporation and the gel was converted into BEA-type zeolite by exposing to water vapor, at 180°C for 12 hours. SEM-EDS and XRD analysis were carried out to characterize the synthesized magnetic BEA-type-zeolite and its adsorption performance was evaluated through methylene blue adsorption test. The result of sample characterization indicated that the amorphous gel was converted to BEA-type zeolite and that magnetite was homogeneously distributed within the synthesized sample. In addition, the magnetic BEA-type zeolite showed high adsorption performance of 125 mg/g against methylene blue. Magnetic BEA-type zeolite with high yield and high adsorption performance were successfully synthesized. Dry-gel conversion method seems to be promising for preparing magnetic zeolites.

Keywords: wastewater treatment, BEA-type zeolite, magnetic particle, composite, dry-gel conversion

INTRODUCTION

The rapid industrialization triggered generation of a vast amount of wastewater from industries, which in many cases contain harmful organic and inorganic substances. Thus, it is essential to purify the wastewater before discharge so as to prevent the adverse effects on human health and the ecosystem. Among various
methods, adsorption by adsorbents has received increasing attention due to its effectiveness, simplicity, and ability to remove a wide variety of harmful substances, even at low concentrations. (Gupta V. K., Carrott P. J. M. et al., 2009)

Zeolites, which are aluminosilicates consist of silica and alumina tetrahedra forming microporous networks with uniform pores, are interesting adsorbents for wastewater treatment. The uniform pores in molecular dimension and the bias in charge due to partial substitution of silicon with aluminum results in interesting adsorption and ion-exchange properties. More than 200 types of frameworks with different the pore size, pore shape and pore connectivity have been discovered until now, enabling us to select the structure type according to the size and shape of the target substance.

Recently, composite materials of zeolites and magnetic materials, namely magnetic zeolites, have attracted increasing attention as adsorbents for wastewater treatment in order to simplify their recovery from the liquid media by magnetic separation after usage. Hydrothermal synthesis method has hitherto been used to synthesize zeolites and previous studies have applied this method to prepare various magnetic zeolites (Hagio T., Kunishi H. et al., 2018). However, they were difficult to control the magnetic particle incorporation since it depended greatly on whether the zeolite nucleates in the vicinity of the magnetic particle or not. If we can control the zeolite synthesis to be in the vicinity of the magnetic particles, magnetic zeolites should be synthesized with high yield and high homogeneity. Therefore, we focused on dry-gel conversion method which involves the conversion of a precursor gel into zeolite through water vapor exposure at high temperature and high pressure (Hari Prasad Rao P.R. and Matsukata M., 1996). By homogeneously dispersing magnetic particle inside the gel in advance and then converting the gel into zeolite, zeolite should be synthesized covering the magnetic particle. Here, we attempt to prepare magnetic BEA-type zeolite by dry gel conversion method for the first time.

MATERIALS AND METHODS

Materials

Colloidal silica containing 30 wt% of silica (HS-30, Sigma Aldrich), aluminum sulfate (Al₂(SO₄)₃, Nacalai Tesque), sodium hydroxide (NaOH, Nacalai Tesque) and tetraethylammonium hydroxide (TEAOH, Tokyo Chemical Industry Co., Ltd.) were used as the silica source, alumina source, alkaline source and structure directing agent (SDA) for BEA-type zeolite synthesis, respectively. Magnetite (Fe₃O₄, Kanto Chemical Co., Inc.) was selected as the magnetic material. Methylene blue (MB, Kishida Chemical Co., Ltd.) was used as a model substance for the adsorption performance evaluation.

Synthesis of magnetic BEA-type zeolite

First, NaOH and TEAOH were added to colloidal silica and stirred for 30 min. Then, Al₂(SO₄)₃ was added to this solution and stirred for another 2 hours. A certain amount of Fe₃O₄ was added to this solution when preparing the magnetic BEA-type zeolite. Then, the mixture was stirred at 353 K until the solutions change into a dry gel. The dried gel was crushed down and sieved, placed in an autoclave containing water without contact, and heated under saturated vapor without direct contact to liquid water at 453 K for 12 hours.
Finally, the product was dried and subsequently calcined at 723 K for 12 hours in air. XRD and SEM-EDS were used for characterization.

MB adsorption test of magnetic BEA-type zeolite

The adsorption performances of the samples were evaluated using samples of 1.0 g/L in MB solution of 150 mg/L. The MB solutions were poured into vessels containing the samples and were subsequently shaken for 24 hours. The adsorbed amount of MB was calculated from the concentration of the MB solutions before and after the adsorption test evaluated using a spectrophotometer (UV-2450, Shimadzu Co., Japan) at a wavelength of 664 nm.

RESULTS AND DISCUSSION

Characterization of synthesized samples

All of the obtained sample with Fe₃O₄ addition showed magnetic separation ability. XRD patterns of the samples with and without Fe₃O₄ addition are shown in Figure 1. They both showed peaks corresponding to those of zeolite with the BEA structure, meaning that the BEA-type zeolite was successfully synthesized regardless of the existence of Fe₂O₃ in the system. In addition, peaks of α-Fe₂O₃ was detected along with Fe₃O₄ in the samples synthesized from gels with Fe₃O₄ addition. The Fe₃O₄ seemed to be partially oxidized during the calcination process; however, it still exhibited magnetic separation ability. From the SEM images of samples with and without Fe₃O₄, almost no difference was observed. The existence of Fe₃O₄ could not be distinguished, implying that the Fe₃O₄ were well covered by the BEA-type zeolite. The results of elemental analysis using SEM-EDS showed homogeneous distribution of Fe and a Si/Al ratio of around 25. The above results indicated that magnetic BEA-type zeolite was successfully prepared via dry-gel conversion method.

![Figure 1 XRD patterns of samples synthesized (a) with and (b) without Fe₃O₄ addition](image)

Evaluation of MB adsorption performance

The MB adsorption performance is shown in Figure 2. The adsorbed amount of MB on the sample with Fe₃O₄ addition was slightly decreased compared to that without it but still maintained a high value of 125 mg/g. The sample with Fe₃O₄ addition includes the weight of iron oxides which barely contribute to the adsorption of MB. Thus, the slight decrease in adsorption performance was probably due to their existence.
CONCLUSION

This study aimed to propose a novel method to synthesize magnetic zeolites with high yield and high homogeneity. Magnetic BEA-type zeolites were synthesized using the dry-gel conversion method for the first time to realize this objective. A precursor gel containing magnetite as the magnetic particle was prepared in advance to ensure magnetite incorporation and the gel was converted into BEA-type zeolite by exposing to water vapor, at 180°C for 12 hours. SEM-EDS and XRD analysis were carried out to characterize the synthesized magnetic BEA-type-zeolite and its adsorption performance was evaluated through methylene blue adsorption test. The result indicated that a homogeneous magnetic BEA-type zeolite with high yield and high adsorption performance were successfully synthesized. Dry gel conversion method seems to be promising for preparing magnetic zeolites.

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