Framework for H₂ storage

POROUS MATERIALS

Metal-organic framework materials (MOFs) have attracted great attention since they were first synthesized in 1998 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 threedimensional 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 California, Berkeley and the University of Texas-Pan American have synthesized a new MOF with a high capacity for H₂ 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 Michigan, Ann Arbor and the University of Texas-Pan American have synthesized a new MOF with a high capacity for H₂ 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 Michigan, Ann Arbor and the University of Texas-Pan American have synthesized a new MOF with a high capacity for H₂ storage (Chen et al., Angew. Chem. Int. Ed. (2005) 44 [30], 4745).

MOF-505, as the new material is known, consists of square Cu₂(CO₂)₄ units linked by rectangular bipyridine-tetracarboxylate (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 CO₂ molecule [Matsuda et al., Nature (2005) 436, 238]. Acetylene (C₂H₂) is an important starting material for making many chemical products and electronic materials, but it is important to separate out CO₂ impurities. C₂H₂ 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 C₂H₂ at a density 200 times greater than the safe compression limit of free C₂H₂ at room temperature. The new hybrid material Cu₂(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 C₂H₂ and CO₂ molecules. However, two noncoordinated oxygen atoms on the pore wall can hydrogen bond to the hydrogen atoms of C₂H₂. This leads to the adsorption of 26 times more C₂H₂ than CO₂ at 270 K and 1.1 kPa. A saturation point is reached very quickly in the adsorption of C₂H₂, 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 NOx and SOx, and the energetically important CH₄ and H₂,” 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 H₂ storage, with fast uptake and release of H₂, fully reversible storage, and a low temperature of adsorption.

Jonathan Wood

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