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Preparation of TiO₂ Photocatalyst Using TiCl₄ as a Precursor and its Photocatalytic Performance

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Abstract: Titania (TiO₂) photocatalysts were prepared by aqueous hydrolysis of TiCl₄ and deposition with NaOH at 400-900°C. The powders obtained have been characterized using X-ray diffraction (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM). The photocatalytic activities of the samples were also examined using the degradation of β-naphthol as a model reaction. As the calcination temperature increases, the anatase and rutile crystallite sizes increase. TiO₂ powder calcined at 700°C exhibits much higher photocatalytic activity than commercial TiO₂ Degussa P-25. The photodegradation rate of β-naphthol using TiO₂ 700°C particles was faster than that using TiO₂ Degussa P-25 as photocatalyst by 2 times. Conversely, prolonged calcination at higher temperatures (900°C) is detrimental to photoactivity.

Key words: Heterogeneous photocatalysis, titania, preparation, photodegradation, β-naphthol

INTRODUCTION

Recently, Heterogeneous photocatalysis through illumination of aqueous suspensions of TiO₂ offers an advanced technology of wastewater treatments for its following advantages: chemical stability of semiconductor TiO₂ in aqueous media and in a wide range of pH values, cheap chemicals in use, no additives required (only oxygen from the air), total mineralization achieved for various organic pollutants, efficiency of photocatalysis with halogenated compounds which are sometimes very toxic to bacteria in biological water treatment (Parra *et al.*, 2002, 2004; Zhao *et al.*, 2004; Zhu *et al.*, 2004; Lee *et al.*, 2003; Taborda *et al.*, 2001; Lachheb *et al.*, 2002; Vulliet *et al.*, 2004; Florêncio *et al.*, 2004; Sivalingam and Madras, 2004; Aguado *et al.*, 2002). Heterogeneous photocatalysis consists of two important steps: the first step is the generation of active species (hole, electron and hydroxyl radical) by light excitation and the second step is the contact of active species with reactant by adsorption of reactant on the catalyst surface or diffusion of active species to the reactant.

There are many methods of producing TiO₂ nanopowders, such as chemical precipitation

(Dhage *et al.*, 2004; Tryba *et al.*, 2003), anodic spark deposition (Meyer *et al.*, 2004), spray pyrolysis (Abou-Helal and Seeber, 2002), sol-gel (Keshmiri *et al.*, 2004; Su *et al.*, 2004; Jung *et al.*, 2004) and hydrolysis (Gablenz *et al.*, 1998; Vorontsov *et al.*, 2001). However, the use of inorganic salt (chloride) precursor rather than organic alkoxide precursor not only can reduce the cost of synthesis, but also can avoid the use of organic solvent to decrease pollution.

The effect of post-heat-treatment temperature on the photoactivity becomes more significant factor, especially when titania is prepared by a liquid-phase reaction route (Chen *et al.*, 2003). The increase of crystallinity is considered as the major reason why the photoactivity is improved by elevating the calcination temperature (Chan *et al.*, 1999). However, very high calcination temperature results in aggregation and/or phase transformation and affects the microstructures as well as the properties of TiO₂ nanoparticles. Anatase-phase TiO₂ crystallites are generally found to be more active than rutile. Recently, it was found that anatase/rutile mixture (7/3) made the best photocatalyst for the oxidation of organic materials in the wastewater treatment (Su *et al.*, 2004).

One important consideration in the TiO₂-photocatalyzed reactions is the adsorption of the organic compounds on the surface of semiconductor particles. It has been reported that adsorption is a prerequisite in the photodegradation of organic compounds (Parra *et al.*, 2004).

The aim of this research is to study the correlation between photocatalytic activity of TiO₂ prepared from TiCl₄ via hydrolysis synthesis at higher temperatures and its several properties, including crystal size and possible reaction site on the surface of TiO₂. To examine the photocatalytic efficiency of the synthesized catalysts and compared with commercial TiO₂ Degussa P-25, photodecomposition of the β -naphthol, a prototype molecule, was studied.

MATERIALS AND METHODS

Materials: All chemicals were used as received without further purification. β -naphthol and titanium tetrachloride TiCl₄ supplied by Fluka (> 99% purity). Acetonitrile and barium hydroxide, respectively, were purchased from Solvachim and Merck. Titanium dioxide Degussa P-25, a known mixture of 80% anatase and 20% rutile form with an average particle size of 30 nm, nonporous with a reactive surface area of 50 \pm 10 m² g⁻¹ and a density of 3.85 g cm⁻³.

Preparation and characterization of catalysts: The nanocrystalline titania catalysts reported in this study have been prepared at room temperature by aqueous hydrolysis of TiCl₄ and precipitated by NaOH (10%). The resulting deposit (hydrated titanium hydroxide) was separated after 24 h by filtration and washed thoroughly with distilled water until the disappearance of Cl⁻ ions from the liquid (tested as AgCl). Subsequently, the solid was dried at 100°C for 24 h in a vacuum system to remove water and then calcined in air for 3 h at temperatures of 400, 700 and 900°C, respectively.

Crystalline phase, particle size and morphology of titania nanocrystals were investigated by X-ray diffraction analysis (XRD) and Scanning Electron Microscopy (SEM), respectively.

XRD was carried out using CuK α (λ = 1.5418 Å) radiation in a Siemens D5000 diffractometer provided with a thin film attachment. SEM measurements were performed using a Jeol apparatus (model T-330A) operating at 10 kV on specimens upon which a thin layer of gold or carbon had been evaporated.

An infrared absorption spectrophotometer (IR) Shimadzu IR-460 was used to determine the specific functional groups.

Irradiation experiments: The experiments were carried out in water at room temperature in a static batch photoreactor of ca. 2 L, consisting of a Pyrex cylindrical flask, open to air, with several apertures to ensure the measurement of pH and of temperature as well as the introduction of oxygen. UV-light was provided by a high pressure mercury lamp (Philips HPK, 125 W) and the infrared radiations were filtered by a circulating water cell (thickness, 2.2 cm) equipped with a Pyrex cut-off filter.

The volume of the aqueous solution introduced into photoreactor was 1 L and the optimum mass of catalyst was 1 g. This quantity was selected as it gives the optimal specific degradation rate using commercial TiO₂ Degussa P-25 as a reference (Assabbane *et al.*, 2000). The initial concentration of β -naphthol was 5 \times 10⁻⁴ mol L⁻¹. Before each photocatalytic test, the suspension at natural pH (~6) was stirred magnetically for 60 min to reach the adsorption equilibrium in the dark prior illumination. Centrifugation or Millipore filters (0.45 μ m diameter) were used to separate titania from the solution before analysis.

Analysis: The quantitative and qualitative analysis of the organic compounds in the samples was performed by high performance liquid chromatography HPLC (Jascotype). The wavelength of detector was 280 nm. A reverse-phase column (length, 25 cm; internal diameter, 4.6 mm) ODS-2 Spherisorb (Chrompack) was used. The mobile phase was composed of acetonitrile (80%) and doubly distilled water (20%). The flow rate was 0.4 mL min⁻¹.

Complete mineralization of organic samples to CO₂ is very often obtained by using the photocatalytic method. The kinetics of the evolution of CO₂ formed was followed by using the method of (Chemseddine and Boehm, 1990), which consists of flushing the CO₂ produced by oxygen into a flask containing 500 mL of barium hydroxide (1.2 \times 10⁻² mol L⁻¹) and to follow the conductivity of the solution with a conductimeter Orion model 150. CO₂ precipitates as BaCO₃, thus decreasing the ionic conductivity in water.

RESULTS AND DISCUSSION

Photocatalyst characterization: In Fig. 1 we show the XRD patterns of TiO₂ powders calcined at various temperatures (400, 700 and 900°C). All samples are crystalline. The XRD pattern of the powder formed at 400°C is characteristic of anatase structure. The XRD peaks become sharper as the calcination temperature is increased. When the TiO₂ was heated up to 700°C, the products became a mixture of anatase and rutile. This

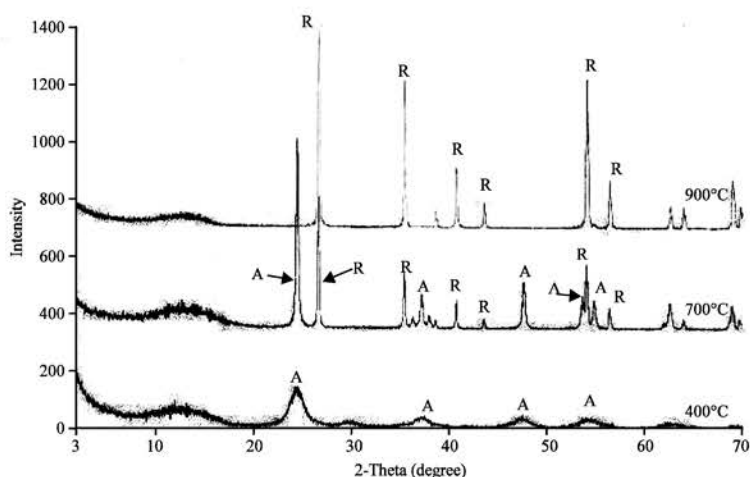


Fig. 1: XRD patterns of powders prepared at different calcination temperatures (A: Anatase, R: Rutile)

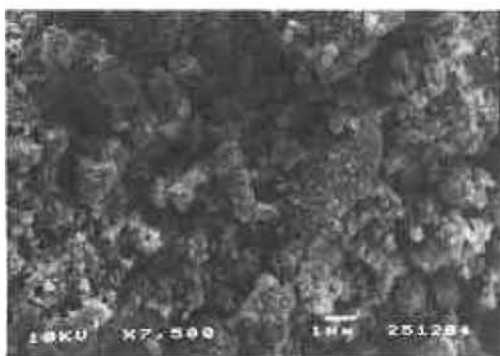


Fig. 2: SEM surface morphology of TiO₂ heat treated at 700°C

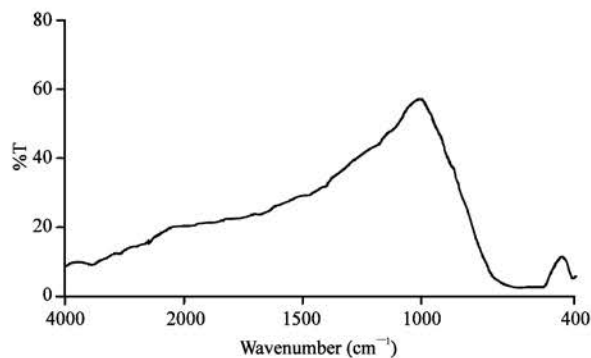


Fig. 3: IR spectrum of TiO₂ powder prepared at 700°C

suggests that there is a phase transformation from anatase to rutile (A-R) which agrees with previous experiments (Su *et al.*, 2004; Chen *et al.*, 2003). The primary formed TiO₂ particles usually contain large portion of defect sites, high temperature facilitates bond breaking as well as atoms rearrangement and therefore the A-R occurs easily. At 900°C the transformation to the rutile phase is complete.

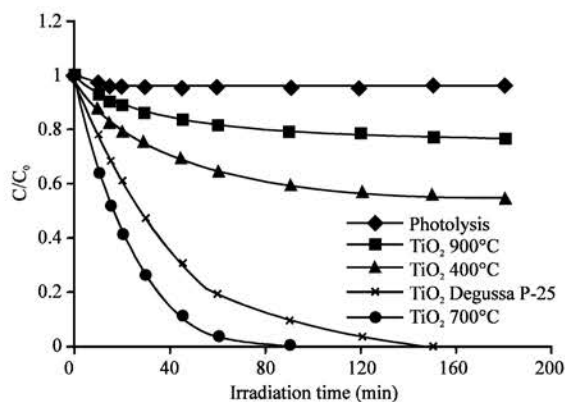


Fig. 4: Kinetics of β -naphthol disappearance in the absence and in the presence of various illuminated TiO₂

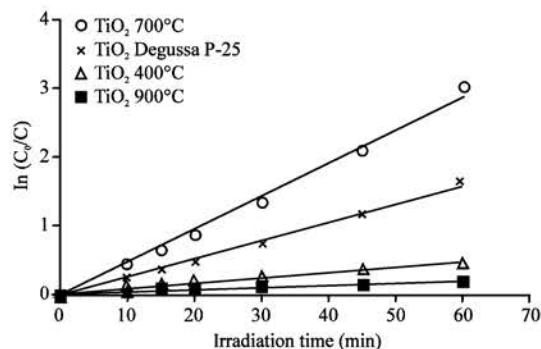


Fig. 5: Linear transform $\ln(C_0/C) = f(t)$ of the kinetic curves from Fig. 4

Crystallinity of the titania powders calcined at various temperatures has been studied. The calculated lattice parameters for anatase are $a = 3.780 \text{ \AA}$ and $c = 9.657 \text{ \AA}$ at 400°C and for rutile are $a = 4.596 \text{ \AA}$ and $c = 2.912 \text{ \AA}$ at 900°C.

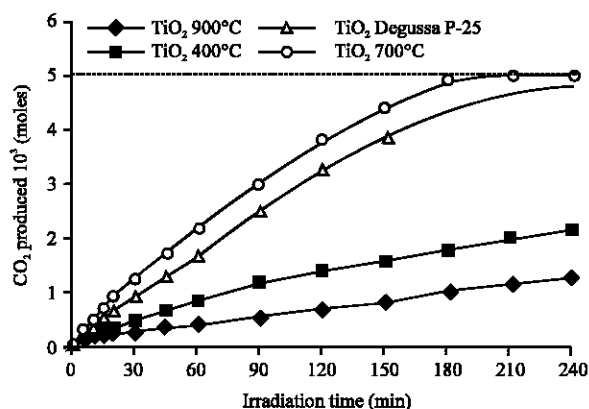


Fig. 6: Kinetics of CO₂ appearance during the photocatalytic degradation of β-naphthol in the presence of various illuminated TiO₂

Table 1: Results of XRD measurements for TiO₂ samples

Calcination temperature (T _c) (°C)	Crystallite size (nm)
400 (A)	7.10
700 (A)	18.70
700 (R)	20.10
900 (R)	28.54

Table 2: Adsorption percentage of β-naphthol on the various TiO₂ samples

Catalysts	Adsorbed (%)
TiO ₂ 700°C	24
TiO ₂ Degussa P-25	16
TiO ₂ 400°C	7
TiO ₂ 900°C	5

Table 3: Apparent first-order rate constants (k_{app}) for different photocatalysts

Photocatalysts	k _{app} (min ⁻¹)
TiO ₂ 700°C	0.046
TiO ₂ Degussa P-25	0.023
TiO ₂ 400°C	0.008
TiO ₂ 900°C	0.004

However, to quantify the crystallite size of TiO₂, the d spacing at 3.52 Å (101) phase for anatase (2θ = 25.4°) and 3.25 Å (110) phase for rutile (2θ = 27.5°) were used. X-ray peak-broadening was analyzed by employing the Debye-Scherrer's Eq. 1 (Guillard *et al.*, 2004; Porter *et al.*, 1999):

$$L = \frac{k'\lambda}{\delta \cos\theta} \quad (1)$$

where L is the crystal size, k' is a constant (= 0.9 assuming that the particles are spherical), λ is the radiation wavelength, δ is the line width at half maximum height of selected peak and θ is the Bragg's angle of diffraction.

The crystallite sizes of each phase present in the samples at various temperatures are listed in Table 1. It is apparent that thermal treatment greatly affects the structure and the size of the resulting TiO₂ crystal. The

crystal sizes for both anatase and rutile increased with increasing of calcination temperature. It has been observed that at higher calcination temperatures, the crystallites formed are larger in size, which can be attributed to the thermally promoted crystallite growth (Chan *et al.*, 1999).

The SEM photograph of the titania sample heat treated at 700°C is shown in Fig. 2. TiO₂ 700°C presents small particles forming spongy like surface and aggregates of different sizes.

In Fig. 3 we show the IR transmission spectrum of TiO₂ powder produced at 700°C. The absorption band at about 440 cm⁻¹ is due to the stretching vibrations of Ti-O-Ti and Ti-O bonds (Chen *et al.*, 2003).

Photocatalytic degradation of β-naphthol

Adsorption in the dark: A good determination of the photocatalytic activity of a sample can only be performed after having reached the adsorption equilibrium, since, otherwise, the initial rate of disappearance of a pollutant would simultaneously include both the initial rate of adsorption and the true, initial photocatalytic rate of reaction.

Under the same conditions as photodegradation, the amounts of β-naphthol (%) adsorbed on the various samples (TiO₂) measured at the end of the previous adsorption period in the dark are reported in Table 2. It is noted that the quantity of β-naphthol adsorbed on TiO₂, which is calcined with 700°C, is more important. Indeed, the capacity of adsorption of β-naphthol is approximately 1.5 times higher for TiO₂ 700°C than TiO₂ Degussa P-25.

The differences of adsorption exhibited by the various samples depended on the calcinations temperature, although the influence of other physicochemical factors cannot be excluded.

Kinetics of β-naphthol disappearance: The decomposition of organic molecules that occurs under irradiation of above synthesized TiO₂ is of great importance. In the present research, the degradation of β-naphthol was selected as a test reaction to verify the photocatalytic activity of different TiO₂ dispersion samples. Figure 4 plots the concentration changes of β-naphthol as a function of illumination time of the TiO₂ samples prepared by calcinating at different temperatures (T_c): 400, 700 and 900°C. It can be observed that the direct photolysis without catalysts can be neglected with less than 4% of conversion within 3 h of UV-irradiation. However, it is found that TiO₂ photocatalysis efficiency increases with the T_c up to 700°C reaching a maxima, i.e., TiO₂ 700°C is the most active to catalyze the

photodegradation of β -naphthol. This catalyst exhibits the highest photoactivity. The total pollutant destruction is occurred within 90 min and 150 min of time irradiation for TiO_2 700°C and TiO_2 Degussa P-25, respectively.

Sample TiO_2 400°C composed primarily of anatase phase. Nevertheless, the broad XRD feature for sample-400°C as shown in Fig. 1 indicated that anatase crystallisation of TiO_2 treated at 400°C was incomplete, hence TiO_2 400°C was expected to exhibit lower photocatalysis efficiency than that of the samples TiO_2 700°C and TiO_2 Degussa P-25.

The catalysts treated at 900°C showed poor activity for β -naphthol decomposition. This catalyst consists of rutile phase only that is known to have less activity than anatase phase. Poor photoactivity of rutile is connected with its fast recombination rate of generated electrons and holes (Tryba *et al.*, 2003).

A better and more quantitative way of presenting the activities of a series of similar catalysts is the use of the rate constant k , which is independent of the concentration used.

The photocatalytic degradation of organic pollutants in water generally follows a Langmuir-Hinshelwood mechanism (Eq. 2) (Assabbane *et al.*, 1997; Herrmann *et al.*, 1997; Chen *et al.*, 2004; Yang *et al.*, 2004; Konstantinou *et al.*, 2001):

$$r = \frac{kKC}{1+KC} \quad (2)$$

where r is the oxidation rate of the reactant ($\text{mol L}^{-1} \text{min}^{-1}$), k is the reaction rate constant ($\text{mol L}^{-1} \text{min}^{-1}$), K is the equilibrium adsorption coefficient (L mol^{-1}) and C is the concentration of the reactant at time t (mol L^{-1}).

At low substrate concentrations, the term KC in the denominator can be neglected with respect to unity and the rate becomes the apparent first order Eq. 3.

$$r = -\frac{dC}{dt} = kKC \quad (3)$$

The integral form, $C = f(t)$ of the rate equation is Eq. 4:

$$\ln \left(\frac{C_0}{C} \right) = kKt = k_{app} t \quad (4)$$

where C_0 is the initial concentration of the reactant (mol L^{-1}) and k_{app} is the apparent rate constant of the pseudo-first order (min^{-1}). The linear transforms \ln

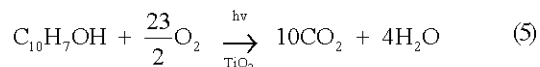
$(C_0/C) = k_{app} t$ of the curves in Fig. 4 are given in Fig. 5. The slopes of the straight lines all of which pass through the origin yield the k_{app} which are given in Table 3.

The photoactivity of the TiO_2 700°C particles determined from the apparent rate constant was much higher than that of commercial TiO_2 Degussa P-25. The UV-light induced photodegradation rate of β -naphthol using TiO_2 700°C particles was faster than that using TiO_2 Degussa P-25, TiO_2 400°C and TiO_2 900°C as photocatalyst by 2, 5.75 and 11.5 times, respectively.

The photoactivity of the four photocatalysts can then be ranked in the following order:

TiO_2 700°C > TiO_2 Degussa P-25 > TiO_2 400°C > TiO_2 900°C.

Kinetics of CO_2 evolution: The evolution of CO_2 as a function of irradiation time in the photocatalytic degradation of β -naphthol is shown in Fig. 6. The same reactivity order was found for the total mineralization followed by CO_2 evolution. Taking into account the fact that complete disappearance of β -naphthol in the irradiated reactor occurs after 90 min for TiO_2 700°C, whereas the stoichiometric (Eq. 5) formation of CO_2 is observed after 210 min under the same working conditions. This implies that total degradation requires a longer time for degrading all the possible reaction intermediate produced involved.



CONCLUSIONS

The microstructure characteristics of TiO_2 powders produced by aqueous hydrolysis of TiCl_4 at higher temperatures were studied using XRD, SEM and IR. Their photoactivities were also evaluated using β -naphthol degradation and mineralization to CO_2 as a test reaction. Anatase phase powders are obtained at the calcination temperature of 400-700°C. As the calcination temperature increased, the particle size increases. At 900°C, the transition to the rutile phase is complete. TiO_2 700°C exhibits the highest photoactivity. The photodegradation rate of β -naphthol using 700°C particles was faster than that using TiO_2 Degussa P-25 as photocatalyst by 2 times. However, it is clear from our measurements that the calcination temperatures used in hydrolysis preparation of TiO_2 samples significantly affect the photocatalysis efficiency of samples in the photodecomposition of β -naphthol. Suitable adsorption capability and better distribution of TiO_2 nanoparticles was the main cause for

the high activity. The results of several tests show that the samples derived from $TiCl_4$ exhibit the best results and the technique presented here seems an economical and fast way for the preparation of a highly active photocatalyst.

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