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Characterisation and activity of sol–gel-prepared TiO_2 photocatalysts modified with Ca, Sr or Ba ion additives

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TiO_2 (anatase)-based photocatalyst powders containing up to 20 mol% calcium, strontium or barium ions were prepared from α-titanic acid by calcining gels prepared from triethanolamine-based sols at 600 °C. The powders were characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM), diffuse reflectance ultraviolet spectrophotometry, nitrogen sorption porosimetry and *in situ* infrared spectroscopy to examine surface adsorbed species. Compositions containing greater than 15 mol% alkaline earth ions resulted in largely amorphous materials. The residual anatase showed decreased crystallite sizes and increased crystallographic cell volumes with increasing concentration of alkaline earth ions, while the BET surface areas of the materials increased from around 80 $m^2 g^{-1}$ (no additive) to 160 $m^2 g^{-1}$ at higher levels of additive. Electronic spectroscopy showed that the band gaps of the materials increased with increasing Ca^{2+} content, due to the decreasing particle sizes. Under the synthesis conditions used, no other crystalline phase was observed, except rutile ($<1\%$ w.r.t. anatase). The photocatalytic decomposition of oxalic acid was used as a model system to determine the relative influences of the additives on the photocatalytic activities. Titania containing 20 mol% alkaline earth ions showed approximately double the photocatalytic activity of similarly prepared anatase without additive. Half of the enhancement occurred for titania samples containing only 2 mol% alkaline earth ions. Comparisons of the physico-chemical properties of the photocatalysts with oxalic acid decomposition rates were carried out to determine the factors influencing the photocatalytic activity.

Introduction

Formation of oxide powders using sol–gel and chemical solution deposition methods has been widely studied, particularly for multicomponent oxides, where intimate mixing is required to form a homogeneous phase at the molecular level. Different hydrolysis and condensation rates for the precursors often thwart this aim and can result in localised enrichment of one or more components. Modification of the starting materials to temper the hydrolysis rates and stabilise the sol has been highly successful, particularly for the chemical solution deposition of thin films. Our interest has been in preparing photoactive titania films and powders from reagents prepared directly from the reaction of α-titanic acid with aminoalcohols.[1] Titanium triethanolamine complexes can be used to form aqueous sols which are non-flammable for safer and less expensive application in industrial processes. In addition, we have been examining the influences on the material properties of the products due to the incorporation of secondary oxides into the product.

The photocatalytic properties of TiO_2 have been the subject of many studies and have attracted attention in a number of applications.[2–8] Properties influencing the photocatalytic activity of TiO_2 particles have been suggested to include the surface area,[4,9] crystallinity, crystallite size and crystal structure.[10–12] Photoactivity enhancement has been proposed and demonstrated using dopant ions or oxides to modify the band gap[13–15] or to act as charge separators of the photo-induced electron–hole pair. Formation of nanometre-sized powders has been achieved[16–19] in an attempt to favour the formation of active defect sites and expose a greater number of reactive surface sites to the reactant molecules. Very recently, sol–gel and templating synthetic methods have been applied to prepare very high surface area porous titania phases. Such materials exhibit regular mesoporous structures,[20,21] but catalytic activities on these high surface area materials are disappointing.[20]

Here, we report the impact of incorporating alkaline earth ions (up to 20 mol%) on the physicochemical properties of sol–gel-prepared titania powders and discuss how these properties influence the photocatalytic activities.

Experimental

Titania powders were produced using a proprietary sol–gel method, utilising titanium triethanolamine complexes prepared from the reaction of α-titanic acid with triethanolamine.[1] Aqueous sols containing calcium, strontium or barium acetate in a range of concentrations up to 20 mol% were prepared. Gelation was achieved by adding concentrated ammonia solution and heating at 50 °C for about 8 h. The gels were fired up to 600 °C in air, heating at a rate of 4 °C min^{-1}, holding at 500 °C for 15 min and then at 600 °C for 5 min after which the powders were removed from the furnace and quenched. This gave a total heating time of about three hours. The calcined powders were crushed using an agate mortar and pestle under similar conditions in an attempt to produce powders with similar ‘fineness’ and particle size distributions. The powdered samples were used for XRD analysis, surface area measurement, diffuse reflectance UV spectroscopy, *in situ* IR spectroscopy and photocatalytic activity testing.

The anatase and rutile contents and crystallite sizes of the materials prepared in this study were determined *via* quantitative X-ray diffraction employing a commercial program, SIROQUANT v2.0,[22] which uses the Rietveld method of powder diffraction analysis. Rietveld scale factors were compared with those of well-crystallised, external titania

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standards to obtain absolute concentrations, hence crystallinity. Data were collected on a Philips PW3700 series diffractometer using Co-Kα radiation. Surface area and pore volumes were determined *via* N_2 sorption at 77 K using a Micromeritics ASAP 2010 sorptometer. Samples were degassed at 523 K for several hours prior to analysis. Surface areas were determined using the BET[23] model, while total pore volumes were calculated at $P/P_o = 0.98$. Pore size distributions (PSD) were determined using the BJH method from the adsorption branch.[23]

Photocatalytic activities were assessed by a simple and convenient method,[5] following the decomposition of oxalic acid in aqueous solution. A batch annular photoreactor was used, consisting of a cylindrical, 500 mL capacity pyrex container, containing a concentrically arranged water-cooled mercury lamp (Hanovia 125 W) within a quartz thumb. The reactor was charged with 400 mL of 0.005 M aqueous oxalic acid and 0.4 g of the catalyst powder, which was kept in suspension by rapid stirring using a magnetic stir bar. Air was bubbled through the suspension at a rate of 40 mL min^{-1} throughout the experiment and a further inlet was used for sampling.

The suspensions were stirred for about 45–60 min in the dark and the residual oxalic acid in solution was determined using a conventional permanganate titration of a filtered sample to calculate the amount of oxalic acid adsorbed on the surface of the catalyst. The mercury lamp was switched on and the oxalic acid concentration was determined every 15–30 min thereafter to measure the rate of photocatalytic decomposition.

Results and discussion

The project aims were to use a sol–gel method to produce titanium–alkaline earth oxide composites and determine the variations in photocatalytic activity (PCA) with composition. A study on the variation of PCA in a range of titanias has demonstrated the difficulty of determining unique correlations due to the interactions between the various physicochemical properties.[24] In this study, we have varied the titania compositions, while maintaining a common synthesis method, in order to discover more information about the factors controlling photoreactivity.

Modification of alcoholic sols prepared from titanium alkoxide using aminoalcohols has been shown to stabilise the sol, reducing or preventing the condensation and subsequent precipitation of titania.[25] In aqueous media, the stabilities of aminoalcohol-based titania sols are dependent on the concentration of titania, the ratio of aminoalcohol to titanium, the pH and temperature. Increasing or reducing the pH (*e.g.* ammonia solution or acetic acid) initiated the gelation of the sols. In these experiments, it was noted that the gelation rate of the sol increased with alkaline earth ion content.

The calcination temperature was limited to 600 °C to avoid significant crystallisation of unwanted phases and to obtain material suitable for efficient photocatalysis. At this temperature, even the undoped sample crystallised as anatase without significant crystallisation of rutile. It is known that dopants can delay the anatase to rutile transformation, allowing >95% anatase to be obtained, even after high temperature calcination. This has been reported to be strongly dependant on the charge and size of the dopant ion.[26] Calcining samples containing high levels of additive at higher temperatures could result in crystallisation, at least in part, of further phases. For comparison, a sample containing 50 mol% Ca began to crystallise the $CaTiO_3$ perovskite phase, even at the low temperatures used here, consistent with related studies.[27]

The method used for determining the photocatalytic activities of the titania materials was to irradiate an aqueous oxalic acid solution containing a suspension of TiO_2 powder.[5] Under the conditions described, the oxalic acid concentration reduced linearly with time until >90% had been decomposed, when the decomposition rate generally slowly reduced. The activity (μmol of oxalic acid decomposed per gram of catalyst per hour) was determined for each sample and compared with various physicochemical properties of the samples in order to determine how the properties of the materials influence the photocatalysis rates. Studies on the influence of temperature and pH on the photodecomposition of oxalate have been discussed previously,[5] and further studies analysing mass transport conditions, concentration of oxalate and catalyst loading have been reported.[28] These suggest that the rate-controlling step in this reaction is a bimolecular surface reaction involving interaction of adsorbed oxalate and peroxyl radicals. Formation of hydrogen carbonate ions increase the alkalinity of the solution with time on-stream.[28] The pH of the oxalic acid solution in our experiments was initially 2.4 (50 mM), rising to 4.0 as the concentration fell below 10 mM.

Increases in the photocatalysis rate with catalyst loading have been suggested to be due to the improved concentration of active sites with the increasing number of particles in solution. Above an optimum level, light shielding and agglomeration due to particle–particle interactions may reduce the photodegradation rate.[29] Light intensity, reactor dimensions, the nature of the particles *etc.*, will all contribute to influence the optimum loading level. In the current study, the optimum loadings between different samples could possibly change, however, the loading of 1.0 g l^{-1} is adjudged to be near enough to the optimum to make differences between samples insignificant, from comparisons with literature observations. For titania particles, optimum loadings have been observed from 0.8 to 3.0 g l^{-1},[30,31] with little change of rate within this range.

X-Ray powder diffraction studies

The major crystalline phase detected in these experiments was anatase, with rutile being observed only in minor (<1%) quantities in some of the samples having higher dopant concentrations. As shown in Fig. 1, the crystallinity of the powders differed greatly depending on the alkaline earth ion content. The calcium-containing samples exhibit an 'S'-shaped curve, showing a relatively flat portion with >95% anatase for less than 5 mol% Ca; a steep portion between 5 and 15 mol% Ca, where the amorphous content increases to >75%; with the remaining portion flattening out to exhibit relatively constant crystallinity up to 20 mol% calcium. Increasing the barium ion content resulted in a much more rapid loss of crystallinity, reaching virtually 100% amorphous content at 20 mol% Ba. Intermediate behaviour was apparent for the strontium-containing materials.

A dopant ion, such as Ca^{2+}, with an ionic radius (1.06 Å) larger than Ti^{4+} (0.64 Å), but smaller than O^{2-} (1.31 Å) can be either isomorphously substituted or interstitially introduced

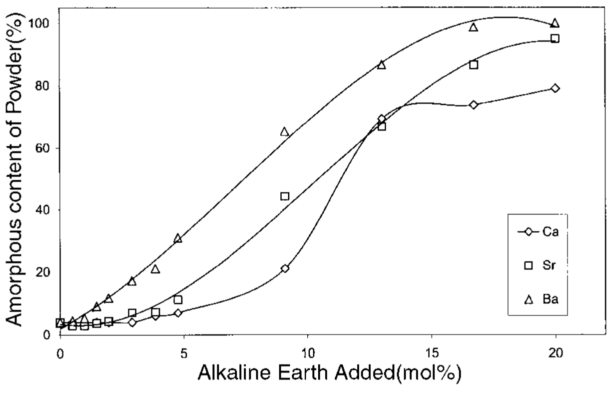

Fig. 1 The effect of increasing alkaline earth ion contents on the crystallinity of sol–gel-prepared titania samples.

into the matrix to produce oxygen vacancies or interstitial Ti^{3+} ions, respectively. This distorts the lattice and affects the unit cell dimensions, and can be observed experimentally by small changes in the Bragg reflection angles in the X-ray diffractogram. Refinement of the anatase cell dimensions within the SIROQUANT program demonstrated an increase in the *a* cell dimension and a small decrease in the *c* cell dimension, with increasing alkaline earth ion concentrations (Fig. 2), resulting in net increases in cell volume along the range. This appears to confirm that these cations are indeed included within the anatase matrix. Titania samples with concentrations of alkaline earth ions above 10–15 mol% are not well crystallised and the major portion of the sample remains amorphous. The relatively small amount of anatase that does crystallise continues to exhibit larger cell volumes, implying a continued increase in the level of incorporation of these ions in the anatase structure. Strontium and barium, being larger than calcium, disrupt the anatase crystallisation at much lower concentrations, reflected in the amorphous contents of the powders and changes in the anatase unit cell dimensions. Although the XRD data show a gradual increase in cell volume, it is not clear whether the concentration of alkaline earth ions in the crystalline phase is the same as that in the amorphous phase.

The anatase crystallite sizes decrease sharply on doping up to 2 mol% with alkaline earth ions (Fig. 3). Further reductions were only moderate for addition of higher levels of additives, particularly for Sr and Ba. Crystallite size measurements became less accurate as the amorphous contents increased, however, the data suggest definite limits to the minimum crystallite size. The facts that the crystallite sizes do not continue to decrease with dopant concentration and no continuum of crystallite sizes to the amorphous phase exists, suggest that the amorphous phase is substantially different from the crystalline phase and not merely a collection of partially formed crystallites too small to be detected by XRD.

N_2 Sorption experiments

Samples containing only 0.5 mol% alkaline earth metal have markedly higher surface areas ($>110\ m^2\ g^{-1}$) compared to the undoped titania (*ca.* $77\ m^2\ g^{-1}$). Further increases in alkaline earth content result in gradual increases in surface area, peaking at around $160\ m^2\ g^{-1}$ (Fig. 4). Total pore volume measurements did not show any significant changes in porosity. The isotherms are typical non-reversible type V curves, which indicate no evidence for significant microporosity, but significant non-specific mesoporosity (*ca.* 10 nm diameter).[23] There is no significant change in the pore size distribution (PSD) with increasing additive concentration. If we assume that the TiO_2 crystallites are themselves non-porous (*cf.* internal porosity, such as in zeolites), then it is reasonable to ascribe the observed porosity to interparticular or textural porosity. Pore sizes are all in the same range for the samples observed, 115 ± 5 Å^3. This is perhaps surprising considering the fundamental differences between the samples containing near 100% anatase compared to samples which are largely amorphous and contain high levels of alkaline earth ions.

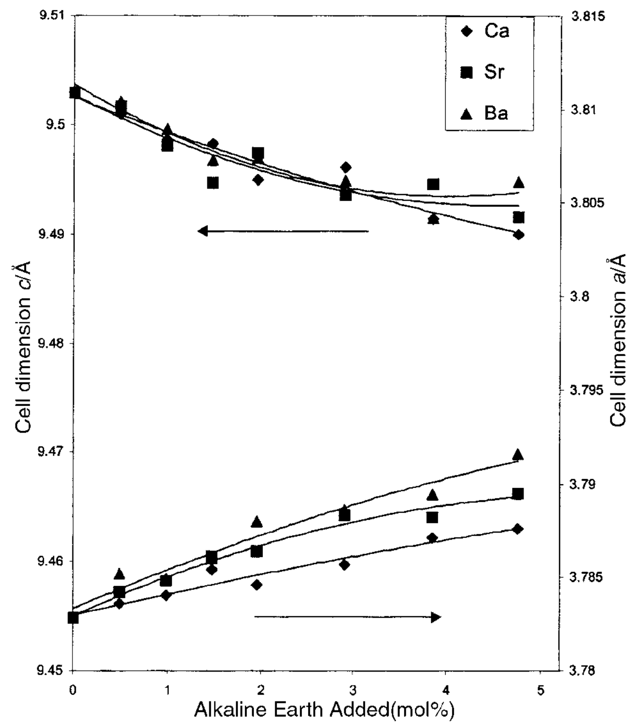

Fig. 2 The effect of increasing intercalation of alkaline earth ions on the anatase cell dimensions.

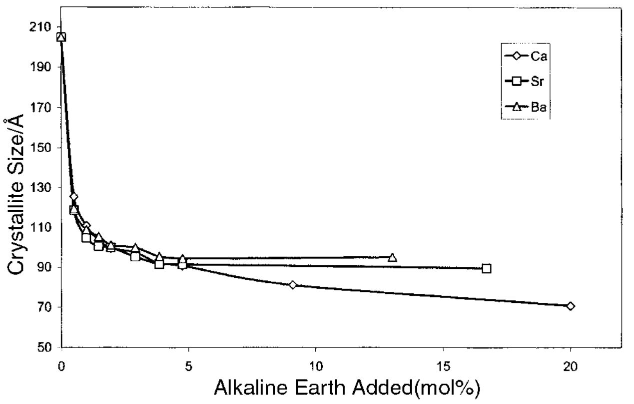

Fig. 3 The influence of increasing alkaline earth ion content on the anatase crystallite sizes.

The relationships between surface area, crystallinity and crystallite sizes are not straightforward. One might expect a major increase in surface area to occur during the transition from crystalline to (largely) non-crystalline material. However, the major change in surface area (77 to $120\ m^2\ g^{-1}$) occurs with <2 mol% additive ion (Fig. 4), whereas the major reduction in crystallinity occurs at higher dopant levels (Fig. 1). As the crystallinity reduces, the surface area increases by only a modest $30–40\ m^2\ g^{-1}$, to peak at around $160\ m^2\ g^{-1}$, with relatively minor differences between the different alkaline earth ions.

Scanning electron microscopy

SEM images of selected examples containing different Ca^{2+} ion concentrations show the morphological changes induced by the addition of alkaline earth cations. Fig. 5(a) shows anatase powder produced with no addition of Ca^{2+}. The sample

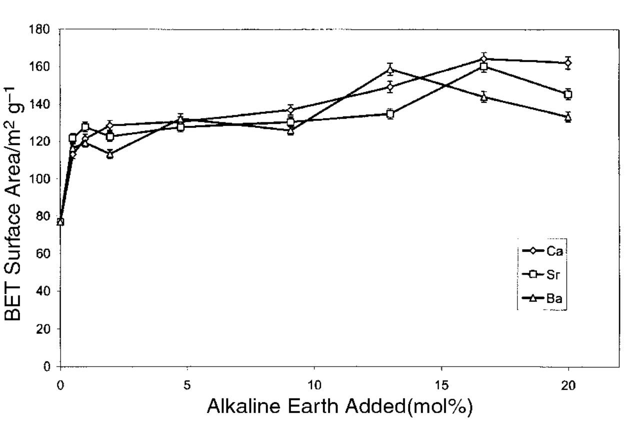

Fig. 4 The influence of increasing alkaline earth ion content on the BET surface areas of sol–gel-prepared titanias.

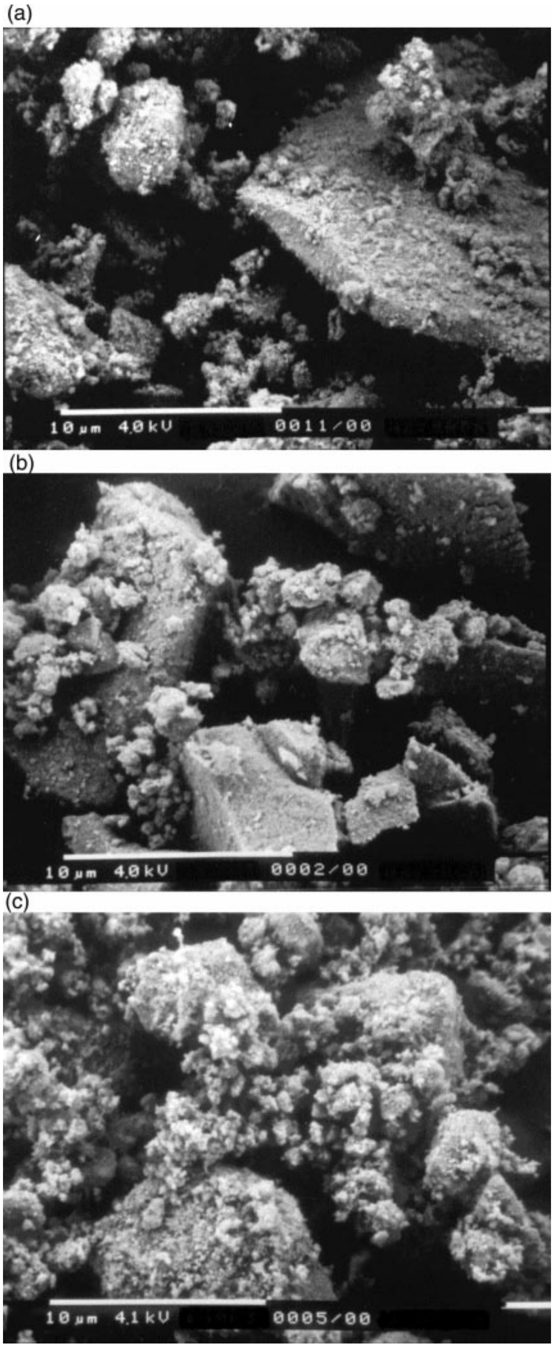

Fig. 5 Scanning electron micrographs of sol–gel-prepared titania: (a) without additive; (b) containing 5 mol% calcium ions; (c) containing 13 mol% calcium ions.

appears as large blocks of coarse material of dimensions from around 1 to above 10 µm. Fig. 5(b) shows a sample containing 5 mol% Ca^{2+}, which displays similar features to Fig. 5(a), with a reduction in the larger particle sizes. Fig. 5(c), on the other hand, shows a powder with a 13.0 mol% Ca^{2+} content. This clearly reveals the altered morphology of a large portion of the powder, which consists of a large proportion of submicron-sized particles.

Diffuse reflectance UV analysis

When the semiconductor crystallite dimensions fall below a critical radius, quantum size effects result in an increase in the band gap and a shift of the band edge to yield larger redox potentials. The amorphous portions of these samples have particle sizes too small to exhibit regular crystallinity and are likely to consist of nanoscale particles. Band gaps were determined from the Kubelka–Munk functions and show increases for the samples containing higher Ca^{2+} ion concentrations (Table 1), reflecting the reduction in crystallite and particle sizes. A larger band gap results in an increased rate constant for the charge transfer, which can result in improved photoefficiencies. Reaction rate enhancement can also be due to the increased migration of electrons and holes to the semiconductor surfaces possible in smaller particles, which allows their participation in the reaction and, thereby, reduces the net electron–hole recombinations.[32,33]

Table 1 The effect of increasing Ca^{2+} content on the band gap of sol–gel-derived titanias calcined at 600 °C

Ca^{2+} content/mol%	Band gap/eV
0	3.23
2	3.27
4.8	3.27
9.1	3.28
13	3.29

Adsorption

The role of substrate pre-adsorption in photodecomposition rates and pathways can be probed using a Langmuir–Hinshelwood kinetic model,[34] and has fuelled debate on whether the photocatalytic decomposition occurs completely on the photocatalyst surface[35] or within a homogeneous phase.[36] A significant degree of pre-adsorption occurred in these experiments, determined by the reduction in the oxalic acid concentration in solution while stirring the suspensions of photocatalyst powders in the dark. Equilibrium occurred in a few minutes, although 30–60 min were allowed for the solution concentration to reach a steady level. The large surface capacity for oxalate ions may simply be a function of pH, where a low pH value results both in a high concentration of free oxalate ions and a high positive charge on the catalyst surface, and where the pH of the solution is below the TiO_2 isoelectric point. The incorporation of alkaline earth ions into the titania will modify the surface charge and thus the adsorption characteristics. The degree of oxalic acid adsorption increases (Fig. 6) for samples containing higher alkaline earth levels, however, the relationships suggest that the alkaline earths play only an indirect role in the adsorption increase. Similarly, the surface areas and amorphous contents do not dictate the degree of surface adsorption.

In situ IR studies

Spectroscopic studies[37–39] have demonstrated the ability to detect the surface binding mode of carboxylates on oxide surfaces. The IR spectrum of oxalate adsorbed onto a TiO_2 surface, measured by *in situ* attenuated total reflectance, has adsorption maxima which agree favourably with the those

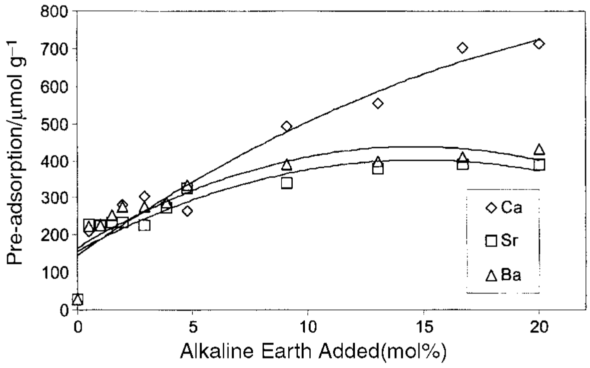

Fig. 6 The effect of increasing levels of alkaline earth ions in sol–gel-prepared titanias on oxalic acid pre-adsorption.

found for the complex $Na_2[TiO(C_2O_4)_2]\cdot 3H_2O$, which contains chelating oxalato ligands bound through each carboxylate group. This differs significantly from free oxalic acid and the oxalate anion in sodium oxalate. Using this technique, the IR spectra of adsorbed oxalate were measured on a range of titanias containing varying calcium ion contents. The IR spectra show absorbances at 1714, 1690, 1642(sh), 1410, 1265, 898 and 805 cm^{-1}, which do not vary significantly from those without calcium[37] and certainly do not show any similarity to the IR spectrum of calcium oxalate, which has three very strong absorptions at 1615, 1320 and 782 cm^{-1}. This implies that the adsorption of oxalate onto the photocatalyst occurs exclusively at the titanium sites, even in those samples containing high levels of calcium. Presumably, the adsorption of oxalic acid occurs at 4 or 5-coordinate titanium cations, and it is likely that an effect of intercalating calcium ions into the structure is to increase the surface concentration of coordinatively unsaturated titanium ions, thus providing further sites for the adsorption of oxalate ions. Studies on titania single crystals have examined the adsorption of a dicarboxylic acid [bis(isonicotinic acid)], suggesting both acid groups are deprotonated, being bound to four 5-coordinate Ti^{4+} ions.[40] Oxalic acid has a very tight bite angle and has the possibility of bridging between two Ti^{4+} ions, or chelating to a single Ti^{4+} ion.

Photocatalysis experiments

Fig. 7 shows how the incorporation of alkaline earth ions into titania across a range of concentrations substantially improves the aqueous photodecomposition of oxalic acid. Approximately half of the photocatalysis enhancement occurred for samples containing 2 mol% alkaline earth ion. Doubling of the activity occurred for samples containing 20 mol%, although, for calcium, the activity reached a plateau below 15 mol% content. For comparison, the activity of standard Degussa P25 is shown on the graph as a horizontal bar.

If substrate pre-adsorption is a prerequisite for efficient photocatalysis, then an important question is whether the increased affinity of the oxalic acid for the catalyst surface results in increased photocatalytic decomposition rates. Fig. 8 shows the relationship between the photocatalytic activity (PCA) and the degree of adsorption of oxalic acid for the three alkaline earth ion types. The traces do not indicate that this type of pre-adsorption is controlling the photocatalysis rate. The additional surface adsorption sites created by the presence of alkaline earth ions are presumably not the type of sites where photodecomposition can occur. The PCAs of the Sr and Ba series differ markedly from that of the Ca-containing samples, suggesting differences on a micro-structural level between the series. The larger Sr^{2+} and Ba^{2+} ions are not accommodated by the titania lattice as readily as the smaller Ca^{2+} ions. This could result in differences in the bonding of the surface titanium species and, thus, the number or nature of the sites available for adsorption.

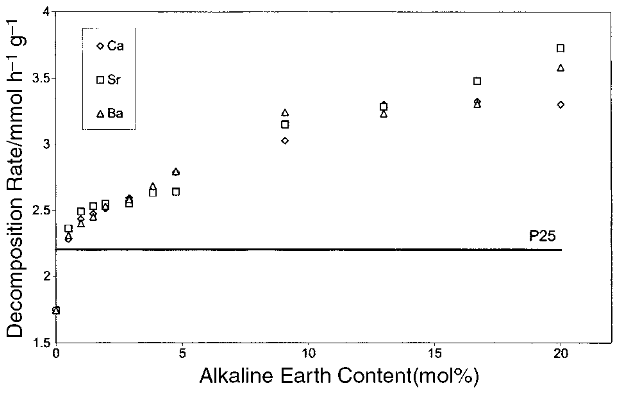

Fig. 7 The effect of increasing levels of alkaline earth ions in sol–gel-prepared titania suspensions on photodecomposition rates of aqueous oxalic acid.

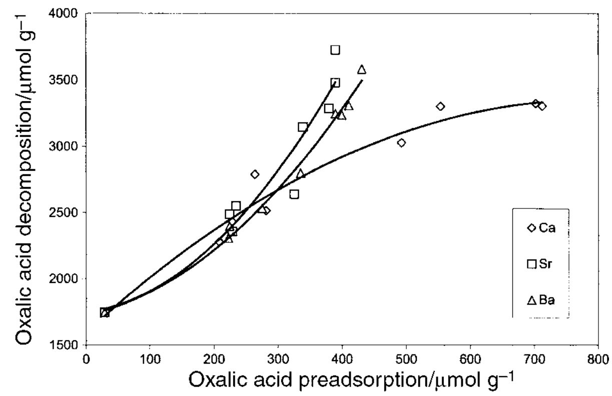

Fig. 8 The relationship between the degree of oxalic acid pre-adsorption and the rate of photodecomposition.

The changing properties of the materials with increasing alkaline earth ion content and the change in PCAs were compared in order to identify important factors influencing the improvement in PCA. When examining these alkaline earth–titania photocatalysts, it might be of benefit to compare them with other binary oxide materials. The photocatalytic activity of titanium dioxide in Ti/Si and Ti/Al binary oxides has been shown to be significantly enhanced in the regions of lower Ti content.[41–43] The Ti species are enriched on the surfaces of the photocatalysts and are proposed to exist as isolated titania moieties having tetrahedral coordination. This results in a diminished radiationless transfer of the photon energy, favouring the photocatalytic processes. In the high titania content range, the presence of silica or alumina was detrimental to the catalyst performance.

The similarity in the shape of the curves showing the surface area development with alkaline earth concentration (Fig. 4), and the PCA with alkaline earth concentration (Fig. 7) suggests that the improvements to PCA could be due to increases in surface areas. Dividing the PCA by the surface area shows a broadly constant activity per square metre across the whole range of alkaline earth concentrations examined (Fig. 9). This result suggests that all of the material present in a particular sample, crystalline or amorphous, is equally active in the photocatalytic decomposition.

While it might be expected that increasing the surface area may have a direct relationship on the PCA, the results suggest that the other changes in the material are less important for photocatalytic efficiency. However, this relationship is only valid for those samples prepared in the manner described above. Comparing P25 photocatalyst, which has a low surface area (50 $m^2 g^{-1}$) and moderate activity (2.25 mmol $h^{-1} g^{-1}$),

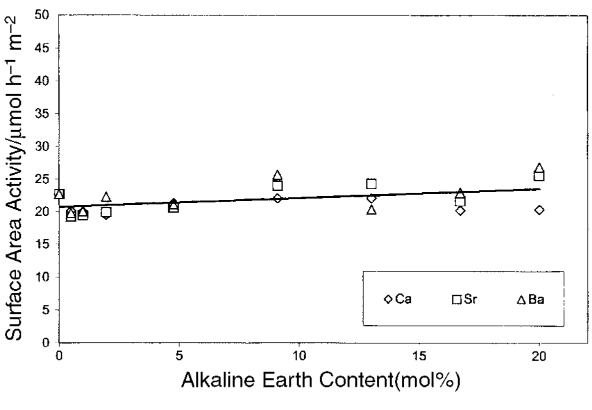

Fig. 9 The relationship between photodecomposition rates per unit surface area and of alkaline earth ion concentration.

with the catalysts containing alkaline earth ions (surface areas up to 145 $m^2 g^{-1}$ and an activity of 3.73 mmol $h^{-1} g^{-1}$ for 20 mol% Sr) shows that the latter would seem to have superior performance. However, if the samples are compared in terms of the activity per unit area, then the P25 photocatalyst has an activity of 45 μmol m^{-2}, compared to our global average of around 28 μmol m^{-2}. This demonstrates that surface area is not the only important factor in determining PCA. Previous studies have pointed out the need to take into account the structural and surface properties of the TiO_2 when comparing photoreactivities.[24] The interactions of different properties are clearly complex and these studies demonstrate the difficulty of isolating a single factor to determine its individual contribution. Continued heating of our samples to develop the crystallinity and particle sizes would also affect crystallite sizes, crystalline phase, surface area, porosity and probably many other factors, making it difficult to determine the root cause of PCA modification. Thus, the observation in this study that the rate of photocatalytic decomposition of oxalic acid is increased by using titanias containing alkaline earth ions can only be regarded as empirical. It is likely that the increase in surface area is important, but high surface area alone does not guarantee high activity.

Conclusions

Inclusion of alkaline earth ion additives into sol–gel-prepared titania increasingly inhibited the crystallisation of anatase ($Ba > Sr > Ca$) as the content was increased to 20 mol% with respect to Ti. Samples with greater than 15 mol% alkaline earth ions appeared largely amorphous under the preparation conditions used, compared to >95% anatase for samples with no additive. Surface areas increased on addition of alkaline earths, although the porosities remained constant. An increase in the adsorption of oxalate occurred for samples with higher alkaline earth contents, although the site of adsorption was exclusively at titanium sites. Photocatalytic activities were significantly higher for samples containing up to 20 mol% alkaline earth ions, even for samples consisting substantially of amorphous material. Although surface area is an important factor in increasing PCA, other physicochemical factors have important roles to play.

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