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Polymorphism in TiO₂ under the influence of CuO and MnO₂

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Titanium dioxide shows polymorphism on heating to a higher temperature. This transformation is strongly dependent on temperature and time of heating. Pure Titania pulp containing amorphous titania was heated at different temperatures and for different times. Above $650 \,^{\circ}$ C the anatase phase evolved and between 900-1000 $^{\circ}$ C, an anatase-rutile transformation occurred. The anatase-rutile transformation in TiO₂ in the presence of CuO and MnO₂ was investigated. The different phases of TiO₂ were determined using powder XRD. Other methods such as chemical analysis, scanning electron microscopy, surface area measurements and crystallite size calculations were used for the characterization of the samples. The transformation temperature was found to be much lowered in the presence of the above metal oxides. Also the method of preparation of metal oxide doped TiO₂ affects the polymorphism.

Key words: Calcination, Sensors, TiO₂, Transition metal oxides, X-ray methods.

Introduction

Titania has been an important gas sensing material, mainly in lamda sensor devices due to its dual response to both oxygen rich and oxygen lean atmospheres. Its stability up to 700 °C makes TiO_2 a suitable gas sensor material for harsh environments, such as the flue ducts of cars [1]. Titania is to date the most suitable photocatalyst, semiconducting material due to its high stability towards photo-corrosion and its relatively favorable band-gap energy. Numerous investigations are in progress for the improvement of the catalytic activity of TiO_2 .

TiO₂ can crystallize in different structures, rutile being the stable one. For high temperature applications of titania as a catalyst, in membranes and sensors a stable anatase phase is necessary. Therefore one of the problems in both catalytic and sensor applications of anatase-based material is its transformation to rutile, a process that depends on both temperature and time. The anatase-rutile transformation doesn't have a transition temperature because there is no phase equilibria involved [2]. Anatase transforms irreversibly and exothermally to rutile in the range 880-1200 K depending on the method of preparation of the sample. The transformation is time and temperature dependent and is also a function of the impurity concentration. Coprecipitation, ion exchange and wet-impregnation are conveniently used for preparing doped titania. The high temperature diffusion technique used to form homo-

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Fax: 91-471 2491712 E-mail: daspnm@rediffmail.com geneously doped TiO₂ easily causes the complete structural transformation of anatase to rutile modification [3]. The rate of transformation of pure anatase was found to be immeasurably slow below 885 K and extremely rapid above 1000 K. The transformation is a nucleation growth process and follows a first order rate law, with an activation energy of ~90 kcal/mol [4]. It was reported that Fe₂O₃ and NiO enhance the anataserutile transformation and the surface area decreases markedly on rutilation. There are significant changes occurring to the surface morphology of titania with rutilation. TiO₂ in the rutile state forms solid solutions with other transition metal oxides and the properties of transition metal oxides are modified by the presence of TiO₂ [5, 6].

This paper presents a study of the influence of different % of CuO and MnO_2 (5 and 15%) on the polymorphism in TiO₂. The samples were prepared by two methods namely co-precipitation using hydrazine hydrate and wet-impregnation. The samples prepared were subjected to heating at different temperatures and for various times in order to investigate the phase transformation in the presence of the above metal oxides. The heated samples were subjected to chemical analysis and characterization was done by powder XRD, scanning electron microscopy, surface area measurements and crystallite size determinations. The results obtained are summarized in this paper.

Experimental Procedure

Chemicals used

TiO₂ pulp (un-calcined pure hydrated TiO₂ containing 75% amorphous TiO₂) obtained from a TiO₂ manufac-

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turing factory, Travancore Titanium Products Ltd. Trivandrum, India, Copper nitrate (A.R. S.d.Fine. Chem. Ltd.), Manganous sulphate (A.R. S.d.Fine. Chem. Ltd.), Manganese dioxide (A.R. S.d.Fine. Chem. Ltd.) Hydrazine hydrate (L.R, S.d.Fine. Chem. Ltd.), Sulphuric acid (98%, Sd.Fine. Chem), Hydrochloric acid (35%, Merck), Ammonium sulphate (L.R, S.d.Fine. Chem).

Sample preparation

 TiO_2 sample doped with 5 and 15% CuO and MnO_2 were prepared using two methods namely co- precipitation and wet- impregnation.

Co-precipitation

5% CuO doped TiO₂ was prepared by taking 40.53 g pure hydrous TiO₂ which contained 37.9 g TiO₂ and mixing it with 758 g ammonium sulphate and 947.5 ml conc. H₂SO₄. The mixture was heated until a clear solution was obtained. It was then cooled and diluted to about one litre. 6.17 g Cu (NO₃)₂ dissolved in distilled water was added to the clear solution and mixed well. Titanium and Cu²⁺ were then precipitated together by the addition of hydrazine hydrate until the pH was ~9. The precipitate so obtained was washed with distilled water till it was free from sulphate ions. It was filtered through Whatman No.42 filter paper, dried in an oven at 110 °C for 3 hours and calcined in a muffle furnace at different temperatures and times.15% CuO doped TiO_2 was prepared as above by taking 35.29 g TiO_2 pulp, 660 g (NH₄)₂ SO₄, 825 ml conc. H₂SO₄ and 21.25 g Cu(NO₃)₂.

Other samples were prepared using the above procedure by taking the following: 5% MnO_2/TiO_2 was obtained by taking 4.12 g $MnSO_4$ and for 15% $MnO_2/$ TiO_2 13.24 g $MnSO_4$ was taken, other materials being the same as above.

Wet-impregnation

5% CuO/TiO₂ was prepared by taking 40.53 g of pure hydrous TiO₂ which contained 37.9 g TiO₂ and 6.17 g Cu(NO₃)₂ dissolved in distilled water was added to it in an agate mortar, mixed thoroughly and dried in an air oven at 110 °C. It was then calcined in a muffle furnace at different temperatures and times. 15% CuO/TiO₂ was prepared as above by taking 35.29 g TiO₂ pulp and 21.25 g Cu(NO₃)₂.

5% MnO_2 doped titania was obtained by taking 40.53 g TiO₂ pulp and 2.10 g MnO_2 and for 15% MnO_2/TiO_2 , 35.29 g TiO₂ pulp and 7 g MnO_2 were taken.

Characterization of the samples

The calcined samples were subjected to chemical analysis using standard procedures. XRD studies were carried out by the powder diffraction technique using a Philips X-ray diffractometer (PW, 1140) with Cu K-Alpha radiation with a wavelength of 1.5418 Å. The percentage of rutile formed was calculated from XRD patterns using the equation: % Rutile=1×100/1+0.794 I_A/I_R

where I_A and I_R are the peak intensities of [101] and [110] planes for anatase and rutile respectively. The 'd' values were compared with standard ASTM values.

The crystallite size of anatase was calculated using the equation crystallite size= $0.9\lambda/\beta \cos\theta$ where λ is the wave length of the X-ray used, β is the half width of the XRD peak and θ the angle of diffraction.

Activation energy calculations were done by plotting a graph between % of rutile against time at different temperatures (T). The time required for a particular rutilation ($t\alpha$) was taken from the graph at each temperature. Another graph between ln t α against 1/T was made, and from the slope of the straight line obtained, the acticvation energy was calculated:

$$\ln t\alpha = -Ea/RT + \ln [A^{-1} \int_0^\alpha d\alpha/F(\alpha)],$$

where ' α ' is the degree of rutilation, t α is the time taken to achieve a transformation degree ' α ' was used for the calculation.

Surface area measurements were done using a Gemini 2360 V4.01 surface area analyzer (Micro Meritics Instrument Corporation, USA).

Scanning electron microscopy studies were done by taking 0.1 g of sample in a test tube, 10 ml of acetone added and ultrasonically dispersed. One drop of this solution was placed on a copper stud, dried in air, made conducting by gold (99%) sputtering and analyzed using a J.S.M - 5600 instrument.

Results and Discussion

Chemical analyses of MnO_2 and CuO doped TiO_2 samples were done as per the standard procedures available in the literature. MnO_2 doped TiO_2 prepared by co-precipitation contained 4.97 and 14.87% MnO_2 and 94.89 and 84.93% TiO_2 while the wet-impregnated samples contained 4.88 and 14.91% MnO_2 and 94.87 and 84.77% TiO_2 respectively for the 5 and 15% doped samples. The CuO doped TiO_2 prepared by co-precipitation contained 4.88 and 14.92% CuO and 94.9 and 84.88% TiO_2 while the wet-impregnated samples contained 4.88 and 14.92% CuO and 94.9 and 84.88% TiO_2 while the wet-impregnated samples contained 4.91 and 14.82% CuO and 94.8 and 84.97% TiO_2 respectively.

Transformation in MnO₂ doped TiO₂

Both the presence and amount of MnO_2 influenced the percentage of anatase and rutile present in the samples. The powder X-ray diffraction patterns of calcined MnO_2 doped TiO₂ samples are shown in Fig. 1. The peak intensities of rutile (2 θ =27.48°) formed from anatase are different in samples prepared by co-precipitation and wet-impregnation. The intensities of anatase (2 θ = 25.30°) diminished while that of rutile increased with temperature, which shows the formation of rutile is Polymorphism in TiO₂ under the influence of CuO and MnO₂



Fig. 1. XRD Patterns of MnO_2 doped TiO₂ heated at different temperatures. (a) Co-precipitated 5% MnO_2/TiO_2 (700°C). (b) Co-precipitated 15% MnO_2/TiO_2 (700°C). (c) Wet-impregnated 5% MnO_2/TiO_2 (750°C). (d) Wet-impregnated 15% MnO_2/TiO_2 (750°C)

favored on heating. In samples prepared by both methods, 15% doped ones gave more rutilation compared to 5% at any particular temperature and time of heating. The onset of rutilation also depends on the method of preparation as well as the amount of MnO_2 doping.

In order to quantify the anatase-rutile transformation, XRD peak intensity ratios were used. The fraction of rutile formed at different temperatures and times of heating was calculated using the equation given above and is tabulated in Tables 1 and 2. It is found that in co-precipitated 5% MnO₂/TiO₂ the onset of rutilation is at 650 °C after 4h heating and 96.4% rutilation was found at 750 °C/10h. In co-precipitated 15% MnO₂ doped TiO₂ on heating at 700 °C for 10h, the rutile formation was almost complete (95.5%) while at 650 °C for 4h, the rutilation was 8.5%. Here the amount of MnO_2 in TiO₂ has a major influence on rutilation. The transformation in wet-impregnated MnO_2 doped TiO₂ was found to be different from that of the co-precipitated system. Here the rutilation was slow and was found to start at 800 °C. 5% doped TiO₂ gave 5.1% rutile at 800° for 4 h heating. The amount of rutile formed was 6.8% for 4 h heating in the case of the 15% MnO₂ doped sample. In the case of the undoped TiO₂ pulp at 800 and 900 °C for 8 h heating, only the anatase phase was present and no rutile was found. But at 1000 °C for 8 h heating, rutilation was complete. Hence here the anatase to rutile transformation takes

Table 1. % of rutile formed during heating of Co-precipitated MnO_2/TiO_2 at different temperatures and times

5% MnO ₂ /TiO ₂				15% MnO ₂ /TiO ₂			
Time of	Rutile formed (%)						
heating (h)	650°C	700°C	750°C	650°C	675°C	700°C	
1	1.0	12.9	28.4	2.2	14.4	26.7	
2	2.1	24.2	48.8	4.3	25.2	46.2	
3	3.2	34.0	63.3	6.5	33.5	60.6	
4	4.1	42.5	73.8	8.5	39.8	71.1	
5	5.3	50.0	81.2	10.7	44.7	78.8	
6	6.2	56.5	86.6	12.6	48.5	84.5	
7	7.1	62.1	90.4	14.5	51.5	88.6	
8	8.2	67.0	93.1	16.4	53.9	91.6	
9	9.1	71.3	95.0	18.2	56.2	93.8	
10	10.3	75.0	96.4	20.1	57.8	95.5	

Table 2. % of rutile formed during heating of Wet-impregnated MnO_2/TiO_2 at different temperatures and times

5% MnO ₂ /TiO ₂			15% MnO ₂ /TiO ₂			
Time of	Rutile formed (%)					
heating (h)	800°C	825°C	850°C	800°C	825°C	850°C
1	0	9.4	41.2	0	16.2	53.5
2	0	17.2	65.5	3.4	29.5	78.4
3	0	24.7	79.4	5.3	40.9	89.9
4	5.1	31.5	88.1	6.8	50.6	95.3
5	6.3	37.7	93.2	8.4	58.4	97.8
6	7.6	43.4	95.9	10.1	65.1	100
7	8.8	48.5	97.5	11.6	70.7	100
8	10.3	53.2	100	13.2	75.4	100
9	11.6	57.4	100	14.7	79.3	100
10	12.8	61.2	100	16.2	82.7	100

place between 900 and $1000 \,^{\circ}$ C. This clearly confirms the fact that doping of TiO₂ by MnO₂ will change the polymorphic transformation in titania and also the transformation temperature was lowered and the method of preparation of doped samples decides the percentage rutilation.

It is well known that the irreversible anatase-rutile transformation in TiO₂ occurs by a nucleation and growth process. The availability of nucleation sites may help to achieve a critical size of particles that leads to crystallization in the rutile phase. Here MnO₂ is believed to assist in the nucleation process and once nucleation is achieved, faster transformation takes place by crystal growth. The nucleation process occurs at the interface between MnO_2 and TiO_2 and the rate of the process is determined by the contact area between the two particles. As compared to wet-impregnated samples, in co-precipitated ones, the availability of MnO₂ in TiO₂ is greater and there is also a uniform distribution of MnO₂ in TiO₂ since both are precipitated from a homogeneous solution. Hence the transformation is greater in the case of co-precipitated samples.



Fig. 2. XRD Patterns of CuO doped TiO_2 heated at different temperatures. (a) Co-precipitated 5% CuO/TiO₂ (700°C). (b) Co-precipitated 15% CuO/TiO₂ (700°C). (c) Wet-impregnated 5% CuO/TiO₂ (750°C). (d) Wet-impregnated 15% CuO/TiO₂ (750°C)

Transformation in CuO doped TiO₂

The XRD patterns of calcined samples are shown in Fig. 2. Peaks from rutile appeared in the patterns of samples prepared by co-precipitation at 750 °C in 5% CuO/TiO₂ and in 15% CuO/TiO₂ at 700 °C. Wetimpregnated samples behaved differently from those co-precipitated. Here also intensities of anatase peaks decreased with temperature and those of rutile increased but the amount of rutile converted from anatase is low even though the onset transformation temperature is the same. At any particular temperature and duration, the rutilation is lower in wet-impregnated samples compared to those co-precipitated. In all the samples, 15% doped samples gave more rutile compared to 5% doped samples at a particular temperature and time of heating. Different fractions of rutile formed at different temperatures and times of heating were calculated and are given in Tables 3 and 4.

It has been reported that ions increasing the oxygen vacancy concentration in the TiO_2 lattice will accelerate the transformation where as ions with a valence higher than four which correspondingly reduce the oxygen vacancy concentration will retard it [2]. During the anatase-rutile transformation, some of the Ti-O bonds are broken to form a distorted structure, which undergoes rearrangement to form stable rutile. When CuO enters into the TiO_2 lattice, a higher temperature favours this, the bond breaking is enhanced. This may result in the rapid transformation from anatase to rutile. Also the

Table 3. % of rutile formed during heating of Co-precipitated CuO/TiO₂ at different temperatures and times

5% CuO/TiO ₂				15% CuO/TiO ₂			
Time of	Rutile formed (%)						
heating (h)	750°C	800°C	850°C	700°C	750°C	800°C	
1	1.6	9.8	25.7	0	12.8	56.2	
2	3.2	18.8	44.8	0	24.1	80.8	
3	4.7	26.8	59.1	1.5	33.8	91.6	
4	6.3	34.2	69.5	2.1	42.3	96.3	
5	7.8	40.6	77.3	2.5	49.7	97.4	
6	9.3	46.5	83.2	3.2	56.2	99.3	
7	10.7	51.7	87.5	3.9	61.8	100	
8	12.2	56.5	90.7	4.8	66.7	100	
9	13.6	60.8	93.1	7.9	71.2	100	
10	15.2	64.7	94.8	10.8	74.8	100	

Table 4. % of rutile formed during heating of Wet-impregnated CuO/TiO_2 at different temperatures and times

5% CuO/TiO ₂			15% CuO/TiO ₂				
Time of	Rutile formed (%)						
heating (h)	750°C	800°C	850°C	700°C	750°C	800°C	
1	1.0	4.1	14.9	2.2	10.8	26.8	
2	2.0	8.0	27.6	4.1	20.5	45.3	
3	2.9	11.8	38.5	6.4	29.1	59.6	
4	3.9	15.4	47.7	8.1	36.8	70.1	
5	4.9	18.9	55.5	10.2	43.6	77.9	
6	5.9	22.3	62.2	11.9	49.8	83.7	
7	6.8	25.4	67.8	13.7	55.2	87.9	
8	7.7	28.5	72.6	15.5	60.1	91.2	
9	8.7	31.5	76.7	17.3	64.4	93.4	
10	9.6	34.3	80.2	19.7	68.2	97.9	

level of rutilation depends on the amount CuO in addition to the method of preparation of doped samples. Therefore doping of TiO_2 with CuO will alter the anatase-rutile transformation in titania. Metal titanate formation was observed in the XRD patterns of MnO_2 and CuO doped TiO_2 . This indicates a reaction between the metal oxide and titania at higher temperature to form their titanates.

Activation energy for polymorphism in doped TiO₂

In MnO₂ doped TiO₂ samples, the activation energy for the transformation was calculated to be 128 kJ/mol for 5% MnO₂/TiO₂ and 109 kJ/mol for 15% MnO₂/ TiO₂ in the case of co-precipitated samples and for wet-impregnated samples 265 and 232 kJ/mol respectively for 5 and 15% MnO₂/TiO₂. In the CuO doped case the activation energy for the transformation was calculated to be 142 kJ/mol for 5% CuO/TiO₂ and 128 kJ/mol for 15% CuO/TiO₂ in the case of co-precipitated samples and for wet-impregnated samples 163 and 139 kJ/mol respectively for 5 and 15% CuO/TiO₂ against a reported value of 380 kJ/mol for undoped TiO₂ [4]. Hence it is clear that there occurs a lowering of the activation energy on doping TiO_2 with MnO_2 and CuO, which accelerates the anatase-rutile transformation. Hence doping of TiO_2 with MnO_2 or CuO causes a structural modification when heated to around 650 °C depending on the nature of the metal oxide. The lowering of the activation energy also plays a major role in the process. The extent of rutilation strongly depends on the nature of the transition metal oxide dopant and the method of preparation. The dopant concentration is also a deciding factor in the polymorphism.

Shannon and Pask [7] have verified that the transformation could equally well be expressed by a first order equation, contracting the interfacial area and nucleation/growth equations, obtaining Ea values of 619. 778 and 811 kJ/mol respectively. Czanderna et al. [8] have described the transformation using a second order rate law and reported Ea=460 kJ/mol, while Rao

Table 5. Variation of Crystallite size and surface area in undoped and MnO_2/CuO doped TiO₂ samples

Sample	Heating Temperature	Surface area (m^2/g)	Crystallite size of anatase (nm)	
	110	162.59	()	
	110	162.58	Amorphous	
	300	109.59	Amorphous	
Undoped T_1O_2	700	27.2	4.8	
	900	9.13	14.2	
	1000	2.54	Anatase absent	
Co prosinitated	110	95.87	Amorphous	
5% MnO ₂ /TiO ₂	700	7.07	10.4	
570 Mile 2/1102	750	2.26	16.5	
a	110	124.36	Amorphous	
Co-precipitated	700	6.4	9.39	
15% MIIO ₂ /11O ₂	750	1.97	17.8	
	110	90.76	Amorphous	
Wet-impregnated	800	10.37	9.77	
570 WIIO ₂ /11O ₂	850	3.42	13.4	
XX7 . 1	110	103.81	Amorphous	
Wet-impregnated	800	7.44	9.4	
1370 WillO ₂ /11O ₂	850	1.16	18.28	
a the t	110	112.3	Amorphous	
Co-precipitated	750	4.93	11.6	
5% CuO/110 ₂	850	1.34	17.76	
a the t	110	132.2	Amorphous	
Co-precipitated	750	6.09	4.33	
15% CuO/110 ₂	850	0.092	31.54	
	110	92.7	Amorphous	
Wet-impregnated	750	12.3	2.39	
5% CuO/110 ₂	850	5.7	10.7	
***	110	119.7	Amorphous	
Wet-impregnated	750	5.5	9.87	
15% CuO/ $11O_2$	850	2.77	15.3	

[4] has applied an exponential transformation rate and calculated Ea=418 kJ/mol.

Surface area and crystallite size measurements (Table 5)

The surface area of doped TiO_2 undergoes a drastic decrease on heating at higher temperatures. In case of MnO₂ doped TiO₂, at 700 °C, the 5% co-precipitated MnO_2 doped sample gave 7.07 m²/g surface area while the 15% doped sample gave a surface area 6.4 m^2/g . The amount of dopant has an influence in the changes of surface area with rutilation. 15% doped samples gave lower surface areas than 5% samples. Also samples prepared by the wet-impregnation method have somewhat higher surface areas than those co-precipitated. However the crystallite size of anatase increases with rutilation, which confirms the growth of particles with rutilation during heating. The surface area and crystallite size of MnO₂ and CuO doped TiO₂ samples along with undoped TiO_2 are shown in Table 5. CuO doped samples also show the same trend. During the anataserutile transformation, there occurs growth of particles. This reflects in a lower surface area and higher crystallite size.

The diffusion of metal oxide into the TiO_2 lattice may result in a lower surface area and a simultaneous increase in crystallite size. The distribution of metal oxide on titania is different for samples prepared by coprecipitation and wet-impregnation. Hence they behaved differently. It was observed that the catalytic activity of doped titania decreases with rutilation. The drastic decrease in surface area with rutilation may result in decreased catalytic activity.

Scanning Electron Microscopic Studies

Scanning electron micrographs of MnO_2 and CuO/TiO_2 before and after rutilation are shown in Figs. 3 and 4. It is seen from the micrographs that in MnO_2 doped TiO₂ before heating, when the anatase phase is present, the surface is somewhat rough and there is a distribution of MnO_2 on the surface of TiO₂ as evident from Fig. 3. The particle surface becomes smooth during heating in the presence of MnO_2 . Also the particle size increased correspondingly with rutilation. The reaction between MnO_2 and TiO₂ during heating to form their corresponding titanates is also confirmed since there is no free MnO_2 on the surface after rutilation. XRD studies also confirm this observation.

In the case of CuO doped TiO₂, there is not much change in the morphology of TiO₂ but the particles are separated as individual ones and some changes in size and shape are observed. These changes may occur due to rutile formation when calcination is carried out. The crystallites seem to expand prior to the transformation to rutile. Therefore it is clear that CuO has some role in deciding the shape of particles. Hence it is evident that the surface morphology of TiO₂ changes with rutilation



15kU ×160 100 mm 5186 RRL SEM (b)

Fig. 3. Scanning Electron Micrographs of MnO_2 doped TiO₂. (a) Before rutilation. (b) After rutilation

in the presence of transition metal oxides and the changes strongly depend on the nature of transition metal oxide doped.

Conclusions

The phase transformation temperature of TiO_2 is affected by the presence of MnO_2 and CuO. The anatase to rutile transformation temperature decreased greatly in the presence of CuO and MnO_2 . The percentage of rutile formed strongly depends on the amount of MnO_2 and CuO present in TiO_2 . The method of preparation of samples plays a major role in deciding the anatase-rutile conversion. The activation energy for the transformation was found to be lowered substantially on doping with MnO_2 and CuO. Also the crystallite size of anatase increased and the surface area decreased sharply with rutilation. The surface morphology of TiO_2 changed by doping with MnO_2 and CuO as well as with rutilation.

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Fig. 4. Scanning Electron Micrographs of CuO doped TiO_2 . (a) Before rutilation. (b) After rutilation

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