**Tailoring the surface chemistry of H3PO4 activated carbons**

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**Abstract**

Activated carbons (ACs) are inexpensive and versatile porous materials useful in a large range of applications such as adsorbents for gas separation, gas storage and water treatment, catalysts, catalyst supports, electrocatalysts, supercapacitors, etc. Besides the aspects related to pore morphology, the surface chemistry also plays fundamental role for ACs performance. In this context, the present work concerns a comprehensive study about the production and characterization of ACs with different surface chemistry. To that, a biomass-based commercial sample of hierarchical micro-mesoporous H3PO4 activated carbon (WV) was taken as starting material. ACs with increased acidity and oxygen content were obtained by means of treatments with a HNO3 solution. On the other hand, an AC with reduced acidity and oxygen content was prepared by heat treating WV under inert atmosphere. Finally, N-doped ACs were prepared by heat treating WV under a NH3-atmosphere up to different temperatures. The obtained materials had their chemical composition carefully evaluated through techniques such as XPS, TPD-MS, elemental analyses and Boehm titration, besides measurements of point of zero charge. The performed work provided valuable understanding on the possibility of fine-tuning the surface chemistry of ACs, so that materials with appropriate properties for a given application can be designed.

*Keywords:* activated carbons; adsorption; surface chemistry; ammonization; surface functionalities

**1. Introduction**

Activated carbons (ACs) are inexpensive and versatile materials that present pronounced porosity and, therefore, large specific surface area. They are very interesting for applications such as adsorbents for gas separation, gas storage and water treatment, catalysts, catalyst supports, electrocatalysts, supercapacitors, etc.1 Besides the aspects related to pore morphology, the surface chemistry also plays fundamental role in the ACs performance. In this context, the present work concerns a comprehensive study on the production and characterization of ACs with different surface chemical composition, so that they can be tailored to have appropriate properties for a given application.

**2. Experimental**

A biomass-based commercial granular micro-mesoporous AC chemically activated with H3PO4 (WV) was taken as starting material. It had its surface modified by means of:

- heat treatment up to 800 oC (2 h; 5 oC min-1) under a N2 atmosphere (N2, 100 mL min-1) (complementary carbonization);

- stirring for 1h with a refluxing solution (∼75 oC) of HNO3 1.0 mol L-1, followed by washing with distilled water until pH of ∼6;

- heat treatment under a NH3 atmosphere (100 mL min-1) up to 400 (4 hours) and 800 oC (1 hour) (5 °C min-1) (ammonization treatment).

The obtained samples were labelled WVC, WVAc, WVN400 and WVN800, respectively. WV and the modified ACs were characterized through techniques such as XPS, TPD-MS, elemental analyses, and Boehm titration, besides measurements of point of zero charge (pzc).

**3. Results and discussions**

*3.1. Characterization of the unmodified AC WV*

The data of chemical composition obtained through XPS (Table 1) shows that the pristine AC WV has a relatively high O content (13.6 wt%) and a quite low N content (0.3 wt%).

Table 1. Chemical composition determined by XPS.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **AC** | **wt%** | | | | | |
| **C** | **O** | **N** | **P** | **Na** | **Si** |
| WV | 83.0 | 13.6 | 0.3 | 1.3 | 1.3 | 0.3 |
| WVC | 86.2 | 8.4 | 0.8 | 2.4 | 1.6 | 0.6 |
| WVAc | 80.1 | 17.0 | 1.7 | 0.8 | - | 0.4 |
| WVN400 | 83.2 | 10.7 | 3.1 | 1.3 | 1.2 | 0.5 |
| WVN800 | 74.9 | 7.2 | 5.1 | 1.2 | 1.0 | 0.6 |

Table 2. Data of pzc and titration.

|  |  |  |  |
| --- | --- | --- | --- |
| **AC** | **pzc** | **Titration (mmol g-1)** | |
| **Acidic** | **Basic** |
| WV | 4.7 | 1.11 | 0.45 |
| WVC | 6.2 | 0.70 | 0.28 |
| WVAc | 1.8 | 1.94 | 0.00 |
| WVN400 | 6.8 | 1.09 | 0.38 |
| WVN800 | 6.2 | 0.33 | 0.75 |

The TPD analysis of WV gave rise to intense emissions (Figure 1). The TPD-CO2 profile (m/z = 44) was deconvoluted into five peaks (Figure 2a). The peaks were assigned as follows. CO2-1 and CO2-2: stronger and weaker carboxylic acids, respectively; CO2-3: carboxylic anhydrides; CO2-4 and CO2-5: lactones. In turn, the TPD-CO profile was deconvoluted into seven peaks (Figure 2b). CO-1 and CO-2: correspond to the fragmentation of the CO2 generated from the decomposition of carboxylic acids; CO-3: carboxylic anhydrides, whose decomposition releases both CO2 and CO; CO-4 and CO-5: C─O─H/C in functions such as phenols and ethers; CO-6 and CO-7: carbonyl functions such as ketones, quinone and pyrone.2,3



Figure 1. TPD profiles of WV for distinct m/z ratios.

 

Figure 2. (a) CO2 and (b) CO-TPD profiles of WV and respective deconvoluted peaks.

In accordance with results of TPD, WV presented an acidic pzc of 4.7. Furthermore, a high content of acidic groups was determined by titration, 1.11 mmol g-1, while the content of basic groups was moderate, 0.45 mmol g-1 (Table 2).

*3.2. Complimentary Carbonization*

As expected, complementary carbonization was followed by considerable weight loss, 12.4 wt%. Taking into account that a TPD analysis is nothing more than a carbonization in small scale, thus the reasons for this weight loss can be identified taking into account the TPD profiles of WV (Figures 1 and 2). In this sense, most of the verified weight loss can be attributed to the decomposition of acidic oxygenated groups, as evidenced by the intense release of CO2 and CO below 800 oC. Furthermore, the release of H2O, H2 and CH4 (m/z = 18, 2 and 16, respectively; Figure 1) has minor contributions. The release of H2O in the range of ~200-320 oC is attributed to the occurrence of condensation reactions involving carboxylic acids and phenols. The release of H2 is intense above around 650 oC due to the condensation of aromatic rings. Finally, The shallow release of CH4 in the range of ~550-900 oC is due to decomposition of aliphatic carbons.

In accordance with the discussions above, WVC presented a lower O content (Table 2) than WV, besides lower acidic and basic contents determined by titration (Table 2). Outstandingly, WVC presented a pzc near the neutrality, 6.2.

*3.3. Treatment with HNO3*

Firstly, it is notable that the treatment of WV with HNO3 pronouncedly increased the acid content, from 1.11 to 1.94 mmol g-1, while the content of basic groups became zero (Table 2). Accordingly, TPD analyses showed that the release of CO2 due to the decomposition of acidic groups increased, while the CO peaks relative to the decomposition of carbonyl groups vanished. As result of these changes, the O content increased from 13.6 to 17 wt% (Table 1) and pzc decreased from 4.7 to 1.8. The presence of some nitrogen (1.7 wt%) in WVAc is due to the formation of NO2 groups, as evidenced by the high resolution XPS N1s spectrum (Figure 3a).

*3.4. Ammonization treatments*

The XPS data show that, as expected, ammonization up to 400 oC led to the insertion of nitrogenated groups, the N content reaching 3.1 wt% (Table 1). Figure 3b shows the high resolution XPS N1s spectrum of the resulting sample (WVN400), which present an envelope that extend from 397 to 402 eV. This envelope was deconvoluted into four peaks. N-X was attributed mainly to moieties containing sp3 nitrogen like amines, amides, lactams and imides (N-X peak). Amides can be formed through the reaction of NH3 with acidic oxygenated functional groups at relatively low temperatures (Figure 4), while condensation reactions lead to the formation of imides and lactams (Figure 5). N-6 and N-5 are attributed to pyridine and pyrrol species, respectively. These species could result from reactions such as those displayed in Figure 6. Finally, the less intense N-Q peak is assigned to quaternary (also called graphitic) nitrogens.4

In accordance with the reactions proposed in Figures 4-6, WVN400 has a lower O content than the pristine AC WV (Table 1) and pzc neared the neutrality (Table 2).



Figure 3. High resolution XPS N1s spectra.



Figure 4. Examples of reactions that give rise to amides during ammonization.



Figure 5. Examples of condensation reactions.



Figure 6. Examples of reactions that lead to the formation of pyrol and pyridine.

Comparing to the treatment up to 400 oC, ammonization up to 800 oC led to a higher insertion of nitrogenated groups, the N content reaching 5.1 wt% (Table 1). This result shows that additional nitrogenation takes place above 400 oC. Supposedly, -NH2 replaces oxygen in phenol/ether groups and the resulting amines participate in a series of additional reactions that increases the content of quartenary, pyrolic and pirydinic moieties, mainly the latter one (Figure 3c). At this point, it is valid to highlight that the N-X peak was shallow in the XPS N1s spectrum of WVN800, which evidences that the groups containing sp3 nitrogen were almost completely converted or decomposed up to 800 oC.

Ammonization up to 800 oC promoted a strong decrease of the acidic content if compared to the treatment up to 400 oC, from 1.11 to 0.33 mmol g-1, while the basic content increased from 0.45 to 0.75 mmol g-1 (Table 2). The increase of basicity can be attributed mainly to the appearing of pyridine groups. In spite of the higher content of basic groups relative, the pzc of WVN800 was near the neutrality, 6.2.

**4. Conclusions**

ACs with different surface chemistry were produced from a commercial AC. A material with increased acidity and oxygen content was obtained through treatment with a HNO3 solution. On the other hand, an AC with lower oxygen content and pzc near neutrality was prepared by heat treating the pristine AC under inert atmosphere at high temperature. Finally, N-doped ACs were obtained by conducing the heat treatment under a NH3-atmosphere up to different temperatures. The performed work provided valuable understanding on the possibility of fine-tuning the surface chemistry of ACs, so that materials with appropriate properties for a given application can be designed.

**Acknowledgements**

The authors thank FINEP (contractual instrument 01.23.0594.00), FAPDF (grant numbers 193.000719/2016 and 0193.001613/2017) and CAPES (Finance Code 001) by financial support.

**References**

[1] Marsh H, Rodríguez-Reinoso F. Activated Carbon, Elsevier, 2006.

[2] Ishii T, Ozaki J-I. Understanding the chemical structure of carbon edge sites by using deuterium-labeled temperature-programmed desorption technique. Carbon 2020; 161: 343-9.

[3] Düngen P, Schlögl R, Heumann S. Non-linear thermogravimetric mass spectrometry of carbon materials providing direct speciation separation of oxygen functional groups. Carbon 2018; 130; 614-622.

[4] Jansen RJJ, Van Bekkum H. XPS of nitrogen-containing functional groups on activated carbon. Carbon 1995: 33;1021-7.