Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry
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Journal Name

ARTICLE

High volumetric uptake of ammonia using Cu-MOF-74/Cu-CPO-27

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Cu-MOF-74 (also known as Cu-CPO-27) was identified as a sorbent having one of the highest densities of Cu(II) sites per unit volume. Given that Cu(II) in the framework can be thermally activated to yield a five-coordinate Cu(II) species, we identified this MOF as a potential candidate for maximal volumetric uptake of ammonia. To that end, the kinetic breakthrough of ammonia in Cu-MOF-74/Cu-CPO-27 was examined under both dry and humid conditions. Under dry conditions the MOF exhibited a respectable performance (2.6 vs. 2.9 NH_3/nm^3 for the current record holder HKUST-1), and under 80 % relative humidity, the MOF outperformed HKUST-1 (5.9 vs. 3.9 NH_3/nm^3, respectively).

Introduction

Nearly 150 million tons of ammonia (NH_3) are produced globally per year[1] to be used as a feedstock in the manufacturing of fertilizers,[2] pharmaceuticals,[3] commercial cleaning products,[4] and as a refrigerant.[5] Among the widely produced toxic industrial chemicals (TICs) identified by the North Atlantic Treaty Organization (NATO), ammonia is ranked high in the hazard index rating due to its toxicity and the risks associated with large scale production and storage – including the potential for spills or explosions – at manufacturing facilities or fertilizer plants.[6] Ammonia is a colourless gas, with a strong and distinctive odour, that causes irritation of the eyes and upper respiratory tract. Prolonged exposure to ammonia at concentrations greater than 50 ppm can cause temporary blindness, pulmonary edema, burns and blisters, and eventually death.[7] As a result, the United States Occupational Safety and Health Administration (OSHA) has set a short-term (15 minute) ammonia exposure limit (STEL) of 35 ppm and an 8 hour time weighted average (TWA) exposure limit of 25 ppm based on recommendations by the National Institute for Occupational Safety and Health (NIOSH).[8] Owing to the potential dangers of both acute and prolonged exposure to ammonia, the development of new materials for the adsorptive removal of ammonia from air is of high importance.[9] To this end, we turn our attention to the use of a Metal-Organic Framework (MOF) as a potential sorbent for ammonia.
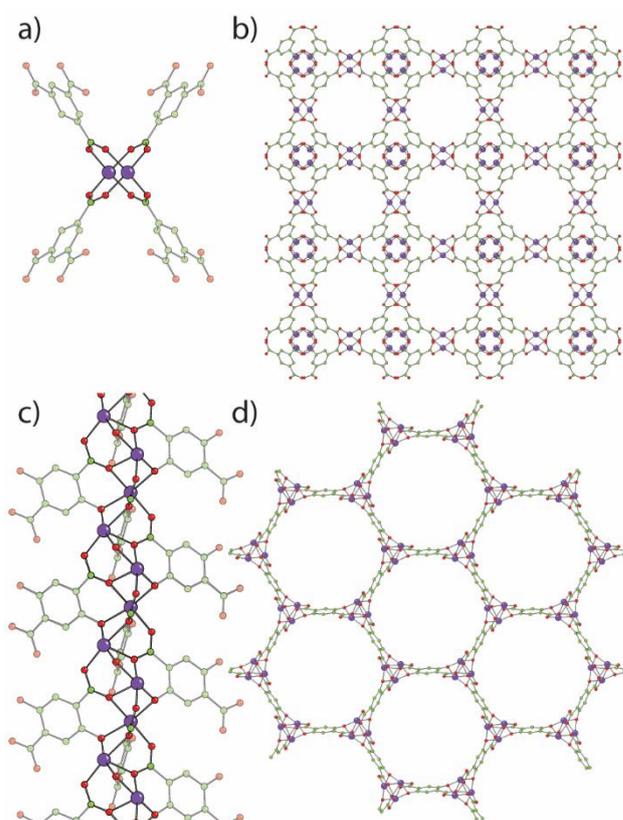

Figure 1: (a) Cu_2-paddlewheel structure of the node of HKUST-1; each Cu(II)-centre is 5-coordinate after thermal solvent removal. (b) 3D cubic structure of HKUST-1. The open metal site of the Cu(II) points into the pore of HKUST-1. (c) 1D chains of Cu(II) centres in Cu-MOF-74 viewed along the *c*-axis, bridged by carboxylate and phenoxide anions; each Cu(II) centre is 5-coordinate after thermal solvent removal. (d) 3D honeycomb structure of Cu-MOF-74 viewed down the *c*-axis. The open metal site of the Cu(II) points into the open pore of Cu-MOF-74.

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MOFs are porous materials made from inorganic cations or clusters and polytopic organic ligands (i.e., linkers).[10] By judiciously choosing the appropriate metal and ligand combination, desired functionalities can be achieved; this has been shown for chemical sensing,[11] chemical separations,[12] gas storage,[13] light harvesting,[14] catalysis[15] and toxic gas adsorption

and degradation.[9a,16,17] With respect to ammonia, the ideal sorbent would have a high density of reactive/adsorption sites for ammonia, and those sites should have a high affinity for ammonia. While the former engenders a high volumetric capacity, the latter ensures that competitive reaction/adsorption of other molecules is minimized. One way to impart a high density of reactive/adsorption sites in a MOF is to incorporate open metal sites, or structural defects, where metal-ammonia bonding can occur.

Recently, HKUST-1, a MOF formed via the coordination of 1,3,5,-benzenetricarboxyate (BTC) moieties to Cu(II) ions has been shown to efficiently absorb ammonia under both dry and humid conditions (see Table 1).[18] The mode of action is the Lewis-acid/base coordination of ammonia molecules to thermally-accessible open sites on the Cu(II) centres. However, while the adsorption sites in HKUST-1 have a high affinity for ammonia, the density of Cu(II) sites ($2.2/nm^3$) is low compared to that in some other MOFs.

To increase the density of adsorption sites while still maintaining high ammonia selectivity, we turned to Cu-MOF-74 (also known as CPO-27), which has one of the highest densities of Cu(II) sites ($4.7/nm^3$) of any known MOF. Cu-MOF-74 is a permanently microporous material consisting of Cu(II) centres coordinated and interconnected via tetra-deprotonated 2,5-dihydroxy-terephthalic acid (BDC-(OH)$_2$; "BDC" = benzene dicarboxylate) (Figure 1). As with HKUST-1, each of the Cu(II) centres of the as-synthesized form of Cu-MOF-74/Cu-CPO-27 also ligates a water molecule. This ligand can be removed by heating the MOF to 250 ° C. Given the high density of open metal sites, coupled with the large variety of metals that can be incorporated (e.g., Zn, Cu, Ni, Co, Mg, Fe), it is not surprising that members of the MOF-74/CPO-27 series are featured in a wide range of investigations of gas storage and/or separation.[19] In fact, the Zn, Ni, Co, and Mg versions have been studied previously for NH$_3$ capture (see Table 1).[20]
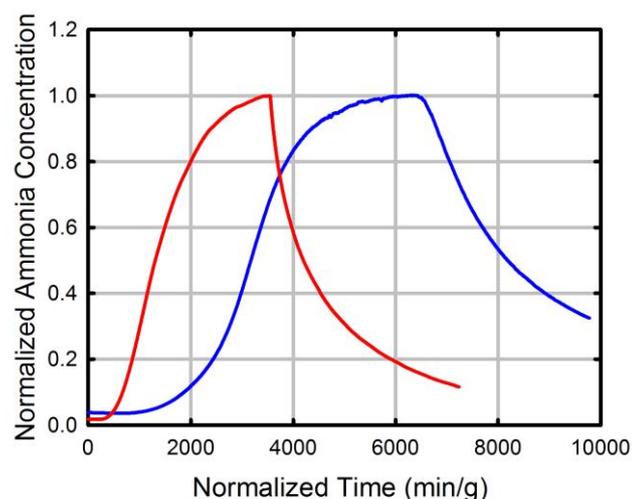

Figure 2: Downstream normalized ammonia concentration as a function of time for Cu-MOF-74 under dry (red curve) and 80 % relative humidity (blue curve).

Experimental

All reagents were purchased and used as received. Cu-MOF-74/Cu-CPO-27 was made according to literature procedures.[21] Surface area characterization was performed at 77 K using a Micromeritics Tristar-II instrument; the observed Brunauer–Emmett–Teller (BET) surface area of 1170 m^2/g was within experimental error of the 1125 m^2/g observed by Calleja et al.[21] Ammonia breakthrough measurements were made with a miniaturized breakthrough apparatus. Approximately 10-15 mg of material was loaded into a nominal 4 mm i.d. fritted glass tube that was subsequently loaded into a water bath for isothermal testing. Prior to testing, samples were dried for one hour at 150 ˚C under a dry air-flow; for "wet" tests they were environmentally equilibrated at 80% relative humidity (RH). A ballast was charged with a predetermined quantity of ammonia and then mixed with a stream of dry (-40°C dew point) or humid (80% RH) air at a rate necessary to achieve a challenge concentration of 2,000 mg/m^3; the total pressure was 1 bar. The stream was then sent through the fritted tube at a flow rate of 20 mL/min, equivalent to a residence time of approximately 0.16 seconds. The effluent stream was sent through a photoionization detector with a 10.6 eV lamp to monitor the ammonia concentration. The corresponding breakthrough curve was integrated to determine the ammonia loading to saturation. A schematic of the apparatus is shown in the Supporting Information (SI; Figure S1). Also in the SI are computed M-NH$_3$ binding energies and M-N bond lengths computed for various M-MOF-74/M-CPO-27 compounds (Figure S2).

Results and Discussions

Figure 2 shows ammonia breakthrough curves for Cu-MOF-74/Cu-CPO-27 under both dry (red) and 80 % relative humidity (blue) conditions.[22] Qualitatively, it can be seen that more ammonia is adsorbed under humid conditions. Quantitatively, we find that Cu-MOF-74/Cu-CPO-27 takes up 3.4 and 7.6 mmol/g of ammonia under 0 and 80 % relative humidity, respectively. Under dry conditions, the adsorption translates to roughly 1 ammonia molecule for every two Cu(II) centres. Given a calculated binding energy of -76 kJ/mol (see SI), the absence of substantially less uptake than one NH$_3$ per Cu(II) centre presumably is due to slow intra-crystalline transport kinetics relative to breakthrough times; similar uptake is observed for Ni-MOF-74/Ni-CPO-27, Zn-MOF-74/Zn-CPO-27 (Table 1).

While the gravimetric uptake and number of ammonia molecules per Cu-centre of Cu-MOF-74/Cu-COP-27 is less than that observed for HKUST-1, the volumetric uptake of 5.9 ammonia/nm^3 at 80 % relative humidity exceeds the 3.9 ammonia/nm^3 observed for HKUST-1 (Table 1). Interestingly, increased relative humidity more than doubles the number of ammonia moieties per Cu(II) centre in Cu-MOF-74 from 0.56 to 1.2.

In volumetric terms, i.e. those most relevant in a gas mask where the weight of the sorbent is negligible in comparison to the weight of the mask, Cu-MOF-74/Cu-CPO-27 outperforms all other MOF materials tested to date at 80% RH as shown in Table 1.[9a,18,20,23,24]

While it would be desirable to determine the origin of the increased affinity for ammonia under humid conditions, post-adsorption powder X-ray diffraction measurements for Cu-MOF-74/Cu-CPO-27 indicate that it loses crystallinity; no such loss in crystallinity is observed for dry Cu-MOF-74/Cu-CPO-27 Peterson et al.[18] observed a similar loss in crystallinity in HKUST-1 after the adsorption of ammonia—a loss that was made worse in the presence of moisture. The loss in structure was attributed to the breaking of Cu-carboxylate bonds, allowing more NH_3 to coordinate to Cu, and forming a presumed ammonium carboxylate salt and a $Cu(OH)_2$ species.[18]

Table 1: Gravimetric, volumetric, and stoichiometric ammonia uptake for various MOFs.

	Gravimetric ammonia uptake (mmol/g)		Volumetric ammonia uptake (NH_3/nm^3)		Uptake Stoichiometry (NH_3/M)	
Relative Humidity	*0 %*	*80 %*	*0 %*	*80 %*	*0 %*	*80 %*
Zn-MOF-74[a]	3.7	2.8	2.9	2.2	0.61	0.46
Cu-MOF-74[b]	*3.4*	*7.6*	*2.6*	*5.9*	*0.56*	*1.2*
Ni-MOF-74[a]	2.3	1.9	1.7	1.4	0.36	0.30
Co-MOF-74[a]	6.7	4.3	5.1	3.3	1.1	0.68
Mg-MOF-74[a]	7.6	1.7	4.5	1.0	0.94	0.21
HKUST-1[c]	6.6	8.9	2.9	3.9	1.3	1.8
IRMOF-3[d]	6.2	-- [g]	2.2	-- [g]	0.46	-- [g]
MIL-100(Fe)[e]	4.3	-- [g]	1.8	-- [g]	-- [g]	-- [g]
DUT-6-(OH)₂[f]	4.7	-- [g]	1.1	-- [g]	-- [g]	-- [g]

[a]As reported;[20]**Error! Bookmark not defined.** [b]This work; [c]as reported;[18]**Error! Bookmark not defined.** [d]as reported;[9a]**Error! Bookmark not defined.**[a] [e]as reported;[23] [f]as reported;[24] [g]data not available. M = metal sites.

Given the loss in structure, attempts to uniquely identify the origin of the increased uptake under humid conditions in Cu-MOF-74/Cu-CPO-27 would likely inadequately reflect the complex nature of the system. However, sorbents that structurally degrade, but that also exhibit high capacities for ammonia, could be of considerable practical interest as active components of single-use filters or abatement systems.

Conclusions

Among MOFs, Cu-MOF-74/Cu-CPO-27 has one of the highest densities of Cu(II) sites per unit volume. Under humid conditions, Cu-MOF-74/Cu-CPO-27 demonstrates the highest volumetric ammonia uptake of any MOF reported to date. Although the MOF shows a loss of crystallinity upon adsorption under humid conditions, for applications in exposure abatement the capacity is more important than the lack of recyclability.

Acknowledgments

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ARTICLE

Table of Content Graphic

The MOF Cu-MOF-74/Cu-CPO-27 was identified as a candidate for high-volumetric ammonia uptake due to the high density of Cu sites.