



# Influence of the thermal treatment on the physicochemical properties and photocatalytic degradation of 4-chlorophenol in aqueous solutions with tungstophosphoric acid-modified mesoporous titania

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## ABSTRACT

Materials based on titania directly modified with tungstophosphoric acid were prepared using titanium isopropoxide as titania precursor and urea as a low-cost pore-forming agent. The obtained mesoporous solids presented an average pore diameter higher than 3.1 nm. The specific surface area decreased when the TPA amount and the calcination temperature increased. All the modified solids only showed the anatase structure of titania by X-ray diffraction, while for the unmodified sample this structure was transformed into the rutile phase from 600 °C on. The crystallite size increased with the calcination temperature, though the TPA-modified samples presented lower values when the TPA amount was increased. The <sup>31</sup>P nuclear magnetic resonance studies showed that the Keggin structure of the tungstophosphate anion was partially transformed when it was thermally treated up to 600 °C, though structure disruption took place at higher temperature. The band gap values estimated from the UV-vis-diffuse reflectance spectra did not show important variation, though they slightly decreased with the TPA content. The 4-chlorophenol degradation was studied in liquid phase, with an air flow continuously bubbled. The degradation behavior of the catalysts as a function of time depended on the TPA amount and the thermal treatment temperature, the samples containing 30% TPA calcined at 500–600 °C and 20% TPA calcined at 600 °C being more effective. The apparent reaction constant, estimated assuming a pseudo-first-order kinetics, followed the same trend. The catalysts can be reused at least three times without an important decrease in the degradation and mineralization degrees.

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## 1. Introduction

Chlorinated phenols constitute an important class of water and air contaminants due to their high toxicity to living organisms, bioaccumulation, strong odor emission and persistence in the environment. They are widely used in the industry and cause severe environmental problems, because they are carcinogens and mutagens. Among them, 4-chlorophenol (4-CP), a known toxic and nonbiodegradable organic compound, is present in the wastewater of pulp and paper, dyestuff, pharmaceutical and agrochemical industries [1].

4-CP is currently removed from the wastewater by conventional treatment methods such as chlorination, adsorption, and biological treatment. However, each method has its shortcomings. For example, chlorination treatments often generate carcinogenic by-products, the spent activated carbon employed in commercial adsorption processes needs to be safely disposed [2] and the biolog-

ical process usually requires a considerably long treatment period to reduce 4-CP to an acceptable level in the final effluent [3].

Photolytic oxidation processes using semiconductor materials have been accepted as a promising alternative to the conventional methods because most of the pollutants can be completely mineralized to CO<sub>2</sub> with suitable catalysts in the presence of UV light. Among the semiconductors employed, TiO<sub>2</sub> is considered to be a good photocatalyst due to its high capacity for degrading toxic and recalcitrant chemical species via relatively simple and low-cost procedures, nontoxicity, easy availability, and long-term stability [4–7].

The photocatalytic degradation of 4-CP has been investigated by many research groups and has become a standard reaction for evaluating various experimental parameters in photocatalysis [8].

Titania performance in the photodegradation of contaminants contained in wastes is influenced by the crystal structure, the crystallinity, the surface area, the porosity, the surface hydroxyl density, and the band gap energy [8–11], among other factors.

The low surface area and the fast recombination of the photoinduced electrons and holes are the main effects that can lead to a low photocatalytic activity. So, an increase in the surface area and

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the separation of electrons and holes can improve the photocatalytic activity of titania. Sol–gel reactions using urea as a low-cost pore-forming agent were found to be a good method to synthesize mesoporous titania with suitable properties to be used as a photocatalyst [12,13].

Transition metals or metal oxides were proved to be electron trappers, thus avoiding the recombination of the electron–hole pairs of TiO<sub>2</sub>-based catalysts [14–17] and improving the photocatalytic activity. In addition, it has been reported that the light absorption is extended to the visible region when large band gap semiconductors are doped with suitable transition metal ions [18].

The increment of the photoactivity of titania samples modified with W has been mainly explained by considering the formation of intermediate W(V) species by means of a transfer of photogenerated electrons [19,20]. This reduced W species could be oxidized to W(VI) by transferring electrons to oxygen [21].

Indeed, several transition metal ions lead to a band gap shift to the visible region when they are impregnated on large band gap semiconductors, allowing the use of light from the visible region of the spectrum.

Heteropolyoxometallates (POM) are widely used as oxidation as well as acid catalysts [22–24]. They are also employed as effective homogeneous photocatalysts in the degradation of organic pollutants in water [25–27].

POM absorb strongly in the near visible and UV region of the light spectrum ( $\lambda < 400$  nm). This absorption corresponds to the ligand-to-metal charge-transfer band and it can generate strongly oxidizing excited state POM\* (reaction (1)). They are able to carry out the oxidation of organic substrates (S) (reaction (2)) directly via charge transfer or H-atom abstraction, or indirectly through the intermediacy of solvent-derived radicals [27]. After that, the corresponding reduced POM are usually reoxidized to their original oxidation state by an electron acceptor such as dioxygen (reaction (3)).



POM have been added to TiO<sub>2</sub> suspensions [28], incorporated into TiO<sub>2</sub> colloids [29], or anchored to TiO<sub>2</sub> by chemical interactions [30] with the purpose of reducing the charge recombination in UV-illuminated TiO<sub>2</sub>. The capacity of POM as acceptors (reaction (5)) of the electrons, generated in the conduction band ( $e_{\text{cb}}^-$ ) together with holes in the valence band ( $h_{\text{vb}}^+$ ), of UV-irradiated TiO<sub>2</sub> suspensions (reaction (4)) was demonstrated by Park and Choi [31] using a photoelectrochemical method. The reduced POM react with O<sub>2</sub> to generate superoxides (reaction (3)).



Unlike these researchers, who have modified the surface of previously prepared TiO<sub>2</sub> with POMs [28–31], we studied the incorporation of tungstosilicic and tungstophosphoric acid into the titania matrix during the TiO<sub>2</sub> gel synthesis, in a similar way to Li et al. [32], but using urea as low-cost template with the purpose of obtaining mesoporous materials [33,34]. We also studied the catalytic activity in the methyl orange photodegradation of the solids annealed in the temperature range 100–600 °C and correlated it with their physicochemical properties [35,36].

As a continuation of this previous work, in the present paper we have extended the temperature range of treatment in order to explore the effect on the crystal structure, textural and physicochemical properties of the tungstophosphoric acid (TPA)/mesoporous titania composites synthesized via HCl

catalyzed sol–gel reactions, where urea is used as a low-cost pore-forming agent.

The aim of our research is to correlate the catalytic activity in the 4-chlorophenol photodegradation with the structural and textural characteristics of the solids, and to discuss the effect of the preparation variables on the pollutant degradation.

## 2. Experimental

### 2.1. Synthesis of TPA-modified mesoporous titania

A titanium isopropoxide (Aldrich, 26.7 g) solution was prepared in absolute ethanol (Merck, 186.6 g) under N<sub>2</sub> atmosphere and at room temperature, continuously stirring for 10 min. Then, 0.33 cm<sup>3</sup> of a 0.28 M HCl aqueous solution was slowly added in order to catalyze the sol–gel reaction. After 3 h, 120 g of a urea–ethanol–water (1:5:1 weight ratio) solution was added, together with an ethanol solution of tungstophosphoric acid (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·23H<sub>2</sub>O, Fluka p.a.) under vigorous stirring. The amount of TPA was varied with the purpose of obtaining a TPA concentration of 0%, 10%, 20% and 30% by weight in the final solid (named TiTPA00, TiTPA10, TiTPA20, and TiTPA30, respectively). The gels were dried at room temperature, and the solids were ground into powder and extracted with distilled water for three periods of 24 h, in order to remove the urea.

Finally, the solids were thermally treated at 100, 500, 600, 700 and 800 °C for 2 h (TiTPAXX<sub>T100</sub>, TiTPAXX<sub>T500</sub>, TiTPAXX<sub>T600</sub>, TiTPAXX<sub>T700</sub>, and TiTPAXX<sub>T800</sub>, respectively, where XX is the TPA concentration).

### 2.2. Sample characterization

The specific surface area, the pore volume and the mean pore diameter of the solids were determined from the N<sub>2</sub> adsorption–desorption isotherms at the liquid-nitrogen temperature, obtained using Micromeritics ASAP 2020 equipment. The solids were previously degassed at 100 °C for 2 h.

The X-ray diffraction (XRD) patterns were recorded with Philips PW-1732 equipment with a built-in recorder, using Cu K $\alpha$  radiation, nickel filter, 20 mA and 40 kV in the high voltage source, and scanning angle between 5 and 60°2 $\theta$  at a scanning rate of 1° per minute.

The solids were studied by transmission electron microscopy (TEM) in a JEOL 100 CXII microscope, working at 100 kV and at a magnification of 80,000 $\times$ . The samples were crushed in an agate mortar, ultrasonically dispersed in isobutanol, and deposited on a carbon-coated copper grid. The particle size distribution of the samples was determined by manual image analysis of a few hundred particles.

The secondary electron micrographs of the samples were obtained by scanning electron microscopy (SEM), using Philips Model 505 equipment.

The <sup>31</sup>P magic angle spinning-nuclear magnetic resonance (<sup>31</sup>P MAS-NMR) spectra were recorded with Bruker Avance II equipment, using the CP/MAS <sup>1</sup>H–<sup>31</sup>P technique. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5  $\mu$ s pulses, a repetition time of 4 s, and working at a frequency of 121.496 MHz for <sup>31</sup>P at room temperature. The spin rate was 8 kHz and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference.

The Fourier transform infrared (FT-IR) spectra of the solids were obtained using a Bruker IFS 66 FT-IR spectrometer and pellets in KBr in the 400–4000 cm<sup>-1</sup> wavenumber range.

The diffuse reflectance spectra (DRS) of the materials were recorded using a UV-visible Lambda 35, Perkin Elmer spectrophotometer, to which a diffuse reflectance chamber Labsphere

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