



	Experiment title: Structure - activity relation in supported metal catalysts: Exploration of XES and HERFD XAS	Experiment number: CH-2464
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Shifts: 18	Local contact(s): Dr. Pieter Glatzel	<i>Received at ESRF:</i>
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Introduction

Supported noble metals are used in industry to catalyze a variety of reactions such as hydrogenation, hydrogenolysis, and oxidation. The catalytic activity of these transition metals differs from one metal to the other. The particle size strongly affects the turn-over frequencies for these reactions, especially in case of supported gold catalysts¹. To understand the origin of the activity and reactivity over these catalysts, we need to understand the geometric and electronic structure of the ensemble of atoms that form the catalytically active site. Insight into the electronic structure of these metal particles helps to reveal the differences in the reactivity of the metal particles with adsorbates as function of particle size. In-situ X-ray emission spectroscopy (XES)^{2,3} explored the possibility of detecting the valence d band of Pt and Au after excitation at the L₃ edges using reference compounds and supported metal catalysts. Combination of XES and XAS provided a full picture of the electronic structure. We aim at detecting the electronic structure and the orbitals that are involved in bonding reactants and intermediates to determine the particle size and support effects.

Experimental

Catalyst Preparation. 1.5 wt% Au/Al₂O₃ was prepared by pore volume impregnation with an aqueous solution of HAuCl₄. After reduction, in TEM, the particles showed a narrow size distribution around 1 nm. 0.6 wt% Au/Al₂O₃ was prepared by deposition precipitation⁴. TEM pictures reveal a broad distribution after calcination in air and successive reduction in H₂. Pt/Al₂O₃, prepared by pore volume impregnation showed a narrow particle size distribution around 1 nm. The reference compounds (Au(OH)₃, Au₂O₃, Au₂S₃, PtCl₄, PtO₂, PtTe₂, PtS₂, Pt(NH₃)₄(NO₃)₂) were obtained commercially from Aldrich, Fluka, and ABCR.

X-ray spectroscopy. The reference compounds were positioned in the beam using a sample holder with kapton (polyamide) tape on both sides. The catalysts (0.6 wt% Au/Al₂O₃, 1.5 wt% Au/Al₂O₃ and 2 wt % Pt/Al₂O₃) were analyzed in kapton tubes. The samples had been treated in H₂ and CO prior to the experiments. The monochromator was equipped with a pair of Si (220) single crystals. The X-ray beam measured 0.3 mm horizontal and 1 mm vertical. The energy was calibrated using gold and platinum foils. The high-energy-resolution fluorescence detection was performed using a horizontal-plane Rowland circle spectrometer, an avalanche photodiode (APD, Perkin Elmer) as detector and Si (933) and Si (951) crystals, for Pt and Au respectively, placed 90° to the sample. A Canberra Si photodiode was mounted to measure the total fluorescence yield simultaneously. The XES spectra were obtained by exciting at the white line intensity from the XAS (L₃ edge) spectra. Each XES scan for reference compounds took 18 minutes. For the low loaded supported metal catalysts, about 15 XES spectra of 11 minutes each were required. To prevent sample damage, each scan was taken on a new spot. The resonant inelastic X-ray scattering (RIXS) planes were also obtained for all the samples. For reference compounds, each RIXS plane took 1 hour and for catalysts 25 min, each but we needed to record 25 planes because of low metal loadings. The data was analyzed with the

help of Matlab codes written by the beam line scientist Pieter Glatzel and the XDAP Software. The FEFF 8 code was used to calculate theoretical XES and XAS spectra in order to interpret the experimental ones.

Results

As an example, Figure 1 shows the XES and XANES of PtCl₄. It shows the white line, peak 1, in XANES, which corresponds to the number of the holes in the d-band. We observe the features at 10 eV, 30 eV, and 50 eV, 2, 3 and 4 respectively, in XANES, where peak 2 represents the anti-bonding state formed due to interaction of platinum

d- orbitals with chloride orbitals. The features between -5 eV and -20 eV in the XES spectra, 5 and 6, correspond to the filled DOS. And the peak at approximately -4 eV corresponds to the peak due to the scattering of the initial X-ray beam.

In Figure 1(b), calculated spectra are broadened manually to compensate for the lifetime broadening of the core hole created in the

filled d-band. The shape of the XAS and XES are well reproduced. The feature at -5 eV in the theoretical XAS cannot be observed in experiment because the Fermi Level cuts through the valence band. The calculated valence band, peaks 5 and 6, is also in good agreement with experimental filled DOS obtained from the XES spectrum. The anti-bonding states in the calculated valence band, 7 and 8, are observed in the experimental XANES (peaks 2 and 3). Similarly for other reference compounds, equally good agreement existed between theory and experiment, except for PtS₂, the origin for which is under investigation.

Also, as a representative example of low loaded metal catalysts we compare the XES of small gold particles of about 1 nm to that of bulk gold in Figure 2. The metal loading of the gold particles was only 1.5 wt%. The measurement took about 3 hours. Figure 2 clearly shows a shift of the d band of small particles towards the Fermi level in comparison to bulk gold, which makes small particles more reactive to form bonds with the adsorbates.

Conclusions

The experiment reveals that we are able to combine the XAS and XES spectra to determine the unfilled and filled d-DOS, which are in good agreement with the theoretical predictions. Supported platinum and gold catalysts of less than 1 wt% can be successfully measured. The use of hard X-rays opens up the possibility of detecting the structure of the valence band under in-situ conditions.

References

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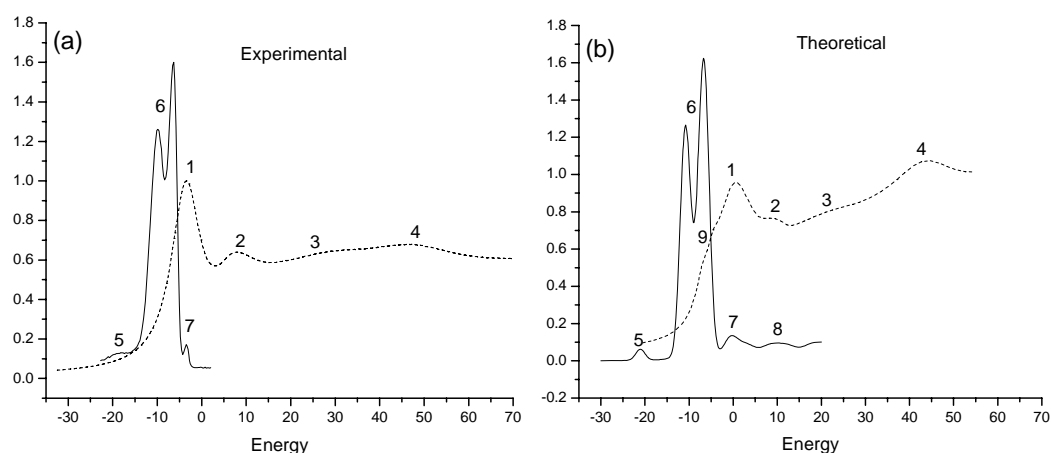


Figure 1: Comparison of experimental and theoretical XES (solid) and XAS (dash) spectra of platinum (IV) chloride

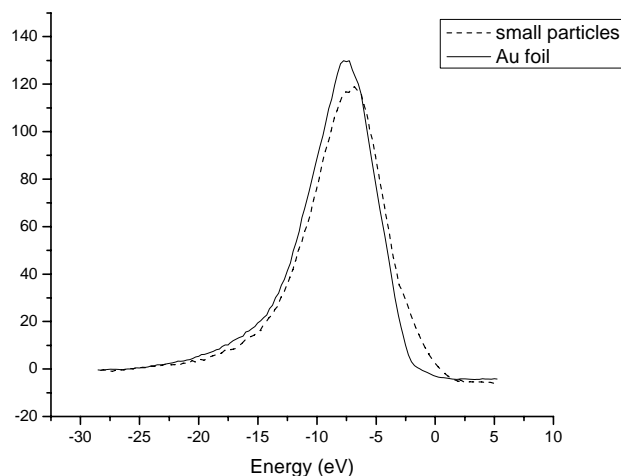


Figure 2: Comparison of XES spectra of small particles with bulk gold.