

High Energy Resolution Fluorescence Detection X-Ray Absorption Spectroscopy: Detection of Adsorption Sites in Supported Metal Catalysts

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Abstract. High energy resolution fluorescence detection (HERFD) X-ray adsorption spectroscopy (XAS) is demonstrated as a new tool to identify the geometry of metal adsorption sites and the orbitals involved in bonding. The type of CO adsorption site on a nanoparticulate Pt-Al₂O₃ catalyst is determined. The orbitals involved in the Pt – CO bonding are identified using theoretical FEFF8.0 calculations. *In situ* application of HERFD XAS is applicable to a large number of catalytic systems and will provide fundamental insights in structure - performance relationships.

Keywords: High Energy Resolution, HERFD XAS, XANES, *in situ*, CO adsorption.

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INTRODUCTION

Optimization of catalytic systems requires a fundamental and detailed understanding of the processes taking place at the catalyst. For heterogeneous catalysts this means the determination of the structures of the catalytically active sites and species. Despite years of research, these structures remain often unknown.

The sensitivity of Pt L edge X-ray Absorption Near Edge Structure (XANES) data for adsorbates on platinum nanoparticles has been reported [1]. The geometry of hydrogen and oxygen adsorption sites was determined by taking difference spectra, i.e. [XANES(Pt cluster + adsorbate) – XANES(Pt cluster bare)], and comparing experimental difference spectra with theoretical ones [1]. The differences in signatures for different adsorption site geometries as such obtained are small and often difficult to interpret.

To detect the subtle variations in XANES upon adsorption of molecules more accurately, spectra with a higher resolution are required. The experimental spectra are broadened because of the finite lifetime of the core hole, resulting in experimental spectra being much broader than the actual density of states (DOS) which is being probed. Monitoring only one fluorescence line with an energy resolution better than

the core hole life time broadening results in high energy-resolution fluorescence detection (HERFD) XANES spectra with a much better resolved fine structure, compared to normal transmission or total fluorescence spectra [2,3].

Here we describe the application of HERFD x-ray absorption spectroscopy for the study of different CO bonding sites structures on platinum nanoparticles. Spectral signatures are related to variations in DOS of the system using the FEFF8 code [4].

EXPERIMENTAL AND THEORY

The 5 wt% Pt sample supported on γ -Al₂O₃ (Condea, 125-250 μ m) was prepared using deposition-precipitation with platinum tetra ammonium nitrate solution in water. The solid was dried and calcined in air/N₂ flow in the following regime: 5 K/min to 393 K; 4 h at 393 K; 5 K/min to 673 K; 4 h at 673 K. Scanning transmission electron microscopy (STEM) shows small platinum particles between 0.5 and 3 nm. The fraction of powder containing 90-125 μ m particles were separated and introduced into the *in situ* reactor for X-ray absorption spectroscopic measurements. The gas atmosphere in the reactor was controlled by five mass flow controllers (Bronkhorst). Highly pure

He, H₂, and 1% CO in He (Air Liquide) were used as the initial gas mixtures. After reduction of the catalyst in H₂ at 473 K the reactor was purged with He and cooled down to room temperature. The catalyst was then put in contact with different gas mixtures under constant flux (10 ml/min) at 298 K. The studies were performed at the high brilliance XAUS-XES beamline ID26 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The electron energy was 6.0 GeV and the ring current varied between 50 and 90 mA. The measurements were performed using two U35 undulators using the 3rd harmonic. The incident energy was selected by means of a pair of liquid nitrogen cooled Si(220) crystals with an energy bandwidth of 0.7 eV. Higher harmonics were suppressed by two mirrors with Cr coating operating in total reflection at 3 mrad. The X-ray beam measured 0.3 mm horizontal and 1 mm vertical with a total flux on the order of 5×10^{12} photons/sec on the sample. The energy was calibrated using a platinum foil. The HERFD was performed with a horizontal plane Rowland circle spectrometer tuned to the Pt L α_1 (9442 eV) fluorescence line. An energy bandwidth of 1.0 eV in the emission detection was achieved using the (660) Bragg reflection of one spherically-bent Ge wafer. An avalanche photodiode (APD) was used as a detector. A Canberra silicon photodiode was mounted to measure the total fluorescence simultaneously.

FEFF8.2 [4] full multiple scattering, self consistent field, calculations were performed using a Hedin-Lundqvist potential and applying the NOHOLE card. The reduction of the core hole lifetime was achieved by using the EXCHANGE card with parameters 0 0 - 1.6.

RESULTS AND DISCUSSION

Figure 1 compares the Pt foil XANES spectra obtained at ambient conditions using total fluorescence and HERFD detection, obtained simultaneously. It clearly shows the enhancement in spectral resolution of applying the HERFD technique; the XANES features are more pronounced and better resolved.

Similar enhancements in spectral resolution and consequently XANES information provided, is obtained for a 5 wt% Pt/Al₂O₃ catalyst. In Figure 2 the total fluorescence and HERFD XANES spectra for the reduced sample in He at room temperature are displayed. Upon changing the gas atmosphere over the catalyst bed to 1% CO in He, a significant change in Pt L₃ whiteline shape is observed. For total fluorescence detection, the CO spectrum shows a shift in energy

and an increased whiteline intensity, broadened at higher energies. The spectrum under CO obtained in HERFD mode displays the energy shift and now reveals a double whiteline feature.

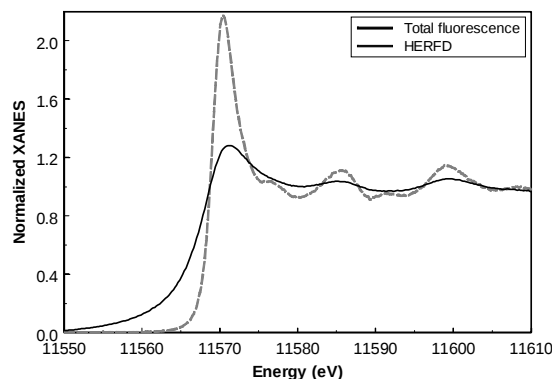


FIGURE 1. Pt L₃-edge normalized XANES data for a Pt foil obtained in total fluorescence and HERFD mode.

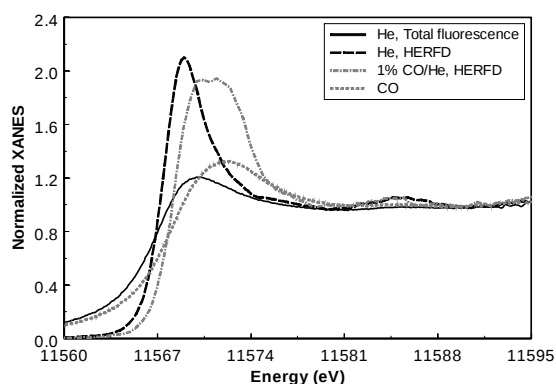


FIGURE 2. Pt L₃ edge normalized XANES data for 5wt% Pt-Al₂O₃ in He, obtained in total fluorescence and HERFD mode, and in 1% CO/He in HERFD mode.

FEFF8.0 calculations are performed in order to identify the geometry of the CO adsorption site. Three different CO adsorption sites on a Pt₆ [1b] cluster were considered: CO atop, CO bridged and CO face-bridging, Figure 3. Whereas total fluorescence XAFS data is accurately calculated with FEFF without using additional experimental resolution corrections, a reduced life time broadening can be simulated using the EXCHANGE CARD. The HERFD XANES data were fitted using an experimental broadening value E_i of -1.6 eV, giving a good approximation to the experiment.

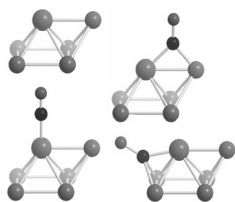


FIGURE 3. Pt_6 -CO cluster simulated with FEFF8.2 (clockwise starting from top left): bare Pt_6 , Pt_6 -CO bridged, Pt_6 -CO face bridged, Pt_6 -CO atop.

The theoretical HERFD XANES data of CO on a Pt_6 cluster are presented in Figure 4. The differences in XANES shape between the bridged and face-bridged bonded CO are very small. The HERFD simulation of the atop CO, however, is very different and shows a double feature in the whitenline.

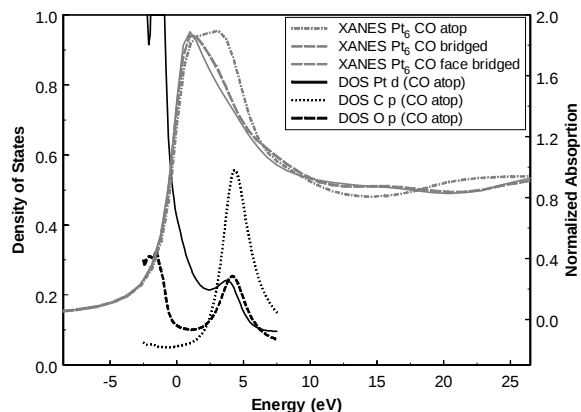


FIGURE 4. Theoretical HERFD Pt L_3 edge XANES for the different CO adsorption sites on Pt_6 and the DOS for the Pt_6 CO atop cluster (Fermi level is calculated at 0 eV).

Comparing the FEFF8.0 (Figure 4) results with the experimental data in 1% CO/He (Figure 2) indicate that the geometry of CO on Pt nanoparticles (under these experimental conditions) is predominantly atop [5]. This distinction is much easier to assign using the HERFD XANES data.

The DOS of the atop CO adsorption site geometry is given in Figure 4. It is evident that the double feature in the Pt L_3 edge whitenline originates from Pt d orbital overlap with C p and O p orbitals. This molecular orbital originates from hybridization of Pt d to the anti-bonding $2\pi^*$ C and O orbitals. This orbital

is only observed for the atop CO since in this conformation the geometry of the orbitals is most favorable for mixing.

CONCLUSIONS

HERFD XAS spectroscopy directly probes the structures of adsorption sites on supported metal nanoparticles. Combined with theoretical FEFF calculations the molecular orbitals involved in metal-adsorbate bonding can be identified. Hence, HERFD XAS spectroscopy is a promising technique for the *in situ* characterization of bonding sites of reactants and intermediates, providing fundamental information on reaction mechanisms and allowing structure-performance relations to be derived.

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