Adsorption (2011) 17: 395–401
DOI 10.1007/s10450-011-9348-0

Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: application for CO_2 separation

Youssef Belmabkhout · Rodrigo Serna-Guerrero · Abdelhamid Sayari

Received: 17 January 2010 / Accepted: 16 February 2011 / Published online: 1 March 2011

Abstract Adsorption of CO_2, N_2, CH_4 and H_2 on triamine-grafted pore-expanded MCM-41 mesoporous silica (TRI-PE-MCM-41) was investigated at room temperature in a wide range of pressure (up to 25 bar) using gravimetric measurements. The material was found to exhibit high affinity toward CO_2 in comparison to the other species over the whole range of pressure. Column-breakthrough dynamic measurements of CO_2-containing mixtures showed very high selectivity toward CO_2 over N_2, CH_4 and H_2 at CO_2 concentrations within the range of 5 to 50%. These conditions are suitable for effective removal of CO_2 at room temperature from syngas, flue gas and biogas using temperature swing (TS) or temperature-pressure swing (TPS) regeneration mode. Moreover, TRI-PE-MCM-41 was found to be highly stable over hundreds of adsorption-desorption cycles using TPS as regeneration mode.

Keywords Adsorption · CO_2 adsorption · CO_2 adsorption selectivity · CO_2 separation · CO_2 removal

1 Introduction

The greenhouse gas emission in the world increased considerably, due mostly to the combustion of fossil fuels for power generation and transportation (Thambimuthu 2002). Although the transition toward more sustainable energy sources is urgently needed for environmental sustainability, fossil fuels are likely to remain the dominant energy supply for the foreseeable future. Therefore, reduction of CO_2 emissions into the atmosphere through capture and sequestration, as well as increased use of low or zero CO_2 emission energy sources like biomethane and other renewable forms of energy, are recognized as major strategies to address global warming.

Gas absorption using alkanolamine solutions is the most common technology for CO_2 scrubbing from large point sources. However, this technology is highly energy intensive and associated with severe corrosion problems (Audus 1997; Meisen and Shuai 1997; Aaron and Tsouris 2005). In contrast, adsorption is recognized to be an attractive alternative for CO_2 removal due to its lower energy requirements (Aaron and Tsouris 2005). Numerous CO_2 adsorbents like zeolites (Cavenati et al. 2005; Konduru et al. 2007; Brandani and Ruthven 2004; Bonenfant et al. 2008) and carbons (Himeno et al. 2005) are used commercially for the removal of CO_2. In addition, considerable research effort has been made in recent years to develop novel CO_2 adsorbents like basic oxides (Feng et al. 2007; Wang et al. 2008; Lee et al. 2008; Symonds et al. 2009), metal-organic frameworks (MOFs) (Millward and Yaghi 2005; Llewellyn et al. 2006, 2008; Yang et al. 2008; Arstad et al. 2008), organosilicas and surface-modified silicas (Zelenak et al. 2008; Harlick and Sayari 2006, 2007; Hicks et al. 2008; Chaffee et al. 2007; Gray et al. 2005; Yue et al. 2008; Belmabkhout and Sayari 2009a; Serna-Guerrero et al. 2008; Chang et al. 2009). The purpose of this endeavor was to develop competitive materials with suitable adsorption capacity and excellent selectivity toward CO_2 versus other gases such as N_2, CH_4 and H_2. In earlier contributions (Harlick and Sayari 2007; Belmabkhout and Sayari 2009a), our group showed

Electronic supplementary material The online version of this article (doi:10.1007/s10450-011-9348-0) contains supplementary material, which is available to authorized users.

Y. Belmabkhout · R. Serna-Guerrero · A. Sayari (✉)
Department of Chemistry and Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada
e-mail: abdel.sayari@uottawa.ca

that triamine-modified pore-expanded MCM-41 silica (TRI-PE-MCM-41) adsorbent exhibits promising properties in terms of CO_2 uptake, rate of adsorption and CO_2/N_2 molar selectivity ratio over a wide range of pressure. Moreover, this material was found to be completely regenerable, thermally stable and tolerant to moisture-containing feeds. In another report (Belmabkhout et al. 2010) dealing with CO_2 adsorption at low partial pressure (<5%), we showed that TRI-PE-MCM-41 exhibits high CO_2 adsorption capacity and CO_2 selectivity over N_2, O_2, CH_4 and H_2, suitable for different gas purification applications. The current work is devoted to the adsorptive properties of TRI-PE-MCM-41 in the presence of mixtures containing high concentration of CO_2, typically from 5 to 50%. Single component adsorption of N_2, CH_4 and H_2 on TRI-PE-MCM-41 was investigated at ambient temperature and at pressures up to 25 bar. Dynamic column-breakthrough experiments of CO_2 in binary mixtures with compositions typical of flue gas, biogas and syngas, was investigated. To evaluate the stability of the material during prolonged operation, extensive adsorption-desorption cycling was carried out. The potential of using TRI-PE-MCM-41 for CO_2 separation in CO_2-rich mixtures was demonstrated.

2 Experimental

2.1 Materials

The detailed preparation procedure and structural characteristics of TRI-PE-MCM-41 were reported in earlier contributions (Harlick and Sayari 2007; Belmabkhout and Sayari 2009a). A brief description of the procedure is provided in the Supporting Information. The surface area, pore volume and pore diameter of TRI-PE-MCM-41 as calculated from nitrogen adsorption data were 367 m^2/g, 0.87 cm^3/g, 9.4 nm, respectively. The adsorption-desorption isotherm of nitrogen on TRI-PE-MCM-41 at 77 K is shown in Fig. S1 (Electronic supplementary material (ESM)).

Carbon dioxide (99.99%), nitrogen (99.999%), helium (99.999), carbon dioxide (0.1; 1; 10; 20%) in nitrogen, methane (99.999%) and hydrogen (99.999%) were supplied by BOC Canada.

2.2 Single component adsorption measurements

As described in Supporting Information, adsorption equilibrium measurements for pure CO_2, N_2, CH_4 and H_2 were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany). Further details about this experimental set-up and procedure may be found elsewhere (Belmabkhout and Sayari 2009b).

2.3 Column-breakthrough measurements of CO_2-containing binary mixtures

The experimental set-up and procedure used for dynamic column-breakthrough measurements were described earlier (Belmabkhout et al. 2010). Details may be found in Supporting Information. The selectivity of CO_2 over species i in the binary mixture of CO_2 and species i was determined using the following equation:

$$S_{CO_2/i} = \frac{x_{CO_2}/x_i}{y_{CO_2}/y_i}$$

where x and y represent the composition of the adsorbed phase and the gas phase, respectively. The experimental relative error estimated from replicate measurements of CO_2 adsorption capacity was ca. 10%.

3 Results and discussion

3.1 Adsorption of single gases

The adsorption isotherms of CO_2, N_2, CH_4 and H_2 onto TRI-PE-MCM-41 at 298 K up to 25 bar are shown in Fig. 1. At the same pressure, the material exhibited very small N_2, H_2 and CH_4 adsorption capacity compared to CO_2 in the same pressure conditions. Nevertheless, the adsorption uptake of CH_4 was slightly higher than N_2 and H_2. It is important to notice that such small uptakes of N_2, H_2 and CH_4 at high pressure are associated with a relative error of ca. 25–50%. It is thus inferred that TRI-PE-MCM-41 has a strong preferential CO_2 adsorption compared to the other gases in a wide range of pressure.

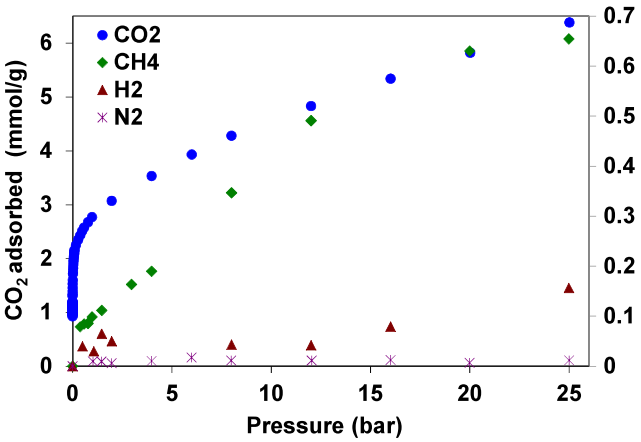

Fig. 1 Adsorption isotherms for CO_2 (Belmabkhout et al. 2010) N_2, CH_4 and H_2 (*right axis*) up to 25 bar at 298 K .

3.2 Column-breakthrough adsorption measurements for CO_2-containing binary mixtures

To evaluate the competition between adsorption of CO_2 and other gaseous species on TRI-PE-MCM-41 under realistic conditions of gas composition, column-breakthrough experiments were carried out using mixtures of CO_2 with N_2, CH_4 and H_2 with compositions akin to a number of industrial gases.

3.2.1 CO_2-N_2 mixture representative of flue gas

The typical CO_2 concentration in flue gas generated in fossil fuel power plants is typically in the range of 5–20%. Therefore, before CO_2 can be sequestered and stored, it must be concentrated using effective separation methods. Figure 2 shows the breakthrough curves of N_2 and CO_2 in the presence of CO_2:N_2 = 20:80 mixture at 298 K and a total pressure of 1 bar using a column containing 0.92 g of TRI-PE-MCM-41 (40–60 mesh particles) and a total flow of 150 mL/min. As seen, N_2 appears in the column downstream immediately after the process has started, indicating a very small adsorption capacity for N_2, if any. No CO_2 was detected downstream the column up to 95 s. The breakthrough of CO_2 was steep and the complete saturation of the packed column occurred at 200 s, corresponding to a CO_2 adsorption capacity of 2.42 ±0.24 mmol/g, in good agreement with the gravimetric capacity (2.30 mmol/g) at the same partial pressure, as reported in Fig. 3. Based on Figs. 1 and 2, it is inferred that the selectivity toward CO_2 over N_2 is very high, approaching infinite value. As shown in Table 1, TRI-PE-MCM-41 exhibits very high selectivity toward CO_2 versus N_2 in comparison to other CO_2 adsorbents like zeolites, activated carbon and MOFs.

3.2.2 CO_2-CH_4 mixture representative of biogas

Biogas is a methane-rich gas mixture that can be used for power generation or transportation fuel. The CO_2 concentration in biogas varies considerably and may reach up to 50%. Therefore, the removal of CO_2 using an effective separation technology is needed to generate biomethane that meets the specifications for injection in the natural gas grid or for use as vehicle fuel. Figure 3 shows the breakthrough profile for CH_4 and CO_2 in the presence of CO_2:CH_4 = 50:50 mixture at 298 K and a total pressure of 1 bar on 1.05 g of TRI-PE-MCM-41 and a total flow of 100 mL/min. Methane appeared in the column downstream as fast as non-adsorbing helium indicating that the adsorption capacity for CH_4 is very small, if any. However, no CO_2 was detected up to 85 s. The breakthrough of CO_2 was abrupt and the complete saturation of the packed column occurred at ca. 300 s, representing a CO_2 adsorption capacity of 2.87 ± 0.28 mmol/g. This finding is in good agreement with the gravimetric capacity of 2.6 mmol/g obtained at the same partial pressure (Fig. 1). Consistent with data in Fig. 1, Fig. 3 shows that the selectivity of CO_2 over CH_4 is very high approaching infinite value. As shown in Table 2, TRI-PE-MCM-41 exhibited one of the highest selectivities toward CO_2 in equimolar mixture with methane, in comparison to other CO_2 adsorbents. No selectivity for CO_2 over CH_4 on amine containing silica is available in the literature. Although it was reported that amino-MIL-53 exhibits high selectivity for CO_2:CH_4 = 50:50 mixture, the CO_2 adsorption capacity at room temperature and 1 bar was small (0.83 mmol/g) in comparison to TRI-PE-MCM-41 (Couck et al. 2009).

3.2.3 CO_2-H_2 mixture representative of syngas

Hydrogen is commonly produced by steam reforming of methane followed by water-gas shift. The resulting hydrogen-rich gas contains, after CO removal, 15–30%

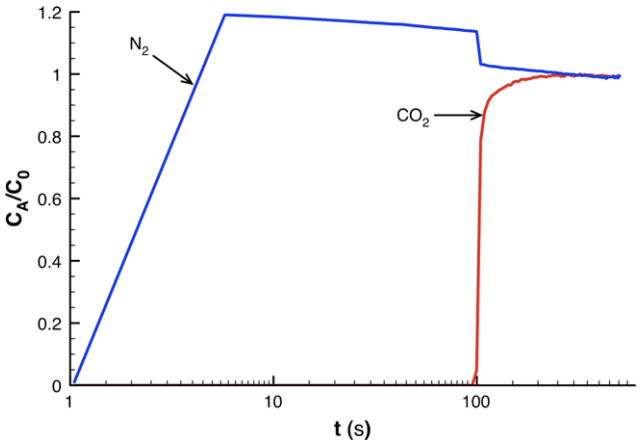

Fig. 2 Column-breakthrough curves for CO_2:N_2 = 20:80 mixture at 298 K and 1 bar over TRI-PE-MCM-41

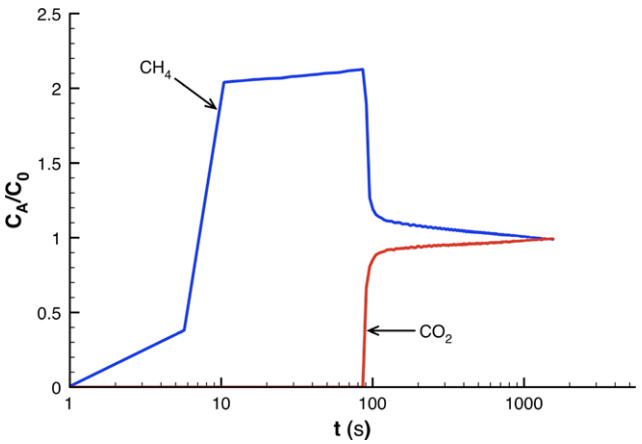

Fig. 3 Column-breakthrough curve for a CO_2:CH_4 = 50:50 mixture at 298 K and 1 bar over TRI-PE-MCM-41

Table 1 CO_2/N_2 selectivity for different materials at room temperature and high CO_2 concentration

Materials	CO_2 concentration/%	CO_2 vs. N_2 selectivity	Reference
13X	50	23	Cavenati et al. 2005
NoritAC	20	14	Dreisbach et al. 1999
Cu-BTC[a] (MOF)	14.9	20	Yang et al. 2007
MCM-41	20	12	Belmabkhout and Sayari 2009b
MCM-41-PEI[b]	4	>1000	Xu et al. 2003, 2005
APS[c]-MCM-48	50	>100	Kim et al. 2005
TRI-PE-MCM-41	20	≈∞	This work

[a]Copper(II) benzene-1,3,5-tricarboxylate
[b]polyethylenimine
[c]aminopropyltriethoxysilane

Table 2 CO_2/CH_4 selectivity for different materials at room temperature at high CO_2 concentration

Materials	CO_2 concentration/%	CO_2 vs. CH_4 selectivity	Reference
13X	50	16	Cavenati et al. 2005
NoritAC	57.4	3	Dreisbach et al. 1999
Cu-BTC[a] (MOF)	50	6	Yang and Zhong 2006
Carborane MOF	50	17	Bae et al. 2008
Amino-MIL 53	50	≈∞	Couck et al. 2009
MCM-41	50	5	Belmabkhout and Sayari 2009b
TRI-PE-MCM-41	50	≈∞	This work

[a]Copper(II) benzene-1,3,5-tricarboxylate

CO_2, which has to be removed. In recent years, tens of patents were issued on the efficient recovery of high purity H_2 using adsorption processes (Sircar and Golden 2000), and considerable effort was made to develop new adsorbents or to modify existing ones in order to increase the primary (H_2) and secondary (CO_2) product recovery while maintaining their high purity (Sircar and Golden 2000). It became a common practice to use more than one type of adsorbents in these processes in order to obtain optimum adsorption capacity and selectivity for the impurities while reducing the co-adsorption of H_2 and improving desorption efficiency (Sircar and Golden 2000). PSA is the most common industrial process for hydrogen purification. The efficiency of the process rests on the selective removal of all the impurities contained in syngas i.e., CO_2, CH_4, CO, H_2O. Because of the deleterious effect of moisture on most industrial CO_2 adsorbents, the feed stream is dried beforehand. The adsorbent bed consists of a layer of activated carbon which adsorbs CO_2, followed by a layer of zeolite 5A for adsorption of CO and CH_4. The main drawback of this process is the hydrogen loss during desorption due mainly to adsorption of H_2 and low selectivity toward CO_2. With hydrogen yield ranging between 75% and 85%, significant amounts of hydrogen are wasted. Recovery of hydrogen in the exhaust stream is generally not attractive because of its low partial pressure. Consequently, these waste gases are rather combusted to recover heat (Sircar and Golden 2000).

One way of improving the yield of H_2 while maintaining high purity is to use a highly selective CO_2 adsorbent like TRI-PE-MCM-41 to separate exclusively CO_2 using a PSA, TSA or PTSA process as shown in Fig. 4. This proposed process uses a single layer of TRI-PE-MCM-41 without any prior drying of the gas feed. After further drying if necessary, the gas stream, now free of CO_2 and moisture, is contacted with a zeolite adsorbent for the effective removal of other impurities, e.g., CO and CH_4, leading to pure hydrogen. The collected CO may undergo methanation, and all the separated methane may be recycled into the steam reforming feedstock for the production of hydrogen or used as fuel for the reforming process.

Figure 5 shows the breakthrough curves of H_2 and CO_2 in the presence of CO_2:H_2 = 20:80 mixture at 298 K and 1 bar on 0.98 g of TRI-PE-MCM-41 and a total flow of 100 mL/min. Hydrogen appeared in the column downstream immediately after the process has started, whereas CO_2 was detected at 198 s. The CO_2 concentration in the effluent reached 80% of the inlet CO_2 concentration in seconds followed by gradual increase until complete saturation of the packed column at 313 s. This corresponds to a dynamic CO_2 adsorption capacity of 2.05 ± 0.2 mmol/g, in fair agreement with the gravimetric capacity of 2.30 mmol/g obtained at the same partial pressure, as shown in Fig. 3. Both Figs. 1 and 5 indicate that the selectivity of CO_2 over H_2 is very high. Literature data on CO_2/H_2 adsorption selectivity are very scarce. As shown in Table 3, TRI-PE-MCM-41 exhibits much higher affinity to CO_2 vs. H_2 than other CO_2 adsorbents.

In summary, under the current conditions, H_2, CH_4 and N_2 behave essentially as non adsorbing gases, leading to practically infinitely high selectivity toward CO_2. Such a

Table 3 CO_2/H_2 selectivity for different materials at room temperature

Materials	CO_2 concentration/%	CO_2 vs. H_2 selectivity	Reference
NaA	1.4	70	Akten et al. 2003
Activated carbon	12.5	47	Cao and Wu 2005
Cu-BTC[a] (MOFs)	50	60	Yang and Zhong 2006
MCM-41	20	32	Belmabkhout and Sayari 2009b
TRI-PE-MCM-41	20	≈∞	This work

[a]Copper(II) benzene-1,3,5-tricarboxylate

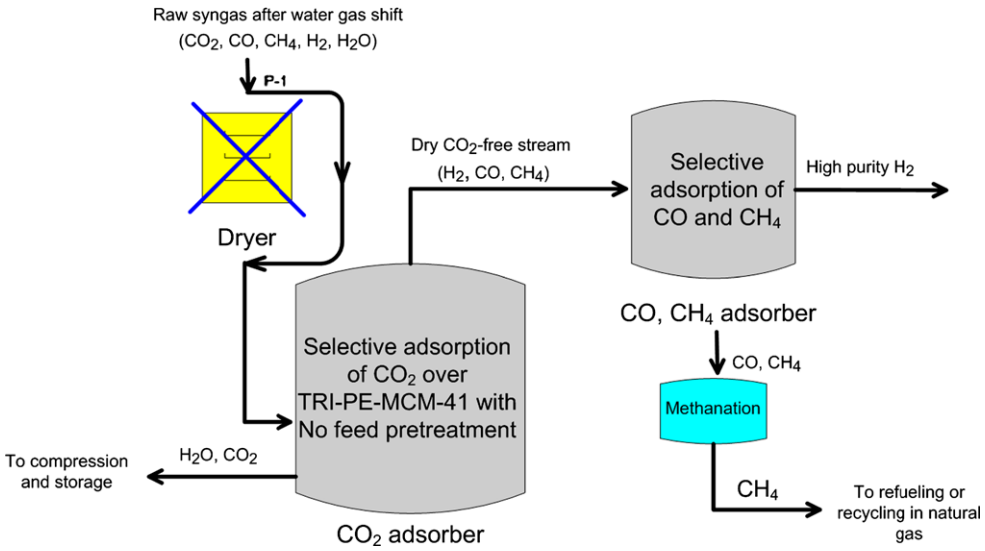

Fig. 4 Proposed approach for the production of high purity hydrogen using highly selective TRI-PE-MCM-41 CO_2 adsorbent

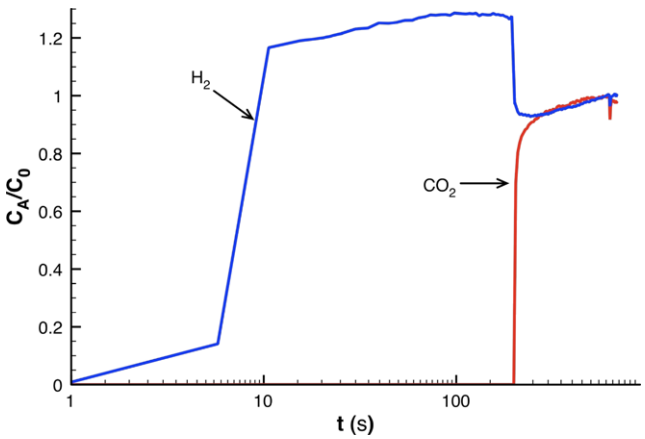

Fig. 5 Column-breakthrough curves for CO_2:H_2 = 20:80 mixture at 298 K and 1 bar over TRI-PE-MCM-41

property is particularly suitable for CO_2 removal from gases such as biogas, flue gas and syngas. Nevertheless, it is important to mention that actual industrial gases contain different impurities, whose effect should be carefully considered. The most ubiquitous impurity is water vapor. Earlier work (Serna-Guerrero et al. 2008; Belmabkhout et al. 2010) showed that adsorption of CO_2 on TRI-PE-MCM-41 is enhanced by the presence of water, most likely because of the formation of bicarbonate (CO_2/N = 1) at the expense of carbamate (CO_2/N = 0.5), which is favored under dry conditions (Serna-Guerrero et al. 2008). Also, we demonstrated that O_2 has no effect on the adsorption of CO_2. Moreover, preliminary data showed that H_2S competes with CO_2 for adsorption sites (Belmabkhout et al. 2009). Admittedly, more work is needed to fully investigate the effect of small concentrations of H_2S, SO_2 and possibly CO.

3.3 Material recycling and stability

For practical applications, the adsorbent should not only possess a high adsorption capacity for CO_2, and high CO_2 selectivity over other species but also exhibit high stability during prolonged operation. Near-equilibrium adsorption–desorption cycles were carried out in the Rubotherm gravimetric set-up using temperature-pressure swing (TPS) regeneration mode to investigate the stability of TRI-PE-MCM-41. In a typical adsorption-desorption cycle, the sample was first exposed to nitrogen at 50 mL/min at 75 °C and 0.1 bar for 30 min. Subsequently, the sample was cooled to 25 °C in flowing nitrogen and the feed gas was switched to pure CO_2, flowing at 50 mL/min for 30 min. The adsorption capacity was assumed to be the weight gain of the sample after 30 min exposure. Figure 6 shows the CO_2 uptake for 200 such adsorption-desorption cycles. Under these conditions, TRI-PE-MCM-41 exhibited remarkable

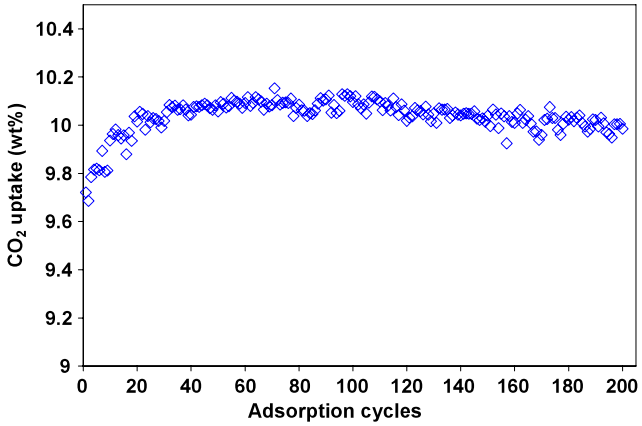

Fig. 6 Adsorption-desorption cycling of pure CO_2 at 25 °C, 1 bar on TRI-PE-MCM-41 using TPS desorption mode (75 °C, 0.1 bar)

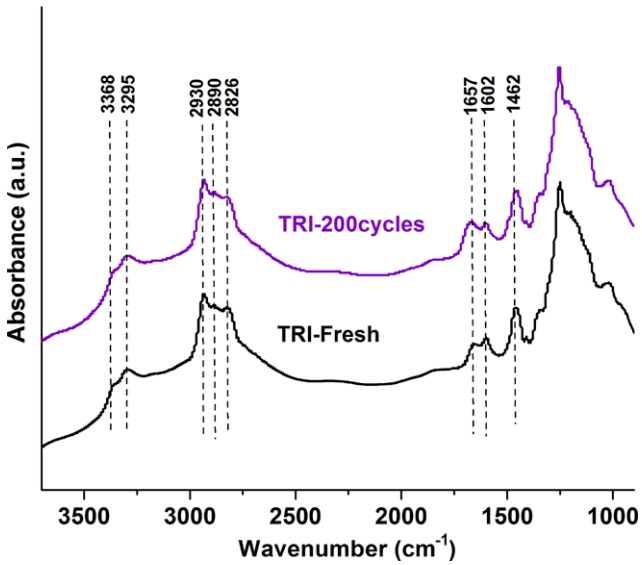

Fig. 7 DRIFT spectra for fresh (TRI-Fresh) and used (TRI-200cycles) samples

stability during extensive TPS cycling over 200 adsorption-desorption cycles. Material regeneration under different conditions was addressed elsewhere (Serna-Guerrero et al. 2010; Belmabkhout and Sayari 2010).

DRIFT spectra (Fig. 7) of the material after cycling (TRI-200 cycles) in comparison to the fresh material (TRI-Fresh) showed that the characteristics bands attributed to vibration of NH_2 (3368, 3295 cm^{-1} and 1657, 1602 cm^{-1}) and CH stretching (2930–2826 and 1462 cm^{-1}) (Chang et al. 2009) exhibited identical intensities. Consistent with the observed high stability (Fig. 6), this indicates that TRI-PE-MCM-41 is not altered under our cycling conditions.

4 Conclusion

Column-breakthrough data showed that TRI-PE-MCM-41 exhibits very high selectivity toward CO_2 in the presence of N_2, CH_4 and H_2 in mixtures with compositions akin to flue gas, biogas and syngas, outperforming many physical and chemical CO_2 adsorbents. The long term stability of TRI-PE-MCM-41 was substantiated via extensive adsorption-desorption cycling. The suitability of TRI-PE-MCM-41 for separation applications using temperature-pressure swing regeneration mode was clearly demonstrated.

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

References

Aaron, D., Tsouris, C.: Separation of CO_2 from flue gas: a review. Sep. Sci. Technol. **40**, 321–348 (2005)

Akten, E.D., Siriwardane, R., Sholl, D.S.: Monte Carlo simulation of single- and binary-component adsorption of CO_2, N_2 and H_2 in zeolite Na-4A. Energy Fuels **17**, 977–983 (2003)

Arstad, B., Fjellvag, H., Kongshaug, K.O., Swang, O., Blom, R.: Amine functionalized metal organic frameworks (MOFs) as adsorbents for carbon dioxide. Adsorption **14**, 755–762 (2008)

Audus, H.: Greenhouse gas mitigation technology: an overview of the CO_2 capture and sequestration studies and further activities of the IEA Greenhouse gas R&D programme. Energy **22**, 217–221 (1997)

Bae, Y.S., Farha, O.K., Spokoyny, A.M., Mirkin, C.A., Punatahnam, S., Hupp, J.T., Snurr, Q.R.: Carborane-based metal-organic frameworks as highly selective sorbents for CO_2 over methane. ChemComm. 4135–4137 (2008)

Belmabkhout, Y., Sayari, A.: Effect of pore expansion and amine functionalization of mesoporous silica on CO_2 adsorption over a wide range of conditions. Adsorption **15**, 318–328 (2009a)

Belmabkhout, Y., Sayari, A.: Adsorption of CO_2 from dry gases on MCM-41 silica at ambient temperature and high pressure. 2: Adsorption of CO_2/N_2, CO_2/CH_4 and CO_2/H_2 binary mixtures. Chem. Eng. Sci. **64**, 3729–3735 (2009b)

Belmabkhout, Y., Serna-Guerrero, R., Sayari, A.: Adsorption of CO_2-containing gas mixtures over amine-bearing pore-expanded MCM-41 silica: applications for gas purification. Ind. Eng. Chem. Res. **49**, 359–365 (2010)

Belmabkhout, Y., Sayari, A.: Isothermal versus non-isothermal adsorption-desorption cycling of triamine-grafted pore-expanded mesoporous silica for CO_2 capture from flue gas. Energy Fuels **24**, 5273–5280 (2010)

Belmabkhout, Y., De Weireld, G., Sayari, A.: Amine bearing mesoporous silica for CO_2 and H_2S removal form natural and biogas. Langmuir **25**, 13275–23278 (2009)

Bonenfant, D., Kharoune, M., Niquette, P., Mimeault, M., Hausler, R.: Advances in principal factor influencing carbon dioxide adsorption in zeolites. Sci. Technol. Adv. Mater. **9**, 013001 (2008)

Brandani, F., Ruthven, D.: The effect of water on the adsorption of CO_2 and C_3H_8 on type X zeolites. Ind. Eng. Chem. Res. **43**, 8339–8344 (2004)

Cao, D., Wu, J.: Modeling the selectivity of activated carbons for efficient separation of hydrogen and carbon dioxide. Carbon **43**, 1364–1370 (2005)

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**, 1095–1101 (2005)

Chaffee, A.L., Knowles, G.P., Liang, Z., Zhang, J., Xiao, P., Webley, P.A.: CO_2 capture by adsorption: materials and process development. Int. J. Greenhouse Gas Control **1**, 11–18 (2007)

Chang, F.Y., Chao, K.J., Cheng, H.H., Tan, C.S.: Adsorption of CO_2 onto amine-grafted mesoporous silicas. Sep. Purif. Technol. **70**, 87–95 (2009)

Couck, S., Denayer, J.F.M., Baron, G., Remy, T., Gascon, J., Kapteijn, F.: An amine-functionalized Mil-53 metal–organic framework with large separation power for CO_2 and CH_4. J. Am. Chem. Soc. **131**, 6326–6327 (2009)

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**, 215–227 (1999)

Feng, B., An, H., Tan, E.: Screening of CO_2 adsorbing materials for zero emission power generation systems. Energy Fuels **21**, 426–434 (2007)

Gray, M.L., Soong, Y., Champagne, K.J., Pennline, H., Baltrus, J.P., Stevens, Jr.R.W., Khatri, R., Chuang, S.S.C., Filburn, T.: Improved immobilized carbon dioxide capture sorbents. Fuel Process. Technol. **86**, 1449–1455 (2005)

Harlick, P.J.E., Sayari, A.: Application of pore-expanded mesoporous silica. 3. Triamine silane grafting for enhanced CO_2 adsorption. Ind. Eng. Chem. Res. **45**, 3248–3255 (2006)

Harlick, P.J.E., Sayari, A.: Application of pore-expanded mesoporous silica. 5. Triamine grafted material with exceptional CO_2 dynamic and equilibrium adsorption performance. Ind. Eng. Chem. Res. **46**, 446–458 (2007)

Hicks, J.C., Drese, J.D., Fauth, D.J., Gray, M.L., Qi, G., Jones, C.W.: Designing adsorbents for CO_2 capture from flue gas-hyperbranched aminosilicas capable of capturing CO_2 reversibly. J. Am. Chem. Soc. **130**, 2902–2903 (2008)

Himeno, S., Komatsu, T., Fujita, S.: Development of a new effective biogas adsorption storage technology. Adsorption **11**, 899–904 (2005)

Kim, S., Ida, J., Guliants, V., Lin, J.Y.S.: Tailoring pore properties of MCM-48 silica for selective adsorption of CO_2. J. Phys. Chem. B **109**, 6287–6293 (2005)

Konduru, N., Lindner, P., Assaf-Anid, N.M.: Curbing the greenhouse effect by carbon dioxide adsorption with zeolite 13X. AIChE J. **53**, 3137–3143 (2007)

Lee, K.B., Beaver, M.G., Caram, H.S., Sircar, S.: Reversible chemisorbents for carbon dioxide and their potential applications. Ind. Eng. Chem. Res. **47**, 8048–8062 (2008)

Llewellyn, P.L., Bourrelly, S., Serre, C., Filinchuk, Y., Férey, G.: How hydratation drastically improves adsorption selectivity for CO_2 over CH_4 in the flexible chromium terephthalate MIL-53. Angew. Chem. Int. Ed. **45**, 7751–7754 (2006)

Llewellyn, P.L., Bourrelly, S., Serre, C., Vimont, A., Daturi, M., Hamon, L., De Weireld, G., Chang, J.S., Hong, D.Y., Hwang, Y.K., Jhung, S.H., Ferey, G.: High uptakes of CO_2 and CH_4 in mesoporous metal-organic frameworks MIL-100 and MIL-101. Langmuir **24**, 7245–7250 (2008)

Meisen, A., Shuai, X.: Research and development issues in CO_2 capture. Energy Convers. Manag. **38**, S37–S42 (1997)

Millward, A.R., Yaghi, O.M.: Metal-organic frameworks with exceptionally high capacity for storage of carbon dioxide at room temperature. J. Am. Chem. Soc. **127**, 17998–17999 (2005)

Serna-Guerrero, R., Da'na, E., Sayari, A.: New insights into the interactions of CO_2 over amine-functionalized silica. Ind. Eng. Chem. Res. **47**, 4761–4766 (2008)

Serna-Guerrero, R., Belmabkhout, Y., Sayari, A.: Further investigations of CO_2 using triamine-grafted pore expanded mesoporous silica. Chem. Eng. J. **158**, 513–519 (2010)

Sircar, R., Golden, T.C.: Purification of hydrogen by pressure swing adsorption. Sep. Sci. Technol. **35**, 667–687 (2000)

Symonds, R.T., Lu, D.Y., Hughes, R.W., Anthony, E.J., Macchi, A.: CO_2 capture from simulated syngas via cyclic carbonation/calcination for a naturally occurring limestone: Pilot-plant testing. Ind. Eng. Chem. Res. **48**, 8431–8440 (2009)

Thambimuthu, K.: Proceeding of workshop on carbon dioxide capture and storage, United nations (UN) Intergovernmental panel on climate change (IPCC) (2002). http://www.climatescience.gov/Library/ipcc/ccs02-workshop_proceedings.pdf. Accessed 15 January 2010

Wang, X.P., Yu, J.J., Cheng, J., Hao, Z.P., Xu, Z.P.: High-temperature adsorption of carbon dioxide on mixed oxides derived hydrotalcite-like compounds. Environ. Sci. Technol. **42**, 614–618 (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**, 29–45 (2003)

Xu, X., Song, C., Andersen, J.M., Miller, B.G., Scaroni, A.W.: Adsorption separation of carbon dioxide form flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent. Fuel Process. Technol. **86**, 1457–1472 (2005)

Yang, Q., Zhong, C.: Molecular simulation of carbon dioxide/methane/hydrogen mixture adsorption in metal-organic frameworks. J. Phys. Chem. B **110**, 17776–17783 (2006)

Yang, Q., Xue, C., Zhong, C., Chen, J.F.: Molecular simulation of separation of CO_2 from flue gas in Cu-BTC metal-organic framework. AIChE J. **53**, 2832–2840 (2007)

Yang, Q., Zhong, C., Chen, J.F.: Computational study of CO_2 storage in metal-organic frameworks. J. Phys. Chem. C **112**, 1562–1569 (2008)

Yue, M.B., Sun, L.B., Cao, Y., Wang, Y., Wang, Z.J., Zhu, J.H.: Efficient CO_2 capturer derived from as-synthesized MCM-41 modified with amine. Chem. Eur. J. **14**, 3442–3451 (2008)

Zelenak, V., Madanicova, M., Halamova, D., Cejka, J., Zukal, A., Murafa, N., Goerigk, N.G.: Amine-modified ordered mesoporous silica: effect of pore size on carbon dioxide capture. Chem. Eng. J. **144**, 336–342 (2008)