Formation Process of Mullite from NH_4^+ -Exchanged Zeolite A

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アンモニウムイオン交換ゼオライト A からのムライトの生成過程

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[Received October 13, 1994; Accepted November 22, 1994]

Zeolite A (NH_4 -A) exchanged with NH_4^+ was used as a precursor of mullite. NH_4 -A was dehydrated and deammoniated by heating up to 300°C and it entered an amorphous state. Mullite crystallized directly from the amorphous phase at above 950°C without forming a spinel phase as an intermediate phase. Since the starting material is zeolite A, which has the tetrahedral framework structure with homogeneous arrangement of Si, Al, and O atoms, these experimental results supported the previous hypothesis proposed for the formation process of mullite.

Key-words : Mullite, Zeolite A, Formation process, NH_4^+ -exchange

1. Introduction

Mullite is the only stable phase in the SiO_2 - Al_2O_3 system at atmospheric pressure.¹⁾ For a long time, many studies on the formation process have been conducted and reported with reference to: (1) Mullite formed directly from the amorphous phase, and (2) SiO_2 - Al_2O_3 spinel phase as an intermediate phase formed before formation of mullite. Formation process (1) was reported in the studies using glasses,^{2),3)} alkoxide hydrolyzed gels,⁴⁾ and spray pyrolyzed powder⁵⁾ as starting materials. Alkoxide hydrolyzed gels,^{6),7)} and kaolin minerals⁸⁾ were used in formation process (2). This difference between formation processes (1) and (2) is considered to depend on the degree of chemical homogeneity of the precursor of starting materials; that is, formation of mullite in the process (1) is easier when the SiO_2 component in the precursor is more miscible with the Al_2O_3 component.⁹⁾ The degree of atomic mixing state in the starting materials, however, was little investigated except for kaolin minerals. In particular, the precursors exhibiting formation process (1) are in the amorphous state. Therefore, arrangement of these atoms was not determined by a structure analysis method such as the X-ray diffraction method.

It is well known that zeolite has a framework structure composed of SiO_4 and AlO_4 tetrahedra. Since the arrangement of Si, Al, and O atoms is a well-mix-

ed state, it is considered to be a good precursor for the formation of mullite. Distribution of Si and Al atoms in the zeolite framework structure obeys Loewenstein's rule,¹⁰⁾ and no Al-O-Al bondings exist in the framework structure.^{11),12)} Therefore, the molar ratio of Si/Al in zeolite is at least one. The chemical formula of zeolite A is generally represented by $\text{Na}_2(\text{AlO}_2)_2(\text{SiO}_2)_2 \cdot 4.5\text{H}_2\text{O}$,^{13),14)} and it is one possessing the composition of the lowest molar ratio of Si/Al in zeolites. The Na^+ is exchangeable and is easily exchanged with NH_4^+ . In this way, the structure of zeolite A exchanged with NH_4^+ is expected to be suitable for mullite formation; however, no investigation has yet been carried out.

The purpose of this study is to examine the formation process of mullite from NH_4^+ -exchanged zeolite A.

2. Experimental procedure

Commercial zeolite A powder (Tosoh Co.; A-4) was used as a crystalline starting material. The Na^+ in the material was replaced with NH_4^+ by the batch method. Zeolite A powder of 100 g was dispersed in 1 dm^3 of the solution dissolving 1 mol $\text{CH}_3\text{COONH}_4$. The exchanging reaction proceeded at room temperature for 24h and was repeated several times by changing to fresh solution. The chemical compositions of treated material were determined by flame spectroscopy for Na, precipitation method for Al_2O_3 and SiO_2 , and indophenol-blue method for NH_3 . Thermogravimetry-differential thermal analysis (TG-DTA) (MAC Science Co.; 2020S) was carried out in air at a heating rate of $10^\circ\text{C}/\text{min}$. The NH_4^+ -exchanged zeolite A (NH_4 -A) was heated for 1h at set temperature by a heating rate of $10^\circ\text{C}/\text{min}$ in order to investigate the thermal transformation. The heated samples were identified by powder X-ray diffraction (XRD) (MAC Science Co.; MXP-3). Infrared absorption spectra (FT-IR) (JEOL; JIR-5500) were measured by the KBr wafer technique. Morphology of the particles in the heated samples was examined by transmission electron microscopy (TEM) (JEOL; 2000EX).

3. Results and discussion

The results of chemical analysis of the NH_4 -A are shown in Table 1. In the NH_4 -A sample, the ratio of NH_4^+ -exchange for Na^+ was 99.0%, and the molar ratio of Si/Al was 1.01.

Figure 1 shows TG and DTA curves of the NH_4 -A. The endothermic peaks around 170°C and 200°C were caused by dehydration and deammoniation, respectively. These assignments were compatible with the thermogravimetric analysis, because the TG curve indicated weight loss at the endothermic peaks on the DTA curve. The broad exothermic peak at about 300°C may be due to the partial oxidation of ammonia.¹⁵⁾ No absorption bands of N-H stretching (3200 cm^{-1}) and bending (1450 cm^{-1}), or H_2O bending (1650 cm^{-1}) were detected in the IR spectra of the sample heated above the broad exothermic temperature. The sharp exothermic peak at 1000°C was attributed to crystallization. This temperature was 20°C higher than that of the other mullite precursors.¹⁶⁾

In order to investigate the process of thermal phase transformation of NH_4 -A, it was heated at various temperatures. X-ray diffraction patterns of

Table 1. Chemical Compositions of NH_4^+ -Exchanged Zeolite A

SiO_2	35.80
Al_2O_3	30.11
Fe_2O_3	0.06
Na_2O	0.19
NH_3	10.41
H_2O	23.24
Total	99.81

$$\text{H}_2\text{O} = \text{lg.loss} - \text{NH}_3$$

Fig. 1. TG and DTA curves of NH_4^+ -exchanged zeolite A.

Fig. 2. X-ray diffraction patterns of NH_4^+ -exchanged zeolite A heated at various temperatures for 1h.

the samples are shown in Fig. 2. The structure of NH_4 -A decomposed at 300°C and became an amorphous state above this temperature. Mullite began to form directly from the amorphous phase at 950°C, without forming a spinel phase as an intermediate phase. The crystallinity of the formed mullite remained in a poor state up to 1200°C and improved at 1400°C. Thermal stability of the crystalline precursor of mullite has an influence on the formation temperature of mullite. For example, sillimanite group minerals in the SiO_2 - Al_2O_3 system have Al_2SiO_5 composition and high homogeneity of Si, Al, and O atoms. In these minerals, such as kyanite¹⁷⁾ and

Fig. 3. TEM photograph of mullite formed from NH_4^+ -exchanged zeolite A by firing at 1400°C for 1h.

andalusite,¹⁸⁾ the structures were stable at around 1200°C in air, and these minerals transformed into mullite upon heating to above 1200°C. On the other hand, the structure of NH₄-A decomposed at low temperature. Therefore, it was possible to form mullite at the lower temperature of 950°C.

Figure 3 shows a TEM photograph of mullite particles formed at 1400°C. The mullite particles had columnar morphology with average size of 40×80 nm, similar to that of the mullite reported previously.¹⁹⁾

These experimental results supported the hypothesis that mullite formed directly from a precursor with a high degree of homogeneity of Si, Al, and O atoms.⁹⁾

(This paper was presented at the Annual Meeting of the Ceramic Society of Japan, April 1993)

Acknowledgements The TEM measurement was done with JEOL-2000EX at Ryukoku University.

References

- 1) I. A. Aksay and J. A. Pask, *J. Am. Ceram. Soc.*, **58**, 507–12 (1975).
- 2) R. Ganz and W. Kronert, *Interceram*, **2**, 136–44 (1982).
- 3) I. Takamori and R. Roy, *J. Am. Ceram. Soc.*, **56**, 639–44 (1973).
- 4) D. X. Li and W. J. Thomson, *J. Mater. Res.*, **5**, 1963–69 (1990).
- 5) S. Kanzaki and H. Tabata, *J. Am. Ceram. Soc.*, **68**, C6–7 (1985).
- 6) D. W. Hoffman, R. Roy and S. Komarneni, *J. Am. Ceram. Soc.*, **67**, 468–71 (1984).
- 7) Y. Hirata, H. Minamizono and K. Shimada, *Yogyo-Kyokai-Shi*, **93**, 36–44 (1985).
- 8) A. J. Leonard, *J. Am. Ceram. Soc.*, **60**, 37–43 (1977).
- 9) K. Okada and N. Otsuka, *J. Am. Ceram. Soc.*, **69**, 652–56 (1986).
- 10) W. Loewenstein, *Am. Mineral.*, **39**, 92–96 (1954).
- 11) J. M. Thomas, C. A. Fyfe, S. Ramdas, J. Klinowski and G. C. Gobbi, *J. Phys. Chem.*, **86**, 3061–64 (1982).
- 12) M. T. Melchior, D. E. W. Vaughan, R. H. Jarman and A. J. Jacobson, *Nature*, **298**, 455–56 (1982).
- 13) T. B. Reed and D. W. Breck, *J. Am. Chem. Soc.*, **78**, 5972–77 (1956).
- 14) L. Broussard and D. P. Shoemaker, *J. Am. Chem. Soc.*, **82**, 1041–51 (1960).
- 15) A. P. Bolton and M. A. Lanewala, *J. Catalysis*, **18**, 154–63 (1970).
- 16) J. A. Pask and A. P. Tomsia, *J. Am. Ceram. Soc.*, **74**, 2367–73 (1991).
- 17) H. Schneider and A. Majdic, *Ceramurgia Int.*, **6**, 61–66 (1980).
- 18) H. Schneider and A. Majdic, *Ceramurgia Int.*, **5**, 31–36 (1979).
- 19) S. Kanzaki, T. Kurihara, S. Iwai, M. Ohashi and H. Tabata, *Yogyo-Kyokai-Shi*, **95**, 1213–18 (1987).