

SYNTHESIS OF A MONOLITH FOR EFFICIENT AMMONIA RECOVERY FROM DILUTE SOURCES THROUGH THE IMMOBILIZATION OF MAGNESIUM AMMONIUM PHOSPHATE CRYSTALS IN MICROCHANNELS

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Summary

Magnesium ammonium phosphate (MAP) is a prospective material for recovering NH_3 from dilute sources. This material is usually obtained as small crystals, so they have to be immobilized in a dispersed state in order to avoid a severe hydraulic resistance. In this work, we attempted to immobilize MAP crystals in a dispersed state by directly synthesizing their crystals within the microchannels of silica microhoneycombs synthesized by the newly developed Ice Templating method. It was confirmed that such immobilization can be achieved, and that the immobilized MAP crystals can efficiently recover NH_3 from a solution without causing a severe hydraulic resistance.

Keywords

Green CRE, Environmental Reaction Engineering, Novel functional materials

Introduction

Magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$: MAP) releases NH_3 when heated to moderate temperatures, and is converted to magnesium hydrogen phosphate (MgHPO_4 : MHP). This MHP can remove NH_3 from fluids containing NH_3 , such as waste water, by being converted back to MAP. So, MAP can be regarded as an efficient material for recovering NH_3 , as it can selectively catch and release NH_3 repeatedly.

As MAP is a nonporous material, its surface area must be increased to efficiently use it. This can be achieved by synthesizing it as small particles, but such particles are likely to cause a severe resistance to fluid flows if they are simply packed in columns when used. Therefore moderate sized pathways must be introduced between the particles to effectively use them. This can be achieved by immobilizing MAP crystals within microchannels, as voids will be naturally formed around the crystals due to the high aspect ratio of the crystals.

Monolithic microhoneycombs synthesized by the Ice Templating method¹, a new micromolding method developed in our laboratory, is thought to be suitable for the support for immobilization, since it has many aligned microchannels with diameters similar to the size of MAP crystals. So in this work, we attempted to immobilize MAP crystals in a monolithic microhoneycomb obtained by the

Ice Templating method, by directly synthesizing them in the microchannels of the monolith.

Experimental

Synthesis of monolithic silica microhoneycombs

A sodium silicate solution was prepared and its pH was adjusted using an ion-exchange resin. The obtained solution was poured into a polypropylene tube and was aged at 303 K. After the solution transformed to a gel, the tube was dipped into liquid nitrogen at a constant rate, and the tube was froze unidirectionally. The completely frozen sample was thawed, and after exchanging the water included in it with *t*-butylalcohol, it was freeze-dried at 263 K.

In situ synthesis of MAP crystals

The obtained silica microhoneycombs were used as the support for immobilization. Solutions respectively containing Mg^{2+} , PO_4^{3-} , and NH_3 were alternately and repeatedly introduced into a microhoneycomb fixed in a tube, and MAP crystals were instantaneously synthesized within the microchannels of the microhoneycomb. After a designated number of introduction sequences, distilled and deionized water was introduced into the microchannels to wash away unreacted material. Then the sample was dried at 303 K.

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The samples were directly observed using a scanning electron microscope (SEM) and analyzed by powder XRD. After heat treatment at 473 K, the samples were exposed to dilute NH_3 solutions, and the ability of the samples to remove NH_3 was evaluated.

Results and Discussion

Morphology

SEM images of the cross sections of a typical sample prior to and after MAP introduction are respectively shown in Figs. 1(a) and 1(b). It can be noticed that crystals are immobilized in a fairly dispersed state within the microchannels of the microhoneycomb. Such results suggest that the crystals generate and grow to the size of the diameter of the microchannels, and are immobilized within them. The crystals formed in the microchannels were confirmed to have a high aspect ratio and moderate spaces were left around them.

NH_3 recovery

The XRD pattern of a typical sample is shown in Fig. 2(a). It can be noticed that the positions of the peaks are identical to those of a MAP reference sample (JCPDS No. 15-0762, Fig. 2(d)) indicating that the crystals synthesized within the microchannels are MAP. This sample was calcined at 473 K. The pattern of the calcined sample is shown in Fig. 2(b). Peaks of MAP disappear, which indicates that MAP was converted to MHP. Next, this calcined sample was exposed to a dilute NH_3 solution (NH_3 : 3000 ppm). It was found that NH_3 can be efficiently recovered from the solution, the amount of which corresponded to about 80 % of the NH_3 needed to convert all the MHP in the sample back to MAP. The XRD pattern of the sample after exposure to a NH_3 solution is shown in Fig. 2(c). It can be noticed that the peaks of MAP reappeared. These results imply that the monolith sample obtained in this work can be used to efficiently recover NH_3 from dilute NH_3 sources.

References

(1) Mukai, S. R.; Nishihara, H.; Tamon, H. Formation of Monolithic Silica Gel Microhoneycombs (SMHs) Using Pseudosteady State Growth of Microstructural Ice Crystals. *Chem Commun.* **2004**, 874

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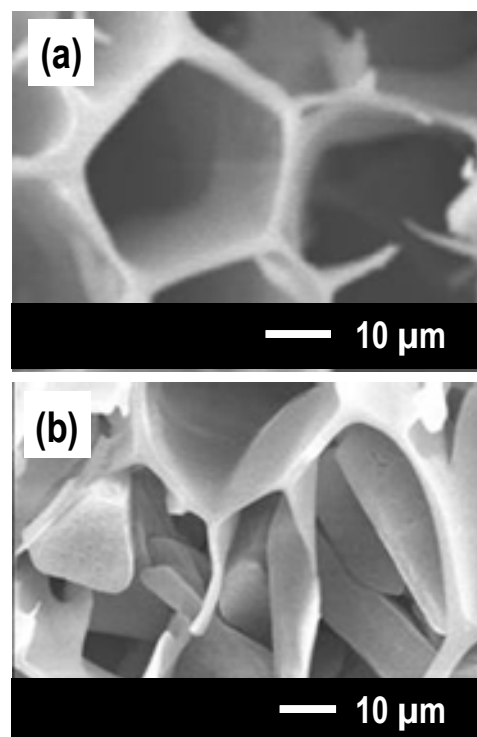


Fig. 1 Cross sectional SEM images of a typical sample obtained in this work
(a) prior to MAP immobilization, (b) after MAP immobilization

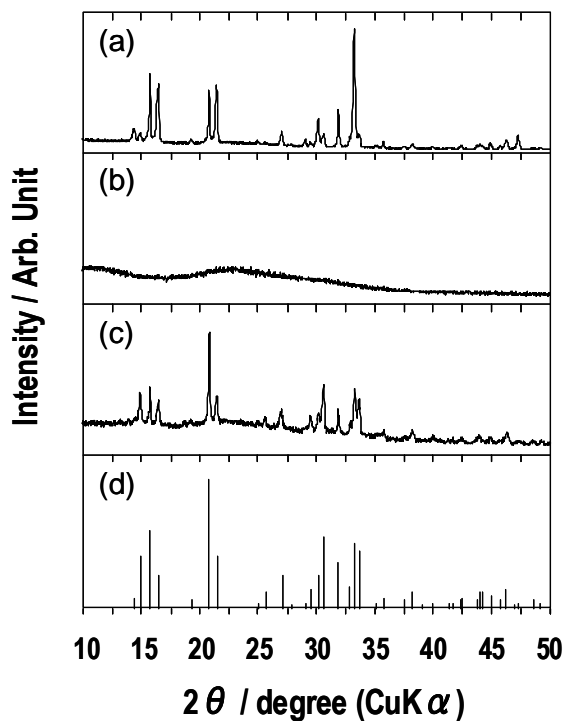


Fig. 2 XRD patterns of a typical sample obtained in this work
(a) as-prepared, (b) after calcination at 473 K, (c) after calcination and exposure to NH_3 solution, (d) MAP reference sample (JCPDS No. 15-0762)