

Effect of the Structure of Ti–Sb–O Catalysts on Their Acid–Base Properties, Surface Oxygen Binding Energy, and Catalytic Properties in Propylene Ammonoxidation

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Abstract—The structure of Ti–Sb–O catalysts, namely, a solid solution of antimony ions in rutile-type TiO_2 and the titanium antimonate TiSb_2O_6 , is characterized by X-ray diffraction, high-resolution electron microscopy, calorimetry, and IR spectroscopy. The structure effects on the acid–base properties and the surface oxygen binding energy are considered, as well as the correlation of these characteristics with the catalytic properties of the Ti–Sb–O system in propylene ammonoxidation. The solid solution has a regular crystal structure. As a consequence, the surface has high concentrations of strong aprotic acid and strong basic sites and is characterized by a high surface oxygen binding energy. In the titanium antimonate structure, extended crystallographic shear defects cause a marked enrichment of the surface with antimony and, accordingly, an increase in the relative concentration of weak aprotic acid sites and a decrease in the surface oxygen binding energy. The changes of the structure and acid–base properties of the surface in passing from the solid solution to TiSb_2O_6 result in an increase in the acrylonitrile selectivity.

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Titanium–antimony oxide catalysts are active and selective in propylene ammonoxidation [1]. The highest activity and the highest selectivity with respect to the desired product, which is acrylonitrile, are shown by titanium–antimony catalysts that are either a solid solution of antimony ions in rutile titanium dioxide or the titanium antimonate TiSb_2O_6 . However, there is still no comprehensive knowledge of the active state of titanium–antimony catalysts because there have been no detailed studies of their microstructure. This lack of information has primarily been due to the low spatial resolution of electron microscopy, which has been unable to study the real structure of ultrafine catalysts. At the same time, it is likely the microstructure of oxide catalysts that governs their catalytically important properties, such as the acid–base properties of the surface and the surface oxygen binding energy. For example, it was demonstrated that, in the case of iron–antimony oxide catalysts, the microstructure of iron antimonate obtained from an equimolar mixture of components differs from the microstructure of iron antimonate obtained from a mixture containing excess antimony oxide [2]. It is the specific features of the real structure of these catalysts that are responsible for the difference between the acid–base properties of their surfaces and between the surface oxygen binding energies. In turn, these differences must give rise to a difference between the catalytic properties of the catalysts in partial oxidation reactions [2] because it is well known that the acid–base surface properties of oxide catalysts

have an effect on their catalytic properties in partial oxidation reactions [2–7]. It is, therefore, a challenging problem to establish a correlation between the real structure of oxide catalysts and their acid–base and surface oxygen binding properties and to elucidate the role of these factors in the catalytic properties of these catalysts in partial oxidation reactions.

Here, we report the effects of the structure of titanium–antimony oxide catalysts on their acid–base properties, surface oxygen bonding energy, and catalytic activity in propylene ammonoxidation.

EXPERIMENTAL

Titanium–antimony oxide catalysts with different component ratios were prepared by coprecipitation from a hydrochloric acid solution of titanium tetrachloride and antimony pentachloride with aqueous ammonia at a constant acidity of pH 7 and $T = 70^\circ\text{C}$ followed by washing the Cl^- ions away from the precipitate with distilled water, drying, and heat treatment in air at 750°C [8].

Electron microscopic examinations were carried out using a JEM-2010 microscope (Japan) with a resolving power of 1.4 Å at an accelerating voltage of 200 kV. Microanalyses were made on a Philips CM-20 electron microscope (Netherlands) equipped with an EDAX DX-4 energy-dispersive spectrometer (Ametek Inc., United States).

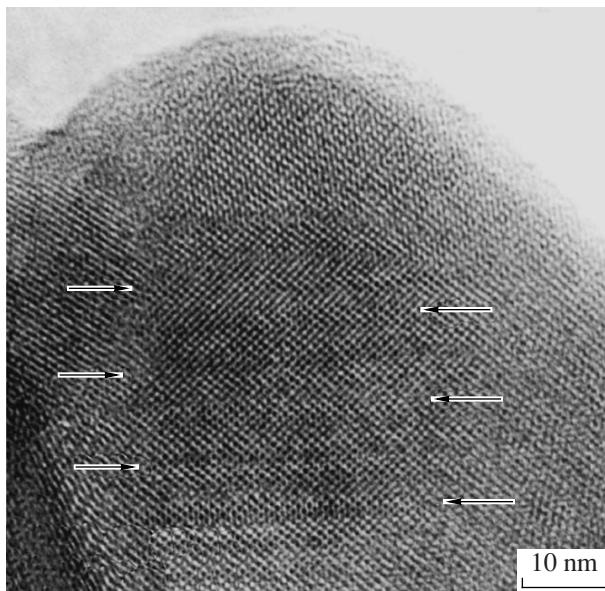


Fig. 1. Electron micrograph of a sample of the solid solution of antimony ions in rutile. The arrows point to the microanalysis area (see Fig. 2).

The surface oxygen binding energy (q_{O_2} , kcal/mol) for the titanium–antimony oxide catalysts was determined calorimetrically from the heat of oxygen uptake by the surface prerduced with carbon monoxide at 450°C. The catalysts were reduced by pulses of a CO–He mixture containing 1–10 vol % CO. Prior to reduction, the samples were heat-treated in oxygen (200 Torr) for 4 h at 450°C and then in vacuo at a residual pressure of 10⁻⁵ Torr for 30 min at the same temperature. Calorimetric experiments were carried out in a Tian–Calvet high-temperature calorimeter connected to a vacuum unit. The extent of reduction of the surface (θ , % ML) was calculated from the amount of oxygen released upon the reduction of the surface with carbon monoxide. The surface area occupied by one oxygen atom was taken to be 7.84 Å² [9].

The acid–base properties of catalysts were studied by recording the IR spectra of adsorbed benzonitrile and deuteriochloroform molecules. The concentration and strength of acid sites were estimated from the spectra of adsorbed deuteriochloroform [3, 10–12].

The catalytic properties of the oxides in propylene ammoxidation were studied using a flow circulation setup. The reaction was conducted in the kinetically controlled regime on a 0.5–1.0 mm size fraction of the catalyst at 450°C. The feed consisted of 2 vol % C₃H₆, 3 vol % NH₃, and 95 vol % air. The feed flow rate was 10 l/h, and the circulation flow rate was 600–1000 l/h. The components of the gas mixture were identified chromatographically. Hydrocyanic acid was determined by argentometric titration [1].

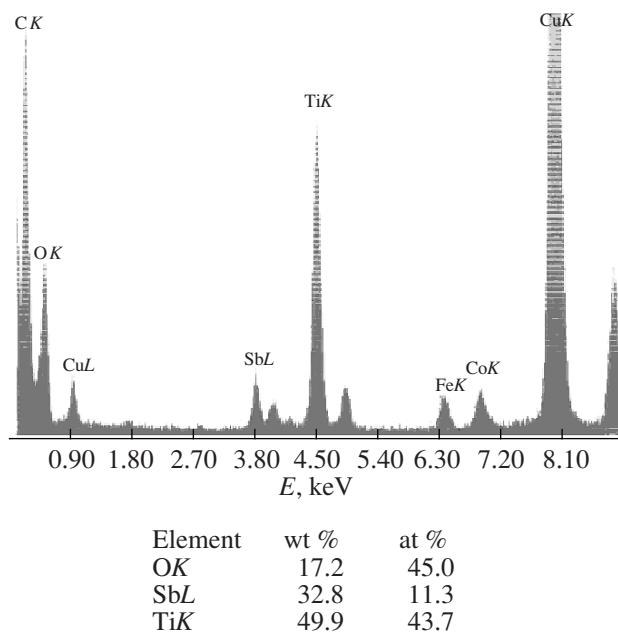


Fig. 2. Elemental composition of the solid solution of antimony ions in rutile.

RESULTS AND DISCUSSION

In an earlier work [8], we demonstrated that the reaction in the titanium–antimony oxide system obtained by coprecipitation yields a solid solution of antimony ions in rutile titanium dioxide (7 mol % Sb₂O₅) and the titanium antimonate TiSb₂O₆ isostructural to priorite. In the composition range 7–50 mol % Sb₂O₅, the system consists of two phases, namely, the solid solution and titanium antimonate. At Sb₂O₅ contents above 50 mol %, the system consists of titanium antimonate and the oxide Sb₆O₁₃. It was demonstrated by X-ray spectroscopy that, in the solid solution and in titanium antimonate, the antimony ions are stabilized in the oxidation states +3 and +5 and titanium is in the oxidation state Ti⁴⁺ [8].

Figure 1 shows an electron micrograph of the solid solution of antimony ions in titanium dioxide. The particles of the solid solution have a regular shape. The spatial structure of the rutile phase crystals is highly ordered. No fine particles of other phases are observed on the surface. According to microanalysis data, the rutile particles contain 11.3 at % Sb (Fig. 2).

Figure 3 shows an electron micrograph of a titanium antimonate sample. Morphologically, this sample is identical to the solid solution sample. Note, however, the high density of extended defects in the particle structure. The micrograph clearly demonstrates the shear nature of these defects: one crystal domain is displaced relative to the other by half the lattice period in the shear direction. It can be assumed that these defects are crystallographic shear defects with a shear vector equivalent to 1/2⟨110⟩(001). This notation means that

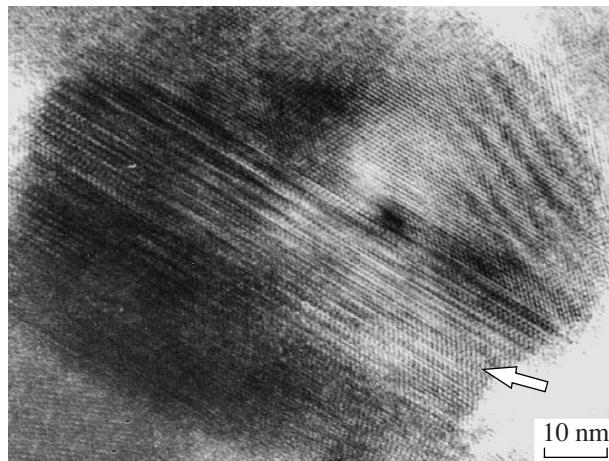


Fig. 3. Electron micrograph of titanium antimonate.

the parts of the crystal are displaced by half the lattice period in the direction $\langle 110 \rangle$ in the plane (001). Microanalysis demonstrated that the surface of this catalyst sample is enriched with antimony (Fig. 4). When performing an elemental analysis of a crystal area rich in such defects, we noticed the following effect: as the accelerating voltage was reduced, the Sb concentration increased up to 72.5 at % versus 64.3 at % at the high accelerating voltage. This effect is explained by the fact that, as the accelerating voltage is decreased, the electron beam penetration depth decreases and the characteristic X-ray signal is generated in a progressively thinner surface layer of the crystal. Therefore, based on microanalysis data, we can assume that the surface of this catalyst sample is enriched with antimony. This enrichment is likely due to the stabilization of excess antimony in defect areas.

Consider the structure effect on the formation of the acid–base properties of the surface and on the surface oxygen binding energy. The acid–base properties of the samples [3] are presented in Table 1. The surface of the solid solution of antimony ions in rutile and the surface of titanium antimonate have two types of aprotic acid

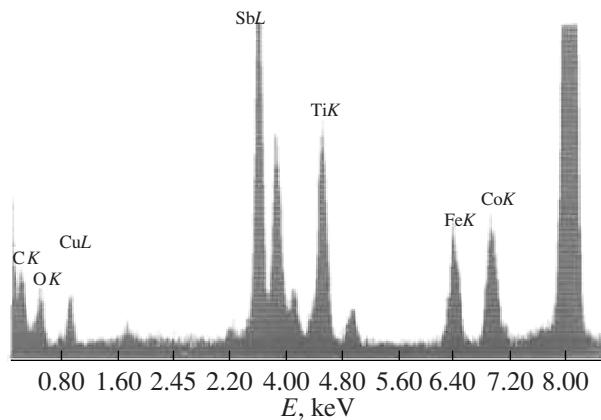


Fig. 4. Elemental composition of titanium antimonate.

sites, namely, strong acid sites, which give rise to a band at 2280 cm^{-1} in the spectrum of benzonitrile, and weak acid sites, which give rise to a band at 2250 cm^{-1} in the same spectrum. According to the literature [11], the strong aprotic acid sites are coordinatively unsaturated surface Ti^{4+} ions and the weak aprotic sites are coordinatively unsaturated surface antimony ions in the oxidation state +3. On passing from the solid solution to titanium antimonate, the concentration of strong aprotic acid sites decreases markedly and the concentration of weak acid sites increases.

Furthermore, the surface of the solid solution sample has two types of basic sites, namely, strong basic sites, which give rise to a band at 2245 cm^{-1} in the spectrum of deuteriochloroform ($\text{p}K_a +2$), and weak basic sites, which manifest themselves as a band at 2255 cm^{-1} in the same spectrum ($\text{p}K_a -3$ [3, 13]). According to the literature [12], the basic sites with $\text{p}K_a +2$ are lattice oxygen ions (O^{2-}), whose energy depends on the energy of the $\text{Me}-\text{O}$ bond in the lattice. The weak basic sites with

Table 1. Acid–base properties of Ti–Sb–O catalysts

Phase composition	$\text{C}_6\text{H}_5\text{CN} \nu_0 = 2229 \text{ cm}^{-1}$		$\text{CDCl}_3 \nu_0 = 2265 \text{ cm}^{-1}$		
	ν, cm^{-1}	$I, \text{cm}^{-1}/\text{m}^2*$	ν, cm^{-1}	$I, \text{cm}^{-1}/\text{m}^2*$	$\text{p}K$
Solid solution of antimony ions in TiO_2	2280 ± 5 (Ti^{4+})	3.8	2245 ± 5	3.46	+2
	2250 ± 5 (Sb^{3+})	3.6	2257 ± 3	3.2	-3
Titanium antimonate	2280 ± 5 (Ti^{4+})	0.5	2240 ± 5	1.1	+2
	2250 ± 5 (Sb^{3+})	4.75	2255 ± 3	3.4	-3

* The $I(\text{cm}^{-1}/\text{m}^2)$ values are obtained by dividing the integrated intensity of the band on the surface area of the sample in the cross section of the light beam: $I = \int_0^\infty \log \frac{J}{J_0} \text{d}v \frac{1}{mS_{\text{sp}}}$, where J_0 and J are transmittances, m is the sample weight (g), S_{sp} is the specific surface area of the sample (m^2/g), and ν is frequency (cm^{-1}).

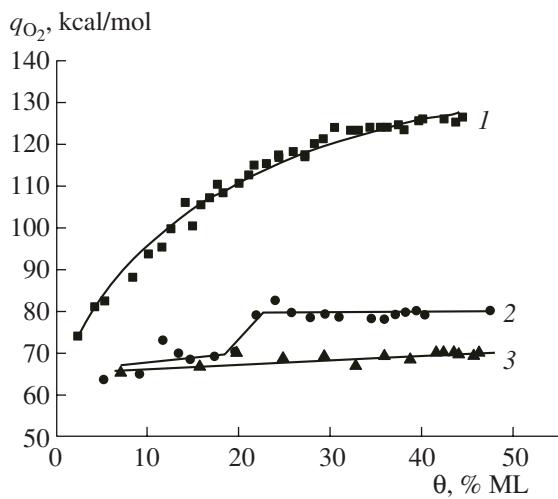


Fig. 5. Effect of the extent of reduction of the surface (θ) on the surface oxygen binding energy for (1) the solid solution of antimony ions in rutile, (2) titanium antimonate TiSb_2O_6 , and (3) Sb_6O_{13} .

$\text{p}K_a - 3$ are oxygen atoms doubly bonded to Sb^{5+} ions. It can be seen from Table 1 that the concentration of the basic sites with $\text{p}K_a + 2$ decreases markedly on passing from the solid solution to titanium antimonate.

Correlation of the microstructural data with the acid–base properties of the surface suggests that the enrichment of the surface with antimony in the case of titanium antimonate causes a decrease in the concentration of strong aprotic acid sites, an increase in the concentration of weak aprotic acid sites, and a decrease in the concentration of strong basic sites.

Figure 5 plots the surface oxygen binding energy as a function of the extent of reduction of the surface for the samples examined and for pure antimony oxide. There is an obvious difference between the solid solution and titanium antimonate in terms of the way the surface oxygen binding energy varies with the extent of surface reduction. For the solid solution, the surface oxygen binding energy increases dramatically from 70 to 125 kcal/mol as the extent of surface reduction increases from 2 to 45% ML. In the case of titanium antimonate, the surface oxygen binding energy remains almost invariable (65–70 kcal/mol) as the extent of surface reduction increases from 3 to 20% ML, rises to 80 kcal/mol at $\theta = 20\text{--}22\%$ ML, and then remains invariable up to $\theta = 46\%$ ML.

In Sb_6O_{13} , the surface oxygen binding energy is 66–70 kcal/mol at $\theta = 7\text{--}42\%$ ML. Note that the q_{O_2} versus θ dependences for pure antimony oxide and titanium antimonate are nearly the same at $\theta < 20\%$ ML and are different at larger θ values.

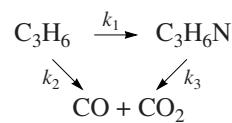
According to calorimetric data, the surface oxygen binding energy for anatase titanium dioxide increases from 80 to 110 kcal/mol as the extent of surface reduction increases from 15 to 20% ML [14]. The surface

oxygen binding energy derived from oxygen thermal desorption data for anatase is 59 kcal/mol [15].

Thus, the modification of titanium dioxide with antimony ions causes considerable changes in the surface oxygen binding energy over a wide θ range. At a given θ , the solid solution of antimony ions in rutile is characterized by a higher surface oxygen binding energy than titanium antimonate. Correlation of these results with the above data suggests that this difference can be accounted for in terms of the catalyst microstructure, which has a marked effect both on the acid–base properties of the surface and on the surface oxygen binding energy.

Let us consider the catalytic properties of the oxides in propylene ammonoxidation in relation to the acid–base properties of the surface and the surface oxygen binding energy. As was demonstrated in earlier works [6, 16–20], partial oxidation reactions require catalysts containing acid and basic sites of certain strengths and the optimum combination of acid–base properties is the determining factor in the interaction between the reactant and the catalyst surface. Extensive data available on the mechanisms of propylene oxidation and oxidative ammonolysis [21–23] indicate that, in the activation of propylene molecules, which is the rate-determining step, the surface oxygen ion O^{2-} , which possesses nucleophilic properties, abstracts a proton from the methyl group of the propylene molecule to yield a carbanion. This bond breaking in the propylene molecule is favored by the polarizability of the allylic C–H bond enhanced by hyperconjugation. It was deduced by analysis of known hydrocarbon oxidation mechanisms [21, 24–26] that, in the reactions in which the rate-determining step is the interaction between the substance being oxidized and the catalyst surface with the formation of a surface intermediate, the surface oxygen binding energy is not of crucial significance. The determining factor in these reactions is the presence of nucleophilic O^{2-} ions, which are responsible for the specific activation of the molecules being oxidized.

According to earlier studies [3], propylene ammonoxidation over the catalyst examined is described by the consecutive–parallel scheme



Acrylonitrile forms from propylene, and carbon oxides form both directly from propylene via the parallel route and from acrylonitrile by its further oxidation via the consecutive route. This description makes it possible to compare the selectivities of the catalysts in partial reactions:

$$S_{\text{C}_3\text{H}_5\text{N}}^0 = k_1/(k_1 + k_2), \quad S_{\text{CO}, \text{CO}_2}^0 = k_2/(k_1 + k_2), \\ b = k_3/(k_1 + k_2),$$

Table 2. Catalytic properties of titanium–antimony catalysts in propylene ammonoxidation

Phase composition	$S_{C_3H_3N}^0$	S_{CO, CO_2}^0	S_{HCN}^0	b
Solid solution of antimony ions in TiO_2	0.77	0.19	0.05	0.047
Titanium antimonate	0.82	0.12	0.05	0.043
Antimony oxide Sb_6O_{13}	0.63	0.14	0.23	0.04

where $S_{C_3H_3N}^0$ and S_{CO, CO_2}^0 are the selectivities with respect to acrylonitrile and carbon oxides, which form via the parallel routes, and b is the further oxidation constant.

For the solid solution of antimony ions in rutile and titanium antimonate, $S_{C_3H_3N}^0 = 0.77$ and 0.82 , $S_{CO, CO_2}^0 = 0.19$ and 0.12 , and $b = 0.45$ and 0.43 , respectively (Table 2). Therefore, the higher acrylonitrile selectivity of titanium antimonate is mainly due to the lower activity of this phase in the parallel formation of total oxidation products. In turn, this is due to the difference between the surface properties of the solid solution and titanium antimonate.

According to the literature, the high selectivity of catalysts with respect to incomplete oxidation products in partial oxidation reactions is due to the loosely bound forms of the initial reactant and reaction products and to the tightly bound oxygen species [6, 27–31]. Whether a tightly or a weakly bound form of the intermediate compound is formed on the surface depends on the strength of the acid sites, and the ratio of these forms determines the reaction route. The surface oxygen binding energy also has an effect on the structure of the surface compound. If the surface oxygen is highly reactive, oxygen-rich complexes will form on the surface and this will lead to the destruction of the π -allyl complex and to its nonselective oxidation. The destructive oxidation of the intermediate compound will also be possible in the absence of loosely bound oxygen provided that the formation of tightly bound species takes place. The desorption of these tightly bound species is necessarily accompanied by the destruction of the carbon backbone [27–32].

There is good reason to believe that, in the antimony-modified titanium dioxide, the appearance of weak aprotic acid sites as coordinatively unsaturated surface Sb^{3+} ions (in addition to strong aprotic acid sites that are coordinatively unsaturated surface Ti^{4+} ions) causes the formation of loosely bound intermediate compounds (in addition to tightly bound surface intermediates) and the latter turn into selective oxidation products. The increase in the relative surface concentration of weak aprotic acid sites on passing from the solid solution to titanium antimonate changes the partial-to-total oxidation rate ratio [3] and raises the acrylonitrile selectivity.

Unfortunately, we have no surface oxygen binding energy data for titanium–antimony oxide catalysts operating in the reaction mixture under steady-state conditions. However, from earlier data concerning the catalytic properties of these oxides at various oxygen partial pressures, it can be inferred that the extent of reduction of the surface of a titanium antimonate catalyst working in a steady-state regime is not higher than 25% ML [1]. The surface oxygen binding energy at this extent of surface reduction is as low as 80 kcal/mol (Fig. 5); nevertheless, it is sufficient for destructive propylene oxidation yielding carbon-containing densification products on the surface. It is likely that, at moderate propylene and ammonia concentrations in the reaction mixture, both titanium–antimony catalysts operate in the oxidized state, with the surface oxygen binding energy not exceeding 65–75 kcal/mol. Under these conditions, the overall propylene conversion rate and the rates of the constituent reaction steps for the Ti–Sb–O catalysts are most likely determined by the acid–base properties of the surface [3]. This assumption is fully consistent with the above claim that, in the reactions in which the rate-limiting step is the interaction between the reactant and the catalyst surface, the determining factor is the presence of nucleophilic oxygen [16, 26].

Thus, the acid–base surface properties, the surface oxygen binding energy, and the catalytic properties of the Ti–Sb–O catalysts in propylene ammonoxidation are governed by their phase composition and microstructure. The catalyst that is a solid solution of antimony ions in rutile titanium dioxide has a regular structure and, as a consequence, sufficiently high surface concentrations of weak aprotic acid and strong basic sites. The crystal structure of titanium antimonate is irregular. It has crystallographic shear defects. The formation of these structural defects causes marked enrichment of the catalyst surface with antimony, favoring the formation of a rather large number of weak aprotic acid sites. As a result, the relative concentrations of strong aprotic acid sites and strong basic sites decrease in passing from the solid solution of antimony ions in TiO_2 to titanium antimonate. This is accompanied by a marked change in the dependence of the surface oxygen binding energy on the extent of surface reduction. The change in the acid–base properties of the surface in passing from the solid solution to titanium antimonate causes a decrease in the overall propylene conversion rate [3] and an increase in the acrylonitrile selectivity.

This is mainly due to the decrease in the rate of acrylonitrile formation via the parallel route.

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