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Studies of Propene Oxidation over Mixed Uranium–Antimony Oxides

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Kinetic studies of the oxidation of propene over a uranium–antimony mixed oxide catalyst (U:Sb = 1:3), together with measurements of the a.c. electrical conductivity of the catalyst, have discriminated between some steps in the redox mechanism. Reduction of the catalyst (activation energy 50 ± 10 kJ mol^{-1}) and desorption of products are accompanied by increases in conductivity, although the initial adsorption of propene has the opposite effect. The conductivity decreases when the reduced catalyst is reoxidised (activation energy 180 ± 10 kJ mol^{-1}). Under reaction conditions, the overall rate is controlled by the production of labile oxygen species at the surface (activation energy 80 ± 1 kJ mol^{-1}).

Catalysts containing mixed oxides of uranium and antimony (denoted U–Sb–O) are known to be active and selective in the oxidation and ammoxidation of alkenes, aromatic hydrocarbons and alcohols.[1–4] With the U–Sb–O system it has been suggested that optimum catalytic efficiency coincides with the maximum concentration of USb_3O_{10}.[5, 6] Higher activities and good selectivities can, however, be achieved in the presence of other metal oxides.[7]

The method of preparation can affect the composition and hence the performance of U–Sb–O catalysts.[6, 8] Evidence has been obtained[9] which suggests that this is due to alterations which are brought about in the defect structure of the U–Sb–O system. Indeed, it has been postulated[7] that the promotion of these catalysts by Ti^{4+} and Zr^{4+} is due to the ready replacement of some Sb^{5+} ions in USb_3O_{10} with such ions, leading to the generation of oxygen vacancies.

In the present work, kinetic studies have been carried out on the oxidation of propene over U–Sb–O catalysts prepared by a standard method. Combined with observations of electrical conductivity, these studies have established a relationship between the defect structure of a catalyst and its performance during propene oxidation.

Experimental

Materials

The uranium–antimony oxide catalyst (U:Sb = 1:3, surface area 2.8 m^2 g^{-1}) was prepared from AnalaR antimony(III) oxide and uranium(VI) dinitrate dioxide hexahydrate (B.D.H. Chemicals Ltd) according to the method of Grasselli and Callahan.[10] It was shown to consist mainly of USb_3O_{10} with relatively small amounts of $USbO_5$ and Sb_2O_4. Propene (Cambrian Chemicals, purity 99.5%), ethene (99.8%) and carbon monoxide

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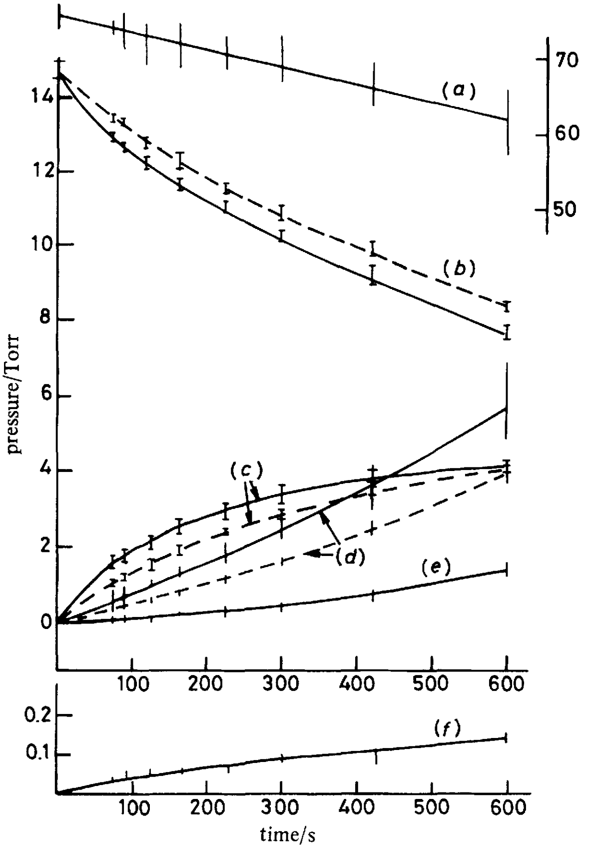

Fig. 1. Oxidation of propene over 0.8 g U–Sb–O catalyst at 654 K, changes in concentrations of reactants and products with time: (*a*) oxygen, (*b*) propene, (*c*) acrolein, (d) carbon dioxide, (*e*) carbon monoxide and (*f*) ethene; (——) catalyst oxidised before each run; (– – –) catalyst evacuated before each run.

(99%, B.D.H. Chemicals Ltd), carbon dioxide and oxygen (B.O.C.) were condensed at 77 K and the middle fractions used. Acrolein (Aldrich Chemical Co. Ltd, 99%) was used without further purification.

Apparatus

The techniques used to study the physicochemical properties (electrical conductivity, thermal behaviour *etc.*) of the uranium and antimony oxides and the binary U–Sb–O system have been described in earlier publications.[9, 11, 12]

Catalytic Properties

Propene oxidation was studied using a conventional static gas-handling system which could be evacuated to *ca.* 5×10^{-4} Torr.† A pressure transducer (SE Laboratories type 180N, 5 pounds per square inch differential) was used to monitor reactants introduced into a vertical reactor (170 cm^3) containing catalyst and a conductivity probe.[12] The temperature of the reactor was automatically controlled to ±0.2 K. Reactions were

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† 1 Torr = 101 325/760 Pa.

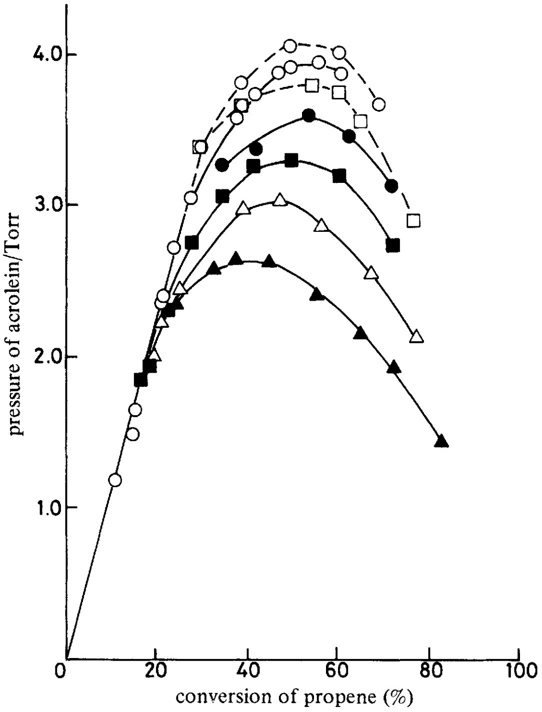

Fig. 2. Formation of acrolein from propene (initial pressure 15 Torr) and oxygen (initial pressure 75 Torr). ○, 652; ●, 675; □, 692; ■, 697; △, 706; ▲, 741 K; (——) 0.8 g catalyst; (– – –) 3.0 g catalyst.

followed by observation of changes in total pressure and by gas-chromatographic analysis. Perkin-Elmer F11 chromatographs with gas-sampling valves were used, with a Porapak T column and a flame ionisation detector for hydrocarbons, and with a silica gel column and a katharometer for oxygen and carbon oxides.

Fresh catalysts were 'conditioned' by exposure to oxygen (24 h) followed by mixtures of propene and oxygen reacting to the extent that at least 55% of the propene was converted. Thereafter, in most kinetic experiments, the catalyst was evacuated (10^{-3} Torr, 300 s), further exposed to oxygen (75 Torr, 300 s) and finally re-evacuated (300 s) prior to each run. The temperatures at which successive experiments were carried out were varied randomly and the reproducibility of the results checked by repetition of certain experiments. As long as the catalyst was reoxidised between kinetic runs, catalytic activity and the yield of acrolein were maintained almost indefinitely. Omission of this step reduced reaction rates but had no effect on the selectivity of acrolein. However, after continuous operation (*ca.* 50 h) without intermittent reoxidation both catalytic activity and selectivity declined very rapidly. Limited deactivation could be reversed by heating in oxygen (90 Torr, 700 K, 12 h).

Results

Reaction Products

At 673 K, and for reaction times up to 300 s, oxidation of propene occurred only in the presence of the catalyst. For longer reaction times, however, traces of ethanol and acrolein, but no oxides of carbon, were detected for reactions in the absence of catalyst.

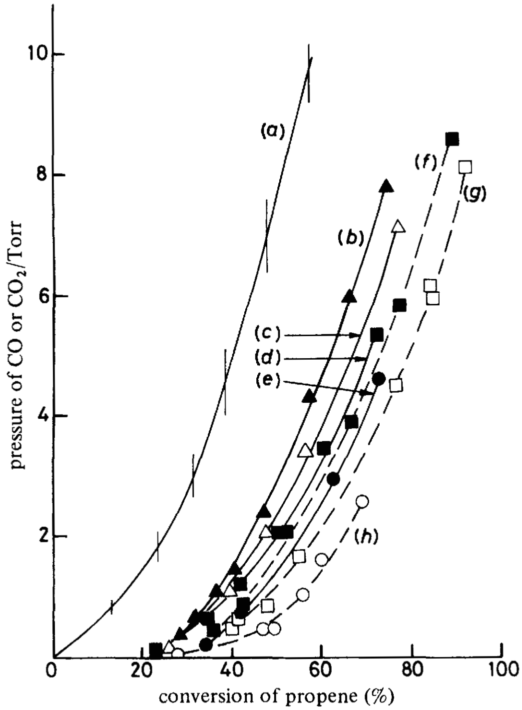

Fig. 3. Formation of oxides of carbon from propene (initial pressure 15 Torr) and oxygen (initial pressure 75 Torr); (*a*) carbon dioxide over 0.8 and 3.0 g of catalyst, 630–740 K; (*b*)–(*e*) (——) carbon monoxide over 0.8 g; (*f*)–(*h*) (– – –) carbon monoxide over 3.0 g; ○, 652; ●, 675; □, 680; ■, 697; △, 706; ▲, 725 K.

Kinetic measurements were made at temperatures between 628 and 741 K using either 0.8 or 3.0 g of catalyst. The reaction, marked by a progressive increase in pressure, was usually followed for 300 s, by which time at least 55% propene had been converted. Typical reactant/product *vs.* time profiles are given in fig. 1 for the oxidation of a 1:5 propene–oxygen mixture at 654 K. (In fig. 1 the error bars are derived from the scatter of data observed in the experiments.) The mean carbon mass balance for runs up to 50% propene conversion was 98.3% (standard deviation 1.1%). At higher conversions, the balances worsened considerably (91% at 70% conversion) and it is likely that some reaction products were not identified.

In all experiments carbon dioxide and acrolein were produced in measurable amounts from the start of reaction. The yield of carbon dioxide increased with increasing propene conversion and much larger amounts were formed from reaction mixtures containing acrolein in addition to the usual amounts of propene and oxygen. Thus, carbon dioxide was formed both directly from propene and by the further oxidation of acrolein. Over the temperature range studied, the yield of carbon dioxide was independent of temperature and of the mass of catalyst. The yield of acrolein at low conversions of propene was *ca.* 75% over both amounts of catalyst, and was independent of reaction temperature (fig. 2). The yield declined at propene conversions exceeding 20% (0.8 g) and 30% (3.0 g).

Carbon monoxide was not detected at propene conversions of <20% (fig. 3). Experiments with added acrolein confirmed that both carbon monoxide and ethylene (formed in small amounts) were secondary products. Slightly more carbon monoxide was produced over the smaller amount of catalyst, suggesting that its formation involved the homogeneous oxidation of acrolein.

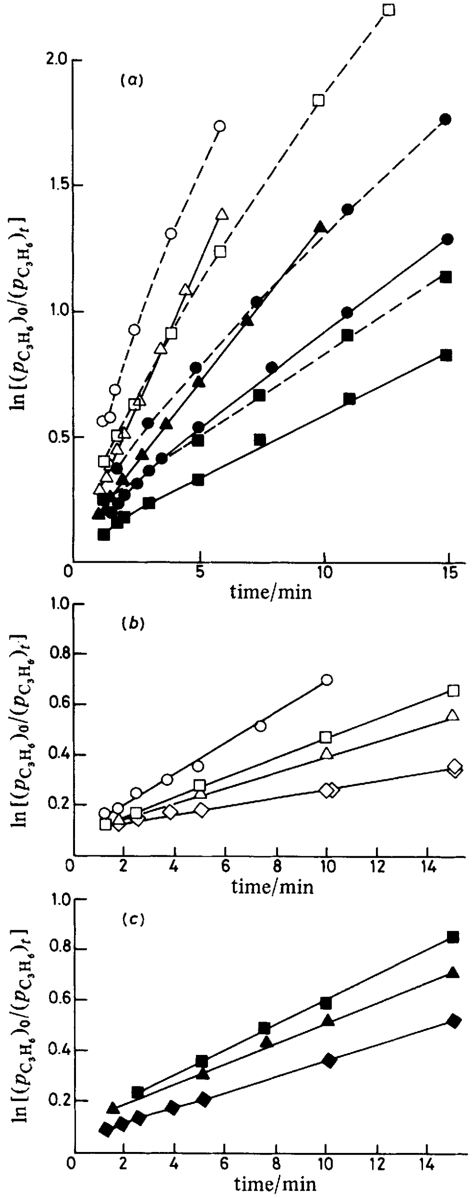

Fig. 4. Rates of conversion of propene. (*a*) Dependence on temperature, 0.8 g of catalyst (——) and 3.0 g of catalyst (– – –); initial pressures: propene 15.0 ± 0.2 Torr, oxygen 75 Torr; ■, 654; ●, 673; □, 692; ▲, 697; ○, 715; △, 725 K. (*b*) 622 K and (*c*) 666 K, dependence on partial pressure of oxygen; initial pressures: propene 15.0 ± 0.2 Torr, oxygen ○, 234; □, ■, 150; △, ▲, 120; ◇, ◆, 75 Torr.

Kinetics

The kinetic experiments showed that, when the catalyst was reoxidised between runs, plots of $\ln[(p_{C_3H_6})_i/(p_{C_3H_6})_t]$ against time (fig. 4) were usually linear after initial curvature. Curvature was more pronounced at lower temperatures and for the larger quantity of catalyst [fig. 4(*a*)]. From the initial slopes and the gradients (k_1) of the linear

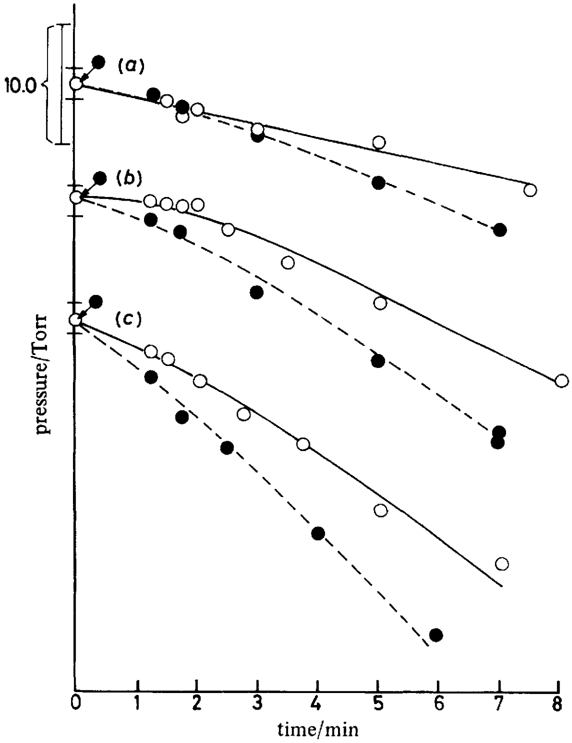

Fig. 5. Consumption of gaseous oxygen during the oxidation of propene (initial pressures: propene 14.8±0.2 Torr, oxygen 75.5±0.5 Torr) (——) 0.8 g catalyst, (---) 3.0 g catalyst; (*a*) 652, (*b*) 675 and (*c*) 700 K.

portions of the curves, activation energies for propene oxidation of 56±5 and 80±1 kJ mol^{-1} were obtained, respectively, for the initial and intermediate stages of reaction over both masses of catalyst. Experiments to assess the effect of oxygen partial pressure on propene oxidation were carried out at 622 and 666 K, with 0.8 g of catalyst and reaction mixtures containing 15 Torr propene and 75–234 Torr oxygen. Except for short reaction times (60 s), plots of ln (propene conversion) against time were linear [fig. 4(*b*) and (*c*)]. The specific reaction rate (taken as the slope of each plot) was proportional to oxygen pressure to the power 1.2±0.1 at 622 K and 0.6±0.2 at 666 K.

In individual kinetic runs, consumption of gaseous oxygen was slow initially, but increased to an approximately constant rate ($r = \Delta p_{O_2}/\Delta t$) at later stages (fig. 5). Gas-phase oxygen accounted for less than half of that incorporated in the products, a result which was confirmed qualitatively by observation of changes in total pressure. Arrhenius-type plots of ln (r) against $1/T$ yielded good straight lines, from which an activation energy of 180±10 kJ mol^{-1} was obtained over both amounts of catalyst.

Measurements of the initial rate of acrolein formation yielded an activation energy of 45±5 kJ mol^{-1}, again over both amounts of catalyst. Overall rate constants (k_2) for the consecutive reaction of acrolein were estimated on the assumption that this process followed first-order kinetics. Since the consumption of propene was first-order (except at early stages), values of k_2 were deduced from the maximum pressure of acrolein, p_A, and the corresponding pressure of propene, p_P. Thus

$$k_2 = k_1(p_P/p_A).$$

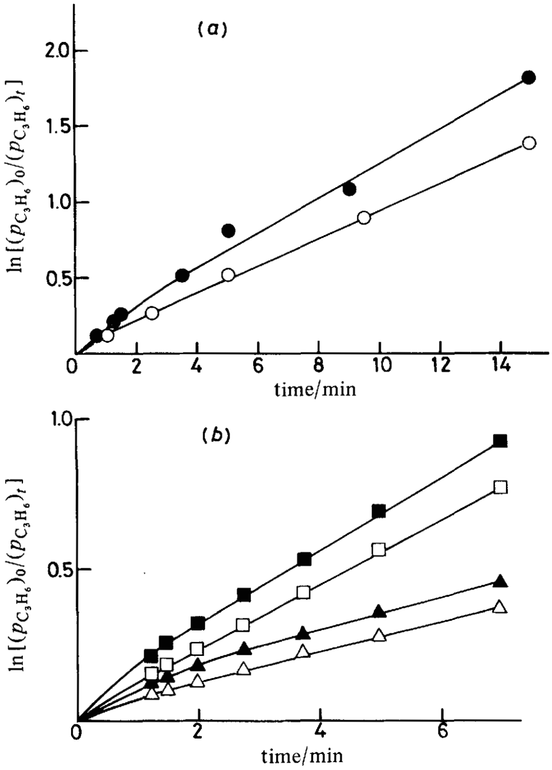

Fig. 6. Rates of conversion of propene over 0.8 g of catalyst, with reoxidation (closed points) and without reoxidation (open points) between kinetic runs; reaction mixtures containing propene (15 Torr) and oxygen (75 Torr); (*a*) first batch of catalyst, ○, ●, 670 K; (*b*) second batch of catalyst, △, ▲, 654; □, ■, 692 K.

Values of k_2 over 0.8 g of catalyst gave a linear Arrhenius plot and the activation energy was 131 ± 5 kJ mol^{-1}.

The treatment of the catalyst between kinetic runs affected to a certain extent the rates of both propene conversion and oxygen consumption. As an alternative to reoxidation between experiments, the catalyst was evacuated for at least 900 s, after which the new reaction mixture was admitted directly. The effect on propene conversion over separate batches of catalyst (0.8 g) is shown in fig. 6. Propene was always converted more rapidly over the catalyst pretreated with oxygen. Evacuation of the catalyst between experiments, without reoxidation, reduced reaction rate by a factor of *ca.* 1.5 at 670 K [fig. 6(*a*)]. At 692 K [fig. 6(*b*)], evacuation of the catalyst without reoxidation between runs reduced the initial rate of propene conversion by a factor of almost two, but at 654 K the effect was very much less. Experiments at 654 K also suggested that the period of evacuation might influence, albeit slightly, the rate and extent of reaction. At equivalent propene conversions, the consumption of gas-phase oxygen was found to be less for catalysts reoxidised between experiments. Finally, the formation of acrolein, CO and CO_2 was unaffected by the reconditioning procedures [fig. 7(*a*) and (*b*)]. In these experiments the yield of acrolein at low conversions was 77.2% (standard deviation 4.7%) over reoxidised catalyst and 76.4% (standard deviation 4.6%) without reoxidation.

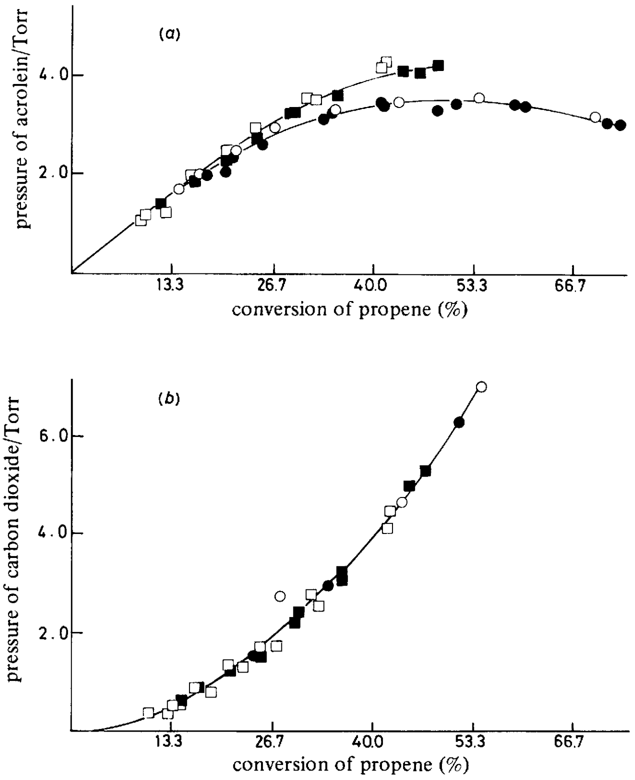

Fig. 7. Effects of catalyst pretreatment on the formation of major products: (*a*) acrolein, (*b*) carbon dioxide; closed points, catalyst reoxidised between runs; open points, catalyst evacuated between runs; □, ■, 654; ○, ●, 692 K.

A.C. Electrical Conductivity Measurements

Measurements of the electrical conductivity of the U–Sb–O catalyst have allowed interactions between the catalyst and certain gases and gas mixtures to be studied. Changes in conductance accompanying exposure of catalysts to gases such as nitrogen, hydrogen, carbon monoxide, propene *etc.* have been described qualitatively elsewhere,[9, 12] but certain important interactions will be described in greater detail below.

Interaction with Propene

Reaction mixtures consisting of propene (*ca.* 3 Torr) in nitrogen (total pressure 90 Torr) were allowed to react with 0.8 g catalyst at 673 K. A probe[12] inserted in the reactor allowed changes in the electrical conductivity of the catalyst to be monitored during reaction (see Experimental section). Before each series of runs the catalyst was exposed to oxygen for at least 12 h at the reaction temperature. Then the first run [curve (i), fig. 8(*a*)] resulted in a fairly rapid increase in conductance; after 60 s, the reaction mixture was pumped away for 300 s, giving a further small increase. When oxygen was admitted the conductance decreased, very rapidly at first but much more slowly thereafter. After 600 s the oxygen was pumped away and replaced by a further portion of reaction mixture. Both the magnitude and the rate of change in conductance were much greater for the first run in the series, (i), than in subsequent runs, (ii), (iii), *etc.* Further, the first run produced a continuous increase in conductance from the outset, whereas later runs

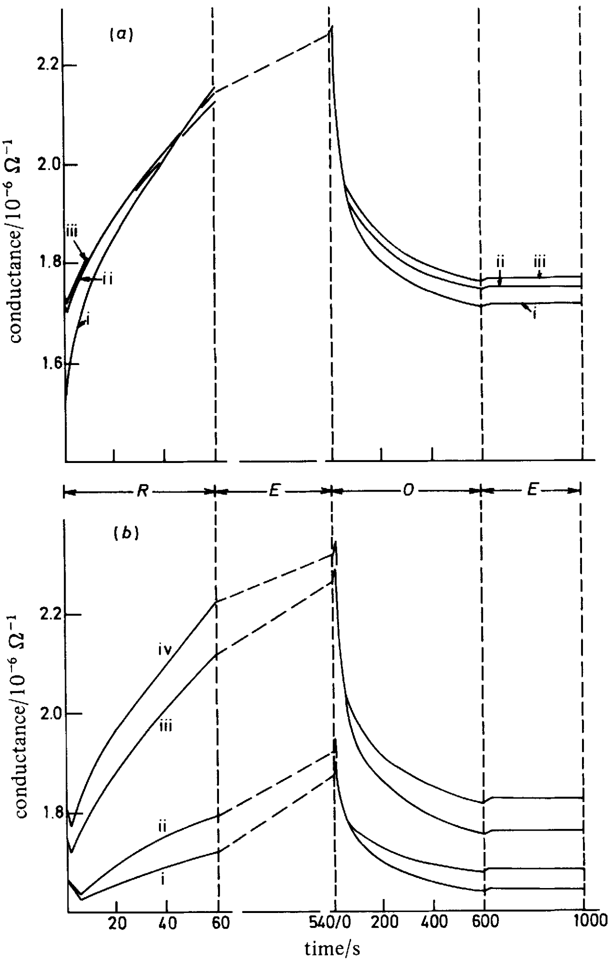

Fig. 8. Changes in electrical conductivity of the U–Sb–O catalyst at 673 K during reduction with propene and subsequent reoxidation (pressure of oxygen 75 Torr); R, reduction; E, evacuation; O, reoxidation. (*a*) Successive runs using mixtures containing propene (3 Torr) and nitrogen (87 Torr); (*b*) runs over conditioned catalyst using mixtures of propene in nitrogen, total pressure 90 Torr, propene pressures (i) 0.66, (ii) 1.3, (iii) 2.6 and (iv) 3.9 Torr.

showed a small initial fall followed by a continuous rise. After three runs followed by reoxidation, the initial value of the conductance was constant and considerably higher than that for the fully oxidised catalyst. Analytical studies and simultaneous measurements of the pressure rise showed that acrolein was the only carbon-containing product of reaction. The effects of varying the pressure of propene (0.7–3.9 Torr) are shown in fig. 8(*b*), in which each trace is for the catalyst conditioned by at least three similar runs. The difference in conductance between the fully oxidised and conditioned states of the catalyst was directly proportional to the initial pressure of propene. Then the rate of increase in conductance, immediately following the small initial decrease, corresponded with an order with respect to propene of *ca.* 1.5. In all experiments, exposure of the catalyst to oxygen after treatment with propene led to a rapid decrease in conductance. A plot of the initial rate of decrease against the total preceding increase in conductance yielded a straight line passing through the origin.

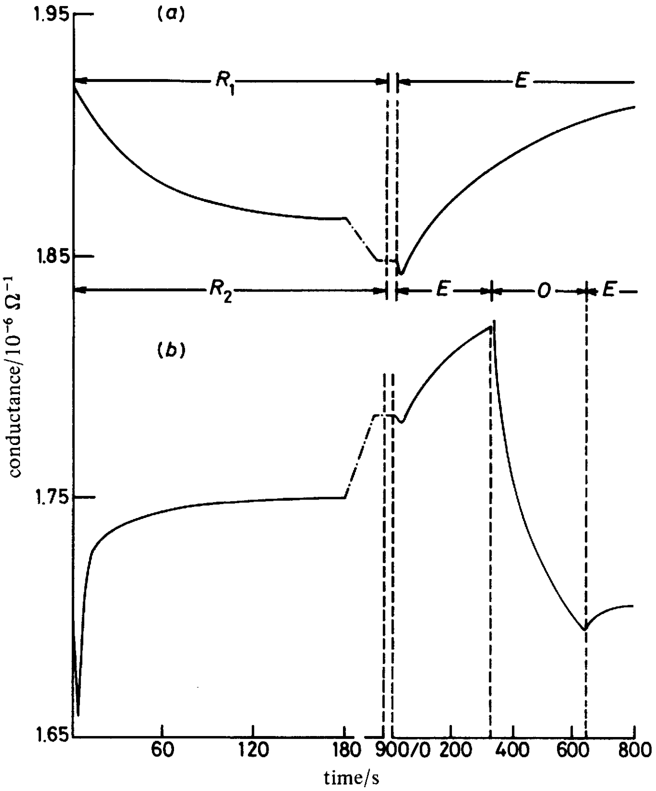

Fig. 9. Changes in electrical conductivity of the U–Sb–O catalyst at 673 K during interaction with propene–oxygen mixtures and subsequent treatment. (*a*) Catalyst evacuated without reoxidation between runs (R_1, 5 Torr propene + 25 Torr oxygen; E, evacuation). (*b*) Catalyst reoxidised between runs (R_2, 5 Torr propene + 15 Torr oxygen; E, evacuation; O, 75 Torr oxygen).

Interaction with Mixtures of Propene and Oxygen

Experiments were carried out to investigate variations in the electrical conductivity of catalyst (0.8 g) exposed to mixtures of propene with oxygen at 673 K, and the effects of the treatment of the catalyst between runs (fig. 9). When the catalyst was conditioned according to the standard procedure and reoxidised between experiments [curve (*b*)], admission of reaction mixture caused an initial decrease in conductance for *ca.* 5 s followed by a rapid increase over the following 15 s. The subsequent increase (over elapsed time 20–900 s) was very slow, but removal of the reactants and products by evacuation caused a larger increase. On exposing the catalyst to oxygen for 300 s, the value of the conductance returned to its pre-reaction level.

Opposite trends were observed for the same catalyst maintained under vacuum between kinetic runs [curve (*a*)]. In these experiments the conductance decreased relatively slowly throughout, and subsequent evacuation caused a similar gradual increase.

Discussion

Products and Yields

Under the conditions used in the present work, the oxidation of propene occurred exclusively by interaction with the U–Sb–O catalyst. Most of the acrolein formed was oxidised to carbon dioxide over the catalyst, but a small proportion underwent homogeneous oxidation to carbon monoxide.

Yields of acrolein (*ca.* 75% at 20% conversion, 623–733 K) were lower than in some previous studies. Delobel *et al.*[13] obtained acrolein yields of *ca.* 80% at 643 K from a pulse-flow reactor study of propene oxidation over a U–Sb–O catalyst (U:Sb = 1:4.6). With pure USb_3O_{10}, Baussart and coworkers[14] obtained 90–97% acrolein at 613 K; Keulks *et al.*[4] obtained 88–90% acrolein over the range 623–713 K for propene conversions <10%. The lower yield found in the present work is probably due to the small amount of $USbO_5$ (active in the total oxidation of propene[10]) contained in the catalyst. For propene conversions >30%, the decreasing yield of acrolein was due to its consecutive reactions.

Kinetics

Analytical data for the consumption of propene over the conditioned (partially oxidised) catalyst did not fit a simple rate expression but corresponded to an order of reaction tending towards 1.0. In contrast, consumption of gaseous oxygen was slow initially and the rate increased as reaction progressed. However, if the catalyst was not reoxidised beforehand, first-order kinetics were observed almost from the outset of each run, and gas-phase oxygen was consumed more rapidly. Under both regimes, even with the large excess of gaseous oxygen, a significant proportion of oxygen in the products originated from the catalyst. This is in agreement with the results of Pendleton and Taylor,[15] who found that initially *ca.* 90% of [^{16}O] acrolein was formed from the reaction of propene with $^{18}O_2$ over $USb_{4.6}O_x$. Our finding that the first-order rate constant for propene consumption increased with increasing oxygen concentration corresponds with the observations of Baussart *et al.*[14] for USb_3O_{10}. These authors proposed a simple model for the process which involves the establishment of an equilibrium between reduced and oxidised surface sites, with both reduction by propene and reoxidation by gaseous oxygen being first-order processes.

The present and previous results[9] are consistent with a mechanism which involves reaction between adsorbed propene and an active form of oxygen in the catalyst (denoted O*). The fully oxidised U–Sb–O catalyst contains a considerable amount of O*, or oxygen convertible to O*, and oxidation of propene over this catalyst is rapid initially but declines as O* is depleted. First-order kinetics correspond to the establishment of a constant surface concentration of O*, the rate of removal of which is then balanced by its replenishment from the gas phase and/or the bulk of the catalyst. Grasselli and Suresh[5] suggested that, prior to the surface reaction, propene is dissociatively adsorbed at unsaturated Sb^V ions forming π-allyl C_3H_5—Sb^V and U^V—OH. (Alternatively, π-allyl C_3H_5—Sb^{IV} and Sb^{III}—OH may be formed over antimonates.[16]) Then the π-allyl species loses a proton to a labile bridging oxide ion in the surface, forming adsorbed C_3H_4. Water is desorbed, leaving a reduced surface. Both metals are maintained in oxidation state (V) by electron-transfer processes, and two electrons are released into the crystal lattice. Subsequently the surface is reoxidised and adsorbed C_3H_4 reacts with the replaced labile oxygen, forming acrolein and releasing two more electrons. The mechanism may be summarised as

$$C_3H_6(g) + \square + O^* \rightarrow C_3H_4(ads) + H_2O(g) \tag{1}$$

$$C_3H_4(ads) + O^* \rightarrow C_3H_4O(ads) \tag{2}$$

$$C_3H_4O(ads) \rightleftharpoons C_3H_4O(g) + \square \tag{3}$$

$$C_3H_4O(ads) + n(O) \rightleftharpoons CO_2, H_2O + \square \tag{4}$$

$$\tfrac{1}{2}O_2(g) \rightleftharpoons O^* \tag{5}$$

$$O_L \rightleftharpoons O^*. \tag{6}$$

In the reactions above, □ represents a surface vacancy at which propene or acrolein may be adsorbed and O_L represents a lattice oxide ion. Oxide ion vacancies have been omitted and the oxygen involved in step (4) cannot be specified at present. Treating adsorbed intermediates and O* as labile species, the following equations are obtained:

$$-\mathrm{d}[C_3H_6(g)]/\mathrm{d}t = k_1\,\theta_{\square}\theta_{O^*}[C_3H_6(g)] \qquad (7)$$

and

$$\mathrm{d}[C_3H_4O(g)]/\mathrm{d}t = -\mathrm{d}[C_3H_6(g)]/\mathrm{d}t - r_4 \qquad (8)$$

where r_4 is the rate of step (4). At low conversions, since acrolein is weakly adsorbed, r_4 is small. The surface concentration of O* for reoxidised catalyst is high, so that the value of 50 ± 10 kJ mol^{-1}, the mean apparent activation energy for initial rates of propene consumption and acrolein formation, characterises the dependence of k_1 on temperature. At later stages of reaction, for equilibrium values of O*:

$$\theta_{O^*} = \frac{r_5 + r_6}{2k_1\,\theta_{\square}[C_3H_6(g)]}. \qquad (9)$$

Hence

$$-\mathrm{d}[C_3H_6(g)]/\mathrm{d}t = (r_5 + r_6)/2. \qquad (10)$$

The activation renergy 80 ± 1 kJ mol^{-1} for the first-order consumption of propene therefore reflects the temperature dependence of the production of O* at the surface. For USb_3O_{10}, Baussart *et al.*[14] obtained an activation energy of 78 kJ mol^{-1} for mixtures containing $C_3H_6:O_2 = 1:5$. Keulks *et al.*[4] obtained 70 kJ mol^{-1} above 673 K, and 124 kJ mol^{-1} at lower temperatures. Keulks suggested that the change in activation energy was associated with either inhibition by acrolein or slow catalyst reoxidation, at low temperatures. A third possibility is a transition between steps (5) and (6) for the replenishment of O*. In the present work, the high activation energy for the consumption of gas-phase oxygen (180 kJ mol^{-1}) indicates that during reaction over the U–Sb–O catalyst, O* is replaced mainly from within the lattice. The equilibrium surface concentration of O* would increase with increasing temperature, corresponding with the observed tendency for propene consumption to follow first-order kinetics more closely at higher temperatures.

Conductivity Measurements

Variations in a.c. conductivity reflect changes in the identity and concentration of charged defects (e^-, h^+, interstitial ions, charged vacancies) in the U–Sb–O catalyst.[9] These changes probably involve $USb_3O_{10} \cdot xSb_2O_4$, although concurrent effects in the small proportion of $USbO_5$ may contribute. We have suggested[9] that interstitial oxide ions, probably O_i^{2-}, play an important part in this reaction.

Reduction of the catalyst by propene would lead to an increase in conductivity, mainly due to the release of electrons:

$$C_3H_6(g) + O_i^{2-} + O_L \rightarrow CH_2{=}CH{-}CHO(g) + H_2O(g) + V_O^{2+} + 4e^- \qquad (11a)$$

or

$$C_3H_6(g) + 2O_L \rightarrow CH_2{=}CH{-}CHO(g) + H_2O(g) + 2V_O^{2+} + 4e^- \qquad (11b)$$

where O_i^{2-} is an interstitial oxide ion, O_L is a lattice oxide ion (previously denoted O_O^{x} [9]) and V_O^{2+} is an oxide-ion vacancy. Desorption of water, which is required initially for the formation of Sb^V sites for the adsorption of propene,[5] also increases conductivity:

$$2OH(ads) \rightarrow H_2O(g) + V_O^{2+} + O_L^{x} + 2e^-. \qquad (12)$$

Also for acrolein

$$C_3H_4O(ads) \rightarrow C_3H_4O(g) + V_O^{2+} + 2e^-. \qquad (13)$$

Conversely, reoxidation of the catalyst, involving either filling oxide ion vacancies or forming interstitial oxide ions, reduces conductivity by replacing electrons with less mobile charged species. The initial adsorption of propene would also reduce conductivity:

$$C_3H_6(g)+O_L+V_O^{2+}+2e^- \rightarrow OH(ads)+C_3H_5(ads). \quad (14)$$

The observed changes in conductivity during reactions are consistent with these processes. Thus the large increase in conductivity when the fully oxidised catalyst was exposed to propene (fig. 8) corresponds to eqn (11*a* and *b*), and processes (12) and (13) would account for the further increase observed when products were desorbed. Reoxidation of the catalyst decreased its conductivity, the process being extremely rapid initially, but slowing considerably when *ca.* 60% of the original increase had been reversed. The small increase in conductivity when the gaseous oxygen used for reoxidation was evacuated shows that a small proportion of oxygen in the reoxidised catalyst is labile. Subsequent exposure of the partially reoxidised catalyst to propene caused a small but well defined decrease in conductivity preceding the much larger increase. It is suggested that this is due to process (14).

Changes in conductivity were very much smaller when the catalyst was exposed to mixtures of propene and oxygen (fig. 9). For the partially oxidised catalyst [curve (*b*)] the rapid initial decrease [process (14)] was reversed almost immediately, after which reduction of the catalyst was slow. Subsequent evacuation and reoxidation of the catalyst was accompanied by changes in conductivity as explained above. When the catalyst was not reoxidised between kinetic runs [curve (*a*)] the initial conductivity was very much higher. Probably the continuous decrease during reaction was due to reoxidation of the considerably reduced catalyst being faster than reduction. Again, evacuation of products increased the conductivity [processes (12) and (13)]. Under both regimes, the very slow changes in conductivity after early stages support the view[13] that under any reaction conditions, equilibrium is established between the rate of reduction and the rate of reoxidation of the catalyst.

The U–Sb–O Catalyst

The catalyst used in this work contained some Sb_2O_4 and was therefore more similar to those containing excess antimony used by Pendleton and Taylor[15] and Delobel *et al.*[12] than to USb_3O_{10} used by Baussart *et al.*[14] and Keulks *et al.*[4] Nevertheless, our observation of both kinetics and conductivity changes correspond closely to results obtained for the pure phase. The major differences in behaviour between U–Sb–O (U:Sb = 1:3) and USb_3O_{10} are, first, that U–Sb–O is readily reduced by propene whereas USb_3O_{10} is not and, secondly, that a considerable proportion of oxygen found in products of reaction over U–Sb–O originates from the catalyst whereas only one or two layers of the surface of USb_3O_{10} participate. The correspondence between activation energies over the two materials points to a similar mechanism for the replacement of O* at the surface. Excess Sb_2O_4 contributes to this process. The transfer of oxide ions through the bulk of the catalyst appears to be the rate-limiting process, although reoxidation of the reduced surface may be the slow step at low temperatures.

The question remains as to the nature of O*. In their mechanism, Grasselli and Suresh[5] suggest that the labile species are superficial oxide ions bridging U and Sb, or two Sb. The changes in a.c. conductivity under reaction conditions, reported above, could be explained in terms of either lattice oxide ions [reaction (11*b*)] or a combination of lattice and interstitial oxide ions [reaction (11*a*)]. However, simultaneous a.c. and d.c. measurements[9] have shown that interstitial oxide ions (O_i^{2-}) are present in the U–Sb–O catalyst, and that these are eliminated when the catalyst is reduced. Therefore we suggest that O_i^{2-} either contributes to or is identified as O*. Thus O_i^{2-} could form intermediates between bulk lattice and superficial oxide ions. Alternatively, O_i^{2-} ions could fulfil the role attributed to the superficial oxide ions.

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