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Two-Dimensional Spatial Resolution of Concentration Profiles in Catalytic Reactors by Planar Laser-Induced Fluorescence: NO Reduction over Diesel Oxidation Catalysts**

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Abstract: *Planar laser-induced fluorescence (PLIF) enables noninvasive in situ investigations of catalytic flow reactors. The method is based on the selective detection of two-dimensional absolute concentration maps of conversion-relevant species in the surrounding gas phase inside a catalytic channel. Exemplarily, the catalytic reduction of NO with hydrogen ($2NO + 5H_2 \rightarrow 2H_2O + 2NH_3$) is investigated over a Pt/Al_2O_3 coated diesel oxidation catalyst by NO PLIF inside an optically accessible channel reactor. Quenching-corrected 2D concentration maps of the NO fluorescence above the catalytic surface are obtained under both, nonreactive and reactive conditions. The impact of varying feed concentration, temperature, and flow velocities on NO concentration profiles are investigated in steady state. The technique presented has a high potential for a better understanding of interactions of mass transfer and surface kinetics in heterogeneously catalyzed gas-phase reactions.*

Optimization of design and operating conditions of catalytic reactors calls for a better understanding of the interactions between the catalytic surface kinetics and the surrounding gaseous flows. The overall reaction rate is often limited by mass transfer of reactants and products to/from the catalytic surface. In particular, in automobile exhaust-gas after-treatment systems, which today use by far the largest fraction of the noble metal consumption worldwide, a better understanding can lead to a substantial reduction of noble metal usage and costs. However, experimental two-dimensional (2D) spatial resolution of species concentrations inside catalytic reactors are usually difficult to obtain and rarely available. Because modern numerical simulations today provide 2D or even 3D species profiles inside reactors,[1] experimental techniques with spatial resolution are also very useful tools in the development and validation of models for catalytic surface as well as gas-phase reaction kinetics.[2]

One-dimensional (1D) spatially resolved concentration and temperature profiles of species inside catalytic reactors have become available within the last years by using the detection capillary sampling technique.[3] Using this sampling technique, catalytic reaction sequences can be understood, at least qualitatively, for instance in the catalytic partial oxidation of hydrocarbons over noble metals.[3a,c,d] However, the invasiveness of this sampling technique makes the quantitative interpretation of the measured profiles a challenging task.[4] Noninvasive and time-resolved investigations of NO reduction in a NO_x storage catalyst have been realized using a combination of diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and Raman spectroscopy with a 1D resolution along the catalytic bed.[5] Improving experiments to 2D-spatial resolution can be achieved by planar laser-induced fluorescence (PLIF). During the past decades, PLIF has become a powerful tool for in situ and noninvasive measurements of species concentrations, mainly in the area of combustion.[6] Combination of numerical simulations and spatially resolved PLIF experiments already led to a more detailed understanding of flames from various burner types as well as catalytically assisted combustion processes.[7] Nevertheless, the use of this technique is limited to fluorescent species within the gas phase (e.g. OH, CH, NO, etc.). Application of PLIF for the investigation of catalytic reactions in emission control devices specifically and catalytic reactors in general under technical conditions is promising but so far quite uncommon.

In this study we investigated the catalytic reduction of NO by hydrogen to ammonia over a commercial diesel oxidation catalyst (DOC) with Pt/Al_2O_3 as catalytically active component according to

$$2\,NO + 5\,H_2 \rightarrow 2\,H_2O + 2\,NH_3. \tag{1}$$

NO PLIF is used to provide absolute 2D NO gas-phase concentrations during the heterogeneous catalytic reduction inside a flow reactor. The field of view of an intensified charge-coupled device (ICCD) camera monitored the 2D LIF signal of the gas phase originated from a thin laser light sheet, which propagates parallel to the surface of the catalyst. The field of view of the camera covers the complete reaction zone. Since the measured fluorescence signals significantly depend on electronic quenching, quenching corrections need to be applied to obtain absolute species concentrations. The relative alteration of the LIF signal due to quenching corrections is less than 20%. All resulting species profiles are obtained by averaging the signal from 100 laser shots to increase the signal-to-noise ratio at steady state operation.

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The pixel-dependent relative standard deviation of the signals from individual laser shots is between 5 % and 9 %. In case of transient processes, the LIF measurements can be carried out on a single shot basis, unfortunately, at the expense of a decrease in the signal-to-noise ratio.

Additionally, the outlet gas flow is analyzed by FTIR spectroscopy and mass spectrometry (MS). The accuracy of the laser-based method can be determined by comparing the LIF results at the outlet side of the catalytic reactor with those obtained by the latter ex situ methods. The determined fluorescence images at steady state are evaluated by ex situ FTIR and MS analyses. Under reactive conditions, the temperature has been gradually increased ($T = 200\,°C$, 250 °C, 300 °C) as well as the flow rate ($\dot{V} = 0.5$ slpm, 1 slpm; slpm: standard liter per minute). Hence the average residence time over the catalyst (length of catalyst = 10 mm, channel height and width = 2 × 20 mm) was 25 ms and 12.5 ms at 300 °C, respectively. Gas inlet mole fractions were 100 ppm NO, 1.000 ppm H_2 diluted in N_2. For nonreactive conditions the temperature was kept at $T = 20\,°C$. At low temperature, no variation in NO concentration was observed in the entire reactor.

The 2D distribution of the NO molecules under reactive conditions at $T = 300\,°C$ (gas temperature = catalyst temperature) is presented in Figure 1. In the entrance region of the reactor, i.e., in front of the catalyst, the NO concentration is homogeneous, neither chemical reactions in the gas phase nor upstream diffusion are observed. Above the catalytic surface, the NO concentration varies significantly due to catalytic reduction of NO to NH_3. Gradients in vertical as well as horizontal directions appear, visualizing the interaction of adsorption of NO on the catalyst with diffusion of NO, mainly toward the catalyst, and convection in flow direction. In the vertical direction, gradients reveal diffusion processes which are additionally influenced by convection of the gas flow. Since no decrease in NO concentration is observed at any point upstream the catalytic section of the reactor, even near the catalytic plate, diffusion in horizontal direction, that is, flow direction, is not significant. Therefore, it can be concluded that the application of a parabolic mathematical model is sufficient to describe the flow in the gas phase, which saves tremendous computational time in comparison with an elliptical model.

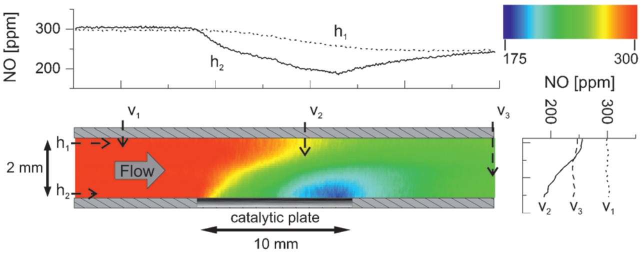

Figure 1. 2D spatially resolved NO concentration within the flow channel for catalytic reduction of NO to NH_3 over a Pt/Al_2O_3 catalyst. Flow rate = 1 slpm, $p = 1$ atm, $T = 300\,°C$, $c_{NO} = 300$ ppm, $c_{H_2} = 1000$ ppm, balance N_2. Vertical and horizontal profiles show absolute NO concentrations at selected positions.

As expected, within the gas phase the vertical NO profiles show minima in direct vicinity to the surface of the catalyst. The lowest NO concentrations are observed near the downstream end of the catalytic plate. Further downstream, the NO concentration gradients slowly begin to disappear due to diffusion. The vertically integrated NO concentration remains constant, again demonstrating that conversion occurs on the catalytic surface only and not in the homogeneous gas phase. The NO concentration determined with PLIF at the outlet of the observed area is in agreement with the data obtained by the ex situ FTIR analysis of the product flow within 0.4 % and 2.0 % deviation.

The impact of operating temperature and flow rate (residence time) on the NO concentration profiles and total NO conversion is presented in Figure 2. NO distributions (PLIF) and ex situ concentrations (FTIR) are recorded at three temperatures ($T = 200\,°C$, 250 °C, 300 °C) combined with two flow rates (0.5 slpm and 1 slpm). The estimated second Damköhler number is in the order of 1. This value and the profiles clearly show that the overall reaction rate is limited by both, surface kinetics and diffusion of the reactants to the catalytic surface in all cases. However, the impact of these two individual processes on NO conversion varies with varying flow rate and temperature. The vertical NO concentration gradients above the catalyst increase with increasing temperature and decreasing flow rate (longer residence time), implying a stronger impact of diffusion on NO conversion. However, the minimum NO concentration measured is 35 ppm. Hence, there is still plenty of NO available in the gas phase close to the catalytic surface, which means that the surface reaction kinetics plays a decisive role for total conversion, as also can be concluded from the increase of conversion with temperature. This impact is even much more pronounced at the higher flow rate of 1 slpm, at which the vertical concentration gradients are rather small. Since hydrogen is present in excess, 1000 ppm H_2 versus 100 ppm NO at the inlet, the hydrogen concentration profiles are not relevant for the discussion above. Comparing the NO maps at different flow velocities for the same temperature and fixed species concentrations further illustrates the direct influence of convection on the NO distribution. Slower flow rates show

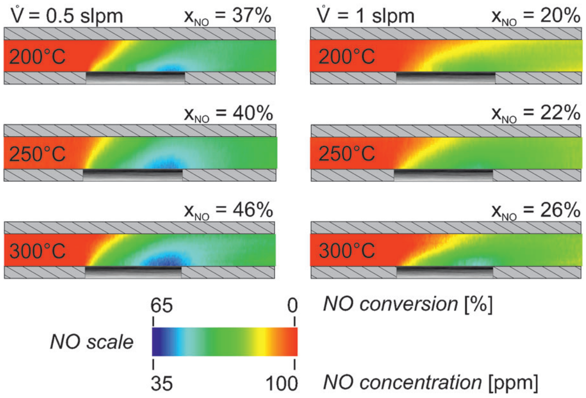

Figure 2. Dependence of the NO distribution on temperature and volumetric flow rate (0.5 slpm left, 1.0 slpm right column). Initial concentrations: $c_{NO} = 100$ ppm, $c_{H_2} = 1000$ ppm, balance N_2. x_{NO} denotes the overall conversion of NO at the outlet.

higher concentration gradients in vertical direction as well as in flow direction. At higher flow velocities, and therefore due to stronger convection, the inlet NO concentration remains roughly constant in the upper part of the channel in the horizontal direction until the middle of the catalyst is reached.

It should be noted that these effects can be overlapped with internal diffusion processes in the catalyst layer, which cannot be studied by the technique presented here. A combination of this experimental technique with numerical simulations of the reactor will elucidate the impact of internal diffusion, similar to recent studies of stagnation flows on catalytic surfaces.[8]

PLIF is shown to be a very valuable technique to measure 2D concentration profiles in catalytic reactors. Here, the technique is applied to determine absolute 2D NO concentration maps for diesel oxidation catalysts. With this study, PLIF is now available for investigations in the field of environmental catalysis, in particular for studies of catalytic devices for the reduction of combustion pollutants from vehicles and other sources.

Experimental Section

The optically accessible flow reactor, which is shown in Figure 3, consists of a rectangular reactor channel (length: 150 mm, depth: 20 mm, height: 2 mm). The latter was realized by milling a slot into a ceramic cylinder (Ø = 20 mm). Commercial Pt/Al$_2$O$_3$ DOCs were used which were placed inside an additional rectangular indentation cut into the bottom of the ceramic channel. The catalysts possess a loading of 5.19 kg m^{-3} (147 g ft^{-3}) and a cell density of 62 cells cm^{-2} (400 cpsi; cells per square inch). To ensure that NO conversion results only from the surface of the catalytic plates and to prevent additional conversion from channels beneath the surface, the entrance of each channel was sealed by ceramic glue. Beneath the bottom surface of the reactor channel a thermocouple was placed inside a drilled hole. An additional thermocouple was placed at the end of the channel to measure the gas temperature. The ceramic channel reactor, together with a catalytic plate, was placed inside a quartz tube. To retain optical access to the area next to and above the catalyst the heating wires as well as the thermal insulation were placed in such an order that a small observation window for the ICCD camera occurs. The reactor was mounted on a translation stage to enable an axial motion with respect to the laser beam. Excitation of NO was performed by laser radiation at 226.68 nm (pulse energy 2 mJ, pulse width 20 ns FWHM (full width at half maximum) by frequency mixing a dye laser (Sirah, PrecisionScan, dye: DCM) at 627 nm (100 mJ, 20 ns FWHM) with the 3rd harmonic (300 mJ, 10 ns FWHM) of a Nd:YAG laser (Spectra-Physics, Quanta-Ray PRO 350). The 2nd harmonic (400 mJ, 10 ns FWHM) of the latter was used to pump the dye laser. Within the temperature range of interest (25–400 °C) the ground state of the chosen P2(12.5) + Q12(12.5) transition (226.68 nm) has an almost constant thermal population.[9] Therefore, the influence of temperature variations could be neglected. In addition to the in situ laser diagnostics, the product gas flow was continuously analyzed by means of online FTIR spectroscopy (MKS MultiGas 2030: NO, N$_2$O, NH$_3$, H$_2$O) and mass spectrometry (V&F H-Sense: H$_2$). The relative error of the utilized ex situ analyzers is $< 2\,\%$. Collisional quenching effects have to be taken into account to obtain absolute concentrations from LIF measurements, because the gas-phase composition changes according to Equation (1). Using the latter formula and the knowledge of the input species concentrations, temperature, and pressure, the concentration of all species involved (NO, H$_2$O, N$_2$, H$_2$, N$_2$O, and NH$_3$) can be derived. Because the appropriate quenching cross sections of these species are available from literature,[10] the LIF signals can be directly converted to absolute NO concentrations.

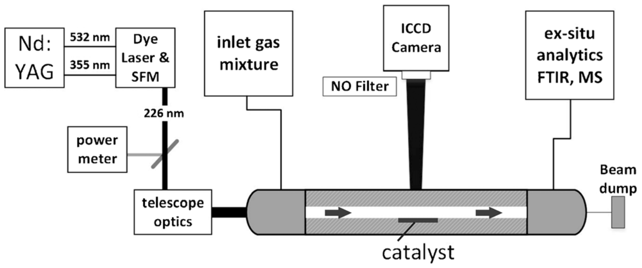

Figure 3. Experimental setup: sketch of the optically accessible flow reactor, laser beam generation, and detection analytics. SFM: sum frequency mixing unit.

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