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TEMPERATURES AND KINETICS OF ANATASE TO RUTILE TRANSFORMATION IN DOPED TiO_2 HEATED IN MICROWAVE FIELD

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Abstract

The influence of aliovalent ions such as Mn, Cr, Fe, Mo, and V on the temperature and kinetics of anatase to rutile phase transformation in TiO_2 heated in microwave field was studied in this work. The results indicated that heat treatment method and dopants considerably affected the anatase-to-rutile phase transition temperature and kinetics of transformation. The activation energy for anatase to rutile transformation of TiO_2 derived from the isothermal data was found to be 328.4 kJ mol^{-1}, which was considerably reduced by the addition of dopants in TiO_2 matrix. The activation energy for Mo, Mn and V doped samples was 252.0, 101.3 and 96.4 kJ mol^{-1}, respectively.

Keywords: activation energy, anatase – rutile phase transformation, microwave processing, TiO_2

Introduction

The irreversible anatase to rutile transformation provides a model example of the phase change in solid-state, which can be studied using simple technique like X-ray diffraction. The kinetics of this transformation has been studied extensively by different investigators and the rate dependent parameters were derived employing different kinetic models [1–7]. The rate of this transformation is, however, dependent on the method of synthesis of TiO_2, its anionic/cationic impurity contents and the reaction atmosphere [5, 8–15]. Among the cations, those, which introduce anion vacancies in the TiO_2 lattice, have been found to increase the rate, with the exception of Al. The additives, which produce titanium interstitials, were found to reduce the rate of transformation [10].

In the present paper, we have investigated the role of mode of heating on anatase to rutile transformation temperature in undoped as well as the samples doped with cations such as Mn, Cr, Fe, Mo, V and Al. The samples were heated in air in conventional electrical resistance furnace in one set of experiments and in microwave (MW) system in the other set. Remarkable difference was observed in the temperature as well as rate of transformation in both undoped and doped anatase samples, depending on the mode of heating i.e. whether the sample was heated in conventional resistance furnace or mi-

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crowave heating system. The activation energy for anatase to rutile transformation was evaluated from specific transformation rates derived from the isothermal data.

Experimental

Several techniques have been recently described for the preparation of titanium oxide including sol–gel process followed by pyrolysis of different types of titania based precursors [16–18]. However, in our present study the undoped and 2 mol% doped TiO_2 samples were prepared by employing controlled precipitation process [19] in which dilute $TiCl_4$ solution was mixed with urea solution in proportion of TiO_2:urea concentration 1:20 moles. The reaction mixture was then heated at ~100°C and refluxed for two to three hours. The resulting reaction mass was cooled and filtered. The precipitate was washed several times with hot de-ionized water till it was free of chloride ions. For preparation of doped TiO_2 in situ doping of precursors was done during precipitation step. For 2 mol% doping of Al/Fe/Mn, their salts viz. $Al(NO_3)_3$/$Fe(NO_3)_3$/$MnSO_4$, respectively, were mixed in dilute $TiCl_4$ solution. Other dopants V/Mo/Cr which could not be precipitated as hydroxides were introduced by mixing salts of dopants viz. NH_4VO_3/$(NH_4)_6Mo_7O_{27}$ and $(NH_4)_2Cr_2O_7$, respectively, with aqueous slurry of $Ti(OH)_4$ using a roller mixer. The precursors were initially vacuum dried and then dried at 110°C followed by heating at 300°C in MW system for 1 h. The samples obtained in the powder form were subjected to heat treatment between 500 to 1100°C in microwave system and conventional electrical furnace with dwell time of 30 min. The microwave system used for heating sample was a commercial microwave oven consisting of magnetron operating at 2.45 GHz with adjustable power settings and full power level of 750 Watts. The system was modified in such a way that the sample temperature could be controlled within ±3°C of the set value through an on/off temperature controller coupled to the magnetron input power source [20]. Calibrated Pt, Pt-13%Rh shielded thermocouple was used for measurement of sample temperature. To avoid sparking, the shield of thermocouple was grounded and to obtain precise sample temperature, the tip of the thermocouple was embedded within the powder sample (weighing ~2–3 g). The samples were kept in a well-insulated sample holder carved from mullite fiberboard. The sample holder was surrounded by four silicon carbide rods located symmetrically around the sample holder. These rods act as pre-heaters for the sample under investigation.

For determination of kinetics of the phase transformation of undoped and selected doped samples, isothermal experiments were carried out for different time intervals at four different temperatures in microwave system. The temperature was measured by calibrated chromel-alumel thermocouple and controlled within ±2°C by controlling the power input to the microwave system using PID temperature controller (Vertex VD 2000). The heat-treated samples were characterized by X-ray diffraction technique and the mass fraction of rutile (α) in TiO_2 was calculated using equation

$$\alpha=\frac{1}{1+0.884(A_{\text{anatase}}/A_{\text{rutile}})}$$

where '$A_{anatase}$' and 'A_{rutile}' represent, respectively, the integral intensities of anatase peak (101) i.e. at 2θ value of 25.4° and rutile peak (110) at 2θ value of 27.5°. 'α' is the extent of the transformation of anatase i.e. mass fraction of rutile in the mixture. The data was plotted using various models proposed for the analysis of α–t curves for the phase transformation reported in [9].

Results and discussion

Figures 1 and 2 compare the effect of dopants on the polymorphic phase transformation of doped and undoped TiO_2 (prepared by using urea as the precipitating agent for $Ti(OH)_4$ precursor) heated in conventional furnace and MW heating system at different temperatures for the dwell time of 30 min. Figure 1 indicates that all the doped and undoped anatase samples heated in resistance furnace start transforming to rutile at ~700°C. However, the completion temperatures of transformation were found to be different for the samples doped with different aliovalent ions. The same samples heated in MW field, however, exhibited drastic differences in the initiation as well as in final conversion temperatures of anatase to rutile (Fig. 2). These differences could be linked to the difference in the mode of heating by the two methods.

The results obtained in the present study, for the furnace heated samples indicated lower transformation temperatures than those reported by Mackenzie [10]. This could be attributed to the difference in the methods of preparation of TiO_2 adopted in our study and that by Mackenzie *et al.* [10] who physically dry mixed the dopants in oxide form in anatase powder. In our study, the dopants were incorporated in the sample during the precipitation stage, ensuring more uniform mixing.

The differences observed in the anatase-to-rutile transformation temperatures in the doped samples could be attributed to the lattice red-ox reactions introduced by the variable valency cations as suggested by Mackenzie [10]. The anion vacancy concen-

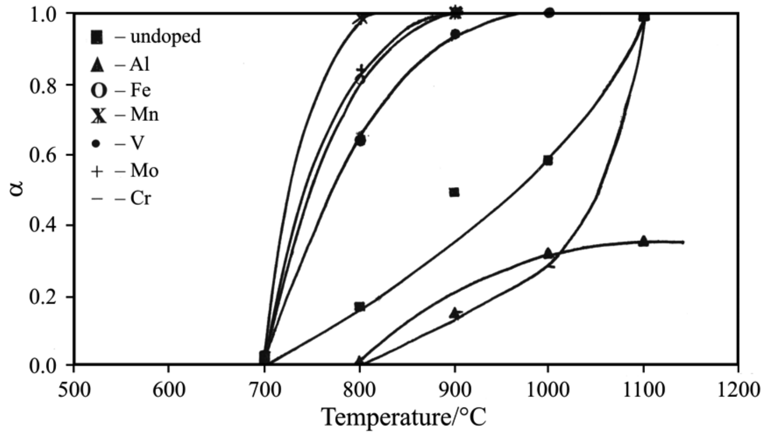

Fig. 1 Effect of dopants on anatase to rutile transformation of TiO_2 when heated in resistance furnace (30 min dwell time) at different temperatures

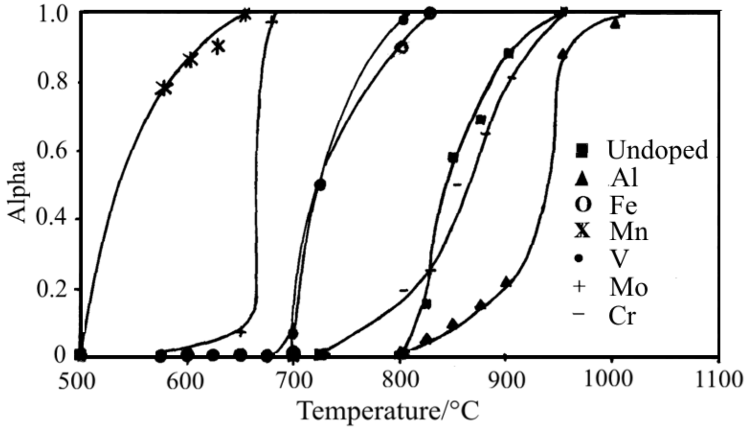

Fig. 2 Effect of dopants on anatase to rutile transformation of TiO_2 when heated in microwave system (30 min. dwell time) at different temperatures

tration introduced in TiO_2 by substituting Ti by lower oxidation state elements results in lowering of anatase to rutile transformation temperature which is much more pronounced in the case of microwave heated samples. Figure 1 suggests that Fe, Mn, V and Mo may very likely exist in lower than +4 oxidation state in the doped samples, thereby lowering down the transformation temperature. However, preliminary ESR study of the Mn, V, Cr, Fe and Mo doped samples indicated these elements to be in the oxidation state of Mn^{2+} or Mn^{3+}, vanadium as V^{4+}, Cr as Cr^{3+}, Fe as $Fe^{2+}$and Mo as Mo^{5+} [21]. The reduction in transformation temperature in Mn, Cr and Fe doped sample could be related to the oxygen vacancies created in the TiO_2 matrix. But this assumption may not be considered as universal since other dopants such as vanadium and molybdenum though in oxidation state of V^{4+} and Mo^{5+}, respectively, still show reduction in anatase to rutile transformation temperature. Mackenzie [10] related reduction in anatase to rutile transformation rate in Cr doped samples (Fig. 1) to its preference for occupying relatively undistorted octahedral sites in TiO_2 lattice. Although the co-ordination of Ti is 6-fold in both anatase and rutile, octahedral sites in anatase are highly distorted, such sites would be unattractive to Cr ion and little exchange would therefore be expected. Al doped anatase samples exhibited increase in transformation temperature to rutile phase. This was attributed to its least efficient vacancy producing nature [10]. Alternately, alumina particles, dispersed among the anatase particles could effectively reduce the probability of interface nucleation at all temperatures [6]. However, this severity of retardation was found to be much reduced when the same Al doped samples were heated in microwave system. This could be due to bulk internal heating nature of the MW technique and the coexistence of better microwave interacting alumina (gamma phase) with anatase, creating anisothermal conditions reported by Roy *et al*. [22].

The kinetic curves obtained from isothermal data in our work were sigmoid shaped (Fig. 3) and similar to those reported by Shannon and Pask [5] and Macken-

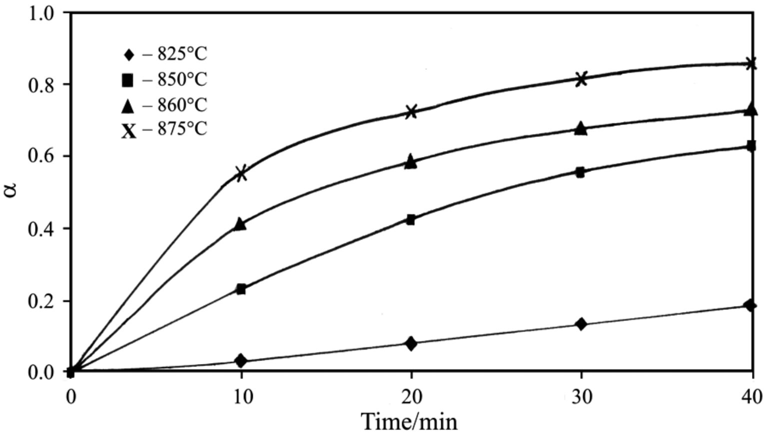

Fig. 3 Kinetic curves for undoped anatase powders isothermally heated in microwave system between 825–875°C

zie [9]. Mackenzie observed that the α–*t* data in such transformations could be fitted to first-order, contracting spherical-interface, random nucleation and rapid growth and overlapping nuclei [9], and nucleation plus crystal growth of overlapping nuclei equations. The initial sigmoid shape indicated that the acceleratory period is dominated by the nucleation of new phase and deceleratory period by growth. The analysis of our data obtained by isothermal heating of undoped and Mo, Mn and V doped TiO_2 showed the best fit with the equation corresponding to the nucleation plus growth of overlapping nuclei kinetic model which could be expressed by the equation

$$[\ln(1-\alpha)]^{1/3}=kt+c$$

The specific transformation rates (k) were derived from the plots of $[\ln(1-\alpha)]^{1/3}$ *vs*. t. A typical plot for anatase-to-rutile transformation for undoped TiO_2 is shown in Fig. 4. The values of k obtained for different sample at different temperatures are listed in Table 1. The activation energies for transformation of undoped and Mn, Mo and V doped samples were then derived from the Arrhenius plots of $\log k$ *vs*. $1/T$ derived from the isothermal data (Fig. 5). The activation energy for the anatase to rutile transformation of undoped sample was found to be 328.4±20.3 kJ mol^{-1} which is marginally

Table 1 The values of k obtained for different samples at different temperatures

Undoped TiO_2		Mn doped TiO_2		Mo doped TiO_2		V doped TiO_2	
T/K	K/s^{-1}	T/K	K/s^{-1}	T/K	K/s^{-1}	T/K	K/s^{-1}
1098	$2.00\cdot10^{-5}$	848	$1.18\cdot10^{-4}$	923	$6.80\cdot10^{-5}$	898	$9.50\cdot10^{-5}$
1123	$4.17\cdot10^{-5}$	873	$1.48\cdot10^{-4}$	948	$1.83\cdot10^{-4}$	923	$1.15\cdot10^{-4}$
1133	$5.50\cdot10^{-5}$	923	$3.67\cdot10^{-4}$	973	$3.67\cdot10^{-4}$	973	$2.50\cdot10^{-4}$
1148	$9.83\cdot10^{-5}$						

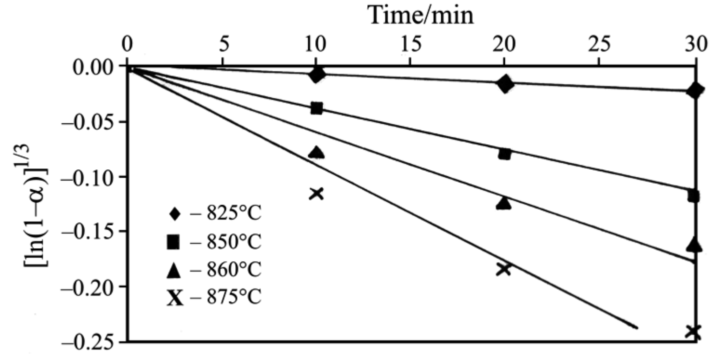

Fig. 4 Plot of $[\ln(1–\alpha)]^{1/3}$ *vs*. *t* of anatase to rutile transformation of undoped TiO_2

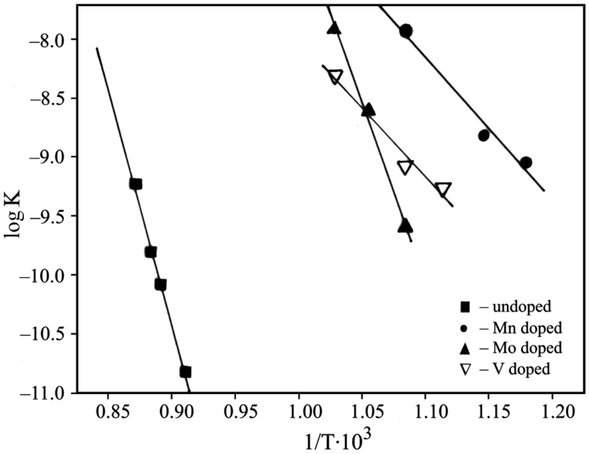

Fig. 5 Arrhenius plot –log*K vs*. $1/T\cdot10^3$ of undoped and Mn, Mo, V doped TiO_2

lower than that reported by Shannon *et al*. and Rao *et al*. [1, 3, 5] derived from their experiments carried out on furnace heated samples, indicating that the type of heating does not alter activation energy. The activation energy values reported by Shannon *et al*. [5] and Rao *et al*. [4] are in the range 350–500 and 350–500 kJ mol^{-1}, respectively. Phenomenal decrease in activation energy was however observed in the present work in the case V, Mo and Mn doped samples. These were 96.4±16.2, 252.0±21.4 and 101.3±16.8 kJ mol^{-1}, respectively.

Conclusions

The following conclusions could be drawn from the present study:

- The microwave processing decreases the temperature of transformation and enhances the rate of transformation of anatase to rutile in the case of doped and undoped TiO_2. The nature of dopant and heating methods dictates the transformation temperature of anatase to rutile.

- The isothermal data for undoped TiO_2 and doped TiO_2 processed in microwave system showed the best fit with the 'nucleation plus growth of overlapping nuclei' kinetic model. The activation energy derived from this data for undoped TiO_2 was 328.4±20.3 kJ mol^{-1}, which is in close agreement with that reported for furnace heated samples (350–500 kJ mol^{-1}) by previous investigators [4, 5] indicating that the type of heating does not alter activation energy significantly. However, the activation energy was reduced from be 328.4±20.3 kJ mol^{-1} for undoped TiO_2 to 96–252 kJ mol^{-1} depending on the dopant used.

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