Catalyst Nanoparticles from a Genetic Algorithm

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Nanoparticles and clusters are known to display unique properties compared to their bulk counterparts depending on their size, structure and composition, e.g. increased (electro-)catalytic activity and novel alloy stoichiometry, but their inherent meta-stability remains a challenge for practical applications. This is particularly true for core-shell type particles or binary compositions such as Pt_xM_y used in electrocatalysis for the oxygen reduction reaction (ORR) [1] and Cu-Au [2] and Cu-Ni [3] alloys for CO_2 fixation into fuels, where an alloying element is used to optimize the binding energy of a reaction intermediate on the surface.

Whereas the stoichiometry and composition of bulk alloys are generally well defined, the particle structure and surface composition will be particular sensitive to the particle size, stoichiometry and reaction conditions. The ability to predict - and ultimately - design stable nanoparticles with specific surface compositions is thus of great importance. Here, we present a new and efficient approach for determining and optimizing the composition and structure of alloy nanoparticles and clusters based on a genetic algorithm and database techniques suitable for density functional theory (DFT) [4, 5] or other electronic structure methods.

In the presented work 309 atoms Cu-Nu and Au-Cu particles were investigated with the genetic algorithm and optimized for composition and structure. The most favorable structure found for the Cu-Ni particle is icosahedral, with a pure Cu shell (162 atoms) and a pure Ni core (147 atoms) [6]. The most preferred Au-Cu particle structure is also icosahedral with a single element core, in this case made from Cu. Different from the Cu-Ni particle the Au-Cu particle prefers a shell structure that is dominated with Au, but has a single Cu atom on each of the particle facets (see figure 1).

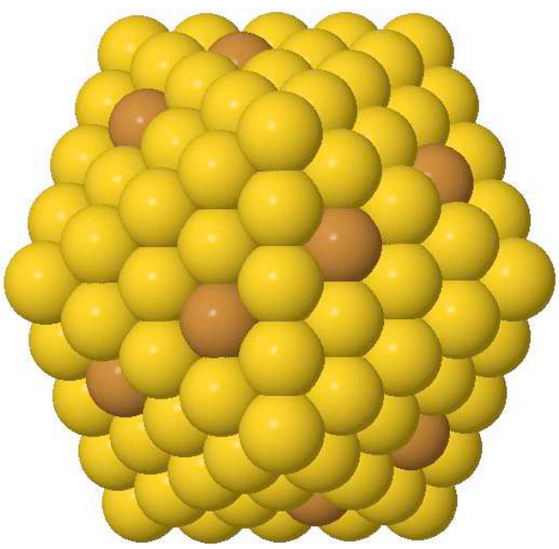

Figure 1: Most preferable structure and composition of a 309 atoms Au-Cu nanoparticle found with help of the genetic algorithm. (Au: yellow, Cu: brown)

The genetic algorithm also makes it possible to investigate what effect reactive conditions have on the catalyst particles, by simulating a reservoir of gaseous species that can be adsorbed onto the particle. In figure 2 a 309 atoms Ni-Cu particle can be seen in a simulated oxygen rich environment. The oxygen binds more favorably to the Ni than the Cu, causing the Ni to be dragged out to the surface of the particle [6].

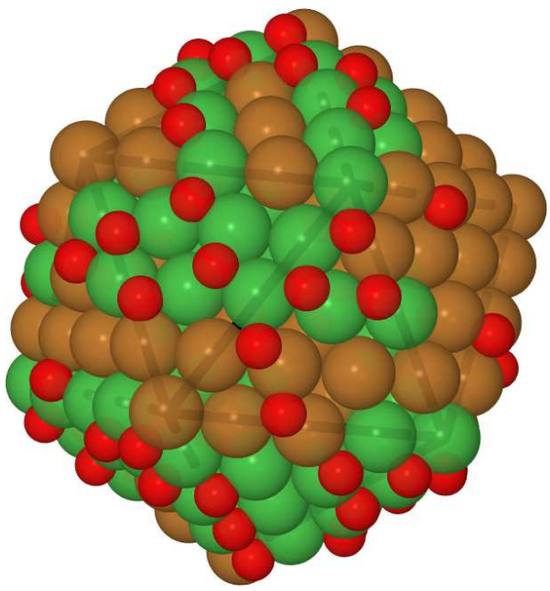

Figure 2: A 309 atoms Ni-Cu particle in a simulated oxygen rich environment. Adsorbed oxygen forms a stronger bond with Ni, compared to Cu, this results in a preferred higher surface concentration of Ni in the particle compared to the same particle in vacuum. (Ni: green, Cu: brown, O: red)

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