Understanding catalytic properties of nanoalloys by using aberration corrected electron microscopy in gaseous environment


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Catalysis is involved in most of industrial chemical processes for refining, pollution control and synthesis of chemicals. Heterogeneous catalysis has always used nanoparticles in order to maximize the surface/volume ratio of active particles. Therefore, “particle size effect” is a well-known concept of catalysis. Moreover, combining metals within catalysts can improve catalytic performances with respect to pure metals, e.g., increased selectivity or resistance to poisoning. The “alloying effect” is classically ascribed to either electronic structure or active site geometry. However, this phenomenon is poorly understood and controlled, due to the difficulty to elaborate homogeneous collections of multimetallic nanoparticles with imposed composition, and to the lack of structural characterization.

Our general objective is to get insights into the interplay between the structure of nanoalloys (Pd-Au, Au-Cu and Pd-Ir on oxide supports) with well-controlled size and composition and their catalytic properties. For that purpose, we have synthesized and characterized supported bimetallic nanoparticles, and analyzed their catalytic behavior by using a MEMS-based technology developed by Protochips Inc.. This MEMS gas cell allows to image and to follow the dynamics of nano-objects in an encapsulated gas environment as a function of the temperature. By combining this technology with our JEOL ARM 200F cold FEG aberration correction microscope, we can obtain images of nano-materials with an information limit better than 0.8 nm under 1 bar gas pressure and at 1000°C (Fig. 1).

From the study of the above systems, we want to address, by using this instrumentation, the following fundamental questions:
- How does the structure of supported nanoalloys depend on particle size and bulk phase diagrams (total miscibility for Pd-Au and Au-Cu vs. miscibility gap for Pd-Ir)?
- How does the chemical structure (ordering, random alloying, partial segregation, core-shell, etc.) of the nanoparticles influence their catalytic properties towards the series of selected prototypic catalytic reactions (oxidation, hydrogenation...)?
- How does the nature of the support drive the structure of the nanoalloys? What is the particle-support interface structure?
- How do temperature and gaseous environment affect the structure of the nanoalloys? Can we gain insights into the atomic mechanisms of sintering, redispersion and strong metal support interaction (SMSI effect)?

The concepts are not new but the methodology is novel and promising thanks to the recent development of gas cells technology that allows reproducing the real operando conditions.
Fig. 1: (a) TiO$_2$ substrate classically used in catalytic reactions with nanoalloys imaged under 1 bar pressure of O$_2$ and at 1000°C (with a JEOL ARM 200F cold FEG microscope equipped with an aberration corrector of the objective lens). (b) Enlargement of the rectangular area in dotted line of (a).