

INFLUENCE OF GAS ATMOSPHERE ON REMOVAL OF SULPHATE GROUPS FROM TITANIUM OXIDE

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Abstract

The studies were devoted to determination of the effect of gas atmosphere and its pressure on the second step of decomposition of hydrated titanium dioxide (HTD) promoted by sulfate groups.

It has been found that thermal decomposition of HTD at temperatures above 300°C consists of a number of processes such as dehydroxylation, desulfuration, recrystallization and sintering of solid grains, photochemical processes (if the decomposition proceeds in the presence of light) and adsorption of gas phase components (in the presence of air or SO₂).

Kinetic parameters characterizing this step of decomposition have been determined for processes carried out in vacuum and in argon or air atmospheres (at a pressure of 13.33 hPa). The kinetic curves of decomposition carried out in the presence of gases capable of being adsorbed on the surface of partly dehydrated HTD are featured by local extrema due to simultaneous processes of decomposition and adsorption of gas components.

Keywords: desulfuration, gas atmosphere, kinetics, thermal decomposition, titanium dioxide

Introduction

Hydrated titanium dioxide of anatase structure is an intermediate product in the sulfate methods of obtaining titanium white – the white pigment used in the paint and lack industry. The grains of the pigment contain some amounts of water and sulfate groups adsorbed and chemisorbed on their surface.

In order to obtain the final product of titanium white HTD is subjected to calcination, where its surface is liberated from the hydroxyl groups and sulfur compounds are removed.

The desulfuration is a process of special importance, since it proceeds in the range of temperature featured by the greatest change in the properties of the product due to the grain growth and the phase transition rutile – anatase.

Investigation of the kinetics of this process and of the effect of various parameters, in particular of composition and pressure of the gas atmosphere, should be useful in optimization of calcination process for obtaining the product of suitable optical, catalytic or photocatalytic properties.

Former studies on the decomposition of HTD [1] were performed in vacuum and in air atmosphere. It has been shown that the process proceeds essentially in two stages. The first stage, proceeding at 20–500°C consists in dehydration of the sample. The second stage of mass loss (500–900°C) is connected with desulfuration of HTD. Thermogravimetric studies and mass spectrometric analysis of gaseous products of the decomposition enabled the identification of the following temperature ranges of dehydration and desulfuration of HTD in vacuum.

20–550°C – dehydration and partial dehydroxylation (elimination of about 92% by mass of H₂O),

550–800°C – second stage of dehydroxylation,

300–720°C – first stage of desulfuration (elimination of about 96% by mass of SO₃),

720–820°C – second stage of desulfuration.

The results of these studies have shown that the process of removal of sulfate groups from the grain surface of HTD begins in vacuum at 300°C and proceeds simultaneously with the dehydroxylation of the sample.

It has been noted also [2], that the process of decomposition of HTD, particularly in temperature range of 300–700°C, is accompanied by recrystallization and growth of crystals, decrease of specific surface and reconstruction of the porous structure. The nature of these transformations depends on temperature, duration, and on composition and pressure of the gas atmosphere involved.

TiO₂ is endowed with semiconductor and photocatalytic properties.

The width of the forbidden zone is 3–3.2 eV [3]. For this reason absorption of UV radiation ($\lambda < 400$ nm) results in a number of photochemical processes proceeding with participation of TiO₂ [4].

The work presents the results of studies on thermal decomposition (desulfuration and dehydroxylation) of HTD in vacuum and in atmospheres of argon, air, and sulfur dioxide under pressures of 13.33 hPa and 26.66 hPa. The role of adsorption and photochemical processes in desulfuration and dehydroxylation of HTD is also discussed.

Experimental

The sample of material was obtained in a sulfate process in Zakłady Chemiczne 'Police'. The sample of composition corresponding to: TiO₂·6.9H₂O·0.066SO₃ had a paste form and was free of activators. The paste was dried at 105°C, then roasted in air for 1 h at 300°C. The obtained product further referred to as UDT/300 had a structure of anatase and was featured by a constant specific surface $S_{\text{BET}(N_2)} = 240 \text{ m}^2 \text{ g}^{-1}$ [1].

Thermogravimetric and kinetic measurements were performed in a glass setup with a quartz spiral as a weighting element. The precision of mass change readings was 10⁻⁵ g.

The TG curves of the sample UDT/300 were recorded in vacuum (10⁻² hPa) at day and artificial lightings and in the dark. The sample of a mass about 40 mg was

partly dehydrated in vacuum for 0.5 h at room temperature and then it was heated with a rate of $5^{\circ}\text{C min}^{-1}$.

The TG curves of the sample UDT/300 were also recorded in argon, air, and sulfur dioxide atmospheres at constant artificial lighting of the measuring setup.

The decomposition was carried out in vacuum up to 320°C , then a suitable amount of a gas was let in and the heating was continued in a gas atmosphere.

The kinetics of desulfuration and dehydroxylation were studied with the use of the same apparatus. Samples of UDT/300 about 40 mg in mass were heated in vacuum up to 320°C with a rate of $5^{\circ}\text{C min}^{-1}$, kept at this temperature for 0.5 h, and then the sample was transferred outside the heating zone of the furnace. After the temperature of measurement has been attained a suitable amount of corresponding gas was let in, the sample placed in the furnace, and the mass loss was recorded within 1.5 h under isothermic and isobaric conditions. The degree of transformation was determined as:

$$\alpha = \frac{\Delta m}{\Delta m_{\max}}$$

where: Δm – loss in mass after a time t , Δm_{\max} – maximum loss in mass.

It has been found that HTD sample ignited in vacuum at 320°C had the following composition:



For all experimental results corrections were made for variations of pressure in the measuring set and for thermodiffusion processes. The values of the corrections were determined by heating samples of coarsely crushed quartz glass under conditions normally applied in measurements for HTD samples.

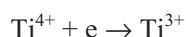
Results and discussion

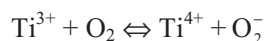
The role of photochemical processes

The TG curves obtained in thermal decomposition of UDT/300 in vacuum, recorded at various conditions of lightening of the measuring set (Fig. 1) have shown that under stronger lightening the processes of dehydroxylation and desulfuration (2nd stage of mass loss) proceed at lower temperatures. The fact may be accounted for a substantial role of photochemical processes in the decomposition of hydrated titanium dioxide. In general opinion [5] the mechanism of decomposition of irradiated TiO_2 involves the formation of electron (e) – hole (h^+) pair.

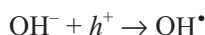


Electrons can participate in generation of surface Ti^{3+} ions.





OH^- groups may donate the electrons with formation of OH^\bullet radicals,



which at increased temperatures may diffuse across the surface or may be desorbed from the TiO_2 surface and participate in reactions involving other OH^- groups (thus leading to desorption of water) or in reactions of catalytic oxidation. Also a possibility of capture of the holes by SO_4^{2-} ions should not be excluded. Some authors [6] have found that sulfate ions affect the photocatalytic oxidation of organic compounds in the presence of TiO_2 .

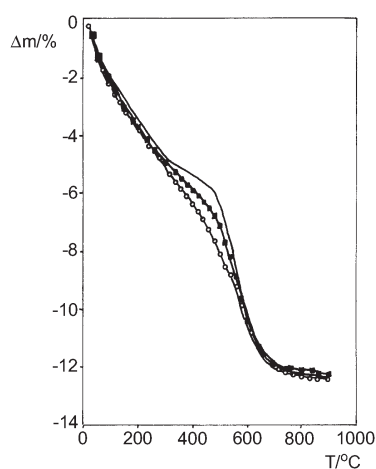


Fig. 1 Thermogravimetric curves of UDT/300 recorded ■ – in vacuum at day; ○ – at artificial lightings and – in the dark

It seems also possible that Ti^{3+} generated photochemically in vacuum are capable of reducing sulfate ions. An indirect proof of complicated nature of SO_4^{2-} transformations in calcination of $\text{TiO}_2/\text{SO}_4^{2-}$ in vacuum may be the changes of IR spectra of the system, as observed by Morterra [7].

Effect of gas atmosphere

As may be seen in Fig. 2, the TG curves recorded in decomposition carried out in the presence of argon, air, or sulfur dioxide within the second stage of mass loss process (dehydroxylation and desulfuration), especially within the temperature range 320–500°C, are shifted toward higher temperatures as compared with the TG curve recorded in vacuum. It has been found also, that in cases where the decomposition is carried out in the presence of gases capable of being adsorbed on defected TiO_2 surface, the overall loss in mass is smaller than observed in vacuum. It results probably from adsorption of oxygen or SO_2 on TiO_2 surface. The decomposition of sulfate

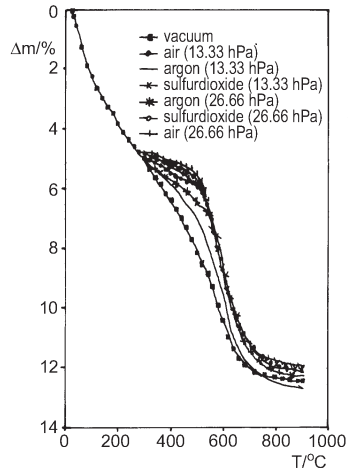


Fig. 2 Thermogravimetric curves of UDT/300 recorded in vacuum and in argon, air and sulfur dioxide atmospheres

groups proceeds in the range of temperatures at which the primary sample has been partly dehydrated and the surface contains vacancies in the coordination shell of Ti^{4+} , non-stoichiometric Ti^{3+} ions, oxygen vacancies and other defects [8] that may become adsorption centers, for molecules occurring in the gas atmosphere. Adsorption of gases results in alteration of the surface TiO_2 layer and may change thermal stability of sulfate and hydroxyl groups.

Effect of gas atmosphere on dehydroxylation and desulfuration kinetics

The results of the studies on kinetics of desulfuration and dehydroxylation of UDT/300 presented in Figs 3–6 show that the kinds of atmosphere gases and their

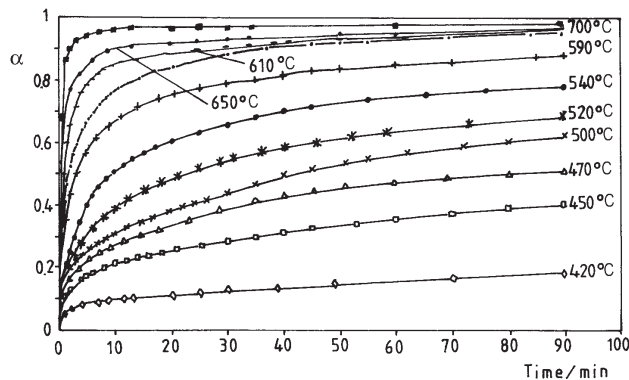


Fig. 3 Kinetic curves of desulfuration of UDT/300 in vacuum

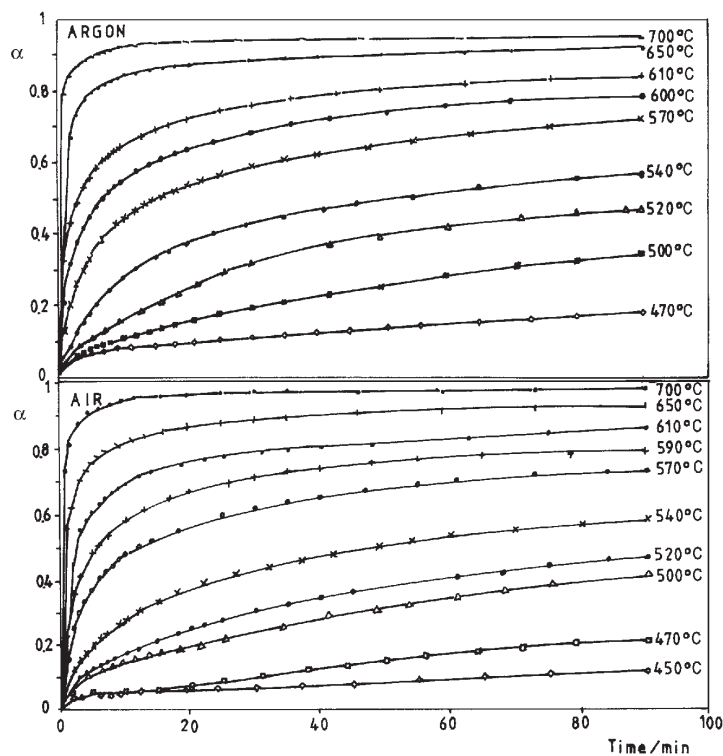


Fig. 4 Kinetic curves of desulfuration of UDT/300 in argon and air atmosphere (13.33 hPa)

pressure have a strong bearing on the course of the process. Kinetic curves of processes carried out in vacuum or under pressures 13.33 hPa argon do not exhibit and evident anomalies, whereas the curves recorded for decompositions under pressures of 26.66 hPa in air and in sulfur dioxide possess local extremes due to simultaneous processes of sample decomposition and adsorption of gases on the TiO_2 surface. A notable feature of the process is that it proceeds mainly on strongly developed solid-gas interface. Hence all factors influencing the structure of the surface layer and the evolution of the porous structure of the sample may have a bearing on the kinetics of the process.

Mathematical description of the kinetics of the process under study is a very complex task. The complexity is a result of simultaneous dehydroxylation and desulfuration of HTD in the temperature region studied and of other processes discussed below.

Our former studies have shown that the decomposition processes are accompanied by recrystallization of the sample material and by sintering of TiO_2 grains. These processes lead to systematic decrease of specific surface from a value of $240 \text{ m}^2 \text{ g}^{-1}$ in a sample calcined at 350°C to $17 \text{ m}^2 \text{ g}^{-1}$ for a product calcined at 700°C , the nature of the changes being dependent also on pressure and composition of the gas atmosphere.

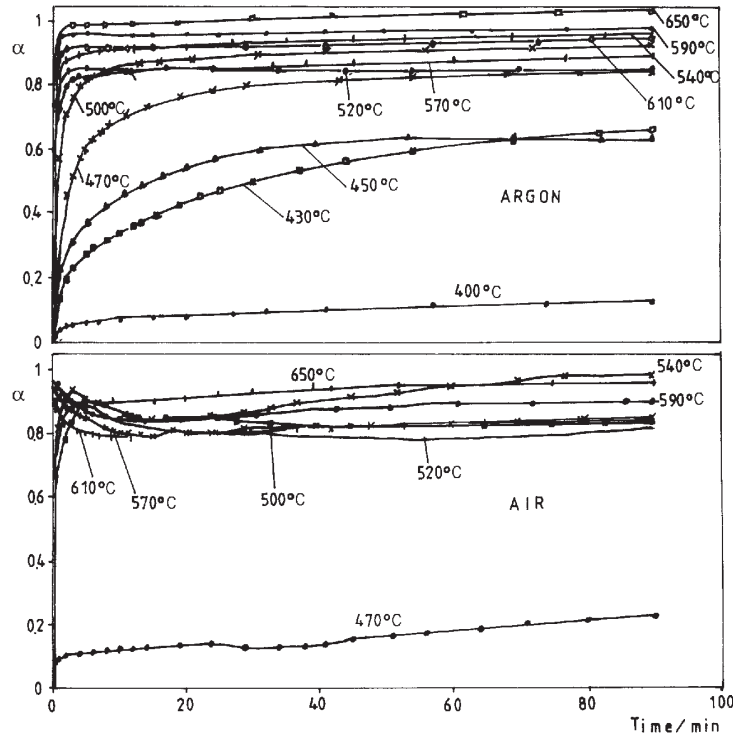


Fig. 5 Kinetic curves of desulfuration of UDT/300 in argon and air atmosphere (26.66 hPa)

The calcination of HTD at temperatures above 300°C, resulting in changes of the sample structure, changes also the conditions of carrying away the gaseous decomposition products from the reaction zone. An additional complication arises from the contribution of free radical reactions in the process of thermal decomposition in presence of light.

It has been found that in the case of thermal decompositions carried out in vacuum or in argon or air at a pressure of 13.33 hPa the kinetic curves obtained in the temperature range tested are best described by the following kinetic equation:

$$\frac{1}{1-\alpha} - 1 = kt$$

The function has been selected basing on statistical criteria and using a program developed by Różycki and Maciejewski [9]. The Arrhenius parameters of the process, namely activation energy and pre-exponential factor, were determined and included in Table 1. Because of the complex nature of the phenomena and reactions occurring one may assume that they give an overall description of the process being investigated.

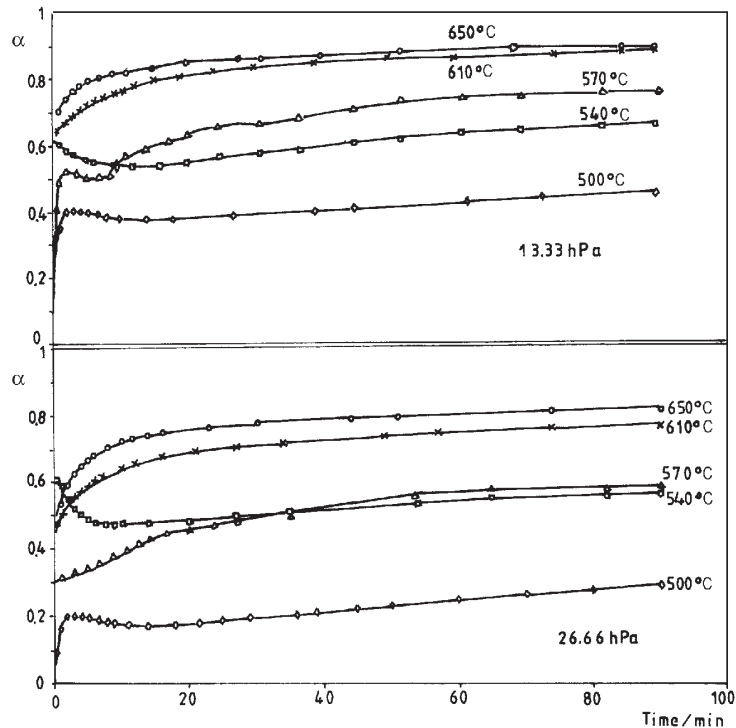


Fig. 6 Kinetic curves of desulfuration of UDT/300 in sulfur dioxide atmosphere

Table 1 Parameters of the Arrhenius equation $k=A\exp(-E/RT)$ calculated by means of the function $g(\alpha) = \frac{1}{1-\alpha} - 1 = kt$ for a process of desulfuration and dehydroxylation in vacuum, in air and in argon

Model	Constant masses		Calculated masses	
	$E_a/\text{kJ mol}^{-1}$	A/min^{-1}	$E_a/\text{kJ mol}^{-1}$	A/min^{-1}
Vacuum				
$g(\alpha)=kt$	107.5	$4.84 \cdot 10^4$	135.9	$5.07 \cdot 10^7$
$g(\alpha)=a+kt$	112.1	$7.06 \cdot 10^5$	144.3	$1.10 \cdot 10^8$
air (13.33 hPa)				
$g(\alpha)=kt$	124.3	$1.90 \cdot 10^6$	146.8	$6.48 \cdot 10^7$
$g(\alpha)=a+kt$	116.3	$4.35 \cdot 10^5$	132.6	$5.95 \cdot 10^6$
argon (13.33 hPa)				
$g(\alpha)=kt$	128.3	$3.09 \cdot 10^6$	131.8	$1.25 \cdot 10^8$
$g(\alpha)=a+kt$	115.3	$3.35 \cdot 10^5$	144.7	$3.18 \cdot 10^7$

No kinetic parameters have been determined for decompositions performed in sulfur dioxide or air atmospheres at 26.66 hPa, since the shape of kinetic curves $\alpha(t)$ was strongly disturbed due to adsorption of the gases on the surface of partly dehy-

drated HTD. An analysis of extreme positions on kinetic curves recorded in the presence of 26.66 hPa air and additional measurements of oxygen adsorption enable to make a supposition that adsorption of oxygen and SO₂ proceeds mostly and is the fastest on active centers left by the hydroxyl groups. A deeper analysis of the effect of kind of atmosphere and its pressure on dehydroxylation and desulfuration of HTD will be feasible after more extensive studies including broader range of gas pressure and precisely determined lightening parameters.

Conclusions

– Thermal decomposition of HTD at temperatures above 300°C comprises a number of processes such as: dehydroxylation, desulfuration, recrystallization, sintering, photochemical phenomena (if the decomposition is carried out for lightened sample) and adsorption of components of gas atmosphere, if the decomposition proceeds in air or in SO₂ atmosphere.

– The kinetic curves of decomposition carried out in vacuum or in atmospheres of air or argon under pressure 13.33 hPa may be described by a kinetic equation $1/(1-\alpha) - 1 = kt$. For the sake of complex nature of phenomena and reactions involved the kinetic parameters determined provide a global characterization of the process.

– Both vacuum and photochemical generation of Ti³⁺ ions and free radical processes (involving OH• radicals) have a substantial effect on the process of dehydroxylation and desulfurization of HTD.

– The kinetic curves of HTD decomposition carried out in the presence of gases capable of being adsorbed on defected TiO₂ surface exhibit a presence of local extremes due to simultaneous processes of decomposition and adsorption components of the gas mixture.

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