Convenient conversion of crystalline layered silicate octosilicate into RWR-type zeolite by acetic acid intercalation

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The intercalation of acetic acid into the crystalline layered silicate octosilicate was found to take place efficiently and give a new type of layered structure. The highly crystalline RWR-type zeolite was successfully prepared by the dehydration–condensation of silanol groups on both sides of the interlayer of the acetic acid-intercalated octosilicate (Ac-octosilicate). The crystallinity of the RWR-type zeolite was strongly dependent on the amount of acetic acid molecules in the interlayer.

1. Introduction

High silica zeolites with small pores have been attractive materials for catalysis, adsorption and separation. Although many researchers have devoted considerable efforts to designing and synthesizing new high silica zeolites, the basic strategy for the control of zeolite topology by direct hydrothermal synthesis has not necessarily been well established. Recently, crystalline layered silicates of zeolitic topology have attracted much attention as precursors for the construction of novel zeolites by the topotactic dehydration–condensation of periodic and reactive silanol groups on both sides of the interlayer and high surface area materials by pillaring or delamination.[1–12] We have also investigated a new strategy for zeolite synthesis from crystalline layered silicates, and recently succeeded in preparing a thermostable zeolite with the novel framework structure CDS-1 (framework type code: CDO).[1] The CDS-1 zeolite was found to be formed from a novel layered silicate PLS-1 by the topotactic dehydration–condensation between silicate layers, consisting of face-sharing pentagon cylinders. The layered silicate octosilicate, also known as ilerite[13] or Na-RUB-18,[14] $Na_8Si_{32}O_{64}(OH)_8 \cdot 32(H_2O)$, is a highly crystalline hydrous sodium silicate, and its intercalation behavior has been considerably studied. More recently, Marler *et al.* reported the formation of a microporous material by a similar method, namely, the conversion of octosilicate intercalated with triethylenetetramine into RUB-24 (RWR-type zeolite).[5] These findings strongly suggest the high potential of converting crystalline layered silicates intercalated with organic molecules into zeolites. However, the detailed characteristics of the intercalated crystalline layered silicate, and the role of intercalated molecules during the zeolitization process, remain unclear. Therefore, in this paper, we have investigated the intercalation of acetic acid into crystalline layered silicate octosilicate (abbreviated as Ac-octosilicate) and then its zeolitization into a RWR-type zeolite by the dehydration–condensation method. The chemical state of acetic acid in the interlayer of Ac-octosilicate is also investigated by a Monte Carlo simulation.

2. Results and discussion

Firstly, the layered silicate octosilicate was synthesized and characterized. As shown in Fig. 1(A)-(a), the XRD diagram of the prepared Na-octosilicate showed no peaks other than those corresponding to the crystalline layered silicate octosilicate reported in the literature.[14] The basal spacing, calculated from the peak corresponding to (004) plane, was 1.11 nm. No impurities or amorphous materials were observed in the SEM image (Fig. 2(a)). Resonance lines at *ca.* −100 and −111 ppm, which were assigned to $HOSi(OSi)_3$ (Q^3) and $Si(OSi)_4$ (Q^4), respectively, were observed in the ^{29}Si MAS-NMR spectrum of Na-octosilicate (Fig. 3(a)). The Q^3/Q^4 peak area ratio was 1.08, almost consistent with the value expected from the octosilicate framework structure.[14,15] These results strongly indicate that the highly crystalline octosilicate was prepared. Therefore, we tried to convert the Na-octosilicate into zeolite by the dehydration–condensation of silanol groups on both sides of the interlayer. However, as can be seen in Fig. 1(B)-(a), only a broad peak corresponding to amorphous materials was observed in the XRD diagram of the Na-octosilicate calcined under vacuum. As the layer structure of Na-octosilicate is maintained by the existence of Na^+ cations and interlayer water molecules, it may be considered that most of the interlayer water molecules are desorbed before dehydration–condensation between the silicate layers, resulting in disordering of the layer structure. Moreover, as the silicate layer needs to have not only silanol groups (Si–OH) but also silanolate groups (SiO^-) for charge balance, NaOH would be formed during calcination at 873 K according to the equation: $SiOH + SiO^- Na^+ \rightarrow SiOSi + NaOH$ The formation of NaOH leads to structural degradation of the octosilicate. The desorption of interlayer water molecules up to 473 K was

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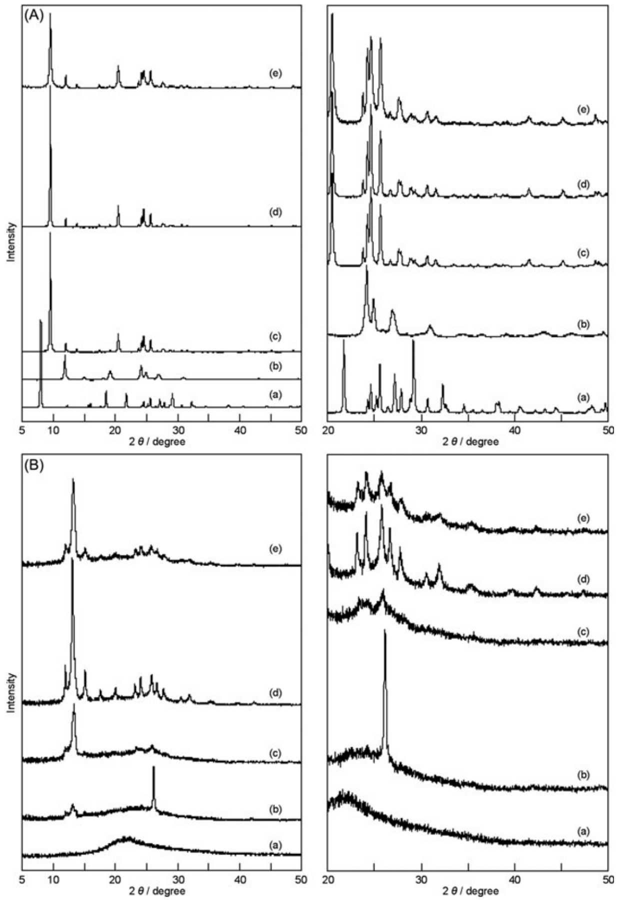

Fig. 1 XRD diagrams of various octosilicates (A) before and (B) after calcination at 873 K for 10 h under vacuum. (a) Na-octosilicate and (b)–(e) Ac-octosilicates prepared using acetic acid aqueous solutions of various concentration; (b) 0.1 M, (c) 1.0 M, (d) 10 M, (e) 17 M.

confirmed by TG-DTA analysis. This fact strongly suggests the necessity for intercalating guest molecules in the interlayer space, which can maintain the layer structure of the octosilicate, until bridging formation by the condensation of silanol groups takes place between the silicate layers. Although several kinds of amine molecule were used for intercalation under acidic conditions,[5] their role remains unclear. Therefore, the possibility of replacing the interlayer water molecules by organic molecules such as ethanol, formic acid, acetic acid and benzoic acid was investigated in detail. It was found that acetic acid molecules are very suitable as intercalation molecules because of their molecular size and acidic nature. The resultant silicate layers possess a hydrophobic character in the interlayer due to intercalated methyl groups, resulting in further intercalation of acetic acid molecules into the interlayer space.

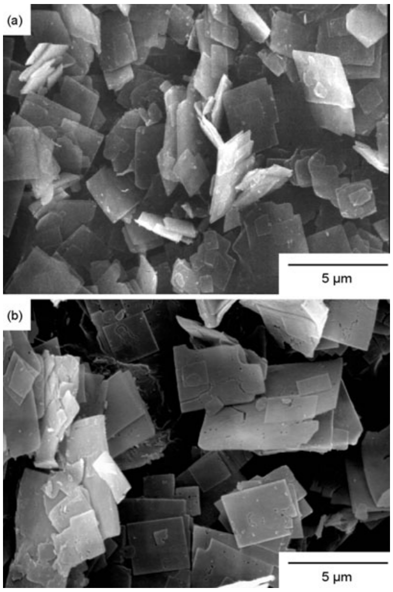

Fig. 2 SEM images of (a) Na-octosilicate and (b) Ac-octosilicate (10 M).

Fig. 1(A)-(b)–(e) shows the XRD diagrams of Ac-octosilicates obtained by treating Na-octosilicate with acetic acid solutions of different concentration. Except for the product obtained with 0.1 M acetic acid aqueous solution, a novel XRD diagram was observed, indicating the intercalation of acetic acid molecules. The XRD diagram of octosilicate prepared with the diluted acetic acid was almost the same as that of H-octosilicate.[16] No morphology change due to acetic acid treatment was observed (Fig. 2(b)). The most probable lattice parameters of the Ac-octosilicate were estimated to be a = 7.4888(5) Å and c = 37.187(4) Å (tetragonal system, FOM(13) = 93.4) by indexing using the program DICVOL04.[17] An acceptable space group, $I4_1/amd$, was derived from the reflection conditions. The lattice constant obtained for the c-axis is an intermediate value between the 44.32 Å of Na-octosilicate (space group $I4_1/amd$)[14] and the 27.06 Å of RWR zeolite (space group $I4_1/amd$).[5] Therefore, we guess that the layer stacking sequence of Ac-octosilicate might be similar to that of Na-octosilicate. From the preliminary Rietveld analysis, the skeleton structure of Ac-octosilicate was found to be in fair agreement with the expected model, but having a shorter interlayer distance.[17] The strong peak, corresponding to the (004) plane of Na-octosilicate, shifted to a high angle (2θ = 9.5°) by the intercalation of acetic acid molecules, indicating a *ca.* 1.8 Å shrinking of each interlayer distance in comparison to Na-octosilicate. From this consideration, the shortest O–O distance between the silanol groups on both sides of the

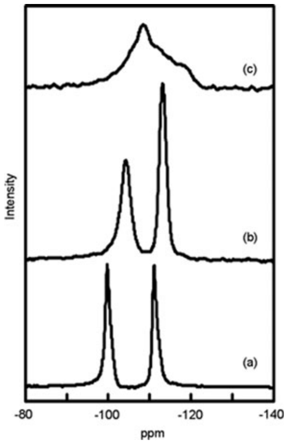

Fig. 3 ^{29}Si MAS-NMR spectra of (a) Na-octosilicate and Ac-octosilicates (10 M), (b) before and (c) after calcination.

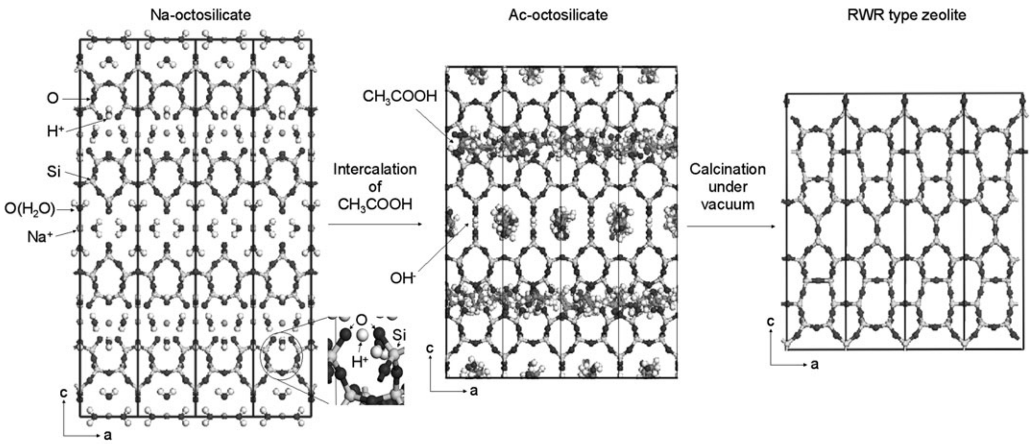

Fig. 4 Predicted crystal structure model of Ac-octosilicate obtained by a Grand Canonical Monte Carlo simulation.

interlayer was calculated to be *ca*. 2.5 Å; the interlayer space would probably be retained by the formation of hydrogen bonding between the silanol groups,[18,19] resulting in the generation of a pseudo micropore structure. Although a shift in the resonance lines corresponding to Q^3 and Q^4 was observed in the ^{29}Si MAS-NMR spectrum of Ac-octosilicate (Fig. 3(b)), the Q^3/Q^4 peak area ratio of 1.10, calculated from the NMR spectrum, was the same as that of Na-octosilicate. These results indicate the effective intercalation of acetic acid molecules without disordering the layered structure of the octosilicate. The intercalated acetic acid molecules are expected to play an important role in the preparation of the RWR-type zeolite by the dehydration–condensation of silanol groups; (1) stabilization of the three-dimensional layered structure, constructing the pseudo micropore with a high crystalline order, (2) ion exchange of Na^+ cation in the octosilicate by H^+ cation from acetic acid, resulting in the protonation of terminal oxygens on the silica surface for bridge formation (Si–O–Si bond) between the silicate layers,[20,21] and (3) exclusion of interlayer water molecules that prevent silanol groups in the interlayer from undergoing a successful dehydration–condensation reaction. Therefore, based on these hypotheses, the expected chemical formula of the Ac-octosilicate without intercalated acetic acid molecules can be speculated to be $Si_{32}O_{56}(OH)_{16}$.[16]

To clarify the intercalation behavior of acetic acid in octosilicate, the influence of acetic acid concentration was investigated. In the case of diluted acetic acid, it was found that only ion exchange of Na^+ cation by H^+ cation proceeded, and the intercalation of acetic acid hardly occurred. The amount of acetic acid molecules intercalated into the interlayer increased with increasing acetic acid concentration, passed through a maximum value at 10 M acetic acid and then decreased again, which was confirmed by TG-DTA and ^{13}C CP/MAS-NMR measurements (not shown here). The numbers of acetic acid molecules per unit cell, calculated from the weight loss over the temperature range 473–673 K in TG curves, were 1.8, 2.5 and 2.3, respectively, when 1 and 10 M acetic acid aqueous solutions and pure acetic acid (17 M) were used.

The chemical state and distribution of acetic acid molecules present in the interlayer, *i.e.* the maximum number of intercalated molecules and their ordering, and the periodicity of silica layer ordering, were estimated by a Grand Canonical Monte Carlo (GCMC) simulation on the basis of the skeleton structure described above. Fig. 4 shows the simulated models of Ac-octosilicate. The number of acetic acid molecules obtained from the GCMC simulation was 4.4 per unit cell. It was found that the acetic acid molecules were parallel to the one-dimensional pseudo-micropore direction with a head-to-tail orientation, and the geometrical layer structure was maintained, even after the intercalation of acetic acid molecules, although the interlayer distance was shrunk. Hence, taking into account the position of the silanol groups on both sides of the interlayer, it is speculated that the dehydration–condensation reaction easily proceeds between the silicate layers.

Next, the possibility of zeolite formation by the condensation of silanol groups was investigated. Prepared Ac-octosilicates were thermally treated at 873 K under vacuum. Fig. 1(B)-(b)–(e) shows the XRD diagrams of Ac-octosilicates after calcination treatment. Except for the sample obtained by 0.1 M acetic acid treatment, each Ac-octosilicate gave a sharp XRD pattern. The peak assigned to the (004) plane of Na-octosilicate shifted to 13.1°. These XRD diagrams of the calcined products were consistent with that of RWR-type zeolite, indicating the successful conversion of Ac-octosilicate into RWR-type zeolite by the formation of bridging between silicate layers through the dehydration–condensation reaction of silanol groups. In the case of diluted acetic acid (0.1 M), the prepared material, probably H-octosilicate without acetic acid molecules, was transformed into a quartz. The crystallinity of the RWR-type zeolite obtained, which was evaluated from the sum of peak widths in the region $2\theta = 20–30^\circ$ and the peak-to-background ratio, was dependent on the number of acetic acid molecules intercalated in the interlayer. The crystallinity was better for the RWR-type zeolite prepared from Ac-octosilicate with an intermediate concentration of acetic acid. The BET surface area of the RWR-type zeolite prepared from Ac-octosilicate (10 M) was 72 $m^2\ g^{-1}$.

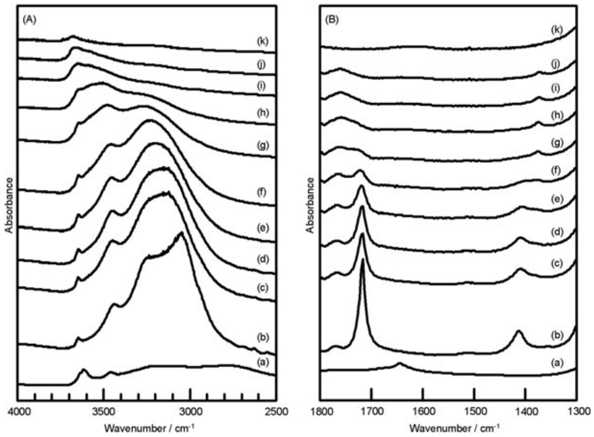

Fig. 5 FT-IR spectra of (a) Na-octosilicate and (b)–(j) Ac-octosilicates evacuated at various temperatures. (a) rt, (b) 343 K, (c) 403 K, (d) 433 K, (e) 473 K, (f) 503 K, (g) 543 K, (h) 573 K, (i) 623 K, (j) 673 K and (k) 873 K.

To confirm the formation of bridging between silicate layers by the dehydration–condensation of silanol groups on both sides of the interlayer, ^{29}Si MAS-NMR spectra were measured. Fig. 3(c) shows a typical ^{29}Si MAS-NMR spectrum of the RWR-type zeolite from Ac-octosilicate (10 M). The broad resonance peaks around −109 and −115 ppm were assigned to Q^4 signals. However, Q^3 signals around −100 ppm were hardly observed, indicating the successful formation of bridging between the silicate layers. As the NMR spectrum shows severely overlapped and very broad resonances, the presence of a small amount of Q^3 species cannot be ruled out. Moreover, to gain further information about the structural transformation process from Ac-octosilicate to RWR-type zeolite, FT-IR spectra were also measured at various temperatures under vacuum. In the FT-IR spectrum at 343 K, the peaks at 3046 and 3234 cm^{-1}, assigned to C–H and O–H stretching vibrations of acetic acid, were observed, whereas those at 3437 and 3645 cm^{-1} were assigned to hydroxyl groups of Na-octosilicate (Fig. 5(A)). With an increase in the evacuation temperature, these peaks from acetic acid molecules broadened and their intensities reduced. However, the peaks were still observed at 503 K. On the other hand, the intensities of the peaks assigned to carbonyl groups (1710 cm^{-1}) and the bending of methyl groups (1410 cm^{-1}) began to decrease above 403 K. These peaks were also still observed at 503 K. Taking into account the fact that a highly crystalline RWR-type zeolite was obtained at 873 K, it seems that the dehydration–condensation of silanol groups in the interlayer begins above 503 K, and as a result, new covalent Si–O–Si bonding forms between the silicate layers. This is confirmed from the fact that the peak intensity at 3437 cm^{-1}, assigned to hydroxyl groups of the octosilicate framework, decreases above 503 K. Only the small peak, assigned to outer surface hydroxyl groups of the octosilicate, was observed at 873 K.

3. Conclusions

The intercalation of acetic acid molecules into the interlayer of crystalline layered silicate octosilicate was achieved, and the highly crystalline Ac-octosilicate was successfully prepared. The conversion of Ac-octosilicate into RWR-type zeolite by the topotactic dehydration–condensation of silanol groups on both sides of the interlayer was strongly dependent upon the amount of intercalated acetic acid molecules. The crystallinity of the RWR-type zeolite obtained increased with increasing number of acetic acid molecules present in the interlayer. It was suggested that one of the important factors for the conversion of crystalline layered silicate into zeolite is how to maintain the layered structure until the formation of bridging begins between the silicate layers by condensation of silanol groups. From all the above results, it was concluded that the intercalation of acetic acid is effective in allowing the formation of RWR-type zeolite by dehydration–condensation.

4. Experimental

Na-octosilicate was synthesized as follows. The starting mixture was prepared from 200 g of colloidal silica (Aldrich, 40%), 26.9 g of NaOH (Merck, 99%) and 59.69 g of distilled water, and then stirred for 30 min until a uniform gel was obtained. The resulting gel was charged into a stainless autoclave equipped with a Teflon liner and kept at 378 K for 23 d. The product was separated from the solution by filtration, washed with distilled water and dried overnight in an oven at 343 K. Next, 0.1 g of the Na-octosilicate was treated with 100 ml of 0.1–10 M acetic acid (AcOH) aqueous solutions or pure AcOH (17 M) at 303 K for 3 d under stirred conditions. The product was filtered off, washed thoroughly with methanol and dried at 343 K for 12 h (Ac-octosilicate). Conversion of the prepared Ac-octosilicate to a RWR-type zeolite was carried out under vacuum at 873 K.

The prepared samples were identified by powder X-ray diffraction (Bruker D8 Advance). The crystal morphology was measured by scanning electron microscopy (SEM, Hitachi S-4000). Textural properties were determined by nitrogen adsorption (Bel Japan Belsorp Mini). Before the adsorption measurements made at 77 K, the powdered zeolites (*ca.* 0.1 g) were heated at 673 K for 10 h in a nitrogen flow. The ^{29}Si MAS-NMR spectra of the samples were recorded using a zirconia rotor with an inner diameter of 7 mm on a Varian VXP-400 at 79.5 MHz. IR spectra were recorded on a FT-IR spectrometer (JEOL JIR-7000) with a resolution 4 cm^{-1} at room temperature. The sample was pressed into a self-supporting thin wafer (*ca.* 6.4 mg cm^{-2}) and placed in a quartz IR cell with CaF_2 windows. Prior to the measurements, each sample was dehydrated under vacuum at 298 K for 2 h.

The modelling of Ac-octosilicate was conducted using a Monte Carlo (MC) method. The MC calculations were performed using the sorption module in Cerius2, developed by Accelrys Inc., USA. The MC method employs the Grand Canonical ensemble and the Burchart-Universal potentials parameter set[22–24] for calculating the interaction between acetic acid molecules and octosilicate. All MC calculations were performed for 10 000 000 cycle steps at 298 K. The accepted total displacement number was set as 0.5. The atomic coordinates of Na-octosilicate were used for constructing the initial framework structure of Ac-octosilcate as an adsorbate for the MC calculations. The silicate layers of Na-octosilicate were kept fixed and translated to account for shrinkage of the basal spacing in Ac-octosilicate. To reduce the influence of the cut-off length on calculations of the interaction between absorbents and absorbate, and between absorbents, twenty-five unit cells with cell lengths $a = b = 37.3579$ Å and $c = 37.2840$ Å were used. Space group $P1$ was applied to the final constructed Ac-octosilicate structure in all MC calculations. Density Functional Theory (DFT) methods were applied for determination of the hydrogen positions in the hydroxyl groups. DFT quantum chemical calculations were performed using the DMol^3 package in Materials Studio (version 3.2), developed by Accelrys, Inc., on an Appro HyperBlade Cluster integrated by Best Systems, Inc.[25,26] The geometry optimization was carried out using a double numerical polarization basis set with polarization functions (DNP), whose accuracy is comparable to Gaussian 6-31G^{++} with a Perdew Burke Ernzerhof (PBE)-type non-local gradient correction functional for exchange and correlation terms.[27,28]

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