A hybrid compound based on porous metal–organic frameworks and polyoxometalates: NO adsorption and decomposition

Feng-Ji Ma, Shu-Xia Liu *, Guo-Jian Ren, Da-Dong Liang, Sha Sha

Key Laboratory of Polyoxometalates Science of the Ministry of Education, College of Chemistry, Northeast Normal University, Changchun 130024, China

ABSTRACT

A new hybrid compound based on porous metal–organic frameworks and polyoxometalates $H_4[(Cu_4Cl)_3(BTC)_8]_2$ $[SiW_{12}O_{40}] \cdot (C_4H_{12}N)_6 \cdot 3H_2O$ (NENU-15, BTC = 1, 3, 5-benzenetricarboxylate) has been hydrothermally synthesized and its crystal structure, stability and porosity have been characterized. The experimental results showed that the introduction of polyoxometalates improved the integral stability of the compound. In addition, NENU-15 was employed in NO removal for the first time. By virtue of the synergistic effect between host frameworks and guest polyoxometalates, it not only displayed good adsorption behavior for NO, but also exhibited superior activity in NO decomposition.

© 2012 Elsevier B.V. All rights reserved.

NO_x (NO and NO_2) arising from automobile exhaust gases and industrial emissions is the major pollutant in the atmosphere, which caused acid rain, photochemical smog, and greenhouse effect. Therefore removal of NO_x has been one of the key environmental subjects in the world nowadays. Since NO is thermodynamically unstable relative to N_2 and O_2, catalytic decomposition is the simplest and cheapest method for its removal [1–3]. In principle, alternative strategies to eliminate NO are based on NO adsorption. Many porous materials such as metal oxides and zeolites have been employed for NO removal [4,5]. Especially, Cu-containing zeolites show peculiar adsorption behavior due to the high activity of Cu sites, and Cu^{2+} has been proved to be important in NO decomposition. Polyoxometalates (POMs), most represented by the Keggin type, also have been used for the NO adsorption and decomposition [6]. POMs are a kind of metal–oxygen cluster compounds with strong Brønsted acidity, showing various advantageous properties [7]. One of the most attractive is that Keggin type POMs could cause the decomposition of the absorbed NO under conditions of rapid heating. However, their applications are limited due to the low specific surface areas.

Metal–organic frameworks (MOFs) are a new class of porous materials consisting of metal ions and organic ligands [8], resulting in high surface areas and tunable pore properties. They have attracted increasing attention due to their potential applications in gas adsorption [9], catalysis [10], sensing [11] and drug delivery [12]. In virtue of the high porosity, they have been used as hosts for encapsulating POMs

to construct new multifunctional hybrid materials [13,14]. However, because of the low stability, there are only few postsynthetically modified MOFs being used in adsorption and release of NO for therapeutic applications [15].

Recently we reported a porous hybrid material based on MOFs and POMs (NENU-11) [16], which displayed good adsorption behavior and decomposition activity for eliminating nerve gas mimic. The porous MOFs with high stability and functional POMs guest, may be an effective material for NO adsorption and decomposition. Herein, we report such a new hybrid compound, $H_4[(Cu_4Cl)_3(BTC)_8]_2[SiW_{12}O_{40}] \cdot$ $(C_4H_{12}N)_6 \cdot 3H_2O$ (NENU-15, BTC = 1, 3, 5-benzenetricarboxylate), and present its potential application in removal of NO. NENU-15 is composed of porous Cu-containing MOFs and Keggin type POMs. The introduction of POMs enhances the thermal stability of MOFs host. Synchronously, Cu ions in MOFs have a synergistic effect as active sites. The results show that NENU-15 displays good adsorption behavior for NO and can realize the decomposition of NO by heating rapidly.

NENU-15 was synthesized in good yield by a hydrothermal method [17]. Single crystal X-ray diffraction analysis of NENU-15 revealed a cubic structure [18], isotypic with that of NENU-11 [16], the chloride-centered square-planar [Cu₄Cl] secondary building units (SBUs) are linked via the BTC ligands to form a 3D open framework. Notably, every Cu^{2+} in SBUs has an exposed coordination site, which is active for adsorbed molecules. The fundamental building unit of the framework is a sodalite-like cage formed by six [Cu₄Cl] squares and eight BTC ligands (Fig. 1a). These cages share the [Cu₄Cl] squares further to construct the cubic framework (Fig. 1c). $[SiW_{12}O_{40}]^{4-}$ anions were located in the cavities formed by the packing of sodalite-like cages (Fig. 1d). The accessible void is estimated by PLATON [19] to be about 24.3% of the total crystal volume.

* Corresponding author. Tel./fax: +86 43185099328.
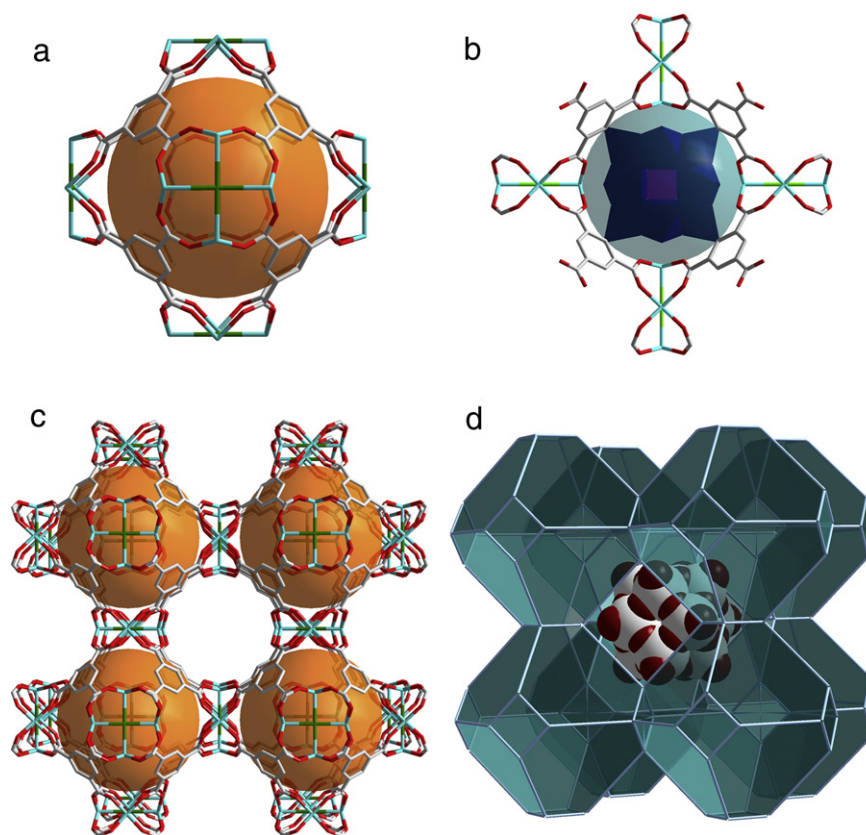 E-mail address: liusx@nenu.edu.cn (S-X. Liu).

Fig. 1. (a) The sodalite-like cage formed by six [Cu₄Cl] squares and eight BTC ligands; (b) the wide-open cavity located $[SiW_{12}O_{40}]^{4-}$ anion; (c) the 3D open framework; (d) the simplified structure of sodalite-type network with POMs.

TGA indicates that the solid is thermally stable up to 350 °C (Figure S2), which is higher than the single framework (~300 °C) [20]. The improvement of thermal stability could be assigned to the encapsulation of POMs [14c,d]. The PXRD pattern of NENU-15 matches the simulated pattern from the single crystal X-ray data (Figure S3), implying that the bulk sample possesses high purity. Moreover, the PXRD patterns at 200 °C and 300 °C further confirm the stability and structural integrity. The results here suggest that incorporating POMs enhances the stability of NENU-15, and more importantly, shows a positive implication for NO adsorption and decomposition.

The permanent porosity was evaluated by N_2 adsorption at 77 K. The sample of NENU-15 was heated at 200 °C under vacuum for 12 h before the adsorption measurements. As shown in Fig. 2, NENU-15 exhibits typical Type-I isotherm for N_2. It increases quickly at the start and reaches a plateau at P/Po = 0.05, indicating the presence of the microporous structure [21]. NENU-15 adsorbs N_2 to 183 cm³ (STP) g⁻¹ at 77 K and 1 atm, with a Brunauer–Emmett–Teller (BET) surface areas of 547 m² g⁻¹. Applying Dubinin–Astakhov (DA) analysis [22] to the isotherm data shows that the pore sizes is distributed around 10.6 Å, corresponding to the result from crystallographic structure analysis (10.8 Å).

Gravimetric adsorption measurements revealed that NENU-15 adsorbed NO 1.74 mmol g⁻¹ at room temperature (Fig. 3). Single MOFs and POMs adsorbed 2.69 and 0.39 mmol/g, respectively. The value of single MOFs is approximate to that of HKUST-1 (~3 mmol/g) and comparable to those of the materials, which have been proposed
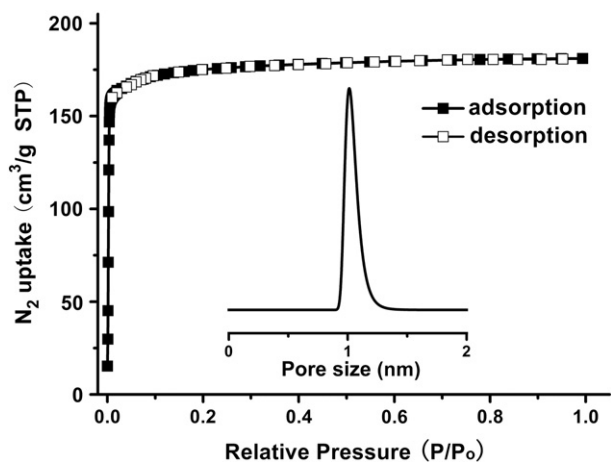

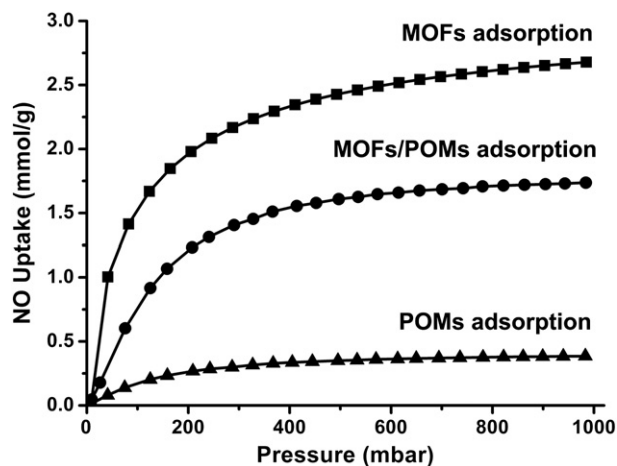**Fig. 2.** N_2 adsorption isotherm at 77 K and pore size distribution.

Fig. 3. NO adsorption isotherms at 298 K.

as NO adsorbents [23]. For NENU-15, the adsorption includes physical and chemical processes, and physical adsorption is primarily due to the porous framework. The chemical adsorption consists of two parts, POMs and exposed Cu sites. It was proposed that NO was adsorbed into POMs as a form of protonated NOH^+ [24]. Meanwhile, there is an accepting orbital in Cu^{2+} (d^9) to support the donation of the electron in the anti-bonding orbital of NO [25]. Both of them are confirmed by IR (Fig. 4). The characteristic peaks at 984, 929, 884 and 807 cm^{-1} are attributable to $\nu(W-O_t)$ and $\nu(W-O_{b/c}-W)$ vibration modes for Keggin anion. The bands at around 1100 cm^{-1} can be regarded as the P–O stretching vibration. The peaks ranging from 1300 to 1900 cm^{-1} are assigned to the MOFs framework. Compared with the IR spectrums of NENU-15 after NO adsorption, several new bands are observed. For POMs, a band at ca. 2260 cm^{-1} is attributable to $\nu(NOH^+)$ [24]; for Cu, a new peak at ca. 1821 cm^{-1} suggests the strong interaction between NO and Cu^{2+} sites [23,25]; the two bands at ca. 1370 and 1300 cm^{-1} could be due to the interaction between NO and the KBr [24b].

Heating NENU-15 after the adsorption measurements, N_2 was found through the mass spectrometry which was coupled with adsorption system. To further investigate the decomposition of adsorbed NO, we performed the test in a fixed-bed reactor at a heating rate of 50 °C min^{-1}. When heating temperature reached 300 °C, an overall nitrogen mass balance showed that 64% of the NO that was absorbed initially in NENU-15 was converted to N_2 (Figure S4). Continued heating to 350 °C produced little change in the conversion. In comparison, nearly 60% of the NO originally contained in single POMs was converted into N_2 upon heating to about 400 °C. For single MOFs, only 11% of the adsorbed NO decomposed at 300 °C, and the framework structure began to collapse at higher temperature. The activity of NENU-15 is greater than that of either MOFs or POMs alone. This indicates that there exists synergetic effect between POMs and Cu in MOFs. The mechanistic details are currently poorly understood, yet the results presented here demonstrate that this kind of new porous material displays the potential application in the removal of NO.

In conclusion, we have presented here a new hybrid compound based on porous MOFs and POMs (NENU-15) and employed it in NO removal for the first time. The open structure with exposed Cu^{2+} sites and POMs guests play important roles in the adsorption of NO. Furthermore, the introduction of POMs improved the thermal stability and brought a positive possibility for NO decomposition. We are going to study the effect of different POMs guests on the adsorption and decomposition of NO.

Acknowledgments

Appendix A. Supplementary material

CCDC-715943 contains crystallographic data. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found online at http://dx.doi.org/10.1016/j.inoche.2012.05.055.

References

[1] J.N. Armor, Environmental catalysis, Appl. Catal., B 1 (1992) 221–256.
[2] B. Harrison, M. Wyatt, K.G. Gough, Catalysis of reactions involving the reduction or decomposition of nitrogen oxides, Catalysis, Royal Society of Chemistry, London, 1982, pp. 127–171.
[3] J.W. Hightower, D.A. Van Leirsburg, The Catalytic Chemistry of Nitrogen Oxides, in: R.M. Klimisch, J.G. Larson (Eds.), Plenum Press, London, 1975, pp. 63–93.
[4] (a) Z. Zhao, X.G. Yang, Y. Wu, Comparative study of nickel-based perovskite-like mixed oxide catalysts for direct decomposition of NO, Appl. Catal., B 8 (1996) 281–297;
(b) J. Zhu, A. Thomas, Perovskite-type mixed oxides as catalytic material for NO removal, Appl. Catal., B 92 (2009) 225–233.
[5] (a) G. Moretti, G. Ferraris, G. Fierro, M.L. Jacono, S. Morpurgo, M. Faticanti, Dimeric Cu(I) species in Cu-ZSM-5 catalysts: the active sites for the NO decomposition, J. Catal. 232 (2005) 476–487;
(b) N.V. Beznis, B.M. Weckhuysen, J.H. Bitter, Cu-ZSM-5 Zeolites for the formation of methanol from methane and oxygen: probing the active sites and spectator species, Catal. Lett. 138 (2010) 14–22;
(c) S. Dzwigaj, J. Janas, J. Gurgul, R.P. Socha, T. Shishido, M. Che, Do Cu(II) ions need Al atoms in their environment to make CuSiBEA active in the SCR of NO by ethanol or propane? A spectroscopy and catalysis study, Appl. Catal., B 85 (2009) 131–138;
(d) K. Mathisen, M. Stockenhuber, D.G. Nicholson, In situ XAS and IR studies on Cu:SAPO-5 and Cu:SAPO-11: the contributory role of monomeric linear copper(I) species in the selective catalytic reduction of NO_x by propene, Phys. Chem. Chem. Phys. 11 (2009) 5476–5488.
[6] (a) R.T. Yang, N. Chen, A new approach to decomposition of nitric-oxide using sorbent catalyst without reducing gas: use of heteropoly compounds, Ind. Eng. Chem. Res. 33 (1994) 825–831;
(b) R. Belanger, J.B. Moffat, The sorption and reduction of nitrogen oxides by 12-tungstophosphoric acid and its ammonium salt, Catal. Today 40 (1998) 297–306;
(c) S. Heylen, S. Smeekens, C. Kirschhock, T. Parac-Vogt, J.A. Martens, Temperature swing adsorption of NO_x over Keggin type heteropolyacids, Energy Environ. Sci. 3 (2010) 910–916.
[7] (a) M.T. Pope, A. Müller, Polyoxometalate chemistry: an old field with new dimensions in several disciplines, Angew. Chem. Int. Ed. 30 (1991) 34–48;
(b) D.L. Long, R. Tsunashima, L. Cronin, Polyoxometalates: building blocks for functional nanoscale systems, Chem. Soc. Rev. 36 (2007) 105–121.
[8] J.R. Long, O.M. Yaghi, The pervasive chemistry of metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1213–1214.
[9] L.J. Murray, M. Dincă, J.R. Long, Hydrogen storage in metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1294–1314.
[10] L. Ma, C. Abney, W. Lin Enantioselective, catalysis with homochiral metal–organic frameworks, Chem. Soc. Rev. 38 (2009) 1248–1256.
[11] G. Lu, J.T. Hupp, Metal–organic frameworks as sensors: a ZIF-8 based Fabry–Pérot device as a selective sensor for chemical vapors and gases, J. Am. Chem. Soc. 132 (2010) 7832–7833.
[12] P. Horcajada, C. Serre, M. Vallet-Regi, M. Sebban, F. Taulelle, G. Férey, Metal–organic frameworks as efficient materials for drug delivery, Angew. Chem. Int. Ed. 45 (2006) 5974–5978.
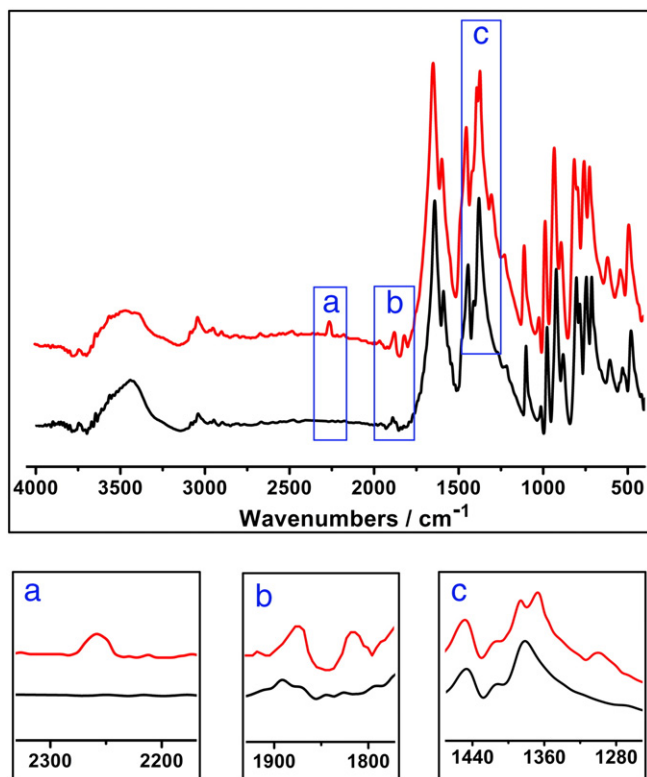

Fig. 4. IR spectra of NENU-15 (black) and NENU-15 with adsorbed NO (red).

[13] (a) X.F. Kuang, X.Y. Wu, R.M. Yu, J.P. Donahue, J.S. Huang, C.Z. Lu, Assembly of a metal–organic framework by sextuple intercatenation of discrete adamantane-like cages, Nat. Chem. 2 (2010) 461–465;
   (b) C.Y. Duan, M.L. Wei, D. Guo, C. He, Q.J. Meng, Crystal structures and properties of large protonated water clusters encapsulated by metal–organic frameworks, J. Am. Chem. Soc. 132 (2010) 3321–3330;
   (c) X.Y. Liu, Y.Y. Jia, Y.F. Zhang, R.D. Huang, Construction of a hybrid family based on lanthanide–organic framework hosts and polyoxometalate guests, Eur. J. Inorg. Chem. 25 (2010) 4027–4033;
   (d) S.Z. Li, D.D. Zhang, Y.Y. Guo, P.T. Ma, J.W. Zhao, J.P. Wang, J.Y. Niu, A series of 3D rare-earth-metal–organic frameworks with isolated guest Keggin silicotungstate fragments as anion templates, Eur. J. Inorg. Chem. 35 (2011) 5397–5404;
   (f) X.L. Wang, H.L. Hu, A.X. Tian, H.Y. Lin, J. Li, Application of tetrazole-functionalized thioethers with different apacer lengths in the self-assembly of polyoxometalate-based hybrid compounds, Inorg. Chem. 49 (2010) 10299–10306.
[14] (a) Y. Yang, S.X. Liu, C.C. Li, S.J. Li, G.J. Ren, F. Wei, Q. Tang, A metal–organic framework based on Wells–Dawson polyoxometalates $[As_2W_{18}O_{62}]^{6-}$ template, Inorg. Chem. Commun. 17 (2012) 54–57;
   (b) C.Y. Sun, S.X. Liu, D.D. Liang, K.Z. Shao, Y.H. Ren, Z.M. Su, Highly stable crystalline catalysts based on a microporous metal–organic framework and polyoxometalates, J. Am. Chem. Soc. 131 (2009) 1883–1888;
   (c) F.J. Ma, S.X. Liu, D.D. Liang, G.J. Ren, C.D. Zhang, F. Wei, Z.M. Su, Hydrogen adsorption in polyoxometalate hybrid compounds based on porous metal–organic frameworks, Eur. J. Inorg. Chem. 24 (2010) 3756–3761;
   (d) F.J. Ma, S.X. Liu, D.D. Liang, G.J. Ren, F. Wei, Y.G. Chen, Z.M. Su, Adsorption of volatile organic compounds in porous metal–organic frameworks functionalized by polyoxometalates, J. Solid State Chem. 184 (2011) 3034–3039.
[15] (a) A.C. McKinlay, B. Xiao, D.S. Wragg, P.S. Wheatley, I.L. Megson, R.E. Morris, Exceptional behavior over the whole adsorption–storage–delivery cycle for NO in porous metal organic frameworks, J. Am. Chem. Soc. 130 (2008) 10440–10444;
   (b) M.J. Ingleson, R. Heck, J.A. Gould, M.J. Rosseinsky, Nitric oxide chemisorption in a postsynthetically modified metal–organic framework, Inorg. Chem. 48 (2009) 9986–9988;
   (c) J.G. Nguyen, K.K. Tanabe, S.M. Cohen, Postsynthetic diazeniumdiolate formation and NO release from MOFs, CrystEngComm 12 (2010) 2335–2338.
[16] F.J. Ma, S.X. Liu, C.Y. Sun, D.D. Liang, G.J. Ren, F. Wei, Y.G. Chen, Z.M. Su, A sodalite-type porous metal–organic framework with polyoxometalate templates: adsorption and decomposition of dimethyl methylphosphonate, J. Am. Chem. Soc. 133 (2011) 4178–4181.
[17] Synthesis of $H_4[(Cu_4Cl)_3(BTC)_8]_2[SiW_{12}O_{40}]\cdot(C_4H_{12}N)_6\cdot 3H_2O$ (NENU-15): A mixture of $CuCl_2\cdot 2H_2O$ (0.18 g, 1 mmol), H_3BTC (0.21 g, 1 mmol) and $K_4SiW_{12}O_{40}\cdot 9H_2O$ (0.32 g, 0.1 mmol) in distilled water (10 mL) was stirred for 30 min. The pH was adjusted to 4.5 by dropwise addition of 50% $(CH_3)_4NOH$ solution. Then the turbid mixture was sealed in a Teflon-lined autoclave and heated at 180 °C for 72 hours, then cooled to room temperature. Cyan cube-shaped crystals were collected with yield 62% based on Cu. Elemental Anal. Calcd (Found %) for $C_{168}H_{130}Cl_6Cu_{24}N_6O_{139}SiW_{12}$: C, 23.94 (23.69); H, 1.55 (1.73); N, 1.00 (1.06); Si, 0.33 (0.41); Cu, 18.09 (17.88); W, 26.17 (26.46). IR (KBr): 3441, 3039, 1886, 1645, 1589, 1479, 1444, 1380, 1103, 976, 925, 885, 806, 784, 747, 715, 612, 532, 482 cm^{-1}.
[18] Crystal data for NENU-15: $C_{288}H_{96}Cl_{12}Cu_{48}N_{12}O_{286}Si_2W_{24}$, Mr = 16243.91, cubic, space group Fm-3 m, a = 30.7911(18) , V = 29193(3) Å^3, Z = 2, Dc = 1.848 mg cm^{-3}, μ = 6.554 mm^{-1}, F(000) = 15192, GOF = 1.011. 57018 reflections measured, 1481 unique (Rint = 0.0289), R1 = 0.0392 (I > 2σ(I)), wR2 = 0.1385 (all data). Data were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) at 296 K. The structure was solved by using the direct method and refined through the full-matrix least-squares method on F2 using SHELXS-97. CCDC-715943 contains crystallographic data.
[19] A.L. Spek, PLATON 99: A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 1999.
[20] Y.X. Tan, Y.P. He, J. Zhang, Pore partition effect on gas sorption properties of an anionic metal–organic framework with exposed Cu^{2+} coordination sites, Chem. Commun. 47 (2011) 10647–10649.
[21] F. Rouquerol, J. Roquerol, K. Sing, Adsorption by powders and porous solids: principles, Methodology and Applications, Academic Press, London, 1999.
[22] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, Academic Press, London, 1982.
[23] (a) B. Xiao, P.S. Wheatley, X.B. Zhao, A.J. Fletcher, S. Fox, A.G. Rossi, I.L. Megson, S. Bordiga, L. Regli, K.M. Thomas, R.E. Morris, High-capacity hydrogen and nitric oxide adsorption and storage in a metal–organic framework, J. Am. Chem. Soc. 129 (2007) 1203–1209;
   (b) S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P.S. Wheatley, R.E. Morris, A. Zecchina, Adsorption properties of HKUST-1 toward hydrogen and other small molecules monitored by IR, Phys. Chem. Chem. Phys. 9 (2007) 2676–2685.
[24] (a) A.M. Herring, R.L. McCormick, S.R. Boonrueng, A Comparison of the Interaction of Nitric Oxide with the Heteropolytungstic Acids $H_3PW_{12}O_{40}$, $H_{0.5}Cs_{2.5}PW_{12}O_{40}$, $HMgPW_{12}O_{40}$, $H_8SiW_{11}O_{38}$, $H_4SiW_{12}O_{40}$, and $H_{10}CoW_{12}O_{42}$, J. Phys. Chem. B 104 (2000) 4653–4660;
   (b) N. Chen, R.T. Yang, Activation of nitric oxide by heteropoly compounds: structure of nitric-oxide linkages in tungstophosphoric acid with Keggin units, J. Catal. 157 (1995) 76–86.
[25] J. Vaylon, W.K. Hall, Studies of the surface species formed from nitric oxide on copper zeolites, J. Phys. Chem. 97 (1993) 1204–1212.