

Cite this: *Chem. Commun.*, 2012, **48**, 347–349

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COMMUNICATION

Facile xenon capture and release at room temperature using a metal–organic framework: a comparison with activated charcoal†Praveen K. Thallapally,^{*a} Jay W. Grate^b and Radha Kishan Motkuri^a

Received 29th July 2011, Accepted 14th September 2011

DOI: 10.1039/c1cc14685h

Two well-known metal–organic frameworks (MOF-5, NiDOBDC) were synthesized and studied for facile xenon capture and separation. Our results indicate that NiDOBDC adsorbs significantly more xenon than MOF-5, and is more selective for xenon over krypton than activated carbon.

The noble gas xenon, Xe, occurs naturally in the atmosphere at 0.087 ppmv, while krypton, Kr, occurs at 1.14 ppmv. Xe is produced industrially as a by-product in the fractional distillation of air to separate nitrogen and oxygen. Xe has nine naturally occurring stable isotopes. Unstable isotopes are produced in the fission of uranium and plutonium, as well as through the radioactive decay of other fission products. Hence, radioactive Xe enters the atmosphere from nuclear detonations, dissolution of the spent fuel in nuclear reprocessing, in the production of medical isotopes, and from nuclear accidents such as the recent catastrophe at Fukushima Daiichi Nuclear Power Plant in Japan.¹ Monitors for radioactive xenon isotopes are stationed around the globe to detect nuclear explosions banned under the Comprehensive Test Ban Treaty² and these systems detected and tracked xenon isotopes from the Japanese nuclear accident.

Industrially, Xe has several uses including commercial lighting. In medicine, Xe can be used for imaging, anesthesia, and neuroprotection. Scientifically, Xe finds use in nuclear magnetic resonance, protein crystallography, and as a propellant in ion propulsion engines.³ Thus, capture and separation of Xe from the atmosphere is important for commercial uses and for atmospheric monitoring. To obtain pure Xe, it is important to separate Xe from its sister noble gas, Kr. Conventional adsorptive approaches to Xe capture and purification have used conventional materials such as zeolites and activated carbon.⁴

Recently a new class of sorbent called metal–organic frameworks (MOF) or porous coordination polymers has been developed.⁵

MOF materials are comprised of metals or metal clusters (“nodes”) coordinated to multi-functional building blocks (“linkers”) and they offer unparalleled levels of permanent porosity (there are numerous MOFs with BET surface areas in the 3000–6000 m² g^{−1} range).⁶ Furthermore, their modular nature and their use of known coordination chemistry offer enormous diversity of structures and properties.⁷ MOFs are therefore uniquely capable of addressing high capacity, selective storage and/or separation of both small and large molecules and there has been an explosion of interest in MOFs in the past decade.⁸

Although there are many reports of gas capture and separation using MOFs, especially for CO₂ capture for carbon sequestration,^{8,9} very few publications have addressed xenon capture and separations.¹⁰ Mueller *et al.* reported higher adsorption of Xe and Kr in containers filled with MOF-5 as compared with empty containers.¹⁰ Similarly, breakthrough experiments conducted by the same group on HKUST showed that a 94/6 molar ratio of Kr and Xe could be purified to 99% Kr with less than 50 ppm of Xe. Recently, Greathouse *et al.* used grand canonical Monte Carlo (GCMC) simulations to model the adsorption of noble gases and found a selectivity of about 2.5–3 for Xe over Kr at 298 K.¹¹ More recently Ryan *et al.* simulated the xenon/krypton separation and screened various MOFs with different topologies and pore sizes using GCMC calculations and concluded that a small pore size and strong adsorption sites are required for preferential separation of Xe over Kr.¹²

In this report, we describe the capture of xenon with selected MOF sorbents, focusing on types with open metal sites, and make comparisons with activated carbon, a conventional material for xenon capture. The MDOBDC (M = Ni, Mg, Zn, and Co) family of MOFs has received a great deal of attention in the recent years due to the high CO₂ capacity (30–36 wt%) at relatively low pressures (1 bar).^{9a,13} The higher adsorptions of CO₂ in these materials were correlated to the presence of a large number of open metal sites in a given unit cell. Therefore we looked at NiDOBDC (see Fig. 1 for the structure) for the sorption of Xe at ambient temperature, compared the uptake and release characteristics with activated charcoal, and examined the selectivity for Xe over Kr. The uptake of Xe by NiDOBDC MOF was approximately twice that of MOF-5, which we examined initially (see ESI†).¹⁴

NiDOBDC was synthesized using the published procedure by combination of a metal nitrate with the organic linker

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† Electronic supplementary information (ESI) available: Details of synthesis and characterization of MOF-5 and NiDOBDC. Gas sorption isotherms of MOF-5 and NiDOBDC. See DOI: 10.1039/c1cc14685h

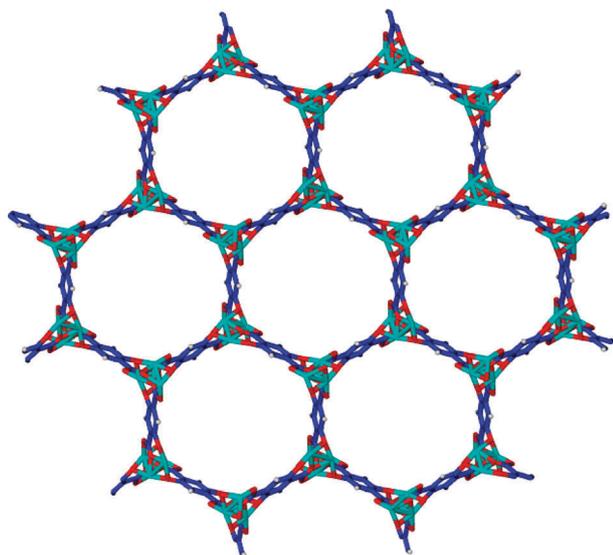


Fig. 1 Honeycomb network structure of NiDOBDC.

2,5-dihydroxyterephthalic acid (DOBDC), in a dimethylformamide (DMF), ethanol and water mixture and the resulting solution was heated at 100 °C for 72 h to obtain a crystalline material. The resulting precipitate was filtered and soaked in methanol for 72 h and then activated overnight at 250 °C under vacuum. DOBDC is a tetrapotic ligand that holds two different types of functional groups of aryloxy and carboxylate to form a linear, hexagonal 1D pore structure. The charcoal was obtained from U.S. Filter 1230C coconut shell activated carbon, and was ground and sieved to 180–250 micron particle size for comparison adsorption studies.

Thermogravimetric analysis (TGA) of NiDOBDC shows a weight loss of 30% from RT to 250 °C corresponding to the loss of solvent molecules (see ESI†). Variable powder X-ray diffraction (PXRD) measurements before and after heating NiDOBDC at 200 °C showed no change in structure, indicating that the sample is stable to solvent desorption (see ESI†). The surface area was determined to be 950 m² g⁻¹ by measurement at 77 K using N₂ adsorption; this value is in agreement with the reported literature (see ESI†).

Gas sorption experiments were performed gravimetrically using the Intelligence Gravimetric Analyzer (IGA) from Hiden instruments. As described in the ESI†, this instrument equilibrates the sample with a given introduced gas pressure, stepping from one preprogrammed set point pressure to the next. Uptake data for Xe, Kr, and N₂ on NiDOBDC and activated charcoal are compared in Fig. 2. The uptake of Xe by NiDOBDC is comparable to that of carbon overall, with superior uptake from 0.25 to 1 bar. At 1 bar, the calculated weight percentage of xenon on NiDOBDC was found to be 55 wt% (Fig. 2) and the desorption was completely reversible (see ESI†). The Xe sorption experiment at RT was repeated several times and the weight percentage was obtained within an error of ±2%. By comparison, the uptake values for the other gases were very small at 1 bar: Kr (3 wt%) and N₂ (1 wt%) respectively (Fig. 2). Neither NiDOBDC nor charcoal has significant uptake for N₂. NiDOBDC is more selective for Xe over Kr, with an uptake ratio of 5–6 for most of the pressure range,

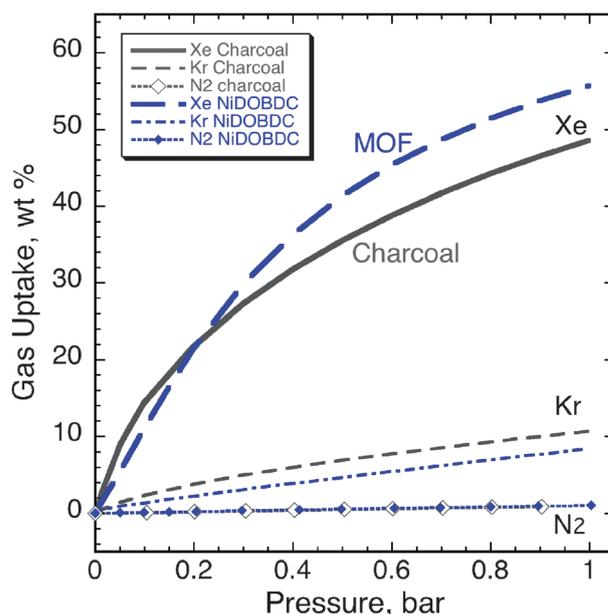


Fig. 2 Xe, Kr and N₂ adsorption isotherms at room temperature in NiDOBDC and activated carbon.

compared to 3.8 for charcoal. Similarly, at 1 bar, the uptake of xenon by MOF-5 is only 26 wt% (see ESI†), which is only about half that of NiDOBDC.

The isosteric heats of adsorption q_{st} at a constant loading for Xe adsorption isotherms at different temperatures (50 °C, 10 °C and 0 °C) using the Clausius–Clapeyron equation. As shown in Fig. 3 q_{st} was relatively constant at around 22 kJ mol⁻¹, indicating gas interactions with a relatively homogeneous pore system. The isosteric energies are found to be consistent with isosteric energies for xenon absorption by other MOFs reported in the literature (15 kJ mol⁻¹, 25 kJ mol⁻¹ and 21 kJ mol⁻¹ for MOF-5, IRMOF-3 and HKUST-1) using a pulsed adsorption measurement technique (TAP-2) that proves the strongest adsorption sites.¹⁵

The uptake data vs. pressure were fitted with the Dubinin–Radushkevich (DR) equation (see ESI†) to calculate the adsorption energies (βE_0), which indicate the interaction strength between the guest molecules and the host surfaces.¹⁶ The βE_0 found for xenon in NiDOBDC, 9.9 kJ mol⁻¹, was

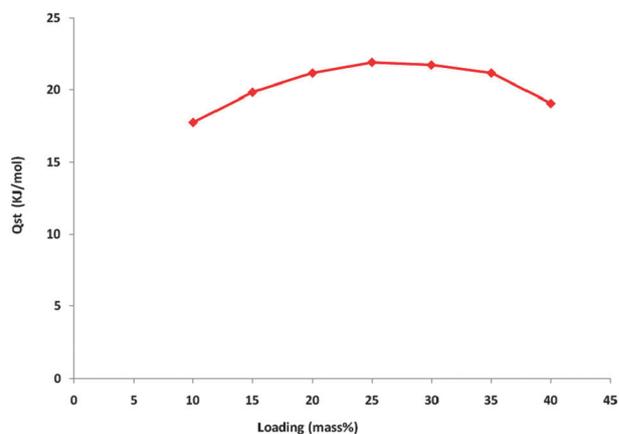


Fig. 3 The isosteric heats of adsorption for NiDOBDC.

greater than that found for activated carbon, 6.6 kJ mol^{-1} (see ESI†). These results indicate that xenon has a stronger interaction with the NiDOBDC framework than with activated carbon surfaces. The βE_0 value plus the heat of vaporization of xenon ($12.64 \text{ kJ mol}^{-1}$) should equal the isosteric heat of adsorption, which is consistent with our values in Fig. 3.

We set out to examine the uptake of Xe by a MOF that has a large number of open metal sites. For example, NiDOBDC has abundant open metal sites with uniform channels. By comparison, MOF-5 has no open metal sites and HKUST has far fewer open metal sites. Examining our own data, the sorption of xenon was indeed much higher for NiDOBDC compared to MOF-5 by a factor of two. As a noble gas atom, the only mechanism for xenon to interact is based on its polarizability. Metal cations are very polarizing, which may enhance the interaction with polarizable adsorbents. In comparison with activated carbon, NiDOBDC has similar adsorption capacities towards Xe but NiDOBDC takes slightly more at 1 bar pressure. Additionally, high surface area, uniform porosity, and high diffusivity make NiDOBDC more attractive. The ability to tune the properties of NiDOBDC by replacing nickel with another transition metal center (Mg, Co, Zn and Mn)¹⁷ or post-functionalization¹⁸ of organic building blocks is also advantageous compared to activated carbon.

In conclusion, we examined the characteristics of NiDOBDC as a sorbent for capturing xenon at noncryogenic temperatures, and found the uptake to be substantially higher than for the typical prototype MOF-5. In comparison to activated carbon, the uptake of NiDOBDC is similar. We also find that the selectivity of the MOF material for Xe over Kr is superior to activated carbon.

This work was supported by Laboratory Directed Research and Development funding. In addition PKT thanks the US Department of Energy—Office of Nuclear Energy. The Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Notes and references

- (a) J. P. Fontaine, F. Pointurier, X. Blanchard and T. Taffary, *J. Environ. Radioact.*, 2004, **72**, 129–135; (b) M. A. Awwal and D. J. Carswell, *Chem. Rev.*, 1966, **66**, 279–295.
- M. Auer, A. Axelsson, X. Blanchard, T. W. Bowyer, G. Brachet, I. Bulowski, Y. Dubasov, K. Elmgren, J. P. Fontaine, W. Harms, J. C. Hayes, T. R. Heimbigner, J. I. McIntyre, M. E. Panisko, Y. Popov, A. Ringbom, H. Sartorius, S. Schmid, J. Schulze, C. Schlosser, T. Taffary, W. Weiss and B. Wernsperger, *Appl. Radiat. Isot.*, 2004, **60**, 863–877.
- (a) K. J. Ooms and R. E. Wasylshen, *Microporous Mesoporous Mater.*, 2007, **103**, 341–351; (b) A. Boutin, M. A. Springuel-Huet, A. Nossou, A. Gedeon, T. Loiseau, C. Volkringer, G. Férey, F. X. Coudert and A. H. Fuchs, *Angew. Chem., Int. Ed.*, 2009, **48**, 8314–8317.
- (a) R. E. Bazan, M. Bastos-Neto, A. Moeller, F. Dreisbach and R. Staudt, *Adsorption*, 2011, **17**, 371–383; (b) M. Bulow, *Stud. Surf. Sci. Catal.*, 1994, **83**, 209–215; (c) K. Munakata, T. Fukumatsu, S. Yamatsuki, K. Tanaka and M. Nishikawa, *J. Nucl. Sci. Technol.*, 1999, **36**, 818–829; (d) D. Ianovski, K. Munakata, S. Kanjo, Y. Yokoyama, A. Koga, S. Yamatsuki, K. Tanaka, T. Fukumatsu, M. Nishikawa and Y. Igarashi, *J. Nucl. Sci. Technol.*, 2002, **39**, 1213–1218.
- K. Biradha, A. Ramana and J. J. Vittal, *Cryst. Growth Des.*, 2009, **9**, 2969–2970.
- (a) M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O’Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469–472; (b) O. K. Farha, A. O. 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**, 944–948; (c) M. J. Zaworotko, *Nature*, 2008, **451**, 410–411; (d) K. T. Holman, *Angew. Chem., Int. Ed.*, 2011, **50**, 1228–1230; (e) M. R. Kishan, J. A. Tian, P. K. Thallapally, C. A. Fernandez, S. J. Dalgarno, J. E. Warren, B. P. McGrail, J. L. Atwood and S. J. Teat, *Chem. Commun.*, 2010, **46**, 9259; (f) S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334–2375; (g) J. A. Tian, R. K. Motkuri and P. K. Thallapally, *Cryst. Growth Des.*, 2010, **10**, 3843–3846.
- (a) R. K. Motkuri, P. K. Thallapally, S. K. Nune, C. A. Fernandez, B. P. McGrail and J. L. Atwood, *Chem. Commun.*, 2011, **47**, 7077–7079; (b) S. Horike, S. Shimomura and S. Kitagawa, *Nat. Chem.*, 2009, **1**, 695–704; (c) P. K. Thallapally, J. Tian, M. R. Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren and J. L. Atwood, *J. Am. Chem. Soc.*, 2008, **130**, 16842–16843; (d) A. J. Lan, K. H. Li, H. H. Wu, D. H. Olson, T. J. Emge, W. Ki, M. C. Hong and J. Li, *Angew. Chem., Int. Ed.*, 2009, **48**, 2334–2338; (e) R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi and T. K. Woo, *Science*, 2010, **330**, 650–653; (f) J. R. Li, R. J. Kuppler and H. C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477–1504; (g) S. Horike, M. Dinca, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854–5855.
- (a) P. K. Thallapally, C. A. Fernandez, R. K. Motkuri, S. K. Nune, J. Liu and C. H. F. Peden, *Dalton Trans.*, 2010, **39**, 1692–1694; (b) P. K. Thallapally, R. K. Motkuri, C. A. Fernandez, B. P. McGrail and G. S. Behrooz, *Inorg. Chem.*, 2010, **49**, 4909–4915; (c) D. Zhao, D. J. Timmons, D. Q. Yuan and H. C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123–133; (d) T. Panda, P. Pachfule, Y. F. Chen, J. W. Jiang and R. Banerjee, *Chem. Commun.*, 2011, **47**, 2011–2013; (e) S. Q. Ma and L. Meng, *Pure Appl. Chem.*, 2011, **83**, 167–188.
- (a) S. R. Caskey, A. G. Wong-Foy and A. J. Matzger, *J. Am. Chem. Soc.*, 2008, **130**, 10870–10871; (b) C. E. Willans, S. French, L. J. Barbour, J. A. Gertenbach, P. C. Junk, G. O. Lloyd and J. W. Steed, *Dalton Trans.*, 2009, 6480–6482; (c) Z. H. Xiang, D. P. Cao, J. H. Lan, W. C. Wang and D. P. Broom, *Energy Environ. Sci.*, 2010, **3**, 1469–1487; (d) R. K. Motkuri, P. K. Thallapally, B. P. McGrail and S. B. Ghorishi, *CrystEngComm*, 2010, **12**, 4003–4006.
- U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastre, *J. Mater. Chem.*, 2006, **16**, 626–636.
- J. A. Greathouse, T. L. Kinniburgh and M. D. Allendorf, *Ind. Eng. Chem. Res.*, 2009, **48**, 3425–3431.
- P. Ryan, O. K. Farha, L. J. Broadbelt and R. Q. Snurr, *AIChE J.*, 2011, **57**, 1759–1766.
- A. O. 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.
- B. Chen, X. J. Wang, Q. F. Zhang, X. Y. Xi, J. J. Cai, H. Qi, S. Shi, J. Wang, D. Yuan and M. Fang, *J. Mater. Chem.*, 2010, **20**, 3758–3767.
- D. Farrusseng, C. Daniel, C. Gaudillere, U. Ravon, Y. Schuurman, C. Mirodatos, D. Dubbeldam, H. Frost and R. Q. Snurr, *Langmuir*, 2009, **25**, 7383–7388.
- X. Lin, A. J. Blake, C. Wilson, X. Z. Sun, N. R. Champness, M. W. George, P. Hubberstey, R. Mokaya and M. Schroder, *J. Am. Chem. Soc.*, 2006, **128**, 10745–10753.
- P. D. C. Dietzel, P. A. Georgiev, J. Eckert, R. Blom, T. Strassle and T. Unruh, *Chem. Commun.*, 2010, **46**, 4962–4964.
- K. K. Tanabe and S. M. Cohen, *Chem. Soc. Rev.*, 2011, **40**, 498–519.