J. Chem. Soc., Faraday Trans. 1, 1982, **78**, 485-494

Preparation, Characterization and Catalytic Activity of Uranium–Antimony Oxide for Selective Oxidation of Propene

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Received 17*th February*, 1981

The selective oxidation of propene to acrolein over USb_3O_{10} was studied in a continuous flow reactor. Our experimental results show that the preparation of a well-defined catalyst of uniform composition depends on the temperature and time of calcination. The kinetic data indicate that acrolein is formed *via* a redox mechanism in which the surface of the catalyst is partially reduced. Mössbauer spectroscopy reveals the presence of Sb^{5+} and Sb^{3+} in the used catalyst. I.r. spectroscopy shows a structural modification.

On the basis of these results we conclude that each steady-state condition is characterized by a vacancy concentration leading to the observed modifications of the catalyst.

Catalysts based on the uranium–antimony oxide system for oxidation or ammoxidation of alkenes are of industrial interest. Fundamental studies on the nature of the catalyst and its behaviour in reaction media are often contradictory or incomplete. It is very difficult to obtain USb_3O_{10} in its pure form. Current processes lead to a heterogeneous compound in which USb_3O_{10} is the major component.[1-3] The physicochemical properties of this catalyst are not well-defined: a previous magnetic study is incomplete[2] and the Mössbauer parameters found by Evans[4] and Birchall[5] are different. For the selective oxidation of propene to acrolein, redox[1,6] and hydroperoxide[7] mechanisms have been propounded. Furthermore, there has so far been no kinetic study using a flow reactor. The aim of the present work is to obtain the catalyst in its pure form, to characterize it before and after the catalytic reaction and to determine the kinetic parameters. This will permit a clarification of the above-mentioned incomplete or controversial issues and a discussion in terms of the reaction mechanism.

EXPERIMENTAL

CATALYST

The reaction of NH_4OH (28%) with a mixture of $UO_2(CH_3COO)_2$, $2H_2O$ and Sb_2O_3 (atomic ratio U/Sb = $\frac{1}{3}$) in concentrated HCl (37%) causes the precursor of the catalyst to be precipitated. The slurry was filtered and the solid was washed with water and dried at 110 °C. Thermal treatment of the precursor under the conditions defined in the results section leads to the catalyst.

PHYSICOCHEMICAL CHARACTERIZATION

The homogeneity and atomic ratio, U/Sb, of the catalyst were determined by electron microprobe analysis (Cameca M.S. 46.)

TEXTURAL CHARACTERIZATION

Pore-size radii and B.E.T. surface area were obtained from a nitrogen adsorption–desorption isotherm at 77 K on a Carlo Erba Sorptomatic instrument. Scanning electron micrographs were obtained with a Stereoscan mark 2 A electron microscope.

STRUCTURAL CHARACTERIZATION

High temperature X-ray diffraction patterns were obtained using a Guinier Lenne camera using Cu K_α radiation in the range 20-1000 °C using variable programs. The infrared experiments used a Beckman I.R. 12 spectrometer in the range 250-4000 cm^{-1}. The samples were examined either in KBr pellets or in a laboratory cell under catalysis conditions, the catalyst being deposited on a AgCl disc.

A description of the i.r. cell has been given in a previous communication.[8]

The oxidation states of uranium and antimony were determined by magnetochemistry and by Mössbauer spectroscopy, respectively. Thermomagnetic studies by the Faraday method were carried out in the range 4.2-673 K. The Mössbauer spectra were recorded and analysed[9] at C.E.N., courtesy of Mr Friedt: the samples contained 10 mg Sb cm^{-2}. The source $^{121}Ca^{m}$ SnO_3 (660 νCi) and the absorbant were maintained at 4.2 K. All isomer shifts are reported with respect to this source.

CATALYTIC CHARACTERIZATION

The differential kinetic measurements were obtained using a conventional Pyrex reactor. The gases were Air Liquide grade (He, O_2, C_3H_6). An Intersmat IGC 15 gas chromatograph using a Porapak Q column provided product analysis. All the experiments were carried out in the temperature range 300-380 °C, with a total flow of 200 cm^3 min^{-1} (s.t.p.) over the catalyst.

RESULTS AND DISCUSSION

PREPARATION OF USb_3O_{10}

To obtain USb_3O_{10} requires the use of a precise temperature and time of treatment. The best technique permitting continuous monitoring of the structural modifications is the Guinier Lenne camera. Fig. 1 shows the precursor evolution as a function of

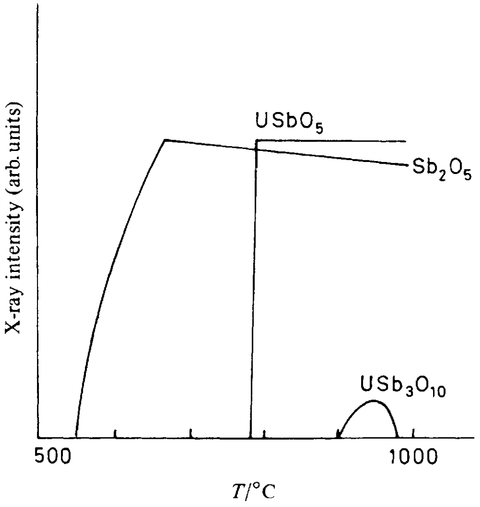

FIG. 1.—Precursor evolution in the range 500-1000 °C.

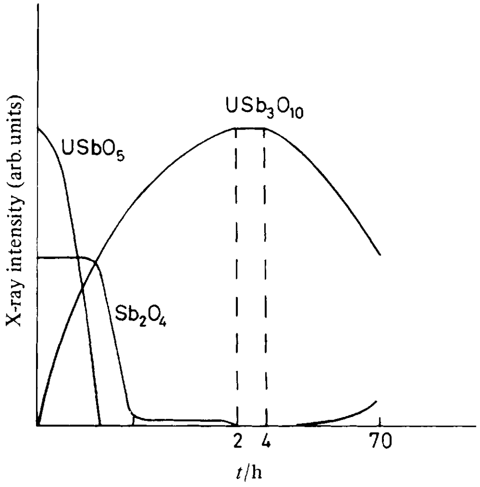

FIG. 2.—Precursor evolution at 900 °C.

the temperature. Under these conditions, it is not possible to obtain pure USb_3O_{10}. This phase appears only in small quantities in the range 900-980 °C, the decomposition of the precursor leading to $USbO_5$ and to an isomorphous phase of Sb_2O_5. To enhance the formation of USb_3O_{10}, the thermal treatment is carried out at 900 °C. The influence of the time of treatment is shown in fig. 2. USb_3O_{10} is formed between two and four hours after reaching 900 °C. After 4 h, USb_3O_{10} is decomposed. The synthesis of USb_3O_{10} under these conditions is the result of the reaction between $USbO_5$, Sb_2O_4 and O_2. The narrow domain of stability of the phase USb_3O_{10} explains the heterogeneity of the compound obtained by most investigators.

CHARACTERIZATION OF USb_3O_{10}

The compounds obtained between two and four hours are the subject of electron microprobe studies. The distribution of U and Sb is homogeneous regardless of the origin of the sample (plate 1). The distribution histograms of U/Sb are always Gaussian (fig. 3). The experimental normal standard deviations are, respectively, 0.15 and 0.12.

The value closer to the theoretical value of 0.11[10] corresponds to the compound heated for four hours in air at 900 °C. This compound was considered as the catalyst. All physicochemical analyses were performed on this product (experimental mean value of U/Sb = 0.34; X-ray diffraction pattern similar to those of Grasselli[11] and Aykan[2]).

The specific surface area of the catalyst is 7 $m^2\ g^{-1}$ and the adsorption–desorption

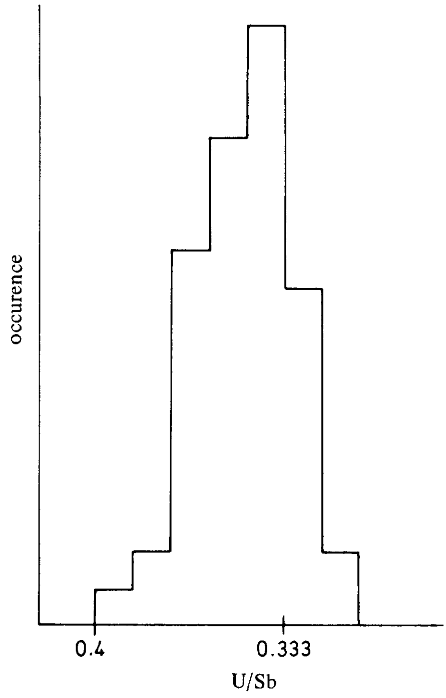

FIG. 3.—Histogram distribution of U/Sb in 'fresh' catalyst (4 h).

isotherm of N_2 (type II B.E.T. classification) allows the solid to be considered as macroporous. This is confirmed by a scanning electron micrograph (plate 2).

^{121}Sb Mössbauer data are summarized in table 1 and fig. 4(*a*).

Comparison with experimental data obtained for Sb_2O_3 and Sb_2O_4 clearly indicates that the antimony is in a pentavalent state in fresh USb_3O_{10}. The Mössbauer parameters for this compound confirm the conclusions of Sleight and Birchall.[5] Magnetochemistry studies show that USb_3O_{10} exhibits weak paramagnetism. The Curie–Weiss law is obeyed: $\chi_{Mc} = 2.66/(T+3.5)$. χ_{Mc} is the molar susceptibility and is corrected for the diamagnetic components Sb^{5+}: 17×10^{-6}; U^{5+}: 28×10^{-6}; O^{2-}: 12×10^{-6} u.e.m.; T is in K. The effective magnetic moment μ_{eff} has a value of 1.77 ± 0.04 μ_B (μ_B is the Bohr magneton). The only state of oxidation of antimony in USb_3O_{10} is Sb^{5+}; therefore, these species are diamagnetic and the paramagnetism

TABLE 1.—^{121}Sb MÖSSBAUER PARAMETERS AT 4.2 K

	quadrupole site				single line		
compound	TQ	SQ	e^2qQ	WQ	TSL	SSL	WSL
USb_3O_{10}[a]	—	—	—	—	0.283	0.659	3.10
USb_3O_{10}[b]	0.0174	−12.40	16.95	3.08	0.2419	0.631	3.08
Sb_2O_4	0.117	−14.12	16.46	3.12	0.127	0.98	3.12
Sb_2O_3	0.2216	−11.95	19.22	2.82	—	—	—

[a] Fresh catalyst; [b] used catalyst. TQ: quadrupole site intensity. SQ: isomer shift (mm s^{-1}). e^2qQ: quadrupole splitting (mm s^{-1}). WQ: width at half maximum (mm s^{-1}). TSL: single line intensity. SSL: isomer shift (mm s^{-1}). WSL: width at half maximum (mm s^{-1}).

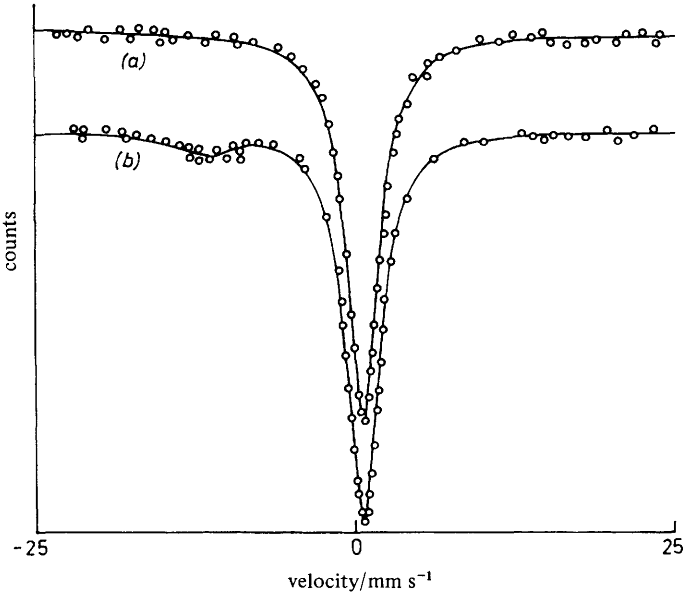

FIG. 4.—Mössbauer spectrum of USb_3O_{10}: (*a*) fresh catalyst, (*b*) used catalyst.

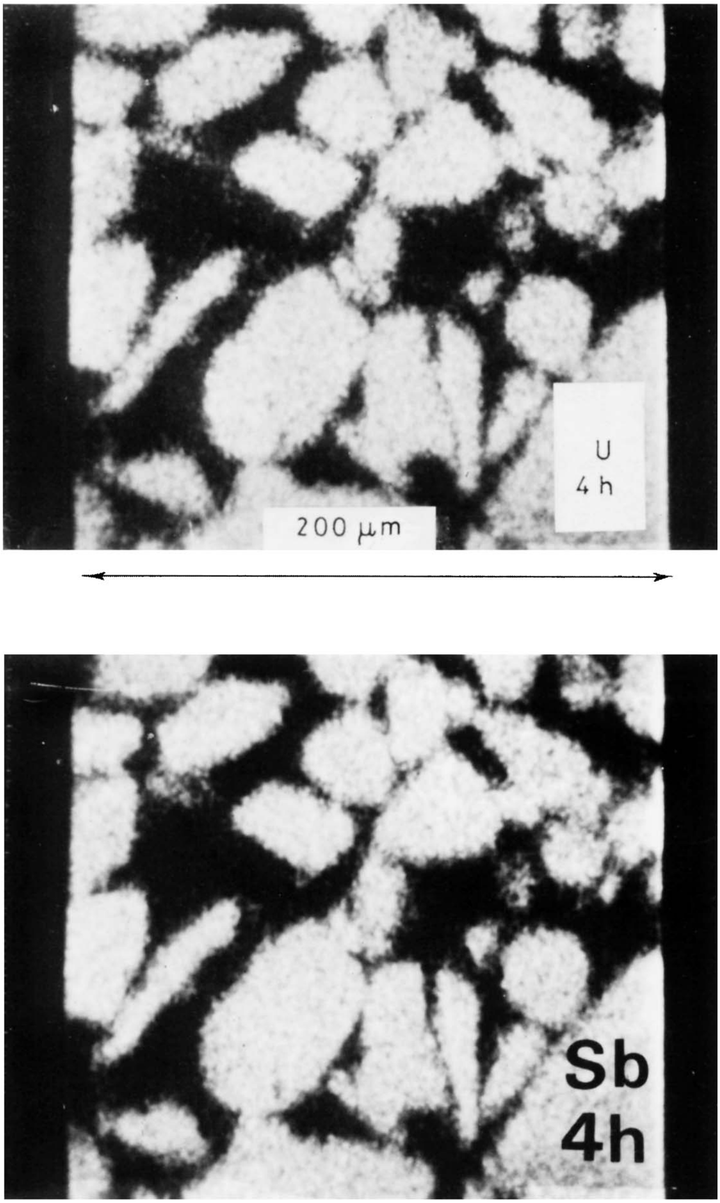

PLATE 1.—X-ray images of (*a*) U and (*b*) Sb in 'fresh' catalyst.

PLATE 2.—Scanning electron micrograph of USb_3O_{10} (magnification × 14000).

of the compound is related to the presence of uranium. The more probable oxidation state is U^{5+}. Two configurations are possible, either $5f^1$ or $6d^1$. In the case $5f^1$, the unpaired electron responsible for the paramagnetism is effectively screened from environmental effects by the overlying s and p electrons. The theoretical expression for the magnetic moment may be expressed by the relation: $\mu_{\text{theoretical}} = g\sqrt{[J(J+1)]} = 2.537\ \mu_B$, where g is the Landé factor and $J = 5/2$.

In the case of $6d^1$, the unpaired electron is on the external level and crystal-field theory involves no orbital contribution. The theoretical expression of the magnetic moment becomes $\mu_{\text{th.}} = \mu_{\text{spin}} = 2\sqrt{[S(S+1)]}$ where $S = 1/2$ and $\mu_{\text{th.}} = 1.732\mu_B$. This value is in good agreement with the experimental value.

In conclusion, the conditions required to obtain a well defined homogeneous catalyst are described above. The mixed oxide presents the X-ray diffraction pattern of USb_3O_{10}, its uniform composition being proved by the electron microprobe study. Moreover, the present work shows that the oxidation states for the two elements U and Sb of the compound are 5+. Note that, in previous studies, every preparation led to mixtures of oxides: USb_3O_{10}–Sb_2O_5,[2] USb_3O_{10}–Sb_2O_4,[3] USb_3O_{10}–Sb_6O_{13}[3] or USb_3O_{10}–$USbO_5$.[1] Only Grasselli postulated the preparation of pure USb_3O_{10} by dissolving the excess antimony oxide from a U–Sb oxide with a high antimony content (U/Sb = 1/9.2) in HCl: this oxide had only been tested as catalyst in the selective ammoxidation of propene.[1]

CATALYTIC ACTIVITY OF USb_3O_{10}

The dependence of the specific area rates of reaction on oxygen and propene partial pressures was examined at 340 °C in the range of $0.266 \leqslant P_{O_2}/\text{atm} \leqslant 0.8$ and $0.133 \leqslant P_{C_3H_6}/\text{atm} \leqslant 0.400$. The results for acrolein formation are presented in fig. 5 and 6.

The relationship between the observed laws and the general laws of a redox reaction is evident. In the concept of a redox cycle[12] the rate of reduction of the catalyst can be written:

$$-\frac{d[C_3H_6]}{dt} = k_{C_3H_6}\, P^{\alpha}_{C_3H_6}\, \theta_{ox}$$

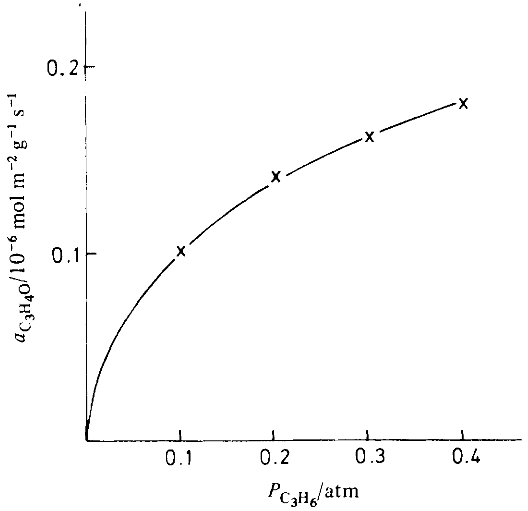

FIG. 5.—Influence of propene partial pressure at 340 °C with $P_{O_2} = 0.5$ atm.

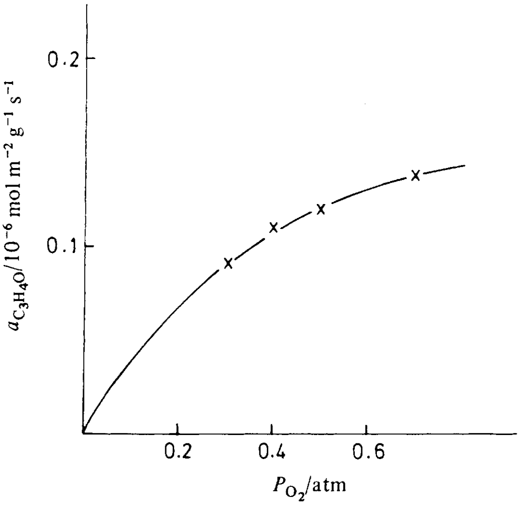

FIG. 6.—Influence of oxygen partial pressure at 340 °C with $P_{C_3H_6} = 0.2$ atm.

where $k_{C_3H_6}$ is the rate constant for catalyst reduction, α is the reaction order of propene for catalyst reduction and θ_{ox} is the fraction of sites oxidized. The rate of reoxidation can be written:

$$-\frac{d[O_2]}{dt} = k_{O_2} P^{\beta}_{O_2} \theta_{red}$$

where k_{O_2} is the rate constant for catalyst oxidation, β is the reaction order of oxygen for catalyst oxidation and θ_{red} is the fraction of sites reduced ($\theta_{ox}+\theta_{red} = 1$). At steady state the rate of catalyst reduction is equal to the rate of catalyst reoxidation:

$$-\frac{d[C_3H_6]}{dt} = -\frac{d[O_2]}{dt} = v$$

$$v = k_{O_2} P^{\beta}_{O_2} \left(1 - \frac{v}{k_{C_3H_6} P^{\alpha}_{C_3H_6}}\right)$$

$$\frac{1}{v} = \frac{1}{k_{O_2} P^{\beta}_{O_2}} + \frac{1}{kC_3H_6 P^{\alpha}_{C_3H_6}}$$

where v is the rate of catalytic reaction. Our experimental results obey this law with $\alpha = \beta = 1$ (fig. 7 and 8). The rate constants are summarized in table 2. Good

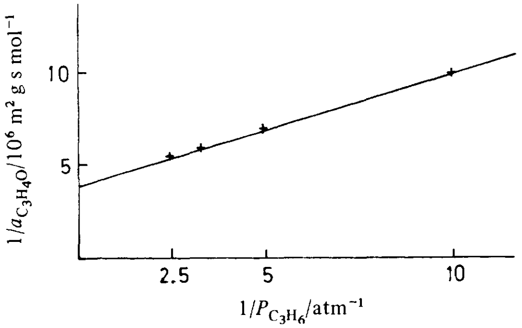

FIG. 7.—Linear form of the rate equation ($P_{O_2} = 0.5$ atm).

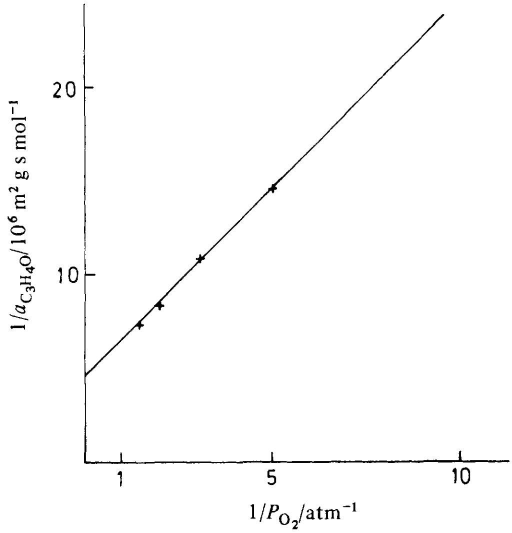

FIG. 8.—Linear form of the rate equation ($P_{C_3H_6} = 0.2$ atm).

TABLE 2.—RATE CONSTANTS FOR REDUCTION AND OXIDATION OF THE CATALYST

	$k_{C_3H_6}$ /10^{-6} mol g^{-1} m^{-2} s^{-1}	k_{O_2} /10^{-6} mol g^{-1} m^{-2} s^{-1}
$P_{O_2} = 0.5$ atm	1.65	0.50
$P_{C_3H_6} = 0.2$ atm	1.16	0.50

TABLE 3.—PROPORTION OF OXIDIZED ACTIVE SITES AGAINST P_{O_2} AND $P_{C_3H_6}$

	$P_{C_3H_6}$/atm		
P_{O_2}/atm	0.100	0.200	0.400
0.266	—	36.4%	—
0.500	60.0%	—	27.5%
0.800	—	63.3%	—

agreement between these constants is observed. The calculations of the fraction of sites oxidized (table 3) are performed with the assumption that k_{O_2} and $k_{C_3H_6}$ remain constant in the range of pressures considered.

The observed kinetics is a composite of reduction and reoxidation of USb_3O_{10}, the sites being neither fully oxidized nor fully reduced.

The Arrhenius plots for the formation of acrolein show that the activation energies (table 4) remain approximately constant regardless of the value of the partial pressure.

TABLE 4.—APPARENT ACTIVATION ENERGY AGAINST PARTIAL PRESSURES

$P_{C_3H_6}$ /atm	P_{O_2} /atm	E_a /kcal mol^{-1}
0.133	0.666	18.6
0.133	0.4	19.8
0.4	0.4	17.2

These values are in agreement with the generally observed values in the case of the selective allylic oxidation of propene.[13]

The influence of temperature and partial pressures P_{O_2} and $P_{C_3H_6}$ on the selectivity for acrolein formation is in accord with the classical laws. This selectivity increases with $P_{C_3H_6}$ and decreases with T and P_{O_2} (table 5). These variations are weak.

It is difficult to make direct comparisons with previous results because of the use of catalysts different from USb_3O_{10}: a 70% $USb_{4,6}O_{13,2}$, 30% SiO_2 catalyst for Grasselli[1] and a compound defined by the ratio U/Sb = $\frac{1}{4}$ for Pendleton.[6] Moreover, no authors determined kinetic parameters (rate constants and selectivity).

TABLE 5.—SELECTIVITY FOR ACROLEIN

T = 340 °C P_{O_2} = 0.5 atm		T = 340 °C $P_{C_3H_6}$ = 0.2 atm		P_{O_2} = 0.4 atm $P_{C_3H_6}$ = 0.133 atm	
$P_{C_3H_6}$/atm	$S_{C_3H_4O}$ (%)	P_{O_2}/atm	$S_{C_3H_4O}$ (%)	T/°C	$S_{C_2H_4O}$ (%)
0.1	89.9	0.1	96.7	300	94.5
0.2	90.2	0.2	92.6	340	91.0
0.3	91.5	0.3	90.5	380	90.0
0.4	92.5	0.4	90		
—	—	0.5	89.9		

After the catalytic tests, physicochemical analyses were carried out in order to investigate the modifications of the catalyst. Whereas X-ray spectra, magnetic susceptibility, histograms of the used catalyst and scanning electron micrographs remain unchanged, the i.r. and Mössbauer spectra exhibit modifications relative to the spectra of the fresh catalyst. These modifications are detected whatever the experimental conditions. The i.r. spectrum shows a weak band at 640 cm^{-1} and a broad shoulder at 1050 cm^{-1} (fig. 9). These modifications are irreversible even after oxygen treatment ($P_{O_2} = 1$ atm, $T \geqslant 340$ °C).

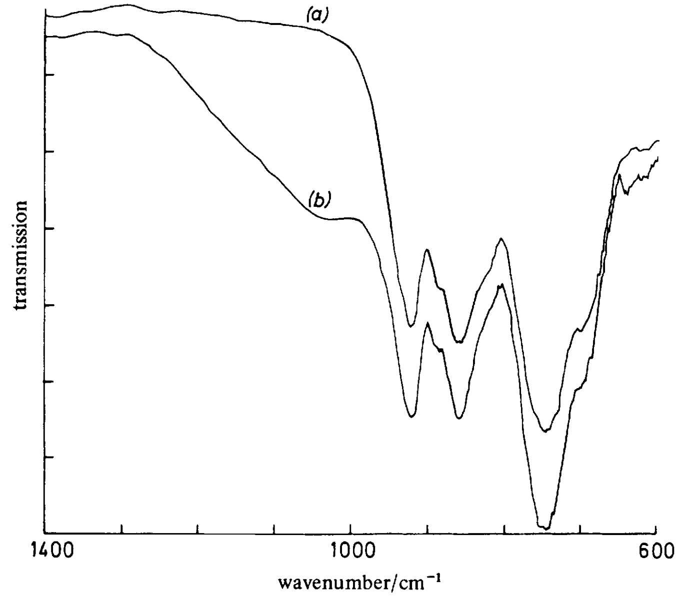

FIG. 9.—I.r. spectra of USb_3O_{10}: (*a*) 'fresh' catalyst, (*b*) 'used' catalyst.

Fig. 4 shows Mössbauer spectra for USb_3O_{10} before and after catalysis. It can be seen that, as a consequence of the interaction with reactant mixtures, the shape of the curve changes and a new absorption peak is detectable.

Assuming that the structure of USb_3O_{10} is similar to the model which has been presented by Grasselli[1] and confirmed by Aykan,[2] structural modification of the solid during the catalysis may be related to the mobility of O_{IV} (Grasselli's terminology). If oxygen vacancies exist when working, they involve modifications of the cationic oxidation state and of the structural state. These evolutions are characterized by i.r. and Mössbauer spectroscopies. Comparison with standard i.r. spectra of uranium oxides, antimony oxides and $USbO_5$ allows the formulation of two hypotheses for the attribution of the two new i.r. absorptions. In the first case, these bands at 1050 and 640 cm^{-1} may be characteristic of vibrations ν_{U-O} and ν_{Sb-O}, respectively, in $USbO_5$. Nevertheless, the absence of a band at 800 cm^{-1}, which is very strong in $USbO_5$, does not confirm this hypothesis. In the second case, we can attribute the band at 640 cm^{-1} to a vibration Sb—O in Sb_2O_4.[14] Mössbauer parameters for the used catalyst indicate the presence of Sb^{3+} and Sb^{5+} (table 1); the values for Sb^{3+} allow us to postulate that this species is in an environment similar to that of Sb^{3+} in Sb_2O_4. Unfortunately the band at 1050 cm^{-1} is not characterized and only UO_2 presents such an absorption in this spectral range. Absence of magnetic susceptibility changes of the 'used' oxide in comparison with the 'fresh' catalyst does not allow confirmation of the presence of UO_2 in the catalyst during the reaction. We propose that a new compound is formed during the catalytic reaction, resulting from a structural change in USb_3O_{10} by O_{IV} departure. Comparison of the electron scanning micrographs of the used and fresh catalysts allows us to affirm that this degradation is not related to a thermal phenomenon, sintering of the samples never being observed.

Two types of mechanisms have been proposed for the selective oxidation of propene on U–Sb–O catalysts. Grasselli[1] and Pendleton[6] proposed a redox mechanism. Pendleton proposed that the lattice is the only direct source of oxygen in acrolein formation. This conclusion is based upon studies of propene oxidation in the presence of $^{18}O_2$. Keulks[7] proposed a hydroperoxide mechanism, this hypothesis being based on the one hand on the low percentage of lattice O^{2-} participating in the product formation (6%) and on the other hand on the fact that he did not detect any changes in the i.r. spectra of the catalyst after reaction ($C_3H_6 + {}^{18}O_2$) in a recirculation reactor.

For our experimental conditions, the hypothesis of a hydroperoxide intermediate is not very probable. Indeed we do not detect any propene oxide in the reaction products. On the other hand the catalytic performances observed in previous microreactor experiments[15] showed the participation of lattice oxygen in the formation of acrolein: the diffusion involves only a part of the O^{2-} layers of the lattice. This participation increases with the temperature. Moreover this paper deals with evolution of the solid and kinetic results, in good agreement with the general redox mechanism. Grasselli[1] proposed that catalyst behaviour is a function of its oxidation state. This information, obtained by a pulse microreactor study, did not allow the characterization of any structural modification. Our study, as distinct from former work, has been carried out with a well-defined phase initially corresponding to USb_3O_{10}. In other respects, it follows the redox cycle. The initial compound evolves during the reaction; some of the Sb^{5+} ions are reduced to Sb^{3+} ions and a part of the lattice is irreversibly destroyed. The reaction process may be explained as follows. First, we consider the first hydrogen abstraction as formation of an allylic complex on the antimony active centre.[13] The second step of the reaction is the second hydrogen abstraction followed by desorption of acrolein with removal of lattice oxygen. The last step of the cycle is the catalyst reoxidation which may be shown as:

In view of this mechanism, the rate constants involve a catalyst in a partially reduced state during the catalysis. Under steady-state conditions, each reactant mixture produces a given vacancy concentration in the underlayers of the oxide. These vacancy concentrations lead to the observed structural modifications, probably due to distortion of the initial unit cell.

We thank J. M. Friedt, Centre de Recherches Nucléaires, Strasbourg, for performing all Mössbauer experiments.

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(PAPER 1/273)