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Highly photocatalytic activity of nanocrystalline TiO₂ (anatase, rutile) powders prepared from TiCl₄ by sol–gel method in aqueous solutions.

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ABSTRACT

In this piece of research, we have synthesized titanium dioxide (TiO₂) powders from titanium tetrachloride (TiCl₄) as an inorganic precursor by applying the sol–gel method. The effect of the calcination temperature in the range 400–800 °C on the photocatalytic performance of TiO₂ nanoparticles was studied. The samples were characterized by TEM, BET surface area measurement, DRS and XRD. They were then used for the photodegradation of two model pollutants – phenol and formic acid – under exposure to UV-A radiation. Despite the fact that the adsorption of both phenol and formic acid on the various TiO₂ nanomaterials followed the Langmuir model, their degradation kinetics followed the Langmuir–Hinshelwood model. The results emphasized a strong increase in the adsorption and in the photocatalytic activity with the TiO₂ calcined at 600 °C which was nearly 1.5 times higher than that of TiO₂-P25 in the case of formic acid. For the degradation of phenol, TiO₂-600 had a similar activity as TiO₂ P25. This is related to their tendency to degrade the intermediate products than the phenol itself. A formal mechanism scheme of phenol degradation has been proposed. The maximum photocatalytic efficiency was reached with the sample calcined at a temperature of 600 °C, while a further increase in temperature depleted the photocatalytic response.

The highest photocatalytic activity of the sample calcined at 600 °C can be attributed to the improvement of the crystallization and the optimal anatase/rutile ratio (96/4).

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1. Introduction

Over the last few decades, there has been a great interest in developing photocatalysts with high catalytic efficiency and good stability for water splitting and removal of organic compounds which have harmful effects on the environment such as the phenolic compounds (Turki et al., 2015), the domestic effluents (Saleh et al., 2016), the pesticides

and the heavy metals in industrial wastewater (Adio et al., 2017; Sani et al., 2017; Saleh and Danmaliki, 2015; Saleh and Al-Saadi, 2015).

To date, a lot of the research work has been interested in photocatalysis for environmental purification (Toumazatou et al., 2017). A heterogeneous photocatalytic system consists of semiconductor particles which are in close contact with a liquid or gaseous reaction medium. In fact, the first step of the photocatalytic process is the pho-

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togeneration of the electron–hole pairs in the semiconductor by light absorption with energy equal to or greater than the associated bandgap. Electrons and holes are capable of being available for redox reactions with the electron-donor or the electron-acceptor species adsorbed on the semiconductor surface (Saleh and Gupta, 2012, 2011; Guillard et al., 2004). Due to metal oxide semiconductors, photocatalysts act as standards for environmental sanitation (Yang et al., 2010).

TiO₂ which is among the most important semiconductors is an ideal photocatalyst owing to numerous advantages such as its excellent photostability, its good mechanical properties, its high selectivity as well as being economical, highly efficient, easily operable, non-toxic and eco-friendly (He et al., 2017; Cargnello et al., 2014). As a matter of fact, an overview of the literature shows that TiO₂ nanoparticles have recently received much attention in various fields, such as industry and academic research (Silva et al., 2015).

Up until now, many strategies have been conducted such as the control of the morphology, the crystalline phase and the crystalline structure with the aim of having very distinguished photocatalytic applications and improving the photocatalytic activity of TiO₂ (Wang et al., 2017). Naturally, TiO₂ consists of anatase, brookite and rutile. Among the three phases, anatase and rutile are the most common ones. The anatase phase generally has a higher photocatalytic performance compared with the other phases (Hamandi et al., 2017). Numerous studies have pointed out that TiO₂ crystals with different phase percentages show a distinct photocatalytic activity (Kho et al., 2010; Xu et al., 2014). Indeed, one of the most photoactive TiO₂ reference materials is TiO₂-P25 which has both anatase and rutile phases (80% and 20% respectively). Numerous studies have attempted to unravel the mechanism of the synergistic effect between anatase and rutile by mixing the phases of nanoparticles with different ratios that leads to many changes, such as the ratio, the structure, the crystallinity, the surface morphology and the particle size (Gao et al., 2014; Xu et al., 2014). The rutile phase has the highest density and is thermally the most stable one, whereas, the anatase is, generally, more photocatalytically active than the rutile (Tehare et al., 2017). Over the past two decades, the work on the phase control has drawn attention just like the synthesis of anatase/rutile TiO₂ (Hua and Lizhi, 2009). In particular, the crystallite phase-dependent synergistic effect is frequently encountered in photocatalysis in which mixed anatase–rutile phases have been reported to show higher activities (Sun et al., 2003). However, heat treatment is generally necessary to form crystallization which modifies the crystallized and thermodynamically stable rutile phase (Turki et al., 2013). Nevertheless, Kawahara et al. proved that, besides its crystallinity and its surface, the rutile–anatase phase junction significantly influences the effectiveness of TiO₂.

Various methods can be used to prepare TiO₂ such as the sol–gel method (Shahi et al., 2016), the electrochemistry (Li et al., 2015), the hydrothermal method (Li et al., 2012), Pulsed Laser Deposition (Millon, 2013) and so forth. The sol–gel method was chosen thanks to its smooth, simple, easy, inexpensive and very efficient operating conditions. In fact, crystalline nanoparticles with a remarkably high level of chemical purity can be made not only by adapting the chemical structure but also by using an inorganic precursor.

In this study, we developed TiO₂ nanoparticles with high photocatalytic activity via the sol–gel method using TiCl₄ as an inorganic titanium precursor. Moreover, the high performance of TiO₂ which has never been mentioned in the literature was due to the combination of three parameters: the use of an inorganic precursor, the calcination temperature and the anatase/rutile coupling. Thus, it is difficult to discover which parameter of these three plays an important role.

This work was devoted to the study of the thermal effect, the optimization of the anatase and rutile phases and the use of an inorganic precursor in the synthesis of TiO₂. The degradation of FA and phenol was studied to evaluate the photocatalytic performances of the synthesized materials. The obtained results were, then, compared to those of TiO₂-P25. The intermediate products of phenol were identified and measured throughout the mineralization tests in order to establish the formal mechanism of photodegradation more effectively.

2. Experimental

2.1. Chemicals

Titanium tetrachloride (TiCl₄) (99.99%) was bought from Sigma–Aldrich while absolute ethanol ($\geq 99.99\%$) was purchased from Merck Millipore (Germany). These reactants, the model pollutants (HCOOH) and phenol were all obtained from Acros Organics and used without further purification. Commercial TiO₂ P25 was bought from Evonik. Ultrapure water ($18\text{ M}\Omega\text{ cm}^{-1}$) was used all through the experiments.

2.2. Synthesis of photocatalysts

The TiO₂ nanoparticles were prepared using the sol–gel method described below. Indeed, 3.9 mL of TiCl₄ was slowly added to 10 mL of absolute ethanol in a reaction vessel. Because of the exothermic reaction, the high volatility of TiCl₄ and the release of hydrogen chloride, this reaction was carried out under fume hood at 0 °C under vigorous stirring. During the mixing process, 0.5 mL of water was then added. The above solution converted from a colorless into a yellow solution which produced TiO₂ nanopowders through the drying process at 85 °C in an oven for 15 h. The obtained TiO₂ nanopowders were eventually treated in a furnace for 2 h at different temperature values (400 °C–800 °C). The initial heating rate was kept at 5 °C/min.

2.3. Characterization

2.3.1. UV–vis diffuse reflectance spectroscopy (DRS)

The irradiance measurement was used to represent the luminous flux received by the photocatalysts. The measurements were taken by UV-Visible diffuse reflectance spectroscopy (DRS) using Avantes AvaSpec-2048 Fiber Optic Spectrometer equipped with a symmetrical Czerny–Turner design with 2048 pixel CCD Detector Array. The spectra were recorded from 250 to 800 nm. A barium sulfate (BaSO₄) was used as a white standard reference. A calibration is necessary before starting the measurements. The calibration lamp used was an Avantes AvaLight-DH-S which is a combined deuterium and halogen light source.

2.3.2. X-ray diffraction (XRD)

The X-ray diffraction (XRD) of each powdery sample was obtained on a PANalytical X'Pert Pro diffractometer with Cu K α radiation ($\lambda = 1.5418\text{ \AA}$) and graphite monochromator. The XRD estimation of the crystallite size was based on the Debye–Scherrer equation:

$$D = 0.9\lambda/\beta\cos\theta$$

where D is the mean grain size (nm), λ is the wavelength of the X-ray radiation (0.154 nm), β is the corrected full width at half maximum height and θ is the diffraction angle.

2.3.3. Specific surface area

The Brunauer–Emmett–Teller (BET) surface area of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 instrument. All the samples were degassed at 300 °C before nitrogen adsorption measurements. The multipoint BET method detected the BET surface area using the adsorption data in the 0.05–0.25 relative pressure (P/P₀) range.

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