

Effect of doping on the phase transformation in TiO₂ - A Review

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Abstract : Titanium dioxide has tremendous applications in different fields like photocatalyst for water and air purification, gas sensor, polymer industry and many more. Particular application of TiO₂ depends on its specific phase. The commonly occurring phases of TiO₂ are anatase, rutile and brookite. There have been extensively study on the transformation from metastable anatase to rutile depending upon verities of factors like dopants, particle size, synthesis conditions etc. In the present review paper the role of doping on the anatase to rutile phase transformation is discussed. Several authors have demonstrated that the dopants like Mn, Ni, Co, Sn, Fe, Nb, Y, Zn and Cr accelerate the transformation while Al, Si, Zr, Ce, Au, Nb and W retard. The underlying mechanism for this dopant induced transformation however is still not clear. The present review paper thus addresses such issues as the oxygen vacancies, lattice strain, co-ordination number etc. of induced by dopants in the phase transformation process.

Keywords: anatase, rutile, phase transformation, dopants

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1. Introduction

In the thousands of titanium compounds, titanium dioxide (TiO₂) has been extensively studied and used in different fields. Titanium dioxide occurs in nature as well-known minerals rutile (tetragonal), anatase (tetragonal) and brookite (rhombohedral), and additionally as two high pressure forms, a monoclinic baddeleyite-like form and an orthorhombic α -PbO₂-like form, both found recently at the Ries crater in Bravia [1-4]. The most common form is rutile, which is also the equilibrium phase at all temperatures. The metastable anatase and brookite phases both convert to rutile upon heating [5, 6].

Titanium dioxide has some important properties like optical (high refractive index), electrical, corrosion resistance, non-toxicity, and chemical inertness in the presence of Acid and basic environment [7-9]. Owing to these properties, TiO_2 has potential applications in photocatalysis, gas sensor, and polymer industry as a white pigment [2, 10-12]. Another interesting application of TiO_2 is its use for destruction of inorganic and organic pollutants present in water [13].

Among the different polymorphs of TiO_2 , the two most common and important phases are anatase and rutile. Most commercially available titanium dioxide powders are either one of these two phases or a mixture of the two. Since the properties like optical and electrical of anatase and rutile are different, it is desirable to be able to control the phase content by understanding the transformation mechanism, as each phase has specific applications. Hence the anatase-to-rutile phase transformation in TiO_2 is an area of both scientific and technological interest. Researchers have attempted to understand and control the anatase–rutile transformation [14-17].

The anatase phase is commonly observed at temperatures in the range of 350–700°C, while higher temperatures promote the growth of the rutile phase. The anatase to rutile transformation (ART) has been proved to depend on many conditions, such as impurity content, particle shape and size, annealing temperature and time, reaction atmosphere, starting phase and reaction conditions [18-22]. According to Tian et al., [23], when ion dopants are used, the transformation depends on the type of dopants, its concentration, distribution, oxidation state, and chemical environment.

In the present review, the effect of impurities in anatase to rutile (A-R) phase transformation is discussed along with the mechanisms. Moreover the role of particle size and synthesis conditions on A-R phase transformation is also briefly outlined.

2. Factors Affecting the Phase Transformations

2.1 Effect of impurities

Table 1 shows some important properties of anatase, rutile and brookite phase of TiO_2 . Doping in TiO_2 changes its different properties, like optical, electrical, magnetic, photocatalytic, electronic and mechanical [24-26]. When dopants are added to TiO_2 , they either substitute at the Ti^{4+} sites or are located in interstitial position of the lattice. When the ionic radius of the doped ion is similar to the radius of the Ti^{4+} (0.745 Å), then there is most likely substitution of the dopant at Ti^{4+} sites within TiO_2 . This substitution occurs in case of

Pt⁴⁺ (0.765 Å), Cr³⁺ (0.755 Å) and V³⁺ (0.78 Å), whereas some other metal dopants such as Co²⁺, Cu²⁺ and Pt²⁺ ions are possibly located in interstitial positions of the lattice rather than directly in Ti⁴⁺ sites because of the relatively large size difference between dopant ions (Co²⁺:0.89 Å, Cu²⁺: 0.87 Å and Pt²⁺:0.94 Å) and Ti⁴⁺ [2,25].

Table 1. Some important properties of TiO₂

Properties	anatase	rutile	brookite
Crystal structure	tetragonal	tetragonal	orthorhombic
Lattice constant (Å ⁰)	$a = 3.784$ $c = 9.515$	$a = 4.5936$ $c = 2.9587$	$a = 9.184, b = 5.447$ $c = 5.154$
Space group	I41/amd	P42/mnm	Pbca
Density (g/cm ³)	3.79	4.13	3.99
Refractive index	2.488	2.609	2.583
Energy Gap (eV)	3.2	3.0	3.14

2.1.1 Impurities accelerating the phase transformation

Arroyo et al., [27] reported that at low dopant concentrations, Mn ions are incorporated in the TiO₂ structure, and the anatase phase is stabilized. At larger concentration however, part of the dopant segregates to the surface of TiO₂ and rutile formation is accelerated, and this results are in accordance with Xu et al., [28]. Li and Jena [29] studied the effect of Ni and Co doping on the phase transformation in TiO₂ and reported that the increased interaction between Co and Ni atoms accelerate the A-R phase transformation rather than their high spin. Moreover the role of Co doping was studied by Tian et al., [23] and according to them Co contents increases the anatase to rutile (A-R) phase transformation of TiO₂ by creating oxygen vacancies.

Song et al., [30] found that the dopant ions like Mn²⁺, Sn⁴⁺, Fe³⁺ and Zn²⁺ ions promote the A-R transformation. They concluded that the influence of metal ion doping on the A-R transformation of the TiO₂ thin layers on muscovite depends on the substitution of foreign ions for Ti⁴⁺ ions in TiO₂ thin layers. Tian et al., [31] reported that Cr³⁺ can effectively promote the formation of oxygen vacancy which influences the A-R transformation. Chao et al., [32] and Serrano

et al., [33] reported that the Ag doping promotes the phase transformation but has a depression effect on the anatase grain growth. According to Othman et al., [34] the increased concentration of Fe promotes phase transformation, but decreases the size of the nanoparticle product.

Yuan and Zhang [35] co-doped Zn and Fe with TiO₂ and observed that this co-doping enhanced the A-R transformation by reducing ART temperature as well as width of the phase transformation temperature widens. Wang et al., [36] prepared Nb and Y doped TiO₂ films by magnetron sputtering method and observed that this co-doping favors the anatase to rutile transformation.

2.1.2 Impurities retarding the phase transformation

Debeila et al., [37] reported the retardation effect of gold on anatase to rutile phase transformation in TiO₂. They observed that this gold is bound mostly on the surface of TiO₂ hence retards the transformation. Ahmad et al., [38] reported that the higher concentration of Nb helps to stabilize the anatase phase. Shi et al., [39] reported that A-R phase transformation temperature increases with increase in Sn²⁺ content.

Yang et al., [40] took ZrO₂ additive with TiO₂ and found that ZrO₂ additive retards the A-R transformation by increasing the strain energy of TiO₂ particles. Xiao et al., [41] prepared Ce doped TiO₂ nanoparticles by hydrothermal process and observed that this doping inhibited the anatase to rutile transformation.

Reidy et al., [42] found that doping with Si, Zr, Al and tertiary mixtures of these produced an elevated ART temperature and they explained that this higher ART temperature is primarily due to the presence of dopant strain fields, which limit mass transport in the system.

Moreover the retardation of the anatase–rutile transformation can be achieved with the following impurities: Al, Si, Mo, Nb and W [2]. Among those dopants, Al-doping in TiO₂ shows retardation of phase transformation from anatase to rutile by stabilizing the surface state of TiO₂ particles and also inhibits grain growth.

2.2 Particle size

The effect of average crystallite size on A-R transformation was studied by many authors. Based on these studies it is now established that a critical size plays an important role in A-R phase transformation. Thus A-R phase transformation will not begin with heating until the critical size is reached [43-

46]. Moreover Zhang and Banfield [18] reported that the rutile phase becomes more stable than anatase for particle sizes greater than 14 nm.

2.3 Synthesis conditions

It is studied that the synthesis conditions like chemicals, peptizing agents etc. affect the phase transformation temperature [47, 48]. Ahonen et al., [49] observed that A-R transformation in air is 973 K, whereas this transformation temperature increases to 1173 K in nitrogen atmosphere.

3. Mechanism of Phase Transformation

The generally accepted theory of the phase transformation is that two Ti-O bonds break in the anatase structure, allowing rearrangement of the Ti-O octahedra, which leads to a smaller volume consequently the rutile phase emerges. The breaking of these bonds is accelerated by lattice disruptions, which can be introduced in a number of ways, such as addition of dopants, variation in the atmosphere (oxygen partial pressure), annealing conditions, and method of synthesis.

It is established that the mechanism for phase transformation of titania is a process of nucleation and growth [46, 50]. Anatase nanocrystals coarsen, grow, and then transform to rutile only when a critical size is reached [18, 46, 51, 52]. It was reported that the smaller the grain sizes, the larger is the lattice deformation. The large lattice deformation facilitates the nucleation process, which lowers the transformation temperature. Moreover as particle size decreases, the surface tension and hydrostatic-like pressures would potentially reduce the strain energy, reducing one of the barriers to transformation in the nanoparticles.

In case of doped TiO₂, some dopant ions reduce mass transport in the system, thereby preventing the materials reaching the critical particle size. Some of these doped materials require higher temperatures compared to undoped materials for the phase transformation. On the other hand other dopant ions, which create oxygen vacancies, accelerate the anatase to rutile phase transformation. Shannon and Pask [53] suggested that processes that increase oxygen vacancies such as the addition of ions of valence less than four and of small ionic radius which can enter the structure via direct substitution, accelerate the A-R phase transformation. Moreover they proposed that an increase of oxygen vacancy concentration reduces the strain energy that must overcome before the rearrangement of Ti-O octahedra occurs. In this aspect monovalent ions are more effective than divalent or trivalent ions for phase transformation

due to creation of more oxygen vacancies. Moreover, both heat treatment and reducing atmosphere increase the concentration of oxygen vacancies which facilitate the Ti-O bond rupture and Ti^{3+} formation in TiO_2 . Ti^{3+} formation hinders ionic movement and hence imposes further constraints on diffusion. Therefore, phase transformation is dominated by effects such as defect concentration [18] and grain boundary concentration [54]. Several kinetic models were used to explain the transformation mechanisms and are represented in Table 2. Each kinetic model is related only to the specific transformation mechanism.

Table 2. kinetic models explaining anatase to rutile phase transformation.

Model	Equation	References
Standard 1st order	$\ln(1-\alpha) = -kt$	[55, 44]
Standard 2nd order	$\frac{1}{(1-\alpha)} - 1 = kt$	[56]
Contracting spherical interface	$(1-\alpha)^{1/3} - 1 = kt$	[53, 57]
Nucleation and growth of overlapping nuclei	$[-\ln(1-\alpha)]^{1/3} = kt$	[53]
One dimensional, linear, branching nuclei and a constant growth	$\ln \alpha = kt + \text{constant}$	[53]
Random nucleation and rapid growth	$\ln(1-\alpha) = kt$	[53]
Where α =fraction of transformation, k =kinetic constant, t =time, b = a constant, n = a parameter relevant to transformation mechanism.		

4. Conclusions

Among the different polymorphous of TiO_2 , anatase and rutile are two important phases regarding the application point of view. Anatase and rutile have different structures, properties and applications. The impact of impurity, particle size and synthesis condition in A-R phase transformation were discussed. Impurities like Mn, Ni, Co, Sn, Fe Zn and Cr accelerate the A-R phase transformation, while Al, Si, Zr, Au, Nb and W retard the transformation. The mechanisms proposed in the literature for A-R transformation influenced by the

dopant ions are discussed. It is shown that the impurities creating oxygen vacancies accelerate the phase transformation on the other hand the impurities present at the interstitial retard the transformation by reducing the mass transport in the crystal. Transformation from anatase to rutile is favorable only when a critical particle size is reached.

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