

Studying adsorption in microporous materials: Influence of pore topology and specific interaction sites

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In this contribution, I will discuss some recent results of molecular simulation studies of adsorption in microporous materials using different levels of theory. In the first part, I will concentrate on an investigation addressing CO₂ adsorption and CO₂/N₂ mixture adsorption in all-silica models of zeolite frameworks. Since only few zeolites are actually available in their all-silica form, it was the main aim of this project to gain insights into the relationships between pore topology and affinity for CO₂. Grand-canonical Monte Carlo simulations were carried out to predict adsorption isotherms, and simulation snapshots from these simulations were used to identify those structural regions in which the CO₂-zeolite interaction is particularly strong.¹ The results obtained for an initial set of 18 topologies were taken as a basis to develop criteria to identify other topologies that might exhibit promising CO₂ adsorption properties. In the derivation of these criteria, we used the concept of natural tilings to decompose each framework into fundamental building blocks. Simulations for additional frameworks identified via this approach revealed very high CO₂ uptakes and CO₂/N₂ selectivities for some cases.²

The second part of this contribution will deal with computational investigations of guest molecules in porous structures using dispersion-corrected density-functional theory (DFT-D). In particular, we studied the interaction of cation-exchanged silicoaluminophosphate SAPO-34 (chabazite-type structure) with C₂ and C₃ hydrocarbons.³ Alkaline, earth alkaline, and transition metal cations were considered, and a detailed analysis of the electron density difference was performed to develop a better understanding of the dominant interactions. Furthermore, we used the difference in interaction energy obtained for unsaturated and saturated hydrocarbons in order to predict which cations should be most beneficial for alkene/alkane separations. In a separate study, the interaction of CO₂ and H₂ with the *sod*-type zeolitic imidazolate framework ZIF-8 (a metal-organic framework) and various substituted derivatives was predicted using a similar methodology.⁴ Here, different adsorption sites in the structure were considered, and the impact of the substituent on the interaction energy at each site was analysed in detail. Finally, we used the DFT-D results to draw some conclusions regarding the impact of the substituent on the hydrogen storage and CO₂/H₂ separation properties.

References:

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