# DFT Calculations Reveal the Rules for the Design of Promising Single-Atom Alloy Catalysts

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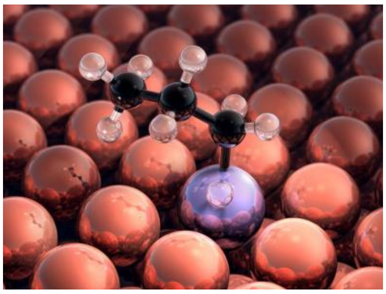
Single-Atom Alloys (SAA) are an emerging class of materials which have shown extraordinary development in recent years for applications in catalysis. They consist of coinage metal nanoparticles (Cu, Ag or Au) doped by substituting distant surface atoms by more active transition metal atoms. This doping strategy turns poorly reactive nanoparticles into catalysts with activities similar to pure transition metal nanoparticles and enhanced resistance to deactivating reactions (e.g. coking), thereby yielding longer lifespan. Despite these attractive properties, SAA catalysts escape the traditional trends used in heterogeneous catalysis (e.g. d-band center). Although this makes their design more complicated, it opens new opportunities in terms of attainable chemistries.

In order to better understand and predict the reactivity of SAAs, we considered two large screening studies aiming at identifying descriptors that capture the binding energy of catalytically relevant adsorbates at their surface. Using DFT calculations, we first identified the atomic charge of the dopant (arising from the electronegativity difference be dopant and the host) and the carbophilicity of the dopant as good descriptors for the binding of adsorbates on SAAs. It turned out that the binding energies of electron-rich adsorbates ($H_2O$, $NH_3$, OH) were well described using the atomic charge of the dopant (electrostatic interaction dominating). For dopant/adsorbate bonds that had a stronger covalent character, the binding energy of carbon was much better descriptor.[1] Our second screening studied aimed at gaining more insight into the binding mechanism of covalently bound species and providing an electronic understanding of the covalent bond. Considering 3d, 4d and 5d dopants in Cu, Ag and Au surfaces, we showed that binding energies were the strongest when the number of electrons brought by the dopant and the adsorbate abide by a rule of 10.[2] We showed that this corresponded to the saturation of the d-orbitals which provided increased stability to the metal/adsorbate bond. We showed that altogether these rules enabled the identification of the right dopant for a reaction of industrial interest, namely the reduction of nitrogen to ammonia.

All in all, these two studies provide unprecedented insights into the reactivity of single atom alloys and can serve as a guide for the design of new catalysts. It also contributed to the paradigm shift of the understandings of chemical bonds on metal surfaces.



C-H activation of propane on RhCu SAA (the Rh dopant is represented in blue)

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[1] R. Réocreux, E. C. H. Sykes, A. Michaelides, and M. Stamatakis, JPCL 13 (2022), 7314-7319

[2] J. Schumann, M. Stamatakis, A. Michaelides, R. Réocreux, Nature Chemistry 16 (2024), 749–754.

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