Further investigations of CO_2 capture using triamine-grafted pore-expanded mesoporous silica

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ABSTRACT

A promising adsorbent for acid gas removal, referred to as TRI-PE-MCM-41, was produced by grafting a triamine-containing silane on an MCM-41-type mesoporous silica whose pores have been enlarged by post-synthesis hydrothermal treatment in the presence of a pore-expander. The CO_2 adsorption capacity was determined gravimetrically, and via column breakthrough measurements. The tolerance of TRI-PE-MCM-41 to moisture in the feed was substantiated by measurements under both equilibrium and dynamic conditions. Using a combination of mass spectrometry and thermogravimetry, it was corroborated that the presence of moisture enhances the CO_2 uptake at equilibrium. Adsorption measurements using fixed bed columns showed that moisture does not affect negatively the CO_2 working adsorption capacity compared to dry streams. Furthermore, since the material hardly adsorbed any N_2 or O_2, the selectivity for CO_2 over N_2 and O_2 was practically infinitely high. Cyclic measurements of pure CO_2 and $CO_2:N_2 = 10:90$ mixture using different regeneration modes shed light on the stability of the material and the influence of adsorption/desorption operating conditions on its performance. It was found that the temperature swing regeneration mode is suitable for desorption above $120\,^{\circ}C$, while regeneration under temperature-vacuum swing may be attractive at lower desorption temperatures.

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1. Introduction

One of the most serious problems facing humanity is to prevent the release of excessive amounts of carbon dioxide, due to its impact on climate change. At present, gas absorption using liquid alkanolamine solutions is industry's preferred technology for CO_2 capture at low temperature, but suffers major drawbacks including high demand of energy and the corrosive nature of the absorbent [1–3]. Adsorption separation is recognized as an efficient and economically attractive candidate to complement or replace the current CO_2 scrubbing processes as it is expected to combine high selectivity and productivity, while offering low energy requirements to regenerate the solid adsorbent [3]. To be competitive, an ideal medium for CO_2 adsorption should combine a number of favorable attributes including: (i) high CO_2 dynamic adsorption capacity, (ii) high selectivity toward CO_2, (iii) low energy requirements for regeneration, (iv) stability to prolonged adsorption–desorption cycling, and (v) tolerance to the presence of moisture in the CO_2-containing feed.

Inspired by liquid amine scrubbing technology, a number of research groups developed solid-supported amines as adsorbents for CO_2 separation [4–8]. Chief among the supports are ordered mesoporous silicas and organosilicas, which have proven to be promising materials in a wide variety of environmental applications. The possibility to incorporate functional groups on their internal surface or within their pore volume has produced highly efficient materials that could lead to alternative separation technologies, including the removal of acid gases from a variety of gas streams [9–17].

Our research group developed a highly promising adsorbent for CO_2 and other acid gases [6,13]. This material, referred to as TRI-PE-MCM-41, consists of a triamine functionalized pore-expanded MCM-41 silica. In our previous efforts, we focused on optimizing the conditions for the preparation of TRI-PE-MCM-41 through surface grafting of aminosilane [6] as well as its adsorptive properties using mostly 5% CO_2/N_2 gas mixture [13]. Limited work on the effect of moisture was also carried out using gravimetric measurements [6]. It was later demonstrated using a propylamine-modified mesoporous silica that TGA may underestimate the actual CO_2 uptake in the presence of moisture [18]. To properly analyze the effect of moisture on CO_2 adsorption at equilibrium, a method coupling gravimetry and mass spectrometry (TGA–MS) was developed. The main purpose of the present work was to expand on our earlier findings to gain an in-depth understanding of

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amine-modified mesoporous silicas as CO_2 adsorbents. Specifically, the current work deals with the following issues: (i) CO_2 adsorption in dry and humid streams at equilibrium using a TGA–MS method, (ii) CO_2 working adsorption capacity and selectivity under dynamic conditions using a fixed bed column, and (iii) behavior of the adsorbent through various adsorption–desorption cycles, studying the effects of adsorption temperature (T_A), desorption temperature (T_D) and desorption pressure (P_D). The adsorbent behavior throughout a number of cycles provided new insights on the stability of the material and its requirements for an efficient regeneration.

2. Experimental

2.1. Materials

Cab-O-Sil M-5 fumed silica from Cabot was used as the silica source. Cetyltrimethylammonium bromide (CTAB, Aldrich) and tetramethyl ammonium hydroxide (TMAOH, 25%, in water, Aldrich) were used as structure directing agent and for pH adjustment, respectively. The post-synthesis pore-expander agent was dimethyldecylamine (DMDA, 97% purity, Aldrich). The grafting agent, obtained from Sigma–Aldrich, was 2-[2-(3-trimethoxysilylpropylamino)ethylamino]ethylamine (herein referred to as TRI-silane). Ultra-high purity grade nitrogen, CO_2 grade 4 purity, and certified gas mixtures of CO_2 balance air were supplied by Linde Canada. All reagents and gases were used without further purification.

2.2. Synthesis of TRI-PE-MCM-41 adsorbent

The pore-expanded mesoporous support was prepared in two steps based on a procedure described elsewhere [19,20]. Briefly, MCM-41 type silica was synthesized at 100 °C using CTAB as structure directing agent in the presence of TMAOH. Pore expansion was achieved through a post-synthesis hydrothermal treatment in the presence of DMDA at 120 °C for 3 days [19,21,22]. After removal of the surfactant template and the pore-expander by calcination, the obtained product was labeled PE-MCM-41.

Incorporation of the amine functionality was achieved via surface grafting following a procedure described elsewhere [6]. A sample of PE-MCM-41 was loaded into a multi-neck glass flask containing 150 mL of toluene. Once a homogeneous mixture was produced, 0.3 mL per gram of distilled deionized water per gram of PE-MCM-41 were added and left stirring for at least 30 min. The glass flask was then submerged in a silicon oil bath set at 85 °C using a temperature controlled stirring hotplate with an external temperature probe. TRI-silane (3 mL per each gram of PE-MCM-41) was subsequently added to the mixture and left stirring for 16 h. The material was filtered and washed with copious amounts of toluene, then pentane. Finally, the recovered solid was dried at 100 °C in a natural convection oven for 1 h and was labeled TRI-PE-MCM-41.

2.3. Characterization

The structural properties of PE-MCM-41 and TRI-PE-MCM-41 were determined by nitrogen adsorption at −196 °C using a Micromeritics ASAP 2020 volumetric apparatus. Prior to measurements, the samples were degassed under vacuum at 150 °C for 5 h. The surface area (S_{BET}) was determined by the BET method, whereas the pore size distribution was calculated using the Kruk–Jaroniec–Sayari (KJS) approach. [23]. The pore volume (V_p) was determined as the amount of liquid nitrogen adsorbed at P/P_0 = ca. 1. The organic content in the sample was measured by thermogravimetric analysis (TGA) on a TA Instruments Q-500 apparatus under flowing nitrogen using a heating ramp of 10 °C min^{-1}

up to 800 °C, followed by complete combustion of the organic material under air at the same heating rate up to 1000 °C. Only the weight loss above 200 °C was taken into account for the calculation of amine content [6].

Single component CO_2 adsorption equilibrium measurements were performed using a Rubotherm gravimetric–densimetric apparatus (Bochum, Germany). More details about the experimental set-up and procedure may be found elsewhere [13]. Briefly, the materials studied (MCM-41, PE-MCM-41 and TRI-PE-MCM-41) were activated at 150 °C under vacuum (5×10^{-4} mbar) for at least 2 h. The temperature was subsequently reduced to ambient and the sample placed in contact with CO_2 under the desired pressure. Equilibration time was allowed until no significant change in the sample weight was observed.

2.4. Adsorption in humid streams

Two different approaches were used to study the performance of TRI-PE-MCM-41 in the presence of humid streams: measurements at equilibrium and measurements under dynamic conditions.

The CO_2 adsorption capacity at equilibrium was determined using the TGA instrument described in Section 2.3, coupled with a Pfeiffer Thermostar mass spectrometer. The experimental procedure involved the following steps: (i) activation of the adsorbent, (ii) adsorption of CO_2, (iii) temperature programmed desorption (TPD) of CO_2, and (iv) decomposition of the organic layer of the adsorbent to determine the amine content of the actual sample. A sample of TRI-PE-MCM-41 of ca. 30 mg was placed in the measurement pan of the TGA and pretreated under flowing N_2 at 150 °C since it has been demonstrated that the grafted amine species are stable up to 250 °C [6] and any CO_2 and moisture adsorbed from ambient air desorbs below 140 °C [24]. In addition, non-hydrolyzed methoxy groups are also removed during the activation step [6]. After pretreatment, the temperature was decreased to 25 °C and the gas stream switched to a mixture of 5% CO_2 balance N_2. To control the relative humidity (RH) in the stream, the mixture of CO_2 in N_2 was bubbled through a glass saturator containing distilled deionized water located in a temperature controlled cooling bath before entering the measurement chamber of the TGA. The flow of 5% CO_2/N_2 mixture was maintained for at least 16 h to ensure that equilibrium was attained. The organic content in the sample was obtained by thermal decomposition as described above.

To properly quantify the amount of CO_2 adsorbed, particularly in the presence of moisture, mass spectrometry (MS) was used in combination with TGA [18], as it has been suspected that the commonly used TGA may underestimate the CO_2 uptake. The mass spectrometer was calibrated against CO_2 using the decomposition of known quantities of $CaCO_3$ under flowing nitrogen at a heating rate of 10 °C min^{-1} in the TGA instrument. After base line correction, a linear relationship between the area of the MS signal corresponding to 44 amu and the total amount of CO_2 was obtained. It was used to quantify the CO_2 released from the adsorbent during TPD.

In addition, breakthrough measurements were performed using the experimental set-up shown in Fig. 1 to investigate the behavior of TRI-PE-MCM-41 in dynamic conditions. Line "A" is used to feed an inert gas, most commonly nitrogen, to activate the sample before each experiment, while line "B" feeds a mixture of 5% CO_2 balance air. The stainless steel column used had an inner diameter of 4.6 mm and a packed length of 120 mm. The column was packed with ca. 1 g of TRI-PE-MCM-41 particles of sizes 40–60 mesh obtained by pressing TRI-PE-MCM-41 powder in a hydraulic press at 450 kg$_f$ cm^{-2}, crushing the obtained pellets and sieving between nets with openings of 40 and 60 mesh. Notice that the pressure used was found to afford pellets without altering the structural properties of the material [22]. The column effluent was monitored using a Pfeiffer Thermostar® mass spectrometer, whose detection limit
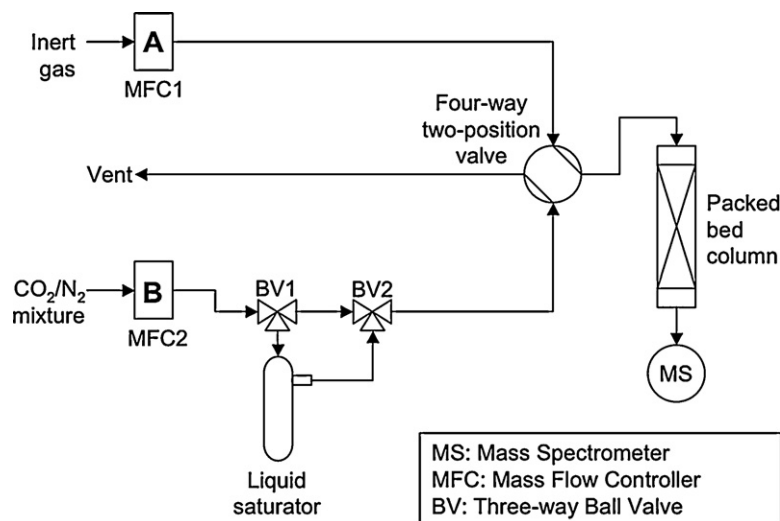
Fig. 1. Experimental set-up for dynamic adsorption measurements.

for CO_2 was estimated to be below 10 ppm. In a typical experiment, the adsorbent was treated at 150 °C for 2 h under a nitrogen flow of 50 mL min^{-1}, then cooled to room temperature and exposed to the CO_2-containing mixture at the same flow rate. The level of humidity was controlled in a similar manner as described for equilibrium measurements using distilled deionized water in a glass saturator submerged in a temperature controlled cooling bath. The complete breakthrough of CO_2 and other species was indicated by the downstream gas composition reaching that of the feed gas.

The adsorption capacity was estimated from the breakthrough curves produced by the MS response using the following equation:

$$n_{adsi} = \frac{FC_{0i}t_{ni}}{W} \tag{1}$$

where n_{adsi} is the dynamic adsorption capacity of any gas i, F is the total molar flow, C_{0i} is the concentration of the gas i entering the column, W is the mass of adsorbent loaded in the column, and t_{ni} is the stoichiometric time corresponding to gas i, which is estimated from the breakthrough profile according to Eq. (2) [25]:

$$t_{ni} = \int_0^t \left(1 - \frac{C_{Ai}}{C_{0i}}\right) dt \tag{2}$$

where C_{0i} and C_{Ai} are the concentrations of any gas i upstream and downstream the column, respectively.

2.5. Adsorption–desorption cycles

To assess the stability of the adsorbent, adsorption–desorption cyclic measurements were carried out on TRI-PE-MCM-41 at different conditions using temperature swing (TS) and temperature-vacuum swing (TVS) regeneration conditions. Because the adsorption–desorption operating conditions may change from one application to another and may depend on the nature of the feed stream, ten adsorption–desorption configurations were explored, as shown in Table 1, and were studied for streams containing pure CO_2 and a CO_2:N_2 = 10:90 mixture.

For example, configuration a represents the conditions that may be found in a TS operation, as desorption occurs under atmospheric pressure and 75 °C under purge gas flowing at 50 mL min^{-1}, whereas configuration b can be associated with a TVS adsorption since regeneration is performed with the aid of vacuum (i.e., $P_D = 0.1$ bar). The experimental procedure was as follows: a sample of ca. 1 g of TRI-PE-MCM-41 was loaded in the Rubotherm apparatus and was exposed to UHP nitrogen at 50 mL min^{-1} for 30 min

at 75, 90 or 120 °C, either under atmospheric pressure or under vacuum (0.1 bar). Subsequently, the sample was cooled down to 25 or 50 °C at isobaric conditions and the feed gas was switched to either pure CO_2 or CO_2:N_2 = 10:90 mixture at 50 mL min^{-1}. The working adsorption capacity (non-equilibrium) was assumed to be the weight gain of the sample after 30 min exposure. The cycle of regeneration and CO_2 adsorption was repeated 10 times for the six sets of adsorption–desorption conditions.

3. Results and discussion

3.1. Characterization of materials

The nitrogen adsorption isotherms of MCM-41, PE-MCM-41 and TRI-PE-MCM-41 are presented in Fig. 2. All isotherms corresponded to the IUPAC Type IV classification, characteristic of mesoporous materials. The structural properties determined by nitrogen adsorption measurements are shown in Table 2. The post-synthesis hydrothermal treatment of MCM-41 afforded a material with significantly larger mean pore diameter (d_p) and V_p without loss in surface area [26]. The pore-expanded support exhibited a d_p of 11.7 nm and a S_{BET} of 1230 m^2 g^{-1}. After grafting, d_p decreased to

Table 1
Cyclic adsorption–desorption configurations.[a]

Configuration	Conditions		
	Adsorption temperature (°C)	Desorption temperature (°C)	Desorption pressure (bar)
a	25	75	1
b	25	75	0.1
c	50	120	1
d	50	120	0.1
e	50	90	1
f	50	90	0.1

[a] Adsorption at atmospheric pressure.

Table 2
Structural properties of mesoporous materials.

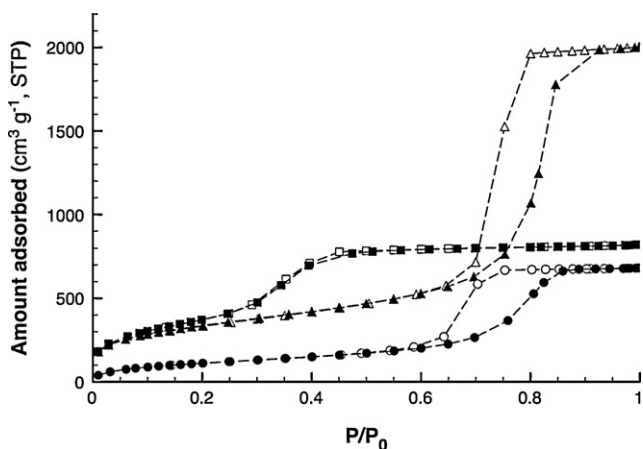| Materials	S_{BET} (m^2 g^{-1})	V_p (cm^3 g^{-1})	d_p (nm)
MCM-41	1490	0.99	3.3
PE-MCM-41	1230	3.09	11.7
TRI-PE-MCM-41	367	0.87	9.4

Fig. 2. Nitrogen adsorption (closed symbols) and desorption (open symbols) isotherms for MCM-41 (squares), PE-MCM-41 (triangles) and TRI-PE-MCM-41 (circles) at 77 K.

9.4 nm, consistent with the occurrence of organic species onto the internal surface. TRI-PE-MCM-41 maintained a relatively large S_{BET} (ca. 367 $m^2 g^{-1}$) and V_p (ca. 0.87 $cm^3 g^{-1}$). The widely open pore structure of surface-modified PE-MCM-41 has been associated with the efficient use of internal functional groups [6,27].

The TGA profile for TRI-PE-MCM-41 is presented in Fig. 3. Since PE-MCM-41 did not undergo any weight loss under TGA up to 1000 °C (not shown), it was inferred that the weight loss for TRI-PE-MCM-41 is associated exclusively with the decomposition of the organic species. This event started at ca. 250 °C, indicating a reasonably high thermal stability. Notice that in some cases, a small weight loss was observed below 200 °C. This was demonstrated to be due to adsorbed water and/or alcohol associated with incomplete hydrolysis of the alkoxysilane [6]. Thus, it was previously established through comparison with elemental analysis, that only the weight loss beyond 200 °C corresponds to the decomposition of the amine-containing chain [6]. Using this method, the amine loading was found to be 7.9 mmol g^{-1}.

Fig. 4 shows the CO_2 adsorption isotherms for MCM-41, PE-MCM-41 and TRI-PE-MCM-41 materials at 25 °C and up to 1 bar. Within the range of CO_2 pressure studied, no significant difference in CO_2 capacity was observed as a result of the hydrothermal pore expansion of MCM-41. However, amine functionalization of the mesoporous silica had a strong impact on the performance of the adsorbent, particularly at very low CO_2 partial pressure. Indeed, TRI-PE-MCM-41 exhibited a high CO_2 uptake in the low
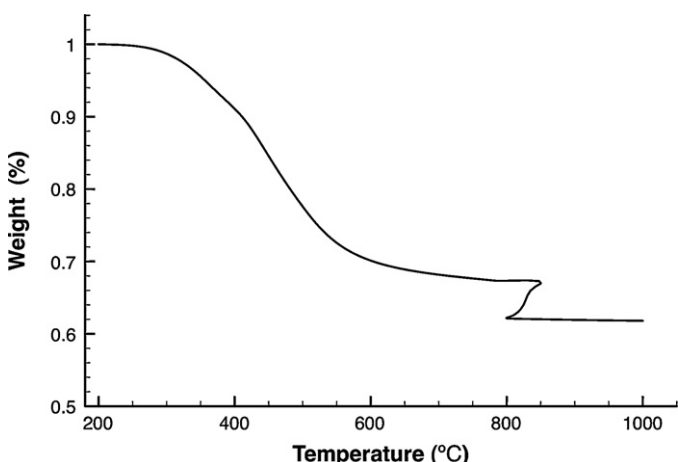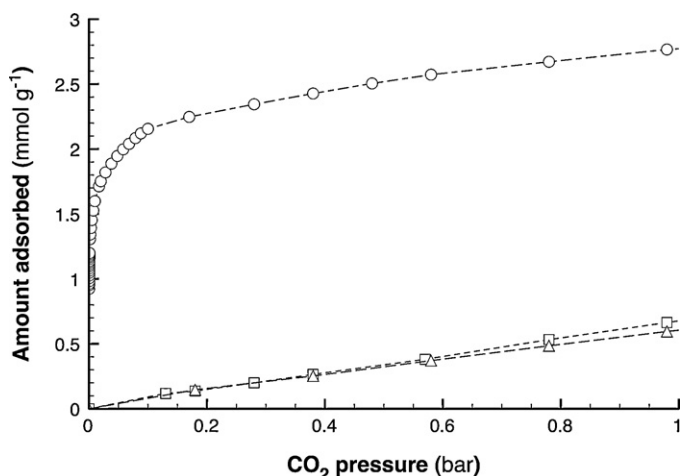

Fig. 4. Adsorption isotherms of CO_2 on MCM-41 (squares), PE-MCM-41 (triangles), and TRI-PE-MCM-41 (circles) at 25 °C.

concentration range, as a result of the interaction of CO_2 with the surface amine sites. The adsorption capacity at 5% of dry CO_2 was 2.05 mmol g^{-1} for TRI-PE-MCM-41, while at the same concentration the capacity exhibited by the non-modified materials was only ca. 0.1 mmol g^{-1}.

3.2. Influence of moisture in the feed

In a previous contribution [18], it was demonstrated that gravimetric analysis often underestimates the CO_2 uptake by amine functionalized materials in humid streams. Thus, to properly assess the influence of moisture on the adsorption of CO_2 on TRI-PE-MCM-41 at equilibrium, mass spectrometry was used. The CO_2 adsorption capacity of TRI-PE-MCM-41 based on the intensity of the 44 amu signal during the TPD of CO_2 adsorbed in the presence of different moisture contents is shown in Fig. 5. The amount of adsorbed CO_2 was found to increase with the concentration of moisture in the feed stream. The CO_2 adsorption capacity was 2.05, 2.19 and 2.51 mol g^{-1} for 0, 27 and 74% relative humidity (RH), respectively. This behavior is in contrast to typical microporous CO_2 physical adsorbents such as 13X zeolite, whose adsorption capacity deteriorates dramatically, even at very low humidity levels (Fig. 5). Enhancement of CO_2 adsorption capacity in wet streams may be explained on the basis of the generally accepted reaction mechanisms between CO_2 and amines, i.e., formation of carbamate
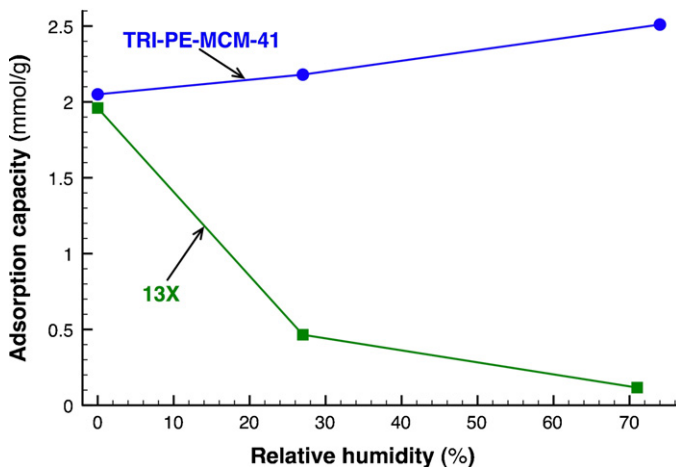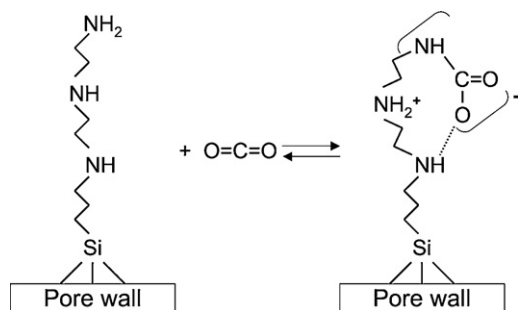

Fig. 3. Thermogravimetric decomposition curve for TRI-PE-MCM-41.

Fig. 5. Adsorption capacity at equilibrium of 5% CO_2/N_2 on TRI-PE-MCM-41 and 13X zeolite at 25 °C in the presence of humidity.

Scheme 1. Carbamate formation pathway on TRI-PE-MCM-41. The dotted line represents a hydrogen bond.

Fig. 7. Adsorption–desorption cycles using TS and TVS configurations *a* and *b* for pure CO_2 and CO_2:N_2 = 10:90 mixture.

(CO_2/N = 0.5) under dry conditions and formation of bicarbonate (CO_2/N = 1) in the presence of moisture. While this promoting effect had been inferred in the past through gravimetric methods, the use of TGA–MS confirms the tolerance of TRI-PE-MCM-41 to moisture, and quantifies the adsorption enhancement.

It is worth mentioning that in dry conditions, the CO_2 to amine ratio (CO_2/N) in the case of TRI-PE-MCM-41 was ca. 0.30, a lower value than the stoichiometric carbamate ratio of 0.5 obtained on grafted primary monoamine [18]. A possible explanation to the lower values of CO_2/N ratio in this case may be associated with recent findings reported by da Silva and Svendsen [28], and Kim and Svendsen [29], who determined the most stable carbamate species formed between CO_2 and various amine molecules. In general, CO_2 forms carbamate with amines that are in close proximity. Further, if the organic species has more than two amine groups, hydrogen bonds may be formed between carbamate and the unreacted amines (Scheme 1), lowering the CO_2/N ratio. Thus, for TRI-PE-MCM-41 two amine groups are likely to react with CO_2 to form carbamate, while the third amine would be inhibited to react further either due to the formation of hydrogen bonds or by steric effects. Consequently, a CO_2/N ratio of 0.33 would be expected from a triamine molecule, a value close to that observed in our adsorbent at dry conditions. The increase of adsorption capacity in the presence of moisture is attributed to the partial formation of bicarbonate species.

With respect to adsorption in packed bed columns, Fig. 6 shows the breakthrough curves of CO_2 at a concentration of 5% balance air under dry conditions and in the presence of 27% RH. The amount of adsorbent was 1 g and the gas stream flow rate was 50 mL min^{-1}. In both cases, N_2 appeared in the column downstream almost immediately after the process has started, indicating a negligi-
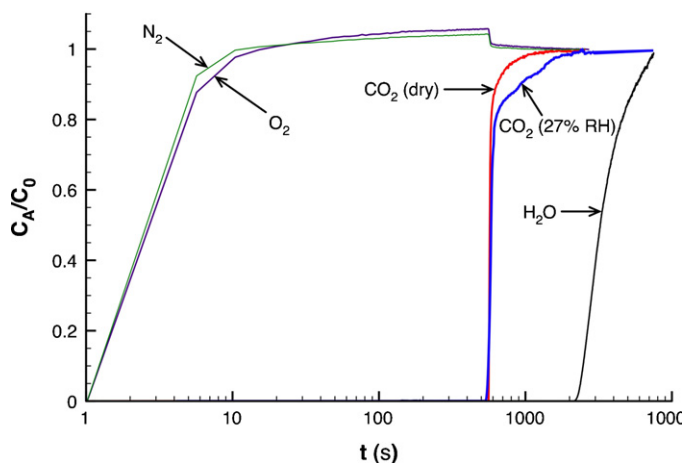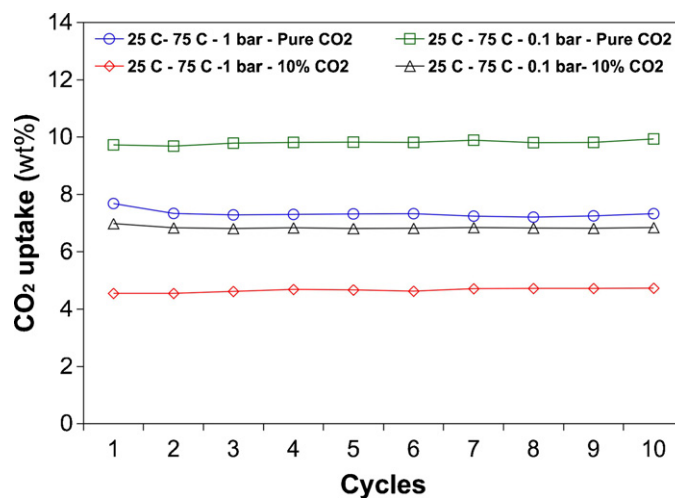
ble adsorption capacity for N_2, in line with the gravimetric data [13]. This was also the case with O_2, whose breakthrough occurred immediately after the start of the adsorption process. No CO_2 was detected downstream the column up to ca. 500 s, demonstrating the high efficiency of TRI-PE-MCM-41 to separate CO_2. The breakthrough of CO_2 was steep and the complete saturation corresponded to a dry CO_2 adsorption capacity of 1.90 ± 0.19 mmol g^{-1}. The CO_2 dynamic adsorption capacity is in good agreement with the gravimetric equilibrium capacity (2.05 mmol g^{-1}) at the same partial pressure, as reported in Fig. 4. From these results, it is concluded that the selectivity of CO_2 over N_2 and O_2 is very high, approaching an infinite value. It is worth mentioning that such selectivity of TRI-PE-MCM-41 toward CO_2 is considerably higher than that exhibited by other typical CO_2 adsorbents like zeolites [30], activated carbon [31] or MOFs [32].

Fig. 6 also shows the breakthrough of water and CO_2 at a RH = 27% under otherwise the same conditions. The calculated dynamic adsorption capacity for CO_2 and water vapor were 1.98 and 2.3 mmol g^{-1}, respectively. As seen, water vapor did not adversely affect the CO_2 adsorption capacity. It is thus inferred that under non-equilibrium adsorption, as far as CO_2 removal is concerned, TRI-PE-MCM-41 is also highly tolerant to moisture. Nevertheless, the anticipated increase in CO_2 adsorption was not observed. As explained in detail in a previous contribution [18], this may be attributed to the comparatively slow kinetics associated with bicarbonate vs. carbamate formation. Thus, observation of enhanced CO_2 adsorption in the presence of water vapor requires a sufficiently long residence time. This requirement does not seem to be achieved under the current dynamic conditions.

3.3. Cyclic measurements

Fig. 7 shows the cyclic adsorption measurements for pure CO_2 and CO_2:N_2 = 10:90 mixture using TS and TVS configurations *a* and *b*, respectively. The adsorption capacity was stable over the ten adsorption–desorption cycles for both pure CO_2 and CO_2:N_2 = 10:90 mixture. Using adsorption at 25 °C and desorption at 75 °C, the adsorption capacity using TVS was ca. 21% and ca. 35% higher than TS for pure CO_2 and CO_2:N_2 = 10:90 mixture, respectively. This may be explained by an incomplete regeneration of adsorption sites at 75 °C and atmospheric pressure. However, the combined effect of T_D = 75 °C and vacuum led to enhanced desorption, thus obtaining a higher CO_2 working capacity. The adsorption capacity of CO_2:N_2 = 10:90 mixture was ca. 40% lower than pure CO_2

Fig. 6. Column breakthrough curves of CO_2 (5% balance air) on TRI-PE-MCM-41 under dry and humid conditions.
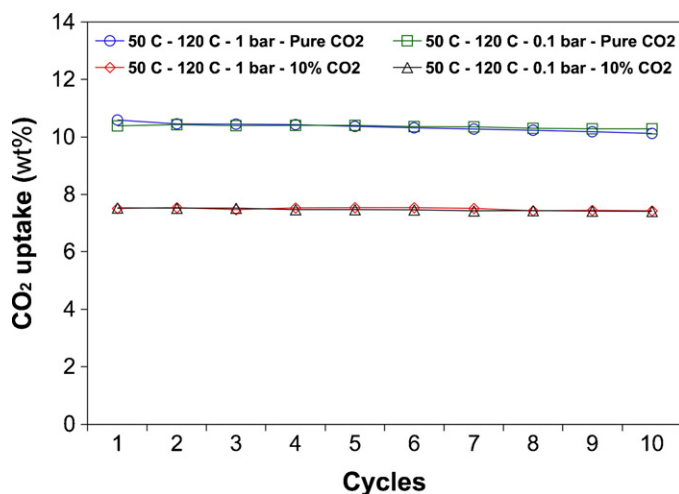
Fig. 8. Adsorption–desorption cycles using TS and TVS regeneration configurations *c* and *d* for pure CO_2 and $CO_2:N_2 = 10:90$ mixture.

using TS configuration *a*, but this difference was only ca. 28% in the TVS configuration *b*. Indeed, the incomplete activation using TS configuration *a*, resulted in less favorable working adsorption capacity than TVS configuration *b*. This clearly shows that TVS configuration *b* is associated with better performances when adsorption and desorption are carried out at relatively low temperature.

Fig. 8 shows the cyclic adsorption measurements for pure CO_2 and $CO_2:N_2 = 10:90$ mixture using TS and TVS configurations *c* and *d*, respectively. Adsorption over the ten cycles can be considered stable since the capacity in cycle 10 was within less than 5% with respect to cycle 1, although a slightly decreasing tendency was observed. With respect to the regeneration configurations, when using adsorption at 50 °C and desorption at 120 °C, the adsorption capacity using either TS or TVS was similar. Accordingly, 120 °C seems to be enough to completely regenerate the adsorbent, leading to a limited effect of vacuum when $T_D \geq 120$ °C is applied. It is important to notice that, although the T_A in configurations *c* and *d* was higher than in *a* and *b*, in terms of adsorption capacity, configurations *c* and *d* outperformed *a* and *b*. These results show that a competitive working adsorption capacity can be obtained even at temperatures higher than ambient if the appropriate regeneration conditions are met.
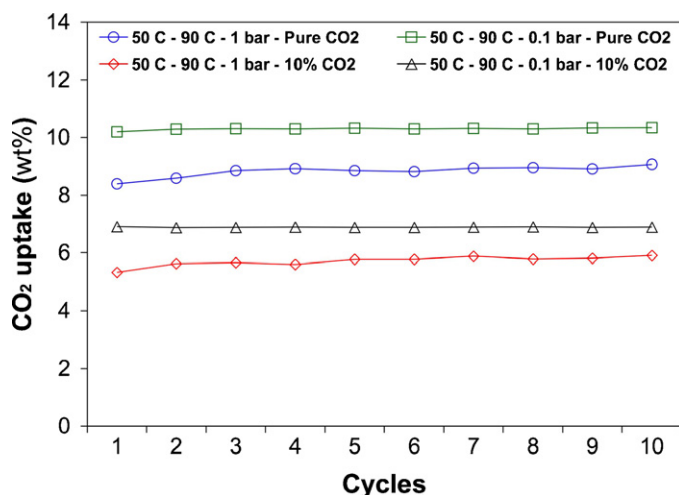
To test the effect of T_D on the working capacity of TRI-PE-MCM-41, cyclic adsorption–desorption measurements using configurations *e* and *f* were performed. While T_A was maintained at 50 °C, in these configurations T_D was decreased to 90 °C. The adsorption capacity throughout ten cycles is presented in Fig. 9. A stable adsorption capacity was observed in all cases. However, the TVS regeneration resulted in a comparatively higher adsorption capacity than when using TS only. These observations are akin to those based on configurations *a* and *b*, suggesting that a comparative advantage of using vacuum during regeneration is only observed when T_D is 90 °C or lower. It is worth noting that configurations *d* and *f* produced very similar adsorption capacity despite the lower T_D used in the latter, particularly in the case of pure CO_2 streams. This suggests that the use of vacuum can lead to a competitive adsorption capacity at low T_D that may be attractive in cases where the use of heat is prohibitive.

Figs. 7–9 show clearly that triamine surface-modified pore-expanded MCM-41 mesoporous silica exhibit different working CO_2 capture performances depending on the regeneration mode used (TS or TVS), T_A and T_D and the CO_2 concentration.

4. Conclusions

This work provides a broad picture of key CO_2 adsorption properties of amine-grafted pore-expanded mesoporous silica. It was demonstrated that, unlike most physical adsorbents, the CO_2 adsorption capacity of TRI-PE-MCM-41 is improved in the presence of moisture while maintaining an infinite selectivity towards CO_2 vs. N_2. Adsorption–desorption cyclic measurements using pure CO_2 and $CO_2:N_2 = 10:90$ mixture showed that TRI-PE-MCM-41 exhibits excellent stability up to $T_D = 120$ °C. It was shown that optimum regeneration strategies for TRI-PE-MCM-41 depend on the temperature of adsorption and desorption, in addition to the adsorbate concentration specific to each intended application. For CO_2 removal at low T_D, for example, temperature-vacuum swing adsorption resulted in a better adsorption working capacity, while at higher T_D, temperature swing adsorption appeared to be a suitable approach.

Fig. 9. Adsorption–desorption cycles using TS and TVS regeneration configurations *e* and *f* for pure CO_2 and $CO_2:N_2 = 10:90$ mixture.

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