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Preparation of novel titania photocatalysts with high activity

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New anatase photocatalysts have been prepared by a hydrothermal technique. The powders have been shown to have a high photocatalytic activity, which is believed to be derived from their high crystallinity and phase purity resulting in fewer defects that can allow pre-emptive recombination of the free electron and positive hole. Bi-phasic particles containing both the anatase and brookite phases have also been prepared, but these have much lower photocatalytic activity. © *2001 Kluwer Academic Publishers*

1. Introduction

As the environment becomes a more and more influential political issue, research into environmentally friendly technologies is also becoming more important. Not least among these issues is the safe destruction of toxic waste. Photocatalysts are a very promising technology in this field, with titania as one of the most powerful and versatile photocatalysts currently known [1]. Titania can be used to catalyse many different reactions in the presence of U.V. light, such as alcohol dehydration, photo-Kolbe oxidations of organic acids [1], oxidation of aromatic compounds [2], degradation of paint pigments [3], and nitrogen oxide reduction [4], and has as a result been studied for many years. The detailed mechanism and factors influencing its activity, however, are poorly understood [1].

The photocatalytic activity in semiconductors is due to the production of an excited electron in the conduction band of the semiconductor, along with a corresponding positive hole in the valence band by the absorption of U.V. radiation. These energetically excited species are mobile, and capable of initiating many chemical reactions, usually by the production of radical species at the semiconductor surface. They are unstable, however, and recombination of the electron and hole can occur very quickly. If recombination occurs too fast (less than one nanosecond), then there is not time for any other chemistry to occur, and no photocatalytic activity is observed. In titania, the species are relatively long lived (around 250 nanoseconds), allowing the electron or hole to travel to the crystallite surface. There various different types of radical are formed, the most common of which is the OH• radical, which is then free to carry out further chemistry at the titania surface. It has generally been accepted that titania powders with a large surface area are desirable, and that those with large crystallite sizes make the best catalysts since they contain fewer defects were premature recombination of electrons and positive holes can occur [5].

There are many different methods for making titania, which is by no means an unusual ceramic, but the photocatalytic activity of powders made by different means can vary widely. Of the three polymorphs of titania, it is generally accepted that the anatase phase is the most active as a photocatalyst, while the rutile phase, which is the thermodynamically stable polymorph, although active, is none the less a poorer photocatalyst. Due to the stability of rutile, most available anatase powders consist of a mixture of the anatase and rutile phases, and occasionally a little brookite too. Therefore, the development of a synthesis method that could selectively produce the anatase phase of titania would be of great use in the development of high activity photocatalysts. A considerable amount of research has gone into determining the factors, which should improve the performance of titania catalysts [6–10].

Hydrothermal processing has been shown to be an effective method for the selective crystallisation of anatase from amorphous titania. Recent papers have described the mechanisms of this reaction, and the factors affecting the rate of crystallisation, and the growth of the crystallites in pure water [11, 12]. At low temperature (up to around 300°C) a solid state epitaxial growth mechanism dominates, and can result in the formation of small amounts of brookite impurities in the anatase product unless a basic solution is used for hydrothermal processing. Above this temperature, a dissolution/precipitation mechanism dominates, producing only anatase, unless a strongly acidic solution is used ($<$pH 4), in which case some brookite and rutile may form. It has been shown that the nature of the amorphous starting material has a strong influence on the rate of crystallisation, and the product phases during hydrothermal treatment. The chloride ion in particular (which is a common contaminant in titania prepared from the convenient hydrolysis of $TiCl_4$) was shown to have a strong influence on the phase produced by hydrothermal treatment, often resulting in the production of small amounts of brookite in the powder, if conditions are not carefully controlled as described above. Control of the hydrothermal processing conditions, therefore, can allow a great deal of control over the physical properties of titania products such as crystallite size, surface area, contamination, morphology and phase. Furthermore, hydrothermal processing has already been demonstrated as a useful method for producing very high activity titania photocatalysts. Komanini has produced titania with activities as high as 3 times that of the standard P25 material from Degussa AG [9, 13, 14].

In the current work, some of the factors affecting the photocatalytic activity of titania powders are examined, by utilising the excellent control which can be obtained over the physical properties of the powder using hydrothermal processing.

2. Experimental

Amorphous titania precursors were precipitated by three different methods, before the resulting powders were crystallised under hydrothermal conditions. The methods for precipitation are as follows:-

A 1.5 M NH_3 solution was added dropwise to 330 ml of 0.9 M $TiCl_4$ solution until the pH was raised from 0.5 to 3.0 (approx. 740 ml). The white precipitate formed was aged for 24 hours before washing with water until the pH reached 7. The amorphous powder (powder A) was then dried for 24 hours at room temperature. This powder contained some adsorped chloride ions and was acidic in nature. In addition, Raman spectroscopy showed that there was some anatase-like short-range order in the powder structure, which was not observed by XRD, implying that the powder contained anatase nuclei.

220 ml of 0.9 M $TiCl_4$ solution was added dropwise to a 7.5 M ammonia solution. The pH fell from 12.5 to 10.9 as the white precipitate formed. The amorphous precipitate was aged for 24 hours before washing until the pH reached 9.2. The amorphous powder (powder B) was then dried for 24 hours at room temperature. This powder contained some adsorped ammonium ions and was basic in nature.

A 0.2 M solution of $Ti(OC_2H_5)_4$ in dry ethanol (550 ml) was added to a 0.6 M solution of water in ethanol (550 ml). After ageing for 25 minutes, the reaction mixture was centrifuged and washed twice with ethanol before drying in a vacuum dessicator (powder C) [15]. This powder contained no inorganic impurities and was neutral.

Hydrothermal crystallisation was carried out in microautoclaves of 50 cm^3 internal volume. The autoclaves were lined with Hastelloy C276, a corrosion resistant alloy, to reduce contamination due to the corrosion of the vessel. A typical crystallisation consisted of treating 300 mg of powder in 25 cm^3 of water for 48 hours, at a variety of different temperatures ranging from 100°C to 350°C.

After hydrothermal treatement, the physical properties of the powders were characterised, and the photocatalytic activity of the powders measured. A step size of 0.006° was used together with a scan speed of 0.5° per minute. The anatase/rutile proportions were measured by the method outlined by Spurr and Myers [16], using the equation $f = 1/(1 + 1.26(I_R/I_A))$. Here f is the weight fraction of anatase, I_R is the intensity of the main rutile XRD peak, and I_A is the intensity of the main anatase XRD peak. They estimated the error in this measurement to be within 1%. The crystallite size of the particles was also estimated using Scherrer's method using the formula $p_m = k\lambda/\beta_{1/2} \cos\theta°$. In this case, p_m is the mean particle diameter, k is a constant (0.89), λ is the wavelength of the X-ray radiation, $\beta_{1/2}$ is the width of the peak at half the peak height in radians, and θ is the diffraction angle of the peak. TEM was used to confirm the value of the constant k. This method is extremely sensitive to the trends in particle size for the same material. The specific surface area was measured using the 3 point BET method using a Yuasa Ionics NOVA 1000 instrument. TG/DTA was carried out on a Seiko SSC5200H system. The TG/DTA apparatus was used to calcine samples by heating at a ramp of 20°C min^{-1} to 1000°C.

In addition to the hydrothermally produced powders, a number of commercially available titania powders were also tested, and all results were compared to the P25 powder available from Degussa A.G., which is the accepted standard against which titania photocatalysts are tested [17].

The photocatalytic activity was measured by the ability of the powder to decompose a 10 vol % acetic acid under illumination by a 400 W mercury lamp. Titania powder (0.35 g) was dispersed in 315 ml of water in a sealed vessel, illuminated by a 400 W high pressure mercury lamp. The system was flushed with nitrogen for 30 minutes and the temperature of the water cooled system allowed to stabilise at $45°C \pm 2°C$. The acetic acid (35 ml) was injected into the vessel under a positive pressure of nitrogen, and the nitrogen flow then adjusted to $\approx$60 ml min^{-1}. The gas exhaust was then bubbled through 1 litre of saturated barium hydroxide solution in a beaker, which was sealed in an empty nitrogen bag. The titania/acetic acid mixture was illuminated for 3 hours. After the lamp was extinguished, the nitrogen flow was continued for a further 30 minutes before the nitrogen bag inlet was finally sealed. The mixture was stirred by a magnetic stirrer throughout. The barium hydroxide solution was allowed to stand for 12 hours to ensure that all the CO_2 produced was precipitated as barium carbonate. The solution was then filtered and dried, and the product weighed to give a quantitative yield of carbon dioxide produced from the decomposition of the acid.

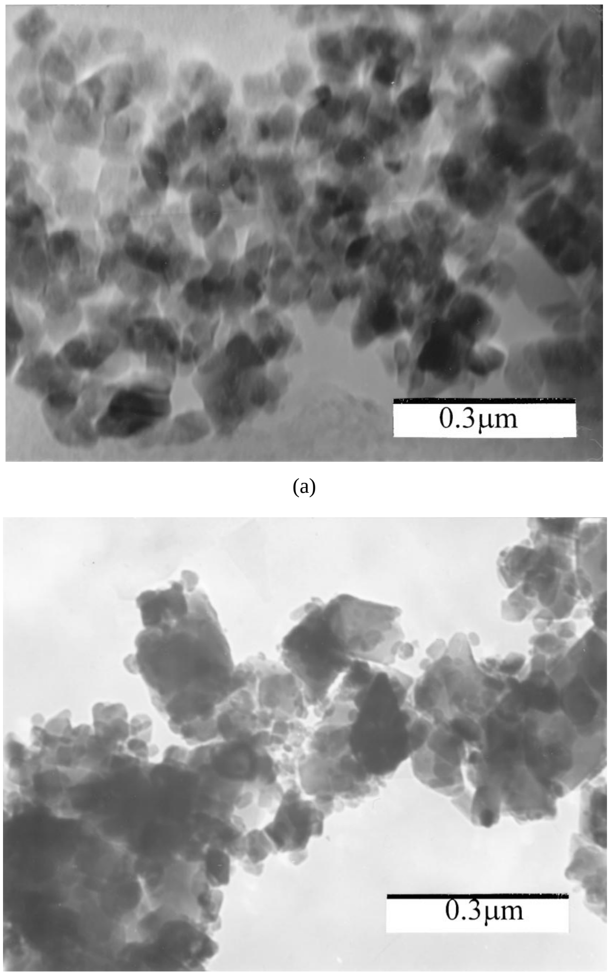
3. Results and discussion

Table I shows the rates of carbon dioxide production for the three amorphous powders A, B, and C, together with their activities after hydrothermal treatment at 350°C for 48 hours. Clearly, the hydrothermal crystallisation of the powders has greatly increased their activity as photocatalysts (by a factor of two). Also significant, however, is the large difference in activity between the different starting materials. Powder B is almost twice

TABLE I Crystallisation conditions, specific surface areas, crystallite sizes, and rates of carbon dioxide production for powders A B and C

Powder	Time (h)	Temp (°C)	Phase	Spec. Surf. area (m^2g^{-1})	Crystallite size (nm)	Rate (moles $g^{-1}h^{-1}$)
A	N/A	N/A	A/AMOR	360	N/A	0.00015
B	N/A	N/A	AMOR	360	N/A	0.00024
C	N/A	N/A	AMOR	360	N/A	0.00087
A	48	350	A	18	51	0.00030
B	48	350	A	32	31	0.00064
C	48	350	A	15	65	0.00178
P25	N/A	N/A	20R, 80A	55	40	0.00045

as active as powder A, even thought the method of synthesis is very similar. This is surprising as anatase is the recognised as the most active polymorph, and is present in A and not C (although in very small amounts). Powder C is almost six times as active as powder A. After hydrothermal treatment, these ratios of activity between the powders remain, although powder B gains a little on powder C. Interestingly, the change in the specific surface areas and crystallite sizes of A and C did not change much relative to each other during hydrothermal treatment, however, powder B did show a significantly lower surface area and higher crystallite size compared to A and C. Of the three powders, only C is more active before calcination than P25, however both B and C are more active after hydrothermal treatment. Powder C is almost 4 times as active as the P25 standard, making it a very promising candidate for photocatalysis applications.



(a)

(b)

Figure 2 TEM micrographs of powder C after hydrothermal treatment for 48 hours at 200°C (a) and 350°C (b).

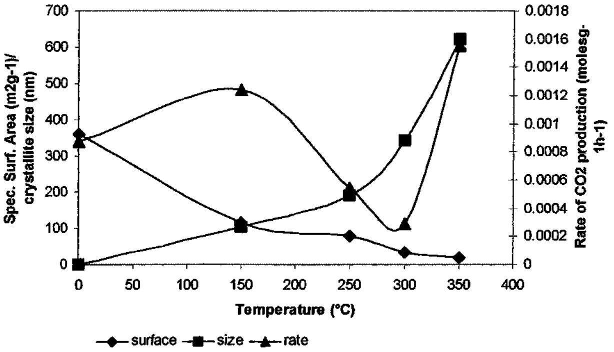


Figure 1 Crystallite size, specific surface area, and rate of carbon dioxide formation for powder C after hydrothermal treatment at different temperatures for 24 hours.

Since the effect of the hydrothermal treatment was largely the same for both the A and C powders, it was decided to focus on powder C for further investigation, since it was free from inorganic contamination, and also the most powerful of the catalysts produced. Fig. 1 shows the changes in crystallite size, specific surface area and photocatalytic activity for powders, hydrothermally treated at different temperatures for 24 hours. Three are clear trends in both the increasing crystallite size and decreasing surface area with increasing hydrothermal treatment temperature, however, the photocatalytic activity has a somewhat complex relationship with the treatment temperature, and shows no clear alignment with either the surface area or the crystallite size. The initial increase in activity can be attributed to the formation of anatase as the titania crystallises under hydrothermal conditions. The activity then falls off with increasing crystallisation temperature and falling surface area. Finally, at a crystallisation temperature of 350°C, the photocatalytic activity sharply increases to its highest level. Clearly these results cannot be explained purely in terms of surface area and crystallite size. The TEM micrographs in Fig. 2 show powder C after hydrothermal treatment at 200°C and 350°C (the most active powder). It can be seen that the increased reaction temperature has resulted in the production of some much larger particles, with the bulk of the particles growing only slightly. This can be attributed to the change in reaction mechanism from the solid state type to dissolution/precipitation, which would result in the elimination of the smallest particles by dissolution, and

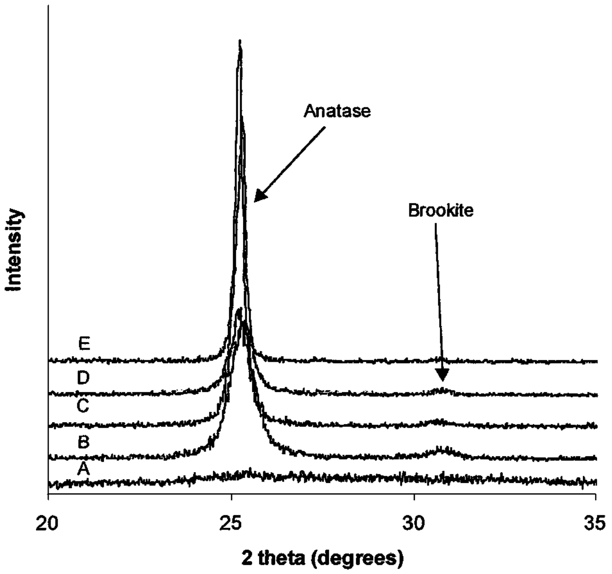


Figure 3 XRD traces of powder C after hydrothermal treatment at different temperatures. A) untreated, B) 150°C, C) 250°C, D) 300°C, E) 350°C.

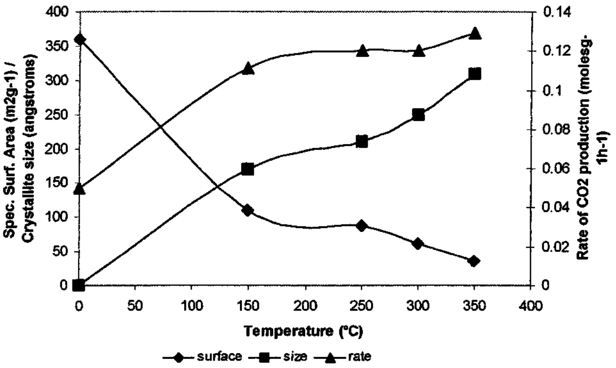


Figure 4 Crystallite size, specific surface area, and rate of carbon dioxide formation for powder B after hydrothermal treatment at different temperatures for 24 hours.

the rapid growth of the largest particles by precipitation of this material. The XRD traces in Fig. 3, however, show that there is a secondary phase present in the powders produced below 350°C. The small peak present at $2\theta = 30.7^\circ$ corresponds to the brookite phase of titania. The presence of this phase also causes the slight shift to higher angle of the anatase peak, since there is an overlapping brookite peak. The brookite phase is not present in the starting material, but is produced as a secondary phase by the solid state reaction mechanism under hydrothermal conditions. When the hydrothermal treatment temperature exceeds 300°C, however, the dissolution/precipitation reaction mechanism then dominates, and the brookite phase is eliminated as described in the introduction.

Fig. 4 shows the specific surface areas, crystallite sizes and activities for powder B, and powder B after various hydrothermal treatments. The trends in surface area and crystallite size are very similar to powder C, but the activity curve for powder B is very different, showing a steady increase in activity with increasing hydrothermal treatment temperature. Since powder B has no brookite present after hydrothermal treatment, regardless of the treatment temperature, it would seem that it is the presence of the brookite phase in powder C, which results in the reduction in photocatalytic activity up until a treatment temperature of 300°C. Above this temperature, the brookite is eliminated and the photocatalytic activity increases greatly.

TABLE II Calcination times, temperatures, and rates of carbon dioxide production for powder C after hydrothermal crystallisation at 350°C for 48 hours

Time (h)	Temperature (°C)	Rate (moles $g^{-1}h^{-1}$)
0	0	0.00087
2	400	0.00073
6	400	0.00052
2	600	0.00058

Although not quantitative, the XRD data does suggest that the amount of brookite present in the powder is very small compared to the amount of anatase. Since the amount of anatase present is therefore increasing with hydrothermal treatment temperature, this suggests that the brookite is interfering with the anatase particles themselves. From this we can deduce that the brookite is present in the same particles as the anatase, since as separate particles they would have little influence. One possible explanation is that the interface between the different phases within the particles provides a site for rapid recombination of electrons and positive holes since such an interface could be regarded as a large crystal defect. This type of recombination before the electron or positive hole reaches the particle surface would significantly reduce the photocatalytic activity.

Komarnini *et al* reported that the activity of his hydrothermally produced titania photocatalysts improved when they were calcined [9]. In this case the activity increased with calcination temperature up until 550°C, beyond which temperature, a decrease in activity was observed. The increase in activity was attributed to a decrease in the number of crystallite defects in the powder; above 550°C, however, the reduction of surface area proved to have a greater effect, and the activity fell. In order to investigate the possible improvement of performance through calcination, powder C was calcined at various temperatures for different times after hydrothermal treatment at 350°C for 48 hours. Table II shows the activities of the powders after calcination. From these results it is quite clear that further calcination of the powder, even at the relatively low temperature of 400°C, in this case, could not improve the activity. Increasing either the time of calcination or the temperature resulted in a decrease in activity. This was probably due to a reduction of surface area on firing, without significant reduction in the number of crystalline defects.

4. Conclusions

High activity titania photocatalysts have been prepared using the hydrothermal method. The high activity is attributed to the high crystallinity of the particles, which have fewer defects at which electrons and positive holes can rapidly recombine and reduce the activity. It has been shown that some of the powders contained biphasic particles consisting of mainly anatase and some brookite. The brookite has been shown to strongly inhibit the photocatalytic activity of the powders. It has been suggested that the interface between the two phases may act as a possible recombination site for the electrons and holes, thus reducing the photocatalytic activity.

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