Ninth Triennial Congress of the WORLD ASSOCIATION OF THEORETICAL AND COMPUTATIONAL CHEMISTS
WATOC 2011

MONTE CARLO SIMULATIONS TO UNDERSTAND "BREATHING" PHENOMENON OF METAL ORGANIC FRAMEWORKS

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Metal Organic Frameworks (MOFs) are a new class of porous materials synthesized from metal clusters connected by organic linkers. One of the promising applications of MOFs is carbon capture from fuel gasses, where CO_2 is adsorbed in the pores of the material. In this presentation, we explore framework flexibility as a possible mechanism for selective and reversible CO_2 adsorption by means of Monte Carlo simulations.

Most MOFs are fairly rigid structures, in the sense that they undergo small changes in volume when external stress is applied. Typical volume changes are of the order of a few percent only. Nevertheless, some MOF materials have an unexpectedly high flexibility and impressively shrink or swell under pressure, temperature or adsorption changes. A well-known example is MIL-53, a structure that shows volume changes of over 40%. In an adsorption experiment, the gas pressure is gradually increased while the amount of adsorbed material in the pores is measured. For MIL-53, the measured adsorption isotherm shows interesting features: when MIL-53 is brought into contact with a gas at increasing pressure, the framework's pores constrict, while at even higher pressures, the pores return to their original geometry. The process, referred to as "breathing", is reversible and shows hysteresis.

Based on Monte Carlo runs, we have constructed a mean-field model to gain insight in the thermodynamics of the breathing. The model shows that the behavior is the result of the different factors at play in a (N_{mof},μ,P,T) ensemble (constant amount of MOF material, constant gas chemical potential, constant gas pressure, constant temperature), i.e. the entropy, the pressure and the resistance given by the adsorbed particles. We further investigate how the MOFs' flexibility could be exploited to design an efficient pressure swing setup.