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Surface modification of activated carbons for CO₂ capture

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Abstract

The reduction of anthropogenic CO₂ emissions to address the consequences of climate change is a matter of concern for all developed countries. In the short term, one of the most viable options for reducing carbon emissions is to capture and store CO₂ at large stationary sources. Adsorption with solid sorbents is one of the most promising options. In this work, two series of materials were prepared from two commercial activated carbons, C and R, by heat treatment with gaseous ammonia at temperatures in the 200-800 °C range. The aim was to improve the selectivity and capacity of the sorbents to capture CO₂, by introducing basic nitrogen functionalities into the carbons. The sorbents were characterised in terms of texture and chemical composition. Their surface chemistry was studied through temperature programmed desorption tests and X-ray photoelectron spectroscopy. The capture performance of the carbons was evaluated by using a thermogravimetric analyser to record mass uptakes by the samples when exposed to a CO₂ atmosphere.

Keywords: Activated carbon, Surface modification, Thermal analysis, CO₂ capture, Adsorption.

INTRODUCTION

The growing awareness of the international community with regard to climate change, has led to the search for technologies designed to reduce greenhouse gas emissions. The growth in energy demand makes it impossible to reduce, in the near term, the use of fossil fuels, which constitute the main source of greenhouse gas emissions. In the short

term, one of the most viable options for reducing carbon emissions consists in capturing and storing CO₂ at large stationary sources, such as power stations, cement plants, refineries, etc.

The current methods of CO₂ capture from flue gas include absorption, adsorption, cryogenic distillation and membrane separation. Adsorption is considered one of the most appealing options for CO₂ capture [1, 2]. However, the efficient capture of CO₂ based on adsorption requires solid adsorbents with a high CO₂ selectivity and capacity. The development of a new generation of materials that can efficiently adsorb CO₂, will undoubtedly enhance the competitiveness of adsorptive separation in flue gas applications.

Porous materials, such as molecular sieves and zeolites, as well as activated carbons, are suitable materials for CO₂ capture by solid sorbent adsorption due to their highly developed porous structure [3, 4]. Activated carbons, in particular, have well developed micro and mesoporosities which are applied in a wide range of industrial and technological processes [5].

The adsorption properties of a solid sorbent are determined by its porous structure and surface chemistry. It has been shown that the capacity of activated carbons to adsorb CO₂ -which is based on physical adsorption- can be increased by introducing nitrogen functional groups into their structure [6-13]. The incorporation of these functionalities may be achieved by two techniques: impregnating the surface with appropriate chemicals or introducing nitrogen into the carbon structure. Impregnation is frequently used although this could lead to the blockage of the porous structure, which would reduce the adsorption capacity of the activated carbon [12]. Nitrogen can be incorporated into the carbon structure by preparing activated carbon from N-containing polymers [7, 14-16] or by heat treatment of the carbons with gaseous ammonia [17, 18].

Reaction with ammonia can be expected to take place at carboxylic acid sites formed by the oxidation of side groups and the ring system. Ammonia decomposes at high temperatures with the formation of radicals, such as NH_2 , NH and H [18, 19]. These radicals may react with the carbon surface to form functional groups, such as $-\text{NH}_2$ -, $-\text{CN}$, pyridinic, pyrrolic, and quaternary nitrogen [19]. In this work two commercial activated carbons were modified by treating them with gaseous ammonia at different temperatures. The aim was to assess the effect of such modifications on the capacity of the carbons to capture CO_2 .

EXPERIMENTAL

Two commercial activated carbons supplied by Norit -here referred to as C and R- were chosen as starting material for the preparation of CO_2 capture adsorbents. C is a wood-based granular carbon manufactured by a phosphoric acid activation process. R, a peat-based steam activated extruded carbon with a diameter of 3 mm, possesses a superior mechanical hardness that makes it suitable for removing low concentrations of contaminants from gases.

Ammonia Heat Treatment

In this work, the activated carbons were treated with gaseous ammonia at different temperatures in a vertical tube furnace. Around 3 g of carbon -dried overnight at 100°C - was placed in a quartz reactor and held under a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ of N_2 for 30 min. When the furnace reached the desired temperature –values between 200 and 900°C - the quartz reactor was introduced. Once the sample had reached the desired temperature the flow was switched from N_2 to NH_3 ($50 \text{ cm}^3 \text{ min}^{-1}$) and then held for 2 h. Next, the sample was removed from the furnace and cooled to 100°C under a flow of ammonia. Finally the flow was changed back to N_2 until room temperature was reached.

The modified carbons were denoted as CN and RN, respectively, followed by the temperature used in the treatment with ammonia, i.e., CN600, RN600.

Chemical and textural characterisation of the samples

Ultimate analysis was carried out in order to determine the amount of nitrogen incorporated into the carbons. The acid/basic character of the samples was estimated by means of the Point of Zero Charge (pH_{PZC}). A mass titration method adapted from Noh and Schwarz was used for this purpose [20]. Helium density was measured in an Accupyc 1330 at 35 °C. N_2 and CO_2 adsorption isotherms at -196 °C and 0 °C, respectively, were carried out in a Micromeritics Tristar 3000. The samples were outgassed at 100 °C under vacuum for 24 h prior to the density and adsorption measurements. The apparent surface areas (S_{BET}) were calculated from the physical adsorption of N_2 using the BET equation in the linear form proposed by Parra et al. [21], and the total pore volumes (V_{p}) were evaluated using Gurvitch's rule ($p/p^0 = 0.99$). Mesopore volume (V_{meso}) comprises pores between 2 and 50 nm according to the IUPAC classification. In this work the mesopore volumes were calculated by applying the DFT method to the N_2 isotherms, assuming slit shaped pores and non-regularisation [22, 23]. The average pore width (D) of the adsorbents was estimated by means of the expression $4V/S_{\text{BET}}$. The micropore volumes (W_0) were calculated by the Dubinin-Radushkevich (DR) method [24] from the CO_2 adsorption isotherms (assuming an affinity coefficient of 0.36), and the average width of the micropore system (L_0) was determined by using the Stoeckli-Ballerini expression [25].

X-ray Photoelectron Spectroscopy (XPS) analysis was performed to characterise the nitrogen functionalities on the ammonia modified carbons. XPS spectra were recorded on a SPECS photoelectron spectrometer equipped with a hemispherical PHOIBOS 100 energy analyser, using $\text{MgK}\alpha$ radiation (energy 1253.6 eV). An X-ray power of 150 W

(11.81 kV) was employed for all the analyses. The vacuum pressure in the analysis chamber was kept below 5×10^{-9} mbar. Pass energies of 50 and 10 eV were used for the low and high resolution scans, respectively. N1s, C1s and O1s envelopes were fitted into Gaussian-Lorentzian component profiles using CasaXPS software.

Temperature-Programmed Desorption (TPD) tests

The ammonia-treated samples were subjected to TPD tests in a Setaram TGA 92 thermogravimetric analyser (TG) coupled to a Nicolet Nexus Fourier Transform Infrared (FTIR) spectrometer. 20 mg of sample was heated at $15 \text{ }^\circ\text{C min}^{-1}$ up to $1000 \text{ }^\circ\text{C}$ under an Argon flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The final temperature was maintained for 30 min. The evolved gases were transferred through a heated interface to the FTIR for analysis.

CO₂ adsorption capacity experiments

The CO₂ adsorption-desorption performance of the samples was evaluated in the TG analyser. The CO₂ adsorption capacity of the samples was determined from the mass uptake recorded when exposed to pure CO₂. Prior to the adsorption measurements, the samples were dried at $100 \text{ }^\circ\text{C}$ in $50 \text{ cm}^3 \text{ min}^{-1}$ of Ar for 1h, and allowed to cool to $25 \text{ }^\circ\text{C}$. Afterwards Ar was changed to $50 \text{ cm}^3 \text{ min}^{-1}$ of CO₂ and the temperature was held at $25 \text{ }^\circ\text{C}$ for 1 h. The temperature was then increased at a heating rate of $0.5 \text{ }^\circ\text{C min}^{-1}$ up to $100 \text{ }^\circ\text{C}$, and the mass change was recorded to evaluate the influence of temperature on CO₂ capture capacity. The sample was kept at $100 \text{ }^\circ\text{C}$ for 1 h and finally the flow was switched to Ar to regenerate the sample.

RESULTS AND DISCUSSION

Ultimate analysis and point of zero charge

The results of the ultimate analysis and the pH_{PZC} of the parent carbons and the ammonia-modified carbons are presented in Table 1. In the case of the C carbons the

product yields decrease as the temperature of the ammonia treatment increases. This indicates that gasification with ammonia takes place at higher temperatures. However, R carbons do not exhibit significant gasification, as shown by the product yields which remain constant with temperature. Ammonia treatment increases the nitrogen content of the carbons, particularly for C-treated carbons, where nitrogen contents of up to 8 wt.% were achieved for the carbon treated at 700 °C. Temperature also influences the degree of nitrogen present in the carbons. The nitrogen content increases with temperature, reaching a maximum at 700 °C for C carbons and 800 °C for R carbons. Higher temperatures resulted in less nitrogen being incorporated into the C-treated samples. The NH₃-carbon reaction can be expected to take place at acidic sites, formed mainly by surface oxides and this reaction may involve carboxylic groups and other oxygen functionalities. The presence of oxygen in the parent carbons plays an important role in determining the extent of the ammonia treatment, as demonstrated by the differences in nitrogen incorporation between the C and R-treated carbons –the oxygen content being 13.7 wt.% for C and only 4.2 wt.% for R-. These results suggest that C is more sensitive to treatment with NH₃.

The acid/basic character of the samples, assessed by the pH_{PZC}, show that reaction with ammonia changed the strong acidic character of C to basic in the C-treated carbons. However, in the case of R, which was already a basic carbon, basicity is not significantly altered by treatment with gaseous ammonia. In addition, no direct link is observed between the pH_{PZC} values obtained for the C and R treated carbons and the nitrogen content of the samples: the highest pH_{PZC} values obtained for the C and R-treated carbons do not correspond to the samples with the largest nitrogen contents.

Textural characterisation

The N₂ adsorption isotherms at -196 °C are presented in Figures 1a and 1b. The C carbons show type IV isotherms, with characteristic hysteresis loops at relative pressures above 0.4, and exhibit both meso and microporosity. The R carbons show type I isotherms which are characteristic of mainly microporous materials. Treatment of the parent carbon C with ammonia gas results in a decrease in the volume of N₂ adsorbed by the C-treated carbons while for R-treated carbons it increases. Table 2 contains the helium densities (d_{He}) measured at 35 °C and the textural parameters calculated from the N₂ and CO₂ adsorption isotherms at -196 °C and 0 °C, respectively. Carbon C presents a helium density of 1.54 g / cm³, which is significantly lower than that of R, 2.14 g / cm³. This difference could be due to their fabrication processes: C is produced by activation with phosphoric acid only at 550 °C, while R is produced through steam activation at temperatures above 800 °C [26, 27]. Thus, heat treatment at temperatures above 600 °C increases the helium densities of the ammonia-treated C carbons but does not alter those of the R carbons. The modification of carbon C by ammonia treatment results in lower BET apparent surface areas, lower total pore (V_p) and mesopore (V_{meso}) volumes and lower average pore widths (D) compared to the parent material. An analysis of the values obtained for the ammonia-treated C carbons shows that these parameters decrease up to 700 °C but at 800 °C the samples appear to recover some porosity, probably due to partial gasification of the carbon by ammonia at higher temperatures. The micropore volumes (W_0) assessed from the CO₂ adsorption isotherms of the ammonia treated samples at 0 °C are lower than that of the parent carbon, C, except for sample CN800, for which a similar value is obtained. The average micropore widths (L_0) calculated for the ammonia-treated C carbons follow the same trend. Ammonia treatment seems to partially block the porous structure of the samples at temperatures up to 700 °C. This effect has generally been attributed to partial

blockage of the microporous system by decomposed products generated during heat treatment with ammonia [18]. At higher temperatures, gasification with ammonia allows the samples to recover porosity.

In order to study the effect of the ammonia-carbon reaction on the texture of the samples, a carbon denoted as C800 was prepared by heat treatment at 800 °C under an inert atmosphere of N₂ instead of NH₃. C800 has the smallest S_{BET} value and pore volume of the C series, which shows that heat treatment alone acts to the detriment of textural development. A comparison of the textural parameters (see Table 2) calculated for C800 (heat-treated under an inert atmosphere) and for CN800 (heat-treated under ammonia flow) shows that ammonia gas promotes the development of porosity in the samples through partial gasification of the carbons.

Modification of carbon R with ammonia increases the BET apparent surface areas and total pore volumes in the ammonia-treated R carbons, except for the sample treated at 400 °C where no significant textural changes with respect to the parent carbon R are observed. Mesopore volumes are negligible in the parent carbon R and the treated samples and the average pore widths remain practically unchanged. On the other hand, the micropore volumes and average micropore widths decrease with temperature. Thus, the observed increase in total pore volume for the ammonia-treated R carbons could be ascribed to an increase in wide microporosity, which cannot be assessed by W₀. It appears, therefore, that when partial gasification with ammonia takes place, it acts preferentially on narrow microporosity, thereby creating a wider microporosity.

Nitrogen functionalities introduced by treatment with ammonia gas at different temperatures

Temperature-programmed desorption (TPD) tests were carried out in order to study the thermal stability of the N-functionalities introduced into the carbon. The only nitrogen-

containing compounds detected for the ammonia-modified carbons were NH_3 and HCN. As expected, in the case of the parent carbons, C and R, no nitrogen compounds were detected.

Figure 2 presents the NH_3 and HCN profiles analysed by FTIR for the ammonia-modified C carbons at different temperatures. The gas intensities have been normalised by the sample mass for comparison purposes. The C samples show different NH_3 and HCN profiles depending on the temperature of the ammonia treatment they have undergone. It is assumed, therefore, that different nitrogen functionalities have been incorporated into the modified C carbons depending on the treatment temperature. The samples treated at the lowest temperatures (i.e., 200 and 400 °C) present the largest NH_3 and HCN emissions. Four main temperature ranges can be distinguished in the NH_3 profiles: low (ca. 300 °C), medium-low (around 400 °C), medium-high (around 650 °C) and high temperature (ca. 800 °C). For each sample two characteristic peaks are observed: CN200 shows a maximum at low temperature, followed by an elbow in the medium-high temperature range; for CN400 a maximum occurs in the medium-high temperature range preceded by a peak at low temperature. The first CN600 and CN800 peaks have shifted towards higher temperatures, appearing in the medium-low temperature range, and in the case of CN800 the first peak is followed by a second one in the medium-high interval. CN700 presents two peaks in the low and high temperature ranges, respectively. In addition, the samples modified with ammonia at the lower temperatures (i.e., CN200 and CN400) exhibit the highest NH_3 emissions, suggesting that the nitrogen incorporated into the carbons treated at these temperatures is associated with more labile functionalities.

HCN profiles were only detected for the samples treated at 200, 400 and 700 °C. This compound evolves from 300 °C for CN200, from 600 °C for CN400 and from 750 °C

for CN700. Single characteristic peaks, occurring at higher temperatures than in the NH₃ profiles are obtained at around 750 °C for CN200 and CN400, and around 900 °C for CN700.

From these results it can be concluded that nitrogen functionalities with different thermal stabilities have been introduced into the carbons as a result of treatment with ammonia gas at different temperatures. At least four types of different nitrogen functionalities may be responsible for NH₃ evolution during the TPD tests, while for HCN only two components can be identified. The nitrogen-containing groups in the C carbons that were treated at the higher temperatures ($T > 600$ °C) appear to be strongly bound, as can be deduced from the maxima of the NH₃ and HCN desorption profiles. Increasing the temperature of the ammonia treatment seems to promote the introduction of more stable nitrogen-functionalities into the carbons possibly because the incorporated N functionalities are transformed with temperature. Upon reaction with ammonia at 200 °C, a number of surface groups on the carbons, but especially the oxygenated ones, may react with NH₃, possibly leading to the formation of amides, imides, imines, amines and nitriles. The addition of ammonia to a carbon double bond only takes place at temperatures of approximately 250 °C and then only to a small extent [27]. It was mentioned above that ammonia gas is thought to decompose at higher temperatures, freeing radicals, such as NH₂, NH and atomic hydrogen [18, 19]. These radicals may attack the carbon with the result that it is gasified to form methane, hydrogen cyanide and cyanogen [18]. Meldrum *et al.* [28] proved by an *in situ* FTIR study, that the reaction of an oxidised activated carbon with gaseous ammonia converts surface cyclic anhydride groups to amide and ammonium carboxylate species. At high temperatures amide would decompose to nitrile through a reversible dehydration reaction. Moreover, amine and alcohol groups may be formed by the reaction of the

ammonia with the epoxide groups that are usually present on oxidised carbon surfaces. The reaction of ammonia with one or more carboxylic acids may lead to amides, lactams and imides. The dehydration, decarboxylation, or decarbonylation of such functional groups may result in pyrroles and pyridines, probably with the formation of nitriles as an intermediate step [17]. It seems clear that oxygenated functionalities on the carbon surface play a determinant role in the incorporation of nitrogen into the carbon surface by ammonia treatment. TPD tests of the R ammonia-treated samples did not show any nitrogen compound evolution. The lower oxygen content of R (4.2 wt.%) may partially explain the lower amount of nitrogen incorporated into the R-modified carbons (up to 2.1 wt. % N). However, it can be seen from the oxygen contents of the samples treated with ammonia (ca. 3 wt. % O) that not all the oxygen is able to react with ammonia. What type of oxygen functionality it is will also play a significant role. In order to obtain more information about the oxygen functionalities on the carbon surfaces, CO and CO₂ profiles were also recorded during the TPD tests. Figures 3 and 4 show the CO and CO₂ emissions analysed by FTIR during the TPD tests of the samples. CO₂ emissions start at earlier temperatures for the R samples, even though significantly lower intensities per milligram of sample are obtained compared to the C samples. In addition, C presents a main CO₂ peak at around 700 °C with a smooth shoulder at approximately 300 °C, while R shows a CO₂ profile with two distinct peaks at around 200 and 500 °C, respectively, and a shoulder at 700 °C. As expected, with the decrease in oxygen content the ammonia treated samples drastically reduce their CO and CO₂ emissions during the TPD tests. CO₂ emissions are negligible for carbons treated at higher temperatures ($T > 600$ °C), particularly for the R-treated samples. Lower temperature ammonia treatment ($T < 600$ °C) results in lower CO₂ intensities compared to the parent carbons and the CO₂ profiles shift towards lower temperatures. This

suggests that oxygen-functionalities in the parent carbon which evolve CO₂ at higher temperatures ($T > 700$ °C) during the TPD experiments, react mainly with ammonia during the heat-treatment at lower temperatures, while ammonia heat-treatment at higher temperatures involves all the CO₂-evolving functionalities in the parent carbons. CO emissions for the parent carbons C and R follow similar profiles with characteristic peaks at around 950 °C and with shoulders at around 800 °C and 850 °C for R and C, respectively. CO profiles for the ammonia-treated samples shift towards lower temperatures compared to the parent carbons. It is also worth noting that the C-modified carbons CN200 and CN400 show CO emissions at lower temperatures (at around 700 °C), outside the temperature range of the parent carbon CO profile. These CO emissions that occur simultaneously with NH₃ and HCN evolution during the TPD tests, result from the decomposition of the labile amide or lactam-like groups formed during the ammonia treatment at lower temperatures. For the remaining C-treated carbons and the R-treated samples the shift of the CO profiles towards lower temperatures, compared to the respective parent carbons, suggests that oxygen functionalities which evolve CO at higher temperatures ($T > 900$ °C) are more reactive towards ammonia. It is generally accepted that CO₂ results from the decomposition of carboxylic acids at low temperatures or from lactones at higher temperatures and that carboxylic anhydrides generate both CO₂ and CO, while phenols, ethers, carbonyls and quinones -i.e. functional groups with one oxygen atom- generate CO. In general, the TPD spectra obtained from carbon materials show composite CO and CO₂ peaks which can be attributed to the contribution of different functionalities [29]. The ammonia heat treatment of C carbon at temperatures lower than 600 °C results in the simultaneous evolution of CO and CO₂ at higher temperatures, together with the evolution of CO at 700 °C. The evolution of CO at 700 °C is probably associated with nitrogen-containing

groups like amides (NH_3 also evolves in the same temperature range). At temperatures higher than $600\text{ }^\circ\text{C}$ ammonia heat treatment results in the loss of the majority of the oxygen functionalities in the parent carbon and the incorporation of nitrogen into more stable functionalities, such as cyclic imides and lactams and/or aromatic rings.

The presence of carboxylic-like functionalities on the parent carbon, R, may be justified by the first CO_2 peak at low temperature ($T \approx 200\text{ }^\circ\text{C}$). However, ammonia treatment of the R carbons appears to be less effective for the incorporation of surface nitrogen functionalities at any temperature.

An XPS analysis was carried out to study the nature of the surface groups present on the carbons. Low-resolution XPS spectra of the ammonia modified carbons at $T > 600\text{ }^\circ\text{C}$ indicate the presence of three main peaks due to carbon, nitrogen and oxygen. For reference purposes the spectra of the parent carbons, C and R, were also recorded. For the R carbons, low-resolution XPS spectra showed small contributions of oxygen and nitrogen. Thus high resolution scans were only conducted on the C carbons.

Figure 5 shows the $\text{N}1s$ spectra of the ammonia modified C carbons, CN600, CN700 and CN800. The shape of the $\text{N}1s$ envelopes of the analysed samples suggests the presence of two main components in all of them. A comparison of the spectra of the different samples shows that, as the ammonia treatment temperature increases, the components become better defined and differentiated from each other. The spectra were curve fitted in order to assess the contributions of specific nitrogen surface groups. The best fit for each spectrum was obtained with two peaks centred at binding energies of around 398.3 and 400.0 eV , respectively (see Table 3). With increasing temperature the binding energies of the fitted peaks #2 of the $\text{N}1s$ spectra shift to higher values while those of the fitted peaks #1 hardly move. Low binding energies may suggest the presence of negatively-charged nitrogen species. According to the literature, peak #1

binding energies probably correspond to pyridine-like structures while peak #2 could be assigned to pyrrole and/or pyridone-like moieties. For peak #2, binding energies vary between 399.9 eV for CN600 and 400.1 eV for CN800, suggesting the possible contributions of different nitrogen structures in each sample. Amide-like moieties (B.E. \approx 399.6-399.9 eV) are rather unstable but lactams and imides (B.E. \approx 399.7 eV) are more persistent [18, 30, 31].

The curve fittings of the C1s and O1s XPS spectra are also presented in Table 3. The curve fitting of the C1s spectra yielded four main components with binding energies at 284.5, 285.6, 286.2-286.7 and 288.8-289.1 eV. These contributions can be assigned to graphitic carbon (284.5 eV), the carbon present in phenolic, alcohol or ether groups (286.1 eV), carbon-nitrogen structures (286.3-287.5 eV), carbonyl groups (287.3 eV), and ester or carboxyl groups (288.7 eV–289.3 eV), respectively [32, 33]. Globally, C carbons present the same type of carbon functionalities, graphitic carbon being the major component.

O1s spectra for the C carbon samples displayed two components with binding energies at 531.5 and 533.3 eV. These binding energies could correspond to oxygen singly bonded to carbon in aromatic rings, in phenols and ethers (533.2-533.8 eV), or to oxygen doubly bonded to carbon in quinone-like structures (531.3 eV) [31-33]. The majority of the O1s envelopes lie between 531 eV and 534 eV. A shift in the signal to higher binding energies may indicate a decrease in functional groups of the carboxylic acid and amide type or it may indicate an increase in groups such as hydroquinones and ethers.

The ammonia heat treatment of the C treated carbons reduce the concentration of surface oxides, mainly phenol and ether-like groups, and simultaneously increase the

number of surface nitrogen moieties and pyridinic and pyrrole-like functionalities, the groups responsible for the strong basic character of the C treated samples.

From the data provided by the XPS analysis and TPD tests valuable information about the fate of nitrogen in the ammonia-treated samples is obtained. Firstly, the temperature of the ammonia treatment determines the type of nitrogen functionalities incorporated into the carbons: below 600 °C amides, imides, imines, amines and nitriles are formed, while above 600 °C nitrogen is preferentially incorporated into aromatic rings which are thermally more stable. Secondly, the presence of oxygen functionalities on the carbon surface has a determinant influence on the extent of the ammonia-carbon reaction. For the C carbons, phenols and ethers seem to be the main oxygen-groups that react with ammonia at $T > 600$ °C.

CO₂ capture tests at atmospheric pressure

Temperature programmed adsorption-desorption tests were carried out to evaluate the influence of temperature on the CO₂ capture capacity of the prepared sorbents. Prior to any CO₂ capture experiment the samples were dried under inert atmosphere to avoid the influence of the moisture present in the samples. Table 4 shows the CO₂ adsorption capacities, at 25 and 75 °C, of the ammonia modified carbons and the parent carbons. The R samples displayed greater CO₂ capacities (wt. %) than the C samples treated with ammonia at the same temperature, especially at 25 °C. This behaviour might be explained by the stronger basic character of the R carbons compared to the C samples and the higher narrow micropore volumes of the R carbons which were calculated from the CO₂ adsorption isotherms at 0 °C. At 75 °C, the CO₂ capture capacities of both series of carbons diminishes, as might be expected for typical adsorption processes, where increasing adsorption temperature acts to the detriment of CO₂ adsorption.

A comparison of the behaviour of the ammonia-modified samples with the parent carbons shows that for the C samples, ammonia heat treatment up to 700 °C reduces the capture capacity of the treated samples. However, treatment temperatures of 700 °C and above result in an enhancement of the capacity of C carbons to capture CO₂. For the R samples, ammonia treatment at the different temperatures increases the CO₂ capture capacity of the R modified samples with respect to the parent carbon, R, but only to a small extent. CN800 and RN800 display the highest CO₂ capture capacities of each series at both 25 and 75 °C. To isolate the effect of the change in surface chemistry on the capture performance of the modified carbons, their CO₂ capture capacities were normalised by the micropore volume (W_0) (see Table 4). Figure 6 shows the temperature resolved CO₂ capture tests for the C and R carbons studied, where CO₂ uptakes are expressed in milligrams of CO₂ adsorbed per cubic centimetre of micropore volume. All the treated carbons present higher CO₂ uptakes per cm³ of micropores than the corresponding parent carbons over the temperature range studied. This clearly indicates that surface modification by ammonia treatment increases the affinity of carbon towards CO₂. For both series the highest CO₂ uptakes per cm³ are obtained for the carbons treated with ammonia at the highest temperatures, CN800 and RN800. However, it should be pointed out that for the C series, CO₂ uptakes per cm³ are not directly related to the nitrogen content. For instance CN600 (3.5 wt.% N) presents a lower CO₂ capture capacity per cm³ than CN200 and CN400 (2.4 and 3.3 wt.% N, respectively). Thus, the CO₂-adsorbent affinity depends not only on the amount of total nitrogen incorporated into the carbons but also on the type of nitrogen functionalities introduced. According to the results, nitrogen on the samples treated with ammonia at temperatures higher than 600 °C can be expected to be incorporated into aromatic rings of the pyridinic and pyrrole-like type. However, no clear differences between CN600,

CN700 and CN800 could be inferred from the characterisation of the nitrogen surface groups by XPS and TPD analysis.

Conclusions

Two commercial activated carbons, C and R, were heat-treated with ammonia at different temperatures, in the 200 - 800 °C range. This treatment introduced nitrogen functionalities into the carbon materials, thereby increasing their basic character. Characterisation of the modified carbons by TPD and XPS showed that ammonia treatment at temperatures higher than 600 °C incorporated nitrogen mainly into aromatic rings, while at lower temperatures nitrogen was introduced into more labile functionalities, such as amide-like functionalities. The CO₂ capture capacities at 25 °C of the treated carbons increased with respect to the parent carbons. In particular in the C series, CO₂ capture capacities rose from 7 wt.% for C to 8.4 wt.% for CN800. Ammonia treatment did not notably change the textural properties of the parent carbons. CO₂ capture capacity is not directly related to the total nitrogen content of the samples but to specific nitrogen functionalities that are responsible for increasing the CO₂-adsorbent affinity.

Thus, any surface modifications of commercial activated carbons should be carefully performed. In this way nitrogen functionalities that promote the CO₂ capture capacities of adsorbents can be incorporated without altering the textural properties of the parent carbon.

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Table 1. Product yield, ultimate analysis and pH_{PZC} of the studied samples

Sample	Product yield (wt %)	Ultimate Analysis (wt.%, daf)				pH_{PZC}
		C	H	N	O	
C	100	82.9	3.0	0.4	13.7	2.8
CN200	103	84.5	2.9	2.4	10.2	6.8
CN400	95	84.9	2.8	3.3	9.0	6.6
CN600	87	91.2	1.7	3.5	3.6	7.8
CN700	86	86.6	1.0	8.1	4.3	8.8
CN800	74	88.7	0.7	6.3	4.3	8.9
R	100	94.7	0.4	0.7	4.2	9.5
RN200	100	95.5	0.3	0.8	3.4	9.7
RN400	100	95.6	0.0	0.9	3.5	9.7
RN600	100	95.8	0.1	1.1	3.0	9.8
RN800	99	94.2	0.1	2.1	3.6	9.6

Table 2. Textural parameters and helium density of the studied samples

Sample	d_{He} (g cm ⁻³)	N ₂ adsorption at -196 °C				CO ₂ adsorption at 0 °C		
		S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	V_{meso} (cm ³ g ⁻¹)	D (nm)	W_0 (cm ³ g ⁻¹)	E_0 (kJ mol ⁻¹)	L_0 (nm)
C	1.51	1361	0.965	0.441	2.84	0.215	26.07	0.74
CN200	1.58	1294	0.925	0.431	2.86	0.181	26.96	0.69
CN400	1.51	1225	0.876	0.397	2.86	0.177	26.92	0.70
CN600	1.69	1095	0.749	0.329	2.74	0.198	27.96	0.65
CN700	1.87	1023	0.686	0.292	2.69	0.206	29.36	0.60
CN800	1.92	1190	0.831	0.354	2.79	0.221	28.97	0.61
C800	1.92	976	0.664	0.288	2.72	0.206	29.36	0.60
R	2.14	942	0.407	0.008	1.73	0.261	28.02	0.65
RN200	2.14	1105	0.470	0.011	1.70	0.252	28.17	0.64
RN400	2.12	948	0.403	0.005	1.70	0.253	28.73	0.62
RN600	2.12	990	0.423	0.008	1.71	0.236	28.89	0.62
RN800	2.14	1072	0.467	0.013	1.74	0.211	30.07	0.58

Table 3. XPS C1s, O1s and N1s fitted peaks for some of the studied samples

Sample	C1s								C total (% at.)
	Fit #1 (eV)	(%)	Fit #2 (eV)	(%)	Fit #3 (eV)	(%)	Fit #4 (eV)	(%)	
C	284.58	64.9	285.86	7.4	286.63	9.6	289.03	6.2	88.1
CN600	284.47	63.8	285.6	13.0	286.74	7.1	289.15	7.6	91.5
CN700	284.54	58.1	285.65	7.1	286.29	13.0	288.85	10.5	88.7
CN800	284.57	61.5	285.71	7.7	286.46	11.1	288.91	10.3	90.6
R	284.53	59.0	285.58	8.0	286.24	14.1	288.86	4.3	85.4
RN600	284.50	53.2	285.56	14.3	286.60	12.3	289.11	4.4	84.2
RN800	284.52	43.6	285.54	20.5	286.65	13.9	289.23	4.6	82.6

Sample	O1s				O total (% at.)
	Fit #1 (eV)	(%)	Fit #2 (eV)	(%)	
C	533.28	7.6	531.54	3.6	11.2
CN600	533.29	3.5	531.63	2.5	6.0
CN700	533.27	3.3	531.49	3.1	6.5
CN800	533.24	2.7	531.52	2.3	5.0

Sample	N1s				N total (% at.)
	Fit #1 (eV)	(%)	Fit #2 (eV)	(%)	
CN600	398.32	0.7	399.91	1.1	1.8
CN700	398.34	1.9	400.07	2.3	4.2
CN800	398.27	1.6	400.08	2.2	3.8

Table 4. CO₂ capture capacities at 25 and 75 °C for the studied samples

Sample	CO ₂ capture capacity (wt.%)		CO ₂ capture capacity / W ₀ (mg CO ₂ / cm ³)	
	25 °C	75 °C	25 °C	75 °C
C	7.0	2.0	326	93
CN200	6.6	1.9	365	105
CN400	6.5	2.0	367	113
CN600	6.5	2.0	328	101
CN700	7.6	2.5	369	121
CN800	8.4	2.7	380	122
R	9.1	2.7	349	103
RN200	9.2	2.9	365	115
RN400	9.6	3.2	379	126
RN600	9.5	2.8	402	119
RN800	9.6	3.2	455	152

Figure captions

Figure 1. N₂ adsorption isotherms at -196°C of the parent activated carbons, C and R, and the corresponding modified samples.

Figure 2. a) HCN and b) NH₃ profiles during the TPD tests of the C-modified carbons

Figure 3. CO₂ evolution during the TPD tests of the studied samples.

Figure 4. CO evolution during the TPD tests of the studied samples.

Figure 5. N1s XPS spectra for CN600, CN700 and CN800.

Figure 6. CO₂ uptakes, normalised by the micropore volume, during the temperature programmed CO₂ capture tests for the studied samples.

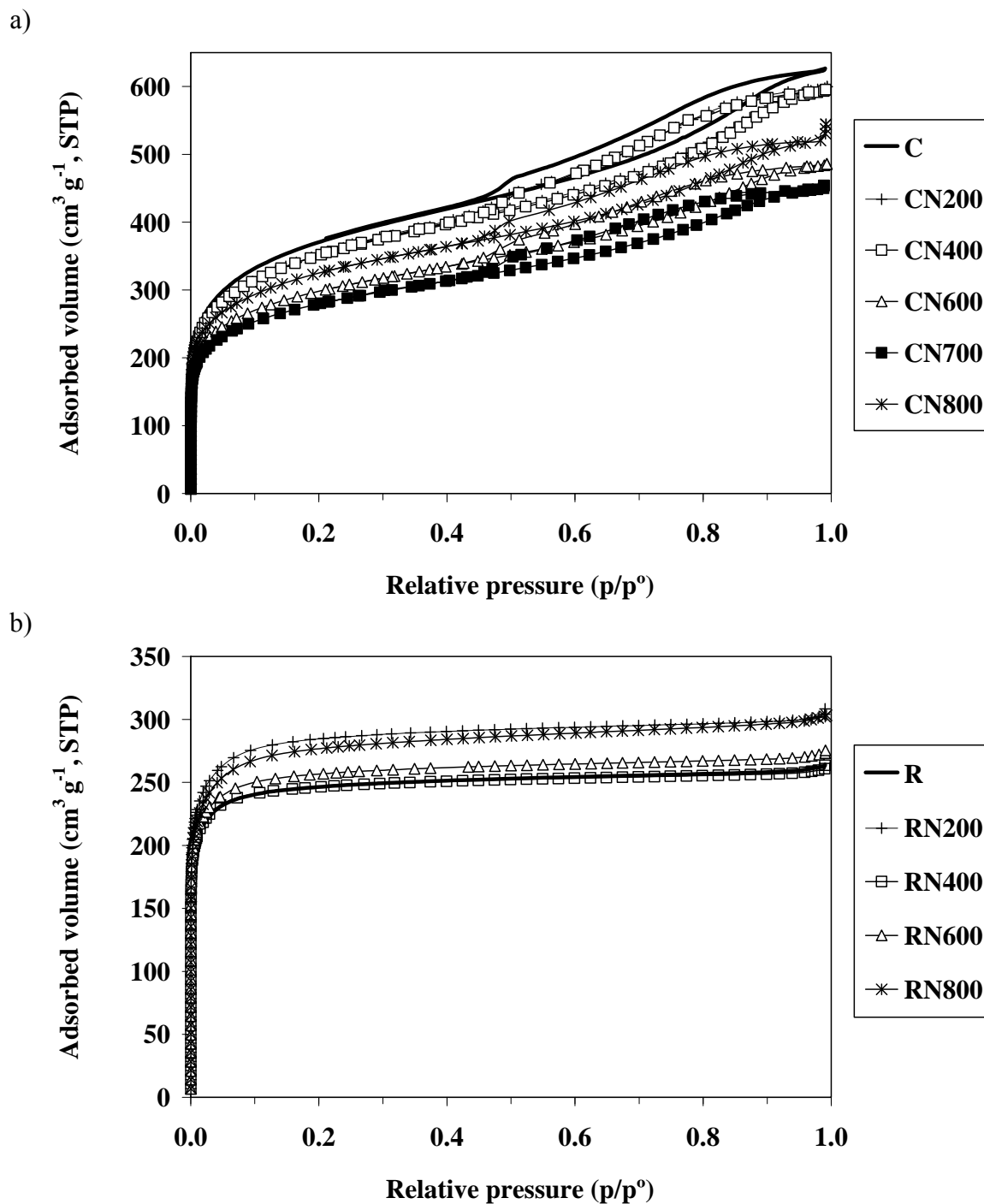
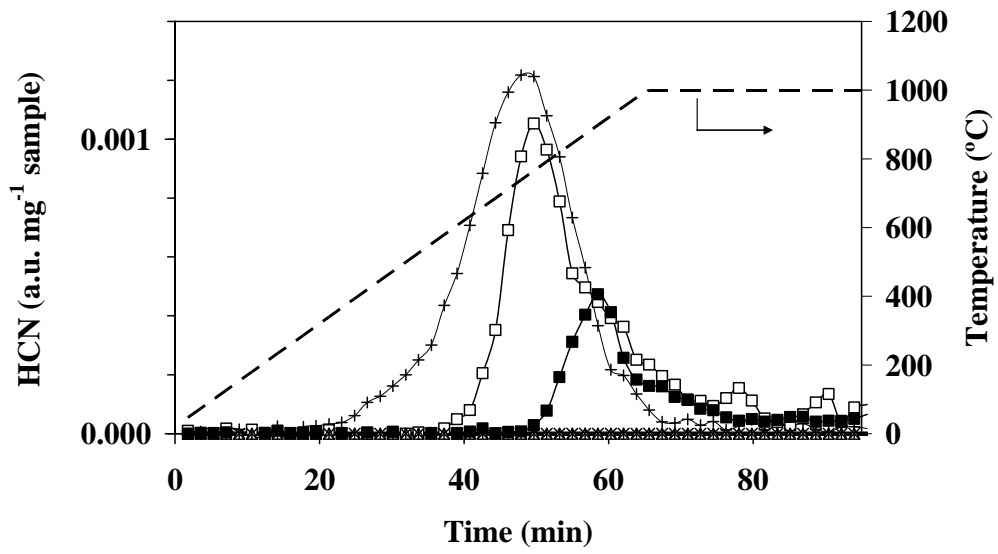


Figure 1 N_2 adsorption isotherms at -196°C of the parent activated carbons, C and R, and the corresponding modified samples.

a)



b)

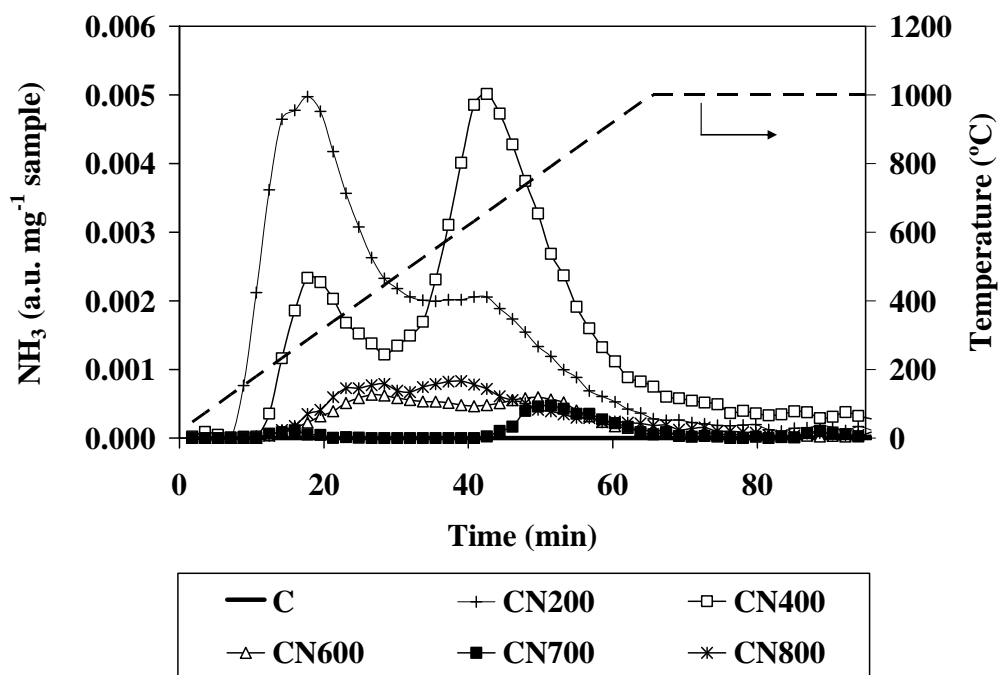


Figure 2. a) HCN and b) NH₃ profiles during the TPD tests of the C-modified carbons.

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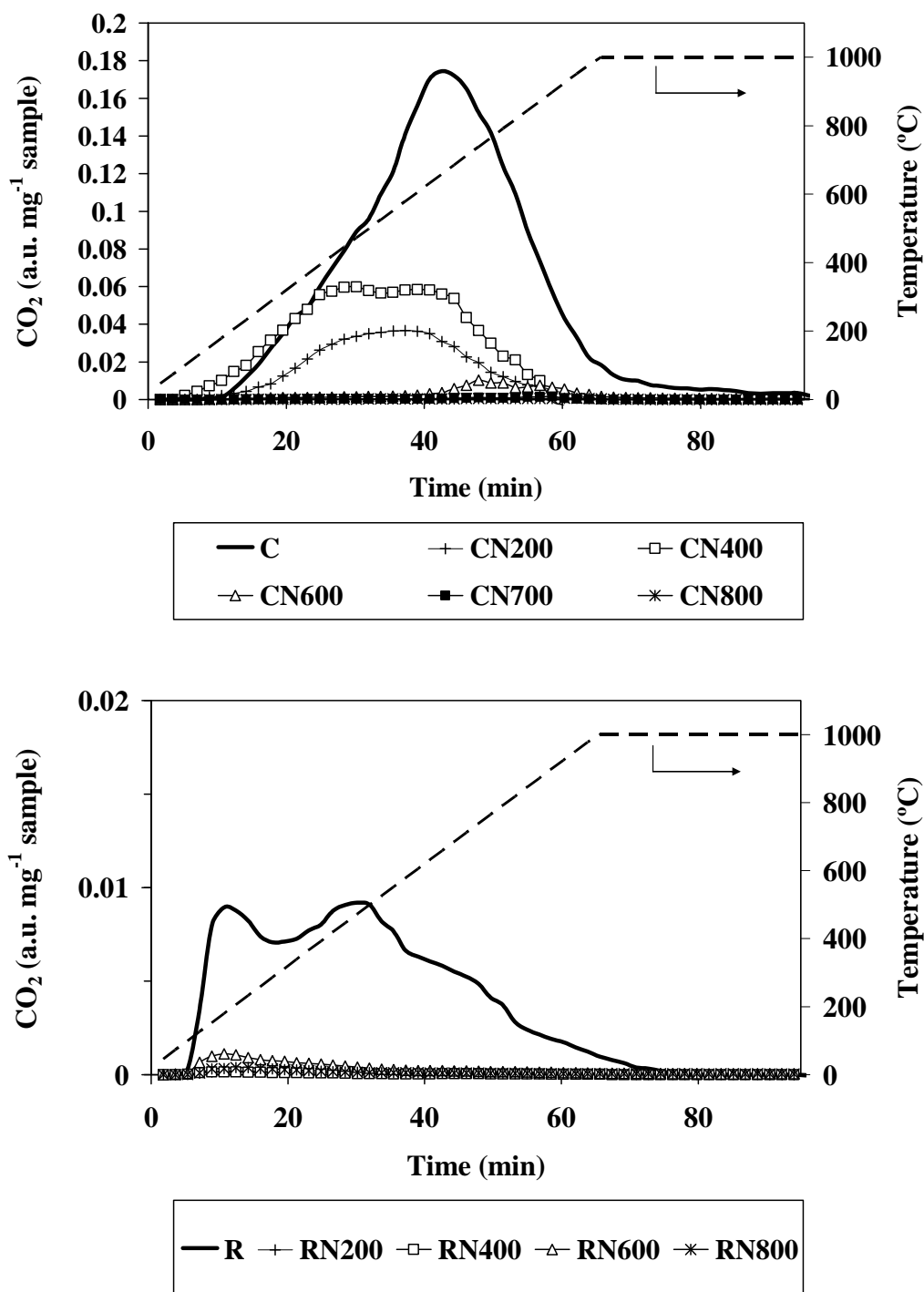


Figure 3. CO₂ evolution during the TPD tests of the studied samples.

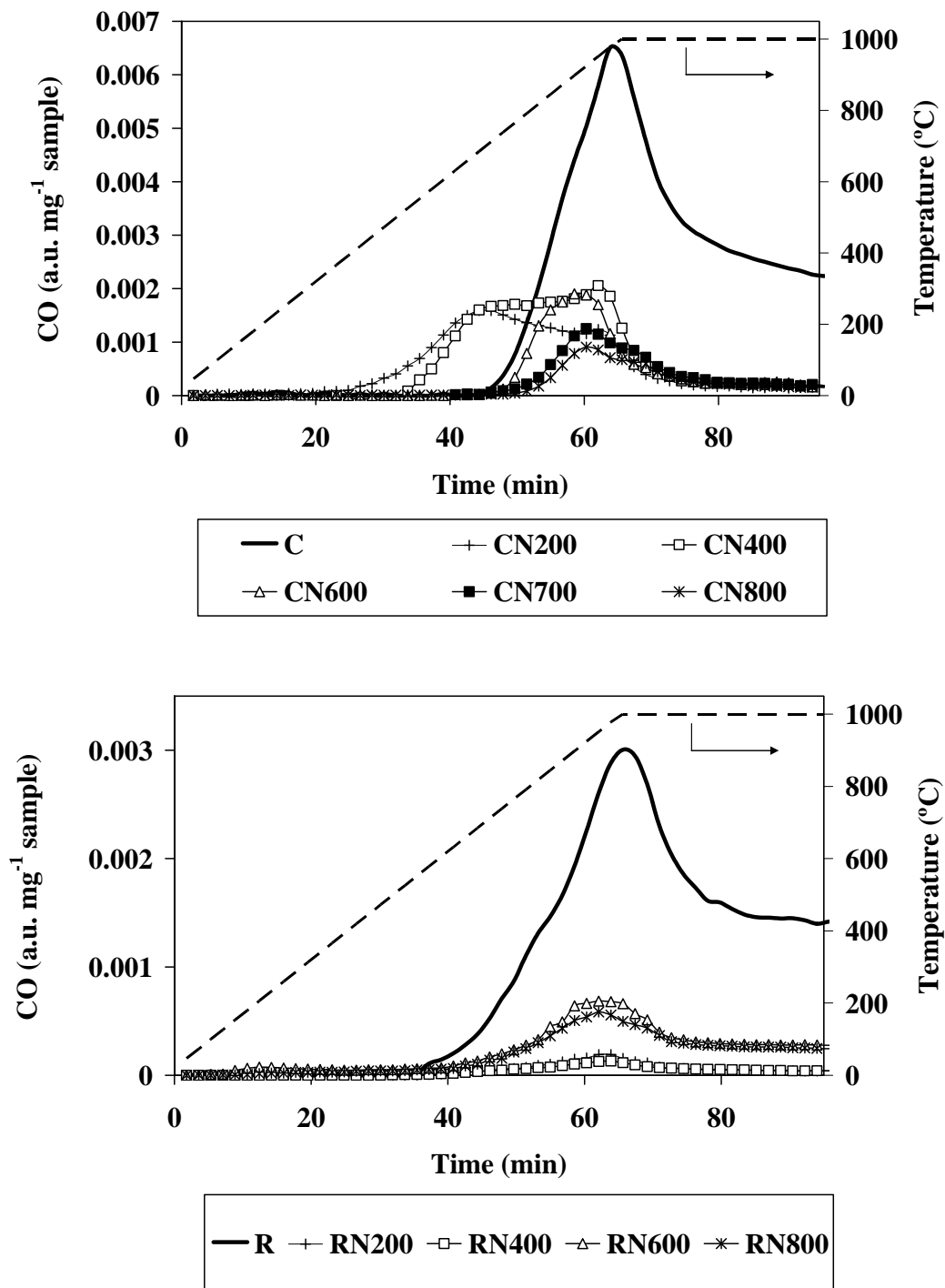


Figure 4. CO evolution during the TPD tests of the studied samples.

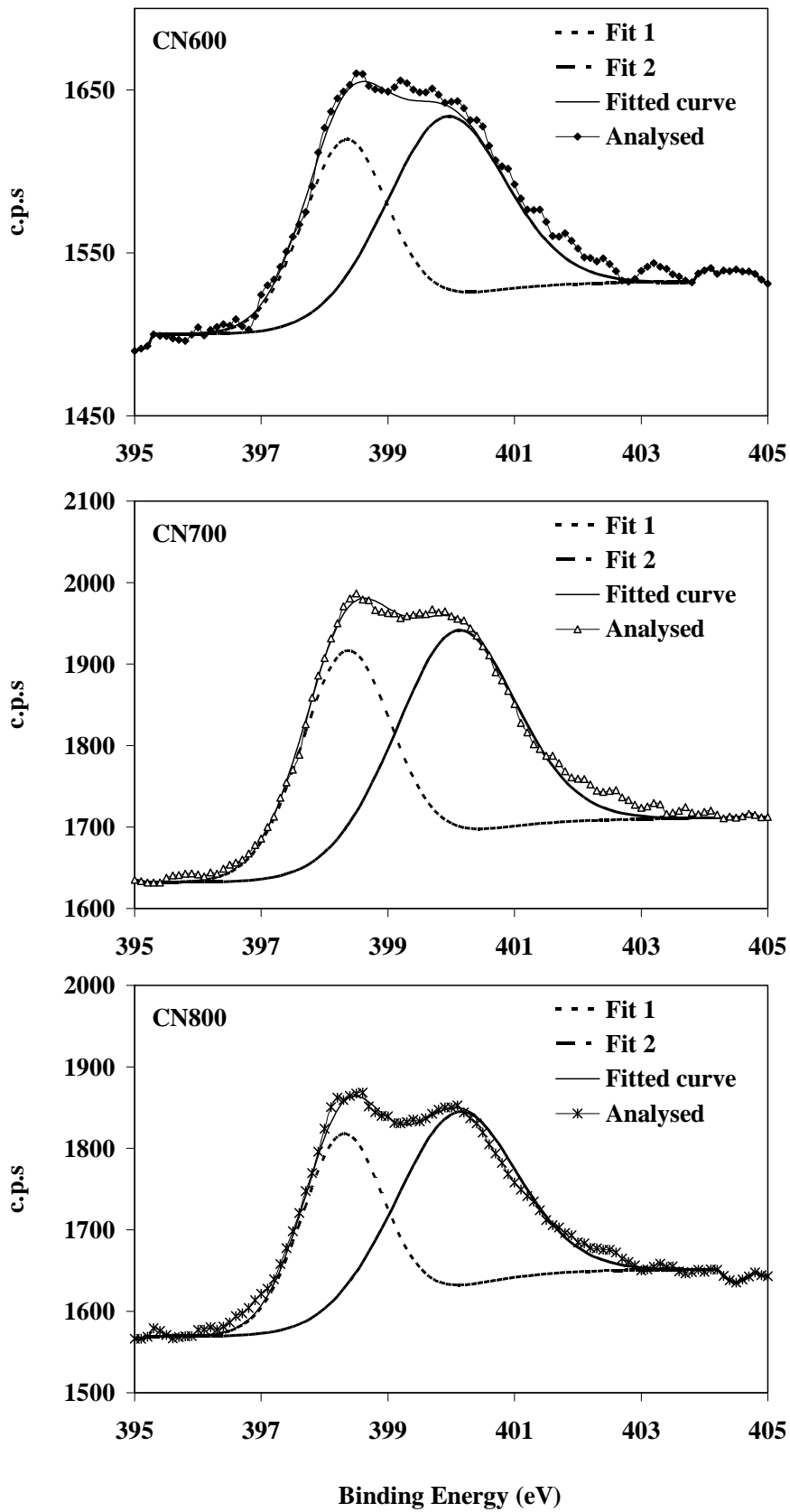


Figure 5. N1s XPS spectra for CN600, CN700 and CN800.

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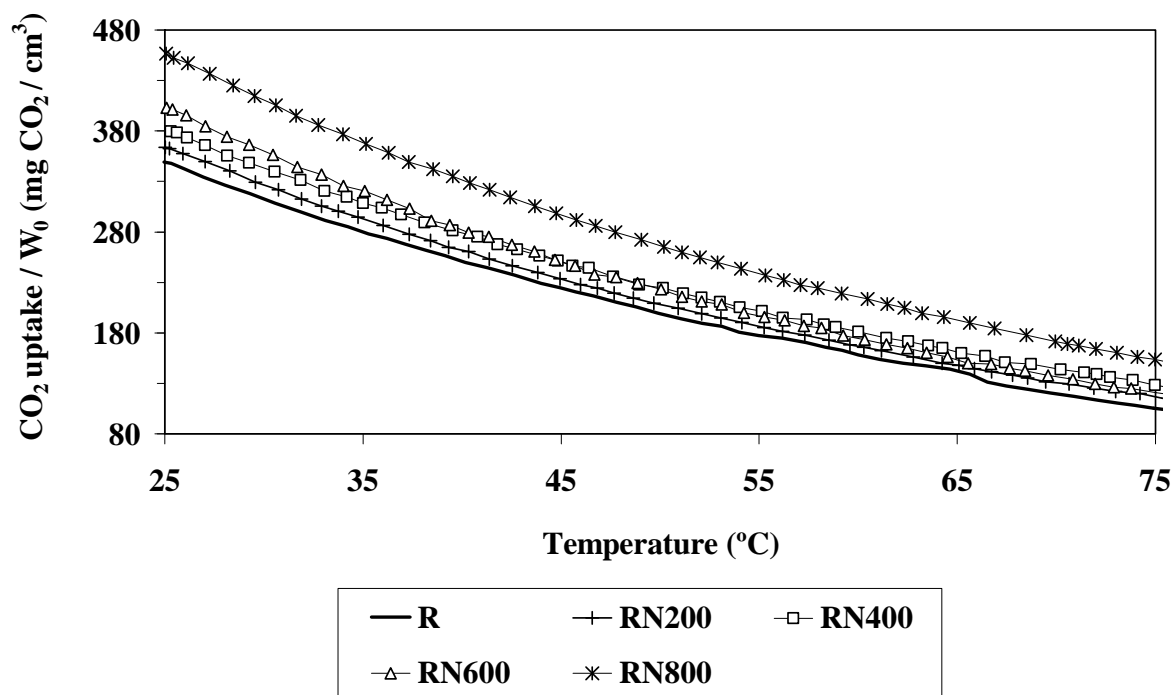
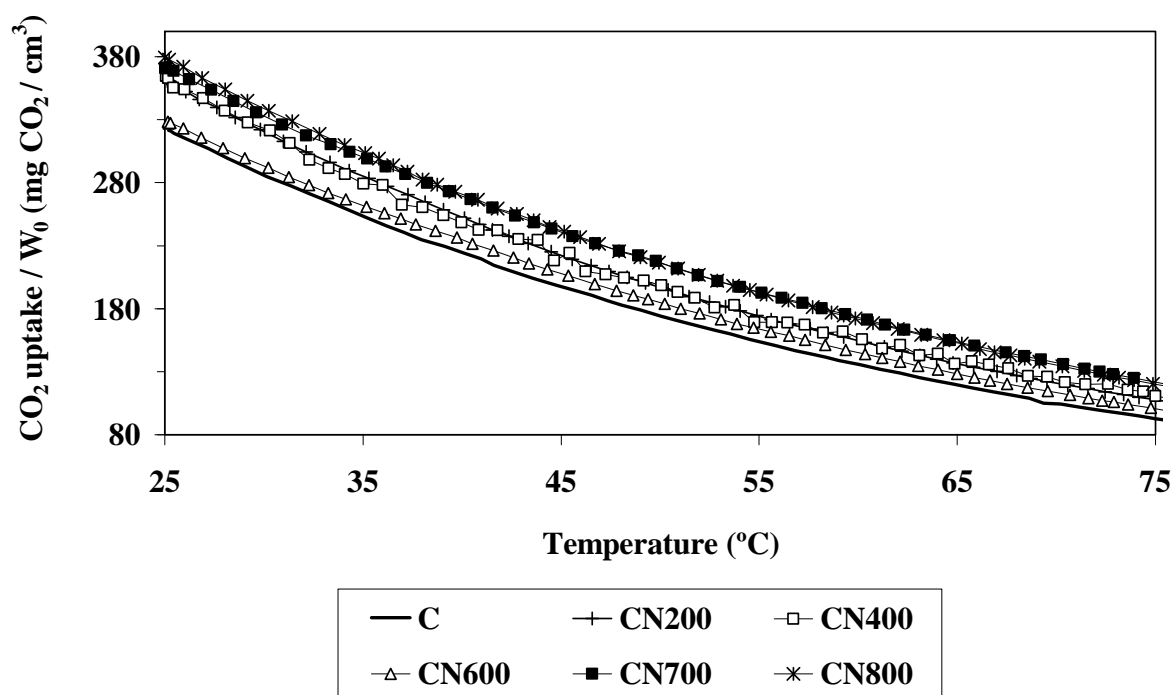


Figure 6. CO₂ uptakes, normalised by the micropore volume, during the temperature programmed CO₂ capture tests for the studied samples.

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