



	<b>Experiment title:</b> Elucidation of the structure-activity relationship in selective oxidation reactions over supported Au catalysts: An <i>in situ</i> XAS study on the Au L <sub>3/2</sub> edges	<b>Experiment number:</b> 01-01-644
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<b>Shifts:</b> 12	<b>Local contact(s):</b> Wouter van Beek	<i>Received at ESRF:</i>
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## Report:

### *Introduction*

Bulk gold is unsuitable for application in heterogeneous catalysis, because of its weak interaction with adsorbates. If gold is highly dispersed and supported on a metal oxide, however, it is catalytically active in selective oxidation reactions, such as the oxidation of CO. It has been suggested that oxidic gold is more active in the CO oxidation than metallic gold<sup>1,2</sup>. The ratio of cationic Au to Au(0) should increase with the O<sub>2</sub>:CO ratio in the reaction mixture.

### *Experimental*

In this project the interaction of oxidic gold and TiO<sub>2</sub>-supported metallic gold particles with O<sub>2</sub>, CO, and a mixture of these is studied under catalytic relevant conditions. 3wt% Au/TiO<sub>2</sub> was prepared by deposition-precipitation, using HAuCl<sub>4</sub>·xH<sub>2</sub>O and TiO<sub>2</sub> Degussa P25 as the starting materials. After drying and calcination at either 423 or 473 K in air, gold particles of 1 to 5 nm were obtained, as determined with TEM. These samples, Au/TiO<sub>2</sub>-423 and Au/TiO<sub>2</sub>-473 (pre-calcined at 423 and 473 K respectively), were studied. Samples were pressed in a pellet and placed in the *in situ* XAS cell. First, X-ray absorption spectra of the Au L<sub>3</sub> and L<sub>2</sub> edge of the starting materials were recorded. Au/TiO<sub>2</sub>-473 was then reduced in 5% H<sub>2</sub>/He at 373 K. The hydrogen was removed and the sample was exposed to flows of CO, O<sub>2</sub> or a mixture of those in He, both at 77 K and 300 K, while recording EXAFS spectra. The interaction of CO with oxidic Au/TiO<sub>2</sub>-423 was studied at 77 K and 300 K. A fresh sample of oxidic Au/TiO<sub>2</sub>-423 was exposed to flows of CO, O<sub>2</sub>, and a mixture of those in He.

## Results

**Table 1. Results of EXAFS analyses**

Sample	shell	C.N.	R (Å)	$\Delta \sigma^2$ (Å <sup>2</sup> )	$\Delta E_0$ (eV)
Au/TiO <sub>2</sub> -473 starting material	O	4.1	1.98	0.0028	-1.97
Au/TiO <sub>2</sub> -473 reduced in H <sub>2</sub> at 373 K	Au	10.8	2.84	0.0010	1.36
Au/TiO <sub>2</sub> -423 starting material	O	3.9	1.98	0.0022	-2.82
Au/TiO <sub>2</sub> -423 reduced in CO at 300 K	Au	9.9	2.85	0.0087	-0.13
Au/TiO <sub>2</sub> -423 reduced in CO and O <sub>2</sub> and mixtures	Au	11.2	2.85	0.0016	2.34

In table 1 the results of the EXAFS analyses of the starting materials and the reduced Au/TiO<sub>2</sub> are shown. From previous experiments we know that after calcination at temperatures higher than 373 K, gold is metallic on TiO<sub>2</sub>. The EXAFS analyses show that during storage under ambient conditions the gold particles re-oxidize. The oxidic gold has the same structure in both starting materials, which is similar to that of bulk Au<sub>2</sub>O<sub>3</sub>. The supported Au(III) reduces to Au(0) in 5% H<sub>2</sub>/He at 343 K (Fig. 1 and 2). Gold particles are formed in which the first Au-Au C.N. is 10.8, corresponding to a particle size of 4 nm<sup>3</sup>. Subsequent exposure to 1% CO/He, at 77 K and 300 K, did not change the structure of the particles and no carbon scattering is detected with EXAFS. In a flow of 1% O<sub>2</sub>/He at 300 K, the gold particles do not re-oxidize (Fig. 3)

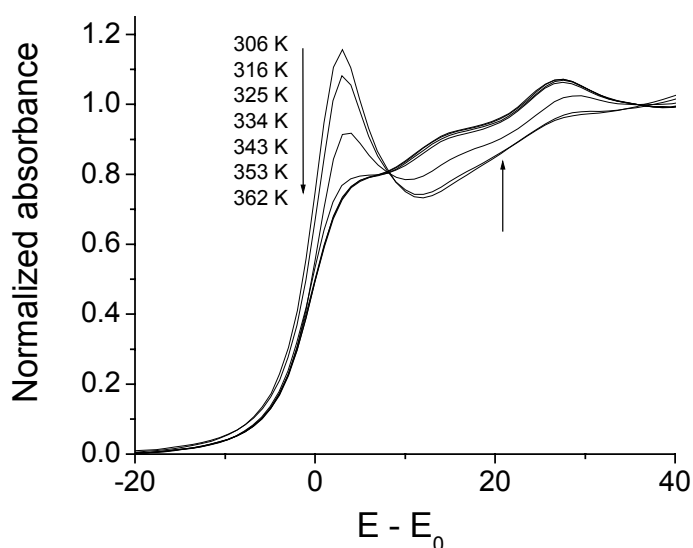


Figure 1. Au L<sub>3</sub> edge of Au/TiO<sub>2</sub>-473. The starting material is heated with 1 K/min in 25 ml/min 5% H<sub>2</sub>/He. Every nine minutes one scan is taken.

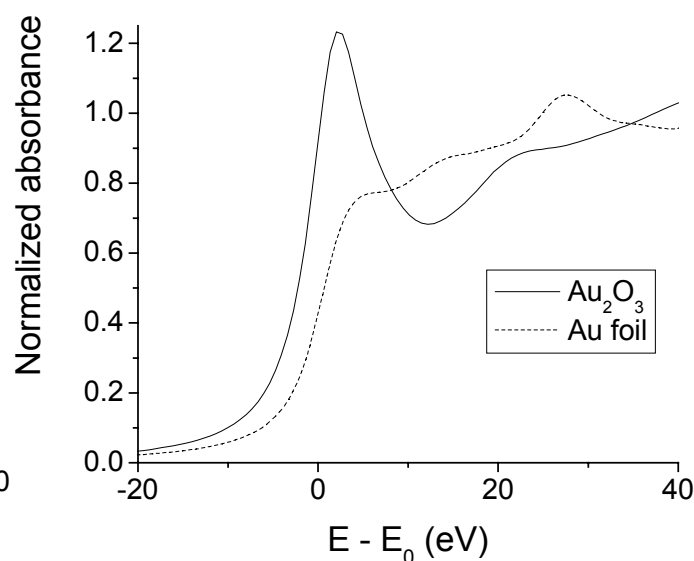


Figure 2. Au L<sub>3</sub> edge of Au<sub>2</sub>O<sub>3</sub> and Au foil.

In a flow of 1% CO/He at 300 K, Au(III)/TiO<sub>2</sub>-423 is converted within one hour to Au(0) (Fig. 4). We propose the following reaction:  $2 \text{AuO}_x + x \text{CO} \rightarrow 2 \text{Au} + x \text{CO}_2$ . Gold particles of 2.5 nm were obtained. In a flow of 5% O<sub>2</sub>/He the oxidic gold particles are also reduced, although at a lower rate than in H<sub>2</sub> or CO. In three hours, half of the oxidic gold is converted to the metal. In a mixture of CO and O<sub>2</sub> in He, oxidic gold decomposes, but slower than in the absence of oxygen. After several treatments with CO/O<sub>2</sub>/He at 300 K, the metallic gold does not re-oxidize in 5% O<sub>2</sub>/He, demonstrating a resistance to oxidation of supported gold. In

this sequence of treatments the particles sinter to an average particle size of 5.5 nm. No interaction with oxygen or carbon monoxide was detected in the EXAFS. The metal particles remained fully reduced.

Gates et al<sup>2</sup> studied gold particles of sizes comparable to ours, supported on MgO. They also find an increasing reduction of Au(III) upon exposure to higher CO partial pressure, whereas a raise of the O<sub>2</sub> partial pressure does not increase the percentage of oxidic gold. In their XANES experiments on the exposure of supported Au(III) to a mixture of CO and O<sub>2</sub>, they claim to see a conversion of Au(III) to Au(I) and Au(0)<sup>2</sup>.

We do not find evidence of the occurrence of Au(I) during treatment of Au/TiO<sub>2</sub> with CO and O<sub>2</sub>.

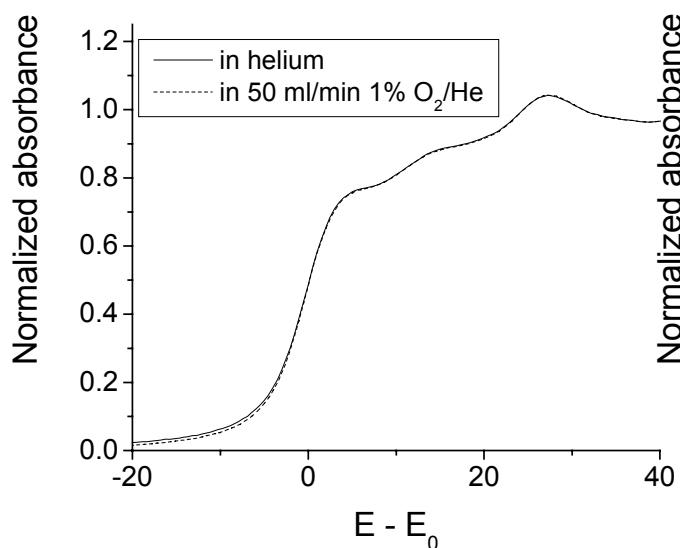


Figure 3. Au L<sub>3</sub> edge of reduced Au/TiO<sub>2</sub>-473 in static helium and in 50 ml/min 1% O<sub>2</sub>/He, 300 K.

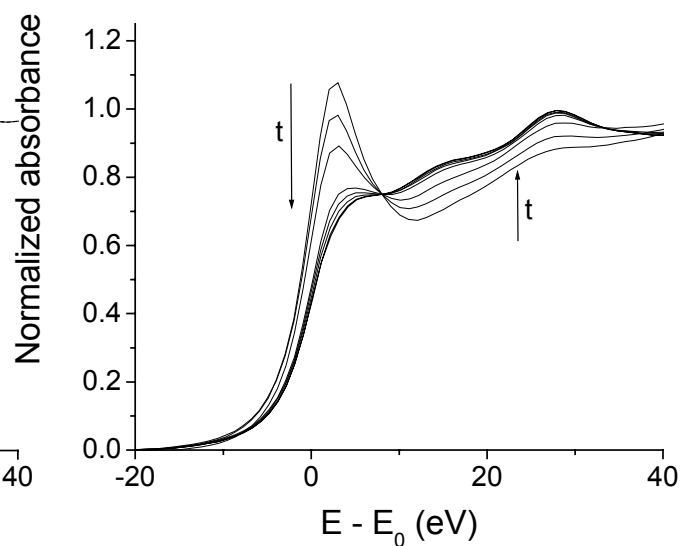


Figure 4. Au L<sub>3</sub> edge of Au/TiO<sub>2</sub>-423 in 50ml/min 5% CO/He, 300 K. Every nine minutes one scan is taken.

### Conclusion

Oxidic gold particles of 1-5 nm in size supported on TiO<sub>2</sub> are stable under ambient conditions. They are readily reduced to metallic gold in 5% H<sub>2</sub> and 1% CO at 300-350 K. Oxidic gold is active as a CO oxidation catalyst. However, the metallic gold particles do not re-oxidize in ≤ 5% O<sub>2</sub> at 300 K. No oxidic gold is detected under these conditions. On the contrary, in gas mixtures with an oxygen content of ≤ 5%, oxidic gold is decomposed, although slower than in the presence of the reducing agents hydrogen and carbon monoxide. The occurrence of Au(I) was not observed.

For the used gold particles of two to six nanometer in size, no adsorption of carbon monoxide or oxygen was observed in the EXAFS. This might mean that either Au particles of this size are too big to interact with these molecules. Another explanation is that we cannot detect the interaction, because it is too weak or because the percentage of gold atoms that acts as adsorption site is too low.

### References

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- (2) J. Guzman, B.C. Gates, *J. Am. Chem. Soc.* 126 (2004) 2672.
- (3) J. de Graaf, A.J. van Dillen, K.P. de Jong, D.C. Koningsberger, *J. Catal.* 203 (2001) 307.