Structural Properties of Sb–Sn–O Mixed Oxide Catalysts

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Mixed oxides of tin and antimony were investigated by X-ray diffraction and Mössbauer spectrometry as a function of chemical composition and of firing temperature. At low calcination temperatures, antimony is present as Sb^{5+} dissolved in the SnO_2 lattice at 5 atom % Sb and a mixture $Sb^{5+} + Sb^{3+}$ at higher concentrations.

Upon calcination a demixing of the solid solution occurs and an antimony oxide phase is formed. From X-ray diffraction, this phase is identified as a bidimensional Sb_2O_4 layer. The balance of electrical charges in the lattice is achieved by two different mechanisms as a function of the Sb content: delocalization of electrons in the conductivity band at low antimony content and reduction of Sb^{5+} to Sb^{3+} at higher antimony percentage. Good selectivities are obtained for propene oxidation when the system is biphasic; it is postulated that the actual catalyst consists of an oriented film of Sb_2O_4 supported by the Sb^{5+}–SnO_2 solid solution.

Mixed oxides of tin and antimony have recently attracted attention concerning their surface composition,[1] acidic properties,[2] isotopic exchange,[3] electrical properties[4] and phase composition.[5]

However, the structure of these solids is still uncertain. It is generally accepted that antimony dissolves in the SnO_2 lattice forming a solid solution, as has been shown by X-ray diffraction[5-9] and electrical conductivity.[4-7, 10] The controversial points are the nature of the antimony oxide phase which appears at 20-30 atom % Sb in samples fired above 973 K and the oxidation state of antimony cations in the solid. Mössbauer spectrometry can provide direct information on the oxidation state and environment of Sb and Sn cations. Some fragmentary results have been reported on this point,[10-13] but unfortunately the investigation was restricted to samples fired at 873 K, whereas it is known that catalytic properties[7-9] and surface composition[1] are noticeably affected by calcination at higher temperatures. Therefore, it appeared of interest to investigate this system in a broader range of temperatures and to try to correlate the results of Mössbauer spectrometry and X-ray diffraction

with catalytic properties for the oxidation of propene into acrolein. The main points to be discussed in this paper are (i) the nature of the antimony oxide phase formed at high temperature, (ii) the oxidation state of antimony and tin cations and the mechanism of balance of electrical charges in the lattice and (iii) the role of calcination in the solid state chemistry and catalytic properties.

EXPERIMENTAL

CATALYSTS

Tin–antimony mixed oxides were prepared by coprecipitation of aqueous solutions of Sn^{4+} and Sb^{3+} chlorides by ammonium hydroxide at pH = 7. The precipitate was filtered, washed and dried overnight at 393 K. The antimony content, expressed as the atomic ratio 100 Sb/Sb+ Sn, was determined by atomic absorption in very good agreement with nominal values. Aliquot parts of each sample were calcined overnight at 773, 1023 and 1223 K under flowing air. The chemical analysis of calcined samples revealed no detectable change in composition due to calcination.

Silica supported antimony was prepared by reacting $SbCl_5$ onto silica, in a similar way to that used previously for molybdenum.[14] The sample was then calcined at 773 K in flowing air.

X-RAY DIFFRACTION

Debye–Scherrer X-ray powder photographs were taken using Cu $K\alpha$ radiation. The phases identified on the samples are listed in table 1.

TABLE 1.—COMPOSITION AND CATALYTIC PROPERTIES OF THE SAMPLES

sample	atom % Sb	temperature of calcination /K	rate of C_3H_6 conversion at 653 K /10^{-8} mol s^{-1} m^{-2}	selectivity for acrolein at 653 K	phases from X-ray diffraction
1	5.0	773	5.2	28	SnO_2
2	5.0	1223	7.6	67	SnO_2
3	18.7	773	1.5	27	SnO_2
4	18.7	1023	7.4	81	SnO_2
5	18.7	1223	4.8	71	$SnO_2 + Sb_2O_4$
6	9.7	773	5.2	28	SnO_2
7	9.7	1023	7.6	67	SnO_2
Sb/SiO$_2$	2.61[b]	773	0.01[a]	30[a]	not determined

[a] At 693 K; [b] wt %.

MÖSSBAUER EXPERIMENTS

Transmission Mössbauer spectra were obtained using conventional devices.

Tin: the source was Ca^{119} SnO$_3$ at room temperature. The calibration was achieved using SnO_2 and β–Sn absorbers. Samples of 6-10 mg Sn cm^{-2} were made by uniformly spreading the powder on a paste board and fixing it with an adhesive tape. Isomer shifts (i.s.) referenced to SnO_2 and quadrupole splittings (q.s.) were calculated using a fit program. Typical errors on these parameters are 0.02 and 0.05 mm s^{-1}, respectively.

Antimony: the source (Ca^{121} SnO$_3$) and the sample (3.5-10 mg Sb cm^{-2}) were both maintained at 77 or 4.2 K. The isomer shift, referred to the source, and e.q. ($e^2 q_Z Q$, assuming $\eta = 0$) were determined using a program which takes into account the thickness of the sample;[15] the respective errors are typically 0.05 and 0.5 mm s^{-1}. The parameters of Sb_2O_3 and Sb_2O_5 were remeasured on well defined oxides.

RESULTS AND DISCUSSION

X-RAY ANALYSIS OF THE SAMPLES

A general agreement exists that antimony is soluble in the SnO_2 lattice up to 20-30 % Sb in the temperature range 773-1123 K, a biphasic system appearing at higher temperatures. However, the nature of the antimony oxide phase formed at higher temperature is still under discussion since α-Sb_2O_4, β-Sb_2O_4 and Sb_6O_{13} have been proposed.

Our own results agree with the existence of the solid solution in this concentration and temperature range and the appearance of an antimony oxide phase at higher temperatures. For two samples, one with 20 atom % Sb content fired at 1223 K in flowing air and the second one with 10 % Sb heated at 1273 K in a sealed tube,

TABLE 2.—COMPARISON OF THE EXPERIMENTAL RESULTS WITH THE SPECTRA OF Sb_2O_4, Sb_2O_4 AND Sb_6O_{13}

Reference spectra: ASTM 11.694, 17.620.

$d/\text{Å}$ exp.	α-Sb_2O_4			β-Sb_2O_4			Sb_6O_{13}		
	$d/\text{Å}$	I/I_1	hkl	$d/\text{Å}$	I/I_1	hkl	$d/\text{Å}$	I/I_1	hkl
	5.90	3	002	5.86	5	200	5.95	30	111
	4.46	9	011	4.47	10	110			
	3.033	5	013	3.03	10	310			
2.947	2.942	45	004	2.912	60	400	2.975	100	222
2.412	2.404	17	020	2.415	30	020	2.576	25	400
	2.112	3	015						
1.865	1.862	25	024	1.860	50	420	1.822	35	440
				1.596	5	130			
1.472	1.469	11	008	1.459	20	800	1.553	30	622
							1.487	8	444
							1.442	6	711, 551
not observed	3.073	100	112	3.23	100	111			
	2.651	25	113	2.873	70	$\bar{3}$11			
	2.235	11	203	2.637	30	$\bar{2}$02			
	1.781	20	221, 205	2.181	30	202			
	1.723	20	116, 222	1.811	50	511, 312			
				1.782	50	$\bar{2}$22			
				1.673	40	$\bar{1}$13, 421			
				1.619	60	$\bar{7}$11, 222			

the X-ray pattern contains lines at 2.947, 2.412, 1.865 and 1.472 Å which may be assigned to α-Sb_2O_4. However, several intense lines of cervantite at 3.073, 2.65, 1.78 and 1.72 Å are lacking. All these missing lines correspond to $h \neq 0$, therefore to a particular axis of the structure. Indeed, if we suppress in the spectrum of cervantite all the lines corresponding to $h \neq 0$ we get the results listed in table 2, which agree with the whole of the experimental results. This is interpreted as arising from α-Sb_2O_4 in the form of a bidimensional film at the surface of the solid.

The observed antimony oxide phase could also be attributed to β-Sb_2O_4 since a similar treatment shows that the experimental pattern agrees with that of β-Sb_2O_4 after suppression of the lines corresponding to $l \neq 0$. In that case, it may

be pointed out that the intense lines of bulk Sb_2O_4 at 3.23, 2.873, 1.811 and 1.619 Å, which correspond to the z-axis, are not observed and the conclusion is again that a bidimensional layer is formed. In fact, the structures of the two polymorphs are very similar and the present finding reflects these analogies. In both cases small displacements are noticed, indicating a weak distortion of the lattice. This was expected since a bidimensional layer would suffer from the influence of the underlying support on lattice spacings.

Kustova *et al.*[8] have attributed the observed spectrum to Sb_6O_{13}, which has an intense line at 2.975 Å, reasonably close to the experimental value of 2.947 Å. This hypothesis appears less probable, because the other line at 2.412 Å would remain unexplained; furthermore, Sb_6O_{13} is known to decompose in this range of temperatures.[6]
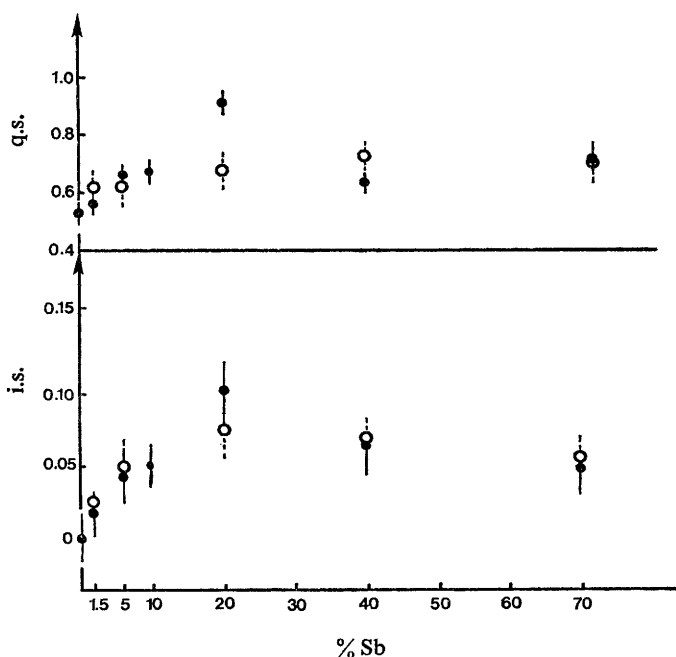

FIG. 1.—Variation of Mössbauer parameters [quadrupole splittings (q.s.) and isomer shifts (i.s.) (in mm s^{-1})] of $^{119}Sn^{4+}$ as a function of chemical composition for samples fired at 773 K. Open and black circles correspond to separate determinations.

Therefore, the novel conclusion of this structure analysis is that the antimony oxide phase formed at the surface of the solid solution consists of a bidimensional layer of Sb_2O_4 for the solid calcined at 1223 K. After calcination at 1023 K this phase is not detected. However, X.p.s. shows a clear Sb enrichment at the sample surface[1] and it may be recalled that X-ray diffraction cannot detect microcrystallites. Therefore, the existence of such a film cannot be excluded at lower firing temperatures. Sintering occurs when the samples are calcined at higher temperatures and the spectrum of three-dimensional Sb_2O_4 is observed as reported by several authors.[6, 8, 9]

MÖSSBAUER SPECTROMETRY OF TIN AND ANTIMONY

The n.g.r. spectrum of ^{119}Sn is similar in pure SnO_2 and Sb-doped catalysts calcined at 773 K. Only small variations of the n.g.r. parameters are observed up

to a Sb content of 10 %, as illustrated in fig. 1.   The formation of reduced tin species is not evidenced.   The larger quadrupole splittings may be accounted for by the distortion of the SnO_2 lattice induced by antimony dissolution, as proposed by Berry and Maddock.[13]

The spectrum of [121]Sb is more complex as illustrated in fig. 2.   In contrast with previous reports,[12] both V and III oxidation states of antimony can be detected, with Sb^{3+}/Sb^{5+} ratios depending on chemical composition and firing temperature.   The n.g.r. parameters and relative proportions (assuming equal Debye Waller factors for the two oxidation states [17]) are listed in table 3.
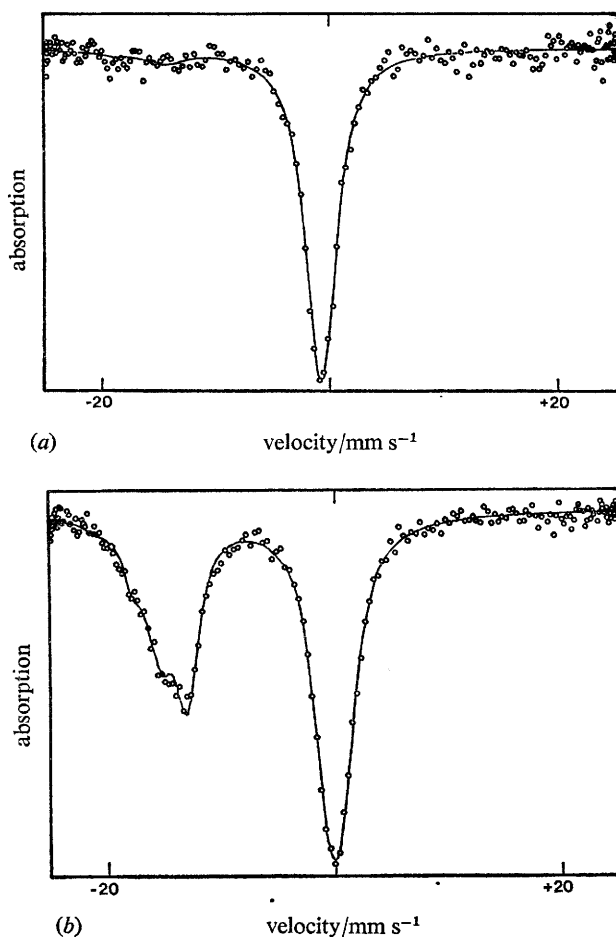

FIG. 2.—Mössbauer spectra of [121]Sb for sample 1 (a) and sample 5 (b).

After calcination at 773 K antimony is found mainly in the Sb^{5+} valence state. The phenomenon is very clear on sample 1 which contains 5 atom % Sb and consists of a solution of Sb^{5+} in SnO_2, in agreement with electrical conductivity measurements. Since no evidence of reduced tin species is found the change balance in the bulk of this sample cannot be achieved either by the substitution of two Sn^{4+} ions by Sb^{5+} and Sn^{2+} (Sn^{3+} oxide has been shown to consist in a mixture of SnO_2 and SnO)[18] or by Sb^{+5} and Sb^{3+}.   Therefore, the delocalisation of the extra electrons in the conduction

band appears more likely. At higher antimony content, some Sb^{3+} appears and the electrical conductivity of the sample, which is maximum at 7-8 % Sb, decreases. Therefore, the domain in which antimony dissolves in SnO_2 in the form of Sb^{5+} exclusively is limited to this value. From X-ray work it has been claimed that up to 20-30 atom % Sb can be dissolved in the lattice.[7-9] This was evidenced by the expansion of the lattice at this Sb content. All of the observations can be understood under the assumption that the charge balance in the lattice is achieved at high Sb content (> 10 %) by the localization of part of the excess electrons at Sb^{5+} cations which are thus reduced to Sb^{3+}. In this model the solid remains a single phase but the nature of the defects in the lattice is controlled by the equilibrium:

$$Sb^{5+} + 2e \rightleftharpoons Sb^{3+}.$$
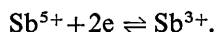
Note that sample 1, calcined at 773 K, contains 98 % of the antimony as Sb^{5+}, therefore the fraction of uncombined Sb, which could be present as Sb_2O_4, is negligible. When calcined at 1223 K whis sample shows an increase in the Sb^{3+} content.

TABLE 3.—N.G.R. PARAMETERS OF Sb^{5+} AND Sb^{3+} SPECIES OBSERVED IN THE CATALYSTS

sample	Sb^{5+}/Sb_{total} /%	Sb^{5+} i.s./mm s^{-1}	e^2q_zQ/mm s^{-1}	Sb^{3+} i.s./mm s^{-1}	e^2q_zQ/mm s^{-1}
1	98	−0.46	3.26		
2	91	−0.58	5.11		
3	93	−0.26	5.98		
4	83	−0.19	6.4	−13.96	17.9
5	71	−0.13	3.85	−14.44	16.7
6	93	−0.24	7.4		
7	87	−0.46	5.05		
$Sb_2O_5{}^a$	100	0.20	4.80		
α-$Sb_2O_4{}^b$	50	0.61	−6.1	−14.36	16.4
$Sb_6O_{13}{}^c$	67	0.8		−14.7	17.0
$Sb_2O_3{}^a$	0			−11.7	18.03
Sb/SiO_2	50	0.53	3.27	−14.8	13.8

^{a} J. P. Devort, *Thesis* (Strasbourg); ^{b} see ref. (16) and (22); ^{c} see ref. (16).

Similar behaviour is found at 10 and 20 % Sb and suggests a decomposition of the solid solution after calcination in air. Indeed, previous X.p.s. data [1] show a fourfold increase in the surface antimony content after the thermal treatment.

Table 3 shows that the n.g.r. parameters of Sb^{3+} in our samples are close to those of Sb_2O_4 or Sb_6O_{13}. The probability of formation of these oxides depends on the temperature of thermal treatments;[16] therefore we have attempted to fit the experimental spectra by constraining the hyperfine interaction parameters to the values known for these oxide phases and analysing independently the remaining Sb^{5+} component. The isomer shift and line width on this latter species are listed in table 4 with the values of the χ^2 test. Sample 5 clearly cannot contain Sb_6O_{13}, as expected from a high temperature of calcination and from X-ray diffraction. The other samples could contain either Sb_2O_4 or Sb_6O_{13}. This computation is, however, of limited value for samples calcined at low temperatures because it assumes that the fraction of antimony dissolved as Sb^{3+} in the SnO_2 lattice is negligible in comparison to Sb^{3+} in Sb_2O_4.

The conclusion of the formation of an Sb_2O_4 phase at high temperature implies separation of an initially homogeneous solid solution. Therefore the thermal treatment does not force the antimony cations into the SnO_2 lattice as proposed by previous authors [9, 19] but rather produces the opposite effect, *i.e.*, a partial extraction of antimony towards the surface.

The actual catalyst would thus consist of a layer of Sb_2O_4 deposited on the solid solution, since the yield of the oxidation of propene into acrolein increases both after high temperature calcination of a Sb deficient sample and by increasing the Sb content. However, the first procedure gives better results and is used industrially.

TABLE 4.—HYPERFINE INTERACTION PARAMETERS OF THE NEW Sb^{5+} SITE OBTAINED FROM A COMPUTER ANALYSIS OF THE SPECTRA WITH THE Sb_2O_4 OR Sb_6O_{13} COMPONENTS CONSTRAINED TO THE LITERATURE VALUES IN THE DATA ANALYSIS

| sample | assuming Sb_2O_4 | | | | assuming Sb_6O_{13} | | | |
	i.s.	width	χ^2	% Sb^{5+} calc.	i.s.	width	χ^2	% Sb^{5+} calc.
2	−0.75	3.1	1	4.5	−0.92	2.76	1	4.1
3	−0.41	3.83	2	20	−0.67	3.54	1.7	19
4	−0.31	3.49	1.7	1.7	−0.59	3.07	1.9	10
5	−1.02	2.36	1.5	13	−13	< 0	16	—
6	−0.31	3.59	1.4	9	−0.43	3.47	1	8
7	−0.78	3.31	1.6	9	−0.94	2.72	2.4	6

The next question concerns the role of the support. Indeed, a comparison between silica supported antimony and Sb–Sn–O catalysts indicates significant influence of the support. Sb/SiO_2, for which n.g.r. shows the presence of an Sb_2O_4 phase, is a poor catalyst. Bulk Sb_2O_4 has a good selectivity but a low activity. Therefore, it can be concluded that SnO_2 does not merely disperse the active phase. The function of the solid solution could be to control the oxidation state of the surface layer through the high conductivity and to stabilize the particular crystalline structure evidenced by X-ray diffraction. The best yield in partial oxidation is obtained after calcination at 1073-1123 K of a solid containing 20 atom % Sb, that is, on a catalyst which is unambiguously biphasic and may contain the oriented Sb_2O_4 phase. Indeed, for optimal catalytic properties the firing conditions of the catalyst are rather critical and calcination at higher temperatures, which causes the growth of bulky Sb_2O_4 crystals, gives worse results, similar to calcination at lower temperatures which keeps the solid solution unmodified.

In summary, we propose a model of the selective Sb–Sn–O catalyst consisting of an oriented film of Sb_2O_4 deposited on the solid solution. From the crystal structure of Sb_2O_4,[20] the surface should contain both Sb^{3+} and Sb^{5+} cations, which appears as a useful assembly for catalysis.

Moreover, the model permits rationalization of the influence of iron on the catalytic properties. Indeed, Fe^{3+} is used as a promotor for this type of catalyst but has been shown to have no effect on activity or selectivity for C_3H_6 oxidation.[21] We believe that iron could play the role of Sb^{3+} in the charge balance and thus stabilize Sb^{5+} cations in the lattice, inhibiting the growth of Sb_2O_4 crystals. Such an effect would be relevant in connection with the life of the catalyst.

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