Hydrothermal Preparation of Bead Type Zeolite Li-A for Use in Recycling the Salt Waste

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1. Introduction

An advanced spent fuel management process based on Li reduction of the oxide spent fuel to a metallic form will generate a LiCl waste.

Zeolite Na-A has been reported as a promising immobilization medium for waste salt with CsCl and $SrCl_2$[1-2]. However, Sodium is accumulated as an ionic form (Na^+-ion) in molten salt during ion exchange step between Na^+-ion in the zeolite-A and Li^+-ion in the molten salt. Therefore, zeolite Na-A need to be replaced by the Li-type zeolite for recycling the salt waste by removing the Cs and Sr ions.

In this study, we prepared the bead type zeolite Li-A hydrothermally from a bead type zeolie 4A by P. Norby and M.C. Mascolo method [3, 4], and its preparation characteristics of zeolite Li-A was investigated.

2. Material and Methods

A bead type zeolite 4A (Merck; analytical grade),was used for the preparation of the zeolite Li-A. A simulated LiCl solution for batch cation exchange reaction was prepared by dissolving the commercial LiCl powder (Aldrich, 99^+%) in 500-ml distilled water. Figure 1 shows experimental apparatuses for the hydrothermal preparation of zeolite Li-A

A bead type zeolite Li-A was prepared hydrothermally from zeolite 4A with the following 2 steps;

1) batch ion exchange step
[500ml,0.5/1.0M LiCl solution + 17g zeolite 4A] mixed at 70 ^oC for 24hr (for a total of three times)
2) Crystallization step
- Vessel: 350ml, S.S 304 pressure vessel
- Time: 72-92hr, - Temperature: 180-285^oC

After two steps, the samples were washed until chloride-free and then, dried at 110 ^oC. The prepared zeolite zeolite Li-A was analyzed by an X-ray diffractometer (XRD, Philips, X'pert MPD), and the Li ion replacement rate was evaluated by Philips X`Pert Graphic & Indentity Program which is a analysis program of material structure with data base on XRD patterns of materials. Several experiments were performed to obtained the 100% Li-exchanged form, zeolite Li-A by the change of LiCl solution concentration, time, and temperature.

(cation exchange) (crystallization step)

Figure 1. Experimental Apparatus for the hydrothermal preparation of zeolite Li-A

3. Results and Discussion

Several experiments were carried out to determine the optimal conditions(temp. et al.) Good results were obtained at the following conditions.

1) Experimental condition 1:

- Ion exchange : 0.5M LiCl solution for 72hr
- crystallization : 200 °C for 72 hr

2) Experimental condtion 2

- Ion exchange : 1.0M LiCl solution for 72hr
- crystallization : 200 °C for 92 hr

XRD patterns for the prepared zeolite Li-A at upper two conditions are shown at Figure 2.

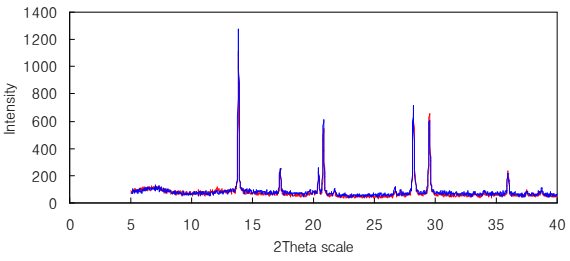

Figure 2. XRD patterns of prepared zeolite Li-A (Condition 1: blue color, Condition2: red color)

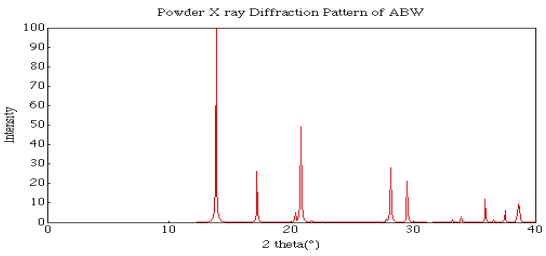

Figure 3. XRD patterns for standard zeolite Li-A

The XRD patterns of prepared zeolite Li-A were compared with that of standard zeolite Li-A(BW) in Figure 3. As shown in XRD patterns in Figure 2 and Figure 3, the prepared zeolite Li-A has similar XRD pattern with that of the standard zeolite Li-A. Based on these results, the prepared zeolite Li-A seems to be almost replaced by Li ion.

4. Conclusions

Na type zeolite, 4A need to be replaced by the Li-type zeolite for recycling the salt waste by removing the Cs and Sr ions. For this purpose, we prepared bead type zeolite Li-A hydrothermally from the bead type zeolite 4A. We have not obtained good results by only batch cation exchange process without crystallization step. However, the 100% Li exchanged zeolites Li-A have been obtained by crystallation reaction at 200 °C for 72hr or 92hr after three cation exchanges in 0.5/1.0M LiCl solution at 70 °C for 24hr. From these results, it was found that the crystallization reaction is very important step for obtaining 100% Li-exchanged form, zeolite Li-A. Our prepared zeolite Li-A have similar XRD patterns with the standard zeolite Li-A(BW), $LiAlSiO_4 \cdot H_2O$ in zeolite data base, so we confirmed that the zeolite Li-A prepared in this study is about 100% Li-exchanged form, zeolite Li-A, the chemical formula of unit cell is $LiAlSiO_4 \cdot H_2O$ like a standard zeolite Li-A(BW).

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