Microsc. Microanal. 25 (Suppl 1), 2019

doi:10.1017/S1431927618015891

Revealing the Surface Energetics and Reactivity of Bimetallic Copper-Gold Catalyst Nanoparticles by *In Situ* Environmental TEM

Jaysen Nelayah[1], Adrian Chmielewski[1], Damien Alloyeau[1], Hakim Amara[2], Jérôme Creuze[3] and Christian Ricolleau[1]

[1.] Université Paris Diderot, Sorbonne Paris Cité, CNRS, Laboratoire Matériaux et Phénomènes Quantiques, UMR 7162, 75013 Paris, France.
[2.] LEM, Unité Mixte CNRS / ONERA, 29 Av. de la Division Leclerc, 92322 Châtillon, France.
[3.] ICMMO - UMR 8182 - Bât. 410, Université Paris-Sud 11, 15 rue Georges Clemenceau, 91405 Orsay Cedex, France.

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 stems 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 will present *in situ* studies of the morphological and chemical transformations of Au, Cu and Cu-Au nanoparticles at elevated temperature both in vacuum and under O_2 and H_2 atmospheres using windowed-cell environmental transmission electron microscope (ETEM).

Supported mono- (Au, Cu) and bimetallic Cu-Au NPs were fabricated by pulsed laser deposition [2]. ETEM experiments were performed on a JEOL JEM-ARM200F spherical-aberration-corrected microscope using a Protochips gas cell. In the first part, we will present an original approach based on bulk plasmon nanothermometry using aluminum nanospheres to determine local temperatures in a gas cell under operation [3]. With access to local temperature under operating conditions, we will assess the thermal homogeneity and stability across the heater region of our Protochips gas cell and the effects of increasing gas pressure on the local temperature.

Then, we will discuss the thermal stability of SiN-supported Au-Cu NPs heated in vacuum up to 800 °C. In particular, we will present a robust methodology to experimentally determine the absolute surface energy of bimetallic nanoalloys using *in situ* TEM imaging. This methodology relies on the real-time monitoring of the evaporation of bimetallic NPs in vacuum and the extension of the Kelvin equation to two-component systems. In Cu-Au nanoalloys in liquid state, the determination of the absolute values of the surface energy suggests that their surface energy follows a Vegard's law-like behavior. These experimental observations are confirmed by Monte Carlo simulations which bring additional insights into the structural stability and thermodynamic properties of Cu-Au NPs both in solid and liquid states [4].

The final part will focus on sintering dynamics and structural evolution of TiO_2-supported Au, Cu and Cu-Au nanoparticles under oxidizing O_2 and H_2 atmospheres up to atmospheric pressure and temperatures up to 600 °C. Figure 2a 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 2b shows the same particle under 0.5 atm of H_2 at 400°C. Under the reductive atmosphere, the cuprite structure remains stable. However, one can observe that the extension (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 respective structural stability under reaction conditions. [5]

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[5] The authors acknowledge funding from the French National Research Agency through the TOTEM project, Grant Number ANR-17-CE07-0031.

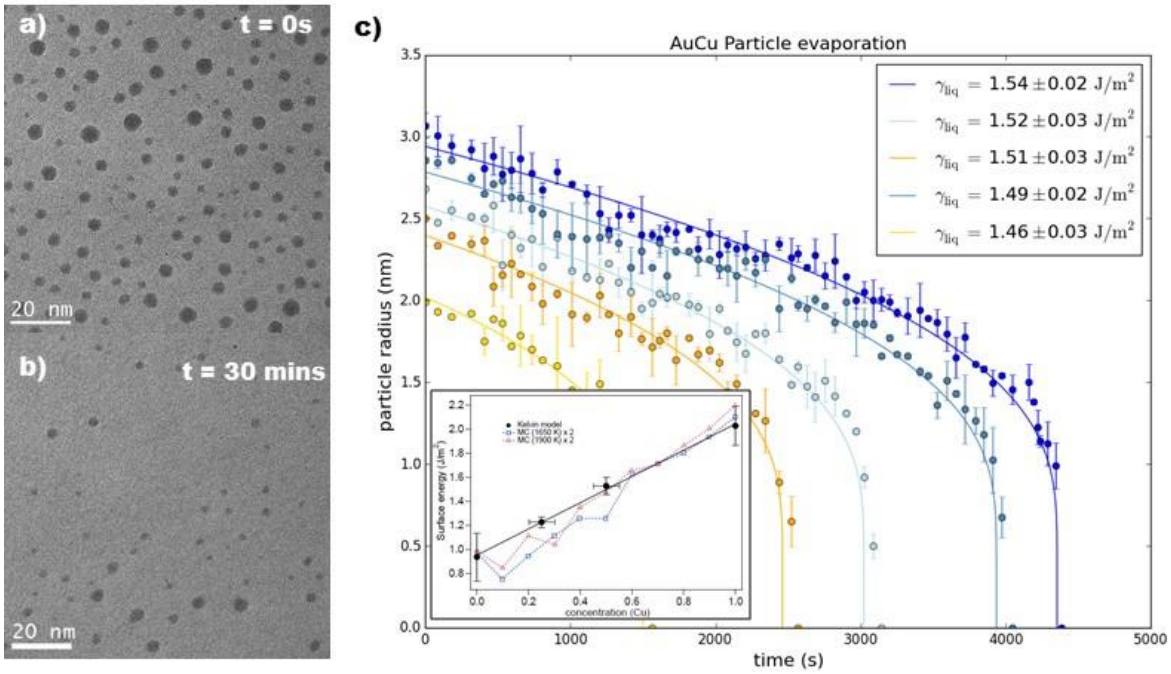

Figure 1. TEM images of the evolution of CuAu NPs at 700 °C at (a) t = 0 s and (b) t = 30 mins. (c)Variation of the radii of six CuAu NPs with time. Insets: corresponding extracted surface energies (right), variation of the surface energy of Cu-Au NPs in liquid state with comosition, blue-red lines are Monte Carlo simulations, the full black line is a linear fit of experimental data (left).

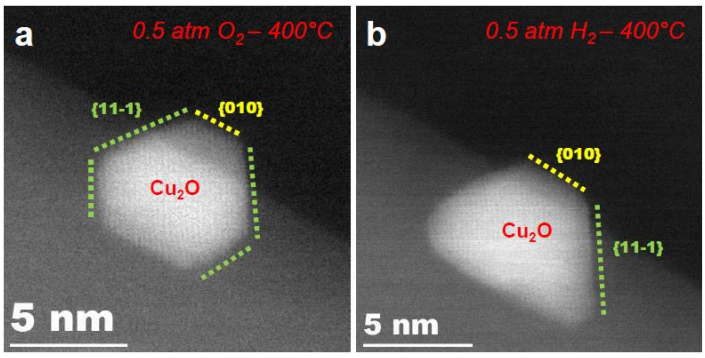

Figure 2. HAADF-STEM images of a rutile-TiO_2 supported Cu nanoparticle under 0.5 atm of (a) O_2 and (b) H_2 gases at 400°C.

https://doi.org/10.1017/S1431927618015891 Published online by Cambridge University Press