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Surface modification of carbon-supported iron catalyst during the wet air oxidation of phenol: Influence on activity, selectivity and stability

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Abstract

Catalytic wet air oxidation (CWAO) of phenol with iron/activated carbon catalysts (Fe/AC) at temperature of 400 K and 8 atm of total pressure is an efficient treatment to oxidize a resistant pollutant such as phenol into biodegradable species, mainly short chain acids. Extended studies employing activated carbon catalysts point out significant changes in the carbon as a consequence of the CWAO process. After the long-term experiments carried out in this work it was concluded that these modifications consist of loss of microporosity, temporary decrease of the mesoporosity, decrease of the carbon/oxygen ratio on the catalyst surface, more acidic pH_{slurry} values, and aggregation of the α-Fe_2O_3 crystallites. The causes that provoke these changes and the reasons why they do not alter significantly the CWAO efficiency were analyzed. The way of exposition of Fe/AC catalyst to the reactants plays an important role in its activity and selectivity towards complete mineralization, namely oxidation to CO_2 and H_2O.

Keywords: Activated carbon; Iron oxide; Wet oxidation; Mössbauer spectroscopy; Phenol

1. Introduction

Activated carbons have been widely used as adsorbent of organic and inorganic pollutants in order to clean waste streams (gas and liquid) coming from very different industrial sectors (food, pharmaceutical, chemical, petroleum, mining, automobile, etc.) [1]. Spent activated carbons have been usually regenerated by steam at high temperatures (1073–1123 K), treatment that increases the price of the overall process. In 1995, Levec and Pintar [2] published a study about the regeneration of activated carbons employing hot water at far lower temperatures (up to 200 °C) than thermal regenerations, avoiding the oxidation of activated carbon itself and abating the desorbed pollutants by wet air oxidation [3]. As a consequence, activated carbon began to be tested as catalyst for wet air oxidation (WAO) process and literature started to appear in this field [4–10].

In the catalytic wet air oxidation process (CWAO), activated carbons have been used as catalyst and also as support. In the latter case, noble metals (Pt, Pd, Ru) have been tested [6,11,12] and in less extension, transition metals Cu, Fe, Ni, Co and Mo [13–16].

The employ of activated carbons as catalyst or support presents improvements comparing to catalysts based on transition and noble metals over conventional supports. For instance, in the CWAO of phenol, the most common pollutant chosen as target compound in the WAO studies, a higher phenol oxidation rate, a higher mineralization and therefore, a less toxic route is achieved [17,18].

However, when activated carbon is used in the CWAO process, significant changes in its textural properties have been

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reported after a given time on stream [10,19,20]. Suarez-Ojeda et al. [10] studied the CWAO of o-cresol, 2Cl-phenol and phenol at 5 g/L in aqueous solution with a commercial activated carbon at 413 K and 2 atm of oxygen in a trickle-bed reactor. In this study, the conversion and BET area of the catalyst after 72 h of time on stream were analyzed and it was found that the highest BET area reduction (98.4% with o-cresol, 91.7% with phenol and 88.6% with 2Cl-phenol) did not correspond to the highest pollutant conversion but to the susceptibility towards coupling reactions on activated carbon, quantified by the critical oxidation potential [21]. These coupling reactions take place mostly during the adsorption step and are stimulated in presence of O_2 and at high temperatures [22,23]. Santos et al. [19] also studied the CWAO of different pollutants with a commercial activated carbon at 433 K and 16 atm of oxygen in a fixed-bed reactor. They also found a decrease in the BET area of the carbon after 120 h of time on stream (34% with p-cresol, 44% with o-cresol, 58% with p-nitrophenol and 35% with o-nitrophenol) and it was observed that, in phenol oxidation, that reduction was almost independent of the time on stream in the range of 80–200 h. The reduction of BET area was significantly lower than the observed by Suarez-Ojeda et al. [10] probably because of the different nature of the carbons and therefore, the different adsorption capacity. Quintanilla et al. [20] in the CWAO of phenol with a commercial activated carbon in a trickle-bed reactor at 400 K and 8 atm total pressure found similar modifications than those given by Suarez-Ojeda et al. [10]. Quintanilla et al. [20] reported decreases of the BET area and the micropore volume of the activated carbon of 90% and 95%, respectively, after 64 h of time on stream. Also, the external area and mesoporosity were diminished. The amount of oxygen surface groups was also increased (CO_2 and CO desorbing upon TPD were multiplied by a factor of 8 and 3.5, respectively).

When iron is incorporated on the activated carbon a substantial increase of phenol and total organic carbon (TOC) conversion was observed. The former increased from 50% in presence of activated carbon to 95% with the carbon-supported iron catalyst and TOC conversion raised from 30% to 65%, both at a space time of 160 $g_{CAT}\cdot h/L$. Also, the presence of Fe enhanced toxicity abatement at sufficiently high space time values [16,20]. This better performance of the carbon-supported iron catalyst is due to both the higher amount of oxygen surface groups, specially the more acidic ones, formed during the calcination process in the catalyst preparation, and the presence of the iron oxide itself since for a given amount of oxygen surface groups, higher conversions were obtained in presence of iron [20].

Moreover, the presence of iron stabilizes the activated carbon since a detrimental effect of wet oxidation on the porous structure of the activated carbons was observed [20]. A 40% reduction in BET area and a 30% in the micropore volume were observed after 216 h of time on stream, whereas the mesoporosity was not affected. The amount of oxygen surface groups was also increased but in less extension than in the activated carbon alone. CO_2 and CO desorbing upon TPD were double after 216 h of time on stream. These phenomena will be analyzed in detail in the present work.

The aim of this work is to study the physico-chemical stability of the carbon-supported iron catalyst (Fe/AC) through the WAO process. For this purpose, a long-term experiment was carried out to investigate the changes in the catalyst surface through time on stream. This experiment was conducted by putting in contact simultaneously the catalyst with the reactants, so that the catalytic bed was saturated in phenol in presence of oxygen (named as SOC experiments). The results have been compared to those found in a previous work [16] where the catalytic bed was first saturated in phenol in nitrogen atmosphere (named as SAC experiments). Therefore, the catalyst stability and activity have been also assessed by modifying the adsorption step (in oxygen or nitrogen atmosphere). The causes of the changes on the surface properties of the Fe/AC catalyst and their possible consequences in the CWAO process have been also investigated.

2. Experimental

2.1. Preparation of the catalyst

A commercial hydrocarbon-derived activated carbon (AC) supplied by Merck (ref.: 102514) has been used as catalyst support in this study. It was previously sieved to a particle size in the range of 0.5–1 mm.

The catalyst was prepared by the incipient-wetness impregnation method employing an aqueous solution of $Fe(NO_3)_3\cdot 9H_2O$ (Panreac) of the required concentration to obtain a Fe loading of 2.5 wt% with a solution volume exceeding by 10% the total pore volume of the support. Impregnation was followed by drying at room temperature for 2 h and overnight at 333 K. The catalyst was then heated up to 473 K within 2 h at two temperature rates (1 h at 0.67 K/min and 1 h at 1.67 K/min) and then calcined at 473 K during 4 h. Fe loading was determined by total reflection X-ray fluorescence spectroscopy (TXRF), using Si–Li detector in a TXRF Extra-II Rich & Seifert spectrometer.

2.2. Catalytic testing for phenol wet oxidation

Catalytic wet oxidation of phenol was conducted in a bench scale wet air oxidation unit with a trickle-bed reactor (TBR) operating in concurrent down-flow of both phases, liquid and gas. Detailed information about the components and operating procedure has been reported elsewhere [16].

Oxidation runs were performed by pumping an aqueous solution of 1000 mg/L of phenol at pH 3.5 (adjusted with H_2SO_4) to the reactor at different flow rates (0.125–2 mL/min) to cover a wide range of space time values (τ). Pure oxygen, continuously fed at 91.5 NmL/min, was used as oxidising agent. The reactor loaded with 2.5 g of catalyst was maintained at 400 K and 8 atm in all the experiments. The set of experiments were carried out by putting fresh catalyst in contact with phenol and oxygen without previous phenol saturation of the catalytic bed; therefore, adsorption and reaction processes take place simultaneously at different rates