High-pressure STM studies of oxidation catalysis

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Appendix II

Ethylene oxidation over Ag(111) and Pt(111)

In this appendix preliminary results are discussed for the partial and total oxidation of ethylene at atmospheric pressure and elevated temperature. Our results indicate that in the case of ethylene epoxidation the active catalyst is a thick, insulating oxide. For the total oxidation of ethylene on Pt(111) the reaction follows a Langmuir-Hinshelwood mechanism.

AII.1 General

Depending on the type of the catalyst and reaction parameter, the oxidation of ethylene can lead to the formation of ethylene oxide (epoxide) or to the formation of CO_2 and water, as seen in Figure A.II.1. The first reaction is also known as the selective or partial oxidation or the epoxidation of ethylene, while the second reaction is called the total oxidation or combustion [1].

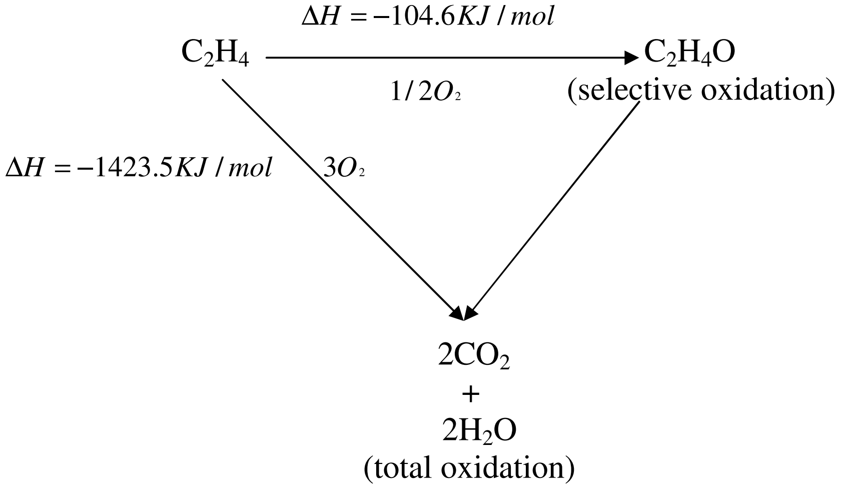

Figure A.II.1: *Schematic representation of the possible reaction paths and products of the* $\boldsymbol{C_2H_4+O_2}$ *reaction.*

In this appendix we show preliminary results obtained with our combination of high-pressure scanning tunneling microscopy and mass spectrometry on both reaction paths, namely partial oxidation of ethylene on Ag(111) and total combustion of ethylene on Pt(111).

AII.2 Partial oxidation of ethylene over Ag(111)

Introduction

Ethylene oxide is one of the most versatile chemical intermediates. With water it forms glycol and polyglicols, with ammonia and amines it forms ethanolamines, which are important solvents. Other important reactions are the polymerisation and the isomerization of ethylene oxide. Silver is the unique catalyst for the oxidation reaction of ethene to ethene oxide. All practical catalysts for the formation of this important compound are silver-based [1-3]. In spite of the existence of a large amount of literature, the data on the adsorption of ethylene, ethylene oxide, water and carbon dioxide on pure metallic silver are conflicting. Also the mechanism of the epoxidation reaction has not been elucidated. Before going into detail we first highlight some properties of silver and silver oxide [4-6]. Silver is the best electrical conducting material and the second best conductor of heat after diamond. The formation of silver oxide proceeds according to:

$$2Ag + 1/2O_2 \rightarrow Ag_2O \qquad \Delta H^\circ = -28kJ/mol$$
$$\Delta G^\circ = -10kJ/mol$$

Silver oxide decomposes above room temperature in air. According to Dushmann, silver oxide needs a partial pressure between 0.56 and 20.8 atm of oxygen pressure to remain stable at temperatures between 446 K and 575 K, where the oxidation reaction occurs [7].

Silver is a good catalyst for ethene epoxidation, because it forms weak bonds with ethene and oxygen. As mentioned above, the origin of the unique catalytic advantage of silver has not yet been clarified. In the last years, most of the existing surface spectroscopic techniques have been used to investigate the oxygen species adsorbed on a silver surface [8-15]. Combining the conclusions from all these investigations it seems that at least four oxygen species adsorbed on the Ag surface exist: molecularly adsorbed oxygen (O_2), superoxide (O^-_2) and peroxide (O_2^{2-}), atomically adsorbed species (O^- and/or O^{2-}) and, finally, subsurface oxygen [16]. Since ethylene does not adsorb on a clean silver surface, a reaction mechanism according to which the adsorbed oxygen on the silver surface reacts with ethylene from the gas phase seems plausible [17].

Van Santen and Kuipers proposed a mechanism for ethene epoxidation in which the selectivity of the reaction depends strongly on the oxygen coverage. At low coverages the oxygen is very strongly adsorbed, whereas at higher coverages the adsorption is much weaker. The reaction enthalpy for the formation of the epoxide from atomic oxygen, at low oxygen coverages is only 50-70 KJ/mol. In this case the total oxidation-a reaction that is much more exothermic –is thermodynamically favoured, whereas epoxidation is hardly possible. At increasing oxygen coverages the charge on the oxygen atoms will decrease and, as a consequence the ethane oxide production increases [18-19].

An industrial catalyst for ethylene epoxidation contains the active element (silver) distributed on a support, usually α-alumina. The role of earth alkali metals is still controversial. It has been proved that in small concentrations potassium acts as a promoter. Also the addition of halogenated organic compounds increases the selectivity of the reaction [18-19].

Most of the fundamental, surface-science research on ethylene epoxidation is focused on the interaction of pure ethylene and oxygen with silver surfaces, usually of single crystals and usually at much lower pressures and temperatures than the conditions under which the industrial process runs. This may not be the best approach, since some of the most important aspects of the process, such as the active form of the catalyst (silver or silver oxide) under actual reaction conditions, cannot be addressed in this way. There is a large database about the various kinds of structures formed by oxygen on silver surfaces from UHV to ambient pressures [8-15].

Results and discussion

As has been explained in the previous chapters of this thesis, our experimental setup allows us to investigate catalytic systems “in situ” under semi-realistic conditions. In studying ethylene epoxidation on Ag (111) at ambient pressures and elevated temperatures, we have encountered several experimental difficulties, which we will point out together with he experimental observations. From the stoichiometric point of view we need a 2:1 C_2H_4:O_2 ratio to run the reaction. Figure AII.2 displays the reaction kinetics from an experiment performed at a constant total pressure of 1.25 bar. In the mass spectrum we follow C_2H_4O by not only recording mass 44 (which could also be CO_2), but also the most abundant fragments at masses 41 (C_2HO), 42 (C_2H_2O) and 43 (C_2H_3O).

As can be seen the temperature and the ratio between the partial pressures of the reactants play a crucial role in the ignition of the reaction. At $t = 6023$ s (indicated by arrow 1) even though the gas is already mixed in the proper, stoichiometric ratio of the reactants, the temperature it was still so low, $T = 403$ K, that the reaction rate was rather modest. Once we increased the temperature to 433 K, the reaction rate for the production of C_2H_4O increased (arrow 2). After a while, at $t = 8830$ s (arrow 3), we decreased the temperature back to 403 K and the mass signal for ethylene oxide decreased accordingly. It has been suggested in the literature that in order to ignite the reaction a silver catalyst needs to be preactivated. In our experiments we have followed the pre-treatment suggested by Tan and coauthors. In order to activate the catalyst and ignite the reaction they annealed the crystal to 425 K in a 6:1 mixture of C_2H_4:O_2 for 2 h [20].

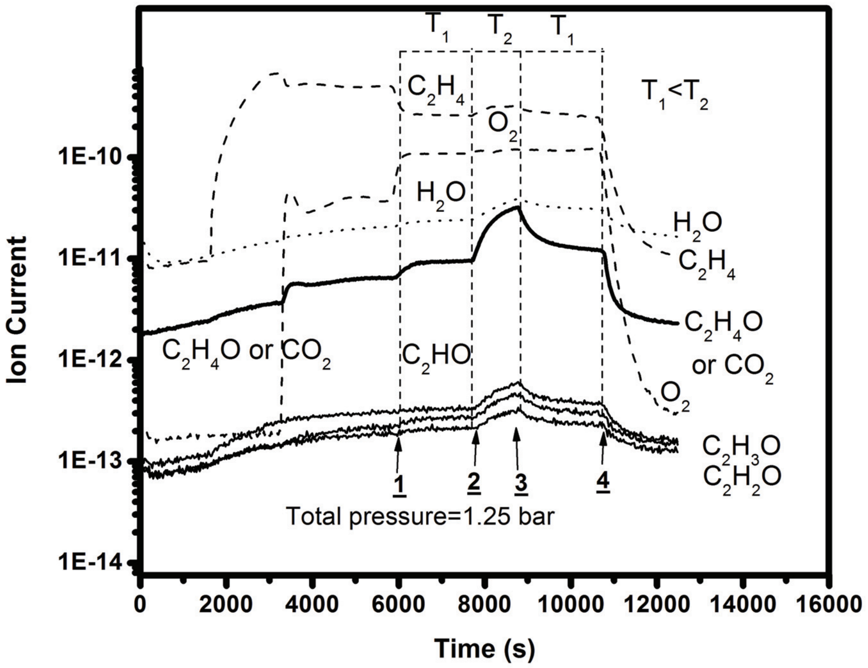

Figure A.II.2: *Kinetics during the epoxidation reaction on Ag (111) at a total pressure of 1.25 bar, recorded while we raised the temperature from 403 K to 273 K. Simultaneously with the increase in the temperature, an increase in the reaction rate is observed.*

The main purpose of this study was to image the surface with scanning tunneling microscopy under reaction conditions and investigate its morphology, in order to identify the active of the catalyst for this reaction. Unfortunately, we did not succeed in t his goal. As described above, the mass spectrometry signals clearly show that we did manage to run the reaction and the desired product, C_2H_4O, has been produced. However, the STM imaging under reaction conditions has been very difficult. Figure A.II.3 reveals that at room temperature both reactant gases (C_2H_4 and O_2) had no effect on the surface structure. Image A was acquired in low vacuum (10^{-2} mbar) at room temperature after the silver surface had been repeatedly cleaned by sputtering ($3x10^{-5}$ mbar Ar^+) and annealing cycles (~1000 K). The surface in image A reflects the morphology of a single crystal with terraces and steps. Image B has been recorded in 1.25 bar of C_2H_4 at room temperature. The sputtering process has produced the vacancy islands with almost triangular shape. In spite of the presence of impurities, the metallic surface still can be easily recognized. Image C has been acquired in 1.25 bar of O_2 at room temperature. As one can see, the surface morphology is close to identical with the one from image B.

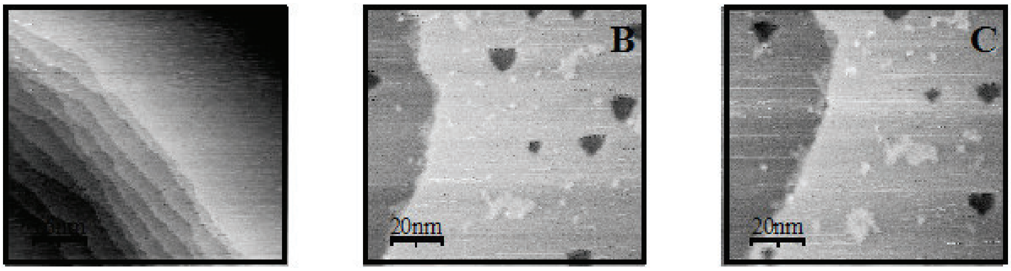

Figure A.II.3: *STM images reflecting the structure of Ag(111) under different conditions at room temperature: (A) low vacuum (10^{-2} bar); (B) 1.25 bar ethene; (C) 1.25 bar oxygen. The sizes of the images are 100 nm x 100 nm (B and C) and 80 nm x 80 nm (A). The tunneling parameters are V_t= 0.2 V and I_t=0.2 nm.*

At high temperature we almost lost the resolution under high-pressure of a C_2H_2 rich-flow. In spite of the poor resolution, steps and terraces could still be recognized, as illustrated in figure A.II.4 (image D). Under an O_2-rich flow or in a mixture of O_2 and C_2H_4 the tip crashed repeatedly into the surface (upper part of image E). Under these conditions it has been impossible to acquire images. The reason for the tip crashes can only be the formation of a thick non-conducting layer on the surface, most probably a silver oxide. The growth of the non-conducting (silver oxide) layer was found to take place very rapidly, within a time interval of few seconds after the oxygen was admitted in the reactor. This process is very reproducible, it happened in all of the 12 experiments at elevated temperatures. The oxygen partial pressure has been varied between 1.25 bar and 200 mbar (close to the lowest pressure allowed by our present gas system).

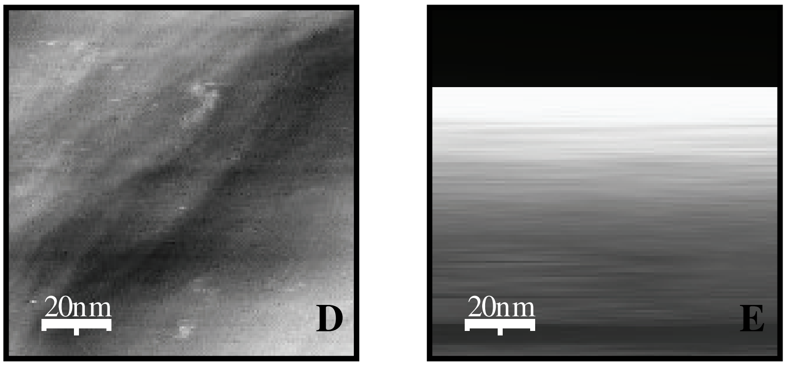

Figure A.II.4: *STM images (100 nm x 100 nm) of Ag(111) exposed to 200 mbar of C_2H_4 at T~450K (image D) and to 200 mbar of O_2 at same temperature (image E). V_t=0.5 V, I_t=0.5 nA.*

We should mention that we have not been able to perform experiments at a higher temperature (the maximum temperature has been 343 K), at which the silver oxide might be unstable and decompose. At present, our only evidence for the formation of the non-conducting silver oxide is the absence of tunneling current and, hence, the reproducible tip crash, but one cannot help wondering whether any of the structures for the silver oxide previously proposed on the basis of low-pressure, surface-science experiments is really relevant for the practical catalysis of ethylene epoxidation? Under industrial conditions, i.e. at high-pressure and high temperature and in the presence of both reactants gases, the current dispute in the literature whether the structure of the surface oxide is p(4x4) [21] or c(3x5√3) [22] might be completely irrelevant.

AII.3 Total oxidation of ethylene on Pt(111)

Oxidation of hydrocarbons over platinum it is one of the key processes in car exhaust conversion and that forms the obvious motive for studying such a reactions. Ethylene it is a good choice for several reasons: it is a very simple hydrocarbon, it interacts with metal surfaces even at moderate temperatures and it gives only few possible oxidation products [23]. In spite of the large amount of experimental data under UHV conditions and near 1 bar, the C_2H_4+O_2 reaction over Pt surfaces is not fully understood. Both Langmuir-Hinshelwood and Eley-Rideal mechanisms have been suggested [24]. All previous studies have agreed on the fact that the main products in the case of the C_2H_4+O_2 reaction over a platinum catalyst are CO_2 and H_2O and very rarely the existence of partially oxidized species has been reported.

The results discussed in this section are based on the measurements performed at a constant total pressure of 1.25 bar and a temperature of 403 K. Figure A.II.5 depicts the reaction kinetics. The following masses have been traced with the mass spectrometer: masses 28 for C_2H_4, 32 for O_2, 44 for CO_2 and 18 for H_2O. We have also followed the signals corresponding to he partially oxidized products. Since we did not notice any variation in their signals, they are not shown in the figure. At t = 6000 s the catalytic system was in an ethylene-rich flow. At t = 7027 s we switched to an O_2-rich flow. The increase in the oxygen signal was followed by a dramatic increase in the CO_2 signal and a more modest increase in the H_2O signal. At first glance the CO_2 production rate shows similar behavior to the CO oxidation over Pt(111). One readily distinguishes the two maxima in the CO_2 production rate marked by arrow number 1 (when we switch from a C_2H_4-rich flow to an O_2 rich flow) and by arrow number 7 (when we switch back from an O_2 rich flow to a C_2H_4 rich flow). These peaks could be attributed to the maxima in the Langmuir-Hinshelwood kinetics when the coverages of the reactant gases are equal. A more careful look at the first peak in the CO_2 production shows that the maximum value does not correspond to equal coverages (θ_{C2H4}= θ_{O2}=0.5). The oxygen pressure is much higher than the ethylene pressure. In the case of the second peak marked by arrow number 7 the Langmuir-Hinshelwood theory applies. The maximum value in the CO_2 production rate corresponds to equal coverages of the reactant gases (θ_{C2H4}= θ_{O2}=0.5). Similar to the CO oxidation over Pt (111), while the catalytic system is in oxygen rich flow the CO_2 signal follows the minor reactant in this case C_2H_4. The arrow number 3 illustrates this conclusion when a small increase in the C_2H_4 signal is followed by a comparable increase in the CO_2 signal. After a while simultaneously with the decrease in ethylene pressure we notice a step down in the CO_2 signal (arrow number 4). The arrow number 6 indicates another increase in the CO_2 signal. This increase is small compared to the Langmuir-Hinshelwood peaks, but could be similar to the sharp peak recorded after the removal of the oxide, during the CO oxidation over Pt (111), mentioned in Chapter 3 of this thesis. If we focus now on the signal of the other product of the reaction H_2O, we again notice two maxima marked by the arrows numbers 2 and 5. Both peaks are acquired in a flow dominated by oxygen. The first maximum in the H_2O signal is recorded after 400 s from the detection of the first maximum in the CO_2 signal when we switch from a C_2H_4 rich flow to an oxygen rich flow. In contrast to this observation the second maximum in the H_2O signal (indicated by arrow number 5) is measured with approximately 286 s before the second peak in the CO_2 production rate indicated by arrow number 7 when we switch from an oxygen rich flow to an ethylene rich flow.

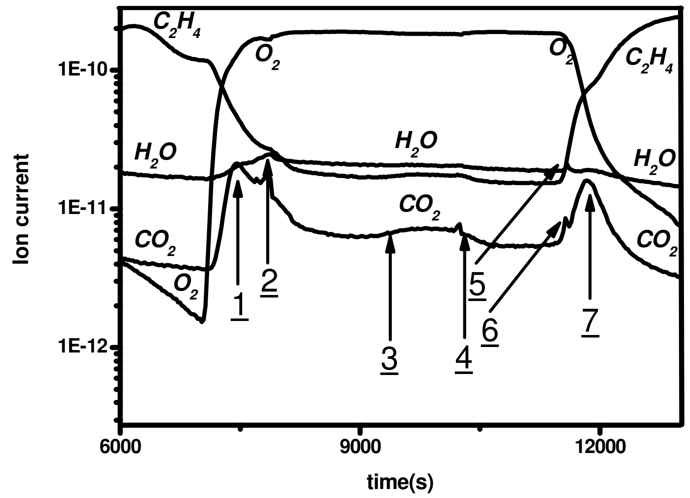

Figure A.II.5: *Reaction kinetics for the total oxidation of ethene on Pt (111) as recorded by the quadrupole mass spectrometer.* P_{total}*=1.25 bar ,T=413 K.*

Simultaneously with the kinetics we also recorded STM images displayed in figure A.II.6. We should mention that before scanning the surface was exposed to a fluctuating mixture of C_2H_2/O_2 for approximately 2 hours at high pressure (1.25 bar) and elevated temperature. After this treatment we switched to C_2H_2 rich flow and then image F has been recorded. Image G has been recorded during the increase in the O_2 signal. Image H has been acquired in O_2 rich flow, while image I has been recorded at after we switch again to C_2H_2 rich flow. As can be seen the resolution of the images is very poor. All the images are showing a very rough surface consisting of "blobby" features. The multiple height profiles performed on these images showed step heights of 2.1-13 Å, witch do not correspond to the step height of Pt (111). At first glance image C (recorded in oxygen rich flow) shows brighter (higher) features compared to the other images, but this difference is not as obvious from the height profiles.

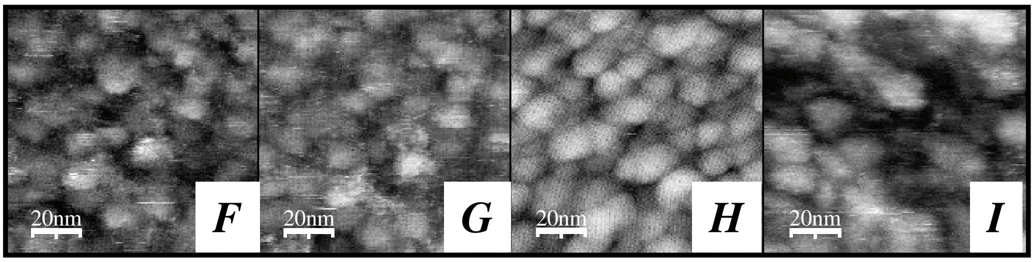

Figure A.II.6: *STM images (100nm×100nm) reflecting the morphology of the Pt (111) surface while exposed to 1.25 bar of C_2H_2 (images F and I) or/and 1.25 bar of O_2 (images G and H).V_t=0.1 V, I_t=0.2 nA.*

Summarizing all the information from the reaction kinetics seem to suggest that for the ethylene oxidation at atmospheric pressures and elevated temperatures over a platinum single crystal, follows a Langmuir-Hinshelwood type of mechanism . Before this experiment the Pt (111) sample has been repeatedly cleaned by sputtering and annealing cycles until a flat, free of impurities surface was obtained. Since the above series of STM images show a rough surface, we can take in consideration the possibility that under the reaction conditions the morphology of the sample has changed dramatically, maybe due to the surface intermediates (more likely carbonaceous species) formed during the reaction. We did not repeat this experiment so we cannot yet state that these data are reproducible.

A.II.4 Conclusions

In this appendix we have reported our results concerning the "in situ" investigation under semi-realistic conditions of two important reactions: ethene epoxidation and ethene combustion. Our experimental observations reveal that in the case of the partial ethylene epoxidation on Ag(111), temperature plays a crucial role in the formation of the desired product (EtO) and, in contrast with the structures proposed for the sliver oxide catalyst based on more traditional surface-science experiments at low pressures, we find evidence for the formation of a thick, insulating oxide layer as the active form of the catalyst under practical conditions. The study of total ethene oxidation on Pt(111) indicates that the reactions follows the Langmuir-Hinshelwood mechanism similar to CO oxidation on Pt(111).

A.II.5 References

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