Structure and acid-basic properties of the surface of titanium oxides modified by phosphorus and aluminum and prepared by the alkoxo method

2.* Study of the active surface of titanium oxides

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The data of temperature-programmed desorption of ammonia from the surface of oxide systems and IR spectroscopy were used to demonstrate that the strength of the surface acid sites in titanium oxides prepared by the alkoxo method and modified by aluminum decreases with respect to that in nonmodified titanium oxide. Modification of titanium oxide with P^{3+} ions from ethriol phosphite almost completely suppresses the acid properties. Modified oxides are able to chemisorb water. XANES data suggest that modification of titanium oxide with phosphorus ions increases the electron density on the titanium atoms and, correspondingly, the basicity of the materials.

Key words: temperature-programmed desorption of ammonia and water, IR spectroscopy, XANES.

A possible way of changing the nature of active sites is introduction into the oxide structure of modifying additives influencing the electron density distribution in the surface layers. Indeed, the individual oxides TiO_2, Al_2O_3, and SiO_2 show relatively weak acidity and are virtually inert in the alkylation of toluene with isopropyl alcohol,[2] whereas in binary and ternary systems, strong acid sites are formed and catalytic properties are displayed. TiO_2—Al_2O_3 systems prepared from isopropoxides by co-precipitation possess both Lewis and Brönsted acidity, the ratio of the concentrations of the sites of these two types being dependent on the composition of the composite material.[3] For mixed TiO_2—SiO_2 oxides, the formation of Si—O—Ti bonds, responsible for the appearance of proton-donating properties, was demonstrated.[4]

This study is devoted to the variation of the acid properties of the surface of titanium oxides modified by phosphorus and aluminum atoms during their preparation by the alkoxo method.

Experimental

Titanium tetra-*n*-butoxide, ethriol phosphite (4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane), and aluminum chloride crystal hydrate were used as oxide precursors.

The procedure for the synthesis of gels was described in a previous publication.[1]

The complex oxides TiO_2/Al (**1**), TiO_2/P (**2**, **3**), and TiO_2/C (**4**) were prepared by calcination of gels formed from stabilized long-lived sols at 450—500 °C. In the synthesis of sample **3**, the "mother liquor" was preliminarily chelated. According to X-ray diffraction data, all the modified oxides were single-phase systems with the anatase structure. In addition, as indicated by thermogravimetric analysis and ^{13}C NMR spectroscopy, nonmodified titanium oxide calcined at 500 °C contained 1.5—1.8% (w/w) residual elemental carbon.

IR spectra were recorded on a UR-20 spectrophotometer. The samples were subjected to heat pretreatment at 100—500 °C *in vacuo*. The temperature was raised with a step of 100 °C, the samples being kept for 2 h at each temperature.

The Ti—K-edge XANES spectra for all samples were recorded at the EXAFS station of the Siberian Synchrotron Radiation Center. The spectra were run in the transmission mode for an electron beam energy of 2 GeV and an average

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current in the acumulator during measurements equal to 80 mA. The X-ray energy was monitored with a channel cut Si(111) monochromator. The harmonics′ rejection was performed using a gold mirror. The X-radiation was recorded using ionized chambers filled with argon. The samples were prepared as pellets with thickness varied to obtain an ~1 step at the absorption edge. The step width in recording the XANES spectra was ~2 eV.

To record the data on temperature-programmed desorption (TPD) of ammonia and water, 0.2-g samples were kept in a dry air stream for 2 h at 550 °C and in a nitrogen stream for 1 h at the same temperature, cooled, and either blown with a 1 : 1 (v/v) mixture of nitrogen and ammonia at room temperature (30 min) or saturated with water vapor at room temperature (30 min). The samples were kept for 1 h at 50 °C to remove the weakly bound adsorbate, cooled to room temperature, and then heated with temperature programming at a rate of 8 K min^{-1} until the adsorbate was completely removed. The TPD data were processed by matching the experimental and calculated patterns of the curves.[5] This method provides determination of the total number of adsorption sites and their distribution over the activation energies of desorption (E_d) in the range from the minimum (E_{min}) to the maximum (E_{max}) value and calculation of the average value for the whole range of desorption energies ($<E>$), which characterizes the average strength of the sites. The ranges of the activation energy of desorption were cut into equal sections (5 kJ mol^{-1} each). Within each section, the sites were considered uniform and their strength was stipulated by one average activation energy corresponding to the middle of the section.

Results and Discussion

Figure 1 shows the IR spectra of the TiO_2/Al sample (**1**) pretreated at various temperatures. The IR spectra of noncalcined Al-containing samples subjected to chelation and treated *in vacuo* at 100 °C were found to exhibit intense absorption bands at 1578 and 1450 cm^{-1} as well as bands at 1395, 1365, 1127, 1110, and 1075 cm^{-1} (see Fig. 1, curve *1*), whose intensity decreased with an increase in the evacuation temperature. These absorption bands disappear almost completely after calcination of the sample in air and *in vacuo* at 500 °C (curve *3*). Comparison of the results obtained with the spectra of metal chelates[6] allows the bands observed at 1578 and 1450 cm^{-1} to be assigned to stretching vibrations of the C$\cdots$C and C$\cdots$O bonds in the β-diketonate molecules, respectively. The other bands belong to the C—H and C—C vibrations of the methyl groups and hydrocarbon chains. The IR spectra of other samples evacuated at 500 °C contained no absorption bands due to organic compounds.

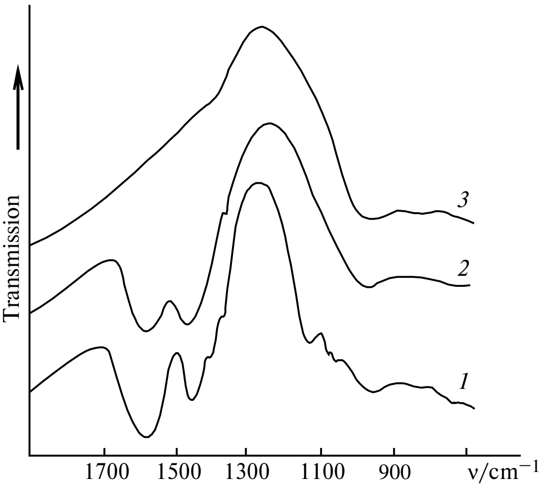


Fig. 1. IR spectra of TiO_2/Al (**1**) evacuated at 100 (*1*), 300 (*2*), and 500 °C (*3*).

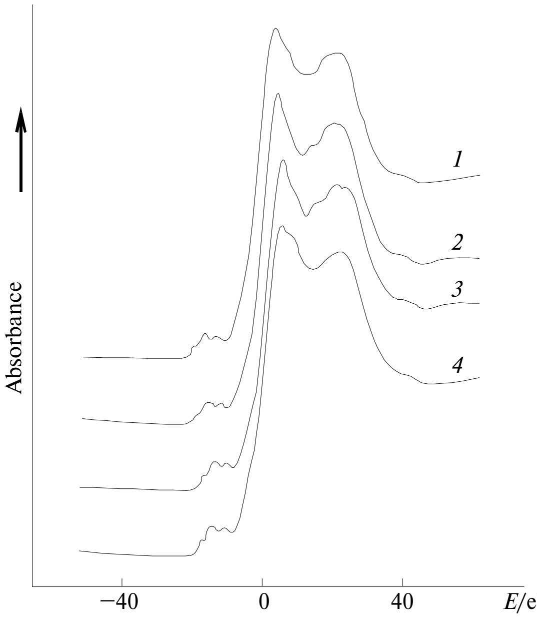


Fig. 2. Titanium K-edge XANES spectra for modified samples: (*1*) TiO_2/P (**3**); (*2*) TiO_2/C (**4**); (*3*) TiO_2/Al (**1**); (*4*) TiO_2/P (**2**).

Figure 2 shows the XANES spectra of the absorption of X-radiation of the titanium K-edge, which give the following intensity ratios of the pre-edge maximum to the size of the K-edge step of titanium absorption, *I* (rel.u.): TiO_2/P (**2**), 0.093; TiO_2/P (**3**), 0.072; and TiO_2/Al (**1**), 0.088.

These values were normalized with respect to pure TiO_2 (anatase).

It is known from the literature that the intensity of the pre-edge maximum characterizes the degree of distortion of symmetry of the titanium environment. In turn, these distortions change the effective charge on titanium.

Thus, it can be seen from the results obtained that the conditions of synthesis markedly influence the symmetry of the oxygen environment and the effective charge of titanium ions in the oxide. The highest effective charge of titanium ions was observed in the phosphorus-modified oxide **2**, whose synthesis did not include the stage of chelation. The charge was lower in the TiO_2 sample (**5**) and in sample **1** and also in phosphorotitanate system **3**, whose synthesis did include chelation.

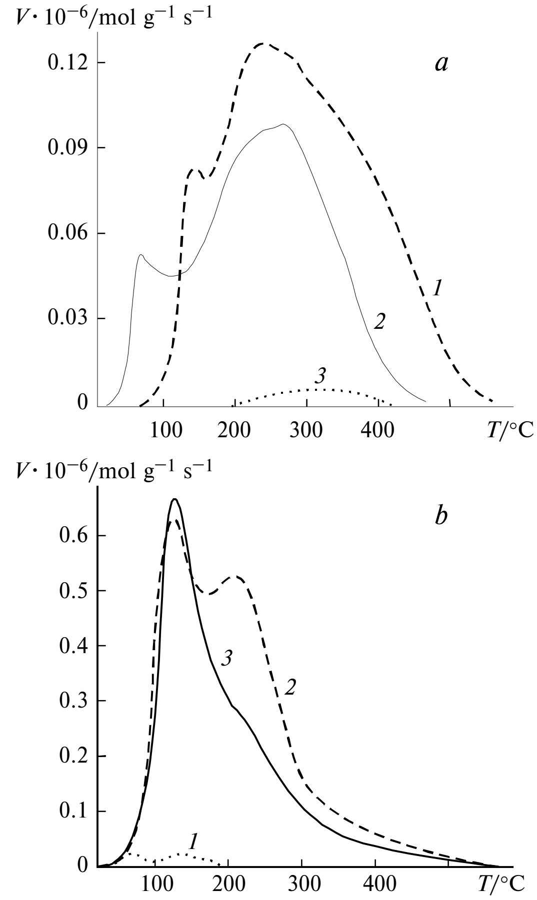


Fig. 3. TPD spectra of adsorbed ammonia (*a*) and water (*b*): (*1*) TiO_2/C (**4**), (*2*) TiO_2/Al (**1**), (*3*) TiO_2/P (**3**).

The results obtained suggest that the titanium atoms in sample **3** are reduced to a greater extent than those in the systems modified with aluminum or phosphorus atoms but prepared without the chelation stage.

Figure 3 shows the TPD curves and Table 1 presents the data on the distribution of sites with different activation energies of desorption and E_d ranges. It is known that the strength of acid sites of heterogeneous systems can be compared using the activation energies of thermal desorption, although the boundary conditions are arbitrary and have been accepted with allowance for earlier studies.[7—9]

The curves of the TPD of ammonia (see Fig. 3, *a*) for the TiO_2 (**5**) and TiO_2/Al (**1**) samples contain two peaks, which can be related, based on E_d values (see Table 1), to weak sites with E_d not higher than 95 kJ mol^{-1} and to medium and strong sites with E_d higher than 95 kJ mol^{-1}. The introduction of aluminum (3 at.%) into the TiO_2 structure decreases both the overall number of acid sites and the number of medium or strong sites. Meanwhile, the number of weak adsorption sites for TiO_2/Al (**1**) somewhat increases. According to published data[7] the molecules of adsorbed ammonia in calcined samples are linked to the surface Ti atoms by coordination bonds. Apparently, the introduction of Al decreases the electron-withdrawing properties of TiO_2.

A completely different situation was observed for the phosphorus-containing system in which the electron density on Ti atoms was increased, according to the XANES study. According to the data of ammonia TPD, on passing to TiO_2/P, the number of acid sites sharply decreases and the E_d range corresponds mainly to sites with medium strength. The decrease in the acidity of oxide systems on treatment of their surface with phosphorus compounds is widely used to modify the zeolite-containing catalysts.[8,9] Under certain conditions, strong acid sites can be removed and the number of medium and weak sites can be simultaneously increased upon introduction of hydrated polyphosphate chains into the structure.[10] However, after the TiO_2/P sample has been calcined in air, the number of sites of ammonia chemisorption still remains very low (see Fig. 3, *a*).

The introduction of aluminum into titanium oxide, like the introduction of phosphorus, results in an increase in the number of sites capable of chemisorbing water (see Fig. 3, *b*, Table 1).

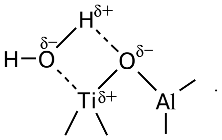
As in the case of ammonia, the thermal desorption curve exhibits two peaks, the high-temperature peak for TiO_2/P being feebly defined. As follows from Table 1, the maximum E_d values for the thermal desorption of water from modified systems are much greater than those for non-modified titanium oxide. The total concentration of sites involved in chemisorption of water in modified samples is more than an order of magnitude greater than that in non-modified TiO_2.

These results indicate that modification of titanium oxide with aluminum and phosphorus results in development of the active surface of the oxide.[1] Although the numbers of active sites for ammonia chemisorption on

Table 1. Distribution of adsorption sites over the activation energy (E_d) of the ammonia (I) and water (II) desorption

System	Number of adsorption sites (μmol g^{-1})						E_d/kJ mol^{-1}					
	Total		with $E_d \le 90\pm5$ kJ mol^{-1}		with $E_d \ge 90\pm5$ kJ mol^{-1}		E_{min}		E_{max}		$<E>$	
	I	II	I	II	I	II	I	II	I	II	I	II
TiO_2/C (**4**)	243	21	16	8	227	13	82	71	184	113	130	93
TiO_2/P (**3**)	5	641	—	229	5	412	114	72	151	185	135	103
TiO_2/Al (**1**)	177	809	33	287	144	522	69	73	168	189	119	106

TiO_2/C and TiO_2/Al are close, the data on the thermal desorption of water demonstrate that the modified system shows a higher capacity for water chemisorption. This may imply that the nature of these sites is different. The incorporation of aluminum ions in the anatase structure does not enhance acidic properties of the coordinatively unsaturated titanium atoms with respect to those in the nonmodified oxide. However, the increased chemisorption capacity toward water might be due to the increase in the proton affinity caused by the increase in the electron density on bridging oxygen atoms (μ-O) in the heterometallic structural fragments (Ti—O—Al). The presence in these fragments of two types of sites, namely, Lewis sites, which tend to enter into electrophilic addition, and μ-O sites, capable of nucleophilic addition, can give rise to a two-center model of water chemisorption, which accounts for strong bonding of water with the surface:



The incorporation of phosphorus atoms into the TiO_2 structure increases the electron density on titanium ions and thus suppresses the acidic properties of the surface.

The observed enhanced chemisorption capacity toward water can be attributed to the hydrolysis of the phosphorus-containing modifying agent,[11] because the products of hydrolysis could accept hydrogen bonds. This assumption is supported by the complex stepwise pattern of desorption of water molecules (see Fig. 3, *b*).

Thus, the introduction of aluminum and phosphorus atoms during the alkoxo synthesis of titanium dioxide with the anatase structure suppresses the acidic properties, while modification with phosphorus enhances the basic properties.

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