



Density Functional Theory Study of the Adsorption Site of CO on Pt(111)

Researchers at the National Institute of Advanced Industrial Science and Technology (AIST), Japan and Accelrys have used MS Modeling's DMol 3 to study the adsorption of CO on the Pt(111) surface.

The study successfully showed the correct site-preference for the CO adsorption site as suggested by experiment.

This finding will enable the design of better catalysts and sensors.

The interaction of CO with metal surfaces has attracted a great deal of interest because it is an important step in many surface and catalytic reactions, such as CO oxidation and hydrogenation.

In particular, the adsorption of CO on Pt surfaces has attracted much attention because of the many potential applications, such as in car exhaust catalysts where it promotes the oxidation of CO to CO₂. The heats of adsorption and local bonding geometries of the interaction have been investigated both experimentally and theoretically.

However, in studies of the CO adsorption on Pt(111), theoretical and experimental results differ. Density functional theory (DFT) predicts adsorption at the the fcc-hollow site, whereas experiments reveal adsorption occurs at the atop site[1,2].

Researchers at the National Institute of Advanced Industrial Science and Technology (AIST), Japan and Accelrys used MS Modeling's DFT code DMol 3 to solve this puzzle, studying the adsorption sites shown in Fig. 1.

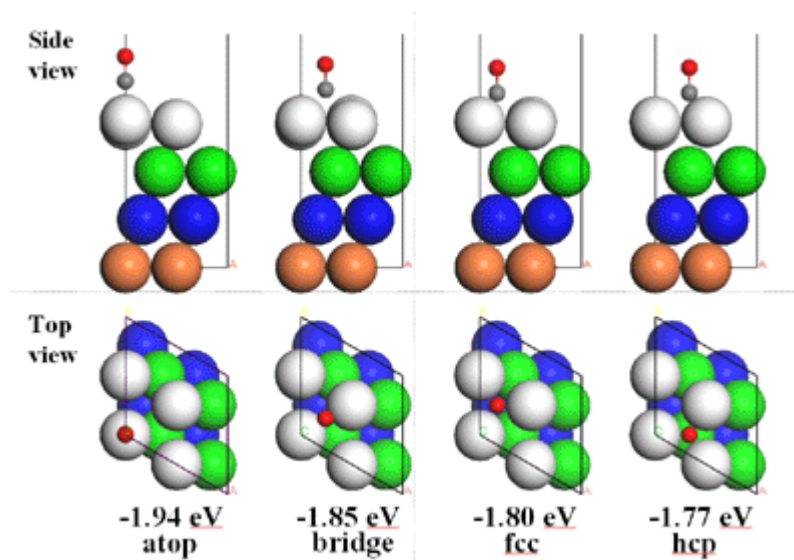


Fig. 1 Side and top views of typical optimized adsorption structures of CO on Pt(111) for the AER-PBE calculation. Numerical values indicate adsorption energies.

Reporting in *Chem. Phys. Lett.* [3], the researchers discovered:

- All electron scalar relativistic (AER) calculations are essential to obtain the correct site-preference, atop followed by bridge and then hollow (fcc and hcp)
- The AER calculations give a deeper Fermi level in good agreement with work function measurements for a Pt surface with all the functionals
- The deeper Fermi level enables the interaction of the LUMO of CO with the metal substrate to be decreased
- This effect suppresses backdonation from the metal substrate to the LUMO of CO, hence it destabilizes fcc-site, that, in

turn, stabilizes the atop-site.

Dr Orita, a senior research scientist at AIST, said "Since localized d-orbitals were expected to be important in the model studied, we chose to use DMol³ for this work, as it is based on localized basis sets, which is more appropriate than DFT codes based on plane wave basis sets."

"As DMol 3 is good at performing geometry optimization, the code enabled us to perform geometry optimization taking account of all the electrons in a system, even when running on a personal computer. Such a low computational cost of performing fast calculations is essential for the practical analyses of changing calculation parameters systematically, such as core treatment, functional, number of slab layer, k-points, and size of unit cell."

References

- [1] P.J. Feibelman *et al.* , *J. Phys. Chem., B* , 105 (2001) 4018.
- [2] G.Kresse *et al.* , *Phys. Rev. B* , 68 (2003) 073401.
- [3] H. Orita *et al.* , *Chem. Phys. Lett.* , 384 (2004) 271 (<http://dx.doi.org/10.1016/j.cplett.2003.12.034>).

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