Oscillatory CO oxidation in exhaust gas catalysts: An X-ray absorption spectroscopy and IR-thermography study

Andreas Gänzler¹, Alexey Boubnov¹, Henning Lichtenberg¹, Oliver Müller², Maria Casapu¹, Ronald Fahren², Jan-Dierk Grunwaldt*¹

¹Karlsruhe Institute of Technology, Karlsruhe, 76131Germany
²University of Wuppertal, Wuppertal, 42097 Germany
*corresponding author:grunwaldt@kit.edu

Introduction

CO oxidation is one of the most extensively studied reactions and significant fundamental knowledge with regard to heterogeneous catalysis was established by examining this reaction in detail, both on powders and single crystals [e.g. (1, 2)]. Furthermore, it is of high importance for exhaust gas applications, where noble metal based catalysts are used to oxidize CO [3-5]. In spite of all the effort, there is still a large gap between fundamental studies at model conditions and the application.

A lot of studies focused on the mechanism of the Pt catalyzed reaction, especially with respect to the occurrence of oscillatory conversion [2, 6]. Most of the results, however, were obtained under ideal conditions, which are very different to those in the application. In situ and operando techniques [7], able to derive information on catalysts under working conditions 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 [8, 9].

This study aims at in-depth understanding of Pt-based model diesel exhaust gas catalysts under real working conditions [10], in particular of phenomena like oscillatory CO oxidation [9]. 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/Al₂O₃ catalysts were prepared by using different precursors and preparation techniques. The catalysts were characterized using BET, AAS, CO- and H₂-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 laboratory reactors at a GHSV = 60,000 h⁻¹ (gas mixture: 0 – 1000 ppm CO, 0 – 1000 ppm NO, 10 % O₂, He). Further activity tests were performed in a capillary microreactor (sieve fraction: 100 - 200 µm) heated by a gasblower, which was used also for the in operando experiments at isothermal conditions at different flows. An infrared camera was used for in operando thermography measurements at isothermal CO oxidation conditions. XAS measurements were conducted at the Pt L-edge at the XAS beamline (ANKA, Karlsruhe, Germany) and at the SuperXAS beamline (SLS, Villigen, Switzerland).

Results and Discussion

In series of Pt/Al₂O₃ catalysts only a few showed oscillatory conversion during CO oxidation light-off experiments. These catalysts were supported exclusively by very small noble-metal nanoparticles (< 3 nm). At isothermal conditions, the stable and reproducibly oscillating CO conversion could be monitored and characterized.

By investigating the dynamics on the microscopic and macroscopic level with IR-thermography and X-ray absorption spectroscopy important conclusions with regard to the mechanism of CO oscillations in a packed bed reactor at isothermal conditions could be drawn. 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). As a complementary tool XAS provided the information regarding the atomic structure and oxidation state of the Pt nanoparticles of the active/non-active catalysts. This enabled to establish correlations between the catalyst structure and activity.

Figure 1. IR-Thermography (left) and XAS (right) during oscillatory CO conditions: Temperature hot spots form at the end of the catalyst bed. Platinum gets oxidized and reduced periodically during oscillatory conversion.

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 secondly 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 and it demonstrates the potential of operando and spatially resolved studies in catalysis.

References

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