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Preparation, characterization and photocatalytic activity of ZnO, Fe$_2$O$_3$ and ZnFe$_2$O$_4$

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Abstract

ZnO, Fe$_2$O$_3$ and ZnFe$_2$O$_4$ were synthesized by precipitation or coprecipitation at constant pH. After aging, washing and drying, the solids were calcined at 800 °C. The samples were characterized by XRD, TGA, N$_2$ physisorption, UV–Vis and TPR. The photocatalytic degradation of phenol was studied in a batch reactor and TiO$_2$ (Degussa, P-25) was used as a reference catalyst. Pure ZnO and Fe$_2$O$_3$ were obtained at 800 °C, whereas ZnFe$_2$O$_4$ and α-Fe$_2$O$_3$ (segregated) were detected in the zinc ferrite sample. TPR experiments showed the reduction peaks in the range of 350–800 °C only with Fe$_2$O$_3$ and ZnFe$_2$O$_4$, attributed to Fe^{3+} to Fe^{2+} reduction and complete dehydroxylation. The photodegradation of phenol (samples calcined at 800 °C) showed small but significant variations that decreased in the order: TiO$_2$ > ZnFe$_2$O$_4$ > ZnO > Fe$_2$O$_3$. Subproducts such as hydroquinone, catechol and benzoquinone were mainly detected. In particular, attention was focused on our prepared materials because after 24 h they did not dissolve as happened with TiO$_2$. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Oxide-materials; Precipitation; Characterization; Phenol photodegradation

1. Introduction

Many conventional methods have been proposed to treat industrial effluents and each method has its shortcomings [1–3]. In the last decade advanced oxidation processes (AOPs) have been shown to be effective for the destruction of refractory pollutants. They are based on the generation of highly reactive and oxidizing hydroxyl radicals. O$_3$/UV, H$_2$O$_2$/UV, Fe$_2$O$_3$/UV and TiO$_2$/air/UV are the main types of AOPs that have been suggested [4]. Various combinations of them are employed for the complete mineralization of the pollutants. Reactive oxygen species play a crucial role in heterogeneous photocatalysis aimed at the degradation of organic compounds [5–14]. The interest in this area is intense and increasing as shown by the number of publications, which is more than 2000 papers on this topic since 1981 [15]. Several semiconductors (e.g. TiO$_2$, Fe$_2$O$_3$, CdS, ZnS and ZnO) and a couple of semiconductor powders [16,17] can act as photocatalysts and they have been applied to a variety of problems of environmental interest in relation to water purification.

Phenol is a major pollutant of surface water and ground water, and there are strict limits on the amounts which can be discharged in the effluent. Owing to its stability and solubility in water, the degradation of this compound to a level of safety in the range of 0.1–1 mg/l is not easy [1,18,19]. The photocatalytic degradation of phenol using TiO$_2$ has been studied extensively and it is the most promising catalyst due to its high efficiency, stability and low cost [20]. Nevertheless, one disadvantage of TiO$_2$ for industrial applications is the necessity of filtration after the photodegradation. ZnO has been reported to be photoactive for phenol and nitrophenol degradation in spite of some photocorrosion effects in the liquid–solid phase [21,22]. α-Fe$_2$O$_3$ has also been investigated in the photodegradation of organic compounds under UV radiation, despite the unfavorable position of its conduction band [23]. ZnFe$_2$O$_4$ has been successfully tested as a heterogeneous catalyst in the oxidative dehydrogenation of *n*-butane to butenes [24] but its use in photocatalysis has not been reported. In this exploratory work, the synthesis, characterization and preliminary photocatalytic results of phenol degradation using ZnO, Fe$_2$O$_3$ and ZnFe$_2$O$_4$ with UV radiation is reported. These results are compared with the conventional TiO$_2$.

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2. Experimental

2.1. Materials

ZnO, Fe_2O_3 and $ZnFe_2O_4$ were prepared by precipitation or coprecipitation of the parent nitrate salts (Baker, 98+%) with an aqueous solution of NH_4OH (50 v/v, Baker) at 50 °C and a constant pH of 8. Once the precipitate was obtained, it was aged without agitation for 24 h. The solids were filtered and carefully washed with demineralized water, dried at 110 °C overnight in a vacuum oven and then calcined in static air at 800 °C for 8 h.

2.2. Methods

X-ray diffractograms were obtained with a D-500 Siemens diffractometer coupled to a copper anode. The Cu $K\alpha$ radiation was selected with a Ni filter. The weight loss of the precursors was obtained in a TGA 51 thermogravimetric analyzer (Dupont 2000). The total surface area of the catalysts was obtained by BET analysis (single point) on a Micromeritics TPD/TPR 2900 analyzer. The UV–Vis (diffuse reflectance) spectra were obtained using a Cary 17D Varian Spectrograph with integrating sphere. The reduction profiles were obtained with samples calcined at 800 °C in a mixture of 10% H_2 and balance Ar in a TPD/TPR-2900 apparatus.

The photodegradation experiments were carried out by dissolving pure phenol (Técnica Química, 99.5%) in de-ionized water at the desired concentration (100 ppm). The catalyst (powder, 80/100 mesh) loading was 1 g/l and appropriate quantities of the suspensions (200 ml) were then transferred to the cells used for irradiation experiments. TiO_2 (Degussa, P-25) was used as a reference catalyst. After homogenization through magnetic stirring and temperature stabilization, the cells were exposed to the UV-lamp (8 W, $\lambda = 254$ nm and intensity = 2.2 mW/cm^2) for 150 min. Phenol analysis was done with a Lambda-25, Perkin Elmer, UV–Vis spectrophotometer (λ_{max} of phenol = 270 nm).

3. Results and discussion

XRD patterns of the samples calcined at 800 °C are shown Fig. 1. In all the catalysts, the expected compounds were characterized by sharp and symmetric peaks, indicating high crystallinity and large particle size. Nevertheless, $ZnFe_2O_4$ catalyst presented the corresponding spinel structure and a small amount of α-Fe_2O_3, which is segregated due to loss of zinc content as $[Zn(NH_3)]^{2+}$ during the washing step [25].

The thermogravimetric analysis curves of ZnO, Fe_2O_3 and $ZnFe_2O_4$ fresh samples (110 °C) are presented in Fig. 2. The ZnO precursor showed a significant weight loss which was around 15% of its original weight, in the range of 120–150 °C attributed to water removal. In the case of Fe_2O_3, the behavior is completely different; two weight

Table 1
Surface areas (SA) and band gap energy (E_g) of photocatalysts

Catalyst	SA[a] (m^2/g)	E_g[b] (eV)
TiO_2 (Degussa P-25)	40.8	3.021
ZnO	16.7	3.117
Fe_2O_3	29.1	1.823
$ZnFe_2O_4$	35.4	1.923

[a] Obtained with samples calcined at 800 °C.
[b] Determined by extrapolation of the rising portion of the spectra of zero absorption.

loss zones were well defined, one from room temperature to 150 °C and another from 150 to 400 °C. This can be interpreted as the elimination of surface water and the conversion of residual nitrates to Fe_2O_3 with 21% of weight loss. $ZnFe_2O_4$ weight loss curve is quite similar to that shown by Fe_2O_3; nevertheless, the weight loss was 19%. Both the samples, Fe_2O_3 and $ZnFe_2O_4$, had a similar weight loss profile and in the range of 400–700 °C no significant weight loss was observed suggesting a recrystallization process [26].

The BET surface areas are compared in Table 1. As expected, the catalysts exhibited different surface areas depending on the amount of surface hydroxyls. The higher surface area of zinc ferrite could be explained in terms of the presence of small surface iron oxide particles whose core is the zinc ferrite. These particles adsorbed the major amount of hydroxyls (FTIR results, not shown here) and repel each other, no further sintering or particle growth was observed. The ferrites surface area is usually 15–10 m^2/g (calcined at 800 °C), although it may increase up to 40 m^2/g with the use of special preparation techniques [24,26].

Fig. 3 shows the UV–Vis diffuse reflectance spectra of the catalysts. The spectra of Fe_2O_3 and $ZnFe_2O_4$ were more or less similar, and the band gap energies reported in Table 1 was lower compared to that reported for Fe_2O_3 (2.16–2.58 eV, [23]). The spectrum profile and the value of band gap energy of ZnO were quite similar to that reported in [22]. It seems that $ZnFe_2O_4$ catalyst presented the same behavior as Fe_2O_3 catalyst which could be explained by the surface enrichment of iron oxide.

The reduction behavior of the oxide forms (samples calcined at 800 °C) examined by TPR showed differences among ZnO, Fe_2O_3 and $ZnFe_2O_4$ samples. As it is shown in Fig. 4a, ZnO sample did not present reduction peaks, which was probably the result of complete dehydroxylation and high thermal stability [24]. The TPR experiment of Fe_2O_3 catalyst presented three not well-resolved reduction peaks at 450, 630 and 780 °C (Fig. 4b) attributed to NO surface reduction, the partial reduction of Fe^{3+} to Fe^{2+}, and dehydroxylation [24]. The TPR profile of $ZnFe_2O_4$ sample presented one broad reduction peak starting at 380 °C and ending at 800 °C, although at higher temperatures (>800 °C), another reduction peak appeared. The H_2 consumption was lower than in Fe_2O_3 which revealed that zinc ferrite was more stable to severe reaction treatments
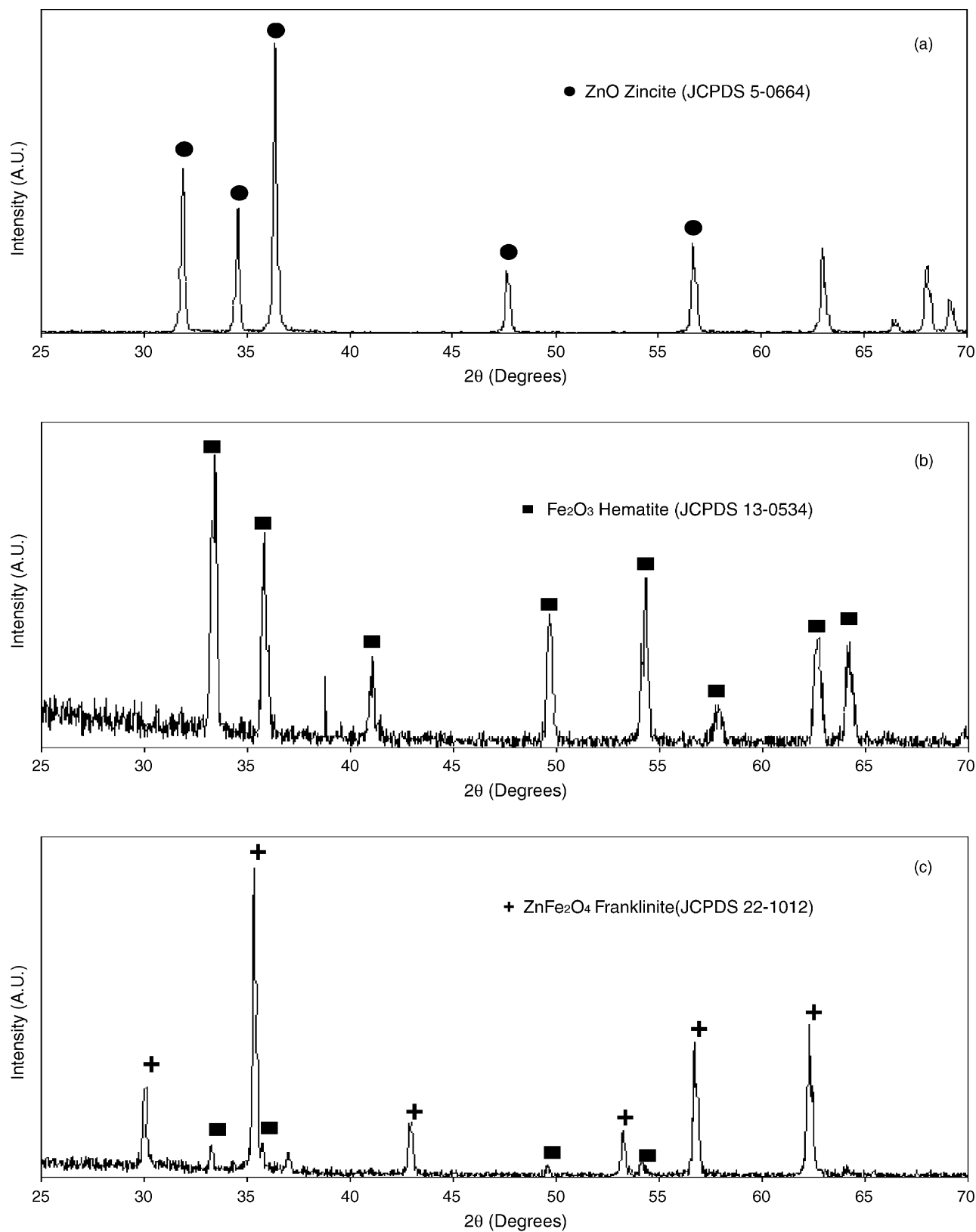
Fig. 1. XRD patterns of samples calcined at 800 °C: (a) ZnO, (b) Fe_2O_3, (c) $ZnFe_2O_4$.
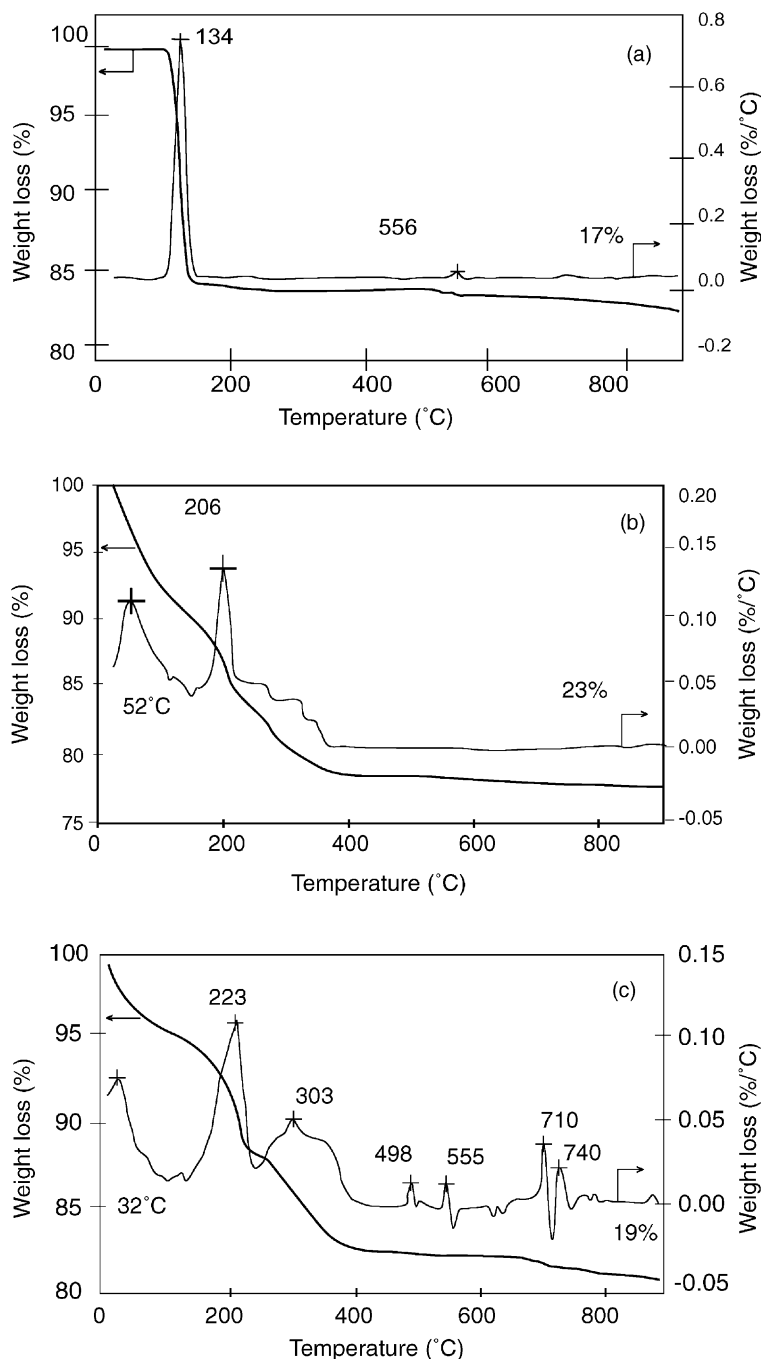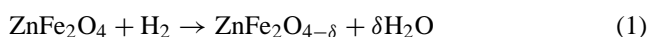
Fig. 2. TGA of precursors dried at 110 °C: (a) ZnO, (b) Fe_2O_3, (c) $ZnFe_2O_4$.

and only at temperatures higher than 800 °C, the structure was modified according to the following reaction:

$$ZnFe_2O_4 + H_2 \rightarrow ZnFe_2O_{4-\delta} + \delta H_2O \qquad (1)$$

In Fig. 5, a comparison of photoactivity among TiO_2 (Degussa P-25), ZnO, Fe_2O_3 and $ZnFe_2O_4$ catalysts at the same operation conditions is shown. Previously, in the absence of illumination or without catalyst, there was no conversion of phenol. As it is shown in Fig. 5, the conversion of phenol after 1 min of illumination followed the decreased order:

$ZnFe_2O_4 > TiO_2 \sim ZnO > Fe_2O_3$. However, after 90 min of illumination, the same trend was not followed; with the TiO_2 commercial catalyst, the conversion of phenol was almost twice than that at 1 min. The photoactivity of ZnO, Fe_2O_3 and $ZnFe_2O_4$ remained constant after 10 min of irradiation time, which was explained in terms of the large amount of subproducts such as hydroquinone, catechol and benzoquinone (determined by GC/MS analysis, not shown here) inhibiting the phenol adsorption. It was also evident that Degussa P-25 TiO_2 generated lower amount of
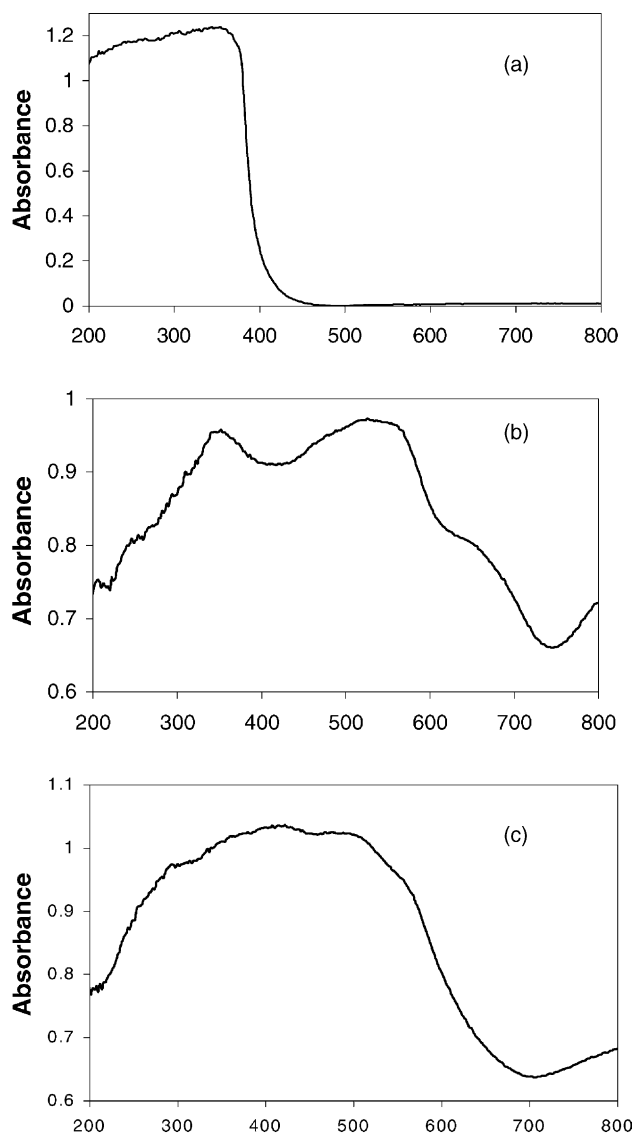
Fig. 3. Absorption spectra of samples calcined at 800 °C: (a) ZnO, (b) Fe_2O_3, (c) $ZnFe_2O_4$.

Fig. 4. TPR profiles of samples calcined at 800 °C: (a) ZnO, (b) Fe_2O_3, (c) $ZnFe_2O_4$.

Fig. 5. Comparison of phenol degradation of samples calcined at 800 °C: (a) ZnO, (b) Fe_2O_3, (c) $ZnFe_2O_4$ and (d) Degussa P-25 TiO_2 as received.

intermediates and the progress of the degradation reaction followed a typical behavior [18]. Although many authors have mentioned that the surface adsorbed water and hydroxyl groups are crucial for photocatalytic reactions [27], it should be considered that among other factors, the kind of phase, surface area, the adsorption capacity, and the surface acid–base properties [21] strongly affect the photoactivity. On the other hand, the operation conditions such as mass of the catalyst, wavelength, temperature, radiant flux, initial concentration of the reactants and oxygen pressure [9] could modify significantly the photoactivity of the catalysts. All these parameters will be considered in a future work with ZnO, Fe_2O_3 and $ZnFe_2O_4$ catalysts in addition to the main advantage of having no need for filtration after the photoactivity test when compared with TiO_2.
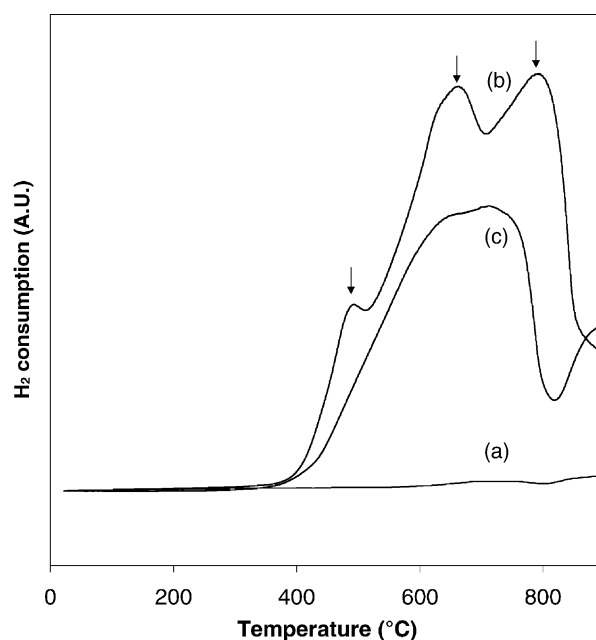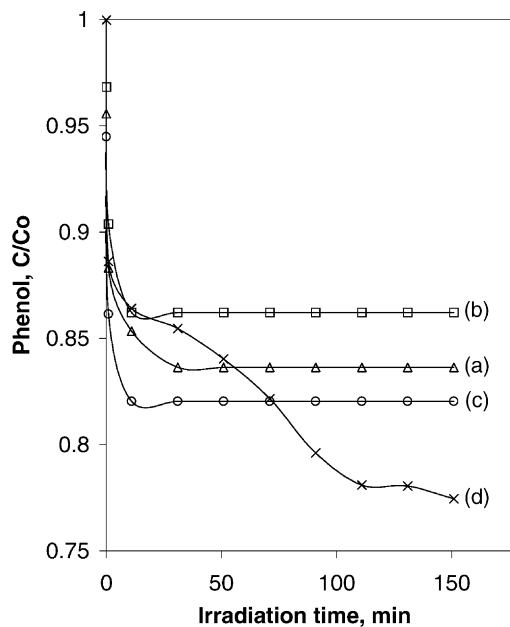
4. Conclusions

ZnO, Fe_2O_3 and $ZnFe_2O_4$ were synthesized by precipitation or coprecipitation, and characterized by XRD, TGA, UV–Vis, N_2 physisorption, TPR, and tested in phenol photodegradation. The results showed a synergism between ZnO and Fe_2O_3, resulting in slightly more active $ZnFe_2O_4$

catalyst than ZnO and Fe_2O_3. The photoactivity of ZnO, Fe_2O_3 and $ZnFe_2O_4$ remained constant after 10 min of irradiation time, which was explained in terms of the large amount of subproducts binding to the surface of the catalysts and inhibiting the phenol adsorption. The decreased order of photoactivity was as follows: $TiO_2 > ZnFe_2O_4 > ZnO > Fe_2O_3$. Future work is in progress in order to find the operation conditions of a higher photodegradation of phenol.

Acknowledgements

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