Synthesis and characterization of mesoporous titania modified with tungstophosphoric acid

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Introduction

Since the photocatalytic degradation of pollutants was introduced, the preparation of photocatalysts with high catalytic performance has attracted much attention. Among several photocatalysts, TiO_2 (in anatasa phase) has been the most widely used because it is easily available, inexpensive, non-toxic, and shows relative high chemical stability. The photocatalytic activity of titania is influenced by the crystal structure, crystalinity, surface area, band gap, porosity and surface hydroxyl group density [1,2]. However, the shortcomings of conventional powder catalysts include low efficiency of light use, difficulty of stirring during reaction and separation after reaction [3]. Hole-electron recombination and low surface area are considered among the most important disadvantages of TiO_2 that result in low photocatalytic activity in practical applications.

Therefore the photo catalytic activity of TiO_2 based catalysts can be improved by separation of the electrons and holes and the increase of the surface area. It is known that doping with suitable metal ions allows extending the light absorption of large band-gap semiconductors to the visible region [4]. Heteropolyoxometalates have been used to modify TiO_2 in order to reduce the charge recombination. They have been added to TiO_2 suspensions [5], incorporated into TiO_2 colloids [6] or anchored to TiO_2 by chemical interactions [7]. In addition, the incorporation of POMs into titania matrix can improve the densities of catalysts and makes it easy to separate them from heterogeneous reaction systems for recycling.

Titania with large surface area was reported to be suitable to obtain high catalytic performance and can be synthesized using urea as low cost template via sol-gel reactions [8].

We present here the preparation and characterization mesoporous titania modified with tunstophosphoric acid (TPA) obtained using urea as low cost pore forming agent, via HCl catalyzed sol-gel reactions.

Materials and Methods

Titaniumisopropoxide (Aldrich, 26.7 g) was mixed with absolute ethanol (Merck, 186.6 g) and stirred for 10 min to obtain a homogeneous solution under N_2 at room temperature, then 0.33 cm^3 of 0.28 M HCl aqueous solution was dropped slowly into the above mixture to catalyze the sol-gel reaction for 1 h. After that, 120 g of urea-alcohol-water (1:5:1 weight ratio) solution was added into the hydrolyzed solution under vigorous stirring to act as template together with ethanol solution of $H_3PW_{12}O_{40}.23H_2O$ (Fluka p.a.). The amount of TPA solution was fixed in order to obtain a TPA concentration of 0, 10, 20 and 30 % by weight in the final material (TiTPA00, TiTPA10, TiTPA20, and TiTPA30, respectively) The gel was kept in a beaker at room temperature till dryness. The solid was grounded into powder and extracted by distilled water for three periods of 24 h, in a system with continuous stirring to remove urea. Finally, the solid was thermally treated at 100, 200, 300, 400, and 500 °C during 2 h. The samples were characterized by BET, FT-IR, XRD, DRS, and TGA-DSC.

Results and Discussion

All the samples are mesoporous with an average pore diameter (D_p) greater than 3.1 nm. The specific surface area (S_{BET}) decreases and the mean pore radius slightly increases when increasing the amount of TPA (Table 1). S_{BET} also decreases when increasing the calcination temperature. The drop of S_{BET} is lower for the samples with higher amount of TPA.

XRD patterns of all the samples, only exhibit the characteristic peaks of anatasa phase at 2θ = 25.3º (101), 37.9º (004), 47.8º (200) and 54.3º. The particle size (D_C) of samples treated at 100 ºC, estimated by XRD using the Scherrer equation, seems to be independent of the TPA content. The crystalinity and D_C increase when the calcination temperature is raised. However, the increment is lower for the samples with higher content of TPA.

According with FT-IR results, the Keggin structure of TPA was preserved during the synthesis and the thermal treatment.

The UV-Vis-DRS spectra of the samples, display an absortion threshold onset that continuously shifts to the visible region with the increment of both TPA content and temperature. The band gap energy (E_g) of TiTPA00 (estimated from UV-Vis-DRS spectra) is similar to that reported for anatasa. E_g decreases as result of the introduction of TPA into the TiO_2 matriz, but remains practically constant with the raise of calcination temperature.

Table 1. Physico-chemical properties of TiO_2TPA samples treated at 100 ºC

Sample	S_{BET} (m^2/g)	D_P (nm)	D_C (nm)	E_g (eV)
TiTPA00	372	3.1	-	3.20
TiTPA10	296	3.4	5.4	3.05
TiTPA20	276	3.6	5.7	3.02
TiTPA30	212	3.9	5.2	2.99

Significance

The results presented in this work showed the influence of the amount of TPA and the calcinations temperature on textural and physicochemical properties of TiO_2 synthesized using urea as template.

According with the results presented in this work, the materials obtained by modification of mesoporous titania with TPA present suitable textural and physicochemical properties to be used as catalysts in the photo degradation of pollutants.

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