JOURNAL OF CATALYSIS **104**, 47–58 (1987)

Selective Oxidation Catalysts Containing Antimony for the Conversion of 1-Butene to Butadiene

II. Selective Oxidation of 1-Butene and CO

G. I. STRAGUZZI, K. B. BISCHOFF, T. A. KOCH, AND G. C. A. SCHUIT

Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Received February 6, 1986; revised August 25, 1986

The selective oxidation of 1-butene to butadiene and the oxidation of CO over a series of $MSbO_4$, with M = Fe, Al, Cr, Co, and Rh, were studied using a fixed-bed, integral reactor system. Activity and selectivity measurements were performed using catalysts which had been prepared by precipitation or impregnation and which had previously undergone extensive characterization. The most selective catalyst for butadiene production was determined to be antimony-impregnated $FeSbO_4$. Post-reaction characterization revealed that the catalysts were stable for prolonged reaction times, the Fe–Sb–O system being the only one able to be reduced under reaction conditions.

1. INTRODUCTION

The ultimate goal of this research was to determine the factors which make binary oxides such as $FeSbO_4$ particularly selective in the oxidation of olefins.

To facilitate a correlation between composition and structure with the ability to perform selective catalytic oxidation, the systems selected for investigation are summarized in Table 1.

By comparison of the catalytic properties of these materials it is possible to elucidate the electronic factor of the metal by changing the chemical composition in a given fixed structure. Simultaneously, each row of the table allows a comparison of the effect of increasing surface concentration of M or Sb as a result of impregnation within an M–Sb pair in each antimonate.

The method proposed was to use as test reactions the oxidative dehydrogenation of 1-butene versus carbon monoxide oxidation. The preparation and characterization of the series has been detailed previously (*1*) and in this paper we provide activity and selectivity data. The determination of the reaction kinetics is a topic for subsequent investigation.

Of the catalysts tested, only iron antimonate has been extensively examined in the literature (*2–5*). There are many hypotheses to explain why the Fe–Sb–O system is a good catalyst for propene and/or butene oxidation. Fattore *et al.* (*6*) proposed that two phases, $FeSbO_4$ and Sb_2O_4, cooperate in producing acrolein from propene, with a higher selectivity than each phase alone. They postulated that the allyl radical formation takes place on Sb_2O_4 and that oxygen ions migrate from $FeSbO_4$ to Sb_2O_4.

Using Mössbauer spectroscopy on the $FeSbO_4$ system, Urlich *et al.* (*7*) found that selective oxidation was increased if the amount of Fe^{3+} was decreased. They concluded that a medium M–O bond strength or reducibility was responsible for a good oxidation catalyst.

Aso *et al.* (*8*) proposed the formation of a specific surface structure to explain the drastic improvement of acrolein selectivity in the Sb-rich region of iron–antimony catalysts. A year later (*9*), they estimated that the surface Sb ions provide adsorption sites

0021-9517/87 $3.00

TABLE 1

Systems Investigated

Antimonate	Structure	Impregnated with extra
$AlSbO_4$	Rutile	Sb, Al, Fe
$CrSbO_4$	Rutile	Sb, Cr, Fe
$FeSbO_4$	Rutile	Sb, Fe
$CoSb_2O_6$	Trirutile	Sb, Co
$RhSbO_4$	Rutile	

for oxygen while the Fe ions stabilize the oxidation state of Sb(V).

Burriesci *et al.* (*10*) subsequently found no evidence for the formation of any other Fe–Sb compound aside from rutile $FeSbO_4$. They suggested that the role of bulk excess antimony in the more selective catalyst was in promoting the formation of structurally distorted and defective $FeSbO_4$, where Fe^{2+} ions were introduced into the rutile structure near oxygen vacancies. Trifiro *et al.* (*11*) suggested that the formation of surface groups such as $O{=}Sb{=}O$ due to the inclusion of excess antimony inside the rutile structure of $FeSbO_4$ could explain the observed increase in selectivity for Sb-rich catalysts.

Thus, surface geometrical, electronic, and bulk structural arguments have been proposed to explain the same features in the system: $FeSbO_4$ with excess antimony is the most active and selective catalyst for ammoxidation of oxidative dehydrogenation of olefins.

In this paper the structural and compositional nature of these catalysts, as revealed by characterization investigations, is related to their distinction catalytic behavior. A correlation was found using the electrochemical potential as a guiding reference for the electronic effect on the elements involved (*12*).

2. EXPERIMENTAL METHODS

2.A. Catalyst Preparation

Catalysts were prepared by solid-state reaction, precipitation, and impregnation techniques, as described by Straguzzi *et al.* (*1*).

2.B. Catalytic Performance: Reaction Studies

2.B.1. Apparatus. The experimental apparatus is depicted schematically in Fig. 1. The flow system was designed to handle two different gas compositions with the same or different flow rates. A four-way valve allowed switching either stream. Each feed gas stream was equipped with a two-stage pressure regulator, pressure gauge, a flow controller (Brooks, Model 8744A) capable of delivering a constant flow with variable downstream pressures, and a rotameter. Stainless-steel tubing, $\frac{1}{8}$-in. o.d., was used for all the gas lines and fittings.

The catalyst was located inside a vertical inert quartz tube (0.8 cm i.d. × 43.2 cm) supported by silicon carbide bed. The reactor tube was surrounded by a nickel sleeve, which served as a heat sink. Three thermocouples were used to monitor and regulate the catalyst bed temperature. One thermocouple, located at the top of the bed, extended to the center of the reactor. The second, in contact with the external wall of the reactor at the same axial position as the first, fed back to a Thermo Electric temperature controller. The third thermocouple, located inside the jacket, was used for safety purposes.

The gas stream was introduced at the top

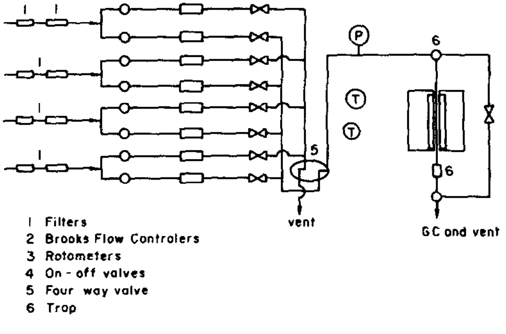

FIG. 1. Schematic diagram of gas manifold and reactor/bypass loops.

of the reactor. The outlet line was wrapped with heating tape and heated to 150°C, to avoid condensation of water produced in the oxidation of 1-butene.

The analytical train consisted of two gas chromatographs. An Antek 700 Series chromatograph, with dual columns, was used for the fixed gases (CO, CO_2 and O_2). A 5700A Hewlett–Packard gas chromatograph was used to analyze all C_4 hydrocarbons. Gas chromatograph detectors output was recorded by integrators.

2.B.2. Experimental techniques. The experimental procedures given in this section are for the isothermal runs used to test for catalyst activity and selectivity.

Before loading the catalyst, the interior of the reactor tube was carefully cleaned using a series of soap, water, and acetone washings. All experiments were made using approximately the same surface area of catalyst. The standard loading was 0.2 g of catalyst well mixed with 1 g of acid-washed SiC of similar particle size.

When the catalyst was loaded, care was taken to locate the thermocouple probe in the middle of the bed. A check of temperature uniformity inside the reactor indicated that the central portion, 10 cm, had a uniform temperature even with gas flows of 100 cm³/min. The upper and lower parts of the reactor were filled with SiC to avoid homogeneous oxidation reactions. Sampling was accomplished by using a 10-port Valco-valve inside a thermoregulated enclosure.

Each catalyst was pretreated before each run. The purpose of the pretreatment was to expose the sample to an oxidizing environment to ensure reproducibility. Every fresh sample was heated at 1°C/min up to 350°C in a stream of 5% O_2 in He flowing at 120 cm³/min. It was held at 350°C for a minimum of 3 h. Meanwhile, feed gases were set in the alternate loop manifold.

2.B.3.1. Oxidation of 1-butene. The 1-butene oxidation studies were carried out over the range of 350–450°C at atmosphere pressure. During the experiments a stream of reaction mixture (6.5% 1-butene, 7% oxygen, balance helium) was passed through the bed at a flow rate of 120 cm³/min. Once the feed gas composition was analyzed, the four-way valve was switched to the reactor line and the reaction was started. Samples were taken every 20 min, for a minimum of 2 h. A standard treatment of the catalyst in 5% O_2–He for 3 h followed each run. Isothermal measurements were made at three different feed compositions to study the effect of the hydrocarbon/oxygen ratio on the activity and selectivity of the catalyst.

2.B.3.2. Oxidation of carbon monoxide. Using the same experimental settings, the stream of reaction mixture contained 3.0% CO, 3.5% oxygen, 93.5% helium. The preliminary studies showed that the CO/O_2 ratio had no effect on the catalytic activity. The reaction was tested for more than 1.5 h; reaction studies were always followed by the standard oxygen–helium treatment.

2.B.3.3. Inhibition studies. These experiments were designed to determine the effect of one reactant upon the reaction of the other. A combined reaction mixture of 6.5% 1-butene, 3% CO, 8.0% O_2, balance helium was passed through the bed at a flow rate of 120 cm³/min. A minimum of three temperatures (350, 400, and 450°C) were tested. Temperature and concentrations were followed for at least 2 h.

3. EXPERIMENTAL RESULTS

3.A. Definition of Terms

The reactor was operated in an integral mode with conversions generally greater than 20%. The definition of conversion, selectivity, and activity are given by the following equations:

For the reaction of 1-butene,

$$\text{Conversion} = 100 \times \{1 - ([\text{butenes}]_t/[\text{butenes}]_0)\}$$

$$\text{Selectivity} = 100 \times \{[\text{diene}]/([\text{diene}] + 0.25 \times [CO_2])\}$$

in which

$[\text{butenes}]_0$ = concentration of butenes before reaction;

$[\text{butenes}]_t$ = concentration of butenes after reaction at time t;

[diene] = concentration of butadiene; and

$[CO_2]$ = concentration of carbon dioxide;

For the reaction of CO,

$$\text{Conversion} = 100 \times \{1 - ([CO]_t/[CO]_0)\}.$$

When comparing different systems,

$$\text{Activity} = \{([\text{butadiene}] + 0.25 \times [CO_2])/(m^2 \cdot h)\}$$

= (moles of butene consumed to form observed oxidation products)/(area × time).

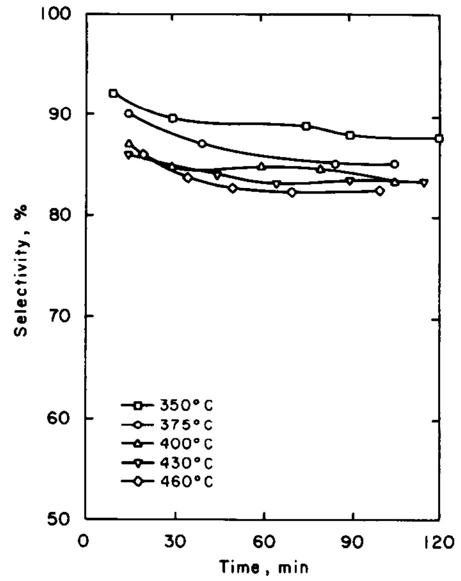

FIG. 3. Effect of temperature on selectivity; $FeSbO_4$; $[1 - C_4/O_2] = 0.9$.

3.B. Iron–Antimony System

3.B.1. $FeSbO_4$. The conversion data taken with $FeSbO_4$ were more extensive than with the other catalysts. Figure 2 presents the effect of the reaction temperature on 1-butene conversion, for a fixed hydrocarbon/oxygen ratio of 0.9. There was no significant activity below 350°C. In the temperature range studied, the initial activity was always close to 100%, declining to a plateau after 30 min on stream. At temperatures above 400°C, when the steady-state conversion was more than 50%, a temperature increase of more than 10°C was measured inside the bed, indicating the presence of hot spots. In Fig. 3 the selectivity to butadiene is presented for the same temperatures.

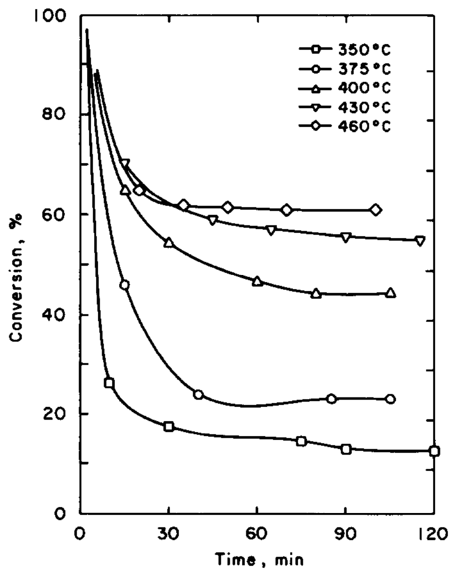

FIG. 2. Effect of temperature on conversion; $FeSbO_4$; $[1 - C_4/O_2] = 0.9$.

Figures 2 and 3 summarize the general behavior. As the temperature increases, the activity increases and the selectivity decreases, staying, however, above 80%.

The effect of the hydrocarbon to oxygen ratio was investigated at 400°C. The results, presented in Fig. 4, show that the conversion of 1-butene increased with the availability of oxygen in the gas phase. This did not affect the selectivity as depicted in Fig. 5. Similar behavior was observed at other temperatures.

Using the previously described pretreatment between measurements, these results

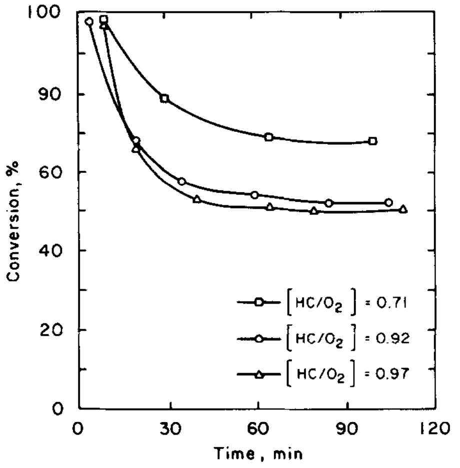

FIG. 4. Effect of HC/O_2 feed ratio on conversion; $FeSbO_4$; 400°C.

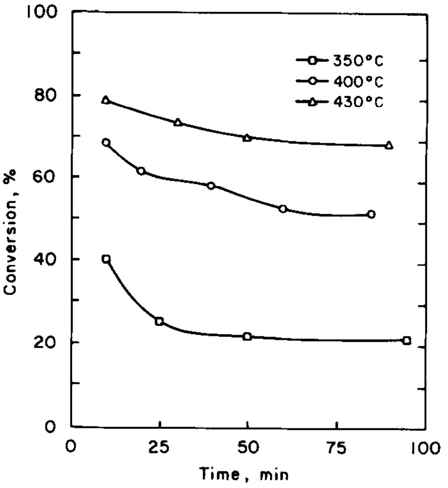

FIG. 6. Effect of temperature on CO conversion; $FeSbO_4$; ([CO]/[O_2]) = 0.8.

were reproducible when measured either increasing or decreasing the reaction temperature, as well as when changing the sample for a fresh one.

The CO conversion data for the temperature range investigated are presented in Fig. 6.

The CO conversions were higher than those for the olefin at the same temperature (compare with Fig. 2). However, when mixed in the feed, the conversion for the carbon monoxide was suppressed without affecting the 1-butene conversion, showing an inhibition effect of the oelfin.

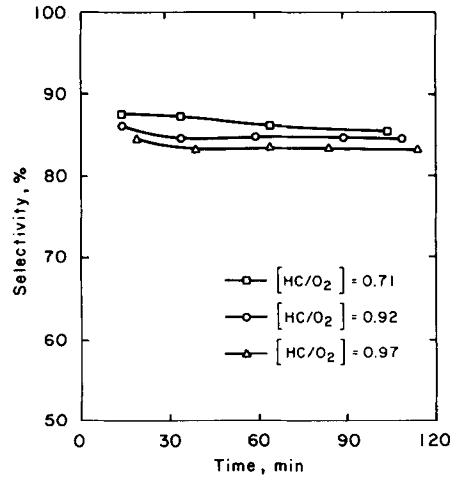

FIG. 5. Effect of HC/O_2 feed ratio on selectivity; $FeSbO_4$; 400°C.

3.B.2. $FeSbO_4$ impregnation. The iron antimonate was impregnated with different amounts of Sb and Fe. Two different batches of $FeSbO_4$ were used. Batch A was pure $FeSbO_4$; while batch B showed traces of FeO in its X-ray diffraction (XRD) pattern, possibly due to a higher calcination temperature (800°C).

On testing the performance of these catalysts, it was found that the reaction temperature and feed composition had similar effects on 1-butene conversion as those reported for $FeSbO_4$. In Fig. 7 the conversion of 1-butene at 400°C and a feed hydrocarbon/oxygen ratio of 0.9 is shown.

Antimony impregnation produced a less active catalyst, while iron impregnation increased the activity. However, the more active the catalyst, the less selective it was for butadiene production. This feature is presented in Fig. 8.

The effect of impregnation on selectivity was opposite to that on activity. Thus, as the X-ray photoelectron spectroscopy (XPS) Sb/Fe ratio increased, the activity decreased and the selectivity increased. This is independent of the bulk phase composition, as shown by batches A (pure

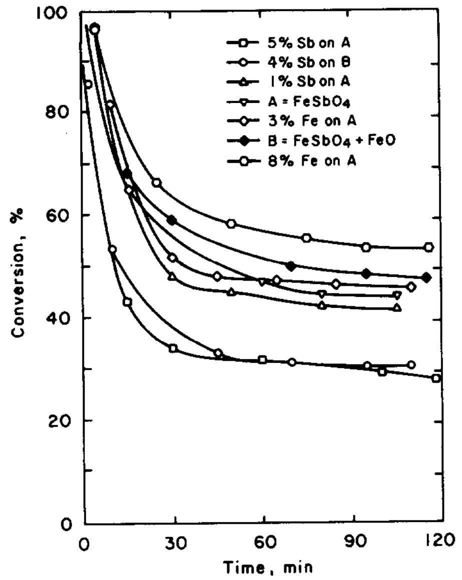

FIG. 7. Conversion of 1-butene at 400°C for impregnated catalysts; $[1 - C_4/O_2] = 0.9$.

$FeSbO_4$) and B ($FeSbO_4$ + traces of FeO). Table 2 summarizes these results.

The conversion of CO, shown in Table 3, decreased as the percentage of impregnation increased regardless of whether the catalyst was impregnated with iron or antimony. However, when CO and 1-butene were fed together, as in the case of nonimpregnated $FeSbO_4$, the CO oxidation was inhibited by the presence of the olefin.

3.B.3. Oxidation state of antimony in Fe–Sb systems. The changes observed in the shape of XPS Sb(3*d*) bands for the used catalysts, and the fact that there was always a 30-min period of initial activity decay in 1-butene oxidation supported the idea of a surface reduction under reaction conditions.

TABLE 2

Summary of Data for 1-Butene Oxidation at 400°C: Feed Ratio $[1 - C_4]/[O_2] = 0.9$

Catalyst (wt%)	Activity (mmol/h · m^2)	Selectivity (%)	XPS Sb 3*d*/Fe 2*p*
8% Fe on A	25	77	2.8
3% Fe on A	22	82	3.0
A = $FeSbO_4$	21	84	3.2
1% Sb on A	17	84	3.3
5% Sb on A	9	92	3.9

TABLE 3

Effect of Impregnation on CO Conversion Steady-State Values for a Feed Ratio $[CO]/[O_2] = 0.8$

Catalyst (wt%)	CO conversion (%)	
	400°C	430°C
A = $FeSbO_4$	53.0	68.6
3% Fe on A	33.9	48.3
5% Sb on A	10.5	15.3

In Fig. 9 the profiles for 1-butene conversion versus time at 400°C and a feed ratio of 0.9 are presented for three samples, each with different initial Sb oxidation state as shown by XPS analysis (*1*).

3.B.4. Fe_2O_3 and Sb_2O_4. 1-Butene conversion data at 400°C are shown for these systems in Fig. 10. The $FeSbO_4$ data were added to facilitate comparisons. Neither Fe_2O_3 nor Sb_2O_4 performed as well as $FeSbO_4$.

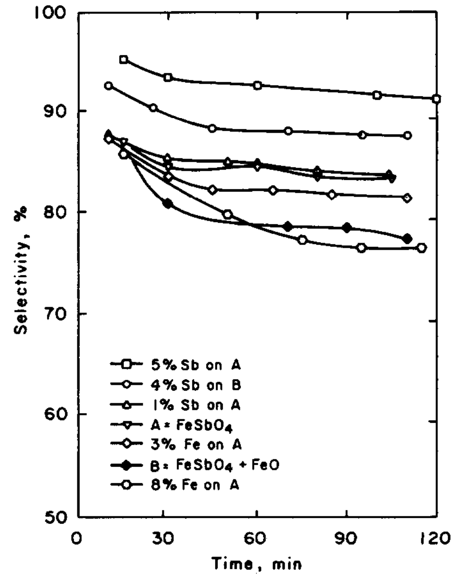

FIG. 8. Selectivity to butadiene at 400°C of impregnated catalysts; $[1 - C_4/O_2] = 0.9$.

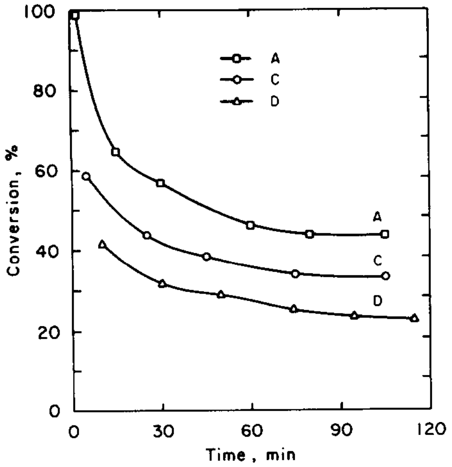

FIG. 9. Effect of pretreatment on 1-butene conversion at 400°C; $[1-C_4/O_2] = 0.9$. A, $FeSbO_4$ heated in flowing air; C, $FeSbO_4$ heated in flowing helium; D, $FeSbO_4$ + Sb(III) heated in flowing helium.

Comparison of the activity of the samples investigated is shown in Table 4. The activity is a better point for comparison than the conversion as it provides a surface area correction. Activities and selectivities are reported at 400°C; and they are arranged in decreasing XPS Sb/Fe ratio and selectivity.

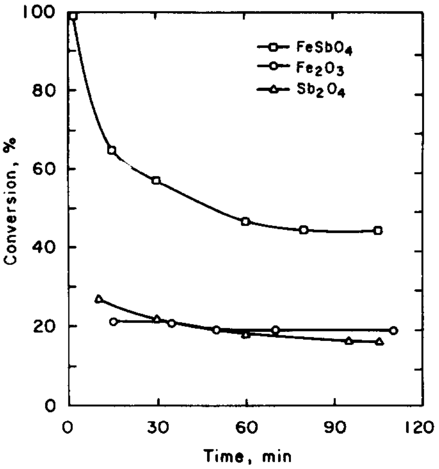

FIG. 10. 1-Butene conversion at 400°C. $[1-C_4/O_2] = 0.9$.

3.C. Aluminum–Antimony System

3.C.1. $AlSbO_4$. The catalyst was tested for 1-butene oxidation at selected temperatures, using a fixed-feed hydrocarbon to oxygen ratio of 0.9. Conversion was always below 25%. At 350°C only isomerization took place. At 400°C, only a tenth of the 20% overall conversion was to butadiene and CO_2, increasing to one quarter of the

TABLE 4

Summary of Data on 400°C for Fe–Sb Catalysts: Feed Ratios: $[1-C_4]/[O_2] = 0.9$; $[CO]/[O_2] = 0.8$

Catalyst	1-Butene oxidation		CO oxidation activity (mmol/m² · h)
	Activity (mmol/m² · h)	Selectivity (%)	
5% Sb on A	9	92	4.4
4% Sb on B	13	88	—
Batch D	11	88	4.4
Batch C	14	85	16.8
1% Sb on A	17	84	—
A = $FeSbO_4$	21	84	36.0
3% Fe on A	22	82	16.6
B = $FeSbO_4$ + FeO	20	78	4.6
8% Fe on B	25	77	—
Sb_2O_4	3	78	7.0
Fe_2O_3	13	33	34.7

24% overall conversion at 460°C. Similarly, for CO oxidation, conversions were below 10% in the temperature range studied.

3.C.2. $AlSbO_4$ impregnation. In general all the Al–Sb catalysts tested were rather inactive for butadiene formation and CO oxidation. None showed initial high conversion, and steady state was reached within minutes. No evidence of hot spots was found. The results are summarized in Table 5. Inhibition of CO oxidation by olefins (1-butene and butadiene) was observed for all catalysts in this series.

3.C.3. $AlSbO_4$ impregnated with $FeSbO_4$. Given the large differences in catalytic performance when iron was isostructurally replaced by aluminum in the rutile antimonate, the following studies were designed to elucidate the structural requirements of the test reaction used. A rather inactive catalyst ($AlSbO_4$) was used as support and impregnated with different amounts of a known active catalyst: $FeSbO_4$. Table 6 presents the results obtained for oxidation reactions at 400°C along with the values of the pure catalyst involved.

TABLE 6

$AlSbO_4$ Impregnated with $FeSbO_4$ Oxidation Reactions at 400°C

Catalyst	1-Butene		CO activity (mmol/m² · h)
	Activity (mmol/m² · h)	Selectivity (%)	
$AlSbO_4$	1.0	75	1.0
2% $FeSbO_4$ on $AlSbO_4$	1.0	76	2.7
15% $FeSbO_4$ on $AlSbO_4$	2.0	86	3.1
$FeSbO_4$	21.0	84	36.0

3.D. Chromium–Antimony System

Chromium antimonate was impregnated with different amounts of Cr, Sb, and Fe. The oxidation activities for 1-butene, CO, and a mixture of these reactants were measured for the series.

Conversions for the olefin were in the 17–40% range. Antimony impregnation did not change the performance of $CrSbO_4$. On the other hand, the chromium-impregnated samples showed a drastic increase in activity and almost no selectivity to butadiene. Carbon monoxide was also detected as an oxidation product and there were low measurable amounts of oxygen in the exit stream. Because of the presence of CO as a product in the olefin oxidation, it was not possible to establish inhibition effects in the combination-feed studies.

Iron impregnation produced an intermediate catalyst; the activity improved with loss of selectivity when compared with pure $CrSbO_4$. No CO was observed as olefin-oxidation product in this case; the inhibition effect of 1-butene over CO oxidation could be measured when both were fed simultaneously. A summary of the oxidation reactions at 400°C is presented in Table 7.

TABLE 5

Effect of Impregnation on $AlSbO_4$ Oxidation Reactions at 400°C

Catalyst (wt%)	1-Butene		CO activity (mmol/m² · h)
	Activity (mmol/m² · h)	Selectivity (%)	
E = $AlSbO_4$	1.0	75	1.0
7% Al on E	<1.0	76	1.0
4% Sb on E	<1.0	76	0.0
7% Sb on E	1.0	80	0.0
7% Fe on E[a]	3.0	70	20.0

[a] Sample calcined in flowing pure oxygen.

TABLE 7

Effect of Impregnation on Chromium Antimonate Oxidation Reactions at 400°C

Catalyst (wt%)	1-Butene		CO activity (mmol/m² · h)
	Activity (mmol/m² · h)	Selectivity (%)	
F = $CrSbO_4$	2	77	7
7% Sb on F	2	76	6
4% Cr on F	35	23	n.a.
7% Cr on F	36	17	140
7% Fe on F	36	56	83

3.E. Cobalt–Antimony System

Catalytic measurements gave a steady-state conversion of 13% for 1-butene at 400°C. The products were equally distributed between isomerization and oxidation reactions. The calculated activity for oxidation products was 6 mmol/m^2 · h, with a selectivity of 47% toward butadiene. Carbon monoxide oxidation gave 97% conversion at 400°C, corresponding to an activity of 117 mmol/m^2 · h. This high activity was suppressed when CO was cofed with 1-butene; a similar behavior was found in most of systems studied.

A sample of the catalyst was impregnated with 6% Co to investigate its effect on the catalytic performance. A conversion of 20% was obtained for 1-butene at 400°C, with only 7% conversion to oxidation products. This gave an activity of 12 mmol/m^2 · h and a butadiene selectivity of 52%. Conversion for CO oxidation was complete, corresponding to an activity of 166 mmol/m^2 · h. This activity prevailed when the olefin was also present in the feed.

3.F. Rhodium–Antimony System

This catalyst converted 25% of 1-butene at 400°C. The oxidation products, mostly carbon dioxide, accounted for 13% of the reaction products with a resulting activity of 2.5 mmol/m^2 · h and a selectivity of 17%. Carbon monoxide oxidation gave an activity of 100 mmol/m^2 · h with 90% conversion. No inhibition effects were observed.

4. DISCUSSION OF RESULTS

Of the catalysts tested, only iron antimonate has been extensively examined in the literature (*2–5*). There is general agreement that an antimony-enriched surface results in a more selective and less active catalyst for oxidation of 1-butene to butadiene (*11*), and for propene conversion to acrolein (*2, 5–9*).

Our results corroborate these findings, giving a clear correlation between the surface metal ratio of the Fe–Sb series and catalytic activity for 1-butene oxidation. Table 3 indicates that, when the XPS Sb 3*d*/Fe 2*p* surface ratio increased, the selectivity increased but the activity decreased. Values for pure Fe_2O_3 and Sb_2O_4 are also shown.

Analysis of these data indicate the presence of different sites involved in the olefin reaction. Iron impregnation apparently generated new oxidation sites while extra antimony decreased the number of unselective sites.

Although the involvement of Sb ions in the reaction cannot be ruled out, the primary function of the antimony appears to be the adsorption of oxygen from the gas phase, i.e., to provide for reoxidation of the catalyst. Aso and co-workers (*8*) showed by a ^{18}O tracer study that the oxygen is accommodated by surface Sb ions preferentially rather than by surface Fe ions.

Comparison of the performance of $FeSbO_4$ with $FeSbO_4$ impregnated on $AlSbO_4$ (Table 4) indicates that involvement of bulk oxygen is necessary for the reaction to proceed and that aluminum antimonate is not able to provide it. In the case of 15% $FeSbO_4$ on $AlSbO_4$, XRD patterns showed the presence of two rutile phases. XPS confirmed the presence of surface iron, but the catalyst behaved more like iron-impregnated aluminum antimonate with very low activity. However, the selectivity resembled that of antimony-impregnated iron antimonate.

According to the data presented, the isomorphous exchange of M in rutile-type $MSbO_4$ produced major differences in the catalytic performance. A summary of steady-state activities (i.e., after more than 30 min on stream when the activity plateau is reached) is shown in Table 8.

All these catalysts showed an antimony surface enrichment as measured by XPS, with a Sb/M ratio greater than 3, with the exception of $AlSbO_4$ which gave 1.2. However, the electronic effect of M within the structure reveals that the activity for butadiene formation is located on the transition

TABLE 8

Summary of Oxidation Reactions at 400°C

Catalyst	1-Butene Activity ($mmol/m^2 \cdot h$)	1-Butene Selectivity (%)	CP activity ($mmol/m^2 \cdot h$)	1-Butene + CO
$AlSbO_4$	1	75	1	CO inhibited
$CrSbO_4$	2	77	7	CO inhibited
$FeSbO_4$	21	84	36	CO inhibited
$CoSb_2O_6$	6	47	117	CO inhibited
$RhSbO_4$	15	17	100	No inhibition
Sb_2O_4	3	78	7	CO inhibited

metal ion and that iron is the most effective. Aluminum and chromium antimonates behaved like Sb_2O_4 (i.e., Sb(III)Sb(V)O_4), being almost inert compared to $FeSbO_4$. Cobalt antimonate was weakly active as well a unselective for 1-butene oxidation, but showed the higher activity of the series for carbon monoxide oxidation. Rhodium antimonate, despite having a rutile structure, behaved differently from the other members of the series. Rhodium antimonate was a very poor olefin dehydrogenation catalyst but had a good performance in CO oxidation.

From the data shown in Table 8 the rate of butadiene produced per unit area and time can be determined. The values for $CoSb_2O_6$ (2.82) and $RhSbO_4$ (2.55) are close to the value for Sb_2O_4 (2.34). All of the rates are very low when compared with the value for $FeSbO_4$: 17.64 mmol of butadiene/$m^2 \cdot h$. Thus, it appears that the theories attributing oxidative dehydrogenation activity to antimony may be eliminated.

A model accounting these results has already been outlined (*12*) and based on the model known as "ensemble" theory, as proposed by Ponec, Sachtler, and van Schaik (*13–15*). This theory was developed to account for changes in activity and selectivity for hydrogenation reactions when varying the ratio of the constituent metals in binary alloys, but it can also be related to these oxides.

Pure Fe_2O_3 is active but not selective because a butene molecule adsorbed on its surface is subject to multiple attacks by the surrounding oxygens. These are all bonded to iron cations and therefore are all active. Large ensembles of contiguous, active oxygens are always present on surfaces of oxidation catalysts containing only transition metal cations. Unless their activity is very low, such surfaces will be nonselective. Ensembles of active oxygens for selective oxidation should therefore be small. They may be reduced in size by replacing active by inactive oxygens of the kind found on the surfaces of antimony oxides. Thus, in the case of selective $FeSbO_4$, each surface Fe cation attached to an active oxygen is surrounded entirely by Sb attached to nonactive oxygens, avoiding overoxidation. The antimony surface enrichment of all $FeSbO_4$ catalysts defines their unique position. The oxidation of CO appears to occur on the same site that is active for the butene oxidation, as evidenced by the inhibition effect of the olefin when both were fed simultaneously. This is plausible since both reactions need only one oxygen. However, such a single active oxygen site cannot be reoxidized by molecular oxygen once it is reduced. The dissociative adsorption of molecular oxygen, as two oxygen anions, requires a larger ensemble of surface metal ions containing at least two anion vacancies. It is proposed that reactivation of the depleted site occurs by migration of a neighboring nonactive oxygen to the anion vacancy next to the transition metal cation. This shift should be accompanied by a simultaneous migration of electrons to Sb^{5+}, the cation related to the originally inactive oxygen, and antimony cations then become reduced to the trivalent oxidation state. Once the concentration of anion vacancies has increased, the adsorption of O_2 may occur by the reaction

$$2\mathrm{Sb}^{3+} + \mathrm{O}_2 \leftrightarrow 2\mathrm{Sb}^{5+} + 2\mathrm{O}^{2-}.$$

Thus, the antimony component ensures that the oxidation is selective by reducing the size of the "active oxygen" ensembles, but it also has a second function which is to allow the reoxidation of the catalyst.

The mechanism proposed for the Fe–Sb system is also able to explain the form of the conversion vs time curves, with an initial high conversion followed by a decline to a steady state. However, in order to explain the relative activities of catalysts containing differing transition metal cations, the ensemble theory must be expanded by ascribing differences in activities at equal ensemble size to changes in the "electronic factor."

The reaction network may be written as

$$\mathrm{C_4H_8} + \mathrm{O}^{2-} \rightarrow \mathrm{H_2O} + \mathrm{C_4H_6} + 2e^- \quad (1)$$

$$2\mathrm{M}^{3+} + 2e^- \leftrightarrow 2\mathrm{M}^{2+} \quad (2)$$

$$2M^{2+} + \mathrm{Sb}^{5+} \rightarrow 2\mathrm{M}^{3+} + \mathrm{Sb}^{3+} \quad (3)$$

$$\mathrm{Sb}^{3+} + \tfrac{1}{2}\mathrm{O}_2 \rightarrow \mathrm{Sb}^{5+} + \mathrm{O}^{2-}. \quad (4)$$

A reasonable measure of the electronic factor for different cations is the electrochemical potential E_0 of these cations and, in particular, the values for reaction (2). Their absolute values are not important for the purposes of this discussion, but their order and relative positions are applicable.

Since reducing Al^{3+} is very difficult, it seems reasonable to assume that its E_0 for a one-electron transfer would also be strongly negative (corresponding to difficult reduction). At the other extreme, the value for Rh^{3+} would be expected to be strongly positive (difficult reoxidation). In both cases, a catalytic cycle involving oxidation and reduction would be quite difficult. The maximum reactivity may be expected to occur around an E_0 value near zero, allowing easy electron transfer in either direction.

A second requirement for the overall reaction to proceed is that electron transfer from a transition metal cation to a nontransition metal cation should be energetically facile (reaction (3)). These conditions are only satisfied by the couple Fe–Sb. Aluminum fails this test because reaction (2) is more likely to occur with $\mathrm{M}^{3+} = \mathrm{Sb}^{3+}$ rather than Al^{3+}. In fact, taking into account the differences in surface area, all the aluminum antimonate activity toward butadiene can be attributed to Sb cations. In the case of Cr, the redox potential is such that its oxidation (step (3)) requires more energy than the one provided by the reduction of antimony. As presented in Table 7, the Cr-impregnated samples were very active but unselective. The consumption of most of the oxygen in the olefin reaction indicates that chromium is able to be reoxidized by gas phase oxygen, carrying the reaction all the way to carbon oxides. When chromium antimonate was impregnated with iron, an active, intermediate selective catalyst resulted. The XPS metallic surface composition gave a ratio Sb : Fe : Cr = 3.8 : 2 : 1 (*1*). Thus, only part of the butadiene produced on the iron could be further oxidized by Cr, resulting in an intermediate selectivity of 56%.

Cobalt antimonate, a trirutile structure with layered order, has Co cations already in the 2+ oxidation state. No evidence was found in the XPS analysis of the post-run samples of either Co^{3+} or Co^{0} oxidation states. Therefore, it must be antimony the replaces M^{3+} in reaction (2). As in the case of rhodium, the lower oxidation state is more stable and reoxidation similar to step (3) is not possible. However, Co and Rh antimonates were the most active catalysts for CO oxidation.

When cations with higher redox potential are available, as in Co and Rh, reoxidation of these sites by gas phase oxygen is feasible even in the olefin reaction. An alternative reaction mechanism must be used to explain the product distribution (*12*), but it is evident that the structure is no longer an important factor in providing a framework for oxygen supply.

5. CONCLUSIONS

A series of antimonate catalysts with tetragonal crystalline structure were studied in an isothermal tubular flow reactor for the selective oxidative dehydrogenation of 1-butene and oxidation of carbon monoxide by properly selecting the operating conditions.

Trends in activity for both reactions with varying catalyst composition run approximately parallel in (tri)rutile systems containing Sb as one of their components, which suggests that both reactions occur on the same site.

An ensemble model, modified for oxides, was used to explain the geometric effect in isostructural rutile-type antimonates. Within this model, antimony may have two functions: to limit the size of the active oxygen ensemble and to adsorb O_2.

The selectivity of 1-butene toward butadiene was connected with the simultaneous presence of different cations in the $MSbO_4$-type series studied. A correlation was found using the electrochemical potential as a guiding reference for the electronic effect of the elements involved.

The activity for butadiene formation was located on M, with Fe being the most effective. It was found also that the binary oxide $FeSbO_4$ was more active and selective than the individual components, i.e., Fe_2O_3 or Sb_2O_4.

For the Fe–Sb pair, the richer the surface in Sb, the more selective and less active was the catalyst. Also, $FeSbO_4$ was the only system that showed a partial reduction of antimony, as Sb^{3+}, in the spent samples.

$CoSb_2O_6$ and $RhSbO_4$ seemed to operate with a different reaction mechanism for both reactions investigated.

REFERENCES

1. Straguzzi, G. I., Bischoff, K. B., Koch, T. A., and Schuit, G. C. A., *J. Catal.* **103,** 357 (1987).
2. Berry, F. J., and Brett, M. E., *J. Catal.* **88,** 232 (1984).
3. Adams, C. R., and Jennings, T., *J. Catal.* **2,** 62 (1963).
4. Sachtler, W. M. H., and de Boer, N. H., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964," Vol. 1, p. 252. Wiley, New York, 1965.
5. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* (*Spec. Suppl.*) **3,** 41 (1954).
6. Fattore, V., Fuhrman, Z. A., Manara, G., and Notari, B., *J. Catal.* **37,** 223 (1975).
7. Urlich, F. J., Kriegsmann, H., Ohlmann, G., and Scheve, J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976," Vol. 2, p. 836. Chem. Soc., London, 1976.
8. Aso, I., Furukawa, S., Yamazoe, N., and Seiyama, T., *J. Catal.* **64,** 29 (1980).
9. Aso, I., Yamazoe, N., Amamoto, T., and Seiyama, T., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980." Elsevier, Amsterdam/New York, 1981.
10. Burriesci, N., Garbassi, F., Petrera, M., and Petrini, G., *J. Chem. Soc., Faraday Trans. I* **78,** 817 (1982).
11. Trifiro, F., Carbucicchio, M., and Centi, G., *J. Catal.* **91,** 85 (1985).
12. Straguzzi, G. I., Bischoff, K. B., Koch, T. A., and Schuit, G. C. A., **25,** 257 (1986).
13. Ponec, V., and Sachtler, W. M. H., *in* "Proceedings, 5th International Congress on Catalysis, Palm Beach, 172," p. 645. North-Holland, Amsterdam, 1973.
14. Sachtler, W. M. H., Ponec, V., and Stephen, J. J., *Surf. Sci.* **47,** 403 (1975).
15. Schaik, J. R. H., van, Dressing, R. P., and Ponec, V., *J. Catal.* **38,** 273 (1975).