

Understanding Fundamental Processes on Au-Ag Catalysts during Oxidation Reactions: a Correlative Microscopy Approach

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Gold catalysts have attracted much attention since the discovery of the remarkable catalytic activity of very small (2-5 nm) supported gold nanoparticles, especially for low temperature oxidation reactions of small organic molecules and CO. More recently, gold-based alloys, in the form of supported and unsupported catalysts, present increased catalytic performances due to synergistic effects between the two metals [1]. Au-Ag alloys are amongst the most promising systems for deNO_x and oxidation catalysis applications. Indeed, on the one hand, silver, with its relatively high chemical activity, can dissociate molecular O₂ providing O(ads) species necessary for oxidation reactions. On the other hand, the relative inertness of gold prevents surface species to undergo complete oxidation and thus enhances the selectivity to desired products, already at low temperatures such as 273 K. The use of alloys in particles of more than 10 nm diameter enables to overcome the well-known issue of size-dependent activity present for pure gold catalysts. The ability to control the surface composition in order to fine-tune the quantity of silver atoms at the surface is mandatory to adjust the catalytic properties of the material. Low concentrations of surface silver will lead to small amounts of O(ads), favoring partial oxidations and high selectivity. An excessive silver concentration will shift the selectivity to complete oxidation products. Besides the influence of the chemical composition on the reaction dynamics, the influence of other physicochemical parameters such as temperature, morphology, size and crystallographic orientation of the samples has to be considered in order to establish a complete picture of the relevant phenomena.

Field Emission Microscopy (FEM) and PhotoEmission Electron Microscopy (PEEM) are used for studying different morphologies and different compositions. FEM needs samples prepared as sharp tips whose extremity mimics a single catalytic nanoparticle. By electropolishing an Au-8.8%at. Ag wire, it is possible to obtain sample diameters of 20-100 nm, which can then be imaged in “Ionization-FIM” mode **Figure 1.a** (top left). In favorable conditions, it is possible to image the surface of the sample with atomic lateral resolution. Comparison with a ball model of the same *fcc* crystal structure (**Figure 1.a** (top right)) allows to determine the crystallographic orientation and the different facets of the sample. In “Emission-FEM” mode, the reaction dynamics are monitored via the local current density of emitted electrons. For a constant field, contrasts arise from local variations of the surface work function that translate variations of the composition of the adsorbed layer. Here, N₂O is used and appears to dissociate over metallic surfaces. O(ads)+H₂ reaction is studied and turns out that the reactivity presents an important structure sensitivity in the temperature range 300-320 K. Bright circles and dark regions, as they can be seen in **Figure 1.a** (bottom), showing zones of localized dissociation of N₂O and reactive interfaces where H₂O is formed. N₂O dissociates over facets of high kink sites density, *i.e.* {012}, forming N₂(g) which readily desorbs and O(ads). Adsorbed oxygen is known to increase the work function of both Au and Ag surfaces, therefore decreasing the brightness of the micrographs. At temperatures higher than 320 K, an increased

mobility of the species leads to the disappearance of structure sensitivity and to an overall homogeneous reactivity, which is seen as a rather homogeneous FEM brightness pattern [2,3] (**Figure 1.b**).

Complementary experiments to FEM/FIM were performed in PEEM in the presence of O₂, H₂ and CH₃OH. On a Au(111) single crystal, Ag has been evaporated to obtain different Ag surface concentrations, from 0 to 3 ML (monolayer). Reference experiments in PEEM and by quadrupole mass spectrometry (QMS) on a pure Au(111) crystal didn't show any catalytic activity. Samples with a silver concentration from 0 to 3 monolayers of silver were prepared and analyzed in a temperature range of 300-473 K. The overall catalytic activity during the experiments was surprisingly low: during PEEM experiments, moderate changes of the brightness were observed and associated to a low reactive sticking coefficient of oxygen. Similarly, in QMS, small variations of the product signals were observed.

The combined use of electron microscopies operating at different length scales and with different samples allowed to get a better understanding of the catalytic properties of Au-Ag materials. To some extent, the complexity gap encountered between studies on model surfaces and catalytic nanoparticles can be bridged. PEEM and FEM experiments indicate that the (111) orientation is of low reactivity whereas vicinal and more open facets are more active. Accordingly, surface morphology seems to be a key factor for explaining the catalytic activity of Au-Ag catalysts. Further work on samples with different architecture and crystallographic structures is necessary [4].

References:

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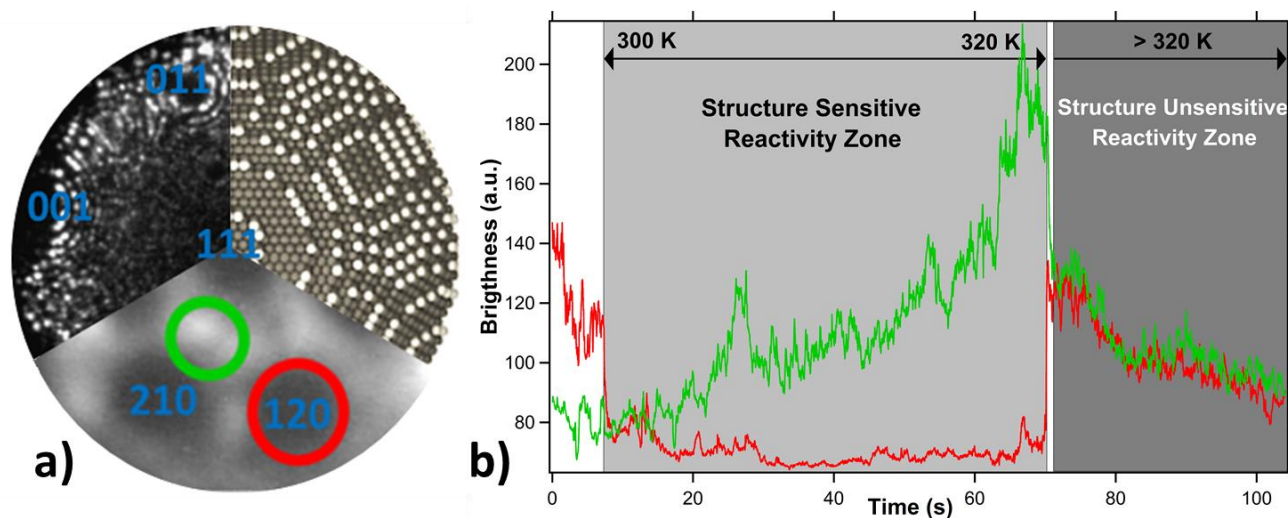


Figure 1. a) Left, top: FIM micrograph of a clean Au-8.8at.%Ag tip. Right, top: Corresponding computed ball model. Bottom: FEM micrograph showing the electron emission pattern during N₂O+H₂ reaction with bright interfaces around the {012} facets indicating water formation at 310 K. Imaging conditions: $P_{\text{tot}} = 3.5 \times 10^{-3}$ Pa, $T = 310$ K, $F = 5.5$ V/nm. **b)** Brightness signal recorded in the red and green circles shown in Fig.1a) illustrating the evolution of the structure dependent reactivity with increasing temperature.