

Synthesis of TiO₂ via hydrolysis of titanium tetraisopropoxide and its photocatalytic activity on a suspended mixture with activated carbon in the degradation of 2-naphthol

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Abstract

Titania (TiO₂) photocatalysts are produced using hydrolysis of titanium tetraisopropoxide (TTIP) at 100–600 °C. The powders are characterized by thermogravimetric analysis (TGA), and X-ray diffraction (XRD). Anatase phase was obtained after calcination at 200 °C. The anatase-rutile transformation takes place at temperatures higher than 400 °C. Adding TiO₂ powders prepared at 600 °C to activated carbon (AC), exhibits much higher photocatalytic activity than commercial TiO₂ (Degussa P-25) alone in degradation of 2-naphthol under the UV-irradiation with O₂. This results shows that an optimum adsorption strength on the co-adsorbent (AC) is needed to improve titania's photoactivity in reactions of organic pollutant degradation in a shorter time.

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1. Introduction

Heterogeneous photocatalysis is a fast growing field of basic and applied research. However, the photocatalytic oxidation of organic compounds by nanocrystalline TiO₂ has received increasing attention since it can achieve the mineralization of a wide variety of organic pollutants to non-toxic mineral products, including carbon dioxide and water [1–4].

There are many methods of producing TiO₂ nanopowders, such as chemical vapor deposition (CVD) [5], the oxidation of titanium tetrachloride [6,7], the sol–gel technique [8], and the thermal decomposition or hydrolysis of titanium alkoxides [9]. Fine, spherical TiO₂ powders with high values of specific surface area were prepared by hydrolyzing titanium tetraisopropoxide (TTIP) with water [10]. Calcination is an important parameter that can be used to increase the photocatalytic activities of both anatase and rutile crystal phases [11].

Noticeably, strong-metal support interaction was first reported for noble metals supported on TiO₂ [12]. Many studies have been devoted to the improvement of titania's photoactivity by adding an inorganic co-adsorbent to the

catalyst, such as silica or zinc oxide [13,14]. Adding activated carbon (AC) to TiO₂ induces a strong beneficial effect because of the high adsorption capacity of AC with organic molecules. Furthermore, the synergistic effect between powdered TiO₂ and powdered AC have been observed of phenol [15] and 4-chlorophenol [16].

One important consideration in the solid-photocatalyzed reactions is the adsorption of the organic compounds on the surface of photocatalyst particles. It has been often reported that adsorption is a prerequisite for highly efficient photodegradation [17]. In this paper, we report on the preparation of TiO₂ powders using hydrolysis of TTIP with water. Also, we compare photocatalytic activity of mixture (TiO₂ synthesized + AC) with commercial TiO₂ (Degussa P-25) in the degradation of 2-naphthol.

2. Experimental

2.1. Preparation of TiO₂ powders

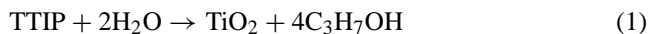
The nanopowders of TiO₂ catalysts, reported in this study, have been prepared by TTIP hydrolysis. TTIP [Ti(OCH(CH₃)₂)₄] (Fluka, purity >99%) was used as a main starting material without any further purification.

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The appreciated amount (10 ml) of TTIP was dissolved in distilled water (5 ml). The concentration of titanium was adjusted to 3 M by HNO_3 . This aqueous solution was stirred at high speed for 1 h. After centrifugation, TiO_2 particles were precipitated. The solids were collected and dried at 70°C during 24 h. Finally, the dried particles were calcined at temperatures of 100, 200, 300, 400, and 600°C for 3 h.

The hydrolysis reaction resulting in the formation of the TiO_2 may be represented by the following reaction:



2.2. Characterization of the samples

Several techniques were used for characterization of the powders. Thermogravimetric analysis (TGA) was performed using a "Labsys TG.DSC 1600 $^\circ\text{C}$ " of SETARAM.

Powder X-ray diffraction analysis (XRD) was carried out using Cu $\text{K}\alpha$ radiation in a Siemens D5000 diffractometer.

2.3. Photocatalytic activity of the catalysts

The photocatalytic test-reaction chosen to characterize the different photocatalysts was the total degradation of 2-naphthol (supplied by Fluka), selected as a model organic pollutant. All the experiments were carried out using a batch photoreactor. This photoreactor was a cylindrical flask made of pyrex optical, transparent to wave-lengths $\lambda \geq 290$ nm. UV-light was provided by a high pressure mercury lamp (Philips HPK 125 W), filtered by a circulating water, and it entered the photoreactor through the bottom window. The analysis of the samples detected in 2-naphthol oxidation were performed by high performance liquid chromatography HPLC (type JASCO). A reverse-phase column (length, 25 cm; internal diameter, 4.6 mm) ODS-2 Spherisorb was used. The mobile phase was composed of 80% acetonitrile to 20% distilled water. The flow rate was 0.4 ml/min, and the detector was set at 280 nm.

TiO_2 (600°C) prepared in this study (0.75 g), and (0.25 g) of commercial AC (from Scharlau, extra pure) were added

under stirring in 1 l of an initial concentration of 2-naphthol (5×10^{-4} mol/l) and maintained in the dark for 90 min. It has been shown that this period was sufficient to reach the adsorption equilibrium. The quantity of 0.75 g was selected as it gives the optimal specific degradation rate using commercial TiO_2 (Degussa P-25) (mainly anatase with a surface area of $50 \text{ m}^2/\text{g}$) as a reference. The amount of 0.25 g AC was chosen to ensure a good adsorption of 2-naphthol. For comparison, experiments were performed with a slurry suspension of powder TiO_2 (Degussa P-25). Furthermore, the reaction was carried out isothermally at room temperature (25°C).

3. Results and discussion

3.1. Characterization of TiO_2 powders

Fig. 1 depicts the thermogravimetric characteristics measured for these particles. Obviously, the weight loss proceeds in stages with increasing temperature, while the most significant loss occurs between 100 and 400°C . The total weight loss monitored up to 400°C is 50.902% for the as-prepared powder. The TGA measurements indicate that the organic phases decompose at temperatures below 400°C . From the TGA data of the as-prepared powders, we presume that TiO_2 is formed. This results have been observed previously [18,19].

In Fig. 2, we show the XRD patterns of as-prepared TiO_2 powders, heat-treated at various temperatures from 100 to 600°C for 3 h. The powder was amorphous. After calcining at 200°C anatase appears at $2\theta = 25.4^\circ$. As the calcination temperature increases (600°C), the rutile peak at $2\theta = 27.5^\circ$ emerges. This suggests that there is a phase transition from anatase to rutile at about 600°C which agrees with previous experiments [10,18]. In addition, the XRD patterns shows that, with increasing firing temperatures, the intensity and sharpness of the TiO_2 peaks grow, indicating an increase in crystallinity and particle size. For more, the photoactivity increases according to the calcination temperature [11].

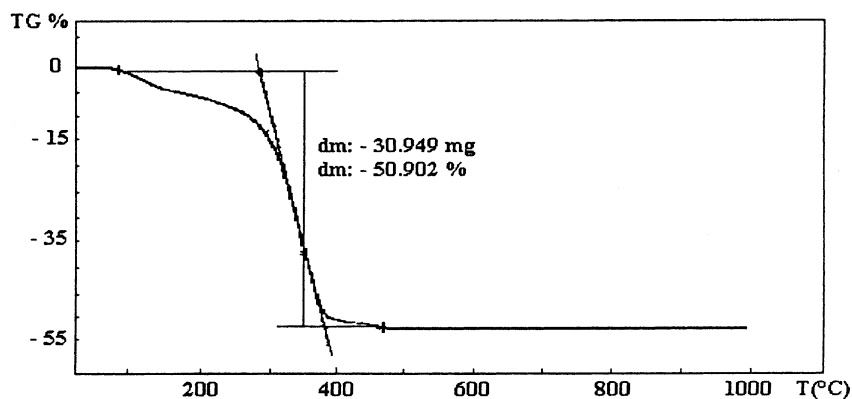


Fig. 1. TG measurements of as-prepared powder.

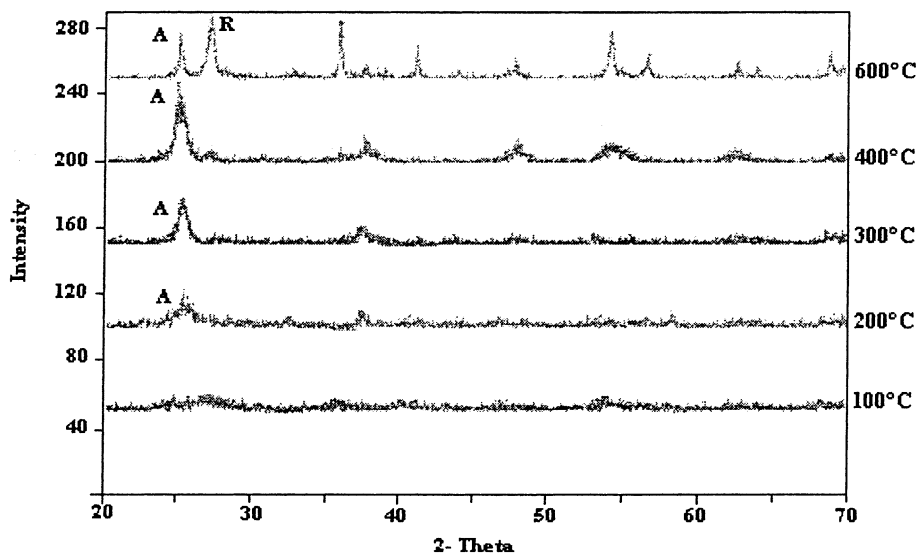


Fig. 2. XRD patterns of powders prepared at different calcination temperatures (A: anatase R: rutile).

However, the powders (TiO_2) produced at 600°C are probably more active.

3.2. Photocatalytic activity of the solids

3.2.1. Adsorption of 2-naphthol

All batch equilibrium experiments were conducted in the dark. 2-naphthol adsorption has been performed at 25°C on neat TiO_2 (Degussa P-25) (0.75 g), on a home prepared titania sample TiO_2 (600°C) (0.75 g), on activated carbon AC (0.25 g), on a suspended mixture of TiO_2 (Degussa P-25) + AC, and on TiO_2 (600°C) + AC with the same respective masses. The kinetics of adsorption are given in Fig. 3 for $C_0 = 5 \times 10^{-4}$ mol/l (initial

concentration of pollutant). A value of about pH 6 was used. It can be observed that most of adsorption occurred within 30 min. The equilibrium concentrations were determined using HPLC after centrifugation and filtration, through Millipore filters ($0.45 \mu\text{m}$ diameter), of the suspension. The amounts of 2-naphthol adsorbed are calculated as follows:

$$n(\text{ads}) = V\Delta C \quad (2)$$

where $n(\text{ads})$ is number of moles adsorbed, ΔC is the difference between the initial concentration, (C_0) and equilibrium concentration, (C_e), and V the volume (1 l).

In Fig. 3, the $n(\text{ads})$ order found for the five solids ($\text{AC} > \text{TiO}_2$ (600°C) + AC \geq TiO_2 (Degussa P-25) + AC \gg TiO_2 (600°C) \geq TiO_2 (Degussa P-25)) suggests that the

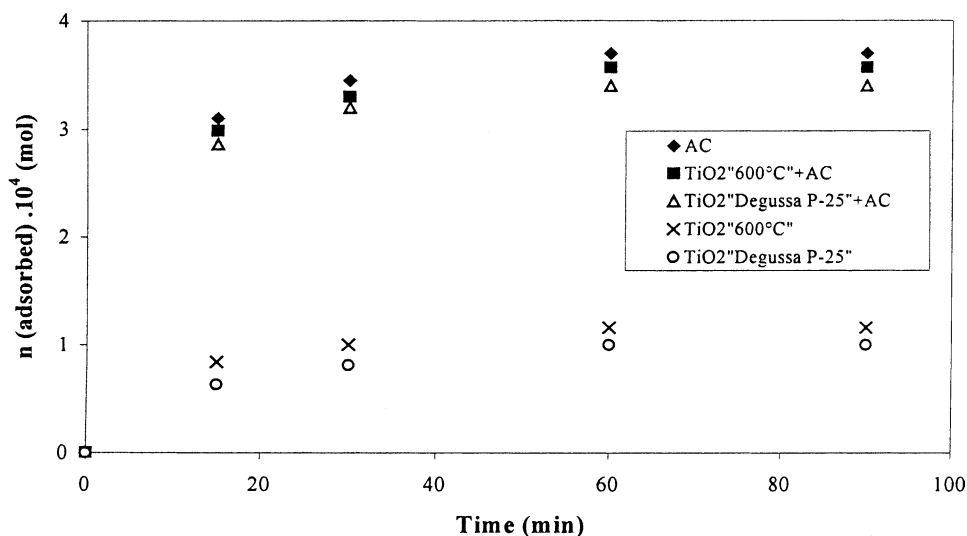


Fig. 3. Kinetics of adsorption of 2-naphthol in the dark for $C_0 = 5 \times 10^{-4}$ mol/l. AC (0.25 g), TiO_2 (Degussa P-25) (0.75 g), TiO_2 (600°C) (0.75 g), TiO_2 (Degussa P-25) (0.75 g) + AC (0.25 g), and TiO_2 (600°C) (0.75 g) + AC (0.25 g).

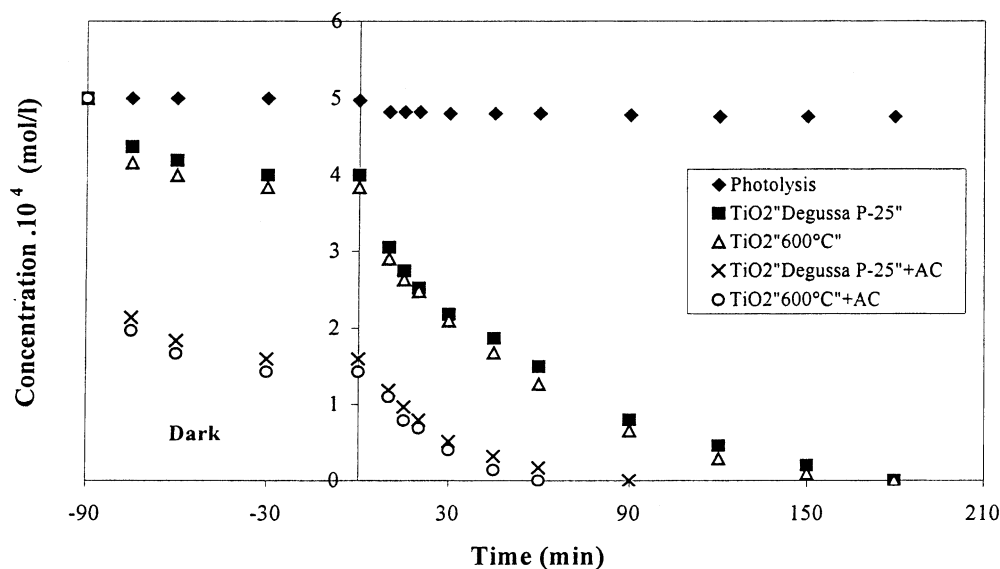


Fig. 4. Kinetics of 2-naphthol disappearance in the dark and photodegradation (UV) in the presence of various solids.

adsorption capacity on AC is much higher than on TiO_2 (600°C) and on TiO_2 (Degussa P-25). But, the amount $n(\text{ads})$ on TiO_2 (600°C)+AC and TiO_2 (Degussa P-25)+AC are respectively slight smaller than on pure AC. The origin of this difference can be ascribed to a strong interaction between TiO_2 particles and AC. This result has been observed by other authors [15,16].

3.2.2. Kinetics of the photocatalytic degradability of 2-naphthol

Fig. 4 shows the kinetics of disappearance, as a function of time, of illuminated 2-naphthol with an initial concentration of 5×10^{-4} mol/l in presence of the different photocatalysts. The period of adsorption in the dark is 90 min.

The direct photolysis without solids could be neglected with less than 4% of conversion after 3 h of UV-irradiation. The total photodegradation of the 2-naphthol was reached in approximately 180 min for TiO_2 (Degussa P-25) and 150 min for TiO_2 (600°C). On the other hand, the irradiated mixture (TiO_2 (Degussa P-25)+AC) and (TiO_2 (600°C)+AC), totally eliminates 2-naphthol in 90 min and 60 min, respectively.

The curves in Fig. 4 are of the apparent first order process as confirmed by the linear transforms $\ln(C_0/C) = f(t)$ of Fig. 5. The apparent first order rate constants (k_{app}) for the four photocatalysts are presented in Table 1. k_{app} has been used as comparison parameter, since it is independent of the used concentration.

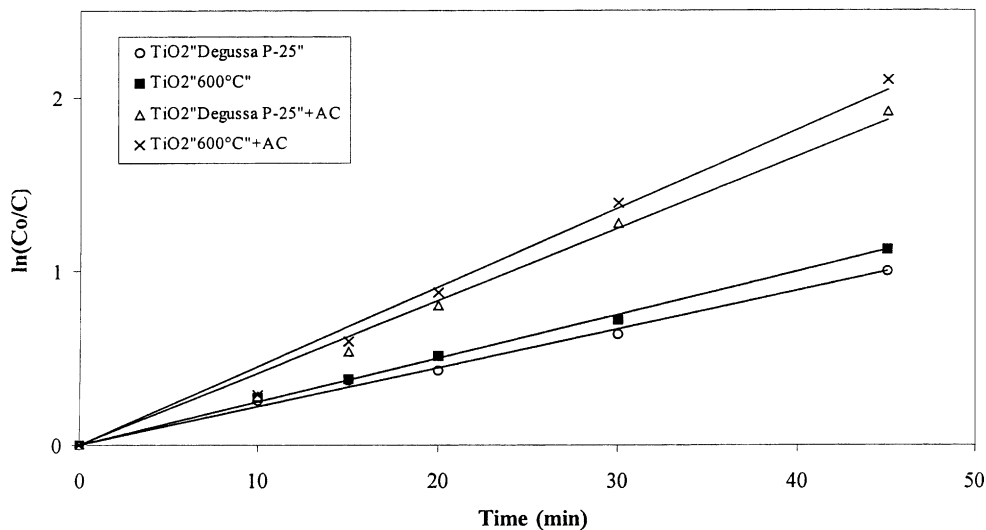


Fig. 5. Linear transform $\ln(C_0/C) = f(t)$ of the kinetic curves of 2-naphthol disappearance for (TiO_2 (Degussa P-25), TiO_2 (600°C), TiO_2 (Degussa P-25) + AC, TiO_2 (600°C) + AC) at 45 min of irradiation.

Table 1
Apparent first-order rate constants (k_{app}) for different photocatalysts

Photocatalysts	k_{app} (min ⁻¹)
TiO ₂ (600 °C) + AC	0.0455
TiO ₂ (Degussa P-25) + AC	0.0415
TiO ₂ (600 °C)	0.0249
TiO ₂ (Degussa P-25)	0.0222

It enables one to determine a photocatalytic activity independent of the adsorption in the dark. The photocatalytic activity of the TiO₂ (600 °C) + AC system determined from the (k_{app}) is higher than that of neat TiO₂ (Degussa P-25).

The photoactivity of the four photocatalysts can then be ranked in the following order: TiO₂ (600 °C) + AC ≥ TiO₂ (Degussa P-25) + AC ≫ TiO₂ (600 °C) ≥ TiO₂ (Degussa P-25).

4. Conclusions

The results reported in this work indicate that:

1. The nanocrystalline TiO₂ powders produced by hydrolysis of TTIP at various temperatures were studied using TGA and XRD.
2. The TiO₂ produced at 600 °C and calcined for 3 h, exhibits the highest photoactivity, which is comparable to that of commercial TiO₂ (Degussa P-25).
3. The calcination at high temperatures is detrimental to the photocatalytic activity of TiO₂.
4. The rates of photocatalytic oxidation of 2-naphthol in aqueous solutions over UV-irradiated solids powders obey pseudo-first order kinetics.
5. The photodegradation order found for the four photocatalysts (TiO₂ (600 °C)+AC ≥ TiO₂(Degussa P-25)+AC > TiO₂(600 °C) ≥ TiO₂ (Degussa P-25)) suggests that their photoactivity is directly related by an important adsorption of 2-naphthol on AC followed by a mass transfer to photoactive titania.

6. In the treatment of waste water, the system TiO₂ (600 °C) + AC enables it to photocatalytically degrade organic pollutant in a much shorter time than with TiO₂ alone.

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