Free energy profile of "breathing" flexible porous frameworks

An Ghysels,[1,2] Veronique Van Speybroeck,[1] Michel Waroquier,[1] Berend Smit[2]

[1] *Center for Molecular Modeling, Ghent University, Belgium*
[2] *Chemical Engineering Department, University of California - Berkeley, CA, USA*
an.ghysels@ugent.be

Metal-organic frameworks (MOFs) are porous crystals consisting of metal clusters connected by organic linkers. The variety in the metal chemistry and the channel topology offer a broad range of applications, from specific catalytic activity to gas separations for green chemistry. A particularly interesting feature of some MOFs like the MIL-53 material, is their ability to "breathe": under the influence of external stimuli like temperature or adsorbate molecules in the pores, the crystal undergoes a large and reversible structural change with a volume decrease of up to 40%. Such materials could be used for temperature-dependent chemical sensors, for energy-efficient repetitive selective gas adsorption, or for chemical-potential driven medicine release in the human body.

To fully exploit the capabilities of the flexible MOFs, a better understanding of the material's behavior under external stimuli is necessary. We have investigated what is the most stable shape of the empty unit cell using periodic DFT calculations that include dispersion corrections. The effect of temperature has been estimated by adding an entropic contribution based on the Einstein oscillator model. Moreover, the insertion of CO_2 and CH_4 adsorbate molecules in the pores of MIL-53(Cr) is studied with a thermodynamic free energy model. This has lead to a phase diagram (large-pore phase versus narrow-pore phase) as a function of the external control variables.

References:

1. Long, J.R. and Yaghi, O. M. *Chem. Soc. Rev.*, 38 (2009) 1213-1214
2. Serre, C., Millange, F., Thouvenot, C., Nogues, M., Marsolier, G. Louer, D.A., Ferey, G. *J. Am. Chem. Soc.*, 124 (2002) 13519-13526
3. Walker, A.M., Civalleri, B., Slater, B., Mellot-Draznieks, C., Cora, F., Zicovich-Wilson, C.M., Roman-Perez, G., Soler, J.M., Gale., J.D. *Angew. Chem. Int. Ed.,* 49 (2010) 7501-7503