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Alkali Metal, Chlorine and other Promoters in the Silver-catalysed Selective Oxidation of Ethylene

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Ethylene oxidation over well characterised Ag(111) surfaces has been investigated by temperature-programmed reaction measurements and by differential batch reactor studies at pressures up to 50 Torr.‡ The influence of chlorine predosing on catalytic activity indicates that a chemisorbed atomic oxygen species is responsible for both partial oxidation and complete oxidation to CO_2+H_2O. This tends to be confirmed by experiments using N_2O as the oxidant, both with the single crystal specimen and with a practical Ag–αAl_2O_3 catalyst in a flow microreactor. Dissolved oxygen, like adsorbed chlorine, is found to be a selectivity promoter. Adsorbed Cs also increases the rate of ethylene oxide production but can also positively influence the overall activity of the system. The results suggest that chlorine and dissolved oxygen promoters principally affect the primary chemistry, whereas the main effect of Cs is on the secondary chemistry (further oxidation of ethylene oxide). This view tends to be confirmed by temperature-programmed reaction measurements and by direct experiments on the influence of Cl and Cs on the isomerisation and combustion of ethylene oxide itself. It is suggested that these effects are primarily electronic in origin and a mechanism based on this view is presented. In the presence of Cs, both CO_2 and NO_x can act as selectivity promoters for the formation of ethylene oxide.

Ethylene epoxidation over silver is a large-scale industrial process of major strategic importance in modern chemical technology. It has therefore been extensively investigated and thoroughly reviewed.[1–3] Nevertheless, the reaction mechanism is still the subject of debate, with much attention focussed on the identity of the crucial epoxidising surface oxygen species. The question of mechanism is obviously of central importance in any discussion of promoter effects.

The Worbs–Sachtler hypothesis[1,4] and variations on it[5] have been particularly influential in guiding much of the thinking in this field. According to this view, an adsorbed dioxygen species $O_2(a)$ is exclusively responsible for epoxide formation, while atomic oxygen O(a) leads to ethylene combustion. Other workers have variously suggested that either $O_2(a)$[6,7] or O(a)[8,9] can give rise to both types of chemistry. Experiments with N_2O have sometimes been carried out in order to examine the oxidation chemistry of the O(a) species deposited by this reagent, but the results have not been unequivocal.[10–12] More recently, detailed and rather direct experiments with Ag powders[13] and single crystals[14] have lent support to the view that O(a) reacts with ethylene to form both ethylene oxide (EO) and CO_2. Experiments with N_2O and chlorine, to be described below, also support this hypothesis, which accordingly forms the basis for our discussion of promoter effects.

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‡ 1 Torr = 101 325/760 Pa.

Experimental

Single-crystal measurements were carried out in a differential batch reactor coupled to an ultra-high-vacuum electron spectrometer chamber; the performance of this system has been described elsewhere.[14] In addition computer-multiplexed temperature-programmed reaction data could be obtained under ultra-high-vacuum conditions after first dosing the specimen with reactants at elevated pressures.[14] The methods used for controlled dosing of chlorine[15] and Cs[16] have already been described. Some auxiliary measurements were carried out using an Ag–αAl_2O_3 catalyst in a laboratory flow microreactor operating at 2.3 atm* with gas chromatographic analysis.[17]

Results

N_2O Experiments

Atomically clean Ag(111) surfaces were found to be completely unselective towards EO formation in the batch reactor; CO_2 and H_2O were the only products formed by C_2H_4–O_2 mixtures. However, if the surface was preconditioned[14] so that it contained a significant amount of dissolved oxygen, O(d), ethylene oxide production commenced with turnover frequencies of the order of 10^{14} cm^{-2} s^{-1} with a selectivity of *ca.* 15% at 10 Torr and *ca.* 500 K. Thus O(d) is a selectivity promoter. Similar observations have been reported for Ag powders.[18]

Such an oxygen-conditioned surface was dosed first with N_2O (6×10^7 L† at 2 Torr, 543 K) and then with varying doses of ethylene at 300 K. Fig. 1 shows the resulting temperature-programmed reaction data; it can be seen that the O(a) deposited by N_2O[17] does indeed lead to the formation of both CO_2 and ethylene oxide. Furthermore, upon exposing the conditioned specimen to a 1:2 N_2O:ethylene mixture in the batch reactor at 6 Torr and 580 K ethylene oxide was produced as summarised in table 1. Concurrent mass spectrometric monitoring of the reactor gas composition showed that the O_2 partial pressure was $< 10^{-4}$ that of the N_2O. There is, therefore, no possibility that the observed EO turnover frequency was due to adventitious O_2 impurity either in the feed gas or produced by *in situ* decomposition of N_2O in the reactor. The second half of table 1 shows the results of N_2O–C_2H_4 reaction over an Ag–αAl_2O_3 catalyst in the flow microreactor; once again, it can be seen that ethylene oxide formation proceeds with a high turnover frequency in the absence of detectable gaseous oxygen. All these observations are consistent with O(a) being the only catalytically relevant oxygen species.

Experiments with Chlorine

Chlorine is the single most important promoter in this system. Experiments involving Cl pre-dosing of the catalyst have in the past been interpreted in favour of the Sachtler mechanism.[1, 4, 19] However, the dioxygen hypothesis runs into yet further difficulty when the effects of chlorine pre-dosing on the deuterium kinetic isotope effect are examined.[20] Fig. 2 shows the efficiency of chlorine pre-coverage in blocking the subsequent chemisorption of O(a). Chlorine coverages were measured by LEED/Auger spectroscopy and oxygen uptake was monitored by the O_2 desorption yield from the oxygen-dosed crystal. Note that the oxygen dosing pressure was the same as that used in the batch reactor studies and that a chlorine precoverage of 0.25 monolayers totally suppresses uptake of O(a) by Ag(111). Fig. 3 shows the effect of progressively increasing Cl pre-

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* 1 atm = 101 325 Pa.

† 1 L = 1 langmuir = 10^{-6} Torr s.

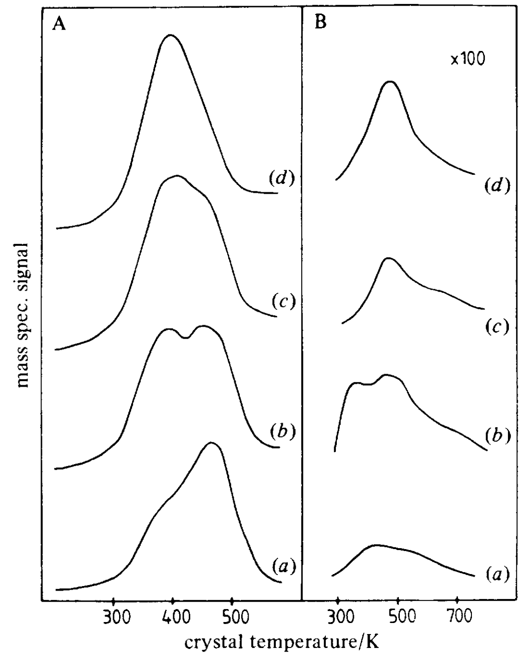


Fig. 1. T.p.r. spectra for (*a*) CO_2 (44 a.m.u.) and (*b*) EO–acetaldehyde (29 a.m.u.) after dosing the crystal with 6×10^7 L of N_2O (543 K, 2 Torr) followed by varying doses of ethylene at 300 K. Ethylene doses: (*a*) 3×10^7, (*b*) 6×10^7, (*c*) 12×10^7 and (*d*) 24×10^7 L.

Table 1. (*a*) Comparison of the rate of ethylene oxide production on Ag(111) from ethylene with nitrous oxide and oxygen in the batch reactor at 580 K

mixture composition/Torr		EO turnover frequency
N_2O	C_2H_4	$/10^{-13}$ molecule cm^{-2} s^{-1}
2	4	3.4
2	2	21.0

(*b*) Production of ethylene oxide and carbon dioxide over the supported Ag catalyst at 537 K with a constant reaction pressure of 2.3 atm and flowrate of 39 cm^3 min^{-1} (g.h.s.v. = 4680) in the laboratory microreactor

mixture composition	rate$/10^{-13}$ molecule cm^{-2} s^{-1}		selectivity
N_2:Et:N_2O	EO	CO_2	(%)
52.0:37.0:11.0	0.8	0.4	79
60.0:37.5:2.5	11.0	22.3	50

coverage on the activity and selectivity of the Ag(111) model catalyst at 550 K. Selectivity rises monotonically with Cl coverage, while overall activity decreases. Most importantly, *all catalytic activity ceases* when the chlorine precoverage reaches 0.25 monolayers. The results illustrated in fig. 2 and 3 therefore suggest that O(a) is responsible for both the partial and the complete oxidation of ethylene.

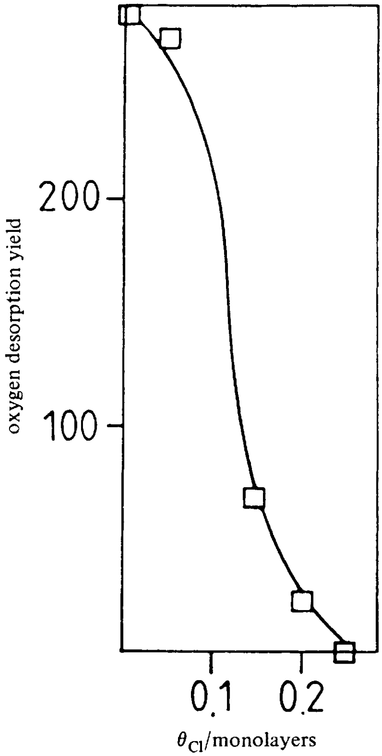


Fig. 2. Variation in the 32 a.m.u. t.p.d. yield for atomically adsorbed oxygen, O(a), with θ_{Cl} after saturating the chlorine precovered surface with oxygen at 298 K, 2 Torr.

Experiments with Cs and Further Experiments with Chlorine

All the measurements to be described were carried out in the absence of surface chlorine. Fig. 4 shows that pre-adsorbed Cs leads initially to an enhanced rate of EO production. In this connection, it should be noted that Ag is known to catalyse the isomerisation of EO (to CH_3CHO).[21, 22] We therefore investigated the effect of Cs on EO isomerisation. Fig. 5 shows that Cs strongly suppresses the rate of EO isomerisation by Ag and since this reaction is thought to be the crucial first step in the further oxidation of EO, it provides a basis for explaining the selectivity enhancement produced by alkali metals. Control experiments have shown[16] that this effect is not merely the result of site-blocking by Cs, because the alkali metal does not significantly affect either the rate or the extent of EO uptake by Ag(111).

Corresponding measurements with chlorine pre-dosing suggest that electronic effects are involved here. Fig. 6 shows that chlorine acts to increase the rate of EO isomerisation, while the control experiments illustrated in fig. 7 show that Cl does not significantly affect the uptake of EO by Ag(111). Fig. 8 shows that under oxidising conditions Cs does indeed inhibit the burning of ethylene oxide. As far as the ethylene chemistry is concerned, fig. 9 shows that Cs also enhances the net rate of CO_2 production. The data of fig. 4, 5, 8 and 9 taken together indicate that there are two routes to CO_2 production; ethylene combustion and EO combustion. Cs appears to enhance the former and suppress the latter; under the present conditions of relatively low selectivity, all the above results are therefore understandable.

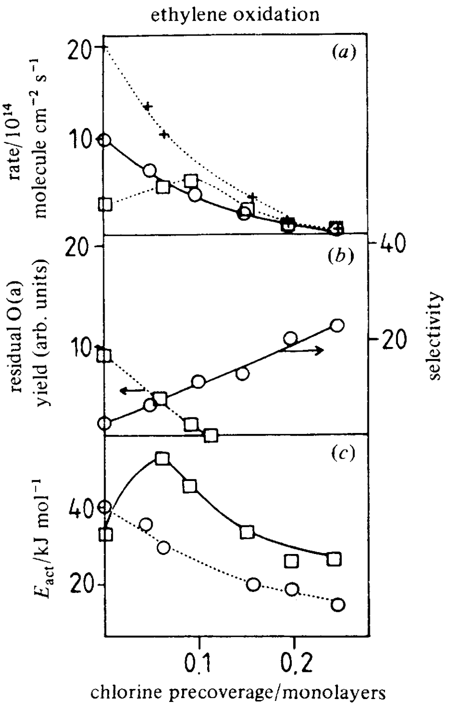


Fig. 3. Reactor data showing the effect of chlorine precoverage on (*a*) the turnover frequencies, (*b*) post-reactor O(a) desorption yield and selectivity and (*c*) activation energies during the oxidation of 4 Torr of ethylene by 2 Torr of oxygen at 550 K. (*a*) +, CO_2; ○, total; □, EO × 10; (*c*) □, EO; ○, CO_2.

Effects of Added CO_2 and Added NO_x

Excessive levels of CO_2 are known to poison the activity of ethylene oxidation catalysts, and it seems likely that this is due to the formation of a surface carbonate species.[8, 9, 23, 24] In the absence of Cs, the Ag(111) model catalyst showed some selective poisoning response to increasing levels of CO_2 [fig. 10(*a*)]. However, in the presence of Cs this effect was considerably more pronounced, leading to appreciable increases in selectivity as the Cs levels increased. Fig. 10(*b*) shows the effect of increasing Cs loading at constant CO_2 partial pressure.

The effect of very low levels of NO_x (in the ppm range) was also investigated. Once again, in the absence of Cs no significant effects were observed except for an overall decrease in activity at high levels of added NO. However, in the presence of surface Cs the selectivity showed a marked positive response to the presence of low levels of NO (fig. 11). In order to obtain some information about the nature of the surface species present under these conditions, a multi-mass temperature-programmed desorption sweep was performed after rapidly withdrawing the specimen from the reactor cell (fig. 12). Note the almost coincident peaks for Cs^+, NO_2^+, NO^+ and O_2^+ signals. Finally, temperature-programmed reaction measurements on a surface dosed with Cs, oxygen, NO and ethylene indicated the presence of a new surface species which released oxygen at relatively low temperature; additional CO_2 peaks at higher temperatures were also found (fig. 13).

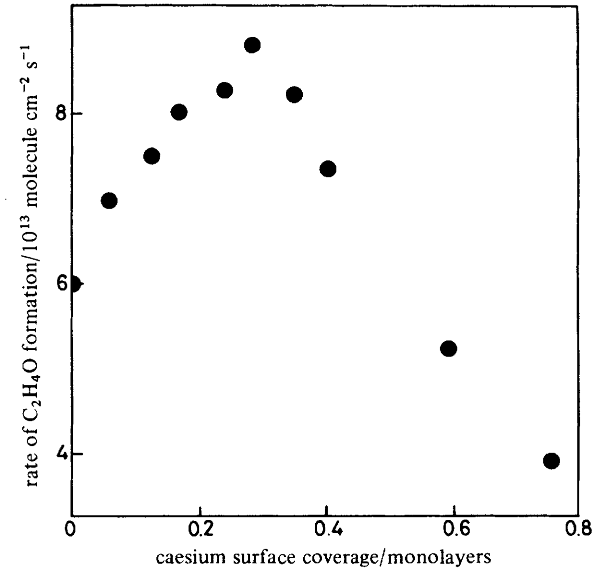


Fig. 4. Variation in the rate of ethylene oxide production with Cs precoverage at 500 K for a 1:1 mixture of C_2H_4:O_2 at a total pressure of 10 Torr.

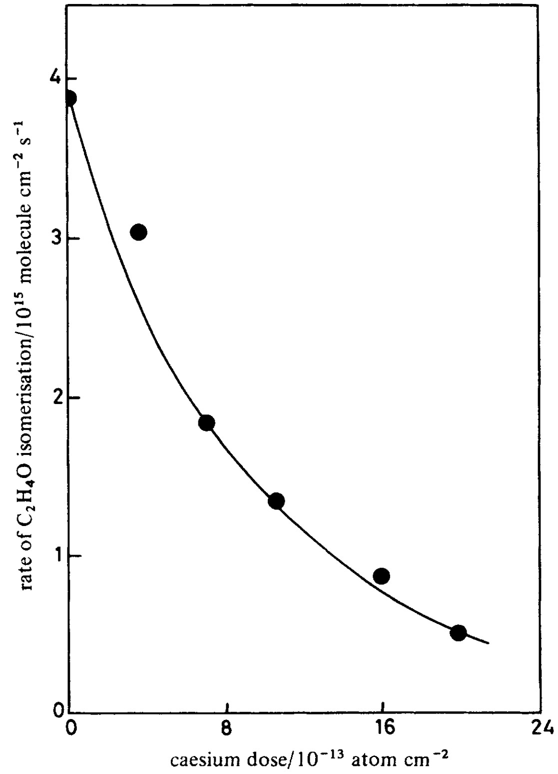


Fig. 5. The effect of preadsorbed Cs on the rate of ethylene oxide isomerisation with 1 Torr of ethylene oxide at 400 K.

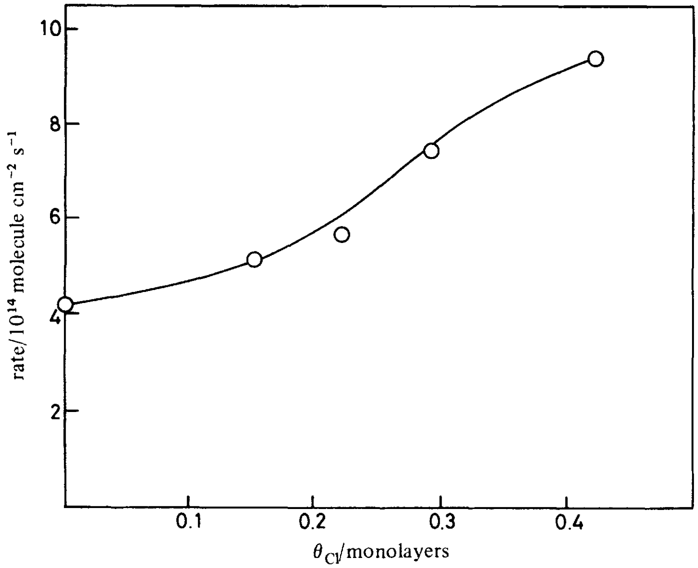


Fig. 6. Variation in the ethylene oxide isomerisation rate with 0.5 Torr of ethylene oxide and varying precoverages of chlorine on the surface at 400 K.

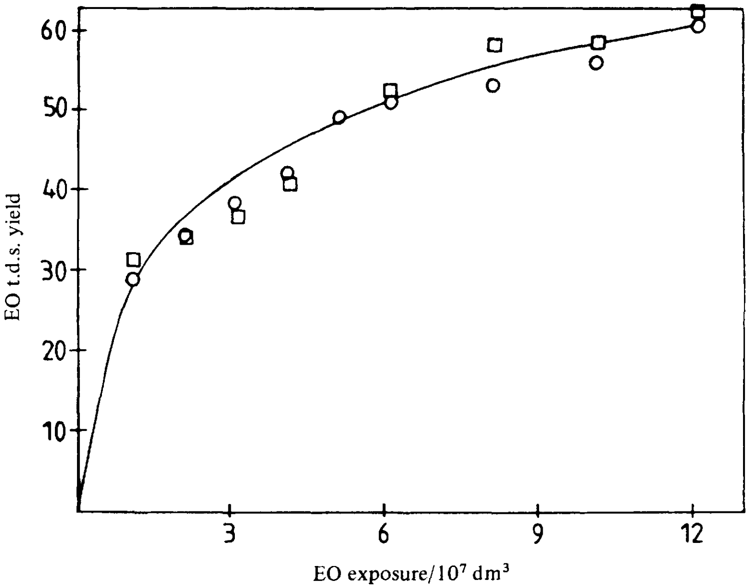


Fig. 7. Room-temperature EO t.p.d. uptake curve on clean and Cl pre-dosed Ag(111) using a dosing pressure of 2 Torr: ○, clean; □, $\theta_{Cl} = 0.07$ monolayer.

Discussion

The results obtained with N_2O and the dependence of catalytic activity on chlorine coverage both tend to reinforce the view that O(a) is responsible for all the observed chemistry. We therefore take this as the basis for our discussion of promoter effects. Given that both Cl(a) and O(d) promote selective oxidation, it seems reasonable to

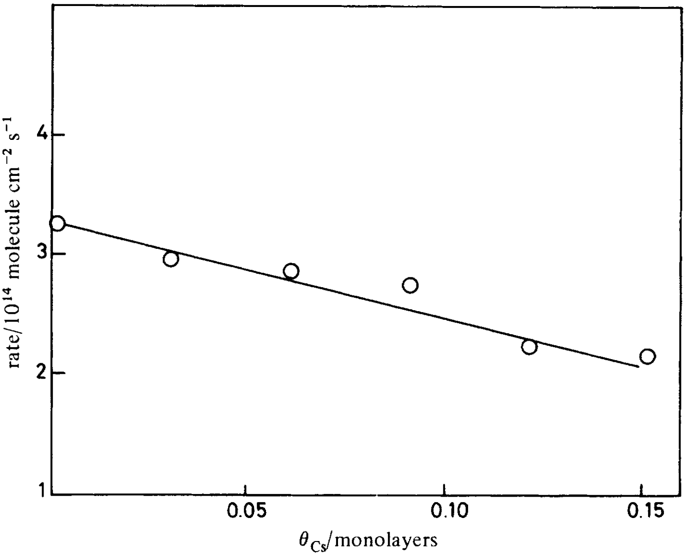


Fig. 8. Variation in the rate of ethylene oxide combustion at 543 K with 0.5 Torr of ethylene oxide and 0.5 Torr of O_2 on a surface with varying precoverages of Cs.

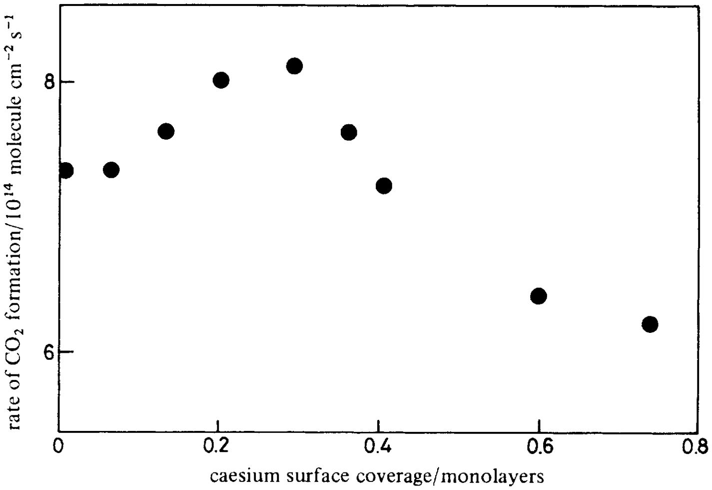


Fig. 9. Variation in the rate of CO_2 production with Cs precoverage at 500 K for a 1:1 mixture of C_2H_4:O_2 at a total pressure of 10 Torr.

propose that they act primarily as electronic promoters. Furthermore, since Cl(a) tends to accelerate the rate of EO isomerisation, its overall positive influence on selectivity must imply that the principal effect of Cl(a) resides in the primary chemistry. The system's behaviour may be rationalised in terms of a simple scheme which calls for the presence of a single type of oxygen species [O(a)] and a single type of chemisorbed ethylene. The primary chemistry involving these two reactants can then proceed down either one of

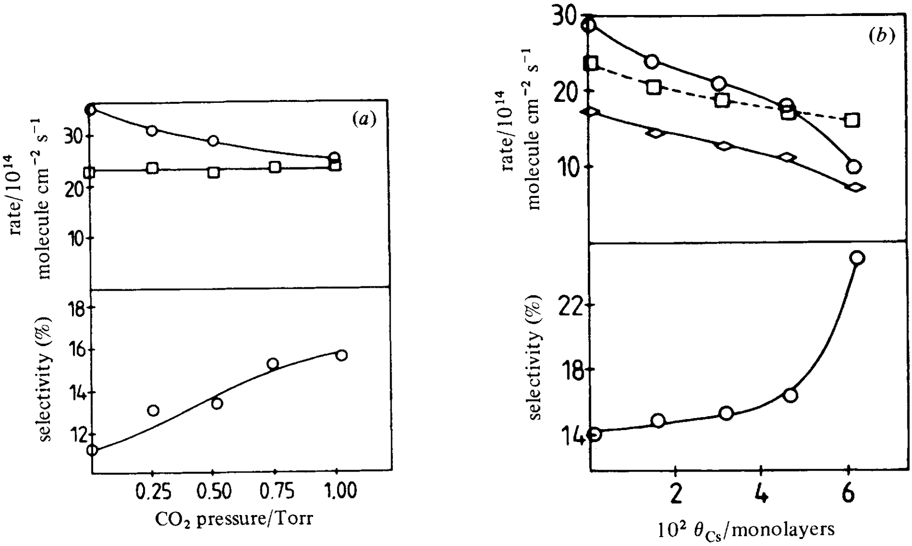
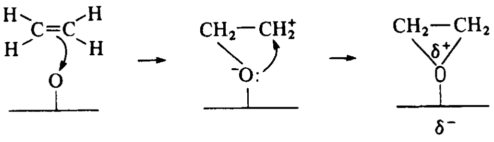
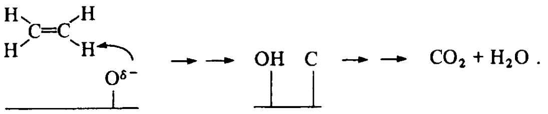


Fig. 10. Reactor data showing the variation in turnover frequencies and selectivity during the oxidation of a 1:1 mixture of ethylene:oxygen at 550 K in the presence of (*a*) increasing CO_2 poisoning and (*b*) 0.5 Torr of CO_2 and increasing Cs precoverages [for rate plots: ○, CO_2; □, EO × 10; ◇, activity].

two competing channels. Either, electrophilic attack by O(a) on ethylene leading to epoxide formation:



or stripping of weakly acidic hydrogens, leading eventually to fragmentation and combustion of the organic moeity:



The first pathway is favoured by the presence of Cl(a) and/or O(d), which compete with O(a) for metal electrons thereby lowering the electronic charge state of O(a) and favouring electrophilic attack on ethylene. Conversely, electron donors such as Cs should favour the second pathway, which results in the direct burning of ethylene. That this is indeed the case would appear to be borne out by the reactor data for CO_2 production on the Cs promoted surface. However, the reactor data for EO isomerisation and combustion strongly suggest that Cs also plays a beneficial role as far as the secondary chemistry is concerned. The opposite effect of Cl(a) in this connection suggests that in the secondary chemistry the promoter effects are also largely electronic in origin.

In the absence of Cs, added CO_2 exerts a relatively weak selective poisoning effect on the total oxidation; the presence of Cs leads to a much more pronounced CO_2 effect with a significant gain in selectivity towards EO formation. CO_2 is known to form a weakly bound surface carbonate when reacted with O(a) at Ag surfaces.[24, 25]

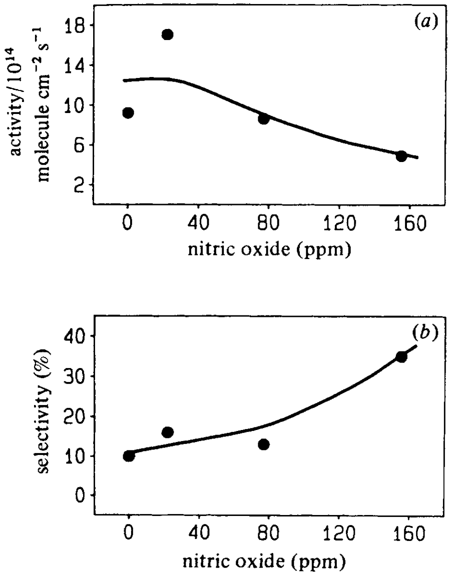


Fig. 11. Reactor data showing the variation in (*a*) activity and (*b*) selectivity with amount of nitric oxide in a 3:1 mixture of ethylene:oxygen at 8 Torr, 550 K, in the presence of 0.13 monolayers of caesium.

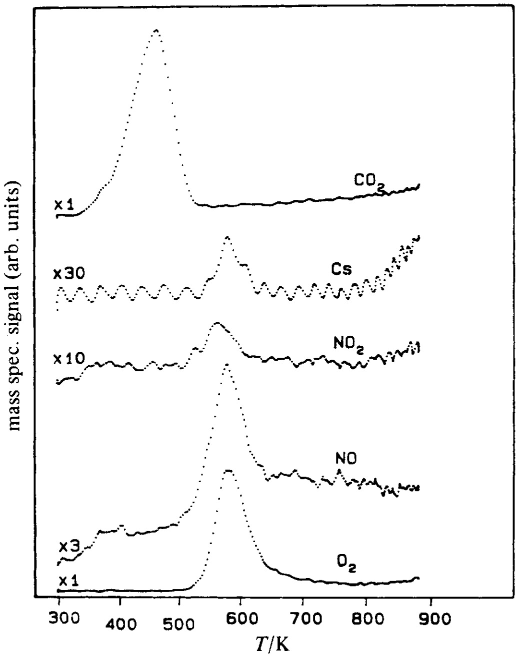


Fig. 12. T.p.d. spectra of CO_2 (44 a.m.u.), Cs (133 a.m.u.), NO_2 (46 a.m.u.), NO (30 a.m.u.) and O_2 (32 a.m.u.) after rapidly withdrawing the specimen from the reactor, where it had been heated to 550 K in a 3:1 mixture of ethylene:oxygen, containing 1000 ppm of NO at a total pressure of 8 Torr.

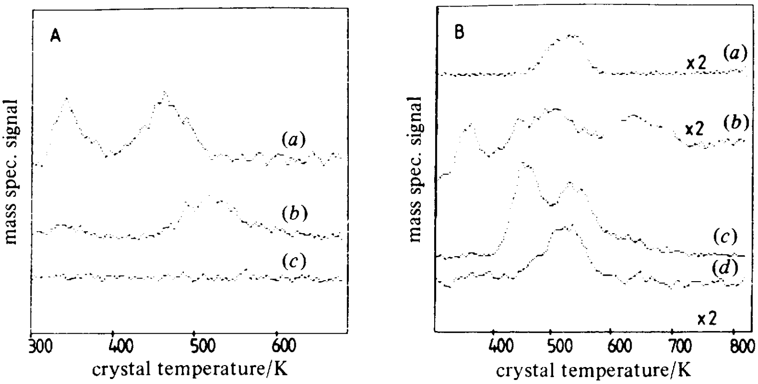


Fig. 13. (A) T.p.r. spectra for (*a*) CO_2 (44 a.m.u.), (*b*) O_2 (32 a.m.u.) and (*c*) NO (30 a.m.u.) after exposing the clean crystal at room temperature to 6×10^7 L of O_2 at 2 Torr, followed by 6×10^7 L of ethylene at 2 Torr. (B) T.p.r. spectra for (*a*) Cs (133 a.m.u.), (*b*) CO_2 (44 a.m.u.), (*c*) O_2 (32 a.m.u.) and (*d*) NO (30 a.m.u.) after exposing a crystal precovered with 0.13 monolayers of caesium to 6×10^7 L of O_2 at 2 Torr, followed by 110 L of NO at 10^{-6} Torr and then 6×10^7 L of ethylene at 2 Torr. All exposures were carried out at room temperature.

Since epoxide formation requires one O(a) per adsorbed ethylene, whereas combustion requires six, it is to be expected that the removal of O(a) by carbonate formation would have a higher-order effect on the combustion reaction. Surface silver carbonate is unstable at reaction temperature, so the steady-state coverage of this species is expected to be fairly low. However, in the presence of Cs a much more stable surface alkali-metal carbonate phase can be formed. This species should reach a substantially greater steady-state coverage, resulting in a substantially greater concomitant depletion of O(a); the enhancement of the CO_2 effect by Cs is therefore understandable.

Promotion of Ag–ethylene epoxidation catalysts by added NO_x has already been reported in the patent literature.[26] The present results are of significance in at least two respects. First, they show that the effect appears only in the presence of surface alkali metal. Secondly, they indicate that it is a phenomenon taking place on the metal component of the catalyst (since no Al_2O_3 is involved in the single crystal experiments). The temperature-programmed reaction data show that Ag surfaces dosed with Cs, O_2, C_2H_4 and NO contain a species which yields gaseous O_2 more readily than 'normal' O(a). Furthermore, the temperature-programmed desorption results obtained after withdrawing the specimen from the reactor suggest that some kind of nitrogen oxyanion is formed at the surface under reaction conditions. The nature of this promotion remains unclear for the moment, but possibilities include the following: (i) a nitrogen oxyanion scavenges some undesired form of surface oxygen, *e.g.* by some kind of redox process, and returns it to the gas phase. (ii) A nitrogen oxyanion participates directly in oxygen transfer to ethylene, resulting in the formation of epoxide.

The first of these possibilities would fit in naturally with the Worbs–Sachtler mechanism, but is not readily accommodated by the mechanistic views proposed here. The second possibility is formally analogous to known homogeneous chemistry in which nitrito-complexes of Pd can catalyse the epoxidation of olefins.[27] Experiments to examine this possibility are in progress.

Conclusions

Chemisorbed atomic oxygen is responsible both for the epoxidation and for the combustion of ethylene on silver catalysts. It is proposed that the charge state of this O(a) is pivotal in determining the relative rates of epoxidation and combustion.

Chlorine acts mainly on the primary chemistry, where it behaves as a selectivity promoter by suppressing ethylene combustion. This may be understood in terms of an 'electronic' effect. O(d) acts in a similar manner.

The principal role of Cs is in the secondary chemistry, where it acts to suppress the isomerisation (and hence the further oxidation) of EO. Again, the origin of this effect appears to be electronic.

CO_2 selectively poisons the combustion of ethylene; the effect is much more pronounced in the presence of Cs. The consumption of O(a) to form surface carbonates of silver (or caesium) is thought to be responsible for this.

Added NO can exert a significant promoter effect, but only in the presence of Cs. Cs salt(s) of nitrogen oxyanions appear to be present on the metal surface during the reaction.

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