Effects of the modification with tungstosilicic acid on the physicochemical properties of mesoporous titania

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Introduction

TiO_2 (titania) is considered as one of the most appropriate semiconductor materials to be employed as a photocatalyst, due to its high activity in the photodegradation of organic compounds, its low cost, low toxicity, and chemical stability [1-2]. The photocatalytic activity of titania is influenced by the crystalline structure, the specific surface area, the porosity, the particle size and the size distribution, the *band gap* (E_g), and the surface density of hydroxyl groups, among other factors [3]. The low specific surface area and the fast recombination of electrons and holes are considered as being mainly responsible for the low photocatalytic efficiency displayed by TiO_2 in practical applications.

Titania with large surface area was reported to be suitable to obtain high catalytic performance and can be synthesized using urea as a low cost template via sol-gel reactions [4].

The photocatalytic activity of TiO_2 based catalysts can be improved by the 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 [5]. Tungstophosphoric acid, a heteropolyacid (HPA) with Keggin structure, has been used to modify TiO_2 in order to reduce the charge recombination. It has been incorporated into TiO_2 colloids [6] or introduced into titania matrix [7]. In addition, the incorporation of HPA into titania matrix can improve the density of the catalysts and make easier their separation from heterogeneous reaction systems for re-use.

Going on with our previous work, as the addition of tungstosilicic acid (TSA) to titania was scarcely studied, we present here the preparation and characterization of TSA-modified mesoporous titania obtained using urea as low cost template, via HCl catalyzed sol-gel reaction

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 solution (1:5:1 weight ratio) was added into the hydrolyzed solution under vigorous stirring to act as template together with ethanol solution of $H_4SiW_{12}O_{40}.23H_2O$ (Fluka p.a.). The TSA amount was fixed in order to obtain a TSA concentration of 0, 10, 20 and 30 % by weight in the final material (named TiTSA00, TiTSA10, TiTSA20, and TiTSA30, respectively). The gel was kept in a beaker at room temperature till dryness. The solid was ground into powder, and extracted by distilled water for three periods of 24 h to remove urea, in a system with continuous stirring. Finally, the solid was thermally treated between 100 and 600 °C during 2 h. The samples were characterized by BET, FT-IR, XRD, DRS, and TGA-DSC.

Results and Discussion

Mesoporous solids were obtained, with an average pore diameter (Dp) higher than 3.0 nm. The specific surface area (S_{BET}) decreased and the mean pore radius slightly increased when increasing the TSA content (Table 1). S_{BET} also decreased when increasing the calcination temperature. The drop of S_{BET} is lower for the samples with higher TSA amount.

The XRD patterns of all the samples only exhibited the characteristic peaks of anatase 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 TSA content. The crystallinity and D_C increased when the calcination temperature is raised. However, the increment was lower for the samples with higher TSA content.

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

The UV-visible DRS spectra of the samples displayed an absorption threshold onset that continuously shifts to the visible region with the increment of both TSA content and temperature. The band gap energy (E_g) of TiTSA00 (estimated from UV-Visible DRS spectra) was similar to that reported for anatase. E_g decreased as a result of the introduction of TSA into the TiO_2 matrix, and also with the raise of the calcination temperature.

Table 1. Physicochemical properties of TiO_2TSA samples treated at 100 ºC

Sample	S_{BET} (m^2/g)	D_P (nm)	D_C (nm)	E_g (eV)
TiTSA00	372	3.1	-	3.20
TiTSA10	296	3.4	5.5	3.00
TiTSA20	276	3.6	5.5	2.98
TiTSA30	212	3.9	5.6	2.96

Significance

The results presented in this work show the influence of the TSA amount and the calcination temperature on the textural and physicochemical properties of TiO_2 synthesized using a low cost pore forming agent. According to these results, the preparation method used, that is a direct modification with TSA of the mesoporous titania, obtained using urea as template, leads to materials with suitable properties to be used as catalysts in the photo degradation of pollutants, such as a lower Eg and a relatively high surface area.

References

1. Sakulkhaemaruethai, S., Pavasupree, S., Suzuki, Y., and Yoshikawa, S., *Mater. Lett*. 59, 2965 (2005).
2. Kyoko, K.B., Kazuhiro, S., Hitoshi, K., Kiyomi, O., and Hironori, A. *Appl. Catal. A: General* 165, 394 (1997).
3. Li, Y., Li, X., Li, J., and Yin, J., *Catal. Commun*. 6, 650 (2005).
4. Pizzio, L.R. *Mater. Lett.* 59, 994 (2005).
5. Anpo, M., *Catal. Surv. Jpn*. 1, 169 (1997).
6. Yoon, M., Chang, J.A., Kim, Y., Choi, J.R., Kim, K., and Lee, S.J., *J. Phys. Chem. B:* 105, 2539 (2001).
7. Fuchs, V. M., Soto,E. L., Blanco, M. N., Pizzio, L. R., *J. Colloid Interface Sci*. 327(2) (2008) 411.