Characterization of Microporous Copper(II) Dicarboxylates (Fumarate, Terephthalate, and *trans*-1,4-Cyclohexanedicarboxylate) by Gas Adsorption

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Some microporous coordination polymers have been synthesized from copper salts and dicarboxylic acids. These stuctures were characterized by gas adsorption methods. The methane adsorption capacities of these coordination polymers were measured under high pressure. The measurement disclosed that these coordination polymers had uniform micropores and methane adsorption capacities almost the same as that of zeolite 5A.

Recently, the chemistry of microporous compounds has been studied extensively in the area of metal coordination polymers because of the feature that their structure can be easily controlled.[1–6] Previously, we reported that copper(II) dicarboxylates had uniform micropores and adsorbed large quantities of gases such as N_2, Ar, O_2, and Xe at low temperatures.[7] However, these copper complexes are not yet well characterized as adsorbents. In this work, a series of copper dicarboxylates were synthesized and characterized by Ar adsorption at 87.3 K, which is more suitable probe to characterize micropore than N_2 probe having quadrupole monent. As the N_2 molecular interacts with the surface through the quadrupole moment, the preadsorbed N_2 molecular near the entrance of the micropore blocked further adsorption. In addition, methane adsorption properties, which have attracted strong interest in the development of new natural gas storage systems,[8] were measured at 298 K. Copper(II) terephthalate {Cu(*p*-$OOCC_6H_4COO$)} (**1**) was synthesized using already published procedures.[7,9] The same methods as **1** were used to synthesize copper(II) fumarate {Cu(*trans*-$OOCC_2H_2COO$)} (**2**) and copper(II) *trans*-1,4-cyclohexanedicarboxylate {Cu(*trans*-1,4-$OOCC_6H_{10}COO$)} (**3**).[9] The temperature dependence of the magnetic susceptibilities of **2** and **3** obeyed the Bleaney–Bowers equation[10] with almost the same magnetic parameters (2*J* and *g*) as **1** and copper(II) acetate monohydrate[11] which has a well-known dimer structure.[12] These results demonstrate that **2** and **3** have the same two-dimensional layers as that of **1** as shown in Figure 1.

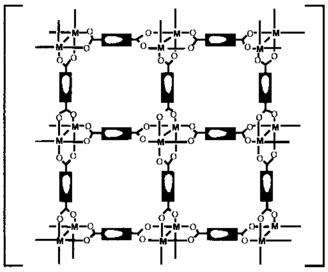

Figure 1. The plausible two dimensional layer of copper dicarboxylate.

These layers would be hold together by the interaction between coppers of one layer and carboxylate oxygens of an adjacent layer. With the stack of these layer, the channeling cavities are formed along one-dimensional direction and can adsorb molecules.[13] High-resolution adsorption isotherms of Ar at 87.3 K were measured in a relative pressure (P/P_0, P_0 = saturation vapor pressure) range from 10^{-6} to 1 using ASAP 2010 volumetric adsorption equipment from Micromeritics. From the resulting date, the BET surface area, micropore volume, pore diameter and pore distribution {using Dubinin–Radushkevitch (DR) methods[14] and Horvath–Kawazoe (HK) methods[15]} were derived to characterize the porosity of the copper complexes (Table 1).

Table 1. Microporosity of copper dicarboxylates obtained by Ar adsorption

Compound	Surface area BET /m^2 g^{-1}	Surface area Langmuir /m^2 g^{-1}	Micropore volume[a] /cm^3 g^{-1}	Pore size[a] /Å
1	545	708	0.22	6.0
2	416	557	0.17	5.4
3	347	456	0.15	4.9

[a] Estimated from the obtained value at P/P_0=0.11, which is associated with a pore size of 20 Å using the HK method.

The adsorption isotherms of the copper complexes are shown in Figure 2. The adsorption isotherms of all compounds show the typical isotherms of Langmuir type, confirming the presence of micropores without mesopores. The sharp rise of argon adsorption at low relative pressures indicates that the micropores are extremely uniform. The rise of argon adsorption at high relative pressures depends on interparticle voids, demonstrating by transmission electron micrographs image of complexes, which indicates the existence of voids of about 10 nm in size between the primary particles.

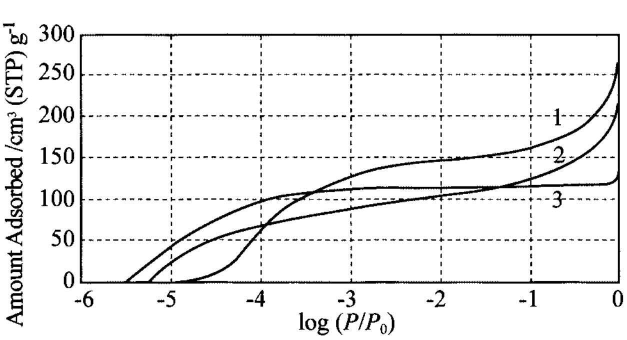

Figure 2. Ar adsorption isotherms at 87.3 K measured on copper dicarboxylates.

The pore size distributions are showed in Figure 3. In all samples, one sharp peak is obtained below 10 Å which indicates that obtained complexes have uniform micropore. To compare experimental values 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 optimized structures were about 6.3, 5.1, and 4.2 Å for **1**, **2**, and **3**, respectively (Figure 4). These calculated values have good agreement with experimental values of HK method. In the case of **1** and **2**, the pore size is larger as the length between carboxylic acid is longer, indicating that the pore size can be controlled freely by varying the kind of carboxylic acid. On the other hand, despite the Cu–Cu distance of **3** is longer than that of **2**, the pore size of **3** is smaller, because of the bulkiness of cyclohexanedicarboxylic acid. The surface area and micropore volume are larger as the pore size is larger.

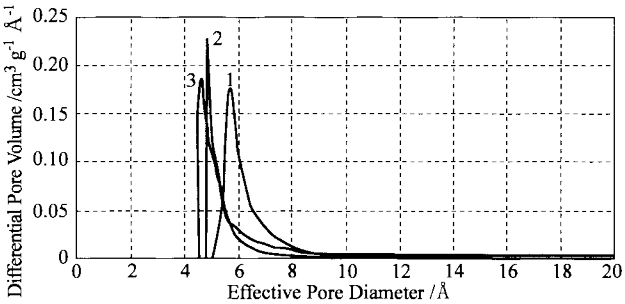

Figure 3. Micropore size distributions for copper dicarboxylates.

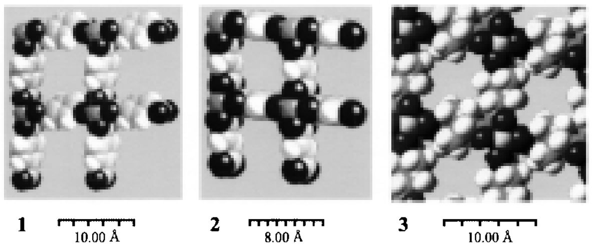

Figure 4. The optimized structures of copper dicarboxylates by simulation.

DR analysis was used to determine the micropore volume and isosteric heat of adsorption in a series of copper complexes. The DR equation is expressed as:

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

where W and W_0 are the amount of adsorption at P/P_0 and the saturated amount of adsorption, E_0 is a characteristic adsorption energy, and the parameter A is Polanyi's adsorption potencial defined as $A = RT\ln(P_0/P)$. The parameter β is the affinity coefficient related to the adsorbate–adsorbent interaction. All DR plots were almost linear in the higher P/P_0 region, giving the micropore volume and βE_0 (Table 2). Micropore volume was calculated from the value of W_0 and liquid argon density by assuming that the adsorbate was adsorbed as a liquid. The micropore volume coincides well with that measured by the HK method for all samples. Furthermore, βE_0 leads to isosteric heat of adsorption $q_{\mathrm{st},\phi=1/e}$ at the fractional filling of $1/e$ by the equation:

$$q_{\mathrm{st},\phi=1/e} = \Delta H + \beta E_0$$

where ΔH (6.52 kJ mol^{-1}) is the heat of vapaorization of the bulk liquid argon at 87.3K. The $q_{\mathrm{st},\phi=1/e}$ values of all samples are from 15 kJ mol^{-1} to 27 kJ mol^{-1}, being greater than that of activated carbon fibers with slit-shaped micropores and zeolites with cylinder-shaped micropores. These results indicate that Ar adsorption on copper complexes is physical adsorption and is stronger than that of activated carbon fibers or zeolites.

Table 2. Characteristic parameters of Ar adsorption isotherms at 87.3 K

Compound	W_0 /cm³ (STP) g⁻¹	Micropore volume/cm³ g⁻¹	βE_0 /kJ mol⁻¹	$q_{\mathrm{st},\phi=1/e}$ /kJ mol⁻¹
1	164	0.21	10.44	16.96
2	119	0.15	9.18	15.70
3	118	0.15	20.05	26.57

The adsorption isotherms of supercritical methane were measured gravimetrically at 298 K up to 3.5 MPa.[16,17] All the adsorption isotherms are of the Langmurian type, indicating that the methane adsoption is monolayer adsorption. At 3.5 MPa, approximately 71 cm³ (STP) (gas volume at standard condition), 82 cm³ (STP) and 60 cm³ (STP) of methane were adsorbed per one gram of dried samples of **1**, **2** and **3**, respectively. These values are almost the same as that of zeolite 5A.

This study has demonstrated that copper coordination polymers (copper dicarboxylates) can be used as a gas adsorbent and has introduced the possibility for a new group of methane adsorbent. Currently, detailed studies are in progress to optimize the structure of complexes for methane adsorption.

References and Notes

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17 The apparatus was equipped with the Cahn-2000 microbalance contained within a SUS steel pressure chamber which was connected with two separate lines for evacuation and adsorbate gas pressurization. After the each sample was set in the apparatus, the adsorbed molecules in the pore and on the surface were removed heating under reduced pressure. After becoming the constant weight, methane was dosed into the adsorption chamber. After each increment for the temperature and sample weight, sufficient time was allowed to stabilize, then the change of the weight of sample was measured. After the buoyancy had been corrected to the obtained amount of the weight change, the absorbed amount was calculated.