



Catalytic properties of carbon materials for wet oxidation of aniline

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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 defoliants.

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 CWAQ 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

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