

Microkinetic analysis of transient ethylene oxidation experiments on silver

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Abstract

A microkinetic model which successfully explains the steady-state kinetics of ethylene oxidation on silver is used to simulate transient surface science experiments. The model explains a number of important TPR experiments in the literature. It is demonstrated that a model with a common intermediate for epoxidation and combustion may explain these experiments, lending further support for the crucial role of oxametallacycles in ethylene epoxidation. It is suggested that the role of subsurface oxygen is to serve as an oxygen reservoir in transient experiments without oxygen atmospheres, but are otherwise unimportant.

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1. Introduction

Since Lefort's discovery of a direct partial oxidation route of ethylene to ethylene oxide on silver, a tremendous amount of work has accumulated in the literature regarding this reaction [1–4]. The reason for this great interest is that ethylene epoxidation by selective oxidation is one of the major petrochemical processes converting several billion US dollars annually [1,2]. Further, ethylene epoxidation is believed to represent the simplest form of kinetically controlled selective oxidation reaction and therefore a natural first step in understanding selective oxidation in general.

Much of the work in the literature has been directed toward establishing the reaction mechanism of ethylene epoxidation and many different more or less complex models have been proposed [3–10]. Especially, transient surface science experiments such as temperature-programmed reactions (TPR) and pulse experiments combined with different surface science characterization tools (XPS, UPS, AES, etc.) play a great role in our understanding of ethylene epoxidation [3,4,7,11–18]. Such experiments indicate that atomic oxygen on silver is active while molecular oxygen is not

[7,11,16–18], that atomic oxygen creates sites for ethylene adsorption [4,7,13,14], that different total oxidation routes exist [7,14], and that subsurface oxygen appears to play an essential role in activating the silver catalyst toward ethylene epoxidation [7,11,12,17,18]. Further, it has been suggested that ethylene cannot adsorb on reduced silver [4,7,13,14,19].

However, the published transient experiments have only been analyzed qualitatively and have therefore not been modeled by a consistent quantitative model such as a microkinetic model. It is generally dangerous to extrapolate the results of transient surface science experiments to real industrial kinetics. In many transient experiments less than a full catalytic cycle takes place per active site, while in steady-state catalysis many catalytic cycles occur on each site. Furthermore, the rate-determining steps and reaction routes may be different under transient and steady-state conditions.

Recently, we published a microkinetic model based on surface science, explaining the steady-state kinetics of ethylene epoxidation, ethylene combustion, and ethylene oxide combustion for a wide range of reaction conditions [20]. In the present work, this model will be used to analyze and simulate various important transient experiments published in the literature. This analysis offers a consistent reinterpretation of TPR experiments and suggests that the role of subsurface oxygen is unimportant in steady-state kinetics but plays a role in transient experiments as an oxygen reser-

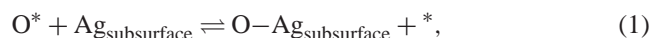
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voir. The successful simulation of transient surface science experiments by the microkinetic model leads to increased confidence that the model contains the essential physics and chemistry to explain ethylene oxidation on silver. Considering that transient kinetic experiments were used to determine many of the parameters of the kinetic model [20] it is not surprising that the model reproduces such experiments. However, it is encouraging that the model with the same parameters reproduces steady-state kinetics as well as offering a consistent reinterpretation of a number of conflicting experiments in the literature. The key idea of the microkinetic model is that both epoxidation and combustion go through a common intermediate, namely an oxametallacycle. It should be stressed that the thermodynamic and kinetic parameters used in the current simulations are identical to those used in the simulation of steady-state kinetics in previous work [20].

2. Methods

The details of the applied microkinetic model have been published elsewhere [20]. The main idea of the model is that a surface oxide (nucleophilic oxygen) is formed and that ethylene and atomic oxygen (electrophilic oxygen) adsorb competitively on the surface oxide. The adsorbed ethylene and electrophilic oxygen react to form an oxametallacycle, which branches into ethylene oxide and acetaldehyde. In the presence of oxygen, acetaldehyde rapidly combusts to CO₂. Ethylene oxide may isomerize to acetaldehyde through the oxametallacycle and combust to CO₂. The oxametallacycle is therefore a common intermediate for ethylene epoxidation, ethylene combustion, and ethylene oxide combustion. Ethylene also combusts through a parallel pathway supposedly through a vinyl alcohol intermediate. However, the parallel ethylene combustion is of minor importance and can be ignored in the present work [20].

In order to take subsurface oxygen into account the microkinetic model is augmented to include the elementary reactions:



These two elementary steps are only included in the microkinetic model in the case where gas-phase oxygen is absent and subsurface oxygen becomes important (Fig. 7). The addition of these reactions ensures that subsurface oxygen can diffuse to the surface as seen experimentally [11] and nucleophilic oxygen can form electrophilic oxygen.

The reaction mechanism applied in the current work is depicted in Table 1. The special notation is explained in detail in [20]; however, in short ^{*} is a metallic silver site consisting of two surface Ag atoms, /O^{*} is a surface oxide site formed by the dissociatively adsorption of oxygen on ^{*}, X^{*} is intermediates on metallic sites, and Y/O^{*} is intermediates on oxide sites. O/O^{*} is an oxygen atom positioned on

Table 1
Reaction mechanism for the microkinetic model

$\text{O}_2(\text{g}) + ^* \rightleftharpoons \text{O}_2^*$	(step 1)
$\text{O}_2^* + ^* \rightleftharpoons 2\text{O}^*$	(step 2)
$\text{O}_2(\text{g}) + 2\text{O}^* \rightleftharpoons 2\text{O}/\text{O}^*$	(step 3)
$\text{C}_2\text{H}_4(\text{g}) + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_4/\text{O}^*$	(step 4)
$\text{C}_2\text{H}_4/\text{O}^* + \text{O}/\text{O}^* \rightleftharpoons \text{CH}_2\text{CH}_2\text{O}/\text{O}^* + \text{O}^*$	(step 5)
$\text{C}_2\text{H}_4\text{O}(\text{g}) + \text{O}^* \rightleftharpoons \text{C}_2\text{H}_4\text{O}/\text{O}^*$	(step 6)
$\text{CH}_2\text{CH}_2\text{O}/\text{O}^* \rightleftharpoons \text{C}_2\text{H}_4\text{O}/\text{O}^*$	(step 7)
$\text{CH}_2\text{CH}_2\text{O}/\text{O}^* \rightleftharpoons \text{CH}_3\text{CHO}/\text{O}^*$	(step 8)
$\text{CH}_3\text{CHO}/\text{O}^* \rightleftharpoons \text{CH}_3\text{CHO}(\text{g}) + \text{O}^*$	(step 9)
$\text{CH}_3\text{CHO}/\text{O}^* + 6\text{O}^* \rightleftharpoons 2\text{CO}_2^* + 4\text{OH}^* + ^*$	(step 10)
$\text{C}_2\text{H}_4(\text{g}) + ^* \rightleftharpoons \text{C}_2\text{H}_4^*$	(step 11)
$2\text{OH}^* \rightleftharpoons \text{H}_2\text{O}^* + \text{O}^*$	(step 12)
$\text{CO}_2^* \rightleftharpoons \text{CO}_2(\text{g}) + ^*$	(step 13)
$\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O}(\text{g}) + ^*$	(step 14)
$\text{O}^* + \text{Ag}_{\text{subsurface}} \rightleftharpoons \text{O}-\text{Ag}_{\text{subsurface}} + ^*$	(step 15)
$2\text{O}^* \rightleftharpoons \text{O}/\text{O}^* + ^*$	(step 16)

The asterisk signifies a metallic silver site, /O^{*} is a surface oxide site, and X^{*} and Y/O^{*} are adsorbed species on metallic silver and surface oxide, respectively.

an oxide site and is also called electrophilic oxygen. All the elementary reactions in the model are assumed to be microscopically reversible and the kinetics is described by Arrhenius expressions. A statistical thermodynamic description is used for all gas-phase molecules and adsorbates. All thermodynamic and kinetic parameters except for the two new steps (steps 15 and 16) are reported in previous work [20]. The parameters for steps 15 and 16 in Table 1 are relevant only to the case when subsurface oxygen diffuses rapidly to the surface and to the surface oxide sites to form electrophilic oxygen.

In order to simulate transient experiments, the mechanism is modeled and solved as outlined previously [20], although the emphasis is of course on the study of the transient solution and that a linear temperature ramp is introduced in the simulation of TPD and TPR experiments,

$$T = T_0 + \beta t, \quad (3)$$

where T (K) is the actual temperature, T_0 is the temperature in the beginning of the experiment β (K/s) is the constant heating rate and t is time (s). Further, a second site balance for the subsurface sites is included in the model:

$$\theta_{\text{Ag}_{\text{subsurface}}} = 1 - \theta_{\text{O}-\text{Ag}_{\text{subsurface}}}. \quad (4)$$

3. Results and discussion

In this section we will analyze and discuss different transient experiments and misunderstandings in the literature in the light of the microkinetic model developed earlier [20].

3.1. Initial sticking

Initially, we will use our microkinetic model to calculate the initial sticking probabilities for various adsorption reactions to get an idea, if it is possible to study these reactions

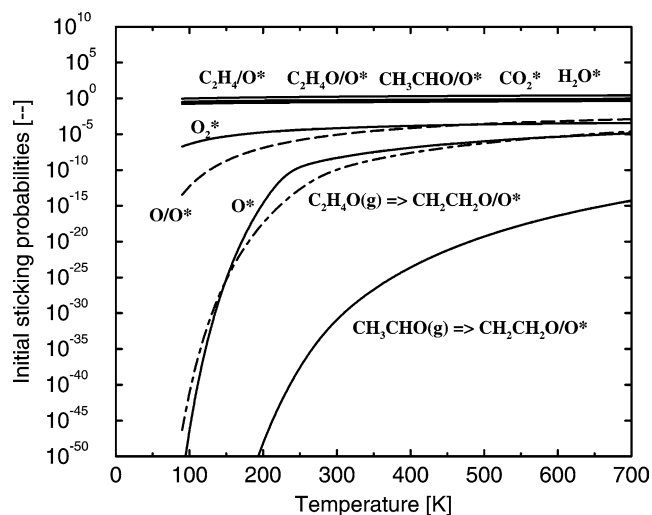


Fig. 1. The calculated initial sticking probabilities of O_2^* , O^* , O/O^* , $\text{C}_2\text{H}_4/\text{O}^*$, $\text{C}_2\text{H}_4\text{O}/\text{O}^*$, $\text{CH}_3\text{CHO}/\text{O}^*$, $\text{CH}_2\text{CH}_2\text{O}/\text{O}^*$, CO_2^* , and H_2O^* versus temperature.

in UHV experiments. In Fig. 1 the initial sticking probabilities for the adsorption of various surface intermediates are shown for different choices of temperature. All the calculated sticking probabilities are less than or equal to unity and are therefore physically realistic. The sticking of ethylene, ethylene oxide, acetaldehyde, carbon dioxide, and water is very high and approaches unity in the whole temperature range; this is consistent with experiments [21–24].

It is observed that the molecular and dissociative sticking of oxygen is very low as also seen experimentally [25]. It is also apparent from the figure that according to the microkinetic model, the dissociative adsorption of oxygen on the surface oxide layer is 1–2 magnitudes faster than the adsorption on metallic silver. Since O/O^* has not been studied by surface science techniques, there is no experimental evidence supporting this claim. However, the sticking of O/O^* can be lowered or increased without collapsing the microkinetic model. In addition, DFT calculations by King and co-workers [26] indicate that the dissociation barrier is lower on surface oxide than on metallic silver.

The sticking probability for the formation of oxametallacycle from ethylene oxide varies from $\sim 10^{-10}$ at 300 K to $\sim 10^{-5}$ at 600 K. This explains the difficulties in studying the oxametallacycle in UHV [27–31]. Furthermore, this shows that ethylene oxide isomerization is a slow process or industrial ethylene epoxidation would not be feasible. The value of $\sim 10^{-10}$ at 300 K is close to the value of $\sim 10^{-8}$ measured by Grant and Lambert [32] for adsorption of ethylene oxide at room temperature. The discrepancy is believed to be due to the uncertainties in measuring such small sticking probabilities experimentally. Finally, an extremely low sticking probability for formation of the oxametallacycle from acetaldehyde is observed, which corresponds well to the fact that acetaldehyde is thermodynamically favored over ethylene oxide.

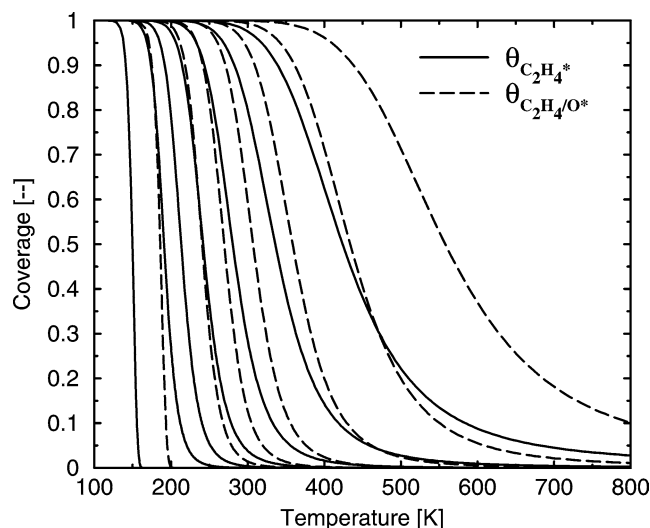


Fig. 2. The simulated equilibrium coverages of ethylene on reduced (C_2H_4^*) and oxidized silver ($\text{C}_2\text{H}_4/\text{O}^*$) versus ethylene pressure and temperature. The ethylene pressures are 0 (left full and dashed curve), 0.001, 0.01, 0.1, 1, 10, and 100 kPa (right full and dashed curve).

Strictly speaking, the calculated sticking probabilities are not predicted by the microkinetic model, but model parameters were chosen in such a way that the model would predict sticking probabilities consistent with experiments [20]. However, it is important to note that the parameters are physically realistic and are able to predict steady-state kinetics as well.

3.2. Adsorption of ethylene

It has been suggested that ethylene will not adsorb on reduced silver but will adsorb in the presence of oxygen. However, TPD experiments on $\text{Ag}(110)$ and $\text{Ag}(111)$ show that ethylene does adsorb on reduced silver at 100 K and desorbs at 140–150 K [21,30,33–35]. Ethylene adsorbed on silver with preadsorbed oxygen desorbs at 160–180 K [21,30,33–36]. This indicates that ethylene does adsorb on both reduced and preoxidized silver, however, the enthalpy of adsorption is greater on the latter. The greater enthalpy of adsorption is probably due to the formation of $\text{Ag}^{\delta+}$ sites by the presence of preadsorbed oxygen, which interact favorably with the π -orbitals of ethylene. Fig. 2 shows simulated coverages of ethylene on reduced and preoxidized silver versus temperature at different pressures. It is clear from the figure that at a given temperature and ethylene pressure, the coverage of ethylene is significantly higher on preoxidized silver than on reduced silver. In UHV ethylene is found to desorb at ~ 150 K on reduced silver and ~ 180 K on preoxidized silver in Fig. 2, which agrees very well with experiments.

The reason for the misunderstanding that ethylene cannot adsorb on reduced silver may be explained in two ways depending on the experiment in question. In one type of experiment, large exposures (10^7 L) of ethylene are applied to a silver sample at room temperature. Afterward the sample

is evacuated to UHV and TPD is performed. In the case of a reduced sample nothing happens in the subsequent TPD, while for the preoxidized sample products of the reaction between ethylene and oxygen evolve. Therefore it appears that at room temperature ethylene only adsorbs on preoxidized silver. However, according to Fig. 2 at room temperature in UHV ethylene is not stable neither on reduced nor on preoxidized silver. The explanation of this paradox is that in the case of preoxidized silver ethylene reacts with oxygen and forms stable intermediates that survive evacuation and subsequently desorb in TPD. Without the presence of oxygen, such reactions are not possible and ethylene does not decompose on reduced silver. This also explains the large ethylene exposure needed to create surface species, which is in contrast to the high sticking probability (~ 1) measured in UHV experiments on single crystals [21]. The large necessary exposure indicates that a slow surface reaction takes place. We will have more to say about these experiments later (Section 3.3).

In the second type of experiments the coverage of ethylene is measured on reduced and preoxidized silver at a chosen temperature and ethylene pressure [19]. From Fig. 2 it is apparent that one can choose a temperature and pressure in such a way that a measurable coverage is present on the preoxidized sample while a negligible amount is present on the reduced sample. From such experiments it would appear that ethylene only adsorbs on preoxidized silver, while more careful experiments will show that ethylene adsorbs on reduced silver too.

Fig. 2 also illustrates that even though an intermediate desorbs at very low temperatures in UHV, it may have a significant coverage at the high pressures of industrial heterogeneous catalysis. This feature is very often overlooked in the literature leading to faulty interpretations. For example, the low heat of adsorption of ethylene (~ 40 kJ/mol) often leads to speculations that ethylene does not adsorb on silver under industrial conditions and instead reacts with oxygen through an Eley–Rideal mechanism (Refs. [3,26] and references therein).

3.3. Simulation of TPR experiments

As noted in the introduction TPR experiments have played a great role in our understanding of ethylene epoxidation. The TPR experiments can be divided into experiments performed in UHV and inert carrier gases and experiments in a reactive oxygen/ethylene atmosphere.

It has not been possible to form ethylene oxide directly in UHV by adsorbing ethylene and oxygen on silver and perform a TPD experiment. This may be due to a number of reasons. First, it is likely that ethylene and/or the active oxygen species desorb before the reaction barrier is climbed. Secondly, it may be difficult to form the active oxygen species in UHV. Fig. 3 shows a simulation of a TPR experiment, where electrophilic oxygen and ethylene is adsorbed on silver at 100 K. It is of no concern here if this initial state of the ex-

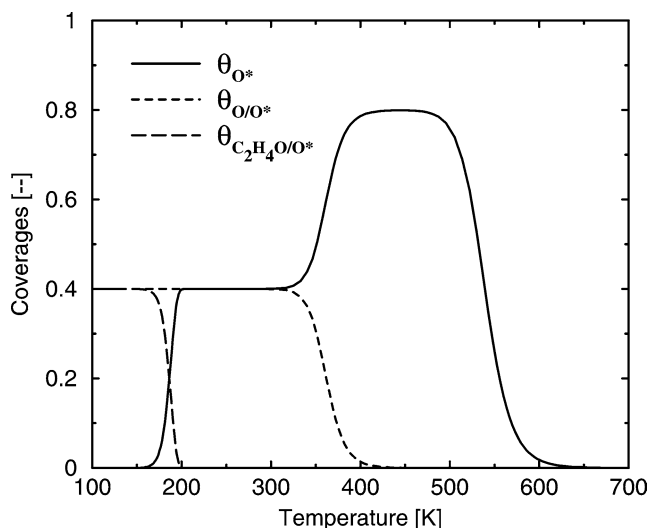


Fig. 3. Simulation of a TPR experiment for preadsorbed electrophilic oxygen (O/O^*) and ethylene ($\text{C}_2\text{H}_4/\text{O}^*$) on silver at 100 K in UHV. $\beta = 10$ K/s, $\theta_{\text{O}/\text{O}^*}^0 = 0.4$, and $\theta_{\text{C}_2\text{H}_4/\text{O}^*}^0 = 0.4$.

periment may be prepared in reality. It is just investigated what the microkinetic model predicts for this hypothetical experiment. As observed from the figure the adsorbed ethylene desorbs (~ 200 K) before any reaction takes place. Later the electrophilic oxygen desorbs at ~ 350 K followed by the desorption of surface oxide oxygen at ~ 550 K. The microkinetic model therefore shows that even if the active species could be adsorbed on silver in UHV, they will desorb before any reaction takes place. This example illustrates how a microkinetic model may be applied to study situations that may not be realized experimentally. This is one of the great strengths of a microkinetic model.

Grant and Lambert [7] performed two types of TPR experiments on Ag(111). First preoxidized Ag(111) was exposed to ethylene ($\sim 10^7$ L) at 300 K. Subsequent TPD resulted in CO_2 desorbing at ~ 380 K, while ethylene oxide did not form. However, by treating the Ag(111) crystal in a 1:6 ethylene:oxygen mixture at 425 K and 1.33 kPa for 1 h it was possible to activate the Ag(111) catalyst. Using the same procedure on the activated catalyst as described above, resulted in an evolution of acetaldehyde and ethylene oxide in a common peak at ~ 360 K. CO_2 still evolved at ~ 380 K but a second peak also appeared at ~ 450 K. The activation of the Ag(111) crystal resulted in the formation of subsurface oxygen. Hence the authors concluded that subsurface oxygen is necessary in ethylene epoxidation supposedly by withdrawal of electron density from surface oxygen and thereby creating electrophilic oxygen that reacts with the π -orbitals of ethylene. Similar results and suggestions have been reached by a number of workers [7,11–14]. The authors [7] interpreted the TPR experiments in the following way: Ethylene is adsorbed on both the preoxidized activated and nonactivated Ag(111) crystal at 300 K. During heating ethylene reacts with preadsorbed oxygen and forms reaction products. Ethylene combusts on both activated and

nonactivated Ag(111). On activated Ag(111) ethylene oxide is formed and some of this ethylene oxide combusts further to CO₂. Therefore two combustion pathways are identified and the authors concluded that subsurface oxygen is necessary for the selective oxidation. However, this interpretation can be questioned. First, as shown earlier (Fig. 2) ethylene is not stable on Ag(111) at 300 K in UHV. Instead some stable intermediates must be formed during the ethylene exposure, which leads to the formation of CO₂, ethylene oxide, and acetaldehyde, respectively, in subsequent TPD. This is a minor detail that does not change the main conclusions from the experiments. It is clear that subsurface oxygen plays a role in these transient experiments, but it is dangerous to conclude that this implies that subsurface oxygen must be important in steady-state kinetics. Campbell [5] pointed out that only one ethylene oxide molecule was formed for each 200 Ag surface atoms in the experiments of Grant and Lambert. This corresponds to a coverage of ~ 0.005 ML. Simulation of the TPR experiment of Grant and Lambert using the microkinetic model results in the following interpretation: During the ethylene exposure to the preoxidized Ag(111) crystal an oxametallacycle coverage builds up as depicted in Fig. 4. It is apparent from the figure that a low coverage of oxametallacycle actually accumulates on the surface. The predicted oxametallacycle coverage by the microkinetic model is a little too low, but considering the great experimental uncertainties and the assumptions in the model, the result is impressive. The current experiment was performed at 300 K, while the microkinetic model explains steady-state kinetics at 450–650 K. As shown in Fig. 4 decreasing the activation barrier for the formation of the oxametallacycle (step 5 in Table 1) 2 kJ/mol from 112 to 110 kJ/mol results in a much higher coverage. Actually, this could suggest that the reason why ethylene oxide is only formed when Ag(111) is activated by subsurface oxygen is that subsurface

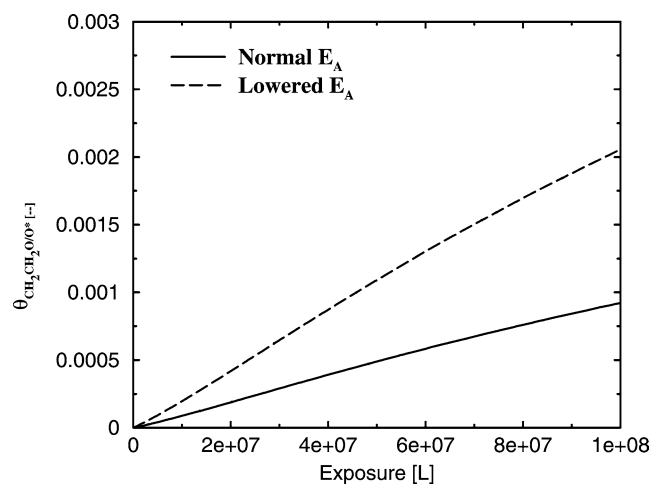


Fig. 4. Calculated development in coverage of oxametallacycle cycle ($\text{CH}_2\text{CH}_2\text{O}/\text{O}^*$) versus ethylene exposure of preoxidized silver at 300 K in a UHV chamber. Two cases are shown, one with the normal activation barrier for step 5 (112 kJ/mol) and another where the barrier is lowered 2 kJ/mol (110 kJ/mol). $P_{\text{C}_2\text{H}_4} = 133$ Pa, $\theta_{\text{O}^*} = 0.25$, and $\theta_{\text{O}/\text{O}^*} = 0.75$.

oxygen decreases the activation barrier referred to above. A small decrease in this barrier would be very important in the room temperature experiments of Grant and Lambert, but would be insignificant at the temperatures of industrial ethylene epoxidation. This is a very simple and likely explanation for the role of subsurface oxygen. This leads to the conjecture that normal atomic surface oxygen is active in industrial ethylene epoxidation as suggested in the microkinetic model of Linic and Barteau [9]. However, due to the titration experiments of Campbell and Paffett [33] and Van Santen and co-workers [12] at 300–600 K this explanation is untenable.

Subsequent TPD of the adsorbed/formed oxametallacycle results in the formation of ethylene oxide and acetaldehyde at ~ 370 K as shown in Fig. 5. This is in agreement with experiments [7,13,14]. Further it is well established that oxametallacycles may form ethylene oxide and acetaldehyde [27–31].

For simplicity, the CO₂ formation is not included in these simulations. However, the microkinetic model may easily account qualitatively for the two peaks of CO₂ formation. The peak at ~ 380 K is a result of the parallel combustion of ethylene by nucleophilic oxygen through a vinyl alcohol intermediate or perhaps another intermediate such as formate. The CO₂ peak at ~ 450 K is due to the further combustion of acetaldehyde formed from the oxametallacycle. It is interesting to note that Grant and Lambert [7] used these experiments to argue that the combustion and epoxidation of ethylene proceed through very different reaction routes. On the other hand, we interpret the experiments successfully by a model where the main part of ethylene combustion and epoxidation goes through a common intermediate. Due to the small conversion and the reaction conditions it is very difficult to estimate the relative importance of different reaction routes in these TPR experi-

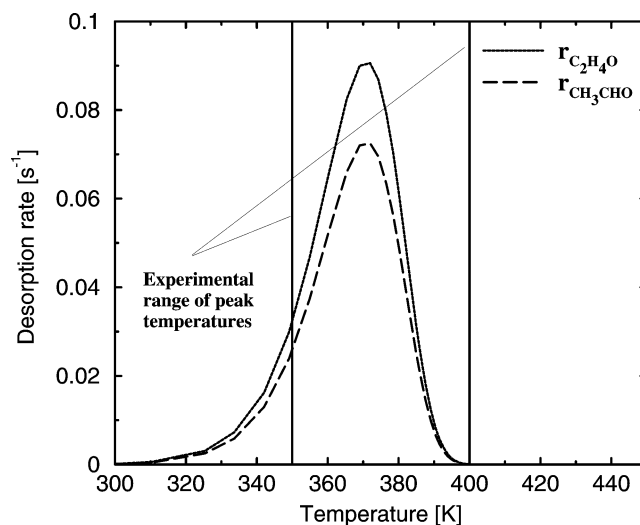


Fig. 5. Simulation of a TPD experiment for adsorbed oxametallacycle ($\text{CH}_2\text{CH}_2\text{O}/\text{O}^*$). $\beta = 10$ K/s and $\theta_{\text{CH}_2\text{CH}_2\text{O}/\text{O}^*}^0 = 0.5$. Experimental reported peak temperatures are in the range 350 to 400 K [7,13,14].

ments. Based on our microkinetic model [20] the parallel combustion is very important at low reactant pressures and this seriously decreases the selectivity at UHV and at the low pressures applied by Grant and Lambert [7]. Grant and Lambert concluded from their experiments that the combustion and epoxidation pathways are very different. However, our model shows that as the reactant pressures increase the parallel combustion of ethylene becomes less important and plays no role under industrial conditions. This explains why Campbell [5] using moderate reactants pressures came to the conclusion that the routes of combustion and epoxidation are very similar, in fact go through a common intermediate. This is also reflected by the fact that Campbell observed selectivities as high as $\sim 40\%$, while Grant and Lambert only achieved selectivities of $\sim 20\%$. This example illustrates a potential pitfall in drawing too strong conclusions from surface science experiments in UHV. In addition, we believe that the above interpretation of the TPR of Grant and Lambert [7] is consistent with the recent experiments of Linic and Barteau [31] and Tysoe and co-workers [35]. In particular, Linic and Barteau found that an oxametallacycle is formed when Ag(111) is heavily dosed with ethylene oxide at 250 K and the oxametallacycle reforms ethylene oxide at ~ 300 K. Correcting for the different heating rates used by Grant and Lambert and by Linic and Barteau the temperatures of ethylene oxide formation are within experimental uncertainties.

Van Santen and co-workers [11,12] performed a series of very important TPR experiments combined with isotopic labeling in reactive atmospheres. These experiments together with the experiments of Grant and Lambert [7] were probably the experiments that convinced most researcher that atomic oxygen is active in both ethylene epoxidation and combustion. Furthermore, Van Santen and co-workers showed that subsurface oxygen is essential to ethylene epoxidation in the absence of gaseous oxygen and that subsurface oxygen exchanges rapidly with surface oxygen and participates in surface reactions. Figs. 6A and 6B depict simulations of such experiments with the microkinetic model for oxygen-rich and oxygen-poor atmospheres, respectively. In these experiments gas-phase oxygen and ethylene were sealed together with silver in a reactor setup. The temperature of the reactor was then raised linearly and the amounts of reactants and products were monitored with time/temperature. The model captures the trends of the experiments with almost quantitative precision. In the beginning of the experiment oxygen and ethylene are consumed in the production of ethylene oxide and CO_2 . Again the experiment suggests that both ethylene epoxidation and combustion go through a common intermediate. At some point all the oxygen is consumed and ethylene starts to be consumed. In the simulation ethylene oxide is isomerized to acetaldehyde which accumulates in the system. However, experimentally the ethylene oxide decomposes to form ethylene and oxygen [11,15,37–41]. The oxygen ends up in CO_2 and the ethylene starts to accumulate in the gas phase

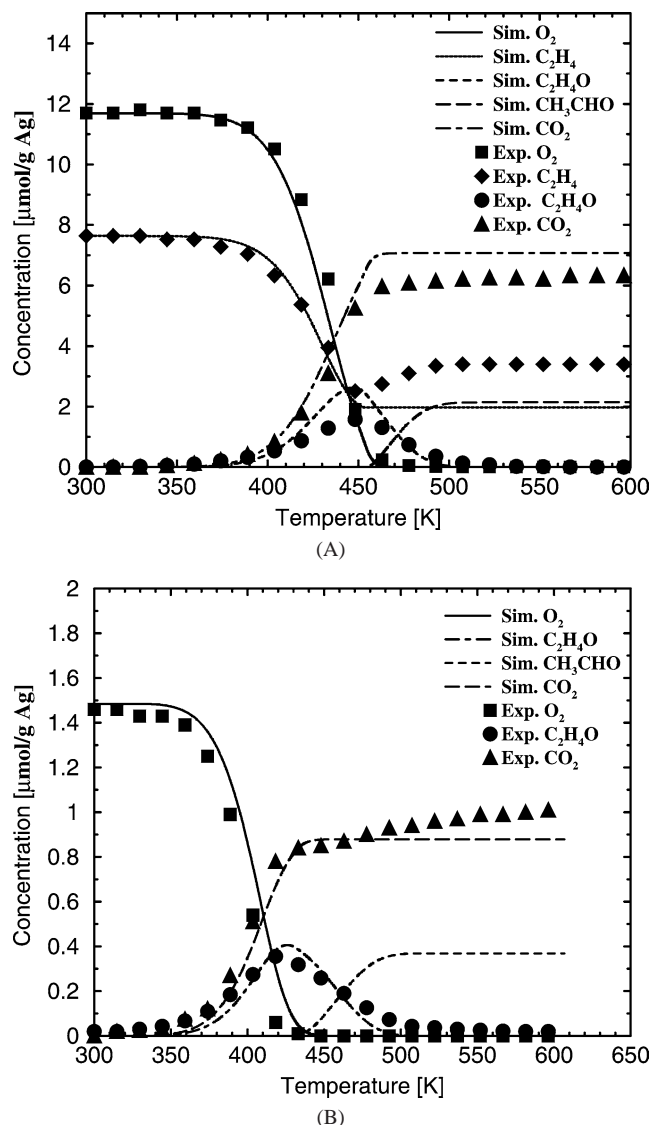


Fig. 6. Simulation of van Santen and de Groot's TPR experiments in reactive atmospheres. (A) Oxygen-rich conditions with $P_{\text{O}_2} = 2.7$ kPa and (B) oxygen-poor conditions with $P_{\text{O}_2} = 0.35$ kPa. Initial ethylene pressure, 1.7 kPa, $1.08 \mu\text{mol/g Ag}$ preadsorbed oxygen, $\beta = 2.3$ K/min. Experimental data points are extracted from [11].

(cf. Fig. 6). In the microkinetic model ethylene oxide does not decompose through the reverse route of the formation of oxametallacycle. However, if the stability of oxygen is increased dramatically in the model such a decomposition becomes possible. This could indicate that the decomposition takes place on special sites (steps or defects) with a high oxygen stability. Adsorption isotherms do show a very high stability of oxygen at low coverages [42]. Also ethylene oxide decomposition seems to increase on smaller silver particles which should contain a large amount of defects [40]. Furthermore, Grant and Lambert [32] did not observe any decomposition of ethylene oxide on Ag(111) single crystals. Ethylene oxide decomposition only takes place in the absence of gaseous oxygen. This could be due

to two reasons. First, the presence of oxygen could poison the defect sites necessary for decomposition. Secondly, the thermodynamic driving force for ethylene oxide decomposition is the formation of O^* which promotes CO_2 formation. In steady-state kinetics of ethylene oxidation oxygen is present and ethylene oxide decomposition is therefore unimportant.

On a more general note the TPR experiments of van Santen and de Groot illustrate an elegant way of circumventing the problem that TPR cannot be performed in UHV (Fig. 3). Of course it is more problematic to interpret such experiments, but if the catalyst is sufficiently characterized it would even be possible to extract important kinetic and thermodynamic parameters for use in microkinetic modeling from such experiments. From a modeling point of view the use of single crystals would be particularly useful, but may be problematic from an experimental point of view.

3.4. The role of subsurface oxygen

It is clear from TPR experiments [7,11–14] and pulse reactor experiments [15–18] that subsurface oxygen promotes the production of ethylene oxide. In the absence of subsurface oxygen only combustion takes place. Most people seem to favor the explanation that subsurface oxygen electronically modifies the surface oxygen, making it more electrophilic and therefore able to attack the double bond of ethylene [3,7]. This is a very reasonable and simple explanation; however, a lot of unexplained aspects exist regarding steady-state kinetics. If subsurface oxygen forms the loosely bonded surface oxygen necessary to explain reaction kinetics [5,43,44] and adsorption isotherms [45,46], a significant decrease in O^* desorption temperature is expected in the presence of subsurface oxygen, which is not observed experimentally [12]. Furthermore, the formation of subsurface oxygen is slow and activated [7,47] and it is therefore doubtful that the uptake of subsurface oxygen is rapid enough to form the active sites necessary under steady-state reaction conditions unless it acts as a static promoter not consumed during reaction. However, experiments show that subsurface oxygen does participate in ethylene oxidation and rapidly exchanges with surface oxygen under reaction conditions [11]. This leads to a new paradox: If subsurface and surface oxygen rapidly exchanges under reaction conditions why does subsurface oxygen around 700 K instead of desorbing at the same temperature as surface oxygen (580 K)? It seems as if subsurface oxygen may rapidly transfer to the surface only if surface oxygen is already present. In the absence of surface oxygen subsurface oxygen first enters the surface at ~ 700 K. A similar effect is observed in the presence of chlorine [6,8,48], which apparently promotes the amount and uptake rate of subsurface oxygen. This may indicate that electronegative species on the silver surface promotes the exchange rate between surface and subsurface oxygen. This promotion may be explained in two ways: The elec-

tronegative surface species changes the subsurface diffusion barrier electronically and/or the severe reconstruction due to the presence of surface O or Cl increases the subsurface diffusion rates. Further, it is not clear what subsurface oxygen is. Recent DFT calculations suggest that in the absence of surface oxygen subsurface oxygen is less stable than gas-phase and surface oxygen, making its existence hard to explain [49]. Some scientists even claim that the subsurface oxygen is really a surface oxygen (Ref. [4] and references therein). In addition, Campbell and co-workers [5,33] investigated the steady-state kinetics on Ag(111) and Ag(110) in a high-pressure cell and rapidly transferred the single crystals to UHV after steady state was obtained [5,33]. In these experiments after transfer to UHV only surface oxygen (O^*) was observed even though subsurface oxygen should be more stable than surface oxygen. This suggests that subsurface oxygen is unimportant under steady-state conditions. It is clear, however, that subsurface oxygen plays a key role in the transient experiments of Grant and Lambert [7] and van Santen and co-workers [11,12].

We suggest that the role of subsurface oxygen in these transient experiments is to serve as an oxygen reservoir that supplies oxygen to the surface oxide.

In Fig. 7 the reaction between ethylene and different oxygen species preadsorbed on silver is simulated. The parameters to describe elementary reaction Eqs. (1) and (2) are chosen in such a way that subsurface oxygen diffuses rapidly to the surface and to the surface oxide sites to form electrophilic oxygen under reaction conditions, this is consistent with the above experimental review. The experimental conditions used in Fig. 7 mirror the conditions used experimentally by van Santen and co-workers [12]. It is clear from the figure that ethylene oxide is only produced if both surface oxide oxygen and subsurface oxygen are present. In the presence of subsurface oxygen it is possible to form electrophilic oxygen that leads to ethylene oxide. In the absence of subsurface oxygen a much smaller fraction of electrophilic oxygen will form and the formed ethylene oxide will combust by the surface oxide oxygen before a new ethylene oxide molecule is formed. Note that the formation of both CO_2 and C_2H_4O go through an oxametallacycle in the simulations and therefore require electrophilic oxygen. It is thus clear that electrophilic oxygen is produced in all three cases but at different rates.

The simulations illustrate that it is possible that the role of subsurface oxygen is merely to act as a oxygen reservoir. However, it does not prove that this is the case.

4. Conclusion

Our microkinetic model which explains, as we have earlier demonstrated, the steady-state kinetics of ethylene oxidation on silver was used here to analyze a number of important transient experiments. This leads to reinterpretations of some important experiments in the literature. It was found

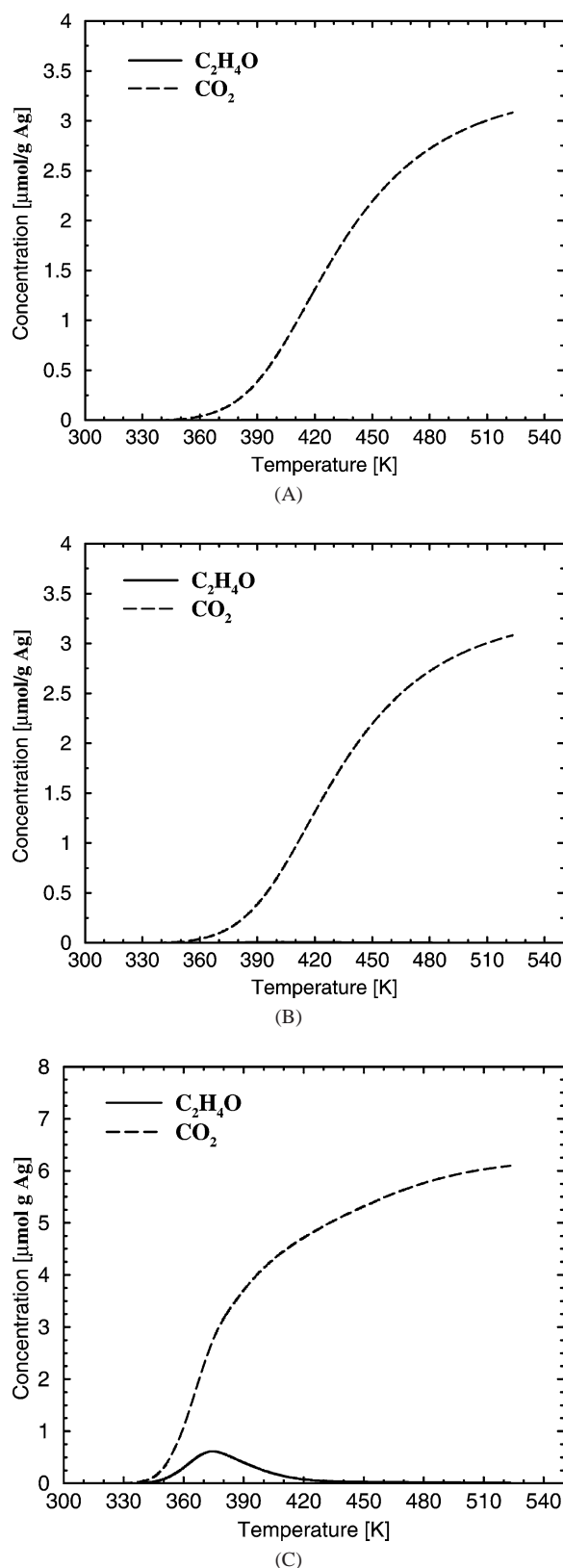


Fig. 7. Simulation of TPR in ethylene atmosphere for a silver catalyst with preadsorbed surface oxide oxygen (A), subsurface oxygen (B), and both surface oxide and subsurface oxygen, (C) $P_{C_2H_4} = 100$ Pa and $\beta = 5$ K/min. Initial coverage of one was used for the respective oxygen species in the simulations.

that ethylene may adsorb on both reduced and oxidized silver and the controversial experiments were rationalized. TPR experiments using ethylene and preoxidized silver were explained successfully by the formation of a common intermediate (the oxametallacycle) in epoxidation and in combustion. The same experiments have earlier been used as proof for mechanisms with very different epoxidation and combustion pathways. Simulations of TPR experiments with reactive atmospheres also supported the existence of a common intermediate in ethylene oxidation. It was suggested that subsurface oxygen only plays a role in transient experiments without oxygen atmosphere where it serves as an oxygen reservoir. This idea was supported by simulations. It may not be surprising that the model explains transient kinetic experiments since a lot of the parameters are established from these transient experiments. However, the model also explains steady-state kinetics and offers a new rationalization of experiments in the literature that previously led to conflicting and inconsistent interpretations. The fact that the microkinetic model not only explains the steady-state kinetics but also transient surface science experiments leads to increased confidence that the model contains the essential physics and chemistry to explain ethylene oxidation on silver. However, as for all microkinetic modeling the model contains some degree of approximation, speculation, and simplification and should be looked upon as a step toward an understanding of ethylene oxidation rather than a complete and perfect model.

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