

Catalytic wet air oxidation of aqueous solution of phenol over Pt/CNF catalyst

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Abstract

The catalytic wet air oxidation (CWAO) of phenol has been studied in trickled bed reactor using 2 wt.% platinum supported on carbon nanofibers (Pt/CNF) as catalyst. The catalyst was prepared by incipient wetness impregnation, and characterized by N₂ adsorption, XRD and TEM. The operational variables studied and their range were: total air pressure, temperature, catalyst load, air and liquid flow rates, and were varied from 1.0 to 3.0 MPa, 413 to 453 K, 0.5-2 g_{cat}, 150-400 mL/min of air and 0.5-2 mL/min of phenol solution, respectively. The initial phenol concentration was 1g/L. After 3h of reaction, phenol conversions were higher than 90% in most of cases, and total organic carbon (TOC) conversions ranged from 30 to 93%. A high stability of the catalyst was also demonstrated. A Langmuir-Hinshelwood kinetic model was used to fit experimental data, obtaining satisfactory results.

It was demonstrated that Pt/CNF is an efficient catalyst for the CWAO of phenol. High phenol conversion and TOC removal can be reached over this catalyst at mild reaction temperature (433 K) and moderate pressure (2.0 MPa).

Keywords: carbon nanofibers, catalytic wet oxidation, kinetic.

1. Introduction

Nowadays, many industries generate large quantities of aqueous wastes containing organic substances that can not be efficiently treated by the conventional methods (physical, physico-chemical, biological and chemical treatments), due basically to their refractoriness and biotoxicity. In fact, treatment of these waters has become a major social, technological, economical and political problem.

To overcome the inconveniences of conventional treatments methods various chemical oxidation techniques have emerged in the last decades, and they are increasingly gaining popularity since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. Among them, the processes industrially used are the non-catalytic wet oxidation and the supercritical oxidation, which require high pressures and temperatures, and consequently high cost. Furthermore, under such extreme conditions, most materials of construction are susceptible to stress corrosion cracking when chloride ions are present in the waste stream (Levec and Pintar, 2007). Moreover, although both procedures have shown high effectiveness, operational conditions cause high operative and installation cost. So that, an interesting alternative is the catalytic wet air oxidation (CWAO), because the catalyst permits a significant reduction of the temperature ($<473\text{K}$) and the pressure ($<3\text{ MPa}$), increasing the oxidation rate of refractory compounds and improving the economy of the process.

Concerning to the type of CWAO catalyst, it is desirable to use a heterogeneous catalyst since a homogeneous one requires an additional separation step. In this sense, various heterogeneous catalysts have been synthesized and tested in the last decades, based mainly on metal oxides of Cu, Zn, Co, Mn, or on noble metals as Ru, Pt, Rh, Ir or Pd. An intensive research effort is therefore needed to develop a more active heterogeneous stable catalyst to enable the CWAO to be used for wastewater treatment. The supports more commonly used in the industry are diverse refractory oxides such as alumina, silica, zeolite, etc. This owes to that they present a series of advantages as the fact of being relatively homogeneous products with stable physico – chemical features.

During the past two decades, carbon nanofibers (CNFs), including multiwalled carbon nanotubes (MWNTs), have attracted extensive interest and attention from both academia and industry. Due to their novel physico-chemical and mechanical properties, CNFs exhibit growing perspectives in a number of potential applications, especially in heterogeneous catalysis (G. Ovejero, 2006). One of the advantages of CNFs used as catalysts and catalyst supports is the possibility of tailoring their microstructures by proper selection of preparation method and controlling their surface chemistry via surface modification (P. Serp, 2003). The mesoporous macrostructure with relatively high specific surface area and almost completely exposed external surface of these materials can be expected to reduce the inner pore diffusion resistance dramatically during the reaction (J. Garcia, 2006).

In the present work, attention is focused on CWAO of phenol solutions in a trickled bed reactor, using Pt supported on CNF as catalyst. The effect of process parameters like temperature, pressure, catalyst load, air flow and liquid flow, has been studied. The experimental data were satisfactory fitted to a Langmuir-Hinshelwood kinetic model.

2. Experimental

The catalytic oxidation of aqueous phenol solution was carried out in a high pressure stainless steel continuous fixed bed reactor (length=300mm, ID 9.2mm), placed in a controlled temperature oven, with an independent inlet system for gas and liquid feed with pressure and temperature control equipment, and separation and sampling system for the outlet products (ICP Microactivity Pro).

The synthesis of catalysts was performed in three steps:

1. - Commercial carbon nanofibers (supplied by Grupo Ingeniería Antolín) were treated with aqueous solution of HNO₃ 5M and were held at reflux for 6h in order to modify the surface chemistry with carboxylic groups. After that, they were washed until neutral pH, and dried overnight at 383K.
2. - The active phase was incorporated by wetness impregnation method using PtCl₄(NH₄)₂ (Aldrich) as precursor and with a final loading of 2 wt.% as Pt.
3. - The activation of the catalyst was carried out by reduction under N₂/H₂ (2:1) atmosphere at 623K.

Once the catalyst (1 g) has been loaded in the reactor and temperature and pressure have reached their set point values, the liquid (phenol aqueous solution, 1g/L) and gas streams (air as oxidation agent) are mixed and then enter the reactor, flowing along the catalyst bed. The exited solution goes to a liquid-gas separation. Samples for analysis were withdrawn after a period of 6 h operation under fixed conditions.

The feed and the reaction products were analyzed to determine the phenol and total organic carbon (TOC) conversion. The phenol concentration in liquid samples was determined by HPLC (VARIAN ProStar 220/230/240) using an UV detector at a wavelength of 254nm. A C18 reverse phase column (Teknokroma) was used as stationary phase to separate the phenol from the partial oxidation products. The mobile phase was a mixture of 35 % acetonitrile and balance distilled water with a flow rate of 1mL/min. TOC content of the solutions before and after reaction was analyzed using a combustion/non dispersive infrared gas analyzer model Rosemount Dohrmann DC-190.

The conversion of phenol and TOC were calculated as follows:

$$X_{Phe} = \frac{[Phe]_0 - [Phe]_t}{[Phe]_0} \times 100$$

$$X_{TOC} = \frac{[TOC]_0 - [TOC]_t}{[TOC]_0} \times 100$$

in which X is percentage conversion, []₀ is the measured concentration value at initial time, and []_t is the measured amount at any other time.

The catalyst was characterised by X-ray diffraction (Siemens D-501), X-ray fluorescence (PHILIPS PW-1480), transmission electron microscopy (JEOL

JEL2010), and N₂ adsorption/desorption isotherms at 77K (Micromeritics ASAP 2010).

3. Results and discussion

- Catalyst characterization

Carbon nanofibers used as support had diameters between 10 and 30 nm and a length of 1 to 10 μm. Two TEM micrographs of CNF and Pt/CNF are shown in Figure 1. The surface groups on the CNF such as –COOH, –OH, –C=O, which are incorporated by oxidation, are important to obtain the interactions required for a good distribution of the metal precursor on the CNF surface. Oxidation of carbon nanofibers in nitric acid gave a larger amount of platinum deposited.

From N₂ physisorption assays, it could be observed that the shape of adsorption/desorption isotherm was type II (IUPAC), and led a 244 m²/g BET surface for CNF, while the metal loading on the support caused a decrease in the surface to 188 m²/g. The high external surface area leads to a significant increase in the surface contact between the liquid reactants (phenol solutions) and the active phase supported on this nanostructured host, which is a prerequisite for its use as catalyst support.

The XRD spectra of Pt/CNT catalysts showed in all cases, two peaks at $2\Phi = 25$ and 45° corresponding to (002) and (100) lines, typical from carbon nanofibers, and a peak at $2\Phi = 39.4$ that belongs to metallic Pt. From this peak, it was possible determine the particle size, resulting in an average size of 10.5 nm, that is in good agreement with the results from the TEM image.

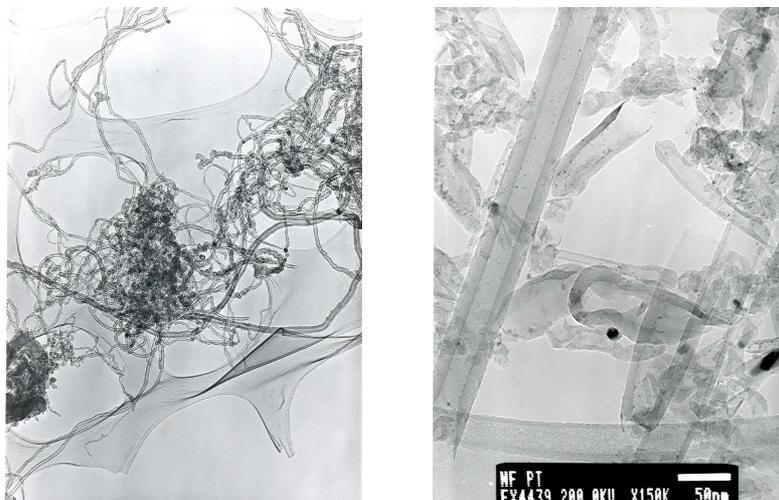


Fig. 1 TEM micrographs of CNF, a) without metal particles and b) with platinum particles supported on.

- Oxidation reactions

The oxidation of phenol was first tested in the absence of any metal and/or carbon support. The reaction was run for 5 h under conditions of 433K, 2 MPa of total pressure and flow rates of 300 mL/min of air and 0.5 mL/min of liquid phase. A phenol conversion of 1.3% was obtained without catalyst and 10 % when the run was

carried out only with the carbon support. Those results are given in Figure 2 where it is represented phenol concentration versus time on stream, in steady-state conditions, and are compared with a run in the same conditions catalyzed by Pt/CNF. As it can be observed, the oxidation reaction mostly occurs when the metal catalyst is present and less than 10 % of phenol conversion is due to non catalytic wet air oxidation or adsorption phenomena over CNFs.

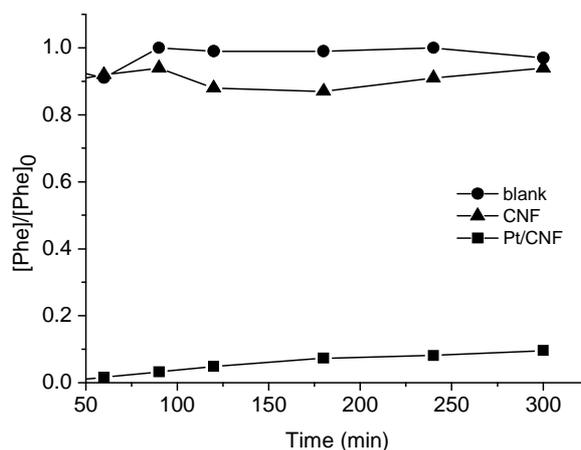


Fig. 2. Phenol oxidation reaction at 433 K with and without Pt/CNF catalyst.

Next, the effect of different operating variables on the CWAO was experimentally tested (Figs. 3-7). Beginning with temperature, Figure 3 shows the low effect of this parameter on the oxidation of phenol when a solution was treated at three different temperatures: 413, 433 and 453 K, while the rest of operational variables were maintained constant. It seems not to improve the amount of removed phenol when the temperature is raised from 413 to 453 K. Nevertheless, the higher the temperature, the higher the amount of phenol molecules that oxide to carbon dioxide as it is shown by the TOC conversion values, specially when the temperature is increased from 413 to 433 K.

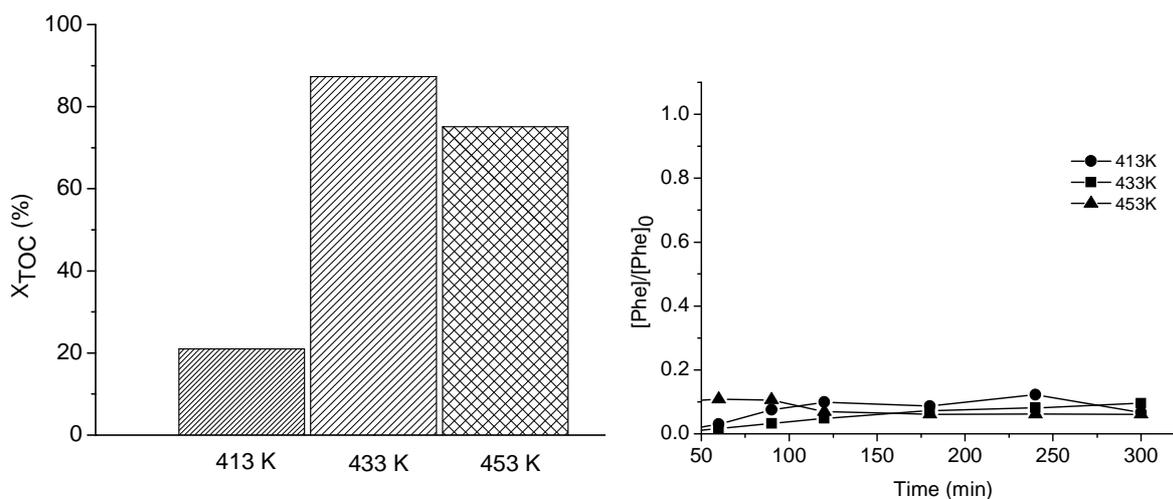


Fig. 3. Effect of temperature on TOC conversion and phenol concentration as a function of the reaction time.

Based on HPLC analysis, it is noted that air could completely oxidized phenol within 100 min at 433 K, while carboxylic acids resulted from CWAO of phenol, are stable and refractory to mineralization into CO_2 and H_2O (Guo and Al-Dahhan, 2006). Those results are due to the fact that an increase in temperature would favour mass transfer of the reactants as well as the oxidation reaction rate, giving a higher phenol conversion (Shing et al., 2004). Experiments were conducted to investigate the formation of CO_2 and it was confirmed that CO_2 constitutes the major part of the carbon balance for these oxidation reactions.

Air pressure was varied from 1.0 to 3.0 MPa. Figure 4 shows that at a phenol concentration of 1 g/L, the air pressure had an appreciable effect in phenol conversion from 1.0 to 1.5MPa, as well as in TOC conversion. Nevertheless, pressures higher than 2.0 MPa do not seem to improve significantly the amount of oxidized phenol. Thus, the maximum TOC conversion occurred at 3.0 MPa (81% after 300 min). Since the catalyst removes from the wastewater most of the TOC, the remaining pollutants can be further treated using biological process (Guo and Al-Dahhan, 2006).

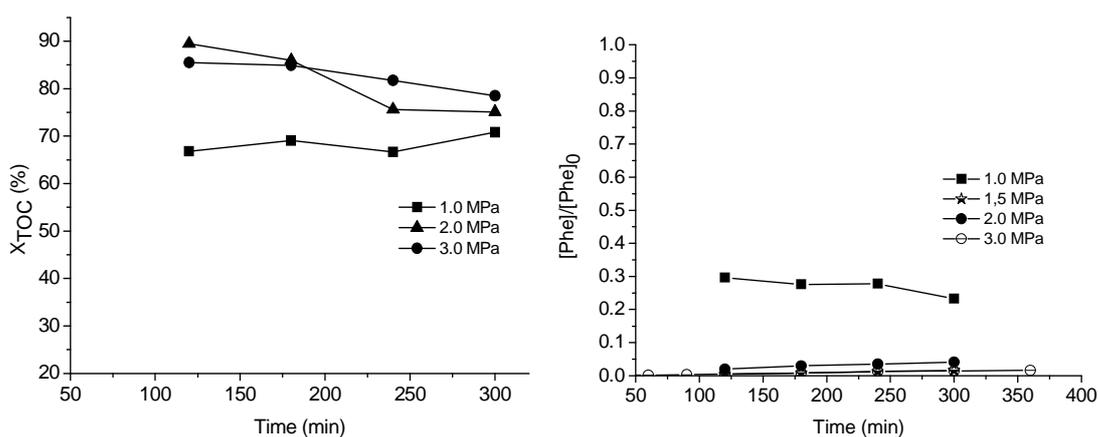


Fig. 4 Effect of pressure on TOC conversion and phenol concentration as a function of reaction time.

The increase of the air pressure applied seems to favour the solubility of the oxygen in the liquid phase until the equilibrium is reached, nearly at 3.0MPa. So that, pressure values higher than 3.0 MPa will not improve phenol oxidation.

The influence of liquid flow rate was also tested at various values: 0.5, 1.0 and 2.0 mL/min of phenol solution (1g/L), and the results obtained are reported in Fig.5. As can be seen, about 75% of organic compounds were converted to CO_2 during the reaction when the phenol flow rate was fixed at 0.5 mL/min, but only about a 50% when the liquid flow rate was increased to 2.0 mL/min. This reduction is attributed to the lower space time; therefore the contact time among the three phases (phenol, catalyst and air) is lower too.

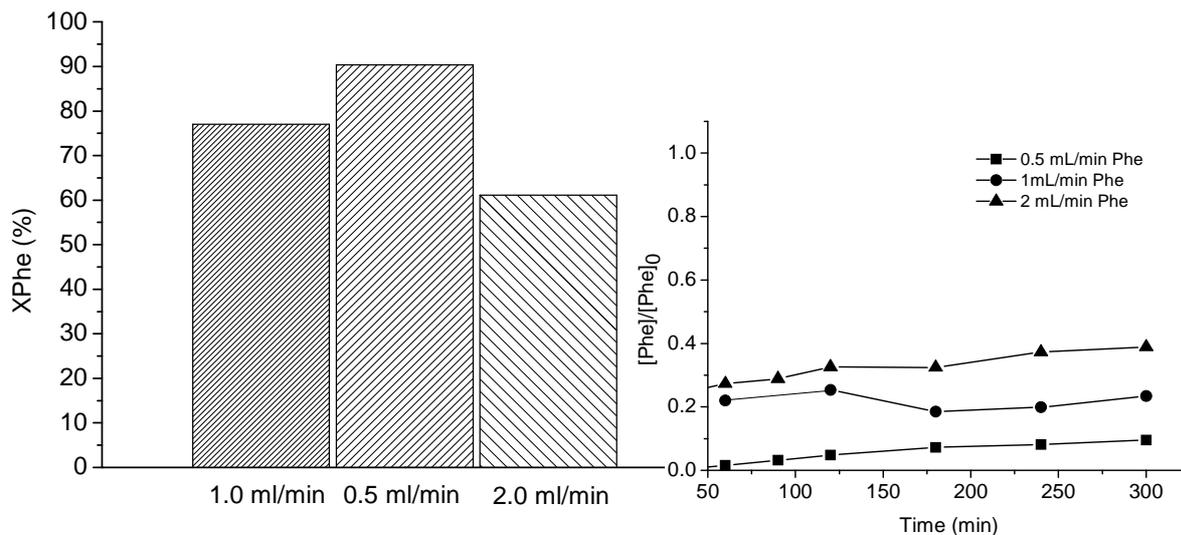


Fig. 5. Effect of liquid flow rate on TOC and phenol conversions as a function of the reaction time.

The effect of catalyst load was investigated in the range of 0.5-2.0 g at 433 K and 2.0 MPa, as shown Figure 6. It can be seen that lower TOC conversion results from lower catalyst load. It is possible to reach the complete phenol oxidation using 2 g of Pt/CNF, and the almost complete mineralization of phenol in the same conditions (93.2%). If it is assumed that wet air oxidation of organic compounds occurs by means of free-radicals chain reaction (Lin et al., 2003), the catalyst will induce free-radicals formation, so the higher the catalyst load, the higher the rate of phenol conversion.

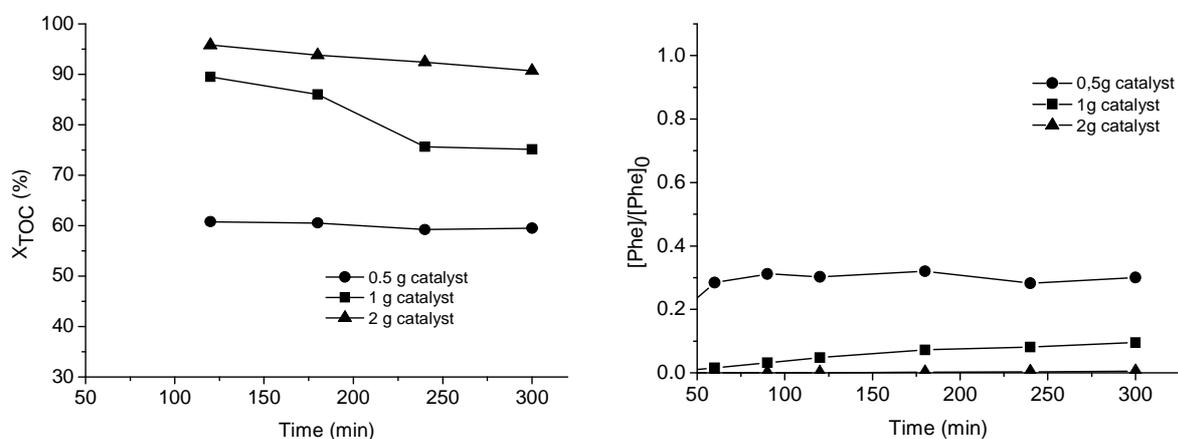


Fig. 6. Effect of catalyst load on TOC conversion and phenol concentration as a function of the reaction time.

Figure 7 reproduce the results of TOC conversion and phenol oxidation obtained when the air flow rates were varied from 150 to 400 mL/min, using 1 g of catalyst, at 2.0 MPa of pressure and a temperature of 433 K.

Apart from this, the best result in TOC conversion is obtained when a flow rate of 300 mL/min is employed, and strangely the worst one when the air flow is increase

until 400 mL/min. Further studies must be done in order to give an explanation to this behaviour.

It is important to notice that an increase of air flow from 150 to 300 mL/min produces a significant effect on the activity of the catalyst for phenol oxidation, but the improvement is negligible when the air flow is higher than 300 mL/min. This trend is similar to pressure effect observed in Fig 4, so that both parameters are closely related.

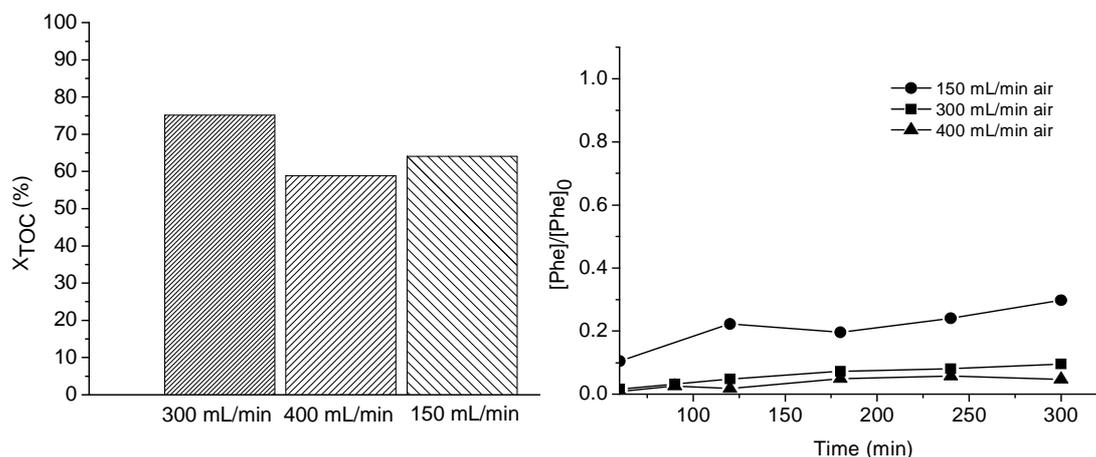


Fig. 7. Effect of air flow rate on TOC conversion and phenol concentration as a function of the reaction time.

The stability of the catalysts is one of the most important aspects in the global evaluation of the performance of a catalyst. Therefore, the platinum catalyst has been used twice in order to evaluate this topic. Before its use, the catalyst was washed with water and dried at 383K overnight. After this treatment, the catalyst was employed in two more phenol oxidation reactions at the same conditions in both of cases. The results can be seen in Fig 8.

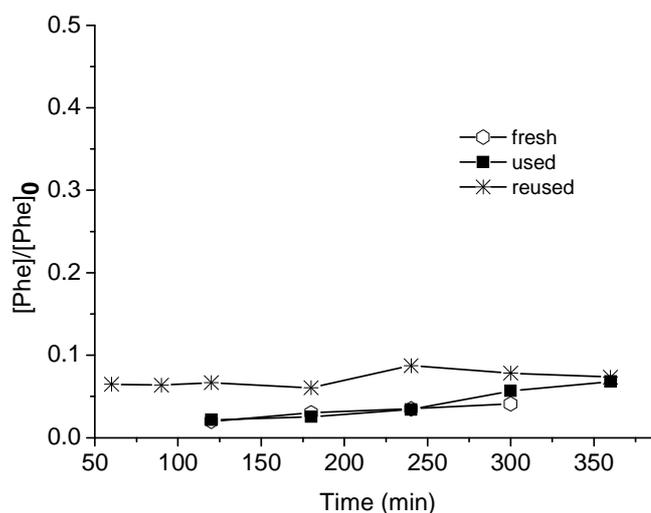


Fig. 8. Phenol oxidation reaction at 433 K, 2.0 MPa, 300 mL/min of air, 0.5 mL/min of phenol, with 1g of fresh, used once and twice Pt/CNF catalyst.

In the oxidation runs presented in Fig. 8, a slight decrease with time in the activity of the reused Pt/CNF catalyst for phenol oxidation is observed. From FRX analysis

carried out over fresh and used catalysts, the difference in platinum weight is less than 0.05%. So, the leaching of active metal was negligible. According to Pintar et al. (2001), heterogeneous catalysts based on precious metals, such as Pt, Ru, Pd, deposited on stable supports are less prone to active ingredient leaching. Phenol is known to form condensation products (dimers) in the liquid phase during CWAO. The irreversible adsorption of these condensation products additionally causes coke catalyst deactivation as observed by Stuber et al. (2005).

- Kinetic model

In a trickled bed reactor, it is assumed that the reaction is only occurring on the solid phase surface. It is necessary for the reactants to transfer into the solid catalytic phase for the reaction to take place (Maugans and Akgerman, 2003). The observed conversion can be interpreted in terms of a first order kinetic scheme, where the rate is directly proportional to the catalyst coverage by the organic substrate. The initial step corresponds to adsorption of phenol, followed by oxidation of the organic molecule, desorption of the oxidized radical and oxygen mediated degradation in solution. Under these conditions, Langmuir-Hinshelwood type kinetics can be assumed:

$$r = \frac{(1/w)kK[Ph]}{1+K[Ph]}$$

where w is the active phase concentration (g_{Pt}/L), k the kinetic rate constant, K the phenol adsorption equilibrium constant and $[Phe]$ the phenol concentration. It is possible to determine the reaction rates as a function of the catalyst weight, depending on phenol concentration variation with time:

$$\frac{W}{F} = \int_0^x \frac{dX_{Phe}}{-r_{Phe}}$$

where W is the catalyst weight (g) and F is the molar flow of phenol (mol/h). This model was solved with the computational program MATLAB, function ODE23, based on a fourth order Runge – Kutta algorithm, resulting the next expression:

$$\frac{W}{F} = \frac{X_{Phe}}{K_1} - \frac{Ln(1-X_{Phe})}{K_1 \cdot K_2 \cdot [Phe]}$$

where:

$$K_1 [g_{Phe} \cdot h^{-1} \cdot g_{cat}^{-1}] = k_{app} \cdot K_{O_2}^{0.5} \cdot C_{O_2}^{0.5}$$

$$K_2 [L \cdot g_{Phe}^{-1}] = K_{Phe}$$

In Fig. 9 experimental data are compared with those calculated from the kinetic model. As expected, experimental and model data are in close agreement, but do not exactly overlap. In both cases, when space time increases the conversion of phenol also increases.

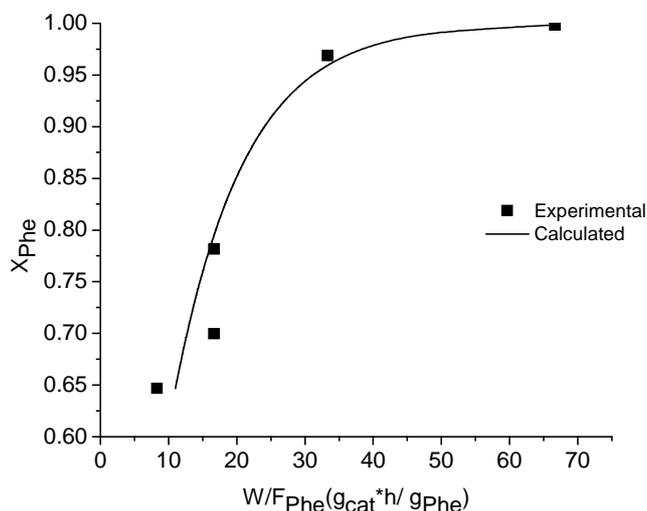


Fig. 9. Phenol conversions as a function of space time (W/F) with Pt/CNF catalyst.

The value of the constants obtained from the model were $0.098 \text{ g}_{\text{Phe}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ (K_1) and $0.057 \text{ L} \cdot \text{g}_{\text{Phe}}^{-1}$ (K_2).

4. Conclusions

It is demonstrated that an effective oxidation of a phenol solution by means of CWAO process in a trickle-bed reactor, using 2 wt.% Pt/NFC as catalyst is possible. The maximum rate of phenol conversion and TOC conversion is observed at high catalyst load.

High phenol conversion and TOC removal can be reached over this catalyst at mild reaction temperature (433 K) and moderate pressure (2.0 MPa), with 1 g of catalyst, and flow rates of 300 mL/min of air and 0.5 mL/min of phenol solution.

In absence of metallic catalyst, phenol oxidation performed was less than 10%.

The same Pt/CNF catalyst can be used several times since the loss of activity is negligible.

The experimental data were satisfactory fitted to a Langmuir-Hinshelwood kinetic model, leading as constants values $0.098 \text{ g}_{\text{Phe}} \cdot \text{h}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$ (K_1) and $0.057 \text{ L} \cdot \text{g}_{\text{Phe}}^{-1}$ (K_2).

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