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Structural Arrangement of Fe–Sb–O Catalysts

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Abstract—In iron–antimony catalysts containing excess antimony oxide and consisting of a mixture of $FeSbO_4$ and α-Sb_2O_4 phases, the structure of iron antimonate changes compared to the catalyst with an equimolar composition, which is the pure $FeSbO_4$ phase. In the presence of excess antimony oxide in the near-surface layer of iron antimonate, extended defects with a structure of crystallographic shift are formed. These accumulate overstoichiometric antimony. Such a structural change is associated with changes in the acid–base properties and the surface oxygen binding strength.

INTRODUCTION

It is known that iron–antimony oxide catalysts are active and selective in several partial oxidation reactions, including the oxidative dehydrogenation of butenes [1–3], propylene oxidation [4], the oxidative dehydrogenation of ethylbenzene [5], the oxidation of methanol and alkylaromatics [6], propylene ammoxidation [6–14], and propane ammoxidation [15]. It was established that catalysts consisting of a mixture of the two phases $FeSbO_4$ and α-Sb_2O_4 are very active and selective in many partial oxidation processes, although the individual iron antimonate phase is highly active but unselective toward the partial oxidation products. The individual antimony oxide phase α-Sb_2O_4 shows low activity and selectivity in partial oxidation [1–14]. The structure of the active component of iron–antimony catalysts has been studied in detail. Various physicochemical methods showed that, in the presence of antimony oxide, the surface of iron antimonate is rich in antimony [1, 7, 9, 11]. Carbucicchio *et al*. [3] proposed that excess antimony completely covers the surface of iron antimonate in the form of highly dispersed oxide α-Sb_2O_4 or a thin layer of antimony. Sala and Trifiro [1] suggested that the $FeSb_2O_6$ phase is formed as a surface compound in which antimony is in the Sb(V) form and iron is in Fe(II) form. This results in an increase in the catalyst selectivity to the partial oxidation products. A Moessbauer spectroscopic study [10] has led to the conclusion that, in the iron–antimony catalysts containing excess antimony oxide, iron antimonate is formed with the disordered rutile structure containing Fe^{2+} ions, which are accumulated near oxygen vacancies. Zenkovets *et al.* [11] showed that, in the catalyst containing excess antimony, the concentration of Sb^{3+} ions increases on the surface. Based on the analysis kinetic data, Carrazan *et al*. [14] assumed that the higher selectivity of iron antimonate containing the crystallites of highly dispersed antimony oxide phase is due to the fact that the surface of iron antimonate modified by antimony is reoxidized by the oxygen of surface antimony oxide during a catalytic reaction, whereas the surface reoxidation by the oxygen of pure iron antimonate or gas-phase oxygen is more difficult.

However, the problem of high catalytic activity and selectivity of iron antimonate in the presence of excess antimony oxide is not yet solved and requires a further study.

In connection with this, the study of the structure (the nature and concentration of defects) of iron–antimony catalysts depending on their chemical and phase composition and the effect of structure on the physicochemical and catalytic properties is very topical.

The goal of this work was to study the structure of iron–antimony oxide catalysts with various compositions and its effect on the acid–base properties and the strength of surface oxygen binding.

EXPERIMENTAL

Iron–antimony oxide catalysts with the compositions $Fe_2O_3 \cdot Sb_2O_5$ and $Fe_2O_3 \cdot 2Sb_2O_5$ were prepared by coprecipitation with an ammonia solution from the solutions of iron nitrate and antimony pentachloride with further washing of the precipitate with distilled water, spray drying, drying in a dry box at 110°C for 12 h and thermal treatment in air at 800°C for 4 h.

XRD analysis of the samples was carried out using a URD-6 diffractometer with CuK_α irradiation. Lattice parameters of iron antimonate were refined using a method described in [16] and the least-squares method applied to six diffraction maximums.

Electron microscopic studies were carried out using a JEM-2010 microscope with an accelerating current of 200 kV and a resolution of 1.4 Å. Microanalytic experiments were carried out using a Philips CM-20 electron microscope equipped with a spectrometer for energy dispersive X-ray analysis (EDXA).

The binding energies of oxygen with the surface of iron–antimony oxide catalysts (q_{O_2}, kcal/mol) were

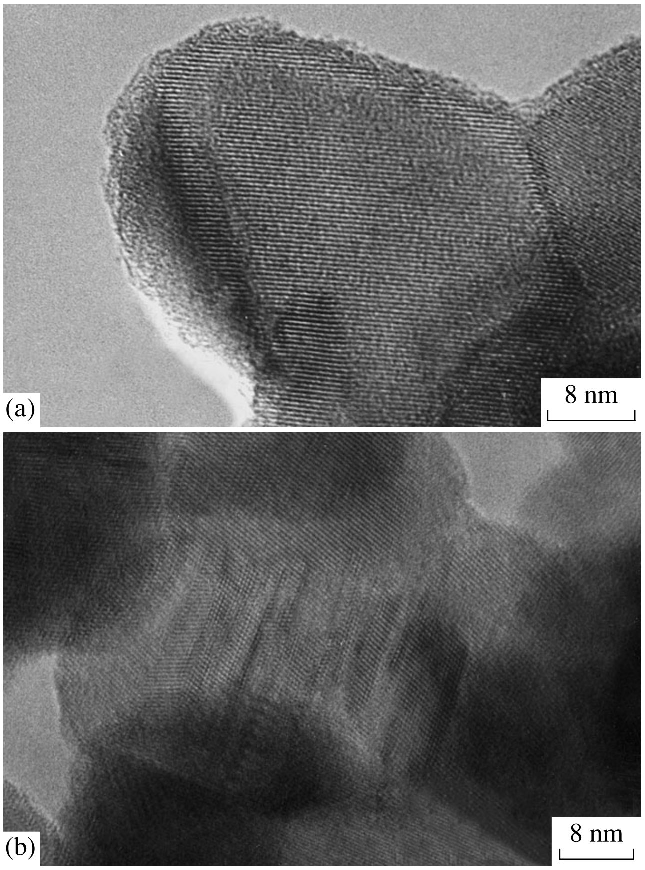

Fig. 1. Electron microscopic image of (a) pure iron antimonate and (b) iron antimonate in the presence of antimony oxide.

determined by calorimetry using the thermal adsorption of oxygen adsorbed on the catalyst surface preliminarily reduced with carbon monoxide at 450°C. Experiments were carried out in a vacuum setup connected to a high-temperature Tian–Calve calorimeter [13]. The extent of surface reduction (θ) in monolayers was calculated from the amount of removed oxygen. The surface area covered by an oxygen atom was taken to be 7.84 $Å^2$. The samples were preliminarily treated in oxygen for 4 h and then in a vacuum for 20–30 min.

RESULTS AND DISCUSSION

According to X-ray data, iron–antimony oxide catalysts of equimolar composition are a well-crystallized phase of iron antimonate $FeSbO_4$. Samples containing excess antimony are mixtures of $FeSbO_4$ and α-Sb_2O_4 phases. Lattice parameters of the phase of pure iron antimonate and iron antimonate in the presence of excess antimony oxide are the same: $a = 4.623(1)$ Å and $c = 3.011(1)$ Å. These values agree with literature data [14].

Figure 1a shows the electron microscopic image of the sample with the equimolar composition, which is the pure $FeSbO_4$ phase. It is seen that the $FeSbO_4$ structure is regular.

Figure 1b shows the image of iron antimonate in the catalyst containing excess antimony and consisting of the mixture of $FeSbO_4$ and α-Sb_2O_4 phases. In this case, the surface of iron antimonate contains shear plane defects in the direction [110]. Such defects are frequent in compounds with rutile structure, such as TiO_2. Defects in the particles of iron antimonate are disordered. Even in a single particle, there are regions with higher and lower densities of defects.

Microanalytical studies showed that, in samples containing excess antimony, the Sb : Fe ratio on various groups of iron antimonate with extended defects is not constant and ranges from 1.4 to 2.1. A typical EDXA spectrum of the sample region where the Sb : Fe ratio is 2 is shown in Fig. 2. Based on these data we assume that overstoichiometric antimony is stabilized in the region of the observed defects.

For the sample of pure iron antimonate with a regular structure the Sb : Fe ratio is close to unity and ranges slightly from 1.00 to 1.04. It is likely that the Sb : Fe ratio higher than unity is due to the insufficiently high calcination temperature of iron antimonate and some disordering of its structure.

Table shows data from [11] on acid–base properties of iron–antimony oxide catalysts consisting of pure iron antimonate or a mixture of iron antimonate and antimony oxide. As shown in [18], the surface of antimony oxide contains only one type of weak acidic aprotic sites registered by IR spectroscopy. These are assigned to the surface coordinatively unsaturated Sb^{3+} ions. Also, basic sites of one type with $pK_a = -3$ were registered.

On the surface of pure iron antimonate, many strong acidic sites are observed. They are characterized by a band in the benzonitrile spectrum at 2270 cm^{-1} and correspond to coordinatively unsaturated Fe^{3+} cations. There are also a few weaker aprotic sites characterized by a band in the benzonitrile spectrum at 2247 cm^{-1}. These correspond to the surface coordinatively unsaturated Sb^{3+} cations. In the catalyst containing $FeSbO_4$ and α-Sb_2O_4, the nature of acid sites does not change, but the concentration of strong aprotic sites (Fe^{3+}) substantially decreases and the concentration of weak acid aprotic sites (Sb^{3+}) increases.

On the surface of pure iron antimonate, there are two types of base sites with $pK_a = 2$ and -3. The catalyst containing excess antimony oxide also has basic sites of two types with $pK_a = 1$ and -3, but the concentration of more basic sites is higher.

Figure 3a shows the dependence of the binding energy of surface oxygen on the degree of surface reduction for the sample containing pure iron antimonate. It is seen that this catalyst can be readily reduced by carbon monoxide. With an increase in the degree of reduction (in percents of a monolayer, θ) from 4 to 12%, the binding energy of surface oxygen

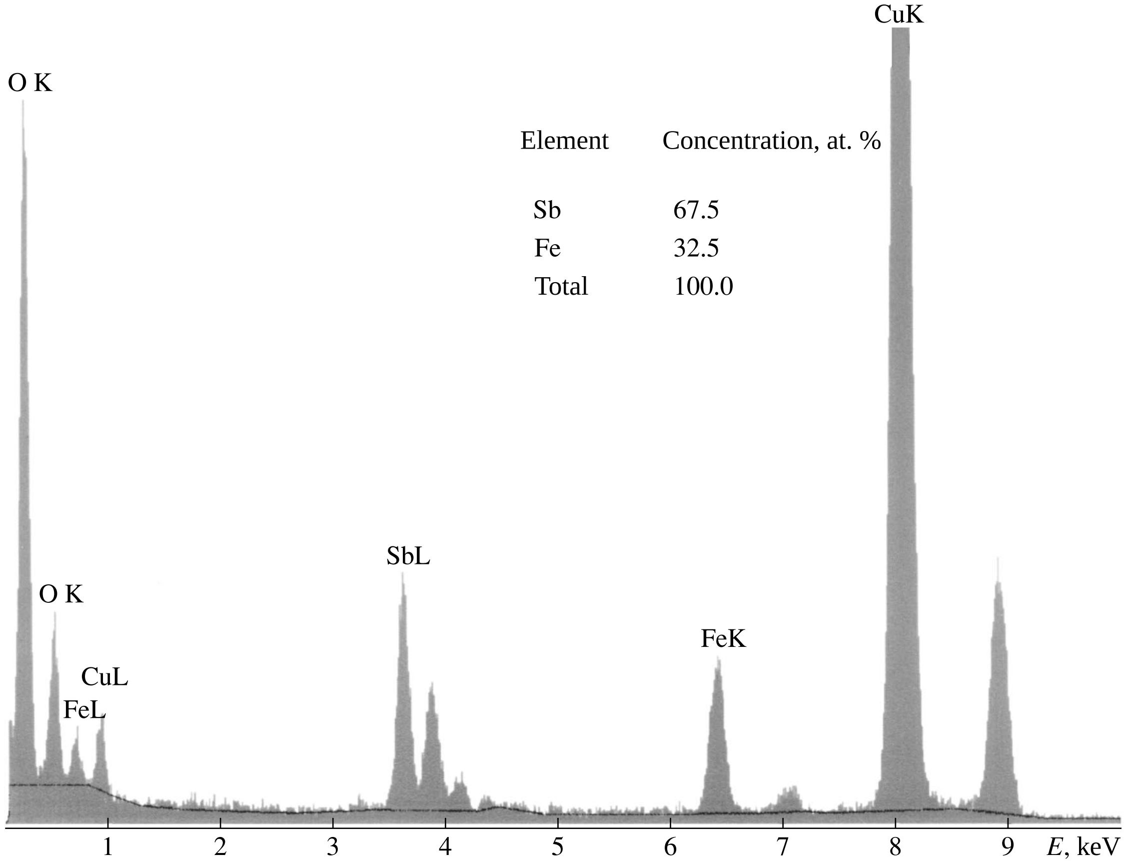

Fig. 2. Typical EDXA spectrum of iron antimonate shown in Fig. 1b.

drastically increases from 74 to 91 kcal/mol. Then, over a broad range of surface reduction degrees up to θ = 63%, the binding energy remains almost constant and drastically increases again with a further increase in θ.

In the case of the catalyst containing $FeSbO_4$ with a defect structure and α-Sb_2O_4, the dependence of the surface oxygen binding energy on the degree of surface reduction is somewhat different (Fig. 3b). In this case,

Phase composition and acid–base properties of the Fe–Sb–O catalysts according to IR spectra of adsorbed probe molecules [7]

Phase composition	Acid sites (according to C_6H_5CN)		Base sites (according to $CDCl_3$ adsorption)		
	ν, cm^{-1}	I, cm^{-1}/m^2*	ν, cm^{-1}	I, cm^{-1}/m^2	pK_a
$FeSbO_4$	2270 ± 5 (Sb^{3+})	1.03	2242 ± 3	0.91	2
	2247 ± 5 (Fe^{3+})	0.19	2259 ± 3	1.36	–3
$FeSbO_4$ + α-Sb_2O_4	2270 ± 5 (Sb^{3+})	0.41	2247 ± 3	2.00	1
	2247 ± 5 (Fe^{3+})	0.52	2258 ± 3	2.61	–3

*The values I were obtained by dividing the integral intensity of the band by the surface area of the sample per unit cross-section of light beam:

$$I = \int_0^\infty \log\frac{T_0}{T} d\nu \frac{1}{\rho S_{sp}},$$

where T_0 and T are transmittences,
ρ is the sample weight, g,
S_{sp} is the specific surface area, m^2/g,
ν is the frequency, cm^{-1}.

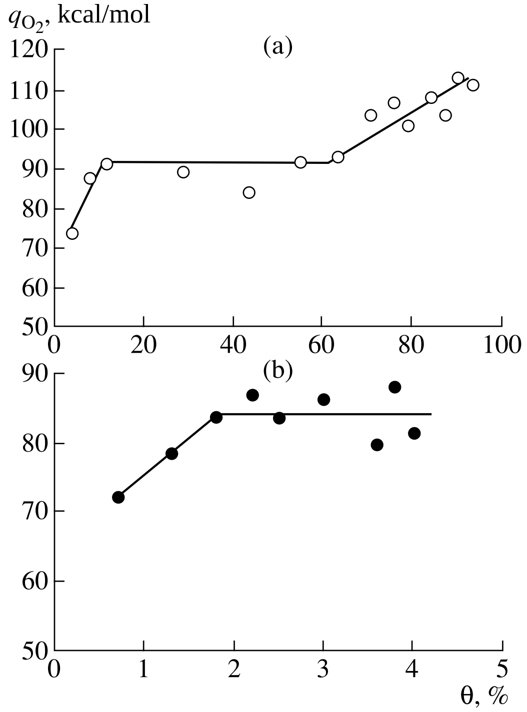

Fig. 3. Dependence of the surface oxygen binding strength on the degree of surface reduction of iron–antimony catalysts with the composition (a) $FeSbO_4$ and (b) $FeSbO_4$ + α-Sb_2O_4 (θ is the percent of a monolayer).

the catalyst surface reduction by carbon monoxide is more difficult and one fails to reduce the surface to a great degree. Even at a high concentration of CO and a prolonged time of reduction, the θ value was at most 4%, and the binding energy of oxygen was 84–86 kcal/mol.

Thus, the catalysts studied have different degrees of reducibility depending on the structure of iron antimonate. The samples of iron antimonate are readily reducible by CO, and the binding strength of surface oxygen is a constant value at relatively high degrees of monolayer reduction. Samples consisting of a mixture of phases $FeSbO_4$ and α-Sb_2O_4 are harder to reduce and have a higher strength of oxygen binding at the same degrees. An increase in the oxygen binding strength with an increase in the concentration of antimony in the iron–antimony catalyst can probably be explained by the difference in the enthalpies of formation of iron and antimony oxides in a given oxidation state. According to [19], the promotion of one oxide compound by another with a higher enthalpy of formation leads to an increase in the oxygen binding energy. For Fe_2O_3, the enthalpy of formation ΔH_{298} is –196.5 kcal/mol. For Sb_2O_4, it is higher: ΔH_{298} = –214.6 kcal/mol [20]. Therefore, we expected that, with an increase in the concentration of antimony in the iron oxide, the binding energy of oxygen would increase, and we observed this in the experiments.

There are also literature data on the binding strength of surface oxygen in iron–antimony catalysts depending on their chemical composition. Thus, the binding strengths of oxygen measured in [21] using oxygen isotope exchange at the degree of exchange $x = 0.01$ were 41 kcal/mol for an iron–antimony sample with an equimolar composition, 64.83 kcal/mol for samples with an Sb : Fe ratio of 2, and 59 kcal/mol for samples with an Sb : Fe ratio of 5 : 1. Although the isotope exchange method mostly provides information on the least bound oxygen, one can see the effect of chemical and phase compositions on the oxygen binding strength. At the same time, the binding strength of surface oxygen obtained from oxygen isotope exchange is the same for samples with an equimolar composition, the samples containing excess antimony, and pure antimony oxide: 45 kcal/mol [22]. According to [17], the strength of surface oxygen binding measured by calorimetry for an $Fe_2O_3 \cdot 2Sb_2O_5$ sample calcined at a lower temperature also depends on the degree of surface monolayer reduction, whereas the strength of oxygen binding at a degree of surface monolayer reduction of 5–6% is much lower than in our case: 48 kcal/mol. With an increase in the degree of reduction from 8 to 25%, it increases to 74% and does not change further up to complete reduction. Note that, in this case, the authors of [17] only managed to reduce the surface by carbon monoxide to θ = 8%. It is likely that somewhat different values of surface oxygen binding strength measured in [17] and in this work are due to the difference in the sample calcination temperatures, which determine the catalyst structures (the nature and concentration of defects) and the conditions of its reduction.

Thus, based on the data obtained, we conclude that, in iron–antimony catalysts containing excess antimony oxide and consisting of a mixture of $FeSbO_4$ and α-Sb_2O_4 phases, the structure of iron antimonate phase changes compared to the catalyst with an equimolar composition, which is the individual $FeSbO_4$ phase. In the presence of excess antimony oxide in the structure of iron antimonate, disordered extended defects in the structure of iron antimonate are formed and have a structure of crystallographic shifts where overstoichiometric antimony is accumulated. Such a change in the structure substantially affects the acid–base properties of the surface and the strength of surface oxygen binding. The concentration of coordinatively unsaturated Sb^{3+} ions, which are weak acid aprotic sites, increases and the concentration of strong aprotic sites, which are coordinatively unsaturated Fe^{3+} ions, decreases. Simultaneously, the number and strength of base sites changes. A change in the surface structure of iron antimonate leads to a change in the binding strength of its surface oxygen. A change in these parameters, which affect the catalytic properties of oxide catalysts, determines the higher selectivity if iron–antimony catalysts containing a mixture of $FeSbO_4$ and α-Sb_2O_4 phases are compared to pure $FeSbO_4$.

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