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Storage and Sorption Properties of Acetylene in Jungle-Gym-Like Open Frameworks

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: The acetylene-sorption properties of six porous coordination polymers (PCPs), $[M_2(L)_2(dabco)]_n$ (dabco = 1,4-diazabicyclo[2.2.2]octane, M = Cu^{2+} (**1**), Zn^{2+} (**2**), L = 1,4-benzenedicarboxylate (bdc; **1a**, **2a**), 1,4-naphthalenedicarboxylate (ndc; **1b**, **2b**), 9,10-anthracenedicarboxylate (adc; **1c**, **2c**)), were investigated. The acetylene sorption isotherms of **1** and **2** measured at 195 K are of type I and show a steep increase at low relative pressures. The sorption properties of carbon dioxide at 195 K were also investigated. Compounds **1** and **2** showed a large difference in onset pressure between acetylene sorption isotherms, although the difference between the carbon dioxide sorption isotherms is not so significant. In particular, **2c** displayed a remarkable affinity for acetylene. The acetylene sorption isotherm at 298 K showed that the adsorption amounts for **2c** and **2b** at 298 K, 1 atm (101 and 106 $mL\,g^{-1}$, respectively) were higher than those of other conventional porous materials. Notably, of the compounds **1** and **2**, the porous crystals **2c** had the highest affinity for acetylene.

Keywords: acetylene · adsorption · copper · microporous materials · zinc

Introduction

The ability to store gas molecules is a typical property of porous materials. Porous coordination polymers (PCPs) constructed from transition-metal ions and bridging organic ligands have resulted in new types of microporous materials suitable for gas storage.[1] One of the advantages of PCPs over conventional porous materials is that their pore size, shape, and functionality can be systematically and predictably controlled through synthetic modification of the organic component.[2] Various PCPs have been studied as gas-storage materials (for gases such as hydrogen,[3] methane,[4] and carbon dioxide[5]), and these results could provide promising guidelines for the design of gas-storage materials.

Acetylene gas is an important starting material for fine chemical products[6] and electric materials.[7] Acetylene is well-known to be a highly reactive molecule: it cannot be compressed above 0.2 MPa as it would explode in the absence of oxygen, even at room temperature.[8] High-density storage of highly pure acetylene at low pressure by a nonvolatile solid matrix could be a key research subject for the preparation of advanced organic materials. Recently, several PCPs showed high levels of selective sorption of acetylene molecules compared with a very similar molecule, carbon dioxide.[9] Although selective acetylene uptake is an attractive function, the adsorbed amounts were small. The adsorption potential becomes deeper with decreasing pore width.[10] On the other hand, a larger pore volume is essential for enhancing the sorption amount. Frameworks exhibiting both a

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deep adsorption potential and large pore volume are desired to facilitate acetylene adsorption at ambient temperature and low pressure. Despite several investigations into PCPs as acetylene-storage materials, systematic and quantitative studies on their sorption properties have not yet been accomplished to clarify a strategy for designing PCPs with high acetylene-storage capacities.

The aim of this paper is to identify the factors that affect acetylene adsorption in the ambient-pressure region. We measured the acetylene sorption properties of six PCP compounds $[M_2(L)_2(dabco)]_n$ (dabco = 1,4-diazabicyclo-[2.2.2]octane, L = dicarboxylate, M = Cu^{2+} (**1**), Zn^{2+} (**2**)), whose pore size and surface properties can be systematically controlled by changing the bridging dicarboxylate ligands, L (Table 1 and Figure 1).[11] Adsorption experiments showed that **2c** (L = 9,10-anthracenedicarboxylate (adc)) had the highest acetylene adsorption capacity at 298 K, 1 atm and thus the highest affinity for acetylene.

Results and Discussion

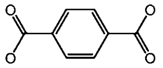
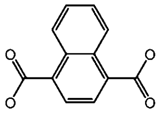
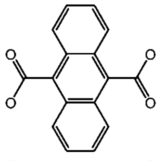
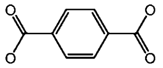
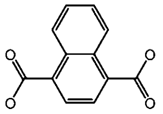
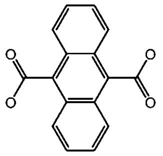
Porous Structures

We prepared host PCP compounds **1** and **2** by the method in the literature.[11b,c,12] The crystal structures of **1** and the corresponding **2** are almost the same, in which two-dimensional (2D) layered structures based on paddle-wheel units are linked with dabco as a pillar ligand (Figure 1). The use of 1,4-benzenedicarboxylate (bdc) gave hosts **1a** and **2a** with a flat and smooth one-dimensional (1D) channel along the *c* axis (pore size = 7.5 × 7.5 Å^2).[12] On the other hand, **1b** and **2b** (L = 1,4-naphthalenedicarboxylate (ndc)) contain narrower 1D undulating channels (pore size = 5.7 × 5.7 Å^2) because of steric hindrance of the naphthalene moiety.[11c,12] In the cases of **1c** and **2c** (L = adc), the large anthracene unit fills the channels, thus resulting in a nonporous undulating 2D sheet. The undulating 2D sheets are connected by dabco pillars to afford 2D channels with cross-sections of 4.8 × 4.3 Å^2.[12,13] The micropore volume (V_m) estimated from N_2 adsorption as well as the crystalline density (ρ_{calcd}) estimated from the cell parameters of **2** are summarized in Table 2. Because of the large size and the alternating orien-

Abstract in Japanese:

$[M_2(L)_2dabco]_n$ (dabco = 1,4-diazabicyclo[2.2.2] octane; L = dicarboxylate; M = Cu^{2+} or Zn^{2+}) の組成を持つ多孔性配位高分子 (PCP) のアセチレンガス吸着挙動を系統的、定量的に評価した。特に、M = Zn^{2+}, L = 9,10-anthracene dicarboxylate の組成を持つ PCP は、室温低圧でアセチレンを 101 ml g^{-1} 吸着し、アセチレンに対して高い親和性を有することを見出した。また、Clausius-Clapeyron 式による吸着等温線の解析から、錯体への吸着が物理吸着によるものであることが示唆された。

Table 1. The PCP compounds $[M_2(L)_2(dabco)]_n$ investigated.

Compound	M	L
1a	Cu^{II}	 bdc
1b	Cu^{II}	 ndc
1c	Cu^{II}	 adc
2a	Zn^{II}	 bdc
2b	Zn^{II}	 ndc
2c	Zn^{II}	 adc

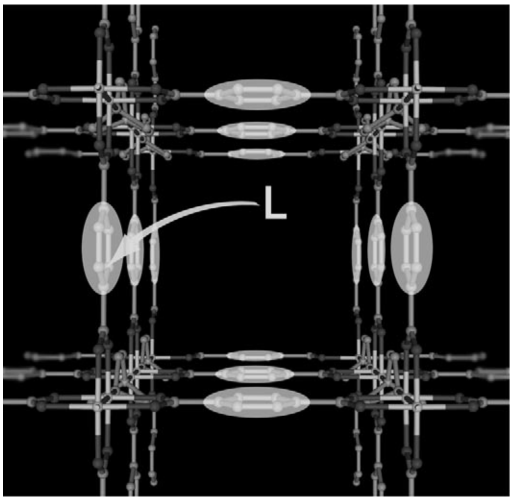


Figure 1. Schematic view of the three-dimensional frameworks of $[M_2(L)_2(dabco)]_n$.

Table 2. Micropore volume (V_m) and crystalline density (ρ_{calcd}).

Compound	V_m [cm^{3}g^{-1}]	ρ_{calcd} [g cm^{-3}]
1a	0.73[a]	0.82[c]
2a	0.75[b]	0.83
1b	0.44[a]	0.97[c]
2b	0.52[b]	0.97
1c	0.28[a]	1.14[c]
2c	0.31[a]	1.15

[a] Obtained from Dubinin–Radushkevich analysis of N_2 adsorption isotherms. [b] Obtained from the literature.[11c] [c] Obtained by using the cell parameters of the corresponding **2**.

tation of adc and ndc, the V_m values were significantly decreased.

Acetylene and Carbon Dioxide Sorption at 195 K

Acetylene sorption isotherms of **1a** and **2a** measured at 195 K are shown in Figure 2a. The equilibrium data exhibit type-I isotherms and show no apparent hysteresis on desorption. The carbon dioxide adsorption isotherms of **1a** and **2a** at 195 K are also of type I (Figure 2b). Acetylene adsorption isotherms for **1b** and **2b** at 195 K are shown in Figure 2c. There is a step in the isotherm for **2b** at low relative pressure ($P/P_0 = 0.035$–0.038). In contrast, the acetylene adsorption isotherm for **1b** was of type I and showed no evidence of any steps in the isotherm. The adsorption isotherms for carbon dioxide on **1b** and **2b** at 195 K are shown in Figure 2d. Comparison of the adsorption isotherms for **1b** and **2b** shows that there are steps in the isotherms at different relative pressures (**1b**: $P/P_0 = 0.35$–0.60; **2b**: $P/P_0 = 0.45$–0.48). The step in the sorption isotherm for **1b** and **2b** could be attributed to a change in the naphthalene rotation mode, as with benzene adsorption of **2b**.[14] The naphthalene ring of the dicarboxylate ion in the guest-free framework of **2b** is disordered over four positions. Solid-state ^{2}H NMR studies revealed that when benzene molecules are densely adsorbed inside the pores at high relative pressure, the adsorbed molecules could interfere with the free rotation of the naphthalene rings, thus resulting in a stepwise sorption isotherm. Similar behavior might be observed in acetylene and carbon dioxide adsorption. Acetylene sorption isotherms for **1c** and **2c** and carbon dioxide sorption isotherms for **1c** and **2c** are shown in Figure 2e and f, respectively. There is a step in the isotherm for acetylene on **1c** at low relative pressure ($P/P_0 = 0.0057$–0.0063), but the other isotherms showed no apparent step. Several flexible PCPs showed such isotherm discontinuities with hysteresis, which was accompanied by a reversible and significant structure change.[15] The flexible and dynamic properties of **1** are quite different from those of **2**.[16] The origin of the step on the isotherm of **1c**, although still unclear, is most likely to be structural change of the host framework.

The adsorption amount of adsorbates on microporous materials can be compared by using the Dubinin–Radushkevich (DR) equation [Eq. (1)]:

$$\ln W = \ln W_0 - (A/\beta E_0)^2 \qquad (1)$$

in which W is the amount of adsorption at a relative pressure P/P_0, W_0 is the saturated amount of adsorption, β is the affinity coefficient, E_0 is the characteristic adsorption energy, and A is the Polanyi adsorption potential defined in Equation (2).[17]

$$A = RT \ln(P_0/P) \qquad (2)$$

At higher relative pressure (P/P_0), the DR plot has a linear relationship, from which the values of βE_0 and W_0 were obtained. The micropore and thermodynamic parameters from the DR analysis are summarized in Table 3. The introduction of a larger aromatic ring resulted in a significant decrease in the adsorption amount (W_0), which may be easily understood and expected from the crystal structures and micropore volume (V_m) obtained from the N$_2$ adsorption data.

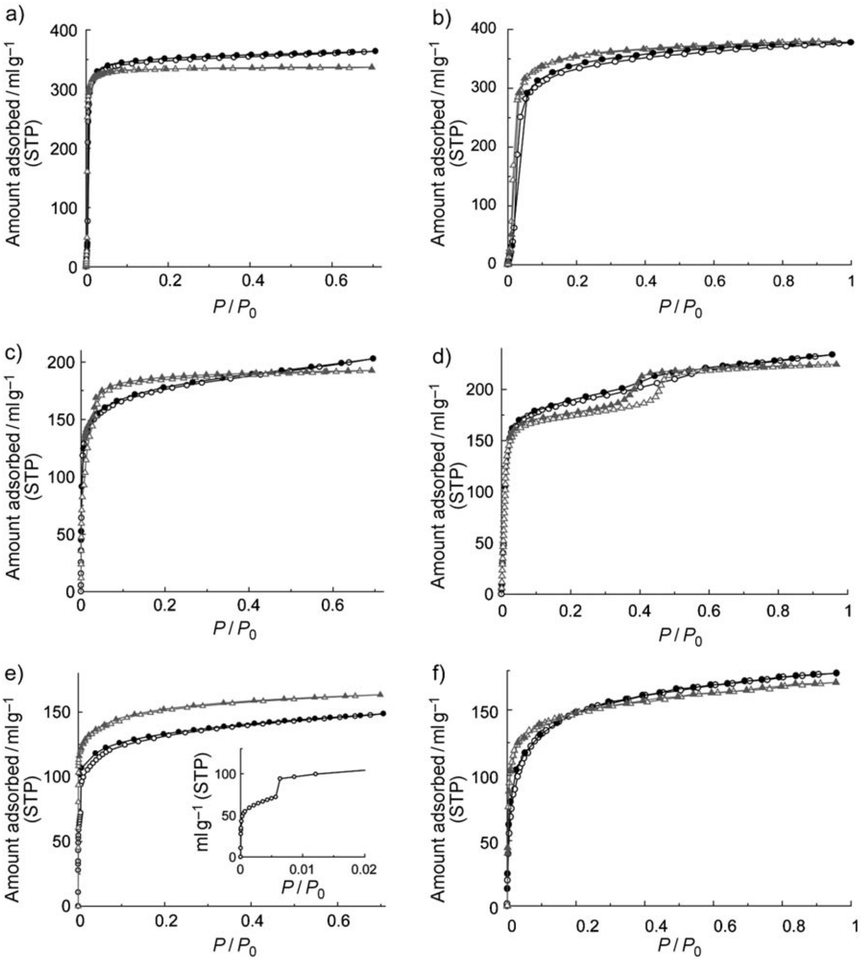


Figure 2. Comparison of sorption isotherms at 195 K for a) acetylene on **1a** (circles) and **2a** (triangles), b) carbon dioxide on **1a** (circles) and **2a** (triangles), c) acetylene on **1b** (circles) and **2b** (triangles), d) carbon dioxide on **1b** (circles) and **2b** (triangles), e) acetylene on **1c** (circles) and **2c** (triangles), and f) carbon dioxide on **1c** (circles) and **2c** (triangles). Open symbols = adsorption, solid symbols = desorption. Inset of e): Acetylene adsorption for **1c** in the low-relative-pressure region.

Table 3. Microporous parameters of **1** and **2** for acetylene and carbon dioxide adsorption from DR analysis.

Adsorbent	Adsorbate	P/P_0[a]	W_0 [mL g^{-1} (STP)]	βE_0 [kJ mol^{-1}]
1a	C_2H_2	0.023–0.15	354.2	20.2
2a	C_2H_2	0.0094–0.034	345.2	22.1
1b	C_2H_2	0.0044–0.031	176.3	14.1
2b	C_2H_2	0.0017–0.027	191.0	10.2
1c	C_2H_2	0.031–0.080	134.0	12.6
2c	C_2H_2	0.00049–0.0072	132.6	27.5
1a	CO_2	0.091–0.26	356.3	10.1
2a	CO_2	0.037–0.23	373.7	11.5
1b	CO_2	0.024–0.19	194.6	12.4
2b	CO_2	0.021–0.28	180.8	13.8
1c	CO_2	0.0061–0.15	163.8	8.0
2c	CO_2	0.010–0.19	152.5	12.3

[a] Pressure range for DR analysis.

Although the graphical presentation of adsorption isotherms shown in Figure 2 is suitable for demonstrating stepwise sorption and comparison of total adsorption amount, this form is not practical for displaying the characteristic features at relative pressures below 0.01. As shown in Figure 3, the use of the Polanyi adsorption potential A (given by [Eq. (2)]) instead of the normal pressure scale displays adsorption data at low pressures much better and demonstrates clearly the difference in the affinity for the adsorbates. The plot of the amount adsorbed against the adsorption potential is often called the characteristic adsorption curve.[17] Because A is proportional to the logarithm of the relative pressure, the potential at initial adsorption corresponds to the onset pressure. A comparison of characteristic adsorption curves in Figure 3 and Figure S1 in the Supporting Information shows that the order of affinity for acetylene and carbon dioxide at initial adsorption is **2c**>**1c**>**2b**≈**1b**>**2a**>**1a**. Interestingly, these PCPs show a large difference in onset pressure between acetylene sorption isotherms, although the difference for the carbon dioxide sorption isotherms is not so significant. In particular, **2c** shows a remarkable affinity for acetylene, because at very low pressures (i.e., $A > 15$ kJ mol^{-1}), the amount adsorbed on **2c** is much higher than for the rest. Generally, the quite narrow micropore, whose width is correct for the size of the adsorbate molecule, has a very deep potential well for the guest and is effective for adsorption in the low-relative-pressure region.[10] The order of the affinity for the adsorbate is consistent with the pore size of the adsorbents. Moreover, the relative pressure at which micropore filling occurs is also dependent on polar groups on the surfaces or interaction sites.[18] Therefore, the origin of the high affinity of **2c** for acetylene is most likely not only the micropore effect but also acetylene–anthracene interactions, because the polarizability of anthracene is known to be $\alpha = 25.4\times10^{-24}$ Å^3, which is much larger than that of benzene or naphthalene.[19] The difference in metal ions may also affect the polarizability.

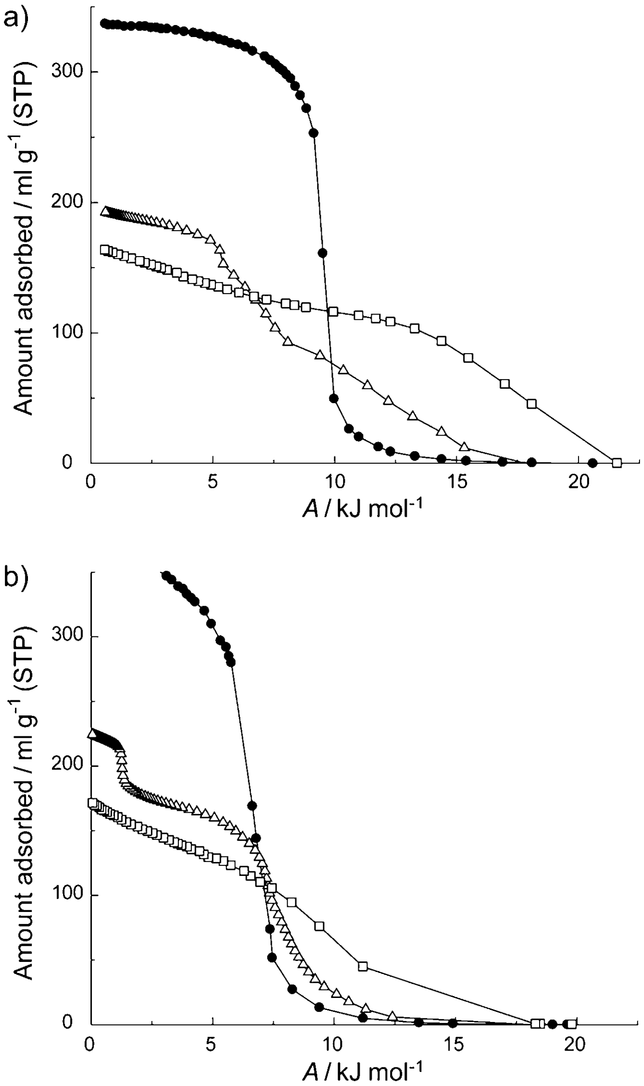


Figure 3. Characteristic adsorption curve of **2a** (solid circles), **2b** (open triangles), and **2c** (open squares) for a) acetylene and b) carbon dioxide at 195 K.

Effect of Temperature on Acetylene-Sorption Properties

To demonstrate the potential application of **1** and **2** for acetylene storage, acetylene sorption isotherms for **1** and **2** were recorded over the temperature range 273–323 K. Sorption isotherms for **1a** and **2a** are shown in Figure 4a and b, respectively. Over these temperatures and pressures, Henry's law is obeyed and the isotherms are close to linear. In contrast, the acetylene sorption isotherms for **1b**, **2b**, **1c**, and **2c** were type I, as shown in Figure 2c–f, respectively. Hysteresis for the adsorption/desorption of acetylene on **1** and **2** is insignificant, except for **1c**. The origin of the hysteresis for **1c** is most likely adsorbent or adsorbate structural change, which is consistent with the step in the acetylene adsorption isotherm for **1c** at 195 K. The adsorption amounts obtained from these isotherms are shown in Table 4. The adsorption amounts for **2b** and **2c** at 298 K, 1 atm (106 and 101 mL g^{-1}, respectively) are higher than those for carbon molecular

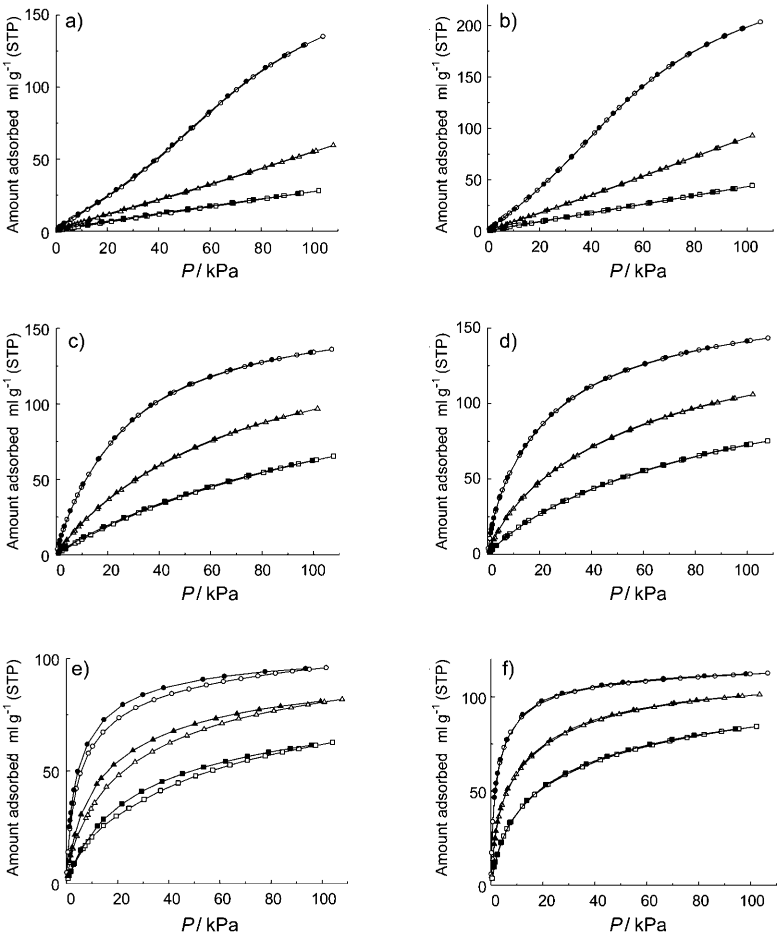


Figure 4. Sorption isotherms for acetylene on a) **1a**, b) **2a**, c) **1b**, d) **2b**, e) **1c**, and f) **2c** at 273 K (circles), 298 K (triangles), and 323 K (squares). Open symbols = adsorption, solid symbols = desorption.

Table 4. Amount of acetylene adsorbed on **1** and **2** over the temperature range 273–323 K at 1 atm.

Adsorbent	Amount adsorbed [mL g^{-1} (STP)]		
	273 K	298 K	323 K
1a	135	60	28
2a	203	93	44
1b	136	97	56
2b	143	106	75
1c	96	82	62
2c	112	101	84

sieves (45 mL g^{-1}),[20] mesoporous silica SBA-15 (36 mL g^{-1}),[21] type-A zeolite (98 mL g^{-1}),[22] and [Mg(HCOO)$_2$]$_n$ (66 mL g^{-1}),[9b] which has the highest acetylene adsorption capacity at 298 K, 1 atm among other PCPs. In particular, the adsorption amount for **2c** was 84 mL g^{-1} even at 323 K, although that of **2b** was 75 mL g^{-1}. The storage density of acetylene in **2c** at 298 K is 0.135 g mL^{-1}, which is equivalent to the density of acetylene at 13 MPa at 298 K and is 65 times larger than the value of the compression limit for the safe storage of acetylene at room temperature, 0.20 MPa: 0.002 g mL^{-1}. The greater uptake capacity of **2c** under ambient conditions is consistent with the high affinity of **2c** for acetylene at 195 K.

The adsorption-potential (A) distribution is a model-independent thermodynamic function and reflects the pore size and shape distribution.[23] Non-normalized adsorption-potential distributions calculated from the sorption isotherms at 273 K are shown in Figure 5. **1a** and **2a** gave sharp peaks, which indicates the existence of uniform micropores. On the other hand, the peak for **2c** is smaller, but the maximum is located at the highest value of the adsorption potential. Comparison of the potential distributions shows that the order of maximum adsorption potential values is **2c** > **1c** > **2b** ≈ **1b** > **2a** > **1a**, which is consistent with the characteristic adsorption curves at 195 K.

The strength of the interaction between the framework and acetylene was studied by using the isosteric enthalpy of acetylene adsorption, which was calculated according to Equation (3) with adsorption isotherms measured at 273, 298, and 323 K:

$$\Delta H_{\text{ads}} = -R\left(\frac{\partial \ln P}{\partial(1/T)}\right)_N \qquad (3)$$

in which ΔH_{ads}, R, P, and N represent the isosteric enthalpy of adsorption, gas constant, pressure, and the uptake of acetylene, respectively. As shown in Figure 6, the isosteric en-

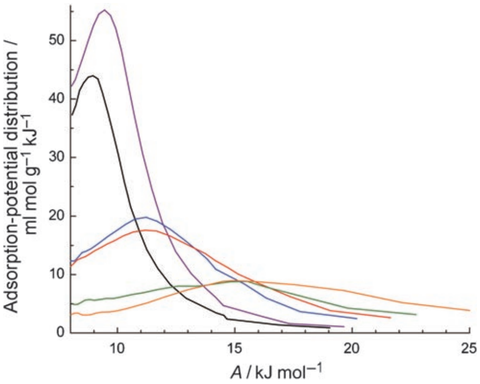


Figure 5. Adsorption-potential distribution for **1a** (black), **2a** (purple), **1b** (blue), **2b** (red), **1c** (green), and **2c** (orange).

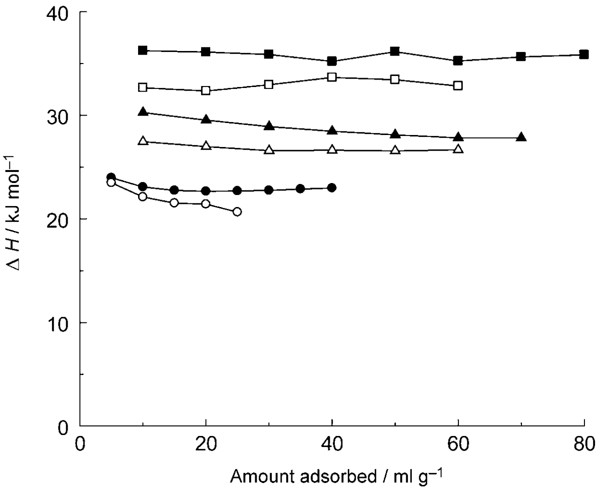


Figure 6. Plot of calculated isosteric enthalpy of adsorption for acetylene on **1a** (open circle), **2a** (solid circle), **1b** (open triangle), **2b** (solid triangle), **1c** (open square), and **2c** (solid square) against the amount of adsorption.

thalpy of adsorption lies in the range 20.6–23.5 kJ mol^{-1} for **1a**, 22.6–24.0 kJ mol^{-1} for **2a**, 26.6–27.5 kJ mol^{-1} for **1b**, 27.8–30.3 kJ mol^{-1} for **2b**, 32.3–33.7 kJ mol^{-1} for **1c**, and 35.2–36.2 kJ mol^{-1} for **2c**. The isosteric enthalpies of adsorption for **1b**, **2b**, **1c**, and **2c** are significantly higher than the latent enthalpy of vaporization for acetylene (1 atm at boiling point) of 20.9 kJ mol^{-1}. The observed value of 36 kJ mol^{-1} for **2c** is smaller than that for $[Cu_2(pzdc)_2(pyz)]_n$ (42.5 kJ mol^{-1}[9a]; pyz = pyrazine, pzdc = pyrazine-2,3-dicarboxylate) and is similar to that for $[Mg(HCOO)_2]_n$ (38.5 kJ mol^{-1}).[9b] The higher enthalpy of acetylene adsorption for $[Cu_2(pzdc)_2(pyz)]_n$ is due to the hydrogen-bonding interactions between the hydrogen atom of acetylene and the oxygen atom on the pore surface. On the other hand, no specific interaction except for van der Waals interactions between adsorbed acetylene molecules and the pore wall of $[Mg(HCOO)_2]_n$ was apparent. This suggests that the high acetylene uptake observed in **2c** is due to physical adsorption, and therefore physisorption could be suitable for high-capacity acetylene storage. Interestingly, the isosteric enthalpy of adsorption for **2c** was unchanged during the adsorption process, although ΔH_{ads} for $[Mg(HCOO)_2]_n$ decreased as the amount of adsorbed acetylene increased. This result indicates that the binding sites of **2c** are relatively uniform.

Conclusions

We have studied the acetylene-sorption properties of six PCPs, **1** and **2**, which have a jungle-gym-like 3D network structure. The capability for the design and size tuning of micropores has permitted the systematic study of acetylene sorption on PCPs. Notably, the porous crystals **2c**, which contain anthracene moieties, had the highest acetylene adsorption capacity and showed the highest affinity for acetylene of the compounds **1** and **2**. These results provide useful information for the understanding and design of PCPs for acetylene storage.

Experimental Section

Materials

The host PCP compounds **1a–c**, $[Cu_2(L)_2(dabco)]_n$,[11f,12] and **2a–c**, $[Zn_2(L)_2(dabco)]_n$,[11a,c,13] were prepared by previously described methods.

Adsorption Measurements

The sorption isotherms of **1a**, **2a**, **1b**, **1c**, and **2c** for acetylene and carbon dioxide at 195 K were recorded on a Quantachrome Autosorb-1 volumetric-adsorption instrument. The sorption isotherms of **2b** for acetylene and carbon dioxide at 195 K were recorded on a BELSORP-18-Plus volumetric-adsorption instrument from BEL Japan, Inc. The acetylene sorption isotherms for all compounds at 273, 298, and 323 K were recorded on a BELSORP-18-Plus volumetric-adsorption instrument.

Acknowledgements

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