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Preparation of high surface area TiO_2 (anatase) by thermal hydrolysis of titanyl sulphate solution

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Abstract

Highly crystalline, ultra fine TiO_2 (anatase) having high surface area has been prepared by thermal hydrolysis of titanyl sulphate solution and characterized using B.E.T surface area measurements, XRD and chemical analysis. The dependence of surface area on concentration of staffing solution, temperature of hydrolysis, duration of boiling and calcination temperature were also studied. As the boiling temperature, duration of boiling and calcination temperature increased, the surface area of TiO_2 formed decreased significantly. On increasing calcination temperature, the crystallite size of TiO_2 also increased and gradually the phase transformation to rutile took place. The onset and completion temperatures of rutilation were 700 and 1000°C, respectively. © 2001 Published by Elsevier Science Ltd.

Keywords: Thermal hydrolysis; Titanyl sulphate; Crystalline; Anatase; Surface area and rutilation

1. Introduction

TiO_2 exists in three crystal modifications, viz. anatase, brookite and rutile. Thermodynamically, rutile is the most stable form. Out of these, anatase has drawn much attention due to its application as catalyst or catalyst support for metal or metal oxide catalysts, used in heterogeneous catalysis, including photocatalysis of industrial and environmental importance. TiO_2 based catalyst was first used commercially in air pollution control equipment in Japan in 1970 [1].

TiO_2 (anatase) is used as a catalyst in amination of methanol, isomerization of 1-butene and β-pinene [2], photo degradation of chlorinated hydrocarbons [3–5], photolysis of water [6] and in degradation of organic water pollutants [7,8].

Metals or metal oxides supported on TiO_2 are used in degradation of chloroflouro carbons [9], photodegradation of dichloroacetic acid [10], partial oxidation of methane to synthesis gas [11], ammonia synthesis [12], carbon monoxide methanation [13], hydro desulphurization [14], reduction of NO_x [15], selective oxidation of *o*-xylene [16], etc.

The catalytic activity, to a great extent, is determined by such physical properties as particle size, surface area, crystallinity, etc. Hence its preparation is fundamental to obtain the properties suitable for catalytic applications.

Most of the above mentioned reactions were found to be carried out on a commercially available TiO_2, known as Degussa p-25, which is a mixture of anatase (70%) and rutile (30%) and has a surface area of 50 m^2/g [17]. The commercial titania fail to provide phase pure anatase and high surface area. The major problem associated with TiO_2 supported catalysts is the phase transformation of anatase to rutile, which involves a decrease in cell volume, an increase in density, mechanical strains and a reduction in surface area leading to an over all degradation of the quality of the catalyst. Hence titania as a catalyst or as a support should be characterized by high surface area and high onset temperature to rutilation.

Several methods are available for the preparation of titania, which include, sol–gel method using titanium tetra alkoxides [8,18], ultrasonic nebulization of $TiCl_4$ [4], hydrothermal crystallization using titanium tetra alkoxides in the presence of organic solvents [19] or by using

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titanium oxychlorides [6]. But it is very difficult to handle $TiCl_4$ or alkoxides, as they vigorously hydrolyse in the presence of atmospheric moisture and the higher price of alkoxides limit their commercialization. Also, pure anatase can not be prepared by hydrothermal crystallization in the presence of chloride ions, which would lead to the formation of rutile phase rather than anatase [20,21].

Hence extensive work has been going on for preparing highly pure anatase having high surface area. Thermal hydrolysis of titanyl sulphate solution, which can give highly pure TiO_2 (anatase) with good crystallinity is a widely used commercial process for the production of pigment grade TiO_2. But the commercial plants add nuclei (seeding agents) to hasten the hydrolysis, which would lead to the precipitation of a mixture of ortho and meta titanic acids and the washed precipitate is normally calcined at very high temperature ca. >1000°C to achieve desired pigmentry properties. Both of these would adversely affect the particle size and surface area. Some adsorbed sulphate and phosphate (which is added to prevent rutilation at high temperature calcination) would also be present as impurity.

A detailed investigation for the preparation of TiO_2 (anatase) by thermal hydrolysis of titanyl sulphate solution under different conditions to obtain better properties in terms of surface area and crystallinity was undertaken and the results are reported here.

2. Experimental

Titanyl sulphate solution, an intermediate product in the commercial preparation of TiO_2 by sulphate route, which is obtained by acidulating ilmenite with sulphuric acid to solubilize titanium as its sulphate, having specific gravity 1.523 at 40°C was supplied by Travancore Titanium Products Ltd, Trivandrum, India. The composition of the solution is given in Table 1.

An 80 ml volume of the above titanyl sulphate solution was taken in a round bottomed flask fitted with a water condenser to which 80 m1 of distilled water was added and refluxed at different temperatures viz. 100±5°C and 200±5°C for different duration, viz. 5 and 7 h each. Usually the thermal hydrolysis of titanyl sulphate is conducted at 100°C [20]. In order to investigate the effect of temperature of hydrolysis on the surface area of TiO_2 formed, we have carried out the hydrolysis at 200±5°C also. It is reported that the hydrolysis will not be complete on boiling for 3 h [20]. Hence the hydrolysis was carried out for 5 and 7 h. The precipitated hydrated TiO_2 was collected in a 1000 ml beaker, washed six times by decantation after adding large quantities of distilled water each time. Finally it was washed with 25% ammonia solution to remove any adsorbed sulphate ions if present. The precipitate was transferred into a large silica crucible and dried in air oven at 110°C for 3 h. The thermal hydrolysis was repeated from titanyl sulphate solutions of different concentrations (by diluting four, six and eight times using distilled water).

The purity of TiO_2 prepared was determined by chemical analysis using standard procedures [22]. Surface area measurements were carried out by BET method using Accusorb Micromeritics, Model 2100 E. Philips Powder Diffractometer, Model PW1710 with Cu Kα radiation was used for XRD studies.

Table 1
Composition of titanyl sulphate solution

Constituents in grams per litre (g/l)	
Total TiO_2	40.0
Reduced TiO_2	2.3
Free H_2SO_4	266.0
Iron	101.0
A/T[a]	1.90
F/T[a]	0.7214

[a] (A = free H_2SO_4, F = Iron and T = total TiO_2).

3. Results and discussion

3.1. Chemical analysis

Chemical analyses results are given in Table 2. The oven dried sample contains 82.0% TiO_2, which shows that the precipitate formed is meta titanic acid ($TiO_2 \cdot H_2O$). From the chemical analysis, it is clear that calcination at 350°C/6 h is necessary to remove water molecule completely. So, all further studies were conducted after calcination at 350°C for 6 h.

3.2. Surface area measurements

The results are shown in Fig. 1. The concentration of titanyl sulphate solution and duration of boiling have a marked effect on the surface area of TiO_2 formed. The samples prepared by diluting the starting titanyl sulphate solution four times have got much higher surface area under our experimental conditions. As the dilution increased further, the surface area of TiO_2 formed was decreased, which could be due to the growth of hydrated titania on boiling the very dilute titanyl sulphate solution. Due to the same reason, similar samples prepared by refluxing for longer duration also showed lower surface

Table 2
Results of chemical analysis

Calcination temp. (°C)	TiO (%)
Oven dried	82.0
270/4 h	86.73
350/4 h	92.83
350/6 h	99.34

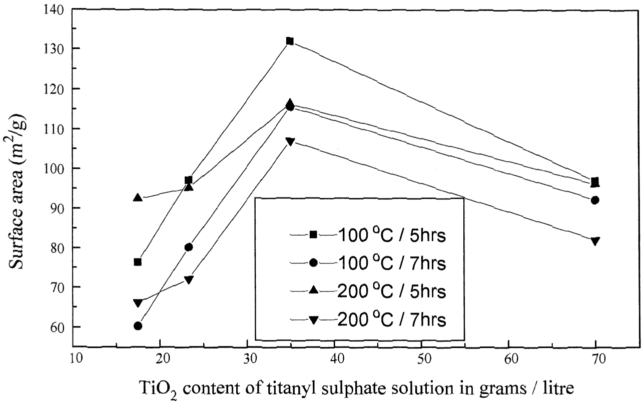

Fig. 1. Surface area of the samples prepared under different conditions.

area. The same was the case when the temperature of hydrolysis was increased.

Out of the above samples, the one having highest surface area was prepared and calcined at different temperatures in order to find out the changes in surface area upon calcination at higher temperatures. A drastic decrease in surface area on increasing calcination temperature was observed, which reveals that TiO_2 particle enlargement is taking place at higher temperatures (Fig. 2).

3.3. XRD studies

The sample having highest surface area was prepared and calcined at different temperatures to conduct the XRD studies for investigating the phase changes occurring while high temperature calcination. The patterns are given in Fig. 3. The XRD pattern of oven dried sample shows that the crystallisation of anatase phase of TiO_2 has started, but the peaks were broad and were not sharp. This would be due to the presence of hydroxyl groups on the surface and it is in agreement with chemical analysis results. Upon calcination at 350°C/6 h, well defined and sharp peaks of anatase were observed in the pattern. So, the calcination at 350°C/6 h is enough for preparing highly pure crystalline TiO_2 anatase by this method. On calcination at 550 and 600°C no phase changes were observed, but when the calcination temperature was increased further to 700°C, the characteristic peaks of rutile were found in the pattern (Fig. 4). The intensity of rutile peaks were increased and that of anatase decreased on increasing the calcination temperature further and there were no peaks of anatase found in the pattern of the sample calcined at 1000°C. Hence it can be concluded that the rutilation started at 700°C and was completed at 1000°C. So the drastic decrease in surface area of these samples as mentioned above could be due to rutilation.

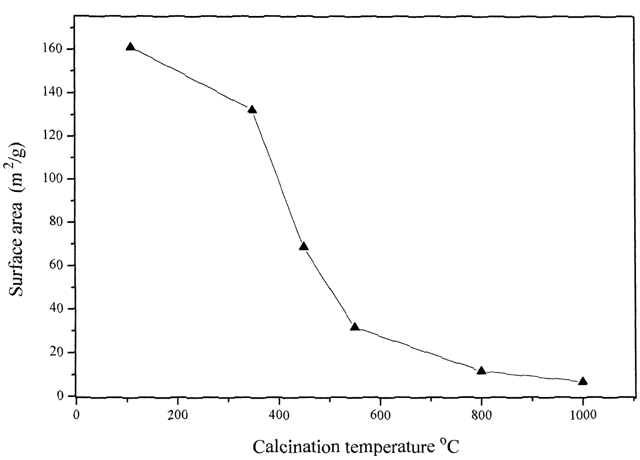

Fig. 2. Changes occurring in surface area with calcination at different temperatures.

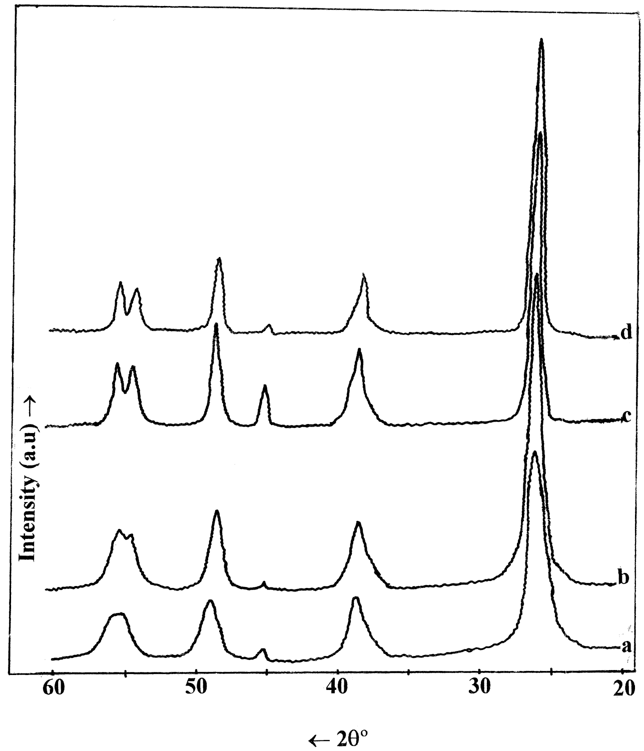

Fig. 3. XRD patterns of titania (a) oven dried, (b) 350°C, (c) 550°C and (d) 600°C for 6 h.

The percentage of rutile and anatase was calculated using the equation [23] $X_R = (1 + 0.794\ I_A/I_R)^{-1}$, where '$X_R$' is the rutile fraction 'I_A' and 'I_R' are the peak intensities of (101) and (110) planes of anatase and rutile, respectively. The results are given in Table 3.

The crystallite size of anatase was calculated in each sample using a computer programme based on the Scherrer relation. For this, we have measured the full width at half height of the peak corresponding to the (101) plane of anatase and the results are given in Table 3. The crystallite size increased on increasing the calcination temperature. In the sample calcined at 600°C, the crystallite size was 17.1 nm, but on increasing the calcination temperature further up to 800°C, no change in crystallite size was observed, but the percentage of rutile was increased. Hence it can be

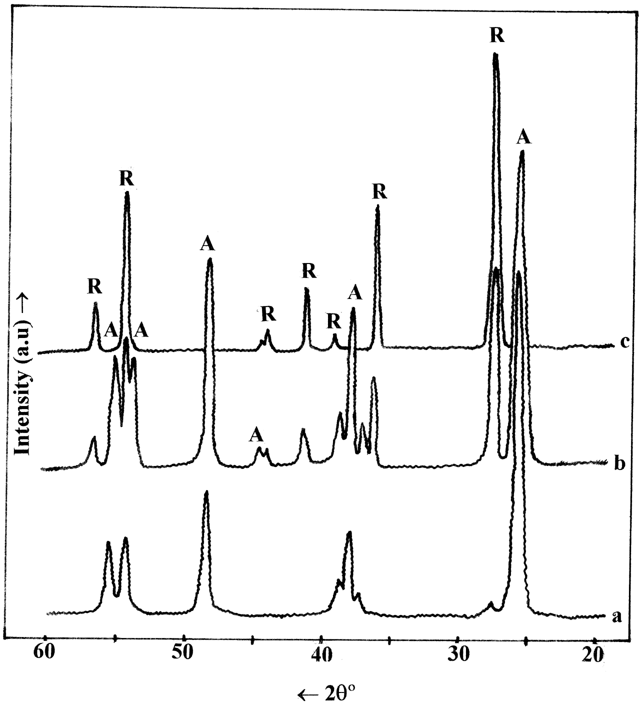

Fig. 4. XRD patterns of titania calcined at (a) 700°C, (b) 800°C and (c) 1000°C for 6 h (A = anatase and R = rutile).

concluded that anatase to rutile phase transformation takes place only after the enlargement of anatase crystallites to a certain size and it is not a simultaneous process.

4. Conclusion

By all the above experiments, it has been concluded that the conditions of thermal hydrolysis of titanyl sulphate solution has a significant effect on the physical properties of TiO_2 formed. Ultra fine TiO_2 (anatase) having high surface area with better crystallinity and high onset temperature of rutilation can be prepared without adding any anti-rutilating agents, by thermal hydrolysis of titanyl sulphate solution of the above mentioned composition, by refluxing at 100±5 for 5 h, after diluting four times to make the TiO_2 content 35 g/l and H_2SO_4 66.5 g/l. Calcination temperature also affect markedly the physical properties and phase transformation. Anatase to rutile phase transformation is not a simultaneous process along with crystallite size enlargement, but, initially, the crystallite size increases and gradually rutilation begins. The onset temperature of rutilation was found to be 700°C. A drastic decrease in surface area was also observed upon rutilation.

Detailed evaluation of the catalytic activity, after loading metal oxides to the TiO_2 prepared by this method is in progress.

Table 3
Anatase, rutile percentages and crystallite size of titania calcined at various temperatures

Calcination temp. (°C)	Phases present (%)		Crystallite size (nm)
	Anatase	Rutile	
350	100	0	9.07
550	100	0	13.96
600	100	0	17.1
700	97.22	2.78	17.1
800	71.15	28.85	17.1
1000	0	100	–

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