Dynamics, Geometry, and Electronic State of Single Ag(I) Site in MFI Zeolite Efficient for Xe Adsorption/Separation

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Xe adsorption/separation technology is needed for expanding the application of Xe existing in the air with only 0.087 ppm.[1, 2] Here, we report MFI zeolite containing a high concentration of single Ag(I) sites capable of Xe separation with 100% selectivity from Kr and O_2 under the near practical condition (**Figure 1**). We designed this material through the environmentally benign ion-exchange procedure. Only the evacuation at around 473 K allowed us to activate this material and use it for Xe adsorption/separation applications. The adsorption site was identified as the single Ag(I) site by a combination of FTIR spectroscopy using CO as a probe molecule, wavelet transform EXAFS, differential adsorption heat of Xe, ^{129}Xe NMR spectroscopy, energy calculation with DLPNO-CCSD(T) method, ^{129}Xe chemical shift calculation at DLPNO-MP2 method, ab initio molecular dynamics simulation, and Kohn-Sham molecular orbital analysis. It was shown that the single Ag(I) site captures the Xe atom via Xe-5p→Ag(I)-5s donation interaction. This driving force originates from the superior acidic property of the Ag(I) ion, endowed by the coordination with the framework AlO_4 tetrahedra in the zeolite. Since the valence orbital energies of Kr are lower than those of Xe, the Kr-4p→ Ag(I)-5s donation interaction is not so strong. Thus, the single Ag(I) zeolite formed in zeolite selectively interacts with Xe even under the co-presence of Kr and enables the selective Xe capture. The present work provides atomic-level insights into how we can create the Xe adsorption/separation functionality using the local geometry of the porous materials.

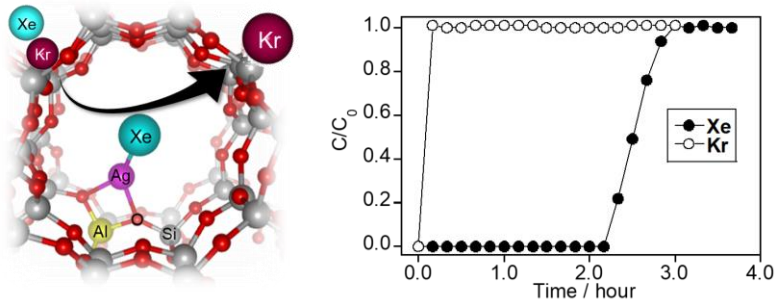

Figure 1. (left) Schematic view of the Xe/Kr separation over the single Ag(I) site in MFI zeolite via the formation of the stable Ag(I)–Xe complex. (right) Breakthrough curves of Xe and Kr observed on Ag(I)/MFI at 298 K under the 50 ppm Xe/ 500 ppm Kr/ 200 kPa O_2 gas mixture.

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