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ABSTRACT

We have combined three techniques, High Energy Surface X-Ray Diffraction (HESXRD), Surface Optical Reflectance, and Planar Laser Induced Fluorescence in an *operando* study of CO oxidation over a Pd(100) catalyst. We show that these techniques provide useful new insights such as the ability to verify that the finite region being probed by techniques such as HESXRD is representative of the sample surface as a whole. The combination is also suitable to determine when changes in gas composition or surface structure and/or morphology occur and to subsequently correlate them with high temporal resolution. In the study, we confirm previous results which show that the Pd(100) surface reaches high activity before an oxide can be detected. Furthermore, we show that the single crystal catalyst surface does not behave homogeneously, which we attribute to the surface being exposed to inhomogeneous gas conditions in mass transfer limited scenarios.

INTRODUCTION

In order to improve our understanding of the underlying mechanisms involved in a heterogeneous catalytic reaction, correlations between the reaction products and the catalyst surface structure are of great importance. Thus, in recent years, there has been an increased interest in so-called *operando* studies in which the catalyst sample is investigated under catalytic operating conditions. In *operando* studies, not only is the exhaust gas probed while the catalyst is exposed to varying temperature or gas conditions, but an attempt is also made to probe the intermediate reaction stages: both spatially, with focus on where any product gas or surface structure changes occur, and temporally, focusing on when these changes occur in relation to changes in experimental parameters such as reactant gas composition or catalyst temperature.

Industrial catalysts, which involve metal nanoparticles or zeolites, are often structurally complex systems and thus difficult to characterize. Atomic scale information on the active sites is therefore difficult to obtain under *operando* conditions. Instead, investigations into specific reaction mechanisms are commonly conducted on single crystal model catalysts with well-defined metallic surfaces.

Furthermore, it has been shown that the surface structure, and therefore also the reaction characteristics of catalysts, can change depending on total pressure of the surrounding gas. Consequently, it is important to perform *operando* experiments in industrially...
relevant gas and temperature conditions (>1 bar, 600-1300 K), even if this adds to the experimental difficulties or increases signal noise. It is otherwise difficult to relate any findings to actual industrial processes.

It is only with the recent advent of high-pressure compatible techniques, such as Surface X-Ray Diffraction (SXRD), Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS), Polarisaton Modulated-Infrared Adsorption Spectroscopy (PM-IRAS) or High-Pressure Scanning Tunnelling Microscopy (HP-STM), that an atomic-scale probing of the surface structure has become possible during the variation of a reaction variable such as gas composition or sample temperature. Other techniques for surface structure determination do exist, but they often require the sample to be in ultra-high vacuum (<10^{-9} mbar) conditions; such limitations render them impractical for operando studies where the catalyst is probed in high pressure (>10 mbar) environments. Operando studies, however, are essential for a knowledge-based development of industrial catalysts.

A caveat of the aforementioned probing techniques is that, while they do provide detailed atomic scale information about the surface, they often probe a limited area of the sample. The structural or chemical changes in this limited area are then often correlated with changes in the global gas composition, as measured by a mass spectrometer (MS) at the reactor outlet. Recent studies, however, have found that the catalyst surface does not always behave homogeneously. This is attributed to variables such as reactor geometry or an inhomogeneous gas distribution around the catalyst effectively exposing distinct parts of the surface to different gas conditions; in particular, at ambient pressure conditions and with a highly active sample, the reaction may become mass transfer limited (MTL). In this situation, the measured catalytic activity is determined by the diffusion of reactants to the catalyst surface instead of the activity of the surface itself. This in turn gives rise to a boundary layer above the sample within which the reactants are almost completely depleted. Hence, in MTL situations, the global average gas composition probed by the MS is not representative of the gas conditions experienced by the catalyst surface. In fact, the conditions might even vary between different points over the catalyst surface. As such, it is of importance to monitor the gas distribution directly over the catalyst, in a spatially resolved fashion, simultaneously with the full sample surface itself. This ensures that the measured atomic scale surface data are representative of the surface as a whole.

Planar Laser Induced Fluorescence (PLIF) is a laser-based species-specific technique that can provide an image of a gas distribution with high spatial and temporal resolution. The technique has been widely employed in combustion diagnostics in the past. More recently, it has also been used for catalysis research. In this study, we have used PLIF to detect CO; through fluorescence in the mid-IR regime. Apart from CO₂, PLIF can also be used to detect other gases of relevance to catalysis such as NO, NH₃, and OH.

High Energy Surface X-Ray Diffraction (HESXRD) is an excellent technique for the fast characterization of surface structures on the atomic level under operando conditions. By using high energy X-rays in combination with a 2D detector, it is possible to create a comprehensive image of the diffraction signal with high temporal resolution. This is especially important in catalysis research to catch the rapid surface changes exhibited as the catalyst activity changes. Due to its photon-in-photon-out nature, HESXRD is not limited by the mean-free-path of electrons as they pass through the gas surrounding the sample. Thus, HESXRD also works well at ambient pressures. The technique is described in more detail in Refs. 6 and 22.

It has recently been shown that the reflectance of LED light by an active catalyst surface will change depending on the surface roughness and the surface oxidation state. This technique is henceforth referred to as Surface Optical Reflectance (SOR). We use SOR to image the entire sample surface at once, which provides a useful overview, almost in the form of a map, of the surface from a macroscopic point of view. From this map, one can then easily see which parts of the surface undergo a change in oxidation state or roughness.

In this work, we have combined SOR with HESXRD and PLIF for detailed surface structure characterization and instant 2D spatially resolved gas phase characterisation during CO oxidation over a Pd(100) single crystal catalyst using a dedicated in situ catalysis chamber. To perform the combined measurements, the entire catalysis chamber, laser, and SOR setups were transported to the high energy X-ray beamline P07 at Petra III at DESY in Hamburg. There, we performed a series of measurements where the reactant gas composition was varied over time. In the experiments, the sample surface was monitored with SOR and HESXRD, while the gas phase was monitored using MS and PLIF. This allowed us to correlate changes in the microscopic surface structure, as seen in the HESXRD signal, with changes in the macroscopic surface structure visualised by SOR. Since SOR gives an overview of the entire sample, it is easy to see where the sample surface structure changes and if the change occurs in a location probed by HESXRD. The high temporal resolution of the techniques also allows for near-instant probing of the surface structure and gas composition which is essential for correlating changes in the surface structure with changes in the product gas composition. Overall, we believe that the presented techniques are valuable to the catalysis community by providing a comprehensive overview of the experimental situation as a whole.

EXPERIMENT

The experimental setup used at the High Energy Materials Science (HEMS) beamline P07 at PETRA III in Hamburg consists of four parts: the catalysis chamber together with its gas system and heater, including a mass spectrometer; the optical setup for the PLIF measurement; a separate optical setup used to create, and image, the LED reflection; and the beamline equipment used for the HESXRD measurement. A schematic diagram of the experimental setup is shown in Fig. 1.

The reactor used in the experiment is an ultrahigh vacuum/ high-pressure flow reactor for surface x-ray diffraction and grazing incidence small angle x-ray scattering studies designed by Leiden Probe Microscopy (LPM), variants of which are commonly used for surface diffraction experiments. The reactor is described in detail in Ref. 28. The reactor chamber has two parts: First, a 25 ml high-pressure flow reactor for catalysis with a boronlic heating element onto which the sample is placed; second, a UHV-part dedicated to sample preparation by means of sputtering and...
The beam was shaped into a laser sheet using a convex cylindrical lens ($f = 100$ mm). In the reactor, the CO$_2$ molecules interact with the beam, resulting in fluorescence at 4.3 $\mu$m. This fluorescence was imaged using a 256 $\times$ 256 pixel LN$_2$-cooled InSb camera (Santa Barbara Focalplane SBF-134). The large, varying thermal background was compensated for by setting up the camera to trigger at 20 Hz, i.e., also between laser pulses, to record the current background, which was subtracted in post-processing on a single-shot basis. In all, we achieved a spatial resolution per pixel of 80 $\mu$m in the image plane and a resolution of around 100 $\mu$m in the normal plane, which was limited by the thickness of the laser sheet. Since the laser has a 10 Hz repetition rate, one snapshot image was recorded every 100 ms with the camera exposure time set to 30 $\mu$s and with a delay of 10 $\mu$s from the laser pulse to avoid any direct laser reflections. To calibrate the PLIF signal to absolute partial pressures, we recorded a series of images where the reactor was filled with a known, homogeneous CO$_2$ distribution, while the sample was heated to various temperatures. The fluorescence yield from these measurements was then compared to data acquired as the catalyst was active. For more in depth information about the PLIF setup and post-processing, refer to Ref. 30.

For the HESXRD measurements, the X-ray energy was set to 77 keV. The sample surface was aligned with the beam such that

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the X-rays impinged on the sample surface at a grazing angle of 0.04°. The use of such a grazing angle, which is below the critical angle for total external reflection (the critical angle for Pd and 77 keV X-rays is 0.0489°), leads to an increase in signal-to-noise ratio and surface sensitivity by drastically reducing the X-ray penetration depth. A large, square-shaped 2D detector, with an area of ~0.17 m² located 1.7 m from the reactor, was used to image the resulting diffraction pattern, giving a comprehensive representation of the sample surface atomic structure along the X-ray line of incidence. The high signal-to-noise ratio enabled us to set the exposure time to as short as 0.5 s, which provided the temporal resolution necessary to monitor transient processes such as oxide formation on Pd(100), confirming previous AP-XPS measurements on the oxidation of Pd(100). Due to the small incident angle, however, the catalyst had to be kept at a constant temperature to not jeopardize the vertical alignment through thermal expansion of the sample.

For the SOR measurement, an LED light (650 nm) was first diffused using a spatial filter to suppress intensity irregularities caused by the internal LED pattern. Next, the light was collimated into a beam before it was directed toward the reactor from above. Two mirrors, each placed at a 10° angle from the reactor, were used to reflect the beam down onto the sample and to catch the reflection, respectively. The reflection was then imaged onto the chip of a CMOS camera (Andor Zyla) by means of a 4f-setup. To avoid misalignment during rotating or tilting of the chamber, which is necessary for the HESXRD measurements, the LED and optics were mounted onto the chamber top-plate itself. During most measurements, this camera was triggered at 10 Hz. In post-processing, all resulting SOR images were divided on a per-pixel basis by an average of a series of images acquired when the surface was reduced, which yields the reflectance difference in per cent. In this way, it is possible to visualise even small reflectivity changes in the spatially resolved image.
Since the three techniques all rely on different detectors and detection apparatus, synchronization between them is key to a successful correlation between the simultaneously acquired data. Figure 2 gives a schematic overview of the lab equipment and triggering setup. A measurement run was initiated by the software controlling the HESXRD detector and diffractometer motors. When the detector began to acquire for the first time during a measurement run, a trigger signal was sent to a separate computer which controlled the flow controllers and logged reactor parameters such as pressure and temperature. This computer polled for a trigger signal every 50 ms; when a signal was detected, acquisition of the reactor parameters began. The same computer also sent signals to the CMOS camera capturing the LED images and to the InSb camera capturing the PLIF fluorescence. The CMOS camera would begin acquiring immediately on reception of the signal, resulting in a maximum delay of 50 ms ($\Delta S$ in Fig. 3) with respect to the start of the HESXRD acquisition, while the InSb camera would begin acquiring on the following laser shot, which might be up to 100 ms later. This resulted in a maximum PLIF delay ($\Delta_{PLIF}$ in Fig. 3) of 150 ms. As the HESXRD detector has an exposure time of 500 ms, these delays were deemed acceptable.

RESULTS AND DISCUSSION

We performed several combined measurements where the PLIF, HESXRD, and SOR techniques were used simultaneously in combination with a traditional mass spectrometer (MS). The experiments were all carried out at constant temperature since a change in temperature would have resulted in a thermal expansion of the sample. This expansion would in turn have necessitated a realignment of the X-ray beam due to its grazing incidence angle—a feat difficult to perform without spoiling the dataset. For this reason, instead of realigning the X-ray beam, the measurements were carried out at a constant temperature.

FIG. 6. Simultaneous SOR (a), HESXRD (b), and PLIF (c) data at three $O_2$:CO ratios corresponding to $t_1$, $t_2$, and $t_3$ in Fig. 4. Note how the oxidization begins to form in the centre-right area and to then spread over the entire sample area during the subsequent minutes. Also note the simultaneous weakening of the CTR corresponding to the metal surface (magenta box), and the simultaneous increase in the oxide peak (cyan). The PLIF signal remains stable since the reaction is mass transfer limited.
of altering the sample temperature, the composition of the gas flow was changed during the measurements in order to probe different catalytic activity regimes for CO oxidation.\textsuperscript{35}

The first part of the experiment was carried out at a sample temperature of 630 K, where, during 10 min, the flown ratio between CO (we used 10\% CO in Ar) and O\textsubscript{2} was varied. Initially, after sputtering and annealing, the as-prepared sample surface was exposed to reducing gas conditions with only CO and Ar but no O\textsubscript{2} being flown. The measurement began with introducing a small amount of O\textsubscript{2} (4 mln/min). The O\textsubscript{2}:CO ratio was initially altered by decreasing the CO flow for 3 min. Subsequently, the CO flow was fixed and the O\textsubscript{2} flow was incrementally increased to alter the O\textsubscript{2}:CO ratio. The ratio was first slowly raised to 1:2, after which it was raised more rapidly until it reached 10:1, as shown in panel (a) in Fig. 4. In this way, the maximum total CO\textsubscript{2} production is kept constant. Argon was used as buffer gas during the entire measurement to keep a constant total flow of 164 mln/min, which resulted in a pressure at the sample of around 180 mbar. Figure 5 shows the mentioned gas flows in more detail.

In order to probe a larger part of reciprocal space with HESXRD, the sample was rotated back and forth 15\degree with each rotation taking 10.3 s. During the rotations, images were acquired at 2 Hz. In post-processing, all images obtained during one rotation were merged, and the maximum of each pixel value during the rotation was used to construct one final image per rotation, resulting in a time resolution of 10.3 s. Subsequently, two regions, one close to the (004) Bragg peak of the PdO(101) bulk oxide and the other on the Pd(111) crystal truncation rod (CTR) originating from the metal surface, were isolated and trended over time.

Panels (b) through (e) in Fig. 4 show the parameters collected during the measurement, while Fig. 6 shows SOR (a), HESXRD (b), and PLIF (c) images at three time points during the measurement (t1-t3). The squares in the images in Fig. 5 correspond to the regions of interest trended in panels (d) and (e) of Fig. 4. The prevalent circular patterns in the reflectivity image are due to an imperfection in the sapphire dome. We further attribute the coarse wavy patterns to dome imperfections.

It is noteworthy that as the O\textsubscript{2}:CO ratio approached 6:1 at t\textsubscript{2}, the surface began to oxidize, which is represented by an increase in the oxide peak intensity with a concurrent decrease in the metal CTR intensity in the HESXRD data, as shown in panel (e). Simultaneously, the reflected SOR intensity of the sample began to decrease, as shown in panel (d). Note that the reflected intensity of the different sides of the sample decreased at different times; in fact, the oxidation spot began to grow in the centre-right after which it spread to cover the full sample surface. The HESXRD signal change due to the oxidation, however, correlates only with a reflectivity decrease in the top right area of the sample. This can be explained by the fact that the X-ray beam is primarily probing that region. Hence, great care must be taken when correlating data representing a limited part of the sample area data with global condition changes, as the probed surface cannot be assumed to change homogeneously, which further emphasises the importance of monitoring the whole surface area. Based on previous studies, we assume that since the oxidation did not begin in the sample centre but was shifted to the right, the sample surface was exposed to a gradient of gas compositions and not, as would be ideal, a homogeneous gas mixture.\textsuperscript{16} Such a gradient is most probably caused by the flow geometry of the reactor, which causes the transport of CO\textsubscript{2} away from the surface to be partially limited by diffusion. Furthermore, we see that the amount of CO\textsubscript{2} produced did not increase substantially during the surface changes, which suggests the reaction to be in MTL. From the data, it is also evident that the CO\textsubscript{2} concentration close to the surface [blue box in Fig. 6(c) and blue trend in Fig. 4(c)] follows a different trend than the CO\textsubscript{2} concentration further away in the direction of the gas outlet (red). There, the PLIF signal instead corresponds well to the signal recorded by the MS, which is to be expected since the MS measures the entire averaged gas mixture leaving the reactor.

With the combination of HESXRD, PLIF, and SOR, it is also possible to accurately determine the time delays involved in the experiment. Since the PLIF signal is instantaneous, it allows for a precise determination of the time it takes for the gas to reach the reactor and HESXRD (b) finally picks up the change in the gas constituents. In this measurement, the O\textsubscript{2} flow is suddenly turned on to initiate the catalytic reaction as shown in (a). A few seconds after the gas change at t = 0, the gas has reached the reactor and the PLIF signal (c) increases as CO\textsubscript{2} production is initiated. Catalyst ignition into MTL is then reached after ~3 s (pink), 1.4 s later (blue), both SOR (d) and HESXRD (e) signals indicate oxide formation. After an additional 1.5 s (green), the MS (b) finally picks up the change in the gas constituents.

![FIG. 7. Simultaneously acquired data showing the timing of the signals. In this measurement, the O2 flow is suddenly turned on to initiate the catalytic reaction as shown in (a). A few seconds after the gas change at t = 0, the gas has reached the reactor and the PLIF signal (c) increases as CO2 production is initiated. Catalyst ignition into MTL is then reached after ~3 s (pink), 1.4 s later (blue), both SOR (d) and HESXRD (e) signals indicate oxide formation. After an additional 1.5 s (green), the MS (b) finally picks up the change in the gas constituents.](https://example.com/figure7.png)
reactor after a change in flow is set at the flow controller. The instantaneous nature of the PLIF and SOR signals also means the combination of techniques is useful for determining whether any oxide formation precedes or succeeds the advent of catalytic activity after a change in gas conditions.

To illustrate the aforementioned concept, we performed a second experiment in which we probed the responses of the various techniques to a change in gas conditions, as shown in Fig. 7. In this short measurement, the sample was first exposed to only CO (50 ml/min), and after a while, the O₂ flow was turned on (200 ml/min). Around one second later, an increase could be seen in the CO₂ PLIF signal as the gas reached the reactor and the catalytic reaction began. Once the PLIF signal no longer increased, which showed that the reaction is in MTL, it took another second for the surface reflectance to begin decreasing as shown by the SOR data, suggesting that surface roughening or oxide formation was taking place. Simultaneous to this decrease, the HESXRD peak corresponding to the metal surface also lost intensity, which confirms the results of a previous study, where PLIF and HESXRD were combined. Finally, after an additional 2 s, the change in gas composition induced by the catalytic reaction became visible in the MS signal.

CONCLUSION

We have successfully built and used a setup combining PLIF, MS, and SOR with HESXRD. We conclude that SOR indicated an inhomogeneous change in the surface during a catalytic reaction. Furthermore, upon transition into the active state, we see that HESXRD and SOR detect a change in surface structure first ~1.5 s after the reaction has entered the MTL. This either indicates that a presence of PdO is not required to drive the reaction into MTL, which is in accordance with a recent study, or that the amount of PdO required to drive the reaction into MTL is initially so small that it cannot be detected immediately. However, in that case, the PdO islands must be smaller than what can be resolved with SOR.

This work shows that the availability of a compact and comparatively inexpensive technique like SOR surveying the global sample surface is highly useful for determining if the behavior of the region probed by a technique such as HESXRD is representative of the whole sample surface. In combination with PLIF, the two techniques provide a complete picture of the macroscopic reaction conditions. We claim that such a complete picture is essential to ensure that any conclusions drawn from correlations between data of macroscopic and microscopic origin are sound. In particular, in operando experiments, the gas is often exchanged fast enough to not evenly diffuse throughout the reactor. This gives rise to gas gradients and surface structure gradients which must be accounted for, especially if the reaction ends up being in MTL. In short, the combination gives a clear overview of the reaction from a macroscopic point of view.

Moreover, SOR is a technique which similarly to PLIF and unlike MS provides delay-free probing of the sample. We have shown that this can be useful to resolve the, at times, sub-second delay between the catalyst ignition and the appearance of a surface oxide. Also, it is often useful to be able to determine the response time of the MS, which is easily done if PLIF data are available.

Another area where both high temporal resolution and the possibility to accurately correlate surface structure with gas composition are important is transient studies of catalytical effects, such as the study of self-sustained catalyst oscillations.

Altogether, we have developed and implemented a combination of SOR and PLIF with HESXRD, which provides detailed macroscopic information on both the sample surface and the surrounding gas, in addition to the atomic surface data provided by HESXRD. The result is a clearer overview of the reaction on a larger scale, which is important to draw sound conclusions in operando studies.

Furthermore, while SOR alone does not give any detailed information about the atomic scale surface composition or atomic structure, it should be possible to correlate the SOR signal with HESXRD data to obtain a calibration which ascribes the appearance of certain surface features to changes in the SOR intensity. Such a calibration could then be used to gain a rudimentary understanding of structural surface changes without the need of expensive synchrotron time. Finally, it may be possible to augment the discussed techniques with ellipsometry, a polarisation based optical technique which has been previously used to extract surface structure information relevant to operando catalysis studies.

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