

Heterogeneous alkene epoxidation: past, present and future

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Abstract

Recent progress in the metal-catalysed heterogeneous epoxidation of alkenes is reviewed with respect to key mechanistic issues, drawing on results obtained with both single crystals and practical dispersed catalysts. New data are also presented and future prospects examined. It is shown that on silver surfaces oxygen adatoms are responsible for all the chemistry—both combustion and selective oxidation. In particular, the minimum necessary and sufficient conditions for epoxidation to occur are π -adsorbed alkene and O_a . Studies with co-adsorbed F, Cl, Br, and I demonstrate that promotion of epoxidation selectivity correlates with halogen electronegativity—supporting the view that this is an electronic effect involving control of the valence charge density on O_a . The observations that (i) selectivity markedly increases with increasing O_a coverage and (ii) alkalis strongly decrease selectivity are in excellent accord with this view. In the presence of alkali, addition of NO_x to the reaction gas leads to formation of adsorbed nitrate species that open an ultra-selective epoxidation channel that involves transfer of oxygen from submonolayer quantities of adsorbed alkali nitrate to alkene, probably by a direct mechanism. Our comprehension of silver surface chemistry suggests that copper should also be an epoxidation catalyst—an expectation borne out in practice. In fact, Cu is more selective than Ag. When allylic hydrogen atoms are present (propene, allylbenzene and its isomers), Cu surpasses Ag by an even greater margin: copper continues to catalyse selective oxidation effectively, whereas silver simply burns these alkenes. The proximity of the C=C bond to the Cu surface is critically important in determining the degree to which epoxidation occurs.

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1. Introduction

The heterogeneous epoxidation of alkenes, especially ethene and propene, is a topic of enduring interest—both from the point of view of fundamental chemistry, and with respect to the importance, or potential importance, of these processes in modern chemical technology. The reactions involved are mechanistically interesting and both epoxides are commercially valuable intermediates. Here, we review a range of topics that are central to an understanding of these processes. We also present new data obtained by a variety of methods and consider future prospects.

Ag-catalysed ethene epoxidation is a mature subject [1]. The technical process employs a catalyst consisting of silver particles supported on α -alumina with addition of ppm levels of a gaseous chlorocarbon that acts to moderate activity and enhance selectivity; generally, controlled amounts of alkali

are also added to the catalyst to further enhance epoxide selectivity to around 80%. Despite intensive academic research stimulated by decades of industrial usage on a global scale, certain aspects of the reaction mechanism are not fully resolved. According to one early but very influential view [2], adsorbed dioxygen is the epoxidising agent whereas oxygen adatoms (O_a) are responsible for combustion. An alternative hypothesis [3], also based on classical measurements, was that all the chemistry is due to O_a , thought to undergo either Eley–Rideal or Langmuir–Hinshelwood reactions with ethene, resulting in epoxidation or combustion, respectively. More recently, single crystal measurements based on very similar methodologies led to strongly divergent conclusions: Campbell and Koel [4] inferred that dioxygen was indeed the selective oxidant; on the other hand, Grant and Lambert [5] claimed that O_a reacted with adsorbed ethene to yield both the epoxide and combustion products. However, this long-standing controversy has been resolved and there is now a consensus that oxygen adatoms are responsible for selective oxidation—although papers still occasionally appear [6]

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in which adsorbed dioxygen is posited as the epoxidising agent. Spectroscopic and reaction data to be presented below demonstrate unequivocally that oxygen adatoms cause both selective oxidation and combustion of styrene adsorbed on Ag(1 0 0).

Another issue that has recently been settled concerns the mode of action of the chlorine promoter in ethene epoxidation. The view used to be [2] that this was a steric or geometric effect—Cl adatoms simply blocked the dissociative chemisorption of oxygen (inhibiting formation of O_a , supposedly an unselective oxidant) thus, enhancing epoxidation selectivity. If correct, this would imply that many different kinds of adatoms should have comparable beneficial effects. By studying the effects of F, Cl, Br, I on ethene epoxidation, we show that selectivity promotion is primarily an electronic phenomenon. Such understanding allowed us to predict that in principle, copper should also be an effective epoxidation catalyst, and indeed this is found to be the case, as we shall show. It also led us to examine the possibility of accessing a new ultra-selective reaction channel on silver surfaces by employing submonolayer quantities of alkali nitrate as the oxygen transfer agent.

Propene epoxide is an even more valuable product than ethene epoxide: it is a strategically important and versatile chemical intermediate whose manufacture accounts for ~10% of total European usage of propene. Two thirds of this is consumed in the manufacture of polyether polyols, the rest being converted to propene glycols, glycol ethers and other materials that have a wide range of applications. However, heterogeneous epoxidation of propene is a much tougher problem to solve: Ag catalysts deliver only very low selectivities over a wide range of conditions and catalyst formulations [7,8]. As a result, propylene epoxide is currently produced by either (i) the old chlorohydrin process [9], environmentally unfriendly because it involves the use of chlorine or (ii) a newer homogenous route [10] that involves co-production of propene epoxide and styrene. It has been proposed, and seems to be generally agreed, [11–16] that the difficulty with propene epoxidation resides in the ease with which an allylic hydrogen atom may be stripped from the molecule, a process that presumably shuts off the epoxidation channel and results in combustion. Therefore, we have examined the oxidation chemistry of allylbenzene, *trans*-methyl styrene and α -methyl styrene on single crystal surfaces of copper and silver. These three isomers are phenyl-substituted propenes: all contain allylic hydrogen atoms, but they differ substantially in their stereochemistry. The differences in their oxidative behaviour on Cu and Ag surfaces, and between each other on Cu(1 1 1), are revealing.

2. Experimental methods

Many of the results summarised below were obtained with single crystal samples examined under ultra high vacuum conditions using a variety of laboratory-based and syn-

chrotron radiation methods, details of which have been published elsewhere [17,18]. The results of laboratory measurements carried out with single-pass fixed bed micro-reactors are also reported, and again the relevant experimental details have been published [19].

3. Identification of the epoxidising agent and the effect of oxygen coverage on selectivity

Ethene desorbs from Ag surfaces before it can react under UHV conditions, therefore higher terminal alkenes that bind sufficiently strongly have been used for UHV studies. These include norbornene [20], 1-butene [21], 2-methylpropene [22], 3,3-dimethyl-1-butene [23], butadiene [24,25] and, especially, styrene (phenyl-ethene) [17,26,27]. Of these, styrene may be regarded as the most important because its chemisorption geometry on silver, determined by NEXAFS, is that of a planar molecule lying parallel to the metal surface with preservation of the olefinic double bond [28] and no tilting or out-of-plane twisting of the olefin function that could endow the molecule with reactive properties significantly different from those of ethene which adsorbs with its C=C bond parallel to the metal surface [18]. This validates the use of styrene as a model terminal alkene for epoxidation studies on silver surfaces.

By using TPR to follow the evolution of gaseous species and synchrotron XPS to follow the time dependence of surface species, we obtained very direct evidence that the minimum necessary and sufficient conditions for the epoxidation of styrene on Ag(1 0 0) are the π -adsorbed alkene and oxygen adatoms (O_a)—no other forms of oxygen were detectable under our conditions, neither dioxygen, nor sub-surface or oxide-like oxygen.

Fig. 1 shows representative TPR data and Fig. 2 shows the results of a detailed analysis of the time and temperature dependence of the C 1s and O 1s XP spectra. When allowance is made for the difference in heating rates between the TPR

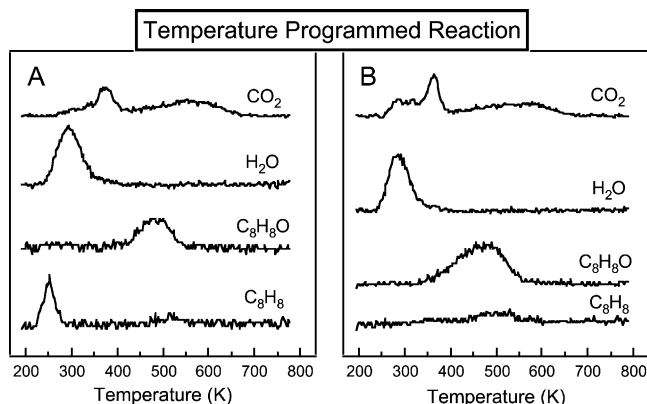


Fig. 1. TPR spectra showing reaction products from co-adsorbed styrene (~0.04 ML) and O_a on Ag(1 0 0) in the presence of (A) 0.035 ML and (B) 0.16 ML of atomic oxygen (the epoxide is unambiguously identified by relative intensities of the $m/z = 39, 65$ and 91 signals).

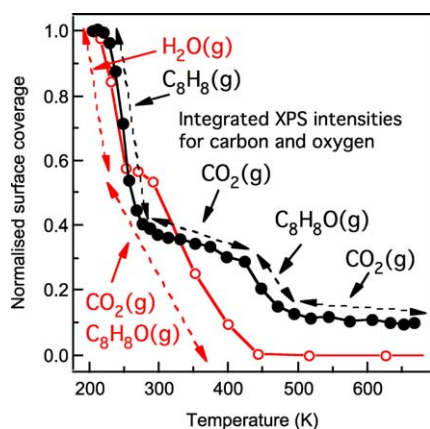


Fig. 2. Time and temperature dependence of C 1s and O 1s normalised integrated intensities during reaction of ~ 0.1 ML of styrene with 0.3 ML of oxygen in the interval 205–667 K: open symbols, O 1s; filled symbols, C 1s.

and TP-XPS measurements, the two types of data are in good accord in regard to the temperature regimes over which the various products are initially formed and subsequently desorbed from the surface. As shown in Fig. 1, the only desorbing species were styrene epoxide, CO_2 and water; at low oxygen coverages there was also desorption of unreacted styrene. In Fig. 2, the O 1s intensity is proportional to the coverage of all oxygen containing surface species—so the observed profile reflects stages in the desorption of H_2O , CO_2 and $\text{C}_8\text{H}_8\text{O}$. The sharp decrease in O 1s intensity commencing at ~ 230 K corresponds to desorption of H_2O , consistent with the TPR results. Comparison with Fig. 1 indicates that over this interval water desorption would have been completed. This is indicated by the first dashed line. CO_2 started to desorb at ~ 260 K, while styrene epoxide was retained on the surface. The intensity decrease between ~ 300 and ~ 425 K is due to CO_2 desorption, followed by styrene oxide desorption (~ 425 to ~ 475 K) and the final stages of CO_2 desorption, as indicated by the second dashed line.

The C 1s intensity profile reflects the desorption of C_8H_8 , CO_2 and $\text{C}_8\text{H}_8\text{O}$. The sharp decrease occurring between 220 and ~ 260 K is consistent with desorption of styrene; beyond this point the only carbon containing species left on the surface should be styrene oxide and carbonaceous fragments. From ~ 260 to ~ 400 K, the C 1s signal continued to decrease, but at a lower rate. This decrease between ~ 260 and ~ 400 K corresponds to combustion of carbonaceous fragments and the consequent desorption of CO_2 (first and second TPR peaks at ~ 300 and ~ 360 K). The decrease between ~ 400 and ~ 500 K corresponds to desorption of styrene oxide (TPR peak at ~ 450 K). Between ~ 500 and ~ 650 K, the small decrease is due to combustion of small amounts of carbonaceous species (third CO_2 TPR peak at ~ 550 K). These results provide compelling proof that the epoxidising species is O_a —hopefully laying this issue to rest once and for all.

A comparison of Fig. 1A and B suggests that increased oxygen coverage results in higher selectivity toward styrene epoxide formation: the epoxide: CO_2 ratio increases with the

extent of O_a precoverage. At a naïve level, this seems surprising as 24 O adatoms are required to burn one molecule of styrene, whereas only one O adatom is needed to epoxidise it—the availability of more O_a should favour more combustion, not less. A systematic study of the coverage dependence of selectivity using both the TPR and the XPS data confirms this effect, as shown in Fig. 3. It is entirely consistent with our view of the reaction mechanism: the higher the oxygen coverage, the lower the valence charge density on any given O_a , thus favouring epoxidation.

4. Role of promoters

4.1. Chlorine and alkalis, separately

In ethene epoxidation, a number of selectivity promoters play a significant role: chlorine, alkalis and NO_x . The most important by far is adsorbed chlorine, a vital ingredient in all technical operations [1]. Early UHV work on Ag single crystal surfaces in which the opposite effects of adsorbed K and Cl on styrene epoxidation were demonstrated [29] pointed to an electronic as opposed to a steric or geometric role for chlorine—in line with the view advanced above that the halogen depletes valence charge density on O_a rendering it more electrophilic and hence favouring O-insertion into the C=C bond, thus epoxidation, rather than C–H cleavage and combustion. With respect to ethene epoxidation, a recent study at atmospheric pressure using Ag thin film catalysts and an entirely different approach—electrochemical promotion (EP)—led to the same conclusion. K and Cl had pronounced and opposite effects on selectivity [19,30]. It is important to note that under both conditions, UHV (styrene) and elevated pressure (propene), we are observing the adverse effects of alkali on the chemistry of the metal phase alone—which is our primary concern here. In the case of Ag/ α -alumina catalysts, the beneficial effects of alkali on selectivity are well known [1]; they may be ascribed to neutralisation of acid sites on the support surface that would otherwise lead to isomerisation

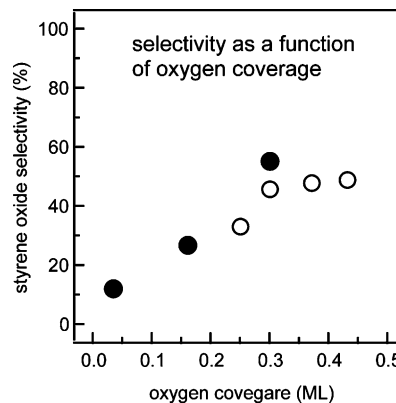


Fig. 3. Selectivity towards styrene epoxide formation as a function of oxygen coverage calculated by two different methods using TPR data (filled circles) and TP-XPS data (open circles).

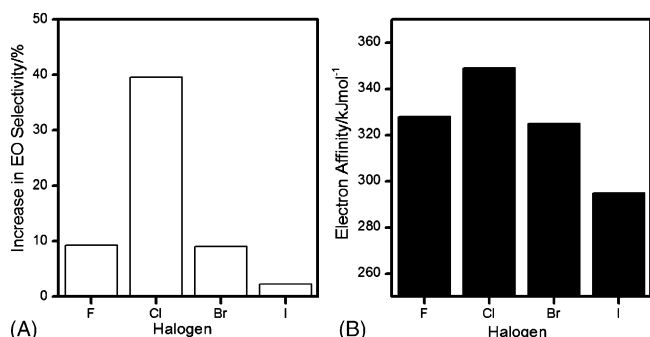


Fig. 4. (A) EO selectivity enhancement at 50% reactant conversion for all four halogens and (B) electron affinities of the halogens (reproduced with permission from reference [31]).

and combustion of the epoxide. These effects are not principal interest in the present context.

Recently, an investigation of the effects of F, Cl, Br and I promotion on ethene epoxidation selectivity was carried out [31] using a silver/ α -alumina catalyst operated at 1 bar pressure. The principal results are summarised in Fig. 4, which illustrates how steady state epoxidation selectivity depends on the identity of the halogen at 50% ethene conversion, all other conditions being held constant. Note the striking correlation with the electron affinities of the halogens, which are also shown in Fig. 4 (the same relative order of selectivities was found throughout the entire range of ethene conversion). These findings strongly support the conclusion that co-adsorbed halogens act to promote selectivity primarily by an electronic effect, as argued earlier.

As noted and discussed above in regard to selectivity, the effect of alkalis on the intrinsic surface chemistry of Ag is uniformly adverse for both styrene under UHV conditions and for ethene at atmospheric pressure—neither molecule contains allylic hydrogen atoms. However, propene behaves very differently [19] as shown in Fig. 5, which contrasts the effects of EP by K on the epoxidation of ethene (A) and propene (B). In these experiments, decreasing catalyst potential (VWR) corresponds to increasing alkali coverage of the Ag surface. Addition of alkali causes ethene epoxidation selectivity to collapse. With propene, clean Ag delivers very

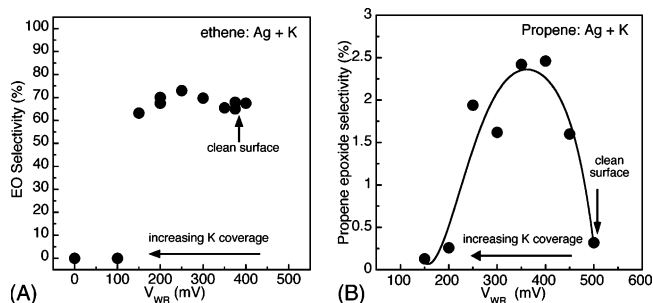
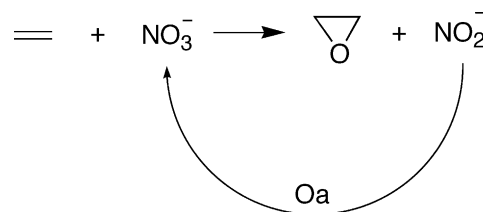


Fig. 5. Electrochemical promotion by K of Ag-catalysed ethene epoxidation (518 K) and propene epoxidation (523 K) at atmospheric pressure: $p_{\text{ethene}}/p_{\text{O}_2} = 2.5$; $p_{\text{propene}}/p_{\text{O}_2} = 0.5$ (adapted with permission from reference [19]).

low epoxide selectivity, as usual. However, addition of alkali causes an initial increase in selectivity by a factor of more than five, followed by a decline. The absolute magnitude of the selectivity increase is not the point; the point is that an actual increase is observed. This is an indication that there are major differences between the oxidative behaviour of ethene and propene on Ag—a point that we shall return to.

Long ago, Grant et al. [32] used a Ag(1 1 1) model catalyst operated at 10 mbar total pressure in a batch reactor to demonstrate that the deliberate introduction of ppm levels of NO_x into the reaction gas resulted in significantly enhanced epoxidation selectivity, but only in the presence of submonolayer quantities of Cs, deposited by vacuum evaporation. Subsequently, by means of control experiments involving vacuum deposition of KNO_2 and KNO_3 on Ag(1 1 1), it was shown [33] that the dosing sequence $\text{K} + \text{O}_2 + \text{NO}$ could be used to produce submonolayer amounts of alkali nitrate on the silver surface. A consistent and plausible explanation of these observations is that (i) NO_x promotion in the presence of alkali is due to the presence of submonolayer quantities of alkali nitrate on the metal surface and (ii) this nitrate somehow facilitates oxygen transfer to the alkene, itself undergoing reduction to nitrite, followed by re-oxidation to nitrate, thus completing the catalytic cycle (scheme below).



More recent EP experiments [30] on ethene epoxidation at atmospheric pressure (Fig. 6) confirmed this behaviour: electro-pumping K to or from the Ag surface in the presence of 20 ppm NO caused substantial reversible increases or decreases, respectively, in epoxidation selectivity. The data also show how reversible the behaviour is (see figure caption).

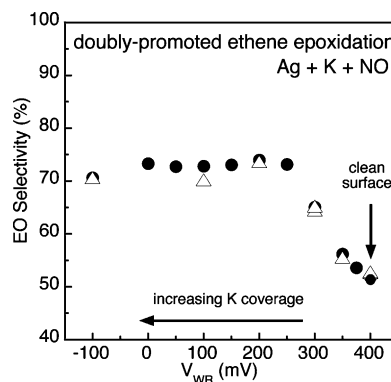


Fig. 6. Electrochemical promotion by K of ethene epoxidation in the presence of 20 ppm NO. Filled circles are data taken while increasing the K coverage by decreasing the catalyst potential. Filled triangles are data taken subsequently while decreasing the K coverage by increasing the catalyst potential: $T = 518 \text{ K}$; $p_{\text{ethene}}/p_{\text{O}_2} = 2.5$ (adapted with permission from reference [30]).

The interesting question is this. Does this oxygen transfer take place by a direct mechanism or is it mediated by the silver surface? Interestingly, when the corresponding experiments were carried out with propene [19], addition of NO_x in the range 0–60 ppm had the opposite effect: in this case, increasing the NO_x concentration decreased epoxidation selectivity. This is another indication that the dominant processes in the oxidation chemistry of ethene and propene on silver differ in important ways.

In order to elucidate further the nature of NO_x promotion, we investigated the reactive properties of nitrated $\text{Ag}(100)$ toward styrene in a well-controlled UHV environment. Fig. 7 shows the styrene oxide yield from the (alkali + oxygen)-pretreated (lower trace) and (alkali + oxygen + NO)-pretreated (upper trace) surfaces. The latter procedure should have led to the formation of sub-monolayer amounts of CsNO_3 in the initial adlayer [33]. In the first case (lower trace), styrene epoxide desorbed at a temperature that is characteristic of reaction between styrene and O_a (~540 K) along with much CO_2 (not shown); recall that the effect of Cs on its own is to reduce epoxidation selectivity. In the second case (upper trace), it is apparent that a new low temperature selective oxidation channel has opened up—the epoxide peaks (arrowed) at 275 and 325 K along with a less pronounced feature at 380 K (as expected, the pathway due to residual O_a was still available, producing the epoxide peak at ~500 K). The corresponding CO_2 fingerprint obtained in this case shows that the low temperature epoxidation channel is close to 100% selective. We therefore, suggest that the remarkable low temperature epoxidation process involves direct transfer of oxygen to the alkene from adsorbed alkali nitrate with simultaneous conversion of the latter to nitrite. The results of recent DFT calculations are consistent with our proposal [34]. A surface-mediated nitrate process ($\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}_a$; $\text{O}_a + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_4\text{O}$) would presumably have produced epoxide at ~540 K or even higher, depending on whether the first or second step was rate

limiting—hence our inference that O transfer from nitrate to alkene is a direct process.

5. Epoxidation catalysed by other metals

5.1. Gold

The discovery of Au/TiO_2 -catalysed propene epoxidation by Haruta and co-workers [35] resulted in an upsurge of activity in this area and the subject has been reviewed relatively recently by Choudhary and Goodman [36]. Much work has been carried out with gold/titania formulations, rather less with gold/Ti silicalite systems, suggesting that Ti-containing species in the support play an important part in the reaction mechanism. Haruta's original work and the often-cited paper by Valden et al. [37] also point to the possible importance of Au metal particle size effects—note that such effects do not appear to be of major significance in catalysis by silver, although morphological effects in Ag-catalysed propene epoxidation were found by Zemichael et al. [38]. In all reported cases of propene epoxidation by Au/titania, co-feeding of hydrogen was found to be necessary—leading to suggestions that the reaction involves in situ formation of hydrogen peroxide. Interestingly, the EP data obtained for propene epoxidation catalysed by K-promoted silver (see above and reference [19]) suggest that peroxy or superoxy surface species may play a part in the selective oxidation process. Intriguingly, a single crystal UHV study by Davis and Goodman [39] found evidence for propene epoxidation by O_a . This shows that neither Au particle size effects, nor the presence of a Ti-containing support, nor co-feeding of hydrogen, nor peroxy species are necessary conditions for Au-catalysed propene epoxidation. In fact, the minimum necessary and sufficient conditions would appear to be the same as those for Ag-catalysed epoxidation— π -adsorbed alkene and O_a . It seems likely, however, that Au/TiO_2 and similar propene epoxidation catalysts are complex systems and it is even possible that more than one reaction pathway operates—for example, one involving O_a , and another involving peroxy species. In this connection, it would be interesting to know the behaviour of Au/TiO_2 towards ethene oxidation, but we have found no relevant reports in the literature.

5.2. Copper

If it is true that the minimum necessary and sufficient conditions for metal-catalysed alkene epoxidation are π -adsorbed alkene and O_a , then under appropriate conditions Cu should be an effective epoxidation catalyst. Single crystal studies on $\text{Cu}(111)$ [40,41] and $\text{Cu}(110)$ [42] with 'non-allylic' alkenes under UHV conditions show that this is indeed the case: in fact, Cu is much more selective than Ag in the epoxidation of styrene and butadiene. But there is a catch. On both Cu surfaces, at sufficiently high oxygen coverages,

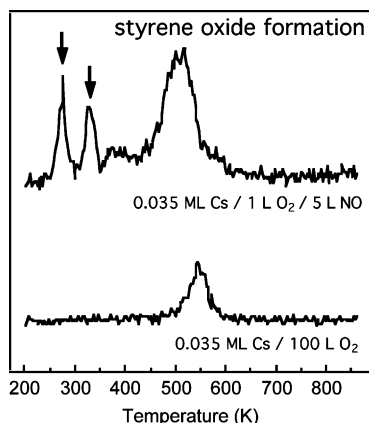


Fig. 7. Styrene epoxide TPR spectra obtained after adsorbing 1 L of styrene (220 K) on cesiated, oxygenated $\text{Ag}(100)$, with (upper trace) and without (lower trace) NO treatment. Arrows indicate new low temperature epoxidation channel.

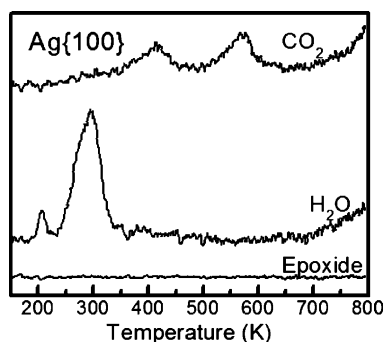
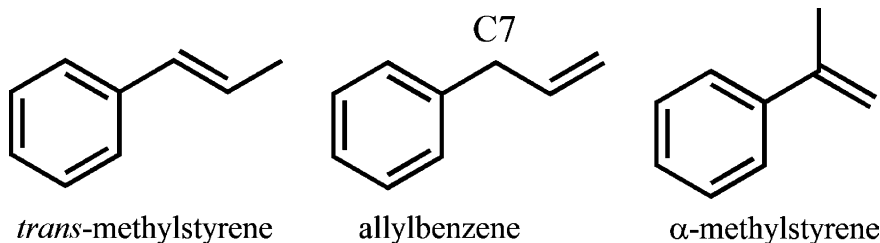


Fig. 8. TPR spectra after dosing Ag{100} with 1 L *trans*-methylstyrene followed by 1000 L oxygen.

nucleation and growth of copper oxide commences and selective oxidation activity is quenched (under steady state conditions in a micro-reactor, copper oxide induces alkene burning [43]). Nevertheless, given the apparent intrinsically higher selectivity of copper compared to silver, we chose to investigate much more demanding systems: the Cu-catalysed selective oxidation of alkenes containing allylic hydrogen atoms.

Accordingly, we performed a comparative study of the oxidation of allylbenzene, π -methylstyrene and *trans*-methylstyrene on Cu and Ag under UHV conditions. These isomeric molecules contain allylic hydrogen atoms and for present purposes are best thought of as three different phenyl-substituted propenes. In other words, we are using them as analogues for propene itself, just as we used styrene as a model molecule for ethene.



The interesting difference is that in these three cases the adsorption geometry of the C=C olefinic bond with respect to the metal surface is likely to vary: simple molecular modelling suggests that *trans*-methylstyrene should lie flattest, with α -methylstyrene somewhat less flat-lying and allylbenzene least flat-lying, with the C=C olefin functionality ‘dangling in space’ away from the surface, due to the stereochemistry at the C7 sp^3 carbon atom. TPR and synchrotron fast XPS studies were carried out on the oxidation of these three molecules on Ag(100) and Cu(111). It was found that in every case, the Ag surface catalysed only burning of the alkene—no selective oxidation was observed. Representative results for *trans*-methylstyrene are shown in Fig. 8 from which it can be seen that only combustion products were observed.

In contrast with this, the Cu surface behaved very differently. With *trans*-methylstyrene and α -methylstyrene, we observed substantial epoxide formation and some combustion,

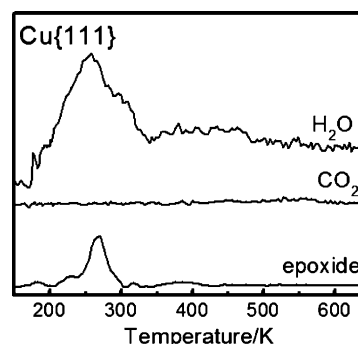


Fig. 9. TPR spectra after dosing Cu{111} with 1 L *trans*-methylstyrene followed by 50 L oxygen.

whilst with allylbenzene very little reaction at all occurred—only a small amount of combustion and no epoxidation at all. Fig. 9 shows typical results for *trans*-methylstyrene. Notice the significant yield of epoxide and the complete absence of CO_2 production.

These striking results confirm that Cu is intrinsically a much more selective epoxidation catalyst than Ag. This may reflect a reduced degree of rehybridisation of the adsorbed olefinic bond on Cu, favouring O-insertion. DFT calculations are in progress in order to examine this point. In the case of Cu, the effects of molecular stereochemistry are interesting and revealing: the unreactivity of allylbenzene indicates that proximity of the C=C function to the metal surface is critically important to epoxidation.

In summary, our single crystal studies show that copper generally delivers higher epoxidation selectivities than silver, and with ‘difficult’ alkenes that contain allylic hydrogen it can hugely outperform silver. Therefore, despite the problems associated with oxidation of the metal in the presence of finite partial pressures of oxygen, copper-based materials are worthy of investigation as partial oxidation catalysts. Clearly, strategies are required for minimising or controlling the extent of Cu oxidation under practical conditions. Obvious avenues include the use of alloys, co-feeding of hydrogen, sequential feeding of oxygen and alkene, and NO_x promotion. All of these approaches are currently being pursued. Recently, we found [43] that at atmospheric pressure in a single-pass micro-reactor, nanoscopic Cu/Au alloy particles were effective for the selective oxidation of propene.

6. Conclusions

1. On silver surfaces, oxygen adatoms are responsible for both combustion and selective oxidation of co-adsorbed alkenes. The minimum necessary and sufficient conditions for epoxidation are π -adsorbed alkene and O_a .
2. The degree to which halogens promote epoxidation selectivity correlates with their electronegativity—supporting the view that this is an electronic effect involving control of the valence charge density on O_a . Additional support for this hypothesis derives from the observations that (i) selectivity increases with increasing O_a coverage and (ii) alkalis have the opposite effect on selectivity compared to halogens and oxygen.
3. In the presence of alkali, addition of NO_x to the reaction gas leads to formation of submonolayer quantities of alkali nitrate. This opens up an ultra-selective epoxidation channel that probably involves direct transfer of oxygen from nitrate to alkene.
4. Our understanding of silver surface chemistry points to copper as a potential epoxidation catalysts—an expectation borne out in practice. In fact, Cu is even more selective than Ag, especially when the alkene contains allylic H atoms.
5. On Cu at least, epoxidation appears to be sensitive to the proximity of the C=C function to the metal surface.

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