Topical Review

2D and 3D imaging of the gas phase close to an operating model catalyst by planar laser induced fluorescence

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Abstract

In recent years, efforts have been made in catalysis related surface science studies to explore the possibilities to perform experiments at conditions closer to those of a technical catalyst, in particular at increased pressures. Techniques such as high pressure scanning tunneling/atomic force microscopy (HPSTM/AFM), near ambient pressure x-ray photoemission spectroscopy (NAPXPS), surface x-ray diffraction (SXRD) and polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) at semi-realistic conditions have been used to study the surface structure of model catalysts under reaction conditions, combined with simultaneous mass spectrometry (MS). These studies have provided an increased understanding of the surface dynamics and the structure of the active phase of surfaces and nano particles as a reaction occurs, providing novel information on the structure/activity relationship. However, the surface structure detected during the reaction is sensitive to the composition of the gas phase close to the catalyst surface. Therefore, the catalytic activity of the sample itself will act as a gas-source or gas-sink, and will affect the surface structure, which in turn may complicate the assignment of the active phase. For this reason, we have applied planar laser induced fluorescence (PLIF) to the gas phase in the vicinity of an active model catalysts. Our measurements demonstrate that the gas composition differs significantly close to the catalyst and at the position of the MS, which indeed should have a profound effect on the surface structure. However, PLIF applied to catalytic reactions presents several beneficial properties in addition to investigate the effect of the catalyst on the effective gas composition close to the model catalyst. The high spatial and temporal resolution of PLIF provides a unique tool to visualize the on-set of catalytic reactions and to compare different model catalysts in the same reactive environment. The technique can be applied to a large number of molecules thanks to the technical development of lasers and detectors over the last decades, and is a complementary and visual alternative to traditional MS to be used in environments difficult to asses with MS. In this article we will review general considerations when performing PLIF experiments, our experimental set-up for PLIF and discuss relevant examples of PLIF applied to catalysis.
Keywords: PLIF, catalysis, CO oxidation

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(Some figures may appear in colour only in the online journal)

1. Introduction

Heterogeneous catalysis is one of the major motivations for the interest in gas-surface interaction with metal surfaces. As applied catalysis is based on a trial and error approach due to the complexity of a technical catalyst, model systems such as low-index single crystal surfaces under ultra high vacuum (UHV) conditions and careful control of the reactant gas abundance on the surface has promoted the understanding of adsorbate-adsorbate and adsorbate-substrate interactions [1, 2]. For instance, CO oxidation on transition metal surfaces, which is an important model system for oxidation catalysis [3], has been extensively studied for many years, but despite the apparent simplicity of the reaction, the details of the reaction pathway is still unclear. While a number of investigations suggests that a surface with chemisorbed oxygen is the most active phase [4, 5], other studies have proposed that the oxidized form of the surface is the most active phase under the pressure and temperature conditions appropriate for real-world catalytic oxidation reactions [6–8] or at the border between a thin oxide and the metal [9]. The details are still under discussion [10–12].

Because of these issues and the need for fundamental knowledge, there is a rapid technical development expanding the literature based on in situ techniques under realistic conditions during catalytic reactions [13–30] as well as novel theoretical approaches [31–35] using model catalysts and semi-realistic conditions.

At the same time, there is an increasing awareness that the details of the reactor geometry is essential for the resulting activity and the resulting structure at the surface. There have been a number of different reactors used for different in situ techniques, and the most common setup is a stainless steel vessel that may reach high vacuum (HV $10^{-7}$–$10^{-9}$ mbar) or even ultra high vacuum (UHV $10^{-10}$ mbar) and operated in a flow or batch mode. In general, it is in principle easy to simulate the gas flows through a vessel using finite element approaches, however the situation becomes significantly more complicated as a catalyst becomes active inside the vacuum vessel, changing the gas composition and flows significantly. There has been some pioneering attempts to simulate this situation [36, 37]. In some cases, the experimental setup is further complicated by the introduction of a differentially pumped electron analyzer close to the sample, as in the NAPXPS set-up.

To this end, we have use planar laser induce fluorescence (PLIF) to investigate the 2D gas distribution with the focus on CO$_2$ and CO in the CO oxidation reaction to investigate the actual gas composition close to the model catalyst surface in a semi-realistic environment as the model catalyst becomes active [19, 36, 38–41]. PLIF is a commonly used technique in combustion related research to investigate the gas composition during combustion such as in a flame and a number of other research fields [42, 43], but has only been limited used in catalysis related research [44–51], and in particular very little work has been done on CO, CO$_2$ and small hydrocarbons. The reason for the limited number of experiments is that these molecules have no or not easily accessible transitions in the UV-visible spectral range, making both excitations and detection more difficult, and has only become feasible in the last decade. In the present review, we explain the experimental facilities needed to perform PLIF and the physical processes involved in the measurements. Our measurements show that for CO oxidation the gas phase composition of CO and CO$_2$ is significantly different close to the active model catalyst surface compared to the composition measured by MS far away from the active catalyst. We show that the gas distribution can also be imaged in 3D.

Furthermore, the spatial resolution of PLIF provides an excellent opportunity to compare different catalysts in the same reactant environment. We present measurements with high spatial and temporal resolution from a ‘curved’ Pd single crystal, revealing differences in the activation temperatures at different parts of the crystal. Also differences in the activation temperature between two different catalysts in the same reactor is presented clearly showing differences between the activation of the two catalysts with different materials composition. Further, we present an experimental solution to how gaseous cross-talk between catalysts can be avoided by placing catalyst in tubes and monitoring the exhaust inside a vacuum vessel, indicating how several catalysts may be tested simultaneously in the same environment.

In addition, the high time resolution of PLIF directly demonstrate the activation or light-off of a catalyst as the temperature is ramped to the ignition temperature. Therefore, the PLIF technique is an excellent tool to visualize gas phase changes during catalysis, also for fundamental studies. To demonstrate this, we present the appearance of the 2D CO$_2$ distribution during self-sustained reaction oscillations over a Pd(100) model catalyst, and propose a model for the changes of the catalyst surface during these oscillations.

As the reactor geometry is important for the gas distribution in the reactor, the technique can also be used to characterize the gas-flow properties in reactors of different designs, as illustrated by the visualization of the 2D CO$_2$ distribution in a stagnation flow reactor as well as in a reactor designed to mimic a common NAPXPS setup.

We also show that the technique can be extended to other reactions and gases relevant for catalysis such as CO and NH$_3$.
2. PLIF

In laser-induced fluorescence (LIF) a laser beam excites the molecule of interest, the excited molecule relaxes by emitting a photon, i.e. fluoresces, and the fluorescence light is then detected. The process is highly selective, meaning that the technique is species specific, targeting a specific molecule. It is also a relatively strong process, allowing for short gate times (ns-µs depending on wavelength region and molecule) and high repetition rates (limited by the laser pulse energy and molecule) but also means that it can be extended to 2D by forming the laser beam into a sheet of light and by detecting the ensuing fluorescence with a 2D detector. When LIF is implemented in a 2D fashion it is often referred to planar laser-induced fluorescence (PLIF), and is then highly spatially resolved along all three dimensions (down to 50 µm), i.e. it yields a cross section of the sought after species. The expression for the LIF signal \( S_{\text{LIF}} \) in the linear excitation regime is given by

\[
S_{\text{LIF}} = \eta \cdot E \cdot g \cdot f(T) \cdot \chi_{\text{ab}} \cdot \frac{P}{k_B T} \cdot \phi,
\]

where \( \eta \) is the experimental collection efficiency, \( E \) is the laser energy, \( g \) is a function that describes the spectral overlap between the laser and the absorption spectral lineshape, \( f(T) \) is the Boltzmann fraction, \( \chi_{\text{ab}} \) is the absorption cross section of the detected species, \( \chi_{\text{ab}} \) is the molefraction of the detected species that together with \( P/k_B T \) gives the number density of the same species and \( \phi \) is the fluorescence quantum yield. The fluorescence quantum yield represents the excited-state emission rates and the collisional interaction and energy transfer between the CO2 and the carrier gas. The expression shows that the detected LIF signal is linearly dependent on the gas density and the fraction of molecules in the state from which the laser excites the molecule, \( f(T) \). This implies that if the signal is carefully analyzed it can be calibrated into partial pressures. The signal is strongly dependent on the number density of molecules which is also taken into account in the analysis process. The number density of molecules \( N \), can be described by

\[
N = \frac{P \cdot V}{(k_B T)}
\]

where \( P \) is the total pressure, \( V \) is the volume, \( k_B \) the Boltzmann coefficient and \( T \) the temperature of the gas. This shows that the number density of molecules and thus the PLIF signal will decrease with the temperature. This is illustrated in figure 1. Figure 1(a) shows how the CO2 PLIF signal 0.5 mm above an active sample changes as the temperature of the sample is ramped up. After the activation of the catalyst identified by a sudden ‘jump’ in the signal, the signal is expected to be constant but a significant decrease of the signal with the temperature is observed. The temperature dependency of the PLIF signal is illustrated in figure 1(b). The PLIF signal plotted is detected at a constant CO2 molefraction and the decrease of the signal is only due to the increase in temperature, affecting both the number density and the population of the probed energy level, which follows the Boltzmann distribution. This temperature dependency is used to analyze the raw PLIF signal shown in figure 1(a) and the resulting corrected PLIF signal is shown in figure 1(c). In the present work we detect CO2, CO and NH3 during catalytic reactions, either as a reactant or a product. Each molecule requires a different experimental set-up due to differences in excitation energies and detection wavelengths. In table 1 we have summarized some of the parameters which needs to be taken into account for each molecule.

3. CO2

In CO oxidation the product is CO2. The CO2 molecule lacks accessible transitions in the UV/visible spectral range, but can be reached through ro-vibrational transitions in the mid-infrared. There are several transitions that can be used in the mid-infrared, e.g. the overtone and combination band at around 2.0 µm (12° → 00°, 0), the combination band at 2.7 µm (00° → (10°) [52] and the fundamental band at around 4.3 µm [53] (figure 2(a)). The overtone and combination band at around 2.0 µm is a weak transition compared to 2.7 and 4.3 µm, limiting the sensitivity. For the fundamental band at 4.3 µm, which was recently demonstrated, the high cross section becomes tricky in larger setups, since the laser beam is strongly attenuated in the ambient air. Owing to these reasons, the combination band at 2.7 µm was chosen in this study, it is stronger than the 2.0 µm band (around 45 times) but still weak enough so as not attenuate the laser radiation too much along the beam path. Throughout our experiments, a laser system operated at 10 Hz generated the IR-laser light by difference-frequency mixing the output from a dye laser (PRSC-D-18, Sirah) at 763 nm with the fundamental frequency from a Nd:YAG laser (PRO 290-10, Spectra Physics) at 1064 nm in a LiNbO3 crystal. The resulting 2.7 µm laser beam had a pulse energy of 4 mJ, a pulse length of 5 ns and an estimated linewidth of 0.025 cm⁻¹. The 2.7 µm laser beam was formed into a laser sheet using sheet forming optics and was used to excite a ro-vibrational transition of the (00° → (10°) of CO2. The CO2 fluorescence was detected by a LN2 cooled, InSb focal plane array (Santa Barbara Focal Plane, SBF-134). Calibration measurements under similar conditions (pressure, flow, temperature and CO2 partial pressures) as in the CO oxidation experiments but at known CO2 partial pressures were carried out for converting the signal to partial pressures, a calibration curve at 150 mbar and room temperature is shown in figure 2(b). Due to mostly re-absorption of the CO2 fluorescence signal the curve bends downwards at around 10mbar CO2 partial pressure, however up to around 4 mbar the curve is close to linear. The CO partial pressure of the incoming gas is therefore kept well below 10 mbar when the PLIF signal should be calibrated to partial pressures. The bending of the calibration curve may result in higher noise level at higher CO2 partial pressures. The calibration curve will change with both total pressure and temperature, however at 150 mbar and room temperature the detection limit of CO2 with the present set-up is about 0.04 mbar, at the same pressure and at 300 °C the detection limit changes to about 0.1 mbar. The calibration...
measurement allows for good estimation of the CO₂ partial pressure produced by the active catalyst but quenching as well as slight re-absorption of the fluorescence in the CO₂ gas between the interrogated region and the camera are not fully compensated for. This does not affect the signal significantly in the present measurements, since relatively low total pressures are used ($<150 \text{ mbar}$). The CO₂ fluorescence signal at $4.3 \mu \text{m}$ is absorbed by the air between the cell and camera and to increase the signal, the path of the fluorescence light can be purged with a non adsorbing gas such as N₂.

3.1. Imaging CO₂

The CO₂ fluorescence, originating from the fundamental band at $4.26 \mu \text{m}$, was imaged perpendicular to the laser sheet onto a 2D focal plane array (FPA) (SBF LP134, Santa Barbara Focal Plane) through an interference filter centered around $4.26 \mu \text{m}$ to discriminate background. To further discriminate the thermal background, an inherent difficulty when working in the mid-infrared regime, the FPA was triggered at 20 Hz, thus taking an extra image between every laser shot, making subtraction of the thermal background possible. The integration for each frame was 15 $\mu \text{s}$ and chosen for efficient collection of the CO₂ fluorescence signal, which is more than 100 $\mu \text{s}$ long at these pressures, while avoiding detector saturation by the thermal background. The temperature of the gas molecules are gradually decreasing with the distance from the sample and an image of the laser sheet at several temperatures was taken. This allows for compensation of the temperature fluctuations in the CO₂ images as well as for steady inhomogeneities in the laser sheet. The CO₂ fluorescence images, with a spatial resolution of 70 $\mu \text{m}$ along all three dimensions (limited by the thickness of the laser sheet), visualized the distribution of CO₂ in the reaction chamber. The experimental set-up is illustrated in figure 3(a). The laser beam was split up and about 10% of the light was led through a reference cell with a known CO₂ concentration. The fluorescence from the reference cell was then detected to compensate for shot-to-shot fluctuations and wavelength jitter. The global gas composition was measured with a mass spectrometer connected via a 70 cm long tube (diameter of $1/8''$) at the outlet of the reactor and the temperature with a type D thermocouple connected to the sample holder.

3.2. Single crystals

Real catalysis is a complicated process, and to gain fundamental information on catalytic processes on the atomic scale to understand surface mediated reaction mechanisms, model systems are used. Single crystal surfaces are the most common model catalysts in surface science since they mimic the extended facets on a catalyst nanoparticle. It is well known that the surface gas interaction is essential for the surface atomic structure on the active catalyst surface. In contrast, the gas phase close to the surface of an active catalyst at semirealistic conditions has not been studied in detail, and should reveal information about the actual gas composition interacting with the surface in the presence of the active catalyst. In figures 4(a) and (b) the CO₂ production over a Pd(1 0 0) single crystal is visualized using PLIF, in a gas mixture of 6 mbar CO, 6 mbar O₂ and 138 mbar Ar. At the start of the experiment, the temperature of the crystal is too low ($<100 \degree \text{C}$) and the catalyst not active, and as a result no CO₂ signal is detected with PLIF or with MS. As the temperature is increased (figure 4(d)) a small increase in the CO₂ production is detected with PLIF (figure 4(c)) and MS (figure 4(d)), indicating a CO poisoned surface [20, 54], inhibiting the oxygen molecule to dissociate on the surface and enable an efficient reaction. The small increase of the CO₂ signal can be explained by a statistical increase of the CO desorption as the temperature is increasing, leaving free surface areas where O₂ can adsorb dissociatively and react. However at a temperature of approximately 270 °C

![Figure 1](image-url)  
Figure 1. (a) The raw PLIF signal detected over a catalyst is plotted as a function of the catalyst temperature. (b) The PLIF signal decreases with $1/T$. (c) The raw data shown in (a) corrected for the decreasing number of gas molecules due to the temperature increase.

| Molecule | Spatial resolution ($\mu \text{m}$) | Temporal resolution (Hz) | Integration time ($\mu \text{s}$) | Excitation wavelength (nm) | Detection Wavelength (nm) |
|----------|-------------------------------|-------------------------|-------------------------------|---------------------------|--------------------------|
| CO₂      | 70                            | 10                      | 20                            | 2.7 4.26                    |
| CO       | 300                           | 10                      | 30                            | 230.1 450–660              |
| NH₃      | 100                           | 10                      | 100                           | 305 565                    |
the CO₂ production increases tremendously, demonstrating that light-off has occurred. This means that the CO coverage is low enough, and the O coverage high enough, for the rate of CO removal (through desorption and reaction) to be higher than the adsorption rate. The result is a sudden lifting of the CO₂ poisoning and an activation of the catalyst. After the light-off, the sample is highly active and a saturation of the CO₂ signal is reached. The images of the CO₂ in figures 4(a) and (b) show a cloud of CO₂ close to the surface with a gradually decreasing CO₂ concentration with the distance from the surface. The CO₂ cloud can be observed at temperatures below light-off, but becomes significantly more visible after light-off. After light-off, the temperature is increased further but the CO₂ production is unchanged indicating that the reaction has reached a mass transfer limited (MTL) regime. In this regime the process is limited by the CO diffusion to the surface and not by the intrinsic activity of the sample. The detected cloud of CO₂ is often referred to as the boundary layer of CO₂ that hinders the CO molecules to reach the surface [36, 37]. At the conditions applied in the experiment shown in figure 4 the CO₂ concentration is significantly higher in a sphere with the radius of approximately 5 mm around the surface. This implies that the gas composition is significantly different within this sphere as compared to the gas inlet or outlet where the partial pressures of the gases present in the chamber is measured. The difference becomes apparent by comparing the partial pressure of CO₂ measured by PLIF just above the surface (black rectangle in figure 4(a)) and the MS sampling the gas at the outlet of the reactor. The result is shown in figures 4(c) and (d) where a maximum of 4 mbar CO₂ is detected by PLIF (figure
4(c)) and the corresponding number measured with MS is 1.5 mbar (figure 4(d)). The PLIF results highlight the necessity of studying the gas phase composition close to the active surface when a reaction experiment under semi-realistic conditions is performed.

3.3. 3D mapping of the gas phase

Two different experimental set-up geometries for excitation and detection were utilized in this study, one where the laser sheet was vertical and the fluorescence light was imaged through the side window, the other with the laser sheet incident in a horizontal fashion, and the fluorescence light collected through the top window, reflected on a mirror positioned as close as possible to the window and again imaged onto the FPA (figure 3(b)). Both geometries used the same optics (a spherical lens with \( f = +200 \) mm and a cylindrical lens with \( f = -40 \) mm), the only difference being that the cylindrical lens was rotated 90°. The possibility of imaging the gas phase from two directions permits to construct a 3D image of the CO₂ gas cloud that surrounds the surface when the sample is highly active and in the MTL regime. In this regime the CO₂ production reach a steady state and do not change significantly in time or with temperature. Several PLIF images can therefore be recorded at this steady state regime without a significant change in the gas distribution over the surface. By moving the laser sheet 1 mm for each image in the vertical (figure 5(a)) and subsequently in the horizontal direction (figure 5(b)), it is possible to generate a 3D representation of the CO₂ cloud surrounding the catalyst surface, see figure 5(c). The 3D image visualize the CO₂ gas close to the surface and it is evident that in a cubical shaped reactor as used in this experiment, the CO₂ concentration is gradually decreasing with the radius from the center of the surface resulting in CO₂ sphere surrounding the surface. The 3D images also reveal a small asymmetry in the fringe of the gas sphere which is a result of the gas flow going from left to right in the figure.

3.4. Self-sustained reaction oscillations

Self-sustained reaction oscillations have been observed in catalytic reactions for many years [55, 56]. Surprisingly, the oscillations in the reactivity appears to occur under fixed temperature and flow conditions and are therefore termed ‘self-sustained’. In the case of CO oxidation, the oscillation has also been correlated to the simultaneous changes in the surface roughness, and as a consequence the number of steps on the surface [15].

To study the oscillation during CO oxidation, a technique which allows for in situ measurement in semi-realistic conditions is required. As demonstrated above, the gas phase is highly important for experiments carried out at semi-realistic conditions. We have visualized the oscillating CO₂ production over a Pd(100) single crystal during CO oxidation from both side and top view. The experiments were performed in a constant oxygen rich gas mixture of 4 ml min⁻¹ CO, 80 ml min⁻¹ O₂ and 16 ml min⁻¹ Ar (mln⁻¹—where n refers to 0 °C and atmospheric pressure) at a total pressure of 150 mbar at a temperature of 240 °C. In an image sequence of 1200 s, as shown in figure 6, the CO₂ production drops and rises twice, demonstrating that the sample is switching between high and low activity. This occurs in steady state conditions and the switching displays a periodic oscillating pattern. The PLIF images in figures 6(a) and (d) show the CO₂ distribution over a low active sample, and the images clearly show that the CO₂ production do not drop to zero but the activity of the sample is lower in this part. The rate of CO conversion is increasing with time in the low active part of the oscillations which is more clear when the PLIF trend is plotted in figure 6(g). The PLIF trend is extracted just above the surface and the partial pressure of CO₂ above the sample increase from approximately 1.5–2.3 mbar in the low activity part. The behavior is similar to the CO poisoned situation described above before light-off, with the difference that the temperature is not observed to be increasing. Figures 6(b) and (e) show the light-off where the catalyst switch to the highly active phase, indicating that CO desorbs from the surface allowing O₂ to dissociate on the surface. As described above, this leads to an increased activity and the sphere of CO₂ is already observed around the surface before the light-off, but is even more pronounced in figures 6(c) and (f) in which the CO₂ distribution in the highly active phase is shown. In the highly active phase the sphere of CO₂ indicates that the sample is in the MTL regime as discussed above. The PLIF trend also shows an almost 100% CO conversion which support the interpretation that the reaction is in MTL by the CO diffusion. The oscillations could also be detected with the MS (figure 6(h)) and the temperature variation of the sample surface (figure 6(i)) of around 5 °C.

Figure 5. Producing 3D images of the CO₂ gas phase in MTL regime by (a) slicing perpendicular to the surface (b) slicing parallel to the surface (c) The resulting 3D reconstruction of the CO₂ sphere.
of the sample surface between the low and high activity was observed due to the exothermal CO oxidation reaction.

Although we have no information on the surface composition, we may speculate on how the nature of the surface may contribute to the self-sustained reaction oscillations. The low activity phase is similar to that observed above, associated with a CO poisoned phase on which the reaction follows the Langmuir-Hinshelwood kinetics (see figure 6(j)). In contrast to the example above, however, the temperature is in this case essentially constant and another mechanism is needed in order to explain the switch to high activity. In accordance with ref [15], we believe that the surface starts in a relatively rough state, with lots of steps. These bind CO harder than flat areas. With time, however, the surface becomes flatter, and the poisoning effect is reduced until the reaction lights-off. (k) At light-off, almost all CO close to the surface is removed, and the surface is exposed to an oxidizing environment resulting in chemisorbed oxygen or a surface oxide on the surface. (l) In the mass transfer limited state, the surface continues to form a thicker oxide, which becomes inactive with the formation of the most stable PdO surface, the PdO(100). With the lower activity, the CO concentration near the surface increases, which reduces the oxide and leaves the surface in a CO poisoned metallic phase with a large density of steps, and the process starts over.

Figure 6. Self sustained reaction oscillations over Pd(100) side view and top view (see also supplementary movie 2 and supplementary movie 3) (a) and (d) very low activity (b) and (e) at light-off (c) and (f) very high activity and in mass transfer limited regime. (g) The PLIF trend as detected just above the samples, a–c indicates the corresponding PLIF images. (h) The MS signal, a–c indicates the corresponding PLIF images. (i) IR-camera recording of the sample temperature, a–c indicates the corresponding PLIF images. (j)–(l) Possible mechanism behind the oscillations. (j) CO binds to the metallic surface, especially at steps, poisoning the catalytic reaction. With time, the surface becomes flatter and the poisoning effect is reduced until the reaction lights-off. (k) At light-off, almost all CO close to the surface is removed, and the surface is exposed to an oxidizing environment resulting in chemisorbed oxygen or a surface oxide on the surface. (l) In the mass transfer limited state, the surface continues to form a thicker oxide, which becomes inactive with the formation of the most stable PdO surface, the PdO(100). With the lower activity, the CO concentration near the surface increases, which reduces the oxide and leaves the surface in a CO poisoned metallic phase with a large density of steps, and the process starts over.
this model lies in the change from an active oxide surface (the PdO(1 0 1)) to an inactive oxide surface PdO(1 0 0). Obviously more measurements are needed to confirm the model, and the difficulties lies in observing a change in a surface structure sensitive signal from small nano-crystallites as the surface switches between active PdO(1 0 1) to inactive PdO(1 0 0).

3.5. Curved crystal

As briefly discussed above in the context of the PdO(1 0 1), under-coordinated sites have been considered to be essential for the reactivity and activity in a number of catalytic reactions [62–64]. Vicinal surfaces have, because of the high step density, been studied intensively to increase the knowledge about the role of under-coordinated sites and steps in chemical reactions [23, 27, 65–72]. On surfaces vicinal to the (1 1 1) the orientation of the steps can be either A-type ((1 1 1) oriented) or B-type ((1 1 0) oriented), and since the step-atoms have different coordination numbers, a difference in the reactivity has been observed [73, 74]. However, a direct comparison of the differences between different step orientations during a catalytic reaction at semi-realistic conditions has not been performed previously due to the limited number of techniques that fulfill the requirements needed to perform such experiments. PLIF hold the spatial and temporal resolution required to make an in situ comparison study during a catalytic reaction. In order to compare the different step orientations, we have studied CO oxidation over a cylindrical shaped Pd(1 1 1) crystal using PLIF. The cylindrical shaped crystal [75–77] expose A- and B-type steps, respectively, see figure 7(a). In a gas mixture of 6 mbar CO, 6 mbar O₂ and 138 mbar Ar when the temperature of the crystal is slowly ramped, the PLIF images reveal that the B-type step have a lower light-off temperature than the A-type step. The PLIF images in figures 7(b)–(d) show the light-off of the two sides respectively. The temperature difference of the light-offs is extremely narrow but by looking at the CO₂ images it is evident that the B-type has the lowest light-off temperature. We also used the advantage of the possibility to extract data locally 0.5 mm above each side and the top of the crystal and the CO₂ trends are plotted in figure 7(e). The plotted trends only show a temperature range of 10 °C corresponding to the light-off sequence of the three different parts of the crystal. The trends clearly show that the reaction is in the MTL regime after light-off but the visualization of the CO₂ distribution over the crystal is a great advantage when the light-off should be determined. The lack of spatial resolution with MS makes it impossible to distinguish from where on the surface the CO₂ originates (figure 7(f)). This is an example illustrating the advantage with the spatial resolution of the gas phase.

As discussed above, the light-off temperature depends on the CO desorption temperature, allowing for oxygen dissociation on the surface. Therefore, it is surprising to find that the stepped parts of the curved crystal has a lower light-off temperature than the extended (1 1 1) surface at the center, since the CO binding would be expected to be stronger at the steps than at the (1 1 1) terraces, and thus a higher desorption temperature. At least, similar light-off temperatures could be expected, since the desorption temperature from the extended (1 1 1) is expected to be similar to the (1 1 1) micro terraces between steps (figure 8(a)). To explain the experimental observations, we rely on Density Functional Theory (DFT) calculations. It is known that the (1 1 1) Pd surface is under tensile stress, and the DFT calculations shows that the (1 1 1) micro
terraces on (223) and (553) surfaces may relax the stress by decreasing the in-plane lattice constant slightly. This relaxation does not occur on extended (111) terraces in the absence of steps. Surprisingly, the difference in relaxation capabilities on extended and micro (111) terraces affects the CO desorption temperature, explaining why the stepped parts of the curved crystals have a lower light-off temperature. However, this would result in that the stepped parts of the curved crystal would have the same light-off temperature, both lower than on the extended (111) surface (figure 8(b)). This is not observed experimentally, since we find that the part of the curved crystal with B-type steps (e.g. (553)-oriented facet) has a lower light-off temperature than the part with A-type steps (e.g. (223)-oriented facet). To explain this discrepancy, the DFT calculations indicate that the B-type side has a stronger CO adsorption energy dependence than the A-type step. At 0.6 ML the CO differential adsorption energy is 1.13 eV for the A-type side while 1.01 eV for the B-type side. Assuming a linear coverage dependence of the differential adsorption energy the repulsion between the adsorbed CO molecules destabilize the CO layer faster on the (553) than on the (223) surfaces. This explains why the light-off is lower for the (553) surface, (figure 8(c)).

The conceptual implications of the above described model are significant for the understanding of catalytic CO oxidation and other oxidation reactions using nano particles. It is already known that the reactivity, for instance in dissociation processes [62, 78], is higher at steps or the corresponding edges between terraces on a nano particle. However, in the case of CO oxidation the O2 dissociation will not happen unless the CO has desorbed, and the desorption temperature will depend on the ability of the nano particle terrace to relax, which in turn depends on the size of the nano particle facet.

3.6. Two powder samples simultaneously

To further demonstrate the spatial resolution and illustrate the versatility of PLIF, figure 9 shows the CO2 distribution over two powder catalyst samples, measured simultaneously in 18 ml min\(^{-1}\) CO, 18 ml min\(^{-1}\) O\(_2\), and 36 ml min\(^{-1}\) Ar at a total pressure of 105 mbar. The samples consist of 2%Pd/CeO\(_2\) (hereafter called the Pd-sample) and 2%Pt1%Pd/CeO\(_2\) (hereafter called the Pt-Pd-sample) pressed powder pellets which are placed 8 mm apart from each other in the reactor. The temperature of the samples are ramped up and down and the PLIF images show that it is possible to distinguish the CO2 distribution around each sample. In the beginning of the experiment (figure 9(a)) none of the samples show any notable CO conversion. At a temperature of 170 °C (figure 9(b)) the light-off of the Pd-sample is observed, resulting in the formation of a CO2 cloud around that sample. As the temperature is further increased, the Pt-Pd sample is observed to become active at about 220 °C (figure 9(c)) and a much larger total cloud of CO2 is now visible. However, the spatial resolution of the experimental set-up is clearly high enough to spatially distinguish which of the two samples that becomes active first. At 250 °C (figure 9(d)), both samples are in the MTL regime indicated by the constant CO2 production even though the temperature is increased further. When the temperature is decreasing, the Pt-Pd sample becomes inactive first (figure 9(e)) and soon followed by the extinction of the Pd-sample (figure 9(f)). The ignition/extinction events for both samples give rise to the corresponding signatures in the PLIF trend, MS signal and temperature data (figures 9(g)–(i)). Obviously the MS signal does not distinguish which catalyst activates first. The PLIF trend, extracted in the area marked with a rectangle over each sample in figure 9(a), clearly show that the Pd sample is highly active in a wider temperature range compared to the Pt-Pd sample. However, the trends also show a gaseous cross-talk between the two catalysts that result in a different gas composition over the Pt-Pd sample, which can have an influence on the light-off temperatures or influencing activation energies extracted from the data. The gaseous cross-talk between the samples demonstrated here with PLIF should be taken into account when performing experiments with several samples in the reactor simultaneously. This experiment shows the potential of having 2D, spatially resolved, non-intrusive measurements of the gas distribution, opening up for simultaneous characterization of more than one sample at a time and direct in situ comparisons. The approach could be beneficial e.g. when studying systems where more than one active
A catalyst is needed to drive different reactions, and how the presence of one catalyst affects the other.

3.7 Three exhaust tubes

Because of the possible interaction of the samples as demonstrated above, we designed a reactor where the samples are separated in three glass tubes to avoid gaseous cross-talk. This could be important if the activity of several samples should be evaluated in a correct way. If several samples can be studied simultaneously and by a direct comparison determine the most active catalyst or the catalyst with the lowest activation/light-off temperature, it could be of interest to catalyst production industry. In the experiment shown in figure 10 we probe the CO₂ production originating from three separate samples simultaneously, and in parallel, by placing the samples into three separated flow tubes. The tubes end inside the middle of the vacuum chamber where the laser sheet was placed as close as possible (<1 mm) to the exits of the tubes, see (figure 10(a)). In this way the gas originating from each individual tube could be probed simultaneously by the laser. Three different catalysts were placed in the tubes, each containing Pd/CeO₂, Pt/CeO₂ and Pt/Al₂O₃, respectively. The experiment was performed in a 1:1 ratio of CO and O₂ at a total pressure of 1 bar which is approximately ten times higher total pressure than in the experiment described in section 3.6. This addresses the possibility of performing experiments in a wide pressure range using PLIF. PLIF, MS and temperature of the samples, measured by a thermocouple, was monitored while the temperature of the samples were increased. At temperatures below 70 °C no PLIF signal was visible indicating that all samples are inactive. A temperatures above 170 °C the tube with the Pd/CeO₂ sample show a CO₂ signal (figure 10(b)) indication catalytic activity. At 100 °C higher temperature the Pt/CeO₂ sample (figure 10(c)) becomes active as evidenced by the detection a CO₂ production from the corresponding tube. The Pt/Al₂O₃ clearly shows the highest activation temperature of 345 °C (figure 10(d)). In this set-up it is also clear that the low flow is directed towards the bottom of the reactor where the outlet is situated, making the detected signal appearing to be not centered in the tubes. The MS signal, as discussed in the experiments shown above, is not able to distinguish from which sample the CO₂ signal is originating (figure 10(e)). The individual CO₂ PLIF trends that can be extracted from each of the samples (figure 10(f)) provides the opportunity to extract quantitative data for the individual catalysts. Three Arrhenius plots (figure 10(g)) can be produced by combining the temperature data and the reaction rate. Activation energy of 0.25 eV, 0.53 eV and 1.05 eV are found for the Pd/CeO₂, Pt/CeO₂ and Pt/Al₂O₃ samples, in good agreement with values reported in the literature [79, 80]. To extract the activation energy using the MS is more...
complicated due to the overlapping CO₂ MS signals inhibiting the extraction of the individual reaction rates for each of the three catalysts.

3.8. CO₂ hydrogenation

PLIF can also be used to visualize the consumption of CO₂ when CO₂ is used as a reactant in a chemical reaction. Figure 11 shows the hydrogenation of CO₂ which also demonstrate that PLIF is a powerful technique when small changes in the gas composition should be detected. In the experiment 1% CO₂, 5% H₂ and 94% Ar is used with a total flow of 200 ml min⁻¹ and a total pressure of 300 mbar resulting in a maximum CO₂ partial pressure of 3 mbar when the experiment start. The sample used in the experiment was a pressed powder pellet that consists of 3% Rh supported by CeO₂. At the time when the temperature is 100 °C no activity of the Rh/CeO₂ catalyst can be observed with PLIF (figure 11(a)) or with MS. As the temperature is increased the catalyst start to consume CO₂ and at 400 °C the lack of signal in the PLIF image is clear (figure 11(b)). The depletion of CO₂ is significant close to the surface and the CO₂ concentration is increasing with the distance from the surface. This shows that also for this reaction, the gas phase close to the surface has a different gas composition within a region similar as for the CO oxidation as was shown above. The CO₂ hydrogenation reaction is
not as efficient as the CO oxidation but the images demonstrate that a cloud with a different gas composition appears close to the surface in this reaction as well. The CO\(_2\) partial pressure close to the surface can be analyzed in more detail and the PLIF signal extracted just above the surface is plotted together with the MS CO\(_2\) signal in figure 11(c). The PLIF trend shows that the partial pressure of CO\(_2\) decreases to below 1 mbar, indicating that the catalyst is active in consuming CO\(_2\) in a CO\(_2\) hydrogenation reaction. Further, the CO\(_2\) MS signal is decreasing insignificantly, since only the CO\(_2\) signal far from the active sample is detected. Concerning the reaction products, several species could be formed, such as methanol and methane. In the present set-up none of the products could be detected by the MS at the outlet. Experiments in which the product is probed by PLIF is planned for the future since PLIF and not through it, as opposed to when a powder catalyst is investigated in a fixed-bed reactor. The results do not reveal the optimal experimental reactor but our studies clearly demonstrate that the gas composition in the reactor is truly dependent on the flow and the geometry of the reactor. The results may also act as a guidance when new reactors are developed.

In figure 12 images of the CO\(_2\) distribution when the reaction is mass transfer limited by CO, from all four reactors are shown. The images of the CO\(_2\) gas phase show that the gas composition is significantly different locally above the catalyst surface as compared to the rest of the chamber. The reactor in figures 12(a) and (b) have a cubical shape with a volume of 240 ml and 23 ml, respectively. Both reactors have a gas inlet and outlet positioned far away from the sample surface where the mass spectrometer is measuring the global composition in the reactor. The images show a similar CO\(_2\) distribution in both reactors with a spherical shaped cloud around the surface with a decreasing gradient of CO\(_2\) with the radius of the sphere. Figure 12(c) shows a stagnation flow set-up which flattens the sphere of CO\(_2\). This is because the tube positioned approximately 5 mm above the surface is used as a the gas inlet with a gas flow of 100 ml\(\text{min}^{-1}\). The opposite is detected in figure 12(d) when a cone positioned 2 mm from the surface is used as the gas outlet. The images show that the CO\(_2\) molecules is flowing through the cone which reshape the sphere significantly. This set-up mimic the flow in a NAPXPS set-up when the nozzle to the XPS analyzer is positioned only a couple of mm from the surface. In NAPXPS experiments, and all other in situ techniques that allows for higher pressure investigation, the most interesting, from a surface science point of view, is the gas molecules interacting with the surface. The high temporal resolution (for each image) as well as high frequency of the images allows for an immediately detection of small changes in the gas phase interacting with the catalyst surface. This information is not easily achieved with other gas phase detecting techniques such as MS, which is often located at the outlet of the chamber and thereby measure the global gas composition in the chamber and not locally over the sample. Capillary MS can be used to measure locally over the surface but a probe might disturb the flow in the chamber.

**Figure 12.** CO\(_2\) gas distribution in the MTL regime in two different reactors and for three different flow configurations, (a) a 240 ml reactor flowing 45 mbar each of CO and O\(_2\) in 90 mbar of Ar with a total pressure of 180 mbar (total flow of 72 ml\(\text{min}^{-1}\)), (b) a 23 ml reactor flowing 6 mbar each of CO and O\(_2\) in 138 mbar of Ar (total flow of 100 ml\(\text{min}^{-1}\)), (c) a 23 ml reactor with a stagnation flow configuration flowing 6 mbar each of CO and O\(_2\) in 138 mbar of Ar (total flow of 100 ml\(\text{min}^{-1}\)), (d) a 23 ml reactor where the outlet is pumped through a 2 mm in diameter cone simulating an APXPS analyzer nozzle and flowing 6 mbar each of CO and O\(_2\) in 138 mbar of Ar (total flow of 100 ml\(\text{min}^{-1}\)).

3.9. **Using PLIF for studies of the gas distribution in model reactors**

The gas molecules interacting with the surface play an important role for the catalytic activity of the surface and it is therefore of great interest to increase the knowledge about the gas phase in the vicinity to the catalyst surface [81]. We have studied the CO oxidation reaction in four different set-ups where the design of the reactors are similar to the ones used when single crystals are studied as model catalysts. These reactors have a geometry that results in a gas flow around the sample and not through it, as opposed to when a powder catalyst is investigated in a fixed-bed reactor. The results do not reveal the optimal experimental reactor but our studies clearly demonstrate that the gas composition in the reactor is truly dependent on the flow and the geometry of the reactor. The results
From the images of the different set-ups we can conclude that in the MTL regime of CO oxidation the CO$_2$ concentration closest to the surface is similar for all set-ups but the shape of the boundary layer formed is dependent on the flow, pressure and geometry of the chamber.

4. CO

CO is one of the reactants together with O$_2$ in the CO oxidation reaction. To probe CO, an electronic transition in the vacuum ultraviolet region needs to be reached. The absorption in the ambient air induces a strong attenuation of the laser beam at these wavelengths. To overcome this problem, a two-photon excitation with a wavelength of 230 nm can be used to reach the $X^4\Sigma^+ (0, 0) \rightarrow B^\Sigma^+$ transition. This is called the Hopfield–Birge band in the CO molecule. Fluorescence in the visible region with the wavelength between 450–660 nm is emitted when the molecule relaxes and the A state is populated as illustrated in figure 13. The two-photon process implies that the fluorescence signal shows a linear to quadratic laser power dependence instead of pure linear as described for the CO$_2$ signal shown above. In the experiment shown in here we used a picosecond laser system consisting of a mode-locked Nd:YAG laser (PL2143C, Ekspla) with external amplifier (APL70-1100, Ekspla). The Nd:YAG third harmonic at 355 nm pumps an Optical Parametric Generator (PG 401-P80-SH, Ekspla), tuned to 230 nm. The laser line width at 230 nm was specified to be 5 cm$^{-1}$ with a pulse energy of typically 0.4 mJ. The repetition rate was 10 Hz and the 80 ps pulse duration provides high peak power, highly beneficial for the two-photon excitation process. The use of a picosecond laser together with the low partial pressure of CO used in the experiments shown in here, reduces the interference of stimulated emission which is considered to be negligible. Calibration measurements were carried out at known partial pressures and at 150 °C. A linear dependency was observed and together with laser pulse energy compensation, the signal in the images was calibrated into partial pressures.

4.1. Imaging CO

The CO fluorescence was imaged perpendicular to the laser sheet onto an ICCD camera (PIMAX 3, Princeton Instruments) using an $f = 50$ mm objective (Nikkor f/1.2) with a 36 mm extension tube mounted on the camera. Images were acquired at a 10 Hz repetition rate with the intensifier gate set to 30 ns. A long-pass filter (GG395, Schott) was used to suppress scattering and fluorescence from surfaces in the reactor. The laser sheet thickness was estimated to 300 μm, which also set the spatial resolution in the image. Laser sheet profiles were recorded at different temperatures for compensation of the thermal gradient in the CO images as well as for steady inhomogeneity in the laser sheet.

4.2. CO oxidation

The work described so far has focused on detecting CO$_2$ during CO oxidation and the CO$_2$ gas phase has been imaged and studied in detail. To understand the gas phase interaction with the catalyst surface in a more complete picture, the CO gas phase has also been visualized during CO oxidation over a Pd catalyst. In figure 14 the CO gas phase was imaged while the Pd(1 1 0) single crystal was heated in a gas mixture of 1:1 ratio of CO and O$_2$. The partial pressures were 26.5 mbar, 26.5 mbar and 53 mbar for CO, O$_2$ and Ar, respectively, resulting in a total pressure of 106 mbar. At the start of the experiment the sample was inactive due to the lack of available sites for O$_2$ dissociation on a CO covered surface. As the temperature was linearly increased as shown in figure 14(d), the rate of the reaction was also increasing with the temperature. At 365 °C a drastic drop was detected in the CO concentration, which indicates the light-off of the reaction and the Pd crystal is highly active. As discussed previously, this occurs when CO desorbs from the surface leaving sites accessible for dissociation of O$_2$. Figure 14(a) shows the CO distribution over the surface at the light-off. A locally lower CO concentration in a
volume in the vicinity of the surface is observed immediately when the crystal switch to the highly active regime. The MS in figure 14(c) shows a global decrease of CO in the chamber and a simultaneous increase in the CO₂ signal confirms that CO is being oxidized. After the light-off the reaction is mass transfer limited by the CO and the CO image in figure 14(b) shows that the volume with significantly lower CO concentration close to the surface is larger than at light-off. The significant consumption of CO at the surface in the MTL regime results in a depletion region of CO locally over the surface. This volume has a similar spherical shape as the CO₂ cloud detected with PLIF in the CO oxidation reaction. The CO PLIF signal extracted in this region, indicated with a black rectangle in figures 14(a) and (b), shows that the CO signal drops 80% from the initial CO partial pressure which can be compared to a 20–30% decrease measured at the outlet with the MS. The CO measurements presented here show the expected opposite behavior with respect to CO₂ in terms of concentration, and also explains the lack of detectable gas phase CO in NAPXPS during MTL conditions [20, 41].

5. NH₃
As for CO, two-photon excitation is used to access the NH₃ molecule. The problem with strong absorption in air of single photon excitation in the vacuum ultraviolet regime, where electronic resonances of the NH₃ is probed, can be avoided by simultaneous absorption of two laser photons. The transition between $X \rightarrow C'$ can therefore be probed by two-photon at 305 nm, followed by population in the A state via fluorescence emissions band at 565 nm, illustrated in figure 15. To generate the 305 nm photons a combined Nd:YAG (Quantaray PRO 250-10, Spectra Physics) and dye laser (Cobra Stretch-G-2400, Sirah) system operating at 10 Hz repetition rate and with 8 ns pulse duration was used. The fundamental wavelength of 610 nm was then frequency doubled to 305 nm using a BBO (beta barium borate) crystal which had a maximum output pulse energy of 35 mJ. A detailed description about the experimental set-up can be found in [82].

5.1. Imaging NH₃
The fluorescence at 565 nm was imaged with an intensified CCD camera (PI-MAX3, Princeton Instruments) with an $f = 50 \text{mm}$ objective (Nikkor f/1.2) or an $f = 150 \text{mm}$ UV lens (B. Halle f/2) mounted on the camera. While continuous background was efficiently suppressed using CCD gates of 100 ns or less, scattered laser radiation was filtered using longpass filters (Schott).

5.2. Hydrogen assisted NH₃ oxidation above a Ag/Al₂O₃ powder catalyst
One important task in the exhaust cleaning of vehicles using diesel engines is the reduction of NOx emissions in the exhaust gases. A three-way catalyst used to oxidize CO and hydrocarbons is not efficient to reduce the NOx due to the oxygen rich conditions. However, several alternatives can be used to reduce the NOx such as traps, hydrocarbon-assisted selective catalytic reduction (HC-SCR) and ammonia-assisted selective catalytic reduction (NH₃-SCR). In the NH₃-SCR process the NH₃ should ideally react with O₂ and NO to form N₂ and H₂O. It has also been shown that H₂ has a promoting effect on the low temperature activity when Ag particles supported by Al₂O₃ are used as the catalyst for the NH₃-SCR process. The role of the H₂ in the reaction mechanism is still under debate and several suggestions have been discussed in the literature such as influence of the chemical state of silver [83–85], removal of reaction inhibitors from the catalyst surface [84, 86] or partial oxidation of the reducing agent [85, 87]. In figure 16 we visualize the promoting effect of H₂ in the oxidation of NH₃ over a Ag/Al₂O₃ powder catalyst by probing the NH₃ with PLIF. In the experiment the temperature of the catalyst is kept to 160 °C and a constant flow of 3.6% NH₃, 90% O₂ with pulses 6%Ar or H₂ at a total pressure of 310 mbar. Figure 16(a) shows a homogenous NH₃ distribution in the image, indicating an inactive catalyst at these conditions. A more interesting result is achieved when H₂ is introduced in the reactor and the reaction and consumption of NH₃ is suddenly initiated. To keep the total pressure constant, the partial pressure of Ar is reduced when H₂ is pulsed into the reactor. The local reduction of NH₃ over the catalyst is clear in the PLIF image shown in figure 16(b). The depletion of NH₃ is significant close to the surface and the MS signals in figure 16(c) show simultaneously an increase of H₂O (green curve) and N₂ (red curve) in the reactor. Figure 16(c) also shows a temperature increase of the sample when H₂ is present in the reactor (pink regions) which is yet another indication of an active catalyst. Together with the MS and temperature the PLIF NH₃ signal is plotted and it is clear that the H₂ effect is reversible in the sense that the NH₃ signal increases again when H₂ is not present in the reactor. These H₂ switches can be repeated several times and the catalyst activity is similar each time.

6. Summary and outlook
In the present review we have shown that it is possible to image different gases in the close vicinity to an active catalyst by the use of PLIF. Recent development of laser and detector technology has enabled this capability. The experiments can be done
by the correct combination of lasers, detector and reactor setup, and it is clear that a combination of expertise is needed for successful measurements. It is essential to combine expertise in laser based techniques with expertise in catalysis or catalytic surface science. By PLIF, the change of the 2D gas distribution can be observed on a timescale better than 0.4 s and with a spatial resolution of 0.1 mm. In this way we can visualize the ignition of the catalyst and the formation of a CO2 cloud or boundary layer in the MTL region around the catalyst. We show that the CO2 cloud may also be imaged in 3D by slicing the CO2 cloud in sheets at different locations by the laser.

The present results were initiated by the need to visualize the gas phase in the proximity of an active CO oxidation catalyst, to demonstrate the change of the gas phase close to the catalyst surface. Such knowledge is needed if a meaningful structure/activity connection is to be made by other techniques available for in situ studies such as HPSTM, SXRD, PM-IRAS, and NAPXPS. At present there is a debate in the catalytic science community concerning the active phase of the late transition metals during CO oxidation, and the measurements presented here demonstrate a significant change in the gas composition which undoubtedly will affect the surface structure, making any structure/activity correlation less obvious. We illustrate the technique by imaging spontaneous reaction oscillations above a Pd(1 0 0) surface.

The spatial resolution of PLIF can be used in several different ways. In the present review, we show how different parts of a curved crystal have different ignition temperatures. An explanation is provided based on DFT calculations indicating different CO desorption temperatures at the (5 5 3), (2 2 3) and (1 1 1) parts of the curved crystal, due to differences in the ability to relax in plane stress and differences in CO coverage. We also show that in the present set-up it is straightforward to differentiate between completely different catalysts placed simultaneously in the same reactor, simply by observing their ignition temperature. By designing a special set-up consisting of tubes, it is possible to reduce gaseous cross talk between catalysts, making individual concentration determinations possible.

During the years that we have developed PLIF for catalysis, we have realized that the method is useful to visualize differences in gas flows for different reactors. In particular we illustrate how the CO2 gas distribution changes when using a cubic reactor, a stagnation flow reactor and a reactor mimicking the more complex NAPXPS reactor.

By choosing the right laser and detector system, gases other than CO2 can in a straightforward manner be visualized. We show this by imaging CO during a CO oxidation reaction and by imaging NH3 in the SCR of NOx by a silver based catalyst. Therefore, it is clear that a large number of molecules can be imaged during catalytic reactions, much of the knowledge already exist in the laser using combustion community.

The present review underlines the potential capacity of PLIF as a technique to visualize catalytic reactions with high spatial and time resolution. However, no information about the chemical or structural composition at the surface is available by PLIF. Therefore, combining other in situ techniques such as PM-IRAS and SXRD with PLIF is an attractive future direction. This approach could yield simultaneous surface structural and gas distribution information, in particular with spatial information.

Since PLIF is sensitive only to the gas phase, it should be interesting to study catalytic reactions which not only depend on the catalytic surface, but also on reactions in the gas phase by radicals. One reaction in which CH3 (methyl) radicals are believed to take part by gas phase reactions is the oxidative coupling of methane. Here methane and oxygen are transformed into ethane or ethene/ethylene and water, but via gas phase reactions with methyl. Imaging methyl close to the catalyst surface during this reaction can possibly only be performed by PLIF.

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