ChemComm

RSC Publishing

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2013, **49**, 2992

Received 31st January 2013,
Accepted 20th February 2013

DOI: 10.1039/c3cc40819a

www.rsc.org/chemcomm

Simultaneously high gravimetric and volumetric methane uptake characteristics of the metal–organic framework NU-111†

Yang Peng,[ab] Gadipelli Srinivas,[ab] Christopher E. Wilmer,[c] Ibrahim Eryazici,[d] Randall Q. Snurr,[c] Joseph T. Hupp,[d] Taner Yildirim*[ab] and Omar K. Farha*[d]

We show that the MOF NU-111 exhibits equally high volumetric and gravimetric methane uptake values, both within ≈75% of the DOE targets at 300 K. Upon reducing the temperature to 270 K, the uptake increases to 0.5 g g^{-1} and 284 cc(STP) per cc at 65 bar. Adsorption of CO_2 and H_2 is also reported. Simulated isotherms are in excellent agreement with those obtained from experiments.

Metal–organic frameworks[1] (MOFs) are a new class of multifunctional, crystalline, porous materials that have received tremendous interest due to their potential applications for high density storage of gases such as hydrogen[2,3] and methane[4,5] and for carbon dioxide capture.[6] Currently, there is no material that meets the on-board H_2 storage targets: 5.5 wt% (gravimetric) and 40 g L^{-1} (volumetric) near ambient temperature.[2b] Similarly, it is a challenge to store methane in vehicles at sufficiently high densities. Very recently the DOE has started a new methane storage program[7] with the following targets: 0.5 g(CH_4) per g(sorbent) for gravimetric capacity and $\rho = 0.188$ g cc^{-1} (11.741 mmol cc^{-1}) for volumetric capacity, which corresponds to the density of compressed natural gas (CNG) at 250 bar and 298 K. The new volumetric target is equal to 263 cc(STP: 273.15 K, 1 atm) per cc, which is significantly higher than the previous target of 180 cc(STP) per cc at 35 bar. For the application of MOFs in carbon capture, recent studies[6] showed that there is no single desired target and that the process variables such as temperature[6b] and pressure[6c] swing determine the optimum sorbent material.

It has been well established that the most important attributes for CH_4 or H_2 storage and carbon capture are the surface area, pore volume and concentration of open metal sites[3] present in MOFs. Recently significant advances have been made in synthesizing new MOFs with record high internal surface areas and pore volumes exceeding 4000 m^2 g^{-1} and 2 cc g^{-1} by utilizing longer organic linkers and copper paddlewheels as the open metal sites. Some of these MOFs are PCN-68[8a]/NOTT-116,[8b] PCN-69[9a]/NOTT-119,[9b] NOTT-112,[10] NU-100[11a,b]/PCN-610,[11c] and NU-111.[12] However most of these studies are limited mainly to synthesis and porosity characterization without studying their detailed gas adsorption properties over a wide range of pressures and temperatures. Clearly understanding the full gas uptake characteristic of these MOFs is important in designing new MOFs with even higher gas uptake properties. Here we show that one of these 2nd generation MOFs, NU-111, has exceptionally high gas uptake properties. The synthesis and X-ray structure of NU-111 have been recently described.[12] It has a noncatenated face-centered-cubic (fcc) lattice, in which the framework nodes consist of Cu-paddlewheels coordinated by the carboxylates of the linkers. The overall structure can be viewed as the packing of three main cages in a fcc lattice as shown in Fig. 1.

The NU-111 sample (about 100 mg) was synthesized and activated at Northwestern University using supercritical CO_2.[12] Temperature-dependent high pressure adsorption measurements

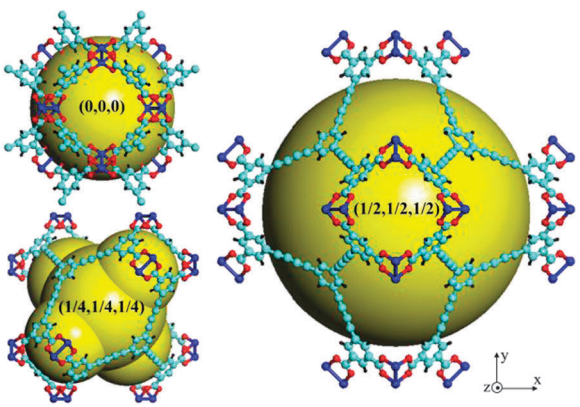

Fig. 1 Three types of cages at the origin (0,0,0), at a tetrahedral site (1/4,1/4,1/4) and at an octahedral site (1/2,1/2,1/2) of the fcc structure of NU-111. There is also a fourth cage[12] which is shown in ESI.† Dark blue, light blue, red, and black colors represent Cu, C, O, and H, respectively.

[a] *NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-6102, USA. E-mail: taner@seas.upenn.edu*
[b] *Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6272, USA*
[c] *Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA*
[d] *Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA. E-mail: o-farha@northwestern.edu*

† Electronic supplementary information (ESI) available: Sorption isotherms and theoretical calculations. See DOI: 10.1039/c3cc40819a

Table 1 The gas uptake characteristics of NU-111 for H_2 (77 K, 65 bar), CO_2 (298 K, 30 bar) and CH_4 (65 bar). The working capacity is defined as the difference in total uptake capacity between 65 bar and 5 bar for CH_4 and H_2. For CO_2, it is defined as 30 bar−1 bar. The density is given in g cc^{-1}

	Excess uptake		Total uptake			Working capacity	
Gas	g g^{-1}	cc cc^{-1}	g g^{-1}	cc cc^{-1}	Density	g g^{-1}	cc cc^{-1}
CH_4 270 K	0.380	217	0.50	284	0.203	0.42	239
CH_4 298 K	0.262	150	0.36	205	0.147	0.31	177
H_2	0.075	341	0.12	546	0.049	0.074	336
CO_2	1.54	321	1.68	350	0.687	1.57	328

were performed at the Center for Neutron Research, National Institute of Standards and Technology (NIST), using a computer-controlled Sieverts apparatus, the details of which have been published elsewhere[13] and are briefly discussed in the ESI.† The gas-uptake characteristics of NU-111 are summarized in Table 1, and the isotherms are shown in Fig. 2.

First, we studied the permanent porosity of activated NU-111 by N_2 adsorption measurements at 77 K (see Fig. S1, ESI†), which yielded an internal surface area of 4930 m^2 g^{-1} and a pore volume of 2.09 cc g^{-1}. These agree well with the values, 4930 m^2 g^{-1} and 2.03 cc g^{-1}, calculated from simulated N_2 isotherms and using PLATON,[14] respectively. The large pore volume of NU-111 was further confirmed by carbon dioxide adsorption measurements at different temperatures as shown in Fig. 2. The CO_2 isotherms at 220 K and 240 K were collected up to the saturation pressure. The maximum adsorption at the saturation pressure yielded pore volumes of 2.00 cc g^{-1} and 2.12 cc g^{-1}, respectively. Both numbers are in excellent agreement with the pore volume measured from the nitrogen isotherm. At 0.15 bar and 298 K (*i.e.*, a condition that is close to flue gas from coal power plants), the CO_2 uptake is about 1.8 wt%, which is lower than MOF-74 (with a high density of open-metal sites) but comparable to Zn-based MOFs reported in a recent CO_2 screening survey.[15] However, NU-111 exhibits a significant CO_2 adsorption, 1.68 g g^{-1} (38 mmol g^{-1}) at 30 bar and 298 K, which is one of the largest uptake measurements reported so far for a MOF (*i.e.* 32.9 mmol g^{-1} for PCN-68[8a] and 40 mmol g^{-1} for NU-100[11a,b]).

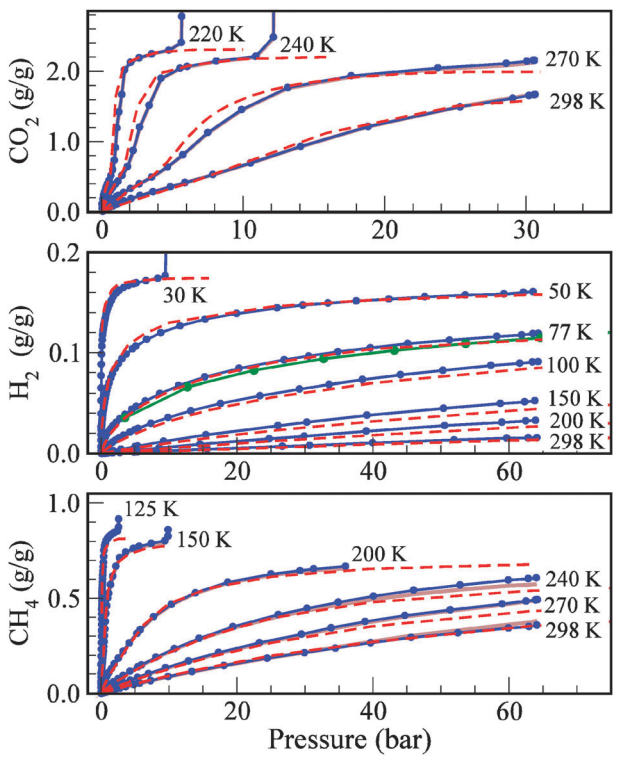

Fig. 2 Total gravimetric gas uptake isotherms at various temperatures for CH_4 (bottom), H_2 (middle), and CO_2 (top). The brown lines (hardly noticeable) in the background are isotherms obtained using He-cold volumes with sample, while the blue lines are isotherms obtained using cold-volumes of empty cells (see ESI† for details). The red dashed lines are simulated isotherms. The green line in H_2-isotherm plot (middle) is taken from ref. 12 and is in excellent agreement with our measurements.

Next we studied the hydrogen uptake properties of NU-111 over a wide temperature and pressure range as shown in Fig. 2. NU-111 exhibits rather high hydrogen adsorption capacity at high pressures. The excess isotherm at 77 K shows a slight maximum near 45 bar (see Fig. S4, ESI†) with 7.8 wt% hydrogen uptake. This value is much lower than the 10 wt% expected from "Chahine's rule"[16a] (*i.e.*, 1 wt% for every 500 m^2 g^{-1}), indicating that this empirical rule which works well for carbons[16b] may not apply for MOFs with very high surface area and large pore volumes. The total hydrogen uptake at 77 K and near 65 bar is 12 wt%. This value is higher than those for NOTT-119[9b] (10.1 wt% at 60 bar) and NOTT-112[10] (10 wt% at 77 bar), comparable to that for PCN-68[8a] (11.5 wt% at 65 bar) and less than that for NU-100[11a] (16.4 wt% at 70 bar) which has much higher surface area and higher pore volume than those of NU-111. We note that both the gravimetric (0.12 g g^{-1}) and the volumetric (0.049 g cc^{-1} = 49 g L^{-1}) uptake values meet the DOE's targets, albeit at 77 K rather than at ambient temperature.

Finally, the high pressure methane sorption data of NU-111 shown in Fig. 2 were collected. The maximum absorption at 125 K is 0.85 g g^{-1} (53.3 mmol g^{-1}), giving a pore volume of 2.12 cc g^{-1}, which is in excellent agreement with the pore volume, 2.09 cc g^{-1}, based on the N_2 isotherm. This suggests that methane is able to access most of the pores available in NU-111 at room temperature, which are accessible by nitrogen at 77 K. At temperatures above 200 K, the total methane uptake does not seem to saturate up to our maximum pressure of 65 bar. The total gravimetric uptake at 298 K and 65 bar by NU-111 reaches 0.36 g g^{-1} (205 cc cc^{-1}), which is very similar to that by PCN-68[8] (0.35 g g^{-1}) and larger than that by NOTT-119[9b] (0.3 g g^{-1}) and it represents the highest gravimetric methane uptake recorded so far for a MOF. However, even though this is a record high value, it is only 72% of the DOE's new gravimetric target of 0.5 g g^{-1}.

The volumetric uptake by NU-111 is also quite impressive. Using the ideal crystallographic density of NU-111 (0.409 g cm^{-3}), we estimate the total methane uptake at 65 bar and 298 K to be 205 cc cc^{-1} (*i.e.* 9.14 mmol cc^{-1}), which is 78% of the DOE's new target of 263 cc(STP) per cc. Nevertheless, it corresponds to a CNG density at P = 186 bar and 298 K. Hence the presence of NU-111 in a CNG tank can reduce the pressure almost three times (assuming no losses due to lower powder packing densities), a significant improvement for practical purposes. The methane storage working capacity, defined here as the difference in uptake between the pressures of 65 bar and 5 bar is 177 cc(STP: 273.15 K, 1 atm) per cc. This is very close to the DOE's old target of 180 cc(STP) per cc and only a few MOFs exhibit such high volumetric uptakes, including PCN-14,[17a] UTSA-20,[17b] and Ni-MOF-74.[3a] However we point out that the gravimetric uptake values of these MOFs are much lower than those

of NU-111 due to higher crystal densities. We emphasize that NU-111 is unique in its equally good volumetric and gravimetric uptakes (both within 72–78% of the DOE targets). Interestingly, the total gravimetric uptake at 270 K and 65 bar reaches the DOE's target of 0.5 g g^{-1} while the total volumetric uptake increases to 284 cc cc^{-1}, 8% higher than the DOE's target. Such strong temperature dependence of the storage capacity suggests that a combination of pressure and temperature swing could be an effective method for methane storage and release.

Fig. 2 also shows isotherms obtained from molecular simulations, which are in excellent agreement with those obtained from experiments and give further confidence to the results reported here. In order to get better insight into the nature of the adsorption sites and interactions in NU-111, we extracted isosteric heats of adsorption (Q_{st}) from the temperature-dependent isotherms shown in Fig. 2 (see Section S4 in ESI† for details). The magnitudes of the Q_{st} values are consistent with those of other Cu-based paddlewheel MOFs. The Q_{st} for all gases have similar behavior with loading. Up to one gas-molecule per Cu-site (3.34 mmol g^{-1}) Q_{st} stays about constant and then starts to decrease up to 12 mmol g^{-1}, which interestingly corresponds to the loading where both Cu- and benzene-sites are occupied. This behavior is probably correlated with the gas–metal site binding.[3] At high gas loading above 12 mmol g^{-1}, Q_{st} for CH_4 and CO_2 starts to increase, which is attributed to the strong gas–gas interaction comparable to gas–MOF interaction.

In conclusion, we have fully characterized the adsorption of NU-111 for H_2, CH_4 and CO_2 over a broad range of pressures and temperatures. We have demonstrated that NU-111 with its BET surface area of 4932 m^2 g^{-1} and high pore volume of 2.09 cc g^{-1} achieves the highest gravimetric methane storage capacity reported so far. The volumetric storage capacity is also very high at pressures near 65 bar. At 270 K, both the gravimetric and volumetric methane storage capacities reach the DOE's new targets. However at 298 K, the gravimetric and volumetric uptake values are about 25% lower than the DOE targets. Nevertheless, the presence of NU-111 in a CNG tank can reduce the pressure about three times (assuming no losses due to lower powder packing densities), which may eliminate the need for expensive multi-state compression at the gas station, yielding significant simplifications and cost reduction. We do emphasize the importance of the working capacity, which requires high uptake at high pressures and low uptake at low pressures. In addition to methane storage properties, NU-111 also exhibits very high H_2 and CO_2 adsorption near 65 bar, which could be important in practical applications such as cryogenic transport of hydrogen and high-pressure carbon capture.

TY acknowledges the support from the U. S. Department of Energy through BES Grant No. DE-FG02-08ER46522. The Northwestern group gratefully acknowledges the DOE Office of Energy Efficiency and Renewable Energy, DOE ARPA-E, and the Stanford Global Climate and Energy Project for support of work relevant to H_2, CH_4, and CO_2, respectively.

Notes and references

1 (*a*) G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191; (*b*) O. M. Yaghi, *et al.*, *Nature*, 2003, **423**, 705; (*c*) H. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695.
2 (*a*) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2012, **112**, 782; (*b*) http://www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html.
3 (*a*) H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2009, **131**, 4995; (*b*) M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876; (*c*) H. Wu, W. Zhou and T. Yildirim, *J. Am. Chem. Soc.*, 2008, **130**, 15268; (*d*) W. Zhou and T. Yildirim, *J. Phys. Chem. C*, 2008, **112**, 8132; (*e*) H. Wu, J. M. Simmons, G. Srinivas, W. Zhou and T. Yildirim, *J. Phys. Chem. Lett.*, 2010, **1**, 1946.
4 (*a*) T. A. Makal, J. R. Li, W. Lu and H.-C. Zhou, *Chem. Soc. Rev.*, 2012, **41**, 7761; (*b*) Y. He, W. Zhou, R. Krishna and B. Chen, *Chem. Commun.*, 2012, **48**, 11813; (*c*) H. Wu, J. M. Simmons, Y. Liu, C. M. Brown, X.-S. Wang, S. Ma, V. K. Peterson, P. D. Southon, C. J. Kepert, H.-C. Zhou, T. Yildirim and W. Zhou, *Chem.–Eur. J.*, 2010, **16**, 5205.
5 (*a*) X. Duan, J. Yu, J. Cai, Y. He, C. Wu, W. Zhou, T. Yildirim, Z. Zhang, S. Xiang, M. O'Keeffe, B. Chen and G. Qian, *Chem. Commun.*, 2013, **49**, 2043; (*b*) K. Seki, *Chem. Commun.*, 2001, 1496; (*c*) K. Gedrich, I. Senkovska, N. Klein, U. Stoeck, A. Henschel, M. R. Lohe, I. A. Baburin, U. Mueller and S. Kaskel, *Angew. Chem., Int. Ed.*, 2010, **49**, 8489; (*d*) U. Stoeck, S. Krause, V. Bon, I. Senkovska and S. Kaskel, *Chem. Commun.*, 2012, **48**, 10841; (*e*) C. Tan, S. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun.*, 2011, **47**, 4487; (*f*) H. J. Park, D.-W. Lim, W. S. Yang, T.-R. Oh and M. P. Suh, *Chem.–Eur. J.*, 2011, **17**, 7251; (*g*) X. Zhao, D. Sun, S. Yuan, S. Feng, R. Cao, D. Yuan, S. Wang, J. Dou and D. Sun, *Inorg. Chem.*, 2012, **51**, 10350; (*h*) D. Yuan, D. Zhao, D. Sun and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357.
6 (*a*) K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae and J. R. Long, *Chem. Rev.*, 2011, **112**, 724; (*b*) J. M. Simmons, H. Wu, W. Zhou and T. Yildirim, *Energy Environ. Sci.*, 2011, **4**, 2177–2185; (*c*) J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, 2011, **4**, 3030–3040; (*d*) C. E. Wilmer, O. K. Farha, Y.-S. Bae, J. T. Hupp and R. Q. Snurr, *Energy Environ. Sci.*, 2012, **5**, 9849; (*e*) L.-C. Lin, A. H. Berger, R. L. Martin, J. Kim, J. A. Swisher, K. Jariwala, C. H. Rycroft, A. S. Bhown, M. W. Deem, M. Haranczyk and B. Smit, *Nat. Mater.*, 2012, **11**, 633.
7 See DOE MOVE program at https://arpa-e-foa.energy.gov/.
8 (*a*) D. Q. Yuan, D. Zhao, S. Sun and H.-C. Zhou, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357; (*b*) Y. Yan, I. Telepeni, S. Yang, X. Lin, W. Kockelmann, A. Dailly, A. J. Blake, W. Lewis, G. S. Walker, D. R. Allan, S. A. Barnett, N. R. Champness and M. Schroder, *J. Am. Chem. Soc.*, 2010, **132**, 4092.
9 (*a*) D. Q. Yuan, D. Zhao and H.-C. Zhou, *Inorg. Chem.*, 2011, **50**, 10528; (*b*) Y. Yan, S. Yang, A. J. Blake, W. Lewis, E. Poirier, S. A. Barnett, N. R. Champness and M. Schröder, *Chem. Commun.*, 2011, **47**, 9995.
10 Y. Yan, X. Lin, S. Yang, A. J. Blake, A. Dailly, N. R. Champness, P. Hubberstery and M. Schröder, *Chem. Commun.*, 2009, 1025.
11 (*a*) O. K. Farha, A. Ö. Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944; (*b*) G. K. H. Shimizu, *Nat. Chem.*, 2010, **2**, 909; (*c*) D. Yuan, D. Zhao, D. Sun and H.-C. Sun, *Angew. Chem., Int. Ed.*, 2010, **49**, 5357–5361.
12 O. K. Farha, C. E. Wilmer, I. Eryazici, B. G. Hauser, P. A. Parilla, K. O'Neill, A. A. Sarjeant, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 9860.
13 W. Zhou, H. Wu, M. R. Hartman and T. Yildirim, *J. Phys. Chem. C*, 2007, **111**, 16131–16137.
14 PLATON (C) 1980–2011 A. L. Spek, Utrecht University, Padualaan 8, 3584 CH, Utrecht, The Netherlands. The van der Waals radii used in the analysis C: 1.70, H: 1.2, Cu: 1.4, N: 1.5, O: 1.52.
15 A. Ö. Yazaydin, R. Q. Snurr, T. H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198–18199.
16 (*a*) E. Poirier, R. Chahine and T. K. Bose, *Int. J. Hydrogen Energy*, 2001, **26**, 831–835; (*b*) G. Srinivas, J. Burress and T. Yildirim, *Energy Environ. Sci.*, 2012, **5**, 6453–6459.
17 (*a*) S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan and H.-C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 1012–1016; (*b*) Z. Guo, H. Wu, G. Srinivas, Y. Zhou, S. Xiang, Z. Chen, Y. Yang, W. Zhou, M. O. Keeffe and B. Chen, *Angew. Chem., Int. Ed.*, 2011, **50**, 3178–3181.

