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Study of the phenol photocatalytic degradation over TiO_2 modified by sulfation, fluorination, and platinum nanoparticles photodeposition

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ABSTRACT

In this work, titanium dioxide has been modified by sulfation, fluorination and simultaneous Pt nanoparticles deposition; the influence of these treatments on the photocatalytic activity of this oxide has been studied. A complete characterization study was carried out and it was observed that sulfation, fluorination and metallization were important factors influencing the TiO_2 properties. The photocatalytic activity of the materials prepared was evaluated in the phenol degradation and it was found that TiO_2 fluorination significantly increased the phenol photodegradation rate, compared with bare TiO_2, sulfated TiO_2 or the commercial TiO_2 Degussa P25. It was also found that Pt photodeposition on sulphated TiO_2 notably increased the photocatalytic activity of this oxide, while Pt on fluorinated TiO_2 did not modify significantly the phenol photodegradation rate.

1. Introduction

Titanium dioxide (TiO_2) heterogeneous photocatalysis has been studied in the decomposition of a wide range of undesirable chemical contaminants and it appears to be a feasible process for water and air pollution control by using solar or artificial light illumination.

TiO_2 properties, such as phase composition and structure, surface hydroxyl groups, particle size, and surface defects play a very important role in the activity of this oxide in photocatalytic reactions. In different studies, some of these parameters have been modified in order to enhance the photocatalytic performance of the TiO_2 [1–8].

It is generally accepted that one major draw-back of TiO_2 as a photocatalyst is the high recombination rate of the electron–hole pair photogenerated, which reduces the photoefficiency of the photocatalytic process.

The sulfation of TiO_2 surface has been reported as an effective method for improving the photoefficiency of this oxide [9–11]. Sulfation pre-treatment leads to a stabilization of the TiO_2 anatase crystalline phase and surface area against sintering during the calcination process. A dehydroxylation process of the excess of adsorbed protons takes place during calcination, leading to the creation of surface oxygen vacancies and promoting the separation of photogenerated charges, thus, improving the TiO_2 photocatalytic efficiency.

As another method for improving the photocatalytic activity of TiO_2, different authors have studied the surface fluorination as a new approach of TiO_2 surface modification [12–18]. Firstly, it has been reported that the surface fluorination of TiO_2 leads to the formation of surface $\equiv$Ti–F groups, these species have a strong electron-withdrawing ability leading to the reduction of the recombination of the photogenerated electrons and holes [14,15,19]. On the other hand, it has also found that surface fluorination of TiO_2 enhances the generation of mobile (unbound) $OH^\bullet$ radicals that are stronger oxidants than the surface adsorbed $OH^\bullet$ radicals [13,17,19,20]. These are the main effects explaining the enhanced photocatalytic activity of fluorinated TiO_2.

Additionally, noble metal deposition has also been a common strategy used to improve the photoefficiency of TiO_2. In this case, the noble metal deposits (usually Au, Pt, Ag, and/or Pd) on TiO_2

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surface act as receptors of the electrons photogenerated in the illuminated TiO_2, thus, reducing the recombination rate and therefore improving the photocatalytic activity of this oxide [2,5,6,8,10,21].

This manuscript describes the synthesis of a series of TiO_2 powders modified by sulfation, fluorination and platinum addition. The main objective of this work has been to study the combination effect of platinization on sol–gel prepared TiO_2 previously sulfated or fluorinated. The photocatalytic activity of the TiO_2 powders prepared was studied in phenol photodegradation used as test reaction. The properties of bare and modified TiO_2 are described in detail and a comparative study of the photocatalytic activity of the TiO_2 powders obtained is also presented.

2. Experimental

TiO_2 used as starting material (bare TiO_2) was prepared by hydrolysis of titanium tetraisopropoxide (Aldrich, 97%) in isopropanol solution (1.6 M) by the slow addition of distilled water (volume ratio isopropanol/water 1:1). The TiO_2 powder was recovered by filtration and dried at 110 °C for 24 h and then this was calcined at 650 °C for 2 h.

Also non calcined TiO_2 powder was modified by sulfation or fluorination treatments, thus, sulfated TiO_2 (S–TiO_2) sample was obtained by immersion of the uncalcined TiO_2 powder in a 1 M sulfuric acid solution under continuous stirring for 1 h, followed by filtration, drying, and calcination at 650 °C for 2 h.

Fluorinated TiO_2 (F–TiO_2) was prepared by adding 10 mM NaF to an aqueous suspension of uncalcined TiO_2. The pH was then adjusted to 3 using a solution of HCl 1 M to maximize the fluoride adsorption. This suspension was stirred for 1 h in the dark. Precipitate was recovering by filtration, dried, and calcined at 650 °C for 2 h.

Photodeposition of platinum was performed over the calcined TiO_2 powders (bare TiO_2, S–TiO_2, or F–TiO_2) using hexachloroplatinic acid (H_2PtCl_6, Aldrich 99.9%) as metal precursor. Under an inert atmosphere (N_2), a suspension of the corresponding TiO_2 sample in distilled water containing isopropanol (Merck 99.8%) which acts as sacrificial donor was prepared. Then, the appropriate amount of H_2PtCl_6 to obtain a nominal platinum loading of 0.5% weight total to TiO_2 was added. Final pH of the suspensions was 3. Photodeposition of platinum was then performed by illuminating the suspension for 120 min with an Osram Ultra-Vitalux lamp (300 W) which possesses a sun-like radiation spectrum with a main emission line in the UVA range at 365 nm. Light intensity on the suspensions was 60 W/m^2 determined by a PMA 2200 UVA photometer (Solar Light Co.). After photodeposition, the powders were recovered by filtration and dried at 110 °C overnight.

Commercial TiO_2 Degussa P25 used as reference material was employed as received.

All the materials were widely characterized using different techniques. Crystalline phase composition and degree of crystallinity of the samples were estimated by X-ray diffraction (XRD). XRD patterns were obtained on a Siemens D-501 diffractometer with Ni filter and graphite monochromator using Cu Kα radiation. Anatase crystallite sizes were calculated from the line broadening of the main anatase X-ray diffraction peak (1 0 1) by using the Scherrer equation. Peaks were fitted by using a Voigt function.

Specific surface area (S_{BET}) measurements were carried out using low-temperature nitrogen adsorption in a Micromeritics ASAP 2010 instrument. Degasification of the samples was performed at 150 °C.

Chemical composition and total platinum content in the samples were determined by X-ray fluorescence spectrometry (XRF) in a Panalytical Axios sequential spectrophotometer equipped with a rhodium tube as the source of radiation. XRF measurements were performed onto pressed pellets (sample included in 10 wt.% of wax).

Light absorption properties of the samples were studied by UV–vis spectroscopy. The UV–vis DRS spectra were recorded on a Varian spectrometer model Cary 100 equipped with an integrating sphere and using $BaSO_4$ as reference. Band-gaps values were calculated from the corresponding Kubelka–Munk functions, $F(R\infty)$, which are proportional to the absorption of radiation by plotting $(F(R\infty) \times h\nu)^{1/2}$ against $h\nu$.

Platinum particle sizes were evaluated by Transmission Electronic microscopy TEM, using a microscope Philips CM 200. For these analyzes, samples were dispersed in ethanol using an ultrasonicator and dropped on a carbon grid.

X-ray photoelectron spectroscopy (XPS) studies were carried out on a Leybold–Heraeus LHS-10 spectrometer, working with constant pass energy of 50 eV. The spectrometer main chamber, working at a pressure $<2 \times 10^{-9}$ Torr, is equipped with an EA-200 MCD hemispherical electron analyzer with a dual X-ray source working with Al Kα ($h\upsilon = 1486.6$ eV) at 120 Wand 30 mA. C 1s signal (284.6 eV) was used as internal energy reference in all the experiments. Samples were outgassed in the prechamber of the instrument at 150 °C up to a pressure $< 2 \times 10^{-8}$ Torr to remove chemisorbed water.

Difusse reflectance infrared Fourier transform spectroscopy (DRIFTS) spectra were recorded on a Thermo Scientific-Nicolet iS10 spectrophotometer. Intervals of 4000–1000 cm^{-1}, a resolution of 2 cm^{-1}, and a forward and reverse moving mirrors speed of 10 and 6.2 kHz, respectively, were used.

Phenol photocatalytic degradation reactions were carried out using a discontinuous batch of 400 mL pyrex reactor enveloped by an aluminum foil, filled with an aqueous suspension (250 mL) containing 50 ppm of phenol (0.53 mM) and photocatalyst (1 g/L). This system was illuminated through a UV-transparent Plexiglas® top window (threshold absorption at 250 nm) by anOsram Ultra-Vitalux lamp (300 W) with sun-like radiation spectrum and a main line in the UVA range at 365 nm, the intensity of the light on photoreactor was 140 W/m^2. In order to favor the adsorption–desorption equilibrium, prior to irradiation the suspension was magnetically stirred for 10 min in dark. Magnetic stirring and a constant oxygen flow of 35 L/h as an oxidant were used to produce a homogeneous suspension of the photocatalyst in the solution. All photocatalytic tests started at pH ca. 6 and the total reaction time was 120 min. During the phenol photoreaction, samples were collected at different times and measured by HPLC, using an Agilent Technologies 1200 chromatograph, which was equipped with UV–vis detector and an Elipse XDB-C18 column (5 μm, 4.6 mm × 150 mm). The HPLC analysis was carried out using water/methanol (65:35) as mobile phase, a flow rate of 0.8 mL/min and 40 °C.

Photolysis test of phenol under UV light and in absence of catalyst were carried out. Under the experimental conditions used in this work, phenol photolysis was not observed.

Total mineralization of phenol with the illumination time was followed by measuring the total organic content (TOC) in a Shimadzu 5000 TOC analyzer.

3. Results and discussion

3.1. Photocatalysts characterization

3.1.1. X-ray diffraction

XRD was used to analyze the effects of fluorination, sulfation, and platinization on the crystallite structure and phase composition of TiO_2 prepared by sol–gel method. Fig. 1A and B shows the XRD patterns of the bare and modified TiO_2.