

DENSITY FUNCTIONAL THEORY IN HETEROGENEOUS CATALYSIS

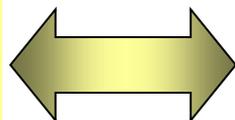
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Brookhaven National Laboratory*

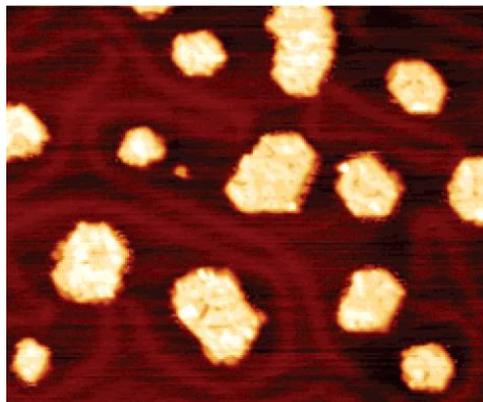


Catalyst discovery

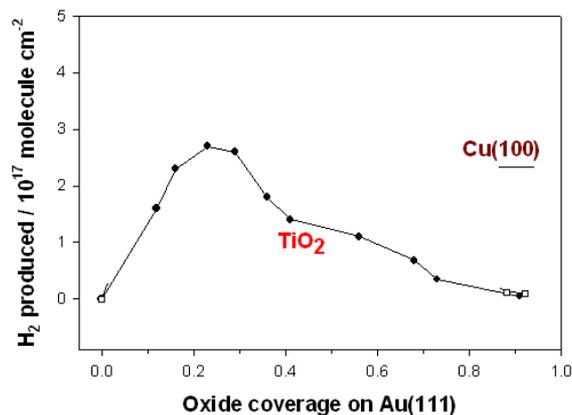
**Synthesis
characterization**



**Experiments
testing**



STM



Experiment

Catalysis has been the ultimate “shake and bake” technology

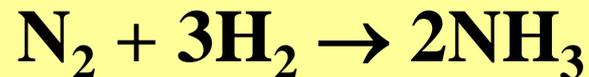
Catalyst discovery: ammonia synthesis



Haber



Fritz Haber won the Nobel Prize in Chemistry in 1918 for his contribution in the development of ammonia synthesis.



Impact today

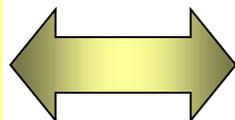
- **Production:**
~**140** million tons/year
- **Application:**
~ **80%** to make fertilizer for feeding
~**48%** of the world population

Catalyst discovery

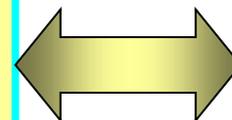
- Haber and Bosch screened **20,000** candidate catalysts over **4,000** different substances to find an iron ore that worked well.

Rational catalyst discovery

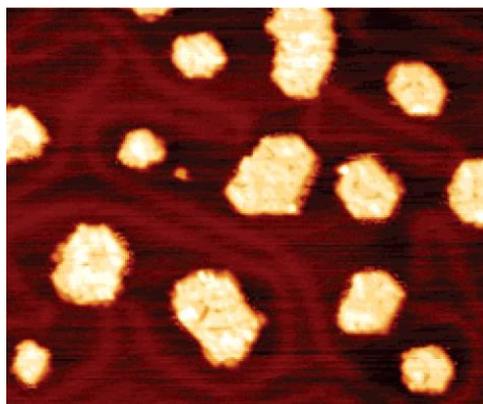
**Synthesis
characterization**



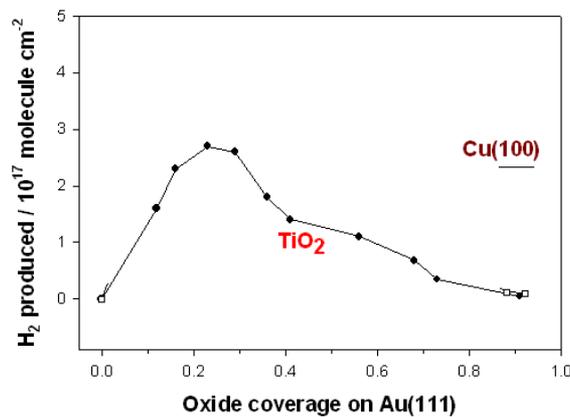
**Experiments
testing**



**Understanding
Improvement**



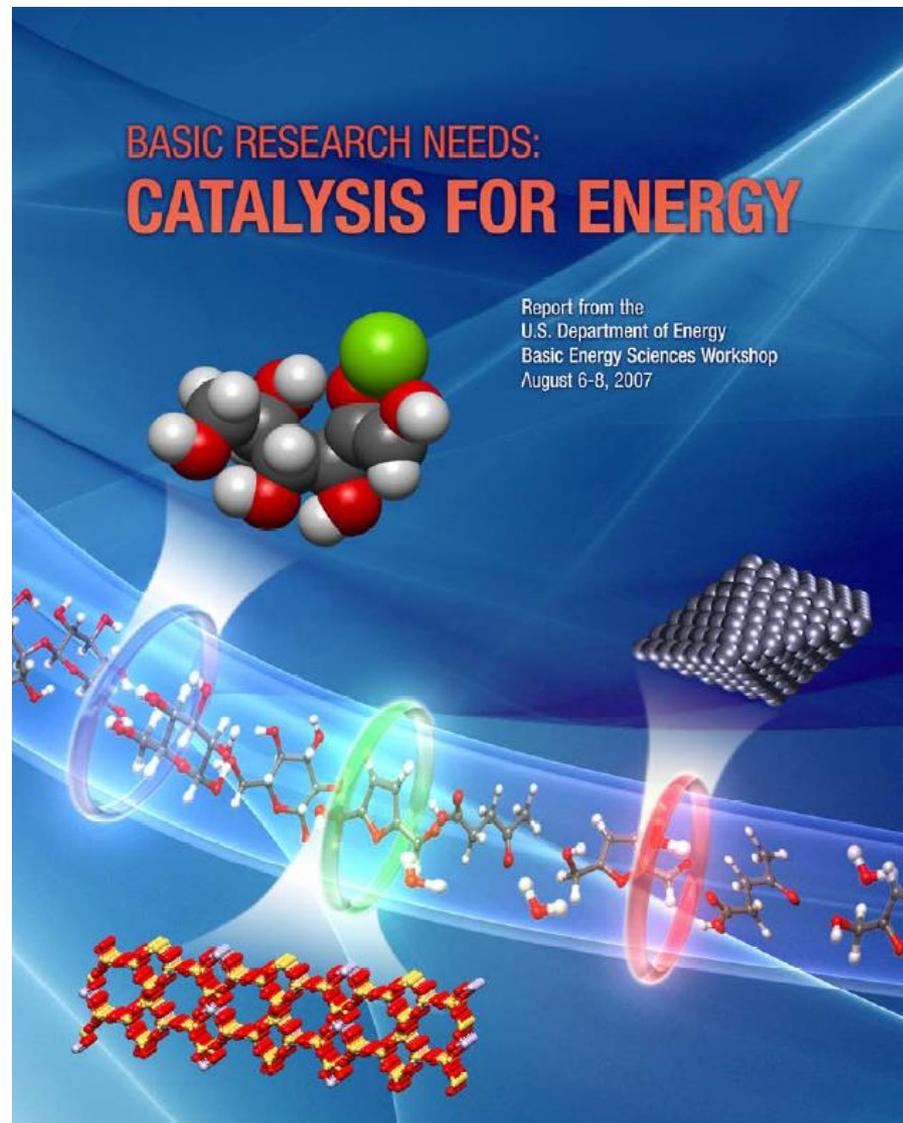
STM



Experiment

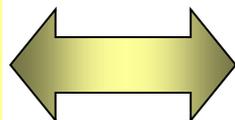
Grand challenges in catalysis for energy

- **Discovery of new catalysts for increasing energy resources and efficiencies, and reducing overall environmental footprints.**
- **Understanding the mechanisms and dynamics of catalyzed transformations.**
- **Catalyst rational design on the basis of understanding.**

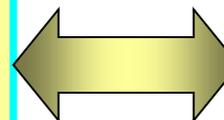


Rational catalyst discovery

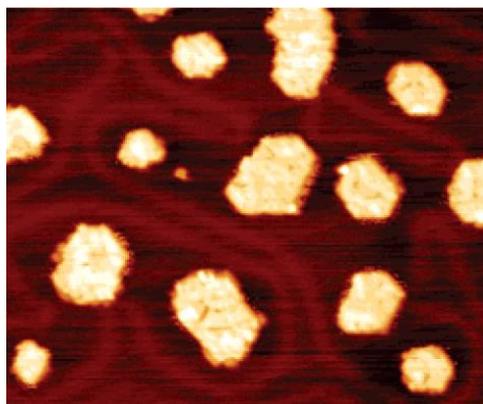
**Synthesis
characterization**



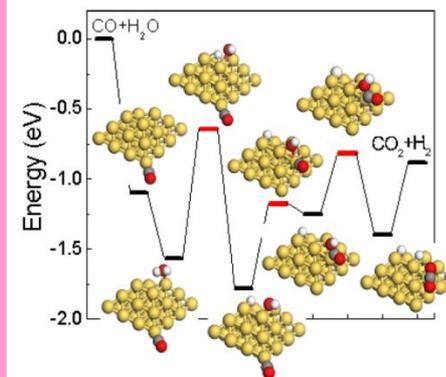
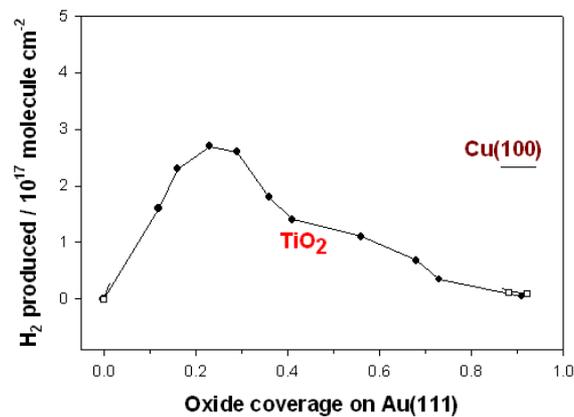
**Experiments
testing**



**Understanding
Improvement**



STM

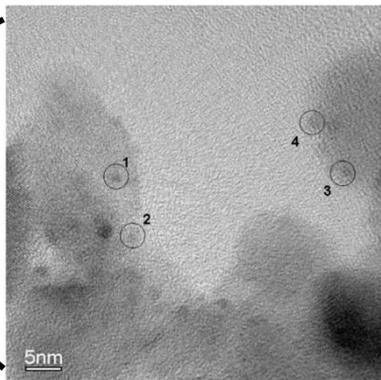


Experiment

Theory

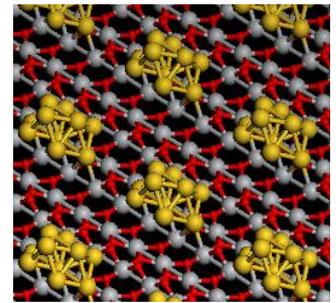
Understanding catalysis in BNL

Real catalysts



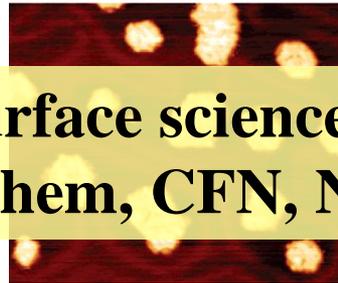
X-ray diffraction (XRD)
X-ray absorption fine structures (XAFS)
Transmission electron microscopy (TEM)

Theoretical models



Density Functional Theory (DFT)
Kinetic Modeling

Understanding catalysis in BNL



**Surface science studies
(Chem, CFN, NSLS-II)**

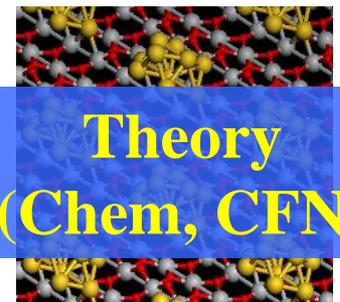
- Photoemission spectroscopy
- Scanning tunneling spectroscopy (STM)
- Photoemission electron microscopy (PEEM)

Model Catalyst

**Fundamental understanding of
the behavior of catalyst:
Rational discovery of better
catalyst**

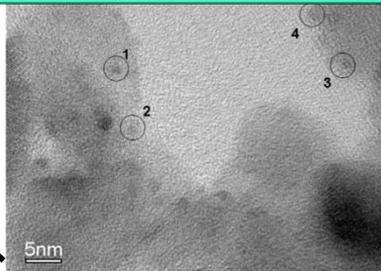
Real catalyst

Theoretical models



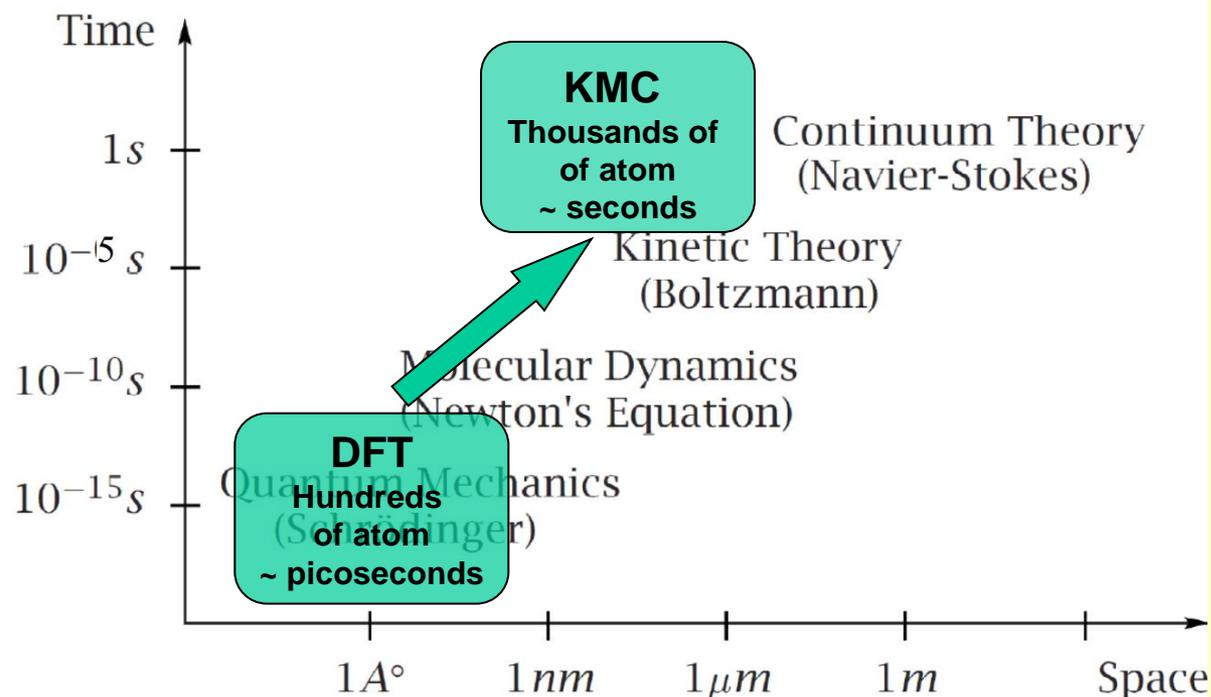
**Theory
(Chem, CFN)**

- X-ray diffraction (XRD)
- X-ray absorption fine structures (XAFS)
- Transmission electron microscopy (TEM)



- Density Functional Theory
- Molecular Dynamics
- Kinetic Modeling

Theoretical studies in catalysis



Density Functional Theory



Structure, Adsorption energy, Reaction pathway, Activation barrier



Kinetic modeling

Reaction rate, Mechanism, Active sites



Rational design of better catalysts

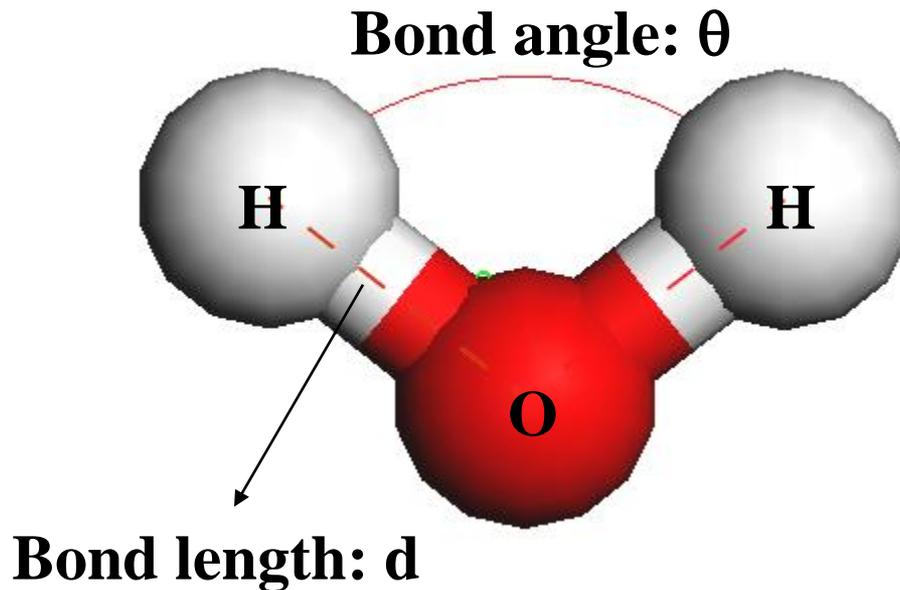
Method

- **Density Functional Theory (DFT) – DMol³, CASTEP or VASP**
- **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**

DFT: structure of molecule or cluster

Structural properties: bond length & angles of molecules with accuracy within 0.05 \AA and $1\text{-}2^\circ$.

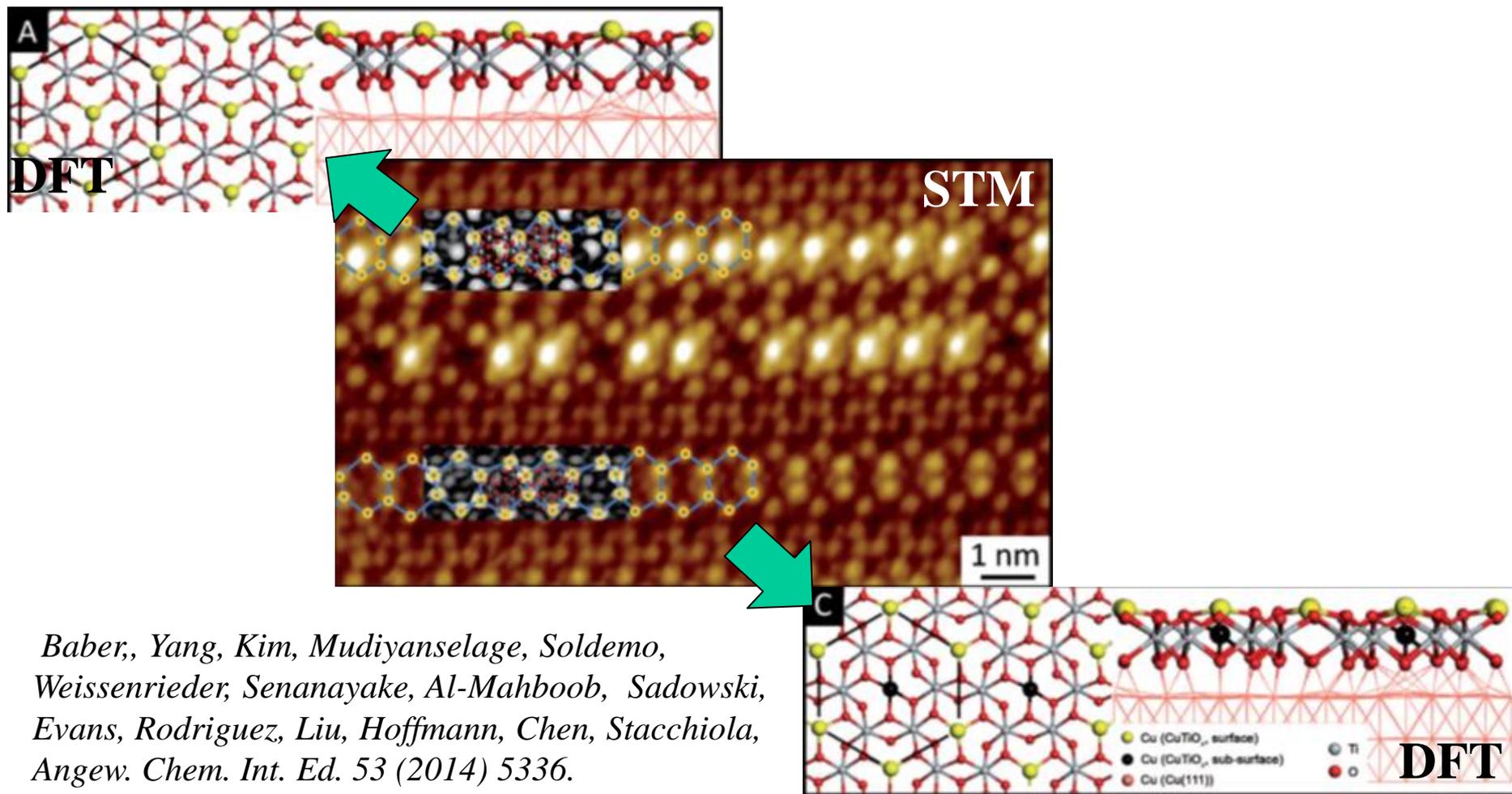
Water Molecule in gas-phase



Simulation: microscope

Complex structures: being able to simulate and well reproduce the microscopic measurements.

$\text{Cu}_2\text{TiO}_3/\text{Cu}(111)$: Scanning Tunneling Microscope (STM)



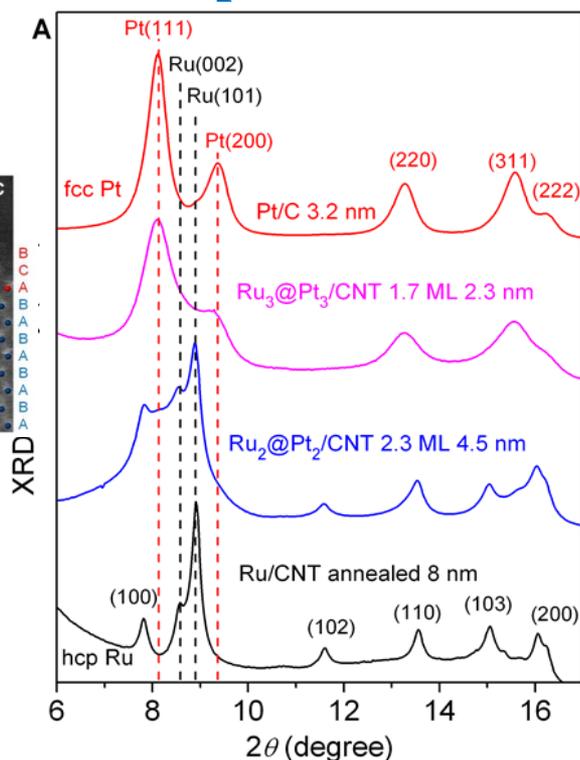
Baber,, Yang, Kim, Mudiyansele, Soldemo, Weissenrieder, Senanayake, Al-Mahboob, Sadowski, Evans, Rodriguez, Liu, Hoffmann, Chen, Stacchiola, Angew. Chem. Int. Ed. 53 (2014) 5336.

Simulation: diffraction

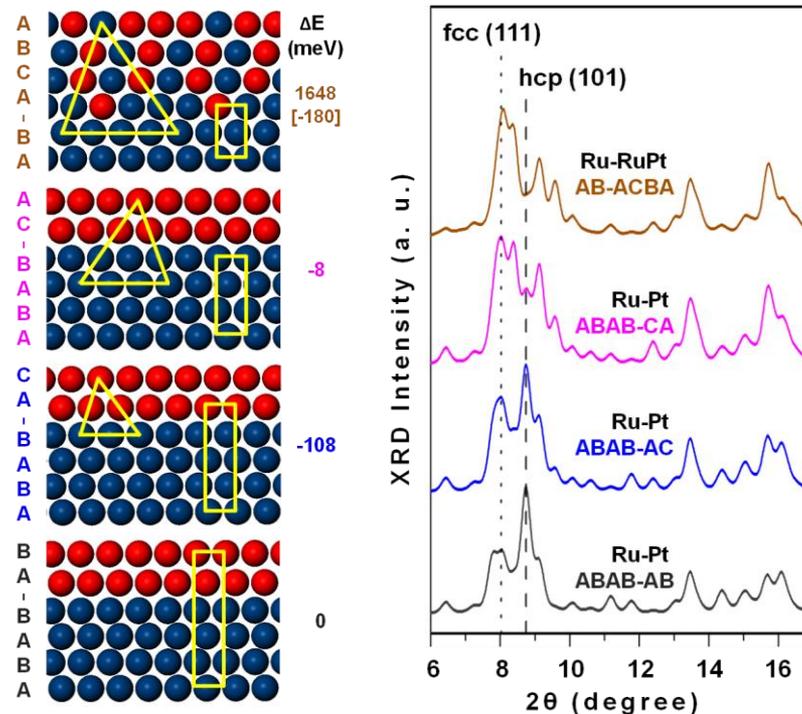
Complex structures: being able to simulate and well reproduce the diffraction pattern.

Pt shell- Ru core NP: X-ray Diffraction (XRD)

Experiment



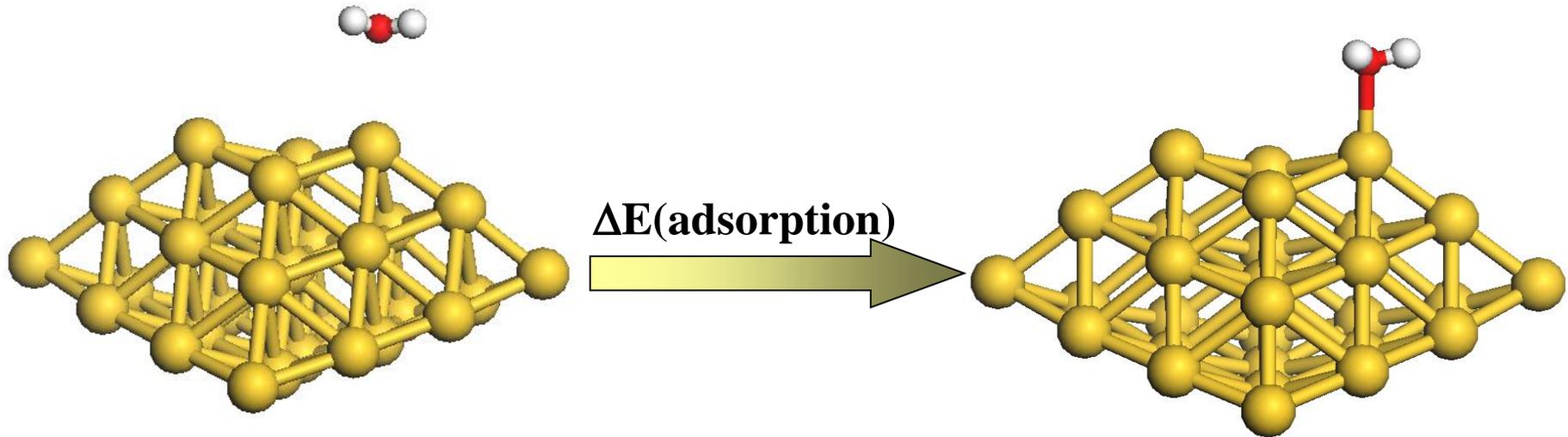
Theory



DFT: adsorption

Adsorption energy and geometry of an adsorbate on a catalyst with accuracy within 0.2-0.3eV.

Water adsorption on Au NP

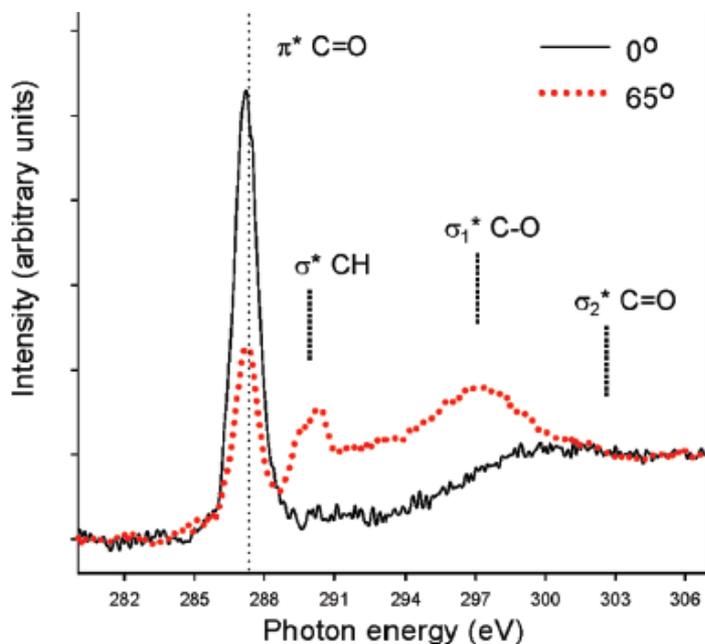


Simulation: spectroscope

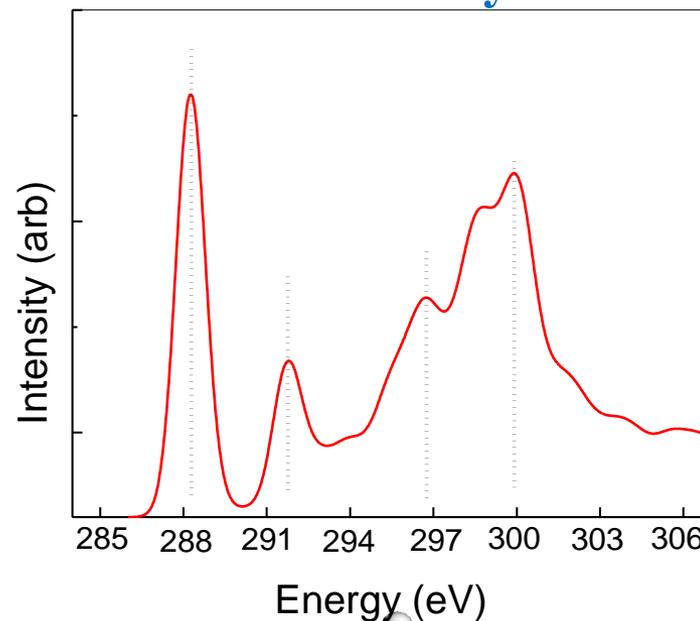
Binding: being able to simulate and well reproduce the spectroscopic measurements.

HCOO/Au(111): X-ray Absorption Spectroscopy (XAS: C K-edge)

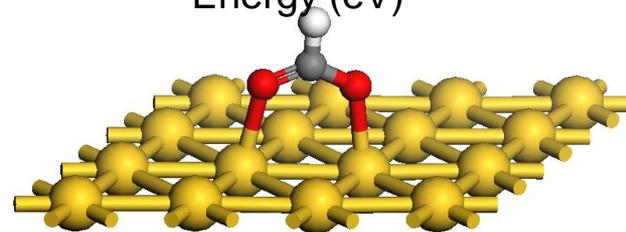
Experiment



Theory



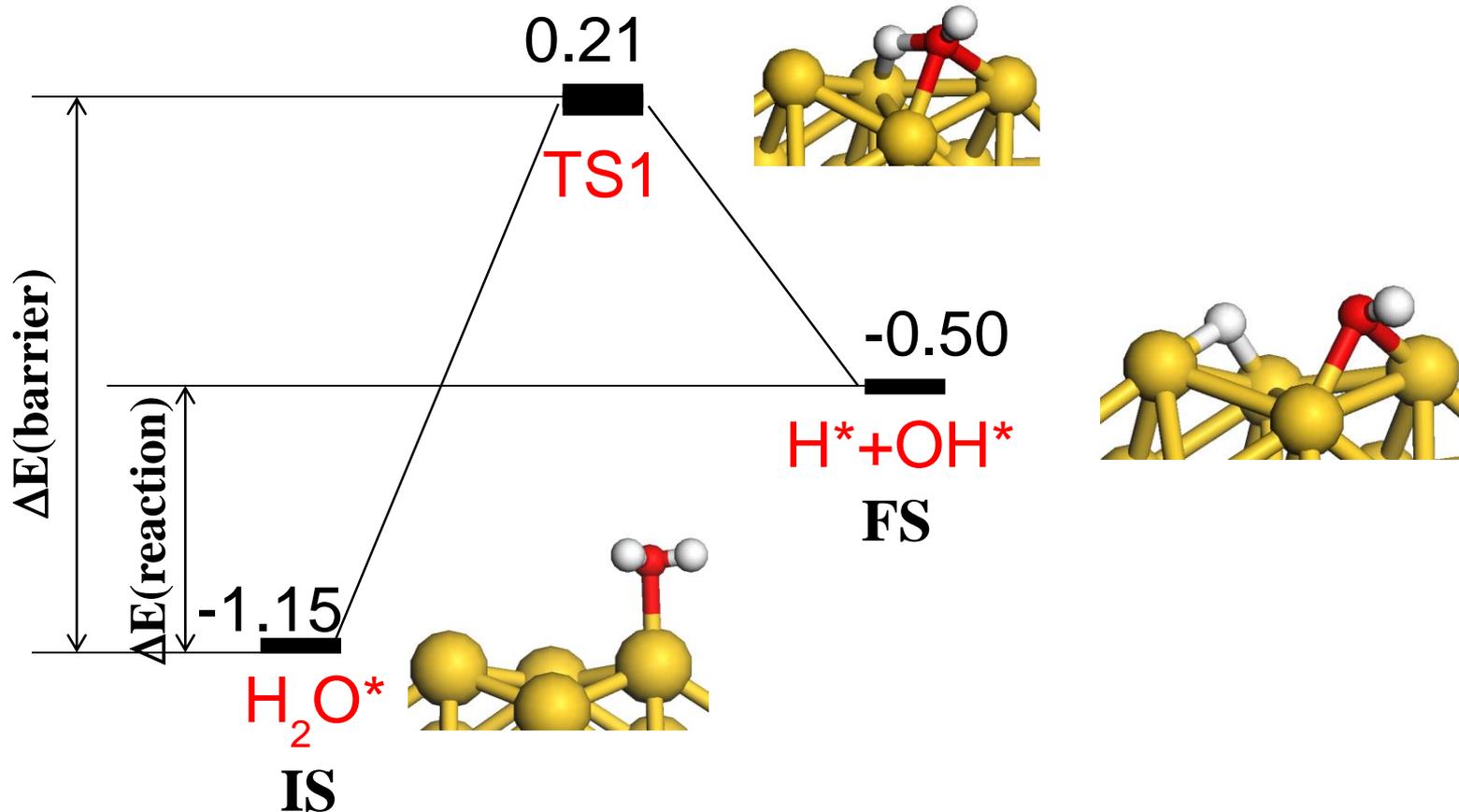
Senanayake; Stacchiola, Liu, Mullins, Hrbek, Rodriguez, *J. Phys. Chem. C* 113 (2009) 19536.



DFT: reaction

Reaction energy and activation barriers

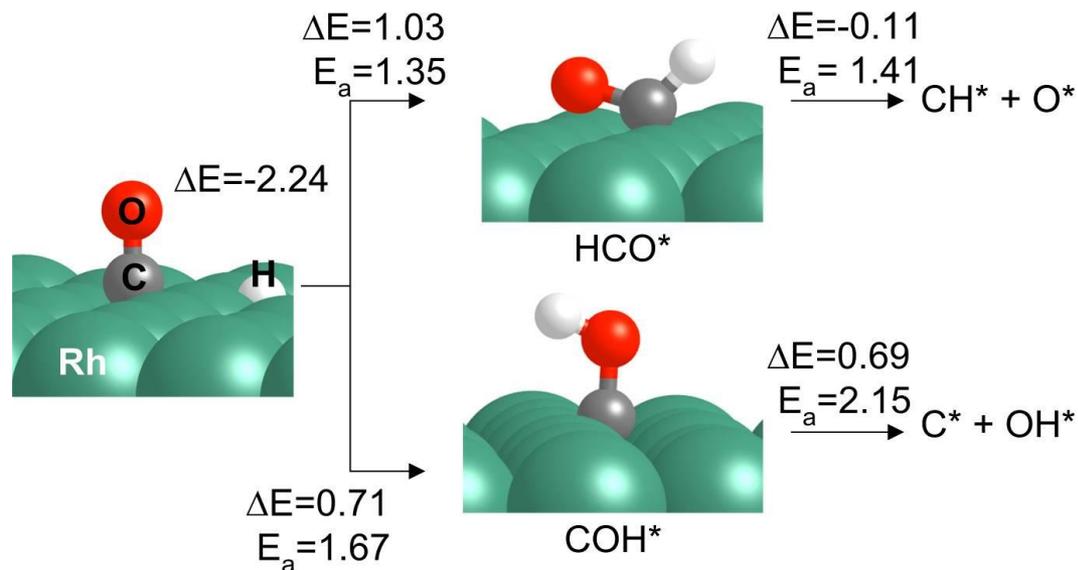
Water dissociation on Au NP



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

Energy in eV

DFT: complex reaction network



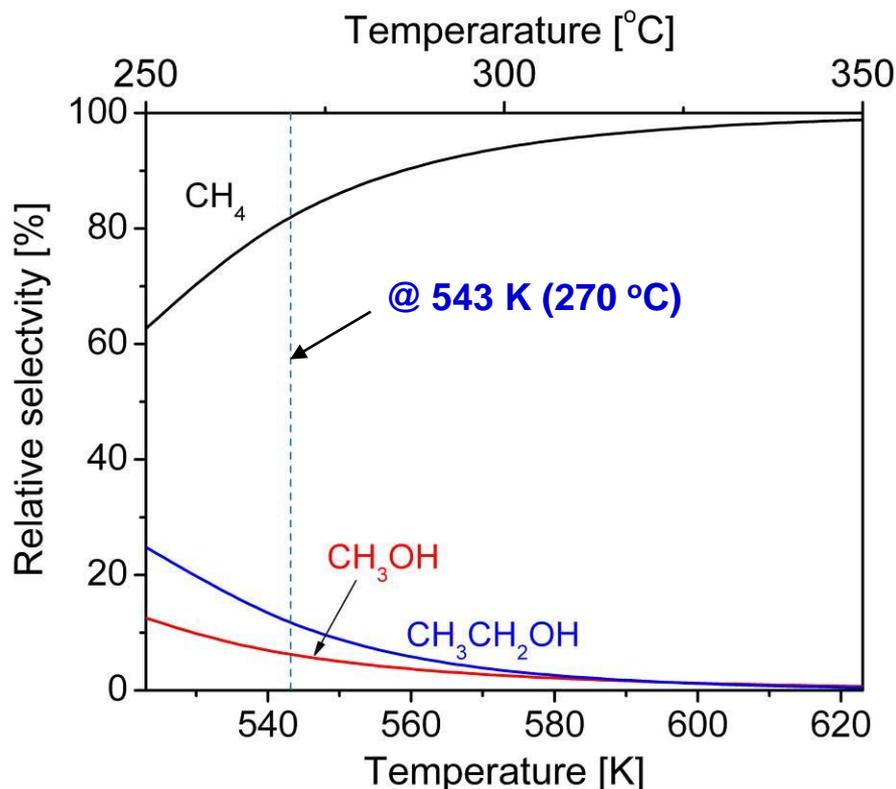
- CO dissociation on Rh(111) is not plausible ($E_a = 3.72\text{eV}$), which has been proposed as a rate-limiting step on supported Rh catalysts.
- HCO is more favorable than COH.

ΔE : reaction energy in eV ; E_a : activation barrier in eV

DFT + kinetic modeling: activity & selectivity



- Experimental conditions
 - $P_{\text{CO}} = 1/3$ and $P_{\text{H}_2} = 2/3$
 - $T = 523 - 623 \text{ K}$
- Surface is mainly covered by CO.
- The production rate of CH_3CHO is ~ 0 .
- Similar to experimental results, CH_4 is the major product under typical experimental conditions, while ethanol and methanol are very low.

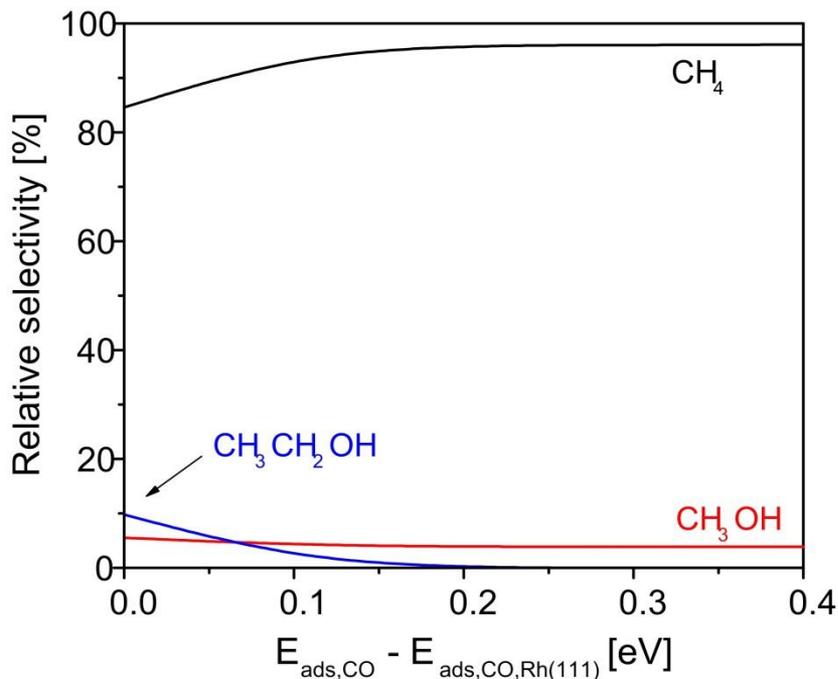


Sensitivity analysis



- Varying each kinetic parameter in the kinetic model by small amount around its original value, while the other irrelevant parameters are held constant.

Varying CO binding energy
→ increasing yield of ethanol
as well as methanol and
methane, but ethanol selectivity
remain the same

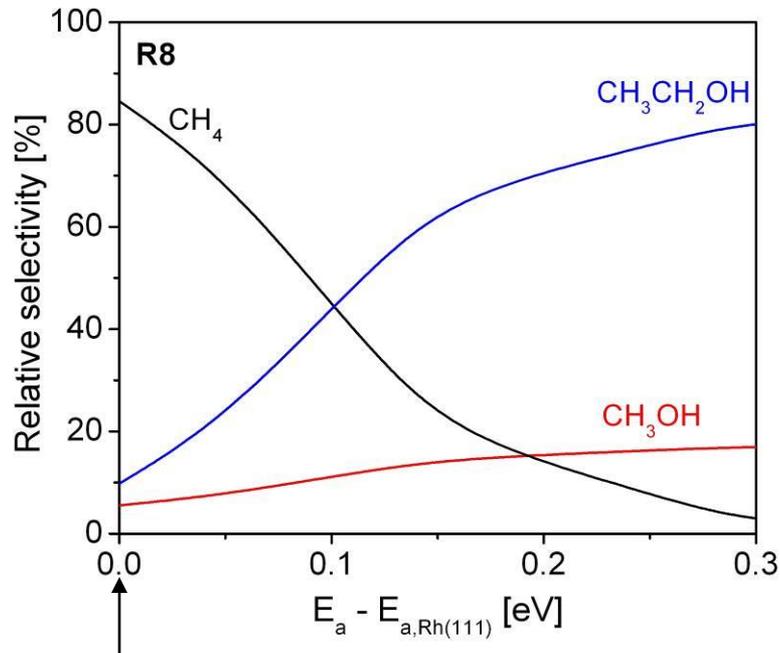
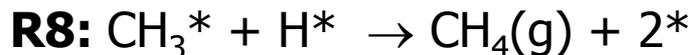


Sensitivity analysis

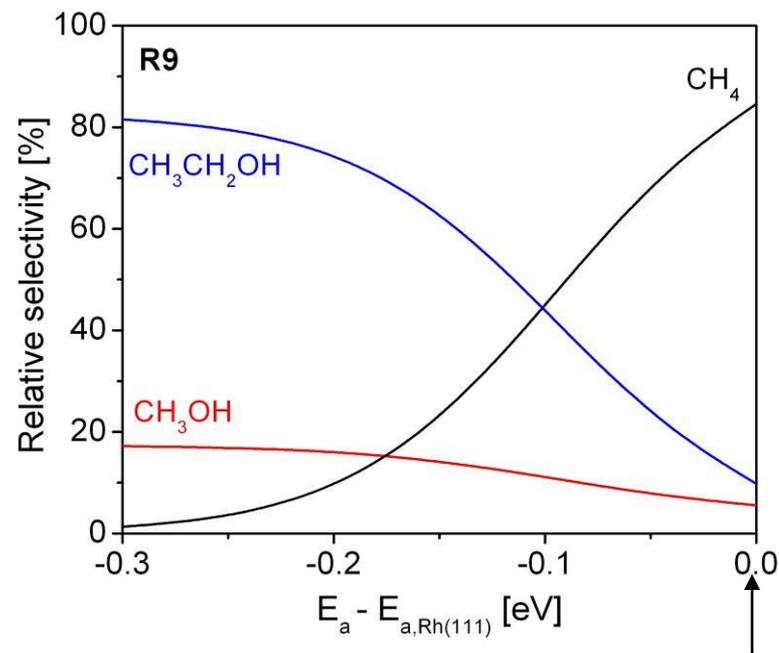


- Other kinetic parameters that improve the ethanol production:
 - H binding energy
 - Barrier for $\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$
 - Barrier for $\text{CO}^* + \text{H}^* \rightarrow \text{HCO}^* + *$
 - Barrier for $\text{CH}_3\text{O}^* + * \rightarrow \text{CH}_3^* + \text{O}^*$
 - Barrier for $\text{CH}_3\text{O}^* + \text{H}^* \rightarrow \text{CH}_3\text{OH}(\text{g}) + 2^*$

DFT + Sensitivity analysis: descriptors



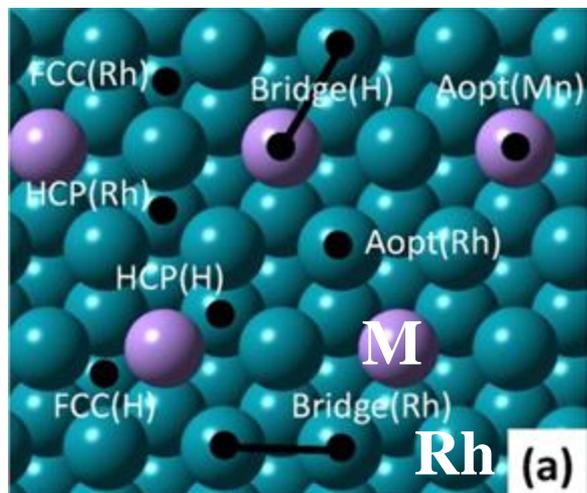
0.80 eV



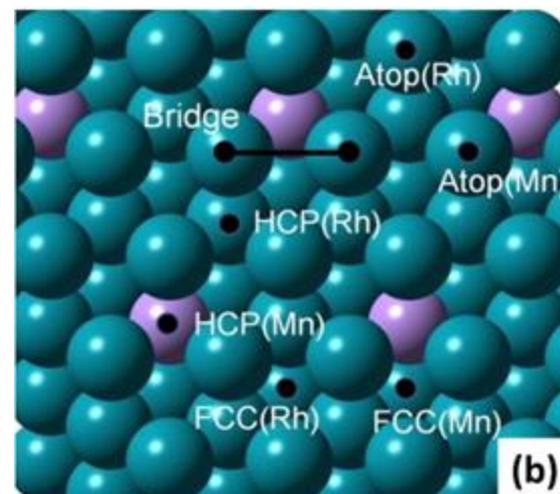
1.15 eV

- Only two variables affect the $\text{C}_2\text{H}_5\text{OH}$ productivity and selectivity significantly. One is the barrier for the CH_4 formation (**R8**); the other is the barrier for CO insertion or C-C bond formation (**R9**).

DFT: catalyst optimization



Segregation

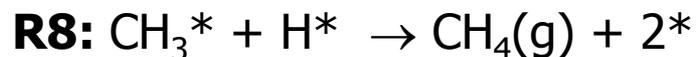


According to the thermodynamics:

- As-prepared: Rh-terminated surfaces.
- Under reaction: Fe stays on the surface layer due to very strong interaction with the reaction intermediates.

Mo and Mn can stay either on the surface layer or in the subsurface.

DFT: catalyst optimization

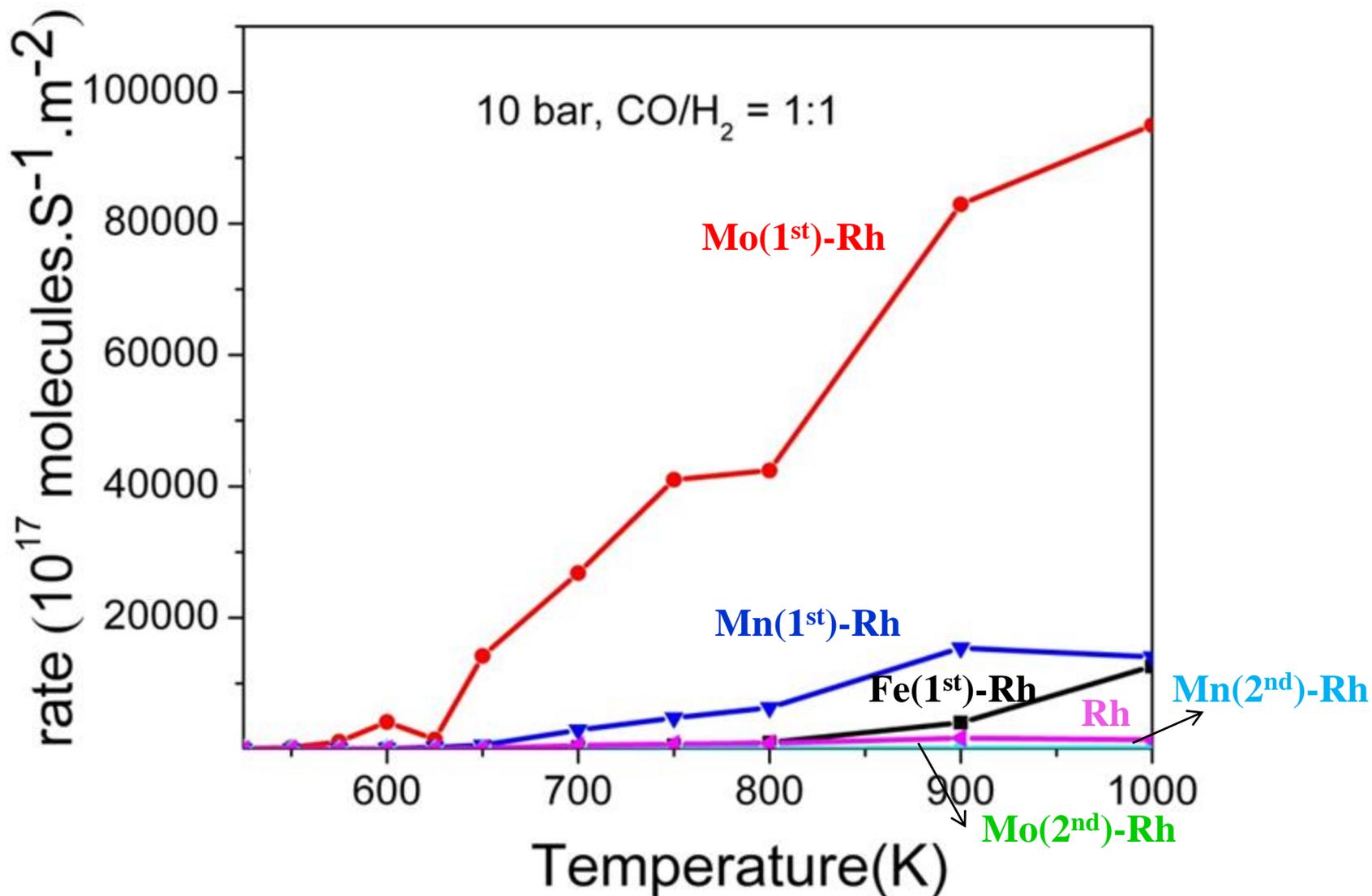


	Rh(111)	Fe(1 st) /Rh(111)	Mo(1 st) /Rh(111)	Mo(2 nd) /Rh(111)	Mn(1 st) /Rh(111)	Mn(2 nd) /Rh(111)
Reaction Energy	-0.25	0.66	0.19	-0.15	0.05	-0.29
Barrier	0.84	1.28	1.13	0.93	1.00	1.20

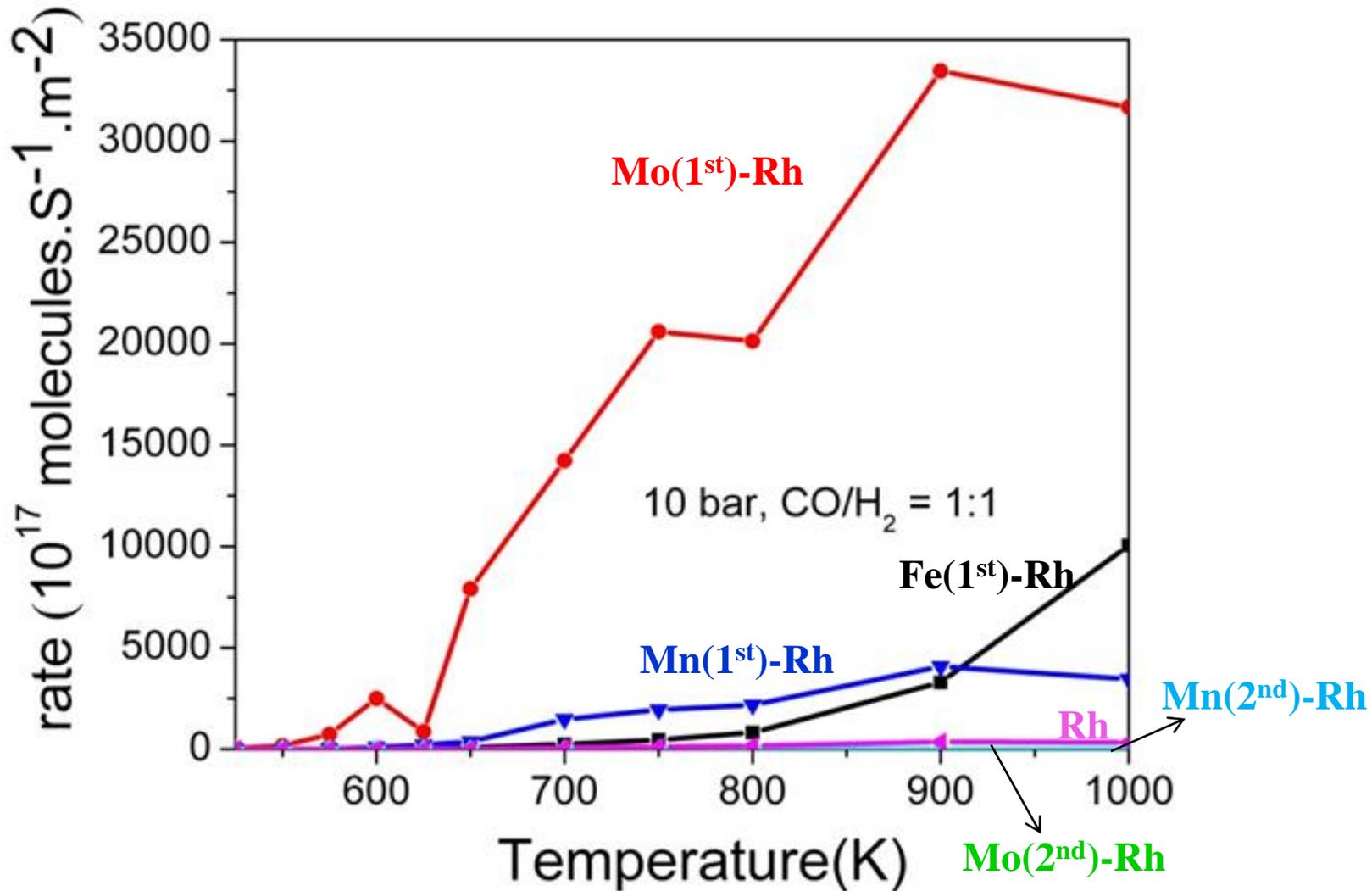
- The reaction energy and activation barriers vary from Rh(111) due to doping metal, no matter whether the dopant is on the surface layer or in the subsurface.
- Doping Fe, Mo and Mn can hinder the methane formation on Rh, where Fe displays the most significant effect.

reaction energy in eV ; barrier in eV

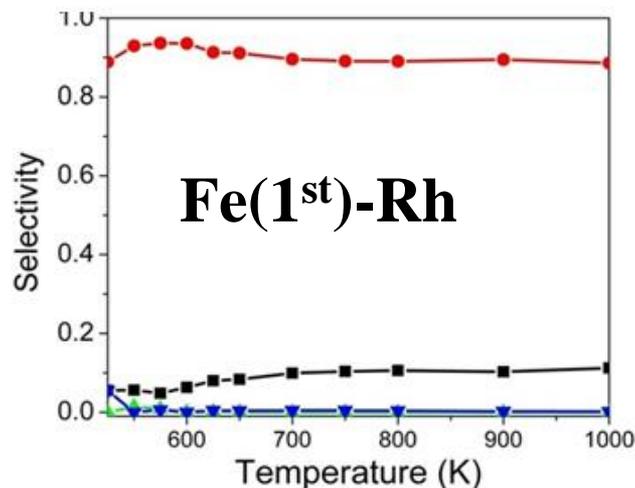
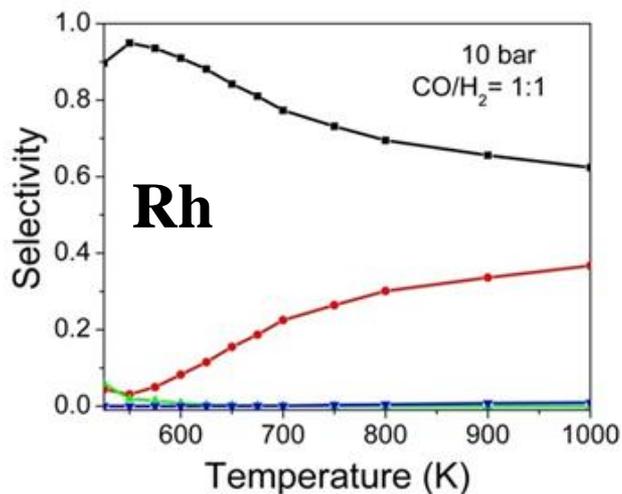
DFT + KMC: activity for CO conversion



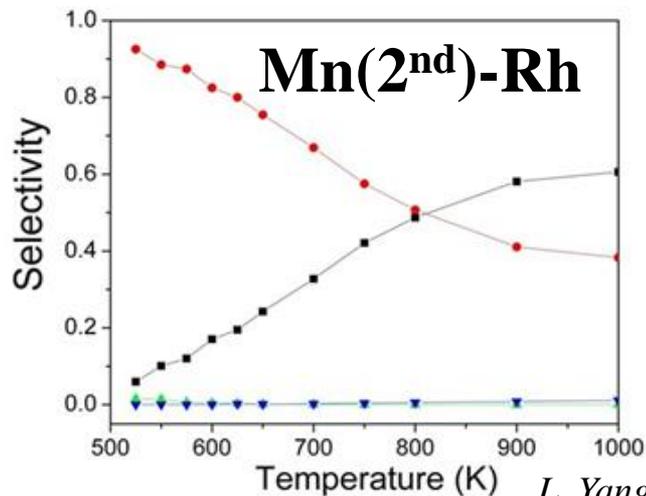
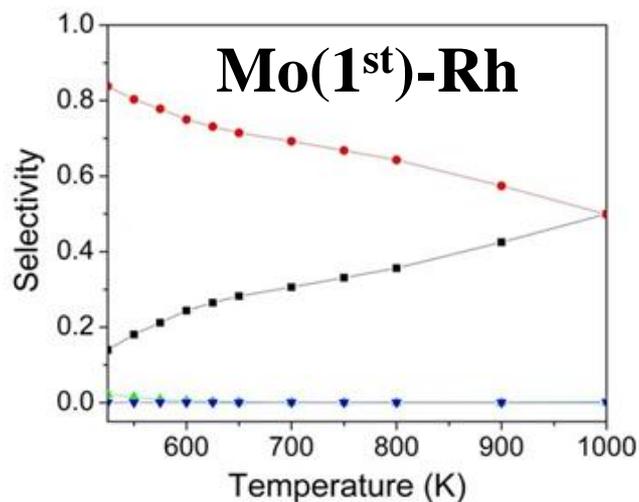
DFT + KMC: activity for ethanol production



DFT + KMC: selectivity



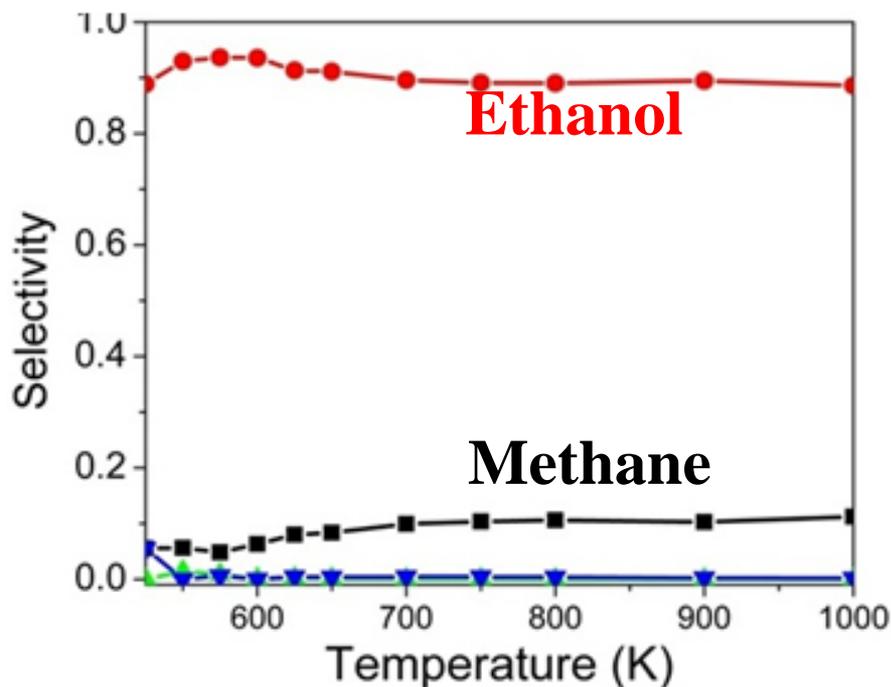
- Methane
- Ethanol
- ▲— Methanol
- ▼— Acetaldehyde



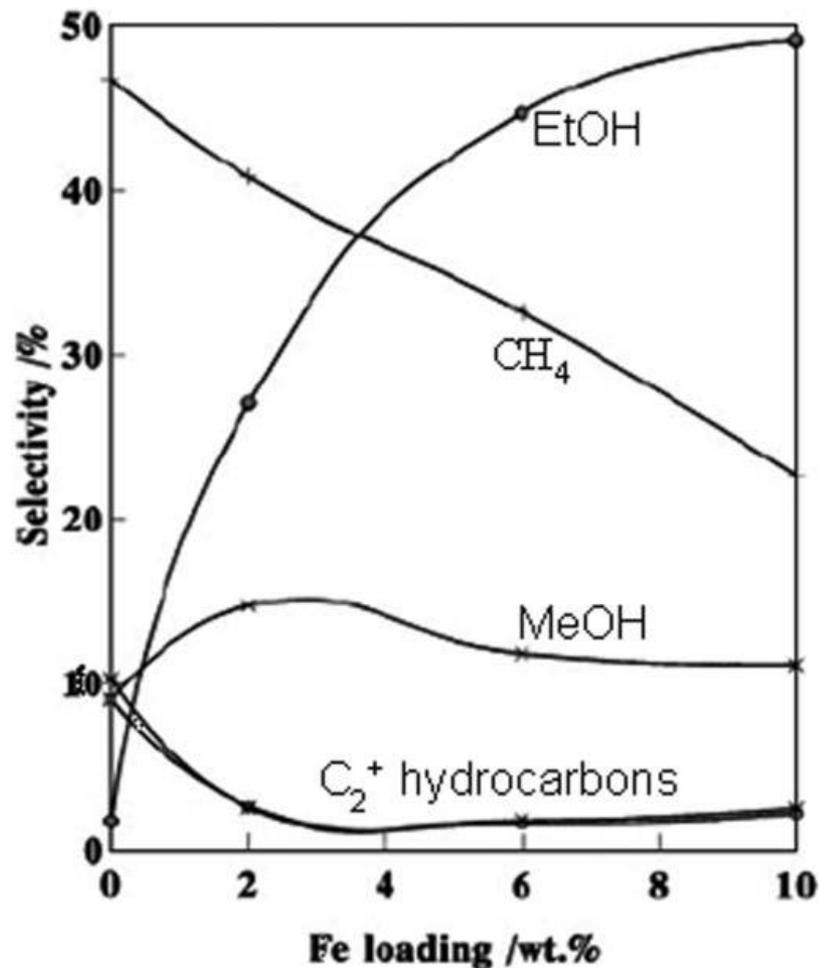
High ethanol selectivity of FeRh



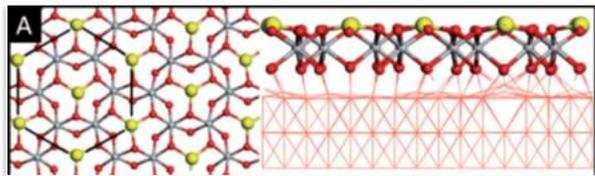
Theory



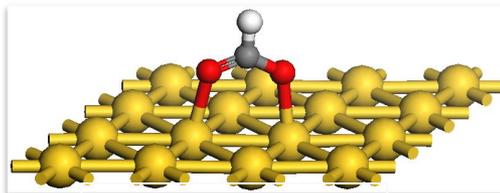
Experiment



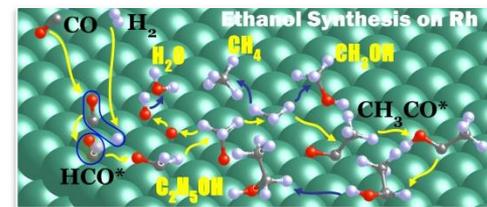
Summary: combined theory



Structure

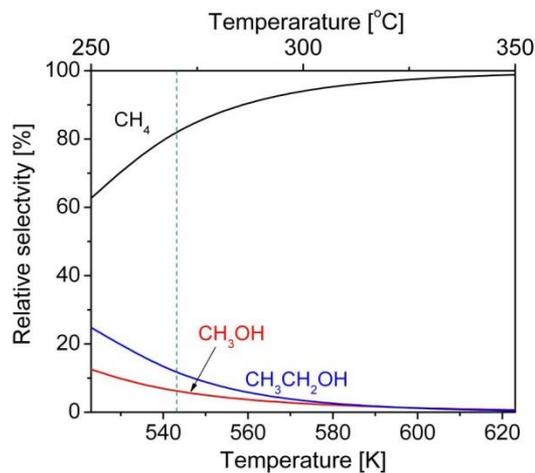


Interaction

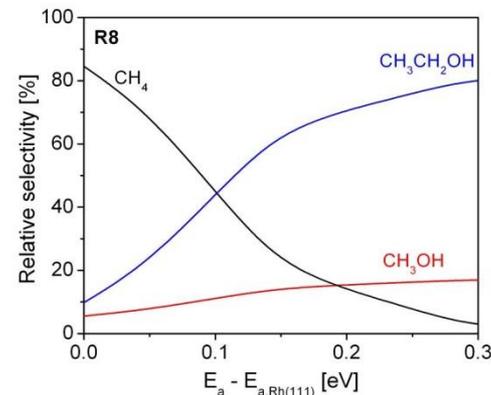


Reaction network

DFT



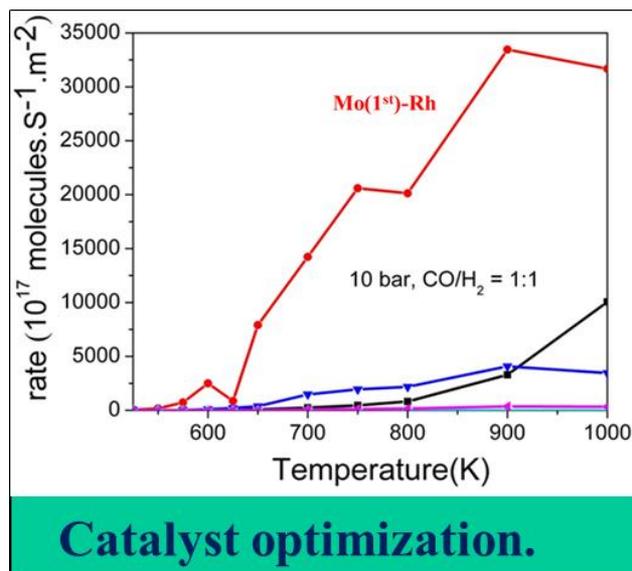
Activity and selectivity



Descriptors

Kinetic Modeling + Sensitivity Analysis

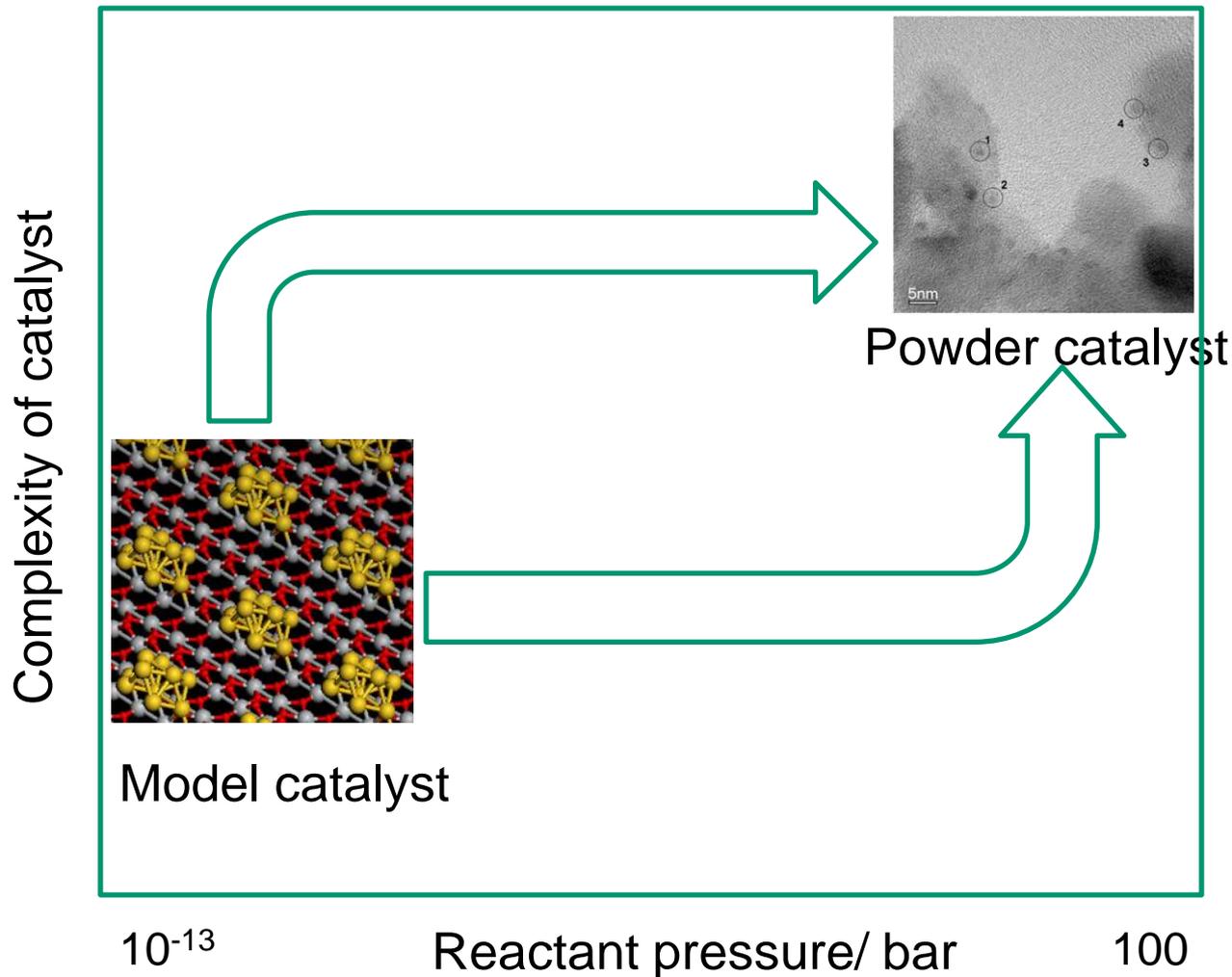
Summary: combined theory



DFT + Kinetic Modeling + Sensitivity Analysis

Challenge: bridge pressure and material gaps

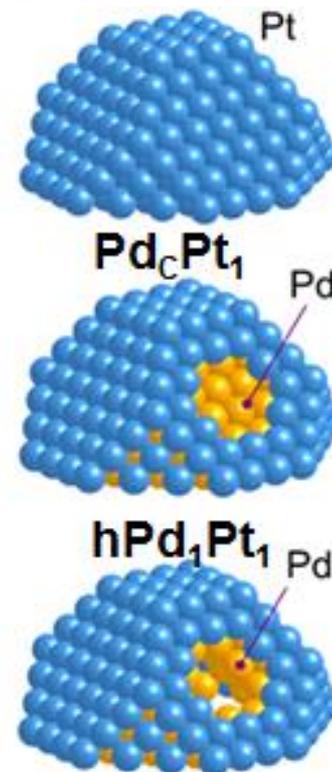
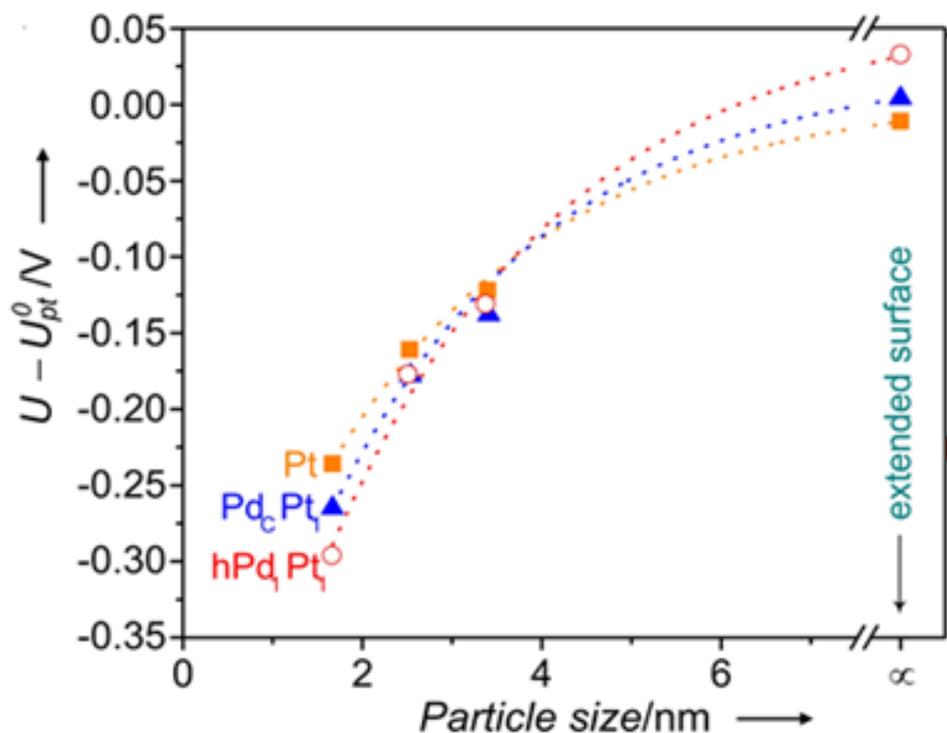
Goal: moving toward modeling more realistic catalysts and reaction conditions



Material gap

- Modeling more realistic catalysts towards bridging material-gap at DFT level: nanoparticles (NPs, e.g. metal and metal oxide)

Small NPs (< 4 nm) : particle models in real shape and size

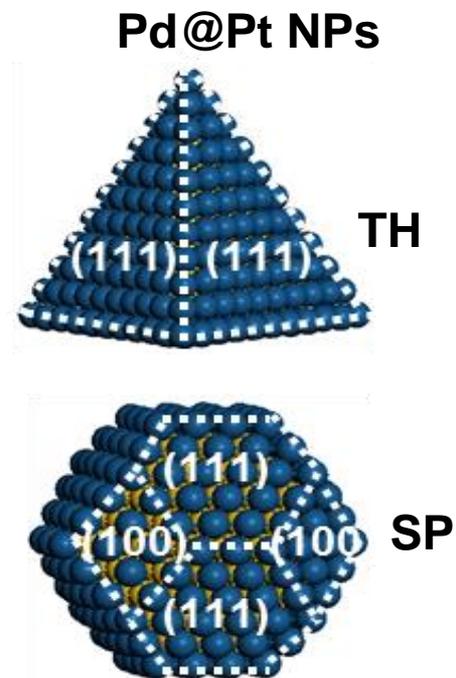
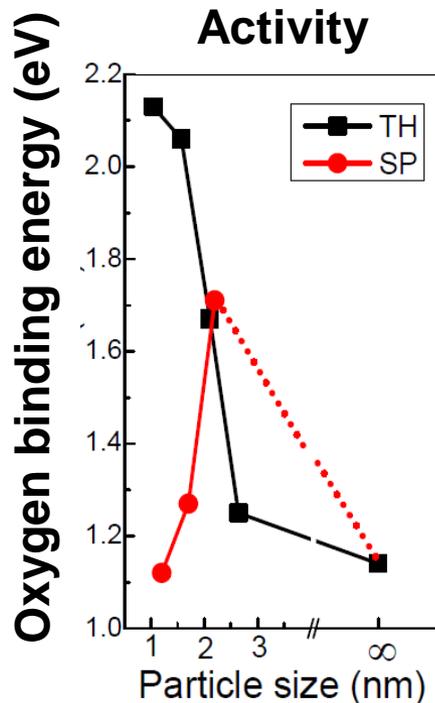
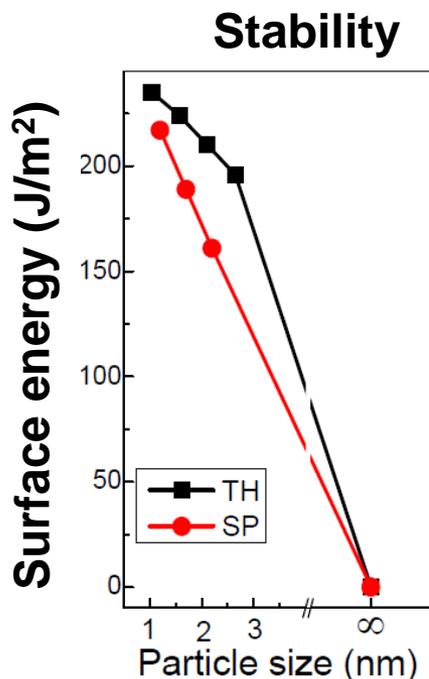


Highlight: the importance of nanosize effect on the stability of particles, even in term of variation from one system to the next.

Material gap

● Modeling more realistic catalysts towards bridging material-gap at DFT level: nanoparticles (NPs, e.g. metal and metal oxide)

Small NPs (< 4 nm) : particle models in real shape and size

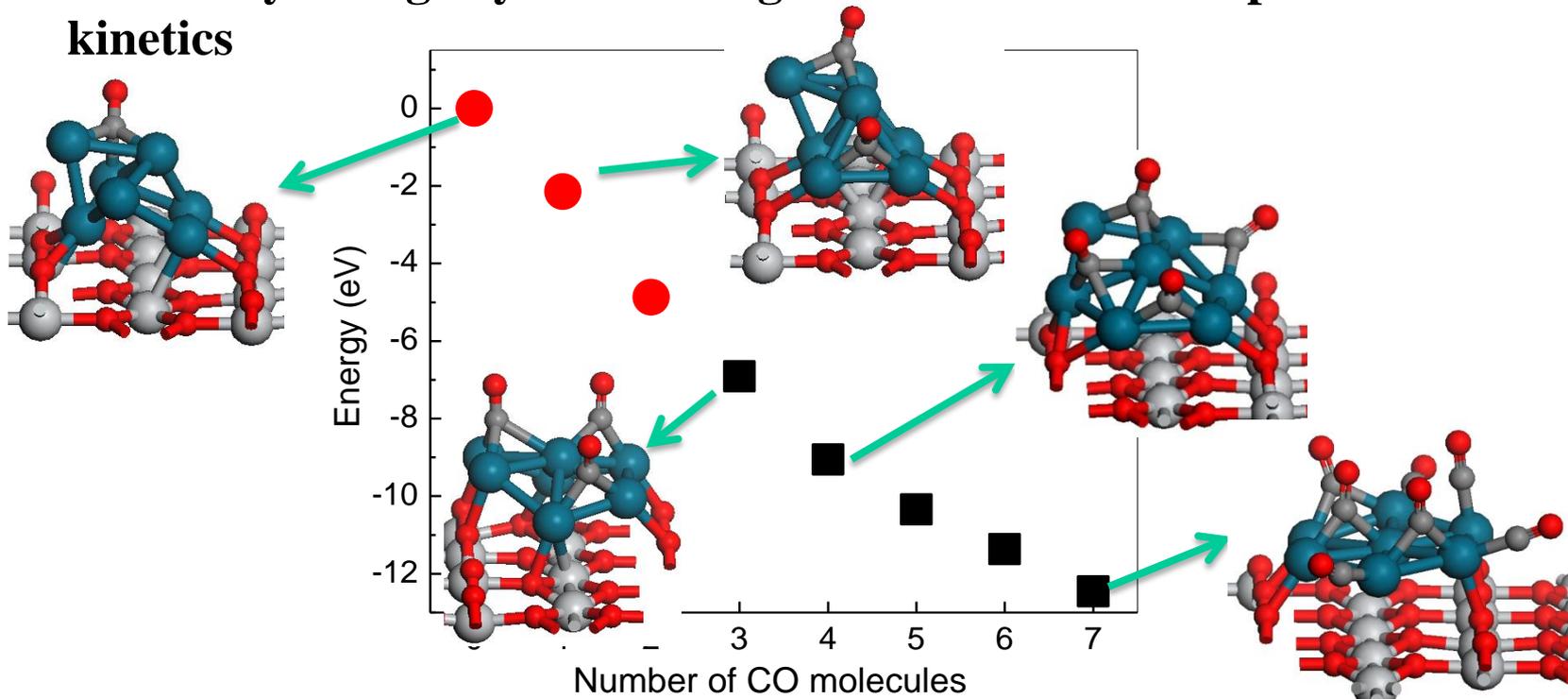


Highlight: the importance of interplay between surface contraction and local structural flexibility of a particle due to finite size and shape in particular at nanoscale.

Pressure gap

● Modeling more realistic reaction conditions towards bridging pressure-gap at DFT level: : considering the pressure of reactants induced

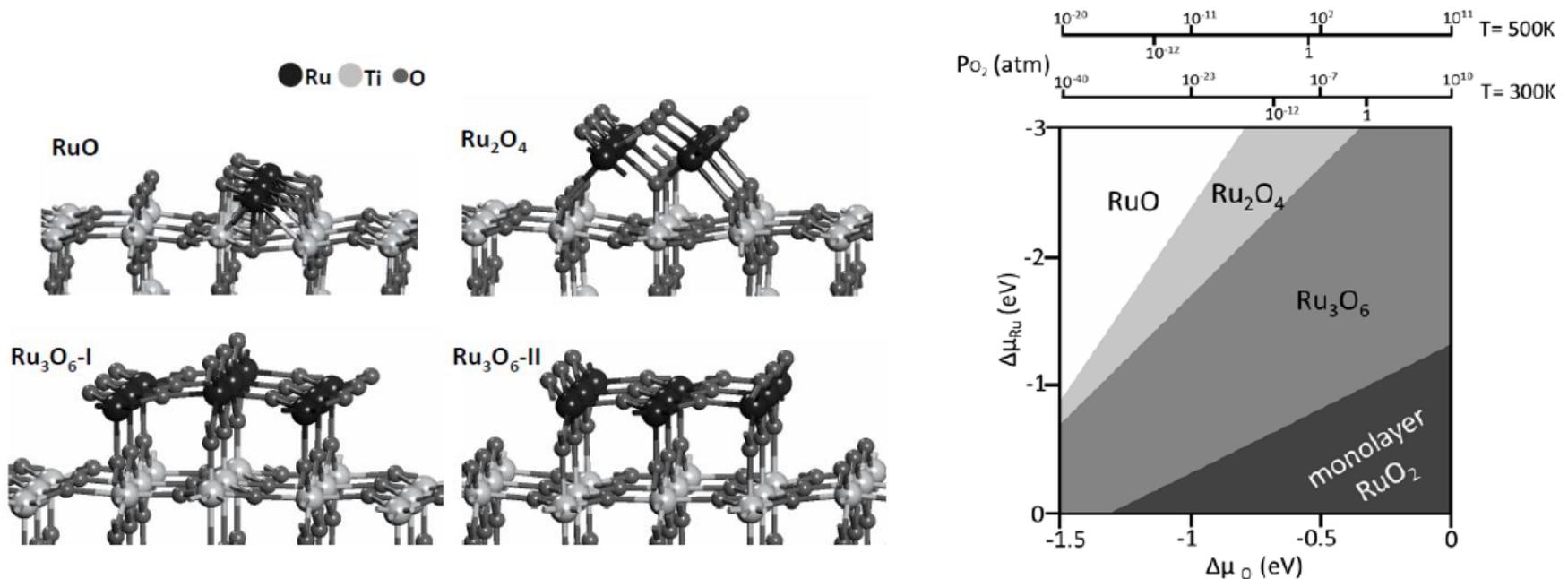
- Structural change by including the coverage effect
- Activity change by considering the effect of co-adsorption on kinetics



Highlight: the significance of pressure effect on the atomic arrangement in particular for small particles and the low-coordinated sites of catalysts.

Pressure gap

- Modeling more realistic reaction conditions towards bridging pressure-gap at DFT level: : considering the pressure of reactants induced
 - Formation of new active phase by determining phase-diagram under different conditions

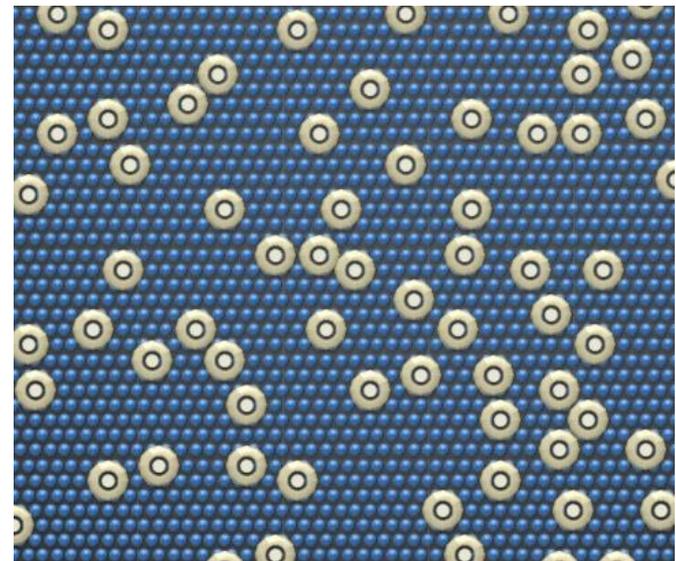
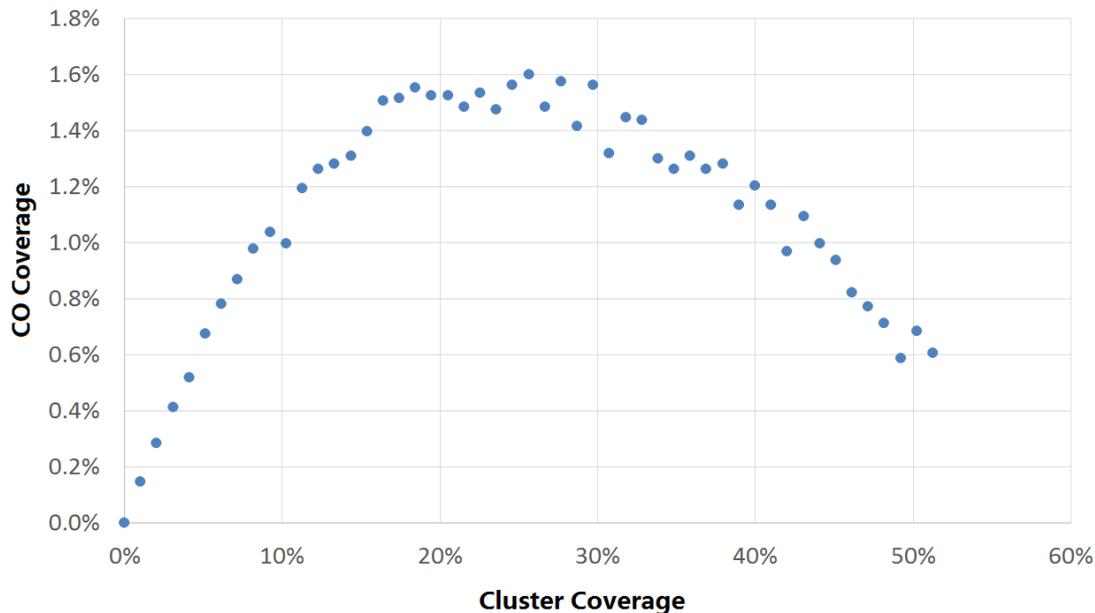


Highlight : the significance of pressure effect on surface composition and structure.

Combined theoretical description of catalysis

● **Modeling more realistic catalysis using KMC based on DFT calculations : estimating**

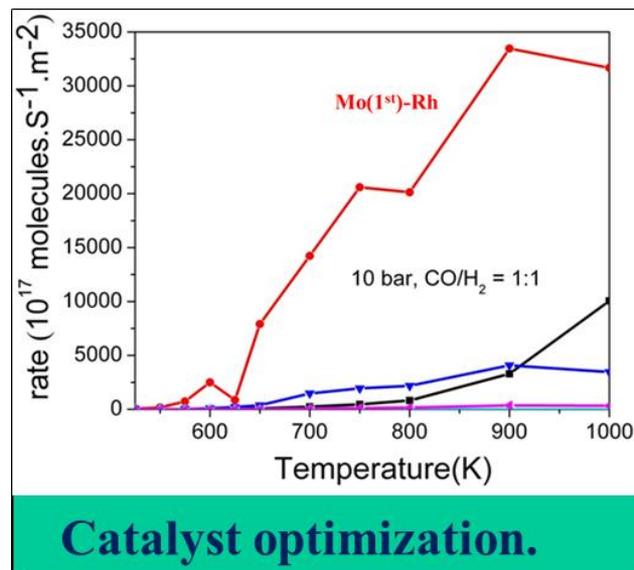
- **yields and selectivity under the experimental pressures and temperatures including the contribution from NPs, supports and the interfaces.**



CO coverage vs. TiO₂ coverage on Cu(111) TiO₂ clusters supported on Cu(111)

Liu, Liu, et al., to be published.

Summary: combined theory

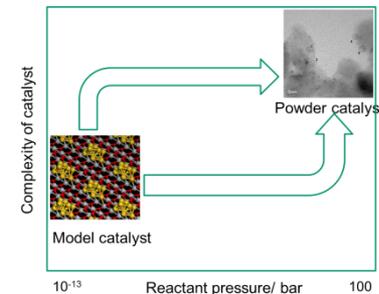


DFT + Kinetic Modeling + Sensitivity Analysis

Future

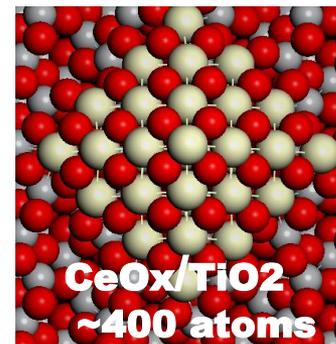
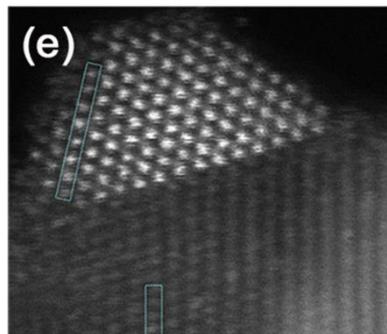
● Model more realistic catalysts and reaction conditions, which allow us to

- Strengthen the experiment-theory connection
- Improve theoretical capability in understanding the reaction mechanism and predicting better catalysts.

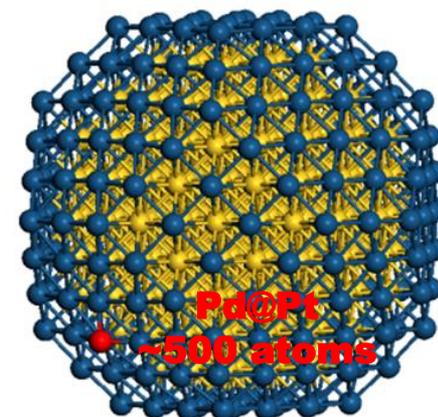
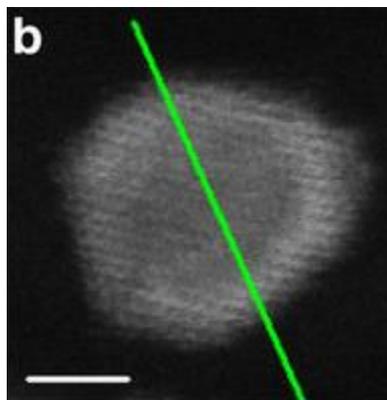


Computational facilities

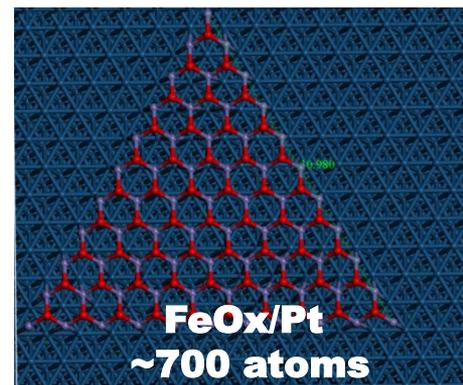
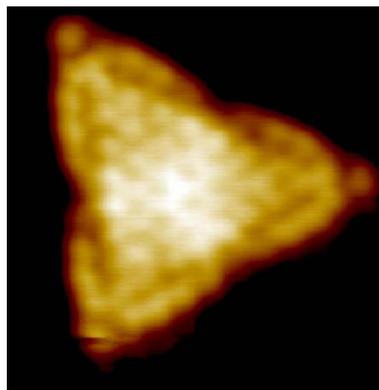
CFN (BNL)



NERSC (LBNL)



NY Blue
BNL



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