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The detailed kinetics and mechanism of ethylene epoxidation on an oxidised Ag/α-Al_2O_3 catalyst

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ABSTRACT

Selectivity in the epoxidation of ethylene over Ag/α-Al_2O_3 catalysts has been shown to be a function of the Ag–O bond strength. The weaker the Ag–O bond is, the more selective it is. Promotion by Cl atoms, which are held under the surface of the Ag, is effected by their weakening the Ag–O bond. Promotion by Cs is effected by its being adsorbed on the Ag sites which form the stronger Ag–O bond, so preventing the formation of the unselective Ag–O bond. The reaction proceeds by the ethylene adsorbing on surface O atoms, forming two types of Ag–O–CH_2–CH_2 intermediates, whose fate is a function of the Ag–O bond strength. The Ag–O–CH_2–CH_2 intermediate formed on the area of the Ag surface having the weaker Ag–O bond (the Ag(1 1 1) surface) has a greater probability of cyclising to form EO than being involved in unselective H abstraction reactions. Conversely, the Ag–O–CH_2–CH_2 intermediate formed on the area of the Ag surface having the stronger Ag–O bond (a stepped surface) will have a greater probability of being involved in unselective H abstraction reactions by the more electronegative surface O atoms than cyclising to form EO. The unselective reaction on both surfaces is a collective reaction of the sea of surface O atoms forming H bonds of different strength to the adsorbed intermediate. The same adsorbed O atom is therefore involved in both the selective and unselective reactions, the extent of which it is involved in each is determined by the Ag–O bond strength. This is an entirely new concept in the partial oxidation of ethylene to ethylene oxide.

1. Introduction

Ethylene oxide (EO) is one of the world's most important industrial chemicals, which, because of its numerous applications, has an annual turnover of about $18 bn. It is produced by partial oxidation and is the most important chemical to be produced by partial oxidation. The process involves passing an ethylene/oxygen mixture (3:1) over an Ag/α-Al_2O_3 catalyst at ~500 K and 1.5 MPa using 1,2-dichloroethene (1,2-DCE) (or vinyl chloride) in ppm quantities in the gas phase and Cs (~300 ppm, w/w on the catalyst) as promoters. Reaction of the 1,2-DCE promoter with the oxidised Ag deposits Cl atoms (~0.2 ML amount) on the surface of the Ag; these Cl atom then migrate under the surface of the Ag [1–4]. In the absence of any promoter, the reaction of ethylene/oxygen mixtures over the Ag/α-Al_2O_3 catalyst produces ethylene oxide at about 50% selectivity. The addition of the Cl promoter increases the selectivity from 50% to 75%. The selectivity of the fully promoted (Cl/Cs) system is ~85%. Since a 1% improvement in selectivity is worth $180 m annually to the producers, elucidation of the reaction mechanism and identification of how the Cl and Cs promoters function within that mechanism is extremely important as a basis for further improvement in selectivity.

It seemed self-evident that the selective oxidation of ethylene to EO would require a special kind of adsorbed oxygen and the first theories of the mechanism reflected this. Kilty et al. propounded that the selective oxygen was a charged chemisorbed molecular oxygen O_2^- and that adsorbed atomic oxygen was unselective [5]. Since it required 6 atomic oxygen species to oxidise ethylene to $2CO_2$ and $2H_2O$ and only one O_2^- species to produce EO, the maximum selectivity predicted by this mechanism was 6/7 (86%). This view remained unchallenged for the next decade until: (i) selectivities in excess of 86% were found experimentally and (ii) Grant and Lambert showed that molecular oxygen could be removed from the Ag(1 1 1) surface by temperature programmed desorption without having any impact upon the production of EO by reaction with atomically adsorbed oxygen [6].

Grant and Lambert's view of the mechanism was that there were two types of adsorbed atomic oxygen: (i) a type which had a low valence charge, making it electrophilic and therefore selective and (ii) a type which was electronegative, having a high valence charge; this species was unselective since it was involved in H abstraction reactions from the adsorbed ethylene,

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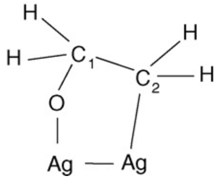
producing H_2O and ultimately oxidising the C fragments to CO_2 [6].

In a complete departure from the notion that it was the nature of the adsorbed oxygen on the surface of the silver which determined selectivity in epoxidation, Barteau and co-workers, as a result of density functional theory (DFT) calculations, posited that selectivity was determined by two nearly equivalent energetic pathways available to an adsorbed oxametallacycle intermediate:



The selective route comprised stretching the O–Ag bond and forming the C_2–O bond. The unselective route had a H atom transferring from C_1 to C_2, forming acetaldehyde whose inevitable fate was CO_2 and H_2O [7]. The Cl promoter, which acted through the surface, was considered to stabilise the selective intermediate relative to the unselective one, while the Cs promoter, which acted through space, was considered to provide the same function.

We have shown previously: (i) that selectivity is a function of the Ag–O bond strength and that the weaker the Ag–O bond is, the more selective it becomes [8], (ii) that the Cl promoter weakens the Ag–O bond, so increasing its selectivity and (iii) that the Cs promoter occupies sites on which the strongest Ag–O bond is formed, preventing its formation and therefore inhibiting the unselective reaction [9]. These experimental data contradict the oxametallacycle mechanism produced by DFT calculations. This paper takes these data as a basis for a new molecular model of the reaction intermediate adsorbed on a fully oxidised Ag surface and shows that selectivity results from the competitive reactions of cyclisation to EO and H abstraction, ultimately to H_2O and CO_2 of the same intermediate and the same adsorbed O atoms.

2. Experimental

The experiments were conducted in a single tube, stainless steel microreactor (0.4 cm id, 20 cm long). It was connected to a quadrupole mass spectrometer via a heated capillary. The reactor could be cooled to 77 K and temperature programmed from 77 to 723 K. The techniques employed were: (i) temperature dependent adsorption, (ii) temperature programmed desorption (TPD) and (iii) temperature programmed surface reaction (TPRS). The gases (O_2, C_2H_4/He(2% C_2H_4) and He) were all 99.995% pure and were used direct from the cylinder. The Ag/α-Al_2O_3 catalyst was prepared using the patented method of complexing silver oxalate (4.6 g in 2.9 cm^3 de-ionised water) with ethylene diamine (1.25 g) and impregnating the α-Al_2O_3 (17.1 g, pore volume 0.3 cm^3) with it, followed by calcination at 373 K for 16 h [10]. Cs promotion was effected by adding CsOH (0.6 g of 10%, w/w to the Ag/ethylene diamine liquid) and then impregnating the α-Al_2O_3 with this, followed by calcinations at 373 K. This produced catalysts with an Ag loading was 10% and Ag surface area was 1.4 $m^2\,g^{-1}$ by O_2 desorption following saturation O_2 dosing (pure O_2, 523 K, 1 h). Promotion of the Cs/Ag/α-Al_2O_3 catalyst by Cl was effected under industrial conditions of 500 K, 1.5 MPa and a gas hourly space velocity of 4750 h^{-1} using a feed composition of C_2H_2 (2%) in air and dichloroethane (ppm). The reaction was stopped by switching flows from the reactant mixture to N_2 and sweeping out the reactor while cooling the catalyst to ambient temperature. All three catalysts, the Ag/α-Al_2O_3, the Cs promoted Ag/α-Al_2O_3 and the Cl promoted Cs/Ag/α-Al_2O_3 had the same Ag loading, ~10%.

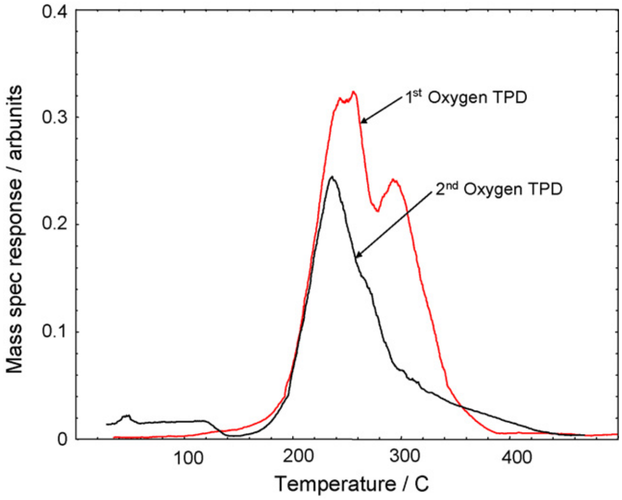


Fig. 1. The (TPD) spectra of O_2 from an Ag/α-Al_2O_3 catalyst: O_2 dosing, O_2 101 kPa, 25 cm^3/min, 1 h, 513 K. Top curve: first desorption. Lower curve: TPD of O_2 dosed on to the catalyst which had been heated to 400 °C to desorb O_2 in top curve.

3. Results

Fig. 1 is the O_2 desorption spectrum obtained following saturation dosing of O_2 (pure O_2, 523 K, 1 h) on to the catalyst. It shows desorption states at 523 K (the α_1-O state) and at 573 K (the α_2-O state). The second O_2 desorption curve (the lower curve in Fig. 1) was obtained by dosing the O_2 (pure O_2, 523 K, 1 h) on to the Ag/α-Al_2O_3 catalyst which has been heated to 723 K in He to produce the upper curve. This heating has caused the Ag to sinter, evidenced by the smaller amount of oxygen desorbed for the same O_2 dose. This sintering has occasioned the loss of the α_2-O state. Lineshape analysis of the leading edge of the α_1-O state, ie plotting the initial rate of desorption versus I/T, gives a desorption activation energy of 140 kJ mol^{-1}; this value shows the desorption to derive from O atoms adsorbed on Ag(1 1 1). That this applies to the whole peak is confirmed by computer simulation of the desorption spectrum shown in the upper curve of Fig. 1. The simulation, required, as input, the desorption activation energies, the order of the desorption (2nd order) and the surface areas of the Ag having a given Ag–O bond strength. The energies used in the simulation were: (i) 140 kJ mol^{-1} obtained from lineshape analysis of Fig. 1 (This value is also identical to the desorption energy of O_2 from Ag(1 1 1).) and (ii) 155 kJ mol^{-1} which is required to simulate the second peak and is thought to derive from desorption of oxygen adsorbed on a stepped Ag surface. For the upper curve of Fig. 1 the areas are: Ag(1 1 1), 1.1 $m^2\,g^{-1}$ and stepped Ag, 0.7 $m^2\,g^{-1}$, while, for the lower curve, the areas are: Ag(1 1 1), 0.96 $m^2\,g^{-1}$ and stepped Ag, 0.06 $m^2\,g^{-1}$. The simulated spectrum replicated the experimental one in terms of peak maximum temperature and in the width of the peaks at half maximum height. This clearly shows that the peaks derive from Ag–O bonds of different strength and also shows that the surface morphology of the freshly prepared Ag is ~50:50 Ag(1 1 1):stepped Ag, while that of the sintered Ag surface is ~100% (Ag(1 1 1)).

It has been suggested that the two oxygen desorption peaks shown in the upper curve of Fig. 1 do not derive from the breaking of two energetically different Ag–O bonds, and that they are the result of the desorption process occurring in two stages in which the majority of the oxygen desorbed in the first peak while the remaining oxygen may have caused a surface reconstruction and desorbed in the second peak. Were the argument to be valid, the second desorption curve shown in the lower part of Fig. 1 would have two peaks as in the upper one since, even though the silver area is smaller, the oxygen was dosed to produce saturation

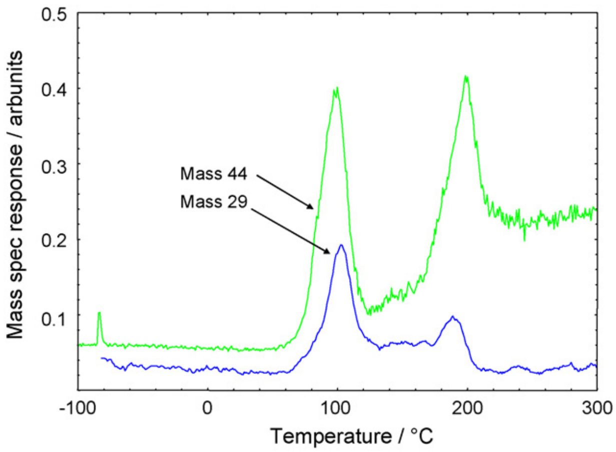


Fig. 2. The temperature programmed reaction of ethylene with an oxidised Ag/α-Al_2O_3 catalyst subtending the α_1-O and the α_2-O states on the surface: $m/z = 29$ is EO; $m/z = 44$ is CO_2 and 0.5 EO.

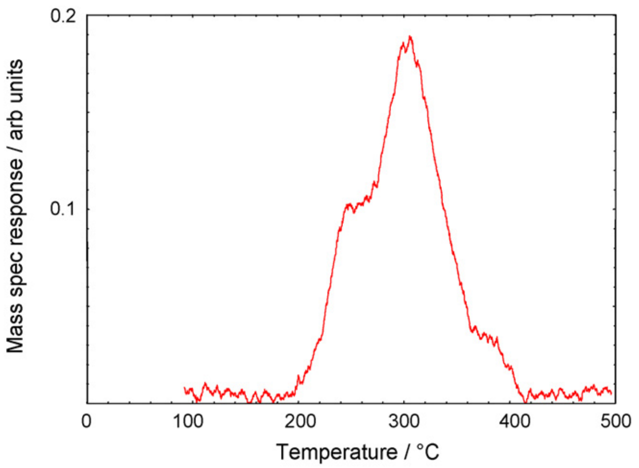


Fig. 3. The TPD spectrum of O_2 from the Ag/α-Al_2O_3 catalyst subtending the α_2-O state principally on the surface.

coverage and so if the argument was valid, the desorption process should occur in two stages, producing two peaks. Only one peak is observed. Measuring the coverage of this α_2-O state as a function of the dosage temperature gives an activation energy to adsorption of 17 kJ mol^{-1} ($\Delta H = 123$ kJ mol^{-1})[8].

Temperature programmed surface reaction of ethylene (2% C_2H_4 in He) with the α_1-O and α_2-O states produced the reaction spectrum shown in Fig. 2. Ethylene oxide (EO) and CO_2 are formed coincidently at 373 and 473 K [8]. The EO/CO_2 peak at 373 K has a selectivity to EO of 57% and has been shown to derive from reaction of ethylene with the α_1-O state [8], while the 473 K EO/CO_2 peak, deriving from the reaction of ethylene with the α_2-O state, has a selectivity of 34%. Selectivity in ethylene epoxidation is therefore an inverse function of the Ag–O bond strength; the weaker Ag–O bond is more selective than the stronger bond. Selectivity is therefore not a function of a branching reaction available to an adsorbed oxametallacycle.

The activation energy for the formation of EO can be obtained by lineshape analysis of the leading edge of the EO peaks. For the 373 K peak it is 60 kJ mol^{-1} and for the 473 K peak it is 170 kJ mol^{-1}.

The coverage of the Ag under industrial operating conditions can be obtained by substituting a value of the heat of adsorption (ΔH) of O atoms of 123 kJ mol^{-1} into the Langmuir isotherm (Eq. (1)) at the operating temperature of 500 K:

$$\theta = \frac{Kp^{1/2}}{1 + Kp^{1/2}} \qquad (1)$$

where $K = A\,e^{\Delta H/RT}$, A (whose value is ~1) is the ratio of the adsorption and desorption factors; the former is the standard collision number Z (~10^{13} cm^3 mol^{-1} s^{-1}) and the latter is the vibrational frequency (~10^{13} s^{-1}) and p is the gas density (mol cm^{-3}) of O_2 at 3 bar. The value of the fractional coverage obtained is 1. It is obvious that this value could be depleted by reaction. The reactive sticking probability of ethylene with the oxidised Ag surface for an activation energy of reaction of 60 kJ mol^{-1} is 5×10^{-7} at 500 K. However, the dissociative O_2 sticking probability on Ag at 500 K is 2×10^{-2} for an activation energy of adsorption of 17 kJ mol^{-1}. This is 10^5 times faster than the rate of removal of the adsorbed O atoms by reaction. Under industrial operating conditions, the ethylene molecule will be adsorbing on a fully oxidised Ag surface. Single crystal and theoretical studies have suggested many possible overlayer structures [11]. Carrying out the calculation of the fractional coverage of the α_2-O state, whose heat of adsorption is greater than that of the α_1-O state by 15 kJ mol^{-1}, also produces a fractional coverage of 1 but, as we have reported previously, the Cs promoter all but eliminates the α_2-O state by its being adsorbed on the stepped surface and so it is not involved in the reaction under industrial conditions.

Fig. 3 is further exemplification that the two O_2 desorption peaks shown in the upper curve of Fig. 1 derive from the breaking of Ag–O bonds of different strengths. The spectrum is obtained by first dosing the O_2 to produce saturation coverage of the Ag with O (O_2, 101 kPa, 523 K, 1 h). The sample is then cooled under the O_2 flow to ambient; the flow is then switched to He and the temperature is raised under the He stream to 503 K where it is held for 10 min before cooling again to ambient. The temperature is then raised to 723 K under He, producing the spectrum shown in Fig. 3. This thermal pre-treatment causes ~80% of the α_1-O state to be lost with the coverage of the α_2-O state to be unaffected. This could only occur if the two O_2 peaks shown in the upper curve of Fig. 1 derived from energetically different Ag–O bonds.

We have also shown that the EO evolving at 373 K is the result of ethylene reacting with the adsorbed O atoms which desorb at 523 K—the α_1-O sate by temperature programmed reaction of ethylene with this O-depleted (α_1-O) oxidised Ag surface [8]. The EO peak evolving at 473 K was unchanged in terms of the amounts of EO and CO_2 produced, i.e. the selectivity is unchanged. Therefore, the EO peak produced at 473 K results from reaction of ethylene with the α_2-O (573 K) adsorbed O atoms. The EO peak produced at 373 K, however, was significantly reduced in amount, showing it to have been formed by reaction of ethylene with the α_1-O state. More importantly, however, the selectivity of the reaction of ethylene with this O-depleted α_1-O state has increased from 57% to 75% [8].

Three important conclusions can be drawn from this. They are: (i) the reaction of ethylene with adsorbed O atoms weakens the Ag–O bond, probably as a result of the heat of formation of the C–O bond of the adsorbed CH_2–CH_2–O–Ag intermediate abstracts the adsorbed O atom from the surface as it forms EO, (ii) the coincident evolution of EO and CO_2 at both 373 and 473 K shows that both the selective and unselective reactions occur at temperatures at which the Ag–O bond is thermally weakened and (iii) the higher selectivity of 75% of the α_1-O state having a lower O atom coverage (20% of saturation) is the result of a reduced amount of H bonding of the adsorbed ethylene to the surface O atoms.

Fig. 4 is a plan view of a molecular model of ethylene bonded as CH_2–CH_2–O–Ag on a fully oxidised Ag_2O_3 surface. The figure shows that there is ample opportunity for the H atoms of the adsorbed ethylene to H bond to the O atoms on the surface. This is made clearer by the elevation view of the same structure (Fig. 5). The H bond of the adsorbed intermediate to the O atoms on the surface

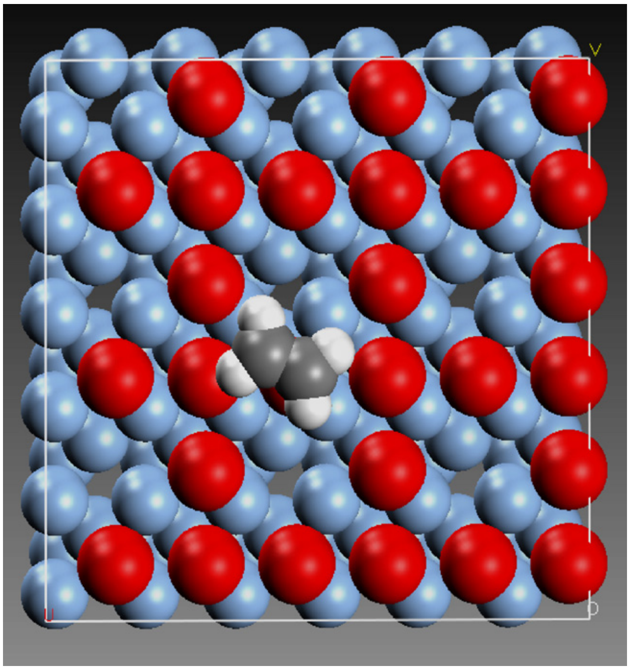


Fig. 4. A plan view of the structure of ethylene bonded to a fully oxidised Ag surface.

of the Ag below it is shown in this figure. The selective reaction to EO occurs by stretching the Ag–O bond so that the O atom bonds to the second C atom of the adsorbed ethylene, so forming EO. The unselective reaction occurs by the sea of surface O atoms which exist below the intermediate (Fig. 5) abstracting H atoms from the adsorbed ethylene producing H_2O and leaving a C residue on the surface which is oxidised to CO_2. In this model it becomes clear why EO and CO_2 are formed simultaneously at a temperature at which the Ag–O bond is weakened. The weaker the Ag–O bond, the more likely it is to stretch and form EO. Also the weaker the Ag–O is likely to be less negatively charged and so forms weaker H bonds to the ethylene. The stronger Ag–O bond will require a higher temperature to stretch to form EO and so will have a higher activation energy for the formation of EO. It will also form stronger H bonds resulting in more H abstraction and consequently lower selectivity. The unselective reaction is a collective reaction of the sea of surface O atoms forming H bonds to the adsorbed intermediate. That the same adsorbed O atom can be involved in both the selective and unselective reactions is a new concept in the partial oxidation of ethylene to ethylene oxide.

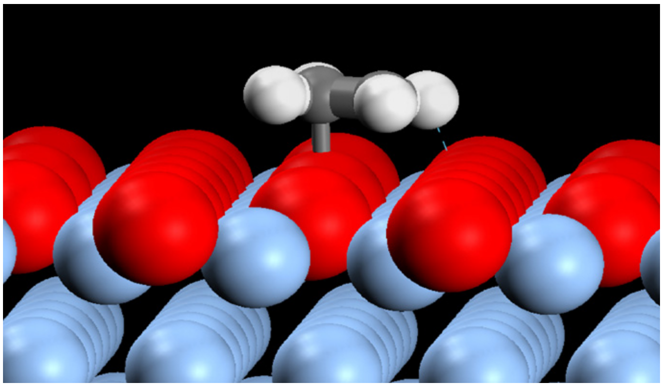


Fig. 5. A vertical view of the structure of ethylene bonded to a fully oxidised Ag surface, showing the H bond of the adsorbed intermediate to the O atom on the surface below it.

This model predicts that promotion would weaken the Ag–O bond. This is, in fact, found experimentally [9]. The O_2 TPD spectrum from a Cl promoted Ag/α-Al_2O_3 catalyst showed that the Cl promoter lowered the O_2 desorption peak maximum from 523 K (Ed = 140 kJ mol^{-1}) to 480 K (Ed = 129 kJ mol^{-1}). (The Cl promoter was dosed on by running the catalyst in a BP pilot plant which produced EO under industrial conditions using 1,2-dichloroethane in ppm amounts as the promoter.) Another point to note is that although inductively coupled mass spectrometry shows the catalyst to contain 0.2 monolayer equivalent of Cl, the amount of O_2 desorbed from the Cl promoted catalyst was identical to that desorbed from the unpromoted catalyst. Temperature programmed Auger electron spectroscopy and temperature programmed XPS have shown that the Cl atoms migrate below the surface of the Ag as the temperature is raised to 500 K [1–4].

Cs is another promoter used industrially. The O_2 TPD spectrum from a Cs promoted catalyst (The Cs is added to the ethylene diamine/Ag complex as CsOH prior to calcining in the preparation.) showed that the Cs promoter had reduced the amount of stronger (less selective) adsorbed O by ~70% and had no effect on the amount or bond strength of the α_1-O state [9].

The promoters therefore act in concert. The Cs inhibits the formation of the stronger, unselective Ag–O bond without affecting the bond strength or the coverage of the weaker, more selective α_1-O state. The Cl is dosed on to the catalyst by reaction of 1,2-dichloroethane with O atoms on a fully oxidised Ag surface and immediately migrates below the surface of the AgO, so preventing its causing site blocking for the adsorption of oxygen and also explaining why CsCl is not formed.

This new concept that the same adsorbed O atom can be involved in both the selective and unselective reactions has up to now not been available to other techniques employed in the investigation of ethylene epoxidation, e.g. IR spectroscopy, calorimetry and single crystal studies. This is because this is the first time that it has been possible to carry out the reaction of gas phase ethylene with the adsorbed oxygen and to measure the selectivity of that reaction. Furthermore, this catalyst, having the unique condition of subtending two Ag–O bonds of different strengths, enables the selectivity of the adsorbed O atoms to be determined in respect of the Ag–O bond strength.

4. Conclusions

(1) Selectivity in the Ag catalysed epoxidation of ethylene is a function of the Ag–O bond strength; the weaker the Ag–O bond is, the more selective it is.
(2) The selective and unselective reactions occur by two nearly equivalent energetic pathways available to the common CH_2–CH_2–O–Ag intermediate. These pathways are: (i) stretching of the Ag–O bond and cyclisisation of the intermediate to form EO and (ii) H bonding of the intermediate to the sea of O atoms on the surface of the Ag, resulting in H abstraction from the intermediate to form H_2O and, ultimately, CO_2.
(3) The weaker Ag–O bond will have a lower activation energy for its stretching to form the cyclic EO product. In addition, it will form weaker H bonds and so will be less likely to abstract H atoms from the CH_2–CH_2–O–Ag intermediate. In combination this will make it a more selective oxidant. Conversely, the stronger Ag–O bond will have a higher activation energy for its stretching to form the cyclic EO product. Since it will be more electronegative, it will form stronger H bonds, leading to a greater propensity for H abstraction, making it, in total, a less selective oxidant.
(4) Promotion of the EO reaction by Cl weakens the Ag–O bond, a result which is consistent with conclusion 2 above.

(5) The Cs promoter is held on the stepped Ag surface where it prevents the formation of the unselective Ag–O bond.

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