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Using combined XAS/DRIFTS to study CO/NO Oxidation over Pt/Al₂O₃ catalysts

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Abstract. Combined X-ray absorption spectroscopy (XAS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) were applied to investigate the interaction between reaction atmosphere, adsorbates and Pt oxidation state of Pt/Al₂O₃ model diesel oxidation catalysts under CO/NO oxidation conditions. The Pt oxidation state was correlated to the adsorbates on the catalyst's surface. Even at low temperature the reaction atmosphere had a strong impact on the oxidation state of the catalyst, and the oxidation state in turn strongly affected CO adsorption on the Pt particles.

1. Introduction

Understanding catalysts at work is a key challenge for the rational design of new catalysts. In the past decades an arsenal of *in situ* techniques was particularly developed to investigate heterogeneous catalysts whose performance is determined by the interaction of numerous factors, e.g. oxidation state and adsorbate coverage [1-3]. However, in order to gain a deeper understanding of catalytic processes under relevant conditions also the reactor design has to be considered, which demands furthermore spatially resolved examination of the catalytic material [1, 4-6]. By combining characterization techniques which provide complementary information about the catalysts structure on different length scales an in depth understanding of catalytic processes under reaction conditions can be established.

Herein, results on the oxidation of CO and NO over a Pt based diesel oxidation catalyst are reported, which were obtained by combining XAS for oxidation state evaluation and DRIFTS for identification of adsorbed species. This combination of techniques allows to probe simultaneously bulk and surface properties of catalysts [7-9], and they were used to unravel the interdependence of the reaction atmosphere, adsorbates and the Pt oxidation state. DRIFTS can not only detect adsorbates on the surface but also provide information on the catalyst's surface structure. The results illustrate that these factors are closely correlated and sensitively depend on each other. This approach can therefore significantly contribute to understand the role of the noble metal oxidation state during these oxidation reactions.



2. Experimental

The model 2 wt.% Pt/Al₂O₃ catalysts were prepared by incipient wetness impregnation using hexachloroplatinic acid (HCP) in an aqueous solution or platinum acetylacetonate (PAA) in acetone as precursors. The samples were dried overnight at 80 °C, calcined at 500 °C for 2h and reduced in 5 % H₂/He at 400 °C for 4h. A Titan 80-300 (FEI Company) FEG electron microscope was used in STEM mode to study the distribution and the size of the resulting Pt nanoparticles on the alumina support.

Simultaneous XAS/DRIFTS experiments were performed at the X18A beamline at the National Synchrotron Light Source (Brookhaven National Laboratory, Brookhaven, USA). The bending magnet radiation was monochromatized by a Si (111) channel-cut crystal monochromator in step scanning mode, to record XANES at the Pt L_{III}-edge (11564 eV, beam with a spot size 0.75mm x 0.75 mm) in transmission mode using ionization chambers. The XANES data was evaluated by linear combination analysis using spectra of a Pt-foil and a PtO₂ reference with the IFEFFIT package [10]. DRIFTS data of the samples were simultaneously recorded using a special setup consisting of a DaVinci arm (Harrick) attached to a modified Praying Mantis DRIFTS accessory (Harrick) [11].

About 40 mg of the respective catalyst (PAA, HCP) was loaded into the sample cup. After pre-reduction in 5 % H₂/He (15mL/min) at 200 °C the catalyst was heated to 450 °C in He and background spectra for DRIFTS were acquired in 50 °C intervals during cooling to room temperature. At room temperature, the catalyst was first exposed to 5000 ppm CO, 10 % O₂ and He and then NO was added resulting in a 15 ml/min flow of 5000 ppm CO, 5000 ppm NO, 10 % O₂ and He. After 30 min the catalyst was heated stepwise (temperature plateaus in 50 °C intervals) to 450 °C and cooled back to 50 °C. At each temperature plateau XANES and DRIFTS data were acquired using the corresponding, previously recorded DRIFTS background spectra. When comparing with other data one should bear in mind that due to the temperature gradients within the DRIFTS cell [12] the actual temperature was usually lower than the set temperature.

3. Results & Discussion

According to the TEM results (Figure 1, left, evaluation of more than 400 particles), impregnation with HCP resulted in small (1.1 nm), finely dispersed Pt particles. Impregnation with acetylacetonate also led to very small Pt particles (1.1 nm), however, several very large particles (~50nm) were also found on this sample (Figure 1, right side).

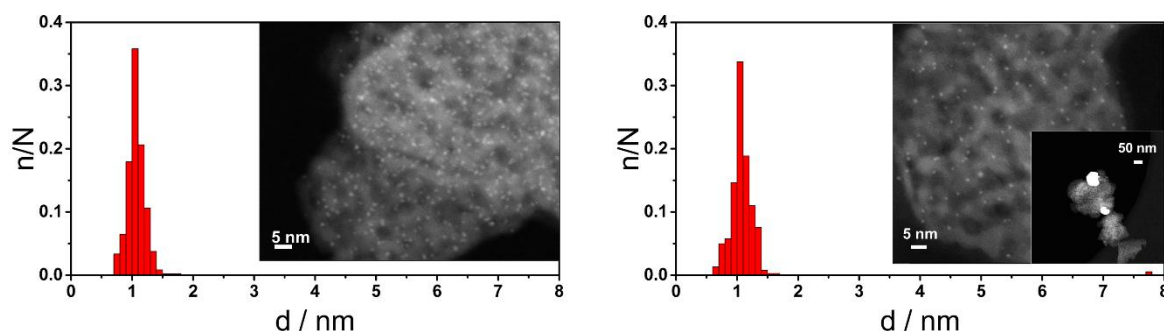


Figure 1. TEM images and respective particle size distribution for 2%Pt/Al₂O₃ catalyst prepared with HCP (left) and PAA (right).

Figure 2 shows XANES and DRIFTS spectra of a pre-reduced catalyst (PAA), simultaneously acquired during the introduction of the reaction mixture at 50 °C in two steps: (1) only CO along with oxygen (blue spectra), (2) addition of NO (red spectra). During the first step the catalyst remained reduced: the XANES spectra did not change and the only visible peak in the DRIFTS spectra at 2096 cm⁻¹ was attributed to CO adsorbed on reduced platinum [13, 14].

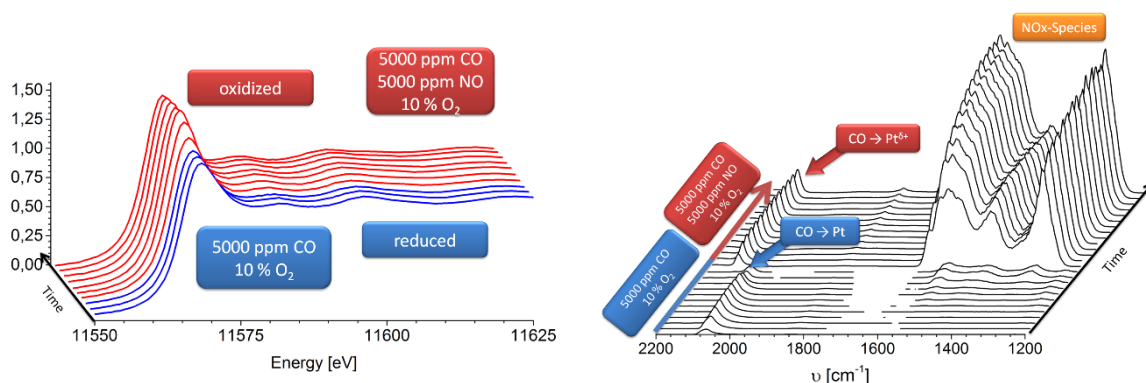


Figure 2. Simultaneously measured XANES (left) and DRIFTS (right) during the introduction of 5000 ppm CO, 10 % O₂, He (blue) over the pre-reduced PAA catalyst, followed by the addition of 5000 ppm NO (red).

After addition of NO the DRIFTS spectra changed significantly. A broad feature between 1200 cm⁻¹ and 1600 cm⁻¹, which can be attributed to NO, NO₂⁻ and NO₃⁻ species adsorbed on the Al₂O₃ support [15, 16], started to dominate the spectra. At 1600 – 1800 cm⁻¹ weak bands, corresponding to linear, non-linear or bent Pt⁰-NO species [17], were observed. The appearance of these features was accompanied by changes in the CO frequency. The peak at 2096 cm⁻¹ vanished while a new peak emerged at 2124 cm⁻¹ representing CO adsorbed on partially oxidized platinum [18]. The DRIFTS spectra suggest that, unlike the previously dosed CO/O₂ feed, the CO/NO/O₂ mixture led to partial oxidation of Pt sites already at room temperature. This is supported by the simultaneously recorded XANES spectra: The Pt-L₃-edge white line increased significantly when NO was added to the reaction mixture. This change in oxidation state at low temperature is probably due to the oxidation of very small Pt particles, which are present in the sample prepared with the PAA precursor [5, 19].

As a next step this interplay between adsorbates and oxidation state was monitored at different temperatures. In Figure 3 the results of the linear combination fitting (LCF) of the XAS data are presented together with simultaneously acquired DRIFTS spectra at several temperature plateaus in the CO/NO/O₂ reaction mixture for the *HCP* (left) and the *PAA* (right) catalysts.

At room temperature the *HCP* sample (Figure 3, left) was covered by CO and NO_x species. CO molecules were adsorbed to Pt sites, which got partially oxidized upon introduction of the reaction mixture, whereas NO_x species covered mainly the Al₂O₃ support. With increasing temperature Pt was further oxidized, while more CO adsorbed to oxidic platinum sites (2129 cm⁻¹). At the same time the DRIFTS bands corresponding to NO_x species adsorbed at Pt sites (1600-1800 cm⁻¹) disappeared and the NO_x coverage on the alumina surface (between 1200 cm⁻¹ and 1650 cm⁻¹) decreased slightly. At elevated temperature (T > 350°C) all adsorbates desorbed, while the catalyst was reduced again even though exposed to an oxidizing atmosphere. During cooling the Pt oxidation state followed a similar profile as during heating. Again, the catalyst was oxidized accompanied by CO adsorption, before Pt was partially reduced during cooling to 50 °C, however, the reoxidation and reduction was shifted to lower temperatures. On the other side NO_x-species on the support adsorbed during heating and cooling in the same manner. According to the LCF results the catalyst ended up slightly more oxidized after the heating-cooling procedure. This was also reflected in the CO adsorption peak, which was slightly shifted to higher wave numbers in the respective DRIFTS spectrum.

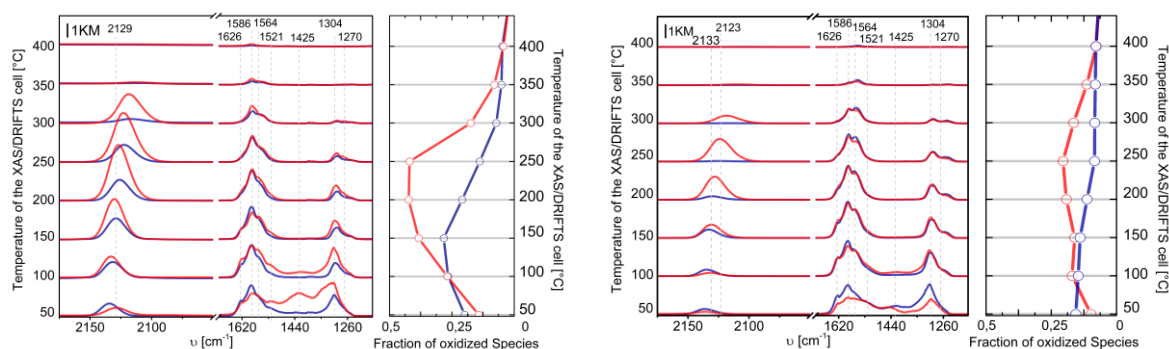


Figure 3. DRIFTS and results of LCF from simultaneously measured XANES/DRIFTS during CO/NO over the 2% Pt/Al₂O₃ catalyst HCP (left) and PAA (right) during heating (red) and cooling (blue).

In case of the *PAA* catalyst changes in the oxidation state of platinum during the CO/NO oxidation temperature cycle were less pronounced, since this catalyst contains also several larger particles (~50 nm) in addition to very small Pt nanoparticles and, accordingly, the fraction of surface Pt atoms, which easily get oxidized is lower. As shown in Figures 2 and 3 the Pt sites were partially oxidized at room temperature in the CO/NO/O₂ mixture. During heating Pt oxidized further also on this catalyst, accompanied by an uptake of adsorbed CO to oxidic Pt sites. At elevated temperatures the Pt oxidation state decreased, as did the CO coverage. When the temperature was decreased again the catalyst remained reduced at elevated temperatures and got partially oxidized at lower temperatures, while CO adsorbed again on oxidic Pt sites. Also on the *PAA* the NO_x adsorption and desorption on the support followed the same trend during cooling and heating. Note that significant concentration and temperature gradients could have evolved along the catalyst bed due to the low gas flow entering the reactor and the rather large diameter of the reactor compared to its length [3, 9]. Therefore, XAS and DRIFTS data might not be any more directly comparable at elevated temperature, even though it was measured in the same cell at the same time.

4. Conclusion

According to these experiments the adsorption of CO appears to be strongly dependent on the Pt oxidation state. Changes in the reaction atmosphere significantly influenced the catalyst's oxidation state already at room temperature. On the other side the oxidation state determined the adsorption on the Pt particles. CO adsorption, which poisons Pt sites with respect to oxygen adsorption and therefore inhibits CO oxidation at low temperatures [5, 19], was found to be significantly more pronounced on oxidized Pt. The combination of XAS and DRIFTS shows the highly sensitive interdependence between the composition of the gas atmosphere, adsorbates and oxidation state, which should be furthermore in close relationship to the noble metal morphology and atomic structure [20]. All these factors are known to influence the catalyst performance and therefore have to be studied and considered, also emphasizing the importance of spatially resolved studies [4, 5].

This study illustrates the interdependence of the reaction gas composition, adsorbates and oxidation state of Pt nanoparticles in exhaust gas catalysts. The combined set-up used for these measurements allowed to see correlations between surface coverage and oxidation state. Features in the IR spectra, which are in turn sensitive to the oxidation state, like the CO band, could be unambiguously assigned. This combination of two powerful characterization techniques can contribute significantly to a better understanding and rational design of catalysts.

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