

Study of the anatase to rutile transformation kinetics of the modified TiO₂

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TiO₂ attracts much interest because of its many potential applications. The use of titanium dioxide strongly depends on its polymorphic form: brookite, anatase, or rutile. Only rutile and anatase play an important role in industry. Anatase as a metastable form undergoes a non-reversible transformation into rutile. Understanding the kinetics of phase transformation and the processes of crystal growth of a material is essential for controlling its structure and, thus, its specific properties. The main purpose of this paper is to explain the anatase to rutile recrystallization kinetics in the modified TiO₂ calcined from industrial hydrated titanium dioxide. The apparent activation energy of anatase to rutile transformation and the average size of titanium dioxide crystallites were determined for the unmodified TiO₂ and TiO₂ modified with P, K, Al, B, Zn, Zr, Ce, Sn, or Sb introduced in the amount of 0.5 mol% and 1.0 mol% when recalculated for their oxides. The growth of TiO₂ crystallites during calcination was strongly inhibited by P, Ce and Zr, and inhibited to a lesser degree by Al, Sn and Sb. B and Zn did not affect the investigated process and K accelerated crystallites growth. The values of apparent activation energy depending on a modifier formed a relationship: Al<Sb<Sn<P<B<Ce<0=Zn=K<Zr. The observed dependencies can be explained by reactions occurring between the modifiers and titanium dioxide.

Keywords: TiO₂, anatase, rutile, modification, phase transformation kinetics.

INTRODUCTION

Titanium dioxide has found many applications in pigment and ceramic industries¹. However, TiO₂ continues to attract much interest also because of its other potential applications such as electronic devices, thin films, batteries, photomaterials for widespread air and water purification, water disinfection and hazardous waste remediation²⁻⁵.

It is well known that an isolated crystalline phase is thermodynamically stable when its free energy is a minimum at a given temperature and pressure^{6, 7}. When the free energy is a local minimum the phase is thermodynamically metastable. A metastable phase moves to the free energy minimum when it overcomes the kinetic restrictions. Such a behavior is often observed in metallic oxides having various polymorphs⁸. The example is polymorphic titanium dioxide which occurs in nature in three modifications, namely, rhombohedral brookite, tetragonal anatase and tetragonal rutile⁹. However, only rutile and anatase are produced industrially in large quantities and play the most important role in the applications of TiO₂. Therefore, they have been intensively studied¹⁰. Brookite is difficult to produce and has no value in the TiO₂ industry¹¹. Moreover, anatase and brookite are thermodynamically metastable with respect to rutile¹². Hence, brookite and anatase undergo a non-reversible transformation into rutile when heated at particular temperature⁶ which depends upon many factors including crystallite size, size distribution, contact area of crystallites, calcination temperature and calcination time, addition of promoters or inhibitors, concentration of the introduced foreign ions, atmosphere, and the presence of rutile nuclei^{13, 14}.

The anatase to rutile phase transformation has been a subject of scientific research and has been widely studied. According to the previous reports the activation energy for anatase to rutile phase transformation involves the activation energy of coarsening of anatase particles, the activation energy of nucleation, and the

activation energy for the growth of nuclei¹⁵⁻¹⁶. A group of kinetic models have been proposed to describe the obtained experimental data. Models, such as standard 1st order or 2nd order, contracting spherical interface, nucleation and growth of overlapping nuclei, one dimensional, linear, branching nuclei and a constant growth, random nucleation and rapid growth, JMAK (Johnson-Mehl-Avrami-Kolmogorov), interface nucleation, and combined interface and surface nucleation, have been proposed in literature¹⁷⁻²². Among a given variety of kinetic equations, the Johnson-Mehl-Avrami-Kolmogorov (also known as the Avrami equation) model is regarded as universal and widely used to describe solid-state phase transformations^{13, 23}. This model is based upon a standard theory that the nucleation process occurs uniformly and randomly, and phase system is infinite in size^{24, 25}. Theoretical models have been studied to modify the Avrami equation in order to take into account additionally other material characteristics, such as non-uniform nucleation, anisotropic particle formation or finite size effect. However, the proposed modifications are still not conveniently applicable.

Understanding the kinetics of phase transformation and the fundamental processes of crystal growth of the material is essentially important for controlling its structure and, thus, its specific properties. Moreover, the comprehension of calcination of a hydrous titanium dioxide is a necessary step in the preparation of commercial material. Hence, the main purpose of this paper is to explain the anatase to rutile recrystallization kinetics in modified TiO₂ calcined from industrial hydrated titanium dioxide. The influence of modifiers on the apparent activation energy of anatase to rutile transformation and on the average size of titanium dioxide crystallites was studied.

EXPERIMENTAL

Sample preparation

The starting material was technical grade hydrated titanium dioxide (HTD) as a concentrated suspension containing 37.4 wt. % of TiO₂ and 3.0 wt. % of rutile nuclei. It was an indirect product from the industrial production of TiO₂ with the sulphate method. The modifiers' solutions were prepared by dissolving reagent-grade H₃PO₄, KOH, Al₂(SO₄)₃, H₃BO₃, ZnSO₄, Zr(SO₄)₂, Ce(NO₃)₃, and SnSO₄ in distilled water and Sb₂O₃ in HCl aqueous solution. Solutions of modifying agents (calculated to P₂O₅, K₂O, Al₂O₃, B₂O₃, ZnO, ZrO₂, CeO₂, SnO₂, and Sb₂O₃) were introduced to HTD. The contents of the additives in relation to TiO₂ were 0.5 and 1.0 mol%.

The obtained pulp after thorough mixing (a mechanical stirrer, 25 rpm, time 0.5 h) was transferred to an evaporating dish and it was then inserted into a laboratory muffle furnace (LM 312.13) and heated to an assumed temperature. The prepared samples, for the investigations of the anatase to rutile transformation were calcined for 0.5, 1.0, 1.5 and 2.0 h at appropriate temperatures in the range 725–910°C.

Sample characterization

The X-ray diffraction analysis (X'Pert PRO Philips diffractometer with CuK_α radiation) was used to determine the phase composition in the calcined titanium dioxide samples and the crystallites size of titanium dioxide. The relative abundance of anatase and rutile phases was calculated from the (101) reflection of anatase and the (110) reflection of rutile. The content of anatase and rutile in the samples was determined from the following equations:

$$W_A = 100/(1+cI_R/I_A) \quad (1)$$

$$W_R = 100/(1+I_A/cI_R) \quad (2)$$

where: W_A and W_R – content of anatase and rutile, I_A and I_R – peak intensities of anatase (101) and rutile (110) and c – coefficient (the ratio of peak intensity (101) 100 wt.% of anatase to the peak intensity (110) 100 wt.% of rutile).

The crystallites average size (D) variation of TiO₂ was determined on the basis of the Scherrer equation:

$$D = \frac{\lambda \cdot K}{\beta \cdot \cos \theta} \quad (3)$$

where: λ – wavelength of CuK_α radiation, K – particle shape factor, β – full width at half maximum of the intensity peak.

The crystallites average size variation of anatase phase was calculated from the (101) reflection of anatase and the (110) reflection of rutile. The width of the peak at half maximum was calculated taking into account the so-called apparatus broadening. This parameter was determined on the basis of the sample of coarse crystalline silicon.

The contents of the modifiers in TiO₂ were verified by ICP–AES analysis (Optima 5300 DV, Perkin Elmer).

Transformation characterization

On the basis of a calculated degree of anatase to rutile transformation depending on time (30, 60, 90 and 120 min) and calcination temperature the rate constant of

anatase to rutile transformation was determined. The constant was calculated using the Avrami equation:

$$\alpha = 1 - \exp(-kt^n) \quad (4)$$

where: α – transformation degree, t – time, n – Avrami exponent, k – reaction rate constant.

The Avrami equation, apart from other kinetic models, is widely and universally used to define phase transformations and crystallization of solids^{13,26}. Then, using the Arrhenius equation and knowing the values of reaction rate constants at different temperatures, the apparent activation energy of recrystallization of anatase to rutile was determined from the dependence of $\ln k$ on $1/T$.

$$k = k_0 \exp(-E_a/RT) \quad (5)$$

where: k – reaction rate constant, k_0 – pre-exponential factor, E_a – apparent activation energy, R – gas constant, T – temperature.

RESULTS AND DISCUSSION

The influence of modifiers on the apparent activation energy of anatase to rutile transformation

The apparent activation energy of anatase to rutile transformation was determined for unmodified TiO₂ and TiO₂ modified with P, K, Al, B, Zn, Zr, Ce, Sn, or Sb introduced in the amount of 0.5 mol% and 1.0 mol% when recalculated for their oxides. The contents of the modifiers introduced to TiO₂ were determined with ICP–AES method. The results of the conducted analysis were consistent with the theoretical assumptions. The obtained results are presented in Table 1.

It was found that an increase in anatase to rutile transformation degree with temperature and calcination time depended on the type of the introduced modifier. In the lower range of temperatures the degree increased to an insignificant degree along the reaction time. In the medium range it was more noticeable and in the high range it was significant. The range of temperatures in which transformation occurred depended on the type

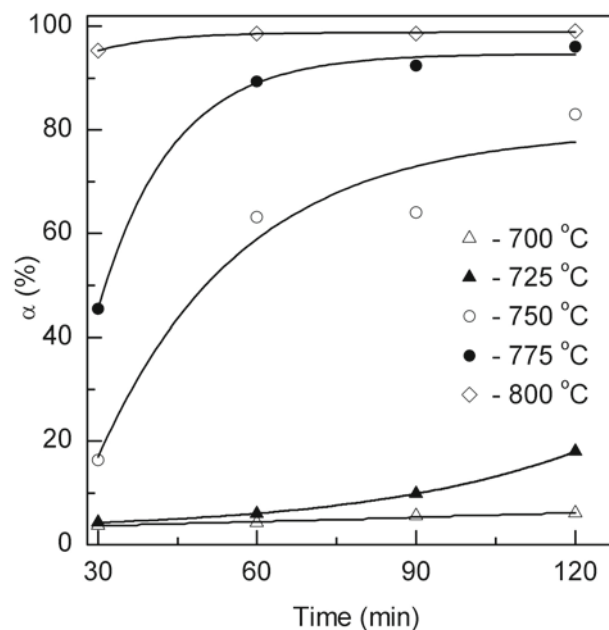


Figure 1. The influence of temperature and calcination time on anatase to rutile transformation degree in unmodified TiO₂

Table 1. The influence of modifiers on the reaction rate constant and apparent activation energy of anatase to rutile transformation

Content of modifier in relation to TiO ₂ [% mol]	Reaction temperature [°C]	Transformation degree/time [%]/[h]				Reaction rate constant [s ⁻¹]	Apparent activation energy [kJ/mol]
		0.5	1.0	1.5	2.0		
Unmodified	725	4	6	10	18	$2.35 \cdot 10^{-5}$	500
	750	16	63	64	83	$2.09 \cdot 10^{-4}$	
	775	45	89	92	96	$4.16 \cdot 10^{-4}$	
0.5 K ₂ O	750	11	24	36	45	$9.30 \cdot 10^{-5}$	505
	775	31	60	69	72	$2.10 \cdot 10^{-4}$	
	800	69	74	79	80	$1.11 \cdot 10^{-3}$	
	825	74	79	83	83	$2.21 \cdot 10^{-3}$	
	850	84	86	89	90	$2.23 \cdot 10^{-2}$	
1.0 K ₂ O	750	8	12	17	18	$1.05 \cdot 10^{-5}$	300
	775	15	22	29	30	$2.96 \cdot 10^{-5}$	
	800	33	39	43	42	$1.76 \cdot 10^{-5}$	
	825	41	45	49	49	$2.02 \cdot 10^{-5}$	
	850	49	54	60	62	$1.23 \cdot 10^{-4}$	
	875	56	65	72	77	$3.31 \cdot 10^{-4}$	
	900	77	85	90	93	$1.28 \cdot 10^{-3}$	
0.5 SnO ₂	740	7	16	33	51	$1.07 \cdot 10^{-4}$	460
	750	14	49	59	79	$1.85 \cdot 10^{-4}$	
	760	28	66	82	89	$2.66 \cdot 10^{-4}$	
	775	67	90	94	95	$6.97 \cdot 10^{-4}$	
1.0 SnO ₂	740	6	14	34	53	$1.13 \cdot 10^{-4}$	420
	750	8	31	60	73	$1.66 \cdot 10^{-4}$	
	760	20	55	81	87	$2.32 \cdot 10^{-4}$	
	775	64	87	93	95	$6.16 \cdot 10^{-4}$	
0.5 ZnO	725	7	12	18	23	$7.83 \cdot 10^{-5}$	550
	750	14	40	76	94	$2.94 \cdot 10^{-4}$	
	775	66	99	99	100	$7.15 \cdot 10^{-4}$	
1.0 ZnO	715	6	13	28	36	$7.78 \cdot 10^{-5}$	500
	725	8	18	34	54	$1.09 \cdot 10^{-4}$	
	735	17	50	92	99	$2.61 \cdot 10^{-4}$	
0.5 B ₂ O ₃	725	5	8	12	21	$3.20 \cdot 10^{-5}$	470
	750	8	30	48	67	$1.49 \cdot 10^{-4}$	
	775	54	86	93	95	$4.68 \cdot 10^{-4}$	
1.0 B ₂ O ₃	725	5	9	12	17	$2.10 \cdot 10^{-5}$	500
	750	8	30	48	66	$1.49 \cdot 10^{-4}$	
	775	43	83	91	95	$3.77 \cdot 10^{-4}$	
0.5 Al ₂ O ₃	750	1	12	18	28	$1.00 \cdot 10^{-4}$	350
	775	21	44	65	73	$1.81 \cdot 10^{-4}$	
	800	68	87	94	95	$7.02 \cdot 10^{-4}$	
1.0 Al ₂ O ₃	775	10	21	30	40	$7.47 \cdot 10^{-5}$	535
	800	44	69	79	83	$3.02 \cdot 10^{-4}$	
	815	69	86	91	94	$7.16 \cdot 10^{-4}$	
0.5 Sb ₂ O ₃	725	7	14	23	33	$6.31 \cdot 10^{-5}$	390
	750	16	55	74	86	$2.18 \cdot 10^{-4}$	
	775	61	91	94	96	$5.84 \cdot 10^{-4}$	

Content of modifier in relation to TiO ₂ [% mol]	Reaction temperature [°C]	Transformation degree/time [%]/[h]				Reaction rate constant [s ⁻¹]	Apparent activation energy [kJ/mol]
		0.5	1.0	1.5	2.0		
0.5 ZrO ₂	775	7	12	25	34	6.55 · 10 ⁻⁵	560
	800	17	46	69	80	1.97 · 10 ⁻⁴	
	825	75	88	91	93	1.25 · 10 ⁻³	
1.0 ZrO ₂	775	5	7	10	11	2.19 · 10 ⁻⁶	525
	800	8	16	29	32	5.69 · 10 ⁻⁵	
	825	31	54	69	78	2.12 · 10 ⁻⁴	
	850	72	90	95	97	7.84 · 10 ⁻⁴	
0.5 CeO ₂	775	7	9	11	13	2.29 · 10 ⁻⁶	485
	800	12	19	33	41	7.40 · 10 ⁻⁵	
	825	32	56	72	80	2.26 · 10 ⁻⁴	
	850	74	91	96	98	8.36 · 10 ⁻⁴	
1.0 CeO ₂	775	6	8	9	10	1.25 · 10 ⁻⁸	575
	800	9	14	21	25	3.10 · 10 ⁻⁵	
	825	19	38	58	65	1.53 · 10 ⁻⁴	
	850	60	87	92	95	5.45 · 10 ⁻⁴	
0.5 P ₂ O ₅	775	5	6	7	7	1.05 · 10 ⁻⁸	450
	825	11	18	25	27	3.12 · 10 ⁻⁵	
	850	20	31	42	49	8.34 · 10 ⁻⁵	
	865	29	45	58	64	1.47 · 10 ⁻⁴	
	880	53	69	76	80	3.10 · 10 ⁻⁴	
1.0 P ₂ O ₅	890	5	13	17	23	2.13 · 10 ⁻⁵	1295
	900	10	17	33	50	9.38 · 10 ⁻⁵	
	910	19	40	73	85	2.05 · 10 ⁻⁴	

of modifier. If it acted as an inhibitor of transformation, the range shifted towards higher temperatures. For example, the influence of temperature and time on anatase to rutile transformation both for unmodified titanium dioxide (Fig. 1) and TiO₂ modified with phosphates which inhibit the analysed process (Fig. 2) is shown. A high transformation degree, 96%, was obtained by calcination of hydrated titanium dioxide without any modifiers at 775°C for 2 h or at 800°C for 0.5 h. A high degree of transformation in the presence of phosphates (93.5%) was obtained at 900°C for 2 h of calcination. It was noticed that a similar degree of transformation was obtained in time 1.5–3 times shorter at temperatures higher than lower by 10–25°C by using various modifying agents.

On the basis of the obtained results a dependence of $\ln(-\ln(1 - a))$ on $1/t$ was drawn in order to determine $1/k$, which was later used in the Arrhenius equation ($1/k$ on $1/T$). This was the basis for calculating the apparent activation energy of anatase to rutile transformation for unmodified titanium dioxide and titanium dioxide with an addition of a given modifiers. The obtained results are presented in Table 1.

The higher the process temperature, the higher values of polymorphous anatase to rutile transformation rate constants were achieved. The values of constants depended on the type and amount of the modifier introduced into TiO₂. Some modifiers did not significantly influence anatase to rutile transformation at a given temperature of

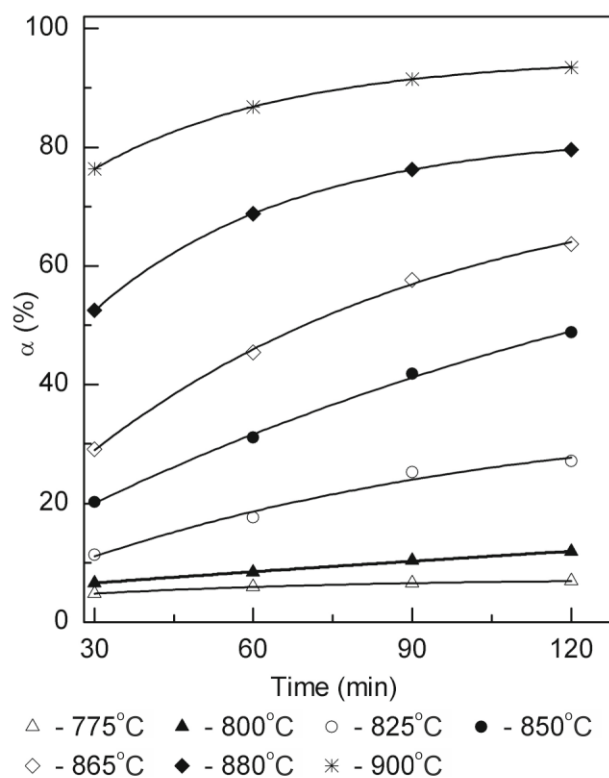


Figure 2. The influence of temperature and calcination time on anatase to rutile transformation degree in TiO₂ modified with phosphorus (0.5 mol% P₂O₅)

the process (boron, antimony, tin), increased the degree of transformation (zinc), limited to a varying extend the degree of transformation (potassium, zirconium, cerium, phosphorus). Out of the above listed modifiers, phosphorus was the greatest inhibitor of anatase to rutile transformation.

In Figures 3 and 4 the influence of modifiers with their identical content in TiO_2 calculated to 1.0 mol% of a given element on the anatase to rutile transformation is compared. Figures 3 and 4 present a comparison of the influence of modifiers and calcination temperature or calcination time on the obtained anatase to rutile transformation degree. An addition of antimony did not change the curve representing anatase to rutile transformation in comparison with unmodified TiO_2 . In the presence of

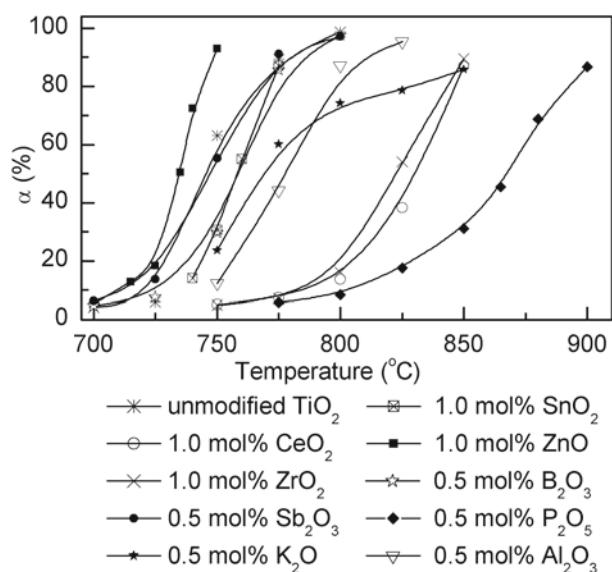


Figure 3. A comparison of the influence of calcination time and modifiers on the anatase to rutile transformation degree in modified TiO_2 (calcination temperature 775°C)

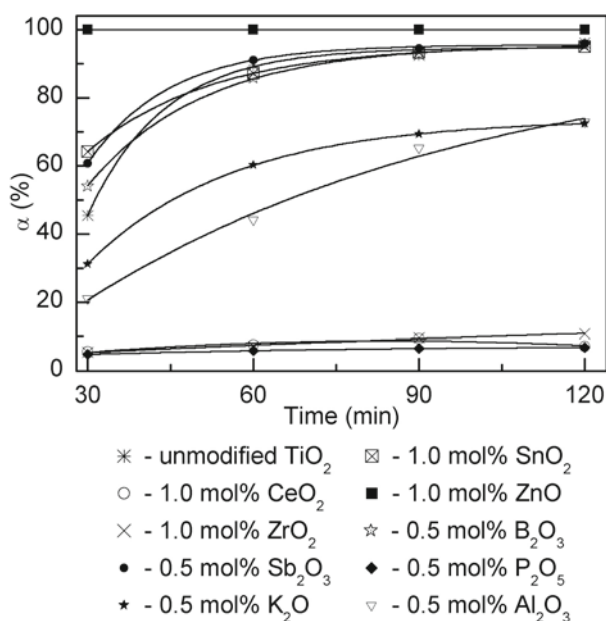


Figure 4. A comparison of the influence of calcination temperature and modifiers on the anatase to rutile transformation degree in modified TiO_2 (calcination time – 60 min)

boron and tin, transformation was slightly inhibited at a lower process temperature. An addition of zinc catalyzed transformation. In the presence of aluminium the transformation curve had a similar character to that of antimony, but at the same temperature a lower degree of transformation was achieved. Zirconium and cerium reacted in a similar way and inhibited transformation to a higher degree than aluminium and potassium. However, the greatest inhibiting influence on anatase to rutile transformation was observed for phosphorus. When we observe the influence of modifiers and calcination time on the increase of transformation degree at a selected temperature of calcination, 775°C , similar conclusions can be drawn. Zinc accelerated transformation, boron, tin and antimony did not affect it, and cerium, zirconium and phosphorus inhibited it to a much higher degree than potassium and aluminium.

The apparent activation energy of anatase to rutile transformation in the presence of selected modifiers (1.0 mol% of a given element) was in the range 350–525 kJ/mol. For unmodified titanium dioxide it was 500 kJ/mol. No similar dependence of apparent activation energy on the type of modifier was observed as distinct from the influence of modifiers on the anatase to rutile transformation degree. It was expected that the values of apparent activation energy depending on a modifier would form a relationship: $\text{Zn} < 0 = \text{B} = \text{Sn} = \text{Sb} < \text{Al} < \text{K} < \text{Ce} = \text{Zr} < \text{P}$. However, the relationship which was actually obtained: $\text{Al} < \text{Sb} < \text{Sn} < \text{P} < \text{B} < \text{Ce} < 0 = \text{Zn} = \text{K} < \text{Zr}$, was much more difficult to interpret. It was observed that usually an increase of the amount of the introduced modifier led to an increase of apparent activation energy. However, this was not the case for potassium. The apparent activation energy for 0.5 mol% K_2O was 505 kJ/mol, and for 1.0 mol% K_2O it was considerably lower – 300 kJ/mol. In the latter case, the range of temperatures spanning the beginning and the end of transformation was wider and the curve demonstrating the dependence of $\ln k$ on $1/T$ was flat. No differences in the effect of temperature on anatase crystallites' size for 1.0 mol% K_2O in comparison with 0.5 mol% K_2O were observed. Moreover, an increasing amount of potassium caused an increase of the final calcination temperature by 50°C . Hence, the lower activation energy for 1.0 mol% K_2O can be connected with the formation and distribution of different phases with potassium. As far as we know K_2SO_4 , which is formed when the starting material originates from sulphate method, can occur on the surface of TiO_2 and therefore can be responsible for the inhibition of anatase-rutile phase transformation²⁷. The increase of phase transformation temperature results in the decay of potassium sulphate and more intense formation of another phase which is K_2TiO_3 . A phase of titanium with potassium locates in the whole volume of titanium dioxide and facilitates rutile formation. This explains a lower activation energy. However, an increase of the amount of phosphorus introduced into titanium dioxide from 0.5 mol% P_2O_5 to 1.0 mol% P_2O_5 resulted in a large increase of E_a from 450 kJ/mol to no less than 1295 kJ/mol. It was found that phosphates introduced into titanium dioxide in the amount of 1 mass.% (0.56 mol%) either stop the phase transformation or inhibit it significantly²⁸.

The observed dependencies can be explained by reactions occurring between the modifiers and titanium dioxide which may produce solid solutions ($\text{Ti}_{1-x}\text{Zr}_x\text{O}_2$, $\text{Ti}_{1-x}\text{Sb}_x\text{O}_2$, $\text{Ti}_{1-x}\text{Sn}_x\text{O}_2$), new compounds containing titanium and an added element (ZnTiO_3 , TiP_2O_7) or oxides of a given modifier (B_2O_3 , Al_2O_3 , ZrO_2 , SnO_2 , CeO_2)^{27, 29-32}. Oxides of the modifiers or their compounds with titanium can be located in intergranular space, cover the surface of grains thus inhibiting the anatase to rutile recrystallization. Nucleation can occur at the phase boundary, on the surface or inside grains. Depending on temperature, one of the models dominates. At a low temperature, phase boundary nucleation prevails, at medium temperatures surface nucleation occurs and at high temperatures nucleation inside grains can be observed. The nucleation activation energy at the phase boundary is smaller than E_a on the surface of grains. And in turn, the nucleation activation energy on the surface of grains is smaller than E_a inside grains³³⁻³⁵.

In order to determine the apparent activation energy of anatase to rutile transformation for TiO_2 modified with phosphorus, or particularly modified with higher amounts of P_2O_5 , material had to be calcined at the temperatures not exceeding 910°C . This is due to the fact that phosphorus, together with titanium, forms titanium pyrophosphate³⁶, which probably covers the surface of grains and transformation can only occur at a high temperature, at which nucleation inside grains dominates. If zinc, boron, tin or antimony were used as modifiers, a lower range of temperatures $725\text{--}775^\circ\text{C}$ was sufficient (like for unmodified TiO_2). Boron probably locates in the interstitial sites of TiO_2 crystal lattice, tin and antimony forms a solid solution, and zinc forms ZnTiO_3 ^{29, 30, 31, 32}. Considering the influence of the investigated modifiers on the degree of anatase to rutile transformation and the value of apparent activation energy, and comparing it to a reaction with unmodified titanium dioxide, a conclusion can be drawn that B_2O_3 , a solid solution of $\text{Ti}_{1-x}\text{Sb}_x\text{O}_2$ (can be obtained at 450°C ³⁷) and ZnTiO_3 (forms at $600\text{--}900^\circ\text{C}$ ³²) are distributed in the whole volume of titanium dioxide grains.

The influence of modifiers on the average size of titanium dioxide crystallites

X-ray diffraction analysis is a method that allows to determine the average size of crystallites of materials up to 100 nm. Above this value, the method can be tentatively used only for the observation of the direction of how crystallites size changes in the calcination of e.g. TiO_2 , including the changes of temperature, the process duration and the type and amount of the modifiers. In the present study, the products contained mainly anatase, anatase and rutile or rutile only depending on the type of the modifier, the temperature and time of the process. Calcination was conducted in a wide range of temperatures from 700°C to 925°C , in which the average size of anatase crystallites sometimes exceeded 100 nm and that of rutile was considerably larger. Therefore, in order to demonstrate the influence of the type of the modifier, the temperature and time of the process on the average size of titanium dioxide crystallites, it was decided that an emphasis should be placed on the changes involving anatase only.

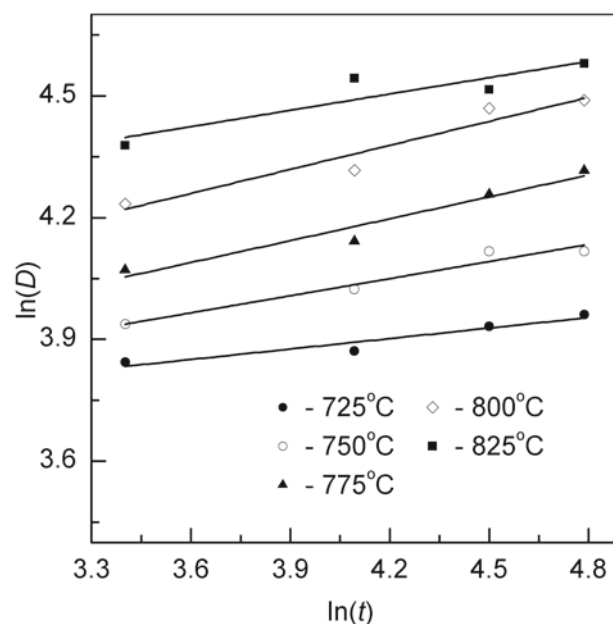


Figure 5. A comparison of the influence of calcination time and process temperature on the average size of anatase crystallites in TiO_2 modified with zirconium (0.5 mol% ZrO_2)

In every case, when the time of the process increased at a given temperature or when the temperature increased at a constant calcination time, the average size of titanium dioxide crystallites gradually increased. It was observed that at a lower range of temperature, when the process lasted between 30 and 60 min, anatase crystallites became larger by 5–10 nm and at a higher range of temperature by 15–20 nm. Figure 5 shows an example of the influence of calcinations time and process temperature on the average size of anatase crystallites for calcination of hydrated titanium dioxide in the presence of zirconium (0.5 mol% ZrO_2). The dependence can be described by an equation proposed by Gesenhues^{33, 34}:

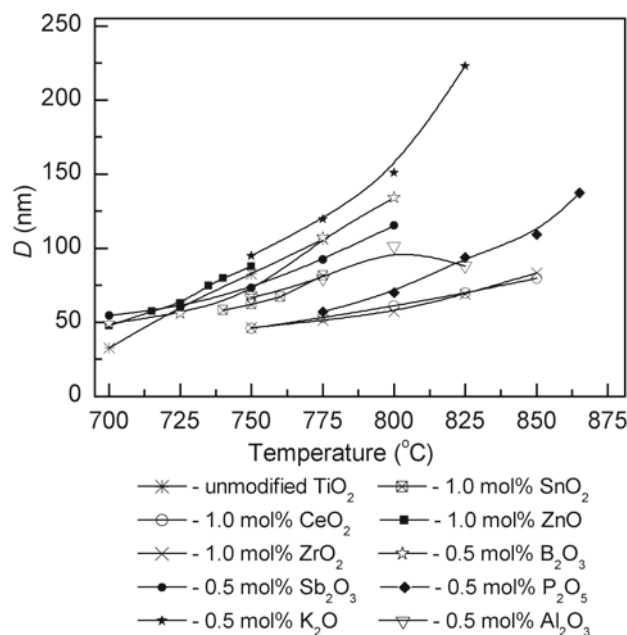
$$D = at^b \quad (6)$$


Figure 6. A comparison of the influence of calcination temperature and modifiers on the average size of anatase crystallites in TiO_2 (calcination time – 30 min)

where D is average size of crystallites [nm], t is time [min], a , b are parameters of model.

When the temperature of the process increased from 725°C to 825°C the average size of anatase crystallites increased from 47 nm to 80 nm and from 53 nm to 98 nm, for 30 and 60 min of calcination time, respectively. In calcination time their size changed from 47 nm to 53 nm and from 80 to 98 nm, at 725°C and 825°C, respectively.

The analysis of the curves presented in Figure 6 shows that the growth of TiO₂ crystallites during calcination was strongly inhibited by phosphorus, cerium and zirconium, and inhibited to a lesser degree by aluminium, tin and antimony. Boron and zinc did not affect the investigated process and potassium accelerated crystallites growth. The average size of anatase crystallites in material calcined from 30 min at 800°C in the presence of zirconium and cerium was 58 nm and in the presence of potassium, anatase crystallites were larger than 100 nm (approximately 150 nm). The influence of the investigated modifiers on crystallites growth was similar to their influence on anatase to rutile polymorphous transformation. It is a known that modifiers that inhibit the growth of crystallites of a given phase of titanium dioxide in calcination process also inhibit anatase to rutile transformation^{34, 38}.

CONCLUSIONS

The study on anatase to rutile transformation kinetics of modified TiO₂ resulted in the determination of the influence of the modifiers on the apparent activation energy of anatase to rutile transformation and on the average size of titanium dioxide crystallites. Calcination was conducted in a wide range of temperatures from 700°C to 925°C. The obtained products contained mainly anatase, anatase and rutile or rutile only depending on the type of the modifier, the temperature and time of the process.

The apparent activation energy of anatase to rutile transformation was determined for unmodified TiO₂ and TiO₂ modified with P, K, Al, B, Zn, Zr, Ce, Sn, or Sb introduced in the amount of 0.5 mol% and 1.0 mol% when recalculated for their oxides. It was found that:

- an increase in anatase to rutile transformation degree with temperature and calcination time depended on the type of the introduced modifier;

- the higher process temperature, the higher values of polymorphous anatase to rutile transformation rate constants were achieved;

- the values of constants depended on the type and amount of modifier introduced into TiO₂,

- boron, antimony, tin did not significantly influence anatase to rutile transformation at a given temperature of the process, zinc increased the degree of transformation, and potassium, zirconium, cerium, phosphorus limited to a varying extend the degree of transformation;

- no similar dependence of apparent activation energy on the type of the modifier was observed as distinct from the influence of modifiers on the anatase to rutile transformation degree;

- the values of apparent activation energy depending on the modifier formed a relationship: Al < S-b < Sn < P < B < Ce < 0 = Zn = K < Zr;

- the observed dependencies can be explained by reactions occurring between the modifiers and titanium dioxide;

- the influence of the investigated modifiers on crystallites growth was similar to their influence on anatase to rutile polymorphous transformation;

- when the time of the process increased at a given temperature or when the temperature increased at a constant calcination time, the average size of titanium dioxide crystallites gradually increased;

- the growth of TiO₂ crystallites during calcination was strongly inhibited by phosphorus, cerium and zirconium, and inhibited to a lesser degree by aluminium, tin and antimony. Boron and zinc did not affect the investigated process and potassium accelerated crystallites growth.

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