



Understanding the activation of a Pt/CeO₂ catalyst for CO and C₃H₆ oxidation by using HERFD-XANES and XES investigations

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Report:

Introduction

Precious metal based catalysts are used for abatement of toxic pollutants in the exhaust gas pipe of vehicles [1]. Pt is commonly applied to oxidize CO and unburned hydrocarbons (HC) produced by gasoline, diesel and natural gas engines. However, there are issues regarding the performance especially at low temperatures (e.g. during the cold start), where most of the emissions are produced. Since many years it has been recognized that a strong interaction between noble metals and reducible supports, such as CeO₂, can be exploited to obtain a higher dispersion of the noble metal particles, which boosts and maintains the catalytic activity [2]. Furthermore, sintered noble metal particles could even be redispersed at high temperatures (>700 °C) by taking advantage of the strong Pt-O-Ce interaction [3]. Lately, a strong positive impact on the light-off temperature for CO oxidation was observed after exposing the catalyst to short rich pulses (reducing atmosphere) at moderate temperatures [4], that is due to pronounced structural dynamics of Pt nanoparticles [5]. However, in order to be able to exploit this phenomenon for further enhancing the performance of exhaust gas catalysts, the characterization of the Pt species in its highly active state and its differences to Pt states with lower activity is highly relevant. In this regard, X-ray photon-in/photon-out methods (e.g. Pt L₃-edge HERFD-XANES, Pt L β₅-XES) are highly attractive, since they have proven a huge potential for accessing the electronic and geometric structure, and especially for unraveling the chemical environment at metal centers *in situ* and *operando* [6-14]. Particularly for Pt-based catalysts the pronounced spectral variations could be correlated with reactant type, structure of the adsorption sites and particle size [6,8,10]. This great potential has been exploited in the present study by monitoring the changes of the interaction between CO and Pt nanoparticles in Pt/CeO₂ and Pt/Al₂O₃ model DOC upon different catalyst pretreatment protocols.

Experimental Section

HERFD-XANES measurements were carried out at the ID 26 beamline of ESRF equipped with three mechanically independent undulators providing a maximal flux of 10^{13} photons per second on the sample. A cryogenically cooled Si (311) double crystal monochromator was used for selecting the photon energy. The emission spectrometer was equipped with five Ge (660) analyzer crystals, spherically bent ($r = 1$ m) and installed in a Rowland geometry with respect to the sample and the detector. The counts of the avalanche photodiode detector were normalized by a photodiode between the slits and the sample. For the acquisition of HERFD-XANES spectra at the Pt- L_3 edge the incident energy was scanned while the fluorescence at the maximum of the Pt $L\alpha$ emission line (9442 eV) was detected. The size of the photon beam was about 150 μm in vertical and 500 μm in horizontal direction and allowed a spatially resolved investigation of the Pt electronic state along the catalyst bed.

The investigated materials, 1% Pt/ Al_2O_3 and 1% Pt/ CeO_2 catalysts, were prepared by incipient wetness impregnation. The catalysts were loaded in a 1.5 mm quartz glass capillary and heated by a hot air gas blower [12]. Gases were supplied using mass-flow controllers (Bronkhorst). An electrically actuated valve (Vici) was used for fast switches between premixed gas flows. The reaction products were monitored with an FTIR spectrometer (MKS Multigas 2030) and a mass spectrometer (Pfeiffer Vacuum).

HERFD-XANES data was acquired after various oxidizing and reducing treatments under CO oxidation reaction conditions at various temperatures. Model reaction conditions (1000 ppm CO, 10 % O_2 , He) and more applied reaction conditions (1000 ppm CO, 500 ppm C_3H_6 , 500 ppm NO, 5 % H_2O , 10 % O_2) were used.

Results and Discussion

Previous experiments demonstrated the sensitivity of the HERFD-XANES technique at the Pt L_3 edge towards changes due to CO adsorption on Pt. This was exploited in the present study, which focused on an assessment of the impact of different pretreatment steps on the Pt electronic state during its following CO oxidation experiment. Significant differences were hereby encountered between Pt/ Al_2O_3 and Pt/ CeO_2 . For example, for the pre-reduced catalyst the HERFD-XANES spectra obtained on the Pt/ Al_2O_3 evolved as expected upon exposure to the CO oxidation mixture at low temperature with the formation of a double peak feature (Figure 1, left), indicating the atop adsorption of CO on Pt [6]. During heating of the catalyst, the decrease of this feature revealed desorption of CO. A similar trend could be observed for Pt on ceria (Figure 1, right), however, as in the case of Pt/ TiO_2 [14], the Pt sites appeared to be different to the ones in Pt/ Al_2O_3 . At low temperatures, the HERFD-XANES spectra did not show the well-defined double-peak feature as in the case of the alumina based catalyst. The spectra were dominated by a maximum at 11568 eV, which probably originated from both, a different CO adsorption mode (probably bridged) involving the Pt- CeO_2 interface [6, 14] and a partially oxidized state due to the interaction with the support.

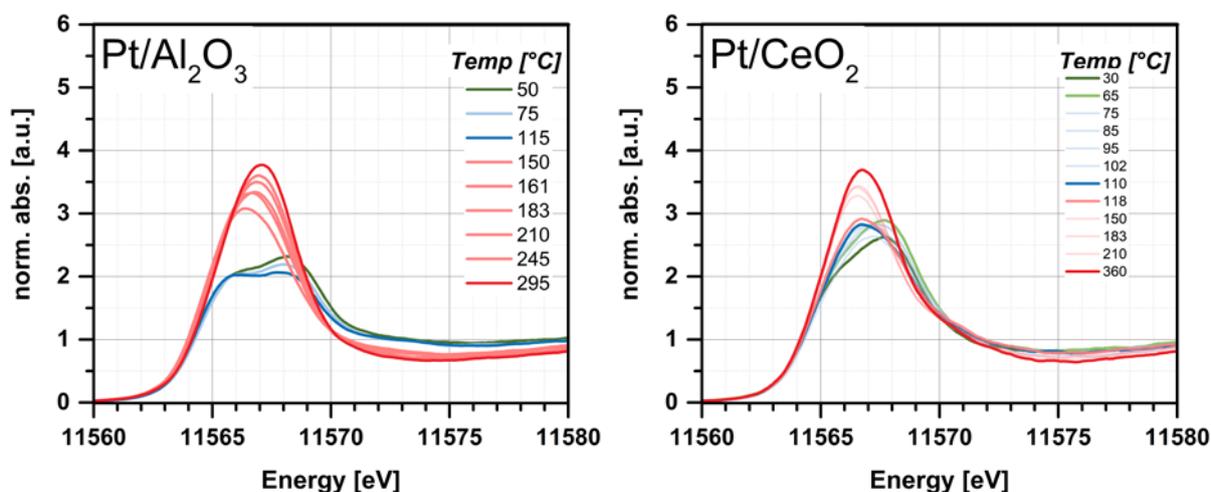


Figure 1: HERFD-XANES spectra obtained at the Pt- L_3 edge on a pre-reduced Pt/ Al_2O_3 (left) and Pt/ CeO_2 (right) catalyst under CO oxidation condition at various temperatures.

When the Pt/CeO₂ catalyst was heated, CO desorption could be detected due to a shift of the white-line maximum, which coincided the CO oxidation light-off and thus the decrease in CO concentration over the catalyst.

By collecting spatially resolved HERFD-XANES spectroscopic data changes in the electronic state arising from differences in the CO adsorption were uncovered along the catalyst bed for the differently pre-treated samples (e.g. oxidizing vs. reducing conditions at 400°C). Hence, the data have provided new and important insight into the specially treated Pt/CeO₂ catalysts, which have a great potential for improved DOC catalysts [5]. To further clarify the impact of the observed activation/deactivation depending on the gas mixture and temperature of catalyst pre-treatment, the obtained information will be supplemented with X-ray emission studies as a next step of our study in near future.

Conclusion

New insight on the Pt electronic state during CO oxidation after various pretreatment steps could be obtained by means of HERFD-XANES investigations. In particular the impact of the support on the noble metal component behavior was strongly reflected in the obtained data, with ceria inducing a different type of interaction between Pt and the adsorbed CO in comparison with that known for the alumina supported catalyst.

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