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Feature Article

Elastic layer-structured metal organic frameworks (ELMs)

Hirofumi Kanoh [a,*], Atsushi Kondo [b], Hiroshi Noguchi [a], Hiroshi Kajiro [c], Aya Tohdoh [d], Yoshiyuki Hattori [b], Wei-Chun Xu [d], Mamoru Inoue [c], Tsutomu Sugiura [c], Kazuhiro Morita [e], Hideki Tanaka [f], Tomonori Ohba [a], Katsumi Kaneko [a]

[a] Graduate School of Science, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan
[b] Division of Chemistry and Materials, Faculty of Textile Science and Technology, Shinshu University, Ueda 386-8567, Japan
[c] Nippon Steel Corporation, Shintomi, Futtsu, Chiba 293-8511, Japan
[d] Institute of Research and Innovation, Takada, Kashiwa, Chiba 277-0861, Japan
[e] New Business Planning Department, Nippon Steel Chemical Co., Ltd., 14-1, Sotokanda 4-chome, Chiyoda-Ku, Tokyo 101-0021, Japan
[f] Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

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ABSTRACT

Elastic layer-structured metal organic frameworks (ELMs) having flexible two-dimensional structure show a gate phenomenon in sorption/desorption of simple gas molecules. The gate phenomenon is accompanied by expansion/shrinkage of the layers. The gas sorption/desorption is not based on a physical adsorption, but on a chemical reaction, which includes high cooperativity. The cooperative reaction could be analyzed thermodynamically. The gate phenomenon showed advantages in separation of CO_2 from mixed gases and in storage of CH_4 owing to easy release of absorbed molecules.

1. Introduction

Organic–inorganic hybrid nanoporous crystals can also be called porous coordination polymers (PCPs) or porous metal organic frameworks (PMOFs) [1,2]. These typically consist of metal ions as a centered core, organic molecules as a ligand, and counter ions as a useful building block. These porous materials have gathered much attention because of their applicability to wide fields such as molecular separation, storage or sensing, catalysis, drug delivering, and so on.

A typical nanoporous crystal is a group of zeolites. Zeolites have robust structures and mainly micropores of about 1 nm. Well-defined nanopores can form in the crystal structures of zeolites. The structure and chemical properties of pores can be modified but very limited. Although zeolites have uniform pores, components of heavier atoms such as Si, Al, or other metals causes a lower porosity, whereas another typical nanoporous material, activated carbon, is highly porous because activated carbon consists mainly of carbon and activation procedures introduce nanostructures into the graphite structure. However, since activated carbon is less crystalline, the nanopores in it are not uniform. In general, activated carbon has wide pore size distribution, except some activated carbon fibers.

In contrast, because of variety in building blocks of metal ions, organic molecules and counter ions, the organic–inorganic hybrid nanoporous crystals have the following advantages [1]: high designability, regularity, and flexibility. These advantages bring about structural diversity, particularly hierarchal structure. The various combinations of building blocks easily enable us to construct different dimensional structures (Fig. 1). Combination of robust and soft frameworks leads to the flexible structures, where the robust frameworks consist of covalent bonds and coordinate bonds, whereas the soft frameworks are based on hydrogen bonds or π–π interaction between aromatic rings. These different bonding modes give rise to hierarchal structures: The lower dominant dimensional structure is composed of robust frameworks and the higher dimensional structures are constituted through the weaker interactions. For example, a two-dimensional (2D) structure (layered structure in Fig. 1c) consists of 2D layers, which contains the stronger bonding in the *x*–*y*-plane and the weaker bonding (or interaction) along *z*-axis through pillaring materials.

Flexible structure induces novel functionalities such as a gate phenomenon [3,4] or breathing effect [5] accompanied by expansion/shrinkage of lattices (an elastic property) [6], or sliding motion [7] and so on. Our recent studies have showed that several MOFs form a similar 2D grid and its stacking structures. We name these materials elastic layer-structured metal organic frameworks (ELMs). In the present paper, we summarize a gate phenomenon of one of ELMs, consisting of $[Cu(bpy)_2(BF_4)_2]_n$ (bpy = 4,4′-bipyridine),

* Corresponding author. Fax: +81 43 290 2788.
E-mail address: kanoh@pchem2.s.chiba-u.ac.jp (H. Kanoh).

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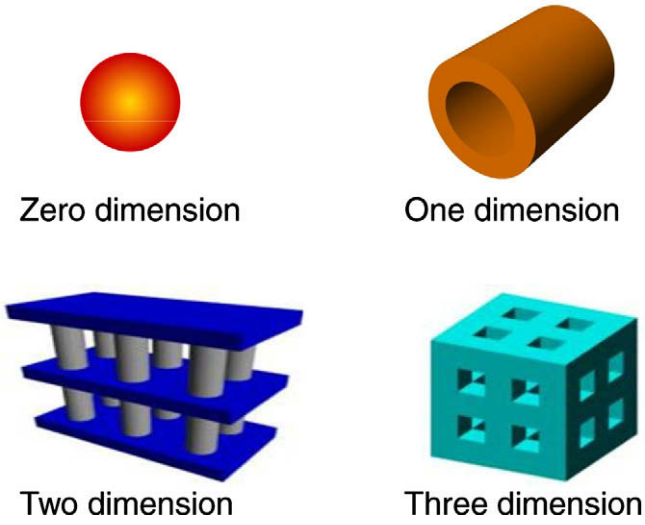

Fig. 1. Hierarchical structure of metal organic framework.

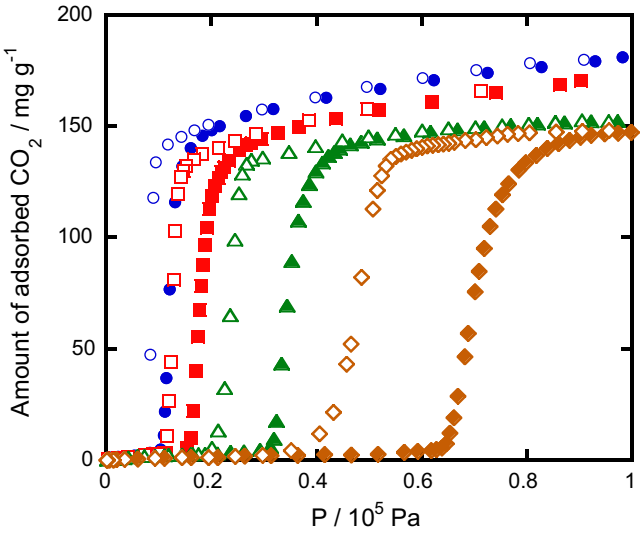

Fig. 3. Temperature dependence of CO_2 absorption on ELM-11. Blue circle: 248 K, red square: 258 K, green triangle: 273 K, and brown diamond: 298 K. Filled: absorption, open: desorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

which is called ELM-11, and show a thermodynamically analytical result about a cooperative clathrate formation in CO_2 absorption of ELM-11. Furthermore, applicability of ELM-11 to separation of CO_2 from a mixed gas and to storage of CH_4 is described. Finally, we briefly introduce recent results of effects of substitution of building units such as metal ions or counter anions on gas adsorptivity and crystal structures of ELMs.

2. $[Cu(bpy)_2(BF_4)_2]_n$ (ELM-11)

2.1. Structure and gate phenomenon

One of $[Cu(bpy)_2(BF_4)_2]_n$ (ELM-11) can be obtained by removal of water molecules from the lattice of $\{[Cu(bpy)(H_2O)_2(BF_4)_2](bpy)\}_n$, which can be prepared by a relatively easy method: Mixing of a $Cu(BF_4)_2$ aqueous solution with a 4,4′-bipyridine (bpy) methanol solution [8], where bpy denotes 4,4′-bipyridine. Blake et al. determined the crystal structure of $\{[Cu(bpy)(H_2O)_2(BF_4)_2](bpy)\}_n$ using a single crystal analysis [8]. $\{[Cu(bpy)(H_2O)_2(BF_4)_2](bpy)\}_n$ forms an interpenetrated structure [3,8,9]. The removal of water molecules from the lattice changes a chemical formula to $[Cu(bpy)_2(BF_4)_2]_n$ and the structure from the interpenetrated type to a 2D layered type [6]. Thus, ELM-11 can be obtained. The 2D layered structure of ELM-11 is indicated in Fig. 2. A bpy molecule bridges two Cu ions in the *x*–*y*-plane and the sequential repetition of the unit form a (quasi) square grid. However, the structure has little space enough to accommodate simple molecules such as N_2 or CO_2, because the stacking layers of the 2D grids shift alternately by a half of the lattice constant and have no straight channel, as shown in Fig. 2a. The interlayer space is not wide enough either for entrance of molecules from the lateral direction: The basal spacing is 0.458 nm (Fig. 2b).

Thus, the 2D layered structure of ELM-11 apparently indicates no open porosity. However, ELM-11 shows unique sorption isotherms of CO_2 at 273 K, as shown Fig. 3, and N_2 and Ar at 77 K: The isotherms show a vertical sorption uptake. We call this behavior a gate phenomenon. The sorption on ELM-11 suddenly begins at a definite sorption pressure (sorption gate pressure) and the sorbed gas is thoroughly desorbed at the desorption gate pressure which is lower than the sorption gate pressure. The isotherm has a rectangular hysteresis loop, which does not correspond to any types of isotherms IUPAC categorizes.

The detailed structure after the CO_2 sorption could be determined by the Reitveld analysis of powder diffraction data obtained by using synchrotron X-ray although the sorption sites of CO_2 are

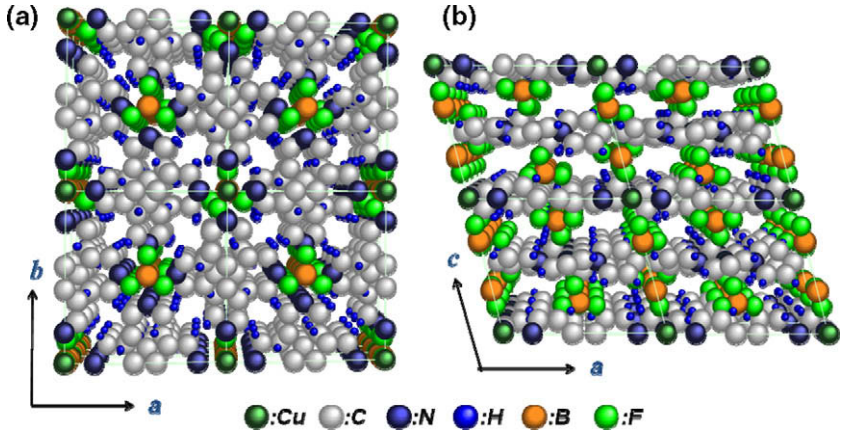

Fig. 2. Crystal structure of ELM-11. Lattice constant: $a = 1.1306$ nm, $b = 1.1466$ nm, and $c = 0.9480$ nm. Angle: $\alpha = 90.5°$, $\beta = 105.0°$, and $\gamma = 89.5°$.