Adsorption (2011) 17: 595–602
DOI 10.1007/s10450-011-9333-7

Nitromethane-water competitive adsorption over modified activated carbon

L. Gonzalo-Chacón · A. Arcoya · I. Rodríguez-Ramos · E. Gallegos-Suárez · A. Guerrero-Ruiz

Received: 26 July 2010 / Accepted: 2 February 2011 / Published online: 18 February 2011

Abstract Modifications of texture and surface properties of a commercial activated carbon (Norit GF-40) were performed by several treatments in order to study their effects on the selective adsorption of nitromethane from nitromethane/water vapor mixtures. Characterisation of the samples by nitrogen adsorption and thermal analysis showed that HNO_3 treatments produce important losses of porosity and surface area, accompanied of an increase of oxygenated functional groups on the surface of carbon, which are progressively removed by heating at temperatures between 573 and 1073 K. All this leads to a drastic decrease of the adsorption capacity per gram of adsorbent with respect to the raw carbon, which offers, on the other hand, the best adsorptive performance. Oxidation by H_2O_2 does not practically affect its textural properties and introduces an important amount of oxygen functional groups at the surface, but changes in the adsorptive properties of carbon are insignificant. Sample oxidised by H_2O_2 and subsequently treated by diethylentriamine shows a decrease in adsorption capacity, without any relevant loss of surface area. The raw carbon treated at high temperature that exhibits the highest surface area and where surface functional groups are absent, showed the greatest adsorption capacity for nitromethane, being much more selective for nitromethane than for water, in nitromethane-water mixtures. Adsorption capacity values for nitromethane on the different samples are related to the extent of the surface area, while water vapour adsorption seems to depend on the population of functional groups at the surface, which may work as adsorption sites.

Keywords Nitromethane · Activated carbon · Selective adsorption · Adsorption capacity

L. Gonzalo-Chacón · A. Arcoya · I. Rodríguez-Ramos (✉)
Instituto de Catálisis y Petroleoquímica, CSIC,
Unidad Asociada Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, UNED-ICP (CSIC), C/ Marie Curie n° 2,
28049 Madrid, Spain
e-mail: irodriguez@icp.csic.es

E. Gallegos-Suárez · A. Guerrero-Ruiz
Dpto. Química Inorgánica y Técnica,
Facultad de Ciencias UNED,
Unidad Asociada Grupo de Diseño y Aplicación de Catalizadores Heterogéneos, UNED-ICP (CSIC), Senda del Rey n° 9,
28040 Madrid, Spain

1 Introduction

Nitromethane is a liquid (BP: 374 K) slightly viscous, colourless, highly polar, which is industrially used as a solvent in chemical reactions, extraction processes and cleaning treatments. As an intermediate in organic synthesis, it is widely used in the manufacture of pharmaceuticals, pesticides, explosives, fibres and coatings. It is also employed in the manufacture of some automotive fuels, as an additive to favour large accelerations (dragsters), and as a solvent for acrylate monomers, such as cyanoacrylate, more commonly known as "super glue" (Boyer and Kuo 2007).

Evaporation of nitromethane at 293 K quickly leads to toxic atmospheres. In those cases environmental purification can be accomplished by adsorption procedures. Adsorption is also appropriate to concentrate and to measure small amounts of nitromethane in air. This latter is achieved by passing nitromethane containing air streams through a suitable adsorbent bed, followed by further desorption of nitromethane for its subsequent identification and quantitative analysis. For an effective practice of this procedure, the effect of the atmosphere humidity has to be considered because water, as nitromethane, is a polar compound, with a very similar boiling point and, therefore, it might interfere

in the selective adsorption of that product. In this sense, nitromethane and water in nitromethane/water mixtures probably compete by the same kind of surface sites, the result of the overall adsorption process being perhaps different to that expected from adsorption of pure compounds. Although silica, modified silica and resins are used as adsorbents, from a practical point of view activated carbons seem to be the more satisfactory ones (Tomaszewski 2003; Gun'ko et al. 2006), because they show a high surface area and an adequate porosity. Moreover, the creation of functional groups at the surface of the carbon materials, otherwise hydrophobic, permits to react them with different kind of organic molecules (Mattson and Mark 1971). The nature and concentration of these groups may be modified by various post-activation treatment methods (Yin et al. 2007), the most important being oxidation.

Nitromethane (CH_3NO_2) is a tautomeric isomer of aci-nitromethane ($CH_2{=}N^+O(OH^-)$). In the gas phase nitromethane is more stable than aci-nitromethane by 14 kcal mol$\sim$ 1. When nitromethane is adsorbed on basic catalysts such as MgO, CaO and γ-alumina, it is adsorbed as the aci-anion ($CH_2NO_2^-$) at room temperature, whereas no aci-anion is formed on acidic zeolites such as H-ZSM-5 (Kheir and Haw 1994; Park et al. 2001). Therefore, adsorption of nitromethane is strongly dependent on the chemical nature of the adsorbent surface.

In this work a commercial activated carbon with high adsorption potential, because of its high surface area (1660 $m^2\ g^{-1}$) and wide porous distribution, was selected as raw adsorbent. Textural and surface properties of this material were modified by mean of different treatments, in order to study the effect of the activated carbon surface chemistry on its adsorption properties. In this sense, formation of oxygenated groups at the surface were induced by oxidation treatments with HNO_3 and H_2O_2 (García et al. 2004), in aqueous solutions, which in addition to functional groups may modify the texture of the material (Molina-Sabio et al. 1991). It is expected that oxidation of carbon by nitric acid and H_2O_2 mainly increases the number of surface oxygen groups (Figueiredo et al. 1999). On the other hand, formation of surface amide bonds by reactions of acidic oxygen groups with molecules with two amine groups, if one of these amine groups remains free, provides the carbon surface with functional groups of basic character (Longhi et al. 2006). Firstly this work is aimed at correlating the surface area and the presence of various groups at the surface of different activated carbons with their adsorption properties for nitromethane and water. In a subsequent stage the competitive adsorption of nitromethane-water mixtures was studied to evaluate how the different treatments of the carbon surface affect the selectivity of the nitromethane adsorption.

2 Experimental

2.1 Materials

Activated carbon (Norit GF-40, 1660 $m^2\ g^{-1}$ and 0.8–1 mm particle size) was used as raw material. From this carbon several modified samples were prepared, as follow: (1) sample CN-2.5M: 20 g of carbon was treated by 200 mL of HNO_3 2.5 M at reflux temperature for 6 h in a soxhlet apparatus; (2) sample CP: carbon was treated by H_2O_2 (33% v/v) for 48 h under stirring at room temperature; (3) sample CP-amina: a portion of the oxidised carbon material CP was suspended in toluene and an excess of diethylenetriamine with respect to the total amount of oxygen surface groups was added. This last suspension was refluxed for 5 h. Under these conditions anchoring of diethylentriamine molecules onto a functional group of carbon, through an amine group, may be expected, while the other amine groups can act as adsorption sites.

After treatments, the solids were successively filtered and washed to remove occluded ions and molecules and finally dried at 393 K over night. Different portions of the prepared samples were heated at 573 and 1073 K for 1 h, in order to reach either a partial or a complete removal of functional groups from the carbon surface. Labels of these samples include the treatment temperature.

2.2 Adsorbents characterisation

Specific surface area and pore size distribution of the carbon samples were deduced from nitrogen adsorption isotherms at 77 K, which were determined in a Micrometritic 2010 equipment, following the BET and BJH methods. Thermogravimetric (TG) analysis of the samples under helium atmosphere was made in order to quantify the content of oxygenated functional groups and their stability at different temperatures. Thermal analysis measurements were performed in a CI Electronics microbalance (MK2-MC5). The samples were heated from room temperature to 1073 K at 10 K min^{-1}. The chemical nature of these functional groups was evaluated by TPD-MS experiments under vacuum in a conventional volumetric apparatus connected to a SRS-200 C mass spectrometer. The sample was evacuated for 30 min at room temperature and then ramped to 1073 K at a 10 K min^{-1} rate.

2.3 Adsorption measurements

Adsorption measurements at room temperature were performed in a continuous flow system. The reactor consists of a glass tube in "U" (0.4 cm ID) where a fixed bed (2 cm length) of adsorbent is placed. Helium containing nitromethane and/or water was fed to the reactor at room

temperature (40 ml min^{-1} total flow). The nitromethane-helium mixture was prepared by bubbling a flow of helium (20 ml min^{-1}) through a saturator-condenser containing nitromethane at 279 K. The flow of nitromethane (13 μmol min^{-1}) was that corresponding to the vapour pressure of this compound in the helium stream at 279 K (10.95 mmHg), obtained from the Antoine's equation. This nitromethane-helium mixture was subsequently diluted with He up to 40 ml min^{-1}. Water was incorporated at room temperature by mean of an injection pump. Flow of water was in the range 0.2–0.3 μL min^{-1}, to match a relative humidity of 25–35% in He in the 40 ml min^{-1}. Under these conditions no condensation of liquids at the walls of apparatus was observed.

Exit gases of the reactor were periodically analysed by an on-line gas chromatograph provided with a thermal-conductivity detector and a Porapack N column. The gas concentration as a function of time, breakthrough curve, was registered. Saturation of the sample is assumed when the exit gas composition is similar to that of the corresponding feed. From the breakthrough curve the adsorption capacity is calculated.

3 Results and discussion

3.1 Characterisation of the samples

Nitrogen adsorption

Adsorption isotherms of N_2 for the raw activated carbon and functionalised samples are given in Fig. 1. The adsorption isotherms are of type I, characteristic of microporous materials although there are clear differences among the different samples. From isotherms, BET surface areas and pore volume distribution summarised in Table 1 were calculated. Analysis of these values permits to quantify the effect of the treatment on the texture of carbon. The "as supplied" carbon (sample C) evidences a wide distribution of pore diameters. Micropores being the major part, but with an important fraction of large micropores and mesopores, as only 77% of pore volume is filled with nitrogen bellow $P/P_0 = 0.1$. Isotherm of sample CN-2.5M denotes an important loss of porosity, affecting to both, micropores and mesopores. Thus, in comparison with sample C, specific surface area of carbon treated by HNO_3 considerably go down to around 600 m^2/g indicating that acid treatment destroys important part of the texture of carbon (Figueiredo et al. 1999; Stavropoulos et al. 2008).

In contrast, isotherm shape of samples treated with H_2O_2(CP) and that functionalised with ethylentriamine (CP-amine) is very similar to that of the parent carbon. Surface area of sample oxidised by H_2O_2 is nearby to that of the "parent" carbon and this also occurs for the pore volume distribution. These results agree with those reported by Sepúlveda-Escribano et al. (1998), who also found that H_2O_2 treatments promote an acid character of the carbon surfaces without significant modification of the textural properties.

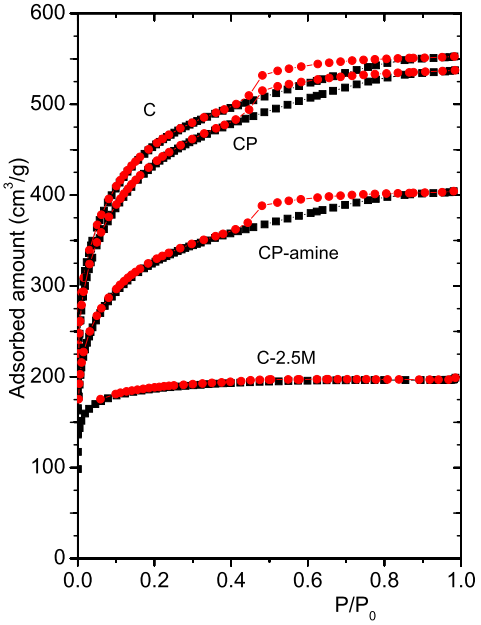

Fig. 1 Nitrogen adsorption isotherms at 77 K

Table 1 Textural characteristics of the different samples

Sample	S_{BET} (m^2 g^{-1})	$V_{0.95}$ (cm^3 g^{-1})	$V_{0.1}/V_{0.95}$	Ash (%)
C	1670	0.86	0.75	8.89
C-573	1660	0.85	0.74	–
C-1073	1710	0.88	0.77	–
CN-2.5M	524	0.29	0.85	1.24
CN-2.5M-573	572	0.30	0.90	–
CN-2.5M-1073	617	0.33	0.92	–
CP	1493	0.77	0.74	2.06
CP-573	1575	0.83	0.73	–
CP-1073	1378	0.69	0.77	–
CP-amine	1190	0.62	0.99	1.68

The pore size distributions calculated from the desorption branch of the N_2 isotherms are given in Fig. 2. These latter match with the analysis of the N_2 isotherms and pore volume distribution (Table 1) performed above. Thus, C, CP and CP-amine samples show bimodal pore size distribution centred at 0.7–0.8 and 3 nm. However, practically total destruction of the porous structure is observed for C-2.5M sample. The thermal treatment at 573 and 1073 K of the samples produces small changes in textural properties as can be seen in

Table 1. The N_2 isotherms of treated samples are not plotted in Fig. 1 for the sake of clarity because they overlap each other.

Thermal analysis measurements

Thermograms of the samples under He atmosphere, depicted in Fig. 3, show the evolution of the functional groups from the surface of the different samples. If we assume that this weight loss only corresponds to decomposition of functional groups, it can be estimated that sample C has the lowest quantity of surface groups, because it exhibits a weight loss bellow 873 K of only 5 wt%. For the rest of samples the registered weight losses are higher and they follow the order C < CP < CP-amine < CN-2.5 M, suggesting a parallel increase in the number of functional groups at the surface by effect of treatments which, on the other hand, are removed by heating. It is clear that, in comparison with CP, the weight loss of CP-amine in the range 473–573 K corresponds to the transformation of surface anchored carboxylate species to amide ones (Silva et al. 2004).

Complementary information about samples C, CP and CP-amine can be attained from the TPD profiles in Fig. 4. For C and CP samples, signals $m/z = 44$ and $m/z = 28$ corresponding to CO_2 and CO, respectively, were registered in the desorption products. The high intensity of CO signal in sample C indicates that the presence of phenolic, carbonylic, eter and quinone groups is majority. For sample CP the am-

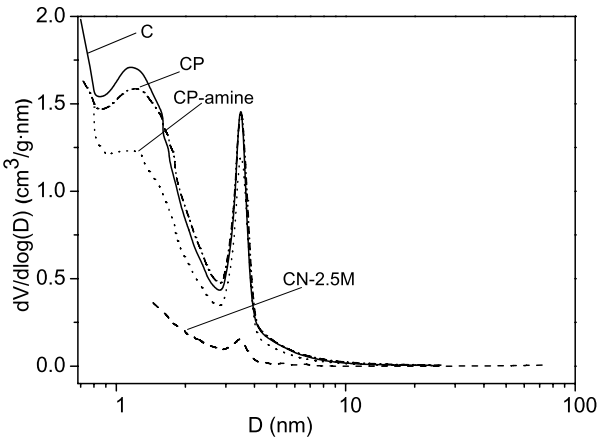

Fig. 2 Pore-size distribution by BJH method

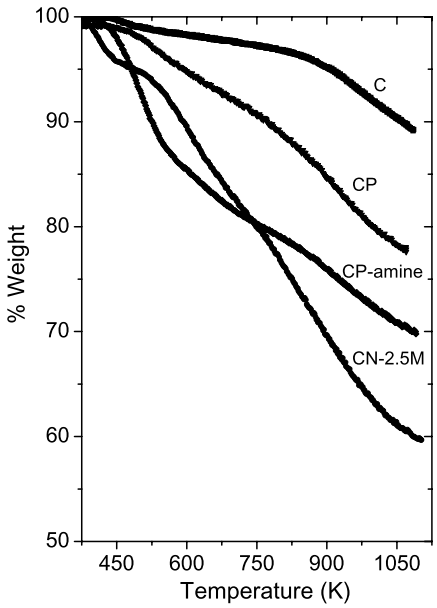

Fig. 3 Thermogravimetric analysis in helium flow

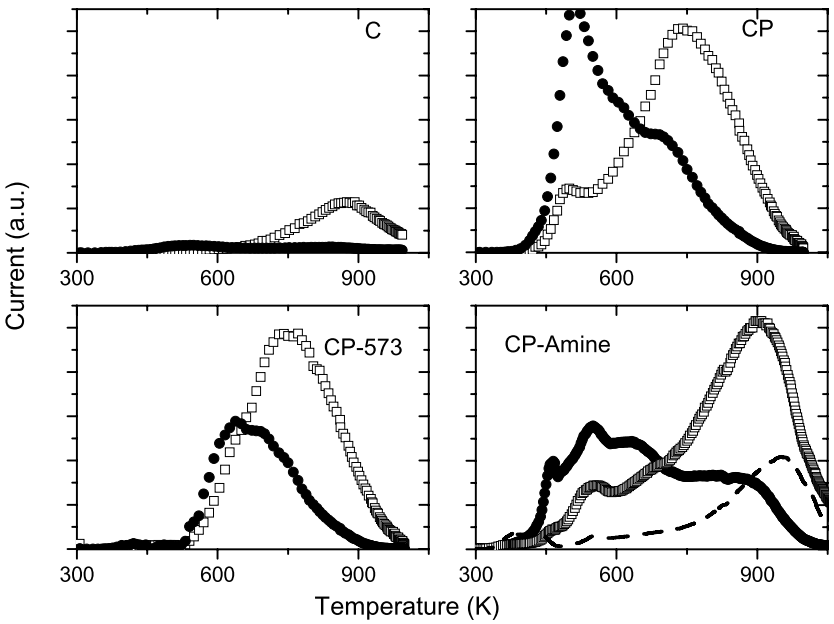

Fig. 4 Temperature programmed desorption profiles corresponding to samples C, CP, CP-573 and CP-amine (●) $m/z = 44$, (□) $m/z = 28$ and (—) $m/z = 27$

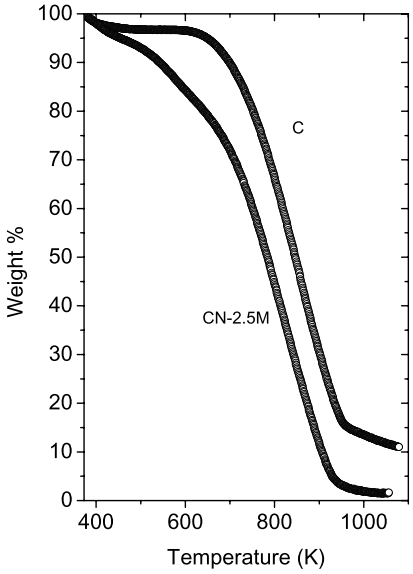

Fig. 5 Thermogravimetric analysis in air flow

plified intensity in the CO and CO_2 profiles, suggests an increase in all the possible functional groups at the surface, including anhydride, lactonic and carboxylic (Figueiredo et al. 1999; Sepúlveda-Escribano et al. 1998) which are formed by effect of H_2O_2 treatment. In a similar way, results of TPD corresponding to CN-2.5M sample (no included) evidence decomposition of carboxyl and phenol groups that were formed by oxidation with HNO_3.

For CP-amine sample an important decrease in the intensity of the $m/z = 44$ signal is observed (Fig. 4). This fact indicates that carboxyl groups are involved in the anchoring of the amine molecules. Furthermore, the signal $m/z = 27$ was detected at high temperatures which seems to point to chemical transformation of anchored amine. The signal $m/z = 27$ has previously been ascribed to desorption of HCN species from nitrogen-treated carbon materials (Boudou et al. 2006).

Thermal treatment of C, CP and CP-amine samples at 1073 K eliminates completely the surface functional groups as was confirmed by TPD experiments where no gases evolution was observed. However, treatment at 573 K mainly reduces the $m/z = 44$ signal in the range of temperature attributed to carboxyl groups (Figueiredo et al. 1999) as shown in Fig. 4 for sample CP-573K.

Thermal stability in air

Additional TG measurements in air render information about the reactivity of the samples in the combustion reaction, as well as of their inorganic material content. Thermograms of samples C and CN-2.5M, given in Fig. 5 as an example, show that oxidation temperature and the subsequent ignition of the latter (∼373 K) is lower than that of the original carbon (623 K) being the behaviour of the other treated samples similar to that of CN-2.5M. On the other hand, quantitative results of TG, summarised in Table 1, show that the percentage of ashes for the treated samples is much lower than that obtained for the parent sample. This indicates that part of the inorganic material in the commercial carbon is removed during the treatments.

Since activated carbons are usually regenerated in air at temperature around 573 K to assure complete desorption of chemisorbed molecules, thermal stability of the samples in air was checked as a previous stage to the adsorption studies. For this purpose the samples were submitted to successive heating-cooling cycles, from room temperature to 573 K and then down to room temperature. After 11 cycles, the weight losses registered for samples C and CP were very similar, only 4 and 6 wt%, respectively. In contrast, samples oxidised with H_2O_2 and subsequently functionalised with diethylentriamine evidenced a weight loss higher than 15% which, moreover, occurs progressively in the early cycles. These results, in agreement with the TG studies, may be attributed to the decomposition of functional groups at the surface and evidence the better stability of the oxygen containing group sample.

Table 2 Nitromethane adsorption capacity at 298 K of the different carbon samples

Sample	AC_W ($g\,g^{-1}$)	AC_S ($g\,m^{-2}$)
C-573	0.575	0.346
C-1073	0.589	0.344
CN-2.5M-573	0.245	0.428
CN-2.5M-1073	0.297	0.481
CP-573	0.591	0.375
CP-1073	0.588	0.427
CP-amine-383	0.415	0.349
CP-amine-573	0.412	0.346

AC_W, adsorption capacity per mass unit

AC_S, adsorption capacity per surface area unit

3.2 Adsorption measurements

Nitromethane adsorption

Results of efficiency of nitromethane adsorption at room temperature are given in Table 2 as adsorption capacity, which is measured when saturation of the solid is achieved. This latter occurs when concentration of nitromethane in the exit gas is similar to that in the feed. Adsorption capacity, relative to the mass of adsorbent (AC_W) is defined as grams of nitromethane adsorbed per gram of carbon. On the other hand, since the samples exhibit very different specific surface areas, adsorption capacity per unit of surface area

(AC_S) is also included. The accuracy of these measurements was estimated to be ±5%.

Activated carbons exhibit two types of adsorption sites, basal and edge carbon atoms, at graphene layers. The edge sites along the imperfections and defects in the graphene planes are the most reactive sites owing to their high densities of unpaired electrons. Therefore oxygen functionalities are located on these highly reactive sites. The thermal treatment of carbon material results in the decomposition of oxygen groups and free active sites at the edges of the graphene layers. The π-electron density of the carbon basal planes is also considered to be chemically active (Bandosz 2009).

Adsorption capacity for nitromethane of samples heated at 573 and 1073 K was measured in order to determine the effect of the different kind of functional groups at the surface, which are decomposed below those temperatures. Heating treatments were done at 573 K, since regeneration treatment of adsorbents is carried out at this temperature, keeping most of the functional groups at the surface, and at 1073 K to obtain information about adsorptive capacity of the samples without any functional groups, because these are almost entirely removed at that temperature.

Results in Table 2 show that ability of the C-573 carbon to adsorb nitromethane is very high, as expected, and highlights that the treatments do not improve significantly the adsorptive capacity of this carbon, but they rather diminish it in the case of CN-2.5M series. However, when comparing the results of adsorption per square meter (last column in Table 2), it is observed an increase in the specific adsorption capacity for samples with lower surface area (CN-2.5M-573 and CN-2.5M-1073). Furthermore, it is noticeable that for each family of samples, the temperature of treatment affect to the values of AC_S, either in those treated with HNO_3 or in that oxidised with H_2O_2, increasing these with the increasing temperature. However, in general, adsorption capacity is more sensitive to the textural changes caused by the treatments than to the number and nature of the functional groups generated at the surface. On the other hand, functionalisation with diethylentriamine (sample CP-amine-573) slightly diminishes the adsorption capacity, both AC_W and AC_S, of sample CP-573. But, differences between the values corresponding to the samples CP-amine-383 and CP-amine-573 are not observed, in spite of the fact that amine was decomposed on this latter, as indicated by the TG profiles above discussed. These unexpected results suggest that basic amine and its decomposition products on the carbon surface do not affect the number of sites available for nitromethane adsorption. All these findings, together with those of thermal stability of the adsorbent, induce to rule out the oxidation treatments as well as the functionalisation of carbon with diethylentriamine, in order to improve the adsorption capacity of the sample C-573. Whereby, the raw carbon heated at 573 and 1073 K were selected to study the adsorption of water and the competitive adsorption for nitromethane-water mixtures.

Table 3 Water adsorption capacity at 298 K of carbon samples heated at 573 and 1073 K

Sample	F_{H_2O} (μL min^{-1})	AC_W (g g^{-1})
C-573	0.2	0.080
C-1073	0.2	0.032
C-573	0.3	0.079
C-1073	0.3	0.032

Water adsorption

Water adsorption was studied over two samples of C carbon previously heated at 573 K and 1073 K, respectively, under helium atmosphere. These temperatures were selected because, as it is said above, 573 K is the temperature for regeneration of adsorbents and 1073 K is the temperature that assures a complete removal of functional groups from the surface. The adsorption capacity values obtained for water flows of 0.2 and 0.3 μL min^{-1} over both samples are summarised in Table 3. As expected, differences in the adsorption capacity values for the two water flows used were not observed we work under equilibrium conditions. However, it seems that the capacity for water adsorption decreases with the increasing pretreatment temperature. This means that the functional groups of carbon surface behave as specific adsorption sites for water, at least in part, in contrast with that observed for nitromethane adsorption (Table 2).

Nitromethane-water competitive adsorption

Comparison of results in Tables 2 and 3 evidences that capacity of carbon for nitromethane adsorption is much higher than for water. Since both molecules exhibit a high polar character, it might occur that for nitromethane/water mixtures, both molecules compete by the same adsorption sites at the surface. On the other hand, adsorption of these molecules on sites of different nature can not be ruled out. In order to delve deeper into these aspects, adsorption of nitromethane-water mixtures was studied. Given that only thermally stable activated carbons can be considered for real applications, and taking into account that regeneration of the adsorbent need high temperature desorption treatments, we have performed the selectivity studies on the original C activated carbon pretreated at 573 K and 1073 K. The C-573 sample contains oxygen surface groups (anhydride and lactonic) while the surface of the C-1073 sample is completely free of surface groups. Figure 6 displays typical breakthrough curves corresponding to the competitive

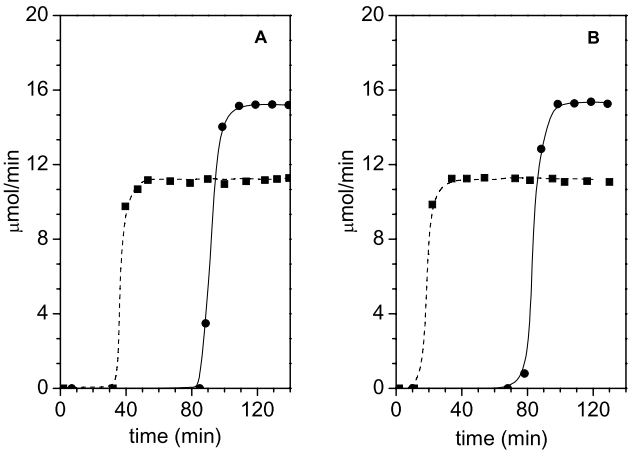

Fig. 6 Breakthrough curves of competitive nitromethane-water adsorption over C-573 (**A**) and C-1073 (**B**) samples. (—●—) nitromethane; (- -■ - -) water

nitromethane-water adsorption on C-573 and C-1073 samples. From the concentration profiles and taking into account the concentration of both adsorbates in the feed, adsorption capacity (AC_W) for each one was calculated and summarised in Table 4. As it can be seen, similar results are obtained for 0.2 µl min^{-1} and 0.3 µl min^{-1} of water, being AC_W for nitromethane much higher than AC_W for water. This latter is, on the other hand, lower than the value obtained for pure water adsorption (Table 3), thus proving the competitive effect of nitrometane, which moreover is favourable for this latter from a practical point of view. This behaviour is in agreement with the polar character of both compounds, i.e., nitromethane, polarity = 3.46 D, (Cataliotti el al. 1992) preferentially adsorbs on carbon surface sites, thus hindering the adsorption of water, polarity = 1.85 D. These results also suggest that an important part of surface sites of carbon are not active for water adsorption. On the other hand, when comparing the results obtained for C-573 and C-1073, it is noted that adsorption of water is much more sensitive to the disappearance of functional groups of carbon than adsorption of nitromethane. This finding can be due to the strong capability of water to interact by hydrogen bonding, which results in a strong interaction with surface groups. By the contrary nitromethane, in spite of its high polarity, has weak ability to interact by hydrogen bonding (Cerdeiriña et al. 2001) although nitromethane adsorption by dipole-π interactions on basal planes of carbon is possible. Thus, the ability of nitromethane to interact with basal planes, besides with the carbon atoms at edges of the graphitic layers, enhances the adsorption capacity of the adsorbent whose surface area is fully used.

Adsorption desorption cycles

On sample C-573 successive cycles of adsorption-desorption of a nitromethane-water mixture were carried out, in order to evaluate its stability. In these cycles adsorption was performed at room temperature, while desorption was achieved under helium stream at 573 K. Results in Table 5 show that adsorption capacity of C-573 for nitromethane keeps up, at least for the four successive cycles performed, thus confirming the viability of this material to be used as reusable adsorbent of nitromethane from nitromethane-water mixtures.

Table 4 Nitromethane-water competitive adsorption at 298 K over carbon pretreated at 573 and 1073 K

Sample	Adsorbate	F_{H2O} (µL min^{-1})	AC_W (g g^{-1})
C-573	Nitromethane	0.2	0.572
	H_2O		0.041
C-1073	Nitromethane		0.558
	H_2O		0.026
C-573	Nitromethane	0.3	0.542
	H_2O		0.049
C-1073	Nitromethane		0.554
	H_2O		0.017

Table 5 Adsorption capacity at 298 K of sample C-573 for nitromethane-water mixtures in successive adsorption-desorption cycles at 0.2 µL min^{-1} flow of water

Cycle	Adsorbate	AC_W (g g^{-1})
1	Nitromethane	0.582
	H_2O	0.052
2	Nitromethane	0.565
	H_2O	0.042
3	Nitromethane	0.565
	H_2O	0.036
4	Nitromethane	0.572
	H_2O	0.042

4 Conclusions

From a commercial activated carbon different adsorbents were prepared by treating this with HNO_3, H_2O_2 and diethylentriamine, followed by heating at 573 and 1073 K. Treatment by HNO_3 2.5 M destroys the porosity of carbon, with considerable decrease in surface area that drastically diminishes the nitromethane adsorption capacity per gram of adsorbent. However, the CN2.5M-573 and CN2.5M-1073 samples present the highest adsorption capacity per surface unit of adsorbent. The presence or not of functional groups on the surface of these two samples excludes the nitromethane adsorption by specific interaction with the oxygen surface groups. Oxidation by H_2O_2 solution does not practically affect either textural or adsorptive properties of

carbon. Subsequent reaction of this latter with diethylentriamine slightly diminishes its adsorption capacity, which means that functionalisation with basic groups does not significantly improve the nitromethane adsorption. The raw carbon exhibits the highest adsorption capacity for both nitromethane, being much more selective for nitromethane than for water in nitromethane-water mixtures. Comparison of adsorption capacity values for nitromethame-water mixtures with those for pure compounds suggests that nitromethane and water compete in part for the same type of sites, but the activated carbon surface exhibits a higher population of selective sites for nitromethane adsorption than for water. Therefore, adsorption capacity for nitromethane is not affected by the presence of water, while the adsorption of this latter is diminished in competitive experiments.

Acknowledgement Authors acknowledge the MICINN Spain (Projects CTQ-2008-06839-C03-01 and 03-PPQ and EUI2008-00185 and -00205) for the financial support.

References

Bandosz, T.S.: Surface chemistry of carbon materials. In: Serp, P., Figueiredo, J.L. (eds.) Carbon Materials for Catalysis, pp. 45–92. Wiley, New Jersey (2009)

Boudou, J.P., Parent, P., Suárez-García, F., Villar-Rodil, S., Martínez-Alonso, A., Tascón, J.M.D.: Nitrogen in aramid-based activated carbon fibers by TPD, XPS and XANES. Carbon **44**, 2452–2462 (2006)

Boyer, E., Kuo, K.K.: Modeling of nitromethane flame structure and burning behaviour. Proc. Combust. Inst. **31**, 2045–2053 (2007)

Cerdeiriña, C.A., Tovar, C.A., González, D., Carballo, E., Romani, L.: Thermodynamics of the nitromethane + 1-butanol system near the upper critical point. Fluid Phase Equilib. **179**, 101–115 (2001)

Figueiredo, J.L., Pereira, M.F.R., Freitas, M.M.A., Órfao, J.J.M.: Modification of the surface chemistry of activated carbons. Carbon **37**, 1379–1389 (1999)

García, T., Murillo, R., Cazorla-Amorós, D., Mastral, A.M., Linares-Solano, A.: Role of the activated carbon surface chemistry in the adsorption of phenanthrene. Carbon **42**, 1683–1689 (2004)

Gun'ko, V., Leboda, R., Turov, V., Zarko, V., Chuico, A.: Oxide, carbon, and carbon/mineral adsorbents for toxic, explosive, and narcotic compounds-synthesis, properties, and applications. In: Blitz, J.P., Gun'ko, V.M. (eds.) Surface Chemistry in Biomedical and Environmental Science, pp. 91–102. Springer, Berlin (2006)

Kheir, A.A., Haw, J.F.: Chemisorption of aci-nitromethane on strongly basic catalysts—an nmr probe of solid basicity. J. Am. Chem. Soc. **116**, 817–818 (1994)

Longhi, M., Bertacche, V., Bianchi, C.L., Fomaro, L.: Preparation and characterization of aminated carbon from a single-step reaction. Chem. Mater. **18**(17), 4130–4136 (2006)

Mattson, J.S., Mark, H.M. Jr.: Activated Carbon. Dekker, New York (1971)

Molina-Sabio, M., Munecas-Vidal, M.A., Rodriguez-Reinoso, F.: Modification in porous texture and oxygen-surface groups of activated carbons by oxidation. Stud. Surf. Sci. Catal. **62**, 329–339 (1991)

Park, S.K., Choo, H., Kevan, L.: Nitromethane decomposition over Cu-ZSM-5 and Co-ZSM-5. Phys. Chem. Chem. Phys. **3**, 3247–3253 (2001)

Sepúlveda-Escribano, A., Coloma, F., Rodriguez-Reinoso, F.: Platinum catalysts supported on carbon blacks with different surface chemical properties. Appl. Catal. A, Gen. **173**, 247–257 (1998)

Silva, A.R., Martins, M., Madalena, M., Freitas, A., Figueiredo, J.L., de Castro, B.: Anchoring of copper (II) acetylacetonate onto an activated carbon functionalised with a triamine. Eur. J. Inorg. Chem. **2004**(10), 2027–2035 (2004)

Stavropoulos, G.G., Samaras, P., Sakellaropoulos, G.P.: J. Hazard. Mater. **151**, 414–421 (2008)

Tomaszewski, W., Gun'ko, V.M., Skubiszewska-Zieba, J., Leboda, R.: Structural characteristics of modified activated carbons and adsorption of explosives. J. Colloid Interface Sci. **266**, 388–402 (2003)

Yin, C.Y., Aroua, M.K., Daud, W.M.A.W.: Review of modifications of activated carbons for enhancing contaminant uptakes from aqueous Solutions. Sep. Purif. Technol. **53**, 403–415 (2007)