ESRF	**Experiment title:** EXAFS study of supported PtAu catalysts and the nature of the hydrogen bonding site: Elucidation of the structure-activity relationship	**Experiment number**: 01 – 01 – 629
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Report:

Supported platinum catalysts are widely used in industry, for example in selective hydrogenation reactions. The Pt particles act as the catalyst and the support keeps the particles highly dispersed. However, the support influences the catalytic properties and stability of the platinum. For example, in the phenylacetaldehyde hydrogenation Pt/SiO_2 yields mainly hydrogenolysis products, whereas Pt/TiO_2 displays selectivity towards phenylethanol[1]. Typical Pt/SiO_2 or Pt/Al_2O_3 catalysts produce 100 % butanal in the hydrogenation of crotonaldehyde. Pt/TiO_2, however, produces crotylalcohol and butanol[1]. This behavior of Pt/TiO_2 is due to a strong metal-support interaction, which is not understood. The activity and selectivity of the platinum particles is also changed when an inactive metal such as gold is added. In the conversion of methylcyclohexane, for example, the activity per active site and the selectivity towards toluene are enhanced[2]. The physical background of this influence is not clear. It can be an ensemble size effect, since gold dilutes the platinum, or an electronic effect. Sachdev et al.[3] ascribed the change in catalytic performance in the reaction of n-hexane with hydrogen to an ensemble size effect. They found that structure-sensitive cracking reactions are suppressed if Au is added to Pt/SiO_2. It is clear that alloying alters the adsorption site of the reactants, leading to a change in selectivity. Thus, supported PtAu particles are potential new catalysts in selective hydrogenation and oxidation reactions.

In this experiment, $PtAu/SiO_2$ and $PtAu/TiO_2$ are studied using *in situ* XAS. The supported bimetallic PtAu nanoparticles are prepared by depositing the $Pt_2Au_4(C\equiv CBu^t)_8$ precursor on the support. Calcination and reduction leads to well-mixed bimetallic particles of one to four nanometer, as shown by TEM. EXAFS experiments of these materials determine the size of the PtAu particles and the local order of the Pt and Au. With *in situ* XANES, the interaction of hydrogen with the metal particles is studied at different temperatures. Hydrogen is a primary reactant and covers the metal surface under typical reactions conditions. The hydrogen adsorption site (on-top, bridged or in three-fold pockets) and binding strength affects the adsorption of other reactants. By means of XANES the H-adsorption modes on supported Pt have been detected and are shown to be a function of the support[4].

The 1wt% Pt / 2 wt% Au / SiO_2 was pressed into a self-supporting wafer and placed in our *in situ* XAS cell. After reduction at 200 ºC, and cooling to room temperature in a hydrogen stream, the cell was closed. XAS spectra were taken of the Pt and Au L_3 and L_2 edges at room temperature.

These edges lie at 11564 eV (Pt L_3), 11919 eV (Au L_3), 13273 eV (Pt L_2) and 13734 eV (Au L_2), thus the EXAFS overlap. The Au edges cannot be used in the EXAFS analysis, because the Pt EXAFS lies partly under these. Because it has the longest useful k-range, the Pt L_3 edge was chosen for the EXAFS analysis. PtAu/SiO_2 in hydrogen at room temperature was analyzed. If the first shell is fitted with a Au contribution a coordination number of nine is found; using a Pt contribution this is eight. The bulk number of neighbours is 12, thus we have small particles of approximately 1.5 nm, as confirmed by TEM measurements. A Pt – 1st neighbour distance of 2.76 Å was found, which coincides with the bulk Pt-Pt distance of 2.80 Å. The bulk Au-Au distance is 2.88 Å. Since we have small particles in which the bond is normally contracted, we cannot draw valid conclusions on the structure of this sample based on these data alone. To do this single metal Pt and Au particles of similar size need to be studied.

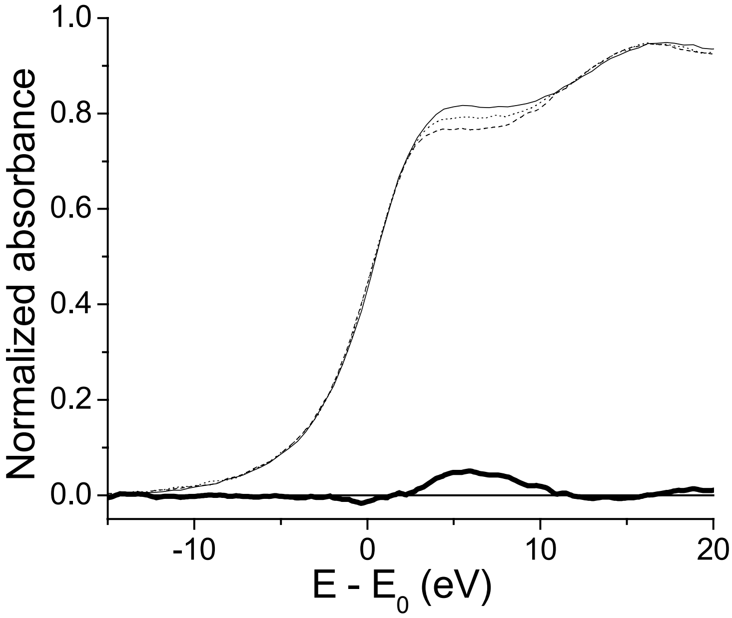

Figure 1. Pt L_2 edge of 1wt% Pt / 2wt% Au / SiO_2 reduced at 200 °C; at room temperature. The edges are aligned at 0.6 of their step height.
—— evacuation at RT;
········ in hydrogen atmosphere;
----- in vacuum, after evacuation at 200 °C (bare metal);
━━ difference of the bare metal with evacuation at RT.

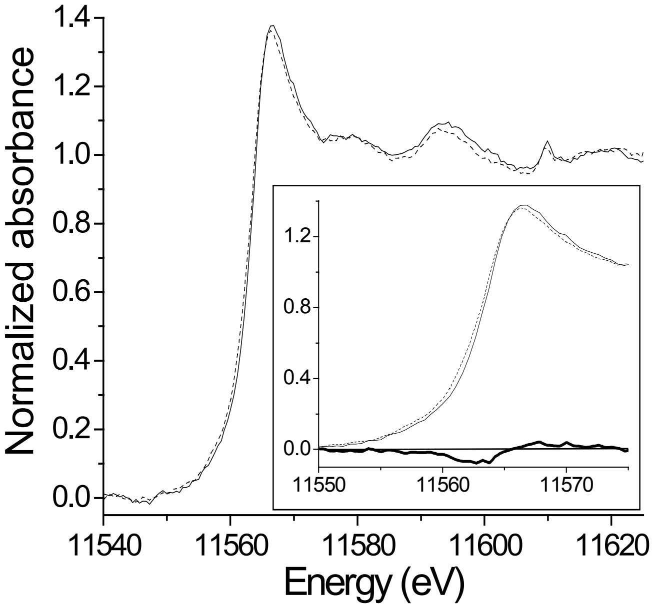

Figure 2. Pt L_3 edge of 0.7wt% Pt / 1.4wt% Au / TiO_2 reduced at 200 °C. The edges are aligned on the position of the Pt foil monitor signal.
—— evacuation at 50 °C; ---- RT, in vacuum, after evacuation at 200 °C; ━━ difference

After the measurement in hydrogen atmosphere at room temperature, the cell was evacuated at room temperature and XAS scans of all four edges were taken at this temperature. Subsequently, the cell was evacuated at RT, 50 °C, 100 °C, 150 °C, and 200 °C and then cooled to room temperature. XANES scans of all four edges were taken at these temperatures in dynamic vacuum. In the Pt L_2 edges a difference is observed between that measured in hydrogen atmosphere and after evacuation at 200 °C (fig.1). Upon evacuation at room temperature, this difference increases. We propose that in hydrogen atmosphere, the hydrogen atoms are mobile. In vacuum, part of the hydrogen desorbs and the remaining hydrogen atoms is localized, therefore we see a stronger effect on the Pt edge. Evacuation at 50 °C decreases the effect of hydrogen on the Pt L_2 edge, because more hydrogen desorbs at this temperature. This does not change the structure of the particles, the Pt – 1st neighbour bond length is still 2.76 Å. After evacuation at 200 °C all hydrogen is removed. To compare the Pt L_2 edges, these edges were aligned on 0.6 of their step height. The L_3 edges of the sample in hydrogen and in vacuum have to be aligned with help of the EXAFS oscillations on their corresponding L_2 edge[5]. The data quality of the Pt L_3 EXAFS is so poor due to glitches that it is not possible to align it on the L_2 edges and thus obtain a properly aligned comparison of the L_3 edges. Therefore, no information can be gained from this edge. In the Au L_3 edge there is a glitch from 13 to 25 eV, exactly in the region of the XANES where we expect a change due to the interaction with hydrogen. This edge can also not be used in the data analysis. In the Au L_2 edges no difference is observed between those measured in hydrogen and after evacuation at 200 ºC. It is concluded that at room temperature hydrogen adsorbs only on the Pt atoms.

For PtAu/TiO_2 containing 1.4 wt% gold and 0.7 wt% platinum, the same experiments were carried out. No difference is observed in the edges measured in hydrogen and after evacuation at 200 ºC. As shown in figure 2, there is a difference in the Pt L_3 edge recorded during evacuation at 50 ºC and after evacuation at 200 ºC. The spectra in this figure could not be aligned on their corresponding L_2 edges, due to the mentioned poor data quality, but it is clear that there is a difference. No effect of hydrogen on the Au edges is observed.

The effect of hydrogen adsorption on PtAu/TiO_2 is less strong than on PtAu/SiO_2. In PtAu/SiO_2 the particle are smaller (1.5 nm versus 3.5 nm in PtAu/TiO_2), therefore a larger fraction of Pt atoms is at the surface. The measured absorption edge is an average of the Pt atoms that bind hydrogen and those that do not. Thus, we observe a larger change in the Pt edge for the smaller Pt particles, even though the hydrogen binding strengths might be the same.

It is concluded that at room temperature hydrogen adsorbs on the Pt atoms of the bimetallic PtAu nanoparticles supported on SiO_2 and TiO_2. In hydrogen atmosphere the hydrogen is delocalized, it moves freely over the surface of the metal particles. Upon evacuation the weakly bonded hydrogen is removed and the bonded hydrogen is localized on specific Pt adsorption sites, which are either on-top, bridged or three-fold. Full-multiple-scattering calculations performed with FEFF8, will enable us to determine the adsorption site as well as the length and strength of the hydrogen-metal bond[4]. The Pt-H bond is strong; evacuation at 50 ºC does not remove the hydrogen. Evacuation at 200 ºC removes all hydrogen. At room temperature no interaction of hydrogen with Au could be observed in the XANES spectra. In the hexane conversion over a PtAu/SiO_2 catalyst similar to ours Chandler *et al.*[6] found that reactions requiring a high amount of surface hydrogen are suppressed. This confirms our finding that only the Pt surface atoms adsorb hydrogen.

To further explore these PtAu/TiO_2 and PtAu/SiO_2 catalysts, the results need to be compared to those for single metal Pt and Au catalysts with similar metal particle sizes on the same supports.

References

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