# Chasing active sites: In operando investigations on a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst during isothermal CO oscillations

<u>Andreas Gänzler</u><sup>1</sup>, Alexey Boubnov<sup>1</sup>, Henning Lichtenberg<sup>1</sup>, Oliver Müller<sup>2</sup>, Maria Casapu<sup>1</sup>, Jan-Dierk Grunwaldt<sup>1\*</sup> <sup>1</sup>Karlsruhe Institute of Technology, Karlsruhe, 76131Germany <sup>2</sup>University of Wuppertal, Wuppertal. 42097 Germany \*corresponding author:grunwaldt@kit.edu

## Introduction

Diesel engines are superior to conventional gasoline engines with respect to fuel efficiency and  $CO_2$  emissions, however, the treatment of the diesel exhaust is a significantly harder task [1, 2]. Therefore multi-component systems are applied in which Pt or Pd based diesel oxidation catalysts (DOC) represent the first stage, with CO oxidation as a major task [3]. Even though studied for decades [4, 5], the noble metal catalyzed reaction is not yet fully understood, especially with respect to more realistic catalysts (supported noble metal particles) and reaction conditions. In this regard, the occurrence of CO conversion oscillations in such catalysts is controversially debated. *In situ* techniques [6], able to derive information without altering reaction dynamics, enable the establishment of structure-activity relationships. Thus, X-ray absorption spectroscopy has already provided important insight into the structural changes underwent by Pt in supported catalysts [7, 8].

This study aims at in-depth understanding of Pt-based model DOCs under real working conditions [9], in particular of phenomena like oscillatory CO oxidation [8]. For this purpose for the first time spatially and time resolved *in situ* X-ray absorption spectroscopy (XAS) and IR-thermography were complementary applied in addition to the catalytic activity tests.

#### Materials and Methods

The model Pt/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by using different precursors and preparation techniques. The catalysts were characterized using BET, AAS, CO- and H<sub>2</sub>-chemisorption, XRD, DRIFTS and XAS. The activity during light-off experiments (50°C to 500 °C) was evaluated with respect to CO, NO and CO/NO oxidation in labreactors at GHSV =  $60,000 \text{ h}^{-1}$  (gas mixture: 0 - 1000 ppm CO, 0 - 1000 ppm NO,  $10 \% O_2$ , He). Further activity tests were performed in a capillary microreactor heated by a Gasblower, which was used also for the *in operando* experiments at isothermal conditions at different flows. A FLIR SC 7000 was used for *in operando* thermography measurements at isothermal CO oxidation conditions. XAS measurements were conducted at the Pt L<sub>3</sub>-edge at the XAS beamline (ANKA, Karlsruhe, Germany) and at the SuperXAS beamline (SLS, Villigen, Switzerland).

### **Results and Discussion**

Stable and reproducible oscillatory CO conversion was obtained at isothermal conditions at the outlet of a packed bed reactor of the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (MS signal). Since CO oxidation is highly exothermic, the active zone of the catalyst bed (hot) could be identified during such oscillations by using IR-thermography (Figure 1). Temperature hot-spot formation was observed, starting at the end of the catalyst bed and migrating towards its inlet. With higher temperature not only its frequency was increased, but also the location of hot spot

formation was shifted towards the beginning of the catalyst bed. Even at very high temperatures, hot spots were formed with high frequency at the start of the reactor, while at the end of the catalyst bed full conversion was found (MS-data).



Figure 1. Thermography images during oscillatory CO conditions. Temperature hot-sports are visualized by difference imaging (left). The actual temperature in the middle of the catalyst bed is shown in (right).

XAS was used to gain a deeper understanding of this behavior on the microscopic level. At low temperatures below the light-off Pt was in metallic state and got oxidized with increasing temperature starting at the end of the catalyst bed. Periodic changes of the Pt oxidation state were observed along the catalyst bed.

By considering the results obtained with MS (integral activity), IR-thermography (location of the active catalyst as function of time) and XAS (spatially and time resolved dynamics of oxidation state and structure of Pt nanoparticles), the Pt oxidation could be linked to the deactivation and Pt reduction to the regeneration of the catalyst.

### Significance

By applying complementary *in situ* techniques, structure-activity relationships could be established by first identifying the active catalyst and second characterizing it. The reduced catalyst was found to push the catalyst into the highly active regime. The effects were less pronounced if larger Pt-particles were present. This helps to design better catalysts for the future.

#### References

- 1. Deutschmann, O. and J.-D. Grunwaldt, Chemie Ingenieur Technik, 2013. 85(5): p. 595-617.
- Lox, E.S.J., Automotive Exhaust Treatment, in Handbook of Heterogeneous Catalysis. 2008, Wiley-VCH Verlag GmbH & Co. KGaA.
- 3. Russell, A. and W.S. Epling, Catalysis Reviews, 2011. 53(4): p. 337-423.
- 4. Ertl, G., Angewandte Chemie International Edition, 2008. 47(19): p. 3524-3535.
- Freund, H.-J., G. Meijer, M. Scheffler, R. Schlögl, and M. Wolf, Angewandte Chemie International Edition, 2011. 50(43): p. 10064-10094.
- 6. Grunwaldt, J.-D., J.B. Wagner, and R.E. Dunin-Borkowski, ChemCatChem, 2013. 5(1): p. 62-80.
- 7. Singh, J., M. Nachtegaal, E.M.C. Alayon, J. Stötzel, and J.A. van Bokhoven, ChemCatChem, 2010. 2(6): p. 653-657.
- 8. Boubnov, A., A. Ganzler, S. Conrad, M. Casapu, and J.D. Grunwaldt, Top Catal, 2013. 56(1-8): p. 333-338.
- Boubnov, A., S. Dahl, E. Johnson, A.P. Molina, S.B. Simonsen, F.M. Cano, S. Helveg, L.J. Lemus-Yegres, and J.-D. Grunwaldt, Applied Catalysis B: Environmental, 2012. 126(0): p. 315-325.