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Tin–antimony oxide catalysts: preparation conditions and properties

R A Lemberanskii, I B Annenkova, Z A Bakhshieva
Azizbekov Azerbaidzhan Industrial University, Baku

ABSTRACT. The influence of preparation conditions of tin–antimony catalysts on their phase composition and olefin-oxidation activity is analysed. Special attention is paid to the influence of the starting compounds, the preparation method and the calcination temperature on the formation of the catalytic surface. The catalyst properties can be regulated by varying their synthesis conditions. Information about the effect of preparation conditions on the properties of the catalysts is scientifically and practically significant for their designed synthesis.

The bibliography contains 44 references.

Contents

I. Introduction 67
II. Influence of preparation method on catalytic activity of tin and antimony oxides 67
III. Influence of calcination temperature on the catalyst phase composition 69
IV. Dependence of catalyst properties on starting Sn- and Sb-containing reagents 69
V. Influence of synthesis conditions on formation of the catalytic surface 71
VI. Conclusion 73

I. Introduction

The economy requires highly active and selective catalysts of reactions, including oxidations, of organic compounds in order to produce the necessary chemical commodities.

The development of a process is an important but not the only condition for preparing an effective catalyst. The synthesis itself is an exceedingly complicated and delicate problem. It requires the strictest observance of the ratio of starting compounds, succession of operations and technical process parameters. This is necessary because the specific structure and given physicochemical, mechanical and catalytic properties are formed during the catalyst preparation. Therefore the numerous investigations of heterogeneous catalysts intentionally include careful studies of the synthesis process, the influence of the preparation method, the nature of the starting materials, the medium, the heat-treatment temperature, and other process parameters on the properties of the synthesised catalysts. An analysis of the results obtained is certainly of interest.

In the present review an attempt is made to generalise and analyse literature data for the influence of such factors on the structure and properties of the tin–antimony oxide system, which is known to contain highly active and selective catalysts of oxidation of olefins into unsaturated aldehydes.

II. Influence of preparation method on the catalytic activity of tin and antimony oxides

Tin–antimony catalysts are especially sensitive to the synthesis conditions. This is particularly evident in the contradictory data for the influence of composition on activity in oxidation and oxidative dehydrogenation of low-molecular-weight olefins.

Traditional preparation methods of such catalysts are rather complicated. They are usually prepared from Sn and Sb oxides that are precipitated separately by the action of boiling concentrated HNO_3 on the metals (or their oxides)[1–4] or of ammonia on HCl solutions of Sn^{IV} and Sb^{III} or Sb^{V} chlorides[5–9] followed by drying of the hydroxide mixture at 120 °C and prolonged (up to 16 h) calcination at 500–1000 °C.[1–5] Vartanov, et al.[10] suggest that the active catalyst phase is formed during the early stages of preparation and possibly even at the time of mixing of the hydroxides.

The prepared catalyst is a complicated heterogeneous system consisting of miscible Sn and Sb oxides over a wide range of Sn/Sb ratios. Data on the boundaries of the miscibility of the oxides are contradictory. Thus, the limiting Sb concentration in the SnO_2 lattice, according to the literature,[2,3,5,8,11–15] varies from 3 to 30 at.%. Such a wide range of concentrations can be explained on one hand by the different methods of determining the oxide solubility limits. X-Ray investigations indicate that Sb is dissolved in the catalyst lattice up to 20–30 at.%. The solid-solution region is limited to 7–8 at.% Sb according to electrical conductivity. On the other hand, the solubility of Sb in SnO_2 depends on the duration and temperature of calcination. It increases with increasing temperature up to 900 °C and then decreases at $t > 100$ °C.[5,13,16]

The question of whether the catalyst components undergo a chemical reaction has not been answered. A chemical compound in the Sn–Sb oxide system could not be detected by X-ray diffraction.[2,3,11] However, it could possibly exist in an X-ray amorphous form. This was confirmed by IR spectrosocpic studies that enabled Alkhazov to detect formation of a chemical compound of proposed composition $8SnO_2.Sb_2O_4$.[17]

Precipitation produces rather highly active and selective Sn–Sb catalysts of mild oxidation of olefins such as propylene into acrolein, isobutene into methacrolein, and oxidative dehydrogenation of butene into divinyl.[10,17–19] Thus, the yield of methacrolein and divinyl is 70% with a selectivity of 80–90% at 400 °C and a gas-mixture flow rate of 3600 h^{-1}. Solid solutions of Sb in SnO_2 in the range 10–20 at.% Sb are most active in mild oxidations.

The method for synthesising Sn–Sb catalysts mentioned above also has drawbacks. It includes many steps and involves formation of toxic and corrosively aggressive side products. The method of synthesising Sn–Sb catalysts from the metal oxides consisting of calcining their mixtures is technically simpler and devoid of these shortcomings. There were concerns about whether the components

reacted in this instance and whether it was extensive enough to form the active phases. Vartanov, et al.[10] confirm that oxides of Sn (SnO_2) and Sb do not react during joint calcination. The possibility of a solid-state reaction between SnO_2 and Sb oxides leading to a solid solution based on rutile has been demonstrated in other studies.[5,13,20]

Rather detailed studies of Sn–Sb catalysts prepared by calcining a mechanical mixture of Sn and Sb oxides have been carried out.[19–21] Oxides of $Sn^{II,IV}$ and $Sb^{III,V}$ were used as starting materials. A moist paste of their mixture was dried at 120 °C and calcined in air at 800 °C for 8 h. Thermographic analysis of the resulting oxide mixtures and X-ray phase analysis of the catalysts suggested with certainty that the starting components reacted during catalyst synthesis. This formed two types of solid solutions. One was based on rutile with the limiting solubility of Sb in SnO_2 of ~15 at.%. The other was a solid solution of Sn (15 at.%) in Sb_2O_4. X-Ray diffraction also detected an X-phase different from each of the starting oxides.

Tests of the samples for gas-phase oxidation of isobutene suggested that the products of reaction of Sn and Sb oxides are the active catalysts. The individual oxides do not catalyse formation of methacrolein. The binary compositions are rather active in this reaction.[19,22] Samples synthesised from SnO_2 and Sb oxides are slightly active.

Systems prepared from SnO and Sb oxides are very active for partial oxidation of isobutene. Compositions in the range of oxide solid solutions 80–90 at.% Sn and 70–80 at.% Sb are most active. The sharp reduction in the yield of CO_2 with the addition of even a small amount of antimony to tin oxides likewise confirms the existence of inter-reaction between the original oxides, but it does not explain the results for dilution of SnO_2 with antimony oxides.

In Fig. 1, the activity for isobutene oxidation of catalysts synthesised from Sn and Sb oxides is compared with that of those prepared by coprecipitation from their metallic powders. The ratios Sn/Sb in the starting materials, the heat-treatment conditions and the isobutene oxidation process are in all instances identical. Catalysts prepared from SnO_2 and Sb oxides have greater selectivity than those synthesised by the usual coprecipitation method. However, they give poorer yields of methacrolein. Samples prepared by calcination of a mixture of SnO and Sb oxides are slightly more selective than those prepared from SnO_2 and Sb oxides although the latter are nonetheless sufficiently selective. The activity of the former for methacrolein formation is much greater than that of the latter and comparable to that of catalysts of metallic Sn and Sb.

Therefore, oxides of $Sn^{II,IV}$ and $Sb^{III,V}$ react when their mixture is calcined. Phases that are active in partial olefin oxidation are formed. Differences in the activity of various series of catalysts indicate that the extent of reaction of the catalyst components and the phases formed are apparently different. These properties depend on the oxides chosen as starting materials and more accurately on the valence of the metal forming the oxide, among other factors. The valence of Sn in the starting oxide has a greater effect on catalyst formation than the Sb valence. In fact, it can be seen from Fig. 1 that samples prepared from various Sb oxides differ little in activity for isobutene oxidation whereas catalysts synthesised for SnO are much better (by about two times) than those prepared from SnO_2.

It is possible that Sn^{2+} becomes easier to oxidise after formation of a solid solution of Sb in the lattice of SnO, which is though to be responsible for oxidation of an olefin to a aldehyde.[13,14] Dissolution of Sb in the previously formed SnO_2 is apparently more difficult. This leads to enrichment of the catalyst surface in Sb as dispersed Sb_2O_4. According to the literature[23] this ensures the high selectivity. The role of surface Sb in selective partial olefin oxidation is also evident in a comparison of the catalytic properties and the surface composition of the Sn–Sb–O system. The experimental data obtained previously[19,21,22] show that samples over a wide range of compositions (10–90 at.% Sb) are sufficiently selective in mild oxidation of isobutene into methacrolein. The selectivity is practically independent of the ratio of starting Sn and Sb oxides. Structural studies of these samples by XPS demonstrated that the surface layer was enriched in Sb by at least two times compared with the bulk.

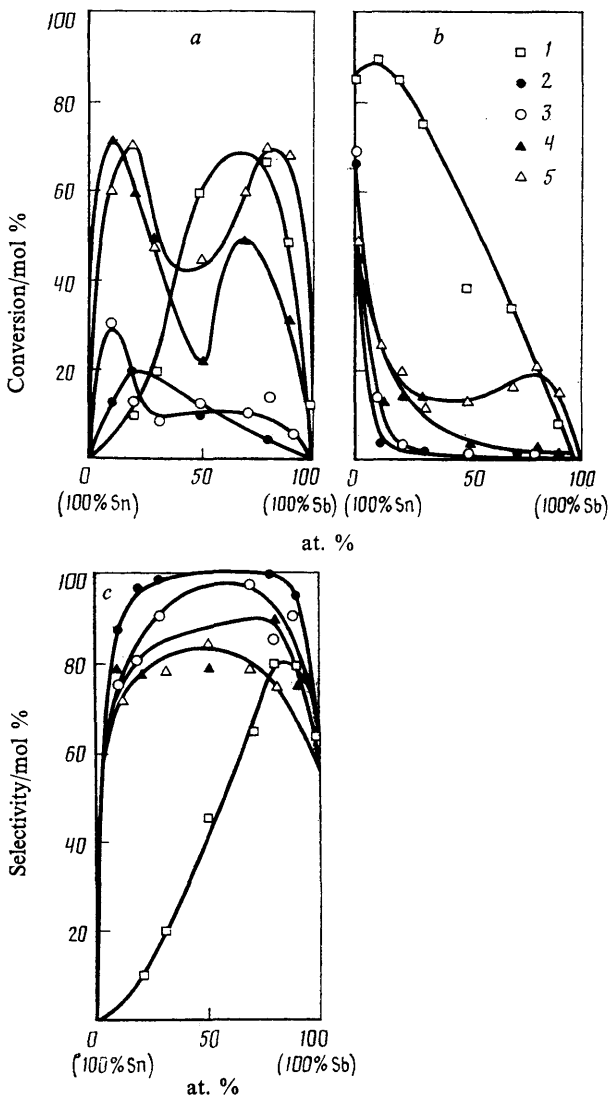


Figure 1. Activity of tin–antimony catalysts of oxidation of isobutene (400 °C): conversion into methacrolein (*a*), conversion into CO_2 (*b*), selectivity for methacrolein (*c*). Catalysts of metallic Sn and Sb (*1*), $SnO_2-Sb_2O_3$ (*2*), $SnO_2-Sb_2O_5$ (*3*), $SnO-Sb_2O_3$ (*4*), $SnO-Sb_2O_5$ (*5*).

III. Influence of calcination temperature on catalyst phase composition

One of the most important process parameters in synthesising catalysts is the calcination temperature, which has a substantial effect on their structure and phase composition and eventually determines their catalytic activity.

The need for high-temperature activation of Sn–Sb catalysts in order to achieve high selectivity for mild oxidation products in olefin oxidations has repeatedly been pointed out.[6,14,16,20,24,25] Various explanations of this need for high-temperature calcination have been offered. According to some,[20,24,26] it is required to increase the solubility of Sb in the SnO_2 lattice. This increases the number and stability of free electrons at high temperatures and also the stability of Sb^V to calcination and redox processes. The improved catalytic properties of the mixed oxides may be a result of both of these factors or only one of them.

Godin, et al.[14] view the role of high-temperature treatment as the destruction of microporosity. This increases the crystallinity and the particle size of the rutile.[9]

In the opinion of Roginskaya, et al.,[16] such heat treatment is necessary to effect the conversion of Sb^V into Sb^{III}.

Sala and Trifiro[20] think that the high-temperature calcination has three different types of effect on the mixed Sn–Sb oxides: a) It sharply increases the extent of SnO_2 modification by Sb, exhibited as increased absorption in the visible spectral region and a greater amount of butadiene formed after oxidative dehydrogenation of *n*-butenes. b) It sharply increases the isomerisation ability due to migration of Sb^V into the SnO_2 lattice and subsequent surface dehydrogenation. c) It decreases the irreversible catalyst mass loss in the redox process caused by the reduction of Sb oxide and partial sublimation of the metallic Sb formed.

The conclusions supported by the experimental data that the solubility of Sb in the SnO_2 lattice increases with increasing calcination temperature are still rejected by certain investigators. According to the literature,[8,15] Sn–Sb catalysts calcinated at high temperatures show a reduced tendency to incorporate Sb into the SnO_2 lattice. Thus, as demonstrated previously,[27–30] the catalytic surface is enriched in Sb. Several authors think[8,15,29,30] that a high calcination temperature induces migration of Sb from the bulk of the rutile to the surface. This forms an equilibrium solid solution of Sb in Sb oxide through thermally excited aggregation of SnO_2 octahedra. The Sb oxide readily volatilises at high temperatures. This leaves on the surface a crystalline solid solution of the rutile type that contains 4 at.% Sb in SnO_2 and up to 25% Sb in the catalyst.

Investigations of Sn–Sb catalyst[27] containing 4 at.% Sb, which according to the literature[8,27] corresponds to the limiting solubility of Sb in SnO_2, did not detect a segregated crystalline Sb oxide phase on the surface of the solid solution, as was described previously.[29] This suggested to Berry and Smith[27] that the enrichment of the surface of Sn–Sb catalyst in Sb after high-temperature calcination is due to concentration of Sb, possibly completely surrounded by Sn, on the SnO_2 rutile surface and is not accompanied by formation of a segregated crystalline surface phase of Sb oxide.

Samples with a high Sb content consist, after calcination at 1000 °C, as demonstrated before,[9] of a rutile solid solution, a small amount of a crystalline substance different from rutile, and significant quantities of an amorphous substance containing Sb. Several investigators[9,30] think that the amorphous phase is formed from Sb that did not enter the solid solution and did not act as a nucleus for formation of Sb_2O_4, which is readily volatiled at high temperatures. The crystalline phase different from rutile was not identified.

Thus we can see that there are various ideas about the surface phase composition formed during high-temperature calcination of Sn and Sb oxides. The question of which phases are responsible for the selective partial olefin oxidation in this catalytic system remains unanswered. The increase of selectivity for mild oxidation of butene[31,32] and propylene[29] of Sn–Sb catalysts due to their high-temperature calcination and the resulting enrichment of the surface in Sb is connected by some authors[14,24,26,32,33] with a solid solution of Sb in SnO_2 and by others[29,34] to the presence on the surface of a catalyst of this solid solution in combination with an Sb oxide phase or to an Sb_2O_4 phase.[23,35] It is also thought[8] that the bulk crystalline SnO_2 lattice is just as important to the occurrence of the catalytic reactions as the presence on the catalytic surface of Sb and Sn ions in close contact with each other.

The majority of investigations of the Sn–Sb oxide system have been carried out with compositions enriched in Sn. The middle region of compositions are still largely unexplored. In the opinion of Kustova, et al.[5] a compound of Sn and Sb oxides is not formed in samples calcined at 500–950 °C. This agrees with previous results.[14] However, Roginskaya, et al.[16] think that an unidentified phase containing 50–80 at.% Sb in addition to a solid solution of Sn is formed in the Sb_6O_{13} structure at 700 °C or in Sb_2O_4 at 900 °C. Structural relationships are unclear even for the Sb–O system in compositions enriched in Sb.

IV. Dependence of catalyst properties on Sn- and Sb-containing starting materials

The choice of Sn- and Sb-containing reagents is an important factor in catalyst formation during its synthesis. This last condition can often change even the influence of heat treatment on the catalyst properties. An investigation of this problem demonstrated[36,37] that high-temperature treatment can produce, depending on the Sn- and Sb-containing compounds chosen as starting materials for the catalyst synthesis, in one instance, samples differing substantially in phase composition and properties. This occurs regardless of an identical Sn/Sb ratio. In another instance catalysts with very similar properties are produced from components with an identical starting ratio.

Lemberanskii, et al.[36,37] studied catalysts of two extreme compositions in which Sn/Sb = 1/9 and 9. These were prepared from metallic Sn and Sb (series A) and from the metal chlorides (series B).

In the region enriched in Sb, the density of series A samples was approximately constant in the calcination temperature range 300–1000 °C at about 6.5–7.0 g cm^{-3}. The specific surface decreased from 6.4 to 4.0 m^2 g^{-1}. The mass change was insignificant. A stronger temperature effect is observed in series B. The density of this series increases continuously and substantially with increasing heat-treatment temperature. It is three times greater for a sample with a calcination temperature of 1000 °C than for one calcined at 300 °C and 1.5 times greater than that of the series A sample of analogous composition. Series B catalysts are more intensely coloured. A large mass loss is observed during heat treatment of series B samples. A significant amount of sample volatilises at all calcination temperatures.

X-Ray phase analysis of calcined catalysts and the phases that were vapourised and then condensed (Fig. 2) showed that series A samples are solid solutions based on Sb_2O_4 (curve *1*). The series B catalysts after calcination at 300 °C are a complicated mixture consisting apparently largely of various chloride compounds. Bands belonging to the pure Sn and Sb oxides are not observed by X-ray diffraction. Starting at 600 °C bands characteristic of SnO_2 (curve *2*) appear in the diffraction patterns and are observed up to 1000 °C. Lines belonging to other Sn and Sb oxides are practically absent. Thus, even at 600 °C the sample is exclusively SnO_2 (poorly formed). At 1000 °C it is already well crystallised SnO_2. The presence of a solid solution of Sb in SnO_2 is possible. It is thought that a significant part of the Sb volatilises as oxides during the calcination. Strong bands of Sb_2O_4 in addition to lines of the other Sb oxides Sb_2O_3 and Sb_2O_5 (curve *4*) are clearly evident in the diffraction patterns of the sublimed phases.

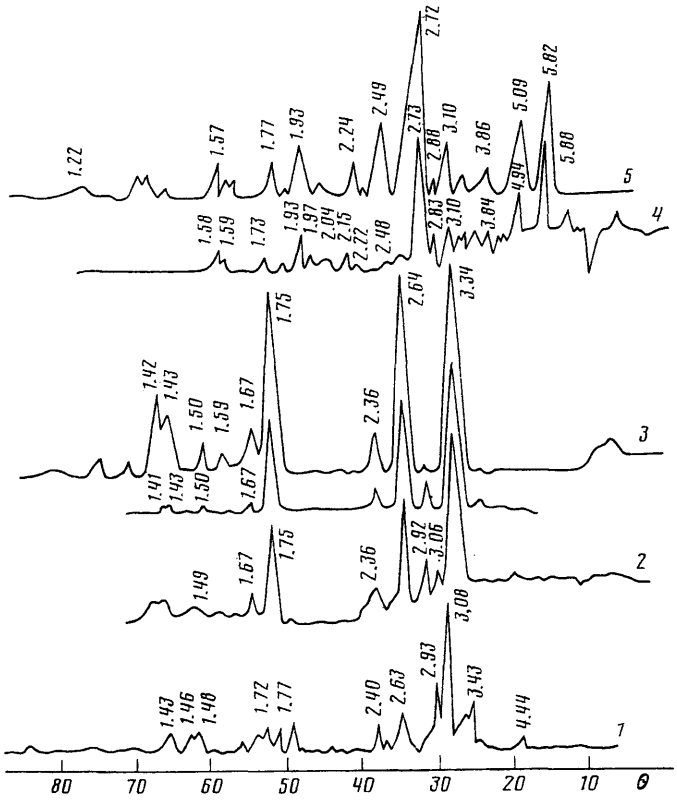


Figure 2. Diffraction patterns of tin–antimony catalysts and sublimed phases: catalysts of metallic Sn and Sb, t_{pr} = 1000 °C, Sn/Sb = 1/9 (*1*); for the curve over the curve *2*, Sn/Sb = 9. Samples of Sn and Sb chlorides, t_{pr} = 1000 °C, Sn/Sb = 1/9 (*2*), 9 (*3*). Sublimed phases of samples of Sn and Sb chlorides, t_{pr} = 600 °C, Sn/Sb = 1/9 (*4*), 9 (*5*).

In the region of compositions enriched in Sn (Sn/Sb = 9), the influence of heat-treatment temperature on catalyst formation depends little on the starting materials and is seen mainly as an intense volatilisation and a large amount of volatilised material. Whereas series A samples lose 5–7% of their mass, series B samples lose 70–80% at 600–1000 °C. The density and bulk mass of samples calcined in the temperature range 600–1000 °C are practically constant. The samples are dark blue, i.e. the catalyst is practically formed even at 600 °C. X-Ray phase analysis of samples with Sn/Sb = 9 demonstrated that the catalyst prepared from the metals is a solid solution of Sb in SnO_2 and that the maximal possible Sb concentration reaches 10–15 at.%.[38] Bands of SnO_2 (curve *3*) are also noted in the diffraction pattern of the sample synthesised from the metal chlorides. Bands characteristic of Sb oxides are not observed and they are not found in the diffraction patterns of the sublimed phases. The amount of sublimed phase is rather large. A comparison of the observed diffraction bands (curve *5*) with previous results[39,40] suggests that this phase contains mainly ammonium chloride and ammonium chlorostannate(IV). Therefore, it seems that all of the Sb is dissolved in the Sn oxide and that the catalyst is a solid solution based on SnO_2, probably in combination with SnO.

Thus, the phase composition of the Sn–Sb catalysts substantially depends on the synthesis conditions. Stucture formation in series A samples, which are prepared from metallic Sn and Sb, is mainly finished up to 600 °C. For series B samples, which are prepared from Sn and Sb chlorides, a longer time and higher temperatures are required and the process is accompanied by a significant loss of catalyst mass. According to thermographic and thermogravimetric analyses, water is lost up to 200 °C. Endotherms are observed in the range 400–500 °C. These are accompanied by large mass losses (65–85%). A Sn compound containing ammonium and chlorine (Sn/Sb = 9) and Sb oxides (Sn/Sb = 1/9) are vapourised. The oxide SnO_2 is more stable.

The high volatility of Sb oxides during heat treatment of series B samples is surely explained by the preparation method. The rate of migration of Sb oxides in series A samples is not so fast and leads only to concentration of Sb on the catalyst surface. Many authors use this to explain the high-temperature activation of Sn–Sb catalysts that is necessary to increase their selectivity for mild oxidation products in olefin oxidation reactions.[6,14,16,20,24,25] therefore, depending on the migration rate of Sb cations, which in turn depends on the starting materials and the catalyst preparation method, the surface of samples in one instance becomes enriched in Sb (series A). In the other instance, even with a high starting Sb content, the surface is depleted of Sb during heat treatment due to volatilisation and becomes enriched in Sn (series B). It is interesting to compare the diffraction patterns of catalysts prepared from Sn and Sb chlorides that have a different ratio of starting materials. In both cases only bands corresponding to SnO_2 are seen (Fig. 2, curves *2* and *3*).

Naturally this cannot affect the catalytic properties of the samples. The test results for isobutene oxidations that are plotted in Fig. 3 confirm this hypothesis.

It can be seen from Fig. 3 that the activity of catalysts of various compositions synthesised from the metals are substantially different. The sample with a high Sn content is significantly more active. Thus, an isobutene conversion of 70 mol% under the chosen oxidation conditions is achieved already at 350 °C whereas it does not exceed 20 mol% at this same temperature on the second sample (Sn/Sb = 1/9). However, the methacrolein yield is much greater at Sn/Sb = 1/9 (60 mol%) than for Sn/Sb = 9, where it does not reach 10 mol%. The sample enriched in Sn in practice catalyses the complete oxidation whereas conversion of olefin into the destructive oxidation products is less than 10 mol% (at 450 °C) on the catalyst

enriched in Sb. This catalyst is selective (up to 90 mol%) for methacrolein formation.

However, a sample of this same composition (Sn/Sb = 1/9) but prepared from metal chlorides is much more active than the series A sample for complete oxidation. It is much less selective for mild oxidation. These samples differ substantially in phase composition. The surface of the series B catalyst is enriched in SnO_2 due to volatilisation of Sb oxides.

In comparing samples with an identical ratio of components that are prepared from different starting materials, it is found that series B samples are always more active than series A samples for oxidation of isobutene to CO_2. The selectivity for methacrolein on them is much lower due to combustion of both isobutene and the methacrolein that is formed (methacrolein is not observed in the reaction products in the studied temperature range on the series B sample with Sn/Sb = 9).

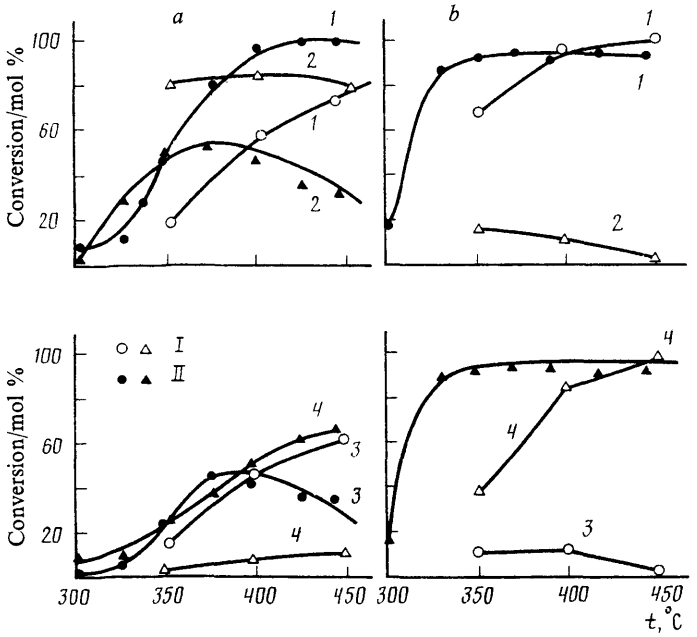


Figure 3. Activity of tin–antimony catalysts [Sn/Sb = 1/9 (*a*) and 9 (*b*)] for oxidation of isobutene (3600 h^{-1}, 5 mol% of *iso*-C_4H_8): series A (from metallic Sn and Sb) (*I*), series B (from Sn and Sb chlorides) (*II*). Total conversion of isobutene (*1*), selectivity for methacrolein (*2*), conversion into methacrolein (*3*), conversion into carbon oxides (*4*).

V. Influence of synthesis conditions on formation of the catalytic surface

The substantial difference in the activity of catalysts prepared by various methods is mainly due to the different nature of the catalytic surface formed under given catalyst synthesis conditions.

High-temperature migration of Sb from the crystal bulk to the catalyst surface has been observed.[8,15,27–30,36,37] The rate of migration and the resulting effects substantially depend on the preparation method of the catalyst. In particular, the starting Sn- and Sb-containing compounds are important. Oxygen necessarily migrates with the Sb and then is redistributed in its various forms on the surface. All of this should change the acid–base characteristics of the catalyst surface and eventually the catalytic properties.

According to Lemberanskii, et al.[36,37] the high oxidising capability of samples prepared from Sn and Sb chlorides, which markedly exceeds that of catalysts from metallic Sn and Sb, is largely controlled by the surface acid–base properties and is explained by their high surface acidity.

This argument is supported by the known fact that the products of complete oxidation are formed at acidic surface centres that depend on surface Sn cations for the Sn–Sb oxide catalysts.[7]

Data for the isomerisation of butene-1 into butene-2 (Fig. 4) confirm this hypothesis.[36,37] The isomerising capability of samples prepared from the chlorides is greater than that for catalysts prepared from the metals. It also appears at lower temperatures. This difference is especially large for the composition with Sn/Sb = 1/9, in which a sharp difference in the phase composition is observed according to X-ray structural analysis.

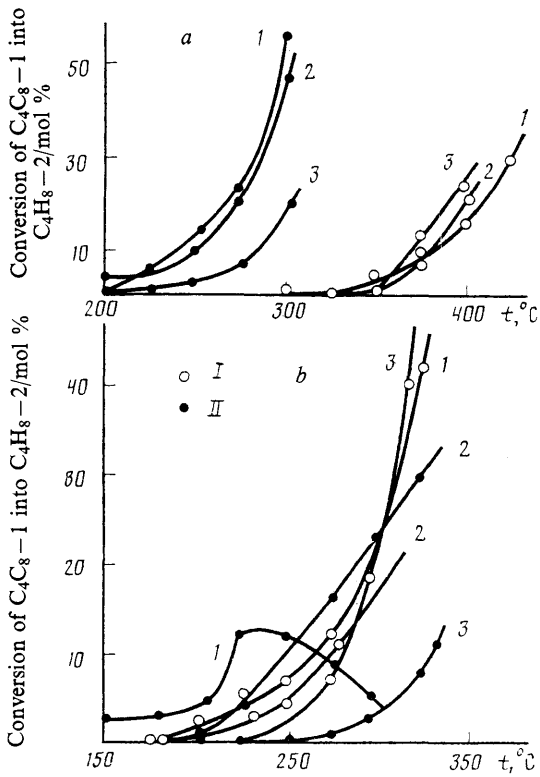


Figure 4. Isomerisation of butene-1 and butene-2 on tin–antimony catalysts (3600 h^{-1}, 5 mol% C_4H_8): Sn/Sb = 1/9 (*a*), Sn/Sb = 9 (*b*). Series A (from metallic Sn and Sb) (*I*), series B (from Sn and Sb chlorides) (*II*); t_{pr}, °C: 600 (*1*), 800 (*2*), 1000 (*3*).

Such results agree with previous studies[20] in which the strong isomerising capability of Sn–Sb catalysts prepared from metal chlorides is explained by the increase in the number of Lewis acid centres formed after dehydration of the surface. This is confirmed

by studies of the isomerisation of butene-1 into butene-2 in an oxidising atmosphere without oxygen in the reaction mixture.[36,41] The experiments were carried out by a response method. An olefin–air mixture was continuously passed at a volume rate of 3600 h^{-1} through a catalyst. After each half minute (analysis time) the reaction products were analysed. After a steady state was attained, the oxygen flow rate was replaced by an equivalent amount of nitrogen to maintain the given volume flow rate. The response of the system to removal of oxygen from the gas phase was followed by continuously analysing the reaction products. After a new steady state was attained, the oxygen flow was started, expelling the nitrogen from the system. The product analyses were stopped after the system again reached a steady state.

Catalysts were prepared by calcining at 800 °C Sn and Sb hydroxides prepared in one instance by the action of concentrated HNO_3 on metallic Sn and Sb and in another by the action of ammonia on the metal chlorides.

It can be seen in Fig. 5*a* that *cis*-butene-1 is formed in greatest yield in an oxidising atmosphere (region *I*) on samples enriched in Sn (curves *1* and *2*). The different activities of the catalysts of the two compositions Sn/Sb = 1/9 and 9 is especially large for samples prepared from the metals (curves *1* and *3*). It is interesting that the isomerisation of butene-1 into *cis*-butene-2 stops on all samples after oxygen is taken out of the gas mixture (region *II*). Subsequent addition of oxygen (region *III*) restores the activity of samples with Sn/Sb = 1/9 to the original value whereas that of samples enriched in Sn (Sn/Sb = 9) does not quite reach the initial value.

Catalysts with a high Sb content are most active in the isomerisation of butene-1 into *trans*-butene-2 (Fig. 5*b*). The yield of *trans*-butane-2 is much less than that of the *cis*-isomer and does not depend on the presence of oxygen in the reaction mixture.

The following conclusions were made by Lemberanskii, et al.[36,41] after analysing their experimental data and results of earlier experiments.

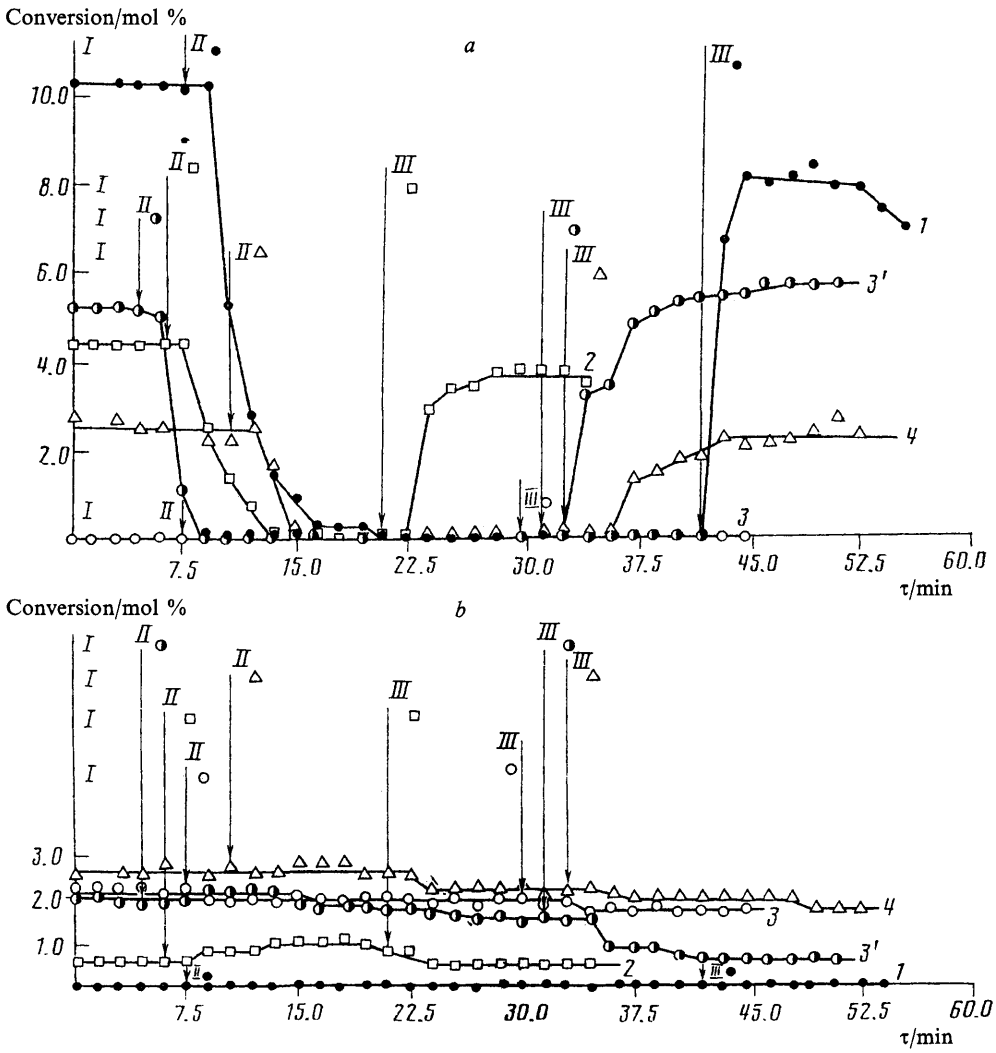


Figure 5. Isomerisation of butene-1 into *cis*-butene-2 (*a*) and *trans*-butene-2 (*b*) on tin–antimony catalysts. Sn/Sb: 9 (*1*, *2*), 1/9 (*3*, *4*). From metallic Sn and Sb (*1*, *3*), from Sn and Sb chlorides (*2*, *4*). O_2 in the gas mixture (*I*, *III*), N_2 in the gas mixture (*II*).

Butene-1 is isomerised into *cis*- and *trans*-butene-2 on Sn–Sb catalysts in an oxidising atmosphere. The yield of *cis*-butene-2 is much greater than that of the *trans*-isomer. Without oxygen in the gas mixture the isomerisation of butene-1 into *trans*-butene-2 continues practically unabated whereas the formation of *cis*-butene-2 is completely inhibited. This certainly indicates that butene-1 is isomerised into *cis*- and *trans*-butene-2 by different mechanisms. In particular, weakly adsorbed molecular oxygen is surely involved in the formation of the *cis*-isomer.

It follows from the experimental data presented that butene-1 is isomerised into *cis*-butene-2 on the catalytic surface enriched in Sn. This is clearly seen by comparing samples prepared from metallic Sn and Sb that differ sharply in composition (Sn/Sb = 1/9 and 9). In the first instance conversion of butene-1 into *cis*-butene-2 is greater; in the second, the *cis*-isomer is not formed under the selected experimental conditions (t = 275 °C). Formation of *cis*-butene-2 is observed on the sample of analogous composition (Sn/Sb = 1/9) that is synthesised from the metal chlorides. However, this does not contradict the preceding observations. It must be considered that according to physicochemical investigations this sample is relatively enriched in Sn due to the fast rate of migration of Sb to the surface and the subsequent volatilisation of Sb, which does not enter the solid solution.[37] The comparison is made with the catalyst of the same nominal composition but prepared from metallic Sn and Sb, where the slower rate of migration of the Sb cations from the bulk limits volatilisation and ensures concentration of Sb on the surface. Therefore, these samples differ in ability to isomerise butene-1 to *cis*-butene-2.

The requisite presence of oxygen in the gas in combination with the catalytic surface enriched in Sn for isomerisation of butene-1 into *cis*-butene-2 indicates that Sn ions are responsible for weakly adsorbed molecular oxygen. This conclusion is confirmed by data for the high activity of SnO_2 and also of Sn–Sb catalysts with surfaces enriched in Sn due to their specific synthesis conditions in complete oxidation reactions requiring the participation of oxygen weakly bound to the catalyst surface.[11,18,22,37,42]

An analysis of previous experimental data[36,37] also suggests that Sb cations are responsible for the conversion of butene-1 into *trans*-butene-2. In fact, butene-1 isomerises into *trans*-butene-2 on the sample enriched in Sb (Sn/Sb = 1/9). No isomerisation is observed on the catalyst with the minimal Sb content (Sn/Sb = 9). This is clearly evident for catalysts prepared from metallic Sn and Sb that are solid solutions of the oxides (Fig. 5*b*, curves *1* and *3*). For samples synthesised from the metal chlorides, formation of the *trans*-isomer becomes noticeable even at Sn/Sb = 9. This is not unexpected if the enrichment of the catalyst surface in Sb as a result of migration from the crystal bulk is considered.

The established fact that Sn and Sb ions are responsible for *cis*- and *trans*-isomerisation, respectively, of butene-1 is of definite interest. It is known that the isomerisation of butene-1 is proposed as a qualitative test for the determination of the total acidity of an oxide catalyst.[43] The study of the acidity of Sn–Sb catalysts by IR spectroscopy of adsorbed ammonia[44] suggested that the Brönsted acidity is caused by Sb ions; the Lewis acidity, by coordinatively unsaturated Sn ions on the surface. Keeping this in mind and recalling the data mentioned above, isomerisation of butene-1 into *cis*- and *trans*-butene-2 can be recommended as a test for Lewis and Brönsted acidity, respectively.

VI. Conclusion

It can be seen from the material presented that the synthesis conditions of Sn–Sb catalysts play such an important role in the formation of their structure and properties that they often dominate over the chemical composition. In fact, the choice of starting Sn- and Sb-containing reagents can affect the rate of high-temperature migration of Sb from the crystal bulk to the surface. This can produce samples with similar or sharply differing catalytic properties depending on the starting ratio of components. In one instance highly selective catalysts of partial oxidation of isobutene into methacrolein are obtained; in the other, active catalysts of complete oxidation.

The optimal synthesis method can be selected on the basis of data for the influence of the method and preparation conditions on the catalyst properties. This method would be fully responsive to economic, technical and ecological demands. For the Sn–Sb oxide system, an analysis of the experimental data indicates that solid-state high-temperature reaction of Sb oxides with SnO should be considered the most rational method of catalyst preparation. This method is technically simple and produces catalysts with sufficiently high activity and selectivity for mild oxidation of olefins that is free of toxic and corrosive starting materials and side products.

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