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Chemical Engineering Journal 95 (2003) 213–220

Chemical Engineering Journal

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The effect of preparation method on the photoactivity of crystalline titanium dioxide particles

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Abstract

The present study shows that acidic conditions during the hydrolysis and condensation of titanium isopropoxide as well as a high water to alkoxide ratio result in crystalline TiO_2 precipitates. Nanosized rutile and anatase particles were prepared at relatively low temperatures ($<100\,^{\circ}C$) and atmospheric pressure. The crystalline particles exhibited improved photocatalytic activity to particles prepared using the conventional alkoxide method.

Surface cleanliness of the prepared particles was found to be highly influential on the photoactivity of the catalyst. The extent and type of washing was found to affect the surface properties of the particles. X-ray diffractometry, photon correlation spectroscopy (PCS), Brunauer–Emmett–Teller (BET) surface area analysis and transmission electron microscopy (TEM) were used to characterise the powders.

Keywords: Photocatalysis; Preparation; TiO_2; Rutile; Anatase

1. Introduction

Organic chemicals are present as pollutants in effluents from both the industrial and domestic sectors [1]. They can also be found in ground and surface waters and have to be either removed or destroyed before discharge into the environment. Over the years, many wastewater treatment processes have been used to treat these organic pollutants. Some include adsorption by activated carbon, air stripping and bio-remediation. Often they involve transferring the pollutants from one waste form to another without completely transforming them into non-toxic wastes. The main advantage that photocatalysis has over other existing technologies is that the organic contaminants are destroyed with no requirement for secondary disposal of concentrated wastes, providing a more environmentally sustainable solution.

The photocatalytic detoxification of wastewater is a promising technology to destroy organic pollutants and in particular for treating dilute wastewater [2–4]. Semiconductor photocatalysis, with a primary focus on titanium dioxide (TiO_2), is a pollutant degradation process that has been applied to a variety of problems. Organic compounds such as alcohols [5], aliphatics [6], aromatics [7], herbicides and pesticides [8,9] have been photocatalytically destroyed in laboratory and field studies. Titanium dioxide, in its anatase phase, is considered to be the most suitable for photocatalytic reactions. It is inexpensive, chemically stable and insoluble under most conditions, which allows for easy removal from the treated water. Additionally, the photogenerated holes and electrons of anatase TiO_2 are highly oxidising and reducing, respectively. Another crystalline form of TiO_2 that has been investigated widely is rutile. However, many researchers have concluded that rutile is a much less active form of titanium dioxide [10,11].

There are different routes that can be used to synthesise anatase and rutile. These include flame synthesis [12], chemical vapour deposition [13], precipitation [14] and the alkoxide sol–gel method [15]. It has been said that the precursor and the method of preparation affect the physico-chemical properties of the synthesised particle [16]. Additionally, for the alkoxide method, heat treatment and washing are two steps that have been observed to affect phase formation and morphology of the prepared particles [17–19].

The alkoxide method involves the formation of non-crystalline (amorphous) titanium dioxide by hydrolysis and condensation of titanium alkoxide. This is followed by the transformation of amorphous titanium dioxide to either crystalline anatase or rutile by calcination at temperatures ranging from 450 to 600 °C. The high temperature results in a decline in surface area (due to sintering and crystal growth) and a loss of surface hydroxyl groups [17]. The

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doi:10.1016/S1385-8947(03)00107-4

washing step has also been found to cause surface modification [18,19]. Cleaning of particles is usually achieved by washing the surface with a solvent, followed by the removal of the solvent by centrifugation. Hague and Mayo [18] reported that the solvent used in particle washing could affect both the chemical composition and crystallinity. It has also been reported that the use of solvents for washing particles can affect the surface charge of particles by bonding onto surfaces of the metal oxide [19]. An alternative washing technique is dialysing particles against double-distilled water [20]. This maybe an effective method for removal of soluble impurities without the introduction of new species.

This paper presents research on the direct synthesis of rutile and anatase at moderate temperatures (<100 °C) as well as the effect of washing technique on particle formation and morphology. The use of these particles as a photocatalyst to destroy organic compounds is investigated.

2. Experimental

All chemicals used were analytical grade and prepared in deionised, distilled water.

2.1. Preparation of anatase by calcination

Titanium butoxide (TBOT, 97%, Aldrich) was used to produce titanium dioxide particles by hydrolysis and condensation of the TBOT precursor. TBOT (0.005 M) precursor dispersed in ethanol was added to a premixed solution of water (0.4 M) and ethanol (EtOH, 17 M) at room temperature. This solution was aged for 3 h to obtain amorphous titanium dioxide particles. These particles were recovered and washed three times with ethanol and twice with water. Centrifugation was used to recover the particles. The particles were then allowed to dry in an oven at 60 °C for 24 h, followed by calcination at 450 °C for 3 h (sample code TH).

2.2. Preparation of rutile and anatase in the absence of calcination

Crystalline titanium dioxide was directly prepared by the hydrolysis and condensation of titanium isopropoxide (TISOP, 97% Aldrich). TISOP was dispersed in isopropanol (PrOH), water and acid at either 60 or 90 °C. The mixture resulted in a final concentration of 0.059 M TISOP, 0.74 M PrOH, 0.56 M nitric acid and 45.2 M water. White precipitates formed instantly. The mixture was stirred for 5 min until the solution became transparent and was aged for 1 h at either 60 or 90 °C to obtain rutile or anatase, respectively. The reaction was stopped after 1 h by quenching the solution in a 0 °C ice bath. The particles were either washed three times with water by centrifugation and redispersion or by dialysis (using Sigma cellulose membrane dialysis tubing) against water at room temperature. These particles were then stored as a stock suspension (sample codes TC-R and TC-A for particles washed by water and TC-60(D) and TC-90(D) for particles washed by dialysis).

2.3. Particle characterisation

The crystalline phase of the prepared particles was determined by X-ray diffraction (XRD) spectroscopy (Siemens D5000 diffractometer). The morphology and size of the particles were examined by transmission electron microscopy (TEM, Phillips CM200). The distribution size of the prepared particles was analysed by photon correlation spectroscopy (PCS, Brookhaven 90+ system). The particle surface areas were determined by nitrogen adsorption using Brunauer–Emmett–Teller (BET) surface area analysis.

2.4. Photoactivity tests

A small batch photocatalytic reaction system which consisted of a spiral photoreactor illuminated by a near-UV illumination lamp (peak wavelength at 360 nm) and a conductivity meter for measuring carbon dioxide generation was used to assess the photocatalytic activity of the prepared particles. A detailed description of the reactor has been given by Matthews [21]. The catalyst loading was 0.1 wt.% and the system was at ambient atmospheric pressure. The photooxidation rate of 100 μg of carbon, added as sucrose, to a 30 ml suspension of the photocatalyst was used as the test reaction. The pH of the suspension was adjusted with perchloric acid ($HClO_4$) to 3.5. By monitoring the rate of formation of carbon dioxide, the rate of mineralisation of the sucrose was determined.

3. Results and discussion

3.1. Particle characterisation

Fig. 1 shows the effect of preparation method on crystalline phase formation. When the system was aged at the lower temperature of 60 °C, characteristic peaks of rutile (major peaks: 27.44, 36.28, 54.28°) were evident (Fig. 1a), while the characteristic peaks of anatase (major peaks: 25.30, 37.80, 48.14°) were evident (Fig. 1b) when the system was aged at 90 °C. Nam et al. [14] and Gopal et al. [22] obtained similar results. For particles prepared using calcination (Fig. 1c), highly crystalline anatase was achieved, as indicated by the sharpness of the peaks.

3.1.1. Formation of crystalline titanium dioxide by conventional alkoxide process

The conventional alkoxide process involved the ageing of ethanolic solutions of titanium butoxide and water. The result was the formation of amorphous titanium dioxide. Heat treatment at 450 °C was required to transform these amorphous titanium dioxide particles into an anatase form.

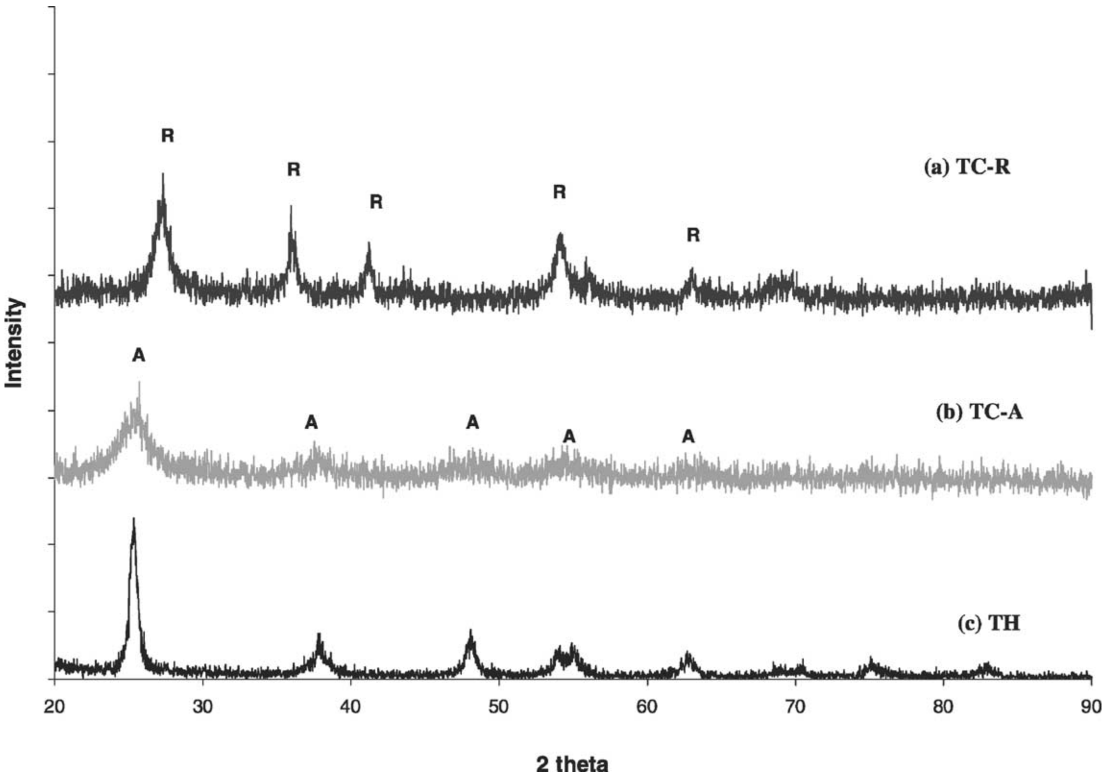


Fig. 1. Effect of reaction temperature on phase formation (a) TC-R (acidified alkoxide method at 60 °C), (b) TC-A (acidified alkoxide method at 90 °C), (c) TH (conventional alkoxide method, calcined at 450 °C for 3 h).

3.1.2. *Formation of the crystalline titanium dioxide by acidified alkoxide process*

The formation of rutile at 60 °C and anatase at 90 °C can be explained by the crystal structure of each phase. Both rutile and anatase have tetragonal structures, which consists of ($TiO_6{}^{2-}$) octahedra. In each of these, the Ti^{4+} ion is surrounded by an irregular octahedron of oxide ions [15] but the linkage of these ($TiO_6{}^{2-}$) octahedra is different. There are two types of linkages involved in the formation of TiO_2 crystals, edge sharing and corner sharing. Rutile involves both types of linkage. Two opposite edges of each octahedron are edge shared forming a linear chain and the chains are linked together via corner oxygen atoms.

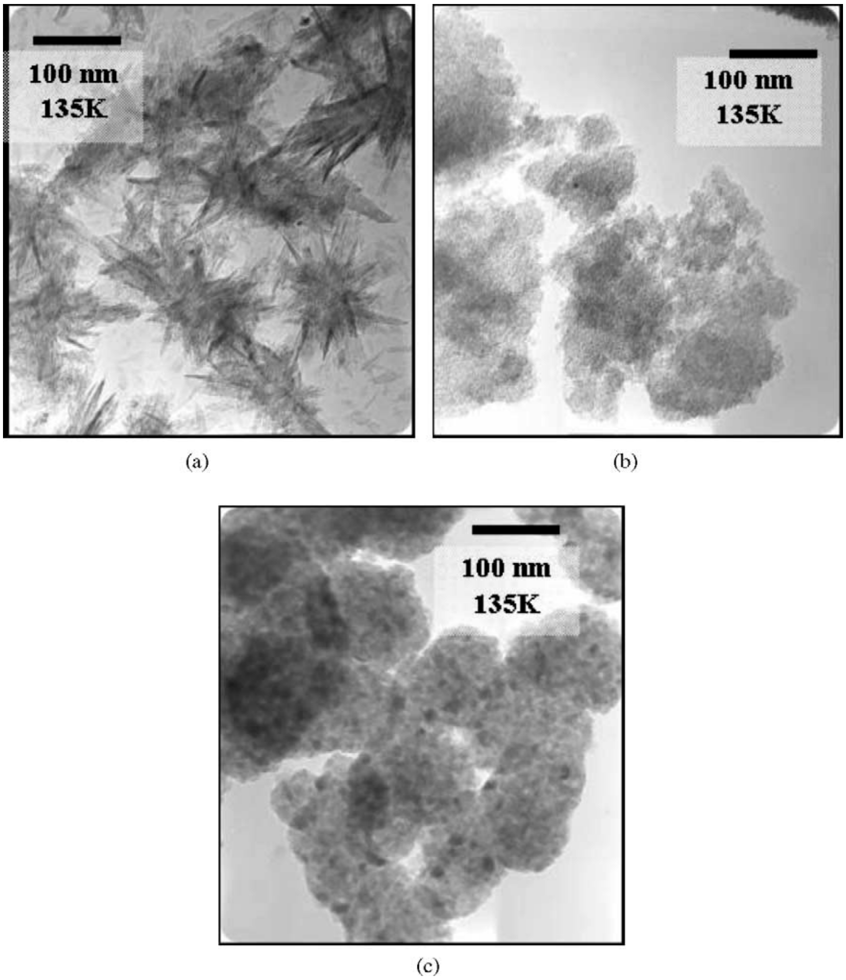
Anatase, however, does not involve corner sharing, but has four edges shared per octahedron [22]. The anatase chains are linked together through shared edges only. The anatase phase is statistically more favourable as there are more edges available to form a bond. Thus, this structure is favoured at the higher collision rates which can be achieved at 90 °C. On the other hand, although the configuration of rutile is thermodynamically more favourable due to the linear arrangement minimising the electrostatic repulsive energy, the formation of corner sharing bonds is more difficult than edge sharing bonds. A slower rate of reaction, which can be achieved at the lower temperature of 60 °C, allows the formation of corner sharing bonds resulting in the rutile structure.

Fig. 2 shows TEM micrographs of crystalline particles prepared under different conditions. For particles prepared by the acidified alkoxide process Fig. 2a and b shows that anatase is made up from agglomerates of nanoparticles whereas the rutile sample is made up of needle shaped particles of approximately 80 nm. The agglomeration of these needle shaped particles leads to the formation of stable spheroids that are approximately 150–200 nm in size. Fig. 2c shows particles prepared by the conventional alkoxide process. The morphology of the particles comprises of small crystals. The prepared particles were characterised and the results given in Table 1.

3.2. *Photoactivity studies*

Photoactivity tests were conducted to assess the photocatalytic ability of prepared particles. The results are given in Fig. 3. The photocatalytic performance of the particles was compared on the basis of the rate of carbon dioxide generated as the sucrose (equivalent to 100 μg of carbon) was oxidised. The photocatalytic performance of the prepared particles decreased in the following order TC-R > TC-A > TH. The photocatalytic results can be explained in terms of the preparation steps involved in the synthesis of these particles.

Heat treatment generates materials of higher crystallinity as indicated by the sharp peaks observed in the XRD pattern of sample TH when compared to TC samples (Fig. 1). However, the process also causes an increase in particle size (600 nm) compared to 150–200 nm for particles prepared



(a) (b) (c)

Fig. 2. TEM micrographs of (a) sample TC-R (rutile) and (b) sample TC-A (anatase) prepared at low temperature using acidified alkoxide process, (c) sample TH prepared using conventional alkoxide process.

Table 1
Description and characteristics of photocatalysts prepared using conventional and acidified alkoxide processes

Sample code	Sample description	Effective diameter (nm)	Specific surface area (m^2/g)	Interpore size (nm)
TC-R[a]	TiO_2, rutile, prepared by the acidified alkoxide process, synthesis at 60 °C	150	95	16.4
TC-A[a]	TiO_2, anatase, prepared by the acidified alkoxide process, by synthesis at 90 °C	200	299	3.5
TH[a]	TiO_2, anatase, prepared by conventional alkoxide process, calcined at 450 °C for 3 h	600	39	N/A

[a] All samples were washed using solvent, followed by centrifugation and redispersion.

by the acidified alkoxide process. It also results in a lower surface area with the specific surface area measured to be 39 m^2/g for heat treated particles compared to 95–299 m^2/g for non-heat treated particles. The lower surface area of sample TH is due to sintering of small crystallite particles at high temperature. Additionally, it has been reported that calcination also reduces the number of hydroxyl groups (one of the highly reactive species responsible for mineralisation of organic contaminants) on the surface of the catalyst, leading to an overall reduction in the photoactivity of the catalyst [17]. The combination of these factors is envisaged to result in lower activity of sample TH when compared with sample TC.

Rutile titanium dioxide particles (TC-R) prepared by the acidified alkoxide process were found to exhibit higher photoactivity than anatase titanium dioxide particles (TC-A) prepared by the same method (Fig. 3). The surface area results did not explain this observation as it was found that anatase 299 m^2/g had a higher specific surface area compared to that of rutile 95 m^2/g (Table 1). The results can be better explained in terms of particle morphology.

The interpore size of the anatase and rutile agglomerates is defined as the distance between primary particles. Fig. 2b shows the anatase morphology comprising of an agglomeration of small primary crystallites (a few nanometers) creating small interpores (3.5 nm). It is postulated that sucrose

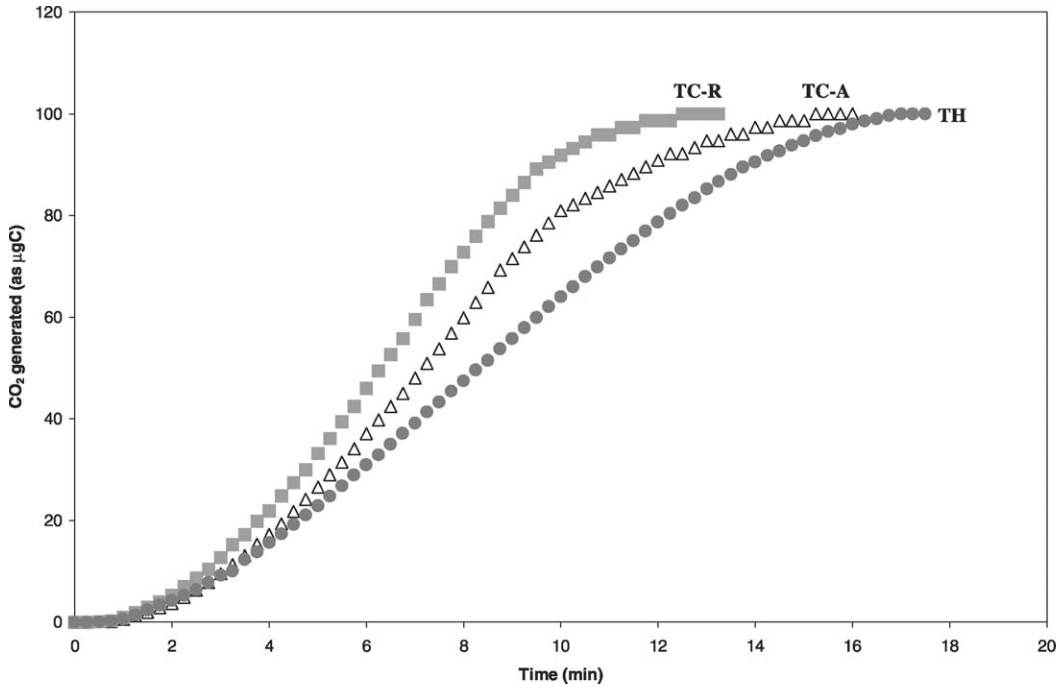


Fig. 3. Results of photocativity testing comparing the activities of different samples. A description of the samples tested is given in Table 1.

cannot penetrate these pores as a result of the bulky nature of the molecule. Rutile on the other hand, has the jagged shaped edges formed by needle-like particles which provide greater external surface sites. The larger pore size (16.4 nm) of rutile particles allows sucrose to access interpore sites. The availability of the surface allows greater exposure and contact between the catalyst, light and substrates and is beneficial for photoreaction. This explains the differences in the surface area between TC-R and TC-A and is postulated to be the primary reason why the rutile particles were observed to exhibit a higher photoactivity than anatase particles.

3.3. *Role of the washing technique*

3.3.1. *Particle characterisation*

Surface reconstruction of nanocrystals is considered to be an important parameter contributing to the performance of the photocatalyst [23]. Often adsorbed surface impurities and unreacted organic groups remain on the surface of titanium dioxide particles after preparation. Thus, appropriate washing techniques for the removal of these impurities was investigated. The presence of organic contaminants is postulated to have adverse effects on the adsorption of sucrose. This is indicated by the adsorbed organic that is present on the anatase particles compared to rutile when prepared by the acidified alkoxide method (Table 2). The amount of organic present was estimated during the carbon burn-off period. The carbon burn-off period is the stage prior to experimental measurements during which organic impurities are destroyed by irradiating the photocatalyst.

The presence of impurities is indicative of the effectiveness of surface cleaning of particles. Table 2 shows that the particles washed using solvent and centrifugation had a high level of impurities which may include adsorbed alcohol or unreacted alkoxide. Therefore, an alternative washing technique, dialysis was investigated. During dialysis, soluble species diffuse across a membrane from a region of high concentration to low concentration until equilibrium is reached. Description and characterisation of particles washed by dialysis are given in Table 2 and the morphology was analysed by TEM (Fig. 4).

Fig. 4a shows numerous clusters of rutile (characterised by needle shaped particles) surrounded by anatase. The primary rutile agglomerates are approximately 200 nm in size and surrounded by agglomerated small anatase particles. The primary rutile agglomerate size for the dialysed system differs to that of the rutile particles washed by centrifugation. This is possibly due to continual growth during dialysis process. However, the process allows the release of impurities that may be trapped on the particle surface or within the pores of the agglomerated structure.

Regardless of the initial reaction temperature, the morphology of the prepared particles shows that the main phase formed after dialysis is anatase. The XRD results presented in Fig. 5 confirmed that the titanium dioxide particles, which further precipitated out during dialysis, were in fact of anatase form. This may be explained by the precipitation process that takes place whilst the particles are being dialysed at room temperature. As discussed earlier after ageing for 1 h the reaction was ceased by placing the system in a 0 °C ice bath. The particles were not recovered and no

Table 2
Description and characteristics of samples used in the photoactivity tests to study the effect of washing technique

Sample code	Sample description	Estimated adsorbed organic (∼μg C)	Effective diameter (nm)
TC-60(D)	TiO_2, acidified alkoxide process at 60 °C, particles washed using dialysis	1.8	350
TC-90(D)	TiO_2, acidified alkoxide process at 90 °C, particles washed using dialysis	1.8	350
TC-R	TiO_2, rutile, acidified alkoxide process at 60 °C, particles washed by centrifugation three times with water	6.2	150
TC-A	TiO_2, anatase, acidified alkoxide process at 90 °C, particles washed by centrifugation three times with water	19.7	200

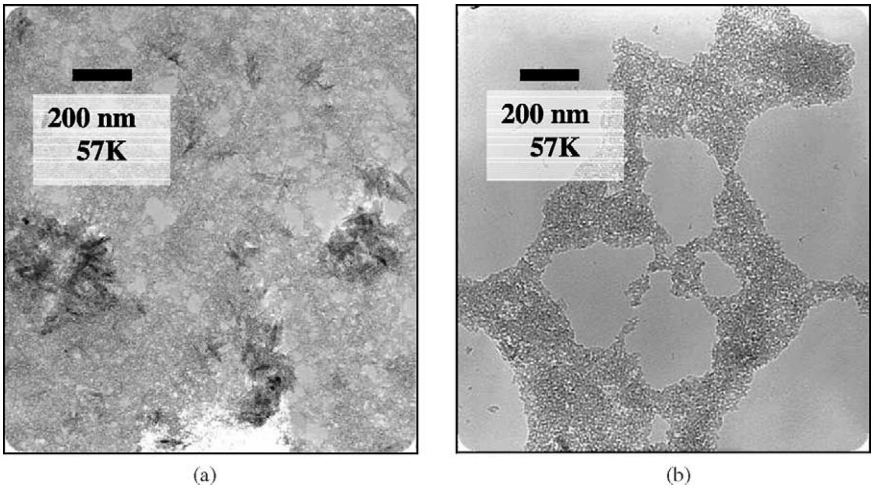


Fig. 4. TEM micrographs of (a) sample TC-60(D) (b) sample TC-90(D) prepared using acidified alkoxide process and washed by dialysis.

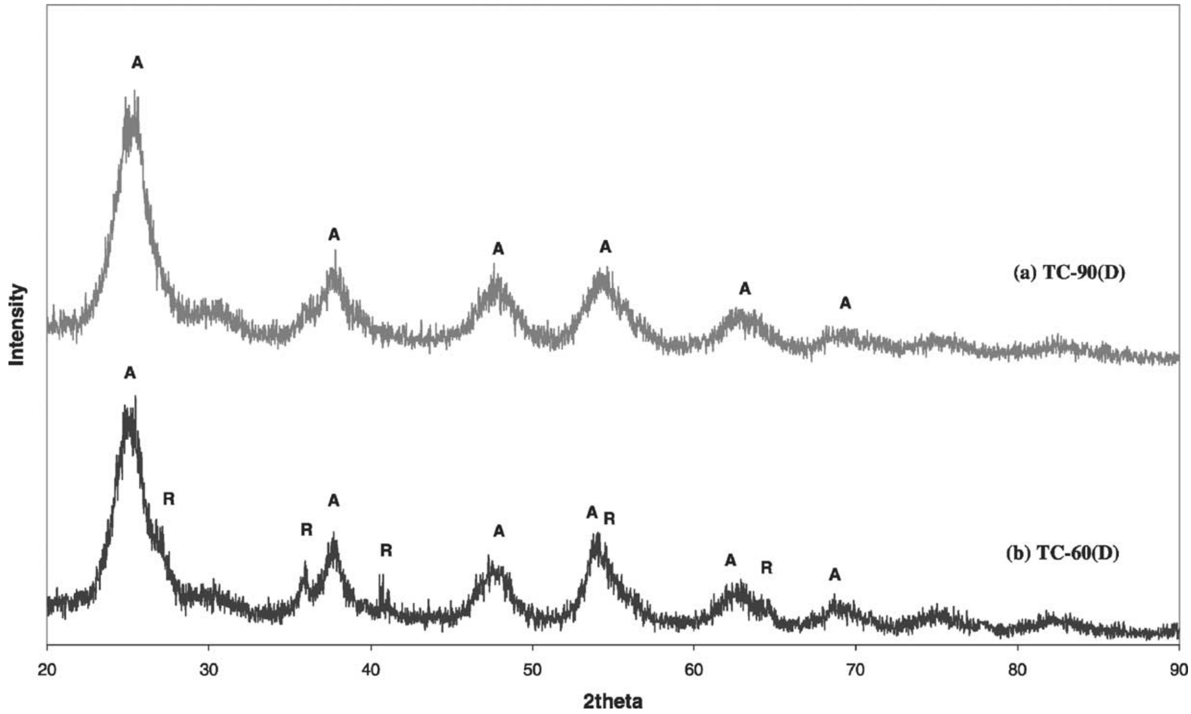


Fig. 5. Effect of dialysis on phase formation (a) TC-90(D) (acidified alkoxide method at 90 °C), (b) TC-60(D) (acidified alkoxide method at 60 °C).

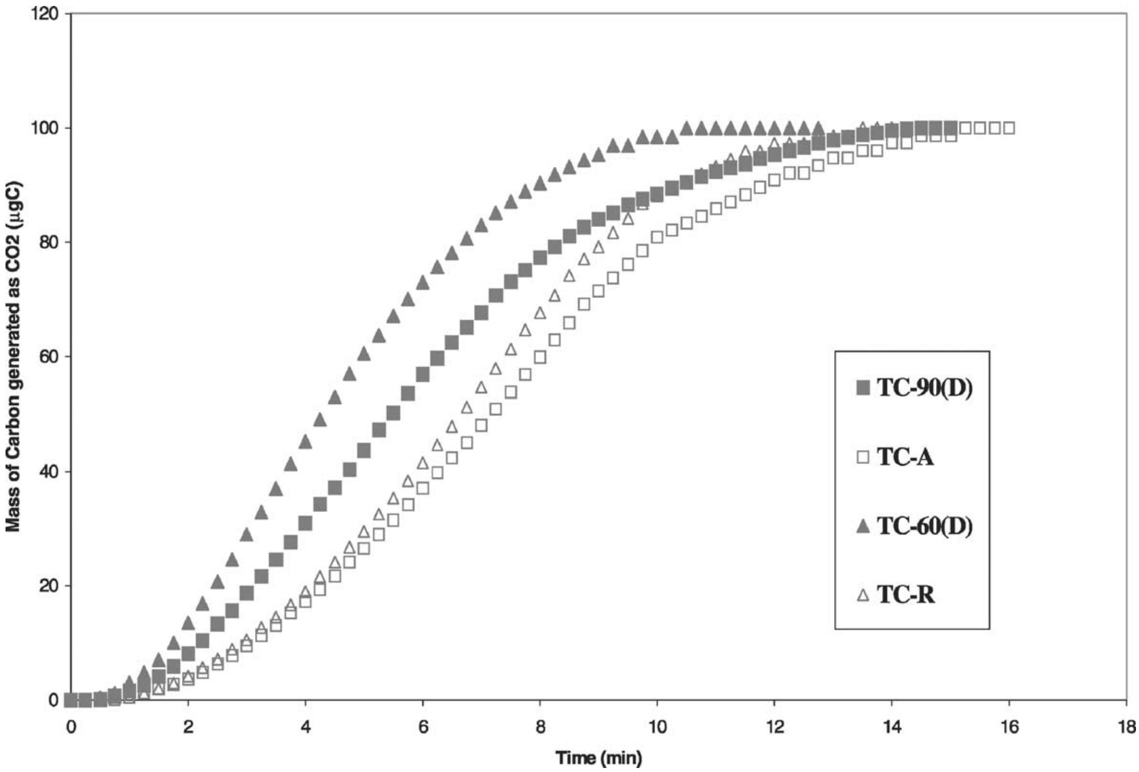


Fig. 6. Results of photocativity testing comparing the activities of samples washed by different method.

solution was discarded before the particles were dialysed at room temperature. Therefore, placing the system in the ice bath merely stops the reaction temporarily and unreacted precursors remained in the system. Thus, when the particles are dialysed at room temperature for 7 days, the reaction of any unreacted alkoxide species is the source of continual particle growth.

The following postulation is put forward to explain the precipitation of TiO_2 in its anatase form (rather than rutile) during dialysis at room temperature. For the dialysis system, firstly, primary rutile particles were formed at reaction temperature of 60 °C (as previously explained). Unreacted precursor and organic impurities remained either adsorbed on the surface of rutile particles or in solution, therefore inducing secondary nucleation. When seed particles (that is, the primary rutile particles) exist in solution, a new scenario is created for the precipitation and formation of the new phase [24]. The reason for the formation of anatase particles at room temperature, during dialysis (rather than rutile) is postulated to be due to the presence of the seed particles resulting in faster reaction kinetics with less energy being required for the nucleation of anatase particles. The growth of anatase particles is postulated to have continued until a point where minimal unreacted precursor remains (1.8 μg of carbon from Table 2). A similar precipitation process can also explain the formation of particles prepared at 90 °C which were also washed by dialysis. In this system, seed particles existing in solution were of anatase rather than rutile. The continued nucleation and growth of anatase particles until all the reactants were consumed was reflected by the yield of 100% compared to the yield obtained by centrifugation batches of 9 and 74% for rutile and anatase, respectively.

3.3.2. Photoactivity studies

Photocatalytic studies were carried out to further understand the implications of the different washing methods on the properties of the prepared particles. The results of these studies are given in Fig. 6, which compares the performance of the particles washed by dialysis with those washed by solvent (all particles were prepared by the acidified alkoxide process).

Fig. 6 shows the photocatalytic activity of the prepared particles decreased in the following order TC-60(D) > TC-90(D) > TC-R > TC-A. One observation from the photoactivity test result is that the particles washed by dialysis exhibited higher photoactivity than those particles that have been washed by centrifugation. Although the size of the dialysed particles (350 nm) is greater than that of non-dialysed particles (150–200 nm), the higher photoactivity exhibited is postulated to be due to the sufficient cleaning process offered by dialysis. Lower carbon burn-off periods and a reduced amount of surface organic indicate this (Table 2). These results show the potential of dialysis as a sufficient washing technique for the removal of organic impurities. While this is yet to be explained, future studies will focus on trying to relate surface properties, carbon burn off and photocatalytic activity with the washing technique.

4. Conclusions

Nanophase crystalline titania particles were prepared by an acidified alkoxide process using titanium isopropoxide as the precursor in an acidic medium. By controlling the reaction temperature, either rutile or anatase can be obtained without the need for heat treatment. The titanium dioxide particles prepared by this method have been compared to titanium dioxide particles prepared by the conventional alkoxide method and have been shown to exhibit higher photoactivity. Thus, the newly adopted particle preparation method is promising in terms of eliminating the undesirable heat treatment that causes increased particle size and lower surface area.

Washing techniques have also been found to affect phase formation and surface properties of the particles. Dialysis is one technique that allows removal of soluble impurities without the introduction of foreign species. Although dialysis has been demonstrated to be a sufficient method for cleaning of particles, the method induces nucleation and growth of new anatase particles. Nevertheless, the formation of anatase nanocrystals at room temperature is relatively new in the particle preparation field. Current studies are focused on improving surface properties by identifying the appropriate washing technique required for a clean catalyst surface.

Acknowledgements

S.S. Watson wishes to thank the Australian government for their financial support by a grant from Australian Research Council and Australian Postgraduate Award. Mr. Steve McEvoy from CSIRO is gratefully acknowledged for providing the use of the photoreactor.

References

[1] M. Lindner, D.W. Bahnemann, B. Hirthe, W. Griebler, Solar water detoxification: novel TiO_2 powders as highly active photocatalysts, Solar Eng. 1 (1995) 399–408.

[2] D.F. Ollis, E. Pelizzetti, N. Serpone, Photocatalysed destruction of water contamination, Environ. Sci. Technol. 25 (1991) 1522–1529.

[3] A. Mills, S. Le Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A 108 (1997) 1–35.

[4] D. Chen, M. Sivakumar, A.K. Ray, Heterogeneous photocatalysis in environmental remediation, Dev. Chem. Eng. Miner. Process 8 (2000) 505–550.

[5] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Photocatalysed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallised TiO_2 suspensions. Part (I). Photocatalytic activity and pH influence, Water Res. 33 (1999) 661–668.

[6] G. Kang, S. Lee, C. Chung, S. Cho, G. Han, B.W. Kim, K.J. Yoon, Characterisation of a TiO_2 photocatalyst synthesised by the solvothermal method and its catalytic performance for $CHCl_3$ decomposition, J. Photochem. Photobiol. A 144 (2001) 185–191.

[7] J.C. Ireland, B. Davila, H. Moreno, Heterogeneous photocatalytic decomposition of polyaromatic hydrocarbons over titanium dioxide, Chemosphere 30 (1994) 965–984.

[8] J. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, Environmental TiO_2-based solar photocatalytic detoxification of water containing organic pollutants. Case studies of 2,4-dichlorophenoxyacetic acid (2,4-D) and of benzofuran, Appl. Catal. B 17 (1998) 15–23.

[9] L. Muszkat, L. Bir, L. Feigelson, Solar photocatalytic mineralisation of pesticides in polluted waters, J. Photochem. Photobiol. A 87 (1995) 85–88.

[10] K. Okamoto, Y. Yamamoto, H. Tanaka, M. Tanaka, A. Itaya, Heterogeneous photocatalytic decomposition of phenol over TiO_2 powder, Bull. Chem. Soc. Jpn. 58 (1985) 2015–2022.

[11] V. Augugliaro, L. Palmisano, A. Sclafani, Photocatalytic degradation of phenol in aqueous titanium dioxide dispersions, Toxicol. Environ. Chem. 16 (1988) 89–109.

[12] S.E. Pratsinis, Flame synthesis of nanosize particles: precise control of particle size, J. Aerosol Sci. 27 (1996) s153–s154.

[13] Z. Ding, X. Hu, P.L. Yue, G.Q. Lu, P.F. Greenfield, Synthesis of anatase TiO_2 supported on porous solids by chemical vapour deposition, Catal. Today 68 (2001) 173–182.

[14] H.D. Nam, B.H. Lee, S. Kim, C. Jung, J. Lee, S. Park, Preparation of ultrafine crystalline TiO_2 powders from aqueous $TiCl_4$ solution by precipitation, J. Appl. Phys. 37 (1998) 4603–4608.

[15] K.Y. Jung, S.B. Park, Anatase-phase titania: preparation by embedding silica and phtocatlytic activity for the decompostion of trichloroethylene, J. Photochem. Photobiol. A 127 (1999) 117–122.

[16] D.S. Bhatkhande, V.G. Pangarkar, A. Beenackers, Photocatalytic degradation for environmental applications—a review, J. Chem. Technol. Biotechnol. 77 (2001) 102–116.

[17] D. Beydoun, Development of a novel magnetic photocatalyst, Ph.D. thesis, Department of Chemical Engineering, UNSW, Sydney, 2000.

[18] D.C. Hague, M.J. Mayo, Controlling crystallinity during processing of nanocrystalline titania, J. Am. Ceram. Soc. 77 (1994) 1957–1960.

[19] M.S. Kaliszewski, A.H. Heuer, Alcohol interaction with zirconia powders, J. Am. Ceram. Soc. 73 (1990) 1504–1509.

[20] A.P. Philipse, M.P.B. van Bruggen, C. Pathmamanoharan, Langmuir magnetic silica dispersions: preparation and stability of surface-modified silica particles with a magnetic core, Langmuir 10 (1994) 92–99.

[21] R.W. Matthews, Kinetics of photocatalytic of organic solutes over titanium dioxide, J. Catal. 111 (1988) 264–272.

[22] M. Gopal, W.J. Moberly Chan, L.C. De Jonghe, Room temperature synthesis of crystalline metal oxides, J. Mater. Sci. 32 (1997) 6001–6008.

[23] P. Madhu Kumar, S. Badrinarayanan, M. Sastry, Nanocrystalline TiO_2 studied by optical, FTIR and X-ray photoelectron spectroscopy: correlation to presence of surface states, Thin Solid Films 358 (2000) 122–130.

[24] S.S. Watson, D. Beydoun, J.A. Scott, R. Amal, Synthesis of novel magnetic photocatalyst by direct deposition of nanosized TiO_2 crystals onto a magnetic core, J. Photochem. Photobiol. A 6009 (2002) 1–11.