AC-HRTEM Imaging of Counter-cations within Zeolitic Nanocavities

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Zeolites consist of covalently bonded aluminosilicate frameworks with regularly arranged nanocavities. Such structural feature brings us various applications of zeolites. As well as nanocavities, cation-exchangeability is also important feature of zeolites. Since the zeolitic frameworks have anionic sites corresponding to [AlO₂]⁻, counter-cations are placed in zeolitic nanocavities. Weakly bound counter-cations can be replaced with another cations even at room temperature. However, the structural information of counter cations within zeolitic nanocavities cannot be acquired in many cases, even though those are indispensable factor for their applications. Especially, structural relationship between polyvalent cations and anionic sites in zeolitic frameworks still has been unclear. Microscopic methods must be suitable for such structural analyses rather than diffractometric methods, because they are applicable also non-periodic structures. High-resolution transmission electron microscopy (HRTEM) has proven as a powerful technique for direct imaging of atomic structures. Recently direct imaging of counter cations of zeolites with an aberration corrected scanning transmission electron microscopy (AC-STEM) have been reported [1]. However, those observations are applicable only to heavy elements of counter cations. High-angle annular dark field (HAADF)-STEM imaging is disadvantageous for light elemental atomic columns. In this study, we tried direct observation of Na cations in NaA zeolite by aberration corrected (AC)-HRTEM. And ab initio molecular dynamics (AIMD) simulations were also performed in order to estimate behavior of Na cation [2].

Figure 1 shows an already known structure of cubic NaA zeolite [3]. There are three kinds of Na⁺ sites within NaA zeolite. Two important sites at 6-membered ring and 8-membered ring are named Na1 and Na2 respectively. Na⁺ at Na2 site are delocalized to four symmetric positions within an 8-membered ring. Commercially available NaA powder was observed by a JEOL JEM2200FS (200kV). Figure 2 shows positive Cs (PCS) image (Cs = +15 µm, Δf = −7 nm) and negative Cs (NCS) image (Cs = −15 µm, Δf = +7 nm). In order to eliminate random noise from AC-HRTEM image, Bragg filter was applied to both images, as shown in Fig. 2 (b, d). Compared with the PCS image, atomic columnar images were sharper in the NCS image. Na⁺ at Na2 sites were imaged as torus-like contrasts in the NCS image caused delocalization in an 8R. This delocalization at Na2 sites was supported also with results of AIMD simulations. Beside Na⁺ at Na2 sites, NCS image of Na⁺ at Na1 sites was streaky though it is localized at center of 6R. This was caused by overlapping of artifact caused by adjacent framework. Such artificial contrast can be reduced by choosing the appropriate projection. Fig. 3 shows NCS image of NaA zeolite projected along [111] direction. Along this projection, framework structure around Na1 site can be almost isotropic. Therefore, Na⁺ at Na1 were imaged as clear dots instead of streaks. This is the first result of direct imaging of Na⁺ captured in zeolitic nanocavities.

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References


FIG. 1. [100]-projected crystal structure of NaA zeolite [3]

FIG. 2. AC-HRTEM micrographs of [100]-projected NaA zeolite. (a) raw and (b) filtered PCS images and (c) raw and (d) filtered NCS images.

FIG. 3. AC-HRTEM micrographs of [111]-projected NaA zeolite of (a) raw and (b) filtered NCS images.