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Relationship between Structure and Activity of Antimony Mixed Oxides in 1-Butene Oxidation[1]

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The mixed oxides of antimony with Sn, Fe, Co, Ni, Mn, Zn, U, Ce, and Cd were prepared and characterized by means of spectroscopic techniques. Fe, Co, Ni, Mn, Zn, Cd and, partially, U were found to form well-defined compounds with Sb oxide. The mixed oxides were tested as catalysts in the 1-butene oxidation. They showed a very different activity but about the same selectivity to butadiene suggesting that the active sites are the same for all compounds. It is proposed that the oxidative dehydrogenation properties of the catalysts are due to two "gem" $Sb^{5+}{=}O$ groups and that the role of the second metal is to adsorb the gaseous oxygen to reoxidize the reduced antimony ions. This reoxidation mechanism can be presented only by mixed oxides showing a particular structure.

INTRODUCTION

In a previous note (*1*) we reported on the structure and on the properties of Bi-molybdates, which are well known and widely used oxidation catalysts. These compounds have been largely employed in the industrial acrylonitrile synthesis for which, in the last 15 yr, also several mixed antimony oxides, such as Sn–Sb, U–Sb and Fe–Sb oxides, came into use. The mixed oxides of antimony with many other metals were further patented as oxidation catalysts (*2*). Several papers have been published to explain the properties of these systems: in a previous work we have proposed that the catalytic activity of a Sn–Sb oxide catalyst can be due to its particular controlled-valence semiconductor character, which leads to stabilization of Sb^{5+} ions without introducing lattice defects (*3*). For the system U–Sb–O Grasselli and coworkers have observed that a well-defined compound, USb_3O_{10}, is responsible for its good catalytic properties (*4,5*). Also for the system Fe–Sb it has been observed, by Boreskov *et al.* (*6*), that catalytic activity can be attributed to a well-defined compound, $FeSbO_4$. In this work we have examined several antimony-based mixed oxides in order to investigate their different or similar properties and the role of the antimony and of the added metals.

EXPERIMENTAL METHODS

Preparation of Catalysts

A pure antimony oxide was prepared by hydrolyzing 1 part by weight of $SbCl_5$ in 10 parts of deionized water. The resulting suspension was then neutralized with ammonia, filtered and dried. The white compound obtained was calcined at 350°C for 2 hr. A part of it was then suspended in water, dried on a rotating evaporator and calcined at 500°C for 15 hr and at 900°C for 1 hr. The mixed oxides were prepared by suspending the required quantity of the pure antimony oxide (calcined at 350°C) in an aqueous solution of $Fe(NO_3)_3\cdot$

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TABLE 1

X-RAY DATA [*d* VALUES (Å) AND RELATIVE INTENSITIES]

Sb 350°C		Sb 900°C		Fe–Sb		Co–Sb		Ni–Sb		Mn–Sb		Zn–Sb		Sn–Sb		Cd–Sb		Ce–Sb		U–Sb	
d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
5.76	13	4.42	6	5.86	3	4.59	8	9.25	9	9.25	7	9.31	4	9.26	7	3.08	4	5.945	18	5.908	16
3.08	15	3.43	21	4.47	7	4.43	6	5.865	4	4.669	7	4.62	2	4.46	5	2.949	100	3.105	16	3.084	11
2.96	100	3.066	70	3.45	11	4.12	14	4.54	3	4.46	5	4.22	4	3.44	17	2.536	35	2.993	100	2.959	100
2.57	35	2.935	100	3.29	62	3.43	15	4.15	7	4.20	10	4.17	7	3.350	28	1.811	90	2.574	28	2.561	24
1.96	9	2.641	25	3.25	40	3.277	100	3.44	9	3.434	9	3.446	14	2.237	15	1.74	4	1.985	7	2.508	5
1.81	51	2.395	15	3.08	24	3.063	30	3.277	100	3.326	100	3.301	86	3.062	36	1.542	100	1.821	42	1.973	6
1.73	12	2.223	8	3.04	12	2.921	23	3.072	54	3.227	22	3.068	42	2.94	100	1.477	15	1.740	7	1.873	3
1.54	50	1.858	30	2.94	100	2.87	7	2.943	45	3.053	57	2.94	100	2.867	7	1.438	5	1.554	32	1.814	37
1.48	13	1.775	28	2.88	18	2.640	13	2.715	2	2.926	39	2.640	11	2.644	26	1.334	8	1.486	8	1.546	34
1.433	2	1.716	37	2.64	14	2.563	72	2.651	15	2.866	11	2.574	67	2.40	10	1.279	10			1.481	12
1.34	9	1.692	12	2.57	40	2.407	11	2.568	72	2.706	6	2.40	8	2.367	3	1.17	50				
1.28	4	1.633	11	2.41	10	2.332	22	2.470	5	2.648	14	2.332	19	2.23	3	1.148	45				
1.177	18	1.588	6	2.32	10	2.25	7	2.407	8	2.595	61	2.25	5	1.862	24	1.045	50				
1.147	14	1.487	10	2.24	8	1.858	12	2.332	18	2.401	12	1.861	16	1.779	18						
1.126	7	1.469	21	2.19	8	1.749	11	2.238	8	2.352	16	1.779	11	1.759	11						
		1.424	15	1.86	19	1.723	67	1.972	3	1.854	14	1.729	54	1.722	10						
				1.815	4	1.646	18	1.864	8	1.776	15	1.650	16	1.691	8						
				1.75	17	1.545	8	1.781	6	1.744	63	1.543	6	1.676	8						
				1.72	43	1.471	17	1.723	74	1.693	9	1.476	9	1.633	7						
				1.69	6			1.695	3	1.644	18	1.470	13	1.487	5						
				1.67	6			1.638	16	1.631	8	1.451	4	1.467	7						
				1.64	12			1.590	2	1.558	6	1.418	11	1.428	5						
				1.62	8			1.535	4			1.408	19								
				1.54	5			1.490	3												
				1.51	5			1.468	19												
				1.49	5			1.429	4												
				1.47	19			1.383	32												
				1.43	7																
				1.39	7																
				1.38	10																
				1.32	5																

$9H_2O$, $Co(NO_3)_2 \cdot H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $SnCl_2 \cdot 2H_2O$, $CeCl_3 \cdot 7H_2O$ and Na_2UO_4, respectively. In the case of Sn, Ce and U the solution was slightly nitric. In all cases the atomic ratio Me/Sb was 1:4. We have chosen this ratio because in preliminary experiments and also from the literature (*6,7*), some of the investigated catalysts (Fe, Ni, Co and Sn–Sb) showed low selectivity and high conversions to carbon dioxide when prepared with ratios Me/Sb > 1:2.2. The Sb oxide excess was a precaution to avoid the presence of free oxides Fe_2O_3, Co_3O_4, NiO, well known as total combustion catalysts. The suspensions were then dried under vacuum in a rotating evaporator to produce a homogeneous distribution of the two ions. The compounds obtained were then calcined at 110°C for 2 hr, at 500°C for 15 hr and at 900°C for 1 hr.

X-Ray Powder Data

X-Ray diffraction patterns were recorded with a Geiger counter Philips spectrogoniometer with Cu–$K\alpha$ radiation.

Infrared Spectra

Infrared spectra were recorded with a Perkin-Elmer Model 457 spectrophotometer using the KBr disc technique.

Determination of Surface Area

The surface area of the catalysts was measured by adsorption of *n*-butanol in a Microscale Mk.II flow microcalorimeter with the technique reported in Ref. (*8*).

Measurements of Catalytic Activity

The catalytic activity was measured for the reaction of oxidation and isomerization of 1-butene. Some measurements were carried out at low temperature (250°C) in a batch reactor as in Ref. (*9*) using 1 g of catalyst and 5% of 1-butene in air. Measurements at high temperatures were carried out in a flow microreactor of quartz. The used quantity of catalyst was 1 g, the reactant gas stream was a 1-butene (2% by volume)–air mixture and the contact time was 1 sec. In both cases the analysis of reaction products was carried out by a C. Erba Fractovap C gas chromatograph, equipped with two columns: the first, 8.5 m long, filled with dimethylsulpholane on Chromosorb P, to separate air, CO_2, 1-butene, *trans*-2-butene, *cis*-2-butene and butadiene; the second, 0.70 m long, filled with molecular sieves, to separate O_2, N_2 and CO.

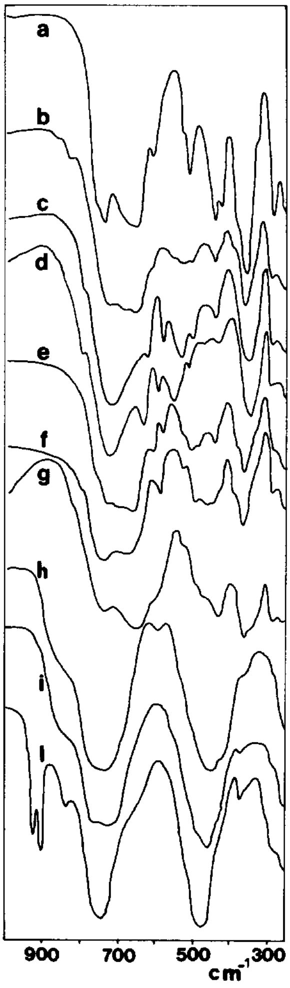

FIG. 1. Infrared spectra of the catalysts calcined at 900°C for 1 hr: (a) Sb oxide, (b) Fe–Sb, (c) Co–Sb, (d) Ni–Sb, (e) Mn–Sb, (f) Zn–Sb, (g) Sn–Sb, (h) Cd–Sb, (i) Ce–Sb, (l) U–Sb.

RESULTS

In Table 1 the X-ray data of the different investigated catalysts are reported. In Table 1 one can observe that the X-ray pattern of antimony oxide, calcined at 350°C, corresponds to that reported for Sb_2O_5 (*10*). The pattern of pure Sb oxide calcined at 900°C corresponds, on the contrary, to that reported for α-Sb_2O_4 (*10*), even if with different intensities (the most intense band is at 2.935, not at 3.07). The mixed oxides Ni–Sb, Co–Sb and Zn–Sb present the d values of the respective antimonates $NiSb_2O_6$, $CoSb_2O_6$, $ZnSb_2O_6$, (*10*) of α and β-Sb_2O_4. These antimonates are well-known compounds, showing a trirutile-type structure (*11*). The X-ray pattern of Fe–Sb presents the d values typical of α-Sb_2O_4, in smaller amount of β-Sb_2O_4 (*10*), and some other peaks that it is impossible to attribute to $FeSb_2O_6$ (*10*), $Fe_2Sb_2O_7$ (*10*) or to $FeSbO_4$ (*12*) owing to the very small difference between the d values of the two antimonates. It is interesting to note that for Fe–Sb, and also for Zn–Sb, the most intense peak ($d = 2.94$) is attributable to α-Sb_2O_4 and not to the antimonate. From the analogies between X-ray patterns of Mn–Sb and the above mixed oxides (peaks at 3.326; 2.595; 1.745; 1.665) we consider that in our Mn–Sb–O system a Mn^{2+} antimonate of the type $MnSb_2O_6$ can be present. A compound of this type, showing a columbite structure, was reported by some authors [(*11*) and related references]. Also in this compound the peaks of α and β-Sb_2O_4 are present. On the contrary, the X-ray pattern of Sn–Sb shows no presence of new compounds, but only of α-Sb_2O_4 with a little amount of β-Sb_2O_4. This fact agrees with what has been found by many authors (*3,13,14*).

Some weak peaks of SnO_2 (at $d = 3.350$, 2.367, 1.759) can also be observed. Cd–Sb shows the d values of the cadmium antimonate $Cd_2Sb_2O_7$ (*10*) and some other peaks (at 3.08, 2.949, 2.536, 1.821, 1.74, 1.542) that can be attributed to Sb_2O_5 (d values at 3.08, 2.96, 2.57, 1.81, 1.73, 1.54). Also $Cd_2Sb_2O_7$ is a known compound showing a weberite-type structure (*15*). The mixed oxides U–Sb and Ce–Sb present only the d values characteristic of Sb_2O_5. In Fig. 1 the ir spectra of the oxides are reported. Pure antimony oxide calcined at 900°C, which from X-ray analysis was found to be α-Sb_2O_4, shows at 610 and 525 cm^{-1} the characteristic bands of this oxide (*3*). The mixed oxides Ni–Sb, Co–Sb and Zn–Sb show at 795, 700–720,

TABLE 2

ANALYTICAL AND SURFACE AREA DATA

Catalyst	Compounds observed	Surface area (m_2/g)
Sb oxide 350°C	Sb_2O_5	39.3
900°C	α-Sb_2O_4	0.4
Fe–Sb	$FeSb_2O_6$ or $Fe_2Sb_2O_7$ + α-Sb_2O_4 + β-Sb_2O_4	11.8
Co–Sb	$CoSb_2O_6$ + α-Sb_2O_4 + β-Sb_2O_4	12.1
Ni–Sb	$NiSb_2O_6$ + α-Sb_2O_4 + β-Sb_2O_4	13.2
Mn–Sb	$MnSb_2O_6$ + α-Sb_2O_4 + β-Sb_2O_4	10.5
Zn–Sb	$ZnSb_2O_6$ + α-Sb_2O_4 + β-Sb_2O_4	5.45
Sn–Sb	α-Sb_2O_4 + β-Sb_2O_4 + SnO_2 (traces)	9.85
U–Sb	Sb_2O_5 + USb_3O_{10} (by ir analysis)	22.7
Ce–Sb	Sb_2O_5	27.4
Cd–Sb	$Cd_2Sb_2O_7$ + Sb_2O_5	29.4

TABLE 3

ACTIVITY DATA IN BATCH REACTOR[a]

Products (moles/ml × 10^{-8}) Catalyst:	Sb 350°C	Fe-Sb	Co-Sb	Ni-Sb	Mn-Sb	Zn-Sb	Sn-Sb	U-Sb	Ce-Sb	Cd-Sb
Butadiene	20.6	44.8	18.05	20.25	4.60	4.14	36.3	13.5	4.70	0.28
t-2-Butene	2.68	6.85	7.70	11.06	3.36	3.86	76.40	289	1.62	6.48
c-2-Butene	5.24	17.85	12.25	20.95	8.35	7.93	106.1	174	1.82	3.82
CO + CO_2	3.9	10.84	6.48	5.31	3.04	3.23	6.50	5.98	17.41	2.81

[a] Experimental conditions: catalyst, 1 g; 5% 1-butene in air; temperature, 250°C; reaction time, 1 hr.

630, 590, 540–510 cm^{-1}, the typical bands of the antimonates $Me^{2+}Sb_2O_6$ (*11*) and some of α-Sb_2O_4 (at 740, 440, 360 and 290 cm^{-1}) in agreement with X-ray patterns. The mixed oxides Fe–Sb and Mn–Sb show ir spectra which are very similar to those of Ni, Co and Zn. Mn–Sb presents, in fact, some bands of Sb_2O_4 (at 740, 650, 610, 500, 440, 360 and 290 cm^{-1}) and some others in the region of the antimonate bands (about 710, 580 and 530 cm^{-1}). This fact supports the hypothesis, advanced on the basis of X-ray data, that in our Mn–Sb system an antimonate of type $MnSb_2O_6$ is present. The ir spectrum of Fe–Sb is very different from that reported for $FeSbO_4$ (*11,16*). It shows, in fact, at 740, 650, 610, 440, 360, and 290 cm^{-1}, the typical bands of α-Sb_2O_4, and at 830, ~700, 590 and 510 cm^{-1} some new bands, present only in the spectra of the compound containing a Sb excess (*17,18,19*), which can be reasonably attributed to the antimonate, being very similar to those of Zn, Co and Ni antimonate. These bands, nevertheless, are different from those of $FeSbO_4$, localized at 675–660, 535–520 and 340–305 cm^{-1} (*11,16*). From this spectrum and from X-ray data, we can exclude the presence, in our Fe–Sb system, of $FeSbO_4$ and hypothesize the presence of $Fe_2Sb_2O_7$, reported by Grasselli (*20*) as a very active and selective oxidation catalyst, or of $FeSb_2O_6$, by analogy with Ni, Co and Zn–Sb. Sn–Sb presents an ir spectrum very similar to that reported for α and β-Sb_2O_4 (*3*), without bands of new compounds, in agreement with X-ray data. The ir spectrum of U–Sb is very interesting; in fact, it accurately resembles that reported by Grasselli and Callahan (*4*) for the active phase USb_3O_{10}, found by them in the system U–Sb–O. Since, from X-rays, the presence of this compound in our U–Sb was not detectable, we assume that it is present in small quantity. Ce–Sb and CdSb show ir spectra very similar to that of

Sb_2O_5 (*3*), in agreement with X-ray pattern data. All the results of chemical characterization are reported in Table 2 together with the values of surface area. From Table 2 we can see that α-Sb_2O_4 has a very low surface area, while Sb_2O_5 shows the highest one. Mixed oxides have values of surface area intermediate between these two. It is of interest to note that U–Sb, Ce–Sb and Cd–Sb, in which, from X-ray and ir analyses it appears that Sb_2O_5 is present, show surface area values higher than those of the other catalysts (about 25 m^2/g).

In Table 3, where the activity data of runs carried out in a batch reactor are reported, it is possible to observe that U–Sb and Sn–Sb are the catalysts giving the greatest amount of isomers, while Fe–Sb, Sn–Sb and also Ni–Sb, Co–Sb and Sb_2O_5 exhibit the highest oxidizing power. Sb_2O_4 was completely inactive also after 5 hr of reaction, as already reported by us (*3*). In Figs. 2, 3 and 4 the amounts of butadiene, 2-butenes and ($CO + CO_2$) formed in experiments carried out in the flow reactor are reported. From these it is possible to observe that the produced amounts of butadiene and carbon oxides change very much from one catalyst to the other, and that U–Sb and Sn–Sb are the only ones which show an appreciable formation of 2-butenes at these reaction conditions. All catalysts, particularly the most active ones, also give small amounts of other oxidized products, such as low molecular weight aldehydes. It is interesting to report that, in these runs, not only α-Sb_2O_4, but also Sb_2O_5, have proved to be inactive at all reaction temperatures.

DISCUSSION

Chemical Characterization

From the X-ray data, and from the high selectivity to butadiene shown by our catalysts, we can exclude the presence of the pure oxide of the added metal for the Fe, Ni, Co, Mn and Sn mixed oxides. It is known that these oxides exhibit a high activity in bulk combustion of olefins (*21*). Since also in Zn–Sb and Cd–Sb a defined compound was observed, for them too it is possible to exclude the presence of the pure metal oxides. In the case of Ce and U, the free oxides must exist, as no defined compound (for Ce) or only a little amount (for U) were observed. It is interesting to note that the method of prepara-

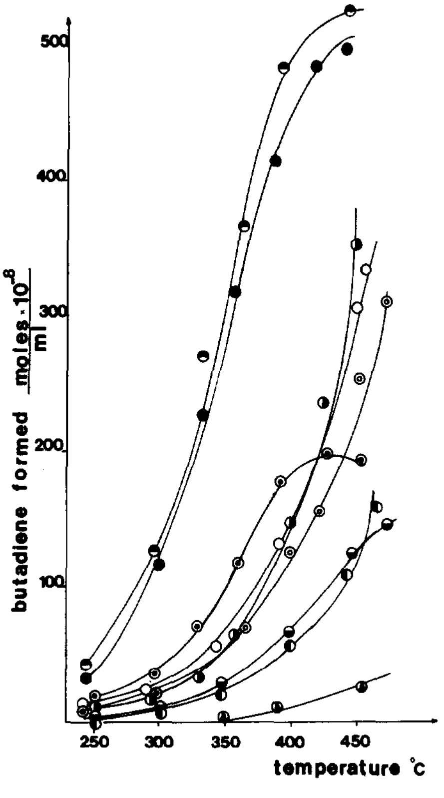

FIG. 2. Amounts of butadiene produced by the catalysts, calcined at 900°C for 1 hr, in flow reactor. Experimental conditions: 2% 1-butene in air; weight of catalyst, 1 g; contact time, 1 sec.

(◓) Fe–Sb;
(◎) Co–Sb;
(◑) Ni–Sb;
(◒) Mn–Sb;
(○) Zn–Sb;
(●) Sn–Sb;
(◉) U–Sb;
(◐) Ce–Sb;
(◕) Cd–Sb.

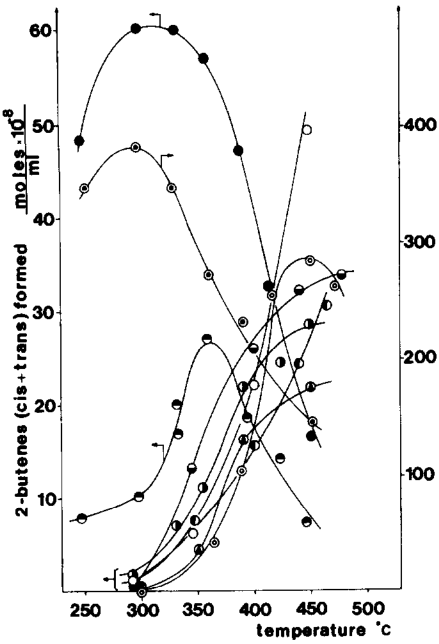

FIG. 3. Amounts of 2-butenes (*cis* + *trans*) produced by the catalysts, calcined at 900°C for 1 hr, in flow reactor. Experimental conditions and symbols as in Fig. 1.

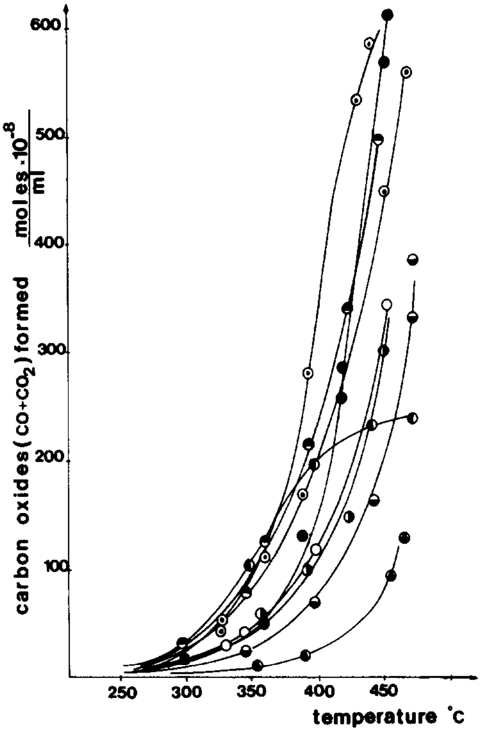

FIG. 4. Amounts of carbon oxides (CO + CO_2) produced by the catalysts, calcined at 900°C for 1 hr, in flow reactor. Experimental conditions and symbols as in Fig. 1.

tion we have used allows us to prepare the antimonates, or mixed antimony oxides, as Wells (*15*) asserts to be the exact denomination, at lower temperatures than the one normally used [900°C for 1 hr rather than 1000°C for 20 hr (*15*)], so reducing sintering. Very probably, the above phenomenon is due to the high surface area of the antimony oxide used in the preparation. It is known that a higher surface area involves a decrease in the temperature at which solid state reactions occur. Looking at Table 2 it is possible to make another interesting consideration. It is known that Sb_2O_5 transforms into α and β-Sb_2O_4 during calcination at 900°C (*3,22,23*). The addition of Zn, Sn, Ni, Co, Mn and Fe oxides to Sb_2O_5 does not influence this transformation; on the contrary, we can assert that their presence favors the partial transformation of α into β-Sb_2O_4. In fact, pure antimony oxide calcined at the same conditions consists of pure α-Sb_2O_4, while not only α but also β-Sb_2O_4 were detected in the mixed oxides by means of X-ray analysis. In the case of Cd, U and Ce, no α and β-Sb_2O_4 but still Sb_2O_5 was observed; moreover, the surface area of these catalysts was very high (like Sb_2O_5). These oxides, therefore, must have a stabilization effect on the surface area and structure of Sb_2O_5. At last consideration is that the antimony oxide, calcined at 900°C, is pure α-Sb_2O_4, different from what was found by us previously, where antimony oxide calcined at 900°C was found to be α and β-Sb_2O_4 (*3*). The formation of pure α-Sb_2O_4 was probably favored by washing with water after calcination at 350°C (see Experimental Methods), which is the only difference introduced in the preparation.

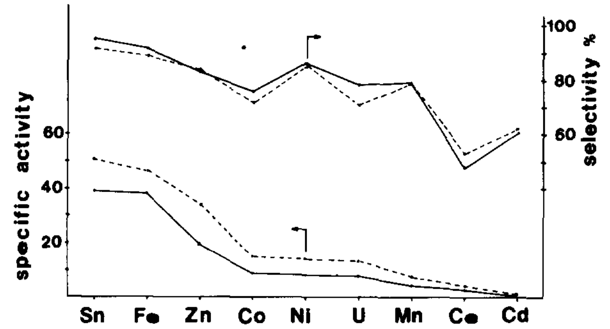

FIG. 5. Specific activity and selectivity of the catalysts at 370°C (—) and at 400°C (---).

$$\text{specific activity: } \frac{\text{butadiene} + (\text{CO} + \text{CO}_2)/4}{\text{surface area}} \; \frac{\text{moles/ml} \times 10^{-8}}{\text{m}^2},$$

$$\text{selectivity: } \frac{\text{butadiene}}{\text{butadiene} + (\text{CO} + \text{CO}_2)/4} \times 100.$$

Catalytic Behavior in Batch Reactor

This type of experiment was carried out to provide information both on the catalyst surface acidity, revealed by the formation of high amounts of 2-butenes at 250°C, and on the initial stage of activity. From Table 3 one can observe that Sb_2O_5 is active in the oxidation and isomerization of 1-butene, while Sb_2O_4 is inactive even after 5 hr of reaction. The fact that Cd and Ce–Sb mixed oxides, which contain Sb_2O_5 (Table 2), give only very small amounts of butadiene and 2-butenes, suggests that Sb_2O_5 could be covered by $Cd_2Sb_2O_7$ and CeO_2, respectively. This "wetting" of Sb_2O_5 can explain the lack of transformation to Sb_2O_4 during calcination at 900°C and perhaps also the stabilization of its surface area. In the case of U–Sb the observed activity can be attributed either to the USb_3O_{10} or to the free Sb_2O_5. Nevertheless, also in this case it is possible to hypothesize a "wetting" of Sb_2O_5 by uranium oxide to explain the lack of transformation to Sb_2O_4 during high temperature treatment.

Catalytic Behavior in Flow Reactor

In order to interpret the catalytic behavior, we have taken two different kinds of kinetic information from Figs. 2, 3 and 4. In Fig. 5 we have reported the specific (i.e., referred to unit surface area) activities and the selectivity to butadiene at 370

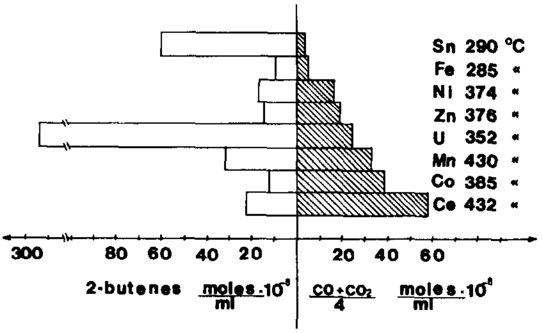

FIG. 6. Amounts of by-products formed at the temperature at which each catalyst gives 100 × 10^{-8} moles/ml of butadiene. Cd–Sb has not been reported since it never reaches this value.

and 400°C. These temperatures were chosen since, in these conditions, almost all the catalysts show activity (Figs. 2, 3 and 4). In Fig. 6 we have reported the temperature at which each catalyst produces a given amount of butadiene (100×10^{-8} moles/ml) and the amounts of by-products formed at the same temperatures. In Fig. 5 it is possible to observe that the catalysts, notwithstanding their present different activities, show, at least at $T \leqslant 400°C$, similar values of selectivity. Low values are only observed for nonactive Cd–Sb and for slightly active Ce–Sb, whose selectivity values can be strongly influenced by analysis errors, by contributions of homogeneous oxidation and of the free cerium oxide.

The relatively low specific activity of U–Sb can be due to the presence of Sb_2O_5 (Table 2), which shows a very high surface area, while the active compound USb_3O_{10} has been found to have a surface area of about 3.5 m^2/g (*5*). If we refer only to this value also U–Sb would show a very high specific activity. Besides, in our U–Sb catalyst, USb_3O_{10} is present in a low amount, and in fact it was revealed only by ir and not by X-rays. The fact that our U–Sb is not very active and presents a high isomerizing power, in contrast with Simons and co-workers' data (*24*), can be attributed to our different preparation method, which is not necessarily the best for this catalyst. In Fig. 6 one can observe that all the catalysts, even when given the same quantity of butadiene, produce very different amounts of 2-butenes and of carbon oxides. No correlations exist between the quantities of isomers and of oxidized products formed. This fact suggests that the active sites responsible for the isomer formation are different from those responsible for the oxidation. It also agrees with what was found by us for a Sn–Sb oxide catalyst at low reaction temperature (*3*). Figure 6 also shows that high carbon oxide amounts are formed by the catalysts that are active at high temperatures. In these experimental conditions, homogeneous oxidation reactions can influence strongly the selectivity values. No discrepancies exist, therefore, between the data of Fig. 5, showing about the same selectivity for all the catalysts, and those of Fig. 6, since the temperatures in Fig. 5

TABLE 4

Compound	Wavenumber (cm^{-1})	Ref.
$SbOF_3$	830	(*32*)
SbO_2F	825	(*32*)
SbO_2Cl	825	(*33*)
$Cl_4Sb\text{-}[SbO_2Cl]_4\text{-}O\text{-}SbCl_4$	809	(*34*)
Sb_2O_5	820	(*3*)
$\alpha\text{-}Sb_2O_4$	—	
Fe–Sb	830	
Co–Sb	795	
Ni–Sb	795	
Mn–Sb	—	
Zn–Sb	795	
Sn–Sb	820	
U–Sb	830	
Ce–Sb	(820)[a]	
Cd–Sb	(820)[a]	

[a] The presence of this band in the two catalysts is very probably due to Sb═O bonds of free Sb_2O_5 itself, whose presence was revealed by X-ray patterns and by the same ir spectra, rather than to Sb═O bonds of new compounds such as antimonates.

are relatively low (370 and 400°C).

The runs, carried out in both the reactors, allow us to deduce the following activity scales for butadiene formation (Fig. 5 and Table 3):

a. Low temperature (batch reactor)

$$\text{Fe–Sb} \geqslant \text{Sn–Sb} > \text{Ni–Sb, Co–Sb, } Sb_2O_5 \geqslant \text{U–Sb} > \text{Mn–Sb, Zn–Sb, Ce–Sb} > \text{Cd–Sb} > Sb_2O_4.$$

b. High temperature (flow reactor)

$$\text{Fe–Sb, Sn–Sb} > \text{Zn–Sb} > \text{Co–Sb, Ni–Sb, U–Sb} > \text{Mn–Sb} > \text{Ce–Sb} > \text{Cd–Sb} > Sb_2O_5,\ Sb_2O_4.$$

Thus the activity scales for the two types of experiments are similar, except for a few discrepancies, the most important of which is the result for Sb_2O_5 which is completely inactive in the flow reactor.

In a previous work we have observed that it is impossible to reoxidize the reduced Sb_2O_5 with gaseous oxygen even at 500°C (*3*). Its inactivity in the flow reactor can therefore be attributed to this impossibility of reoxidation.

Nature of the Oxidizing Sites

Since all the active catalysts show about the same selectivity to butadiene (Fig. 5) and consist of compounds containing pentavalent antimony, we think that the active oxidation sites are the same for all the catalysts and are tied to Sb^{5+}. This fact is in agreement with what has been advanced by some authors (*3,25,26,27*) for a Sn–Sb catalyst and by Grasselli and Suresh (*5*) for a U–Sb catalyst. Moreover, almost all the pure oxides of the added metals are active in the deep oxidation of olefins to carbon dioxide and are not selective for the formation of butadiene (*21*). This fact is a confirmation of the above hypothesis.

The role of the added metal is, in our opinion, to make easier (or to catalyze) the reoxidation of the antimony ions reduced during the previous interaction with the olefin. In view of what is stated above it is important to point out that these oxides are able to adsorb and to activate the gaseous oxygen (*28, 29*). Therefore, we can assert that they show that very property which is lacking in Sb_2O_5. To explain the reoxidation mechanism we report below the structure of the different antimonates present in our compounds:

a. $Me^{2+}Sb_2{}^{5+}O_6$ (Me^{2+} = Fe, Co, Ni, Zn) compounds show a trirutile-type structure (*11*) in which the following situation:

$$-Me^{2+}-Sb^{5+}-Sb^{5+}-Me^{2+}-Sb^{5+}-Sb^{5+}-Me^{2+}-$$

is present (*30*).

b. $MnSb_2O_6$ shows a columbite-type structure (*11*) in which chains of the type

$$\begin{gathered}-Sb^{5+}-Sb^{5+}-Sb^{5+}-Sb^{5+}-Sb^{5+}-\\-Me^{2+}-Me^{2+}-Me^{2+}-Me^{2+}-Me^{2+}\end{gathered}$$

are present (*30*).

c. USb_3O_{10} shows the following structure (*5*):

$$\begin{gathered}-U^{5+}-Sb^{5+}-U^{5+}-Sb^{5+}-U^{5+}-Sb^{5+}-U^{5+}-\\-Sb^{5+}-Sb^{5+}-Sb^{5+}-Sb^{5+}-Sb^{5+}-Sb^{5+}-.\end{gathered}$$

d. $Cd_2Sb_2O_7$ presents, on the contrary, a completely different, and very complicated, weberite-type structure (*15*).

e. In the case of Sn–Sb mixed oxides, showing a solid solution structure (*3, 13–15*), it is possible that a situation such as (a) or (c), showing two neighboring Sb^{5+} ions, can be present. This hypothesis was already advanced by us for a high temperature treated Sn–Sb (atomic ratio 4:1) mixed oxide (*3*) and by Stroeva and coworkers (*26*), always for the same catalyst.

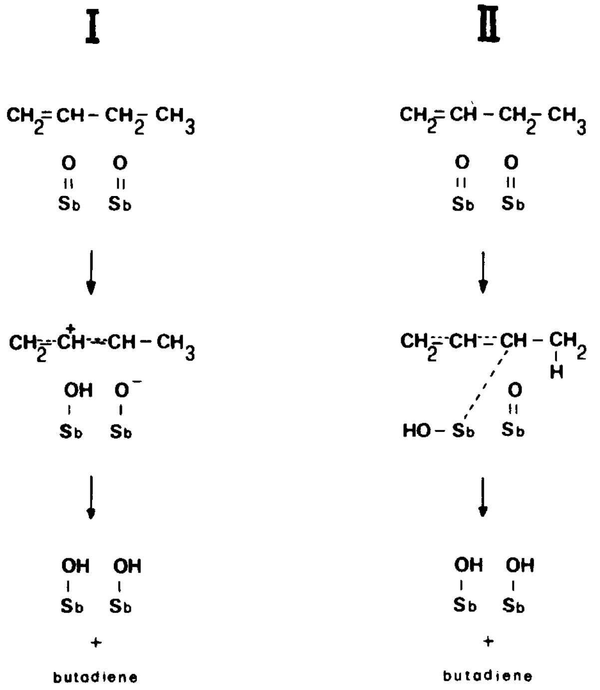

FIGURE 7.

The closeness of Sb^{5+} ions to the metal ions can make easier the reoxidation of the former reduced form, either by direct oxidation by the second metal, as in USb_3O_{10} (*5*), whose reduced ions are then oxidized by the gaseous oxygen, or by formation of particular adsorbed oxygen species, transferred to antimony through peroxidic bridges. A mechanism of this type was proposed by Cimino and Pepe (*31*) for the system CoO–MgO and NiO–MgO. It is very interesting to point out that $MnSb_2O_6$, which is not very active (Figs. 2 and 5), shows a chain structure closely related to that of $USbO_5$, the less active phase found by Grasselli and Callahan (*4*) in U–Sb mixed oxides. We think that the presence of two neighboring Sb^{5+} ions, as in trirutile compounds and, perhaps, in Sn–Sb, can be a promoting factor for the catalytic activity in olefin oxidation of these compounds.

It has been reported for USb_3O_{10} that the olefin can be adsorbed, in allylic form, on a Sb^{5+} ion and that the dehydrogenation occurs on the contiguous U^{5+} ions (*5*). A similar mechanism can be operating also in our active antimonate, where the two neighboring Sb^{5+} ions can be responsible for the oxidative dehydrogenation. This hypothesis was advanced also by Stroeva and co-workers (*26*) for a Sn–Sb mixed oxide.

As regards Fe–Sb mixed oxides we think that $FeSbO_4$, showing a rutile-type structure, is a catalyst of deep oxidation, as demonstrated by the data of Fe–Sb 1 : 1 reported by Boreskov *et al.* (*6*) and Shchukin *et al.* (*7*) and also confirmed by us (*17*). We explain the increase in selectivity presented by Fe–Sb oxides with ratio 1 : 2 (*6,7,17*) by the formation of a compound of the type $FeSb_2O_6$, showing a trirutile-type structure, or $Fe_2Sb_2O_7$, according to Grasselli (*20*). Also for this author a structure showing "two gem Sb^{5+}" presents a higher selectivity than a structure of the type -Me–Sb–Me–Sb (*20*).

With regard to the nature of the active

sites tied to Sb^{5+} ions, we have already reported that the only active antimony oxide, Sb_2O_5, presents Sb–O double bonds (*3*). From ir spectra (Fig. 1) it is possible to observe that the active compounds present, in the range 795–830 cm^{-1}, a small band that can be attributed to Sb=O (*32–34*). To support this interpretation, we have reported in Table 4 the wavenumbers at which the Sb=O bands occur, together with those of our compounds. These double bonds, presented by two contiguous Sb^{5+} ions, can play an important role in the hydrogen allylic abstraction from olefins, as hypothesized for oxidation catalyst based on Mo (*28*) and W (*35*) mixed oxides. The importance of double bonds is confirmed by the fact that in USb_3O_{10} they are present not only on Sb^{5+}, as revealed by the ir band at 830 cm^{-1}, but also on U^{5+}, as revealed by the ir band at 935 cm^{-1}. Uranyl compounds, in fact, were found to present bands in this wavenumber region (*36*). In this catalyst the two neighboring $U^{5+}{=}O$ and $Sb^{5+}{=}O$ groups can behave as the two $Sb^{5+}{=}O$ groups, present in other mixed oxides.

The possible mechanisms, operated by the two gem $Sb^{5+}{=}O$ sites, can be those shown in Fig. 7. In the first case the formation of an allylic ester occurs, by analogy with the noncatalytic oxidation of olefins by compounds containing Me=O bonds, such as SeO_2 and perchromates (*37–39*). In the second case the formation of a σ-allylic bond occurs. In both mechanisms the second $Sb^{5+}{=}O$ group makes easier the abstraction of a second hydrogen atom from the allyl, without movement of the hydrocarbon molecule on the catalyst surface.

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