



## Effect of the type of acid used in the synthesis of titania–silica mixed oxides on their photocatalytic properties



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### ABSTRACT

TiO<sub>2</sub>–SiO<sub>2</sub> mixed oxides were synthesized by the sol–gel technique using three different acids, i.e., acetic, sulfuric, or chlorhydric acid. Their photocatalytic behavior was evaluated on the phenol oxidation in liquid phase and correlated with the characterization results. It was found that the kind of acid used during the preparation strongly influences the phase composition and stability of the TiO<sub>2</sub> phases incorporated in the silica structure as well as the photocatalytic activity. In all cases, silica introduced a dispersive effect that stabilized the TiO<sub>2</sub> crystalline phases upon calcination at 700 °C. SO<sub>4</sub><sup>2-</sup> and CH<sub>3</sub>COO<sup>-</sup> ions stabilized the anatase phase at high calcination temperatures (700 °C) leading to samples with the highest photoactivities. Cl<sup>-</sup> ions induced the formation of traces of rutile and brookite resulting in a lower photoactivity. The highest photoactivity was achieved with the catalyst synthesized with acetic acid and calcined at 700 °C (TS1-700-ace). The photocatalytic performance of this material was even better than that obtained with the commercial catalyst Degussa P-25.

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### 1. Introduction

Photocatalytic degradation of pollutants with TiO<sub>2</sub> has become one of the most promising technologies to protect the environment. One of the challenges currently faced by photocatalysis is the optimization of TiO<sub>2</sub> in such a way that photocatalysis will be more applicable at a practical level [1]. The three main polymorphs of TiO<sub>2</sub>, i.e., anatase, brookite, and rutile, exhibit different physical properties such as refractive index, chemical and photochemical reactivity which in turn are closely related with the crystalline structure, morphology, and particle size.

In most of the research works on the topic, the crystalline anatase phase appears to be more photoactive than rutile and brookite. The difficulty to obtain pure anatase phase lies in the fact that rutile is the polymorph thermodynamically more stable, and although anatase is kinetically stable it is easily transformed into rutile at temperatures ranging from 500 to 1000 °C [2]. According to that, the development of new methods of synthesis in which the shape, size, and TiO<sub>2</sub> crystalline phases can be controlled is an important task to be achieved in the field of photocatalysis [3].

It has been reported that the kind of acid catalyst used in the synthesis of TiO<sub>2</sub> dramatically affects the crystallization process, inducing the formation of one or another phase. In this regard, acids like HCl or HNO<sub>3</sub> induce the formation of brookite and rutile and even a mixture of the three phases, whose relative proportions depend on the range of acidity, temperature, titanium concentration, and reaction time [4,5]. It is difficult to obtain pure brookite phase and it is usually synthesized in combination with other crystalline phases [6].

On the other hand, it has also been found that acid peptization with sulfuric acid retards the transition from anatase to rutile and, in addition, sulfated titanium oxide exhibits a highlighted photocatalytic activity [7–9]. The remarkable behavior displayed by sulfated materials has been ascribed to their large surface area, anatase crystalline phase, and the increment of the acid properties. Colón et al. [10] have established that sulfate ions stabilize the anatase phase up to 700 °C, obtaining highly defective materials due to the creation of oxygen vacancies through a dehydroxylation process of an excess of adsorbed protons. The loss of surface oxygen ions as well as the predominant anatase phase seems to be the determinant factors for the high photocatalytic activity showed by sulfated materials, improving the charge carrier's separation and the diffusion of the same to the surface [10].

Li et al. [11] studied the effect of the SO<sub>4</sub><sup>2-</sup> dopant over TiO<sub>2</sub> synthesized by the sol–gel method under supercritical and

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conventional conditions of drying, and also evaluated the photocatalytic properties of the oxides on the phenol degradation. The obtained results showed that the most influent factors over the photocatalytic properties of the  $\text{SO}_4^{2-}/\text{TiO}_2$  oxides were the presence of pure anatase phase, high surface area, large pore volume and pore size, crystalline defects (oxygen vacancies), and specially the surface acidity.

Moreover, it is well known that the addition of ligands or modifying compounds such as  $\beta$ -diketones (e.g., acetylacetone) or carboxylic acids (acetic acid) allows to control the hydrolysis reaction rate of titanium alkoxides (highly reactive) in the sol–gel synthesis, avoiding the precipitation of undesirable phases. In this sense, acetic acid is usually employed as modifying or stabilizing agent in the sol–gel synthesis, since this compound reacts chemically with the titanium alkoxide at atomic level to give a new precursor. The steric effect of the acetate ligand and the increase in the number of coordination of Ti lead to a decrease in the rate of the hydrolysis reaction [12–14].

In the last years, titania–silica mixed oxides have become a new alternative in photocatalytic processes. Their main applications are based on the ability to act as catalyst and support in a wide variety of reactions. They exhibit characteristic properties from both single oxides such as photocatalytic activity, high surface area, thermal stability, and mechanical strength. In addition, as a result of the interaction between  $\text{SiO}_2$  and  $\text{TiO}_2$  at atomic level synergic effects are generated including quantum size and support effect as well as the formation of new catalytic acid sites [15–18].

$\text{TiO}_2$ , especially in its anatase crystalline form, is the most widely used material in studies of photocatalytic degradation. However, aspects such as particle size and poor surface area have motivated the development of supported systems in which  $\text{SiO}_2$  has emerged as an appropriate support for improving the photocatalytic process, since it is a chemically inert material with large surface area and transparent to UV radiation.

In this study  $\text{TiO}_2$ – $\text{SiO}_2$  were synthesized by the sol–gel technique and the effect of three different acids on the phase composition and photocatalytic activity was studied. In addition, the effect of calcining the samples at 500 and 700 °C was also investigated. The photocatalytic behavior was evaluated on the phenol oxidation in liquid phase and correlated with the obtained characterization results. The influence of silica on the crystalline phases and its role as a retarding agent in the crystallization process was also established.

## 2. Experimental

### 2.1. Catalyst preparation

$\text{TiO}_2$ – $\text{SiO}_2$  mixed oxides were synthesized through the sol–gel technique using tetraethoxysilane (TEOS, Aldrich 98%) and titanium tetraisopropoxide (TTIP, Aldrich 97%) as silica and titania sources, respectively. The synthesis procedure involved two stages of hydrolysis of each alkoxide. In the first step, the hydrolysis of TEOS in isopropanol was performed by adding distilled water previously acidified with acetic, sulfuric, or chlorhydric acid, under the following molar ratios: TEOS:water:isopropanol:acid = 1:20:8:0.4. The solution was then left at room temperature for 14 h to promote hydrolysis and gelation of the silicon alkoxide. In the second step, the hydrolysis of a solution of TTIP in isopropanol was carried out by adding acidified distilled water. Final molar relation TTIP:water:isopropanol:acid was 1:12:14:1. After gelation time, the two solutions were mixed to obtain a transparent  $\text{TiO}_2$ – $\text{SiO}_2$  sol and it was stirred for 1 h at room temperature. After that, heating at 65 °C was carried out to obtain a transparent gel. Additional drying at 110 °C was performed to allow the formation of a xerogel

structure. The xerogel was ground into fine powders and calcined at 500 and 700 °C for 2 h in static air. The molar ratio Ti/Si was 1. The samples were labeled as TS1–CT–acid, where TS1 is referred to titania silica (Ti/Si = 1), CT is the calcination temperature (500 or 700 °C) and the word acid is associated with the type of acid used in the synthesis, i.e., ace (acetic), sul (sulfuric), and clor (chlorhydric).  $\text{SiO}_2$  blank was also synthesized under the same conditions, avoiding the addition of the titania source, in order to make some comparisons.

### 2.2. Characterization of the catalysts

XRD patterns were obtained on a Siemens D-501 diffractometer with Ni filter and graphite monochromator, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Crystallite sizes of the different phases were estimated from the line broadening of the corresponding X-ray diffraction peaks using the Scherrer equation. Peaks were fitted using a Voigt function.

BET surface area and porosity measurements were performed using a Micromeritics Gemini V, by means of  $\text{N}_2$  adsorption at 77 K. Prior to the analysis, the samples were degassed under  $\text{N}_2$  flowing at 100 °C for 2 h, followed by a vacuum treatment at the same temperature for 1 h.

Thermogravimetric analyses and differential thermal analyses (TGA/DTA) were recorded using a STA 1600 Platinum Series instrument (LINSEIS).

Infrared (IR) spectra of the materials were recorded with a Varian 660 spectrometer, using KBr pellets as matrix for the powder samples.

UV–vis diffuse reflectance absorption spectra were acquired with a Varian spectrometer model Cary 100 equipped with an integrating sphere, using  $\text{BaSO}_4$  as reference. All the spectra were recorded in diffuse reflectance mode. Since the Kubelka Munk function can be considered proportional to the radiation absorption, the bandgaps were calculated from the spectra recorded by plotting  $(F(R)h\nu)^{1/2}$  vs.  $h\nu$ , according to the method proposed by Tandon and Gupta [19].

The isoelectric points of the catalysts were not measured. But, it has been reported that the isoelectric points of these kind of materials are located around 4–6. Due to the fact that the silica creates Lewis acid sites, the isoelectric points of  $\text{SiO}_2$ -modified  $\text{TiO}_2$  oxides are lower than those of pure  $\text{TiO}_2$  and decrease with increasing  $\text{SiO}_2$  content [20]. The surface charge of the photocatalyst can influence the adsorption of phenol (pKa 9.95 at 25 °C). Brezová et al. and Chiou et al. [21,22] found that for  $\text{TiO}_2$  the degradation of phenol is very effective in mild acidic solutions and that between pH 2.0 and 10 only small changes in the phenol degradation rates were observed. Because of this, all the experiments were carried out under autogenous pH of the phenol solution (pH 5.5).

### 2.3. Photocatalytic experiments

The photocatalytic activity of the prepared samples was tested through the phenol oxidation in water (50 ppm) at a catalyst concentration of 1 g/L, in a Pyrex immersion well reactor. The UV light source was provided by a medium pressure Hg lamp (400 W) supplied by Applied Photophysics, which has a main emission line of 365 nm. The lamp was placed inside the batch reactor surrounded by a double borosilicate glass jacket where a water stream keeps the temperature of the solution constant. During the photooxidation process (2 h), an oxygen flow was used to maintain homogeneously suspended the catalyst in the solution. Samples of 2 mL volume were withdrawn at different time intervals, then filtered (Millipore Millex25 0.45  $\mu\text{m}$  membrane filter) and analyzed by UV–vis spectrometry at 270 nm (characteristic phenol band). Prior to exposure to UV light, the photocatalysts were mixed with the phenol solution

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