Design and Gas Adsorption Property of a Three-Dimensional Coordination Polymer with a Stable and Highly Porous Framwork

Kenji Seki,* Satoshi Takamizawa,[†] and Wasuke Mori*[†]
Department of Research and Development, Osaka Gas Co., Ltd., 6-19-9 Torishima, Konohana-ku, Osaka 554-0051
[†]*Department of Chemistry, Faculty of Science, Kanagawa University, Hiratsuka, Kanagawa 259-1293*

(Received January 18 , 2001; CL-010056)

A three-dimensional coordination polymer was synthesized from porous copper(II) terephathlate and triethylenediamine (TED) as a pillar ligand, which has a higher porosity and higher capacity for methane adsorption than zeolites and porous coordination polymers reported previously.

Recently, a great deal of attention has been directed toward the use of coordination polymers in the design and synthesis of new porous materials.[1–8] Because of their structural controllability, these porous materials will be attractive adsorbents for gas storage. So some groups have been researching in this field.[6–8] However, the use of these coordination polymers as alternative adsorbents for gas storage to activated carbons or zeolites presents problems with respect to porosity and structure stability. So in order to improve the porosity and stability, a coordination polymer having a three-dimensional network structure bridging a two-dimensional layer of porous copper(II) terephthalate[1] synthesized previuouly with TED as a pillar ligand, are synthesized and characterized by Ar adsorption at 87.3 K in this work. In addition, methane adsorption properties, which have attracted strong interest in the development of new natural gas storage systems, are evaluated at high pressure at 298 K.

A three-dimensional coordination polymer of Cu(1,4-$OOC–C_6H_4–COO)\cdot 1/2C_6H_{12}N_2$ (**1**) was synthesized by a heterogeneous reaction between porous copper terephthalate (**2**)[1] and TED.[9] The resulting temperature dependence of the magnetic susceptibilities for the obtained coordination polymer indicates the existence of the same dinuclear structure[10] as that of **2** which have a two-dimensional structure of dicarboxylic acids bridging the center copper ions. Based on the result and elemental analysis, it is supposed that the two-dimensional layer bridging the copper(II) ions with the dicarboxylate ions are linked with TED as pillar ligands to give a three-dimensional structure (Figure 1).

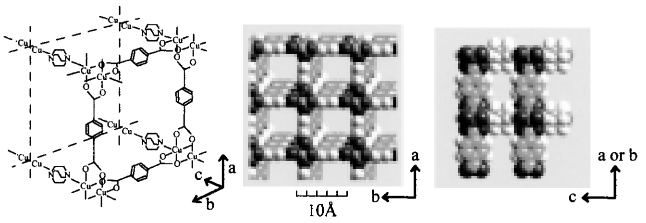

Figure 1. The plausible three dimensional structure for **1**.

The stability of this network structure was studied by X-ray powder diffraction (XRPD) and thermal gravimetric (TG) analysis, as plotted in Figure 2. The TG curve of **1** illustrates the release of the adsorbed molecules when sampling in air up to about 343 K, followed by the thermal decomposition of the structure at 523 K. No chemical decomposition was observed between 343 K and 523 K. The structure of this stable phase was studied by measuring the XRPD pattern at R.T., 473 K and 523 K. These results demonstrate that the porous network structure is retained up to 523 K in the absence of the included guest molecules. Figure 3 also shows that the observed XRPD pattern agrees with the simulated pattern of the optimized plausible structure by using Cerius2, indicating the structure of the obtained compound is confirmed to be the plausible structure.

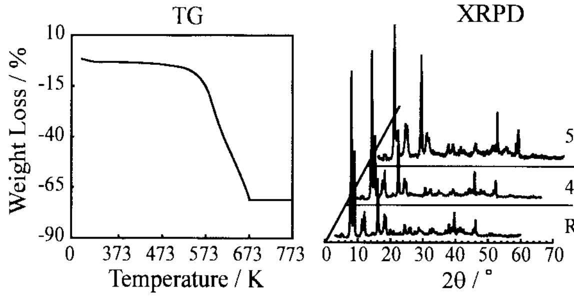

Figure 2. The TG curve and the XRPD patterns for **1**.

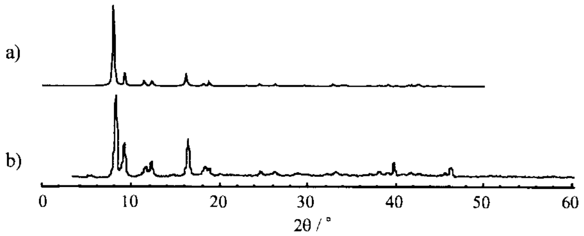

Figure 3. a): Simulated XRPD pattern for dried **1**.
b): Experimental XRPD pattern at 473 K.

To examine the porosity of **1**, high-resolution adsorption isotherm of Ar at 87.3 K was measured in a relative pressure range from 10^{-6} to 1 using ASAP 2000M volumetric adsorption equipment from Micromeritics. The adsorption isotherm is shown in Figure 4. The adsorption isotherm of **1** shows typical isotherm of Langmuir type, confirming the presence of micropores without mesopores. From the data, the BET surface area, micropore volume, pore diameter, and pore distribution {using Dubinin–Radushkevitch (DR) methods[11] and Horvath–Kawazoe (HK) methods[12]} were derived to characterize the porosity of **1**. The results are summarized in Table 1.

The pore size distribution is shown in Figure 4. One sharp peak is observed at 7.4 Å, indicating that the obtained coordination polymer has uniform micropores. To compare experimental valus of pore size with calculated values, the plausible structures were optimaized by molecular mechanic (MM) and molecular dynamics (MD) of Cerius2 and the pore sizes were calculated. The effective pore sizes calculated from these opti-

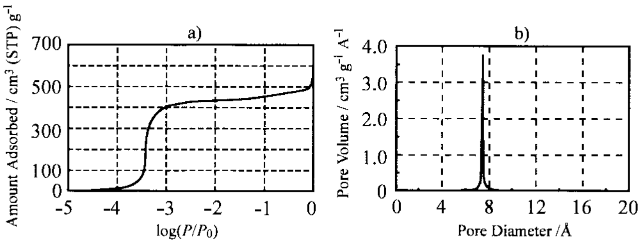

Figure 4. a): Ar adsorption isotherm for **1**; b): Micropore size distribution for **1**.

Table 1. Microporosity of coordination polymers obtained by Ar adsorption

		Micropore volume/cm³ g⁻¹		
Compound	S.A./m² g⁻¹	HK[a]	DR	Pore size/Å
1	1548	0.58	0.58	7.4
2	545	0.22	0.21	6.0

[a]Estimated from the obtained value at P/P_0=0.11 which is assiciated with the value of 20 Å pore size.

mized structures was about 7.4 Å (Figure 1). This calculated values have good agreement with experimental value of HK method. The effective pore size of **1** is larger than that of **2** reported previously. This difference is explained by the difference in the way of stacking of the two-dimensional layer bridging the copper(II) ions with dicarboxylate ions between **1** and **2**.[13] **1** has a narrower pore size distribution than **2** because of regular stacking of two-dimensional layers by the insert of pillar ligands. The surface area and micropore volume are much greater than that of **2**, indicating that construction of coordination polymers having a three-dimensional network structure is an effective method in improving porosity.

The adsorption isotherms of methane were measured gravimetrically up to 3.5 MPa. Figure 5 plots the methane adsorption isotherm of **1** at 298 K. The adsorption isotherm is the Langmurian type, indicating that methane adsorption is the monolayer adsorption. Approximately 180 cm³ (STP) of methane were adsorbed per 1 g of dried samples of **1** at 3.5 MPa. This value is much higher than those of **2** {about 71 cm³ (STP) g⁻¹ at 3.5 MPa} and zeolite 5A (**3**) {about 83 cm³ (STP) g⁻¹ at 3.5 MPa}.[8]

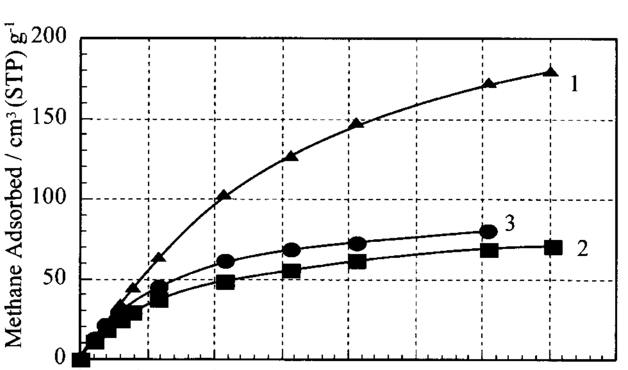

Figure 5. High pressure methane adsorption isotherms at 298 K.

High pressure adsorption of supercritical methane in micropore field has been studied by the extended DR equation.[14] The DR plots was linear in all regions, indicating that methane adsorption is micropore-filling, giving the satureted vapor pressure of the quasi-vaporized supercritical methane P_{0q} and the characteristic adsorption energy βE_0. Furthermore, the βE_0 leads to isosteric heat of adsorption $q_{\mathrm{st},\phi=1/e}$ at the fractional filling of $1/e$. Obtained parameter, W_L, βE_0 and $q_{\mathrm{st},\phi=1/e}$ are summarized in the Table 2.

Table 2. Characteristic parameters of methane adsorption isotherm at 298 K

Compound	W_L[a] /cm³ (STP) g⁻¹	βE_0 /kJ mol⁻¹	$q_{\mathrm{st},\phi=1/e}$ /kJ mol⁻¹	P_{0q} /MPa
1	303	8.02	16.19	33.9

[a]The inherent micropore volume determined by the Langmuir plot.

The $q_{\mathrm{st},\phi=1/e}$ values of **1** is 16.19 kJ mol⁻¹, being the same as that of activated carbon fibers with slit-shaped micropores and zeolites of with cylinder-shaped micropores. The $q_{\mathrm{st},\phi=1/e}$ value indicates that the methane adsorption of copper complexes is physical adsorption and the mechanism is that of micropore filling.

This study has demonstrated that the construction of a three-dimensional network structure is an effective method in improving porosity. A coordination polymer having a three-dimensional network structure bridging the two-dimensional layer of copper (II) terephthalate by TED as a pillar ligand has a higher porosity and higher methane adsorption capacity than zeolites and other porous coordination polymers.

References and Notes

1 W. Mori, F. Inoue, K. Yoshida, H. Nakayama, and S. Takamizawa, *Chem. Lett.*, **1997**, 1219.

2 W. Mori and S. Takamizawa, *J. Solid State Chem.*, **152**, 120 (2000).

3 S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, and A.G.Orpen, I. D. Williams, *Science*, **283**, 1148 (1999).

4 H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, *Nature*, **402**, 276 (1999).

5 H. Li, M. Eddaoudi, T. L. Groy, and O. M. Yaghi, *J. Am. Chem. Soc.*, **120**, 8571 (1998).

6 M. Kondo, T. Okubo, A. Asami, S. Noro, T. Yoshitomi, S. Kitagawa, T. Ishii, H. Matsuzaka, and K. Seki, *Angew. Chem. Int. Ed.*, **111**, 190 (1999).

7 S. Noro, S. Kitagawa, M. Kondo, and K. Seki, *Angew. Chem. Int. Ed.*, **39**, 2081 (2000).

8 K. Seki, S. Takamizawa, and W. Mori, *Chem. Lett.*, in press.

9 A methanol solution (10 cm³) of copper(II) sulfate pentahydrate (0.31 g) was added to a methanol solution (200 cm³) of terephthalic acid (0.21 g) and formic acid (2.0 cm³). After the mixture was allowed to stand for several days at 313 K, toluene solution (12.5 cm³) of triethylenediamine was added to the mixture, which was then allowed to react at 433 K in autoclave for 1 h. A light blue precipitate was collected, washed with mehanol, and dried at 373 K under vacuum. Anal. Found: C, 46.12; H, 3.44; N, 4.97%. Calcd for $Cu(OOC\text{–}C_6H_4\text{–}COO)\cdot 1/2C_6H_{12}N_2$: C, 46.57; H, 3.54; N, 4.94%.

10 J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

11 S. J. Gregg and K. S. W. Sing, "Adsorption, Surface Area, Porosity," 2nd ed., Academic Press, London, UK (1982).

12 G. Horvath and K. Kawazoe, *J. Chem. Eng. Jpn.*, **16**, 470 (1983).

13 In the case of **1**, the benzene rings are parallel to the direction of channel, while the benzene rings of **2** lean to the direction of pores because of the steric hindrance between the adjacent layers, demonstrated by the plausible structures optimaized by molecular mechanic (MM) and molecular dynamics (MD) of Cerius2.

14 K. Kaneko, K. Murata, K. Shimizu, S. Camara, and T. Suzuki, *Langmuir.*, **9**, 1165 (1993).