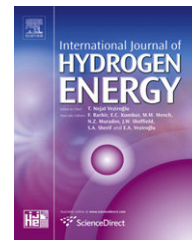


Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Increased volumetric hydrogen uptake of MOF-5 by powder densification

J.J. Purewal<sup>a,b</sup>, D. Liu<sup>a,b</sup>, J. Yang<sup>a</sup>, A. Sudik<sup>a,\*</sup>, D.J. Siegel<sup>b</sup>, S. Maurer<sup>c</sup>, U. Müller<sup>c</sup>

<sup>a</sup> Ford Motor Company, Research and Advanced Engineering, MD 1170/RIC, P.O. Box 2053, Dearborn, MI 48121, USA

<sup>b</sup> Mechanical Engineering Department, University of Michigan, 2250 G. G. Brown Laboratory, 2350 Hayward St., Ann Arbor, MI 48109, USA

<sup>c</sup> BASF SE, Chemicals Research and Engineering, 67056 Ludwigshafen, Germany

## ARTICLE INFO

### Article history:

Received 20 November 2010

Received in revised form

25 February 2011

Accepted 3 March 2011

Available online 16 April 2011

### Keywords:

Hydrogen storage

Metal-organic frameworks

Adsorbents

Thermal conductivity

Materials processing

## ABSTRACT

The metal-organic framework MOF-5 has attracted significant attention due to its ability to store large quantities of H<sub>2</sub> by mass, up to 10 wt.% absolute at 70 bar and 77 K. On the other hand, since MOF-5 is typically obtained as a bulk powder, it exhibits a low volumetric density and poor thermal conductivity—both of which are undesirable characteristics for a hydrogen storage material. Here we explore the extent to which powder densification can overcome these deficiencies, as well as characterize the impact of densification on crystallinity, pore volume, surface area, and crush strength. MOF-5 powder was processed into cylindrical tablets with densities up to 1.6 g/cm<sup>3</sup> by mechanical compaction. We find that optimal hydrogen storage properties are achieved for  $\rho \sim 0.5$  g/cm<sup>3</sup>, yielding a 350% increase in volumetric H<sub>2</sub> density with only a modest 15% reduction in gravimetric H<sub>2</sub> excess in comparison to the powder. Higher densities result in larger reductions in gravimetric excess. Total pore volume and surface area decrease commensurately with the gravimetric capacity, and are linked to an incipient amorphization transformation. Nevertheless, a large fraction of MOF-5 crystallinity remains intact in densities up to 0.75 g/cm<sup>3</sup>, as confirmed from powder XRD. Predictably, the radial crush strength of the pellets is enhanced by densification, increasing by a factor of 4.3 between a density of 0.4 g/cm<sup>3</sup> and 0.6 g/cm<sup>3</sup>. Thermal conductivity increases slightly with tablet density, but remains below the single crystal value.

Copyright © 2011, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Research over the past 10 years has revealed the considerable potential for hydrogen storage in high surface area, microporous metal-organic frameworks (MOFs)—three-dimensional, crystalline solids constructed from a periodic array of metal clusters and multi-topic organic struts. In particular, frameworks consisting of tetrahedral [Zn<sub>4</sub>O]<sup>6+</sup> units connected via rigid multi-topic carboxylate linkers have been shown to adsorb large amounts of hydrogen reversibly at low

temperature and moderate pressure [1–4]. A specific compound, Zn<sub>4</sub>O(BDC)<sub>3</sub> (BDC = 1,4-benzene dicarboxylate), termed MOF-5 serves as the prototypical material in an extensive series of frameworks. MOF-5 can adsorb large amounts of hydrogen at low temperatures on a gravimetric basis, up to 10 wt.% absolute at 77 K [5,6]. With conventional synthesis methods, however, MOF-5 is obtained as a loose powder consisting of small crystallites. Powders have low density and poor thermal conductivity, major drawbacks from an engineering perspective. By mechanical compaction, MOF powders can be

\* Corresponding author.

converted into shaped bodies, such as pellets, which have higher densities and are easier to handle [7].

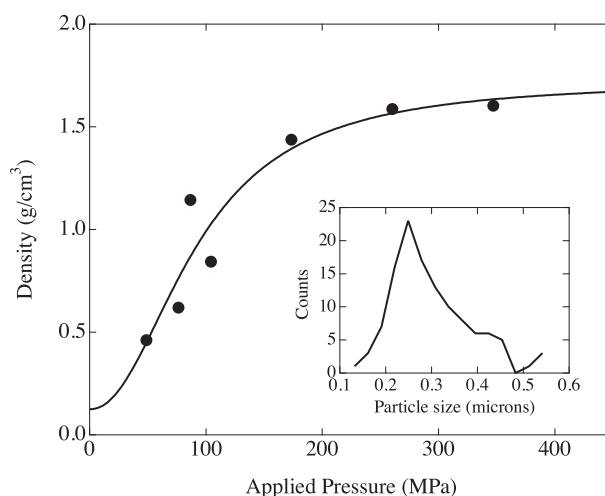
It has been previously found that densification of MOF-177 produces a decrease in the internal surface area, becoming particularly acute when the compacted powder density exceeds the single crystal density [8]. The degradation of intracrystalline porosity in MOF-177 is linked to an amorphization transformation brought on by mechanical compaction. Since amorphization in MOF-5 is thought to occur at a low applied pressure [9], this leads to the question of whether powder densification can actually be an effective method for improving volumetric hydrogen capacity.

While gravimetric and volumetric excess adsorption are the most commonly reported properties for hydrogen storage materials, they are not the only figures of merit for material performance. Total volumetric hydrogen storage, for example, is equal to the net amount of hydrogen gas (both adsorbed and free) contained within a fuel tank filled with MOF-5 powder or pellets. The difference in total volumetric storage between an upper and a lower pressure is approximately equal to the amount of hydrogen that can be delivered from a storage tank which is operated isothermally between those pressure limits. Secondly, the hydrogen refueling rate depends on the rate at which the sorbent material can be cooled to its base operating temperature. The thermal conductivity of pristine MOF-5 single crystals is already an order-of-magnitude smaller than the targeted value. The question of whether the density of MOF-5 pellets can be varied in a way that optimizes several key properties for a hydrogen storage material is the basis of the present work. In this study, MOF-5 powder was processed into pellets of varying bulk density. The effect of density on specific surface area, thermal conductivity, crush strength and hydrogen adsorption capacity is described.

## 2. Materials and methods

Powder samples of MOF-5 were prepared and desolvated as described previously [4,10]. In the following discussion we will often refer to three variations of MOF-5 density: (i) The *bulk powder density*, determined after the powder settles to a stable formation following light tapping, is measured at  $\rho_b \sim 0.13 \text{ g/cm}^3$ , and is strongly impacted by the aggregate packing (and void space) between individual crystallites. (ii) The *skeletal density*, determined by helium pycnometry (AccuPyc 1330, Micromeritics), is  $\rho_{sk} = 2.03 \text{ g/cm}^3$ , excludes pore volume from the volume used in the density calculation (i.e., only space taken up by the MOF linker and secondary building unit are considered part of the MOF volume). (iii) The *theoretical single crystal density* is given by  $\rho_c = 0.605 \text{ g/cm}^3$ , and represents the idealized limit of a bulk powder with a packing fraction of unity (i.e., no voids between crystallites).

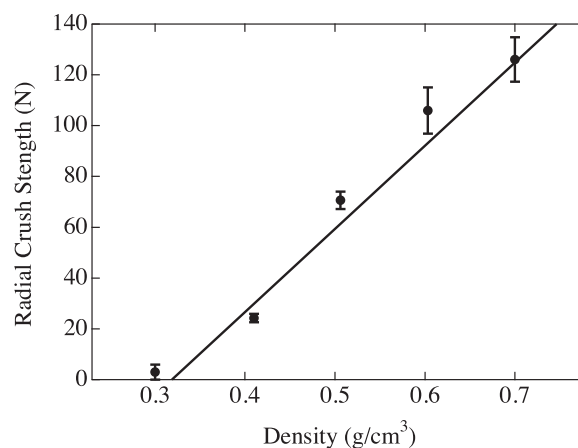
Pellets were prepared with bulk densities between  $0.27$  and  $0.79 \text{ g/cm}^3$  from desolvated MOF-5 powder with a cylindrical punch and die set having a bore diameter of either  $6.35 \text{ mm}$  or  $4.5 \text{ mm}$ . A specified mass of powder was loaded into a cylindrical die and compressed using a manual pellet press (Reflex Analytical). The resulting pellets are cylindrical with flat ends. By raising or lowering the anvil which supports the die, it is



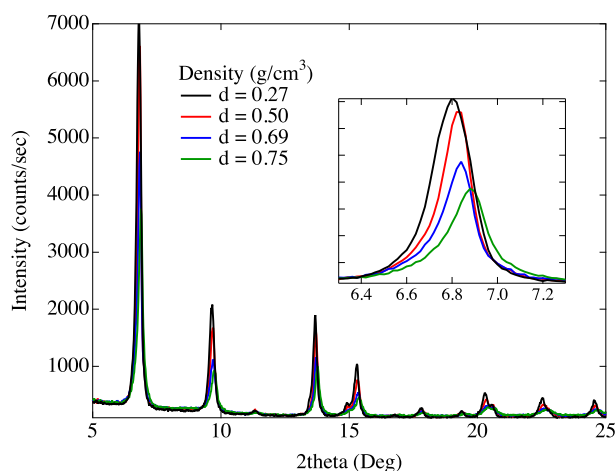
**Fig. 1 – Density of individual pellets versus forming pressure. Inset: Particle size distribution of the MOF-5 powder used to prepare pellets.**

possible to control the penetrating depth of the punch and thereby control the final pellet thickness. Pellet bulk densities are calculated from the mass and physical dimensions of individual pellets. Maximum error in the measured pellet density is approximately 3%.

Since MOF-5 is known to decompose in humid air [5], all handling of the material was done inside a high-purity glovebox with a humidity of less than  $0.1 \text{ ppm}$ . Particles of MOF-5 cohere well and it is not necessary to introduce binder additives to form pellets. Individual pellets typically weigh less than  $100 \text{ mg}$ , so it is necessary to produce a set of pellets of constant density in order to obtain a cumulative mass large enough for adsorption measurements. The variation of the measured density within a single set of pellets was largest for the  $0.41 \text{ g/cm}^3$  set, which had a standard deviation of approximately 3% of the mean. For all other sets the standard deviation was less than 1%. An additional set of pellets (used only in the pressure versus density calibration curve shown in Fig. 1)



**Fig. 2 – Radial crush strength of MOF-5 pellets as a function of pellet density.**



**Fig. 3** – Powder X-ray diffraction patterns for MOF-5 pellets. Inset: magnified view of the 6.8° peak.

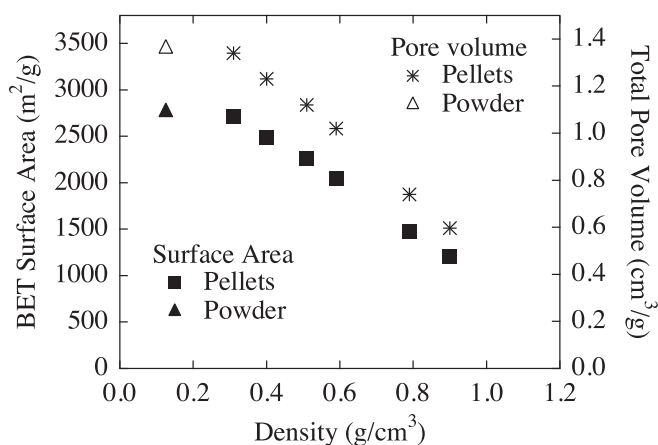
was prepared using a 6 mm die set and a 12 ton hydraulic press (Carver, 4350 manual pellet press). This bench-top press was located outside of the glovebox. To minimize exposure of the MOF-5 to humid air, dry nitrogen gas was blown across the die set during pressing.

Hydrogen adsorption measurements were performed with an automated Sieverts-type apparatus (PCT Pro 2000, Setaram). To collect isotherms at 77 K, the sample holder was submerged in a liquid nitrogen bath using a continuous-flow cryostat (CryoPro 2000, Setaram). Further details of hydrogen volumetric uptake measurements are available elsewhere [10]. Surface area and pore volume measurements were performed by nitrogen adsorption at 77 K with a Micromeritics ASAP 2420.

Thermal diffusivity measurements were performed with a commercial xenon flash thermal diffusivity instrument (Anter Flashline, FL3000S2) operating at 700 W, using 12 mm diameter pellets with an average thickness of 2 mm. The pellets were kept in a N<sub>2</sub> atmosphere during measurements. A thin layer of silver paint was applied to the top surfaces of the pellets to prevent them from fracturing during measurement. The lower surfaces of the pellets were coated with graphite. Heat capacity measurements were performed on individual 4.5 mm pellets with a DSC (SENSYS DSC, Setaram), using a heating rate of 5 °C/min and a He carrier gas flow of 20 ml/s.

Crush strength measurements were performed on a mechanical testing system (Instron model 3366) equipped with a 500 N load cell following the procedure described ASTM D4179-01. For radial crush tests, pellets of diameter 0.635 cm and height  $0.49 \pm 0.01$  cm were compressed on their side between two platen anvils at a rate of 0.5 mm/min until mechanical failure, detectable as a drop in applied load. Typically the pellets broke in half. Measurements were collected for 5 pellets of a given density.<sup>1</sup>

<sup>1</sup> ASTM D4179-01 recommends a sample set of 50–200.



**Fig. 4** – MOF-5 pellet BET specific surface area (■) and total micropore volume (\*) versus density. The BET surface area (▲) and total micropore volume (△) of powder MOF-5 is also shown.

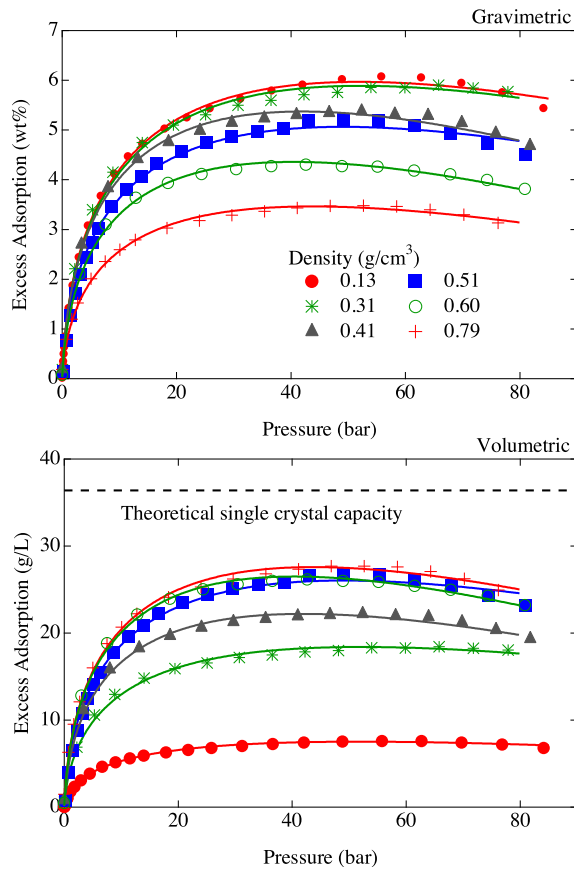
X-ray diffraction measurements were collected on a Scintag X2 powder diffractometer, using Cu K $\alpha$  radiation, with a step size of 0.02° and a rate of 2 s/step.

### 3. Results and discussion

Final pellet densities versus applied pressure (using pellets prepared with a 6 mm die and 12 ton hydraulic press) are summarized in Fig. 1. The applied forces varied from 1.3 kN to 9.8 kN. As expected, the density does not increase indefinitely, but instead approaches a limiting value of  $\rho_{\max} \sim 1.7$  g/cm<sup>3</sup>. This is nearly three times the single crystal density ( $\rho_c = 0.605$  g/cm<sup>3</sup>). It should be noted that pellet properties can depend on particle sizes of the starting powder, as well as on the holding time and release rate of the applied pressure. As shown in the inset of Fig. 1, the MOF-5 particle sizes varied between 0.15  $\mu$ m and 0.5  $\mu$ m, with a maximum at 0.25  $\mu$ m [10]. The holding time for applied loads was typically 1 min, but it was not possible to control the pressure release rate with the manual pellet presses.

Mechanical strength is an important consideration in determining an optimum pellet density. Pellets with inadequately low densities tend to crumble and break apart upon repeated handling. This is undesirable for pellets that have been designed to optimize heat transfer, kinetics, hydrogen density and other properties. The radial crush strengths of several sets of identically sized MOF-5 pellets (within an error of 1%) are compared in Fig. 2. Pellets with a density of 0.31 g/cm<sup>3</sup> show almost no resistance to compressive loads applied along their radius. However, tablets with larger densities have greatly improved crush strength. For the 0.41 g/cm<sup>3</sup> pellets, the average crush strength was 24 N. This increases to 71 N and 106 N for pellets having densities of 0.51 g/cm<sup>3</sup> and 0.60 g/cm<sup>3</sup>, respectively.

Fig. 3 shows powder XRD curves for MOF-5 tablets with varying densities. While the intensities of the diffraction peaks decrease with density, there are no other notable changes in

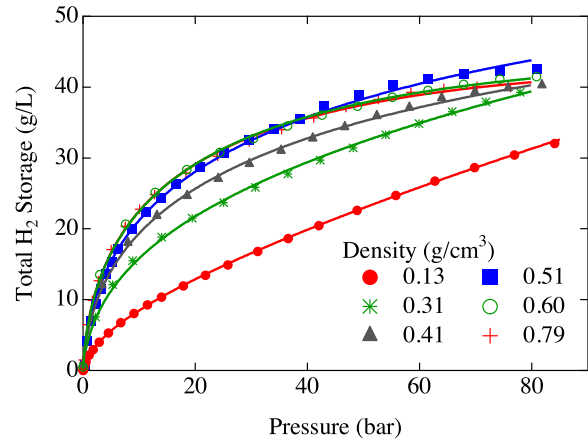


**Fig. 5 – Excess hydrogen adsorption by MOF-5 powder ( $\rho_b = 0.13 \text{ g/cm}^3$ ) and of several MOF-5 pellets of indicated densities at 77 K. Gravimetric adsorption (top) expressed as a mass fraction  $m_{\text{H}}/m_{\text{sample}} \times 100$ , and volumetric adsorption (bottom). Fits to the modified D-A model are shown.**

the XRD patterns except for a slight increase in the diffuse scattering.<sup>2</sup> Although the MOF-5 crystal structure is believed to collapse to an amorphous phase at an applied pressure of 3.5 MPa [9], this transformation is not observed here. Based on the calibration curve in Fig. 1, a density of 0.75 g/cm<sup>3</sup> corresponds to an applied pressure of around 80 MPa. While the consistent decrease in diffraction intensity does indicate a progressive transformation from crystalline to amorphous, even at 0.75 g/cm<sup>3</sup> a considerable fraction of the crystalline phase remains intact.

Compacting MOF-5 powder into pellets reduces the surface area relative to the powder. The variation of N<sub>2</sub> BET specific surface area versus pellet density is shown in Fig. 4. For MOF-5 pellets with  $\rho = 0.31 \text{ g/cm}^3$ , there is a 2% decrease in surface area compared to the powder ( $\alpha_{\text{BET}} = 2762 \text{ m}^2/\text{g}$ ). Pellets with densities of 0.51 g/cm<sup>3</sup> and 0.90 g/cm<sup>3</sup> exhibit a 18% and 57% decrease in surface area, respectively. Trends in total pore volume closely follow those for surface area.

<sup>2</sup> The small peak shift visible in the inset of Fig. 3 is due to sample displacement error which was caused by small differences in the heights of the prepared pellets.



**Fig. 6 – Total hydrogen storage by MOF-5 powder ( $d = 0.13 \text{ g/cm}^3$ ) and MOF-5 tablets of specified densities at 77 K. Fits to the modified D-A model are shown.**

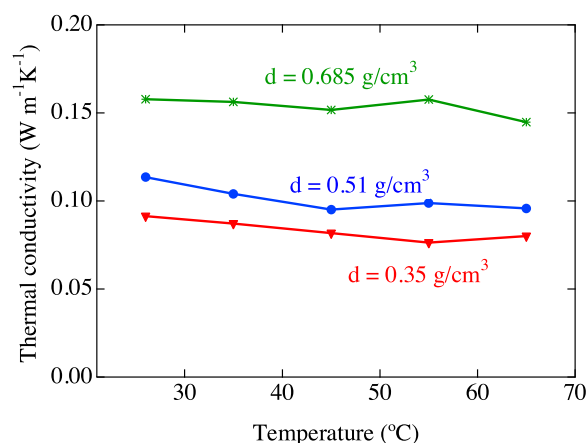
Excess hydrogen adsorption capacity at 77 K for many known sorbents scales with BET specific surface area [11]. Based on the results in Fig. 4, it is reasonable to expect similar trends in the hydrogen uptake for different sample densities. Excess hydrogen adsorption isotherms for MOF-5 powder and pellets are shown in Fig. 5, along with fits to a modified D-A model [12].<sup>3</sup> Maximum excess gravimetric uptake is unchanged in the 0.31 g/cm<sup>3</sup> pellet relative to the powder. However, decreases of 15% and 42% are observed for the 0.51 g/cm<sup>3</sup> and 0.79 g/cm<sup>3</sup> samples, respectively. Volumetric excess adsorption<sup>4</sup> is substantially increased for the densified pellets. The maximum volumetric excess adsorption is increased by a factor of 2.5 ( $V_{\text{max}} = 18.4 \text{ g/L}$ ) for the 0.31 g/cm<sup>3</sup> sample relative to the powder. The increase is a factor of 3.5 ( $V_{\text{max}} = 26.0 \text{ g/L}$ ) for the 0.51 g/cm<sup>3</sup> sample. This is approximately 70% of theoretical single crystal capacity of 36.4 g/L, as calculated from the gravimetric capacity of MOF-5 powder at 77 K (our measurement:  $n_{\text{max}} = 29.8 \text{ mol/kg}$ ) and from the single crystal density ( $\rho_c = 0.605 \text{ g/cm}^3$ ).

The total amount of hydrogen storage by MOF-5 pellets (defined as the excess adsorption plus the gas phase H<sub>2</sub> within the void space of the pellets) is plotted in Fig. 6. Relative to MOF-5 powder, total storage at 80 bar is increased by 26% in the 0.31 g/cm<sup>3</sup> sample and by 40% in the 0.51 g/cm<sup>3</sup> sample. On the other hand, if desorption occurs isothermally at 77 K by a pressure decrease from 80 bar to 3 bar, then the total hydrogen delivery is increased by 13% in the 0.31 g/cm<sup>3</sup> sample, versus 17% for the 0.51 g/cm<sup>3</sup> sample.

Preliminary thermal conductivity data for MOF-5 tablets was measured at 26, 35, 45, 55 and 65 °C for three densities. Results are shown in Fig. 7. The thermal conductivity ( $k$ ) was

<sup>3</sup> The modified D-A model is fitted independently for each sample. The D-A parameters  $\alpha$ ,  $\beta$  and  $\rho_0$  are taken from fits to data for MOF-5 powder at 77 K, 83 K, 95 K, 106 K, 122 K, and 183 K [10]. These parameters are held constant in the fits to the pellet data, allowing only  $n_{\text{max}}$  and  $v_a$  to vary for individual samples.

<sup>4</sup> Volumetric adsorption is calculated here as the excess hydrogen adsorption divided by the total volume occupied by the pellets, excluding void space between pellets.



**Fig. 7 – Preliminary thermal conductivity measurements of MOF-5 pellets of indicated densities plotted versus temperature.**

determined from the measured thermal diffusivity ( $\alpha$ ) and heat capacity ( $c_p$ ) using the equation

$$k = \alpha \times \rho \times c_p, \quad (1)$$

where  $\rho$  is the density. Increased pellet density apparently enhances the conductivity by decreasing the amount of interstitial voids within the pellet. Gains from increased density are modest, however, and pellet conductivities are well below the single crystal value of 0.31 W/mK at room temperature [13].

Forming MOF-5 bulk powder into pellets involves compromises between crush strength, gravimetric adsorption and volumetric adsorption. Pellets with  $\rho = 0.79 \text{ g/cm}^3$ , for example, have the largest excess volumetric  $\text{H}_2$  capacity and the greatest crush strength, but also have the lowest excess gravimetric  $\text{H}_2$  adsorption. The  $0.51 \text{ g/cm}^3$  pellets appear to deliver the best compromise between these three factors among the densities considered here. In fact, when considering total hydrogen delivery between a 3 bar and 80 bar operational pressure range, the  $0.51 \text{ g/cm}^3$  pellets provide the greatest enhancement with respect to the bulk powder. The decreases in MOF-5 surface area and gravimetric  $\text{H}_2$  adsorption as a function of density, as well as the increases in volumetric  $\text{H}_2$  adsorption, closely follow the trends previously observed for MOF-177 [8].

Varying the density of MOF-5 pellets does not appear to have a large effect on the thermal conductivity. In order for MOF-5 monoliths to cool down, or warm up, rapidly within hydrogen storage systems by thermal conduction, the thermal conductivity should be approximately an order-of-magnitude larger. Introducing additives such as expanded natural graphite is a topic for future work.

#### 4. Conclusion

We report a significant increase in the volumetric excess hydrogen uptake of MOF-5 via powder densification. Optimal storage properties are achieved for densities  $\rho \sim 0.5 \text{ g/cm}^3$ , yielding a 350% increase in volumetric  $\text{H}_2$  density (relative to the powder), with only a modest 15% reduction in gravimetric

excess capacity. The decrease in specific surface area with density is apparently linked to the degradation of the intracrystalline porosity of MOF-5 due to amorphization. Nevertheless, a substantial fraction of MOF-5 crystalline phases remains intact even at a bulk density of  $0.75 \text{ g/cm}^3$ , well above the single crystal density. The radial crush strength of the prepared pellets increases monotonically with density, increasing by a factor of 4.3 between  $\rho = 0.41 \text{ g/cm}^3$  and  $\rho = 0.60 \text{ g/cm}^3$ . Thermal conductivity increases slightly with tablet density, but remains below the single crystal value.

#### Acknowledgments

The authors acknowledge Angela Harris (Ford) for help with the crush test measurements and Giovanni Cavataio (Ford) for help with the surface area measurements. Financial support was provided by U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, grant no. DE-FC36-GO19002.

#### REFERENCES

- [1] Yang J, Sudik A, Wolverton C, Siegel DJ. High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery. *Chem Soc Rev* 2010;39:656–75.
- [2] Li H, Eddaoudi M, O'keeffe M, Yaghi OM. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* 1999;402:276–9.
- [3] Rowsell JLC, Millward AR, Park KS, Yaghi OM. Hydrogen storage in functionalized metal-organic frameworks. *J Am Chem Soc* 2004;126:5666–7.
- [4] Müller U, Schubert M, Teich F, Puetter H, Schierle-Armdt K, Pastre J. Metal-organic frameworks—prospective industrial applications. *J Mater Chem* 2006;16:626–36.
- [5] Kaye S, Dailly A, Yaghi O, Long J. Impact of preparation and handling on the hydrogen storage properties of  $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})_3$  (MOF-5). *J Am Chem Soc* 2007;129:14176–7.
- [6] Zhou W, Wu H, Hartman MR, Yildirim T. Hydrogen and methane adsorption in metal-organic frameworks: A high-pressure volumetric study. *J Phys Chem C* 2007;111:16131–7.
- [7] Hesse M, Mueller U, Yaghi O. Shaped bodies containing metal-organic frameworks, U.S. Patent 7,524,444 B2, 2009.
- [8] Zacharia R, Cossement D, Lafi L, Chahine R. Volumetric hydrogen sorption capacity of monoliths prepared by mechanical densification of MOF-177. *J Mater Chem* 2010;20:2145–51.
- [9] Hu YH, Zhang L. Amorphization of metal-organic framework MOF-5 at unusually low applied pressure. *Phys Rev B* 2010;81:174103.
- [10] Sudik A, Yang J, Maurer S, Leung E, Zio MD, Purewal J, Gearheart C, Siegel DJ, Müller U. To be published (2011).
- [11] Panella B, Hirscher M, Pütter H, Müller U. Hydrogen adsorption in metal-organic frameworks: Cu-MOFs and Zn-MOFs compared. *Adv Funct Mater* 2006;16:520–4.
- [12] Richard M-A, Bénard P, Chahine R. Gas adsorption process in activated carbon over a wide temperature range above the critical point. part 1: modified Dubinin-Astakhov model. *Adsorption* 2009;15:43–51.
- [13] Huang B, Ni Z, Milward A, McGaughey A, Uder C, Kaviani M, et al. Thermal conductivity of a metal-organic framework (MOF-5): Part ii. measurement. *Int J Heat Mass Transfer* 2007;50:405–11.