ESRF	**Titre de l'expérience:** **Size and structure dependences on the catalytic activity for CO oxidation of gold nanoparticles supported on an unreducible α–Al_2O_3(0001) substrate**	**Experiment number**: 32-02-696
Beamline: BM32	**Date of experiment:** from: 11/06/2009 to : 16/06/2009	**Date of report**: 30.10.2009
Shifts: 18	**Local contact(s)**: Odile ROBACH	*:*

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The goal of this experiment was to approach the role of the substrate on the correlation between the size and the catalytic activity of supported gold nanoparticles.

A preliminary study of the real-time growth mode of Au/Al_2O_3(0001) in ultra-high vacuum has been undergone as function of substrate temperate and evaporation rate. Calcium contamination of the surface due to segregation from the bulk was observed. We spared the beamtime to conclude our study on the gold nanoparticles on TiO_2.

Indeed, all our reactivity measurements, in the frame of carbon monoxide (CO) oxidation, at the laboratory exhibit a maximum of activity as a function of the deposited gold amount (see figure 1). GISAXS measurements allow the correlation of this maximum to particles with a diameter of about 3 nm.

So, the aim of these experiments, with our setup mounted on the BM32 beamline, was to collect data to understand this maximum. This corresponds to equivalent gold thicknesses below 0.5 monoatomic planes.

For such low coverage the nanoparticles are not stable, and we showed that their distribution is strongly anisotropic.

This is illustrated by the GISAXS patterns on figure 2. The upper patterns are in UHV and at room temperature. Changes were not observed at room temperature even under gas pressure.

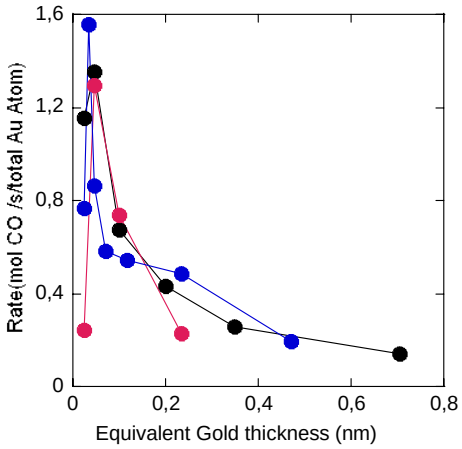

Figure 1 *: CO Conversion rate as a function of the deposited gold amount deposited on TiO_2(110) during 3 series of measurements at 473 K and when 20 mbar of oxygen + 0.2 mbar CO are introduced in the x-ray reactor-chamber*

At 473 K, particles become bigger and their density decreases. This is probably due to the thermal activation. When CO is added to Argon, no change is observed. But when it is added to oxygen a new sintering occurred. This can be linked to the local heating induced by the CO oxidation reaction itself.

We also observed that the GISAXS patterns and their evolution are direction dependant as also shown on figure 2. The distance between particles is initially higher along the dense rows of the TiO_2(110) surface than perpendicularly. The effect of gases is also stronger in this direction, indicating a larger mobility of the gold atoms along the rows.

Quantitative analysis is under progress to determine in each situation the size of the particles, their density to correlate them to the activity for CO oxidation.

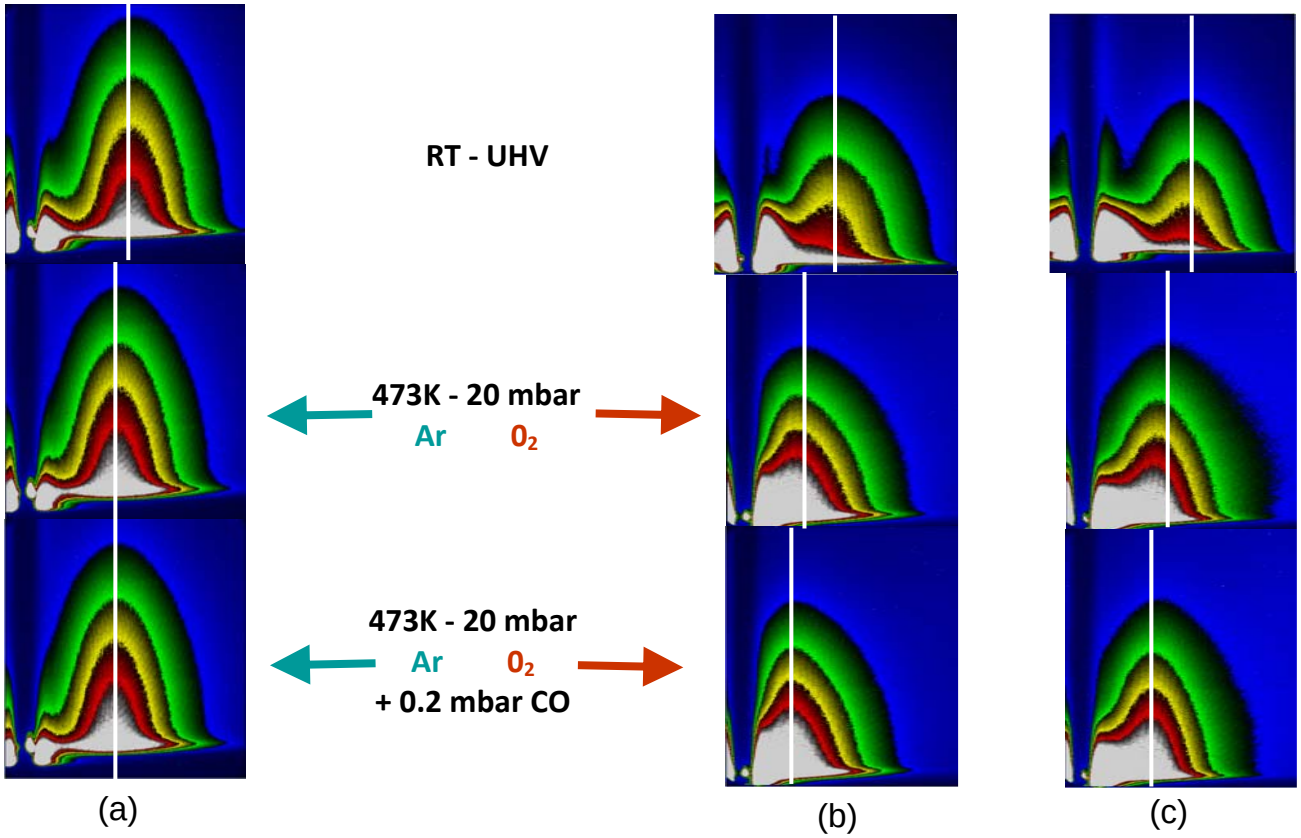

Figure 2 : *Evolution of the GISAXS patterns of a 0.04nm gold equivalent thicknesses, (a) and (b) in the direction parallel to the dense TiO_2 rows and (c) perpendicularly. In (a) Oxygen was replaced by the inert Argon.*

Together with GISAXS, we also collected diffracted intensity. This is illustrated on Figure 3 which shows its evolution along an azimuth scan through an in-plane gold peak. We observed three peaks : the central one, corresponding to the (111) epitaxy of gold with its dense rows parallel to the one of the TiO_2(110) substrate, and two satellites at ±4.5° which are attributed to rotational gold epitaxy.

For the highest diameter the satellites are small relatively to the central one. The diffracted intensity does not evolve significantly under oxygen and during reaction conditions. For the smallest particles, in UHV the peaks are broad and weak; but under reaction the lonely satellites grow up. For intermediate diameter the three directions have roughly the same importance.

Regarding the lattice parameters, deduced from a preliminary analysis, those for the smallest particles with the rotational epitaxy, are deformed compared to the gold bulk ones with a dilatation in one direction and a small contraction in the two others. Such a result must be founded by a systematic quantitative analysis to determine if it can be correlated to the high catalytic activity of the supported gold nanoparticles.

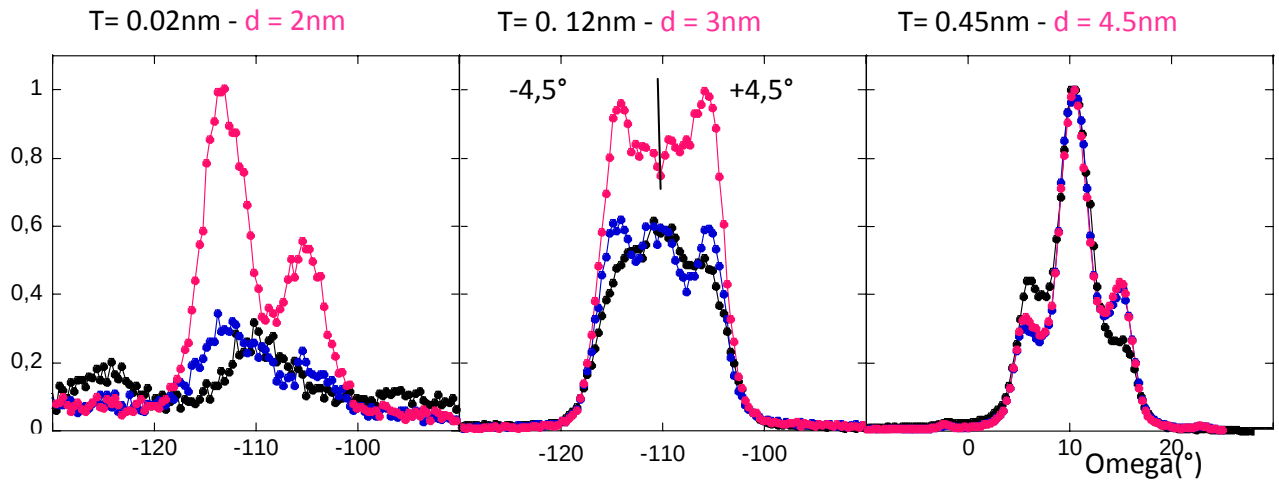

Figure 3 *: Evolution of the diffracted intensity for an azimuth scan around an in-plane gold peak,(i) black curve : in UHV at Room temperature, (ii) blue one: under 20 mbar O_2 at 473K and (iii) pink : 20 mbar O_2 + 0.2 mbar CO at 473K .T is the equivalent gold thickness and d the diameter under the reactive mixture as deduced from GISAXS.*