



	Titre de l'expérience: Size and structure dependence of the catalytic activity of supported gold nanoparticles for CO oxidation	Experiment number: 32-02-688
Beamline: BM32	Date of experiment: from: 10/06/2008 to : 16/06/2008	Date of report: 26.09.2008
Shifts: 24	Local contact(s): Odile ROBACH	
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In the previous experiments, equivalent gold thickness between 0.4 to 3 gold monolayers (ML), were explored (RE n° SI1459, n° 32 02 648 and ref [1]). The quantitative analysis of the GISAXS pattern was performed using the dedicated *IsGISAXS* software [2]. The growth was found 3D and the particles were best modeled by a truncated sphere. The size of the nanoparticles, in UHV, ranged from 2 to 5 nm. The reaction rate per Au atom measured at 470 K was seen to increase as the cluster size decreases. Particles of size lower than 3 nm were stable under oxygen but sintering occurs when CO is added at 470K. That dimension coincides with the switch which was previously observed from nucleation-growth, with particles pinned on defects, to coalescence where particles become independent of defects [3]. However we did not succeed to simultaneously measure the activity and the size of the clusters by GISAXS. The link between them was obtained by complementary experiment at the laboratory.

During the June campaign at ESRF on BM32, we succeeded to do simultaneously such measurements; moreover we also performed GIXS (or Surface X-ray diffraction) and get the structure and the lattice parameter in the gold nanoparticles. We extend our study to smaller coverage, down to 0.1 ML.

Figure 1 shows examples of collected GISAXS patterns. For coverage, higher than 0.4 gold ML, there is one correlation peak on each side of the beam shutter footprint (which masks the reflected beam). In that case the interparticles spacing is centered around one value. In the case of thinner coverage, as illustrated for 0.2ML, there are two correlation peaks which correspond to two distances (one being close to the beamshuter). This is consistent with STM images (see right hand of figure 1), recorded for similar coverage, that shows clusters localized along the step of the substrate terraces, with two mains distances: along the step and perpendicularly.

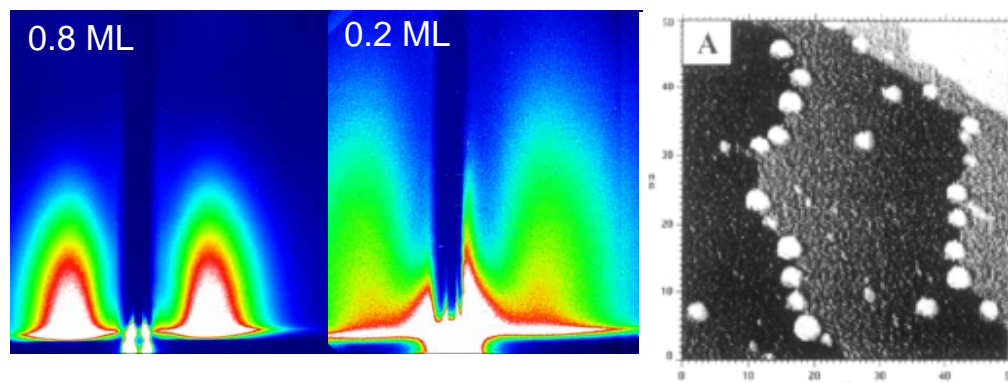
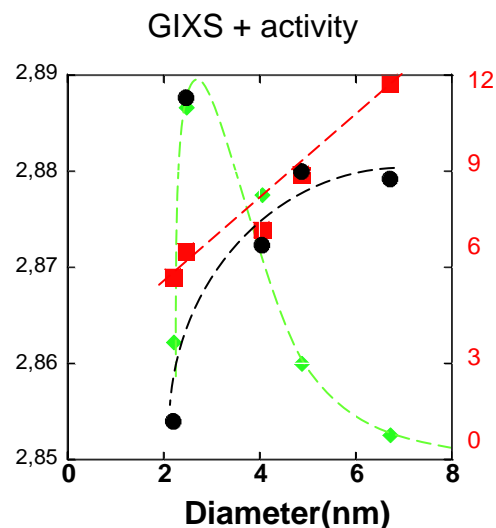
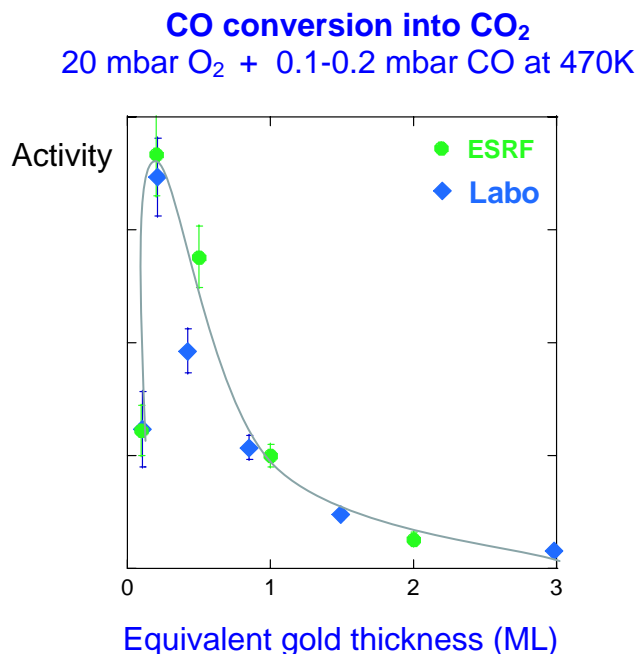


Figure 1: GISAXS pattern for gold equivalent thickness of 0.8 and 0.2 ML. The STM image corresponds to 0.1 ML (from [4]).

As previously, we observed, that under exposure to millibars of the reactive gas, particles were stable for equivalent coverage thicker than 1 ML, even under the reactive mixture O₂+CO at 470K. This 1 ML corresponds to particles with 3 nm size. Below they are instable and sintering occurred. Data were collected under CO and O₂ alone, and CO+O₂ at several temperatures in order to understand the sintering driving force, especially to determine the role of the increase of the local temperature due to the exothermic conversion of CO into CO₂. The analysis is presently under progress.

Whatever the gold coverage thickness, we were able to measure at 470K the CO conversion into CO₂ even for 0.1 ML. Figure 2 shows the rate per Au atom as a function of the deposited quantity. The results, obtained during the preparation at the laboratory follow the same variation as this found at ESRF during x-ray measurements, with a maximum for around 0.2ML. On figure 3, the rate (green curve) is plotted with nanoparticles parameters, as deduced by GIXS performed in the same time as the reactivity: diameter (horizontal axis), cluster height (red curve with the right hand vertical axis) and gold nanoparticles lattice parameter (black curve with the left hand vertical axis).



- Vertical axis of the black curve : $d_{\text{Au-Au}}$ in Å (left hand)
- vertical axis of the red curve : gold nanoparticles height in number of atomic plane (right hand)

The ESRF experiments being recent, the whole analysis is not complete, but first very important conclusions can be already drawn:

- The rate of CO conversion into CO₂ presents a maximum around 2.5 – 3 nm
- At the maximum, the particles clearly kept a 3D-character with at least 6-7 atoms-heights.
- A significant lattice contraction is evidenced.

The rate variation confirms the maximum in turnover frequency (TOF) observed by Valden *et al* [4] but it discards the metal non-metal transition (quantum size effect) as suggested by these authors.

On the other side it seems to be contradictory to Lopez *et al* [5] who attribute the activity to the increase of low coordinated sites concentration when decreasing the size, with no maximum. However, previous work shows that surface activity diminishes with a lattice contraction [6].

The open questions are thus: Is the measured lattice contraction enough to explain the observed drop of the activity for the smaller sizes? Does the substrate reducibility play a role or not in the behaviour of the activity versus size curve?

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