



## A Density Functional Theory Study of the Effect of Alloying on the Surface Reactivity of Catalysts

Researchers at Queens University, Belfast, University of Cambridge, and Tamkang University have used Accelrys' density functional theory (DFT) - based CASTEP program to study the effect of alloying on the surface reactivity of catalysts.

Industry has long exploited the technique of alloying metals in order to increase the surface reactivity of catalysts. Good examples include copper-platinum alloys, used extensively for the oxidation of carbon monoxide in, for example, automobile exhaust catalysts. However, pure copper catalysts show little affinity for carbon monoxide, whilst, on the other hand, pure platinum catalysts are inhibited by their over-affinity for carbon monoxide as they are quickly 'poisoned' - the excess of carbon monoxide at the catalyst surface prevents the approach of oxygen molecules and thus the oxidation reaction is inhibited. The copper-platinum alloys provide a viable alternative to the pure metals. In addition it has recently been discovered alloys containing Pt(111) instead of Pt or Cu offer significant catalyst performance enhancement. With this keen interest, it is highly desirable to understand how this alloying modifies the catalyst surface and the subsequent role in reactions.

Dr. Peijun Hu and team, aiming to shed light on this alloying effect on catalyst reactivity, used Accelrys' CASTEP program to undertake a comparative DFT study of CO oxidation on Cu<sub>3</sub>Pt(111), Pt(111), and Cu(111). The following key issues were investigated:

- The alloying effect on the bonding/adsorption sites - the adsorption of CO and O<sub>2</sub>
- The alloying effect on the bonding energies of CO and O<sub>2</sub> - CO oxidation
- Reaction pathways/mechanisms and the effect of alloying

The CASTEP simulations resulted in the following observations:

- CO preferentially adsorbs on a top site of Pt
- Oxygen preferentially adsorbs on a fcc hollow site of 3 Cu atoms on Cu<sub>3</sub>Pt(111)
- The adsorption energies of CO (or O<sub>2</sub>) are lower on the alloy surface than on the pure metal surface
- The transition states for CO oxidation on the alloy and on the two pure metals were identified and the reaction barriers calculated. It was found that the activation barrier for the reaction on the alloy was lower as compared to the pure metals. This result indicates that the Cu<sub>3</sub>Pt alloy would be a better catalyst than pure Pt or Cu - advantageous considering the relatively high cost of pure Pt
- The physical origins of the results were revealed to be due to the fact that a strong corrugated potential energy surface for the CO diffusion on the alloy leads to the CO activation from the initial state to the transition state being an important factor contributing to the reaction barrier.

### Reference

1. C. J. Zhang, R. J. Baxter, P. Hu, A. Alavi, and M. H. Lee, A density functional theory study of carbon monoxide oxidation on the Cu<sub>3</sub>Pt(111) alloy surface: Comparison with the reactions on Pt(111) and Cu(111), *J. Chem. Phys.*, 2001, **115** (11), 5272-5277.

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