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Zeolites

Intraframework Migration of Tetrahedral Atoms in a Zeolite**

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Abstract: *The transformation from a disordered into an ordered version of the zeolite natrolite occurs on prolonged heating of this material in the crystallizing medium, but not if the mother liquor is replaced by water or an alkaline solution. This process occurs for both aluminosilicate and gallosilicate analogues of natrolite. In cross experiments, the disordered Al-containing (or Ga-containing) analogue is heated while in contact with the mother liquor of the opposite analogue, that is, the Ga-containing (or Al-containing) liquor. Therefore, strong evidence for the mechanism of the ordering process was obtained, which was thus proposed to proceed by intraframework migration of tetrahedral atoms without diffusion along the pores. Migration is first triggered, then fuelled by surface rearrangement through reactions with the mother liquor, and stops when an almost fully ordered state is attained. Classical dissolution–recrystallization and Ostwald ripening processes do not appear to be relevant for this phase transformation.*

Zeolites are microporous, crystalline solids constructed by corner-sharing SiO_4 and AlO_4^- tetrahedra, yielding a three-dimensional four-connected network, and are widely used as industrial adsorbents, ion exchangers, and catalysts.[1] Their performance depends primarily on the size, shape, and dimensionality of the intracrystalline channels and cavities, which allow the diffusion of chemical species, but also on the Si/Al ratio and the Al distribution over the tetrahedral sites (T-sites) of the framework. The zeolite framework determines the physicochemical properties of the surface surrounding the pores with which the diffusing chemical species interact. Chemical modifications of the tetrahedral framework, such as isomorphous substitution of Si or Al by other tetrahedral elements, are possible by modifications during zeolite synthesis and by post-synthetic treatments with species that diffuse along the pores and react with the framework.[2] Therefore, the chemistry and industrial applications of zeolites generally appear to be determined by their pores. Herein, however, we present clear experimental evidence for extensive intraframework T-atom migration that proceeds without pore diffusion of the migrating species; this migration contributes to a disorder-to-order process that significantly modifies the physicochemical properties of the zeolite. Limited migration of T-atoms during post-synthetic zeolite treatments has previously been proposed to explain, for instance, the SiO_2 island formation in silicoaluminophosphate molecular sieves, including SAPO-5 (framework type AFI) and SAPO-37 (FAU), the Si/Al distribution in dealuminated zeolite Y (FAU) at high temperature, the healing of defects in YNU-2 (MSE) upon steaming, or, very recently, the B/Al exchange in zeolite beta (*BEA).[2a,3] In all of these cases, the migrating species likely diffuse along the pores.

Natrolite (NAT) is a naturally occurring zeolite with an ideal chemical composition of $|Na_{16}(H_2O)_{16}|[Al_{16}Si_{24}O_{80}]$ and contains a pore system that consists of eight-ring channels intersected by nine-ring channels.[4] For this family of small-pore zeolites, several compositions that incorporate Al, Ga, and Ge at the T-sites have been reported.[5] We have previously described the synthesis of gallosilicate natrolites (Ga-NATs) and their in situ disorder–order transformation, which is well understood from a thermodynamic point of view. However, the exact transformation mechanism remains to be elucidated.[6] In this process, the initial Ga-NAT phase, which is denoted TNU-3, contains Ga and Si in a random distribution over the available T-sites. An increase in the temperature of the hydrothermal treatment under crystallization conditions leads to an increase in the degree of Si–Ga ordering, with one particular T-site being preferentially occupied by Si. An almost complete order is attained in the material denoted TNU-4. What is really puzzling is that this transformation, which brings about no significant changes in the bulk Si/Ga ratio of the zeolite, occurs at a given temperature without phase segregation, without changes in yield, and without noticeable changes in the crystal habit and size. Thus, intermediate phases appear to be single phases with an intermediate degree of ordering rather than physical mixtures. Whereas these characteristics point to a solid-state process, this transformation cannot be induced by heating the solid at the crystallization temperature in water or in a hydroxide solution. The degree of ordering also greatly affects the physicochemical properties of the resulting Ga-NAT zeolites: As the degree of Si–Ga ordering increases, the cation exchange capacity and the water adsorption/desorption ability decrease, and the thermal stability increases.[7]

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Very recently, we have developed a robust method to synthesize the aluminosilicate analogue Al-NAT and found that the initial Al-NAT phase, denoted PST-3, has an almost completely disordered distribution of Si and Al, but transforms in situ into an almost completely ordered version, PST-4, with an increase in crystallization time or temperature.[8] Similarly to the case of Ga-NAT materials, ab initio calculations suggest that this transformation is also driven simultaneously by the preference of Si to occupy one of the crystallographically distinct T-sites (the low-multiplicity site), and of Al to occupy half of the other site (the high-multiplicity site) in the NAT topology to avoid negatively charged tetrahedral couples (Loewenstein's rule).[9] However, these thermodynamic driving forces do not tell us how the in situ disorder–order transformation occurs, which, also in the aluminosilicate, brings about no phase segregation, no changes in yield, and no noticeable changes in the crystal habit and size. We were not able to detect any transformation when the disordered NAT material was heated at 200 °C for seven days in the absence or presence of water or hydroxide solution. Whereas this failure to observe any transformation strongly suggests that the crystallization medium is required, the process cannot be simply considered to be dissolution of a metastable disordered phase and recrystallization into a more stable ordered phase by Ostwald's rule of stages because of the reasons given above.

The synthesis of Al-NAT zeolites stimulated us to perform several sets of cross experiments that are relevant to the disorder–order transformation mechanism and provide valuable insights into its nature. In such experiments, which are now accessible for the first time after the development of Al-NAT synthesis, Ga (or Al) atoms were used as a probe to monitor the disorder–order transformation of Al-NAT (or Ga-NAT). In the first set of cross experiments, we used the gallosilicate mother liquor (Ga-NAT-ML; $SiO_2/Ga_2O_3 = 30$ and $Na_2O/Ga_2O_3 = 75$) that was obtained after crystallization of the Ga-NAT material at 150 °C for seven days.[4] The most disordered Al-NAT zeolite (i.e., PST-3) was added at $0.2\,g\,mL^{-1}$ to the resulting clear solution. After heating the mixture at 150 °C for different time intervals, the solid products and the solution phase were separated by centrifugation. The time evolution of the degree of Si–Al ordering was followed by powder X-ray diffraction (XRD; Supporting Information, Figure S1) and multinuclear magic-angle-spinning (MAS) NMR spectroscopy (Figure S2). Very interestingly, a transformation into an almost fully ordered form has occurred after 14 days, with no noticeable changes in the crystal morphology or size (Figure S3). A series of materials obtained from these cross experiments were also investigated by transmission electron microscopy (TEM) elemental mapping (Figure 1; see also Figure S4). The mappings show that the Ga species that were initially found in solution were incorporated extensively at the surface of the zeolite crystal (Figure 1), whereas Al species in the crystal surface were severely depleted after 3 days. This suggests that dissolution/recrystallization processes occur only on the zeolite surface without more extensive dissolution of the crystals, whereas the initial Ga incorporation occurred by substitution of Al at tetrahedral sites (Figure S2). Moreover, at longer heating times, Ga progressively penetrated from the surface into the core of the zeolite crystals, and eventually became uniformly distributed throughout them. Further evidence for the surface rearrangement was provided by X-ray photoelectron spectroscopy (XPS; Figure S5). After one day, the crystal surface showed a very small amount of Al and considerable Ga enrichment; the surface Al content increased with heating duration. However, the Ga content remained almost constant for seven days and then dramatically decreased. This again supports that Ga at the surface migrated into the crystal core by replacing Al in the bulk.

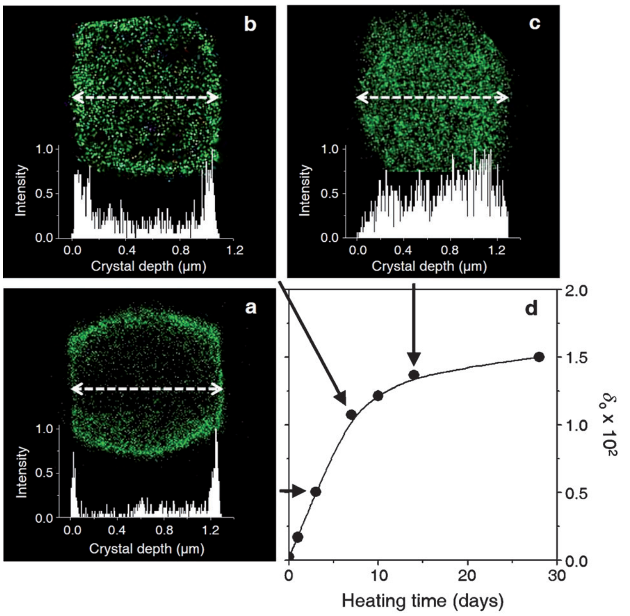

Figure 1. Ga TEM elemental mapping and concentration profiles across approximately 1.2 μm-long crystals in the solid products obtained after heating PST-3, the most disordered Al-NAT zeolite, in the gallosilicate mother liquor at 150 °C and $0.2\,g\,mL^{-1}$ for a) 3, b) 7, and c) 14 days. The mother liquor was obtained by centrifuging the Ga-NAT synthesis mixture after heating at 150 °C for 7 days. d) Time evolution of the orthorhombic distortion (δ_o) of the zeolite. δ_o is defined as $(b-a)/(b\times a)^{0.5}$, where b and a are the unit cell parameters obtained from the orthorhombic indexing (see Table S7 in Ref. [8]).

The ^{71}Ga NMR spectrum of the starting Ga-NAT-ML solution exhibits only one line at approximately 200 ppm, which corresponds to tetrahedral Ga species. However, no signal attributable to octahedrally coordinated Ga was observed (Figure S6), as expected from the very basic nature ($pH > 13.5$) of the starting solution in which the concentration of cationic Ga species must be negligible. We also found that the tetrahedral Ga species in the starting solution were fully incorporated into the solid, whereas tetrahedral Al atoms in the framework were extracted from the Al-NAT zeolites, as confirmed by ^{27}Al and ^{71}Ga NMR spectroscopy (Figure S6) and elemental analysis (Figure S7) of the mother liquor recovered after three days of heating. Moreover, the ^{71}Ga MAS NMR spectra of the solid products (Figure S2) only show resonances in the chemical shift range characteristic of framework tetrahedral Ga atoms. Finally, considering the van der Waals radius (3.2 Å) of GaO_4^- tetrahedra, their diffusion along the small eight-ring $(2.6\times$

3.9 Å) or nine-ring (2.5 × 4.1 Å) channels in the NAT framework, which are additionally crowded with water and Na^+ ions, must be extremely hindered.[8] All of these observations support that the migration of framework Ga atoms from the surface of Al-NAT crystals into their core occurs in the solid state.

As demonstrated above, Ga migration into the PST-3 crystals is accompanied by T-atom ordering. To investigate the extent of the association of these two events, that is, ordering and migration, the almost fully ordered PST-4 zeolite was kept in contact with the Ga-NAT-ML solution in a similar way as described above. SEM images of the products revealed the appearance of holes in the crystals, with the extent of this effect increasing as heating duration increased (Figure S8). More importantly, electron mapping images show that Ga incorporation into the ordered phases occurred mainly on the surface, possibly by dissolution/recrystallization processes associated with the appearance of holes. However, migration of Ga into the PST-4 crystals was not clearly visible even after 14 days of heating (Figure 2). This implies that Ga migration from the crystal surface into the core only occurs when the solid phase is disordered. Therefore, the driving force for this intriguing phenomenon appears to be the same as that for the ordering process, i.e., preferential siting and Loewenstein's rule.

In the second set of cross experiments, we heated the disordered Ga-NAT material (i.e., TNU-3) immersed in the aluminosilicate mother liquor (Al-NAT-ML) that was left over after the crystallization of Al-NAT at 150 °C for seven days, and observed a similar trend (Figures S9–S12). However, the rate of T-atom ordering was much faster for the Ga-NAT material in the Al-NAT-ML solution than for the Al-NAT material in the Ga-NAT-ML solution. This may be rationalized by a faster surface rearrangement in the former material that is due to the more basic nature of Al-NAT-ML. We also observed that the ordering process occurred much faster in the Ga-NAT material treated with Al-NAT-ML than in the Al-NAT zeolite immersed in its own mother liquor with a high pH value (for the direct synthesis, see Figure S4 in Ref. [8] and Figure S10). This again supports that T-atom migration does not occur by diffusion along the zeolite pores, because the Ga species cannot be smaller than the corresponding Al species. If T-atom ordering occurred along the zeolite pores, a faster process would have been observed for Al-NAT.

Interestingly, for both sets of cross experiments, bulk compositional changes (Figures S7 and S12) occurred faster than the ordering process (Figure 1 d; see also Figure S10), highlighting that the evolution of ordering is instead related to that of the chemical profile along the zeolite crystal (Figures 1 a–c, see also Figure S9), that is, to T-atom migration.

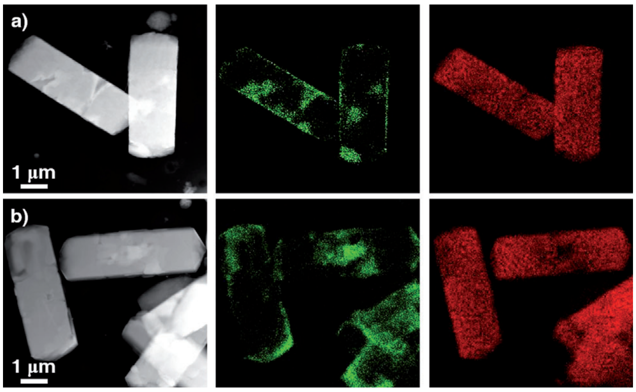

Figure 2. TEM images (left) and Ga (middle) and Al (right) TEM elemental mapping. The solid products obtained after heating the almost fully ordered Al-NAT zeolite (i.e., PST-4) in the Ga-NAT-ML solution at 150 °C for a) 3 and b) 14 days. The mappings show that no migration into the core occurs when the Al-NAT zeolite is already ordered.

To account for all of the results given here, we propose that the driving force for T-atom ordering in the zeolite framework may allow a tetrahedral T(III) (i.e., Al or Ga) atom to exchange positions with a neighboring T-atom that is located deeper in the crystal, which enables propagation into the core of the crystal (Figure 3). In the presence of an alkaline solution that contains Si and Al or Ga, some T-atom substitution occurs at the outer surface of the zeolite crystals, resulting in violations of Loewenstein's rule (i.e., Al–O–Al, Ga–O–Ga, or Ga–O–Al bonds) and/or Al/Ga atoms at T_1 sites, which is allowed under kinetic control. Thermodynamically, it would be favored to obey Loewenstein's rule by exchanging positions of Ga atom with a neighboring T-atom that is located deeper in the crystal. The incorporation of

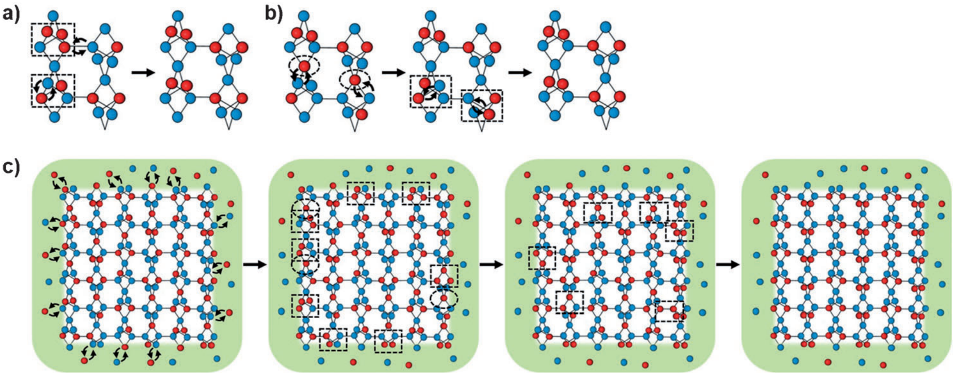

Figure 3. Schematic illustration of the intraframework T-atom migration in NAT-type zeolites. Red and blue circles represent T(III) (i.e., Al or Ga) and Si atoms, respectively (O omitted for clarity). a) T-atom substitution (dashed squares) with a neighboring T-atom deeper in the crystal minimizes the energy cost of violating Loewenstein's rule. b) T-atom substitution (dashed circles) that accounts for the preference of Si atoms to be located at the low-multiplicity sites, with T(III) atoms occupying half of the high-multiplicity sites to obey Loewenstein's rule. c) In situ disorder–order transformation in a zeolite crystal viewed along the [100] axis. No preference to either of the two substitution processes described above was assumed to exist during intraframework T-atom migration.

a new T(III) species from the solution into the zeolite crystal surface first triggers and then fuels the T-atom migration into the crystal because of the preference of Si to occupy the low-multiplicity site and the preference of Al or Ga to occupy half of the high-multiplicity sites to obey Loewenstein's rule. We propose a solid-state migration of Si, Al, and Ga that takes place along the framework without Ostwald ripening or "classical" dissolution/recrystallization processes. Nonetheless, this transformation is still "liquid-mediated"[6] in the sense that the process is fostered by rearrangements at the outer crystal surface in contact with the mother liquor. The mother liquor may be needed because a simple alkaline solution would simply produce leaching of T-atoms.

Finally, no ordering process that led to a 100% ordered material has ever been observed during Ga-NAT[6] or Al-NAT[8] synthesis: Multinuclear MAS NMR spectroscopy always detected some residual disorder (Figure 3 in Ref. [8]). Our proposed T-atom migration pathway can explain the incompleteness of the ordering process. The T_2 and T_3 sites in the NAT framework are topologically equivalent to each other, and they become distinguishable only when preferentially occupied by Si or Al/Ga (as in the orthorhombic *Fdd*2 phase). Therefore, a substitution process that starts at different ends of the crystals and propagates through the core has some probability of resulting in misfit, in which opposite sides of the crystal "choose" a different high-multiplicity site for Si preferential siting. This misfit would lead to a degree of residual disorder (Figure S13). Furthermore, no completely disordered phase has ever been observed either; we reason that this is because T-atom ordering overlaps with the crystallization process.

In summary, the overall results of our work suggest that the chemistry of zeolites may be even richer than already acknowledged, and that intracrystalline migration of tetrahedral species without diffusion along the pores is possible and may bear significant implications on the physicochemical properties of this important class of crystalline solids.

Experimental Section

The synthetic Al-NAT and Ga-NAT materials were prepared as previously described.[6,8] In the first set of cross experiments, we obtained a gallosilicate mother liquor (Ga-NAT-ML) solution with $SiO_2/Ga_2O_3 = 30$ and $Na_2O/Ga_2O_3 = 75$ by centrifuging the Ga-NAT synthesis mixture that had been heated at 150 °C for 7 days. After adding the almost disordered Al-NAT zeolite PST-3, which had been crystallized at 100 °C for 1 day,[8] to this solution at 0.2 g mL^{-1}, the resulting mixture was stirred at ambient temperature for 1 hour, charged into Teflon-lined 23 mL autoclaves, and then heated at 150 °C for different periods of time. The solid and solution phases were separated by centrifugation. In the second set of cross experiments, an aluminosilicate mother liquor (Al-NAT-ML) solution with $SiO_2/Al_2O_3 = 250$ and $Na_2O/Al_2O_3 = 900$ was obtained by centrifuging the Al-NAT synthesis mixture that had been heated at 150 °C for 7 days. Then, the most ordered Ga-NAT material TNU-3, which had been crystallized at 100 °C for 3 days,[6] was mixed with the Al-NAT-ML solution at 0.2 g mL^{-1} and treated as described above.

Cell parameters were obtained by full-profile fitting of the synchrotron powder diffraction data obtained at the Pohang Acceleration Laboratory (PAL) source. High-resolution transmission electron microscopy (HRTEM) images with energy-dispersive X-ray (EDX) chemical mapping were obtained with an omega-filter-equipped JEOL JEM-2200FS transmission electron microscope operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on a VG Multilab 2000 spectrometer employing a Mg Kα X-ray source (1253.6 eV). Typically, five scans were accumulated, and all of the binding energies were referenced to the C 1s line at 284.6 eV, which results from adventitious carbon. The ^{27}Al and ^{71}Ga solution NMR measurements were carried out in 5 mm quartz tubes using a Bruker DRX-500 spectrometer. Further details on the characterization are given elsewhere.[8]

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