ESRF	**Experience title:** **Investigation by GISAXS of the influence of H_2 on the CO oxidation on TiO_2-supported gold nanoparticles.**	**Experiment number**: SI 1459
Beamline: BM32	**Date of experiment:** from: 23/01/2007 to : 29/01/2007 from: 31/01/2007 to : 8 /02/2007	**Date of report**: 1/10/2007
Shifts: 24	**Local contact(s)**: Odile ROBACH	*Received at ESRF:*

Names and affiliations of applicants :
Marie-Claire Saint-Lager, Pierre Dolle, Stéphanie Garaudee, *Institut Néel-MCMF CNRS- Grenoble*
Rémi Lazzari, Jaques Jupille, Miguel Mantilla, *Institut des NanoSciences de Paris – CNRS-UniversitéParis 6-7*

The beamtime allocated by the ESRF committee followed the one allocated by the CRG committee, we report here only on a part of the whole results, the other part being the object of the Experimental Report n° 32-2-648.

GISAXS, as well as GIXS, were performed under several conditions: under oxygen, CO pressures between 1 to 100 mbar, as well as under CO + O2 reactive mixture (total pressure 10 to 20 mbar) with the ratio CO:O2 between 1:2 and 1:100; GIXS are discussed in the other report.

Several gold deposit thicknesses were explored from 0.5 to 7Å. For the larger nanoparticles, we detect no change in the GISAXS pattern. In contrast for the smaller ones – the more reactive- we observed an evolution as shown for an 1 Å gold deposit recorded at room temperature (figure 1) and at 200°C (figure 2). This thickness corresponds to a particles size of 1-2 nm. The two figures show that the main effect occurs under the reactive mixture pressure (panels c). A deeper analysis is needed to quantify the effect, the first explanation being a sintering of the nanoparticles i.e. an increase of their size and a decrease of their density. These changes are more pronounced at 200°C.

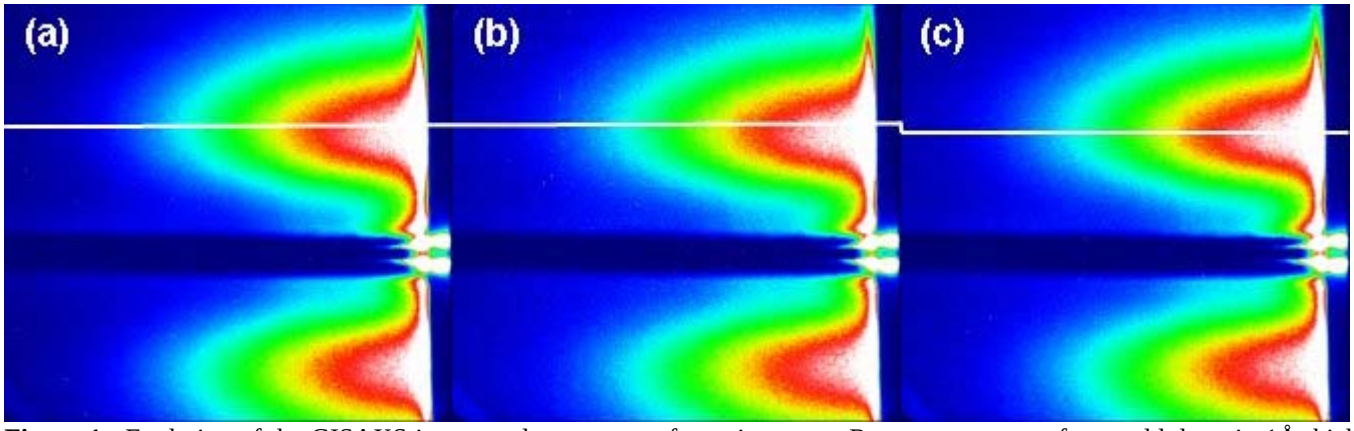

Figure 1 : Evolution of the GISAXS image under pressure of reactive gas at Room temperature for a gold deposit, 1Å thick, (a) in UHV, (b) under 20 mbar O_2 and (c) during CO oxidation (20mbar O2 + 0,1 mbar CO).

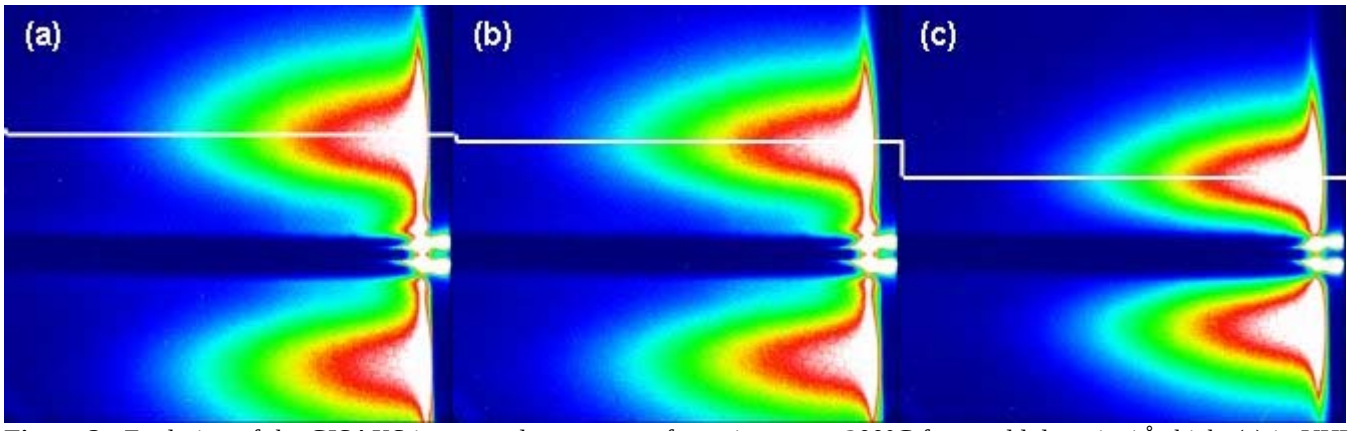

Figure 2 : Evolution of the GISAXS image under pressure of reactive gas at 200°C for a gold deposit, 1Å thick, (a) in UHV, (b) under 20 mbar O_2 and (c) during CO oxidation (20mbar O2 + 0,1 mbar CO).

The images above show that the same pressure of oxygen alone has not the same effect. We also observed that the influence on the particles morphology of CO pressure alone is negligible, even at higher pressure, than in the reactive mixture as illustrated on figure 3.

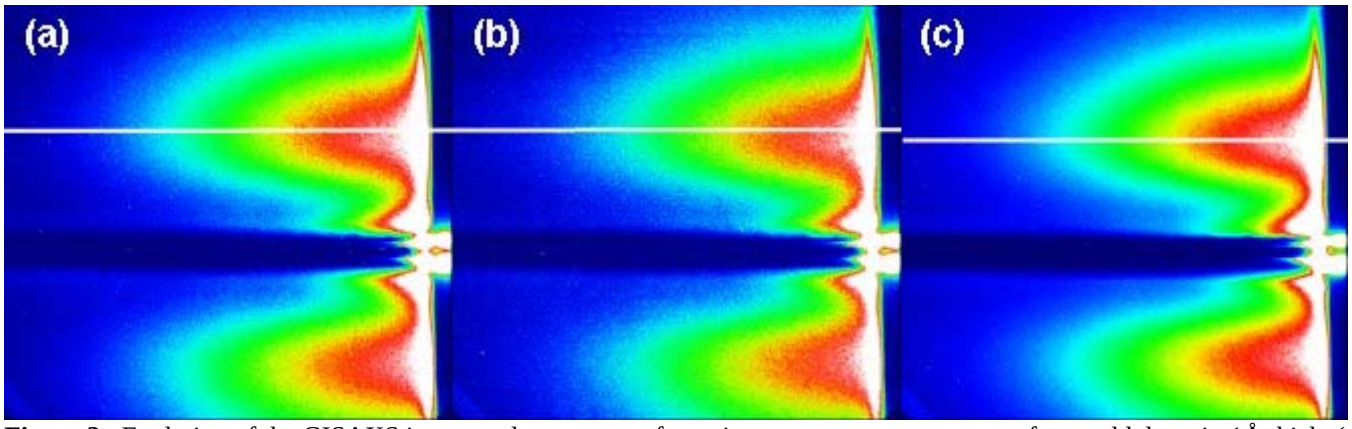

Figure 3 : Evolution of the GISAXS image under pressure of reactive gas at room temperature for a gold deposit, 1Å thick, (a) in UHV, (b) under 10 mbar O_2 and (c) during CO oxidation (20mbar O2 + 10 mbar CO).

Anyway even if these effects stay subtle at room temperature it is clear that pressure of reactive molecule induces morphological changes of the nanoparticles. As reported in RE n° 32-2-648, we also observed modification of their crystallography. But here an increase of their size needs:

(i) either an exchange of gold atoms from one aggregate to the other ; this phenomenon called Ostwald ripening is due the gradient of chemical potential between small and big particles that might be influenced by the adsorbed gases.

(ii) or an enhanced mobility of the whole cluster under gases.

Surprisingly enough, it is only for particles of 1-2 nm that change in morphology are observed. But this effect stays small and does not forbid to stabilize gold nanoparticles actives for CO oxidation.

We also measure the reactivity of the gold nanoparticles as illustrated on figure 4. The partial pressure of oxygen, CO and CO2 was followed by a mass spectrometer connected to the x-ray reactor through a leak valve[1].

We observed that the reactivity increases as particle size decreases without decrease at low size. This is in contrast with published STM measurements which evidence a maximum activity for 3nm particles[2].

Moreover, these measurements allowed an optimization of the partial pressure ranges for reactivity measurements, showing in particular that the turnover varies as d^n, where d is the particle diameter and n is an exponent lying between 1 and 2.

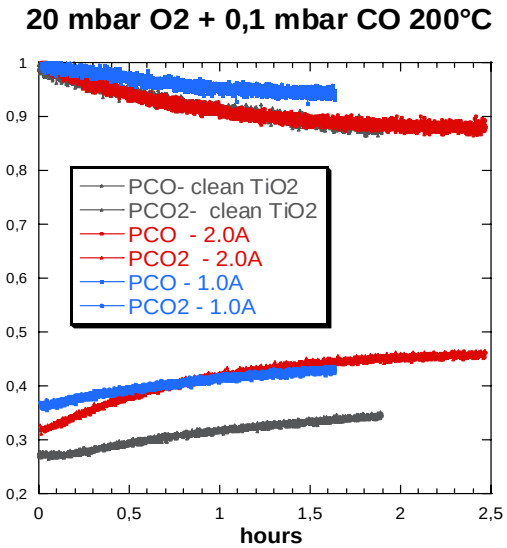

Figure 4 :
Variation of the 28 and 44 mass signal as recorded by the spectrum analyser during exposure of gold deposit 1 and 2 Å thick.

Such observations open a way to establish a *quantitative* relationship between size and reactivity that is a clue to answer the strongly debated pathway of reaction. This is one of the aim of a further proposal.

[1]M.C. Saint-Lager *et al* Rev. Sci. Inst. 78, (2007) 083902

[2] M. Valden, X. Lai and D. W. Goodman, Science 281 (1998) 1647.