ESRF	**Experiment title:** Adsorption of hydrogen on supported Pt and Au catalysts: An *in situ* XAS study on the L_3 and L_2 edges	**Experiment number:** 01-01-661
Beamline: BM01B	**Date of experiment:** from: 30/06/2004 to: 02/07/2004	**Date of report:** 28/02/2005
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Introduction

Bulk gold is the least reactive metal considering the adsorption of atoms and molecules on the metal surface, but its properties change remarkably when it is highly dispersed and supported on a metal oxide [1]. Supported gold nanoparticles act as catalysts in oxidation reactions[1], but gold is also active in reactions involving hydrogen, such as the hydrogenation of alkenes, alkadienes, alkynes, and ketones, in hydrogenolysis, and in dehydrogenation reactions [2]. Chemisorption of hydrogen on supported gold catalysts is occasionally mentioned in literature and small or no amounts of chemisorbed hydrogen are reported [2]. We aim to provide insight into the chemisorption of hydrogen on supported gold nanoparticles under catalytic relevant conditions, by studying the chemisorption and Au-H interaction. To identify that the hydrogen is chemisorbed on the gold particles, the Au-H bond has to be observed. This can be achieved with X-ray absorption spectroscopy (XAS). It is well established and often observed that the chemisorption of hydrogen induces significant changes in the Pt L_2 and L_3 X-ray absorption near-edge structures (XANES) of supported Pt particles [3]. Here the adsorption of hydrogen on Au/Al_2O_3 as studied with *in situ* X-ray absorption spectroscopy is reported and compared to Pt/SiO_2.

Experimental

Catalyst preparation. Gold particles supported on γ-Al_2O_3 (Condea) were prepared by incipient wetness impregnation with an aqueous solution of $HAuCl_4$. The chlorine was removed by bringing the powder in excess water, stirring the slurry at 343 K and maintaining the pH at eight. The resulting white powder was dried at 363 K and stored in darkness. The gold content was 0.43 wt%. Pt/SiO_2 was prepared by adding an aqueous solution of tetraammine platinum nitrate (PTA) to a slurry of SiO_2 in a NH_4OH solution of pH 10. After adsorption of the PTA, the powder was filtered, washed, and dried at 373 K. The 1 wt% Pt/SiO_2 samples were pre-reduced at 423 K (Pt/SiO_2-A) or 873 K (Pt/SiO_2-B).

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 H_2 and cooled down in a H_2 flow to 298 K. At this temperature, XAS data for the L_3 and L_2 edge were collected in static hydrogen atmosphere. Subsequently, the cell was evacuated at 473 K for two hours to remove the adsorbed hydrogen. L_3 EXAFS and L_2 XANES spectra were collected under dynamic vacuum ($<10^{-4}$ mbar) at 298 K. All spectra were recorded in transmission mode using ion chambers. The incident X-rays are monochromated by a Si(111) channel-cut monochromator and harmonics are rejected by a chromium-coated mirror. 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 ($1.5 < R < 3.5$ Å), using a k weighting of 3. Experimentally calibrated theoretical references of gold and platinum foils, Au_2O_3, and PtO_2 obtained with the FEFF8 code were used. The pre-edge subtracted and normalized XANES spectra were aligned to remove initial state core level shifts and final state screening effects. The L_2 edges of the samples with and without chemisorbed hydrogen have the same shape at the onset, and thus were aligned on this onset. Ramaker *et al.* [4] state that after alignment the Pt L_2 edges overlay each other over about 60% of the height of the edge-step and therefore align the L_2 edges on 0.6 of their step height. This does not lead to a proper alignment of the Au L_2 edges, because they have a different shape compared to the Pt L_2 edges. A good alignment of the Au L_2 edges was obtained by aligning these on 0.4 of their step height. This also gave a good alignment of the Pt L_2 edges, thus the same procedure was used for Pt. The energy of the point in the L_2 edges having an intensity of 0.4 was set to zero. The L_3 EXAFS was then aligned on the corresponding L_2 EXAFS in the region between 50 and 120 eV over the edge using a least-squares method.

Results

The results of the EXAFS analyses for the samples measured in vacuum and in hydrogen atmosphere are listed in Table 1. The particle size is determined from the coordination number, assuming spherical particles. In Figure 1 the measured EXAFS function and its Fourier Transform, including the best fit, of Au/Al_2O_3 are shown. Pt-O and Au-O contributions of about 0.1 oxygen neighbors per metal atom could be fitted, but the amount is considered below significance. For spherical particles, a metal-oxygen coordination number of not more than 0.5 is expected for metal particles of 1 nm, assuming that a metal atom in contact with the support coordinates to two oxygen atoms. For bigger particles, the expected metal-oxygen *C.N.* is even lower. The interatomic distances in both the Pt and Au samples are lower than in the bulk, which is expected for small particles. This contraction of the distance in small particles is caused by the increased electron density between the atoms, due to dehybridisation of the spd metal orbitals [5]. This effect increases with decreasing particle size. The Pt-Pt interatomic distance of the small Pt particles increases upon chemisorption of hydrogen, because of the electron-withdrawing properties of hydrogen. For Au/Al_2O_3 a slight effect of hydrogen adsorption on the Au-Au interatomic distance is observed.

Table 1. Results of the first shell EXAFS analyses (k^3 weighting)

sample	**conditions**	**C.N.** [a]	**ΔR(Å)** [b]	**$\Delta\sigma^2(10^{-4}Å^2)$**	**ΔE_0(eV)**	**particle size (nm)**
Pt/SiO_2-A	in vacuum [c]	7.4	-0.06	35	1.4	1.2
	in hydrogen [d]	8.4	-0.02	20	1.9	
Pt/SiO_2-B	in vacuum [c]	11	-0.02	4	-1.8	5
	in hydrogen [d]	9.7	-0.02	-11	1.7	
Au/Al_2O_3	in vacuum [c]	4.3	-0.14	12	1	1
	in hydrogen [d]	5.3	-0.13	23	-2	

[a] Pt-Pt coordination number for Pt/SiO_2; Au-Au coordination number for Au/Al_2O_3. [b] *ΔR* is defined as the difference between the metal-metal distance found for the sample and that found for the metal foil, using the same Pt or Au reference.
[c] $1.5 < R < 3.5$ Å, $3 < k < 12$ Å^{-1}. [d] $3 < k < 8$ Å^{-1}

Due to the chemisorption of hydrogen, large differences occur in the Pt L_3 and L_2 edges of Pt/SiO_2-A and Pt/SiO_2-B, that are similar to those previously shown in literature [3]. The effect on the $L_{3,2}$ edges of Pt/SiO_2-A is larger, because the effect induced by hydrogen depends on the particle size. In Figure 2, the $L_{3,2}$ edges of Au/Al_2O_3 collected in hydrogen and in vacuum are compared. The differences as shown in the figure are obtained by subtracting the L_3 and L_2 edges in vacuum from those in hydrogen. A change is observed in both edges upon addition of hydrogen between zero and 25 eV over the edge. This range is the same as where the changes in the Pt edges appear. For Au, the intensity of the change in the edges is smaller than for Pt.

Conclusion

The *in situ* XAS experiments prove that hydrogen chemisorbs on the gold particles. Addition of hydrogen to Au/Al_2O_3 induces a change in the Au L_3 and L_2 X-ray absorption near-edge structures, similar to the change that occurs in the Pt $L_{3,2}$ edges upon hydrogen chemisorption. This makes *in situ* XAS also a tool for obtaining hydrogen binding sites on supported gold catalysts [4].

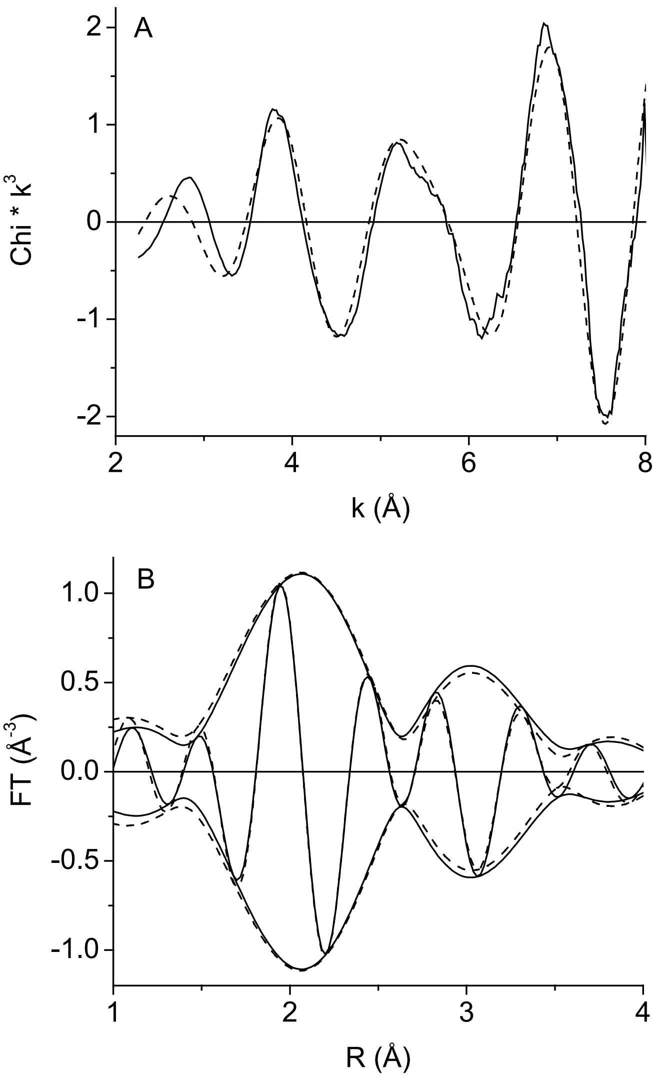

Figure 1. A. k^3-weighted EXAFS function of Au/Al_2O_3 in hydrogen (solid line) with best fit (dashed line) and **B.** corresponding Fourier transform (solid line) with best fit (dashed line) (R-space fit, $1.4 < R < 3.55$ Å, k^3 weighted, $3 < k < 8$ Å^{-1}). The fit parameters are as in Table 1.

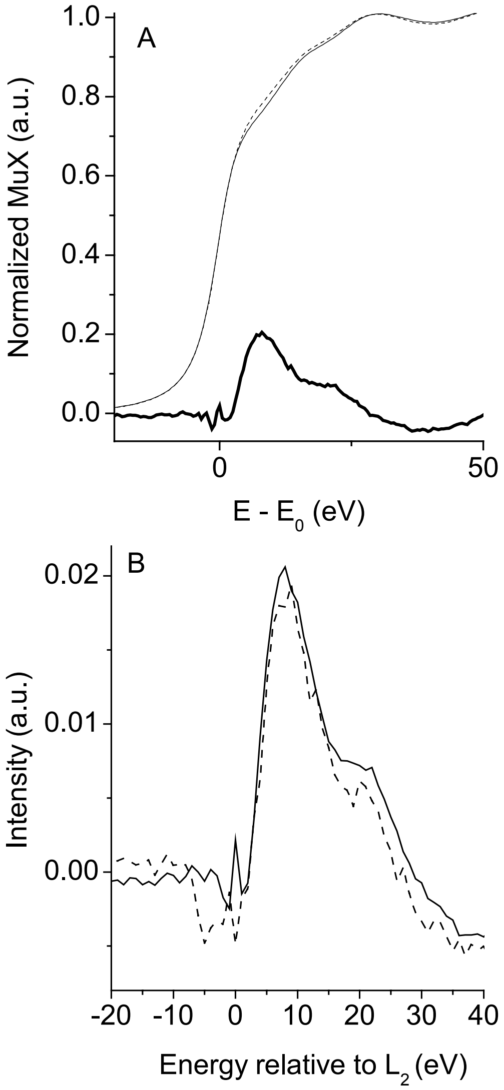

Figure 2. A. Au L_3 of Au/Al_2O_3 at 298 K measured in hydrogen after reduction at 473 K (dashed line), in dynamic vacuum after hydrogen removal by evacuation at 473 K (solid line), and the difference multiplied by ten (thick solid line). **B.** Differences in the Au L_3 (solid line) and Au L_2 (dashed line) edges induced by hydrogen (298 K).

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