Microporous and Mesoporous Materials 243 (2017) 239–246

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Synthesis and crystal structure analysis of a novel microporous barium-containing silicate AES-20

Katsutoshi Yamamoto [a], [*], Takuji Ikeda [b], [**], Chiaki Ideta [a], Koji Watanabe [a], Takuma Nakaoka [a]

[a] Faculty of Environmental Engineering, The University of Kitakyushu, 1-1 Hibikino, Wakamatsu-ku, Kitakyushu 808-0135, Japan
[b] Research Institute for Chemical Process Technology, National Institute of Advanced Science and Technology, 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan

ARTICLE INFO

Article history:
Received 15 December 2016
Received in revised form
10 February 2017
Accepted 10 February 2017
Available online 13 February 2017

Keywords:
Barium-containing silicate
Layered silicate
X-ray structure analysis
Microporous

ABSTRACT

A novel microporous barium-containing silicate AES-20 was successfully synthesized, and its crystal structure was determined based on the *ab-initio* structure analysis from powder X-ray diffraction data. AES-20 was composed of unique silicate layers having 8- and 5-rings and interlayer barium atoms pillaring the silicate layers. AES-20 was obtained through the hydrothermal synthesis in the presence of lithium cations, which were involved in AES-20 as extra-framework species. The 8-ring micropore in AES-20 is smaller than a nitrogen molecule but larger than a carbon dioxide molecule, suggesting the application to a size-selective adsorbent for carbon dioxide removal.

1. Introduction

Development of novel crystalline microporous silicate materials is important because they can be utilized as size-selective catalysts or adsorbents owing to their molecular-sized uniform micropores. Admitting that one of the most fruitful and the most common strategies to obtain novel microporous silicates would be the use of organic structure-directing agents, actually the incorporation of heteroatoms is also a promising approach. In particular, the incorporation of hetero-coordinated, that is non-tetrahedral, atoms is worthy of attention, since it can produce unique structures that cannot be constructed only from tetrahedral atoms.

ETS-10 as well as ETS-4 [1,2] would be the first synthetic microporous silicates containing hetero-coordinated atoms in the framework. In these materials, octahedrally-coordinated titanium atoms are incorporated in their crystalline structures, and because of the presence of such non-tetrahedral species they are able to have unique topologies. Monteregianite [3] and rhodesite [4] are natural minerals that also incorporate hetero-coordinated framework atoms. These minerals are composed of the same structured silicate layers, and the silicate layers are bridged with 6-coordinated yttrium atoms in monteregianite or 6-coordinated calcium atoms in rhodesite. AV-1 and AV-2 [5] are their synthetic analogues synthesized by Rocha et al. AMH-3 [6] and CAS-1 [7] are novel synthetic calcosilicate materials whose structures are similar to but clearly different from that of rhodesite; CAS-1 has two-dimensional 8-ring channels like rhodesite.

We also have synthesized crystalline microporous silicates containing hetero-coordinated atoms [8–12]. In our cases, alkaline-earth metals were employed as hetero-coordinated species, and mechanochemical reaction was applied in the precursor preparation process [13–15]. AES-1, which has been demonstrated to have the same topology as CAS-1 [9], is a calcium-containing microporous silicate crystallized from a precursor prepared by the mechanochemical reaction of calcium hydroxide and fumed silica. By using this mechanochemically prepared precursor, AES-1 is crystallized at as low temperature as 150 °C. AES-18 and AES-19 are novel strontium-containing microporous silicate materials. Also in this case, precursor materials are prepared through the mechanochemical reaction of fumed silica and strontium hydroxide and successively converted into a crystalline material by the hydrothermal treatment.

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[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: katz@kitakyu-u.ac.jp (K. Yamamoto), takuji-ikeda@aist.go.jp (T. Ikeda).

http://dx.doi.org/10.1016/j.micromeso.2017.02.034
1387-1811/

The advantage of the incorporation of hetero-coordinated atoms is not only that it can create a novel structure but also that unique properties might be added to silicate matrix. In this regard, it is noteworthy that Rocha et al. succeeded in synthesizing AV-5 and AV-9. These materials had hetero-coordinated lanthanide atoms such as cerium, europium, and terbium introduced in monteregianite-like silicate structures and showed interesting photoluminescence properties [16,17]. These materials have really motivated us to develop novel barium-containing silicates because lanthanide-doped barium silicate materials have been actually utilized as novel photonics materials such as phosphors or scintillators [18–21].

In this study, we report the successful synthesis of a novel microporous barium-containing silicate material AES-20. The physicochemical properties and the X-ray crystal structure analysis of this material are also reported.

2. Experimental

2.1. Synthesis of AES-20

AES-20 was initially synthesized from a mechanochemically mixed precursor like other alkaline earth metal-containing AES materials [9,11,12]. 1.00 g of fumed silica Aerosil 200V (Nippon Aerosil) and 1.05 g of barium hydroxide octahydrate (Wako) were charged in a 45 ml silicon nitride milling pot together with seven 15 mm silicon nitride balls and allowed to react mechanochemically using a Fritsch P-5 planetary ball mill operated 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. 0.060 g of lithium hydroxide monohydrate (Wako) was dissolved in 1.32 g of water, and 0.5 g of the mechanochemically reacted powder was dispersed in the solution. The resulting suspension with a molar ratio of SiO_2: $Ba(OH)_2$: LiOH: H_2O = 1: 0.2: 0.35: 20 was hydrothermally treated in a 22 ml Teflon-lined stainless autoclave at 150 °C for 7 days under stirring conditions. The product was filtered, washed with distilled water, and dried at room temperature.

AES-20 was synthesized also without mechanochemical reaction. In this case, fumed silica and barium hydroxide were dispersed in aqueous solution of lithium hydroxide and hydrothermally treated under the same conditions.

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. Thermogravimetric and differential thermal analysis (TG-DTA) was conducted under atmospheric conditions at the heating rate of 5 K min^{-1} with a Rigaku ThermoPlus TG8120 apparatus. The nitrogen adsorption isotherm at −196 °C and the water and carbon dioxide adsorption isotherms at 25 °C were collected with a Bel Japan Belsorp max instrument. Adsorption measurements were conducted after the pretreatment at 200 °C under vacuum for more than 2 h in all cases. The equilibrium time for each measuring pressure was 300 s in nitrogen and water adsorption measurements and 500 s in carbon dioxide measurement. In water adsorption measurement, saturated water vapor was employed as adsorbate. Carbon dioxide adsorption was measured up until 0.1 MPa instead of saturated pressure. The UV–vis spectra were recorded with a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere attachment ISR-2600. The scanning electron micrographs (SEM) were taken at a low accelerated voltage of 1.0 kV and a working distance of 3 mm by means of a Hitachi S-4800 field emission-type microscope equipped with a Bruker Quantax energy dispersive X-ray spectrometry (EDS) system for chemical composition analysis.

Local structures of constituent elements were investigated by the solid-state magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) technique. ^{1}H MAS, ^{29}Si DDMAS and $\{^{1}H\}\rightarrow{}^{29}Si$ CP/MAS NMR spectra of the sample were recorded on a Bruker AVANCE III 400WB at 400.1 MHz for ^{1}H and at 79.5 MHz for ^{29}Si. Additionally, ^{6}Li and ^{7}Li MAS NMR spectra were collected at 58.9 MHz and 155.5 MHz, respectively. In all samples, a zirconia rotor with an inner diameter of 4 mm was used, and their spinning rates were 6 kHz for ^{29}Si and 14 kHz for ^{1}H, ^{6}Li and ^{7}Li. Each spectrum was accumulated with following conditions; pulse length of 3.5 μs, recycle delay of 4 s and 32 scans for ^{1}H, pulse length of 2.5 μs ($\pi/4$ pulse), recycle delays of 30 s and 12800 scans for ^{29}Si DDMAS, contact time of 6 ms, recycle delays of 4 s and 10240 scans for ^{29}Si CP/MAS, pulse length of 2 μs, recycle delay of 2 s and 10240 scans for ^{6}Li, and pulse length of 2 μs, recycle delay of 5 s and 8 scans for ^{7}Li. Tetramethylsilane for ^{1}H and ^{29}Si nuclei and 1.0M LiCl in D_2O solution for ^{6}Li and ^{7}Li nuclei were used as chemical shift references.

2.3. Crystal structure analysis

For the crystal structure analysis, high quality XRD data were collected at room temperature with a Rigaku SmartLab instrument operated at 40 kV and 50 mA equipped with a position sensitive D/teX Ultra2 detector in the Bragg-Brentano geometry using Cu $K\alpha_{12}$ radiation. Samples were packed into aluminum holders with a thickness of 2.0 mm. Because the X-ray absorption of AES-20 containing Ba atoms was very large, an absorption-independent para-focusing reflection optics was adopted. The opening width of an incident divergence slit was fixed at 1/6°.

The crystal structure of AES-20 was determined by *ab-initio* structural analysis from powder diffraction data. Indexing of reflections with the program Conograph [22] 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 observed diffraction peaks were extracted by the hybrid-pattern decomposition (HyPD) method using a versatile pattern fitting program RIETAN-FP [23]. Obtained $|F_{obs}|^2$ data were analyzed by the maximum-entropy Patterson method (MEP) [24] using the program ALBA [23], where the Patterson function was combined with the maximum-entropy method (MEM) to improve $|F_{obs}|^2$ data of overlapped reflections. An initial structural model was analyzed by the powder charge-flipping (pCF) method (Superflip [25]) and the direct method (EXPO2014 [26]) using the improved $|F_{obs}|^2$ dataset.

Lattice and structural parameters based on the initial model were refined by the Rietveld method, and the structure model was modified by trial and error. Extra-framework sites, i.e. adsorbed H_2O, were found in an electron density distribution map obtained by MEM analysis using the program Dysnomia [27,28]. All structural models and electron density maps were visualized by the program VESTA3 [29]. Additionally, we applied the bond valence sum 3D mapping method (abbreviated as BVS3D) to verify the validity of distribution of Ba^{2+} obtained by the structure refinement and to predict whether Ba^{2+} can migrate in a crystal structure [30]. The BVS3D calculation was carried out by using the program PyAbstania coded by Nishimura [31].

3. Results and discussion

3.1. Synthesis conditions and resulting phases

Table 1 and Fig. 1 exhibit the synthesis conditions and the XRD patterns of several alkaline earth metal-containing silicates. As