



# Near Surface Alloys for Improved Water–Gas–Shift Catalysis



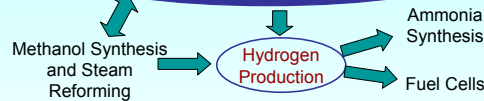
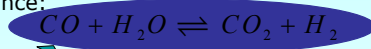
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## Motivation

The **Low-Temperature Water-Gas-Shift (WGS) Reaction** is of significant industrial and environmental importance:



A two-step process is currently practiced because of commercial catalysts limitations:

➤ **Low temperature step** to push the equilibrium toward hydrogen production

➤ **High temperature step** to provide faster kinetics

Therefore, there is a need for a **better catalyst** for small scale applications (e.g.: on-board reformers for **hydrogen fuel cell-powered** vehicles)

## A Cu/Pt Near Surface Alloy (NSA)

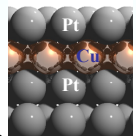
For the low-T step, Cu and Pt based catalysts have been used.

- **Cu** – drawbacks: is pyrophoric; “poisoned” by formate (HCOO) intermediate; has a high H<sub>2</sub>O activation barrier;
- **Pt** – drawbacks: poisoned by carbon monoxide (CO) and sulfur (S)

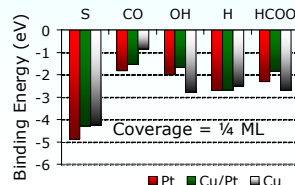
Density Functional Theory (DFT) calculations of binding energies for key reaction intermediates on a model Cu/Pt(111) surface show a very promising trend for CO, OH, HCOO, and S, compared to pure Cu(111) and Pt(111).

➤ OH, HCOO bind **significantly weaker** on Cu/Pt(111) compared to Cu(111) surface.

➤ CO, S and OH bind **significantly weaker** on Cu/Pt(111) than pure Pt(111) surface.

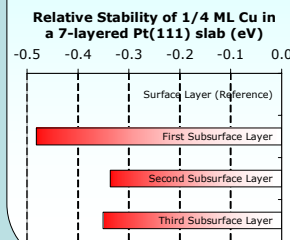


Cross-section view of the model Cu/Pt(111) surface



## Thermodynamic and kinetic Accessibility of the alloy

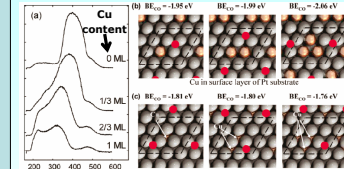
DFT calculations show that the two key processes for incorporation of Cu atoms into a Pt particle: (1) **surface vacancy formation on Pt**, and (2) **diffusion of Cu from surface to subsurface of Pt**, have an activation energy barrier of ~3 eV.



Thermodynamics favors Cu residing **below the Pt surface**, particularly in the **first subsurface layer**. These results are corroborated by XPS.

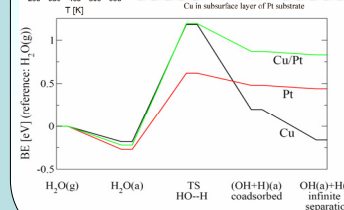
As a result, Cu/Pt alloy seems to be both thermodynamically and kinetically accessible upon annealing at T > 700 K

## CO Binding and H<sub>2</sub>O activation

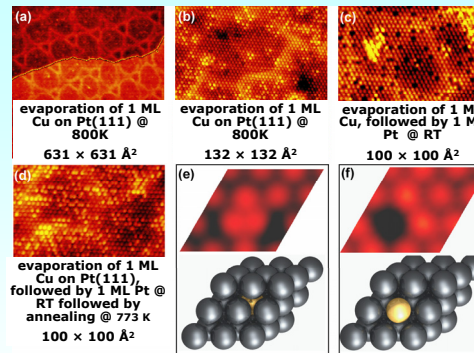


➤ TPD indicates that with **increasing Cu coverage CO-desorption Temperature decreases**, a trend found with DFT **only** if Cu exists in the **subsurface** layer

➤ DFT shows Cu/Pt NSA **activates H<sub>2</sub>O** – the **RLS** for WGS- with a barrier similar to Cu, and yet binds the H<sub>2</sub>O dissociation products much weaker to **facilitate subsequent elementary steps**.



## Chemical ID via STM + DFT



DFT-simulated STM images (e and f) show that **Cu in Pt surface** appears as a **dark spot**, whereas **Cu in subsurface of Pt** appears as **bright spots**, as observed in **High-resolution STM images** in (a)-(d) of Cu/Pt NSA's prepared with different protocols.

## Conclusions

### Cu/Pt NSA

- is **thermodynamically** and **kinetically** accessible at the experimentally used annealing temperatures
- binds CO weaker than pure Pt, and binds formate weaker than Cu -- **reduced potential for poisoning by dominant reactive intermediates**
- activates H<sub>2</sub>O with low activation energy barrier, and binds the reaction products weakly, **facilitating further reactions**
- is more **S and CO tolerant** than Pt, a desirable attribute for low-temperature WGS catalysts.

### Acknowledgements:

