Adsorption Microcalorimetry Applied to the Characterisation of Adsorbents for CO₂ Capture

F. Wilton Miranda da Silva,[1] Débora A. Soares Maia,[2] Ronan S. Oliveira,[1] Juan Carlos Moreno-Piraján,[3] Karim Sapag,[2] Célio L. Cavalcante,[1] Giorgio Zgrablich[2] and Diana C. S. Azevedo[1]*

1. 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
2. Instituto de Física Aplicada (INFAP/CONICET), Universidad Nacional de San Luis, San Luis, Argentina
3. Grupo de Investigación en Sólidos Porosos y Calorimetría, Departamento de Química, Universidad de Los Andes, Bogotá, Colombia

The present work presents the design, assembly and experimental validation of a microcalorimetric device coupled to a volumetric adsorption setup applied to the characterisation of adsorbents for carbon dioxide (CO₂) capture. Three adsorbents were evaluated for CO₂ adsorption at 273 K in the pressure range of vacuum to 101 kPa. The data for CO₂ on zeolite 13X agreed well with the available data reported in the literature, thus validating the device, which also provided reproducible results with an activated carbon sample. For the amine-modified zeolite, the differential enthalpy at lower coverage was increased by a factor of 1.7 as compared to the zeolite matrix. This points out to the potential of such technique to characterise heterogeneities introduced by amine impregnation. However, the adsorption uptake was decreased by factor of 2.7 at 101 kPa. This fact suggests that amino groups may be blocking some physisorption sites, leading to restricted chemisorption on the outer surface. Thus, the main novelty of this study is the simultaneous measurement of adsorption isotherms and respective differential enthalpy curves for amine-impregnated adsorbents, which may be considered a fingerprint of the modified surface chemistry. This work has been carried out in the framework of a cooperation project between three South American universities and is part of the effort to develop and fully characterise adsorbent materials intended for CO₂ capture.

Keywords: adsorption microcalorimetry, differential enthalpy, CO₂ capture

INTRODUCTION

The emissions of pollutant gases from the burning of fossil fuels are the main sources of greenhouse gases (GHG), which is believed to lead to the global warming. Among the GHGs, carbon dioxide (CO₂) is the major contributor in regards to the amount released in the atmosphere, although methane and chlorofluorocarbons have more pronounced greenhouse effect per unit mass (Yang et al., 2008). The high emission of CO₂ is mainly due to power plants run on fossil fuel (Lee et al., 2002; Grande and Rodrigues, 2008; Knofel et al., 2008), but there is growing demand for CH₄/CO₂ separation (natural gas and biogas upgrading) and CO₂ separation from syngas (especially that intended for Fischer-Tropsch synthesis and for H₂ use in fuel cells).

Separation technologies have been studied for CO₂ capture in pre-combustion and post-combustion scenarios, such as amine-based absorption, membrane-based separation, adsorption and cryogenic separation (Ebner and Ritter, 2009). In this context, adsorption may be a potentially attractive alternative to capturing CO₂ from stationary sources and offshore applications. Various

adsorbents have been investigated for such matter, such as zeolites, activated carbons, MOF's (metal-organic frameworks) and amine-grafted silicas (Bastin et al., 2008; Grande and Rodrigues, 2008; Merel et al., 2008; Choi et al., 2009). Furthermore, adsorbents modified with amines have been investigated as potential materials for CO_2 capture above room temperature (typically 348 K) and at low partial pressures of CO_2 (Chatti et al., 2009; Su et al., 2010; Bezerra et al., 2011). These are the conditions often found in flue gas, which also contains humidity and other contaminants (NOx, SOx), a challenging scenario with technological solutions yet to be found (Ebner and Ritter, 2009).

Regardless the final application, the accurate determination of the equilibrium equation of state (adsorption isotherms) and differential enthalpies as a function of coverage are fundamental requirements for the analysis and design of an adsorption separation process (Ruthven, 1984). Moreover, it is necessary to characterise the adsorbent material from a morphological and surface chemistry point of view, in order to understand which factors determine adsorption selectivity and capacity. Microcalorimetry combined with some other technique to measure adsorption equilibrium (e.g., volumetric devices) is an important experimental tool to determine the equilibrium relations and characterising adsorbents with respect to its energetic heterogeneity (Dunne et al., 1996a; Llewellyn and Maurin, 2005; García-Cuello, 2009; Garcia-Cuello et al., 2009; Bulánek et al., 2011).

The differential adsorption enthalpy evolved as a function of loading reveals the degree of heterogeneity of gas–solid interactions, which is an important aspect in the characterisation of adsorbents (Dunne et al., 1996a; Rouquerol et al., 1999). A decrease in the differential adsorption enthalpy with increasing coverage is typical of heterogeneous adsorbents that bear adsorption sites with different surface energies. The highest adsorption enthalpy at nearly zero coverage followed by a decrease is due to the preferential interaction of the adsorbate gas with stronger energy sites progressively occurring before interaction with weaker energy sites. Such behaviour occurs with most solids of industrial importance, such as zeolites and activated carbons. On the other hand, an increase in the differential adsorption enthalpy with increasing coverage is typical of homogeneous adsorbents (e.g., graphite). Cooperative (sorbate–sorbate) interactions between adsorbed molecules increase as the loading increases while the gas–solid energy remains constant (Dunne et al., 1996a; Llewellyn et al., 2005).

In order to design adsorption and desorption processes, the differential adsorption enthalpy is used for the calculation of energy balances in packed columns (Ruthven, 1984; Zimmermann and Keller, 2003). For instance, the differential adsorption enthalpy is the main source of energy required to regenerate the adsorbent from the column, which is the major operating cost in a temperature swing adsorption (TSA) process (Dunne et al., 1996a).

The general purpose of this work is to present the design, the assembly and the experimental validation of an adsorption microcalorimetry system for simultaneous measurements of isotherms and differential enthalpies of adsorption applied to the characterisation of the adsorbents for adsorption of CO_2. In the present study, a zeolite 13X (Z13X) and a microporous-activated carbon were employed for validating and checking reproducibility of system. Z13X was modified upon impregnation with monoethanolamine (MEA) and the effects of a modified surface chemistry on CO_2 adsorption were characterised by this technique. The adsorbents were tested for CO_2 adsorption at 273 K under the pressure range of vacuum to 101 kPa.

The measurement of fundamental adsorption data (equilibrium and kinetics), ordinarily required for process design and optimisation, has been the main research focus of the Brazilian research group on Adsorptive Separation Processes, GPSA (in Portuguese, *Grupo de Pesquisa em Separações por Adsorção*). Started in 1994 by Prof. Célio Cavalcante and Prof. Diana Azevedo from Universidade Federal do Ceará (UFC), GPSA has been engaged in the study of such topics as gas adsorption for separation (Bazan et al., 2008; Dantas et al., 2011a,b) and storage purposes (Bastos-Neto et al., 2005; Rios et al., 2009), preparative chromatography for biomolecules recovery (Sousa et al., 2009) and liquid-phase purification processes in petrochemical and biofuels applications (Luna et al., 2008). For the last 5 years, GPSA has built partnerships with national and international research groups aiming at a better understanding of adsorption from a molecular point of view, which has led to fruitful associations with Argentinian Institute of Applied Physics (INFAP/CONICET) from Universidad Nacional de San Luis (UNSL) and the Grupo de Investigación de Sólidos Porosos y Calorimetría (GSPC) of the Department of Chemistry at Universidad de los Andes (UniAndes) in Colombia. At this point, it is worth mentioning the active cooperation program between INFAP-CONICET/UNSL and GPSA/UFC (2008–2011), which was mainly focused at graduate student exchange, funded by CAPES (Brazil) and SPU (Argentina). The expertise of the Colombian team (GSPC) on the manufacture of calorimetric devices for various purposes has led to the construction of three identical apparatus installed in the three universities, to be validated against one another. The results to be shown in this study were obtained in the devices installed at UNSL and UFC. The samples studied herein were synthesised or modified at UNSL (activated carbons) and UFC (amine-modified zeolite). Molecular simulation studies are presently being carried out at INFAP and GPSA to propose adsorption mechanisms for the observed differential adsorption enthalpy as a function of coverage. These studies are out of the scope of the present work, which is mainly intended to show the features of the adsorption microcalorimetric device and original experimental data that may be extracted from such setup.

EXPERIMENTAL

Adsorbents

Three types of samples were used to test the reproducibility and accuracy of the assembled apparatus, an activated carbon (B10n), a pure and an amine-modified Z13X shaped in spherical pellets. The microporous-activated carbon sample (B10n) was prepared by chemical activation using phosphoric acid as activating agent, according to the experimental procedure reported by Maia et al. (2010). The B10n sample was pre-washed with a 10% (weight) sulphuric acid solution and then rinsed with distilled water (neutral pH) before the chemical activation step. The impregnation was carried out at 358 K for 2 h upon immersion in phosphoric acid solution at a concentration of 26% (w/w). After impregnation, the sample was dried and submitted to a one-step carbonisation, with a heating rate of 10 K/min, under nitrogen, until reaching 723 K. After carbonisation, the sample was washed with distilled water up to pH 6 and dried.

Zeolite KOSTROLITH 13X was supplied by CWK Chemiewerk Bad Kostritz (Bad Kostritz, Germany) in the form of spherical pellets of approximately 2 mm diameter. It was used as a reference material to validate the calorimetric system with data found in the literature. A sample of Z13X impregnated with MEA was prepared following the procedure described by Bezerra et al. (2011). About

2.0 g of the zeolite, previously regenerated at 623 K, were soaked in 50 mL MEA solution (10% vol. in methanol) at 298 K for 72 h. Then the solids were filtered and dried at 423 K in an inert (N_2) atmosphere. This sample will be referred to as Z13X/MEA.

Textural Characterisation

Porous texture analysis of the samples has been carried out by nitrogen isotherms at 77 K in Autosorb-1 MP (Quantachrome, Boynton Beach, FL) volumetric adsorption equipment. Specific surface area was determined according to the BET method and the micropore volume was estimated using the Dubinin–Radushkevich (DR) equation (Rouquerol et al., 1999). The total pore volume was calculated as the adsorbed volume at $P/P_0 \approx 0.98$, assuming the pores are totally filled with liquid adsorbate. Prior to each characterisation experiment, the samples were outgassed in situ. Here, the B10n, Z13X and Z13X/MEA were heated up to 423 K, 723 K and 393 K, respectively, with a rate of 1 K/min under high vacuum (turbomolecular pump) for 12–16 h.

Adsorption Microcalorimetry

Prior to each adsorption experiment, the samples were outgassed and heated up to 423 K in the case of B10n and 723 K for Z13X for 12–16 h. To avoid the possibility of degradation of the incorporated amine, the Z13X/MEA sample was outgassed at 393 K. The adsorption experiments were carried out at 273 K.

The heat evolved during each adsorption step was measured using a Tian-Calvet microcalorimeter (model CA-100; ITI, Del Mar, CA). This apparatus comprises two identical calorimetric chambers to accommodate the reference and the adsorption cells. In each chamber, there is a thermopile which is installed in electrical opposition to the other. Each thermopile was electrically calibrated by Joule effect, as described in a previous work (Garcia-Cuello et al., 2009), in order to determine the calorimetric constant K of the equipment, which converts the areas of voltage peaks to thermal energy units.

The microcalorimeter was connected to an adsorption volumetric setup to measure simultaneously the adsorption isotherm and the differential enthalpy curve. The volumetric system was built in stainless steel and fit the adsorption and reference chambers of the microcalorimeter, as shown in Figure 1. The adsorption setup includes a vacuum pump (model E2M1.5; Edwards, UK), a pressure transducer (model 2002; Teledyne Hastings Instruments, Hampton, VA) that operates in the range from 10^{-5} to 133 kPa, diaphragm valves, a calibrated cylinder and two microcalorimetric cells. The sample cell is identical to the reference cell, as a ''twin-like'' calorimeter (Calvet and Prat, 1963). The volume of each part of system was determined by expansion experiments with helium.

For the simultaneous measurement of the isotherm and the differential enthalpy curve, the calorimetric cell containing the sample must be carefully inserted in the calorimetric chamber, as shown in Figure 1. In this manner, the adsorption isotherm is evaluated by measurements of the gas pressure transducer (5) initially (after applying a pressure increment with valve V closed) and upon equilibration with the sample (valve V open), at a known temperature. The volumetric method is the most employed one to determine gas adsorption isotherms and is comprehensively described by Gregg and Sing (1982) and Rouquerol et al. (1999).

The heat evolved from the sample due to adsorption is dissipated through the thermopiles, giving rise to a voltage signal, E, recorded over the time until the return of the thermopile output signal to its base line (Solinas and Ferino, 1998). This thermoelectric potential is recorded by a multimeter, allowing for readings of 0.1 μV resolution, which is connected to a computer by means of a RS-232 interface.

The total heat (Q) produced by an event may be calculated from Equation (1) (Calvet and Prat, 1963):

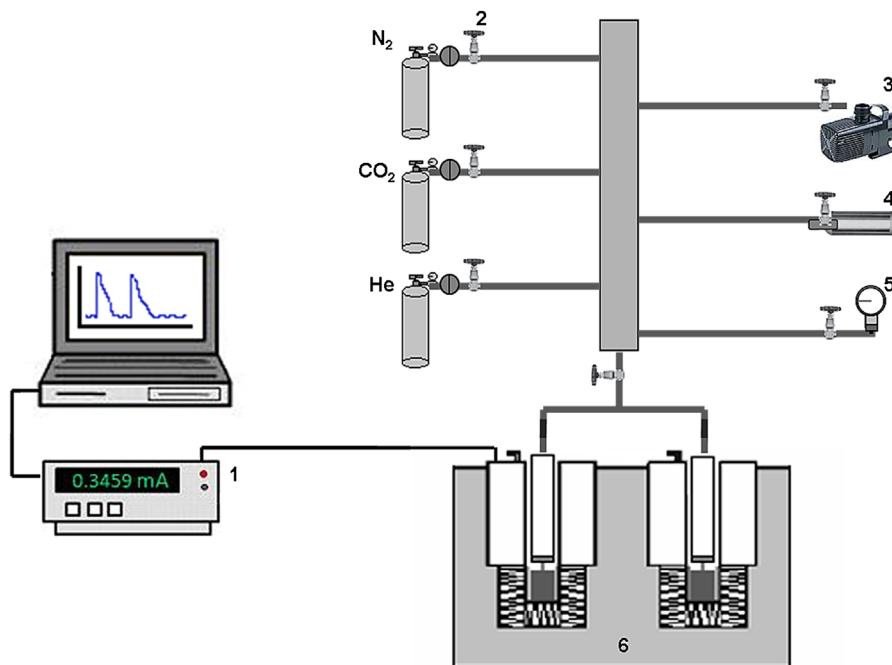$$Q = K \int_{t1}^{t2} E \, \mathrm{d}t \tag{1}$$

Figure 1. Scheme of the adsorption microcalorimetric system. (1) Multimeter, (2) diaphragm valve, (3) vacuum pump, (4) reference volume, (5) pressure gauge, (6) microcalorimeter. [Color figure can be seen in the online version of this article, available at http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1939-019X]

Table 1. Textural characteristics of the adsorbents

Adsorbents	BET surface area (m^2/g)	Micropore volume DR (cm^3/g)	Total pore volume (cm^3/g)
B10n	1019	0.40	0.41
Z13X	581	0.31	0.45
Z13X/MEA	121	0.05	0.15

Figure 2. Nitrogen adsorption isotherms at 77 K on: (a) B10n-activated carbon; (b) zeolite 13X and (c) amine-modified zeolite 13X (Z13X/MEA).

where K is the microcalorimeter constant determined from previous calibration procedures.

In order to evaluate the adsorption differential enthalpy from calorimetric data, the so-called discontinuous procedure was employed (Rouquerol et al., 1999), which consists of injecting discrete quantities of gas in successive steps to the adsorbent. Under these conditions, the differential enthalpy ($\Delta h_{ads}T,n$) of adsorption is calculated according to Equation (2) (Rouquerol et al., 1999; Llewellyn and Maurin, 2005):

$$\left(\frac{dQ_{rev}}{dn^\sigma}\right)_{T,A} + Vc\left(\frac{dp}{dn^\sigma}\right)_{T,A} = \Delta h_{ads}T, n \qquad (2)$$

where dQ_{rev} is the heat reversibly exchanged with the surroundings at temperature T measured by the calorimeter, dn^σ is the adsorbed amount due to pressure increase dp and Vc is the dead volume of the cells. In practice, the term Vc is evaluated by experiments with helium and the sample, assuming that helium is not adsorbed at low pressure at room temperature (experimental conditions of all measurements).

RESULTS AND DISCUSSION

Textural Characterisation of the Adsorbents

Table 1 summarises the textural properties for the activated carbon (B10n) and the zeolite samples Z13X and Z13X/MEA, as obtained from nitrogen isotherms at 77 K. The activated carbon sample (B10n) shows the highest specific surface area, which is typical of chemically activated carbons from lignocellulosic precursors (Rios et al., 2009). The nitrogen adsorption isotherm at 77 K for activated carbon is shown in Figure 2a. According to the IUPAC classification, the activated carbon isotherm is classified as Type I, which is typical in microporous materials (Sing et al., 1985). It is observed that the B10n sample reaches its saturation capacity (maximum adsorbed quantity) of N_2 at 77 K at about 0.1 relative pressures, which is due to the high fraction of micropores in the material (97%).

Zeolite 13X is well known as a microporous material, thus, it is also expected to show Type I N_2 isotherms. This is true for both samples Z13X and Z13X/MEA, up to 0.4 partial pressure (Figure 2b and c). However, there is a considerable increase of adsorbed N_2 above 0.7 relative pressure, which resembles the shape of a Type 2 isotherm. This may be explained by the existence of a considerable macropore fraction, due to the conformation of microporous crystals into pellets. It is also observed a reduction in the BET surface, in the micropore and total pore volume for amine-modified Z13X, which indicates that the molecules of MEA may have partially filled the pore volume. This adverse impact on textural properties upon impregnation has already been reported in literature (Chatti et al., 2009; Bezerra et al., 2011).
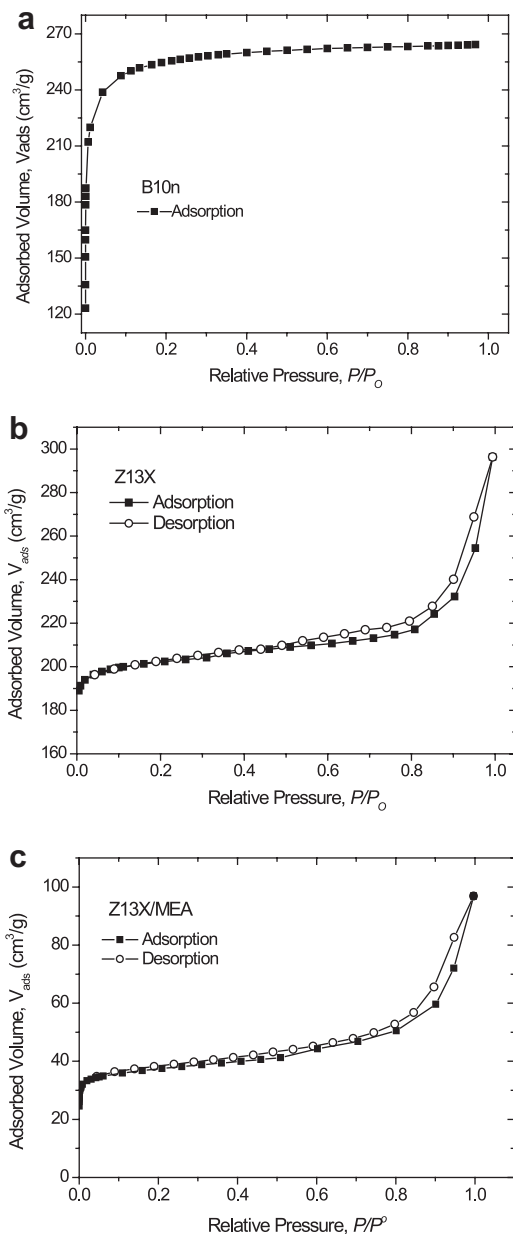
Adsorption Microcalorimetry

Adsorption of CO_2 on zeolite 13X

Several adsorption studies have been reported with zeolitic adsorbents, particularly faujasites, due to their technological importance in the chemical industry, mainly in catalysis, gas separation/purification, gas storage and ion exchange processes (Llewellyn, 2000; Zimmermann and Keller, 2003; Maurin et al., 2005). In this work, the differential calorimetric curve of Z13X was used to validate the *in-house* microcalorimetric device, since there is wide availability of adsorption and calorimetric data reported in the scientific literature for this system.

The differential enthalpy of adsorption $\Delta h_{ads}T,n$ as function of the CO_2 uptake for the Z13X is depicted in Figure 3. The initial enthalpy of adsorption is high and decreases to reach a *plateau*
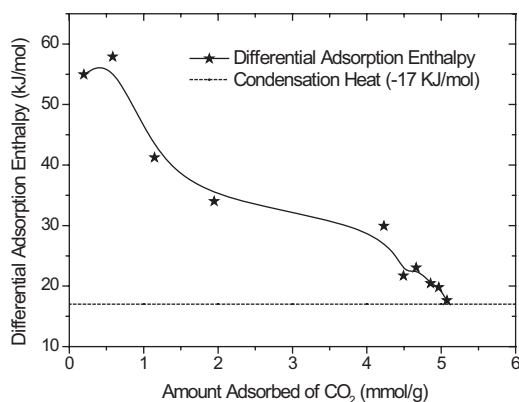
Figure 3. Differential adsorption enthalpy of CO_2 at 273 K on zeolite 13X.

Figure 5. Comparison between the differential adsorption enthalpies of CO_2 on zeolite 13X.

with increasing CO_2 coverage. This is due to the preferential interaction of CO_2 with the stronger sites, which are filled before the weaker sites. This behaviour is typical for microporous adsorbents according to the classification of differential enthalpy curves proposed by Llewellyn and Maurin (2005).

In the range of 4 and 5 mmol/g, the differential enthalpy decreases from −30 to −17 kJ/mol. Above 5 mmol/g of adsorbed CO_2, the differential heat of adsorption decreases down to −17 kJ/mol, approaching the heat of condensation of CO_2 (Arrigo et al., 2010). This behaviour is likely to indicate that the microporous filling process has been completed and the adsorption process occurs on the wider pores with eventual CO_2 condensation. This is in agreement with the measured adsorption isotherm (Figure 4).

To validate the microcalorimetric system, the differential enthalpy curves obtained in this study are compared to those reported in the literature (Figure 5). It is observed that the three curves are similar in shape and magnitude. In the 4–5 mmol CO_2/g range, it is observed that our data fully agree with those reported by Zimmermann and Keller (2003). Furthermore, in this interval, both data obtained in this study and by Zimmermann and Keller (2003) deviate from the data of Dunne et al. (1996b). Such behaviour may be a consequence of the difference between the material composition, since the measurements of Dunne et al. (1996b) were made on pure crystal Z13X, whereas the measurements of this work and that of Zimmerman and Keller's (2003) were made on zeolite pellets, which usually include up to 20%
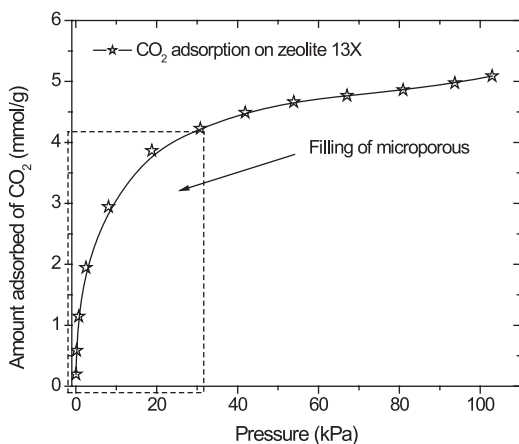
(weight) of binder in their shaping. In pure crystals, which are ideally 100% microporous, CO_2 condensation does not occur and hence the curve remains at higher enthalpy values than the heat of condensation of CO_2.

Table 2 shows a comparison with literature data of differential adsorption enthalpy values at zero coverage, for Z13X and some aluminosilicate reference materials. It may be observed that the differential adsorption enthalpy of CO_2 on aluminosilicate materials varies in the range of −65 to −32 kJ/mol at low coverage. This first experimental point is very sensitive to the experimental conditions, making it difficult to establish a rigorous comparison between the different systems or data from different methods and laboratories. In addition, it is important to observe that, generally speaking, the differential adsorption enthalpy for zeolites is dependent on the Si/Al ratio and the compensation cation, because these define the location and strength of adsorption sites in the matrix (Bulánek et al., 2010). For instance, Plant et al. (2007) compare Z13X to zeolite NaY and they state that CO_2 affinity at low coverage is lower for the latter due to different Si/Al ratios.
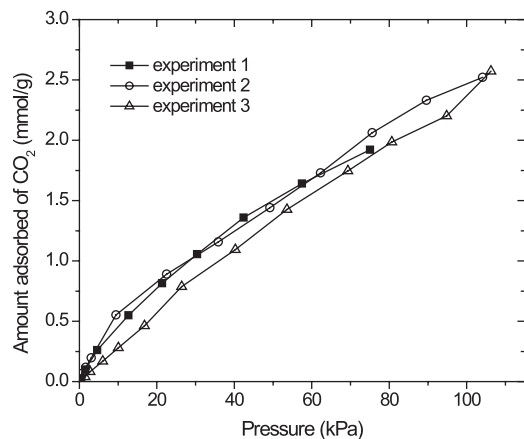
Adsorption of CO_2 on activated carbon

To evaluate the reproducibility of the microcalorimetric system, three adsorption experiments of CO_2 at 273 K were done on activated carbon (B10n). The adsorption isotherms and the calorimetric curves obtained are shown in Figures 6 and 7. Isotherms 1 and 2 were highly reproducible, whereas isotherm 3 presented a lower adsorption capacity, as shown by Figure 6. However, all of the three isotherms presented the same shape and tendency. The deviation for experiment 1 is likely to be due to incomplete outgassing of the sample, which decreased its adsorption uptake. Comparing the isotherms obtained for the Z13X (Figure 4) and for the activated carbon (Figure 6), it is noticeable that zeolitic adsorbents reach nearly its maximum capacity of adsorption (saturation) at low pressures. Nevertheless, in the same interval, the isotherm behaviour for carbon is approximately linear. This behaviour is attributed to the fixed size of micropores due to well-defined crystal structure of the zeolite, unlike activated carbons, which have amorphous pore structure and usually display a wide pore size distribution (PSD).

Figure 7 shows the curves of differential adsorption enthalpy for the activated carbon B10n. It can be observed that the differential adsorption enthalpy varies from −60 to about −20 kJ/mol and becomes roughly constant for high loadings. This result is probably due to the initial filling in the smaller pores, which bear

Figure 4. Adsorption isotherm of CO_2 at 273 K on zeolite 13X.

Table 2. Differential adsorption enthalpies of CO_2 at nearly zero coverage for zeolite 13X and some aluminosilicate reference materials

Sample	$-\Delta h_{ads}$ (kJ/mol)	Experimental conditions	Refs.
Zeolite FER	60–45	Calorimetric measurement at 307 K	Bulanék et al. (2010)
Zeolite ZSM-5	48	Calorimetric measurement at 303 K	Bonelli et al. (2000)
Zeolite NaY	32	Calorimetric measurement at 300 K	Plant et al. (2007)
	49	Calorimetric measurement at 304 K	Dunne et al. (1996b)
	48	Calorimetric measurement at 300 K	Plant et al. (2007)
Zeolite	65	Calorimetric measurement at 298 K	Zimmermann and Keller (2003)
13X	55	Calorimetric measurement at 273 K	This work

Figure 6. Adsorption isotherms of CO_2 at 273 K on activated carbon.

higher interaction energy with the CO_2, releasing higher heats of adsorption at low coverage. After that, adsorption occurs on wider pores, which release lower differential adsorption enthalpy. This decreasing behaviour is frequently observed in microporous carbons produced by well-known suppliers, like Norit or Maxsorb. Himeno et al. (2005) estimated the adsorption enthalpy at nearly zero coverage for these samples from the slopes of van't Hoff plots and found values in the range of −25 to −15 kJ/mol. They also showed that the adsorption enthalpy at low coverage is related to the pore size. The PSD of the activated carbon B10n was reported by Maia et al. (2010) and they concluded that this carbon is essentially microporous with a narrow PSD, which is
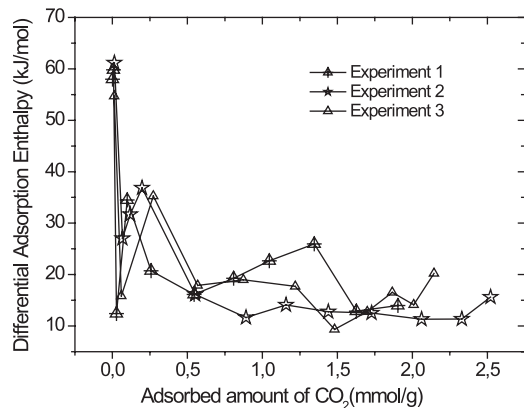
coherent with the relatively high value of differential adsorption enthalpy at low coverage measured for this sample.

Adsorption of CO_2 on sample Z13X/MEA

The impact of chemical modifications on the surface of amine-modified zeolite was evaluated by microcalorimetric measurements. The adsorption isotherm and differential adsorption enthalpy of CO_2 at 273 K are shown in Figures 8 and 9, respectively. The shape of the isotherms for pure and amine-modified Z13X is similar. However, in this pressure range and at this relatively low temperature, the functionalised zeolite has a lower adsorption capacity, as described by Bezerra et al. (2011). This fact suggests that the zeolite modification process with amine may have both filled and blocked some sites which are responsible for the physisorption of molecules of CO_2. It is well known that physisorption is significant essentially at room and lower temperatures. In such case, high surface area and pore volumes are vital to provide high uptakes. Nevertheless, as shown in the textural characterisation, both the surface area and pore volume of the modified zeolite were decreased significantly, a trend already reported in literature. Jadhav et al. (2007) reported that small MEA loadings (2.9, wt%) on zeolite allows for the enhancement in CO_2 adsorption. However, at higher loading (25, wt.%), capacity decreased due to a detrimental effect on their textural properties.

In Figure 9, it is shown that the differential adsorption enthalpy for the amine-modified Z13X is higher than that of the pure zeolite at nearly zero CO_2 coverage. At zero coverage, the maximum value is −95 kJ/mol, indicating a very strong interaction with CO_2. This fact can be attributed to preferential chemical interaction of CO_2

Figure 7. Differential adsorption enthalpy of CO_2 at 273 K on activated carbon B10n.
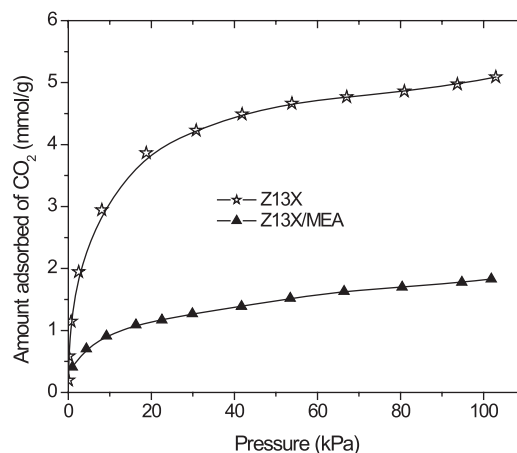
Figure 8. Adsorption isotherms of CO_2 at 273 K on pure and amine-modified zeolite 13X.
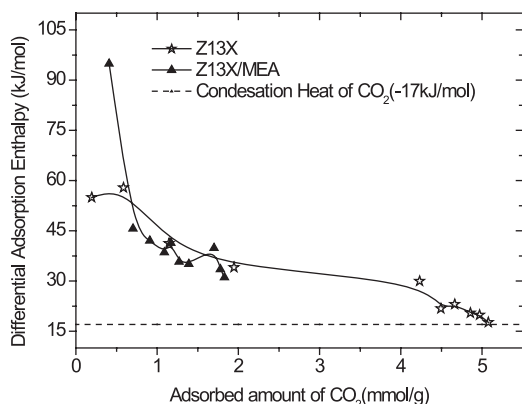
Figure 9. Comparison between the differential adsorption enthalpies of CO_2 on pure and amine-modified Z13X.

with amine surface groups impregnated in Z13X, the order of magnitude being comparable to that of a chemical reaction between CO_2 and a primary amine to form carbamates (Kim and Svendsen, 2007; Mello et al., 2011). Combining this finding with the drastic reduction in adsorption uptake, these suggest that most amine is blocking micropores where CO_2 would be physisorbed in an otherwise pure zeolite and amine groups available for chemisorption seem to be mostly located in the macroporous structure. In fact, CO_2 adsorption isotherms for these impregnated zeolites measured at higher temperatures (75°C) shows an increased uptake with respect to the uptake at lower temperatures (Bezerra et al., 2011). This also confirms that chemisorption is likely to be occurring, since chemical reactions are usually activated processes.

As shown previously, for the Z13X, the adsorption enthalpy converges to the condensation heat of CO_2 at higher CO_2 coverage (-17 kJ/mol), which is typical of the physisorption process. However, for the Z13X/MEA at high coverage of CO_2, the differential adsorption enthalpy levels off for values between -31 and -42 kJ/mol, with relatively constant values at $1-1.9$ mmolCO_2/g adsorbed. This behaviour is coherent with the existence of chemisorption sites which have higher interaction with the CO_2 than the physisorption sites from pure matrix. Because the aminogroups available for chemisorption seem to be mainly located on outer surface (macropores), and a monolayer of CO_2 is expected to be formed on such sites, overall CO_2 uptake is decreased and CO_2 is prevented from condensing at high coverage. A similar range of initial adsorption enthalpy of CO_2 was found (-90 to -100 kJ/mol) for titania (Knofel et al., 2009) and mesoporous silicas such as SBA-16 (Knofel et al., 2007) and MCM-41 (Mello et al., 2011) modified with 3-aminopropyltriethoxysilane (APTES). For impregnated MCM-41, the initial adsorption enthalpy increased by a factor of 3 as compared to the pristine material. At zero coverage, the adsorption enthalpy was -98 kJ/mol, whereas it was -32 kJ/mol for the starting material. This result indicates a stronger interaction of CO_2 with amine groups, with enthalpies of the order of magnitude of a chemisorption process. Moreover, nuclear magnetic resonance performed on APTES-functionalised MCM-41 after CO_2 adsorption experiments showed evidence that carbamates were formed as the product of the reaction between CO_2 and amine groups (Mello et al., 2011). These results are in accordance with the data reported in the present study, thus confirming the potential of adsorption microcalorimetry coupled to manometry as a technique to characterise heterogeneities in adsorbents introduced by amine impregnation.

CONCLUSIONS

As the joint work of three South American universities, a Tian-Calvet adsorption microcalorimeter built *in-house* has been presented and applied to the direct measurement of the heat evolved upon CO_2 adsorption on porous solids. The differential adsorption enthalpy as a function of coverage was measured for an activated carbon, a pure and an amine-modified Z13X. The curves at 273 K for Z13X agreed quite well with the available data in the literature, validating the microcalorimetric system. The comparison of the curves of adsorption enthalpy measured for the pure and the modified zeolite showed that the adsorption enthalpy at lower CO_2 coverage for the Z13X/MEA is higher than that for the pure zeolite, suggesting the occurrence of chemisorption. This fact shows the usefulness of the microcalorimetric technique in detecting the surface heterogeneity on adsorbents due to impregnation by amine groups and suggests that amino groups may have a detrimental impact on textural properties and hence on uptake by physisorption. On the other hand, impregnated MEA, possibly located in larger pores, contributes to chemisorption of CO_2, preventing it from condensing at higher loadings. Finally, in order to check the reproducibility of the system, three CO_2 adsorption isotherms at 273 K were carried out on the activated carbon sample. The replicates of isotherms and respective calorimetric curves follow similar and reproducible trends, providing evidence that this adsorption microcalorimeter may be a sensitive and useful apparatus for the characterisation of adsorbents for CO_2 capture.

NOMENCLATURE

E	voltage signal (V)
dp	pressure increase (Pa)
dn^{σ}	adsorbed amount (mol)
dQ_{rev}	differential heat (J)
Q	total heat (J)
K	microcalorimeter constant (W/V)
t	time (s)
Vc	dead volume (m³)
$\Delta h_{ads} T,n$	differential enthalpy of adsorption (J/mol)

REFERENCES

Arrigo, R., M. Havecker, S. Wrabetz, R. Blume, M. Lerch, J. Mcgregor, E. P. J. Parott, J. A. Zeitler, L. F. Gladden, A. Knop-Gericke, R. Schlogl and D. S. Su, ''Tuning the Acid/Base Properties of Nanocarbons by Functionalisation Via Amination,'' J. Am. Chem. Soc. **132**, 9616–9630 (2010).

Bastin, L., P. S. Bárcia, E. J. Hurtado, J. A. C. Silva, A. E. Rodrigues and B. Chen, ''A Microporous Metal-Organic Framework for Separation of CO_2/N_2 and CO_2/CH_4 by Fixed-Bed Adsorption,'' J. Phys. Chem. C **112**, 1575–1581 (2008).

Bastos-Neto, M., A. E. B. Torres, D. C. S. Azevedo and C. L. Cavalcante, Jr., ''Methane Adsorption Storage Using Microporous Carbons Obtained from Coconut Shells,'' Adsorption **11**, 911–915 (2005).

Bazan, R. E., M. Bastos-Neto, R. Staudt, H. Papp, D. C. S. Azevedo and C. L. Cavalcante, Jr., ''Adsorption Equilibria of Natural Gas Components on Activated Carbon: Pure and Mixed Gas Isotherms,'' Ads. Sci. Technol. **26**, 323–332 (2008).

Bezerra, D. P., R. S. Oliveira, R. S. Vieira, C. L. Cavalcante, Jr. and D. C. S. Azevedo, ''Adsorption of CO_2 on Nitrogen-Enriched Activated Carbon and Zeolite 13X,'' Adsorption 17, 235–246 (2011).

Bonelli, B., B. Onida, B. Fubini, C. O. Arean and E. Garrone, ''Vibrational and Thermodynamic Study of the Adsorption of Carbon Dioxide on the Zeolite Na−ZSM-5,'' Langmuir 16, 4976–4983 (2000).

Bulánek, R., K. Frolich, E. Frýdová and P. Cicmanec, ''Microcalorimetric and FTIR Study of the Adsorption of Carbon Dioxide on Alkali-Metal Exchanged FER Zeolites,'' Top. Catal. 53, 1349–1360 (2010).

Bulánek, R., K. Frolich, E. Frýdová and P. Cicmanec, ''Study of Adsorption Sites Heterogeneity in Zeolites by Means of Coupled Microcalorimetry with Volumetry,'' J. Therm. Anal. Calorim. 105, 443–449 (2011).

Calvet, E. and H. Prat, ''Recent Progress in Microcalorimetry,'' Pergamon Press, Oxford (1963).

Chatti, R., A. K. Bansiwal, J. A. Thote, V. Kumar, P. Jadhav, S. K. Lokhande, R. B. Biniwale, N. K. Labhsetwar and S. S. Rayalu, ''Amine Loaded Zeolites for Carbon Dioxide Capture: Amine Loading and Adsorption Studies,'' Microp. Mesop. Mater. 121, 84–89 (2009).

Choi, S., J. H. Drese and C. W. Jones, ''Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources,'' Chem. Sus. Chem. 2, 796–854 (2009).

Dantas, T. L. P., F. M. T. Luna, I. J. Silva, Jr., D. C. S. Azevedo, C. A. Grande, A. E. Rodrigues and R. F. P. M. Moreira, ''Carbon Dioxide/Nitrogen Separation Through Adsorption on Activated Carbon in a Fixed Bed,'' Chem. Eng. J. 169, 11–19 (2011a).

Dantas, T. L. P., F. M. T. Luna, I. J. Silva, Jr., A. E. B. Torres, D. C. S. Azevedo, A. E. Rodrigues and R. F. P. M. Moreira, ''Carbon Dioxide Nitrogen Separation Through Pressure Swing Adsorption,'' Chem. Eng. J. 172, 698–704 (2011b).

Dunne, J. A., R. Mariwala, M. Rao, S. Sircar, R. J. Gorte and A. L. Myers, ''Calorimetric Heats of Adsorption and Adsorption Isotherms. 1. O_2, N_2, Ar, CO_2, CH_4, C_2H_6 and SF_6 on Silicalite,'' Langmuir 12, 5888–5895 (1996a).

Dunne, J. A., M. Rao, S. Sircar, R. J. Gorte and A. L. Myers, ''Calorimetric Heats of Adsorption and Adsorption Isotherms. 2. O_2, N_2, Ar, CO_2, CH_4, C_2H_6 and SF_6 on NaX, H-ZSM-5, and Na-ZSM-5 Zeolites,'' Langmuir 12, 5896–5904 (1996b).

Ebner, A. D. and J. A. Ritter, ''State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries,'' Sep. Sci. Technol. 44, 1273–1421 (2009).

Garcia-Cuello, V. S., ''Diseño Construcción y Puesta a Punto de un Microcalorímetro de Adsorción,'' Master Thesis, Universidad Nacional de San Luis, Argentina (2009).

Garcia-Cuello, V., J. C. Moreno-Piraján, L. Giraldo-Gutiérrez, K. Sapag and G. Zgrablich, ''A New Microcalorimeter of Adsorption for the Determination of Differential Enthalpies,'' Microp. Mesop. Mater. 120, 239–245 (2009).

Grande, C. A. and A. E. Rodrigues, ''Electric Swing Adsorption for CO_2 Removal from Flue Gases,'' Int. J. Greenhouse Gas Control 2, 194–202 (2008).

Gregg, S. J. and K. S. W. Sing, ''Adsorption, Surface Area and Porosity,'' Academic Press, London (1982).

Himeno, S., T. Komatsu and S. Fujita, ''High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons,'' J. Chem. Eng. Data 50, 369–376 (2005).

Jadhav, P. D., R. V. Chatti, R. B. Biniwale, N. K. Labhsetwar, S. Devotta and S. S. Rayalu, ''Monoethanol Amine Modified Zeolite 13X for CO_2 Adsorption at Different Temperatures,'' Energy Fuels 21, 3555–3559 (2007).

Kim, I. and H. F. Svendsen, ''Heat of Absorption of Carbon Dioxide (CO_2) in Monoethanolamine (MEA) and 2-(Aminoethyl)ethanolamine (AEEA) Solutions,'' Ind. Chem. Res. 46, 5803–5809 (2007).

Knofel, C., J. Descarpentries, A. Benzaouia, V. Zelen, S. Mornet, P. L. Llewellyn and V. Hornebecq, ''Functionalised Micro/Mesoporous Silica for the Adsorption of Carbon Dioxide,'' Microp. Mesop. Mater. 99, 79–85 (2007).

Knofel, C., V. Hornebecq and P. L. Llewellyn, ''Microcalorimetric Investigation of High-Surface-Area Mesoporous Titania Samples for CO_2 Adsorption,'' Langmuir 24, 7963–7969 (2008).

Knofel, C., C. Martin, V. Hornebecq and P. L. Llewellyn, ''Study of Carbon Dioxide Adsorption on Mesoporous Aminopropylsilane-Functionalised Silica and Titania Combining Microcalorimetry and In Situ Infrared Spectroscopy,'' J. Phys. Chem. C 113, 21726–21734 (2009).

Lee, J. S., J. H. Kim, J. T. Kim, J. K. Suh, J. M. Lee and C. H. Lee, ''Adsorption Equilibria of CO_2 on Zeolite 13X and Zeolite X/Activated Carbon Composite,'' J. Chem. Eng. Data 47, 1237–1242 (2002).

Llewellyn, P., ''Characterisation of Microporous Materials by Adsorption Microcalorimetry,'' Membr. Sci. Technol. Ser. 6, 213–230 (2000).

Llewellyn, P. L. and G. Maurin, ''Gas Adsorption Microcalorimetry and Modelling to Characterise Zeolites and Related Materials,'' C. R. Chim. 8, 283–302 (2005).

Llewellyn, P. L., G. Maurin, T. Poyet, N. Dufau, R. Denoyel and F. Rouquerol, ''Do the Differential Enthalpies of Adsorption Vary Between 77 K and 302 K? An Experimental Case Study of Argon and Nitrogen on Two Faujasite Type Zeolites,'' Adsorption 11, 73–78 (2005).

Luna, F. M. T., A. A. Pontes-Filho, E. D. Trindade, I. J. Silva, Jr., C. S. Azevedo and C. L. Cavalcante, Jr., ''Removal of Aromatic Compounds from Mineral Naphthenic Oil by Adsorption,'' Ind. Eng. Chem. Res. 47, 3207–3212 (2008).

Maia, D. A. S., K. Sapag, J. P. Toso, R. H. López, D. C. S. Azevedo, C. L. Cavalcante, Jr. and G. Zgrablich, ''Characterisation of Activated Carbon from Peach Stones Through the Mixed Geometry Model,'' Microp. Mesop. Mater. 134, 181–188 (2010).

Maurin, G., P. L. Llewellyn, T. Poyet and B. Kuchta, ''Adsorption of Argon and Nitrogen in X-Faujasites: Relationships for Understanding the Interactions with Monovalent and Divalent Cations,'' Microp. Mesop. Mater. 79, 53–59 (2005).

Mello, M. R., D. Phanon, G. Q. Silveira, P. L. Llewellyn and C. M. Ronconi, ''Amine-Modified MCM-41 Mesoporous Silica for Carbon Dioxide Capture,'' Microp. Mesop. Mater. 143, 174–179 (2011).

Merel, J., M. Clausse and F. Meunier, ''Experimental Investigation on CO_2 Post-Combustion Capture by Indirect Thermal Swing Adsorption Using 13X and 5A Zeolites,'' Ind. Eng. Chem. Res. 47, 209–215 (2008).

Plant, D. F., G. Maurin, I. Deroche and P. L. Llewellyn, ''Investigation of CO_2 Adsorption Qin Faujasite Systems: Grand Canonical Monte Carlo and Molecular Dynamics Simulations Based on a New Derived $Na^+−CO_2$ Force Field,'' Microp. Mesop. Mater. 99, 70–78 (2007).

Rios, R. B., F. W. M. Silva, A. E. B. Torres, D. C. S. Azevedo and C. L. Cavalcante, Jr., ''Adsorption of Methane in Activated Carbons Obtained from Coconut Shells Using H_3PO_4 Chemical Activation,'' Adsorption **15**, 271–277 (2009).

Rouquerol, F., J. Rouquerol and K. Sing, ''Adsorption by Powders & Porous Solids,'' Academic Press, San Diego (1999).

Ruthven, D. M., ''Principles of Adsorption and Adsorption Processes,'' Wiley, New York, U.S.A. (1984).

Sing, K. S. W., D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, ''Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity,'' Pure Appl. Chem. **57**(4), 603–619 (1985).

Solinas, V. and I. Ferino, ''Microcalorimetric Characterisation of Acid–Basic Catalysts,'' Catal. Today **41**, 179–189 (1998).

Sousa, A. S., A. P. Guimařaes, C. V. Gonçalves, I. J. Silva, Jr., C. L. Cavalcante, Jr. and C. S. Azevedo, ''Purification and Characterisation of Microbial Hyaluronic Acid by Solvent Precipitation and Size-Exclusion Chromatography,'' Sep. Sci. Technol. **44**, 906–923 (2009).

Su, F., C. Lu, S. C. Kuo and W. Zeng, ''Adsorption of CO_2 on Amine-Functionalised Y-Type Zeolites,'' Energy Fuels **24**, 1441–1448 (2010).

Yang, H., Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland and I. Wright, ''Proguess in Carbon Dioxide Separation and Capture: A Review,'' J. Environ. Sci. **20**, 14–27 (2008).

Zimmermann, W. and J. U. Keller, ''A New Calorimeter for Simultaneous Measurement of Isotherms and Heats of Adsorption,'' Thermochim. Acta **403**, 31–41 (2003).