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Synthesis and crystal structure analysis of a novel strontosilicate AES-19 having two dimensional eight-membered ring micropores

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ABSTRACT

A novel microporous strontium-containing silicate material AES-19 was successfully synthesized by mechanochemical method in which a precursor material was prepared through the solid-phase mechanochemical reaction of parent materials and crystallized by the hydrothermal treatment in an alkaline solution. The crystal structure analysis demonstrated that AES-19 was composed of a unique silicate layer having a two-dimensional eight membered ring micropore system and that interlayer six-coordinated strontium atoms connected the silicate layers.

1. Introduction

Crystalline microporous materials such as zeolites having molecular-sized uniform micropores have been widely utilized as size-selective catalysts or adsorbents. Their pore structures, such as pore sizes, shapes, and dimensions, greatly affect their physicochemical properties, so a lot of efforts have been made to synthesize novel structures of microporous materials. Among various approaches to obtain novel zeolites, the use of organic structure-directing agents such as bulky quaternary ammonium cations would be the most successful strategy [1], and various novel zeolites have been actually yielded.

Nevertheless, the incorporation of heteroatoms is another effective strategy to obtain novel zeotypes; several novel zeolites having 3MR-containing *lov* (spiro-5) or *vsv* composite building units [2] have been synthesized by the incorporation of zinc [3–5], lithium [6], or beryllium [7], and various germanosilicate or germanate zeolites having *d4r* composite building unit have also been prepared [8–12]. Among heteroatom-containing silicates, ETS-4 and ETS-10 [13,14] synthesized by researchers of Engelhard seem curious in particular because 6-coordinated octahedral titanium atoms are incorporated in these materials. That is, titanium atom is not merely a heteroatom but a “hetero-coordinated” atom. Because of the presence of the non-tetrahedral species in the framework, three-letter codes for zeolite materials cannot be given to these materials [15]. However, because of the presence of this strange framework species, they can construct characteristic frameworks that cannot be built by a zeolite composed only of tetrahedral species. This fact suggests that the introduction of non-tetrahedral heteroatoms could be a promising approach to build novel microporous zeotypes.

Hetero-coordinated atom-incorporated microporous materials can be found in natural minerals as well as in synthetic substances. Rhodesite [16] is a calcosilicate mineral having a two-dimensional eight membered ring (8MR) micropore system. In this mineral, calcium atoms are incorporated in the framework as 6-coordinated species. A synthetic calcosilicate CAS-1 [17] has a crystal structure closely related to that of rhodesite similarly to have 6-coordinated calcium atoms and two-dimensionally intersected 8MR micropores. Likewise, 6-coordinated yttrium atoms are incorporated in a mineral montregianite [18,19] whose silicate layer is isostructural to that of rhodesite. AV-1, a synthetic analog of montregianite, has been already reported [20], and the incorporation of lanthanoids isostructurally substituted for yttrium has been also reported [21,22]. We also have recently reported the synthesis of several silicate materials containing alkaline-earth metal atoms as hetero-coordinated species [23–25]. These materials, including a structure-solved microporous calcosilicate AES-1 that is an isostructure of CAS-1, were crystallized from precursors prepared through mechanochemical reaction [26–28] of silica and alkaline-earth metal hydroxides.

In this work, we report on a strontium-containing silicate AES-19, one of the materials reported in the previous paper as an unknown material [24]. Also in this case, a precursor material was

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prepared through the mechanochemical reaction of fumed silica and strontium hydroxide and successively converted into a crystalline material by the hydrothermal treatment. The X-ray crystal structure analysis demonstrated that this material was a novel microporous strontosilicate material having two-dimensional 8MR micropores.

2. Experimental

2.1. Synthesis of AES-19

Fumed silica Aerosil 200V (Nippon Aerosil) and strontium hydroxide (Wako) were employed as silicon and strontium sources, respectively. These source materials were mixed at the molar ratio of SiO_2:$Sr(OH)_2$ = 1:0.2 and charged into a milling pot made of silicon nitride together with silicon nitride balls. The pot was set in a Fritsch P-5 planetary ball mill, and the mixture was allowed to react mechanochemically through the milling at 400 rpm for the total milling time of 24 h. The milling was conducted at autogenous temperature for 15 min followed by the pause for 15 min before another 15 min of milling to avoid the overheating of samples. The mechanochemically reacted mixture was dispersed in an aqueous solution of potassium hydroxide (Wako) at the molar ratio of SiO_2:$Sr(OH)_2$:KOH:H_2O = 1:0.2:0.35:20 and hydrothermally treated in a Teflon-lined stainless autoclave at 150 °C for 7 days under stirring conditions. The resulting product was filtered, washed with distilled water, and dried at room temperature.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of the synthesized samples were collected with a PANalytical X'Pert PRO MPD diffractometer operated at 45 kV and 40 mA equipped with a high-speed X'Celerator detector. The scanning electron micrographs (SEM) were taken with a Hitachi S4100L field emission-type microscope. Thermogravimetric and differential thermal analysis (TG–DTA) was conducted at the heating rate of 2 K min^{-1} with a Rigaku ThermoPlus TG8120 apparatus. The nitrogen adsorption isotherm at −196 °C was collected with a Bel Japan Belsorp-mini II instrument. The water and carbon dioxide adsorptions were measured at 25 °C with a Bel Japan Belsorp max instrument. Adsorption measurements were conducted after the pretreatment at 200 °C under vacuum for 3 h in all cases.

2.3. Crystal structure analysis

For the crystal structure analysis, high quality XRD data were collected at room temperature with a Bruker D8-Advance with Vαrio1 diffractometer operated at 40 kV and 50 mA equipped with a Ge(1 1 1) monochromator and a linear position-sensitive VÅNTEC-1 detector (8° 2θ) in a modified Debye–Scherrer geometry using Cu $K\alpha_1$ radiation. Samples were sealed into borosilicate capillary tubes with an inner diameter of 0.5 mm. The X-ray absorption of the sample tube containing Sr atom was corrected based on its μr value (μ: linear absorption coefficient, r: sample radius), which was determined at 0.858 by the measurement of transmittance.

The crystal structure of AES-19 was determined by ab initio structural analysis. Indexing of reflections with the programs N-TREOR built in the program EXPO2009 [29] successfully gave lattice parameters and indices of the reflections. A space group was determined from reflection conditions derived from these indices. Observed integral intensities, $|F_{obs}|^2$, of all diffraction peaks were extracted preliminary by the hybrid-pattern decomposition (HyPD) method using the program RIETAN-FP [30]. The HyPD method is a new advanced technique as the whole pattern fitting, which is combination analysis of the Le Bail method and individual profile fitting (only integrated intensities). In HyPD, Le Bail analysis and the subsequent refinement of integrated intensities are carried out cyclically, giving the best fit finally. Then, a structural model for AES-19 was constructed by combination of the powder charge-flipping method using the program Superflip [31].

Lattice and structure parameters of AES-19 were refined by the Rietveld method using RIETAN-FP on the basis of the above structural model. A split pseudo-Voigt profile function and a background function of Legendre polynomials with 11th order were used in the refinement. Partial profile relaxation with a modified split pseudo-Voigt function was applied to some reflections with highly asymmetric profiles. In the early stage of the refinement, we imposed restraints upon all the Si–O bond lengths, i.e., l(Si–O) = 0.160 ± 0.002 nm, all the O–Si–O bond angles, i.e., ϕ(O–Si–O) = 109.47 ± 3.0°. Furthermore, indistinct extraframework atoms were found in an electron density distribution map obtained by the maximum entropy method (MEM) combined with Rietveld analysis, namely so called the MEM/Rietveld method. The MEM analysis was carried out by means of the program Dysnomia [32]. Structural model and electron density map was visualized by the program VESTA [33].

3. Results and discussion

We have already reported the synthesis of a microporous calcosilicate AES-1 [24] (Fig. 1a), and under the same synthesis conditions AES-19 (Fig. 1b) was obtained from a mechanochemically prepared precursor containing strontium (Fig. 1c) in lieu of calcium. From a simple mixture of starting materials without mechanochemical reaction, a mixture of AES-19 and α-quartz was obtained (Fig. 1d), indicating that mechanochemical reaction not only amorphized the starting materials but also formed a uniformly mixed composite [24]. A precursor having a lower

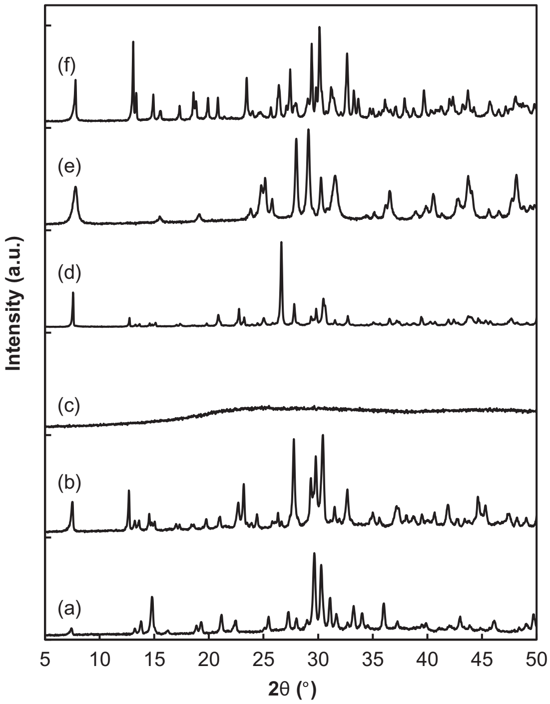

Fig. 1. XRD patterns of (a) calcosilicate AES-1, (b) AES-19, (c) mechanochemically reacted precursor, (d) a product synthesized without mechanochemical reaction, (e) AES-36 synthesized from a precursor with Sr/Si ratio of 0.4, and (f) AES-17 crystallized in NaOHaq.