



Research Paper

Synthesis, characterization and photocatalytic activity of TiO₂ supported natural palygorskite microfibers

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ARTICLE INFO

Article history:

Received 9 November 2010

Received in revised form 11 March 2011

Accepted 16 March 2011

Available online 23 March 2011

Keywords:

Palygorskite

TiO₂

Photocatalysis

Inorganic–inorganic nanocomposites

Orange G pollutant

ABSTRACT

This study deals with the synthesis of TiO₂ supported Moroccan palygorskite fibers and their use as photocatalyst for the removal of Orange G pollutant from wastewater. The TiO₂–palygorskite nanocomposite synthesis was accomplished according to a colloidal route involving a cationic surfactant as template (hexadecyltrimethylammonium bromide) assuring hence organophilic environment for the formation of TiO₂ nanoparticles. The clay minerals samples were characterized before and after functionalization with TiO₂. Anatase crystallizes above ca. 450 °C and remarkably remains stable up to 900 °C. In contrast, pure TiO₂ xerogel obtained from titanium tetraisopropoxide (TTIP) showed before calcination a nanocrystalline structure of anatase. By increasing the temperature, anatase readily transforms into rutile beyond 600 °C. The remarkable stability at high temperature of anatase particles immobilized onto palygorskite microfibers was due to the hindrance of particles growth by sintering. Homogeneous monodisperse distribution of anatase particles with an average size of 8 nm was found by TEM and XRD onto palygorskite fibers. This anatase particle size remains below the nucleus critical size (ca. 11 nm) required for anatase–rutile transition. The TiO₂ supported palygorskite sample annealed in air at 600 °C for 1 h exhibits the highest photocatalytic activity towards the degradation of Orange G compared to nanocomposite samples prepared under different conditions as well as pure TiO₂ powders obtained from the xerogel route or commercially available as Degussa P25.

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1. Introduction

Heterogeneous photocatalysis has emerged as an alternative advanced oxidation process for water decontamination. Indeed, due to the generation of strong oxidant species (holes h⁺ and radicals ·OH) upon UV irradiation of semiconductor oxides, heterogeneous photocatalysis is able to decompose and to mineralize bio-recalcitrant organic pollutants in the form of CO₂ and H₂O (Carp et al., 2004; Fujishima et al., 2000; Fujishima and Zhang, 2006; Herrmann, 1999; Paz, 2006; Robertson, 1996).

Practically, the commercial TiO₂ nanopowder Degussa P25, made up of anatase (80%) and rutile (20%), is the most active photocatalyst used in wastewater treatment (Herrmann, 1999; Nieto-Suárez et al., 2009). Nevertheless, TiO₂ powder nanoparticles easily agglomerate which reduces photonic efficiency for most degradation processes to less than 10% (Houari et al., 2005) and needs to implement costly microfiltration processes for recovering micron sized aggregated

particles from water decontaminated by TiO₂ slurry (Carp et al., 2004; Herrmann, 1999; Houari et al., 2005; Liu et al., 2009). Therefore, researches recently have focused on improving photocatalysis activity by the development of TiO₂ supported photocatalysts.

Several routes have been explored to prepare TiO₂ supported photocatalysts on a variety of supports such glass fibers (Robert et al., 1999), carbon (Herbig and Lobmann, 2004), beads (Jung et al., 2005), membranes (Kim et al., 2007) and glass micro-fiber fabrics (Sarantopoulos et al., 2007, 2009). Generally, the efficiency of the overall photocatalytic process decreases as the catalyst is immobilized because the illuminated surface area is smaller by several orders of magnitude (Fernandez-Ibanez et al., 1999). Thus, porous materials or more generally materials exhibiting high specific surface areas like silica gels (Chuan et al., 2004), zeolites (Reddy et al., 2003), activated carbons (Herrmann et al., 1999; Nagaoka et al., 2002) and clay minerals (An et al., 2008; Aranda et al., 2008; Feng et al., 2003; Houari et al., 2005; Liu et al., 2009; Nieto-Suárez et al., 2009) were considered as alternative supports. Among the clay mineral family, the smectite group was the most common support used to perform TiO₂ supported photocatalyst. Indeed, owing to their lamellar structure, their high specific surface area and microporous volume, as well as their adsorption properties (Bouberka et al., 2008; Xu et al., 2008), these

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clay minerals were involved in the development of TiO_2 interlayer pillared clays (Ti-PILC) and have been considered as attractive solutions (An et al., 2008; Feng et al., 2003; Houari et al., 2005; Khalfallah Boudali et al., 1994). However, the photocatalytic activity of these materials was lower with respect to that of anatase (Fujishima and Zhang, 2006). This is likely due to the amorphous or poorly crystalline structure of the TiO_2 pillars due to highly acidic sol precursors ($\text{pH} < 1.8$) used in the preparation of Ti-PILC (Liu et al., 2009). Furthermore, the acidic conditions needed for the hydrolysis of Ti precursor, e.g. TiCl_4 or titanium tetraisopropoxide (TTIP), are so severe that they induce the dissolution of clay minerals. Thus, researches were more recently focused on developing soft methods for functionalizing clay minerals with TiO_2 .

In this respect, An et al. (2008) have published the immobilization of commercial TiO_2 Degussa P25 on the surface and interspatial regions of montmorillonite. Beforehand, the clay was transformed into hydrophobic sample by ion exchange reaction with a cation surfactant, the hexadecyltrimethylammonium bromide (CTAB). Likewise, Aranda et al. (2008) have reported a colloidal route involving in situ soft controlled hydrolysis (using water addition and a few drops of HCl) of titanium alkoxide precursor onto surfaces of sepiolite, a fibrous clay mineral, beforehand converted into organophilic material by CTAB surfactant (Aranda et al., 2008). Upon calcination, the CTAB, acting as template of TiO_2 particle formation, was eliminated leading to the distribution of oxide particles onto sepiolite microfibers. It is worth noting that the formation of stable active TiO_2 anatase onto sepiolite fibers was observed only after doping with sulfur (Aranda et al., 2008). The success of the colloidal procedure for the nanocomposite preparation, i.e. oxide particles attached to clay mineral, depends on the nature of clay minerals (Letaïef et al., 2006). Although palygorskite and sepiolite are both fibrous clay minerals, their structural features are different (Brigatti et al., 2006). Indeed, sepiolite is a microfibrillar magnesian silicate with small crystal size, large specific surface area ($\approx 335 \text{ m}^2/\text{g}$ for the sample from Yuncillos (Toledo, Spain) exploited by TOLSA S.A. (Aranda et al., 2008; Ruiz-Hitzky, 2001), three tetrahedral silica chains in ribbons and pure trioctahedral character. In contrast, palygorskite is a microfibrillar magnesian silicate containing noticeable amounts of Al and/or Fe with large crystals size, low specific surface area ($\approx 153 \text{ m}^2/\text{g}$ for the sample from Serradilla (Cáceres, Spain) exploited by TOLSA S.A. (Blanco et al., 1989)), and two tetrahedral silica chains in ribbons with a predominant dioctahedral character. These different features could cause disparities in their behaviors against functionalization with TiO_2 and subsequently the photocatalytic activity of the nanocomposite.

The present work reports on the synthesis and characterization of active anatase TiO_2 photocatalyst supported onto palygorskite fibers. This nanocomposite material was prepared via a colloidal route and anatase particles were found remarkably stable up to 900°C without intentional doping of titania. Different samples were prepared depending on the annealing treatment and a TiO_2 -palygorskite nanocomposite was found exhibiting photocatalytic activity higher than that of the commercially available Degussa P25 TiO_2 powder towards the removal of the organic dye Orange G (OG) considered as model pollutant.

2. Experimental

2.1. Clay purification

Natural raw clay (labeled Pal) was sampled from Marrakech High-Atlas region. It was reported to be particularly rich into palygorskite (Benaboud et al., 1996; Daoudi, 2004; Daoudi et al., 2009). These samples were first crushed and sieved through a $20 \mu\text{m}$ sieve. They contain about 31 wt. % of carbonates. Thereafter, 20 g of clay powder was treated under stirring at room temperature with 200 cm^3 of sodium acetate buffer solution having a pH of 4.5. This treatment has

the advantage to avoid the alteration of the clay mineral fraction (Shariatmadari, 1998). The samples were washed by successive centrifugations (4000 rpm for 10 min) to remove acid and acetate traces (tested by measurements of pH and conductivity of supernatants). The carbonate amount was decreased to ca. 25 and 20% after 1 h and 3 days of treatment, respectively. Homoionic sodium mineral sample (labeled Na^+ -Pal) with an average particle diameter lower than $2 \mu\text{m}$ was isolated from raw clay according to a procedure described elsewhere (Rhouta et al., 2008).

2.2. Preparation of TiO_2 supported palygorskite nanocomposite

All chemicals including titanium tetraisopropoxide (TTIP) and hexadecyltrimethylammonium bromide (CTAB) were purchased from Aldrich and used as received without further purification. The preparation of TiO_2 supported palygorskite nanocomposite was achieved according to an adapted colloidal procedure previously described (Aranda et al., 2008). Briefly, organo-clay sample (CTA^+ -Pal) was first prepared at 50°C for 48 h by ion exchange reaction of Na^+ -Pal aqueous dispersion (3 g in 300 cm^3) with 0.2 g of CTAB (3 cationic exchange capacity, CEC). Thereafter, 5 cm^3 of TTIP was added to a dispersion of 1 g of CTA^+ -Pal in isopropanol (7 cm^3). Finally, water was added drop wise under stirring until the spontaneous formation of a gel. The gel (labeled CTA^+ -Pal-Ti) was dried at 60°C for 2 days and thereafter calcined at different temperatures ($^\circ\text{C}$) and times (h). The samples were designated as CTA^+ -Pal-Ti-T-t, where T is the calcination temperature and t the time (e.g., CTA^+ -Pal-Ti-600-1 is a sample functionalized with TiO_2 annealed in air at 600°C for 1 h).

In parallel, TiO_2 xerogel (labeled Ti-gel) was prepared according to the above conditions, i.e. hydrolyzing a mixture of 5 cm^3 of TTIP and isopropanol (50% v/v) by slow addition of increasing amounts of water. The xerogel sample was dried at 60°C for 2 days and heated in air at different temperatures. The powder samples obtained were designated Ti-gel-T-t (e.g. Ti-gel-600-1 is a TiO_2 powder prepared by the xerogel route and calcined in air at 600°C for 1 h).

2.3. Characterization techniques

The CEC of the purified palygorskite fraction (Na^+ -Pal) was evaluated by titration of the clay minerals with the cationic surfactant CTAB. The point of zero charge (PZC) was determined from the analysis of the curve depicting the streaming induced potential (SIP) variation versus the added amount of surfactant. The SIP measurements were carried out by using a Müttek Instrument (Particle Charge Detector, PCD) as described elsewhere (Jada et al., 2006).

The different samples were characterized before and after functionalization with TiO_2 by different techniques. The structural changes of TiO_2 was analyzed in situ versus the temperature by X-ray diffraction (XRD) through the two-theta range $2\text{--}60^\circ$ using a Bruker D8 Advance diffractometer equipped with a Vantec Super Speed detector and a MRI radiation heating chamber (Bragg-Brentano configuration; Ni filtered Cu K_α radiation). The diffractograms were recorded every 50°C from the room temperature to 950°C . An isotherm was maintained at each level for 40 min to carry out the analysis then the temperature was increased using a ramp of 1°s^{-1} . XRD at room temperature was recorded in the same angular range using a Seifert XRD 3000TT diffractometer equipped with a graphite monochromator (Bragg-Brentano configuration; Cu K_α radiation). Differential thermal analysis (DTA) and thermo-gravimetric (TG) studies were performed using a Labsys apparatus (Setaram) with 60 mg of clay powder analyzed at temperatures ranging from 25 to 1000°C with a heating rate of $10^\circ\text{C min}^{-1}$. A Jeol JSM 6400 scanning electron microscope (SEM) equipped with an Oxford energy dispersive spectrometer, EDS (Si-Li detector; MK program) and a JEOL JEM 2010 transmission electron microscopy (TEM) equipped with a

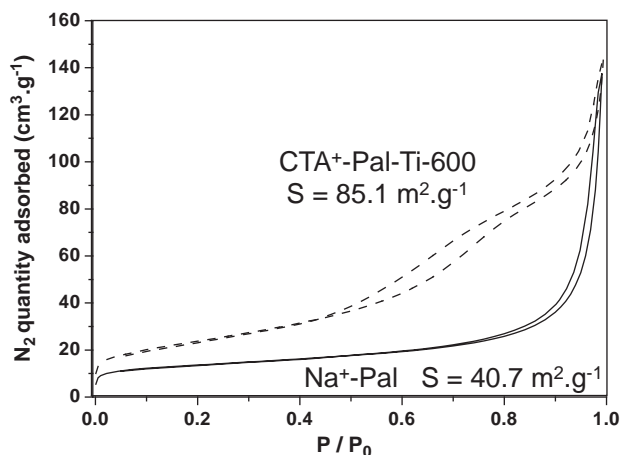


Fig. 2. N_2 adsorption-desorption isotherms of Na^+ -Pal and CTA^+ -Pal-Ti-600-1 samples.

endothermic effect is observed occurring at $110^\circ C$ associated with weight loss of $\approx 5\%$. This is due to the removal of physisorbed water and part of zeolitic water filling tunnels (Önal and Sarıkaya, 2009 and Huang et al., 2007). Another endothermic peak is observed between 160 and $330^\circ C$ at a maximum of $248^\circ C$ with weight loss around 2%. This is ascribed to the elimination of the remaining zeolitic water (Önal and Sarıkaya, 2009) and/or to water coordinated to octahedral

edge cations (Huang et al., 2007). Between 330 and $590^\circ C$, a broad endothermic effect is observed with a maximum at $480^\circ C$ associated with weight loss of $\approx 3\%$. This peak could be attributed to the loss of the residual coordinated water and/or of crystalline water by dehydroxylation of the inner octahedral cations (Huang et al., 2007). According to Huang et al., 2007, the broad profile of this peak could be explained by overlaps with secondary peaks due to the dehydroxylation corresponding to the different occupations of octahedral sites, e.g. Fe^{3+} , Al^{3+} , Mg^{2+} , or the vacancy. For temperatures ranging from 600 to $830^\circ C$, a complex endothermic effect is observed made up of four sub-peaks with maxima at 755 , 787 , 796 and $814^\circ C$, with mass loss of about 15%. These secondary peaks could be ascribed to a series of phenomena of the removal of carbonates (calcite and/or ankerite) and also probably to transformation reaction of ankerite to calcite (Dasgupta and Phil, 1965). An endothermic peak at $822^\circ C$ with mass loss about 4% is further observed which could be ascribed to the removal of the remaining crystalline water by dehydroxylation (Önal and Sarıkaya, 2009). The exothermic peak observed at approximately $855^\circ C$ without any weight loss corresponds to recrystallisation of palygorskite.

3.1.1.4. FTIR. The infrared spectrum of the Na^+ -homoionic clay mineral (Na^+ -Pal) (Fig. 4) is similar to that reported in literature for palygorskite (Blanco et al., 1989; Chahi et al., 2002; Suárez and García-Romero, 2006). Indeed, the absorption bands observed between 3000 and 3800 cm^{-1} correspond to the stretching of the hydroxyl groups (Al and / or Fe and/or Mg) OH. The peak centred at 3620 cm^{-1} , ascribed to OH stretching mode in Al-Al-OH, is particularly characteristic of palygorskite (Suárez and García-Romero, 2006; Blanco et al., 1989). The absorption bands centred at about 3430 and 3270 cm^{-1} correspond to the vibration of physisorbed water (surface and zeolitic) which interacts with each other because of the hydrogen bridges (Blanco et al., 1989). The band at 1660 cm^{-1} with a shoulder at 1640 cm^{-1} is ascribed to the bending modes of coordinated, absorbed and zeolitic water (Blanco et al., 1989; Önal and Sarıkaya, 2009; Suárez and García-Romero, 2006). In agreement with thermal analysis (Fig. 3) and XRD analysis (Fig. 1), the peak at 1440 cm^{-1} confirms the remaining carbonate impurities (Rhouta et al., 2008). The small band at 1200 cm^{-1} is a characteristic of palygorskite because it doesn't appear in any silicates except sepiolite. It is ascribed to Si-O-Si bond between alternative ribbons at the point of periodical inversion apical oxygen in tetrahedral within the structure of fibrous minerals (palygorskite and sepiolite). Absorption bands observed between 950 and 800 cm^{-1} correspond to bending vibration of structural hydroxyl groups (Al and/or Fe and/or Mg)-OH. The intense peaks observed in ranges $[985, 1100\text{ cm}^{-1}]$ and $[400, 750\text{ cm}^{-1}]$ are

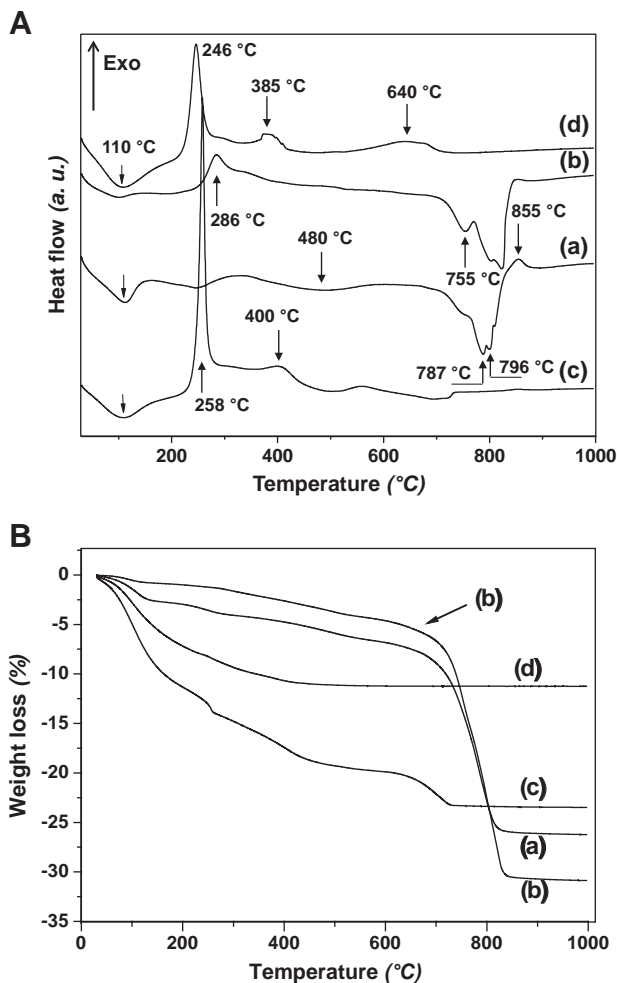


Fig. 3. Differential thermal analysis (A) and thermo-gravimetric (B) of (a) Na^+ -Pal, (b) CTA^+ -Pal, (c) CTA^+ -Pal-Ti and (d) Ti-gel. The DTA thermograms are shifted vertically for clarity.

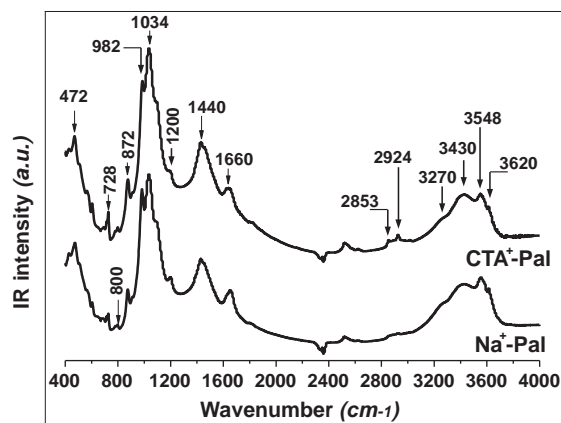


Fig. 4. FTIR spectra of different samples before and after modification with CTA^+ and functionalization with TiO_2 .

ascribed to stretching and deformation modes respectively of Si–O and/or Al–O bonds.

3.1.2. CTA⁺-Pal

3.1.2.1. Thermal analysis. The Na⁺-exchanged clay mineral fraction (Na⁺-Pal) has been modified by exchanging the charge compensating cations (Na⁺) in palygorskite with cationic surfactant species (CTA⁺) to obtain an organo-clay CTA-palygorskite sample (CTA⁺-Pal). The thermal analysis proves the formation of CTA modified palygorskite (Fig. 3). Indeed, the comparison of CTA⁺-Pal thermogram with that of the pristine sample (Na⁺-Pal) shows an additional exothermic peak at about 286 °C (Fig. 3A) associated with a weight loss of ca. 1.6% (Fig. 3B), which corresponds likely to the release of surfactant by pyrolysis. Moreover, the endothermic effect at 110 °C is assigned to desorption of the physisorbed water (Fig. 3A). Consistently, the corresponding weight loss (Fig. 3B) is lower for the surfactant modified CTA⁺-Pal sample owing to its organophilic character (1.3%) in comparison with that of the hydrophilic pristine Na⁺-Pal clay mineral (ca. 3%).

3.1.2.2. FTIR. The success of organophilic modification of palygorskite is further supported by FTIR spectroscopy analysis. Indeed, with respect to the pristine clay mineral (Na⁺-Pal), Fig. 4 shows the presence of additional absorption bands at 2924 cm^{−1} and 2853 cm^{−1} ascribed to asymmetric and symmetric stretching vibrations of C–H groups. These bands appear to be less intense which indicates that the amount of cationic surfactant retained by palygorskite is low due to its small CEC (8 meq/100 g). The corresponding deformation bands, appearing in the 1500–1200 cm^{−1} range, are likely overlapped in the large band centred at 1430 cm^{−1} of carbonate.

3.1.2.3. XPS. The Fig. 5 shows typical XPS spectra of the different types of samples. The peak intensities of the elements characteristic of palygorskite, namely O 1s, Si 2s, Si 2p, Na 2s and Al 2s decrease upon the silicate modification with CTAB surfactant while that of C 1s increases (compare spectra a and b). The increase of carbon content from 28 to 38 at.% is consistent with the covering of the surface of palygorskite fibers with CTA (Table 1). The chemical modification of clay minerals with ammonium surfactants is well known to produce organo-clay (OC) minerals exhibiting high affinity towards organic species, hence making them interesting for adsorption of these compounds (Bouberka et al., 2008; Lagaly et al., 2006; Park et al., 2011). Thus, the CTA modified palygorskite (CTA⁺-Pal) offers an organophilic environment favorable to hydrolysis and polycondensa-

Table 1

Surface composition determined by XPS of different samples before and after modification with CTA and functionalization with TiO₂.

Sample	Si 2s (at. %)	O 1s (at. %)	C 1s (at. %)	Ti 2p _{3/2} (at. %)
Na ⁺ -Pal	29	43	28	0
CTA ⁺ -Pal	26	36	38	0
CTA ⁺ -Pal-Ti	0	34	58	8
CTA ⁺ -Pal-Ti-600-1	0	53	28	19

tion of TTIP (Aranda et al., 2008) yielding to the synthesis of a xerogel precursor sample (CTA⁺-Pal-Ti) as described in the experimental section.

3.1.3. CTA⁺-Pal-Ti

3.1.3.1. ICP and XPS. The ICP analysis has revealed an increase of Ti amount from about 0.14 wt. % in the pristine sample (Na⁺-Pal) to 25.5 wt. % in as-prepared CTA⁺-Pal-Ti precursor sample. XPS analysis of the sample CTA⁺-Pal-Ti has confirmed the presence of titanium (Ti 2p core level due to polycondensed species of titanium) while the elements characteristic of the palygorskite disappeared except oxygen that is still present with approximately the same content (36 and 34 at. % for CTA⁺-Pal and CTA⁺-Pal-Ti respectively) (Table 1). The intensity of C 1s significantly increases for CTA⁺-Pal-Ti compared to CTA⁺-Pal due to the presence of isopropanol solvent, remaining isopropoxy groups and CTA surfactant in the CTA⁺-Pal-Ti sample: the carbon content increases from 38 to 58 at.% (Table 1).

3.1.3.2. Thermal analysis. The XPS results are further supported by the TG-DTA analysis. In fact, an exothermic peak at 258 °C, close to that observed at 286 °C for CTA⁺-Pal corresponding to the decomposition of organic matter, is observed for CTA⁺-Pal-Ti with a weight loss significantly higher (7.6%) than for CTA⁺-Pal (1.6%) (Fig. 3). This is due to the fact that for the CTA⁺-Pal sample a decomposition of CTAB surfactant occurs while for the CTA⁺-Pal-Ti sample there is in addition a decomposition of remaining isopropoxy species. Another exothermic peak is observed for CTA⁺-Pal-Ti at ca. 400 °C which likely corresponds to the transition of amorphous hydroxo-oxo polycondensed Ti phase to crystalline TiO₂. These two exothermic peaks are also observed for the pure TiO₂ xerogel sample but they are slightly shifted to lower temperatures at 246 °C and 385 °C. As for CTA⁺-Pal-Ti sample they correspond to the removal of isopropanol solvent and the crystallization of as-prepared amorphous titania, respectively (Fig. 3).

3.1.4. TiO₂-palygorskite nanocomposites

3.1.4.1. In situ XRD. The above results are consistent with in situ XRD analysis versus the temperature (Figs. 6 and 7). Indeed, as for the Na⁺-Pal sample (Fig. 1), the room temperature XRD pattern of CTA⁺-Pal-Ti reveals the presence of palygorskite (evidenced by several corresponding reflections, especially the basal reflection d(110) at 1.056 nm (2θ=8.36°)), ankerite and traces of quartz (Fig. 6). Any peak of crystalline TiO₂ phase is observed in this sample at room temperature. By increasing the temperature, the diffraction peaks of ankerite disappear and are no more observable above 700 °C (see for instance the main reflection at 2θ=31°) (Figs. 6 and 7). This is in good agreement with thermal analysis (Fig. 3), which has shown an endothermic peak at ca. 750 °C associated to a weight loss of about 15% of ankerite remained in the pristine clay mineral (Na⁺-Pal).

The characteristic (110) reflection of palygorskite at low angles (ca. 8.36°) is still observable upon heat treatment at 300 °C (Fig. 6) while any peak of crystalline TiO₂ phase is observed in this sample at this temperature. Nevertheless, this reflection is no more observable above 350 °C due likely to its low intensity compared to those of other crystalline phases (Figs. 6 and 7). This does not mean that the

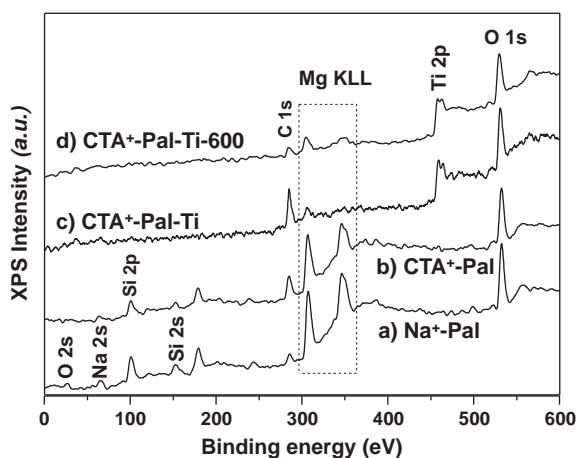


Fig. 5. XPS spectra of different samples before and after modification with CTA⁺ and functionalization with TiO₂.

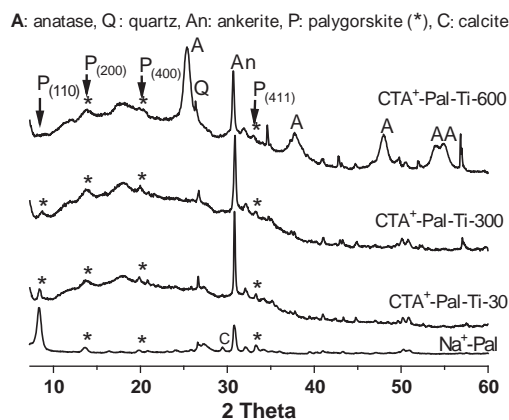


Fig. 6. XRD patterns of CTA⁺-Pal-Ti precursor sample before and after heat treatments at 300 and 600 °C showing the observation of (110) reflection of palygorskite in the as-elaborated sample as well as after its heat-treatment at 300 °C and the still observation of some harmonics reflections of palygorskite after heat treatment at 600 °C.

structure of palygorskite is destroyed at this temperature. Indeed, the diffractograms obtained from oriented flat plates of the Na⁺-exchanged palygorskite (Na⁺-Pal) have confirmed that the (110) reflection is still observable after annealing at 500 °C (Fig. 1b). Moreover, several other reflections of the palygorskite, especially the (411) peak at ca. 33°, remain observable up to 700 °C (Figs. 6 and 7). This gives evidence for a good thermal stability of the palygorskite up to at least 700 °C without significant structural folding (Huang et al., 2007). Furthermore, these diffractograms have revealed that TiO₂ begins to crystallize above 450 °C in the form of anatase (JCPDS file 99-201-5379) as evidenced by the appearance of the (101) and (200) reflections at ca. 25 and 48°, respectively.

3.1.4.2. Crystallites sizes determination. Fig. 8 depicts the influence of the annealing temperature of CTA⁺-Pal-Ti samples on the average crystallite sizes of anatase determined from the full width at half maximum (FWHM) of the (101) and (200) peaks according to Scherrer's equation. Both curves show similar crystallite sizes of anatase in the two directions and the same dependence with the temperature. When anatase begins to be detected around 500 °C the crystallites size is

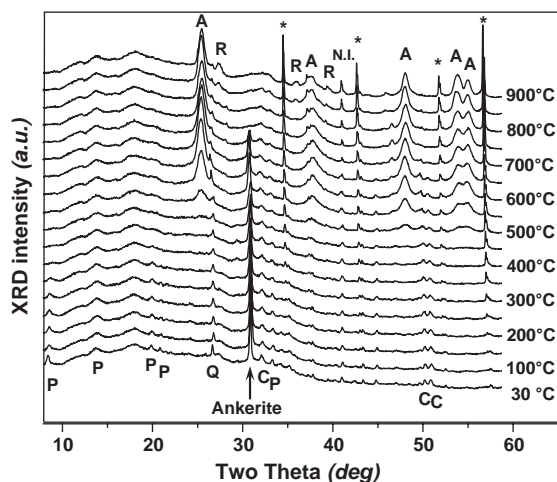


Fig. 7. Complete XRD patterns at different temperatures in air of TiO₂-palygorskite nanocomposites (CTA⁺-Pal-Ti) showing the formation of anatase (A) and traces of rutile (R) by increasing the temperature along with the disappearance of ankerite (P: palygorskite; Q: quartz; C: calcite; N.I.: not identified; * alumina from the sample holder).

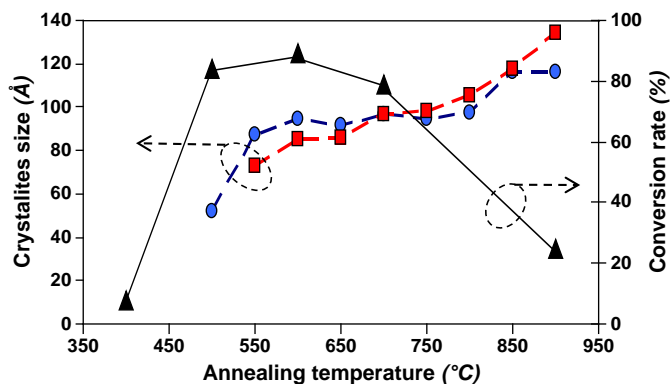


Fig. 8. Influence of the annealing temperature of CTA⁺-Pal-Ti samples on the crystallites size of anatase and on the photocatalytic conversion rate of OG in 1 h (triangles). The average crystallites sizes were determined from (101) and (200) XRD reflections of anatase (circles and squares, respectively).

approximately 5 nm and it increases to reach a plateau at 8–9 nm in the temperature range 550–800 °C. It is noteworthy that no crystallite growth is observed in this broad temperature range. Beyond 800 °C, a noticeable increase of the average crystallite size is observed to reach 12 nm at 900 °C. By contrast with previous work (Aranda et al., 2008), the anatase crystallites formed on the palygorskite fibers remain remarkably stable up to 900 °C with a very small average crystallite size as evidenced by the Fig. 7. A few amounts of rutile just began to be formed above 850 °C as evidenced by the weak peaks assigned with the JCPDS file 99-100-4705.

3.1.4.3. TEM. The remarkable stability of anatase crystallites on palygorskite fibers is further confirmed by TEM analyses. Fig. 9 shows the growth of monodisperse spherical anatase nanoparticles on the surface of palygorskite fibers formed after annealing in air at 600 °C of an as-prepared CTA⁺-Pal-Ti sample. The anatase particles form a uniform thin film covering entirely the fibers. Their average size is in the range 8–12 nm in good agreement with XRD data. EDX analyses pointed on a coated palygorskite fiber have shown large amounts of titanium compared to the bare palygorskite fibers. The elemental compositions (Si, Mg, Al, Fe) were in good agreement with that of the palygorskite confirming its good stability at 600 °C as demonstrated with XRD analysis (Figs. 6 and 7). Selected area electron diffraction carried out on palygorskite fibers coated with nanoparticles clearly has shown the ring pattern of anatase (Fig. 9c). High resolution electron microscopy has confirmed the quasi spherical shape and the nanometric size of the anatase crystallites as evidenced by crystallites exhibiting a reticular distance of ca. 0.3 nm corresponding to the {101} reflection of anatase (Fig. 9d).

Fig. 10 shows TEM analyses of a TiO₂-palygorskite nanocomposite sample after annealing in air at 900 °C (CTA⁺-Pal-Ti-900-1). Microstructural differences are observed with respect to the sample annealed at 600 °C (CTA⁺-Pal-Ti-600-1). The TiO₂ particles developed onto palygorskite fibers upon heat-treatment at 900 °C are significantly larger (20–50 nm) (Fig. 10a) than those observed upon annealing at 600 °C (≈8 nm) (Fig. 9). Furthermore there are domains without palygorskite fibers where oxide particles form aggregates. The average particle size in these aggregates is significantly larger (100–200 nm) than those attached to palygorskite fibers (Fig. 10c). EDX analysis of the particles in the aggregates reveals they are free TiO₂ nanoparticles while EDX analyses of the small one (Fig. 10a) confirm that the palygorskite fibers are covered with TiO₂ as evidenced by the presence of Si, Al, Mg and Fe in addition to Ti. This also suggests the palygorskite fibers remain stable even after heat-treatment at 900 °C.

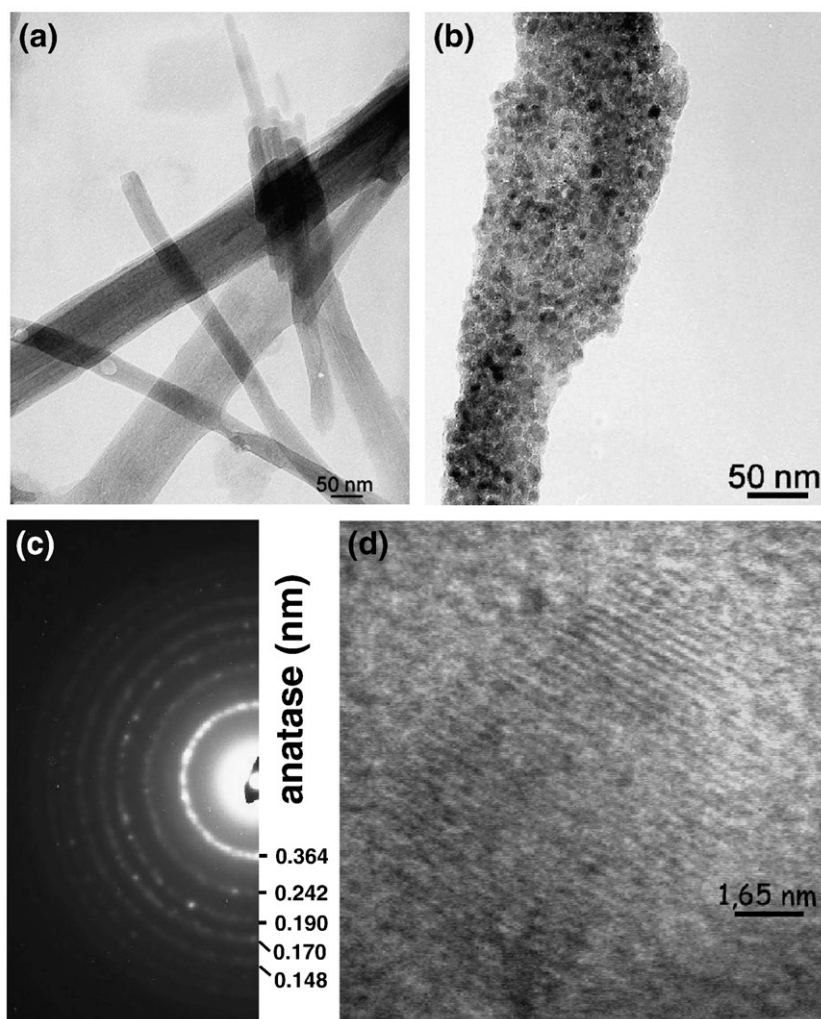


Fig. 9. TEM micrographs of Na⁺-Pal (a) and CTA⁺-Pal-Ti-600-1 (b) samples. Selected area electron diffraction pattern indexed with anatase (c) of a CTA⁺-Pal-Ti-600-1 sample and high resolution electron micrograph (d) showing a nodular anatase nanoparticle (8–12 nm in diameter) and the {101} planes with a reticular distance of ca. 0.3 nm.

Selected area electron diffraction performed on particles in aggregates exhibit a dot pattern corresponding to the [111] zone axis of rutile according to JCPDS file 01–1292 (Fig. 10d). This contrast with the ring pattern obtained from coated palygorskite fibers (Fig. 10b), that is similar to the one obtained for the sample annealed at 600 °C (Fig. 9c), and that is clearly assigned to anatase (JCPDS file 01–0562). On the other hand, it is worth noting to observe in the Fig. 10b diffraction rings at 0.444 and 0.267 nm which are ascribed to (400) and (411) reflections respectively of palygorskite, which proves the structure of clay mineral fibers is not folded. As mentioned above, the grains of anatase do not grow excessively when they are attached to clay mineral fibers compared to free particles. This prevents their transformation into rutile phase as observed for free particles that form aggregates.

3.1.4.4. XPS. The XPS analysis carried out on TiO₂ supported palygorskite nanocomposite annealed at 600 °C has revealed that the C 1s intensity decreases due to the decomposition of organic components as isopropanol solvent, surfactant (CTAB) and remaining isopropoxy species (Fig. 5d) in agreement with thermal analysis (Fig. 3). The carbon content considerably decreases from 58 at. % for CTA⁺-Pal-Ti to 28 at. % for CTA⁺-Pal-Ti-600-1 which is the same value found for the pristine clay mineral fraction Na⁺-Pal (Table 1). This removal of organic matter from TiO₂ functionalized clay mineral is consistent with the white color of the CTA⁺-Pal-Ti-600-1 sample in

contrast to those treated at lower temperatures (<400 °C) which appeared black due to the formation of carbon upon surfactant calcination. As proposed by Aranda et al. (2008), the surfactant molecule (CTAB) acts as template for anchoring TiO₂ to the clay mineral. Therefore, heat-treatment conditions should be appropriately chosen to assure the minimization of carbon contamination in the material in order to enhance the photocatalytic activity. On the other hand, upon annealing of the functionalized clay mineral, the relative amounts of titanium and oxygen increase from 8 and 34 at. % to 19 and 53 at. %, respectively (Table 1). Like in the pristine clay mineral (Na⁺-Pal), the N₂ adsorption–desorption isotherm obtained for the TiO₂-palygorskite calcined at 600 °C is of type II but with a hysteresis of types H3/H4 according to the IUPAC classification (Fig. 2). The surface area increases by a factor of 2 to reach the value of 85.1 m² g^{−1}.

3.1.5. Pure TiO₂ xerogel and oxide powders

3.1.5.1. In situ XRD. Pure titania xerogel (Ti-gel) prepared under the conditions described in the experimental section has been analyzed in situ by XRD versus the temperature up to 900 °C (Fig. 11). Unlike as-prepared titanium functionalized CTA modified palygorskite sample (CTA⁺-Pal-Ti) that did not exhibit crystalline TiO₂ phase before calcination (Figs. 6 and 7), the XRD pattern at room temperature of TiO₂ xerogel gives evidence for crystalline anatase with broad peaks at

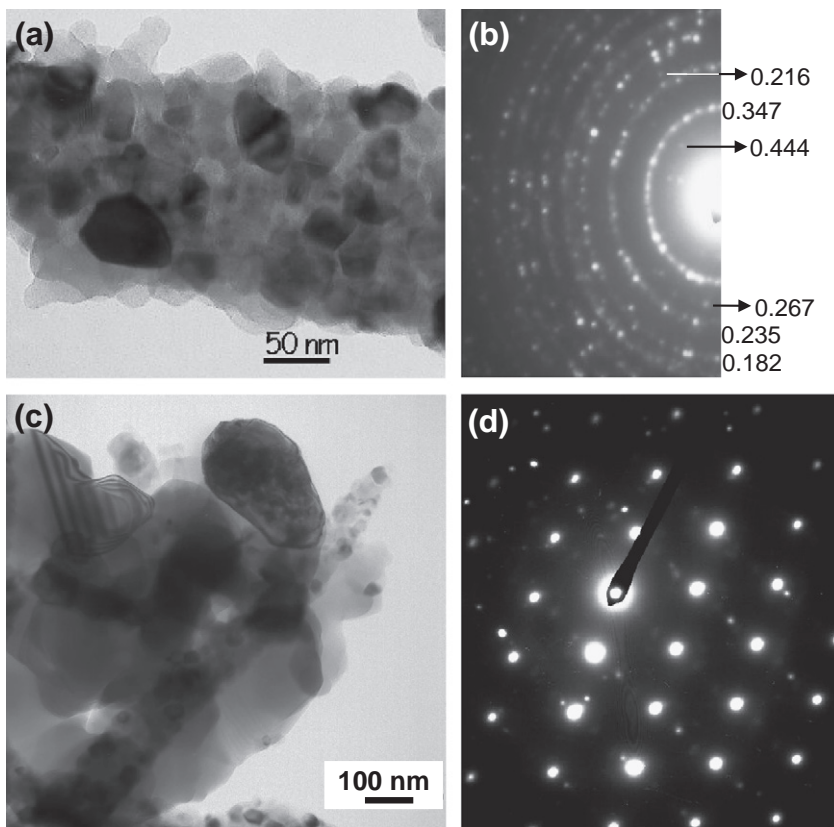


Fig. 10. TEM micrographs of CTA⁺-Pal-Ti-900-1 sample showing anatase nanoparticles (20–50 nm in diameter) on a palygorskite fiber (a) and corresponding selected area electron diffraction pattern indexed with anatase (b). The rings pointed with an arrow correspond to palygorskite. Free oxide crystallites 100–200 nm in diameter (c) and corresponding selected area electron diffraction pattern indexed with rutile (d).

reticular distance equals 0.351, 0.237, 0.189 and 0.168 nm. As the temperature increases, the crystallinity of anatase is improved as supported by the higher intensity and lower FWHM of the XRD peaks. The anatase/rutile transition is observed around 600 °C, in good agreement with thermal analysis (Fig. 3), and the total transformation into rutile is effective beyond 650 °C.

3.1.5.2. Crystallites sizes determination. Fig. 12 represents the variations of crystallites sizes of pure TiO₂ xerogel determined from the FWHM of (101) anatase and (110) rutile XRD reflections. In contrast

to as modified palygorskite CTA⁺-Pal-Ti sample (Fig. 8), the average crystallite size of anatase continuously increases from 5 nm for as-prepared TiO₂ xerogel sample to 30 nm after annealing at 650 °C. Beyond this temperature, the rutile phase appears with crystallites size of ca. 40 nm which rapidly grow with the annealing temperature to reach 130 nm at 900 °C. These results prove the remarkable effect of the palygorskite fibers in stabilizing TiO₂ anatase phase at high temperatures and this could be due to particle size effects. Indeed, thermodynamic calculations predicted that rutile is the most stable phase at all temperatures and pressures up to 6×10^6 kPa (Carp et al., 2004). However the small differences of the Gibbs free energy (4–20 kcal mol^{−1}) between both phases suggest that metastable anatase

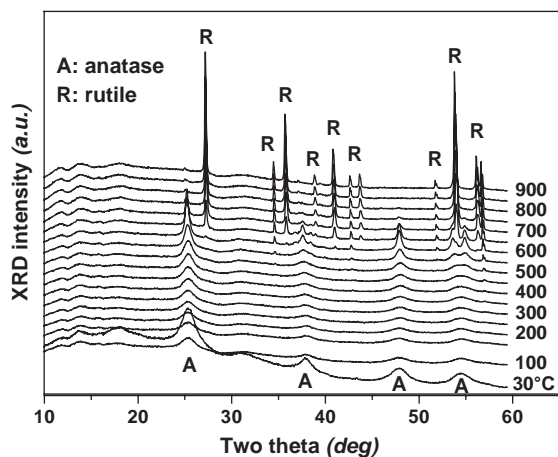


Fig. 11. In situ XRD in air of a pure TiO₂ xerogel sample as a function of the annealing temperature in the range 30–900 °C showing the transformation of anatase (A) to rutile (R) at ca. 600 °C.

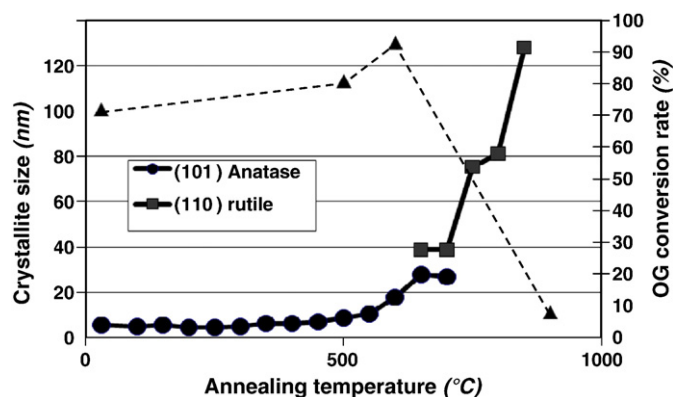


Fig. 12. Variation of the average crystallites size of anatase (circles) and rutile (squares) from a pure TiO₂ xerogel sample and of the photocatalytic conversion rate of OG (triangles) as a function of annealing temperature. Crystallite sizes were determined from (101) and (110) for anatase and rutile, respectively.

can be stabilized at normal pressure and temperature as frequently observed. This is the case when particle size decreases to sufficiently low values due to predominant surface effects, e.g. surface free energy and surface stress depend on particle size (Zhang and Banfield, 1998). In this context, it has been suggested that anatase is more thermodynamically stable at sizes smaller than 11 nm while rutile is the most stable at sizes greater than 35 nm (Zhang and Banfield, 2000). From a physical point of view, the transition temperature and the rate of transformation depend on the rate of sintering of the primary anatase particles to reach the critical size (Banfield et al., 1993; Kumar et al., 1994; Wang and Ying, 1999).

TEM images of Fig. 9 give evidence for a high nucleation rate of TiO_2 on the surface of palygorskite fibers. As a result, anatase particles are monodisperse with a mean size smaller than the critical size of ca. 11 nm. The anatase crystallites have been formed around 500 °C due to the removal of organic species which limits their size and leads to a nodular morphology and stable grain boundaries. As the critical nucleus size of rutile was reported to be at least three times larger than that of anatase (Kumar, 1995), the homogenous dispersion of TiO_2 anatase particles on the palygorskite fibers with an average size smaller than 11 nm likely delays the sintering and growth of the particles even at temperature as high as 900 °C. Thus, the particle sizes remain smaller than the nucleus critical size required for anatase–rutile transition as evidenced by XRD (Fig. 8) and TEM analyses (Fig. 9). The anatase particles in the TiO_2 xerogel already exist at room temperature (Fig. 11) leading to a higher density, which facilitates sintering and growth by increasing the temperature. The critical size for anatase/rutile transition is readily reached at ca. 550 °C as shown by XRD data (Fig. 12).

3.2. Photocatalytic activity

3.2.1. Palygorskite based materials derivatives

The photocatalytic decomposition kinetics of the different samples before and after functionalization has been tested against the degradation of OG in aqueous solution (Fig. 13). The pristine palygorskite Na^+ -Pal sample has no noticeable effect to reduce the OG concentration. This means there is no photocatalytic activity as expected since there is no component known to exhibit such properties in this compound, and this means also that adsorption of this model pollutant is negligible on this sample in good agreement with our recent work (Bouna et al., 2010). This confirms OG dye compound satisfies the requirement for this photocatalytic test. Similarly as-prepared

Ti-supported CTA^+ -Pal-Ti sample is almost inactive since only about 15% of OG is removed in 150 min. This low decrease of the dye concentration in the aqueous solution is due to adsorption since no TiO_2 anatase has been formed at this stage as deduced from XRD analysis (Figs. 6 and 7). Moreover, the CTA^+ -Pal-Ti sample has an organophilic character and consequently a greater affinity toward adsorption of organic compounds (Bouberka et al., 2008; Lagaly et al., 2006; Park et al., 2011). The functionalized clay mineral samples have been annealed in air at different temperatures for 1 h to promote the formation of crystalline TiO_2 nanoparticles.

The sample treated at 400 °C has a slightly better behavior than the untreated one but there is no evidence for photocatalytic activity since the OG degradation is very slow (Fig. 13). Anatase is not yet formed at 400 °C (Fig. 7) and there is a significant carbon contamination from the surfactant pyrolysis, which gives a dark grey color to the material. The nanocomposite materials annealed at 500 °C and even better at 600 °C exhibit important photocatalytic activity since the OG initial amount disappear in ca. 90 min. The treatment at 700 °C induces a lower efficiency than at 500–600 °C and this is worse for the sample annealed at 900 °C for which only 50% of the initial dye amount was degraded in 150 min. This behavior can be correlated to the formation of active anatase nanoparticles as observed by XRD above 450 °C and to the crystallization of the less active rutile phase at high temperatures.

Table 2 shows the conversion rate of OG after a photocatalytic test for 1 h except otherwise specified. The treatment in air at 500 °C for 5 h improves only slightly the photocatalytic activity (88% of OG removed) compared to that performed for 1 h (85% of OG removed). The best efficiency is observed for the sample treated at 600 °C for 1 h (89% of OG removed) then the activity decreases by increasing the annealing temperature but they are still active at 900 °C (25% of OG removed). This behavior is likely due to the good thermal stability of anatase when the temperature and the annealing time increases and to the structural changes. The best photocatalytic activity is observed for samples calcined in the temperature range 500–600 °C for which the average crystallite size of anatase is 8 nm (Fig. 9). The decrease of photocatalytic activity above this temperature range could be due to the increase of anatase crystallite size and, at 900 °C, to the onset of rutile formation.

3.2.2. Photocatalytic activity of TiO_2 -palygorskite nanocomposite compared to pure TiO_2 powders

The photocatalytic activity of TiO_2 supported palygorskite nanocomposites (CTA^+ -Pal-Ti-600-1 sample) has been compared to pure TiO_2 powders: (i) commercial Degussa P25 and (ii) TiO_2 obtained by the xerogel route. Fig. 14 depicts the OG proportion normalized by the mass of titanium really present in each sample that has been converted during photocatalytic tests in 30 min. These results clearly show that the TiO_2 supported palygorskite nanocomposite prepared by heating in air at 600 °C is the most efficient. This supported photocatalyst exhibits an activity twice higher than those of the pure TiO_2 powders (Degussa P25 and Ti-gel-600-1). The small size and the better dispersion of TiO_2 nanoparticles immobilized on the palygorskite fibers prevent agglomeration, which maintains a high specific surface area and accounts for this good efficiency. Before calcination at 600 °C, TiO_2 xerogel sample (Ti-gel) is more active than

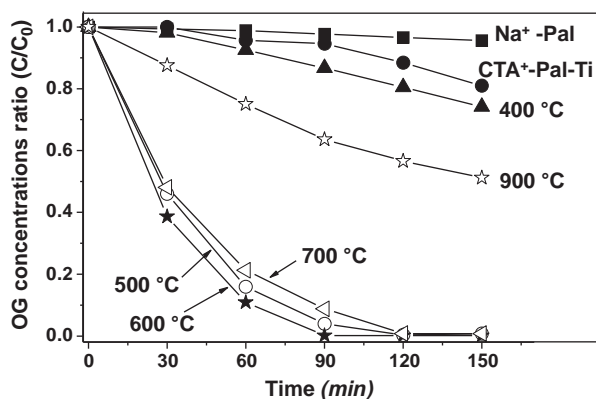


Fig. 13. Change in OG concentration (where C_0 and C are the OG concentrations, respectively, at the initial time $t=0$, and after an elapsed time t of the photocatalytic reaction) versus irradiation time of Na^+ -exchanged palygorskite (Na^+ -Pal), organo palygorskite functionalized precursor (CTA^+ -Pal-Ti) and different TiO_2 -palygorskite nanocomposites obtained upon annealing for 1 h at different temperatures in the range 400–900 °C.

Table 2

Orange G proportion removed from aqueous solutions during a photocatalytic test in 1 h for different samples before and after functionalization and heat treatment in air.

Sample	Na^+ -Pal	CTA^+ -Pal-Ti	400 C-1 h	500 C-1 h	500 C-5 h	600 C-1 h	700 C-1 h	900 C-1 h
% of removal of OG	1.24	4.37	7.46	84.07	88.05	89.07	78.76	24.96

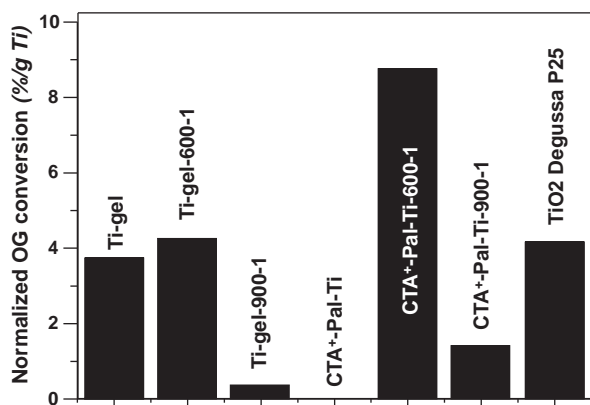


Fig. 14. Comparison of Orange G proportion normalized by mass of titanium converted by photocatalysis using different catalysts in 30 min.

untreated Ti-supported palygorskite (CTA⁺-Pal-Ti). As evidenced by XRD versus the temperature this is due to the presence of crystalline anatase in the TiO₂ xerogel prepared at room temperature (Fig. 11) while annealing above 500 °C is required for crystallization of anatase in CTA⁺-Pal-Ti sample (Fig. 7). The heat treatment at 600 °C of the TiO₂ xerogel slightly improves the photocatalytic activity due to the improvement of the anatase crystallization which exhibits average crystallite size of ca. 20 nm (Fig. 12). Beyond this temperature, the photocatalytic activity drastically drops as the anatase crystallite size increases causing the formation of the less active rutile phase (Fig. 12). For instance, the xerogel precursor calcined at 900 °C exhibits photocatalytic efficiency significantly lower than that of TiO₂ supported palygorskite obtained at the same temperature. This behavior is ascribed to the formation of rutile which is almost the single phase starting from TiO₂ xerogel (Fig. 11) while only traces are found in CTA⁺-Pal-Ti-900-1 sample for which anatase is still the dominant phase (Fig. 7).

4. Conclusions

The preparation of inorganic–inorganic nanocomposites, TiO₂ supported onto natural fibers of Moroccan palygorskite, by a sol-gel method using a cationic surfactant as template was achieved. XRD versus temperature has demonstrated that TiO₂ crystallizes above 450 °C in the form of anatase, which remarkably remains stable up to 900 °C. The stabilization of this TiO₂ phase is due to the nanometric size of the particles immobilized onto palygorskite fibers, which prevents sintering and growth beyond the nucleus critical size (ca. 11 nm) required for the anatase–rutile transition. This is supported by XRD and TEM analyses, which have shown homogeneous and monodisperse distribution of nodular anatase nanoparticles (average size 8 nm) onto palygorskite fibers for sample annealed in air at 600 °C for 1 h.

This sample exhibits the highest photocatalytic activity against the removal of OG selected as model pollutant in aqueous solution, even compared to pure TiO₂ powders as commercial Degussa P25 and TiO₂ powder originating from xerogel route. All characterizations allow concluding that for this best photocatalyst sample (CTA⁺-Pal-Ti-600-1) the structural folding of palygorskite is not significant, the carbon contamination is minimized and the anatase nanoparticles are thermally stable, smaller than 10 nm, well dispersed and immobilized on the surface of palygorskite fibers. Besides, this supported photocatalyst easily flocculate so that it is readily removable from treated solutions. This work contributes to the valorization of natural clays and to the preservation of water by efficient treatment of waste waters.

Acknowledgements

The financial supports from the “Convention de coopération CNRST-Maroc/CNRS-France” (chemistry project No 04/08), the “Programme de Coopération Scientifique Interuniversitaire de l'Agence Universitaire de la Francophonie” (No 63 13PS826) and the “Programme d'Action Intégrée Volubilis” (No MA-08-185) are gratefully acknowledged. Authors thank Drs. E. Ruiz-Hitzky and P. Aranda (Instituto de Ciencia de Materiales de Madrid, CSIC, Spain) for fruitful discussions on clay minerals and Pr Mohamed Saïd Mehahed for his help in revising the English language of the paper.

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