Binding energies of hydrogen molecules to lantern-type dinuclear M(BDC)(DABCO)$_{1/2}$

Tohru Takei, Jiro Kawashima,[1] Takato Ii,[1] Akihiro Maeda,[1] Tetsushi Ohmura,[1]
Masao Ichikawa,[2] Mitsuya Hosoe,[2] Izuru Kanoya,[2] and Wasuke Mori*[1]

[1]Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka 259-1293
[2]Honda R & D Co., Ltd., Wako Research Center, Chuo, Wako 351-0193
Fax: 81-463-58-9688, e-mail: wmori@kanagawa-u.ac.jp

The hydrogen adsorption properties and uptake capacities of three-dimensional (3-D) microporous materials of lantern-type dinuclear M(BDC)(DABCO)$_{1/2}$ (M = Co(II), Cu(II), Zn(II), BDC = 1,4-benzenedicarboxylate, DABCO = 1,4-diazabicyclo[2.2.2]octane, Co(BDC)(DABCO)$_{1/2}$ **1**, Cu(BDC)(DABCO)$_{1/2}$ **2**, Zn(BDC)(DABCO)$_{1/2}$ **3**) were investigated at different temperatures of 77 K and 87 K and pressures up to 0.1 MPa. The results from hydrogen adsorption experiments conducted at 77 K and 87 K show that all complexes have a relatively high hydrogen uptake. The isosteric heats of hydrogen adsorption data calculated based on the Clausius-Clapeyron equation are consistent with these observations, indicating strong adsorbent-adsorbate interactions. The results indicated that the hydrogen heats of adsorption were 5.9-6.5 kJ/mol, 6.3-7.9 kJ/mol, and 5.6-6.0 kJ/mol for **1**, **2**, and **3**, respectively.

Key words: lantern-type, dinuclear, micropore, hydrogen adsorption, heat of adsorption

1. INTRODUCTION

Porous metal–organic frameworks (MOFs) have become competitors to other porous materials such as zeolites[1-2] and carbon materials.[3-5] They are synthesized in a building block approach from metal or metal oxide vertices interconnected by organic linkers.

Hydrogen storage has been a consistently topical and controversial focus of materials research over the past few decades. Recent studies have confirmed that MOFs can store considerable quantities of hydrogen at 77 K.[6-13] Hydrogen storage materials fall into two categories: those that dissociate the molecules and chemically bind them as hydrides and those that physisorb the molecules on their surface. Clearly, the most important attributes of the second category are high surface area and strong binding potential. Of the various materials under consideration, ordered porous materials such as MOFs are considered capable of fulfilling this role. Recently, Yaghi and co-workers reported on the considerable potential for hydrogen storage in microporous coordination solids with robust 3-D frameworks and high surface areas.[6-9] One key feature that characterizes most MOFs is the relatively low enthalpy of adsorption change associated with the hydrogen uptake. This energy usually lies in the range 4.7-7.5 kJ/mol, significantly lower than the estimated 15 kJ/mol required for reversible hydrogen uptake at ambient temperatures and fuel-cell operating pressures between 1.5 and 30 atm.[14]

Previously, we reported that copper(II) dicarboxylates,[15-17] molybdenum(II) dicarboxylates,[18] and ruthenium(II,III) dicarboxylates,[19-20] which have lantern-type structures, reversibly occluded large amounts of gases such as N$_2$, Ar, O$_2$, CH$_4$, and Xe. The uniform linear micropores of these adsorbents were assumed as having been constructed by the stacking or bonding of two-dimensional (2-D) lattices of dinuclear transition-metal dicarboxylates. Furthermore, it has been found that mononuclear copper(II) BDC-pyridine, which has a regular one-dimensional (1-D) structure, occludes large amounts of gases.[21-22] We recently reported the hydrogen adsorption properties for MOFs of the type M(BDC)(DABCO)$_{1/2}$.[13] The general method for synthesizing a 3-D porous complex is shown in Fig. 1.
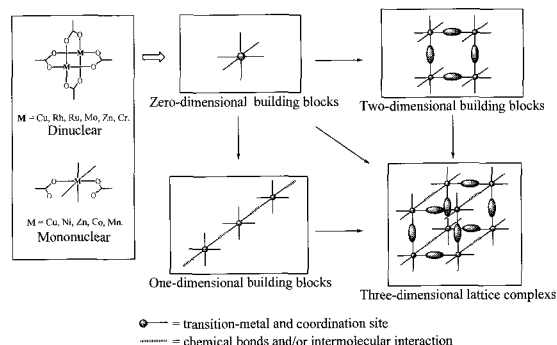

Fig. 1 3-D lattice organized by the assembly of lower dimensional building blocks.
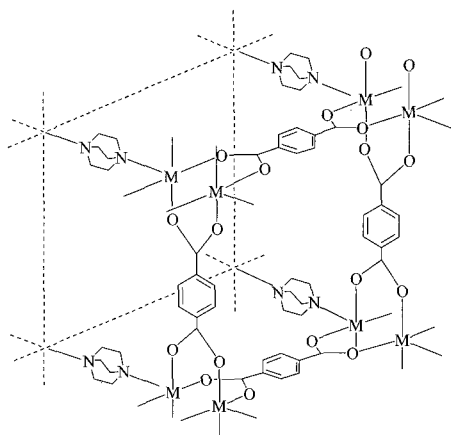
Fig. 2   Plausible lantern-type 3-D dinuclear structure for M(BDC)(DABCO)$_{1/2}$ (M = Co(II), Cu(II), Zn(II)).

In this paper, we report the hydrogen adsorption properties for MOFs of the type M(BDC)(DABCO)$_{1/2}$(M = Co(II), Cu(II), Zn(II)), which has a regular 3-D structure.(Fig. 2) All complexes were investigated at different temperatures of 77 K and 87 K and pressures up to 0.1 MPa. In addition, we present the hydrogen heat of adsorption, which is a very important factor in the application of these hydrogen storage materials, evaluated at 77 K and 87 K.

2. EXPERIMENTAL

2.1 Synthesis

Cobalt(II)   1,4-benzenedicarboxylate-DABCO {Co(BDC)(DABCO)$_{1/2}$}(1) was synthesized using already published procedures.[13] The same methods as 1 were used to synthesize copper(II) 1,4-benzenedicarboxylate-DABCO {Cu(BDC)(DABCO)$_{1/2}$}(2) and zinc(II) 1,4-benzenedicarboxylate-DABCO {Zn(BDC)(DABCO)$_{1/2}$}(3).[23]

2.2 H$_2$ adsorption measurement

Hydrogen adsorption isotherms were measured using an ASAP2010 volumetric adsorption apparatus provided by Micromeritics Co., Ltd. Before the adsorption measurements, the samples were degassed under a vacuum at 373 K. Hydrogen adsorption isotherms were measured up to 0.1 MPa.

3. RESULTS AND DISCUSSION

Lantern-type dinuclear M(BDC)(DABCO)$_{1/2}$ (M = Co(II), Cu(II), Zn(II)), has been synthesized in a two-step reaction,[13] which is a new synthetic method compared with the previously reported synthetic method.[15-20] In addition, the reactions are reproducible and can be readily scaled up.

Analysis of the temperature dependence of hydrogen adsorption by MOFs provides further insights into the influences exerted by their structural features. Isosteric analysis of adsorption isotherms collected at various temperatures enables an estimation of the coverage-dependent isosteric heat of hydrogen adsorption, where the behavior of this function
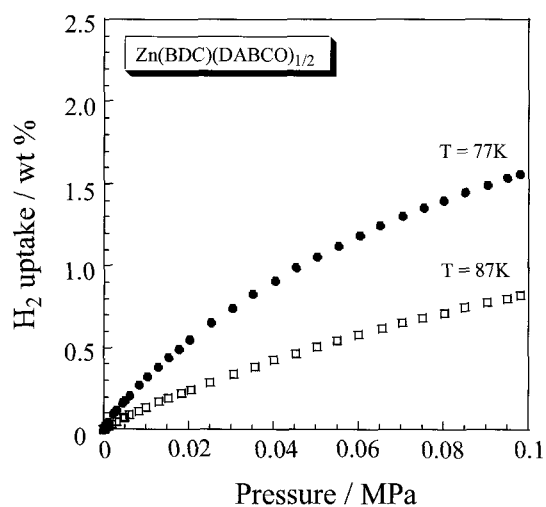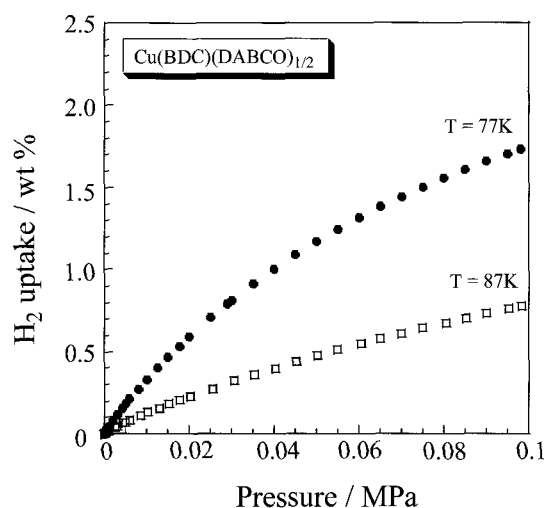

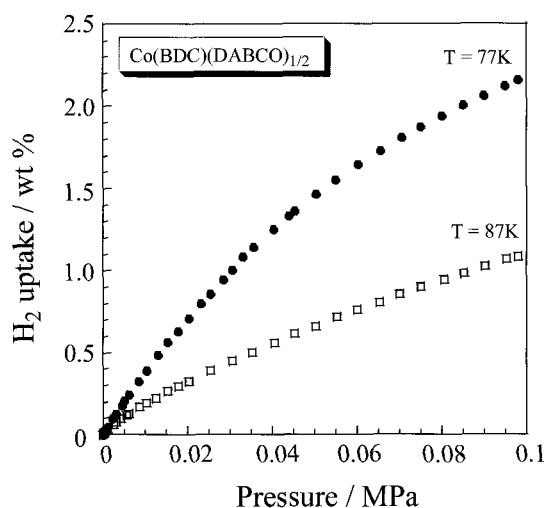Fig. 3   Hydrogen adsorption isotherms for M(BDC)(DABCO)$_{1/2}$ (M = Co(II), Cu(II), Zn(II)) at 77 K and 87 K. At 77 K data is indicated by filled circles, at 87 K data by open squares. Top: Co(BDC)(DABCO)$_{1/2}$, Middle: Cu(BDC)(DABCO)$_{1/2}$, Bottom: Zn(BDC)(DABCO)$_{1/2}$.

Table 1. Summary of gas adsorption data.

materials		$N2_{BET}$ [m²/g]	$N2_{Lang}$ [m²/g]	$N2_{vol}$ [cm³/g]	Ar_{dia} [Å]	HL_{77K} [wt %]	HL_{87K} [wt %]	ΔH_{ads} (kJ/mol)
Co(BDC)(DABCO)₁/₂	1	1595	2120	0.77	6.13	2.28	1.09	5.9-6.5
Cu(BDC)(DABCO)₁/₂	2	1300	1703	0.63	5.96	1.67	0.78	6.3-7.9
Zn(BDC)(DABCO)₁/₂	3	1165	1488	0.63	6.18	1.54	0.81	5.6-6.0
IRMOF-1[8-10]		2900	3362	1.04	c.a. 8[b]	1.32	—	4.7-5.2
Prussian blue analogues[11]		560-870	—	—	—	1.4-1.8	—	5.3-7.4
Activated Carbon[5]		—	—	0.18-0.74	—	—	—	3.9-5.2

[a] Acronyms: $N2_{BET}$, $N2_{Lang}$ are the BET, Langmuir surface areas by measuring nitrogen gas; $N2_{vol}$ is pore volume by measuring nitrogen gas; Ar_{dia} is pore diameter by measuring argon gas; HL_{77K} is the maximum amounts of hydrogen adsorbed at 0.1 MPa, 77 K; HL_{87K} is the maximum amounts of hydrogen adsorbed at 0.1 MPa, 87 K; ΔH_{ads} is isosteric heats of hydrogen
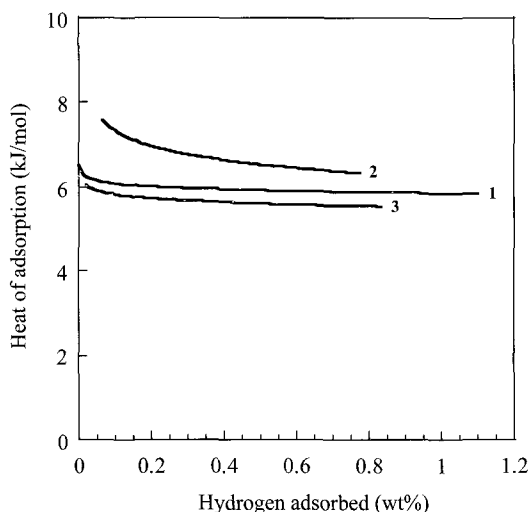
[b] This value is measured by X-ray crystallography.

Fig. 4 Enthalpy of hydrogen adsorption for M(BDC)(DABCO)₁/₂ (M = Co(II) **1**, Cu(II) **2**, Zn(II) **3**) calculated from fits of their 77 K and 87 K isotherms.

is determined by the relative magnitudes of the adsorbent-adsorbate and adsorbate-adsorbate interaction.

Hydrogen adsorption in three different MOFs, **1**, **2**, and **3**, were investigated at temperatures 77 K and 87 K. Fig. 3 shows the resulting hydrogen adsorption isotherms up to 0.1 MPa at 77 K and 87 K. Table I lists the adsorption properties of all complexes. As expected, the amount adsorbed decreases significantly with temperature. All complexes display approximately a Type-I isotherm in the IUPAC classification scheme. Under these conditions, hydrogen adsorption isotherms are not saturated because these temperatures are above the critical temperature (33 K for hydrogen).

The strength of the interaction with the framework was probed by measuring a second hydrogen sorption isotherm for each compound at 87 K. Taking both the 77 K and 87 K data, a variant of the Clausius-Clapeyron equation[24] was then used to calculate the enthalpy of adsorption as a function of the quantity of hydrogen adsorbed.

As expected, the behavior of the isosteric heat of hydrogen adsorption is shown to gradually decrease in value as a function of the amounts adsorbed. As shown in Fig. 4, the enthalpies of adsorption lie in the ranges 5.9-6.5 kJ/mol for **1**, 6.3-7.9 kJ/mol for **2**, and 5.6-6.0 kJ/mol for **3**, significantly higher than the enthalpy of vaporization of hydrogen (0.99 kJ/mol at its boiling

point). These values are nearly equal to the previously reported hydrogen adsorption enthalpies of 4.7-5.2 kJ/mol for IRMOF-1(Zn₄O(BDC)₃),[8] 5.3-7.4 kJ/mol in the dehydrated Prussian blue analogues M₃[CO(CN)₆]₂ (M = Mn, Fe, Co, Ni, Cu, Zn),[11] and 3.9-5.2 kJ/mol for variously functionalized activated carbons.[5] A possible explanation for the different values for the heat of hydrogen adsorption in the three samples could be different pore sizes. It is known from theoretical calculations on carbon structures that hydrogen adsorption is favored in small micropores. If we assume that this is also the case for MOFs, it would be reasonable to assume that hydrogen is more strongly adsorbed in **2**, which has an effective pore size of 5.96 Å, the smallest of the three complexes.

As observed for all complexes, the low-pressure region of the adsorption isotherm is strongly dependent on the strength of the interaction between the hydrogen molecules and the adsorbent. Therefore, the difference in the storage capacity at low pressures for different materials can also be attributed to different heats of adsorption.

4. CONCLUSIONS

We have reported on hydrogen storage at different temperatures in three different MOFs, M(BDC)(DABCO)₁/₂ (M = Co(II), Cu(II), Zn(II)). All complexes were synthesized using new procedures. The magnitude of the measured heat of adsorption for both temperatures gives clear evidence that hydrogen is physically adsorbed in the MOFs.

At low temperature and low-pressure, **2** has the highest hydrogen heat of adsorption (6.3-7.9 kJ/mol) of all the complexes. MOFs with smaller pores systematically show a considerably stronger adsorbent-adsorbate interaction. It is might be that the difference of the hydrogen heat of adsorption for MOFs depends on pore size.

These results showed that high surface area and more suitable pore size are important under low-pressure. Therefore, the major challenge is to synthesize MOFs having an optimum pore size without decreasing the specific surface area and pore volume.

References and Notes

[1] H. W. Langmi, A. Walton, M. M. Al-Mamouri, S. R. Johnson, D. Book, J. D. Speight, P. P. Edwards, I. Gameson, P. A. Anderson, I. R. Harris, *J. Alloys Compd.*, **356**, pp710-715, (2003).

[2] A. Zecchina, S. Bordiga, J. G. Vitillo, G.

Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen, K. P. Lillerud, *J. Am. Chem. Soc.*, **127**, pp6361-6366, (2005).

[3] B. Panella, M. Hirscher, S. Roth, *Carbon*, **43**, pp2209-2214, (2005).

[4] H. G. Schimmel, G. J. Kearley, M. G. Nijkamp, C. T. Visser, K. P. de Jong, F. M. Mulder, *Chem. Eur. J.*, **9**, pp4764-4770, (2003).

[5] X. B. Jhao, B. Xiao, A. J. Fletcher, K. M. Thomas, *J. Phys. Chem. B*, **109**, pp8880-8888, (2005).

[6] L. N. Rosi, J. Eddaoudi, T. D. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science*, **300**, pp1127-1129, (2003).

[7] A. G. Wong-Foy, A. J. Matzger, O. M. Yaghi, *J. Am. Chem. Soc.*, **128**, pp3494-3495, (2006).

[8] J. L. C. Rowsell and O. M. Yaghi, *J. Am. Chem. Soc.*, **128**, pp1304-1315, (2006).

[9] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, J. Kim, *Nature*, **423**, pp705-714, (2003).

[10] B. Panella, M. Hirscher, H. Pütter, U. Müller *Adv. Funct. Mater.*, **16**, pp520-524, (2006).

[11] S. S. Kaye and J. R. J. Long, *J. Am. Chem. Soc.*, **127**, pp6506-6507, (2005).

[12] D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem. Int. Ed.*, **43**, pp5033-5036, (2004).

[13] T. Takei, T. Ii, J. Kawashima, T. Ohmura, M. Ichikawa, M. Hosoe, Y. Shinya, I. Kanoya, W. Mori, *Chem. Lett.*, **36**, pp1136-1137, (2007).

[14] S. K. Bhatia and A. L. Myers, *Langmuir*, **22**, pp1688-1700, (2006).

[15] W. Mori, F. Inoue, K. Yoshida, H. Nakayama, S. Takamizawa, M. Kishita, *Chem. Lett.*, **12**, pp1219-1220, (1997).

[16] K. Seki, S. Takamizawa, W. Mori, *Chem. Lett.*, **4**, pp122-123, (2001).

[17] K. Seki, S. Takamizawa, W. Mori, *Chem. Lett.*, **4**, pp332-333, (2001).

[18] S. Takamizawa, W. Mori, M. Furihata, S. Takeda, K. Yamaguchi, *Inorg. Chem. Acta*, **283**, pp268-274, (1998).

[19] S. Takamizawa, K. Yamaguchi, W. Mori, *Inorg. Chem. Commun.* **1**, pp177-178, (1998).

[20] S. Takamizawa, T. Ohmura, K. Yamaguchi, W. Mori, *Mol. Cryst. Liq. Cryst.*, **342**, pp285-290, (2000).

[21] T. Ohmura, W. Mori, M. Hasegawa, T. Takei, A. Yoshizawa, *Chem. Lett.*, **32**, pp34-35, (2003).

[22] T. Ohmura, W. Mori, M. Hasegawa, T. Takei, T. Ikeda, E. Hasegawa, *Bull. Chem. Soc. Jpn.*, **76**, pp1387-1395, (2003).

[23] Elemental analysis calcd for $C_{11}H_{10}CoN_1O_4$ (**1**): C, 47.33; H, 3.61; N, 5.02%. Found: C, 47.27; H, 3.58; N, 4.91%. Elemental analysis calcd for $C_{11}H_{10}CuN_1O_4$ (**2**): C, 46.56; H, 3.55; N, 4.94%. Found: C, 46.53; H, 3.47; N, 5.14%. Elemental analysis calcd for $C_{11}H_{10}ZnN_1O_4$ (**3**): C, 46.26; H, 3.53; N,

4.90%. Found: C, 46.21; H, 3.30; N, 4.97%.

[24] R. T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley, New York (2003).