Trends in the Catalytic CO oxidation Activity of Nanoparticles

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Introduction
While extended gold surfaces are generally considered chemically inert [1], nanosized (<5 nm) gold particles can be very effective catalysts for a number of oxidation reactions [2-5]. There are reports of similar size effects for silver catalysts [6]. The origin of the nano-effects in the catalytic properties of these metals is widely debated [5], and no consensus has been reached yet. Based on a set of density functional theory calculations we compare the catalytic activity for the CO oxidation reaction over extended surfaces and small nano-particles of a number of metals.

Materials and Methods
The results are based on density functional theory (DFT) calculations. The Kohn-Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies up to 408eV (30 Ry). The density cutoff is 816 eV. The core electrons are treated with Vanderbilt non-local ultrasoft pseudopotentials.[8] Exchange-correlation potential and energy are described employing the RPBE generalized gradient correction self-consistently.[7] Finally the DFT results are combined with a microkinetic model .[9]

Results and Discussion
In figure 1a and 1b, we present a measure of the catalytic activity for the CO oxidation over (a) extended surfaces and (b) metal nano-clusters. For the extended surfaces the activity is calculated at high temperature conditions (T=600K, p_{O2}=0.33 bar and p_{CO}= 0.67 bar) and for the metal nano-clusters at low temperature conditions (T=273 K, p_{O2}=0.21 bar and p_{CO}=0.67 bar). While Pt and Pd are the most active catalyst for extended surfaces at high temperatures, Au is the most active for very small particles at low temperature. The calculations capture the special catalytic properties of nano-sized particles observed experimentally. The adsorption energies shift substantially depending on the coordination number of the metal atom. Adsorption on the low coordinated metal atoms in the nano-clusters is stronger than adsorption on the highly coordinated metal atoms in the extended surfaces. This is the dominant reason why gold becomes the best catalyst for small nano particles.

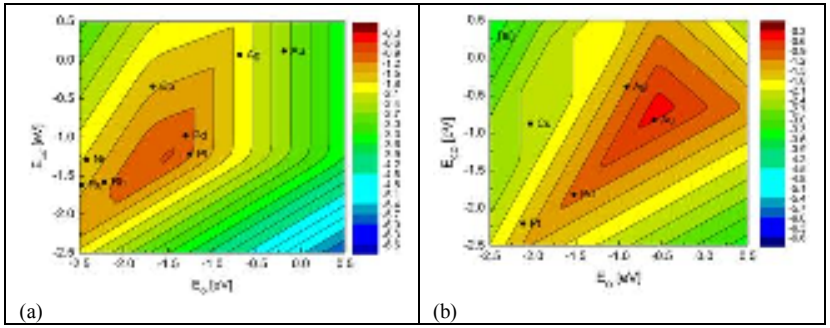

Figure 1, Contour plot of a measure of the catalytic actvity for CO oxidation as a function of the CO and O adsorption energies on (a) 111 surfaces and (b) 12-atom clusters. The values for some elemental metals are shown.

Significance
The present analysis suggests that the maximum in reactivity moves toward more noble metals, when the coordination number of the metal atoms is lowered. The results suggest that similar results can be obtained for other catalytic reactions.

References
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