

Triamine-grafted pore-expanded mesoporous silica for CO₂ capture: Effect of moisture and adsorbent regeneration strategies

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Published online: 7 August 2010
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Abstract Adsorption of carbon dioxide (CO₂) was investigated on triamine-grafted, pore-expanded MCM-41 mesoporous silica (TRI-PE-MCM-41). Measurements of adsorption capacity using mass spectrometry showed an enhanced CO₂ adsorption capacity in humid streams compared to dry CO₂. This was corroborated with breakthrough experiments, which also showed that TRI-PE-MCM-41 offered a practically infinite selectivity towards CO₂ over nitrogen. Cyclic measurements of pure CO₂ and CO₂:N₂ = 10:90 mixture using different regeneration modes showed that amine-grafted PE-MCM-41 is particularly suitable for CO₂ removal using temperature swing adsorption (TSA) at adsorption temperatures higher than ambient, while temperature-vacuum swing adsorption (TVSA) may be attractive at ambient temperature.

Keywords CO₂ capture · Adsorption capacity · Adsorption selectivity · Adsorbent regeneration · TSA · TVSA

1 Introduction

Carbon dioxide (CO₂) has drawn particular attention for being the main anthropogenic contributor to climate change. Gas absorption using alkanolamine solvents is nowadays the preferred technology used industrially for CO₂ scrubbing. However, this technology is recognized to have several drawbacks due to its high demand of energy and the corrosive nature of the absorbent (Audus 1997; Meisen and

Shuai 1997; Aaron and Tsouris 2005). Consequently, extensive efforts have been devoted in recent years to the development of novel strategies to prevent the release of greenhouse gases, particularly CO₂ into the atmosphere (Yang et al. 2008a). Compared to other separation technologies, adsorption is recognized as an efficient and economically attractive candidate to complement or replace the current absorption processes (Aaron and Tsouris 2005). The adsorption approach is expected to combine high selectivity and productivity, while offering low energy requirements to regenerate the solid adsorbent.

An ideal medium for CO₂ adsorption should combine different properties including: (i) high CO₂ dynamic adsorption capacity, (ii) high selectivity toward CO₂, (iii) low energy requirements for regeneration, (iv) stability to prolonged adsorption-desorption cycling, and (v) tolerance to the presence of moisture. Inspired by liquid amine scrubbing technology, a number of research groups developed solid-supported amines as adsorbents for CO₂ separation (Birbara et al. 2002; Gray et al. 2007; Harlick and Sayari 2007; Jones et al. 2007; Olah et al. 2008). However, the effect of various conditions relevant to industrial applications, such as the presence of humidity in the feed stream and the stability of the adsorbent through repetitive adsorption-desorption cycles are yet to be investigated.

In this paper, the adsorption of CO₂ on amine-grafted mesoporous silica type MCM-41 with enlarged pores was investigated at equilibrium and under dynamic conditions in dry and humid streams. The behavior of the adsorbent through various adsorption-desorption cycles was also monitored, and the effects of adsorption temperature (T_A), desorption temperature (T_D) and desorption pressure (P_D) were studied.

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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%, balance 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, CO₂ grade 4 purity, and certified gas mixtures of CO₂ balance N₂ were supplied by Linde Canada. All reagents and gases were used without further purification.

2.2 Synthesis of mesoporous adsorbent (TRI-PE-MCM-41)

The pore-expanded mesoporous support was prepared in two steps based on a procedure described elsewhere (Sayari et al. 1998; Kruk et al. 2000). Briefly, MCM-41 type silica was synthesized at 100 °C using CTAB as structure directing agent in the presence of TMAOH. A pore expansion procedure followed, using DMDA as swelling agent at 120 °C for 3 days (Sayari et al. 1999, 1998; Serna-Guerrero and Sayari 2007). The surfactant template and expander agent were removed by heating the material at 550 °C under flowing nitrogen followed by calcination in air for 5 h at the same temperature. The obtained product was labeled PE-MCM-41.

Incorporation of the amine functionality was achieved via surface grafting following a procedure described elsewhere (Harlick and Sayari 2007). 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 PE-MCM-41 of distilled deionized water was 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 gram of silica) 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 77 K using a Micromeritics ASAP 2020 volumetric apparatus.

Prior to measurements, the samples were degassed under vacuum at 150 °C for 5 hours. The surface area was determined by the BET method, whereas the pore size distribution was calculated using the Kruk-Jaroniec-Sayari (KJS) approach (Kruk et al. 1997). The pore volume was determined as the amount of liquid nitrogen adsorbed at $P/P_0 = \text{ca. } 1$. 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 considered as propylamine loss (Harlick and Sayari 2007).

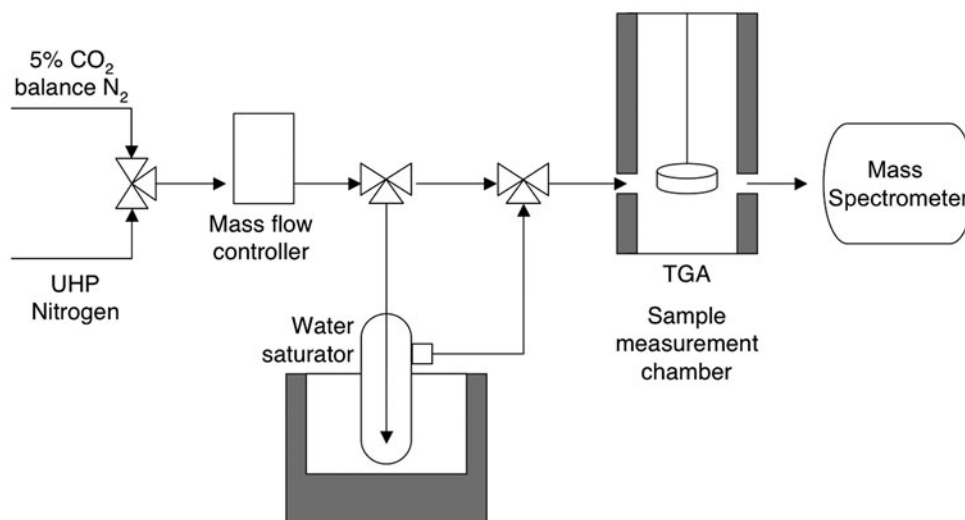
Single gas adsorption equilibrium measurements for CO₂ were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany). More details about this experimental set-up and procedure may be found elsewhere (Belmabkhout and Sayari 2009). Briefly, the materials studied (MCM-41, PE-MCM-41 and TRI-PE-MCM-41) were activated at 423 K 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 CO₂ under the desired pressure. Equilibration time was allowed until no significant change in the weight of the sample recorded by the Rubotherm microbalance 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 CO₂ adsorption capacity at equilibrium was measured using the above-mentioned TGA instrument coupled with a Pfeiffer ThermoStar mass spectrometer. The experimental procedure for this analysis involved the following steps: (i) activation of the adsorbent, (ii) adsorption of CO₂, (iii) temperature programmed desorption (TPD) of CO₂ and (iv) decomposition of the organic layer of the adsorbent to determine the actual amine content of the 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 N₂ at 150 °C since it has been demonstrated that the grafted amine species are stable up to 250 °C (Harlick and Sayari 2007) and any CO₂ and moisture adsorbed from ambient air desorbs below 140 °C (Khatri et al. 2006). In addition, non-hydrolyzed methoxy groups are also removed during the activation step (Harlick and Sayari 2007). After pretreatment, the temperature was decreased to 25 °C and the gas stream switched to a mixture containing 5% CO₂ balance N₂. To control the relative humidity (RH) in the stream, the mixture of CO₂ in N₂ was bubbled through a glass saturator

Fig. 1 Schematic representation of the experimental setup used for adsorption measurements



containing distilled deionized water in a temperature controlled cooling bath before entering the measurement chamber of the TGA, as shown in Fig. 1. The flow of CO₂ mixture continued 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 CO₂ adsorbed, particularly in the presence of moisture, a method using mass spectrometry (MS) was used (Serna-Guerrero et al. 2008), as it has been suspected that the commonly used gravimetric analysis may underestimate the CO₂ uptake. The MS was calibrated using different amounts of CO₂ obtained by decomposition of known quantities of high purity CaCO₃ under flowing nitrogen at a heating rate of 10 °C min⁻¹ in the TGA instrument. A blank experiment was used for baseline correction. Simultaneous TGA measurements allowed precise determination of the amounts of CO₂ released. The established linear relationship between the area of the 44 amu MS signal after baseline correction and the amount of CO₂ was used to quantify the CO₂ released from the adsorbent during temperature programmed desorption (TPD).

In addition, breakthrough measurements were performed using the experimental set-up shown in Fig. 2 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% CO₂ balance N₂. The stainless steel column used has 120 mm in length and 6.4 mm of inner diameter. The column effluent was monitored using a Pfeiffer ThermoStar® mass spectrometer, whose detection limit for CO₂ was estimated to be below 10 ppm. In a typical experiment, the adsorbent was treated at 120 °C for 2 hours under a nitrogen flow of 50 mL min⁻¹, then cooled to room temperature, finally switching the feed gas to the mixture containing CO₂ at the same flow rate. The level of humidity was controlled in a similar manner as described for

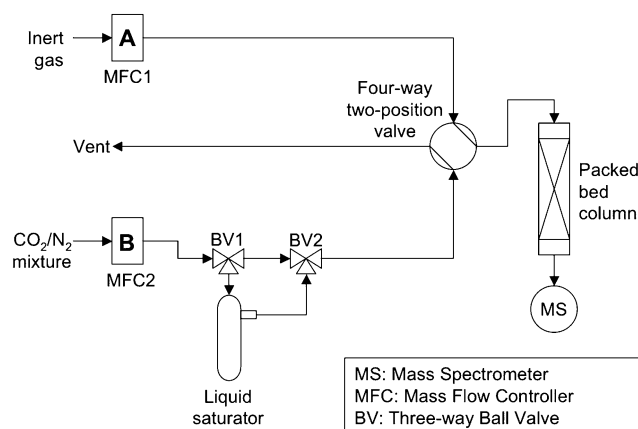


Fig. 2 Experimental setup for dynamic adsorption measurements

equilibrium measurements using distilled-deionized water in a glass saturator submerged in a temperature-controlled cooling bath. The complete breakthrough of CO₂ 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:

$$n_{\text{adsi}} = \frac{F C_{0i} t_{ni}}{W} \quad (1)$$

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 (2) (Claudino et al. 2004):

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

Table 1 Cyclic adsorption-desorption configurations

Configuration	Conditions			
	Adsorption temperature (°C)	Desorption temperature (°C)	Adsorption pressure (bar)	Desorption pressure (bar)
<i>a</i>	25	75	1	1
<i>b</i>	25	75	1	0.1
<i>c</i>	50	120	1	1
<i>d</i>	50	120	1	0.1
<i>e</i>	70	150	1	1
<i>f</i>	70	150	1	0.1

where C_{0i} and C_{Ai} are the concentrations of any gas i up-stream 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 adsorption (TSA) and temperature vacuum swing adsorption (TVSA) configurations. Because the adsorption-desorption operating conditions may change from one application to another and may depend on the nature of the feedstock, six adsorption-desorption configurations were selected, as shown in Table 1, and were studied using pure CO₂ and a CO₂:N₂ = 10:90 mixture.

For example, configuration *a* represents a typical TSA, as desorption occurs under atmospheric pressure and 75 °C under purge gas flowing at 50 mL min⁻¹, whereas configuration *b* is a TVSA since regeneration is performed under 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, 120 or 150 °C, either under atmospheric pressure for TSA experiments or under vacuum (0.1 bar) for TVSA measurements. Subsequently, the sample was cooled down to 25, 50, or 70 °C at isobaric conditions and the feed gas was switched to either pure CO₂ or CO₂:N₂ = 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. This procedure (i.e., regeneration and CO₂ adsorption) was repeated over 10 cycles for the six sets of adsorption-desorption conditions.

3 Results and discussion

3.1 Characterization

The structural properties of MCM-41, PE-MCM-41, and TRI-PE-MCM-41 as determined by nitrogen adsorption

Table 2 Structural properties of mesoporous materials determined by nitrogen adsorption

Materials	S_{BET} (m ² /g)	V_p (cm ³ /g)	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

measurements are shown in Table 2. As can be seen, the post-synthesized hydrothermal treatment of MCM-41 afforded a material with significantly larger pore size and volume without loss in surface area (S_{BET}). The pore-expanded support exhibited a mean pore diameter (d_p) of 11.7 nm and a S_{BET} of 1230 m² g⁻¹. After grafting, the mean pore size decreased to 9.4 nm. TRI-PE-MCM-41 maintained a relatively large surface area (ca. 367 m² g⁻¹) and pore volume (ca. 0.87 cm³ g⁻¹). The typical amine loading of TRI-PE-MCM-41 determined by TGA was 7.9 mmol g⁻¹. The widely open pore structure of surface-modified PE-MCM-41 has been associated with the efficient use of internal functional groups (Harlick and Sayari 2007; Reynhardt et al. 2005).

Figure 3 shows the CO₂ adsorption isotherms for MCM-41, PE-MCM-41 and TRI-PE-MCM-41 materials at 298 K and up to 1 bar. Within the range of CO₂ pressure studied, no significant difference in CO₂ capacity was observed as a result of the hydrothermal pore-expansion of MCM-41. However, functionalization of the mesoporous silica had a strong impact on the performance of the adsorbent, particularly at very low CO₂ partial pressure. Indeed, TRI-PE-MCM-41 exhibited a high CO₂ uptake in the low concentration range, as a result of the interaction of CO₂ with the surface amine sites. The adsorption capacity at 5% of dry CO₂ was 2.05 mmol g⁻¹ for TRI-PE-MCM-41, while at the same concentration the capacity exhibited by MCM-41 and PE-MCM-41 was only ca. 0.1 mmol g⁻¹.

Fig. 3 Adsorption isotherms of CO_2 on MCM-41 (squares), PE-MCM-41 (triangles), and TRI-PE-MCM-41 (circles)

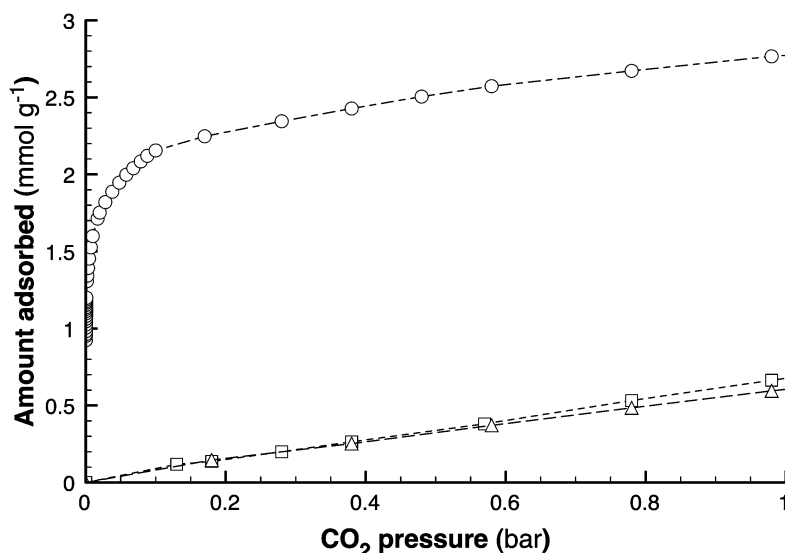
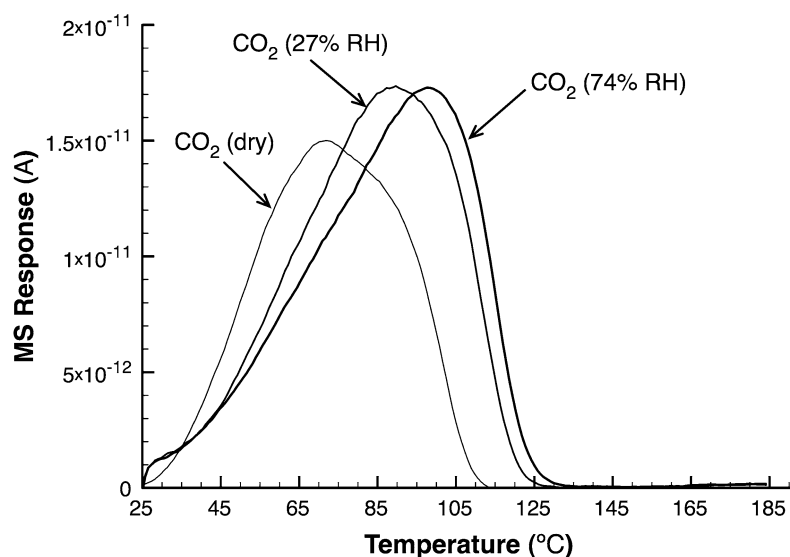


Fig. 4 TPD profiles of CO_2 released after adsorption on TRI-PE-MCM-41 under various levels of humidity



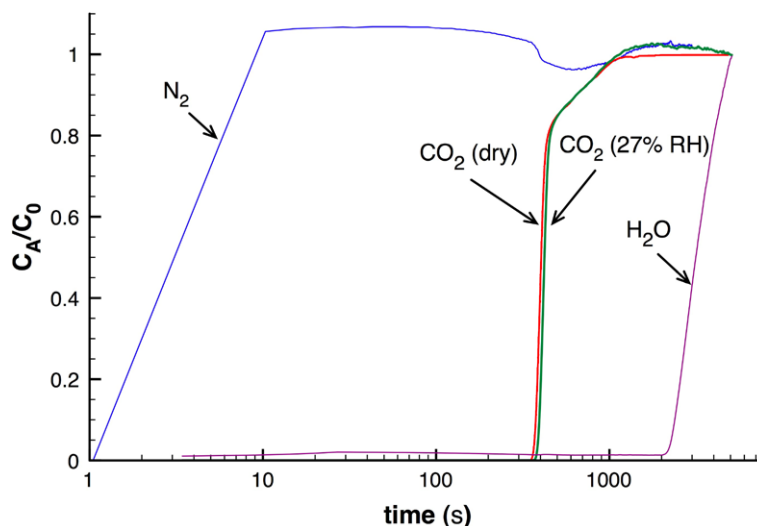
3.2 Humid CO_2 adsorption

The 44 amu signals recorded by MS during TPD of CO_2 adsorbed on TRI-PE-MCM-41 in the presence of different moisture contents are presented in Fig. 4. In a previous work (Serna-Guerrero et al. 2008), 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, mass spectrometry was used in this work. 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 2.12, 2.44 and 2.51 mol g^{-1} for 0, 27 and 74% relative humidity (RH), respectively. 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 ($\text{CO}_2/\text{N} = 0.5$) under dry conditions and partial formation of bicarbonate ($\text{CO}_2/\text{N} = 1$) in the presence of moisture. Interestingly, this is the first time that the promoting effect of moisture is observed directly by mass spectrometry on mesoporous silica grafted with organic molecules containing primary and secondary amine groups.

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. 0.27, a lower value than that observed during the formation of carbamate species on grafted primary monoamines, i.e., 0.5 (Serna-Guerrero et al. 2008). A possible explanation to the lower values of CO_2/N ratio in this case can be found in the works of da Silva et al. (2006) and Kim et al. (2007) where the most stable carbamate species formed between CO_2 and various liquid amine molecules were de-

Fig. 5 Breakthrough curves of CO₂ (5% balance N₂) on TRI-PE-MCM-41 under dry and humid conditions



terminated. According to such studies, when more than one amine group is present in the molecule, the CO₂ forms carbamate with two amine groups that are in close proximity from each other, but it also forms hydrogen bonds with adjacent secondary amines. Thus, for the tri-amine molecule in TRI-PE-MCM-41 two amine groups would react with CO₂ to form carbamate, while the third amine would be inhibited to react further due to the formation of hydrogen bonds, resulting in a CO₂/N ratio of 0.33, a value close to that observed in our adsorbent at dry conditions. With respect to the interaction with humid streams, unlike physical adsorbents, the adsorption capacity of TRI-PE-MCM-41 is not hindered by the presence of moisture and, on the contrary, it was improved in ca. 15% with respect to dry streams. The increase in 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. 5 shows the breakthrough curves of CO₂ at a concentration of 5% balance N₂ under dry conditions and in the presence of 27% RH. As seen, N₂ appears in the column downstream almost immediately after the process has started, indicating a very small adsorption capacity for N₂, if any. Within an accuracy of 10 ppm, no CO₂ was detected downstream the column up to ca. 250 s, demonstrating the high efficiency of TRI-PE-MCM-41 to separate CO₂. The breakthrough of CO₂ was steep and the complete saturation corresponded to a CO₂ adsorption capacity of 1.90 ± 0.19 mmol/g. The CO₂ 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. 3. From these results, it is concluded that the selectivity of CO₂ over N₂ is very high, approaching an infinite value. It is worth mentioning that the selectivity of TRI-PE-MCM-41 toward CO₂ versus N₂ is considerably higher than that exhibited by other typical CO₂ adsorbents like zeolites (Cavenati et al. 2004),

activated carbon (Dreisbach et al. 1999) or MOFs (Yang et al. 2008b), and even other amine-grafted adsorbents such as polyethylenimine-containing MCM-41 silica (Xu et al. 2003) and 3-aminopropyltriethoxysilane-grafted MCM-48 (Kim et al. 2005). Figure 5 shows that the breakthrough profile of CO₂ is not affected negatively under humid streams demonstrating that, although a significant uptake of water was observed, TRI-PE-MCM-41 is highly tolerant to moisture when removing CO₂.

3.3 Cyclic measurements

Figure 6 shows the cyclic adsorption measurements for pure CO₂ and CO₂:N₂ = 10:90 mixture using TSA and TVSA configurations *a* and *b*, respectively. The adsorption capacity was stable over the ten cycles for these adsorption-desorption configurations for both pure CO₂ and CO₂:N₂ = 10:90 mixture. Using adsorption at 25 °C and desorption at 75 °C, the adsorption capacity using TVSA was ca. 21% and ca. 35% higher than TSA for pure CO₂ and CO₂:N₂ = 10:90 mixture, respectively. The adsorption capacity of CO₂:N₂ = 10:90 mixture was ca. 40% lower than pure CO₂ using TSA configuration, but this difference was only ca. 28% in the TVSA configuration. This clearly shows that TVSA configuration is associated with better performances than TSA when adsorption and desorption are performed at relatively low temperature.

Figure 7 shows the cyclic adsorption measurements for pure CO₂ and CO₂:N₂ = 10:90 mixture using TSA and TVSA configurations *c* and *d*, respectively. The adsorption capacity was once again stable over the ten cycles for the two adsorption-desorption configurations for both pure CO₂ and CO₂:N₂ = 10:90 mixture. Using adsorption at 50 °C and desorption at 120 °C, the adsorption capacity using either TSA or TVSA was similar. It is important to notice that, although the T_A in configurations *c* and *d* was higher than that

Fig. 6 Adsorption-desorption cycles using TSA and TVSA configurations *a* and *b* for pure CO₂ and CO₂:N₂ = 10:90 mixture

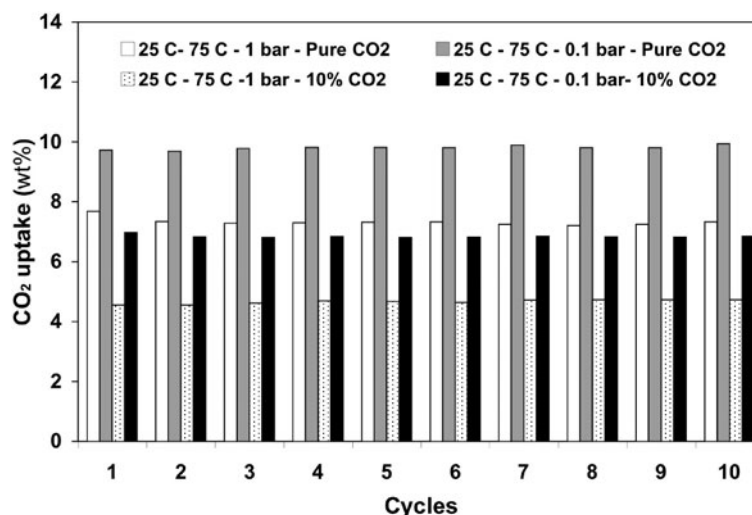
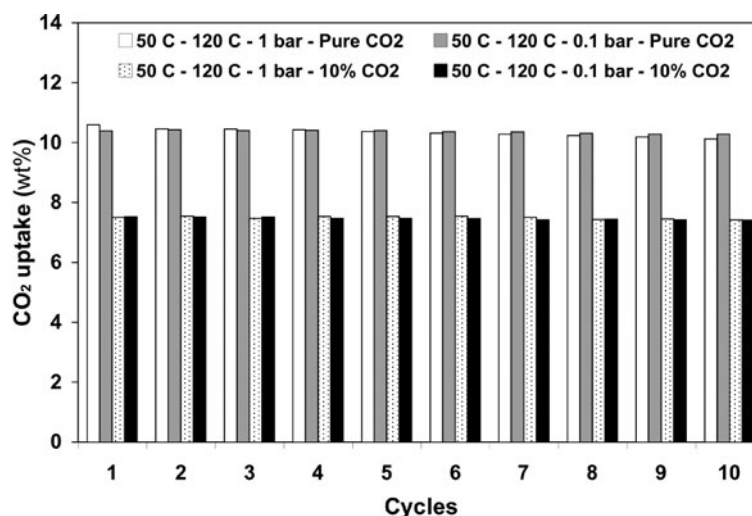


Fig. 7 Adsorption cycles using TSA and TVSA regeneration configurations *c* and *d* for pure CO₂ and CO₂:N₂ = 10:90 mixture



in configurations *a* and *b*, in terms of adsorption capacity, configurations *c* and *d* outperformed largely configurations *a* and *b*. This may be due to the higher T_D (120 °C) used in configurations *c* and *d*, showing that improved working adsorption capacity can be obtained at temperatures higher than ambient if the appropriate regeneration conditions are met.

Figure 8 shows the cyclic adsorption measurements for pure CO₂ and CO₂:N₂ = 10:90 mixture using TSA and TVSA configurations *e* and *f*, respectively. Using adsorption at 70 °C and desorption at 150 °C, the working adsorption capacity using TVSA was ca. 15% higher than TSA in the case of pure CO₂ but identical in the presence of CO₂:N₂ = 10:90 mixture. The average difference between the working adsorption capacity of CO₂:N₂ = 10:90 and pure CO₂ was only ca. 20% in the case of TSA vs. ca. 30% in the TVSA case. However, configurations *e* and *f* exhibited the lowest working CO₂ adsorption capacity. Additionally, and

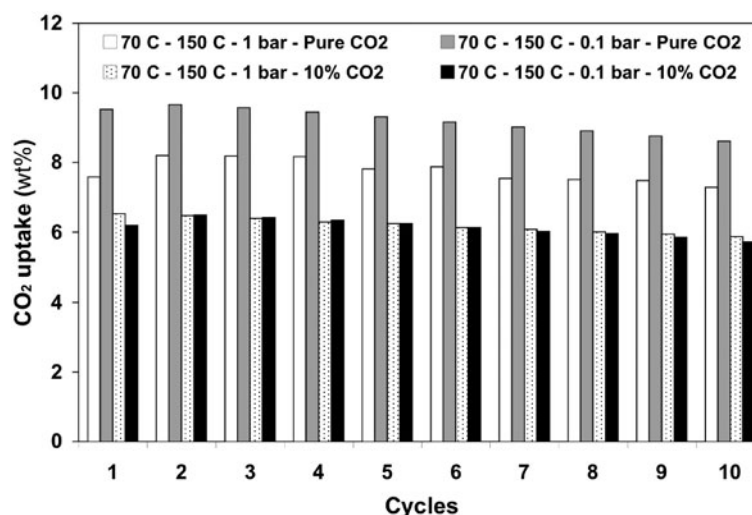
unlike configurations *a*, *b*, *c* and *d*, a steady decrease of working adsorption capacity was observed over the ten cycles for both pure CO₂ and CO₂:N₂ = 10:90 mixture, estimated on ca. 10% between cycles. This suggests that 150 °C is not appropriate as desorption temperature for TRI-PE-MCM-41.

Figures 6, 7 and 8 show clearly that triamine surface-modified pore-expanded MCM-41 mesoporous silica exhibit different working CO₂ capture performances depending on the regeneration mode used (TSA or TVSA), T_A and T_D . The best CO₂ removal performance observed for TVSA was configuration *b* while for TSA it was configuration *c*.

4 Conclusions

This work shows a broad picture of key CO₂ adsorption properties of amine-grafted pore-expanded mesoporous sil-

Fig. 8 Adsorption cycles using TSA and TVSA regeneration configurations *e* and *f* for pure CO₂ and CO₂:N₂ = 10:90 mixture



ica. Adsorption experiments using a packed bed column showed that it is possible to produce high purity gases over TRI-PE-MCM-41 with an efficient use of the column, as indicated by the steep shape of the breakthrough curve. It was demonstrated that, unlike most physical adsorbents, the CO₂ adsorption capacity of TRI-PE-MCM-41 is improved in the presence of moisture while maintaining an infinite selectivity towards CO₂ versus N₂. Adsorption-desorption cyclic measurements using pure CO₂ and CO₂:N₂ = 10:90 mixture showed that TRI-PE-MCM-41 exhibits excellent stability up to $T_D = 120^\circ\text{C}$. It was shown that an appropriate set of regeneration conditions for TRI-PE-MCM-41 depends on the temperature of adsorption, specific to each intended application. Indeed, TRI-PE-MCM-41 could be used to treat gas streams at temperatures higher than ambient if the appropriate regeneration conditions are met. For CO₂ removal at ambient temperature, for example, temperature-vacuum swing adsorption resulted in a better adsorption working capacity, while at higher T_A , temperature swing adsorption appears to be a suitable approach.

Acknowledgements The financial support of the Natural Science and Engineering Council of Canada (NSERC) and Canadian Institute of Health Research (CIHR) is acknowledged. A.S. thanks the Federal Government for the Canada Research Chair in *Nanostructured Materials for Catalysis and Separation* (2001–2015). R. S-G. thanks the Mexican National Council for Science and Technology (CONACYT) for a graduate studies scholarship.

References

- Aaron, D., Tsouris, C.: Separation of CO₂ from flue gas: A review. *Sep. Sci. Technol.* **40**, 321 (2005)
- Audus, H.: Greenhouse gas mitigation technology: An overview of the CO₂ capture and sequestration studies and further activities of the IEA greenhouse gas R&D program. *Energy* **22**, 217 (1997)
- Birbara, P., Filburn, T., Michels, H., Timothy, N.: Sorbent system and method for absorbing carbon dioxide (CO₂) from the atmosphere of a closed habitable environment. US Patent 6,364,938 (2002)
- Belmabkhout, Y., Sayari, A.: Effect of pore expansion and amine functionalization of mesoporous silica on CO₂ adsorption over a wide range of pressure and temperature. *Adsorption* **15**, 318 (2009)
- Cavenati, S., Grande, C.A., Rodrigues, A.E.: Adsorption equilibrium of methane, carbon dioxide, and nitrogen on zeolites 13X at high pressures. *J. Chem. Eng. Data* **49**, 1095 (2004)
- Claudino, A., Soares, J.L., Moreira, R.F.P.M., Jose, H.J.: Adsorption equilibrium and breakthrough analysis for NO adsorption on activated carbons at low temperatures. *Carbon* **42**, 1483 (2004)
- da Silva, E.F., Svendsen, H.F.: Study of the carbamate stability of amines using ab initio methods and free-energy perturbations. *Ind. Eng. Chem. Res.* **45**, 2497 (2006)
- Dreisbach, F., Staudt, R., Keller, J.U.: High pressure adsorption data of methane, nitrogen, carbon dioxide and their ternary mixture on activated carbon. *Adsorption* **5**, 215 (1999)
- Meisen, A., Shuai, X.: Research and development issues in CO₂ capture. *Energy Convers. Manag.* **38**, S37 (1997)
- Gray, M.L., Champagne, K.J., Soong, Y., Filburn, T.: High capacity immobilized amine sorbents. US Patent 7,288,136 (2007)
- Harlick, P.J.E., Sayari, A.: Applications of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO₂ dynamic and equilibrium adsorption performance. *Ind. Eng. Chem. Res.* **46**, 446 (2007)
- Khatri, R.A., Chuang, S.C.C., Soong, Y., Gray, M.: Thermal and chemical stability of regenerable solid amine sorbent for CO₂ capture. *Energy Fuels* **20**, 1514 (2006)
- Kim, S., Ida, J., Gulians, V., Lin, J.Y.S.: Tailoring pore properties of MCM-48 silica for selective adsorption of CO₂. *J. Phys. Chem. B* **109**, 6287 (2005)
- Kim, I., Svendsen, H.F.: Heat of absorption of carbon dioxide (CO₂) in monoethanolamine (MEA) and 2-(aminoethyl)ethanolamine (AEEA) solutions. *Ind. Eng. Chem. Res.* **46**, 5803 (2007)
- Kruk, M., Jaroniec, M., Sayari, A.: Application of large pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements. *Langmuir* **13**, 6267 (1997)
- Kruk, M., Jaroniec, M., Sayari, A.: New insights into pore-size expansion of mesoporous silicates using long-chain amines. *Microporous Mesoporous Mater.* **35–36**, 545 (2000)
- Jones, C.W., Hicks, J.C., Fauth, D.J., Gray, M.: Structures for capturing CO₂, methods of making the structures and methods for capturing CO₂. US Patent application 20070149398 (2007)
- Olah, G., Goepert, A., Meth, S., Prakash, S.: Nano-structure supported solid regenerative polyamine and polyamine polyol adsorbents for the separation of carbon dioxide from gas mixtures including the air. Int. Patent Application WO2008/021700 A1 (2008)

- Reynhardt, J.P.K., Yang, Y., Sayari, A., Alper, H.: Polyamidoamine dendrimers prepared inside the channels of pore-expanded periodic mesoporous silica. *Adv. Funct. Mater.* **15**, 1641 (2005)
- Sayari, A., Kruk, M., Jaroniec, M., Moudrakovski, I.L.: New approaches to pore size engineering of mesoporous silicates. *Adv. Mater.* **10**, 1376 (1998)
- Sayari, A., Yang, Y., Kruk, M., Jaroniec, M.: Expanding the pore size of MCM-41 silicas: use of amines as expanders in direct synthesis and postsynthesis procedures. *J. Phys. Chem. B* **103**, 3651 (1999)
- Serna-Guerrero, R., Sayari, A.: Applications of pore-expanded mesoporous silica. 7. Adsorption of volatile organic compounds. *Environ. Sci. Technol.* **41**, 4761 (2007)
- Serna-Guerrero, R., Da'na, E., Sayari, A.: New insights into the interactions of CO₂ with amine-functionalized silica. *Ind. Eng. Chem. Res.* **47**, 9406 (2008)
- Xu, X., Song, C., Andersen, J.M., Miller, B.G., Scaroni, A.W.: Preparation and characterization of novel “molecular basket” adsorbents based on polymer-modified mesoporous molecular sieve MCM-41. *Microporous Mesoporous Mater.* **62**, 29 (2003)
- Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, B.R., Bland, A.E., Wright, I.: Progress in carbon dioxide separation and capture: A review. *J. Environ. Sci.* **20**, 14 (2008a)
- Yang, Q., Zhong, C., Chen, J.F.: Computational study of CO₂ storage in metal-organic frameworks. *J. Phys. Chem. C* **112**, 1562 (2008b)