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CH_4 storage and CO_2 capture in highly porous zirconium oxide based metal–organic frameworks†‡

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Received 2nd July 2012, Accepted 14th August 2012
DOI: 10.1039/c2cc34714h

A series of porous Zr oxoclusters-based MOFs was computationally explored for their gas storage/capture performances. The highly porous UiO-67(Zr) and UiO-68(Zr) solids show exceptionally high CH_4 and CO_2 adsorption capacities under operating conditions that make these thermal, water and mechanical resistant materials very promising for physisorption-based processes.

The anthropogenic emission of CO_2 from fossil fuel burning in power plants and automobile transport is a growing environmental and economic issue. CH_4 is another strategic gas of considerable interest. Apart from its negative greenhouse effect, this latter species, which is the main component of the natural gas, is also considered as a cleaner energy carrier than petroleum oil because of its higher hydrogen-to-carbon ratio and a resulting much lower carbon emission.[1] Indeed, the search for safe and high-capacity CH_4 storage and CO_2 capture systems has been a long-standing challenge that has triggered tremendous studies with the aim to improve the existing related technologies. It is well established that the physisorption-based processes involving porous solids offer an efficient storage/capture alternative with the ability to release the adsorbed gases easily.[2] Among this class of materials, porous metal–organic frameworks (MOFs) have attracted substantial attention during the past decades in the field of gas adsorption/separation both experimentally[3] and theoretically.[4] Such an intriguing family of coordination materials corresponds to crystalline hybrid media built up from inorganic metal-ion subunits connected by polytopic organic ligands. Through a judicious choice of these organic and inorganic moieties, many MOFs were designed with ultra-high porosity, including MIL-101,[5a] MOF-177,[5b] MOF-205,[3a] PCN-14,[5c] UMCM-2,[5d] that have further shown high CO_2 and/or CH_4 uptakes.[3a,5c,6] However, the majority of these promising materials suffers either from a relatively poor stability under humidity or would require a high energy cost for regeneration that are both severe drawbacks for practical applications.[3c,d] Indeed, tailoring more stable, chemically-resistant MOF frameworks combined with high adsorption performance is still nowadays a great challenge for the MOF community.

Here, we focus on an emerging class of zirconium-based MOFs derived from the UiO-66(Zr) topology. This isoreticular series includes the existing UiO-67(Zr),[7a] UiO-68(Zr)[7a] and Zr-AzoBDC[7b] solids where 4,4′-BPDC, TPDC and AzoBDC ligands substitute the parent BDC organic node of UiO-66(Zr), respectively, that are completed by a newly synthesized Zr-MOF involving Cl_2AzoBDC as a linker (Fig. 1). The hydroxylated forms of these analogue materials are built up from the inorganic block Zr_6-octahedra $[Zr_6O_4(OH)_4]$ bounded to twelve organic linkers, leading to a three dimensional periodic structure in which each centric octahedral cage (Fig. 1a) is connected to eight corner tetrahedral cages (Fig. 1b) through triangular windows. The parent UiO-66(Zr) has been recently shown to be stable up to 450 °C under air, unaltered upon water adsorption[8a] and mechanical pressure,[7a] easily regenerable[8a,b] and selective for the CO_2–CH_4 mixture with a high working capacity.[8c] The four other analogues are also porous MOFs (see the structural features provided in Table S3 in the ESI‡). The solvothermal synthesis of the UiO-67(Zr), Zr_6-AzoBDC and its 3,3′,4,4′-Cl_2AzoBDC functionalized analogue have been carried

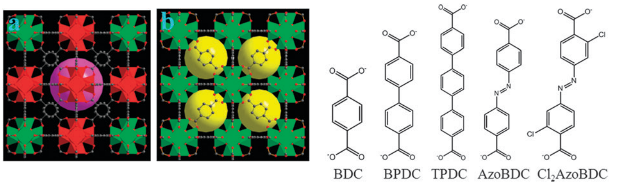

Fig. 1 Illustration of the Zr-MOFs crystalline structure: (a) octahedral cage, (b) tetrahedral cages. H atoms were omitted for clarity. The large spheres represent the void regions inside the cages (Zr polyhedra: red for octahedral cage, green for tetrahedral cages; C, gray; O, red). The extended organic linkers are also presented.

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† This article is part of the ChemComm 'Metal-organic frameworks' web themed issue.

‡ Electronic supplementary information (ESI) available: Details of experiments and molecular simulations. CCDC 889529–889533. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc34714h

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out and the resulting solids activated and characterized. As a further step, their thermal, water and mechanical stabilities have been assessed (see ESI‡), revealing that this class of solids is stable up to 450 °C, in water at room temperature overnight and exhibits a fair mechanical stability upon application of uniaxial pressure.

In light of such favourable porosities and properties, a step further consisted of exploring *via* a predictive approach the adsorption capacities of this extended series of Zr-MOFs for CH_4 and CO_2 under industrially relevant conditions. This modelling effort is based on a preliminary computational assisted structure determination strategy conducted in tandem with X-ray powder diffraction (XRPD) experiments to propose plausible structure candidates for each investigated Zr-MOF. Indeed, starting with the parent UiO-66(Zr), the crystallographic structure for each Zr-MOF analogue was first built using a ligand replacement strategy[9] based on the unit cell parameters deduced from XRPD experiments. The resulting structures were further refined using a density functional theory (DFT) geometry optimization procedure (details of the computational methodology are described in the ESI‡). The geometry optimized structures and their corresponding structural features are provided in Fig. S8 and Table S3 (see ESI‡). The theoretical accessible surface areas and pore volumes vary from 1020 to 4240 $m^2\ g^{-1}$ (0.45 $cm^3\ g^{-1}$ to 1.82 $cm^3\ g^{-1}$) when one goes from UiO-66(Zr) to UiO-68(Zr) and further decrease for Zr_6-AzoBDC (3640 $m^2\ g^{-1}$ and 1.38 $cm^3\ g^{-1}$) and Zr_6-Cl_2AzoBDC (2885 $m^2\ g^{-1}$ and 1.13 $cm^3\ g^{-1}$). Except from the parent UiO-66(Zr) where a very good agreement is obtained between the experimental and predicted geometric features, some discrepancy can be noticed for the other solids (see ESI‡) mainly due to the presence of residual Zr oxide and/or incomplete activation of the sample. This observation strongly suggests that the *optimal* adsorption performances of these Zr-MOFs can be only achieved *via* a computational approach. This information will further orientate the synthesis effort to be deployed for optimizing the activation procedure of the most promising solids.

Grand Canonical Monte Carlo simulations (see ESI‡) were performed to predict the *optimal* adsorption uptakes for CH_4 and CO_2 in this series of Zr-MOFs for a wide range of pressure at 303 K. For gas uptake and delivery purpose, the total adsorbed amount is a more relevant quantity compared to the excess one.[4b] Further from an application standpoint, it is more meaningful to express the adsorption uptakes of different materials in terms of volume than mass as the densities of the adsorbents vary.[10] For this reason, the adsorbed amounts were converted into cm^3 (STP) cm^{-3} (STP defined by IUPAC: 1 bar and 273 K) using the crystallographic density of each MOF. Primarily, UiO-66(Zr) was selected as a model material since its experimental and simulated geometric features concur very well (see Table S1, ESI‡).

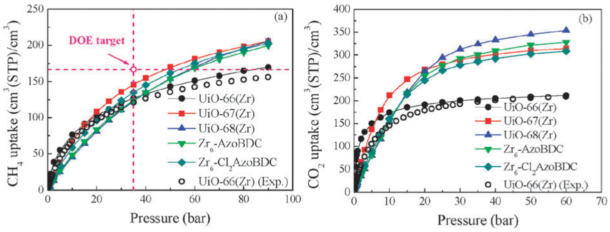

Fig. 2 Simulated adsorption isotherms for (a) CH_4 and (b) CO_2 in the five Zr-MOFs at 303 K. The experimental data are also provided for UiO-66(Zr) as a comparison.

Fig. 2 shows a very good agreement between the adsorption isotherms simulated for this material and the corresponding experimental data obtained by gravimetry measurements (see ESI‡). Such a validation step allowed us to confidently carry out further explorations for the whole series of Zr-MOFs. Fig. 2 thus also reports the absolute adsorption isotherms for CH_4 and CO_2 in the remaining four Zr-MOFs. Table 1 summarizes the predicted adsorption capacities at the pressures considered in practical applications (CH_4: 35 bar,[5c] CO_2: 40 bar[4b]) that are compared with the performances of other adsorbents including MOFs, activated carbons and zeolites. As indicated in this table, among these Zr-MOFs, UiO-67(Zr) shows the highest storage capacity for CH_4 (146 cm^3 (STP) cm^{-3}) at 35 bar. It should be noted that the target set by the U.S. department of Energy (DOE) for such an application is 180 cm^3 (STP') cm^{-3} where STP' denotes 1 bar and 298 K.[11] To match the current IUPAC definition used in this work, this objective corresponds to a value of 167 cm^3 (STP) cm^{-3}.[11a] Together with the results shown in Fig. 2, one can argue that the storage capacities of both UiO-67(Zr) and Zr_6-Cl_2AzoBDC are only slightly below the DOE requirement. Further, Table 1 emphasizes that UiO-67(Zr) outperforms most of the well-known MOFs reported so far except the Cu(II)-paddlewheel based Cu-BTC, UTSA-20 and PCN-14, and the CPO-27(Ni) containing Ni(II) coordinatively unsaturated sites (cus).

Indeed, while these three last MOFs show the best performances, their structures are known to be dramatically altered upon water adsorption[3c,12] in contrast to what have been demonstrated

Table 1 Adsorption uptakes for CH_4 (35 bar)–CO_2 (40 bar) and working capacity predicted in the Zr-MOFs at ambient temperature *vs.* the values in other adsorbents including MOFs, zeolites and activated carbons

		$V_{\text{adsorption uptake}}$ (cm^3 (STP) cm^{-3})		$V_{\text{working capacity}}{}^{a}$ (cm^3 (STP) cm^{-3})	
Materials	*T*/K	CH_4	CO_2	CH_4	CO_2
UiO-66(Zr)	303	127	205	105	116
UiO-67(Zr)	303	146	301	138	266
UiO-68(Zr)	303	123	333	118	313
Zr_6-AzoBDC	303	124	223	122	209
Zr_6-Cl_2AzoBDC	303	135	293	127	267
Mesoporous MOFs					
MIL-101(Cr)[6a]	303	103	340	64	197
MOF-200[3a]	298	61	267	59	263
MOF-205[3a]	298	114	310	111	305
UMCM-2	303	128	357	123	346
PCN-68[14a]	298	117	281	112	264
NU-100[4b]	298	—	327	—	310
Microporous MOFs					
MOF-5[3a,6b]	298	126	326/293	124	312/283
MOF-177[3a,6b]	298	124	357/332	122	349/328
MIL-47(V)[14b,e]	303	145	250[b]	132	214
Cu-BTC[14c]	298	180	278	153	200
PCN-14[5c]	290	230	—	210	—
CPO-27(Ni)[14d]	298	214	331	160	142
UTSA-20[14f]	300	195	323[c]	173	226
Other conventional adsorbents					
AC Maxsorb[13a]	298	74	166	64	147
Zeolite 13X[13b]	298	128	185[d]	112	69

[a] Calculated from the difference of the adsorption amounts adsorbed in MOFs at 1 and 10 bar for CH_4 and at 1 and 40 bar for CO_2. [b] Measured at 20 bar. [c] Measured at 35 bar. [d] Measured at 32 bar.

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above for UiO-67(Zr). In addition, this Zr-MOF shows a storage capacity for CH_4 which is much higher than other conventional adsorbents such as the activated carbon (AC) Maxsorb[13a] and the zeolite 13X,[13b] thus UiO-67(Zr) is particularly promising for such an application.

The situation slightly differs for the CO_2 capture with UiO-68(Zr) showing the highest adsorption capacity (333 cm^3 (STP) cm^{-3}) among these five Zr-MOFs which considerably exceeds the performances of the usual AC and zeolites as emphasized in Table 1. Such an exceptionally high adsorption uptake has been reported in other existing MOFs. However, some of them suffer from severe drawbacks such as the Zn(II)-based solids like MOF-5, MOF-177, MOF-205 and UMCM-2 for which the structures built up from a Zn-dicarboxylate connectivity undergo a complete loss of crystallinity after exposure to moisture that would considerably limit their industrial uses. This restriction should also hold true for the NU-100 and UTSA-20 due to their structural analogies to Cu-BTC in terms of the secondary building units (SBU). Further, in practical applications, the working capacity, defined as the difference in the capacities between the adsorption and desorption (1 bar was chosen here) pressures, is another crucial criteria for evaluating the performance of a porous material for CO_2 gas capture as the higher the working capacity the higher the productivity.[10] As shown in Table 1, the resulting working capacity for UiO-68(Zr) is very high and remains similar to its adsorption uptake (313 *vs.* 333 cm^3 (STP) cm^{-3}). Such a behavior which is consistent with an adequate non-rectangular shape of the corresponding CO_2 adsorption isotherm[10] (Fig. 2) deviates from those obtained for another class of competitive hybrid materials, *i.e.* the cus containing MOFs, for CO_2 capture as for instance the CPO-27(Ni) and the water-resistant MIL-101(Cr) which show working capacities that are drastically decreased by $\sim$57% and 42%, respectively, compared to their uptakes. These lower working capacities are related to the more sudden increase of the adsorption isotherms in the domain of low pressure, in line with much higher CO_2 adsorption enthalpies for both MIL-101(Cr) (-45 kJ mol^{-1})[6a] and CPO-27(Ni) (-40 kJ mol^{-1})[14d] *vs.* the value simulated here for UiO-68(Zr) (-20 kJ mol^{-1}) (see ESI[‡]). This result also suggests that this Zr-MOF can be potentially regenerated without requiring costly operating conditions.

In conclusion, the MOF-type UiO-67(Zr) and UiO-68(Zr) with ultra-high porosity are predicted to be very promising materials for the CH_4 storage and CO_2 capture respectively. Beyond their exceptionally high adsorption uptakes at pressures considered in practical applications, these materials show very good working capacities and involve medium ranged CO_2 adsorption enthalpy values suggesting a potential regenerability under mild conditions. Further, it has been experimentally established that these Zr-oxides MOFs show high thermal, fair mechanical and water stabilities; however their geometric features are still below the theoretical ones. This latter observation suggests that an effort for optimizing the activation protocol of such materials *via* for instance a modulator approach[15] deserves to be deployed in order to attain the predicted outstanding performances prior to pave the way for their uses in physisorption based processes.

The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2007–2013) under grant agreement no. 228862. The financial support of the Beijing Nova (2008B15), "Hubert Curien Cai Yuanpei" (24038XC) programs and Natural Science Foundation (21136001) is also greatly appreciated.

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