Crystal structure transformation of TiO_2 in presence of Fe_2O_3 and NiO in air atmosphere

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Abstract. TiO_2 is produced and marketed in two main grades viz. anatase and rutile. Both anatase and rutile have their own pigmentry properties and hence cannot be substituted by each other. Pure anatase on heating at higher temperatures undergoes crystallographic rearrangement to form rutile. This transformation in presence of NiO and Fe_2O_3 under air atmosphere was studied using XRD and SEM. The transformation temperature was found to be reduced much in presence of NiO and Fe_2O_3 and the extent of lowering was higher for NiO than Fe_2O_3 . The activation energy for this transformation was also calculated. The method of preparation had major influence on the transformation.

Keywords. Anatase; rutile; transformation; crystallographic rearrangement; activation energy.

1. Introduction

TiO_2 is the stable form of titanium. It is also one of the top 20 inorganic chemicals of industrial importance and is an important pigment material used (A Status report prepared under the National Register of Foreign Collaborations, Govt. of India 1993). It exists in three different forms; anatase, rutile and brookite. Rutile is the stable form while anatase and brookite are meta stable. Anatase on heating transforms irreversibly to rutile. This transformation does not have a transformation temperature since there is no phase equilibrium involved (Gennari and Pasquevich 1998). Therefore, anatase to rutile transformation temperature varies, which strongly depends on many factors such as presence of impurity, deviation of stoichiometry, surface area, particle size, atmosphere etc (Yoganarasimhan and Rao 1962).

Yoganarasimhan and Rao (1962) have reported that sulphate ions have pronounced inhibiting action on anatase–rutile transformation. They studied the transformation in anatase prepared by the hydrolysis of titanium sulphate and found that transformation occurs at higher temperature than that for pure anatase. The rate of transformation of spectroscopically pure anatase is exponential with activation energy of ~ 90 k.cal/mol and the transformation temperature 400–1000°C. Impurities having inhibiting action are chloride, sulphate, flouride (Rao *et al* 1959; Yoganarasimhan and Rao 1962), whereas transition metal oxides like Fe_2O_3 , CuO , MnO_2 etc have accelerating power on anatase–rutile transformation (Shannon and Pask 1965; Mackenzie 1975). It has been

revealed that ions increasing the oxygen vacancy concentration in TiO_2 lattice will accelerate the transformation (Shannon and Pask 1965).

Since during anatase–rutile transformation, rupture of some of the Ti–O bonds in anatase occurs to form a distorted octahedral arrangement of each tetragonal structure, which causes an increase in density, decrease in cell volume, mechanical strain and decrease in surface area leading to an overall degradation in physical properties of anatase (Gennari and Pasquevich 1999).

In the present study, the anatase–rutile transformation in presence of NiO and Fe_2O_3 has been investigated. The activation energy of transformation is also calculated. The samples were prepared by two different methods, viz. co-precipitation and wet-impregnation, in order to investigate the influence of preparation method on this transformation. The kinetics of the transformation is also studied.

2. Experimental

2.1 Materials

Samples were prepared using TiO_2 pulp (uncalcined pure hydrated TiO_2 containing 78.6% TiO_2) obtained from a TiO_2 manufacturing factory, Travancore Titanium Products Ltd. Thiruvananthapuram, India, ferric nitrate (A.R. S.D. Fine Chem. Ltd) and nickel nitrate (A.R. S.D. Fine Chem. Ltd).

2.2 Methods of preparation

2.2a Preparation of $\text{Fe}_2\text{O}_3/\text{TiO}_2$: The samples were prepared by two methods, viz. co-precipitation and wet-impregnation.

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2.2b Co-precipitation using hydrazine hydrate: 11.45 g of pure hydrous TiO_2 which contained TiO_2 (anatase) (8 g) and ammonium sulphate (160 g) were taken in a 250 ml beaker. 200 ml conc. H_2SO_4 was added and heated till a clear solution was obtained. It was then cooled and diluted to about 1 l. 5.05 g ferric nitrate dissolved in 25 ml distilled water was also added. The mixture was stirred well. Titanium and iron were then precipitated together by adding hydrazine hydrate till pH was 9. The precipitate was decanted, washed with distilled water till the washings were free from sulphate ions and filtered using Whatman No. 42 filter paper. The precipitate was dried in an oven for 3 h at 110°C , ground well, made into different portions in silica crucibles and calcined at different temperatures and time in muffle furnace.

2.2c Wet-impregnation: 11.45 g pure hydrous TiO_2 was taken in a 250 ml beaker. 5.05 g ferric nitrate dissolved in 25 ml distilled water was added to it and made into a paste by mixing thoroughly. It was then dried in an oven for 3 h at 110°C , ground well, made into different portions in silica crucibles and calcined at different temperatures and durations in a muffle furnace.

2.2d Preparation of NiO/TiO_2 : The samples were prepared by two methods viz. co-precipitation and wet-impregnation.

2.2e Co-precipitation using hydrazine hydrate: The procedure followed for the preparation was the same as given in the case of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ except that 8.1 g nickel nitrate was used in place of ferric nitrate.

2.2f Wet-impregnation: Preparation of NiO/TiO_2 was done using the same procedure as followed for $\text{Fe}_2\text{O}_3/\text{TiO}_2$ by adding 8.1 g nickel nitrate instead of ferric nitrate.

3. Chemical analysis

Chemical analysis of the samples was done as per the standard procedures available in literature (Kolthoff *et al* 1961, 1962). TiO_2 was estimated using aluminium reduction method. Fe_2O_3 was estimated by titration against potassium dichromate after reduction with stannous chloride. Nickel was estimated gravimetrically with dimethyl glyoxime after precipitating out titania using ammonium hydroxide.

4. X-ray diffraction studies

The X-ray diffraction studies were carried out by the powder diffraction technique using a Philips X-ray

Figure 1. A. XRD patterns of co-precipitated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples calcined at a. 700°C for 6 h, b. 700°C for 10 h, c. 900°C for 6 h and d. 900°C for 10 h and B. XRD patterns of wet-impregnated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples calcined at a. 700°C for 6 h, b. 700°C for 10 h, c. 900°C for 6 h and d. 900°C for 10 h.

diffractometer (PW, 1140) with $\text{CuK}\alpha$ radiation with a wavelength of $1.5418 \text{ \AA}$.

X-ray diffraction of all the samples calcined at different temperatures and durations were done. In order to study the kinetics of anatase to rutile transformation,

the percentage of rutile formed was calculated in each sample and the 'd' values were compared with the standard ASTM values.

For calculating percentage of rutile formed, the following equation was used (Gennari and Pasquevich 1998)

$$\text{Percentage of rutile} = 100/1 + 1.26 I_R/I_A,$$

where I_A and I_R are the peak intensities of [101] and [110] planes of anatase and rutile, respectively.

Table 1a. Rutile % formed on calcination of co-precipitated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples at different temperatures and time.

Temperature (°C)	Time of heating (h)	Rutile (%)
700	6	39.3
700	8	60.7
700	10	61.3
800	6	64.3
800	8	75.5
800	10	76.8
900	6	89.2
900	8	92.7
900	10	98.7

Table 1b. Rutile % formed on calcination of wet-impregnated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples at different temperatures and time.

Temperature (°C)	Time of heating (h)	Rutile (%)
750	6	22.6
750	8	26.4
750	10	28.3
800	6	45.3
800	8	48.5
800	10	51.8
900	6	89.2
900	8	90.3
900	10	91.4

5. Scanning electron microscopic studies

0.1 g of sample was taken in a test tube, 10 ml of acetone was added and sonicated to disperse the particle. One drop of this solution was placed on a copper stud, dried in air, made conducting by gold (99%) sputtering and was analysed using J.S.M-5600 instrument.

6. Surface area measurement

The surface area measurements were done using a GEMINI III 2375 Surface area analyser (Micro Meritics Instrument Corporation, USA) based on standard principle (Hiemenz 1986).

7. Results and discussion

7.1 Fe_2O_3 doped TiO_2

Chemical analysis of $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples showed that the Fe_2O_3 contents were 9.10% and 10.32% in co-precipitated and wet-impregnated samples, respectively. The TiO_2 contents were 90.6 and 89.2%, respectively. The XRD patterns of the co-precipitated and wet-

Figure 2. a. Plot of $\ln ta$ against $1/T$ for co-precipitated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples and b. plot of $\ln ta$ against $1/T$ for wet-impregnated $\text{Fe}_2\text{O}_3/\text{TiO}_2$ samples.

impregnated samples are shown in figures 1A and B, respectively.

In all the samples there were peaks corresponding to anatase, rutile and pseudo brookite while no peaks were found for α -Fe₂O₃. It was obvious that Fe₂O₃ enhanced rutilation. In co-precipitated samples the enhancement was higher than that in wet-impregnated ones, since in co-precipitated samples there was uniform distribution of Fe₂O₃ as both were precipitated from a homogeneous solution.

It was found that in both the samples, rutilation increased with temperature. The conversion was different at different temperatures. In co-precipitated samples, this

conversion was higher than that in wet-impregnated ones. The rutile percentage in both the above samples at different temperatures and durations were calculated and are shown in tables 1a and b, respectively.

The activation energy for anatase–rutile transformation, calculated from the slope of the plot shown in figures 2a and b gave a value of 10.9 k.cal/mol for co-precipitated sample and 21.8 k.cal/mol for wet-impregnated samples against a reported value of 90 k.cal/mol for pure anatase (Gennari and Pasquevich 1998).

Hence Fe₂O₃ enhances rutilation by lowering activation energy. The lowering effect is higher for co-precipitated samples than that of wet-impregnated ones.

Surface area measurements showed that surface area of samples decreased sharply on calcination at 900°C for 10 h in both the samples due to rutilation as shown in table 2. The decrease was higher in co-precipitated samples because of higher rutile percentage.

Scanning electron micrographs of co-precipitated and wet-impregnated samples calcined at 900°C for 10 h are shown in figures 3a and b.

It was found that the particles were very fine and much less agglomerated in wet-impregnated samples compared

Table 2. Surface area of Fe₂O₃/TiO₂ samples prepared by co-precipitation and wet-impregnation.

Method of preparation	Surface area (m ² /g)	
	Before calcination	After calcination at 900°C/10 h
Co-precipitation	251.8	2.48
Wet-impregnation	242.93	2.53

Figure 3. a. SEM of co-precipitated Fe₂O₃/TiO₂ samples calcined at 900°C for 10 h and b. SEM of wet-impregnated Fe₂O₃/TiO₂ samples calcined at 900°C for 10 h.

Figure 4. A. XRD patterns of co-precipitated NiO/TiO_2 samples calcined at a. 700°C for 4 h, b. 700°C for 8 h, c. 800°C for 4 h and d. 800°C for 8 h and B. XRD patterns of wet-impregnated NiO/TiO_2 samples calcined at a. 750°C for 4 h, b. 750°C for 8 h, c. 900°C for 4 h and d. 900°C for 8 h.

Table 3a. Rutile % formed on calcination of co-precipitated NiO/TiO_2 samples at different temperatures and time.

Temperature (°C)	Time of heating (h)	Rutile (%)
700	4	45.6
700	6	50.1
700	8	56.3
750	4	68.4
750	6	71.2
750	8	74
800	4	89.1
800	6	91.4
800	8	92.5

Table 3b. Rutile % formed on calcination of wet-impregnated NiO/TiO_2 samples at different temperatures and time.

Temperature (°C)	Time of heating (h)	Rutile (%)
750	4	31.5
750	6	54.3
750	8	64.1
800	4	62.8
800	6	74.2
800	8	80.4
900	4	62.2
900	6	83.1
900	8	93.5

to co-precipitated ones, which could be due to lower rutile %. The particles in each sample prepared by the above two methods were different in size and shape. No individual Fe_2O_3 particles were seen in any of the micrographs. This is in agreement with XRD studies since there is no peak corresponding to Fe_2O_3 found in any of the XRD pattern.

From the above data it is clear that Fe_2O_3 enhances rutilation by lowering activation energy and the enhancement effect varies with method of preparation of samples. The changes in % of the Fe_2O_3 would change the

activation energy to different extents depending on the method of preparation. Surface area decreased sharply with rutilation. During calcination Fe_2O_3 reacts with TiO_2 to form pseudo brookite.

7.2 NiO doped TiO_2

Chemical analysis revealed that the samples of NiO doped TiO_2 prepared by co-precipitation and wet-impregnation contain 18.8% and 17.91% of NiO , respectively. The TiO_2 contents were 80.92 and 81.32%,

Figure 5. a. Plot of $\ln t_a$ against $1/T$ for co-precipitated NiO/TiO₂ samples and b. plot of $\ln t_a$ against $1/T$ for wet-impregnated NiO/TiO₂ samples.

Table 4. Surface area of NiO/TiO₂ samples prepared by co-precipitation and wet-impregnation.

Method of preparation	Surface area (m ² /g)	
	Before calcination	After calcination at 700°C/8 h
Co-precipitation	416.18	17.86
Wet-impregnation	403.1	18.27

respectively. XRD patterns of calcined samples prepared by co-precipitation and wet-impregnation are shown in figures 4a and b, respectively.

It was observed that rutilation increased with increase of temperature. In all the samples there were peaks corresponding to anatase, rutile and nickel titanate. There were no peaks for NiO. Hence NiO reacted with TiO₂ during calcination to form nickel titanate. The percentage of rutile formed in co-precipitated and wet-impregnated samples calcined at different temperatures and durations are shown in tables 3a and b, respectively.

It was found that the percentage of rutile is higher in co-precipitated samples than that of wet-impregnated ones at a given condition. It is due to lower distribution of NiO on TiO₂ compared with that in co-precipitated ones. However, the variation in rutilation was found to be higher than that reported for undoped TiO₂ (Gennari and Pasquevich 1998) which is due to the presence of NiO.

The activation energy for anatase–rutile transformation as calculated from the slope of the plot shown in figures 5a and b gave a value of 6.62 k.cal/mol for co-precipitated sample and 10.33 k.cal/mol for wet-impregnated sample against a reported value of 90 k.cal/mol for pure anatase (Gennari and Pasquevich 1998).

The lowering of activation energy is higher in co-precipitated samples as compared to that of wet-impregnated samples. It would be due to uniform distri-

bution of NiO on TiO₂ in co-precipitated samples as compared to wet-impregnated ones.

The surface area measurements shown in table 4 reveal that the surface area decreases drastically on rutilation. Here also the decrease is higher in co-precipitated samples due to higher rutilation.

Scanning electron micrographs of calcined samples prepared by co-precipitation and wet-impregnation are shown in figures 6a and b.

It was found that the particles were very fine and much less agglomerated in wet-impregnated samples as compared to co-precipitated ones. Lower rutile percentage in wet-impregnated samples could be the reason as mentioned earlier. Particles were found to be approximately similar in size and shape in each sample. No separate NiO particles could be seen in any of the micrographs. Hence it is obvious that NiO has reacted with TiO₂ on calcination. XRD studies also support these observations.

It was also found that the enhancement of rutilation by NiO is higher than that for Fe₂O₃ even though both enhance rutilation by calcination at higher temperature and durations. NiO would be increasing oxygen vacancies in TiO₂ crystal lattice to higher extents than Fe₂O₃. These oxygen vacancies are responsible for the enhancement of transformation and lowering of activation energy as reported earlier (Gennari and Pasquevich 1998).

Figure 6. a. SEM of co-precipitated NiO/TiO_2 samples calcined at 700°C for 8 h and b. wet-impregnated NiO/TiO_2 samples calcined at 700°C for 8 h.

8. Conclusions

The following conclusions can be drawn from this investigation.

Anatase–rutile transformation is enhanced by the presence of both NiO and Fe_2O_3 in the order $\text{NiO} > \text{Fe}_2\text{O}_3$. XRD analysis proved that rutilation is increased on increasing temperature and duration of calcination. Also both NiO and Fe_2O_3 react with TiO_2 during calcination to form corresponding titanates. Method of preparation has a significant influence on quantity of rutile formed during calcination, since co-precipitated samples gave higher rutile % than wet-impregnated ones at any temperature and time of calcinations. The activation energy is lowered much, on doping with Fe_2O_3 and NiO , than for pure anatase in the order $\text{NiO} > \text{Fe}_2\text{O}_3$. Surface area measurements confirmed that the surface area decreased markedly upon rutilation.

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