

Improved Fe₂O₃/Al₂O₃ systems for the oxidation of a model organic pollutant using H₂O₂ as oxidant

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Abstract Different Fe₂O₃/Al₂O₃ catalysts (4 wt% Fe) were prepared and characterized by N₂ physisorption, SEM-EDX, TGA and XRD. The systems were tested for the oxidation of high concentration phenol solutions (5 g/L) in a batch reactor at 50 °C, using H₂O₂ as oxidant. In order to enhance the catalyst stability two strategies were combined: an elevated temperature of calcination (900 °C) and pre-treatments with different organic acids (acetic, oxalic acid). The stability of the catalyst was improved significantly (leaching levels were reduced by up to 70%), with a good performance over the global oxidation process: mineralization levels of ca. 50% with oxidant consumption efficiencies of around 75%.

Introduction

Environmental catalysis for water pollution abatement still appears as a «Research & Development» field plenty of challenges. During the last decades, the progress of chemical treatments has led to the emergence of the Advanced Oxidation Processes (AOPs). The AOPs can be broadly defined as aqueous phase oxidation methods based on the intermediacy of highly reactive species such as hydroxyl radicals, leading to the destruction of the target pollutant [1]. For laboratory-scale experiments, phenol is frequently chosen as a model organic pollutant due to its high toxicity and resistance to traditional detoxification techniques [2-4]. Different AOPs have been applied to effectively treat phenolic wastewaters, including the classic Fenton's reagent [2, 5-6]. However, the homogeneous Fenton process is usually conducted at acidic conditions to maintain the iron species in solution and different drawbacks strongly limit its industrial implementation (down-stream treatment to adjust the pH, sludge separation, etc.). For this reason, current research has focused on the development of heterogeneous Fenton-like catalysts, by immobilizing transition metal cations (primarily iron, but not exclusively) over different solid supports [2, 7].

The design of appropriate catalysts must consider the activity and also the stability of the active phase in the reaction conditions of the Catalytic Wet Peroxide Oxidation (CWPO). Among low-cost materials, the potential of alumina supported systems has been limitedly explored [8-11]. We have studied iron-alumina catalysts with promising results at mild reaction conditions (70°C, 1 atm); the catalyst stability was significantly enhanced by means of a high temperature thermal treatment [10]. We observed that both higher iron contents and catalyst loadings have a positive impact on mineralization levels and oxidant consumption efficiencies.

In the present work, we continued investigating Fe₂O₃/Al₂O₃ systems for the CWPO of phenol. This time the strategy was to perform the tests at a lower temperature (50 °C), with an optimized catalyst concentration and iron content (approximately ten times higher than those previously investigated). The objective was to reach higher degradation rates, minimizing the impact of leaching processes. For this purpose, pelletized catalysts were prepared with a 4 wt% Fe and different acid pre-treatments. A relatively concentrated phenol initial charge (5 g/L) was selected, which imposes more demanding reaction conditions in order to test the resistance to solubilization of the iron species.

1 Experimental/methodology

Catalyst preparation and characterization

A Fe₂O₃/Al₂O₃ catalyst was prepared by wet impregnation using iron citrate (Sigma-Aldrich) and gamma Al₂O₃ spherical pellets (SASOL, diameter of 2.5 mm). The catalyst designed as 4Fe900 was dried at 110°C (24 h) and calcined at 900 °C for 4 h, in air atmosphere. Two additional catalysts were prepared by treating 4Fe900 catalyst with different organic acids (acetic and oxalic acid). The acid treatment was performed by immersion of the catalyst pellets into an aqueous acid solution. The molar ratio [organic acid]/[Fe] was 4, and the contact time was 24 h at room temperature. The catalysts were further washed with distilled water, dried at 110°C (24 h) and recalined at 900 °C (4 h). The samples were labelled as 4Fe900ac and 4Fe900ox, corresponding to the acetic and the oxalic acid treatment, respectively.

The catalysts were characterized by N₂ physisorption, Scanning Electronic Microscopy SEM-EDX, Thermogravimetric Analysis (TGA) and X-Ray Diffraction (XRD), using the equipment and procedures

described elsewhere [10]. The iron content of fresh and used samples was determined by a standard colorimetric test (FerroVer® Iron Reagent, HACH), with a previous nitric acid extraction of the solid samples. Final leaching levels were estimated by comparing the initial and final iron contents of the used catalysts.

Reaction tests

Reaction experiments were carried out for 6 hours in an agitated batch reactor at atmospheric pressure and moderate temperatures (40-70 °C). In a typical run, a mass of 1 g of catalyst was put into 100 mL of 5g/L of phenol aqueous solution under continuous stirring at 50 °C. The resulting initial oxidant concentration corresponds to the stoichiometric $[H_2O_2]/[phenol]$ molar ratio of 14. Liquid samples were taken at different time intervals. Phenol and hydrogen peroxide remaining concentration were determined by standard procedures; Total Organic Carbon (TOC), pH and UV-VIS spectrum (600-200 nm range) were also measured. More detail of these determinations was included in a previous work [10].

2 Results and discussion

Characterization of the catalysts

The characterization results indicate that the thermal treatment induced a reduction in the surface area of the alumina (Table 1). We observed that after the thermal treatment, only a fraction of the total iron present is able to be extracted by nitric acid attack (NAA), probably due to migration of Fe to inner or more defective regions of the support, as corroborated by SEM-EDX. The calcination at 900 °C might induce stronger iron-alumina interactions stabilizing the iron species onto the support. The formation of mixed oxides Fe-Al-O (not detected through the characterization techniques employed) should not be completely discarded. However, it was reported that spinel-like phases are thermodynamically hindered at the pressure/temperature conditions selected for the catalysts preparation in the present study [12].

As expected, the catalysts treated with organic acids exhibited lower iron contents. The acid pre-treatment removed an iron fraction which was probably formed by the more labile Fe species. This treatment also induced a moderate increase of the surface area of the catalysts, as reported in Table 1.

Despite these differences, the surface mapping of all the samples showed a regular distribution of iron species onto the catalyst. This is in agreement with XRD results: only gamma-alumina characteristic peaks were observed. Due to the low concentration/good dispersion of Fe, no iron-containing phases were detected.

Table 1. Summary of characterization results for the catalysts and the support

Fresh Samples	BET surface area (m ² /g)	Total Fe content (%)	Fe extracted by NAA (%)	Phases detected by XRD
Al ₂ O ₃	208	-	-	γ-Al ₂ O ₃
Al ₂ O ₃ (900°C)	138	-	-	γ-Al ₂ O ₃
4Fe900	116	4.2	1.8	γ-Al ₂ O ₃
4Fe900ac	135	3.8	1.4	γ-Al ₂ O ₃
4Fe900ox	138	3.8	1.4	γ-Al ₂ O ₃

Preliminary reaction results in the absence of phenol

The ability of this alumina-based system to promote oxidant decomposition (in the absence of organic compounds) was evaluated. Reaction tests were performed using 4Fe900 catalyst in the temperature range 40-70 °C. The experimental data were contrasted against a kinetic model in which the rate of peroxide decomposition was assumed to be first order reaction with respect to the H₂O₂ concentration. The resulting reaction rates are shown in Table 2 (with linear regression coefficients R²). The apparent activation energy for hydrogen peroxide decomposition was evaluated as 52.1 kJ/mol. The results are reasonable, compared with literature reports [13-14]. In a previous work we found a lower apparent activation energy (39.5kJ/mol), at similar operating conditions using a Fe₂O₃/Al₂O₃ catalyst (4% Fe) calcined at 400 °C [15]. The higher calcination temperature of 4Fe900 would be the main responsible of its lower decomposition rates and higher activation energy.

Table 2. First order rate constant values for H₂O₂ decomposition with 4Fe900 at different temperatures ([Cat] = 9.1 g/L; [H₂O₂]₀ = 0.672 mole/L)

Temperature (°C)	Reaction rate (min ⁻¹)	R ²
40	0.0058	0.9865
50	0.0109	0.9952
60	0.0153	0.9994
70	0.0365	0.9921

CWPO of phenol aqueous solutions

First, the CWPO performance of 4Fe900 catalyst was studied (Figure 1). A complete phenol conversion and a final TOC reduction of near 50% were achieved. The oxidant consumption rate was moderate during the CWPO process, resulting in a final oxidant efficiency of 67% (calculated as is defined in the footnote to the Table 3). The Fe leaching level for the used catalyst was also determined: 20% of iron lixiviation was registered after 6 h of reaction. In spite of the high calcination temperature used for 4Fe900, its leaching degree could not be neglected. It must be noted that the advanced oxidation occurred at strong acidic conditions (pH evolution, Figure 1a). Although the phenol was totally converted, its mineralization was only partial. In order to complete the mass balance, accumulation of intermediate species must be taking into consideration. It is widely accepted that these intermediates are primary ring compounds (mainly catechol and hydroquinone) and organic acids generated after subsequent ring-opening [5]. The UV-Visible spectra from Figure 1b confirmed this reaction pathway. At the initial time, the spectrum showed a main peak at 271 nm, characteristic of phenol. As the oxidation process advanced, the peak at 271 nm diminished and the absorbance in the visible region increased (this was associated with the formation of brownish quinone-like compounds). After 6 h of reaction, the signal of phenol completely disappeared and the color of the reaction solution turned clearer, though not colorless (a remaining absorbance in the visible range was registered, consistent with a partial oxidation). The presence of more refractory short-chain organic acids formed at the final oxidation steps is considered the major responsible of uncomplete mineralization levels at long CWPO reaction times. Due to the high initial concentration of phenol, the accumulation of the different intermediate species was significant, producing a marked pH drop (the pH remained near 2 during the last 3 hours of reaction time). In the context of this adverse operation conditions, the lixiviation degree registered for 4Fe900 was acceptable.

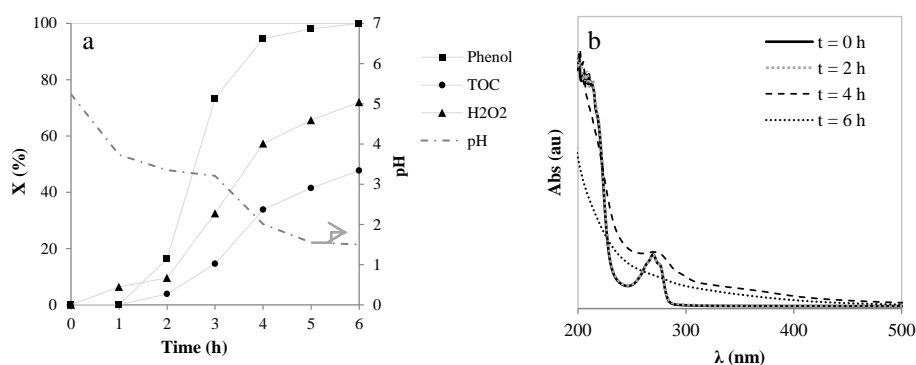


Fig. 1. CWPO results using 4Fe900 at 50 °C: a) Phenol, TOC and H₂O₂ conversions and pH evolution vs. reaction time; b) UV-VIS spectra ([phenol]₀=0.048 mole/L; [cat]=9.1 g/L; [H₂O₂]₀=0.672 mole/L)

Second, the effect of an acid pre-treatment was explored. The nature of the organic acids was chosen in order to expose the catalyst to a similar environment than the developed during phenol oxidation. Acetic and oxalic acids are known as refractory intermediates formed at advanced stages of the oxidation process; particularly the oxalic acid which is recognized as the major responsible of the active species solubilization [9]. The 4Fe900ox and 4Fe900ac samples were used at 50 °C and final leaching levels were determined. The reaction results are presented in Table 3. For the treated samples, a very slight decrease in the conversions was registered, compared with 4Fe900. The hydrogen peroxide conversions proved to be more sensitive to the lower content of labile iron; phenol conversion and TOC reduction remained practically unmodified for 4Fe900ox and 4Fe900ac. However two important improvements were observed: the H₂O₂ consumption efficiencies were increased and the iron leaching levels were notably reduced.

Table 3. CWPO results after 6 h of reaction time at 50 °C: Effect of acid pre-treatment of the catalyst

Samples	X _{Phenol} (%)	X _{H₂O₂} (%)	X _{TOC} (%)	η H ₂ O ₂ * (%)	Fe Leaching (%)
4Fe900	100	70	47	67	20.4
4Fe900ac	100	62	49	79	6.2
4Fe900ox	98	63	46	73	10.9

$$* \eta_{H_2O_2} (\%) = \frac{g_{TOC_{converted}} \cdot g_{H_2O_2_{initial}}}{g_{TOC_{initial}} \cdot g_{H_2O_2_{converted}}} \cdot 100$$

The oxidant efficiency was enhanced due to a slower hydrogen peroxide consumption rate that did not affect the TOC reduction levels. It has been previously reported that the use of substoichiometric oxidant concentrations might improve the efficiency of the CWPO process when the oxidation reaction does not reach completion [10].

From these results, an alternative for future research would be to use lower initial doses of H₂O₂ to optimize the reaction conditions.

In terms of catalyst stability, the results obtained for 4Fe900ox and 4Fe900ac were very promising: after the addition of an acid-immersion step, the leaching levels of the catalysts were reduced by up to 70% (for 4Fe900ac). Again, the low pH of the reaction medium (due to the presence of short-chain organic acids) imposed unfavorable conditions that strongly favor the solubilization of the iron species. Thus, the lixiviation levels of 6-10% registered for the treated catalysts were highly satisfactory. It should be considered that after reaction, the final iron contents of the three catalysts were comparable. However, the additional step of acid treatment represented an important improvement: as a fraction of the labile Fe species were removed during the pretreatment, minor levels of leached iron were reached during the CWPO reaction. The treated catalysts exhibited similar conversions and mineralization degree than 4Fe900, with a much lower resulting concentration of iron in solution. By means of two simple procedures (a high temperature thermal treatment and an acid immersion) the catalytic performance was enhanced, especially in terms of stability. Nevertheless, it is necessary to extend the understanding of the effect of the organic acid nature. So far, the characterization techniques employed could not detect significant differences between both treated catalysts in order to support distinctive experimental behavior.

As previously mentioned, one of the central aspects to evaluate the stability of the catalysts in CWPO reactions is the resistance to the solubilization of the active phase. However, the lixiviation of the active phase would not be the only contribution to catalyst deactivation. As the CWPO reaction proceeded, the formation of brown deposits onto the catalyst surface was observed; this might be associated to reaction intermediates accumulation. The used samples were preliminary analyzed by TGA and a weight loss of approximately 5.3% was registered between 150-500 °C (under air current). This temperature range might be directly related to the oxidation of deposited organic species.

Further work is under way in order to optimize both the reaction conditions and the catalyst systems in order to minimize deactivation processes at aggressive operation conditions.

3 Conclusions

The Fe₂O₃/Al₂O₃ catalysts resulted active for the CWPO of phenol, at mild operation conditions. After a thermal treatment at 900 °C, the leaching of the active phase was moderate (20%) with relatively high mineralization and oxidant consumption levels. The lixiviation levels were promising, taking into account the strong acidic reaction medium of the oxidation process.

A simple previous treatment of the catalyst with organic acids was used as an original strategy to improve catalyst stability. The phenol, TOC and oxidant conversions of the treated catalysts resulted good and remained comparable to those of the untreated catalyst. The acid pre-treatments improved both the oxidant consumption efficiency and the stability of Fe₂O₃/Al₂O₃ catalysts, reducing the leaching in a 47% for 4Fe900ox and a 70% for 4Fe900ac.

At high initial concentration of phenol, the important accumulation of partially oxidated products might contribute to catalyst deactivation due to the formation of organic deposits onto the catalysts surface.

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