Atomistic Simulations of CO2 and N2 Diffusion in Siliceous Zeolites

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To efficiently separate CO2 from multi-species gas streams, sorbents must have high CO2 selectivity, and CO2 mobility within the materials must not be a limiting factor. Zeolites are one attractive option as sorbents due to their variety of structures, availability, and thermal and chemical stability.

This work presents a series of studies of diffusion of CO2 and other relevant gases within all-silica zeolites.* In particular, we describe how diffusion of CO2 and N2, both as single components and as binary mixtures, in three zeolites with identical chemical composition but differing pore structures, silicalite, ITQ-3, and ITQ-7, was studied using atomistic simulations. In all materials CO2 diffuses slower than N2 but otherwise the behavior of these gases within ITQ-7 and silicalite is quite different than within ITQ-3. In ITQ-7 and silicalite, the loading dependence of diffusion is very similar for CO2 and N2, the apparent activation energies for diffusion of each adsorbate are similar in the two materials, and the diffusion properties of adsorbed mixtures can easily be understood. In contrast, none of these are true within ITQ-3. Free energy and potential energy profiles are used to uncover the roots of these differences. The preferential sites of adsorption for CO2 and N2 are the same within ITQ-7 and silicalite but not within ITQ-3. In ITQ-3, CO2 molecules preferentially adsorb in the windows that separate the material's cages, whereas for N2 this is the site of the largest barrier to diffusion. As a consequence CO2 hinders N2 diffusion very effectively. Our analysis suggests that this behavior might be common for adsorbates that interact strongly with a material that has narrow windows between cages.

In these projects, we aim to understand and characterize at the molecular level how carbon dioxide and other small gas molecules behave in pores of zeolites. The behavior of gas mixtures within adsorbents such as zeolites is hard to determine experimentally; this presents a clear opportunity for atomistic computer simulations studies as the ones outlined above to contribute to the search for useful materials. Furthermore, this research offers a singular opportunity to gain fundamental understanding to assess and guide the design and identification of zeolites for selective separations of CO2 from complex gas streams in a variety of industrial processes.

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