



Synthesis of hectorite–TiO₂ and kaolinite–TiO₂ 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 TiO₂ supported on hectorite and kaolinite. Deposition of TiO₂ on the clay mineral surface was conducted by using a sol–gel method with titanium isopropoxide as precursor. Anatase TiO₂ 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–TiO₂ 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–TiO₂, as compared with the untreated material. Photocatalytic performance of clay–TiO₂ 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–TiO₂ composites was comparable to that observed using pure commercial TiO₂ (Degussa P25).

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1. Introduction

Heterogeneous photocatalytic oxidation of pollutants over TiO₂ surfaces has been widely employed for air and water remediation due to its effectiveness, lack of toxicity and low cost (Ollis and Al-Ekabi, 1993; Hoffmann et al., 1995; Pichat, 2003). TiO₂-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 pollu-

nants. It is particularly critical to improve the degradation of hydrophobic compounds such as aromatic and aliphatic hydrocarbons, for which bare TiO₂ 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 TiO₂ photocatalytic degradation to enhance the removal of organic pollutants (Mogyorósi et al., 2002). Intercalation of TiO₂ 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 TiO₂ particles and active oxidants generated upon light absorption, clay–TiO₂ composites can lead to increased photocatalytic activity (Yoneyama et al., 1989; Kaneko et al., 2001; Mogyorósi et al., 2003; Kun et al., 2006). Photocatalytic activity of TiO₂-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 TiO₂ 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

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evaluation of their photocatalytic efficiency for the removal of two model hydrophobic VOCs, which are commonly present in indoor air: toluene and *D*-limonene ($C_{10}H_{16}$, 1-methyl-4-(1-methylethenyl)-(S)-cyclohexene). The photocatalytic performance of clay-TiO₂ composites was compared with that of a standard material (Degussa P25 TiO₂).

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(OC₃H₇)₄ (97%) was purchased from Sigma-Aldrich (USA), absolute ethanol ($\geq 98\%$) from Riedel-de Haen (Switzerland), hydrochloric acid (reagent grade, 37%) from Aldrich (USA). All stock solutions were prepared using nanopure water (Barnstead ultrapure water system, 17.6 M Ω -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 TiO₂ (P25) from Degussa (Germany).

2.2. Sample preparation

2.2.1. TiO₂ sol stock dispersion

A TiO₂ sol stock dispersion was prepared by mixing titanium tetraisopropoxide, Ti(OC₃H₇)₄, with hydrochloric acid, nanopure water and absolute ethanol, as reported elsewhere (Langlet et al., 2003). This sol dispersion showed the following characteristics: a Ti(OC₃H₇)₄ concentration $C=0.4$ M, a H₂O/Ti(OC₃H₇)₄ molar ratio of 0.82, and a pH=1.27. For preparation of nanocomposites, the TiO₂ stock dispersion was diluted with absolute ethanol to give a 0.05 M concentration of Ti(OC₃H₇)₄.

2.2.2. Clay-supported TiO₂

A clay-water dispersion (1% w/w) was stirred for 2 h. An aliquot of TiO₂ sol was added to the dispersion, to obtain a final TiO₂ content of 70% w/w. The slurry was stirred for 24 h. The resulting dispersion was centrifuged at 3800 rpm for 10 min. The solid phase was washed with nanopure water followed by triplicate centrifugation. The resulting clay-TiO₂ composite was dispersed in a 1:1 water: ethanol solution, prior to hydrothermal treatment in an autoclave at 180 °C for 5 h. The product was centrifuged once again at 3800 rpm for 15 min, and oven-dried at 60 °C for 3 h.

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 Noam analytical system and a Cu K α 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). N₂-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-TiO₂ and hecto-TiO₂ 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-TiO₂ and two samples of hecto-TiO₂ were digested in a 3:1 mixture of 29 M HF and 15 M HNO₃ in Teflon digestion cups by heating on a hot plate for 48 h. Samples were dried down and treated with ~2 drops of HNO₃ and then 2 drops of HClO₄. Samples were then treated with aqua regia (3:1 HCl+HNO₃). Digested samples were then dried in oven to constant mass at 100 °C and cooled to room temperature in a desiccator. Upon cooling, 2% HNO₃ 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

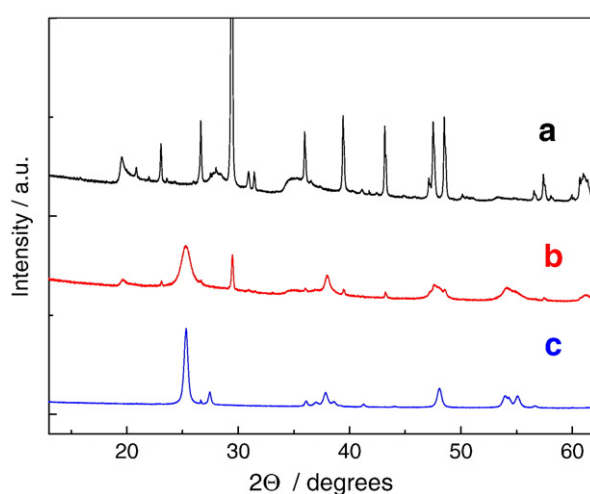


Fig. 2. XRD patterns of (a) hectorite; (b) hecto-TiO₂; (c) P25.

Emission Spectroscopy) by dilution ~1:2 for kao-TiO₂ and ~1:20 for hecto-TiO₂. 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-TiO₂ 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-cm² 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 μ m. 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 ($\lambda_{max}=360$ nm) with an irradiance on the film surface of 1.4 mW cm⁻². 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⁻¹. 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 cm⁻¹, without interference from other matrix bands. For *D*-limonene, the band at 2917 cm⁻¹ was chosen to monitor its depletion from the surfaces due to photocatalytic oxidation.

3. Results and discussion

3.1. Structural properties

Fig. 2 show XRD patterns for the hectorite samples. Spectra for hecto-TiO₂ (Fig. 2b) exhibited characteristic reflections of anatase (γ -TiO₂,

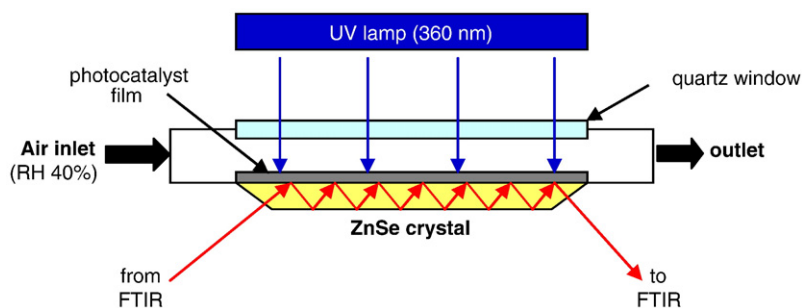


Fig. 1. ATR-FTIR photocatalytic flow reactor.

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