Simultaneous Imaging of Gas Phase over and Surface Reflectance of a Pd(100) Single Crystal during CO Oxidation

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Supporting Information

ABSTRACT: A direct correlation between the reaction activity and the surface structure of a catalyst is generally needed to better understand the mechanisms behind the heterogeneous catalysis process. In this work, we employed planar laser-induced fluorescence (PLIF) to spatially resolve the CO2 distribution just above a Pd(100) surface, and simultaneously monitored the optical reflectance of the surface, during CO oxidation. We show that when the reaction is in the mass transfer limited regime, the inhomogeneity of the gas composition over the sample can lead to an inhomogeneity of the surface reflectance change arising from oxide formation and surface roughening. The combination of PLIF and surface reflectance also makes it possible to spatially resolve and simultaneously follow the dynamics of the gas phase and the surface on a subsecond time scale during self-sustained reaction oscillations of a Pd(100) surface, providing insights into the gas–surface interaction.

INTRODUCTION

For a fundamental understanding of the mechanisms behind heterogeneous catalysis, a direct correlation between the reaction activity and the surface structure of a catalyst is generally needed, which calls for the so-called operando studies of catalysis.1,2 The past decades have seen a growing number of spatially revolved techniques developed for gas and/or surface characterization of heterogeneous catalyzed reactions.3 CO oxidation catalyzed by Pd single crystals, being one of the most common model systems, has been studied for a long time.4,5 In recent years, a number of in situ surface-sensitive techniques have been developed to study the model system, particularly at increased pressures, for example, high-pressure scanning tunneling microscopy/atomic force microscopy (HPSTM/AFM),6,7 polarization-modulated infrared absorbance spectroscopy (PM-IRAS),8 ambient-pressure X-ray photoelectron spectroscopy (AP-XPS),9–12 and surface X-ray diffraction (SXRD).13–15 Studies have shown that a palladium oxide may be formed on a Pd(100) surface under CO oxidation, depending on the temperature, total pressure, and O2/CO ratio. Because of the oxide formation, an increase of the surface roughness has been found.15,16

Onderwaeter et al. have recently developed a reflectometer to study the optical reflectance change of a Pd(100) surface during CO oxidation.19 They have shown that the surface reflectance of the Pd(100) sample decreases during reaction and attribute this to the formation of a palladium oxide layer on the surface. In a more recent paper,20 with modeling and experimental results, Onderwaeter et al. conclude that the decrease of reflectance results both from the formation of a palladium oxide layer and an increase of the surface roughness and is dominated by the latter under CO oxidation reaction.

In their first paper,19 a decrease of the reflectance is observed to start from the center of the sample surface and spread radially across almost the entire sample, which is attributed to a temperature gradient over the sample due to the heating. In their experiment, the reaction was in the so-called mass transfer limited (MTL) regime, where the reaction rate is mass transfer limited by one of the reactants impinging onto the surface. It has been shown both theoretically and experimentally that when the reaction is in the MTL regime, the gas composition above the surface changes significantly, compared to that in the non-MTL regime.21–23 This could in turn change the surface structure since it is sensitive to the gas composition.

Here we have developed a surface reflectance setup similar to that reported in refs 19 and 20 and report successful oxidation and reduction experiments with the corresponding changes in surface reflectance of a Pd(100) surface. To move forward, we combine the surface reflectance with planar laser-induced fluorescence (PLIF), a gas detection technique that can spatially resolve gases close to a sample surface in real time. PLIF has been shown to be able to detect gases close to a catalyst sample with high spatial and temporal resolution.24–27 During CO oxidation, we find that the change of the surface reflectance is closely related to the CO2 concentration above the surface, which is highest at the center of the active model catalyst from where the surface reflectance change starts. Since

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a high CO₂ concentration corresponds to a high O₂/CO ratio and therefore a more oxidizing environment in the MTL regime, we conclude that the change of the gas phase due to the activity of the catalyst is responsible for the radial dynamics of the change of the surface reflectance.

In addition, we have used the combination of surface reflectance and PLIF to study self-sustained reaction oscillations of CO oxidation over the Pd(100) surface. Self-sustained reaction oscillations have been studied in catalytic reactions for many years.28,29 Previously, Hendriksen et al. have proposed that these reaction oscillations involve two main processes on the surface, roughening and smoothening.30,31 Recently, Onderwaater et al. from the same group have revisited the reaction oscillations and showed that there are fast and intermediate oscillations superimposed on the regular ones, adding a new aspect to the scenario.32 As surface reflectance is sensitive to the palladium oxide formation and surface roughness, and since PLIF and surface reflectance provide similarly high spatial and temporal resolutions, the catalytic activity and the surface morphology can be correlated during the oscillation process.

**METHODS**

**Sample and Reactor.** The sample under investigation is a Pd(100) single crystal with dimensions of 4 × 4 mm² and a thickness of 2 mm. The cleaning procedure of the sample can be found in ref 23. The sample was heated by a boracite heater, also used as the sample holder, the temperature of which was measured by a type-D thermocouple. The dependence of the surface reflectance on the sample temperature can be found in the Supporting Information.

A schematic picture of the setup is shown in Figure 1. A cubical chamber of volume 23 cm³ with four windows for optical access was used for PLIF and surface reflectance measurements. Gases were supplied to the reactor by individual mass flow controllers (Bronkhorst EL-FLOW), and the gas pressure in the reactor was regulated by a digital pressure controller (Bronkhorst EL-PRESS) at the gas outlet. The gas composition in the reactor was monitored by a quadruple mass spectrometer (Pfeiffer, QME 220), which was connected to the outlet of the reactor by a 70 cm long gas tube (D = 1/16 in.). An automatic leak valve was used to control the amount of gas from the outlet leaking into the mass spectrometer for analysis and to keep the pressure in the mass spectrometer stable at 5 × 10⁻⁶ mbar. A more complete description of the gas system can be found in ref 23. The mass spectrometry (MS) signal is calibrated by normalizing the MS CO signal to a known initial partial pressure, and the CO₂ signal is scaled to match the observed conversion of CO.

**PLIF.** The experimental setup and detection scheme for the CO₂ PLIF have been described in detail previously.33,34 The detection of CO₂ was realized by exciting the (00°0) → (10°1) combination band at ∼2.7 μm and collecting the fluorescence from the fundamental band at ∼4.3 μm. The fundamental 1064 nm laser beam with ∼350 mJ/pulse from an injection seeded single-mode Nd:YAG laser was used to pump a broad-band infrared optical parametric oscillator (IR OPO; GWU, versaScan-L 1064), generating a signal beam at ∼1.7 μm and an idler beam at ∼2.7 μm, with ∼8 and ∼7 mJ/pulse, respectively, both operating at 10 Hz. As shown in Figure 1, the idler beam was shaped into a thin laser sheet of ∼5 mm height by a spherical lens (f = +500 mm) and a cylindrical lens (f = +100 mm) and then sent through the reactor just above the catalyst. The full width at half-maximum (FWHM) of the idler beam is around ∼10 cm⁻¹, which is broad enough to cover a number of rovibrational lines in the (00°0) → (10°1) transition.

![Figure 1. Schematic illustration of the experimental setup for simultaneous measurements of PLIF and surface reflectance of a Pd(100) sample during CO oxidation.](image-url)
of CO₂. The CO₂ fluorescence was then imaged by a liquid nitrogen cooled IR camera (Santa Barbara Focal Plane, SBF LP134). An interference filter inside the camera, centered at 4.26 μm, was used to suppress the strong thermal background. The exposure time was set to 30 μs to minimize the background and favor the fluorescence signal. Quantification of the detected PLIF signal is achieved by calibration measurements with known CO₂ partial pressures at corresponding temperatures and total chamber pressures to real measurements.

Surface Reflectance. As illustrated in Figure 1, light from a light-emitting diode (LED; Thorlabs M62SL3) is first collimated and spatially filtered by two spherical lenses (f = +100 mm) and a small pinhole (diameter 100 μm) and then sent to a beam splitter above the reactor. The splitter reflects 50% of the collimated beam onto the sample and transmits 50% of the beam reflected by the sample toward a complementary metal oxide semiconductor (CMOS) camera (Andor Zyla). Another pair of spherical lenses (f = +200 mm) and an aperture were used for imaging the sample surface with a bright-field 4f configuration. The camera can be operated at a repetition rate up to 200 Hz, limited by the transfer rate of the data. In this study, the repetition rates were chosen according to the nature of the reaction processes, i.e., a lower rate for the oxidation process and a higher rate for the reduction process.

### RESULTS AND DISCUSSION

**Oxidation and Reduction.** We have performed an oxidation and reduction experiment similar to that by Onderwaater et al.20 Our results are qualitatively very similar, and we use the results for the more complex CO oxidation experiments described below. The oxidation experiment was performed using a sample temperature of 320 °C and a total pressure of 125 mbar with flows of 4 mL/min of O₂ and 36 mL/min of Ar (corresponding to initial partial pressures of 12.5 mbar of O₂ and 112.5 mbar of Ar). The reduction experiment was initiated after the oxidation experiment by switching the gas flow to 4 mL/min of CO and 36 mL/min of Ar (corresponding to initial partial pressures of 12.5 mbar of CO and 112.5 mbar of Ar). Hereinafter, the reflectance change ΔR is defined as \((I − I₂)/I₀\), where \(I₀\) is the reflected intensity at the start of the experiment and \(I\) the subsequently measured intensity. Prior to the oxidation experiment, the sample was exposed to a pure CO environment to ensure that the surface was oxide free. The results from the oxidation and reduction experiments are shown in Figure 2. Figure 2a shows how the reflectance changes at \(t₁ = 10\ s\), \(t₂ = 48\ s\), and \(t₃ = 120\ s\) during the oxidation process (\(t = 0\) defined as when O₂ was introduced). The change of the surface reflectance as a function of the oxidation time from three different regions (marked by white rectangles) is shown in Figure 2b. Between \(t₁ = 10\ s\) and \(t₂ = 48\ s\), the reflectance decreases at a greater speed, while, after \(t₂ = 48\ s\), the decrease of the reflectance is much slower. Our results agree very well with those of Onderwaater et al.20 According to their model, the decreased reflectance can be attributed to a combination of the formation of a surface oxide and an increased surface roughness. They conclude that an increase of the oxide thickness is mainly responsible for the faster decrease of reflectance and self-terminated after a certain thickness, followed by a roughening process which is responsible for the slower decrease of reflectance. As can be seen from Figure 2b, no significant difference in the surface reflectance, at the different regions of the surface, can be observed during the oxidation in pure oxygen.

Turning to the reduction process shown in Figure 2c,d, the surface reflectance increases rapidly after the introduction of CO (indicated by the arrow) and almost restores its original value after \(t₃ = 30\ s\). Interestingly, we can also see the trace of switching the flow in the middle image in Figure 2c i.e., the gas flows from the bottom right corner to the top left corner of the sample surface. See also Movies M1 and M2 showing the oxidation and reduction measurements, respectively, in the Supporting Information.

**CO Oxidation and Gas-Phase Dependence.** As mentioned above, the surface chemical composition is sensitive to the gas composition close to the surface, and any spatial inhomogeneity of the gas composition could lead to an inhomogeneity of the surface. We have shown in previous studies that the CO and CO₂ distributions across the Pd surface vary significantly in the MTL reaction region.20 We therefore

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**Figure 2.** Surface reflectance changes of the sample during the oxidation and reduction processes in pure O₂ and CO, respectively. (a) Snapshots of the surface reflectance at \(t₁ = 10\ s\), \(t₂ = 48\ s\), and \(t₃ = 120\ s\) during oxidation of the surface. (b) Change of the surface reflectance at different regions of the surface indicated by the white squares in (a). (c) Snapshots of the surface reflectance at \(t₁ = 7\ s\), \(t₂ = 12\ s\), and \(t₃ = 30\ s\) during reduction of the surface. (d) Change of the surface reflectance at different regions of the surface indicated by the white rectangles in (c). The arrow in (d) indicates when the gases are switched from pure O₂ to pure CO.
investigated the oxidation of the Pd(100) surface under the reaction conditions, particularly in the MTL regime, by measuring the gas composition close to the surface using PLIF and the surface reflectance simultaneously. The results are shown in Figure 3. In the experiment, the sample was kept at 320 °C and 125 mbar, with flows of 30 mL/min of O2, 2 mL/min of CO, and 18 mL/min of Ar. This corresponds to initial partial pressures of 75 mbar of O2, 5 mbar of CO, and 45 mbar of Ar, with a 15:1 O2/CO ratio, meaning that the reaction is under the O2-rich condition. A mass spectrometer was used to monitor the global gas concentration and to ensure that the reaction was in the MTL regime. Figure 3a, b shows how the surface reflectance changes at t1 = 50 s, t2 = 400 s, and t3 = 800 s during the oxidation process (t = 0 is defined as the time at which the gases were switched from pure Ar to CO and O2 mixtures). As can be clearly seen, the reflectance change on the sample surface is not homogeneous. Instead, the reflectance at the center of the sample decreases at a much greater speed, compared to that at the corners of the sample. This is emphasized by the trends in Figure 3b, which shows how the reflectivity changes in each of the three squares in Figure 3a. The corresponding CO2 gas distribution is shown in Figure 3c by a 10-shot averaged PLIF image recorded at t = 50 s, visualizing the CO2 distribution above the sample, which does not change significantly during the reaction process. A CO2 boundary layer over the surface can clearly be seen. A normalized (to the initial CO partial pressure, 5 mbar) horizontal CO2 profile at 0.5 mm above the sample is plotted in Figure 3d. Both parts c and d of Figure 3 clearly show that the CO2 distribution above the sample is not homogeneous, but decreases radially from the center of the surface. This also means that the O2/CO ratio is the highest at the center of the surface and decreases radially toward the edges. Combining the results from surface reflectance and gas-phase measurements, we attribute the inhomogeneous development of the surface reflectance to the inhomogeneity of the gas composition above the surface. According to ref 20, the decrease of reflectance is a result of both surface oxide formation and increased surface roughness, and is dominated by the latter. The higher O2/CO ratio at the center of the sample results in a faster palladium oxide formation and a quicker roughening compared to that at the corners of the sample, explaining the radial dynamic development of the surface reflectance signal from the surface. A small difference in the reflectance change between the two edges of the sample (top left and bottom right), as can be seen in Figure 3a, is due to the gas flow, which results in slightly different gas compositions over the two edges.

It is worth noting that the spots present in Figure 3a are not artifacts from the imaging system, but instead real objects present on the surface. They are not present from the start of the oxidation/roughening process during the reaction, but gradually appear as a decrease of the surface reflectance during the process at a much greater speed than the rest of the surface. Interestingly, they become significantly more pronounced under the reaction conditions, compared to the pure O2 condition. We speculate that these spots are areas with a high density of steps on the surface, which become oxidized/rougher more easily under the reaction conditions, and are difficult to reduce completely in a pure CO environment, due to the formation of a highly stable PdO surface such as the oxygen-terminated PdO(100).35

Surprisingly, as mentioned above, the CO2 PLIF profile close to the surface does not change considerably during the inhomogeneous oxidation/roughening process of the surface (see the Supporting Information). As the surface clearly simultaneously consists of a number of different oxygen-rich phases during the oxidation/roughening process, it is difficult to isolate a single phase responsible for the high activity and the nonchanging CO2 distribution detected by PLIF. It is possible that only small areas of the surface with, for instance, chemisorbed oxygen are able to maintain the high activity.36 It may also be that specific orientations of the PdO, such as the PdO(101) with coordinately oxygen unsaturated sites, is responsible for the high activity.18

To further demonstrate the sensitivity of the surface structure to the gas composition, we performed the oxidation and reduction experiments at different O2/CO ratios. The oxidation experiment was performed at a 4:1 O2/CO ratio, with flows of 4 mL/min of O2, 1 mL/min of CO, and 45 mL/min of Ar (corresponding to initial partial pressures of 10 mbar of O2, 2.5 mbar of CO, and 112.5 mbar of Ar). The reduction experiment was performed at a 1:4 O2/CO ratio, with flows of

Figure 3. Surface reflectance changes of the sample and CO2 distribution above the surface during CO oxidation under O2-rich conditions (15:1 O2/CO ratio). (a) Snapshots of the surface reflectance change at t1 = 50 s, t2 = 400 s, and t3 = 800 s. (b) Change of the surface reflectance at different regions of the surface indicated by the white rectangles in (a). (c) A 10-shot averaged PLIF image showing the CO2 distribution over the sample surface, acquired over 1 s. (d) Normalized horizontal CO2 profile 0.5 mm above the sample. The dashed lines show the positions of the center and the edges of the sample.
of O2, 4 mL/min of CO, and 45 mL/min of Ar (corresponding to initial partial pressures of 2.5 mbar of O2, 10 mbar of CO, and 112.5 mbar of Ar). In both experiments, the sample was kept at 320 °C and 125 mbar and in the highly active phase. The results are summarized in Figure 4. Similar to Figure 3a, Figure 4a shows the inhomogeneous reflectance change on the surface during the oxidation process, but with a difference in shape and size, comparing snapshots at t3 = 800 s. Comparing the trends between Figures 3b and 4b, it is clear that the reflectance decreases at similar rates at the center of the surface, while at very different rates at the edges of the surface, i.e., much slower in Figure 4b. When the gas is switched from the O2-rich to the CO-rich condition, the palladium oxide is reduced. As shown in Figure 4c,d, during the reduction process, the surface reflectance increases and returns almost to the initial state after 60 s. See also Movies M3 and M4 in the Supporting Information.

To explain the difference in reflectance change between the two oxidation processes in Figures 3a and 4a, we compare the gas composition just above the sample surface between the two cases, as shown in Figure 5. The horizontal CO2 partial pressure profile (blue) in Figure 5a,b is obtained by integrating the CO2 PLIF signal 0.5 mm above the sample surface, similar to Figure 3b. Given the known initial O2/CO ratio in the gas mixture, the corresponding CO and O2 profiles just above the surface are calculated, assuming that two CO2 molecules correspond to two CO2 molecules and one O2 molecule, as shown in Figure 5a,b. With the calculated CO and O2 profiles, the O2/CO ratio profile just above the active catalyst can also be calculated, as plotted in Figure 5c. The cross sections of the reflectance image acquired at t = 800 s during the oxidation process for the two cases have been plotted in Figure 5d to show the correlation with the corresponding gas composition (O2/CO ratio). In each case, the gradients of the gas composition and the reflectance change are much smaller in the higher O2/CO ratio case than in the lower O2/CO ratio case, resulting in an overall larger decrease in the reflectance over the entire surface. As a result, we can see a more spread out reflectance decrease over the surface in Figure 3 than in Figure 4. However, the dependence of the reflectance change on the O2/CO ratio does not seem to be linear. Therefore, the large difference in the O2/CO ratio between the two cases does not result in a large difference in the reflectance change at the center of the surface, but a much more obvious difference at the edges.

**Self-Sustained Reaction Oscillations.** It has been proposed by Hendriksen et al. that self-sustained reaction oscillations above a Pd(100) during CO oxidation involve two main processes on the surface, roughening and smoothening.33 We have demonstrated above, using the same approach as Onderwaater,19,20 how the change of the surface reflectance can be related to the oxidation (roughening) and reduction (smoothening) processes, which in turn are affected by the gas composition close to the surface depending on the initial O2/CO ratios and the activity of the catalyst. Here, we combine the surface reflectance with PLIF to correlate the surface roughness/oxidation to the gas-phase composition close to the surface during self-sustained reaction oscillations. The results are summarized in Figure 6. The experiment was performed by supplying a constant heating current, which heated the sample to around 240 °C. The total chamber pressure was kept at 150 mbar with flows of 4 mL/min of CO, 80 mL/min of O2, and 16 mL/min of Ar (corresponding to initial partial pressures of 6 mbar of CO, 120 mbar of O2, and 24 mbar of Ar), resulting in a 20:1 O2/CO ratio. Both the PLIF trend in Figure 6a and the MS trends in Figure 6b show an alternating change of the gas phase, indicating that the sample is undergoing self-sustained reaction oscillations. Figure 6c shows the alternating changes in the surface reflectance, which correlate perfectly to the observed gas-phase changes. Due to the exothermic nature of the reaction, the sample temperature is also oscillating, as can be seen in Figure 6d. See also the Supporting Information.

It can be seen from the CO2 PLIF image in Figure 6e that a very small amount of CO2 is detected in the case of an almost inactive catalyst at time t1. As a consequence, a large amount of CO is present close to and on the surface, and the reflectance image in Figure 6f shows that the surface is smooth. Using an

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**Figure 4.** Surface reflectance changes of the sample during the oxidation and reduction process at 4:1 and 1:4 O2/CO ratios, respectively. (a) Snapshots of the surface reflectance changes during oxidation at t1 = 100 s, t2 = 500 s, and t3 = 800 s. (b) Change of the surface reflectance at different regions of the surface, indicated by the white rectangles in (a). (c) Snapshots of the surface reflectance during reduction at t1 = 10 s, t2 = 15 s, and t3 = 40 s. (d) Change of the surface reflectance at different regions of the surface, indicated by the white rectangles in (c). The arrow in (d) indicates when the gases are switched to reduction conditions.
image recorded from a reduced Pd sample as a reference, the reflectance change is zero over the entire surface. We therefore conclude that the surface is metallic, smooth, and nearly saturated with CO at t₁. As the surface becomes active, as evidenced by the PLIF trace in Figure 6a, there is a sudden decrease of the surface reflectance trace as shown in Figure 6c. We attribute this sudden decrease of the reflectance to the formation of a thin palladium oxide layer, which is consistent with the observation by Onderwaater et al.,20 supported by STM and SXRD experiments.16,17 When the reaction reaches the MTL regime, there is a large amount of CO₂ produced close to the surface, as evidenced by the PLIF images in Figure 6f,g. This results in an increase of the O₂/CO ratio, and as described above, the sample becomes increasingly oxidized/roughened in the MTL regime. As can be seen from the surface reflectance trace from the center of the sample (red) in Figure 6c, there is a decreasing trend from t₁ to t₂, demonstrating that the surface roughness/oxidation increases when the reaction is in the MTL regime. However, as was also described above, the roughening/oxidation process is not homogeneous over the entire surface, as can be seen from the images in Figure 6i,j. The observation further confirms that the gas-phase inhomogeneity results in a surface oxide/roughness inhomogeneity. As the entire sample becomes increasingly rough and oxidized, at a critical point, the surface suddenly becomes inactive, supporting the previous observations by Hendriksen et al.31 At this point, the amount of CO is increasing, reducing and smoothening the surface, and the process repeats itself. See also Movie M5 in the Supporting Information.

It is worth noting that the changes of the surface reflectance are very small (around 0.4%) in this experiment compared to the experiments shown above (about 30%). This is because the sample was heated to a much lower temperature (around 240 °C) in the oscillation experiment; thus, it is more difficult for the surface to get oxidized/roughened. To enhance the signal-to-noise ratio, 40 images acquired over 20 s are therefore averaged to obtain Figure 6h–j. It is also interesting to see that the center of the surface reflectance change is slightly shifted from the center of the sample. This is due to the flow of the gas, as illustrated by the top view CO₂ PLIF image in Figure 6k, which was recorded from a separate measurement but with the same sample environment.

Figure 5. Measured CO₂ and calculated CO and O₂ partial pressure profiles (smoothed) at 0.5 mm above the sample surface for (a) the 15:1 O₂/CO ratio case and for (b) the 4:1 O₂/CO ratio case. (c) Comparison of calculated O₂/CO ratio profiles above the sample surface between the two cases. (d) Correlation between the gas composition and the reflectance change over the sample surface for the two cases, where a higher O₂/CO ratio yields a lower reflectance over the surface for the same condition.
SUMMARY AND OUTLOOK

In this work, we have combined measurements of the surface reflectance and PLIF to investigate the Pd(100) surface during CO oxidation. When the reaction is in the MTL regime, the surface exhibits an inhomogeneous surface reflectance change and the gas distribution close to the surface is also inhomogeneous. We attribute the inhomogeneity in the surface reflectance to the inhomogeneity in the gas phase and interpret that, with a higher O2/CO ratio at the center of the sample, the surface oxide grows faster and as a consequence is roughened by the reaction more quickly, compared to that at the edges of the sample. Such an inhomogeneity of the surface and the gas phase also implies that care should be taken when we are comparing surfaces under the reaction conditions using traditional surface-sensitive techniques, where either a small surface area is probed as in AP-XPS and STM or a large area is probed as in SXRD. From our previous work, the gas distribution can strongly depend on the gas flows, total pressures, and even reactor geometries. Therefore, it would be interesting to investigate how the surface reflectance changes with these parameters. In the oscillation experiment, the simultaneously collected information on the gas phase and the surface reflectance clearly illustrates the roughening and smoothening processes involved in the oscillations. Both the PLIF and surface reflectance techniques provide high spatial (on a macroscopic scale) and temporal resolutions, making it possible to directly correlate the gas phase and surface both spatially and temporally. As the surface reflectance is a relatively simple technique, it would in principle not be difficult to integrate it with diffraction-based techniques, such as SXRD for evaluation of its sensitivity to surface oxides and surface roughness.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b08108.

Temperature dependence of the surface reflectance and PLIF and MS trends during the oxidation process (PDF)
Movie M1 showing the surface reflectance change during oxidation in pure O2 (AVI)
Movie M2 showing the surface reflectance change during reduction in pure CO (AVI)
Movie M3 showing the surface reflectance change during oxidation under O2-rich conditions (AVI)
Movie M4 showing the surface reflectance change during reduction under CO-rich reaction conditions (AVI)
Movie M5 showing the simultaneous measurement of PLIF and surface reflectance during oscillations (AVI)
Catalytic Reaction Conditions. Spectroscopy and Simultaneous Activity Measurements under 77 K.

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