RMA-3: synthesis and structure of a novel Rb-aluminosilicate zeolite†

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RMA-3 (Rubidium Microporous Aluminosilicate-3) was hydrothermally synthesized from rubidium–aluminosilicate gels without using any organic or inorganic additives, and its structure determined by XRD Rietveld analysis was confirmed as a novel framework topology containing two 8-membered ring pore-openings with dimensions of 0.49 × 0.37 nm and 0.34 × 0.38 nm.

The fundamental method of synthesizing aluminosilicate zeolites is the hydrothermal treatment of aluminosilicate gel in alkaline media without an organic structure-directing agent (OSDA). A lot of alkali-metal aluminosilicate zeolites have been synthesized without OSDA, and several ones such as A, X, Y, L, mordenite, *etc.* are commercially available. Most of these aluminosilicate zeolites are synthesized in Na-, K- and (Na + K)-ions media. However, only a few aluminosilicate zeolites incorporating rubidium ions *e.g.* Rb–D, Rb–M[1] and Rb–analcime,[2] have been reported.

At present, the focus is on large-pore zeolites containing the pores constructed with 12-MR (membered ring) or more, and those with high Si/Al ratio or non-aluminosilicate for new catalysts and adsorbents.[3] Therefore, new zeolites such as VPI-5,[4] $AlPO_4$-8,[5] UTD-1,[6] CIT-5,[7] IM-12,[8] ECR-34[9] have recently been synthesized with OSDA and in some cases with OSDA in fluoride containing media such as ITQ-15,[10] ITQ-17,[11] ITQ-21.[12] Consequently, hydrothermal synthesis of zeolite in a simple alkaline metal ion as alkaline source has rarely been reported recently. Although there exist some reports of zeolite synthesis with the simultaneous addition of OSDA and rubidium ion, such as VPI-9,[13] ECR-18[14] and SSZ-42,[15] sufficient clarity with respect to knowledge of mineralizing, structure-directing and templating effects of rubidium ion is not available. In the present study, the synthesis of microporous Rb-aluminosilicate zeolites is investigated in order to obtain the phase relationship of aluminosilicate zeolite phases, and to examine the above effects of rubidium ion without using any OSDA. Herein, we report the synthesis and structure of a novel Rb-aluminosilicate zeolite RMA-3 with a two-dimensional pore system of 8-MRs.

The trial of zeolite synthesis of Rb–aluminosilicate was performed using gels with the wide range of composition expressed as the following general molar ratios: $x\mathrm{RbOH} \cdot \mathrm{Al(OH)_3} \cdot y\mathrm{SiO_2} \cdot z\mathrm{H_2O}$, where x/y was varied in the range 0.2–1.0, y in 2–35 and $z/y = 30$. The gels were prepared by dissolving $Al(OH)_3$ (C3005, 99.6%, Sumitomo Chemical Co., Ltd.) in 50 wt% solution of RbOH (Aldrich) by heating on a hot plate, then, amorphous silica powder produced by wet process (Nipsil, $SiO_2 = 88\%$, $H_2O = 12\%$, Nippon Silica Ind.) was added, and the mixture was stirred until a homogeneous gel slurry was obtained. The gel slurry was charged into an 80 cm^3 stainless steel autoclave and heated at 438 K for 180 h under an autogenous pressure while being rotated at 50 rpm. The obtained solid product was washed with distilled hot water and dried at 373 K. The sample was identified by XRD (MacScience MXP-3). The chemical composition of the sample was determined by elemental analysis of Rb, Al and Si using an inductively coupled plasma analyzer (Perkin-Elmer Optima-3000). Field emission scanning electron microscopy (FE-SEM, HITACHI S-4500) was used to characterize particle size and morphology of the obtained crystals. Solid state MAS NMR spectra were measured using a Bruker AMX-500 spectrometer. The ^{27}Al spectra were recorded at room temperature at 130.268 MHz, with a spinning rate of 11 kHz, by single pulse technique. Also, the ^{29}Si spectra were recorded at 99.417 MHz, with a spinning rate of 7 kHz. Water sorption capacity on the sample was determined by thermogravimetric analysis (MacScience TG-DTA 2000). Nitrogen adsorption isotherms at 77 K were measured using an automatic volumetric apparatus (BEL Japan, BELSORP 28SA). Gas adsorption isotherms at 298 K were measured using the same equipment. High-resolution XRD data for structure analysis were collected on a MacScience MXP-3TA HRII powder diffractometer using monochromatic Cu $K\alpha_1$ radiation ($\lambda = 1.540598$ Å) at RT. Measurement conditions were as follows: a Bragg–Brentano geometry using a flat specimen was rotated at 20 rpm, the 2θ collection range and step size were $7.5° < 2\theta < 100°$ and 0.015°, respectively. *Ab-initio* structure determination, Rietveld refinement, MPF (MEM-based pattern fitting)[16] analysis and visualization were carried out using EXPO,[17] RIETAN-2000[18] and VENUS packages[19] including a program PRIMA for electron density analysis using the maximum entropy method (MEM),[20] respectively.[21]

RMA-3 was synthesized from gels having general molar compositions described above, where x/y was in the range 0.55–0.70, and y in 6–12. Typical composition of RMA-3 is $Rb_2O \cdot Al_2O_3 \cdot 7.2SiO_2 \cdot 4.2H_2O$, and the variation in the SiO_2/Al_2O_3 ratio is as low as 7.0–7.8, which is compatible with the values calculated from the integrated intensities of the ^{29}Si MAS NMR spectra by curve fitting. ^{27}Al MAS NMR spectra of RMA-3 show only one symmetrical peak attributed to the tetrahedral Al atom, and this shows that all the aluminium atoms are incorporated into the framework. On the other hand, in the low x/y region of the gel in the trial synthesis, pure Rb–mordenite (Rubidium Microporous Aluminosilicate-1) was obtained, and a higher y region of that, Rb–offretite (Rubidium Microporous Aluminosilicate-4) was crystallized. Detailed results of these zeolites will be reported in other papers.[24] Fig. 1 shows the SEM

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† Electronic supplementary information (ESI) available: Details of structure solution and refinement for RMA-3. See http://www.rsc.org/suppdata/cc/b5/b502254a/

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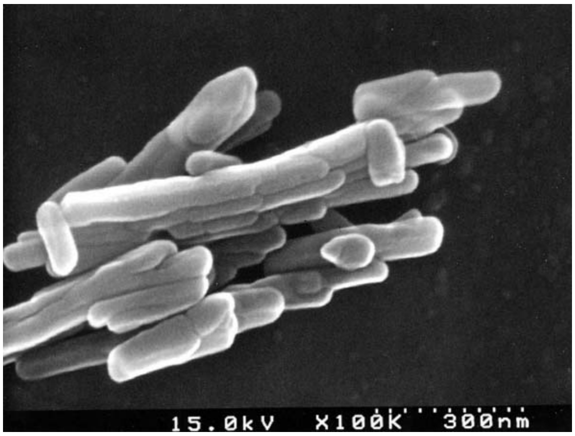

Fig. 1 SEM image of RMA-3 crystals.

image of an aggregation of rod-like RMA-3 micro-crystals (Also see ESI†).

Space group and lattice parameters for RMA-3 are orthorhombic system *Pmma* (No. 51), and $a = 0.99653$ (4) nm, $b = 0.75717(3)$ nm, $c = 0.93031(4)$ nm and $V = 0.70196(5)$ nm^3, respectively. The observed number of reflections was 443. Framework topology and the positions of the main rubidium ions were revealed by a direct method. The crystal structure model of RMA-3, illustrated in Fig. 2, has a novel topology. Two sub-building units (SBU) with 4-MR, 6-MR and 8-MR, *i.e.* $4^2 6^2 8^2$ and $4^6 8^4$ constitute the framework, as shown in Fig. 3. The inner space of the two-dimensional channels is filled with rubidium ions.‡

From the MPF analysis, the electron density distribution image, as shown in Fig. 4 suggested that small amount of water molecules is distributed near rubidium ions. The total number of adsorbed water molecules is estimated to be *ca.* 5.3 molecules per unit-cell. The existence of adsorbed water molecules is supported by a weight loss of *ca.* 8 wt% up to 423 K from the TG-DTA curve. Furthermore, covalent bonds between Si(Al) and O atoms were clearly observed. For this structure analysis, Si/Al value was determined to be *ca.* 3.6 by ICP-AES analysis. Then, the contribution of the Si/Al value was included in this refinement as a virtual chemical species. Two Rb^+ ion sites are distributed on the central point of SBU1 and on the center of 8-MR plane of SBU2 with $g(Rb1) = 0.92$ and $g(Rb2) = 0.42$, respectively, as illustrated in Fig. 3. These facts suggest that Rb1 functions as both an SDA and a cation, although Rb2 probably functions only as a cation. Finally, the chemical formula and molecular weight, M, for RMA-3 calculated from refined occupancies and multiplicities were found to be $Rb_{2.7}Al_{2.6}Si_{9.4}O_{24}\cdot 5.3H_2O$ and 1039.04, respectively. Observed, calculated and difference patterns for the XRD data of RMA-3 were plotted against 2θ as shown in Fig. 5. Obtained R-factors were sufficiently low, *e.g.* $R_{wp} = 7.81\%$, $R_I = 2.72\%$, $R_F = 2.56\%$ and $R_{exp} = 1.65\%$.

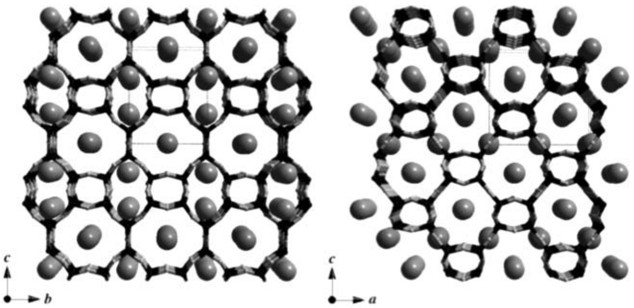

Fig. 2 Structural model for RMA-3 with novel topology. Left: [100], right: [010] direction, respectively. Water molecules are ignored for convenience.

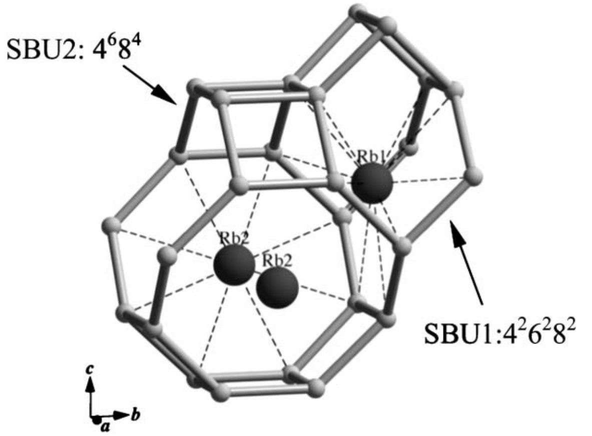

Fig. 3 Fragment of framework structure of RMA-3 including two SBU's and two Rb sites are illustrated. Interatomic distance l(Rb–O) has a range from 0.319 to 0.379 nm.

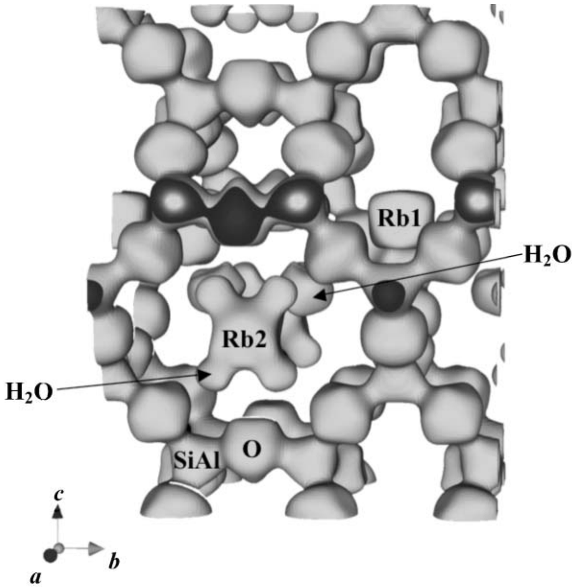

Fig. 4 Electron density distribution in RMA-3 illustrated along [100] direction. Equi surface density level is set to 0.8 e Å^{-3}.

The pore openings of RMA-3 are two 8-MRs with dimensions of 0.49 × 0.37 nm along [100] and 0.34 × 0.38 nm along [010]. Adsorption isotherms of O_2, N_2, CH_4 and CO_2 at 298 K are shown in Fig. 6. Adsorption capacities of these gases at 101.3 kPa are smaller than those of NaA, because of the small void volume for the large framework density of 17.1 of RMA-3 and the existence of large rubidium ions in the channels. N_2 gas adsorption isotherm of RMA-3 at 77 K shows a small BET surface area of 43 m^2 g^{-1} and micropore volume of 0.02 cm^3 g^{-1}. These results indicate that rubidium ions block the pores for adsorption and

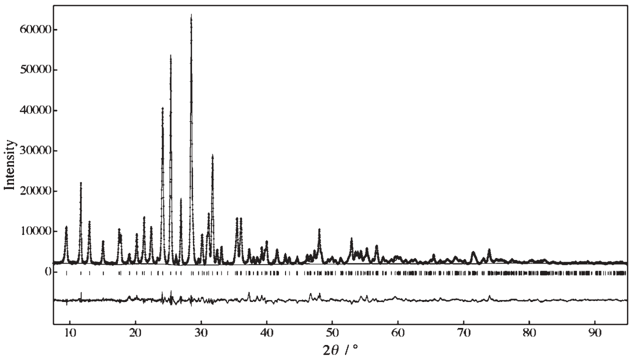

Fig. 5 Observed, calculated, and difference patterns for Rietveld refinement of RMA-3.

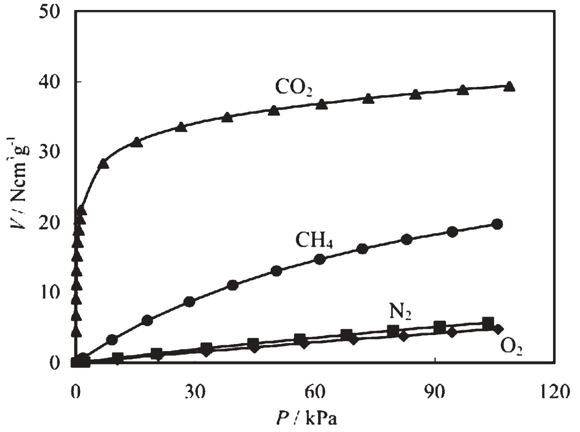

Fig. 6 Adsorption isotherms of CO_2, CH_4, N_2, and O_2 on RMA-3 at 298 K.

diffusion of N_2 molecules at that temperature. On the other hand, RMA-3 shows very high thermal stability up to 1273 K.

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‡ CCDC 264995. See http://www.rsc.org/suppdata/cc/b5/b502254a/ for crystallographic data in CIF or other electronic format.

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21 At first, the integrated intensities of the as-synthesized compound were extracted by using the Le Bail method[22] with the Rietveld program RIETAN-2000, and then, extracted integrated intensities were refined and repartitioned by the maximum-entropy patterson program ALBA[23] again. The split pseudo-Voigt function of Toraya was used as a profile function. Partial profile relaxation with a modified split pseudo-Voigt function was applied to parts of (nearly) isolated reflections with anisotropic broadening and/or highly asymmetric profiles in the low 2θ region, which dramatically improved fits between their observed and calculated profiles. An 11th-order Legendre polynomial was fit to the background. Observed integral intensities were introduced in the direct method program SIRPOW build in EXPO.[17] Although relabeling of some atoms were necessary, a structural model, in which cage type framework were formed by $(SiAl)O_4$ tetrahedra, was readily found. On the other hand, location of Rb ions and adsorbed water molecules were estimated by an electron density distribution analysis by the MEM/Rietveld analysis. In this work, MEM analyses were carried out using a program PRIMA. The spatial resolution was 128 × 96 × 128 pixels per unit cell. MEM is, *per se*, model-free, and can provide values of isolated reflections consistent with a good starting model. After the first MEM analysis, electron density distribution is redetermined by MPF method,[16] which is the structure refinement utilizing the combination of whole-pattern fitting (RIETAN-2000) and MEM analysis. MEM analyses and whole-pattern fitting are alternately repeated (REMEDY cycles) until *R* factors in the latter no longer decrease. Structural models were revised by full examination of density maps, if necessary. Modifications of structural models were repeated until a revised structural model agreed well with density maps resulting from the above iterative procedure.
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