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Study of the Formation Features of the Active State in Supported Pt/TiO₂ CO Oxidation Catalysts Doped with Alumina

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Abstract

The anatase phase of titanium dioxide TiO₂ is metastable and irreversibly converts to rutile at a temperature above 700 °C. This is accompanied by a significant decrease in the specific surface area and a change in the porous structure. Modification of titanium dioxide by the addition of alumina leads to the formation of the nanocrystalline structure of anatase and to a significant increase in the temperature of anatase to rutile phase transition up to 950 °C. After high-temperature annealing, the Al₂O₃-TiO₂ sample is characterized by a higher specific surface area and a better developed porous structure than those of pure anatase with the regular crystal structure. The high thermal stability of the anatase phase in supported Pt/(Al₂O₃-TiO₂) catalysts under calcination provides a high dispersion of platinum particles, which leads to the rather high catalytic activity of these catalysts in CO oxidation.

Keywords: anatase, rutile, alumina, nanocrystalline structure, CO oxidation

INTRODUCTION

Titanium dioxide of anatase modification is widely used as an adsorbent, photocatalyst for detoxication of hazardous organic impurities in the air and water [1–4], as supports in supported metal and oxide catalysts used in various processes of heterogeneous catalysis, and as sensors [5–8]. These kinds of applications are mainly due to the fact that anatase possesses highly developed specific surface area and developed porous structure. At the same time, the anatase modification of TiO₂ is metastable and is irreversibly transformed into rutile with temperature rise to 700–750 °C, which causes changes in the crystal structure, substantial decrease in specific surface area and, as a consequence, worsening of the catalytic properties of catalysts supported in TiO₂ [8–12].

The method of titanium dioxide preparation and its modification with the additives of some

elements have a substantial effect on the temperature of the phase transition of anatase into rutile. It is demonstrated that the addition of small amounts of silicon dioxide into titanium dioxide at the stage of preparation causes a substantial increase in the temperature of the phase transition of anatase into rutile [13–19]. It was established that with the use of initially temperature-resistant modifying compounds, such as cerium or yttrium oxides, the thermal stability of the anatase phase increases, too. In this situation, the method of preparation should exclude the formation of oxide cerium-titanium or yttrium-titanium compounds under the chosen conditions of thermal treatment [20, 21].

The authors of [22–24] studied the formation of the Al₂O₃-TiO₂ system obtained using the sol-gel method. It was demonstrated that in the region of high concentrations of aluminium oxide, aluminotitanium compounds are formed during annealing. In the region close to the equimolar

component ratio, aluminium oxide particles get agglomerated on the surface area of TiO_2 particles up to their complete encapsulation thus preventing agglomeration. This promotes an increase in the temperature of the phase transition of anatase into rutile and the specific surface area of the system. With high TiO_2 concentrations, a sample with low specific surface area is formed.

The goal of the present work was to study the effect of the addition of aluminium oxide on the thermal stability of titanium dioxide with anatase structure and the catalytic properties of supported catalysts $\text{Pt}/(\text{Al}_2\text{O}_3-\text{TiO}_2)$ obtained on its basis, in the oxidation of CO.

EXPERIMENTAL

Methods of the preparation of supports and catalysts

The samples of titanium dioxide modified with Al_2O_3 additive in the amount of 1–10 mass % were synthesized by impregnating over the water-absorbing capacity of TiO_2 xerogel obtained according to the industrial sulphuric technology [25], with the solution of tert-butyl aluminium, followed by drying and annealing in the air under temperature variation within the range 200–1000 °C for 4 h. Supported $\text{Pt}/(\text{Al}_2\text{O}_3-\text{TiO}_2)$ catalysts were prepared by impregnating over the water-absorbing capacity of the obtained supports annealed at 500 °C in the air, with the solution of platinum nitrate, subsequent drying and thermal treatment in the air at a temperature of 500 or 750 °C for 2 h. Platinum content in the catalysts was fixed at 1 mass %.

Methods of investigation

Analysis of the chemical composition of catalysts was carried out by means of atomic emission spectrometry with inductively coupled plasma with the help of an Optima 4300 DV spectrometer (PerkinElmer, USA).

Specific surface area of the samples (S_{sp}) was measured by means of argon thermodesorption at 77 K using a Sorbi-M instrument (LC META, Russia) over four points of sorption equilibrium. The porous structure of the samples was studied using a traditional method of low-temperature (77.4 K) nitrogen adsorption with the help of a DigiSorb-2600 instrument (Micromeritics, USA).

Phase analysis (XRD) was carried out using a D8 Advance diffractometer (Bruker, Germany) with monochromatic CuK_α -radiation within the

range $2\theta = 15\text{--}90^\circ$. Coherent scattering domain size (D_{CSD}) for anatase was determined according to Sherrer equation using the half-width of the diffraction peak (200) [26]. The parameters of TiO_2 lattice were refined by least mean squares method using the Polikristall software [27] with 3–7 lines depending on the degree of separation of the diffraction peaks within the angle range $50\text{--}70^\circ$ over 2θ .

Studies by means of scanning electron microscopy (SEM) were carried out with a JEM 2010 instrument (JEOL, Japan) with the resolution of 1.4 Å and accelerating voltage 200 kV. The elemental analysis of the samples was carried out using dispersive spectroscopy (EDX) with a microanalytical attachment with energy dispersive EDAX DX-4 detector (Ametek Inc., USA). The area of the region under analysis was 100 nm², the sensitivity of element detection was 0.1 mass %.

The state of platinum was studied by means of X-ray photoelectron spectroscopy (XPS). The spectra were recorded with a photoelectron spectrometer SPECS (SPECS GmbH, Germany) with AlK_α -radiation ($h\nu = 1486.6$ eV, 205 W). The scale of bonding energies (E_b) was calibrated over the peaks of the core levels of metal gold and copper: $\text{Au}4f_{7/2}$ (84.0 eV) and $\text{Cu}2p_{3/2}$ (932.67 eV). All spectra were recorded with the energy of analyzer transmission 20 eV with a step of 0.1 eV. Deconvolution of the photoelectron peaks of $\text{Pt}4f$ into separate components was carried out using the XPSPeak 4.1 software [28] subtracting the background according to Shirley's method [29]. The contours of peaks were approximated by Gaussian and Lorentzian functions, and the constant of spin-orbital splitting was 3.35 eV.

The catalytic properties of samples in the oxidation of CO were studied with the help of the flow-circulation set-up BI-CATr(oxy) (Russia) with the catalyst fraction 0.25–0.5 mm. The composition of the reaction mixture was: 1 vol. % CO, 10 vol. % O_2 , and the rest was N_2 . The rate of reaction mixture input was $4.46 \cdot 10^{-3}$ mol/min. The reaction mixture was heated to the necessary temperature with the rate of 1.7 °C/min, which allowed us to exclude the errors connected with non-uniform heating of the catalyst. The rate of circulation of the reaction mixture was 1000 L/h, which provided the mode of complete mixing (with no thermal and concentration gradients in the catalyst layer).

The composition of the initial and resulting reaction mixture was analyzed by means of chromatography. The activity of catalysts was characterized by the temperature at which a

50 % conversion of CO is achieved (T_{50}). Conversion values were determined from the curve of conversion dependence on temperature.

RESULTS AND DISCUSSION

Formation of titanium dioxide modified with aluminium oxide additive

The XRD data on titanium dioxide modified with aluminium oxide depending on the temperature of its annealing are presented in Table 1. The anatase phase is conserved in non-modified titanium dioxide during annealing at a temperature of 700 °C, while rutile admixture is detected along with anatase when temperature is increased to 750 °C. Modification of titanium dioxide with aluminium oxide results in a substantial increase in the thermal stability of anatase. For instance, in the samples containing less than 10 mass % of Al₂O₃, only anatase phase is observed during annealing up to 950 °C. In the samples containing 10–15 mass % Al₂O₃, anatase

phase and the traces of Al₂O₃ are observed at this annealing temperature. It should be noted that the unit cell parameters of anatase in all the samples do not change after modification with aluminium oxide and are equal to: $a = 0.3787$ nm and $c = 0.9524$ nm. On this basis, we may assume that the solid solution of Al₂O₃ in TiO₂ with anatase structure is not formed.

The electron microscopic image of the initial titanium dioxide xerogel is shown in Fig. 1, *a*. One can see that the sample is composed of fine anatase particles 3–6 nm in size, loosely packed in coarse aggregates about 100 nm in size. After annealing at a temperature of 500 °C, TiO₂ is a well ordered anatase structure with particle size 20–50 nm (see Fig. 1, *b*). One can see in Fig. 1, *c* that the modification of titanium dioxide by the addition of aluminium oxide leads to the formation of nanocrystalline anatase structure composed of irregularly accreted anatase particles 5–6 nm in size, with the formation of interblock boundaries between them, where the clusters of aluminium oxide are likely to be stabilized. As a consequence,

TABLE 1

Effect of the temperature of annealing of TiO₂ modified with Al₂O₃ additive on the phase composition

Chemical composition, mass %	Phase composition			
	Annealing temperature, °C			
	350	500–600	750	950
100 TiO ₂	Anatase	Anatase	Anatase, rutile	Rutile
1 % Al ₂ O ₃ –99 % TiO ₂	«	«	Anatase	Anatase
3 % Al ₂ O ₃ –97 % TiO ₂	«	«	«	«
5 % Al ₂ O ₃ –95 % TiO ₂	«	«	«	«
10 % Al ₂ O ₃ –90 % TiO ₂	«	«	«	Anatase + Al ₂ O ₃ traces
15 % Al ₂ O ₃ –85 % TiO ₂	«	«	«	«

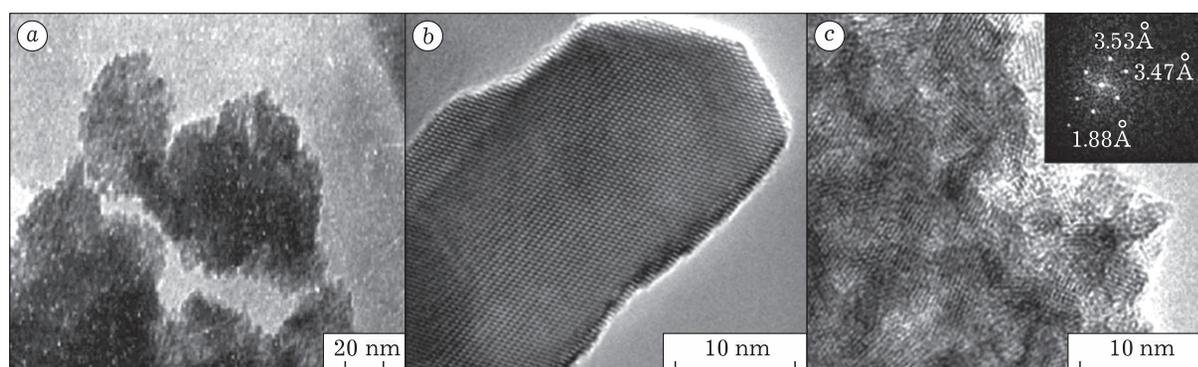


Fig. 1. High-resolution electron microscopic images of the samples of initial TiO₂ xerogel (*a*); non-modified TiO₂ annealed at 500 °C (*b*); 5 mass % Al₂O₃–95 mass % TiO₂ annealed at 500 °C, and its Fourier image with the indication of interplanar distances of anatase in the insert (*c*).

anatase structure is strongly disordered in the region of interblock boundaries. The nanocrystal structure of anatase is conserved during annealing of these samples at a temperature of 750 and 950 °C, but the size of anatase crystallites increases to 10–15 and 30–40 nm, respectively.

It was established in [12, 30–33] that the temperature of the phase transition of anatase into rutile is to a high extent dependent on the size of anatase crystals. It was demonstrated that

the initial size of anatase particles affects the temperature of the phase transition from anatase into rutile. It is stated on the basis of thermodynamic evaluation that anatase modification is thermodynamically more stable in nanometer-sized TiO_2 with particle size 15–45 nm (depending on the content of micro-impurities), and rutile modification becomes more stable with a further increase in the size of anatase crystals. On the basis of these data and the results obtained in our work, we may assume that an increase in the temperature of anatase to rutile phase transition caused by titanium dioxide modification by adding aluminium oxide is explained by the formation of nanocrystalline anatase structure in which the size of anatase particles at a temperature of 950 °C does not reach the critical value determining the phase transition of anatase into rutile.

Modification of titanium dioxide by adding aluminium oxide affects also the type of the dependence of specific surface area and the size distribution of pore volume on calcination temperature (Fig. 2, 3). With an increase in temperature, the specific surface area of pure titanium dioxide decreases more sharply in comparison with the samples modified with aluminium oxide, which is due to the higher dispersion of anatase particles. With an increase in the content of aluminium oxide, the size of anatase particles in annealed samples decreases, which promotes an increase in specific surface

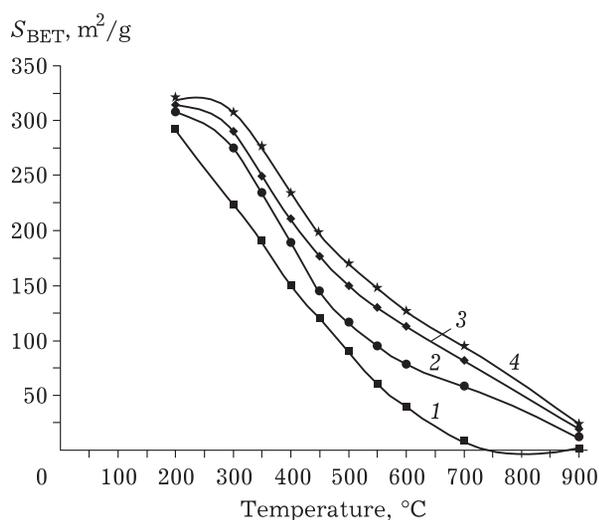


Fig. 2. Dependence of specific surface area (S_{BET}) on annealing temperature for samples: non-modified TiO_2 (1), 1 mass % Al_2O_3 –99 mass % TiO_2 (2), 5 mass % Al_2O_3 –95 mass % TiO_2 (3), 7 mass % Al_2O_3 –93 mass % TiO_2 (4).

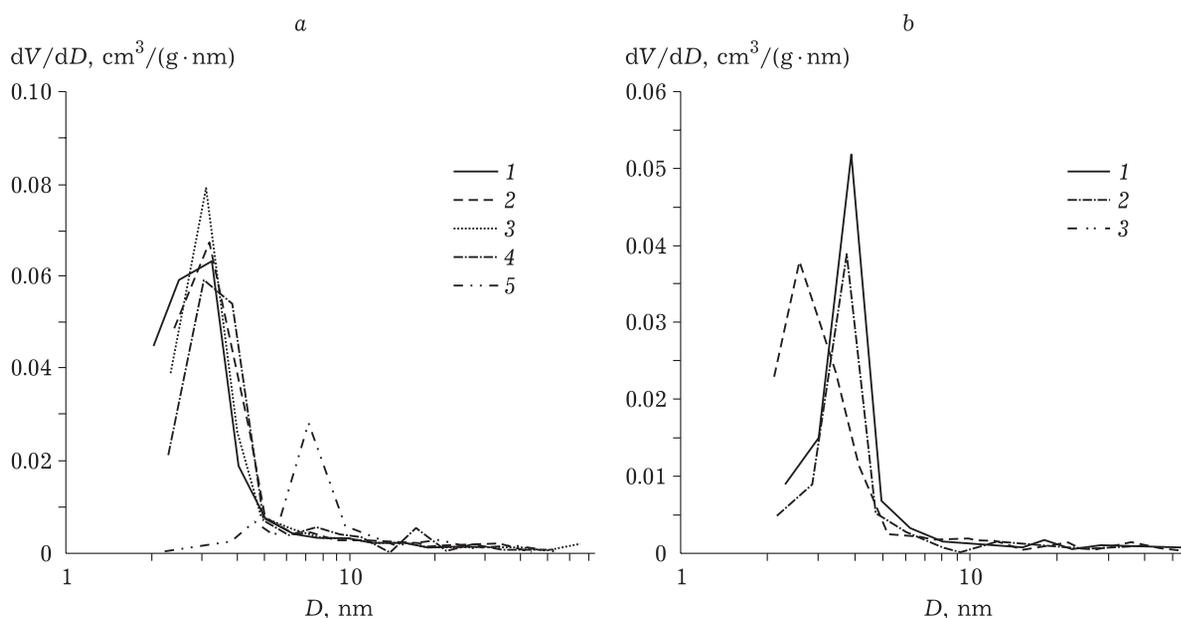


Fig. 3. Pore size distribution for samples: a – “pure” TiO_2 annealed at a temperature of 350 (1), 450 (2), 500 (3), 550 (4) and 700 °C (5); b – 5 mass % Al_2O_3 –95 mass % TiO_2 annealed at 350 (1), 500 (2) and 800 °C (3).

area. For “pure” titanium dioxide, an increase in annealing temperature to 700 °C leads to an increase in prevailing pore size from 3 nm to 7–10 nm. In the case of titanium dioxide modified with aluminium oxide, the average pore size remains at a level of 3–4 nm with an increase in the temperature of thermal treatment to 800 °C. Therefore, the support has anatase structure and is characterized by rather developed pore structure at so high annealing temperature.

Physicochemical and catalytic properties of Pt/(Al₂O₃-TiO₂) catalysts

Supports containing non-modified TiO₂, with the composition 5 mass % Al₂O₃-95 mass % TiO₂ and 10 mass % Al₂O₃-90 mass % TiO₂ with anatase structure were used to prepare supported catalysts Pt/(Al₂O₃-TiO₂). According to XRD data, catalysts obtained on the basis of TiO₂ modified with Al₂O₃ additive represent anatase phase after annealing at 500 and 750 °C. The catalyst obtained on the

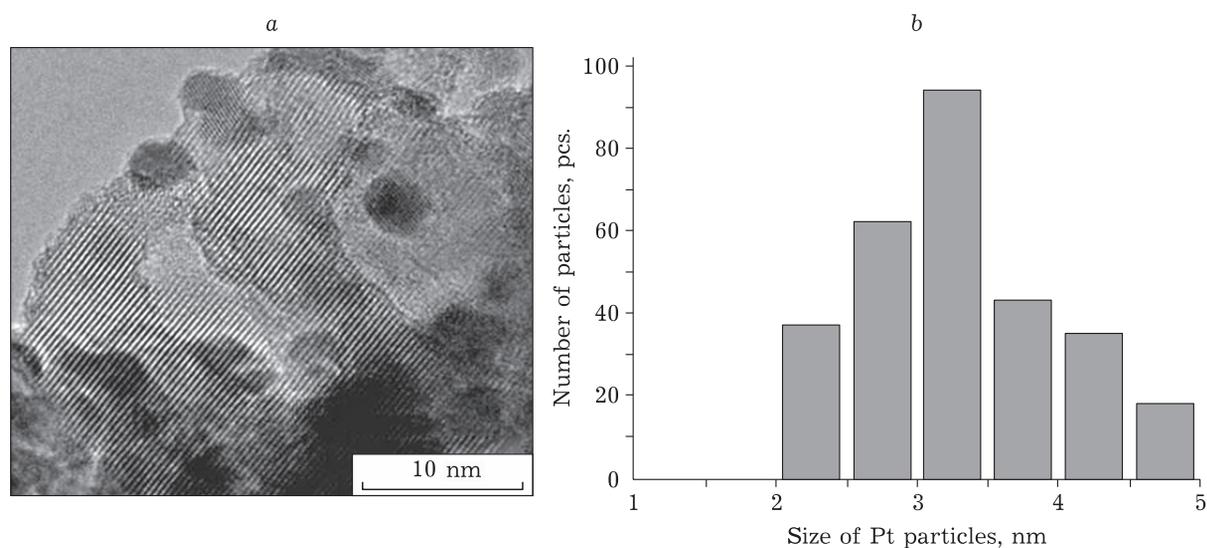


Fig. 4. High-resolution electron microscopic image (a) and the size distribution of Pt particles (b) in the sample with 1 mass % Pt/TiO₂ annealed at 500 °C.

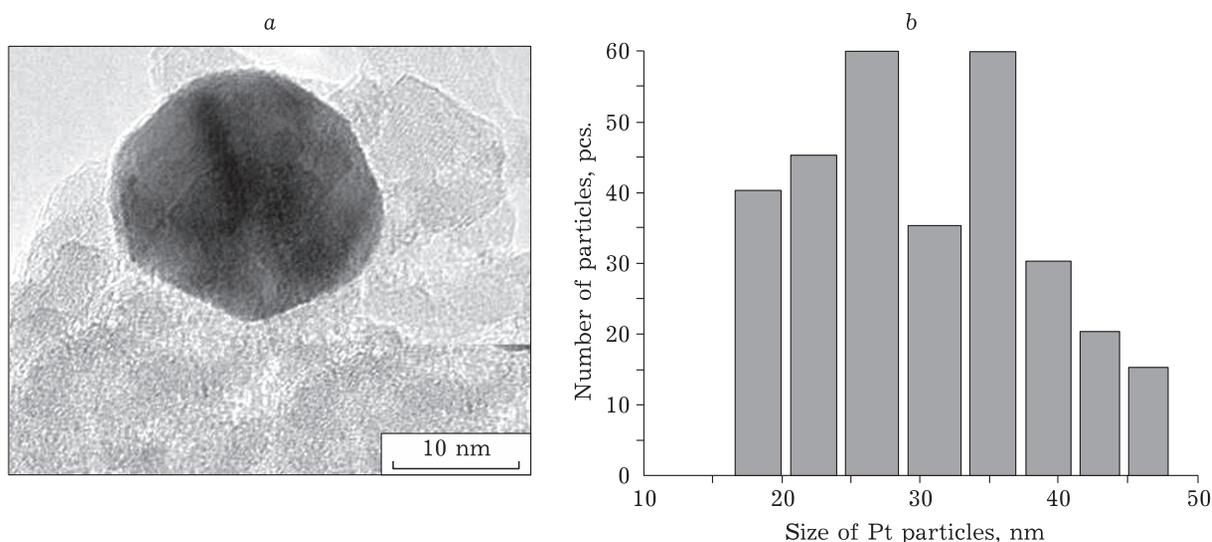


Fig. 5. High-resolution electron microscopic image (a) and the size distribution of Pt particles (b) in the sample with 1 mass % Pt/TiO₂ annealed at 750 °C.

basis of non-modified TiO_2 after annealing at $500\text{ }^\circ\text{C}$ contains only anatase phase, too, but after thermal treatment at $750\text{ }^\circ\text{C}$ it additionally contains trace amounts of rutile phase.

Electron microscopic photographs of the obtained catalysts and the size distribution of platinum particles are shown in Fig. 4–7. Figure 4 shows that the prevailing particle size in the Pt/TiO_2 catalyst annealed at $500\text{ }^\circ\text{C}$ is $1.5\text{--}5\text{ nm}$. After annealing at $750\text{ }^\circ\text{C}$, particle size increases to $20\text{--}50\text{ nm}$, while in the catalyst based on modified titanium dioxide $\text{Pt}/(5\text{ mass } \% \text{ Al}_2\text{O}_3\text{--}95\text{ mass } \% \text{ TiO}_2)$ annealed $500\text{ }^\circ\text{C}$ the prevailing size of platinum particles is $0.5\text{--}0.8\text{ nm}$ (see Fig. 6, b), while after annealing at $750\text{ }^\circ\text{C}$ it is $1.0\text{--}2.5\text{ nm}$ (see Fig. 7, b).

It follows from XPS data (Table 2) that two main states of platinum with bonding energy $E_b(\text{Pt}4f_{7/2})$ are recorded in the obtained catalysts. The first state with $E_b = 71.1\text{ eV}$ is characteristic of metal platinum Pt^0 , and the second state with $E_b = 72.1\text{ eV}$ corresponds to the presence of $\text{Pt}^{\delta+}$. According to the data shown in Table 2, for the same Pt content in the catalyst, the electron state of platinum is a substantial extent determined by aluminium content. For instance, in the catalyst containing no aluminium additive platinum is mainly stabilized in the stage of Pt^0 . In the catalysts obtained on the basis of $\text{Al}_2\text{O}_3\text{--TiO}_2$ supports, the fraction of platinum in $\text{Pt}^{\delta+}$ state increases with an increase in aluminium content.

The data shown in Fig. 8 illustrate the catalytic properties of the catalysts in the reaction of CO oxidation. One can see that Pt/TiO_2 and $\text{Pt}/(\text{Al}_2\text{O}_3\text{--TiO}_2)$ catalysts differ from each other in their catalytic properties. The Pt/TiO_2 catalyst annealed at $500\text{ }^\circ\text{C}$ is less active in comparison with the $\text{Pt}/(5\text{ mass } \% \text{ Al}_2\text{O}_3\text{--}95\text{ mass } \% \text{ TiO}_2)$ catalyst annealed at the same temperature. In the first case, T_{50} is $130\text{ }^\circ\text{C}$, while in the second case it is $100\text{ }^\circ\text{C}$. After thermal treatment of these catalysts at a temperature of $750\text{ }^\circ\text{C}$, the catalytic activity of the first catalyst decreases substantially ($T_{50} = 206\text{ }^\circ\text{C}$), while for the second catalyst it remains rather high ($T_{50} = 118\text{ }^\circ\text{C}$).

It follows from the comparative analysis of SEM data and the catalytic properties of the obtained catalysts that an increase in the size of platinum particles to $20\text{--}40\text{ nm}$ in the Pt/TiO_2 catalyst after annealing at $750\text{ }^\circ\text{C}$ leads to substantial worsening of catalytic properties. A well ordered crystal structure of anatase does not provide high thermal stability of platinum

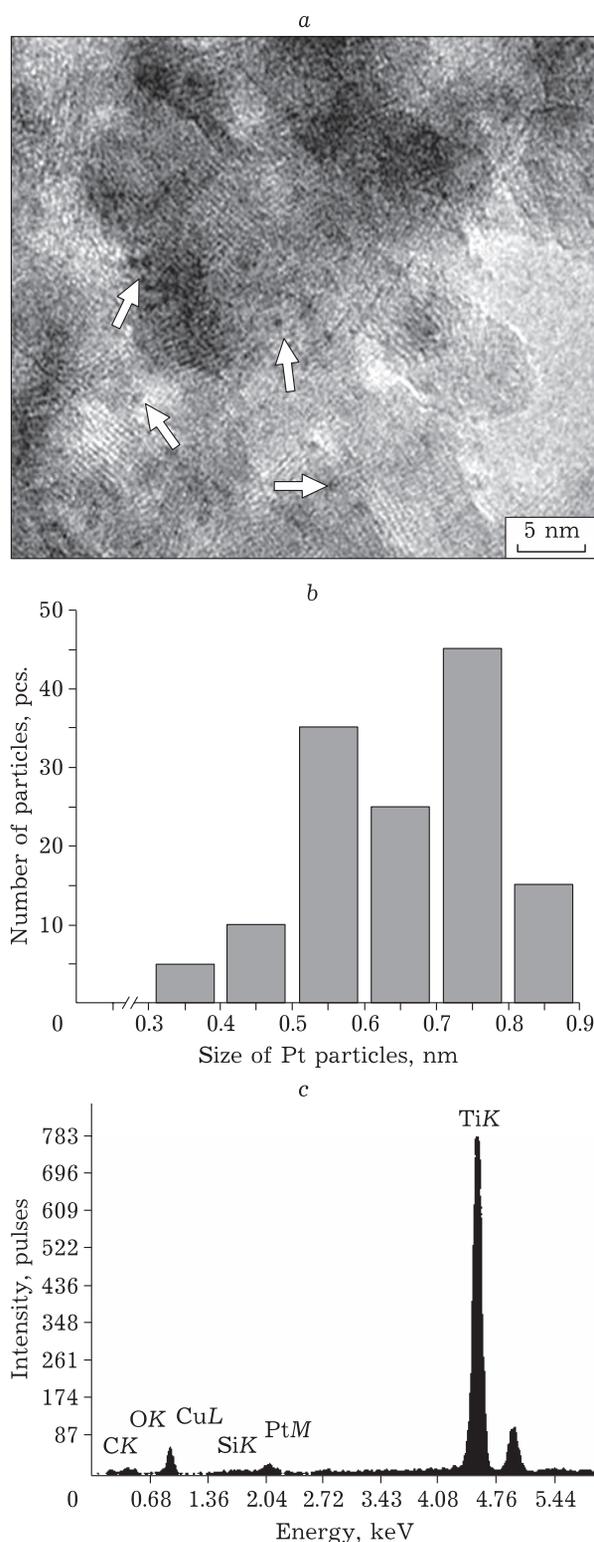


Fig. 6. High-resolution electron microscopic image (a), the size distribution of Pt particles (b) and the data of chemical analysis (EDX) (c) of the sample with 1 mass % Pt/ (5 mass % $\text{Al}_2\text{O}_3\text{--}95\text{ mass } \% \text{ TiO}_2$) annealed at $500\text{ }^\circ\text{C}$. Arrows indicate the visible platinum particles.

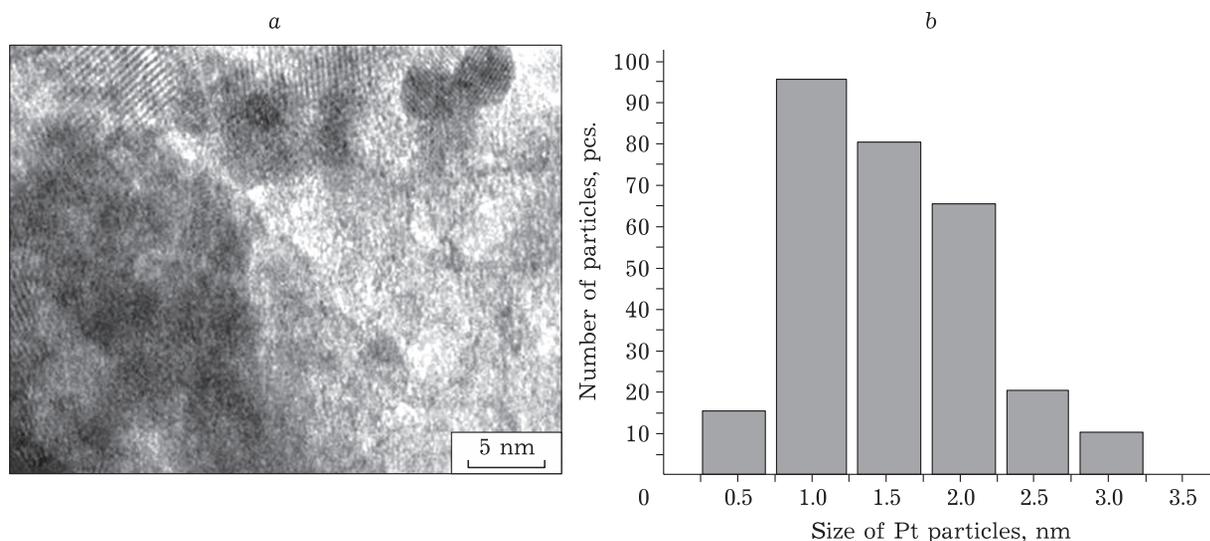


Fig. 7. High-resolution electron microscopic image (a) and the size distribution of Pt particles (b) in the sample with 1 mass % Pt/(5 mass % Al₂O₃-95 mass % TiO₂) annealed at 750 °C.

particles during high-temperature annealing. In the case of Pt/(Al₂O₃-TiO₂) catalyst, anatase structure remains nanocrystalline after annealing at 750 °C, which is provided by the formation of fine platinum particles 2–3 nm in size.

CONCLUSION

Modification of titanium dioxide by adding aluminium oxide leads to the formation of nanocrystalline anatase structure composed of fine anatase crystallites growth together in the incoherent manner, with the formation of interblock boundaries between them, with aluminium oxide clusters stabilized on these boundaries. The formation of nanocrystalline structure promotes an increase in thermal stability of anatase and a sub-

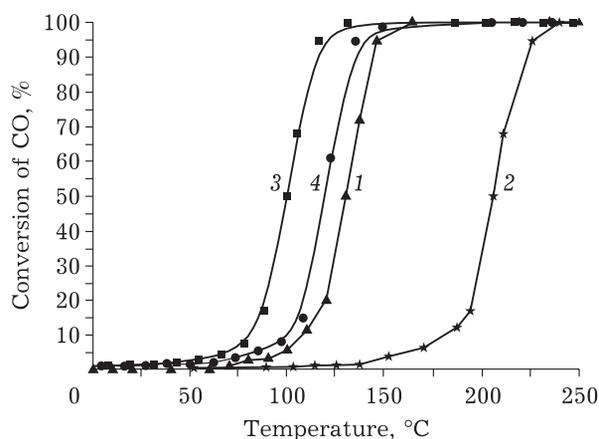


Fig. 8. Catalytic properties of Pt/TiO₂ samples annealed at a temperature of 500 (1), 750 °C (2), and Pt/(5 mass % Al₂O₃-95 mass % TiO₂) annealed at 500 (3) and 750 °C (4) in the reaction of CO oxidation.

TABLE 2

XPS data on the electron states of Pt with $E_b(\text{Pt}4f_{7/2})$ and their concentrations in the catalysts under investigation

Chemical composition, mass %	$E_b(\text{Pt}4f_{7/2})$, eV	Concentration, %	Pt ^{δ+} /Pt ⁰
1 % Pt/TiO ₂	71.7 (Pt ⁰)	69.6	0.44
	72.1 (Pt ^{δ+})	30.4	
1 % Pt/(5 % Al ₂ O ₃ -95 % TiO ₂)	71.7 (Pt ⁰)	67.5	0.54
	72.1 (Pt ^{δ+})	36.5	
1 % Pt/(10 % Al ₂ O ₃ -90 % TiO ₂)	71.7 (Pt ⁰)	57.9	0.73
	72.1 (Pt ^{δ+})	42.1	

stantial increase in the temperature of phase transition from anatase into rutile. The use of the obtained supports with nanocrystalline anatase structure for the preparation of supported Pt/(Al₂O₃-TiO₂) catalysts allows a substantial enhancement of their thermal stability and catalytic activity in the oxidation of CO in comparison with the supported Pt/TiO₂ catalyst.

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