The influence of the catalyst on the CO formation during catalytic wet peroxide oxidation process

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Abstract

Herein, the formation of CO as a harmful product upon the Catalytic Wet Peroxide Oxidation (CWPO) process is studied in presence of different solid catalysts: an activated carbon-supported Fe (Fe/AC), a metal-free catalyst based on Graphene Nanoplatelets (GNP), and 1.6 wt.% Fe containing Cr_2AlC MAX-phase catalyst. The evolution of the gas effluent during the CWPO has been compared to that obtained in the Fenton process.

CO yield was significantly higher in the homogeneous Fenton where CO concentration reaches a maximum of ca. 6651 mg/Nm^3, a far from negligible concentration bearing in mind the emission limit value for CO according to Directive 2010/75/EU is 150 mg/Nm^3 (as 10-minutes average value). By contrast, in presence of Fe/AC and, notably, GNP and MAX catalysts, a more progressive phenol and aromatics intermediates oxidation resulted in a much lower CO maximum concentration in the gas phase at the exit of the reactor of ca. 2454 mg/Nm^3, 170 mg/Nm^3 and 187 mg/Nm^3, respectively.

The CWPO process with GNP and MAX phase, though require longer reaction times than Fenton, were able to achieve high mineralization degrees with significantly lower CO selectivity. Hence, when compared to homogeneous Fenton oxidation, CWPO results in a better process sustainability during the treatment of high-loaded phenolic wastewaters by decreasing the hazardous CO gaseous emissions avoiding this way the secondary pollution during the oxidation process.

Keywords: Carbon monoxide, Metal-free catalysts, catalytic wet peroxide oxidation, Fenton oxidation, graphene, MAX phase

1. Introduction

Nowadays, Advanced Oxidation Processes (AOPs) are considered efficient technologies for the decontamination of water with recalcitrant compounds [1,2,3,4]. In AOPs, *in situ* generated hydroxyl radicals ($HO\cdot$) are the main responsible for abatement of pollutants through different by-products which can be eventually oxidized until CO_2 and H_2O [5]. Nevertheless, one of the main concerns regarding AOPs is the potential formation of harmful oxidation intermediates that, occasionally, can present even more toxicity than their parent pollutants [6,7,8,9].

Many works have focused on the possible formation of hazardous by-products in the liquid phase [9,10,11] but, unfortunately, the analysis of potential harmful products that can be released to the gas phase has not been conveniently addressed. In this sense, few studies dealing with air purification by photocatalytic oxidation have revealed that carbon monoxide is always present as a final oxidation product along with CO_2, [12,13,14]. Also, we have recently demonstrated that significant amounts of CO are also produced during Fenton oxidation processes [15,16]. These works have shown the critical effect of the type of oxidizing pollutant and operational conditions on the carbon monoxide formation during the AOPs.

On the other hand, among all the AOPs technologies, Catalytic Wet Peroxide Oxidation (CWPO) emerge as an attractive alternative to the employment of dissolved Fe in Fenton process. In this sense, CWPO can generate hydroxyl radicals (HO·) by the effective decomposition of H_2O_2 with an appropriate heterogeneous catalyst, thus allowing to work in wide range of pH limiting the generation of Fe sludge, one of the main limitations of the homogeneous Fenton process [17]. Over the last decades many works have been devoted to the study of iron-based materials (Heterogeneous Fenton), where iron are usually supported on different materials such as activated carbons [17,18], pillared clays [19] alumina [20] or zeolitic materials [21], among others. At present, the trend of CWPO processes is the search and the development of more stable and efficient materials capable to avoid iron or other metal leaching [17,22]. In this regard, different works focused on design of metal-free catalysts as promising alternatives to metal-based catalyst [23,24,25,26]. Graphene and graphene oxide (GO) are good examples of these new metal-free materials for the abatement of pollutants in water by the CWPO processes [22].

Herein, the efficiency upon the Catalytic Wet Peroxide Oxidation (CWPO) process with different catalysts, with special attention to carbon monoxide production as a harmful in the gas phase, is discussed and compared to that obtained in the homogeneous Fenton process. Three catalyst with substantial differences have been selected: (i) a conventional metal-based catalysts based on Fe supported on Active carbon (Fe/AC),

(ii) one metal-free catalysts with a 2-dimensional structure consisted on Graphene Nanoplatelets (GNP) and (iii) a Fe doped MAX-phase based on Cr_2AlC which combines both metallic and ceramic properties and can catalyze several oxidative reactions [27].

The results of this work provide new valuable data regarding the importance of monitoring the gas phase generated during the treatment of high-loaded wastewaters, and indicate that the appropriate selection of the catalysts can improve the environmental sustainability of the CWPO process decreasing the secondary pollution during the oxidation process.

2. Experimental

2.1 Catalysts preparation

Table 1 summarizes the main properties of the employed catalysts. Briefly, the iron supported activated carbon catalysts (Fe/AC) with a nominal iron content of 4% w/w was prepared by incipient impregnation at room temperature with an aqueous solution of iron nitrate in a commercial activated carbon, supplied by Merck (Cod. 102514; d_p: 1.5 mm). The sample was dried 12 h at 70 ºC and finally, heat treated at 200 ºC in air atmosphere for 4 h. As can be observed in Table 1, the catalysts presented high surface area, around 930 m^2/g, and relatively high oxygen content due to the final heat-treatment in air atmosphere. More preparation details are provided elsewhere [28].

Graphene nanoplatelets (GNP), obtained from Angstron Materials Inc., was employed as received in powder form. GNP presented a through-plane dimension of 50-100 nm and low oxygen content (less than 1 %) and relatively low S_{BET} ($\leq 40\ m^2/g$) (Table 1).

Cr_2AlC MAX powders were synthesized from the reaction of their elemental constituents (chromium, aluminium and graphite) at high temperature (1350 ºC) in argon atmosphere, according to the procedure described elsewhere [J. Gonzalez-Julian, S. Onrubia, M. Bram, O. Guillon, "Effect of sintering method on the microstructure of pure Cr_2AlC MAX phase ceramics, J. Ceram. Soc. Jpn. 124 (4) 415-420 (2016)]. The compacted MAX specimen was planetary milled with zirconia balls to achieve a mean particle size of 0.9 µm. The powders, with a S_{BET} value of 10 m^2/g, had a purity of 97.1%, determined by inductively coupled plasma-optical emission spectroscopy (ICV-OES), and contained a 1.6 wt.% of Fe that came from the raw chromium constituent and 1.2 wt.%. of oxygen.

2.2 CWPO experiments

CWPO experiments were carried out in a high-pressure reactor (BR-300, BERGHOF) which was operated in continuous mode for the gas effluent, further details are given elsewhere [15,16]. In order to analyse the gas produced during the process, 1 L/min N_2 stream was continuously introduced into the reactor. The gas effluent exit containing the CWPO or Fenton off-gas effluents generated along the oxidation process were conducted to an CO and CO_2 detector, where the instant concentrations were recorded. The selected operating conditions were in all cases maintained: 1000 mg/L of initial phenol concentration, the stoichiometric amount of hydrogen peroxide (5000 mg/L), T = 80 ºC, atmospheric pressure and 5 g/L of catalyst in CWPO experiments or 100 mg/L of Fe^{2+} in the Fenton trials. An initial pH of 3 was selected in order to appropriately compared the CWPO experiments with the Fenton process.

2.3 Analytical methods

Liquid samples from the reactor were analysed at different reaction times. Phenol and aromatic by-products were quantified by high performance liquid chromatography (Thermo Fisher Scientific) using a C18 column (Eclipse Plus C18, 150 x 4.6 mm, 5 μm) at 323 K with a 4 mM aqueous sulfuric acid solution at 1 $mL\cdot min^{-1}$ as mobile phase. Short-chain organic acids were analysed by ion chromatography (IC) equipped with a conductivity detector (Metrohm 883 IC) using a Metrosep A supp 5 column (250 x 4 mm) as stationary phase and 0.7 $mL\cdot min^{-1}$ of an aqueous solution of 3.2 mM Na_2CO_3 and 1 mM $NaHCO_3$ as the mobile phase. Total organic carbon (TOC) in solution was measured using a TOC analyser (Shimadzu, mod. TOC-Vsch). H_2O_2 concentration was determined by colorimetric $TiOSO_4$ method using a UV2100 Shimadzu UV–vis spectrophotometer.

CO and CO_2 were continuously monitored, thus gas exiting the reactor at 1 $L\cdot min^{-1}$ (containing the CWPO and Fenton gaseous products and the N_2 carrier) was analysed using an Ultramat 23 infrared detector (Siemens). CO_2 and CO signals in ppmv were recorded every 6 s. The accumulated amounts of CO_2 and CO produced (in mg) along the oxidation processes were estimated by integration of concentration profiles.

3. Results and discussion

3.1 CWPO performance

The evolution of TOC, phenol, aromatics, acids and the accumulated amount of CO and CO_2 for the Fenton oxidation and the CWPO with Fe/AC, GNP and MAX catalysts have been represented in Figure 1 and 2, respectively.

As can be noted in Figure 1, in the homogeneous Fenton reaction, phenol and aromatics were rapidly degraded at the first stages of the reaction, hereafter the oxidation process continued with the short chain organic acid and, as expected, CO_2 and TOC curves evolve similarly. On the contrary, carbon monoxide was mostly produced at the first minutes of the reaction, fact that is attributed to the complete oxidation of the aromatics intermediates, being these species the main responsible for the CO production [15]. Interestingly, although TOC elimination with the Fe/AC catalyst was noticeable higher than in the homogeneous Fenton process, CO_2 and CO evolved to a much lesser extent. In this sense, as can be seen in the carbon mass balance, represented in Figure 3, in the Fenton process nearly all the TOC eliminated fits with the CO/CO_2 produced, while a great imbalance between the TOC remaining in the liquid phase and the CO/CO_2 released was observed in the Fe/AC catalyst. This can be directly attributed to the strong adsorption capacity of the activated carbon used as support in the Fe/AC catalyst [29]. It should remarked that the abrupt end of the oxidation process with Fe/AC at approximately 30 min of reaction time, corresponds to the stage when hydrogen peroxide was completely consumed, likely due to the high concentration of active carbon employed in the CWPO with the Fe/AC catalyst [18,30]. Hence, although an 85 % of TOC disappearance was achieved with Fe/AC catalyst, uniquely the 30 % of the initial TOC was mineralized to CO_2 (see Figure 3).

As can be seen in Figure 2, although CWPO process with GNP and MAX catalysts achieved lower TOC degradation rates than the Fenton process, both catalysts maintained relatively high mineralization efficiencies attaining TOC conversions of 45.9 and 53.8 %, respectively, at 80 min of reaction time. The carbon mass balance (see Figure 3) shown that, at the end the process, TOC disappearance in the liquid phase was equivalent in a large extent to the final mineralization products (CO and CO_2). Hence, all TOC disappearance with GNP and MAX catalysts can be directly attributed to the mineralization to CO and CO_2 and no evidence of TOC adsorption was observed in either catalysts.

Lastly, it can be emphasized that although GNP and MAX presented a similar trend in the TOC curves and CO_2 evolution which continuously evolved along the oxidation process, only when MAX catalyst was employed phenol and aromatics were completely oxidized. This can explain why CO trends towards an asymptotic value when MAX was employed in the CWPO process [15].

3.3 Carbon monoxide selectivity

In order to gain an insight into the role of the catalyst nature on the CO selectivity during the CWPO, temporal profiles of the accumulated amount of CO and CO_2 have been represented in Figure 4. Additionally, the CO selectivity, expressed as mg of CO in gas phase per mg of carbon dioxide produced, is represented in Figure 5.

It can be noted in Figure 4 that, in the phenol CWPO upon Fe/AC catalyst, CO was rapidly produced at the beginning of the reaction, coinciding with the complete removal of the aromatic species (see Figure 1), main step involved in the CO production [15]. This behavior is similar to that found for Fenton oxidation. On the contrary, lower degradation rates for phenol and aromatics took place in CWPO processes upon GNP and MAX catalysts, thus CO production was limited at the beginning of the reaction and a more progressive release of CO can be observed.

Interestingly, CO selectivity (represented in Figure 6) was significantly lower in the CWPO comparing to the Fenton. This is indicative that the presence of a solid surface, and then the introduction of an adsorption step in the reaction mechanism, affects the extension of the reactions involved in the oxidation pathway. Bearing in mind that, regardless the oxidative mechanism implicated in the CO, this harmful species could be further oxidized to CO_2 via attack by $^{\cdot}OH$ radicals [31]. In this sense, it may be reasonable to conclude that when heterogeneous reactions take place more slowly, CO oxidation can be produced at the surface of the catalyst and more chances for to CO to be oxidized to CO_2 are before it can leave the liquid surface and released in the gas phase.

CO selectivity seems to be substantially affected by the catalyst nature (i.e.: metallic based materials, metal free, catalyst supports….) employed in the CWPO, where different pathways of the surface which can inhibit or favor the formation of CO. In this sense, the relatively low CO yield achieved with the Fe/AC compared to Fenton can be directly ascribed to the strong adsorption detected with this catalyst as above discussed. Thus, while the adsorption of aromatic intermediates species adsorption is favored over the acids on the carbonaceous surface in the Fe/AC catalyst [], acids are easily released and oxidized minimizing the CO yield [15].

On the other hand, a different oxidation pathway could explain the lower selectivity found in MAX systems compared to GNP catalyst. In this sense, MAX exhibited a predominant selectivity to catechol instead of hydroquinone or p-benzquinone (see Figure S1 of the Supporting Info) while, as usually occurs in carbon-based catalysts [], phenol oxidations proceed mainly through p-benzoquinone/hydroquinone intermediates in the GNP, being the former more selective to CO in accordance with our previous work [15].

3.4 Analysis of harmful CO continuous emissions

A practical consequence of the above discussed CO yields can be observed in Figure 8, where the continuous CO and CO_2 emissions have been represented for the homogeneous Fenton oxidation (Figure 8a) and for the CWPO process with Fe/AC, GNP and MAX and catalysts (Figure 8b, c and d, respectively). As can be seen in the Fenton process, fast ring opening of aromatics intermediates occurred at the initial stages of the reaction and CO release mainly took place at short reaction times (< 5 min). Hence, CO concentration reach a maximum of ca. 5450 ppmv (6720 mg/Nm^3), a far from negligible concentration bearing in mind that the emission limit value for CO according to Directive 2010/75/EU is 150 mg/Nm^3 (as 10-minutes average value) []. By contrast, in presence of Fe/AC and, in a much greater extent, GNP and MAX catalysts, a significantly lower oxidation rate and a progressive phenol and aromatics intermediates oxidation resulted in a much lower CO maximum concentration released to gas phase. Hence, CO concentration reached a maximum of ca. 1,990 ppmv (2,454 mg/Nm^3), 152 ppmv (187 mg/Nm^3) and 138 ppmv (170 mg/Nm^3), for the Fe/AC, GNP and MAX pahse, respectively .

According to the above results, the decrease of the instantly and the average CO emission values period of time was in the case of the Fenton process 2.7, 39.5 and 35.4 times higher than that obtained with the Fe/AC, GNP and MAX phase catalyst respectively. Therefore although a slightly lower degree of mineralization were achieved as expected in the CWPO process, these heterogeneous systems are capable to, on the one hand, maintain good TOC removal efficiencies while, on the other, results in a minorization CO productions and instantly CO emission resulting in a substantial decrease of the hazardous gaseous emissions.

4. Conclusion

This work highlights the noticeable concentrations of CO that are emitted in the gas phase generated during the treatment of high-loaded wastewaters by thermal advanced oxidation treatments such as CWPO. The formation of CO during the CWPO of phenol upon different solid catalysts have been studied, and the following conclusions can be drawn:

- Although CWPO process with GNP and MAX catalysts achieved lower TOC degradation rates than the Fenton process, both catalysts maintained high mineralization efficiencies attaining TOC conversions of 45.9 and 53.8 %, respectively, when compared to the homogeneous process (59.1 %).
- CO production was limited in CWPO processes at the beginning of the reaction and a more progressive release of CO was observed. Besides, the CO yield was found to be significantly lower in the CWPO process compared to that obtained in the homogeneous Fenton.
- Interestingly, when phenol oxidation was tested, CWPO MAX exhibited a predominant selectivity to catechol, which is less selective to CO than hydroquinone, usually found to be predominant aromatic intermediate in carbon-based catalysts as GNP and Fe/AC catalysts. For its part, low CO selectivity in the Fe/AC can be directly ascribed to the strong adsorption capacity of aromatic intermediates of AC.
- As a practical consequence, the high CO cocnentratios achivieded in the Fenton process (6720 mg/Nm^3) can be reduced to notably in presence of GNP and MAX catalysts resulted in a much lower CO maximum concentration 187 mg/Nm^3 and 170 mg/Nm^3, respectively.

, CWPO novel catalysts as GNP and MAX phase, though require longer reaction times than Fenton to achieve similar oxidation degrees, are less selective to CO and can significantly limit carbon monoxide concentrations released upon the oxidation process. Hence, when compared to homogeneous Fenton, CWPO results in a better sustainability decreasing the hazardous gaseous emissions and the secondary pollution found during the oxidation process.

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