Micro-cubic glass from pseudomorphism after thermal treatment of ammonium-exchanged zeolite A

Hirohisa Yamada\textsuperscript{a,*}, Shingo Yokoyama\textsuperscript{a}, Yujiro Watanabe\textsuperscript{b,1}, Hikaru Uno\textsuperscript{c,2}, Kenji Tamura\textsuperscript{a}

\textsuperscript{a}Ecomaterials Center, National Institute for Materials Science, 1-1Namiki, Tsukuba, Ibaraki 305-0044, Japan
\textsuperscript{b}College of Environmental Engineering and Architecture, Kanazawa Institute of Technology, 7-1 Ohigigaoka, Nonoichi, Ishikawa 921-8501, Japan
\textsuperscript{c}Faculty of Engineering, Hosei University, 3-2-7 Kajinocho, Koganeishi, Tokyo 184-8584, Japan

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Abstract

Isothermal treatments of the ammonium-exchanged Na–zeolite A were carried out at 400 °C for different durations up to 1000 min in the air. The products were characterized by XRD, SEM, AFM, FT-IR, DTA and nitrogen adsorption measurement. The results confirmed that the amorphous pseudomorphism occurred, showing the tweed-like patterns on the surface of cubic solid. These characterizations supported the existence of thin surface layer of zeolite crystal as a microvessel, which was consistent with the previous hypothesis. The amorphous transformation was taking place by the mechanism, in which the zeolite framework reacted with hydrogen decomposed from ammonium ions. The obtained micro-cubic glass should be useful as an eco-functional material, such as the fixation of harmful ions.

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1. Introduction

Zeolite is crystalline, hydrated aluminosilicate with exchangeable cations. The aluminosilicates portion of the structure is a three-dimension open framework consisting of a network of AlO\textsubscript{4} and SiO\textsubscript{4} tetrahedra linked to each other by sharing oxygen atoms. They have periodic and molecular-sized pores and channels in their unique structures \cite{1}. The chemical composition of zeolite can be generally represented by the oxide formula M\textsubscript{2n}O:Al\textsubscript{2}O\textsubscript{3}:xSiO\textsubscript{2}:yH\textsubscript{2}O, where M is the cation of valence n which compensate the negative charge of the framework, x is larger than 2, depending on the type of zeolite, and y varies from 0 to 10.

More than 100 different species of natural and synthetic zeolites have been identified \cite{2}. Linde type A zeolite with Na ions as an exchangeable cation (Na–zeolite A) which general formula is Na\textsubscript{12}Al\textsubscript{12}Si\textsubscript{12}O\textsubscript{48}:27H\textsubscript{2}O, has the minimum Si/Al ratio among zeolites and high cation-exchange capacity. Zeolite A is easily synthesized with well-shaped cubic morphology and a few \textmu m in size.

In the heat treatment of zeolite A, the interesting phenomenon was observed. After the treatment at about 1000 °C and 30 min, the potassium-exchanged Na–zeolite A turns into an X-ray and IR-amorphous (Na, K)-aluminosilicate \cite{3}. While the changes are taking place, the external shape of the original zeolite A crystals, as observed by scanning electron microscopy, remains apparently unperturbed. This phenomenon is recognized as amorphous pseudomorphism. Pseudomorphism is defined to be a phase transformation into another phase of different crystal structure or composition without any changes in the external form of the original phase \cite{4,5}. Pseudomorphism occurs often in many natural and synthetic materials. Noncrystalline ‘pseudomorphs’ after originally crystalline material are known as well \cite{6}. The most common example of such minerals is zircon (ZrSiO\textsubscript{4}), which becomes amorphous by prolonged irradiation by the uranium which is sometimes
present in zircon. Amorphous pseudomorphism after heat treatment of K-exchanged Na–zeolite A was explained by
the hypothesis of thin surface layer of zeolite crystal serving as a microvessel, inside which the amorphous transform-
ation takes place. This is an unproven hypothesis which has to be confirmed or rejected in further investigations.

In the present study, we paid attentions to the zeolite A with ammonium ion. Ammonium-ion exchange and
subsequent heat-treatments are popular way for obtaining protonated zeolite. The obtained product has been recog-
nized to be amorphous and useless one. The objectives of the present work are: (i) to study the amorphous
pseudomorphism after zeolite-LTA with ammonium-cations under isothermal treatment at 400 °C by varying the
duration from 0 to 1000 min, (ii) to characterize precisely the obtained solid after pseudomorphosis by using XRD,
SEM, AFM, FT-IR, DTA and nitrogen adsorption measurement.

2. Experimental

Synthetic Na–zeolite A was supplied as powders by Wako Pure Chemical Industries, Ltd, Japan. One gram of
Na–zeolite A was added to 100 mL aqueous solution containing 1 M NH₄Cl. The suspension was stirred at
room temperature overnight, and then suspension was filtered with a 0.45 μm membrane filter (Millipore,
0.45 μm HA-type). The procedures were repeated three times. The separated solid was then added to distilled water,
stirred, filtered and washed with distilled water at room temperature. The procedures were repeated five times.
Finally the reacted solid was separated, washed with 500 mL of distilled water and dried in an oven at 50 °C
for 12 h.

The isothermal treatments were carried out in the air by an electric furnace. The ammonium-exchanged zeolite A in
porcelain crucible was put into the furnace at 400 °C for desired duration 0–1000 min, and then pulled out from the
furnace for quenching at ambient condition.

The untreated Na–zeolite A, the ammonium-exchanged zeolite A and the isothermal treated samples were
characterized by the powder X-ray diffraction (XRD) method with Fe Kα radiation (RIGAKU: RINT 2200), by
the scanning electron microscopy (SEM) (JEOL S-5500), by the atomic force microscopy (AFM) (SHIMAZU
SPM9500), FT-IR spectrometer (Parkin-Elmer Ins., SPEC-
TRUM 2000), DTA analysis (SEIKO, Exstar 6000) and the
nitrogen adsorption isotherm measurement (BEL JAPAN,
Inc., BELSORP 28SA).

3. Results and discussion

Fig. 1 showed the DTA curves of the untreated Na–zeolite A and the ammonium-exchanged zeolite A.

The DTA curve of the untreated Na–zeolite A was compared with that of the typical zeolite A. The weak
endothermic shoulder at about 50 °C may be due to desorption of loosely held water molecules in the zeolite.
The appearance of the endothermic minima at about 170 °C is due to dehydration of the hydrated sodium ions located in
the cages of the zeolite A framework. Two exothermic peaks at about 850 and 900 °C corresponded to the
amorphization and crystallization of carnegieite, respect-
ively [7].

The primary effect of the heating of the ammonium-
exchanged zeolite A was also the desorption of zeolitic
water below 200 °C. The peak temperature of dehydration for the ammonium-exchanged zeolite A was higher than that
of the Na–zeolite A, because of the difference of the
hydration energy for ammonium ions and Na ions in zeolite
A. As recognized in the previous study, the thermal
transformation depends considerably on the type of
exchangeable cations in the zeolite structure [8]. The
newly appeared endothermic peak at about 300 °C was
related to the decomposition of ammonium ions located in
the zeolite framework.

No characteristic peak was observed up to about 1200 °C
where the crystallization of mullite took place as indicated by the exothermic peak [9]. No distinct feature was
observed in DTA curve at 400 °C for the ammonium-
exchanged zeolite A. Therefore, the isothermal treatment of
the ammonium-exchanged zeolite A was carried out at
400 °C for further investigation.

Fig. 2 showed that the XRD patterns of the untreated
Na–zeolite A, the ammonium-exchanged zeolite A and the
product after the isothermal treatment at 400 °C for 10 min.
The XRD pattern of the untreated zeolite A was typical one
for Na–zeolite A with no trace of impurity. After the
ammonium-exchange treatment, the peak intensity and
position of XRD pattern were changed according to the
ion-exchange in zeolite framework [10]. After the
isothermal treatment at 400 °C for 10 min, the XRD peaks
related to zeolite-LTA structure were disappeared and
the amorphous halo was appeared. XRD analyses confirmed that the obtained products after the treatments at 400 °C were X-ray amorphous phase, being independent on the heating durations.

Fig. 3 indicated the FT-IR spectra of the untreated Na–zeolite A, the ammonium-exchanged zeolite A and the product after the isothermal treatment at 400 °C for 10 min. In the FT-IR spectra of the untreated Na–zeolite A, the characteristic bands for zeolite framework at 560 cm⁻¹ due to the external vibration of double four-rings, 1000 cm⁻¹ for the internal vibration of T(Si, Al)–O asymmetric stretching, 660 cm⁻¹ for the internal vibration of T(Si, Al)–O symmetric stretching and 460 cm⁻¹ for the internal vibration of T–O bending were observed (Fig. 3) [11]. The band related to OH was also appeared at about 1600 cm⁻¹.

The bands obtained for the untreated zeolite A were also observed for the ammonium-exchanged zeolite A. It indicated that no remarkable changes were observed in the microenvironment of the framework during the process from Na-type to the ammonium-exchanged type. The additional band was appeared at about 1400 cm⁻¹, which was related to ammonium ions in the framework.

After the isothermal treatment, the bands at 560 cm⁻¹ for double four-rings, 1000, 660 and 460 cm⁻¹ for the internal vibration of T–O bondings were either broadened or disappeared. The appearance of broad bands at 710 and 470 cm⁻¹, which are characteristic to amorphous aluminosilicate, i.e. the loss of the crystallinity of zeolite A was obtained [12–15].

The SEM images in Fig. 4 indicated the interesting phenomenon, i.e. pseudomorphism: a phase transformation into another phase of different crystal structure or composition without any changes in the external form of the original phase. Both the untreated Na-zeolite A and the ammonium-exchanged zeolite A showed the typical cubic morphology with the original crystallinity which was defined by XRD method. The product after the isothermal treatment at 400 °C also showed the cubic shape, being independent on the heat duration. The combination of SEM and FT-IR observations confirmed that the amorphous pseudomorphism was occurred for the ammonium-exchanged sample treated at 400 °C. These observations are compared with the previous study [3]. The potassium-exchanged zeolite A showed a pseudomorphic transformation into an X-ray- and IR-amorphous aluminosilicate when heated at about 1000 °C for 30 min. In contrast to structural changes, the particles of the resulting amorphous (Na–K)-aluminosilicate have the same shape and size (as can be estimated from the micrograph) as the starting zeolite. This phenomenon can be explained by the property of thin surface layer of zeolite crystal, which is different from that of bulk crystal. In their hypothesis, the thin surface layer of zeolite crystal played an important role as a microvessel to make amorphous aluminosilicate by pseudomorphism.

The present SEM and AFM (Fig. 5) studies confirmed the existence of the special thin surface layer, i.e. special surface morphology of zeolite crystal after the isothermal treatment. Comparing the smooth surface for the untreated and ammonium-exchanged zeolite A, the tweed-like patterns on the surface of cubic solid was appeared on the SEM images after the isothermal treatment. The gathering of tiny hills of which height was a few 100 nm on the surface was observed on the AFM images after the isothermal treatment. The relationship between the SEM images and AFM images was not completely explained, but
Fig. 4. SEM images of (a), (b) the untreated Na–zeolite A, (c), (d) the ammonium-exchanged zeolite A and (e), (f) the product after the isothermal treatment at 400 °C for 10 min.

Fig. 5. AFM images of (a) the untreated Na–zeolite A and (b) the product after the isothermal treatment at 400 °C for 10 min.
these distinct surface features were closely related to the amorphization of zeolite A during heating caused by structural changes at molecular level, i.e. by breaking of Si–O–Al bonds between different building units of the zeolite structure. The breaking of bands of Al–O–Si bondings in zeolite structure was originated with hydrogen ions which were obtained by the decomposition from ammonium ions in the zeolite structure.

No distinct mesopore was recognized by the nitrogen adsorption measurement for the isothermal treated product. This feature was explained that the thin surface layer of the zeolite crystal may cover and block the microstructure of zeolite. Therefore, the obtained material should be appreciable to fixation of harmful ions inside, which was partly exchanged with ammonium ions before the isothermal treatment.

4. Conclusion

In the present study, zeolite A with ammonium ion was treated at 400 °C for different lengths of time. Ammonium-ion exchange and subsequent heat-treatments are popular way for obtaining protonated zeolite. The products were characterized by XRD, FT-IR, SEM, AFM and nitrogen adsorption measurement. The results confirmed that the amorphous pseudomorphism occurred, showing the tweed-like patterns on the surface of cubic solid. These characterizations supported the previous hypothesis, and also indicated that the zeolite framework reacted with hydrogen decomposed from ammonium ions. The observations are very interesting as solid-state reactions and await further elucidation in terms of the specific mechanism. Because the outside surface of the zeolite crystal serves as a microvessel, this material may be useful for absorption of harmful ions inside the structure.

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