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Synthesis and characterization of Li-type EDI zeolite

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Abstract

A Li-type EDI zeolite (Li-EDI) was successfully synthesized in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system using a silica–alumina mixed sol as the starting material in the absence of other chemical species. The characterization of the obtained Li-EDI was compared with that of the Li-exchanged Linde F zeolite (K-type EDI zeolite). Starting gels with the batch composition of $x Li_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 275H_2O$ ($x = 2–5$) were prepared by adding a LiOH solution to a silica–alumina mixed sol. A hydrothermal reaction of the gels was carried out at various temperatures. Li-EDI formed from all of the batches in the range of 60–100 °C. However, the ABW-type zeolite co-crystallized in the composition of Li_2O/Al_2O_3 of 2.0–3.0 above 90 °C. The crystal morphology of Li-EDI was a prism shape. The average particle size of Li-EDI is 0.69 μm in length and 0.23 μm in width. The crystal structure of the Li-EDI collapsed at 300 °C, which indicated that the thermal stability of Li-EDI is significantly lower than that of the Linde F zeolite, which is stable up to 1000 °C.

Keywords: Powders-chemical preparation; Thermal properties

1. Introduction

Several types of zeolites with the EDI-type framework (EDI zeolite)[1] are known, such as edingtonite occurring as a natural zeolite and Linde F as a synthetic zeolite. A number of syntheses of Linde F were carried out in the $K_2O–Al_2O_3–SiO_2–H_2O$ system.[2,3] EDI zeolites were also obtained in the systems including Li, such as $Li_2O–BaO–Al_2O_3–SiO_2–H_2O$,[4] $Li_2O–Rb_2O–Al_2O_3–SiO_2–H_2O$,[5] $Li_2O–Cs_2O–Al_2O_3–SiO_2–H_2O$,[5,6] and $(TMA)_2O–Li_2O–Al_2O_3–SiO_2–H_2O$[6] (TMA: tetramethylammonium). Last year, the Li-type EDI zeolite was synthesized in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system in the presence of an amine using microwave heating techniques.[7]

In the present study, a Li-type EDI zeolite was successfully synthesized in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system using a silica–alumina mixed sol as the starting material in the absence of other chemical species. The characterization of the obtained Li-type EDI zeolite, such as crystal structure, morphology, thermal property, and chemical composition, was compared with that of the Li-exchanged Linde F zeolite.

2. Experimental procedure

A sol as the starting material was prepared by mixing the acidic silica sol (SiO_2: 20%, Nissan Chemical Ind., snowtex-O) with the acidic alumina sol (Al_2O_3: 10%, Nissan Chemical Ind., alumina sol-200). Subsequently, hydrous gels with the batch composition of $x Li_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 275H_2O$ ($x = 2–5$) were obtained by adding LiOH solution to the silica–alumina mixed sol. A hydrothermal reaction of the hydrous gels was carried out at 60–100 °C in sealed Teflon containers. At the end of the reaction, the products were separated from the mother liquors by filtration, washed with distilled water and dried at 50 °C. The products were identified by X-ray diffractometry (XRD) (Rigaku, RINT2500). Their morphologies were observed by scanning electron microscopy (SEM) (JEOL, JSM-7400F).

The chemical compositions of the products were determined by flame photometry for Li, and by a gravimetric method for SiO_2 and Al_2O_3. The H_2O content was deter-

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mined by the weight loss from ignition at 1000 °C for 1 h. A thermogravimetry–differential thermal analysis (TG–DTA) (Mac Sience; 2020S) was carried out in air at the heating rate of 10 °C min^{-1} using α-alumina as the reference. The zeolite samples were heated for 1 h at a set temperature then at the heating rate of 10 °C min^{-1} in order to investigate their thermal stability and transformation. The heated samples were identified by XRD.

The properties of the Li-type EDI zeolites were compared with those of the Li-exchanged Linde F zeolites. This Linde F zeolite was prepared from the hydrous-gel of $6K_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}120H_2O$ at 100 °C for 48 h. The K^+ in the materials were replaced with Li^+ by the two-step batch method as follows due to the low selectivity for Li^+ by the Linde F zeolite: a 100 g portion of the zeolite powder was dispersed in 1 dm^3 of $NaNO_3$ solution with the concentration of 1.0 mol dm^{-3}; the cation exchange reaction proceeded at room temperature for 24 h and was repeated several times by changing with fresh solution; the treated materials, Na-exchanged Linde F, were washed with distilled water and dried at 40 °C. Subsequently, the Na-exchanged Linde F was treated in the same manner with $LiNO_3$ used in place of $NaNO_3$.

3. Results and discussion

3.1. Synthesis of zeolites

In this study, the SiO_2/Al_2O_3 ratio in the batch composition was held constant at 2 to obtain lower silica zeolites. Fig. 1 shows a formation diagram of the zeolites in the batch with Li_2O/Al_2O_3 ratios of 2.0–5.0 within 24 h at various temperatures. The Li-type EDI zeolite formed from all of the batches in the range of 60–100 °C. The ABW zeolite, however, co-crystallized in the batch composition with Li_2O/Al_2O_3 ratios of 2.0–3.0 above 90 °C as shown by the open circles in Fig. 1.

In the $Li_2O–Al_2O_3–SiO_2–H_2O$ system, the Li-type EDI zeolites have never been synthesized and the ABW zeolites are formed exclusively from the batch with the SiO_2/Al_2O_3 of 2.[8–11] The reason for this was explained by the fact that the hydrothermal stability of ABW in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system is higher than that of EDI. The hydrothermal stability of the zeolites generally increases with an increase in the framework density.[12] The framework densities of the EDI and ABW structures are 16.6T/nm^{-3} (T = Al and Si) and 19.0T/nm^{-3},[1] respectively. The synthesis of the zeolites in the $2.5Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}275H_2O$ at 100 °C was carried out as a function of time to confirm the hydrothermal stability between EDI and ABW. The XRD patterns of the products are shown in Fig. 2. At the reaction time of 1 h, EDI mainly formed along with a small amount of ABW. The XRD intensities for EDI decrease with time, on the contrary, that of ABW increases with time, which indicates that EDI was transformed into ABW. This result proves that the hydrothermal stability of ABW is higher than that of EDI.

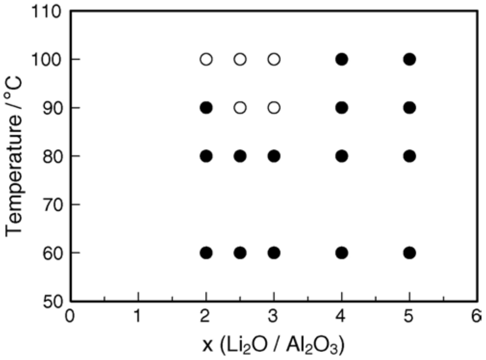

Fig. 1. Formation diagram of zeolites in the batch of $xLi_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}275H_2O$ within 24 h: (●) EDI; (○) EDI + ABW.

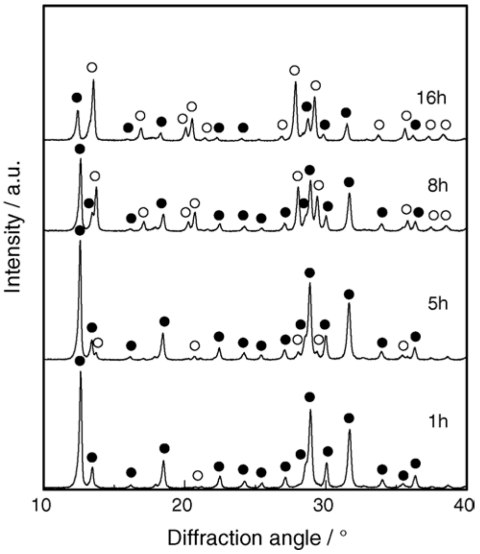

Fig. 2. X-ray diffraction patterns of products obtained from the batch of $2.5Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}275H_2O$ at 100 °C: (●) EDI; (○) ABW.

In other studies with reference to the synthesis of zeolites in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system, the starting materials such as aluminium hydroxide–silica acid,[8] metakaolin[9,10] and zeolite A[11] were lower in reactivity, and hence a nucleus of ABW having a higher stability than that of EDI occurred in these starting materials, but no EDI.

3.2. Characterization

Fig. 3 shows the XRD patterns of the as-synthesized Li-type EDI zeolite (Li-EDI) made from the gel containing $5Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}275H_2O$ at 90 °C for 16 h and Li-exchanged Linde F. The XRD pattern of Li-EDI is the same as that of the Li-exchanged Linde F. It is known that the cation-exchange of Linde F causes marked alteration in the X-ray diffraction pattern.[13] However, the refinement of these crystal structures have never been done. Further studies are necessary to investigate the structures of the Li-EDI and Li-exchanged Linde F in detail.

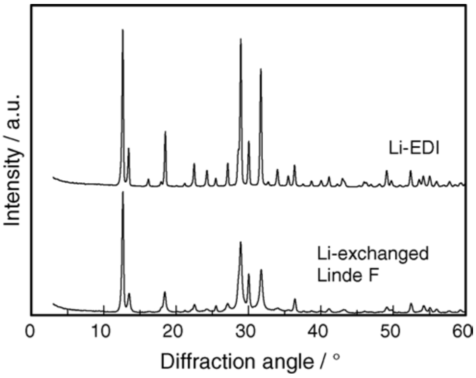

Fig. 3. X-ray diffraction patterns of Li-EDI and Li-exchanged Linde F zeolite. Batch comp.: $5Li_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}275H_2O$; temperature: 90 °C; time: 16 h.

The chemical analysis of Li-EDI is shown in Table 1. The SiO_2/Al_2O_3 of Li-EDI is equal to 2.00, which indicates that the composition of Li-EDI was the lowest silica content among the zeolites and suggests that Li-EDI has a higher cation exchange capacity. Linde F possesses an excellent selectivity for NH_4^+, hence it has been become a candidate material for the removal of NH_4^+ from waste water.[14] However, Linde F also exhibits a relatively high selectivity for K^+.[15] In contrast, the selectivity for Li^+ in Linde F is lower.[15] Therefore, Li-EDI is expected to be used as a removal material for NH_4^+.

The Li-type EDI zeolite synthesized in the $Li_2O–Al_2O_3–SiO_2–H_2O$ system in the presence of an amine (amine-Li-EDI) has the SiO_2/Al_2O_3 value of 2.40, because the amine and/or its decomposition products are presumed to play the role as a template.

Fig. 4 shows the SEM images of Li-EDI. The crystal morphology was prism shaped which is the same as that of the Linde F zeolites. The average particle size is 0.69 μm in length and 0.23 μm in width. The crystal morphology and the particle size in the products obtained under all the synthesis conditions in this study are the same.

The TG and DTA curves of Li-EDI and the Li-exchanged Linde F are shown in Fig. 5. Fig. 6 shows the XRD patterns of Li-EDI heated at various temperatures. The crystal structure of Li-EDI collapsed at 300 °C, which corresponds to the dehydration temperature, resulting in the formation of an amorphous material. This indicates the simultaneous collapse of the framework structure and the dehydration. Such processes are also known for the Li-, Na-, Sr-, and Ba-type Linde F materials.[3,16] On the other hand, the structure of the as-synthesized Linde F (K-type) is thermally stable up to 1000 °C. In the Li-EDI heated at 750 °C, γ-eucryptite[17] crystallized. This result indicates that the exothermic peak at 780 °C can be assigned to the crystallization of γ-eucryptite. The γ-eucryptite is transformed into β-eucryptite above 900 °C, resulting in the formation of a single phase of β-eucryptite at 1000 °C. This transformation gives the endothermic peak at 1000 °C on the DTA curve as shown in Fig. 5. The endothermic peak at 1300 °C is confirmed to correspond to the melting point, because a glassy specimen was observed after the measurement by TG–DTA. This result suggests that Li-EDI is expected to be suitable for the forma-

Table 1
Chemical composition of Li-EDI

	Mass%
SiO_2	36.79
Al_2O_3	31.18
Li_2O	9.00
H_2O	23.47
Total	100.44

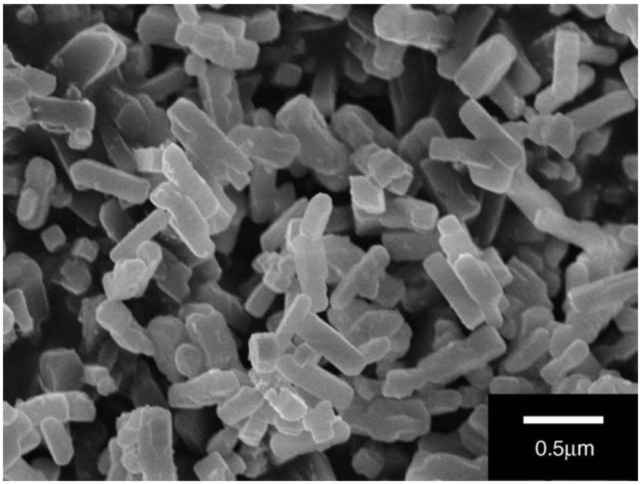

Fig. 4. Scanning electron micrograph of Li-EDI.

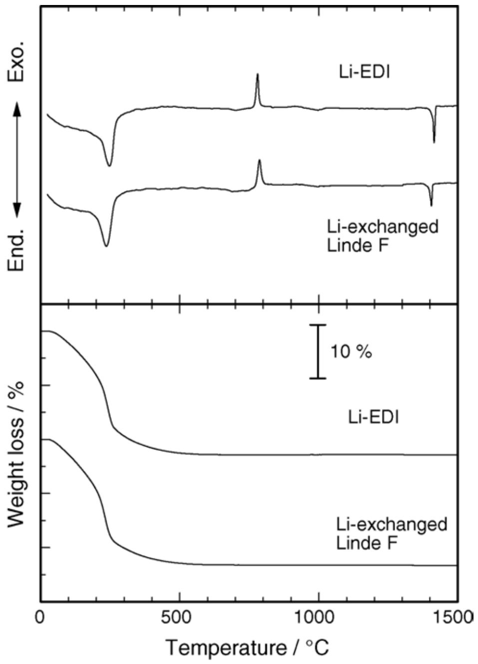

Fig. 5. TG and DTA curves of Li-EDI zeolite and Li-exchanged Linde F.

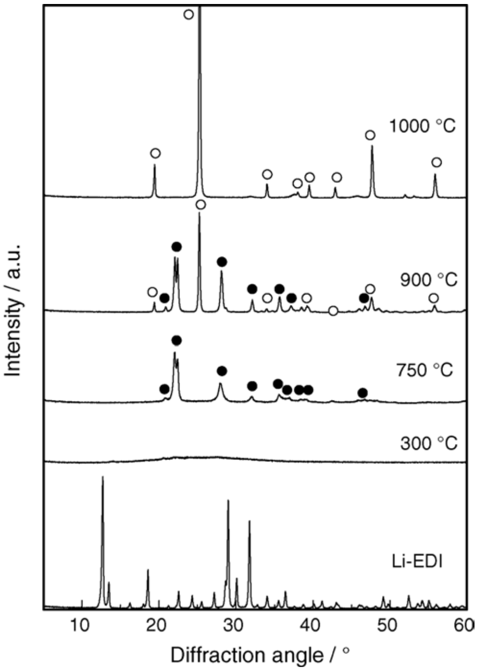

Fig. 6. X-ray diffraction patterns of Li-EDI heated at various temperatures for 1 h: (●) γ-eucryptite; (○) β-eucryptite.

tion of β-eucryptite ceramics having a low thermal expansion coefficient.[18]

On the other hand, the TG and DTA curves of the Li-exchanged Linde F have the same profiles as that of Li-EDI as shown in Fig. 5, but we reported that γ-eucryptite and β-eucryptite simultaneously crystallized in the Li-exchanged Linde F at 720 °C.[16] The difference in the thermal-transformation process between Li-EDI and the Li-exchanged Linde F may be attributed to the small amount of Na and K in the Li-exchanged Linde F.

Sathupunya et al.[7] reported that amine-Li-EDI becomes an amorphous material at 300 °C; however, β-eucryptite crystallized into the amorphous form above 500 °C. β-eucryptite formed a solid solution in the Si/Al ratio range of 1.0–1.6 in the $LiAlSiO_4$–SiO_2 joint system.[19] Since the SiO_2/Al_2O_3 of the amine Li-EDI is 2.40, β-eucryptite crystallized.

4. Conclusion

The Li-type EDI zeolite was successfully synthesized in the Li_2O–Al_2O_3–SiO_2–H_2O system, which has been never reported using a silica–alumina mixed sol as the starting material. Since the reactivity upon zeolitization of the silica–alumina mixture sol is higher than those of the other starting materials reported so far, the EDI zeolites have a lower hydrothermal stability compared to the ABW zeolites generated in the Li_2O–Al_2O_3–SiO_2–H_2O system.

The SiO_2/Al_2O_3 of Li-EDI is equal to 2.00 indicating that the silica content of Li-EDI is the lowest among the zeolites. Li-EDI became an amorphous material at 300 °C, which showed that the thermal stability of Li-EDI is significantly lower.

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