

(S)TEM analysis of structural modifications at nano-sized Au||ceria-oxide interfaces

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Structural investigation of Heterogeneous Catalysts has benefited from the new capabilities of aberration corrected equipment. It is also true that catalysts are often a source of new challenges for Electron Microscopy. More particularly, aberration corrected microscopes have been exploited to analyse fine details of the surface of catalyst nanoparticles [1], very recent examples having dealt with such characterization even under environmental conditions [2]. It is also well established that in the case of supported catalysts, in which a substrate is used to disperse the catalytically active phase, the support material can largely influence the behaviour of the supported phase. In the case of supported metal catalysts such modification is associated to so called metal-support interaction effects. Though such interaction can take place through different mechanisms it seems reasonable that metal||support interface is the place through which it is established. From this, it turns that characterizing the structure of such interfaces is a requirement to understand in full detail the behaviour of this type of systems. This is a quite challenging task in the case of supported catalysts given not only the usual size of the interfaces involved, of just a few nanometers, but also to the intrinsic characteristics of this type of materials, complex aggregates of largely overlapping nanocrystals randomly oriented with respect to the electron beam.

In this contribution we present the results of an in-depth study of structural modifications taking place at the interface of Au nanoparticles supported on a reducible $\text{Ce}_{0.5}\text{Tb}_{0.12}\text{Zr}_{0.38}\text{O}_2$ mixed oxide catalyst after activation in a reducing environment at mild temperatures, 200°C. A structural analysis based on HREM and STEM-HAADF images recorded in aberration corrected microscopes is complemented with parallel analysis of the oxidation state of Ce in the catalyst by STEM-EELS. Microscopy data are used to rationalize the changes observed in the chemical properties of the 1.5% wt Au/ $\text{Ce}_{0.5}\text{Tb}_{0.12}\text{Zr}_{0.38}\text{O}_2$ catalyst after reduction at 200°C, in particular the CO adsorption capacity inhibition observed after this particular treatment. The whole set of results obtained by (S)TEM allows establishing a clear correlation between catalyst pretreatment–interface structure and chemical properties. They also illustrate the high potential of the AC-(S)TEM approach in the analysis of metal-support interaction effects, even in the most difficult cases.

Measurement of CO adsorption capacity of the 1.5% wt Au/ $\text{Ce}_{0.5}\text{Tb}_{0.12}\text{Zr}_{0.38}\text{O}_2$ catalyst by volumetric methods indicate a decrease in the total CO adsorbed onto the metal phase close to 50% after reduction in H_2 at 200°C, as compared to the values observed for the same catalyst oxidised at 250°C. A comparative analysis of AC-HREM and AC-HAADF images obtained on both, the oxidised and reduced, catalysts, performed by measurements of distances observed in intensity profiles recorded along lines crossing the interface between gold nanoparticles and support, evidenced slight differences in the distance between the last cation plane at the support side of the interface and the first plane of metal atoms at the nanoparticle, Figure 1. Such differences, with values in the range 0.028 – 0.035 nm are clearly visible by the shift of the trace corresponding to the reduced catalyst with respect to that of the oxidised one. To allow for sub-pixel resolution and thus improve the accuracy of distance measurements, all the intensity profiles were fitted to sets of Gaussian functions. Distance measurements were then obtained from differences between the

corresponding optimized maxima values resulting from fitting. Likewise, in the case of AC-HAADF images, the column ratio mapping technique was applied to improve accuracy in their quantitative analysis.

From the analysis of a large number of interfaces on both catalysts, a statistically significant difference of this interface structural parameter could be established. Thus, the average values obtained for the two catalysts were 0.298 ± 0.003 nm (oxidised) and 0.285 ± 0.005 nm (reduced). These two distance ranges do not overlap this meaning that they are clearly distinct. In fact, 85% of the measurements made on the oxidised catalyst were larger than the average value of the reduced one. Likewise, 77% of the measurements made on the latter were smaller than the average value observed for the oxidised catalyst. These results evidenced a rapprochement of the Au nanoparticles towards the support surface in the reduced catalyst, this suggesting a tighter binding of the nanoparticles after reduction.

Quantitative analysis of fine structure details of STEM-EELS data recorded on the two catalysts evidenced the presence of larger amounts of reduced Ce^{3+} species at the gold||ceria-oxide interfaces of the reduced catalyst. This result suggests that the structural change could be linked to support to metal electron transfer effects, which is in good agreement with previous Au-4f XPS results. Moreover, a detailed analysis, by nanoparticle modeling, of the distribution of Au atoms at the surface of the whole ensemble of nanoparticles present in the catalyst allows us interpreting, in exact quantitative terms, the decrease of CO adsorption capacity as due to deactivation of just the metal atoms located at the metal-support interface, very likely as a response of the metal-support electronic interaction effect detected by AC-microscopy.

References

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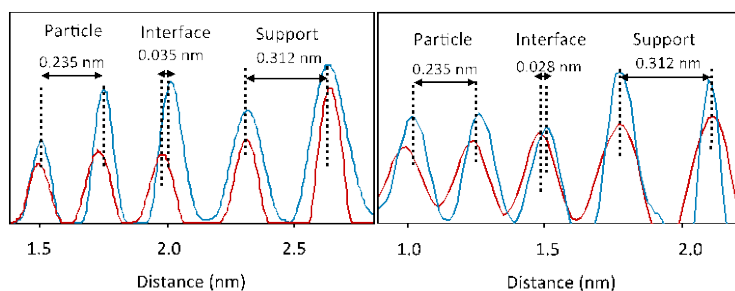


Figure 1.- Superposition of intensity profiles recorded from the AC-HAADF images (left) of the oxidized catalyst (dark trace) and the reduced catalyst (light trace); (right) the same but starting from AC-HREM images. In both plots, maxima corresponding to the oxide support have been aligned.

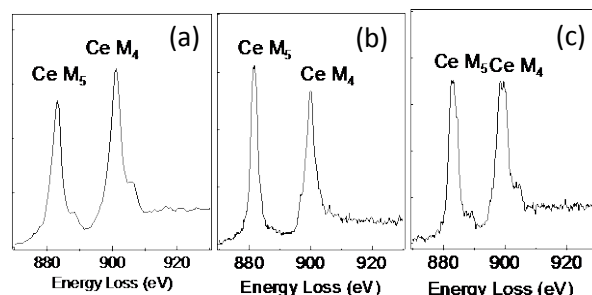


Figure 2.- EELS: (a) oxidized catalyst at metal-support interface sites; (b) reduced catalyst at metal-support interface sites; (c) reduced catalyst at support sites near the metal particles.