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Nanostructured hybrid TiO_2-C for the photocatalytic conversion of phenol

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ABSTRACT

The photocatalytic activity of hybrid TiO_2-C materials prepared by solvothermal synthesis was studied using phenol as test molecule. The influence of furfural, chitosan and saccharose as carbon precursors was verified. Characterization was performed by N_2 adsorption isotherms, XRD, DR/UV–vis and SEM. The carbon precursor affects the surface area and the XRD patterns of TiO_2-C. First and second order reaction rates approaches were used to estimate the photocatalytic activity. TiO_2-C materials showed an increase up to 4.4 higher photoactivity than commercial TiO_2. The present results suggest that hybrid TiO_2-C nanostructured materials can be potentially used as eco-friendly and low-cost heterogeneous photocatalysts under UV–vis irradiation.

1. Introduction

An important share of the pharmaceutical industry use phenol derivatives in some way during the reaction-steps. Unfortunately, the associated wastewaters of these processes became an outstanding environmental issue. In this sense, one relevant challenge for science concerns to the study and the development of novel advanced oxidation processes (AOP's) for the remediation of polluted waters (Andreozzi et al., 1999; Giménez et al., 2016). There are different technologies for the removal of pollutants, like adsorption, bio- and chemical degradation, being heterogeneous photocatalysis one of the AOP's.

TiO_2 has been widely reported as the best photocatalyst for purifying water and air (Herrmann et al., 1993; Legrini et al., 1993). However, TiO_2 has important scale-up limitations such as the low photons absorption (ca. 6%) of solar spectra and its synthesis methods are commonly expensive and not eco-friendly. In addition, the surface area of commercial TiO_2 is commonly low, and therefore it is limited for the treatment of low volume and low concentration of pollutant to be efficiently use as photocatalysts for the treatment of wastewaters.

Many enforces have been performed for the enhancement of TiO_2 photoactivity such as doping with noble metals (He et al., 2002), with p-block elements (Dozzi and Selli, 2013), with nonmetals (Foo et al., 2013), and the use of inorganic co-supports (Anderson and Bard, 1995). Activated carbon (AC) has received an increasing attention in the photocatalytic conversion of organic aromatic molecules such as phenol (Andrade et al., 2014; Velasco et al., 2014a) and 4-chlorophenol (Cordero et al., 2007a; Matos et al., 2009) among others because it is able to solve most of the scale-up limitations of TiO_2.

Previous works have shown that heteroatoms in the surface of AC play an important role upon the photoactivity of TiO_2-C binary materials. The influence of heteroatoms such as oxygen (Matos et al., 2010a, 2015a; Velasco et al., 2014a), sulfur (Bandosz et al., 2012) and nitrogen (Matos et al., 2013a; Bandosz et al., 2016) have been reported. It has been also recently reported that the presence of these heteroatoms in the pore framework of AC are responsible of its intrinsically photochemical reactivity (Bandosz et al., 2012; Velasco et al., 2014b; Gomis-Berenguer et al., 2016).

In addition to conventional activated carbons, an increasing attention in the photocatalytic activity of hybrid TiO_2-C nanostructured materials prepared by solvothermal synthesis has been reported (Matos et al., 2010b; Shen, 2015; Shet and Vidya, 2016). The solvothermal synthesis overcomes the problems in the conventional synthetic methods for the production of TiO_2 such as chemical vapor deposition which is very expensive and classic sol–gel (Jung, 2008) which does not permit the control of crystalline phase nor lead to high surface areas. The solvothermal

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technique was introduced to synthesize some ceramic oxides including nanocrystal TiO_2 powders (Kominami et al., 1996, 1999; Wang et al., 2001; Kang, 2003; Zhang et al., 2003; Wahi et al., 2006; Yang et al., 2009; Hung and Hoaz, 2012; Shen, 2015; Shet and Vidya, 2016). These studies showed that solvothermal synthesis not only have the advantages of low cost hydrothermal synthesis (Hung and Hoaz, 2012), but also avoided contaminations from ion species dissolved in water, which improved the surface area (Wahi et al., 2006) and quality of reactive facets (Yang et al., 2009) of TiO_2 nanocrystals with remarkable photo-efficiency in energy production and environmental remediation. Having in mind the advantages of the solvothermal synthesis, in the present work, three different C-doped TiO_2 hybrid materials were prepared by this methodology and the photocatalytic activity was tested by following the kinetics of phenol conversion under UV–vis irradiation. Furfural, chitosan and saccharose were used as carbon precursors and the photoactivity of TiO_2-C materials were compared against that on a commercial TiO_2.

2. Experimental procedure

2.1. Materials and synthesis of Hybrid TiO_2-C photocatalysts

Furfural, chitosan, saccharose, titanium (IV) isopropoxide and phenol were analytical grade and purchased from Sigma–Aldrich. Absolute ethanol was purchased from VWR. TiO_2-P25 (Evonik, ex-Degussa) was employed as standard photocatalyst for comparative reasons. It consist of mainly Anatase phase (ca. 70%), non-porous polyhedral particles of ca. 30 nm mean size and BET surface area 45 $m^2\,g^{-1}$.

In earlier works, our group have reported the catalytic and photocatalytic activity of hybrid TiO_2-C nanostructured materials (Matos et al., 2010b) prepared by solvothermal synthesis (Titirici et al., 2007). In summary, in a typical solvothermal synthesis, 1 g of furfural (Fu) and 1 g of titanium (IV) isopropoxide were dissolved in 18 mL of ethanol. The resulting solution was sealed into a glass vial inside a Teflon-lined autoclave, followed by solvothermal treatment at 180 °C overnight. The resulting brown solid was separated from the solution by filtration following washing several times with absolute ethanol. The material was dried under static air at 100 °C by 2 h. Similar samples were prepared by using chitosan (Ch) or saccharose (Sac) as carbon source. Samples were denoted Fu-C-TiO_2, Ch-C-TiO_2, Sac-C-TiO_2, respectively, for each carbon precursor.

2.2. Characterization

Textural characterization was performed by N_2 adsorption–desorption isotherms at 77 K. The full isotherms in the range of 4×10^{-3} kPa to 84 kPa were measured in a Micromeritics ASAP-2020. Surface area, micropore area and volume, and pore diameters were obtained by Brunauer–Emmet–Teller (BET) (Brunauer et al., 1938), Harkins–Jura (HJ) (Harkins and Jura, 1944) and Horvath–Kawazoe (HK) (Horvath and Kawazoe, 1983). HJ and HK methods were employed because hybrid TiO_2-C materials would contain simultaneously slits and spherical pores. Diffuse reflectance ultraviolet/visible spectra (DR/UV–vis) of samples were recorded at 300 K in the wavelength range 200–800 nm using a UV–Vis–NIR spectrophotometer (Cary 5000, Varian). Powder X-ray diffraction (XRD) patterns were recorded in the range of $2\theta = 2–90°$ with a Cubix-PRO diffractometer from PANalytical with CuKα (1.54056) radiation and processed with the PW1877 program (Philips). Scanning electron microscopy (SEM) micrographs were collected in a JEOL 6300 microscope operating at 20 kV, 2×10^{-9} Å beam current and15 mm as working distance.

2.3. Phenol adsorption in the dark and photocatalytic test

The experimental set-up is shown in Fig. 1 (Miranda et al., 2013). In summary, phenol conversion reactions were performed using an open-to-air batch reactor (250 mL) made of Pyrex using a 300 W UV–vis arc lamp (Ultravitalux Osram). The intensity of the incident UVA and visible light on the solution was measured with an HD2302 photometer (Delta OHM) using LP 471 UVA and LP 471 RAD sensors (spectral responses 315–400 nm and 400–1050 nm respectively). In the oxidation tests, an air flow was employed what produces a homogenous suspension of the catalyst in the solution. The photocatalytic tests were performed at 25 °C under stirring of 0.1 g photocatalysts in 200 mL phenol, with 5 ppm initial concentration (ca. 53.2 μmol L^{-1}, ca. 10.64 μmol). Samples were maintained in the dark for 15 min to complete adsorption at equilibrium prior the irradiation. After filtration, phenol aliquots were analyzed following the characteristic 270 nm band of phenol using a Spectrophotometer UV–vis Shimadzu UV-1800, and the phenol concentrations were estimated using a standard calibration curve. Two different kinetic approaches were verified and the first-order apparent rate-constant (k_{app}) and the second-order reaction-rate (k_2) were estimated as the best kinetic parameters (Turchi and Ollis, 1990; Herrmann et al., 1993) to compare the photocatalytic activity against that on commercial TiO_2-P25. The experiments were performed by duplicate and the reproducibility of results was better than 95%.

3. Results and discussion

3.1. Characterization of photocatalysts

3.1.1. Morphology of TiO_2-C materials

Fig. 2 shows the SEM images of the TiO_2-C samples. It can be seen spherical particles with several sizes, indicating nanoparticle coalescence and the development of an aggregate structure. This is in agreement with the coalescence mechanism induced by void growth in porous solids (Koplik and Needleman, 1988). Fig. 2A and C showed that samples prepared from furfural and saccharose, respectively, are composed by aggregated particles assembled into spheres with a mean particle size of about 1.8 μm and 2.6 μm for Fu-TiO_2-C and Sac-TiO_2-C. By contrast, Fig. 2B does not shows a preference of particle growth by coalescence suggesting a non-stable structure for this sample. Spheres are hardly observed in Fig. 2B. So, the morphology in the Ch-TiO_2-C sample was clearly different to the other samples and this can be explained

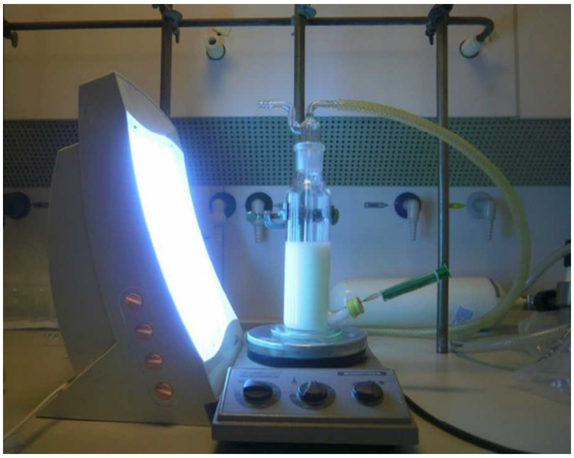

Fig. 1. Experimental set-up for the phenol photoconversion.