Thermodynamics of framework breathing: free energy model for flexible porous crystals

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The porous metal-organic framework MIL-53(Cr) may vary its cell parameters drastically while retaining its crystallinity under influence of external stimuli such as temperature and adsorption of guest molecules [1]. The hysteresis of 'framework breathing' between the large-pore and narrow-pore shapes of the material is not yet fully understood in the thermodynamic picture [2, 3, 4]. We propose a generic parametrized free energy model for the osmotic thermodynamic potential including three contributions: host free energy, guest-guest interactions, and host-guest interactions [5]. Our approach allows to determine the stable states on a two-dimensional free energy landscapes as a function of shape and adsorbed amount of guest molecules. The new model correctly reproduces the structural transitions along the experimental CO_2 and CH_4 isotherms. Assuming a first order phase transition and collective behavior, our model moreover successfully explains the adsorption versus desorption hysteresis as a consequence of the creation, stabilization, destabilization, and disappearance of a second free energy minimum. Finally we decouple the gas chemical potential μ and mechanical pressure P as two independent thermodynamic variables and predict the complete (μ, P) phase diagram for CO_2 adsorption in MIL-53(Cr).

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