PLATINUM CATALYSTS SUPPORTED ON MWNT FOR LIQUID PHASE DEGRADATIVE OXIDATION OF NITROGEN CONTAINING COMPOUNDS

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Since their discovery [1], carbon nanotubes (CNT) have attracted great interest from both a fundamental and an applied point of view, due to their high mechanical strength and unique electrical and thermal properties [2]. These characteristics are also interesting in the context of using CNT as a support for heterogeneous catalysts in liquid-phase reactions. Some examples of this type of application using multiwalled carbon nanotubes (MWNT) have been reviewed recently [3]. Our experience with carbon supported noble metal catalysts applied to catalytic wet air oxidation (CWAO) of liquid effluents [4] prompted us to prepare platinum catalysts supported on surface oxidized MWNT, to be used in the liquid phase degradative oxidation of nitrogen containing compounds, such as aniline and azo dyes.

The catalysts Pt1, Pt2 and Pt3 were prepared by excess solution impregnation, using different metallic precursors dissolved in various solvents, respectively $[PtI_2(CO)_2]$ in toluene, H_2PtCl_6 in water and $[Pt(CH_3)_2(C_8H_{12})]$ in hexane. The metal dispersion (D_M) was determined by H_2 pulse chemisorption (Table 1). The prepared catalysts were then tested in the CWAO of aniline. The aniline conversion ($X_{Aniline}$), TOC abatement (X_{TOC}) and selectivity towards CO_2 formation (S_{CO2}) obtained after 2 h of reaction at 200ºC and 6.9 bar of oxygen partial pressure are resumed on Table 1.

Table 1 – Catalytic wet air oxidation of aniline, at 2 hours conversion

Catalyst	**D_M (%)**	**$X_{Aniline}$ (%)**	**X_{TOC} (%)**	**S_{CO2} (%)**
No catalyst	-	45.0	27.4	60.8
MWNT	-	54.0	45.7	84.6
Pt1	16.5	98.5	66.2	67.2
Pt2	26.8	99.4	78.3	78.8
Pt3	27.4	99.5	65.0	65.3

All prepared catalysts exhibit very good activity (aniline conversion > 98% at 2 h of reaction time), which can be attributed to the high surface area (175 m^2/g) and to the complete absence of micropores in the MWNT, providing an efficient surface contact between aniline and the active sites. Although, the non-catalytic wet air oxidation of aniline cannot be neglected under the reaction conditions employed, it is obvious that supporting platinum on MWNT significantly increases both aniline and TOC conversions. The activity of these catalysts depends on the type of precursor used in their preparation, decreasing in the order $[Pt(CH_3)_2(C_8H_{12})]$ > H_2PtCl_6 > $[PtI_2(CO)_2]$, which is in agreement with the D_M (Table 1). The S_{CO2} decreases in the order H_2PtCl_6 > $[PtI_2(CO)_2]$ > $[Pt(CH_3)_2(C_8H_{12})]$. The highest S_{CO2}, 78.8% after 2 h of reaction, was obtained with the catalyst prepared with H_2PtCl_6. This catalyst was selected for further studies with azo dyes.

The oxidative degradation of aqueous solutions of three dyestuffs – Chromotrop 2R (C), Erionyl Red B (ER) and Solophenyl Green Ble 155% (SG), mono-, di- and trisazo dyes, respectively – was carried out using the Pt2 catalyst at 150ºC and 6.9 bar of oxygen partial pressure. The results obtained are given in Table 2. It was observed that the organic dyes could not be decomposed under these conditions in the non-catalytic process. In the presence of the Pt2 catalyst, the dye conversion and solution TOC were significantly enhanced. After 2 h of reaction, almost 100% conversion was obtained for all azo dyes. The efficiency of TOC abatement decreased in the order di- > mono- > tris-, a total color bleaching being observed for all solutions.

Table 2 – Catalytic wet air oxidation of azo dyes at 150ºC, 2 hours residence time.

Azo dye	**Catalyst**	**X_{Dye} (%)**	**X_{TOC} (%)**	**S_{CO2} (%)**
C	No	0	0	-
	Yes	100	63.5	63.5
ER	No	28.0	0	0
	Yes	99.5	78.1	78.5
SG	No	0	0	-
	Yes	99.5	21.2	21.3

These results show the potential capabilities of MWNT as a support for metal catalysts, in particular for liquid-phase oxidation reactions.

Acknowledgment. This work was supported by Fundação para a Ciência e a Tecnologia POCTI/FEDER (POCTI/EQU/33401/2000 and POCTI/1181/2003) and by CRUP (F-12/03). JG acknowledges Becas Internationales Universidad Complutense/ Flores Valles for finantial support.

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