Dealumination of small-pore zeolites through pore-opening migration process with the aid of pore-filler stabilization

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Small-pore zeolites are gaining increasing attention owing to their superior catalytic performance. Despite being critical for the catalytic activity and lifetime, postsynthetic tuning of bulk Si/Al ratios of small-pore zeolites has not been achieved with well-preserved crystallinity because of the limited mass transfer of aluminum species through narrow micropores. Here, we demonstrate a postsynthetic approach to tune the composition of small-pore zeolites using a previously unexplored strategy named pore-opening migration process (POMP). Acid treatment assisted by stabilization of the zeolite framework by organic cations in pores is proven to be successful for the removal of Al species from zeolite via POMP. Furthermore, the dealuminated AFX zeolite is treated via defect healing, which yields superior hydrothermal stability against severe steam conditions. Our findings could facilitate industrial applications of small-pore zeolites via aluminum content control and defect healing and could elucidate the structural reconstruction and arrangement processes for inorganic microporous materials.

INTRODUCTION
Tuning the compositions of chemical species in functional materials is crucial for obtaining the desired properties; in particular, postsynthetic tuning of chemical compositions is in high demand. Zeolites, which are crystalline microporous materials composed of TOx (T = Si, Al, and so on) tetrahedra, represent one of the most challenging research topics. Several factors, such as the atomic composition and concentration of defects, determine their application in various fields, including adsorption, catalysis, and ion exchange. Small-pore zeolites are characterized by their 8-rings (8R) as the largest pores (Fig. 1A) (1, 2). Among the 255 different zeolite structures, 51 are categorized as small-pore zeolites (3). Figure 1B illustrates representative small-pore zeolite structures with three-letter codes given by the Structure Commission of the International Zeolite Association: CHA, AEI, AFX, ERI, and RHO. These zeolites have attracted increased attention owing to their remarkable catalytic behavior; for example, CHA, AEI, and AFX zeolites are promising catalysts for the selective catalytic reduction of NOx with NH3 (NH3-SCR) (4, 5); they exhibit ~20% higher NO conversion compared with the medium-pore ZSM-5 and large-pore zeolite beta catalysts (6–8). CHA and ERI zeolites are potential catalysts for methanol-to-olefin conversions (9, 10).

Optimizing the Si/Al ratio is important for efficient industrial applications because the amount of framework Al (FAI) species determines the properties, including hydrophobicity and acidity, and thus affects the catalytic behavior and hydrothermal endurance (11–14). The Bronsted acid sites formed around the aluminum atoms in H+-form zeolites are known to be the source of a zeolite’s catalytic activity; however, excessive numbers of these sites cause unfavorable side reactions, such as the formation of pore-blocking aromatic compounds during methanol-to-olefins conversion, leading to catalytic deactivation (12). Moreover, zeolites with low Si/Al ratios tend to degrade easily by elimination of FAI species (15). At the same time, too high Si/Al ratios may not always be favorable, depending on the application, such as NH3-SCR. Although a higher Si/Al ratio generally enhances the hydrothermal stability, it also leads to fewer ion exchange sites, especially paired Al atoms that are ion exchange sites for divalent cations such as Cu or Fe, the active sites in SCR. In a previous study in which SCR performances of CHA zeolites with different Si/Al ratios were compared, high NOx conversion was only achieved when the Si/Al ratio was 9 or below, while a marked decrease in conversion rate was observed when the Si/Al ratio was 12.5 (16). Hence, commonly used methods involve tuning the Si/Al ratios to the optimum values. However, direct synthesis of small-pore zeolites with high Si/Al ratios requires special starting materials, such as hydrofluoric acid (17–19) or zeolites (20–23) starting materials for interzeolite conversion (24). Although organic structure-directing agents (OSDAs) are necessary for synthesis of many of small-pore zeolites, synthesis of zeolites with high Si/Al ratios requires more complex OSDAs, such as imidazolium-based or bicyclic OSDAs, which lead to a marked increase in cost (20–22, 25). For instance, most reported synthetic protocols for AFX zeolite afford products with Si/Al ratios less than 5, except for...
some cases wherein bulky organic molecules are used as OSDA and the Si/Al ratio of the product is 8.4 (20). The use of complex OSDAs, which requires a multiple-step synthesis procedure, increases the synthesis cost of zeolites and hinders the industrial scale production.

We performed postsynthetic dealumination of small-pore zeolites (Fig. 1C) (26). Dealumination is extensively used in the mass production of commercial high-silica zeolites because highly siliceous zeolite can be obtained by dealumination of zeolites with low Si/Al ratios, which can be synthesized without using expensive OSDAs or hydrofluoric acid (27). Moreover, dealumination can be achieved via economical and sustainable processes, such as steaming and acid treatment, neither of which require expensive pressure-resistant reaction vessels nor produce highly toxic wastewater (28, 29). The use of atmospheric pressure during the process enables easy scaling-up of the production process. Several studies have reported on the dealumination of the most commonly used large-pore zeolites (i.e., with 12-rings as the largest pores), including FAU, MOR, and *BEA zeolites (30–33).

Post-synthetic tuning of the bulk Si/Al ratio consists of two steps: dealumination, in which FAI species are eliminated from the structure to form extra-framework Al (EFAI) species, and extraction, in which EFAI species are transported to the liquid phase through micropores (34). Most studies have evaluated the dealumination step because the extraction step was sufficiently fast for their research targets, viz zeolites with pores larger than 10-rings (10R). However, for small-pore zeolites, extraction of EFAI species [kinetic diameter, 5.0 Å (35)] is difficult owing to the limited mass transfer due to the narrow 8R micropores (3 to 4 Å); therefore, postsynthetic tuning of bulk Si/Al ratios has never been accomplished with preserved zeolite crystallinity. Steam dealumination of these small-pore zeolites has been reported previously (36, 37), which eliminated FAI species from CHA, RHO, and KFI zeolites while preserving crystallinity via steaming treatments at 500° to 600°C. However, EFAI species that may block the zeolite pores and suppress catalytic performance remained in the zeolite structure (~85% of total Al atoms in CHA zeolite case). Removal of such EFAI species in CHA zeolite by acid washing reduced the relative crystallinity. Steaming at higher temperatures (>700°C) degraded the crystal structures. Consequently, novel methodologies for extracting the remaining EFAI without collapsing the framework are crucial for the successful dealumination and tuning of Si/Al ratios of small-pore zeolites.

Recently, we reported a liquid-mediated, postsynthetic defect-healing method (38) wherein tetraethylammonium (TEA) cations were used as pore filler to stabilize the zeolite structures, while fluoride compounds were added to enable the reconstruction of aluminosilicate structures. Consequently, we tried to stabilize the zeolite structure using organic pore fillers under dealumination conditions, wherein framework reconstruction occurs. In zeolite synthesis, organic additives are used to obtain the desired products. Apart from performing structure-directing roles during crystallization, these organics function as pore-filling agents (39–41) and occupy the pores in the zeolite structure, which stabilizes the frameworks (42). With the exception of a few studies on large-pore zeolites (43), these organic compounds are removed by calcination before further postsynthetic treatment or use in catalysis and adsorption, and the stabilization role of the organic cations in the as-synthesized zeolite has been overlooked. In this study, we report the compositional tuning of small-pore zeolites by leaching in
acidic solution based on the framework stabilization using pore-filling organic compounds. Furthermore, we performed defect-healing treatment to achieve enhanced hydrothermal stability because defects formed during the dealumination may cause structural degradation and catalytic deactivation (44, 45). This strategy was inspired by the two effects of the steaming process: removal of aluminum atoms from the framework and defect healing through silicate migration (Fig. 1C) (46). The former step is realized via treatment in acid solution with pore fillers, and the latter is achieved through liquid-mediated treatment in the presence of ammonium fluoride and TEA hydroxide (TEAOH). The enhanced hydrothermal stability of the obtained zeolite is demonstrated using an NH₃-SCR test after exposure to high-temperature steam (800°C).

RESULTS

Acid treatment of small-pore zeolites

The as-synthesized zeolites contained organic cations and inorganic cations in their pores. Organic cations are usually eliminated by calcination before dealumination (30) because they occupy zeolite pores, which may hinder the extraction of EFAl species. The dealumination of AFX zeolite [scanning electron microscopy (SEM) image shown in fig. S1A; particle size, 5 to 15 μm] was performed after calcination at 550°C. The Si/Al ratio increased from 3.6 to 12 upon treatment in acidic solution, which indicates the removal of more than 50% of aluminum species. However, the relative crystallinity, calculated from the peak area of the x-ray diffraction (XRD) patterns of the samples before and after acid leaching (fig. S2; see Materials and Methods for the definition of relative crystallinity) decreased drastically to 8%, indicating the deterioration of the crystalline structure.

Stabilization of the zeolite framework is essential to maintain its structure during acid treatment and to achieve dealumination with preserved crystallinity. The organic compounds act as pore fillers, which enhances the thermodynamic stability of the framework (39, 40). This inspired us to exploit the stabilization effect of organic compounds during the acid treatment. The as-synthesized AFX zeolite containing organic molecules [N,N′-bis-triethylpentanediyldiammonium dibromide (Et₆-diquat-5); see fig. S3A] was treated in 0.5 M sulfuric acid solution. The bulk Si/Al ratio of the AFX zeolite (Fig. 2A) increased from 3.6 to 9.1 upon acid treatment for 2 hours, confirming the dealumination of the AFX zeolite. The extraction of aluminum species from the solids was confirmed using 27Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy (Fig. 2C). In the NMR spectra of the sample before acid treatment, tetrahedral aluminum species [56.5 to 58.5 parts per million (ppm)] are observed, while octahedral (EFAl) species (approximately −1.5 ppm) are barely observed. During the first 10 min of acid treatment, a gradual shift of the FAI peak, possibly due to uneven dealumination from two different T sites in the AFX structure, is observed in the presence of a peak from EFAl. The intensity of the EFAl peak gradually decreased during further acid treatment, suggesting that the extraction of EFAl species occurred owing to the treatment. The micropore volume calculated from the nitrogen adsorption-desorption isotherm (fig. S4) using the t-plot method showed no notable change (from 0.21 to 0.22 cm³ g⁻¹) upon acid treatment for 2 hours. At the same time, the relative crystallinity calculated from the XRD patterns (fig. S5) decreased to 96% (Fig. 2B). Considering the nearly

![Fig. 2. Changes in Si/Al ratio, crystallinity, and Al configurations.](image-url)

(A) Si/Al ratio and (B) relative crystallinity calculated from XRD patterns of AFX (red), AEI (light blue), CHA (pink), ERI (light green), and RHO (purple) zeolite after acid leaching for 0 to 120 min. 27Al MAS NMR spectra of acid-leached (C) AFX, (D) CHA, (E) ERI, and (F) RHO zeolites. AlIV and AlVI denote the peaks of tetrahedral and octahedral Al species, respectively. AS, as-synthesized.
constant micropore volume during the acid treatment, the decrease in XRD peak intensity was attributed to the formation of structural defects and changes in composition, rather than to the collapse of the crystal structure \((47)\). Removal of Al atoms from both inner and outer parts of the particles was confirmed using cross-sectional transmission electron microscopy energy dispersive x-ray spectroscopy (TEM-EDS) and SEM-EDS images (figs. S6 and S7). To investigate the effect of particle size on the dealumination rate, AFX zeolite with smaller particle size (100 to 200 nm) was also synthesized according to a previously reported procedure \((22)\) and then dealuminated. The Si/Al ratio in this case increased from 4.6 to 9.3, similar to the results shown in Fig. 2A. The changes in the pore volume and the crystal structure caused by dealumination are discussed further in the following section.

Subsequently, a similar dealumination strategy was applied to other small-pore zeolites: AEI-, CHA-, ERI-, and RHO-type structures [SEM images shown in fig. S1 (B to D)]. For the AEI and ERI zeolites, the Si/Al ratios increased from 4.7 to 8.5 and from 6.0 to 7.8 by acid treatment for 2 hours, respectively (Fig. 2A). The RHO zeolite was dealuminated from Si/Al = 4.1 to Si/Al = 12. Conversely, the change in the aluminum content of the CHA zeolite was limited (Si/Al = 4.2 to 5.2). The crystallinity was preserved in ERI, CHA, and AEI zeolites, with relative crystallinities of 120, 113, and 89%, respectively (Fig. 2B and XRD patterns shown in figs. S8 to S11). The apparent increase in the peak intensities in the XRD patterns could be related to the removal of a thin layer of the remaining amorphous solid precipitated on the surface of the crystals or the presence or absence of inorganic cations, which filled the zeolite pores. However, the RHO zeolite starts degrading after 10 min of the acid treatment, and the crystallinity decreased to 48% after 2 hours of acid treatment. This could be attributed to the stabilization of OSDA, which is insufficient for the RHO zeolite structure to maintain its crystallinity during the composition change. In the \(^{27}\text{Al}\) MAS NMR spectrum of the CHA zeolite (Fig. 2D), the peak at ~56 ppm corresponds to the tetrahedral Al species in the zeolite framework. The peak at ~0 ppm, corresponding to EFAI, was observed during the first 10 min of acid treatment. Although some of the Al atoms are rapidly removed from the framework, a decrease in the peak intensity of the octahedral Al species was not observed during the acid treatment of CHA zeolite, suggesting that the EFAI species remained in the pores. In the ERI zeolite (Fig. 2E), the peak areas of the EFAI species were small, indicating removal of a limited number of Al species from the structure. Figure 2 also illustrates the relationship between aluminum extraction and crystal degradation in the RHO zeolite. EFAI species rapidly increased after brief contact with the acidic solution (~0 min in Fig. 2F) but began to decrease after 10 min. Conversely, the relative crystallinity remained at ~100% during the initial acid treatment and began to decrease after 10 min. This indicates that degradation of the crystal structure in the RHO zeolite was caused by the transport of the EFAI species through the zeolite pores.

To elucidate the mechanism of dealumination, the charge balance between the negatively charged zeolite framework and the extra-framework cations (Fig. 3A) was calculated. Zeolite frameworks are negatively charged when Si(IV) atoms are substituted by Al(III) atoms. These negative charges are balanced by the positive charges of the organic and inorganic cations in the pores when the structure contains no defects. The number of aluminum atoms and inorganic cations was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic adsorption spectroscopy (AAS), and the number of organic cations was calculated from the thermogravimetry results (fig. S12). The charge balance diagram for the AFX zeolite is shown in Fig. 3B. The number of OSDA molecules here has been doubled because the OSDA in these cases is a divalent cation (fig. S3A). In the as-synthesized AFX zeolite, the total positive charge of sodium and OSDA cations was balanced by the negative charge of the FAI species. At 0 min of acid treatment, which stands for simple mixing and subsequent separation of the acid solution and zeolite without any stirring or heating, 53% of sodium cations had already been removed from the zeolite pores. By extending the treatment period to 30 min, 83% of sodium cations were extracted to the liquid phase; subsequently, the sodium cation content did not change substantially. The content of OSDAs in the zeolite did not change notably during the acid treatment, suggesting the presence of OSDA cations in the pores, which stabilizes the framework throughout the treatment. This is reasonable considering the large size of the OSDA molecules \(\text{[e.g., the diameter of } \text{TeA}^- \text{cations is } 0.74 \text{ nm \ (48)}\]), the structure of OSDA molecules being unaffected during acid treatment was confirmed by \(^{13}\text{C}\) cross-polarization (CP) MAS NMR spectroscopy (fig. S13). In addition, FAI species were removed from the structure to form EFAI species (Fig. 2C). According to the charge balance diagram in Fig. 3B, after 5 min, the content of cations was equivalent to only 69% of the total number of aluminum atoms, which also confirms that the EFAI species in the form of almost neutral \(\text{[e.g., } \text{Al(OH)}_3^- \text{]} \text{ or cationic (e.g., } [\text{Al(OH)}_2]^+ \text{]} \text{] aluminum species are balanced by the remaining FAI species and defect sites (Si–O–)}\). Removal of these EFAI species was rather gradual, i.e., it took 10 min of the acid treatment for 40% of aluminum atoms to be extracted in the liquid phase. Subsequently, the extraction of Al species proceeded continually, and the final Si/Al ratio was 9.1 after 2 hours of the acid treatment, corresponding to the removal of 54% of Al species. Figure 3 (C to E) presents the charge balance diagram during the acid treatment of CHA, ERI, and RHO zeolites, respectively. In their as-synthesized form, the number of aluminum atoms (negative charge, if included in the framework) and organic and inorganic cations (positive charge) were well balanced. Similar trends (as for the AFX zeolite) were observed in the ERI and RHO zeolites: rapid extraction of inorganic cations within a few minutes, followed by removal of Al species, which took ~60 min. In the acid treatment of the CHA zeolite, a rapid decrease of sodium cations was observed, and 83% of sodium cations were removed by mixing zeolite and acid solution followed by immediate separation (0 min in the charge balance diagram). Removal of potassium cations required longer times, but 95% of them were extracted after 10 min of the acid treatment. Owing to the fast extraction of inorganic cations, a peak of octahedral aluminum species with considerable intensity appeared at 0 min in the \(^{27}\text{Al}\) MAS NMR spectra (Fig. 2D). However, the removal of aluminum atoms from the CHA zeolite was slower than that of other zeolites. Even after 2 hours of the acid treatment, no notable decreases in the peak intensities of octahedral aluminum species were observed, and 83% of the aluminum atoms remained as the FAI or EFAI.

High-energy x-ray total scattering (HEXTS) measurements were conducted on the as-synthesized and acid-leached AFX and RHO zeolites [total scattering factors \(S(Q)^2\) presented in figs. S14 and S15 and reduced pair distribution functions, \(G(r)^2\), presented in Fig. 4 (A and B)]. The peaks at 1.6, 2.6, and 3.1 Å in \(G(r)\) correspond
to the correlation of T-O, O-O, and T-T atom pairs, respectively (49). For the T-O correlation, an increase in the intensity and a slight shift to a shorter distance were observed by the acid treatment in both zeolites. This could be attributed to the uniform T-O bond length followed by the elimination of the Al-O bonds (~1.7 Å), which are slightly longer than the Si-O bonds (~1.6 Å) (50). The peaks at 3.6 to 4.4 Å could be assigned to the correlation between a T atom and the second O atom. The T-O<sub>2nd</sub> correlation in 4-rings (4R) and six or larger rings (≥6R) could be observed at 3.6 to 3.8 Å and 3.9 to 4.4 Å, respectively. In the range of T-O<sub>2nd</sub> correlation

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**Fig. 3. Change of charge balances during dealumination.** (A) Scheme of charge balance between FAI atoms and cations. Change in the number of aluminum atoms and inorganic and organic cations per unit cell in (B) AFX, (C) CHA, (D) ERI, and (E) RHO zeolites. The number of OSDA molecules in AFX and ERI zeolites (marked with ¶) is doubled, as they are divalent cations (see fig. S3).
(≥6R, 3.9 to 4.4 Å), a similar peak shift was observed in both the AFX and RHO zeolites upon acid treatment. Contrastingly, a substantial decrease in the peak intensity was observed in the range of the T-O 2nd correlation (4R, 3.6 to 3.8 Å) of G(r) of the RHO zeolite, while only a slight decrease was observed in the AFX zeolite. The decrease in peak intensity in the range of T-O 2nd correlation (4R, 3.6 to 3.8) may be attributed to the destruction of building units, such as double eight ring (d8r) or double six ring (d6r). Plots of G(r) of samples after 5 and 60 min of acid treatment (fig. S16) show that these structural changes start after less than 5 min, which is sooner than the start of structural degradation of the RHO zeolite. The difference in the peak intensities of the AFX and RHO zeolites suggests that d8r units in the RHO structure were destroyed or at least distorted by dealumination, while most of the d6r units in the AFX structure were preserved. Figure S5 shows our proposed scheme for dealumination and extraction of EFAI species in small-pore zeolites, which is discussed in detail in the 'Discussion' section.

Argon adsorption measurements were conducted on the AFX zeolites before and after the acid treatment in their calcined form (fig. S16) and the high-silica AFX zeolite obtained via the acid treatment should have a considerable number of structural defects. Therefore, defect healing via liquid-mediated treatment using an aqueous solution of ammonium fluoride and TEAOH (38) was performed on the acid-leached AFX zeolite. The XRD patterns of the AFX zeolite before and after the treatment indicate that the crystallinity was preserved during the treatment (fig. S17). The relative crystallinity of self-defect healing of AFX zeolite

The AFX zeolite will be further discussed, as it showed the highest Si/Al ratio with preserved crystallinity after acid dealumination. The high-silica AFX zeolite obtained via the acid treatment should have a considerable number of structural defects. Therefore, defect healing via liquid-mediated treatment using an aqueous solution of ammonium fluoride and TEAOH (38) was performed on the acid-leached AFX zeolite. The XRD patterns of the AFX zeolite before and after the defect healing indicate that the crystallinity was preserved during the treatment (fig. S17). The relative crystallinity of

![Fig. 4. HEXTS measurements and Ar adsorption results.](image)

Reduced pair distribution function G(r) of as-synthesized and acid-leached (2 hours) (A) AFX and (B) RHO zeolites. Black and red lines correspond to the as-synthesized and acid-leached samples, respectively. Argon adsorption isotherms of AFX zeolite samples in (C) linear and (D) semilogarithmic scale. The black, blue, green, and orange lines and symbols correspond to the as-synthesized sample and samples after the acid treatment for 5, 30, and 120 min, respectively. Before adsorption measurement, OSDA molecules were removed by calcination at 550°C.
the acid-leached sample was 100% after treatment, and the higher concentration of the treatment solution resulted in higher crystallinity and the formation of the *BEA phase (fig. S18). The Si/Al ratio decreased from 9.1 to 8.9 owing to desilication by ammonium fluoride. The preserved structure of OSDA molecules occluded in zeolite pores were confirmed by using $^{29}$Si CP MAS NMR spectroscopy (fig. S13). The $^{29}$Si MAS NMR spectra (Fig. 6A) demonstrate the increase and decrease in defects caused by the acid and the defect-healing treatments. The peaks between −98 to −100, −104 to −105, and −110 to −112 ppm correspond to the Q⁴ (2Al), Q⁴ (1Al), and Q⁴ (0Al) species, respectively, and the peak at −102 ppm corresponds to Q⁵ Si species [Si(OH)(OSi)]⁵ (53). Notably, the intensity of peaks decreased by dealumination and increased by defect healing, possibly because of the formation of structural defects and pore opening during dealumination; therefore, any change of bonding partner or bond angles and length affected the state of electronic shielding of each atom and thus broadened the peak in $^{29}$Si MAS NMR spectra. Acid leaching led to framework dealumination, as indicated by the decrease in Q⁴ (2Al) and the formation of silanol defects, which was confirmed by the formation of the Q⁵ peak in the CP NMR spectra. The Q⁵ peak disappeared after the defect healing, illustrating the decrease of silanol defects through silicate migration during the liquid-mediated treatment. The Fourier-transformed infrared (FT-IR) spectra (fig. S19) and $^1$H MAS NMR spectra (fig. S20) also confirm this increase and decrease of defects. In the FT-IR spectra, peaks corresponding to isolated silanol groups, Brønsted acid sites, and silanol nests are observed at 3740, 3650, and 3500 cm⁻¹. The peak corresponding to isolated silanol groups and silanol nests grew in intensity upon acid treatment and shrank upon defect-healing treatment. In the $^1$H MAS NMR spectra of the as-synthesized samples, a large peak was observed at 3.9 ppm, attributed to the H-bonded water. After acid leaching, a small peak is observed at 4.3 ppm, which could be attributed to silanol nests (47). Although this peak was also observed after defect-healing treatment, its intensity was decreased.

According to the thermogravimetric curves (fig. S12), the amounts of adsorbed water in the as-synthesized sample, the sample after acid treatment, and the sample after acid and defect-healing treatments were 12, 13, and 6.2%, respectively. The amount of adsorbed water decreased upon defect-healing treatment, indicating the hydrophobicity of the treated zeolite due to the presence of a smaller number of defects.

Regarding the role of TEAO⁺ and F⁻ during the defect-healing treatment, the results of our previous study (38) suggest that the former stabilizes the zeolite framework, whereas the latter reconstructs the zeolite structure to heal defects by silicate migration. In this study, however, the presence/absence of TEAOH and NH₄F did not cause substantial variation in relative crystallinity of the solid phase (XRD patterns and IR spectra shown in figs. S21 and S22). When the liquid phase contained only NH₄F, relative crystallinity was 94%; however, treatments with TEAOH solution and pure water yielded relative crystallinities of 98 and 96%, respectively. This difference could be attributed to the presence of OSDA molecules in the pores and the difference in Si/Al ratio. In this study, liquid-mediated treatment was conducted on zeolites containing OSDA molecules in the pores, which should have worked as a stabilizing agent during the treatment, instead of the TEA cations. Liquid-mediated treatment of H⁺-form AFX zeolite yielded a relative crystallinity of 87%, which is much lower than that obtained by the treatment of zeolites containing OSDA molecules (XRD patterns shown in fig. S23). Although the relative crystallinity obtained herein is similar to the case when pure water was used as the treatment medium, the decrease in silanol defects was limited. These results indicate that pure water treatments can be used for improving the stability of small-pore zeolites, although the current study was focused on treatment with NH₄F and TEAOH to realize enhanced stability.

**Evaluation of hydrothermal stability**

Hydrothermal stability tests were conducted on AFX zeolite with its as-synthesized form, acid-leached form, and AFX zeolite after the acid and the defect-healing treatments (Fig. 6B; XRD patterns shown in figs. S24 to S26). All samples were converted to the H⁺ form before the tests. The as-synthesized AFX zeolite was degraded by steaming, and the crystal structure collapsed above 750°C. Contrastingly, the zeolite stabilized by the acid leaching and the defect-healing treatment preserved the Bragg peaks of the crystalline phase even at 800°C. The dealuminated AFX zeolite without any defect-healing treatments exhibited high hydrothermal stability owing to the suppression of the elimination of FAI atoms, which is the main cause of framework destruction during hydrothermal treatment. This demonstrates the advantage of the proposed acid dealumination method, which enables enhanced hydrothermal stability of H⁺-form zeolites with an economical and sustainable procedure. Conversely, defect-healing treatment did not affect the hydrothermal stability of the H⁺-form zeolites, as the number of silanol defects does not affect the stability of H⁺ form of low-silica zeolite (38).

**Evaluation of NH₃-SCR activity**

The effect of the current postsynthetic treatments on the hydrothermal stability of Cu-exchanged zeolites was evaluated by NH₃-SCR tests. When the same Cu loading was used for all samples, 7.3 and 6.1 weight % (wt%) of Cu could be loaded onto AFX zeolite after acid treatment and after acid treatment followed by defect healing; on the other hand, 3.6 wt% of Cu could be loaded onto the as-synthesized form. By adjusting the loading condition, catalyst with 6.8 wt% Cu loading was prepared from the as-synthesized AFX zeolite and was used in the catalytic test discussed in the subsequent section.

Figures S27 and S28 show the XRD patterns of fresh and hydrothermally aged (at 800°C for 7 hours) Cu-exchanged form of the as-synthesized AFX zeolite, the acid-leached one, and the one obtained after acid leaching followed by defect-healing treatment. Figure 6C shows the NO conversion during the SCR test of fresh and hydrothermally aged AFX zeolites. In the SCR with fresh catalysts, acid-leached AFX zeolite showed higher NO conversion at low temperatures (<250°C) compared to the as-synthesized zeolite. Moreover, when the samples after hydrothermal aging were tested, the acid-leached sample with subsequent defect healing performed better than the as-synthesized zeolite in all temperature ranges. In contrast to the results for H⁺-form zeolites, the hydrothermal stability of acid-leached and Cu-exchanged zeolites was improved because of the defect-healing treatment, and this may be attributed to the different degradation mechanisms of the H⁺-form and Cu-exchanged zeolites. The former is mainly degraded by the dealumination of FAI atoms, and the latter is degraded because of the formation of the CuO₅ cluster (15, 54). The decrease in the amount of silanol...
groups by the defect-healing treatment prevents the formation of such CuO₃ species and enhances the hydrothermal stability of Cu-exchanged zeolites. Furthermore, acid site densities of the as-synthesized AFX zeolite, the acid-leached one, and the one obtained after acid leaching followed by defect-healing treatment were 1.6, 1.0, and 1.0 mmol g⁻¹, respectively, measured by ammonia temperature-programmed desorption (NH₃-TPD). This result may indicate increased accessibility of acid sites by pore opening. Although the accessible acid sites decreased by 35% after the dealumination process, the decrease was smaller than the decrease in the number of Al atoms (54%). This indicates increased accessibility of acid sites by pore opening, which could be another factor that contributed to realizing enhanced catalytic activity.

**DISCUSSION**

Mechanistic studies on the dealumination of zeolites with medium (or larger) pores have been reported in recent years. According to computational studies, when zeolites are exposed to steam or acidic solutions, the Si-O-Al linkages are first hydrolyzed one by one to form EFAl species (29, 55). These EFAl species should exist in the form of Al(OH)₃(H₂O) (a typical scheme of dealumination is shown in fig. S29) (28, 56, 57). Furthermore, these EFAls were extracted in the liquid phase via leaching in acidic solution after steaming (58) or extending acid treatment (34). A similar phenomenon was observed in the initial few minutes of the acid treatment in this work. Some of the inorganic cations (such as Na⁺ in AFX, CHA, and RHO zeolites and K⁺ in CHA zeolite) were rapidly removed, while other inorganic cations (such as K⁺ and Cs⁺ in ERI and RHO zeolites) and most organic cations were preserved in the zeolite pores (Fig. 3, B to E). Typically, the removal of inorganic cations proceeds for less than 10 to 30 min. The ion exchange process results in the formation of FAI balanced by protons. This proton-balanced FAI is easily removed from frameworks via hydrolysis catalyzed by protons (56, 57). However, extraction of EFAl species in the liquid phase is difficult for small-pore zeolites because of the insufficient diffusion rate in narrow micropores (2) and requires almost 60 min (Fig. 2A).

The type and number of the cations that could be removed depended on the framework topology (Fig. 3, B to E). Although most of the cations were removed from the AEI and CHA zeolites, 13% of the sodium cations remained in the AFX zeolite even after 120 min of acid treatment. In the ERI and RHO zeolites, 42% potassium cations and 67% cesium cations remained after the acid treatment, respectively. This could be explained in terms of framework topology and OSDA occupancy. In AEI and CHA zeolites, the numbers of OSDA cations per aft and cha cavity were 0.65 and 0.68, respectively, which shows the presence of “empty” cages that are not filled by OSDA cations. The inorganic cations and protons can move freely between the empty cages considering the three-dimensional channel system of these structures. In the AFX structure, two types of cages, viz. aft and gme cages, are present; the latter is too small for OSDA cations to be included. The number of OSDA cations in the AFX sample was 0.67 per aft cage. Hence, the inorganic cations and protons could be transported via gme cages and empty aft cages. In contrast, the irremovable cations in ERI and RHO should be trapped in the closed cages of their structures (can cages in the ERI structure and d8r in the RHO structure) that are not connected to other cages via eight or larger rings (59, 60). The 13% of sodium cations remaining after the acid treatment of AFX zeolite may have been stuck in aft cages that are co-occupied by OSDA cations.

![Fig. 5. Schematic illustration of proposed POMP.](image)
Aluminum species were protonated and partly removed from the structure via these ion exchange processes to form EFAl species; these were gradually transported through zeolitic pore channels and extracted to the liquid phase. The crystallinities of AFX, AEI, CHA, and ERI zeolites were preserved during this acid treatment; however, when calcination of the zeolite was conducted before acid treatment to remove OSDA cations, the same treatment resulted in almost complete amorphization of the structures (fig. S2). These results indicate that the compositional tuning of small-pore zeolites with preserved crystallinity proceeds only when the zeolite structures are stabilized by the OSDA cations. The destruction of pores of zeolite structures could be attributed to the absence of wide channels (larger than 12 rings) in small-pore zeolites for the transportation of EFAl species. The 8R channel of the framework is too narrow for EFAl species, such as Al(OH)$_3$, to be transported through without causing extensive damage to the structure (35, 57). To rationalize the transportation of EFAl species, a novel process named pore-opening migration process (POMP) has been suggested as the proposed mechanism (Fig. 5A). To ensure that the EFAl species can be transported through the small pores, the 8Rs should be partially opened and micropores of zeolite should be widened, as observed in the argon adsorption isotherms (Fig. 4D). The ability to load larger amounts of Cu onto acid-leached zeolites could also be attributed to the pore opening during the dealumination process. This partial pore opening could be attributed to the void of T sites formed by dealumination or dynamic cleavage and reconnection of T-O bonds (53, 61). Simultaneously, migration of EFAl species breaks the crystal frameworks through interactions with the surrounding atoms of zeolite structures (62, 63).
Without the stabilization effect of OSDA cations occluded in the cavities, cleavage of T-O-T bonds and loss of pore-filling EFAI species lead to the destruction of the crystal structures.

Despite the proposed POMP scheme, the RHO zeolite was degraded by this treatment even when OSDAs were present in the pores, which may be attributed to the presence or absence of d8r building units. The crystal structures of the AFX, AEI, and CHA zeolites are composed of interconnected d8r (Fig. 1B). The ERI zeolite also has a d6r structure. Because EFAI species were transported through 8R, d6r units could have been preserved in these zeolites (Fig. 5B). Contrastingly, the RHO structure consists of d8r building units connected to each other (Fig. 1B). The damage to 8R during transportation of EFAI species directly leads to the collapse of d8r building units, inducing a substantial decrease in crystallinity (Fig. 5B). This is consistent with the experimental result, wherein the degradation of the RHO structure occurred after 10 min of acid treatment, just after the extraction of EFAI species, and the same was confirmed using the HEXTS measurement (Fig. 4A). In the AFX and RHO zeolites, a peak shift was observed between 3.9 and 4.4 Å, which may be due to the destruction (or at least distortion) of large rings, such as 8R. However, a notable decrease in the peak intensity in the range of the T-O-T correlation in 4R (3.6 and 3.8 Å) was confirmed using the HEXTS measurement (Fig. 4A).

During transportation of EFAl species directly leads to the collapse of building units connected to each other (Fig. 1B). The damage to 8R zeolites (Fig. 5B). Contrastingly, the RHO structure consists of d8r building units connected to each other (Fig. 1B). The damage to 8R during transportation of EFAl species directly leads to the collapse of d8r building units, inducing a substantial decrease in crystallinity (Fig. 5B). This is consistent with the experimental result, wherein the degradation of the RHO structure occurred after 10 min of acid treatment, just after the extraction of EFAI species, and the same was confirmed using the HEXTS measurement (Fig. 4A). In the AFX and RHO zeolites, a peak shift was observed between 3.9 and 4.4 Å, which may be due to the destruction (or at least distortion) of large rings, such as 8R. However, a notable decrease in the peak intensity in the range of the T-O-T correlation in 4R (3.6 and 3.8 Å) was confirmed using the HEXTS measurement (Fig. 4A).

Without the stabilization effect of OSDA cations occluded in the cavities, cleavage of T-O-T bonds and loss of pore-filling EFAl species lead to the destruction of the crystal structures. Despite the proposed POMP scheme, the RHO zeolite was degraded by this treatment even when OSDAs were present in the pores, which may be attributed to the presence or absence of d6r building units. The crystal structures of the AFX, AEI, and CHA zeolites are composed of interconnected d6r (Fig. 1B). The ERI zeolite also has a d6r structure. Because EFAI species were transported through 8R, d6r units could have been preserved in these zeolites (Fig. 5B). Contrastingly, the RHO structure consists of d8r building units connected to each other (Fig. 1B). The damage to 8R during transportation of EFAl species directly leads to the collapse of d8r building units, inducing a substantial decrease in crystallinity (Fig. 5B). This is consistent with the experimental result, wherein the degradation of the RHO structure occurred after 10 min of acid treatment, just after the extraction of EFAI species, and the same was confirmed using the HEXTS measurement (Fig. 4A). In the AFX and RHO zeolites, a peak shift was observed between 3.9 and 4.4 Å, which may be due to the destruction (or at least distortion) of large rings, such as 8R. However, a notable decrease in the peak intensity in the range of the T-O-T correlation in 4R (3.6 and 3.8 Å) was confirmed using the HEXTS measurement (Fig. 4A). In the AFX and RHO zeolites, a peak shift was observed between 3.9 and 4.4 Å, which may be due to the destruction (or at least distortion) of large rings, such as 8R. However, a notable decrease in the peak intensity in the range of the T-O-T correlation in 4R (3.6 and 3.8 Å) was confirmed using the HEXTS measurement (Fig. 4A).

Materials and Methods

Aerosil 200 fumed silica (Evonik), LUDOX AS–40 colloidal silica (Sigma-Aldrich), SNOWTEX 40 colloidal silica (Nissan Chemical), FAU zeolite (Si/Al = 5.1; Tosoh HSZ-350HUA), 50 wt% aqueous solution of sodium hydroxide (Fujifilm Wako Pure Chemical), 25 wt% sodium hydroxide solution (Kishida Chemical), 50 wt% aqueous solution of potassium hydroxide (Fujifilm Wako Pure Chemical), 50 wt% aqueous solution of cesium hydroxide solution (Sigma-Aldrich), ammonium fluoride (Fujifilm Wako Pure Chemical), aluminum nitrate nonahydrate (Fujifilm Wako Pure Chemical), aluminum hydroxide (Kyowa Chemical Industry), sodium aluminate (Fujifilm Wako Pure Chemical), aluminum sec-butoxide (Fujifilm Wako Pure Chemical), 35 wt% N,N′-dimethyl-3,5-dimethylpiperidinium hydroxide (DMDMPOI), (see fig. S3D), 1 M sulfuric acid (Fujifilm Wako Pure Chemical), ammonium nitrate nonahydrate (Fujifilm Wako Pure Chemical), and silicon carbide (High Purity Chemicals) were used as received.

AFX zeolite was synthesized using Et6-diquat-5 (fig. S3A) as an OSDA, which was synthesized according to a previously reported procedure (65). Deionized water, sodium hydroxide solution, Aerosil 200 fumed silica, Et6-diquat-5, and aluminum nitrate nonahydrate were mixed to obtain a reaction mixture with the composition of 1 SiO2:0.017 Al2O3:1 NaOH:0.1 Et6-diquat-5:40 H2O. The mixture was stirred at 25°C for 24 hours and then transferred to a Teflon-lined stainless-steel autoclave (Parr, model 4749), which was heated in an air-circulated oven for 7 days at 150°C. The solid product was collected by filtration, washed with deionized water, and dried at 80°C.

For the synthesis of AEI zeolite, water, 35 wt% DMDMPOI solution, 25 wt% sodium hydroxide solution, and aluminum hydroxide were mixed to obtain a clear solution. Subsequently, SNOWTEX 40 colloidal silica was added dropwise, and CHA zeolite (Si/Al = 12) was added as the seeds. The composition of the reaction mixture was 1 SiO2:0.077 Al2O3:0.38 NaOH:0.084 DMDMPOI:18 H2O. The synthesis was performed at 180°C for 24 hours under the rotation of 15 rpm. The solid product was collected by filtration, washed with deionized water, and dried at 100°C.

For the synthesis of ERI zeolite sample for dealumination, aluminum sec-butoxide was dissolved in 50 wt% aqueous solution of potassium hydroxide, followed by dropwise addition of hexamethonium bromide solution and LUDOX AS–40 colloidal silica. The whole mixture was stirred at 25°C for 2 hours and aged at 90°C for 20 hours. Subsequently, the ERI zeolite seed (10 wt% of SiO2) obtained using the charge density mismatch approach (see the Supplementary Materials) was added to the mixture, which was transferred to a tubular reactor (66). The chemical composition of the reaction mixture was 1.63 hexamethonium bromide:7.8 KOH:0.8...
CHA zeolite was synthesized via an interzeolite conversion method. FAU zeolite (Tosoh HSZ-350HUA), 25% aqueous solution of TEAOH, 50 wt% aqueous solution of sodium hydroxide, and sodium aluminate were added to this solution, and the mixture was heated at 80°C for 2 hours to obtain a clear solution. Subsequently, LUDOX AS-40 colloidal silica was added dropwise. The composition of the reaction mixture was 10 SiO$_2$:1.0 Al$_2$O$_3$:1.8 Na$_2$O:0.3 Cs$_2$O:0.5 18-crown-6:100 H$_2$O. The reaction mixture was stirred at 25°C for 24 hours, after which it was transferred to a Teflon-lined autoclave. The synthesis was continued for 3 days at 120°C. The solid product was collected by filtration, washed with deionized water, and dried at 80°C.

For the RHO zeolite synthesis, 18-crown-6 was mixed with deionized water and stirred until it dissolved completely. Fifty weight % sodium hydroxide solution, 50 wt% cesium hydroxide solution, and sodium aluminate were added to this solution, and the mixture was heated at 80°C for 2 hours to obtain a clear solution. Subsequently, LUDOX AS-40 colloidal silica was added dropwise. The composition of the reaction mixture was 10 SiO$_2$:1.0 Al$_2$O$_3$:1.8 Na$_2$O:0.3 Cs$_2$O:0.5 18-crown-6:100 H$_2$O. The reaction mixture was stirred at 25°C for 24 hours, after which it was transferred to a Teflon-lined autoclave. The synthesis was continued for 3 days at 120°C. The solid product was collected by filtration, washed with deionized water, and dried at 80°C.

For the acid treatment of AFX, CHA, ERI, and RHO zeolites, 0.5 g of the as-synthesized zeolite or the calcined zeolite sample was dispersed in 5 ml of deionized water, followed by addition of 5 ml of 1 M sulfuric acid. For the acid treatment of AEL zeolite, 3 g of the AEL zeolite sample was dispersed in 30 g of 1.1 M aqueous solution of sulfuric acid. The slurry was stirred at 80°C for 2 hours. The solid product was collected by centrifugation, washed with deionized water, and dried at 80°C.

For liquid-mediated defect healing (38), ammonium fluoride was dissolved in 25% aqueous solution of TEA, followed by addition of deionized water, if needed. The chemical composition of the treating solution was xNH$_4$F:x TEAOH:150 H$_2$O (x = 1 or 10). The treatment solution (0.5 to 1 g) was added to the zeolite solution, and the mixture was sealed in a Teflon-lined autoclave. The treatment was conducted at 170°C for 24 hours. The solid product was collected by filtration, washed with deionized water, and dried at 80°C.

Before the stability tests, the zeolite samples were converted to H$^+$-form by calcination for 5 hours at 600°C with the ramp rate of 110°C min$^{-1}$ in dry air and ion exchange in 1 M ammonium nitrate solution, followed by another calcination step. The stability tests were conducted with an in-house-built experimental system. The samples were ramped for 75 min to the target temperature (700°C to 900°C), and exposed to steam-containing air for 3 hours. The water was fed by syringe pump to achieve an appropriate water content (10 volume % at the atmospheric pressure).

Copper-exchanged AFX zeolites were prepared as follows. The AFX zeolite samples were calcined for 5 hours at 600°C with the ramp rate of 1.9°C min$^{-1}$ in dry air and ion-exchanged by 1 M ammonium nitrate solution to obtain their ammonium form. Subsequently, the samples were dipped in 3% copper acetate solution at 90°C for 2 hours once (in the case of dealuminated AFX zeolite) or twice (in the case of as-synthesized AFX zeolite) and calcined again. The hydrothermal aging was conducted in the same equipment as hydrothermal stability tests. The temperature and period of the hydrothermal aging was 800°C and 7 hours, respectively, and the ramp rate was 11°C min$^{-1}$. In the SCR experiments, the Cu-exchanged zeolite sample (10 mg) mixed with silicon carbide (12 mg; particle diameter, 2 to 3 μm) was held in a quartz tube with the inner diameter of 4 mm using glass wool. As a pretreatment, a mixture of gases (5% oxygen and balance nitrogen, controlled by mass flow controllers) was introduced in the reactor tube, followed by heating of the reactor system to 150°C. The catalytic evaluation was conducted at the temperatures of 150° to 500°C with the step of 50 K in a mixture of gases containing nitric oxide (300 ppm), ammonia (300 ppm), water (3%), oxygen (5%), and nitrogen (balance). The flow rate of gas and gas hourly space velocity was 100 cm$^3$ min$^{-1}$ and 2.08 × 105 hours$^{-1}$, respectively. The conversion rate was characterized by a chemiluminescent NOx analyzer (ECL-88A, Yanaco).

Powder XRD patterns of the samples were collected on an Ultima IV x-ray diffractometer (Rigaku) using CuKα radiation (λ = 0.15406 nm, 40 kV, 40 mA) at a scanning rate of 10° min$^{-1}$ and a scanning step of 0.02°. The crystallinity of each phase was calculated on the basis of the area of selected peaks (table S1). Particle sizes and morphologies of the products were observed using field emission SEM (JEOL JSM-7000F) with an accelerating voltage of 15 kV after coating the samples with osmium. The elemental distribution inside particles was analyzed by TEM-EDS and SEM-EDS. TEM-EDS measurements were performed using a JEM-F200 (JEOL) microscope with an accelerating voltage of 200 kV, after burying the samples in epoxy resin (Gatan G2) and slicing them using a focused ion beam system. SEM-EDS measurements were performed using an ultrahigh-resolution SU9000 (Hitachi High-Tech) system equipped with a silicon drift EDS analyzer (EDAX, AMETEK). Here, accelerating voltage was set at 10 kV to excite the electron of each atom of the sample (silicon and aluminum). Before the SEM-EDS, cross-sectional surface of the zeolite sample was prepared using a broad argon ion-milling system (IM4000Plus, Hitachi High-Tech) without any kind of metal coatings applied on the samples. Nitrogen and argon adsorption-desorption measurements were carried out with BELSORP MAX (MicrotracBEL) and Autosorb-iQ2-2MP (Anton Paar) instruments. Before the N$_2$ adsorption-desorption measurements, samples were calcined in air using a muffle furnace, where the zeolite samples were heated under gradual escalation from the ambient temperature to 550°C for 5 hours, and kept at 550°C for 5 hours. For preparation of samples for Ar adsorption measurements, the zeolite samples were heated at 400°C for 4 hours under the flow of N$_2$ gas, followed by calcination at 550°C for 5 hours. The pretreatment for degassing was conducted at 400°C for 24 hours for measurements with the BELSORP MAX and at 150°C for 30 min and at 350°C for 240 min when the Autosorb-iQ2-2MP was used. The measurement of nitrogen and argon adsorption was conducted at liquid nitrogen and argon temperature (normal boiling point, −196°C and −186°C, respectively). Acid site densities were determined using NH$_3$-TPD (MicrotracBEL BELCAT II). For this, samples were heated at 400°C for 60 min at a ramping rate of 10 K min$^{-1}$ under flowing He [50 standard cubic centimeter per minute (sccm)] to desorb any adsorbed species. NH$_3$ was loaded at 100°C for 30 min under flowing NH$_3$ (5.16%) and He (balance), and the system was purged using He for 30 min. Measurements were taken at 100° to 600°C with a ramping rate of 10 K min$^{-1}$ in 30 sccm He, and desorption of NH$_3$ was measured using a thermal conductivity detector. The elemental composition of the samples was determined by flame AAS (Hitachi High-Tech Z-2000) for quantification of K and Cs, and ICP-AES (Thermo iCAP 300) for quantification of other elements. The samples
were dissolved in mixed solution of hydrochloric and hydrofluoric acid. The solid-state MAS NMR measurements were conducted by a JNM-ECA 500 instrument (JEOL, Japan). Unless specified otherwise, all of the measurements were conducted on samples in their as-synthesized, acid-leached, or stabilized form without any further post-synthetic treatments. The $^{27}$Al MAS NMR spectra were recorded at 130.33 MHz with a $\pi/2$ pulse length of 3.2 μs, a recycle delay of 5 s, and a spinning frequency of 10 kHz. The $^{13}$C CP MAS NMR spectra were recorded at 125.77 MHz with a recycle delay of 1 s, and a spinning frequency of 10 kHz. The $^{29}$Si CP MAS NMR spectra were recorded at 500.16 MHz with a $\pi/2$ pulse length of 3.6 μs, a recycle delay of 2.8 s, and a spinning frequency of 10 kHz. FT-IR spectra were recorded as averages of 16 scans at 4 cm$^{-1}$ resolution using a JASCO FT-IR-6600 spectrometer with a mercury cadmium telluride detector. The powder samples placed in a pan were heated at 500°C for 1 hour at the ramping rate of 5 K min$^{-1}$ in flowing N$_2$ (100 cm$^3$ min$^{-1}$) to remove the adsorbed water. After cooling down to 25°C, the FT-IR measurement was conducted with the diffuse reflectance method. The HEXTS measurements were conducted at the BL04B2 high-energy XRD beamline (SPring-8, Japan). The scattering patterns of the samples were collected at room temperature under vacuum conditions. The obtained scattering patterns were corrected and normalized by various factors to calculate the total structure factor, $S(Q) = 4\pi\sin(\theta)/\lambda$ (49, 67). The reduced pair distribution functions, $G(r)$, were obtained by implementing Fournier transformation, as expressed in the following equation:

$$G(r) = \frac{2}{\pi} Q_{\text{max}}^2 Q S(Q) - 1) M(Q) \sin Qr dQ$$

$$M(Q) = \sin Q \Delta r / Q \Delta r$$

The energy of the incident x-ray was 61.2 keV, and the maximum $Q$ ($Q_{\text{max}}$) collected was 25.7 Å$^{-1}$ for AFX zeolite and 17.7 Å$^{-1}$ for RHO zeolite.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abc3093

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Acknowledgments: HEXTS measurements conducted at beamline 0482, SPring-8 were approved by Japan Synchrotron Radiation Research Institute under the proposal numbers 2020A0687 and 2021A1152. Funding: This work was partly supported by New Energy and Industrial Technology Development Organization Moonshot Project; Japan Society for the Promotion of Science (JSPS) KAKENHI Grant-in-Aid for Transformative Research Areas(A) (JP20P0206/20H05880); and the Materials Processing Science project (”Materialize”) of Ministry of Education, Culture, Sports, Science and Technology (JPMXP021912801). T.Y. is a research student of the University of Tokyo and Mitsubishi Chemical Corporation (no. P2021-178746A, and T.W. Competing interests: T.W. Writing (original draft): T.Y., K.I., and T.W. Writing (review and editing): T.Y., K.I., T.S., T.O., Y.H., Y.K., H.Y., Q.H., T.K., C.A.J.F., Z.L., R.O., Y.Y., K.O., Y.S., A.E., and T.T. Supervision: K.I. and T.T.