EAAOP-1

CHANIA, 7-9 SEP 06

## BOOK OF ABSTRACTS

# Environmental Applications of Advanced Oxidation Processes

## Chania, September 2006

Co-organised by:
**Technical University of Crete**
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# Catalytic properties of carbon xerogels for wet oxidation of aniline

**B. Machado[1], A. Ribeiro[1], I. Moreira[1], M. Rosário[1], H. Gomes[1,2], J. Figueiredo[1], J. Faria [1]***

[1] Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2] Departamento de Tecnologia Química, Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-857 Bragança, Portugal

* corresponding author: email: jlfaria@fe.up.pt

**Keywords**: catalytic wet oxidation; aniline; carbon xerogels

## Abstract

Wet air oxidation (WAO) is an old process developed in the middle of the XX century, but still the centre of very active and contemporary research especially in what concerns catalyst development. In ideal conditions soluble hydrocarbons can be oxidized in aqueous solution to carbon dioxide and water. Organic pollutants with heteroatoms are more challenging, because they require harsh conditions for complete oxidation and pose the risk of increased toxicity in case of incomplete degradation. Among known critical pollutants there is aniline, which presents carcinogenicity and toxicity (reproductive, developmental, neural and acute) to humans and to aquatic organisms. It is also a model compound for pesticide like molecules.

Our previous interest in the catalytic WAO (CWAO) of aniline using metal supported catalysts (Gomes et al, 2004) prompted us to study the development of highly mesoporous materials which can be very efficient not only as catalytic supports, but as catalysts themselves.

Using the conventional sol-gel approach (formaldehyde to resorcinol ratio of 2:1) we have fabricated different carbon xerogels with various degrees of mesoporous surface area. The materials were characterized by $N_2$-adsorption, TG analysis and SEM. We synthesized four different base materials. They were further activated in order to explore the effect of the surface oxidation on the activity and stability of the materials. They in the CWAO of aniline aqueous solutions and the results quantified in terms of substrate conversion and TOC removal. The experimental apparatus for WAO consisted of batch high pressure reactor described elsewhere (Gomes et al, 2004).

A recent review concerning carbon materials for CWAO (Stuber et al, 2005), shows that the studies on the stability of these materials has been considerably neglected. This is mainly due the fact that experiments of this nature are time consuming. We made repetition trials adding fresh substrate to the reactor in order to test the continued material performance. We compared the activity of the synthesized materials with that of different commercial activated carbons.

As representative example, a carbon xerogel with a mesoporous surface area of 199 $m^2$/g ($S_{MES}$=776 $m^2$/g) led to a complete aniline conversion after one hour oxidation, with a corresponding TOC removal of 83% (measured after 3 hours), under conditions of 200ºC and 6,9 bar oxygen partial pressure (air used oxidant, total pressure 50 bar). The selectivity towards $CO_2$ was calculated indirectly, from the TOC measurement as being 84%.

We concluded that the conversion is directly related with the mesoporous character of the material. However the performance does not depend only on the texture, but also on the degree of surface oxidation of the carbon xerogel, which we found to be determinant in the stability of the material under the operating conditions.

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# Catalytic properties of carbon xerogels for wet oxidation of aniline

**B. Machado[1], A. Ribeiro[1], I. Moreira[1], M. Rosário[1], H. Gomes[1,2], J. Figueiredo[1], J. Faria[1*]**

[1] Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal, jlfaria@fe.up.pt (J. Faria[*])
[2] Departamento de Tecnologia Química e Biológica, Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-857 Bragança, Portugal, htgomes@ipb.pt (H. Gomes)

**Abstract** The main objective of this work was to develop carbon materials suitable to be used efficiently in catalytic wet air oxidation (CWAO) processes. Accordingly, carbon xerogels with different mesoporous surface area and chemistry were prepared by the conventional sol-gel approach and tested in the CWAO of aniline at 200ºC and 6.9 bar of oxygen partial pressure. The developed materials showed high activity in aniline and total organic carbon removal, a clear increase in the removal efficiency relatively to non-CWAO being observed. At 200ºC, almost complete aniline conversions were obtained after one hour oxidation with high selectivity to non-organic compounds. The materials were characterized by thermogravimetric analysis, $N_2$ adsorption and scanning electron microscopy, in order to relate their efficiency to the chemical and textural characteristics. It was concluded that the removal efficiency increases with the mesoporous character of the materials and with the concentration of oxygen containing functional groups at their surface. The results obtained indicate that mesoporous carbon xerogels are promising catalysts for CWAO processes.

**Keywords** aniline; carbon xerogels; catalytic wet air oxidation; mesoporous catalysts; sol-gel; surface chemistry

## Introduction

Wet air oxidation (WAO) is an old process developed in the middle of the XX century, but still the centre of very active and contemporary research especially in what concerns catalyst development for the catalytic process (CWAO). CWAO consists in the total oxidation of the organic species present in effluents to $CO_2$, $N_2$ and $H_2O$ at relatively mild conditions of temperature and pressure (125-220ºC, 5-50 bar), using oxygen or air as the oxidising source, providing that a suitable catalyst is used. The quest for highly efficient catalysts was always a main research objective in the studies devoted to CWAO. As they are easily removed by filtration from the treated solution, heterogeneous catalysts presenting high activity and stability have been particularly investigated over the years (Bhargava et al., 2006). Good catalytic systems, especially supported noble metal catalysts, were used for the oxidation of model compounds (mainly phenol and carboxylic acids) as well for the oxidation of wastewaters. Following this research line, previously we reported the development of platinum catalysts supported on different carbon materials, and their excellent results when applied to the removal of aniline by CWAO (Gomes et al., 2004). Interestingly, we have noticed that the aniline removal efficiency and the selectivity to non-organic compounds obtained when using these supported Pt catalysts increased with the mesoporous character and with the concentration of surface oxygen functional groups of the corresponding support. Other research groups also reported on carbon materials as promising catalysts to the CWAO of aromatic compounds, such as phenol and aniline (Santiago et al., 2005; Santos et al., 2006) and of nitrogen containing compounds, such as ammonia and amines (Aguilar et al., 2005). The development and application of carbon materials in CWAO, either as a catalytic support or directly as a catalyst, was recently reviewed (Stuber et al., 2005).

All the results and findings reported prompted us to study the development of highly mesoporous materials, possessing appreciable surface oxygen functional groups, which can be very efficient not only as catalyst supports, but as catalysts on their own. Accordingly, in this work we developed carbon xerogel (CX) materials with different texture and surface chemistry and tested them in the CWAO of aqueous aniline solutions. Due to their controllable preparation procedure, CX materials can be tailored to achieve high mesoporous surface areas and, by proper oxidation treatments (either in liquid or in gas phases), the amount and nature of oxygen surface functional groups on their surface can also be easily modified (Samant et al., 2004). Aniline was chosen as test molecule, because it is an aromatic compound of practical interest to treat, presenting carcinogenicity and toxicity (reproductive, developmental, neural and acute) to humans and to aquatic organisms. It is widely used in the chemical industry, mainly in the synthesis of rubber additives and polymers such as isocyanate intermediates and polyurethanes. Additionally, derivatives of aniline are used as herbicides, fungicides, animal repellents and defoliants.

## Methods

### Preparation of carbon xerogels

Aqueous organic gels were prepared by polycondensation of resorcinol with formaldehyde (1:2), adapting the procedure described elsewhere (Job et al., 2004). Accordingly, 9.91 g of resorcinol (Aldrich, 99%) were added to 18.8 mL of deionised water in a glass flask. After complete dissolution, 13.5 mL of formaldehyde solution (Sigma, 37 wt.% in water, stabilized with 15 wt.% methanol) were also added. In order to achieve the desired initial pH of the precursor solution, sodium hydroxide solution was added dropwise under continuous stirring and pH monitoring. The gelation step was allowed to proceed at 85ºC during 3 days. The appearance of the gels varies from light brown, when the initial precursor solution pH was fixed in 5.0, to dark red, when it was set to 6.0. At this point, the consistency of the material allows the samples to be shaped as desired (ground to small particles ca. 1 mm). The gels were further dried in a oven from 60ºC to 150ºC during several days, defining a heating ramp of 20ºC/day. After drying, the gels were pyrolyzed at 800ºC under a nitrogen flow (100 mL/min) in a tubular vertical oven. Four different carbon xerogel (CX) samples (CX01 to CX04, as defined in Table 1.1) were produced, varying the initial precursor solution pH in the range 5.0-6.0. The precise control of this parameter was found to be determinant in the development of the mesoporous character of the CX materials (Job et al., 2004).

### Activation and characterization of carbon xerogels

In order to introduce oxygen functional groups at the surface of the previously prepared CX materials and to increase their mesoporous character, gas phase activation was used, according to previous work (Figueiredo et al., 1999). About 2 g of each sample was heated to 400ºC in a tubular vertical oven, at a heating rate of 10ºC/min, under an $O_2$ diluted in $N_2$ (5% $O_2$) atmosphere, during 6 hours. Burn-off (BO) values ranging between 4% and 10% were obtained for all samples (Table 1.1). The materials obtained before and after activation were further characterized to asses their degree of mesoporosity and oxygen surface functional groups concentration. Textural characterization was based on the analysis of the materials $N_2$ adsorption-desorption isotherms, determined at -196ºC with a Coulter Omnisorp 100CX apparatus. Specific BET surface areas ($S_{BET}$) were calculated, as well as the micropore volumes ($V_{MIC}$) and the non-microporous surface areas (mainly mesoporous, $S_{MES}$) determined by the t-method, using the standard isotherm for carbon materials proposed by Rodríguez-Reinoso (Rodriguez-Reinoso et al., 1987). Surface analysis for topographical characterization was carried out by scanning electron microscopy (SEM) with a Jeol JSM-6301F (15 keV) electron microscope. The sample powders were mounted on a double-sided adhesive tape and observed at different magnifications under two different detection modes, secondary and back-scattered electrons. To quantify the concentration of oxygen functional groups introduced at the materials surface, thermogravimetric analysis (TGA) was performed using a Mettler M3 balance. For that purpose, the samples were first heated in $N_2$ from 30ºC to 900°C at 25°C/min, allowing the quantification (mass loss) of the functional groups present on the materials surface, which decompose upon heating. After 7 minutes at 900ºC in $N_2$, the gas feed was changed to air in order to burn the carbon samples and determine their fixed carbon and ash contents.

### Oxidation procedure

The oxidation reactions were performed in a 160 mL stainless steel high pressure reactor (model 4564, Parr Instrument Co. Ltd., Illinois, USA) equipped with a magnetically driven stirrer (a rotation speed of 500 rpm was chosen to ensure proper mass transfer of air in the liquid phase) and a thermocouple. The reactor was heated by an electrical heating mantle controlled by a temperature controller unit (model PID 4842, Parr Instrument Co. Ltd., Illinois, USA).

Typically, in an oxidation run, 70 mL of water and the desired amount of catalyst (for CWAO runs) were placed inside the reactor and heated to the reaction temperature (200ºC). Then, 5 mL of aniline solution were added trough an injection system, the aniline solution concentration being calculated to give a concentration of 2 g/L inside the reactor. In order to ensure homogeneous mixing, the first sample was only withdrawn a few seconds after the aniline injection and reactor pressurization with air (50 bar of total pressure, corresponding to an oxygen partial pressure of 6.9 bar, or 38% of excess oxygen relative to the stoichiometric amount needed for complete aniline mineralization).

### Product analysis

Periodically, 1 mL of liquid sample was withdrawn from the reactor to be further analyzed for aniline concentration and TOC content. Aniline concentration was determined by injecting samples on a GC chromatograph (DANI GC-1000)

equipped with a capillary column (WCOT Fused Silica 30 m, 0.32 mm i.d., coated with CP-Sil 8 CB low bleed/MS 1 µm film). The samples TOC content was measured in a TOC analyzer (Shimadzu 5500A). This equipment determines in separate runs the sample total carbon (TC) by combustion at 700ºC over a Pt catalyst bed and the total inorganic carbon (TIC) by sample treatment with phosphoric acid. TOC is obtained subtracting TIC from TC. For both GC and TOC analysis, three reproducible injections (variance less than 3%) were considered. With the experimental values of aniline concentration and TOC content, it is possible to calculate the reaction selectivity towards non-organic compounds, according to a protocol described elsewhere (Gomes et al., 2004).

## Results and discussion

### Materials characterization

The $N_2$ adsorption-desorption isotherms at -196ºC were determined for all the prepared CX materials before and after their activation with $O_2$. The curves obtained after activation are represented in Figure 1.1. From their observation it can be concluded that all the prepared materials are strongly mesoporous, a well defined histeresis being obtained, particularly for the CX04 sample, which was prepared using an initial precursor solution pH of 6.0, suggesting a higher mesoporous surface area when compared to the other CX materials. It should be noticed that CX04 was activated to a higher burn-off (Table 1.1), which can explain the development of a more extensive mesoporosity when compared with the other materials.
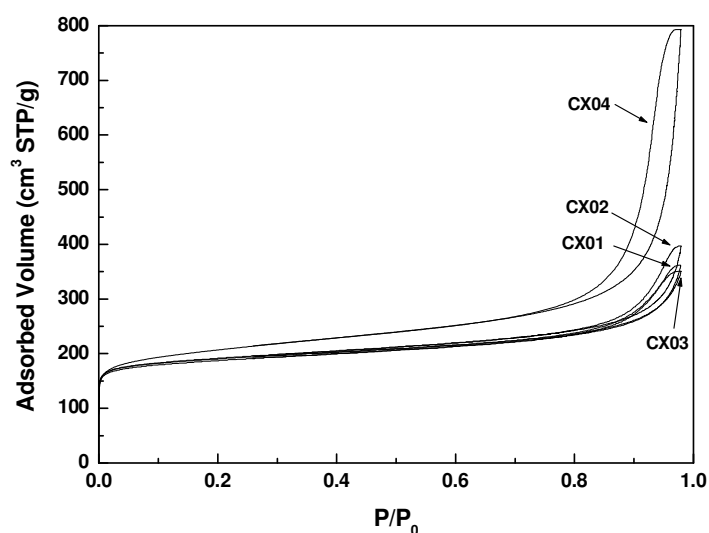


**Figure 1.1** $N_2$ adsorption-desorption isotherms at -196ºC on the prepared CX materials after activation with $O_2$

The textural properties of the materials were determined and are collected in Table 1.1 before and after activation with $O_2$. The textural properties of the activated carbon Norit ROX 0.8 (ROX) are also included for comparison purposes, as it was also tested in the CWAO of aniline. Analysis of Table 1.1 shows that before activation with $O_2$, all CX samples have a significant mesoporous surface area, and that oxidation of CX had a strong impact on the textural properties of the materials, particularly on their mesoporosity. On the other hand, ROX presents much higher microporosity and lower mesoporosity when compared to the activated CX samples.

The uniformity of the mesopores formed during CX preparation (after activation with $O_2$) was assessed by visual inspection of micrographs obtained by SEM. A uniform pore distribution all over the surface was observed for all the prepared samples (Figure 1.2).

**Table 1.1** Initial CX preparation pH, specific BET surface areas ($S_{BET}$), micropore volumes ($V_{MIC}$) and non-mesoporous surface areas ($S_{MES}$) calculated by t-plot, before and after activation with $O_2$ and burn-off observed in the activation of the CX materials

| Catalyst | Initial pH | $S_{BET}$ (m²/g) | $S_{MES}$ (m²/g) | $V_{MIC}$ (cm³/g) | BO (%) |
|----------|-----------|------------------|------------------|-------------------|--------|

| | | before | after | before | after | before | after | |
|---|---|---|---|---|---|---|---|---|
| ROX | - | 900 | - | 114 | - | 0.32 | - | - |
| CX01 | 5.0 | 628 | 722 | 102 | 139 | 0.21 | 0.23 | 4.0 |
| CX02 | 5.3 | 620 | 736 | 124 | 152 | 0.20 | 0.23 | 4.2 |
| CX03 | 5.5 | 633 | 734 | 89 | 129 | 0.21 | 0.24 | 4.4 |
| CX04 | 6.0 | 625 | 773 | 171 | 230 | 0.18 | 0.22 | 9.6 |
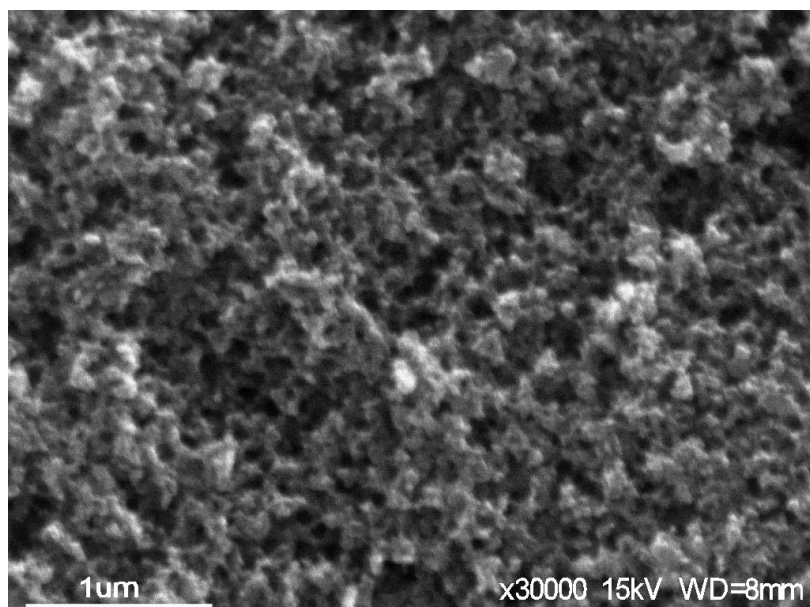


**Figure 1.2** SEM micrograph of a carbon xerogel sample after activation with $O_2$ (CX01 magnified 30k X)

In order to quantify the concentration of oxygen containing functional groups present on the surface of all the prepared CX materials and ROX, their thermogravimetric decomposition (TGA) was monitored under inert and oxidizing atmosphere. From the corresponding mass loss evolution with temperature and atmosphere, the amounts of volatiles, fixed carbon and ash were determined (Table 1.2). The volatiles content is attributed to oxygen containing surface functional groups, produced during the materials activation stage by reaction between the oxygen and fixed carbon in the materials matrix, which decompose upon heating.

**Table 1.2** Volatiles, fixed carbon and ash contents of all the prepared CX materials, before and after activation with $O_2$ and of ROX, obtained by TGA (dry basis)

| Catalyst | Volatiles (wt.%) | | Carbon (wt.%) | | Ash (wt.%) | |
|---|---|---|---|---|---|---|
| | before | after | before | after | before | after |
| ROX | $6.9 \pm 0.1$ | - | $91.2 \pm 0.1$ | - | 1.9 | - |
| CX01 | $3.9 \pm 0.6$ | $17.0 \pm 0.4$ | $96.1 \pm 0.6$ | $83.0 \pm 0.4$ | 0.0 | 0 |
| CX02 | $4.6 \pm 0.3$ | $17.1 \pm 0.9$ | $95.4 \pm 0.3$ | $82.9 \pm 0.9$ | 0.0 | 0 |
| CX03 | $4.4 \pm 0.7$ | $16.4 \pm 0.3$ | $95.6 \pm 0.2$ | $83.6 \pm 0.3$ | 0.0 | 0 |
| CX04 | $3.7 \pm 0.9$ | $13.7 \pm 0.2$ | $96.3 \pm 0.9$ | $86.3 \pm 0.2$ | 0.0 | 0 |

Analysis of Table 1.2 indicates that the CX materials before activation possess a modest surface chemistry (mean concentration of 4.2 wt.%), which apparently decreases as the pH of the initial precursor solution used in their preparation increases. This tendency shall be confirmed in future works by performing complementary analyses, such as elemental analysis, to quantify the total oxygen content, and by temperature programmed desorption, in order to identify and quantify the types of oxygen functional groups. Upon activation of the CX materials, the concentration of oxygen functional groups increases considerably (mean concentration of 16.0 wt.%). Another interesting observation to take into account is that the CX materials have no mineral impurities. This characteristic contrasts with the ROX material, which has a non negligible ash content (1.9 wt.%). In terms of surface oxygen functional groups, ROX contains roughly half of that observed in the CX materials after activation.

Summarizing the observations gathered from textural and chemical characterization, it is concluded that the increase of the initial precursor solution pH used in the preparation of CX materials leads to an increase of their mesoporous character and to a decrease in the concentration of oxygen functional groups present on their surface. Comparing CX characteristics with ROX, it is concluded that CX materials are highly mesoporous and contains a considerable concentration of oxygen functional groups, while ROX is essentially microporous and contains an appreciably lower amount of oxygen.

## Oxidation reactions

The prepared CX and ROX materials were tested in the CWAO of aniline aqueous solutions (2 g/L) at 200ºC and 6.9 bar of oxygen partial pressure. The results obtained are shown in Figure 1.3, from where it can be concluded that the non-CWAO of aniline at the given conditions cannot be neglected. In Table 1.3 the same results are summarized in terms of aniline conversions ($X_{ANL}$) after 1 h and 5 h of reaction, together with the selectivity to non-organic compounds ($S_{NOC}$), calculated from the total organic carbon conversion values ($X_{TOC}$) after 5 h of reaction and the initial aniline removal rates ($r_0$).
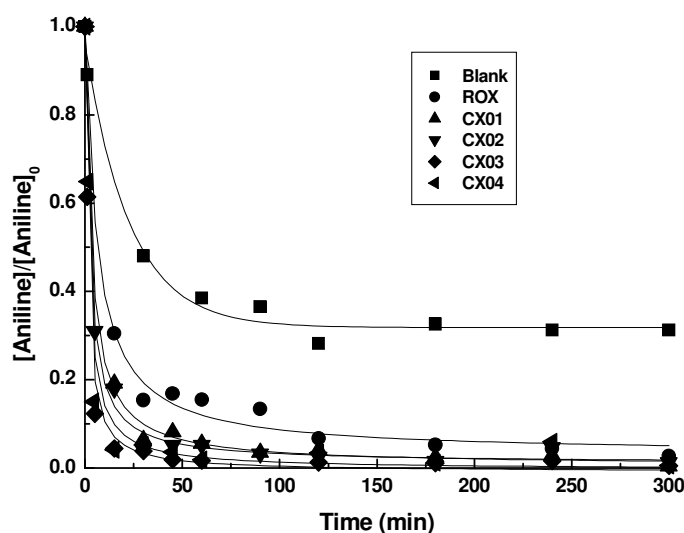


**Figure 1.3** WAO/CWAO aniline removal curves at 200ºC and 6.9 bar of oxygen partial pressure obtained in the absence of catalysts and in the presence of the prepared CX and of the ROX materials

From Table 1.3, it is observed that the aniline conversion obtained in the absence of catalysts is 68.7% after 5 h of reaction (61.5% after 1 h). In terms of TOC removal, a lower efficiency can be observed after 5 h of reaction, with 45.3% TOC conversion being obtained, which gives a selectivity to non-organic compounds of 65.9%. The significant removal of aniline observed in the experiment performed without any catalyst indicates that this compound can be easily degraded at the given conditions. However, further removal of intermediate oxidation products (more recalcitrant and non-biodegradable) is more difficult to achieve without the aid of a suitable catalyst.

With the introduction of carbon materials in the reaction system (0.8 g), a clear increase of the aniline removal efficiency can be observed in Figure 1.3, when compared to the non-catalytic experiment, either using ROX or the prepared CX materials. This increase in aniline removal may be interpreted in terms of adsorption and catalytic activity of the materials. Comparing the CX materials with ROX, it is observed that the former are more efficient to remove aniline than the latter. The difference in the observed performance between both types of carbon materials may be explained by the higher mesoporous character and higher concentration of oxygen functional groups present in CX materials, as reported previously (Gomes et al., 2004). Comparing the performances of the different CX materials for aniline removal, no clear distinction is observed between them in Figure 1.3. However, calculating the initial aniline removal rates achieved with each sample (shown in the last column of Table 1.3), it is possible to distinguish differences in performance between the prepared CX materials, being clearly concluded that it increases (except for CX04) with the use of CX prepared using a higher initial precursor solution pH. As an example, the initial aniline removal rate observed with the catalyst CX01 is 0.636 g.L$^{-1}$.min$^1$, whilst with the catalyst CX03 the initial aniline

removal rate more than doubles (1.567 $g.L^{-1}.min^{1}$). This is clear evidence that the CX preparation procedure influences significantly the materials textural and/or surface chemical characteristics, leading to different catalytic behaviour. Taking a closer look at the aniline removal curves we can distinguish two distinct steps. Initially (first 20 minutes of reaction), there is a sharp aniline removal, due to a possible coupled contribution of adsorption and catalytic activity of the materials. In a second step (after 20 minutes of reaction), the aniline removal continues to decrease slightly, due only to catalytic activity. In order to better understand the influence of the materials textural and chemical characteristics on the adsorption behaviour and catalyst activity, future experiments are planned at different temperatures, as well as more detailed chemical characterization to identify and quantify the types of functional groups present on the materials surface. In a recent published work devoted to the CWAO of aqueous methyl and dimethylamines, using activated carbons as catalysts, the observed catalytic activities and adsorption behaviour were related to the presence of oxygenated functional groups on the activated carbons, being proposed that the quinonic surface groups were those responsible for the catalytic activities, while carboxylic, lactone and anhydride groups were responsible for the adsorption behaviour (Aguilar et al., 2005).

**Table 1.3** Aniline conversions after 1 h and 5 h of reaction, TOC conversions and selectivity to non-organic compounds after 5 h of reaction and initial aniline removal rates obtained in the WAO/CWAO experiments at 200ºC and 6.9 bar of oxygen partial pressure

| Catalyst | $X_{ANL}$ (%, 1h) | $X_{ANL}$ (%, 5h) | $X_{TOC}$ (%, 5h) | $S_{NOC}$ (%, 5h) | $r_0$ ($g.L^{-1}.min^{-1}$) |
|---|---|---|---|---|---|
| Blank | 61.5 | 68.7 | 45.3 | 65.9 | 0.056 |
| ROX | 85.2 | 97.0 | 92.5 | 95.4 | 0.323 |
| CX01 | 98.9 | 99.6 | 87.1 | 87.4 | 0.636 |
| CX02 | 94.8 | 98.7 | 86.3 | 87.5 | 0.875 |
| CX03 | 98.3 | 99.5 | 88.7 | 89.1 | 1.567 |
| CX04 | 98.1 | 99.4 | 85.9 | 86.4 | 1.170 |

Referring again to Table 1.3, the increase in the aniline removal efficiency upon the introduction of the carbon materials is clearly evidenced. Aniline conversion after 1 h of reaction increases from 61.5% (68.7% after 5 h) obtained in the non-catalytic experiment to 85.2% (97.0% after 5 h) when the ROX material was used and to almost complete conversions when the CX materials were used. When comparing the TOC conversion obtained in all experiments after 5 h of reaction, it can be observed that the introduction of the carbon materials also increases considerably the removal of the intermediate compounds resulting from aniline oxidation. It should be noticed that in the experiment performed without any catalyst the reaction samples collected as the reaction proceeded acquired an increasingly intense orange colour, suggesting the formation of nitrogen intermediate compounds, whilst when using the carbon materials the collected samples remained non coloured, suggesting that either the reaction proceeds trough a different reaction mechanism path, or the formed intermediates are easily adsorbed at the materials surface. The TOC conversion observed after 5 h of reaction when using the ROX material increased from 45.3% (with a corresponding selectivity to non-organic compounds of 65.9%) when no catalyst was used to 92.5% (selectivity to non-organic compounds of 95.4%). When the CX materials were used, the TOC conversion values obtained after 5 h, although lower than those obtained with the ROX material, are also very high, a mean value of 87% (average selectivity to non-organic compounds of 87.6%) being obtained. The differences observed in the TOC removal efficiencies of ROX and CX materials may be ascribed to a better removal of the intermediate compounds resulting from aniline oxidation by adsorption on the surface of the ROX material. Overall rationalization of the results seems to indicate the occurrence of a different adsorption/reaction mechanism behaviour when the ROX material or the CX materials are used. At a first glance, it seems that the CX materials possess higher intrinsic catalytic activities than the activated carbon, and that they are correlated to their mesoporous surface area and surface chemistry.

In order to optimize the CX catalyst load needed for the CWAO of aniline, further experiments were performed with CX04, decreasing the catalyst mass. The results obtained are shown in Figure 1.4. It can be observed that by reducing the catalyst mass from 0.8 g to 0.4 g, the aniline removal pattern is not significantly altered, being reasonable to state that the catalyst performance is independent of catalyst load in this range. A further decrease in the catalyst mass to 0.2 g, apparently led to worse aniline removal efficiency, but after 180 minutes of reaction, aniline conversion was also almost complete. Although the catalyst load was notoriously decreased, the aniline removal efficiency remained high, which suggests that the CX materials may play a primary role in the initial step of the mechanism of aniline degradation, allowing its adsorption and generation of reactive radicals, which will further react with other aniline molecules until their complete degradation, similar to what was proposed in previous works for the CWAO of low molecular weight carboxylic acids, using metal supported catalysts (Gomes et al., 2002). The aniline conversions

obtained after 1 h and 5 h of reaction, the TOC conversion and the selectivity to non-organic compounds after 5 h of reaction and the initial aniline removal specific rates obtained in each experiment are gathered in Table 1.4.
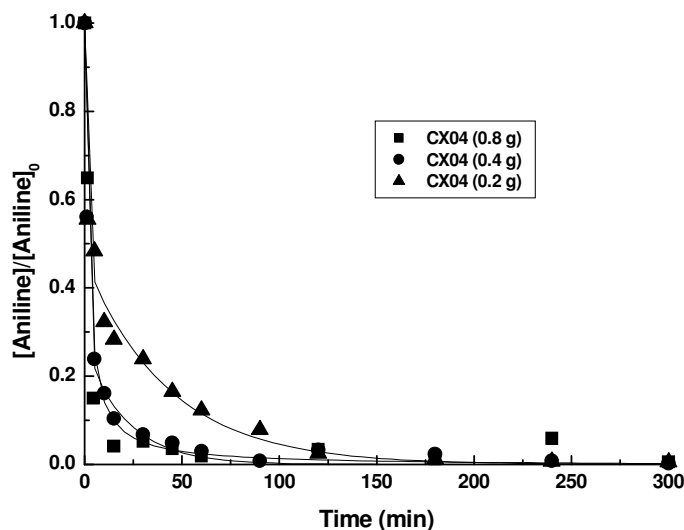


**Figure 1.4** CWAO aniline removal curves at 200ºC and 6.9 bar of oxygen partial pressure obtained using different CX04 catalyst loads

Analysis of the data shown in Table 1.4 supports the previous observations. The aniline conversion after 1 h of reaction is almost complete in both experiments performed with 0.8 g and 0.4 g of CX04 (~97.6%), rather similar values of TOC conversion and selectivity to non-organic compounds being observed after 5 h of reaction (~87.8% and 88.2%, respectively). When 0.2 g of catalyst was used, the aniline conversion observed after 1 h of reaction decreases to 87.7%, but almost complete aniline removal is also observed after 5 h (99.5%). Taking into consideration the parameters TOC conversion and selectivity to non-organic compounds, the use of 0.2 g of CX04 lead to lower values at the end of reaction (79.2% and 79.6% for TOC conversion and selectivity, respectively), suggesting that the available active centres of CX04 needed to assist in the adsorption/initial activation of the aniline oxidation intermediates are not sufficient to guarantee their oxidation, because they are occupied with aniline molecules for a longer time. In spite of the apparently lower aniline reaction rate observed when using only 0.2 g of CX04, comparison of the initial aniline removal specific rates ($r_0$, normalized with the catalyst load) shows that they increase with decreasing catalyst load, suggesting that the mechanism of aniline removal with this material is not purely heterogeneous, but involves an initial fast adsorption activation to reactive radicals at the material surface, followed by rapid desorption to the liquid phase, where the reaction will proceed via a radical mechanism. This liquid phase reaction shall be the limiting step, justifying, the rapid aniline removal at the very beginning of the reaction and subsequent lower reaction aniline removal rate.

**Table 1.4** Aniline conversion after 1 and 5 h of reaction; TOC conversion and selectivity to non-organic compounds after 5 h; and initial aniline removal specific rates obtained in the CWAO experiments performed with CX04 at variable catalyst mass

| CX04 mass (g) | $X_{ANL}$ (%, 1h) | $X_{ANL}$ (%, 5h) | $X_{TOC}$ (%, 5h) | $S_{NOC}$ (%, 5h) | $r'_0$ ($g_{aniline} \cdot g_{CX}^{-1} \cdot min^{-1}$) |
|---|---|---|---|---|---|
| 0.8 | 98.1 | 99.4 | 85.9 | 86.4 | 0.110 |
| 0.4 | 97.0 | 99.7 | 89.7 | 90.0 | 0.240 |
| 0.2 | 87.7 | 99.5 | 79.2 | 79.6 | 0.421 |

Comparing the results obtained in this work with others published in the literature (Oliviero et al., 2003; Gomes et al., 2004, 2005; Barbier et al., 2005; Garcia et al., 2005) devoted to the CWAO of aniline using metal supported catalysts, we found that they are comparable or even better in some cases, showing that carbon xerogels are promising catalysts for CWAO. Although we suspect that their catalytic activity is strongly influenced by their mesoporous character and

surface chemistry, further research shall be performed to fully understand the variables pertinent to the efficiency of the CX materials.

## Conclusions

Carbon xerogels prepared by the conventional sol-gel method were tested in the CWAO of aniline at 200°C and 6.9 bar of oxygen partial pressure, and found to be promising to use in CWAO processes. Almost complete removal of aniline was obtained with all the prepared carbon xerogel samples after 1 h of reaction, which performed better than the commercial activated carbon Norit ROX 0.8. This removal efficiency was attributed to both adsorption and catalytic activity of the materials, the conversion being directly related to their mesoporous character and surface chemistry. Experiments performed with different masses of carbon xerogel allowed to conclude that the CWAO of aniline with these materials proceeds via a radical mechanism in the homogeneous phase, after an initial and essential step of adsorption and radical activation on the materials surface.

## Acknowledgments

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