UNIVERSITEIT GENT

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Modelling gas separation in zeolites and MOFs: Understanding the role of pore topology and specific interaction sites

LECTURES

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Modelling gas separation in zeolites and MOFs: Understanding the role of pore topology and specific interaction sites

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Molecular simulation methods are a widely employed method to study the adsorption of gases and their mixtures in microporous materials, such as zeolites and metal-organic frameworks (MOFs). Topics of particular relevance include those related to gas storage (hydrogen, methane) and gas separation (removal of carbon dioxide, separation of alkane/alkene mixtures). This contribution will report recent simulation results, emphasising the interplay between structural properties and adsorption behaviour. The first part will focus on the impact of zeolite topology on the CO_2/N_2 separation properties, studying siliceous zeolites as model systems. The second part will deal with the peculiar aspect of gas adsorption at coordinatively unsaturated metal sites in MOFs.

In the simulation study of siliceous zeolites, a new, semi-empirical parameter set is introduced in order to achieve a more accurate representation of electrostatic interactions: Here, the point charges representing the zeolite framework are obtained from density-functional theory (DFT) calculations, using the REPEAT method. Together with empirical Lennard-Jones parameters, this parameter set allows for an unambiguous decomposition of the total interaction into an electrostatic and a dispersive part. The parameters are used to predict CO_2/N_2 mixture adsorption in a variety of siliceous zeolites, permitting the calculation of working capacities and adsorption selectivities. For those systems that exhibit a high CO_2/N_2 selectivity, the carbon dioxide adsorption sites are investigated in detail. It is shown how specific building units that lead to a high affinity for CO_2 can be identified, and the concept is corroborated by performing additional calculations for other zeolites that incorporate these building units. Finally, it is discussed how the concept can be extended to zeolites with extra-framework cations, which are more relevant for real-world applications.

The second part of this contribution deals with the adsorption of small molecules at the coordinatively unsaturated copper sites of MOFs with Cu_2 paddle wheels, specifically $Cu_3(btc)_2$ (btc = 1,3,5-benzenetricarboxylate). Initially, it is shown how simulations using standard force-field parameters fail to predict the hydrogen adsorption isotherm and the preferred adsorption sites in this system. A pragmatic approach that uses low-level DFT calculations to obtain improved parameters for the Cu-H_2 interaction is then presented. It is shown how the new parameters, despite neglecting some significant interactions in the DFT calculations, lead to a massively improved description of the adsorption isotherm. A conceptually similar strategy is employed for propylene, where some additional aspects must be considered due to the size of the molecule. Finally, some (tentative) DFT results for the interaction of functionalised Cu_2 paddle-wheel systems with adsorbed molecules are presented.