

## HIGHLY DENSE & SELECTIVE ACETYLENE ACCOMMODATION IN METAL-ORGANIC MICROPOROUS MATERIAL

The recent advent of metal(organic microporous materials (MOMs), as new functional microporous adsorbents has attracted the attention of chemists [1,2] owing to scientific interest in the creation of unprecedented regular nano-sized spaces and in the finding of novel phenomena, as well as commercial interest in their application for storage, separation and heterogeneous catalysis. One of the advantages of MOMs, over other microporous materials such as activated carbons, is designability, which provides a variety of surface properties. This prominent feature leads us to expect that MOMs will show a high adsorption capability for specific molecules. However, few useful concepts and strategies for the specific adsorption of smaller molecules have been established to date. Here, we have found superb sorption of acetylene molecules on the functionalized surface of an MOM and show an enhanced “confinement effect,” which can be achieved by precisely and regularly arranged double hydrogen bonding sites in a nano-sized pore wall, applicable to a highly stable, selective adsorption system [3].

Acetylene ( $C_2H_2$ ) is one of the key molecules as a starting material for many chemical and electric materials. In order to obtain highly pure  $C_2H_2$  for the preparation of these materials, the separation of  $C_2H_2$  from a mixture gas containing carbon dioxide ( $CO_2$ ) impurities without a large expenditure of energy is an important subject. However the separation is considerably difficult because these molecules are quite similar to one another in equilibrium sorption parameters, related physico-chemical properties, and molecular size and shape (Fig. 1). In addition, acetylene is well known as a highly reactive molecule and, therefore, it cannot be compressed above 0.2 MPa; otherwise, it explodes without oxygen, even at room

temperature. With this background, more feasible and safe materials for  $C_2H_2$  separation are required.

The complex **1** [ $Cu_2(pzdc)_2(py_2)$ ] (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine) is a suitable adsorbate for the adsorption of  $C_2H_2$  and  $CO_2$  molecules due to their permanent one-dimensional channel, with a cross section of  $4 \times 6$  Å. In addition, **1** has oxygen atoms in its pore surface, which act as basic adsorption sites for guest molecules. Accordingly, it is expected that **1** would exert an effective sorption ability for  $C_2H_2$  molecules because  $C_2H_2$  molecules have a linear form with acidic hydrogen atoms at both ends ( $pK_a = 25$ ). The adsorption isotherms of  $C_2H_2$  and  $CO_2$  at 270, 300 and 310 K were measured on anhydrous **1** (Fig. 2). A marked difference between  $C_2H_2$  and  $CO_2$  adsorption isotherms was observed. The adsorption isotherms of  $C_2H_2$  show a steep rise in the very low-pressure region and reach saturation, whereas those of  $CO_2$  indicate gradual adsorption. The saturation-adsorbed amount of  $C_2H_2$  corresponds to just one molecule per unit pore. The maximum ratio of the amount adsorbed of  $C_2H_2$  relative to that of  $CO_2$  absorbed is 26.0 (at 1.1 kPa) at 270 K, indicating that **1** adsorbed  $C_2H_2$  more preferentially than  $CO_2$ .

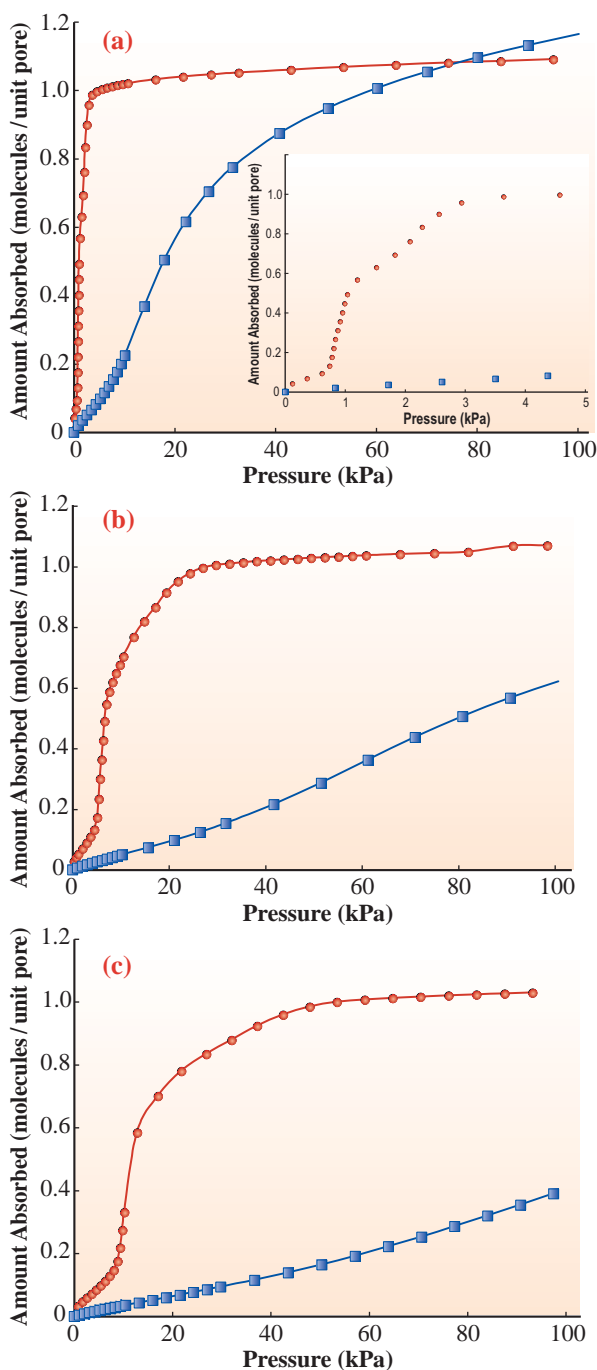
To elucidate the mechanism of the high adsorption ability for  $C_2H_2$  molecules in **1**, we determined the structure and electron density of **1** with adsorbed  $C_2H_2$  molecules by the MEM (maximum entropy method)/Rietveld analysis using synchrotron X-ray powder diffraction (XRPD) data of **1** with  $C_2H_2$  at 10 kPa at 170 K (Fig. 3), beamline BL02B2. Only one  $C_2H_2$  molecule locates in the middle of the channels. Surprisingly, the density of adsorbed  $C_2H_2$  in the pore is equivalent to the value of an imaginary state of acetylene at 41 MPa at room temperature and is 200 times larger than the value of the compression limit for the safe use of  $C_2H_2$  at room temperature, 0.20 MPa.

In the channels,  $C_2H_2$  molecules align along the *a*-axis, and each end of the  $C_2H_2$  molecule is oriented to two non-coordinated oxygen atoms on the pore wall. We can recognize a few electrons ( $0.21 \text{ eÅ}^{-3}$ ) between the hydrogen atom of  $C_2H_2$  and the free oxygen atom, indicating that O---H—C hydrogen bonds exist. These interactions strongly fix the  $C_2H_2$  molecule in a periodic unit pore and isolate the  $C_2H_2$  in the 1D-channel, which enhances the “confinement effect” and enables stable accommodation.

	$C_2H_2$	$CO_2$
Molecular Size	5.5 Å	5.3 Å
Critical Temperature	308.2 K	304.2 K
Standard Boiling Point	189.2 K	194.7 K

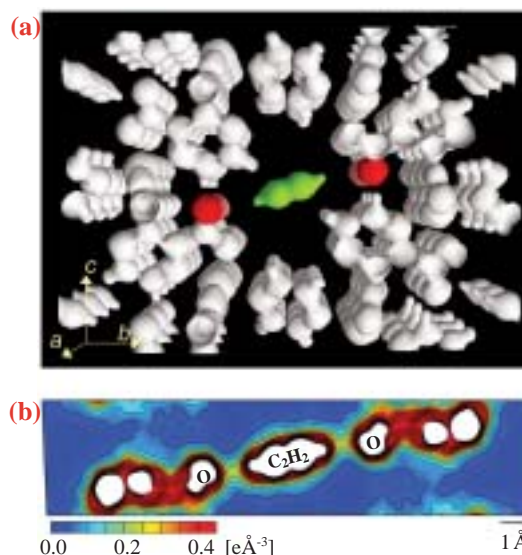
Fig. 1. Molecular size and thermodynamic properties of  $C_2H_2$  and  $CO_2$ .

The specific sorption ability of **1** for  $C_2H_2$  is ascribed to the binding of the acetylene molecule in two basic oxygen atom sites, which are ideally arranged on a regular micropore surface. Usually, small molecules such as  $CO_2$  are adsorbed in the micropore only by the deep van der Waals type



**Fig. 2.** Adsorption isotherms for  $C_2H_2$  (red circles) and  $CO_2$  (blue squares) on **1**. The pressure range is from  $10^{-4}$  to 100 kPa and the temperatures is 270 K (inset shows a lower pressure region) (a), 300 K (b) and 310 K (c).

potential energy well. However, these functional sites of flexible MOMs attain optimal chemical bonding with specific adsorbates and significantly enhance the “confinement effect.” According to the results, when the multiple specific interaction-sites are located at suitable positions on a regular micropore, a specific adsorption system to the target molecule can be realized. This new guideline for the specific adsorption system on microporous materials will be applicable to a wide range of target molecules.



**Fig. 3.** MEM electron density views. (a) MEM electron densities of  $C_2H_2$  adsorbed **1** at 170 K as equal-density contour surface along  $a$ -axis. The equicontour level is  $1.0 \text{ e}\text{\AA}^{-3}$ . The central  $C_2H_2$  molecule and oxygen atoms are in yellow-green and red, respectively. Other atoms are in white. (b) MEM electron density distribution views on two-dimensional section along molecular axis of  $C_2H_2$  molecule down the  $a$ -axis.

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## References

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