Tuning metal sites of DABCO MOF for gas purification at ambient conditions

Somboon Chaemchuen\textsuperscript{a,b}, Kui Zhou\textsuperscript{a,b}, Nawsad Alam Kabir\textsuperscript{a,b}, Yao Chen\textsuperscript{a,b}, Xiaoxing Ke\textsuperscript{c}, Gustaaf Van Tendeloo\textsuperscript{d,e}* , Francis Verpoort\textsuperscript{a,b,d,e,}\textsuperscript{*}

\textsuperscript{a} Laboratory of Organometallics, Catalysis and Ordered Materials, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Center for Chemical and Material Engineering, Wuhan University of Technology, Wuhan, China
\textsuperscript{b} Department of Applied Chemistry, Faculty of Sciences, Wuhan University of Technology, Wuhan 430070, China
\textsuperscript{c} Department of Applied Chemistry, Faculty of Sciences, Wuhan University of Technology, Wuhan 430070, China, EMAT (Electron Microscopy for Materials Science), University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium
\textsuperscript{d} Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation
\textsuperscript{e} Ghent University, Global Campus Songdo, 119 Songdomunhwa-Ro, Yeonsu-Gu, Incheon, Republic of Korea

\textbf{A R T I C L E I N F O}

Article history:
Received 23 June 2014
Received in revised form 9 September 2014
Accepted 12 September 2014
Available online 20 September 2014

Keywords:
MOFs
CO\textsubscript{2} adsorption
Mixed ligand
DABCO
Metal effect

\textbf{A B S T R A C T}

Metal–organic frameworks (MOFs) have emerged as new porous materials for capture and separation of binary gas mixtures. Tuning the metal sites in MOF structures has an impact on properties, which enhance affinity of gas adsorption and selectivity (e.g., surface area, cavity, electric field, etc.). The synthesis and characterization of a M-DABCO series (M = Ni, Co, Cu, Zn) of MOFs are described in this study. The experiments were conducted using multicomponent gas mixtures and the Ideal Adsorbed Solution Theory (IAST) was applied to determine the CO\textsubscript{2}/CH\textsubscript{4} selectivity. Experimental adsorption isotherms were fitted with a model equation to evaluate the characteristic adsorption energy (Isosteric, Q\textsubscript{st}) of this series. The Ni metal in the M-DABCO series reveals the best performance concerning CO\textsubscript{2} adsorption and CH\textsubscript{4}/CO\textsubscript{2} selectivity at ambient conditions based on IAST calculations. The combination of characterizations, calculations and adsorption experiments were used to discuss the metal impact on the adsorption sites in the M-DABCO series at ambient conditions.

\textcopyright 2014 Elsevier Inc. All rights reserved.

1. Introduction

The development of metal–organic frameworks (MOFs) has opened the window toward new potential materials. Additionally, MOF-research is fueled by their extraordinary compositional and structural variety, permanent porosity, ultralow densities, well-defined pores and channels. The high internal surface area is one of the foremost attributes of MOFs and has been shown to be highly desirable in many potential applications involving gas storage and separation, etc. [1–3]. MOFs have received much attention as materials for separation of gas mixtures, e.g., CO\textsubscript{2} and CH\textsubscript{4} [4–7]. From industrial point of view, separation of CH\textsubscript{4}/CO\textsubscript{2} gas mixtures is interesting since it is found in a variety of industrial off-gases: in process streams reforming, coal gasification, partial oxidation of hydrocarbon, natural gas processing, etc. [8]. Furthermore, differences in electrostatic properties between gases (CH\textsubscript{4} is non-polar, CO\textsubscript{2} has a quadrupole moment) and MOF materials are of fundamental interests. At ambient temperature and pressure up to 42 bars, certain MOFs show a CO\textsubscript{2}/CH\textsubscript{4} sorption selectivity of 8–10 and a CO\textsubscript{2} uptake between 2–35 mmol/g [4,9], which is much higher than the corresponding values of zeolites and activated carbon [4,6]. Moreover, these materials have attracted much attention due to their tunable structures, low enthalpy of adsorption and high affinity for CO\textsubscript{2} [10–16]. Exploring their performances for applications in adsorption, separation, and purification, MOFs have attracted intense interests of many researchers working in the field of green energy such as H\textsubscript{2} storage, natural gas purification, biogas upgrading and so on.

Biogas is an alternative green energy source that can be upgraded and applied as fuel for energy in daily life. Biogas itself is a mixture consisting mainly of CH\textsubscript{4} (60\%), along with CO\textsubscript{2} (40\%) and some trace gases (H\textsubscript{2}O, N\textsubscript{2}, H\textsubscript{2}S, etc.) [17]. In order to use biogas, it needs to be cleaned or upgraded, a treatment whereby carbon dioxide is separated from methane. MOFs are composed of organic bridging ligands coordinated to metal-based nodes. Both, the metal and organic linkers, have a distinct effect
on gas adsorption properties. Suitable MOFs for a particular requirement may be synthesized by choosing an appropriate metal center and organic linker. Several types of MOFs structures can be prepared using a variety of metals, such as M$_2$(DOBDC) [18,19], M-BTT [20,21], MIL-53 [22,23], and MIL-88 [24], etc. Numerous studies have quantified how the CO$_2$ isosteric heats of adsorption change when replacing the metal atom for a given MOF topology [25–29]. Consequently, the metal site can significantly influence the CO$_2$ interaction [26,28–30]. Although several studies have been reported, there are still significant opportunities to tune CO$_2$–MOF interactions by using different metals to affect the metal center–CO$_2$ interaction.

Although many MOFs have been prepared using one single kind of organic linker, the use of two different linkers, opens up more possibilities to tune the pore size and chemical functionalities independently [31]. MOFs synthesized using a mixed-ligand system of O- and N_donors often lead to so-called pillared-layer structures, which received much attention for potential use as adsorbent materials. Pillared-layer MOFs consist of two types of organic linkers, typically aromatic dicarboxylates and diamines, where the 2-D layers formed by metal ions and dicarboxylates are pillared by diamines. Mixing of terephthalic acid (BDC) and 1,4-diazabicyclo[2.2.2]octane (DABCO) with metal salts is one series of mixed ligand systems to synthesize microporous MOF materials (Scheme 1). BDC is a common rigid ligand applied in MOFs, which often leads to a simple cubic topology. Chen et al. reported a unique α-Po-type of microporous 3D primitive cubic MOFs $\text{M}[(\text{COO})_2]_{\text{L}}\text{G}_{\text{x}}$ ($\text{M}^{2+} = \text{Cu}^{2+}$ and $\text{Zn}^{2+}$, $\text{R}(\text{COO})_2 = \text{dicarboxylate linker, L = bidentate pillar linker, G = guest molecules}$) of which the micropores were systematically tuned [32]. Such three dimension primitive cubic MOFs can be easily self-assembled by the paddle-wheel clusters $\text{M}_2(\text{COO})_4$ using a dicarboxylate linker and a bidentate pillar linker. It is expected that by the incorporation of different combinations of dicarboxylate and pillar linkers, a series of microporous MOFs with systematically varied micropores will be readily constructed. The micropores can be further tuned by making use of interpenetration; thus, rationally designed microporous MOFs for highly selective separation and purification of small molecules can be fulfilled. The M-DABCO series is a group of pillared-layer isostructural MOFs materials in which two metal atoms are connected with four BDC forming the paddle wheel and in combination with two DABCO ligands the framework can be constructed as shown in Scheme 1 [33–38]. The properties of Zn$_2$, Cu$_2$, Ni-DABCO for H$_2$ storage are determined by the Henry’s constants and they present small values, low adsorption enthalpies at zero coverage and therefore require mild regeneration conditions compared to MOFs with Mg-DOBDC, MIL-101, Cu-BTC, etc. [33,39]. The water tolerance of this MOF type is one of the advantages, which was exhibited by this series. This stability could be explained by the fact that the metals present in the paddle wheel cluster of M-DABCO series are coordinated to oxygen and nitrogen atoms and no free coordination sites are readily available for H$_2$O to interact with. Moreover, the non-polar aromatic benzene group connected to the metal–oxygen and nitrogen chains is highly hydrophobic [35]. For the reasons mentioned above, this type of MOFs is considered for the application of CO$_2$ adsorption in the presence of moisture. However, the structures are unstable and collapsed at high (>60%) humidity water vapor sorption at 25°C [34].

Herein we present the synthesis and characterization of the M-DABCO series with variable metal site ($\text{M} = \text{Zn, Ni, Co, Cu}$) together with their gas adsorption (N$_2$, CO$_2$, CH$_4$) properties of these materials. Combination of the structural characterizations, experimental adsorption results and adsorption modeling is used to demonstrate the metal effect on the gas mixture separation of CO$_2$ and CH$_4$ at ambient conditions, which is still missing in literature until today. The results of the corresponding study allow identifying the effect of metal substitution. More studies of this type would allow a greater understanding of the role of the metals in facilitating the adsorption properties of metal–organic frameworks for CO$_2$ and CH$_4$ separation at ambient condition. We believe that the results of this work are essential in order to fine tune and synthesize MOFs with desired adsorption properties.

2. Experimental

2.1. Synthesis of M-DABCO series

All reagents and solvents employed were commercially available (Aladdin) and used without further purification. All samples were prepared using solvothermal methods from a solution of the starting materials, which included the nitrate salt of the metal ions, 1,4-benzenedicarboxylate (BDC) and 1,4-diazabicyclo[2.2.2]octane (DABCO) ligand. The procedure to synthesize M-DABCO ($\text{M} = \text{Ni, Co, Cu, Zn}$) were modified from those described in literature [33,34].

Ni-DABCO was synthesized from a mixture of BDC (3 mmol, 498 mg), DABCO (2.49 mmol, 279 mg) and Ni(NO$_3$)$_2$·6H$_2$O (3 mmol, 872 mg) in 60 mL of DMF in a conical flask and stirred at room temperature for 20 min, followed by sonication of 20 min. The mixture was transferred into a Teflon-lined autoclave and heated to 110°C for 24 h. Thereafter the mixture was cooled down to room temperature. The green colored solid product was

---

Scheme 1. The self-assembly of the paddle-wheel cluster $\text{M}_2(\text{COO})_4$ using the dicarboxylate BDC and the bidentate pillar ligand DABCO to construct three dimensional cubic MOFs (M-DABCO series).
then filtered and washed thoroughly with DMF to remove unreacted reagents followed by drying at room temperature (25–30 °C) under vacuum overnight. The dried material was transferred into a vacuum desiccator for further use.

The procedures for Cu-DABCO and Co-DABCO were similar to the synthesis of Ni-DABCO. The nitrate salt of Cu(NO₃)₂·3H₂O (3 mmol, 725 mg) and Co(NO₃)₂·6H₂O (3 mmol, 873 mg) were used instead of Ni(NO₃)₂·6H₂O, respectively. The mixture was heated in a Teflon-lined autoclave at 120 °C for 48 h. The synthesis of Zn-DABCO was made use of the zinc nitrate salt. Zn(NO₃)₂·6H₂O (5.41 mmol, 1609 mg), BDC (5 mmol, 830 mg) and DABCO (2.5 mmol, 280 mg) were mixed in 60 ml of DMF and transferred to a Teflon-lined autoclave which was heated at 120 °C for 48 h. The product recovery and storage steps for Cu-, Co-, and Zn-DABCO were similar to those of Ni-DABCO.

2.2. Measurements

Activation of the materials was done by in situ evacuation under vacuum at 110 °C overnight to obtain porous materials ready for the characterizations. The powder X-ray diffraction spectra (XRD) were collected using an Empyrean instrument from PANalytical applying a monochromatic Cu Kα radiation at ambient conditions. TEM investigation of Ni-DABCO was carried out in a Philips CM20 microscope operated at 200 kV. The Ni-DABCO powder (Ni-DABCO) was crushed and dispersed in water-free ethanol. The solution was then ultrasonic for 3 min before dropping onto a Cu-grid with lacey carbon film. Imaging and diffraction of the structure was performed at low electron dose in order to minimize beam damage to the sample. Thermogravimetric analyses (TGA–DSC) were carried out using a Netzsch (STA449c/3/G) instrument. Thermogravimetric analyses (TGA–DSC) were performed using a heating rate of 5 °C min⁻¹ under inert atmosphere (N₂-flow). Scanning electron microscopy (SEM) from JEOL (JSM-5610LV, 0.5–35 kV) was used to investigate the texture of the materials. The low-pressure gas adsorption isotherms were measured by the volumetric method on a Micrometics instrument (ASAP2020). In all gas adsorption measurements 60–100 mg of sample was used. For the CO₂, CH₄ and N₂ gas adsorption analyses gases of purity > 99.999% were applied. Prior to the adsorption measurements, the samples were evacuated at 180 °C under vacuum (initial activation) for about 3 h. The micro pore surfaces were calculated by the Brunauer–Emmett–Teller (BET) and Langmuir method. The linearized BET and Langmuir equation were fit to the data within the range 0.02 < P/P₀ < 0.2 and P/P₀ > 0.99 was considered for the pore volume.

3. Results and discussion

3.1. Structure

It is a basic teten of MOFs structure that, in the assembly of various shaped geometric units, frameworks with highly symmetric vertices and ideally one kind of link (“edge transitive”) would be most likely to form. High-resolution powder X-ray diffraction (XRD) has been used to observe the local geometry and conformation of the crystalline phase of the M-DABCO series and the resulting spectra are presented in Fig. 1a. The main peak of all members of this M-DABCO series appears before 10° (2θ), 8.3° to be exact, unmistakably correlating with a MOF crystal structure. The strong intensity for the (100)-peak in all samples clearly reveals that the obtained patterns are derived from supported metals and ligand building blocks completing the MOF structure of the M-DABCO member. Considering the crystallographic construction, the 3D structure is formed by square-grid of metal-BDC layers further interlinked by DABCO ligands. Within this 3D structure the two windows of interlacing channels are supposed to be of similar sizes within M-DABCO series (Co-DABCO; 7.6 × 7.6 and 5.1 × 3.7 Å; Zn-DABCO and Cu-DABCO; 7.5 × 7.5 and 4.8 × 3.2 Å, Ni-DABCO; 7 × 7 and 4 × 4 Å) [36,38].

Structural investigation of the Ni-DABCO MOF, which served as an example for the M-DABCO series, was also performed by transmission electron microscopy (TEM) to confirm the crystallinity of the Ni-DABCO series. A diffraction pattern along main zone axis of [010] is shown in Fig. 1b. The flake from which the diffraction pattern was acquired is shown in the inset. The indexation of the diffraction pattern is in good agreement with the XRD results, as indicated in the Fig. 1a, i.e., (100) and (001) lattice distances. The sharp diffraction spots indicate high crystallinity of as-synthesized Ni-DABCO. However, the structure is sensitive to electron beam. Although low dose was carefully applied onto the MOF flake, the diffraction pattern degraded shortly after a limited exposure time.

In order to get deeper insight into the induced textures, the samples were characterized by scanning electron microscopy (SEM). The crystals showed cubic and rod-bars shapes composed of M-DABCO after activation at 110 °C under vacuum as shown in SEM images (Fig. 2). All the samples with high crystallinity possess the correct structure in which the coordinately saturated site of the metal atoms create a 3D pillared-layer framework, as seem in Scheme 1. By studying the SEM images of the M-DABCO series, a distinct crystalline growth and particle size distribution of 1–50 µm is confirmed. The particle shapes of Zn and Cu-DABCO are cube-like, while the shape of the Ni-DABCO crystals is needle- or rod-like. Co-DABCO however, shows a mixture of cube- and rod-shape. In addition, a small amount of ball shape particles is present next to the cube and rod structures of Co-DABCO. This structure might be correlated with the small new peaks as shown in XRD result (2θ < 8.3° and 14.8° (111)).

3.2. Thermal stabilities

Thermo gravimetric analysis (TGA) was performed to assess the architectural stability of the M-DABCO. The results of M-DABCO (M: Zn, Co, Cu, Ni) samples are depicted in Fig. 3. The first weight loss occurs between 50 and 200 °C (a-zone) and can be attributed to the removal of solvent (DMF) and/or water molecules from surface and cavities of the samples, roughly corresponding with the temperature of the boiling point of DMF (153 °C) and water (100 °C). The next main weight loss is found in the range of 350–550 °C (b-zone, the temperatures are explicitly based on the DTG curves) indicating the metal organic framework decomposition. Zn-, Ni-, and Co-DABCO of this MOF series possess a thermal stability up to 350 °C, while Cu-DABCO sample is less thermal stable within this M-DABCO series. The weight loss of Cu-DABCO takes off at 275 °C in the b-zone resulting in decomposition of its structure (Fig. 3) [33,34].

Ni-DABCO displays the highest thermal stability and robustness compared with the other members of this series. The thermogravimetric profile of Ni-DABCO shows a structure collapse (structure decomposition) at a temperature higher than 425 °C. The air stability of two members of this DABCO series has been reported before. Ni-DABCO was investigated after exposure to air for several months and no remarkable differences in the XRD pattern were found [35]. This indicated that the crystal structure of Ni-DABCO possesses an impressive stability under ambient atmosphere. In case of Co-DABCO small grains are observed on the crystal surface after bringing the crystals into contact with air for several days [38]. Upon exposure to air, the decomposition was also visually detectable since a color change prevails from purple to pink. Structural collapse was further confirmed from surface area measurements, which showed a decrease of the surface area and
pore size. All these observations clearly indicate the sensitivity of Co-DABCO against moisture.

For the activation of the M-DABCO MOFs, to achieve high micro porosity, evacuation of the materials at 180 °C under vacuum for 3 h was performed. The effect of solvent removal (material activation) under different conditions was investigated by thermogravimetric analysis (see Fig. S1). For fresh Zn-DABCO the first weight loss (around 35%) appeared from 50 to 250 °C corresponding to the loss of guest solvent molecules (DMF) and/or water from the surface and channels/pore. A steady plateau is reached from 250 to 350 °C before complete decomposition of the framework. While activated Zn-DABCO showed a weight loss due to structural decomposition (b-zone, up to 350 °C), no weight loss was observed at temperatures lower than 250 °C (a-zone). Analysis of the frameworks after activation by XRD and TG clearly indicates that removal of solvent molecules has no influence on the framework integrity. Identical phenomena for the other M-DABCO MOFs in this study were observed.

Fig. 1. (a) XRD patterns of the M-DABCO series, with only Co-DABCO having a (111) reflection, which might be correlated with the small amount of ball shape particles. (b) Diffraction pattern obtained from a crushed sample of Ni-DABCO. The flake, inserted as an inset, is oriented along [010] zone axis.

Fig. 2. SEM images of the M-DABCO series: (a) Zn-DABCO, (b) Cu-DABCO, (c) Ni-DABCO, (d) Co-DABCO.
3.3. Surface properties

The porosity and surface area of this M-DABCO series were determined by nitrogen adsorption–desorption at \(-196\, ^\circ C\). Before gas adsorption measurements, all samples were evacuated under vacuum without damage of their structure (material activation). All samples exhibit a permanent microporosity as evidenced by the reversible type I adsorption isotherms corresponding to microporous materials, according to the IUPAC classification [40]. The initial steep step of all samples increases in the volumetric uptake before 0.02 \(P/P_0\) followed by a quick saturation step at relative low pressure which signifies micropore filling as shown in Fig. 4. All adsorption isotherms of the M-DABCO samples are steep for the initial \(N_2\) uptake and without hysteresis, indicating a high micro-porosity of the structure and high stability of the framework [41,42]. A comparison with existing literature data of the surface area and porosity properties of M-DABCO series in MOF materials have been summarized in Table 1. The surface area and porosity properties for the Zn-, Ni-, Cu-DABCO samples are in the same range to the values reported in literature [33,34]. From the M-DABCO samples prepared in this study the Ni-DABCO sample reaches the highest surface area (Table 1), demonstrates the best \(N_2\) uptake of 528 cm\(^3\) g\(^{-1}\) at \(P/P_0 = 0.99\) and shows a fully reversible physiosorption isotherm in the M-DABCO series. The maximum nitrogen uptake capacities for Co-, Zn-, and Cu-DABCO amounts to 481, 454, and 445 cm\(^3\) g\(^{-1}\), respectively.

One of the most important properties of MOFs is its high porosity (fraction of void volume to total volume), which involved number of adsorptive sites within a given material. This work illustrates the role of the metal center in mixed ligand MOFs (DABCO and BDC) in the building unit of the MOFs exhibiting exceptional surface area and porosity. According to our experimental results, we found that Ni-DABCO possesses the largest pore volume (Table 1). Previously, it has been demonstrated that the amount of gas uptake/adsorption can be correlated with the pore volume of MOF materials [43]. Furthermore, the flexibility of a M-DABCO framework might effected the adsorption of small gases similar as in IRMOF-1 [44]. Within the metal series of DUT-8 (NDC and DABCO ligands), the total gas uptake was obviously caused by the different degrees of flexibility and stability of the MOF framework within the series. The different metal atoms had a pronounced influence upon the total gas uptake [45].

3.4. Gas adsorption

This work attempts to measure at ambient conditions (room temperature and low pressure) the adsorption of \(CO_2\) and \(CH_4\) to evaluate the porosity and the response of the M-DABCO frameworks during adsorption. The obtained isotherms can generate meaningful data since the current process for \(CO_2/CH_4\) separation (e.g., biogas upgrading, etc.) is performed in nearly the same conditions. For these measurements the M-DABCO samples were activated in the conditions in which their structures remain unchanged (see thermal gravimetric results, Fig. 3 and Fig. S1). The activated M-DABCO samples already show significant gas adsorption at low relative pressure condition. The \(CO_2\) and \(CH_4\) adsorption isotherm were measured at 25 \(^\circ C\) and pressure up to 1 Mpa to elucidate the effect of the metal identity on the gas uptake in this iso-structural series of MOFs, see Fig. 5a and b. The \(CO_2\) and \(CH_4\) adsorption isotherms rapidly increase with a linear tendency. The sequence of the total \(CO_2\) capacity in the M-DABCO series is Ni-(2.17 mmol) > Zn-(1.87 mmol) > Cu-(1.45 mmol) > Co-(1.02 mmol) and for the total \(CH_4\) capacity it becomes Co-(0.57 mmol) > Cu-(0.51 mmol) > Ni-(0.51) > Zn-(0.48 mmol), clearly emphasizing the effect of each metal to gas adsorption. The Ni-DABCO sample showed the highest \(CO_2\) adsorption in the DABCO series at ambient conditions, which could be attributed to the highest surface area of this member in this series (BET results, Table 1 and Fig. 4). The desorption isotherms of \(CO_2\) and \(CH_4\) show no evidence of hysteresis (Figs. S2–S5), indicating a typical physiosorption behavior in micropores, indicating its potential suitability for applications in pressure swing adsorption (PSA) or temperature swing adsorption (TSA) processes.

At ambient conditions, the \(CO_2\) adsorption results on Ni-DABCO measured in this work are slightly higher than that reported by Liang et al. [35] but comparable to the results described by Arstad et al. [22], Ni-DABCO can adsorbed \(CO_2\) (2.2 mmol g\(^{-1}\)) at nearby ambient conditions which is higher than that on IRMOF-1 (0.98 mmol g\(^{-1}\)), IRMOF-3 (1.4 mmol g\(^{-1}\)), MOF-177 (1.1 mmol g\(^{-1}\)), ZIP-8 (1.3 mmol g\(^{-1}\)) and MIL-47 (1.5 mmol g\(^{-1}\)) [47]; it is comparable to that on AC (Norit R1) (2.2 mmol g\(^{-1}\)) [48], H-mordenite (2.2 mmol g\(^{-1}\)) [49], Na-ZSM-5 (1.9 mmol g\(^{-1}\)) at 0.72 bar [50] and silicalite (2.3 mmol g\(^{-1}\)) [51]. The loading of Ni-DABCO for \(CO_2\) at ambient conditions is lower compared to MOFs containing open metal sites, e.g., CuBTC (5.5 mmol g\(^{-1}\)) [52], MIL-101 (2.5 mmol g\(^{-1}\)) [52] and MgDOBDC (7.8 mmol g\(^{-1}\)) [26]. However, Ni-DABCO is easier to regenerate at mild conditions than those MOFs bearing open metal sites,
which will be discussed in the isosteric heats of adsorption analysis section.

In the next step all samples were evaluated for the selective uptake of CO\(_2\) over CH\(_4\), which is related to the separation application (e.g., biogas upgrading, natural gas purification, etc.). The selectivities were calculated from the isotherms by the Ideal Adsorption Solution Theory (IAST) [53], which has been proved to be valid for calculating the gas selectivity of adsorbents such as MOF materials from the single-component adsorption isotherms of a gas mixture via modeling techniques. In this method, the isotherms of each sample are collected at the same temperatures and Ideal Adsorption Solution Theory (IAST) is applied in order to predict the expected selectivity of the material. The selectivity \(S_{A/B}\) in a binary mixture of components \(A\) and \(B\) is defined in Eq. (1) (The calculation model and parameters have been described in the Supporting information).

\[
S_{A/B} = \frac{x_A}{x_B}/\frac{y_A}{y_B}
\]

where \(x_i\) and \(y_i\) are the mole fractions of component \(i\) \((i = A, B)\) in the adsorbed and bulk phases, respectively.

To calculate the CO\(_2\)/CH\(_4\) selectivity of the M-DABCO series for the separation application for biogas upgrading, typically composed of 40% CO\(_2\) and 60% CH\(_4\), mixtures were calculated at ambient conditions (25°C, pressure up to 1 MPa) using the IAST. The results are shown in Fig. 6, an increase in pressure raises the selectivity of the heavier species except for Co-DABCO (small change). At the highest pressure (1 MPa), Ni-DABCO exhibits the best selectivity and based on these conditions Ni-DABCO is followed by Zn-> Co-> Cu-DABCO, respectively. Additionally, the selectivity tendency on this MOF is increasing significantly at high pressure.

Furthermore, the adsorptive selectivity (thermodynamic separation) arises from the difference in affinity of the various components of the gas mixture to be adsorbed on the pore surface of the metal–organic frameworks. For selectivity based upon a

<table>
<thead>
<tr>
<th>Name</th>
<th>Surface area (m(^2) g(^{-1}))</th>
<th>Pore volume (cm(^3) g(^{-1}))</th>
<th>Pore size (nm)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-DABCO</td>
<td>1450</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>1725</td>
<td>0.85</td>
<td>–</td>
<td>[67]</td>
</tr>
<tr>
<td></td>
<td>1870</td>
<td>0.69</td>
<td>1.67</td>
<td>This work</td>
</tr>
<tr>
<td>Ni-DABCO</td>
<td>1705</td>
<td>0.82</td>
<td>–</td>
<td>[35]</td>
</tr>
<tr>
<td></td>
<td>1904</td>
<td>0.98</td>
<td>–</td>
<td>[33]</td>
</tr>
<tr>
<td></td>
<td>2120</td>
<td>0.82</td>
<td>1.78</td>
<td>This work</td>
</tr>
<tr>
<td>Cu-DABCO</td>
<td>1400</td>
<td>0.71</td>
<td>–</td>
<td>[68]</td>
</tr>
<tr>
<td></td>
<td>1616</td>
<td>0.70</td>
<td>1.67</td>
<td>This work</td>
</tr>
<tr>
<td>Co-DABCO</td>
<td>2022</td>
<td>0.75</td>
<td>1.64</td>
<td>This work</td>
</tr>
</tbody>
</table>

* A relative pressure range of \(P/P_0 > 0.99\) was used.

---

**Table 1**
The surface area, pore volume and pore size of the M-DABCO series.

**Fig. 5.** Adsorption isotherms for CO\(_2\) (a) and CH\(_4\) (b) on M-DABCO series measured at ambient conditions (25°C, pressure up to 1 MPa (1 atm)).

**Fig. 6.** Selectivity calculations of CO\(_2\)/CH\(_4\) with pressure of 40% of CO\(_2\) and 60% of CH\(_4\) at ambient conditions (25°C, pressure up to 1 MPa (1 atm)).
physisorptive adsorption mechanism, the separation relies on the gas molecules having different physical properties, such as the polarizability or the quadrupole moment, resulting in a higher adsorption enthalpy of certain molecules over others. Due to electrostatic interactions the polarizability of CO$_2$ is higher resulting in a higher adsorption capacity for CO$_2$ compared to that of CH$_4$ under the same conditions. Therefore, due to the polarizability of CO$_2$, the adsorption of CO$_2$ on the M-DABCO series is higher than the CH$_4$ adsorption. In comparison with other MOFs, e.g., Cu-BTC and MIL-101, the metal centers of those MOFs are fully coordinated and so the contribution of electrostatic interaction is much less resulting in a lower adsorption of CO$_2$ on the latter. The adsorption capacities of those MOF materials (Cu-BTC and MIL-101) follow the order CO$_2$ > CH$_4$ > CO > N$_2$ over the entire experiment range [54].

Adsorption characteristics in MOFs depend on the geometry of the linker as well as on the saturation (coordination) level of the metal atom [55]. The adsorption of CO$_2$ on MOF materials is not due to chemisorption, but may be attributed to ionic interactions. This is in agreement with the report of Caskey et al. who stated that the higher ionic character of the Mg-O bond in Mg-DODBC attributed to the relatively higher CO$_2$ uptake [26]. Yazaydın et al. suggested from the obtained experimental results that the CO$_2$ uptake increases with a decreasing M-O bond length in the framework of M-DODBC MOFs [46], which was also confirmed by electronic calculations by Park et al. [56]. The order of these bond lengths, which may be considered as an indication for the affinity of metals in this coordination state toward oxygen, is Ni-O (2.55 Å) < Co-O (2.72 Å) < Zn-O (2.71 Å) < Cu-O (2.82 Å). Therefore, the metal effect in the M-DABCO series provides changes in adsorption and selectivity (for binary gas mixture (CO$_2$/CH$_4$)). It can be concluded that the effect of the metal sites is the key factor to contribute to the local electric field effects and interactions (binding energy of CO$_2$ adsorption).

3.5. The isosteric heats of adsorption analysis

The CO$_2$ isosteric heats of adsorption is a critical parameter that has a significant influence over the performance of a given adsorbent material for capture and separation applications. The magnitude of the isosteric heats of adsorption dictates the affinity of the pore surface toward CO$_2$, which in turn plays a crucial role in determining the adsorptive selectivity and the energy required to release the CO$_2$ molecules during regeneration. Optimization of the binding strength between CO$_2$ and MOFs (adsorbent) can be applied to control lowering the energy requirements of the separation process [57]. Isosteric heats of adsorption ($Q_{st}$) is a frequently expressed heat of CO$_2$ adsorption as a function of the quantity of CO$_2$ adsorbed. The analysis of adsorption isotherms collected at various temperatures allows an estimation of the coverage-dependent isosteric heats of adsorption ($Q_{st}$), where the behavior of this function is determined by the relative magnitudes of the adsorbent–adsorbate and adsorbate–adsorbate interactions. The $Q_{st}$ values are computed using the Virial-Type Model for predicting CO$_2$ isosteric heats of adsorption as discussed elsewhere in literature [58]. All the isotherms could be fitted satisfactorily with a simple Virial-Type model and the more complicated models did not lead to a notably better fit to the experimental data. Errors were propagated by taking into account the covariance of the fitting parameters. The model used in this work is readily expressed by Eq. (2) (Parameters are described in the Supporting information).

$$Q_{st} = RT^4 \left( \frac{\partial \ln P}{\partial T} \right)_n$$

Adsorption isotherms of CO$_2$ were collected using a volumetric technique from fitting at 0 and 25 °C for the M-DABCO series. As expected, the amount adsorbed CO$_2$ increases significantly with diminishing temperature for all samples (as shown in Figs. 52–55). The coverage dependencies obtained via calculation are presented graphically in Fig. 7. Zn- and Cu-DABCO show a gradual increase of their isosteric heats of adsorption values as function of the amounts adsorbed, while for Co- and Ni-DABCO their values heighten with increasing adsorbed amounts of CO$_2$, especially for Co-DABCO. The CO$_2$ isosteric heats of adsorptions ($Q_{st}$) for various metal sites in the M-DABCO series are binding energies, increasing from 17 to 30 kJ mol$^{-1}$ at saturated loading. The $Q_{st}$ at zero coverage for the M-DABCO series are Co- > Ni- > Zn- > Cu-DABCO as 20.8, 19.1, 18.4 and 17.5 kJ mol$^{-1}$, respectively. At the saturated CO$_2$ adsorption, the values of $Q_{st}$ are Co-(29.8 kJ mol$^{-1}$) > Ni-(25.8 kJ mol$^{-1}$) > Zn-(22.4 kJ mol$^{-1}$) > Cu-(21 kJ mol$^{-1}$). This clearly indicates that different metals of M-DABCO series display a different affinity to carbon dioxide interaction under low CO$_2$ coverage. At the highest CO$_2$ adsorption, the values of $Q_{st}$ are Co-(29.8 kJ mol$^{-1}$) > Ni-(25.8 kJ mol$^{-1}$) > Zn-(22.4 kJ mol$^{-1}$) > Cu-(21 kJ mol$^{-1}$). This can be explained due to the presence of various metal sites in M-DABCO series and a different metal might significantly tune the interaction between CO$_2$ and adsorbent materials and thus the binding energy between CO$_2$ and the adsorbent, which even increase significantly at high pressure [33,34]. In addition, the isosteric heats of adsorption of Co-DABCO does not follow the trend observed in the M-DABCO series. The presence of small peaks and two-phase mixture (rod and cube shape) might be responsible for this different behavior.

To explain the isosteric heats of adsorption phenomena in the M-DABCO series one should focus on the adsorbed molecules interacting with the surface of adsorbent material. Using a sorbent consisting of two types of pores (macropores and micropores) will display different adsorption mechanisms. Macropores will offer “primary adsorption sites” to gas molecules, while the micropores cannot directly adsorb molecules form the gas phase. Instead, they are filled by diffusion processes of primary adsorbed molecules reaching eventually the open end of such a pore and there they are adsorbed on “secondary sites” [59]. Furthermore, at higher surface coverages or adsorption loading, adsorbed molecules often are not completely isolated from each other but interact with each other (adsorbed–adsorbed interactions) [60,61]. Based on the described model above, isosteric heat of adsorptions of molecules adsorbed via a diffusion process at zero coverage is lower than the isosteric heats of adsorption obtained from primary adsorption sites and adsorbed–adsorbed interaction and are increasing when more adsorbed molecules are present in the adsorption process.
The isosteric heats of adsorption of CO$_2$ on the M-DABCO series are lower than Cu$_2$(BTC)$_2$ (30 kJ mol$^{-1}$) [47], and much lower than the heat of adsorption reported for CO$_2$ with MIL-100 (60 kJ mol$^{-1}$) [63], MIL-101 (44 kJ mol$^{-1}$) [63] and zeolite 13X (49 kJ mol$^{-1}$) [50], indicating a relatively weak interaction of CO$_2$ with the surface. The $Q_n$ values can be attributed to the coordinately saturated metal sites and only marginal effects are observed due to change of the metal atom in the framework. The lower values for these MOF series are probably beneficial from the perspective of a reduced energy requirement for adsorbent regeneration. Specifically, the use of a material that binds CO$_2$ too strongly would increase the regeneration cost owing to the large quantity of energy required in order to break the MOF framework–CO$_2$ interactions. On the other hand, if the isosteric heats of adsorption is too low, although the material would be more readily regenerated, the purity of the captured CO$_2$ would be lowered owing to the decreased adsorption selectivity, moreover, the volume of the adsorbent beds would also be increased due to the lower density of CO$_2$ adsorption.

Based on the electrostatic potential distribution from computational simulations Xu et al. were able to demonstrate that the preferential adsorption sites for CO$_2$ are located around the corners of the metal sites [18]. The electrostatic potential involved on the metal sites (clusters) has the ability to distribute the selectivity of mixed gas. In addition, in the low pressure range MOFs can adsorb more which is usually governed by the metal site [19]. The estimation of the local electrostatic effects due to a positive charge developed on the metal sites interacting with CO$_2$, this calculated energy, in the absence and presence of a point charge of d-metal levels have been described in literatures [56,64]. The occupied electronic structure of metal sites alters the different CO$_2$ binding affinity. A systematic simulation study for CO$_2$ adsorption in MOFs at low pressure (e.g., 1 bar) is usually associated with the CO$_2$ binding affinity [65]. Here, the M-DABCO series has been tuned to enhance the CO$_2$ adsorption by metal substitution by considering M = Zn, Cu, Co and Ni. Our results demonstrate the following trend for CO$_2$ adsorption: Ni > Zn > Co > Cu-DABCO and these results also correlate with the binding energy of CO$_2$ adsorption on M-DOBDC [56]. Therefore, we can conclude that the effect of the metal sites is the key factor which contribute to the local electric field effects and interactions (binding energy of CO$_2$ adsorption), and in this way predictions of some of these transition metals often can be made.

Additional insights into properties of the DABCO series in correlation with the CO$_2$ uptake can be extracted from the study from Frost et al., who proved that the gas uptake in MOFs falls into three regimes [66]. At low pressures the CO$_2$ uptake correlates with the isosteric heats of adsorption; at intermediate pressures the CO$_2$ uptake corresponds with the MOF surface area and at the highest pressures the CO$_2$ uptake matches with the free volume available within the MOFs. Our results report a correlation between the CO$_2$ adsorption (Fig. 5a) and the surface area properties (Fig. 4 and Table 1) and isosteric heats of adsorption at ambient pressure. Alternatively, the adsorptive selectivity can arise due to chemical interactions between certain components of the gas mixture and surface functionalities of the metal–organic framework. Functionalties that recognize certain molecules based on their propensity for participating in specific chemistry can result in much higher selectivities than those obtained from a purely physisorptive mechanism. For example, the susceptibility of the carbon atom in CO$_2$ to be attacked by nucleophiles has led to the investigation of materials possessing strong Lewis bases, such as amines. The interaction of CO$_2$ with an amine can result in a C-N bond as observed in the aminos aminium solvents, resulting in highly selective adsorption of CO$_2$ over CH$_4$.

4. Conclusion

Next to the synthesis and characterization, a systematic evaluation of the effects of metal identity on the surface area and gas adsorption/selectivity of three-dimensional pillared-layer of M-DABCO (M = Ni, Co, Cu, Zn) was performed. The highlight in this study was the introduction of different metal atoms in the M-DABCO series. The highest surface area and pore volume was found for Ni-DABCO, which is advantageous to the CO$_2$ adsorption and CO$_2$/CH$_4$ selectivity in M-DABCO MOF materials. The saturated metal site in the DABCO series can significantly change/improve the gas adsorption and selectivity behavior at ambient conditions. This is attributed to the adsorptive properties that can be dramatically tuned based on the charge density present at the metal coordination site. The adsorption capacity, selectivity and isosteric heats of adsorption calculations were compared with available literature data for a variety of adsorbents. It follows that the M-DABCO series is attractive for a PSA based separation process at ambient condition.

The “design” of MOFs has been somewhat controversial and it is difficult to determine whether or not a final MOF product is rationally designed. The understanding developed here can lead to new routes to higher MOFs–adsorbate binding energies through coordinated design of both optimal metal centers and ligands. The adsorption capacity is a complex interplay of many factors including the framework density, free volume, porosity, and accessible surface area. Through this undertaking, the structural characteristics that most strongly influence the metal accessibility play a key role in designing more efficient CO$_2$ adsorption and selectivity (CO$_2$/CH$_4$) of MOFs which may be elucidated and should be studied in the future.

Acknowledgements

The authors would like to express their deep appreciation to State Key Lab of Advanced Technology for Materials Synthesis and Processing for financial support (Wuhan University of Technology, 2013-KF-5). F.V. acknowledges the Chinese Central Government for an “Expert of the State” position in the program of “Thousand talents” and the FWO-Flanders for financial support (G.0081.10N). X. Ke and G. Van Tendeloo are grateful to funding from the European Research Council under the seventh Framework Program (FP7), ERC Advanced Grant number 246791-COUNTAMOS. Special thanks also goes to the Ratchadapiseksomphot Endowment Fund 2013 of Chulalongkorn University (CU-56-387-CC).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2014.09.038.

References
