Influence of Thermal Aging on the Activity of a Heterogeneous Photo-fenton Catalysts

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A new photo- Fenton catalyst has been manufactured from synthetic layered clay laponite (Laponite RD) by the pillaring technique. Eight different catalyst samples were prepared: four without thermal aging (WTA) calcined at 523 K, 623 K, 723 K and 823 K, and other four with thermal aging (TA) calcined at the same temperatures. The samples have been characterized by XRD and SEM/EDS techniques, and through the bulk chemical analysis. The results of this characterization have been previously reported [8]. This paper presents the results regarding the activity of the catalyst samples, determined for the phenol degradation in water by the photo- Fenton process, using an aqueous solution of 0.1 mM concentration in the presence of 

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The high effectiveness of the photo- Fenton process is attributed to the formation of hydroxyl radicals (HO•) in the reaction (1), and the regeneration of Fe(II) ions by photo- reduction of Fe(III) ions (2):

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{hv} = \text{Fe(OH)}^{2+} + \text{HO} \cdot \] (1)

\[ \text{Fe(OH)}^{2+} + \text{hv} = \text{Fe}^{2+} + \text{HO} \cdot \] (2)

Despite its effectiveness, the homogeneous photo- Fenton process has an important drawback for practical application to large water flow rates, caused by sludge formation in the final neutralization step [1]. Therefore, new heterogeneous Fe-based catalysts have been prepared and tested [2- 7].

The first heterogeneous photo- Fenton catalyst was prepared by immobilization of Fe (III) ions on a Nafion membrane [2]. This is not practical because of the high cost of the Nafion membrane (over $2000/kg). Another idea was a Fe (III) catalyst supported on a resin [3]. Noorjahan et al. [4] immobilized the Fe (III) ions on a HY zeolite by impregnation and calcinations. Suspending Fe (III) - HY in aqueous solution polluted with phenol was irradiated with UV light. The effect of three main factors (Fe loadings, H2O2 dose, pH) were studied. They found that a dose of only 0.25% Fe (III)- HY in water was efficient to degrade phenol at pH 6. The reaction rate was higher than in the homogeneous Fenton, due to the synergetic role of the zeolite. In addition, the pH could be in a wider range. The main drawback of this catalyst is the low mineralization degree of the phenol in water.

A new bentonite clay- based Fe- nanocomposite (Fe-B) as a heterogeneous catalyst for photo- Fenton discoloration and mineralization of Orange II dye in water was prepared [5]. XRD analysis revealed that the Fe-B mainly consisted of hematite (Fe2O3) and quartz (SiO2) crystallites. The Fe concentration determined by XRF was of 31.8%. The catalytic activity of Fe- B was evaluated in the degradation of Orange II 0.2 mM in water. For optimal conditions (1.0 g Fe-B/L, 10mM H2O2, pH3, and 1.8 W UV-C source) a complete discoloration and a 50-60% mineralization were achieved in less than 60 and 120 min, respectively.

The main drawback of this catalyst is the low stability due to the Fe leaching. The same authors [6] improved the catalyst stability by coating with a compact nano composite film. A new laponite clay-based Fe nanocomposite as heterogeneous photo- Fenton catalyst was prepared [7], and tested in the mineralization process of an azo-dye Acid Black 1 (AB 1) in water, in the presence of H2O2 and UV light. Under the optimal reaction conditions found by the authors (0.1 mM AB1, 6.4 mM H2O2, 1.0 g catalyst/L, pH3, 8W UV-C) they achieved a complete discoloration and a 90% mineralization after 90 min reaction time, and a complete TOC removal after 4 cycles of 2h reaction time. These encouraging results determined us to prepare a similar catalyst and to test it in process of the degradation of phenol in water.

Experimental part

The synthetic laponite clay (Laponite RD) was supplied by Brescia S.R.L. and used as starting material to prepare a series of Fe-Lap-RD catalysts. The laponite RD powder has a specific area of 370 m²/g. The rest of the chemicals employed in the experiments were supplied by Merck (H2SO4, 98% and H2O2, 35%), Sigma-Aldrich (Na2CO3, KI, KH2PO4, NaOH, phenol and Fe(NO3)3, 9H2O). The water used was of Milli-Q quality.

A series of Fe-Lap-RD catalysts was prepared through a reaction between a solution of iron salt and a dispersion of laponite RD clay. Firstly an aqueous dispersion of laponite RD clay was prepared by adding 2 g laponite RD to 100 mL H2O under vigorous stirring. Secondly, sodium carbonate was added slowly as a powder into a vigorously stirred 0.2 M solution of iron nitrate so that a molar ratio of 1:1 for [Na+]/[Fe3+] was established. The obtained solution was added very slowly into the dispersion of laponite clay prepared in the first step until a ratio of 11 mmol Fe3+ per gram clay was achieved [6]. The suspension was stirred 2 h and then divided into two portions. One portion was kept in an oven at 373 K for two days. For simplicity this portion will be referred as “thermally aged” (TA). Another portion, referred as “without thermal aging” (WTA) was stirred for two days at room temperature to allow sufficient
intercalation of the clay. After that, the precipitate of each portion was collected by centrifugation and washed several times with deionised water to ensure that all the Na+ ions were removed. The recoveries were dried at a temperature of 373 K for 24 h and further divided into four equal portions. The two portions underwent a calcination process at different temperatures for 24 h. The calcination temperatures were 523, 623, 723, and 823 K. For simplicity, the clays will be referred as: WTA-T for the clays obtained without thermal aging and TA-T for the clays prepared by thermal aging; T represents the calcination temperature used in this study: 523, 623, 723, and 823 K. The characterization of catalyst samples by chemical analysis, SEM/EDS, XRD and DTA was described in a previous paper [8].

The photocatalytic activity of each pillared clay was evaluated in the process of mineralization and conversion of a 0.1 mM phenol solution in the presence of 5 mM H2O2, 1 g/L catalyst and UV irradiation using a Unilux Philips lamp (15 W UV-C, λ = 254 nm). Irradiation was carried out in magnetically stirred, cylindrical Pyrex quartz cell (4 cm diameter, 2.3 cm height) containing 10 mL solution, at room temperature. The pH was adjusted to 3 using a H2SO4 solution. This is the optimal pH in the homogeneous photo-Fenton process [1]. The start of the reaction was considered to be the moment when the cell was put under the UV-C lamp. After irradiation the catalyst was separated from the solution by filtration with Hydrophilic PTFE Millex-LCR filter (pore diameter 0.45 . 10-9 m).

The conversion of phenol was measured using a Merck-Hitachi HPLC. The column used was a RP-C18 LichroCarp (Merck, length 125 mm, diameter 4mm) packed with Li-Chrospher 100 RP-18 (5 . 10-9 m diameter). Isocratic elution was performed with a 30/70 mixture of acetonitrile / aqueous phosphate buffer (0.05 M, pH 2.8). The mineralization of phenol was measured using a Shimadzu TOC 5000 Analyzer. The leaching iron (Fe3+ and Fe2+) from the catalysts was measured using a UVVIS Cary 100 Scan spectrophotometer and a special Merck reagent named Spectroquant. The experimental determinations were carried out at a wavelength of 565 nm. Because the reaction was still going on after the irradiation time was over, it was necessary to use a stopping reagent, which contained 0.1 M Na2SO3, 0.1 M KH2PO4, 0.1 M KI and 0.05 M NaOH. The stopping reagent was injected in the sample solution immediately after filtration, using a 1:1 volumetric ratio.

Results and discussions

The evolution of the phenol conversion degree \( \left( X_{\text{Ph}} = 1 - \frac{C_{\text{Ph}}}{C_{\text{Ph0}}} \right) \) with time in the presence of the four WTA catalyst samples is represented in the figure 1. The lowest is for the uncatalyzed process, which is a UV/H2O2 advanced oxidation reaction. The results show that the phenol destruction is between 95% and 99% in less than 90 s irradiation time. The calcinations temperatures have a slight influence. The highest rate was obtained with the catalyst sample calcinated at 723 K. The results presented in the figure 2 with the thermal aged catalysts are similar. The conversions are slightly higher than for WTA probes, and the best results correspond to the TA catalyst calcinated at 623 K. The optimal calcinations temperature was confirmed by the magnitude of the apparent first-order
rate constants (table 1) derived by the integral method from figure 3. A practical result is that thermal aging allows the reduction of the optimal calcinations temperature from 723 to 623 K.

Conclusions
A new heterogeneous photo- Fenton catalyst has been prepared by the intercalation and pillaring of a laponite clay with iron salt. Eight different catalyst samples were prepared: four without thermal aging (WTA) calcined at 523 K, 623 K, 723 K and 823 K, and other four with thermal aging (TA) calcined at the same temperatures.

The activity of catalyst samples was evaluated by the phenol conversion ($X_{\text{Ph}}$) versus reaction time in the presence of 5mM H$_2$O$_2$, 1g/L catalyst, pH 3, 303 K. The phenol conversion was almost complete (99.5%) with the TA-623 in a rather short reaction time.

The kinetic curves have been farther processed by the integral method and the apparent first-order rate constant has been identified. This had a maximum ($4.12 \cdot 10^{-2} \text{ s}^{-1}$) for WTA calcined at 723 K. The TA samples had also a maximal activity ($k = 5.28 \cdot 10^{-2} \text{ s}^{-1}$) but for lower calcinations temperature (623K). The thermal aging allows obtaining a greater rate constant with a lower calcinations temperature. This finding has a significant economic importance for the practical application of the process to phenol contaminated water treatment.

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