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Study of CO_2 adsorption in functionalized carbon

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Abstract We evaluated the ability of CO_2 adsorption in functionalized activated carbons granular and monolithic type, obtained by chemical activation of African palm stone with H_3PO_4 and $CaCl_2$. We made a comparison between two methods of incorporation of nitrogen groups: the impregnation method with NH_4OH solution and NH_3 gasification. The materials were texturally characterized by N_2 adsorption at 77 K, the isotherms shows obtaining microporous materials with surface areas between 545–1425 $m^2\,g^{-1}$ and pore volumes between 0.22 to 0.53 $cm^3\,g^{-1}$. It was established that with the methodologies used for functionalization is increased content of nitrogen groups, was achieved a higher proportion of such groups when carrying out the process in liquid phase with NH_4OH. The incorporation of nitrogen groups in the material generates an increase of up to 65 % in the CO_2 adsorption capacity of the MCa2 (Monolith prepared with $CaCl_2$ solution at 2 %) sample. Was reached a maximum adsorption capacity of 344 $mgCO^2\,g^{-1}$ in the MCa2FAL (sample MCa2 functionalized with NH_4OH solution) sample.

Keywords Activated carbon · Chemical activation · Functionalization · CO_2 adsorption

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1 Introduction

The formation of carbon dioxide (CO_2) and its accumulation in the atmosphere are a widespread concern in most industrialized countries, mainly due to the contribution of this gas to global climate change.

The generation of carbon dioxide (CO_2) is inherent to combustion when fossil fuels are used, the effective capture of emissions of CO_2 from industrial and commercial operations is seen as an important strategy that has the potential to achieve a significant reduction in atmospheric levels of CO_2. This capture is based in the separation of CO_2 contained in flue gases produced in power plants and industrial processes. All technologies that can be used for CO_2 capture required the use of separation techniques for translate the currents where the CO_2 appears as a dilute gas in other currently highly concentrated streams of CO_2, with the right conditions for transport and storage (Andersson et al. 2005).

Adsorption is considered one of the most attractive options for CO_2 capture (Sjostrom and Krutka 2010). However, the efficient CO_2 capture based on adsorption requires solid adsorbents that not only present a high adsorption capacity but also high selectivity for retaining CO_2 preferentially over other gases. The development of a new generation of materials that can absorb this gas efficiently, will undoubtedly enhance their separation from other adsorbates (e.g., CH_4, N_2, etc.) in industrial applications.

Thus, the main objective to reduce CO_2 emissions on an industrial scale is the development of a means of capturing low-cost, high selectivity and high adsorption capacity even at moderate temperatures (at this point should be borne in mind that flue gas is at temperatures between 50 °C and 100 °C) and that allow a controlled desorption so that the amount of adsorbed CO_2 can be used in other types of processes. Porous materials, such as molecular sieves, zeolites and activated carbons are suitable materials for CO_2 capture due to their highly developed porous structure (Chaffee et al. 2007).

In general, activated carbons (CAs) have a well developed porous structure which gives them a high surface area and high pore volume, when compared with other porous solids. In some processes the activated carbon surface chemistry is not sufficiently "active" to allow the establishment of specific adsorbate-adsorbent interactions. In such cases, appropriate modification of carbon materials surface chemistry by the incorporation of surface groups (heteroatoms), may contribute to improve the adsorption process (Figueiredo et al. 1999). In this regard, various studies have shown that the ability of activated carbon for adsorption of an acid molecule such as CO_2—which relies on physical adsorption—can be increased by introducing nitrogen functional groups in its structure (Gray et al. 2004; Thote et al. 2010).

In this work were prepared, characterized and functionalized granular and monolithic carbonaceous materials for the carbon dioxide adsorption. For this was used as precursor material African palm stone (*Elaeis guineensis*) which was activated with two types of agents: H_3PO_4 and $CaCl_2$ at different concentrations. These prepared materials, were functionalized in gas phase with NH_3 and liquid phase with NH_4OH, with the intention to incorporate surface basic groups (nitrogen groups) and subsequently, were studied in the CO_2 adsorption at 273 K and until 1 bar.

2 Experimental section

2.1 Materials preparation

In the series prepared, the impregnation of African palm stone was performed on relation 2 mL of solution/1g precursor. Were taken two portions of precursor, one of these was mixed with solutions of H_3PO_4 (series GACP) at different concentrations (from 32 % −36 % −40 % −48 % w/v), at a temperature of 358 K for 2 hours with a subsequent drying at 393 K for approximately 10 hours. The other portion was impregnated initially with $CaCl_2$ (series MCa), were used solutions at 2 %, 3 %, 5 % 7 % w/v and subsequently each one was impregnated with a solution at 32 % H_3PO_4 (to facilitate the compaction of the monoliths) the impregnation was performed at 358 K for 6 hours, then the temperature was increased to 393 K for approximately 8 hours. These conditions were selected according to previous work (Nakagawa et al. 2007; Juárez-Galán et al. 2009). The synthesis of honeycomb monoliths requires a process of compaction, in which the precursor impregnated is leads to a uniaxial press and is subjected to a pressure of 4500 psi and a temperature of 423 K during 30 seconds. The activation was conducted in a horizontal furnace Carbolite®, the impregnated precursors with H_3PO_4 are supported in a quartz container under N_2 flow of 80 mL min^{-1}, at a heating rate of 1 K min^{-1} until 723, remaining in this temperature during 2 hours. The materials activated with $CaCl_2$ are subjected to a flow of 100 mL min^{-1} CO_2 at a heating rate of 3 K min^{-1} to 1073 K, remaining in this temperature during 6 hours, then is done a heating to 873 K for 2 hours in N_2 atmosphere to remove excess CO_2 from the materials (Juárez-Galán et al. 2009).

Subsequently, the solids that were activated with H_3PO_4 washed with hot distilled water to remove residues of impregnation until neutral pH and conductivity between 5 and 10 ms cm^{-1}; the carbonized with $CaCl_2$ initially washed with 1 M HCl solution and then with hot distilled water. Finally, the carbonaceous materials are dried in an oven at 383 K for 12 hours and stored in plastic containers in a nitrogen atmosphere.

2.2 Functionalization

Based on the results of the characterization that was performed on all activated carbons obtained and shown in a previous work (Vargas et al. 2012), were chosen the materials with higher CO_2 adsorption capacity in each series and were subjected to the processes described below.

2.2.1 *Impregnation method*

Were taken 3 g of the samples anteriorly selected, which previously dried overnight at 373 K, and were impregnated with 80 mL of ammonium hydroxide (NH_4OH) concentrated (28–30 %) at a temperature of 353 K in reflux for 24 hours. After this time the solution was filtered and the carbonaceous materials were washed with distilled water to remove excess ammonium hydroxide superficial. Finally, the carbons were dried at 373 K for 6 hours (Plaza et al. 2007; Pirngrube et al. 2009).

2.2.2 *Gasification method*

For the functionalization of the carbonaceous materials by gasification, was carried out a treatment with gaseous ammonia in a horizontal furnace. About 3 g of carbon were dried overnight at 373 K, then are supported in a quartz container and introduced into the reactor, heating was started under N_2 flow of 80 mL min^{-1} for 30 min. When the oven reaches a temperature of 1073 K, the N_2 flow is changed to NH_3 (50 mL min^{-1}) and maintained for 5 hours. The sample is cooled to 373 K under a flow of ammonia. Finally the flow is switched back to N_2 until it reaches room temperature (Pirngrube et al. 2009; Plaza et al. 2009, 2011; Przepiòrski et al. 2004).

The functionalized samples are identified along the paper by the same conventions used in each series, followed by the lettering: FAL (functionalization with ammonium hydroxide solution) and FAG (functionalization with ammonia gas) according to the sample

2.3 Characterization

The textural properties of the synthesized monoliths were analyzed using N_2 adsorption measurements at 77 K in a volumetric system (Quantachrome, Autosorb 3-B). Before the adsorption experiments, samples were submitted to an outgassing treatment at 523 K for 24 h. The volume of micropores, V_0 (N_2) and the volume of narrow micropores ($V_n(CO_2)$; pores <0.7 nm) was obtained by application of the Dubinin-Radushkevich equation to the nitrogen adsorption data (Ni liquid density $= 0.808\ \mathrm{g\,cm^{-1}}$) and dioxide carbon adsorption data (CO_2 (273 K) liquid density $= 1.023\ \mathrm{g\,cm^{-1}}$), respectively. The total pore volume, V_t, was obtained from the amount adsorbed at a relative pressure P/P^0 of 0.99 while the mesopore volume, V_{meso}, was obtained from the difference between the total pore volume and the micropore volume (Marsh and Rodríguez-Reinoso 2005). Additionally we determined the total basicity and acidity of the materials by Boehm titrations in which about 100 mg of adsorbent was immersed in 25 mL of solutions NaOH and HCl 0.1 M in plastic containers of 50 mL, the solutions are left to 298 K, stirred manually twice a day for 48 hours; occasionally N_2 is bubbled on solutions in order to remove atmospheric CO_2 and finally aliquots of these solutions are titrating with acid or base solutions with previously standardized (Boehm 2002). We also performed an analysis of infrared spectroscopy for this purpose 0.1 g of the activated carbons were ground and mixed with potassium bromide (to remove dispersers effects of large crystals). This powder mixture is compressed into a mechanical press to form a translucent disc through which can pass the light ray spectrometer. Then we read on a Thermo-Nicolet 6700 FT-IR (Kohl et al. 2010). Finally we performed immersion calorimetry in solutions of HCl and NaOH 0.1 N, for determining the enthalpy of immersion, were weighed about 100 mg of sample and placed in a glass ampoule coupled to the calorimetric cell designed for this purpose. Were then added 8 mL of the solvents mentioned. The cell was placed in the main reservoir of heat, and then was left to stabilize the temperature of the calorimetric set for about 1 hour, or the time needed for stabilization of the calorimeter, after was performed of immersing the sample in solution and were recorded thermal changes until that the baseline stabilized again, finally we recorded an after-period during 20 minutes. And the measure ended with the electrical calibration experience (Silvestre-Albeiro et al. 2001; Vargas et al. 2011).

The adsorption capacity for CO_2 in the different activated carbon monoliths at 273 K and until 1 Bar was measured using a volumetric system (Quantachrome, Autosorb 3-B). Before the adsorption experiments, the different samples were outgassed at 423 K for 4 h.

3 Results and discussion

3.1 Textural characteristics

Textural characteristics of the carbonaceous materials were determined by N_2 adsorption measurements at 77 K. Each series presented different behaviors associated with the type of activating agent used, the surface areas are between 542–1425 $\mathrm{m^2\,g^{-1}}$ and the pore volume between 0.22 to 0.53 $\mathrm{cm^3\,g^{-1}}$. Within the series found that the CAGP48 and MCa2 samples have the best adsorption capacity, and therefore were used for the functionalization process.

Figure 1 shows adsorption isotherms for the original and functionalized carbonaceous materials. In Fig. 1a is observed that the isotherms obtained for the samples are type I according to the IUPAC classification (Sing et al. 1985),

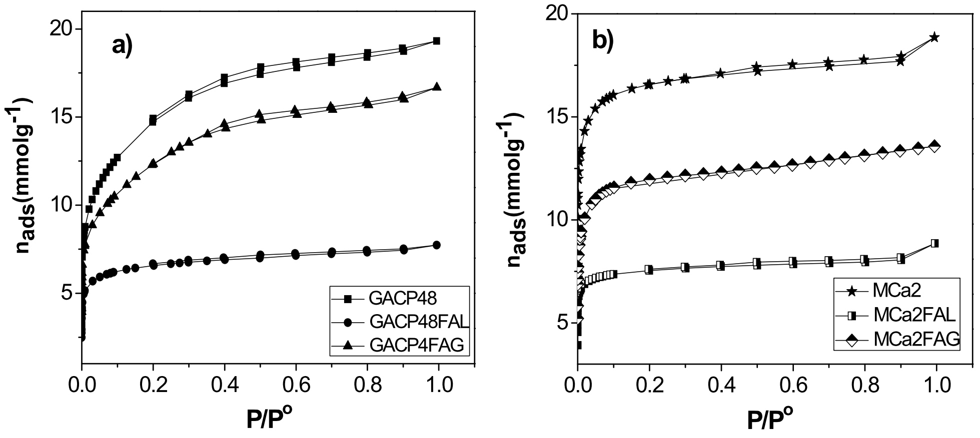

Fig. 1 Nitrogen adsorption isotherms for original and modified samples (**a**) GACP, (**b**) MCa2

Table 1 Textural parameters for carbonaceous materials obtained from the N_2 adsorption isotherm at 77 K and CO_2 adsorption isotherm at 273 K

Sample	N_2 adsorption data at 77 K				CO_2 adsorption data at 273 K
	S_{BET} (m^2g^{-1})	V_0 (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	$V_{0.99}$ (cm^3g^{-1})	V_n (cm^3g^{-1})
GACP48	1137	0.40	0.27	0.67	0.20
GACP48FAG	944	0.33	0.25	0.58	0.22
CAGP48FAL	542	0.22	0.05	0.27	0.30
MCa2	1425	0.53	0.12	0.65	0.50
MCa2FAG	1030	0.38	0.08	0.46	0.53
MCa2FAL	658	0.25	0.05	0.30	0.64

CAGP48 and CAGP48FAG materials presents an open elbow at low relative pressures ($P/P^0 < 0.1$), indicating a pore size distribution in the samples, while the CAGP48FAL sample has a closed elbow characteristic of materials with narrow porosity. Meanwhile in Fig. 1b the isotherms obtained for the original and functionalized samples MCa2, MCa2FAG and MCa2FAL are type I with closed elbow own of a narrow pore distribution. In both samples the functionalization processes generate a decrease in BET area and pore volumes. From the nitrogen adsorption isotherms can be seen that the functionalization in both cases decrease the textural characteristics of the original samples, the change with ammonia gas is between 17–27 %, while the functionalization with ammonium hydroxide leads to decrease a 52 % the surface area and pore volume of materials. This decrease can be attributed to a block in the carbon matrix produced by the nitrogen surface groups that generated during the reaction with ammonia and ammonium hydroxide.

Table 1 shows the textural characteristics of the carbonaceous materials, as discussed above, is observed a decrease in surface area, micropores, mesopores and the total volume. By contrast with the functionalization of materials, narrow micropore volume (V_n) obtained from the adsorption isotherm of CO_2 to 273 K, which corresponds to the volume of pores below ∼0.7 nm (Garrido et al. 1987), increases. For CAGP48FAL, MCa2FAL and MCa2FAG samples this value is greater than the total volume of micropores (V_0) determined by N_2 adsorption that measured all pores of size less than 2 nm, this behavior reflects the existence of kinetic constraints for the N_2 access in narrow microporosity.

3.2 Chemical characteristics

3.2.1 Infrared spectroscopy

Figure 2 shows the FTIR spectra of the original and functionalized samples. In the spectra of Figs. 2a and 2b are noted three bands of interest: one located between 3200 to 3600 cm^{-1}, associated with O–H stretching vibration in alcohols and carboxylic acids, are observed in addition, a series of peaks between the wave number of 1420 and 1700 cm^{-1} of moderate intensity, attributable to lengthening of the functional groups of type, C=O and C=C, which may correspond to the presence of ketones, esters, aldehydes and carboxylic acids (Shin et al. 1997). And a band between 860–1270 cm^{-1} characteristic of C–O stretching. The spectra of the CAGP48 and CAGP48FAG samples are similar to each other, as are the spectra of the MCa2 and MCa2FAG samples, indicating that treatment with ammonia does not substantially modify the surface chem-

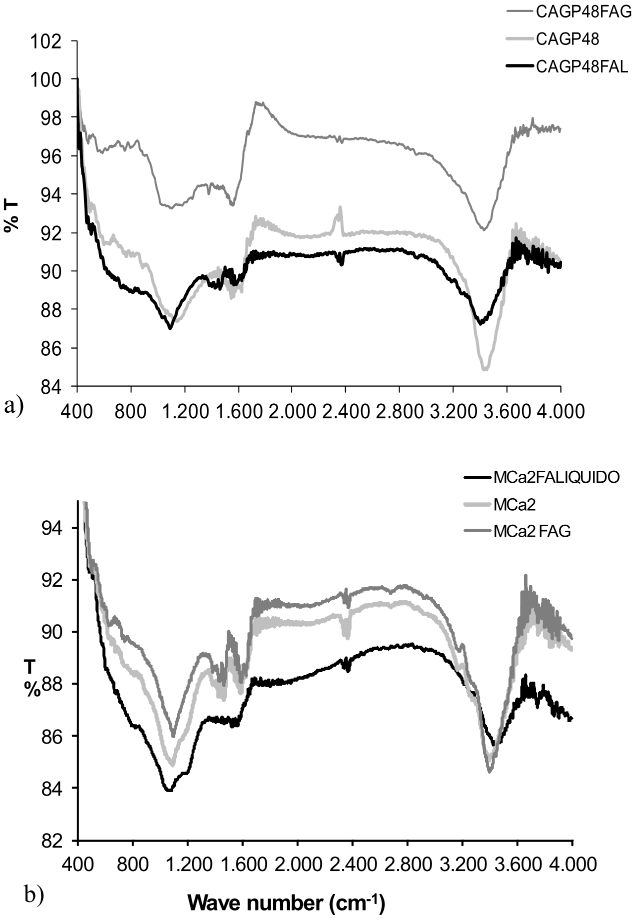

Fig. 2 FTIR spectra for original and modified samples (**a**) GACP, (**b**) MCa2

Table 2 Total acidity and basicity of samples together with immersion enthalpies of the original and functionalized samples in acidic and basic medium

Sample	Total acidity (μmol g^{-1})	Total bacisity (μmol g^{-1})	$-\Delta H$ imm HCl (J g^{-1})	$-\Delta H$ imm NaOH (J g^{-1})
GACP48	434	138	10.20	28.34
GACP48FAG	340	144	15.69	22.48
CAGP48FAL	328	183	24.19	20.63
MCa2	553	54	6.43	32.40
MCa2FAG	184	129	12.24	16.39
MCa2FAL	134	164	20.31	14.87

istry of carbon materials, however in the CAGP48FAG and MCa2FAG samples, can be seen the presence of a low intensity band at 1190 cm^{-1} characteristic of the CN group. The CAGP48FAL and MCa2FAL samples presents a different spectrum compared to the original samples CAGP48 and MCa2; the band located between at 3200 to 3600 cm^{-1}, associated with O–H stretching vibration in carboxylic acids and alcohols has a lower intensity with respect to the other two samples, likewise between 1420–1700 cm^{-1} shows the decrease of the signals corresponding to C=O and C=C, moreover is observed a better defined peak in the MCa2FAG sample in 1190 cm^{-1} characteristic of the CN group, meanwhile CAGP48FAL sample has a band of low intensity at 1400 cm^{-1} characteristic of the amino group (Plaza et al. 2007). According to the spectra is observed that the functionalization with ammonium hydroxide generates the greatest changes in surface chemistry of the materials which can be associated with the reactions between the groups at the surface of the original carbon and ammonium hydroxide used to the amendment.

3.2.2 Chemical characteristic and immersion calorimetry

Table 2 shows data for the total acidity and basicity together with the immersion enthalpies in HCl and NaOH 0.1 N solutions, obtained for the original and functionalized activated carbons.

Acidity values ranging from 134–553 μmol g^{-1} and basicity between 54–183 μmol g^{-1}. It is observed that the functionalization process using both methods generates a decrease of the total acidity of the materials and an increase in the basicity. Also it is evident that the incorporation of basic groups is favored by the acidity of original material, because with ammonium hydroxide modification in the MCa2 sample that has an acidity of 553 μmol g^{-1}, is achieved the triple its initial basicity (MCa2FAL), while in the CAGP48 sample which has a acidity of 434 mmol g^{-1}, only increases its basic character one third part of the original value (CAGP48FAL Sample).

Additionally in the table are shows the enthalpic data for the samples. Immersion calorimetry is a technique in which is measured the thermal effects resulting of immersing a solid in a solvent usually non-polar type with which the solid generally do not react (Silvestre-Albeiro et al. 2001; Vargas et al. 2011). This heat of immersion or wet heat is related to the formation of an adsorbed molecules layer of liquid on the solid surface, together with the wetting of the adsorbed layer. The heats of immersion of a solid specific in liquids with different chemical properties (acidic and basic solutions) can be used to establish or confirm specific interactions with groups on the surface of the solid.

The enthalpies in acid medium are between −6.43 and −20.31 J g^{-1} and in basic medium are between −16.39 and −32.40 J g^{-1}, is observed that with the functionalization process increases the interaction between the solid and the acid generating a higher enthalpic value, and enthalpy decreases in basic medium.

3.3 CO_2 adsorption at 273 K

As mentioned earlier, the CO_2 adsorption has become very important in recent years due to the impact it has on the environment. In this connection are required materials not only with a low cost, but also have a high selectivity to the molecule, for which are made chemical modifications that enhance the interaction of the gas with the solid adsorbent. In this perspective was evaluated CO_2 adsorption capacity of original and functionalized carbonaceous materials, for this measured was used a volumetric equipment, the experiments of adsorption were made at 273 K and until 1 bar.

Figure 3 shows the CO_2 adsorption isotherms obtained for the materials. It is appreciated that in functionalized samples there are increased the adsorption capacity of the gas. In according with previous work the form of CO_2 adsorption isotherms at 273 K is related to the mechanism of adsorption. Accordingly the isotherms of the original and modified samples as have a tendency near of the rectilinear, that can be related with a CO_2 absorption mechanism wherein the surface coverage is associated with pore sizes greater than two times the molecular dimension CO_2 (Martin-Martínez et al. 1995).

Table 3 shows the amounts of CO_2 adsorbed. Is observed an adsorption capacity between 105–334 mgCO_2 g^{-1}. The highest retention of gas are obtained for CAGP48FAL and MCa2FAL samples. It is evident that the functionalization with ammonia generates an increase in CO_2 adsorption capacity between 13–18 %, whereas with ammonium hydroxide the increase is greater, obtaining a 47–65 % more of CO_2 adsorbed. The MCa2FAL sample is capable of adsorbing 334 mgCO_2 g^{-1}, this value is satisfactory, considering that there have been adsorbed amount of ∼380 mgCO_2 g^{-1}, in carbon molecular sieves with a surface area of 3100 m^2 g^{-1} and a V_n above 1.40 cm^3 g^{-1} (Wahby et al. 2010).

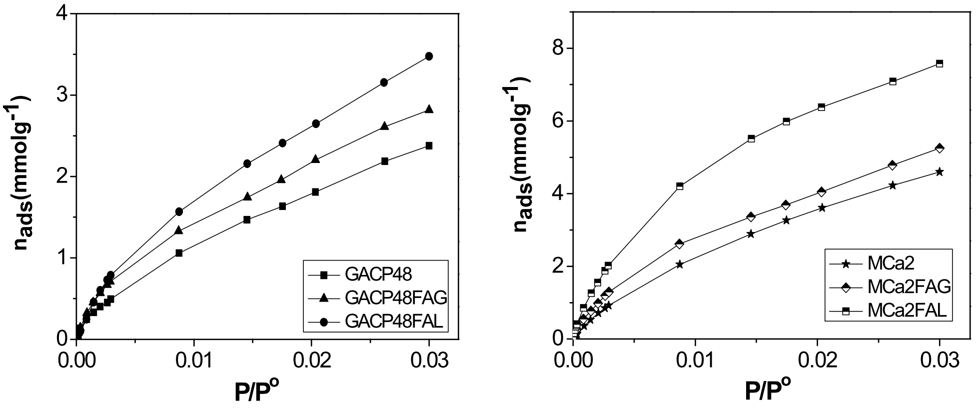

Fig. 3 CO_2 adsorption isotherms at 273 K and until 1 bar

Table 3 CO_2 adsorbed amount ($mgCO_2\,g^{-1}$) at 273 K and 1 bar of samples

Sample	CAGP48	CAGP48FAG	CAGP48FAL	MCa2	MCa2FAG	MCa2FAL
$mgCO_2\,g^{-1}$	105	124	153	203	230	334

4 Conclusions

We studied the CO_2 adsorption capacity in unmodified and functionalized activated carbon through gasification and impregnation technique. Was obtained surface areas between 161–1425 $m^2\,g^{-1}$ and pore volumes between 0.09 to 0.53 $cm^3\,g^{-1}$. It was found that functionalizations generate a decrease in the textural characteristics of the materials caused by a blockage of the porosity of the material due to the groups generated by the chemical modification. The results obtained using the three characterization techniques employed: FTIR, Boehm titration and immersion calorimetry, show that the functionalization processes used are able to modify the surface chemistry of the materials, increasing the content of nitrogen groups in the carbonaceous solids. Furthermore it was established that the most effective method of functionalization, in this study is in liquid phase with ammonium hydroxide.

Finally adsorption tests showed that the amount CO_2 adsorbed is increased with the incorporation of nitrogen groups in the carbon matrix. Such functionalization generates an increase between 13 to 65 % in the CO_2 adsorption capacity of the solids. It reached a maximum adsorption capacity of 334 $mgCO_2\,g^{-1}$ in the sample MCa2FAL.

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