Hydrogen Storage in Metal-Organic Frameworks

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INTRODUCTION

Materials exhibiting reversible hydrogen adsorption with high gravimetric and volumetric capacities are sought for use in on-board storage systems of hydrogen fuel cell-powered vehicles. Microporous metal-organic frameworks with high internal surface areas have been shown to display excellent storage properties, but only at cryogenic temperatures. Methods for synthesizing frameworks containing coordinatively-unoccupied metal centers are therefore being developed as a means of increasing the H₂ adsorption enthalpy. In particular, we seek to synthesize thermally-robust, high-surface area materials with a high concentration of open metal coordination sites. By adjusting the electronic structure of the metal ions, it is expected that an optimal H₂ binding enthalpy in the range ~15 to ~20 kJ/mol can be achieved, leading to a high H₂ storage capacity at room temperature and safe pressures of up to 100 bar.

RESULTS AND DISCUSSION

We have utilized a number of strategies for generating open metal coordination sites on the internal surfaces of microporous metal-organic frameworks. Our approaches involve the insertion and activation of metal carbonyl units on the aromatic components of existing frameworks, as well as the design of new frameworks using bridging ligands that facilitate the generation of open metal coordination sites. For example, the reaction of Zn₂O(BDC)₂ (MOF-5) with Cr(CO)₅ has been shown to generate (arene)Cr(CO)₃ units that can be photoactivated to bind H₂. Alternatively, the use of triangular azolate-based bridging ligands has been shown to result in a sodalite-type structure with solvated metal centers within the framework that can be activated to bind H₂. Further studies have involved frameworks such as M(dobdc) (M = Mg, Fe;dobdc = 2,5-dioxido-1,4-benzenedicarboxylate), which exhibit surfaces featuring an extremely high density of open M²⁺ coordination sites.

The resulting compounds have been characterized by a variety of techniques, including gas adsorption measurements, neutron powder diffraction (see Figure 1 for an example of the type of results obtained), inelastic neutron scattering spectroscopy, and infrared spectroscopy.

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REFERENCES