Synthesis and characterization of four new halloysite–TiO2 nanocomposites.

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SYNTHESIS AND CHARACTERIZATION OF FOUR NEW HALLOYSITE–TiO$_2$ NANOCOMPOSITES

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Abstract

The synthesis as well as the characterization of small-sized TiO$_2$ particles supported on Halloysite are presented. Halloysite from Utah, USA as well as from Limnos, island Greece, were used to synthesize two nanocomposites for each halloysite with TiO$_2$ to halloysite weight ratios of 80:20 and 60:40 and compare with published data of well formed nanocomposites of intermediate proportion (70:30) that were previously studied. All nanocomposites were prepared by deposition of anatase (TiO$_2$) on the halloysite tubes using a sol–gel method under hydrothermal treatment at 180 °C. Phase composition, particle morphology and physical properties of these samples were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Attenuated Total Reflection using Fourier Transform Infrared spectroscopy (ATR-FTIR) and N$_2$ surface area analysis by BET. Preparation of all halloysite–TiO$_2$ nanocomposites led to the anticipated good dispersion of anatase particles on halloysite surfaces. ATR-FTIR results revealed the formation of hydrogen bonding between anatase and the outer surfaces of halloysite tubes. All halloysite-TiO$_2$ nanocomposites largely showed interparticle mesopores of about 5.7nm and high SSAs.

Key words: Anatase, clay minerals, Photocatalytic activity.
1. Introduction

It is well known that TiO$_2$ nanoparticles have good catalytic activities because of their large specific surface areas where reactions take place (Zhao et al., 2006). Titanium dioxide, especially in the form of anatase, has proven to be the most suitable semiconductor for widespread environmental applications such as the degradation of oil spills and the decomposition of many organic molecules as well as other air pollutants (Hoffmann et al., 1995; Michael et al., 1995; Fujishima et al., 2000; Martínez-Ortiz et al., 2003). TiO$_2$ powders, however, easily agglomerate into larger particles, reducing their photocatalytic activities (Zhao et al., 2006).

Clay minerals are attractive materials for adsorption and catalysis (Chmielarz et al., 2011) and when composited with TiO$_2$, they have been used in aqueous dispersions to enhance the removal of organic pollutants by photocatalytic degradation (Mogyorósi et al., 2002; Kibanova et al., 2009), as well as to increase the photocatalytic activities in decomposing air pollutants (e.g. Nikolopoulou et al., 2009; Papoulis et al., 2010; Papoulis et al., 2013a; Papoulis et al., 2013b). Previous investigations revealed that using clay minerals with microfibrous (Aranda et al., 2008; Karamanis et al., 2011) or tubular morphology (Papoulis et al., 2010; Papoulis et al., 2013a; Papoulis et al., 2013b) as a template and TiO$_2$ as the photocatalyst led to significantly increased TiO$_2$ photocatalytic activity in decomposing many pollutants.

The dispersion of anatase nanoparticles onto halloysite surfaces under mild conditions is a promising method to resolve the agglomeration problem of TiO$_2$ (Papoulis et al., 2010; Papoulis et al., 2012). Recent studies showed that halloysite-TiO$_2$ nanoparticles have excellent photocatalytic activities in decomposing both inorganic and organic air pollutants (Papoulis et al., 2010; Papoulis et al., 2013b).

In present work, we describe the synthesis and characterization of nano-sized TiO$_2$ particles supported on two different halloysites (weight ratios of TiO$_2$ to Halloysite were 80:20 and 60:40) by using a novel method under mild conditions, which does not involve calcinations or stabilizing agents. The results are compared with recently published data for well prepared nanocomposites of different TiO$_2$-Halloysite proportions (70-30) that show very high photocatalytic activities in decomposing air and organic pollutants (Papoulis et al., 2013b). The aim of this study was to prepare well formed clay-based nanocomposites that could have increased photocatalytic efficiency in decomposing inorganic and organic air pollutants.

2. Materials and Methods

2.1. Sample Preparation

A halloysite sample from Utah, USA and a halloysite sample from Limnos island were used in this study. Both the samples were size fractionated to obtain <2 μm by gravity sedimentation followed by centrifugation to separate solid from liquid.

2.2. TiO$_2$ Stock Sol Dispersion

A TiO$_2$ sol dispersion was prepared by mixing titanium tetraisopropoxide, Ti(OC$_3$H$_7$)$_4$, with hydrochloric acid, nanopure water (3D) and absolute ethanol (Langlet et al., 2003). The TiO$_2$ stock dispersion was diluted in absolute ethanol to give a 0.05 M concentration of Ti(OC$_3$H$_7$)$_4$. 

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2.3. Halloysite-supported TiO$_2$

An aliquot of TiO$_2$ sol was stirred for 2 h and then the (1% w/w) halloysite-water dispersion was added to the TiO$_2$ dispersion in order to obtain the desirable TiO$_2$ content. The slurry was stirred for 24 h and the resulting dispersion was centrifuged for 10 min (3800 rpm) followed by three times centrifuge washing (with 3D water). The halloysite–TiO$_2$ composites were then dispersed in a 1:1 water:ethanol solution, prior to hydrothermal treatment in an autoclave for 5 h at 180 °C. The products were centrifuged for 15 min (at 3800 rpm) and oven-dried for 3 h (at 60 °C).

2.4. Characterization

The phase compositions of untreated and TiO$_2$ treated halloysite samples were determined by X-ray diffraction (using a Bruker D8 advance diffractometer, with Ni-filtered CuKα radiation). XRD patterns were obtained from oriented or random powder samples in a 2θ range of 2° to 60° at a scanning rate of 2°/min. Random powder mounts for selected samples were prepared by gently pressing the powder into the cavity holder. Oriented clay powder samples were prepared by the dropper method. Halloysite-TiO$_2$ morphology was examined with a SEM LEO SUPRA 35VP.

Attenuated total reflection infrared (ATR/FTIR) measurements were made with the ATR Miracle accessory of PIKE technologies (diamond crystal) attached to the EQUINOX 55 FT-IR spectrometer ( Bruker). Nitrogen adsorption-desorption isotherms for each sample degassed at 100 °C for 3 hours were obtained at 77K using Autosorb$^1$ (Quantachrome corporation). Brunauer-Emmet-Teller (BET) surface areas and pore size distribution were determined from the isotherms. Pore size distribution of each sample was obtained using density functional theory (DFT) method in which a N$_2$ adsorption branch model was selected.

3. Results and Discussion

3.1. X-Ray Diffraction

Both halloysite samples (from Utah and Limnos island), as it has been reported in previous studies, are pure with no detectable impurities, if any (not detected by XRD) (Papoulis et al., 2013b). Figure 1 shows the XRD patterns of the four nanocomposites prepared in this study from both halloysites compared with nanocomposites 70-30. All patterns show the presence of dehydrated halloysite and anatase, confirming their phase purity (Figure 1). The XRD patterns of all nanocomposites showed all the characteristic reflections of anatase ($\gamma$-TiO$_2$) at 25.3°, 37.9°, 47.6°, 54.8° 2θ, which intensity decreasing by decreasing TiO$_2$ amount. Additionally the intensity of the 001 reflection of dehydrated halloysite is increasing with increasing amount of dehydrated halloysite. The XRD patterns also indicated that the temperature of 180 °C involved in the synthesis of halloysite-TiO$_2$ nanocomposites did not modify the native mineral structure of dehydrated halloysite. It is well known that heating halloysite at 100-350 °C sharpens the basal reflection (001) and reduces the spacing but never to as low as the characteristic reflection of kaolinite (7.14 Å) (Brindley and Robinson, 1946; Joussein et al., 2005). In this study, the basal reflections of both halloysites after treatment were detected at 7.29 Å (Figure 1).

3.2. ATR-FTIR Spectra

The ATR-FTIR spectra of all four TiO$_2$-treated halloysites compared with nanocomposites 70-30 from both areas are generally similar (Figure 2), while the intensities of halloysite reflections are lower in the nanocomposites and especially in the nanocomposites with the lower amounts of halloysite (20%) in them. The reflections of the spectra confirm that the structures of both dehydrated halloysites were not changed after treating with TiO$_2$. None of the characteristic bands of dehydrated halloysite (Joussein et al., 2005; Bobos et al., 2001) were affected except the Si–O broad stretching band which shifted from about 997 cm$^{-1}$ (Papoulis et al., 2010) to more than 1000 cm$^{-1}$ (Figure 2) in all nanocomposites. The shifting of the Si–O broad stretching band increased with increasing amount of anatase (Figure 2). This shift is an indication of the formation of...
hydrogen bonding between TiO$_2$ and the outer surfaces of halloysite tubes (tetrahedral sheet) which becomes stronger in the more anatase rich nanocomposites. The ATR-FTIR spectra of all nanocomposites confirmed that the treatment temperature of 180°C during the synthesis of halloysite-TiO$_2$ nanocomposites did neither destroy halloysites nor modified their native dehydrated halloysite mineral structure.

Figure 1 – XRD patterns of the four new Halloysite-TiO$_2$ nanocomposites (60-40, 80-20) from both areas compared with the two previously studied nanocomposites (70-30) a) nanocomposites using halloysite from Utah and b) nanocomposites using halloysite from Limnos (H: halloysite, A: anatase).

Figure 2 – ATR-FTIR Spectra of Halloysite-TiO$_2$ nanocomposites compared with the two previously studied nanocomposites (70-30) (Lim: Limnos).

3.3. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

In this investigation we present SEM micrographs of the four nanocomposites compared with nanocomposites 70-30 (Figure 3), while the morphologies of both halloysites have already been previously reported by us (Papoulis et al., 2010; Papoulis et al., 2013b). It should be noted that the halloysite tubes from Limnos island appear to be well formed (Papoulis et al., 2010), while those from Utah are not curved and rolled up that perfectly. The latter morphology, therefore, suggests
that more halloysite surfaces are available for TiO$_2$ nanoparticles to be dispersed in the sample from Utah (Papoulis et al., 2013b).

SEM observations of all nanocomposites showed that many uniform TiO$_2$ grains of about 10-30 nm were deposited on the external surfaces of halloysite tubes of all nanocomposites (Figure 3). The TiO$_2$ nanoparticles were found to be distributed very well on both halloysite external surfaces but not homogeneously (Figure 3) although homogeneous distribution of TiO$_2$ grains on halloysite tubes was anticipated (Papoulis et al., 2013b). TiO$_2$ nanoparticles seem to cover, at least partially, the lumen of most halloysite tubes (Figure 3). By increasing the amount of TiO$_2$ content, the deposited TiO$_2$ particles were found to be aggregated on the surfaces of the halloysite tubes (Figure 3) while decreasing the amount of TiO$_2$ led to aggregation of halloysite tubes from both sources.

**Figure 3 – SEM micrographs of Halloysite-TiO$_2$ nanocomposites from Utah (a: 60-40, b: 70-30, c: 80-20) and Limnos island (d: 60-40, e: 70-30, f: 80-20) (arrows: anatase nanoparticles partially covering halloysite lumen).**
3.4. Determination of Specific Surface Areas (SSAs) and Porosity

Adsorption–desorption isotherms of nitrogen and pore size distributions for all four halloysites–TiO$_2$ nanocomposites compared with nanocomposites 70-30 are presented in Figures 4 and 5 and Figures 6 and 7, respectively. The isotherm shapes for all nanocomposites are of the same type (type IV) indicating both meso and micropores (IUPAC classification, 1994) (Sing et al., 1985; Sing et al., 2004). The different size of the hysteresis observed is due to the different proportions of halloysite and anatase, two minerals with major differences in size, shape and SSA. Additionally the two different halloysites are characterized by differences in size and SSA. The total pore volumes of the nanocomposites with halloysite from Utah were found to be significantly higher while the SSAs were found to be slightly smaller than those of the nanocomposites with halloysite from Limnos (Figures 6, 7). This could be attributed to the presence of more interparticle pores (macroporous) of the first samples while the second type of samples show more mesopores at about 5.7 nm (Figures 6, 7) and retained the higher SSA (of halloysite from Utah) due to a better TiO$_2$ distribution on halloysite external surfaces. All nanocomposites largely showed mesopores of about 5.7 nm, while the macropores found in starting halloysite material (Papoulis et al., 2010) were considerably reduced apparently due to partial covering of the lumen of halloysite tubes by TiO$_2$ nanoparticles.

![Figure 4 - Adsorption-desorption isotherms of nitrogen for nanocomposites using halloysite from Utah compared with the two previously studied nanocomposite (70-30).](image1)

![Figure 5 - Adsorption-desorption isotherms of nitrogen for nanocomposites using halloysite from Limnos compared with the previously studied nanocomposite (70-30).](image2)
4. Conclusions

Preparation of four new halloysite–TiO$_2$ nanocomposites using two different halloysites led to good dispersion of anatase on the external surfaces of halloysite tubes. Both halloysites were not destroyed by the treatment temperature, while the formation of hydrogen bonding between the outer surfaces of halloysite tubes and TiO$_2$ was detected. All nanocomposites largely showed interparticle mesopores of about 5.7nm. The characteristics of the nanocomposites presented here compared with the characteristics of already tested samples in different TiO$_2$-Halloysite proportion (70-30) that were presented in our recently published paper (Papoulis et al., 2013b) suggest promising photocatalytic activities in decomposing organic as well as inorganic air pollutants.

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6. References


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