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Atomic resolution observation of zeolitic framework and captured cations using low-dose OBF STEM technique

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Zeolite is a common porous material with a unique framework structure and periodically aligned nanosized pores. Zeolites have a wide range of industrial applications such as gas separation, catalysis, and ion exchange. In these applications, the material properties emerge from the interaction between the host zeolitic framework and guest materials, such as molecules or ions. However, zeolites are very weak to electron irradiation, and it is difficult to analyze this interaction at the atomic scale using electron microscopy.

Recently, we developed an optimum bright-field scanning transmission electron microscopy (OBF STEM) technique for low-dose observations [1]. OBF STEM uses a segmented-type STEM detector and can achieve a dose efficiency that is two orders of magnitude higher than that of annular bright field (ABF) STEM, a conventional phase-contrast-based STEM technique. Furthermore, the OBF STEM images can be acquired in real-time in sync with the probe scanning, which makes low-dose data collection much easier. It was shown that low-dose OBF STEM can visualize the atomic structure of zeolitic frameworks for both T (=Si or Al) and O sites, even in lattice defects such as twin interfaces. Furthermore, the Na-captured LTA-type sample, which is one of the most beam-sensitive zeolites, was observed using OBF STEM, which visualizes extra-framework Na sites with a lower occupancy of approximately 1/4 [2].

We then applied the low-dose OBF technique to the Cs-exchanged LTA-type zeolites. Cs exchange is a very important application for the removal of hazardous chemicals, and understanding how Cs species are captured inside this material is of great importance. The atomic structures of the Na- and Cs-captured LTA samples were investigated using high resolution TEM (HRTEM) in the literature [3]. However, because of the higher Al content inside the LTA framework (Si/Al=1), which decreases the electron illumination resistance, the attainable spatial resolution remains limited. In this study, we observed Cs-LTA zeolites using the OBF STEM technique with high spatial resolution (~1 Å) under low-dose conditions, with the aim of revealing the interactions between host zeolitic frameworks and captured guest cations.

We prepared Cs-exchanged LTA-type zeolite samples using the ion-exchange procedure of a commercially available Na-captured LTA zeolite sample with a CsCl aqueous solution. The Cs-LTA sample was gently crushed using an agate mortar and then dispersed onto a TEM grid with a carbon support film. We then observed the Cs-LTA sample using the OBF STEM technique with aberration-corrected STEM equipped with a segmented detector. To suppress the irradiation damage, the probe current was set to 0.16 pA, which is more than two orders of magnitude lower than the usual STEM observation conditions.

Figure 1(a) shows the OBF STEM image of the Na-LTA zeolite sample. The LTA-type has a cubic shape framework, and eight-membered rings (8MRs) can be observed along the [100] zone-axis. In Na-LTA-type zeolites, the Na cations captured inside the 8MRs split into four sites, with an occupancy of approximately 1/4 [4]. In addition to the clear visualization of the T and O atomic sites inside the LTA framework, the OBF image shows a slight contrast around the center of 8MR, corresponding to the captured Na cations [2]. We then observed the Cs-captured sample from the [100] zone-axis using OBF STEM, as shown in Figure 1(b). The OBF image contrast at the center of the 8MRs changed into a distinct sharp one compared with the Na-LTA case, indicating that the captured Cs cations were rigidly confined into the LTA framework instead of splitting into multiple sites with low occupancy. This observation agrees well with the literature using HRTEM and density functional theory (DFT) calculations [3], showing the capabilities of OBF STEM to directly observe captured cation sites inside zeolites at the atomic scale.

We applied a low-dose OBF STEM technique to the Cs-exchanged LTA-type zeolite samples. The atomic structure was clearly visualized for not only the LTA framework structures but also the captured Cs sites, identifying the different behavior of the captured cations in comparison to the Na-LTA case. This result shows that the OBF STEM technique is promising for the atomic-scale analysis of zeolites, including extra-framework cations.

Graphic:

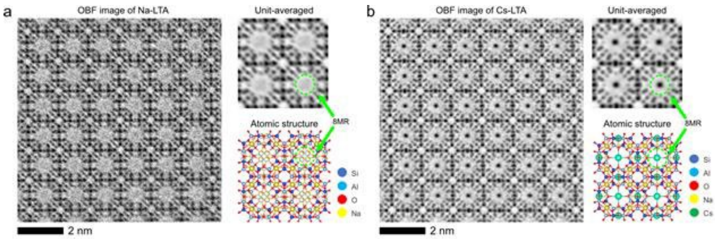

Figure 1. OBF STEM images of (a) Na- and (b) Cs-LTA zeolites. The experimentally acquired raw images, their unit-averaged OBF images, and corresponding atomic structure models are shown, respectively.

Keywords:

OBF-STEM, low-dose, zeolite, counter-cation

Reference:

[1] K. Ooe et al., Ultramicroscopy 220 (2021) 113133.
[2] K. Ooe et al., Science Advances 9 (2023) eadf6865.
[3] K. Yoshida et al., Microporous and Mesoporous Materials 259 (2018) 195-202.
[4] J.J. Pluth and J.V. Smith, Journal of American Chemical Society 102 (1980) 4704-4708.