# Stressing the benefits of combining 3D and 2D (S)TEM studies for physical-chemical parameters estimations of heterogeneous catalysts: when quantification is addressed

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The application of electron tomography in the field of heterogeneous catalysis has grown considerably in recent years. Whereas initial applications were mainly focused on obtaining qualitative information (mostly related with nanocrystal morphologies or spatial distribution of catalyst particles), more recent works begin to explore the possibility of going beyond by extracting also quantitative information from 3D reconstructions. In particular, procedures to extract numbers out of these reconstructions to characterise physical-chemical parameters relevant to this type of materials as it is the case of metal loading and/or specific surface area. Hence, there is strong interest to improve these quantification procedures and recent advances related either to the 3D reconstruction techniques or image processing has been published very recently. [1-4]

The reliability of these 3D procedures have been demonstrated; in some cases, by comparison with well-established macroscopic techniques. It is frequent in this case that, even counting on high quality reconstructions, a certain mismatch is observed between parameters obtained by electron tomography and those coming from macroscopic techniques. As we propose in this contribution, to understand these differences and also to improve the estimations based on the microscopic approach, the simultaneous use of 2D and 3D electron microscopy techniques is necessary; this combination providing additionally a much more accurate methodology to quantify catalyst physical-chemical parameters. In addition, we intend also to illustrate how the two approaches (2D vs 3D) provide the complementary information required to get a more detailed view of catalyst materials. To illustrate these ideas we will discuss different cases in which the synergy of combining 2D and 3D studies to get accurate quantifications and characterization is evidenced.

First case refers to a Au/CeZrTbOx catalyst which it was investigated with the purpose of quantifying several key parameters supposedly related to its catalytic performance: specific surface area of the cerium mixed oxide support and, on the other hand, the metal loading and spatial distribution of the gold active nanoparticles. These studies were carried out using HAADF-STEM based tomography and the corresponding 3D reconstruction was achieved using the SIRT algorithm, followed by manual segmentation. Concerning the specific surface area values determined from the 3D reconstructions of the CeZrTbOx support, a quite good agreement was found with the experimental value determined by the B.E.T., nitrogen physi-sorption, method. In the estimation of gold total loading, resolution of the 3D reconstructions allowed a good segmentation of the two components of the catalyst (metal and support) even in this case which involves a metallic phase supported on a heavy oxide (Figure 1). From the segmented volumes of metal and support crystallites, the gold metal loading could be estimated, but a value differing by 33% to that determined by direct chemical methods (ICP) was observed. This difference stems from the fact that 3D reconstructions did not consider particles contained within the larger fraction of sizes which in fact were observed in the 2D histogram established from HREM and HAADF-STEM images. When the 3D loading value is corrected with the contribution to the total mass of the larger particles, which can only be very precisely done in a reasonable time on the basis of the 2D histrogram, a quite good agreement with the ICP value was observed. These results point out the importance of using simultaneously 2D and 3D information to obtain accurate estimates of supported phase loadings, in

cases like the one discussed here where coexistence of both small and medium sized particles are present in the catalyst, a quite common situation.

Focusing now on the determination of spatial distribution of the dispersed nano-sized gold particles, the 3D studies of the same catalyst mentioned before, did show a strong preferential location onto nanocrystal boundaries and stepped regions of the oxide support (Figure 1). The 3D reconstructions indicated also that the surface crystallography of the CeZrTbOx mixed oxide support was dominated by {111} facets, consisting mainly of octahedral crystallites, of just a few nanometers, joined to one another, possibly by twinning on {111} facets. 2D HREM images showed that the structural stability for such arrangement could reside on the epitaxial growth of the metal nanoparticles onto the underlying oxide support, as shown in Figure 1-Right. Boundaries and stepped regions allow increasing the contact area between metal and support. Therefore, the atomic resolution information provided by HREM studies allowed in this case understanding those features characterized by the 3D studies, another way in which the complementarity of both techniques becomes extremely useful. Further examples will also be shown which support the complementary, rather than exclusive, character of the two, 2D vs 3D, approaches.

It is finally also important to point out that quantitative estimates based on 3D STEM as those mentioned in this abstract, rather than to be used as alternatives to other well established macroscopic techniques, should be always aimed at providing clues about how well the nanostructural data obtained, either by 2D or 3D (S)TEM analysis represent the actual macroscopic material. This is of large importance in the case of materials intrinsically as heterogeneous as catalysts frequently are.

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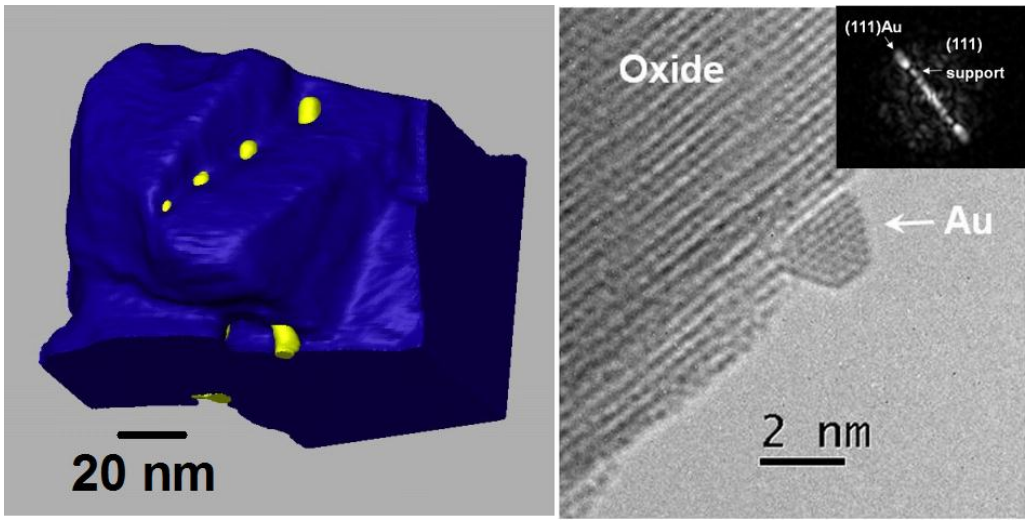


***Figure 1.*** *(Left) 3D reconstruction of Au/CeZrTbOx catalysts. (Right) HREM micrograph showing epitaxial relationships between a gold nanoparticle and the cerium-based support crystallite.*