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Photothermocatalytic oxidation mechanisms of Pt-TiO₂ and Au-TiO₂ studied by operando XANES and XES

Experiment number:
CH-4576

Beamline: ID20	Date of experiment: from: 25 Nov 2015 to: 02 Dec 2015	Date of report: <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Blanka Detlefs	

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Report:

Introduction

Pt-based catalysts are extensively used in many different applications such as oxidation and environmental catalysis, reforming catalysts in petrochemistry, and in “hydrogen economy” acting in both production of hydrogen via e.g. catalytic partial oxidation and its utilization in fuel cells. Thus, application of Pt catalysts sets a demand for characterization techniques able to adequately reproduce Pt structure and dynamics in the state relevant to catalysis. As Pt catalysts are very dynamic and easily change upon variation of external conditions *in-situ* or *operando* characterization techniques are required. X-ray spectroscopy is ideal for *such* studies due to the penetrating ability of X-rays which allows using many different X-ray window materials and opens the way to producing *in-situ* cells tailored for the specific reaction. High-Energy-Resolution Fluorescence Detected X-ray Absorption Near Edge Structure (HERFD-XANES) provides information on the local electronic and geometric structure of Pt sites. HERFD-XANES provides much sharper spectral features than in the conventional X-ray Absorption Spectroscopy (XAS) which originate from the decreased final state core-hole broadening of one particular fluorescence channel. Thus, changes can be better discriminated by HERFD-XANES. While XANES probes electronic structure of unfilled states, X-ray Emission Spectroscopy (XES) in the Valence-to-Core (V2C) region is a complementary technique probing the electronic density of filled valence orbitals. We used *operando* HERFD-XANES and V2C XES complemented by XANES modeling to describe the state and dynamics of Pt sites in working Pt/Al₂O₃ and Pt/TiO₂ catalysts during thermal- and photoactivated oxidation of CO.

Experimental Section

2.2 wt.% Pt/Al₂O₃ was synthesized by incipient-wetness impregnation of SCFa-230 (Sasol) γ -Al₂O₃ with hexachloroplatinic acid [1]. Pt/TiO₂ was made by wet impregnation of hydrothermally-made TiO₂ (anatase with (100), (001), and (101) exposed facets [2]) with hexachloroplatinic acid. *Operando* XAS / XES measurements were performed at ID20 beamline (ESRF, Grenoble, France). X-ray beam generated by 3 u26 undulators was monochromatized using Si (111) double crystal and Si (311) channel-cut pre- and post-

monochromators. A secondary emission spectrometer (Rowland geometry) using a Si (844) reflection of a spherically bent (1m) analyzer crystal and a Timepix detector was used to record HERFD-XANES and XES at Pt L₃ absorption (scanning incident energy with the emission spectrometer set to the maximum of the Pt L_{β3} emission line) and Pt L_{β5} emission lines (keeping incident energy at the maximum of the “white line” of the absorption spectrum and scanning the energy of the emitted X-rays). Photon flux at the sample position was approx. $5 \cdot 10^{12}$ photons/sec and the total instrumental energy bandwidth approx. 1.5 eV. Pressed and sieved catalysts (100-200 μm) were loaded in the Harrick cell originally designed for IR and UV-Vis diffuse reflectance studies with a 60 μm thick flat mica window [3]. The catalysts were pretreated (reduced) for 15 min at 180 °C in 5% H₂/He, after which the gas feed was changed to 10% O₂/He and, subsequently, 1000 ppm CO/10% O₂/He, and stepwise heating was performed. Schott KL 2500 lamp was used as a light source for photocatalysis in the light-assisted experiments. HERFD-XANES and XES spectra were recorded after changing the gas atmosphere and/or temperature. CO conversion was monitored online using an MKS 2030 FTIR gas analyzer. HERFD-XANES spectra were modeled using multiple scattering FEFF 9.6.4. *ab initio* code [4].

Results and Discussion

The exemplary HERFD-XANES and V2C-XES spectra of Pt/Al₂O₃ and Pt/TiO₂ catalysts (no qualitative difference was noticed for different Pt/TiO₂, therefore spectra of one catalyst based on TiO₂ (100) are reported here) measured at room temperature during switching of gas atmospheres are reported in Fig. 1. The XANES spectra of Pt/Al₂O₃ changed significantly from hydrogen-containing to oxygen-containing feed resulting in an increase of a “white line” from ~1.5 to almost 8 and a small shift of the maximum absorption to higher energy. Further addition of CO to the feed resulted in a slight but noticeable decrease of the “white line”. Even more changes were observed in V2C XES with appearing of the so-called crossover peak at 11.558 keV upon interaction with oxygen and its decrease after admission of CO. On the contrary, XANES spectra of Pt/TiO₂ showed less than 25% increase in the “white line” intensity resulting from admission of oxygen and a significant decrease and broadening of the “white line” after admission of CO. Similarly, slight changes were observed in the XES spectra, where the crossover peak, although not resolved, was present even in the spectrum of the reduced sample. During stepwise heating of both Pt/Al₂O₃ and Pt/TiO₂ the spectra changed between the O₂ and CO + O₂-like states showing more oxidized features at higher conversions of CO.

Small spherical model Pt₁₃ and Pt₁₉ clusters with bare surface or terminated with O and CO served for modeling the spectra. Moreover, a single Pt site bound to an oxygen atom from the support was modelled. Both models resulted in a good qualitative agreement with HERFD-XANES spectra of Pt/TiO₂ while appearance of the crossover peak in V2C XES (arising from mixing of O 2p and Pt 5d orbitals [5]) suggested strong interaction between Pt and oxygen atoms from the titania support even for the sample under reducing conditions, i.e. a model of a single or oligonuclear Pt site bound to titania surface. Changes in the spectra of Pt/TiO₂ could only be attributed to changes in adsorbed species (Fig. 2b). In contrast, for Pt/Al₂O₃ modelling by using bare changes in adsorbed species was not sufficient. While using bare Pt₁₉ cluster resulted in a good fit with the XANES spectrum of the reduced catalyst a bulk oxide model such as PtO₂ was required to fit the spectrum under oxygen (Fig. 2a). Admission of CO resulted in the decreased “white line” which supported partial reduction of Pt. However, no broadening of the “white line” due to interaction with CO was observed (as found for Pt/TiO₂ and for Pt/Al₂O₃ elsewhere [6]). This interaction could in our case be masked by much stronger changes due to restructuring of Pt.

Combination of thermal and photoactivation resulted in up to about 10% (Pt/Al₂O₃) and 20% (Pt/TiO₂) increase in CO conversion at 70 °C thus converting additional 100 and 200 ppm CO correspondently. At the same time HERFD-XANES was not able to detect changes in between light-on and light-off conditions at the relevant temperatures below 100 °C (Fig. 3a). On the contrary changes in the intensity of the emission peaks in V2C XES was noticed for all studied catalysts (Fig. 3b) which highlights the importance of combining *operando* XAS and XES. The reason for changes in the V2C XES spectra under light irradiation will be determined after modeling of the spectra which is underway.

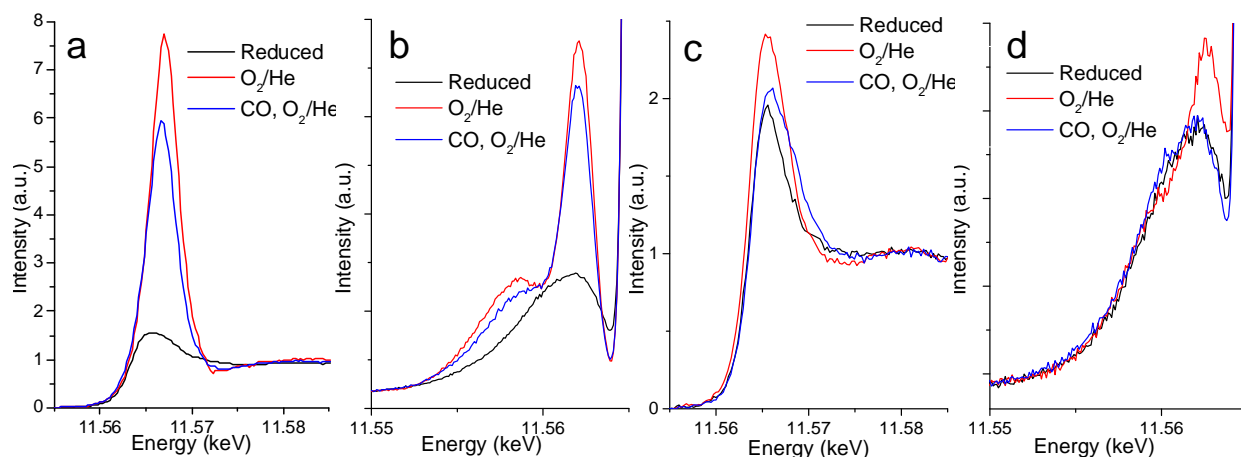


Figure 1. HERFD-XANES spectra of (a) Pt/Al₂O₃ and (c) Pt/TiO₂-100, and V2C XES spectra of (b) Pt/Al₂O₃ and (d) Pt/TiO₂-100) measured at 30 °C under 5% H₂/He, 10% O₂/He, and 1000 ppm CO/10% O₂/He.

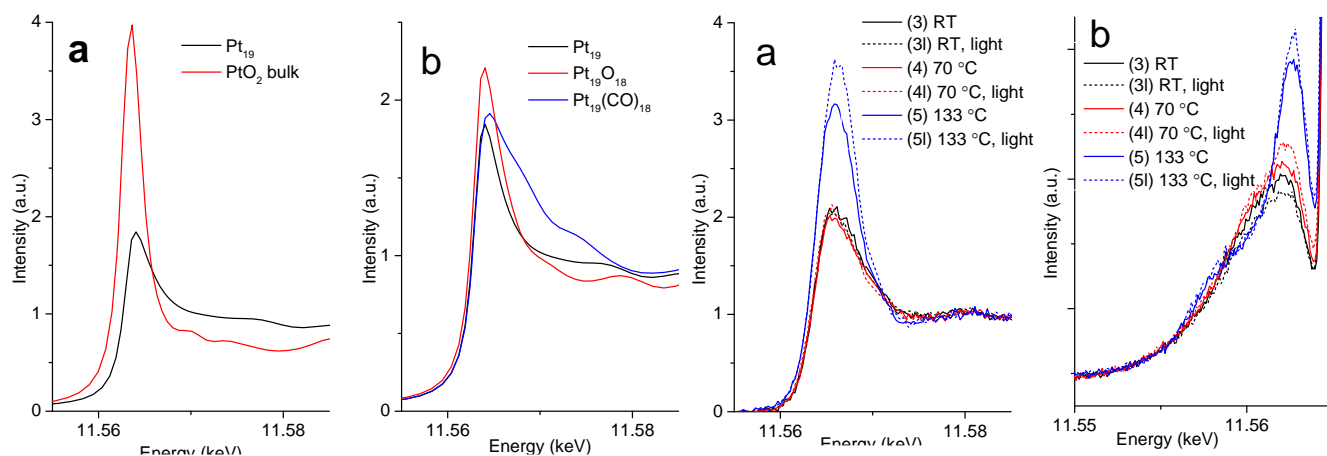


Figure 2. Calculated HERFD-XANES spectra of (a) bulk PtO₂ model in comparison with a Pt₁₉ spherical cluster model and (b) bare Pt₁₉ cluster compared to Pt₁₉ with chemisorbed oxygen or CO.

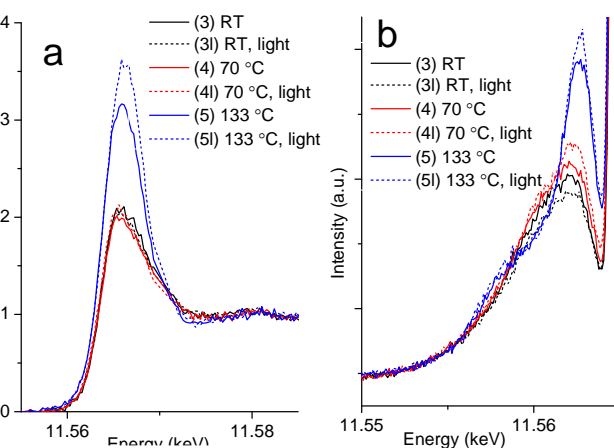


Figure 3. Changes in the (a) HERFD-XANES and (b) V2C XES spectra of Pt/TiO₂-101 during thermal and photothermal oxidation of CO. While changes between thermal and photothermal mechanisms are almost negligible in the XANES spectra, significant variations in intensity of emission bands occur.

Conclusions

A combination of *operando* HERFD-XANES and V2C XES complemented by modeling allowed observing drastic differences in the behavior of Pt sites in Pt/Al₂O₃ and Pt/TiO₂ catalysts during oxidation of CO. While changes in the structure of Pt could be attributed to a complete restructuring (bulk oxidation/reduction) of Pt clusters supported on alumina, titania stabilized Pt sites and the spectral differences could be attributed only to the different adsorbed species. Light irradiation changed electronic structure and activity of Pt catalysts, the exact description of the changes requires XES modeling.

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