



A study on the potential application of natural phosphate in photocatalytic processes

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ABSTRACT

In an attempt at increasing surface area of the resulting solids, different titanium-based systems were synthesized on natural phosphate through the sol–gel process using diverse ageing conditions (reflux, magnetic stirring, sonication or microwaves) and tested for gas-phase selective photooxidation of propan-2-ol. The best results were obtained for the system aged under ultrasounds which was ascribed to its lower band-gap energy. Moreover, the synthesis of TiO₂ on natural phosphate seemed to produce retardation in crystallization as well as a change in titanium and phosphorus electronic environments (as determined by XPS) which in the case of the sonicated system resulted in an improved catalytic behavior as compared to pure titania. All in all, the present piece of research shows that provided that its surface area can be increased natural phosphate can be used as support for a photocatalytic active phase thus widening the scope of its application.

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1. Introduction

Photocatalysis is usually set as an example of Green Chemistry Technology [1]. In fact, the name of the discipline itself (as represented in Fig. 1) refers to two of the so-called 12 Principles of the Green Chemistry [2]: (i) “photo” means light energy and if we succeed in using sun-light, we will contribute to energy economisation (6th Principle of Green Chemistry) and (ii) moreover, catalytic processes are preferable to the stoichiometric ones (9th Principle).

Morocco possesses 75% of the world's phosphate reserves. It is the world's first exporter (28% of the global market) and third producer (20% of global production).

Although phosphates are mainly used in the industry of fertilizers, they have been successfully utilized as catalysts (either alone or conveniently-modified) in a wide range of organic reactions [3]. Some examples include Michael-addition [4], Knoevenagel [5] and Claysen-Schmidt [6,7] condensations, Diels–Alder reaction [8], Beckmann rearrangement [9,10] or transesterifications [11].

The present piece of research is aimed at exploring the possibility of widening the scope of applications of Moroccan natural phosphates through the incorporation of a photocatalytic active phase. Resulting systems will be tested for gas-phase selective photooxidation of propan-2-ol. This way two of the goals of Green Chemistry would be achieved: (i) valorisation of natural resources

(Moroccan natural phosphates) and (ii) development of selective oxidations, at room temperature and ambient pressure through the use of light and a catalyst rather than using less environmentally-friendly stoichiometric oxidants (e.g. potassium dichromate or permanganate).

2. Experimental

2.1. Synthesis of the different titania-based systems

Natural phosphate (NP) came from an extracted ore in the region of Khouribga (Morocco). The fraction of 100–400 μm grain size was washed with water, calcined at 900 °C for 2 h, washed again, calcined at 900 °C for 0.5 h and ground (63–125 μm). The structure of NP is similar to that of carbonate hydroxyfluorapatite as shown by X-ray diffraction pattern and chemical analysis. Titanium was then incorporated to NP through the sol–gel process using titanium isopropoxide [Ti(OCH(CH₃)₂)₄] as the precursor and the precipitation method described elsewhere [12]. Initially, several systems with a titanium nominal content of 1%, 3%, 5%, 8%, 10% and 20% (expressed as g of TiO₂ per g catalyst) were synthesized. Resulting systems exhibited negligible photocatalytic activity, which was ascribed to their low surface area (1–3 m²/g). In an attempt at increasing surface area, synthetic method was modified through substitution of dipicolinic acid by HNO₃ as an agent to adjust pH at 2.5 (Fig. 2A). Moreover, once the gel had been formed on NP, it was divided into four portions which were sub-

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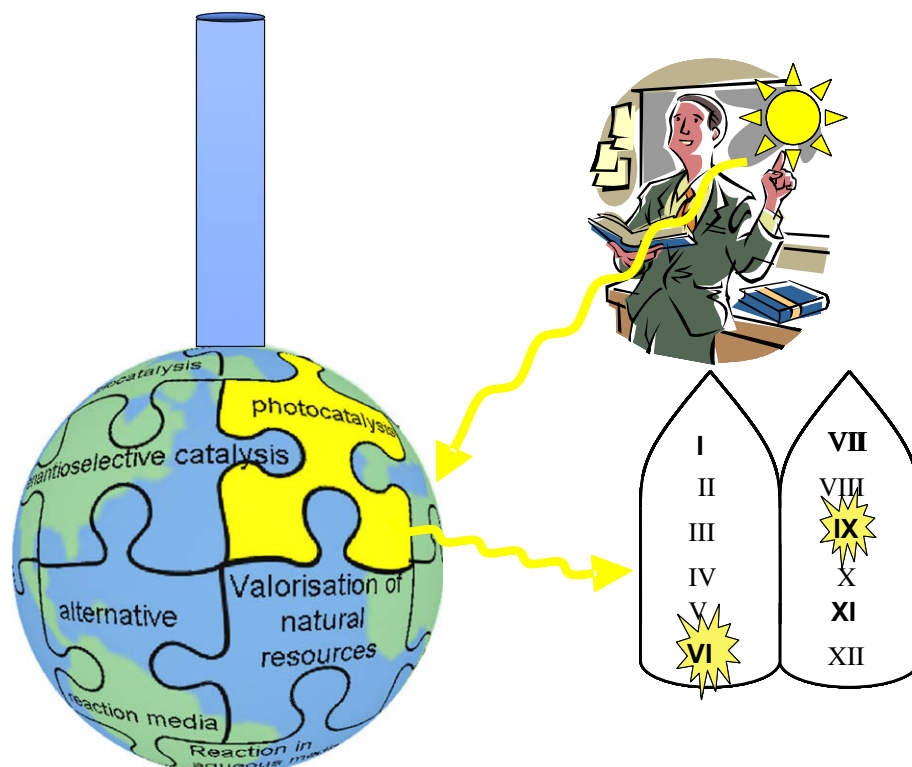


Fig. 1. Schematic representation of photocatalysis in the context of Green Chemistry, represented by the so-called 12 Principles.

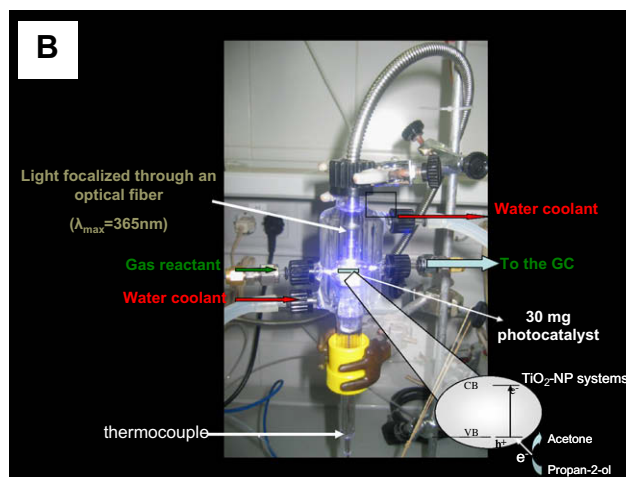
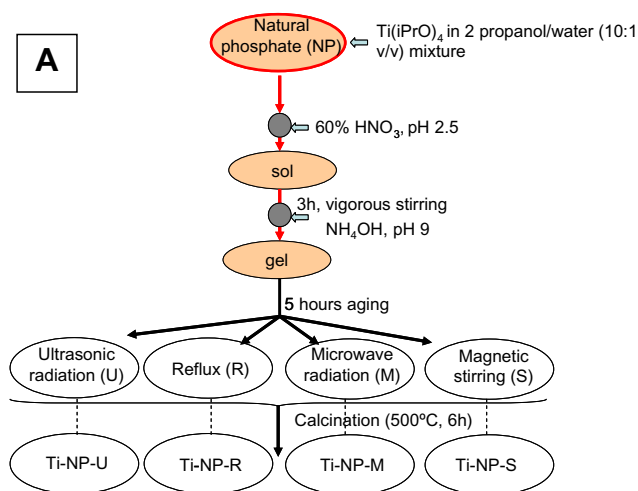


Fig. 2. (A) Schematic representation of synthetic procedure to obtain the different titanium-based systems used in the present work. (B) Photoreactor used in the present study together with a schematic representation of the process.

mitted at different ageing conditions for 5 h: reflux (R), magnetic stirring (S), microwave oven (M) or ultrasounds (U). For these new systems TiO_2 nominal content was 16.66%. Microwave treatment was performed in a CEM Focused Microwave™ Synthesis system (Model Discover) operating at continuous microwave power of 140 W. In the case of the system aged under sonication, an Ultrasonic Homogenizer (4710Series, Cole–Palmer Instrument Co. 300 W, 20 kHz, operated in the continuous mode) was used. Furthermore, the mixture was kept at 0 °C to avoid solvent evaporation. After ageing, resulting systems were calcined at 500 °C for 6 h in static air.

For comparative purposes, pure TiO_2 (labeled as TiO_2 -ref) was synthesized as a reference material in a similar way as Ti-NP-R.

2.2. Characterization

Elemental analyses were made on a ICP-MS ELAN-DRC-e (Perkin–Elmer), after dissolution of the samples in a H_2SO_4 :HF:H₂O (1:1:1) mixture. Atomic spectroscopy standards (PE Pure Plus, Perkin–Elmer) were used for calibration.

As far as EDX analyses are concerned, they were performed on a JEOL JSM-6300 SEM apparatus operating at an accelerating voltage of 20 keV with a resolution of 65 eV. EDX values corresponded to the average value of four measurements carried out at different areas of the solid with an amplification of 5000×.

Thermogravimetric analysis and differential thermal analysis were recorded on a Setaram Setsys 12 instrument. Temperature

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