



	Experiment title: Selective hydrogenation by supported noble metal catalysts: In-situ XAS study of the metal-hydrogen interaction	Experiment number: CH-1789
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Names and affiliations of applicants (* indicates experimentalists): Prof. dr. Roel Prins, dr. Jeroen van Bokhoven, Eveline Bus* ETH Zürich, Institut für Chemie- und Bioingenieurwissenschaften, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland		

Introduction

The catalytic and physical properties of supported noble metal catalysts are studied in our group as part of a larger project concerning the structure-activity relationship in supported metal catalysis. The aim is to gain control of the selectivity by designing and synthesizing unique catalysts. The test reaction is hydrogenation. Platinum is usually the catalyst in this reaction, because it is very active. This high activity may be a disadvantage if the reactant contains multiple double bonds. Platinum hydrogenates all double bonds, but the intermediates may have added commercial value. Our goal is to design a catalyst, which selectively hydrogenates only some of the double bonds and stops the hydrogenation at an intermediate. A possible method is to vary the adsorption strength of the intermediates and the products. If the desorption of the intermediate is faster than its reaction, it will not react further. Another possibility is to alter the geometry of the adsorption site. The adsorption strength and the geometry of the active site can be changed by alloying. Platinum has different catalytic properties when an inactive metal such as gold is added. The physical background of this influence of gold on platinum is unclear. It may be an ensemble-size or structural effect (Pt is diluted) or an electronic effect. The added gold is considered to be inactive in the catalytic process, since it interacts weakly with the reactants [1]. It was found recently that the properties of gold change remarkably when is highly dispersed and supported on a metal oxide [2]. The supported gold nanoparticles are catalytically active in both oxidation and hydrogenation reactions. Hence, gold cannot be considered an inactive additive in catalysis over PtAu particles. Supported gold nanoparticles are interesting new catalysts in selective hydrogenation reactions. The adsorption strength of the gold atoms is weak, thereby facilitating desorption of any desired intermediate products.

Hydrogen is a primary reactant in hydrogenation reactions. The hydrogen coverage and the strength of the hydrogen-metal bond influence the activity and selectivity. Insight into the hydrogen-metal interaction is gained by means of *in situ* XAS at the metal L_3 and L_2 edges [3]. Here, the hydrogen-metal interaction of Pt/SiO₂, Au/Al₂O₃ and PtAu/SiO₂, with metal particles of 1 to 2 nm is studied. The change in the metal L_3 , L_2 , and L_1 X-ray absorption near-edge structure (XANES), as well as the coordination number, interatomic distance, and disorder in the supported metal particles is determined as function of the hydrogen coverage.

Experimental

Catalyst preparation. Gold particles supported on γ -Al₂O₃ (Condea) were prepared by incipient wetness impregnation with an aqueous solution of HAuCl₄, and subsequent hydrolysis of the precursor to remove Cl. The 0.43 wt% Au/Al₂O₃ precursor was dried at 363 K and stored in darkness. Pt/SiO₂ was prepared by adding an aqueous solution of tetra ammine platinum nitrate (PTA) to a slurry of SiO₂ in a NH₄OH solution. After adsorption of the PTA, the powder was filtered, washed, and dried at 373 K. The 1 wt% Pt/SiO₂ sample was pre-

reduced at 423 K. PtAu/SiO₂ was synthesized using the organometallic complex Pt₂Au₄(C≡CBu^t)₈ as precursor. The complex adsorbed spontaneously from hexane on SiO₂. After calcination at 300 °C a catalyst containing 1 wt% Pt and 2 wt% Au was obtained.

X-ray absorption spectroscopy. The sample was pressed in a self-supporting wafer and placed in a stainless steel *in situ* XAS cell. The cell was connected to a gas-flow system, temperature controller, and vacuum pump. The samples were reduced at 473 K in flowing H₂, cooled down in a H₂ flow to 298 K and the cell was pressurized to 2 bar. L₃ EXAFS and L₂ and L₁ XANES spectra were collected at this pressure and subsequently at apparent hydrogen coverage of 0, 0.5, 0.7, 0.8, 0.9 and 1. The apparent coverage is the ratio between the amount of adsorbed hydrogen at a certain pressure and the adsorbed amount at 1 bar, as determined in hydrogen chemisorption experiments in our laboratory. Three spectra were taken at an apparent coverage of 1: at 0.8, 1, and 2 bar. After the experiment at 2 bar, the cell was evacuated (<10⁻⁵ mbar) at 473 K or 573 K (for Pt/SiO₂) for two hours to remove the adsorbed hydrogen. After cooling to 298 K, hydrogen was dosed to obtain the desired coverages. All spectra were recorded in transmission mode using ion chambers. The incident X-rays were monochromated by a Si(111) channel-cut monochromator and a chromium-coated mirror rejected higher harmonics. XAS data analysis was carried out using the XDAP software package. The absorption data were pre-edge and background-subtracted using standard procedures. The spectra were normalized on the height of the edge-step at 50 eV over the edge. Multiple shell fitting was performed in R-space, using a k weighting of 3. Experimentally calibrated theoretical references of gold and platinum foils obtained with the FEFF8 code were used. Although it is likely that surface atoms vibrate anharmonically, harmonic vibrations are assumed in the fitting. The pre-edge subtracted and normalized XANES spectra were aligned to remove initial state core level shifts and final state screening effects.

Results

For Pt/SiO₂ the Pt L₃ and L₂ XANES change due to the chemisorption of hydrogen, as previously shown in literature. A minor change also occurs in the L₁ XANES. The change depends on the hydrogen pressure or the apparent coverage, as shown for the Pt L₂ edge in figure 1. The extended X-ray absorption fine structure (EXAFS) of the Pt L edges also changes. Fitting of the EXAFS function shows that in vacuum, the Pt-Pt bond is only 2.70 Å, compared to a bulk distance of 2.78 Å. This contraction of the distance is expected for these small particles (~ 2 nm) and is caused by the increased electron density between the atoms, due to dehybridization of the spd metal orbitals [4]. The Pt-Pt interatomic distance increases upon chemisorption of hydrogen (Figure 2A), because of the electron-withdrawing properties of hydrogen [5]. Furthermore, the coordination number increases and the Debye-Waller factor decreases with increasing hydrogen coverage (Figure 2B,C). This suggests a change in the particle shape, most likely from a pancake shape in vacuum, to a spherical particle in hydrogen atmosphere.

Changes were also detected in the Au L₃ and L₂ edges of Au/Al₂O₃ in the presence of hydrogen. The intensity of the change increases with increasing hydrogen pressure and thus coverage. The intensity of the hydrogen-induced change in the Au edges is smaller than that in the Pt edges, although the particle size is similar. No change in the Au L₁ could be observed, probably because it has too little intensity. The Au-Au interatomic distance is 2.76 Å, which is 0.09 Å less than that found for a gold foil. The coordination number is 6.7, which corresponds to a particle size of 1.2 nm. The Debye-Waller factor is 0.005 Å⁻¹, thus higher than for Pt particles of similar size. For Au/Al₂O₃ these variables do not change with hydrogen pressure. Thus, although hydrogen adsorbs on these small gold particles and induces a change in the Au L edges, the particle shape is not altered.

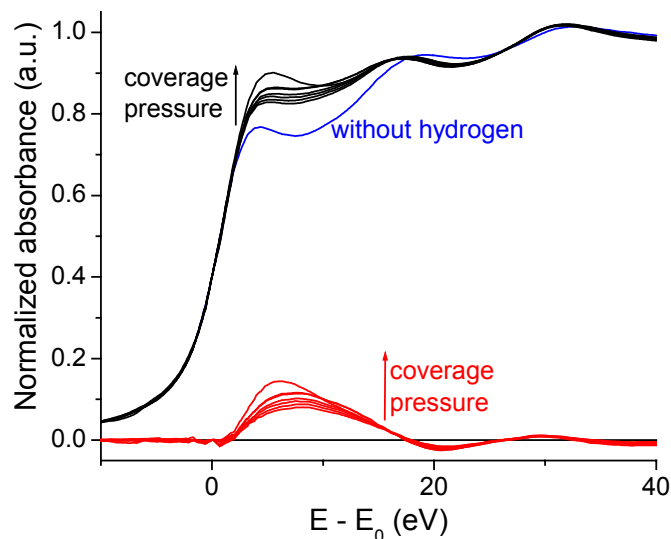


Figure 1. Pt L₂ edge of 1 wt% Pt/SiO₂ at 298 K at apparent hydrogen coverages of 0 (blue), 0.5, 0.7, 0.8, 0.9 and 1 (black) and the difference between the L₂ edges in hydrogen and that in vacuum (red).

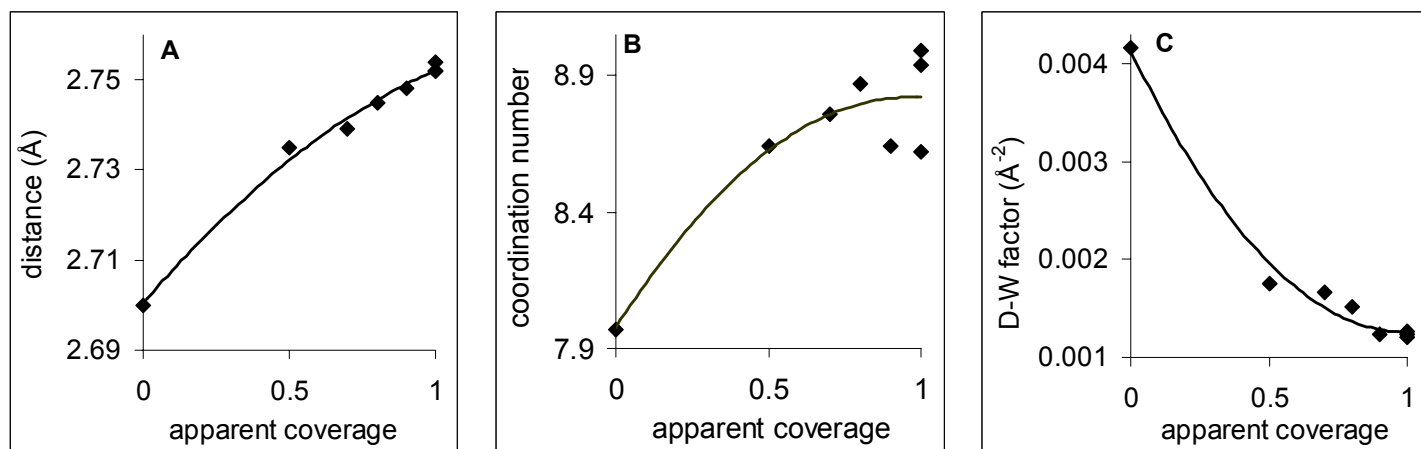


Figure 2. **A.** Pt-Pt distance, **B.** coordination number, and **C.** Debye-Waller factor in Pt/SiO₂ as function of the apparent hydrogen coverage, as obtained by EXAFS analysis of the Pt L₃ edge. $3 < k < 12 \text{ \AA}^{-1}$, $1.5 < R < 3.5 \text{ \AA}$, k weighting of 3, fitting in R-space. At an apparent coverage of 1, three points are given: for hydrogen pressures of 0.8, 1, and 2 bar.

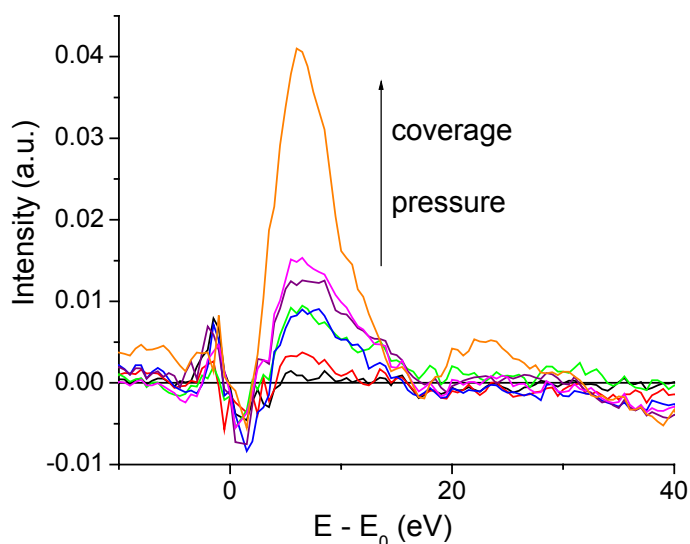


Figure 3. Difference of the Pt L₂ edges of PtAu/SiO₂ in hydrogen, at H coverages of 0.5, 0.7, 0.8, 0.9, and 1, with that in vacuum, 298 K.

When adsorbing hydrogen on supported PtAu alloy particles, a change in the L₃ and L₂ edges of both metals is observed, although the change is much less intense for Au than for Pt. The change in the Pt edges is less intense than for pure Pt particles (Figure 3), although the particle size is similar. In the fitting of the EXAFS, no distinction could be made between Pt and Au, since the backscattering amplitude and phase shift are similar. The EXAFS of the Pt L₃ edge was fitted with a Pt-Pt reference, and that of the Au L₃ edge with a Au-Au reference. Pt has 10 nearest neighbours in vacuum, which decreases to 9 in 1 bar hydrogen. This trend is opposed to that found for Pt/SiO₂. It suggests that the Pt atoms move to the surface of the particle, to be able to form a Pt-H bond, which is stronger than the Au-H bond. The number of nearest neighbours of Au is 7 and does not change with hydrogen coverage. Thus, the shape of the particle also changes.

Conclusion

The chemisorption of hydrogen induces a change in the Pt L_{3,2,1} XANES of 2 nm-sized Pt particles supported on SiO₂. The same change is observed in the Pt and Au L_{3,2} edges of Au/Al₂O₃ and PtAu/SiO₂, having particles of similar sizes. The shape and disorder of the Pt particles changes upon hydrogen adsorption. Furthermore, the contracted Pt-Pt bonds relax. These changes in the particle are not found for Au/Al₂O₃. The local geometry around the Pt atoms in PtAu alloy particles changes due to hydrogen adsorption, but in a different way than in pure Pt particles. The alloying with Au changes the interaction of supported Pt nanoparticles with hydrogen.

References

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