

DENSITY FUNCTIONAL STUDY OF WATER-GAS-SHIFT REACTION ON METAL-OXIDE CATALYSTS

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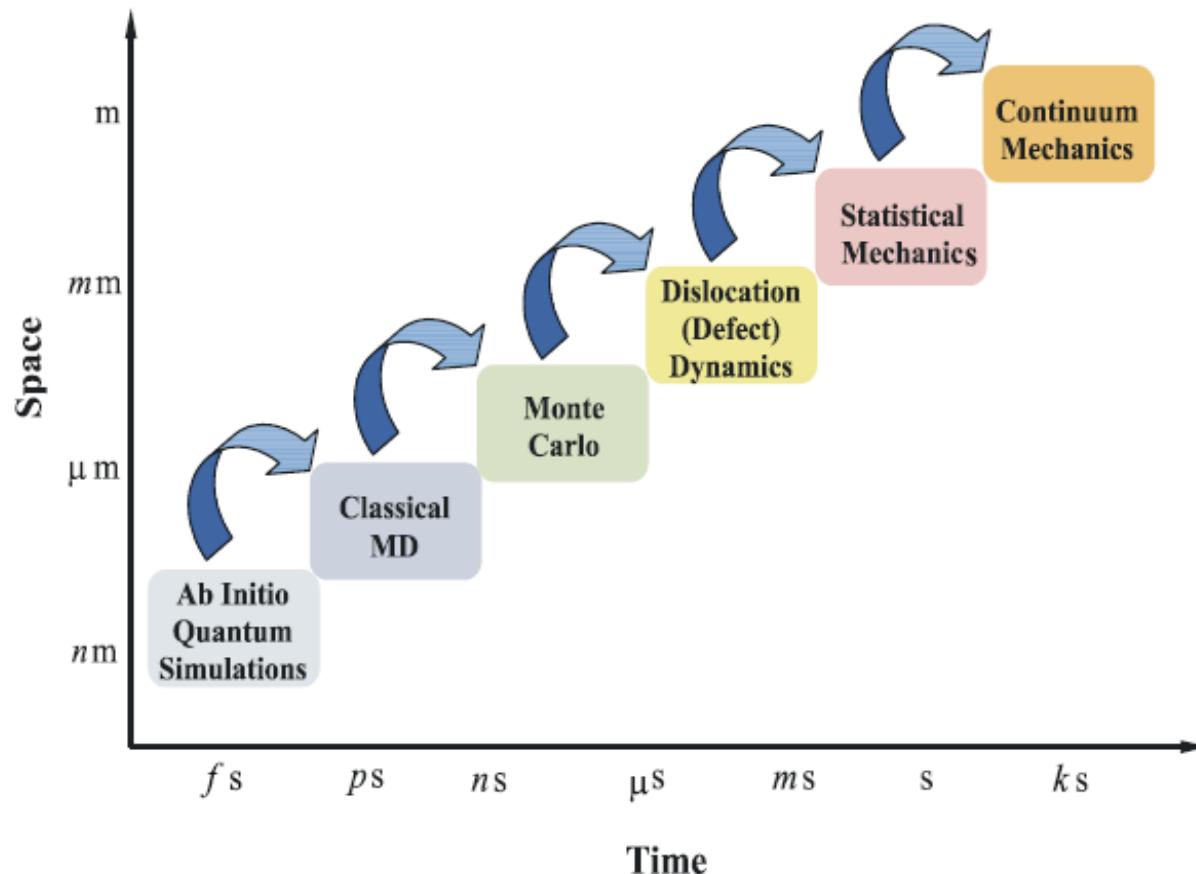
Center for Functional Nanomaterials, Brookhaven National Laboratory



EPSCoR Program Review

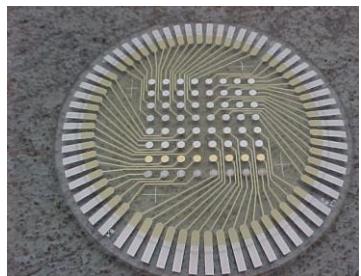


Theoretical studies of materials



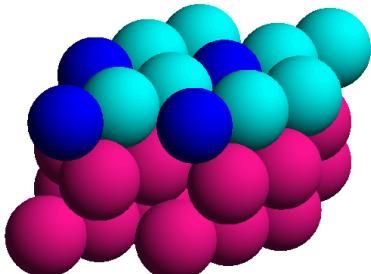
Role of theory in material development

H₂/CO electrooxidation in fuel cells



**Synthesis
characterization**

PtRuM
ternary alloys



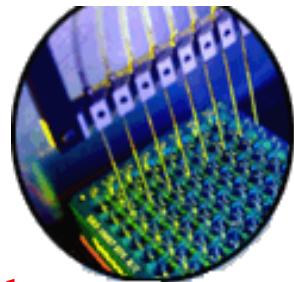
Confirm the
theoretical predictions

Predict better
catalysts

**Experiments
testing**

Theory

PtRu
bimetallic alloy

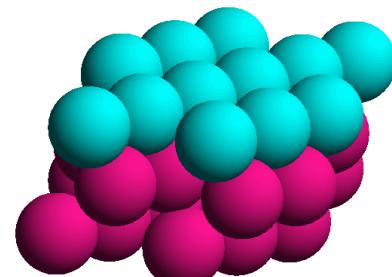


Describe and
understand the
catalytic activity of
proven catalysts

Liu, et al., *Electrochimica Acta* 48 (2003) 3731.

Liu, et al., *J. Phys. Chem. B* 107 (2003) 11013.

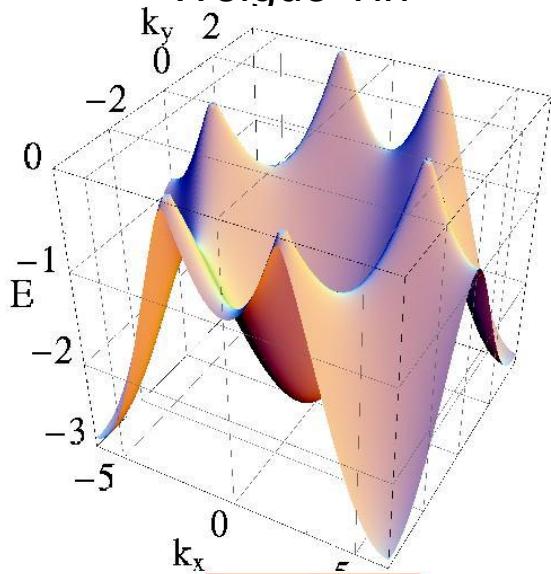
Liu, et al., US patent No. 6,663,998.



Material Theory under Basic Energy Sciences at Brookhaven National Laboratory

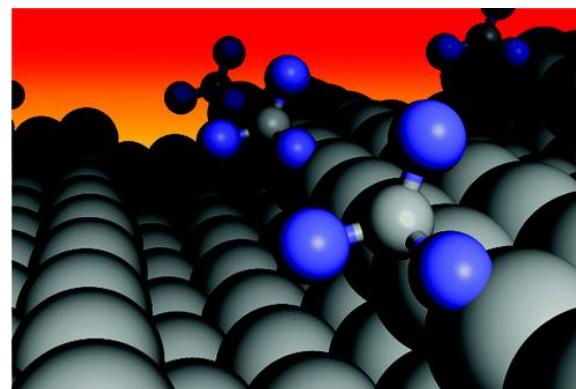
Condensed Matter Physics & Materials Science

Alexei Tsvelik
Robert Konik
Wei Ku
Sergei Maslov
Weiguo Yin



Center for Functional Nanomaterials

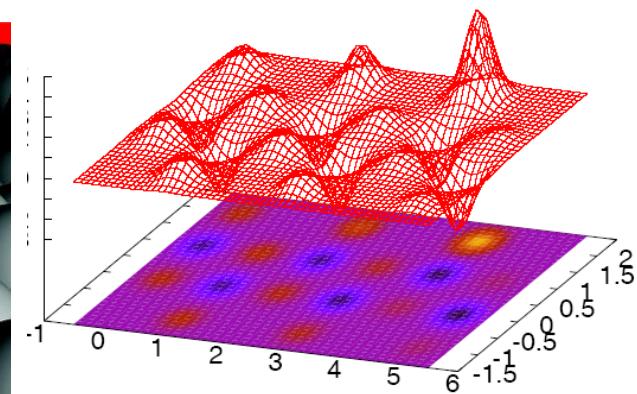
Mark S. Hybertsen
Qin Wu
James T. Muckerman*
James Davenport*
Ping Liu*



Chemistry

James T. Muckerman*
Huagen Yu
Ping Liu*

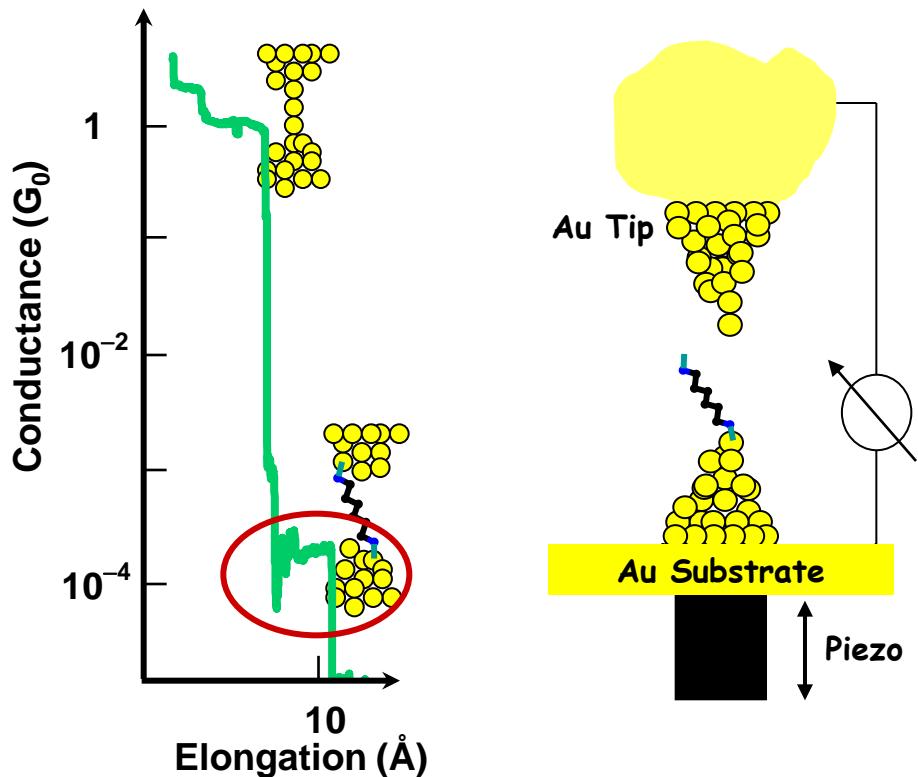
* Joint appointment



Single molecule junction evolution under stress

Joint project between Columbia Univ. and BNL (CFN)

Experimental Approach

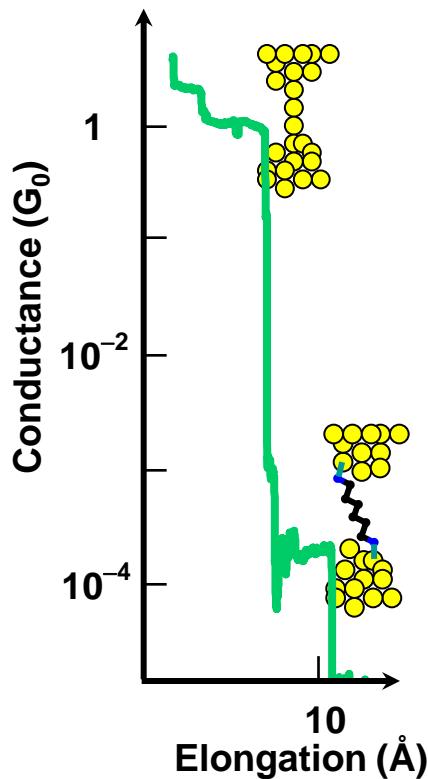


Single molecule junction evolution under stress

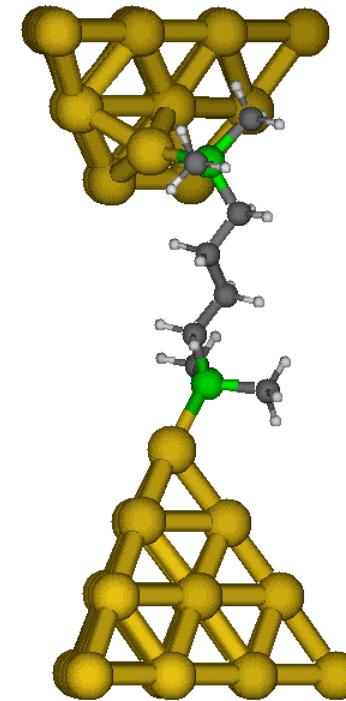
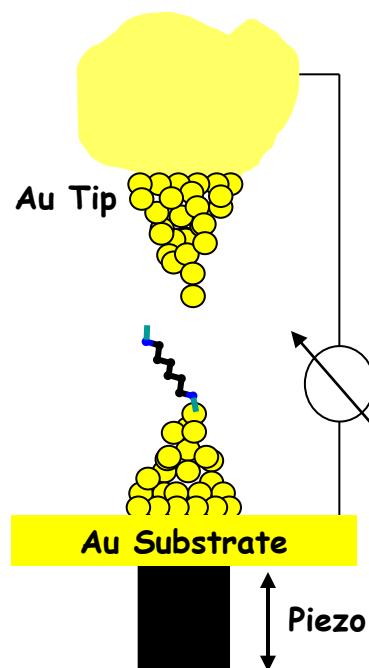


Joint project between Columbia Univ. and BNL (CFN)

Experimental Approach



Calculated Adiabatic Trajectory



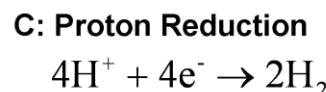
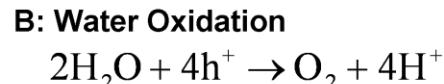
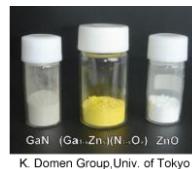
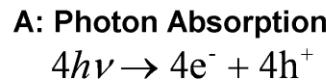
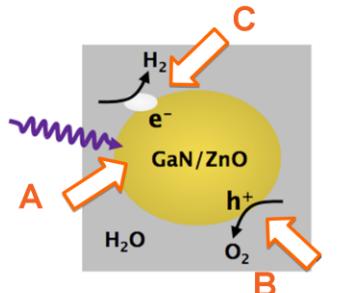
Kamenetska, Koentopp, Whalley, Park, Steigerwald, Nuckolls, Hybertsen & Venkataraman,
PRL 102, 126803 (2009)

Courtesy from M. Hybertsen

Solar water splitting simulation

Joint Theoretical Project between Stony Brook & BNL (Chemistry & CFN)

Photocatalytic Water Splitting: GaN/ZnO Alloy Particles

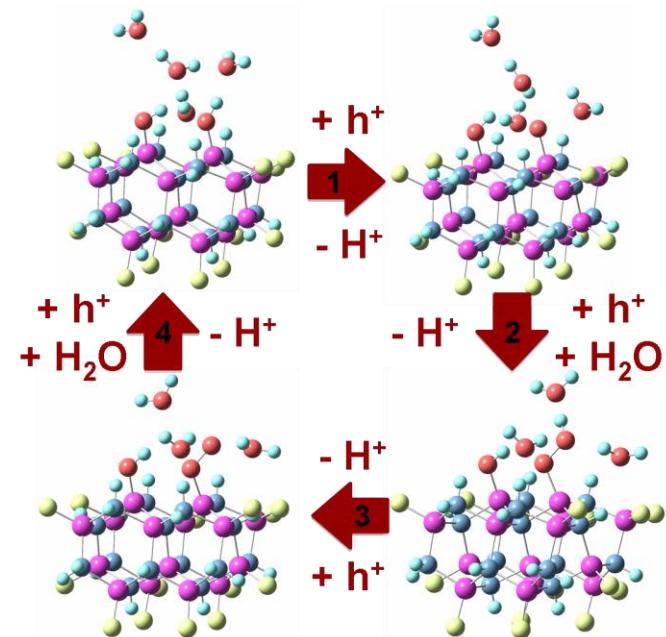


Reaction Step	ΔG (eV)
$*OH^- + h^+ \rightarrow *O^\cdot - + H^+$	2.8
$*O^\cdot - + H_2O + h^+ \rightarrow *OOH^- + H^+$	1.0
$*OOH^- + h^+ \rightarrow *O_2^- + H^+$	1.6
$*O_2^- + H_2O + h^+ \rightarrow *OH^- + O_2 + H^+$	-0.7
Net: $2H_2O + 4h^+ \rightarrow O_2 + 4H^+$	4.7

X. Shen, J. Wang, L. Li, Y.A. Small, P.B. Allen, M. V. Fernandez-Serra, M.S. Hybertsen and J.T. Muckerman

GaN(1010) – Water Interface: Model Oxygen Evolution Process

What are the structures of the water fragments at each reaction step ?



Research interests

- Establishing a molecular level understanding of catalysis and developing, in strong combination with experiments, new catalysts using theoretical methods
- Specific themes are
 - (i) the cleaning of conventional oil-derived fuels: hydrodesulfurization, hydrodenitrogenation
 - (ii) the production, conversion and use of non-conventional fuels such as hydrogen and alcohols: alcohol synthesis from carbon dioxide, water-gas-shift reaction, electrochemical reactions in fuel cell, ...

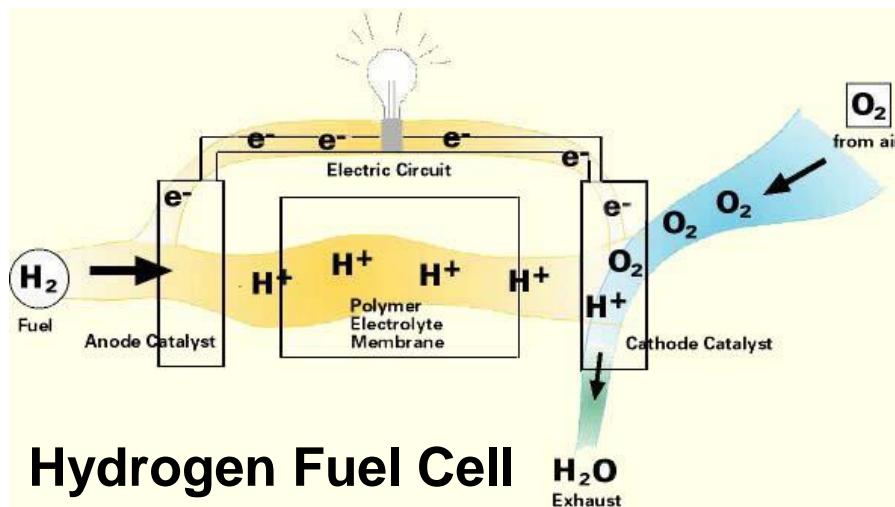
Water-gas-shift (WGS) reaction



- WGS reaction is a part of steam reforming of hydrocarbons



- Increasing interest due to its emerging application for
 - onboard purification &
 - production of hydrogen for fuel cell vehicles.



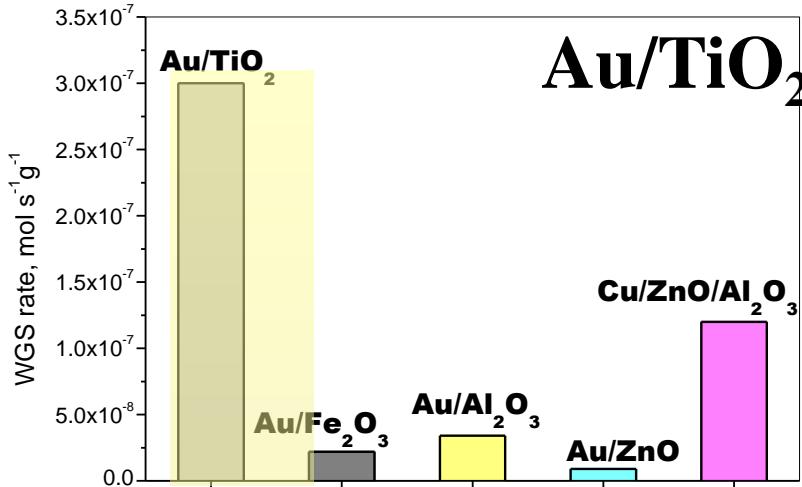
Catalysts for WGS reaction

- Conventional catalysts:

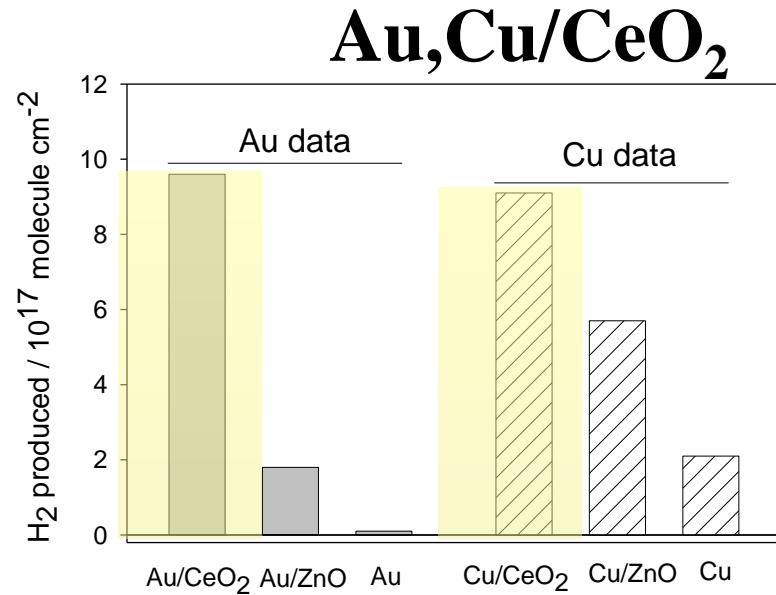
- Mixture of Fe-Cr oxides at 350-500°C
- Zn-Al-Cu oxide at 180-250°C

- New generation catalysts:

- Metal/oxide



Sakurai, Ueda, Hrbek, Kobayashi, Haruta, Chem. Commun. (1997) 271.



Rodriguez, Liu, Hrbek, Evans, Perez, Angew. Chem. Int. Ed. 46 (2007) 1329.

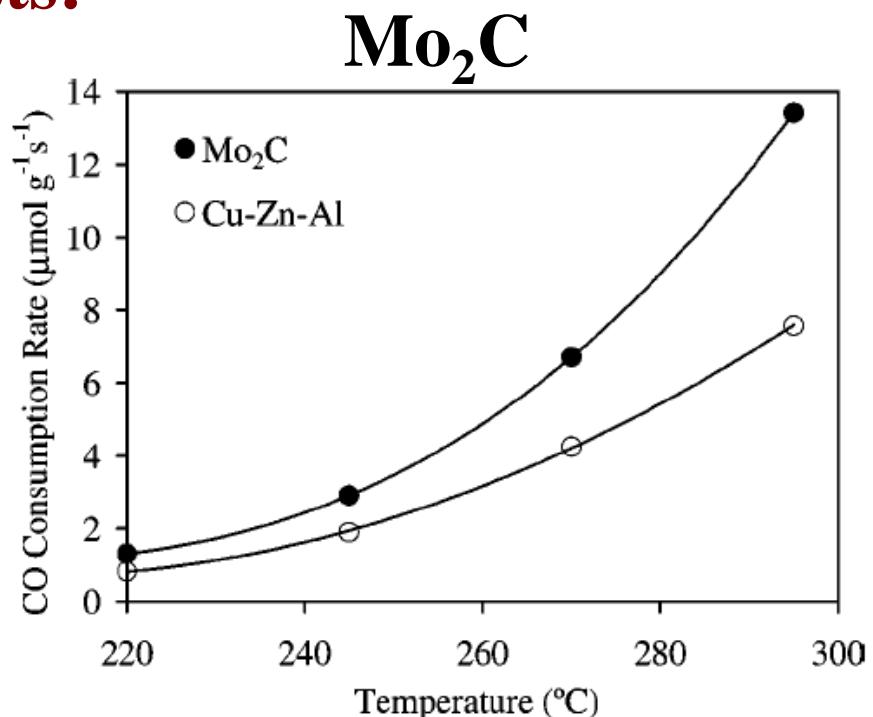
Catalysts for WGS reaction

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- New generation catalysts:

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- Metal carbide



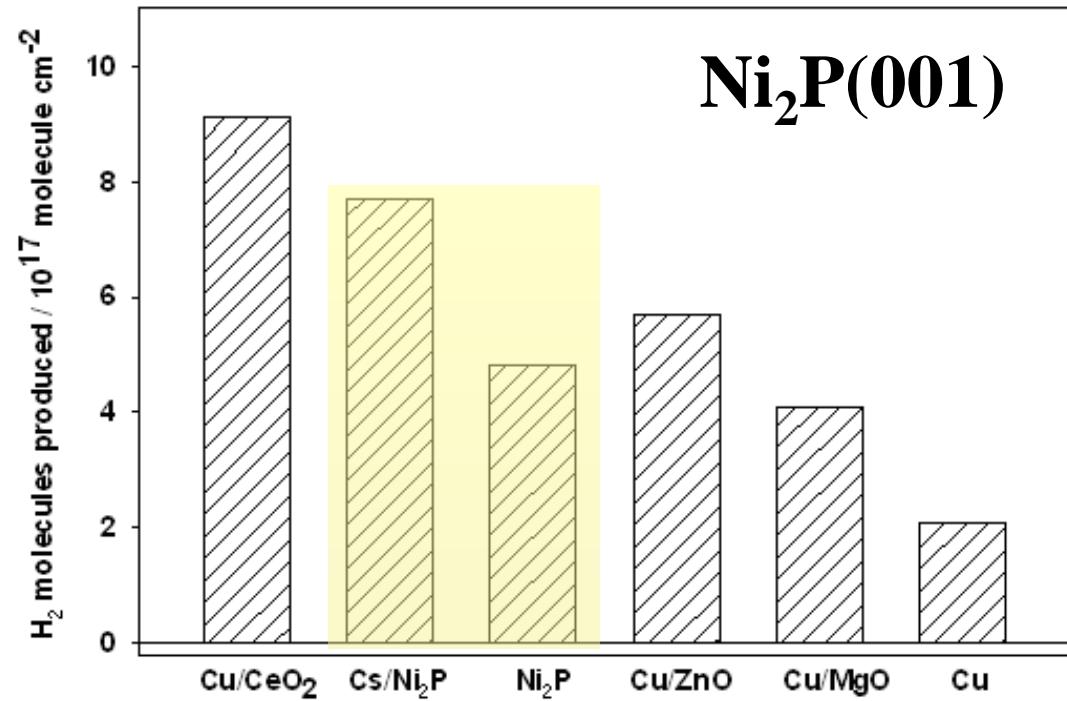
Catalysts for WGS reaction

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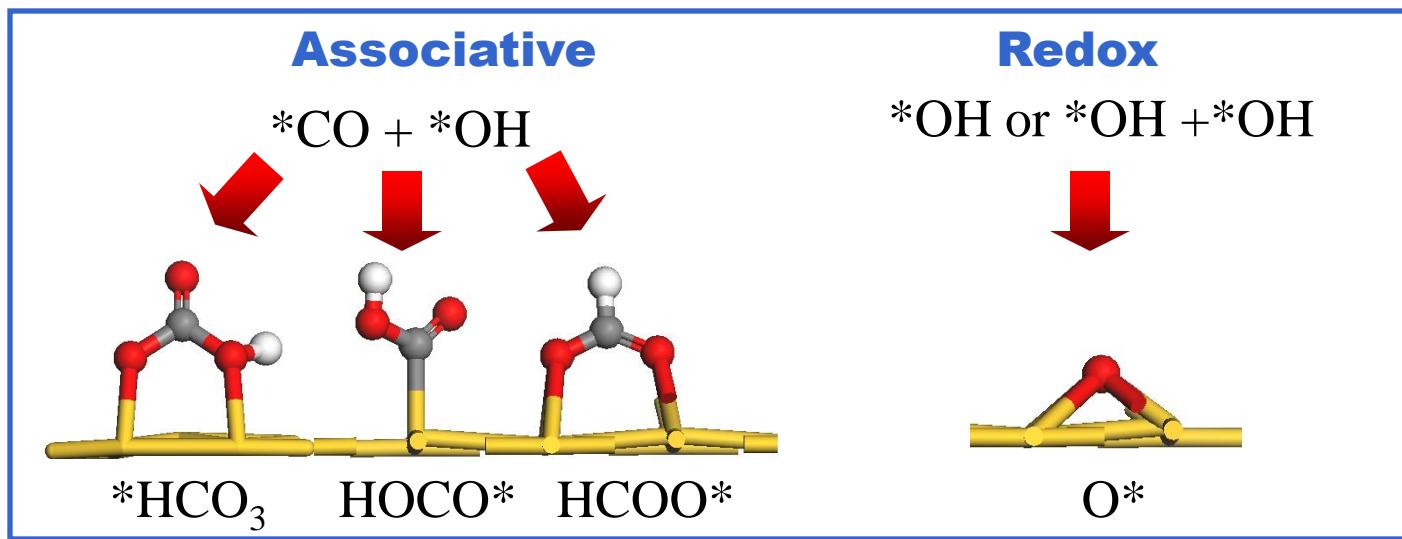
- New generation catalysts:

- Metal/oxide
- Metal carbide
- Metal phosphide



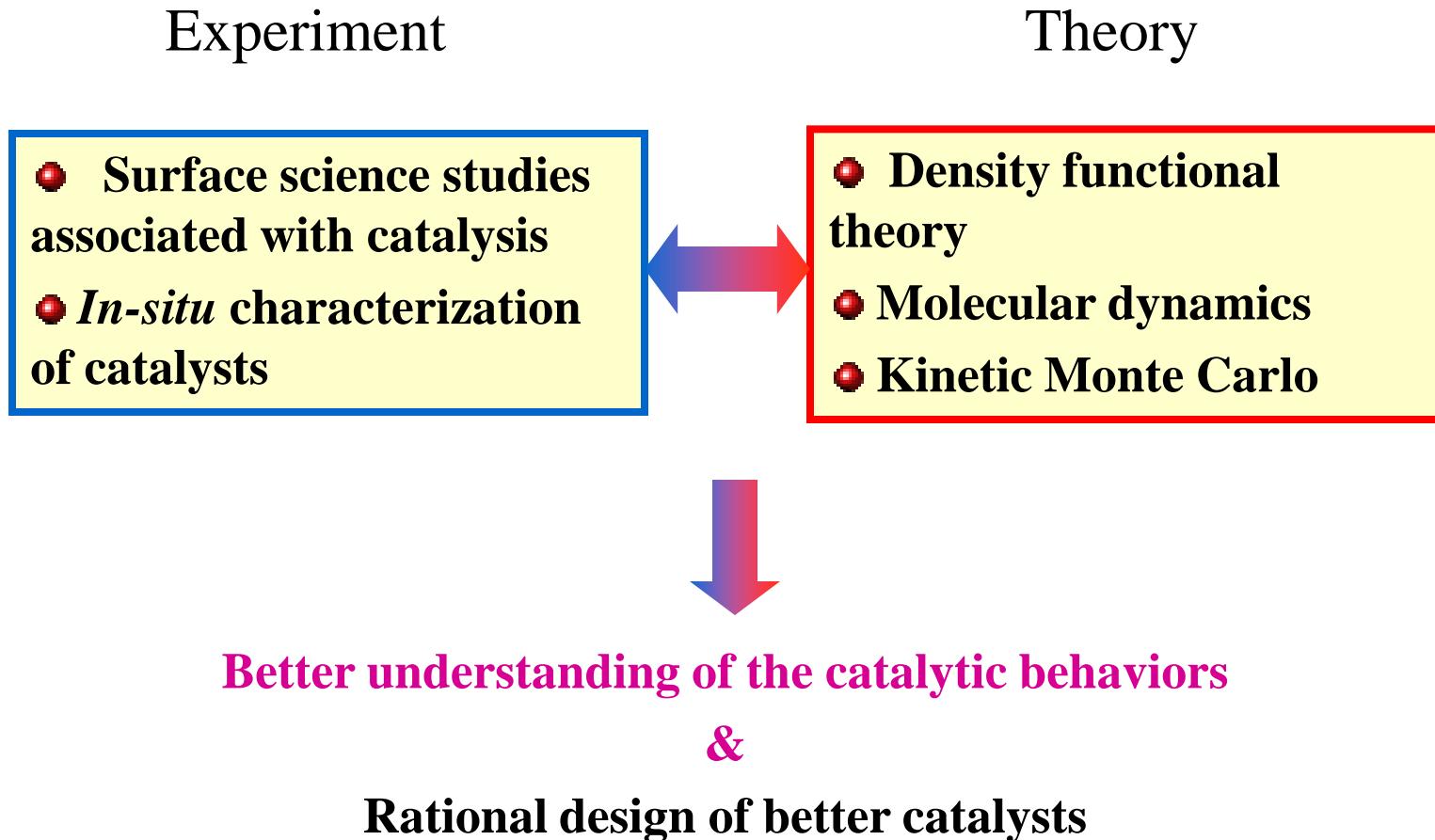
Challenges in WGS studies

● Mechanism



- Active species
- Relation between atomic and electronic structures and WGS activity

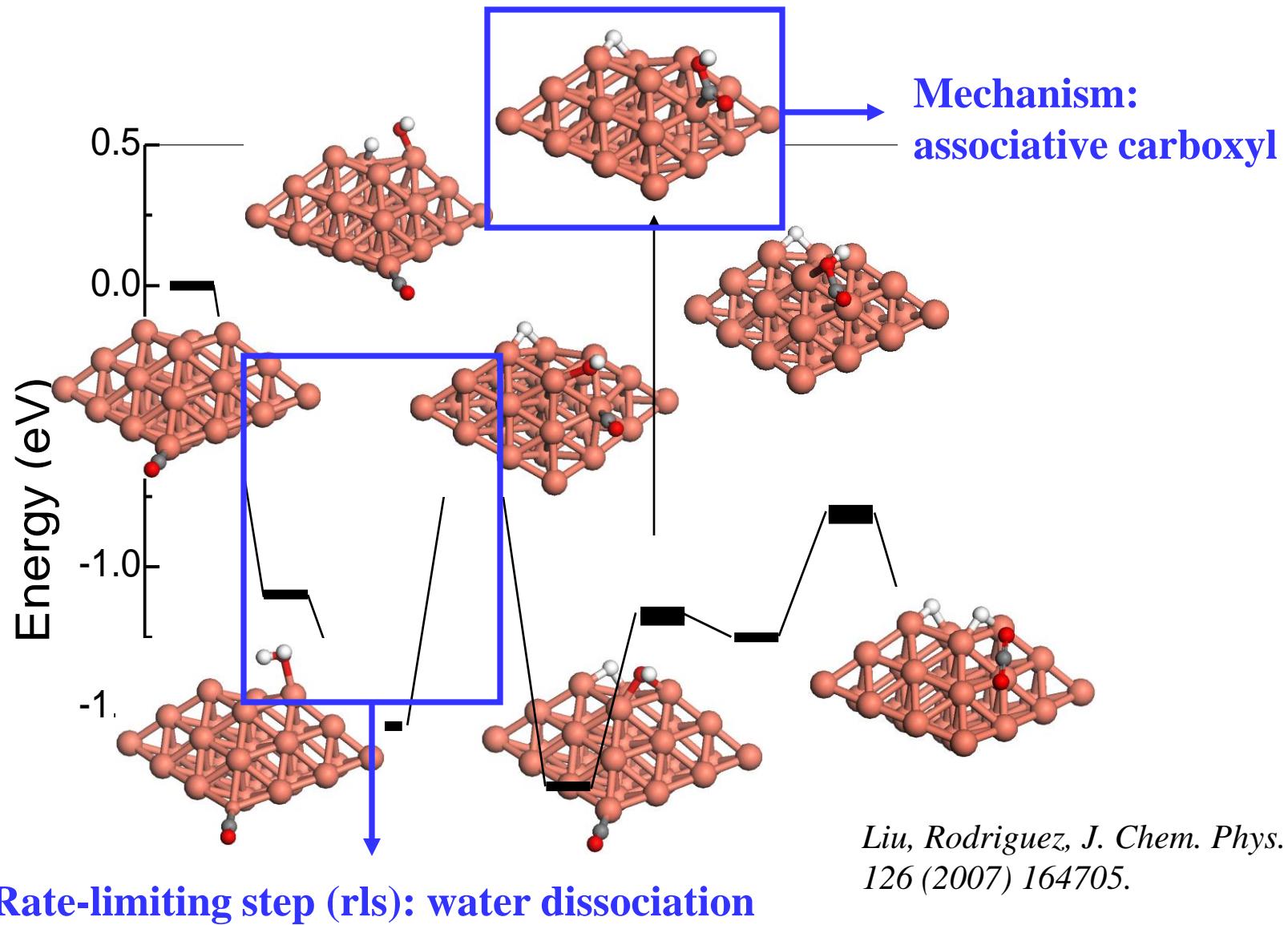
Integral approach to catalysis



Method

- Density Functional Theory (DFT) – DMol³ or CASTEP
- Periodic self-consistent PW91-GGA or RPBE-GGA
- All electrons, effective core potential, ultra-soft Vanderbilt pseudo-potentials
- Numerical basis sets, plane wave basis sets
- Spin polarization as needed
- Linear Synchronous Transit and Nudged Elastic Band method for locating transition state

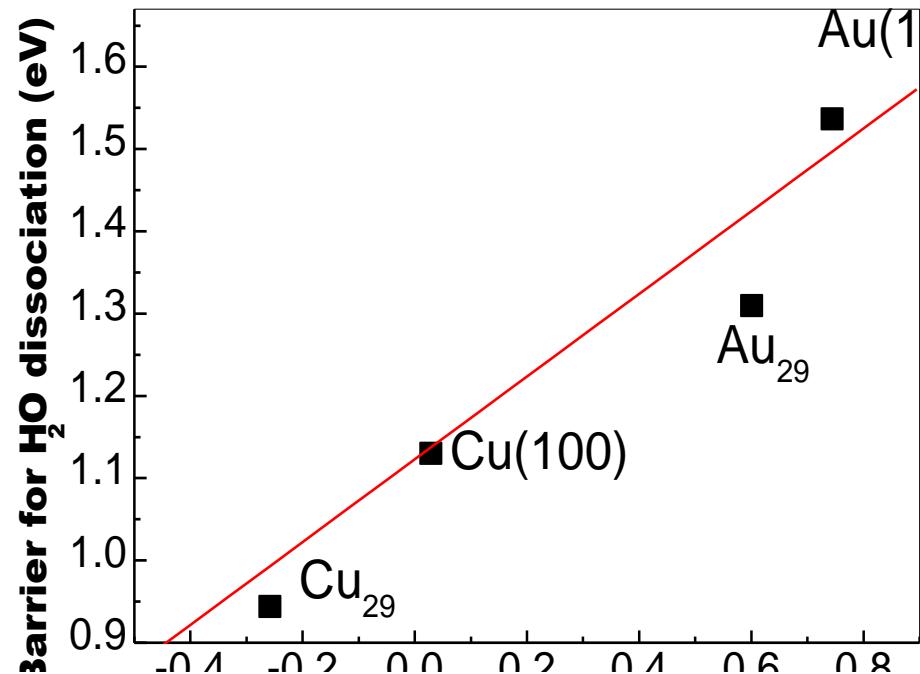
WGS reaction on Cu₂₉



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

WGS reaction on Au_{29} , Cu(100) and Au(100)

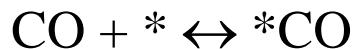
	Mechanism	rls
Cu_{29}	Carboxyl	H_2O dissociation
Au_{29}	Carboxyl	H_2O dissociation
Cu(100)	Redox	H_2O dissociation
Au(100)	Carboxy1	H_2O dissociation



Micro-kinetic model for WGS reaction

WGS reaction on Cu₂₉

Kinetics



(1)



(2)

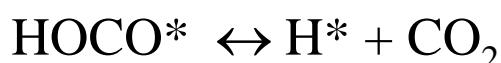


(3) rls

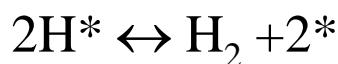
Reaction rate



(4)



(5)



(6)

$$\theta_{\text{CO}} + \theta_{\text{H}_2\text{O}} + \theta_{\text{OH}} + \theta_{\text{OCO}^*} + \theta_{\text{H}} + \theta_* = 1$$

$$r = k_0 \exp\left(-\frac{\Delta E_{a3}}{k_B T}\right) P_{\text{H}_2\text{O}} K_2 \theta_*^2 \left(1 - \frac{P_{\text{H}_2} P_{\text{CO}_2}}{K_{\text{gas}} P_{\text{H}_2\text{O}} P_{\text{CO}}}\right)$$

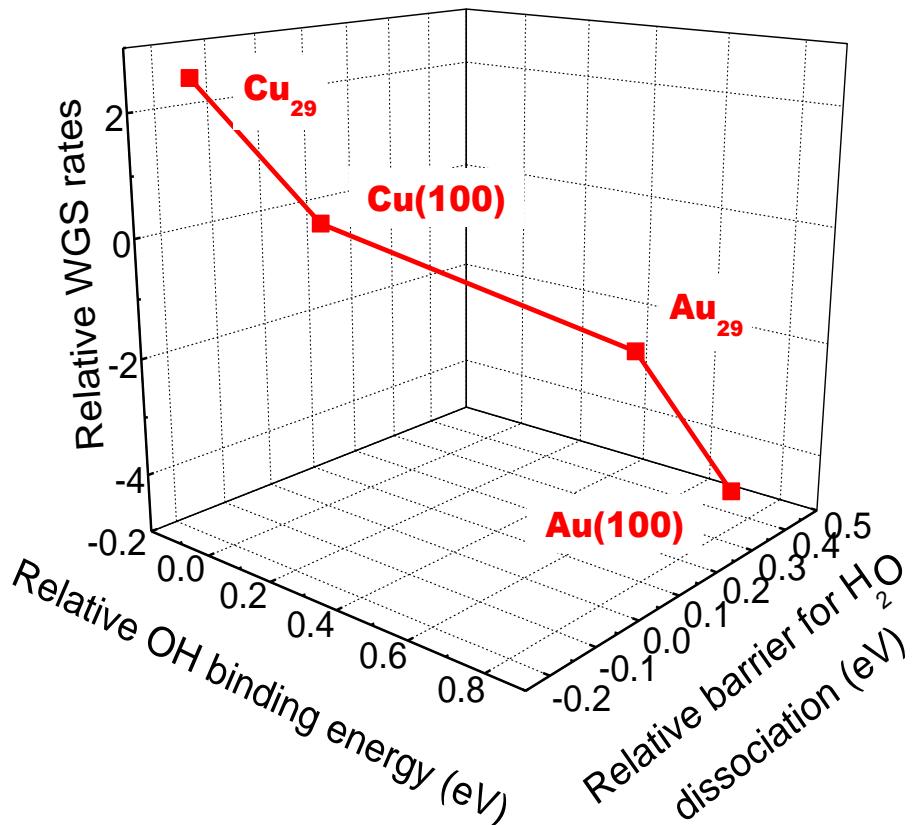
Parameters

$$K_n = \exp[-(\Delta E_{ads}^n - T\Delta S_n)/k_B T]$$

$$\theta_* = \frac{1}{1 + P_{\text{CO}} K_1 + P_{\text{H}_2\text{O}} K_2 + \frac{P_{\text{CO}_2}}{P_{\text{CO}} K_1 K_4 K_5} \sqrt{\frac{P_{\text{H}_2}}{K_6}} + \frac{P_{\text{CO}_2}}{K_5} \sqrt{\frac{P_{\text{H}_2}}{K_6}} + \sqrt{\frac{P_{\text{H}_2}}{K_6}}}$$

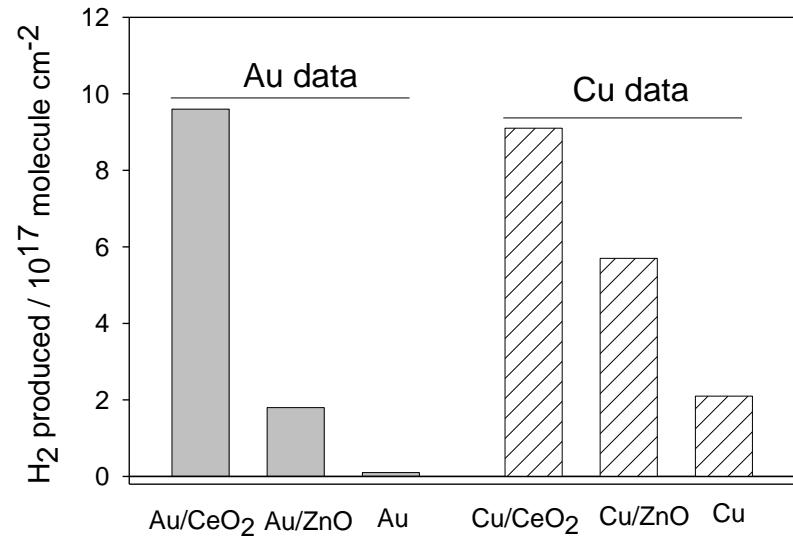
WGS reaction rates

Theory



19 Torr of CO, 9 Torr of H_2O , 1 Torr of CO_2 and 1 Torr of H_2 at 625K

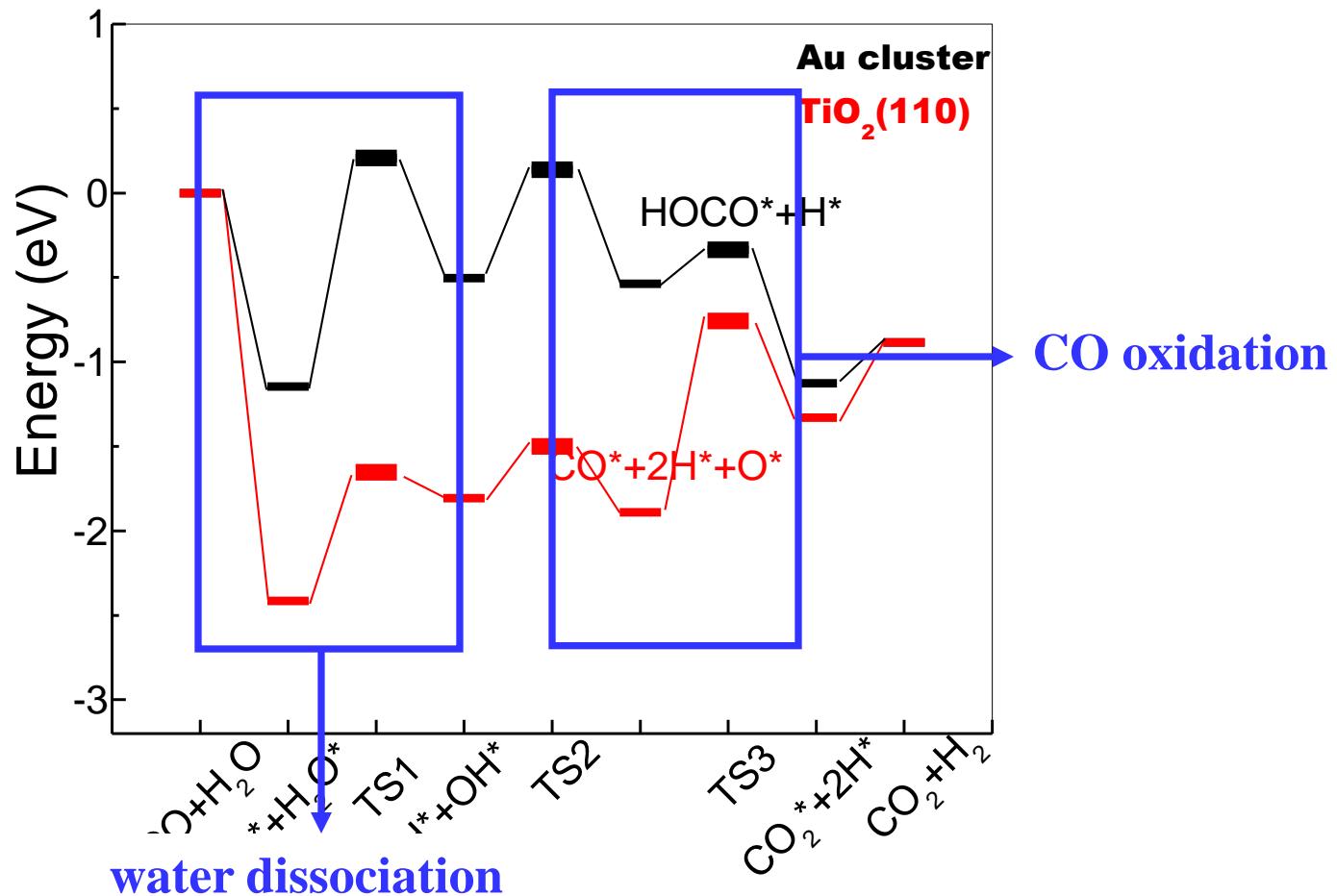
Experiment



Rodriguez, Liu, Hrbek, Evans, Perez,
Angew. Chem. Int. Ed. 46 (2007) 1329.

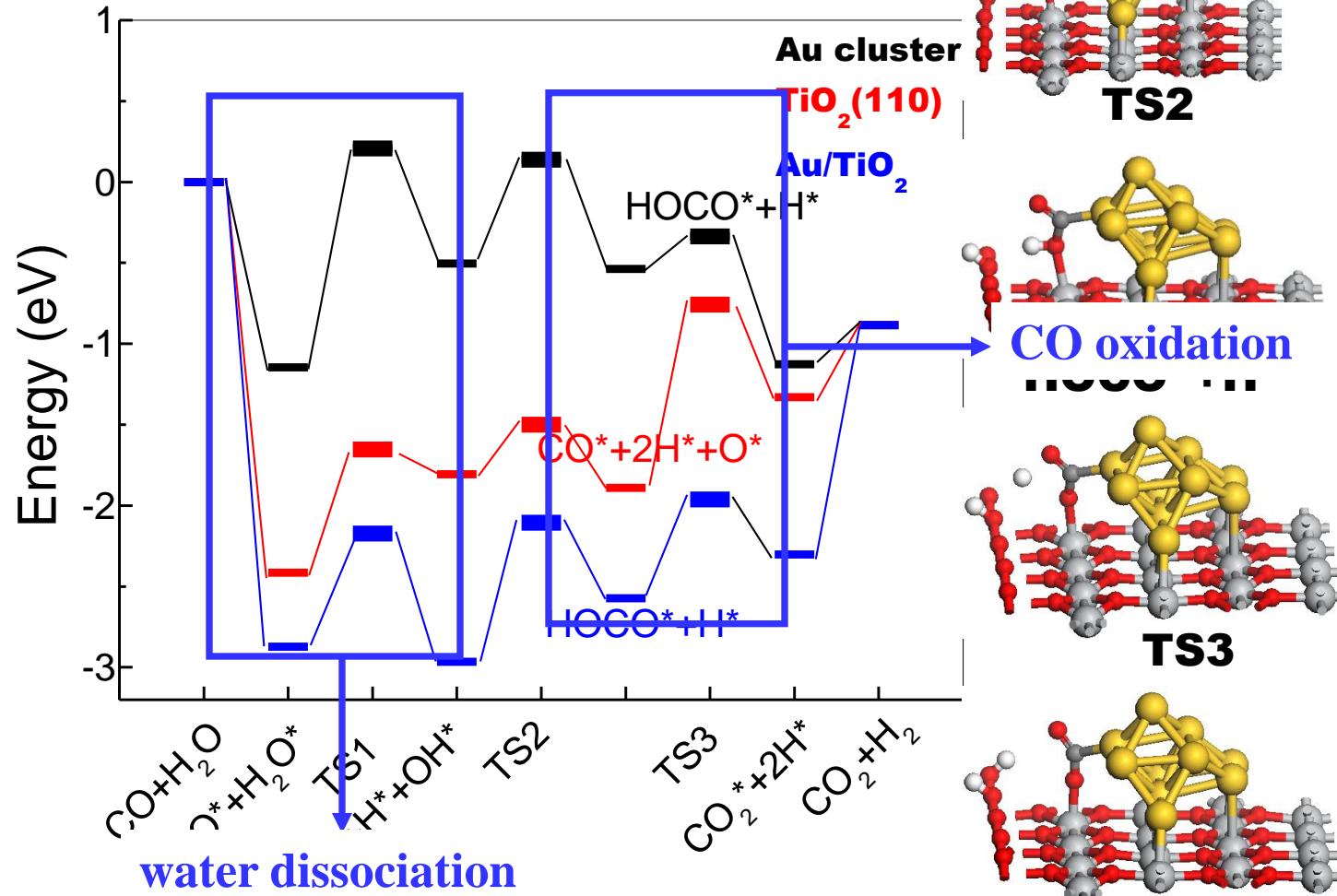
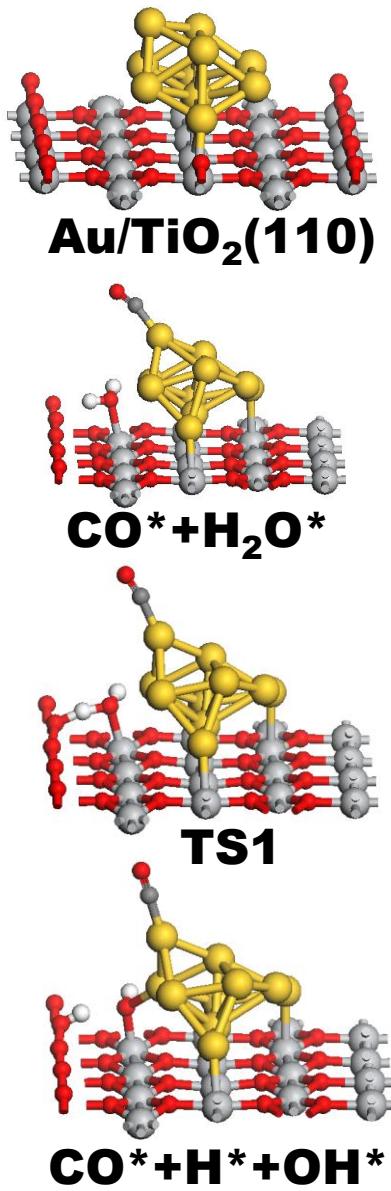
Consistency between experiment and theory for the WGS activity: $\text{Cu}/\text{ZnO} > \text{Cu} > \text{Au}/\text{ZnO} > \text{Au}$

WGS reaction on Au/TiO₂(110)



Rodríguez, Evans, Graciani, Park, Liu, Hrbek, Sanz, *J. Phys. Chem. C* 113 (2009) 7364.

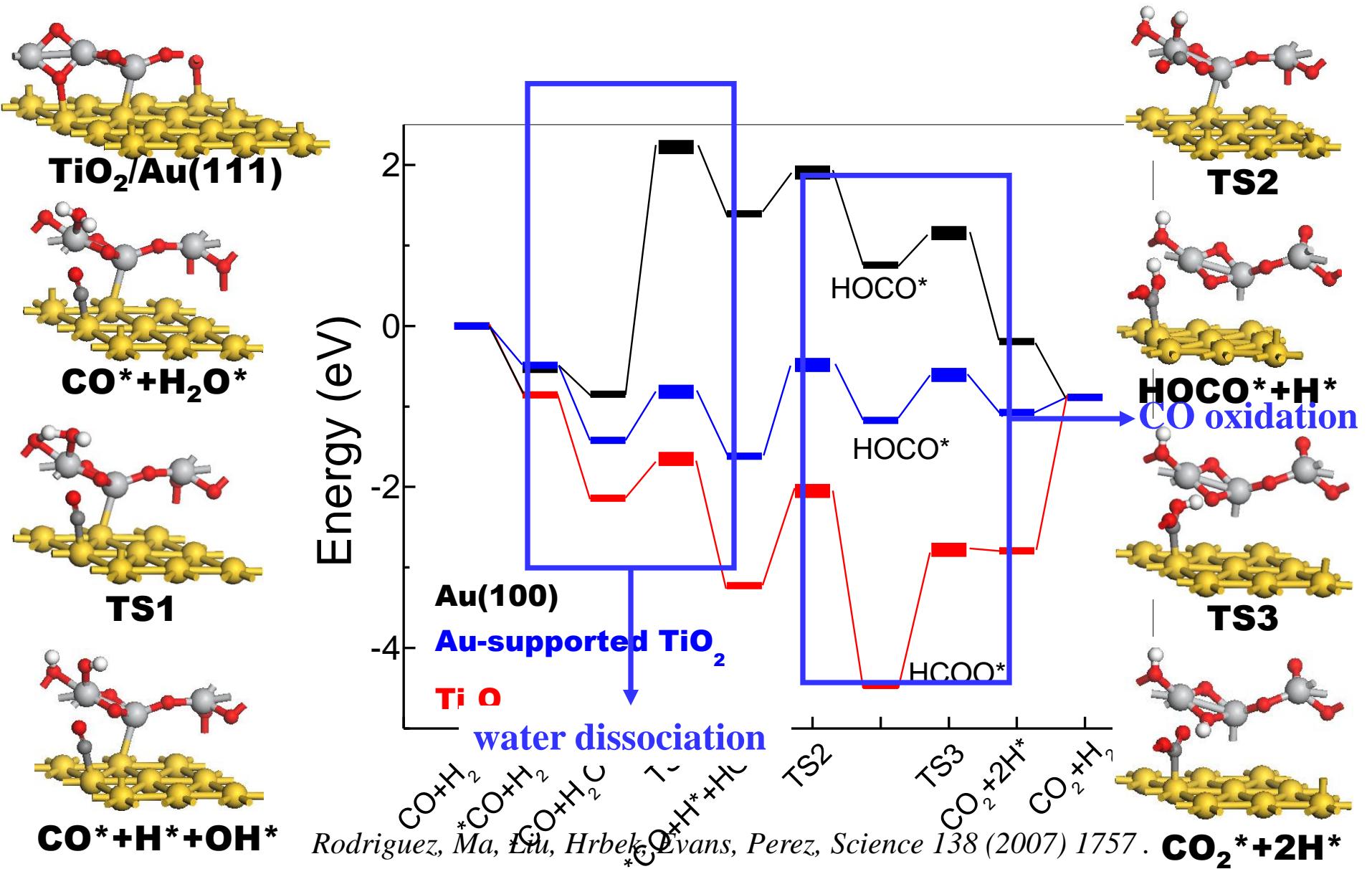
WGS reaction on Au/TiO₂(110)



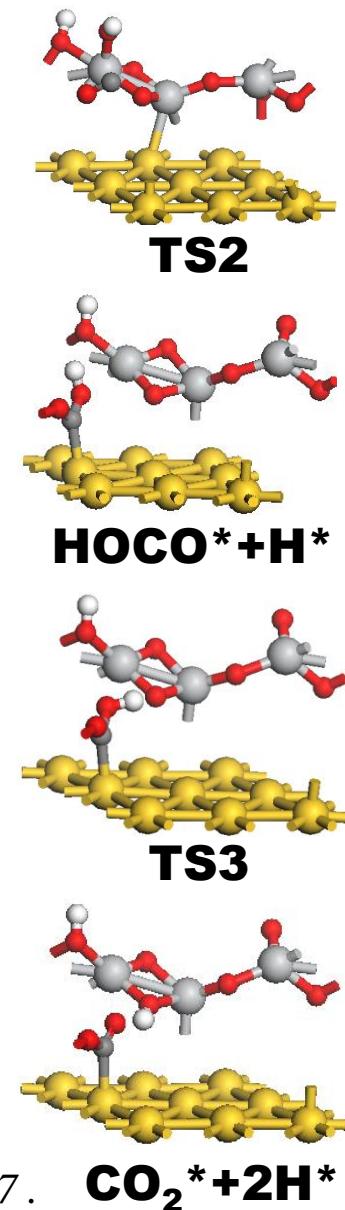
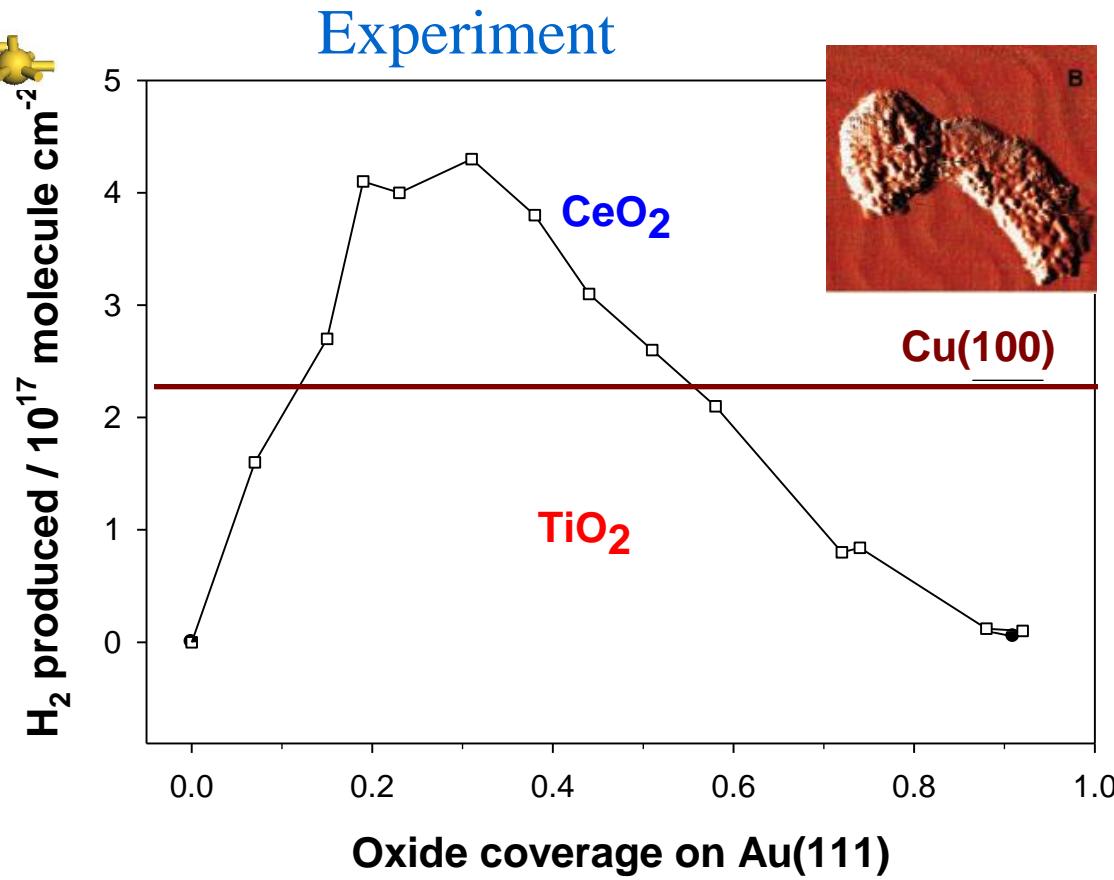
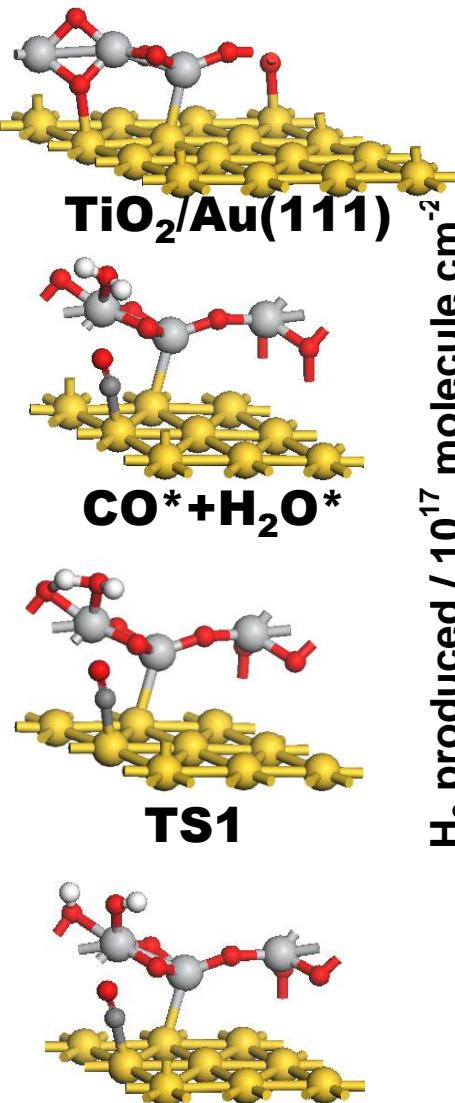
Rodríguez, Evans, Graciani, Park, Liu, Hrbek, Sanz, *J. Phys. Chem. C* 113 (2009) 7364.

CO₂* + 2H*

WGS reaction on $\text{TiO}_2/\text{Au}(111)$



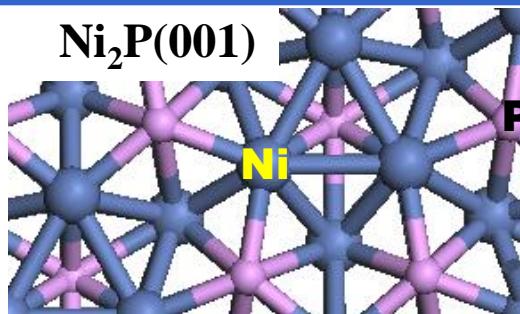
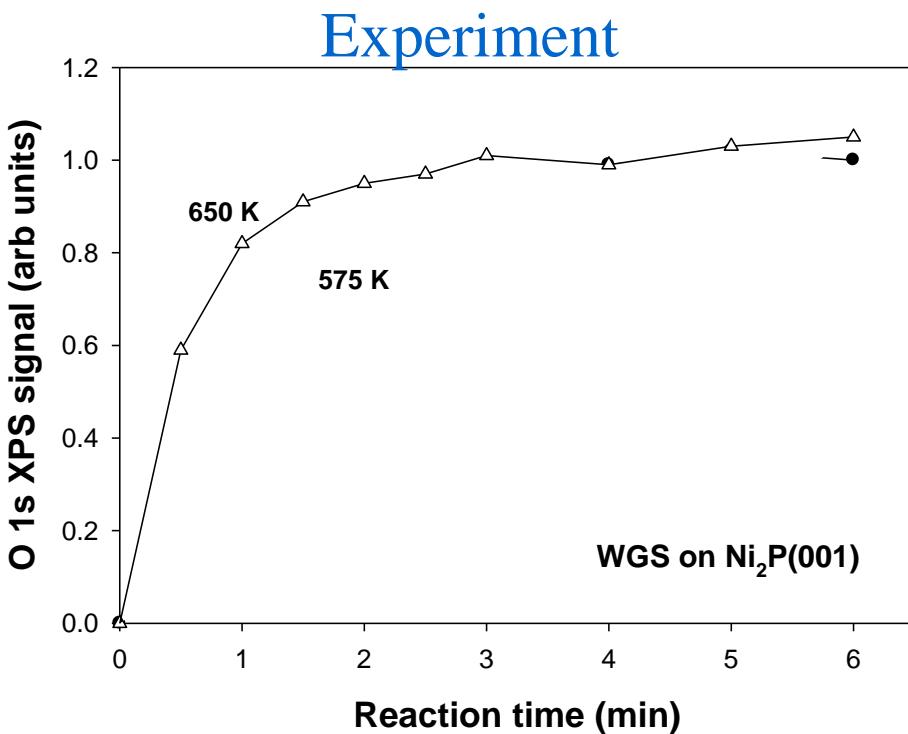
WGS reaction on $\text{TiO}_2/\text{Au}(111)$



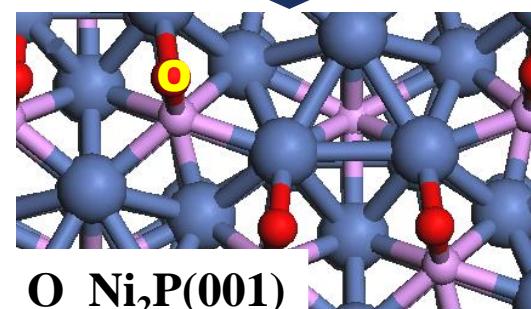
Rodriguez, Ma, Liu, Hrbek, Evans, Perez, Science 138 (2007) 1757.



WGS reaction on $\text{Ni}_2\text{P}(001)$



Clean surface does not catalyze the WGS reaction , due to the strong P-O and Ni-O interactions.

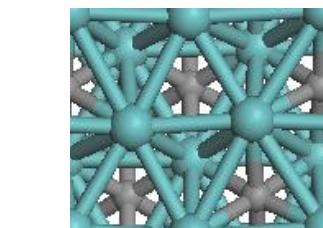
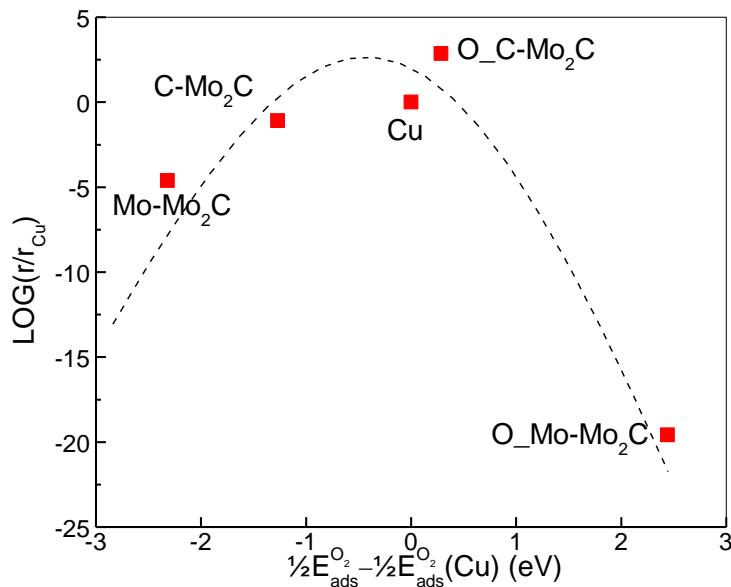


$\text{O}_-\text{Ni}_2\text{P}(001)$

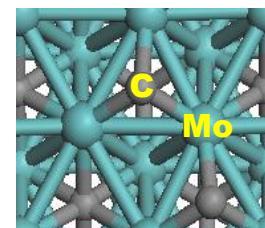
Liu, Rodriguez, Takahashi, Nakamura, J.
Catal. 262 (2009) 294.

The high activity of Ni_2P observed experimentally is due to the formation of a Ni oxy-phosphide in the surface during the WGS reaction.

WGS reaction on Mo₂C(001)



Mo-terminated Mo₂C(001)
(Mo-Mo₂C)

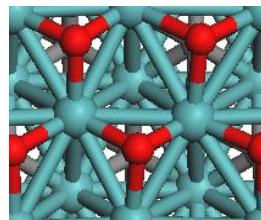


C-terminated Mo₂C(001)
(C-Mo₂C)

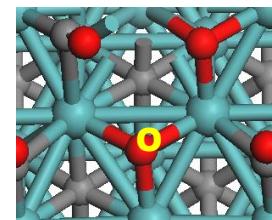
Neither of the surfaces catalyze the WGS reaction as well as Cu, due to the strong Mo-O and C-O interactions.



Surface oxidation



O-covered Mo_{Mo₂C}
(O_{Mo-Mo₂C})



O-covered C_{Mo₂C}
(O_{C-Mo₂C})

19 Torr of CO, 9 Torr of H₂O, 1 Torr of CO₂ and 1 Torr of H₂ at 625K

Liu, Rodriguez, J. Phys. Chem. B 110 (2006) 19418.

The high activity of Mo₂C observed experimentally is due to the formation of a Mo oxy-carbide in the surface during the WGS reaction.

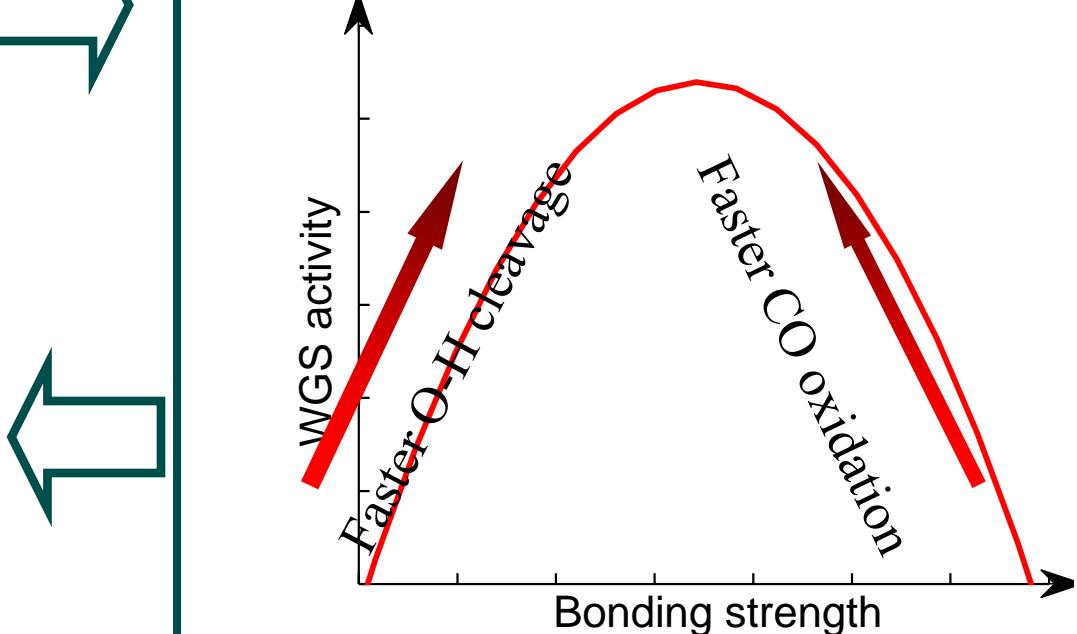
Rational design of better WGS catalysts

The good WGS catalyst should be active enough to dissociate water, but still being able to oxidize and remove CO efficiently.

Single-functional catalysts

- Single-active site directly functions all the steps in the WGS reaction
- The improvement of the WGS activity is limited due to the compromise of water dissociation and CO oxidation

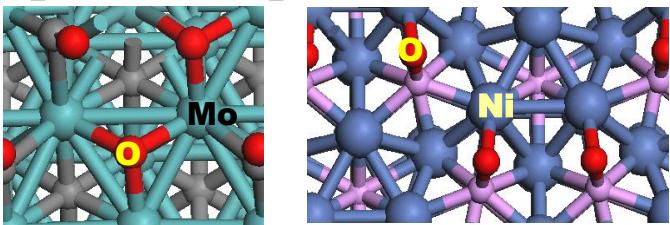
- Materials with only one component participating the reaction



Rational design of better WGS catalysts

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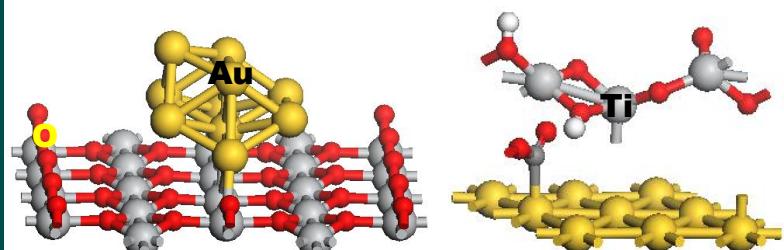
- Compounds with at least two exposed components



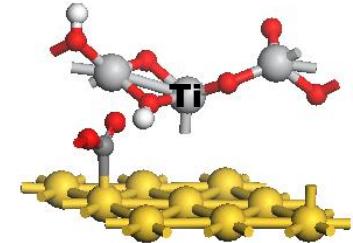
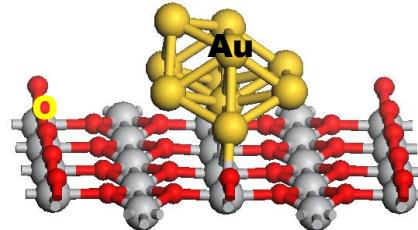
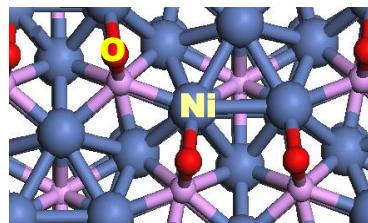
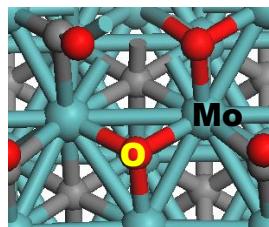
Multi-functional catalysts

- Multi-active sites participate the WGS reaction directly, where each functions different steps

● Composite materials



Rational design of better WGS catalysts



Experiments testing

Synthesis characterization

Theory

Predict better catalysts???

The high WGS performances rely heavily on the cooperation between **oxygen** and **metal centers** with moderate activity

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