

A simple red-ox titrimetric method for the evaluation of photo-catalytic activity of titania based catalysts

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Abstract. A simple red-ox titrimetry method has been developed for rapid evaluation of the photo catalytic activity of TiO₂ based photo-catalysts. The analytical procedure employs monitoring the kinetics of a simple one electron transfer reduction reaction of conversion of Ce⁴⁺ to Ce³⁺ in dilute aqueous solution in presence of sunlight. The photo-catalytic activity of TiO₂ synthesized by two different routes was evaluated by the above technique. The effect of surface area, crystallite size and polymorphic contents on the photo-catalytic activity of TiO₂ was also studied employing this method.

Keywords. Red-ox titration; photo-catalysis; titanium dioxide; catalytic activity; synthesis of titania; microwave processing.

1. Introduction

Titanium (IV) oxide is the most promising semiconductor photo-catalyst and has been investigated extensively in recent years for wide ranging applications. The diverse applications of this magic material have been covered exhaustively in the reviews recently published (Fox and Dulay 1993; Hagfeldt and Gratzel 1995; Hoffmann *et al* 1995; Linsebigler *et al* 1995; Rajeshwar 1996; Fujishima *et al* 2000) from different reputed laboratories.

The evaluation of catalytic activity of TiO₂ used as a photo-catalyst has been frequently made by using sophisticated analytical equipments like GC, HPLC, ICP/MS etc (Okamoto and Yasunori 1985; Dube and Darshane 1993; Prairie *et al* 1993; Murugesan 2001). These equipments and the chemicals required for the analysis are expensive and beyond the budgetary limits of normal teaching institutions. In the present work, we have developed a simple method for rapid scanning of a large number of TiO₂ based photo-catalysts prepared under varying experimental conditions in a relatively short duration in R&D laboratories having basic analytical facilities. The method suggested here could also be adopted to study the photo-catalytic activity of other transition metal oxide based catalysts. For establishing this technique, we have monitored a simple one-electron transfer red-ox reaction involving photochemical reduction of Ce⁺⁴ to Ce⁺³ in dilute ceric sulphate solution. The results presented in this paper show that the technique can be used for rapid scanning of a number of photo-catalyst samples in a reasonably short duration.

2. Experimental

2.1 Preparation of hydroxide precursor

The TiO₂ used in this investigation was prepared from TiCl₄ solution (Merck, Synthesis grade with purity, > 99%). Dilute TiCl₄ was prepared by controlled addition of concentrated TiCl₄ in ice cooled demineralized water. The concentration of TiCl₄ in dilute solution was maintained around 2–3 molar. Ti(OH)₄ precursors were precipitated from this solution by employing two different processes, viz. (i) controlled precipitation using urea and (ii) hydrolysis of dilute TiCl₄ solution.

In controlled precipitation process, dilute TiCl₄ solution was mixed with urea in proportion of TiO₂ : urea 1 : 20 moles and heated at ~ 100°C. The reaction mixture was refluxed for 2–3 h to ensure completion of the reaction. The precipitate was cooled, filtered and washed several times with hot demineralized water till it was free of chloride ions.

In hydrolysis process, the stock solution of TiCl₄ was further diluted five to six times with demineralized water. The solution was refluxed at 100°C for 3 h and cooled to room temperature. Refluxed solution resulted in the formation of a precipitate that settled down on cooling. The supernatant liquid from the slurry was decanted slowly and it was re-mixed with fresh demineralized water. Dilute ammonia was then added to this solution drop wise, under stirring condition till its pH was neutral (pH ≅ 7). The precipitate so obtained was filtered and washed with demineralized water till free of chloride ions.

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2.2 Preparation of TiO₂ from hydroxide precursor and characterization

The hydroxide precipitates obtained by both the methods were vacuum dried at room temperature followed by controlled heat treatment at 110°C and 300°C in microwave system (MW) for 1 h. This resulted in the formation of titanium oxide (TiO₂), which was characterized by X-ray diffraction technique using CuK- α radiation (Phillips X'Pert X-ray diffractometer). The crystallite size '*t*' of TiO₂ heat treated at different temperatures was evaluated from the half width 'B' of the most prominent peak at 50% intensity using the Debye–Scherrer relation (Cullity 1967) given by

$$t = \frac{0.9\lambda}{b \cos q_B}, \quad (1)$$

where λ is the wavelength of the radiation (Å) used and $2q_B$ represents the angle at which the peak is recorded.

The weight fraction of rutile in TiO₂ prepared by different methods was calculated using the following equation (Zhang and Banfield 2000)

$$a = \frac{1}{1 + 0.884 (A_{\text{anatase}}/A_{\text{rutile}})}, \quad (2)$$

where A_{anatase} and A_{rutile} represent respectively the integral intensities of anatase (101) and rutile (110) peaks and a the extent of transformation of anatase i.e. weight fraction of rutile in the mixture.

The surface area of resulting product was measured by BET method employing nitrogen gas adsorption unit (SMART SORB-90) manufactured and supplied by M/s Smart Instrument Co., Dombivali, Maharashtra.

2.3 Preparation of standard solutions of ceric sulphate and ferrous ammonium sulphate

A dilute ceric sulphate solution (4×10^{-4} N) was prepared by dissolving the known amount of oven dried (150°C, 15 min) ceric sulphate crystals in 3N H₂SO₄ solution. The percentage conversion of the Ce⁴⁺ to Ce³⁺ as a function of

time was determined by back titrating the residual Ce⁴⁺ in solution employing ferrous ammonium sulphate (as a reducing agent) and ferroin as an indicator. The standard ferrous ammonium sulphate solution was prepared by dissolving the freshly re-crystallized ferrous ammonium sulphate in dilute H₂SO₄ solution (3N).

2.4 Kinetics of conversion of Ce⁴⁺ to Ce³⁺ in presence of sunlight

The experiment to study the kinetics of conversion of Ce⁴⁺ to Ce³⁺ in presence of sunlight was performed as follows:

25 ml of the ceric sulphate solution was taken in 100 ml beaker to which weighed amount of TiO₂ powder was added. The amount of TiO₂ powder added varied from 25 to 150 mg. The ceric sulphate solution containing TiO₂ powder was exposed to sunlight and stirred continuously to get uniform dispersion. The solution containing the slurry was exposed to sunlight for different lengths of time and unconverted Ce⁴⁺ was estimated by titrating the solution against ferrous ammonium sulphate using ferroin as an indicator. Preliminary results obtained indicated that the amount of TiO₂ needed for complete conversion of Ce⁴⁺ to Ce³⁺ contained in 25 ml of solution was about 150 mg. In all the subsequent experiments 150 mg of TiO₂ was added to 25 ml of the ceric sulphate solution.

For comparison of photo activity of TiO₂ prepared by different routes, the experiments were conducted on different samples on the same day at the same time to eliminate any uncertainty resulting from non-identical conditions of the sunlight on different days.

3. Results and discussion

3.1 Physical properties of TiO₂ photo-catalysts

Table 1 summarizes the physical properties such as phase composition and crystallite size derived from X-ray diffraction (XRD), and BET surface area of the powders

Table 1. Comparison of powder characteristics of the samples obtained by different methods.

	Sample A		Sample B	
	A-1	A-2	B-1	B-2
Process	Controlled precipitation		By hydrolysis	
Heat treatment	110°C for 60 min (MW)	300°C for 60 min (MW)	110°C for 60 min (MW)	300°C for 60 min (MW)
Phases identified by XRD	Anatase	Anatase	Anatase (40%) + rutile (60%)	Anatase (33%) + rutile (67%)
Surface area (m ² /g)	198	100	180	82
Crystallite sizes (Å)	45	118	77 (a) 110 (r)	130 (a) 132 (r)

a, anatase; r, rutile.

obtained employing different experimental conditions. The relative amount of anatase and rutile (**a**) in the powder obtained by hydrolysis process was calculated from XRD using (2). The calculations indicated that at 110°C, **a** was 60% while at 300°C the same increased to 67%. The crystallite size of anatase phase in samples A and B increased with increasing temperature (table 1). The relative increase in the crystallite size in pure anatase was higher than that for the same phase in the mixture. The crystallite size for pure anatase increased from 45 Å at 110°C to 118 Å at 300°C, whereas that for anatase in the mixture it increased from 77 Å at 110°C to 130 Å at 300°C.

The surface area of TiO₂ prepared by controlled precipitation method having anatase phase (sample A-1) decreased from 198 m²/g to 100 m²/g by increasing the heat treatment temperature from 110°C to 300°C (sample A-2). The mean surface area of the mixture of anatase and rutile obtained by hydrolysis, however, decreased from 180 m²/g at 110°C to 82 m²/g at 300°C (table 1). The order of magnitude of decrease in the surface area in both powders was almost the same (~ 50%).

3.2 Photo catalytic reactivity

The plots depicted in figures 2–5 indicate the percentage conversion of Ce⁴⁺ to Ce³⁺ as a function of time for the samples obtained by controlled precipitation and by hydrolysis route. Figures 2 and 3 compare the reactivity of anatase phase with the mixture of anatase and rutile obtained under identical experimental conditions at 110°C and 300°C, respectively. Figures 4 and 5 highlight the influence of heat treatment of TiO₂ on the resulting kinetics.

All the plots of conversion of Ce⁴⁺ to Ce³⁺ in solution, in presence of TiO₂ prepared by different methods (figures 2–5), showed that the percentage of Ce³⁺ in solution increased continuously with time. The extent of increase was found to depend mainly on the temperature at which the sample was prepared and also on the polymorphic form of TiO₂ in the sample. TiO₂ prepared by heating Ti(OH)₄, obtained by dilution method, to 110°C (sample B-1) (figure 1b) contained nearly 60% rutile phase and was found to be much more reactive compared to the sample obtained from Ti(OH)₄ precipitated by urea route and heated to the same temperature (110°C) (figure 2). This latter sample consisted only of anatase phase (sample A-1) (figure 1a). It is interesting to note that the reactivity of the mixture of anatase and rutile prepared at 110°C (sample B-1) is substantially higher compared to that of the single anatase phase (sample A-1) despite the fact that the mean surface area of the mixture is 180 m²/g compared to 198 m²/g for the single anatase phase prepared also at 110°C. The oxides obtained from the same hydroxide precursor after heating to 300°C in MW for 60 min however, showed reverse trend in their

photocatalytic activity. Sample A-2 consisting of a single anatase phase (figure 1c) showed higher reactivity (figure 3) as compared to the mix phase powder containing nearly 67% rutile phase (figure 1d) (sample B-2). The mean surface area of the mixture prepared at 300°C is 82 m²/g compared to 100 m²/g for the single anatase phase. The decrease in reactivity of the mixture with increasing temperature could be understood both in terms of the decrease in the mean surface area of the sample as well as the increase in the rutile content of the mixture, which is known to be less reactive compared to the anatase phase (Karakitsou and Verykios 1993; Mihaylov *et al* 1993; Mills *et al* 1993a, b; Noda *et al* 1993; Ohtani and Nishimoto 1993; Martin *et al* 1994).

The enhanced reactivity of anatase with increasing temperature (figure 4) observed in the present study corroborates with the results of previous investigators (Nishimoto *et al* 1985; Mills and Morris 1993; Mills *et al* 1993a; Tanaka *et al* 1993). Mills and Morris (1993) attributed this increase to the increase in mean crystallite size of the phase with increasing temperature. Our results also show a similar trend in the values of the mean crystallite

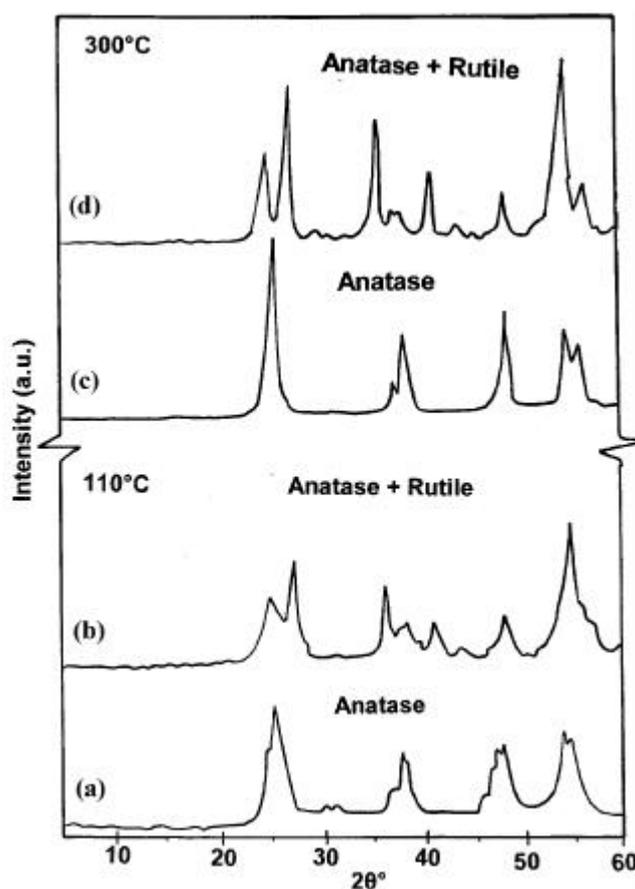


Figure 1. XRD patterns of anatase phase and anatase + rutile mixture prepared by microwave heating to 110°C and 300°C of Ti(OH)₄ precursor obtained by urea precipitation and hydrolysis method, respectively for 60 min.

size derived from X-ray diffraction data. The crystallite size of anatase increased from 45 Å at 110°C to 118 Å at 300°C (table 1).

The photochemical reactivity of anatase phase and the mixture of anatase and rutile phases prepared by heating their precursors at 110°C and 300°C, respectively are compared in figures 4 and 5. The decrease in the reactivity of the mixture heat treated at 300°C (figure 5) could be attributed more to the increase in rutile content of the mixture (67% compared to 60% at 110°C), which is considered to be less reactive than the anatase phase (Karakitsou and Verykios 1993; Mihaylov *et al* 1993; Mills *et al* 1993a, b; Noda *et al* 1993; Ohtani and Nishimoto 1993; Martin *et al* 1994). If mean crystallite size was the only factor controlling the reactivity of the sample, then on the basis of the increased mean crystallite size of the anatase as well as the rutile component in the mixture (table 1), the mixture also should exhibit higher reactivity at higher temperature. The decrease in reactivity of the mixture with increasing temperature could thus be understood more on the basis of the decreased surface area and increased rutile content in the sample prepared at high temperature.

One of the interesting features of this investigation is the parabolic dependence of the amount of Ce^{4+} converted on time (figure 6), suggesting that some kind of diffusion controlled process is involved in the reduction process. The parabolic nature of the plot was independent of whether the TiO_2 sample was monophasic (anatase) or biphasic (anatase + rutile mixture). The possibility of such diffusion controlled bimolecular photochemical reaction has been documented (Rohatg-Mukherjee 1992). However, due to limited data it is not possible at this stage to propose any detailed mechanism for the process.

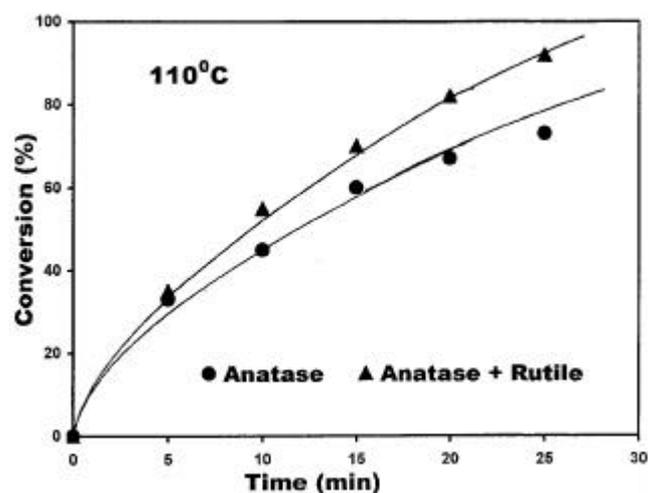


Figure 2. Plot of percentage conversion of Ce^{4+} to Ce^{3+} as a function of time (min) for the anatase phase and anatase + rutile mixture prepared by microwave heating at 110°C for 60 min.

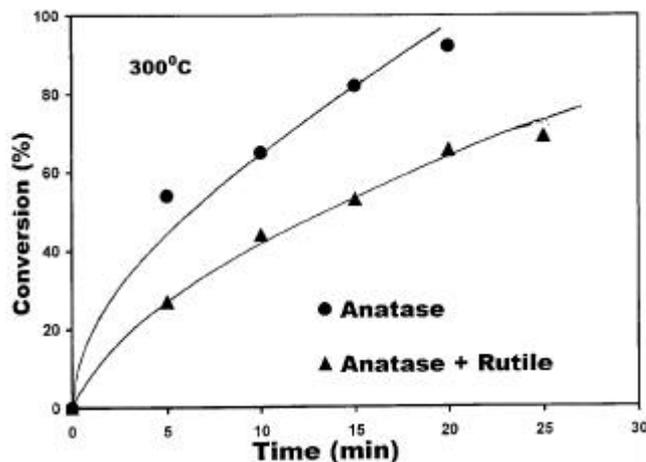


Figure 3. Plot of percentage conversion of Ce^{4+} to Ce^{3+} as a function of time (min) for the anatase phase and anatase + rutile mixture prepared by microwave heating at 300°C for 60 min.

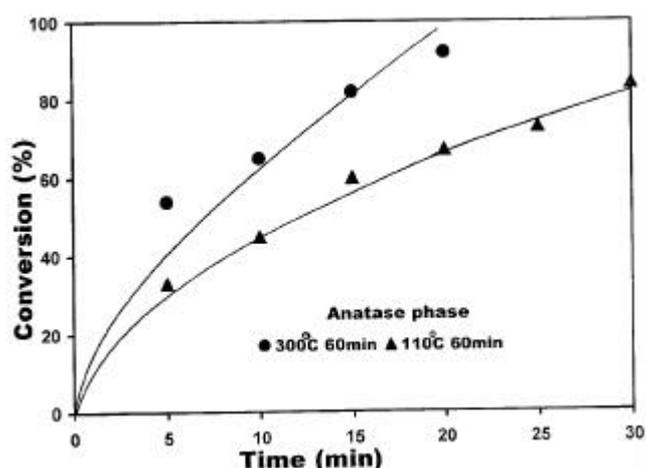


Figure 4. Plot of percentage conversion of Ce^{4+} to Ce^{3+} as a function of time (min) for the anatase phase prepared by microwave heating at 110°C and 300°C for 60 min.

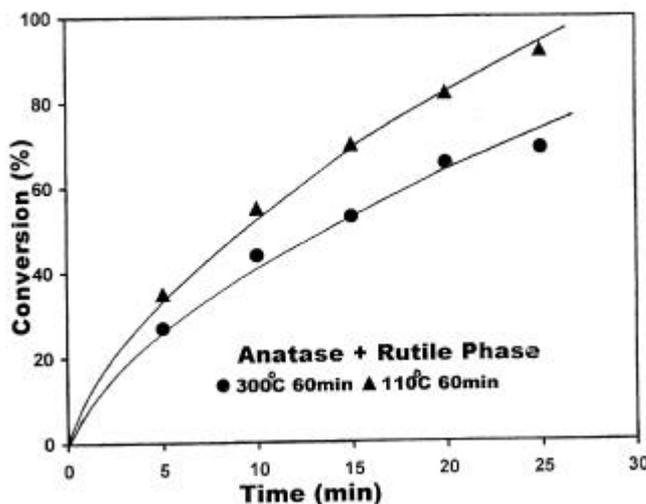


Figure 5. Plot of percentage conversion of Ce^{4+} to Ce^{3+} as a function of time (min) for anatase + rutile mixture prepared by microwave heating at 110°C and 300°C, respectively for 60 min.

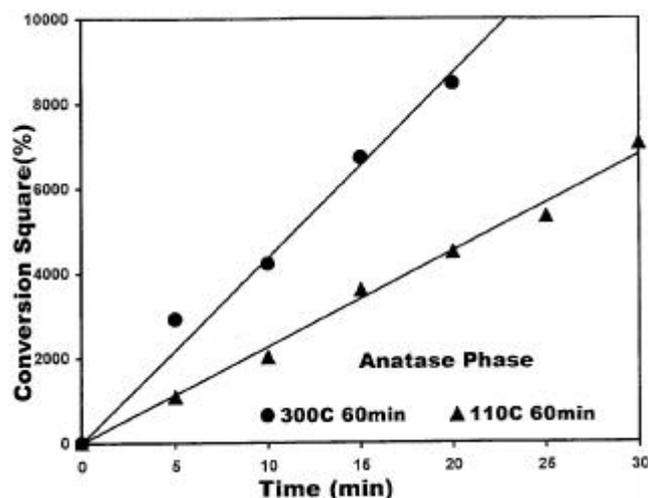


Figure 6. Plot of conversion square of Ce^{4+} to Ce^{3+} as a function of time (min) for the anatase phase prepared by microwave heating at 110°C and 300°C for 60 min.

4. Conclusions

The results of this investigation suggest that it is possible to study photocatalytic activity of TiO_2 catalysts in presence of sunlight using simple red-ox titration technique. The study also reveals that the reactivity of the mixture of anatase and rutile phases prepared via hydrolysis route is relatively higher compared to that of anatase phase prepared under identical condition when the temperature of heat treatment of the hydroxide precursor is relatively low (i.e. 110°C). The sintering of anatase and rutile mixture with increasing temperature results in the reduction of its reactivity, probably due to decrease in mean surface area and increase in its rutile content with increasing temperature. Anatase also sinters with increasing temperature, but its continuous conversion to rutile simultaneously could result initially, in the creation of an interface between anatase and rutile phases, which could probably be catalytically more reactive. Such enhanced reactivity at the point of phase transitions in the materials has been a common phenomena in solid state reactions (Hedvall 1966). This reactivity can, however, decrease when the

TiO_2 in the anatase form transforms to rutile substantially, as it happens above 600°C .

References

- Cullity B D 1967 *Elements of X-ray diffraction* (USA: Addison-Wesley Publishing Company Inc.)
- Dube G R and Darshane V S 1993 *J. Mol. Catal.* **79** 285
- Fox M A and Dulay M T 1993 *Chem. Rev.* **93** 341
- Fujishima A, Rao T N and Tryk D A 2000 *J. Photochem. and Photobiol. C: Photochem. Rev.* **1** 1
- Hagfeldt A and Gratzel M 1995 *Chem. Rev.* **95** 49
- Hedvall J A 1966 *Solid state chemistry* (Amsterdam: Elsevier Scientific Publication)
- Hoffmann M A, Martin S T, Choi W and Bahnemann D W 1995 *Chem. Rev.* **95** 69
- Karakitsou K E and Verykios X E 1993 *J. Phys. Chem.* **97** 1184
- Linsebigler A L, Lu G and Yates J T 1995 *Chem. Rev.* **95** 735
- Martin S T, Morrison C L and Hoffmann M R 1994 *J. Phys. Chem.* **98** 13695
- Mihaylov B V, Hendrix J L and Nelson J H 1993 *J. Photochem. Photobiol. A: Chem.* **72** 173
- Mills A and Morris S 1993 *J. Photochem. Photobiol. A: Chem.* **71** 285
- Mills A, Morris S and Davis R 1993a *J. Photochem. Photobiol. A: Chem.* **70** 183
- Mills A, Davis R H and Worsley D 1993b *Chem. Soc. Rev.* **22** 417
- Murugesan V 2001 *Proceedings on workshop on catalysis on sustainable development through catalysis* (Mumbai: Catalyst Society of India) p. 17
- Nishimoto S, Ohtani B, Kajiwara H and Kagiya T 1985 *J. Chem. Soc., Faraday Trans.* **1** 81
- Noda H, Oikawa K and Kamada H 1993 *Bull. Chem. Soc. Jpn* **66** 445
- Ohtani B and Nishimoto S 1993 *J. Phys. Chem.* **97** 920
- Okamoto Ken-ichi and Yasunori Yamamoto 1985 *Bull. Chem. Soc. Jpn* **58** 2015
- Prairie Michael R, Evans Lindsey R, Stange Bertha M and Martinez Sheryl L 1993 *Environ. Sci. Technol.* **27** 1176
- Rajeshwar K 1996 *Chem. & Ind.* **12** 14
- Rohatg-Mukherjee K K 1992 *Fundamentals of photochemistry* (Delhi: Wiley Eastern Publ.)
- Tanaka K, Hisanaga T and Rivera A P 1993 in *Photocatalytic purification and treatment of water and air* (eds) H Al Ekabi and D F Olis (Amsterdam: Elsevier) p. 337
- Zhang H and Banfield J F 2000 *J. Mater. Res.* **15** 437