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Thermal Stability and Decomposition Products of Mg-exchanged Na-LTA Zeolite for Heat Pump Use

Noriaki Nakayama, Yasuhiro Hayashi, Keiko Fujiwara, Tadato Mizota

Faculty of Engineering, Yamaguchi University, Ube 755-8611, Japan
Fax: 81-836-85-9601, e-mail: nakayamn@yamaguchi-u.ac.jp

The thermal stability of Mg^{2+} exchanged Na-A-type zeolites (Mg-LTA) usable for the zeolite-water heat pump system has been investigated by TG-DTA, XRD, and TEM. Eight samples with different Mg compositions from x = 0.0 to 0.84 in the formula of $(Na_{1-x}Mg_{x/2})AlSiO_4 \cdot yH_2O$ were examined. DTA curves show endo-thermic peaks at round 100-200°C due to the dehydration and exo-thermic peaks above 800°C due the decomposition of framework structure. The composition dependence of peak temperature is relatively small. Mg ion exchange does not cause the degradation of framework structure even for the highest Mg composition. The samples with x>0.50 show a sharp DTA peak at around 850°C and a broad one at around 950°C. The framework structure is collapsed into amorphous state at the temperature of the former peak. At around the temperature of the latter peak, fine crystallites of $MgAl_2O_4$ spinel phase with the radii less than 100nm begin to grow embedded in the amorphous component. $MgAl_2O_4$ spinel phase is Mg poor in composition and its structure is disordered.

Key words: Zeolite A, thermal decomposition, fine particle, disordered spinel, TEM

1. INTRODUCTION

LTA zeolites with high water content and high hydration enthalpy are promising heat adsorbents usable for the zeolite-water heat pump system [1-4]. The Mg exchanged Na-LTA (Mg-LTA) shows the considerable increase of the water content compared with Na-LTA, which results in the high heat exchange ability, although the hydration enthalpy (ΔH_h) is similar to the case of Na-LTA. As the increase of average cationic charge decreases the total number of cations in the zeolite cavity, the ion-exchange increases the water content. Fujiwara and Mizota have prepared a series of Mg-exchanged Na-LTA samples with Mg content in the range from x=0.05 to 0.89 in the formula of $(Na_{1-x}Mg_{x/2})AlSiO_4 \cdot yH_2O$ [5] and investigated the dehydration process and the hydration enthalpy [6]. The water content in weight increases from 22% for Na-LTA to 30% for Mg-LTA with x=0.89. The hydration enthalpy is almost independent on the Mg composition in the temperature range lower than 150°C suitable for the zeolite-water heat pump operation.

In this report, we describe the thermal stability of Mg-LTA and its dependence on the Mg concentration. We have also investigated the decomposition products of Mg-LTA zeolite. As for the decomposition products of LTA zeolite ion-exchanged with divalent cations such as Co^{2+} or Ni^{2+}, Schmidt and Weidenthaler [7,8] have recently reported the formation of fine particles of spinel type $CoAl_2O_4$ or $NiAl_2O_4$ embedded in the amorphous matrix. Similar fine particles are obtained depending on the Mg concentration also in the case of Mg-LTA,.

2. EXPERIMENTAL

As the starting materials, two commercial LTA zeolites were used: NA100P ($Na_{1.04}Al_{0.98}Si_{1.00}O_4 \cdot 2.19H_2O$) and GA100P ($Na_{0.50}Mg_{0.28}Al_{0.97}Si_{1.00}O_4 \cdot 2.59H_2O$) from Nippon Chemical Industry Co. LTD. Two gram of starting material was treated with $MgCl_2$ aqueous solution ($200cm^3$). To obtain the sample with x=0.40, GA100P was treated with NaCl solutions. The details of ion-exchange experiments for the sample used in the present experiments are listed in Table I. 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 Mg content was analyzed by atomic absorption spectrometry. The dehydration process was examined by using a TG-DTA apparatus with an infra-red furnace. The phase identification was made by powder XRD using Cu-Kα radiation. The microstructures were characterized by transmission electron microscopy (TEM). The semi-quantitative chemical analysis was also performed in a TEM (JEOL JEM-2010F) by energy dispersion fluorescent X-ray analysis (EDX).

Table I The conditions of ion-exchange experiments and the water content of Mg-LTA: $(Na_{1-x}Mg_{x/2})AlSiO_4 \cdot yH_2O$

x	starting material	$MgCl_2$ solution	Tempe-rature	dura-tion	water content, y
0.0	NA100P	–	–	–	2.19
0.05	NA100P	0.003 M	40°C	3 h	2.23
0.17	NA100P	0.01M	40°C	3 h	2.36
0.40	GA100P	1.0M NaCl	40°C	3 h	2.41
0.53	GA100P	–	–	–	2.58
0.62	GA100P	0.50M	25°C	6 h	2.54
0.73	GA100P	0.10M	70°C	5 h	2.73
0.84	GA100P	0.50M	70°C	24 h	2.79

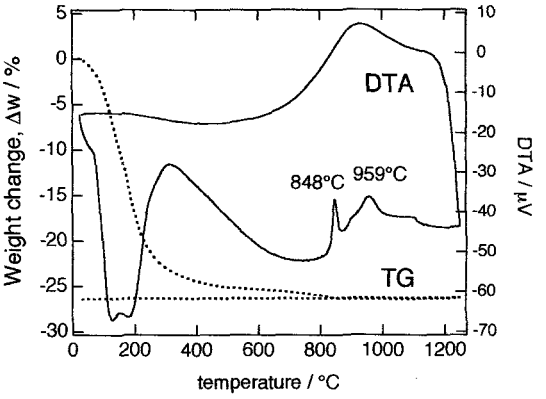


Fig.1 TG-DTA curves for Mg-LTA with x = 0.62

3. RESULTS and DISCUSSION

3. 1. Thermal stability of a typical sample with x=0.62

Figure 1 shows TG-DTA curves measured in air with the heating rate of 20K/min for a typical sample with x=0.62. The DTA curve shows endo-thermic peaks at 126 and 198°C and exo-thermic peak at 848 and 959°C. From the TG curve, the endo-thermic peaks can be attributed to those caused by the dehydration. The appearance of two dehydration peaks is the typical feature of Mg-exchanged LTA as reported previously [5]. The exo-thermic peak at 848°C corresponds to the collapse of the framework structure as revealed by the XRD patterns shown in Fig. 2.

Figure 2 shows XRD patterns of four samples with x=0.62 after the TG-DTA measurements up to 800, 890, 1000, and 1250°C, respectively. The calculated XRD patterns of MgO and $MgAl_2O_4$ are also shown in the figure. After the TG-DTA measurements, samples were rapidly cooled (typically by a rate of 100 K/min) to room temperature. The measurements were performed using a sample holder made of Al_2O_3 single crystal to detect the amorphous component. The XRD pattern of a sample heated up to 800°C is similar to the starting sample but the one of a sample heated up to 890°C shows no sharp peak but a broad peak at around 25° in 2θ. Thus the DTA peak at 848°C corresponds to the collapse of LTA framework into an amorphous state. The relatively broad DTA peak at 960°C is due to the partial crystallization from the collapsed amorphous state. The XRD pattern of a sample heated up to 1000°C shows sharp peaks at 2θ= 44.9 and 65.4° although the broad peak remains at around 2θ= 25°. Two broad and weak peaks are also at around 2θ= 37 and 60° and a sharp and weak peak at 2θ= 38.6° are also seen in the diffraction pattern. When the sample is heated up to 1250°C, broad peaks at 2θ= 36.9 and 59.4° increase their intensity. However a very broad peak at around 2θ= 25° still remains.

As mentioned above, Mg-LTA with x=0.62 is collapsed on heating above 850°C into an amorphous state and then decomposed into amorphous and crystalline component. The crystalline component is assigned to the spinel phase although XRD pattern suggests some defect structures.

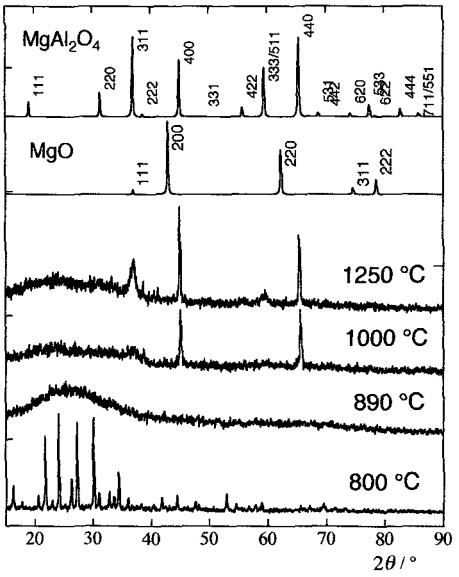


Fig.2 Observed XRD patterns of Mg-LTA with x = 0.62 heated up to 800, 890, 1000, 1250 °C and calculated one of MgO and $MgAl_2O_4$

The intense diffraction peaks at 1000°C may be indexed as 200 and 220 peak of MgO with NaCl type structure. However, the lattice parameter calculated from two sharp peaks is 4.03Å, which is much smaller than the lattice parameter of MgO (a-4.213Å). The observed lattice paramter is close to the half of the $MgAl_2O_4$ with spinel structure (a=8.080Å) and then the two sharp peaks can be index as 400 and 440 peaks of spinel structure. Two broad peaks in the XRD pattern at 1250°C can be indexed as the 311 and 511 peaks of spinel phase with the same lattice parameters for 400 and 440 peaks. However, the other peaks of spinel-type structure, which show fairly large intensity, are not seen. These observations suggest the obtained crystalline phase is close to $MgAl_2O_4$ in composition but the crystal structure is heavily disordered. The close resemblance in the packing of oxygen atoms in both the spinel and NaCl type structure suggests that the metal site occupancies are disordered. The short range ordered spinel-type structure has been revealed by using TEM as will be mentiond in section 3.3.

3.2. Compositional dependence.

Figure 3(a) shows DTA curves of all the samples. All of them show endo-thermic peaks in the range from 100 to 200°C due to the dehydration and also exo-thermic peaks above 800°C due the collapse of framework structure. Figures 3(b) and (c) show the compositional dependence of peak temperatures. The peaks due to the dehydration at around 200'C do not show apparent compositional dependence. The well-defined peaks in the lower temperature range in between 120 and 140°C appear for the samples with $0.17 \leq x \leq 0.72$, although other samples show the corresponding shoulders. These peaks evidences the usefulness of Mg-LTA as the heat absorbent for zeolite-water heat pump operating at the zeolite bed temperature below 150'C.

The peak temperature corresponding to the collapse of the framework structure is also almost independent on the Mg concentration. Mg ion exchange does not cause the degradation of framework structure at high temperature even for the highest Mg composition. The samples with $x>0.50$ show a sharp DTA peak at around 850°C and a broad single peak at around 950°C. However, samples with $x \leq 0.40$ shows rather complex DTA anomalies, suggesting some difference in the decomposition reaction. Figure 4 shows XRD patterns after the DTA measurements up to 1100°C for typical four samples with the different Mg content. The samples with $x>0.50$ shows XRD patterns similar to the one for x=0.62 in Fig. 2, indicating that the decomposition products are composed of amorphous component and crystalline component with defect spinel structure. On the contrary, the samples with $x<0.50$ show

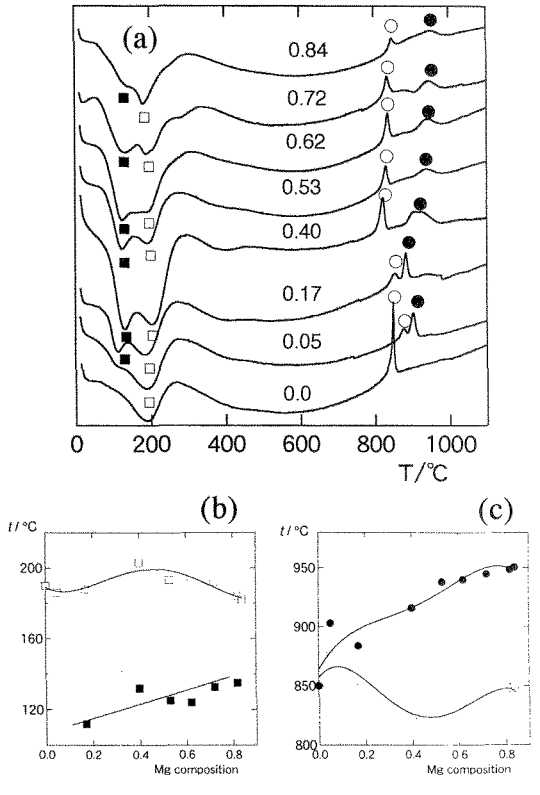


Fig . 3 DTA curves for Mg-LTA (a) and variation of peak temperature with the Mg content (b) and (c)

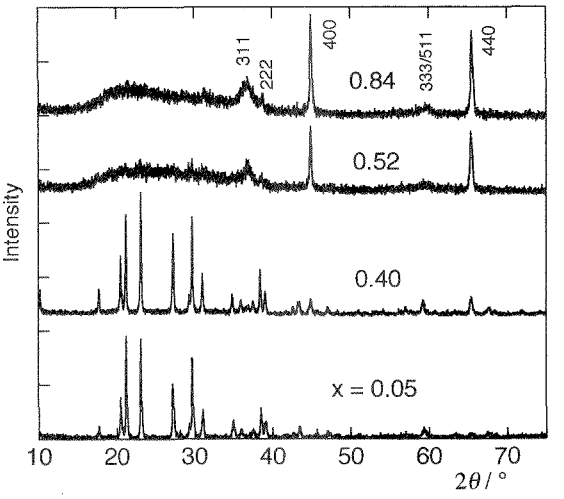


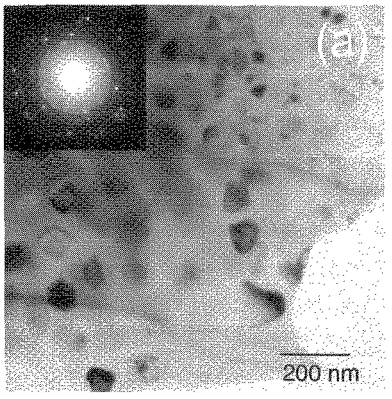
Fig. 4 XRD patterns of Mg-LTA with x=0.05, 0.40, 0.50 and 0.84 heated up to 1100°C

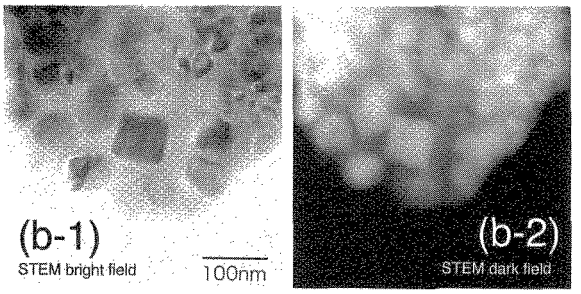
many sharp peaks, which can be indexed as those of $NaAlSiO_4$ with $P6_3$ symmetry (nepheline in the mineral name with lattice dimensions of a=10.05Å and c=8.38Å). The observed lattice parameters for x=0.40 are a=9.977Å and c=8.345Å. The difference in the lattice constant with the reported value suggests the incorporation of Mg atoms in the $NaAlSiO_4$ lattice. Thus the defect spinel phase is obtained as a crystalline component of decomposition product when the Mg composition in LTA is enough high, namely Mg/Al atomic ratio greater than 0.25.

3.3. Microstructures of decomposition product for $x>0.5$

Figure 5 shows electron diffraction (ED) patterns and TEM images of a sample with x=0.84 heated up to 1100°C. The ED pattern in Fig.5(a) composed of sharp diffraction spots, diffraction rings and hallo background. The image indicates that small crystallites are embedded in a particle with its size of a few micrometer. The size of the crystallite ranges from several nano-meter to about 100nm. Most of the crystallites show rectangular shape. The STEM dark field image in Fig. 5(b) suggests that the volume fraction of the crystalline component is rather high. The ED pattern in Fig. 5(c) taken from a single crystallite can be indexed as [001] zone ED pattern of spinel structure. However, the 220 spots and its equivalents are weaker than the 400 spots and its equivalents, although 220 spot of regular spinel is much stronger. Correspondingly, the high-resolution lattice image in Fig. 5(c) shows regular {400} lattice fringes with the spacing of 2Å throughout the crystallite but the {220} lattice fringes with the spacing of 2.8Å are disturbed from place to place. These observations indicate the short-range ordered spinel-type structure. All the samples with $x>0.5$ showed similar microstructures.

The short range ordering may be ascribed to the lower concentration of Mg than the regular spinel composition $MgAl_2O_4$. It is well known that the partial γ-Al_2O_3–$MgAl_2O_4$ solid solution with the cation disorder and vacancies is formed in the Al_2O_3–MgO pseudo-binary





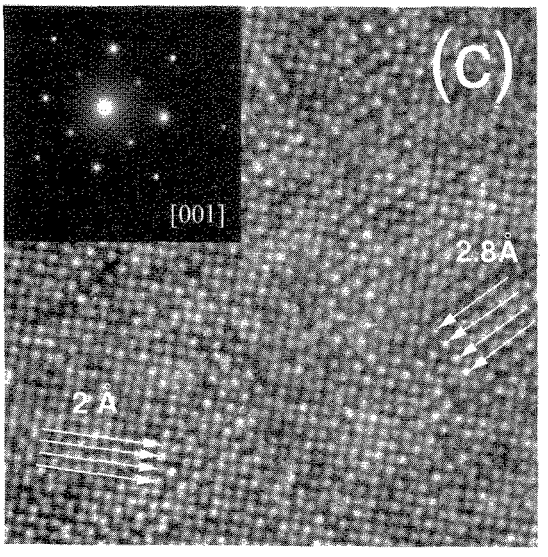


Fig. 5 TEM observations for Mg-LTA with x=0.84 heated up to 1100°C; (a) an ED pattern of a particle and its bright field image, (b) a bright and a dark field image of the same region observed in the STEM mode, (c) An ED pattern and the lattice image of a single crystallite embedded in a particle

system [9]. The composition of the crystallites was checked by EDX analysis in TEM as shown in Fig. 6. The spectrum (a) obtained from a fairly wide region gives an atomic ratio of Mg:Al:Si=18:44:38 close to the net composition. However, the spectrum (b) obtained from the limited region including a embedded single crystallite shows the small Si-Kα peak intensity and gives an atomic ratio of Mg:Al:Si=26:59:15, suggesting the Mg poor state. In the decomposition products of

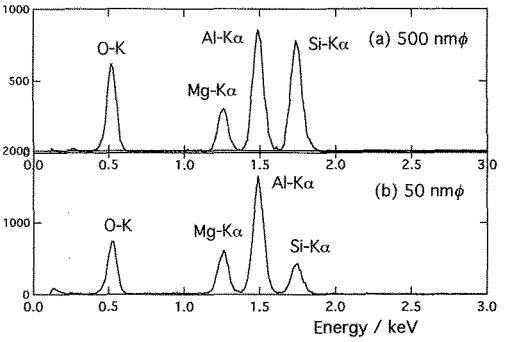


Fig. 6 EDX spectra of Mg-LTA heated up to 1100°C (x=0.84) The spectrum (a) was obtained from the region of about 500nmϕ and the spectrum (b) was obtained from the region of about 50nmϕ including a single crystallite.

Mg-LTA, fine crystallites of $Mg_{1-x}Al_{2+2x/3}\square_{x/3}O_4$ with short range ordered spinel structure are embedded in the SiO_2-based amorphous matrix.

4. SUMMARY

Mg-LTA's show their thermal stability up to 800°C almost independently on the Mg composition up to highest composition of x=0.84. The ion-exchanged Mg-LTA with high water content and thermal stability is promising as the heat adsorbent usable for zeolite-water heat pump system. The decomposition product of Mg-LTA is also interesting because well dispersed $MgAl_2O_4$ fine particles are embedded in a glass matrix. As reported for the decomposition product of Co-LTA, a high surface area is expected if the glass matrix were dissolved out in the alkaline solutions [8].

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