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Rutilation in nickel oxide-doped titania prepared by different methods

S. Riyas [a], G. Krishnan [b], P.N. Mohan Das [a,*]

[a] *Regional Research Laboratory (CSIR), Trivandrum 695 019, India*
[b] *Department of Chemistry, University College, Trivandrum, India*

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Abstract

Titanium dioxide shows polymorphism on heating at high temperature. This strongly depends on temperature and duration of heating. When amorphous titania pulp was heated at different temperatures and time between 900 and 1000 °C, anatase–rutile transformation occurred. This transformation under the influence of different percentages of NiO was studied by preparing samples by two different methods. The transformation temperature was found to be lowered in the presence of the above metal oxide. Also the method of preparation of metal oxide-doped TiO_2 affects the polymorphism. The different phases of TiO_2 were determined using powder XRD. Other methods such as chemical analysis, scanning electron microscopy, surface area measurements and crystallite size calculation were used for the characterization of the samples.

Keywords: Anatase; Rutile; Co-precipitation; Wet-impregnation

1. Introduction

Nanocrystalline solids, which occur as polymorphs of low density, can be expected to transform to a dense polymorphic form at high pressures and temperatures [1]. On heating, amorphous titania transforms to nanocrystalline titania with the desired properties [2]. Quantitative analysis of the transformation kinetics of amorphous titania to anatase has been attempted only in liquid media under hydrothermal conditions or for titania films. Thermal hydrolysis is used to prepare high surface area anatase from titanyl sulphate solution [3]. Both dry and hydrothermal heat treatments of sol–gel amorphous titania have been used to produce nanocrystalline titania [4]. Titania is to date the most suitable photo catalyst semiconducting material due to its high stability towards photo corrosion and its relatively favourable band-gap energy. Numerous investigations are in progress for the improvement of the catalytic activity of TiO_2.

TiO_2 crystallizes in the metastable anatase and brookite besides the stable rutile structure. The rutile form of TiO_2 is the most stable and both anatase and brookite transform to rutile on heating. The anatase–rutile transformation does not have a transition temperature because there is no phase equilibria involved [4]. 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.

Co-precipitation, ion-exchange, and wet-impregnation are conveniently used for preparing doped titania. The high temperature diffusion technique used to form homogeneously doped TiO_2, easily causes the complete structural transformation of anatase to rutile modification [5]. 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 the first-order rate law, with activation energy of ~90 kcal/mol. It was reported that Fe_2O_3 and NiO enhance the anatase–rutile transformation and the surface area decreases markedly on rutilation. There are significant changes occurring to the surface morphology of titania with

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* Corresponding author. Tel.: +91 471 515250; fax: +91 471 491712.
E-mail address: daspnm@rediffmail.com (P.N. Mohan Das).

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rutilation [6]. The effect of Cr_2O_3 doping on anatase–rutile transformation in TiO_2 was also reported earlier. The activation energy for the transformation was much lowered in presence of Cr_2O_3 [7]. TiO_2 in the rutile modification forms solid solutions with other transition metal oxides and the properties of transition metal oxides are modified by the presence of TiO_2.

The effect of doping TiO_2 with different percentages of NiO (5 and 15%) on the anatase–rutile transformation has been studied. The doped 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 time in order to investigate the phase transformation in the presence of the above metal oxide. The heated samples were subjected to chemical analysis and characterized by powder XRD, scanning electron microscopy, surface area measurements and crystallite size determinations. The results obtained are discussed in this paper.

2. Experimental

2.1. Chemicals used

TiO_2 pulp (uncalcined pure hydrated TiO_2 containing 75% TiO_2) was obtained from a TiO_2 manufacturing factory, Travancore Titanium Products Ltd. Trivandrum, India. Nickel nitrate, hydrazine hydrate, sulphuric acid, hydrochloric acid, and ammonium sulphate of AR grade were used.

2.2. Sample preparation

TiO_2 doped with 5 and 15% NiO was prepared using two methods namely co-precipitation and wet-impregnation.

2.2.1. Co-precipitation

5% NiO/TiO_2 was prepared by taking 40.53 g of pure hydrous TiO_2, which contained 37.9 g TiO_2 and mixing with 758 g ammonium sulphate and 947.5 ml conc. H_2SO_4. The mixture was heated until a clear solution was obtained. It was then cooled and diluted to about 1 l. Nickel nitrate (4.95 g) dissolved in distilled water was added to the clear solution and mixed well. Titanium and Ni^{2+} 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 h, and calcined in a muffle furnace at different temperatures and time. 15% NiO/TiO_2 was prepared as above by taking 35.29 g TiO_2 pulp, 660 g $(NH_4)_2SO_4$, 825 ml conc. H_2SO_4, and 27.2 g $Ni(NO_3)_2$.

2.2.2. Wet-impregnation

5% NiO/TiO_2 was prepared by taking 40.53 g of pure hydrous TiO_2, which contained 37.9 g TiO_2 in an agate mortar and 4.95 g nickel nitrate dissolved in distilled water was added to it, mixed thoroughly and dried in an air oven at 110 °C. It was then calcined in a muffle furnace at different temperatures and time. 15% NiO/TiO_2 was prepared as above by taking 35.29 g TiO_2 pulp and 27.2 g $Ni(NO_3)_2$.

2.3. Characterization of the samples

The calcined samples were subjected to chemical analysis using standard procedures [8,9]. XRD studies were carried out by the powder diffraction technique using a Philips X-ray diffractometer (PW, 1140) with Cu Kα radiation with a wavelength of 1.5418 Å. The percentage of rutile formed was calculated from XRD patterns using the equation [10]:

$$\text{Rutile}\,(\%) = (1 \times 100/(1 + 0.794))(I_A/I_R)$$

where I_A and I_R are the peak intensities of [1 0 1] and [1 1 0] 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 wavelength of the X-ray used; β, half width of XRD peak; and θ, angle of diffraction.

Surface area measurements were done using Surface area analyzer (GEMINI III 2375 Micro Meritics Instrument Corporation, USA) based on standard principle.

Scanning electron microscopy studies were done using Scanning Electron Microscope (JEOL J.S.M.-5600 instrument). One gram 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 analyzed.

3. Results and discussion

Chemical composition of samples of both 5 and 15% NiO/TiO_2 was established as 4.88 and 14.72% NiO and 94.7 and 84.8% TiO_2, respectively, in co-precipitated samples and 4.79 and 14.78% NiO and 94.8 and 84.9% TiO_2, respectively, in wet-impregnated samples. The evolution of the phase transformation in NiO/TiO_2 was analyzed using X-ray diffraction. When NiO/TiO_2 samples were heated in air, the diffraction patterns of anatase gradually diminished in intensity and was finally displaced by the characteristic rutile pattern. XRD Patterns of NiO-doped TiO_2 heated at different temperatures and time are shown in Figs. 1 and 2.

The extent of anatase–rutile transformation was calculated using the equation mentioned earlier. It is found that in co-precipitated 5% NiO/TiO_2 the onset of rutilation is observed at 700 °C for 8 h heating and 94.7% rutilation was found at 850 °C/8 h. The transformation changes with the method of preparation of NiO-doped TiO_2. In co-precipitated 15% NiO-doped TiO_2 on heating at 700 °C for 8 h, the

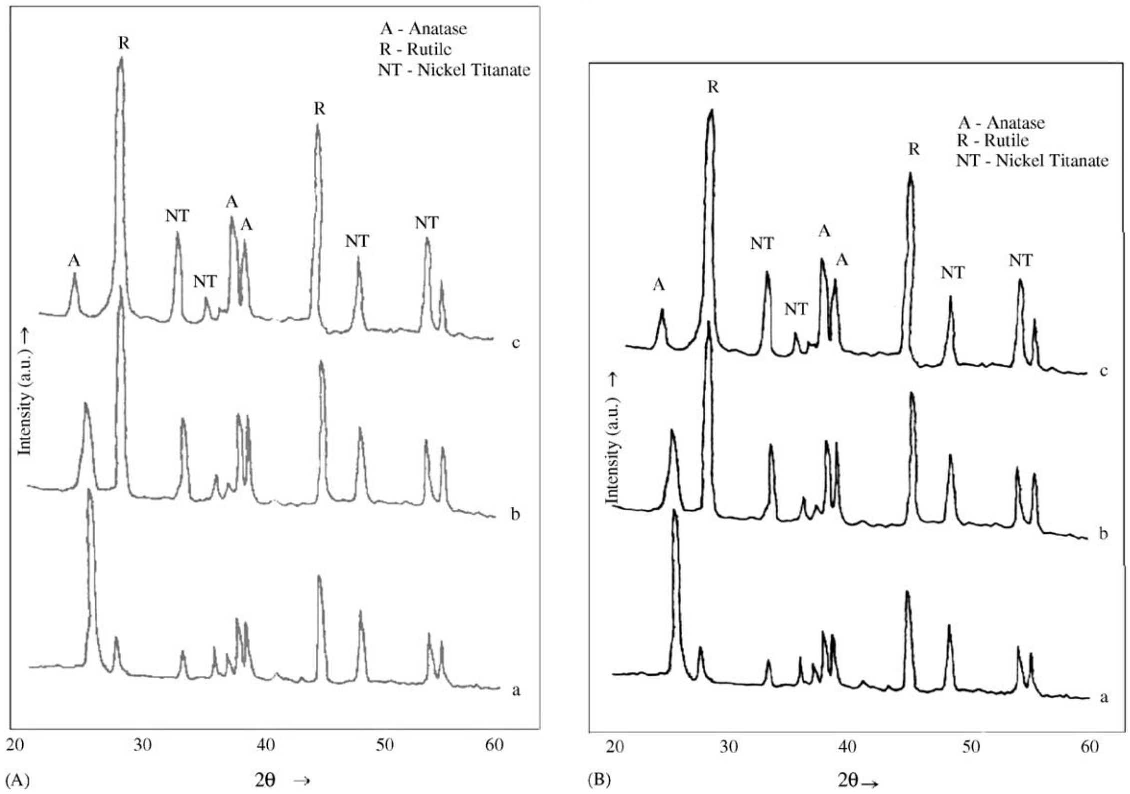

Fig. 1. XRD patterns of co-precipitated NiO-doped TiO_2 heated for 6 h at: (a) 700 °C; (b) 800 °C; and (c) 850 °C (A: 5% and B: 15%).

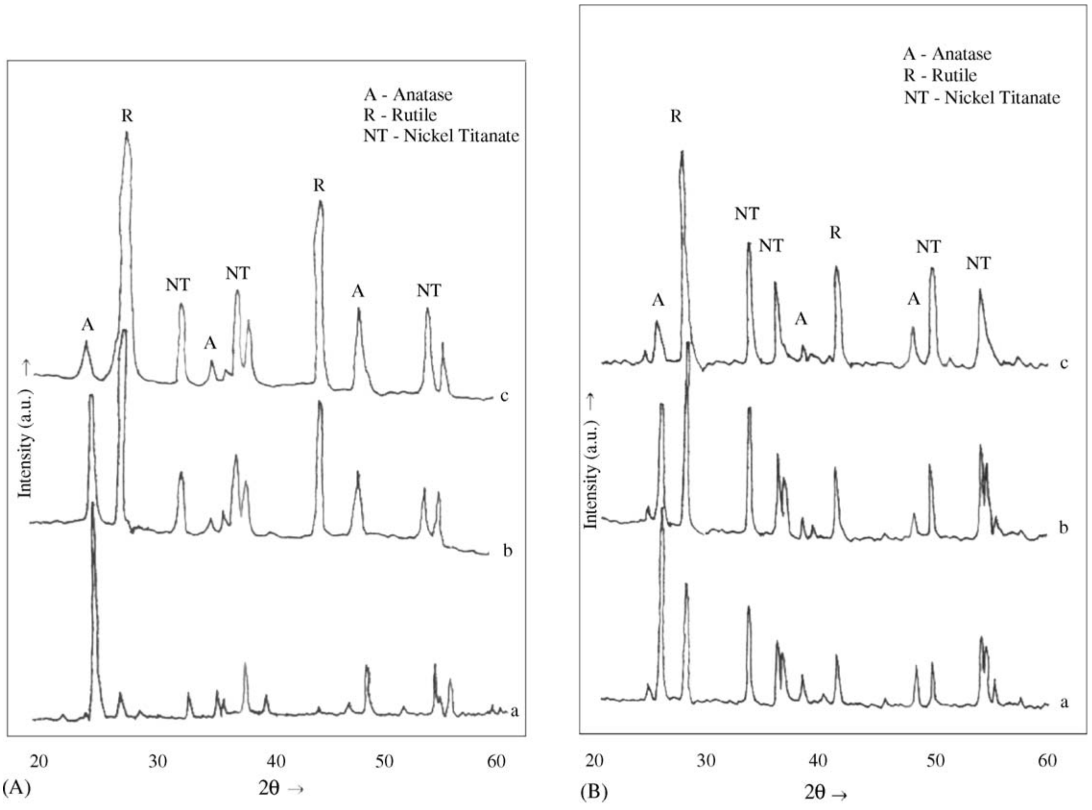

Fig. 2. XRD patterns of wet-impregnated NiO-doped TiO_2 heated for 6 h at: (a) 850 °C; (b) 875 °C; and (c) 900 °C (A: 5% and B: 15%).

Table 1
Percentage of rutile formed during heating of co-precipitated NiO/TiO_2 at different temperatures and time

Time of heating (h)	Rutile formed (%)					
	5% NiO/TiO_2			15% NiO/TiO_2		
	700 °C	800 °C	850 °C	700 °C	750 °C	800 °C
1	0	13.2	30.8	1.2	26.8	52.5
2	1.6	26.9	52.2	2.5	31.9	61.3
3	2.4	35.4	66.9	3.7	38.0	72.4
4	3.2	39.8	77.1	4.9	42.7	80.6
5	4.1	44.1	84.2	6.2	45.4	84.6
6	4.9	46.8	89.1	7.4	48.8	90.2
7	5.6	49.7	92.4	8.5	53.0	97.6
8	6.4	51.9	94.7	9.7	54.1	99.9
9	7.2	54.7	96.4	10.8	55.4	100
10	8.1	62.4	97.5	12.3	61.6	100

rutile formation was 9.7% while at 800 °C for 7 h, rutilation is complete (Table 1). The transformation in wet-impregnated NiO-doped TiO_2 was found to be different from that of co-precipitated system. Here rutilation was slow and found to start at 850 °C/8 h in 5% NiO-doped TiO_2 sample. The amount of rutile formed was 54.7% for 8 h heating in the case of 15% doped sample. (Table 2) To analyse the effect of Ni^{2+} on the anatase–rutile transformation, the transformation in the case of undoped TiO_2 pulp must be known. At 800 and 900 °C for 8 h heating, only anatase phase is present and no rutile was found in undoped TiO_2 pulp. But at 1000 °C for 8 h heating, rutilation was found to be complete. Hence, here anatase to rutile transformation takes place between 900 and 1000 °C. Therefore, it is clear that NiO enhances the crystallographic rearrangement in TiO_2.

It is believed that Ni^{2+} introduces oxygen vacancies due to its dissolution in the anatase lattice initially at the surface of titania. Then as temperature increases migration of it into the bulk occurs. The mobility of the vacancies should favour the rutile nucleation in both the surface and the bulk of anatase particles. The conversion is different in different samples. In co-precipitated samples, the conversion occurs at lower temperature than in the wet-impregnated.

Table 2
Percentage of rutile formed during heating of wet-impregnated NiO/TiO_2 at different temperatures and time

Time of heating (h)	Rutile formed (%)					
	5% NiO/TiO_2			15% NiO/TiO_2		
	850 °C	875 °C	900 °C	850 °C	875 °C	900 °C
1	1.7	9.2	22.6	9.4	16.3	43.6
2	3.3	17.6	40.1	17.9	29.9	68.2
3	4.8	25.3	53.7	25.7	41.4	82.1
4	6.6	32.2	64.2	32.7	50.9	89.9
5	8.2	38.5	72.3	39.1	59.2	94.3
6	9.8	44.2	78.6	44.8	65.7	96.8
7	11.3	49.3	83.4	50.3	71.3	98.1
8	12.8	54.2	87.1	54.7	75.9	100
9	14.3	58.3	90.1	58.9	79.9	100
10	15.7	62.1	92.3	62.8	83.1	100

Nucleation of rutile starts with in the interface between two contacting NiO and TiO_2 and the nucleation rate is determined by the probability of contact between the two. The lower distribution of NiO with TiO_2 in wet-impregnated samples slows down the transformation temperature. In the case of co-precipitated samples, there is uniform distribution of NiO on TiO_2 since both are precipitated from homogeneous solution.

Anatase–rutile transformation is found to increase with the amount of NiO, since nucleation process is determined by the contact between NiO and TiO_2. As the concentration of NiO increases, the probability of contact between the two increases, which increases the transformation rate. Also the oxygen vacancies are created more rapidly with higher NiO percentage. In samples heated above 700 °C there are peaks for nickel titanate and no peak for NiO, which shows that on heating at higher temperature NiO reacts with TiO_2 to form titanate.

Another factor for the enhanced transformation is the activation energy for the transformation. It was calculated to be 44.4 kcal/mol for 5% NiO/TiO_2 and 36.6 kcal/mol for 15% NiO/TiO_2 in the case of co-precipitated samples and for wet-impregnated ones 68.3 and 59.4 kcal/mol, respectively, for 5 and 15% NiO/TiO_2 against a reported value of 90 kcal/mol for undoped TiO_2 [11]. From the above it is evident that NiO enhances rutilation in TiO_2 by lowering the activation energy and the accelerating effect depends on the method of preparation of doped sample as well as the concentration of dopents.

The surface area of NiO-doped TiO_2 undergoes drastic decrease on heating at higher temperatures as evident from Table 3. The crystallite size increases with rutilation. The changes in surface area and crystallite size are higher for co-precipitated samples than for the wet-impregnated ones. It is due to rutilation during heating. Rutilation is accompanied by enlargement of particle, which resulted in lower surface

Table 3
Variation of crystallite size and surface area in undoped and NiO-doped TiO_2 samples

Sample	Heating temperature (°C)	Surface area (m^2/g)	Crystallite size of anatase (nm)
Undoped TiO_2	110	162.58	Amorphous
	300°/6 h	109.59	Amorphous
Co-precipitated 5% NiO/TiO_2	110	137.7	Amorphous
	700	13.8	9.4
	850	6.8	27.7
Co-precipitated 15% NiO/TiO_2	110	192.7	Amorphous
	700	11.2	11.8
	800	1.9	31.6
Wet-impregnated 5% NiO/TiO_2	110	103.5	Amorphous
	850	17.7	13.9
	900	9.2	19.3
Wet-impregnated 15% NiO/TiO_2	110	125.2	Amorphous
	850	13.8	17.3
	900	6.2	22.1

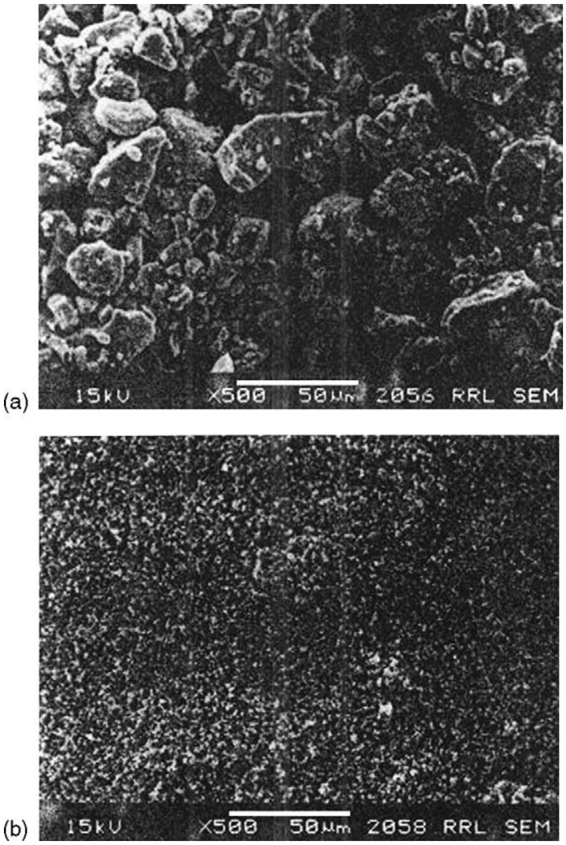

Fig. 3. SE micrographs of NiO-doped TiO_2 before calcinations: (a) co-precipitated and (b) wet-impregnated.

area and higher crystallite size. It was observed that the catalytic activity of doped titania decreases with rutilation. It may be due to the drastic decrease in surface area with rutilation.

To understand the morphological changes scanning electron micrographs of NiO-doped TiO_2 before and after rutilation were analyzed. Here, titania particles are found to be aggregated in the pure form (anatase). On heating some rearrangement occurs to form rutile. During this conversion, the aggregates of particles would be converted into agglomerates where the particles are rigidly joined. The surface of both anatase and rutile samples were found to be rough before doping NiO. SE micrographs of NiO-doped TiO_2 prepared through different methods before and after heat treatment are shown in Figs. 3 and 4.

It is seen from the micrographs that in co-precipitated NiO-doped TiO_2, the particle becomes fine and the surface becomes cloudy during heating. This is due to rutilation during heating in the presence of NiO. While in wet-impregnated NiO-doped TiO_2, there is not much change during the heating. Hence, it is clear that in wet-impregnated samples rutilation does not occur during the heating. XRD studies also support this observation. It may be due to the difference in distribution of NiO on TiO_2. In co-precipitated samples there is uniform distribution of NiO on TiO_2, since both are precipitated from a uniform solution.

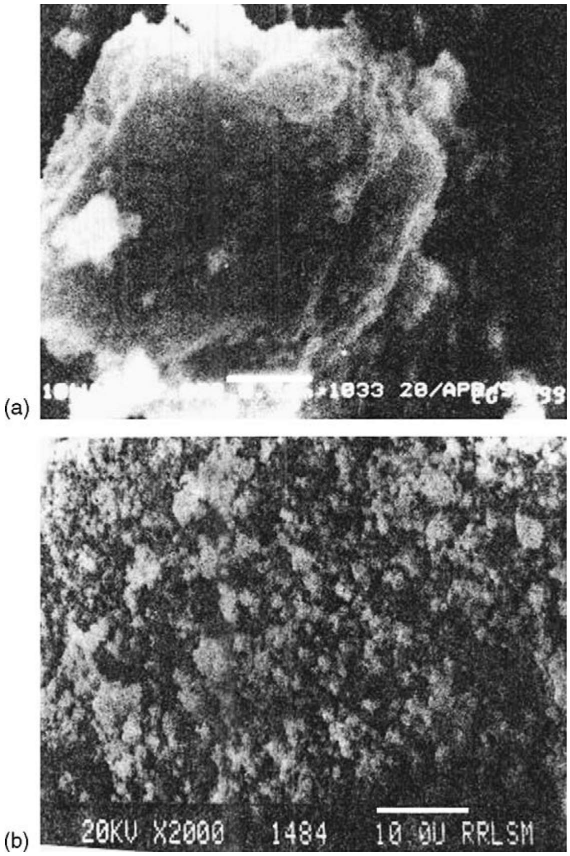

Fig. 4. SE micrographs of NiO-doped TiO_2 after heating: (a) co-precipitated and (b) wet-impregnated.

Hence, it is evident that the surface morphology of TiO_2 changes upon rutilation under the influence of NiO. This is supported by surface area and crystallite size measurements.

4. Conclusions

From the above studies it can be concluded that:

1. On heating at higher temperature TiO_2 undergoes anatase to rutile transformation;
2. Anatase to rutile transformation temperature is decreased in presence of NiO;
3. Rutilation depends on the quantities of NiO and the method of preparation of NiO-doped TiO_2 samples;
4. The surface area decreases on rutilation;
5. The surface morphology of TiO_2 changes with rutilation.

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