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Microscopic Theory of Hysteretic Hydrogen Adsorption in Nanoporous Materials

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Recently, significant progress has been made in the development of novel microporous materials such as metal−organic frameworks (MOFs).[1] Because of their high surface areas, MOFs are ideal materials for gas storage application such as for hydrogen storage.[2] Out of recent intensive studies, one of the phenomena,[3] that is the hysteretic H_2 adsorption observed in some of the MOF systems, has attracted much attention. This is because, for certain ranges of applied pressure, the amount of H_2 molecules sorbed by the host is higher on desorption than on adsorption. Thus, H_2 molecules that are adsorbed at high pressures can be stored at lower pressures beyond the equilibrium density. The H_2 hysteresis was first observed by Férey et al.[3a] in the MOFs of metal-(1,4-benzenedicarboxylate) [MIL-53 or M(BDC), M = Cr, Al]. The hysteretic H_2 adsorption and related kinetics were systematically studied by Zhao et al.[3b] in nanoporous MOFs. More recently, a study by Choi et al.[3d] elegantly demonstrated wide H_2 adsorption hysteresis and its sensitive dependence on temperature in the MOF of Co(1,4-benzenedipyrazolate) [Co(BDP)]. Although both M(BDC) and Co(BDP) consist of one-dimensional channels with nanoscale pores, they exhibit very different structural dynamics during H_2 adsorption/desorption; the M(BDC) is nearly intact after hydrogenation, whereas the desolvated, thus collapsed, Co(BDP) becomes open as external H_2 pressure increases. The observed hysteresis in the flexible Co(BDP) was attributed to the adsorption-induced structural change, i.e., pore opening/closing.[3d] The hysteresis in the rigid M(BDC), however, implies that an intrinsic hysteretic mechanism may be involved other than the pore opening/closing.

Hysteresis, as a characteristic history-dependent response of non-equilibrium systems to changes of external forces, is a prevalent phenomenon in many ostensibly different systems such as ferromagnets, Li-ion batteries, and gas adsorbents. The external force (μ), i.e., magnetic field or chemical potentials of Li ions and gas adsorbates, drives the systems to have the equilibrium density (x) of spins, Li ions, or adsorbates, respectively. Usually the equilibration process in such systems is kinetically hindered, leading to the hysteresis. Because x and μ are *conjugate* variables of the free energy, one can analyze the thermodynamics of hysteresis in terms of either of these quantities.

In gas-adsorption experiments, the adsorbed gas density x at a given temperature T is regulated by an applied external pressure p. The pressure p and chemical potential μ of a gas reservoir have a simple thermodynamic relation, $\mu(T) = \mu_o(T) + k_BT \ln(p/p_o)$, where k_B and p_o are the Boltzmann constant and the standard-state pressure, respectively. As p exponentially depends on μ and T,[4] it is reasonable that p-x hysteresis was very sensitive to temperature changes.[3d] In contrast, the adsorption curves as a function of μ or the μ-x isotherms at different temperatures are more or less converged to one with a hysteresis width $\Delta\mu$ of ~10 meV (Figure 1).[4]

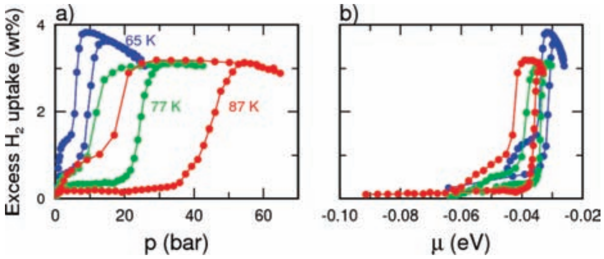

Figure 1. Hysteretic H_2 adsorption in Co(BDP) in p-x and μ-x isotherms. The data in (a) are taken from ref 3d.

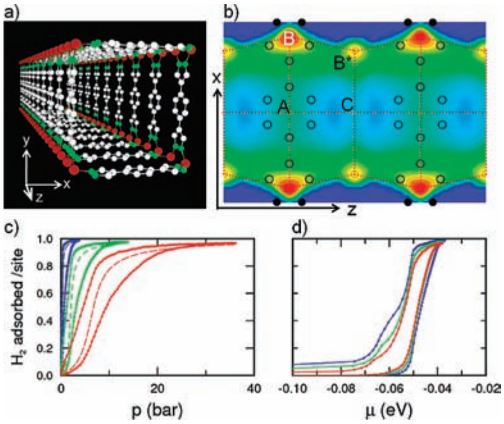

Figure 2. (a) A one-dimensional channel model of Co(BDP) MOF.[3d] (b) First-principles H_2 adsorption energy map on the BDP units in the Co(BDP). The positions of C and N atoms in the BDP are marked by open and filled circles, respectively. (c, d) Simulated isotherms of H_2 adsorption at 65 (blue), 77 (green), and 87 K (red).

Here, we present a microscopic theory of the hysteretic H_2 adsorption confined in small-pore systems. As a model system, we used an uncollapsed Co(BDP) MOF (Figure 2a) that is adopted from the Co(BDP)·2DEF·H_2O framework,[3d] but our main conclusions do not depend on details of MOF models as long as the H_2 adsorption is associated with small-pore diffusions.

Figure 2b shows the adsorption energy map for a H_2 adsorbate on the BDP units of the Co(BDP) MOF. The *ab initio* adsorption energy was calculated within the generalized gradient approximation (GGA) to the spin-polarized density-functional theory, as implemented in the PWSCF package.[5] To better describe the van der Waals interaction, we used recently developed pseudopotentials augmented with local atomic potentials.[6] Three different adsorption sites (A−C) were identified with adsorption energies (E_{ad}) of 81, 154, and 70 meV/H_2, respectively, for the H_2 orientation heading to the zx-plane (Figure 2b). The site denoted by B* (E_{ad} = 132 meV/H_2) corresponds to side-on adsorption to the different BDP units in the yz-plane. For N_2 molecules, we found much stronger adsorption with E_{ad} = 109 to 261

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meV/N_2, which explains why the N_2 adsorption occurs at lower pressures than the H_2 adsorption does.[3d]

To simulate the H_2 adsorption/desorption isotherms, we performed grand-canonical Monte Carlo (GCMC) simulations[7] using two-dimensional lattice models based on the identified adsorption sites A to C. The periodic $L_z \times L_x$ lattices were constructed by repeating the 2 × 8 unit cell along the z direction by $L_z/2$ times. The lattice has a short periodicity ($L_x = 8$) in the x direction associated with the small pore size of the channel. The free energy of the system was approximated by the Ising-like model,[7] where H_2 adsorption/desorption is described by spin flips under the effective external field given as a sum of chemical potential and adsorption energy. For better comparison with the experiment, the rescaled adsorption energy was used in GCMC.[4]

Two H_2-adsorption scenarios were simulated:

Open-Surface Dynamics. The adsorption sites are freely accessible by H_2 regardless of small pores, and thus the equilibration proceeds *via direct* exchange of H_2 between the lattice and external gas reservoir at given p and T. This may be able to happen if the H_2 diffusion along the pore channel is fast enough. Because the inter-H_2 interaction is very weak, the lattice model quickly arrives at its equilibrium within 25 Monte Carlo steps (MCS) *per site* in the GCMC simulations of $T = 77$ K. Thus, adsorption/desorption hysteresis is not observed as indicated by the dashed lines in Figure 2c. This corresponds to the cases of activated carbons[3b] and giant-pore MOFs,[2b] where no hysteresis is reported.

Small-Pore Dynamics. The Co(BDP) framework pores are too small (1 × 1 nm^2) to transport H_2. Thus, for the inner part of the MOF, the direct H_2 exchanges between the external reservoir and adsorption sites cannot occur frequently. Instead, during the adsorption cycle, H_2 molecules will diffuse through intersite hopping from near-surface regions to the inner part, whereas the diffusion occurs in the reverse way on the desorption cycle. To study the effect of the intersite diffusion on hysteresis, we divided the system by three parts: two surfaces of $L_z = 10$ lattice layers at each side and an encompassed bulk region with a channel length L_z. For a given p, the surface layers are almost instantaneously equilibrated with the reservoir as governed by the above open-surface dynamics. The H_2 diffusion (either surface-to-bulk or within bulk region) was simulated using Kawasaki dynamics,[7] in which molecules hop to adjacent unoccupied adsorption sites following the Metropolis algorithm. A similar approach was developed to investigate the dynamics of fluids in mesoporous glasses.[8] Figure 2c shows the simulated H_2 isotherms for $L_z = 1000$. Pressure was controlled at a constant sweep rate with a total simulation time of $\sim 2 \times 10^7$ MCS per site. At $T = 65$, 77, and 87 K, we obtained a similar size of hysteresis width $\Delta\mu$ (~10 meV) in the μ-x isotherm.

Based on the simulated (Figure 2c−2d) and measured (Figure 1a−1b) isotherms, the simple small-pore diffusion model captures most intrinsic features of the hysteresis, including the general temperature dependence in the p-x domain. However, we also notice some differences in theory and experiment. (1) The observed isotherms in Figure 1b show a down-shift of the adsorption chemical potentials for the increased temperatures. This can be explained in part by considering the vibrational entropy of the adsorbed H_2 molecules, which reduces the free energy of the adsorbates (and thus adsorption chemical potentials) with increasing T. (2) The measured H_2 adsorption in Co(BDP) occurs more abruptly than our simulations do. The simulated isotherms rather resemble those of the M(BDC), which is rigid during hydrogenation.[3a] So, the abrupt adsorption in the Co(BDP) and thus enhanced hysteresis can be attributed to the H_2-induced pore opening[3d] at high pressures.

Finally, we compare transient adsorption in open-surface and small-pore systems upon stepwise change of the external pressure at 77 K. With the equilibrium state ($x = 0.27$) at $p = 1.67$ bar as an initial state, we traced the transient adsorption at $p = 1.94$ bar until the system reaches 99% (open surfaces) or 90% (small pores) of the new equilibrium state ($x = 0.43$). For the open-surface dynamics, the necessary simulation time is nearly constant for various system sizes (L_z) ranging from 100 to 2000 (Figure 3). On the other hand, in small-pore systems such as Co(BDP), the equilibration time scales nearly quadratic with increasing the channel length. So, macroscale adsorbent systems can exhibit adsorption hysteresis during a finite rate pressure sweep (v). For instance, we estimated that a model system with 1-cm-long small-pore channels will show an isotherm with a hysteresis width $\Delta\mu$ of ~10 meV as in Figure 2, when the pressure sweep rate $v \approx 6$ mbar/s. Here, we used 1 MCS/site $= 1/[\omega_{H2} \exp(-\Delta E_d/k_B T)]$, where ω_{H2} is the oscillation frequency (10 THz) of H_2, ΔE_d is the diffusion energy barrier of 6 meV,[3d] and T is 77 K.

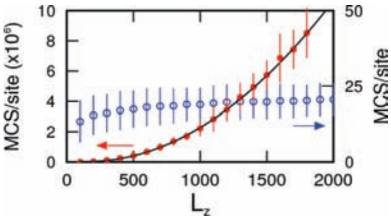

Figure 3. Characteristic equilibration time (MCS per site) for transient adsorption based on small-pore (filled circles) and open-surface dynamics (open circles) at 77 K, showing different scaling behaviors for the system size L_z. A solid line is a fitting of the small-pore data in a quadratic form.

In conclusion, we reveal that the hysteretic H_2 adsorption and its sensitive dependence on temperature are the intrinsic characteristics of diffusion-controlled small-pore systems. The hysteresis theory is generally applicable for other gas storages and Li-ion-based batteries and supercapacitors.

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Supporting Information Available: Simulation details of GCMC. This material is available free of charge via the Internet at http://pubs.acs.org.

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