Available online at www.sciencedirect.com

Applied Catalysis B: Environmental 54 (2004) 175–182

APPLIED CATALYSIS B: ENVIRONMENTAL

www.elsevier.com/locate/apcatb

Carbon nanotubes and xerogels as supports of well-dispersed Pt catalysts for environmental applications

H.T. Gomes[a,b], P.V. Samant[a], Ph. Serp[c], Ph. Kalck[c], J.L. Figueiredo[a], J.L. Faria[a,*]

[a] *Laboratório de Catálise e Materiais/Departamento de Engenharia Química, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[b] *Departamento de Tecnologia Química, Escola Superior de Tecnologia e de Gestão do Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-857 Bragança, Portugal*

[c] *Laboratoire de Catalyse, Chimie Fine et Polymères—Ecole Nationale Supérieure d'Ingénieurs en Arts Chimiques Et Technologiques, 118 route de Narbonne, 31077 Toulouse Cedex 04, France*

Received 8 December 2003; received in revised form 25 April 2004; accepted 13 June 2004

Abstract

Different types of carbon materials including multi-walled nanotubes (MWNT), carbon xerogels (CX) and activated carbon (AC) were used as supports to prepare platinum catalysts (1% w/w), which were tested in the treatment of aqueous aniline solutions by catalytic wet air oxidation (CWAO). The prepared materials and catalysts were characterized by several techniques (SEM/EDS, TEM, N_2 adsorption, TPD and H_2 chemisorption). All catalysts presented a very high activity for the removal of aniline and total organic carbon (TOC). Catalyst activity and selectivity toward CO_2 formation were found to depend on the nature of the support and concentration of oxygen containing functional groups on the surface of the materials.

Keywords: Multi-walled carbon nanotubes (MWNT); Carbon xerogels; Activated carbon; Carbon supported catalysts; Catalytic wet air oxidation (CWAO); Aniline.

1. Introduction

Carbon materials are often used as support for preparing metal-based catalysts. Carbon occurs in many allotropic forms, which includes fullerenes [1,2] and carbon nanotubes [3–7]. The discovery of carbon nanotubes triggered an intense research activity concerning their preparation, characterization and applications [8]. Carbon nanotubes can be produced in two forms, single-walled nanotubes (SWNT) or multi-walled nanotubes (MWNT). As a result of their mechanical and electronic properties, exciting new breakthroughs in materials and engineering science are expected. Exploring their ability as support for production of efficient heterogeneous catalysts is one of the current objectives of research. Although some examples of this type of application started to be referred [9–14], systematic studies comparing the performances of different forms of carbon as catalyst support are now required.

Other types of carbon materials with characteristic textural properties are the carbonized resorcinol/formaldehyde resins referred in the pioneering work on the synthesis of organic aerogels [15], normally designated by carbon aerogels and xerogels [16]. These materials have attracted an enormous attention, due to the possibility of fine-tuning their textural properties during the sol–gel method employed for their preparation.

Because morphology and size do play an important role in the dispersion of the metal phase [17], the present study aims at comparing the efficiency of different metal catalysts supported on carbon xerogel (CX), MWNT and activated carbon (AC) in an environmental application.

The treatment of aniline containing effluents by wet air oxidation (WAO) has been reported and aims at the total

---

* Corresponding author. Tel.: +351 225 081 645; fax: +351 225 081 449.
E-mail address: jlfaria@fe.up.pt (J.L. Faria).

0926-3373/$ – see front matter
doi:10.1016/j.apcatb.2004.06.009

Nomenclature

List of symbols

$[TOC]_0$	Initial TOC concentration (g/L)
$[TOC]_A$	TOC concentration of oxidized aniline (g/L)
$[TOC]$	TOC concentration at a given time (g/L)
$[TOC]_{CO_2}$	TOC concentration leaving as CO_2 (g/L)
$[A]_0$	Initial aniline concentration (g/L)
$[A]$	Aniline concentration at a given time (g/L)
X_A	Aniline conversion
X_{TOC}	TOC conversion
S_{BET}	BET surface area (m^2/g)
V_μ	Micropore volume (cm^3/g)
$S_{non\text{-}\mu}$	Non-microporous surface area (m^2/g)
D_M	Metallic dispersion (%)
d_P	Pt particle diameter (nm)
CO	CO released by TPD (μmol/g)
CO_2	CO_2 released by TPD (μmol/g)
CO/CO_2	Ratio between CO and CO_2 released by TPD
Total O_2	Total O_2 released by TPD (μmol/g)
W	Platinum concentration (g_{Pt}/L)
k	Kinetic rate constant (mol L^{-1} min^{-1})
K	Aniline adsorption constant (L/mol)
r	Reaction rate (mol min^{-1} $g_{Pt}{}^{-1}$)
r_0	Initial reaction rate (mol min^{-1} $g_{Pt}{}^{-1}$)

oxidation of the organic species present in the effluent to CO_2, N_2 and H_2O under relatively severe conditions of temperature and pressure (220–320 °C, 50–200 bar), using oxygen or air as oxidant [18–20]. Although very efficient, WAO involves high capital costs and costly safety measures, mainly due to materials corrosion, which requires the construction of large volume pressure reactors with special metal enriched alloys. This led to the development of catalysts capable of bringing the process conditions to more amenable values (125–220 °C, 5–50 bar) in order to reduce energy consumption and the corresponding processing costs. Several catalysts were studied in the last decades. Initially, homogenous catalysts were found to be very efficient, but their use for wastewater treatment entails a further separation step in the process in order to remove them from the final treated effluent. On the other hand, heterogeneous catalysts can be easily removed by filtration and they will be the best choice if they are active, stable and selective to harmless end products. Effective systems are reported for oxidation of model compounds (phenol, carboxylic acids) [21–23]. In a previous work of our group, carbon supported platinum catalysts were found to present such desirable characteristics [24].

Among the existing treatment technologies, catalytic wet air oxidation (CWAO) is an efficient option for the treatment of aniline containing wastewaters. Aerobic biodegradation of aniline can be achieved only at very low concentrations (up to 350 mg/L) without being toxic to nitrifying microorganisms [25]. Aniline is a key component in the production of polyurethane, it is used in the manufacture of dyes (including azo dyes) and intermediates for herbicides, other pesticides and rubber chemicals, such as vulcanization accelerators and antioxidants [26,27], thus being found in several types of wastewaters, including those from the textile industry. Due to the extreme toxicity of aniline, these wastewaters require further treatment. The US Environmental Protection Agency (EPA) has suggested a limit of 262 μg/L of aniline in water, based on health effects [27].

In the present paper, the preparation of Pt catalysts (1%) supported on CX, MWNT and AC by the method of incipient wetness (IW) is described. Their activities are then determined in the CWAO of aniline. Supports with different textural and surface chemical characteristics were used in order to correlate the support properties with the catalytic activity and selectivity towards CO_2 formation.

2. Experimental

2.1. Support preparation

Three different carbon based supports were used in the preparation of heterogeneous platinum catalysts, namely, MWNT, CX and an AC.

MWNT were prepared by chemical vapor deposition (CVD) of ethylene, using alumina-supported iron as catalyst [28]. The composite material obtained from the CVD production step, consisting of nanotubes, iron and alumina, was then purified by a sulphuric acid treatment. The aim of this step was to accomplish the total dissolution of alumina and the partial elimination of iron contained in the tubes. The final material has a purity of 97%. The nanotubes were further oxidized with HNO_3 (18% v/v) for 3 h in order to create oxygenated functional groups at their surface [10], which will act as anchoring sites for the platinum complexes. Finally, it was washed with water under reflux until neutrality (pH ≈ 6) of the rinsing waters and dried overnight at 110 °C.

The CX precursor was synthesized by the conventional sol–gel approach, using formaldehyde and resorcinol (2:1) and aqueous solution of sodium carbonate as catalyst in a ratio 200:60. The solution was mixed uniformly and kept for 1 day at room temperature and the gel was further cured at 50 °C and 90 °C for one day at each temperature. The red brown opaque solid gel was then cut, chopped and sectioned into the desired shape and size (around 1–2 mm). In order to promote additional cross-linking of the gel, 5% acetic acid was added to the solvent during the initial water to solvent (acetone) exchange. The excess water was then removed from the gel by several extractions with acetone for 10 h to obtain acetone filled gel. The acetone filled gel is then further exchanged several times with cyclohexane to remove the solvent from the gel for 10 h. Cyclohexane from the pores of the gel is removed slowly by evaporating at ambient temperature and then further by exposing it to hot air at about 50 °C for 2–3 h. The gel was carbonized at 800 °C under nitrogen flow of 150 mL/min for 6 h, with heating rate of 10 °C/min. The presence of sodium catalyses the pyrolysis reaction, hence, sodium from the carbonized gel is extracted, using HCl in a Soxhlet for 6 h, which was subsequently washed with demineralised water several times till pH 6–7, and dried overnight in oven at 110 °C.

The AC used was Norit ROX 0.8 in pellet form (0.8 mm diameter, 3–4 mm length), washed with hot hydrochloric acid during 12 h under reflux in order to remove mineral impurities. Later, it was washed with water under reflux until neutrality (pH 6) of the rinsing waters and finally dried overnight at 110 °C.

2.2. *Catalyst preparation*

Platinum (1%, w/w; Pt) catalysts supported on the different carbon materials were prepared by IW impregnation, using H_2PtCl_6 as metal precursor. After impregnation, the catalysts were dried overnight at 110 °C. Prior to reaction the catalysts were heat treated in nitrogen at 400 °C for 2 h, reduced in hydrogen at 350 °C for 3 h and flushed with nitrogen at 350 °C for 30 min in order to remove physisorbed hydrogen.

2.3. *Catalyst characterization*

The carbon supports were characterized by temperature programmed desorption (TPD). The samples were placed in a U-shaped quartz reactor and heated up to 1100 °C. CO and CO_2 evolution was recorded using a quadrupole mass spectrometer (Spectramass). The micropore volume (V_μ) and the non-micropore surface area ($S_{\text{non-}\mu}$) were calculated from the N_2 adsorption isotherms at 77 K obtained after outgassing at 350 °C under vacuum in an automatic analyzer (Coulter Omnisorp 100 CX) by using the *t*-method. The catalysts metal dispersion was measured by H_2 chemisorption at room temperature, using the same equipment. Scanning electron microscopy (SEM) on a JEOL JCM-35C (15 keV) was used for topographical and analytical characterization. Transmission electron microscopy (TEM) observations were performed on a Philips CM12 instrument (120 keV), using carbon-coated copper grids.

2.4. *Oxidation procedure*

The oxidation reactions were performed in a 160 mL, 316 stainless steel high-pressure reactor (model 4564, Parr Instrument Co. Ltd., IL, USA) equipped with a magnetically driven stirrer and a thermocouple. The reactor was heated by an electrical heating mantle controlled by a temperature controller unit (model PID 4842, Parr Instrument).

Typically, in an oxidation run, 75 mL of the aniline solution (2 g/L) and 0.8 g of catalyst (for CWAO runs) were placed inside the reactor. After 7 min flushing with N_2 in order to remove dissolved oxygen, the reactor was heated to the reaction temperature. Once the set temperature was achieved, the first sample was withdrawn, and then the reactor was pressurized with air. At this point the time of reaction was initialized. Periodically, 1 mL of liquid sample was collected from the reactor to undergo product analysis.

2.5. *Product and data analysis*

Aniline concentration during reaction 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 TOC content of the samples was determined in a TOC-analyzer (Shimadzu 5500A). This equipment determines in separate runs the sample total carbon (TC) by combustion at 700 °C 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 2%) were considered.

With the experimental values of aniline concentration and TOC, it is possible to calculate the reaction selectivity towards CO_2 according to a similar protocol previously established for phenol oxidation [29]. The initial TOC concentration ($[\mathrm{TOC}]_0$) and the TOC concentration removed due to aniline oxidation ($[\mathrm{TOC}]_\mathrm{A}$) are given by:

$$[\mathrm{TOC}]_0 = [\mathrm{A}]_0 \times \left(\frac{72}{93}\right) \qquad (1)$$

$$[\mathrm{TOC}]_\mathrm{A} = ([\mathrm{A}]_0 - [\mathrm{A}]) \times \left(\frac{72}{93}\right) = X_\mathrm{A}[\mathrm{TOC}]_0 \qquad (2)$$

where $[\mathrm{A}]_0$ is the initial aniline concentration, [A] the aniline concentration at a given time (72/93) the ratio carbon to total mass in the aniline molecule and X_A the aniline conversion.

The difference between the initial and the TOC value at a given time ([TOC]) is attributed to carbon leaving as CO_2:

$$[\mathrm{TOC}]_{\mathrm{CO_2}} = [\mathrm{TOC}]_0 - [\mathrm{TOC}] \qquad (3)$$

Thus, from the definition of selectivity towards CO_2:

$$\mathrm{CO_2}\ \text{selectivity} = \frac{[\mathrm{TOC}]_{\mathrm{CO_2}}}{[\mathrm{TOC}]_\mathrm{A}} = \frac{X_\mathrm{TOC}}{X_\mathrm{A}} \qquad (4)$$

where X_TOC is the conversion of TOC.

3. Results and discussion

3.1. *Catalyst characterization*

The BET surface area, the micropore volume and the surface area determined by the *t*-plot are shown in Table 1.

Table 1
Textural characterization of different carbon supports and corresponding platinum catalysts with their metallic dispersions

Material	S_{BET} (m^2/g)	V_{μ} (cm^3/g)[a]	$S_{non-\mu}$ (m^2/g)[a]	D_M (%)	d_P(nm)
MWNT	175	0.001	175	–	–
CX	724	0.110	524	–	–
AC	1053	0.405	113	–	–
Pt/MWNT	169	0.001	169	26.6	3.82
Pt/CX	662	0.138	325	29.2	3.48
Pt/AC	1064	0.409	125	25.0	4.06

[a] Determined by the *t*-plot.

As expected, the support with highest BET surface area is AC (1053 m^2/g). The reason lies essentially on the microporous character of the material with only 10.7% of the surface area due to non-microporous area. On the other hand, CX has a large percentage of mesopores contributing to the BET surface area (around 70% of the 724 m^2/g).

The MWNT support has the smallest BET surface area (175 m^2/g). Due to the production mechanism of this material, MWNT are essentially non-porous ($S_{BET} = S_{non-\mu}$) with all the observed surface area owed to adsorption on the external surface of the tubes [10]. The surface area agrees with the calculated geometric area suggesting that the MWNT have both ends closed and their structure has not been strongly affected by the nitric acid treatment.

The amounts of oxygen containing functional groups were evaluated by TPD and the results obtained are shown in Fig. 1.

It is clear from the profiles obtained that the more oxidized materials correspond to CX and AC. However, MWNT contain oxygenated groups along their surface walls to a non-negligible extent. This is an important observation, because it leads to the conclusion that carbon nanotubes can be non-destructively oxidized along their sidewalls and subsequently, covalently functionalized. It is also worth mentioning that the TPD profiles of MWNT are quite distinct from AC or CX suggesting that different types of functional groups are present.

Analysis of Table 2 shows that there are significant differences between the amounts and types of oxygen containing functional groups in the supports. MWNT have

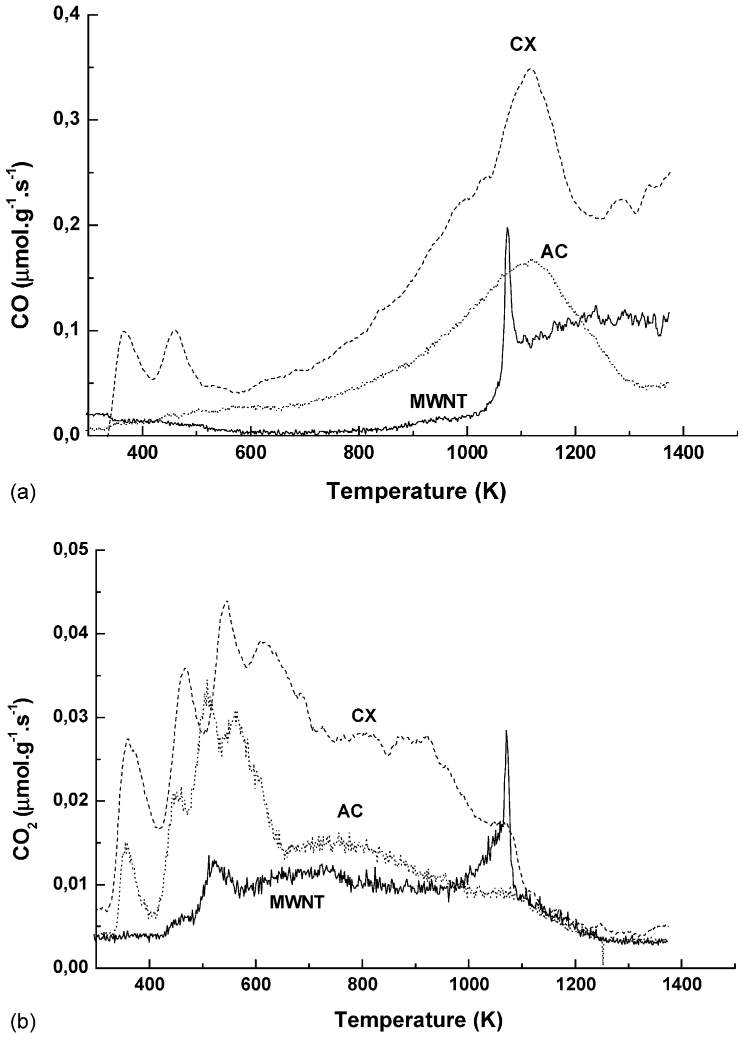


Fig. 1. Profiles of (a) CO and (b) CO_2 evolution during the TPD of different carbon materials.

Table 2
Total amounts of CO and CO_2 released by TPD during chemical characterization of the different carbon materials

Support	CO (μmol/g)	CO_2 (μmol/g)	CO/CO_2	Total O_2 (μmol/g)
MWNT	26	59	0.44	72
CX	709	217	3.27	572
AC	472	106	4.45	342

lower concentration of oxygen containing functional groups (72 $\mu mol_{O_2}/g$), CO_2 evolving oxygen groups predominating. CX and AC have larger amounts, respectively, 572 and 342 $\mu mol_{O_2}/g$, CO evolving oxygen groups predominating. Due to the amount of oxygen present at their surfaces, CX and AC are expected to exhibit stronger acidic character.

Impregnation with Pt leads to very similar metal dispersions in all the materials (D_M ranging from 25 to 29%) and consequently, the calculated diameter (d_P) of the Pt crystallites (assuming spherical geometry) is also similar (Table 1).

On the other hand, there were no drastic changes in the surface area of the resulting catalysts. In the case of CX, there is an increase on the reported V_μ that is produced at the expense of the mesoporous structure.

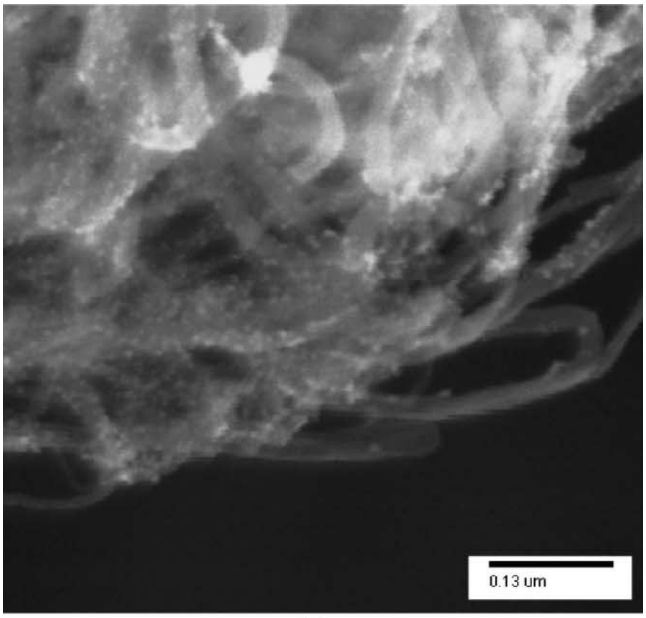
In most cases, the introduction of platinum can lead to catalytic gasification of the carbon material during the H_2 reduction step and is responsible for the increase in BET surface area of the AC based catalyst, although in this case, the increase in the micropore volume is more modest. Further support for the occurrence of gasification comes from the observation that methane was released during the reduction process in the preparation of the catalyst.

For MWNT the differences are too small to be significant. Some area is lost due to the introduction of platinum onto the surface, however that can be calculated to be not greater than 0.8 m^2/g (corresponding to the available metal surface area).

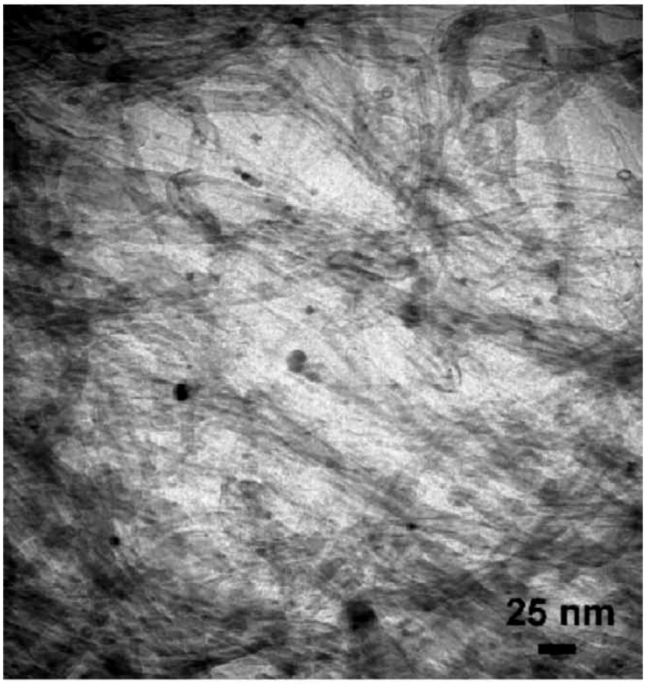
The good metal dispersion of all prepared catalysts was confirmed by the SEM/EDS and TEM analyses. SEM and TEM micrographs show that the platinum particles are very well distributed over the carbonaceous supports. The calculated average size of the particles was between 3.5 and 4.1 nm (Table 1), based on the measured dispersions. For Pt/CX and Pt/AC, Pt particles homogeneously distributed could be observed at lower magnifications. For Pt/MWNT, due to the fluffy nature of the material with a tendency to aggregate, higher magnifications were required to observe the Pt crystallites, which were masked by the material arrangement. The platinum particles on Pt/MWNT are clearly visible on SEM (Fig. 2a) and TEM (Fig. 2b) micrographs. The presence of Pt on the catalyst was confirmed by EDS analysis all over the sample.

3.2. Oxidation reactions

The prepared catalysts were tested in the CWAO of aniline at 200 °C and 6.9 bar of oxygen partial pressure. The results obtained are given in Fig. 3, where a run without catalyst is also shown for comparison purposes.



(a)



(b)

Fig. 2. Micrographs of the Pt/MWNT catalyst by (a) SEM and (b) TEM.

It can be observed from Fig. 3 that the oxidation of aniline occurs to some extent in the absence of catalyst, with 45.1% conversion after 2 h of reaction and 60.8% selectivity towards CO_2 formation. Observation of an increasingly intense orange color during the progression of the reaction suggested the formation of intermediate azoic compounds [22] accounting for the low selectivity of the non-catalytic WAO.

The observed conversion can be interpreted in terms of a pseudo first order kinetic scheme, were the rate is directly

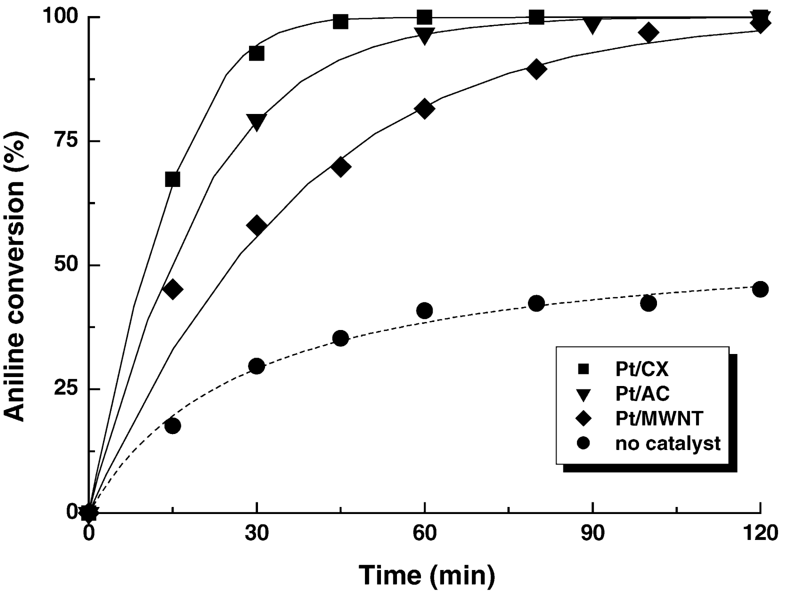


Fig. 3. Aniline conversion in the catalytic and non-catalytic WAO of aqueous solutions.

proportional to the catalyst coverage by the organic substrate (except in the case of non-catalytic WAO). The initial step corresponds to adsorption of aniline, followed by oxidation of the organic molecule, desorption of the oxidized radical and oxygen mediated degradation in solution [30]. Under these conditions, Langmuir-Hinshelwood type kinetics can be assumed:

$$r = \frac{(1/W)kK[\mathrm{A}]}{(1+K[\mathrm{A}])} \qquad (5)$$

where W is the active phase concentration (g_{Pt}/L), k the kinetic rate constant, K the aniline adsorption equilibrium constant and [A] the aniline concentration. The results of the fit are expressed in terms of the lines drawn in Fig. 3 (except for the non-catalytic case) and the corresponding values of k and K are given in Table 3. The initial rate (r_0, Table 3) is defined as the specific reaction rate per gram of metal when the reaction time is close to zero, which is when the concentration of aniline approaches its initial value. The initial rate (r_0) values were calculated fitting the kinetic model to all the experimental points. Analyzing the data, we can conclude that the initial reaction rates ($r = r_0$ for $t = 0$) decrease in the order Pt/CX > Pt/AC > Pt/MWNT. As the reaction proceeds (higher aniline conversion), the rates of reaction (r) obtained for each catalytic system decrease with the decreasing of aniline concentration in solution. From 0 to 100% of aniline conversion, the measured reaction rates follow the same order as obtained for the initial reaction rates.

It is worth mentioning that the kinetic rate constant is higher in the case of Pt/MWNT, while the equilibrium constant for adsorption is very low, resulting in a low overall initial rate. For the other catalysts the effect is quite the opposite. Thus, due to a more regular structure, MWNT will allow to produce well-dispersed catalysts at higher metal loads, making it possible to take advantage of the observed high reaction rates reported here.

It is clear that the introduction of the catalyst led to an almost complete conversion of aniline in the three cases: comparing the conversion after 2 h of reaction ($X_{2\,\mathrm{h}}$, Table 3) for all catalysts we can observe that almost no difference exists between them. After 2 h of reaction 100% conversion of aniline was obtained with Pt/CX and Pt/AC catalysts, and 98.8 % conversion with the Pt/MWNT catalyst. Trying to correlate the observed catalyst activities with the textural and chemical characteristics of the respective supports (Tables 1 and 2), it is clear that the activity is favoured by the mesoporous character of the support and by the concentration of oxygen bearing functional groups present on its surface. These characteristics facilitate aniline adsorption on the support surface for subsequent reaction at the

Table 3
Reaction data for the CWAO of aniline, using platinum supported on different carbon materials at 200 °C and 6.9 bar of oxygen partial pressure

Catalyst	r_0 (10^{-3} mol min^{-1}g$_{\mathrm{Pt}}$$^{-1}$)	k (10^{-3} mol L^{-1} min^{-1})	K (L mol^{-1})	$X_{2\,\mathrm{h}}$ (%)	CO_2 selectivity (2 h, %)
Pt/MWNT	5.0	2.37	13.4	98.8	86.9
Pt/CX	8.5	1.42	82.9	100	92.7
Pt/AC	7.1	1.75	35.0	100	94.5
No catalyst	–	–	–	45.1	60.8

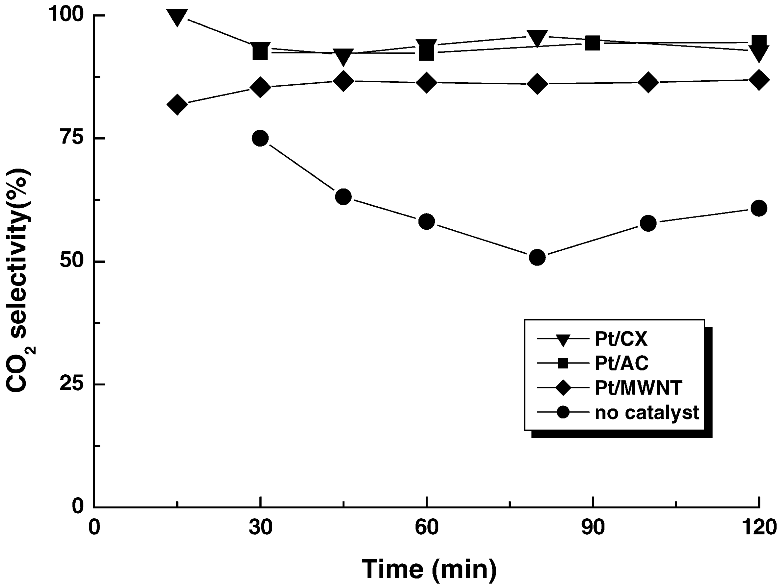


Fig. 4. Selectivity towards CO_2 formation in the catalytic wet air oxidation of aniline, using platinum supported on different carbon materials.

metal active sites. Higher mesoporous area allows easier diffusion of reactants than in microporous environments. Due to resonance effects [31], aniline develops a significant basicity, favoring adsorption on acid supports.

The calculated selectivity to CO_2 (Table 3) follows the aniline conversion, with the selectivity values increasing in the same order. For each catalyst, the selectivity is practically constant in time, which is another advantage of CWAO when compared to WAO (Fig. 4).

Simultaneous analysis of Figs. 3 and 4 leads to the conclusion that Pt/CX and Pt/AC catalysts are very active and selective (selectivity of around 95% after 2 h of reaction). No coloration was developed during the course of the reaction. Nevertheless Pt/MWNT is also very active, its performance is slightly inferior, only 98.8% conversion being registered. During the catalytic experiment with Pt/MWNT, a faint orange color developed as the reaction proceeded (selectivity of 87% after 2 h of reaction), indicating the occurrence of some stable intermediates. The CWAO of aniline is known to lead to the formation of some azo compounds (hydrazobenzene, azobenzene and azoxybenzene), nitrogenous aromatic compounds (*p*-aminophenol, nitrobenzene, *p*-nitrophenol and nitrosobenzene) and other aromatics (phenol, hydroquinone, catechol and benzoquinone) [32]. However, due to their mechanical strength the carbon MWNT are expected to be very resistant in longer cycles of catalyst re-use.

4. Conclusion

Pt catalysts supported on different carbon materials by IW impregnation showed a very high efficiency for the CWAO of aniline. Practically complete removal of aniline was obtained at 200 °C with all the catalysts after 2 h of reaction. Although, all catalysts are very active, they presented different selectivity toward CO_2 formation, Pt/CX and Pt/AC being more selective than the Pt/MWNT catalyst. Nevertheless, this work represents one of the first applications of MWNT in environmental protection. Additionally, the results obtained suggest that better supported-catalysts can be produced at higher metal loading. Indeed, high loading and well-dispersed nanotube-supported catalysts have been already recently reported [14].

A global analysis of the results based on the comparison of initial rates leads to the conclusion that the activity and the selectivity to CO_2 of the Pt supported catalysts increases with the mesoporous character of the materials and with the concentration of oxygen containing functional groups on the surface of the support.

Environmental protection is a great challenge to be faced by industry, since the environmental regulations will certainly impose more stringent limits in the future, which will may justify the use of more sophisticated catalysts. The results obtained confirm the potentialities of these new carbon materials as supports for the development of highly active heterogeneous catalysts.

Acknowledgment

This work was supported by Fundação para a Ciência e a Tecnologia, POCTI and FEDER (Projects POCTI/EQU/33401/2000 and POCTI/118/2003) and by CRUP (F-12/03).

References

[1] H.W. Kroto, J.R. Heath, S.C. Obrien, R.F. Curl, R.E. Smalley, Nature 318 (1985) 162.

[2] H.W. Kroto, Nature 329 (1987) 529.

[3] S. Iijima, Nature 354 (1991) 56.

[4] S. Iijima, T. Ichihashi, Y. Ando, Nature 356 (1992) 776.

[5] S. Iijima, T. Ichihashi, Nature 363 (1993) 603.

[6] M. Terrones, N. Grobert, J. Olivares, J.P. Zhang, H. Terrones, K. Kordatos, W.K. Hsu, J.P. Hare, P.D. Townsend, K. Prassides, A.K. Cheetham, H.W. Kroto, D.R.M. Walton, Nature 388 (1997) 52.

[7] S. Iijima, Physica B 323 (2002) 1.

[8] C.N.R. Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, Chem. Phys. Chem. 2 (2001) 78.

[9] B. Rajesh, K.R. Thampi, J.M. Bonard, N. Xanthopoulos, H.J. Mathieu, B. Viswanathan, J. Phys. Chem. B 107 (2003) 2701.

[10] R. Giordano, P. Serp, P. Kalck, Y. Kihn, J. Schreiber, C. Marhic, J.-L. Duvail, Eur. J. Inorg. Chem. (2003) 610.

[11] K. Hernadi, L. Thien-Nga, E. Ljubovic, L. Forro, Chem. Phys. Lett. 367 (2003) 475.

[12] J.P. Tessonnier, L. Pesant, C. Pham-Huu, G. Ehret, M.J. Ledoux, Scientific Bases for the Preparation of Heterogeneous Catalysts, vol. 143, 2002, p. 697.

[13] J.M. Nhut, R. Vieira, L. Pesant, J.P. Tessonnier, N. Keller, G. Ehret, C. Pham-Huu, M.J. Ledoux, Catal. Today 76 (2002) 11.

[14] P. Serp, M. Corrias, P. Kalck, Appl. Catal. A 253 (2003) 337.

[15] R.W. Pekala, J. Mater. Sci. 24 (1989) 3221.

[16] E.J. Zanto, S.A. Al-Muhtaseb, J.A. Ritter, Ind. Eng. Chem. Res. 41 (2002) 3151.

[17] A.T. Bell, Science 299 (2003) 1688.

[18] G. Chen, L. Lei, P.-L. Yue, Ind. Eng. Chem. Res. 38 (1999) 1837.

[19] L. Lei, G. Chen, X. Hu, P.-L. Yue, Water Environ. Res. 72 (2000) 147.

[20] X. Hu, L. Lei, G. Chen, P.L. Yue, Water Res. 35 (2001) 2078.

[21] L. Oliviero, J. Barbier Jr., D. Duprez, A. Guerrero-Ruiz, B. Bachiller-Baeza, I. Rodríguez-Ramos, Appl. Catal. B 25 (2000) 267.

[22] L. Oliviero, J. Barbier Jr., D. Duprez, Appl. Catal. B 40 (2003) 163.

[23] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Catal. Today 75 (2002) 23.

[24] H.T. Gomes, J.L. Figueiredo, J.L. Faria, Appl. Catal. B 27 (2000) 217.

[25] S.H. Gheewala, A.P. Annachhatre, Water Sci. Technol. 36 (1997) 53.

[26] Petrochemicals Manufacturing, Pollution Prevention and Abatement Handbook, World Bank Group, July 1998, pp. 371.

[27] J. Sarasa, S. Cortés, P. Ormad, R. Garcia, J.L. Ovelleiro, Water Res. 36 (2002) 3035.

[28] M. Corrias, B. Caussat, A. Ayral, J. Durand, Y. Kihn, P. Kalck, P. Serp, Chem. Eng. Sci. 58 (2003) 4475.

[29] S.S. Lin, C.L. Chen, D.J. Chang, C.C. Chen, Water Res. 36 (2002) 3009.

[30] H.T. Gomes, J.L. Figueiredo, J.L. Faria, P. Serp, P. Kalck, J. Mol. Catal. A 182–183 (2002) 48.

[31] M.B. Smith, J. March, March's Advanced Organic Chemistry. Reactions, Mechanisms, and Structure, Wiley, New York, 2001.

[32] L. Oliviero, H. Wahyu, J. Barbier Jr., D. Duprez, J.W. Ponton, D. Metcalfe, D. Mantazavinos, Trans. Inst. Chem. Eng. 81 (2003) 384.