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The activity and selectivity of oxygen atoms adsorbed on a Ag/α-Al_2O_3 catalyst in ethene epoxidation

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The bonding of the oxygen species held on a Ag/α-Al_2O_3 catalyst has been studied by temperature programmed desorption and their reactivity in ethene epoxidation by temperature programmed reduction using ethene as the reductant. The Ag/α-Al_2O_3 catalyst was produced by the thermal decomposition of a Ag oxalate/α-Al_2O_3 precursor. Oxygen desorbs from this Ag/α-Al_2O_3 catalyst in two states, one (peak maximum temperature 520 K) having a desorption activation energy of 140 kJ mol^{-1}–oxygen desorbing from Ag(111), and one (peak maximum temperature 573 K) having a desorption activation energy of 155 kJ mol^{-1}–oxygen desorbing from a highly stepped or defected Ag surface. Temperature programmed reduction of the two oxygen states existing on the surface of the Ag/α-Al_2O_3 catalyst using ethene as the reductant produced two peaks at 373 and 473 K in which ethene epoxide and CO_2 evolved coincidently. The peak at 373 K derives from the reduction of oxygen atoms adsorbed on Ag(111). The higher temperature peak (473 K) corresponds to the reduction of oxygen atoms adsorbed on highly stepped or defected Ag surface. The selectivity to ethene epoxide for the 373 K peak is ~57%, while that of the 473 K peak is 34%. The coincident evolution of ethene epoxide and CO_2 shows that the selective and unselective reaction pathways have a common surface intermediate–probably an oxametallacycle. The higher selectivity of the oxametallacycle formed by the bonding of ethene to the weaker Ag—O bond is considered to result from its having a lower activation energy to cyclisation than that produced by ethene bonding to the higher Ag—O bond.

KEY WORDS: ethene epoxidation; oxametallacycle; silver/alumina catalyst.

1. Introduction

Silver is unique in its ability to oxidize ethene to ethene epoxide in high selectivity. Identification of the origin of this high selectivity has proved to be difficult. There are two aspects which are determining in respect of this high selectivity. These are: (i) the nature of the chemisorbed oxygen involved in the selective oxidation and (ii) the reaction pathway resulting from the interaction of this chemisorbed selective oxygen with ethene.

Kilty and coworkers believed that the selective chemisorbed oxygen was a charged molecular species, O_2^- [1]. Using infrared spectroscopy, they claimed to have identified an adsorbed ethene peroxy species (CH_2—CH_2—O—O—Ag) by the interaction of ethene with molecular oxygen adsorbed on Ag [1]. The ethene peroxy complex was observed to decompose at 383 K and was proposed to be the precursor to ethene epoxide. Atomic oxygen was considered to be an unselective oxidant [1]. The mechanism resulting from these conclusions (reactions (1) and (2) below) predicts a maximum selectivity of 6/7 (86%)

$$C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O + O_{(a)} \qquad (1) \times 6$$

$$6C_2H_4 + 6O_{(a)} \rightarrow 2CO_2 + 2H_2O \qquad (2)$$

It was not until the mid-1980s that the limiting selectivity of 86% was exceeded and so this mechanism was given considerable credence for several years.

Campbell and coworkers studied ethene epoxidation on model Ag(110) and Ag(111) single crystals using a combined microreactor/surface science apparatus [2–6]. From their observation of measurable rates of ethene epoxidation when no adsorbed atomic oxygen species were observed [3] and from the fact that titration of preadsorbed oxygen produced only CO_2 [2], Campbell and co-workers concluded that an adsorbed molecular oxygen species was the oxidant. The mechanism they proposed, however, was that a common intermediate produced by the interaction of adsorbed ethene and O_2^- was responsible for the production of ethene epoxide and CO_2 [2].

Later, however, noting that the molecular oxygen species on Ag(111) and Ag(110) were different (the molecular oxygen species on Ag(111) was found to be superoxide-like, O_2^- (a), in nature, whereas that on Ag(110) was peroxy-like, O_2^{2-} (a), in nature) but that their rates of ethene epoxide production were similar, Campbell decided against molecular oxygen being the oxidant [6]. He further propounded that the adsorbed molecular oxygen species acted to create a high surface coverage of a "special" state of adsorbed atomic oxygen and it was this special oxygen state that was the oxidant.

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The reaction mechanism relating to this special state was that the adsorbed ethene reacted with it in a rate determining step to form a common intermediate which then forms ethene epoxide or fragments to CO_2 and H_2O [6].

Cant and Hall also concluded that a molecularly adsorbed oxygen species was the oxidant and that it formed an intermediate with adsorbed ethene which was common to the formation both to ethene epoxide and to CO_2 [7]. Their experiments were conducted using *cis* or *trans* 1,2-d_2-ethene and they found 92% *cis*/*trans* equilibration in the ethene epoxide produced. These results showed that the addition of oxygen to the C=C bond of ethene was not concerted and that at some stage in the reaction co-ordinate there is free rotation about a C—C single bond which is formed during the reaction [7].

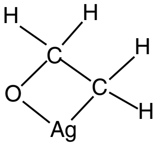
Lambert and coworkers showed that the molecular oxygen species could be removed from the surface of Ag(111) by temperature programmed desorption without having any impact on the subsequent production of ethene epoxide by reaction with the atomically adsorbed oxygen [8,9]. They proposed that it was the valence charge state of this atomically adsorbed oxygen that determined reaction selectivity. The valence charge state of the atomically adsorbed oxygen was considered to be determined by chloride promoters or by subsurface oxygen atoms. A lower valence charge density on $O_{(a)}$ was thought to make it a better electrophile, favouring electrophilic attack on adsorbed ethene and hence epoxidation (reaction Scheme 1). A higher charge density on $O_{(a)}$ was thought to result in H abstraction from ethene and hence combustion (reaction Scheme 2).

It should be noted that reaction scheme 1 does not allow for rotation about the C=C bond in the ethene and so the mechanism could not account for Cant and Hall's observation of 92% *cis*/*trans* equilibration in the ethene epoxide produce when starting with 100% *cis* or *trans* 1,2-d_2-ethene.

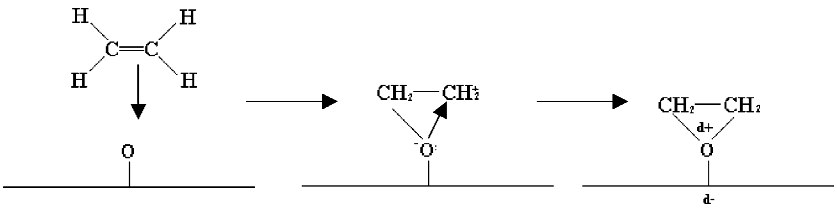
Force and Bell used infrared spectroscopy to identify the adsorbed species existing on the surface of a Ag/SiO_2 catalyst during ethene epoxidation from which they produced a mechanism for the reaction [10,11]. They proposed that atomically adsorbed oxygen was the oxidant and that it reacted with adsorbed ethene to form $CH_2—CH_2—O—Ag$ which was a common intermediate responsible for the formation of both ethene epoxide (by cyclisation of the intermediate) and of CO_2 and H_2O (by H migration to form $CH_3—CH—O—Ag$ which was completely combusted).

Recently, Linic and Barteau have added considerable detail to our understanding of ethene epoxidation over Ag [12–14]. They studied the adsorption and decomposition of ethene epoxide on Ag(111) using temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) [12]. Adsorption of ethene epoxide at 130 K was found to be molecular; the molecule desorbed at 200 K on temperature programming. Adsorption at 250 K caused ring opening to produce an intermediate which, on temperature programming, produced ethene epoxide, ethene, water and ethanol coincidently at 300 K [12]. Simulation of the HREELS spectrum of this intermediate by density function theory (DFT) calculations showed it to be the oxametallacycle (Intermediate 1) [12].

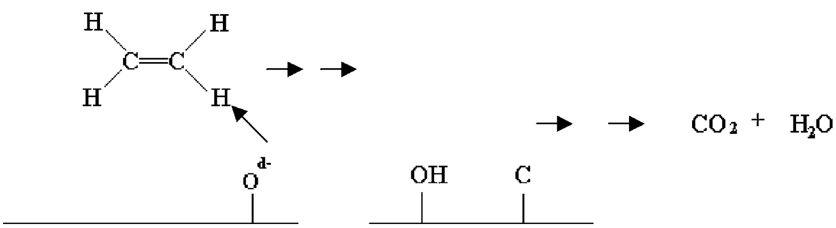
Construction of the reaction coordinate using DFT showed that transition state 1 (TS1) was the transition state formed by the interaction of gas phase ethene with



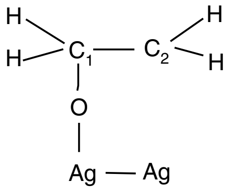
Intermediate 1.



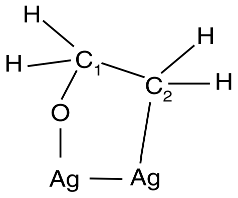
Reaction Scheme 1.



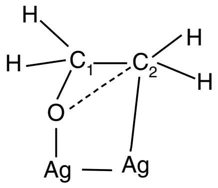
Reaction Scheme 2.



TS1



Intermediate 2



TS2.

adsorbed oxygen; this then formed a stable oxametallacycle (Intermediate 2). The metallacycle is the common intermediate which forms ethene epoxide by the stretching of the Ag—O bond, the breaking of the C_2—Ag bond and the formation of the C_2—O bond (TS2). It also forms CH_3CHO by 1,2-hydrogen shift [13,14].

The purpose of the present paper is to investigate the mechanism of the forward reaction of ethene and adsorbed oxygen on a Ag/α-Al_2O_3 catalyst which has two Ag—O bonds of different bond strengths. The intention is threefold. It is (i) to determine the desorption activation energies of each of these bonds, (ii) to determine the selectivities of these bonds in the formation of ethene epoxide and (iii) to confirm that in the forward reaction of ethene epoxidation both ethene epoxide formation and CO_2 production proceed through a common intermediate.

2. Experimental

2.1. Preparation of the silver oxalate impregnated α-Al_2O_3 catalyst

Before impregnation with the silver oxalate, the α-Al_2O_3 support (supplied by bp Chemicals) was crushed using a pestle and mortar and then sieved, retaining the 300–350 μm sized material. The method employed for impregnating the α-Al_2O_3 support with Ag using silver oxalate ($C_2O_4Ag_2$) as the Ag salt has been patented by bp [15]. The silver oxalate (4.6 g) was added to distilled, de-ionised water (2.86 cm^3) in a beaker (50 cm^3). This was maintained at 313 K using a water bath and stirred using a magnetic stirrer to achieve a slurry. Ethylene diamine (1.25 g) was added dropwise with continuous stirring. The slurry was filtered and the Ag/ethylene diamine complex containing liquid was retained. The α-Al_2O_3 support was added to the Ag/ethylene diamine liquid in a bottle which was shaken to achieve good mixing and penetration of the pore volume of the support by the liquid. The material was dried overnight at between 353 and 373 K for 16 h.

This patented method of preparation of Ag/α-Al_2O_3 catalysts is the basis for the preparation of Ag/α-Al_2O_3 catalysts which, with appropriate amounts of alkali promoter, are used industrially for the production of ethene epoxide.

2.2. The gases

Helium (99.999%) was supplied by Linde. It was passed through a Chromapack Gas Clean moisture trap before use. Oxygen (99.995%) was supplied by the British Oxygen Company (BOC). It was passed through a moisture trap before use. Ethene in helium (2% ethene) was supplied by Air Products and was 99.995% pure. It was passed through a moisture trap and an oxygen trap (Oxyclear) before use.

2.3. The microreactor system

The multipurpose microreactor used in these experiments has been described in detail previously [16]. It is a single stainless steel tube, 20 cm long and 0.4 cm internal diameter. It is housed in a metal heating block. The reactor is connected, on-line, to a mass spectrometer (Hiden Analytical, Warrington, England) *via* a heated capillary. The reactor can be cooled to 77 K and temperature programmed from 77 to 1100 K using a Newtronics controller.

Two types of experiment were performed in this study:temperature programmed desorption (TPD) [17] and temperature programmed reduction (TPR) [16].

3. Results and discussion

3.1. The desorption of oxygen from the Ag/α-Al_2O_3 catalyst

The Ag/α-Al_2O_3 catalyst (0.25 g) produced by the decomposition of the silver oxalate/α-Al_2O_3 material was heated from ambient to 513 K at 10 K min^{-1} under O_2 (101 kPa, 25 cm^3 min^{-1}), held at that temperature for 1 h and then cooled to ambient under the O_2 flow. During this O_2 treatment the exit flow from the reactor was vented rather than being passed to the mass spectrometer. This preserved a low $m/z = 32$ level in the mass spectrometer and so minimized the time required for the establishment of a suitable $m/z = 32$ background signal on the mass spectrometer when the flow was switched from O_2 to He and was re-directed to the mass spectrometer.

Two O_2 desorption peaks are obtained: (i) a low temperature oxygen desorption peak having a peak maximum temperature of 523 K and (ii) a high temperature oxygen desorption peak having a peak maximum temperature of 573 K. Bal'zhinimaev [18] has published a similar oxygen TPD spectrum from a supported Ag catalyst. He attributed the lower temperature peak to oxygen desorbing from regular surface and the higher peak to oxygen desorbing from imperfect or defect regions of the surface [18].

The total amount of O_2 desorbing in these two peaks is 1.146×10^{19} atom g^{-1}. The surface Ag atom density calculated from the unit cell dimensions is 1.193×10^{15} Ag atom cm^{-2} or an area of 8.38×10^{-16} cm^2 Ag^{-1}. Since saturation coverage of Ag by O atoms is 0.67 monolayer [4] then each O atom corresponds to a Ag area of 12.5×10^{-16} cm^{-2}. The O_2 desorption peak corresponded 1.146×10^{19} O atom (g catalyst)$^{-1}$ and so the Ag area of the Ag/α-Al_2O_3 catalyst is 1.43 m^2 (g catalyst)$^{-1}$. Since the Ag loading 10% by weight, the area of the Ag per gram Ag is 14.3 m^2 (g Ag)$^{-1}$. This corresponds to an Ag particle size of 4×10^{-6} cm or 400 Å. This small particle size is consistent with the surface being highly stepped.

Figure 1 (black curve) is the oxygen desorption spectrum obtained after re-dosing the Ag/α-Al_2O_3 catalyst which had produced the O_2 TPD spectrum shown in figure 1 (red curve) with oxygen in an identical manner to that described above and temperature programming in He. One peak with a peak maximum at 513 K is observed; this peak has a shoulder at 543 K and a tail at 573 K. The silver surface area has roughly halved. The loss in area results from the loss of the highly stepped surfaces.

This loss of the more highly stepped surfaces on the first heating to 723 K is more clearly demonstrated in the computer simulations of the desorption spectra shown in figure 1. The simulations shown in figure 2 are obtained using the Polanyi–Wigner equation (equation 1) by inputting values for the desorption activation energies (E_d), the desorption pre-exponential (A) and the initial oxygen atom coverages ($O_{(a)}$). Equation 1 is solved at 1 K intervals from 273 to 773 K. The rate of desorption is calculated at 274 K and the amount of material which has desorbed in the 1 K time interval (6 s, heating rate 10 K min^{-1}) is calculated by multiplying the rate of desorption by the time interval. This amount is now subtracted from the initial oxygen atom coverage and the process is repeated.

$$\frac{-d(O_{(a)})}{dt} = \frac{2(dO_2)}{dt} = A\,e^{-E_d/RT} O^2_{(a)}, \qquad (3)$$

where $O_{(a)}$ (atom cm^{-2}) is the coverage of the silver surface by adsorbed oxygen atoms t (s) is time A (cm^2 molecule^{-1} s^{-1}) is the desorption pre-exponential term E_d (J mol^{-1}) is the desorption activation energy $\frac{(dO_2)}{dt}$ (molecule cm^{-2} s^{-1}) is the rate of molecular oxygen evolution R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the temperature.

The inputs for these simulations are shown in table 1. The desorption activation energies of 140 and 145 kJ mol^{-1} are those reported in the literature for O_2 desorption from Ag(111) and Ag(110), respectively [19–21]. The third desorption activation energy of 155 kJ mol^{-1} is one which was required to be used to fit the experimental data. This high value is considered to derive from oxygen atoms being adsorbed on a highly stepped surface. The value of the desorption pre-exponential term used to fit both peaks (2 cm^2 molecule^{-1} s^{-1}) is a standard value for second order recombinative desorption. The areas of the Ag surface designated as Ag(111), Ag(110) and stepped for the simulated first desorption (curve 2a) are listed in row 3. Fifty five percent of the oxygen is adsorbed on the (111) surface, 10% percent on the (110) face and 35% percent

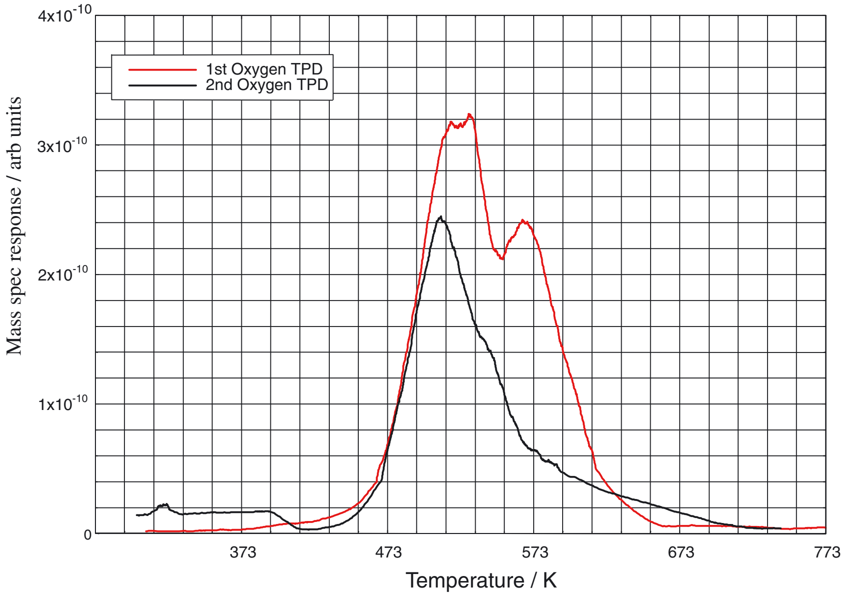


Figure 1. The oxygen desorption spectra from the Ag/α-Al_2O_3 catalyst.

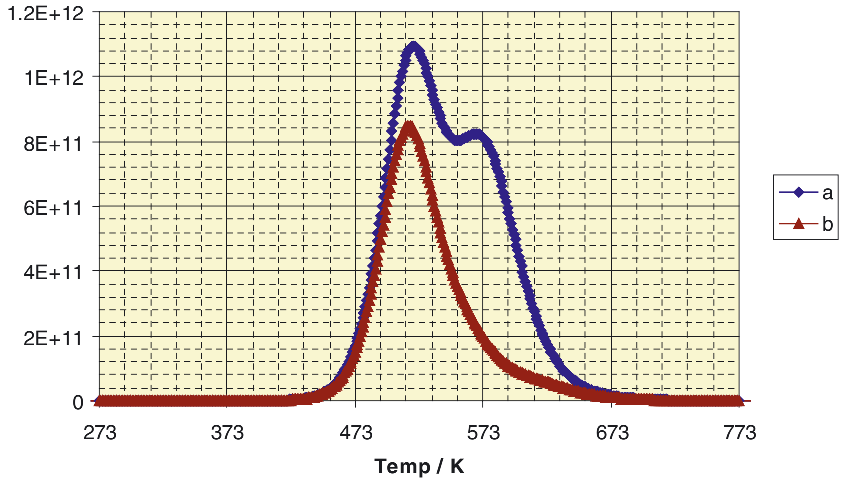


Figure 2. Simulated oxygen desorption spectra from the Ag/α-Al_2O_3 catalyst: curve a first heating, curve b second heating.

on the highly stepped surface. (Since we believe that the method of dosing oxygen on to the surface (pure O_2, 101 kPa, 25 cm^3 min^{-1}, 1 h, 513 K) produced a saturated surface, these coverages are simply a statement of the surface morphology of the initial state of the Ag existing for the first desorption.)

The simulated second desorption (curve 2b) is achieved using the same values of the desorption activation energies as those used for curve 2a, but with a reduced Ag area (60% of the original value) and with a different surface morphology (Ag(111) 80%, Ag(110) 15% and highly stepped surface 5%). Sintering engenders the loss of the highly stepped surface. These oxygen atoms which are bonded differently on the different crystal faces of the Ag are expected to have different activities and different selectivities. The oxygen atoms which are bonded more strongly on the highly stepped surfaces are probably more negatively charged than those on the Ag(111) face and so are likely to be less selective in the ethene epoxidation reaction which requires an electrophilic oxygen species.

These simulations (figure 2, curves a and b) calculated using the desorption activation energies for the Ag(111) and Ag(110) obtained from single crystal studies together with a small contribution from a "high index" desorption activation energy reproduce both the peak maximum temperature and the full width half maximum values of the experimental curves shown in figure 1 (red and black curves) and so provide reasonable confidence in the interpretation of the data in terms of the morphology of the surface of the Ag in the Ag/α-Al_2O_3 catalyst.

Table 1
Desorption activation energies, pre-exponential terms and surface areas used as inputs for oxygen TPD simulations

Peak	Ag(111)	Ag(110)	High index face/ defect sites
Activation energy to desorption	140 kJ/mol	145 kJ/mol	155 kJ/mol
A-factor (cm^2 $molecule^{-1}s^{-1}$)	2×10^{-3}	2×10^{-3}	2×10^{-3}
First desorption	1.1 m^2/g	0.2 m^2/g	0.7 m^2/g
Second desorption	0.96 m^2/g	0.18 m^2/g	0.06 m^2/g

That the two oxygen TPD peaks of figure 1 (red curve) derive from two kinetically different adsorbed oxygen species is nicely demonstrated in figure 3. This oxygen TPD spectrum is obtained by dosing the oxygen on to a fresh sample of the Ag/α-Al_2O_3 catalyst in the manner used as standard (O_2, 101 kPa, 25 cm^3 min^{-1} 513 K, 1 h and cooling under the O_2 to ambient). The flow was then switched to He (101 kPa, 25 cm^3 min^{-1}) and the temperature was raised to 503 K (10 K min^{-1}) where it was held for 4 min. The catalyst was then rapidly cooled to ambient before temperature programming was recommenced.

Figure 3 shows that this treatment has resulted in a significant lowering of the amount of oxygen desorbing in the 523 K peak (Ag(111)) while the amount desorbing in the 573 K peak is virtually unaltered. It is clear that heating the oxygen dosed catalyst to 503 K and holding there for 4 min, has simply desorbed most of the weakly held oxygen, the temperature of 503 K being too low to cause much loss of oxygen from or any sintering of the highly stepped surface.

3.2. *Temperature programmed reduction of the adsorbed oxygen by ethene*

The Ag/α-Al_2O_3 catalyst was dosed to saturation with oxygen in the method adopted as standard raising the temperature from ambient to 513 K under pure O_2 (101 kPa, 25 cm^3 min^{-1}), holding the catalyst under the

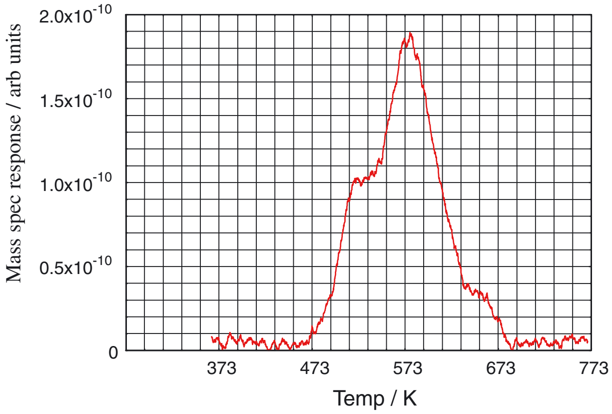


Figure 3. The oxygen desorption spectrum from the Ag/α-Al_2O_3 catalyst after having desorbed the low temperature oxygen peak by heating in He to 503 K.

O_2 flow for 1 h at 513 K and lowering the temperature to ambient under the O_2 flow when the flow was switched to He (101 kPa, 25 cm^3 min^{-1}).

This produced an oxidized Ag surface having two types of adsorbed oxygen one of which desorbed at 523 K and the other at 573 K. This catalyst was then cooled further to 173 K under the He flow. After 173 K was reached, temperature programming was begun at 10 K min^{-1} and 2 min after the start of the temperature programming, the He flow was switched to an ethene/He flow (2% ethene, 101 kPa, 25 cm^3 min^{-1}) following m/z ratios 18, 29 and 44 on the mass spectrometer. The temperature programmed reduction spectrum is shown in figure 4. (Due to considerable noise on the $m/z = 18$ (H_2O) signal, it showed no structure and so is not reported in any of the temperature programmed reduction profiles figures 4–6).

Two reaction peaks are observed: (i) at 373 K comprising two virtually coincident peaks of m/z ratios 29 (CHO^+) and 44 (C_2H_4O ethane oxide and CO_2) and (ii) a $m/z = 29$ peak at 463 K with a near coincident $m/z = 44$ peak at 473 K. Due to the carcinogenic nature of ethene epoxide, it was not possible to feed it to the mass spectrometer to obtain its cracking fraction. A cracking fraction has been published, however, by the National Institute of Standards and Technology (NIST) [22] and its value of a 2:1 ratio of the 29 peak to the 44 peak will be used here to estimate the selectivities (ethene epoxide produced/ethene converted)of the two peaks in the TPR spectrum in figure 4, acknowledging that the cracking fraction of ethene epoxide will vary somewhat from one mass spectrometer to another. The selectivities so produced, however, will give a clear indication of the nature of the reactivity of the two oxygen species.

The height of the $m/z = 29$ peak in the 373 K peak is 1.7×10^{-10} units and so contributes 0.85×10^{-10} units to the $m/z = 44$ peak. The $m/z = 44$ peak of the 373 K peak is 3.4×10^{-10} units and so the amount of CO_2 in this peak is $3.4 \times 10^{-10} - 0.85 \times 10^{-10} = 2.55 \times 10^{-10}$ units. The selectivity to ethene epoxide of the oxygen in the 373 K peak is therefore $1.7 \times 10^{-10}/\ (1.7 \times 10^{-10} + 2.55 \times 10^{-10}/2$ (2 molecules of CO_2 are produced per ethene converted)) = 57%. Carrying out the same calculation for the 473 peak having a $m/z = 29$ peak height of 0.8×10^{-10} units and a $m/z = 44$ peak heights of 3.2×10^{-10} units gives a selectivity of the oxygen in this peak of $0.8 \times 10^{-10}/(0.8 \times 10^{-10} + 3.2 \times 10^{-10}/2) =$ 34%. Allowing for the inaccuracies in the determination, it is clear that oxygen in the high temperature peak is significantly less selective than that in the low temperature peak. Also the values of these selectivities correspond with others obtained on unpromoted Ag [23,24].

An estimate of the activation energy for the reaction of an adsorbed ethene molecule with the adsorbed

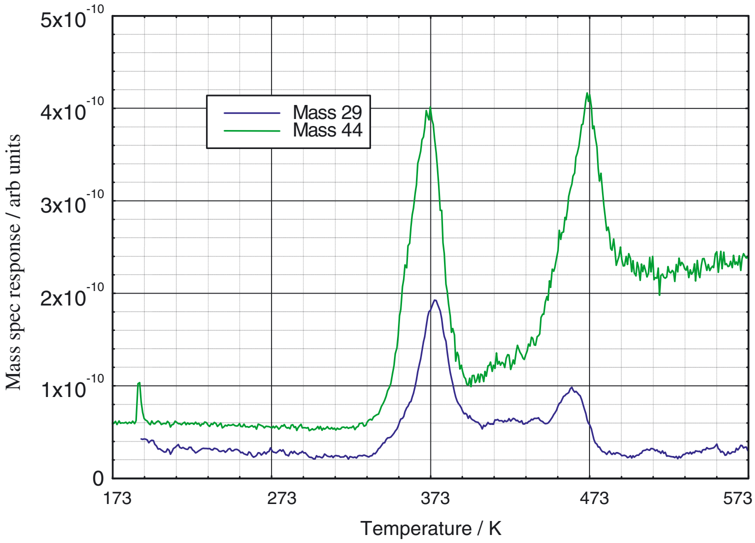


Figure 4. Temperature programmed reduction (TPR) by ethene of the oxygen atoms adsorbed on the Ag/α-Al_2O_3 catalyst.

oxygen atoms to form ethene epoxide can be obtained by line shape analysis of the early rising part of the ethene epoxide peaks. Linic and Barteau's analysis of the reaction coordinate shows the reaction to be first order in adsorbed oxygen. If the analysis is carried out over a small temperature range, it can be considered to be independent of the amount of adsorbed ethene, for two reasons: (i) the reaction is carried out in a flow of ethene (2% or a dosage of 1.5×10^7 ML s^{-1}) and this will maintain the equilibrium coverage of ethene and (ii) the heat of adsorption of ethene is small (42 kJ mol^{-1}) [2] and so the equilibrium coverage will not change greatly over a small temperature range. For the 373 K peak, a plot of ln (rate of ethene epoxide formation/oxygen coverage) against $1/T$ over the temperature range 333–361 K gives an activation energy of reaction of 60 kJ mol^{-1}; for the 473 K peak, the same plot carried out over the temperature range 433–451 K gives an activation energy of 170 kJ mol^{-1}.

Campbell and Paffett attempted to produce ethene epoxide by exposing pre-adsorbed oxygen adlayers (half monolayer and saturation) on Ag(110) to ethene at various temperatures in the range 300–600 K using ethene partial pressures in the range 1–10 Torr (1 Torr = 133 Pa). In no case was any amount of ethene epoxide detected [2]. It is unclear why, in our case using an identical saturation coverage (we know there is no subsurface oxygen produced by our dosing conditions), ethene epoxide was detected at selectivities comparable to those found in steady state rate measurements. The difference may relate to the pressure of ethene used here 2.03×10^3 Pa compared with values in the range of 1.33×10^2 to 1.33×10^3 Pa in Campbell's work. It could also relate to Campbell's experiment being conducted in a batch mode where the product ethene epoxide was exposed to Ag(110), having a high coverage of oxygen so that any ethene epoxide produced would be further oxidized to CO_2.

3.3. The mechanism of the reaction of ethene with oxygen adsorbed on Ag

In considering the nature of the interaction of the ethene with the oxygen atoms adsorbed on the Ag surface of fresh Ag/α-Al_2O_3, it must be remembered that these experiments are carried out anaerobically on an Al_2O_3 supported Ag whose surface is oxidized to saturation level, i.e. it contains 0.67 monolayer of adsorbed oxygen atoms. Furthermore, these oxygen atoms are adsorbed on two distinct regions (on Ag(111) and on a stepped surface or defects) each occupying roughly equal areas. The desorption activation energies of the adsorbed oxygen atoms on the two surfaces are distinctly different (140 kJ mol^{-1} Ag(111) and 155 kJ mol^{-1} on stepped or defect surface), giving rise to different activation energies for the ethene/$O_{(a)}$ interaction.

The interaction of ethene with $O_{(a)}$ on Ag(111) produces ethene epoxide with a reaction selectivity of ~57%, a value which is roughly twice that of the reaction of ethene with $O_{(a)}$ on the stepped Ag surface.

Since ethene epoxide and CO_2 are evolved at the same temperature, they must have a common rate limiting step. Possible sources of this common rate limiting step could be either the adsorption of ethene or the diffusion of the ethene through the catalyst to reach the Ag particles. Remembering that the experiment involved heating the surface oxidized Ag/α-Al_2O_3 catalyst in ethene from 193 K at 10 K min^{-1} until the reaction took place at 373 and 473 K rules out the possibility of diffusion to the active centre as the common rate determining step. It would have taken 18 min for the reactants to reach the active centre for the 373 K peak and 28 min to reach the 473 K peak. Diffusion to the active centre would have occurred at the same time for both active centres and so would have produced only one peak. It would also have occurred in a much shorter period of time (<1 min) on such a low surface area catalyst in 2% ethene. For adsorption of ethene to be the common rate limiting step a delay of 18 min for adsorption on to the 373 K active centre would require an adsorption activation energy of ~120 kJ mol^{-1} while that for adsorption after 28 min on the 473 K site is ~160 kJ mol^{-1}. These adsorption activation energies are unrealistically high and so exclude adsorption of ethene as the common rate limiting site.

The most plausible common rate limiting step is the branching reaction pathway of a common intermediate. On the basis of their DFT calculations, Linic and Barteau have published that TS1 is the transition state for the initial interaction of a gas phase ethene molecule and oxygen atom adsorbed on Ag [14]. This then forms a stable oxametallacycle (Intermediate 2) [14]. Intermediate 2 is the common intermediate which Linic and Barteau claim is responsible both for the formation of ethene epoxide by the breaking of the C_2—Ag bond during the formation of the C_2—O bond and for the formation of acetaldehyde (the precursor to CO_2 and H_2O) by a 1,2-hydrogen shift [13]. Experimental evidence for this calculated reaction coordinate was provided in part by the decomposition of ethene epoxide on Ag(111) [12].

This coincident evolution of ethene epoxide and CO_2 in two peaks at 373 and 473 K resulting from the reaction of ethene with oxygen atoms having different Ag—O bond strengths, coupled with the lower selectivity of the stronger Ag—O bond, provides compelling evidence that the forward ethene epoxidation reaction occurs through a common intermediate–the oxametallacycle (Intermediate 2). The lower selectivity of the more strongly adsorbed oxygen species probably results from the stronger Ag—O bond in the

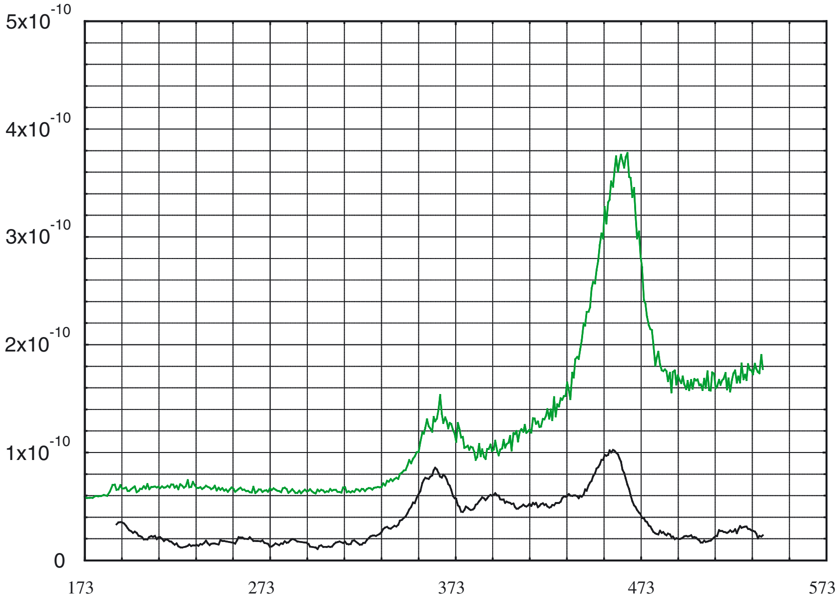


Figure 5. Temperature programmed reaction of the oxidized Ag/α-Al_2O_3 catalyst having removed 80% of the 523 K oxygen species–the black line is the $m/z = 29$ signal (ethene epoxide) and the green line is the $m/z = 44$ signal (CO_2).

oxametallacycle having a higher activation energy to stretch to form the cyclic epoxide species than the weaker Ag—O bond.

Figure 5 is the temperature programmed reduction by ethene of an oxidized Ag/α-Al_2O_3 catalyst which had been pretreated so as to produce the oxygen desorption spectrum shown in figure 3, i.e. the oxygen had been initially dosed on to saturation as described previously and then the temperature was raised from ambient to 503 K under a He stream and held at 503 K for 4 min before being rapidly cooled to ambient. This has the effect of reducing the amount of oxygen desorbing in the 523 K peak to 20% of its original value while leaving that desorbing at 573 K at about 90% of its original value. The temperature programmed reduction of this oxidized surface again results in two peaks in which ethene epoxide and CO_2 evolve coincidently, again indicating their origination in the branching reaction pathways of a common intermediate. The selectivity of the 363 K peak is increased from 57% to 75% while that of the 463 K peak is roughly unchanged at 34%. The low coverage of adsorbed oxygen on the Ag(111) face (~ 0.13 ML) has resulted in an increase in selectivity. This lowering

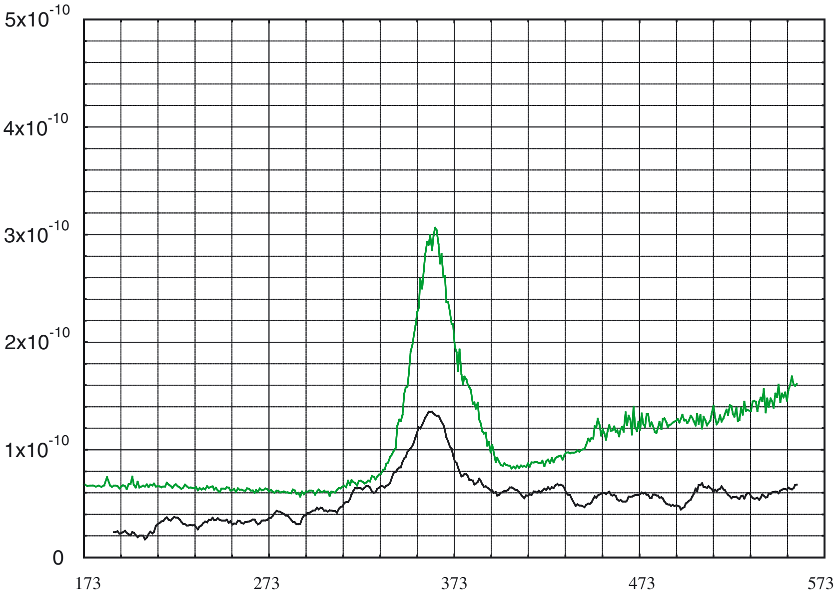


Figure 6. Temperature programmed reduction by ethene of the oxidized Ag/α-Al_2O_3 catalyst from which the 573 K desorbing oxygen species has been removed–the black line is the $m/z = 29$ signal (ethene epoxide) and the green line is the $m/z = 44$ signal (CO_2).

of the peak maximum temperature for ethene epoxide production from 373 K (figure 4) to 363 K (figure 5) by lowering the oxygen coverage, indicates a lowering of the activation energy for cyclisation, probably as a result of a slight weakening of the Ag–O bond at low oxygen coverages.

Figure 6 is the temperature programmed reduction by ethene of an oxidized Ag/α-Al_2O_3 catalyst which had been pretreated so as to produce the oxygen desorption spectrum shown in figure 1 (black curve). (figure 1 (black curve) had been produced by dosing oxygen to saturation coverage on to a Ag/α-Al_2O_3 catalyst, the Ag having been sintered by heating the catalyst to 873 K in a He stream.) The morphology of the sintered Ag surface is 80% Ag(111), 15% Ag(110) and 5% stepped or defected surface (Table 1). Temperature programmed reduction of the saturation oxygen coverage of this Ag surface produces one peak at 373 K in which ethene epoxide and CO_2 are evolved coincidently, deriving from the two reaction pathways available to a common intermediate. The selectivity of this single oxygen species is 49%. This should be compared with a selectivity of 57% for the oxygen which desorbs from the same Ag(111) surface but which also has oxygen adsorbed on a higher index surface (figure 5). The origin of the higher selectivity of the Ag surface having both types of oxygen could be because the more strongly bound oxygen atoms produces more electropositive Ag^+ sites for the adsorption of ethene. The stronger C_2—Ag bond in the oxametallacycle could predispose it to cyclise rather than to undergo a 1,2-hydrogen shift.

4. Conclusions

(1) The Ag surface of a Ag/α-Al_2O_3 catalyst produced from a silver oxalate/α-Al_2O_3 precursor has roughly equal areas of Ag(111) morphology and of a stepped or defected surface as evidenced by the activation energies of the two oxygen desorption peaks (140 and 155 kJ mol^{-1}).

(2) The oxygen atoms adsorbed on the Ag(111) and stepped surfaces of the Ag/α-Al_2O_3 catalyst have different reactivities to ethene and different selectivities to ethene epoxide. The oxygen adsorbed on Ag(111) reacts with ethene at 373 K with an activation energy of ~60 kJ mol^{-1} and with a selectivity to ethene epoxide of ~57%. The oxygen adsorbed on the stepped and defected Ag surface reacts with ethene at 473 K with an activation energy of ~170 kJ mol^{-1} and with a selectivity to ethene epoxide of 34%.

(3) High temperature treatment of the Ag/α-Al_2O_3 catalyst causes the Ag area of the catalyst to sinter, losing half its area and virtually all of the stepped and defected surfaces.

(4) In the reaction of ethene with both types of adsorbed oxygen on the Ag/α-Al_2O_3 (oxalate precursor) catalyst, CO_2 is evolved coincidently with ethene epoxide. Therefore both ethene epoxide and CO_2 production must derive from a common rate limiting step, the most likely one being the branching reaction pathway of a common intermediate, probably an oxametallacycle.

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