Coordination Polymers

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Kinetic Gate-Opening Process in a Flexible Porous Coordination Polymer**

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Recently, there has been growing interest in the nature of flexible and dynamic porous coordination polymers (PCPs) that reversibly change their structures and properties in response to guest adsorption.[1] After one of the present authors predicted their importance,[2] many flexible PCPs have been prepared in only a decade. So-called structural dynamism has been identified as a key principle for high selectivity,[3] accommodation,[4] and molecular sensing.[5] One of the most interesting phenomena in flexible PCPs is stepwise adsorption caused by the guest-induced framework transition.[3,4,6] In particular, a gate effect occurs when the framework structure changes during the adsorption process from a closed structure to an open one at a specific pressure, which generates an S-shaped or sigmoidal adsorption profile. The onset pressure at which the gates of the closed-structure grooves become open is referred to as the gate-opening pressure (P_{go}) and is related to the structural transformation of the host framework.[7] Interestingly, the value of P_{go} shows a guest dependency.[8] This difference between adsorbates suggests that flexible PCPs have potential applications in many fields, including separation, sensors, and switching materials. In particular, small gaseous adsorbates, such as O_2, Ar, and N_2, are attractive targets for research, first because the differences in sorption behavior between such similar gas molecules have attracted wide commercial interest for processes such as air separation, and also because of scientific interest as a result of their simple structures and small differences in physical properties.[9]

However, several questions remain unanswered. Why does adsorption not occur below P_{go}? What determines P_{go}? How can the difference in P_{go} for different guests be enhanced? Generally, a sigmoid isotherm with small hysteresis has been understood to be the result of cooperative phenomena.[10] Several flexible PCPs actually show isotherm discontinuities at high relative pressure, with large hysteresis, where kinetics would play an essential role.[11,12] In spite of their importance, few attempts have been made to determine the kinetics of the gate effect.[11,13] Herein, we present the synthesis, crystal structure, and gas sorption properties of a flexible PCP, $\{[Cd(bpndc)(bpy)]\}_n$ (**1**; bpndc = benzophenone-4,4′-dicarboxylate, bpy = 4,4′-bipyridyl), which shows a large difference in P_{go} between O_2, Ar, and N_2 (Figure 1). To understand the mechanism behind the differences between similar gases, we treat this phenomenon with the aid of a new diffusion model in which adsorption proceeds through the formation of an intermediate. Kinetic analysis revealed that the formation of the intermediate, which can be described as a gate-opening process, governs P_{go} and enhances the difference between gases.

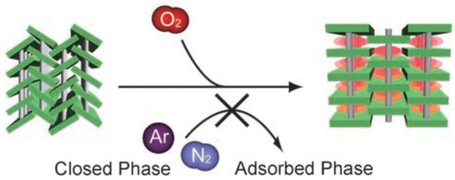

Figure 1. Adsorption at low pressure.

The solvothermal reaction of $Cd(NO_3)_2{\cdot}4H_2O$, H_2bpndc, and bpy in dimethylformamide (DMF) produced the solvated framework compounds $\{[Cd(bpndc)(bpy)](dmf)(H_2O)\}_n$ (**1**⊃Solvents). Single-crystal X-ray analysis demonstrated that cadmium ions are connected by bpndc to produce 1D double-chain structures of $\{[Cd(bpndc)]\}_n$ along the *c* axis, and are linked by bpy along the *b* axis to give a 2D sheet motif (Figure 2a and b). The 2D layers are mutually interdigitated to create a 3D assembled framework (Figure 2c). This is similar to previously reported PCPs that show a flexible nature.[14] The 3D structure of **1**⊃Solvents consists of a

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

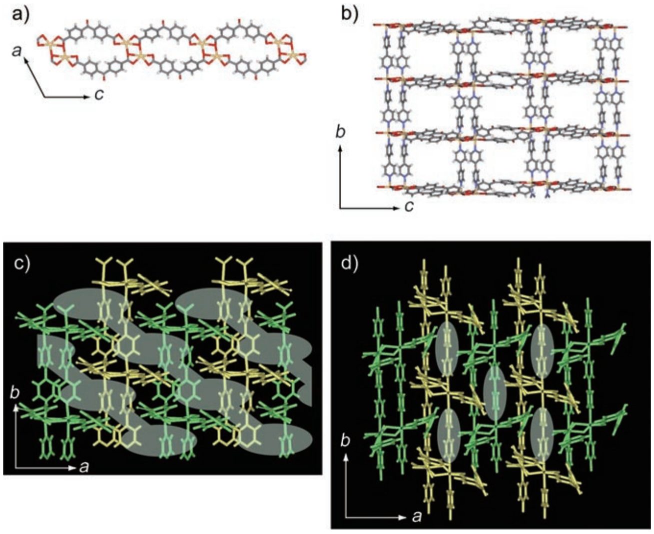

Figure 2. Crystal structures of **1**⊃Solvents and **1** showing a) 1D double chain of $\{[Cd(bpndc)]\}_n$, b) 2D layer structure of **1**⊃Solvents (gray, purple, red, and yellow are C, N, O, and Cd, respectively), c) 3D assembled structure of **1**⊃Solvents, and d) 3D assembled structure of **1**. Solvents are omitted for clarity. Cavities and windows are highlighted.

unidirectional set of nonintersecting linear arrays of cavities ($12\times7\times4$ Å^3) with narrow connecting windows (with cross sections of about 2×6 Å^2) along the [110] or [1−10] directions, as shown in Figure 2c and Figure S3a in the Supporting Information. The void volume V_{void} is 29.4% of the total crystal volume, as calculated using the Platon program.[15] The solvent-accessible volume of the cavity is 403.4 Å^3, which includes two water and two DMF molecules.

Thermogravimetric (TG) analysis of **1**⊃Solvents showed the release of solvent molecules with increasing temperature up to 140°C, to produce the guest-free phase **1** (Figure S1 in the Supporting Information). No further weight loss was observed between 140 and 230°C, which indicates that the guest-free phase was stable. As the X-ray powder diffraction (XRPD) pattern of **1** shows sharp diffraction peaks (Figure S2 in the Supporting Information), the porous framework was largely maintained, even without guest molecules, and **1** retains its single-crystallinity. Single-crystal diffraction data were then collected. The crystal structure of **1** was solved in space group $P2_1/a$, which is different from the space group for **1**⊃Solvents ($C2/c$). The c axes in **1** correspond to half of the c axes in **1**⊃Solvents. The cell volume per Z value decreases by 14.3%, which indicates a dramatic contraction of the framework. Crystal structure analysis revealed that the 2D layer motif is maintained. On the other hand, shrinking of the layer gap along the a axis by about 0.9 Å occurred, which is attributable to a gliding motion of the 1D double-chain moieties (Figure 2d).

The interesting aspect of the desolvated structure is the presence of interlayer noncovalent interactions. There is close contact between hydrogen atoms of bpndc and the ketone oxygen or aromatic carbon atoms of neighboring bpndc (d(H–O) = 2.89 Å, d(H–C) = 3.44 and 3.53 Å). The void spaces are separated by interlayer interactions, and zero-dimensional cavities are created, isolated from each other, with a size of about $6\times5\times3$ Å^3. The solvent-accessible volume of this cavity is 132.6 Å^3 and V_{void} is 11.3% of the total crystal volume, as estimated by Platon.[15]

We measured the adsorption isotherms of O_2, Ar, and N_2 by volumetric adsorption (Belsorp-18, BEL Japan) at various temperatures (77, 90, and 100 K) to study the effect of structural transformation. The isotherms at 90 K showed a sudden increase at gate-opening pressures P_{go} of O_2, Ar, and N_2 at 3.9, 40.1, and 55.3 kPa, respectively, and attained saturation (Figure 3a).[16] It is surprising that the small

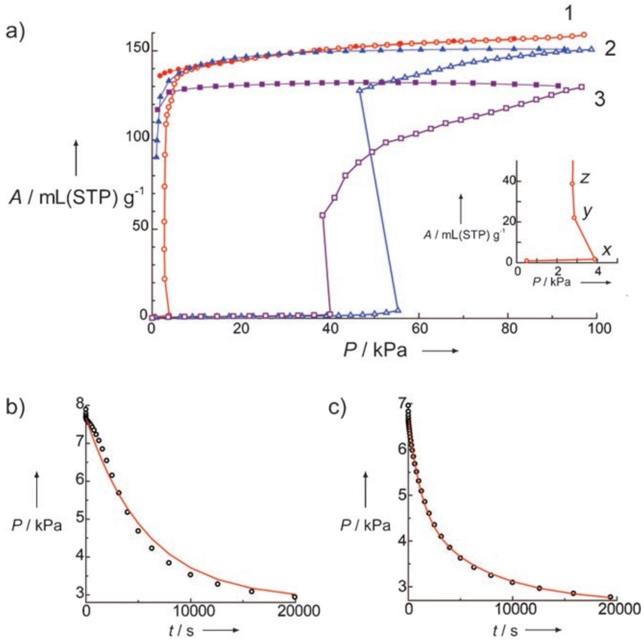

Figure 3. a) Sorption isotherms for adsorbates in **1** at 90 K. 1) O_2 adsorption (red open circles) and desorption (red filled circles); 2) N_2 adsorption (blue open triangles) and desorption (blue filled triangles); 3) Ar adsorption (purple open squares) and desorption (purple filled squares). Inset: O_2 adsorption isotherm at low pressure. b,c) Comparison of calculated profiles for the pressure versus time graphs from the DE model (red lines) with the experimental profiles (○) for b) point x to point y of the inset in (a), and c) point y to point z.

difference in physical properties between these gas molecules should have such a large effect on P_{go}. On the other hand, desorption isotherms showed adsorption volumes decreasing at lower pressures and large hysteresis loops in the N_2 and Ar isotherms. Adsorption measurements at 77 and 100 K showed that P_{go} increased as the measurement temperature increased (see the Supporting Information). The adsorption volumes of O_2, Ar, and N_2 at 90 K were 158.8, 129.5, and 150.7 mL g^{-1}, respectively, when the pressure approached 100 kPa. These isotherms reveal that the gas molecules cannot diffuse into the isolated cavities of **1** at pressures below P_{go}. At P_{go}, the gates of the grooves of **1** open and the structure is transformed from closed phase to open phase.

To observe the structure transition of **1** under gas pressure, we performed in situ XRPD experiments under various gas atmospheres (Figure S4 in the Supporting Information). Cell parameters of the O_2-adsorbed form were determined by Le Bail analysis to be $a = 15.1588(4)$, $b = 11.7324(1)$, and $c = 30.9112(6)$ Å, $\beta = 104.430(3)$, and $V = 5324.10$ Å^3, with space group $P2_1/c$. This is close to the cell parameters of **1**⊃Solvents ($a = 15.52(3)$, $b = 11.79(2)$, $c = 30.92(6)$ Å; $\beta = 103.87(2)$, $V = 5492$ Å^3), which indicates that the O_2-adsorbed form is open and expanded. Powder patterns for N_2- and Ar-adsorbed forms showed structures similar to those of the O_2-adsorbed form.

To clarify the origin of the shape of the adsorption isotherms and the large difference in P_{go} between similar gas molecules, we analyzed the adsorption phenomena from a kinetic point of view. Figure 3 b and c show how pressure decays, during O_2 adsorption, from point x to point y and from point y to point z, as labeled in the inset of Figure 3 a. In these volumetric measurements, pressure change is proportional to the adsorption volume. Within these interdigitated structures, there are barriers as a result of diffusion both through the windows and along the pore cavities.[14,17] This can be described by a double-exponential (DE) equation.[18] The pressure decay from point y to point z follows the DE equation with good accuracy, thus indicating that the kinetic behavior of this process is dominated by diffusion (Figure 3 c). On the other hand, the pressure decay curve at P_{go} from point x to point y has an inflection point and cannot be described by the DE model (Figure 3 b). This type of decay curve has been reported in flexible PCPs[19,20] and the pseudo-plateau at the beginning of this curve suggests the existence of a certain "growing process".

To describe the decay curve that includes the pseudo-plateau, another diffusion process could be introduced. In this model, adsorption proceeds through the formation of an intermediate [see Figure 4; Eq. (1)]:

$$\mathrm{C} \xrightarrow{k_{go}} \mathrm{I} \xrightarrow{k_{d1}, k_{d2}} \mathrm{A} \tag{1}$$

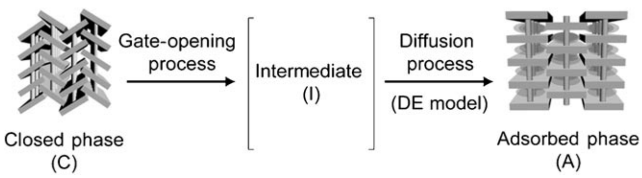

Figure 4. The gate-opening (GO) model.

Here, a closed phase C is transformed to an intermediate I, which can adsorb gas molecules. The formation of I can be referred to as the gate-opening process. We will suppose that gas molecules adsorb only on the crystal surface during the gate-opening process, and therefore that the adsorption volume during this process is quite small and does not affect the pressure. The gate-opening process (C to I) can be described by a first-order rate law (with rate constant k_{go}). The intermediate I, formed from C, adsorbs gas and decays to the adsorbed form A. This diffusion process can be described by the DE model (with rate constants k_{d1} and k_{d2}). We call this model the gate-opening (GO) model. To describe pressure decay in volumetric measurements using the GO model, we introduce the GO equation where P is the pressure at time t, P_e is the pressure at equilibrium, and P_i is the initial pressure [see the Supporting Information for its derivation; Eq. (2)]:[21]

$$P = \left(\frac{k_{go} \exp(-k_{d1} t) - k_{d1} \exp(-k_{go} t)}{2\,(k_{go} - k_{d1})} + \frac{k_{go} \exp(-k_{d2} t) - k_{d2} \exp(-k_{go} t)}{2\,(k_{go} - k_{d2})} \right) (P_i - P_e) + P_e \tag{2}$$

We collected kinetic data by one-point volumetric adsorption measurements. The pressure P_i of an adsorbate was introduced into the evacuated sample cell and allowed to equilibrate at P_e. We monitored the pressure change with time for various values of P_i at different temperatures. A comparison of the profile calculated according to the GO equation with the experimental profile for O_2 adsorption at 90 K with $P_i = 11.8$ kPa is shown in Figure 5 a. It is apparent that the GO model provides a good description of the kinetics for adsorption with structure transformation.

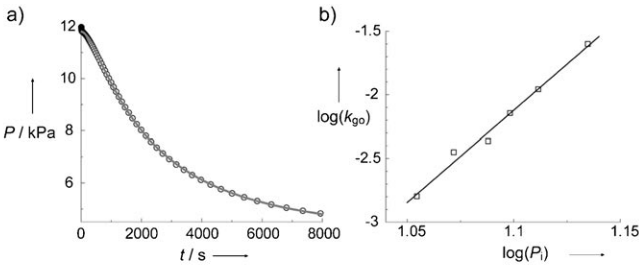

Figure 5. a) Variation of pressure with time for adsorption of O_2 at 90 K with $P_i = 11.8$ kPa (○) and the calculated profile for the GO model (gray line). b) Plot of the logarithm of k_{go} (O_2 adsorption at 90 K) against the logarithm of P_i.

The kinetic data obtained from one-point measurements of O_2 adsorption on **1** at 90 K with various initial pressures ($P_i = 11.3$, 11.8, 12.5, 12.9, and 13.6 kPa) also followed the GO model, thus affording an experimental estimate of k_{go}. The kinetic data are given in the Supporting Information. A plot of the logarithms of the experimental k_{go} values against the logarithms of P_i is a straight line with slope 14.5 (Figure 5 b), which indicates that we could write $k_{go} = k'_{go}(P_i)^a$ in the measurement region (where a is the slope of the line). The abruptly changing adsorption isotherms of **1** are explained by the large pressure dependency of k_{go}, as follows. When P_i is much lower than P_{go}, the gate-opening process does not proceed (k_{go} is nearly zero) and the diffusion process does not start. When the pressure is close to P_{go}, however, k_{go} increases very rapidly and adsorption then occurs. Adsorption does not occur below P_{go} because gate opening is required before the diffusion process can begin. In other words, the kinetic behavior of the gate-opening process determines P_{go}.

We also measured the adsorption kinetics of **1** with different gases (O_2, N_2, and Ar) at 90 K. The adsorption of Ar on **1** with $P_i = 45.3$ kPa followed the GO model well ($k_{go} = 4.7 \times 10^{-4}$, $k_{d1} = 1.3 \times 10^{-5}$, $k_{d2} = 3.4 \times 10^{-6}$). The pressure decay of N_2 for various values of P_i (59.0, 72.5, and 90.4 kPa) followed the GO equation, but with large errors because the gate-opening process is slow and pressure decay affects k_{go}.[21] The small k_{go} values for N_2 and Ar adsorption indicate that the P_{go} of N_2 and Ar are dominated by the gate-opening process. If this process did not exist, adsorption would occur under lower pressure conditions. The gate-opening process dramatically increases the difference in P_{go} between similar gases. Comparison of the kinetic data shows that the order of k_{go} for the same pressure is $O_2 > Ar > N_2$, which is consistent with the guest dependency of P_{go}. This order is also consistent with that of the boiling points (90.2, 87.3, and 77.4 K for O_2, Ar, and N_2, respectively), which suggests that the intermolecular interaction force of the guest molecules governs this process.

We also carried out one-point O_2 adsorption measurements at various temperatures (88, 90, 92, and 95 K with P_i in the range 11.80–11.93 kPa). As the temperature increased, the value of k_{go} decreased, which is consistent with the temperature dependency of P_{go} (see the Supporting Information). Such anti-Arrhenius behavior was observed in clathration reactions of an organic host.[13] Anti-Arrhenius behavior is usually indicative of a multistep mechanism (see the Supporting Information).[22] The features of the gate-opening process can be summarized as follows: 1) the adsorption volume is quite small; 2) k_{go} shows a strong dependency on pressure (or concentration of adsorbate); 3) an adsorbate with a higher boiling point provides a larger k_{go}; and 4) k_{go} decreases with increasing temperature. These features should be attributable to the condensation of adsorbate on a crystal surface, and some structural transformation might then be induced.

In conclusion, we have prepared a flexible PCP that shows abrupt changes in its adsorption isotherms with guest-dependent gate-opening pressure. We also demonstrated that the kinetics of the gate-opening process provides for large differences in onset pressure between similar gas molecules. These kinetic analyses indicate that the gate-opening process could be associated with the condensation of adsorbate on a crystal surface. Modification of a crystal surface could provide new mechanisms for adsorption phenomena. A detailed understanding of the gate-opening process would be the key to further fine-tuning of the gas-adsorption performance of PCPs.

Experimental Section

Synthesis of **1**⊃Solvents and **1**: A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (1.0 g, 3.24 mmol), H_2bpndc (0.88 g, 3.26 mmol), and bpy (0.50 g, 3.20 mmol) was suspended in DMF (40 mL) and heated in a round-bottomed flask at 120 °C for 1 day. A colorless crystalline precipitate **1**⊃Solvents was formed. These crystals were collected, washed with ethanol, and dried in a vacuum at 120 °C, which resulted in guest-free solid **1**. Elemental analysis of **1** calcd (%) for $C_{25}H_{16}CdN_2O_5$: C 55.93, H 3.00, N 5.22; found: C 55.68, H 3.40, N 5.30.

Physical measurements: TG analyses were performed using a Rigaku Thermo plus TG 8120 apparatus in the temperature range between 303 and 773 K in a N_2 atmosphere and at a heating rate of 10 K min^{-1}. Elemental analyses were performed on a Thermo Finnigan EA1112 apparatus. XRPD data of **1**⊃Solvents and **1** were collected on a Rigaku RINT-2200HF (Ultima) diffractometer with $Cu_{K\alpha}$ radiation. In situ synchrotron radiation experiments were performed at SPring-8 with the approval of JASRI as a Nanotechnology Support Project of MEXT (Proposal No. 2006A1677/BL02B2). The adsorption isotherm for N_2, Ar, and O_2 was measured with BELSORP-18 volumetric adsorption equipment attached to a closed-cycle helium cryostat (BEL Japan, Inc.).

X-ray structure determination: Measurements were made on a Rigaku Mercury CCD system with $Mo_{K\alpha}$ radiation. In all cases, the structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 (SHELXL-97).[23] All non-hydrogen atoms were anisotropically refined, while all hydrogen atoms were placed geometrically and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom.

Crystal data for **1**⊃Solvents: $C_{28}H_{23}CdN_3O_7$, $M_r = 625.89$, monoclinic, space group $C2/c$, (#15), $a = 15.52(3)$, $b = 11.79(2)$, $c = 30.92(6)$ Å, $\beta = 103.87(2)$, $V = 5492(18)$ Å^3, $Z = 8$, $T = 173$ K, $\rho_{calcd} = 1.514$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.845$ cm^{-1}, $2\theta_{max} = 50.0°$, $\lambda(Mo_{K\alpha}) = 0.71070$ Å, 11161 reflections measured, 4726 unique, $4227 > 2\sigma(I)$ were used to refine 347 parameters, no restraints, $R(R_w) = 0.0450$ (0.0908), GOF = 1.124. Crystal data for **1**: $C_{25}H_{16}CdN_2O_5$, $M_r = 536.80$, monoclinic, space group $P2_1/a$, (#14), $a = 13.758(7)$, $b = 11.753(5)$, $c = 15.648(7)$ Å, $V = 2352.8(18)$ Å^3, $Z = 4$, $T = 223$ K, $\rho_{calcd} = 1.515$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 0.966$ cm^{-1}, $2\theta_{max} = 50.0°$, $\lambda(Mo_{K\alpha}) = 0.71070$ Å, 12226 reflections measured, 3978 unique, $3366 > 2\sigma(I)$ were used to refine 298 parameters, no restraints, $R(R_w) = 0.0997$ (0.2175), GOF = 1.202. CCDC-671180 and CCDC-671181 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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