

Design of an adsorbent with an ideal pore structure for methane adsorption using metal complexes

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Three-dimensional metal complexes synthesized from copper dicarboxylates and triethylenediamine (TED), which have an ideal pore size for methane adsorption, have higher methane adsorption capacity than the theoretical maximum for activated carbons.

Methane is a primary component of natural gas, which is an important candidate for clean transportation fuels. The storage of methane on adsorbents has been pursued actively as an alternative to high pressure compressed gas storage. However, it was concluded that none of the conventional adsorbents tested showed sufficient methane storage to meet that required for commercial viability.^{1–5} The analysis of pore structure of adsorbents indicated that for even carbons as the best methane adsorbent, there is a large percentage of mesopores and macropores where methane adsorption does not occur sufficiently.² Therefore, to achieve higher adsorption capacity, it is essentially necessary that the micropore volume must be maximized, while the mesopore and macropore volume must be minimized as far as possible.

Recently, a great deal of attention has been directed toward the use of metal complexes in the design and synthesis of new porous materials.^{6–11} Because of their structural controllability, these porous materials will be attractive adsorbents for methane storage. However previously reported complexes are not suitable owing to low adsorption capacities. Herein, a new type of methane adsorbent with ideal pore structure and sufficient adsorption capacity is reported.

Novel metal complexes $[\{Cu(O_2CRCO_2) \cdot 1/2TED\}_n]$ ($R = 4,4'$ -C₆H₄C₆H₄ **1** or *trans*-C₆H₄CH=CH **2**) were synthesized by a heterogeneous reaction between porous copper dicarboxylates⁶ and TED.[†] The temperature dependence of the magnetic susceptibilities for the metal complexes obtained indicates that the existence of the same dinuclear structure as that of copper(II) acetate monohydrate and porous copper(II) dicarboxylates *i.e.* a two-dimensional structure of dicarboxylic acids bridging central copper ions. Based on these results and elemental analysis, it is suggested that the two-dimensional layer bridging the copper(II) ions with dicarboxylate ions are linked with TED as pillar ligands to give a three-dimensional structure (Fig. 1).

The stability of this network structure was studied by X-ray powder diffraction (XRPD) and thermal gravimetric (TG) analysis. The TG curve of **1** illustrates the release of the adsorbed molecules up to *ca.* 373 K, followed by thermal decomposition of the structure at 513 K. No chemical decomposition was observed between 373 and 513 K. The

structure of this stable phase was studied by measuring the XRPD pattern at room temp., 473 K and 513 K. These results demonstrate that the porous network structure is retained up to 513 K in the absence of the included guest molecules. Similarly the network structure of **2** is retained up to 473 K in the absence of the included guest molecules.

Fig. 2 shows that the observed XRPD pattern of **1** is in very good accordance with a simulated pattern of the optimized plausible structure generated using Cerius2, indicating that the structure of **1** is similar to that shown in Fig. 1.

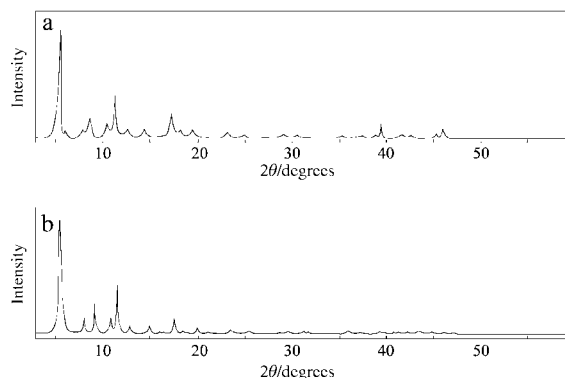


Fig. 2 X-Ray diffraction patterns of **1**. (a) Experimental X-ray powder diffraction after removal of the included guest molecules. (b) Simulated X-ray powder diffraction of the optimized structure using Cerius2.

To examine the porosity of **1** and **2**, high-resolution adsorption isotherms of Ar at 87.3 K were measured in a relative pressure (P/P_0) range from 10^{-6} to 1 using ASAP 2000M volumetric adsorption equipment from Micromeritics. These adsorption isotherms of **1** and **2** (Fig. 3) show typical isotherms of Langmuir type, confirming the presence of micropores without mesopores. Analyses of these isotherms yielded BET surface areas of 3265 and 3129 m² g⁻¹, micropore volumes of 1.18 and 1.07 cm³ g⁻¹ and effective pore sizes of 10.8 and 9.5 Å for **1** and **2**, respectively (using Dubinin–Radushkevitch methods¹² and Horvath–Kawazoe methods¹³).

The pore size distributions are sharp with one sharp peak at 9.5 Å for **2**, indicating that the obtained metal complexes have uniform micropores. On the other hand, for **1**, the pore size distributions exhibit two peaks. This result does not indicate the existence of two kinds of pores, but rather the existence of two adsorption sites having different values of adsorption potential

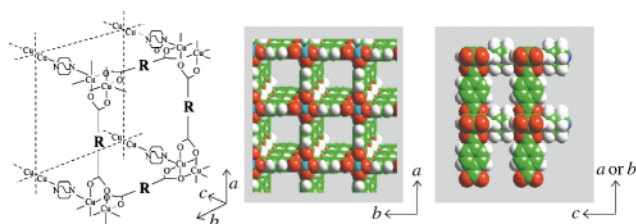


Fig. 1 A plausible three-dimensional structure for the complexes.

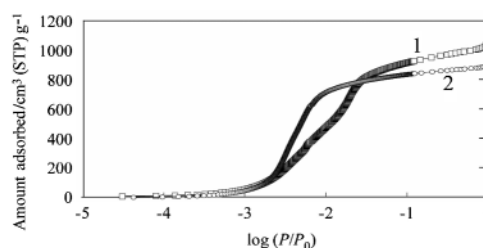


Fig. 3 Ar adsorption isotherms at 87.3 K for the coordination polymers.

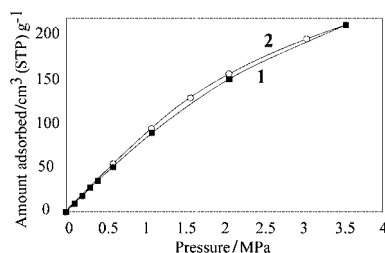


Fig. 4 High-pressure adsorption isotherms of methane at 298 K on metal complexes.

in one pore. These sites are the corner and the edge of the square pore. HK methods can not be used to calculate the pore size distributions for pores of the more than >8 Å width.¹⁴ To compare experimental values of the pore size with calculated values, the plausible structures were optimized by molecular mechanic (MM) and molecular dynamics (MD) of Cerius2 and the pore sizes were calculated. The effective pore size calculated from the optimized structure of **2** was *ca.* 9.4 Å (Fig. 1). This calculated value is in good agreement with the experimental HK value indicating the structure of the obtained complexes is as suggested. The bigger the size of dicarboxylic acid as a ligand, the larger the porosity and pore size, indicating that the porosity and pore size can be controlled by the starting materials. These surface areas and pore volumes are much larger compared with those of other coordination polymers, zeolites and commercial activated carbons already reported, and are the same as those of special high surface area activated carbons. These coordination polymers have adequate porosity to adsorb methane as well as a suitable pore size distribution which is nearly ideal for methane adsorption.

The adsorption isotherms of methane were measured gravimetrically up to 3.5 MPa. Fig. 4 shows methane adsorption isotherms of **1** and **2** at 298 K. The adsorption isotherms are of Langmuir type. Approximately 212 cm³ (STP) and 213 cm³ (STP) of methane were adsorbed per g of dried samples of **1** and **2** at 3.5 MPa. These values are much higher than that of zeolite 5A [*ca.* 83 cm³ (STP) g⁻¹ at 3.5 MPa] and nearly the same as that of the high surface area activated carbon AX-21, a methane adsorbent with the highest capacity among conventional materials.²

The samples were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 5(a) and (b) show SEM image of particles of **2**, indicating that the particles are plate forms of *ca.* 0.2 μm in width, these particles aggregate and particles of *ca.* 7 μm in size are formed. Fig. 5(c) shows a surface AMF image of **2**. Nanocrystallites of *ca.* 100 nm in size were observed on the surface, considered to be the primary particles.

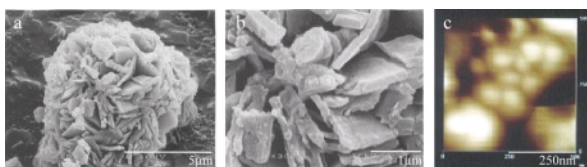


Fig. 5 SEM and AFM images of coordination polymer **2**.

Moreover, in order to characterize pore structures and material density, mercury intrusion penetration was measured from 1 to 60 000 psia with a Micromeritics instrument. Fig. 6 shows the result of mercury porosimetry for **2**, which is in good accordance with those of SEM and AFM, with regard to voids between particles, *i.e.* the voids between the secondary particles (plate forms) correspond to peak a of 0.1–5 μm and the voids between the primary particles correspond to peak b of 6–20 nm. The apparent density (0.983 g cm⁻³) of the primary particles is

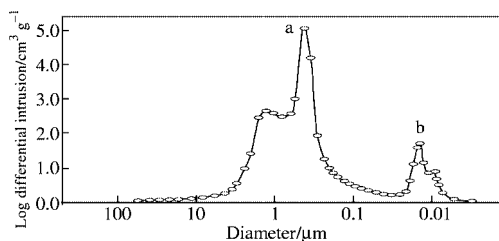


Fig. 6 Mercury penetration curve for **2** (differential intrusion vs. pore diameter).

calculated from the result of mercury porosimetry by assuming that peaks a and b are derived from voids between particles. The practical parameter, *v/v*, expressing the gas storage capacity [*v/v* is the volume of gas (at 298 K and 0.1013 MPa) divided by the volume of the tank] was estimated to be 225 from the density and the amount of adsorbed methane per weight of dried sample. On the other hand, adsorption simulations predict that the theoretical maximum for methane storage capacity of carbon, the structure of which consists of parallel planes of graphite with an optimum slit width 11.4 Å, is *v/v* = 198, for void-free monolithic carbon.¹⁵ Thus the amount of adsorbed methane for **2** surpasses the theoretical maximum storage capacity of carbon calculated under the same conditions due to the high density of the complex.

The results of the present work have important implications since practical utilization of the coordination polymer for new adsorptive gas storage may be feasible.

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Notes and references

† **1**: An ethanol solution (15 cm³) of copper(II) acetate monohydrate (0.095 g) was added to a dimethylformamide solution (30 cm³) of styrene dicarboxylic acid (0.096 g) and formic acid (0.3 cm³). After the mixture was allowed to stand for several days at 313 K, a toluene solution (12.5 cm³) of triethylenediamine was added to the mixture, which was then allowed to react at 373 K in an autoclave for 1 h. A light blue precipitate was collected, washed with methanol, and dried at 373 K *in vacuo*. Anal. Found: C, 49.34; H, 2.70; N, 4.42. Calc. for Cu(O₂CC₆H₄CO₂)·1/2C₆H₁₂N₂: C, 50.90; H, 2.96; N, 4.42%.

2: This complex was prepared using the procedure described for **1**. Anal. Found: C, 56.52; H, 3.55; N, 3.52. Calc. for Cu(O₂CC₆H₄CO₂)·1/2C₆H₁₂N₂: C, 57.22; H, 3.11; N, 3.93%.

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