Chemical Engineering Science 65 (2010) 3695–3698

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Shorter Communication

Amine-bearing mesoporous silica for CO_2 removal from dry and humid air

Youssef Belmabkhout, Rodrigo Serna-Guerrero, Abdelhamid Sayari *

Department of Chemistry and Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

ARTICLE INFO

Article history:
Received 12 August 2009
Received in revised form
16 February 2010
Accepted 24 February 2010
Available online 1 March 2010

Keywords:
Adsorption
Selectivity
Separations
Purification
Air
Porous media

ABSTRACT

This work demonstrates the potential use of triamine-grafted pore-expanded mesoporous silica TRI-PE-MCM-41, for the removal of CO_2 from nitrogen, oxygen and water vapor-containing mixtures. In addition to unprecedentedly high CO_2 uptake at low pressure, high adsorption rate and stability, this material exhibited very high selectivity for CO_2 over N_2 and O_2, regardless of the presence of moisture. It is thus highly suitable for use in CO_2 removal from air, for example in air purification and in closed-circuit breathing systems.

The atmospheric air used for the cryogenic separation of nitrogen and oxygen has to be free from carbon dioxide to avoid any potential blockage of heat-exchange equipment due to frozen CO_2 during the liquefaction process (Rege et al. 2000, 2001). Moreover, because trace amounts of CO_2 degrade the electrolyte in alkaline fuel cells (AFC), the oxygen used as feedstock for fuel cells has also to be CO_2-free (Kordesch et al., 2000). In addition there is a significant level of interest to remove CO_2 from air to combat the greenhouse gas effect (Lackner and Wright, 2009; Stolaroff et al., 2008; Nikulshina et al., 2009).

Efficient removal of CO_2 at low concentration is also key for the proper operation of closed-circuit breathing systems (CCBSs) (Ernsting, 1999). Such systems are used in confined spaces such as submarines and aerospace shuttles (Satyapal et al., 2001), in mining as well as in rescue missions, diving (Moore, 2007), and also in medical applications (Dosch, 2006). Indeed, oxygen intake by humans is used at a rate of ca. 25%, the rest being exhaled in a ca. 5% CO_2-containing gas. If the exhaled gas is to be recycled using a CCBS, it is necessary to remove the carbon dioxide in the breathing loop to avoid its presence at concentrations considered hazardous to human health (Dosch, 2006). According to the United States Occupational Safety and Health Administration, the threshold limit value (TLV) of CO_2 is 0.5% and its short-term exposure limit (STEL) during 15 min is 3%. With these exposure limits in mind, an adsorbent used in a breathing system is considered to be exhausted when the concentration of CO_2 downstream the scrubber lies in the range of 0.1–0.5% (Murray et al., 1999; Shunji et al., 2003).

Adsorption is widely used for CO_2 removal from mixtures containing N_2 and O_2 (Major et al., 1965, Aaron and Tsouris, 2005). A large variety of CO_2 solid sorbents have been reported in the literature including oxides (Lee et al., 2008), zeolites (Cavenati et al., 2004), activated carbons (Himeno et al., 2005), metal-organic frameworks (MOFs) (Millward and Yaghi, 2005; Llewellyn et al., 2006; Yang et al., 2008), organo-silicas and surface-modified silicas (Harlick and Sayari, 2007; Hicks et al., 2008; Huang et al., 2003; Xu et al., 2005; Chaffee et al., 2007; Gray et al., 2005; Yue et al., 2008). However, the removal of low CO_2 concentration from gas streams via adsorption was rarely addressed (Major et al., 1965; Rege et al. 2000, 2001). The current work deals with the removal of low concentration, from ppm level to few percent, of CO_2 in N_2, O_2 or mixtures thereof using adsorption over a triamine-functionalized pore-expanded mesoporous silica, referred to as TRI-PE-MCM-41. To the best of our knowledge, this is the first time that an amine-functionalized silica is used for the removal of ppm levels of CO_2 from air. The adsorption isotherm for dry CO_2 was determined at 298 K up to 0.05 bar and was compared to the corresponding CO_2 adsorption data on 13X zeolite. Column-breakthrough measurements were also carried out to determine the selectivity of CO_2 over N_2 and O_2 in the absence and presence of moisture.

The adsorbent used, TRI-PE-MCM-41, consisted of a pore-expanded mesoporous MCM-41 silica whose surface has been functionalized using a triaminesilane. The detailed preparation procedure and structural characteristics of TRI-PE-MCM-41 may be found elsewhere (Harlick and Sayari, 2007, Belmabkhout and Sayari,

---

* Corresponding author. Tel.: +1 613 5625483; fax: +1 613 5625170.
E-mail address: abdel.sayari@uottawa.ca (A. Sayari).

0009-2509/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ces.2010.02.044

2009). The BET surface area, pore volume and pore size of TRI-PE-MCM-41 were 367 m^2/g, 0.87 cm^3/g and 9.4 nm, respectively. Zeolite 13X, supplied by Sigma-Aldrich, exhibited a surface area of 658 m^2/g and a pore volume of 0.31 cm^3/g. Pure CO_2 adsorption equilibrium measurements were performed using a Rubotherm gravimetric-densimetric apparatus (Belmabkhout and Sayari, 2009; Belmabkhout et al., 2009). The experimental set-up used for dynamic breakthrough measurements and the data handling methodology were described earlier (Serna-Guerrero and Sayari, 2007). Additional details may be found in supporting information (Fig. S1). Typically a 120 mm long × 4.2 mm ID stainless steel column, filled with ca. 1 g 40–60 mesh adsorbent particles, was used. The material was activated under dry helium at 373 or 423 K and then exposed to CO_2-containing feed flowing at 100 mL/min.

Fig. 1 shows the adsorption isotherm for CO_2 on TRI-PE-MCM-41 at low CO_2 partial pressure and room temperature compared to the most common CO_2 adsorbent, namely 13X zeolite. As seen, TRI-PE-MCM-41 outperformed 13X zeolite below ca. 0.05 bar. Fig. 1 shows also that the lower the partial pressure of CO_2, the higher the difference between the CO_2 adsorption capacity for TRI-PE-MCM-41 and 13X zeolite. Moreover, in contrast to TRI-PE-MCM-41, the performance of 13X was not only strongly dependent on the high activation temperature (473–673 K), but also very sensitive to the presence of moisture (Harlick and Sayari, 2006, Brandani and Ruthven, 2004, Bonenfant et al., 2008). Literature data show that under the same conditions, the adsorption capacities for plain MCM-41 (Belmabkhout et al., 2009), carbon-based materials (Himeno et al., 2005) and MOFs (Millward and Yaghi, 2005; Bastin et al., 2008) in the low pressure range are very small compared to TRI-PE-MCM-41 and 13X. Moreover, as shown in Fig. S2 (Supporting Information) and elsewhere (Belmabkhout and Sayari, 2009), both nitrogen and oxygen as well as carbon-free air (CFAir) behave essentially as non-adsorbing gases over TRI-PE-MCM-41. Fig. S3 (Supporting Information) shows also that the kinetics of CO_2 adsorption at low CO_2 concentration (1000 ppm) is fast with 90% of the total adsorption capacity reached within 15 min time.

Zeolite 13X is the most used adsorbent for the pre-purification of air, with a CO_2 capacity of 0.5 mmol/g at 400 ppm and 295 K (Rege et al., 2000, 2001) provided that the feed is strictly dry. As shown in Fig. 1, the current TRI-PE-MCM-41 exhibited a CO_2 capacity twice as high, i.e., ca. 0.98 mmol/g at ca. 400 ppm and 298 K.

To assess the effect of competition between CO_2, and the main air components N_2 and O_2 for adsorption on TRI-PE-MCM-41, column-breakthrough experiments were carried out using mixtures of CO_2 with N_2, and CFAir with concentrations relevant to air purification and CCBS applications. Fig. 2 shows the breakthrough curves for N_2, O_2 and CO_2 in the presence of CO_2:CFAir = 0.03:99.97 mixture at 298 K and a total pressure of 1 bar on TRI-PE-MCM-41 activated at 423 K. As seen, O_2 and N_2 appeared in the column downstream almost immediately after the process has started, indicative of very small adsorption capacity for N_2 and O_2, if any. No CO_2 was detected downstream the column up to a contact time of 167 min. Complete saturation of the packed column occurred after ca. 328 min, representing a final CO_2 adsorption capacity of 0.9 ± 0.09 mmol/g. These findings show that the selectivity of CO_2 over N_2 and O_2 is extremely high.

Based on both CO_2 adsorption capacity and selectivity at very low pressure, TRI-PE-MCM-41 outperformed not only zeolite 13X, but also other physical adsorbents such as carbons and MOFs. It is thus inferred that TRI-PE-MCM-41 is a promising material for air purification applications.

Fig. 3 shows the breakthrough curves for CO_2, N_2 and O_2 using a CO_2:Air = 5:95 mixture at 298 K and 1 bar. In this case, TRI-PE-MCM-41 was activated at 373 K instead of 423 K to investigate the effect of activation temperature on CO_2 adsorption properties. As seen, O_2 and N_2 were detected downstream the column immediately, suggesting that (i) the

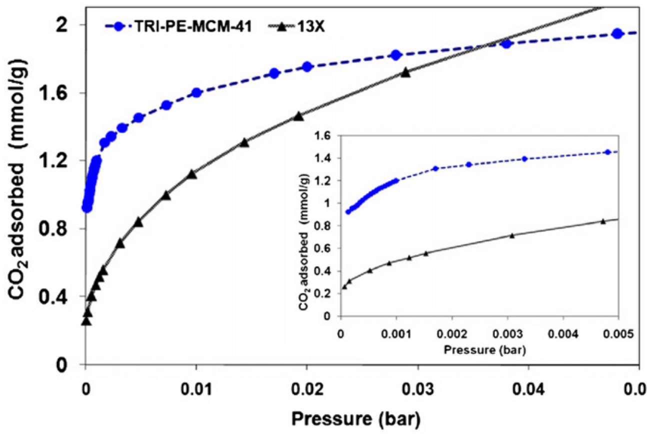

Fig. 1. CO_2 adsorption isotherm for TRI-PE-MCM-41 at 298 K compared to zeolite up to 0.05 bar; inset: close-up at very low pressure.

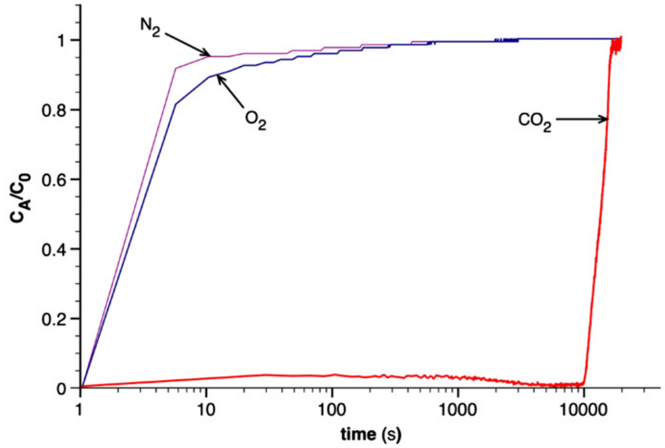

Fig. 2. Column-breakthrough curves for CO_2:CFAir = 0.03:99.97% mixture at 298 K and 1 bar.

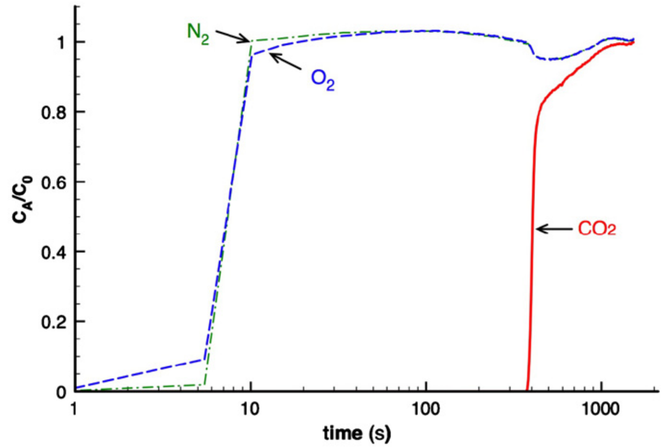

Fig. 3. Column-breakthrough curves for CO_2:Air = 5:95 mixture at 298 K and 1 bar in dry conditions.