Ammonoxidation of carbon materials for CO₂ capture

M.G. Plaza, F. Rubiera, J.J. Pis, C. Pevida*

Instituto Nacional del Carbón (INCAR), CSIC. Apartado 73, 33080 Oviedo, Spain

*corresponding author e-mail: cpevida@incar.csic.es

Abstract

Ammonoxidised carbons were produced from three different starting materials: an activated carbon obtained from wood by chemical activation using the phosphoric acid process, a steam activated peat-based carbon, and a char obtained from a low-cost biomass feedstock, olive stones. Nitrogen was successfully incorporated into the carbon matrix of the different materials, the amount of nitrogen uptake being proportional to the oxygen content of the precursor. At room temperature the CO₂ capture capacity of the samples was found to be related to the narrow micropore volume, while at 100 °C other factors such as surface basicity took on more relevance. At 100 °C all the ammonoxidised samples presented an enhancement in CO₂ uptake compared to the parent carbons.

Keywords: Ammonoxidation; Carbon Materials; Adsorption; CO₂ capture.

1. Introduction

Carbon Capture and Storage (CCS) has been attracting much attention in recent years due to the urgent need to cut down greenhouse gas emissions. According to the International Energy Agency (IEA), CCS could contribute up to 19 % of the cumulative effort to reduce energy-related CO₂ emissions [1]. Postcombustion capture from coal power plants has great potential for reducing CO₂ emissions and the installation of several new 1400 GW coal power plants is planned before 2030 [2]. However, postcombustion capture is faced with two difficult challenges: a low CO₂ partial pressure and huge volumetric flow rates, which increase the cost of the separation stage.

Amine scrubbing could be used as an alternative for this stage, but it has serious drawbacks, such as high energy requirements and corrosion.

Adsorption has been proposed as another attractive option as it could reduce the cost associated with the capture step [3-17]. Among the adsorbents that could be used to carry out the separation of CO₂ are activated carbons. These offer a number of advantages, such as ease of regeneration, low cost, high CO₂ adsorption capacity, and high CO₂/N₂ selectivity. Many attempts have been made to enhance the postcombustion capture performance of common adsorbents by chemically modifying their surface; among these, nitrogen enriched carbons have shown an enhancement in the CO₂ capture capacity [18-25]. Nitrogen-rich carbons present other applications related to the protection of the natural environment. For instance, they have been applied to reduction of NO [26-28], to removal of pollutants of acidic character such as SO₂ and H₂S [29, 30], to adsorption of metal ions from the liquid phase [31], and, more recently, to the production of electrodes in electrochemical capacitors with improved performance [32, 33].

Although nitrogen is not abundant in natural carbon materials, there are several ways to produce nitrogen-rich carbons: by pyrolysis of nitrogen containing polymers [23, 25], by impregnation [18, 19, 24, 34], or by reaction with ammonia [20, 35-40]. Ammoxidation or the reaction of activated carbons with ammonia-air gas mixtures is another method that can be used to carry out the nitrogen enrichment of carbon materials [35-37, 41-46].

In this work three different carbon materials were subjected to ammoxidation: two different types of commercial activated carbons and a char obtained in our laboratory from a low-cost biomass feedstock, olive stones. Modification of the surface chemistry was evaluated by means of ultimate analysis, the estimation of the point of zero charge,

DRIFT spectroscopy, and temperature programmed desorption tests with evolved gas analysis. The effect of ammoxidation on the texture of the samples was assessed from the N₂ and CO₂ adsorption isotherms at -196 and 0 °C, respectively. Finally, the CO₂ capture performance of the samples was determined using a thermogravimetric analyser.

2. Experimental

The samples were dried overnight at 100 °C prior to the ammoxidation treatment. Around 6 g of sample was placed in a quartz reactor and swept with 50 cm³ min⁻¹ of N₂ for 30 min. Then, the reactor was introduced in a vertical tube furnace, previously heated to the desired temperature. Once the sample reached that temperature, the N₂ flow was replaced by 50 cm³ min⁻¹ of a gas mixture containing ammonia and air at a ratio of 1:2, and held for 2 h. Afterwards, the reactor was removed from the furnace and allowed to cool down. Finally, the samples were placed in a forced air oven at 100 °C for 1 h in order to desorb the weakly adsorbed ammonia. The samples were named after the starting carbon used followed by the letters NO and by the temperature of the treatment (e.g., CNO200 stands for sample C ammoxidised at 200 °C).

The effect of the temperature of the treatment was studied with two different types of commercial activated carbons supplied by Norit: Norit C Gran and Norit R 2030 CO₂. The first carbon, Norit C Gran, is produced by chemical activation of wood at 550 °C using the phosphoric acid process, while the second, Norit R 2030 CO₂, is a peat-based carbon activated with steam at 900 °C. They will be referred to as C and R, respectively.

In addition, an agricultural by-product abundant in Spain, olives stones, was selected as a low-cost feedstock for producing ammoxidised carbons. The raw stones were ground and sieved, and a particle size of between 1 and 3 mm was selected for the experiments.

The first step, carbonisation, was carried out at 600 °C in a N₂ flow with an average char yield of 24 %. The resulting char was denoted as O.

The nitrogen uptake of the samples was determined by ultimate analysis. The change in the ratio of acidic to basic groups was evaluated from the point of zero charge (pH_{PZC}), determined by a mass titration method adapted from Noh and Schwarz [47]. The modification of the surface chemistry was also studied by DRIFT spectroscopy and temperature programmed desorption tests (TPD) together with evolved gas analysis, using a thermogravimetric analyser coupled to a FTIR spectrometer via a heated interface.

The effect of ammoxidation on the porous texture of the samples was assessed from the N₂ and CO₂ adsorption isotherms at -196 and 0 °C, respectively, obtained using a volumetric apparatus. Prior to the adsorption measurements, the samples were outgassed overnight at 100 °C under vacuum. The use of both adsorbates provided complementary information. Whereas the adsorption of CO₂ at 0 °C and up to 1 bar is restricted to pores narrower than 1 nm, N₂ adsorption at -196 °C covers wider pore sizes but suffers from diffusion limitations in the narrowest pores. The apparent surface area of the samples was evaluated from the N₂ adsorption isotherms by means of the BET equation (S_{BET}), and the total pore volume (V_{p}) was assessed from the amount of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume (V_{DR}) and narrow micropore volume (W_0) (pore width below 0.7 nm) were estimated by applying the Dubinin-Radushkevich method to the N₂ and CO₂ adsorption isotherms, respectively. The mean micropore width and narrow micropore width (L_{DR} and L_0 , respectively), were calculated using the Stoeckli-Ballerini empirical relation [48].

Finally, the CO₂ capture capacity of the prepared samples was assessed using a Setaram TGA 92 thermogravimetric analyser, which recorded the mass uptake of the samples in CO₂ flow.

3. Results and discussion

3.1. Characterisation of the C series

To select the temperature of ammoxidation, the starting carbons were subjected to temperature programmed oxidation tests at a heating rate of 15 °C min⁻¹ in 50 cm³ min⁻¹ of air. Figure 1 shows the corresponding TG and DTG curves of carbon C. Oxygen chemisorption takes place between 200 and 300 °C, as can be seen from a slight mass gain. Above 300 °C, the reactivity of the carbons in oxygen is excessively high and so 300 °C was the maximum temperature studied.

Table 1 presents the results of the ultimate analysis and the pH_{PZC} of the prepared samples. Oxygen content has been calculated by difference. Carbon C has a high oxygen content and a strong acid character due to the phosphoric acid production process. The ammoxidised samples have similar oxygen contents to the starting carbon, but significantly higher nitrogen contents which increase with temperature: 5.0 and 9.2 wt.% at 200 and 300 °C, respectively. During ammoxidation, the carbon is also oxidised, thus replacing the oxygen consumed in the reactions with ammonia [36]. From a comparison of these results with a previous work by our group on the modification of C by heat treatment in the presence of pure ammonia gas [20], it was found that nitrogen uptake is significantly higher when the NH₃ treatment is carried out in the presence of air (ammoxidation); sample C treated for 2 h with 50 cm³ min⁻¹ of NH₃ in the absence of air (amination), at 200 and 400 °C, presented only 2.4 and 3.3 wt.% of N, respectively.

In order to study the nature of the functionalities created by ammoxidation, the DRIFT spectra of samples C, CNO200 and CNO300, were recorded on a Nicolet Magna IR-560 spectrometer, fitted with a diffuse reflectance accessory and a MCTA detector. 128 interferograms with a resolution of 4 cm^{-1} were acquired. The corresponding spectra are depicted in Figure 2. For comparative purposes, sample CN200, obtained by amination at $200\text{ }^{\circ}\text{C}$ [20], has been included in this figure. The spectra of the ammoxidised samples present a band at 2225 cm^{-1} , which is more intense in the case of CNO300, and is ascribed to nitriles [38]. The starting carbon, C, displays a band at 1700 cm^{-1} , which is characteristic of carboxyls and lactones, and a sharp band at 1600 cm^{-1} , related to aromatic carbon stretching with electronegative substituents (i.e., oxygen) nearby, quinones or carbonates [49, 50]. If the spectra of the ammoxidised samples are compared with the spectrum of the starting carbon, it can be seen that an overlap occurs between the bands at 1600 and 1700 cm^{-1} . This is attributed to the formation of amides from the reaction of NH_3 with surface carboxyls during ammoxidation, as the amides absorb infrared radiation in the region between 1630 and 1680 cm^{-1} [35, 51]. Neither nitriles nor amides were found in the CN200 spectrum. Therefore it is the presence or absence of air in the reactive atmosphere that must affect the type and amount of surface functionalities formed upon reaction with ammonia.

Ammoxidation causes a shift in pH_{PZC} (see Table 1), due to the incorporation of basic nitrogen functionalities. This increase in pH_{PZC} is similar to that attained by amination, despite the higher nitrogen uptake achieved by ammoxidation. This is partly due to the fact that ammoxidation favours the formation of amides, which are very weak bases, as mentioned earlier. Moreover, during the amination treatment, acidic oxygen groups are consumed in the reaction with ammonia, but this time the oxygen is not replaced and so there is an increase in the pH_{PZC} .

In order to study in more detail the surface chemistry of the ammoxidised carbons, temperature programmed desorption tests were carried out at a heating rate of $15\text{ }^{\circ}\text{C min}^{-1}$ up to $1000\text{ }^{\circ}\text{C}$, in $50\text{ cm}^3\text{ min}^{-1}$ of Ar flow rate. Figure 3 shows the corresponding profiles of the evolved NH_3 , HCN, CO and CO_2 . NH_3 emissions present two well defined maxima, at 210 and $680\text{ }^{\circ}\text{C}$. The low-temperature ammonia most probably comes from the decomposition of labile amines, while at higher temperatures it comes from the decomposition of amides and lactams [35, 46]. The HCN emissions are maxima at around $730\text{ }^{\circ}\text{C}$. These emissions arose very likely from the decomposition of nitriles, observed in the DRIFT spectra of the samples, but they may also have come from the decomposition of amides, lactams, and imides [35, 46]. The ammoxidised samples present CO emissions with maxima at $665\text{ }^{\circ}\text{C}$, outside the temperature range of the starting carbon, C. This low-temperature CO is emitted simultaneously to NH_3 , so it probably originates from the decomposition of amide-like functionalities [46]. From the CO_2 profiles, it can also be seen that the CO_2 -evolving groups (carboxyls, anhydrides and lactones) have reacted preferentially with ammonia. The bulk oxygen content does not diminish, despite the consumption of the acidic surface oxides. This is due to the simultaneous chemisorption of oxygen as CO-evolving groups, such as amides and lactams.

Figure 4 presents the N_2 and CO_2 adsorption isotherms of the ammoxidised samples at -196 and $0\text{ }^{\circ}\text{C}$, respectively. The C series represents the Type IV nitrogen isotherms, with the contributions of micro and mesoporosity. It can be observed that there is a reduction in the N_2 and CO_2 adsorbed volumes with increasing ammoxidation temperature. In addition, the CO_2 adsorption isotherm of CNO300 shows a more pronounced curvature which indicates the narrowing of the pore width. This point is corroborated by the calculated textural parameters presented in Table 2, where it can be

seen that the ammoxidation treatment reduced the porous volume of the starting carbon by narrowing the existing pores (see the decrease in L_{DR} and L_0). This reduction in pore volume, which becomes more pronounced with increasing temperature, may have been due to the surface groups introduced and to the deposition of decomposed products.

3.2. Characterisation of the R series

As can be seen from Table 1, the RNO series exhibits a lower nitrogen uptake than the corresponding CNO series. This is probably due to the lower oxygen content of the R carbon. It was previously mentioned that NH_3 reacted preferentially with the CO_2 -evolving groups, so that R has a significantly smaller amount of these groups (see Figure 5). Although R was a basic carbon to begin with, it can be seen from Table 1 that the ammoxidised samples present a slightly higher pH_{PZC} .

The textural characterisation of the RNO series (Figure 6) indicates that the porous system of the starting carbon, R, was virtually unaffected by the ammoxidation treatment. R is essentially microporous, with a Type I nitrogen adsorption isotherm (Figure 6a), and a mean pore width (L_{DR} and L_0), which is significantly narrower than that of carbon C (cf. Table 2).

3.3. Characterisation of the biomass series

The greatest nitrogen uptake was attained by the ammoxidation at 300 °C of the two commercial activated carbons. For this reason, 300 °C was the temperature selected for carrying out the ammoxidation of the char obtained from the olive stones. ONO300 displays a higher nitrogen and oxygen content than the starting char, O, indicating that the simultaneous chemisorption of nitrogen and oxygen took place during the ammoxidation treatment. From the shift observed in the pH_{PZC} of the ammoxidised sample, it can be deduced that the incorporation of basic groups prevailed.

Sample O aminated (treated with NH_3 in the absence of air) at 400 °C, exhibited a nitrogen content of 0.9 wt.% [52], which is significantly lower than the 2.6 wt.% attained by ammoxidation at 300 °C. Thus, the presence of air in the reactive atmosphere must promote the incorporation of nitrogen into the carbon matrix.

When the different carbons were compared, it was found that nitrogen incorporation by ammoxidation at 300 °C depends very much on the oxygen content of the starting carbon (see the linear trend in Figure 7).

The TPD test of ONO300 displayed NH_3 and HCN emissions (Figure 8) with maxima at 690 and 720 °C, respectively, that come from the decomposition of amides, lactams and nitriles. The shape of the NH_3 and HCN profiles match those of the CNO series (Figure 3), except for the absence of low-temperature NH_3 from the decomposition of amines.

The starting char, O, presents incipient microporosity, which is inaccessible to nitrogen molecules at -196 °C, due to diffusion limitations (note that W_0 is higher than V_p in Table 2). Samples O and ONO300 show narrower microporosity than carbons C and R, as can be seen from the curved shape of their CO_2 adsorption isotherms (Figure 9) and also from the mean narrow micropore width, L_0 . ONO300 exhibits a higher narrow micropore volume, W_0 , than the starting char, indicating that gasification occurred to some extent during the ammoxidation treatment. However, ONO300 still suffer from N_2 diffusion limitations at -196 °C.

3.4. Assessment of CO_2 capture capacity

Figure 10 summarises the CO_2 capture capacities of the studied samples at 25 and 100 °C and 1 bar. They were evaluated in a thermogravimetric analyser from the mass gain of the samples when they were exposed to $50 \text{ cm}^3 \text{ min}^{-1}$ of CO_2 . As expected, CO_2 capture capacity decreases with increasing temperature. From the figure it can be seen

that ammoxidation affects the CO₂ capture capacity of the studied samples in different ways. In the case of carbon C, ammoxidation reduced the porous volume of the starting carbon, which might explain the decrease in the CO₂ capture capacity of CNO200 and CNO300 at room temperature. However, at 100 °C, sample CNO300 exhibits a CO₂ capture capacity slightly higher than that of C. This may be due to its surface chemistry that plays a more active role when temperature increases. On the other hand, RNO200 and RNO300, whose texture was unaltered by ammoxidation, present a slight increase in CO₂ capture capacity, which may be due to the incorporation of nitrogen functionalities. Finally, ONO300 presents a significantly enhanced CO₂ capture capacity, due to the combined effect of a higher narrow micropore volume and a favourable surface chemistry.

An approximately linear relationship between the narrow micropore volume and the CO₂ capture capacity of the samples can be seen in Figure 11a. However, it should be noted that the regression coefficient is significantly better at 25 °C than at 100 °C. It seems that at 100 °C, other parameters, such as surface basicity, also influence the CO₂ capture performance of the adsorbents (see Figure 11b).

The CO₂ capture performance of ammoxidised samples is similar to that of the aminated samples (prepared by causing the carbons to react with dry ammonia in the absence of air) at low temperature. Sample O, aminated at 400 °C, presented a CO₂ capture capacity of 6.8 and 1.9 wt.% at 25 and 100 °C, respectively, slightly lower than that of ONO300 (6.9 and 2.0 wt.%) [52]. The C and R samples aminated at 200 °C, displayed a CO₂ capture capacity at 25 °C of 6.6 and 9.2 wt.%, respectively, very close to the 6.5 and 9.2 wt.% of CNO200 and RNO200. However, better results were obtained by amination at high temperature, due to the combined effect of a suitable surface

chemistry (predominance of pyridinic-like functionalities) and a higher porosity development [20, 52].

4. Conclusions

It was observed that the presence or absence of air in a reactive atmosphere (ammoxidation vs. amination) significantly affects the type and amount of surface functionalities formed upon reaction with ammonia. During ammoxidation, the formation of nitriles and amide-like functionalities is favoured and a greater amount of nitrogen is incorporated onto the carbon surface.

Ammoxidation implies the simultaneous chemisorption of nitrogen and oxygen. However, nitrogen uptake by ammoxidation at 300 °C was found to be proportional to the oxygen content of the starting carbon. Ammonia seems to react preferentially with the CO₂-evolving groups of the starting carbon, such as carboxyls, while the remaining oxygen mainly forms part of CO-evolving groups, such as amides or lactams.

Ammoxidation treatment enhances CO₂ capture to a similar extent than amination at low temperature, despite the differences in nitrogen uptake and the type of functionalities formed by the two modification methods.

CO₂ capture capacity is related to the narrow micropore volume of the samples, and this relationship is approximately linear at room temperature. However, above room temperature, the trend deviates from linearity due to the influence of other factors, such as surface basicity.

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References

- [1] International Energy Agency, Energy Technology Perspectives, IEA, 2008.
- [2] Q. Schiermeier, Putting the carbon back, *Nature* 442 (2006) 620-6.
- [3] M.T. Ho, G.W. Allinson, D.E. Wiley, Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption, *Ind. Eng. Chem. Res.* 47 (2008) 4883-90.
- [4] D. Ko, R. Siriwardane, L.T. Biegler, Optimization of pressure swing adsorption and fractionated vacuum pressure swing adsorption processes for CO₂ capture, *Ind. Eng. Chem. Res.* 44 (2005) 8084-94.
- [5] S.-H. Cho, J.-H Park, H.-T. Beum, S.-S. Han, J.-N. Kim, A 2-stage PSA process for the recovery of CO₂ from flue gas and its power consumption, in: S.-E. Park, J-S Chang, K-W Lee (Eds.), *Studies in Surface Science and Catalysis*, Elsevier; 2004, pp. 405-10.
- [6] W.-K. Choi, T.-I. Kwon, Y.-K. Yeo, H. Lee, H. Song, B.-K. Na, Optimal operation of the pressure swing adsorption (PSA) process for CO₂ recovery, *Korean. J. Chem. Eng.* 20 (2003) 617-23.
- [7] J.H. Park, H.T. Beum, J.N. Kim, S.H. Cho, Numerical analysis on the power consumption of the PSA process for recovering CO₂ from flue gas, *Ind. Eng. Chem. Res.* 41(2002) 4122-31.
- [8] Y. Takamura, S. Narita, J. Aoki, S. Hironaka, S. Uchida, Evaluation of dual-bed pressure swing adsorption for CO₂ recovery from boiler exhaust gas, *Sep. Purif. Technol.* 24 (2001) 519-28.
- [9] M. Ishibashi, H. Ota, N. Akutsu, S. Umeda, M. Tajika, J. Izumi, A. Yasutake, T. Kabata, Y. Kageyama, Technology for removing carbon dioxide from power plant flue gas by the physical adsorption method, *Energy Convers. Manage.* 37(1996) 929-33.

- [10] G.D. Pirngruber, S. Cassiano-Gaspar, S. Louret, A. Chaumonnot, B. Delfort, Amines immobilized on a solid support for postcombustion CO₂ capture-A preliminary analysis of the performance in a VSA or TSA process based on the adsorption isotherms and kinetic data, *Energy Procedia* 1 (2009) 1335-42.
- [11] J. Zhang, P.A. Webley, P. Xiao, Effect of process parameters on power requirements of vacuum swing adsorption technology for CO₂ capture from flue gas, *Energy Convers. Manage.* 49 (2008) 346-56.
- [12] A.L. Chaffee, G.P. Knowles, Z. Liang, J. Zhang, P. Xiao, P.A. Webley, CO₂ capture by adsorption: materials and process development, *Int. J. Greenh. Gas Con.* 1 (2007) 11-8.
- [13] N. Tlili, G. Grévillet, C. Vallières, Carbon dioxide capture and recovery by means of TSA and/or VSA, *Int. J. Greenh. Gas Con.* 3 (2009) 519-27.
- [14] J. Merel, M. Clausse, F. Meunier, Experimental investigation on CO₂ post-combustion capture by indirect thermal swing adsorption using 13X and 5A zeolites, *Ind. Eng. Chem. Res.* 47 (2008) 209-15.
- [15] C.A. Grande, R.P.P.L. Ribeiro, A.E. Rodrigues, CO₂ capture from NGCC power stations using electric swing adsorption (ESA), *Energ. Fuel.* 23 (2009) 2797–803.
- [16] C.A. Grande, A.E. Rodrigues, Electric swing adsorption for CO₂ removal from flue gases, *Int. J. Greenh. Gas Con.* 2 (2008) 194-202.
- [17] M. Radosz, X. Hu, K. Krutkramelis, Y. Shen, Flue-gas carbon capture on carbonaceous sorbents: toward a low-cost multifunctional carbon filter for "green" energy producers, *Ind. Eng. Chem. Res.* 47 (2008) 3783-94.
- [18] M.M. Maroto-Valer, Z. Lu, Y. Zhang, Z. Tang, Sorbents for CO₂ capture from high carbon fly ashes, *Waste. Manage.* 28 (2008) 2320-8.

- [19] M.M. Maroto-Valer, Z. Tang, Y. Zhang, CO₂ capture by activated and impregnated anthracites, *Fuel Process. Technol.* 86 (2005) 1487-502.
- [20] C. Pevida, M.G. Plaza, B. Arias, J. Fermoso, F. Rubiera, J.J. Pis, Surface modification of activated carbons for CO₂ capture, *Appl. Surf. Sci.* 254 (2008) 7165-72.
- [21] J. Przepiórski, M. Skrodzewicz, A.W. Morawski, High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption, *Appl. Surf. Sci.* 225 (2004) 235-42.
- [22] C. Pevida, C.E. Snape, T.C. Drage, Templated polymeric materials as adsorbents for the postcombustion capture of CO₂, *Energy Procedia* 1 (2009) 869-74.
- [23] C. Pevida, T.C. Drage, C.E. Snape, Silica-templated melamine-formaldehyde resin derived adsorbents for CO₂ capture, *Carbon* 46 (2008) 1464-74.
- [24] M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, CO₂ capture by adsorption with nitrogen enriched carbons, *Fuel* 86 (2007) 2204-12.
- [25] T.C. Drage, A. Arenillas, K.M. Smith, C. Pevida, S. Piippo, C.E. Snape, Preparation of carbon dioxide adsorbents from the chemical activation of urea-formaldehyde and melamine-formaldehyde resins, *Fuel* 86 (2007) 22-31.
- [26] M.-C. Huang, H. Teng,, Nitrogen-containing carbons from phenol-formaldehyde resins and their catalytic activity in NO reduction with NH₃, *Carbon* 41 (2003) 951-7.
- [27] T. Grzybek, J. Klinik, B. Samojeden, V. Suprun, H. Papp, Nitrogen-promoted active carbons as denox catalysts. 1. The influence of modification parameters on the structure and catalytic properties, *Catal. Today* 137 (2008) 228-34.
- [28] C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, Heterogeneous reduction of nitric oxide over synthetic coal chars, *Fuel* 84 (2005) 2275-79.

- [29] J.P. Boudou, M. Chehimi, E. Broniek, T. Siemieniowska, J. Bimer, Adsorption of H₂S or SO₂ on an activated carbon cloth modified by ammonia treatment, *Carbon* 41 (2003) 1999–2007.
- [30] J. Bimer, P.D. Salebut, S. Berleo_zecki, J.P. Boudou, E. Broniek, T. Siemieniowska, Modified active carbons from precursors enriched with nitrogen functions: sulfur removal capabilities, *Fuel* 77 (1998) 519–25.
- [31] S. Biniak, M.G. Pakulea, S. Szymanski, A. Swiatkowski, Effect of activated carbon surface oxygen- and/or nitrogen-containing groups on adsorption of Copper(II) ions from aqueous solution, *Langmuir* 15 (1999) 6117–22.
- [32] R. Pietrzak, K. Jurewicz, P. Nowicki, K. Babel, H. Wachowska, Microporous activated carbons from ammoxidised anthracite and their capacitance behaviours, *Fuel* 86 (2007) 1086–92.
- [33] K. Jurewicz, R. Pietrzak, P. Nowicki, H. Wachowska, Capacitance behaviour of brown coal based active carbon modified through chemical reaction with urea, *Electrochim. Acta* 53 (2008) 5469–75.
- [34] M.L. Gray, Y. Soong, K.J. Champagne, J. Baltrus, R.W. Stevens Jr, P. Toochinda, S.S.C. Chuang, CO₂ capture by amine-enriched fly ash carbon sorbents, *Sep. Purif. Technol.* 35 (2004) 31–6.
- [35] R.J.J. Jansen, H. van Bekkum, Amination and ammoxidation of activated carbons, *Carbon* 32 (1994) 1507–16.
- [36] R. Pietrzak, XPS study and physico-chemical properties of nitrogen-enriched microporous activated carbon from high volatile bituminous coal, *Fuel* 88(2009) 1871–7.
- [37] R. Pietrzak, H. Wachowska, P. Nowicki, K. Babel, Preparation of modified active carbon from brown coal by ammoxidation, *Fuel Process. Technol.* 88 (2007) 409–15.

- [38] C.L. Mangun, K.R. Benak, J. Economy, K.L. Foster, Surface chemistry, pore sizes and adsorption properties of activated carbon fibers and precursors treated with ammonia, *Carbon* 39 (2001) 1809-20.
- [39] P. Vinke, M. van der Eijk, M. Verbree, A.F. Voskamp, H. van Bekkum, Modification of the surfaces of a gas activated carbon and a chemically activated carbon with nitric acid, hypochlorite, and ammonia, *Carbon* 32 (1994) 675-86.
- [40] G.M.K. Abotsi, A.W. Scaroni, Reaction of carbons with ammonia: effects on the surface charge and molybdenum adsorption, *Carbon* 28 (1990) 79-84.
- [41] L. Wachowski, M. Hofman, Application of TG-DTG analysis in the study of the ammoxidised carbon materials, *J. Therm. Anal. Calorim.* 83 (2006) 379-83.
- [42] K. Jurewicz, K. Babel, R. Pietrzak, S. Delpeux, H. Wachowska, Capacitance properties of multi-walled carbon nanotubes modified by activation and ammoxidation, *Carbon* 44 (2006) 2368-75.
- [43] K. Jurewicz, K. Babel, A. Ziółkowski, H. Wachowska, Capacitance behaviour of the ammoxidised coal, *J. Phys. Chem. Solids* 65 (2004) 269-73.
- [44] K. Jurewicz, K. Babel, A. Ziółkowski, H. Wachowska, Ammoxidation of active carbons for improvement of supercapacitor characteristics, *Electrochim. Acta* 48 (2003) 1491-8.
- [45] K. Jurewicz, K. Babel, A. Ziółkowski, H. Wachowska, M. Kozłowski, Ammoxidation of brown coals for supercapacitors, *Fuel. Process. Technol.* 77-78 (2002) 191-8.
- [46] R.J.J. Jansen, H. van Bekkum, XPS of nitrogen-containing functional groups on activated carbon, *Carbon* 33 (1995) 1021-7.
- [47] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, *J. Colloid Interf. Sci.* 130 (1989) 157-64.

- [48] F. Stoeckli, L. Ballerini, Evolution of microporosity during activation of carbon, *Fuel* 70 (1991) 557-9.
- [49] P.E. Fanning, M.A. Vannice, A DRIFT study of the formation of surface groups on carbon by oxidation, *Carbon* 31 (1993) 721-30.
- [50] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Modification of the surface chemistry of activated carbons, *Carbon* 37 (1999) 1379-89.
- [51] B. Stohr, H.P. Boehm, R. Schlogl, Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate, *Carbon* 29 (1991) 707-20.
- [52] M.G. Plaza, C. Pevida, B. Arias, J. Feroso, M.D. Casal, C.F. Martín, F. Rubiera, J.J. Pis, Development of low-cost biomass-based adsorbents for postcombustion CO₂ capture, *Fuel* 88 (2009) 2442-7.

Tables

Table 1 Point of zero charge and chemical analysis of the samples

Sample	pH _{PZC}	Ultimate analysis (wt. %, daf)			
		C	H	N	O*
C	2.8	82.9	3.0	0.4	13.7
CNO200	6.4	79.2	2.5	5.0	13.3
CNO300	6.1	75.0	2.0	9.2	13.8
R*	9.5	94.7	0.4	0.7	3.9
RNO200**	10.1	95.7	0.1	1.0	2.9
RNO300**	9.7	94.4	0.2	1.7	3.4
O	8.7	93.0	2.2	0.3	4.5
ONO300	9.2	89.2	1.9	2.6	6.3

*Calculated by difference; **Sulfur content = 0.3 wt. %

Table 2 Textural parameters and helium density of the samples

Sample	d_{He} (g cm^{-3})	N_2 adsorption at $-196\text{ }^\circ\text{C}$				CO_2 adsorption at $0\text{ }^\circ\text{C}$	
		S_{BET}	V_{p}	V_{DR}	L_{DR}	W_0	L_0
		($\text{m}^2 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	($\text{cm}^3 \text{g}^{-1}$)	(nm)	($\text{cm}^3 \text{g}^{-1}$)	(nm)
C	1.51	1361	0.97	0.51	2.9	0.22	0.74
CNO200	1.56	1189	0.89	0.43	2.4	0.18	0.69
CNO300	1.61	964	0.70	0.35	2.4	0.16	0.63
R	2.14	942	0.41	0.37	1.1	0.26	0.63
RNO200	2.14	999	0.42	0.37	1.0	0.26	0.63
RNO300	2.13	950	0.40	0.37	1.0	0.26	0.62
O	1.65	43	0.03	—	—	0.17	0.59
ONO300	1.62	120	0.05	—	—	0.20	0.57

Figure 1. Combustion profile of carbon C in $50 \text{ cm}^3 \text{ min}^{-1}$ of air flow at a heating rate of $15 \text{ }^\circ\text{C min}^{-1}$.

Figure 2. DRIFT spectra of samples C, CNO300, CNO400 and CN200 [20].

Figure 3. NH_3 (a), HCN (b), CO (c) and CO_2 (d) evolution profiles of series CNO during heating at $15\text{ }^\circ\text{C min}^{-1}$ up to $1000\text{ }^\circ\text{C}$ in $50\text{ cm}^3\text{ min}^{-1}$ of Ar.

Figure 4. Adsorption isotherms of N_2 at $-196\text{ }^{\circ}\text{C}$ (a) and CO_2 at $0\text{ }^{\circ}\text{C}$ (b) for the CNO series.

Figure 5. CO₂ evolution profiles of RNO series during heating at 15 °C min⁻¹ up to 1000 °C in 50 cm³ min⁻¹ of Ar.

Figure 6. Adsorption isotherms of N₂ at -196 °C (a) and CO₂ at 0 °C (b) for the RNO series.

Figure 7. Relationship between the nitrogen uptake of the ammoxidised samples at 300 °C and the oxygen content of the starting carbon material.

Figure 8. NH_3 (a), HCN (b) evolution profiles of ONO300 during heating at $15\text{ }^\circ\text{C min}^{-1}$ up to $1000\text{ }^\circ\text{C}$ in $50\text{ cm}^3\text{ min}^{-1}$ of Ar.

Figure 9. CO₂ adsorption isotherms at 0 °C of samples O and ONO300.

Figure 10. CO₂ capture capacities of the studied samples evaluated in a thermogravimetric analyser at 1 bar in 50 cm³ min⁻¹ of CO₂ flow rate.

Figure 11. Relationship between the CO₂ capture capacity and: (a) the narrow micropore volume, W_0 , and (b) the point of zero charge, pH_{PZC} .