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The role of the carbonaceous deposits in the Catalytic Wet Oxidation (CWO) of phenol

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Abstract

Different Ce—Mn composites have been used as catalyst for the Catalytic Wet Oxidation (CWO) of Phenol under different operating conditions in the range of 80–160 °C and 0.5–2 MPa P_{O_2}. High mineralization performances were observed by operating at moderate temperatures (130–160 °C) and oxygen partial pressures (1–2 MPa). The mechanism proposed for the mineralization process includes the initial polymerization of phenol with the rapid formation of a carbonaceous deposit on the catalytic surface (favoured by the presence of Mn), which is later oxidized to CO_2 and H_2O (the richest Ce catalysts being more active in this process). At milder conditions, i.e. temperatures below 110 °C, no mineralization was observed and only the first process operates producing the irreversible polymer deposition until the total activity loss of the catalyst for phenol elimination.

Keywords: Phenol; Catalytic Wet Oxidation; Wastewater; Ce—Mn composites; Carbonaceous deposit; Deactivation; Mechanism; TEM

1. Introduction

Drinking water abundance in the Earth has dramatically decreased during the previous decades, indicating a high level of exploitation and contamination of the existing water resources. Diverse industrial (petrochemical, pharmaceutical and agro-alimentary) and also domestic activities produce liquid effluent with highly bio-toxic and refractory organic pollutant that has to be treated before discharge in the environment. New health standards and environmental regulations become more and more severe for the disposal. In this sense, wastewater treatment would play an important role in the zero-discharge policy that governments want to apply.

Wet Oxidation (WO) can be considered as an efficient method to mineralize organic compounds in liquid effluents with medium Chemical Oxygen Demand ($5 < \text{COD} < 100$ g l^{-1}), thus converting this process in the basis of a very attractive technology for the treatment of industrial waste streams which are too dilute to be incinerated and yet too toxic to be biologically treated. Nowadays, there are more than 150 plants worldwide that use this technology and different industrial processes have been patented [1,2]. The use of catalyst in this process (Catalytic Wet Oxidation, CWO) can reduce the severity of the WO conditions and makes the processes more attractive for industrial applications. In fact, WO and CWO processes have been successfully applied to the treatment of wastewaters from textile/paper industries [3,4], food industries, chemical and pharmaceutical industries [5,6] and the alumina industry [7,8]. Good performances have been also observed using synthesized substrates such as ammoniacal and phenolic solutions [9,10]. Heterogeneous ceria-based catalysts have attracted attention for these purposes because of their excellent performance, often attributed to their capacity to exchange oxygen with the reaction environment [11]. Among the catalysts used for CWO processes, heterogeneous Ce/Mn composite oxides stands out because of their high catalytic activity [12]. Nevertheless, it has been reported that they often suffer from activity loss,

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which is frequently attributed to the formation of a carbonaceous deposit on the surface of the catalytic particles [13–15]. In this work, we demonstrate that the carbonaceous deposit can be oxidized and instead of being the origin for the apparent deactivation, this process can be considered as the initial step for the total mineralization of phenol. The role of the Ce and Mn in the formation/oxidation of the deposits is also discussed.

2. Experimental section

2.1. Material synthesis

Cerium–Manganese composite oxides, with Ce/Mn atomic ratios of 85/15 (CM85), 50/50 (CM50), 15/85 (CM15) and 0/100 (CM0) were prepared by coprecipitation from an aqueous solution of manganese (II) and cerium (III) nitrates (Merck), followed by drying at 100 °C and calcination in air at 500 °C for 1 h. The characterization of the samples was previously report [16].

2.2. Characterization techniques

Transmission Electron Microscopy (TEM) measurements were performed on a FEI CM200Feg microscope with a structural resolution of 0.23 nm.

2.3. Catalytic tests

The reactions were carried out in a 500-mL autoclave equipped with a pollutant injector, a valve for sampling, a magnetic stirrer and a pressure gauge. In a typical run, the autoclave was charged with 250 ml of distilled water, 0.5–2.0 g of catalyst and a certain pressure of oxygen (0.5–2.0 MPa). A concentrated solution of phenol was injected at the reaction temperature (80–160 °C). Total Organic Carbon (TOC) was measured by using a Shimadzu TOC analyzer and phenol concentration was determined by gas chromatography. The carbon content on the catalyst surface was quantified by CHN elemental analysis (Carlo Erba, model 1106).

3. Results and discussion

Two ranges of temperatures and P_{O_2} have been considered for which reaction occurs with or without real mineralization of phenol into CO_2 and H_2O. Results obtained for these two ranges are now described and referenced as mild (90–110 °C and 0.5 MPa P_{O_2}) and moderate (130–160 °C and 1.0–2.0 MPa P_{O_2}). Fig. 1 shows the evolution of the phenol reduction percentage in several experiments performed with the CM50 catalyst at mild conditions and different g phenol/g catalyst ratios. As it can be seen, the complete removal of the pollutant was only achieved with the lowest phenol concentration, while low phenol and TOC reduction was observed for more concentrated phenol solutions. In the latter case, the degradation profiles levelled off, thus indicating the total activity loss of the catalyst, after reaction times of 50–100 min. It should be remarked that similar TOC and phenol conversions values were obtained for experiments with similar phenol concentration-catalyst loading ratio (1900/1 and 3800/2).

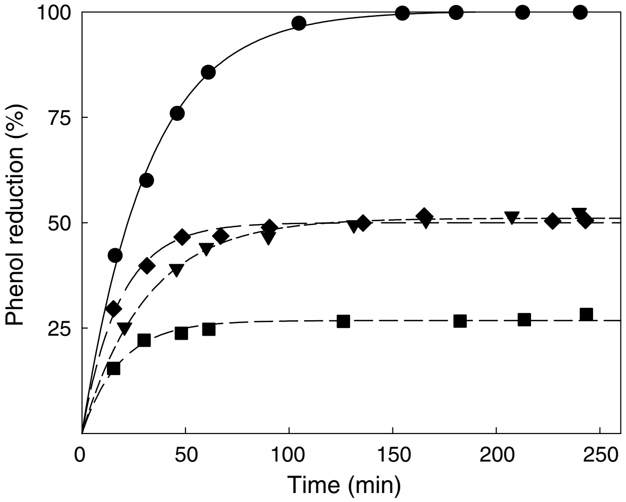

Fig. 1. Phenol elimination using CM50 catalyst at 90 °C and 0.5 MPa $P(O_2)$ and the following initial phenol to catalysts ratios (ppm of carbon/g of catalysts): 500/1 (●), 1900/1 (◆), 3800/2 (▼) y 3800/1 (■).

In order to elucidate the reason for this activity loss, the catalysts were recovered after reaction and characterized by TPD, TPO, and TEM. Fig. 2 shows a typical HREM image obtained for a used catalyst. A thick carbonaceous layer (20 nm) is observed covering the entire sample, what in principle, could be argued as the principal cause for the collapse of the catalyst in accordance to [6]. The carbon contents of the recovered samples, summarized in Table 1, are similar for all the aged catalyst, which it is in good agreement with the hypothesis of a surface collapse occurring after deposition of a certain amount of carbonaceous layer. Table 1 also shows the carbon balances for the experiments presented in Fig. 1. As it can be deduced from these data, the total amount of carbon removed from solution

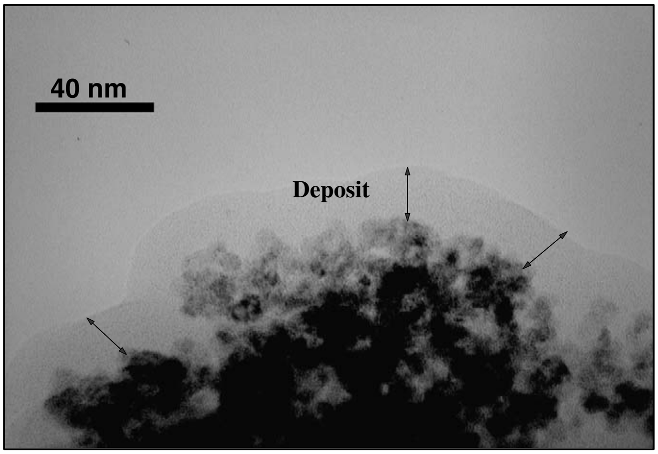

Fig. 2. TEM image of CM50 after reaction (◆).

Table 1
Carbon balances for experiments presented in Fig. 1

C_0/m$_c$[a]	ΔC_{TOC}/m$_c$[b]	C_d/m$_c$[c]	D[d]
500/1	486	479	124
1900/1	986	960	249
3800/1	1040	982	255
3800/2	1010	970	252

[a] Initial phenol concentrations/mass of catalyst ratios (ppm carbon/gram of catalyst).

[b] TOC removal per gram of catalyst after 4 h (ppm carbon/gram of catalyst).

[c] TOC removal due to the carbonaceous deposit (ppm carbon/gram of catalyst).

[d] Carbon amount per gram found in the used catalyst (mg of carbon/gram of catalyst).

exactly corresponds with the carbon content of the formed C-layer, thus indicating that, at the operated conditions, phenol is fully converted into carbonaceous deposit, and not mineralized to CO_2 and H_2O. The activity loss of the catalyst for phenol elimination is observed once the collapse of the surface for deposit adsorption is achieved. In the case of the CM50 catalyst, this occurs for a deposit containing 250 mg of carbon per gram of catalyst. Similar values were obtained for the all series of Ce—Mn composites. These results, shown in Table 2, indicate that the amount of carbon per m^2 deposited on the catalyst, before its collapse, increases with Mn content. In fact, only negligible amount of carbon was found for pure CeO_2 catalyst, which, moreover, does not exhibit any activity under these conditions. Therefore Mn can be considered as responsible for the carbonaceous deposit formation. Table 2 also includes the values for phenol and TOC removal, as well as a quantification of the carbonaceous deposits. According to these data, we can assume that carbon mineralization (expressed as C_{CO_2} in Table 2) is almost negligible operating at mild conditions.

In order to get some insight into the nature of the carbonaceous deposit, TPO and TPD experiments were performed on the "deactivated" catalysts. Results obtained in a typical run by using these techniques are shown in Figs. 3 and 4, respectively. Oxygen consumption observed in the TPO experiment is linked to the burn-off of the carbonaceous materials. CO_2 and H_2O are the unique products formed on this process, thus indicating the hydrocarbon-like nature of the deposit. Similar results were obtained by Larachi by running also TPO experiments on Ce—Mn oxides used as catalysts in WAO processes [15]. Regarding the origin of such a deposit, it could be formed by the oxidative polymerization of phenol occurring on the catalyst surface, as suggested in [17]. Kim [18] has recently confirmed by FTIR and NMR that the C-deposits have a mainly aromatic nature, which it is in good agreement with the polymerization hypothesis.

Table 2
Carbon balances for experiments carried out with different Ce—Mn composites at mild (90 °C and 0.5 MPa $P(O_2)$) and moderate conditions (160 °C and 2 MPa $P(O_2)$)

	Sample	ΔC_P/m$_c$[a]	ΔC_{TOC}/m$_c$[a]	C_d/m$_c$[b]	C_{CO_2}[c]	D/S[d]
Mild	CM0	631	620	615	0.3	19.4
	CM15	1069	1021	986	1.9	6.8
	CM50	1005	986	960	1.5	3.7
	CM85	825	792	770	1.1	3.6
Moderate	CM0	–	900	680	17	–
	CM15	1892	1474	600	46	–
	CM50	1887	1525	652	46	–
	CM85	1762	1424	737	38	–

The initial phenol to catalysts ratio was (ppm of carbon/g of catalysts) 1900/1.

[a] Phenol (C_P) and TOC removal per gram of catalyst after 4 h (ppm carbon).

[b] TOC removal due to the carbonaceous deposit (ppm carbon).

[c] Percentage of carbon removed due the real mineralization.

[d] Carbon amount per surface unit in the used catalyst after its collapse (mg of carbon/m^2).

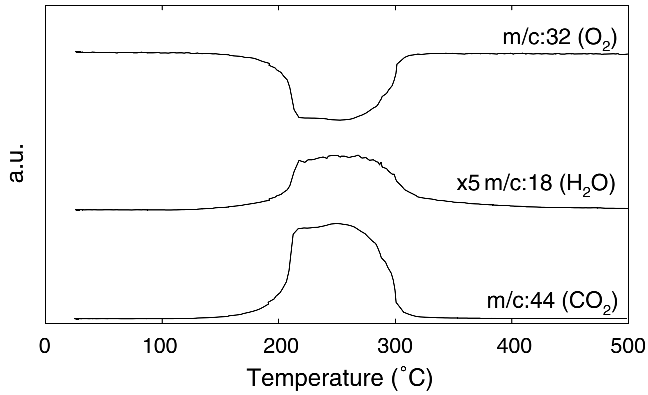

Fig. 3. TPO-MS profiles of used CM50. The sample was pre-treated at 125 °C in He flow, in order to remove physisorbed water. The CWO conditions were Reaction time: 240 min; Initial phenol concentration: 500 ppm; Partial oxygen pressure: 0.5 MPa; Temperature: 90 °C.

As deduced from Fig. 3, the carbonaceous deposit can be fully oxidized to CO_2 and H_2O by calcination above 250 °C. We have also evidenced that, after this treatment, the collapsed catalyst recovered its initial catalytic activity, thus confirming the role of the carbonaceous deposit on the activity loss for phenol elimination.

No evidences for phenol desorption were obtained during TPD experiments conducted on these catalysts. Only H_2 evolution was observed (Fig. 4a), in the temperature range 400–900 °C, as a consequence of the deposit carbonization induced by the TPD experiment. Fig. 4b shows traces obtained during a further TPO experiment following the previous TPD. The CO_2 formation and the absence of water signal in this TPO corroborate the hypothesis of the carbonization of the deposit during the TPD, and its further oxidation in the subsequent TPO measurement. These evidences indicate that is not phenol, but a polymer what is strongly absorbed on the catalyst surface, probably forming a complicate net surrounding all the catalyst particles, as seen in Fig. 2.

The results obtained under moderate operation conditions are considerably different. Fig. 5 shows the evolution with time of phenol concentration in a CWO experiment of phenol ($C_0 = 1900$ ppm) over CM15 at 160 °C and oxygen

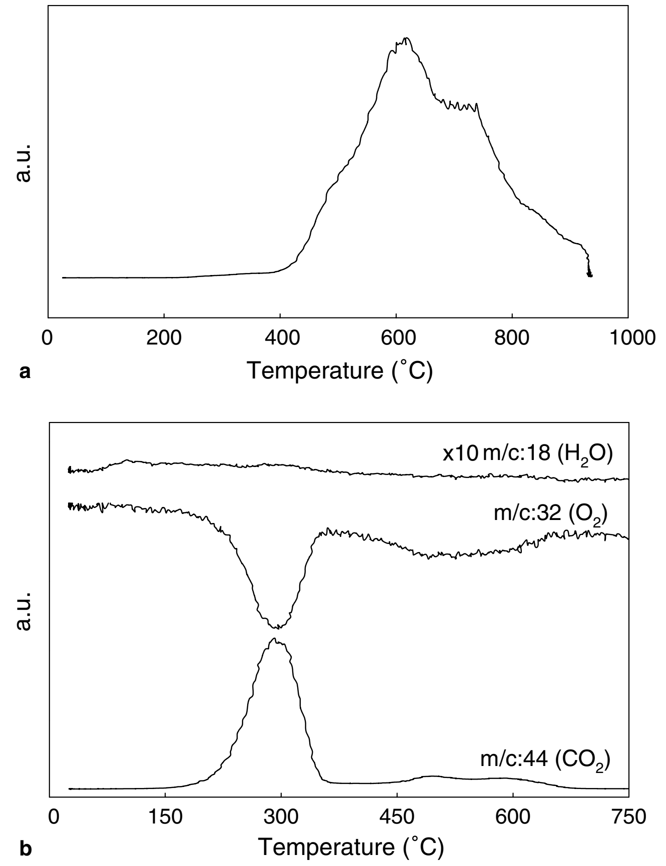

Fig. 4. DPT-MS of hydrogen (a) and subsequent TPO (b) of used CM50. The CWO conditions were Reaction time: 240 min; Initial phenol concentration: 500 ppm; Partial oxygen pressure: 0.5 MPa; Temperature: 90 °C.

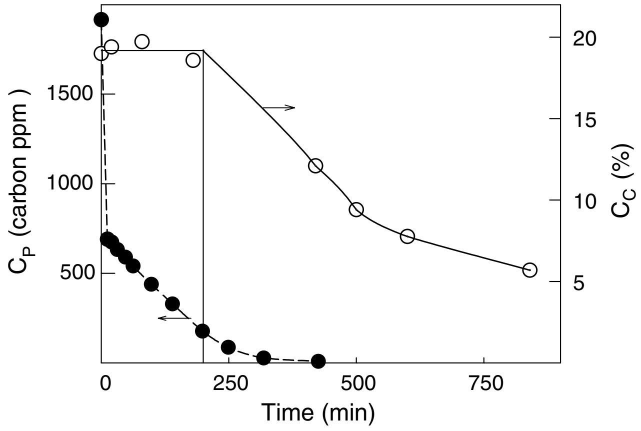

Fig. 5. Evolution of phenol concentration (●) and weight percentage of carbon deposit over the catalyst surface (○) using one gram of the sample CM15 at 160 °C and 2.0 MPa $P(O_2)$ and an initial phenol concentrations of 1900 ppm of carbon.

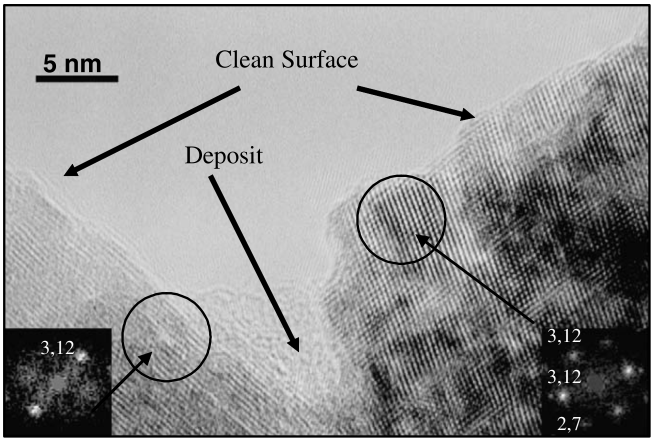

Fig. 6. TEM image of CM15 after reaction using one gram catalyst at 160 °C and 2.0 MPa $P(O_2)$ and an initial phenol concentrations of 1900 ppm of carbon. Digital diffraction patterns (inset images) can be indeed to a ceria fluorite-like structure.

partial pressure of 2.0 MPa. Conversion of 100% of phenol is obtained after 400 min of reaction. The TEM images of the used catalyst indicate that, in this case, most of the surface is C-free and only a residual amount of carbon remains (Fig. 6), in agreement with the evolution for carbon content in the catalyst, expressed as weight percentage, in Fig. 5. The phenol and TOC removal values for the all series of investigated catalysts are summarized in Table 2. As expected, catalytic activity increased by working at moderate conditions, the CM15 and CM50 catalysts showing the higher values for both, phenol and TOC elimination. Values for product distribution and carbon mineralization (expressed as C_{CO_2}) are also included in this table. It should be noticed that carbon mineralization, that is conversion of phenol into CO_2 and H_2O, is only achieved by working at moderate conditions.

Regarding phenol evolution depicted in Fig. 5, three different stages can be identified: (I) Drastic reduction, (II) Linear elimination, and (III) Slow exhaustion. First stage coincides with the formation of the C-deposit, which is a fast process occurring at the very beginning of the reaction. This reduction exactly corresponds with the maximum amount of polymer adsorbed on the catalyst, leading to the catalyst deactivation observed at milder operation conditions ($\sim$250 mg of carbon/g of catalyst). Once the deposit is formed, a linear evolution for phenol removal is observed (stage II), thus accounting for a constant reaction rate for this process. This may indicate that the fraction of covered active sites on the catalyst stays invariable, which is in agreement with the carbon content in the solid remaining also constant. Thus, we can conclude that, in this stage, the deposit is being simultaneously eliminated by oxidation and regenerated by polymerization from phenol remaining in solution. When phenol is exhausted, the deposit cannot be regenerated and the carbon content of the catalyst begins to decrease due to the oxidation of the deposit.

Acetic acid was found as intermediate compound during reaction, thus corroborating that, operating at these conditions, the mineralization of phenol is taking place. The acetic acid concentration in the media increases in the initial stages of the reaction and subsequently decreases during stage III. This indicates that the Ce—Mn composites are also active for the removal of this refractory acid, which is considered as the limitation step in the CWO of big organic molecules as phenol, ethyl glycol, etc [19]. In this sense, Ce—Mn oxides are efficient catalysts for the CWO of different organic compound, also refractory, thus having a promising future for treating real industrial effluents.

The all series of Ce—Mn oxide catalysts exhibited a similar behavior, the slope in the linear region being dependent on the catalyst composition. This slope might be related to the rate of the polymer oxidation reaction, i.e. to the real oxidation capacity of the catalyst. The catalytic activity sequence in this region was as follows (TOC removal rate is indicated in parenthesis as ppm min^{-1}):

$$\text{CM85}(2.4) \approx \text{CM50}(2.2) > \text{CM15}(1.7) \gg \text{CM0}(0.9).$$

According to these data, the richest Ce samples exhibit the higher activity. This can be related with the well known redox properties of the ceria (Ce^{3+}/Ce^{4+}), which would facilitate the processes involved in the oxidation of the organic compound [2].

4. Summary

Our research indicates that operating at low temperature and oxygen partial pressure, all phenol removed from the solution is transformed in a C-layer of about 20 nm formed on the catalyst surface, leading to its total apparent deactivation. The ultimate capacities for the collapse of the catalysts surface increases with Mn contents. No mineralization reaction takes at this operation conditions. On the contrary, phenol removals near to 100%, even for high phenol concentration, were achieved by operating at moderate temperatures (130–160 °C) and oxygen partial pressures (1–2 MPa). The mechanism proposed for the process includes the initial polymerization of phenol with the formation of a deposit on the catalytic surface (favoured by the presence of Mn), followed by its oxidation into small organic molecules, i.e. acetic acid, as intermediate step for the further mineralization into CO_2 and H_2O (the richest Ce catalysts being more active in these oxidation processes).

In conclusion, Ce—Mn composites show a high and stable activity for phenol and acetic acid wet oxidation at moderate condition, which are still far bellow that the conditions used in the conventional wet oxidations processes. This excellent behavior can be explained by the role of Mn and Ce at the different stages of the proposed mechanism for the wet oxidation of phenol.

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