



Catalytic properties of carbon materials for wet oxidation of aniline

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ARTICLE INFO

Article history:

Received 26 November 2007

Received in revised form 10 February 2008

Accepted 12 February 2008

Available online 4 March 2008

Keywords:

Aniline

Carbon xerogels

Catalytic wet air oxidation

Mesoporous catalysts

Surface chemistry

ABSTRACT

A mesoporous carbon xerogel with a significant amount of oxygen functional groups and a commercial activated carbon, were tested in the catalytic wet air oxidation of aniline at 200 °C and 6.9 bar of oxygen partial pressure. Both carbon materials showed high activity in aniline and total organic carbon removal, a clear increase in the removal efficiency relatively to non-catalytic wet air oxidation being observed. The best results in terms of aniline removal were obtained with carbon xerogel, an almost complete aniline conversion after 1 h oxidation with high selectivity to non-organic compounds being achieved. The materials were characterized by thermogravimetric analysis, temperature programmed desorption, N₂ adsorption and scanning electron microscopy, in order to relate their performances to the chemical and textural characteristics. It was concluded that the removal efficiency, attributed to both adsorption and catalytic activity, is related to the mesoporous character of the materials and to the presence of specific oxygen containing functional groups at their surface. The effect of catalytic activity was found to be more important in the removal of aniline than the effect of adsorption at the materials surface. The results obtained indicate that mesoporous carbon xerogels are promising catalysts for CWAO processes.

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1. Introduction

Wet air oxidation (WAO) is a mature process developed in the third quarter of the XX century, but still the centre of very active and contemporary research, especially in what concerns catalyst development [1–4]. Catalytic wet air oxidation (CWAO) consists in the total oxidation of the organic species present in effluents to CO₂, N₂ and H₂O under relatively mild conditions of temperature and pressure (125–220 °C, 5–50 bar), using oxygen or air as the oxidising source, provided that a suitable catalyst is used. The quest for highly efficient catalysts was always a main research objective in the studies devoted to CWAO. Heterogeneous catalysts presenting high activity and stability have been investigated over the years [5–8], since they can be easily removed by filtration from the treated solution. Good catalytic systems, especially supported noble metal catalysts, were used for the oxidation of model compounds (mainly phenol and carboxylic acids) as well as the oxidation of waste waters [9–12]. Following this research line, we have previously reported the development of platinum catalysts supported on different carbon materials and their excellent

results when applied to the removal of aniline by CWAO [13]. Interestingly, we have noticed that the aniline removal efficiency and the selectivity to non-organic compounds obtained with such supported Pt catalysts were dependent on the mesoporous character and on the concentration of surface oxygen functional groups of the corresponding support. Other research groups also reported on carbon materials as promising catalysts for the CWAO of aromatic compounds, such as phenol and aniline [14–17] and of nitrogen containing compounds, such as ammonia and amines [18,19]. The development of carbon materials and their application in CWAO, either as a catalyst support or directly as a catalyst, was recently reviewed [20].

All the reported results and findings prompted us to study the development of 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 prepared a mesoporous carbon xerogel (CX) with a well developed surface chemistry and tested it in the CWAO of aqueous aniline solutions. A commercial activated carbon (ROX, from Norit) was used as standard for comparison purposes. Due to their controllable preparation procedure, CX materials can be tailored to achieve high mesoporous surface areas, and the amount and nature of oxygen functional groups on their surface can also be easily modified by proper oxidation treatments (either in liquid

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or in gas phases) [21]. Aniline was chosen as test molecule because of its hazardous properties, 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 defoliantes.

2. Experimental

2.1. Preparation of carbon xerogel

The carbon xerogel was prepared by polycondensation of resorcinol with formaldehyde (1:2), adapting the procedure described elsewhere [22]. 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 (6.1), sodium hydroxide solution was added dropwise under continuous stirring and pH monitoring. The precise control of this parameter was found to be determinant in the development of the mesoporous character of CX materials [22]. The gelation step was allowed to proceed at 85 °C during 3 days. After this period the gel was dark red and the consistency of the material allowed the sample to be shaped as desired (ground to small particles ca. 0.1 mm). The gel was further dried in an oven from 60 to 150 °C during several days, defining a heating ramp of 20 °C/day. After drying, the gel was pyrolyzed at 800 °C under a nitrogen flow (100 mL/min) in a tubular vertical oven.

2.2. Activation and characterization of CX

In order to introduce oxygen functional groups on the surface of the previously prepared CX material and to increase the mesoporous character, gas phase activation was used [21,23]. The material was heated to 400 °C in a tubular vertical oven, at a heating rate of 10 °C/min, under a flow of O₂ diluted in N₂ (5% O₂), during 6 h. A burn-off of 5.4% was obtained. The material was characterized before and after activation to assess the degree of mesoporosity and surface oxygen functional groups concentration. Textural characterization was based on the analysis of the N₂ adsorption–desorption isotherms, determined at –196 °C 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 Rodriguez-Reinoso et al. [24]. 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 on the materials surface, thermogravimetric analysis (TGA) was performed using a Mettler M3 balance. For that purpose, the samples were first heated in N₂ from 30 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 min at 900 °C in N₂, the gas feed was changed to air in order to burn the carbon samples and determine their fixed carbon and ash contents. The concentration of oxygen functional groups present at the carbon materials surface was also quantified by temperature programmed desorption (TPD), heating the samples from room

temperature to 1100 °C under helium atmosphere. The amounts of CO and CO₂ desorbed from the carbon samples were monitored with a SPECTRAMASS Dataquad quadrupole mass spectrometer, allowing the identification and quantification of the oxygen functional groups after analysis of the corresponding TPD spectra using the peak assignment and deconvolution procedures described elsewhere [23].

2.3. Oxidation procedure

The oxidation reactions were performed in a 160 mL stainless steel high pressure reactor (model 4564, Parr Instrument Co. Ltd., IL, 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.).

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. Then, 5 mL of aniline solution were added through the 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 at 200 °C, 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.

2.4. Product analysis

Liquid samples of 1 mL were periodically withdrawn from the reactor to determine aniline concentration and TOC content. Aniline concentration was measured by GC in a DANI GC-1000 chromatograph using 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) and a FID detector. TOC content was measured in a TOC analyzer (Shimadzu 5500A). This equipment determines in separate runs the sample total carbon (TC) by combustion over a Pt catalyst bed at 700 °C and the total inorganic carbon (TIC) by sample treatment with phosphoric acid. TOC is obtained by subtracting TIC from TC. For both GC and TOC analysis, three values with a variance less than 3% were considered. With the aniline concentration and TOC content, it is possible to calculate the reaction selectivity towards non-organic compounds, according to a procedure described elsewhere [13].

Concerning other reaction intermediates, their presence was searched by means of a computer-controlled Hitachi Elite LaChrom HPLC system equipped with a Diode Array Detector (L-2450) and one solvent delivery pump (L-2130) at a flow rate of 1 mL/min. Nitrobenzene and nitrophenols were investigated using a Purospher Star RP-18 column (250 mm × 4.6 mm; 5 μm particles) with an isocratic method of a A:B (40:60) mixture of 3% acetic acid and 1% acetonitrile in methanol (A) and 3% acetic acid in water (B).

3. Results and discussion

3.1. Materials characterization

The N₂ adsorption–desorption isotherms at –196 °C were determined for the CX material before and after activation with O₂ and for ROX. The curves obtained are presented in Fig. 1. From their observation it can be concluded that all materials contain mesopores, a well defined hysteresis being obtained, particularly for the

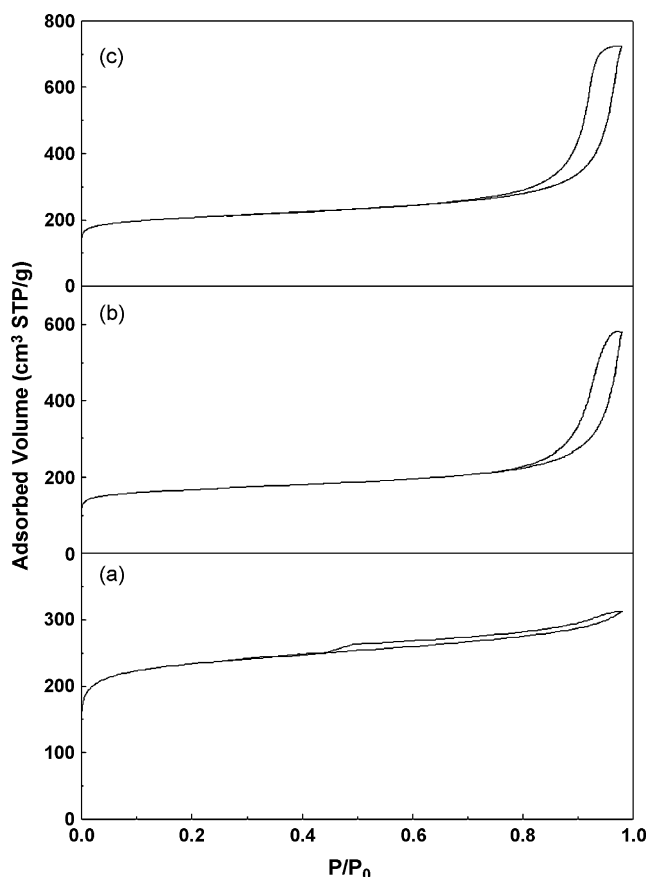


Fig. 1. N_2 adsorption–desorption isotherms at $-196\text{ }^\circ\text{C}$: (a) ROX, (b) CX before activation and (c) CX after activation.

CX sample after activation, suggesting a higher mesoporous surface area when compared to the other materials.

The textural properties of the materials were determined from the analysis of the corresponding N_2 adsorption–desorption isotherms and are collected in Table 1.

Analysis of Table 1 shows that before activation with O_2 CX has a reasonable mesoporous surface area and that oxidation has a strong impact on the textural properties of the material, particularly on the mesoporosity. On the other hand, ROX presents much higher microporosity and lower mesoporosity when compared to the activated CX sample. The uniformity of the mesopores formed during CX preparation was assessed by visual inspection of micrographs obtained by SEM. A uniform pore distribution all over the surface was observed.

In order to quantify the concentration of oxygen containing functional groups present on the surface of the carbon materials, 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 2). The volatiles content is attributed to surface oxygen containing functional groups which decompose upon heating.

Table 1
Specific BET surface areas (S_{BET}), micropore volumes (V_{MIC}) and non-microporous surface areas (S_{MES}) of ROX and of CX before and after activation

Catalyst	S_{BET} (m^2/g)		S_{MES} (m^2/g)		V_{MIC} (cm^3/g)	
	Before	After	Before	After	Before	After
ROX	900	–	110	–	0.32	–
CX	630	780	160	210	0.19	0.23

Table 2

Volatiles, fixed carbon and ash contents of the carbon materials obtained by TGA (dry basis)

Catalyst	Volatiles (wt.%)		Carbon (wt.%)	
	Before	After	Before	After
ROX ^a	6.9 ± 0.1	–	91.2 ± 0.1	–
CX ^b	3.7 ± 0.9	13.7 ± 0.2	96.3 ± 0.9	86.3 ± 0.2

^a Ash: 1.9 wt.%.

^b Ash free.

Table 3

Amounts of CO and CO_2 , volatiles (CO + CO_2) and CO/ CO_2 ratios, obtained from the TPD spectra of ROX and of the prepared CX material before and after activation with O_2

Catalyst	CO ($\mu\text{mol}/\text{g}$)		CO_2 ($\mu\text{mol}/\text{g}$)		CO + CO_2 (wt.%)		CO/ CO_2	
	Before	After	Before	After	Before	After	Before	After
ROX	1160	–	330	–	4.7	–	3.5	–
CX	280	3740	70	470	1.1	12.5	4.0	8.0

Analysis of Table 2 indicates that the CX material before activation possess a modest surface chemistry (concentration of 3.7 wt.%). Upon activation, the concentration of oxygen functional groups increases considerably (concentration of 13.7 wt.%). Another interesting observation to take into account is that the CX samples have no mineral impurities. This characteristic contrasts with the ROX material, which has a non-negligible ash content (1.9 wt.%). In terms of oxygen functional groups, ROX contains roughly half of that observed in the CX material after activation. The previous observation was confirmed by temperature programmed desorption (TPD). The TPD spectra of the CX material after activation with O_2 and of ROX are shown in Fig. 2, a much higher concentration of oxygen functional groups of CX being observed relatively to ROX.

The total amounts of CO and CO_2 released for the prepared CX and ROX are gathered in Table 3. The analysis of the CO/ CO_2 ratios shows that the CX samples have higher predominance of CO releasing oxygen functional groups compared to ROX, and that this predominance increases upon activation with O_2 . The TPD results also allowed the identification of the functional groups present at the materials surface by peak assignment and deconvolution procedures, as described elsewhere [23]. For the fit lines shown in Fig. 2, the release of CO_2 was attributed to carboxylic anhydrides, lactones and carboxylic acids. In the case of ROX, both low temperature and high temperature decomposing carboxylic acid groups were considered, to better describe the release of CO_2 at temperatures between 150 and 400 $^\circ\text{C}$. The release of CO was attributed to carboxylic anhydrides, phenols and quinones. Table 4 summarizes the concentration of the different oxygen functional groups present at the carbon materials surface. It is evidenced that CX possess mainly phenol and quinone groups, with correspondingly higher CO/ CO_2 ratios, when compared to ROX. The small differences between the CO and CO_2 values given in Table 3 and the sum of the individual CO and CO_2 values in Table 4 arises from small amounts of unidentified oxygen functional groups present at the materials surface.

Summarizing the observations gathered from textural and chemical characterization, it is concluded that the CX material after activation with O_2 is predominantly mesoporous and contains a considerable concentration of oxygen functional groups, while ROX is highly microporous and contains an appreciably lower amount of oxygen.

3.2. Oxidation reactions

3.2.1. Effect of catalyst texture and surface chemistry

The prepared CX (after activation with O_2) and ROX materials were tested in the CWAO of aniline aqueous solutions (2 g/L) at

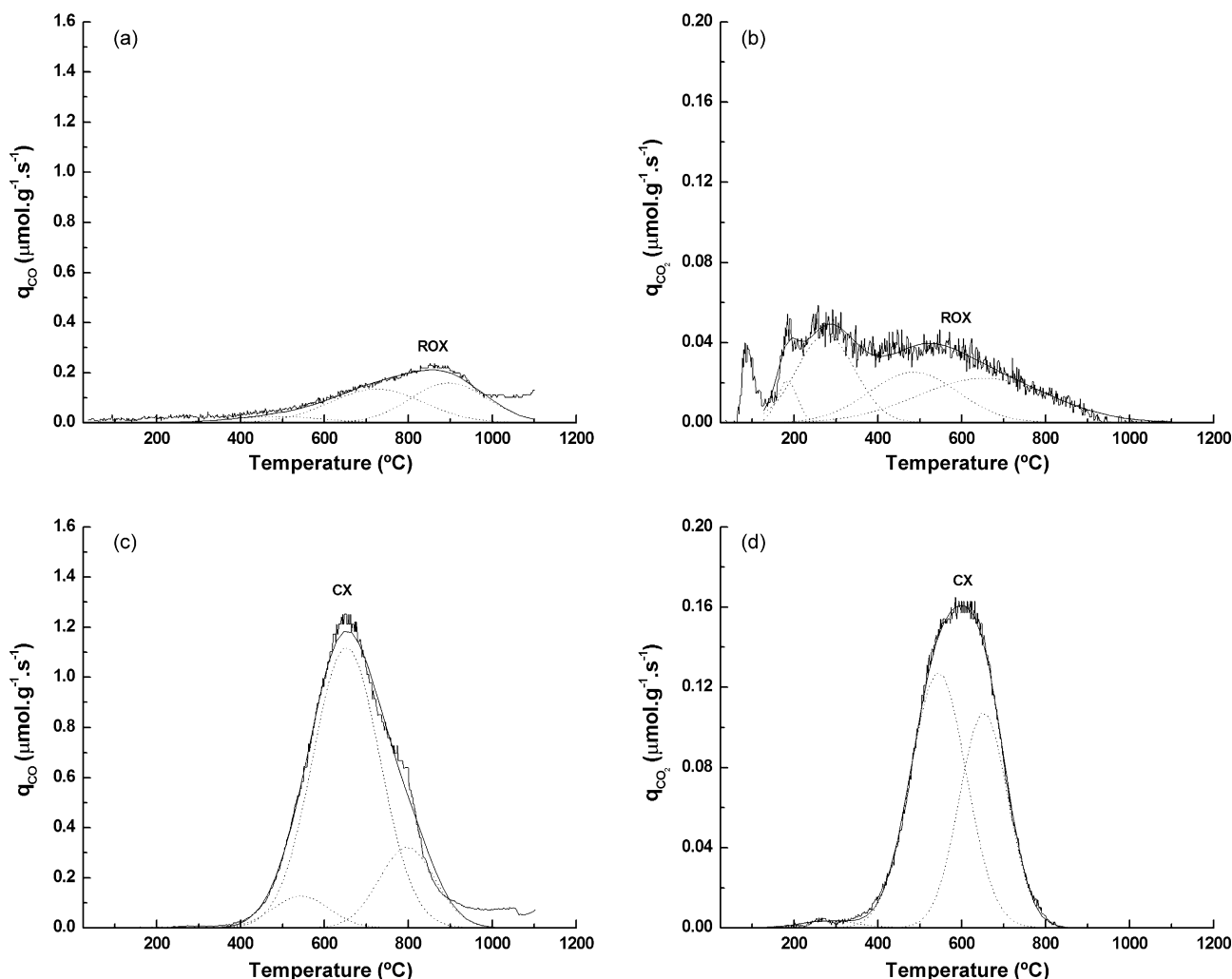


Fig. 2. TPD spectra and deconvolution (dotted lines): (a) CO and (b) CO₂ evolution for ROX; (c) CO and (d) CO₂ evolution for CX after activation.

Table 4

Concentrations of the different oxygen functional groups released by TPD during chemical characterization of ROX and of the CX material after activation with O₂

Catalyst	CO		CO and CO ₂		CO ₂	
	Phenol (μmol/g)	Quinone (μmol/g)	Anhydride (μmol/g)	Lactone (μmol/g)	Carboxylic acid (μmol/g)	
ROX	440	440	80	100	110	
CX	2700	650	250	190	7	

200 °C and 6.9 bar of oxygen partial pressure. The results obtained are shown in Fig. 3 where it is observed that the non-catalytic WAO of aniline at the given conditions cannot be neglected. However, it is evident that the introduction of carbon materials in the reaction system (0.8 g) is needed in order to increase the aniline removal efficiency. Table 5 reports aniline conversions (X_{ANL}) after 1 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).

In the non-catalytic WAO of aniline the rate of conversion decreases markedly with the time, apparently almost levelling-off after 3 h. Similar findings were reported in equivalent experiments of non-catalytic WAO of aniline [25]. After a long time of reaction (5 h) the conversion is 69%. In terms of TOC removal at the same time (5 h) the TOC conversion is only about 45%, which results in a selectivity to non-organic compounds of 66%. The significant removal of aniline obtained in the experiment performed without any catalyst indicates that this compound can be degraded at the given

Table 5

Aniline conversions (X_{ANL}) after 1 and 5 h of reaction, TOC conversions (X_{TOC}) and selectivity to non-organic compounds (S_{NOC}) after 5 h of reaction, and initial aniline removal rates (r_0) obtained in the WAO/CWAO experiments at 200 °C and 6.9 bar of oxygen partial pressure

Catalyst	$X_{ANL, 1h}$ (%)	$X_{ANL, 5h}$ (%)	$X_{TOC, 5h}$ (%)	$S_{NOC, 5h}$ (%)	$r_0 \times 10^{-2}$ (mg g _{cat} ⁻¹ min ⁻¹)
Blank	62	69	45	66	–
ROX	85	97	92	95	0.3 ± 0.1
CX	98	99	86	86	1.1 ± 0.3

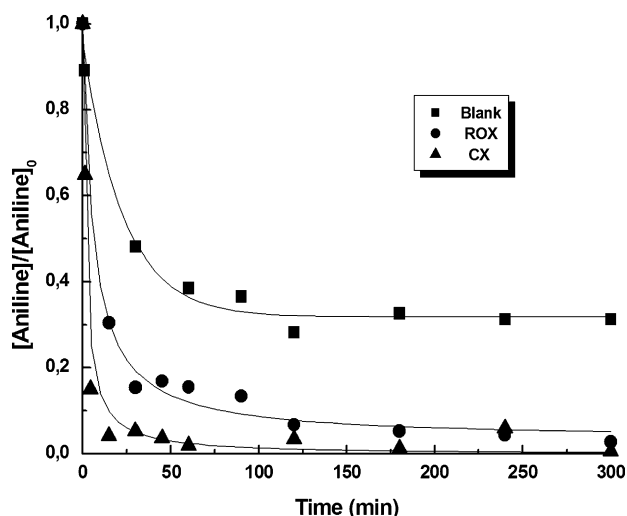


Fig. 3. WAO/CWAO aniline removal curves at 200 °C and 6.9 bar of oxygen partial pressure obtained in the absence of catalysts and in the presence of ROX and CX materials.

conditions. However, further removal of more recalcitrant oxidation products is difficult to achieve without the aid of a suitable catalyst.

Aniline conversion after 1 h of reaction increases from 62% (69% after 5 h) obtained in the non-catalytic experiment to 85% (97% after 5 h) when the ROX material was used and to almost complete conversion when the CX material was used. This increase in aniline removal may be interpreted in terms of adsorption and catalytic activity of the materials. Comparing CX with ROX, it is observed that the former is more efficient to remove aniline than the latter. The initial aniline removal rates (r_0) achieved with each sample are shown in the last column of Table 5. The initial aniline removal rate increases from $30 \text{ mg}_{\text{cat}}^{-1} \text{ min}^{-1}$ with the ROX catalyst, to $110 \text{ mg}_{\text{cat}}^{-1} \text{ min}^{-1}$ with the CX catalyst. The overall efficiency of both carbon materials should reflect a combined effect of their mesoporous character and surface oxygen functionality (as measured by the CO/CO_2 ratio obtained by TPD). In CWAO of aqueous

methyl and dimethylamines using activated carbons as catalysts, the observed catalytic activity was related to the presence of oxygenated functional groups on the activated carbons, being proposed that the quinone surface groups (releasing CO by TPD) were those responsible for the catalytic activities, while carboxylic, lactone and anhydride groups, releasing CO_2 , were responsible for a catalytic activity inhibition [19]. In a recent study [26] we discovered that the CX catalyst undergoes surface modification (decrease of the CO/CO_2 ratio) when used in the CWAO process, supporting our interpretation on the catalytic role of the groups releasing CO by TPD.

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 samples collected as the reaction proceeded acquired an increasingly intense orange colour, suggesting the formation of nitrogen containing intermediate compounds, whilst when using the carbon materials the collected samples remained non-coloured, suggesting that the reaction proceeds through a different reaction mechanism. HPLC analysis of the reaction samples were performed for both WAO and CWAO, confirming the occurrence of different intermediate compounds. The analysis failed to detect nitrobenzene, 4-nitrophenol, 1,3-benzoquinone and 3-aminophenol. Some traces which could correspond to phenol, hydroquinone, azobenzene, azoxybenzene and 4-aminoazobenzene were detected but not positively identified due to the very minute amounts present in solution. In addition, there are other unidentified trace compounds. The reported CWAO of aniline using a Ru/CeO_2 catalyst [25] includes a wide range of organic by-products, such as phenazine, acridinamine, formamidoacridine, azobenzene, azoxybenzene, oxanilide, phenylformamide, phenylacetamide, nitrobenzene, nitrosobenzene, nitrophenol, nitrosophenol, phenol, hydroquinone, catechol, benzoquinone and carboxylic acids. These intermediates are involved in a complex reaction network and may not be detected in a given experiment due to their reactivity, or because they are not identified by the analytical method. Our findings are in line with two of the proposed routes for the CWAO of aniline [25]: (a) the oxidative removal of the aniline group

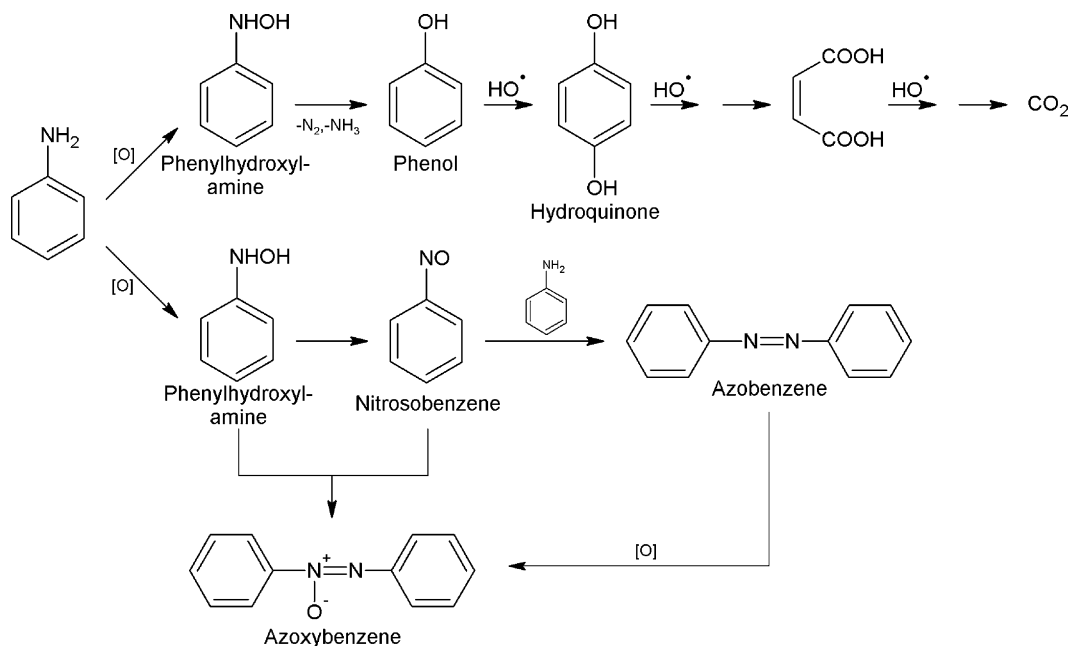


Fig. 4. Possible routes for aniline CWAO in the presence of ROX and CX materials.

Table 6
Results published in the literature concerning works devoted to the CWAO of aniline

Catalyst	Po ₂ (bar)	T (°C)	g _{anil} /g _{cat}	Reaction time (h)	X _{ANL} (%)	S _{NOC} (%)	Reference
Ru/CeO ₂	20	160–230	0.46	3	93–100	–	[28]
Pt/MWNT Pt/CX Pt/AC	6.9	200	0.19	2	99–100	87–95	[13]
MCM-41 VMCM-41 (Cr)MCM-41 (Cu)MCM-41	6.9	200	0.19	2	41–96	58–76	[29]
Ru/CeO ₂	20	160–230	0.46	3	80–100	73–96	[30]
MWNT Pt/MWNT	6.9	200	0.19	2	46–100	79–85	[31]
CX ROX	6.9	200	0.19	5	97–99	86–95	This work

followed by hydroxylation and ring cleavage and (b) the formation of di-aromatic compounds (Fig. 4). The oxidizing species are oxygen either in the bulk or adsorbed (which we represented by [O]) and the hydroxyl radical HO• readily formed under CWAO conditions.

Although the theoretical reaction network [25] predicts the primary products formed in the presence of O₂ and H₂O alone to be diphenylamine, nitrosobenzene, nitrobenzene and phenol, they are not necessary detectable. In our case phenylhydroxylamine is a key intermediate, which can be oxidised to nitrosobenzene and provide the route to the di-aromatics, or hydroxylated to hydroxylaminophenol leading to the formation of phenol, by the release of N₂ and NH₃ (most probably NH₄⁺ under the CWAO conditions). Phenol will undergo oxidation through hydroquinone formation, which normally leads to benzoquinone, but under CWAO conditions is readily cleaved and oxidized, thus difficult to isolate experimentally.

The TOC conversion observed after 5 h of reaction when using the ROX material increased from 45% (with a corresponding selectivity to non-organic compounds of 66%) when no catalyst was used to 92% (selectivity to non-organic compounds of 95%). When the CX material was used, the TOC conversion value obtained after 5 h, although lower than that obtained with the ROX material, is also very high, 86% (selectivity to non-organic compounds of 86%) being obtained. The differences observed in the TOC removal efficiency of ROX and CX may be ascribed to a better removal of the intermediate compounds resulting from aniline oxidation by adsorption on the surface of the ROX material. The mesoporous nature of CX explains the better aniline removal results, because the adsorption and degradation of somewhat bulky molecules, like aniline, are favoured at the surface of mesoporous materials. The microporous nature of ROX favours the adsorption and degradation of smaller oxidation intermediate molecules, with a better TOC removal being obtained with this material, when compared to CX.

Overall rationalization of the results seems to indicate the occurrence of a different adsorption/reaction mechanism when the ROX material or the CX material is used. At a first glance, it seems that the CX material possesses higher intrinsic catalytic activity than the activated carbon and that this is related to the specific surface chemistry.

3.2.2. Effect of catalyst mass and reaction temperature

In order to better understand the adsorption/reaction mechanism occurring in the CWAO of aniline with the use of the CX material, further experiments were performed, decreasing the catalyst mass. It was observed that, reducing the catalyst mass from 0.8

to 0.4 g, the aniline removal pattern was 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 min 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 play a primary role in the initial step of the aniline degradation mechanism, 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 [27].

The influence of temperature on the CX aniline removal efficiency was also studied to conclude about the contributions of catalytic activity and adsorption of the material on the global aniline removal mechanism. Both removal contributions are affected by temperature, but in opposite ways. When temperature is decreased, catalyst activity is decreased and surface adsorption is increased. When temperature is increased, the reverse occurs. When the reaction temperature was reduced from 200 to 160 °C, an evident decrease of the aniline removal efficiency was observed, being concluded that the effect of catalyst activity of the CX materials is more important than the effect of adsorption.

The results obtained in this work are compared with others published in the literature [13,28–31] using metal supported catalysts (Table 6). The performances are comparable or even better in some cases, showing that carbon xerogels are promising catalysts for CWAO.

4. Conclusions

A carbon xerogel prepared by the conventional sol–gel method was tested in the CWAO of aniline at 200 °C and 6.9 bar of oxygen partial pressure and found to be a good catalyst for CWAO processes. Almost complete removal of aniline was obtained 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 related to their mesoporous character and specific surface chemistry. The higher mesoporosity of the carbon xerogel, in contrast with the microporous nature of Norit ROX 0.8, explains the better aniline removal results, due to favoured adsorption and degradation of large molecules on mesoporous materials. The microporous nature of ROX favours the adsorption and degradation of smaller oxidation intermediate molecules, explaining the

better TOC removal values obtained with this material. Experiments performed with different masses of carbon xerogel allowed to conclude that the CWAO of aniline with this material involves an initial and essential step of adsorption and radical activation at the material surface. By analysis of the influence of temperature on the global aniline removal efficiency it was found that the effect of catalytic activity is more important than the effect of adsorption at the carbon xerogel surface.

Acknowledgements

The authors gratefully acknowledge Fundação para a Ciência e a Tecnologia for financial assistance (projects POCI/58252/EQU/2004, POCTI/1181/2003 and SFRH/BD/16565/2004), with contribution from FEDER. AMTS acknowledges the financial support from POCI/NO10/2006. AR, IM and MR are no longer affiliated to LCM.

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