Cite this: Chem. Commun., 2012, 48, 759-761

www.rsc.org/chemcomm

COMMUNICATION

H₂ storage and CO₂ capture on a nanoscale metal organic framework with high thermal stability[†]

Jian Zhang,^{*a*} Lixian Sun,^{*ac*} Fen Xu,^{*b*} Fen Li,^{*a*} Huai-Ying Zhou,^{*c*} Ying-Liang Liu,^{*d*} Zelimir Gabelica^{*e*} and Christoph Schick^{*f*}

Received 17th August 2011, Accepted 20th November 2011 DOI: 10.1039/c1cc15106a

A nanoscale aluminium-based metal organic framework (NMOF) with high thermal stability has been synthesized, which shows high H_2 and CO_2 uptake capacities and an excellent selectivity for CO_2 over N_2 and O_2 .

Metal–organic frameworks (MOFs) have attracted considerable attention in recent years for gas storage,¹ separation,² and catalysis applications.³ Traditionally, syntheses of MOFs have been mainly focused on yielding high quality single crystalline samples suitable for structural analysis. Nevertheless, nanosizing is a very effective strategy for the development of new materials with novel and often improved properties compared to traditional materials.^{4,5} Recently, a few groups had reported the syntheses of nanosized MOF crystallites (NMOF), which are an attractive new class of materials used for innovative applications in drug delivery, imaging probes, photonics and biosensing.⁶

Because bulky porous MOFs already proved to be very performing for gas sorption, separation and purification, their nanoscale counterparts are expected to exhibit interesting, novel and even enhanced gas sorption properties due to textural or morphological changes such as an increased crystallite interface area or a decreased diffusion distance.^{7,8} The porous nanosized MOF MIL-101 prepared using the microwave method exhibits a large uptake and significantly rapid sorption kinetics of benzene, making it a potential candidate for the sorptive removal of volatile organic compounds (VOCs) and other unwanted organic contaminants.⁷ Tanaka *et al.* reported a

NMOF (CID-1) built up from Zn(II) metallic ions linked to isophthalate and 4,4'-bipyridyl ligands, showing methanol adsorption capacities almost identical to its bulky counterpart (CID-1 macrocrystals), but the shapes of the methanol sorption isotherms differed significantly and the adsorption kinetics increased dramatically.⁸

In this study, we focus on a porous Al-based metal organic framework [Al(OH)(NDC), NDC stands for 1,4-naphthalenedicarboxylic acid] that involves a three-dimensional network with two types of 1D square-shaped channels.⁹ Here, we report original synthesis conditions leading to nanosized Al(OH)(NDC)·DMF particles prepared using Al(NO₃)₃·9H₂O and H₂NDC under solvothermal (DMF) conditions.

The morphologies and the particle sizes of NMOF were investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM and TEM pictures clearly reveal that nanoscale MOF particles (<100 nm) are obtained when DMF is used as a solvent (NMOF), as shown in Fig. 1.

The crystalline nature of NMOF was confirmed by powder X-ray diffraction (PXRD) (Fig. 2a). PXRD patterns of our NMOF samples are identical to the pattern of Al(OH)(NDC) reported by Comotti *et al.*,⁹ thereby confirming the same structural topology of all these solids. Moreover, most of the diffraction peaks of the NMOF samples are broadened due to the restricted size of its crystallites (about 51 nm, calculated by the Scherrer equation using the 8.4° peak as reference).

The IR spectrum (Fig. S1, ESI[†]) of as-synthesized and dried (50 °C) NMOF sample confirms the Al(OH)(NDC) composition as ascertained by the typical vibrational bands in the region 1400–1700 cm⁻¹ that characterize carboxylic functions. The IR



Fig. 1 (a) SEM image and (b) TEM image of NMOF as synthesized.

^a Materials and Thermochemistry Laboratory, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, 116023, China. E-mail: lxsun@dicp.ac.cn; Fax: +86-0411-84379213; Tel: +86-0411-84379213

 ^b Faculty of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian, 116029, China. E-mail: xufen@lnnu.edu.cn
 ^c Dept Mat Sci & Engn, Guilin Univ Elect Technol, Guilin 541004, China

^d Dept Chem, Jinan Univ, Guangzhou 510632, Guangdong, China

^e Université de Haute Alsace, ENSCMu, Lab. LPI-GSEC, 3, Rue A. Werner, F-68094, Mulhouse Cedex, France

Rue A. werner, F-08094, Mulhouse Cedex, France

^J Institute of Physics, Universität Rostock, Rostock D-18059, Germany † Electronic supplementary information (ESI) available: Additional details of the synthesis of NMOF, low-pressure gas adsorption measurements, determination of isosteric heats of adsorption, hydrogen adsorption kinetics measurements, IR spectra, and other physical measurements. See DOI: 10.1039/c1cc15106a



Fig. 2 (a) Experimental PXRD patterns and (b) TG profile of NMOF (heating rate: $5 \,^{\circ}\text{C min}^{-1}$ in air flow).

spectrum shows the presence of free –C=O bands of the DMF moieties at 1670 cm⁻¹ (Fig. S1a, ESI†), confirming the incorporation of the DMF molecules within the pores. In the case of NMOF after activation, the absence of the absorption band around 1670 cm⁻¹ indicates that the DMF has been totally removed from the channels after activation at 200 °C overnight (Fig. S1b, ESI†), although TG data indicate that DMF is completely evacuated only at ~300 °C.

The TG curve of the as synthesized and dried (50 °C) NMOF shows two main events occurring between the room temperature and 750 °C at a heating rate of 5 °C min⁻¹ under air flow (Fig. 2b). A gradual weight-loss step of 20% corresponds to the removal of one guest DMF molecule per Al(OH)(NDC) (calc.: 21%) from the large nanochannels of NMOF. A long plateau up to 500 °C with almost no weight losses is recorded thereby illustrating the high thermal stability of the frameworks for NMOF. The second event, observed above 500 °C, corresponds to the sudden oxidative degradation of the linkers from the framework, Al₂O₃ being the only residual solid at the end of the calcination process.

To further illustrate the thermal stability of NMOF, we performed the PXRD measurements of the as-synthesized samples in air at elevated temperature (Fig. 3). When the sample is heated to 200 °C, the intensity of the XRD peaks remarkably increases due to the enhancement of the electron density contrast caused by the removal of DMF molecules from the pores.⁹ Before the NMOF framework collapses (about 500 °C), no phase transition is detected. The results from TG characterization and PXRD measurements confirm the high thermal stability and the rigidity of the NMOF.



Fig. 3 Results of the temperature-dependent PXRD study of as synthesized NMOF in air.



Fig. 4 (a) N_2 sorption isotherms and (b) H_2 sorption isotherms. In the isotherms, solid and open markers represent adsorption and desorption points respectively.

To acquire more information about the porous structure, N_2 sorption isotherms were recorded for NMOF at 77 K (Fig. 4a). The isotherm profile (Fig. 4a) of NMOF was of type I, confirming a microporous behavior.¹⁰ H₄-type hysteresis loop (*P*/*P*_o range 0.80–1.00) was observed for the nanosized Al(OH)(NDC) material corresponding to the filling of intercrystalline mesopores created upon nanocrystallite packing. The N₂ volume adsorbed by NMOF is 163 cm³ g⁻¹ at 0.005 *P*/*P*_o (Standard Temperature and Pressure, STP) (Fig. 4a), which is far higher than that reported in the literature.⁹ The BET specific surface area (*S*_{BET}) of NMOF is 761 m² g⁻¹.

The uptake capacities for H₂ (kinetic diameter = 2.8 Å) were measured at 77, 87, and 97 K (Fig. 4b). The H₂ adsorption amount on nanocrystalline Al(OH)(NDC) was 142 cm³ g⁻¹ (12.7 mg g⁻¹) at 77 K and 817 mm Hg (Fig. 4b), a value higher than those measured for most of the nanosized MOFs or CPs, such as ICP-3 (or -5), Cr-BDC, CPP-3, Carborane-Co(II)-3 (or -4) under the same conditions.¹¹ Furthermore, the H₂ uptake capacity of NMOF is also higher than that of microcrystalline Al(OH)(NDC) (MMOF) prepared by the hydrothermal synthesis (see Fig. S2, ESI†). The results confirm that our solvothermal synthesis procedure with DMF solvent is more efficient than the literature recipe.⁹

To better understand the interaction between adsorbates and the framework, the isosteric heat of adsorption for H₂ as a function of H₂ uptake was determined using the Clausius– Clapeyron equation. As shown in Fig. S3 (ESI[†]), the heat of adsorption is ~6.3 kJ mol⁻¹ and constant for NMOF.

The high-pressure hydrogen storage performance was also measured with a commercial pressure-composition isotherm (PCI) unit provided by Advanced Materials Corporation (Fig. S4a, ESI†). The hydrogen uptake of NMOF at 77 K and 30 atm reaches 21.9 mg g⁻¹. Moreover, the kinetics of adsorption of H₂ on NMOF was measured at 77 K. Fig. S4b (ESI†) shows the kinetic curve for H₂ uptake *versus* time. The H₂ adsorption rate of NMOF reveals that within the short time of about 100 s, H₂ adsorption reaches ~98% saturation.

To examine the separation capability of NMOF for various gases, single-component gas sorption experiments were carried out on CO₂ (3.3 Å), CH₄ (3.8 Å), N₂ (3.64 Å) and O₂ (3.46 Å) at 273 K and up to 777 mm Hg (Fig. 5a).

The uptake capacities for CO_2 were measured at 273 K (Fig. 5a) and 298 K (Fig. 55, ESI[†]). The CO_2 isotherm is completely reversible at 273 K, exhibiting a steep rise at low pressures, and reaches a maximum of 71 cm³ g⁻¹ (139 mg g⁻¹)



Fig. 5 (a) Gases sorption isotherms on NMOF at 273 K and (b) heat of adsorption isotherms at different CO_2 and CH_4 loadings. In the isotherms, solid and open markers represent adsorption and desorption points respectively.

at 273 K and 777 mm Hg, which is higher compared to the corresponding values of some representative MOFs and ZIFs.¹² The specific surface area of NMOF calculated by CO₂ adsorption data is 767 m² g⁻¹, which are in agreement with the value of NMOF based on the N₂ adsorption. We also calculated the isosteric heat of adsorption (Q_{st}) for CO₂ using adsorption data collected at 273 and 298 K by the Clausius–Clapeyron equation. Q_{st} for CO₂ is ~23 kJ mol⁻¹ in the adsorption region from 5 cm³ g⁻¹ to 35 cm³ g⁻¹ (Fig. 5b).

The CH₄ uptake capacity of NMOF is 19 cm³ g⁻¹ at 273 K and 777 mm Hg. Q_{st} for CH₄ is ~18 kJ mol⁻¹, which is much lower than that for CO₂. We attributed the significant difference in the adsorbed amounts and the heats of adsorption for CO₂ and CH₄ to the fact that CO₂ has a quadrupole moment, whereas CH₄ is nonpolar, so the stronger affinity of CO₂ for the material adsorption sites, as compared to CH₄.

Comparatively, the N₂ and O₂ uptakes at 273 K and 777 mm Hg were only 4.5 cm³ g⁻¹ and 5.2 cm³ g⁻¹, respectively. The initial slopes of CO₂, CH₄, N₂ and O₂ adsorption isotherms were calculated, and the ratios of these slopes were used to estimate the adsorption selectivity for CO₂ over CH₄, N₂ or O₂.¹³ From these data (Fig. S6, ESI†), the calculated CO₂/CH₄ selectivity was 4.4:1, CO₂/N₂ selectivity was 19.6:1 and CO₂/O₂ selectivity was 18.8:1 at 273 K.

In summary, here we reported for the first time a synthesis procedure yielding pure uniformly nanosized Al(OH)(NDC) (NMOF) crystallites with high thermal stability. NMOF can adsorb 12.7 mg g⁻¹ and 21.9 mg g⁻¹ hydrogen at 77 K under about 1 atm and 30 atm, respectively. Moreover, the kinetics experiment indicates that nanocrystalline NMOF adsorbs H₂ up to ~98% saturation within about 100 s at 77 K. It shows high CO₂ sorption capacity and excellent selectivity for CO₂ over N₂ and O₂. It is concluded that NMOF is a promising candidate for H₂ storage, for CO₂ capture, and for gas separation.

This work was financially supported by the "973 Project" (2010CB631303), NSFC (20833009, 20903095, 20873148, U0734005, 51071081, 51071146, 51101145 and 51102230), LNSFC (No. 20102224), Liaoning BaiQianWan Talents Program (No. 2010921050), Liaoning Education Committee (L2010223) and IUPAC (Project No. 2008-006-3-100). The authors would like to thank Dr Zheling Zhang and Jeffrey Yang (Quantachrome Instruments, USA) for helpful discussions.

Notes and references

- (a) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127–1129; (b) M. Dinca, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876–16883; (e) M. Latroche, S. Surble, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J. H. Lee, J. S. Chang, S. H. Jhung and G. Férey, *Angew. Chem., Int. Ed.*, 2006, **45**, 8227–8231.
- 2 J. B. Lin, W. Xue, J. P. Zhang and X. M. Chen, *Chem. Commun.*, 2011, 47, 926–928.
- 3 L. X. Shi and C. D. Wu, Chem. Commun., 2011, 47, 2928-2930.
- 4 A. Carne, C. Carbonell, I. Imaz and D. Maspoch, *Chem. Soc. Rev.*, 2011, 40, 291–305.
- 5 G. Z. Yuan, C. F. Zhu, Y. Liu and Y. Cui, *Chem. Commun.*, 2011, 47, 3180–3182.
- 6 (a) W. J. Rieter, K. M. L. Taylor, H. Y. An, W. L. Lin and W. B. Lin, J. Am. Chem. Soc., 2006, **128**, 9024–9025; (b) A. M. Spokoyny, D. Kim, A. Sumrein and C. A. Mirkin, *Chem. Soc. Rev.*, 2009, **38**, 1218–1227; (c) W. B. Lin, W. J. Rieter and K. M. L. Taylor, Angew. Chem., Int. Ed., 2009, **48**, 650–658.
- 7 S. H. Jhung, J. H. Lee, J. W. Yoon, C. Serre, G. Férey and J. S. Chang, *Adv. Mater.*, 2007, **19**, 121–124.
- 8 D. Tanaka, A. Henke, K. Albrecht, M. Moeller, K. Nakagawa, S. Kitagawa and J. Groll, *Nat. Chem.*, 2010, 2, 410–416.
- 9 A. Comotti, S. Bracco, P. Sozzani, S. Horike, R. Matsuda, J. Chen, M. Takata, Y. Kubota and S. Kitagawa, J. Am. Chem. Soc., 2008, 130, 13664–13672.
- 10 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, 57, 603–619.
- (a) Y. M. Jeon, G. S. Armatas, J. Heo, M. G. Kanatzidis and C. A. Mirkin, Adv. Mater., 2008, 20, 2105–2110; (b) Z. F. Xin, J. F. Bai, Y. M. Shen and Y. Pan, Cryst. Growth Des., 2010, 10, 2451–2454; (c) O. K. Farha, A. M. Spokoyny, K. L. Mulfort, S. Galli, J. T. Hupp and C. A. Mirkin, Small, 2009, 5, 1727–1731; (d) W. Cho, H. J. Lee and M. Oh, J. Am. Chem. Soc., 2008, 130, 16943–16946; (e) Y. M. Jeon, G. S. Armatas, D. Kim, M. G. Kanatzidis and C. A. Mirkin, Small, 2009, 5, 46–50.
- 12 (a) H. Furukawa, J. Kim, N. W. Ockwig, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2008, 130, 11650–11661;
 (b) R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, Science, 2008, 319, 939–943;
 (c) E. Neofotistou, C. D. Malliakas and P. N. Trikalitis, Chem.-Eur. J., 2009, 15, 4523–4527; (d) A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O'Keeffe and O. M. Yaghi, Acc. Chem. Res., 2010, 43, 58–67.
- (a) J. An, S. J. Geib and N. L. Rosi, J. Am. Chem. Soc., 2010, 132, 38–39; (b) R. Banerjee, H. Furukawa, D. Britt, C. Knobler, M. O'Keeffe and O. M. Yaghi, J. Am. Chem. Soc., 2009, 131, 3875–3877.