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### **Title**

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### **Publication Date**

2008-08-05

Peer reviewed

**Synthesis of Hectorite-TiO<sub>2</sub> and Kaolinite-TiO<sub>2</sub> Nanocomposites with Photocatalytic Activity for the Degradation of Model Air Pollutants.**

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## **Abstract**

We studied the synthesis and photocatalytic activity of small-sized TiO<sub>2</sub> supported on hectorite and kaolinite. Deposition of TiO<sub>2</sub> on the clay mineral surface was conducted by using a sol-gel method with titanium isopropoxide as precursor. Anatase TiO<sub>2</sub> particles formation was achieved by hydrothermal treatment at 180 °C. Material characterization was conducted using XRD, SEM, XPS, ICP-OES, BET and porosimetry analysis. Efficiency in synthesizing clay-TiO<sub>2</sub> composites depended strongly on the clay mineral structure. Incorporation of anatase in hectorite, an expandable clay mineral, was found to be very significant (> 36 wt.% Ti) and to be followed by important structural changes at the clay mineral surface. Instead, no major structural modifications of the clay were observed for kaolinite-TiO<sub>2</sub>, as compared with the untreated material. Photocatalytic performance of clay-TiO<sub>2</sub> composites was evaluated with ATR-FTIR following the oxidation of adsorbed toluene and d-limonene, two model air pollutants. In either case, the photocatalytic removal efficiency of these hydrophobic substrates by the synthesized clay-TiO<sub>2</sub> composites was comparable to that observed using pure commercial TiO<sub>2</sub> (Degussa P25).

**Keywords:** photocatalysis, clays, hectorite, kaolinite, VOCs, toluene, d-limonene, titania, indoor pollutants.

## 1. Introduction

Heterogeneous photocatalytic oxidation of pollutants over TiO<sub>2</sub> surfaces has been widely employed for air and water remediation due to its effectiveness, lack of toxicity and low cost (Pichat, 2003; Hoffmann et al, 1995; Ollis and Al-Ekabi, 1993). TiO<sub>2</sub>-based photocatalysts are being increasingly used for indoor air cleaning in commercial applications (Hodgson et al., 2007), and are being tested as additives of cementitious building materials because of their self-cleaning properties and urban depollution potential (Strini et al., 2005). In this light, it becomes of interest to develop novel materials with enhanced photocatalytic performance for the removal of airborne organic pollutants. It is particularly critical to improve the degradation of hydrophobic compounds such as aromatic and aliphatic hydrocarbons, for which bare TiO<sub>2</sub> was shown to be less effective than for polar species (e.g., alcohols) (Hodgson et al., 2007).

In aqueous dispersions, clays have been used in combination with TiO<sub>2</sub> photocatalytic degradation to enhance the removal of organic pollutants (Mogyorósi et al, 2002). Intercalation of TiO<sub>2</sub> nanoparticles in the clay mineral structure is envisioned to entail benefits on the photocatalytic yields, providing resistance to aggregation. By hosting organic solutes and ensuring their effective interaction with TiO<sub>2</sub> particles and active oxidants generated upon light absorption, clay-TiO<sub>2</sub> composites can lead to increased photocatalytic activity (Kun et al, 2006; Mogyorósi et al, 2003; Kaneko et al., 2001; Yoneyama et al., 1989). Photocatalytic activity of TiO<sub>2</sub>-pillared clays has been reported in aqueous solution, but few studies evaluated the degradation of gaseous substances (Ooka et al., 2004; Pichat et al., 2005).

In this paper we describe the synthesis and characterization of small-sized TiO<sub>2</sub> particles supported on two different clay minerals using a novel method under mild conditions, which does not require stabilizing agents nor clay calcination. We performed a preliminary evaluation of their photocatalytic efficiency for the removal of two model hydrophobic VOCs, which are commonly present in indoor air: toluene and d-limonene (C<sub>10</sub>H<sub>16</sub>, 1-methyl-4-(1-methylethenyl)-(S)-cyclohexene). The photocatalytic performance of clay-TiO<sub>2</sub> composites was compared with that of a standard material (Degussa P25 TiO<sub>2</sub>).

## **2. Experimental**

### ***2.1. Materials***

Kaolinite (KGa-1b) from Washington County, Georgia, USA and hectorite (SHCa-1) from San Bernardino County, California, USA, were purchased from the Source Clays Repository of the Clay Minerals Society (Washington, DC) and have been characterized previously (Mermut and Cano, 2001). Both clay minerals were used as received. Tetraisopropoxide Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> (97%) was purchased from Sigma-Aldrich (USA), absolute ethanol (≥98%) from Riedel-de Haen (Switzerland), hydrochloric acid (reagent grade, 37%) from Aldrich (USA). All stock solutions were prepared using nanopure water (Barnstead utrapure water system, 17.6MΩ-cm). For the photocatalytic experiments toluene (Sigma-Aldrich, >99.5%) and d-limonene (Aldrich, 96%) were used as model reactants without further purification. Acetone (GC grade, B&J) was used as solvent. The photocatalytic performance of the samples was compared to that of TiO<sub>2</sub> (P25) from Degussa (Germany).

## ***2.2. Sample preparation***

### *2.2.1. TiO<sub>2</sub> sol stock dispersion.*

A TiO<sub>2</sub> sol stock dispersion was prepared by mixing titanium tetraisopropoxide, Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>, with hydrochloric acid, nanopure water and absolute ethanol, as reported elsewhere (Langlet et al., 2003). This sol dispersion showed the following characteristics: a Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> concentration C= 0.4 M, a H<sub>2</sub>O/ Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> molar ratio of 0.82, and a pH = 1.27. For preparation of nanocomposites, the TiO<sub>2</sub> stock dispersion was diluted with absolute ethanol to give a 0.05 M concentration of Ti(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>.

### *2.2.2. Clay-supported TiO<sub>2</sub>*

A clay-water dispersion (1% w/w) was stirred for 2 hours. An aliquot of TiO<sub>2</sub> sol was added to the dispersion, to obtain a final TiO<sub>2</sub> content of 70% w/w. The slurry was stirred for 24 hours. The resulting dispersion was centrifuged at 3,800 rpm for 10 minutes. The solid phase was washed with nanopure water followed by triplicate centrifugation. The resulting clay-TiO<sub>2</sub> composite was dispersed in a 1:1 water: ethanol solution, prior to hydrothermal treatment in an autoclave at 180°C for 5 hours. The product was centrifuged once again at 3,800 for 15 minutes, and oven-dried at 60°C for 3 hours.

## ***2.3. Characterization***

The samples were analyzed using a Philips PW2400 wavelength dispersive x-ray fluorescence spectrometer. Sample morphology was studied using a scanning electron

microscope (SEM) JEOL JSM 5600LV, equipped with Noarn analytical system and a Cu K $\alpha$  monochromator from a Phillips (X'Pert) diffractometer. Surface elemental composition was obtained by X-ray photoelectron spectrometry (XPS) (PHI 5400 with Al X-ray source) performed on pellets prepared with each of the synthesized composites, as well as the reference material (P25). N<sub>2</sub>-BET and pore size distribution analysis of native and modified clays and of P25 was carried out using a surface gas adsorption analyzer (TriStar 3000, Micromeritics).

Total (bulk) Ti content in the kao-TiO<sub>2</sub> and hecto-TiO<sub>2</sub> samples was determined in digested samples by Inductive Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis with a Perkin Elmer Optima 5300 DV. Two samples of kao-TiO<sub>2</sub> and two samples of hecto-TiO<sub>2</sub> were digested in a 3:1 mixture of 29 M HF and 15 M HNO<sub>3</sub> in Teflon digestion cups by heating on a hot plate for 48 hours. Samples were dried down and treated with ~2 drops of HNO<sub>3</sub> and then 2 drops of HClO<sub>4</sub>. Samples were then treated with aqua regia (3:1 HCl + HNO<sub>3</sub>). Digested samples were then dried in oven to constant mass at 100 °C and cooled to room temperature in a desiccator. Upon cooling, 2% HNO<sub>3</sub> with trace HF were added, dried a second time, and after cooling 0.1% HF was added to completely dissolve the samples. Duplicate samples were used for ICP-OES (Inductive Coupled Plasma – Optical Emission Spectroscopy) by dilution ~1:2 for kao-TiO<sub>2</sub> and ~1:20 for hecto-TiO<sub>2</sub>. Each sample was analyzed using 5 replicates, and the relative standard deviation was at 2% and less, indicating the results being in the 95% confidence interval.

#### ***2.4. Evaluation of photocatalytic activity***

The photocatalytic activity of the clay-TiO<sub>2</sub> composites and P25 was evaluated using Attenuated Total Reflection Fourier Transformed Infrared Spectroscopy (ATR-FTIR), following a method described for aqueous systems (Mendive et al., 2001). The ATR flow cell used in this study (illustrated in Fig. 1) consisted on a flat 4-cm<sup>2</sup> ZnSe crystal covered by an airtight enclosure provided with a quartz window. A thin layer of each tested material was deposited on the surface of the ATR crystal by applying 1–2 mL of a suspension of the photocatalyst in acetone, and allowing for complete evaporation of the solvent. The amount of photocatalyst used in each study was determined gravimetrically with a precision of 1-5 %. The films mass was typically between 10 and 30 mg, corresponding to estimated average film thickness of 3-6 μm. Toluene and d-limonene were used as test compounds in the determination of the photocatalytic removal efficiency of the clays. Toluene was applied directly on the surface of the film, while d-limonene was mixed with the suspension of the photocatalyst in acetone. In the case of toluene, the film was irradiated under static ambient air (RH ~40%). For d-limonene, a 2 mL/min flow of ambient air was circulated over the film before and during UV irradiation. Irradiation of the samples was performed with a longwave UV light ( $\lambda_{\text{max}} = 360 \text{ nm}$ ) with an irradiance on the film surface of 1.4 mW cm<sup>-2</sup>. FTIR spectra were collected using a Nicolet Magna 760 spectrophotometer with a MCT-A detector and a KBr beamsplitter, in the range 4000-650 cm<sup>-1</sup>. Spectra of surface-bound species were collected before and during irradiation at time intervals of 2-20 min. FTIR signatures corresponding to toluene and d-limonene were used to determine their photocatalytic surface depletion rate. Quantitative analysis of toluene surface concentration during

irradiation was carried out at  $3027\text{ cm}^{-1}$ , without interference from other matrix bands. For d-limonene, the band at  $2917\text{ cm}^{-1}$  was chosen to monitor its depletion from the surfaces due to photocatalytic oxidation.

### **3. Results and discussion**

#### ***3.1. Structural properties***

Figures 2 show XRD patterns for the hectorite samples. Spectra for hecto-TiO<sub>2</sub> (Fig. 2b) exhibited characteristic reflections of anatase ( $\gamma$ -TiO<sub>2</sub>, namely,  $25.3^\circ$ ,  $37.9^\circ$ ,  $47.6^\circ$ ,  $54.8^\circ$   $2\Theta$ ), same as P25 (Fig. 2c), in comparison with hectorite (Fig. 2a). Also the presence of calcite as a common impurity was observable in (Fig. 2b) ( $2\Theta = 29.4^\circ$ ) while the clay mineral pattern decreased in intensity. Diffractograms of the kaolinite samples are shown in Figure 3. By contrast with hectorite, reflections of anatase in the kao-TiO<sub>2</sub> sample, were not well-defined and superimposed with the typical kaolinite reflections. Changes in the kaolinite pattern before and after the insertion of TiO<sub>2</sub> are evident (Fig. 3), but the incorporation of anatase is not indicated. The basal spacing of the original and modified clay minerals did not show significant changes indicating that the TiO<sub>2</sub> nanoparticles are not situated in the interlayer space of the clays. The basal spacing value for both native and modified samples were  $4.5\text{ \AA}$  and  $7.1\text{ \AA}$  for hectorite and kaolinite, respectively.

The temperature of  $180^\circ\text{C}$  involved in the synthesis did not modify the native clay mineral structure (Guggenheim and Koster van Groos, 2001; González Jesús et al., 2000). Instead, temperatures in excess of  $900\text{ }^\circ\text{C}$  would be required to produce any irreversible change (Murad, 2003; Dubois et al., 1995). Therefore the prepared clay-TiO<sub>2</sub> composites were compared to the native clay minerals without further thermal treatment.

Figure 4 shows SEM images of the hectorite samples before and after TiO<sub>2</sub> addition. Images indicate changes in surface morphology after treatment, in consistency with TiO<sub>2</sub> incorporation into the clay mineral aggregates. No changes were observed for the kaolinite samples (Fig. 5).

EDS analysis conducted on the surface of hecto-TiO<sub>2</sub> and kao-TiO<sub>2</sub> revealed the presence of Si, Ti, O, Mg, Ca atoms, and O, Si, Al, Ti atoms, respectively. Because surface heterogeneity was evident, no attempts of obtaining quantitative information of surface composition were made.

### ***3.2. Bulk and surface TiO<sub>2</sub> composition***

Bulk Ti concentration data indicated significant anatase incorporation into hectorite, but not into kaolinite, for which Ti levels were comparable before and after TiO<sub>2</sub> addition (Table 1). As determined by XPS, surface Ti in hecto-TiO<sub>2</sub> and kao-TiO<sub>2</sub> were found to be 2.7% and 1 % (atomic ratio), respectively.

### ***3.3. BET and porosimetry analysis***

In the case of hectorite, TiO<sub>2</sub> deposition contributed to a ~130% increase of the specific BET surface area and the surface area of hecto-TiO<sub>2</sub> was much larger than that determined for P25. By contrast, the specific surface area of kaolinite was relatively small, and only increased by ~30% after TiO<sub>2</sub> deposition, remaining in levels that were

significantly lower than P25. BJH-pore area distribution changes upon TiO<sub>2</sub> deposition are shown in Figure 6 and Table 1. For hectorite, most of the new specific pore surface corresponded to the smallest pores (below 30 nm, with a significant fraction below 10 nm). For kao-TiO<sub>2</sub> most of the new pore surface area generated during the synthesis was related to the larger pores (> 100 nm).

### **3.4. Photocatalytic activity**

#### *3.4.1. FTIR spectra of toluene.*

The initial FTIR spectra of toluene and d-limonene adsorbed on each of the studied photocatalysts is shown in Figure 7. In Figure 7a, we illustrate characteristic bands for toluene at (1) 3100-2800 cm<sup>-1</sup>, (2) 1700-1400 cm<sup>-1</sup>, (3) 1100-1000 cm<sup>-1</sup>, and (4) 750-680 cm<sup>-1</sup> assigned to alkyl and aromatic C-H stretching vibration, C-C stretching mode of the aromatic ring, C-H in-plane bending, and C-H out of plane bending vibrations, respectively.

Toluene spectra adsorbed on P25 film showed bands corresponding to toluene exclusively, and a broad absorption band of P25 below 900 cm<sup>-1</sup>. Similar features were observed for toluene adsorbed on hectorite-TiO<sub>2</sub>, where the broad signal at 1000-1200 cm<sup>-1</sup> corresponds to absorbance of the silicate framework. Samples of kao-TiO<sub>2</sub> showed intense kaolinite bands in the regions 3750-3600 cm<sup>-1</sup> and 1200-900 cm<sup>-1</sup>, the latter as in hectorite corresponding to the asymmetric stretching vibration of Si-O-Si groups.

#### *3.4.2. FTIR spectra of d-limonene.*

The characteristic bands are at (1) 3000-2800  $\text{cm}^{-1}$  and (2) 1700-1300  $\text{cm}^{-1}$  corresponding to C-H stretching, and C-C stretching and C-H bending vibrations, respectively (Figure 7b). Figure 8 exemplifies spectral changes occurring due to irradiation of d-limonene adsorbed onto hecto-TiO<sub>2</sub> surfaces.

#### 3.4.3. Photooxidation of toluene and d-limonene.

The observed pseudo-first order photooxidation rate constants normalized with the film mass ( $k/m$ ) and with the TiO<sub>2</sub> mass ( $k/m'$ ), were calculated from the time-dependent concentration changes of each material, and are listed in Table 1. The latter shows clearly that, in the case of kaolinite composites, a small proportion of TiO<sub>2</sub> caused the largest relative effect. The reaction kinetics depended on the initial concentration of analyte. For the case of d-limonene, since the initial concentration was higher, the kinetics was initially of zeroth-order, then of pseudo-first order. For toluene, only pseudo-first order kinetics was observed. Data reported in Table 1 correspond to pseudo-first order rates for both compounds. Growth of new FTIR signatures corresponding to formation of surface-bound d-limonene oxidation products was observed in the range 1720-1590  $\text{cm}^{-1}$  (Figure 9). Absorption at 1716  $\text{cm}^{-1}$  likely corresponded to the formation of a surface-bound oxidation byproduct containing a C=O group, and signals near 1600  $\text{cm}^{-1}$  to byproducts containing carboxylate groups. The relative intensity of these byproduct signals varied between P25 and clay-TiO<sub>2</sub> substrates, suggesting that reaction mechanisms and product stability were different in each case. The ATR-FTIR method used in this study did not allow observing the spectral signature of volatile oxidized species such as formaldehyde or CO<sub>2</sub> (a mineralization product), which do not remain adsorbed onto the photocatalyst

film. Benzaldehyde has been reported as one of the primary products of photocatalytic oxidation of toluene (d'Hennezel et al, 1998; Disdier et al, 2005). However, our method did not allowed to detect surface-bound benzaldehyde, if this byproduct was formed during reaction of toluene.

It is worth noting that IR signatures corresponding to the clay minerals functional groups remained unchanged over the course of the experiment. In contrast, intensity of the IR characteristic bands of toluene or d-limonene decreased as a function of irradiation time.

#### **4. Conclusions**

The efficiency in synthesizing clay-TiO<sub>2</sub> composites depended on the clay mineral structure. Incorporation of anatase in hectorite was found to be very significant (> 36 wt.% Ti) and led to morphological changes (Figure 4). Hecto-TiO<sub>2</sub> composites favored the adsorption and enhanced the photocatalytic degradation of VOCs. Deposition of TiO<sub>2</sub> on the external surface of kaolinite was modest, however the photocatalytic activity was enhanced. For either composite, the photocatalytic activity was similar to that of the P25 TiO<sub>2</sub> particles.

#### **Acknowledgements**

DK thanks the support of a DGAPA-UNAM scholarship. The authors express gratitude to P. Fernandez and P. Santiago-Jacinto (UNAM) for technical support, to R. Hernandez-Reyes (UNAM, SEM), to D. Lucas and A.T. Hodgson (LBNL-EETD), to B.

Gilbert (LBNL-ESD) for XRD data acquisition and interpretation, to M. Salmeron and V. Altoe (LBNL-MSD, XPS), to J.T. Larsen (LBNL-ESD, ICP-OES) and to V. Battaglia and X. Song (LBNL-EETD, BET analysis). This project was supported in part by UNAM (PAPIIT Project No: IN116007-2) and by LBNL (LDRD Project # 366088). All work at LBNL was conducted under US DOE Contract No. DE-AC02-05CH11231.

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## List of figures

Figure 1. ATR-FTIR photocatalytic flow reactor. (page 7)

Figure 2. XRD patterns of (a) hectorite; (b) hecto-TiO<sub>2</sub>; (c) P25. (page 8)

Figure 3. XRD patterns of kaolinite, kao-TiO<sub>2</sub> and their difference. (page 8)

Figure 4. SEM images: (a) hectorite; (b) hecto-TiO<sub>2</sub>. (page 8)

Figure 5. SEM images: (a) kaolinite; (b) kao-TiO<sub>2</sub>. (page 8)

Figure 6. Pore area distribution. (a) hectorite and hecto-TiO<sub>2</sub>; (b) kaolinite and kao-TiO<sub>2</sub>; (c) P25. (page 9)

Figure 7. ATR-FTIR spectra corresponding to (a) toluene and (b) d-limonene adsorbed on P25, kao-TiO<sub>2</sub> and hecto-TiO<sub>2</sub> films. (page 10)

Figure 8. Spectra of d-limonene adsorbed on hecto-TiO<sub>2</sub> during UV irradiation. On the insert: time dependent absorbance changes at 2917 cm<sup>-1</sup>. (page 10)

Figure 9. Time-dependent changes in the spectra of d-limonene and its surface-bound oxidation products adsorbed to (a) P25 film; (b) hecto-TiO<sub>2</sub> film. (page 11)

**Table 1.**

**Characterization and photocatalytic performance of clay-TiO<sub>2</sub> composites, P25 (reference) and native clay minerals.**

	<b>Hecto-TiO<sub>2</sub></b>	<b>Kao-TiO<sub>2</sub></b>	<b>P25</b>	<b>Hectorite</b>	<b>Kaolinite</b>
<b>TiO<sub>2</sub> size (nm)</b>	9.6	n.d. <sup>(a)</sup>	17.4	–	–
<b>BET surface area (m<sup>2</sup> g<sup>-1</sup>)</b>	139.5	15.9	60.7	59.9	12.5
<b>Average pore volume (cm<sup>3</sup> g<sup>-1</sup>)</b>	0.457	0.670	0.308	0.105	0.091
<b>Average pore width (nm)</b>	10.5 – 11.0	125 – 136	19.5 – 21.4	11.4 – 13.1	25.2 – 27.4
<b>Ti content (wt.%)</b>	36.4 ± 1.6	1.72 ± 0.07	59.9 <sup>(b)</sup>	0.039 ± 0.005 <sup>(c)</sup>	1.674 ± 0.004 <sup>(c)</sup>
<b>Surface elemental composition by XPS (%)</b>	<b>O</b> 67.5 <b>Al</b> 16.7 <b>Mg</b> 5.9 <b>Si</b> 5.5 <b>Ti</b> 2.7 <b>Ca</b> 1.6	<b>O</b> 71.8 <b>Al</b> 17.7 <b>Si</b> 9.5 <b>Ti</b> 1.0	<b>O</b> 79.6 <b>Ti</b> 20.4	n.d.	n.d.
<b>Oxidation rate per film mass 10<sup>3</sup> x k/m (min<sup>-1</sup> mg<sup>-1</sup>)</b>	0.709 (T) 1.04 (L)	0.677 (T) 0.590 (L)	0.639 (T) 1.33 (L)	no reaction	0.108 (L)
<b>Oxidation rate per TiO<sub>2</sub> mass 10<sup>3</sup> x k/m' (min<sup>-1</sup> mg<sup>-1</sup>)</b>	1.16 (T) 1.71 (L)	23.6 (T) 20.5 (L)	0.639 (T) 1.327 (L)	no reaction	3.86 (L)

n.d.: not determined; T: results for toluene; L: results for d-limonene.

(a) due to poor XRD resolution; (b) stoichiometric value; (c) Mermut and Cano, 2001.