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Pure and (zinc or iron) doped titania powders prepared by sol–gel and used as photocatalyst

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Abstract

Pure and doped (zinc and iron) nanocrystalline titania powders were prepared by the sol–gel route. Doping tends to change the existing crystalline phases and their degree of crystallinity, but particle size distribution and morphology of the particles are also affected. In the pure titania system, the main crystalline phase is anatase but rutile is also present. The doped (Zn and Fe) titania crystallizes only as anatase. The undoped titania shows a bimodal distribution of particles size: fine (20–40 nm) and coarse (300–500 nm) grains. The doped TiO_2 powder also exhibits a much more uniform particle size distribution, with all grains under 40 nm.

The photocatalytic efficiency of suspended powders was tested on the decolouration of Orange II aqueous solutions under visible artificial light irradiation. The maximum decolouration reached by the pure TiO_2 was 81% at a rate of 3.6×10^{-3} min^{-1}. Iron doping decreases the photocatalytic activity; the maximum dye degradation was only 43% at a rate of 1.3×10^{-3} min^{-1}. On the contrary, the performance of Zn-doped titania was better, having a decolouration rate of 17.7×10^{-3} min^{-1}.

Keywords: Sol–gel; Nanocrystalline titania; Metal-ion doping; Orange II decolouration; Visible light photocatalysis

1. Introduction

Recent studies have demonstrated that photocatalysis can be used to destroy dye compounds, using semiconductor photocatalysts under light irradiation [1–4]. When illuminated with an appropriate light source, the photocatalyst generates electron/hole pairs, with free electrons produced in the empty conduction band leaving positive holes in the valence band. The photogenerated electron/hole pairs are capable of initiating a series of chemical reactions at the catalyst surfaces, which involve adsorbed organic pollutants that are decomposed and generate relatively harmless end products; carbon dioxide and water are the main final products, together with NO_x and HCl for organic compounds containing nitrogen and chlorine. UV radiation is commonly used as the stimulating source, but visible light (artificial, or sunlight) was also tested by several authors [5–10].

Among the various semiconductor materials, titania has been extensively studied due to its unique properties such as high chemical stability, thermal stability, non-toxicity, excellent functionality, low cost and high photocatalytic activity [3]. These properties can be improved substantially by the use of nanostructured titania. Nanocrystalline titania has been widely studied for application in photocatalysis, and several works on the preparation of TiO_2 nanocrystals have been reported [2,6,7,11–14]. The photocatalytic behaviour of titania depends on the crystal structure, lattice defects, specific surface area and particle size/morphology, among other factors. Anatase crystallites, for instance, show a relatively higher photocatalytic activity than rutile, which can result from the superior adsorptive affinity for organic compounds of anatase, and its lower recombination rate [1]. Also, the decreasing of particle size has an influence on electrochemical potentials of the photo generated charge carriers, thus the interest in the preparation of nano-sized titania particles.

Recently, titania doped with different ions was presented as an alternative way to increase its efficiency as photocatalyst [7,13,15–19], since doping species can act as hole and/or electron traps [20]. The sol–gel process has been proved to be

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suitable to prepare homogeneous pure and doped titania powders with nanometric size [2,11–13,15–19].

2. Experimental procedure

2.1. Powders preparation and characterization

As precursors, titanium (IV) isopropoxide (Fluka), zinc nitrate hexahydrate (Riedel – de Haën) and iron nitrate nonahydrate (Merck) were used. Absolute ethanol PA (Panreac) was used as the solvent and ammonium hydroxide, 25% NH_3 (Riedel – de Haën) was utilized to precipitate the sols.

Undoped TiO_2 powders were prepared by the sol–gel route as follows: a solution of absolute ethanol (EtOH) and titanium isopropoxide (TiPr) (molar ratio EtOH/TiPr = 30.3) was sonicated for 7.5 min and then distilled water was added (molar ratio H_2O/TiPr = 3.2). After sonication for 45 min, ammonium hydroxide was abruptly added (molar ratio NH_3/TiPr = 1.56) and the final solution was sonicated for more 30 min.

TiO_2 doped powders with composition in Zn equal to 0.1 mol% and composition in Fe equal to 2 mol%, were prepared by the sol–gel route in the same way. The iron and zinc precursors were dissolved in the above given amount of distilled water.

The final solutions were centrifuged for 15 min at 7000 rpm. After decantation and addition of absolute ethanol (molar ratio EtOH/TiPr = 5.0), further centrifugation, for 15 min at 7000 rpm was carried out.

After decantation, the resulting powders were dried at 60 °C (24 h) and heat treated at 500 °C for 2 h.

The powders were characterized in terms of existing crystalline phases by XRD (Rigaku Geigerflex diffractometer, CuK_α radiation between 0° and 80°). The powder morphology was studied by scanning electron microscopy (SEM-Hitachi, SU 70) equipped with energy dispersion spectroscopy (EDS–EDAX with detector Bruker AXS, software: Quantax), which was used to evaluate the compositional homogeneity. The specific surface area of the prepared powders was evaluated by BET (Micrometrics Gemini).

2.2. Photocatalytic activity measurements

The photocatalytic activity of prepared powders was tested for the degradation of Orange II (Fluka AG, Buchs, Switzerland, di-sodium salt) azo dye solutions. Orange II aqueous solutions were prepared with a concentration of 20 mg/L by dissolving the dye in tap water, resulting in a pH ≈ 7. The photocatalytic reactions were carried out in a cylindrical batch reactor (Fig. 1) developed previously [8,9], consisting of a lamp (Philips ML – 160 W) that radiates in the visible region (between 400 and 600 nm). The correct dimensions of the reactor limited the increase of the bath temperature (<10 °C) during visible light irradiation. The effect of the powders in suspension (1 g/L) on the photocatalytic activity was monitored by measuring the absorbance of the respective reacting solutions. Samples (about 5 mL) were collected at different time intervals (up to 7.5 h). The UV–Vis absorption spectra were recorded using a Shimadzu UV-3100 spectrometer and distilled water as reference. Photolysis and dark experiments (i.e. in the absence of the catalyst and without radiation, respectively) were performed under similar experimental conditions.

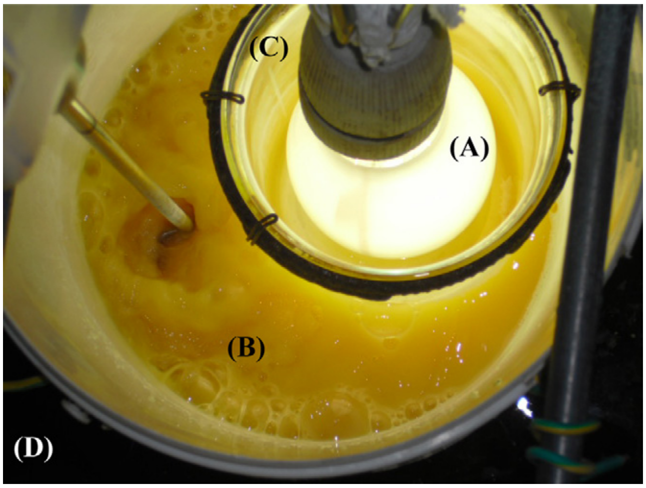

Fig. 1. View of the reactor set-up used during the photocatalytic experiments: (A) lamp (Philips ML – 160 W); (B) suspension of the powders in the Orange II solution with stirring; (C) glass protector; (D) cooling water tank.

3. Results and discussion

XRD patterns of the prepared powders are presented in Fig. 2. In the undoped TiO_2 heat-treated at 500 °C the main crystalline phase is anatase, however, the presence of rutile is clearly detected. On the contrary, anatase is the only crystalline phase detected in the doped TiO_2 samples, leading to the conclusion that the doping inhibited the formation of rutile (Fig. 2). The use of iron resulted in a decrease of the powder crystallinity (insert in Fig. 2).

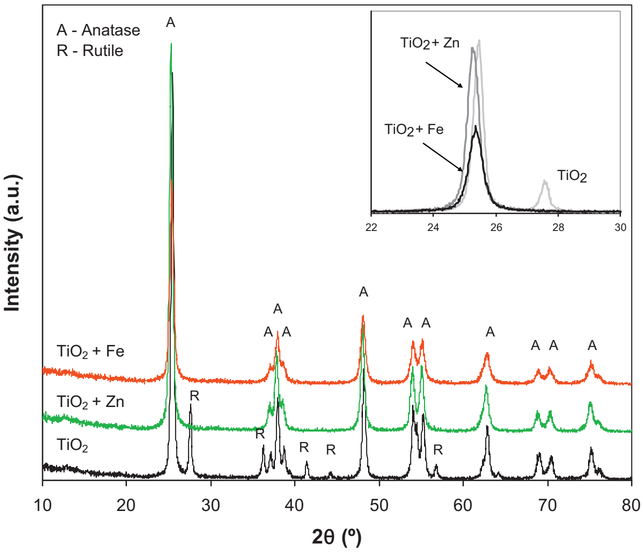

Fig. 2. XRD spectra of the powders.

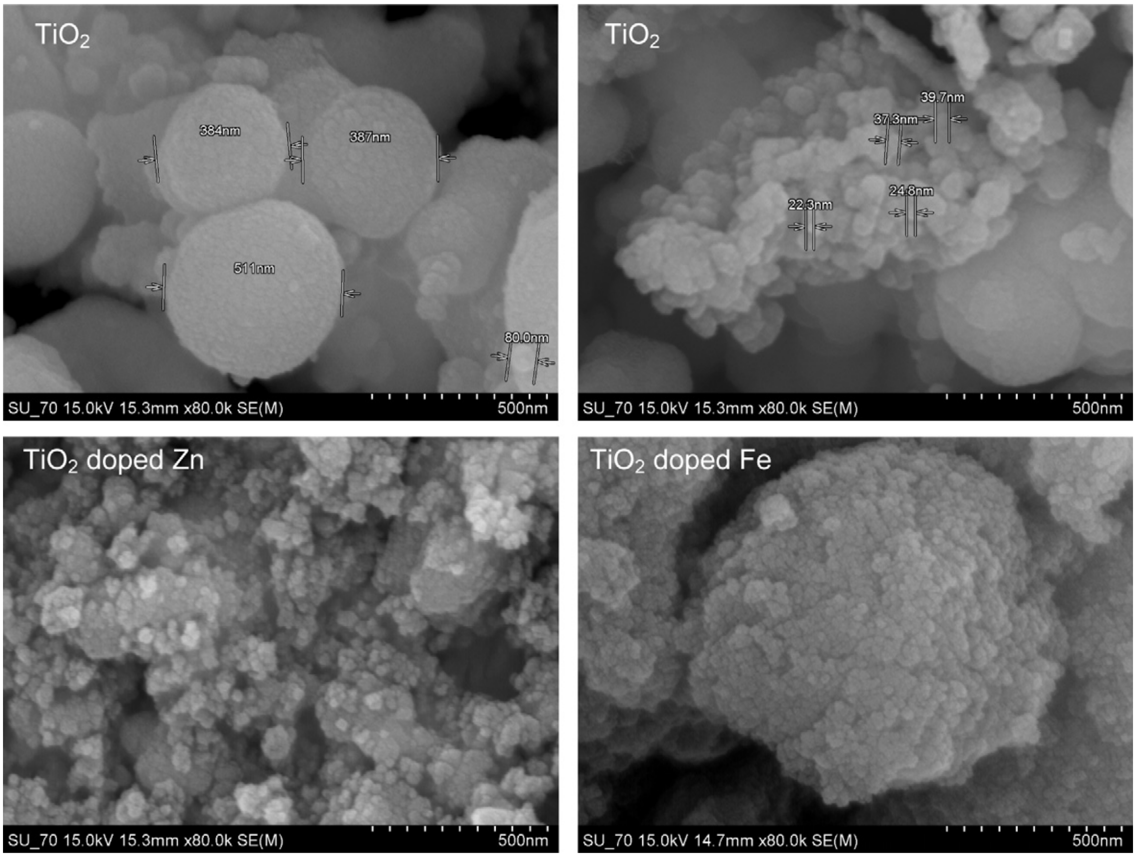

Fig. 3. SEM images of the pure TiO_2 and that doped with Zn and Fe.

The particle sizes of the prepared powders are all submicron (Fig. 3). The undoped TiO_2 consists of fine particles (20–40 nm) together with coarser ones (300–500 nm). The Zn and Fe doped powders are more uniform in size and are much finer (<40 nm), so the specific surface area (SSA) of the doped materials is higher than that of undoped titania. However, the doped titanias presents a tendency to agglomeration, which is more notorious for the Fe doped titania (Fig. 3), having the agglomerates a diameter bigger than the coarser titania ($\approx$1000 nm). This is reflected in the values obtained for the specific surface areas. The undoped titania has a SSA of 7 m^2/g; Fe and Zn doped titanias exhibit, respectively, 15 m^2/g and 41 m^2/g.

Prior to the photocatalytic degradation of Orange II solutions in the presence of the TiO_2 powders, control experiments were performed. These were carried out without the powder (direct photolysis) and in the presence of TiO_2 but in dark conditions. Direct photolysis of the dye is ineffective, resulting in a photodegradation degree of less than 5%, after a reaction time of 7 h. A similar behaviour was observed for dark conditions.

On the contrary, an effective decolouration was observed when titania powders were dispersed in the Orange II solutions. Its effect is seen in Fig. 4, showing the evolution of the absorbance spectra of the Orange II solutions, with the powders in suspension, after increasing exposure times. In this figure it is possible to see that the tested powders have diverse photodegradation efficiencies.

The characteristic absorbance peak of Orange II dye is located at 486 nm ($\lambda_{\text{máx.}}$ = 486 nm) and therefore the material's photocatalytic activity can be followed over its evolution with the exposition time. Plotting the discolouration percentage $[(A_0 - A)/A_0] \times 100$ (where A is the absorbance at 486 nm after some exposure time and A_0 is its initial value) versus time (Fig. 5), it is possible to compare the photocatalytic behaviour of the powders in suspension. The maximum decolouration attained was, respectively, 81%, 98% and 43% for undoped titania and that doped with Zn and Fe. Doping TiO_2 with Zn promoted a decrease of the time necessary to reach 50% of discolouration from $\approx$3 h to only 40 min. However, iron doping led to a clear decrease of photodegradation efficiency.

As referred to in previous publications [21], it is possible to calculate the apparent rate constant (k_a) of the photodegradation reaction, since it generally follows a Langmuir–Hinshelwood mechanism. The reaction rate is proportional to the photocatalytic material coverage of the dye molecules, which can be determined through the equation $\ln(A_0/A) = k_a t$, where k_a (min^{-1}) is the apparent rate constant and t (min) is the time. A good correlation ($R^2 > 0.97$) was obtained (Fig. 6), suggesting that the reaction kinetics follow a pseudo-first order rate law. The Zn doping promoted only a slight increase (from 81% to 98%) of the maximum decolouration achieved. Nevertheless, the apparent rate constant (k_a) is almost six times higher ($k_a = 3.2 \times 10^{-3}\ \text{min}^{-1}$ versus $k_a = 17.7 \times 10^{-3}\ \text{min}^{-1}$, insert in Fig. 6), so the time necessary to reach a certain degree of

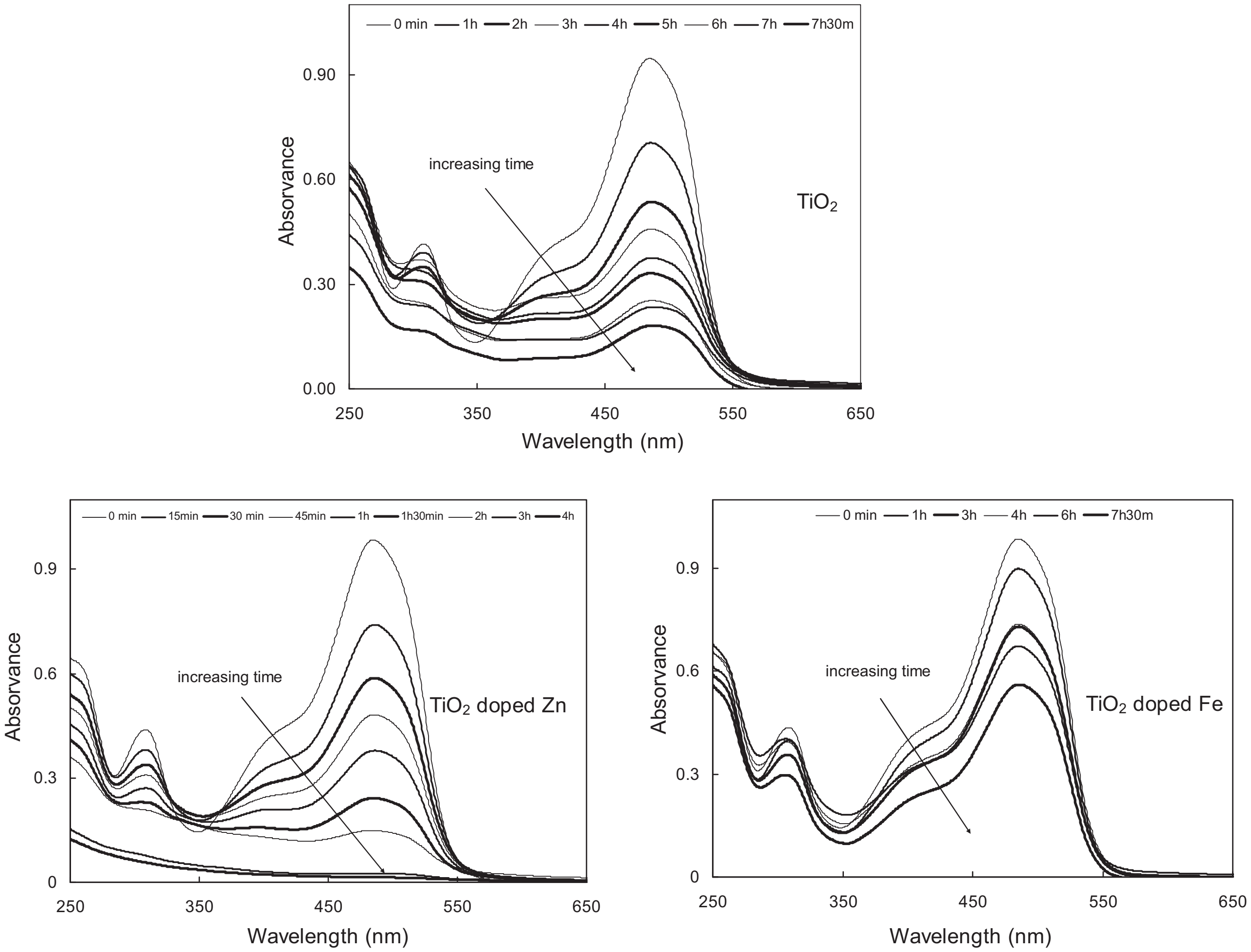

Fig. 4. Decolourisation of Orange II dye solution with the TiO_2 powders in suspension.

discolouration is significantly smaller for the Zn doped TiO_2. Adversely, the k_a value obtained for the Fe doped titania is smaller ($k_a = 1.3 \times 10^{-3}$ min^{-1}, insert in Fig. 6), showing the detrimental effect of iron on the photocatalytic behaviour.

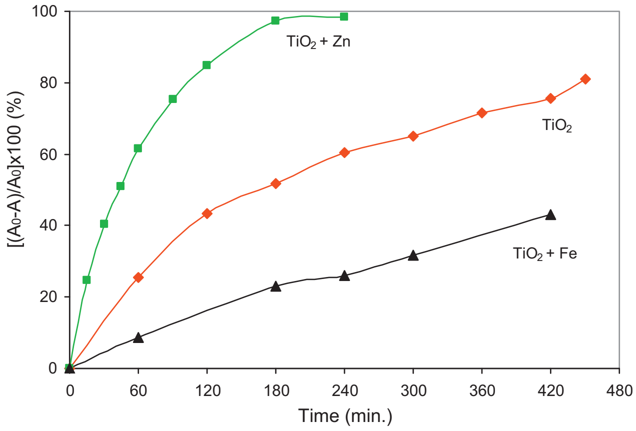

Fig. 5. Attenuation (%) of the 486 mm absorbance peak with the exposition time.

As refereed to in the literature [1], there are several parameters controlling the photocatalytic activity of a titania-based powder. Two of these are the nature of existing crystalline phases, and the specific surface area, and both seemed to change upon Zn doping. The anatase polymorph is much more efficient than rutile, and the photocatalytic activity directly depends on the specific surface area. According to this, the increase of photocatalytic activity of Zn-doped titania can be related to the inhibition of rutile formation (Fig. 2), and also to the increase of the powder's specific surface area (Fig. 3). Good results for Zn-doped TiO_2 prepared using a stearic acid gel method were also obtained by Chen et al. [17], where the observed behaviour was rationalized in terms of the role of Zn in the TiO_2 monocrystals and also on changes of specific surface area.

The Fe doped TiO_2 also consists of anatase only (Fig. 2), and the particle size is smaller than that of undoped titania (Fig. 3); however, it exhibited a decrease in photocatalytic activity. This behaviour can be related to the propensity that the powder has to agglomerate (Fig. 3), which promotes a decrease of the exposed surface area. A decrease of the crystallinity was also observed (insert in Fig. 2), which can also contribute to the observed behaviour.

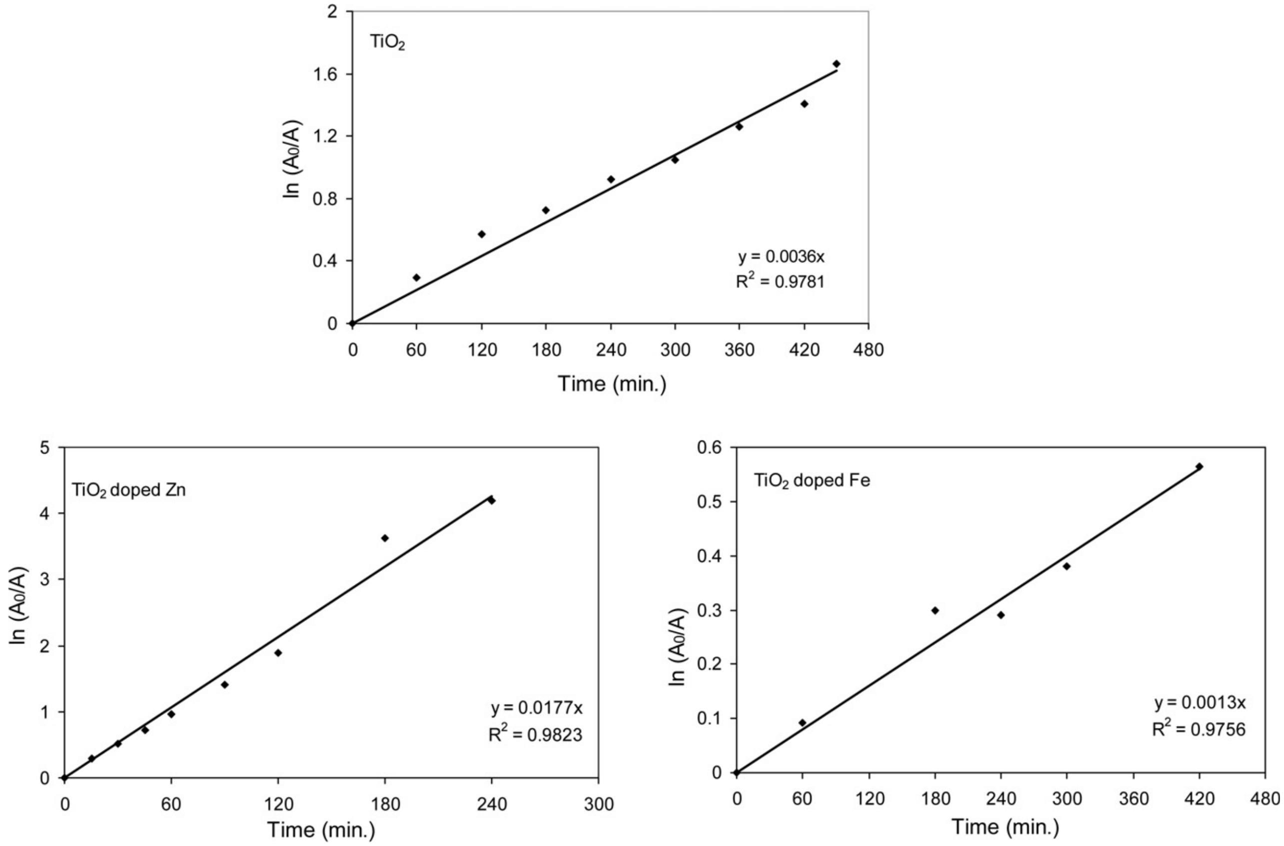

Fig. 6. Linear transform ln $A_0/A = f(t)$ of the kinetic curves. Inserted values correspond to the slope (reaction rate, k_a) and correlation factor (R^2).

4. Conclusions

Nanosized undoped TiO_2 and zinc and iron doped TiO_2 powders were prepared using a sol–gel based process.

In the undoped titania, besides anatase some rutile was also detected. The presence of Zn or Fe inhibited the rutile formation; the doped titania crystallizes only as anatase.

The undoped titania consists of a polydisperse mixture of small particles (20–40 nm) and coarser grains (300–500 nm). The doped titania powders are much more uniform in size and are composed of particles under 40 nm. However, the doped titanias exhibit some tendency to agglomeration, mainly the Fe doped titania.

The maximum decolourisation reached by the undoped TiO_2 is 81% at a rate of 3.6×10^{-3} min^{-1}. Iron doping promoted a decrease of the photocatalytic activity. On the contrary, titania doping with Zn significantly improved the photocatalytic activity. The maximum decolourisation degree reached was 98% at a rate of 17.7×10^{-3} min^{-1}. The observed behaviour was related to the crystalline phases present, degree of crystallinity and exposed surface area.

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