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TiO$_2$ photocatalysts deposited on fiber substrates by liquid phase deposition

Bettina Herbig, Peer Löbmann*

Fraunhofer-Institut für Silicatforschung, Neunerplatz 2, 97082 Würzburg, Germany

Abstract

Hybrid organic–inorganic fibers and carbon fibers were coated with TiO$_2$ by *liquid phase deposition* (LPD). Continuous films were easily accessible on untreated carbon fibers after short mineralization times, whereas the density of nucleation sites on the hybrid substrates was increased by hydroxylation. The photocatalytic activity of TiO$_2$ powder prepared by LPD was investigated and the material showed its best performance after heat treatment at 300–400 °C. Due to their better thermal stability at these temperatures, carbon fiber filaments were predominantly used as substrates for LPD TiO$_2$. The photocatalytic activity of the coated fibers per illuminated surface area was found to be higher than that of LPD particles and even higher than that of commercial TiO$_2$ powders normally used in suspension for photocatalytic wastewater treatment.

1. Introduction

Within the recent years, the application of photocatalytic materials has increasingly been addressed by many research groups and companies for the removal of numerous organic pollutants from water and air [1–3]. Due to its high stability against photocorrosion and its environmental non-toxicity, TiO$_2$ in its anatase modification has become the most important material for that use. When suspended particles are applied for water purification, the resulting highly active surfaces are advantageous, because of their availability for reactants and photons. Nevertheless, technical problems may arise from undesirable particle agglomeration, the necessary particle-fluid separation after radiation treatment for the reuse of the catalyst and for obtaining a clean, powder-free water [4]. If the titania is applied to a substrate and immobilized, the resulting surface area and activity are reduced. Therefore, it is advantageous to deposit TiO$_2$ on continuous support media with high surface areas such as fibers and fabrics.

Most vacuum-based technologies such as sputtering are basically limited to the line-of-sight deposition of materials and cannot easily be applied to such rather complex geometries. TiO$_2$ precursor solutions used in sol–gel coating technologies [5] will wet fiber filaments and fabrics completely. The uniformity of such films, which is essential for high qualities and good adhesion, will however be low due to the formation of liquid menisci between adjacent fibers during drying.

Alternatively, partially crystalline TiO$_2$ can directly be prepared from supersaturated solutions by liquid-phase deposition (LPD) [6]. A good understanding of the deposition mechanism on self-assembled monolayers (SAMs) has been developed [7–9]. Recently, it has been shown that planar polystyrene substrates [10,11] and even polymer microcapsules [12] can be coated. These results indicate that LPD should be a viable method for TiO$_2$ thin film formation on the curved surface of fibrous materials. In this paper we describe the coating of hybrid organic–inorganic hollow fibers (ORMOCER®, [13]) as well as carbon fibers and the photocatalytic activity of the resulting materials is compared to commercially available TiO$_2$ materials.

2. Experimental

2.1. Materials and film deposition

ORMOCER® hollow fibers were prepared by a method described previously [14]. Their surfaces were hydroxylated

* Corresponding author. Tel.: +49-931-4100-404;
fax: +49-931-4100-599.
E-mail address: loebmann@isc.fhg.de (P. Löbmann).

by immersing in an aqueous sodium persulphate solution (15 mass%, Fluka) at 80 °C for 60 min. Carbon fibers were purchased from Soficar S. A. (France), organic residues from the manufacturing process were removed by heat treatment at 500 °C for 10 min in air atmosphere.

A coating procedure adopted from Koumoto et al. [6,11] was used by immersing untreated and hydroxylated fibers (ORMOCER®) and multifiber filaments (carbon) in LPD coating solutions. The coated substrates were removed from the supersaturated solutions after various deposition times, rinsed in deionized water and subsequently air-dried. In order to investigate the photocatalytic activity of TiO₂ prepared by LPD, TiO₂ particles homogeneously precipitated in solution were separated by centrifugation, washed twice with deionized water and dried at 50 °C over night. Samples of the precipitates were annealed at different temperatures in air atmosphere for 180 min, respectively.

2.2. Structural characterization

Surface characterization was carried out by scanning electron microscopy (SEM) (Hitachi S 800, field emission scanning electron microscope with SE-detector). The surface coverage with TiO₂ was evaluated using image analysis.

Film thicknesses were determined at fractured samples. Quantitative X-ray diffraction measurements on homogeneously precipitated powder samples were performed according to a procedure described elsewhere [10].

2.3. Measurement of photocatalytic activity

Dichloroacetic acid (DCA) was used as a model compound, since it has a very low vapor pressure, is soluble in water at any concentration and its photocatalytic degradation can easily be monitored by measurement of the amount of chloride ions formed during the photocatalytic experiments [15].

The photochemical experiments were performed in a tubular quartz glass reactor filled with 2 l of aqueous solution containing 1 g DCA/l. Solutions were thermostated (maximum 30 °C), vigorously stirred by a magnetic stirring bar and continuously bubbled with air. TiO₂ precipitates treated at various temperatures were suspended in DCA solution (50 mg/l). Alternatively, TiO₂ coated carbon multifiber filaments were immersed into the DCA solution without and after previous heat treatment at ambient temperature.

Illumination was started following a dark period of 10 min, which was sufficient to attain adsorption equilibrium of DCA. Measurement of chloride concentration took place after 5 min of lamp start run. Illumination was carried out with a middle pressure mercury lamp (Heraeus, 150 W) in combination with a lamp protection tube of borosilicate glass, which eliminated UV-radiation below $\lambda = 300$ nm.

For reference measurements on the photocatalytic activity, commercially available TiO₂ powders (P25, Degussa) were employed. In order to compare the photocatalytic ac-

tivity of suspended and supported systems, the surface area of the respective photocatalytic material illuminated in the batch reactor per liter of DCA solution has been assessed in model calculations. The photocatalytic activity was defined as the quotient of chloride concentration (mg/l) after 180 min of illumination and illuminated surface area per liter DCA solution (m²/l).

The illuminated volume of DCA solution (V_{illVol}) in the tubular reactor can be calculated through $V_{illVol} = (r_{RR}^2 - r_{PT}^2) \times \pi \times l$, where r_{RR} is the inner radius of the reactor, r_{PT} is the outer radius of the protection tube and l is the light emitting length of the lamp. For a TiO₂ particle of the LPD process globular shape can be assumed, surface area and particle volume were calculated using the average particle radius (1.9 μm) as determined by SEM. Considering the skeletal density of anatase (3.90 g/cm³), the specific surface of LPD particles can be estimated to be approximately 0.81 m²/g. For a concentration of 50 mg TiO₂ particles/l DCA solution, 25.4 mg of particles are in the illuminated volume of the DCA solution and are responsible for DCA degradation in 2 l solution. In these experiments, thus there are 12.7 mg particles illuminated and provide an effective surface of 0.005 m²/l DCA solution, considering that particles were illuminated at one side. The effective surface areas of P25 suspensions were calculated through the same procedure for an average particle diameter of 21 nm and various concentrations of P25 suspensions (1.2, 5, 10, and 100 mg/l).

The surface area of coated carbon multifiber filaments can be calculated through $OF_{KF} = 2 \times (r_{KF} + r_{LPD}) \times \pi \times l \times n_{KF} \times n_{KB}$, where r_{KF} is the average carbon fiber radius (2.5 μm), r_{LPD} the film thickness of TiO₂ (400 nm), l the light emitting length of the applied lamp (44 mm), n_{KB} (9) the number of carbon multifiber filaments, and n_{KF} (6000) the number of carbon fibers a carbon filament consists of. This surface area is responsible for DCA degradation in 2 l solution. Considering that illumination of fibers in circular arrangement around the lamp is just taking place at one side, the effective surface area of carbon fibers can be determined to 0.011 m²/l DCA.

These model calculations allow the comparison of photocatalytic activity of suspended (TiO₂ particles) systems. Transmission measurements of P25 suspensions with different TiO₂ particle concentrations ensured that a suspension with 5 mg P25/l provides a comparable transmission as a suspension of 50 mg LPD TiO₂ particles/l. Because of the good transmission of TiO₂ particle suspensions, effects of shading were not taken into account and model calculations were used for comparison of photocatalytic activity of so called suspended and supported (deposited on fiber substrates) systems.

3. Results and discussions

ORMOCER® fibers were used as substrates because of the expected high environmental stability of these

materials. An increased resistance of the hybrid inorganic–organic composition towards photocatalytic degradation by the TiO_2 coating compared to purely organic polymers was anticipated. Additionally, ORMOCER®s can be processed into a vast variety of shapes such as coatings, fibers and even hollow fibers.

Fig. 1 shows the surfaces of ORMOCER® hollow fibers after different mineralization times. Material deposition originates at single sites after 2 h (a), the diameter of the separated deposits ranges from 200 to 270 nm. The further mineralization proceeds predominantly by hemispherical growth of existing seeds rather than new nucleation (b). Due

Fig. 2. SEM image of an ORMOCER® hollow fiber hydroxylated by aqueous sodium persulphate solution after 2 h exposure to TiO_2 LPD solution.

to the low density of nucleation sites, the sample surface is not completely covered within 6 h of LPD (c).

The density of nucleation sites is significantly increased by hydroxylation of the ORMOCER® fiber surface. Surface coverage of LPD TiO_2 is nearly being completed after 2 h of mineralization time (Fig. 2). The size of the seeds is close to those observed on untreated surfaces after equal mineralization times (Fig. 1a). Quantitative information about the coverage of the different samples as a function of mineralization time was obtained by image analysis of the respective SEM micrographs, these data are given in Fig. 3. Additionally, the thicknesses of the films were measured at fractured fibers (Fig. 4).

The results confirm a growth mechanism that recently had been proposed for the deposition of TiO_2 by LPD on polystyrene surfaces [11]: in the early stages, the inorganic material nucleates at specific sites, from which a spherulitic growth continues. X-ray diffraction experiments and transmission electron microscopy revealed that the radius of such hemispherical particles coincides with the *C*-axis of anatase.

Fig. 1. SEM images of untreated ORMOCER® hollow fibers after (a) 2 h, (b) 4 h and (c) 6 h exposure to LPD TiO_2 solutions: in the early stages, the inorganic material nucleates at specific sites, from which a hemispherical growth continues rather than new nucleation occurs.
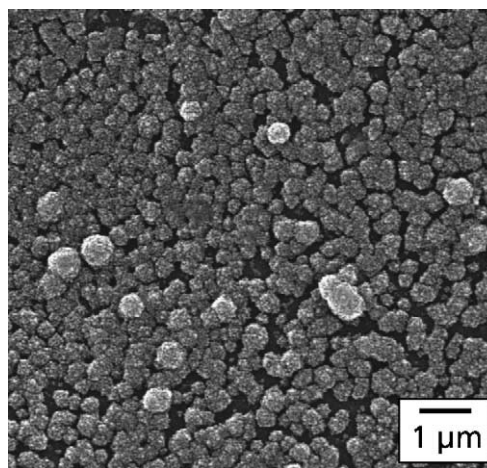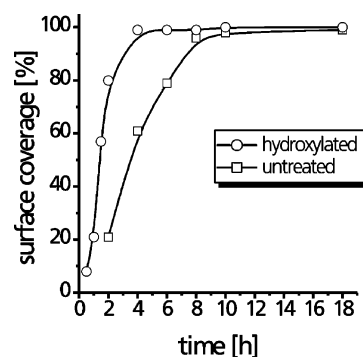

Fig. 3. Surface coverage of untreated and hydroxylated ORMOCER® hollow fiber surfaces as a function of LPD time. Lines are drawn as guide to the eyes.
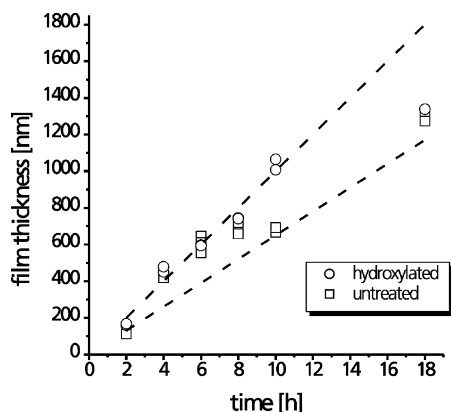
Fig. 4. TiO$_2$ film thickness on ORMOCER® hollow fiber surfaces as a function of LPD time. The dashed lines mark the range of growth rates (65–100 nm/h) that previously have been measured for film deposition on polystyrene [11].

A connective film is formed as soon as neighboring grains get in touch and the subsequent increase in film thickness is dominated by vertical growth. The observed material deposition rates between 65 and 100 nm/h are in good agreement with the film growth detected on the fibers (Fig. 4).

On functionalized polystyrene hydrophilicity was not necessarily associated with a high density of nucleation sites [11] as suggested by many authors for thin film deposition on self-assembled monolayers [16,17]. When carbon fibers, which are expected to have rather hydrophobic [18] surfaces, were exposed to LPD solutions, continuous films were readily observed after short mineralization times. A typical sample mineralized for 2 h is displayed in Fig. 5a. The thickness of the film was determined to be 200 ± 15 nm, the further growth rate of approximately 100 nm/h for longer exposures is consistent with the previous results on hybrid fibers (Fig. 4). After 4 h of mineralization time, some cracks become visible on the film surface (Fig. 5b). De Guire and co-workers [9] made similar observations for planar films on self-assembled monolayers. After 6 h of LPD coating some spherical particles, which obviously originated from homogeneous TiO$_2$ precipitation in solution [11], have settled on top of the fiber coating (Fig. 5c). Even though the crack width appears to increase, the films do not delaminate from the surfaces.

The diameter of carbon fibers (5 μm) is smaller than that of the ORMOCER® material used in this study (700 μm), the coating of filaments of carbon fibers should therefore provide significantly higher surface areas for wastewater treatment. Since it is known from the literature that the photocatalytic activity of TiO$_2$ prepared by LPD largely depends on the respective crystallinity and grain size, in a first step particles homogeneously precipitated from supersaturated solutions were examined.

Powders homogeneously precipitated in solution were isolated after 24 h, three samples were subsequently annealed at higher temperatures. Their crystallinity as determined by X-ray diffraction is given in Fig. 6. The inset shows the SEM
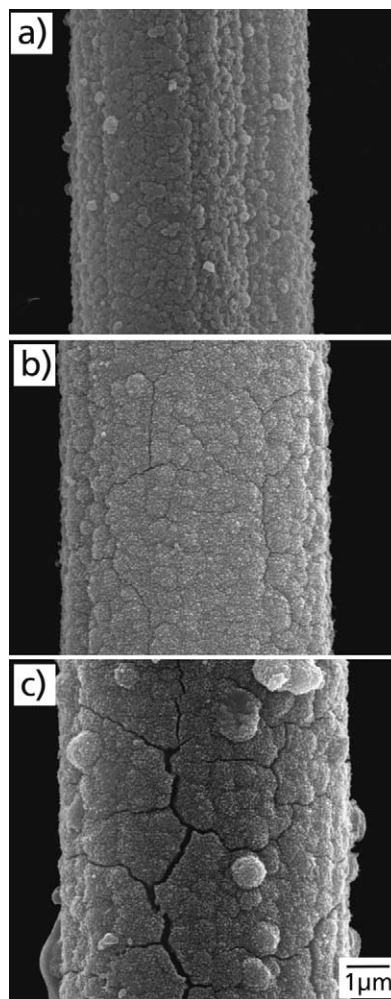

Fig. 5. SEM images of carbon fiber after (a) 2 h, (b) 4 h and (c) 6 h exposure to a TiO$_2$ LPD solution.
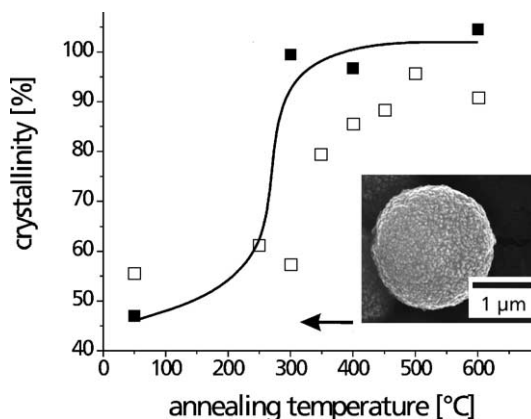

Fig. 6. Crystallinity of TiO$_2$ powders collected from an LPD solution as a function of annealing temperature (■) compared to the results of previous studies (□) [10]. The line is drawn as a guide to the eyes, the SEM image of a typical particle is displayed as an inset.
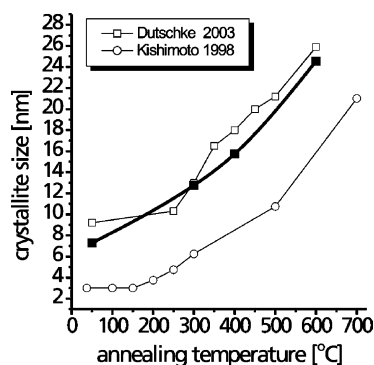
Fig. 7. Crystallite size of TiO₂ LPD powders determined from the peak width of the (1 0 1) X-ray diffraction peak by the Scherrer equation. The size is given as a function of annealing temperature and compared to previous results obtained by Kishimoto et al. (○) [19] and Dutschke et al. (□) [10].

image of a typical particle as prepared at 50 °C, the morphology is not significantly altered at higher temperatures.

Even though the initial crystallinity of the material directly after mineralization is somewhat lower than previously reported [10] (Fig. 6), the powders are fully crystalline after treatment at 300 °C or above with regard to the anatase modification of TiO₂. In Fig. 7, the respective sizes of the crystallites determined from the signal width of the (1 0 1) peak of anatase are also compared to other studies. Generally, the size of the crystallites increases with annealing temperature. The values determined in this work are in good agreement with the measurements on material recently prepared in our laboratories [10], but the crystals are significantly larger than those synthesized by Kishimoto et al. [19]. Obviously the TiO₂ material prepared in separate batches or by different groups shows similar general behavior, differences though may well be attributed to small variations of the experimental procedures.

The photocatalytic degradation of dichloroacetic acid was measured with suspensions of LPD particles, the concentration of chloride ions was taken as a measure for the decay of the model substance (Fig. 8a). Even though the as-prepared powders show a small activity, the decomposition is significantly increased by annealing of the powders. If the Cl⁻-concentrations after 180 min irradiation are compared (Fig. 8b), the powders show the highest activity when treated at 300 °C or 400 °C. This behavior was also observed by other authors and their assumption that a high crystallinity along with a small crystal size is beneficial [19], was thus confirmed.

The images of as-prepared particles (inset Fig. 6) do not differ from powders annealed at higher temperatures, even though an increase in crystallite size was measured by XRD. On the other side, N₂-sorption experiments on as-prepared as well as on annealed powders gave specific surface areas below 8 m²/g indicating that the particles have no significant inner surface and porosity on the length scale of the crystallites (2–25 nm). It therefore should be taken into consideration that the decrease in photocatalytic activity above 400 °C is not necessarily caused by a decrease in specific surface area, but is possibly due to changes in surface topography at higher temperatures.

Regardless of the details of the respective changes upon annealing, the TiO₂ thin films prepared by LPD should be deposited on a support with high surface area, that at least can withstand thermal treatment at 300–400 °C. For both reasons, carbon fibers (5 μm diameter) are preferable to ORMOCER® hollow fibers (∅ 700 μm), since the latter posses a lower surface area per unit volume and show strong shrinkage/disintegration above 200 °C.

Carbon fibers that had been coated with TiO₂ by liquid phase deposition, were annealed at 350 °C in air atmosphere (Fig. 9a). Even though the cracks within the film are broadened in comparison to the as-coated samples (Fig. 5b), the TiO₂ does not delaminate. By treatment at 600 °C in air atmosphere, the carbon fiber can even be removed completely, while the inorganic coating remains in fibrous shape (Fig. 9b). The resulting tubular TiO₂ material is very brittle though.
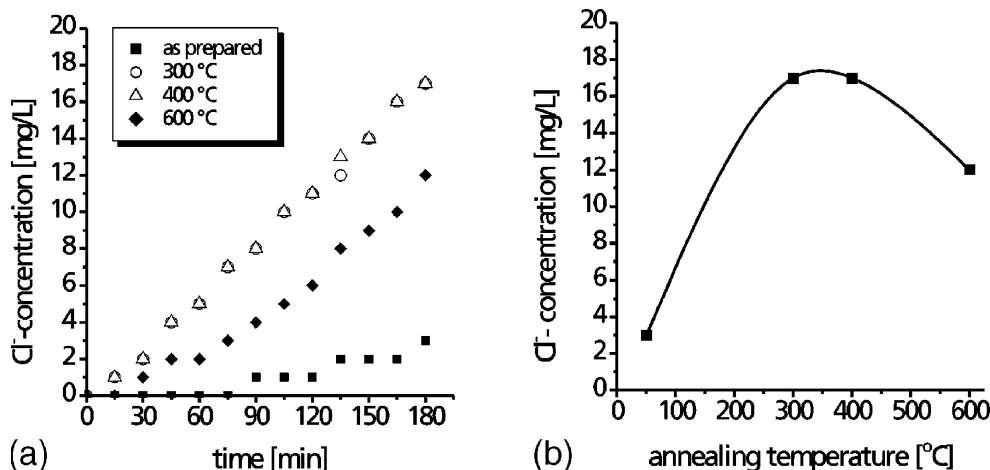

Fig. 8. Results of the photocatalytic decomposition of DCA by suspensions of LPD TiO₂ particles annealed at different temperatures: concentration of chloride ions as a function of time (a); final concentrations of Cl⁻ after 180 min irradiation as a function of treatment temperature of the TiO₂ particles (b).
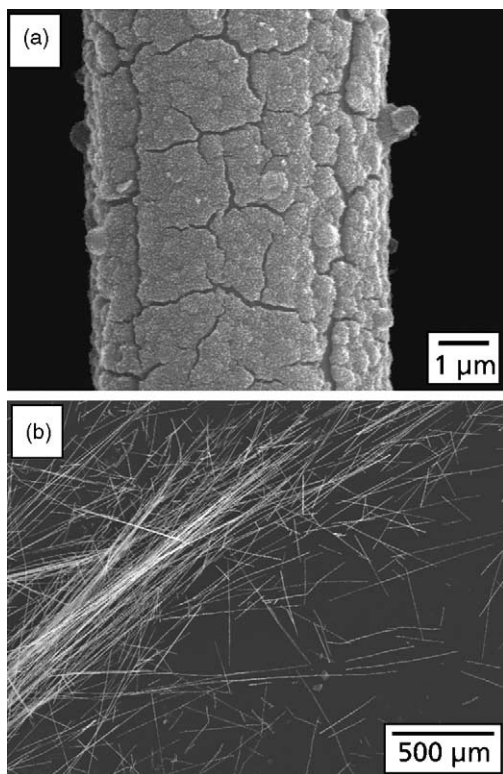
Fig. 9. Carbon fibers coated with TiO_2 after 4 h of liquid-phase deposition and annealing at 350 °C (a) and 600 °C (b) under ambient conditions for 3 h.

Carbon fiber filaments each containing approximately 6000 single fibers were coated with TiO_2 by liquid-phase deposition and some of the samples were subsequently treated at 300 °C. LPD powders had shown their highest photocatalytic activity after curing at this temperature. The photocatalytic activity of these samples was again evaluated by the decomposition of DCA (Fig. 10). The degradation of the model substance was enhanced compared to the experiments with suspended particles (Fig. 8) and the annealing of the deposited TiO_2 significantly improves the activity. Since the direct comparison of the degradation experiments
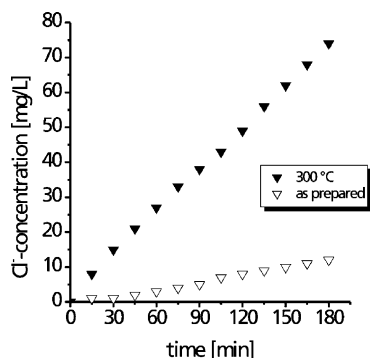

Fig. 10. Results of the photocatalytic decomposition of DCA by carbon fibers coated with TiO_2. The concentration of chloride ions as a function of time is given for experiments in the presence of as-coated fiber filaments and samples annealed at 300 °C.
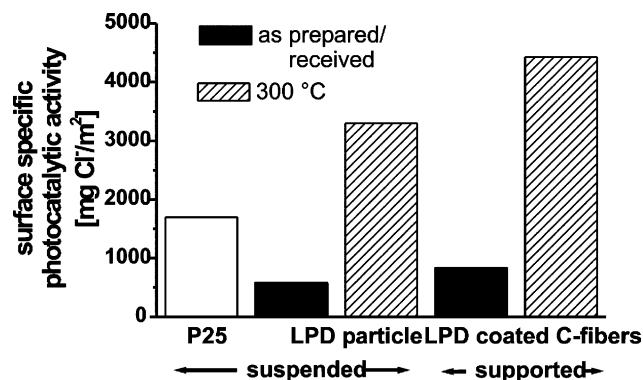

Fig. 11. Cl^--concentration per square meter of illuminated catalyst surface area after irradiation for 180 min taken as a measure for the respective photocatalytic activity (see Section 2 for details).

is difficult, all previous results were re-calculated and normalized to the concentration of chloride ions per square meter of illuminated catalyst after 180 min irradiation.

Degradation measurements of DCA were performed on P25 suspensions of various concentrations (1.2, 5, 10, and 100 mg/l). The photocatalytic activity of LPD particles and LPD TiO_2 supported on carbon fibers were compared to the suspension of P25 (5 mg/l) providing the optimum relation of chloride concentration (mg/l) after 180 min of illumination and illuminated surface area (m^2/l) and therefore the optimum surface specific photocatalytic activity. LPD particles after heat treatment at 300 °C show a higher photocatalytic activity in comparison to as-prepared LPD particles and in addition a higher activity as P25 (Fig. 11). Fig. 11 also demonstrates a higher photocatalytic activity of carbon multifiber supported LPD TiO_2 after heat treatment at 300 °C in comparison to the suspended systems of LPD particles and P25.

4. Conclusion

ORMOCER® fibers can be homogeneously coated by LPD, a surprisingly high nucleation rate and film adhesion is also observed on carbon fibers. Due to their smaller diameter and thus increased specific surface area and their better thermal stability below 400 °C, these substrates may be highly suitable as filaments or fabrics for the supported application of TiO_2 in photocatalysis. TiO_2 prepared by liquid phase deposition exerts best photocatalytic activity after thermal treatment at 300 and 400 °C both applied as suspension or as a coating on carbon fibers. Comparative measurements suggest that the surface specific photocatalytic activity of LPD-derived TiO_2 is higher than that of commercially available P 25.

Acknowledgements

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