TiO_2 thin film synthesis from complex precursors by CVD, its physical and photocatalytic properties

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Abstract. Photocatalytic TiO_2 films on glass and quartz plates were obtained by the chemical vapour deposition using $Ti(dpm)_2(Opr^i)_2$ complex compound (CC-CVD method) in a standard vacuum apparatus at $1.2–2.0 \times 10^{-4}$ mbar. The substrate temperature was stabilised in the range of 450–600 °C. The growth rate varied from several nanometres to several dozen of nanometres per minute. Structural information on TiO_2 thin films was obtained from synchrotron radiation experiments. High-resolution grazing incidence X-ray diffraction (GIXRD) experiments were performed at the high-resolution powder diffractometer at the DESY/HASYLAB beamline B2 (Hamburg, Germany). Thin films deposited on either single-crystal Si wafers or on amorphous quartz substrates were analysed. The photocatalytic activity of the TiO_2 thin films was studied using a photocatalytic reactor. The fungicide Fenarimol was chosen as chemical indicator and its degradation kinetics was followed by High-Performance Liquid Chromatography (HPLC).

1. INTRODUCTION

Great interest has been recently provoked by the technology of water purification of organic compounds, such as pesticides, using photocatalysis by semiconductors, such as titanium dioxide (TiO_2). This technology typically reduces toxic organic compounds to non-toxic inorganic compounds, such as carbon dioxide, water, ammonium or nitrates, and chloride ions.

In order to avoid the use of TiO_2 powder, which entails later separation from water, various researchers started to investigate ways of immobilising TiO_2 particles, for example in thin film form [1, 2]. Actually the thin film technique is becoming a standard for preparation of TiO_2-based photocatalysts. One of the advantages of thin film photocatalysts is that the catalyst layer may be connected to an external power source to reduce the recombination of UV-activated electrons and holes and thus, the efficiency of the catalyst is increased [3].

Among the modern methods of thin solid film preparation, the method of Chemical Vapour Deposition (CVD) is one of the most flexible, applicable when it is necessary to prepare doped films or multi-layer structures. In addition, CVD *in vacuo* will permit, to easily combine sulphides of metals with oxides to prepare multi-layer conducting/photocatalytic structures like $In_2S_3(In_2O_3 : S)/TiO_2$ [4].

It is generally believed that the presence of a ready-made fragment of the material to be deposited (such as $O - Ti - O$) in the source molecule accelerates the kinetics of thin film growth, and effectively permits to reduce the synthesis temperature. Moreover, the $O - Ti - O$ groups promote the oxide phase formation irrespective on the O_2 presence in the gas phase [5].

One of the important problems is the selection of the optimum source compounds for TiO_2 films. Among them $TiO(dpm)_2$, $Ti(OR)_4$ and $Ti(dpm)_2(OR)_2$ were used [6, 7]. Lately, $Ti(dpm)_2(OPr^i)_2$ (dpm = 2,2,6,6-tetramethylheptane-3,5-dione, Pr^i = isopropyl) found a wide application as a starting compound for TiO_2 containing films prepared by different methods (MOCVD, sol-gel, sputtering) [8, 9]. Data on the thermal behaviour in condensed phase of some commercially available samples of this substance have recently been reported [10, 11].

The main purpose of the present paper is to study the growth processes of TiO_2 thin films and their structural properties using the $Ti(dpm)_2(OPr^i)_2$ complex as CVD precursor and to study the photocatalytic activity of the resulting films.

In this work, the fungicide Fenarimol—{α-(2-chlorophenyl)-α-(4-chlorophenyl)-5-pyrimidine-methanol}—was chosen as chemical indicator. Its photochemical behaviour in aqueous solutions under sunlight has been studied in our laboratories, including kinetics and photoproducts, and is now reasonably well known [12–15], thus making its chemical behaviour in the photocatalytic TiO_2 system a good starting point. These experiments were also compared with kinetics studies in aqueous TiO_2 suspensions irradiated by sunlight or by a Xenon arc lamp.

2. EXPERIMENTAL

The thermal properties and the thermal decomposition reaction of $Ti(dpm)_2(OPr^i)_2$ in vacuum were described in detail earlier [16].

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The TiO_2 films were obtained in a standard vacuum apparatus ($\sim 5 \times 10^{-7}$ mbar). Vaporisation was conducted from an open surface evaporator. The temperature of the vapour source was varied in the range of 90–210 °C, and the substrate temperature was stabilised in the range of 450–600 °C. The pressure of the volatile decomposition products of the starting compound was $1.2–2.0 \times 10^{-4}$ mbar depending on the deposition parameters, with the system working in the molecular vapour stream regime. The size of the vacuum chamber allowed the evaporator—substrate distance to be varied from several centimetres to 40 cm.

Different types of glass and fused quartz plates of 78.5 cm^2 were used as substrates. All substrates were cleaned carefully using a specially developed procedure right before loading. The film thickness was determined by weight. It was found to be between 100 and 300 nm. The growth rate could be varied from several nanometers to several tens of nanometers per minute.

The High-resolution grazing incidence X-ray diffraction (GIXRD) method was used to study the crystal structure of the prepared samples. The GIXRD experiments were performed at the high-resolution powder diffractometer at the DESY/HASYLAB beamline B2 (Hamburg, Germany). We used grazing incidence angles α_i between 0.9 and 1.0 degrees. The synchrotron radiation wavelength was $\lambda = 0.11371$ nm.

A photoreactor apparatus was developed in order to follow the kinetics of Fenarimol degradation with and without photocatalytic action of the TiO_2 thin films (see Figure 1). The volume of the irradiated solution was 7.9 ml with 1 mm optical thickness; a water filter with fused quartz windows was used in order to avoid an excessive heating of the solution. The photocatalytic process in water requires the presence of O_2 as electron acceptor, thus a continuous flow of air was injected by means of an air pump.

The light intensity has been measured using a Sola-Scope I spectroradiometer (Solatell) and a IL700 A radiometer (International Light) with a SEE240 UVB detector (sensitivity curve maximum at 294 nm, half power points at 282 and 304 nm). The photon flux intensity of 3.45 Ein $h^{-1}\,l^{-1}$ used in the quantum yield calculations was obtained integrating the spectroradiometer results in the 280–340 nm range and taking into account the illuminated reactor area of 75.4 cm^2 and its total volume of 10.4 cm^3. The wavelength range was limited by the spectrum of the lamp and by absorption of the deposited film. The exact spectral shape of the TiO_2 film absorbance curve was not accounted for in the light intensity calculations and might introduce 20% of error into the absolute quantum yield values.

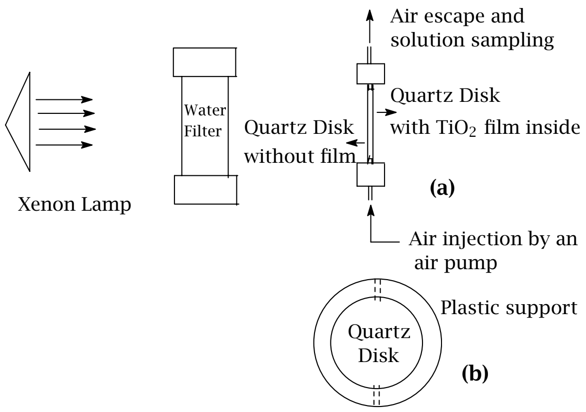

Figure 1. *Sample solution irradiation diagram. (a) photoreactor cell profile view; (b) photoreactor cell front view.*

Fenarimol (Riedel, 99.7%) 5 mg/l solutions were prepared in bidistilled water.

Before irradiation, the Fenarimol solution was left in contact with the reactor cell about 12 h in the dark in order to achieve the adsorption equilibrium of the pesticide between the solution and the cell surfaces.

During irradiation, 100 μl samples were taken every 0.5 h or 1 h, and immediately analysed with a HPLC system (Merck-Hitachi 655A-11 system with 655A-22 UV detector) under the following experimental conditions: LichroCART 125-4 column; Lichrospher 100 RP-18, 5 μm; acetonitrile eluent (Merck Lichrosolv) 65%, bidistilled water 35%; 1.1 ml/min flow; detection at 220 nm.

Eleven different types of TiO_2 thin films, deposited on different substrates at different temperatures, were tested (Table 1). The total irradiation time was between 3 and 5 hours for each sample.

To compare the reaction rates to that of the TiO_2 P25 powder (Degussa), the same amount by weight (7 mg) was deposited on a quartz substrate, by evaporation from a TiO_2 aqueous suspension, and tested in the same way.

3. RESULTS AND DISCUSSION

3.1. Preparation and studies of TiO_2 *films.*

The structural phases that can be formed in a titanium dioxide sample are the amorphous phase, the metastable crystalline forms, brookite and anatase, and the high-temperature stable anatase phase [17]. The three metastable forms all occur in nature, although rutile is the most common. It should be noted that other oxides, Ti_2O, TiO, Ti_2O_3, Ti_3O_5 and Ti_nO_{2n-1} ($n = 4, \ldots, 10$) may be formed at low oxygen concentrations.

The transition from the amorphous to the anatase form usually requires temperatures close to 300 °C. The phase transition anatase → rutile occurs in the range 600–800 °C upon heating of a TiO_2 powder sample [18, 19], the reverse transition does not occur upon cooling because of the high activation energy. In the case of bulk samples, the anatase-to-rutile phase transition occurs at temperatures over 800 °C.

Beyond the well-known use of the metastable anatase phase in a broad range of photocatalytic processes, supporting evidence for the enhanced catalytic

Table 1. TiO_2 *thin-films deposition conditions.*

Sample identification	Substrate	Film Thickness (nm)	Deposition Temp (°C)
R1	Glass (2 mm)	100	450
R2	Glass (2 mm)	90	420
R3	Glass (2 mm)	110	480
R4	Glass (2 mm)	200	450
R5	Striped Glass	11	450
R6	Quartz	170	435
R7	Quartz	60	465
R8	Quartz	85	450
R9	Quartz	25	400
R10	Quartz	240	450
R11	Quartz	200	520
R12	Ceramic Glass	100	450
R13	Ceramic Glass	170	465

activity of nanostructured mixed-phase titania was recently found [20]. Therefore, one of our preliminary aims was to determine the optimal deposition and processing parameters that would lead to the formation of either single-phase anatase or anatase-rutile phase mixtures in the thin film samples.

Although previous CVD deposition runs on ordinary glass substrates at 520–550 °C, have produced polycrystalline anatase modifications as verified by X-ray qualitative analysis [16], further attempts to reproduce this polycrystalline form on other substrates, that would be stable at the deposition temperature, were not successful.

Single-phase rutile (R) films were obtained after CVD deposition at temperatures close to 500 °C (Figure 2) on Si wafer substrates. Post-synthesis annealing does not modify the structure of the as-deposited films since rutile is the stable high-temperature phase.

For samples deposited on fused quartz substrates, a representative grazing incidence X-ray diffraction pattern is shown in Figure 3. Along with Bragg reflections corresponding to the major (R) rutile phase, several low-intensity anatase diffraction peaks could also be detected. Further annealing of these TiO_2 films in order to increase the oxygen thin film content, lead to the disappearance of the minor anatase phase (A)—Figure 4, so that single-phase rutile films were obtained. For several samples thermally annealed at approx. 900 °C, preferential orientation along the 110 crystallographic direction could be noticed (Figure 4, top).

In order to investigate in more detail the texture effects present in thin-film samples annealed at high-temperatures above the anatase-to-rutile transition, a series of X-ray diffraction experiments were performed at the BW4 wiggler beamline (DESY/HASYLAB) using two-dimensional image-plate detectors. A standard Al_2O_3 (NIST-647a) powder reference sample was used for the energy calibration of the incoming synchrotron radiation beam and of the detector-sample distance.

The image-plate X-ray diffraction pattern of a multilayer sample after annealing for 2 hours at 650 °C shows only weak preferred orientation effects (Figure 5). This indicates that thick (750 nm) homogeneous

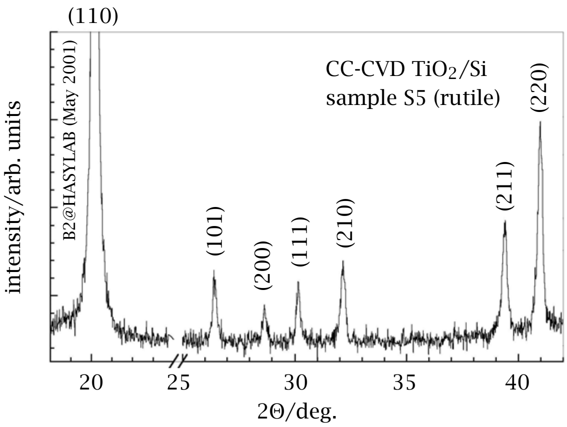

Figure 2. *GIXRD pattern of as-deposited* TiO_2 *film on* Si *wafer substrate. Single-phase rutile films are obtained in the as-deposited state. Deposition temperature 520° C, film thickness* ≈ 500 *nm.*

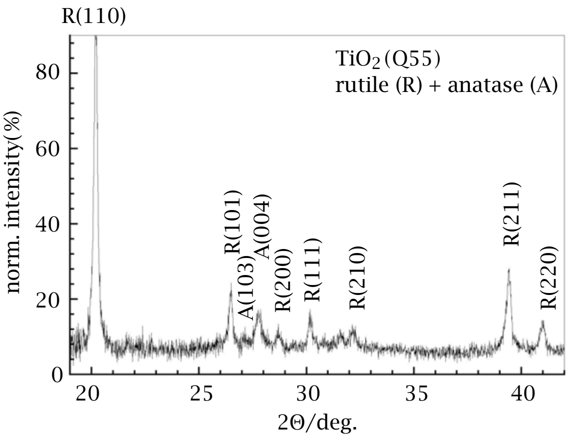

Figure 3. *GIXRD pattern of as-deposited* TiO_2 *film on quartz. Both rutile (R, dominant phase) and anatase (A) phases are present. Deposition temperature 450° C, film thickness* ≈ 300 *nm.*

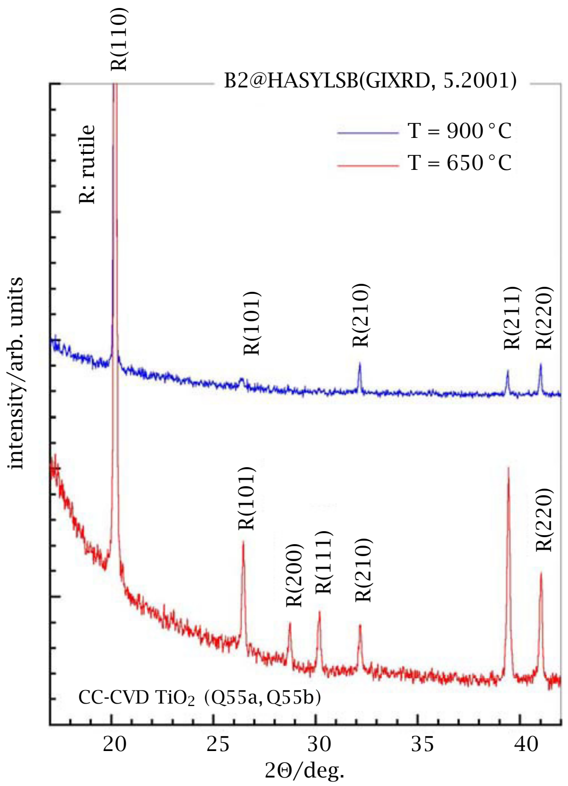

Figure 4. *GIXRD pattern of* TiO_2 *films annealed at 650° C (bottom) and 900° C (top) respectively. Single-phase rutile films are obtained (sample* Q55*, glass substrate).*

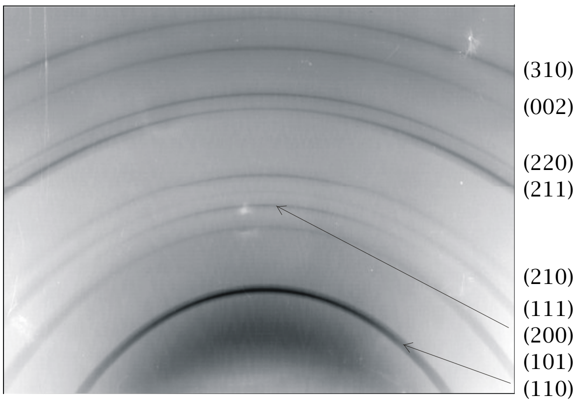

Figure 5. *Image-plate diffraction pattern of the* Q65 *sample(quartz substrate, deposition temperature 520° C, thickness 750 nm) after 2 hours at 650° C.*

films may nevertheless be produced by CC-CVD deposition followed by an adequate post-synthesis annealing procedure.

Our results demonstrate a shift to lower temperatures for rutile deposition compared with the usually 700 °C for TiO_2 powder formation by annealing, thus we tried to use a lower deposition temperature to obtain the anatase form. However, the $Ti(dpm)_2(OPr^i)_2$ precursor doesn't decompose below 400 °C so that TiO_2 could not be deposited at too low temperatures.

3.2. Phocatalytic activity of TiO_2 *films.*

At present, the mechanism of photocatalytic activity is not well understood. The schematic concept of the photocatalytic reaction which includes the valence electron excitation in semiconductor materials and the formation of $H^\bullet$ and $OH^\bullet$ radicals on the material surface does not explain why TiO_2 is a better photocatalyst than other semiconductors like ZnO, Fe_2O_3, MgO etc. Moreover, TiO_2 materials synthesised using different methods [21, 22] exhibit different photocatalytic properties. Indeed, materials synthesised by the sol-gel method with an essentially amorphous structure and the 75/25 anatase/rutile structural ratio show a photocatalytic activity comparable with the Degussa P25 TiO_2 (80/20 anatase/rutile ratio) but higher than that of the pure anatase powders. These studies suggest that photocatalytic performance should be dependent on several parameters including the particle size, the surface area and the ratio between the anatase and rutile crystal phases.

Rutile, however, has generally been assumed to have larger crystallite size and lower photocatalytic activity as compared to anatase. The difference in the lattice structure causes different mass densities and electronic band structures of the two TiO_2 forms. As a result, the band gap increases and the band edges shift to larger redox potentials making the anatase form of TiO_2 a much better catalyst than the rutile form. However, opinions are divided as regards the reasons for the observed activity decrease resulting from annealing the powder samples between 600 and 700 °C, accompanied by anatase transformation into rutile. Some authors [18] believe this is due to the gradual increase of the rutile fraction when the annealing temperature is increased. However, Mills *et al.*, explain the catalytic activity decrease by a drop in the specific surface area of the TiO_2 due to particle sintering, rather than to the anatase to rutile transformation, which occurs at temperatures above 700 °C [19]. This means that there exists a reasonable correlation between photocatalytic activity and the surface area of the particles in the dispersion. On the other hand, some authors indicated that the rutile phase of TiO_2 might be active or inactive according to the TiO_2 synthesis conditions [23].

Considering the polemics arising from the previous discussion, it was also important to test the catalytic activity of the rutile thin films, obtained by CVD deposition using the $Ti(dpm)_2(OPr^i)_2$ complex as TiO_2 precursor.

The problem of the rutile 110 surface activity was recently studied both experimentally and theoretically. Based on the experimental results, it has been variously proposed that water adsorbs (a) molecularly

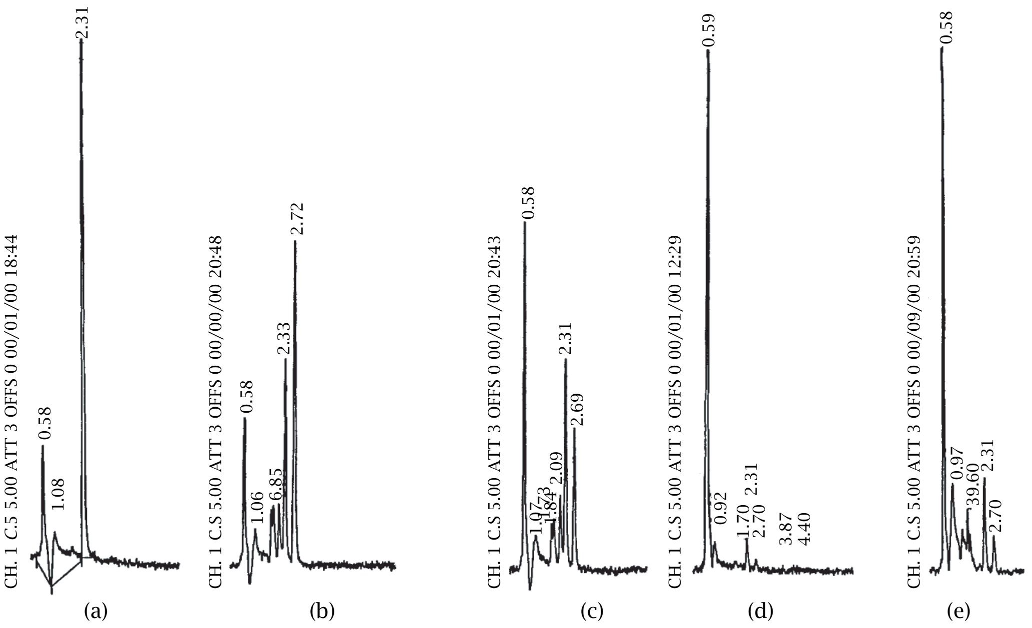

Figure 6. *Degradation of Fenarimol (5 mg/l, in water) monitored by HPLC. (a) Before irradiation. (b) 3 h of irradiation, no photocatalist. (c) 3 h of irradiation in contact with* TiO_2 *thin film deposited on ceramic glass at 450° C by CVD. (d) 2.5 h of irradiation in contact with a* TiO_2 *thin film deposited in quartz by evaporation of water from a* TiO_2 *suspension. (e) 1.5 h of irradiation in contact with a* TiO_2 *water suspension.* ***Notes:*** *The* TiO_2 *amounts in the water suspensions and on the ceramic glass were identical. Chromatographic peak retention times: 0.58 - non-retained compounds; 2.31 - Fenarimol; 2.70 - Fenarimol photoproduct resulting from direct photodegradation; smaller peaks - other degradation products.*

on the 110 surface and only dissociates at defect sites [24], (b) dissociatively at low coverages and thereafter molecularly [25], (c) ether molecularly or dissociatively depending on temperature [26]. One point of consensus is that if dissociation does occur, it is only at small concentrations. It was recently calculated by I. D. Lindan, *et al.* [27], using first principles density-functional methods that a monolayer of H_2O on the rutile 110 surface would contain water in both molecular and dissociated forms. With this results it is possible to conclude that the 110 surface should be photocatalytically active. As it was already mentioned, the CVD thin films annealed at high temperatures have the same 110 crystal orientation, so it should be expected this 110 termination would be also present in films prepared at lower temperatures.

One can note that the film thickness varies with the variation in substrate and temperature (Table 1). The three simultaneous variables make it difficult to get a clear quantitative picture for the Fenarimol degradation velocity. For example the fungicide adsorption degree may also be influenced. Instead, more valuable information can be obtained comparing the photoproducts formation by chromatographic analysis.

Previous studies have shown that Fenarimol, when irradiated by sunlight or by a Xenon lamp, photodegrades into several photoproducts [15], which suffer further degradation into minor and polar molecules eluted within the solvent peak of the chromatogram and indistinguishable in our analysis conditions.

The photocatalytic activity of our TiO_2 thin-films was estimated by the growth of the chromatographic peak of the non-retained compounds. This peak increases not only due to the decreasing area of the Fenarimol peak, but above all due to the degradation of all the intermediary photoproducts. In our photoreactor two concurrent degradation processes occur—direct photodegradation and photocatalytic degradation, thus the chemical stability of the intermediate photoproducts will depend on the photocatalytic activity of the TiO_2 thin films.

Of all the films tested, the TiO_2 films prepared at 450 °C on ceramic glass substrates were the only samples to exhibit the photocatalytic activity. Figure 6 shows a typical chromatogram of different samples: not irradiated (a), irradiated without TiO_2 (b) and irradiated in contact with TiO_2 (Degussa P25) (d,e). It is worth noticing that Figure 3 shows evidence of a mixed TiO_2 structure with a small amount of the anatase, instead of the pure rutile form observed in the other deposition conditions. Considering that the other thin films have shown no evidence of photocatalytic activity, we attribute the catalytic effect of the R12 sample (Table 1) to the slight amount of anatase present.

Table 2 presents the quantum yield data for the R12 sample as compared to the control and the Degussa P25

Table 2. *Quantum yields φ for Fenarimol photolysis and product formation. The products are labeled according to chromatographic retention times.*

	Control: Ceramic Glass without film $\varphi \times 10^3$	R12 $\varphi \times 10^3$	Powder film (sample (d) of Figure 6) $\varphi \times 10^3$
Fenarimol	0.48	0.50	6.46
Rt272	0.35	0.14	0.87
Rt058	0.22	0.41	4.92

Note: The product concentrations were quantified assuming equal absorbance values for all the compounds involved, a reasonable assumption given that the total area of all the peaks remains constant within 20%. Additional errors of the quantum yields are due to the uncertainties related to the exact film absorption spectrum, as explained in the text.

powder results. The quantum yields were calculated based on the photon flux measurements. These data demonstrate that the product formation yields sum up to give Fenarimol decomposition yield within 20%, which lies within the margin of error of the equal absorbance assumption made in product quantification—see the note to the Table. These data show the photocatalytic activity of the R12 sample, manifested in the product ratio change: the Rt272 product is formed with lower relative yield, while the Rt058 product—with a higher relative yield, as compared to the control. This is the same tendency as we see in the product ratio characteristic of the TiO_2 film obtained from the Degussa P25 powder, as opposed to the control, where only the direct photolysis takes place.

4. CONCLUSIONS

The use of the complex compound $Ti(dpm)_2(OPr^i)_2$, as precursor for TiO_2 thin films deposition using the CC-CVD method, with deposition temperatures between 400 and 520 °C, leads to the formation of TiO_2 rutile phase, which shows no photocatalytic activity. The sample R12 shows photocatalytic activity, however quite low as compared to the P25 powder, which we attribute to low anatase contents.

Further effort is in progress to improve the anatase phase deposition, taking advantage of alternative techniques such as plasma and photo-assisted CC-CVD methods.

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