

On the role of Cs, Cl and subsurface O in promoting selectivity in Ag/ α -Al₂O₃ catalysed oxidation of ethene to ethene epoxide

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Abstract

The role of Cs and Cl in promoting selectivity in ethene epoxidation over a Ag/ α -Al₂O₃ catalyst was examined by determining their effect, singly and in combination, on the kinetics of adsorption and desorption of oxygen on that catalyst. Cs has been shown to be bound to a stepped surface of the Ag that constitutes 0.7 m² g⁻¹ of the total Ag area, which is 1.9 m² g⁻¹. It thereby blocks the adsorption of oxygen on to this surface. The Cs has no effect on the bonding, activity, or selectivity of the oxygen on the Ag(111) surface of the Ag, which constitutes 1.1 m² g⁻¹ of the Ag area. The overall effect of Cs is to increase the selectivity of the Ag, because the stepped surface has an ethene epoxide selectivity of only 33%, compared with 57% for the Ag(111) surface. Cl dosed onto the Cs/Ag/ α -Al₂O₃ in an industrial reactor at BP using dichloroethane did not affect the amount of oxygen adsorbed on the Ag surface; therefore, it is located under the Ag surface. Its electron-withdrawing effect from the Ag(111) surface increases the activation energy of oxygen adsorption from 17 to 24 kJ mol⁻¹; however, it also decreases activation energy oxygen desorption from 140 to 129 kJ mol⁻¹, thus lowering the heat of adsorption from 123 to 105 kJ mol⁻¹. The overall effect of this lowering of the heat of adsorption means that the activation energy for cyclising the surface intermediate to produce ethene epoxide is lowered relative to the unselective pathway, thereby increasing selectivity. Subsurface oxygen has no effect on the kinetics of the desorption of surface oxygen, but it does reduce the activity and selectivity of surface oxygen to ethene epoxide.

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1. Introduction

In an earlier paper on ethene epoxidation, we reported that Ag/ α -Al₂O₃ catalysts prepared by impregnation of the α -Al₂O₃ support by silver oxalate (C₂O₄Ag₂) gave rise to a surface morphology of Ag with roughly equal areas of Ag(111) and a highly stepped Ag surface [1]. Temperature-programmed desorption (TPD) of oxygen from this surface

produced two peaks in the oxygen desorption spectrum, one at 523 K, corresponding to a desorption activation energy (E_d) of 140 kJ mol⁻¹ resulting from the recombinative desorption of O atoms from the Ag(111) face, and the other at 573 K, corresponding to a desorption activation energy of 155 kJ mol⁻¹ resulting from the recombinative desorption of O atoms from a stepped Ag face.

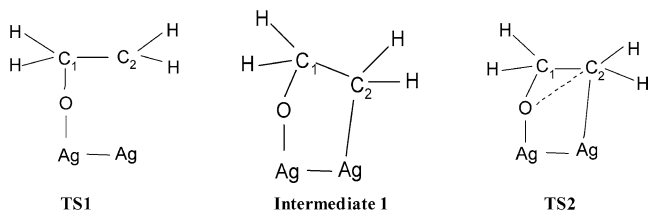
The temperature-programmed reduction of these two oxygen states by ethene produced two peaks in which ethene epoxide and CO₂ evolved coincidentally. Reduction of the O atoms adsorbed on the Ag(111) surface by ethene occurred at 373 K with an activation energy of 60 kJ mol⁻¹ and a selectivity to ethene epoxide of 57%; reduction of the O atoms adsorbed on the stepped Ag surface by ethene occurred at

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473 K with an activation energy of 170 kJ mol^{-1} and a selectivity to ethene epoxide of 33% [1]. In the absence of alkali (e.g., Cs) or halogen (e.g., Cl) promoters, taking into account the surface populations of the Ag(111) and stepped Ag surfaces, the overall selectivity of this Ag/ α -Al₂O₃ catalyst to ethene epoxide is predicted as $\sim 48\%$, in accord with what is found industrially [2,3].

The higher ethene epoxide selectivity of the 523 K desorbing O₂ peak was rationalized in terms of the reaction mechanism. Linic and Barteau constructed the reaction coordinate for ethene epoxidation using density functional theory (DFT) calculations [4,5]. They investigated the reverse reaction experimentally by studying the adsorption and decomposition of ethene epoxide on Ag(111) using TPD and high-resolution electron energy loss spectroscopy (HREELS) [6]. They concluded that transition state 1 (TS1) was formed by the initial interaction of ethene with oxygen adsorbed on Ag; this transition state then formed a stable oxametallacycle intermediate:



It was our contention that the intermediate 1 species gave rise to the coincident evolution of ethene epoxide and CO₂, and that the weaker Ag–O bond of the 523 K desorbing O₂ peak gave rise to a lower activation energy for the stretching of the Ag–O bond to form the cyclic transition state TS2 relative to the stronger Ag–O bond of the 573 K desorbing O₂.

These findings indicate that promoters, which increase the selectivity of ethene epoxide formation, do so by weakening the Ag–O bond strength and/or blocking the adsorption of oxygen on to the stepped Ag surface. It is well known that using a chlorine-containing hydrocarbon (e.g., C₂H₂Cl₂) in the gas phase in ppm quantities increases the selectivity to ethene epoxide from 48% to $\sim 75\%$, whereas the addition of Cs to the catalyst (which must be used in conjunction with CH₂Cl₂) increases the selectivity from 75 to $\sim 85\%$. This paper reports the effects of Cl and Cs on the kinetics of adsorption and desorption of O₂ on a Ag/ α -Al₂O₃ catalyst and explores the role of these promoters in improving selectivity in ethene epoxidation.

2. Experimental

2.1. Preparation of the silver oxalate-impregnated α -Al₂O₃ catalyst

The method of impregnating the α -Al₂O₃ support with silver oxalate has been patented by BP and described in de-

tail in a previous paper [1,7]. The silver oxalate (4.6 g) was added to distilled deionised water (2.86 cm³) in a beaker held at 313 K. The mixture was stirred continuously to achieve a slurry. Ethylene diamine (1.25 g) was added dropwise to the slurry, which was stirred continuously. The slurry was filtered, and the undissolved, uncomplexed silver oxalate was discarded. The liquid containing the Ag/ethylene diamine complex was retained. The α -Al₂O₃ support was added to the Ag/ethylene diamine liquid in a bottle, which was then shaken vigorously to achieve good mixing. The material was dried overnight at 353–373 K, to give a Ag/ α -Al₂O₃ catalyst with a silver loading of $\sim 10\%$ w/w.

2.2. Cesium-promoted Ag/ α -Al₂O₃ catalyst

The Ag/ethylene diamine complex was prepared as described earlier. Cesium promotion was effected by adding CsOH (0.06 g of 10% w/w) to the Ag/ethylene diamine liquid. The α -Al₂O₃ support was then added to Cs/Ag/ethylene diamine liquid, and the material was dried overnight at 353–373 K. This method gave a Ag/ α -Al₂O₃ catalyst (10% w/w) with a Cs promoter level of 300 ppm w/w.

2.3. Chlorine-promoted Cs/Ag/ α -Al₂O₃ catalyst

The chlorine-promoted Cs/Ag/ α -Al₂O₃ was prepared under industrial conditions in a unit run by BP. The reaction was carried out at 500 K at 1.5 MPa and a gas hourly space velocity of 4750 h⁻¹ using a feed composition of C₂H₄ (2%) in air and dichloroethane (ppm). The reaction was stopped by switching flows from the reactant mixture to N₂ and sweeping out the reactor while cooling the catalyst to ambient temperature. The catalyst was discharged and a representative sample was crushed, retaining the 300–350 μm material. The intention here was to obtain a catalyst that had the exact level and nature of Cl promoter as that which produced selectivity to ethene epoxide on the order of 80%. This was considered important because Campbell et al. showed that depositing Cl onto Ag(110) by dosing gas phase Cl₂ at 300 K resulted in areas of the Ag(110) that were chlorided and areas that were Cl free [8]. The Cl-free areas of the Ag(110) showed no evidence of the adsorbed Cl and behaved like clean Ag(110) in terms of the kinetics of adsorption and desorption of oxygen on it [8].

2.4. The gases

Helium (99.999%; Linde), was passed through a Chromapack Gas Clean moisture trap before use. Oxygen (99.995%; British Oxygen Company) was passed through a moisture trap before use.

2.5. The microreactor system

The multipurpose microreactor used in these experiments was as described previously [9]. It is a single stainless steel

tube (2 cm long, 0.4 cm i.d.) housed in a metal heating block. The reactor is connected on-line to a mass spectrometer (Hiden Analytical, Warrington, UK) through a heated capillary. The reactor can be cooled to 77 K by pumping liquid N₂ through the metal block; it can also be heated to 1100 K in a temperature-programmed mode using a Newtronics controller. The thermocouple used to register the temperature of the catalyst and communicate it to the controller was embedded in the catalyst bed.

3. Results and discussion

3.1. The kinetics of adsorption and desorption of oxygen on the unpromoted Ag/ α -Al₂O₃ catalysts

Fig. 1 (red line) shows the TPD spectrum of O₂ from a fresh sample of the Ag/ α -Al₂O₃ catalyst. The oxygen was dosed onto the Ag by heating the Ag/ α -Al₂O₃ (0.25 g) from ambient to 513 K at 10 K min⁻¹ under pure O₂ (101 kPa, 25 cm³ min⁻¹); the catalyst was held at 513 K under the O₂ flow for 1 h before being cooled to ambient temperature under the O₂ flow. The flow was then switched to He, and the O₂ desorption spectrum was obtained by heating the catalyst under the He flow at 10 K min⁻¹ from ambient temperature to 773 K.

Close inspection of the first O₂ desorption spectrum in Fig. 1 (red line) shows that the peak maximum temperature of the low-temperature desorption peak is quite broad, ranging from 513 to 523 K. The O₂ desorption spectrum, shown by the black line in Fig. 1, is obtained by treating O₂ as described earlier onto the Ag/ α -Al₂O₃ catalyst that

had been heated to 773 K to produce the desorption spectrum shown by the red line. The spectrum shown by the black line has only one peak maximum at 513 K. Heating the Ag/ α -Al₂O₃ catalyst to 773 K sintered the Ag, resulting in a loss of the state that gives rise to the 570 K desorption peak maximum—the stepped surface—and thus a sharpening of the 513/523 K peak.

Fig. 2 shows the O₂ desorption spectra obtained by exposing the sintered Ag/ α -Al₂O₃ catalyst to pure O₂ (101 kPa, 25 cm³ min⁻¹) for 5 min at 353 (blue line), 383 (green line), 423 (red line), and 453 K (black line). After each 5-min exposure, the catalyst was rapidly cooled to ambient temperature in the O₂ flow, the flow was switched to He, and temperature programming was begun.

Fig. 2 shows that the fraction of the dosing O₂ that was adsorbed increased with increasing adsorption temperature, and so the adsorption of O₂ on the Ag was activated. The Ag area of the sintered Ag/ α -Al₂O₃ catalyst was determined in the following manner. Oxygen was dosed on to the catalyst (O₂ 101 kPa, 60 min, 25 cm³ min⁻¹), producing a limiting (saturation) coverage. Campbell and Paffett [10] found that the saturation coverage of Ag(111) by O atoms was a 0.67 monolayer. The Ag surface atom density calculated from the unit cell dimensions was 1.19×10^{15} Ag atoms cm⁻². Therefore, saturation oxygen atom coverage of Ag(111) was $0.67 \times 1.19 \times 10^{15}$ O atoms cm⁻², equivalent to 12.5×10^{-16} cm² Ag(111)/O atom or 25×10^{-16} cm² Ag(111)/O₂ molecule desorbed. (We have shown that the sintered catalyst surface is Ag(111) [1].) The amount of O₂ desorbed from 0.25 g of the sintered Ag/ α -Al₂O₃ catalyst was 0.6×10^{18} molecules or 2.4×10^{18} molecules O₂ g⁻¹.

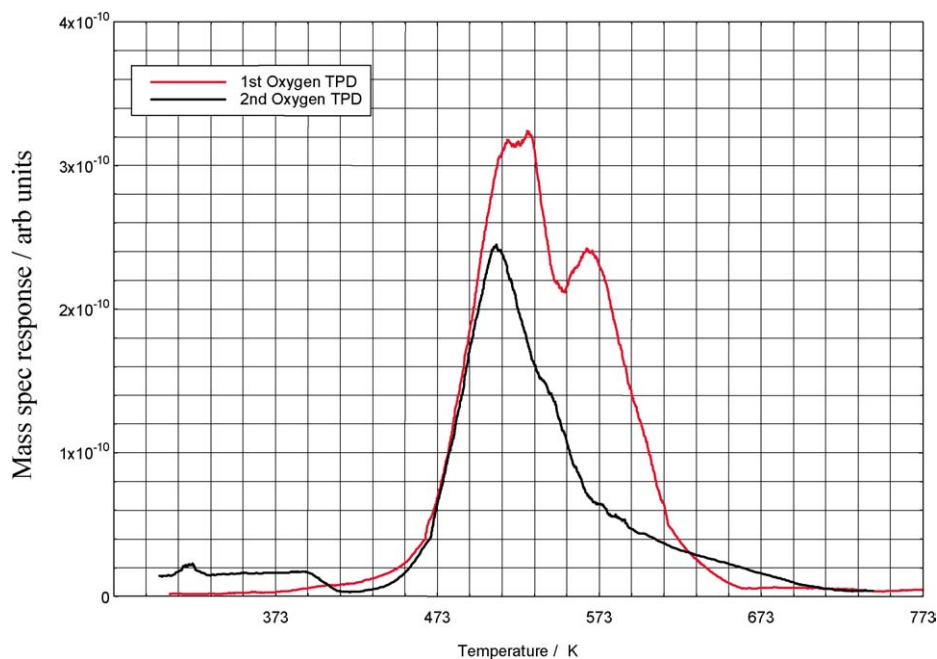


Fig. 1. The oxygen desorption spectra from the unpromoted Ag/ α -Al₂O₃ catalyst.

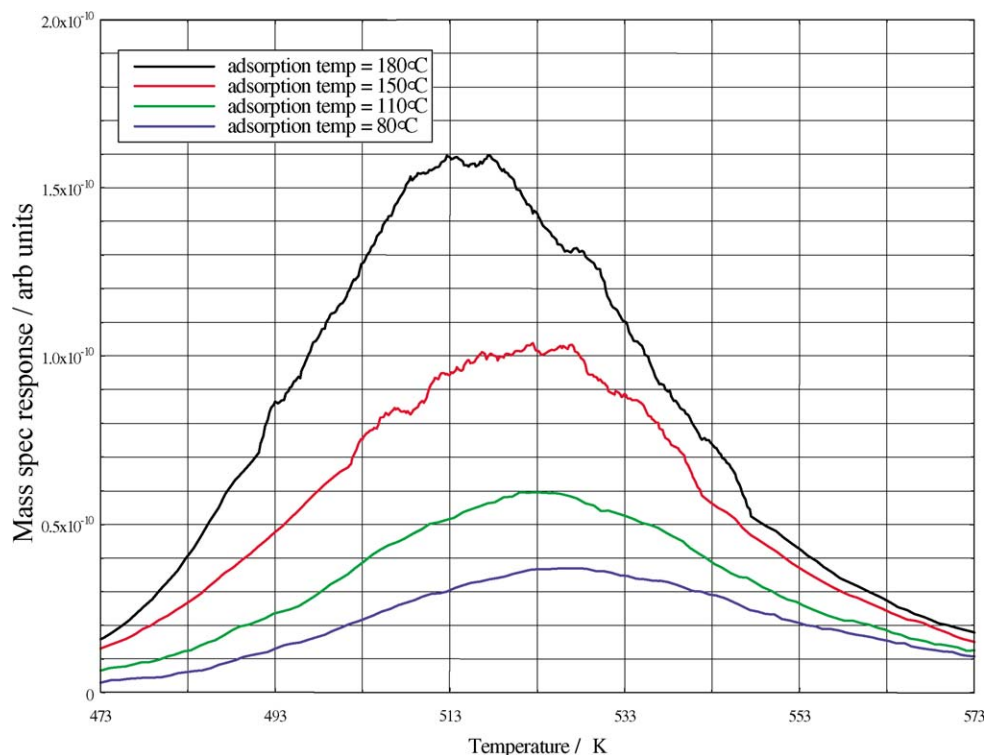


Fig. 2. The oxygen desorption spectra obtained by exposing the sintered Ag/ α -Al₂O₃ catalyst to pure O₂ for 5 min at 353, 383, 423 and 453 K.

The silver metal area of the sintered Ag/ α -Al₂O₃ catalyst was then 0.6 m² g⁻¹.

The activation energy (E_a) for oxygen adsorption can be calculated on the sintered Ag/ α -Al₂O₃ catalyst from a plot of the logarithm of the amount of O₂ desorbed for each dosing temperature against the reciprocal of the dosing temperature on the following basis. The Ag area on the sintered catalyst was 0.6 m² g⁻¹, and so for an Ag surface atom density of 1.19×10^{15} atoms cm⁻², there are 1.8×10^{18} Ag sites on 0.25 g of the Ag/ α -Al₂O₃ catalyst loaded into the reactor. The total oxygen atom dosage in the 5-min flow of O₂ (101 kPa, 25 cm³ min⁻¹) was 6×10^{21} atoms; thus, even at saturation coverage of the Ag, the depletion of the amount of gas phase O₂ dosed was only 0.03%. A plot of the logarithm of the amount of O₂ desorbed, corresponding to the amount adsorbed, for each dosing temperature against the reciprocal of the dosing temperature, gives a value of 17 ± 1 kJ mol⁻¹ for the adsorption activation energy.

The temperatures of the maxima of the desorption peaks shown in Fig. 2 decreased from 525 K for the lowest coverage peak to 513 K for the highest coverage peak. This and the fact that the peaks are symmetric demonstrate that the desorption is second order [11]. Therefore, a plot of $\ln(\text{desorption rate}/\text{coverage}^2)$ versus $1/T$ gives the activation energy for desorption (E_d). Table 1 lists the activation energies to desorption for each of the adsorption temperatures so obtained. Table 2 lists the relationship between the coverage of the Ag(111) surface of the unpromoted Ag/ α -Al₂O₃ catalyst and the adsorption temperature.

Table 1

Activation energies for oxygen desorption from the unpromoted Ag/ α -Al₂O₃ catalyst obtained by line shape analysis of the oxygen desorption peaks of Fig. 2

Adsorption temperature (K)	Gradient of the line	Activation energy to desorption (kJ mol ⁻¹)
353	-16861	140.2
383	-16628	138.4
423	-16767	139.4
453	-16971	141.1

Table 2

Relationship between the coverage of the Ag(111) surface of the unpromoted Ag/ α -Al₂O₃ catalyst by atomic oxygen (monolayers) and the adsorption temperature

Adsorption temperature (K)	Coverage of the Ag(111) of the unpromoted Ag/ α -Al ₂ O ₃ surface by O atoms (monolayers)
353	0.11
383	0.17
423	0.28
453	0.45

The value of E_d is 139.8 ± 1.4 kJ mol. Therefore, the heat of adsorption of oxygen on the Ag/ α -Al₂O₃ catalyst ($\Delta H = E_a - E_d$) is 123 ± 1.4 kJ mol⁻¹. These values for the desorption activation energy and the heat of adsorption of oxygen on the sintered Ag/ α -Al₂O₃ catalyst are consistent with the surface being predominantly Ag(111) [12,13].

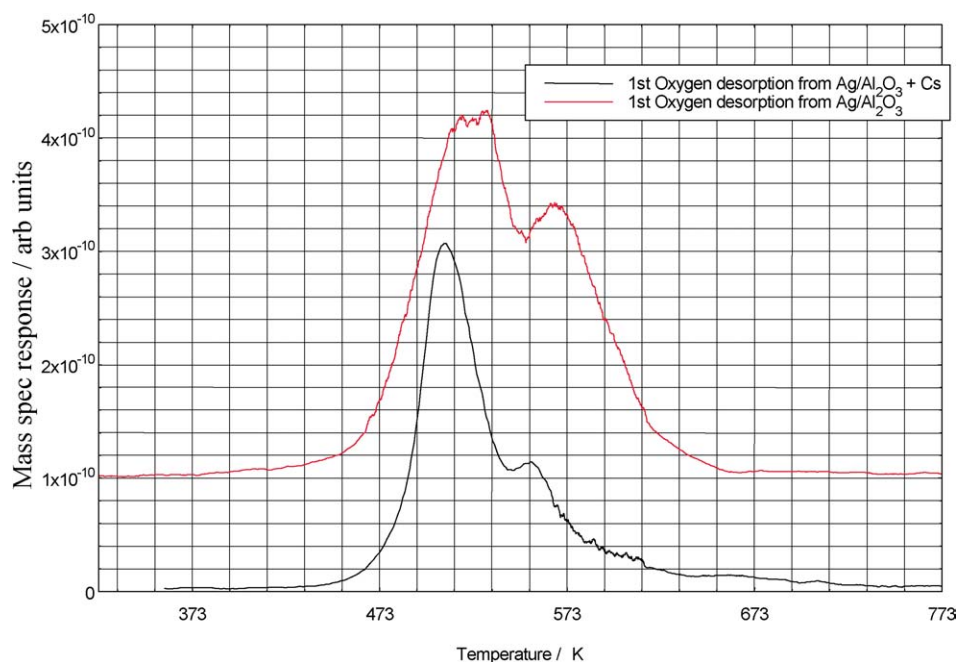


Fig. 3. Oxygen desorption spectra from unpromoted (red line) and Cs-promoted (black line) Ag/ α -Al₂O₃ catalyst.

3.2. The kinetics of adsorption and desorption of oxygen on Cs-promoted Ag/ α -Al₂O₃ catalysts

The black curve in Fig. 3 represents the O₂ desorption spectrum from the Cs-promoted Ag/ α -Al₂O₃ catalyst prepared as described in Section 2. The oxygen was dosed onto the catalyst to saturation by temperature programming the catalyst from ambient to 513 K at 10 K min⁻¹ in a pure oxygen flow, and the catalyst was held at that temperature for 1 h before the temperature was decreased to ambient under the oxygen flow. For comparison, the red curve in Fig. 3 depicts the O₂ desorption spectrum from an as-prepared sample of unpromoted Ag/ α -Al₂O₃ catalyst. Fig. 3 clearly shows that adding Cs (300 ppm w/w) to the Ag/ α -Al₂O₃ catalyst reduced the amount of O₂ desorbing at 570 K by a factor of 3 or more, but had no effect on the amount or the peak maximum temperature of the O₂ desorbing at 513 K.

We had associated the 570 K O₂ desorbing peak with O adsorbed on a stepped Ag surface [1]. Therefore, as would seem perfectly reasonable, the Cs was located on the stepped Ag surface. Furthermore, the Cs was stable in that position and also appeared to stabilize the Ag surface from sintering, as can be seen in Fig. 4, which compares the first and second O₂ desorption spectra. The area of the Ag(111) face was reduced by 7% by heating to 773 K, whereas that of the Cs-doped stepped face was reduced by 10%. (The O₂ desorption spectrum of an unpromoted Ag/ α -Al₂O₃ catalyst that had been sintered by heating to 773 K showed a near-complete loss of the 570 K desorption peak.) The Cs adsorbed on the stepped surface did not affect the peak maximum temperature of the O₂ desorbing from the Ag(111) face. This is in sharp contrast to the findings of Campbell,

who reported that adsorption of oxygen onto a Cs-doped Ag(111) face produced a surface cesium “oxide” (\sim CsO₃) that decomposed at \sim 610 K, producing Cs and O₂ in the gas phase [14]. We found no desorption of O₂ at 610 K. Grant and Lambert, in contrast, found multiple O₂ desorbing states depending on the Cs coverage of the Ag(111) [15]. We found no states other than that from clean Ag(111). Thus it seems clear that there was no Cs on the Ag(111) surface of the Ag/ α -Al₂O₃ catalyst. Campbell’s observation that Cs makes the Ag(111) face less active but more selective for ethene epoxidation [14] and Grant and Lambert’s apparently contradictory observation that Cs enhances both the total activity and selectivity for ethene epoxidation [15] are not relevant to our study where no Cs exists on the Ag(111) face of the Cs-doped Ag/ α -Al₂O₃ catalyst.

We showed in an earlier paper [1] that ethane epoxide selectivity was only 33% for the 570 K O₂ desorption peak and 57% for the 513/523 K peak, giving an overall selectivity of 47%. Lowering the surface population of the less-selective face by a factor of 3 would predict an increase in overall selectivity from 47 to 55%. This magnitude of increased selectivity achieved by adding Cs is roughly the same as that found industrially in the doubly (Cs + Cl)-promoted catalyst, where the addition of Cs- to a Cl-promoted system increased selectivity from \sim 75 to \sim 85%.

The normal operating conditions for Al₂O₃-supported Ag catalysts are 500 K and 1.5 MPa. These conditions will not sinter or anneal the unselective stepped surface, and so for commercial catalysts, prepared from the silver oxalate precursor patented by BP, adding Cs to the catalyst to block the activity of the unselective stepped surface is essential.

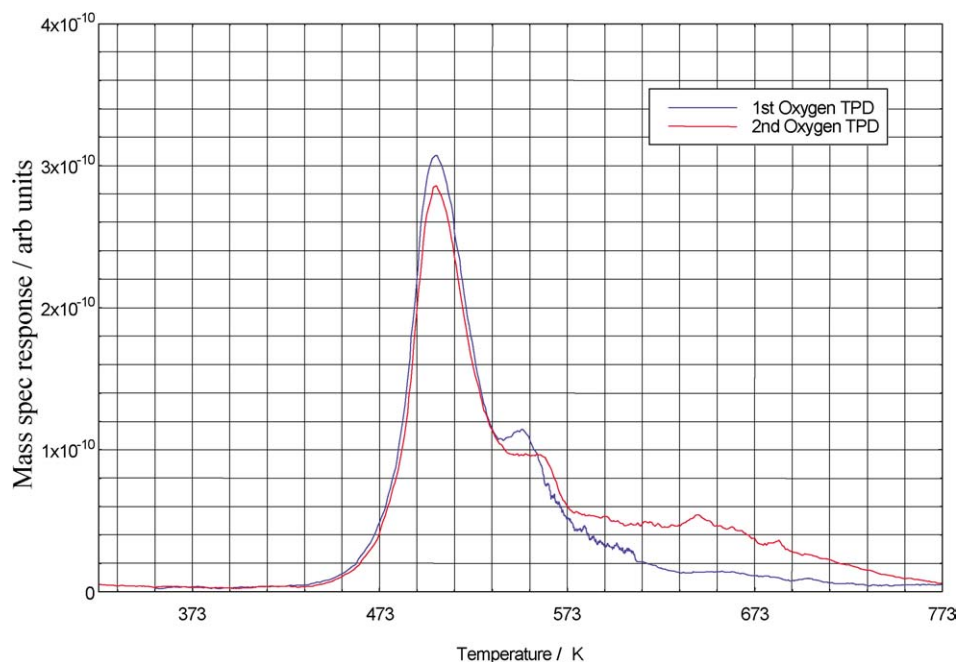


Fig. 4. Oxygen desorption spectra from the Cs-promoted Ag/ α -Al₂O₃ catalyst showing that Cs stabilises the surface morphology.

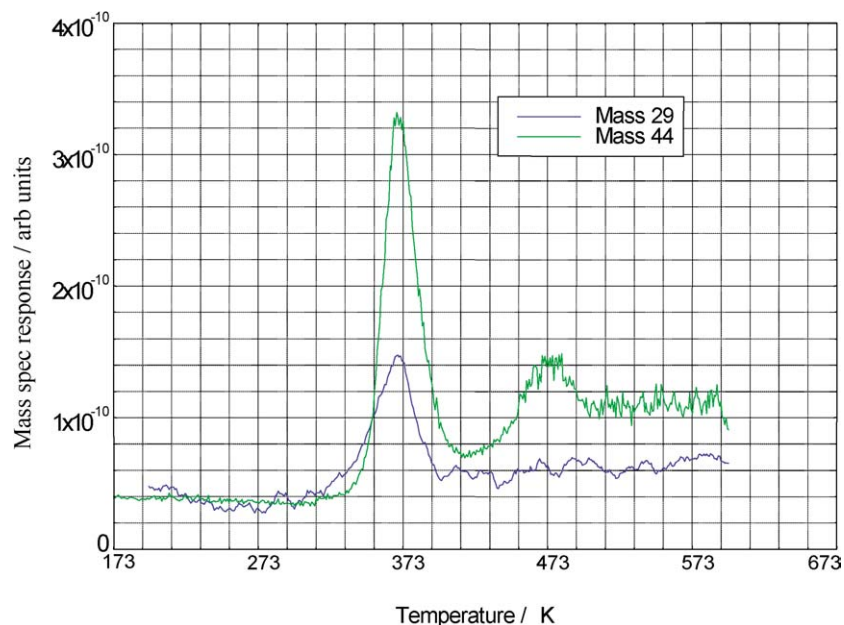


Fig. 5. Temperature-programmed reaction of ethene with the oxygen adsorbed on the Cs-promoted Ag/ α -Al₂O₃ catalyst.

3.3. Temperature-programmed reaction of ethene with oxygen adsorbed on the Ag(111) surface of the Cs-promoted Ag/ α -Al₂O₃ catalyst

Fig. 5 provides corroborative evidence that the role of Cs is simply one of site blocking and that Cs has no electronic-promoting effect that would increase the selectivity of ethene epoxide formation. This figure shows the temperature-programmed reaction TPR spectrum of ethene with the oxygen adsorbed on the Cs-promoted Ag/ α -Al₂O₃ catalyst.

The oxygen was dosed on to the Cs-promoted Ag/ α -Al₂O₃ catalyst to saturation coverage using the method described earlier, which was used to produce the surface species giving rise to the desorption spectra shown in Fig. 3 (black line) and Fig. 4.

Once the catalyst was cooled to ambient temperature under the oxygen flow and was switched the flow to He, the catalyst was then further cooled to 173 K under He. The temperature was then programmed up to 193 K at 10 K min⁻¹ under the He flow, at which point the flow was switched to

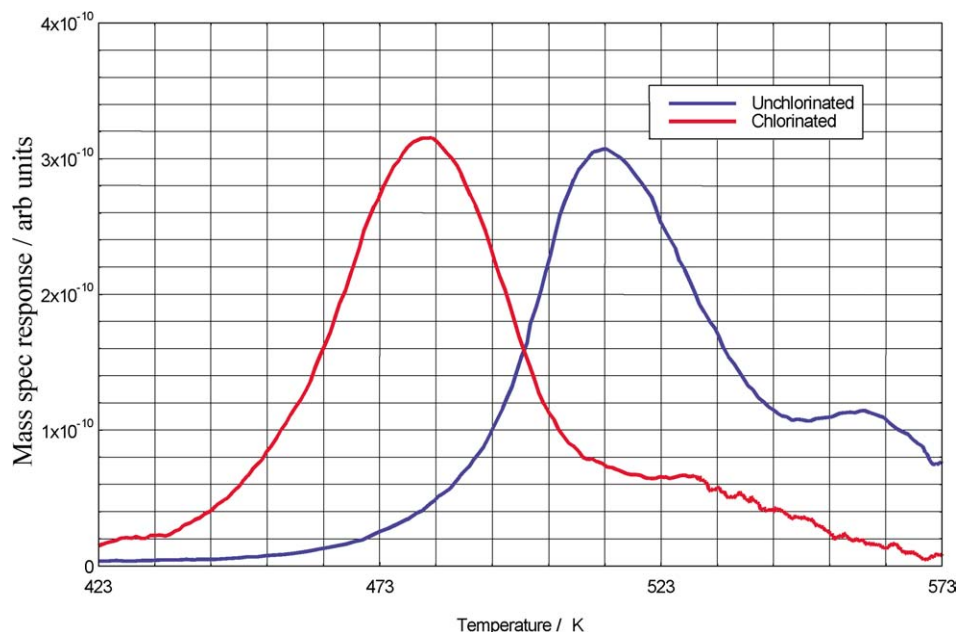


Fig. 6. Oxygen desorption spectra from a Cs-promoted Ag/ α -Al₂O₃ catalyst (blue line) and from a Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst (red line).

an ethene/He flow (2% ethene, 101 kPa, 25 cm³ min⁻¹) and the temperature raised to 573 K at the same heating rate.

Fig. 5 shows that ethene epoxide ($m/z = 29$) and CO₂ ($m/z = 44$) evolved coincidentally at 373 K, as had been shown previously by ethene TPR of oxygen adsorbed on unpromoted Ag/ α -Al₂O₃ catalyst [1]. The selectivity of the 373 K peak obtained for the Cs-promoted Ag/ α -Al₂O₃ catalyst calculated from Fig. 5 was only 40%, lower than the value of 49% found for the unpromoted catalyst [1]. These selectivities are calculated in Fig. 5 using a flat baseline at 0.4×10^{-10} units. If a sloping baseline is used to connect the ethene epoxide and CO₂ peaks, then the selectivities of the 373 K peak for the Cs-promoted Ag/ α -Al₂O₃ catalyst are both 44%. In either case, therefore, it is clear that the Cs adsorbed on the stepped Ag surface does not promote the kinetics of the selective reaction pathway of the adsorbed oxametallacycle adsorbed on the Ag(111) face. As explained earlier, the observations of Campbell [14] and of Grant and Lambert [15] on the role of Cs on Ag(111) in promoting ethene epoxidation on that surface do not apply to the present study.

That the Cs promoter operates by blocking adsorption of oxygen on to the stepped Ag surface is clear from Fig. 5. The surface population of the 473 K peak in which ethene epoxide and CO₂ were formed coincidentally with a selectivity to ethene epoxide of 33% during ethene TPR of the unpromoted Ag/ α -Al₂O₃ catalyst [1] decreased to only 20% of the unpromoted value by Cs promotion.

3.4. The kinetics of adsorption and desorption of oxygen on a Cl- and Cs-promoted Ag/ α -Al₂O₃ catalyst

The blue curve in Fig. 6 is the O₂ desorption spectrum from a Cs-promoted Ag/ α -Al₂O₃ catalyst that has no Cl

on it. The red curve in Fig. 6 is the O₂ desorption spectrum from a Cl-promoted Ag/Cs/ α -Al₂O₃ catalyst, with the Cl promoter deposited on the Ag by reaction of 1,2-dichloroethane (ppm) with the partially oxidized Ag surface obtaining during ethene epoxidation at 500 K and 1.5 MPa in a C₂H₄/air (2% C₂H₄) mixture. The O₂ dosage (O₂, 101 kPa, 25 cm³ min⁻¹, 513 K, 1 h) was the same for both, the dosage that produced saturation coverage (0.67 ML) of the Ag by O atoms. We have demonstrated that Cs promotion simply blocks O₂ adsorption on the stepped surface of the Ag/ α -Al₂O₃ catalyst, but does not affect the kinetics of desorption of O₂ from the Ag(111) face.

Promotion by Cl lowers the O₂ desorption peak maximum temperature from 513 to 481 K. Significantly, however, it has no effect on the amount of oxygen adsorbed; the amount of oxygen desorbing from the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst is exactly the same as that from the Cl-free Cs/Ag/ α -Al₂O₃ catalyst. This finding is somewhat surprising, because inductively coupled plasma mass spectrometry showed a Cl atom content of the Ag component of the catalyst of 0.2 monolayer equivalent. X-ray photoelectron spectroscopy measurements by Lambert et al. [16] showed that the Al₂O₃ support did not pick up any Cl under halocarbon treatment, and so the Cl is associated with the Ag.

Several conclusions can be drawn based on these findings, including the following: (i) The Cl did not block sites (as did the Cs) and thus was not on the external surface of the catalyst; (ii) the Cl diffused below the surface of the Ag, as Bowker et al. reported [13]; (iii) promotion by Cl was electronic; and (iv) Cl promotion functioned to lower the Ag–O bond strength. The distinct difference in the behaviour of the Cl atoms observed here (i.e., subsurface, not site blocking) and that observed by Campbell and Paffett

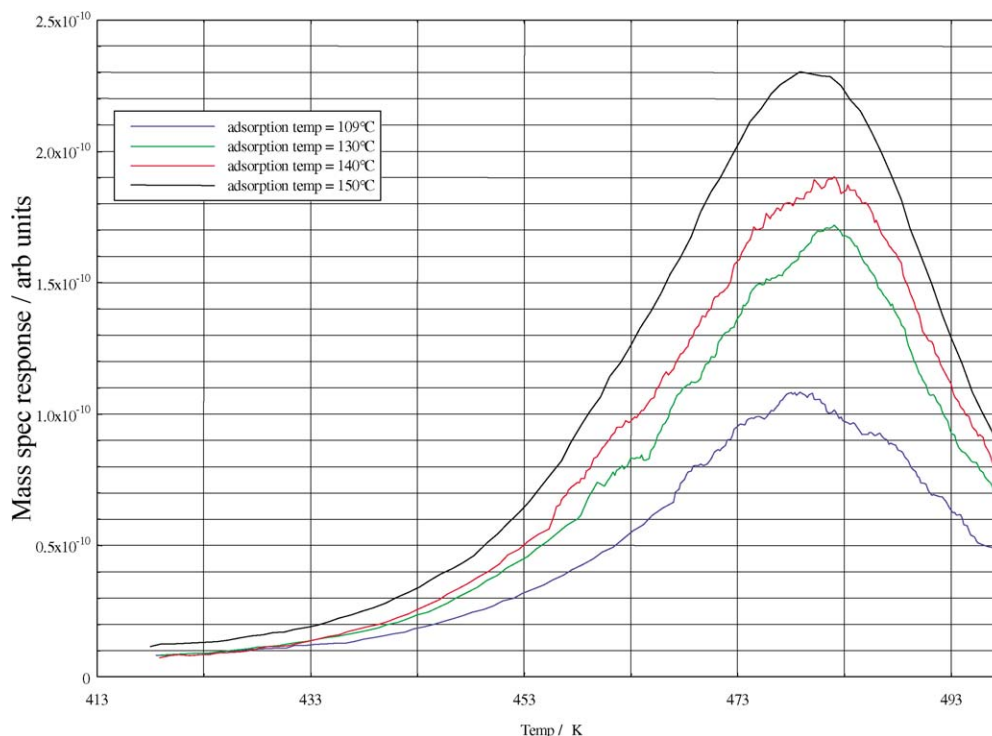


Fig. 7. Oxygen desorption spectra obtained by dosing O₂ on to the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst for 5 min at 382, 403, 413 and 423 K.

(i.e., site blocking, ordered surface overlayer) [8] can be explained by the difference in the methods of dosing the Cl atoms on to the catalyst. Campbell and Paffett dosed on the Cl atoms using gas phase Cl₂ at 300 K to produce an ordered Cl overlayer discernible by LEED [8]. In contrast, Lambert et al. promoted an Ag/ α -Al₂O₃ catalyst with Cl by injecting CH₂Cl₂ into C₂H₄ (18.6 kPa)/O₂ (7 kPa)/He (75.4 kPa) at 518 K, which to some extent mirrored our method of Cl dosing [16]. Lambert et al. [16] also reported that Cl increased selectivity but also caused site blocking. This apparent contradiction can be explained by the fact that initially the Cl is dosed onto the surface by reaction, at which point Lambert et al. recorded the change in activity and selectivity on-line by mass spectrometry and gas chromatography. Bowker and Waugh [17] and Piao et al. [18] showed that migration of Cl from the surface of Ag(111) into the bulk is activated. Therefore, depositing the Cl in a plant over the time period necessary to produce optimum performance will produce subsurface Cl by the slow activated migration of Cl from the surface of the Ag(111) into the bulk. Pulsing the CH₂Cl₂ will produce surface Cl that will need time to migrate into the bulk.

By simply comparing the temperature of the O₂ desorption peak maximum of the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst (481 K) with that of a Cl-free Cs/Ag/ α -Al₂O₃ catalyst for which a desorption activation energy of 140 kJ mol⁻¹ has been calculated by line shape analysis (513 K), it is possible to calculate a value of 130 kJ mol⁻¹ for the value of the desorption activation energy of O₂ from the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst.

Table 3

Relationship between the coverage of the Ag(111) surface of the Cl promoted Cs/Ag/ α -Al₂O₃ catalyst by oxygen atoms (monolayers) and adsorption temperature

Adsorption temperature (K)	Coverage of the Ag(111) of the Cl promoted Cs/Ag/ α -Al ₂ O ₃ surface by O atoms (monolayers)
382	0.21
403	0.34
413	0.36
423	0.46

A more rigorous method for determining the desorption activation energy of O₂ from a Cl-promoted Ag/ α -Al₂O₃ catalyst is to perform line shape analysis of the O₂ desorption peaks produced by dosing O₂ for the same length of time at different adsorption temperatures on to the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst. Fig. 7 shows the O₂ desorption spectra obtained by dosing O₂ (101 kPa, 25 cm³ min⁻¹) for 5 min onto the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst at the adsorption temperatures 382 K (blue line), 403 K (green line), 413 K (red line), and 423 K (black line).

As was observed in carrying out the same experiment on a Cl-free Ag/ α -Al₂O₃ catalyst (Fig. 2), so here, with the Cl-promoted catalyst, increasing the adsorption temperature resulted in increased O₂ adsorption. Table 3 lists the coverage of the Ag(111) surface of the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst as a function of the adsorption temperature. Comparing Table 3 with Table 2 shows that the surface coverages by O atoms of the Cl-promoted Ag(111) were the same as

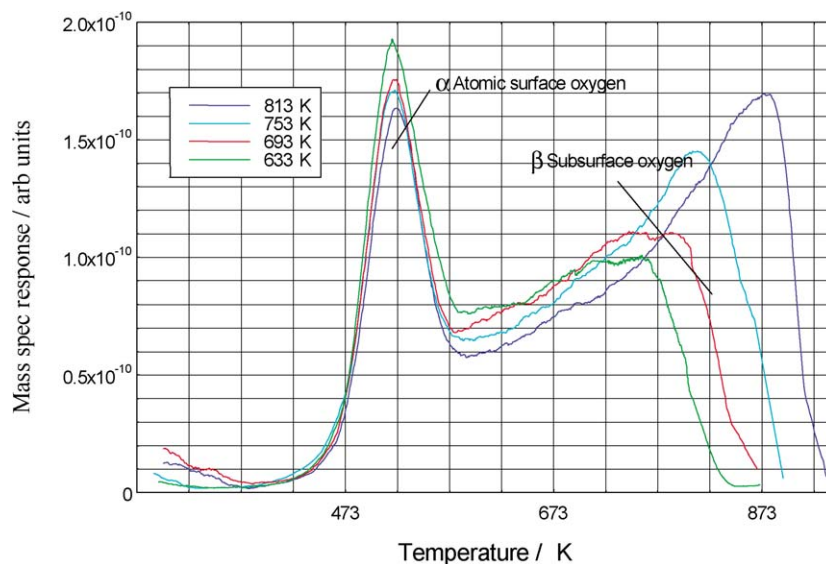


Fig. 8. The oxygen desorption spectra from an unpromoted Ag/ α -Al₂O₃ catalyst containing between 1.6 and 2.8 monolayers of subsurface oxygen.

those for the unpromoted Ag(111) at the same adsorption temperature, providing additional evidence that the Cl promoter is subsurface.

As explained earlier, plotting the logarithm of the amount adsorbed versus the reciprocal of the adsorption temperature is a valid way to obtain the adsorption activation energy. The value obtained from this method was $23.7 \pm 1 \text{ kJ mol}^{-1}$, which is 7 kJ mol^{-1} higher than that obtained for a Cl-free Cs/Ag/ α -Al₂O₃ catalyst. This increased adsorption activation energy for the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst is consistent with subsurface Cl withdrawing electrons required for the dissociative adsorption of O₂ from the surface region.

Line shape analysis on the Cl-promoted O₂ desorption (Fig. 7), done by plotting $\ln(\text{desorption rate}/\text{coverage}^2)$ versus K/T gave a desorption activation energy of 129 kJ mol^{-1} , a value only 1 kJ mol^{-1} lower than that obtained using the peak maximum temperature. The heat of adsorption of O₂ on Ag was reduced from 124 kJ mol^{-1} on a Cl-free Cs/Ag/ α -Al₂O₃ catalyst to 105 kJ mol^{-1} on the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst.

The oxametallacycle (intermediate 1) is the key intermediate in the formation of ethene epoxide on Ag, and selectivity in this reaction is determined by the propensity of that intermediate to cyclise relative to its propensity to undergo 1,2-hydrogen shift [3,4]. In an earlier paper [1] in which we found two O₂ desorption peaks at 523 and 573 K, with the lower desorption peak having an ethene epoxide selectivity of 57% compared with a value of 33% for the 573 K peak, we argued that the increased selectivity for the weaker Ag–O bond meant that the intermediate that it formed had a greater propensity to cyclise than did the intermediate formed by bond of the ethene to the stronger Ag–O bond. It is a logical extension of this work that weakening the Ag–O bond strength will result in greater selectivity to ethene epoxide. Here we find that Cl promotion does just that, which ac-

counts for its positive effect in promoting higher selectivity in Ag-catalysed ethene epoxidation.

In the case of ethene epoxidation over Ag/ α -Al₂O₃ catalysts prepared from a silver oxalate precursor, the promoters Cl and Cs act independently and additively. Industrially, it is found that electronic promotion by subsurface Cl weakens the Ag–O bond strength and raises the selectivity from 47 to $\sim 75\%$. The Cs promoter located on the stepped Ag surface blocks the adsorption of the less-selective oxygen atoms on this surface and raises the selectivity to $\sim 85\%$.

3.5. The kinetics of oxygen desorption from an unpromoted Ag/ α -Al₂O₃ catalyst containing 1.6–2.8 monolayers of subsurface oxygen

The existence of subsurface oxygen in Ag has been reported previously [19–21]. It desorbs from the Ag over a range of temperatures above that at which surface oxygen desorbs. It has been proposed that subsurface oxygen exerts an electronic effect on the surface oxygen and acts as a promoter in the same way as Cl does. Indeed, Backx et al. [22] have claimed that subsurface oxygen in Ag is essential for the epoxidation of ethene.

We have investigated the effect of subsurface oxygen in Ag on the desorption kinetics of surface oxygen. If it had a promoting effect, then we would expect to see the peak maximum temperature for surface oxygen desorption decreasing from 513/523 K to the value (481 K) found for promotion by Cl.

Fig. 8 shows the oxygen desorption spectra obtained after dosing O₂ (101 kPa, $25 \text{ cm}^3 \text{ min}^{-1}$) onto the Ag/ α -Al₂O₃ catalyst for 1 h at 633 K (green curve), 693 K (red curve), 753 K (blue curve), and 813 K (black curve). After the oxygen was dosed for 1 h at the desired adsorption temperature, the catalyst was cooled to ambient temperature under O₂

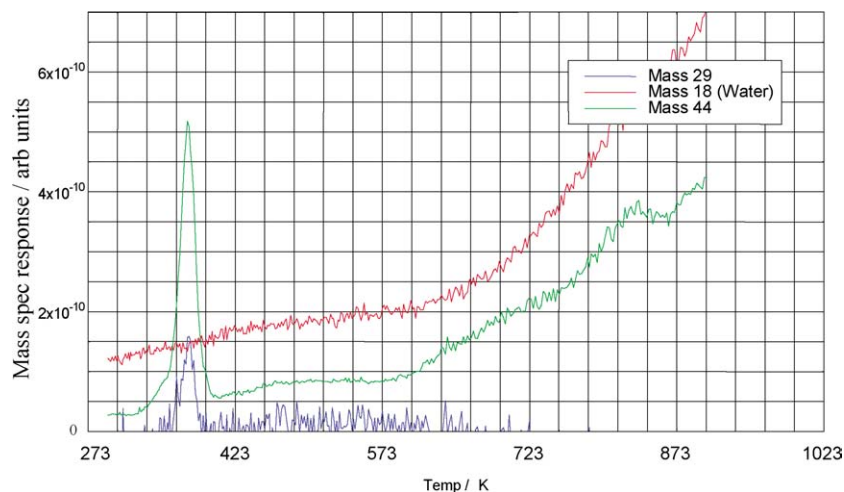


Fig. 9. Temperature-programmed reaction of ethene with surface and subsurface oxygen of the unpromoted Ag/ α -Al₂O₃ catalyst.

Table 4

The relationship between the number of monolayers of subsurface oxygen and the adsorption temperature

Adsorption temperature (K)	Amount of subsurface oxygen (surface monolayer equivalents)
633	1.6
693	2.0
753	2.3
813	2.8

flow. The flow was then switched to He, and the spectra were obtained by raising the temperature at 10 K min⁻¹ from ambient to 923 K.

The figure shows large, apparently zero-order peaks originating at ~590 K for all adsorption temperatures. These peaks maximized at ~760 K for the lowest coverage and increased to 873 K for the highest coverage. They represent the desorption of O₂ from the subsurface of the Ag. Table 4 lists the adsorption temperatures and the corresponding amounts of subsurface oxygen calculated in surface monolayer equivalents, using a value of 1.19 atoms cm⁻² as the surface Ag atom density and an Ag area of 1 m² g⁻¹.

However, Fig. 8 shows that the surface oxygen peak maximum was unaffected by this subsurface oxygen. Its value remained fixed at 520 K regardless of the amount of subsurface oxygen in the range of 1.6–2.8 monolayers. Thus the subsurface oxygen does not weaken the surface Ag–O bond as Cl does and so will not promote the increased selectivity to ethene epoxide that subsurface Cl does.

3.6. TPR of ethene with surface and subsurface oxygen on the unpromoted Ag/ α -Al₂O₃ catalyst

Fig. 9 shows the TPR spectrum obtained by passing an ethene/He (2% ethene, 101 kPa, 25 cm³ min⁻¹) stream over the unpromoted Ag/ α -Al₂O₃ catalyst that had been dosed with pure O₂ for 1 h at 773 K. This produced >2.3 monolayers of subsurface oxygen atoms, as well as saturation cov-

erage of the oxygen state that desorbed at 523 K, the oxygen desorbing from Ag(111) (see Fig. 8).

One peak can be observed at 373 K in which ethene epoxide and CO₂ evolve coincidentally. The selectivity of ethene epoxide in this peak was only 40% using a flat baseline and 44% using a sloping baseline for the CO₂ peak. Reaction of the ethene with subsurface oxygen was completely unselective, producing only CO₂ and H₂O. Thus the subsurface oxygen was unselective of itself and did not promote an increase in selectivity of the adsorbed oxygen.

Lambert et al. [16] showed that the promotional effect in ethene epoxidation of the halogen series, F, Cl, Br, and I, correlates with the electron affinity of the halogen. Cl, with an electron affinity of –349 kJ mol⁻¹, is the most selective, whereas I (electron affinity = –295 kJ mol⁻¹) shows only negligible promotional activity [16]. It is not surprising, therefore, that subsurface O (electron affinity = –141 kJ mol⁻¹) [23] does not exhibit any promotional activity.

4. Conclusions

1. The Cs promoter is bound to the stepped surface of the Ag component of the Ag/ α -Al₂O₃ catalyst. (This stepped surface constitutes 0.7 m² g⁻¹ of the total Ag area of 1.9 m² g⁻¹ [1].)
2. Held in that position, the Cs promoter blocked adsorption of oxygen onto that surface. However, it did not affect the activity to ethene or selectivity to ethene epoxide of the oxygen adsorbed on the Ag(111) surface.
3. Oxygen adsorbed on the stepped Ag surface was only 33% selective, compared with a value of 57% on the Ag(111) surface, which constitutes 1.1 m² g⁻¹ of the 1.9 m² g⁻¹ total Ag area [1]. Therefore, blocking adsorption of oxygen on to the stepped Ag surface will increase the overall selectivity of the Ag surface to ethene epoxide formation.

4. Because the Cl promoter did not block the adsorption of oxygen on the Ag(111) surface of a Cs/Ag/ α -Al₂O₃ catalyst, we conclude that it is held under the surface of the Ag.
5. The Cl promoter is electronic in its function and withdraws electrons from the surface Ag atoms. Evidence for this is found in the increase in the activation energy for adsorption of oxygen on to the Ag(111) surface from 17 kJ mol⁻¹ for Cs/Ag/ α -Al₂O₃ to 24 kJ mol⁻¹ for Cl-promoted Cs/Ag/ α -Al₂O₃.
6. The Cl promoter lowered the desorption peak maximum temperature from 513 K for the Cs/Ag/ α -Al₂O₃ catalyst to 481 K for the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst. Thus, the activation energy for the desorption of oxygen from the Ag(111) surface was lowered from 140 kJ mol⁻¹ for the Cs/Ag/ α -Al₂O₃ catalyst to 129 kJ mol⁻¹ for the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst.
7. Decreasing the heat of adsorption of oxygen on the Ag(111) face of the Cs/Ag/ α -Al₂O₃ catalyst from 123 to 105 kJ mol⁻¹ for the Cl-promoted Cs/Ag/ α -Al₂O₃ catalyst decreased the activation energy for cyclisation of the surface intermediate relative to the activation energy of the unselective pathway, which remained unchanged, and so increased the selectivity to ethene epoxide.
8. Subsurface oxygen had no effect on the desorption kinetics of the oxygen held on the Ag(111) surface of the Ag/ α -Al₂O₃ catalyst. It also had no effect on the activity and selectivity of the oxygen on the Ag(111) surface to reaction with ethene to form ethene epoxide.

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