Chemical Engineering Journal 253 (2014) 486–492

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Kinetics of wet peroxide oxidation of phenol with a gold/activated carbon catalyst

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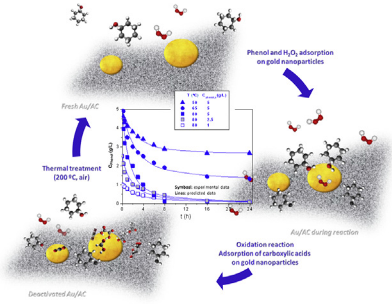
HIGHLIGHTS

- Au/AC is an active and efficient catalyst for CWPO of phenol.
- The Au/AC catalyst provided a good performance within a wide pH range (from acidic to neutral).
- The activity of Au/AC can be recovered by a thermal treatment at 200 °C in air.
- A kinetic model including catalyst deactivation has been developed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 26 January 2014
Received in revised form 14 May 2014
Accepted 15 May 2014
Available online 27 May 2014

Keywords:
Gold nanoparticles
Catalytic wet peroxide oxidation
Phenol
Deactivation
Kinetic model

ABSTRACT

Gold nanoparticles supported on activated carbon (Au/AC) have been tested in catalytic wet peroxide oxidation using phenol as target pollutant. In the current work, the effect of several operating conditions, including initial pH (3.5–10.5), catalyst load (0–6 g/L), initial phenol concentration (0.1–5 g/L), hydrogen peroxide dose (4–100% of the theoretical stoichiometric amount) and reaction temperature (50–80 °C) has been investigated. The results show that the Au/AC catalyst would be useful at relatively high pollutant to catalyst ratios (at least 0.4 w/w) and it can work efficiently within a wide range of pH (3.5–7.5). The catalyst suffers rapid deactivation but its activity can be completely restored by an oxidative thermal treatment at low temperature (200 °C). A kinetic model is presented, capable of describing the experimental results. This model is based on a rate equation of order one for hydrogen peroxide consumption and two for phenol oxidation and includes the catalyst deactivation and its temperature dependence.

1. Introduction

Catalytic wet peroxide oxidation (CWPO) is a well-known process used for the abatement of water pollutants [1,2]. Like other advanced oxidation processes (AOPs), it is based on the action of hydroxyl and hydroperoxyl radicals produced, in this case, upon catalytic decomposition of hydrogen peroxide under relatively mild operating conditions (50–130 °C, 1–5 atm) in the presence of a solid catalyst. However, the difficulty of developing suitable catalysts is pointed out in the literature [3–5], being currently the factor limiting the industrial application of CWPO. This still remains as an important challenge for research on the topic.

Current trends are addressed to the development of supported and un-supported metal nanoparticles, being the most studied iron, manganese and gold nanoparticles [5]. Recent studies on the catalytic applications of gold nanoparticles show that CWPO is a promising area in that respect [6–9]. So far, gold nanoparticles deposited on hydroxyapatite (Au/HAP) [6], diamond (Au/npD) [8] or activated carbon (Au/AC) [9] have shown fairly high activity. However, frankly different efficiencies of hydrogen peroxide consumption were observed with those catalysts, which are attributed to the nature of the support, crucial for the activity of gold [9].

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http://dx.doi.org/10.1016/j.cej.2014.05.063

In our previous studies [9,10], a reaction mechanism and an oxidation pathway for phenol with Au/AC catalyst were proposed based on the experimental evidences. CWPO proceeds through a complex scheme of reactions involving a number of intermediates, such as aromatic compounds (mainly resorcinol, hydroquinone and p-benzoquinone) and low molecular weight carboxylic acids (maleic, malonic, oxalic, acetic and formic), according to the following steps: (i) adsorption of phenol and, preferentially, hydrogen peroxide on the gold-support interface, (ii) production of hydroxyl and hydroperoxyl radicals mainly on the gold surface though in some extension also occurs on the carbon surface and (iii) reaction between hydroxyl radicals and phenol molecules on the gold surface. The hydroxyl radicals are also released to the liquid phase where they react with phenol in solution. Parasitic reactions involving recombination of radical species, can take place yielding hydrogen peroxide as well as oxygen and water.

According to that mechanism, and considering only the main reactions for CWPO of phenol, the following reaction scheme is likely to occur:

- Hydrogen peroxide decomposition into hydroxyl and hydroperoxyl radicals in the presence of gold nanoparticles by a redox cycle:

$$H_2O_2 + Au^0 \rightarrow {}^{\cdot}OH + OH^- + Au^+ \tag{1}$$

$$H_2O_2 + Au^+ \rightarrow {}^{\cdot}OOH + H^+ + Au^0 \tag{2}$$

- Phenol oxidation by radical species into aromatic compounds, low-molecular carboxylic acids, carbon dioxide and water can be described by:

$$\text{Phenol} + {}^{\cdot}OH + {}^{\cdot}OOH \rightarrow \text{Aromatics} + \text{Acids} + CO_2 + HO_2 \tag{3}$$

In the current work, the attention is focused on the potential application of the Au/AC catalyst in CWPO. With this purpose, the effects of several operating conditions, *viz.* initial pH, catalyst load, initial phenol concentration, hydrogen peroxide dose and reaction temperature are investigated and the stability of the catalyst studied, as well as its regeneration. A kinetic model has been developed describing the rates of phenol oxidation and hydrogen peroxide decomposition which includes the catalyst deactivation and its temperature dependence.

2. Materials and methods

2.1. Catalyst

The 0.8 wt% Au/AC catalyst (Sample n°: 106C) was provided by World Gold Council and used as received. The characterization of the catalyst is summarized in Table 1, according to the data provided by the supplier with the exception of the BET surface area (S_{BET}), the external or non-microporous surface area (A_{ext}) and the elemental carbon analysis. The two former were obtained from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar apparatus on the sample previously outgassed overnight at 150 °C to a reduced pressure <10^{-3} torr. Elemental analyses were carried out in a LECO Model CHNS-932 analyzer.

2.2. Oxidation experiments

The CWPO experiments were performed batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of phenol solution at the desired pH (adjusted with HCl or NaOH) were placed in the reactor with the catalyst and heated up to the reaction temperature. After that, 5 mL of an adjusted concentration of hydrogen peroxide aqueous solution were added and the stirring at 1200 rpm started. Previous to the analysis of the reaction samples, the catalyst was separated by filtration (0.45 μm Nylon filter) and dried at 60 °C. All the experiments were performed by duplicate being the standard deviation always less than 5%.

The oxidation runs were performed at different initial pH (3.5–10.5), phenol concentration (0.1–5 g/L), temperature (50–80 °C), catalyst loading (0–6 g/L) and H_2O_2 dose (4–100% of the theoretical stoichiometric amount for complete phenol mineralization, namely 5 $g_{H_2O_2}/g_{Phl}$. Previous to the oxidation runs, the fresh catalyst was contacted with a phenol solution under the same experimental conditions as in the corresponding CWPO runs but in the absence of hydrogen peroxide for adsorption equilibration.

Table 1
Physico-chemical properties of Au/AC catalyst.

Support		Activated carbon
	Carbon type	Camel X40S
	Origin	Vegetal
	Specific surface area, S_{BET} (m^2/g)	934
	External area, A_{ext} (m^2/g)	56
	C (%)	76.6
	O (%)	20.6
Gold		
	Au content (wt.%)	0.8
	d_{Au} (nm)	10.5 ± 6.7
	Au^0 (at.%)	75
	Au^+ (at.%)	12.5
	Au^{3+} (at.%)	12.5

2.3. Analytical methods

Liquid samples from the reactor were analyzed by different procedures. Phenol and aromatic by-products were determined by high performance liquid chromatography, HPLC (Varian, mod. ProStar), low molecular weight acids by anionic suppression ionic chromatography, IC (Metrohm, mod. 761 Compact IC) and total organic carbon (TOC) using a TOC analyzer (O. I. Analytical, model 1010). Hydrogen peroxide was determined by colorimetric titration with a UV 2100 Shimadzu UV–VIS spectrophotometer using the titanium sulfate method [11]. A more detailed description of these analytical procedures can be found elsewhere [9].

3. Results and discussion

3.1. Mass transfer considerations

Experiments at different stirring velocities within the range of 200–1500 rpm showed the absence of limitation due to the external diffusion (see Fig. S1 of Supporting Information). The stirring velocity was set at 1200 rpm for all the following experiments. The Weisz-Prater criterion has been used to check whether internal diffusion could be rate-controlling:

$$\Phi = \eta \cdot \varphi^2 = \left(\frac{\text{observed rate}}{\text{diffusion rate}}\right) = \left(\frac{r_{obs} \cdot L_s^2}{D_{eff} \cdot c_s}\right) \cdot \left(\frac{n+1}{2}\right) < 0.15 \tag{4}$$

Assuming pseudo-second order kinetics ($n = 2$), as will be further demonstrated, the above expression is simplified to:

$$\Phi = \eta \cdot \varphi^2 = \left(\frac{k_{obs} \cdot C_{phenol} \cdot L_s^2}{D_{eff}}\right) \cdot \left(\frac{3}{2}\right) \tag{5}$$

The observed kinetic rate constant for phenol oxidation, $k_{obs} = 6 \cdot 10^{-5}$ L/(g_{Ph} h), was calculated using a power-law pseudo-second order model at the highest temperature (80 °C) and catalyst