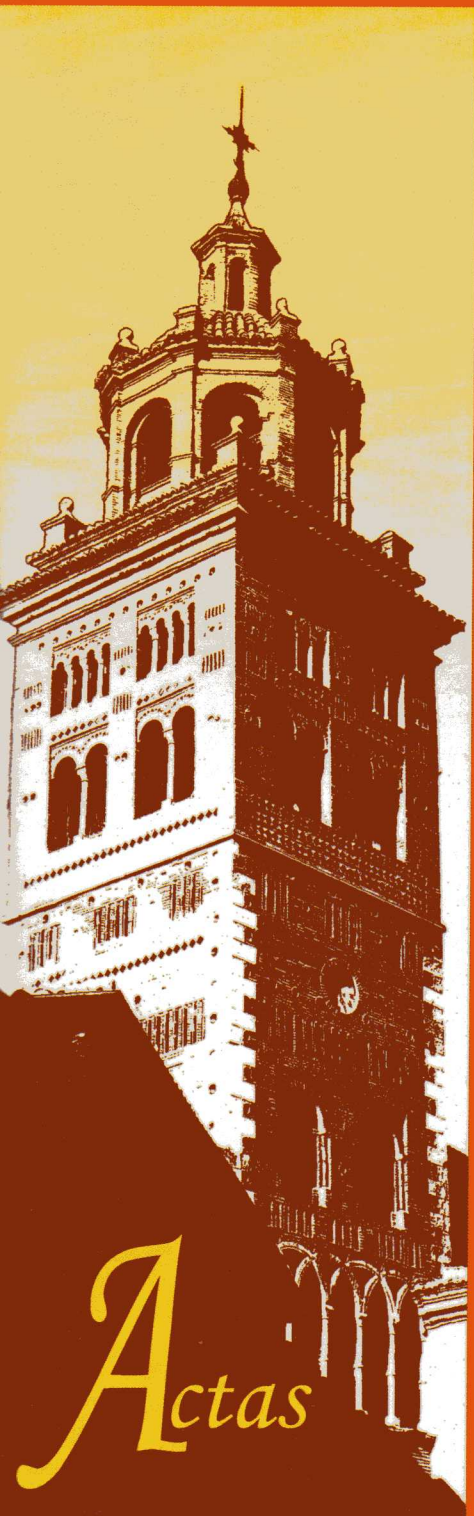
GRUPO ESPAÑOL CARBÓN

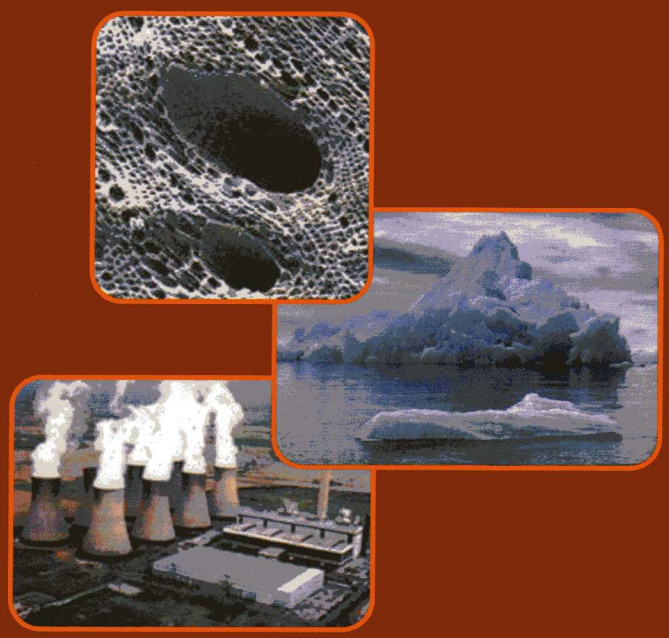
IX Reunión del Grupo Español del Carbón

22-24 Octubre 2007

Teruel

Sede Territorial de la Diputación General de Aragón





Actas

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EFFECT OF TEXTURAL AND CHEMICAL PROPERTIES OF CARBON MATERIALS IN THE CATALYTIC WET AIR OXIDATION OF ANILINE

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Keywords: carbon xerogels; mesoporous catalysts; surface chemistry

1. Introduction

Previous works reporting the use of carbon materials in the oxidative treatment of aromatic compounds and of nitrogen containing compounds seem to indicate that their catalytic activity is intimately related to their surface chemistry and porous texture [1-3]. In this work we prepared a mesoporous carbon xerogel (CX) material with a significant amount of oxygen functional groups and tested it in the Catalytic Wet Air Oxidation (CWAO) of aqueous aniline solutions. A commercial activated carbon (ROX, from Norit) was used as standard for comparison purposes. The results will have predictive value in establishing relationships between structure and catalyst efficiency in CWAO.

2. Experimental

The carbon xerogel material was prepared by polycondensation of resorcinol with formaldehyde (1:2), using an initial precursor solution pH of 6.1, followed by oxidation with O_2 at 400ºC, adapting the procedure described elsewhere [4]. The carbon materials were characterized by thermogravimetric analysis (TGA), temperature programmed desorption (TPD), N_2 adsorption and scanning electron microscopy (SEM). The oxidation reactions were performed in a 160 mL stainless steel high pressure reactor (model 4564, Parr Instrument Co. Ltd., Illinois, USA). Liquid samples were withdrawn from the reactor at given times to quantify aniline concentration and total organic carbon (TOC) content.

3. Results and discussion

Textural and chemical characterization shows that the prepared CX material presents a strong mesoporous character and appreciable concentration of oxygen functional groups (Table 1). In comparison to activated carbon, the CX material is more mesoporous (ROX is essentially microporous) and contains a significant concentration of oxygen functional groups (greater than ROX), as determined by TGA and by integration of the CO and CO_2 TPD spectra (Figure 1).

Table 1. Textural characterization, chemical characterization and reaction results obtained with the carbon materials in the CWAO of aniline.

Catalyst	S_{MES} (m^2/g)	CO (μmol/g)	CO_2 (μmol/g)	CO/CO_2	$X_{ANL,\ 1\ h}$ * (%)	$X_{TOC,\ 5\ h}$ * (%)	$r_0 \times 10^{-2}$ ($mg_{anl}.g_{cat}^{-1}.min^{-1}$)
ROX	110	1160	330	3.5	85	92	0.3 ± 0.1
CX	210	3740	470	8.0	98	86	1.1 ± 0.3

* For the blank experiment (no catalyst): $X_{ANL,\ 1\ h}$ = 62 % and $X_{TOC,\ 5h}$ = 45 %.

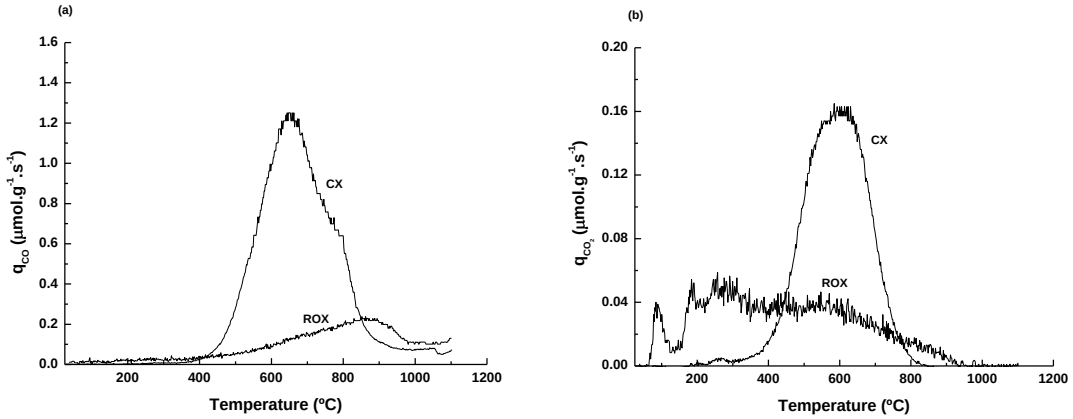

Figure 1. TPD spectra of the carbon materials: (a) CO evolution; (b) CO_2 evolution.

The CWAO of aniline at 200ºC and 6.9 bar of oxygen partial pressure in the presence of CX lead to almost complete aniline conversion after one hour and to high TOC removal at the end of reaction, as shown in Table 1. The conversion of aniline is higher for CX relatively to ROX, which can be associated with the higher mesoporosity of CX. On the other hand, the microporous nature of ROX favors the adsorption and oxidation of smaller intermediate compounds, leading to a more efficient TOC reduction.

In addition, the differences in the surface chemistry of both materials are also expected to influence the observed performances in aniline removal. The overall efficiency should reflect a combined effect of the materials 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 catalyst [3], 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 as CO by TPD) were those responsible for the catalytic activities, while carboxylic, lactone and anhydride groups, releasing as CO_2, were responsible for a catalytic activity inhibition [3]. Thus, catalytic activity in carbon materials seems to be favored by higher CO/CO_2 ratios. Further reaction runs with CX, varying catalyst mass and the reaction temperature, put in evidence that the effect of catalytic activity in the efficiency of this material is more pronounced than the effect of adsorption.

As a final conclusion, the mesoporous texture of CX with specific surface chemistry leads to a faster conversion of aniline like aromatic compounds, making them a potential alternative to the conventional activated carbon catalysts used in CWAO processes.

4. Acknowledgments

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

5. References

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