Synthesis of TiO_2 and Ag/TiO_2 catalysts by solvothermal and photo-deposition method for hydrogen production from ethanol

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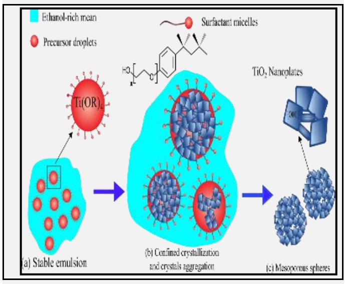

In this work, the solids were synthesized under solvothermic conditions and then via photo-deposition with 0.5 wt.% Ag/TiO_2. The as-prepared powders were characterized by UV–visible diffuse reflectance spectroscopy (DRS-UV–vis), BET area, X-ray diffraction (XRD) and Scanning electron microscopy (SEM). The photocatalytic tests showed that the sample prepared with 0.5 wt.% Ag/TiO_2 presented higher hydrogen activity (24.68 µmol H_2) compared to the other photo-catalysts synthesized via solvothermal. Thus, it indicates a greater fraction of photons in the UV region and visible with the addition of Ag in the catalyst composition. The results demonstrate that the proposed method synthesizes pure and crystalline anatase TiO_2 square nanoplates that form nanostructured spheres with well controlled size, structure, and morphology.

Introduction

The use of the solvothermal method has been reported as a strategy to obtain structurally ordered chipboard in the form of spheres or nanotubes for example [(1,2)]. Developments of such oriented structures contribute to the modification of physical properties, such as surface area and porosity of the powders, thus affecting the flow of reagents and gaseous products onto the surfaces of the particles during catalytic applications [(2,3,4)].

Studies have reported that nanostructured TiO_2 particles of different morphologies have played an important role in photoelectricity and photocatalysis. TiO_2 particles with well-defined morphologies were synthesized by solvothermic route with effective control of the alcoholysis rate [(5,6)].

The rapid recombination of photogenerated electron/hole (e^-/h^+) pairs and poor activation by visible light due to their relatively high band gap (3.2 eV) of TiO_2 limits the use of solar energy for H_2 production [7,8]. Therefore, alternatives have been studied to improve the response to visible light and inhibit the recombination of electron/hole pairs, such as the use of co-catalysts (Pt, Ag, Pd, Rh) in the form of nanoparticles to improve the response to visible light and inhibit charge recombination [7,9,10]. Finally, the performance of the Ag-TiO_2 nanoplates was compared with TiO_2 nanoplates synthesized with non-ionic surfactant Triton® X-100.

In this work, we studied the influence of the physical and chemical variables on the solvothermic synthesis in the genesis of the crystalline nanostructures of the new photocatalysts, to understand and improve the growth of TiO_2 photocatalysts. The physical parameters were evaluated, with the final objective of preparing anisotropic structures of high crystallinity.

Material and Methods

The TiO_2, Ag/TiO_2 with and without Triton® -X were prepared by the solvothermal and photo-deposition method. 3.0 mL of $Ti(OC_4H_9)_4$, 97.0%, Sigma Aldrich, 0.5 mL of H_2SO_4, 98.06%, Dinâmica, 18.0 mL of CH_3COOH, 99.7%, VETEC were mixed with 30.0 mL of C_2H_5OH, 98.4%, Neon. Then, the solution was transferred into a 125 mL autoclave and kept at 170/180 ºC for 24 hours. The precipitated were centrifuged, washed with distilled water, and dried at 70 ºC 12 hours.

The photo-deposition method of Ag-decorated TiO_2 nanoplates (Ag-TiO_2) was prepared with 0.052 g $AgNO_3 \cdot 6H_2O$, which was dissolved in 60.0 mL of C_2H_5OH, and 0.050 g of TiO_2. The solution was transferred to closed glass ampoule at room temperature. Inertization was carried out for 20 min and after the suspension was stirred at 4000 rpm and irradiated with a LED UV-visible 28 W lamp (LED Grow full spectrum, λ = 380 to 780 nm) for 3 hours. The solution was filtered, washed and dried at 80 °C for 24 hours The samples were prepared to obtain a 0.5% Ag/TiO_2 170/180. In order to explore the effect of a non-ionic surfactant, it was added 0.5 mL of the (t-Oct-C_6H_4-$(OCH_2CH_2)_xOH$, x = 9-10, Triton® X-100, Aldrich) previously dissolved in C_2H_5OH, and the resulting solid product was denoted as TiO_2 with surfactant.

Catalyst characterization.

The optical properties were determined by Diffuse reflectance spectroscopy in the UV-visible region of 190 to 900 nm using a Labsphere diffuse reflectance accessory. The powder phase composition was identified by XRD using a diffractometer Bruker D8 Advance X-ray, CuKα radiation (λ= 0.1538 nm). The angle of diffraction was varied from 4° to 90° using a step size of 0.04°. SEM was used to study the morphology, particle-size, crystal structure and composition. The examination was performed using a Hitachi microscope (TM-1000 Tabletop Microscope 1000).

Photocatalytic activity was evaluated in a Pyrex glass reactor (247 mL) working at room temperature. The photocatalyst (15 mg) was transferred to the reactor and dispersed in an aqueous solution (150 mL) and 0.15 mol L^{-1} C_2H_5OH. The photocatalyst was irradiated with a Xe arc lamp (150 W, ozone free, LOT Oriel GmbH & CO KG). Samples of the evolved gases were analyzed by GC with TCD (Varian chromatograph Model Star 3400 CX) equipped with a 5A molecular sieve using Ar as the carrier gas.

Results and Discussion

UV-Vis Diffuse Reflectance Spectroscopy. The analysis showed that the Ag-TiO_2 with surfactant provided a decrease in the band gap to 3.26 eV compared to the other: Ag-TiO_2 without surfactant of 3.28 eV; TiO_2 3.43 eV; and TiO_2* 3.49 eV [5].

Powder X-ray Diffraction (XRD) Analysis. It was observed the diffraction angles of 25.40°; 38.05°; 48.06°; 54.12°; 55.06°; 62.79°; 69.05°; 70.23° and ~~e~~ 75.28° with diffractions of crystallographic planes (101), (004), (200), (105), (211), (204), (116), (220) and ~~e~~ (215), characteristic of the anatase TiO_2 structure (JCPDS 01-071-1166). The TiO_2 (1 0 1) particle size registered was TiO_2 (10.8 nm), TiO_2 170 (13.7 nm) and TiO_2 185 (17.0 nm). The broadening of the diffraction peak of the (004) plane indicates a reduction in the size of the crystallites along the c axis, perpendicular to the {001} faces, suggesting the formation of anatase TiO_2 nanoparticles with exposed {001} faces [(11)]. The photo deposition of Ag did not cause any difference in relation to the XRD of pure TiO_2, the mass of Ag (5 wt.%) deposited was below the minimum detection level [30], but the presence of Ag was confirmed by energy dispersive EDS spectroscopy.

The morphology of the catalysts was investigated by SEM, Figure 1. The images reveal that the spherical-shaped particles indicate that the Ag-TiO_2 without surfactant forms irregular agglomerates. While, for Ag-TiO_2 synthesized with surfactant, the particles were homogeneously distributed over the sample support.

Photocatalytic activity evaluation. Figure 2 shows photocatalytic activity, The Ag photo deposition has a significant influence on H_2 production. The Ag-TiO_2 catalysts with/without Triton®-X showed greater activity. This can be explained considering that the Fermi level of Ag is lower than that of TiO_2. The photoelectrons generated in Ag can be easily transferred to TiO_2. This can inhibit the recombination of electron/hole pairs (e-/h+) on the TiO_2 surface [12]. In general, photocatalysts synthesized with surfactant showed better activity compared to those synthesized without surfactant. This may be associated with an increase in surface area and an increase in exposed {001} faces in relation to {101} faces. In general, all TiO_2 presents activity of H_2 production < 1 µmol/g cat?

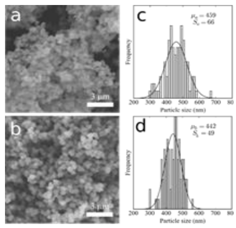

Figure 1 - SEM image and particle size distribution

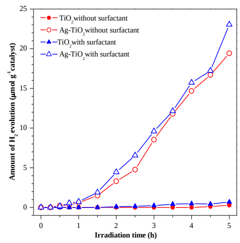

Figure 2 - Hydrogen production on anatase TiO_2 nanoplates.

Conclusions

Nanostructured spherical-like anatase Ag-TiO_2 particles formed by nanoplates with exposed {001} facets were successfully produced under solvothermal conditions with well-controlled morphology and particle sizes followed by the photo deposition of Ag nanoparticles for the formation of Ag-TiO_2. Our study represents an essential step for future research on the fluoride-free synthesis of nanostructured TiO_2 particles with exposed {001} facets.

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