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Efficient photocatalysts by hydrothermal treatment of TiO_2

A.I. Kontos [a], I.M. Arabatzis [a], D.S. Tsoukleris [a], A.G. Kontos [a,b], M.C. Bernard [c], D.E. Petrakis [d], P. Falaras [a,*]

[a] *Institute of Physical Chemistry, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Athens, Greece*
[b] *Physics Department, School of Applied Mathematical and Physical Sciences, National Technical University of Athens, Zografou University Campus, 15780 Athens, Greece*
[c] *UPR 15 du CNRS "Physique des Interfaces et Électrochimie", Université Pierre et Marie Curie, 75252 Paris Cedex 05, France*
[d] *Department of Chemistry, University of Ioannina, Ioannina 45110, Greece*

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Abstract

Mixed phase nanocrystalline TiO_2 powders (anatase–rutile) (Degussa P25) were prepared by hydrothermal modification. The preparation procedure took place at 200 °C for 1–10 days in an autoclave system with water as the solvent. Thus, different degrees of modification were achieved. TiO_2 water modified nanocrystalline thin films were immobilized on glass substrates by applying a doctor-blade's deposition technique. A variety of spectroscopic [UV–vis reflectance, infra-red (IR), Raman, structural X-ray diffraction (XRD), N_2 absorption (BET)] and microscopic [atomic force microscopy (AFM), scanning electron microscopy (SEM)] techniques were applied to characterize the modified films. A model textile industry pollutant (methyl orange) was used in order to evaluate the photocatalytic efficiency of the modified material. Our results show that the photocatalytic activity of the modified films is improved by a factor of 2 when we extend the hydrothermal treatment up from 1 to about 4 days in the autoclave system. Scratch tests revealed favorable interconnection of the titania nanoparticles as well as significantly higher adhesion to the glass substrate for the modified films, in comparison to the original P25 material.

Keywords: TiO_2 nanocrystalline thin films; Hydrothermal treatment; AFM; Photocatalyst activity; Methyl orange; Adherence; Pollutant degradation

1. Introduction

Titania is one of the most studied semiconductors for photocatalytic reactions due to its low cost, ease of handling and high resistance to photoinduced decomposition [1,2]. The photocatalytic activity of titania varies depending on its crystal phase, particle size and crystallinity. Among the common crystalline forms of titania, anatase is generally recognized to be the most active phase as opposed to the rutile and brookite forms [3,4]. Regarding the particle size, TiO_2 photocatalysis follows the trend of common heterogeneous processes, i.e. smaller particles induce higher surface to volume ratio, thus enhanced photocatalytic rates are achieved [5,6].

In general, hydrothermal synthesis is a prospective method to obtain nanocrystalline titania particles, where polymorphism, particle size and crystallinity could be controlled by the hydrothermal conditions [7,8]. Moreover, it is a low temperature technique for materials development, widely applied in industrial processes for ceramic synthesis [9]. The hydrothermal technique requires autoclave instrumentation and relies on the extensive heating of the nanoparticles diluted over an aqueous solution or slurry. Fine-tuning of the semi conducting nanoparticle size and specific active area critically affects the desired properties of the photocatalysts by varying the surface to volume ratio, by affecting the photo excited charge transfer and by influencing the surface hydroxyl concentration. Recent research activity in the field of materials chemistry reveals the crucial role of water on the final properties of titanium dioxide nanoparticles [2]. Water molecules express their nucleophile character, inducing the semiconductor particles decrease under elevated temperature and pressure conditions, similar to those achieved in an autoclave. In this way, the energy band structure becomes discrete and titania nanoparticles exhibit optical and photocatalytic properties superior to those of the source

* Corresponding author. Tel.: +30 210 6503644; fax: +30 210 6511766.
E-mail address: papi@chem.demokritos.gr (P. Falaras).

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material [10]. Furthermore, it is well established that amorphous titania develops its photocatalytic properties after heating at temperatures above 450 °C in an ambient environment. Surprisingly, the crystallization temperature for the anatase crystalline phase under hydrothermal conditions is only 200 °C [11,12]. This observation proves that water molecules can induce structural changes more efficiently, consuming less energy. The solution based hydrothermal treatment assures flexibility of the synthetic procedure, as time consuming steps of paste preparation are reduced by dissolving necessary reagents prior to heating. Thus, thin nanocrystalline titania films can be easily produced and subsequently they are expected to present uniformity, adherence and sufficient photocatalytic activity.

Hydrothermal treatment of an aqueous mixed paste containing titania powder has been recently used for the development of mechanically stable nanocrystalline films. The titania particles appear chemically interconnected and present good adhesion to the plastic substrates [13]. The modified films were used in dye-sensitized solar cells presenting very good efficiency. Although, the interconnection of the nanoparticles favors the mechanical stability of the films, the development of agglomerated particles at the film surface is detrimental for the photocatalytic process [10,14]. Advantages and disadvantages of particle chemical interconnection have to be judged according to the specific application.

This work describes the hydrothermal treatment of a commercial titania powder. The material is autoclaved in water at 200 °C for various days, producing materials with different degrees of modification. TiO_2 water modified nanocrystalline thin films were stabilized on glass substrates [15]. The photocatalyst immobilization presents certain advantages over the heterogeneous catalysis of slurries because (a) it does not require separation or filtration steps, (b) it can be easily adopted in continuous flow systems and (c) it is not very sensitive to particle agglomeration. The samples were structurally characterized by XRD and Raman spectroscopy. The specific surface area was determined by N_2 absorption–desorption isotherms while microscopy techniques (SEM and AFM) were used for defining the films morphology, roughness and fractal dimension as well as the size of nanoparticles. IR spectroscopy and UV–vis reflectance were applied in order to examine the influence of the surfaces properties on the surface hydroxyl content and the optical absorption of the materials. To evaluate the photocatalytic efficiency of the modified nanocrystalline titania films (1, 2, 3, 4 and 10 days), the photodegradation of the well known organic azo-dye methyl orange (MO), a typical pollutant in the textile industry [16], was investigated as model compound under near UV irradiation (350 nm).

The hydrothermal procedure of titania powder at relatively low temperature ensures finely tuning the properties of the modified titania particles by only varying the duration of the treatment without the danger of the anatase phase transformation to rutile. Thus, optimum properties like increased roughness and complexity of the photocatalyst surfaces, and amplified hydroxyl content per unit area can be combined with improved interconnection of the nanoparticles and adhesion to the substrate. Control of the above factors by fine tuning of the autoclave parameters can lead to efficient immobilized titania photocatalysts. This is essential for future synthesis of titania pastes in bulk, industrial quantities.

2. Experimental

Two grams of nanocrystalline Degussa P25 powder were mixed with 50 ml water and were autoclaved at 200 °C and pressure 14 bar for 1, 2, 3, 4 and 10 days. Thin films with a thickness of about 4 μm were immobilized on glass substrates by applying a simplified doctor-blade's deposition technique [15]. In particular, 0.5 g TiO_2 powder (Degussa P25) was grinded with 1 ml of water containing 0.1 ml acetylacetone producing a viscous paste. The paste was diluted by very slow addition of 1.7 ml of water. Finally, one drop of Triton X-100 was added and the paste was smeared on a glass substrate immobilized by an adhesive tape strip, which determines the film thickness. After drying at 100 °C for about 10 min, the film is annealed in an oven at 450 °C for 30 min.

Scratch tests have been performed using an ASTM D-3359 test kit. For visual inspection, we used a Karl Suss optical microscope in the reflection mode. The crystallinity of the photocatalysts was analyzed with an X-ray diffractometer (Siemens D-500, Cu Kα radiation). Raman measurements were carried out with a triple Jobin–Yvon spectrometer equipped with a microscope, a CCD detector and a 514.5 nm Argon laser excitation line. Diffused reflectance and transmittance spectra of the titania films were recorded in the range of 200–800 nm using a Hitachi U-4001 spectrometer equipped with an integrated sphere.

Detailed surface images were obtained by means of a scanning electron microscope (SEM) with numerical image acquisition (LEICA S440). Surface morphology, roughness and fractality of the modified titania films were examined with a digital Instruments Nanoscope III atomic force microscope (AFM), operating in the tapping mode (TM).

All the powders were characterized by nitrogen absorption-desorption isotherms at 77 K using a commercial SORPOMATIC/FISONS 1900 apparatus. Prior to each absorption–desorption measurements the samples were degassed at 473 K under $P = 10^{-2}$ mbar for 24 h. The specific surface areas were determined on a routine basis using the linear part of BET equation at $0.05 < (P/Po) < 0.15$–0.25.

Finally, the powders were characterized by FT-IR spectroscopy. The powder samples were mixed with KBr in standard quantities and pressed in transparent pellets. The pellets were subsequently annealed in 120 °C for 24 h in order to remove any free water. Then the samples were

measured using a Nicolet 550 Magna-IR-TM spectrometer in the region of 400–4000 cm^{-1} with 32 successive scans.

The photocatalytic activity of the TiO_2 films was evaluated by degradation of methyl orange (4-[(4-dimethylamino) phenyl-azo]). Photocatalysis experiments were carried out at round-bottomed photocatalytic cells. The cell glass permits radiation pass when wavelength is over 320 nm. A laboratory constructed irradiation system equipped with four F15W/T8 black light tubes (Sylvania GTE) was used. Aqueous solutions of methyl orange (4 ml) were photolyzed in the presence of modified TiO_2 thin films, under magnetic stirring. The films initially deposited on (3.5 cm × 2.6 cm) microscopy glass substrates were adjusted accurately in a surface area of 1.0 cm^2, by cutting the microscopy glass slides with a diamond knife. All solutions were O_2 bubbled for 2 h prior to use in order to achieve dissolved oxygen saturation. Initial pollutant concentration was set to 2.056×10^{-5} M. Analytical determination of the azo-dye pollutant was carried out spectrophotometrically at 466.5 nm (ε_{MO} = 25,100 M^{-1} cm^{-1}).

3. Results and discussion

Structural, morphological and spectroscopic analysis of the modified materials was carried out. All characterization methods, apart from the BET analysis and the IR spectroscopy, were applied in the films.

Characteristic X-ray diffraction patterns of the different samples are shown in Fig. 1. The anatase (A) reflections dominate but rutile (R) is also present as the original material TiO_2 Degussa P25 contains both phases (approximately 75% anatase and 25% rutile). The inset picture zooms at the A(1 0 1) anatase and R(1 1 0) rutile peaks in the region of 20–30°; the sequential order of the patterns

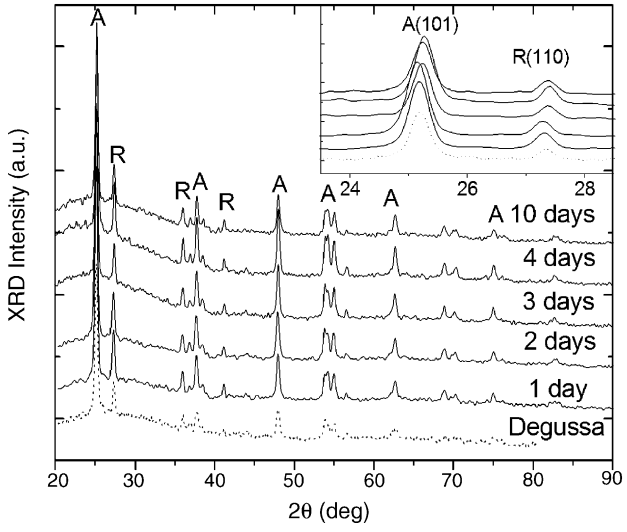

Fig. 1. The XRD patterns of titania films based on Degussa P25 autoclaved for various time periods.

remains the same as that in the main figure. The ratio of the two peak intensities was approximately the same, under the experimental error, for all samples indicating similar weight percentage of the anatase to rutile phase. Furthermore, the grain size was determined from the width at half maximum (w) of the A(1 0 1) peak according to the Scherrer formula ($D = 0.9\lambda/w \cos\theta$) [17]. Values of $D = 25 \pm 1$ nm were estimated for all samples.

Several Raman vibrational modes were well resolved on all spectra (not shown). The main modes 195, 393, 514 and 637 cm^{-1} correspond to the predominant anatase phase [18]. The minor rutile phase is revealed by a broad peak at 446 cm^{-1}. The intensity ratio of the 195 to 446 bands is comparable for all spectra indicating similar anatase to rutile phase ratio for all samples.

Characteristic SEM images of three samples (2, 4 and 10 days in the autoclave) at 10 μm magnification are presented in Fig. 2. The images show that the films exhibit a microgranular and rough surface. By increasing the autoclave treatment from 1 to 4 days, a marginal decrease of the dispersed particles size, which further become more homogenous in shape is observed. On the contrary, large particles are formed resulting in inhomogeneous films by extending the autoclave treatment to 10 days. Images of the surface have been also taken with a higher magnification covering an area of 200 nm × 200 nm upon the films. The surfaces form a sponge like structure with substantial improvement of their quality (homogeneity without 'hills' and 'calderas') after 4 days treatment in the autoclave.

The quantitative stoichiometric analysis of the secondary X-ray emission verifies the atomic ratio of Ti:O = 1:2. The analysis did not reveal any quantity of carbon upon the surface. This is due to the heat treatment of the films (final temperature = 450 °C), which removes all the organic solvent and modifier species.

In parallel to the SEM images, AFM images for the above three samples are shown in Fig. 2, too. These images show comparable results to the SEM ones verifying the better uniformity for the 4 days autoclaved sample. Several AFM images of each sample have been characterized in order to obtain representative values of the mean roughness, fractal dimension and mean size of the surface nanocrystals. Different measurements on each sample present negligible differences. This indicates that the results characterize the whole film and not a specific area. Mean results are summarized in Table 1 together with results from the photocatalytic experiments (to be presented later on this section). The roughness of the films decreases by prolonging the hydrothermal treatment while the fractal dimension is not very much affected. Finally the surface nanoparticles size is significantly bigger than that estimated by the XRD measurements. This is due to the agglomeration of the nanoparticles at the surface in grains with large size that can be up to several hundred nanometers, as shown in the SEM images. This parameter presents a minimum for the sample, which has

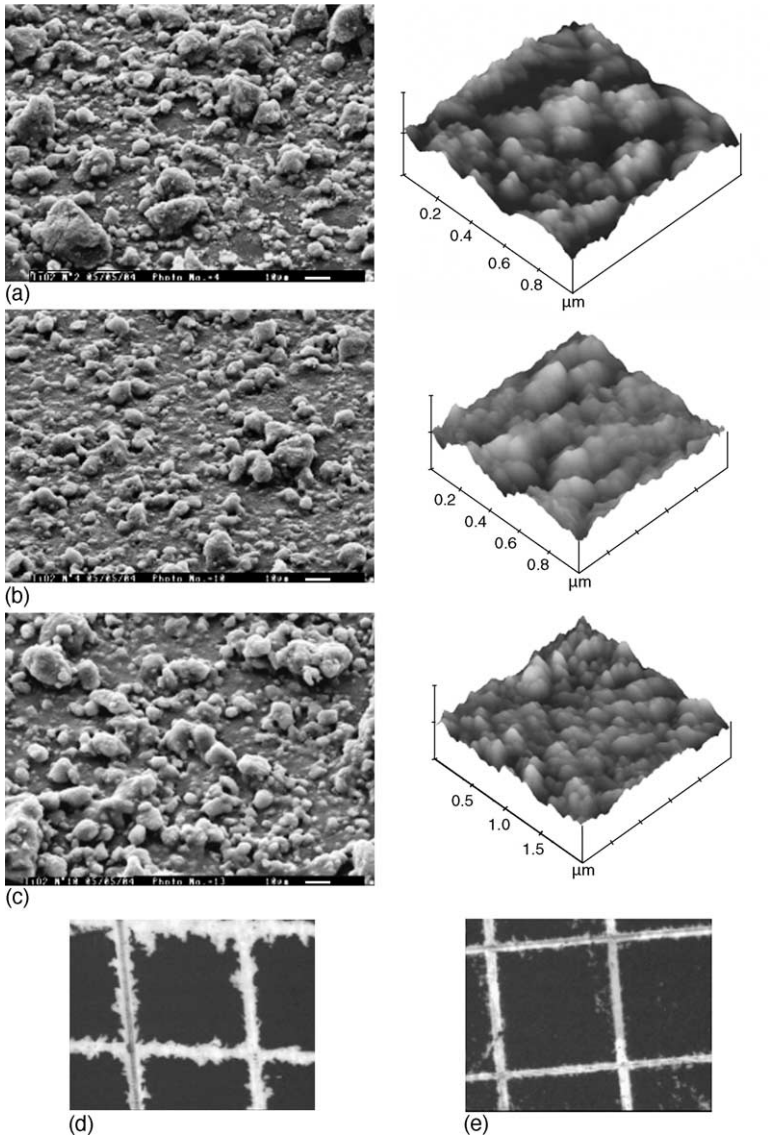

Fig. 2. SEM (left) and AFM (right) images from autoclaved titania films after 2 (a), 4 (b) and 10 (c) days hydrothermal treatment. Optical images on scratched titania films made from original Degussa P25 (d) and 4 days hydrothermally treated (e) materials (distance between parallel scratches is about 1.5 mm).

been autoclaved for 4 days. In Fig. 2(d and e), we also present optical microscopy images after performing the scratching tests on the obtained films. While all films present visually good adhesion, a detailed view under the optical microscope reveals severely scratched edges of the unmodified Degussa films. On the contrary, the autoclaved ones show well-defined edges. This demonstrates that via the autoclave treatment, the TiO_2 particles are chemically interconnected and adhere better to the glass substrate in comparison to the untreated Degussa P25 source material. This is very important for a number of applications, especially in heterogeneous photocatalysis on thin films, where the immobilization of the catalyst plays the most crucial role.

Table 1
Apparent first order photocatalytic reaction constant (k_{app}) of methyl orange on TiO_2 films

	Degussa P25	Degussa autoclave (2 days)	Degussa autoclave (4 days)	Degussa autoclave (10 days)
k_{app} (10^{-3} min^{-1})	7.9	1.11	1.65	1.18
Roughness (nm)	24.7	23.6	16.2	16.3
Fractal dimension	2.17	2.16	2.10	2.14
Mean particle size (nm)	88	93	61	73
SSA (m^2/g)	55	36.6	37.7	34.9

Characteristic properties derived from AFM on titania films and nitrogen isotherms on titania nanopowders, respectively.

The specific surface area (SSA) of the nanopowders has been calculated from the absorption–desorption isotherms. The results have shown significantly reduced values of SSA for the modified titanias in comparison to Degussa P25 (see Table 1), which is attributed to the agglomeration of the titania nanoparticles.

The IR spectra show similar features for all samples. IR transmittance is limited by strong absorption in the high frequency region as well as absorption of water molecules at about 1630 and 3420 cm^{-1}, and due to normal stretching vibrations of TiO_2 in the range of 550–653 cm^{-1}. Absorption in the spectral range of 700–1000 cm^{-1} has been assigned to the surface vibrations of the Ti–O bonds [19]. Shifting of the absorption band edge above 700 cm^{-1} has been related to the deformation of the TiO_2 bonds in the surface due to hydroxyl groups, water molecules or other ligands, which are attached on the surface of the TiO_2 nanoparticles [20].

Comparison of the raw spectra in Fig. 3 shows minor differences. To obtain more information in the region of interest (700–1000 cm^{-1}), first derivative spectra have been produced and are shown in the inset figure. In this way, we are able to observe systematic broadening of the absorption band or equivalently shifting of the transmittance edge. The derivative spectra mark the turning point of the transmittance edge at about 850 cm^{-1}. This point is indicated by an arrow in the raw spectra of the untreated Degussa powder in Fig. 3. Upon increasing the duration of autoclave treatment up to 4 days, the transmittance edge turning point shows a monotonic frequency shift from −27 to −4 cm^{-1} relative to the corresponding one of the Degussa powder. Moreover, it is interesting to examine the intensity of the transition peak in the derivative spectra, which corresponds to the abruptness of the transmittance edge. As shown in the inset figure, the transition peak intensity increases with the duration of the autoclave treatment. At 4 days, it reaches approximately the one observed for the Degussa P25. The prolonged autoclave treatment up to 10 days has opposite effect to the behavior of this peak with (a) increased shift to −10 cm^{-1} and (b) reduced intensity, relative to the one of Degussa P25. Therefore, the IR data, even though they present marginal changes, they clearly indicate an increase of molecular absorbed species on the TiO_2 surface induced by the extension of the autoclave treatment up to 4 days. These results are in accordance with the improvement of the photocatalytic performance for this particular sample.

In Fig. 4, we present the sum of the reflectance (R) and transmittance (T) data near to the absorption edge 300–600 nm. The sum spectra are insensitive to the exact thickness of the films and similar in shape. The absorption edge was estimated by extrapolating the reflectance curve at low and high frequency and by taking the cross point of the two extrapolated lines; an example of this calculation is shown upon the graph for the 10 days autoclaved film. In this way, similar energy gaps, within an uncertainty of ±3 nm, were obtained for all different films as well as the Degussa reference, invariant of the autoclave treatment duration. The absorption of the films at wavelengths above 600 nm is stabilized at about 22% of the incident light which is clearly bigger than the 14% obtained for unmodified Degussa; these values do not take into account the contribution of the glass substrate. Furthermore, the absorption of the films in the spectral range between 300 and 600 nm increases progressively with the duration of the autoclave treatment. This is in agreement with the yellowish tone of the samples color after subsequent autoclave treatment. The increased absorption can be related with total reflected and transmitted light losses. Since the crystallographic mixture of phases and the grain size remains the same for all samples, we may attribute the scattering losses to progressively more dense structure of the samples as soon as we increase the autoclave treatment [21], in accordance with the BET measurements and the morphological characterization.

The films activity was evaluated through photocatalysis experiments that took place in aqueous solutions of methyl

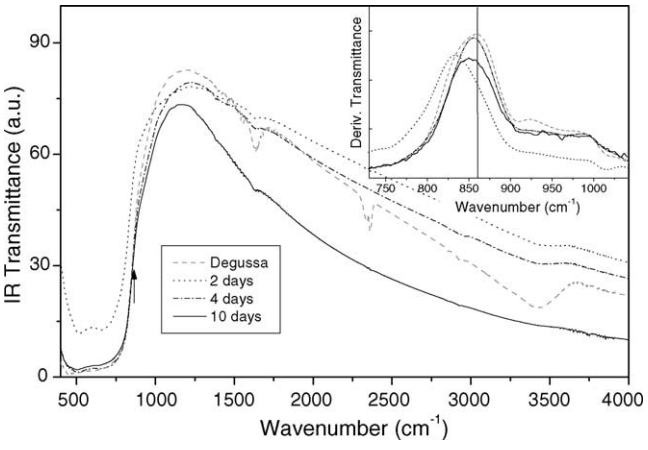

Fig. 3. IR spectra of Degussa P25 and various autoclave treated samples. Derivative curves, at the 700–1100 cm^{-1} range, are shown in the inset figure. Straight line marks the transmittance edge frequency of the Degussa powder.

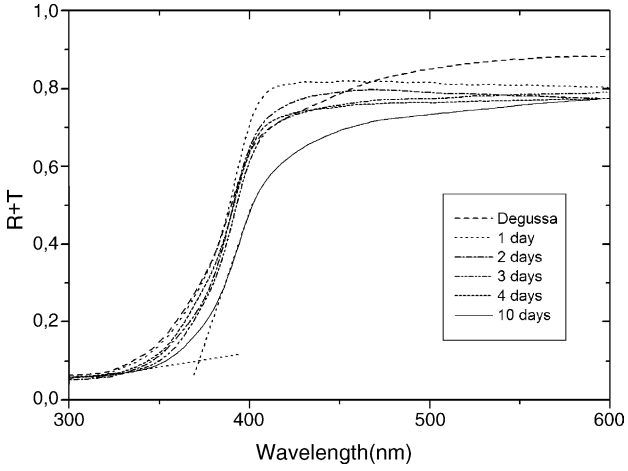

Fig. 4. Total reflectance and transmittance of the titania films autoclaved for different time duration.

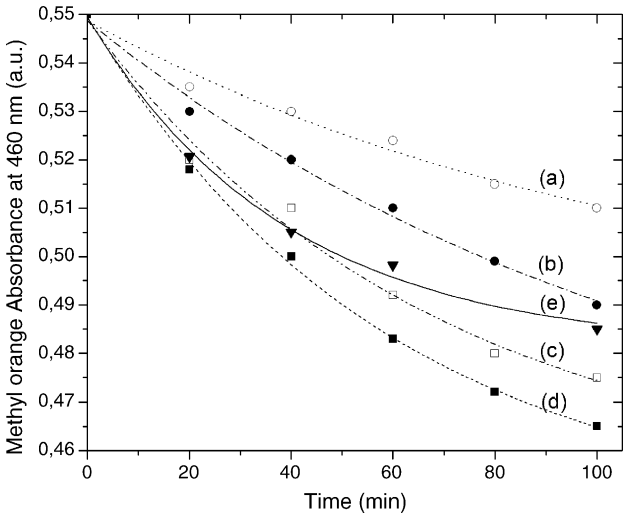

Fig. 5. Photodecomposition kinetics of methyl orange using TiO_2 thin film catalysts: 1 (a), 2 (b), 3 (c), 4 (d) and 10 (e) days of hydrothermal treatment of Degussa P25 at 200 °C.

orange. The pollutant solution was first photolyzed in the absence of the photocatalyst in order to examine its stability. These experiments verified that the azo-dye is not decomposed even after long-time irradiation under UV-illumination at 350 nm. The photocatalytic activity of the films was then expressed as the % pollutant decomposition. Each experimental set of measurements was repeated twice giving similar results.

The photocatalytic experiments (Fig. 5) indicate a gradual decrease of pollutant concentration in the presence of the TiO_2 photocatalysts, upon increasing the duration of the hydrothermal treatment of the titania powders up to 4 days. However, this behavior is not monotonic, since excess hydrothermal treatment up to 10 days causes decrease of the photocatalytic activity (see Fig. 5(e)).

Detailed analysis of the photocatalysis kinetics proves that the methyl orange concentration decrease upon illumination is fitted well with first-order exponential decay curves; hence it follows first-order reaction kinetics. It is well established [22] that photocatalysis experiments follow the Langmuir–Hinshelwood model, where the reaction rate R is proportional to the surface coverage θ (Eq.(1)):

$$R = -\frac{dC}{dt} = k_r\theta = \frac{k_r KC}{1 + KC} \quad (1)$$

where k_r is the reaction rate constant, K the adsorption coefficient of the reactant at the surface of the film and C its concentration. When C is very small, the KC product is negligible with respect to unity so that Eq. (1) describes first-order kinetics. The integration of Eq. (1) with the limit condition that at the start of irradiation, $t = 0$, the concentration is the initial one, $C = C_0$, gives:

$$-\ln\left(\frac{C}{C_0}\right) = k_{app}t = k_r Kt \quad (2)$$

where k_{app} is the apparent first-order reaction constant. Values of k_{app} for the various samples deduced from the graphs of Fig. 5 and Eq. (2) are given in Table 1.

Changes in k_{app} are attributed, via Eq. (2), to corresponding variations in the K values, i.e. to the different absorption of the reactant in the surface of the semiconductor nanoparticles or equivalently to different surface coverage θ. This explanation of the photocatalytic mechanism is further supported by the morphological characterization of the samples by SEM and AFM where the films autoclaved for 4 days have shown the smaller agglomerated particles size. High quality of the films, without agglomeration in the size scale of the roughness, is prerequisite for enhanced photocatalytic activity [10].

The above explanation is further supported by the IR measurements, which have shown increase of titania surface coverage by hydroxyl groups after 4 days in the autoclave system. This is well understood, if one takes into account that the photocatalysis mechanism involves the participation of surface hydroxyls (OH^-). In fact, illumination of the TiO_2 films by photons of energy greater than the band gap energy (E_g = 3.2 eV) creates pairs of electrons (e^-) and holes (h^+) following the reaction:

$$TiO_2 + h\nu \rightarrow TiO_2(e^-, h^+)$$

In the valence band, the photogenerated holes migrate to the interface and react with OH^- adsorbed onto the TiO_2 to create hydroxyl radicals ($^\bullet OH$):

$$(TiO_2)\cdots OH^- + h^+ \rightarrow {}^\bullet OH$$

The $^\bullet OH$ radicals present extremely strong oxidizing properties and are able to decompose the MO pollutant. It is then expected that materials rich in surface hydroxyls (and therefore in resulting $^\bullet OH$ radicals) present, respectively, high photocatalytic activity.

However, one must have in mind that the heterogeneous photocatalysis is a surface process and the hydrothermally treated catalysts have different surface characteristics. This results in differences in the total titania surface area exposed to the light beam and that available for pollutant adsorption. The above model is consistent with the highest photocatalytic activity observed for the non-treated (original) material, which presents the higher specific surface area as well as the larger amount of chemically absorbed water and hydroxyl content. Although we have managed to control the hydrothermal conditions for improving the photocatalytic properties without affecting neither the structure nor the nanoparticle size of the titania films, we still observe much lower apparent reaction constants than the one of Degussa P25 (see k_{app} values in Table 1). The characteristics of the modified titania films are also compatible with the relative strong photocatalytic efficiency observed for the hydrothermally treated catalysts for 4 days treatment and justifies the relative activity decrease observed in the case of extended stay (10 days) in the autoclave.

4. Conclusions

Hydrothermal treatment of commercial titania powder Degussa P25, in an autoclave at 200 °C for 1, 2, 3, 4 and 10 days, respectively, produces materials with different degrees of modification in specific pore volume and surface area. These materials can be immobilized on glass substrates in the form of nanocrystalline titania thin films by applying a simplified doctor-blade's deposition technique.

The films exhibit optimum interconnection of the nanoparticles and adhesion to the glass substrates in scratch tests and outperform over Degussa P25 in the mechanical aspects of immobilization. Photocatalytic degradation of methyl orange azo-dye under UV-illumination indicates a gradual decrease of pollutant concentration in the presence of the TiO_2 photocatalysts, dependent on the duration of the hydrothermal treatment of the titania powder. An optimum hydrothermal treatment corresponds to a titania films made from powders autoclaved for 4 days. Further increase of the duration of hydrothermal treatment results in a significant decrease of both surface area and hydroxyl content and therefore leads to a decrease of the photocatalytic efficiency.

The roughness and complexity of the thin film surface shows a dependence on the hydrothermal treatment. An attempt has been made to associate the nucleophile attack of water molecules with the surface characteristics and the surface concentration of hydroxyl groups determined by FT-IR spectroscopy. It is strongly proposed that the hydrothermal treatment of the titania powder induces modifications to the film roughness, surface area, agglomerated particle size and hydroxyl content of the photocatalyst. The above factors strongly influence the overall ability of capturing photons and producing oxidizing species on the immobilized titania materials, thus affecting their photocatalytic efficiency.

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