

# Surface science and the silver-catalyzed epoxidation of ethylene: an industrial perspective

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## Abstract

Key surface science studies relating to the silver-catalyzed epoxidation of ethylene are reviewed from the perspective of industrial catalyst development. Fundamental studies using primarily Ag(111) and Ag(110) single crystals have provided evidence for the key role of atomic rather than molecular oxygen in both the epoxidation and combustion reactions. Model studies employing higher alkenes are also discussed as they reveal the importance of C–H bond reactivity in the combustion pathways. The influence of alkali and halide promoter species via electronic and geometric effects is discussed. Recent STM and in situ Raman studies of oxygen, chlorine and CO<sub>2</sub> adsorption on Ag surfaces showing dynamic silver restructuring and the identification of reactive surface species are highlighted as an area that will further the understanding of the epoxidation reaction by providing key structural information. Such information would not only benefit computational modelling efforts, but could also lead to more rational catalyst development processes. © 1998 Elsevier Science B.V.

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## 1. Introduction

The silver-catalyzed reaction of ethylene and oxygen to form ethylene oxide (EO) has been the subject of an extensive number of surface science studies, not only because of the industrial importance of the epoxide, which is largely converted into ethylene glycol or a variety of other derivatives and had an estimated world production of over  $11 \times 10^6$  t in 1995 [1], but also because the subtle complexities underlying this seemingly straightforward reaction system have defied simple interpretation of typical surface science and catalytic data. Ethylene may

react with oxygen to form either ethylene oxide (selective oxidation) or carbon dioxide and water (total combustion) as illustrated in Fig. 1. In addition, the product ethylene oxide may also undergo further oxidation to carbon dioxide and water. The difficulty in understanding the chemistry associated with these three pathways arises from the variety of oxygen species that can be formed on silver [2], and the situation is further complicated in industrial practice by the use of co-fed chlorine moderators as well as a broad range of catalyst promoters to enhance selectivity to the desired partial oxidation product.

Previous surveys of both single-crystal Ag and silver catalyst work provide excellent coverage of published research in this field. A

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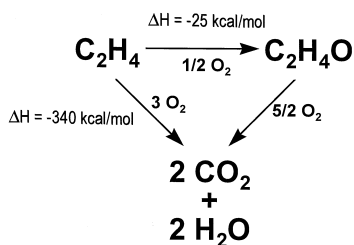


Fig. 1. Reaction network for ethylene epoxidation and competing combustion reactions.

comprehensive review by van Santen and Kuipers [3] considers both surface science and catalytic studies related to the mechanism of ethylene epoxidation up to approximately 1987. Sajkowski and Boudart [4] have discussed the effects of silver particle size and surface orientation, and conclude that epoxidation does not meet the standard criteria for structure sensitivity at industrially relevant temperatures and pressures. A more recent review by Zhang [5] focuses on evidence supporting a key role for atomic oxygen as the reactive species in the partial oxidation mechanism, while a review by Ayame [6] supports the possible reactions of both  $\text{O}_2^-$  and  $\text{O}^-$  to form ethylene oxide. The intent of this paper is not to attempt another broad review of this subject, but rather to highlight a selection of recent surface science studies that, from an industrial perspective, have provided important insights into various aspects of the silver-catalyzed epoxidation reaction.

To date, the most important advances in the development of silver epoxidation catalysts have, to the best of our knowledge, largely been through empirical means. Commercially available catalysts have been reported to operate with selectivities in the 80% range, although patent examples and academic studies [7–9] have claimed experimental selectivities well over the 85.7% upper limit (6/7 stoichiometry) corresponding to a mechanism in which only molecular oxygen reacts to form ethylene oxide [10]. To illustrate the progress that has been achieved since the discovery of the plain supported Ag catalyst in 1931, clean silver surfaces

have an initial selectivity to EO of around 40% [3]. A significant increase of 15 to 20% in selectivity is gained simply by the continuous addition of a chlorine-containing hydrocarbon species to the gaseous reactants as a moderator, which also acts to depress overall reaction rates [11,12]. Alkali or alkaline earth promoters, such as cesium, provide another substantial improvement, in the range of 10% [7,13]. While these components account for most of the increased selectivity of industrial catalysts since the Ag-based process was first commercialized, the commodity nature of the business and the resulting sensitivity of the economics to raw material prices—principally that of ethylene—generally make it worthwhile to implement new catalysts offering seemingly minor gains of only a few percentage points or less in selectivity. As a result, although additional step-change improvements in catalyst technology are still likely, at least some degree of commercial development effort is concentrated on making incremental gains in performance through, for example, new promoter combinations or methods of catalyst preparation [14–17].

## 2. The mechanism of ethylene epoxidation

The Ag(110) and (111) planes have been the subject of the majority of surface science studies related to epoxidation, with one of the key issues being the role of various oxygen species in the overall mechanism, particularly whether atomic or molecular oxygen reacts to form EO. Structure sensitivity and the roles of promoters and moderators have also been intensively investigated. A major difficulty in studying epoxidation on Ag single crystals is inducing ethylene and oxygen to react under low pressure conditions. On Ag(111), Grant and Lambert [18] found that co-adsorption of ethylene and oxygen at room temperature leads only to combustion products. In order to activate the Ag(111) surface for epoxidation, it was necessary to first

anneal the single crystal to 425 K in a 6:1 mixture of oxygen and ethylene at 10 Torr for 1 h. Because this treatment is known to form subsurface oxygen, this was interpreted as evidence that this species is somehow necessary for epoxidation on Ag(111). Similarly, ethylene and oxygen adsorbed at low temperature onto Ag(110) under UHV conditions do not react at all, and Roberts and Madix [19] attribute this to the desorption of ethylene at a temperature below that required for its activation. Consequently, to circumvent these limitations, many studies have incorporated a high-pressure cell for reacting ethylene and oxygen over the single crystal, followed by transfer of the sample to ultra-high vacuum (UHV) for characterization.

After activation of their Ag(111) crystal, Grant and Lambert [18] used temperature-programmed reaction (TPR) to observe the reaction of chemisorbed ethylene and atomic oxygen in UHV. The essential role of adsorbed atomic oxygen in epoxidation, as well as the competing ethylene combustion reaction, was demonstrated by several observations. First, the yield of ethylene oxide and the basic features of the TPR spectra were found to be independent of the coverage of chemisorbed dioxygen, which is present under the same reaction conditions, but can be removed by annealing. Fig. 2 shows TPR data for EO formed on Ag(111) with (a) and without (b) dioxygen. Clearly, EO is produced even in the absence of the desorption-limited low temperature  $O_2$  peak. In contrast, the yield of EO was found to be proportional to the coverage of atomic oxygen. The amount of EO formed in TPR, and the rate of EO formation in a high-pressure reactor were found to increase significantly when  $C_2D_4$  was substituted for  $C_2H_4$ , suggesting that C–H bond cleavage is the rate-limiting step in the combustion to  $CO_2$ . In addition, the presence of a secondary pathway to  $CO_2$  formation from EO decomposition was demonstrated by adsorbing and reacting EO itself. It was shown that the residual amount of surface atomic oxygen after complete oxidation of EO is inversely proportional to the EO expo-

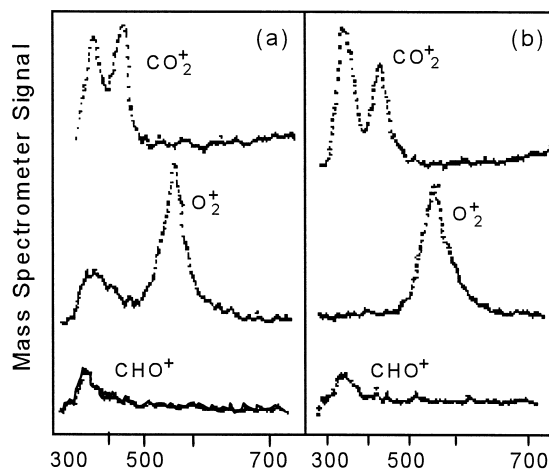


Fig. 2. Multimass TPR spectra for  $C_2H_4$  oxidation on activated Ag(111). (a) In the presence of dioxygen. (b) Without dioxygen.  $CHO^+$  is the ion monitored to detect EO formation; other masses in the fragmentation pattern were monitored to confirm this assignment (from Ref. [18]; reprinted with permission from *J. Catal.*, Academic Press).

sure, indicating that atomic oxygen also participates in the total oxidation of EO to  $CO_2$  and  $H_2O$ . After depletion of this atomic oxygen, subsurface oxygen was found to be capable of diffusing to the surface to form additional  $CO_2$ . Notably, these studies also demonstrate that all three reaction paths can occur over silver alone, indicating that EO burning is not necessarily due solely to the properties of the catalyst support.

Although atomic oxygen was first proposed to be the reactive species on silver catalysts over 50 years ago [20], previous studies were not able to clearly distinguish between an atomic or molecular oxygen mechanism. Grant and Lambert convincingly explained their results by using a mechanism in which adsorbed ethylene reacts with chemisorbed atomic oxygen to form either EO or  $CO_2$ . They suggest that the competition between the two pathways in this primary reaction is controlled by the charge on atomic oxygen. When dissolved oxygen or other electron-withdrawing moderators such as chlorine are present, the production of EO through electrophilic attack of the olefin double bond by

atomic oxygen is favored. Conversely, in the presence of species that contribute valence charge to silver and hence atomic oxygen, the oxygen preferentially attacks a C–H bond in ethylene, leading ultimately to combustion products. In a secondary reaction, EO may undergo further oxidation by adsorbed atomic oxygen to form additional  $\text{CO}_2$ . This widely accepted mechanism qualitatively explains many observations about the catalytic system and the effects of moderators and promoters. An added detail proposed by Campbell and Koel [21], among others, is that both EO and  $\text{CO}_2$  arising from ethylene burning are formed from a common ethylene–oxygen adduct. Their reasoning is based on similarities in the observed kinetic parameters for the two processes, suggesting the same rate-determining step in both pathways.

While providing strong evidence that atomic oxygen is the active species in ethylene epoxidation, whereas molecular oxygen is merely a spectator, the Grant and Lambert work required ‘activating’ the Ag(111) crystal by annealing at high pressures in a mixture of ethylene and oxygen. Using a somewhat different approach, three surface science studies employing higher alkenes under better-defined conditions not only demonstrate the applicability of the atomic oxygen mechanism to alkene epoxidation in general, but also provide insight into the importance of C–H bond reactivity in the competing combustion reactions. In the first study, Roberts and Madix [19] co-adsorbed norbornene and atomic oxygen on Ag(110). The higher binding energy of norbornene enables reaction to the epoxide under UHV conditions. Norbornene oxide was formed during temperature-programmed reaction at a temperature above the norbornene molecular desorption temperature as shown in Fig. 3. Since atomic O was the only oxygen species present on the Ag(110) crystal during reaction, this shows that atomic oxygen must be the species reacting to form the epoxide. Additionally, because the bridgehead allylic hydrogens in norbornene have a low gas-phase acidity compared to those of propylene or butene, it

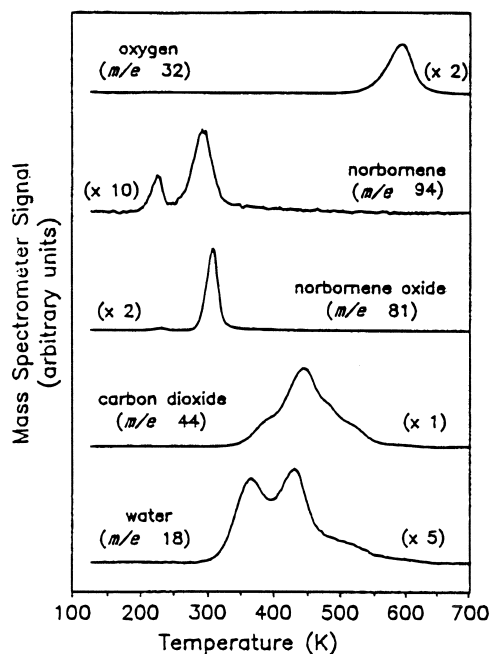


Fig. 3. Temperature-programmed reaction of norbornene in the presence of excess surface oxygen atoms on Ag(110). The oxygen coverage was approximately 0.2 monolayers. The heating rate was 12 K/s. Multiplication factors are referenced to the carbon dioxide spectrum and are corrected for degree of fragmentation in the mass spectrometer (reprinted with permission from Ref. [19]; ©1988 American Chemical Society).

was postulated that high C–H bond acidity favors C–H bond scission and subsequent reaction to combustion products in the higher linear alkenes.

A second model study is the epoxidation of styrene on Ag(111) [22]. Styrene was found to form styrene oxide and combustion products when reacted with chemisorbed atomic oxygen on this surface. The presence of the electron-donating phenyl group and the absence of allylic hydrogens, which would make the alkene susceptible to H-abstraction and hence combustion, are thought to account for the relatively high selectivity observed for epoxidation (60%). Interestingly, in the presence of adsorbed K, an electropositive species, the selectivity declined to 0% while with electronegative Cl, it improved to 93%. These effects are consistent with the electronic effect mechanism described

earlier—these species may be affecting the selectivity for epoxidation by altering the charge on atomic oxygen, thereby influencing its propensity for electrophilic attack of the olefin double-bond. Consistent with the dominance of electronic effects in this system, thermal desorption showed that K also decreased the binding energy of styrene, while it was increased with Cl. In a similar study by Mukoid *et al.* [23], epoxidation of 3,3-dimethyl-1-butene (DMB) on atomic oxygen-precovered Ag(111) in the presence of Cl was found to be exceptionally efficient (> 99%). Although no epoxidation was observed in the presence of K or on an unpromoted surface, this startling selectivity is again attributed to the lack of allylic hydrogens in the olefin. In addition to influencing the charge present on atomic oxygen, Cl and K were found to alter the binding energy of DMB just as they did with styrene.

To compare the trends in selectivity reported for these model systems at low pressure with those obtained under catalytic conditions, Ossipoff and Cant [24] have compiled reaction rates, selectivities, and kinetic orders for ethylene, propylene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, benzene, cyclohexene, norbornene, 1-methylcyclohexene, 4-methylcyclohexene, and styrene over silver sponge catalysts. Cyclic compounds were found to be much less reactive than noncyclic species. The reaction rate was also found to decrease with increasing molecular size, which the authors suggest is due to higher olefin surface coverage, causing less oxygen to be available for reaction. Consistent with the single-crystal results, the selectivity of noncyclic olefins was found to depend on whether abstractable hydrogens were present on nearby carbons. On the other hand, the effect of gas-phase acidity on reaction rate was not pronounced in these experiments, but the authors conclude that competitive adsorption between the olefin and atomic oxygen masks the acidity effect at the high pressures in the catalytic studies. This is an important point, because it indicates that surface science studies

may be uniquely suited for probing the intrinsic reactivity of the molecules, independent from coverage and adsorption effects that can mask these properties under continuous operation at higher pressures. Also, the reaction of norbornene to form benzene on the sponge catalyst rather than norbornene oxide as observed in UHV single-crystal work, was rationalized as oxidative removal of a ring carbon followed by rearrangement to benzene, which is evidently favored at high pressures [25]. Despite these discrepancies, the single-crystal studies employing higher alkenes still provide solid evidence in favor of the atomic oxygen mechanism because the reactions are taking place under conditions where only chemisorbed atomic O is present, and in the absence of any support-related effects. Although alternative pathways seem to be preferred for specific olefin substrates at pressures more similar to those practised industrially, the low-pressure work is clearly capable of shedding light on the roles of moderators and promoters, as well as the characteristics of the olefin that determine its reactivity.

A complementary approach used to demonstrate the plausibility of the atomic oxygen mechanism involves the use of  $N_2O$  instead of  $O_2$  as the oxygen source in ethylene epoxidation. Tan *et al.* [26] first characterized the decomposition of  $N_2O$  on Ag(111), and then studied the epoxidation of ethylene on this surface and over a  $Ag/\alpha-Al_2O_3$  catalyst both in UHV and in a high-pressure reactor.  $N_2O$  was found to produce both chemisorbed atomic oxygen and dissolved atomic oxygen when decomposed at temperatures > 300 K on Ag(111). Significantly, molecular dioxygen is not formed. In the presence of preadsorbed atomic oxygen,  $N_2O$  was found to readily dissociate. This dissociation is also enhanced by low levels of dissolved oxygen, although higher levels suppress it. After dosing  $N_2O$  at 550 K onto the Ag(111) single crystal and then exposing it to ethylene at high pressures, ethylene oxide and acetaldehyde were produced during temperature-programmed reaction. This demonstrates that EO can be directly

produced from atomic oxygen formed from dissociation of  $N_2O$ , in the absence of molecular  $O_2$ . Studies at high pressure with the single crystal showed that the turnover rate to EO when using  $N_2O$  as the oxygen source was approximately 1/7 that from using  $O_2$  itself. The lower rate from  $N_2O$  is attributed to inhibition of its dissociation by the high levels of dissolved oxygen present under the reaction conditions.

As mentioned above, a clean unmodified silver surface exhibits a maximum selectivity to EO of  $\sim 40\%$  [3] and the chemisorption rates of  $C_2H_4$  and  $O_2$  are both relatively slow. The weak binding of  $C_2H_4$  on clean Ag may be enhanced by the addition of electronegative elements such as Cl, which are thought to increase positive charge on silver ( $Ag^{\delta+}$ ), and in fact, this behavior is observed for the higher alkenes [22,23]. In industrial practice, chlorinated hydrocarbons, such as 1,2-dichloroethane, are added in trace amounts to the feed gas. At low Cl feed rates, the activity and selectivity of the catalyst are increased, while at higher feed rates, the activity decreases due to surface site blocking by chloride [27]. Therefore, an optimum surface coverage of chloride moderator is necessary to achieve the best combination of activity and selectivity under given reaction conditions. Due to the low gas-phase levels of Cl modifiers needed to improve selectivity, usually in the ppm range, exact concentration control may be rather difficult. To allow wider chloride ranges for easier operation, chloride scavengers such as ethane are added to the feed gas to promote Cl removal from the surface. A dynamic equilibrium may then be established by adsorption/desorption of Cl species on the catalyst surface during reaction at steady state.

The role of chlorine in the epoxidation of ethylene on Ag single crystal surfaces has been the subject of investigations by numerous groups. Campbell [28] found that although the effect of Cl coverage on selectivity to EO is generally similar for the Ag(110) and Ag(111) crystallographic planes, there are some differ-

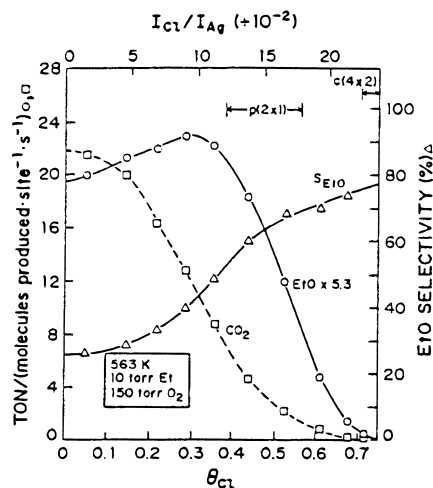


Fig. 4. Steady-state reaction rates and selectivity versus chlorine coverage on Ag(110) at 563 K, 10 Torr ethylene, and 150 Torr  $O_2$  (from Ref. [21]; reprinted with permission from J. Catal., Academic Press).

ences in the detailed responses. At low surface Cl coverages, the turnover numbers for EO production indicate either a small activity decrease [29] or increase [21], depending on the experimental conditions. Fig. 4 shows the effect of chlorine coverage on steady-state reaction rates and selectivity for Ag(110) under conditions where the secondary EO burning reaction is thought to be minimal. Because selectivity is observed to increase significantly around 0.4  $\theta_{Cl}$ , Campbell and Koel [21] propose that the efficiency-enhancing role of Cl occurs primarily through surface site-blocking via an ensemble effect in which  $CO_2$  production requires more free Ag sites than epoxide formation. On the other hand, Grant et al. [30] have proposed the role of chlorine to be primarily electronic in origin. In this view, epoxide formation is favored over ethylene combustion by the presence of adsorbed Cl that competes with adsorbed oxygen for metal electrons, thereby lowering the electronic charge of O(a) and favoring electrophilic attack of  $C_2H_4$ , leading to EO. This mechanism could also account for the observed increase in selectivity with chlorine coverage.

The influence of alkali species, and in particular the interactions between alkali and other promoter species added to industrial catalysts to enhance performance, has been less extensively studied and is not as well understood. Some surface science work has been reported on the effects of cesium, a commonly used selectivity promoter for silver catalysts. Considering solely electronic effects, cesium might be expected to lower the selectivity of the ethylene-to-EO reaction through a donation of electronic charge to atomic oxygen. Indeed, on Ag(111), Cs was found to increase the amount of CO<sub>2</sub> produced from ethylene combustion during temperature-programmed reaction, but to decrease CO<sub>2</sub> associated with EO combustion [31]. Grant and Lambert attribute this to the increased electron density on oxygen inhibiting ring-opening of the epoxide and its subsequent decomposition. A second study focusing on the combustion of ethylene oxide also supports this conclusion [32]. Notably, Campbell's studies on the same crystal plane suggest that the behavior of cesium may be more complex than presented in this relatively straightforward interpretation, with some evidence for the formation of a CsO<sub>3</sub> species which could exert quite different electronic and/or geometric effects [33]. More recent studies have found that Ag(110) undergoes a (1 × 2) reconstruction upon adsorption of Cs [34,35], and that Cs increases the uptake of CO<sub>2</sub> by silver in the presence of oxygen [36]. The latter response could decrease EO burning by inhibiting the formation of additional CO<sub>2</sub>. In actual catalysts, cesium may also influence selectivity by neutralizing reactive sites on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. A recent study [37] contrasted the interaction of cesium and silver with alumina films and found that cesium can form a strong chemisorptive bond with this surface, whereas silver aggregated into particles on the alumina and did not cause large perturbations in its electronic structure.

Another example illustrating the importance of competing ethylene and EO combustion on catalyst selectivity, especially when multiple

promoters are present, is a recent study of a cesium–rhenium–silver model system [7]. Electrolytic silver samples were used to compare the effects of cesium and/or rhenium on catalyst performance. The optimum selectivity and activity were observed for silver promoted with both cesium and rhenium. Thermal desorption spectra indicated that rhenium, which is thought to exist on the silver surface as an oxyanion, weakens the interaction between atomic oxygen and silver. Work function measurements showed that cesium increases the electron density on adsorbed oxygen while rhenium decreases it. The authors conclude that Cs acts to suppress EO combustion while at the same time Re mitigates the alkali's detrimental effect on ethylene combustion by weakening the interaction between atomic oxygen and silver, thereby leading to the highest overall selectivity for the combined Ag–Cs–Re system.

There are numerous published examples of high-selectivity epoxidation systems that go beyond the primary catalyst components discussed so far. One intriguing area of study is the NEMCA effect (non-Faradaic electrochemical modification of catalytic activity). In one recent report [38], silver films deposited on  $\beta''$ -Al<sub>2</sub>O<sub>3</sub>, a Na<sup>+</sup> ion conductor, were promoted in situ by Na and Cl to give an epoxidation selectivity of 88%. The addition of 1,2-dichloroethane as a Cl source was found to be necessary to prevent deactivation due to the formation of sodium carbonate from CO<sub>2</sub> and Na. This extraordinary optimum was located by varying the catalyst potential, and hence Na coverage, and is theorized to correspond to the stabilization of adsorbed Cl on Ag by sodium, possibly via the formation of a silver–oxychloride surface complex that in turn creates sites for the adsorption of weakly bound electrophilic oxygen that promotes the reaction to EO.

Remarkably high selectivities have also been observed for catalysts using gaseous NO as a co-fed promoter [8]. A study of the Ag/K/O/NO system using Ag(111) and Ag(110) crystals, as well as a Ag/Al<sub>2</sub>O<sub>3</sub> cata-

lyst has been reported [39]. Photoelectron spectroscopy indicates that alkali nitrite species are formed on Ag single crystals after exposure to NO, whereas alkali nitrate on silver along with an alkali–NO species on alumina are generated with the supported catalyst. When oxygen is present, the formation of nitrate from NO is favored in both cases. After heating to temperatures used for epoxidation, both nitrite and nitrate are decomposed, and the authors speculate that this could provide a source of surface oxygen for highly efficient reaction to EO. A strong poisoning action of CO<sub>2</sub> on these catalysts is proposed to proceed via competing carbonate formation on the silver surface.

### 3. Linking model systems with real catalysts

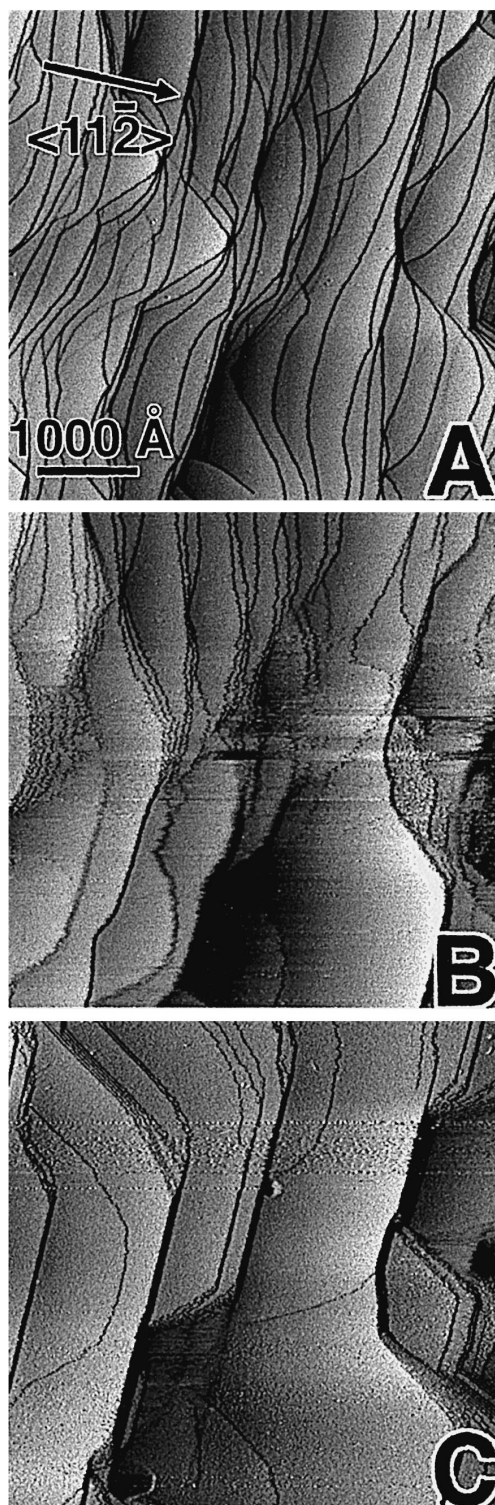
While single-crystal studies have provided enlightening mechanistic details such as the active form of oxygen for epoxidation and the electronic/geometric effects of promoters, molecular-level characterization of the actual silver surface under catalytically relevant conditions has proven to be an elusive goal. ‘Activation’ processes for both single crystals and catalysts, and proposals of unique and unusual species composed of varying combinations of silver, oxygen, chloride, and alkalis abound in the literature. The development of surface science techniques capable of probing these systems at an atomic level, such as scanning tunnelling microscopy (STM), may provide the means to investigate these theories. Several recent STM studies have examined the effects of various adsorbates on the structure of silver surfaces and have observed significant surface rearrangement as the result of exposure to oxygen, chlorine, and CO<sub>2</sub>.

The formation of –Ag–O–Ag– chains along the [001] direction on Ag(110) after exposure to oxygen at room temperature was detected by STM several years ago [40]. This phenomenon is now known as the ‘added-row’ reconstruction. Ag(111) has also been reported to restructure

upon oxygen exposure, at least at temperatures above 800 K [41]. More recently, STM has been utilized to study the dynamics of oxygen-induced faceting on Ag(110) surfaces [42,43]. Ozcomert et al. [43] obtained STM ‘motion picture’ images acquired as the Ag(110)2° → [001] surface undergoes nucleation and growth of facets during exposure to oxygen at room temperature. During 138 min of exposure to oxygen, the silver surface first shows small fluctuating terraces, followed by the growth of stable terraces and finally stable (110) facets amid step bunches. The growth of facets is thought to be thermodynamically controlled because their formation can be completely reversed by the depletion of oxygen via titration with CO at room temperature. The susceptibility to faceting was found to depend on which initially stepped surface was used. A kinetic analysis of the added-row reconstruction during oxygen exposure indicates that Ag atoms are supplied from steps at the rate of 3 atoms/s per site at room temperature; at high oxygen pressure, the formation of the silver–oxygen overlayer is sustained by the creation of pits in the Ag(110) terraces [44]. Significantly, the silver–oxygen chains were found to fluctuate at room temperature unless pinned by impurities or steps. In all, these studies clearly indicate that silver surfaces undergo extensive dynamic changes during exposure to oxygen, even at room temperature.

Interestingly, chlorine adsorption has also been found to induce dynamic restructuring of silver surfaces. STM studies by Frank and Hamers [45] show real-time restructuring of (111)-textured silver films upon dosing Cl<sub>2</sub>. Fig. 5 shows STM images of Ag(111) terraces acquired during room-temperature Cl<sub>2</sub> exposure ( $\theta_{\text{Cl}} \leq 0.38$ ) in which the formation of large terraces and step arrays (microfacets) from narrower terraces and monatomic steps is observed. Thus, exposure to chlorine somehow restructures the surface into wider terraces interspersed with higher steps. Not only are the microfacets stable to temperatures as high as 830 K, but they could also be prepared under a variety of





different conditions. It is thought that the Cl atoms are present on the flat terraces but are too mobile to be directly imaged at room temperature. Nevertheless, Cl-induced changes in the structure of the silver surface could clearly influence its reactivity by creating unique geometric or electronic sites for epoxidation or influencing the stability of key adsorbates. Extension of this work and that on the oxygen–silver system to higher temperatures and with subsequent ethylene exposure could provide additional insight into the nature of the catalytic surface during epoxidation.

STM has also been utilized to study the formation of carbonate species on oxygen-precovered Ag(110) by the reaction of CO<sub>2</sub> [46]. As mentioned earlier, surface carbonate derived from the CO<sub>2</sub> generated in the combustion reactions has been postulated as one mechanism for the inhibition of silver catalysts. From NEXAFS (near-edge X-ray adsorption fine structure) studies, carbonate is known to adsorb parallel to within 10° on the oxygen precovered Ag(110) surface [47,48]. Depending on the initial oxygen coverage during CO<sub>2</sub> exposure, the STM results show that either all of the available oxygen can be converted to carbonate, with the transformation proceeding along the –Ag–O–Ag– added-row [001] direction, or the surface can be reconstructed into separate carbonate and oxygen phases. The reaction starts at the step edges; more specifically, the terminal oxygen atoms of the added rows are the most reactive. The reaction with CO<sub>2</sub> stops when the surface no longer has terminal oxygens and the carbonate and oxygen reconstructed phases coexist in the final structure. Heating leads to CO<sub>2</sub> desorption. Detailed analysis of the STM images indicate that two oxygen atoms are required for the creation

Fig. 5. Real-time STM monitoring of Cl<sub>2</sub> exposure on Ag(111) at room temperature. Dose started after Fig. 1a. Time between images is 6 min. Steps are seen to initially roughen then bunch into two distinct periodicities. Dosing pressure:  $2 \times 10^{-9}$  Torr. Image size:  $4000 \times 4000$  Å (from Ref. [45]; reprinted with permission from J. Catal., Academic Press).

of the carbonate reconstruction, and further suggest that the oxygen atom that is not incorporated in the carbonate desorbs after recombination with another oxygen atom.

In summary, these STM studies bring a new level of understanding to the adsorption and reaction of oxygen, chlorine and CO<sub>2</sub> on silver. The direct observation of surface reconstruction, and most importantly, identification of reactive species, such as the terminal oxygens of the silver–oxygen added rows in the formation of carbonate, demonstrate that reaction may occur most readily at only a small fraction of the atomic oxygen sites on the silver surface. Clearly, these reactions are potentially much more complex than expected, but STM provides a powerful tool for directly observing these reactive species, and promises to enhance our mechanistic understanding of the epoxidation system.

In situ Raman spectroscopy is another technique that has great potential for illuminating the reactive species involved in epoxidation at elevated temperatures and pressures. Bao *et al.* [49] reported the first Raman investigation of Ag(111) and Ag(110) exposed to oxygen and ethylene under conditions close to those practised commercially. The three Ag–O vibrational bands that were found after exposing silver to oxygen and annealing to high temperature were assigned as adsorbed atomic oxygen at 954 cm<sup>-1</sup>, subsurface atomic oxygen at 802 cm<sup>-1</sup>, and atomic oxygen dissolved into the bulk at 632 cm<sup>-1</sup>. Based on changes in the Raman spectrum, Ag(110) was postulated to form (111) facets after long oxygen exposures. When exposed to ethylene, the band at 802 cm<sup>-1</sup> disappears, presumably due to reaction of the proposed subsurface oxygen species with ethylene. The 632 cm<sup>-1</sup> band also decreases in intensity, indicating that bulk oxygen can diffuse towards the surface for reaction. The ability to perform in situ spectroscopic characterization of these model systems, especially when combined with isotopic labelling to unambiguously identify surface species, may be able to provide answers

to long-standing questions about the nature of the oxygen and ethylene species involved in epoxidation.

While STM and Raman spectroscopy are prominent examples of techniques capable of providing atomic-level information regarding the Ag-catalyzed epoxidation reaction, an *ex situ* approach more commonly practised in industry is to use traditional surface science tools, such as various electron spectroscopies, to characterize working epoxidation catalysts, and particularly to rationalize changes in catalyst activity or selectivity over time. Due to incompletely understood aging effects, sustaining initial catalyst performance can frequently be as valuable as improving early-life results. An ongoing example of this type of analysis is Minahan and Hoflund's study of Cs-promoted supported-Ag catalysts [50,51]. Of course, a limiting factor in this approach is the ability to develop an unambiguous interpretation of the data given the complexity of the real-world systems. Single-crystal studies thus play a crucial role in supporting such work by facilitating analogies to simplified models.

#### 4. Conclusions

While we have not tried to be comprehensive in noting recent surface science work in the field of Ag-catalyzed epoxidation chemistry, the studies that are summarized here clearly demonstrate that much progress has been achieved in elucidating and understanding the basic reaction steps and the mechanistic roles of promoters and moderators, particularly in the absence of complicating effects due to high pressures, temperatures, competing adsorption and support materials. Thanks to these fundamental studies, long-debated questions such as the importance of atomic vs. molecular oxygen in the epoxidation reaction have largely been laid to rest. Furthermore, newly available in situ techniques offer the promise of obtaining detailed information on the state of the catalyst under operating

conditions. STM experiments in particular have already shown that under the influence of chlorine or oxygen, the Ag surface is far more dynamic than ever imagined. This technique may eventually provide the ability to ascertain the local environment of the reactive oxygen species in epoxidation. Such structural information has obvious value in refining theoretical treatments of this reaction, an area that, perhaps because of the complicated interactions between silver and oxygen alone, has received only moderate attention of late. Another potentially rewarding approach that may be applied to this reaction system is the deliberate formation of suspected surface intermediates from suitable precursors in order to evaluate their mechanistic plausibility. Though not specifically addressing the mechanism for ethylene epoxidation itself, Jones and Barteau [52] have, for example, decomposed 2-iodoethanol on Ag(110) to form a hydroxyethyl intermediate that they propose goes on to form an oxametallacycle.

Nevertheless, while these studies may someday lead to the rational discovery and development of improved epoxidation catalysts, it is important to note that they may not yet have the sensitivity needed to discern the subtle changes that produce the small selectivity differences upon which much of industrial catalyst development still depends. For example, the concentrations of moderators and promoters in industrial catalysts are finely adjusted at the ppm level, with differences of as little as 100 ppm or less between commercially acceptable and unacceptable formulations. Whether structural or electronic in basis, resolving the slight but economically significant perturbations implied by these adjustments may pose a formidable challenge for the methods of surface science.

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## References

- [1] Kirk-Othmer Encyclopedia of Chemical Technology 4th edn., Vol. 9, Wiley, USA, 1994, p. 915.
- [2] F. Besenbacher, J.K. Nørskov, *Prog. Surf. Sci.* 44 (1993) 5.
- [3] R.A. van Santen, H.P.C.E. Kuipers, *Adv. Catal.* 35, Academic Press, London, 1987, p. 265.
- [4] D.J. Sajkowski, M. Boudart, *Catal. Rev. Sci. Eng.* 29 (1987) 325.
- [5] S. Zhang, *Shiyu Huagong* 24 (1995) 586.
- [6] A. Ayame, *Shokubai* 38 (1996) 205.
- [7] J. Deng, J. Yang, S. Zhang, X. Yuan, *J. Catal.* 138 (1992) 395.
- [8] P. Hayden, R. Clayton, J. Bamforth, A. Cope, European Patent 3642 (1979) to ICI PLC.
- [9] L.A. Kapičak, A.W. Naumann, T.M. Notermann, E.M. Thorsteinson, US Patent 4,994,588 (1991) to Union Carbide Chemicals and Plastics.
- [10] H. Worbs, PhD Thesis, Technische Hochschule Breslau, 1942.
- [11] G.H. Law, H.C. Chitwood, US Patent 2,279,469 and 2,279,470 (1942) to Carbide and Carbon Chemicals.
- [12] V.E. Ostrovskii, N.V. Kul'kova, M.S. Kharson, M.I. Temkin, *Kin. Kat.* 5 (1962) 469.
- [13] R.P. Nielson, J.H. LaRoche, US Patent 4,012,425 (1977) to Shell Oil.
- [14] M.M. Bhasin, US Patent 4,908,343 (1990) to Union Carbide Chemicals and Plastics.
- [15] T. Yamamoto, S. Nagase, H. Tanabe, Kawasaki, US Patent 5,077,256 (1991) to Nippon Shokubai Kagaku Kogyo.
- [16] A.M. Lauritzen, US Patent 4,761,394 (1988) to Shell Oil.
- [17] E.M. Thorsteinson, M.M. Bhasin, S.R. Seyedmonir, U.S. Patent 5,187,140 (1993) to Union Carbide Chemicals & Plastics Technology.
- [18] R.B. Grant, R.M. Lambert, *J. Catal.* 92 (1985) 364.
- [19] J.T. Roberts, R.J. Madix, *J. Am. Chem. Soc.* 110 (1988) 8540.
- [20] G.H. Twigg, *Trans. Faraday Soc.* 42 (1946) 284.
- [21] C.T. Campbell, B.E. Koel, *J. Catal.* 92 (1985) 272.
- [22] S. Hawker, C. Mukoid, J.P.S. Badyal, R.M. Lambert, *Surf. Sci.* 219 (1989) L615.
- [23] C. Mukoid, S. Hawker, J.P.S. Badyal, R.M. Lambert, *Catal. Lett.* 4 (1990) 57.
- [24] N.J. Ossipoff, N.W. Cant, *Catal. Lett.* 16 (1992) 149.
- [25] N.W. Cant, E.M. Kennedy, N.J. Ossipoff, *Catal. Lett.* 9 (1991) 133.
- [26] S.A. Tan, R.B. Grant, R.M. Lambert, *J. Catal.* 104 (1987) 156.
- [27] G.L. Montrasi, G.C. Battison, *Oxidation Comm.* 3 (1983) 259.
- [28] C.T. Campbell, *J. Catal.* 99 (1986) 28.
- [29] C.T. Campbell, M.T. Paffett, *Appl. Surf. Sci.* 19 (1984) 28.

- [30] R.B. Grant, C.A.J. Harbach, R.M. Lambert, S.A. Tan, J. Chem. Soc., Faraday Trans. 1 83 (1987) 2035.
- [31] R.B. Grant, R.M. Lambert, Langmuir 1 (1985) 29.
- [32] S.A. Tan, R.B. Grant, R.M. Lambert, J. Catal. 106 (1987) 54.
- [33] C.T. Campbell, J. Phys. Chem. 89 (1985) 5789.
- [34] C.J. Barnes, M. Lindroos, D.J. Holmes, D.A. King, Surf. Sci. 219 (1989) 143.
- [35] R. Döhl-Oelze, E.M. Stuve, J.K. Sass, Solid State Commun. 57 (1986) 323.
- [36] J.M. Campbell, S. Reiff, J.H. Block, Langmuir 10 (1994) 3615.
- [37] J.A. Rodriguez, M. Kuhn, J. Hrbek, J. Phys. Chem. 100 (1996) 18240.
- [38] Ch. Kkaravasilis, S. Bebelis, C.G. Vayenas, J. Catal. 160 (1996) 205.
- [39] R.M. Omerod, K.L. Peat, W.J. Wytenburg, R.M. Lambert, Surf. Sci. 269–270 (1992) 506.
- [40] T. Hashizume, M. Taniguchi, K. Motai, H. Lu, K. Tanaka, T. Sakurai, Surf. Sci. 266 (1992) 282.
- [41] X. Bao, J.V. Barth, G. Lehmppfuhl, R. Schuster, Y. Uchida, R. Schlögl, G. Ertl, Surf. Sci. 284 (1993) 14.
- [42] T. Hashizume, J.E. Rowe, R.A. Malic, K. Motai, K. Cho, J. Kishimoto, T. Sadurai, J. Vac. Sci. Technol. B 12 (1994) 1809.
- [43] J.S. Ozcomert, W.W. Pai, N.C. Bartelt, J.E. Reutt-Robey, J. Vac. Sci. Technol. A 12 (1994) 2224.
- [44] W.W. Pai, J.E. Reutt-Robey, Phys. Rev. B 53 (1996) 15997.
- [45] E.R. Frank, R.J. Hamers, J. Catal. 172 (1997) 406.
- [46] I. Stensgaard, E. Laegsgaard, F. Besenbacher, J. Chem. Phys. 103 (1995) 9825.
- [47] M. Bader, B. Hillert, A. Puschmann, J. Haase, A.M. Bradshaw, Europhys. Lett. 5 (1988) 443.
- [48] R.J. Madix, J.L. Soloman, J. Stöhr, Surf. Sci. 197 (1988) L254.
- [49] X. Bao, B. Pettinger, G. Ertl, Ber. Bunsenges. Phys. Chem. 97 (1993) 3.
- [50] D.M. Minahan, G.B. Hoflund, J. Catal. 158 (1996) 109.
- [51] D.M. Minahan, G.B. Hoflund, J. Catal. 162 (1996) 48.
- [52] G.S. Jones, M.A. Barteau, J. Vac. Sci. Technol. A 15 (1997) 1667.