Atomistic Simulations of CO_2 and N_2 in Silica Zeolites: the impact of pore size and shape

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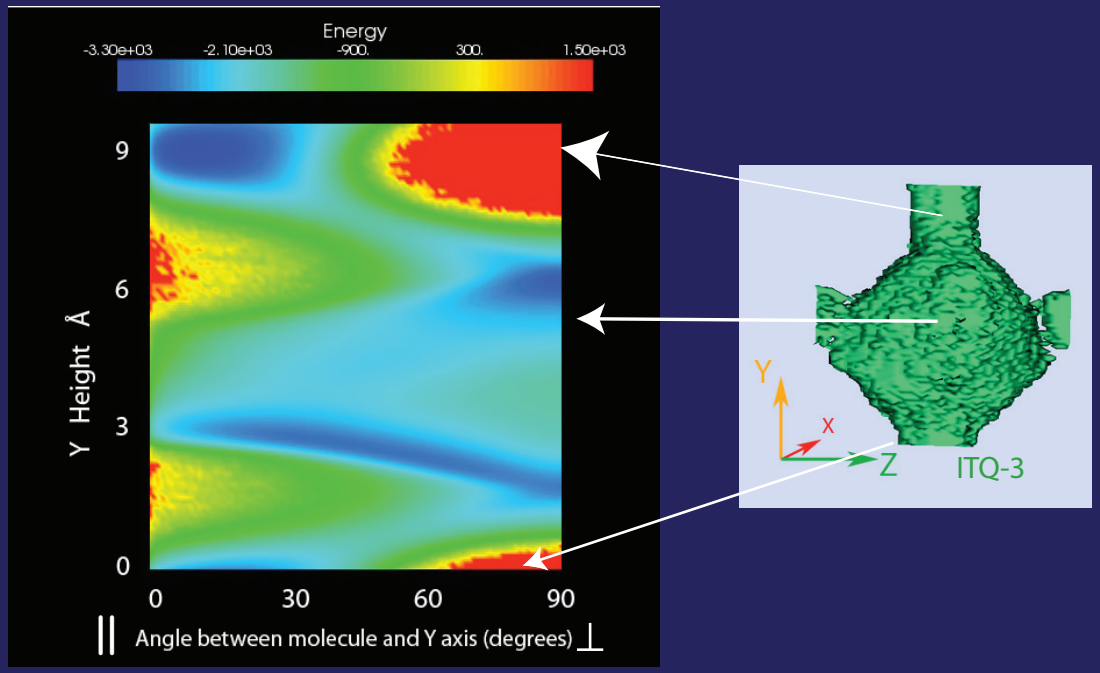
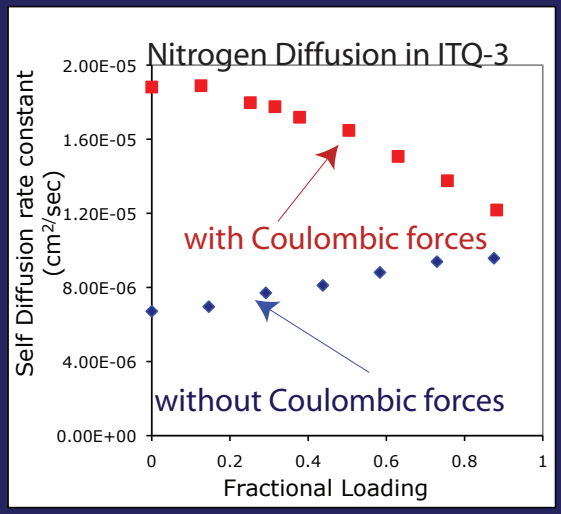
To efficiently separate CO_2 from multi-species gas streams, sorbents must have high CO_2 selectivity. Zeolites are one attractive option due to their variety of structures, availability, and thermal and chemical stability. We use atomistic modeling techniques to understand and characterize at the molecular level how carbon dioxide and other small gas molecules behave in pores of a variety of zeolites to aid in the identification of adsorbents selective for CO_2.

To investigate the influence of pore geometry on adsorption, selectivity, and diffusion we simulate the behavior of CO_2, N_2 and CO_2/N_2 mixtures within zeolites with identical chemical composition (SiO_2) but different structures. We have shown that the details of the behavior depend greatly on the geometry of the different zeolites. In particular, within zeolites with large cages connected by narrow channels CO_2's and N_2's behavior is unique and quite different from that of species without quadrupole moment.





ITQ-3 is a zeolite with cages connected by narrow channels that very selectively adsorbs CO_2 over N_2. The free energy profile (above) shows that the path a CO_2 molecule traverses as it diffuses in the y-direction is very much determined by the rugged landscape. This path requires molecular re-orientation which results in a barrier to diffusion located -peculiarly- at the entrance to the narrow channels rather than the channel itself.

The behavior of N_2 in these materials is also quite unexpected: when coulombic interactions are neglected diffusion rates decrease, contradicting the usual assumption that weaker interactions should result in faster diffusion. The solution to this puzzle lies in the diffusion free energy profiles. These profiles (not shown) indicate that when coulombic forces are present the interaction of N_2 with the walls in the narrow pores is so attractive that the free energy barrier to diffusion, located at these "bottlenecks", becomes smaller. Free energy profiles can also be used to understand the different dependence of diffusion rate on loading seen in the graph above.