

# Atomic and electronic structure analysis of Pd@Ag core-shell nanoparticles by large-scale DFT calculations

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Large-scale density functional theory (DFT) can play an important role to clarify the active sites of catalytic reactions in metallic nanoparticle systems by investigating the site- and size-dependence of atomic and electronic structures and reaction properties. Our large-scale DFT code CONQUEST [1] can treat large systems containing more than several thousands of atoms by using local orbitals and a linear-scaling ( $O(N)$ ) method. CONQUEST achieves  $O(N)$  by using the locality of density matrices with the density matrix minimization method. Local orbitals, which are called support functions, are used to express the density matrices.

The computational cost scales cubically to the number of the support functions, both in the  $O(N)$  and the conventional diagonalization calculations. Therefore, to reduce the number of support functions without losing accuracy, we have introduced multi-site support functions (MSSF) [2,3]. MSSFs are the linear combinations of pseudo-atomic orbitals from a target atom and its neighbor atoms in a cutoff region.

$$\phi_{I\alpha}(r) = \sum_K^{neighbours} \sum_{\mu \in K} C_{I\alpha, K\mu} \chi_{K\mu}(r)$$

MSSFs correspond to local molecular orbitals so that the number of required support functions can be the minimal. While the  $O(N)$  method is not guaranteed to be applicable for metallic systems, the multi-site method can be applied for metallic systems stably.

In this study, we have investigated the selective semihydrogenation of alkynes with core-Pd/shell-Ag (Pd@Ag) nanoparticles by using the multi-site method. Pd@Ag accelerates the hydrogenation from alkyne to alkene but prevent the overhydrogenation from alkene to alkane [4]. To clarify the catalytic mechanism of Pd@Ag, we investigated the atomic and electronic structures of Pd, Ag and Pd@Ag nanoparticles. It is found that the surfaces of Ag nanoparticles are charged negatively, while that of the Pd nanoparticle is partially charged negatively. We will also report the electronic structure dependence of Pd@Ag on the Ag-shell thickness and the effect from the Pd/Ag interface to the particle surface.

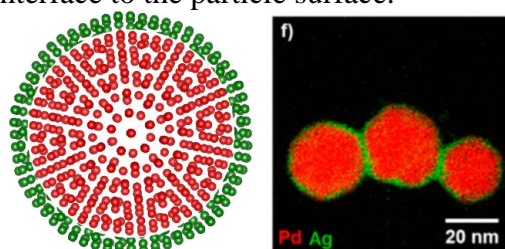


Figure 1: Simulation model and experimental image [4] of Pd@Ag nanoparticles.

## References

1. <http://www.order-n.org/>
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3. A. Nakata, D. R. Bowler, T. Miyazaki, *J. Chem. Theory Comput.* **10** (2014) 4813.
4. T. Mitsudome, T. Urayama, K. Yamazaki, Y. Maehara, J. Yamasaki, K. Gohara, Z. Maeno, T. Mizugaki, K. Jitsukawa, K. Kaneda, *ACS Catal.* **6** (2016), 666.