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An Investigation of the Relationship between the Bulk and Surface Composition of Tin and Antimony Mixed Oxide Catalysts and the Oxidative Dehydrogenation of 1-Butene to Butadiene

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The influence of calcination temperature on the performance of tin–antimony catalysts has been investigated. It is shown that the specific activity for the formation of butadiene from 1-butene may be directly related to the concentration of antimony cations at the surface. It is proposed that isolated antimony cations surrounded entirely by tin ions in nearest neighbor sites constitute an active site for the formation of butadiene.

INTRODUCTION

Antimony–tin mixed metal oxide catalysts have been developed commercially (*1–3*) for the oxidation of propylene to acrolein, the ammoxidation of propylene to acrylonitrile, and the dehydrogenation of butenes. A number of investigations of this system have been reported and postulates made about the physical parameters governing the catalysis, but few definite conclusions can as yet be drawn. It is generally observed that only catalysts subjected to high temperatures at the preparative stage exhibit high selectivity and some authors have associated this with the necessity to form solid solutions. Lazukin *et al.* (*4*) report the presence of Sb(III) and Sb(IV) in solid solution in SnO_2. Godin *et al.* (*5*) and Crozat and Germain (*6*) postulate that the active sites for the selective oxidation of propylene consist of octahedrally coordinated Sb(V) ions dissolved in the Sn(IV) oxide lattice in association with the redox couple Sn(V)–Sn(III). Similarly Sala and Trifirò (*7, 8*) propose that Sb(V) = 0 groups are necessary for oxidative dehydrogenation, the tin providing a mechanism for the reoxidation of Sb(III). Roginskaya *et al.* (*9*), however, have proposed that Sb(III) is the active species being formed preferentially at high temperatures. Sn(IV) has also been proposed as the active site (*10, 11*) with antimony either labilizing the Sn–O bonds (*10*) or being involved in the abstraction of allylic hydrogens (*11*).

Our work on the solid state (*12*) and surface properties (*13*) of these catalysts has shown that the coprecipitation preparative procedure gives a homogeneous but relatively amorphous material which is slowly crystallized as the catalyst is calcined at higher temperatures. The calcination conditions normally adopted, however, do not effect complete crystallization or bulk equilibrium. Furthermore, the surface composition of these catalysts has been found to depend on bulk composition, calcination period, and calcination temperature, becoming increasingly enriched

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in antimony at higher temperatures. Bulk crystallization and surface segregation processes therefore depend critically on the calcination conditions adopted during catalyst activation. With this in view we have reinvestigated the catalytic properties of the system employing the oxidation of 1-butene as a model reaction.

EXPERIMENTAL

Tin–antimony oxide catalysts were prepared by coprecipitation as described previously (*12*), ground to a 30/60 mesh size, and heated in air either for 16-hr periods in the temperature range 400 to 1000°C or at 1000°C to constant weight (2–3 weeks). Catalyst activity for the selective oxidation of 1-butene by these materials was then determined employing a tubular microreactor system with glc analysis.

The microreactor consisted of a 30 × 1.2-cm glass-lined steel tube with 0.5 g of catalyst occupying about 2.5 cm at the center, the remaining space being filled with 10/30 mesh fused silica chips. This was heated by a surrounding rectangular brass block containing cartridge heaters regulated by a Eurotherm controller with a chromel/alumel thermocouple situated as close as possible to the catalyst.

Chemically pure grade gases in the volume ratio 50% air:45% nitrogen:5% 1-butene were fed to the reactor and regulated by passing through restrictors at pressures controlled by Foxborough valves to give a contact time of 1 sec during experiments. Two ten-port Taylor/Servomex pneumatically operated control valves were used to take "on-line" samples of feed gases and products which were analyzed on a Pye G.C.D. thermal conductivity unit. Oxygen, nitrogen, and carbon monoxide were separated by a 5-m molecular sieve 13X column and carbon dioxide and the C_4's by a 1-m Carbopack C 0.19% picric acid column, followed by 5 m of 20% propylene carbonate on chromosorb P at 35°C. Provision was also made for the determination of liquid oxidation products; aldehydes and ketones were separated on a 4-m column of 10% Carbowax 1540 on acid-washed chromosorb W, and acids on a 1-m column of 10% P.E.G. Adipate with 1% sebacic acid on acid-washed dimethyldichlorosilane-treated chromosorb W.

Individual catalysts were tested at 50°C temperature points in the range 150 to 400°C, taking three samples for each reaction temperature. For the purpose of presenting and discussing our results we have defined the specific activity for the formation of a product under our experimental conditions to be the yield of product obtained per unit surface area per unit time.

Surface and bulk properties were determined by X-ray protoelectron spectroscopy (XPS) and powder X-ray diffraction as we have reported elsewhere (*12, 13*) while surface areas were determined by the conventional B.E.T. nitrogen adsorption method.

OBSERVATIONS

Our catalytic results are generally in good agreement with those previously reported in the literature where corresponding catalyst preparation and evaluation conditions have been employed (*7, 11*). Thus materials calcined for 16 hr at high

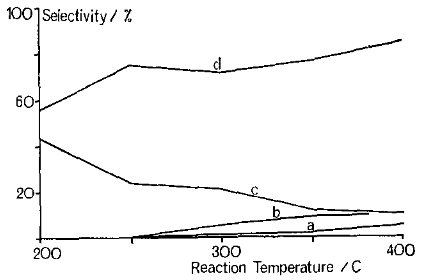

FIG. 1. Apparent selectivity as a function of reaction temperature for a catalyst of nominal composition $Sn_{0.8}Sb_{0.2}O_2$ calcined for 16 hr at 800°C. (a) CO_2, (b) *trans*-2-butene, (c) *cis*-2-butene, (d) butadiene. Total conversion increases from 3% at 200°C to 70% at 400°C.

temperatures (800–1000°C) were both active and selective for the oxidative dehydrogenation of 1-butene to butadiene. Carbon dioxide and *cis-* and *trans*-butene were also formed in significant amounts but the other gaseous and liquid products together accounted for less than 1% of the reaction and will be disregarded for the purpose of the present paper. Figure 1 represents a typical set of results for apparent selectivity as a function of reaction temperature obtained with a catalyst containing 20 atom% Sb.

Consideration of our results has shown that the specific activity for the formation of butadiene varies as a function of the calcination temperature to which the catalyst had been subjected. Specific activity, therefore, varies with the bulk structure (*12*) and surface composition (*13*). Figure 2 illustrates a typical result. The trends were observed to be similar over the temperature range 300 to 400°C and so for the purposes of comparison we have chosen to discuss the results obtained at 400°C. Although this reaction temperature gave rise to high conversions under certain circumstances it has the advantage of minimizing the influence of errors in the surface area determination. The above definition of specific activity

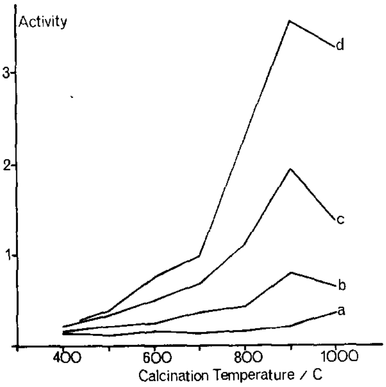

FIG. 2. Specific activity for butadiene formation in μmoles m^{-2} min^{-1} as a function of calcination temperature after 16-hr heat treatments. Reaction at (a) 200, (b) 300, (c) 350, (d) 400°C.

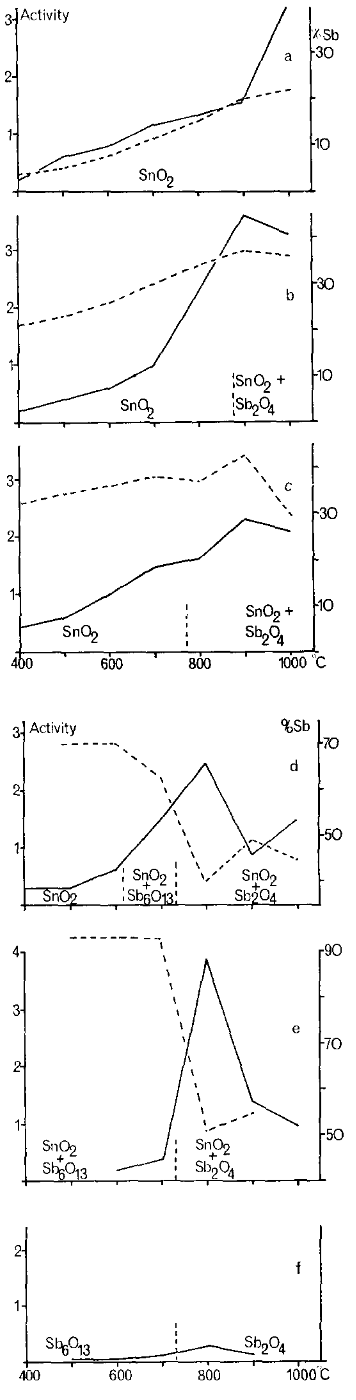

FIG. 3. The relationship between specific activity for the formation of butadiene (solid line, μmoles m^{-2} min^{-1}), surface antimony composition (broken line, atom%), and catalyst calcination temperature (a) 4, (b) 20, (c) 40, (d) 68, (e) 83, (f) 100 atom% Sb bulk composition.

TABLE 1

The Relationship between Specific Activity and Surface Antimony Concentration for Catalysts Calcined for 14 Days at 1000°C[a]

Surface composition (atom% Sb)	Specific activity $\times 10^6$ moles m^{-2} min^{-1}				Selectivity to CO_2 at 400°C (%)
	To Butadiene at			To CO_2 at 400°C	
	300°C	350°C	400°C		
0	0	0.4	1.25	2.65	66
11.7	0.15	0.92	2.28	1.34	36
14.0	0.22	0.90	1.90	0.53	21
23.7	0.34	1.06	2.44	0.49	13
25.5	0.53	1.33	3.65	0.43	11

[a] Total conversion at 350°C varies between 5 and 15%.

strictly applies at high conversion only if the reaction is zero order in butene pressure. However, the possibility of a higher reaction order and the use of high conversions should not invalidate qualitative discussion of the observed trends. The activity data for selected catalyst compositions are collected in Figs. 3 a–f together with the corresponding surface compositions determined by XPS (*13*) and the crystalline phases present as distinguished by X-ray diffraction (*12*).

It is apparent that when the rutile-like SnO_2 phase may alone be distinguished in catalysts by X-ray diffraction, the specific activity for the formation of butadiene increases as antimony segregates to the reaction surfaces at higher calcination temperatures. The pure oxides Sb_6O_{13} and Sb_2O_4 alone, however, were found to be relatively inactive while the appearance of these phases in particular catalysts at the higher calcination temperature generally resulted in significant changes in the trends in activity and surface composition.

Although there is a close parallel between catalytic activity and the surface concentration of antimony, the relationship is not quantitative over the entire range of catalysts calcined for 16 hr. This may be associated in part with the presence under certain conditions of two bulk phases in varying proportions. Investigations of the solid state properties of this system (*12*) have shown that the conventional 16-hr calcination procedure produces nonequilibrated material of poorly defined crystallinity. Bulk equilibrium is in fact very difficult to achieve in this system. However, prolonged calcination (14–21 days) in air at 1000°C does result in the formation of a highly crystalline monophasic solid solution of antimony in tin oxide, since any excess Sb_2O_4 is volatilized at this temperature. Furthermore, the surface composition of this material may be varied to give antimony concentrations up to a maximum of about one cation in four (*13*). We have, therefore, examined the catalytic behavior of this solid solution as a function of surface antimony composition. The results are given in Table 1. Specific activity for the formation of butadiene appears to vary almost linearly with surface antimony concentration and there is a corresponding but nonlinear decline in the activity for CO_2 formation with increasing antimony.

DISCUSSION

Since the best structurally defined catalytic materials that we have studied were those calcined for prolonged periods at 1000°C, we shall first discuss the catalytic results obtained with these materials. Consideration of the relationship between surface segregation of antimony in this system and the nucleation of the Sb_2O_4 phase has led us to propose that at high temperature antimony is distributed in the surface to minimize Sb–Sb interactions (*13*). Since the activity for the formation of butadiene was observed to increase beyond the basic activity of pure SnO_2 in proportion to the concentration of added surface antimony, we propose that activity for butadiene formation may be associated with the presence of individual surface antimony cations surrounded entirely in nearest neighbor positions by tin cations. Antimony cations in adjacent nearest neighbor sites would not, therefore, be active in selective oxidation. This proposition is supported by the observation that the pure antimony oxides are relatively inactive. Similarly, since the yield of CO_2 decreased rapidly with decreasing tin concentration at the surface, activity for the formation of CO_2 may be associated with the presence of tin ions at the surface surrounded only by other tin cations.

The catalysts calcined for 16-hr periods, which correspond to the materials most commonly investigated in the literature, form a rather more complex picture. Not only is the bulk structure very poorly crystalline but phase separation may be incomplete and bulk equilibrium is not achieved. However, we shall discuss salient features of their catalytic properties in the context of the structural characterization and proposed model.

The catalyst containing 4 atom% Sb (Fig. 3a) corresponds most closely to the catalysts equilibrated at 1000°C, since this composition corresponds to the solid solution limit of antimony in SnO_2. Although the catalyst is poorly crystalline, the surface antimony concentration and catalytic activity are closely related. The specific activity observed for butadiene formation at higher antimony compositions and low calcination temperatures (Figs. 3b and c) was not significantly increased with respect to the 4 atom% value, even though the surface concentration of antimony was necessarily greater. Since the catalysts were prepared by coprecipitation, the surface after calcination at low temperatures may be considered to consist of a random array of tin and antimony ions. The probability of any individual antimony cation being surrounded entirely by tin cations is therefore much reduced. At higher calcination temperatures, however, as the surface ions are thermally rearranged and more antimony migrates to the surface the specific activity for butadiene formation would be expected to increase and approach the maximum value, as was observed experimentally.

Although it is clear that at 1000°C surface concentrations of antimony in excess of 25 atom% may not be sustained because nuclei of Sb_2O_4 form and are volatilized, it is not necessarily obvious for low calcination temperatures at which stage surface segregation processes result in the formation of free Sb_2O_4. The only evidence would appear to be the presence of Sb_2O_4 in the X-ray diffraction patterns. It may be envisaged that up to 50 atom% antimony may be accommodated at the reaction surface without reducing the activity for butadiene formation if the antimony cations occupy non-nearest neighbor surface sites. Since free Sb_2O_4 is relatively inactive, a surface layer might be expected to inhibit catalytic activity. However, Sb_2O_4 does sinter readily, so that the separation of the Sb_2O_4 phase might effectively remove excess antimony which would otherwise inhibit catalytic activity. The situation for catalysts of high antimony bulk composition is thus rather complex, but the activity pattern displayed in Fig. 3e does indicate that phase separation results in the generation of new reaction surfaces which support suitable cationic environments for enhanced activity. A detailed investigation of the primary kinetics of butene oxidation over tin–antimony oxides which has been carried out in this Laboratory (*14*) correlates well with this work and will be published shortly.

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REFERENCES

1. British Patent 864666, 1960, Distillers.
2. British Patent 902952, 1962, Distillers.
3. U.S. Patents 3094565, 1963; 3142170, 1964; 3244642, 1966, Distillers.
4 Lazukin, V. I., Belousov, W. M., and Rubanik, M., *UK. Khim. Zh.* **32**, 231, 1966.
5. Godin, G. W., McCain, C. C., and Porter, E. A., "Proc. IV Int. Congr. on Catalysis" (Moscow 1968), Vol. I, p. 271. Akadémiai Kiadó, Budapest, 1971.
6. Crozat, M., and Germain, J. E., *Bull. Soc. Chim. Fr.* 1125, 1973.
7. Sala, F., and Trifirò, F., *J. Catal.* **34**, 68, 1974.
8. Sala, F., and Trifirò, F., *J. Catal.* **41**, 1, 1976.
9. Roginskaya, Ur. E., Dublin, D. A., Stroevan, S. S., Kulkova, N. V., and Gelbshtein, A. E., *Kinet. Katal.* **9**, 1143, 1968.
10. Wakabayashi, K., Kamiya, Y., and Ohta, A., *Bull. Chem. Soc. Japan* **40**, 2172, 1967.
11. Trimm, D. L., and Gabbay, D. S., *Trans. Faraday Soc.* **67**, 2782, 1971.
12. Pyke, D. R., Reid, R., and Tilley, R. J. D., submitted for publication.
13. Cross, Y., and Pyke, D. R., *J. Catal.* **57**, 000 (1979).
14. McAteer, J. C., *Trans. Far. Soc. I.* (in press).