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Structural and fractal characterization of tungstophosphoric acid modified titanium dioxide photocatalyst

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ABSTRACT

This article presents the comparison of structural and fractal properties of nanocrystalline titanium dioxide (TiO_2) and TiO_2 modified with tungstophosphoric acid (TiO_2/HPW) and their impact on the photocatalytic degradation of hazardous water pollutants. TiO_2 and TiO_2/HPW samples were synthesized by a combined sol-gel and hydrothermal processing. The XRD analysis of pure TiO_2 samples revealed that phase composition was mainly dependent on the calcination temperature, changing from amorphous TiO_2 to crystalline anatase and rutile by increasing the temperature. On the other hand, the XRD of TiO_2/HPW samples calcined at temperatures above 600 °C showed crystalline peaks associated to formation of WO_3 and $WO_{2.92}$ crystalline domains. The N_2 adsorption-desorption isotherm and pore size distribution of TiO_2/HPW samples detected the existence of mesoporous characteristic with very narrow bimodal pores in the mesoporous region.

The structural heterogeneity of samples was analyzed by means of pore size distribution functions, while the variation in fractal dimension were determined from the nitrogen adsorption isotherms, using the modified Frenkel-Halsey-Hill method. The results demonstrate that the approach is capable of characterizing complex textures such as those present in the TiO_2 and TiO_2/HPW photocatalysts. Besides, the effect of calcinations condition on photocatalytic properties of the samples was also investigated. The highest efficiency with respect to methyl orange photodecomposition was observed for TiO_2/HPW photocatalysts calcined at 700 °C.

1. Introduction

Titanium dioxide or titanium oxide based materials have shown great potential as powerful photocatalysts for various significant reactions due to their chemical stability, nontoxicity and high reactivity [1–4]. Nanocrystalline TiO_2 performance in the photodecomposition of organic pollutants in water solution is dependent on factors such as: surface area, porosity, crystalline structure and band gap [5]. Low surface area and fast recombination of photoinduced electrons and holes are the main effects that can lead to a low photocatalytic activity [6,7]. In reverse, an increase of the surface area and better separation of electrons and holes can improve the photocatalytical activity of TiO_2.

The structural, morphological and photocatalytic properties of TiO_2 nanocrystals are strongly dependent of the synthesis process [8–12]. Sol-gel processing has become one of the most successful techniques for preparing powders or gels of TiO_2 with photocatalytic properties [13,14]. Nevertheless, TiO_2 materials obtained by sol-gel processing are either amorphous or not well crystallized and consequently, they must undergo a suitable treatment to obtain active photocatalysts.

An enhancement of crystallinity can be obtained by thermal treatment but the temperature must be carefully selected. Low calcination temperatures result in incomplete crystallization, while high calcination temperatures cause undesirable phase transformations. By increasing the calcination temperature, poorly crystalline TiO_2 nanoparticles prepared at low temperature progressively crystallizes to photocatalytically active anatase TiO_2 phase, while further increase of calcination temperature irreversibly transforms anatase into scarcely active rutile TiO_2 phase [15,16]. Therefore, a key goal is to prepare anatase nanoparticles with high surface area, uniform particle size, pore structure, and high anatase-to-rutile transformation temperature [17].

It has been shown that introduction of small amount of impurities into TiO_2 induces a change in the structural, catalytic and optical properties [18]. Thus far, coupling of TiO_2 to WO_3 has been widely studied in order to improve the photocatalytic performances of TiO_2. The performance of TiO_2-WO_3 coupled materials (either powders or thin films) mainly depends on the porosity of obtained structure, i.e. specific surface area of the material [19–22]. In this respect, the variety

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of fractal dimensions of a xerogel material can provide valuable information about the irregularity of the surface or roughness of porous structure. Fractal dimension (D_S) parameter is used to quantitatively assess fractal geometry, and it represents a measure of the irregularities on the surface of a solid. For an irregular surface the fractal dimension acquires values between two and three, where the lower limit corresponds to a perfectly smooth surface, while the upper limit corresponds to a totally irregular or rough surface [23]. One of the simplest relationships used to determine D_S of a solid, based on the adsorption data, was proposed by Avnir and Jaroniec from the Frenkel-Halsey-Hill equation and by means of the extension of Dubinin-Raduskevich's isotherm [24–26]. Among the methods described in the literature, those based on fractal analysis have proved themselves excellent for the investigation of either naturally occurring or synthesized complex textures [27–29].

The main goal of this study was to compare the structural and textural properties of nanocrystalline TiO_2 and TiO_2 modified with tungstophosphoric acid which are obtained by combining sol-gel and hydrothermal methods. We also investigated the influence of calcination temperature on textural properties, phase transformation and photodecomposition of methyl orange (MO) in order to gain deeper insight into the roughness of pore structure using of the theory of fractals. We applied modified Frenkel-Halsey-Hill method to determine the surface fractal dimension of prepared samples which is directly related to their photocatalytic performance.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (Sigma Aldrich) and tungstophosphoric acid (Sigma Aldrich) were used for synthesis of pure TiO_2 and TiO_2/HPW powders in this study. Methyl orange (azo dye) was used as a model compound for photocatalytic tests. All chemicals were of analytical grade and were used without further purification.

2.2. Catalyst preparation

Amorphous TiO_2 and TiO_2/HPW powders were prepared by a sol gel method. Titanium isopropoxide was used as the precursor of titanium dioxide, hydrochloride acid as the catalyst and isopropyl alcohol as the solvent. For the synthesis of both types of samples, titanium isopropoxide (5.6 ml) was slowly dissolved in isopropyl alcohol (30 ml). After that, an appropriate amount of $H_3PW_{12}O_{40}$ (20%) was dissolved in water and then added into solution drop by drop. The resulting mixture was heated to 45 °C until homogeneous hydrogel was formed. This hydrogel was subsequently heated to 200 °C at a heating rate of 2 °C/min and after that washed with hot water three times. The wet gel was calcined at 500, 600, 700 and 800 °C for 3 h, which resulted in the formation of TiO_2 and TiO_2/HPW nanocrystalline photocatalysts. According to calcination conditions synthesized samples were labeled as: T_{500}, T_{600}, T_{700}, T_{800} for TiO_2 and T/HPW_{500}, T/HPW_{600}, T/HPW_{700} and T/HPW_{800} for TiO_2/HPW photocatalysts.

2.3. Characterization techniques

The phase structure of the obtained catalysts was analyzed by X-ray diffraction method (XRD), using a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, with Ni-filtered CuK_α radiation (40 kV, 30 mA, λ=1.54178 Å). Diffraction data were acquired over the scattering angle 2θ from 10° to 80° with a step of 0.020° and an acquisition rate of 2°/min. The diffractogram were used to identify the crystalline phase and evaluate the crystallite size by the Scherrer equation [30].

UV–Vis diffuse reflectance spectra (DRS) of catalysts were recorded using UV–vis spectrophotometer (Specord M40 Carl Zeiss). Photoluminescence (PL) spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer at room temperature, with a 450 W xenon lamp as the excitation light source. The obtained spectra were corrected for the spectral response of the measuring system and spectral distribution of the Xe lamp.

N_2 adsorption-desorption isotherms of TiO_2 and TiO_2/HPW samples were measured with an automatic adsorption apparatus (Sorptomatic 1990 Thermo Finnigan) at 77 K. All samples were degassed under vacuum at 120 °C for 12 h before the measurement. The total pore volume (V_{tot}) was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.98. Micropore volumes (V_{mic}) were determined according to the theory of micropore volume filling process and the logarithmic form of Dubinin-Radushkevich equation [31]. The specific surface areas (S_{BET}) were calculated by fitting the adsorption data to Brunauer–Emmett–Teller (BET) equation in the linear range relative to p/p_O (0.05–0.35) [32]. The pore size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method using the N_2 desorption isotherms [33].

The surface fractal dimension of catalysts is calculated using Frenkel-Halsey-Hill (FHH) model [34]. The method is based on the analysis of multilayer adsorption on the fractal surface of the material. Theoretical analysis leads to the expression:

$$\ln\left(\frac{V}{V_m}\right) = C + A\ln\left[\ln\left(\frac{P_0}{P}\right)\right] \quad (1)$$

where, V is the volume of adsorbed gas at equilibrium pressure P, V_m is the volume of gas in a monolayer, and P_o is the saturation pressure of the gas. The constant C is a pre-exponential factor, and A is a power law exponent dependent on surface fractal dimension, D_S, and the mechanism of adsorption.

Therefore, on the plot of ln(V) vs. ln(ln P_O/P)), the slope of the linear segments should be equal to A, and the fractal dimension, D_S, depends on the values of A. In the case of the capillary condensation regime, the fractal dimension equation is given by the following equation:

$$A = D_S - 3 \quad (2)$$

The photocatalytic activity of the pure TiO_2 and TiO_2/HPW samples calcined at various temperatures was analyzed by photocatalytic decomposition of methyl orange as a model compound. The reaction was carried out in an open cylindrical thermostated Pyrex cell of 6.8 cm in diameter, corresponding to surface area accessible to light of 36.3 cm^2. A 100 ml of 8 mg/L aqueous solution of methyl orange was placed in a cell containing 100 mg of either TiO_2 or TiO_2/HPW samples and suspensions were irradiated for different intervals of time. Irradiation of the solutions was performed under lamp that simulates solar radiation (Solimed BH Quarzlampen), with a power consumption of 300 W, housed 25 cm above the top surface of the solution. Illumination intensity on the top of the photocatalytic reactor was 850lx. Prior to illumination, the suspensions were magnetically stirred in the dark for 30 min to achieve adsorption–desorption equilibrium. The suspensions aliquots of 2 ml were taken in five minute intervals, filtered through a 0.20 μm syringe membrane filter into standard quartz cuvettes with optical path of 1 cm and the concentration of the MO was monitored by measuring the absorbance of the samples using a UV–vis spectrometer (Thermo Electron Nicolet Evolution 500).

The photodegradation reaction kinetics of MO can be described by a Langmuir - Hirshelwood (LH) model according to the report [20]. The apparent rate constant has been chosen as the basic kinetic parameter for the TiO_2 and TiO_2/HPW samples since it enables determination of photocatalytic activity independent on the previous adsorption period in the dark and the concentration of solute remaining in the solution. The degradation of MO under simulated solar light performed in the photodegradation experiment followed the first-order kinetics expressed as: