

# Stroboscopic operando spectroscopy of the dynamics in heterogeneous catalysis by event-averaging

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## Article

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# Abstract

Heterogeneous catalyst surfaces are highly dynamic entities that respond rapidly to changes in their local gas environment, and the dynamics of the response is a decisive factor for the catalysts' action and activity. Few probes are able to map catalyst structure and local gas environment simultaneously under reaction conditions at the time scales of the dynamic changes. Here we use the CO oxidation reaction over a Pd(100) surface exposed to pressures of 3 and 100 mbar of a CO + O<sub>2</sub> gas mixture to demonstrate how such studies can be performed by time-resolved ambient pressure photoelectron spectroscopy. Central elements of the method are cyclic gas pulsing and software-based event-averaging by image recognition of spectral features. For the CO oxidation reaction over Pd(100) our main finding is that that all surface phases – the CO-covered Pd surface, a surface oxide and a thick PdO<sub>x</sub> phase – catalyse the CO oxidation reaction, in dependence on the supply of gas phase reactants.

## Introduction

One of the key questions in heterogeneous catalysis is how the catalyst structure, composition and function relate to each other. The fact that the structure of a catalyst is dynamic rather than static as the reaction is initiated causes a major challenge in the endeavour of understanding of catalysis. The dynamics is strongly influenced by the exact reaction conditions in terms of temperature, pressure and gas composition [1][2]. These conditions may fluctuate with time and therefore to derive the complete mechanisms occurring on a particular catalysts, whether this be the automotive three-way catalyst or catalysts for power-to-X technologies [3], cannot be attained without a profound understanding of the dynamics of the catalyst material. The fluctuations can be produced by external stimuli, but also by changes being induced by the action of the catalyst itself [4][5].

Changes in the local gas composition above the catalytically active surface [6] and its influence on the structure and activity of the catalyst are particularly difficult to address experimentally. The reason is that this requires experimental methods that simultaneously can probe the structure, catalytic activity and local gas composition with a time resolution comparable to the timescale of the structural changes. While picosecond time resolution is necessary if the elemental steps of a catalytic cycle are to be probed [7], millisecond to second time resolution is sufficient to follow structural surface changes of the catalyst, such as phase transitions, surface roughening and segregation. Therefore, methods that allow video-rate frequencies or slightly beyond render the possibility to follow the dynamic restructuring of the catalyst surface. Imaging techniques that use strong probe signals, such as scanning tunnelling microscopy, transmission electron microscopy or low energy electron microscopy, can provide time-lapsed surface images at video-rate frequencies in both ultrahigh vacuum and ambient conditions. However, these techniques do not provide access to activity and local gas composition and can become challenging for detailed surface information when the catalyst temperature is elevated. In contrast, ambient pressure x-ray photoelectron spectroscopy (APXPS) [8] probes both the surface structure and its local gas composition, which also gives direct information on the catalytic activity. However, it uses a relatively

weak light-based probe signal, which implies that video-rate frequency mapping results in a low signal-to-noise ratio, which significantly hinders a proper analysis of the time-resolved data.

Here, we demonstrate how the fundamental problem of a low signal-to-noise ratio in time-resolved APXPS can be overcome by event-averaging over many surface phase transitions. In the experiments we use a sample compartment with a small gas volume to expose the sample surface to a rapidly oscillating gas composition with a repetition period between 14 and 145 s. In this way, we force the catalytic surface to periodically switch back and forth between phases with different activities as the catalytic reaction proceeds. The electron energy analyser in the APXPS system is used to simultaneously and continuously monitor the surface chemical reaction, phase transitions and gas phase composition at frame rates of up to 17 Hz. Image recognition and lock-in techniques are applied to the raw data to form an event-averaged signal of many phase change events on the surface. Ultimately, we demonstrate that one can record spectra with 60 ms time resolution. By averaging over more than 500 events, we can achieve time-resolved spectroscopic characterization of the catalytic sequence with an excellent signal-to-noise ratio and with an effective acquisition time of  $\approx 30$  s.

As a model system, we use the CO oxidation reaction over the Pd(100) surface prototypical for new experimental *in situ* tools for catalysis. Examples of this include planar laser-induced fluorescence (PLIF) [9], high-energy surface x-ray diffraction (HESXRD) [10], high-pressure scanning tunnelling microscopy (HPSTM) [11] and APXPS [12]. The reaction is also of fundamental interest since chemisorbed structures, thin surface oxides and bulk oxides all can co-exist at reaction conditions. Which surface is most active has been debated for decades, cf. the recent review by van Spronsen *et al.* [13]. Thus, *in situ* HPSTM [14], SXRD [15], APXPS [12] and HESXRD [16] studies in combination with mass spectroscopy have shown that the formation of various oxides on the Pd(100) surfaces coincides with the rapid increase in the CO<sub>2</sub> production. This observation has been interpreted as evidence for the oxides being more active than the metallic surface. In contrast, older studies by Gao *et al.* that used polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) ([17] and references in [13]) found that the CO<sub>2</sub> production decreased upon oxidation of the Pd(100) surface. Gao *et al.* pointed out that the highly reactive metallic surface state often is transient in high-pressure reactions and that it therefore easily can be overlooked. A recent study by Gustafson *et al.* carefully compared oxidized and chemisorbed phases and concluded that thin Pd oxide films are at least as active as the metallic surface, while thicker oxides are less active [18]. Other recent temperature-programmed reaction spectroscopy studies by Weaver *et al.* [19] and Mehar *et al.* [20] on Pd(111) and Pd(100) compared the intrinsic CO oxidation activity at UHV conditions and concluded that the chemisorbed oxygen phase is two to three times more active than a multilayer PdO(101) film supported on Pd(111) [19], while a multilayer PdO(101) film is more active than a single-layer PdO(101) film grown on Pd(100) [20]. Dynamic measurements with a time resolution comparable to the timescale of the phase change on the surface would provide a powerful method to investigate the transition between chemisorbed and oxidized phases and can potentially be used to reveal transient phases [17].

Here, we present data on the CO oxidation reaction over a Pd(100) surface at 3.2 mbar and 100 mbar total pressure. Gas pulses are used to drive the surface into different states, and time-resolved, event-averaged APXPS data are obtained and analysed. We find that the local CO and O<sub>2</sub> partial pressures just above the surface are the driving force for surface restructuring, and we demonstrate that there is a short time frame in which a transient metallic, CO-covered surface is highly active for CO oxidation, before the local gas composition forces the formation of a thin surface oxide. Finally, we discuss how the combination of gas pulsing and event-averaging of data can be applied to other surface science techniques used in catalysis research to obtain time-resolved data with a sufficiently high signal-to-noise ratio to be analysed.

## Results

### *Method*

In our experiments performed at the HIPPIE beamline, MAX IV Laboratory, Lund, Sweden, we exposed a Pd(100) single crystal surface to alternating pulses of CO-rich and O<sub>2</sub>-rich gas mixtures with CO:O<sub>2</sub> mixing ratios of 2.7:1 and 1:2.7, respectively. The pressure was kept constant at 3.2 mbar and the sample temperature at 550 K ± 10 K. The duration of the CO-rich pulse was 45 s and that of the O<sub>2</sub>-rich one 100 s, resulting in a total pulse period of 145 s. By exposure to the periodically varying pulses, the surface was brought to oscillate back and forth between an inactive and active surface state for the CO oxidation reaction, as verified by mass spectrometry that probed the gas entering the nozzle of the electron analyser (see figure S1 and further experimental details of the pulsing parameters in the SI).

The surface was exposed sequentially to 58 combinations of a CO-rich and an O<sub>2</sub>-rich pulse. During the exposure we continuously recorded the O 1s x-ray photoelectron (XP) spectra. The spectra were measured at a frequency of 6.75 Hz using the “fixed acquisition mode” of the electron energy analyser. This mode makes use of the energy dispersion of the analyser, which allows fast acquisition of entire spectra at fixed analyser voltages. Figure 1A shows an image plot of 810 spectra (equal to an acquisition time of 120 s) acquired during one complete surface oscillation cycle induced by the gas pulse variation. The spectral features originate both from the gas phase molecules probed in a volume 0 – 50 μm above the sample surface (strong features above 535 eV binding energy) and from the surface atoms and adsorbed molecules (weak features below 533 eV binding energy). The spectra marked by two dotted lines *i* and *ii* in Fig. 1A are shown in Fig. 1B. Clearly, a poor signal-to-noise ratio makes peak decomposition in these spectra impossible. The standard solution for further component analysis would normally be to bin the dataset in Fig. 1A at the expense of time resolution. Information about how fast the phase change occurs on the surface, on hidden transient phases and on how the catalytic properties change during the phase change would get lost. We note that the experiments were performed at an APXPS beamline with one of the most intense photon fluxes in the world, which renders further improvement of the signal-to-noise ratio by choice of photon source unrealistic at the present stage.

In the following we will show that calculation of the event-averaged signal of the experimental data from all 58 gas pulses instead of the time-averaged signal of a single pulse provides a suitable pathway towards a much-improved signal-to-noise ratio. This then makes possible a detailed component analysis without loss of time resolution. In principle, it would be possible to obtain such an event-averaged signal by relying on the delay between the gas pulse and the measurement. Such an approach would require, however, that all pulses are identical and that a given surface transition from one phase to another happens at a certain delay for all pulses. Neither of the conditions can be guaranteed to be fulfilled in the experiment. There might, for example, exist history effects in the gas dosing system, resulting in a gas composition that changes slightly over time, or in the state of the surface, caused e.g. by segregation. In such cases a pulse-probe measurement would fail and lead to incorrect conclusions about the surface dynamics. Instead, we rely on the use of a locking signal that defines the transition event from the active to the inactive surface phase for CO oxidation and vice versa. Appropriate locking signals are expected to be found at the beginning and the end of the CO pulse. These two events need to be considered separately since the lengths of the different parts of the gas pulse vary slightly over time (cf. Fig. S2 and S3 in the SI).

Any feature in the image plot of figure 1A that signals a phase transition on the surface can potentially be used as the locking signal, as the time-resolved data were recorded continuously. Examples of such features in the raw data can be the appearance or disappearance of a signal or the changed intensity of a component due to adsorption of molecules or oxide formation. It can also be a work-function shift on the surface, which is visible as an apparent binding energy shift of the gas phase components [21]. By trial-and-error of different locking signals, we found that the work function-induced shift of the gas phase O 1s peak of CO<sub>2</sub> (start of CO pulse as the partial pressure of CO<sub>2</sub> here is high) and O<sub>2</sub> (end of CO pulse as the partial pressure of O<sub>2</sub> here is high) is the most suitable locking signal. These shifts are visible as clear image contrasts within the dotted rectangles in Fig. 1A, and one stamp-image within each rectangle is chosen. An image-recognition algorithm loops over the raw data and searches for the best match between these stamp signals in all of the data (see movie M1.mp4 in the SI). Using this method, we can determine the absolute time of each phase transition event on the surface with a time resolution that corresponds to the sampling frequency of the experiment, 148 ms in the present experiment. Hence, the data from all 58 pulses can be properly time-aligned and the event-averaged signals at the start and end of the CO-pulse can be constructed by averaging the time-aligned data of all 58 pulses. Finally, the two event-averaged image signals are merged together to form the full event-averaged image constructed based on measured sample-work function changes. The corresponding signal is displayed in figure 1C.

It is clear that the above averaging algorithm has resulted in a very much improved signal-to-noise ratio without any loss in time resolution. This is already clear from consideration of the image plot in Fig. 1C and even clearer from the appearance of the two spectra i and ii in Figure 1D, which were extracted from Fig. 1A as indicated. Deconvolution of these spectra into components is now possible with high precision and certainly this is a dramatic improvement in comparison to what can be done on the data in Fig. 1B. Similar event-averaged data for C 1s and Pd 3d<sub>5/2</sub> are shown and discussed in the SI (figures S4 and S5).

We demonstrate the capability of the method with a second dataset of CO oxidation over a thicker PdO<sub>x</sub> oxide formed at higher pressure. The dataset was recorded on the POLARIS instrument at DESY (cf. SI for a description of the setup) [22]. The setup takes advantage of a double-cone for gas dosing together with a very short sample-cone distance on the order of 30 μm, which leads to the creation of a “virtual cell”, in which the flow onto the sample creates a local high-pressure pillow with μm dimensions. A total flow of 1800 sccm was used and resulted in a local gas pressure of ~100 mbar in the virtual cell.

Figure 2 uses a similar layout as figure 1 and summarizes the CO oxidation experiments at 100 mbar. Here, the gas pulse length was reduced to 14 s, which was made possible by the very short gas-exchange time of the virtual cell. For the measurements at the POLARIS setup a pulsing pattern of 8 s oxidation in pure O<sub>2</sub> and 2 s reduction in 8:1 CO:O<sub>2</sub> was used. To avoid direct mixing of CO and O<sub>2</sub> in the gas inlet line, prohibited at the DESY facility, 2 s of 1:8 O<sub>2</sub>:He was used at each side of the CO-rich pulse. During the experiments the crystal was kept at a stable temperature of 803 ± 2 K, as the rapid gas compositions oscillations left a short time window for the crystal to cool or heat due to absence or presence of exothermic heat from the CO oxidation reaction.

The short gas pulse length allowed us to measure and average over more than 500 pulses within the same measurement time as was used for 58 gas pulses in the first experiment. Since the gas dosing was very reproducible with the high gas flows and since the changes on the surface are slower in this case only one stamp-signal was used (again marked with a dotted rectangle in panel A). Instead of using the work-function shift as was done in figure 1, here we found that the Pd 3p<sub>3/2</sub> component of the metallic surface was the optimum locking signal. In fact, the gas phase signals are difficult to see in raw data before event-averaging.

Clearly, the comparison of the two topmost panels of figure 1 and 2 demonstrates how noisy raw data recorded in a transient gas flow by event-averaging can be transformed into high-quality data with dramatically improved signal to noise ratio.

### ***Interpretation of the results***

The low-noise 0.1 s data in Figs. 1D and 2D, derived using the above method, are well suited for further analysis, since they contain simultaneous information on all gas phase species, the surface-adsorbed CO species and the oxidation state of the surface. The time-dependent gas composition just above the sample surface can be obtained from the curve fitted intensity of the gas phase components divided by the number of oxygen atoms of each molecule and normalized to the total pressure of the cell. The results obtained from curve fitting on the order of 800 (Fig. 1) and 200 (Fig. 2) event-averaged spectra, respectively, are summarized in Figs. 1E and 2E. Note that partial pressures are shown with vertically stacked y-axes to the left in both cases meaning that the partial pressure of CO is zero at t = -40 s in Fig. 1E. The entirety of curve fitting results is available from movies M2.mp4 and M3.mp4 in the SI.

The surface components in Fig. 1D are the Pd 3p<sub>3/2</sub> line (blue), the signal in grey at 531.4 eV binding energy due to adsorbed CO and the two components at 528.7 eV and 529.3 eV (orange), which we attribute to a (Ö5'Ö5)R27° surface oxide (hereafter named Ö5 oxide). The assignment agrees with previous studies [12][23]. The sum of the intensities of the Ö5 oxide components is shown as orange data points in Fig. 1E together with the time-dependent intensity of the surface CO peak. Both curves are normalized to the value of highest intensity.

In contrast, in Fig. 2D we find a surface O 1s component at 529.9 eV due to a thick PdO<sub>x</sub> phase, displayed in orange colour, and the Pd 3p<sub>3/2</sub> line in blue. The former signal is present in oxygen-rich conditions only. Its varying intensity correlates well with the position of the Pd 3p<sub>3/2</sub> component, which changes between 533.2 eV in oxygen-rich and 532.0 eV in CO-rich conditions. First of all, this implies that the surface in CO-rich conditions is entirely reduced to its metal state. Secondly, the palladium oxide phase in O<sub>2</sub>-rich conditions must be thicker or comparable to the probing depth of approximately 17 Å (see SI for details) since the bulk-metal phase cannot be discerned anymore, as is visible from the observation that the entire Pd 3p<sub>3/2</sub> peak shifts. This conclusion is further supported by the Pd 3d<sub>5/2</sub> data in Fig. S6 in the SI, which suggest a PdO<sub>x</sub> thickness of 25 Å.

A comparison of the data in Figs. 1 and 2 makes it clear that the high O<sub>2</sub> pressures of 100 mbar leads to a much higher degree of oxidation of the Pd surface than in the experiments performed at 3 mbar, in which only a surface oxide is formed. This difference notwithstanding, in both cases exposure of the surface to CO-rich conditions leads to a complete oxide removal, most clearly demonstrated by the Pd 3d data in Fig. S6.

Regarding the 1 mbar experiment (Fig. 1), the observed formation of a Ö5 oxide on Pd(100) at the present experimental conditions has been verified by several techniques before, including APXPS [12][23]. It is well known that the surface system is in the so-called CO mass-transfer limit in this pressure regime [5][17], with the formation of CO depletion layer. Previously it has, however, not yet been possible to determine the exact dynamics of the catalytic process and in particular what happens in the transition region into and out of the mass-transfer limit. The high time resolution and good signal-to-noise ratio of the data in Fig. 1D allows us to provide such analysis now.

Fig. 1E shows that the CO pulse starts to arrive at the surface at around -25 s and that the CO<sub>2</sub> production increases. The increased CO content in the pulse then presses more and more CO through the CO depletion layer above the surface. This CO reaches the surface where it reacts instantaneously to CO<sub>2</sub> within the time resolution of the experiment; thus, the CO<sub>2</sub> production follows suit. Eventually, only little O<sub>2</sub> remains above the surface, so that the system tips over into the O<sub>2</sub> mass transfer limit and the Ö5 oxide is not replenished anymore. At t=0 s, the supply of O atoms from the Ö5 oxide to the CO oxidation reaction leads to a fast disappearance of the oxide signal; now, instead CO covers the entire surface - poisons it - and thus stops the reaction to CO<sub>2</sub>. The switch-over in surface coverage from oxygen to CO is very rapid, so rapid, indeed, that the transition cannot be resolved: the shift from an oxygen- to CO-

covered surface occurs in less than 163 ms. These observations show that the  $\text{NiO}$  oxide is extremely resistant to CO-induced extinction under the experimental conditions: it converts all CO to  $\text{CO}_2$  as long as sufficient  $\text{O}_2$  is available in the gas phase to replenish the oxide. Conversely, once this is not the case anymore, the phase transition from the oxide-covered surface to the CO-poisoned surface is very rapid.

The CO partial pressure reaches its maximum at  $t = 20$  s, after which the local CO pressure starts to decrease.  $\text{CO}_2$  production is resumed first when the CO partial pressure has dropped to  $\sim 1$  mbar (at  $t = 38$  s). At  $t = 47.0$  s the  $\text{CO}_2$  pressure starts to increase rapidly until the  $\text{NiO}$  oxide signal reappears at  $t = 50.8$  s, marking the transition from the CO-covered to the  $\text{NiO}$  oxide-covered surface. Clearly, right before this transition, the surface is highly active for CO oxidation, although it is primarily covered by CO with no or only little  $\text{NiO}$  oxide on the surface. Indeed, the primarily CO covered transient surface is sufficiently active to bring the system into the CO mass-transfer limit.

The time-resolved and event-averaged data show that the  $\text{NiO}$  oxide is very hard to reduce at the mbar conditions of the experiment. The reduction sets in first when the gas composition above the sample surface is dominated by  $\text{CO}_2$  and the surface system is in the oxygen mass-transfer limit. Similarly, the reverse transition from a CO- to the  $\text{NiO}$  oxide-covered surface happens only when the surface system is in the CO mass-transfer limit. Once the surface phase transition happens it is fast and occurs within less than 163 ms. We find that the  $\text{NiO}$  oxide always is very active, while the metallic CO-covered surface may be very active, but only if the partial pressure of  $\text{O}_2$  is sufficiently high.

Essential for being able to draw these conclusions is the fact that we can probe the surface and the local gas composition right above the surface, both of which are equilibrated, with sub-second time resolution. It would be difficult, if not impossible, to do the same by a combination of gas and surface characterization techniques that do not probe the same spot at the same time, such as mass spectrometry combined with a surface sensitive technique. There exist other approaches to overcome these hinders, such as a combination of carefully synchronized PLIF for local gas phase probing and HESXRD [24] or surface reflectance [19] for surface analysis. It is interesting to note the similarity of the present results to those of Blomberg *et al.* [24], who exposed a Pd(100) crystal to a gas mixture of 6 mbar CO and 24 mbar  $\text{O}_2$  at a sample temperature of 473 K. They found by PLIF that  $\text{CO}_2$  production reached saturation approximately 2.5 s before any sign of the  $\text{NiO}$  oxide was observed by HESXRD. The finding matches well with the present results. The fact that a high  $\text{O}_2$ :CO ratio is required before the  $\text{NiO}$  oxide develops is also well in line with a recent study by Gustafson *et al.* [18], who also concluded that the  $\text{NiO}$  oxide is at least as active for CO oxidation as the metallic surface. While the study by Gustafson *et al.* concluded that the surface oxide *must* be as active as the oxide and the study by Blomberg *et al.* concluded that the surface is not fully oxidized when the ignition of the catalyst occurs, the chemisorbed phase present on the metallic surface when ignition occurs is left untouched. The reason for this is clear. These previous studies did not have the ability to probe oxide, chemisorbed phases and localized gas composition simultaneously with high time resolution. As pointed out by Gao *et al.* [17] more than 10 years ago the complexity of high-pressure reactions, and especially the limitations of mass transfer,

results in high reaction rate states which often are transient. Here, we show that this indeed is the case, and surprisingly the majority of the surface is CO-covered according to fig. 1E when ignition occurs. First, when the mass transfer limit is reached and no CO is found near the surface the CO desorbs and the surface oxide develops rapidly.

Turning to the results of the 100 mbar experiment summarized in Fig. 2, we find that the front of the arriving CO-rich pulse of 2 s duration is entirely consumed by the CO oxidation reaction (Fig. 2E): a CO<sub>2</sub> cloud above the surface builds up between  $t = 0.0$  to  $t = 0.1$  s, and the CO<sub>2</sub> pressure reaches 100 mbar. The reaction is catalysed by the PdO<sub>x</sub> phase that is present at the surface at  $t = 0.0$  s. The complete conversion of CO is accompanied by a reduction of the oxide, which is fully consumed within  $\sim 250$  ms. The surface becomes metallic, but remains active for the direct conversion of the 8:1 CO:O<sub>2</sub> feed gas (i.e. now the reaction is limited by the oxygen supply). The tailing-off of the CO-rich pulse goes along with a second increase of the CO<sub>2</sub> production to 100 mbar. We attribute this second phase of high CO production rate to the gas mixture becoming stoichiometric. Clearly, at this point, no PdO<sub>x</sub> surface phase is observed; the metallic Pd surface is sufficiently active for the complete combustion of all incoming CO. The re-oxidation of the surface to PdO<sub>x</sub> at the end of the CO-rich pulse is much slower than the reduction of the oxide upon arrival of the pulse (cf. a further analysis of the event-averaged Pd 3d<sub>5/2</sub> data in the SI and its comparison to the PdO<sub>x</sub> signal as determined from the O 1s and Pd 3d signals).

The finding that CO<sub>2</sub> production is observed when a thick PdO<sub>x</sub> oxide is found on the surface matches well recent SXRD study of Shipilin *et al.* [26]. In this study different Pd oxide phases were observed with SXRD while in the mass transfer limit for the CO oxidation reaction. In low excess of oxygen in the feedgas the authors observed growth of PdO islands atop a  $\sqrt{5}$  surface oxide, while a thick and polycrystalline PdO film were observed with a high excess of oxygen in the feedgas. While the study of Shipilin *et al.* used the composition of the feedgas to tune the gas atmosphere that the surface equilibrates to, we measure it directly and clearly show that high pressure of pure oxygen is a requirement for development of the thicker PdO<sub>x</sub> oxide. In fact, this is exactly what we would predict based on the observed kinetics for the oxide removal and growth. As the oxide growth is slow, while reduction is fast, just a little CO in the near surface region will prohibit growth of bulk oxides. In contrast, the  $\sqrt{5}$  oxide growth proceeds fast and does not require high pressure of oxygen for seconds to form.

## Summary

We present a new method to generate event-averaged APXPS data from cyclic gas pulse experiments using a triggering signal obtained by image-recognition and originating from true changes on the surface. The event-averaging process removes times delays induced by history effects in the gas pulsing system or the sample due to e.g. segregation. This stands in contrast to what can be achieved if gas pulsing is used for triggering the measurement. The method is suitable for non-periodic studies: for example, it becomes possible to study self-sustained oscillations that are non-periodic in nature [5][27].

We have applied the here developed method to the catalytic oxidation of carbon monoxide over a Pd(100) surface at ~mbar pressures and have used it to study the rapid transition between the CO-covered metallic and oxidized surface. The transition is so rapid that it would have been impossible to investigate it without the event-averaging method. The  $\text{PdO}_5$  surface oxide turns out to be extremely resistant to reduction at 550 K, which first sets in once  $\text{O}_2$  is nearly absent in the gas phase above the surface. Upon reduction the surface become metallic and CO poisoned within less than 150 ms. It remains inactive at low  $\text{O}_2$  pressure, but turns active for a short time when the local oxygen pressure becomes sufficiently high. Once the CO mass transfer limits is reached, CO desorbs and the  $\text{PdO}_5$  surface oxide reappears again within 150 ms.

CO oxidation experiments over a Pd(100) surface at 100 mbar pressure and within a virtual cell with  $\mu\text{m}$ -dimensions allow a much faster repetition rate and therefore averaging over more than 500 events. The event-averaging method improves the data set to such a degree that the gas phase components, which are completely hidden in the noise in the single-event data, become fully analysable. As in the mbar experiments we find a rapid removal of the PdOx phase under reaction-induced  $\text{O}_2$ -poor conditions. The re-oxidation requires a high pressure of pure oxygen gas and is a significantly slower process.

In the experiments, we use an oscillating gas composition to create forced surface phase oscillations. Many other sample environment parameters could be used in future experiments, such as the total gas pressure or the sample temperature. The method of image-recognition to generate a true surface triggering signal can be applied to any time-lapsed APXPS experiment [28] and even any surface science technique that makes use of a fast detector. The only requirement is that the time-resolved data contain features that can be identified by image recognition. The application to SXRD (see, e.g., [26] and consider rapid gas pulsing and event-averaging applied to movies of diffraction patterns) or PLIF [25] and many other techniques should be straight forward. The method presented here opens entirely new avenues for time-resolved catalysis, as experiments with hitherto unseen stroboscopic vision of surface changes in response to changes in the local sample environment now become possible.

## Declarations

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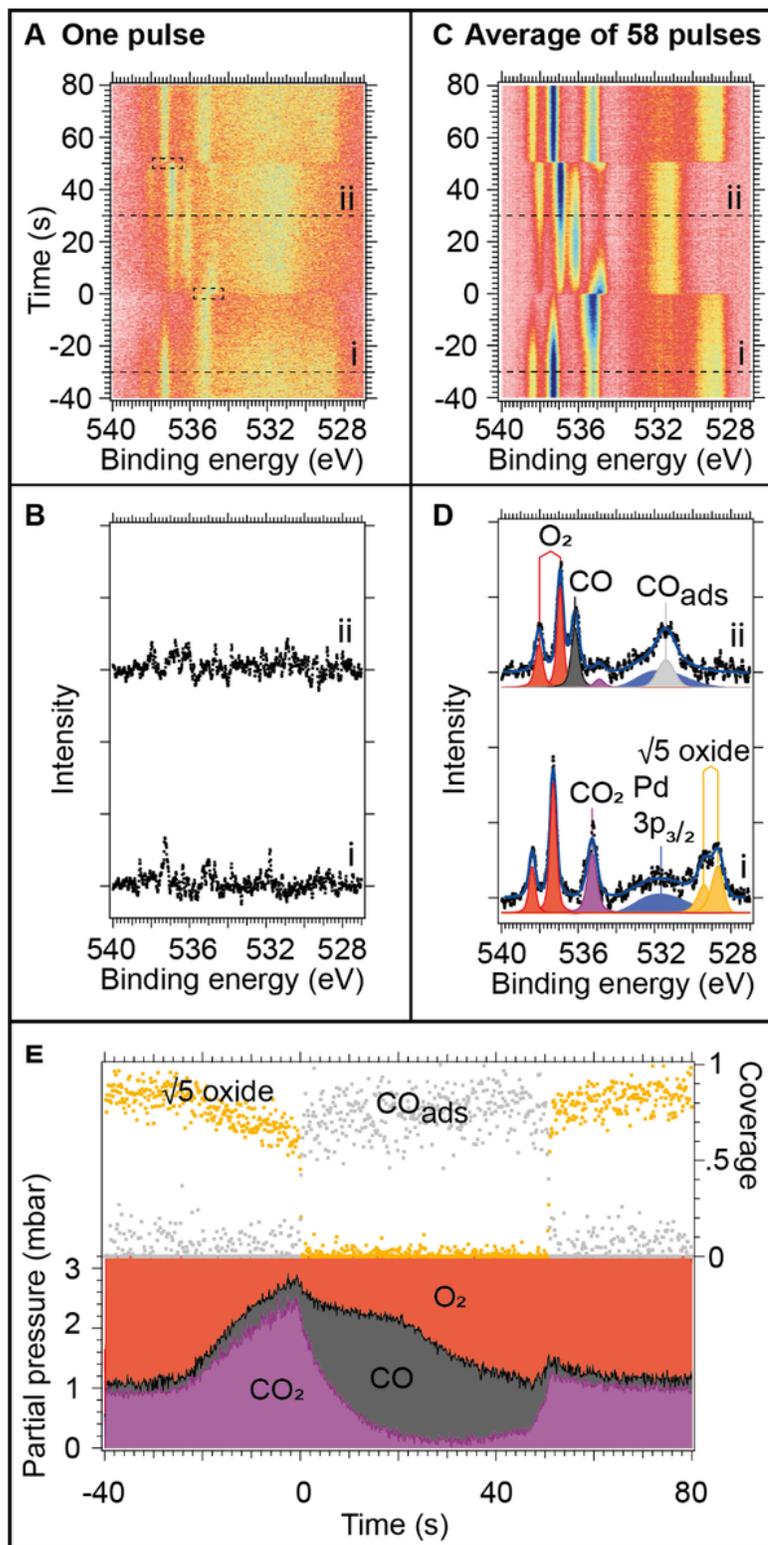
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## Figures



**Figure 1**

Image plots of time resolved O 1s data acquired with a photon energy of 650 eV before (A) and after (C) event-averaging 58 pulses. B and D show single spectra recorded along the dotted lines i and ii in panel A and B and the curve fitting and peak assignment for the event-averaged data. The pressures,  $\sqrt{5}$  oxide, and adsorbed CO as obtained by curve fitting are shown in (E). Partial pressures are shown on vertically stacked y-axes – i.e. at  $t = -40$  s the partial pressure of CO is zero.

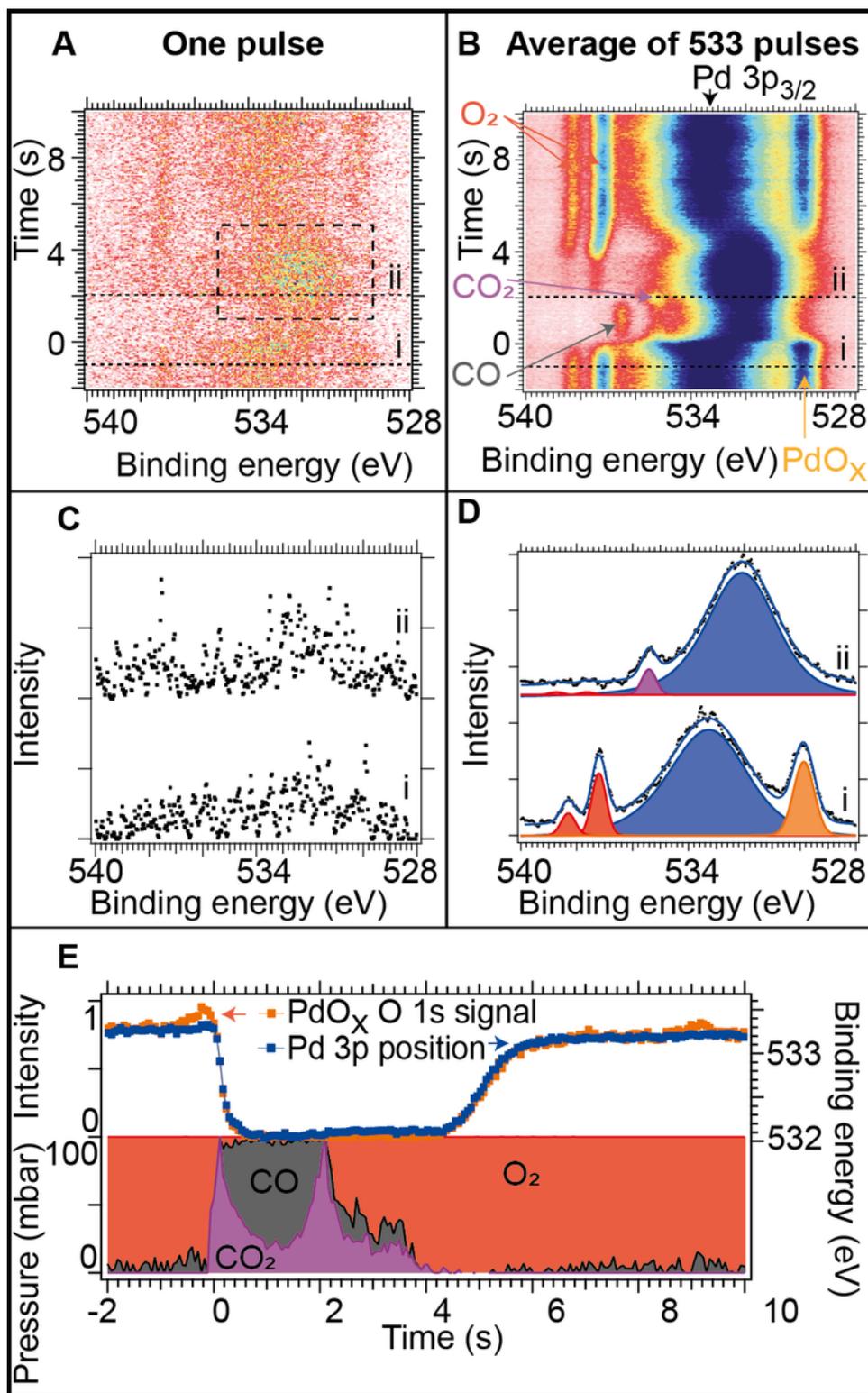


Figure 2

Image plots of time resolved O 1s data acquired with 17 Hz and a photon energy of 4.6 keV before (A) and after (B) event-averaging 533 pulses. Examples of single curve fitted spectra before (C) and after event-averaging (D) are shown in the panels below for the spectra highlighted with i and ii in panel A and B. The pressures, PdO<sub>x</sub> signal, and position of Pd 3p<sub>3/2</sub> peak as obtained by curve fitting are shown in (E). Partial pressures are shown on vertically stacked y-axes.

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