In-situ E-TEM study of bimetallic TiO_2 supported copper-gold nanocatalysts under oxydizing (O_2) and reducing (H_2) atmosphere

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Supported bimetallic copper-gold nanoparticles (NPs) are of interest to heterogeneous catalysis as they often perform better than their monometallic counterparts in many oxidizing and reducing reactions [1]. If the effects of the metal alloying on the catalytic performances of Cu-Au NPs are undeniable, the origin of these effects is still largely unknown. This stem from the lack of direct observations of the NPs in their reaction environments, *i.e.*, at high temperature and high pressure. In this contribution, we present *in situ* gas TEM studies of the morphological and chemical transformation of Au, Cu and Cu-Au nanoparticles under oxidizing (O_2) and reductive (H_2) atmospheres as a function of gas pressure and temperature, using windowed-cell environmental transmission electron microscope (E-TEM).

Mono- (Au, Cu) and bimetallic Cu-Au NPs were fabricated by pulsed laser deposition [2] and deposited on rutile-TiO_2 nanorods [3]. *In-situ* E-TEM was performed in an environmental-cell designed by Protochips Inc. using state-of-the-art Micro-Electro-Mechanical System technologies and were conducted in gas environment up to atmospheric pressure and a temperature of 600 °C. Figure 1a shows an HAADF-STEM image of a Cu NP under 0.5 atm of O_2 at 400 °C. In these environments, the initial metallic structure (Cu^0) of the NP is fully oxidized to a cuprite structure (Cu_2O). The resulting morphology is a truncated octahedron, bounded by (111) and (100) facets. Figure 1b shows the same particle under 0.5 atm of H_2 at 400°C. Under reductive atmosphere, the cuprite structure remains stable. However, one can observe that the (111) and (100) facets have slightly changed. This implies a change in surface energy of these two facets, induced by the change of the reaction medium.

Similar temperature- and gas-induced structural changes have been observed in Au and Cu-Au NPs. These observations will be presented and discussed to highlight the effect of alloying gold and copper on their structural stability in reactive conditions.

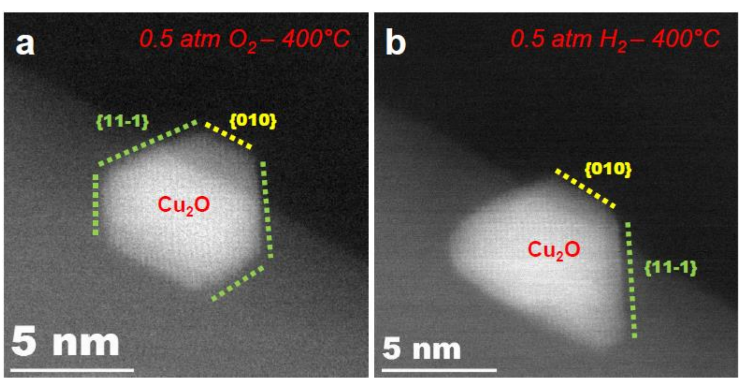

Figure 1. STEM-HAADF images of a rutile-TiO_2 supported Cu nanoparticle under 0.5 atm of O_2 (a) and H_2 (b), at 400°C.

References:
[1] C.L. Bracey, P.R. Ellis and G.J. Hutchings, "*Application of copper-gold alloy in catalysis: current status and future perspectives*", Chem. Soc. Rev., 38, pp. 2231-2243 (2009) .

[2] H. Prunier et al., Phys. Chem. Chem. Phys., (2015),17, 28339-28346.

[3] CH. Li et P. Afanasiev, Mater. Res. Bull. 46 (2011), p.2506-2514.