

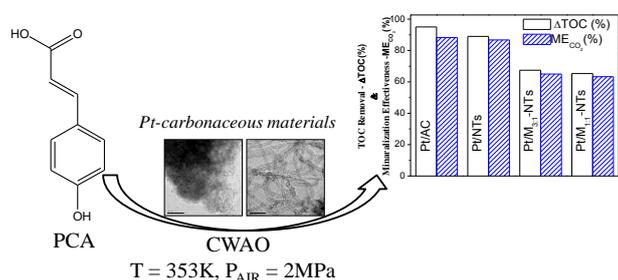
Enhanced Catalytic Activity of Platinum Carbonaceous Materials in Catalytic Wet Air Oxidation of Poly Phenolic Substrate - *p*-coumaric Acid

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Abstract:



The activity of carbon-supported platinum catalysts towards the catalytic wet air oxidation (CWAO) of *p*-coumaric acid (PCA) under the mild conditions (in air, $T = 353\text{ K}$, $P = 2\text{ MPa}$) was investigated. An nearly complete conversion of PCA with more than 90% of total organic carbon abatement (ΔTOC) to the less harmful CO_2 and H_2O , with respect to their initial activities were observed for all the catalysts investigated regardless of the type of the support utilized, namely activated carbon (AC), pristine (NTs) and modified carbon nanotubes (MNTs). The best performance is obtained using Pt/AC and Pt/NTs with the TOC removal of 95% and 89% respectively. The comparative catalytic study with their sole supports has also been studied. The discussion of the results with the literature data shows that the efficient catalysts Pt/AC and Pt/NTs are the gifted systems for the CWAO of PCA under mild conditions.

Keywords: Catalytic Wet Air Oxidation, *p*-coumaric acid, platinum catalysts, Carbon Nanotubes, Activated Carbon.

INTRODUCTION

The most important scientific and technical challenges facing humanity in the 21st century not only concern the supply of secure, clean, sustainable energy but also wastewater remediation for re-use purpose. Water, one of the world's most valuable resources, is under constant threat due to climate change and resulting drought. On the other hand the explosive population growth significantly increases fresh water demand for industrial and domestic activities. In this scenario it become absolutely mandatory the development of technologies for the treatment of wastewater and recycling. Industrial waste significantly contributed to the pollution of the environment through organic materials which are known

as Persistent Organic Pollutants, which could be existed quite a long time in the environment. Most of the industrial wastewater contains of 23% of poly phenolic compounds (Ojeda et al. 2004). This situation is mainly due to their high solubility in water. *p*-coumaric acid, whose chemical structure is closely related to that of bio-recalcitrant polyphenolic fraction present in the olive oil processing and wine-distillery waste water, has been already taken as target molecule for CWAO studies (Mantzavinos et al. 1996, Milone et al. 2006, Minh et al. 2006, Neri et al. 2002, Perkas et al. 2005). Several technologies are available to remove industrial organic wastes, such as biological, thermal and chemical treatments. The biological method is unsuccessful; due to the long dwelling time of microorganisms to degrade the pollutants (Kim et al. 2011). CWAO is one of the chemical oxidation methods, which is effectively able to convert the hazardous, toxic and high concentrated organic pollutants to CO_2 and H_2O (Levec et al. 1997).

The development of heterogeneous catalysts containing high activity and stability has been focused over the last years (An et al. 2001, Cao et al. 2003, Lin et al. 2002, Liu et al. 2001, Pintar et al. 2004), since they can be easily recovered by the filtration from the reaction mass. The metal supported catalysts for CWAO show serious deactivation problems, including poisoning (Kim et al. 2011), fouling (Keav et al. 2010), and leaching (Yang et al. 2015). In addition, the support material may undergo stability problems, such as dissolution in reaction medium or poor chemical resistance. Consequently the expansion of deactivation resistant catalysts has been studied (Keav et al. 2014, Arena et al. 2012). Moreover the use of noble metal catalysts for liquid phase oxidation is favored since no leaching or dissolution of the active metal occurs even in hot and acidic conditions (Aksoylu et al. 2003, Arena et al. 2012). Supported platinum catalysts seem to be hopeful (Gaalova et al. 2010, Hernandez et al. 2012, Torres et al. 2011) compared with other noble metal catalysts reported for liquid phase oxidation. The use of carbon materials in CWAO of phenolic fractions has been extensively studied (Liotta et al. 2009, Liu et al. 2013, Rocha et al. 2011, 2014, Wang et al. 2014). However, carbon support is presenting a strong resistance in acidic media (Hadrami et al. 2004). What is more the carbon supported platinum catalysts are having strong metal/support interactions (Panizza et al. 2006) avoiding two of the major catalyst problems in CWAO, namely leaching and sintering. Metal catalysts based

on platinum on various supports have been tested in the CWAO of PCA (Liotta et al. 2009, Milone et al. 2006, Minh et al. 2006, Perkas et al. 2005).

Recently, we have tested metal-free carbonaceous materials featured by different textural properties as catalysts for the degradation of PCA under mild conditions (in air, $P = 2\text{MPa}$ and $T = 353\text{K}$) (Milone et al. 2011). Our study has evidenced that pristine CNTs, together with the commonly used AC, exhibit better catalytic performances than oxidized CNTs. AC and CNTs allow achieving an nearly complete removal of PCA in 5 h with a ΔTOC higher than 85% and, additionally the removal of organic carbon occurs mainly through the mineralization to CO_2 rather than the adsorption on the catalyst surface, thus improving the catalyst lifetime and reducing the energy and time consuming regeneration processes required for catalyst re-use.

The aim of the work is to study the catalytic behavior in the CWAO of PCA of the catalysts obtained by dispersing 1 wt% of platinum on the previously studied carbonaceous materials, namely AC, pristine and modified CNTs. Several analysis techniques are utilized to thoroughly characterize the catalysts in order to correlate their specifics and their catalytic behavior.

METHODS

Materials

Carlo Erba supplied AC support (CAS 7440-44-0). CNTs supports (NTs) were prepared by catalytic chemical vapor deposition of isobutane ($\text{i-C}_4\text{H}_{10}$) over 29 wt% $\text{Fe}/\text{Al}_2\text{O}_3$ catalyst. Modified CNTs supports ($\text{M}_{\text{N:S}}\text{-NTs}$) were obtained by liquid phase oxidation of the parent CNTs in $\text{HNO}_3+\text{H}_2\text{SO}_4$ mixture with different nitric:sulfuric acid volume ratio (N:S = 3:1 and 1:1). A detailed description of the procedures of CNT synthesis and functionalisation can be found elsewhere (Donato et al. 2009, Santangelo et al. 2012).

Platinum catalysts were prepared by wet impregnation method. Supports were uniformly wetted with an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Alfa-Aesar, 99.95%) having an amount of platinum salt suitably calculated to obtain catalysts with a nominal metal content of 1 wt%. After impregnation, the supports were dried at 353K for overnight. In order to obtain active Pt sites (Gomes et al. 2000, Milone et al. 2006) the samples were reduced at 473K under (60 mL min^{-1}) stream of H_2 for 1 hr.

All the reagents used were analytical grade.

Sample Characterization

The amount of metal content on the catalyst and the metal leaching in reaction medium during the catalytic test are determined by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Analyst 200 instrument. The amount of metal is calculated from the calibration curve, which is obtained from the standard metal solutions.

Specific surface area (SSA) of carbonaceous supports and platinum catalysts was determined by Brunauer-Emmett-Teller (BET) method using a Surface Area Analyzers – Qsurf Series – Micromeritics. Adsorption-desorption of dinitrogen at 77 K was carried out after out-gassing (10^{-4} mbar) the samples at 363 K for 2 h. Results obtained are reported in **Table 2a**.

X-ray diffraction (XRD) patterns of the solids were recorded using an Ital Structures diffractometer. Analyses were performed in step scan mode (step: 0.02° , counting time: 2s/step) using nickel filtered $\text{Cu K}\alpha$ radiation source. The powder samples were mounted on Plexiglas holders. Crystalline phases were identified by comparison with the reference data from ICDD (International Centre for Diffraction Data) files.

Dispersion and average size of the reduced nanoparticles (NPs) were evaluated by transmission electron microscopy (TEM). A JEOL JEM 2010 analytical electron microscope (LaB₆ electron gun and 200 kV accelerating voltage), equipped with a Gatan 794 Multi-Scan CCD camera for digital imaging was utilized. The reduced catalysts were ground in an agate mortar, suspended and sonicated in isopropanol for 5 minutes. A drop of the obtained suspension was placed on a carbon coated copper grid. TEM micrographs were taken after the solvent evaporation. For each catalyst several hundreds of metal NPs visible on the micrographs were measured by a computerized system. The average Pt NP size was hence calculated as $d_{\text{Pt}} = \frac{\sum N_i d_i}{\sum N_i}$, N_i being

the number of the NPs with diameter d_i ; the width of their distribution was calculated as the standard deviation

$$\sigma = \sqrt{\frac{\sum (d_i - d_{\text{Pt}})^2}{\sum N_i}}$$
 of the data. Results obtained are reported in **Table 2a**.

The surface chemistry of supports and catalysts was investigated by temperature programmed desorption (TPD) analysis (Milone et al 2011). Measurements were carried out using a flow reactor equipped with a quadrupole mass spectrometer (HPR 20 Hiden Analytical Instrument). Samples (30 mg) were placed in a U-shaped quartz tube inside an electrical furnace and heated at 10 K min^{-1} up to 1373 K under 30 cc min^{-1} of He flow. The decomposition products 28 (CO), 30 (NO), 44 (CO_2) and 64 (SO_2) were monitored. At the end of each measurement a calibration with pure gases was performed. The amounts of gases (CO, NO, CO_2 and SO_2) released from the specimens, as determined by integration of the corresponding TPD profiles, are reported in **Table 2a**.

In addition, aiming to express their acid-basic character via a single number, the pH at point zero charge (pH_{ZPC}) of the supports was also measured by the procedure reported elsewhere (Milone et al. 2011, Utrilla et al. 2001). Nitrogen was bubbled through the solution to stabilize the pH by preventing the dis-solution of CO_2 . Results obtained are reported in **Table 2a**.

The amount of carbon removed by adsorption on the catalysts (C_{ads}) was evaluated by temperature-programmed oxidation

(TPO) as difference between the amount of CO₂ evolved during the combustion of used and fresh catalysts. The experiments were carried out in a Chemisorb 2750 Micromeritics instrument. All samples were analyzed in the temperature range 298–1273K increasing temperature at 10 K min⁻¹. Catalyst (0.05 g), placed in a quartz reactor, was exposed to a stream of 20 cc min⁻¹ mixture of O₂ and He purified with molecular sieves and oxygen absorbent traps.

C_{ads}(%) was calculated as

$$C_{ads}(\%) = \frac{m_{cat} \left[\left(\frac{CO_{2(U)}}{m_U} \right) - \left(\frac{CO_{2(F)}}{m_F} \right) \right]}{C_0} \cdot 100$$

where CO_{2(U)} and CO_{2(F)} are the moles of CO₂ measured from TPO analysis of the used (U) and fresh (F) catalysts; m_{cat} is the mass (g) of catalyst used in the reaction; m_U and m_F represent the masses (g) of used and fresh catalysts analyzed by TPO; C₀ indicates the moles of C introduced into the reaction vessel at beginning of the reaction.

Catalytic Activity

The reaction was carried out in air at 353 K. The aqueous solution of PCA (4.5 mM, concentration corresponding to the maximum solubility of PCA at ambient temperature) was placed in an autoclave (Parr mod. 4560) equipped with a magnetically driven stirrer and connected to an air cylinder in order to maintain the pressure constant (P = 2Mpa) throughout the experiment. The reaction vessel (200 mL) and all the internal parts in contact with the reaction mixture were made in Teflon in order to avoid the metal contamination. To minimize dead reaction time due to the heating up, the catalyst (0.5 g) was soaked into 100 mL of solvent, and the reaction temperature was increased up to 353 K. Then, 25 mL of solution containing the substrate was introduced into the reaction vessel through the gas entrance tube. Liquid samples were periodically withdrawn from the reactor and analyzed. Used catalysts were recovered after the reaction by filtration, washing with cold water and drying under vacuum at 353 K for 3 h.

The progress of the reaction was followed by sampling a sufficient number of micro samples and analyzing them by high performance liquid chromatography (HPLC). An Agilent 1100 series instrument equipped with a photo diode array detector was used. The reaction products were separated in a Symmetry C18 column (4.6 mm x 250 mm) using solution of 81% ultra pure water (Millipore) water and 19% HPLC grade acetonitrile (Aldrich) (isocratic method). The total flow was kept a 0.7 mL min⁻¹. HPLC was served for both identification

and quantification purposes. Calibration curve for the reagent was obtained analyzing reference sample under the above reported experimental conditions.

The conversion of PCA was calculated as

$$PCA_{conv}(\%) = \frac{C_0 - C_t}{C_0} \cdot 100,$$

where C₀ and C_t are the initial concentration of PCA and its concentration at time t, respectively.

Total organic carbon (TOC) content was determined with a Shimadzu 5050 TOC analyzer.

Quality Control

Calibration of each instrument was performed before the analysis. The best calibration curve with the R² value 0.995 was chosen for the analysis. The quality control validation parameters investigated were the limits of detection (LOD), limits of quantification (LOQ), precision (Relative Standard

Table 1. Quality Control Parameters of the Instruments: Limit of Detection (LOD), Limit of Quantification (LOQ), Precision and Spiked recovery

Instrument	LOD	LOQ	*Precision (RSD%)	+Recovery (%)
HPLC (mg/L)	2.5	6	1.32	98.60
TOC (mg/L)	1	3	1.05	99.30
TPO	-	-	1.83	99.01
BET	-	-	1.28	98.20

$$* RSD\% = \frac{\text{Standard Deviation of Sample Results (S)}}{\text{Average of Sample Results}};$$

$$+ \text{Recovery}\% = \frac{\text{Spiked Sample Result}}{\text{Average of Actual Spiked Amount}}$$

Deviation - %RSD), and accuracy (Recovery %) (Currie et al. 1995). HPLC and TOC instruments were validated with the different concentrated solutions. TPO and BET surface area analyzer were validated with the adsorption of known quantity of carbon on Alumina support and with the standards respectively. The values are tabulated in **Table 1**.

RESULTS AND DISCUSSION

Specifics of catalysts

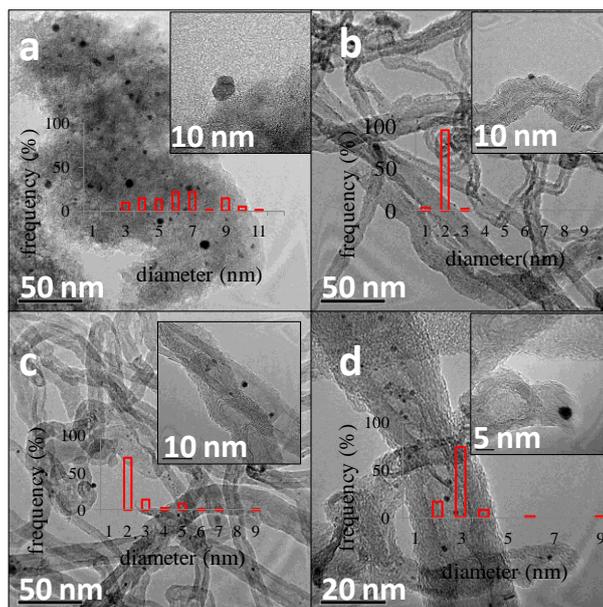


Figure 1. TEM images of Pt/AC (a); Pt/NTs (b); Pt/M_{3:1}-NTs (c); Pt/M_{1:1}-NTs (d); inset of figures represent the HRTEM images for crystalline nature of platinum particle and Particle size distribution

Table 2. Codes, specifics and their catalytic activity of the investigated catalysts

(a) Codes and Specifics								
Code	Pt loading (wt.%)	Mean Pt ± S.D (nm)	pH-point charge (pH _{ZPC})	zero	Specific Surface Area (m ² g ⁻¹)		CO ₂ (μmol g _{cat} ⁻¹)	CO (μmol g _{cat} ⁻¹)
					Fresh SSA ₀	After first cycle SSA ₁		
Pt/AC	0.97	5.7 ± 2.0	10.0		608	352	121	137
Pt/NTs	0.96	1.5 ± 0.3	7.0		194	188	11	11
Pt/M _{3:1} -NTs	0.96	2.2 ± 0.9	2.5		192	189	91	126
Pt/M _{1:1} -NTs	0.97	3.1 ± 1.1	2.3		148	128	359	456
(b) Catalytic Activity; Actual removal rate of PCA (κ _{PCA}), measured rate of PCA (κ _{PCA} ^{app}), adsorption rate* (κ _{ads}), TOC abatement ΔTOC, Carbon adsorbed C _{ads} , Mineralization Effectiveness ME _{CO₂} , Metal leaching Fe and Pt								
Catalyst	κ _{PCA} (μmol min ⁻¹)	κ _{PCA} ^{app} (μmol min ⁻¹)	ΔTOC (%)	C _{ads} (%)	ME _{CO₂} (%)	Fe (mg/L)	Pt (mg/L)	
Pt/AC	34.1	36.6	94.8	6.6	88.2	-	-	
Pt/NTs	29.8	30.7	89.2	2.5	86.7	-	-	
Pt/M _{3:1} -NTs	28.0	28.9	67.4	2.4	65.0	1.7	7.8	
Pt/M _{1:1} -NTs	18.2	18.9	65.3	2.0	63.3	1.8	8.0	

* κ_{ads} is calculated as $\frac{PCA_0 C_{ads}}{m_{cat} t 100}$, where PCA₀ = 5.6 × 10⁻⁴ mol, m_{cat} = 0.5 g and t = 30 min.

The codes and textural properties of the investigated catalysts are reported in **Table 2a**. The measured Pt content is in good accord with the nominal one. Loading metal on the supports causes a decrease in the surface area (SSA) due to the so-called pore blocking effect (Gomes et al. 2004, Park et al. 2010, Reinoso et al. 1998, Taboada et al. 2009), namely the insertion of the metallic NPs into pores of the supports (see inset of **Figure 1**). The decrease of SSA in Pt-loaded catalysts is in the same order as with the parent supports, i.e. Pt/AC > Pt/NTs > Pt/M_{3:1}-NTs > Pt/M_{1:1}-NTs.

The TEM photographs and the particle size distribution of various catalysts are shown in **Figure 1a-d**. TEM images that show the morphologies of the Pt particles on the various catalysts. The dark spots observable in the figure correspond to the Pt particles. The random distribution of dark spots is observable on the side walls of the CNTs. The high magnification TEM images (inset of Figure 1) represent the crystalline nature of the platinum particle. The histograms (inset of **Figure 1a-d**) evidence the narrow distribution of platinum particles.

The TEM photograph of the catalyst Pt/AC shows the

platinum particles are dispersed on the support AC with the mean particle size of 5.48 nm, however the mean metal particle size dramatically reduces from 5.48 nm to the range 1.5-3.1 nm, using CNTs catalysts despite its lower SA (Nousir et al. 2008). Moreover, it can be seen that the particle sizes of CNTs catalysts increase slightly from Pt/NTs to Pt/M_{1:1}-NTs with the decrease in pH_{ZPC} of the support (**Table 2a**) which agreed with the previous findings (Reinoso et al. 1998). However, particle size measured for Pt/AC does not fit into this correlation, which indicates the different type of the carbonaceous support.

Figure 2a(i-iv) shows the XRD patterns of the investigated catalysts. The peaks at 2θ angles of 26° and 43°, corresponds respectively to the reflections of C (002) and C (100) planes (Park et al. 2010, Taboada et al. 2009,) of the support, in all the Pt catalysts. Instead, the signal due to the diffraction of Pt (111) planes (Knupp et al. 2008, Milone et al. 2006) at 2θ = 40° is clearly visible only in Pt/AC catalyst where the metal NPs have greater size (**Table 2a**). The good agreement between XRD and TEM results suggest that the platinum is well dispersed using the Wet Impregnation method.

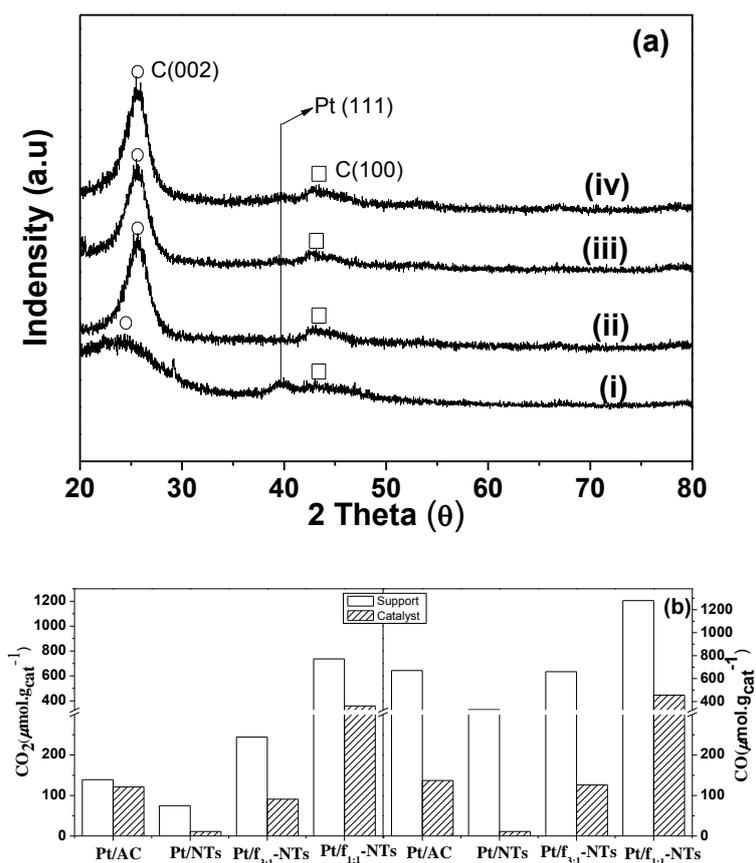


Figure 2. XRD [Pt/AC- a(i); Pt/NTs – a(ii); Pt/M_{3:1}-NTs - a(iii); Pt/M_{1:1}-NTs - a(iv)] and Comparative TPD profile of the investigated catalysts with their supports

The amounts of CO and CO₂ released from the specimens, as determined by integration of the TPD profiles, are represented in the **Figure 2b**. It compares the TPD profile of the investigated Pt catalysts and the parent supports. The latter was discussed thoroughly in our previous work (Milone et al. 2011). The absence of SO₂ (not shown in Figure 2) in the Pt catalysts, shows that the desorption of SO₂ species during the Pt metal reduction. Lower amounts of CO₂ and CO pertain to Pt loaded catalysts. The decrease of the CO₂ release may be due to desorption of less stable carboxylic groups during the reduction of the metal. The decrease in CO concentration suggests that the anchoring of hexachloroplatinic anion is mainly on the carbon surface basic sites (Fraga et al. 2002, Okhlopkova et al. 2009, Reinoso et al. 1998).

Catalytic Activity

CWAO of PCA operated in air at 353K and 2 MPa leads to the formation of secondary reaction products (SRP) (**Figure 3**). During the reaction with the catalyst Pt/AC, the formed SRP were p-HBAld and p-HBA. HQ and MA were also added for Pt/NTs. The selectivity of these products indicated that the reaction could follow the path way (A) as reported in **Scheme 1**. Whereas the reaction with the catalysts Pt/M_{3:1}-NTs and Pt/M_{1:1}-NTs, produced additionally 3,4-DHBAld and 3,4-DHBA with the above intermediates, likely to follow the path way (A) and (B) as in **Scheme 1**. These findings agree with the mechanism proposed by Minh et al. 2006. The different pathways of the investigated catalysts expecting the different rates of the catalysts.

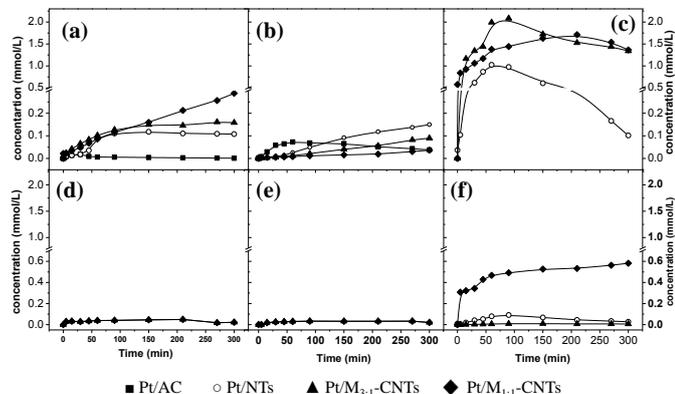


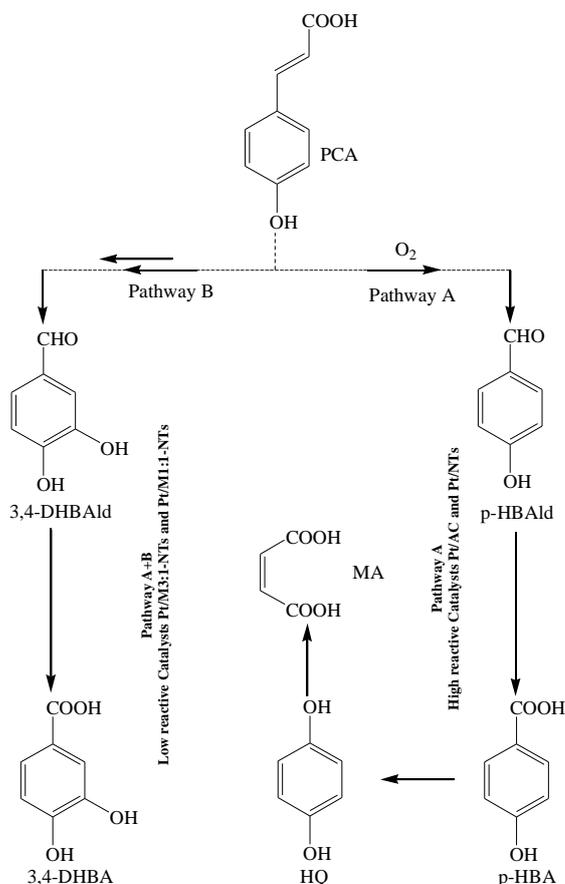
Figure 3. Secondary Reaction Products (in mmol/L) formed during the reaction (a) p-HBAld; (b) p-HBA; (c) HQ; (d) 3,4-DHBAld; (e) 3,4-DHBA, (f) MA

Figure 4a demonstrates PCA concentration (%) as a function of reaction time. All the investigated catalysts show nearly complete removal of the substrate from the solution, regardless the samples tested. Blank experiment (absence of catalyst), in order to evaluate the non catalytic process, shows only 23% of PCA removal. The results indicate that the degradation of PCA is strongly favored only in the presence of catalysts.

Table 2b reports the amount of organic carbon removed by

adsorption onto the catalyst surface with respect to the initial amount introduced into the reaction vessel, $C_{ads}(\%)$, evaluated by TPO analysis as described in section 2.2. The adsorption capacity ($C_{ads} \%$) increases with the increase in surface area of the catalysts and is in the order Pt/AC > Pt/NTs > Pt/M_{3:1}-NTs > Pt/M_{1:1}-NTs (**Table 2b**). Surface area of the spent catalyst (SSA_1) recovered upon one catalytic cycle is reported in **Table 2a**. It shows Pt/AC that suffers the higher loss ($\approx 42\%$) in agreement with the higher amount of adsorption on carbon. A much lower decrease in SSA_1 can be observed for the catalysts Pt/NTs ($\approx 3\%$) and Pt/M_{3:1}-NTs ($\approx 2\%$). Moderate loss is observed for Pt/M_{1:1}-NTs ($\approx 14\%$) in accord with the C_{ads} .

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Scheme 1. Simplified Mechanism of PCA oxidation [from Ref. 26]

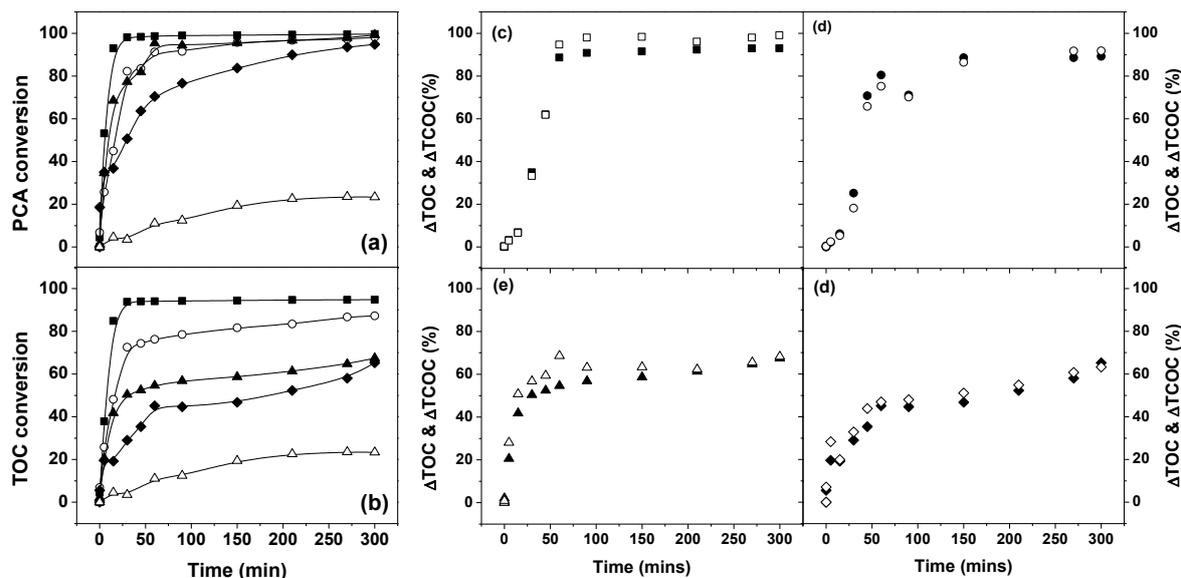


Figure 4. PCA concentration (a) and TOC removal (b) Vs Time for the investigated catalysts (■) Pt/AC, (○) Pt/NTs, (▲) Pt/M_{3:1}-NTs, (◆) Pt/M_{1:1}-NTs, (Δ) no-catalyst; comparison of TOC Vs TMOc (c-f)

Rates of the Reaction

The apparent rate of removal of κ_{PCA}^{app} is calculated as follow:

$$\kappa_{PCA}^{app} (\text{mol g}_{cat}^{-1} \text{ min}^{-1}) = \frac{PCA_0 \left(1 - \frac{C_t}{C_0}\right)}{m_{cat} t}$$

where PCA_0 stands for the initial amount of PCA ($5.6 \cdot 10^{-4}$ mol), m_{cat} is the amount of catalyst and C_t/C_0 represents the fraction of the reagent detected at time t . Assuming that the carbon adsorption completes within the first 30 minutes of reaction, the actual rate of removal (κ_{PCA}) is obtained by subtracting the adsorption rate κ_{ads} from κ_{PCA}^{app} . Results obtained are, reported in **Table 2b**, and it indicates that κ_{ads} ranks in the order Pt/AC > Pt/NTs > Pt/M_{3:1}-NTs > Pt/M_{1:1}-NTs. This suggests that the adsorption does not affect the reactivity of the catalysts. The higher reaction rates of the catalysts Pt/AC and Pt/NTs follow the mechanism path way (A) and lower rates of the catalysts Pt/M_{3:1}-NTs, Pt/M_{1:1}-NTs follow the mechanism path way (A) and (B) as expected in scheme 1.

TOC Removal

The catalysts efficiency toward the removal of the organic

The catalysts efficiency toward the removal of the organic reagent and products, evaluated as total organic compound abatement, ΔTOC (%), is calculated as:

$$\Delta TOC(\%) = \frac{TOC_0 - TOC_F}{TOC_0} \cdot 100$$

TOC_0 and TOC_F correspond to the TOC values of the solution before and after 5 h reaction, respectively.

Figure 4b shows the highest efficiency pertains to Pt/AC and Pt/NTs showing after 5 hrs, a TOC conversion of 95%, 89% respectively. But the catalysts Pt/M_{3:1}-NTs and Pt/M_{1:1}-NTs show a less organic compound removal capacity of 67 and 65% after 5 hrs, respectively, even observed the complete removal of PCA during the reaction time. A possible explanation for the lesser removal of organic compound can be elucidated by the comparison between of TOC and Total measured organic carbon (TMOc).

Figure 4(c-f) shows a comparison between TOC measurements and total measured organic carbon (TMOc), calculated from HPLC analysis as a function of time; where TMOc is defined as the sum of the organic contributions measured from all the individually detected intermediates. From **Figure 4(c-f)**, it can be seen that TMOc is slightly higher than that of TOC and are in good agreement with each other, which demonstrates that more than 90% of the intermediates are successfully detected and identified in all the reactions. **D.P.Minh et al. 2006** observed that the discrepancies between TOC and TMOc were due to the formation of the oligomers of PCA. The current study ruled out the formation of such product. The lesser removal of ΔTOC (%) for the Pt/M_{N:S}-NTs catalysts, indicates that PCA oxidation mainly leads to the formation of intermediates (Rocha et al. 2014, Yang et al 2008)

Since the main routes for elimination of organic carbon from the solution are mineralization through the complete oxidation to the less harmful CO_2 and adsorption onto the catalysts, the mineralization effectiveness of the catalysts (ME_{CO_2}) is evaluated by applying the following mass balance equation

$$\Delta TOC (\%) = ME_{CO_2}(\%) + C_{ads}(\%).$$

The occurrence of the mineralization contribute is of significance for the selection of a good catalyst for pollutant

removal and moreover it guarantees an enhancement of the catalyst lifetime in the absence of other factors than adsorption that can compromise the catalysts performance, and reduces the energy and time consuming regeneration processes required for catalyst re-use.

As in **Table 2b**, all the investigated catalysts show more than

90% of ΔTOC (%) is mainly due to mineralization of organic compounds to CO_2 with respect to their initial activities. The higher ME_{CO_2} may be due to the presence of iron impurities (Milone et al. 2011, Quintanilla et al. 2007, 2008), and the presence of platinum metal (Milone et al. 2006).

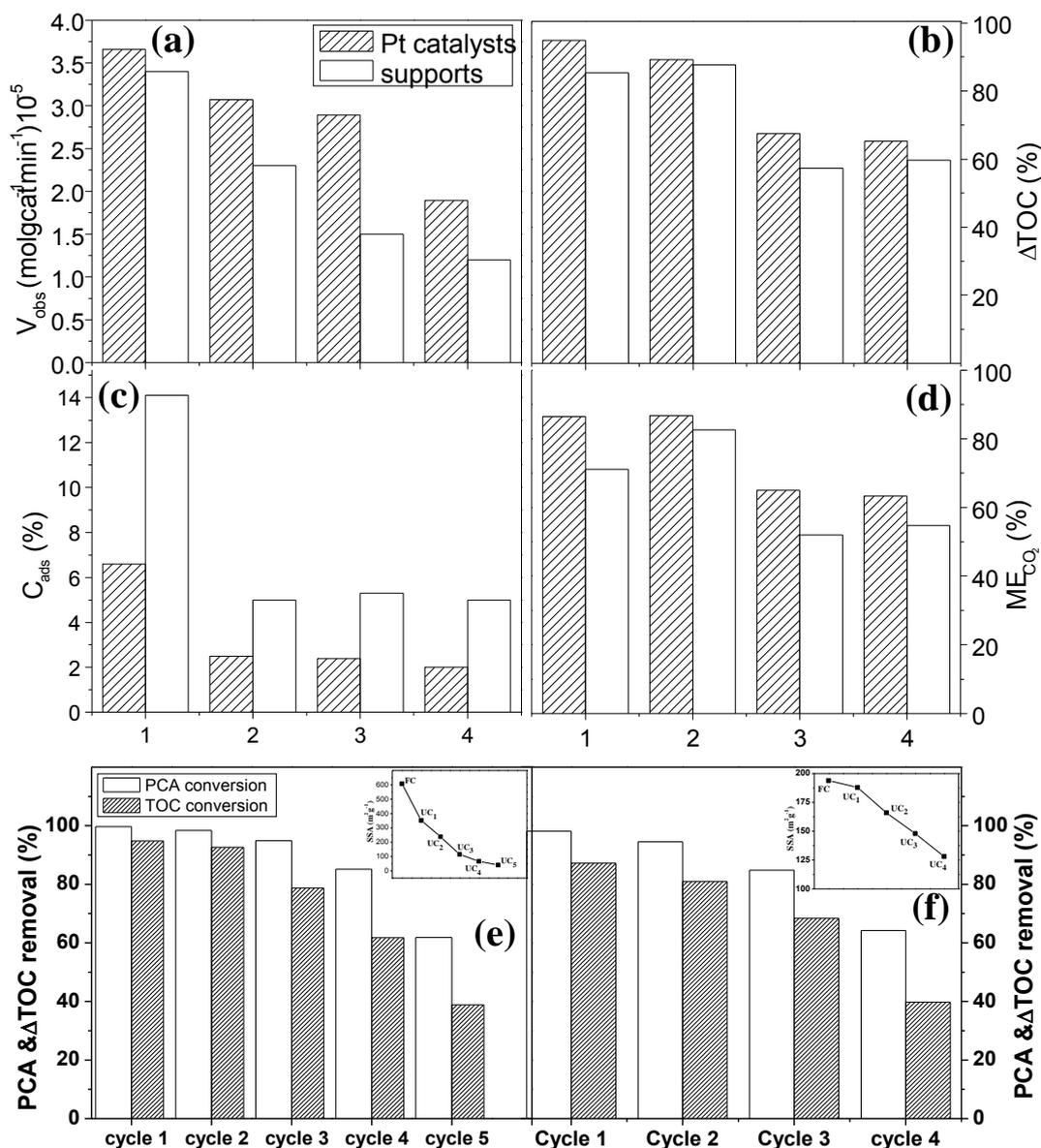


Figure 5. Comparative catalytic activity of investigated catalysts with their sole supports (a) reaction rate; (b) TOC removal ΔTOC %; (c) adsorption of organic carbon C_{ads} %; (d) mineralization effectiveness ME_{CO_2} (%). In the Figure 1,2,3,4 represent Pt/AC, Pt/NTs, Pt/ $\text{M}_{3:1}$ -NTs, Pt/ $\text{M}_{1:1}$ -NTs respectively with their sole supports; Recycle Experiments of investigated catalysts; (a) Pt/AC, (b) Pt/NTs

Leaching Experiment

It is interesting to note that during the experiments with the catalysts Pt/M_{3:1}-NTs, Pt/M_{1:1}-NTs, the reaction medium become yellow colored. As discussed earlier, it is not due to the formation of oligomers of PCA. It is expecting that the dissolution of their supports, due to their hydrophilic nature. It is studied from the blank reaction without PCA under the experimental conditions, and then filtered the reaction medium through 0.2µm syringe. The filtered samples are yellow in color, indicate the dissolution of support; and analyzed by TOC to measure the dissolved carbon content of the support. The **Table 2b** shows the considerable dissolution of carbon in the reaction medium under the reaction conditions and it increases with the increase in pH_{ZPC(s)} of the supports, which reflects the hydrophilic nature of the supports Pt/M_{3:1}-NTs, Pt/M_{1:1}-NTs.

The metal leaching from the catalyst is important, because it is a direct cause of catalyst deactivation. The analysis of the reaction solution after the catalytic tests by atomic absorption spectroscopy evidences the presence of Fe and Pt. The **Table 2b** shows the considerable leaching of Fe and Pt metals of the catalysts Pt/M_{3:1}-NTs and Pt/M_{1:1}-NTs. The mineralization effectiveness ME_{CO₂}(%) of these catalysts (65-67%) increased about 25% when compared the activity with their sole supports. It may be due to, homogenous activity of the leached metals. The experimental results show that the extent of Fe and Pt metal leaching is strongly dependent on the pH_{PZC(S)} (pH at point zero charge) of the support. The metal leaching of the catalysts increases with the increase in acidity of the supports, which agrees with the literature data (Mantzavinos et al. 1996, Zhang et al. 1999). But there is no Fe leaching observed in the CWAO of PCA in the case supports as catalysts (Milone et al. 2011) indicates that the loading of Pt lowers the SMSI effect (Strong Metal Support Interactions) between the metal and the support.

Influence of Platinum on the catalytic activity

The addition of platinum plays an important role on the catalytic activity of the catalysts. **Figure 5(a-d)** reports the influence of Pt on the catalytic activity of the catalysts when compared to their sole supports. It shows clearly that the presence of Pt mainly catalyze the reaction and leads to increase in catalytic activity in terms of rates of the reaction K_{PCA} (**Figure 5a**), TOC abatement ΔTOC% (**Figure 5b**) and mineralization effectiveness ME_{CO₂} (%) (**Figure 5d**). The amount of carbon removed by adsorption (C_{ads} %) was found to be reduced by the addition of Pt (Figure 5c), which indicates that the presence of platinum favors the oxidation of PCA and intermediates rather than their adsorption (Pintar et al. 2004).

Performance of used catalysts

In order to understand the re-usability of the catalysts, cyclic experiments were performed with used Pt/AC and Pt/NTs catalysts. Thus the catalysts were subjected to same reaction conditions several times. For each cycle, the catalyst

recovered from the reaction vessel by filtration was washed with water and dried at 353K for 2 hrs later reduced under H₂ (60 mL min⁻¹, 473K) for 1 hr. The results are summarized in **Figure 5(e-f)**. No considerable loss of activity was observed up to 4 consecutive runs for Pt/AC (Figure 5e), however in 5th cycle, its activity declined to 62% of PCA conversion with the TOC abatement of 39% (Figure 5b).

For Pt/NTs the same catalytic performance was achieved up to 3 cycles (**Figure 5a and 5b**). But it lowered to 64% of PCA conversion with the TOC removal of 40%. The decrease in catalytic activity can be attributed to the loss in SSA_{UC} (inset of Figure 5a and 5b) which was observed after each cycle is solely due to the adsorption of organic compounds (Ojeda et al. 2007, Stuber et al. 2005), which leads to the decrease in active platinum sites. Moreover the treatment after each cycle could lead to denature of the catalysts such as increase in platinum particle size and aggregation of platinum particles; confirmed the crucial for the drastic reduction of accessible reaction sites hence observed the deactivation of the catalysts (Villa et al. 2010).

These results concluded that the catalyst Pt/AC show better results for at least 4 cycles, and Pt/NTs for 3 cycles towards PCA conversion and TOC abatement capacity.

Comparison of Results

In conclusion, it is valuable to note that among the catalysts investigated Pt/AC and Pt/NTs catalysts show best catalytic performance towards PCA conversion and TOC removal. The direct comparison of the current study with the earlier studies is bit difficult, because of the different experimental conditions. However the comparisons (Table 3) are made based on the PCA conversion, TOC removal and mineralization effectiveness.

Table 3. Comparison of present activity data with other reported data Temperature (T), Pressure (P), TOC Removal ΔTOC(%), Mineralization Effectiveness ME_{CO₂} (%)

Reference	Conditions		Catalyst	ΔTOC (%)	ME _{CO₂} (%)
	T (K)	P (MPa)			
Milone et al. 2006	353	2	Pt/CeO ₂	90.0	55.0
Perkas et al. 2005	463	5	Pt/TiO ₂	90.0	-
Minh et al. 2006	413	5	Ru/TiO ₂	-	70.0
Present work*	353	2	Pt/AC*	95.0	88.2
			Pt/NTs*	89.2	86.7

One of the most efficient catalytic systems in the CWAO of PCA under the same conditions as the present work ($P = 2$ atm, $T = 353$ K, $PCA = 4.5$ mM) is Pt/CeO₂ (Milone et al. 2006), Pt/AC in the current study presented a higher ΔTOC (%), 95%; and Pt/NTs showed a close ΔTOC (%) of 89.2% against 90% over Pt/CeO₂, and additionally the highest mineralization effectiveness, 88.2% and 86.7% against 55%.

Another reference catalyst is Pt/TiO₂ studied by Perkas et al. 2005 under harsh conditions ($P=5$ MPa, $T = 463$ K); it had a ΔTOC (%) of 90%, however Pt/AC and Pt/NTs showed ΔTOC (%) of 95 and 89.2% under mild experimental conditions.

Finally it should be pointed out that Pt/AC and Pt/NTs had better mineralization effectiveness than the best performing Ru/TiO₂ and Ru/ZrO₂ catalysts tested under more severe reaction conditions ($P=5$ MPa, $T = 413$ K) (Minh et al. 2006) than those used in the present work. Indeed with Ru catalysts only 70% of mineralization is achieved, while Pt/AC and Pt/NTs allow higher values of 88.2% and 86.7% under mild conditions.

CONCLUSION

The results of the present study in CWAO of PCA, shows the complete conversion of PCA at 5 hrs of contact time for all the investigated platinum catalysts under mild conditions ($T=353$ K, in air $P=2$ MPa). Among the catalysts investigated Pt/AC, Pt/NTs had a mineralization effectiveness, ME_{CO_2} (%) of 87-88% which reduces to 63-65% for Pt/ $M_{N,S}$ -NTs. The stability data of the most active catalysts Pt/AC and Pt/NTs show the better catalytic activity towards PCA conversion and TOC removal for at least 3-4 catalytic cycles. The catalytic activity of the platinum catalysts shows the enhanced behavior with respect to their sole supports. Metal leaching of the catalysts increases with the increase in acidity of the supports. The performance of the used catalysts shows the decrease in loss of SSA.

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