Physical and Chemical Properties of Supported Platinum Clusters

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Introduction
In several applications of heterogeneous catalysis the active catalyst are transition metal particles dispersed on porous ceramic supports. From a computational chemistry point of view these systems are challenging. They consist of different kinds of chemical bonds, ranging from metallic to covalent and ionic which all have to be described with high accuracy. Moreover, the geometrical symmetry of the system is low, making the problems computationally demanding. These issues have resulted in a slow development of the theoretical understanding of supported metal particles and the metal-oxide interphase and it is only recently that these systems have been addressed from first principles [1-3].

In the present contribution we present results for the physical and chemical properties of small platinum clusters supported on MgO(100) and BaO(100). The systems are technologically important, for example, in oxidation of methanol in presence of NH3 (Pt/MgO) and NOX storage catalysts (Pt/BaO). Our results shed light on important issues such as catalyst deactivation due to sintering, the influence of the support on the chemical properties of platinum as well as the modification of the platinum/metal-oxide interface upon adsorption of CO.

We use the Density Functional Theory (DFT) [4] in the pseudo potential - plane wave implementation [5]. Slab geometries with periodic boundary conditions are employed to model the oxide surfaces. To investigate the role of different approximations to exchange and correlation effects we have performed calculations in both the Local Density Approximation (LDA) and a gradient corrected functional (PBE).

Results
The performance of our computational approach was investigated by calculations of structural (lattice constant, relaxation, rumpling) and energetic (surface energy, bulk modulus) properties of the bulk and different surfaces for MgO, BaO and Pt. In all cases our results compare favorably with previously reported theoretical as well as experimental data. The small effects of relaxation in MgO allowed us to model the surface with only two layers. For BaO, on the other hand, the surface was modeled with three layers.

The characterization of the metal/metal-oxide bond included calculation of the charge difference. In Figure 1 we show the results for a single platinum atom adsorbed atop an oxygen anion on BaO(100). The oxygen site was found to be the stable geometrical configuration.
Figure 1. The charge difference ($\Delta \rho = \rho_{\text{system}} - \rho_{\text{MgO}} - \rho_{\text{Pt}}$) for one platinum atom adsorbed on BaO(100). Platinum is blocked by the iso-surfaces. The dark iso-surface indicates charge gain, whereas bright indicates charge depletion. The iso-surfaces are at $\pm 0.05$ e/Å$^3$. The curve to the right is the integrated charge density along the coordinate of the surface normal (e/Å). Only the region near the Pt atom is displayed.

The charge redistribution upon adsorption is to largest extent caused by minimization of Pauli repulsion. Charge is depleted from the oxygen out-of-plane component, as well as metal states directed towards oxygen. O-states in the surface plane gain charge, so is metal states not directed towards the surface. From the integrated $\Delta \rho$ it is clear that a net charge transfer occur from the oxygen to the platinum. The character of the metal/metal-oxide bond obtained for the monomer was found to transfer to larger clusters.

Comparing the absolute binding energies for platinum clusters on MgO(100) and BaO(100) we find that the clusters are ~1.5 eV more strongly bound on BaO(100). On both supports the large difference in relative stability between the different sites for the monomer (the oxygen site is favored by ~1 eV) makes atomic diffusion an improbable event. For Pt$_2$ on MgO, however, our results suggest the possibility of a roll diffusion similar to the one recently proposed for Cu$_2$ on MgO(100) [1].

The charge redistribution displayed in Figure 1 also have large effects for CO adsorption energies. In comparison with the gas phase systems the CO adsorption energy was found to increase by ~1 eV. The difference was tracked to both more efficient $5\sigma$ donation and $2\pi$ backdonation.

References