Microporous and Mesoporous Materials 156 (2012) 115–120

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Adsorptive capturing and storing greenhouse gases such as sulfur hexafluoride and carbon tetrafluoride using metal–organic frameworks

Irena Senkovska [a,*], Elisa Barea [b], Jorge Andrés Rodríguez Navarro [b], Stefan Kaskel [a]

[a] *Department of Inorganic Chemistry, Technical University of Dresden, Germany*
[b] *Departamento de Química Inorgánica, Universidad de Granada, Granada, Spain*

ARTICLE INFO

Article history:
Received 19 October 2011
Received in revised form 7 February 2012
Accepted 13 February 2012
Available online 25 February 2012

Keywords:
Metal–organic frameworks
High pressure adsorption
Sulfur hexafluoride
Carbon tetrafluoride
Greenhouse gas

ABSTRACT

High pressure excess adsorption isotherms of sulfur hexafluoride (SF_6) and tetrafluoromethane (CF_4) on metal–organic frameworks $Cu_3(btc)_2$ (HKUST-1, btc – benzene-1,3,5-tricarboxylate), $Fe_3FO(H_2O)_2(btc)_3$ (MIL-100), $Cr_3F(H_2O)_2O(1,4\text{-bdc})_3$ (MIL-101, 1,4-bdc – 1,4-benzenedicarboxylate), $Co_2(1,4\text{-bdc})_2(dabco)$ (dabco-1,4-diazabicyclo[2.2.2]octane), $Ni_2(2,6\text{-ndc})_2(dabco)$ (DUT-8, 2,6-ndc – 2,6-naphthalenedicarboxylate), $Ni_2O_5(btb)_2$ (DUT-9, btb – benzene-1,3,5-tribenzoate), $Zn_4O(btb)$, and ($Zn_4O(dmcpz)_3$) (dmcpz – 3,5-dimethyl-4-carboxypyrazolato) at 298 K were investigated using volumetric methods. Up to 1 bar pressure (at 298 K), microporous MOF with open metal sites HKUST-1 shows the best performance in SF_6 adsorption and microporous $Zn_4O(dmcpz)_3$ in CF_4 adsorption. At high pressure, mesoporous MIL-101 and DUT-9 have the highest storage capacities for both gases among the MOFs investigated.

1. Introduction

Sulfur hexafluoride (SF_6) represents the best insulating gas available in the electrical industry, with excellent dielectric and arc-quenching properties. It is also used in several other applications, including thermo-acoustic insulator for windows, and as a contrast agent in medical applications. SF_6 plasma is also used in the semiconductor industry as an etchant, etc. Tetrafluoromethane (CF_4) is used in the semiconductor industry for cleaning of processing chamber, for dry etching and for chemical vapor deposition process. However, the extremely stable nature of the SF_6 and CF_4 molecules with lifetimes in the atmosphere of 3200 or 50,000 years, respectively, together with their high efficiency as infrared absorbers make them to the very powerful greenhouse gases (so called high global warming potential gases (high GWPs)). CF_4 or SF_6 are respectively 6500 or 22800 times more potent than CO_2 in terms of their capabilities to trap heat in the atmosphere over a hundred year period [1].

Hence, efficient methods are needed for handling, recovering, and storing such gases after industrial use. Several methods were proposed for separation, including pressure swing adsorption (PSA), membrane separation and temperature swing adsorption (TSA) [2–4]. All mentioned methods involve the use of porous material. However, the different requirements should be fulfilled by adsorbent for different techniques; amongst others, the adsorption behavior at different pressures in crucial. Several theoretical calculation and practical studies of CF_4 or SF_6 adsorption have been carried out on different porous materials such as pillared clays [5], zeolites [6–9], microporous carbons [10–12], carbon nanotubes [13,14] and metal–organic capsules [15] up to now. Metal–organic frameworks (MOFs) represent a new class of hybrid materials built up from metal clusters and organic linkers. The well defined pore size and wide pore size variety make MOFs very attractive adsorbents [16,17]. Additionally, these materials hold records in terms of specific surface areas and pore volumes, and have shown a huge potential, amongst others for gas storage applications, including SF_6 and CF_4 [18,19].

In this study we investigated the CF_4 or SF_6 adsorption capability of several representative MOFs.

HKUST-1 or $Cu_3(btc)_2$ [20] (btc – benzene-1,3,5-tricarboxylate) was chosen because it is one of the most frequently investigated MOFs so far, showing interesting properties in hydrogen, methane and carbon dioxide storage, gas separation, and catalysis. HKUST-1 has a trimodal pore size distribution. The larger and more hydrophilic type of pores consists of cages built up of 12 $Cu_2(COO)_4$ paddle wheel secondary building units with copper open metal sites pointing inside the cavity. These pores have a diameter of approximately 13.5 Å (Fig. 1a). The second pore type has a diameter about 11 Å. The third type of pores is smaller, with 5 Å in

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[*] Corresponding author. Address: Department of Inorganic Chemistry, Technical University of Dresden, Bergstr. 66, D-01062 Dresden, Germany. Tel.: +49 351 46332564; fax: +49 351 46337287.

E-mail address: irena.senkovska@chemie.tu-dresden.de (I. Senkovska).

1387-1811/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2012.02.021

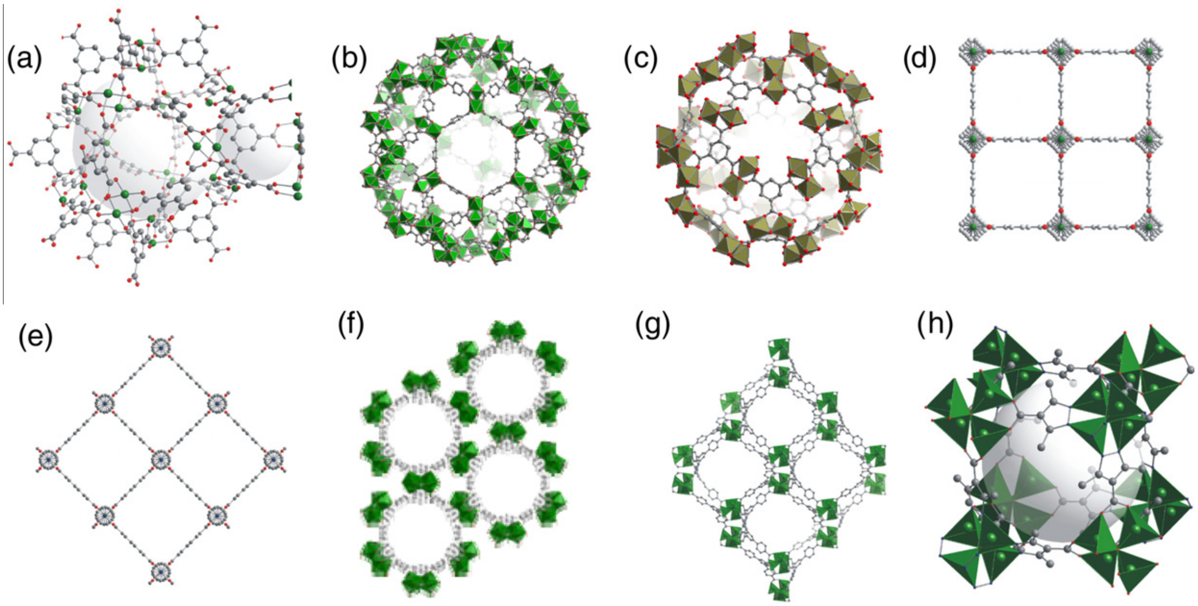

Fig. 1. Crystal structures of investigated MOFs: (a) $Cu_3(btc)_2$, (b) MIL-101(Cr), (c) MIL-100(Fe), (d) $Co_2(1,4\text{-bdc})_2(dabco)$, (e) DUT-8, (f) DUT-9, (g) $Zn_4(btb)_2$, and (h) $Zn_4O(dmcpz)_3$.

diameter. The second and third pore types are less hydrophilic as the pore interior is fenced by the organic linkers. HKUST-1 has a moderate stability at high humidity level [21].

MIL-101 or $Cr_3F(H_2O)_2O(1,4\text{-bdc})_3$ [22] (MIL – Matérial Institut Lavoisier) is a zeolitic, water stable [21,23] mesoporous chromium terephthalate. The structure is composed of supertetrahedra (ST) as building blocks forming two types of mesoporous cages of 29 and 34 Å in diameter (Fig. 1b). The ST themselves have a microporous character with a pore size of 8.7 Å and consist of three chromium trimers connected through the terephthalate linkers. The specific pore volume exceeds 2.02 $cm^3\ g^{-1}$. Due to the high inner surface area and the mesoporous character, MIL-101 is a good candidate for various applications, including high pressure gas adsorption.

MIL-100(Fe) or $Fe_3FO(H_2O)_2(btc)_2$ [24] is a water stable [21,25] mesoporous iron(III)trimesate. Like MIL-101 it has two types of mesopores with cages of 25 and 29 Å in diameter (Fig. 1c). These cages are also formed by ST, constructed from iron trimers linked by the tricarboxylate linkers. Here, the pore diameter of the ST is slightly smaller than in MIL-101 with 6.6 Å in diameter. Nitrogen physisorption measurements revealed a total specific pore volume of 0.9 $cm^3\ g^{-1}$. The iron compound should be more suitable for industrial use than copper or chromium based MOFs regarding toxicity.

$Co_2(1,4\text{-bdc})_2(dabco)$ [26] framework is composed of binuclear Co_2-units with a paddle wheel structure, bridged by the 1,4-benzenedicarboxylate (1,4-bdc) di-anions to form a distorted 2D square-grid $[Co_2(1,4\text{-bdc})_2]$ layers. The axial sites of the Co_2-paddle wheels are coordinated by nitrogen atoms from the 1,4-diazabicyclo[2.2.2]octane (dabco) ligand (so called pillar ligand) connecting the 2D layers into a 3D structure. The overall topology can be described as a primitive cubic net (**pcu**). The channels of 7.6 × 7.6 Å in diameter (Fig. 1d) are interconnected by the smaller channels approximately 5.1 × 3.7 Å in size. The networks of such pillar layered MOFs often show flexible behavior [27,28].

DUT-8 [29,30] (DUT – Dresden University of Technology, $Ni_2(2,6\text{-ndc})_2(dabco)$) is a 3D structure with a primitive cubic net topology (**pcu**) similar to $Co_2(1,4\text{-bdc})_2(dabco)$. Two types of channels are present in the structure: 9.6 × 9.6 Å (Fig. 1e) and 2.5 × 7.4 Å (taking the van der Waals radii of the carbon atoms into account). The specific feature of DUT-8(Ni) is the structural transformation observed by gas adsorption and pronounced pore opening and "gate pressure" effect for N_2 (at 77 K up to 1 bar), *n*-butane (at 298 K) and CO_2 (at 298 K up to 50 bar).

DUT-9 [31] $Ni_5O_2(btb)_2$ (btb – benzene-1,3,5-tribenzoate), is a mesoporous MOF developed in our group. The structure contains $Ni_5O_2(CO_2)_6$ clusters, linked *via* btb linkers into a 3D network. Two different types of pores are present in the structure of DUT-9: a smaller one approximately 13 Å in diameter and a larger one with a diameter of approximately 25 Å. Both are arranged in an alternating fashion giving rise to hexagonal channels throughout the whole crystal structure (Fig. 1f). The specific pore volume calculated from the nitrogen adsorption isotherm is 1.77 $cm^3\ g^{-1}$ (Fig. S1f).

$Zn_4O(btb)_2(H_2O)_{3.5}(DMF)_{0.5}$ includes $Zn_4O(COO)_6$ clusters as SBU (similar to MOF-5) connected by btb linkers into an extended three dimensional framework with anatas (**ant**) topology. In spite of two interpenetrating nets presented in the structure, the pores of approximately 14 Å are available (Fig. 1g). The crystal structure of the compound was described by Caskey et al. [32], but no information about the porosity of the MOF has been reported. Using the supercritical CO_2 drying (SCD), we obtained a microporous material with total pore volume of 0.9 $cm^3\ g^{-1}$ (Fig. S1g).

Unfortunately, the compounds $Co_2(1,4\text{-bdc})_2(dabco)$, [22] DUT-8, DUT-9, and $Zn_4O(btb)_2$ are water sensitive and should be handled under dry atmosphere.

Finally, a hydrophobic MOF, Zn_4O(3,5-dimethyl-4-carboxypyrazolato)$_3$ ($Zn_4O(dmcpz)_3$) [33] has the structure motive of MOF-5 (primitive cubic net topology (**pcu**)) (Fig. 1h), but in opposite to MOF-5, this material exhibits remarkable thermal, mechanical, and chemical (amongst others hydrothermal) stability. The compound has pores with diameter of approximately 6.5 Å which are accessible through the 4.0 × 4.0 Å windows.

2. Experimental

2.1. Materials preparation

All chemicals were used as received without further purification. H_3btb (benzene-1,3,5-tribenzoic acid) was prepared according to a procedure described in the literature [34,35]. *N*,*N*-dimethylformamide (DMF) and *N*,*N*-diethylformamide (DEF) were