



# Composite $\text{H}_3\text{PW}_{12}\text{O}_{40}$ - $\text{TiO}_2$ catalysts for toluene selective photo-oxidation

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## ABSTRACT

A series of composite systems based on titania and growing quantities of tungstophosphoric acid are prepared and characterized using infrared, nuclear resonance, UV–visible, photoluminescence, and photoelectron spectroscopies, transmission electron microscopy as well as x-ray diffraction and porosimetry techniques. These techniques showed evolution of the tungstophosphoric acid species supported into titania while this majority component of the system suffers minor changes. The activity and stability of the composite samples for gas phase toluene photo-oxidation under UV and sunlight-type irradiation conditions was measured by means of the reaction rate and the photonic efficiency parameter. The modeling of the radiation field was accomplished by numerically solving the radiative transfer equation. The photo-activity of the composite materials showed a significant selectivity towards the transformation of the hydrocarbon into a partially oxidized product, benzaldehyde. Both the activity and selectivity of the titania are significantly affected by the presence of tungstophosphoric acid species. The physico-chemical characterization was able to point out to the leading role of specific polytungstate species in driving the enhancement of the activity and selectivity of the reaction, rendering stable, highly active and selective photo-catalysis.

## 1. Introduction

Heterogeneous photocatalysis is an advanced oxidation process that uses semiconductors broadly applied in the degradation and transformation of organic pollutants [1,2], production of hydrogen using light and bio-molecules [3], conversion of  $\text{CO}_2$  into high value-added industrial chemicals and hydrocarbon fuels [4,5] as well as degradation of biological microorganisms [6].

One family of materials potentially interesting corresponds to the Polyoxometallates (POMs). POMs correspond to a wide class of functional materials consisting on nanoscale transition metal oxide clusters [7]. The most explored POMs are the heteropolyacids (HPAs); they are customarily classified starting from the unit “parent” polycations, being the Keggin ( $\text{XM}_{12}\text{O}_{40}^{n-}$ ), Dawson ( $\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$ ), Lindquist ( $\text{M}_6\text{O}_{19}^{n-}$ ), and Anderson ( $\text{XM}_6\text{O}_{24}^{n-}$ ) structures among the most utilized as functional materials in chemistry [7,8]. The Keggin anions contain a heteroatom X ( $\text{X} = \text{P}, \text{Si}$ ) as the center of a  $\text{XO}_4^{n-}$  unit and the so-called addenda atom, commonly W or Mo, constructing the external coordination shell of the unit. In particular, the heteropolyacid  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anion displays a size of ca. 1 nm and consists on a  $\text{PO}_4^{3-}$  tetrahedron surrounded by four  $\text{W}_3\text{O}_9$  groups formed by edge-sharing octahedra. Heteropolyacids with Keggin structure are strongly acidic

and present significant stability when supported on high surface area oxides [8–10].

Among Keggin heteropolyacids functional uses, homogeneous but particularly heterogeneous photocatalysis have emerged as a field of intense research. The combination with titanium oxide corresponds to the most widely analyzed photo-catalytic combination [8–13]. Apart from introducing new acidic and cationic functionalities to a titania support, the photocatalytic properties of the composite material can be improved (with respect to the titania or heteropolyacid single references) not only by a simple effect of the heteropolyacid dispersion (and thus increase of potential active sites availability to reactants) but also as a fact that the Keggin structure can behave itself as a photocatalyst upon light excitation of the so-called oxygen-to-metal charge transfer. Excited Keggin polytungstate anions correspond to strong oxidant species compared with their electronic ground state due to the higher energy of the corresponding electronic levels. In addition, excitation of this material allows a more efficient use of visible light with respect to titania alone materials [8–11]. As a result of the fitness of the above mentioned physico-chemical properties for functional use in photocatalytic processes, improved performance with respect to titania counterparts in photo-degradation of organic compounds has been frequently reported under UV and/or visible light illumination

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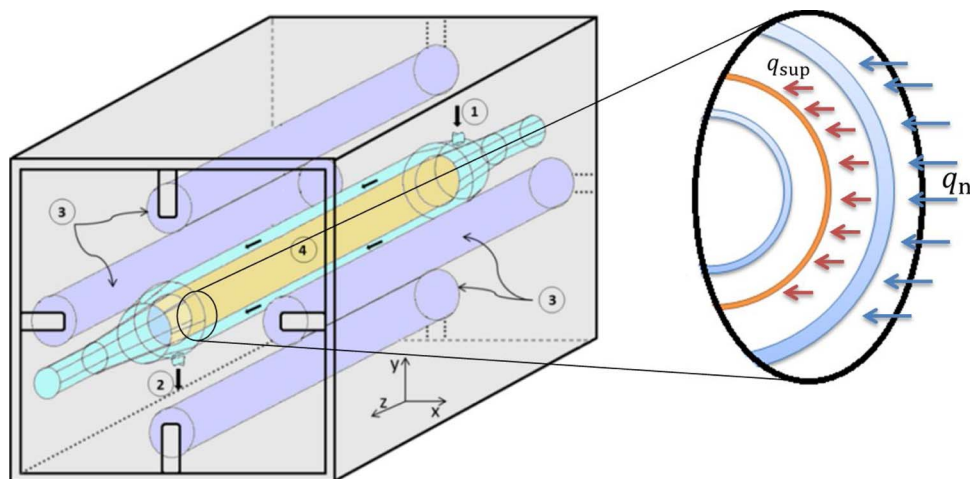


Fig. 1. Photocatalytic annular reactor. (1) gas inlet, (2) gas outlet, (3) lamps, (4) catalyst sample.

[8,11,14–19]. Less common is however the use of heteropolyacids-titania composites in selective photo-transformations. Nevertheless, as a representative example we can highlight the work of García-López et al. in 2-propanol photo-assisted (or photo-thermal) catalytic dehydration, a reaction facilitated by the acidity of the composite system [20].

Here we presented a study of the evolution of the toluene selective photo-oxidation to benzaldehyde through a series of samples having different surface concentration of the heteropolyacid as a benchmark test. Photo-catalytic production of benzaldehyde has been attempted from benzyl alcohol [21], but the achievement of such reaction starting from the corresponding hydrocarbon would be significantly more appealing from an economical point of view. As detailed in this contribution, almost complete selectivity towards to partial oxidation can be obtained using composite  $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{-TiO}_2$  composite catalysts. The complete physico-chemical characterization of the materials using X-ray diffraction, UV-visible, photoluminescence, X-ray photoelectron, infrared and nuclear magnetic spectroscopies together with microscopy would allow to rationalize the result as a function of the polytungstate species present at the titania surface, their electronic and structural effects in the support properties as well as the composite material as a whole.

## 2. Experimental

### 2.1. Preparation of the samples

A titanium isopropoxide (Aldrich, 26.7 g) solution was prepared in absolute ethanol (Merck, 186.6 g) under  $\text{N}_2$  atmosphere and at room temperature, continuously stirring for 10 min. Then, 0.33 mL 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 w/w) solution was added, to act as a mesoporous forming agent, together with an ethanol solution of tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$ , Fluka p.a.) under vigorous stirring. The amount of TPA was varied with the purpose of obtaining a TPA concentration of 10, 20 and 30% by weight in the final solid (named  $\text{TiO}_2$  for the reference and  $\text{TiO}_2$  TPA10,  $\text{TiO}_2$  TPA 20, and  $\text{TiO}_2$  TPA30, 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 500 °C for 2 h.

### 2.2. Characterization techniques

The Brunauer–Emmett–Teller (BET) surface areas and average pore volumes and sizes were measured by nitrogen physisorption (Micromeritics ASAP 2010). XRD profiles were obtained with a Seifert

D-500 diffractometer using Ni-filtered  $\text{Cu K}\alpha$  radiation with a  $0.02^\circ$  step and fitted using the Von Dreele approach to the Le Bail method [22]; particle sizes and microstrain were measured with XRD using the Williamson–Hall formalism. FT-IR spectra of the supports and catalysts were obtained in the  $400\text{--}4000\text{ cm}^{-1}$  wavenumber range using Bruker IFS 66 FT-IR spectrometer and pellets in KBr. The  $^{31}\text{P}$  MAS-NMR spectra were recorded using the CP/MAS  $1\text{H}\text{--}^{31}\text{P}$  technique with Bruker Avance II equipment. A sample holder of 4 mm diameter and 10 mm in height was employed, using 5  $\mu\text{s}$  pulses, a repetition time of 4 s and working at a frequency of 121.496 MHz for  $^{31}\text{P}$  at room temperature. The spin rate was 8 kHz and several hundred pulse responses were collected. Phosphoric acid 85% was employed as external reference. UV-vis diffuse-reflectance spectroscopy experiments were performed on a Shimadzu UV2100 apparatus using nylon as a reference. XPS data were recorded on  $4 \times 4\text{ mm}^2$  pellets, 0.5 mm thick, prepared by slightly pressing the powdered materials which were out-gassed in the prechamber of the instrument at room temperature up to a pressure  $< 2 \times 10^{-8}$  Torr remove chemisorbed water from their surfaces. The SPECS spectrometer main chamber, working at a pressure  $< 10^{-9}$  Torr, was equipped with a PHOIBOS 150 multichannel hemispherical electron analyzer with a dual X-ray source working with  $\text{Ag K}\alpha$  ( $h\nu = 1486.2\text{ eV}$ ) at 120 W, 20 mA using C 1 s as energy reference (284.6 eV). Transmission electron microscopy (TEM) and X-ray energy dispersive spectra (XEDS) were recorded on a JEOL 2100F TEM/STEM microscope using a copper sample holder (Lacey/Carbon 200 Mesh, Copper (Cat. # LC200-CU) from Electron Microscopy Science – emsdiasum). Photoluminescence spectra were measured at room temperature on a Fluorescence Spectrophotometer (Perkin Elmer LS50B).

## 3. Photo-catalytic experiments

Gas-phase photo-oxidation of toluene (Aldrich, spectroscopic grade) were carried in a continuous flow annular photoreactor (Fig. 1) and using a set-up described elsewhere [23,38]. Table 1 shows details of reactor configuration and experimental conditions. Activity and selectivity for the gas-phase photooxidation were tested in a continuous flow annular photoreactor containing ca. 40 mg of photocatalyst as a thin layer coating on a pyrex tube. The corresponding amount of catalyst was suspended in 1 mL of ethanol, painted on a pyrex tube (cut-off at ca. 290 nm), and dried at RT. The reacting mixture ( $100\text{ ml min}^{-1}$ ) was prepared by injecting toluene ( $\geq 99\%$ ; Aldrich) into a wet (ca. 75% relative humidity) 20 vol.%  $\text{O}_2/\text{N}_2$  flow before entering to the photoreactor, yielding an organic inlet concentration of ca. 700 ppmv. After flowing the mixture for 6 h (control test) in the dark, the catalyst was irradiated by four fluorescent daylight lamps (6W, Sylvania F6W/D) with a radiation spectrum simulating sunlight (UV content of 3%; main emission lines at 410, 440, 540, and 580 nm, symmetrically positioned

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