

Temporal Analysis of Products Experiments at Atmospheric Pressure: The Epoxidation of Ethylene on Silver

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Dedicated to Prof. Dr. Frerich J. Keil on the occasion of his 70th birthday

A high-speed pulse reactor setup for the study of chemical reactions which are catalyzed by a fixed bed is described. The benefits of this method compared to stationary-state measurements are demonstrated using the example of ethylene epoxidation on elemental silver. It is shown that the intrinsic catalyst reactivity depends strongly on oxygen loading and has a pronounced maximum for a loading of about 50 %. In contrast, the selectivity is independent thereof. The relevance of the method for research in catalysis and its relation to the well-established temporal analysis of products approach are illustrated and discussed.

Keywords: Epoxidation, Ethylene oxide, Pulse reactor, Silver, Temporal analysis of products

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1 Introduction

The design of catalytic chemical reactors including the prediction of conversion, selectivity, and release or consumption of heat requires a set of reaction rate expressions which describe the chemistry in a specific range of temperature, pressure, and composition. From an engineering point of view any such set of reasonable accuracy is sufficient for all practical purposes. However, to progress on the path towards rational catalyst design or to perform systematic catalyst manipulation, a more detailed understanding of the elementary steps, in particular those that govern selectivity, is needed.

The temporal analysis of products (TAP) approach to chemical kinetics is a well-established method, which can be used to study in detail the kinetic network behind chemical reactions on catalysts, including adsorption and desorption. This method uses high-speed valves to dose small amounts of reagents onto the catalyst bed. In this way, the central issue of the problem, i.e., chemical rates, is addressed in a rather direct way because chemical reactions are followed in real-time – quite in contrast to steady-state kinetics where chemical rates are deduced from the difference of two time-invariant quantities: the incoming and outgoing flow rates of chemical species. Detailed information on TAP can be found in the reviews by Gleaves et al. [1, 2] and references therein.

Both qualitative as well as quantitative information on catalytic reactions can be gained rather directly through TAP. However, this method has one inherent drawback, namely, its reliance on very low gas pressures. In the idle

state, the catalyst is in fact exposed to a vacuum in the range of 10^{-8} mbar. The low pressures are necessary because only under these conditions the flow of the applied gas pulses (some 10^{14} molecules per pulse) is well described by Knudsen diffusion alone. The diffusive propagation of an inert, i.e. non-adsorbing, gas pulse through the catalyst bed can then serve as “measuring stick” [1] to which the rates of surface events like adsorption, reaction, and desorption can be compared.

The initial preparation of a catalyst surface under TAP conditions can be cumbersome as it sometimes requires hundreds or even thousands of gas pulses when sticking probabilities are low [3,4]. In this paper, experimental results on the development of a method quite akin to TAP, in which the catalyst is not exposed to a vacuum and in which the reactants can be fed into the reactor in the form of arbitrary rectangular pulses, is described. It is called TAP at atmospheric pressure, or atmTAP for short. The professional TAP user might object that the presented method is not TAP at all, yet the authors think that the literal meaning implied in TAP is nevertheless appropriate and that it shall be used here for the lack of a more distinguished term. The question of whether or not such a pulse reactor system can

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deliver information up to par or perhaps even superior to classical TAP is addressed.

In the atmTAP applied in this work, the vacuum is replaced by a transient stream of reagents entrained in a constant carrier gas stream. The reagents can be switched on and off while the total volumetric flow remains constant. If the reagent concentrations are low enough, the change in contact time with extent of reaction can be neglected. Furthermore, if the contact time is sufficiently short, dispersion effects are minimized and the reactor behaves like a plug-flow reactor. Thus, useful kinetic parameters are obtained rather directly from the measurements without recourse to complex modeling. Catalyst conditioning is now straightforward and also a switch from steady-state operation to pulsed or periodic operation can be immediate. Moreover, the steady-state can be perturbed by concentration jumps in one of the reagents. This can also be useful in the study of adsorption properties as detailed in [5].

Conceptually, the atmTAP is a pulse reactor working under constant pressure and flow. Two main obstacles have to be overcome if the maximum amount of information is to be extracted from the measurements. First, the time resolution of the gas analysis system must be high enough and the measured signals have to be proportional to the real concentrations and second, the rise time of a reagent pulse has to be sufficiently short. As will be explained in the subsequent sections, it can be claimed that measurements with a time resolution in the subsecond regime are definitely feasible and further improvements would most likely allow measurements with a pulse width well in the low millisecond regime.

Finally, it should be pointed out that the design expounded in this article is only one out of many ways in which such an experiment can be set up; there is an almost endless list of combinations of equipment which could be used instead. Some users might, e.g., find multiport valves more suitable than the solenoid ones suggested here, especially if higher pressures are desired. However, the ones used in this work have the benefit of being small, easy to use, and economic. The design is also convenient and versatile especially in comparison to the use of sample loops which limit the operation to pre-defined amounts of substance and require a change of the loop if a change in pulse duration is desired.

As a test case for the atmTAP, the time-honored epoxidation of ethylene on silver was chosen. This reaction has been studied quite thoroughly (see the review by van Santen and Kuipers [6] and the references therein) since it is the prototypical partial oxidation reaction in heterogeneous catalysis. The sole interaction of oxygen and silver shows great complexity [7, 8] in the sense that several distinct oxygen species occur on and below the silver surface. The interaction of the silver-oxygen system with ethylene and the effects of promoting/inhibiting elements on the reaction are still, and despite the apparent simplicity of the reaction, the topic of present-day fundamental research and no consen-

sus on the mechanism has yet been reached. A rather peculiar aspect of this reaction is the rather substantial kinetic isotope effect (C_2H_4 vs C_2D_4), which does not only figure in the reaction to CO_2 where it is expected but also in the epoxidation step in which (apparently) no hydrogen bonds are broken or created [9]. Here, the kinetic isotope effect is in fact inverse, i.e., the reaction becomes faster when hydrogen is substituted by deuterium. At low pressure (10 Torr) on single crystal surfaces, the effect reaches an unusually high value of 6.5 [10].

2 Instrument Design and Function

The atmTAP instrument consists of three main sections: a gas feed system which generates rectangular reagent pulses of arbitrary duration, a tubular fixed bed reactor, and a gas analysis system.

2.1 Gas Feed System

The core of the apparatus is a small ($26 \times 16 \times 26$ mm) metal block onto which two pairs of 3/2-way solenoid valves [11] are mounted as shown in Fig. 1. A set of mass flow controllers (MFCs) provides the four streams A – D of equal volumetric flow rate. Typically, a pure inert gas like helium or argon is connected to A and C, while the streams B and D contain the reagents diluted in the same carrier gas. When the solenoid valves are not energized, i.e., in the idle state, the gases A and C flow into the reactor while B and D are sent to the exhaust (vent) via the back end of the block. If now the pair of valves connected to A and B is switched, the reagent containing gas B passes through the reactor while the pure inert gas A is redirected to the exhaust, i.e., the flow into the reactor changes from A/C to B/C and analogously if the opposite valve pair switches. Thus, there are four states of the system: A/C, B/C, A/D, and B/D.

In the experiments described in this paper, A and C are pure helium, B is ethylene in helium and D is oxygen in helium giving rise to the four states: He/He, C_2H_4/He , O_2/He , or C_2H_4/O_2 . The solenoid valves are switched with the help of solid-state relays which in turn are triggered by a USB-connected microcontroller according to a pulse sequence defined by the user in a Python program.

At the beginning of any experiment, the needle valve is adjusted so that both pressure transducers give the same reading while the system is in the A/C state, i.e., the pressure drop over the needle valve equals the pressure drop over the catalyst bed. Instead of a needle valve, a pressure regulator may also be used. The pressure drop over both reactor and valve should be equal to within 1 mbar or less since otherwise the mass flow controllers would adjust their settings to the new pressure drop after the valves have been switched leading to irregular flow conditions and, thus, unpredictable fluctuations in the reagent concentrations.

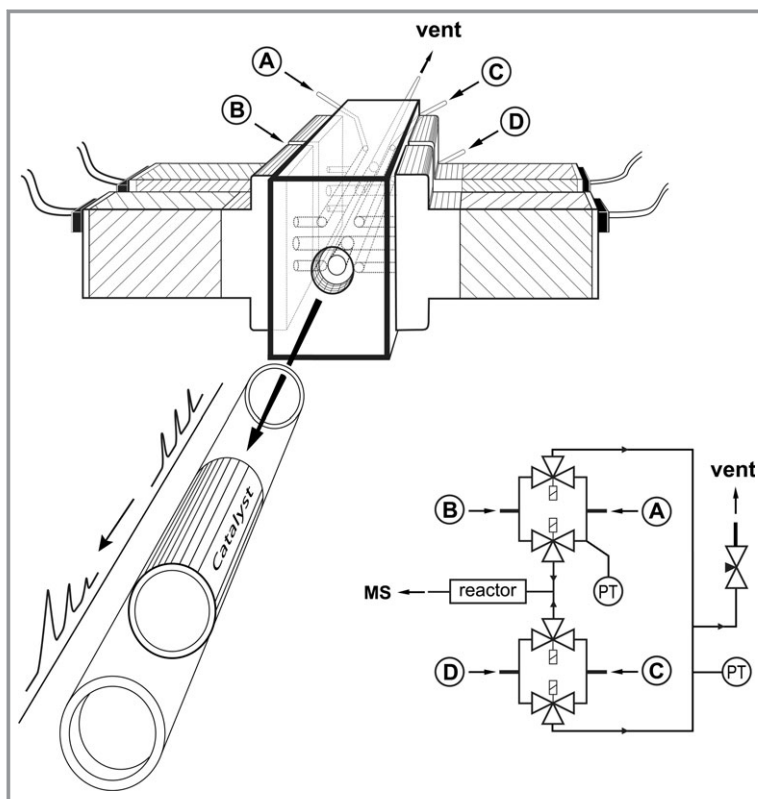


Figure 1. The gas feed system and its flowchart. The central block onto which the 3/2-way solenoid valves [11] are mounted has dimensions of $26 \times 16 \times 26$ mm. In the idle state, the gases A and C pass through the reactor while B and D flow into the exhaust line (vent). Upon switching, e.g., the pair of valves connected to A and B, the streams A and B exchange their flow path: B is redirected into the reactor while now A is sent to the exhaust. The needle valve is adjusted in such a way that the pressure drop over the reactor and the pressure drop over the valve, as indicated by the pressure transducers PT, become equal. In this way, the mass flow controllers are not perturbed upon switching the valves and the flow remains constant. A fraction of the reactor effluent is passed on to a mass spectrometer (MS) for online gas analysis.

These effects are particularly severe if gases are being mixed online instead of being provided by a static premix from a bottle, which is the less flexible but in principle preferred method.

2.2 Reactor

A short metal cylinder (not shown) with a central bore and axial O-ring seals serves as an adapter which connects the block with the reactor tube (glass, ID 6 mm, OD 8 mm). The distance between the end of this adapter and the catalyst packing is filled with glass wool and/or an inert packing. Downstream of the catalyst, a second glass wool plug is inserted to hold the catalyst in place. A (split) brass block with integrated heating cartridges serves as an oven for the reactor tube. A thermocouple is introduced via a narrow channel in such a way that it is in contact with the glass tube and the oven at the central position of the catalyst packing.

2.3 Gas Analysis

To sample a fraction of the gas at the reactor outlet, a 1/16" stainless steel tube protrudes right into the reactor and is brought into contact with the downstream glass wool plug. The opposite end of the tube is connected via a needle valve to a Teflon transfer line which leads directly into the inlet system of a homebuilt molecular beam mass spectrometer [12]. In this system, a part of the sampled gas is formed into a molecular beam which is directed right into the ionization head of the quadrupole mass spectrometer [13]. In this way, the detected ion signal of a species is proportional to its concentration in the beam and the signal transients are largely unaffected by the average residence time of a molecule in the vacuum chamber itself.

The used quadrupole mass spectrometer (qMS) is able to deliver a new data point about every 2 ms; however, the resulting signals are usually too noisy to be practically useful and a somewhat longer acquisition time in the order of 10–50 ms is chosen depending on the signal intensity of the monitored species. Thus, the upper limit in time resolution is in the order of 10 ms with respect to the detection of a single species by the qMS. Since a qMS can only measure a single ion mass at a time, the monitoring of several species is only possible sequentially and, therefore, the time resolution gets worse with the number of species monitored. As will be shown in the next section, the method is currently not limited by this problem, because the transients are still broad enough to be resolved completely. However, in future experiments it

may eventually be necessary to be able to detect more species at a faster rate. Using a time of flight mass spectrometer might prove beneficial in this case.

2.4 General Design Guidelines

During the design and construction of the current atmTAP setup, a couple of rules have established: tube diameter transitions, dead volumes in fittings and valves, and unnecessarily long tubing must be avoided to minimize pulse broadening. If transitions in tube diameter cannot be avoided, they should at least be smooth, i.e., conical. These requirements will sound familiar to anyone dealing with gas or liquid chromatography. In fact, the use of small diameter, low dead volume fittings, and tubing as used in GC work are recommended rather than the more common large-diameter Swagelok-type fittings.

Dispersion effects inside the reactor cannot be eliminated completely but they can be reduced. In particular, the resi-

dence time in the reactor should be minimized, i.e., the packing should be short and the gas flow should be high. For a fast detection (in the sense that signals are not broadened unnecessarily), mixing in the transfer lines must be avoided. If transfer capillaries are used, it should be born in mind that gas retention, as in GC capillary columns, is likely to occur which leads to misleading results in pulse experiments.

Furthermore, a molecular beam MS is not the only possible option and maybe not even the preferred one since it requires a somewhat large vacuum chamber with powerful turbopumps. Some commercially available gas analysis systems feature response times of less than 1 s which might be fast enough for some applications; but here it should also be thoroughly checked whether gas retention in the transfer line is an issue by pulsing into the system all species which are relevant for the studied reaction.

2.5 System Response

To analyze the quality of the reagent pulses produced by the valves, the gas was sampled directly at the exit of the valve block. The response obtained when switching the stream from helium at 100 sccm (standard cubic centimeter per minute referring to 20 °C and 1013.25 hPa) to ethylene (1 % C₂H₄ in He) for 0.25, 0.5, or 1.0 s is shown in Fig. 2a. The signal intensity for the 1.0-s case corresponds to the steady-state concentration when ethylene is always on. The experiment showed that for switching times shorter than 0.25 s this steady-state signal intensity is not reached.

Fig. 2b is a magnification of the 0.25-s pulse showing that the full width at half maximum actually corresponds to the switch time of the valve. The rising flank of the 1.0-s pulse shown in Fig. 2c has a rise time (10 to 90 %) of 120 ms.

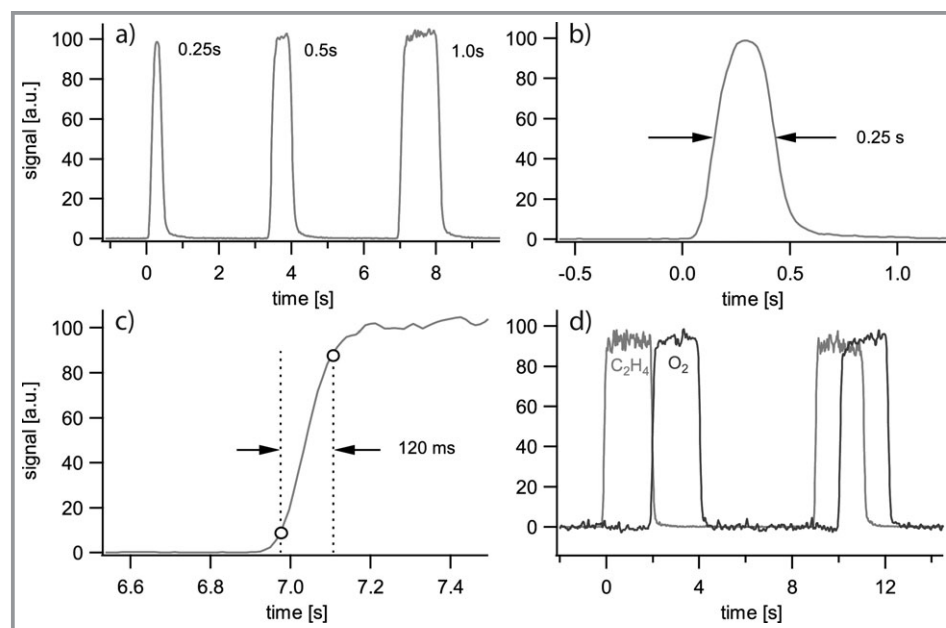


Figure 2. a) System response when a stream of helium is switched to ethylene in helium for valve switching times of 0.25, 0.5, and 1.0 s. b) Magnification of the 0.25-s pulse. c) Magnification of the rising flank of the 1.0-s pulse. The rise time (10–90 %) is 120 ms. d) Ethylene and oxygen pulses of 2 s duration with an offset of either 2 or 1 s. All system responses shown are measured without a catalyst packing.

Whether this value is limited by the valves (through the actuation transient and the internal dead volume) or by the used gas analysis system is currently unknown. A catalyst packing increases the rise time further due to dispersion effects. The pulsing of two reagents is shown in Fig. 2d where 2 s wide rectangular pulses of oxygen and ethylene are superimposed with a delay of either 2 or 1 s.

2.6 Pulse Quantification

The amount N_i of a specific species i in a pulse is given by the duration Δt of the pulse, the concentration c_i and the volumetric flow \dot{V} by the product $c_i \dot{V} \Delta t$. This is an approximation, because it neglects the transients of the pulse and thus is valid only for sufficiently long pulses. Accounting for the transient behavior is straightforward, the signal $S_i(t)$ of a species is related to N_i by:

$$N_i = c_i \dot{V} \int dt \frac{S_i(t)}{S_{i,\max}} \quad (1)$$

where $S_{i,\max}$ is the steady-state value of S_i , i.e., when species i is constantly on, and $S_i \rightarrow 0$ as $c_i \rightarrow 0$ is required.

3 Temporal Analysis of Products Measurements

3.1 System Configuration and Experimental Conditions

For the atmTAP experiments the volumetric gas streams used are A/C: 50 sccm He, B: 0.02 or 0.002 sccm C₂H₄,

1 sccm Ar in He, D: 1 sccm O₂, 1 sccm Ar in He (with reference to 20 °C and 1013.25 hPa). The total volumetric flow is 50 sccm in all four cases. Because two out of four streams enter the reactor, the total flow into the reactor is 100 sccm at any time. Hence, the molar fractions of the reactants amount to 0.02 or 0.002 % for C₂H₄ and 1 % for O₂. A single MFC delivers He to lines A and C via two throttling capillaries which split the stream into two equal portions. The gases B and D are mixed online via MFCs. Again, only one MFC is used for He, and the stream is split by another pair of throttling capillaries.

The gas purities are 3.5 for C₂H₄, 4.8 for Ar, and 5.0 for He and O₂. An oxygen trap is installed in the He line which reduces the oxygen content of the carrier gas to ppb levels. The used catalyst is elemental silver powder (500 mg, purity 99.95 % based on metal content, Alfa Aesar, 100 mesh) and the length of this bed is approximately 8 mm. Together with the inner diameter of the reactor tube of 6 mm and the density of silver this leads to a gas exchange rate over the bed of about 16 Hz at the used 200 °C and ambient pressure. The catalyst powder is sandwiched between a 40-mm glass wool plug (downstream) and a packing of alpha alumina spheres (upstream) which also serves as a pre-heating zone for the incoming gas.

The signal rise time of an argon pulse at room temperature (as defined in Fig. 2c) now amounts to 600 ms. The dispersion due to the packing is thus clearly noticeable but it is still sufficiently small for the measurements presented here. For experiments in which this parameter is more critical, the total length of the packing should be reduced.

CO₂ is detected on mass 44 at an electron kinetic energy of 50 eV. 44 is the only viable mass number since the CO₂ ion fragments are too low in intensity to be practically useful. Unfortunately, the target molecule of the reaction, ethylene oxide (EO), has the same nominal mass as CO₂ and thus both species cannot be distinguished by a qMS. However, they easily could be distinguished by a high-resolution reflectron time-of-flight (TOF), Orbitrap, or Fourier transform ion cyclotron resonance (FTICR) MS since the exact (single isotope) masses differ quite a bit: 44.0262 and 43.9893 u for EO and CO₂, respectively. The two other most abundant ion fragments of EO occur on mass 15 and 29. However, in the experiment, it turned out that near-threshold ionization of EO offered the best signal-to-noise ratio and least background. Therefore, it was decided to selectively detect EO on mass 44 at an electron energy of 15 eV where the ionization cross section of CO₂ is still negligible (the ionization potential of EO is 10.6 eV and that of CO₂ 13.7 eV [14]). To obtain the signal corresponding to CO₂ alone, the contribution due to EO has to be subtracted; the required relative ionization cross sections for 15 and 50 eV are measured by directly introducing EO into the system.

Ethylene is detected on mass 26 or 28 at ionization energies of 50 or 15 eV, respectively. The small contribution of ethylene oxide fragments at these masses are neglected since only a small fraction of about 2 % of the total ion count of

ethylene oxide fragments appears at the masses 26 to 28 at 50 eV. Argon is detected on mass 40. The relative detection efficiencies of the species are determined by introducing defined gas mixtures of the pure components together with argon as a common standard into the system.

3.2 Catalyst Conditioning

The fresh catalyst is first heated under He flow to a temperature of 200 °C. During this period, CO₂ is released from the catalyst surface due to the decomposition of surface carbonates. Upon switching to O₂ in He, there is a marked increase in CO₂ signal intensity from the oxidation of residual hydrocarbons which decays within several minutes. The catalyst is then treated with C₂H₄ and O₂ for several hours. In the days and weeks following this initial period, different pulse and also steady-state experiments are performed and no significant changes in reactivity are observed. In these experiments the temperature never exceeds 300 °C. Special attention must be paid to the pre-conditioning procedure. It may be the case that the used catalyst batch had not yet reached a real steady state, which in some cases can require a time on stream of several hundreds of hours.

4 Results and Discussion

Some basic questions about catalyst properties and reaction mechanisms can be answered quickly using the atmTAP experiment, e.g., if the presence of gas phase oxygen is necessary for the reaction. This is not the case when the reaction starts with an oxidized surface. Moreover, it is immaterial whether or not ethylene is pulsed together with oxygen, provided the ethylene concentration is not too high and the pulse is short. The product species' response is the same in both cases; hence, ethylene mainly reacts with oxygen already present on the surface. Under steady-state conditions, a switch to a different oxygen isotope would be necessary to elucidate this question as is done in steady-state isotopic transient kinetic analysis (SSITKA) experiments. TAP experiments also benefit from the use of isotope-labeled reagents; however, the use of (expensive) isotopes can often be avoided by an appropriate design of the pulse sequence.

Another important question is how stable the surface oxygen is. The oxygen stored on and in the catalyst is indeed rather stable: even purge intervals of several minutes hardly change the response to a pulse of ethylene. This is also expected, otherwise experiments in a standard TAP system [15] would not be feasible.

A further question regarding the interaction of the surface with the hydrocarbon is if ethylene does adsorb on Ag and how strong the adsorption is. Indeed it adsorbs strongly on the fully oxidized Ag surface and this can be observed easily provided the ethylene concentration is low enough. It is observed that a low concentration pulse of ethylene takes

several minutes to elute at room temperature, i.e., despite its short length of only 8 mm, the Ag packing acts like a chromatographic column. In contrast, the experiment also shows that ethane does not adsorb at all proving that the strong interaction with the silver surface is a specific feature of the C=C bond of ethylene.

A systematic experiment which illustrates this effect is shown in Fig. 3. Here, the catalyst is initially treated with oxygen in helium at 200 °C. After 30 min, the packing is cooled down to room temperature while maintaining the oxygen flow. The temperature is then raised to 35 °C under helium and the chromatography experiment is started. A 1.0-s pulse of ethylene (0.002 % in He) together with argon is sent over the packing and the elution of both species is followed in time; every such experiment is repeated five times and the results are averaged. A plot of the elution curves for 35, 45, and 55 °C is shown in Fig. 3a.

The so-called retention time of a pulse is the mean time for the elution of the substance from the column. The valve is switched at time $t = 0$ s. Hence, the retention time is actually a species-specific mean residence time. The net

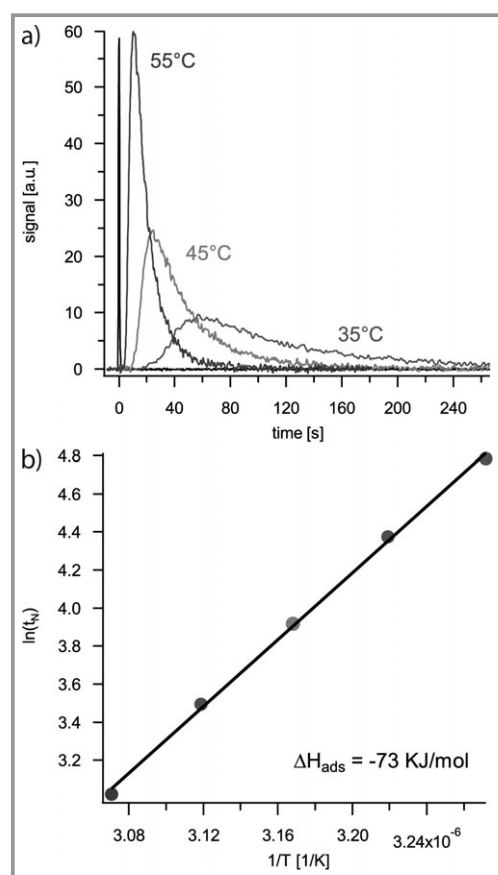


Figure 3. a) Elution curves of ethylene with respect to a non-adsorbing component (argon at $t = 0$ s) for 35, 45, and 55 °C. b) Plot of the logarithm of net retention time t_N versus $1/T$ for 35, 45, 50, and 55 °C. From the slope of the curve ($-\Delta H/R$), the enthalpy of adsorption was determined to be -73 KJ mol^{-1} .

retention time t_N is defined as the difference between the retention time of an adsorbing (ethylene) and a non-adsorbing component (argon). Therefore, t_N is equal to the time a molecule spends on the catalyst surface on average. It can be shown that in the limit of infinite dilution, a plot of the logarithm of t_N vs $1/T$ yields $-\Delta H_{\text{ads}}/R$ as slope, ΔH_{ads} being the heat of adsorption. A derivation of this relation starts with the Clausius-Clapeyron equation and makes use of the theory of chromatography at infinite dilution, see, e.g., [16]. For the five temperatures measured here (35, 40, 45, 50, and 55 °C), the slope corresponds to a value of -73 KJ mol^{-1} for the heat of adsorption as shown in Fig. 3b. The adsorption energy of ethylene on silver depends strongly on surface oxygen coverage. Using density functional theory (DFT) study, Özbek et al. [17] calculated values of +3, -38, -83, and -86 KJ mol^{-1} for adsorption of ethylene on an oxygen vacancy for oxygen precoverages of 25, 50, 75, and 100 %, respectively.

It should be noted that, apart from adsorption enthalpies, isotherms can be determined with the help of the atmTAP apparatus in a rather straightforward manner as well. To this end, breakthrough curves need to be measured as a function of the ethylene concentration. The amount adsorbed is then inferred from the area above the breakthrough front. Determination of isotherms before and after a series of experiments is quite easy and can be used to monitor changes in catalyst surface area without having to transfer the catalyst to a dedicated machine.

There is an ongoing discussion in the literature about different oxygen species on silver [18, 19] and their reactivity. To shed light on this issue, a simple titration experiment with fairly dilute (0.02 %) and short ethylene pulses was carried out. The pulse sequence used is depicted in Fig. 4. A 120-s O_2 pulse oxidizes the catalyst and is followed by a 30-s purge period where only He flows and all gas phase O_2 is removed. Then, an array of 60 ethylene pulses, each of 0.5 s duration and with a separation of 5 s, is fed into the reactor. Thus, the surface/subsurface oxygen of the catalyst is consumed step-by-step while at the same time the reactivity is probed. Since the number of ethylene molecules in the pulse and also the residence time is sufficiently small, the change of the catalyst surface by a single pulse can be neglected while a larger number of such pulses change the state of the catalyst significantly. In TAP parlance, a single low-concentration pulse constitutes a state-defining experiment while a sequence of such pulses is a state-altering experiment [1]. This idea carries over to the conducted atmTAP experiments which allow probing the reactivity as a function of surface state. Moreover, by using a sufficiently short ethylene pulse, it can be expected that separation of the initial irreversible adsorption step from the subsequent surface reaction steps will be possible in time. Another interesting feature of titrating surface oxygen in this way is that a measure for the total number of active centers per gram catalyst is obtained, which constitutes a potentially useful marker for catalyst optimization strategies. The

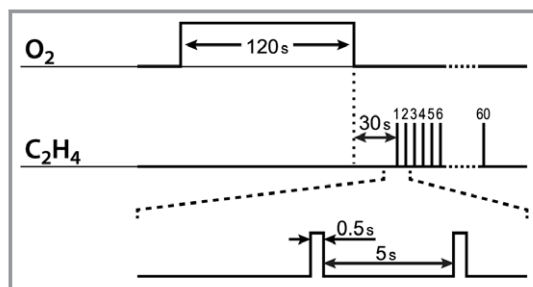


Figure 4. Pulse sequence used in the experiment.

whole pulse sequence is repeated five times and the signals are averaged.

The response of the catalyst to the pulse sequence is shown in Fig. 5. There is a marked maximum in conversion and in the EO product signal. This maximum is not resolved at higher ethylene concentrations for which the oxygen would be consumed too quickly. Furthermore, there is a broadening of the CO₂ response as the surface/subsurface oxygen is depleted (Fig. 6), whereas the pulse shape of the EO signal remains narrow over the whole sequence, i.e., the CO₂ evolution continues while the ethylene pulse has long passed the reactor. Two effects could be responsible: either the rate of formation of CO₂ is simply getting lower as the oxygen is being depleted or it is a chromatographic effect as already described above for ethylene. It is well known that CO₂ chemisorbs on oxygen-covered Ag [8] as carbonate and also that isotope exchange with C¹⁸O₂ is very quick [20]. Hence, there is a strong interaction with the surface and this may well depend on the state of the surface.

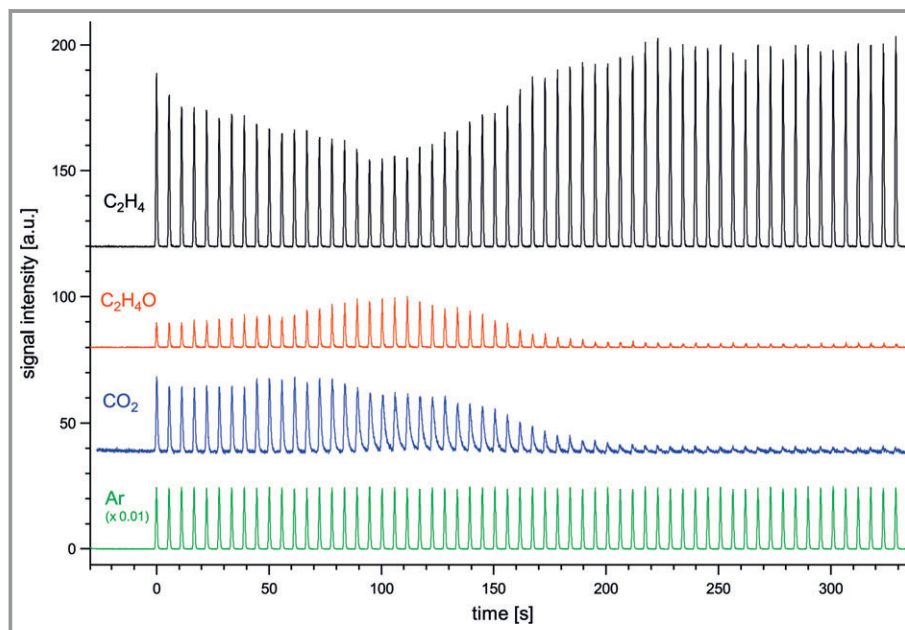


Figure 5. Pulse response of the fully oxidized silver catalyst at 200 °C, 1 bar, and a total flow of 100 sccm. The argon signal is multiplied by 0.01 to match the overall scale. The ethylene fraction at the inlet of the valve system is 0.02 %.

An additional experiment was conducted in which CO₂ is pulsed as a function of the surface oxygen concentration. This experiment shows that the pulse broadening is indeed (mainly) governed by a chromatographic effect.

To properly quantify the per-pulse conversion, selectivity, and product yields, the area under each peak is shown in Fig. 7. It can clearly be seen that not only the conversion to EO but also to CO₂ features a pronounced maximum and that the per-pulse selectivity actually remains approximately 40 % throughout the whole sequence even though the overall chemical activity of the surface changes radically with the pulse number. The value of 40 % is in line with the reported selectivity for elemental silver powder [6]. Experiments at twice the flow rate, i.e., 200 sccm, yield the same selectivity of about 40 % throughout, while the conversion per pulse is of course lower.

To rationalize this finding in terms of a reaction mechanism, two reaction schemes (Fig. 8) are considered that contain only the most essential intermediates. In discussing both schemes, the catalyst packing is assumed to be homogeneous in composition at all times. The oxygen content, denoted symbolically by θ , changes, but only to a little extent, due to a single pulse and, therefore, the reactivity of the surface is fully specified by the apparent rate constants $k_i(\theta)$ which are constants only in the case of very small changes of θ . Furthermore, it is obvious that the proposed reaction schemes certainly do not apply directly to the steady state (or to high concentration pulses) since the postulated reaction steps would not be independent anymore in this case due to the blocking as well as chemical modification of sites by intermediates.

In the two-site model (A), two distinct sites/oxygen species are present on the surface initially, which are responsible for either partial (*1) or total (*2) oxidation (Fig. 8). In this scheme, the formation of either adsorbed EO (C₂H₄O*) or acetaldehyde (CH₃CHO*) depends solely on which kind of site an ethylene molecule encounters in the first reactive collision. Here, the choice of intermediate species is somewhat arbitrary and both could indeed be replaced by abstract entities X*¹, Y*² leaving open their exact nature. What matters is that X*¹ and Y*² follow the same reaction sequence.

If two distinct and largely independent sites/oxygen species existed on the surface, they should react with different rate constants and, thus, would show a specific (exponential) decay with the

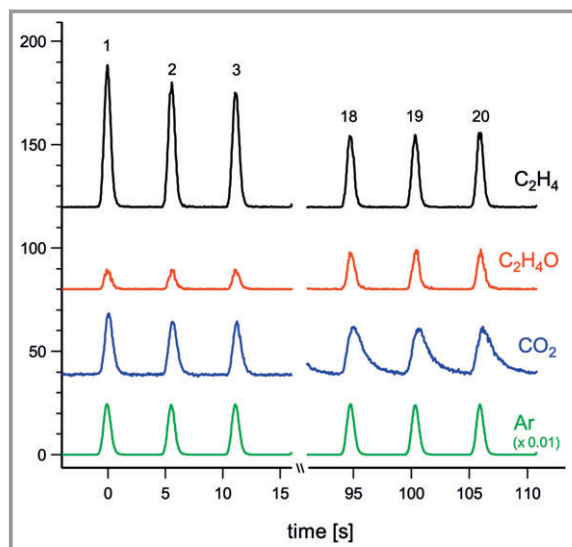


Figure 6. Magnification of the data shown in Fig. 5; pulses 1–3 and 18–20.

pulse number. Moreover, even if the rate constants were similar, the (presumably) differing initial populations of these species would make the fraction of molecules reacting one way or the other – and hence, the selectivity to EO given by $k_1/(k_1 + k_3)$ – dependent upon the pulse number. This is clearly not the case here. While it cannot be ruled out that the used calibration is off by a few percent, the authors are confident that the values are reasonable because the evaluation of the selectivity by two independent ways gave the same result: the first is based on the ethylene consumption and the EO production, while the second employs

the EO and CO₂ production only; the latter values had the better signal-to-noise ratio and are plotted in Fig. 7.

According to DFT calculations by Özbek and van Santen [21], there also exists a direct path with no energy barrier towards adsorbed EO, i.e., gas phase ethylene reacts with adsorbed oxygen without an intermediate to form adsorbed EO in an Eley-Rideal type of mechanism. If such an additional path played a significant role, it should also leave some signature in the obtained data which it does not. Furthermore, the direct path is not compatible with the strong inverse kinetic isotope effects which have been measured.

The two sites *1 and *2 posited in reaction scheme A in Fig. 8 can also be interpreted as realizations of so-called “electrophilic” and “nucleophilic” oxygen species, a popular conjecture frequently stated in many papers [7, 19, 22]. The results obtained here can only be harmonized with this

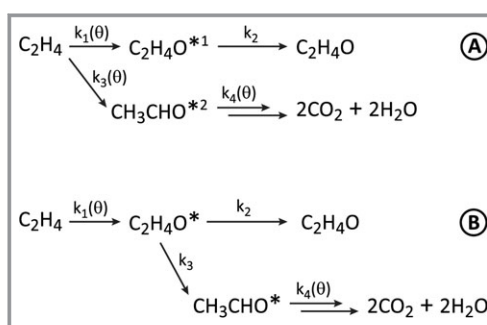


Figure 8. The proposed reaction sequences for the case of either two independent sites/oxygen species *1 and *2 (A) or a single type of site * (B). The parameter θ stands symbolically for the active surface/sub-surface oxygen content and the $k_i(\theta)$ are the associated (apparent) rate constants.

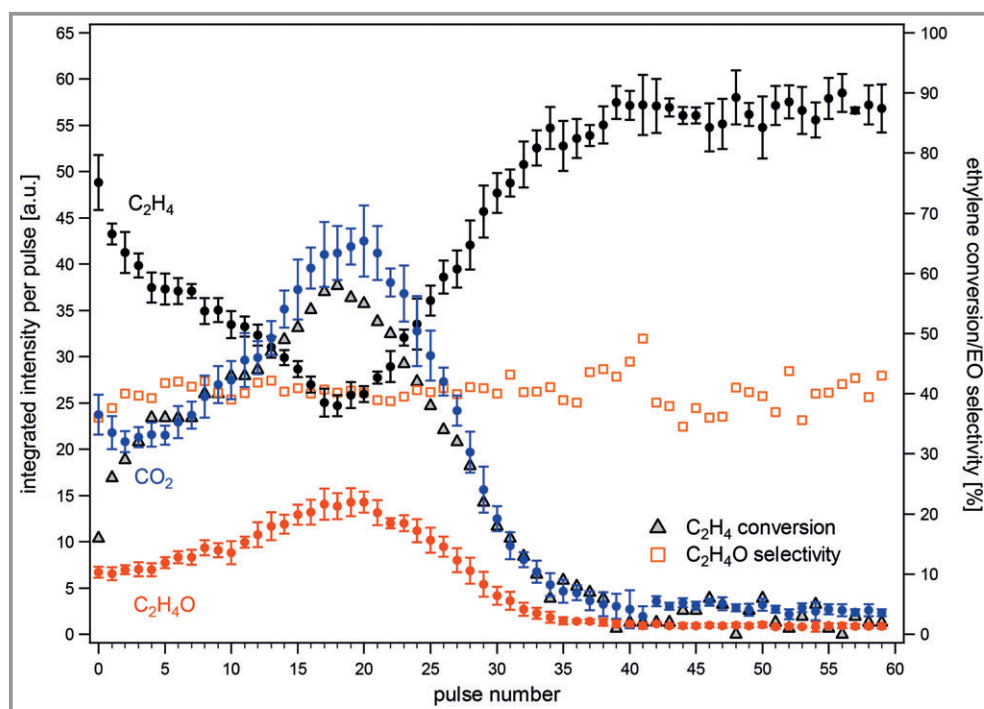


Figure 7. Integrated signal intensity of the data in Fig. 5 for ethylene, EO, and CO₂ (left axis) together with the per-pulse conversion and selectivity (right axis) as a function of pulse number. The error bars represent the per-pulse conversion and selectivity (2σ) as estimated from five successive runs of the experiments.

conjecture if it is demanded that both oxygen species are subject to rapid interconversion and, hence, are in equilibrium with each other at all times. However, this additional proposition is actually not supported by the X-ray photoelectron spectra presented in [19], which shows that also a single species can be prepared selectively.

In the single-site model (B), the fate of the ethylene molecule is not determined by the first reactive collision but rather by a secondary process which occurs at the “landing site” as shown in Fig. 8. The model assumes that the branching ratio k_2/k_3 of EO and CO₂ does not depend on the oxygen coverage θ but only the initial step with rate constant $k_1(\theta)$ does. The subsequent steps subsumed under $k_4(\theta)$ also depend on θ because here adsorbed acetaldehyde CH₃CHO* is further oxidized to CO₂, presumably via acetic and oxalic acid as proposed in [10]. These steps should depend rather strongly on θ since the local periphery of the molecule being oxidized has to provide five more oxygen atoms in total and these will have to diffuse in some way to the local site from lateral positions or from the subsurface region. Alternatively, the molecule has to diffuse to regions where oxygen atoms are available.

In 2003, Linic and Barteau [23] proposed on grounds of DFT calculations that the common intermediate (C₂H₄O*) is a so-called “oxametallacycle” (OMC) in which one carbon atom is bound to a silver site while the other carbon is bound to an adsorbed oxygen atom, thus, forming a cycle. This OMC can now either isomerize to EO, which then desorbs, or it can undergo a hydrogen shift to form acetaldehyde which is quickly oxidized further. Linic and Barteau estimated a selectivity of 41–43% in the temperature range of 400–500 K which agrees surprisingly well with the results of this study. Furthermore, the mechanism explains the inverse kinetic isotope effect mentioned in the introduction; replacing hydrogen by deuterium slows down the hydrogen shift, i.e., the isomerization to acetaldehyde. This increases the rate towards EO while decreasing the rate towards CO₂. As a result, the selectivity rises. Since 2003, additional experiments and calculations have been published which support the OMC hypothesis [21, 24, 25]. In particular, Özbek et al. [26] have found in their DFT calculations that the energy barrier from the OMC towards EO and acetaldehyde hardly depends on the oxygen coverage which is in agreement with the finding of the present study that the selectivity does not depend on pulse number.

The other interesting aspect of the experiment can now also be understood, namely, the initial increase of catalyst activity with decreasing oxygen coverage. Since OMC formation requires a free metal site to form, a high oxygen loading corresponds to a smaller number of active sites. Thus, the optimal oxygen surface coverage, i.e., the point of highest activity, lies somewhere between complete and zero. With the data in Fig. 7 and the corresponding oxygen balance (as determined from the production of C₂H₄O, CO₂, and H₂O) it can be determined to be precisely 50%. Assuming that all reactive oxygen atoms are initially located on

surface sites, the reactivity of the surface is highest when exactly half of the sites are covered with oxygen atoms. However, it is known that also subsurface oxygen can react by refilling the surface sites and, hence, the value of 50% is potentially biased to some extent. The diffusional kinetics of subsurface oxygen can actually be investigated with the atmTAP apparatus and further experiments in this direction are currently in progress.

5 Additional Comments

In heterogeneous catalysis, observations may well depend on the total time on stream and the prevailing chemical conditions during this time. The experiments conducted in this study will not be an exception and it is imaginable that the results would change on a timescale of several hundred hours.

A general and important aspect of the atmTAP approach that is probably not obvious and is worth to be mentioned should also be pointed out. The use of short pulses with sufficiently low concentrations allows drawing conclusions about the intrinsic reactivity of an as-prepared/conditioned catalyst surface. The absence of both ongoing surface processes from side reactions and the blocking of sites by intermediates simplifies the kinetic reaction network considerably and allows the disentanglement of various reaction steps. In particular, a comparison of the experiment with ab initio calculations appears feasible under these conditions since such calculations normally do not include the complications which arise due to surface intermediates as they inevitably occur under steady-state conditions.

The atmTAP is a fairly versatile instrument that quickly reveals many catalyst properties, which would never be observable in a steady-state kinetics setup, and yields valuable clues about the different processes which should be included in or excluded from a kinetic model. Such experiments are helpful in the process of “guessing” the mechanism. Furthermore, the apparatus can also be used to study adsorption/desorption properties of the participating species via pulse retention measurements and frontal analysis.

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Symbol used

c_i	[mol L ⁻¹]	concentration of species i
ΔH_{ads}	[kJ mol ⁻¹]	heat of adsorption
k_i	[s ⁻¹]	rate constant of reaction i
N_i	[mol]	amount of a specific species i
R	[J K ⁻¹ mol ⁻¹]	universal gas constant
S_i	[a.u.]	signal of species i
$S_{i,\text{max}}$	[a.u.]	steady-state value of S_i
t	[s]	time
Δt	[s]	duration of the pulse
t_N	[s]	net retention time
\dot{V}	[mL min ⁻¹]	volumetric flow

Greek symbol

θ	[mol g _{cat} ⁻¹]	oxygen loading of the catalyst
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Abbreviations

atmTAP	TAP at atmospheric pressure
DFT	density functional theory
EO	ethylene oxide
FTICR	Fourier transform ion cyclotron resonance
MFC	mass flow controller
qMS	quadrupole mass spectrometer
SSITKA	steady-state isotopic transient kinetic analysis
TAP	temporal analysis of products
TOF	time-of-flight

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