High Pressure Hydrogen Sorption Isotherms on Microporous Fluorinated Metal Organic Frameworks (FMOF) and BPL Carbon Using High-Pressure TGA (TGA-HP)

Qian Mather and A. F. Venero
TA Instruments-Waters LLC, 159 Lukens Drive, New Castle, DE 19720, USA

Prof. Mohammad Omary,
University of North Texas, Denton, TX, USA

ABSTRACT

This paper discusses the use of high-pressure TGA (TGA-HP) to investigate the hydrogen storage capacity of a novel fluorinated metal organic framework (FMOF).

INTRODUCTION

Hydrogen is attractive as the clean energy source of the future and as a potential replacement for fossil fuels due to the absence of harmful exhaust emissions and compatibility with fuel cells. The challenge for adopting hydrogen as a fuel source is the need for practical, portable storage systems.[1] Potential hydrogen storage technologies include containers of compressed or liquefied H_2, carbon nanotubes, metal hydrides and metal organic frameworks (MOFs), which store hydrogen via physisorption or chemisorption. The Department of Energy (DOE) has set aggressive targets for hydrogen storage capacity at near-ambient temperatures and pressures. At present, none of the currently-available candidate storage materials possess the combination of high hydrogen densities, low desorption temperatures, fast kinetics, and low-cost needed for automotive applications that meet the DOE criteria. Recently, new microporous metal-organic frameworks (MOFs) were found to be promising candidates for hydrogen storage.

Porous MOFs are constructed through the assembly of metal-containing clusters with multidentate organic ligands via coordination bonds into a three-dimensional structure with well-defined pore size and morphology. Because of their high surface area, controlled pore size and functionality, high gas sorption capacities are observed. Tunable pore size and functionality of pore-wall chemistry enable specific applications.

Since the hydrogen storage capacity of candidate materials increases at high pressures and low temperatures, current research on porous MOFs has been focused around pressures of 20-80 bar and at liquid nitrogen temperatures (77 K). These conditions create challenges for laboratory measurements of hydrogen uptake. Disadvantages of traditional volumetric methods include potential leakage at high pressure, temperature gradient effects on the measured pressure and uncertainty in measuring the skeletal sample volume. In contrast, the advantage of high-pressure thermo-gravimetric analysis (TGA-HP) is direct measurement of mass uptake without the above-mentioned drawbacks.

High-Pressure TGA is an excellent tool to investigate the efficiency of a material for absorbing and storing gases such as hydrogen, at a variety of temperatures and pressures. The TA Instruments TGA-HP series products are specialty gravimetric analyzers designed to provide unique capabilities for high-pressure, ultra-high vacuum, and high-temperature under static or dynamic reactive atmospheres. These instruments are designed for sorption studies using water vapor, organic vapors, hydrogen, methane and carbon dioxide as well as permanent gases and corrosive gases. Using dynamic and static methods, the TGA-HP series provides the capability of studying isothermal or isobaric measurements under conditions of high pressure or high vacuum, and high temperature. Typical applications include:

- General gas/solid and vapor/solid reactions
- Oxidation/reduction of metals
- Gas adsorption/desorption studies
- Diffusion and permeation studies
- Reaction kinetics
- Degradation of ceramics
- Catalysts, zeolites, activated carbons and other specialty materials
- CO_2 sequestration
- Coal gasification
- Methane storage

EXPERIMENTAL PROCEDURES

A TA Instruments TGA-HP50 was used to conduct hydrogen sorption measurements on porous FMOF samples synthesized by Omary et al[2]. The TGA-HP50 utilizes a recording microbalance with a sensitivity of 0.5 µg which provides excellent accuracy for measurement of minute weight changes. A sample size of 100 mg FMOF was loaded into an aluminum sample pan. An equilibrium criteria of < 0.003 wt% change over 5 min was utilized in order to determine the appropriate transition point to successive pressure steps. Pressure was stepped from 500 torr (0.67 bar) to 50,000 torr (67 bar). Temperature control at 77 K was achieved using a custom liquid nitrogen Dewar surrounding the reactor tube. Due to the temperature differential between the sample and reference sides, the buoyancy effect was not negligible and was corrected via the standard method of executing the exact same experimental run in helium (helium does not physisorb on surfaces, so any weight change detected is due solely to buoyancy). The volume of the sample was calculated using a density of 1.78 g/cm^3 obtained from XRD measurements[2]. The measurement precision of pressure transducer is 0.01 torr and the temperature is measured with a precision of 0.01°C. The data acquisition interval was every 2 min or after 0.01 wt% change. For both H_2 and He runs, samples were outgassed until weight was stabilized. BPL carbon was outgassed at 0.01 torr at 325°C for 30 min.

RESULTS & DISCUSSION

The fluorinated MOF sample synthesized by Omary et al. consists of silver tetrazole clusters that assemble to create fluorinated microporous channels, and smaller cavities. A space filling representation is provided in Figure 1.

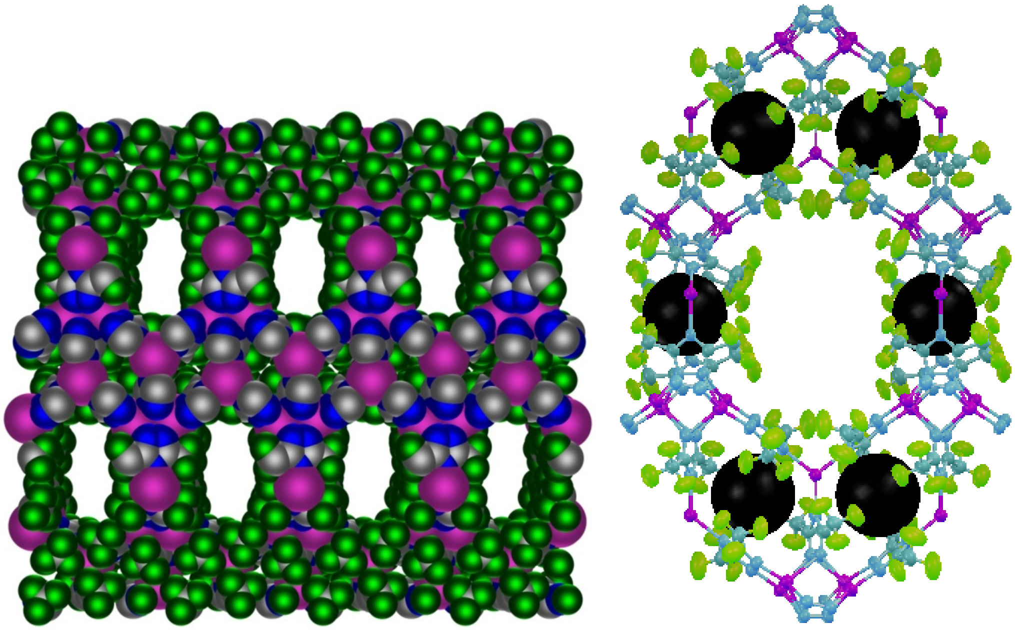

Figure 1: (a) a space-filling representation of the large fluoro-lined channels (~ 12.2×7.3 Å) and (b) a perspective view of the small cavities (~ 6.6×4.9 Å), denoted by black spheres, surrounding the large channels.

The excess H_2 adsorption storage capability of BPL carbon and the FMOF sample is shown in Figure 2. Note how the gravimetric adsorption is quantified over a wide pressure range from sub-atmospheric to nearly 70 bar. Interestingly, the hydrogen sorption isotherm of FMOF shows a two-step filling profile at low pressure. It is reasonable to assign the first uptake to filling of gas molecules into the larger fluorinated micropore channels; whereas the second step of the sorption is assigned to the small pores since the size of the latter can accommodate the dynamic size of the H_2 molecules. Hysteresis is seen in the hydrogen sorption process, with a plateau during pressure drop that lasts until 14 bar pressure is reached. This hysteresis could be exploited in order to allow sorption at high pressure, but storage at low pressure. The gravimetric capacity of hydrogen within the FMOF at 77 K and 30 bar was measured for 1.72 wt% which is 31 kg/m^3 using skeletal density of 1.78 kg/m^3 obtained from XRD measurement. This is close to the DOE 2010 target of 45 kg/m^3. In comparison, BPL

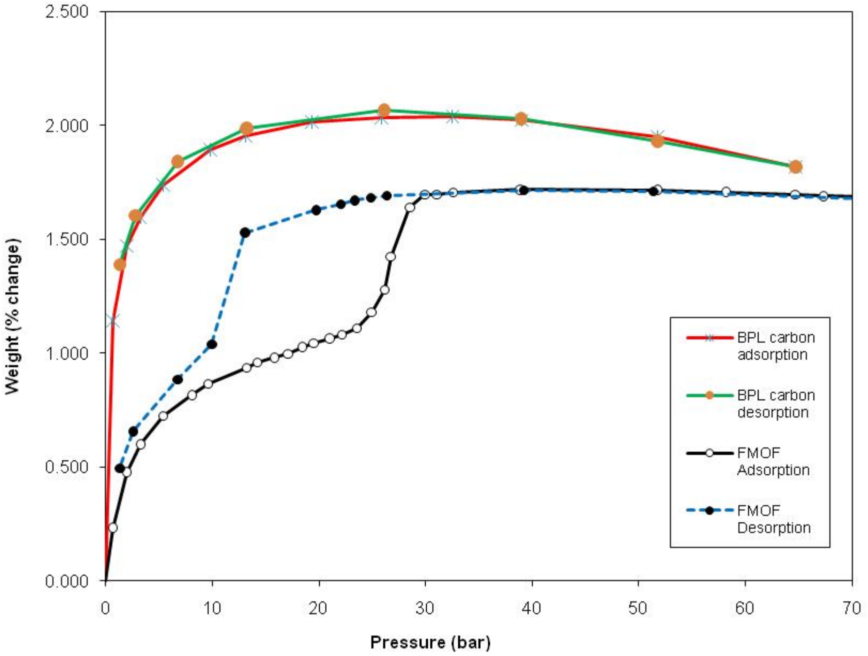

Figure 2: H_2 uptake onto BPL carbon and FMOF at 77k

carbon H_2 sorption showed a reversible type I isotherm with a maximum of ~2 wt% at 30 bar. Usually for micropore filling, small pores are filled first and larger pores later.

It is difficult to explain the isotherm and the hysteresis results presented here. One hypothesis is that structure morphological change occurs during sorption. This is supported by a physical appearance change in the sample: before the sorption test the sample is composed of large granules and by the end of test it is a fine powder. Crystallographic studies[3] have shown the order of filling of N_2 on adsorption sites vs. temperature. It is reported that the small cavities in the FMOF are accessible only after the major channel is filled. The high flexibility of silver coordination allows large framework expansion or contraction without any apparent bond breaking. The change in bond lengths and angles results in a large anisotropic unit-cell expansion or contraction that is reflected in the size and shape changes of the channels and cages. From this “breathing” effect, it is postulated that H_2 adsorption is similar to previously observed N_2 adsorption in FMOF (not shown here); a two-step mechanism where small cavities are filled after the large channels are filled. To obtain a quantitative analysis of the pore size distribution and pore volume, it is advisable to utilize a number of probe gas molecules with different sizes, for which the TGA-HP series are perfectly suited.

CONCLUSIONS

These experiments demonstrate that the TGA-HP series high-pressure gravimetric analyzer is ideal for performing sorption experiments at high pressure or high vacuum and low temperature with good accuracy and repeatability for demanding applications such as the study of hydrogen sorption.

REFERENCES

1. http://www.eoearth.org/article/Hydrogen_storage
2. C. Yang, X. Wang and M. Omary, *J. Am. Chem. Soc.*, **2007**, 129, 15454-15455.
3. C. Yang, X. Wang and M. Omary, *Angew. Chem.,* **2009**, 121, 2538-2543.

TA Instruments

United States
159 Lukens Drive, New Castle, DE 19720 • Phone: 1-302-427-4000 • E-mail: info@tainstruments.com

Canada
Phone: 1-905-309-5387 • E-mail: shunt@tainstruments.com.

Mexico
Phone: 52-55-5200-1860 • E-mail: mdominguez@tainstruments.com

Spain
Phone: 34-93-600-9300 • E-mail: spain@tainstruments.com

United Kingdom
Phone: 44-1-293-658-900 • E-mail: uk@tainstruments.com

Belgium/Luxembourg
Phone: 32-2-706-0080 • E-mail: belgium@tainstruments.com

Netherlands
Phone: 31-76-508-7270 • E-mail: netherlands@tainstruments.com

Germany
Phone: 49-6196-400-7060 • E-mail: germany@tainstruments.com

France
Phone: 33-1-304-89460 • E-mail: france@tainstruments.com

Italy
Phone: 39-02-2742-11 • E-mail: italia@tainstruments.com

Sweden/Norway
Phone: 46-8-555-11-521 • E-mail: sweden@tainstruments.com

Japan
Phone: 813-5479-8418 • E-mail: j-marketing@tainstruments.com

Australia
Phone: 613-9553-0813 • E-mail: sshamis@tainstruments.com

India
Phone: 91-80-2839-8963 • E-mail: india@tainstrument.com

China

Phone: 8610-8586-8899 • E-mail: info@tainstruments.com.cn

Taiwan
Phone: 886-2-2563-8880 • E-mail: skuo@tainstruments.com

Korea
Phone: 82.2.3415.1500 • E-mail: dhrhee@tainstruments.com

To contact your local TA Instruments representative visit our website at www.tainstruments.com