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Anomalous interaction between propylene and Ag cation in zeolites

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Recently, Ag-exchanged zeolite X (Ag-X) membrane was found to be promising for propylene/propane separation [1]; however, the separation mechanism providing the high C3H6 selectivity is still unclear. To elucidate this mechanism, it is essential to identify the positions of the Ag cations in the zeolite X framework, and to clarify the adsorption behavior of C3H6 on Ag-X by molecular modeling. In this study, in situ synchrotron X-ray powder diffraction of Ag-X was measured, and the positions of Ag cations were identified by the Rietveld and MEM analyses, and then the obtained structure was used to understand the adsorption mechanism of C3H6 by ab initio molecular dynamics (MD) simulation.

In situ XRPD measurements were carried out at SPring-8 (BL02B2). The Rietveld analysis (RIETAN-FP) of the obtained XRPD pattern was successfully performed (Rwp = 7.7, S = 1.5), and the fractional coordinates (I–VI sites) and occupancies of Ag cations were identified. In addition, the electron distribution of the Ag cation was observed at each site by the MEM analysis (Dysnomia), which shows the validity of the Rietveld analysis. The only Ag cation sites that should contribute to C3H6 adsorption are the IV, V, and VI sites. The ratio of Ag cations in these sites to total Ag cations was 0.53. On the other hand, the number of adsorbed C3H6 molecules per Ag cation was estimated to be ca. 0.55 from the low relative pressure region of the C3H6 adsorption isotherm (313 K). In other words, if we assume that one C3H6 molecule is adsorbed per Ag cation, the ratio of Ag cations that can contribute to C3H6 adsorption is 0.55, which is in good agreement with the result from the Rietveld analysis.

Ab initio MD simulation based on the Ag-X structure from the Rietveld method showed that the 12-membered ring channels of Ag-X were blocked by the adsorbed C3H6 molecules on Ag cations and the C3H6 molecules diffused by hopping between the Ag cations. This blocking should prevent the diffusion of propane inside Ag-X, which does not have a specific interaction with the Ag cation and contribute to the high C3H6 selectivity of the Ag-X membrane. The most interesting finding revealed by this ab initio MD simulation is that the Ag cations exhibit extremely specific motion, resembling the role of a “pump”that releases and diffuses the adsorbed C3H6.

References:

1. M. Sakai et al., ACS Appl. Mater. interfaces 12 (2020) 24086–24092; 11 (2019) 4145–4151.

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