Formation process of Sr-celsian from precursor zeolites

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Introduction

The materials with the composition of SrAl2Si2O8 have been expected as a refractory and an electric material, due to the high melting point (1650°C), the low thermal expansion coefficient \((3.7 \times 10^{-6} \text{K}^{-1} \text{ from } 20 \text{°C to } 1200 \text{°C})\), and the low dielectric constant.\(^2\) The crystal phases of SrAl2Si2O8 have three polymorphs: monoclinic \((\text{space group: }P2_1/c)^3\) and hexagonal \((\text{space group: }P6_{3}mmn)^4\) forms only as synthesized, and slawsonite \((\text{space group: }P2_1/a)^5\) as natural mineral. Monoclinic form, hexagonal form, and slawsonite, are the same in the crystal structure as three polymorphs of celsian \((\text{BaAl2Si2O8})\), which are monocelsian, hexacelsian, and paracelsian.\(^6\) Therefore, the compounds of SrAl2Si2O8 also are called Sr-celsian, and these three polymorphs are called Sr-monocelsian, Sr-hexacelsian, and Sr-paracelsian, respectively. Sr-monocelsian and Sr-hexacelsian have been synthesized through the crystallization of glasses,\(^7\) hydrothermal reaction,\(^8\) and the solid-state reaction from a mixture of kaolin minerals and SrCO\(_3\).\(^9\) SrSO\(_4\).\(^10\)

Zeolites are aluminosilicate hydrates having the general formula of \(M_{2n} \cdot O\cdot Al_{2} \cdot SiO_{2} \cdot yH_{2}O\), where \(M\) is an exchangeable cation to maintain charge neutrality, \(n\) is valence number of \(M\)-ion. The framework structure of zeolites is composed of both AlO\(_4\) and SiO\(_4\) tetrahedra in the various ratios. The Löwenstein rule\(^11\) prohibits Al–O–Al bond in the zeolite framework, therefore the composition of zeolites is Si/Al \(\geq 1\). When a zeolite is heated, the crystal structure collapses, resulting in the formation of an amorphous phase and then the recrystallization to some nonzeolitic species of which the framework density is higher than that of zeolites. Due to these characterizations, zeolites as the precursor in the formation of aluminosilicate compounds have the following many advantages:\(^12\) (1) The distribution of Al, Si, M, and O atoms in zeolites is in a well-mixed state due to the Löwenstein rule; (2) The desired composition of the starting material easily prepared by selecting zeolite with the required Si/Al ratio and by exchanging the cation in zeolite to the required metal cation; (3) Zeolites are synthesized at low temperatures around 100°C, and are widely used for many industrial and technological applications, and hence low-cost materials.

Two kinds of zeolites with different crystal structures with the same chemical composition of SrO·Al\(_2\)O\(_3\)·2SiO\(_2\)·xH\(_2\)O prepared by an ion-exchange technique were used as a precursor of Sr-celsian. One was Sr-exchanged Linde F zeolite (Sr–F), the other was Sr-exchanged Linde F zeolite (Sr–F). The Sr–A almost became an amorphous material at 400°C, and then generates a small amount of Sr-hexacelsian from the amorphous material at 500°C. The amount of Sr-hexacelsian steeply increased and a small amount of Sr-monocelsian also formed at 1000°C. On the other hand, the Sr–F nearly becomes an amorphous material at 500°C, owing to the hexacelsian - to - monocelsian phase transformation. The reason for the crystallization of Sr-hexacelsian at 500°C only from Sr–A was explained in terms of the similarity in framework structures of zeolite A and Sr-hexacelsian.

Experimental procedure

Two kinds of zeolites, zeolite A ((Na\(_2\)O·Al\(_2\)O\(_3\)·SiO\(_2\))·27H\(_2\)O) (framework type code: LTA\(^13\)) and Linde F zeolite ((K\(_2\)O·Al\(_2\)O\(_3\)·SiO\(_2\)h)·25H\(_2\)O) (framework type code: EDI\(^16\)), were used as starting materials. Both of these zeolites have the molar ratio of Si/Al = 1 with the different crystal structures. The zeolite A was a commercial powder (Tosoh Co., A–4). The Linde F zeolite was synthesized from the hydro-gel of 6K\(_2\)O·Al\(_2\)O\(_3·2SiO\(_2·120H\(_2\)O at 100°C for 48 h. The Na\(^+\) in the zeolite A and K\(^+\) in the Linde F zeolite were replaced with Sr\(^{2+}\) by the batch method as follows: A portion of zeolite powder of 100 g was dispersed in 1 dm\(^3\) of 0.5 mol·dm\(^{-3}\) Sr(NO\(_3\))\(_2\) solution;
The cation exchange reaction proceeded at room temperature for 24 h and was repeated several times by changing with fresh solution. The treated zeolites were washed with distilled water and dried at 40°C. The chemical compositions of Sr-exchanged zeolites were determined by inductively coupled plasma emission spectrometry (Shimadzu Co., ICPS-8000) for Sr and Ba, by flame spectrophotometry (HITACHI Ltd., Z-5010) for Na and K, and by a gravimetric method for Si and Al.

Thermogravimetry-differential thermal analysis (TG–DTA; MAC Science Co., 2020S) was carried out in air at a heating rate of 10°C·min⁻¹. The Sr-exchanged zeolites were heated in air at set temperature with a heating rate of 10°C·min⁻¹ in order to investigate the thermal transformation. The heated specimens were identified by powder X-ray diffractometry (XRD; MAC Science Co., MXP-3A), and the morphology was observed with scanning electron microscope (SEM: JEOL Ltd., JSM-5410).

3. Results

3.1 Chemical composition

The results of chemical analysis in the Sr-exchanged zeolite A and Linde F zeolite (Sr–F) are shown in Table 1. The chemical formulas of Sr-exchanged zeolites are Sr₂₋₀.₉₆Na₀.₀₁Al₁.₉₂Si₂.₀₈O₈·₅.₁₅H₂O in Sr–A and Sr₂₋₀.₉₁Ba₀.₀₄K₀.₀₁Al₂.₀₂Si₂.₀₁O₈·₃.₆₄H₂O in Sr–F, respectively, which indicated these materials have the same cation-composition as Sr-celsian. The presence of Ba in Sr–F was due to the uptake of trace Ba in the Sr(NO₃) solution by Linde F zeolite with the high selectivity for Ba.¹⁷

3.2 Thermal analysis

Figure 1 shows TG and DTA curves of Sr–A and Sr–F. Endot-
these structures are stable up to 700\degree C. Com\textsubscript{1}lyzed gel was necessary to heat at temperatures above 1000\degree C, the formation of Sr-hexacelsian from glasses and alkoxido hydro-

The difference in the framework structure of precursor zeolites in Sr-celsian, Sr-exchanged zeolites were heated at various temperatures for 1 h. Figure 2 shows the XRD patterns of products obtained from Sr–A. When Sr–A was heated at 400\degree C, the crystal structure of zeolite A was almost decomposed and only trace of the reflection of the (100) plane is observed. A small amount of Sr-hexacelsian forms at 500\degree C. The amount of Sr-hexacelsian slightly increased up to 600\degree C and was constant from 600\degree C up to 1000\degree C. In zeolite A exchanged with alkaline metal cations and Ca\textsuperscript{2+} ion, these structures are stable up to 700\degree C–900\degree C. It was found that the thermal stability of Sr–A was significantly lower. The formation of Sr-hexacelsian from glasses and alkoxido hydro-

The XRD patterns of Sr–F heated at various temperatures are shown in Fig. 3. Sr–F nearly becomes an amorphous material at 300\degree C corresponding to the dehydration temperature. This indicates that the collapse of the framework structure occur simultaneously with the dehydration. Such collapse process is also known in Li, Na, Ca, and Ba type Linde F zeolites. Sr-

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Fig. 4. Scanning electron micrographs of Sr-exchanged zeolites heated at various temperatures for 1 h. a) Sr–A, b) Sr–A at 500\degree C, c) Sr–A at 1000\degree C, d) Sr–F, e) Sr–F at 500\degree C, f) Sr–F at 1000\degree C.

3.3 Thermal transformation

In order to investigate the crystallization process of Sr-celsian, Sr-exchanged zeolites were heated at various temperatures for 1 h. Figure 2 shows the XRD patterns of products obtained from Sr–A. When Sr–A was heated at 400\degree C, the crystal structure of zeolite A was almost decomposed and only trace of the reflection of the (100) plane is observed. A small amount of Sr-hexacelsian forms at 500\degree C. The amount of Sr-hexacelsian slightly increased up to 600\degree C and was constant from 600\degree C up to 1000\degree C. In zeolite A exchanged with alkaline metal cations and Ca\textsuperscript{2+} ion, these structures are stable up to 700\degree C–900\degree C. It was found that the thermal stability of Sr–A was significantly lower. The formation of Sr-hexacelsian from glasses and alkoxido hydro-

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3.4 SEM observation of heated specimens

Figure 4 shows the scanning electron microphotographs of the specimen heated at various temperatures. In both of Sr–A and Sr–F heated at 500\degree C, there is no change in morphologies compared with starting materials, zeolite A and Linde F zeolite. The specimens heated at 900\degree C also maintained the morphologies of starting materials, which is not shown in Fig. 4. These results suggest that the crystal size of Sr-hexacelsian formed from Sr–A at 500\degree C is smaller than that of the zeolite A used as the starting material. When both of the Sr-exchanged zeolites were heated at 1000\degree C, these morphologies became spherical in shape.

4. Discussion

The difference in the framework structure of precursor zeolites with the same chemical composition resulted in the difference in the formation process of Sr-celsian. In particular, Sr-hexacelsian formed only from Sr–A at 500\degree C. The reason for this result is explained in terms of the similarity in the framework structure between Sr-hexacelsian and zeolite A. Zeolites have a common subunit of structure which is a specific array of TO\textsubscript{4} tetrahedra (T = Si or Al). These subunits have been called secondly building unit (SBU). As shown in Fig. 5, the framework of Sr-hexacelsian consists of single 6-membered rings of TO\textsubscript{4} tetrahedra, and that of zeolite A also has single 6-membered rings of TO\textsubscript{4} tetra-

In contrast, the framework of Linde F zeolite is composed of complex 4 = 1 unit (T\textsubscript{4}O\textsubscript{16}) and single 8-membered rings of TO\textsubscript{4} tetrahedra and has no single 6-membered ring of TO\textsubscript{4} tetra-

These SBUs probably remained in the amorphous materials obtained from Sr-exchanged zeolites around 500\degree C, though the long range order of zeolite A structure broke down. Consequently, the single 6-membered rings of TO\textsubscript{4} in Sr–A promoted the nucleation of Sr-hexacelsian, and Sr-hexacelsian inherited the single 6-membered rings of TO\textsubscript{4} from zeolite A as a precursor.

At 1000\degree C, Sr-hexacelsian mainly formed from Sr–F, along
with a small amount of Sr-monocelsian, and the amount of Sr-hexacelsian increased and Sr-monocelsian slightly formed in Sr–A. These results prove that the exothermic peaks at 1030°C on DTA curves (Fig. 1) are mainly attributed to the formation of Sr-hexacelsian. The metastable forms, Sr-hexacelsian, usually nucleated more readily than stable forms, Sr-monocelsian. The metastable forms, Sr-hexacelsian, are ascribed to the simpler structures of the high symmetry modification of Sr-hexacelsian. As shown in Fig. 4, the morphologies of both zeolite monocelsian and hexacelsian, have lower kinetic barriers for nucleation. In contrast, the low symmetry monocelsian, are made of three-dimensional networks in which the Al and Si are at least partially ordered in a special orientation. Owing to these structural differences, the high symmetry Sr-hexacelsian, have lower kinetic barriers for nucleation. As shown in Fig. 4, the morphologies of both zeolite samples heated at 1000°C became spherical in shape, which indicates the formation of a liquid phase. Since the compound of SrAl2Si2O8 composition has a glass transition temperature of 883°C,23) the amorphous materials became a supercooling liquid above around 900°C. The liquid phase facilitates the crystallization of Sr-hexacelsian around 1000°C.

In other studies13,14 with reference to the thermal transformation of Sr-exchanged zeolite A, Sr-hexacelsian formed at 1000°C, but no crystallization at 500°C. The difference in the transformation between this study and others may be due to impurities, heating schedule, and atmosphere, etc. Further studies are necessary to investigate the difference in the crystallization process of Sr-hexacelsian from Sr-exchanged zeolite A.

According to the previous work22) of the transformation of Ba-exchanged zeolite A (Ba–A), the crystal system of celsian (BaAl2Si2O8) formed at 500°C was monoclinic. The framework of monocelsian consists of single 4- and 8-membered rings of TO4 as shown in Fig. 5.23) Consequently, the SBU in Ba–A, single 4- and 8-membered rings of TO4, promoted the nucleation of monocelsian. The framework in zeolite A is thus similar to both structures of monocelsian and hexacelsian. The zeolite A as starting material in the previous work22) is the same as that of this work. Therefore, exchangeable cations in precursor zeolites, that are Sr2+ and Ba2+, give the difference in the thermal transformation process of celsian. We focus on the site selectivity of cations in zeolite A, that is, the occupant sites of Sr2+ and Ba2+. Three kinds of cation sites, that is, six-, eight-, and four-membered oxygen rings site, exist in zeolite A crystal framework as shown in Fig. 5, which are named site I, II, and III, respectively.24,25) In the unit cell of Na type zeolite A (Na2O·Al2O3·SiO2·27H2O), the site I and site II are occupied by eight and three Na+ ions, respectively. The twelfth Na+ ion occupies site III. The site selectivity of cations in zeolite A are decided by the cation-lattice interaction energies. Zeolite A is divided into two structures, ionic and covalent. The cation-lattice interaction energies consist of the electrostatic, polarization, dispersion, repulsion, and charge transfer energies. Ogawa et al.26) calculated these energies for the cations at the single 6- and 8-membered rings of TO4 in a simplified model of zeolite A. Consequently, the cation-lattice interaction energies for Sr2+ and Ba2+ are calculated as listed in Table 2. As a result, Sr2+ prefers the site I, whereas Ba2+ prefers the site II. Consequently, six Sr2+ ions in the unit cell of Sr–A occupies the site I. In unit cell of Ba–A, all of the site II are occupied by Ba2+ ions and the residual three Ba2+ ions are present at the site I. The cations at the site III seems to be energetically the most unstable of the cations in zeolite A, thus no divalent cation exist at the site III. As shown in Fig. 5, Sr2+ or Ba2+ is located on the six-membered oxygen rings in the hexacelsian structure, whereas on the eight-membered rings in the monocelsian structure. The location of Sr2+ in Sr–A is similar to hexacelsian. On the other hand, that in Ba–A is similar to monocelsian. Therefore, the Sr-hexacelsian crystallized in Sr–A at 500°C.

5. Conclusion

We found that Sr-hexacelsian was formed at 500°C from Sr–A. The similarity in the framework structure between Sr-hexacelsian and zeolite A, being the presence of single 6-membered rings of TO4 tetrahedra, promoted the nucleation of Sr-hexacelsian at 500°C. Therefore, Sr-hexacelsian inherited the single 6-membered rings of TO4 from zeolite A as a precursor. Furthermore, all of Sr2+ in Sr–A is present at the site I on six-membered oxygen rings, and the Sr2+ of Sr-hexacelsian structure is also located on the six-membered oxygen ring. The similarity location of Sr2+ also promoted the nucleation of Sr-hexacelsian at 500°C in Sr–A.

References