

# Adsorption of CO<sub>2</sub> on nitrogen-enriched activated carbon and zeolite 13X

Diogo P. Bezerra · Ronan S. Oliveira ·  
Rodrigo S. Vieira · Célio L. Cavalcante Jr. ·  
Diana C.S. Azevedo

Received: 15 May 2010 / Accepted: 4 January 2011 / Published online: 14 January 2011  
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**Abstract** Adsorption may be a potentially attractive alternative to capturing CO<sub>2</sub> from stationary sources in the context of Carbon Capture and Sequestration (CCS) technologies. Activated carbon and zeolites are state-of-art adsorbents which may be used for CO<sub>2</sub> adsorption, however physisorption alone tends to be insignificant at high temperatures. In the present work, commercial adsorbents have been impregnated with monoethanolamine (MEA) and triethanolamine (TEA) in order to investigate the effect of the modified surface chemistry on CO<sub>2</sub> adsorption, especially above room temperature. Adsorption isotherms for CO<sub>2</sub>, N<sub>2</sub> and CH<sub>4</sub> were measured in a gravimetrically system in the pressure range of UHV to 10 bar, at 298 and 348 K for activated carbon and zeolite 13X supports. The adsorbed concentration of CO<sub>2</sub> was significantly higher than those of CH<sub>4</sub> and N<sub>2</sub> for both adsorbents in the whole pressure range studied, zeolite 13X showing a remarkable affinity for CO<sub>2</sub> at very low pressures. However, at 348 K, the adsorbed concentration of CO<sub>2</sub> decreases significantly. The supports impregnated with concentrated amine solutions and dried in air suffered a detrimental effect on the textural properties, although CO<sub>2</sub> uptake became much less susceptible to temperature increase. Impregnations carried out with dilute solution followed by drying in inert atmosphere yielded materials with very similar textural characteristics as compared to the parent support. CO<sub>2</sub> isotherms in such materials showed a significant change with similar capacities at 348 K as com-

pared to the original support at 298 K in the case of activated carbons. The impregnated zeolite showed a decrease in adsorbed phase concentration in low pressures for a given temperature, but the adsorbed amount also seemed to be less affected by temperature. These results are promising and indicate that CO<sub>2</sub> adsorption may be enhanced despite high process temperatures (e.g. 348 K), if convenient impregnation and drying methods are applied.

**Keywords** CO<sub>2</sub> adsorption · Zeolite 13X · Activated carbon · Amine impregnation

## 1 Introduction

It is widely acknowledged that CO<sub>2</sub> emissions play a major role in global warming and related climate change issues (IPCC 2005). The development of suitable Carbon Capture and Sequestration (CCS) technologies, mainly for post-combustion processes, is urgently needed. The Intergovernmental Panel on Climate Change (IPCC) reported that, by the end of this century, there could be a global average temperature increase between 1.4 and 5.8 K and sea level rise of 9 to 88 cm (Jadhav et al. 2007).

To reduce the amount of CO<sub>2</sub> released into the atmosphere, state-of-the-art available CCS technologies are amine-based absorption, membrane-based separation, adsorption and cryogenic separation. These technologies can be applied to large point sources of CO<sub>2</sub>, such as pre- and post-combustion power plants, and in large industrial process, for instance, separating it from natural gas, coal bed methane or biogas.

CO<sub>2</sub> adsorption is successfully used in CO<sub>2</sub>/H<sub>2</sub> separation to treat streams from water-gas shift reactors (Ebner and Ritter 2009) but, to date, it is still not a feasible option

D.P. Bezerra · R.S. Oliveira · R.S. Vieira · C.L. Cavalcante Jr. ·  
D.C.S. Azevedo (✉)  
Grupo de Pesquisa em Separações por Adsorção (GPSA),  
Department of Chemical Engineering, Universidade Federal do  
Ceará, Campus Universitário do Pici, Bl. 709, 60455-760,  
Fortaleza, CE, Brazil  
e-mail: [diana@gpsa.ufc.br](mailto:diana@gpsa.ufc.br)

as capture technology from stack gases, where the amount of CO<sub>2</sub> varies from 4% to 15% by volume (Figueroa et al. 2008), temperatures are moderately high (e.g. 348 K) and presence of competitors, as water, approximately 5–7% (D’Alessandro et al. 2010). A suitable adsorbent must be cheap, selective for CO<sub>2</sub> despite (high) process temperature, have high surface area and pore volume together with fast intraparticle diffusion and reversible adsorption (ideally upon pressure swings). Additionally, such characteristics must be constant throughout a large number of cycles in the long run. Activated carbons, zeolites, pillared clays, metal oxides and their surface modifications have been widely reported for CO<sub>2</sub> capture (Drage et al. 2009; Xiao et al. 2008; Choi et al. 2009). These adsorbents may retain CO<sub>2</sub> via weak physisorption and/or strong chemisorption interactions. On a recent comprehensive review about the subject, Ebner and Ritter (2009) suggest that a near-term goal to be pursued concerning adsorbents for CO<sub>2</sub> capture should be to develop materials that can operate at elevated temperatures in the presence of sulfur bearing compounds and possibly steam, with working capacities at elevated temperatures in the range of 3–4 mmol/g, that is, 132–176 mg/g.

Activated Carbon (AC) has been proposed as a potential adsorbent due to its low cost, natural affinity for CO<sub>2</sub> and to the possibility of tailoring textural properties and surface chemistry. Zeolite 13X has also been extensively reported as an adequate adsorbent for CO<sub>2</sub> adsorption due to its high affinity for polar molecules at low partial pressures. However, for both adsorbents, physisorption tends to be insignificant at high temperatures, which may pose a serious drawback for CO<sub>2</sub> adsorptive capture from flue gases. Siriwardane et al. (2005) reported that CO<sub>2</sub> adsorption capacity for zeolite 13X, 4A and activated carbon were about 160, 135 and 110 mg/g adsorbent, respectively, at 298 K and 1 atm CO<sub>2</sub> partial pressure, which is a quite high value for the activated carbon, but no data at higher temperatures were reported. CO<sub>2</sub> adsorption behavior of zeolites under high pressure conditions was also investigated by Cavenati et al. (2004). The adsorption capacities of zeolites 13X were evaluated in the pressure range up to 50 bar at three different temperatures. Isotherms obtained at 293, 308 and 323 K show that CO<sub>2</sub> uptake at a given pressure decreases significantly even with a small increase of the operating temperature.

In order to operate at relatively high temperatures and keep high separation selectivity, modifications in the surface chemistry of adsorbents have been proposed, most of which seem to lead to some degree of chemisorption. Amine impregnation (Drage et al. 2007; Maroto-Valer et al. 2005; Przepiórski et al. 2004) or anchoring (Knowles et al. 2006; Zheng et al. 2005; Plaza et al. 2007) on different supports show promise to improve CO<sub>2</sub> adsorption and selectivity, because they confer a basic character to the surface,

which may potentially enhance CO<sub>2</sub>-solid interaction. Caution should be exercised in the introduction of these amines into the porous structure of the solid so as to reach an even dispersion of the amino-groups and avoid collapsing or clogging the porous volume available for diffusion and adsorption.

The simplest method to impregnate amines is to physically mix the amine in solution with the support under given temperature, stirring and time conditions, followed by solvent removal by evaporation or filtration. The first amine-impregnated silica used to capture CO<sub>2</sub> was reported by Xu et al. (2002). They described the impregnation of MCM-41 with polyethyleneimine (PEI) to generate an adsorbent named as “molecular basket”. CO<sub>2</sub> adsorption capacity was significantly increased for high loadings the PEI, despite the sharp decrease in textural properties. Chatti et al. (2009) studied the immobilization of MEA on zeolites 13X for CO<sub>2</sub> capture. They used three amine impregnation routes and investigated the effect of different parameters—such as solvent, stirring time and synthesis temperature—on the CO<sub>2</sub> uptake. At 1 bar and 348 K, using a volumetric apparatus, the measured adsorption uptakes were 37 mg/g and 49 mg/g for the unmodified zeolite 13X and the zeolite 13X/MEA (50%), respectively. Note that a rather high amine loading was used and the textural properties of the impregnated zeolite were damagingly affected (surface area decreased from 386 to 15 m<sup>2</sup>/g).

Thote et al. (2010) synthesized an *in situ* nitrogen enriched carbon for CO<sub>2</sub> capture using soy beans as the starting lignocellulosic raw material in order to generate basic sites on the activated carbon provided by the starting material itself. They performed breakthrough experiments with an inlet gas mixture of 15% vol. CO<sub>2</sub> balanced with helium at 1 bar. The N-enriched carbon had suitable textural properties for gas adsorption (ABET—811 m<sup>2</sup>/g, microporous) with breakthrough saturation capacities of 41 and 22 mg/g at 298 and 348 K, respectively. Nevertheless, most of the figures found in literature for CO<sub>2</sub> uptake are still relatively far from the desired targets.

In the present study, two commercial adsorbents (zeolite 13X and a microporous activated carbon) were impregnated with amines—monoethanolamine (MEA) and triethanolamine (TEA)—under different procedures. Pristine and modified materials were analyzed by N<sub>2</sub> adsorption/desorption isotherms at 77 K and thermo-gravimetric techniques in order to characterize the textural and structural modifications induced on the adsorbents by the amino-impregnation. The adsorbents were tested for CO<sub>2</sub> adsorption in two temperatures (298 and 348 K) under the pressure range of UHV to 10 bar using a gravimetric setup.

**Table 1** Summary of amine impregnation conditions on zeolite 13X and activated carbon

Support	Amine (conc. in % vol.)	T and time of immersion in impregnant solution	Filtration	Drying conditions	Key
AC	TEA (98%)	393 K/3 hours	No	393 K until complete solvent evaporation	AC/TEA
	MEA (0.2%)	298 K/72 hours	Yes	423 K/4 hours N <sub>2</sub> atmosphere	AC/MEA
Zeolite 13X	MEA (0.2%)	298 K/72 hours	Yes	423 K/4 hours N <sub>2</sub> atmosphere	ZEO13X/MEA(1)
	MEA (50%)	333 K/3 hours	Yes	423 K/4 hours in air	ZEO13X/MEA(2)

## 2 Experimental

### 2.1 Adsorbents

Two commercial adsorbents were used in this study: granular activated carbon from Mead Westvaco (USA) and zeolite 13X pellets from Klostrolith (German), with an average diameter of 2 mm.

### 2.2 Amine impregnation

The amine impregnation on zeolites 13X and activated carbon (AC) were carried out under different approaches (Jadhav et al. 2007; Son et al. 2008 and Chatti et al. 2009), which are summarized in Table 1, using monoethanolamine (MEA) and triethanolamine (TEA) as the nitrogen source. About 2.0 g of the adsorbent, previously regenerated at 623 K (zeolite) or 423 K (AC), were soaked in 50 mL of MEA and TEA solutions of various concentrations (see Table 1). Amine solutions were prepared in water for AC impregnation and in methanol, for zeolite modification. Solids remained in contact with the solutions under agitation for the time and at temperatures indicated in Table 1. The materials were separated from the amine solution either by filtration or evaporation to dryness. Then, modified sorbents were dried at 423 K, some in air and others under inert atmosphere (nitrogen flow).

### 2.3 Characterization of the amine-loaded adsorbents

Analytical techniques were used to characterize the chemical and textural modifications induced in impregnated zeolite 13X and activated carbon. Nitrogen adsorption/desorption isotherms were measured using an Autosorb-1 MP apparatus (Quantachrome, U.S.A.) for the determination of such textural properties as surface area, total pore volume, micropore volume, mean pore diameter and pore size distribution (in the case of ACs). The impregnated adsorbents were initially regenerated at 423 K, to avoid amine

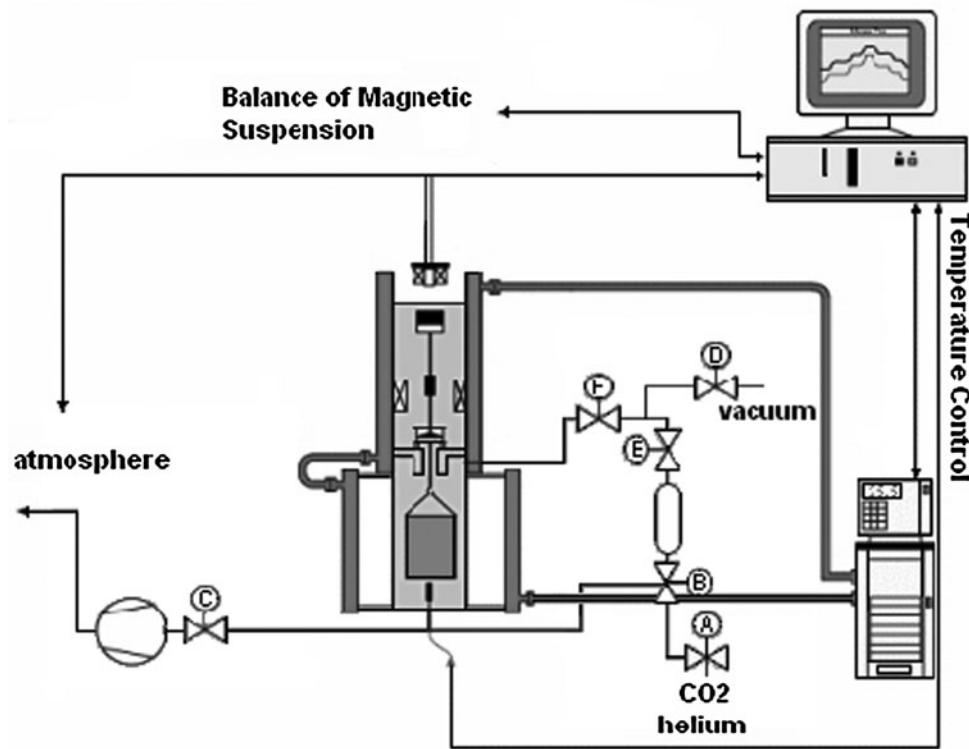
volatilization, and then subjected to stepwise N<sub>2</sub> relative pressure increases and decreases at 77 K. The specific surface area was calculated by the BET equation, micropore volume and average pore width were determined by using the Dubinin–Radushkevich equation assuming slit pores for activated carbon and cylindrical pores for zeolites and pore size distribution (only activated carbon) was assessed from the density functional theory using slit pore geometry and particle–particle interaction potentials (Rouquerol et al. 1999).

The samples were also characterized using thermogravimetric analysis (TG) to study their thermal stability and dehydration characteristics. The measurements were performed using a Shimadzu TGA 50 equipment, with a heating rate of 10 °C/min, in a dynamic N<sub>2</sub> atmosphere with approximately 5.0 mg of sample. The temperature range of 298–1073 K was used for TGA analyses.

### 2.4 Gravimetric method

Adsorption equilibrium studies were performed using a magnetic suspension balance by Rubotherm (Bochum, Germany). The gravimetric setup is shown in Fig. 1. The adsorbents were degassed in situ at 423 K until no mass variation in the system was observed (except for pristine zeolite 13X, which was regenerated at 623 K). After that, the measuring chamber was cooled down to the experiment temperature (298 or 348 K) and the gas pressure (CO<sub>2</sub>) was increased stepwise (UHV until approximately 10 bar). Mass variation at equilibrium ( $\Delta m$ ) was recorded for each pressure step. For each sample, a previous experiment with helium (non-adsorbed) was carried out in order to determine the specific volume of the solid phase of the sample ( $V_s$ ) and the “bucket” volume ( $V_b$ , characteristic of the suspended parts inside the chamber). The sum of these volumes was used to account for the buoyancy effects on measurements with adsorbing gases.

**Fig. 1** Gravimetric setup for gas adsorption experiments at high pressures



For a given gas pressure  $P$ , the excess adsorbed phase concentration may be calculated according to:

$$m_{ex}(P, T) = \Delta m(P, T) + (V_b + V_s) \cdot \rho(P, T) \quad (1)$$

where:  $m_{ex}$  is the excess uptake (g/g sample);  $\Delta m$  is the mass difference sensed by the equipment (g/g sample);  $V_b$  is the specific volume of the balance suspended components ( $\text{cm}^3/\text{g}$  sample);  $V_s$  is the specific volume of the sample solid phase ( $\text{cm}^3/\text{g}$  sample);  $\rho$  is the gas density ( $\text{g}/\text{cm}^3$ );  $P$  is the pressure (bar); and  $T$  is the temperature (K). Further details on data handling for gravimetric adsorption measurements at high pressures may be found elsewhere in Dreisbach et al. (2002) and Bastos-Neto et al. (2005).

In order to describe the behavior of the adsorption isotherm, equilibrium data were correlated using the Langmuir-Freundlich equation, expressed as follows.

$$\frac{q}{q_s} = \frac{bP^m}{1 + bP^m} \quad (2)$$

where  $q$  is the adsorbed concentration (g/g);  $P$  is the gas pressure (bar);  $q_s$  is the maximum/saturation adsorbed concentration (g/g);  $b$  is the Langmuir dissociation constant (1/bar) and  $m$  is a fitting parameter related to the surface heterogeneity of the adsorbent. For  $m = 1$ , the classical Langmuir equation, originally proposed for energetically homogeneous surfaces, is encountered.

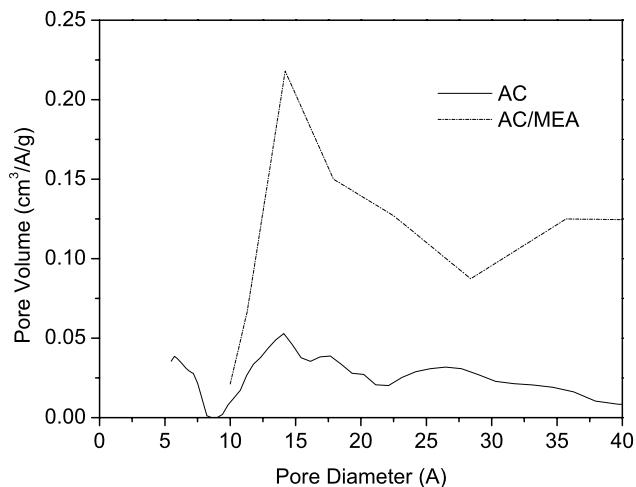
### 3 Results and discussion

#### 3.1 Characterization

Table 2 summarizes the textural characteristics for the pristine and modified adsorbents, as calculated from  $\text{N}_2$  adsorption isotherms. The surface area for the starting activated carbon was the highest (over  $1500 \text{ m}^2/\text{g}$ ) with a wide pore size distribution, judging from the fact that the micropore volume is less than half of the total pore volume. AC modified with TEA suffered a drastic decrease in all textural properties, indicating that the amine may have almost completely blocked the porous structure of the support. On the other hand, the impregnation carried out with dilute MEA solution and drying under inert atmosphere led to a solid with nearly intact textural characteristics, very similar to those measured for the starting carbon, except for the micropore volume, which was significantly increased. This may have been caused by the uniform deposition of amino groups on adsorbent, most likely in meso and macropores of the original support as well as some degree of micropore development under the action of the amine and temperature (Gargiulo et al. 2007). In fact, the pore size distribution of these materials—shown in Fig. 2—confirms that, upon impregnation, a much larger fraction of the pores has dimensions in the range of 10 to 20 Å. Nevertheless, it may also be observed that a significant fraction of pores, those

**Table 2** Textural characteristics of the samples

Sample	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Average pore width (Å)
AC	1727	1.204	0.578	13
AC/MEA	1749	1.181	0.940	13
AC/TEA	8	0.018	0.003	41
ZE013X	515	0.454	0.298	11
ZE013X/MEA(1)	491	0.456	0.277	11
ZE013X/MEA(2)	19	0.013	0.001	11

**Fig. 2** Pore size distributions as determined from Density Functional Theory for AC and AC/MEA samples, the latter as impregnated according to Table 1

smaller than 8 Å which were initially present in the carbonaceous support AC, disappeared after amine impregnation in AC/MEA.

A similar behavior was found for zeolite 13X concerning textural properties of the modified materials. The parent zeolite ZEO13X and the modified sample ZEO13X/MEA(1) have similar surface areas around 500 m<sup>2</sup>/g and micropore volume close to 0.5 cm<sup>3</sup>/g, both typical values found for faujasites. The average pore width also did not change after MEA impregnation using a dilute impregnant solution and drying under inert atmosphere, suggesting that the pore openings are mostly intact. On the other hand, the impregnation performed with concentrated MEA had a pronounced detrimental effect on the textural properties of the resulting material. Micropore volume was the most drastically reduced parameter: less than 1% of that of the pristine zeolite, which leads us to believe that the bulk of the porous network is damaged, very likely due to MEA obstruction. The remaining surface area and total pore volume possibly account only for pellet macropores and external area.

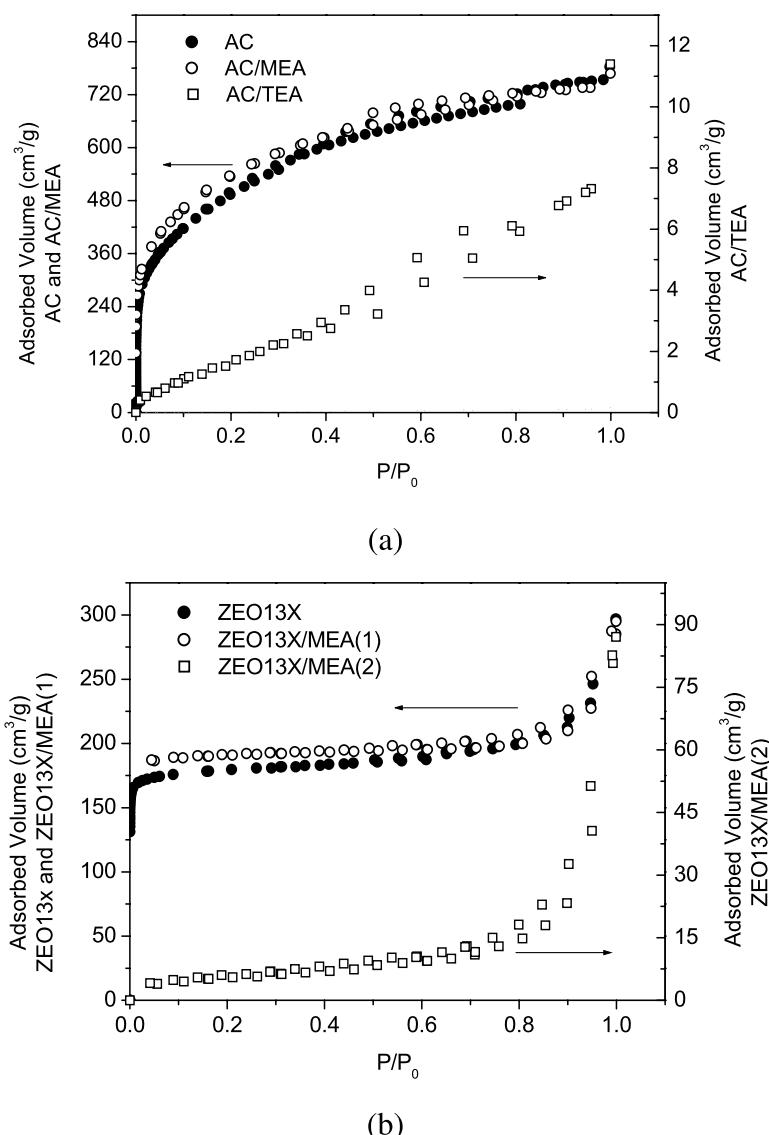
The nitrogen adsorption isotherms at 77 K for zeolites and activated carbon (starting supports and modified adsorbents) are shown in Fig. 3. The activated carbon samples

showed smooth type I isotherms, with a continuous increase in the adsorbed volume, from relatively low pressures up to  $p/p_0 = 1$ , which indicates a larger pore distribution. As expected, the N<sub>2</sub> isotherm of the AC sample impregnated with MEA showed a similar shape as the starting AC, except for a slightly steeper slope in the low pressure range, which corroborates with its higher fraction of micropores, as indicated in the PSD shown in Fig. 2. Sample AC/TEA had a nearly insignificant N<sub>2</sub> uptake with an indistinguishable isotherm shape, confirming that the porous structure was collapsed as a result of an inadequate impregnation procedure.

The N<sub>2</sub> isotherm of zeolite 13X shows an abrupt increase in the adsorbed volume at low relative pressures, followed by a constant adsorbed volume in the range of relative pressure of 0.1 to 0.8, a typical behavior of solids that present constant pore size and microporous crystalline structure. The increase in relative pressures near 1.0 is probably due to the presence of macropores as a result of pellet conformation, necessary to facilitate the diffusion in the micropores, and to allow its use as packing in adsorption columns for industrial process. The modified sample ZEO13X/MEA(1) shows nearly the same behavior as the parent support. However, for the sample loaded with a high concentration of MEA—ZE013X/MEA(2)—textural properties were negatively affected, a similar result to that found by an Indian group that has been working on MEA impregnation in zeolites (Jadhav et al. 2007; Chatti et al. 2009). They have varied the concentration of the impregnating amine solution from 2 to 50% wt (in methanol), but using a much larger solid/liquid ratio than in the present work. In nearly all cases, a pronounced decrease in surface area and pore volume was observed. Because textural properties practically did not change for samples AC/MEA and ZEO13X/MEA(1), thermogravimetric analysis were performed with these samples and compared to the parent materials in order to check whether the amine was actually incorporated in the adsorbents.

The curves of relative mass loss determined in TGA are shown in Fig. 4 (a) and (b) for activated carbons and zeolites, respectively. The pre-adsorbed moisture along with other volatiles (methanol or water used as solvent for amine-impregnation) were initially desorbed, specially for

**Fig. 3** Nitrogen adsorption/desorption isotherms at 77 K for parent and modified activated carbons (a) and zeolites (b)

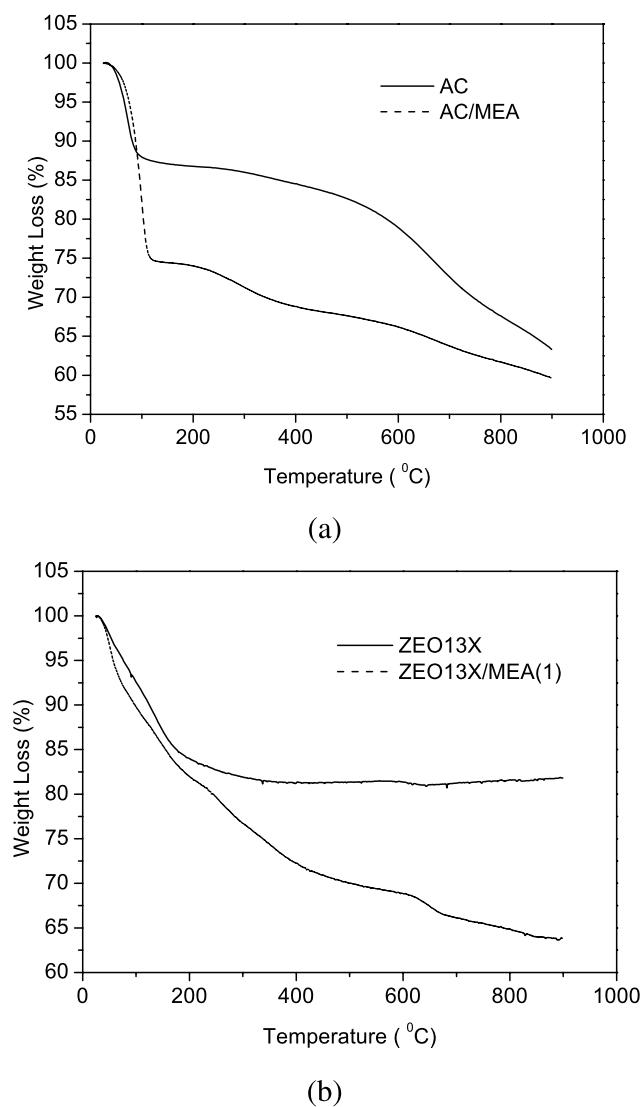


modified samples, which show larger weight loss in both cases. The activated carbon exhibits a fast degradation peak near 373 K, indicative of its hydrophobic character. This peak was steeper and slightly delayed for modified carbon AC/MEA, suggesting that amine impregnation was successful and gave the surface a more hydrophilic character. For this sample, a very smooth inflection point is observed between 473 K and 573 K, which is likely to be due to amine desorption and volatilization. The zeolites samples show a continuous weight loss, especially for the unmodified sample, indicating its extremely hydrophilic character. The modified sample has a higher mass loss at the same temperature as the parent zeolite due to volatilization of adsorbed methanol remaining from the impregnation (at lower temperatures) and possibly MEA. Nevertheless, it was not possible to spot a clear degradation peak at temperatures around or higher than 443 K (boiling point of monoethanolamine)

indicating all the amino groups are probably retained on the surface at this temperature. Because mass loss is very similar up to 423 K for parent and modified zeolites, these results suggest that MEA-impregnated zeolites may be more robust materials with respect to adsorption at moderately high temperatures such as those ordinarily found in stack gases.

### 3.2 Adsorption isotherms on zeolites 13X and activated carbon

The adsorption isotherms of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> at 298 K and 348 K on un-modified zeolite 13X and activated carbon are shown in Fig. 5. In the whole pressure range and both temperatures, the uptakes of CO<sub>2</sub> were always higher than those of CH<sub>4</sub> and N<sub>2</sub>. However, at 348 K and 1 bar, CO<sub>2</sub> adsorbed concentration does not exceed 150 mg/g (3.4 mol/kg) for the zeolite and 30 mg/g (0.68 mol/kg) for the activated



**Fig. 4** TGA curves for the parent and MEA-impregnated activated carbon **(a)** and zeolite 13X **(b)**, respectively

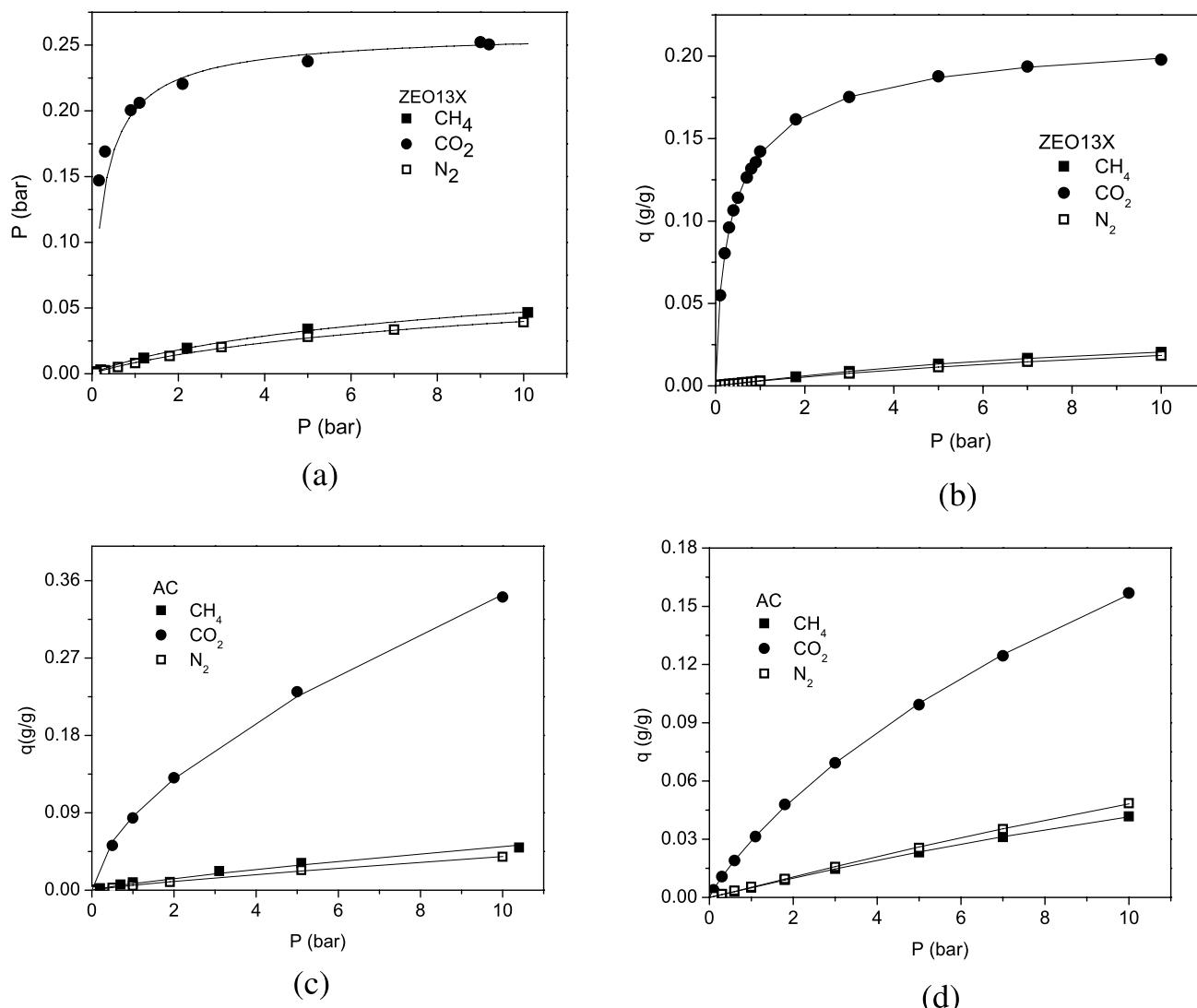
carbon. This is far below the suggested targets (Ebner and Ritter 2009), especially for activated carbon. Moreover, although there is relatively little uptake of the other gases as compared to CO<sub>2</sub>, adsorption under multicomponent conditions will eventually reduce further the figures obtained for pure CO<sub>2</sub>. Within the scenario of post combustion capture, zeolite 13X seems to be the best adsorbent choice in view of the low CO<sub>2</sub> partial pressures. However, uptake and selectivity at higher temperatures must be improved.

On the other hand, at high pressures, CO<sub>2</sub> adsorbed concentration on activated carbon far exceeds that of zeolites due to its much more extended surface area and specific pore volume. Similar results are shown by Sircar et al. (1996), who reported that most of the microporous activated carbons tested adsorb more CO<sub>2</sub> than zeolite 5A at 303 K and pressures in the order of magnitude of several bars.

Thote et al. (2010) were the few authors to report a surprisingly high CO<sub>2</sub> uptake for an N-enriched activated carbon—110 mg/g—at 298 K and 1 atm. This figure converts to 2.5 mol/kg, which is comparable to those measured for zeolites 13X (160 mg/g) and 4A (135 mg/g). Nevertheless, results at higher temperatures are not shown and, from our own results (Fig. 5), unmodified activated carbons are more prone to capacity decrease with increasing temperature than zeolites.

The CO<sub>2</sub> adsorption isotherms for the AC samples (supports and modified adsorbents) at 298 and 348 K are shown in Fig. 6, with a zoom of the low pressure region (up to 1 bar). As expected, the activated carbon impregnated with TEA had a much lower CO<sub>2</sub> uptake than the other two samples, due to its very poor texture (Table 2). However, an interesting behavior was observed with the rise in temperature: CO<sub>2</sub> uptakes were not as reduced as expected when physisorption is the only retention phenomenon. Regarding the sample AC/MEA (that kept favorable textural characteristics), it adsorbed less CO<sub>2</sub> than the parent AC at 298 K, possibly due to the disappearance of pores narrower than 10 Å (see Fig. 2). Pores of such dimension are greatly responsible for gas physisorption, which is expected to be the governing retention mechanism at this temperature. However, at 348 K, the impregnated sample adsorbs more CO<sub>2</sub> than the parent AC. Moreover, if we compare the isotherms for sample AC/MEA at 298 and 348 K, CO<sub>2</sub> uptakes increases with increasing temperature, which is counter-intuitive if only physical adsorption is considered. Actually, amine-impregnation is claimed to be a convenient strategy to increase CO<sub>2</sub> adsorption at moderately high temperatures. Amino groups change the adsorbent surface, providing specific adsorption sites for CO<sub>2</sub> of stronger nature than dispersion (van der Waals) forces. If this is an activated interaction and textural properties are not significantly affected upon impregnation, it is possible to enhance CO<sub>2</sub> uptake despite temperature increases in a certain range, as has also been observed by other authors (Chatti et al. 2009; Jadhav et al. 2007; Khatri et al. 2006). Therefore, MEA impregnation does have potential to produce adsorbents that maintain high uptakes despite moderately high temperatures.

Amine impregnations carried out in zeolite 13X showed similar trends as those discussed previously. In Fig. 7, the adsorption isotherms of unmodified (parent) and modified zeolite are shown at 298 and 348 K. The sample prepared by impregnation with a dilute MEA solution and dried in inert atmosphere—ZEO13X/MEA(1)—showed a decrease in CO<sub>2</sub> uptake at 298 K when compared to the parent support, but not as pronounced as the uptake reduction observed for ZEO13X/MEA(2), the sample with poor textural properties (see Table 2). At 348 K and a sufficiently high pressure, both impregnated zeolites adsorb more CO<sub>2</sub> than at 298 K.



**Fig. 5** Adsorption isotherms of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> at 298 K (on the left) and 348 K (on the right) for unmodified samples zeolite 13X (a)/(b) and activated carbon (c)/(d). Points are excess uptakes as mea-

sured in a gravimetric setup and the lines represent the fitted (least-squares) Langmuir-Freudlich equation

This happens at 6 bar for ZEO13X/MEA(1) and at 1 bar for ZEO13X/MEA(2). These results are in accordance with the studies carried out by Yue et al. (2006) which showed an increase in CO<sub>2</sub> adsorbed amount on SBA-15 impregnated with tetraethylengenetamine (TEPA) when the temperature increased from 308 to 373 K, which is discrepant considering only exothermic physisorption. Choi et al. (2009) argue that for high amine loadings and low temperatures, this behavior could be attributed to a strongly diffusion-controlled process, particularly at 298 K. In other words, CO<sub>2</sub> would diffuse quite slowly in heavily amine-loaded material at low temperature and its uptake would seem exceptionally low. However, this does not seem to be the case in the present study because porous structure remained unaltered for ZEO13X/MEA(1), because this material was obtained

with a very dilute amine solution (0.2% vol) and textural properties remained nearly unaltered. Another approach to explain the increase in CO<sub>2</sub> uptake with a rise in temperature is that chemical reactions occur between amino groups and CO<sub>2</sub> to produce species carbonates (Satyapal et al. 2001; Arenillas et al. 2005) according to the following equations.

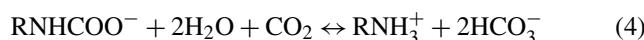
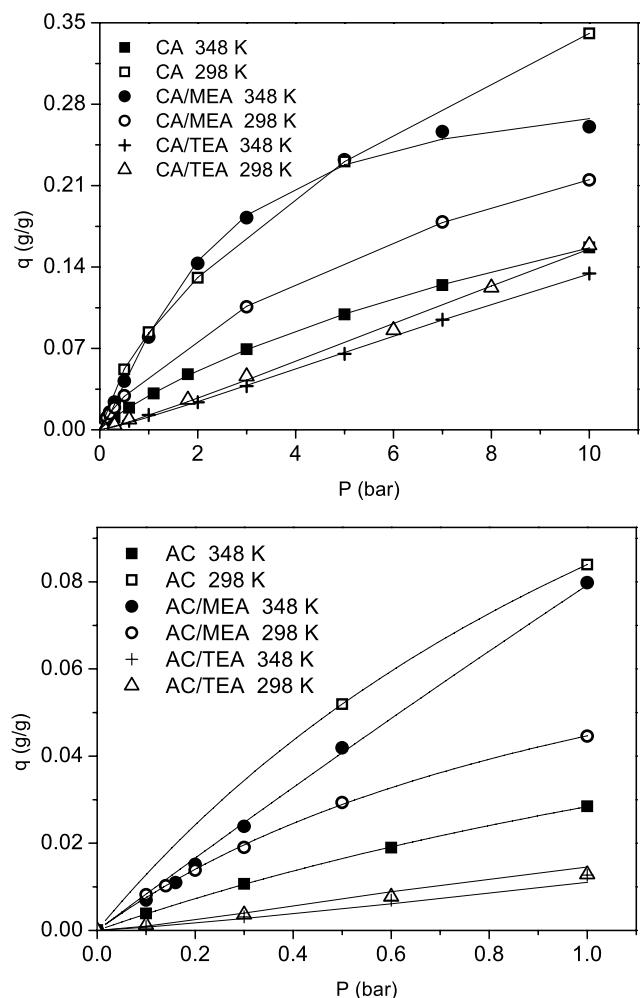


Table 3 shows CO<sub>2</sub> uptakes obtained in this study as compared to other values found in the literature. Reported literature data is usually obtained from breakthrough experiments under dynamic conditions at nearly atmospheric pressure. In general, the data obtained in this work matches that found



**Fig. 6** Adsorption isotherms on parent and amino-impregnated activated carbons at 298 K and 348 K. Points are excess uptakes as measured in a gravimetric setup and the lines represent the fitted (least-squares) Langmuir-Freundlich equation. The plot on the bottom is a magnification of the pressure range from UHV up to 1 bar

by other authors with promising results at 348 K for modified zeolite in low pressures and modified AC at higher pressures.

### 3.3 Equilibrium adsorption modeling

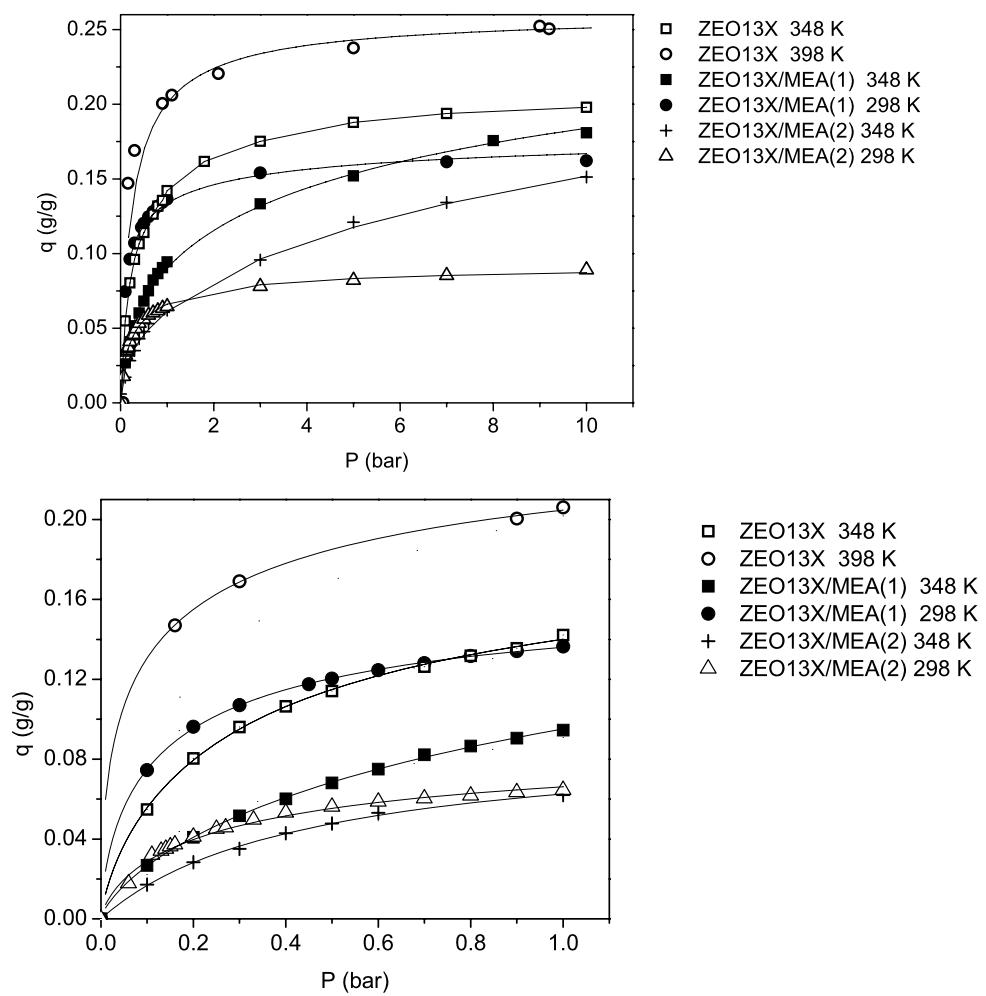
All adsorption isotherm data were correlated by the Langmuir-Freundlich (LF) equation, which managed to fit experimental results quite well ( $R^2 > 0.99$  in nearly all cases). The LF model parameters are summarized in Table 4 and some interesting observations may be drawn from them. The results show that the pristine activated carbon AC is the adsorbent with the highest  $\text{CO}_2$  saturation adsorption capacity  $q_m$  (as  $P^m \gg 1/b$ ), but low  $b$  values, which means that such uptake—more than 30 kmol/kg—will only be achieved at very high pressures. This material may be suitable for natural gas purification in offshore platforms, where tem-

peratures are usually low and pressure exceeds several bars. Upon amine-impregnation, modified AC samples have an increase in the  $b$  parameter, which indicates a stronger adsorbent/adsorbate interaction as expected, but not enough to compete with zeolite 13X (raw and modified) at low pressures. On the other hand, zeolite 13X do not show as high  $q_m$  values for  $\text{CO}_2$  adsorption data, but large values of  $b$ , especially at low temperatures, which reflect on the steep initial slope of the isotherm. The only noticeable exception is ZEO13X/MEA(2) at 348 K, which shows a completely inverse trend with reference to LF parameters: high values of  $q_m$  and a very low value of  $b$ . As a result uptake increases quite slowly with partial pressure. In fact, one of the outstanding effects of amine-impregnation on zeolites is changing the shape of  $\text{CO}_2$  isotherm to a less rectangular one, particularly at higher temperatures, which tends to increase the uptake at high pressures and decrease it at low pressures (as compared to the parent support). With regards to parameter  $m$ , it varies at random, bearing no meaningful physical significance. Therefore, at the present stage, the Langmuir-Freundlich model should be only taken as a fitting mathematical equation, which may be particularly useful in designing cyclic separation processes, such as PSA. To envision the potential of amine-impregnated zeolite 13X to capture  $\text{CO}_2$  from flue gases, let us consider the optimized 1-bed, 4-step PSA separation cycle proposed by Ko et al. (2005). The feed concentration is 15% vol  $\text{CO}_2$  and the cycle operates with a high pressure ( $P_H$ ) step of 14 atm and a low pressure ( $P_L$ ) step of 0.88 atm. Under such conditions, and using a regular 13X zeolite, 98%  $\text{CO}_2$  is recovered with a productivity of 908 LSTP/hr/kg. According to the excellent review of Ebner and Ritter (2009), this is one of the best PSA performances reported in scientific literature. If we look at  $\text{CO}_2$  uptakes of ZEO13X and ZEO13X/MEA(1) at the reported  $P_H$  and  $P_L$  values (taking into account the feed concentration of  $\text{CO}_2$ ), the impregnated sample still has a lower capacity in the upper pressure, but a much lower retention than ZEO13X in the low pressure (0.1 bar). As a follow-up research work, other aspects should be looked into, such as varying the concentration of impregnating amine (between 0.2 and 50%) and investigating reversibility of the isotherm and diffusional aspects.

### 4 Conclusion

Commercially available zeolite 13X and activated carbon have been modified by amine impregnation using different protocols aiming to increase  $\text{CO}_2$  uptake, especially at higher temperatures and relatively low pressures (up to 10 bar). Impregnations carried out with dilute amine solutions and drying/activation in inert atmosphere have shown to be effective since resulting modified samples have similar textural properties as compared to the starting materials, with

**Fig. 7** Adsorption isotherms on parent and amino-impregnated zeolite 13X at 298 K and 348 K. Points are excess uptakes as measured in a gravimetric setup and the lines represent the fitted (least-squares) Langmuir-Freundlich equation. The plot on the bottom is a magnification of the pressure range from UHV up to 1 bar



**Table 3** Maximum adsorbed amount of CO<sub>2</sub> at different temperatures and pressures

Adsorbent	Adsorbed amount (mg/g)						Reference	
	298 K			348 K				
	0.1 bar	1 bar	10 bar	0.1 bar	1 bar	10 bar		
AC	10	83	340	4	31	156	This study	
AC/MEA	8	45	214	7	75	260	This study	
AC/TEA	—	14	158	—	12	134	This study	
Activated carbon—MEA	—	68 <sup>a</sup>	—	—	50 <sup>b</sup>	—	Maroto-Valer et al. (2008)	
In situ N-enriched activated carbon	—	110	—	—	—	—	Thote et al. (2010)	
ZEO13X	83	206	255	54	142	197	This study	
Zeolite 13X	—	211	264	—	—	—	Cavenati et al. (2004)	
Zeolite 13X	—	160	—	—	—	—	Thote et al. (2010)	
ZEO13X/MEA(1)	74	136	162	26	94	180	This study	
ZEO13X/MEA(2)	32	64	89	17	62	151	This study	
Zeolite 13X—MEA	—	—	—	—	49 <sup>c</sup>	—	Chatti et al. (2009)	

<sup>a</sup>at 303 K;

<sup>b</sup>at 343 K;

<sup>c</sup>pure gas, measured in a volumetric apparatus

**Table 4** Adsorption parameters from Langmuir-Freundlich equation

Adsorbent	Temperature (°C)	Gas	$q_m$ (mg/g)	$b$ (bar $^{-1}$ )	$m$
AC	298	CO <sub>2</sub>	1400	0.06	0.70
		CH <sub>4</sub>	131	0.07	0.90
		N <sub>2</sub>	131	0.04	1.00
	348	CO <sub>2</sub>	537	0.06	0.85
		CH <sub>4</sub>	204	0.03	1.00
		N <sub>2</sub>	190	0.03	1.08
ZEO13X	298	CO <sub>2</sub>	259	5.20	1.05
		CH <sub>4</sub>	70	0.16	1.08
		N <sub>2</sub>	63	0.15	1.05
	348	CO <sub>2</sub>	220	1.77	0.71
		CH <sub>4</sub>	40	0.09	1.10
		N <sub>2</sub>	42	0.07	1.01
AC/MEA	298	CO <sub>2</sub>	552	0.10	0.82
	348		241	0.08	0.99
AC/TEA	298	CO <sub>2</sub>	470	0.09	0.81
	348		297	0.07	0.98
ZEO13X/MEA(1)	298	CO <sub>2</sub>	147	11.1	0.94
	348		124	2.98	0.81
ZEO13X/MEA(2)	298	CO <sub>2</sub>	96	2.26	0.69
	348		1140	0.05	0.52

thermal stability and hydrophilic character compatible with the incorporation of the amine. CO<sub>2</sub> isotherms were measured for the parent supports and modified materials in the pressure range of 0.1 to 10 bar and temperatures of 298 and 348 K. As a general trend, amine-modified adsorbents have a lower CO<sub>2</sub> uptake at 298 K as compared to the parent support but, for the same impregnated sample, adsorbed CO<sub>2</sub> increases with a rise in temperature. This behavior is probably due to the occurrence of some extent of chemisorption to form carbonates. The amine impregnation on 13X zeolite causes a distinct change in the shape of CO<sub>2</sub> isotherms, which becomes less rectangular with a steady increase as pressure rises, so that no distinct saturation plateau is observed up to 10 bar. Hence, a suitable impregnation protocol may eventually produce a modified zeolite adsorbent that is suitable for CO<sub>2</sub> capture from flue gases with high recovery.

**Acknowledgements** The present work was carried out thanks to financial support provided by CNPq (Brazilian Ministry for Science and Technology) and Petrobras.

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