

Redox chemistry of Au on metal-doped Calcium Oxide: A comprehensive model for factors governing the dopant-induced stabilization

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The co-presence of electron donors and acceptors within an oxide has been shown to lead to a strong interaction between the species¹. This interaction manifests itself, for example, in a larger binding energy of Au (electron acceptor) onto a Mo (electron donor) -doped CaO compared to a pristine oxide². The binding energy of the metal to the oxide surface is one of the key factors affecting the growth mode and shape of the catalytically active metal particles. For rationalizing the notable increase (1.5-2.5 eV, depending on the adsorption site) of the binding energy of Au onto a CaO surface after Mo-doping, we employ density functional theory calculations and introduce a scheme that breaks the adsorption energy into contributions from the ionocovalent bond formation between the Au and the CaO surface, electron transfer (Mo → Au) induced modifications in the Mo-oxide and Au-oxide adhesions, and electrostatic interaction between the Au and Mo through the dielectric. Comparing the different contributors, the energy gain upon the electron transfer (redox reaction between Au and Mo) is clearly the highest. Coulombic interaction plays a role only at the relatively small Au-Mo distances (<10 Å), but redox induced stabilization survives constant upon increasing Au-Mo distances. Moreover we find that Mo can empty its valence states completely adopting an oxidation state of +6. Replacing Mo with Cr reduced the stabilization effect for Au adsorption and our results show that maximum oxidation state of Cr is +4. By varying the dopant metal we are able to show that the stabilization effect correlates well with the third ionization energy of dopant in gas-phase.

References

- ¹H. Metiu, S. Chretien, Z. Hu, B. Li and X. Sun, *J. Phys. Chem C* **116**, 10439 (2012).
- ²X. Shao, S. Prada, L. Giordano, G. Pacchioni, N. Nilius and H.-J. Freund, *Angew. Chem. Int. Ed.* **20**, 11525 (2011).