

Preparation of Rare Earth Containing Na-A-Type Zeolites with High Water Content

Noriaki Nakayama, Aika Masuda, Keiko Fujiwara, Tadato Mizota and Yutaka Ueda*

Faculty of Engineering, Yamaguchi University, Ube 755-8611, Japan

Fax: 81-836-85-9601, e-mail: nakayamn@yamaguchi-u.ac.jp

* ISSP, University of Tokyo, Kashiwa 277-8581, Japan

Na-A-type zeolites (Na-LTA) ion-exchanged with trivalent rare earth ions (RE^{3+} : La^{3+} , Dy^{3+} and Yb^{3+}) have been prepared. Pristine LTA powders were treated with dilute 0.01M $RECl_3$ aqueous solution at 40°C for 3 hours. XRD patterns of solid products indicated that the zeolite framework was retained. The chemical analysis of Na in the supernatant solution gave 17, 33, and 40% of Na ions exchanged with La^{3+} , Dy^{3+} and Yb^{3+} , respectively. The topochemical incorporation of rare earth ions in the individual zeolite particles was confirmed by qualitative EDX analyses in a TEM. The water content measured by TG analysis increased with the increase of the ion exchanged amount. Yb exchanged Na-LTA with the smallest RE^{3+} and the highest exchange amount showed the highest water content ($Na_{7.4}Yb_{1.8}Al_{11.6}Si_{12.2}O_{48} \cdot 34.7H_2O$).

Key words: Zeolite LTA, Rare Earth, Ion exchange, TEM, XRF

1. INTRODUCTION

Rare earth ion-exchanged faujasite-type zeolites (FAU) have been long used for cracking catalysts in petroleum refining [1]. The structural details of rare earth ions in FAU have been investigated by various methods. However, reports on the rare earth ion-exchanged A-type zeolite (LTA) are very scarce and it has been believed that the large and trivalent rare earth ions cannot enter the zeolite cages in LTA smaller than those in FAU. The only one system, Eu(II) exchanged LTA, has been synthesized and investigated by X-ray diffraction[2], ESR[3], and Mössbauer Spectroscopy[4]. Recently, the incorporation of rare earth elements into LTA has been reported as a promising method for the nuclear waste disposal [5,6]. The rare earth ion-exchanged LTA is also interesting for the application of LTA to the zeolite-water heat pump system [7,8]. The Mg exchanged Na-LTA shows no remarkable increase of the hydration enthalpy (ΔH_h) but considerable increase of the water content compared with those of Na-LTA, which results in the high heat exchange ability [9-11]. As the increase of average cationic charge decreases the total number of cations in the zeolite cage, the ion-exchange increases the water content. The trivalent rare earth ions, if they are incorporated in the zeolite cage, are therefore expected to be more effective to increase water content. We have tried to exchange the Na ions in LTA with the heavy rare earth ions, Dy and Yb, with the ionic radii smaller than

that of Eu. To investigate the effect of ionic size, we also examined the La containing system. The hydrated ions of Dy^{3+} and Yb^{3+} in aqueous chloride solutions have also been reported to have the size and the coordination number smaller than those of La and Eu [12]. The characterization of reaction products by XRD, analytical TEM and TG-DTA indicated the formation of heavy rare earth ion-exchanged LTA with high water content.

2. EXPERIMENTAL

Na-LTA powder ($Na_{12.36}Al_{11.98}Si_{12.24}O_{48} \cdot 26.7H_2O$) was treated with 0.1M or 0.01M aqueous solution of $RECl_3$ (RE : La, Dy, and Yb). One gram of Na-LTA was reacted in the 200ml $RECl_3$ solution at 40°C for 3 hours. The obtained products were filtrated and washed with de-ionized water. They were dried at 40°C for 24 hours and then kept under the water vapor pressure equilibrated with the saturated NH_4Cl aqueous solution at 25°C. The content of the Na in the supernatant solution was analyzed by atomic absorption spectrometry to evaluate the ion-exchange amount. The phase identification was made by powder XRD using Cu-K α radiation. The microstructures of the solid product were characterized by TEM. The semi-quantitative chemical analysis was also performed in a TEM (JEOL JEM-2010FM) by energy dispersion fluorescent X-ray analysis (EDX). The dehydration process was examined by TG-DTA.

Table I Ion exchange ratio (molar percent of leached Na) and water content of RE-LTA

RE (ionic radius)	RECl ₃ solution	exchange ratio	water content in weight	water molecules in the unit cell
La (1.16Å)	0.1 M	23%	-	-
Dy (1.03Å)	0.01 M	17%	22.0%	28.5 H ₂ O
Yb (0.99Å)	0.1 M	86%	-	-
	0.01 M	33%	23.1%	31.0 H ₂ O
	0.1 M	86%	-	-
	0.01 M	40%	24.4%	34.7 H ₂ O

3. RESULTS and DISCUSSION

3.1 Exchange amount and XRD patterns

The results of atomic absorption spectrometry for the supernatant solution are listed in Table I. Fairly large amount of Na was leached from Na-LTA. Assuming the topochemical ion-exchange of RE ions with the Na ions in LTA, the amount of RE ions in the solid LTA phase is one third of the eluted total amount of Na in the supernatant solution. In the followings, we define the ion-exchange ratio as the molar ratio of Na eluted in the solution to Na in the pristine LTA. The ion-exchange ratio is larger for samples treated with 0.1M solutions and also increases in the order of La, Dy and Yb. Namely, it increases with decreasing the ionic radius of the rare earth ions. Powder XRD patterns shown in Fig.1 indicate that the products with the ion-exchange ratio more than 50% contains large amount of amorphous-like phases. The samples treated with 0.01M RECl₃ solutions show sharp and intense diffraction peaks, which can be indexed as LTA type structures. In the case of the sample treated with 0.01M YbCl₃ solution, XRD pattern shows broad background at around $2\theta=30^\circ$. Hereafter, we call these three samples treated with 0.01M RECl₃ solutions as La-LTA, Dy-LTA, and Yb-LTA, respectively. The lattice constants of LTA phases are shown in Fig. 1. The lattice constants of Dy-LTA, and Yb-LTA are slightly smaller than the pristine Na-

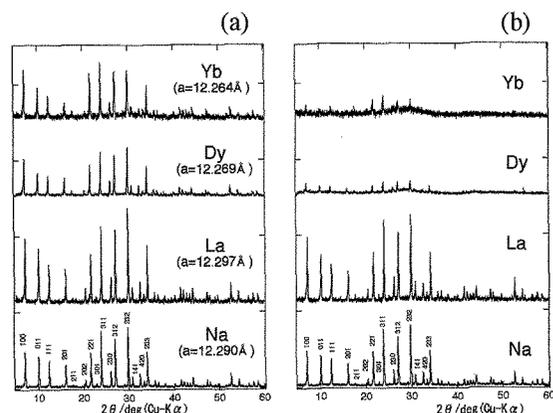


Fig. 1 X-ray diffraction patterns of Na-LTA treated with 0.01M(a) and 0.1M(b) RECl₃ aqueous solutions

LTA, which may suggest the lattice contraction due to the cation number decrease or the elution of the Al atoms in the framework. Above results suggest the topo-chemical ion-exchange of Na-LTA treated with 0.01M RECl₃ solutions.

3.2 TEM and EDX characterization

Figure 2 shows the TEM images of Dy-LTA. Dy-LTA particles have similar shape and size to those for pristine Na-LTA as shown in the low magnification image in Fig.2(a), although a few small crystallites are seen on the surface of the LTA crystallite. Some particles were aggregated as shown in Fig.2(b). The lattice image in Fig. 2(c), taken from a region near the circle A in Fig.2(b), indicates fairly good crystallinity. The incorporation of Dy ions in the LTA particle was confirmed by EDX analysis. Figure 3 shows EDX spectra of the 4 marked regions of a particle in Fig.2(b). The relative intensities of Al-K α , Si-K α and Dy-L α lines are almost similar although the intensity ratio of Dy-L α to Si-K α lines ranges from 0.14 to 0.23. A semi-qualitative analysis without standard samples using Cliff-Lorimer ratio thin section method gives a rough compositional ratio of Na: Al: Si: Dy = 5.1: 12.4: 12: 1.6, which agrees with the composition (Dy³⁺_{1.4}Na_{8.2})[Al₁₂Si₁₂]O₄₈ calculated from the leached Na amount in the supernatant solution. EDX analyses were

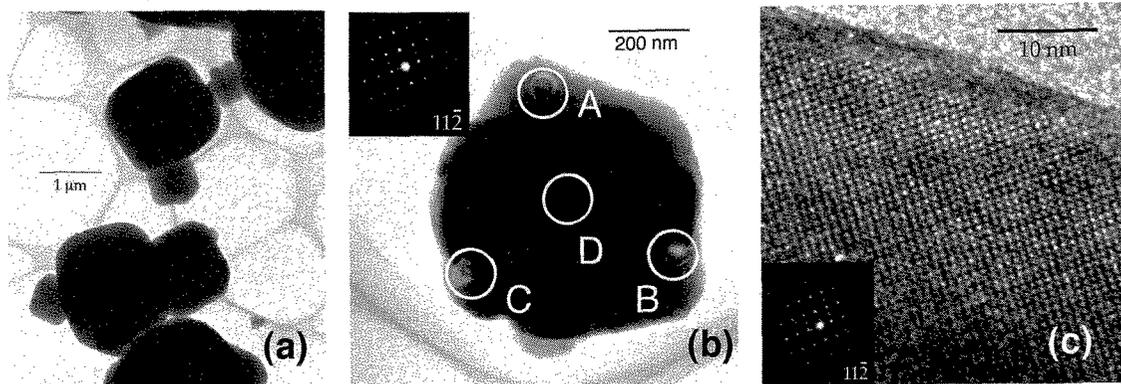


Fig.2 TEM images of Dy-LTA; The lattice image (c) was taken near the region A in the image (b).

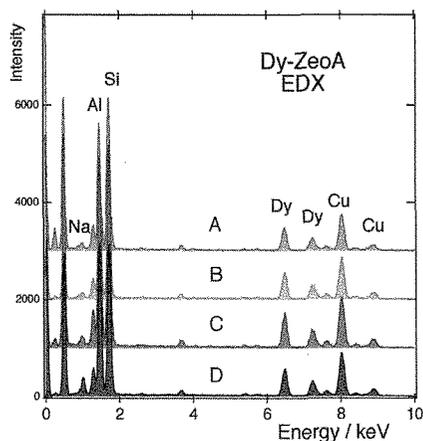


Fig.3 TEM-EDX spectra of Dy-LTA for the 4 regions of a particle shown in Fig. 2(b)

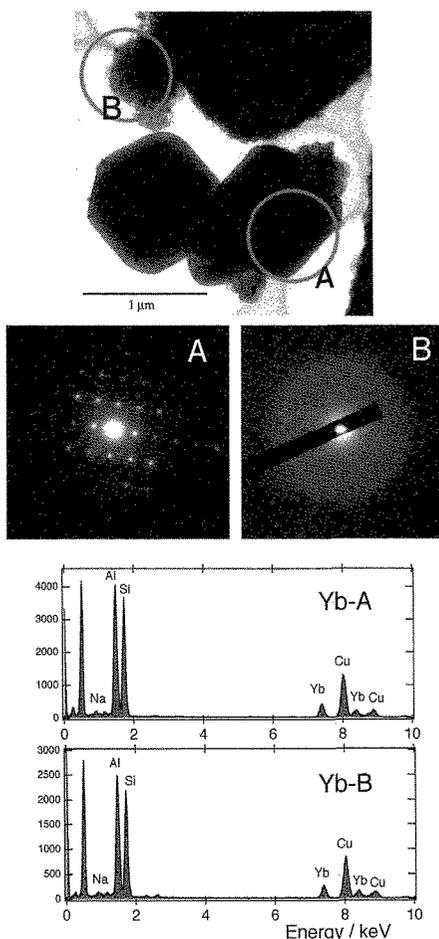


Fig. 4 A TEM image of Yb-LTA and the electron diffraction patterns and EDX spectra of two typical particles

performed for other several particles giving similar results. Above results indicate that most of the Dy ions are topochemically exchanged with Na ions in the LTA with some variation of the composition.

Both TEM and EDX analyses for La-LTA and Yb-LTA

gave almost similar results. EDX spectra for La-LTA give the *RE* composition (typically La:Si=0.5:12 in molar ratio) lower than Dy-LTA. Those for Yb-LTA revealed the *RE* composition similar to Dy-LTA. In the case of Yb-LTA, amorphous-like particles were observed in addition to LTA particles as shown in Fig.4. The electron diffraction patterns of the rectangular shaped particles are net-type ones which can be indexed as those of LTA-type structure. The particles with the irregular shape, such as particle B in Fig.4, which seems to be an aggregate of nano-sized fine particles, give halo patterns from the amorphous structure. Despite the difference in the electron diffraction patterns, the EDX spectra indicate almost similar compositional ratio as shown in Fig. 4. This shows that the amorphous particles are not formed by the hydrolysis of $RECl_3$ solution. For small particles, the high ion-exchange ratio with trivalent rare earth ions about 40% seems to cause the degradation of crystallinity to form amorphous phase.

3.3 TG-DTA analyses and the water content

Figure 5 shows TG and DTA curves on heating for La-LTA, Dy-LTA, and Yb-LTA, compared with those of pristine Na-LTA. From room temperature to 230°C, TG curves show steep decrease in weight and DTA curves shows large and wide endothermic peak due to the dehydration. The weight decreases gradually up to 400°C and at above 600°C the weight change is negligible. The weight change ratio increases in the order of La, Dy and Yb, namely with increasing ion-exchange ratio or with decreasing ionic radius. The molar ratios of water calculated from the TG weight change, y in the chemical formula $(RE,Na)_xSi_{12}Al_{12}O_{48}yH_2O$, are 28.5, 31.0, and 34.7 for La, Dy, and Yb-LTA, respectively. These values are fairly larger than the value, $y=26.7$, for the pristine Na-LTA. Particularly, the molar water content of Yb-LTA is compatible with that of Mg-LTA ($y=34.2$ for a 68% ion-exchanged sample [11]) which shows high heat exchange ability for zeolite-water heat pump system. However, the water content in weight is smaller because of the larger atomic weight of Yb. The water content in weight is shown in Fig. 6 as a function of ionic radius.

The dehydration process has been changed by *RE* ion exchange. The peak temperatures of DTA and DTG curves indicate the slight lowering of dehydration temperature as shown in Fig 6. The thermal stability at high temperature has been also changed by *RE* ion exchange. The pristine Na-LTA shows a sharp exothermic peak in the DTA curve 853°C, which is caused by the phase change from dehydrated LTA to $NaSiAlO_4$ (a mixed phase of nepheline and canegieite). *RE*-ion exchanged LTA shows two DTA peaks at higher temperatures above 880°C. These peaks also correspond to the phase change from dehydrated LTA. X-ray diffraction patterns of samples after DTA measurements indicated that the main phase was $NaSiAlO_4$. As a by-product, $Al_2Yb_2O_9$ for Yb-LTA or Dy_2SiO_5 for Dy-LTA was observed. The formation of aluminate or silicate also indicates that the rare earth ions are incorporated in the

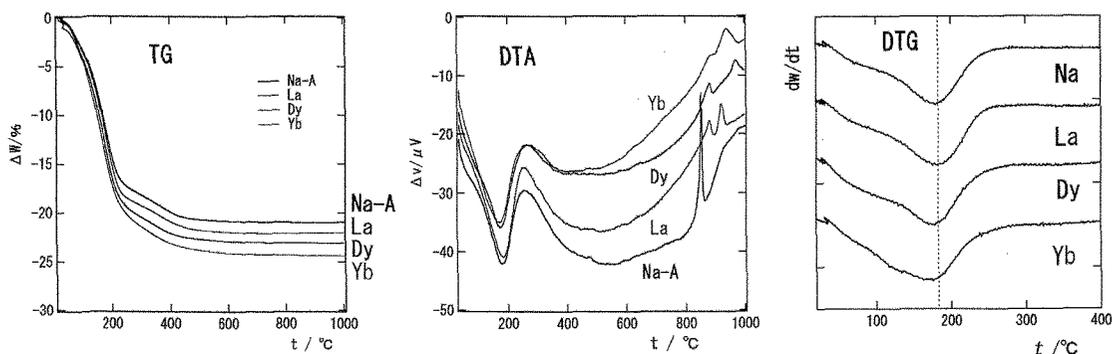


Fig. 5 TG, DTA, and DTG curves of La, Dy, Yb-LTA and pristine Na-LTA

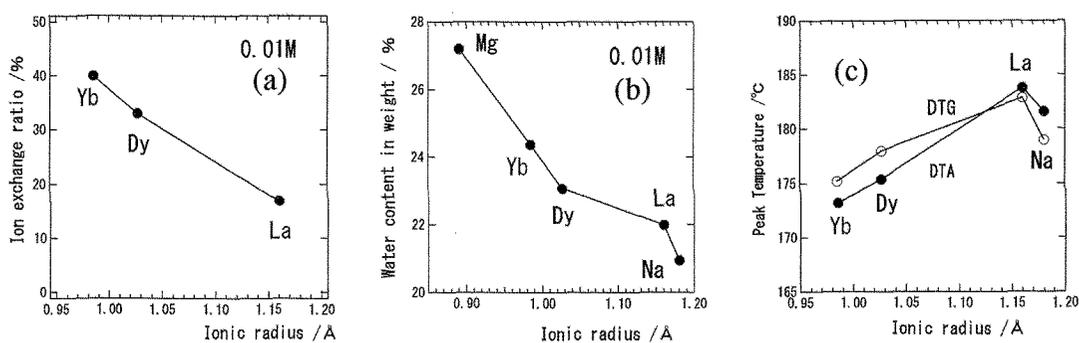


Fig. 6 Ion-exchange ratio (a), the water content in weight (b), and DTA / DTG peak temperatures (c) versus ionic radius of RE or Na

LTA cages, because the LTA ion-exchanged by transition metals like Co^{2+} also shows similar DTA peaks and aluminate formation above 900°C [13].

4. SUMMARY

We could prepare RE ion-exchanged Na-LTA zeolites by treating dilute 0.01M RECl_3 solutions up to the ion exchange ratio about 30-40%, although some microscopic compositional inhomogeneity exists. The ion exchange ratio increases with decreasing the ionic radius of rare earth ions (Fig.6). The ion-exchange ratio higher than 40% causes the degradation LTA framework structure to the amorphous-like structure. The high ionic charge of the rare earth ion causes the decrease of the number of metal ions in the LTA cages and the increase of water content. Highest water content was attained for Yb-LTA with the small RE ionic radius. DTA and DTG curves indicate the lowering of dehydration temperature. RE ion-exchanged Na-LTA zeolites are expected to be effective as the absorbent usable at low temperatures. The present results suggest that the careful setting of preparation conditions, such as the pH control or the solution flowing during ion-exchange reaction, lead to the high quality heavy rare earth ion exchanged LTA zeolite, although a recent report claims the surface hydroxide formation in the case of ion-exchange by light rare earth ions, La^{3+} and Ce^{3+} [14].

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