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Synthesis of Bulk Zeolite by Modified Hydrothermal Process and Its Characterization

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Abstract

Fabrication of bulk zeolite such as silver ion exchanged Y-zeolites was attempted by the modified hydrothermal processing. The present synthetic processing was modified from thermal hot-pressing developed by Yamasaki. Using this process, we were successful for the dense bulky silver ion exchanged Y-zeolite. In this study the microstructure of bulk FAU zeolite were observed by FE-SEM, XRD and XAFS. Also, the relation of microstructure and properties were discussed.

Key words: ion exchange, zeolite, FAU-type, bulk, hydrothermal hot-pressing

1 Introduction

Zeolites with possess well-defined three-dimensional (3D) micropores have been much attention for applications as catalysis carrier, gas separation, adsorption and ion exchanger. Especially, Ag^+ ion-exchanged zeolites are quite unique materials with actions such as photochemical/thermal cleavage of water into H_2 and O_2 [1], photo-oxygen production from water [2], and photocatalytic decomposition of NO [3, 4]. Silver ions can be reduced intrazeolitically by heating [5, 6], by reaction with reducing agents [7], or by sorption of metal atoms [8]. Tsutsumi and Takahashi reported that the Ag^+ ions in zeolite Y can be reduced to bulk clusters of Ag^0 after treatment with alcohol and alkylbenzene above 300 °C [9]. It was, however, restricted the applications because zeolites are obtained as a powder only and was not able to obtain a solidified body except for small single crystalline zeolite [10]. Thus, many researches have tried to make powder consolidation and thin film for expansion of applications of zeolite. However, there is still a problem that microporous structure was not able to be retained for bulky or filmy zeolite synthesized in conventional method, because they contain a lot of parts of amorphous and portion of micropores structure were filled with amorphous phase. Therefore, practical use of zeolites has not been achieved yet.

Our group has proposed to obtain solidified zeolite bulk using Hydrothermal Hot-pressing (HHP) method. The HHP technique is a method by which hard solid bodies of powders can be produced in a short time and at a relatively low temperature under saturated vapor pressure [11]. Nakahira et al. reported that densified and translucent bulky Y-zeolite was synthesized using HHP technique [12]. Hence, the purpose in this paper is to attempt to synthesize Ag^+ ion exchanged Y-zeolite (refer as Ag-Y-zeolite) by this HHP technique and reveal the

microstructure of bulky Ag-Y-zeolite observed by FE-SEM. Moreover, the local structure of the Ag^+ ion in Ag-Y-zeolite bulk compared to Ag-Y-zeolite powder observed by XAFS.

2 Experimental

2.1 Ion Exchange Reaction

Ag-Y-zeolite sample was prepared by conventional ion-exchange technique using $1.0 \times 10^{-2} \text{ M}$ AgNO_3 solution and Na-Y-zeolite (HSZ-320NAA, particle size; 0.3 to 0.4 μm , $\text{SiO}_2/\text{Al}_2\text{O}_3=5.5$, specific surface area; 860 m^2/g , Tosoh Co.) under stirring at 70 $^\circ\text{C}$ for 10 h. After filtration, the powder was dried at 323 K overnight. When the zeolite is in the exchange medium, equilibrium is established;

2.2 Hydrothermal hot-pressing

Ion exchanged Ag-Y-zeolite powder were used as a starting powder. Figure 1 showed an autoclave for HHP in this study. Ag-Y-zeolite powder (0.75 g) was added to 20 wt% of various concentration of NaOH solution, which was placed into the autoclave. This autoclave containing sample was heated at 423 K at the rate of 10 K/min under the pressure with 40 MPa for 2 h. After HHP treatment, the autoclave was cooled to a room temperature and the product removed from the autoclave. Products treated by HHP method were washed and dried at 323 K for more than 12 h. Some Ag-Y-zeolite bulks were calcined in H_2 at 773 K for 2 h.

2.3 Characterizations

Products prepared by HHP were identified by powder X-ray diffractometry (XRD, RINT2500, Rigaku) with $\text{CuK}\alpha$ radiation, operating at 40 kV and 50 mA. The microstructures of products were observed by field emission scanning electron microscopy (FE-SEM, S-4500, HITACHI). Nitrogen adsorption isotherms at 77 K were obtained by automatic gas adsorption measure apparatus (BELSORP18PLUS-SPL, Japan BEL). Some pieces of product were pretreated at 403 K for 12 h. Specific surface area of products was calculated by a Langmuir plot. The Ag K-edge XAFS spectra were obtained in the fluorescence mode at 298 K.

3 Results and Discussion

The effect of NaOH concentration on the microstructure of Ag-Y-zeolite sample by HHP was examined. Under various synthetic conditions of HHP, Ag-Y-zeolite bulks were obtained. Strong Ag-Y-zeolite bulks obtained with 5 M NaOH solution on HHP, which bulk density was approximately 1.80 g/cm^3 . Although bulk density of Ag-Y-zeolite bulk with 1 M NaOH solution was 1.03 g/cm^3 , it is likely suggested that the addition of low concentration NaOH solution could not led to appropriate hydrothermal condition. Thus, optimum NaOH concentrations on HHP existed for preparing dense Ag-Y-zeolite bulks.

Figure 2 shows SEM images of HHP-treated samples with 1 or 5 M NaOH solution before/after heat treatment in H_2 . SEM observation indicated that HHP-treated samples with 1 M NaOH before/after heat treatment in H_2 showed some voids and they were porous and not densified. On the other hand, HHP-treated samples with 5 M NaOH before/after heat treatment in H_2 showed a very dense bulk surface without defects such as pinholes and

Fig. 1 Autoclave for hydrothermal hot-pressing.

Fig. 2 SEM images of HHP-treated samples with 1 *M* NaOH (a) before, (b) after heat treatment in H_2 , and with 5 *M* NaOH (c) before, (d) after heat treatment in H_2 .

Fig. 3 XRD patterns of (a) Y-zeolite powder, (b) Ag-Y-zeolite powder, (c) Ag-Y-zeolite powder calcined 500 °C in H_2 , (d) Ag-Y-zeolite HHP bulk calcined 500 °C in H_2 .

Fig. 4 XANES spectra of (a) Ag foil, (b) Ag_2O , (c) Ag-Y-zeolite powder, (d) Ag-Y-zeolite powder calcined 500 °C in H_2 , (e) Ag-Y-zeolite HHP bulk calcined 500 °C in H_2 .

cracks. It is founded that the successful synthesis condition for preparing the densest bulk HHP-treated sample is done under 5 *M* NaOH solutions. Thus, this dense and pinhole-free microstructure consisting of fine zeolite crystals are successfully obtained.

Ag-Y-zeolite samples were evaluated by XRD, as shown in Fig. 3. The XRD results showed that all products were identified as Y-zeolite. The peak width of Ag-Y-zeolite HHP bulk calcined 500 °C in H_2 around 2

$\theta = 38^\circ$ (marked as $\downarrow$) was extended slightly. This is thought to be due to overlapping of the identified peaks of Y-zeolite and Ag metal, which indicated to produce Ag metal by the reduction of Ag^+ ions. Specific surface area of Ag-Y-zeolite powder, and Ag-Y-zeolite bulk prepared by HHP with 1 and 5 M NaOH solution were $810 \text{ m}^2/\text{g}$, $605 \text{ m}^2/\text{g}$ and $695 \text{ m}^2/\text{g}$, respectively. This result showed that a high specific surface area of dense bulk zeolite solidified upon HHP treatment was comparable with that of the Ag-Y-zeolite powder as a starting material.

Fig. 4 shows the XANES spectra of Ag-Y-Zeolite powder and bulk and reference materials such as Ag_2O and Ag foil. Shapes and positions of the bands due to multiple scattering in XANES spectrum of the (c) Ag-Y-zeolite powder and (d) Ag-Y-Zeolite powder calcined 500°C in H_2 were quite different from those of (a) Ag foil and (b) Ag_2O . This indicates that the large clusters of Ag_2O or Ag metal are not formed within zeolite cavities. XANES spectrum of (e) Ag-Y-zeolite HHP bulk calcined 500°C in H_2 was similar to that of (a) Ag foil, which implies that there are silver metal due to reduction of Ag^+ ions.

4 Conclusion

In this paper, solidified bulky Ag-Y-zeolite could be successfully synthesized by HHP treatment for short term. It was founded that the dense Ag-Y-zeolite by HHP was obtained under 5 M NaOH solution as solvent. Solidified Ag-Y-zeolite bulk by HHP with 5 M NaOH solution was identified as Y-zeolite polycrystalline and had significantly large surface area over $600 \text{ m}^2/\text{g}$. Moreover, it was revealed that observed by the local structure of the Ag^+ ion, silver metals were existed in Ag-Y-zeolite bulk prepared by HHP. Using HHP methods, the solidification of other zeolites, such as MFI and MOR etc, have also confirmed. Therefore, this HHP is significantly applicable to solidify many porous materials like zeolites and mesoporous materials with high surface area. Successful synthesis of dense and bulky Ag-Y-zeolite with significantly high surface areas by HHP method will lead to new applications as efficient photocatalysts for the decomposition of NO_x (NO and N_2O) into N_2 and O_2 .

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