# *Theory-Experiment Interface in Catalysis: Fundamental Studies to Understand the Behavior of Active Sites*

**José A. Rodriguez**

## Collaborators:

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**$$ US-DOE**

*Chemistry Department*

## Outline

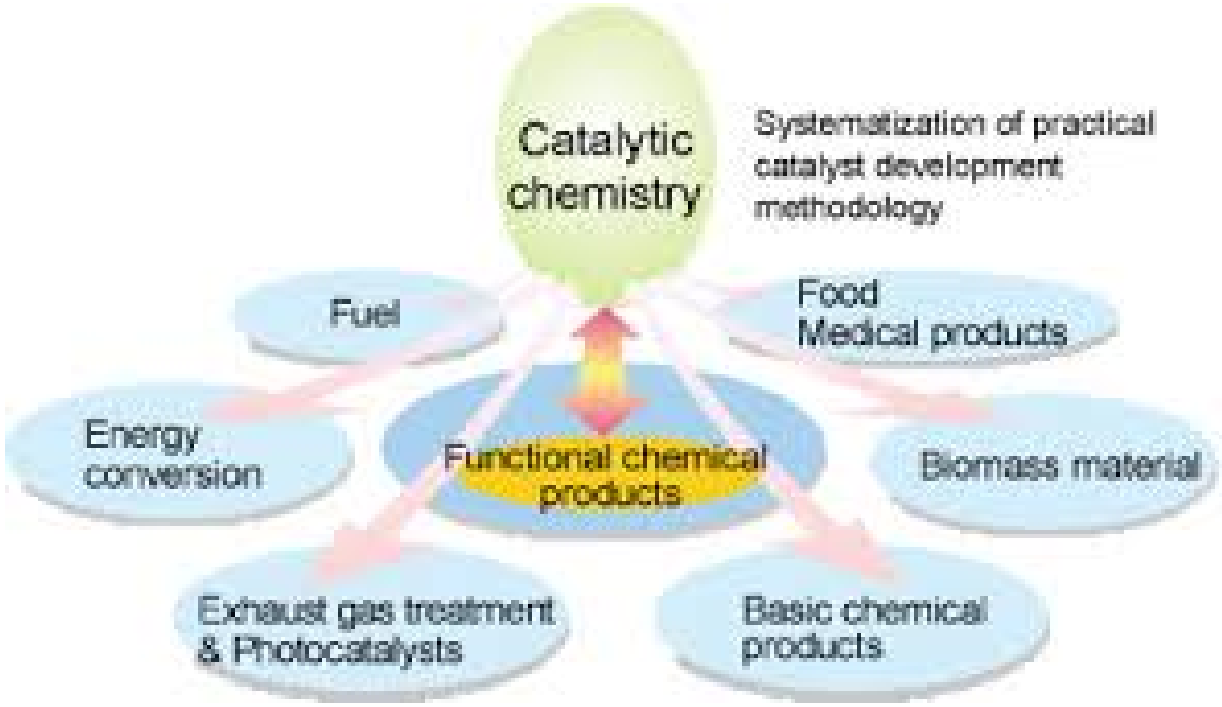
- **Motivation: Theory within a multi-technique approach in the study of complex catalysts**

- **Studies of the water-gas shift reaction**
  - **role of metal-oxide interface**
  - **reaction mechanism**

- **Studies of $CO_2$ hydrogenation to methanol**
  - **role of metal-support interaction**

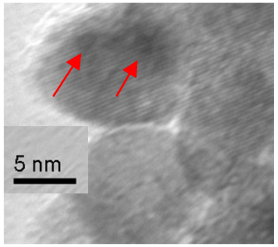
- **Studies of desulfurization processes**
  - **role of metal-support interaction**

## Motivation: Catalysis has many technological applications

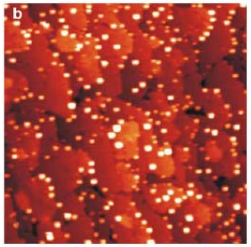



**Catalytic processes are essential for the functioning of the modern world**

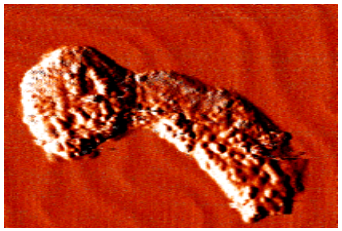
# Heterogeneous catalysts are complex systems



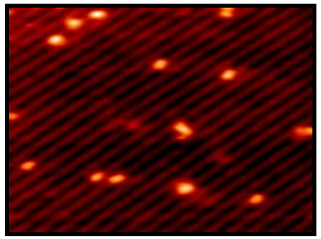

TEM: Au-$CeO_2$ powder



STM: Au on $CeO_2$(111)



STM: $CeO_x$ on Au(111)



STM: Au/$CeO_x$/$TiO_2$(110)

**The phenomena responsible for the catalytic properties of these materials are not well understood:**

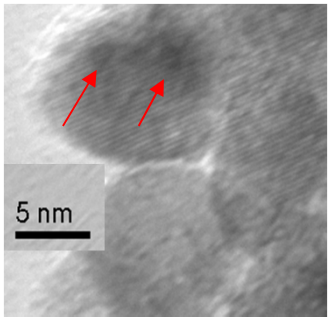
- **active phase**
- **role of the catalyst components**
- **size effects**
- **reaction mechanism**


**Rodriguez, Hanson, Senanayake, Stacchiola, Phys. Chem. Chem. Phys. 15 (2013) 12004**

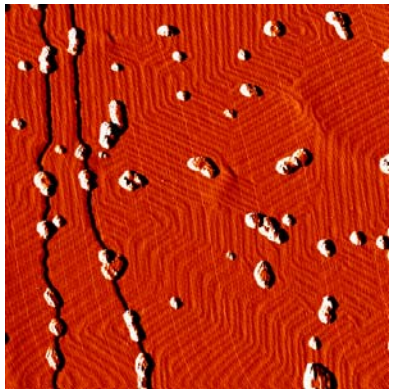
**Senanayake, Liu, Rodriguez, Stacchiola et al, *Angew. Chem.* 52 (2013) 5101**

**Challenge:** **We need to characterize chemical transformations occurring in a wide range of materials and reaction times**

TEM image
Au/$CeO_2$




**powder catalyst**

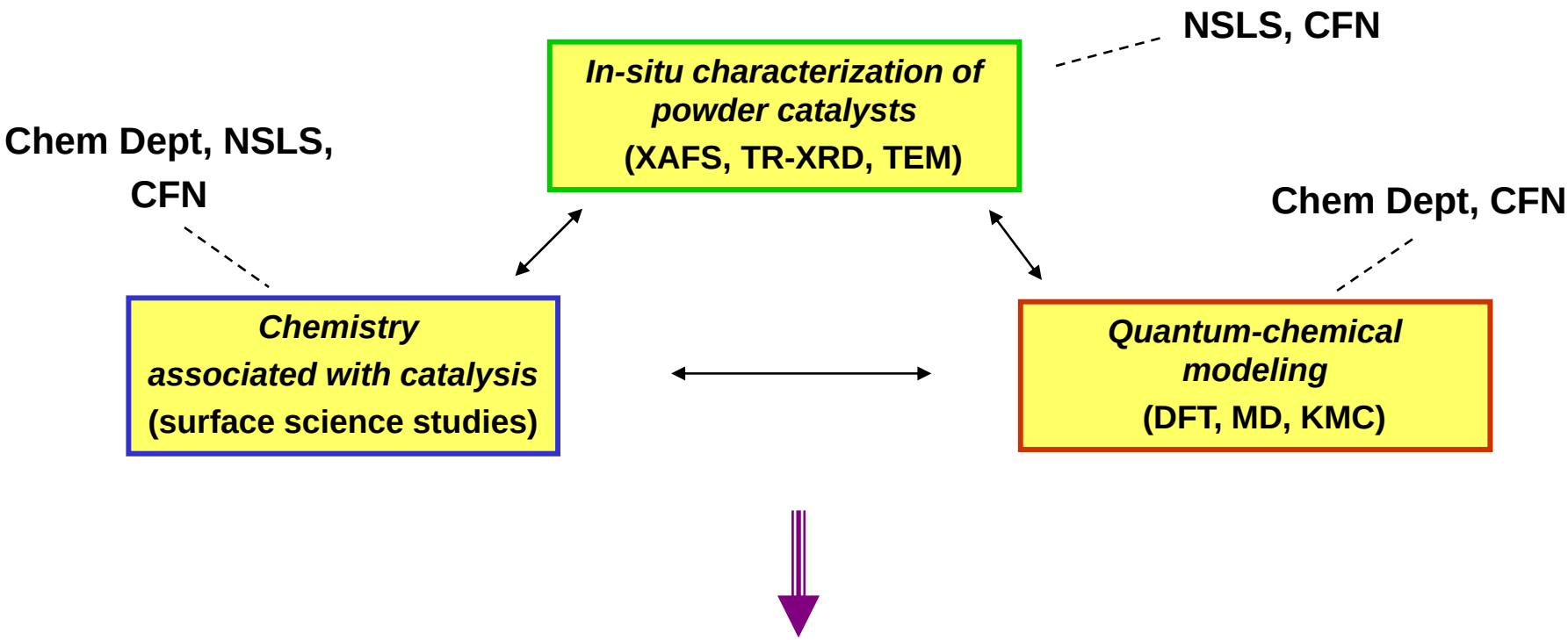


200 nm x 200 nm

STM image
for $CeO_x$/Au(111)

**model single crystal**

## Integrated approach to catalysis:




**Fundamental understanding of the behavior of active sites:**

**Rational design of better catalysts**

**Theory** $\longrightarrow$ **Conceptual frame in catalysis science**

- **It can help with the interpretation of experimental results**
- **It can predict the behavior of catalytic materials**
- **It can be useful for developing basic patterns of reaction**

## Examples of studies integrating theory and experiment

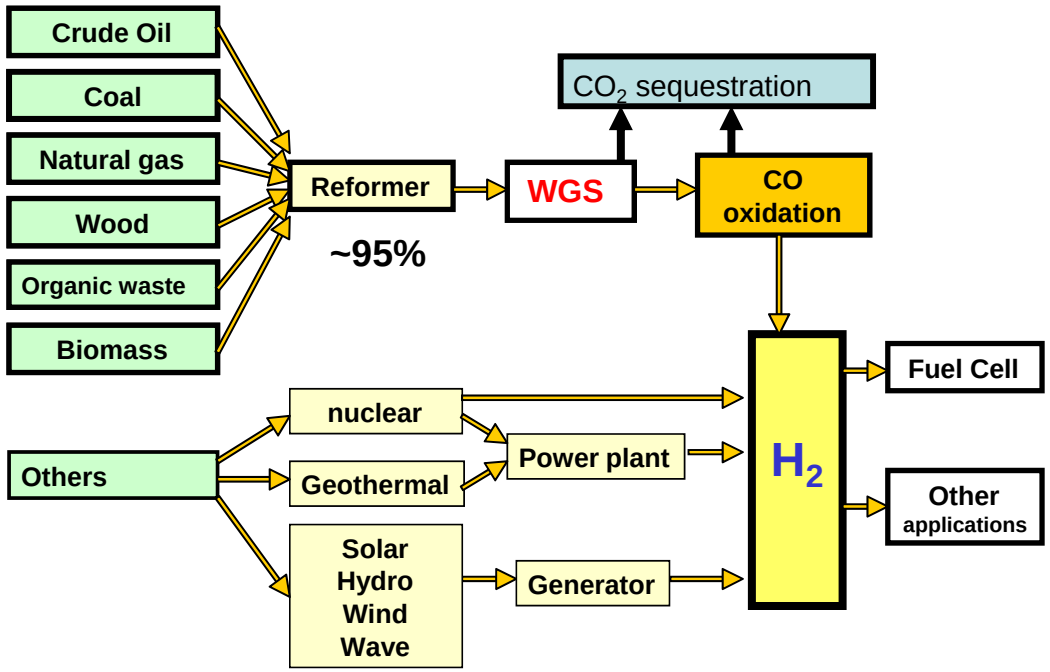
- **Studies of the water-gas shift reaction**
  - **role of metal-oxide interface**
  - **reaction mechanism**

- **Studies of $CO_2$ hydrogenation to methanol**
  - **role of metal-support interaction**

- **Studies of desulfurization processes**
  - **role of metal-support interaction**

- **Studies of the water-gas shift reaction**
  - **active phase**
  - **role of metal-oxide interface**
  - **reaction mechanism**

# Motivation:




**Most hydrogen is currently derived from the steam reforming of hydrocarbons:**

$$C_nH_m + nH_2O \rightarrow nCO + (n\text{-}m/2)H_2$$

**The reformed fuel contains 1-10% CO, which degrades the performance of the Pt electrode used in fuel cell systems.**

**The water-gas shift ($CO + H_2O \rightarrow H_2 + CO_2$) is used to remove the CO.**

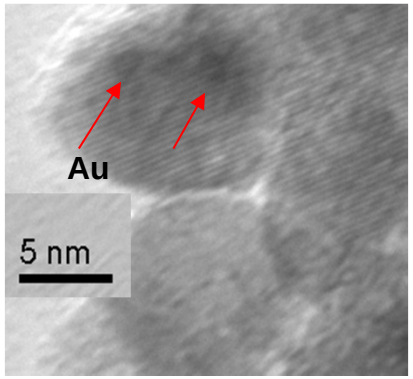
## Traditional WGS catalysts:

- Cr-Fe oxides, high temperature (> 250 C)
- Cu-Zn oxides, low temperature (< 250 C)

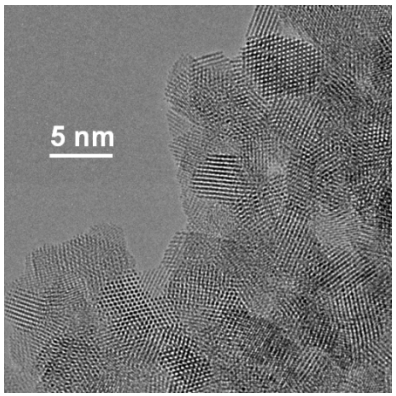
**More active and more stable catalysts need to be found**

## New generation WGS catalysts:

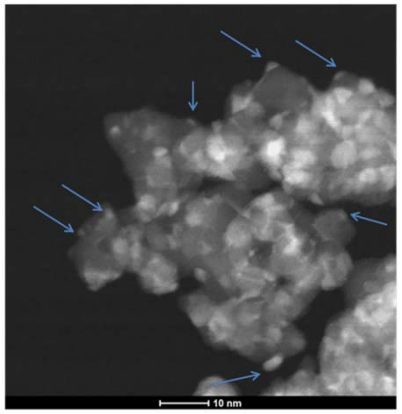
- Au, Cu and Pt on $CeO_2$ and $TiO_2$




**$Au/CeO_2$**

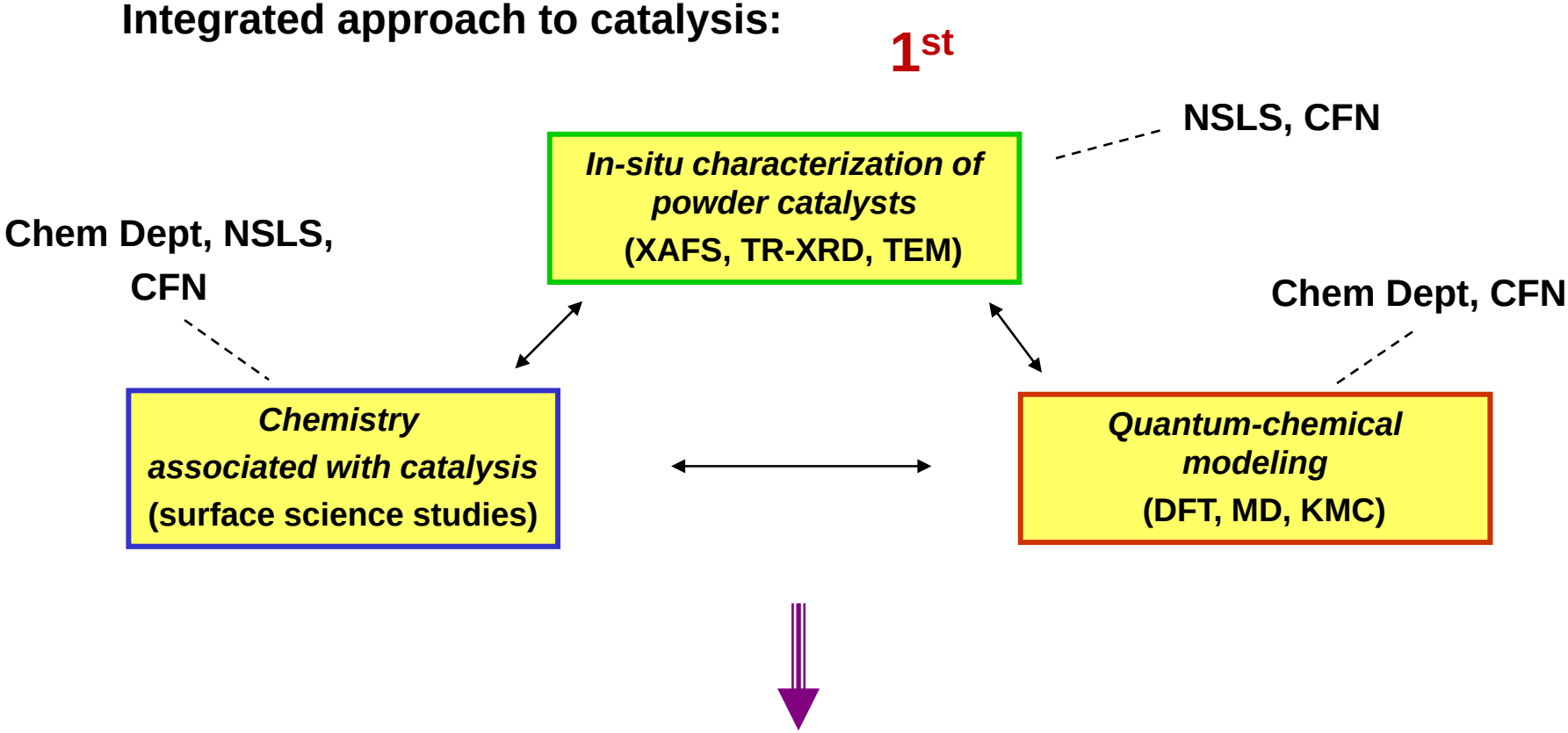



**$Ce_{1-x}Cu_xO_2$**



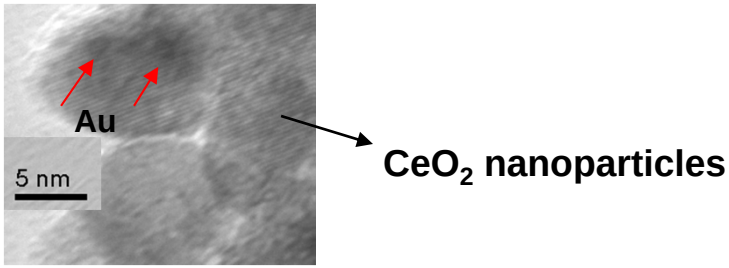

**$Pt/CeO_{x/}TiO_2$**

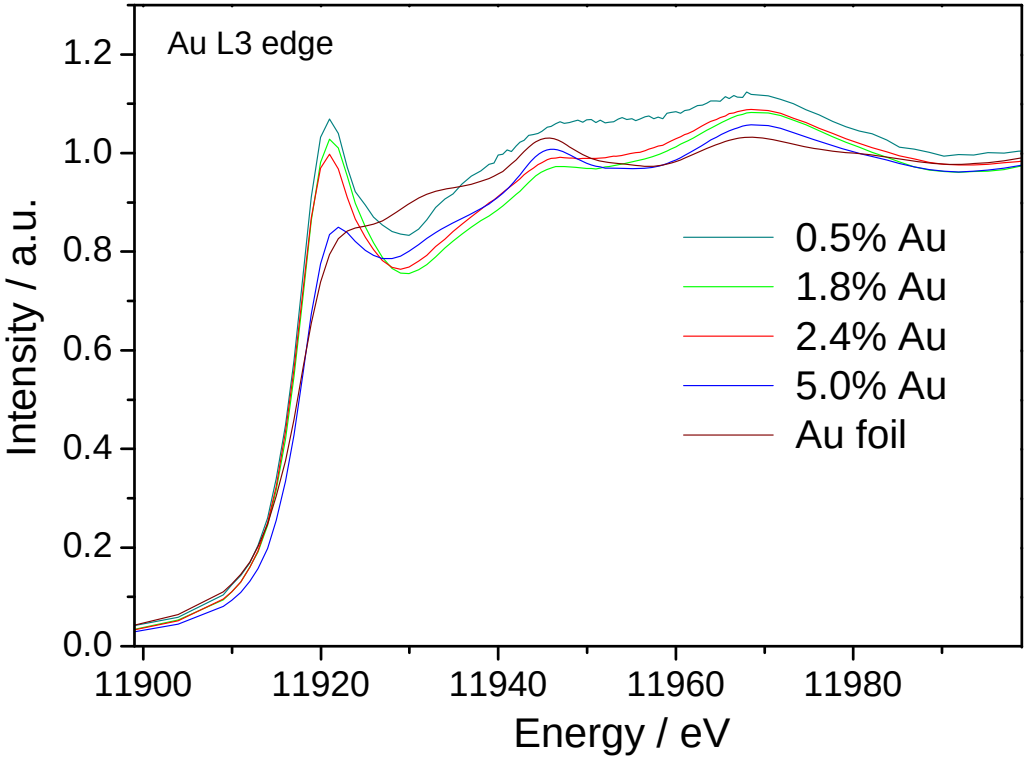
## Integrated approach to catalysis:




**Fundamental understanding of the behavior of active sites:**

**Rational design of better catalysts**



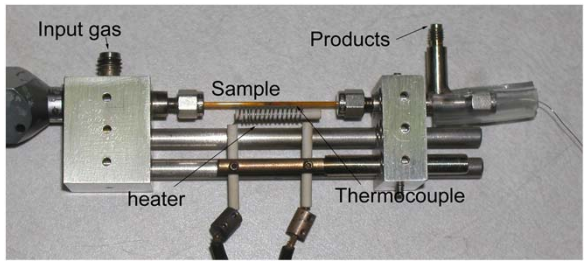

powder Au/$CeO_2$ catalysts

Before reaction, as prepared:

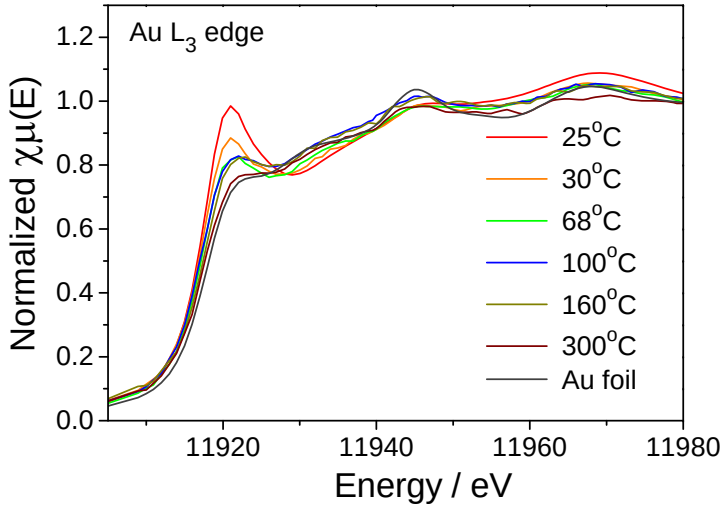
The relative amount of $AuO_x$ increases when the total amount of gold decreases.

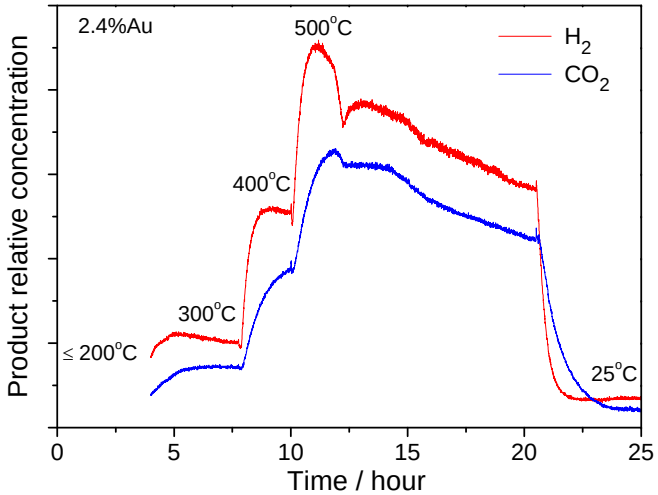
## $AuO_x/CeO_2$ under water-gas shift reaction: $CO + H_2O \rightarrow H_2 + CO_2$

**NSLS X19A**

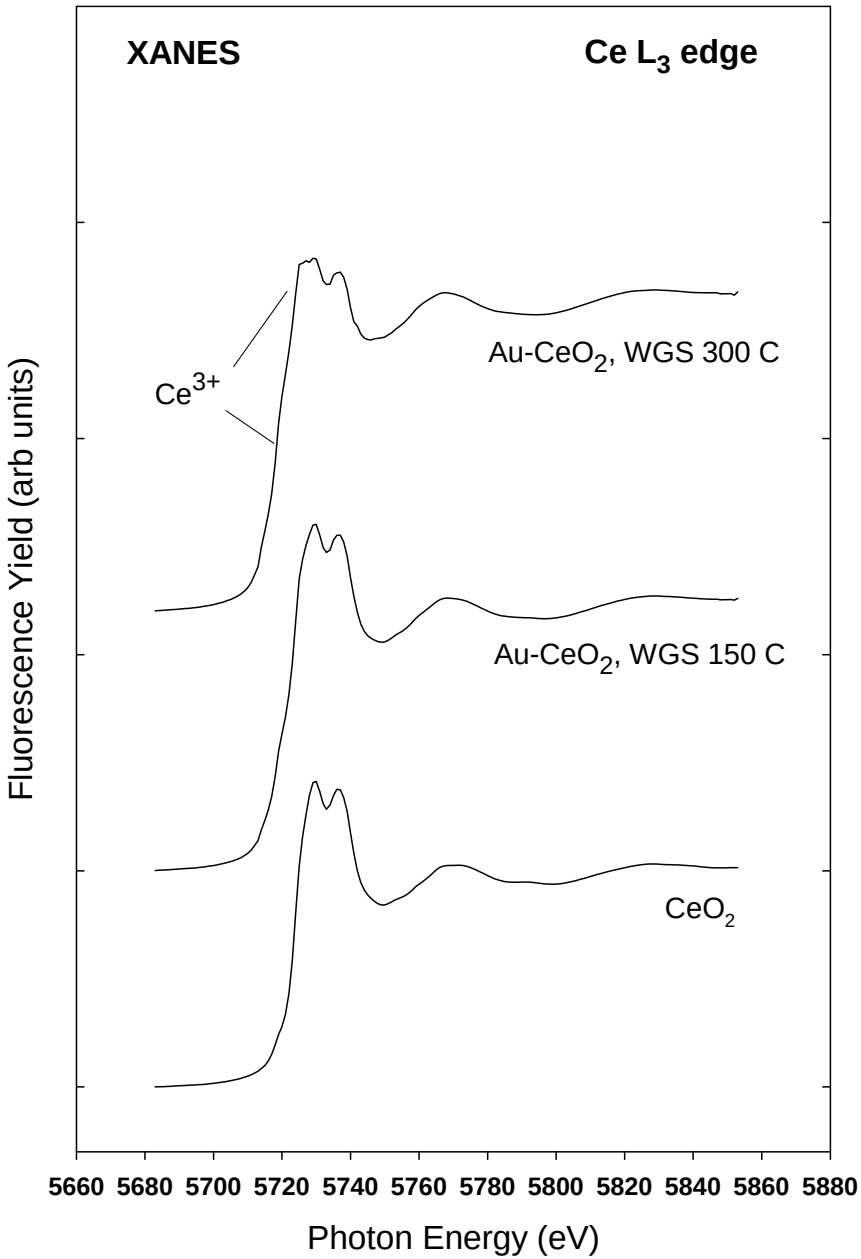



**flow micro-reactor**




*In-situ* measurements under atmospheric pressure for WGS reaction. The $AuO_x$ becomes Au. The active phase consist of metal nanoparticles dispersed on $CeO_{2-x}$.



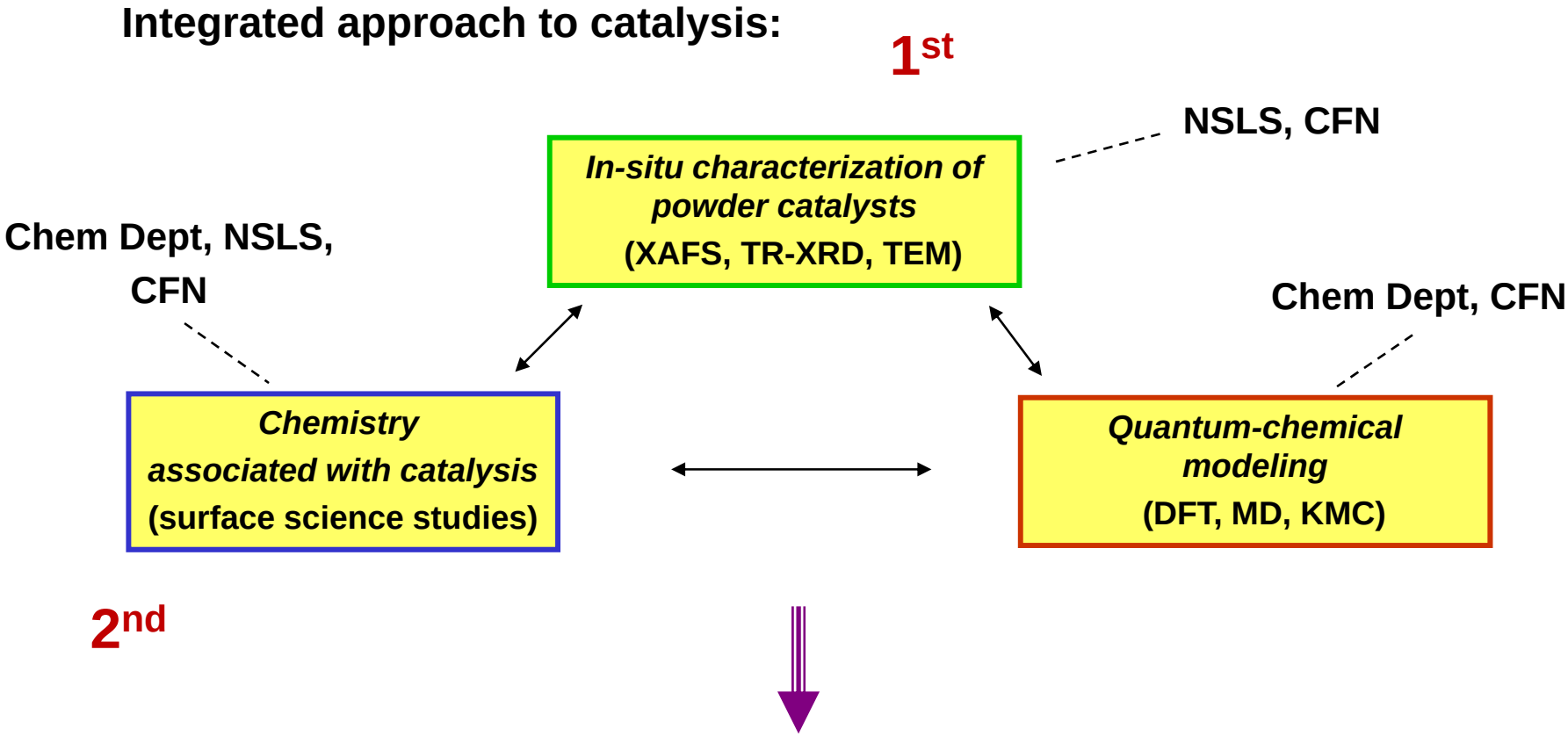

*In-situ* XANES at Ce $L_3$-edge

Ceria is reduced under reaction conditions.

## Summary

***In-situ*** **XANES and XRD studies show that the active phase of Au-$CeO_2$ catalysts for the WGS reaction consist of metal nanoparticles dispersed on partially reduced $CeO_{2-x}$**

**Integrated approach to catalysis:**




**Fundamental understanding of the behavior of active sites:**

**Rational design of better catalysts**

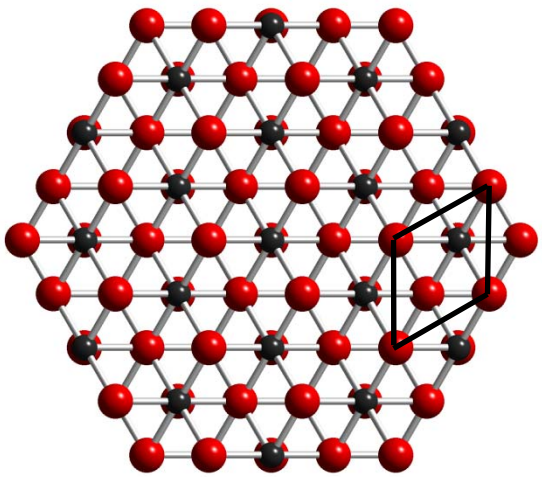
**Water-gas shift reaction on:**

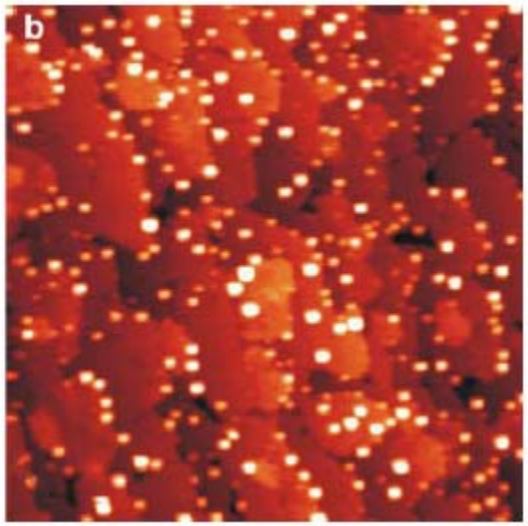
- **Au nanoparticles supported on $CeO_2(111)$, $ZnO(000\bar{1})$ and $TiO_2(110)$**

## Model systems: Au and Cu on $CeO_2(111)$

### $CeO_2(111)$ structure

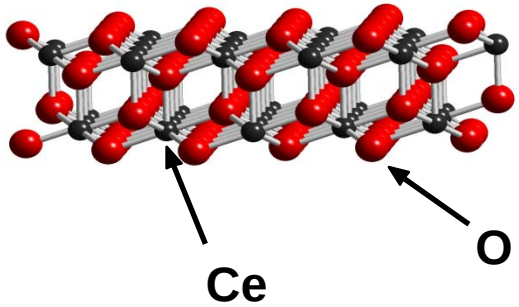
Top view





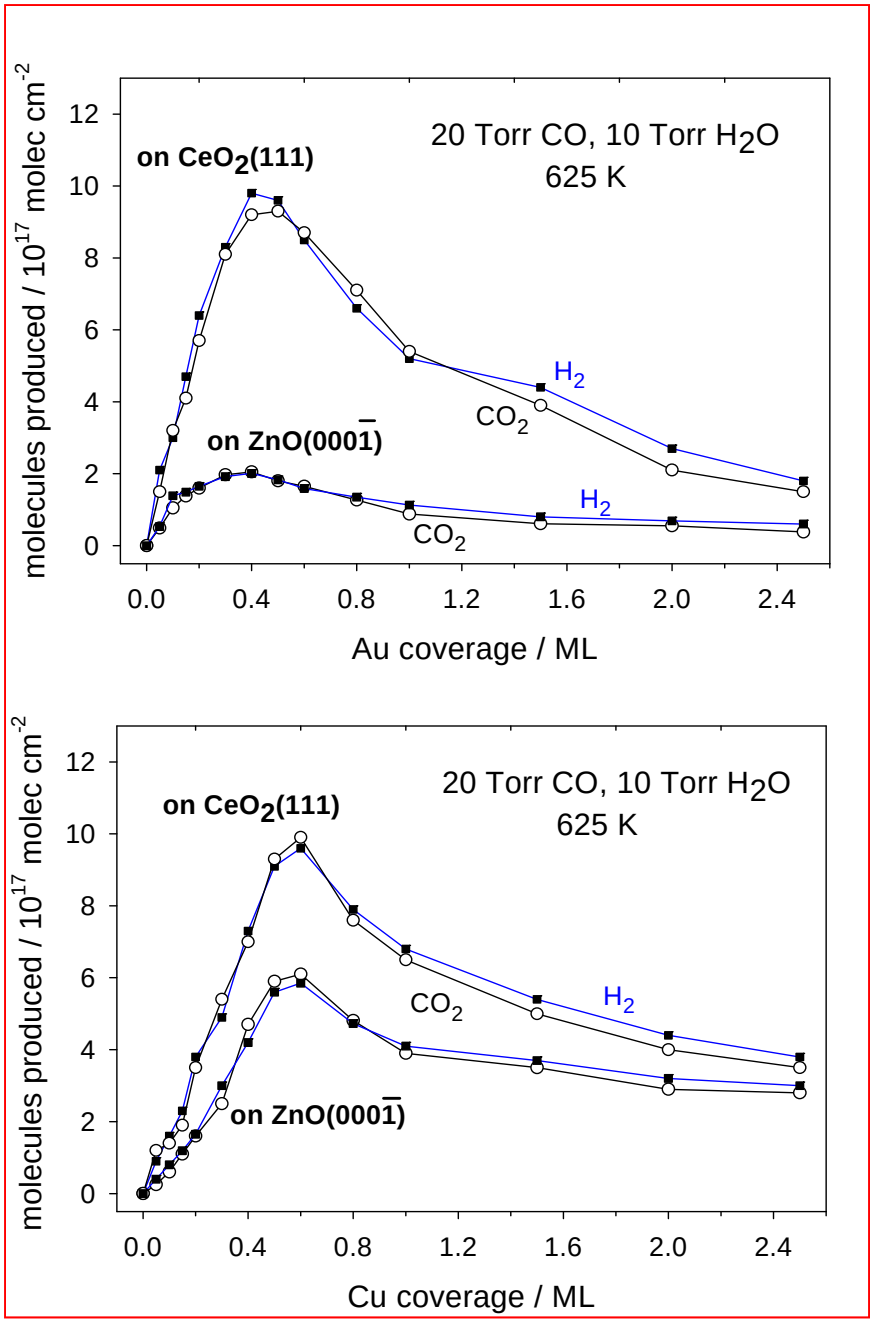

150x150 $nm^2$

Side view




**For Au on $CeO_2(111)$ , the results of STM show 3D islands of Au with sizes of 2-4 nm (0.3-0.8 ML)**

- Freund et al, Catal. Lett. 114 (2007) 8.



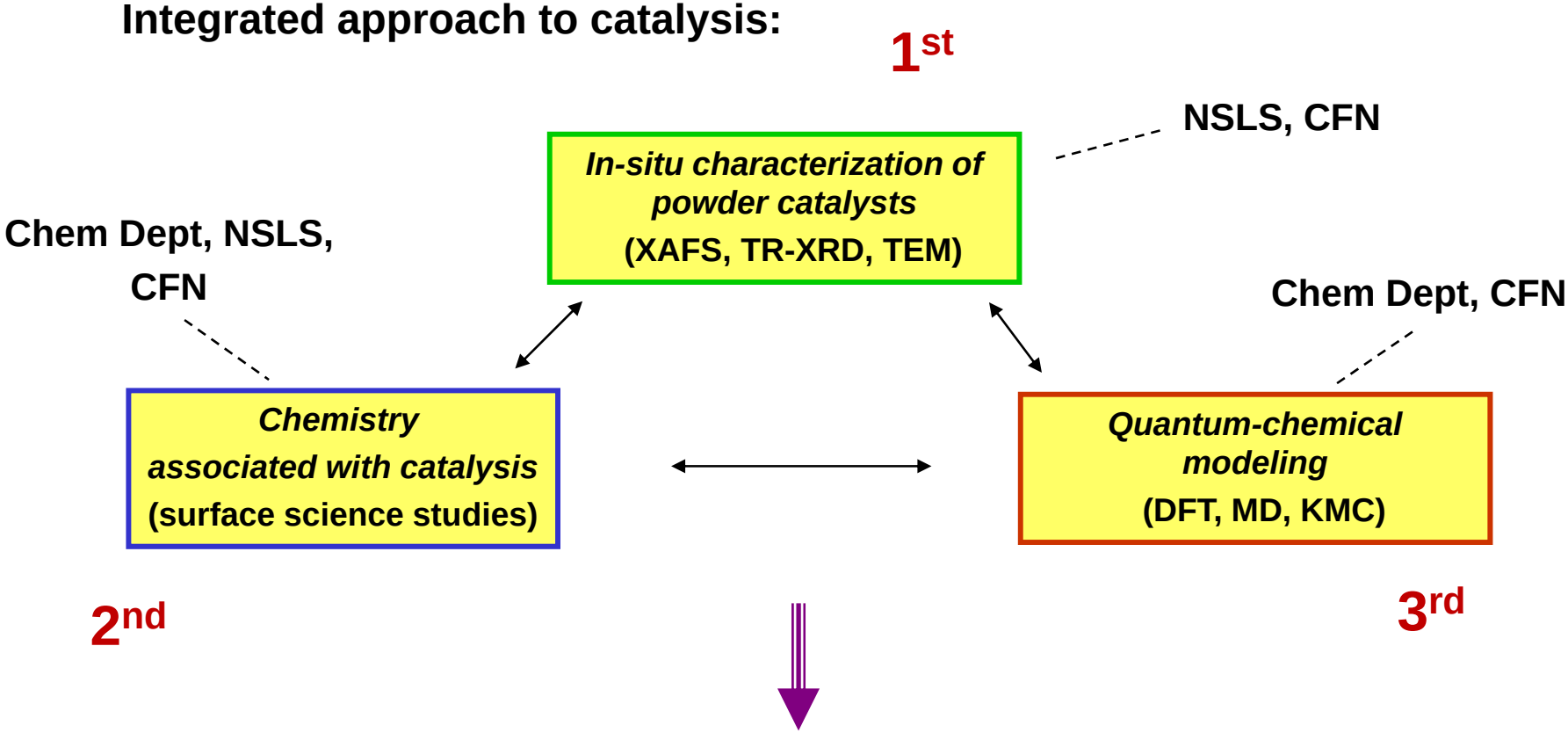

**After exposing Au/$CeO_2$(111) surfaces to mixtures of {CO + $H_2O$} under WGS reaction conditions, post-reaction XPS characterization shows Au and partially reduced $CeO_{2-x}$(111)**

Rodriguez, Liu, Hrbek et al,
Angew. Chemie, 46 (2007) 1329

**Particle size matters: At the maximum activity metal particles with 2-4 nm in size.**

**Question: What is the role of the oxide?**

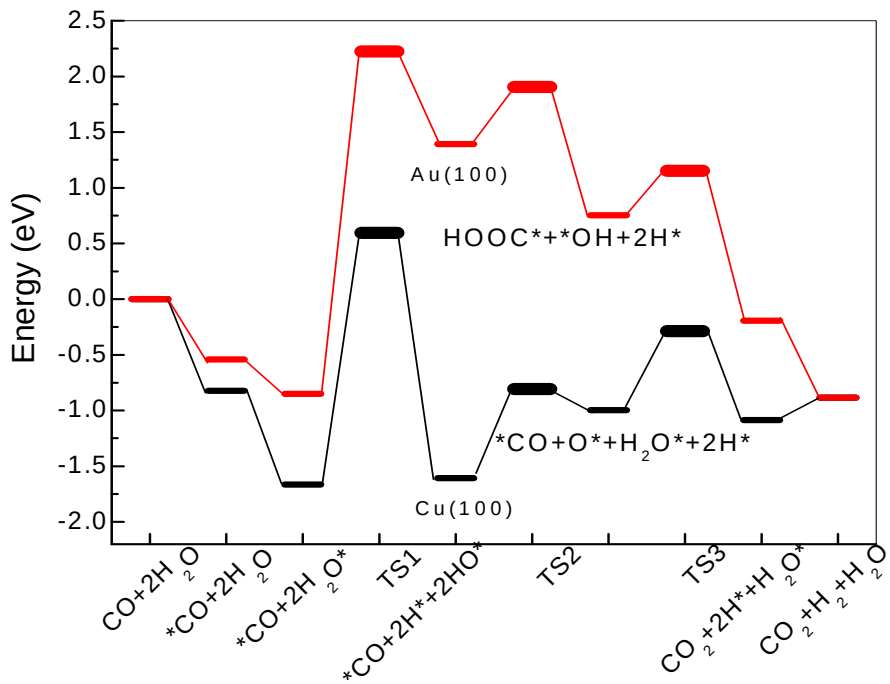
## Integrated approach to catalysis:




**Fundamental understanding of the behavior of active sites:**

**Rational design of better catalysts**

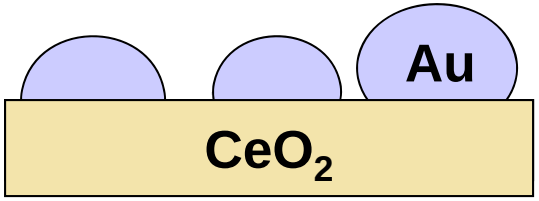
# DFT results for WGS on Cu and Au systems



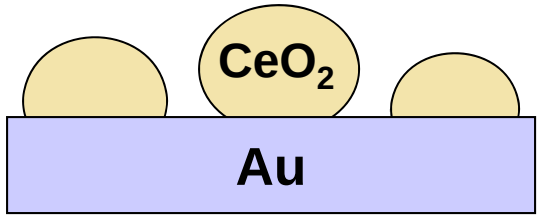

**Liu and Rodriguez, J. Chem. Phys. 126 (2007) 164705**

**Au(100) and Au(111) do not dissociate water well, but subsequent steps of the WGS are fine.**

**Can an oxide help with the dissociation of water?**




***conventional***



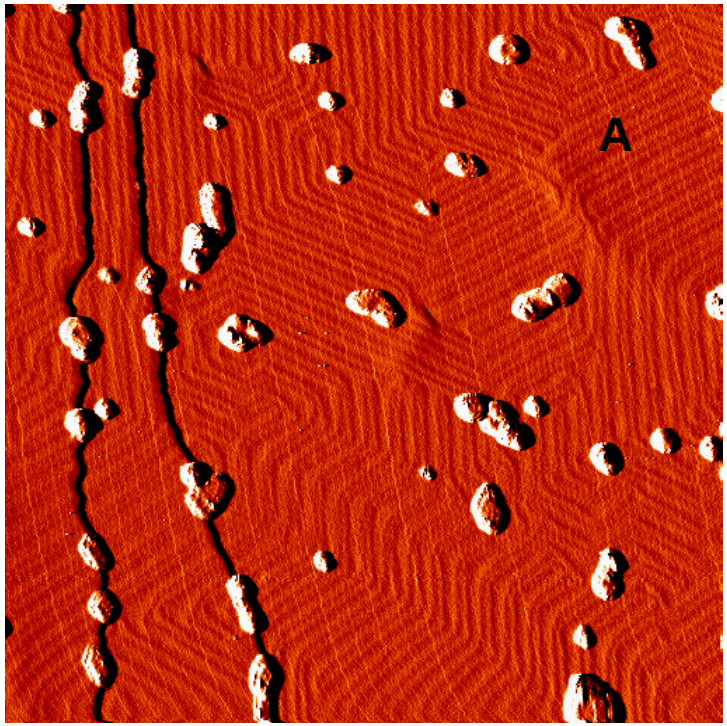

***inverse***

**On the inverse oxide/metal catalyst, the reactants can interact with defect sites of the oxide nanoparticles, metal sites, and the metal-oxide interface. Excellent for studying the role of the oxide.**

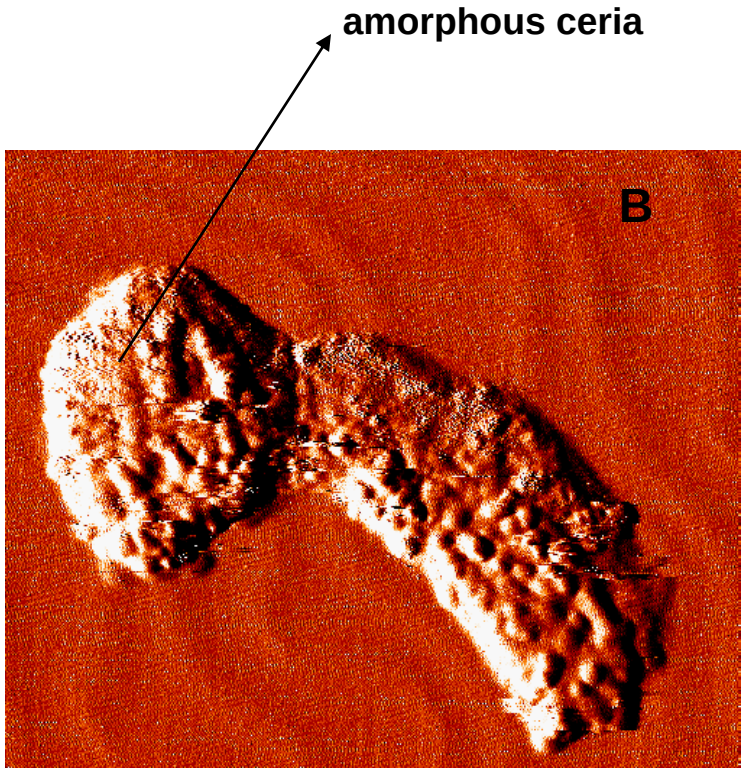
**Rodriguez et al, Angew. Chem. Int. Ed. 48 (2009) 8047**

# Water-gas shift reaction on $CeO_x$/Au(111) and $CeO_x$/Cu(111)

## Images of scanning tunneling microscopy for nanoparticles of $CeO_2$ dispersed on a Au(111) surface

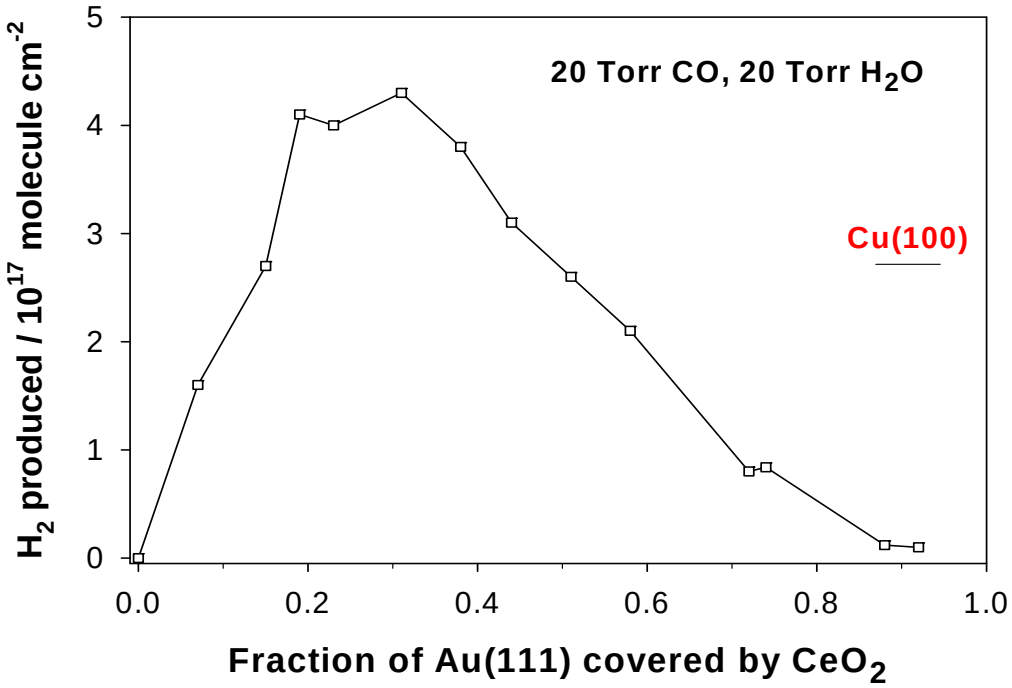



200 nm x 200 nm



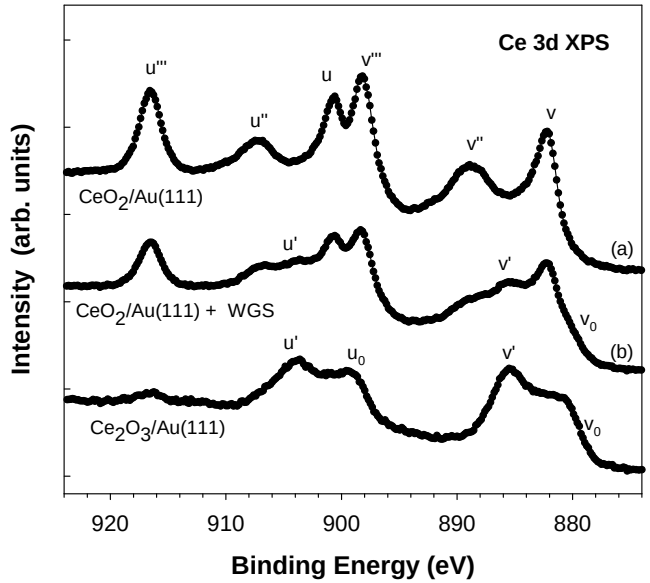

30 nm x 25 nm

**Model catalyst for the water-gas shift**

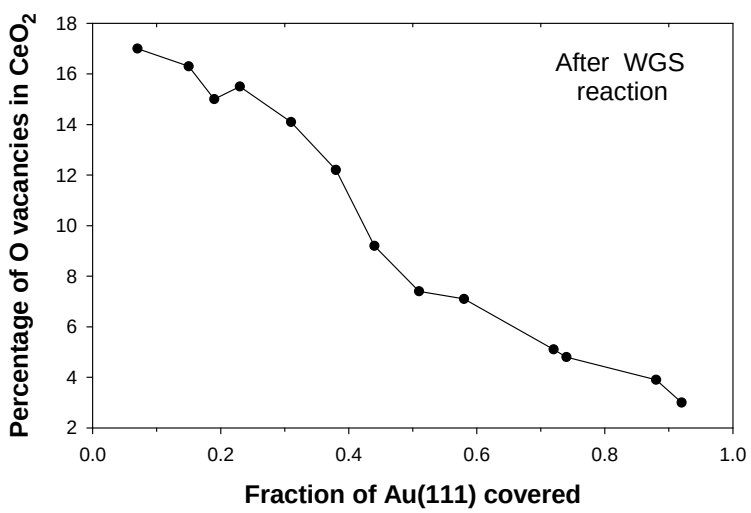



**Production of hydrogen through the water-gas shift ($CO + H_2O \rightarrow H_2 + CO_2$) on $CeO_2$/Au(111) catalysts**

**Rodriguez et al, Science, 318 (2007) 1757**




**Photoemission indicates that there is a correlation between the concentration of O vacancies in the ceria nanoparticles and the catalytic activity**



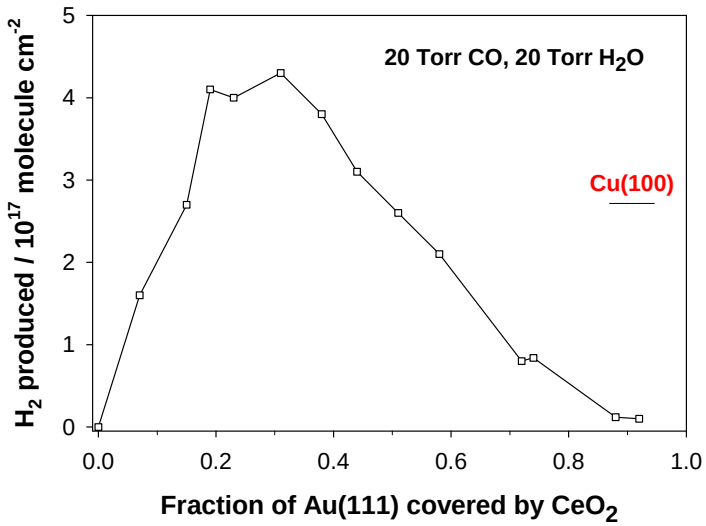
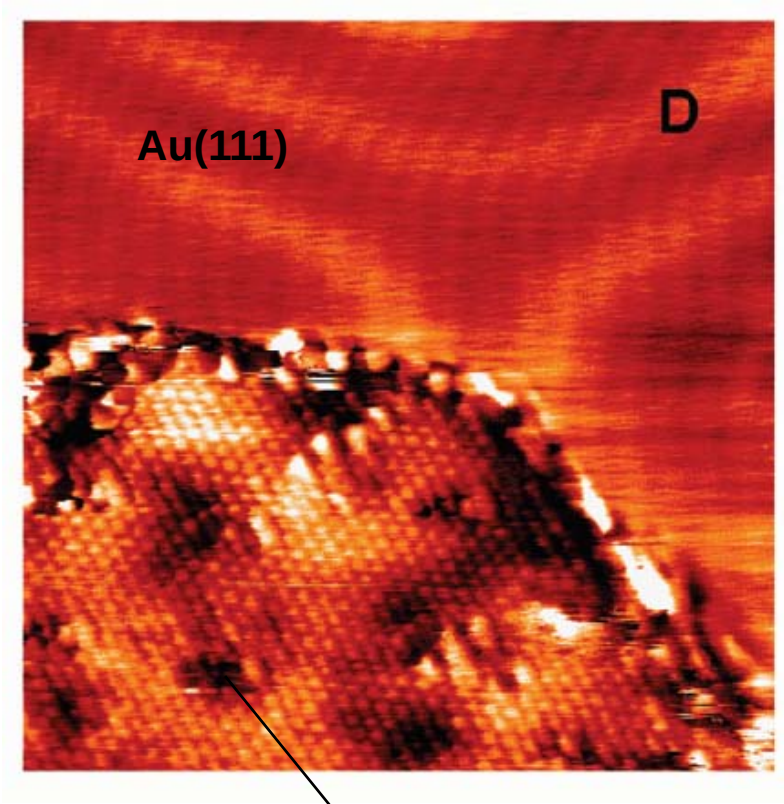




**Fig 3**

**Rodriguez et al, Science, 318 (2007) 1757**

**Image of scanning tunneling microscopy for nanoparticle of $CeO_{2-x}$ dispersed on a Au(111) surface**



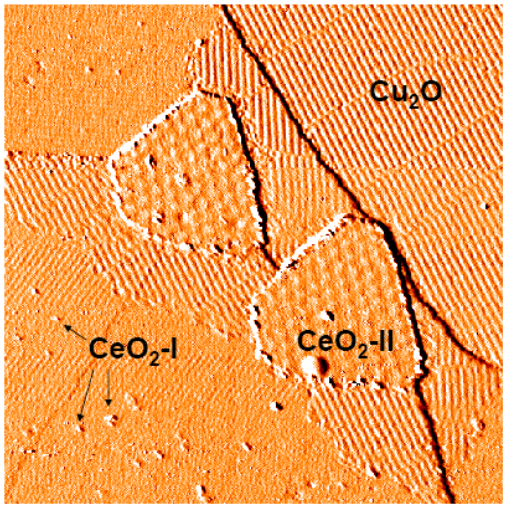

**30 nm x 30 nm**

**$CeO_{2-x}$ with clusters of O vacancies. It dissociates water.**

**Bifuntional catalyst:**

**Water dissociates on O vacancies of the oxide, CO adsorbs on Au sites located nearby, and subsequent reaction takes place at the metal-oxide interface**

# WGS on $CeO_x$/Cu(111)

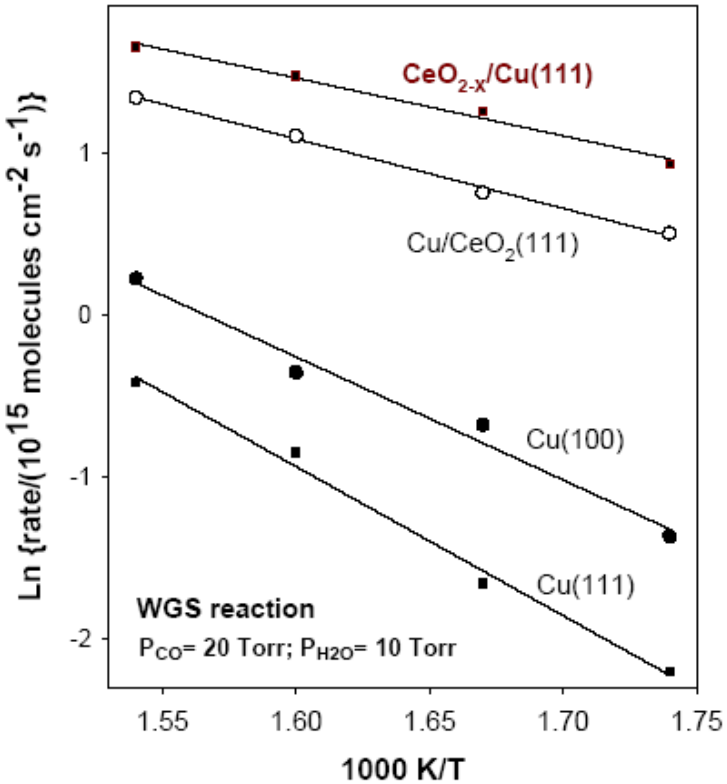



150nm x 150nm

**under reaction**

**$Cu^{1+} \rightarrow Cu^0$**

**$Ce^{4+} \rightarrow Ce^{3+}$**

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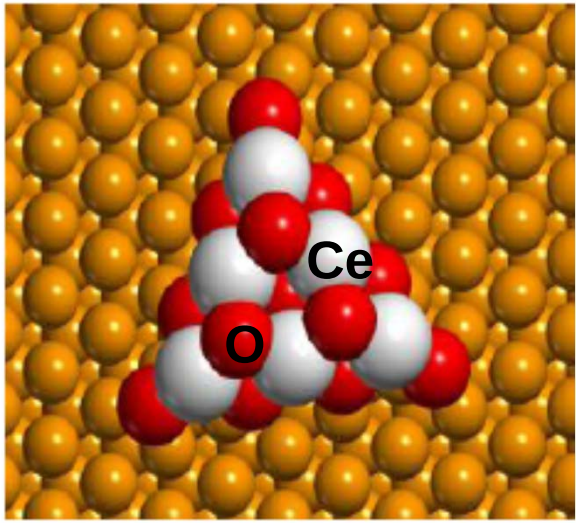
**Water dissociates on O vacancies of the oxide, CO adsorbs on Cu sites located nearby, and subsequent reaction takes place at the metal-oxide interface**

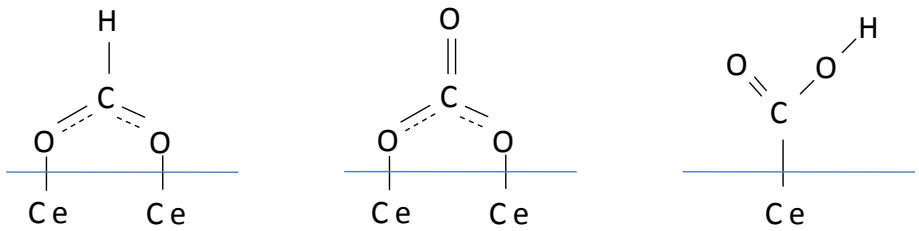
**Rodriguez et al, Angew. Chem. Int. Ed. 48 (2009) 8047**

## DFT studies using model catalysts



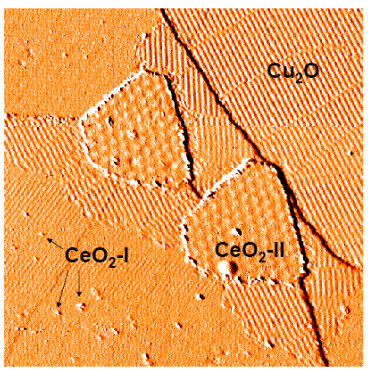

**Nanoparticles of ceria in contact with Cu(111) is very active for the dissociation of $H_2O$ and do not bind the OH groups very strongly.**

# Highlight: Metal-oxide interfaces play a key role in the binding and generation of reaction intermediates




*Formate* *Carbonate* *Carboxyl*

**Possible intermediates for WGS**

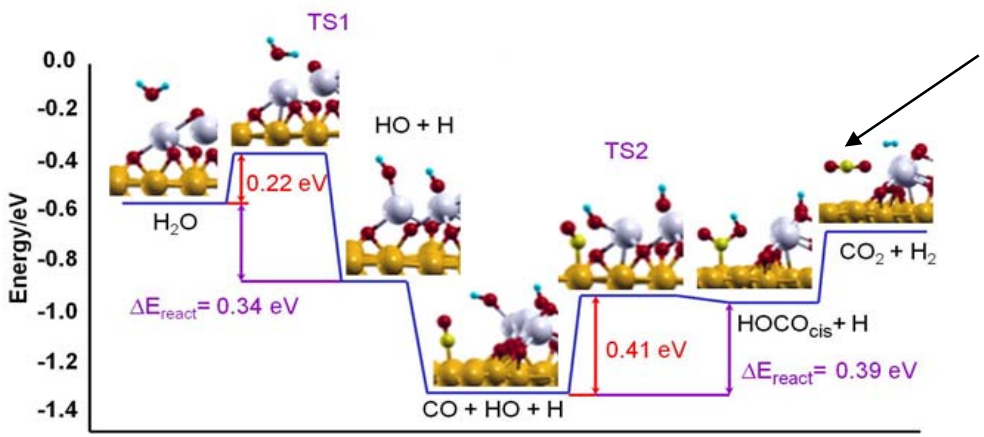



150nm x 150nm

**under reaction**

**$Cu^{1+} \rightarrow Cu^0$**

**$Ce^{4+} \rightarrow Ce^{3+}$**




**$CO_2^-$ seen with NAP-XPS, IR**

**Calculated structures and energies for the WGS reaction path on $CeO_x$/Cu(111)**

**Senanayake, Liu, Rodriguez, Stacchiola et al, *Angew. Chem.* 52 (2013) 5101**

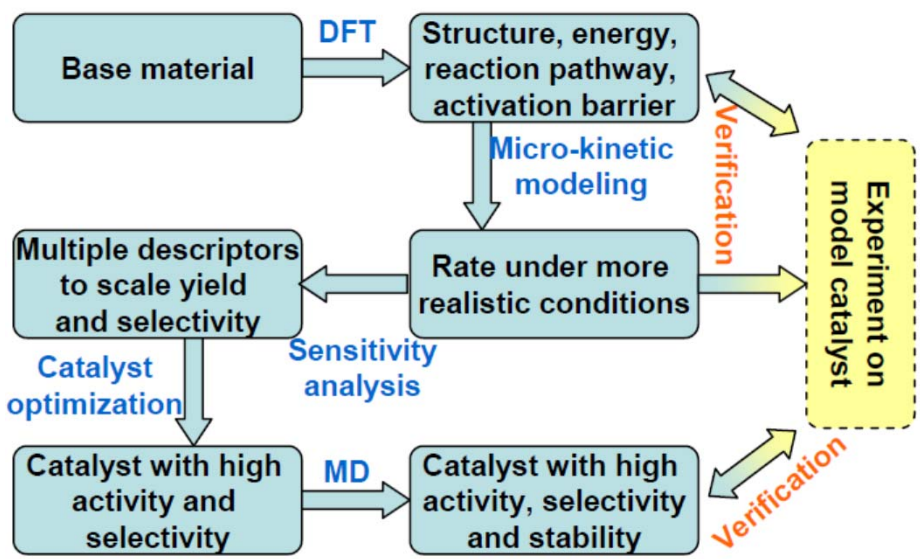
# Future work

***Computer modeling*:**

**1) DFT calculations of adsorption energies and transition states on nanoparticles and extended surfaces**

**2) Microkinetic modelling of reaction rates**

**3) Molecular dynamics and kinetic Monte Carlo studies**




**Ping Liu's work**

- **Studies of $CO_2$ hydrogenation to methanol**
  - **on metal-oxide systems**
  - **on metal-carbide systems**

# $CO_2$ hydrogenation on metal-carbide and metal-oxide interfaces

**The synthesis of C1-C4 alcohols through the hydrogenation of $CO_2$ is an attractive route for the production of clean fuels.**

**The main limitation for the industrial synthesis of higher alcohols from $CO_2$ has been the lack of a selective and durable catalyst that allows an efficient production of the alcohols.**

**Major issues are the activation of $CO_2$, the cleavage or hydrogenation of the C-O bonds, and the formation of C-C bonds for the selective formation of C2-C4 alcohols.**

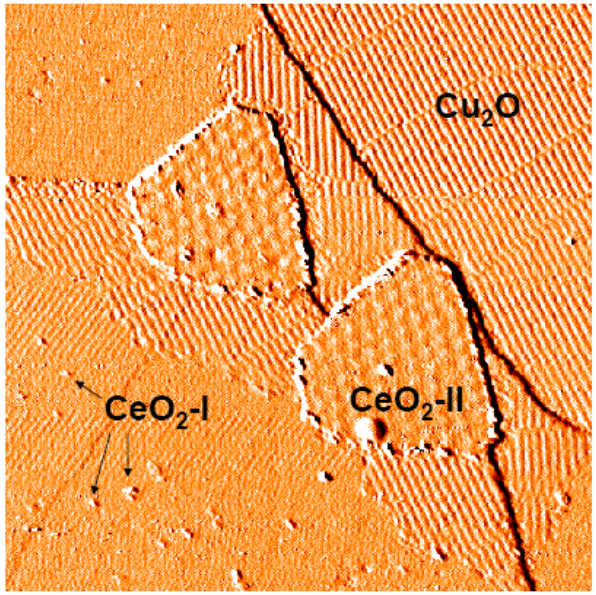
**- J.J. Spivey and A. Egbebi, *Chem. Soc. Rev.* 2007, *36*, 1514.**

**Major advance: Activation of $CO_2$ on metal-carbide and metal-oxide interfaces**

**- Rodriguez, Liu et al, J. Phys.Chem. Lett. 3 (2012) 2275.**

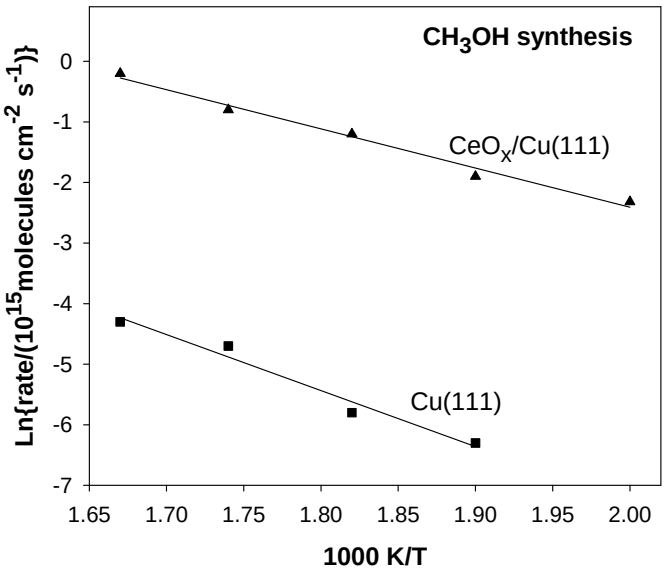
**- Stacchiola, Senanayake, Liu, Rodriguez et al, Angew. Chem. 52 (2013) 5101.**

# Methanol synthesis on $CeO_x$/Cu(111)




150nm x 150nm

$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$




**under reaction**

**$Cu^{1+} \rightarrow Cu^0$**

**$Ce^{4+} \rightarrow Ce^{3+}$**

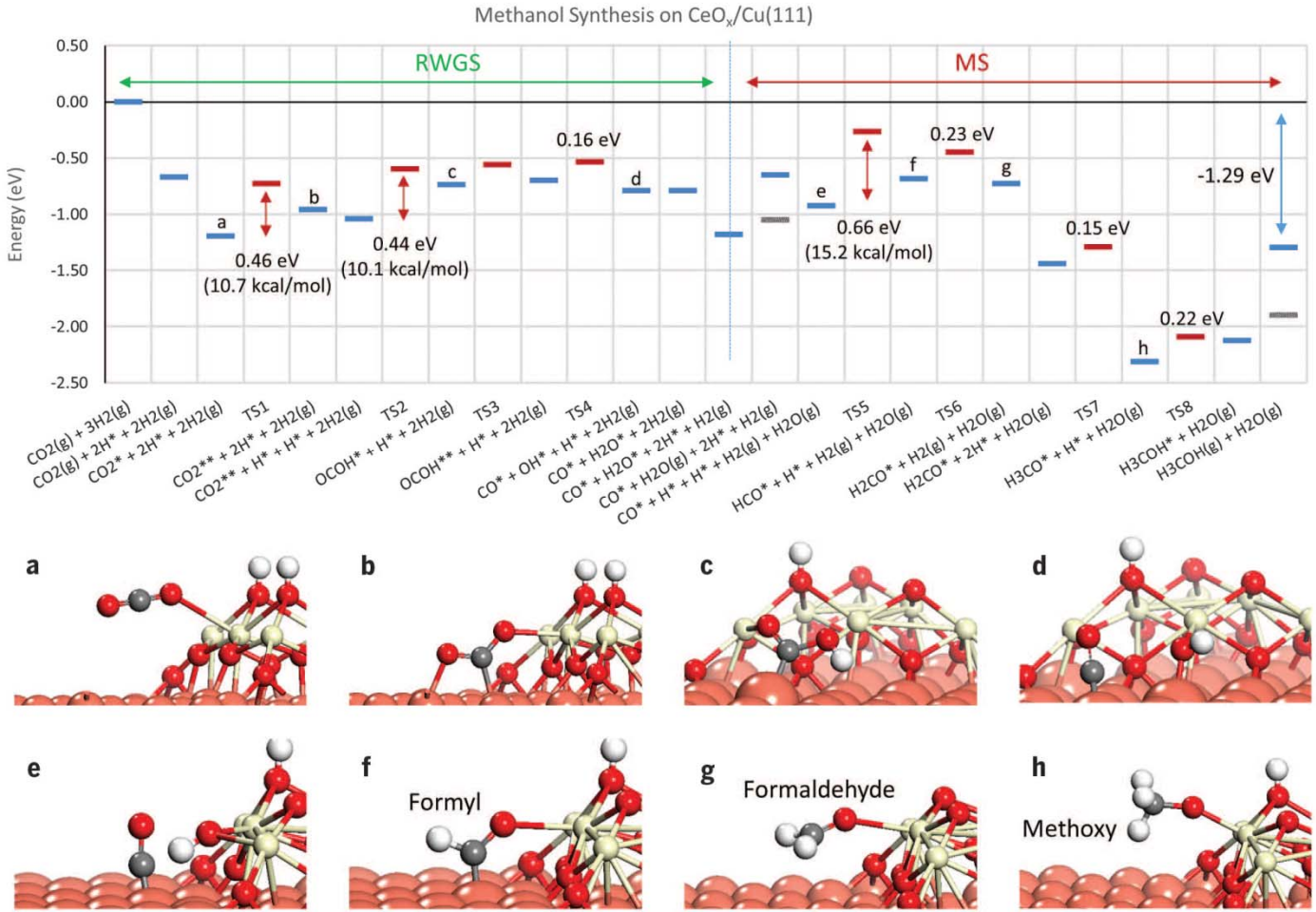
$P(CO_2)$= 0.5 atm $P(H_2)$= 4.5 atm
Top trace : 20% of Cu covered by ceria

The ceria nanoparticles enhance the reactivity of the copper surface, oxide plays active role

**One needs to optimize performance of the metal-oxide interface**

**Rodriguez et al, Science 345 (2014) 546**

DFT results

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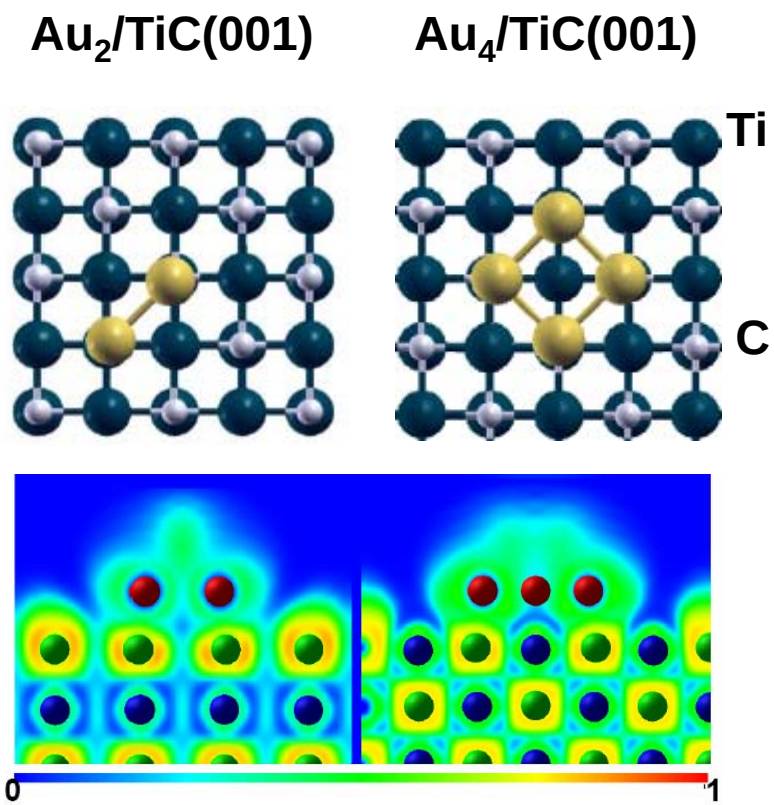
**Rodriguez et al, Science 345 (2014) 546**

## DFT results




Electron density plots

**Au atoms in contact with TiC show a big polarization of electrons that enhances chemical reactivity of the metal**

Rodriguez et al, J. Am. Chem. Soc. 131 (2009) 8595.

# Metal- Carbide interfaces: $CO_2$ hydrogenation to methanol

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

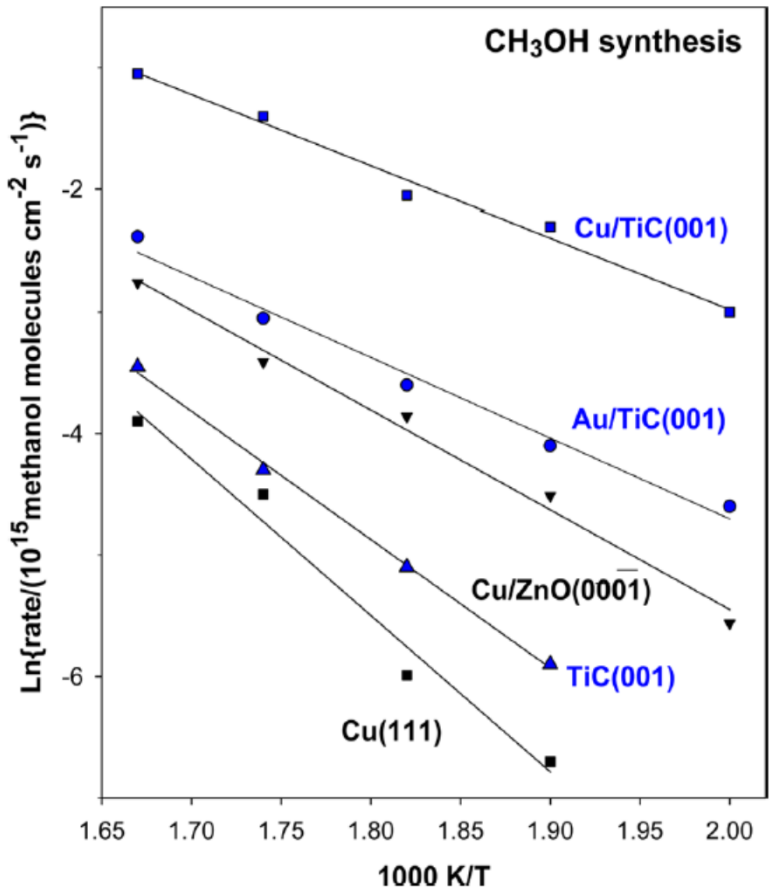
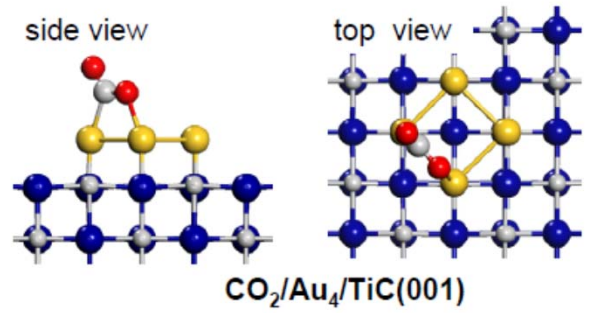
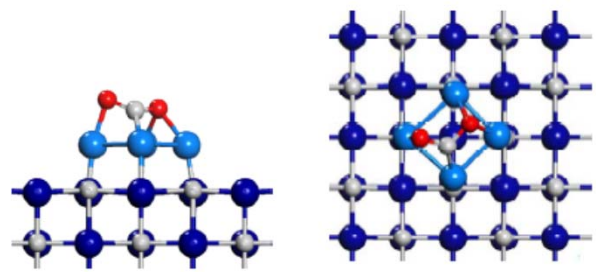



**Figure 1.** Arrhenius plot for methanol synthesis on Cu(111), a ZnO(000$\bar{1}$) surface precovered with 0.2 ML of Cu,[9] clean TiC(001), and titanium carbide precovered with 0.1 ML of Au or Cu. In a batch reactor, the catalysts were exposed to 0.049 MPa (0.5 atm) of $CO_2$ and 0.441 MPa (4.5 atm) of $H_2$. The reported values are for steady state rates measured at temperatures of 600, 575, 550, 525, and 500 K.




$CO_2/Au_4/TiC(001)$

$E_{ads}$= -0.7 eV



$CO_2/Cu_4/TiC(001)$

$E_{ads}$= -1.1 eV

On Au(111) or Cu(111) no $CO_2$ bonding

**Cu and Au clusters in contact with TiC are quite active for the bonding and hydrogenation of $CO_2$.**

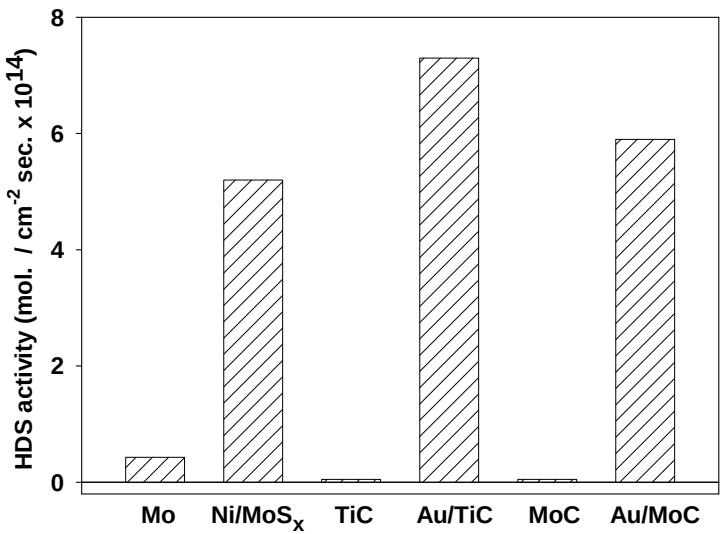
Rodriguez, Liu et al, J. Phys.Chem. Lett. 3 (2012) 2275.

- **Studies of desulfurization processes**
  - **role of metal-support interaction**

# Desulfurization on metal-carbide interfaces

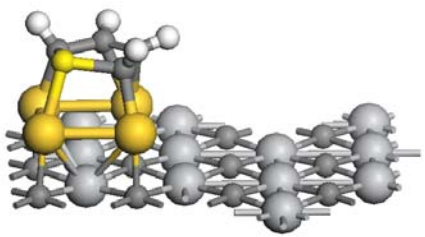
**Sulfur-containing molecules are common impurities in oil and other fossil-derived fuels. Recent legislation emphasizes the need for reducing the sulfur content in oil-derived fuels:**
**From 40-70 ppm to 5-10 ppm**

**More active catalysts are being search for hydrodesulfurization**




**1 Torr $C_4H_4S$, 500 Torr $H_2$**

**600 K**

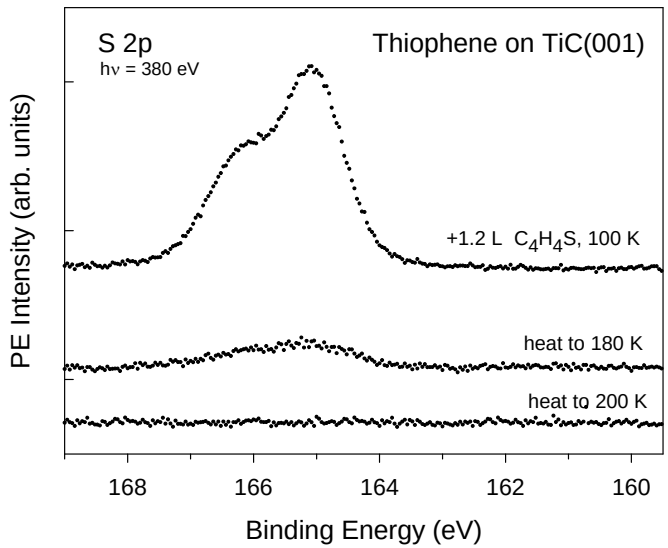


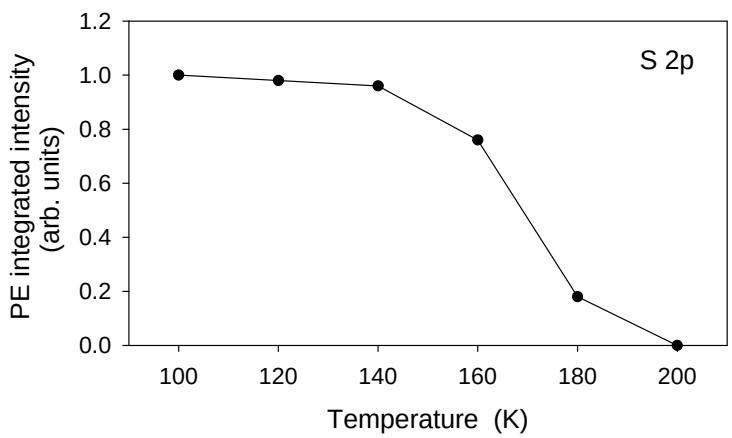
**$C_4H_4S/Au_4/TiC(001)$**

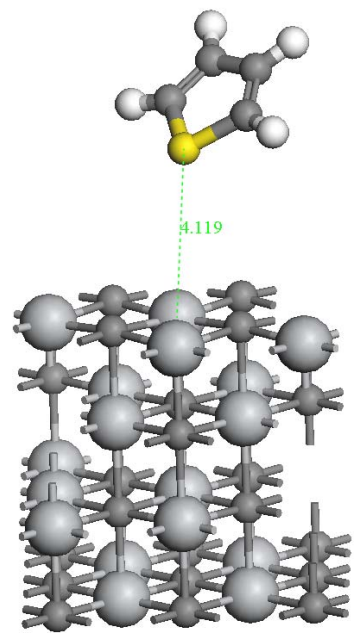
**Au/TiC and Au/MoC display a HDS activity that is comparable or higher than that of conventional Ni/MoS$_x$**


**J.A. Rodriguez, P. Liu et al, *J. Am. Chem. Soc.* 131 (2009) 8595.**

**J.A. Rodriguez, P. Liu et al, *Catalysis Today*, 166 (2011) 2-9**



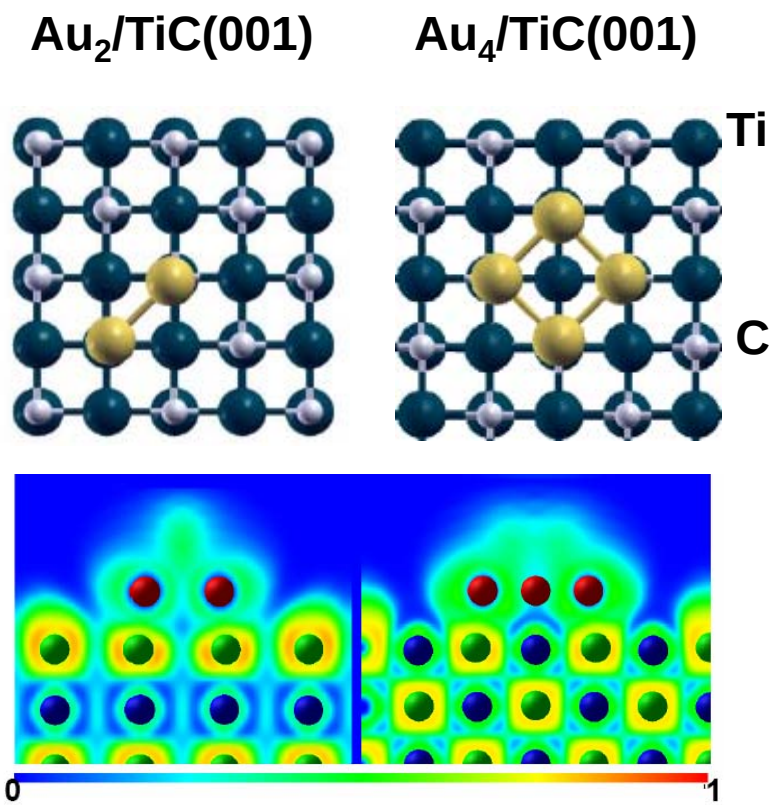




**The bonding interactions of thiophene with TiC(001) are very weak.**

Rodriguez et al, J. Am. Chem. Soc. 131 (2009) 8595.

## DFT results

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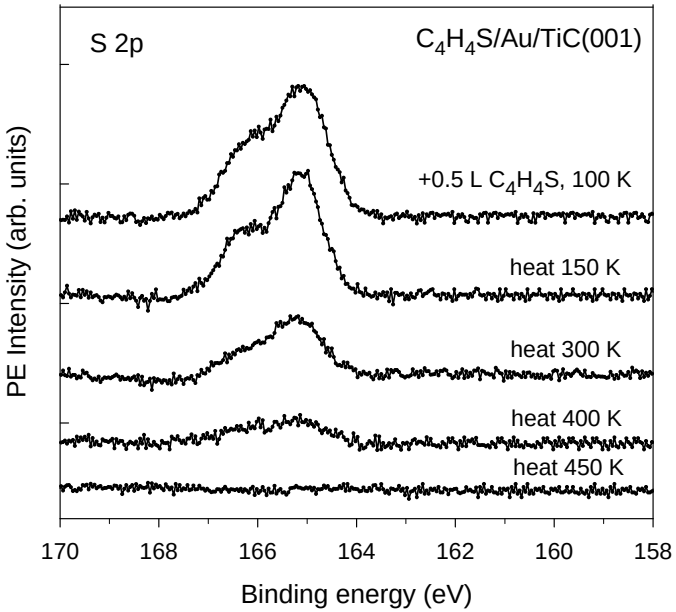
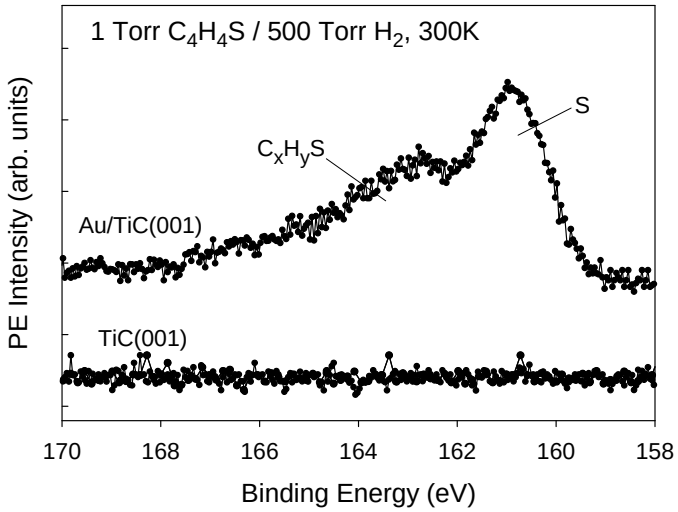
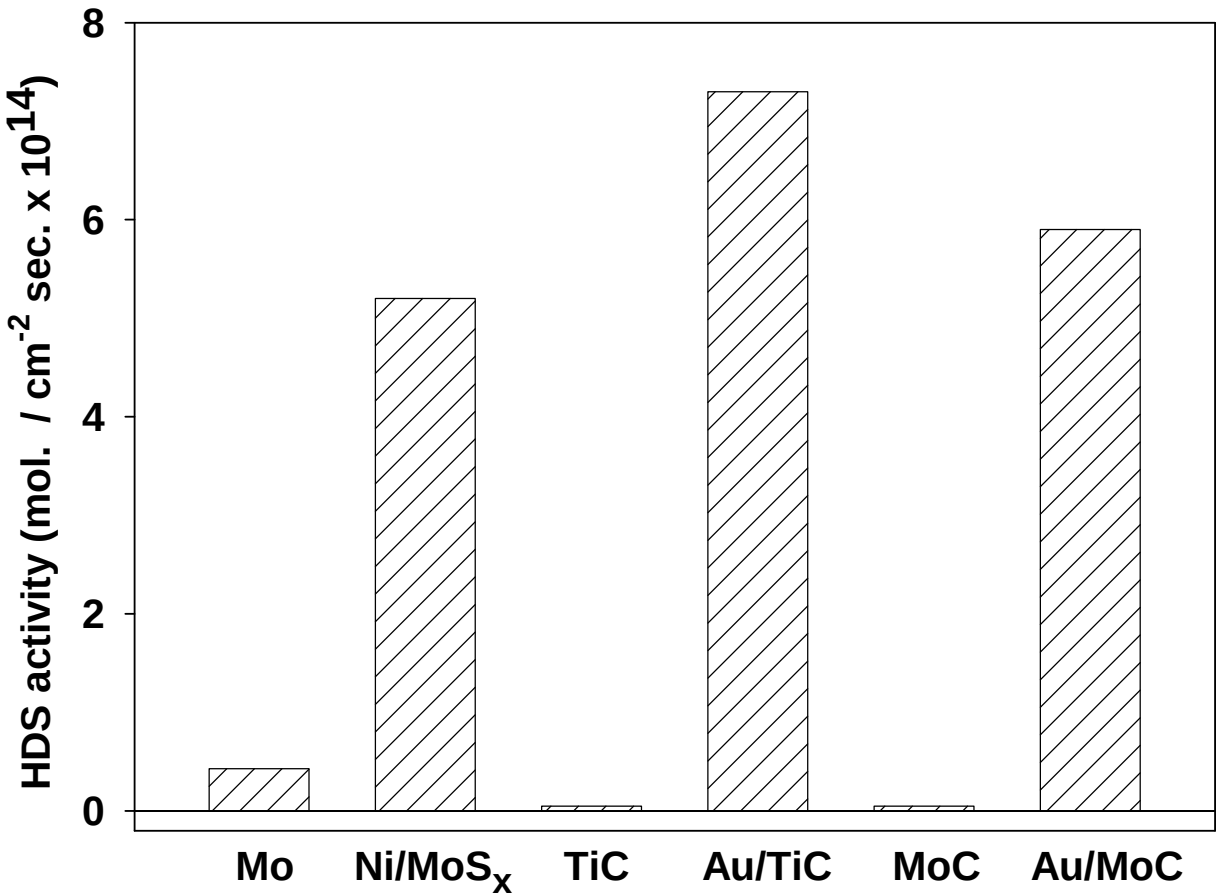
Rodriguez et al, J. Am. Chem. Soc. 131 (2009) 8595.



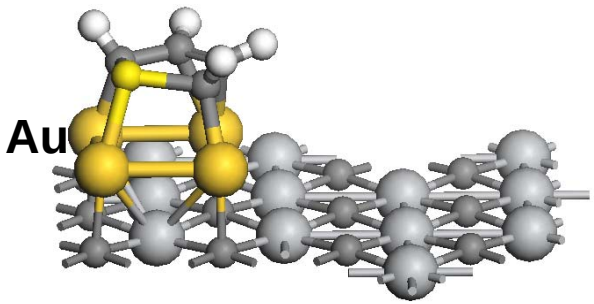




**The addition of small amounts of Au to TiC enhances the bonding of thiophene and makes possible HDS reactions.**

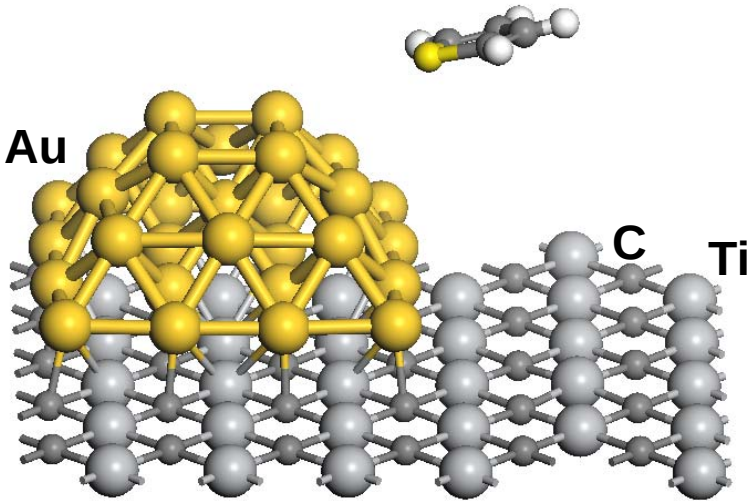
Rodriguez et al, J. Am. Chem. Soc. 131 (2009) 8595.




**Au/TiC and Au/MoC display a HDS activity that is comparable or higher than that of conventional Ni/MoSx catalysts.**




**Au4/TiC(001)**




**Au29/TiC(001)**

**Active for HDS**

**No-active for HDS**

Rodriguez et al, J. Am. Chem. Soc. 131 (2009) 8595.

# Conclusion

**Theory can be quite useful in the study of catalytic processes**

- **It can help with the interpretation of experimental results**
- **It can predict the behavior of catalytic materials**
- **It can be useful for developing basic patterns of reaction**