



Chemical modification of carbon powders with aminophenyl and aryl-aliphatic amine groups by reduction of *in situ* generated diazonium cations: Applicability of the grafted powder towards CO₂ capture

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ABSTRACT

Aminophenyl, p-aminobenzyl and p-aminoethylphenyl groups were grafted at the surface of carbon Vulcan XC72R by spontaneous reduction of the *in situ* generated diazonium cations from the corresponding amine. X-ray photoelectron spectroscopy and elemental analysis confirmed an amine loading of about 1 mmol/g. The grafting of amine functionalities leads to a decrease of specific surface area from 223 to about 110 m²/g with a drastic loss of microporosity. Acid–base properties of the surface are also affected by the modification. Aminophenyl grafted groups make the surface more acidic while aryl-aliphatic amines groups tends to render it more basic. The grafted layer shows in each case a good thermal stability up to 250 °C. The affinity of the modified powder towards CO₂ and N₂ has been evaluated by thermal swing adsorption. The maximum adsorption capacity of CO₂ of modified carbons is lower than the unmodified carbon but the presence of the amine functionalities involves a better selectivity of the material towards CO₂ adsorption in comparison of N₂ adsorption.

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1. Introduction

Carbonaceous materials are widely used in different applications such as inks, sorbents, electrode materials, and support for catalysts [1]. Surface modification of carbons allows the direct modulation of their physicochemical properties to improve their suitability in various applications. Different possible treatments of the surface include thermal treatment under various atmospheres [2,3], oxidation [4], irradiation [5], or chemical modification such as grafting [6] or depositing a thin layer on the surface [7]. For the last two methods, the growing popularity of the diazonium salt chemistry has to be mentioned. Pinson and co-workers first described in 1992 the electrochemical reduction of diazonium salt leading to the grafting of aryl groups at a carbon surface [8]. Furthermore, the spontaneous modification of carbonaceous materials in presence of diazonium salts has also been reported [6,9–15].

Among various functionalities, amino groups are useful in different applications from biology (biochips [16,17]) to environment (acid gas sorbent [18,19] and heavy metal recovery [20,21]). Amines are particularly useful for the removal of carbon dioxide in post-combustion processes [19]. Adsorption processes are one of the most attractive technique to capture CO₂, but to be efficient,

solid sorbents must have a high CO₂ adsorption capacity and a high selectivity, combined to an easy regeneration [19,22]. Mesoporous silicas are commonly modified by aminosilanes to this purpose and such modification typically leads to a monolayer of amine on the surface of silica [23,24]. Depending on the surface area and the porous structure, amine loading can be as high as 1–5 mmol/g and the capture of CO₂ depending on the composition of flue gases varies from 0.1 to 2.3 mmol/g [24–27]. Porous carbonaceous materials are also promising materials for CO₂ sorbent application due to their highly developed porous structure, low cost, and their large choice in the form of the support that can improve the facility of handling. To improve the material selectivity, nitrogen functional groups can be introduced in different ways. For example, impregnation of carbon powders by nitrogen enriched polymers has been reported [28]. Another way to enrich carbons with nitrogen is to prepare the activated carbon with a nitrogen containing polymer or to introduce nitrogen species by a high thermal treatment under ammonia [29]. Finally, grafting of amino groups on carbon support by diazonium chemistry has been reported on glassy carbon [30] and carbon nanotubes [31] and on carbon powder [15]. However, these materials have never been tested for CO₂ capture.

Here, we report the modification of carbon powder Vulcan XC72R by reaction with the corresponding diazonium cations of these three diamines: paraphenylenediamine, aminobenzylamine and aminoethylamine. The *in situ* diazotization of these molecules leads to the attachment of aryl groups containing a primary amine.

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These compounds have been characterized by elemental analysis, X-ray photoelectron spectroscopy, thermogravimetric analysis, adsorption isotherms under nitrogen and carbon dioxide. Furthermore, their potential as a CO₂ sorbent has been evaluated by means of a thermogravimetric analyzer as well as their selectivity towards CO₂ (vs. N₂).

2. Experimental section

2.1. Carbon surface modification

All the reagents (Vulcan XC72R (Cabot), hydrochloric acid (Fisher), sodium nitrite and all the diamines (Aldrich)) were used as received.

Typically, 500 mg of carbon Vulcan XC72R (Cabot) was added in 50 mL of deionized water (Barnstead Nanopure II). The powder was dispersed by vigorous stirring during about 15 min. Then, 0.1 eq of diamine was introduced, followed by 0.1 eq of solid sodium nitrite and finally 5 mL of concentrated HCl. The resulting mixture was stirred overnight and filtered over a nylon membrane having pores of 0.47 μm (GE Osmonics). Finally, the powder was washed with successive aliquots of water, DMF, MeOH and acetone and allowed to dry overnight under vacuum at 40 °C.

Three diamines were used to modify carbon Vulcan XC72R: paraphenylenediamine, 4-aminobenzylamine and 4-aminoethylaniline. The modification was carried *in situ* as the diazonium cations are directly formed from the corresponding amine and then reduced by carbon without prior isolation. The respective resulting modified powders are named Vulc-NH₂, Vulc-ABA and Vulc-AEA. (Scheme 1).

2.2. Characterization methods

2.2.1. X-ray photoelectron spectroscopy (XPS)

The XPS measurements were performed on an Axis Ultra spectrometer (Kratos Analytical) at the Alberta Centre for Surface Engineering and Science (ACES), University of Alberta. The base pressure in the analytical chamber was lower than 2×10^{-8} Pa. Monochromatic Al Kα source ($h\nu = 1486.6$ eV) was used at a power of 210 W. The analysis spot was 700×400 μm. The resolution of the instrument is 0.55 and 0.70 eV for Ag 3d Au 4f peaks, respectively. Survey scans were collected for binding energy ranging from 1100 eV to 0 with an analyzer pass energy of 160 eV and a step of 0.33 eV for a dwell time of 100 ms. For the high-resolution spectra,

the pass-energy was 20 eV with a step of 0.1 eV and dwell time of 200 ms. The number of scans was varied from 8 for C1s to 15 for O1s and 70 for N1s.

2.2.2. Thermogravimetric analysis under nitrogen (TGA)

TGA analyses were conducted with a Seiko TGA/DTA 6200 instrument. The temperature scan was kept between 40 and 1000 °C at a rate of 10 °C/min under a flow of nitrogen (extra dry, Praxair) at 100 mL/min for all the samples.

2.2.3. Adsorption isotherms

The isotherms were conducted on an Autosorb AS-1 instrument (Quantachrome Instrument, USA) using nitrogen at 77 K or CO₂ at 273 K as an adsorbate and the ASWIN1 software was used for data analysis. Samples (40–50 mg) were degassed for 12 h under vacuum at ambient temperature prior analysis. The volume of N₂ adsorbed was recorded for relative pressure from 10^{-5} to 1 and the volume of CO₂ adsorbed was recorded for relative pressure ranging from 10^{-6} to 0.03. The saturation pressure for CO₂ was considered as 26200 torr.

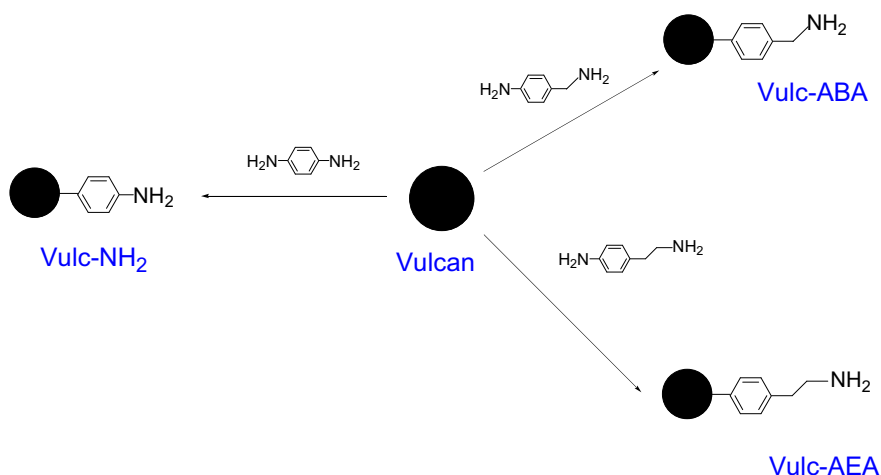
2.2.3.1. Nitrogen adsorption isotherm. The BET isotherm was used to obtain the specific surface area of the carbon powder and the *t*-method micropore analysis [32] was used to obtain microporous and external surfaces. The *t*-method compares the thickness (statistical thickness *t*) of the layer adsorbed at a given partial pressure in comparison with a known non porous solid taken as a reference. The statistical thickness is related to the quantity of gaz adsorbed n^a and the one needed to form a monolayer n_m^a (extrapolated from the BET equation).

$$t(\text{nm}) = 0.354(n^a/n_m^a) \quad (1)$$

t has been calculated with the Carbon-Black equation.

$$t(\text{Å}) = 0.88(P/P_0)^2 + 6.45(P/P_0) + 2.98 \quad (2)$$

Extrapolation of the *t*-plot where the adsorbed volume is plotted against the statistical thickness of the layer adsorbed gives the surface developed by meso- and macropores, called the external surface area. When, this one is different from the BET surface area, a contribution of micropores is expected and their surface associated is obtained by difference between the BET surface area and the external surface area. Micropore volumes were calculated using the α_s -method. This method has been developed by Sing [33] is similar to the *t*-method except that a quantity adsorbed at a



Scheme 1. Modification of carbon Vulcan XC72R by *in situ* generated diazonium cations of paraphenylenediamine, 4-aminobenzylamine and 4-aminoethylaniline. Multilayer formation that may occur by the modification process has not been represented for the sake of clarity.

chosen partial pressure $n_{0,4}^a$, generally $P/P_0 = 0.4$, replace the quantity of nitrogen needed to form a monolayer in the Eq. (1). α_s -method has the advantage to take into consideration interaction between adsorbate and adsorbent.

2.2.3.2. CO_2 adsorption isotherm. Microporous surface are given using Dubinin–Radushkevitch method, which is commonly used for the treatment of CO_2 adsorption isotherms [34]. Cross-sectional area of CO_2 molecules was taken as 21 Å/molecule.

2.2.4. pH at the point of zero charge (pH_{PZC}) measurement

This measurement used a pH drift-method [35]. 150 mg of carbon powder was solubilized in 50 mL of 0.01 M NaCl. Nitrogen was bubbled through the solution to prevent CO_2 dissolution. Then, the pH was adjusted at the following values: 2, 4, 6, 8, 10, 12, with HCl or NaOH solutions (concentrations varied from 5×10^{-3} to 1 M). The vial was sealed and the solution stirred during 48 h. The final pH was then recorded and plotted against the initial pH. The pH_{PZC} is the point where the final pH equals the initial pH. Because the curves have a S-shape, the pH_{PZC} is also equal to the pH at the plateau. More information concerning the factors that influence acid–base properties of carbonaceous materials can be found as Supplementary data.

2.3. CO_2 and N_2 adsorption measurements

Adsorption measurements were performed with a thermogravimetric analyzer, allowing to follow the mass gained or lost during the process. First, powders were heated under nitrogen upon 250 °C at 10 °C/min and kept at this temperature during 90 min.

This step allowed the desorption of adsorbed species, particularly water and traces of CO_2 (as they are present in air). The powders were then allowed to cool to 120 °C at 10 °C/min under nitrogen. At this moment, the mass recorded for the sample is taken as the reference mass that will be used in the further calculation. Since a mass loss is noticeable during this step, elemental analysis of each powder was performed to take into account the quantity of amine left on the surface (see Supplementary data, Table S1). Three adsorption/desorption cycles were then performed. The adsorption step began at 120 °C under either CO_2 or N_2 . The powder was cooled from 120 to 40 °C and kept at 40 °C for 60 min. The desorption step was always conducted under nitrogen. The powder was heated from 40 to 120 °C and kept at 120 °C for 90 min. All heating and cooling rates were 10 °C/min while all gas flow were 100 mL/min. Experiments to reach the maximum of adsorption under N_2 or CO_2 were conducted by following the same procedure, except that only one adsorption/desorption cycle was performed, and each step lasted 5 h.

3. Results and discussion

3.1. Characterization of the grafted powders

3.1.1. Surface composition

XPS survey for the unmodified carbon shows the characteristic C1s (284.5 eV) and O1s (532 eV) peaks, while modified carbons each present an additional peak for N1s at 400 eV which suggests the presence of amino functionalities (Fig. S1). Fig. 1 shows N1s core level spectra for the unmodified and modified carbons. The N1s core level spectra are similar for all the modified carbons,

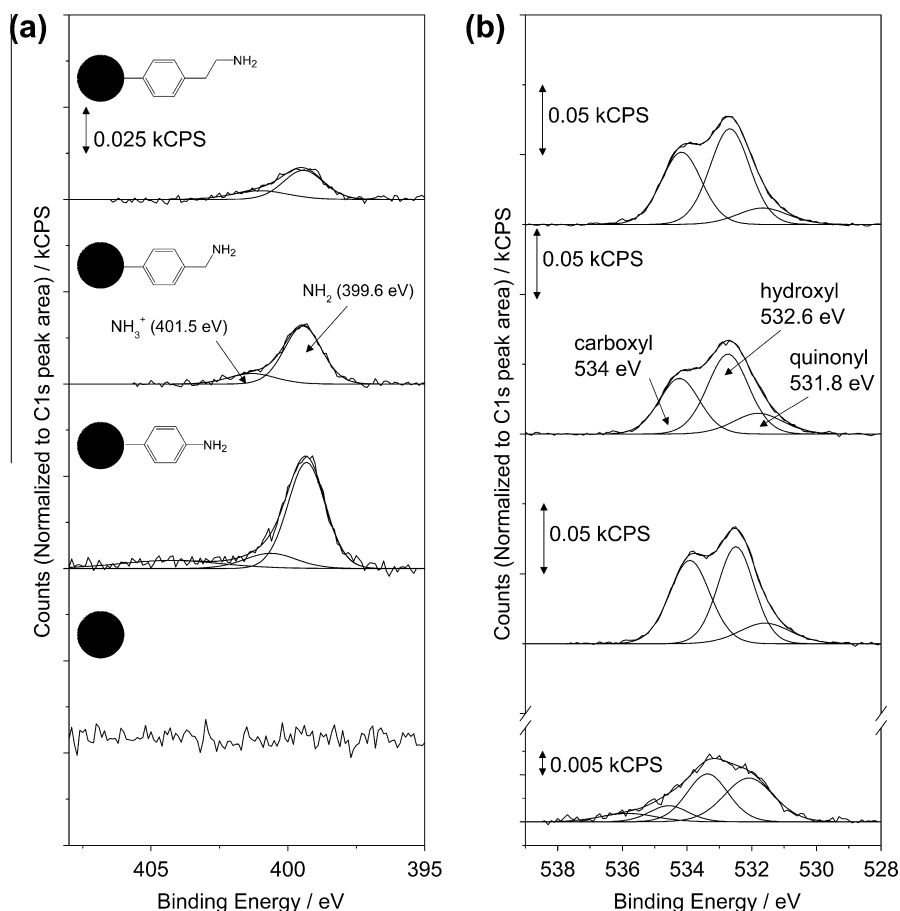


Fig. 1. (a) N1s core level spectra and (b) O1s core level spectra of unmodified Vulcan XC-72R, aminophenyl-, aminobenzyl- and aminoethyl-modified Vulcan XC-72R.

presenting one peak that can be fitted in two components. The first one, at 399.6 eV is due to the amine in its neutral form, while the second one at 401.5 eV can be attributed to the ammonium species (protonated form) [36]. It should be noted that for all modified carbons, a linkage of an aryl molecule to the surface by an azo bond is possible. This would result in a small contribution in the N1s core level spectra at 400 eV [13,15]. However, the presence of azo bonds cannot be confirmed by XPS when their N1s component overlapped with that of species such as amine [13,15]. The relative nitrogen concentration, evaluated from XPS data, is around 1.5 at.% and consistent with elemental analysis data (Table 1) and with previous studies for carbon modified with nitrogen containing species [13,15]. Therefore, the aryl grafted group represents about 10 wt.% or 1 mmol/g of the total mass of the modified carbons. The nitrogen percentage estimated by XPS is slightly higher than that determined by elemental analysis, confirming the localization of the grafted moieties at the carbon surface. Vulc-ABA and Vulc-AEA present a smaller amount of nitrogen than Vulc-NH₂ at their surface, indicating a less efficient grafting process for the aliphatic aromatic compounds. This points to a difference in reactivity between aminophenyl and aryl-aliphatic diazoniums. The higher grafting level for the aminophenyl modified carbon is consistent with the more positive reduction potential value of the corresponding diazonium relative to those bearing an aliphatic amine [30,37]. Interestingly, modified carbons show an increase of oxygen species at the surface (from 1.4 to 5–7 at.%) even if the grafted moieties do not contain any oxygen (Table 1). O1s spectra for modified carbons can be fitted with three components at 531.8, 532.6 and 534 eV which are also present in the unmodified one. Those components can be attributed to quinonyl, hydroxyl and carboxylic acid functionalities, respectively, which are commonly present at the surface of carbons [38]. Unmodified Vulcan presents also a small peak around 535 eV attributable to adsorbed water on the surface. The increase of oxygen at the surface accompanying the modification may be due to the oxidizing conditions of the reaction. A slight increase of the oxygen concentration has been previously observed for phenyl and azobenzene modified Vulcan [13]. Notably, the increase of the oxygen concentration is more important for the modified carbons of the present study, presumably because they are more hydrophilic. The presence of carbonate species that form complexes with amino functionalities at the surface may also contribute as their presence is confirmed by a very small peak at 289.3 eV in the C1s spectra of modified carbons while it is unnoticeable for the unmodified carbon. The O1s peak for carbonate anions is usually found around 531.4 eV and thus would overlap with the quinonyl peak [36].

3.1.2. Porosity analysis

Adsorption isotherms measured under nitrogen are shown in Fig. 2. Vulcan presents a type I + II isotherm at low and high pressure range, respectively, as defined in the IUPAC classification [39]. The rapid increase of the adsorbed volume at low partial pressure indicates the presence of a high amount of micropores. From the isotherm, a BET surface area of 221 m²/g can be extracted which

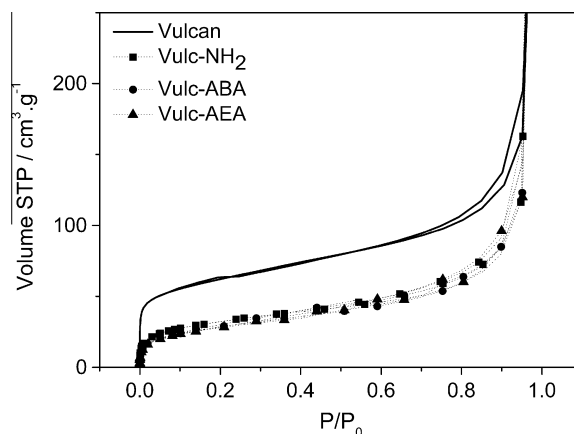


Fig. 2. Nitrogen adsorption isotherms of unmodified and aminophenyl-, aminobenzyl-, aminoethyl-modified Vulcan XC-72R.

is consistent with literature data [40]. After modification, one can observe a decrease in the volume adsorbed at low relative pressure ($P/P_0 < 0.1$), corresponding to a decrease in microporosity. Accordingly, the BET surface area decreases to about 100 m²/g following modification. It is interesting to notice that the trend is the same for all modified carbons and is similar of what has been observed for nitrophenyl [14], and cyanophenyl [15] grafted carbon by the same reaction on Vulcan and on other carbons [41]. An even more important decrease of the BET surface area has been recently reported for high surface area activated carbon (Norit) impregnated with alkyl amines [28]. To separate the contribution of micropores to the surface relative to the surface generated by mesopores and macropores, the *t*-method has been used. The results, obtained by using the Carbon Black equation (Eq. (2)) to calculate the statistical thickness (refer Section 2 for details), are presented in Table 2. The microporous surface, which is accounting for half of the total surface in Vulcan, represents only 10–35% of it after modification, depending on the grafted moieties. As suggested in a previous study [14], the aryl groups are localized at the entrance of micropores smaller than 1 nm or will be filling them preventing a further access to nitrogen adsorbate. Consequently, the BET surface area decreased and furthermore, the microporous surface is strongly affected.

Gas adsorption isotherms measured with nitrogen often leads to an underestimation of the microporosity due to the lower mobility of nitrogen at low temperature and whose diffusion in small size pores is inhibited [42]. To access the microporosity, isotherms can be measured under carbon dioxide. Carbon dioxide has a cross section similar to nitrogen but since the experiment is performed at 273 K, the CO₂ molecules are more mobile. On the other hand, isotherms under carbon dioxide can be affected by the presence of any interaction of this gas with the modified carbon. Isotherms measured with carbon dioxide are shown in Fig. 3. Due to technical limitations, the adsorption is limited to a pressure range that cannot reach atmospheric pressure. In these conditions,

Table 1

Atomic composition by XPS and elemental analysis, weight percentage corresponding to the amine functionality or the aryl group obtained by elemental analysis and weight loss at 700 °C measured by thermogravimetric analysis under nitrogen.

	XPS					Element analysis				TGA
	%C	%N	%O	%Cl	%S	%C	%N	%wt NH ₂	%wt aryl groups	wt loss at 700 °C
Vulcan	98.3	0.0	1.4	0.0	0.3	97.1	–	–	–	1.4
Vulc-NH ₂	90.6	2.6	6.7	0.1	0.0	94.2	1.4	2.0	11.2	5.2
Vulc-ABA	92.1	1.3	6.5	0.04	0.0	93.5	0.8	1.2	7.8	4.6
Vulc-AEA	93.4	0.7	5.7	0.07	0.0	97.9	0.9	1.4	9.9	3.4

Table 2
BET, external and microporous surface area obtained by analysis of the nitrogen adsorption isotherm and microporous volume obtained by either nitrogen or carbon dioxide adsorption isotherm.

	BET surface area m ² /g	External surface area ^a m ² /g	Microporous surface area ^a m ² /g	Microporous volume	
				From N ₂ adsorption ^b cm ³ /g	From CO ₂ adsorption ^c cm ³ /g
Vulcan	221	124	97	3.5 10 ⁻²	4.3 10 ⁻²
Vulc-NH ₂	113	69	44	1.7 10 ⁻²	2.5 10 ⁻²
Vulc-ABA	104	76	28	1.8 10 ⁻³	3.0 10 ⁻²
Vulc-AEA	102	90	12	2.9 10 ⁻²	3.0 10 ⁻²

^a External surface is obtained by application of the *t*-method analysis with the Carbon-Black equation on the nitrogen adsorption isotherm. Microporous surface is determined by difference between the BET surface area and the external surface area.

^b Obtained by extrapolation of the linear part of α_s -plot of nitrogen adsorption isotherm.

^c Obtained by application of the Dubinin-Radushkevich theory to the CO₂ adsorption isotherm.

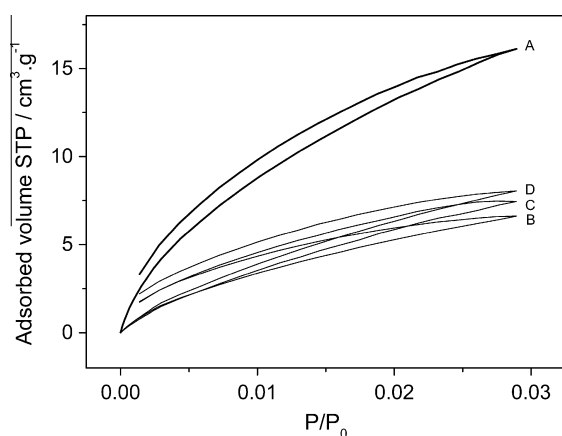


Fig. 3. CO₂ adsorption isotherms at 273 K of (A) unmodified and (B) aminophenyl-, (C) aminobenzyl-, (D) aminoethyl-modified Vulcan XC-72R.

unmodified Vulcan presents an isotherm corresponding to the beginning of a type I isotherm, characteristic of the filling of micropores of unimolecular size by carbon dioxide [28]. The isotherm shape is similar for modified carbons, but in this case the type I shape could also be a consequence of chemisorption. As it has already been observed for measurements under nitrogen, the amount of carbon dioxide adsorbed in micropores decreased after modification. Comparing the volume adsorbed in the micropores under nitrogen (α_s -method) and under carbon dioxide (Dubinin-Radushkevich method) reveals that a larger amount of micropores is indeed reached when CO₂ is used (Table 2). This trend is accentuated for Vulc-ABA and Vulc-AEA and may signify the presence of narrow micropores or a form of constriction at their entrance for those compounds [34]. It should be noted that the microporous volume of our modified carbons is significantly smaller than those reported for other carbons used to trap CO₂ [29,43,44]. An hysteresis can be observed between the adsorption and desorption branches of the isotherm. The lag between the two branches is more pronounced after modification. Even though this phenomenon is not clearly assessed in the literature, it demonstrates a difference in kinetics of adsorption and desorption. The same phenomenon has been previously observed for carbons impregnated by amines [28]. It suggests a higher affinity of the surface towards carbon dioxide after modification, or an irreversible adsorption accompanying chemisorption.

3.1.3. Surface pH

Plots of final pH as a function of initial pH are presented in Fig. 4 and show the classical S-shape [35]. From these plots, the pH_{PZC} can be determined. The pH_{PZC} represents the pH for which there is no charge density at the surface. For the unmodified Vulcan, a

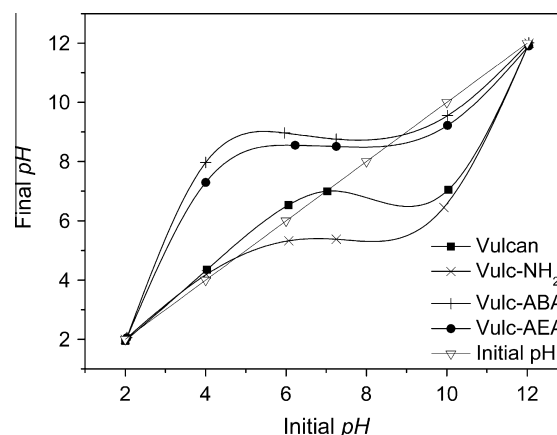


Fig. 4. Plot of final pH against initial pH of suspensions of unmodified and aminophenyl-, aminobenzyl-, aminoethyl-modified Vulcan XC-72R. Isoelectric points are taken as the point where the s-shaped curves cross the initial pH curve.

value of 7 is observed. This value should be taken with appropriate care, because the carbon does not disperse well in the electrolyte. The pH_{PZC} of Vulc-NH₂ is 4.5 while those of Vulc-ABA and Vulc-AEA are 9.4 and 9.1, respectively. When comparing the pH_{PZC} and the pKa for the corresponding amine in solution, (e.g. aniline for the aminophenylamine grafted, benzylamine for ABA and aminoethylbenzene for AEA), (Table 3) it is interesting to notice that these values are very similar. One can deduce that aminophenyl-modified surfaces are more acidic than unmodified surfaces whereas the ABA and AEA modified surfaces are more basic. The similarity between the pZc and the pKa tends to indicate that the grafting on carbon surface does not have a strong impact on the pH properties of the molecules themselves. This correlates the results obtained by a previous study on glassy carbon, where the pKa of ABA and AEA electrochemically grafted was found to be 10 and 10.5, respectively [30]. The presence of basic functionalities, particularly nitrogen functionalities may contribute to the adsorption of acidic CO₂. This has already been observed for SO₂ capture [45]. Therefore, a

Table 3

Values of pZc for the unmodified and aminophenyl-, aminobenzyl-, aminoethyl-modified Vulcan XC-72R and the pKa of the free form of the amines.

	pZc	pKa (corresponding amine in solution) ^a
Vulcan	7	–
Vulc-NH ₂	4.5	4.87
Vulc-ABA	9.4	9.34
Vulc-AEA	9.1	9.83

^a Aniline for Vulc-NH₂, benzylamine for Vulc-ABA and β -phenylethylamine for Vulc-AEA.

difference in CO₂ adsorption is expected between Vulc-NH₂ and Vulc-ABA and Vulc-AEA.

3.1.4. Thermal stability of the grafted powders

Thermogravimetric analysis of the unmodified and modified powders was performed under nitrogen and representative thermograms are presented in Fig. 5. Unmodified Vulcan shows a slight degradation below 700 °C which is mainly due to the departure of oxygenated species that are commonly found at the surface [46]. Above 700 °C, the rate of degradation increases and corresponds to the beginning of the oxidation of carbon due to the presence of trace amount of oxygen in our TGA analyzer. Modified carbons present a continuous mass loss with the increase of temperature. The onset of the degradation for modified carbon is attributed to the departure of the grafted layer. For each modified carbon, the total mass loss at 1000 °C reach 6–8%, which almost corresponds to the mass loss of the unmodified carbon. Nevertheless, to be more accurate, the difference between the mass lost at 700 °C for a modified carbon relative to unmodified Vulcan were compared to avoid the problem associated with the competitive departure of grafted species and oxidation of carbon [15]. In this case, after subtracting the contribution of unmodified Vulcan, a mass loss of 2–4% is attributable to grafted species. This represents a small quantity compared to the loss expected with the departure of aryl groups (~10%) but still larger than that expected for the simple departure of only the amine attached to the phenyl ring (Table 1). A recent study hypothesized that in the case of aminophenyl groups, the mass loss could be explained by the departure of oxygenated functionalities present at the carbon surface in addition to the amine functionalities [15]. A similar mechanism is expected for Vulc-ABA and Vulc-AEA. Nonetheless, these mass losses contrast with those reported for activated carbons impregnated with alkyl amines [28]. The later are consistent with the complete departure of the amine species following heating at 400 °C. This provides some indirect evidence for the covalent grafting of the amine at the carbon surface by modification with the diazonium chemistry.

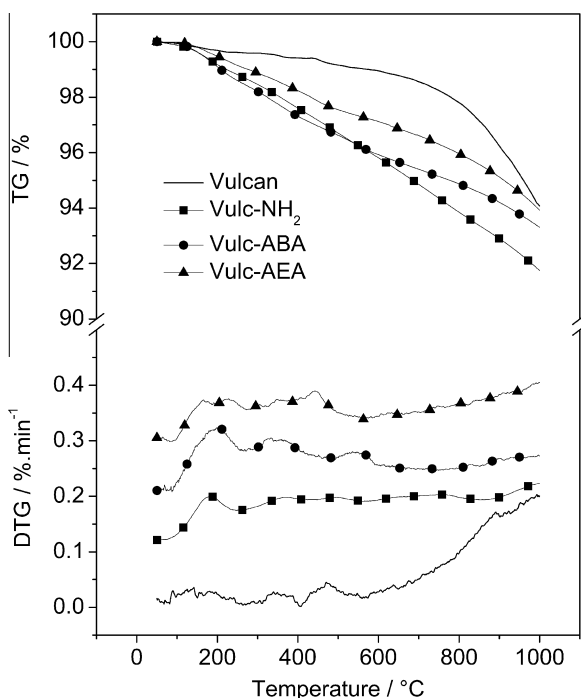


Fig. 5. Thermal stability study of unmodified and aryl-modified carbons under N₂ (100 mL/min). The graph presents the mass loss upon heating from 40 to 1000 °C at 10 °C/min (TG) and its derivative (DTG). Note that all DTG curves should begin at 0%/min but they have been shifted upward to help the reading.

A closer look at the derivative curve of mass loss (DTG) shows the existence of several degradation processes represented by a peak in the curve. A first step is observable for all the modified carbon between 100 and 250 °C, and then followed by two or three steps before 700 °C that are ill-defined compared to the first one. A knowledge of the changes occurring to the surface upon heating between 100 and 250 °C is particularly important considering the potential use of the materials as CO₂ sorbents. Indeed, while the adsorption of CO₂ is often made at ambient temperature, the desorption step that regenerates the sorbent usually takes place at 120–200 °C [47]. Therefore, to get a better insight of the chemical transformation occurring to modified carbon upon heating, elemental analysis and XPS measurements were performed after the powders have been heated at different temperatures: 120, 285, 460 and 1000 °C.

The nitrogen content measured by elemental analysis after heating is shown in Fig. 6. The curves present normalized data to the highest amount of nitrogen detected for each method (elemental analysis or XPS) following heat-treatment. Therefore, it is worth mentioning that a lower percentage determined by XPS compared to elemental analysis data does not necessarily mean a lower amount of nitrogen in absolute values. Vulc-ABA and Vulc-AEA present a continuous decrease of the nitrogen concentration. However, Vulc-NH₂ seems to be more stable as the nitrogen content does not decrease much before 285 °C. Fig. 6 also shows an unexpected feature for the variation of the nitrogen content measured by XPS. Indeed, a significant increase of the nitrogen content is found following heat-treatment at 120 °C. This is observed despite a loss of nitrogen quantified by elemental analysis. Since elemental analysis measures the bulk properties of a material and XPS probes only the surface, we hypothesize that diffusion of the grafted groups or adsorbed and unbound species from the interior to the external surface of the material might be occurring at 120 °C. XPS will be helpful to understand the reaction occurring to the grafted amine species upon heating at higher temperature (*vide infra*).

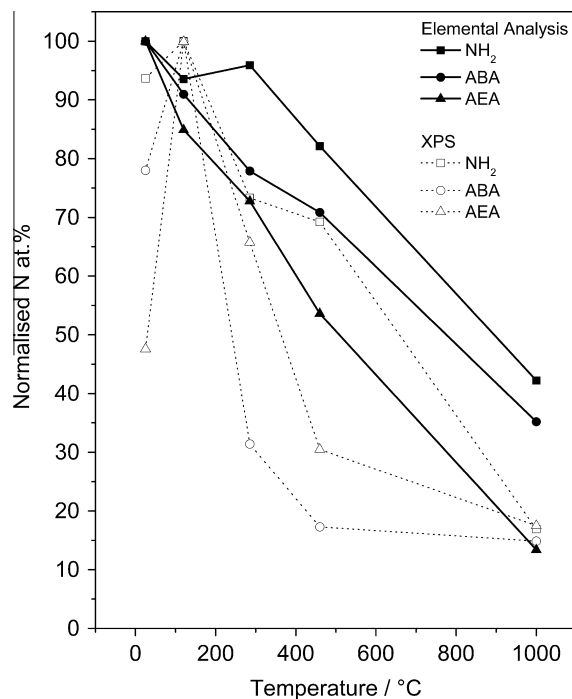


Fig. 6. Evolution of the relative nitrogen content of the various carbons upon heating, as determined by elemental analysis (full line) and XPS (dotted line).

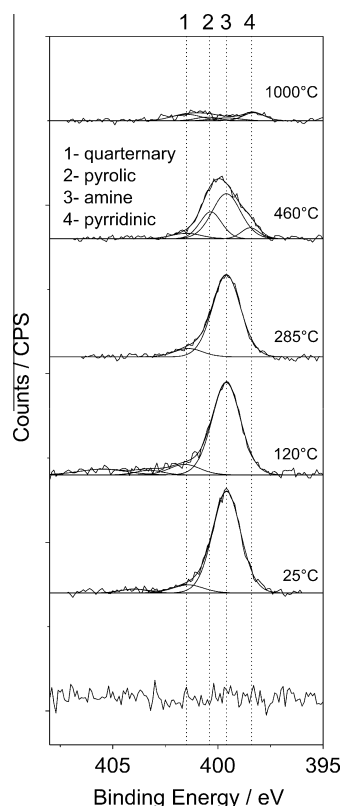


Fig. 7. N1s core level spectra of unmodified Vulcan (bottom curve) and aminophenyl-modified Vulcan after heat treatment at (a) 25 °C, (b) 120 °C, (c) 285 °C, (d) 460 °C and (e) 1000 °C.

Fig. 7 presents the N1s core level spectra of Vulc-NH₂ heated at different temperatures. The shape of the peak remains unchanged until 285 °C, confirming that even if there is a loss of nitrogen, no change occur to the amine functionality itself. Thus, the loss of nitrogen suggests a release of a small quantity of arylamine species (cleavage of a C–C bond between the aryl bond and the carbon at the surface). However, this hypothesis is very unlikely because the mass represented by aryl group would be far larger than the one actually lost. Consequently, the smaller nitrogen loss points towards a cleavage of the C–N bond between the amine and the aryl groups. For Vulc-NH₂ heated at 460 °C, the N1s core level spectrum becomes broader. The component attributed to amine still represents 60% of the nitrogen species but peaks associated to pyridinic N-6 (398 eV), pyrrolic N-5 (400 eV) and quarternary nitrogen N-Q (401.5 eV) appears. These species are commonly generated by reaction of ammonia with carbon at temperature higher than 400 °C [28,48]. Amination allows the introduction of nitrogen species at a carbon surface by reaction between ammonia and surface oxides to form ammonium salts and amine groups. The reaction is usually carried at temperature higher than 400 °C and leads to their dehydration and dehydrogenation to produce amide, nitrile, pyridine or pyrrole-like functionalities. This again may suggest a degradation mechanism by cleavage of C–N bond and reaction of residual NH₂ species with the surface or a migration of amine on the surface by reaction with surface oxides especially carboxylic groups to form amide like species that will decompose in pyrrole-like and pyridinic species upon heating. Finally, only traces of nitrogen are found for the aminophenyl-modified Vulcan heated to 1000 °C.

The overall evolution of the N1s core level spectra of Vulc-ABA (Fig. S2) and Vulc-AEA (Fig. S3) shows a similar trend than Vulc-NH₂. Nevertheless, the aryl-aliphatic amines grafted are less stable

as one fourth of the total nitrogen quantity is removed by heating at 285 °C. Further description can be found in the [Supplementary data](#).

Although the degradation mechanism remains not fully understood, these results provide useful information on the thermal stability of the grafted layer. Thermal stability is mandatory in adsorption measurements when powders are heated under nitrogen to regenerate the surface, and then submitted to adsorption and desorption cycles, the later being usually performed at relatively moderate temperature (the temperature for the regeneration of the sorbent is usually chosen between 120 and 250 °C).

3.2. Carbon dioxide adsorption: capacity and selectivity

Fig. 8a shows the quantity of CO₂ adsorbed at 40 °C and then desorbed at 120 °C by the powders. Unmodified Vulcan shows the best adsorption capacity (0.34 mmol/g) while after modification of the surface, the quantity of CO₂ adsorbed decreases to 0.24 mmol/g for Vulc-NH₂ and to 0.16 mmol/g for Vulc-ABA and Vulc-AEA. The decrease of CO₂ adsorption seems to be mainly due to the loss of microporosity. This has previously been observed on amine impregnated samples where the blocking of porosity was affecting drastically the adsorption capacity [28,49]. This indicates that the predominant mechanism of adsorption is physisorption which is expected for temperature as low as 40 °C and atmospheric pressure. The contribution of amine to CO₂ chemisorption may not be visible due to the high concentration (100%) of the CO₂ flow. Indeed, Plaza et al. [44] noticed that the effect of surface area diminishes for low CO₂ partial pressure, while the impact of chemisorption on amines and adsorption on narrow micropores may then appear more important. It is interesting to notice that the maximum adsorption capacity is reached approximately in the same period of time (~2 h) for all carbons even if the adsorption kinetics seems to be slower after modification (the slope decreases).

The sorbent is regenerated by heating at 120 °C under N₂ atmosphere. The rate of desorption is fast as only a few minutes are needed to remove 75% of the adsorbed gaz. The unexpected features that appears at the beginning of the desorption step may be due to an apparatus artefact and is discussed further in [Supplementary data](#) section. Interestingly, for unmodified Vulcan, a significant amount of CO₂ seems to be still trapped by the powder following the desorption step performed under N₂ (0.05 mmol/g). On the other hand, for the amine modified carbons most of the adsorbed CO₂ is removed. This is somewhat surprising considering that the adsorption isotherms under CO₂ (Fig. 3) showed an hysteresis between the adsorption and desorption branches that suggested the trapping of CO₂ by the modified carbon after desorption at low pressure and because an increase of CO₂ entrapped after modification has already been observed on amine impregnated carbon [28]. Again, the loss of microporosity after modification and an adsorption mechanism predominantly based on physisorption may explain why the amount of residual CO₂ entrapped in the modified powders is smaller. At moderate temperature and ambient pressure, it is still possible to have CO₂ molecules entrapped in micropores. The apparent discrepancy observed when comparing to the adsorption isotherm is due to the fact that removing CO₂ by diminishing the pressure as in the gas adsorption isotherm measurements may empty the micropores leaving only CO₂ molecules linked to amines by chemisorption. On the other hand, increasing the temperature will render the interaction between CO₂ and amines (as supposed in the mechanism given in [Scheme 1](#)) unstable and eliminate the contribution by chemisorption. However, the relatively low temperature of regeneration may not be sufficient to remove CO₂ entrapped in narrow micropores. Consequently, the amount of CO₂ remaining at low partial pressure

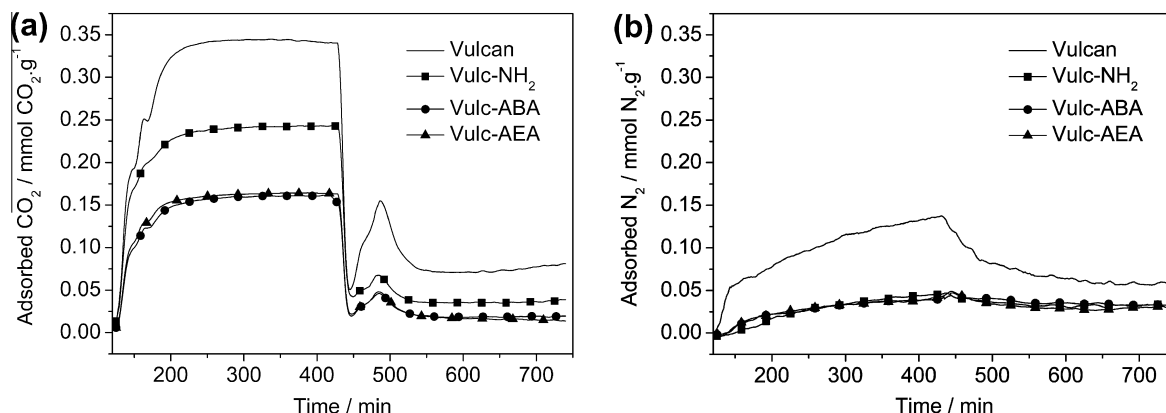


Fig. 8. (a) CO₂ and (b) N₂ adsorption capacity at 40 °C and desorption at 120 °C of the unmodified and aryl-modified carbons. Before adsorption, the powders are maintained at 285 °C during 90 min to ensure the removal of weakly adsorbed species and humidity. Then, the powders are cooled to 120 °C where the adsorption step begins. During the adsorption step the powders are cooled from 120 to 40 °C at 10 °C/min and kept at 40 °C for 5 h.

(adsorption isotherm experiment) would essentially result from chemisorption while in the temperature swing adsorption, the remaining CO₂ amount will be due to physisorption. The amount of CO₂ adsorbed and desorbed are both reproducible if the powders are submitted to adsorption and desorption cycles. More details about reproducibility can be found in [Supplementary data \(Fig. S4\)](#).

[Fig. 8b](#) shows the adsorption of nitrogen on unmodified and modified powders in the same conditions as CO₂ adsorption. The selectivity of the material towards CO₂ in presence of nitrogen is an important factor, considering the conditions of releasing CO₂ in real applications of post-combustion process (5–15% of CO₂ in N₂). The adsorption of nitrogen occurs in the micropores of unmodified carbon, but after modification this adsorption is, like CO₂ adsorption, very unlikely because the grafted groups block the entrance of these micropores. If the experiment time is the same as for the one performed with CO₂, the adsorption of nitrogen on unmodified and modified carbon does not reach a maximum. The amount of adsorbed N₂/amount of adsorbed CO₂ ratio (determined from the maximum adsorbed values of [Fig. 8](#)) decreases from 0.4 to 0.2 after modification with aminophenyl groups which means that modification of carbon seems to improve the selectivity towards CO₂. This is in agreement with the adsorption isotherms under CO₂ where the hysteresis suggests some affinity of the powder towards CO₂ and that this affinity increased after modification.

It is interesting to compare the affinity towards CO₂ of the different modified carbons. To this end, the ratio between the number of CO₂ molecules adsorbed and the number of molecules of grafted amines was determined and shown in [Fig. 9](#). This ratio characterizes the adsorption efficiency. The mechanism proposed by Gray et al. [47] suggests that in absence of water, carbon dioxide reacts with amine to form the carbamate as presented in [Supplementary data \(Scheme S1\)](#). Thus, the ratio between the quantity of CO₂ adsorbed and the amine available should be between 0.5 and 1 if each amine reacts with a CO₂ molecule. This obviously does not take into account the amount of CO₂ adsorbed by physisorption. [Fig. 9](#) shows that Vulc-AEA has a higher ratio of CO₂ adsorbed by grafted amine (0.86) than Vulc-ABA (0.43) and Vulc-NH₂ (0.23). A better affinity towards Vulc-AEA and Vulc-ABA compared to Vulc-NH₂ was expected because of the basic character of their surface. On Vulc-NH₂, that exhibits an acidic surface, chemisorption is not expected to occur. The amount adsorbed by Vulc-NH₂ may then be considered as the amount adsorbed by physisorption. By subtracting that part to the ratio obtained for Vulc-ABA and Vulc-AEA, a more accurate ratio for the chemisorption can be given. The corrected ratio for Vulc-ABA and Vulc-AEA would then be 0.43 and 0.2 which is relatively low for a pure CO₂ stream. The discrepancy

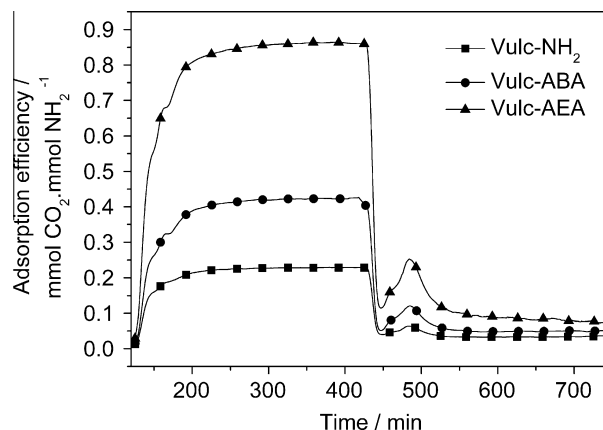


Fig. 9. Adsorption efficiency during adsorption at 40 °C and desorption at 120 °C. The adsorption efficiency is defined as the ratio between the amount of molecules of CO₂ adsorbed vs. the amount of molecules of amine available at the surface. The last one has been calculated from the amount of nitrogen determined by elemental analysis after the preparation of the surface for adsorption (see [Fig. 8](#) and Section 2 for more details). These values are given in the [Supplementary data \(Table S1\)](#).

between Vulc-AEA and Vulc-ABA could not be predicted by pH_{pzc} measurements. The surface pH is expected to have a higher impact at lower partial pressure of CO₂.

The amount of CO₂ captured by Vulcan powder is relatively low if compared to literature data. Numerous studies on amine modified silica have shown a CO₂ capacity of up to 2.36 mmol/g for stream with a low proportion of CO₂ (5% in N₂) [23]. On carbon supports, the adsorption capacities are generally lower even for supports of comparable specific surface area [28,29,44]. The materials prepared in this work behave like impregnated carbons. The loss of microporosity induced by the modification implies a decrease of the adsorption capacity. Hence, the first conclusion may be that this kind of modification is not the best approach to prepare efficient and competitive CO₂ scrubber. However, impregnated carbons shows a degradation of all the amine layer around 400 °C [28] while covalent grafted layer shows a notable stability of the amine functionality up to 285 °C and a progressive incorporation of the nitrogen in the carbon material after 460 °C. Several studies on carbon or silica support have elucidated the factors influencing the adsorption [50–52]. The work on silica is particularly useful to determine the best characteristics for the grafted layer as the raw material does not adsorb CO₂ itself [25,53]. Thus, the presence of humidity, the regeneration temperature, the CO₂

partial pressure, the amine loading and the basicity of the surface have to be considered when evaluating the adsorption capacity.

In this work, the adsorption measurements were carried out at low temperature where the physisorption is predominant. An approach for using carbon support at their full potential would be to control the grafting process in such a way that the intrinsic microporosity of the carbon support will be kept. The grafted layer would then make the material selective while the adsorption process would occur essentially by physisorption. The main difference between carbon and silica support is due to the porosity of the raw material. High surface area and microporous carbons are usually selected because they should be characterized by a high adsorption capacity. Silica supports are usually mesoporous, and their adsorptive properties after modification have been further enhanced by increasing their pore size distribution [23,24]. This ensures a higher loading of grafted molecules in the pores whereas micropores of carbon support tend to be blocked after modification. Similarly, mesoporous carbons may then enhance the adsorptive properties of the carbon, allowing a higher amount of grafted moieties and so a higher CO₂ adsorption capacity. This has been recently demonstrated with nitrogen-doped carbon monoliths which showed a very high CO₂ adsorption of 3.13 mmol/g of carbon at ambient temperature [43].

4. Conclusion

Aminophenyl and aryl-aliphatic groups have been successfully grafted at the surface of Vulcan by spontaneous reduction of the *in situ* generated corresponding diazonium cations. The grafting efficiency depends on the nature of the amine and is lower in the case of aryl-aliphatic amine. The purpose of this paper was to evaluate if the diazonium chemistry could be used to synthesize new CO₂ solid sorbent, as this modification method has never been reported in the open literature before for this application. As already observed in the case of impregnated aminated compounds [28], the grafting of those amine groups drastically decreased the intrinsic porosity of the carbon. However, covalent grafting affords materials that are more thermally stable at temperatures below 250 °C. A detailed description of the consequence of modification of Vulcan, with aminophenyl and aryl-aliphatic amine was presented. One interesting results is the possibility to tune the pH surface properties by a simple change of the para substituent of the aryl groups. This opens the way of further use of such modified supports in different fields other than CO₂ capture.

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Appendix A. Supplementary material

XPS survey spectra of unmodified and aminophenyl-, amino-benzyl-, aminoethylphenyl-modified Vulcan XC72R (Fig. S1); Information and discussion concerning the surface pH of modified carbons; N1s core level spectra of unmodified Vulcan (bottom curve) and aminobenzyl-modified Vulcan after heat treatment at (a) 25 °C, (b) 120 °C, (c) 285 °C, (d) 460 °C and (e) 1000 °C (Fig. S2); N1s core level spectra of unmodified Vulcan (bottom curve) and aminoethyl-modified Vulcan after heat treatment at (a) 25 °C, (b) 120 °C, (c) 285 °C, (d) 460 °C and (e) 1000 °C (Fig. S3); Nitrogen content of the modified carbon obtained by ele-

mental analysis just after the synthesis (initial) and after the pre-treatment step prior to the adsorption experiments. (Table S1); Description of the apparatus artefact; Reproducibility of the measurements (Fig. S4); Description of the model of Gray et al. [47] for reaction of amine with CO₂.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2011.03.019.

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