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Correlations between X-Ray Photoelectron Spectroscopy Data and Catalytic Properties in Selective Oxidation on Sb–Sn–O Catalysts

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A series of Sb–Sn–O catalysts has been studied by X-ray photoelectron spectroscopy (XPS) as a function of Sb content (from 1.7 to 39.7 atom%) and activation temperature. At low activation temperature (500°C) surface and bulk compositions are comparable, while at higher activation temperatures strong surface enrichment in Sb occurs. Detailed analysis of the XPS line shapes shows that two phases may exist at the surface of the catalyst. The first one, which is observed at low Sb content and low activation temperature (500°C), is assigned to Sb(V) in solid solution in the SnO_2 lattice. The second one, which is observed for Sb contents larger than 5% or for high-temperature activations, is assigned to an Sb_2O_4 phase. Catalytic properties for selective oxidation of propylene were studied in the 350 to 400°C range. The selectivity for acrolein increases when surface Sb content is increased either by enhancement of the Sb concentration or by higher activation temperature. It is then postulated that the catalytic phase, which gives selective oxidation, consists of an Sb_2O_4 phase lying at the surface of a solid solution of Sb(V) in SnO_2.

INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is a technique sensitive to the uppermost layers (≃20 Å) of solid materials and consequently is a very suitable tool for characterizing catalysts. This technique has already been applied successfully to determine phase segregation under controlled treatments. For instance, for oxidation catalysts consisting of TiO_2 doped by V or Mo ions, the migration of part of these ions toward the surface, resulting in V_2O_5 or MoO_3 particles lying on the surface, was clearly demonstrated by XPS (*1*, *2*) to occur at high temperature (800°C). Grzybowska *et al.* (*3*) applied XPS to study the different bismuth molybdate phases; they showed that, in the conditions of catalytic oxidation of propylene, the surface composition of the three molybdate phases reflects that of the bulk whereas after vacuum or reducing treatment the three compounds show similar values of the surface Bi/Mo ratio.

Antimony oxide–tin oxide catalysts are known to be selective for the oxidation and ammoxidation of olefins (*4*). The selectivity varies from 25 to 80% as a function of the Sb content, but some controversy still exists on the influence of the chemical composition on catalytic properties (*5*). It appeared then of interest to apply XPS to try to bring some new insight on

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TABLE 1

XPS Data in eV (±0.2 eV) for Sb–Sn–O Catalysts as a Function of Sb Content and Calcination Temperature[a]

Samples: percentage Sb–calcination temperature (°C)	Sb $3d_{\frac{3}{2}}$			O 1*s* + Sb $3d_{\frac{5}{2}}$	Sb $3d_{\frac{3}{2}}$ − Sn $3d_{\frac{5}{2}}$
	E_b	γ	asymmetry		
1.5– 500	540.4	1.74	0.94	530.7	53.7
1.5– 950	540.0	1.83	1.02	530.6	53.3
5 – 500	540.1	2.14	1.34	530.7	53.4
5 – 950	539.9	1.73	1.05	530.6	53.2
5 –1100	540.0	1.82	1.03	530.6	53.2
10 – 500	540.1	2.18	1.22	530.6	53.3
10 – 825	539.8	1.86	1.10	530.5	53.1
10 – 950	539.7	1.80	1.06	530.4	53.0
20 – 500	539.9	1.92	1.12	530.5	53.2
20 – 750	539.8	1.94	1.25	530.5	53.1
20 – 950	539.7	1.82	1.03	530.5	53.0
40 – 500	539.9	1.82	1.08	530.5	53.2

[a] γ is the linewidth at half height evaluated in eV and the asymmetry parameter is the ratio γ_1/γ_2, γ_1 and γ_2 being defined in Fig. 1.

the surface composition of these solids and on the electronic state of antimony which is believed to be the active site for catalysis. A correlation with catalytic properties, mainly selectivity for propylene oxidation to acrolein, was also attempted.

EXPERIMENTAL METHODS

Catalysts. The catalysts were prepared by coprecipitation of aqueous solutions of the chlorides by ammonium hydroxide at pH = 7. The precipitate was filtered, washed, and dried overnight at 120°C. The antimony content, expressed as the atomic ratio Sb/(Sb + Sn), was varied in a wide range from 1.7 to 39.7%. Aliquot parts of each sample were calcined overnight at 500, 750, 950, and 1100°C under flowing air. The chemical analysis of calcined samples revealed no detectable change in composition due to calcination.

XPS experiments. A sample holder was covered with indium and the catalyst in a powder form was pressed on it. The samples were introduced into a Hewlett–Packard HP 5950 A spectrometer and outgassed at room temperature at a pressure down to 10^{-9} Torr.

Negligible charge effect was observed for all the samples and therefore the flood gun was not used. The spectrometer, which belongs to the Centre Commun ESCA of the Université Claude Bernard (Lyon), was monitored by computer and the different spectra were accumulated from 5 min up to 2 hr depending on their intensity. The experimental spectra were then treated by computer for smoothing, subtraction of the background, and determination of the peak areas.

Catalytic oxidation of propylene. A classical flow microreactor at atmospheric pressure was operated at low conversion, less than 5%. The reaction mixture was $C_3H_6/O_2/N_2 = 1/1/5.5$ and the temperature range 350 to 400°C. The products were analyzed by on-stream gas chromatography as described previously (*6*).

RESULTS AND DISCUSSION

XPS results are reported in Table 1 for the binding energy values referenced to that of Sn $3d_{5/2}$ which was taken equal to 486.7 eV in SnO_2. Charge effects could occur (*7*) for such oxide materials. However, pure SnO_2 which is an *n*-type semiconductor was observed not to give rise to a charge effect since its binding energy values were the same as in the literature and use of the flood gun did not change line positions or widths and shapes. For Sb–Sn–O samples conductivity measurements were performed and showed that conductivity was increased by Sb incorporation by several orders of magnitude with respect to pure SnO_2. No charge effects were observed for such conducting samples. The choice of a reference level is important and in the present case cannot be really unambiguous, if an internal element is chosen, since a chemical shift could also occur for Sn $3d$ levels. Such a difficulty has been discussed widely in the literature and a source of confusion arises from the fact that the levels of the elements (Au $4f_{7/2}$ from evaporation or C $1s$ from contamination) used for calibration differ by as much as 1 eV according to different authors (*7*). Data from the literature for Sn and Sb oxides are given for comparison in Table 2 and values are corrected by reference to the widely assumed values of 84.0 eV for Au $4f_{7/2}$, 87.7 eV for Au $4f_{5/2}$, and 285.0 eV for C $1s$.

It is worth noting at this stage that Mössbauer studies performed on our samples (*12*) showed that Sn underwent no detectable reduction due to charge compensation resulting from Sb(V) incorporation into the SnO_2 matrix. It seems therefore reasonable to take Sn $3d$ levels as internal references. The last column in Table 1 gives the separation between Sn $3d_{5/2}$ and Sb $3d_{3/2}$ levels, which does not suffer from possible charge effects or from the choice of a reference level. It then clearly appears that this separation decreases as the Sb content increases. Note that increasing reduction of Sn should decrease its $3d$ level values and therefore increase the Sb $3d$–Sn $3d$ separation in contrast with experiments (Table 1). Note also that each experiment was performed several times with different samples of the same batch. The data of Table 1, column 2, were then obtained with a reproducibility better than 0.1 eV. It may therefore be concluded that absolute values of binding energies (Table 1, column 2) have a definite meaning, even if chemical shifts are not significant with respect to the spectrometer accuracy.

The Sb $3d_{3/2}$ peaks have been analyzed as far as their shapes are concerned. Their asymmetry, given in Table 1, column 4, has been evaluated as the ratio γ_1/γ_2 where γ is defined in Fig. 1. It then clearly appears by deconvolution that the largest asymmetry corresponds to the largest linewidth and that the Sb peaks are due to the overlapping of two peaks at 540.4 and 539.8 eV as shown in Fig. 1. Following such an assumption, it may be concluded that:

(i) The samples at low Sb content (1.5%) and low activation temperature (500°C) mainly give the former peak at 540.4 eV with a small amount of the second one (asymmetry toward smaller binding energy values).

(ii) Samples with Sb content in the 5 to 20% range and low activation temperature (500°C) mainly give the second peak at 539.8 eV with a more or less significant amount of the first one (asymmetry toward larger binding energy values and larger linewidth).

(iii) All samples activated at high temperatures (>750°C) mainly give the second peak.

The binding energy values for the above two peaks are very close to those given in Table 2 for Sb_2O_5 and Sb_2O_4, respectively. Moreover, such an asymmetry observed in the peaks is in agreement with that observed by Orchard and Thornton (*13*), who have shown that for Sb_2O_4 the XPS peaks correspond to the overlapping of two signals with 0.6 eV separation, a half width of 1.9 and 1.7 eV, respectively, and a ratio of intensity of 1.6 to 1. These two signals were assigned to Sb (III) and

TABLE 2

XPS Data for Sn and Sb Lines from Literature as a Function of Oxidation State and Corrected by Reference to Au $4f_{7/2} = 87.7$ or C $1s = 285.0$ eV

Compounds	Sb $3d_{3/2}$ or Sn $3d_{5/2}$	O 1*s*	Reference level	Reference	Corrected Sb $3d_{3/2}$ or Sn $3d_{5/2}$	Corrected O 1*s*	Remarks
Sn metal	484.1	—	284.6 (C 1*s*)	*8*	484.5	—	
SnO	485.9	—	87.0 (Au $4f_{7/2}$)	*9*	486.6	—	
	485.8	529.9	284.6 (C 1*s*)	*8*	486.5	530.6	
SnO_2	486.0	—	87.0 (Au $4f_{7/2}$)	*9*	486.7	—	
	486.3	530.3	284.6 (C 1*s*)	*8*	486.7	540.7	
$Na_2Sn^{IV}O_3$	487.0	531.3	284.6 (C 1*s*)	*8*	487.4	531.7	
Sb metal	537.8		285.0 (C 1*s*)	*10*	537.8		
Sb_2O_3	539.6		285.3 (C 1*s*)	*11*	539.3		
	539.4		285.0 (C 1*s*)	*10*	539.4		
Sb_2O_5	540.6		285.3 (C 1*s*)	*11*	540.3		
	540.2		285.0 (C 1*s*)	*10*	540.2		
Sb_2O_4	(III) 540.0 (?)		285.3 (C 1*s*)	*11*	(III) 539.7 (?)		Average gives 539.8
	(V) 540.5				(V) 540.2		for Sb_2O_4 (III + V)
$NaSb^VO_3$	539.2		285.0 (C 1*s*)	*10*	539.2		

Sb (V) ions, respectively. However, it is known that binding energy values are sensitive to the covalent character of a metal–oxygen bond, larger covalency resulting in smaller binding energy values (*14*).

It follows that the decrease observed in Table 1, column 2, when Sb content increases, could indicate an increase in the covalency character of the M–O bond. However, in such a case one would expect the line symmetry not to change in the whole range of samples, in contrast with experiment and a continuous trend to smaller binding energy values when Sb content increases. Consequently, the presence of two different phases seems to us more probable. The two different signals could correspond to Sb (IV) or Sb (V) in the SnO_2 matrix (solid solution) and Sb_2O_4, respectively. However Mössbauer studies were performed on such systems (*12*). Sb (V) ions were detected in large majority for low Sb content. Sb (III) ions were detected in very small amount but their intensity sharply increased both with Sb content and activation temperature. Moreover, conductivity measurements showed that conductivity was sharply increased by

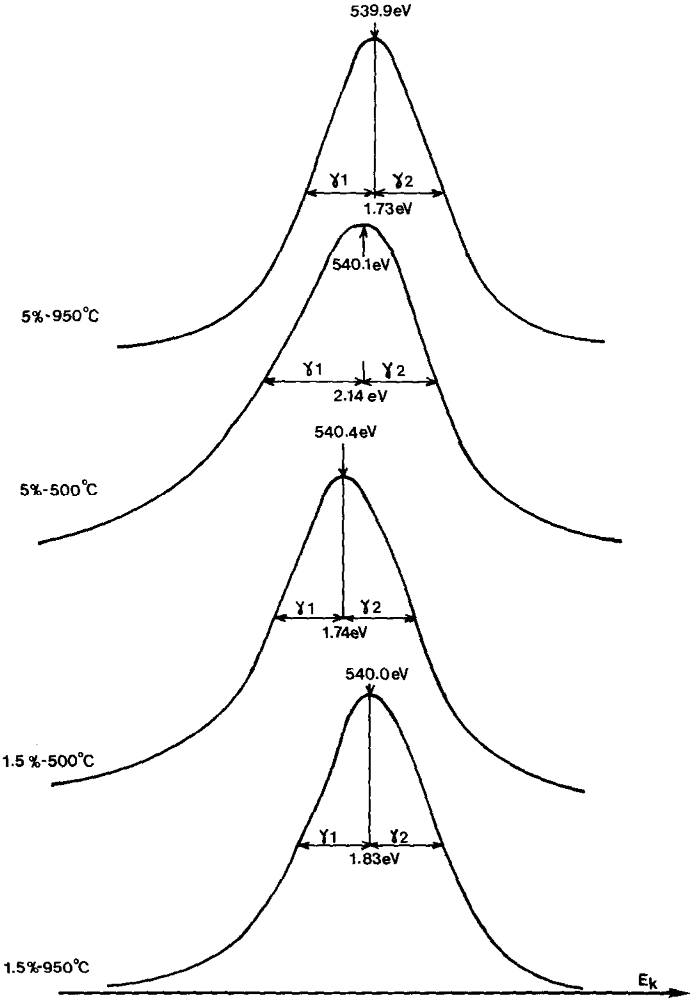

FIG. 1. XPS peaks of Sb $3d_{3/2}$ levels for different Sb–Sn–O catalysts as a function of Sb content and activation temperature indicated in the curves.

TABLE 3

Effect of Calcination Temperature on Surface Concentration in Sb Deduced from XPS Line Intensities and on Catalytic Properties (Activity and Selectivity) for Propene Oxidation

1	2		3		4	5	6	7
Samples: percentage Sb–calcination temperature (°C)	Sb/(Sb + Sn)% from 4*d* lines in XPS	Amplification factor	Sb/(Sb + Sn)% from 3*d* lines in XPS	Amplification factor	Chemical analysis (%)	Specific surface area (m² g⁻¹)	Rate of propylene conversion V × 10⁻⁸ mol sec⁻¹·m⁻²	Selectivity for acrolein (%)
0 (SnO_2)	0		0		0	25	7.9	22
1.5– 500	3.5	1.9	2.9	3.9	1.7	31.5	4.1	25
1.5– 950	6.6		11.1			3.6	10.8	48
5 – 500	4.5	2.9	5.1	3.5	5.0	45	5.2	28
5 – 950	13.0	3.8	17.6	4.7		11	7.6	67
5 –1100	17.2		24.0			1.8	8.7	48
10 – 500	8.8	2.6	10.0	3.2	9.7	62	3.8	40
10 – 825	23.3	3.0	31.8	3.2		10	5.2	73
10 – 950	26.3		31.8			5	5.5	66
20 – 500	18.7	1.4	20.1	1.6	18.7	87	1.5	27
20 – 750	26.1	1.3	32.1	1.8		29	7.4	81
20 – 950	23.6		35.0			4.8	4.8	71
40 – 500	42.9		45.9		39.7	99	2.7	68
100 (Sb_2O_4)	100				100	2.7	0.3	54

incorporation of Sb (V) ions in the SnO_2 matrix. It follows that one can conclude that the two phases may reasonably be assigned to Sb (V) in SnO_2 (solid solution) and Sb_2O_4 phase.

Quantitative data from XPS results are reported in Table 3, the atomic Sb/(Sn + Sb) ratios being calculated from the XPS line intensities (I) using the approximate relationship:

$$\frac{n_1}{n_2} = \frac{I_1}{I_2} \cdot \frac{\sigma_2}{\sigma_1} \left[\frac{Ek_2}{Ek_1}\right]^{\frac{1}{2}}$$

where n_i, Ek_i, and σ are, respectively, the number of atoms of element i, the kinetic energy value corresponding to the line considered, and the cross-section calculated theoretically (*15*).

Two striking features appear clearly. First, for samples activated at 500°C the XPS data (column 3) are very close to those obtained from chemical analysis (column 4) indicating that the surface composition is similar to that of the bulk. Second, a strong migration of antimony toward the surface of the catalyst particles occurs during heating at high temperatures ($\geqslant$750°C). This migration is particularly important at low Sb content since a fourfold increase is observed.

It may be noted that the XPS results obtained from 4*d* lines (column 2) with higher kinetic energy values with respect to those from 3*d* lines (column 3) indicate smaller differences in surface concentration as a function of activation temperatures. This result arises from the fact that a deeper layer was analyzed from 4*d* electrons than from 3*d* electrons, which is in excellent agreement with our conclusions that migration of Sb occurred by calcination and that phase segregation was observed.

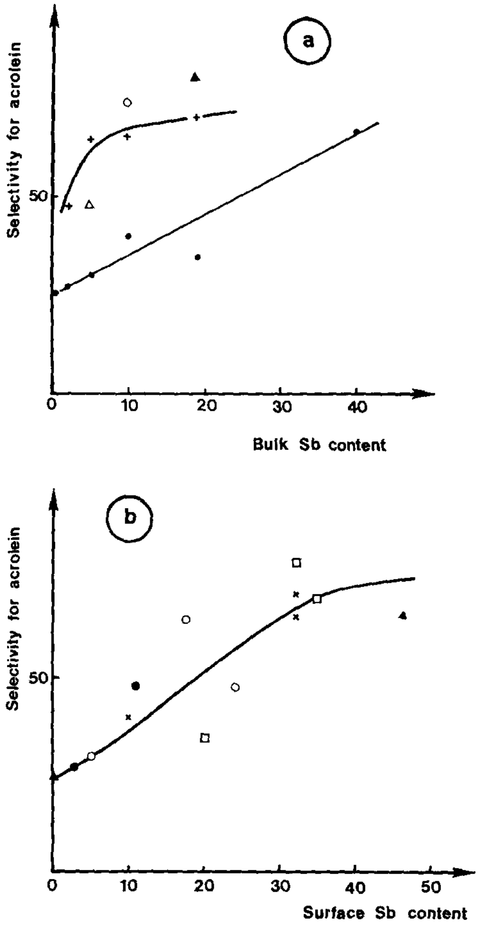

FIG. 2. Selectivity for acrolein formation at 380°C for Sb–Sn–O catalysts. (a) As a function of nominal Sb content (calcination temperature: ●, 500°C; ▲, 750°C; ○, 825°C, +950°C; △, 1100°C). (b) As a function of surface Sb content as determined by XPS (bulk content: ▲, 0%; ●, 1.5%; ○, 5%; ×, 10%; □, 20%; △, 40%).

X-ray analysis (*16–18*) has shown previously that for low Sb content ($\leqslant$10%) and whatever the calcination temperature, the material corresponds to a solid solution of Sb (V) in SnO_2. At higher Sb content ($\geqslant$25%) an additional phase of Sb_2O_4 (α and β) was detected. Note at this stage that at intermediate Sb content (25%) the Sb_2O_4 phase was detected only for high calcination temperatures (*17*).

Finally an Sb_2O_4 phase was detected at high Sb content by X-ray analysis which is sensitive to the bulk whereas XPS is sensitive only to the uppermost layers of the material and the binding energy values for the two XPS peaks correspond to Sb_2O_5 and Sb_2O_4. These results are a very strong indication that two different phases are detected by XPS. Our interpretation is in agreement with that of Orchard and Thornton (*13*). Following their conclusion the Sb_2O_4 phase in our conditions should lead in XPS to a single peak with a linewidth of 1.7 to 1.9 eV due to Sb (III). When Sb (V) ions are also present the line peaks are asymmetric and broader up to 2.3 eV which is in agreement with our data given in Table 1, column 3. The first one (peak at 540.4 eV) corresponds to Sb (V) in solid solution in SnO_2 and the second one (peak at 539.8 eV) to a Sb_2O_4 phase dispersed at the surface of the solid solution. The discrepancy between X-ray and XPS data certainly represents differences between the bulk and the surface of the solid particles.

It therefore appears important to consider the surface composition as determined by XPS rather than the nominal one to discuss catalytic properties. The catalytic results for selective oxidation of propene at 380°C are reported in Table 3 (column 6 and 7) in terms of selectivity for acrolein and rate of propylene conversion.

Figure 2 reports the selectivity for acrolein versus bulk or surface Sb content. Two main features appear:

(i) The change in selectivity is not directly related to the opposite change in surface area as suggested previously (*19*).

(ii) The selectivity increases with surface content in Sb, which is particularly striking when samples are calcined at high temperature.

The low activity of bulk Sb_2O_4 and the decrease of the catalytic activity per unit area at high Sb content led previous authors (*17–19*) to reject the hypothesis that Sb_2O_4 could be the active phase. They proposed that the active sites are Sb (V) ions in the solid solution.

Although we are conscious that the XPS technique cannot unambiguously characterize a given phase in the way that the X-ray technique can, the XPS data indicate that the catalytic selectivity increases when the solid surface is enriched in Sb in a form that we tentatively assign to an Sb_2O_4 phase. One can then conclude that the selective catalyst consists of a Sb_2O_4 phase lying on the surface of the solid solution of Sb (V) in SnO_2. The surface area of such an Sb_2O_4 phase could not be determined independently of the total surface area of the catalysts which may explain why no correlation between catalytic properties and surface area could be established.

Our results can be compared to those obtained for Mo–TiO_2 catalysts (*2*) where incorporation of Mo ions was followed using three physical methods, namely, XPS, UV, and ESR spectroscopies. It was indeed observed that calcining a sample containing 0.5% Mo in anatase at 800°C leads to transformation of anatase into rutile and insertion of Mo ions in the TiO_2 particles in the form of Mo (V) ions. Moreover, the surface is enriched in Mo by a factor of 10 to 20, the surface layer being presumably in the form of MoO_3. The catalyst is therefore composed of MoO_3 deposited on an Mo (V) doped rutile.

The conclusion of the present work is that the highly selective catalyst Sb–Sn–O is composed of a Sb_2O_4 phase lying on a solid solution of Sb (V) in SnO_2 and that the surface composition in Sb as determined by XPS bears a closer correspondence with catalytic performance than the nominal composition.

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