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Dephosphatation under UV light of water by Ti-PILC with activation by secondary species (La, Se, and Rb)<sup>☆</sup>

*Déphosphatation d'une eau polluée sous irradiation UV avec une argile montmorillonite intercalée au Ti activée par addition d'espèces secondaires (La, Se et Rb)*

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## ABSTRACT

Me/Ti-PILC catalysts (Me: La, Se, Rb) were prepared with 60% in weight of Ti-species and 3% in weight of Me-secondary species added under ultrasounds. All materials were characterized by XRF, XPS, XRD, BET, HR-TEM/EDS, FEG-SEM and UV-vis. Three kinds of Ti-oxide nanoparticles were identified: (1) Ti-pillars within the clay layers, (2) rutile nanoflowers, and (3) anatase. In UV-vis spectra, no significant change in the band-gap was observed. In La and Se samples, small variations of the anatase XRD lines are associated with cationic diffusion after deposition of secondary species and calcination. An O1s XPS-peak (533.5 eV) is attributed to oxygen vacancies generated by this diffusion. Phosphate photo-removal in water was studied using phosphoric acid solution (75.97 g L<sup>-1</sup>). Dephosphatation is significantly improved in the presence of Me-species as La/Ti-PILC > Se/Ti-PILC > Rb/Ti-PILC > Ti-PILC. Partial dephosphatation by adsorption is possible in the dark but is strongly improved by UV irradiation. With a La catalyst and under UV irradiation, phosphates (6.6 × 10<sup>-3</sup> mol L<sup>-1</sup>) were recovered in less than 70 min. Therefore, Me/Ti-PILC have a great potential as photocatalysts for the treatment of wastewaters and the recovery of phosphates.

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## R É S U M É

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Les catalyseurs Me/Ti-PILC (Me: La, Se, Rb) ont été préparés avec 60% en poids de Ti et 3% en poids d'espèces secondaires métalliques Me dispersées sous ultrasons. Tous les matériaux ont été caractérisés par FX, SPX, DRX, BET, HR-MET/EDS, FEG-MEB et UV-vis. Trois types d'oxydes de Ti ont été identifiés: 1) piliers de Ti à l'intérieur des couches d'argile, 2) nanofleurs rutile, 3) anatase. Dans les spectres UV-vis, aucun changement significatif de la bande interdite n'a été observé. Dans les Diffractogrammes RX des échantillons au La et Se, de faibles déplacements des raies de l'anatase sont observés et sont dus à la diffusion cationique. Un pic SPX de O1s (533.5eV) est attribué à des lacunes d'oxygène générées par cette diffusion. La photo-élimination des phosphates dans l'eau a été étudiée en utilisant une solution d'acide phosphorique (75.97 g.L<sup>-1</sup>). La déphosphatation est significativement améliorée en présence d'espèces Me, dans l'ordre: La/Ti-PILC > Se/Ti-PILC > Rb/Ti-PILC > Ti-PILC. Une déphosphatation partielle par adsorption est possible dans l'obscurité, mais elle est fortement améliorée par une irradiation UV. Avec le catalyseur au La et sous irradiation UV, 6,6 × 10<sup>-3</sup> mol L<sup>-1</sup> de phosphates ont été récupérés en moins de 70 min. Par conséquent, les solides Me/Ti-PILC ont un grand potentiel en tant que photocatalyseurs pour le traitement des eaux usées et la récupération des phosphates.

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## 1. Introduction

Phosphorus containing species are now most often included in fertilizers and are necessary for agriculture [1,2]. Large amounts of phosphate wastes in water are also due to soaps and detergents and to mining wastes [3] and metallurgical industries [4,5]. Because the price of phosphates steadily increases, various treatments have been developed for their recovery. The methods in use include biological treatments [6], physical treatments [7], or chemical treatments such as precipitation or crystallization of phosphate-containing solids, like Ca-phosphate for instance [8,9]. Adsorption is comparatively the cheapest and most efficient technique [10]. To improve phosphate recovery, several active solids have been studied in recent years, in particular: iron-coated natural and engineered sorbents [11], slag materials [12], bauxite [13], ashes from coal and petroleum coke combustion [14], goethite [15], La-impregnated silica gel [16], natural calcite [17], B<sub>2</sub>O<sub>3</sub> on borosilicate glasses [18], natural calcium-rich sepiolite [19], La-doped natural vesuvianite (double silicate of calcium and aluminum) [20], and La-doped natural bentonite clays [21].

Nano-titania, because of its availability, low cost and good stability, is considered as an important solid for the treatment of wastewater. However, nano-titania particles easily agglomerate and lose their activity. To overcome this problem and stabilize titania nanoparticles, natural porous solids, zeolites and clays have been tested [22,23]. The two latter types of materials have Al and Si species in framework positions and their porous volume is filled by water and compensating cations. Recent publication showed that a zeolite, with native charge-compensating cations exchanged by Ti-species, had enhanced properties for phosphate removal from water [24]. In contrast to zeolites, the exchange of the natural cations of clays can lead to an increase of porous volume associated with an improved adsorption

capacity. This “pillaring” principle has been explored with mixed alumina/lanthanum-pillared montmorillonite [25] and with alumina clusters introduced between the layers of a natural bentonite clay from Northeast Brasil [25]. Synthesizing titania pillars within montmorillonite to obtain a pillared inorganic layered compound (Ti-PILC) has also been reported in the studies of the Tianhong Mining Company (China) [26]. Montmorillonite is an expandable layered aluminosilicate mineral whose chemical composition depends on soil composition and hydration and on climate, and which can be represented by the general chemical formula: (EC)<sub>x+y</sub>(Si<sub>8-x</sub>Al<sub>x</sub>)<sup>IV</sup>(Al<sub>4-y-z</sub>Fe<sub>y</sub>Mg<sub>z</sub>)<sup>VI</sup>O<sub>20</sub>(OH)<sub>4</sub> · nH<sub>2</sub>O (with IV: T<sub>d</sub> site and VI: O<sub>h</sub> site) [27], where EC are exchanged compensating interlayer cations (EC: Ca<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup> and even traces of Ti<sup>4+</sup>) and x, y, and z characterize metallic substitutions in the Si tetrahedral and Al octahedral sites [28–31]. The montmorillonite used here comes from the Maghnia region in Algeria. The preparation of Ti-PILC consists in exchanging the positive natural charges between a sodic-enriched version of the clay and colloidal titanium Ti(IV) polymeric complexes [32]. After calcination, TiO<sub>2</sub> pillars are formed, the porous volume increases and an improvement of arsenic absorption capacity was observed [16]. Possible applications of Ti-PILC for photocatalytic reactions were also reported, for methylene blue degradation for instance [33].

The mechanism of UV-light activation has been studied in detail with pure commercial titania semi-conducting oxide (Degussa P25) [34]; its energy gap is given by the equation  $E = hc/\lambda$  (the band gap of semiconductor is essentially the energy gap between the valence and conduction bands). This model, based on a band-gap of 3.1 eV, classically assumes that upon absorption of UV-light, the electrons located in the valence band (VB) are promoted into the conduction band (CB, e<sup>-</sup>CB) leaving positive holes (h<sup>+</sup>-VB) in the valence band. These electrons and holes migrate on the titania surface where they react respectively

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