

In-situ investigation of the interaction of surface kinetics with transport processes over catalytic surfaces by planar laser-induced fluorescence

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Abstract

Planar laser-induced fluorescence (PLIF) enables non-invasive, in-situ investigations of chemical reactions in the gas-phase above a catalytic surface in flow reactors by detecting variations in species concentration. By excitation of conversion relevant species, e.g. NO or OH, two-dimensional (2D) concentration maps can be obtained which lead to a more detailed understanding of the conversion relevant mechanisms. In this study, we present an experimental configuration to determine 2D NO-concentrations maps during the catalytic reduction to NH₃ by hydrogen inside an optically accessible flow reactor. The NO-concentration profiles elucidate the interaction of surface kinetics and transport processes and their dependence on reactant concentrations, temperatures and flow velocities.

Introduction

The ability to observe ongoing reactions in industrial reactors and catalytic converters using spatial resolved in-situ methods can provide new information about these complex chemical reaction system as well as transport phenomena. Further development and optimization of reactor systems such as automotive exhaust gas converters are of high interest regarding the worldwide growing demand on more efficient usage of resources and a reduction of air pollutants. Experimental two-dimensional (2D) information about gas-phase species concentrations inside heterogeneous catalytic converters are usually difficult to obtain and rarely available. Since modern numerical simulations today provide 2D- or even 3D species profiles inside reactors [1], 2D experimental techniques are very useful tools for the development and validation of models describing the reaction kinetics at the catalytic surface or in the gas-phase[2].

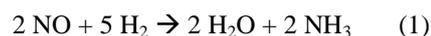
One-dimensional (1D) spatially resolved species concentrations and temperature profiles inside catalytic reactors have become available within the last years by using different detection strategies.[3-5] Catalytic partial oxidation of hydrocarbons to H₂/CO mixtures (i.e., syngas) within honeycomb monoliths have been investigated by a capillary sampling technique yielding 1D gas-phase compositions as well as temperature profiles.[4] However, the insertion of mechanical probes may influence the fluid flux and therefore the chemical reactions.[6] Non-invasive and time-resolved investigations of NO reduction in a NO_x storage catalyst have been carried out using a combination of diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) and Raman spectroscopy with 1D resolution along the catalytic bed.[7] Advancing to a 2D spatial resolution can be realized by planar laser induced fluorescence (PLIF). During the past decades, PLIF has become a powerful tool for in-situ and non-invasive

measurements of species concentrations, mainly in the area of combustion.[8, 9] 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.[10-13] Nevertheless, the utilization of this technique is limited to fluorescent species within the gas-phase (e.g. OH, NO, CH). Successful application of PLIF in chemical reactors for investigation of catalytic reactions under realistic conditions is promising but quite uncommon in the field of catalysis.[14]

In the following, we applied in-situ PLIF to obtain 2D absolute NO gas-phase concentrations during the heterogeneous catalytic reduction inside a flow reactor. The field of view of the intensified LIF CCD-camera (ICCD) images the gas-phase in front of the catalyst, above and after the catalyst. In addition the gas flow was monitored by means of FTIR (NO, N₂O, H₂O, NH₃) and mass spectrometry (H₂), to determine final species concentrations. Hence, the latter techniques were used to verify the experimental results obtained by the PLIF measurements.

Since the fluorescence signals are strongly influenced by electronic quenching, it is mandatory to consider quenching corrections if absolute species concentrations are desired.

In this study, we investigated the catalytic reduction of NO by hydrogen to ammonia according to



All measured fluorescence images refer to steady state conversions of NO verified by ex-situ FTIR analysis.

Experimental

The optically accessible flow reactor, which is shown in Figure 1, consists out of a rectangular reactor

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channel (length: 150 mm, depth: 20 mm, height: 2 mm). The latter was realized by milling a slot into a solid ceramic cylinder ($\varnothing = 20$ mm). An additional rectangular indentation is cut into the bottom of the ceramic cylinder in which the catalytic active material is embedded. For this purpose, commercial Pt/Al₂O₃-diesel oxidation catalysts (DOC) were cut into slices possessing the height of a single channel, a length of 10mm and a width of 20mm. The cutting was carried out without damaging the upper surface and washcoat of the catalytic plate. Afterwards the catalytic slice is placed inside the rectangular indentation in the bottom of the ceramic channel. To ensure that NO conversion results exclusively from the surface of the catalytic plates and to prevent additional conversion from other channels inside, the entrance of each channel was sealed by ceramic glue. The commercial catalysts possess a loading of 147g/ft³ and a cell density of 400 CPSI (channels per square inch). The ceramic channel reactor in combination with the catalytic plate was placed inside a quartz tube. Thermocouples were used inside the reactor and beneath the catalyst to monitor the gas phase temperature as well as the temperature of the catalytic plate. To remain optical access to the area next to and above the catalyst, the heating wires as well as the thermal insulation were specially placed in order to realize a small observation window for the ICCD camera.

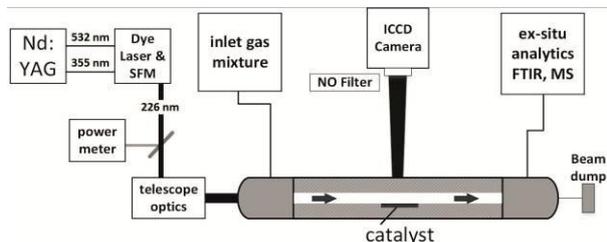


Figure 1: Experimental setup: sketch of the optically accessible flow reactor, laser beam generation and detection analytics. SFM: sum-frequency mixing unit.

The experimental rig was mounted on a translation stage to enable axial motion with respect to the laser beam. The gas flows were dosed and controlled by mass flow controllers (Bronkhorst). The gas mixture was heated before entering the reactor using a preheater stage to ensure a homogeneous gas temperature and uniform mixing. Excitation of NO was performed via laser radiation at 226.68 nm. For this purpose, P2(12,5) + Q12(12,5)-transitions within the NO-A-X(0,0) band, shown in Figure 2, have been chosen. The involved ground state levels possess an almost constant population within the temperature range (25 °C – 400 °C) used for the catalytic conversion. The laser beam was formed into a planar laser light sheet using telescope optics (LaVision) before entering the reactor. To improve the beam quality razor blades cut the outer regions of the laser sheet. For signal correction purposes, laser pulse fluctuations were recorded by an energy

monitor. Furthermore, Rayleigh scattering of the laser beam was measured to consider spatial inhomogeneities of the laser beam intensity or inhomogeneities in the sensitivity of the image intensifier/CCD-chip of the ICCD camera. The NO-A-X(0,2) and NO-A-X(0,3) fluorescence emission at 248 nm was detected by the ICCD-camera using an appropriate band pass filter (cw = 248 nm, FWHM 10 nm). The field of view of the camera covers the complete reaction zone. Since the measured fluorescence signals significantly depend on electronic quenching, appropriate corrections need to be applied to obtain absolute species concentrations. The relative alteration of the actually LIF-signal due to quenching corrections is less than 20 %. All measured species

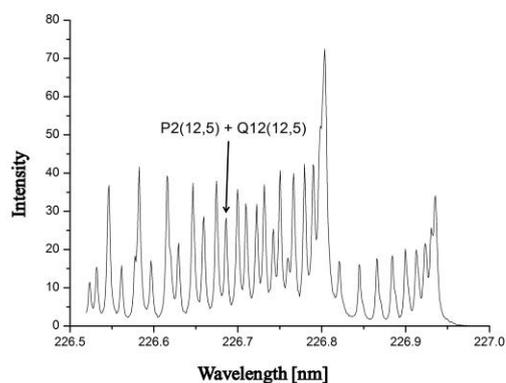


Figure 2: Excitation spectrum of NO.

profiles are obtained by averaging the signal from 100 laser shots to increase the signal to noise ratio at steady state operation. 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. The pixel-dependant relative standard deviation of the signals from individual laser shots is between 5 % and 9 %. The experiments were carried out within the linear LIF regime. Thus the fluorescence signal can be expressed as

$$F = CN_1^0 I_v \frac{A_{21}}{A_{21} + Q_{21}}$$

F: fluorescence signal; C: summary of constant factors such as collection solid angle, focal area; I_v: intensity of the laser beam; A₂₁: Einstein coefficient for spontaneous emission; Q₂₁: quenching rate. In addition to the in-situ 2D laser diagnostics, the product gas flow was continuously analyzed by means of online FTIR- (MKS MultiGas 2030: NO, N₂O, NH₃, H₂O) and mass-spectrometry (V&F H-Sense: H₂). The relative error of the utilized ex-situ analysers is < 2 %. Collisional quenching effects are taken into account to obtain absolute concentrations from LIF-measurements, because the gas-phase composition changes – and therefore the quenching rate – 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, H₂O, N₂, H₂, N₂O and NH₃) can be derived. Appropriate quenching cross sections of these species are available from literature.[15-17] Thus, the LIF-signals can directly be converted into absolute NO-concentrations.

Results

Experimental data has been measured for various reaction parameters under both, reactive and non-reactive conditions. The temperature has been gradually increased from T=25°C, T=200°C, T=250°C and T=300°C. H₂ gas inlet mole fractions were 1000ppm and three different amounts of NO (100ppm, 200ppm and 300ppm) diluted in N₂. The volumetric flow rates were 0.5 slpm and 1 slpm (slpm: standard liter per minute). Thus, the average residence time over the catalytic plate was 25ms and 12.5ms for 300°C, respectively. The NO LIF measurements were done under steady state reaction conditions, which were monitored by the ex-situ analytics. Reference images of homogeneously distributed NO flows under non-reacting conditions (without H₂) were recorded for every given temperature, NO concentration and flow rate. The addition of hydrogen into the gas mixture initiates the NO reduction at temperatures $\geq 200^\circ\text{C}$. After reaching steady state conversion associated fluorescence images were recorded. All fluorescence images were corrected for laser intensity fluctuations, background scattering and laser sheet/camera sensitivity inhomogeneities. Figure 3 shows a homogeneously distributed flow of 100ppm NO under non-reacting conditions at T = 25°C. As expected, the 2D-distribution reveals no gradients in any direction because NO is not reduced under the given reaction conditions. Similar NO distributions were obtained, if NO concentrations, temperatures and flow rates are varied.

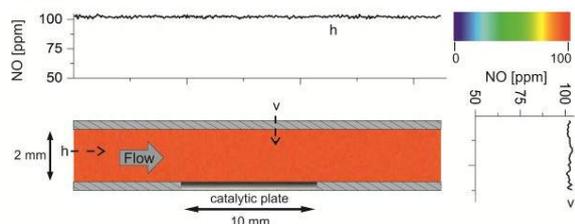


Figure 3: 2D NO distribution under non-reacting conditions. $c_{\text{NO}} = 100\text{ppm}$, $T = 25^\circ\text{C}$.

At low temperatures ($T < 200^\circ\text{C}$) the presence of H₂ has no influence on the measured NO profiles. At higher temperatures ($T > 200^\circ\text{C}$) NO reduction is observed by both, ex-situ analytics (FTIR/mass spectrometry) as well as in-situ NO PLIF. Figure 4 presents spatially resolved NO-concentration profiles during the catalytic reduction of NO to NH₃ at $T = 300^\circ\text{C}$, $c_{\text{NO}} = 300\text{ppm}$ and $c_{\text{H}_2} = 1000\text{ppm}$. In front of the catalyst the NO concentration is homogeneous, neither chemical reactions in the gas-phase nor upstream are observed. Above the catalyst significant gradients of NO appear in horizontal as well as vertical direction. NO is converted

as a result from the ongoing reduction with H₂ to NH₃. The reaction is taking place on the catalytic surface exclusively which can be concluded from the observed gradients. From the measured 2D NO profiles direct information about diffusion, adsorption, conversion and product-desorption phenomena are obtained. In vertical direction gradients reveal among the other phenomena diffusion processes which are additionally influenced by convection of the gas flow. As expected, lowest NO concentrations are observed in direct vicinity to the catalytic surface. Further downstream, behind the catalyst, the gradients slowly disappear due to diffusion. The NO concentration determined with PLIF at the outlet of the observed area agrees with the data obtained by ex-situ FTIR-analysis of the product flow. The overall deviation between the in-situ determined concentrations and the ex-situ determined concentrations is between 0.4% and 2.0%. Figure 5 shows the impact of temperature and flow rate variations for the catalytic reduction of NO over Pt/Al₂O₃ catalysts. The influence of these experimental parameters can be observed on the one hand by the total conversion x_{NO} measured with the conventional FTIR analytics, and on the other hand, by PLIF. The latter

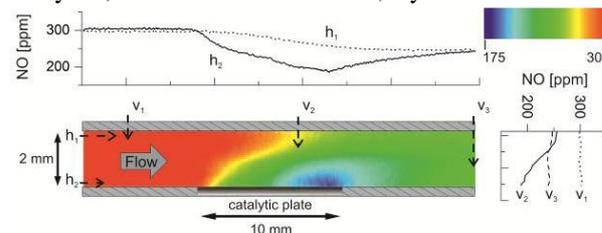


Figure 4: 2D NO distribution during steady-state NO reduction to NH₃ with H₂. $c_{\text{NO}} = 300\text{ppm}$, $c_{\text{H}_2} = 1000\text{ppm}$, $T = 300^\circ\text{C}$. [18]

reveals the influence in a much more detailed way, namely in-situ and two-dimensionally resolved. The influence of variation of just a single parameter can directly be observed by a corresponding change of the 2D NO distributions. As shown in Figure 5, NO distributions were recorded at three different temperatures ($T = 200^\circ\text{C}$, 250°C , 300°C) and two flow rates (0.5 slpm and 1.0 slpm). For all measured cases,

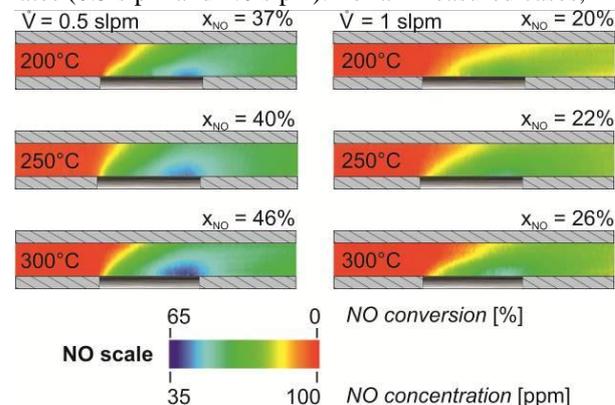


Figure 5: Impact of temperature and flow rate on the NO-distribution. $c_{\text{NO}} = 100\text{ppm}$, $c_{\text{H}_2} = 1000\text{ppm}$, x_{NO} : total conversion of NO. [18]

the measured profiles imply that the overall reaction rate is limited by surface kinetics as well as diffusion of the reactants to the catalytic surface. In vertical direction the NO gradients in direct vicinity to the surface increase with increasing temperature and decreasing flow rate, indicating an increasingly stronger impact of diffusion on NO conversion. However, the temperature dependent surface reaction kinetic has a significant impact on the overall conversion. The increase of conversion with temperature and the incomplete conversion of NO conversion (maximum conversion is 65 %, see blue colored areas in Figure 5), implies a limitation of the reaction kinetics. At the higher flow rate (1 slpm) this impact becomes even more pronounced, because the gradients clearly show even more limitations of diffusion and reaction kinetics. The estimated Damköhler number is on the order of 10^0 , also indicating a limitation of the reaction rate by surface kinetics and diffusion.

Comparing the two different flow velocities further illustrates the influence of convection on the NO-distribution. For slower flow rates the observed concentration gradients were steeper in vertical direction as well as in horizontal direction. At higher flow rates the inlet concentration of NO remains roughly constant in the upper part of the channel until the middle of the catalytic plate.

The effect of collisional quenching on experimentally obtained NO profiles is presented in Figure 6.

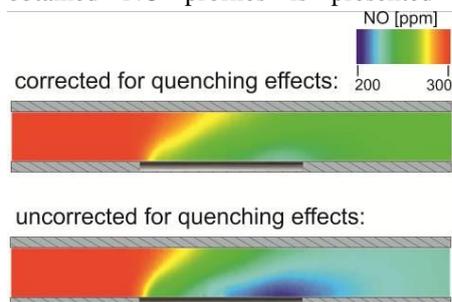


Figure 6: Effect of collisional quenching on 2D LIF signals. $c_{\text{NO}} = 300\text{ppm}$, $T = 200^\circ\text{C}$

Along the catalytic reactor the chemical environment is changing due to the ongoing reduction reaction. This has to be considered during signal processing. H_2O , which is a strong quencher, is formed during the catalytic reduction and therefore strongly influences the measured LIF signals. Stronger quenching of excited NO results in weakened NO signals. Thus the obtained NO concentration is artificially lower than the actual concentration, if quenching effects are neglected. Figure 6 illustrates this effect for the reduction of 300ppm NO at 200°C . Without an appropriate quenching correction considering all relevant molecules, which are present in the gas-phase, the obtained conversion is much higher than the actual one. As a consequence, the final NO concentration at the outlet is not in agreement with the NO concentration determined by FTIR. Therefore, it is mandatory to account for collisional quenching effects

to obtain correct concentration profiles from the measured LIF signals.

Conclusions

It is shown, that PLIF is a very valuable technique for in-situ investigations of catalytic reactors. Determination of absolute 2D concentration profiles of NO during its catalytic reduction to NH_3 provided detailed information about the influences of temperature and flow rate on the interaction of diffusion and surface kinetics. An increase of the temperature generally leads to higher conversion and steeper concentration gradients. Both, the diffusion and the surface reaction kinetics are limiting factors for the NO conversion and play a decisive role for the chemical system.

Comparison of NO-distributions at different flow rates showed the direct influence of convection on the NO-distribution inside the reactor. For chemical systems possessing variations in the molecular environment due to conversion of reactants and formation of products, an appropriate correction for collisional quenching of the LIF signals is needed. Simultaneous measurements of product concentrations by conventional ex-situ analytics (FTIR and mass spectrometry) proved to be a valuable reference method to the in-situ PLIF measurements.

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References

1. O. Deutschmann, Modeling and simulation of heterogeneous catalytic reactions : from the molecular process to the technical system, Wiley-VCH, Weinheim, 2012.
2. M. Reinke; J. Mantzaras; R. Schaeren; R. Bombach; W. Kreutner; A. Inauen, Proceedings of the Combustion Institute 29 (2002) 1021-1029
3. D. Livio; C. Diehm; A. Donazzi; A. Beretta; O. Deutschmann, Appl. Catal., A 467 (2013) 530-541
4. A. Donazzi; D. Livio; M. Maestri; A. Beretta; G. Groppi; E. Tronconi; P. Forzatti, Angew Chem Int Edit 50 (17) (2011) 3943-3946
5. R. Horn; K. A. Williams; N. J. Degenstein; A. Bitsch-Larsen; D. Dalle Nogare; S. A. Tupy; L. D. Schmidt, J. Catal. 249 (2) (2007) 380-393
6. M. Hettel; C. Diehm; B. Torkashvand; O. Deutschmann, Catal. Today 216 (0) (2013) 2-10
7. A. Urakawa; N. Maeda; A. Baiker, Angew Chem Int Edit 47 (48) (2008) 9256-9259
8. A. C. Eckbreth, Laser diagnostics for combustion temperature and species, Gordon & Breach, Amsterdam, 1996.
9. K. Kohse-Höinghaus, Prog. Energy Combust. Sci. 20 (3) (1994) 203-279

10. B. C. Connelly; M. B. Long; M. D. Smooke; R. J. Hall; M. B. Colket, *Proceedings of the Combustion Institute* 32 (2009) 777-784
11. M. Forsth; F. Gudmundson; J. L. Persson; A. Rosen, *Combustion and Flame* 119 (1-2) (1999) 144-153
12. M. B. Davis; M. D. Pawson; G. Veser; L. D. Schmidt; G. Veser, *Combustion and Flame* 123 (1-2) (2000) 159-174
13. M. Reinke; J. Mantzaras; R. Schaeren; R. Bombach; A. Inauen; S. Schenker, *Proceedings of the Combustion Institute* 30 (2005) 2519-2527
14. A. Zellner; R. Suntz; O. Deutschmann, *Chemie Ingenieur Technik* 86 (4) (2014) 538-543
15. M. R. Furlanetto; J. W. Thoman; J. A. Gray; P. H. Paul; J. L. Durant, *J Chem Phys* 101 (12) (1994) 10452-10457
16. J. B. Nee; C. Y. Juan; J. Y. Hsu; J. C. Yang; W. J. Chen, *Chem Phys* 300 (1-3) (2004) 85-92
17. T. B. Settersten; B. D. Patterson; J. A. Gray, *J Chem Phys* 124 (23) (2006)
18. A. Zellner; R. Suntz; O. Deutschmann, *Angew Chem Int Edit* 54 (2015) DOI: 10.1002/anie.201410324R1