



Multilayer TiO₂/SiO₂ thin sol–gel films: Effect of calcination temperature and Na⁺ diffusion

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ABSTRACT

The detrimental effect of Na⁺ ion diffusion originating from soda-lime glass substrate during calcination on the properties of TiO₂ thin sol–gel films can be eliminated by a barrier layer between the glass substrate and the final TiO₂ film. This work deals with two layer films consisting of a barrier layer (SiO₂ or TiO₂) and a final layer (TiO₂) deposited on soda-lime glass as a substrate. Particular emphasis was given to the effect of calcination temperature on both barrier and final layer.

It was found that photocatalytic properties of titania thin films depend directly on the amount of crystalline anatase which is produced during calcination. It was proved that the SiO₂ layer is a much better barrier against Na⁺ ion diffusion than the TiO₂ layer. Furthermore using a SiO₂ barrier the final titania layers are active even when calcined at 300 °C. With the application of a SiO₂ barrier we can increase the activity of titania layers more than 20 times and moreover 200 °C is sufficient to form a stable and functional SiO₂ barrier. It was also shown that when SiO₂ barrier is used, no Na⁺ ion diffusion is possible.

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1. Introduction

For the preparation of transparent TiO₂ photocatalyst films the sol–gel method is often used. Sol–gel technology is a low temperature method of preparing metal oxide films by a chemical route. Precursors of these films consist of organometallic chemicals, mainly metallic alkoxides or metal colloid solutions. After deposition (by dip-coating) layers are calcined to obtain an anatase crystalline structure. The calcination temperature [1,2], alkoxide concentration and loading of catalyst [3–5] are the most important parameters influencing the photocatalytic activity of sol–gel titania layers.

The main advantage of using a sol–gel technique is the achievement of good control of surface properties such as composition, thickness and topography [6,7]. This method allows preparation of materials with exceptional purity, homogeneity and composition and is also used for direct catalyst modification by dopants [8–10].

An important factor that determines the photocatalytic efficiency of titania films is the type of substrate. The detrimental effect of sodium contamination of the TiO₂ catalyst layer, originating from the soda-lime glass substrate during heat treatment, has previously

been reported [6]. In this regard, various explanations were given: (a) Na⁺ ions increase the temperature of anatase formation and increase the particle size [11,12], (b) they promote the recrystallization of the anatase to rutile [13], (c) they perturb the crystallinity of TiO₂, prevent the formation of the anatase phase, and produce recombination centers of photogenerated electron–hole pairs [14], (d) they produce either sodium titanate (Na₂O_xTiO₂) or a brookite phase [15], (e) they cause bonding or a shift of the oxygen anions resulting in the partial reduction of Ti(IV) to Ti(III) [16], and finally (f) they adsorb CO₂ in air to form carbonate and cause an increase in amount of carbon in the film [17].

The crystallographic (e.g., phase, crystallinity, size) and structural properties (e.g., surface area, pore volume) of TiO₂ particles or layers greatly affect their photocatalytic activity [18,19]. The calcination procedure is critical to control the physicochemical properties of TiO₂ catalysts [20,21]. For higher photocatalytic activity of TiO₂ sol–gel layers high calcination temperatures are usually needed. An optimum was observed in the calcination temperature for titania layers [3]. This optimum is connected with crystal phase change of amorphous TiO₂ to anatase (around 500 °C) and of anatase to rutile (around 800 °C) [18,22,23]. When using soda-lime glass as a support there is a limitation in the calcination temperature due to the softening point ($T_s = 734$ °C) which means that, around this temperature, the substrate is unstable [24].

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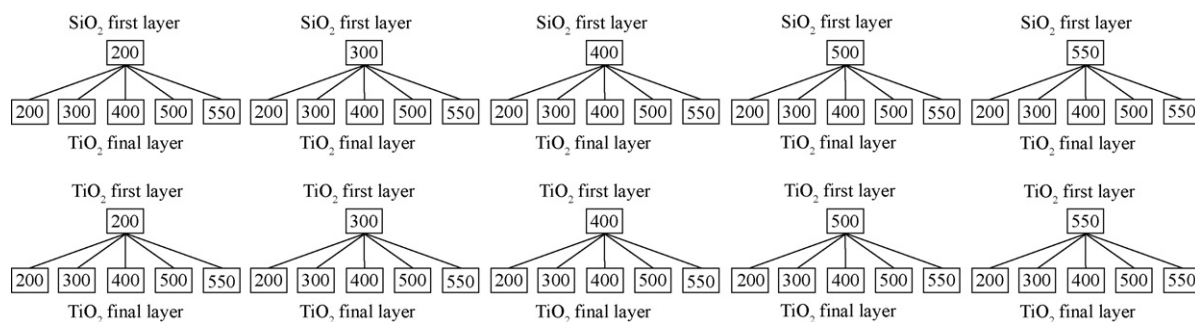


Fig. 1. Tree of multilayer composition and the calcination temperatures [°C].

The aim of this work was the preparation of photocatalytically active sol–gel TiO_2 coatings on soda-lime glass substrates by dip-coating. Particular attention was given to the barrier effect of either the SiO_2 or TiO_2 interlayer placed between the glass substrate and the final TiO_2 layer and calcination temperature of individual layers.

2. Experimental details

2.1. Chemicals

Titanium(IV) isopropoxide (97%; Sigma–Aldrich) and tetraethyl orthosilicate TEOS (purity 98%; Fluka) were used to prepare the titania and silica in the $\text{TiO}_2/\text{SiO}_2/\text{glass}$ films. Absolute ethanol (p.a. Penta) and ethyl acetoacetate (purity p.a. 99%; Fluka) used as solvents and hydrochloric acid (p.a. 36%; Penta) and nitric acid (p.a. 65%; Penta) were used as sol–gel catalysts. 4-Chlorophenol 4CP ($\geq 99\%$) was supplied by Sigma–Aldrich.

2.2. Preparation of thin multilayer films

The SiO_2 layers were prepared by the following sol–gel method. 10 g of the TEOS solution were diluted with 15 cm^3 of ethanol and the product was stirred for 90 min. Small amounts of pure H_2O (2.5 cm^3) together with concentrated nitric acid (0.5 cm^3) were then added to produce the sol, which was stirred for 1 h and then stored for up to 1 month under cool, dark conditions and used as required.

The TiO_2 thin film layer was prepared using Ti-isopropoxide as the Ti precursor in a sol–gel method, based on that reported by Haga et al. [25], but with slightly modified reaction conditions in order to produce titania films with an optimum activity. Thus, under vigorous stirring, 7 g of Ti-isopropoxide solution were added drop-wise to 10 cm^3 of ethanol to create an initial titania sol. 10 cm^3 of ethanol together with 2 g of ethyl acetoacetate and hydrochloric acid were then added to this solution, followed by stirring for 24 h, and the produced titania sol was stored for up to 3 months under cool, dark conditions and used when required.

For the study of the effect of the SiO_2 barrier layer on the photoactivity of titania layers, a SiO_2 barrier layer was first deposited on the microscopic (75 mm \times 25 mm \times 1 mm) soda-lime glass substrate using a dip-coating technique (withdrawal rate: 60 mm min^{-1}) and SiO_2 sol. The set of different $\text{SiO}_2/\text{glass}$ substrates was then prepared by calcination in an oven at different temperatures (200, 300, 400, 500 and 550 °C) for 3 h. The TiO_2 layers were deposited using dip-coating (withdrawal rate: 60 mm min^{-1}) on $\text{SiO}_2/\text{glass}$ substrates (glass with SiO_2 layer, calcined at different temperatures) and then $\text{TiO}_2/\text{SiO}_2/\text{glass}$ layers were prepared by calcination at different temperatures (200, 300, 400, 500 and 550 °C) for 3 h.

As can be seen in Fig. 1, a large number of samples prepared using various temperatures was obtained, e.g., $\text{TiO}_2/\text{SiO}_2/\text{glass}$,

$\text{TiO}_2/\text{TiO}_2/\text{glass}$ (titania layer was used as barrier = two layers of TiO_2) and $\text{TiO}_2/\text{glass}$ (titania layer directly on glass).

2.3. Titania sol and layer characterization

The thermostability—thermogravimetric and differential thermal gravimetric analysis (TG–DTA) of the materials was examined by a SETARAM–SETSYS Evolution TG–DTA/DSC 18 with mass spectrometry (MS) detector. The presence of crystalline phases was determined by X-ray diffraction using an X’Pert PRO θ – θ powder diffractometer with parafocusing Bragg–Brentano geometry using $\text{Cu K}\alpha$ radiation. The surface morphology and layer thickness were determined by scanning electron microscopy (SEM, Hitachi S4700) and an Ocean Optics USB4000 diode array photometer with a fibre optic reflectance probe (NanoCalc). The amounts of the diffused ions from the substrate into the TiO_2 and SiO_2 layers were determined by glow discharge atomic emission spectrometry (GDS; Horiba GD-Profilier 2).

2.4. Model compound photocatalytic degradation

The photocatalytic assisted oxidation of the 4CP in the presence of dissolved oxygen, using the titania films was performed as follows. The TiO_2 film under test was suspended in a glass cuvette (2.0 cm path length \times 3.0 cm \times 5.0 cm depth) into which was added an aqueous solution of 4CP model compound (10^{-4} M, pH = 4.5, 25 cm^3). All irradiations were carried out using UVA light (1.5 mW cm^{-2}) from an 11 W BLB Sylvania Lynx light source (wavelength range from 320 to 390 nm with maximum at 355 nm). During the reaction the solution was stirred well and the temperature was kept constant at 20 °C. The concentration of 4CP was determined by UV–VIS spectrophotometry (Varian Cary 100) and high performance liquid chromatography (HPLC Shimadzu LC-10ADvp with SPD-M10Avp UV/VIS photodiode array detector).

In the photocatalytic degradation studies of 4CP prior to irradiation with UVA, the solution was left in contact with the titania film under test for 45 min in the dark to ensure 4CP adsorption equilibrium was achieved. A simple spectroscopic analysis of the dye solution before and after this equilibration step revealed that in all cases less than 1% of the compound tested was adsorbed by the titania films.

3. Results and discussion

3.1. Characterization of titania layers

All the prepared films were compact, uniform and transparent. SEM analysis showed some difference in the layer structure when a SiO_2 barrier is used. In this case the agglomerates are smaller and also large crystals are clearly visible. No cracks formation or other abnormalities in titania layer homogeneity were observed by SEM.

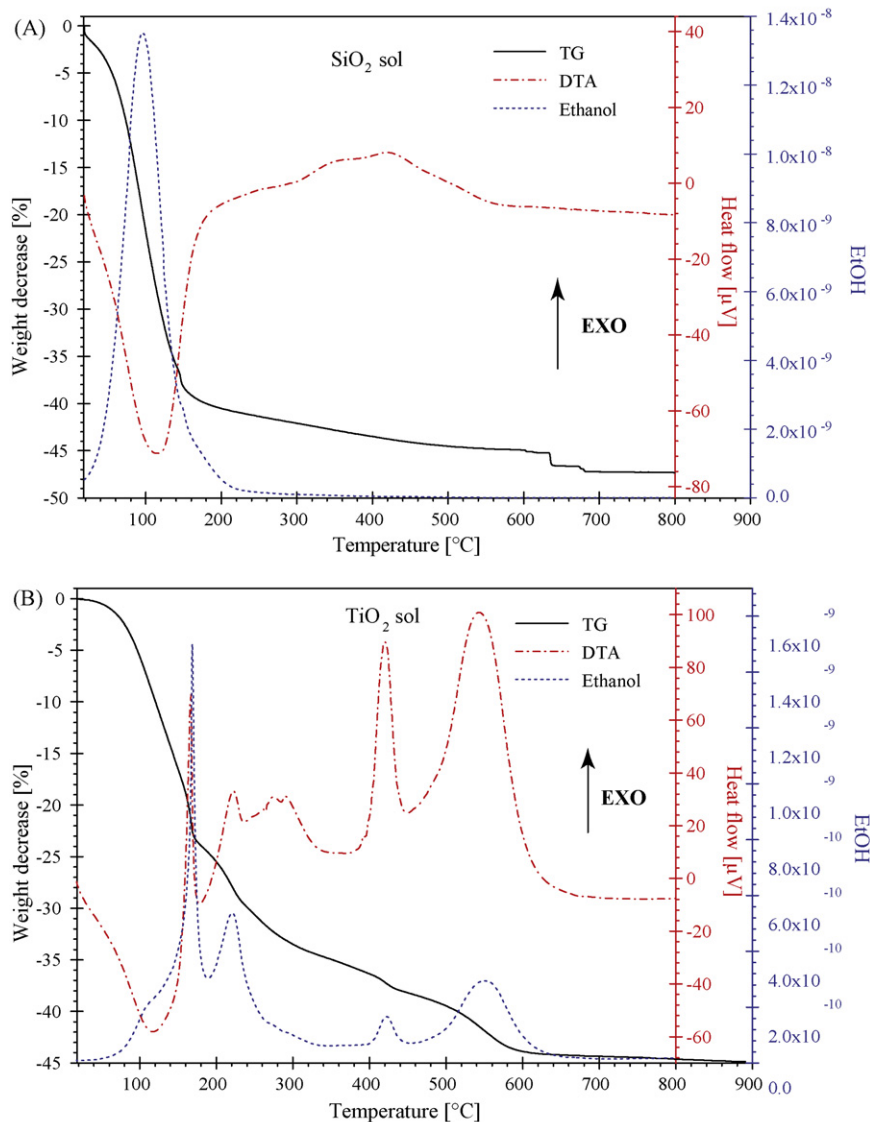


Fig. 2. TG and DTA curves of (A) SiO_2 and (B) TiO_2 xerogel dried at 25 °C. The concentration of ethanol measured by MS during the analysis is also shown.

All the layers exhibited an excellent adhesion to the supports. Typical interference spectra associated with thin films were evident, a feature which allowed the thicknesses of the titania layer films to be calculated from the reflectance spectra using NanoCalc software [26]. When the $\text{TiO}_2/\text{SiO}_2/\text{glass}$ system was used, the thickness of the SiO_2 barrier was around 50 ± 2 nm and the thickness of the final titania layer was 65 ± 2 nm. As observed earlier, there is a linear dependence of layer thickness on the number of layers prepared by subsequent dip-coating [26,27]. This means, that when the TiO_2 barrier was used together with the final titania layer, the overall thickness of $\text{TiO}_2/\text{TiO}_2/\text{glass}$ system was 130 ± 2 nm.

Results of the TG/DTA analysis of the SiO_2 and TiO_2 xerogel prepared by drying the sols for 2 days at room temperature are shown in Fig. 3A and B. During the TG/DTA analysis of the SiO_2 xerogel, all significant changes occurred up to 200 °C (Fig. 2A). Between 25 and 150 °C approximately 40% weight decrease was observed. This can be attributed to evaporation of the physically adsorbed water and other chemicals, especially ethanol (which corresponds to the ethanol peak detected by MS detector at 100 °C). Above this temperature all ethanol is evaporated and the weight decrease is very

small (only 5% up to 600 °C). The DTA curve contains no peaks and therefore we do not expect change in structural and mechanical properties of the film.

The TG/DTA curves for TiO_2 xerogel are more complicated than those for SiO_2 (Fig. 2B). The weight loss below 110 °C corresponds to the removal of adsorbed water and ethanol. The second weight loss at about 180 °C is attributed to the removal of chemically adsorbed ethanol. The third weight loss, between 190 and 400 °C, is attributed to the removal of organics and structural hydroxyls, which increases the number of bridging oxygen atoms and thus the monolithic nature of the gel matrix [28]. The literature results indicate that the most abundant release of organic fraction takes place in the temperature range 100–400 °C and the heat treatment temperature needed to obtain the crystalline TiO_2 -anatase phase generally remains between 400 and 500 °C [29,30]. According to these results we can expect structural and mechanical changes of TiO_2 films during increase in the annealing temperature.

Fig. 4 shows that the titania layers analyzed by X-ray diffraction are at-most 120 nm thick and the analyzing beam penetrates about 30 μm deep into the glass or $\text{SiO}_2/\text{glass}$ substrate. Therefore

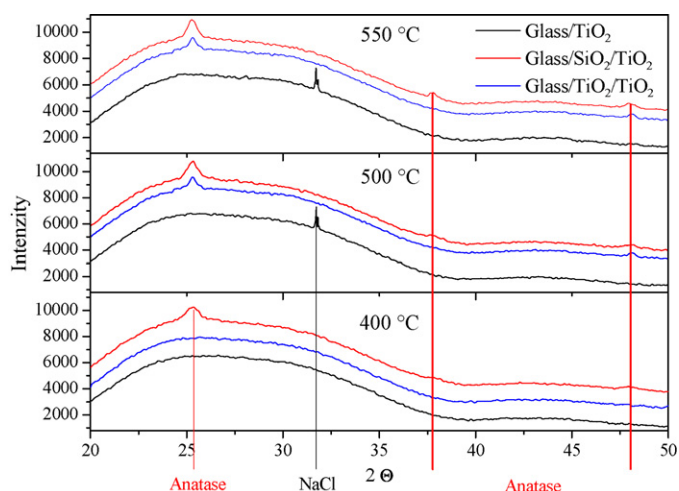


Fig. 3. RTG diffraction of titania layers for different calcination temperatures. SiO₂ and TiO₂ barrier layers were annealed at 550 °C. The peaks of the anatase phase are well defined and match with (JCPDS 21-1272).

the contribution to the X-ray layer pattern from the amorphous substrate is clearly seen as a large hump in the 2θ angular range 20–40° (Fig. 3). The peaks of the anatase phase are well defined and are matched with the PDF card 21-1272 [31]. No peaks corresponding to the rutile phase were observed, which is in agreement with reports that the phase transformation from anatase to rutile occurred at 1000 °C when HCl was used as catalyst in sol-gel formation [23].

On TiO₂/glass samples, where a TiO₂ layer is deposited directly on the glass substrate without any barrier, X-ray diffractograms showed no lines corresponding to anatase crystalline structure. The absence of anatase lines does not mean that it is not present. The detection limit of anatase decreases with decreasing titania layer thickness and anatase crystallite size, which means that in thin layers with anatase crystallite size less than 10 nm, it is very hard to observe anatase lines in the X-ray pattern. For TiO₂/SiO₂/glass samples the amorphous phase is still dominant, but we can prove anatase crystal formation starting from 400 °C and the anatase peak area is slightly increased with increasing temperature (around 10% for an increase from 400 to 550 °C). The size of anatase crystallites (calculated according to the Scherrer equation) is increasing with temperature, about 6 nm between 400 and 550 °C (Table 1). The same behaviour of crystallite size increase with increasing calcination temperature was observed previously [32], but the crystalline size changed only about 3 nm with temperature change from 400 to 600 °C. For the TiO₂/TiO₂/glass samples, anatase crystals were also detected, but in this case they initially appeared at 500 °C, and the anatase peak area was three times lower than that for SiO₂ barrier (Table 1). Note that the thickness of the TiO₂ layer in TiO₂/TiO₂/glass samples is 130 nm; this means that it is two times higher than in TiO₂/SiO₂/glass samples, and even if the first titania layer is serving as barrier, the total amount of TiO₂ is doubled. It is surprising that, for a single 60 nm thick layer with SiO₂ barrier,

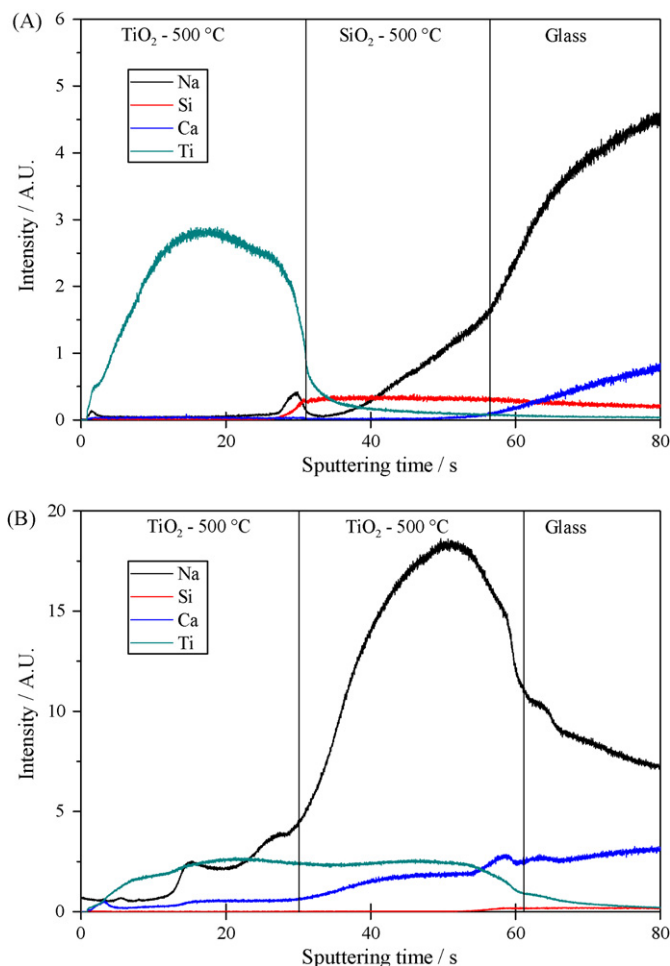


Fig. 4. GDS Na(I), Ca(II), Ti(IV) and Si(II) depth profiles for TiO₂/SiO₂/glass (A) and TiO₂/TiO₂/glass (B) layers calcined at 550 °C.

the area of the anatase peak is higher than that for a 130 nm titania layer (TiO₂/TiO₂/glass).

As already mentioned Na⁺ ions diffusing from the glass support to TiO₂ film may influence photoinduced activity. Therefore the determination of the sodium concentration profile in thin film deposited on glass is of great interest. When the SiO₂ layer is studied, we can approximately recognize the interface between the glass and the SiO₂ layer by Ca(II) detection. It can be seen that Ca²⁺ diffusion to the SiO₂ layer is negligible and we also observe only a very small amount of Na(I) in the SiO₂ bulk. As a consequence, the SiO₂ barrier layer act as very effective protection against Na⁺ and Ca²⁺ ion diffusion from soda-lime glass substrate. In contrast, from Fig. 5b we can see an increase in Na(I) concentration in the TiO₂ bulk (3 times) in relation to the Na(I) concentration in the glass substrate, when only TiO₂ layer is used as a single layer. But the amount of Na(I) in the outer part of titania film is 2 times lower than in the glass substrate. Tada and Tanaka [30] measured the Na(I) profile in

Table 1

Anatase peak area and anatase crystallite size [nm] for different titania substrates and calcination temperatures of final titania layer. The TiO₂ or SiO₂ barrier layers were calcined at 550 °C.

Final calcination	Anatase peak area $2\theta = 25.3^\circ$		Anatase crystallite size [nm]	
	TiO ₂ /SiO ₂ /glass	TiO ₂ /TiO ₂ /glass	TiO ₂ /SiO ₂ /glass	TiO ₂ /TiO ₂ /glass
300	0	0	0	0
400	899	29	13	0
500	950	302	16	18
550	1009	740	19	25

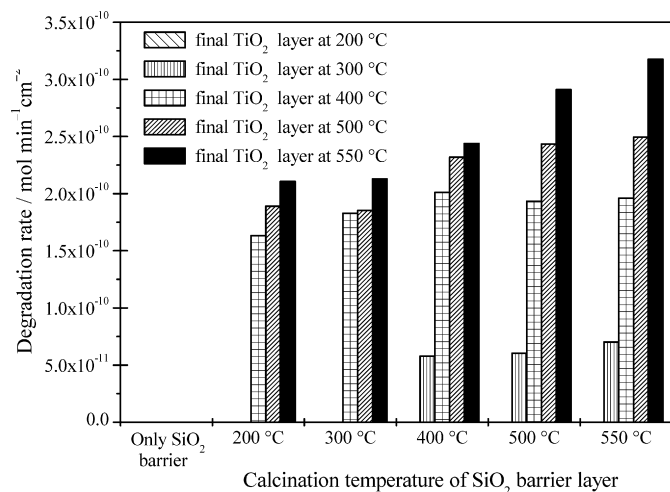


Fig. 5. Effect of SiO₂ barrier: different calcination temperatures of the SiO₂ barrier layer are on x-axis and the degradation rates of the 4CP R [mol min⁻¹ cm⁻²] for different calcination temperatures of the final TiO₂ layer are in columns.

a single titania sol-gel layer deposited on soda-lime glass and calcined at 500 °C using XPS. They also observed an increased amount of Na(I) in the titania layer, but the maximum was not in the bulk of the titania layer, but on the outer surface. This difference may be due to the measurement technique, but our results obtained by GDS reflect Na⁺ ion diffusion in a more realistic way.

GDS records for one layer of TiO₂ film on SiO₂ pre-coated glass (Fig. 4a) reveal very significant suppression of sodium ion diffusion to the titania bulk and the concentration of Na(I) in titania layer is almost zero. When a titania layer is coated on a TiO₂/glass substrate—two titania layers are present (Fig. 4b); we can still see Na⁺ ion diffusion to the final layer, but the concentration is much lower than in the TiO₂ layer close to glass substrate and in the glass. It is interesting that similarly as in the single titania layer (TiO₂/glass) the concentration of Na(I) has a maximum in the first titania barrier layer.

3.2. Photocatalytic measurements

No significant change in the decomposition rate of 4CP was observed within a pH range of 2.9–6.0 [33]. Our reactions started at pH = 4.5 and at the end of 4CP degradation it was around 3.8 so we do not expect either speciation or adsorption on titania layer. It means that using 4CP model compound we can correctly compare photocatalytic activity of titania films calcined at various temperatures. The dependence of 4CP concentration on irradiation time was measured for all tested samples. From the linear part of such curves the initial rate R [mol min⁻¹ cm⁻²] of 4CP degradation was then calculated.

Fig. 5 shows the effect of different calcination temperatures of the SiO₂ barrier layer (x-axis) and different calcination temperatures of the final TiO₂ layer (columns) on the degradation rate R of 4CP [mol min⁻¹ cm⁻²]. It can be seen that the photocatalytic activity of a single SiO₂ layer (without TiO₂ final layer) is negligible. Secondly it is clear that the calcination temperature of the SiO₂ barrier has no significant effect on the photocatalytic activity of the final titania layer. This is not surprising because the TG/DTA analysis of SiO₂ xerogel (Fig. 2A) showed no release of organic or weight loss of the material for temperatures above 200 °C. Also GDS results showed that the SiO₂ layer is a very effective barrier against Na⁺ and Ca²⁺ ions. From Fig. 5 it further follows that with increasing calcination temperature of the final titania layer in TiO₂/SiO₂/glass samples, starting from 300 to 550 °C, the photocatalytic activity increases. This can be explained by anatase crystal formation and

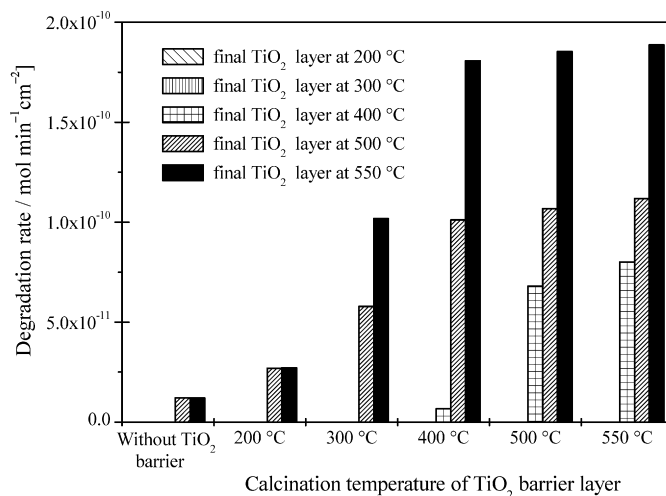


Fig. 6. Effect of TiO₂ barrier: different calcination temperatures of the TiO₂ barrier layer are on x-axis and the degradation rates of the 4CP R [mol min⁻¹ cm⁻²] for different calcination temperatures of the final TiO₂ layer are in columns.

its increasing amount at temperatures higher than 400 °C (Fig. 3, Table 1).

It is interesting that when the SiO₂ barrier layer in TiO₂/SiO₂/glass samples is calcined at 400, 500 and 550 °C, the titania layer is photocatalytically active even when calcined at 300 °C. This is possibly due to the formation of very small crystals of anatase which could not be detected by XRD.

Fig. 6 shows the effect of different calcination temperatures of the TiO₂ barrier layer (x-axis) and different calcination temperatures of the final TiO₂ layer (columns) on the degradation rate R of 4CP.

When the TiO₂ layer was used as a single layer (TiO₂/glass), very low photoactivity was observed only for 500 and 550 °C calcination temperatures (Fig. 6); for lower temperatures the photocatalytic activity was negligible. The degradation rate of 4CP on TiO₂/glass samples (550 °C) is 26 times smaller than on TiO₂/SiO₂/glass (SiO₂ barrier 550 °C, TiO₂ final layer 550 °C). This is in agreement with the generally accepted fact that Na⁺ ion diffusion decreases the activity. Guillard et al. [14] observed sixfold smaller activity of sol-gel titania layers on soda-lime glass than on pyrex or silicon. This difference was ascribed to the presence of Na, Mg and Ca atoms in soda-lime glass while in Pyrex no such atoms were detected. The difference in activities (26 times and 6 times) can be explained by the fact that our layers are almost 4 times thinner than those prepared by Guillard. This finding is supported by Watanabe et al. [34] who reported that the difference in photoactivity of the TiO₂ film formed on soda-lime glass and SiO₂ pre-coated soda-lime glass is more pronounced when the TiO₂ film thickness is smaller.

Here we must mention, that after calcination of final titania layer in the TiO₂/TiO₂/glass system both, barrier and final titania layer are at the end calcined at the same temperature. The following result will show, that the effect of calcination temperature on the properties of titania barrier layer is very important. When the TiO₂/TiO₂/glass samples were studied (Fig. 6), no photocatalytic activity was observed for final titania layers calcined at 200 and 300 °C and the calcination temperature of the titania barrier had no effect.

If we now focus to the samples where the final TiO₂ layer was calcined at 550 °C, we can see that when the titania barrier is calcined at temperatures ≤ 400 °C, the photocatalytic activity of such samples increased linearly with temperature, but if the titania barrier is calcined at temperatures ≥ 400 °C, the photoac-

tivities are almost the same. This phenomenon is also the same for TiO₂/TiO₂/glass samples where the final layer is calcined at 500 °C.

This effect of TiO₂ barrier calcination temperature on photocatalytic activity of the final titania layer is in good correlation with our TG/DTA results, which show that, at temperatures from 300 to 550 °C, the TiO₂ barrier is not thermally stable and, when the final titania film is deposited and calcined, it is not well protected from metal ions diffusion.

Now we will focus on different calcination temperatures of the final titania layer in TiO₂/TiO₂/glass where the TiO₂ barrier is calcined at 550 °C (Fig. 6). We can see that, with increasing calcination temperature, the degradation rate increases, e.g., almost twice (by a factor of 1.7) with increasing temperature from 500 to 550 °C. This agrees well with our XRD measurement which shows that the amount of anatase in the layers calcined at 550 °C is 2.4 times higher than at 500 °C. Mathews et al. [35] also observed an increase in photoactivity with annealing temperature. This is explained, not only by the change in crystal structure of the films, but also by the change in surface morphology. They concluded that increase in calcination temperatures from 400 to 600 °C leads to an increase in the surface roughness and thus to an increase in effective surface area which, in turn, improved the photocatalytic activity. In our case the possible effect of the surface roughness could be excluded because for all calcination temperatures the surface roughness was equal to 3 ± 1 nm.

The strong positive effect of the SiO₂ barrier would be even more pronounced taking into account that, in the case of TiO₂ as barrier layer, we have two times larger amount of TiO₂ photocatalytic material in the film.

3.3. Relation between Na(I), crystallinity and photoactivity of titania layers

By GDS analysis (not shown in graphical form) we have found that for TiO₂/glass samples calcined at 200 °C the amount of Na(I) in the titania layer is the same as in the glass substrate. The Na⁺ diffusion coefficient at 400 °C in alkali silicate glass (transformation temperature $T_g = 478$ °C) is about one order of magnitude higher than that for 300 °C [36]. As a consequence we can expect an increased diffusion of Na⁺ ions in glass at calcination temperatures around 400 °C. When a TiO₂/glass sample is calcined at 550 °C the amount of Na(I) is 3 times higher than in soda-lime glass substrate. This means that the Na⁺ ions can diffuse easily from glass into the bulk of the TiO₂ layer and their diffusion coefficient in the titania layer at the calcination temperature is due to organic compounds present in the layer even higher than in the glass. This is in agreement with our TG/DTA analysis in Fig. 3B, where we can see some removal of organic even at 600 °C.

On the other hand when SiO₂/glass samples were analyzed by GDS, the amount of Na(I) in the SiO₂ layer was negligible and the calcination temperature has no significant effect on the Na(I) amount in the layer. For SiO₂ sol it was experimentally proved (TG/DTA analysis; Fig. 2A) that above 200 °C there were no organic compounds and the inorganic SiO₂ structure was completed. Thus, diffusion of Na⁺ ions from glass during the calcination was suppressed. As a consequence, when Na⁺ ions are on the surface or in the titania layer, they repressed the crystallinity of TiO₂, but when a SiO₂ underlayer is used, the anatase crystal phase was detected by XRD.

Table 1 shows that the crystallite size in samples where a SiO₂ barrier is not present (TiO₂/TiO₂/glass), is higher than in TiO₂/SiO₂/glass samples. This is in good correlation with the results of Nam et al. [12] who observed higher crystallite size of anatase crystals when Na⁺ ions were added to titania powder (prepared by the sol-gel process) before calcination. For TiO₂/glass samples no anatase crystalline phase was detected and, as described above, the

concentration of Na(I) in the layer was so high that a NaCl crystal peak was detected in the titania layer calcined at 500 and 550 °C (Fig. 4). Nam et al. [12] observed NaCl crystal formation in TiO₂ powder prepared from acidic Ti-isopropoxide sol, where NaOH and HCl was added. In our case, where no additional Na⁺ ions are added, NaCl must be formed after the deposition of titania sol on the glass support and following annealing of the layer. For lower temperatures (200, 300 and 400 °C) where Na⁺ ion diffusion is low no NaCl peaks were detected.

From our results it is clear that the photocatalytic activity is mainly dependant on the amount of anatase and the anatase crystallite size; this is the reason why very low activity was determined when Na(I) was detected. As a consequence, for photocatalytically active titania layers prepared by the sol-gel method on soda-lime glass, a SiO₂ barrier layer is necessary. The final TiO₂ can be relatively thin and even lower temperatures can be used for calcination. In contrast, for TiO₂ layers coated directly on the substrate, higher thicknesses and also higher temperatures are needed to reach sufficient photoactivities.

4. Conclusion

The major observations of this study can be summarized as follows. (i) Due to the presence of Na(I) (proved by GDS), TiO₂ single layers with no barrier (TiO₂/glass) calcined at 500 and 550 °C show very low photoactivity. (ii) TiO₂ layers with SiO₂ barrier, TiO₂/SiO₂/glass, have more than 20 times higher photocatalytic activity than those without a barrier (TiO₂/glass). (iii) The calcination temperature of the SiO₂ barrier itself is not so important, and it was found that 200 °C is enough to stop metal ion diffusion from the glass substrate.

The results show that the SiO₂ layer is a much better barrier than TiO₂. This is due to the fact that thermal diffusion of metal ions from the alkaline-containing substrate into the outer titania layer during calcination is much slower in the SiO₂ barrier layer than in the TiO₂ barrier layer.

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