Temperature-triggered gate opening for gas adsorption in microporous manganese formate†

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Microporous manganese formate shows temperature-triggered gate opening for nitrogen and argon adsorption, which is not due to a structural change of the framework but due to dynamic opening of the pore aperture and/or sufficient kinetic energy of the adsorbates to overcome a diffusion barrier above a critical temperature.

Metal–organic frameworks[1] (MOFs) with regular, controllable pore sizes and shapes, have attracted much attention in recent years because of their potential applications in many areas including gas storage,[2] separation and catalysis.[3] In particular, the potential utility of MOFs in storage, transportation, separation and purification of important industrial gases such as hydrogen,[2a–k] methane[2l–o] and acetylene[2p,q] has been well demonstrated. The effects of the size, shape and chemical nature of the pore wall on the gas sorption capacity and selectivity of MOFs have been investigated. Furthermore, X-ray diffraction and neutron scattering studies have been performed to elucidate gas binding sites inside the micropores.[2q,r,4] To design efficient MOFs for gas storage and related applications, nevertheless, we need to better understand the gas adsorption mechanism of MOFs. Herein we report the unusual temperature-dependent gas adsorption behavior of MOFs, which may be attributed to dynamic opening of the pore aperture and/or sufficient kinetic energy of adsorbates to overcome a diffusion barrier above a critical temperature.

Microporous metal formates $M(HCOO)_2$ (M = Mn^{2+} (**1**),[2c,5a] and Mg^{2+} (**2**)[2q,5e,6]) are low-cost, readily-synthesized MOFs with permanent porosity and high thermal stability.§ They have an isomorphous structure containing one-dimensional zigzag channels (Fig. 1) in which various guest molecules such as 1,4-dioxane and tetrahydrofurane (THF) can be included.[2c,5a,6] We have demonstrated that guest-free **1** selectively adsorbs gases with a small size such as H_2, CO_2 and C_2H_2.[2c,q] At 77 K, for example, **1** showed a type I adsorption isotherm for H_2 with a maximum uptake of 100 $cm^3\ g^{-1}$ at 1 atm, but no appreciable sorption of N_2 (Fig. 2) or Ar.[7] The selective gas sorption was ascribed to the small aperture (3.64 Å)[8] of the channels in **1** which discriminates gases with small kinetic diameters[9] such as H_2 (2.8 Å) from those with larger kinetic diameters[9] such as Ar and N_2 (3.4 and 3.64 Å, respectively).[2c] In extending this work to other metal formates, we expected that **2** would also show no appreciable sorption of N_2 since **2** has essentially the same crystal structure with a slightly *smaller* aperture of the channels (3.36 Å).[8] To our surprise, however, the nitrogen sorption measurement of **2** at 77 K revealed a type I isotherm with quick saturation at low pressures and a high uptake of N_2 (116 $cm^3\ g^{-1}$; 1.8 N_2 molecules per unit pore)[10] at 1.0 atm (Fig. 2, Fig. S1†). Puzzled by the totally different N_2 sorption behavior of **1** and **2** at 77 K, we decided to investigate the gas adsorption at higher temperatures. As far as N_2 sorption is concerned, **2** behaves like a typical microporous material: the amount of N_2 sorption decreased with increasing temperature. At 196 K, for instance, the N_2 uptake of **2** was 50 $cm^3\ g^{-1}$ or 0.8 N_2 molecules per unit pore at 1 atm (Fig. 2). Surprisingly, however, **1**, which did not adsorb N_2 at 77 K as described above, showed a significant uptake of N_2, 40 $cm^3\ g^{-1}$ or 0.8 N_2 molecules per unit pore, the same amount of the gas as **2**, at 196 K and 1 atm (Fig. 2).[11]

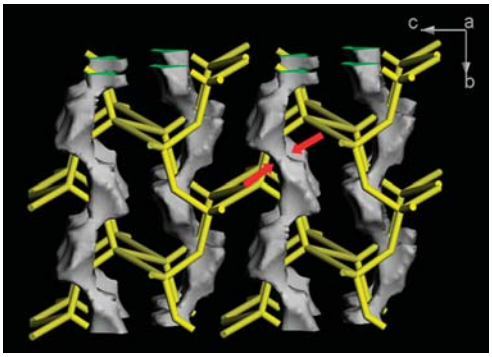

Fig. 1 1D zigzag channels with narrow necks (red arrow) in **1** and **2** (diameter 3.64 and 3.36 Å, respectively). Only M(II) centers are connected (yellow wire) to show the framework topology.

To better understand the unusual temperature dependent N_2 sorption in **1** we carried out a temperature-programmed

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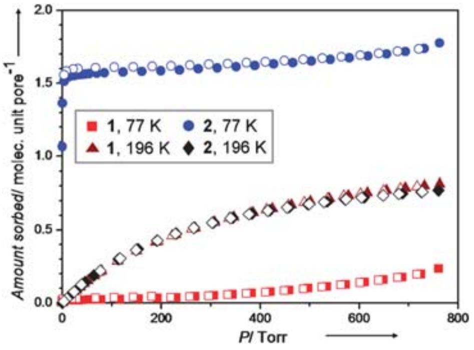

Fig. 2 Nitrogen sorption isotherm[10] for **1** and **2**: **1**, 77 K (squares), **1**, 196 K (triangles), **2**, 77 K (circles), **2**, 196 K (diamonds). Solid symbol = adsorption, open symbol = desorption.

desorption (TPD) study.¶ The N_2-TPD profiles of **1** and **2** are quite different as compared in Fig. 3. Most notably, the total amount of desorbed N_2 in **2** monotonously decreases with increasing adsorption temperature,[12] whereas that in **1** is insignificant until ~100 K, but increases until ~140 K and then drops off as the temperature further increases (Fig. 4), indicating that the gate opens around 110 K. Although the gate opening phenomenon in MOFs triggered by pressure has been well documented,[2r,13] this is a rare example of gate opening triggered by temperature in MOFs.[14,15]

We first thought the gate opening might be due to a temperature-triggered structural change. However, comparing the single crystal X-ray structure of **1** at 90 and 196 K revealed no significant change in the structure including cell parameters and pore size (Table S1†),[16] which indicated that the temperature-triggered gate opening is not due to a static structural change of the framework.[17] One explanation for the unusual behavior is that **1** has a "kinetically closed" pore[18] toward N_2, which becomes open at a high temperature. More specifically, above a critical temperature (~110 K in this case), (1) N_2 molecules have sufficient kinetic energy to overcome a diffusion barrier to diffuse into the channel,[9,15,18] and/or (2) the large amplitude lattice vibration opens the aperture dynamically to allow N_2 molecules to diffuse into the channel.[9,19] At present we do not know which factor is dominant, but both factors appear to be operative.

A similar temperature-dependent sorption behavior was observed for Ar in **1** (Fig. 4), which presumably has the same origin. However, it is interesting to note that **1** showed normal gas sorption behavior for O_2 despite the fact that the kinetic diameter[9] of O_2 (3.46 Å) is slightly *larger* than that of Ar (3.4 Å). Thus, the kinetic diameters proposed by Breck[9] and widely used in understanding the size-exclusive sorption behavior of porous materials with uniformly sized pores and channels, fail to explain the apparently contradicting selective sorption behavior of **1**. In fact, other parameters such as the minimum dimensions (MIN-1 and MIN-2) of molecules proposed by Webster *et al.*[20a] better explain the selective sorption of O_2 over Ar in **1** at a temperature below 140 K; the minimum dimensions of O_2 (MIN-1, 2.930 Å; MIN-2, 2.985 Å)[20a] are smaller than those of Ar (MIN-1, 3.51 Å; MIN-2, 3.63 Å).[20b]

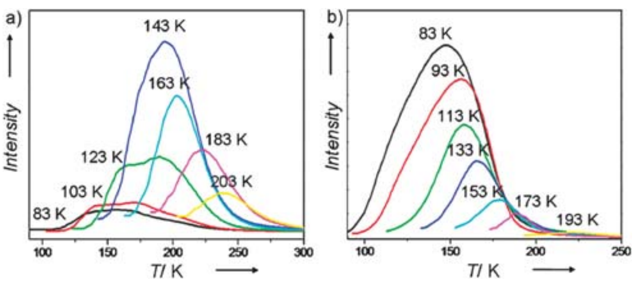

Fig. 3 Temperature-programmed desorption (TPD) profiles of N_2 for **1** (a) and **2** (b). The temperatures above the graphs indicate the gas sorption temperatures.

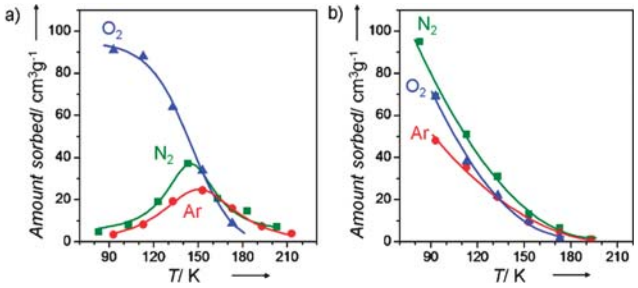

Fig. 4 Total amounts of gases desorbed for **1** (a) and **2** (b) as a function of temperature.

The nitrogen sorption of other metal formates $M(HCOO)_2$ ($M = Fe^{2+}$, Co^{2+}, Ni^{2+} and Zn^{2+}) at 77 K has been examined. Similar to Mg formate, all the transition metal formates except Mn formate (**1**) showed a type I isotherm at 77 K (Fig. S2† and ref. 5*b*,*d*). A careful inspection of the aperture sizes of the channels in the metal formates revealed that **1** has the *largest* aperture size (3.64 Å) (Table S3†). These observations raise the following questions. Despite the largest aperture size, why does only **1** show the temperature-triggered gate opening behavior? What is special about manganese formate? Although we do not have definite answers to the questions at the moment, we suspect that the framework of **1** may have the "least flexible" aperture among the series from the thermal (vibrational) motion point of view, or have an unusually high diffusion barrier from the kinetic point of view, leading to the unique temperature-dependent gas sorption behavior. To test this conjecture further studies, including vibrational analysis of the framework, and the temperature-dependent aperture-size distribution using *ab initio* molecular dynamics simulations, are in progress.

In conclusion, microporous manganese formate exhibits unusual temperature-dependent nitrogen and argon adsorption. It illustrates a temperature-triggered gate opening, which is not due to a structural change of the framework but presumably due to dynamic opening of the pore aperture and/or sufficient kinetic energy of adsorbates to overcome a diffusion barrier above a critical temperature. Such temperature-triggered gate opening/closing behavior of MOFs may find useful applications in gas separation and purification.

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Notes and references

§ **1**·1/3THF and **2**·1/3dioxane were synthesized according to our procedure published previously.[2c,q] **1**·1/3THF was evacuated at 150 °C for 2 days under dynamic vacuum, and **2**·1/3dioxane at 200 °C for 10 days under dynamic vacuum to remove the guests. Complete removal of the guests has been confirmed by elemental analysis and NMR.

¶ Low temperature temperature-programmed desorption (TPD) experiments were carried out in a fixed-bed tubular reaction system equipped with a specially designed heater for control between 77 K and 373 K and a thermal conductivity detector. The detailed procedure for TPD is described elsewhere.[21] Before TPD experiments, **1** and **2** were activated by heating slowly from rt to 200 °C under vacuum ($<10^{-5}$ Torr). After the gas adsorption (N_2, Ar and O_2) at a designated temperature, the sample was evacuated to remove the physisorbed gas at the same temperature under vacuum ($<10^{-2}$ Torr). Once the baseline of the integrator became stable, a TPD run was started with flowing He (carrier gas) at a heating rate of 10 K min^{-1} from 83 K to 300 K.

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8 The diameter corresponds to that of the largest probe atom, which can be fitted to the narrowest part of the channel based on the X-ray crystal structure at 90 K. Calculated with Materials Studio modeling software.

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10 A unit pore in **1** or **2** is defined by the pore occupied by a guest molecule (dioxane or THF) before activation, and surrounded by 3 formula units.

11 In our previous paper (ref. 2*c*), we reported no appreciable sorption of N_2 at 195 K. Later, however, we found that the sample of **1** was not fully degassed after a CO_2 sorption study. The new N_2 sorption data presented here were obtained with freshly prepared, fully evacuated samples and confirmed by repeated experiments with samples from different batches of **1**.

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