

DFT global optimisation of gas-phase and MgO-supported sub-nanometre AuPd clusters

Challenges

To identify the different geometrical features of AuPd sub-nanometre clusters and rationalize their catalytic activities on MgO(100) surface.

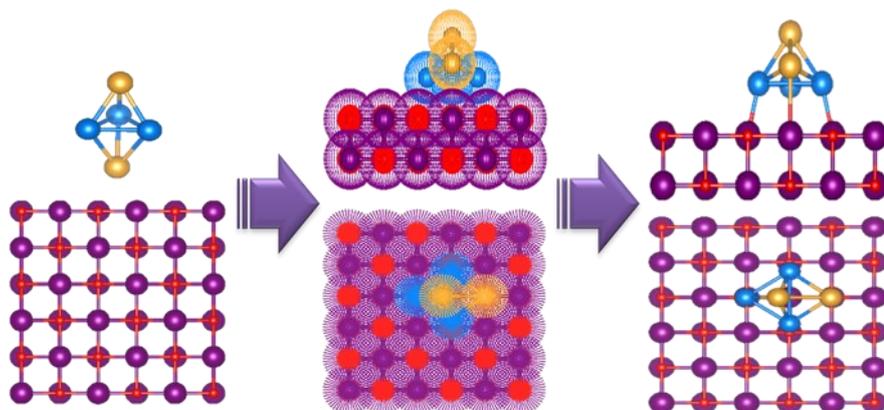
Background

The ability to control the surface and structural properties of nanostructures in the nanometre range and their suitable integration with different scientific research concepts have attracted widespread interest from researchers because of their use in many emerging technological applications. AuPd nanostructures, in particular, have been investigated previously for a number of applications, including catalytic applications. AuPd catalysts have been found to be promising candidates for a wide variety of chemical reactions, such as cyclohexane oxidation, NO reduction, CO oxidation, direct synthesis of hydrogen peroxide, and synthesis of aldehydes from primary alcohols.

Results

The use of the Birmingham Parallel Genetic Algorithm directly at the DFT level (BPGA-DFT) approach has successfully allowed the global optimization of free and MgO(100)-supported N=4-10 Au, Pd, and AuPd clusters. Significant structural differences between gas-phase and surface-supported are revealed by global optimization in the presence of a MgO slab in addition to the clear homotop swap behaviour in mixed AuPd clusters, in order to increase the number of stabilising Pd-O bonds. For singly doped clusters, the GM structures were confirmed by homotop reminimisation.

The BPGA-DFT calculations show that the Pd and Pd-rich clusters prefer 3D structures, while structural transitions occur for Au configurations from 2D to 3D upon adding more than one Pd atom. The planar structures of free Au global minima are all found to remain planar on the MgO(100) surface, with some deviation from the planarity for supported Au₉ and Au₁₀. They are also found to lie roughly perpendicular to the MgO surface, due to the "metal-on-top" effect. Global minima for the gas phase Pd clusters are all found to be different from their supported structures with the exception of Pd₄, which retains its tetrahedral structure. The energetics show the strong tendency of free Au-Pd clusters to alloy, with the exception of N=6, which confirms our magic size hypothesis of pure Pd and Au clusters at this size and reveal that the Pd and Pd-rich clusters tend to have the most negative adsorption energies. This could improve catalytic performance by suppressing cluster sintering.



Case study



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Product Used

VASP
Birmingham Parallel Genetic
Algorithm
Blue-BEAR high-performance
computer ARCHER facilities

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