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Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide

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Abstract Three different porous metal organic framework (MOF) materials have been prepared with and without uncoordinated amine functionalities inside the pores. The materials have been characterized and tested as adsorbents for carbon dioxide. At 298 K the materials adsorb significant amount of carbon dioxide, the amine functionalised adsorbents having the highest CO_2 adsorption capacities, the best adsorbing around 14 wt% CO_2 at 1.0 atm CO_2 pressure. At 25 atm CO_2 pressure, up to 60 wt% CO_2 can be adsorbed. At high pressures the CO_2 uptake is mostly dependent on the available surface area and pore volume of the material in question. For one of the iso-structural MOF pairs the introduction of amine functionality increases the differential adsorption enthalpy (from isosteric method) from 30 to around 50 kJ/mole at low CO_2 pressures, while the adsorption enthalpies reach the same level at increase pressures. The high pressure experimental results indicate that MOF based solid adsorbents can have a potential for use in pressure swing adsorption of carbon dioxide at elevated pressures.

Keywords Metal organic frameworks · Amine functionality · Carbon dioxide · Adsorption

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1 Introduction

At present, CO_2 is separated from low pressure flue gases or from high pressure natural gas by using a liquid or solution as absorbent (Nunge and Gill 1963). The process typically works in the temperature interval between 313 K (absorption) and 393 K (desorption). Main drawbacks of the solvent based absorption processes are high energy requirements and possible environmental issues due to loss of alkanolamine as a consequence of its high volatility. Separation processes based on solid sorbents might be an alternative, and during the last decade a number of silica, zeolite, carbon and polymer based sorbents have been developed (Leal et al. 1995; Xu et al. 2002; Kim et al. 2005; Harlick and Sayari 2006; Huang et al. 2003; Delaney et al. 2002; Zheng et al. 2005; Hiyoshi et al. 2005; Khatri et al. 2005; Chang et al. 2003; Siriwardane et al. 2001; Harlick and Tezel 2004; Satyapal et al. 2001). However, a main drawback of many of these is their relatively limited surface areas, their limitation in structural design, and the limited possibility for surface modification.

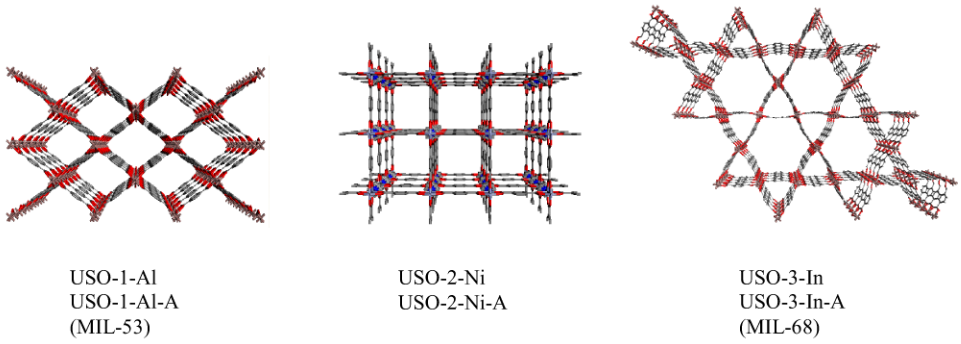
Metal organic frameworks (MOFs, also called coordination polymers) are a relatively new class of porous materials with high diversity. Such materials are built up by metal atoms (ions) linked together by multifunctional organic ligands. The high diversity is a consequence of the linkage between the inorganic and organic chemistry where the whole substitution chemistry of organic synthesis can be coupled with the inorganic elemental and cluster chemistry. During the 1990s the field has developed on the academic level (Hagrman et al. 1999; Batten and Robson 1998; Zaworotko 2000; James 2003; Kitagawa et al. 2004). During the last years couple of years MOF materials has been tested for applications such as gas storage (Noro et al. 2000;

Rowsell and Yaghi 2005; Millward and Yaghi 2005), catalysis (Mueller et al. 2006; Dai 2004; Ohmori and Fujita 2004; Gómez-Lor et al. 2005), enantiomeric separation (Seo et al. 2000), and gas separation (Uemura et al. 2005). The wide structural diversity of MOFs makes it possible to construct materials with extreme surface areas (Chae et al. 2004) and to tailor the material properties and thus its affinity towards specific gas molecules (Uemura et al. 2005; Fletcher et al. 2005; Sudik et al. 2005; Bourrelly et al. 2005; Ramsahye et al. 2007). Consequently, it should be possible to develop large capacity and high selectivity MOF based sorbents.

MOF synthesis is in most cases carried out using a solvent, and as synthesised, the pores of the MOF is filled with solvent molecules. Since the MOFs are to be used for removal of carbon dioxide from a gas stream, it is of importance that the porous structure is maintained when the solvent molecules are removed upon heating. This is certainly not always the case, so special care must be taken to assure that the structure does not collapse. The thermal stability of MOF materials is expected to be lower that of Zeolites and zeolite analogues. The main reason for this is lower metal-linker binding energies as compared to the strong Si–O and Al–O bonds in the Zeolites. Nevertheless, many MOF materials show relatively high thermal stabilities, and decomposition often occurs at temperatures above 573 K which is sufficient for the present application.

We have prepared three different highly porous MOF structures shown in Scheme 1. The three different structures have each been prepared in two versions with and without amine substituents on the organic linker. This has been done in order to analyse the effect of such functionalities upon sorption behaviour. The adsorption capacities for carbon dioxide have been measured from vacuum to 25 atm CO_2 pressure. The results will be discussed from the perspective of the material properties such as amine functionality, specific surface area and pore volume. The results obtained for the MOFs will be compared to other solid adsorbents such as amine-grafted silicas.

Scheme 1

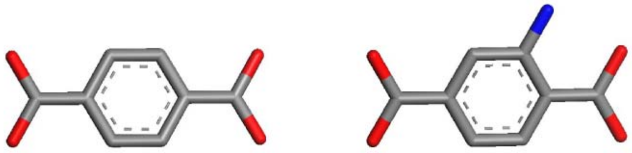


2 Experimental

2.1 Adsorbent synthesis

All materials were prepared using either 1,4-benzenedicarboxylic acid (1,4-bdc) or 1,4-bdc having one amine substituent; 1,4-dicarboxylic-2-amino-benzene, as shown in Scheme 2.

USO-1-Al (Al(OH)(1.4-bdc)·0.8DEF) and USO-1-Al-A (amine functionalised) were prepared in a similar manner as described by (Loiseau et al. 2004) using the following modifications: A mixture of 10 ml diethylformamide (DEF) and 2 ml ethanol was used as solvent. 1,4-benzene dicarboxylic acid (1,4-bdc) (1.00 mmol) and $AlCl_3 \cdot 6H_2O$ (1.5 mmol) was added and the reaction was carried out at 383 K for 24 hours. USO-2-Ni ($Ni_2(1.4\text{-}bdc)_2(dabco)\cdot 4DMF\cdot 0.5H_2O$) and USO-2-Ni-A (amine functionalised) were prepared is a similar manner as the Zn analogue described by (Dybtsev 2004) with the following modifications: 1,4-bdc (1.00 mmol), 1,4-diazabicyclo[2.2.2] octane (DABCO) (0.83 mmol) and $Ni(NO_3)_2 \cdot 6H_2O$ (1.00 mmol) was added to 20 ml dimethylformamide (DMF) in a Teflon lined autoclave. The mixture was heated to 383 K for 24 hours. USO-3-In (In(OH)(1.4-bdc)·1.25DEF) and USO-3-In-A (amine functionalised) were prepared in a similar manner as described by (Barthelet et al. 2004) using the following modifications: A mixture of 4 ml DEF and 8 ml ethanol was used as solvent. 1.4-bdc (1.50 mmol) and $In(NO_3)_3 \cdot H_2O$ (0.75 mmol) was added and the reaction was carried out at 383 K for 24 hours. All materials were characterized by thermogravimetric analysis (TG) and powder X-ray diffraction. Full characterization details will by published elsewhere (Kongshaug and Fjellvåg 2008).



Scheme 2

For comparison, we also prepared an aminosilyl grafted MCM-41 material as follows: MCM-41 was prepared as described by (Beck et al. 1992; Kresge et al. 1992). The as synthesized material was calcined at 813 K overnight in air to remove rests of template. When cooling down to ambient temperature the gas was switched to pure nitrogen and the material was kept inert during the following reaction steps. The measured specific surface area of the calcined MCM-41 was 1300 m^2/g. 1.0 g of MCM-41 was transferred to a Schleck tube containing a magnetic stirrer. 20 ml toluene was added, then 1.0 ml $(EtO)_3Si(CH_2)_3NH_2$. The slurry was refluxed (393 K) overnight. The solid was filtrated and washed two times with 20 ml portions of pentane. Then the powder was dried under vacuum for two hours yielding the adsorbent called MCM-41-NH_2.

2.2 Testing of adsorption

Low pressure isotherms were recorded by using a Quantachrome Autosorb-1 instrument. Specific surface area and pore volume measurements were carried out by using nitrogen at 77 K using liquid nitrogen as coolant, while carbon dioxide isotherms were collected at 298 K. Estimates of differential adsorption enthalpy using the isosteric method isotherms collected at 303 K and 323 K were obtained by using a thermostatted bath. The MOF samples were pretreated under high vacuum at 423 K for two hours prior to the adsorption experiments. Specific surface areas were derived using the BET method, while micropore volumes were estimated from t-plots and Estimates on the differential enthalpies of adsorption were calculated by using the isosteric method (Rouquerol et al. 1999). High pressure isotherms were recorded using an in-house built instrument described by (Blom et al. 2004).

2.3 Computational details

Quantum chemical calculations were carried out using the Gaussian 03 suite of programs (Frisch et al. 2004). The hybrid functional B3LYP was used in conjunction with 6-31G(s,p) basis sets.

3 Results and discussion

The metal organic frameworks, USO-1-Al, USO-2-Ni and USO-3-In and their amine functionalised analogues, all form stable, microporous three dimensional structures. The structures are shown schematically in Scheme 1 while the specific surface areas and pore volumes are given in Table 1. USO-1-Al and USO-3-In have one-dimensional pores, while USO-2-Ni has a three dimensional pore system. The effective pore sizes are around 8 Å for USO-1-Al, 10 Å for USO-2-Ni, while the large pores in USO-3-In are 7 Å. Based on simple Van-der-Waals considerations we find that the smallest pores in USO-3-In are inaccessible for both N_2 and CO_2.

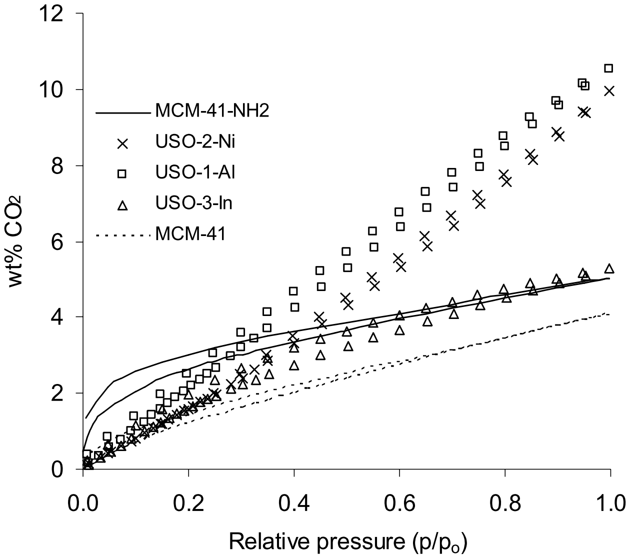


Fig. 1 CO_2 isotherms from vacuum to 1 atm pressure at 298 K for three MOFs and silylamin grafted MCM-41 (MCM-41-NH_2). Both adsorption and desorption curves are shown ($p_0 = 1.0$ atm)

Solid adsorbents for carbon dioxide removal have to a large degree been based on porous silicas such as MCM-41 or SBA-15 materials having aminosilane groups grafted to the pore surface. Such materials having mono-amine surface groups typically have carbon dioxide capacities in the range 3 to 9 wt% at 1 atm CO_2. (Knowles et al. 2005a, 2005b). Their DTA study show that the adsorption enthalpy of CO_2 increases from around 35 kJ/mole for unfunctionalized MCM-41 to around 52–56 kJ/mole with amine functionalities. Figure 1 shows the CO_2 isotherms measured for our base case MCM-41-NH_2 material together with the three unfunctionalised MOFs and unfunctionalised MCM-41. MCM-41-NH_2 clearly show better adsorption properties as compared to the amine free MCM-41, especially at low pressures where the curve shape of the MCM-41-NH_2 indicate significantly stronger adsorption energy. The amount of carbon dioxide adsorbed at atmospheric pressure of CO_2 for the MCM-41-NH_2 material is around 5 wt%, typical for this class of materials, while the capacity of the best unfunctionalised MOF materials exceeds this at least with a factor of two.

In order to resemble the amine grafted silica adsorbents we chose to prepare MOFs having uncoordinated amine substituents by using a amine functionalised 1,4-bdc linker in the MOF synthesis. Powder X-ray diffraction showed that the amine functionalised MOFs USO-1-Al-A, USO-2-Ni-A and USO-3-In-A are isostructural (not considering the amine substituents) to their non-functionalised analogues.

Table 1 Specific surface areas (SSA) and pore volumes (PV) derived by nitrogen adsorption measurements at 77 K using BET and t-plot methods, respectively

	USO-1-Al	USO-1-Al-A	USO-2-Ni	USO-2-Ni-A	USO-3-In	USO-3-In-A
SSA (m^2/g)	1300	960	1925	1530	930	16
PV (ml/g)	0.42	0.25	0.74	0.50	0.34	na[a]

[a] na = not applicable

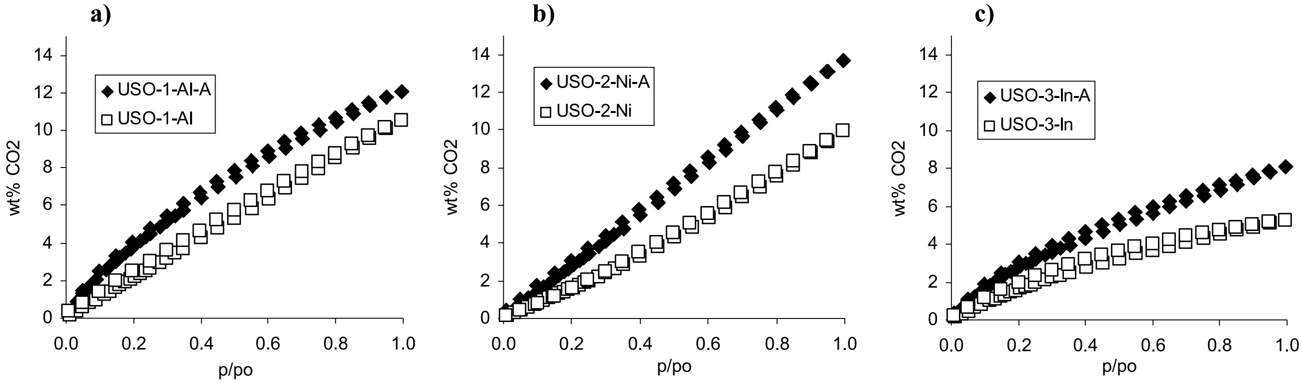


Fig. 2 CO_2 adsorption and desorption isotherms of amine functionalised and theirs analogous non-functionalised MOFs at 298 K. Both adsorption and desorption curves are shown ($p_0 = 1.0$ atm)

However, the crystalinity of the amine functionalised MOFs are systematically lower as indicated by the reduced surface areas in Table 1.

CO_2 isotherms for the amine functionalised and non-functionalised MOFs are shown in Fig. 2a–c. Despite the lower specific surface areas of the functionalised MOFs their adsorption capacities for CO_2 are higher than the non-functionalised materials for all cases. As for the MCM-41 systems, the isotherms for the amine functionalised materials USO-1-Al-A and USO-3-In-A show increased steepness of the inner part of the isotherms indicating an increase in average adsorption energy upon functionalisation. For USO-2-Ni-A this increase is less pronounced. The adsorption is fully reversible as indicated by the overlap of the adsorption and desorption part of the curves shown in Fig. 2.

For USO-1-Al and USO-1-Al-A isotherms were recorded at 303 and 323 K to estimate the differential adsorption enthalpies by using the isosteric method. Figure 3 show the isotherms at these two temperatures, while in Fig. 4 the differential adsorption enthalpy is plotted as a function of relative pressure. The differential adsorption enthalpy for USO-1-Al-A is high (around 50 kJ/mol) at low CO_2 pressures and levels off at increasing pressure converging towards 25 kJ/mol at $p/p_0 = 0.5$. The curve for USO-1-Al is different showing constant differential adsorption energy of around 30 kJ/mol independent of the CO_2 pressure. The latter value is slightly lower than 36 kJ/mol reported by (Ramsahye et al. 2007) for the same material, and it is also lower than the adsorption enthalpies of 35 kJ/mol reported for non-functionalised MCM-41 (Knowles et al. 2005a, 2005b). The limiting differential adsorption enthalpy of 50 kJ/mol obtained for USO-1-Al-A at low CO_2 pressures is close to the reported adsorption enthalpies of amine functionalized MCM-41 of 52–56 kJ/mol.

A number of studies on aminosilane grafted silica sorbents have proposed that carbamate species are formed upon CO_2 sorption. In Scheme 3 the most relevant possible reactions have been drawn at dry conditions and in the presence of water.

Quantum chemical modelling of the interaction between CO_2 and the amine group of aniline (see Scheme 4) indicate that the interaction has a binding energy of about 20 kJ/mole (Arstad et al. 2007). The equilibrium distance between the N-atom and the C-atom of CO_2 is 298 pm while the shortest O-H distance is 288 pm which are close to the sum of the Van-der-Waals radii of the atoms (Pauling 1960). The estimated limiting differential adsorption enthalpy of around 50 kJ/mol for USO-1-Al-A can be rationalized by adding up the different Van-der-Waals interactions around an adsorbed CO_2 molecule inside the pores. For the amine functionalised MOFs the adsorbed CO_2 molecule can obtain a higher total adsorption energy that for the non-functionalized analogues which mainly can be attributed to the relatively high Van-der-Waals interaction with the amine functionality. At increase CO_2 pressure the differential adsorption enthalpy become similar to that of USO-1-Al, consistent with a de-

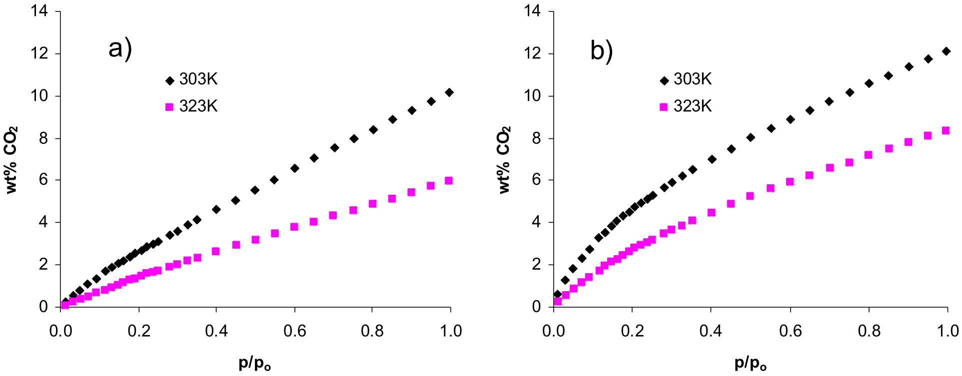
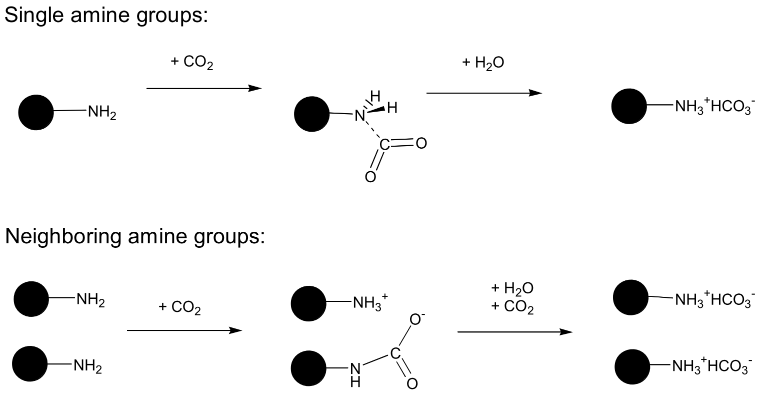


Fig. 3 CO_2 isotherms of **a** USO-1-Al and **b** USO-1-Al-A measured at 303 and 323 K ($p_0 = 1.0$ atm)



Scheme 3

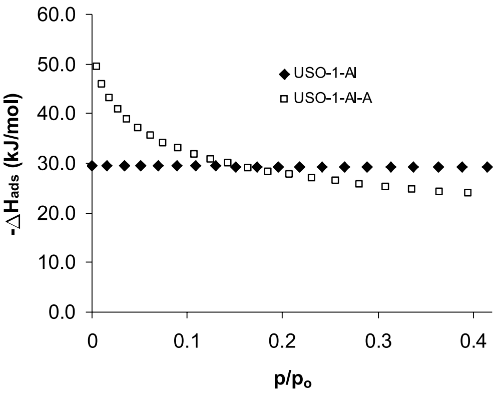
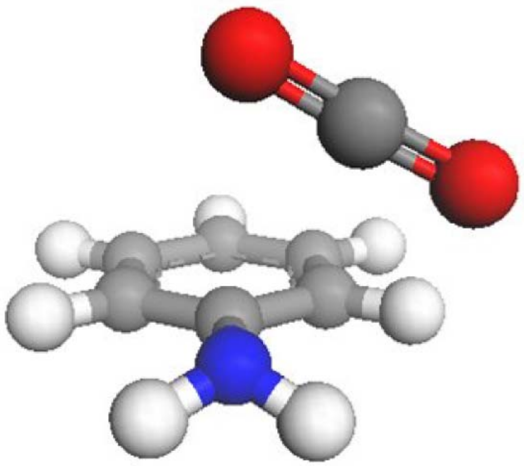


Fig. 4 Estimated differential adsorption energies of USO-1-Al and USO-1-Al-A from the isosteric method using the data shown in Fig. 3. ($p_0 = 1.0$ atm)



Scheme 4

creased influence of the amine sites since these sites already are occupied.

Carbamate species are the kind of moieties that most probably is formed when soluble alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA) are used for liquid absorption of CO_2 (Versteeg et al. 1996). In principle, such moieties can be formed in the reaction between CO_2 and the amine group of the MOF directly; however, quantum chemical modelling of the reaction between CO_2 and ammonia has shown that the barrier for carbamate formation is as high as 60 kJ/mol in the presence of 2 water molecules (Arstad et al. 2007). Also the formation of carbonic acid from CO_2 and 2 water molecules is unfavorable, having activation barrier of around 100–115 kJ/mole (Lewis and Glaser 2003); In bulk water the activation energy for carbonic acid formation is measured to 70 kJ/mole (Magid and Turbeck 1968). Amine groups can, in a similar manner as water, catalyse the formation of carbonic acid, lowering the activation energy for the reaction between one CO_2 and

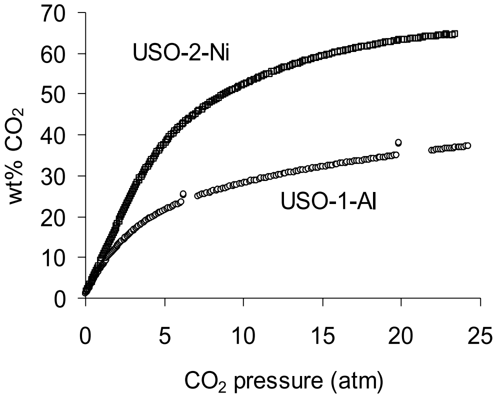


Fig. 5 High pressure CO_2 isotherms of USO-1-Al and USO-2-Ni at 298 K

one water molecules to about 65–78 kJ/mol depending on the kind of amine used (Swang and Blom 2008). As a consequence neither carbonic acid nor carbamate species will be formed under dry conditions and even in the presence of traces of water the formation of these species have high barriers and will not be formed in significant amounts at ambient temperature. Carbamate species can, under dry conditions, only be formed in cases where different amine functionalities have the possibility to interact (see lower reaction in Scheme 3), either by the use of flexible di- or triamine fragments or by having oligomeric or polymeric amine fragments as a viscous liquid phase on a support. In this case the molecules/chains can move relative to each other and thus act as catalysts for carbamate formation for each other in a similar manner as described for the liquid MEA system (Arstad et al. 2007).

Encouraged by the observations at low CO_2 pressures showing that saturation is far from achieved at 1 atmosphere CO_2 for the MOF adsorbents, we carried out measurements at elevated pressures. The results from these measurements are shown in Fig. 5.

While USO-1-Al and USO-2-Ni show similar adsorption at low pressures (see Fig. 1), the two materials diverge at higher CO_2 pressures: USO-1-Al give a maximum adsorption capacity of around 35 wt% at 25 atm CO_2 pressure, while USO-2-Ni reaches more than 60 wt% CO_2 at the same conditions. We believe the difference in capacities of the two adsorbents is a direct consequence of the different pore volumes of the two materials, 0.45 and 0.75 ml/g; the chemical affinity of the pore walls of the two materials should be quite similar since the same linker has been used in both materials. This is similar to the observations of H_2 adsorption in MOF materials where a linear relation is observed between the H_2 adsorption capacity (at 77 K) and the specific surface area of the material (Wing-Foy et al. 2006).

4 Conclusions

We have prepared a selection of MOF adsorbents that maintain open porosity upon desolvation and the open structures have been tested as low temperature adsorbents for CO_2. The best adsorbents reach carbon dioxide capacity levels of 14 wt% at atmospheric pressures of CO_2 and as high as 60 wt% at 25 atm at CO_2 pressure and 298 K. At low partial pressure of CO_2, the highest CO_2 adsorption capacities are obtained with the MOF adsorbents having uncoordinated amine functionalities within the pores. Such functionalities increase the adsorption energy of carbon dioxide. Quantum chemical modelling confirms that CO_2 is adsorbed with a relatively low energy (around 20 kJ/mole) to an amine group. In addition, in the relatively narrow pores of the present MOFs an adsorbed molecule will have additional interactions with other parts of the pore. At low CO_2 pressures the differential enthalpy of adsorption is estimated to around 50 kJ/mole for an amine functionalized MOF (USO-1-Al-A), while the adsorption enthalpy is estimated to 30 kJ/mol for the isostructural MOF without amine functionalities. At increase CO_2 pressures the differential adsorption enthalpies of the two materials become similar. There is no evidence that CO_2 is absorbed forming carbonic acid or carbamate moieties for the amine functionalised MOFs, which we believe is a natural consequence of the amine groups being spatially separated avoiding bis-amine reactions forming simultaneous ammonium and carbamate species in the presence of CO_2. At elevated CO_2 pressures the observed adsorption capacities show a linear relationship to the specific surface area and pore volume of the adsorbents. The high adsorption capacities at elevated CO_2 pressures together with the possibility to make MOF materials having extreme surface areas indicate that niche applications of MOF adsorbents may be found for removal of CO_2 from high pressure gas mixtures.

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