Framework for H_2 storage

POROUS MATERIALS

Metal-organic framework materials (MOFs) have attracted great attention since they were first synthesized in 1999 because their extraordinary level of porosity and large surface area hold promise for gas adsorption and storage. The materials consist of metal oxide units linked into a three-dimensional framework by organic molecules, which allows MOFs to be designed with compositions and pore sizes suitable for different applications. Omar M. Yaghi and colleagues at the University of Michigan, Ann Arbor and the University of Texas-Pan American have synthesized a new MOF with a high capacity for H_2 storage [Chen *et al.*, *Angew. Chem. Int. Ed.* (2005) **44** (30), 4745].

"The high surface areas and functionalities of porous MOFs hold promise for both physisorption and chemisorption of hydrogen molecules," explains Banglin Chen of the University of Texas. "We developed a straightforward strategy to incorporate open metal sites for potential chemisorption of H_2, together with the high surface area and pore size for efficient physisorption."

MOF-505, as the new material is known, consists of square $Cu_2(CO_2)_4$ units linked by rectangular biphenyltetracarboxylate (bptc) blocks. The extended network has two sizes of pores, one with a diameter of 8.3 Å surrounded by the inorganic units and the other 10.1 Å in size surrounded by bptc units. This gives a total accessible free volume of 37.1%.

MOF-505 is able to take up 2.47 wt.% hydrogen at 77 K and 1 atm pressure. This is the highest yet recorded under these conditions and is an important milestone toward achieving the 2010 target of 6.0 wt.% proposed by the US Department of Energy, says Chen.

Jonathan Wood

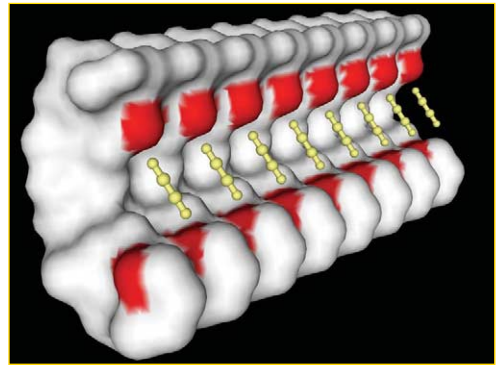
Pores separate and store gas

POROUS MATERIALS

One advantage of metal-organic microporous materials (MOMs) is the ability to incorporate organic functional groups into the pore walls. Properties such as hydrophilicity or chirality can be introduced for applications in storage, separation, and heterogeneous catalysis. Japanese researchers have synthesized an MOM that specifically absorbs and stores acetylene over the similarly sized CO_2 molecule [Matsuda *et al.*, *Nature* (2005) 436, 238]. Acetylene (C_2H_2) is an important starting material for making many chemical products and electriconic materials, but it is important to separate out CO_2 impurities. C_2H_2 is also highly reactive and explodes at pressures >0.2 MPa.

Not only is the new MOM capable of separating the two gases, it permits stable storage of C_2H_2 at a density 200 times greater than the safe compression limit of free C_2H_2 at room temperature.

The new hybrid material $Cu_2(pzdc)_2(pyz)$, where pzdc is pyrazine-2,3-dicarboxylate and pyz is pyrazine, has pores 4-6 Å in size. This pore diameter is suited to both C_2H_2 and CO_2 molecules. However, two noncoordinated oxygen atoms on the pore wall can hydrogen bond to the hydrogen atoms of C_2H_2. This leads to the adsorption of 26 times more C_2H_2 than CO_2 at 270 K and 1.1 kPa.



Acytelene molecules (yellow) bound to noncoordinated oxygen atoms (red) on the MOM pore wall. (Courtesy of Susumu Kitagawa.)

A saturation point is reached very quickly in the adsorption of C_2H_2, even at low pressures. A 1:1 ratio is achieved between the number of adsorbed molecules and the available pore sites. This gives the high acetylene storage density observed.

"We are going to design and synthesize various MOMs targeting other molecules such as environmental pollutant gas molecules NO_x and SO_x, and the energetically important CH_4 and H_2," Susumu Kitagawa of Kyoto University told *Materials Today*.

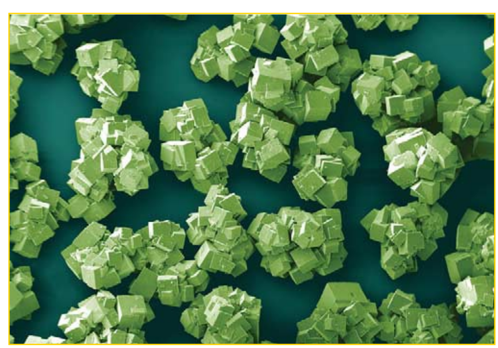
Jonathan Wood

BASF develops MOF materials

CONFERENCE REPORT

Ulrich Müller described BASF's progress in commercializing metal-organic framework materials (MOFs) at the 2005 International Conference on Materials for Advanced Technologies in Singapore. BASF became interested in MOFs because of their remarkable surface areas. MOFs can also be synthesized with readily available, cheap chemicals. The company now has a pilot plant that yields 20 kg of MOF from a synthesis of 2-3 hours. ZnO is simply mixed with a solution of ethylene terephthalate in a suitable solvent that can be recycled. The MOF forms as a precipitate, which is shaped into tablets after filtration and drying.

BASF are not looking to sell the MOFs as raw materials, rather they will work with partners to develop systems for gas purification and storage. Müller explained that the MOF structure allows the maximal storage of gas on a per-volume basis. Filling a gas canister with MOF tablets allows you to store three times more propane for use as an outdoor source of fuel. MOFs are also extremely promising for H_2 storage, with fast uptake and release of H_2, fully reversible storage, and a low temperature of adsorption.



'Nanocubes' of MOF materials. (Courtesy of BASF.)

Jonathan Wood