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Photocatalytic activity of titanium dioxide coatings: Influence of the firing temperature of the chemical gel

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Abstract

Heterogeneous photocatalysis can be exploited for the decomposition of micro-organisms which have developed on the surfaces of building materials. In this work, the efficiency of titanium dioxide coatings on fired clay products is examined. The sol–gel method is used to synthesize a fine TiO_2 powder with a specific surface area of $180\,m^2\,g^{-1}$. Thermal treatment of the chemical gel at 340 °C leads to crystallisation in the anatase phase and with further temperature increase, crystallite growth. For thermal treatments in the range 580–800 °C, there is a progressive transition from anatase to rutile. However, despite a decrease in specific surface area of the powder attributed to aggregation/agglomeration, the coherent domain size deduced from X-ray diffraction measurements remains almost constant at 23 nm. Once the transition is completed, increase of thermal treatment temperature above 800 °C leads to further crystallite growth in the rutile phase. The thermally treated titania powders were then sprayed onto fired clay substrates and the photocatalytic activity was assessed by the aptitude of the coating to degrade methylene blue when exposed to ultraviolet light. These tests revealed that the crystallite size is the important controlling factor for photocatalytic activity rather than the powder specific surface area or the anatase/rutile polymorph ratio.

1. Introduction

In addition to aesthetic considerations, the development and proliferation of micro-organisms on clay products can cause mechanical and chemical damage to the material. Titanium dioxide is well known as an active catalyst for degradation of dyes[1–4] and in the metastable form anatase, it is currently the most commonly used catalyst for the photodegradation of organic pollutants.[5] More generally, the anatase allomorph of titanium dioxide is a wide bandgap semiconductor that has been used in a wide range of applications, including photocatalysis,[6–8] dye-sensitized solar cells[9,10] intercalation of lithium ions in batteries[11,12] and in electrochromic displays.[13,14]

Titanium dioxide synthesis processes require in general high temperature and pressure conditions, and lead to a mixture of anatase and rutile crystals.[15] The sol–gel technique can be effectively used to control the size of the crystallites and the anatase to rutile ratio. Furthermore because it is a lower temperature synthesis route, the cost in energy associated with the synthesis of anatase crystals is decreased.

The role of the particle size is important because it intervenes in a competition between mechanisms: the decrease of the average particle size increases the number of surface sites for charge transfer but also causes an increase of the rate of recombination of the surface charge, which can slow down the degradation of the organic compounds by photocatalysis. In this case, according to Dodd et al., the charge carriers accumulate near the particle surface and the process of recombination becomes faster than the interfacial charge transfer.[16]

This paper describes the preparation of anatase and rutile particles synthesized with a sol–gel method[17] and the impact of various physical and chemical parameters, such as the crystallinity, the anatase to rutile ratio,[1,18] the crystallite size and the specific surface area[19,20] of the crystals on their photocatalytic activity. To investigate how the photocatalytic activity of titania powder is influenced by these parameters, thermal treatments of the synthesized powders were made from 350 °C to 1100 °C. The powders were then characterized by X-ray diffraction and BET

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specific surface area measurements. The main parameter controlling the characteristics of anatase powders is the temperature of the thermal treatment of the chemical gel.

2. Experimental

2.1. Sol–gel synthesis of anatase crystals

The chemical synthesis used in this study was adapted from a method originally reported by Uekawa and Kajiwara.[17] In a nitrogen atmosphere, 2 mL of titanium isopropoxide (Alpha Aesar, 97%) was poured into a 50 mL flask at room temperature. 30 mL of anhydrous ethanol (VWR Prolabo) was rapidly added. At this point, fine white precipitates often formed in the clear solution. 0.15 mL acetic acid (VWR Prolabo, 99.8%) was added, and the solution was stirred for 5–10 min until the precipitates dissolved and the solution became clear and colourless. 8 mL of aqueous hydrogen peroxide (VWR Prolabo, 33%) was then added, resulting in a bright orange transparent solution containing a titanium peroxide product.[21,27] The total solution volume was completed to 50 mL by adding anhydrous ethanol. The solution colour slowly changed from orange to transparent yellow after approximately 5 h reaction time at room temperature. The above solution was aged at 75 °C for 72–96 h. After 30 min of heating, the solution became translucent yellow and noticeably more viscous. After approximately 60 min, an opaque, pale yellow gel had formed. At the end of the aging stage, aggregates of dark orange particles were obtained.[21]

In order to obtain titanium dioxide crystals of various sizes, the powders were then heated at different temperatures comprised between 200 °C and 1100 °C for 1 h (temperature ramp: 5 °C/min).

2.2. Sample preparation

Substrates in the form of square slabs were cut, with dimensions 4 cm × 4 cm × 1 cm, out of a commercial fired clay product. Next, 10 g of the dioxide powder was dispersed in 90 g of distilled water. The suspension was then mixed for 15 min in a tubular agitator before being sprayed onto the fired clay substrates. Samples were subsequently heated at 100 °C for 2 h (temperature ramp: 10 °C/min) to achieve adherence of the coating.

2.3. Analysis

The specific surface area of dioxide powders was measured using the BET method with a FlowSorb II (Micromeritics) instrument.[27] All samples were treated at 300 °C for 3 h, prior to measurements, to evacuate all previously absorbed gases.

In order to assess particle size and the anatase content of the dioxide powders, X-ray diffraction (XRD) measurements were performed on a Debye Scherrer diffractometer using a copper source and a monochromator located in front of the sample. The sample was planar and studied in reflexion. The diffracted rays were collected by a curved detector (INEL CPS 120) over a period of 12 h. The monochromatic beam is centred on the CuK_α line ($\lambda = 1.5418$ Å).

The size of the coherent domains has been determined using the simplified Scherrer equation (1)

$$\frac{0.9\lambda}{\Delta(2\theta)\ \cos(\theta)} \tag{1}$$

where λ is the wavelength ($\lambda = 1.5418$ Å) and θ is the diffraction angle.[5]

The mass fractions of the rutile phase (W_R) and anatase phase (W_A) of the titanium dioxide powders have been calculated using Eqs. (2) and (3):

$$W_\mathrm{A} = \frac{1}{1 + 1.265 I_\mathrm{R}/I_\mathrm{A}} \tag{2}$$

$$W_\mathrm{R} = \frac{1}{1 + 0.8 I_\mathrm{A}/I_\mathrm{R}} \tag{3}$$

where I_R is the intensity of the strongest peak of rutile, corresponding to the crystallographic direction [1 1 0]; $2\theta = 27.438$ Å and I_A, the intensity of the strongest peak of anatase, corresponding to the crystallographic direction [1 0 1]; $2\theta = 25.281°$.[5] No evidence was observed in the X-ray pattern for the presence of brookite.

To determine the evolution of titanium dioxide powders with temperature, differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) was made using a Setsys 24 (Setaram) instrument from room temperature to 1200 °C with a temperature ramp of 5 °C/min. Measurements were conducted in air using a calcined alumina powder for reference.

The photocatalytic activity of the coatings made with these crystals was then evaluated using a procedure involving the UV decomposition of methylene blue. The coated samples were soaked in a 10^{-5} M methylene blue solution for 30 min. The methylene blue degradation was monitored using a UV–vis spectrophotometer (Elmer Perkin Lambda 40). Since the samples are solid and opaque, the absorption measurements are made with an integrating sphere which collects the reflected beam from the sample. Samples were exposed to UV light ($\lambda = 366$ nm) for 2 h, and measurements were recorded at regular time intervals. The methylene blue adsorption spectra for a fired clay substrate exhibited three peaks, centred on 555 nm, 600 nm and 660 nm which are attributed to the presence of H-aggregates, dimers and monomers respectively of methylene blue. The relation between absorption of light, A, and concentration of the absorbing species, C, is described by the Beer–Lambert law:

$$A = \varepsilon b C \tag{4}$$

where b is the optical path length in cm and ε is the extinction coefficient in $\mathrm{cm}^{-1}\,\mathrm{L}\,\mathrm{mol}^{-1}$. The extinction coefficient for each species is assumed to be the same.[13–18] The ratio of concentration of methylene blue, at a time t, C_t to the concentration at time zero, C_0, is given by the ratio of the measured absorption A_t at time t to the initial absorption A_0. Though there is an interdependent relationship between the three species, it has been found convenient to choose the strong dimer peak to represent

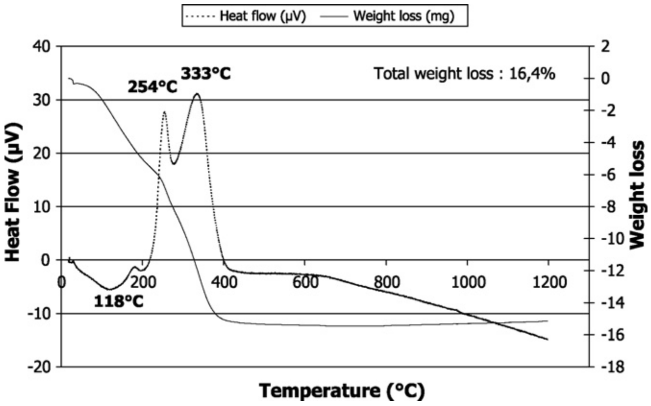

Fig. 1. DTA-TGA analysis of a titanium dioxide chemical gel.

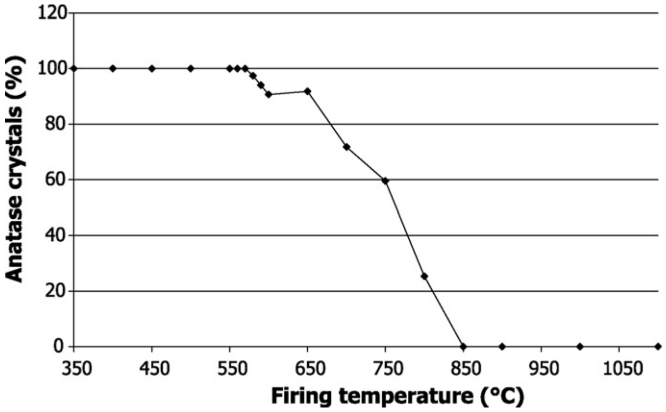

Fig. 2. Evolution of the anatase content as a function of the firing temperature.

the concentration of methylene blue. In fact, a slight red shift can be detected in the 600 nm dimer peak explained by the conversion of dimers into monomers. The absorption ratio A_t/A_0 of this peak has therefore been studied as a function of irradiation time.[22]

3. Results and discussion

3.1. Crystallisation of anatase

Thermal analysis of the chemical gel obtained from the sol–gel synthesis, before any calcination, gave information on crystallisation in the powder. The DTA curve (Fig. 1), presents three peaks associated with a cumulative mass loss of approximately 15.5%. The first peak located at 118 °C is endothermic and corresponds to the evaporation of the excess water present in the chemical gel. The strong peaks at 254 °C and 333 °C are exothermic. They correspond respectively to the decomposition of alcohol residue and to the crystallisation of anatase particles due to a reorganization of the Ti–O bonds.[21] XRD analysis of the powders obtained after heating treatments at 250 °C and 340 °C has shown that anatase does not crystallise below 250 °C but confirmed that crystallites have been formed in the powder once 340 °C is attained.

In the rest of the paper, the powder called synthesized anatase corresponds to a gel calcined at a temperature equal to or above 340 °C.

3.2. Influence of thermal treatment of the chemical gel on the anatase content and the size of the coherent domains of anatase particles

Due to the fact that the photocatalytic activity of titanium dioxide powder is influenced by factors such as the crystallinity of the anatase phase[1,18] and the specific surface area,[19,20] we have investigated the influence of the thermal treatment temperature on the physical and chemical characteristics of the gel.

As a starting point, the X-ray data was analysed in order to determine the anatase/rutile ratio as a function of thermal treatment temperature (Fig. 2). Since anatase crystallites are metastable, the transition temperature is not fixed and varies with the synthesis method used. In the synthesis of ultrafine titania by the sol–gel method, during coarsening of the nanocrystalline anatase, anatase transforms to rutile only after growing to a certain size (14 nm in diameter), and once rutile is formed, rutile coarsens much faster than anatase.[23,24] In the present case, the first rutile crystallites appear after treatment at 580 °C. Below 580 °C, the content of anatase crystals in the powder is close to 100% (within the detection limit of XRD). For treatment temperatures of the chemical gel comprised between 580 °C and 850 °C, there is a progressive transition from anatase to rutile. Then at thermal treatment temperatures of the chemical gel above 850 °C, the anatase content is below the detection level (100% rutile).

XRD analysis of the powders also gives information on the evolution of the size of coherent domains as a function of the treatment temperature (Fig. 3). In fact, the size of coherent domains has been determined from each diffraction peak corresponding to the crystallite phase studied. However, due to the hypothesis made on the XRD size evaluation (the size of the coherent domains corresponds to the size of well organized particles at the crystallographic scale), it is important to note that the size of coherent domains should be smaller than the size of aggregated particles. In this work, the evolution of the size of coherent domains of anatase and rutile crystals can be divided

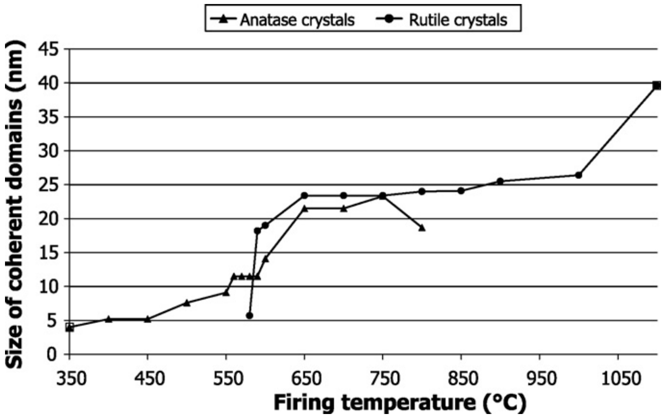

Fig. 3. Evolution of the size of coherent domains of the powder particles synthesized as a function of the firing temperature.

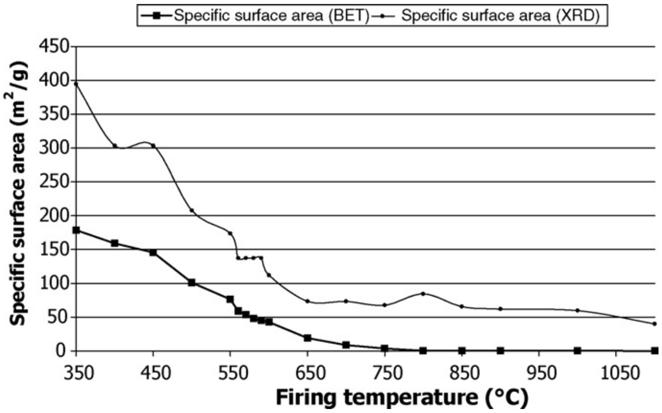

Fig. 4. Evolution of the specific surface area of crystals obtained by sol–gel synthesis as a function of the firing temperature of the chemical gel.

into four temperature ranges. As indicated by peaks in the diffraction pattern, thermal treatment at temperatures between 350 °C and 400 °C results in crystallisation of anatase particles, which however remain very small. Then from 400 °C to 580 °C, there is a significant increase in the size of the anatase crystallites corresponding to reduction of surface free energy of the powder. In the next temperature range from 580 °C to 800 °C, where there is a progressive transition from anatase to rutile, the coherent domain sizes are similar and remain almost constant with thermal treatment temperature. This observation that the anatase to rutile conversion starts at a temperature of approximately 580 °C, which in turn corresponds to an anatase coherent domain size of 12–15 nm matches well with the previous work of Banfield and coworkers.[23–25] We might deduce that the available free energy is now consumed by the phase transition. Finally above 800 °C, once the transition is finished, increase of the thermal treatment temperature yields a further increase in coherent domain size.

3.3. Influence of firing temperature of the chemical gel on specific surface area of anatase powders

Further information is given by measurement of the specific surface area of the powders as a function of the treatment temperature (Fig. 4). This decreases from a starting value of 180 $m^2 g^{-1}$ for powder treated at 350 °C to 0.1 $m^2 g^{-1}$ for powder treated at 1100 °C, corresponding to a substantial change in powder reactivity. The initial decrease for treatments up to 600 °C can be explained essentially by anatase crystallite growth. To a first approximation, the anatase crystallites are assumed to be spherical. This is not strictly true but according to Masson et al.,[28] titania crystallites evolve from a slightly anisotropic shape when below 600 °C towards a more equiaxed shape at 800 °C. For a spherical particle of diameter D the equivalent specific surface area Sp is given by

$$\mathrm{Sp} = \frac{6}{\rho D} \qquad (5)$$

where ρ is the crystallite density. Table 1 compares calculated equivalent specific surface area values using the size of coherent domains obtained by XRD for D to the measured values. Though the ratio is not equal to 1, which can probably be attributed to different assumptions used in the two approaches, it remains almost constant between 2 and 3 up to 600 °C implying that the specific surface area is controlled by crystallite growth. Higher temperature thermal treatments than lead to a divergence in behaviour expressed by a strong increase in the ratio. Providing the anatase and rutile crystallite surfaces absorb nitrogen in a similar way for the BET experiment,[29] the specific surface area of the powders continues to decrease with temperature despite the fact that crystallite growth has been halted by the anatase to rutile transition. This suggests that another mechanism is operating; aggregation/agglomeration of crystallites, to reduce the powder reactivity as temperature of thermal treatment is increased. In fact, some studies have shown that the kinetics of phase transformation and particle coarsening are related to the nanoparticle aggregation state.[25]

As a general rule, thermal treatment of a powder drives several mechanisms in parallel: for example, crystallite growth, aggregation, agglomeration and pore elimination. According to the physical and chemical conditions within the powder, inhibition of a mechanism will allow the remaining mechanism(s) to become predominant. We note that once the phase transition is completed, crystallite growth with increased thermal treatment temperature starts up again.

3.4. Influence of firing temperature of the chemical gel on the photocatalytic activity of the coatings made with the powder obtained

The characterisation of the titania powders revealed strong changes in the anatase/rutile ratio, crystallite size and the specific surface area as a function of thermal treatment temperature. Finally, spectrophotometric measurements have been made to evaluate the photocatalytic behaviour of fired clay substrate coatings prepared from these powders. This was based on the ability of the titania coating to decompose methylene blue when exposed to UV light.

Analysis of the absorption spectrum of methylene blue deposited on the surface of samples revealed that methylene blue is preferentially adsorbed as dimers and that the physical and chemical characteristics of the coating do not influence its adsorption. The rate of decomposition of methylene blue, based on the height of the dimer peak, is plotted as a function of thermal treatment temperature in Fig. 5. It should be compared to a value of $-(29.5 \pm 4) \times 10^{-5}\ \mathrm{min}^{-1}$ for substrates without titania coatings. The strong increase in decomposition rate from 350 °C to 450 °C can be explained by crystallisation of the anatase particles which is necessary in order to achieve photocatalytic behaviour.

In the temperature range 450–560 °C, the increased anatase crystallite sizes with the corresponding decrease of specific surface area then reduce the decomposition rate. However, the range of thermal treatments from 580 °C to 1000 °C yields surprising information when compared to currently expressed literature opinions.[26] The transition of anatase crystallites into rutile crystallites and the further decrease in specific surface area of the

Table 1
Specific surface area (DRX)/specific surface area (BET) ratio as a function of the heat treatment temperature.

Temperature (°C)	Crystal size (nm)	Specific surface area (Sp) measured by BET method	Specific surface area (Sp) estimated by XRD method	Sp(BET)/Sp(XRD)
350	4	394.74	178.6	2.2
400	5.2	303.64	159.1	1.9
450	5.2	303.64	145.7	2.1
500	7.6	207.76	101	2.1
550	9.1	173.51	76.2	2.3
560	11.5	137.30	59.05	2.3
570	11.5	137.30	53.7	2.6
580	11.5	137.30	47.7	2.9
590	11.5	137.30	45.3	3.0
600	14.1	111.98	42.7	2.6
650	21.5	73.44	18.9	3.9
700	21.5	73.44	8.7	8.4
750	23.3	67.77	3.7	18.3
800	24	84.44	0.4	211.1
850	24.1	65.52	0.2	327.6
900	25.5	61.92	0.2	309.6
1000	26.4	59.81	0.2	299.0
1100	39.6	39.87	0.1	398.7

powder does not result in further decrease in photocatalytic activity. In fact, the decomposition rate, within a certain experimental scatter, remains constant just like the crystallite size. Only the thermal treatment at 1100 °C with significant increase in the rutile crystallite size leads to a reduced decomposition rate. We deduce that the crystallite size of the titania powder is the important controlling factor for photocatalytic activity rather than the powder specific surface area or the anatase/rutile polymorph ratio.

In other words, the crystallite size intervenes in the mechanism of decomposition of methylene blue. Two possibilities can be considered. The first is that the crystallite size affects the number of active sites for decomposition at the interface between the methylene blue layer and that of the titania. The second refers to a role in the supply of species for the decomposition reaction. This reaction is quite complex involving generation of electrons and holes followed by formation of hydroxyl and super oxide radicals. For example, the migration of holes and electrons to the crystallite surface, related to crystallite size, could act as the slow step in this overall process. In this scheme, based on the absence of change in decomposition rate of the powder specific surface area for thermal treatments above 600 °C, further transport of species along grain boundaries and surfaces to reactions sites does not seem to be limiting.

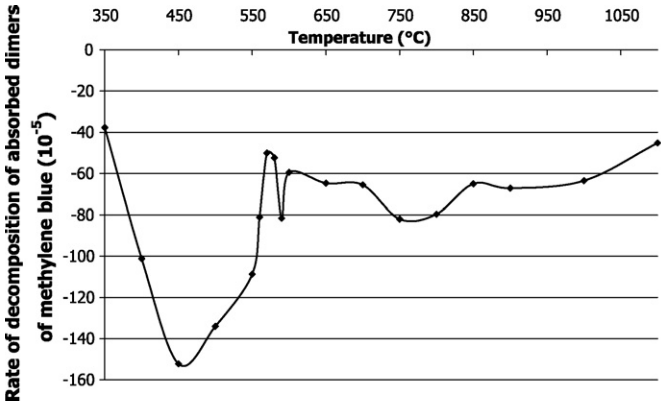

Fig. 5. Evolution, as a function of the firing temperature of the chemical gel, of the rate of decomposition of methylene blue adsorbed on the surface of fired clay substrates.

4. Conclusion

Fine titania powders have been prepared using the sol–gel method. The physical and chemical characteristics of these powders are strongly sensitive to the temperature of thermal treatment of the chemical gel. First, a temperature of 340 °C must be attained before the powder crystallises into the anatase phase. Thermal treatment between 400 °C and 580 °C leads to crystallite growth corresponding to the increase of temperature and reduction of surface free energy of the powder. From 580 °C to 800 °C, there is a progressive transition from anatase to rutile but the crystallite size now remains almost constant. In contrast, the decrease of specific surface area measured by the BET method suggests that aggregation/agglomeration of crystallites in the powder occurs. Once the transition is completed, increase of thermal treatment above 800 °C leads to further crystallite growth as indicated by X-ray diffraction measurements. Finally, the photocatalytic activity of titania coatings on fired clay products was evaluated as a function of the thermal treatment temperature. From these results, we deduce that the crystallite size of the titania powder is the important controlling factor for photocatalytic activity rather than the powder specific surface area or the anatase/rutile polymorph ratio.

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