

# Mechanism of the Effect of Thermal Treatment on the Formation of Strong Acid Sites in the Surface Layers of Sulfated Metal Oxides

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**Abstract**—Strong acid catalysts were synthesized by the impregnation of hydrated  $\text{ZrO}_2$  and  $\text{TiO}_2$  with sulfuric acid followed by thermal treatment at different temperatures. The surface acidity and crystallochemical characteristics of the catalysts were studied by potentiometry and X-ray diffraction analysis, respectively. It was found that the surface acidity gradually increased as the temperature of thermal treatment was increased from 350 to 600°C for  $\text{SO}_4^{2-}/\text{ZrO}_2$  or to 200°C for  $\text{SO}_4^{2-}/\text{TiO}_2$ ; this increase correlated with the degrees of crystallinity of the samples. A hypothesis was proposed to explain the gradual accumulation of acid sites in the surface layer in the course of thermal treatment. It was assumed that, because of crystallographic changes that caused the weakening or even rupture of  $\text{Zr}-\text{O}-\text{S}$  and  $\text{Ti}-\text{O}-\text{S}$  bonds in modified surface layers, these layers exhibited an enhanced reactivity in contact with water vapor. Subsequently, this resulted in the formation of strongly acidic grafted  $\text{M}-\text{O}-\text{SO}_3-\text{H}^+$  groups.

## INTRODUCTION

Metal oxides ( $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , etc.) modified with sulfate anions are of considerable interest because they exhibit the properties of strong acid catalysts or even solid superacids in the following reactions: the hydration of unsaturated hydrocarbons; esterification and acylation; the alkylation of aromatic compounds; and, what is most important, the low-temperature isomerization and cracking of paraffins [1–3]. It is well known that the synthesis of these materials consists in the impregnation of corresponding hydrated metal oxides with small amounts of  $\text{H}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  followed by drying and calcination in air at elevated temperatures (500–700°C).

At the same time, although a great number of studies were performed with the use of various physicochemical techniques, the mechanism of formation of strong acid sites on the surface of sulfated metal oxides remains unclear.

Thus, as early as 1979, Hino *et al.* [1] described the high catalytic activity of sulfated oxides and explained the appearance of superacid sites on the surface of  $\text{ZrO}_2$  by the strong inductive effect of  $\text{SO}_4^{2-}$  anions on the ability of Zr atoms for the coordination bonding of water. According to Hino *et al.* [1], this water exhibited the properties of Brønsted acid sites. Komarov and Sinilo [4] studied the nature of the catalytic activity of sulfated  $\text{ZrO}_2$  using IR spectroscopy and gravimetry; they concluded that the strong acceptor  $\text{SO}_4^{2-}$  anions play a crucial role in the formation of surface acidity.

Clerfield *et al.* [5] related the acidity of  $\text{SO}_4^{2-}/\text{ZrO}_2$  catalysts to the formation of bridging sulfate groups. Based on IR-spectroscopic data, Kustov *et al.* [6] and Morterra *et al.* [7] made a conclusion that strong acid sites on the surface are protons bound to sulfate groups, which is consistent with published data [8].

In this work, potentiometric titration and X-ray diffraction analysis were used to develop the concept of the generation of strong acid sites on the surfaces of sulfated  $\text{ZrO}_2$  and  $\text{TiO}_2$  due to crystallochemical changes in near-surface layers in the course of crystallization as the temperature of thermal treatment was increased. In this case, published data [2, 3, 9] were taken into consideration. In these publications, the formation of Brønsted acid sites on sulfated  $\text{ZrO}_2$  and  $\text{TiO}_2$  samples was directly related to the crystallization; that is, to the formation of a tetragonal form in the case  $\text{ZrO}_2$  and an anatase structure in the case of  $\text{TiO}_2$ .

Potentiometric titration is the most informative and convenient technique for studying the acidity of surface functional groups. Potentiometry is a classical technique for determining the  $\text{pK}$  values of acids and bases in solutions. It is also widely used for evaluating the acidity of cation-exchange resins, which are solid acids in chemical nature; in the course of ion-exchange sorption they can substitute various cations for the protons of surface functional groups [10, 11]. However, there is no published data on the potentiometric studies of the sulfated hydroxides of polyvalent metals.

The hydrated oxides  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  are typical inorganic amphotolytic ion exchangers, which

exhibit the properties of anion exchangers at low pH values and of solid acids (cation exchangers) in neutral or alkaline solutions. Potentiometric titration was used for evaluating the acidity of surface hydroxyl groups in rutile and anatase [11–13] and the acidity of hydrated iron and zirconium oxides [12, 14]. Thus, the appearance of strong Brønsted acid sites on the surfaces of oxides modified with sulfate ions [2, 3, 9] will primarily manifest itself in potentiometric titration curves.

To determine the role of crystallization processes in the formation of surface acid sites, hydrated zirconium and titanium oxides were synthesized and the potentiometric titration curves of these samples were obtained after modification with sulfuric acid followed by calcination in air at different temperatures.

## EXPERIMENTAL

To prepare the oxides  $\text{ZrO}_2$  and  $\text{TiO}_2$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and  $\text{TiCl}_4$  salt solutions (0.4 M) and equivalent amounts of a 6 M  $\text{NH}_4\text{OH}$  solution were used. The reaction mixtures were stirred for 5 h at room temperature. Next, the resulting precipitates were filtered off and washed with hot demineralized water to remove excess salt. After drying at 120°C for 10 h, the samples were impregnated with a 0.5 M  $\text{H}_2\text{SO}_4$  solution (30 ml/g of a corresponding oxide) and then calcined in air for 5 h at temperatures from 200 to 600°C. According to elemental analysis data, the sulfur contents of the  $\text{ZrO}_2$  and  $\text{TiO}_2$  samples calcined in air at 350°C were 2.8 and 3.5%, respectively.

The individual sample method, which was described in detail elsewhere [15], was used in the potentiometric titration. The pH measurements were performed using an OP-211/1 pH meter (Hungary). Equal volumes (20 ml) of a solution containing 10 ml of a supporting electrolyte (0.2 N NaCl) and different amounts of a titrant (0.1 N NaOH or HCl) were added to each of the test samples. A blank experiment (without a test sample) was performed analogously. Potentiometric titration curves are usually plotted on the equilibrium solution pH–titrant volume added coordinates. In this study, the pH dependence of the amount of absorbed ions ( $\text{Na}^+$  or  $\text{Cl}^-$ ) was analyzed, which is more illustrative. The adsorption of  $\text{Na}^+$  or  $\text{Cl}^-$  ions ( $A$ , mg-equiv/g) was determined from the equation

$$A = \frac{\Delta VC}{m},$$

where  $m$  is the sample weight, g;  $C$  is the titrant concentration, mg-equiv/l; and  $\Delta V$  is the difference between titrant volumes in the blank experiment and in the experiment with a sample at a given equilibrium pH value (this difference was determined graphically). In this case, the value of  $A$  was taken equivalent to the sur-

face concentration of exchange protons ( $\text{OH}^-$  anions) at the equilibrium pH value measured.

The X-ray diffraction spectra were recorded on a DRON-3 diffractometer (Burevestnik, St. Petersburg) in a discrete mode (scanning step of 0.05°; exposure time of 3–5 s) using  $\text{CuK}_\alpha$  radiation (voltage of 30 kV; anode current of 20 mA).

## RESULTS

**$\text{ZrO}_2$  modified with  $\text{H}_2\text{SO}_4$ .** Figure 1a demonstrates the potentiometric titration curves of initial  $\text{ZrO}_2$  and the samples modified with  $\text{H}_2\text{SO}_4$  and then calcined at 350, 400, 500, and 600°C. It can be clearly seen that the initial hydrated  $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$  (predried at 120°C for 3 h) sorbed  $\text{Cl}^-$  anions at  $\text{pH} < 5$  (titration with HCl) and  $\text{Na}^+$  anions at  $\text{pH} > 5$  (titration with NaOH); that is, the isoelectric point of this inorganic amphotelyte lies at  $\text{pH} \sim 5$ , which is consistent with published data [12, 16].

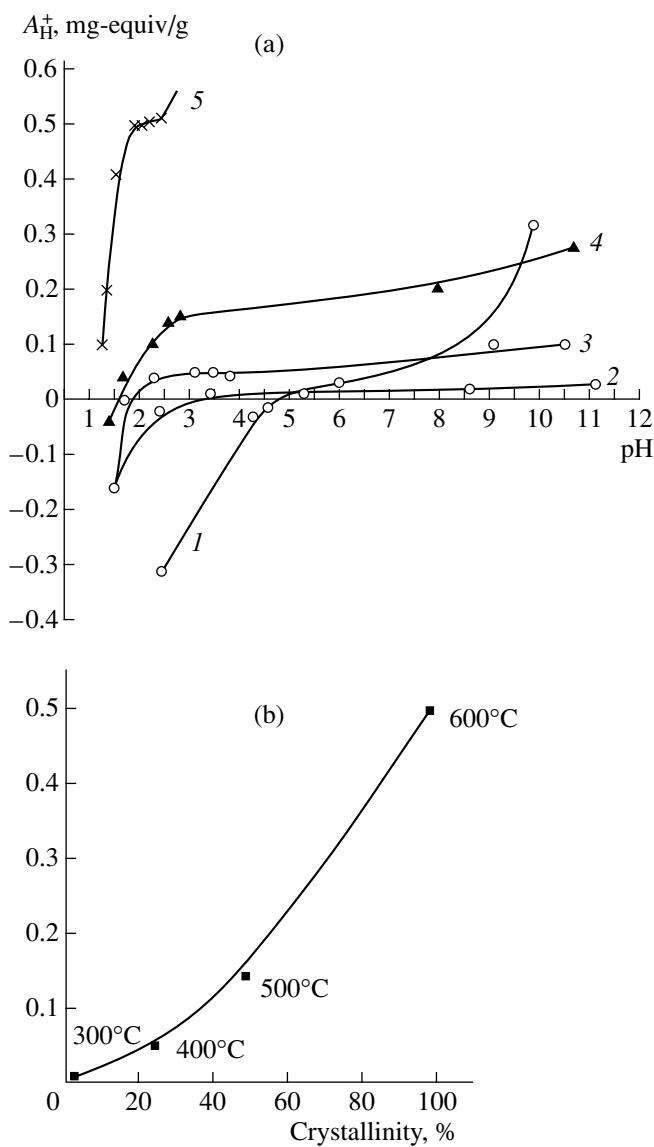
Note that the minimum temperature of thermal treatment (350°C) was chosen with consideration for the fact that  $\text{H}_2\text{SO}_4$  decomposes at 300°C; that is, the samples calcined at  $T \geq 350^\circ\text{C}$  were free of impurity  $\text{H}_2\text{SO}_4$  unreacted with the oxides.

It can be clearly seen that the acidic function was practically absent from the sample of  $\text{SO}_4^{2-}/\text{ZrO}_2$  calcined at 350°C because it scarcely sorbed cations, sorbed anions to a much lesser extent (than the initial sample), and its isoelectric point was at  $\text{pH} \sim 3$ .

The calcination of  $\text{SO}_4^{2-}/\text{ZrO}_2$  at higher temperatures gradually increased (as  $T$  was increased up to 600°C) the acidity of the samples. In this case, the isoelectric points of the  $\text{SO}_4^{2-}/\text{ZrO}_2$  samples calcined at 400 and 500°C was at  $\text{pH} \sim 1.7$ , whereas it was at  $\text{pH} \sim 1.3$  for the sample calcined at 600°C. The cation-exchange capacity for this pH value was as high as  $\sim 0.5$  mg-equiv/g. This high cation-exchange capacity at  $\text{pH} \sim 1.3$ , as well as the shape of the potentiometric titration curve, unambiguously indicate that the  $\text{SO}_4^{2-}/\text{ZrO}_2$  sample calcined at 600°C was a very strong acid (however, probably not a superacid) with  $\text{p}K_a \sim 1.3$ .<sup>1</sup>

The X-ray diffraction patterns of the initial samples and the samples calcined after treatment with  $\text{H}_2\text{SO}_4$  suggest that the partial crystallization of the samples began at only 400°C, which is consistent with published data [9]. The initial sample and the sample of  $\text{SO}_4^{2-}/\text{ZrO}_2$  (350°C) were X-ray amorphous. Figure 2 demonstrates the typical X-ray diffraction patterns of

<sup>1</sup> According to Helfferich [10], the value of pH approximately corresponds to the value of  $\text{p}K_a$  for half of the capacity of ion-exchange sites of the same type.



**Fig. 1.** (a) Potentiometric titration curves of ZrO<sub>2</sub> samples treated with H<sub>2</sub>SO<sub>4</sub> and calcined at different temperatures,  $T$ , °C: (1) initial sample, (2) 350, (3) 400, (4) 500, and (5) 600. Supporting electrolyte: 0.1 N NaCl. (b) The concentration of strong acid sites (at pH 2.5) as a function of the degree of crystallinity of ZrO<sub>2</sub>/SO<sub>4</sub> samples.

the initial sample and the samples of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (400, 500, and 600°C). These diffraction patterns indicate that an almost completely crystallized tetragonal modification of ZrO<sub>2</sub> was formed at 600°C. Figure 1b also demonstrates the concentration of surface acid sites in the samples of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> (the cation-exchange capacity at pH 2.5) as a function of the calculated degree of crystallinity of the samples. The parabolic function obtained unambiguously indicates a direct correlation between the appearance of strongly acidic functional groups on the surface of SO<sub>4</sub><sup>2-</sup>/ZrO<sub>2</sub> and its crystallization, which is consistent with published data [9, 17].

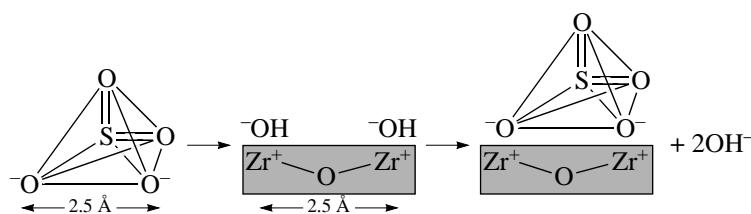
**TiO<sub>2</sub> modified with H<sub>2</sub>SO<sub>4</sub>.** In the case of TiO<sub>2</sub>, a somewhat different behavior was observed (Fig. 3). Along with hydrated ZrO<sub>2</sub>, the initial TiO<sub>2</sub> was found to be an amphotelyte with an isoelectric point at pH ~ 8, which is consistent with published data [11–13]. At the same time, the potentiometric titration curves of samples calcined at 300, 400, and 450°C practically coincided. These results indicate that TiO<sub>2</sub> modified with H<sub>2</sub>SO<sub>4</sub> is also a sufficiently strong acid with  $pK_a \sim 1.4$ . The cation-exchange capacity of this strong solid acid at pH 2.5 is also sufficiently high and amounts to ~0.65 mg-equiv/g. As the temperature of calcination was increased to 550°C, the cation-exchange capacity of this material halved; this was most likely due to the thermal degradation of surface sulfated complexes.

The shapes of the curves in Fig. 3, as well as the concept developed in this work, demonstrate that the formation of strong acid sites on sulfated TiO<sub>2</sub> was complete at temperatures lower than 300°C.

The X-ray diffraction analysis of the synthesized samples suggests that the samples calcined with sulfuric acid even at 300°C were crystalline (anatase) because of easier crystallization of amorphous TiO<sub>2</sub> impregnated with H<sub>2</sub>SO<sub>4</sub> as compared with the corresponding amorphous ZrO<sub>2</sub> [9, 17].

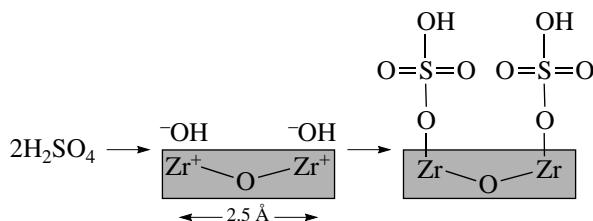
## DISCUSSION

The results obtained using potentiometry and X-ray diffraction analysis are in qualitative agreement with published data [2, 3, 9, 17]. They unambiguously indicate that the appearance of strong Brønsted acid sites on the surfaces of sulfated disperse ZrO<sub>2</sub> and TiO<sub>2</sub> oxides is directly related to the crystallization in the course of calcination. At the same time, to reveal the reasons for this interrelation, the mechanism of sorption of SO<sub>4</sub><sup>2-</sup> ions on the initial hydrated oxides and the corresponding structural and chemical transformations in the surface layers of sulfated samples in the course of calcination should be considered in detail. In particular, both the molecular structure of SO<sub>4</sub><sup>2-</sup> anions and the crystal chemistry of the hydrated oxide surfaces should be taken into consideration. Thus, the distance between oxygen atoms in the tetrahedral SO<sub>4</sub><sup>2-</sup> anion is 2.52 Å [18]. The atoms of Ti and Zr and, consequently, the OH<sup>-</sup> groups bound to them occur at approximately the same distance on the surface of amorphous hydrated Zr and Ti oxides. In my opinion, this circumstance is responsible for a favorable structural conformity in the anion-exchange sorption of SO<sub>4</sub> on the surfaces of hydrated ZrO<sub>2</sub> and TiO<sub>2</sub>. That is, two neighboring OH<sup>-</sup> anions are mainly replaced by a doubly charged SO<sub>4</sub><sup>2-</sup> anion (Scheme 1); this can be conditionally designated as doubly charged substitution.



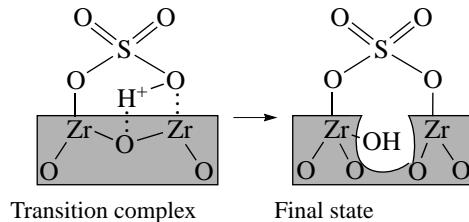
In the production of superacids, the surface modification of amorphous  $\text{ZrO}_2$  and  $\text{TiO}_2$  with sulfuric acid takes place in the same manner except that the reaction results in the release of two  $\text{H}_2\text{O}$  molecules.

Of course, structural unconformities, which exclude the “ideal” occurrence of reactions in accordance with Scheme 1, are possible in the presence of surface defects. That is, singly charged substitution is also possible (Scheme 2).



Scheme 2.

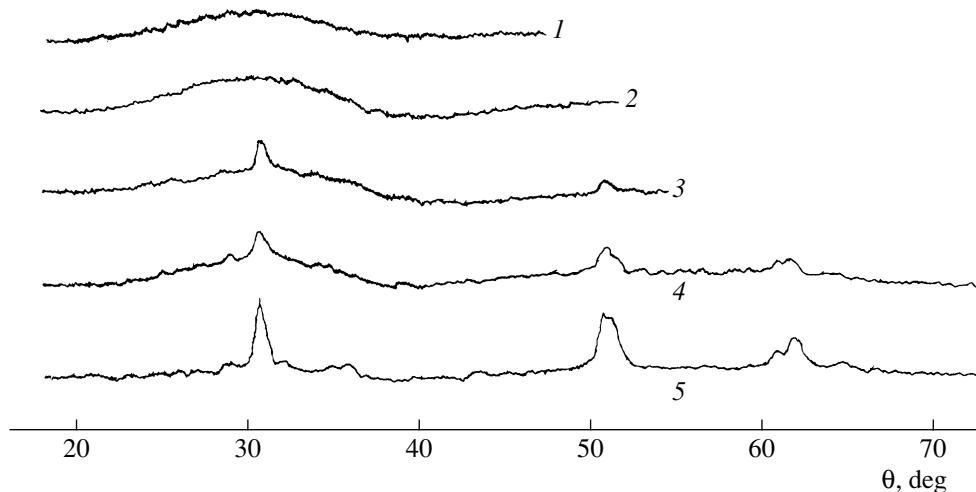
However, as the temperature is increased, surface hydrosulfonate groups, which were formed in accordance with Scheme 2, cleave neighboring  $\text{Zr}-\text{O}-\text{Zr}$  bonds to form ultimately the same bridging groups of doubly charged substitution (Scheme 3).



Scheme 3.

Schemes 1 and 3 explain the run of curve 2 in Fig. 1a, which suggests the absence of strongly acidic groups from the surface upon calcination at  $350^\circ\text{C}$ .

It is well known that freshly formed amorphous  $\text{TiO}_2$  and  $\text{ZrO}_2$  dissolve in sulfuric acid; this implies the occurrence of the process through the stage of elementary acts in accordance with Scheme 3. Naturally, in the synthesis of superacids, a portion of  $\text{H}_2\text{SO}_4$  molecules cleave near-surface  $\text{M}-\text{O}-\text{M}$  bonds in accordance with Scheme 3. The near-surface layer of a particular thickness containing sulfate (Scheme 1) or hydrosulfonate (Scheme 2) groups is formed depending on the acid amount used. Moreover, it is likely that this process can explain an increase in the surface area of sulfated samples in the course of thermal treatment, which was observed by Arata [9].

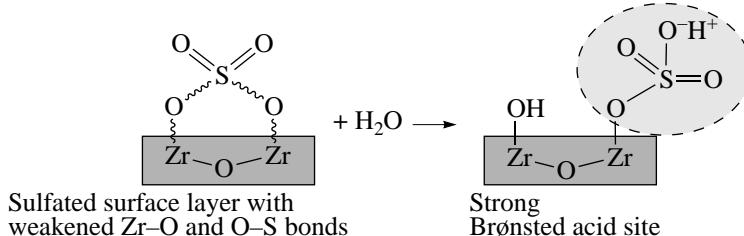


**Fig. 2.** X-ray diffraction patterns of  $\text{ZrO}_2$  samples treated with  $\text{H}_2\text{SO}_4$  and calcined for 2 h at different temperatures,  $T$ ,  $^\circ\text{C}$ : (1) initial sample, (2) 350, (3) 450, (4) 500, and (5) 600.

Taking into account the above considerations, let us discuss special features of crystallization in surface-sulfated oxides responsible for the appearance of strong Brønsted acid sites.

It is well known that the recrystallization or crystallization of amorphous materials begins at an interface; at structural defect sites; or on the surface, which is also a defect of a crystal lattice or amorphous material. In the sulfation of a surface (Scheme 1) or in the formation of a sulfated near-surface layer (Schemes 2, 3), the process of crystallization is hindered, as was actually observed experimentally [9, 17]. However, this process begins at higher temperatures because it most likely

arises in the bulk of particles (at sites that are free of sulfo groups); hence, it is hindered. A lattice rearrangement that occurs in this case has a significant effect on the crystal chemistry of a sulfated near-surface layer. Namely, the process of crystallization, which develops from the bulk of particles, inevitably displaces Zr and Ti atoms bound to the surface and near-surface sulfo groups (Schemes 1, 3). In turn, this causes either cleavage or stress (weakening) of Zr–O–S and Ti–O–S bonds. Finally, the formation of strongly acidic hydro-sulfate groups (Brønsted sites), which have highly active protons [6], takes place in contact with water vapor (on calcination in air) (Scheme 4).



Scheme 4.

The runs of curves 3–5 in Fig. 1a, as well as data shown in Fig. 2, clearly demonstrate the evolution of crystallization processes in sulfated  $\text{ZrO}_2$  and the formation of strong acid sites, which is associated with crystallization.

$\text{TiO}_2$  begins to crystallize at much lower temperatures than  $\text{ZrO}_2$ . Therefore, the potentiometric titration curves of  $\text{TiO}_2$  samples calcined at 300, 400, and 450°C after impregnation with  $\text{H}_2\text{SO}_4$  practically coincide

because the crystallization was complete at 150–200°C. A sample of  $\text{TiO}_2$  calcined at 150°C was washed to remove excess  $\text{H}_2\text{SO}_4$ ; thereafter, its potentiometric titration curve was constructed. The run of curve 4 in Fig. 3 indicates that hydrosulfate groups grafted to the surface of  $\text{TiO}_2$  did not degrade in the course of washing with water (cf. Scheme 2); in this case, strong Brønsted acid sites were also formed.

Thus, sulfated samples were synthesized by the impregnation of hydrated  $\text{ZrO}_2$  and  $\text{TiO}_2$  with sulfuric acid. The development of the surface Brønsted acidity in the course of their crystallization during thermal treatment in air at 150–600°C was studied in detail with the use of potentiometric titration.

A mechanism was proposed and experimentally substantiated for the formation of strong Brønsted sites. This mechanism is based on the concept that, in the course of the hindered crystallization of sulfated samples, the surface Zr–O–S and Ti–O–S bonds undergo cleavage, deformation, and weakening, which are responsible for their enhanced reactivity toward water vapor with the formation of the strongly acidic hydro-sulfate groups  $\text{M}-\text{O}-\text{SO}_3^-\text{H}^+$  on the surface.

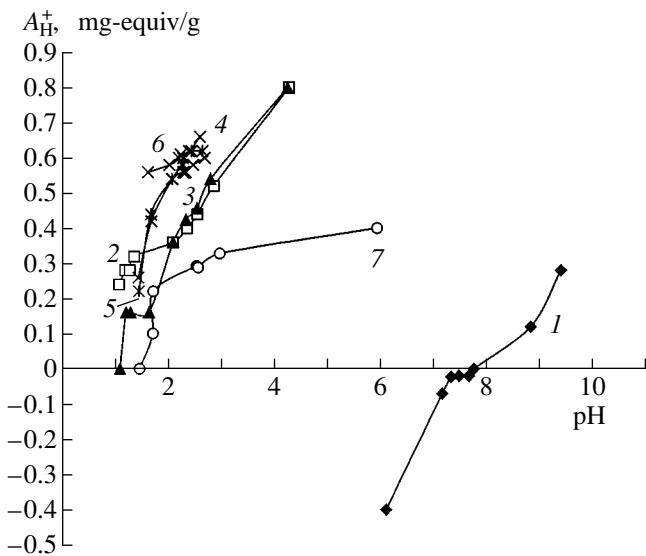


Fig. 3. Potentiometric titration curves of  $\text{TiO}_2$  samples treated with  $\text{H}_2\text{SO}_4$  and calcined at different temperatures,  $T$ , °C: (1) initial sample, (2) 150, (3) 200, (4) 300, (5) 400, (6) 450, and (7) 550. Supporting electrolyte: 0.1 N  $\text{NaCl}$ .

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