Modelización de propiedades fisico-químicas de sistemas de interés catalítico

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Modeling for Theoretical Catalysis Group

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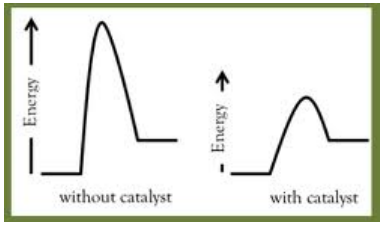
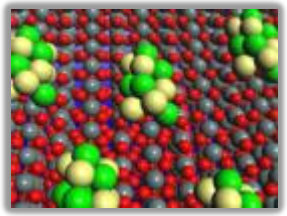
Till 2010: Humboldt University Berlin, Berlin, Germany

Heterogeneous catalysis



- Catalysts work by providing lower activation barrier
- Metal or oxide catalysts are typically supported

  → increase surface area & lower cost



- support-catalyst interaction affects reactivity

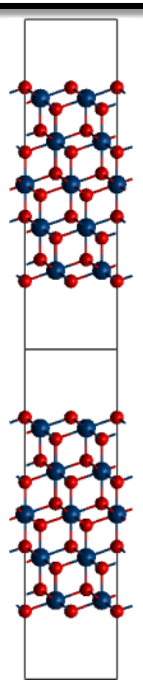
Understanding catalysis at the atomic level ↔ Rational design

Problems → the structural complexity of most catalysts
the pressure gap – UHV vs. real conditions

Solutions → suitable experimental and theoretical model systems

Theoretical modelling

Surface models

Periodic approach: supercell or slab geometry →  (2×2) CeO_2(111)

Methods

Density Functional Theory DFT

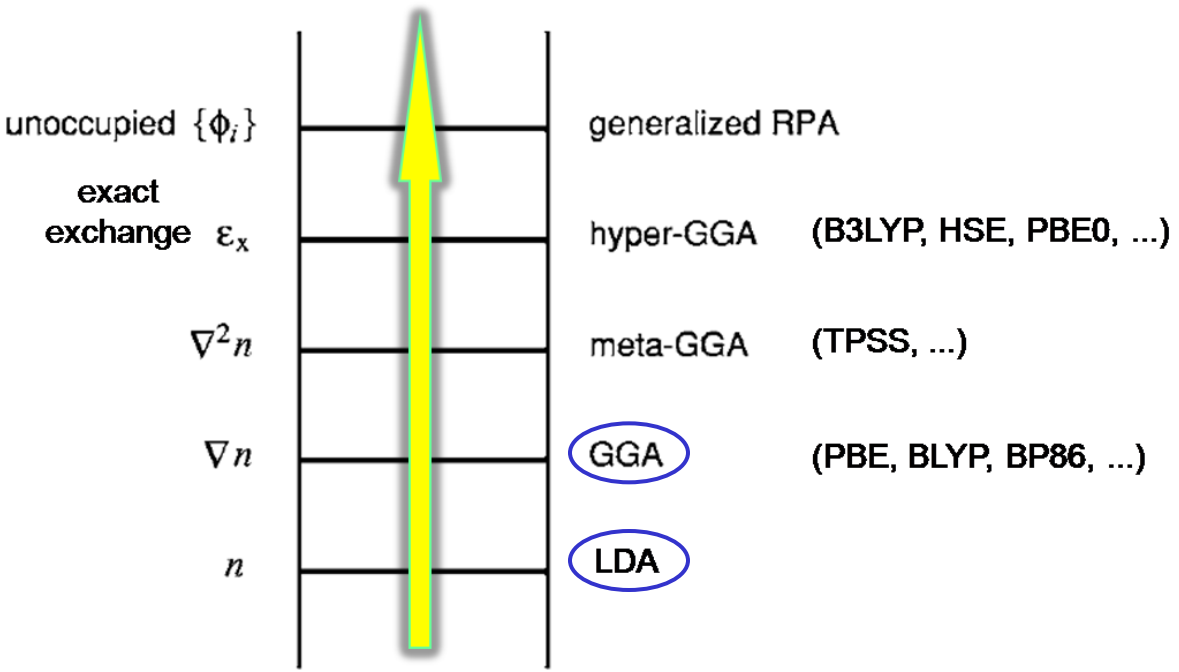
Vienna Ab initio Simulation Package, VASP

Total energy $E[n] = T_s[n] + E_{ext}[n] + E_{Hartree}[n] + E_{xc}[n]$

↑ electron density

↑ unknown exchange-correlation potential

DFT: The Jacob's ladder



J. P. Perdew, A. Ruzsinszky, J. Tao, V. N. Staroverov, G. Scuseria, G. I. Csonka, JCP 123, 062201 (2005)

Electron self-interaction not fully cancelled

Local Density (LDA) and Generalized Gradient (GGA) Approximations

Defficiencies
- Overestimation: Electron delocalization, metallic character, atomization energies
- Underestimation: Band gaps, energy barriers

„cheap" solution: DFT (LDA/GGA)+U on-site Coulomb repulsion

„expensive" solution: Hybrid-DFT exact-exchange

Bath Abbey

Systems: Creation of computational model catalysts

Nature

- ❑ Metal
- ❑ Oxide
- ❑ Metal/Oxide

Aggregation

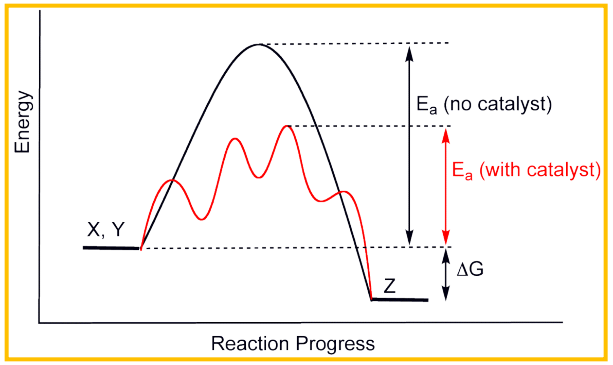
- ❑ Surfaces & Interfaces
- ❑ Supported nanostructures –clusters → complex systems

Everything should be as simple as it can be but not simpler!
Einstein

Questions: Structure ↔ Function

Active Site

- Structure , electronic and vibrational properties –STM, XPS, IR
- Surface termination – mind pressure gap! → DFT+Statistical Thermodynamics
  DFT+Monte Carlo
- Support effect – not always innocent!
- Chemisorptive properties – TPD



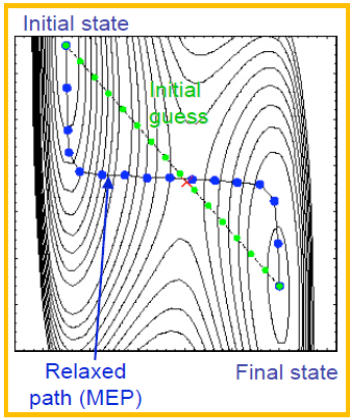
Function

- Reactivity Parameters → 'Probing' chemical reactivity

  e.g., O defect formation energy

  ⇒ Best model catalyst candidate

- Reaction Mechanisms → Nudged Elastic Band Method



Slide courtesy of Graeme Henkelman

Selected Examples

Oxide Surfaces

- $V_2O_5(001)$
  - ✓Prediction of missing-row defect structure @ reducing conditions → confirmed
  - ✓Explanation MIT transition at the surface

PRB 70, 045422 (2004)
PRL 99, 226103 (2007)

- $CeO_2(111)$
  - ✓Prediction of localization of excess charge away from the defect → confirmed
  - ✓Explanation of (2×2) subsurface vacancy ordering
  - ✓Understanding mechanism for partial alkyne hydrogenation

PRL102, 026101 (2009)
PRL 106, 246801 (2011)
PRL 110, 246101 (2013)
J. Phys. Chem. C 118, 5360 (2014)

Oxide/Oxide

- VO_x/CeO_2
  - ✓Elucidation of monolayer catalyst structure
  - ✓Understanding support effect on reactivity

Angew. Chem. Int. Ed. 48, 8006 (2009)
JACS 132, 2345 (2010)
J. Phys. Chem. C 115, 7399 (2011)

Metal/Oxide

- $Au/Al_2O_3/NiAl$
  - ✓Elucidation of electronic structure – counting electrons

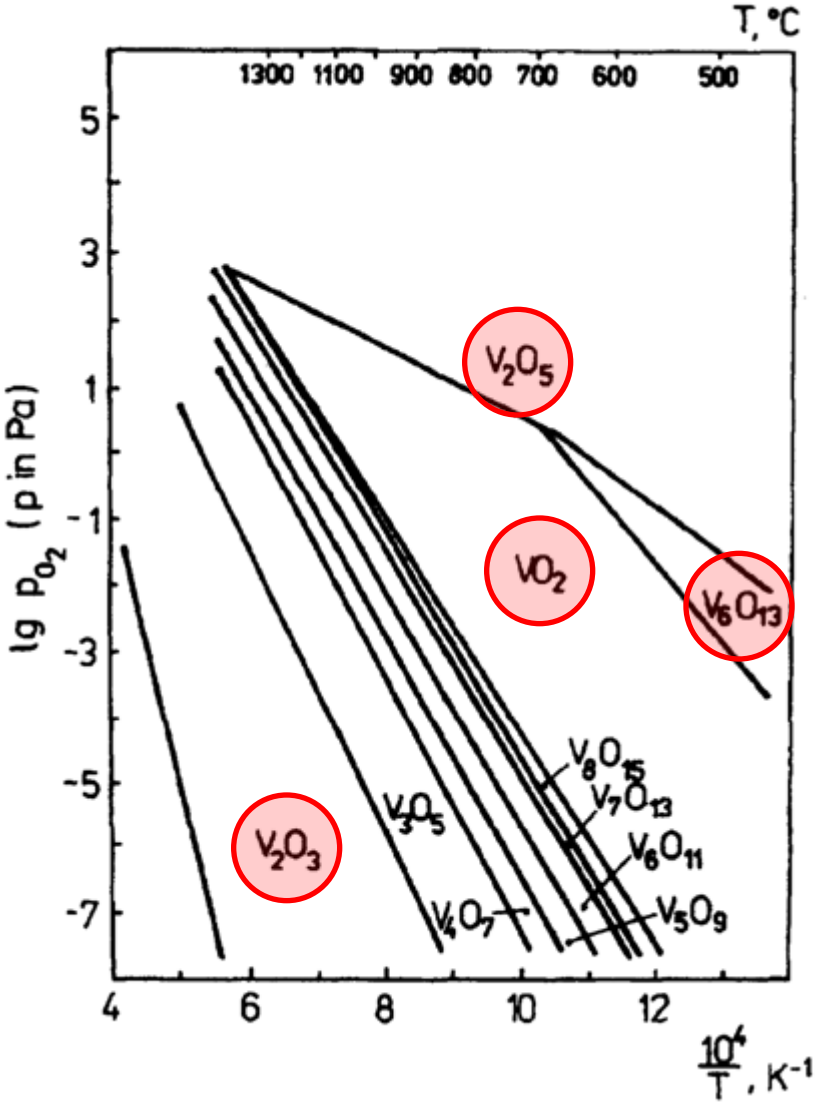
PRL 100, 096802 (2008)

- Ni/CeO_2
  - ✓Explanation of Ni coverage dependence on reactivity for water-gas shift

J. Phys. Chem. C 117, 8241 (2013)

Vanadium oxide bulk phases

- VO_x large variety of oxidation states
  V_2O_5 (5+), VO_2 (4+), V_2O_3 (3+), VO (2+)



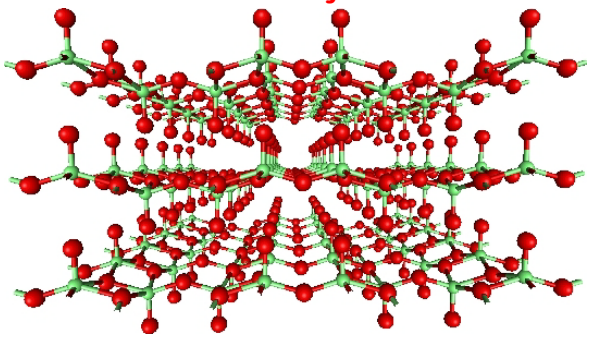
Most vanadium oxide bulk phases exhibit a metal-insulator transition

- V_6O_{13}: V^{4+},V^{5+} MIT @ 150 K
- V_2O_3: V^{3+} MIT @168 K
- VO_2: V^{4+} MIT @ 340 K
- V_2O_5: V^{5+} no MIT

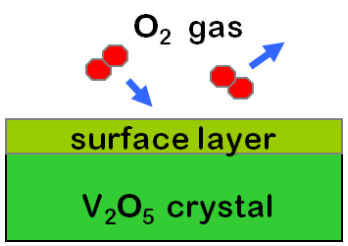
V_2O_5(001): defect structure and MIT transition

V_2O_5(001)

Vanadyl O



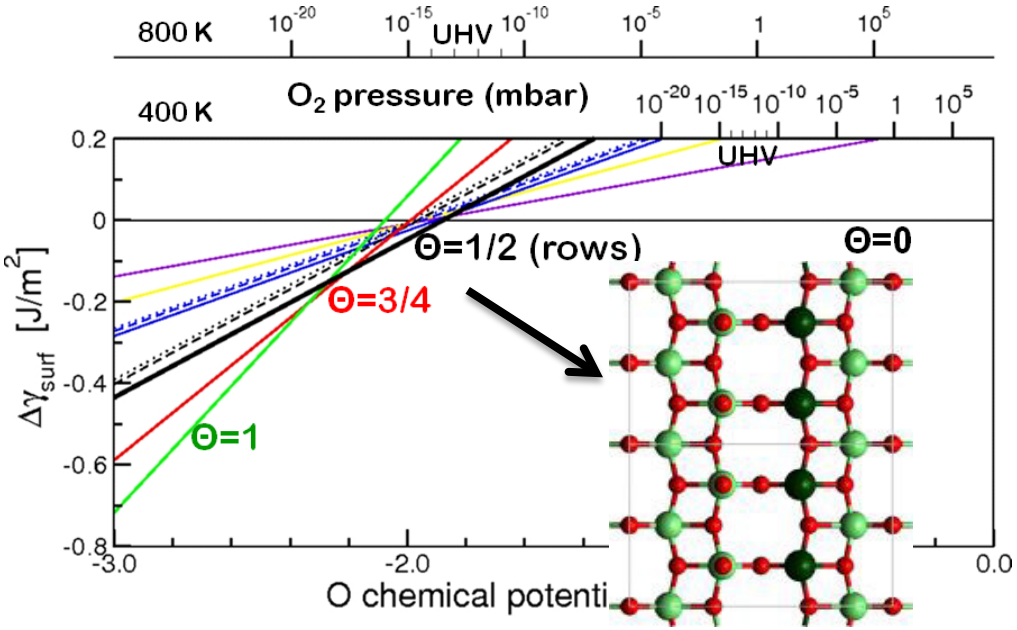
V^{5+} insulator



DFT-GGA+ statistical thermodynamics

$$V_2O_5^{\text{clean}} \rightleftarrows V_2O_5^{\text{reduced}} + N_{def}\ ½\ O_2$$

$$\Delta\gamma_{surf}(T,p) \approx N_{def}\left[E_f^{½O_2}(\Theta) + ½\,\Delta\mu_{O_2}(T,p)\right]/A$$



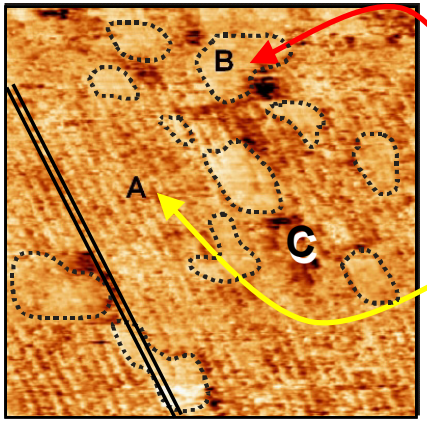
- DFT predicts the ease of reduction in the direction of the rows
  Explanation in terms of defect-induced lattice relaxation effects

PRB 70, 045422 (2004)
PRL 99, 226103 (2007)

V_2O_5(001): defect structure and MIT transition

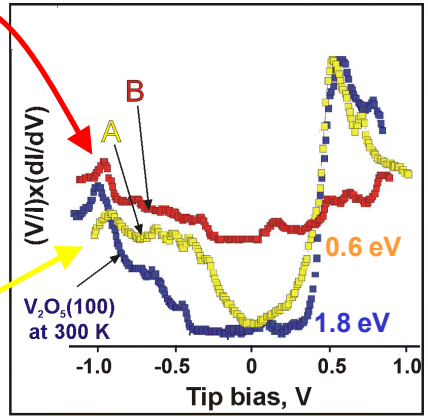
PRB 70, 045422 (2004)
PRL 99, 226103 (2007)

STM @350K

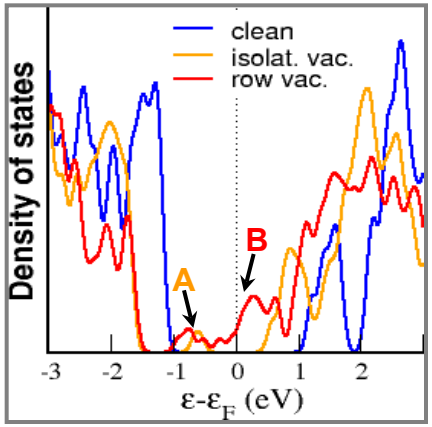


50x50 nm^2 -1.3 V 0.24 nA

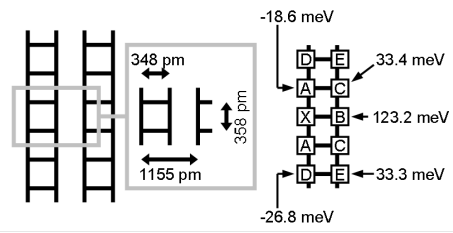
STS @350K



DFT+U U=3 eV

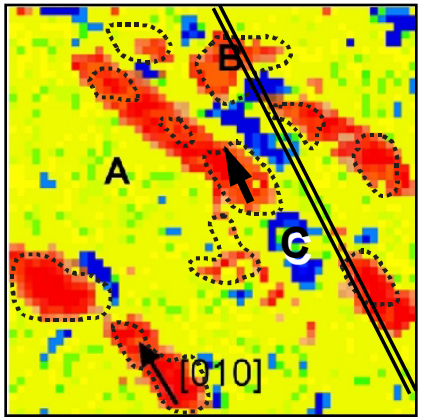


Monte Carlo network

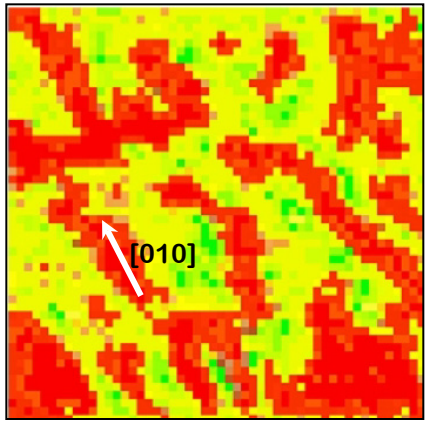


50 double rows
150 sites/row
15,000 sites

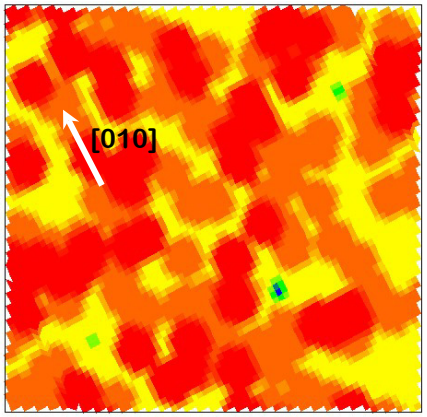
@350K



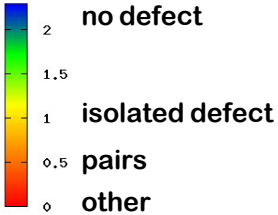
@400K



7% reduced sites @300 K



58x54 nm^2



surface insulator-metal transition

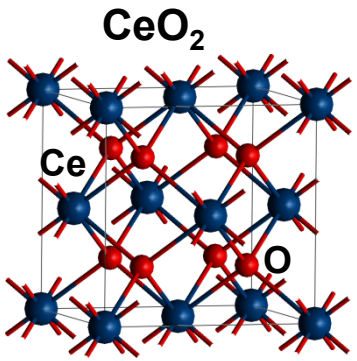
350-400 K

Bandgap map

Monte Carlo simulated Bandgap map

The facile reduction along [010] constitutes a prediction!!

CeO_2: a challenge for DFT – f-electron systems



insulator Ce^{4+} (f^0)

❑ Catalysis, Ion Conductor, Gas Sensor, Fuel Cell Component

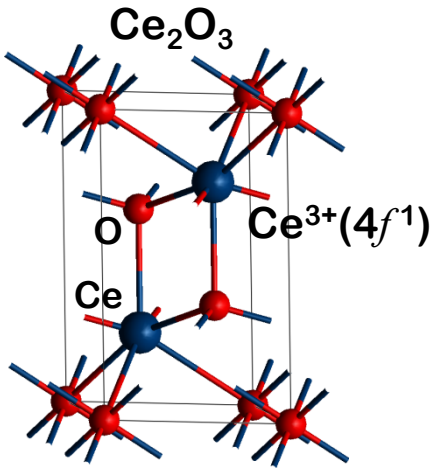
Ceria **reducibility** is **key** to its functionality

Ce^{4+} (f^0) ↔ Ce^{3+} (f^1)

Kresse, Blaha, Da Silva, Ganduglia-Pirovano, PRB 72 (2006)

Da Silva, Ganduglia-Pirovano, Sauer, Bayer, Kresse, PRB 75 (2007)

Ganduglia-Pirovano, Hofmann, Sauer, Surf. Sci. Rep. 62,219 (2007)



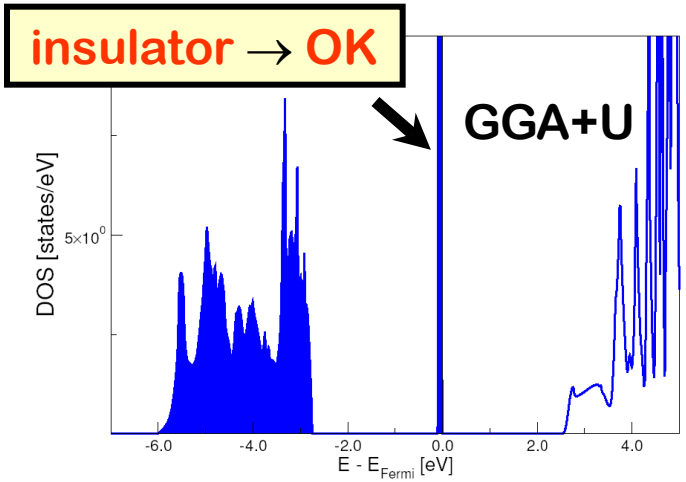
antiferromagnetic insulating ground state

DFT: ~~GGA~~

GGA+U; Hybrid

Accurate description?

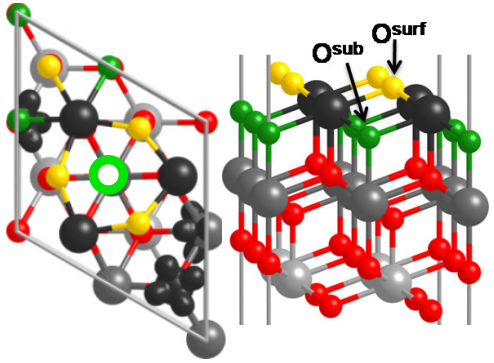
Predictive power?



$CeO_2(111)$: Near-surface oxygen defect structure

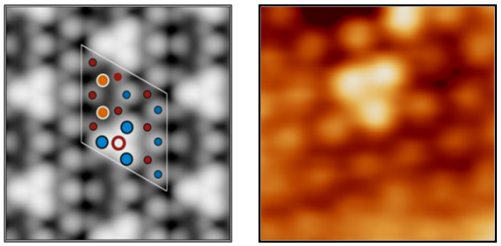
- DFT predicts a tendency of Ce^{3+} ions to be away from the defect

NNN-NNN



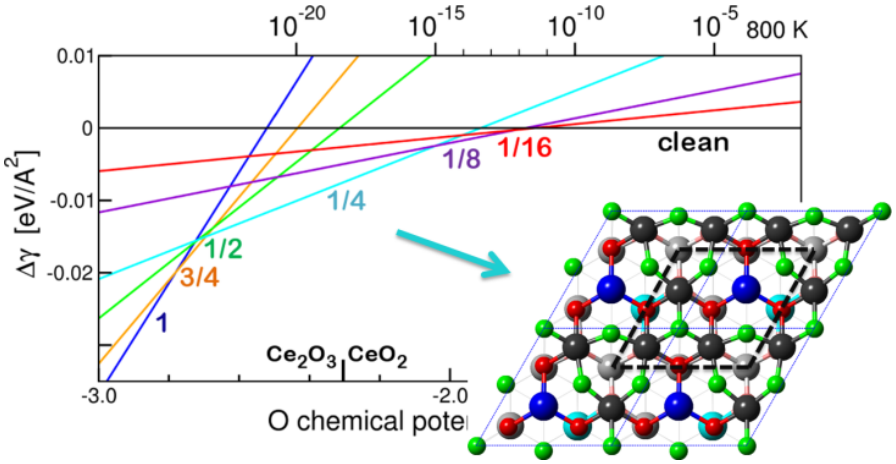
PRL102, 026101 (2009)

- STM/STS +DFT confirm the tendency of defects to bind to Ce^{4+} ions



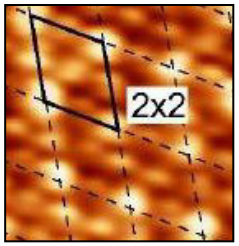
PRL 106, 246801 (2011)

- DFT predicts a preference for subsurface O defects (1/16 ≤ Θ ≤ 1ML)



PRL 110, 246101 (2013)

- DFT + statistical thermodynamics predict a (2×2) subsurface vacancy structure → repulsion!



- Explanations in terms of defect-induced lattice relaxation effects –Ce^{3+} is larger

Ceria as stand-alone catalyst

Angewandte Communications

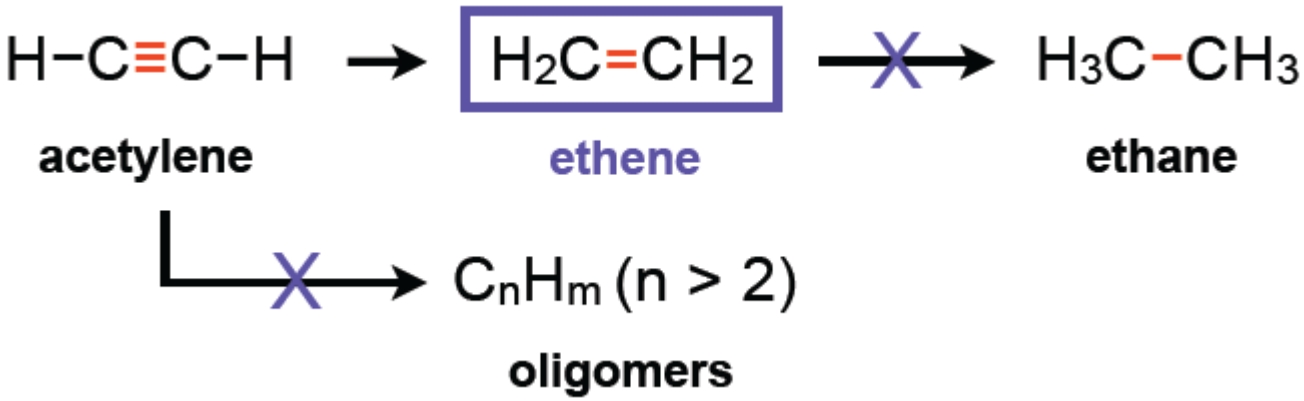
Angew. Chem. Int. Ed. **2012**, 51, 8620 –8623

Heterogeneous Catalysis

DOI: 10.1002/anie.201203675

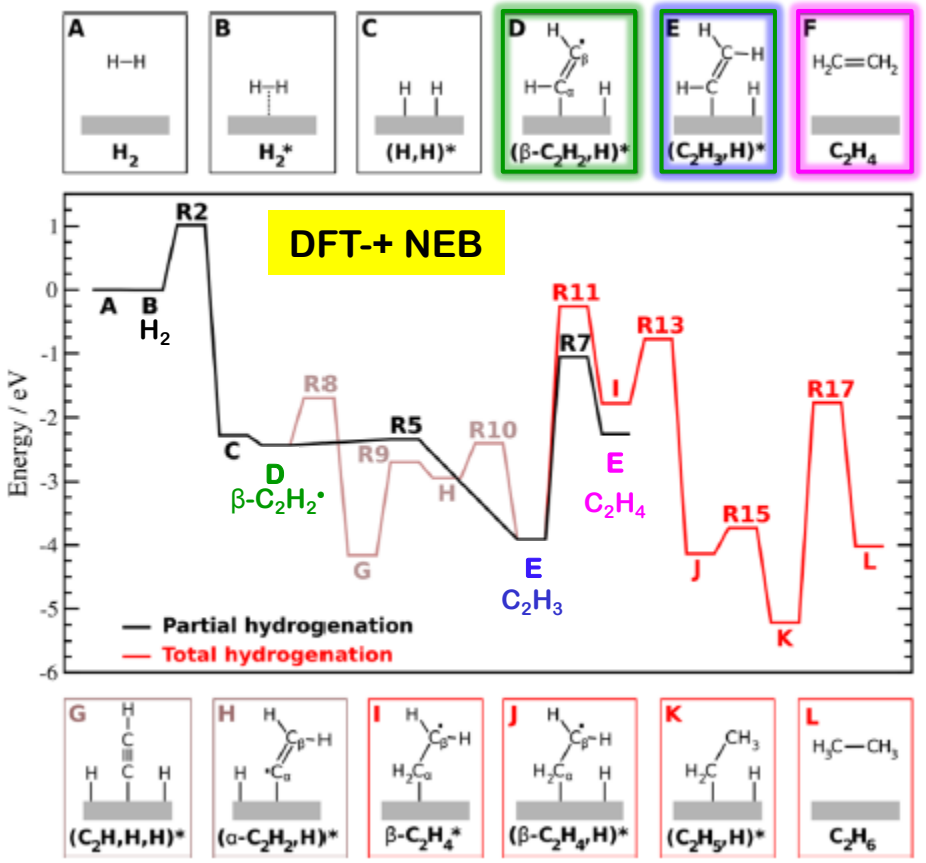
Ceria in Hydrogenation Catalysis: High Selectivity in the Conversion of Alkynes to Olefins**

*Gianvito Vilé, Blaise Bridier, Jonas Wichert, and Javier Pérez-Ramírez**
Institute for Chemical and Bioengineering
Department of Chemistry and Applied Biosciences, ETH Zurich



- Partial alkyne hydrogenation: crucial step for purification of olefin streams
- Conventional catalysts: Pd-based

Hydrogenation reaction mechanism



- ❑ H_2 dissociation → limiting step
- ❑ Highly reactive β-C_2H_2• radical species – Ce^{3+} – hydrogenated to form C_2H_3 → "barrierless"
- ❑ Oligomer formation only at low H_2/C_2H_2 ratios

Oxide supported vanadia –VO_x– catalysts

- VO_x large variety of oxidation states

  V_2O_5 (5+), VO_2 (4+), V_2O_3 (3+), VO (2+)

V^{2+} V^{3+} V^{4+} V^{5+}

- Important catalysts in oxidation reactions

  -SO_2 to SO_3 in the production of sulfuric acid
  -benzene to maleic anhydride (polyester resins)
  -oxidative dehydrogenation alkanes to alkenes, methanol to formaldehyde

Reducibility is key to their catalytic function

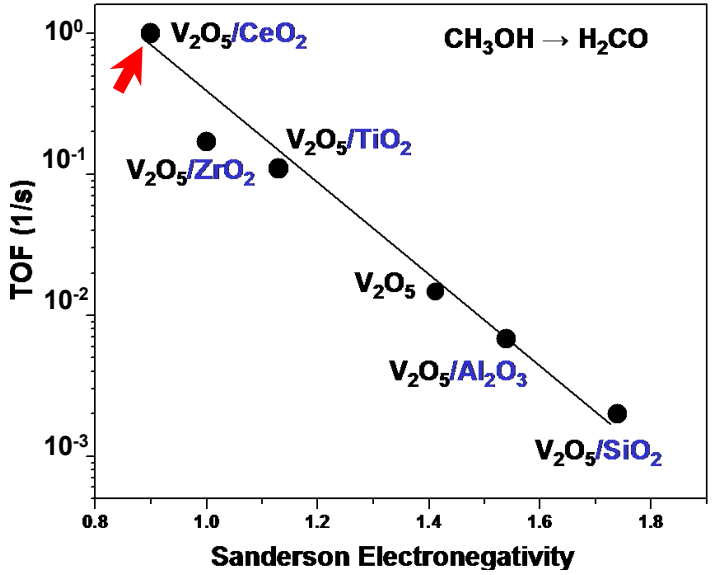
$$C_3H_8 + [V^{5+}O] \longrightarrow C_3H_7 + [V^{4+}OH] \longrightarrow [V^{3+}]\cdots H_2O \longrightarrow [V^{3+}]$$

propane; $-C_3H_6$ propene; $-H_2O$

Reactivity Parameter

O defect formation $[V^{5+}O] \xrightarrow{-\frac{1}{2}O_2} [V^{3+}]$

- The specific support affects the structure and catalytic performance

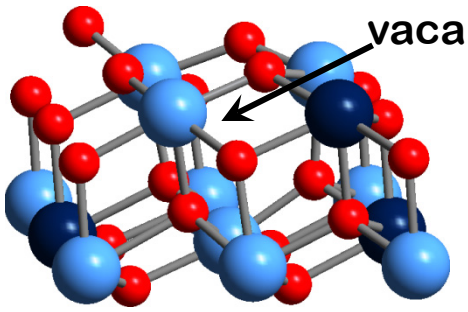


I. Wachs, Catal. Today, 100, 79 (2005)

Reactivity: The origin of the support effect

Angew. Chem. Int. Ed. 48, 8006 (2009)
JACS 132, 2345 (2010)
J. Phys. Chem. C 115, 7399 (2011)

$CeO_{2-x}(111)$

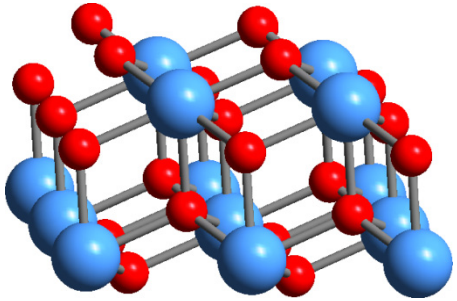


$2\times Ce^{3+}$

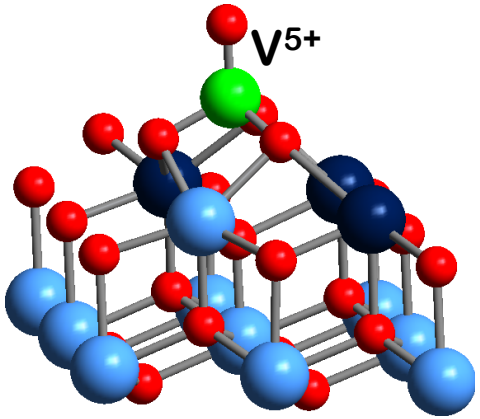
$-\frac{1}{2}\ O_2$

$+1.87$ eV

$CeO_2(111)$



$VO/CeO_2(111)$

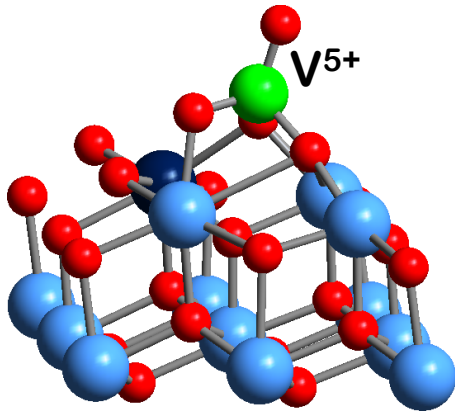


$3\times Ce^{3+}$

$-\frac{1}{2}\ O_2$

$+0.79$

$VO_2/CeO_2(111)$

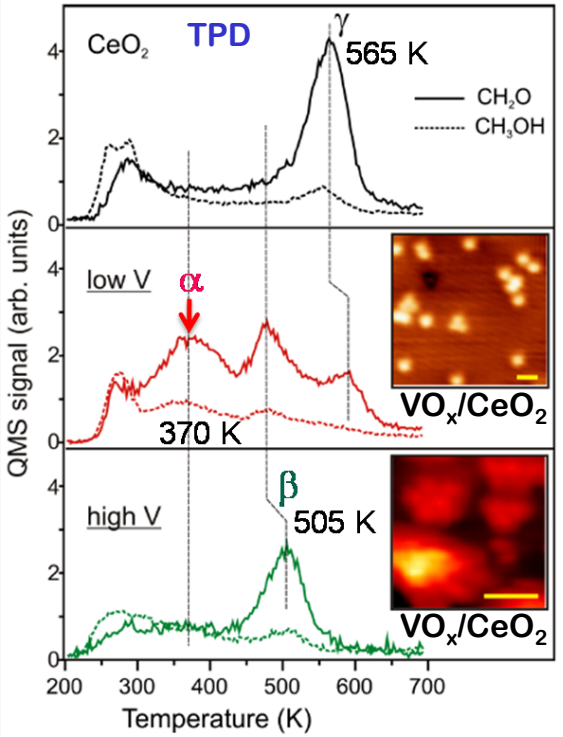


$1\times Ce^{3+}$

PBE+U [eV]

Reactivity

$CH_3OH \rightarrow CH_2O$

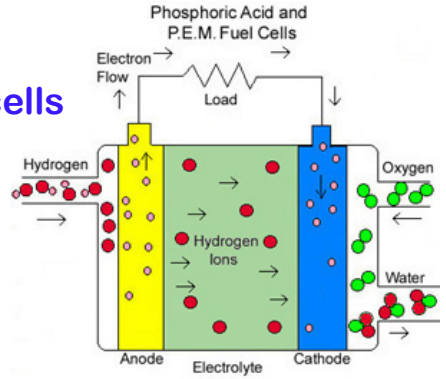


Origin of the high catalytic activity is the ability of ceria to stabilize reduced states by accommodating electrons in localized f-states, which is promoted by the vanadia species

Oxide supported metal catalysts

- Hydrogen is expected to play an important role in future energy scenarios

Fuel cells



- H_2 production
  - Steam reforming of hydrocarbons: $C_nH_m + nH_2O \rightarrow nCO + (n-m/2)H_2$
  - Fuel contains 1-10% CO → Pt electrode degradation
  - **Water-gas shift:** $CO + H_2O \rightarrow H_2 + CO_2$

WGS catalysts

- classic catalyst formulation: mixed Fe and Cr or Cu and Zn oxides → drawback: long preconditioning
- new catalysts: metal–Pt, Au–particles supported by reducible oxides–TiO_2, CeO_2

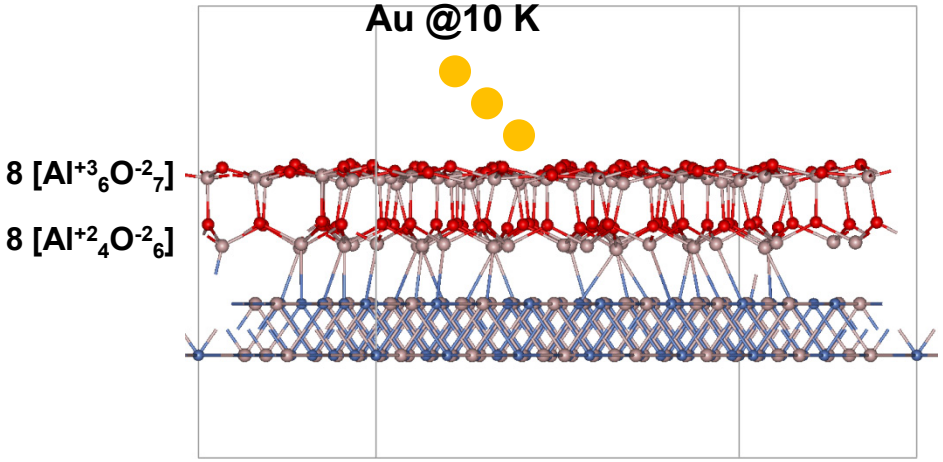
Fu et al., Science 301 (2003) 935

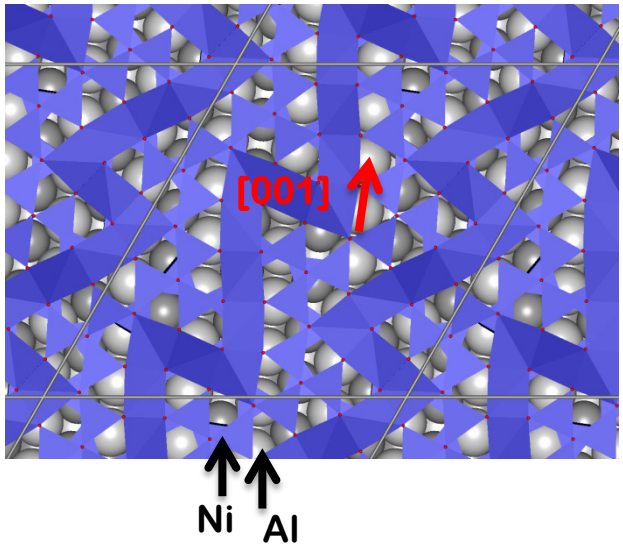
Bifunctional: CO adsorbs on metal
H_2O dissociates on oxide

- cluster size
- charge of the metal cluster
- metal/oxide support interface

Counting electrons on oxide supported Au chains

The model: Au on a thin alumina on NiAl(110)





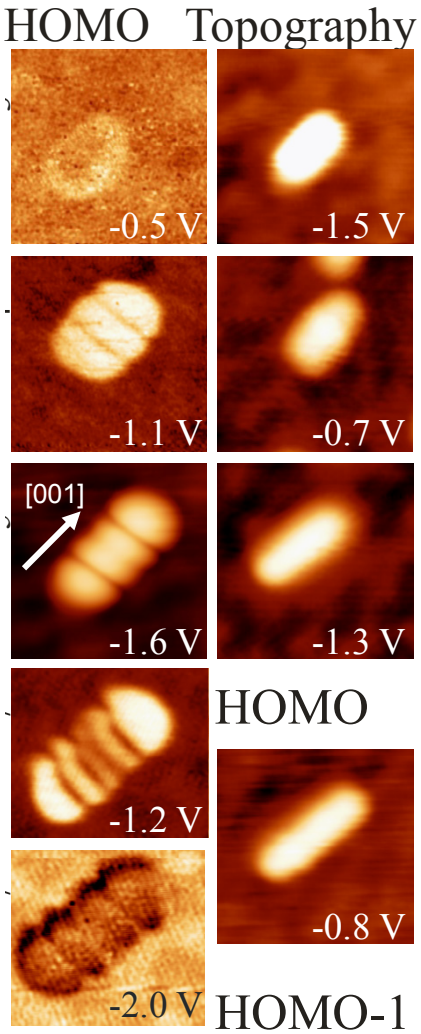
Support structure:

Kresse, Schmid, Napetschnig, Shishkin, Köhler, Varga, Science 308, 1440 (2005)

Kulawik, Nilius, Freund, PRL 96, 036103 (2006)

Self-assembly Au chains: STS & STM

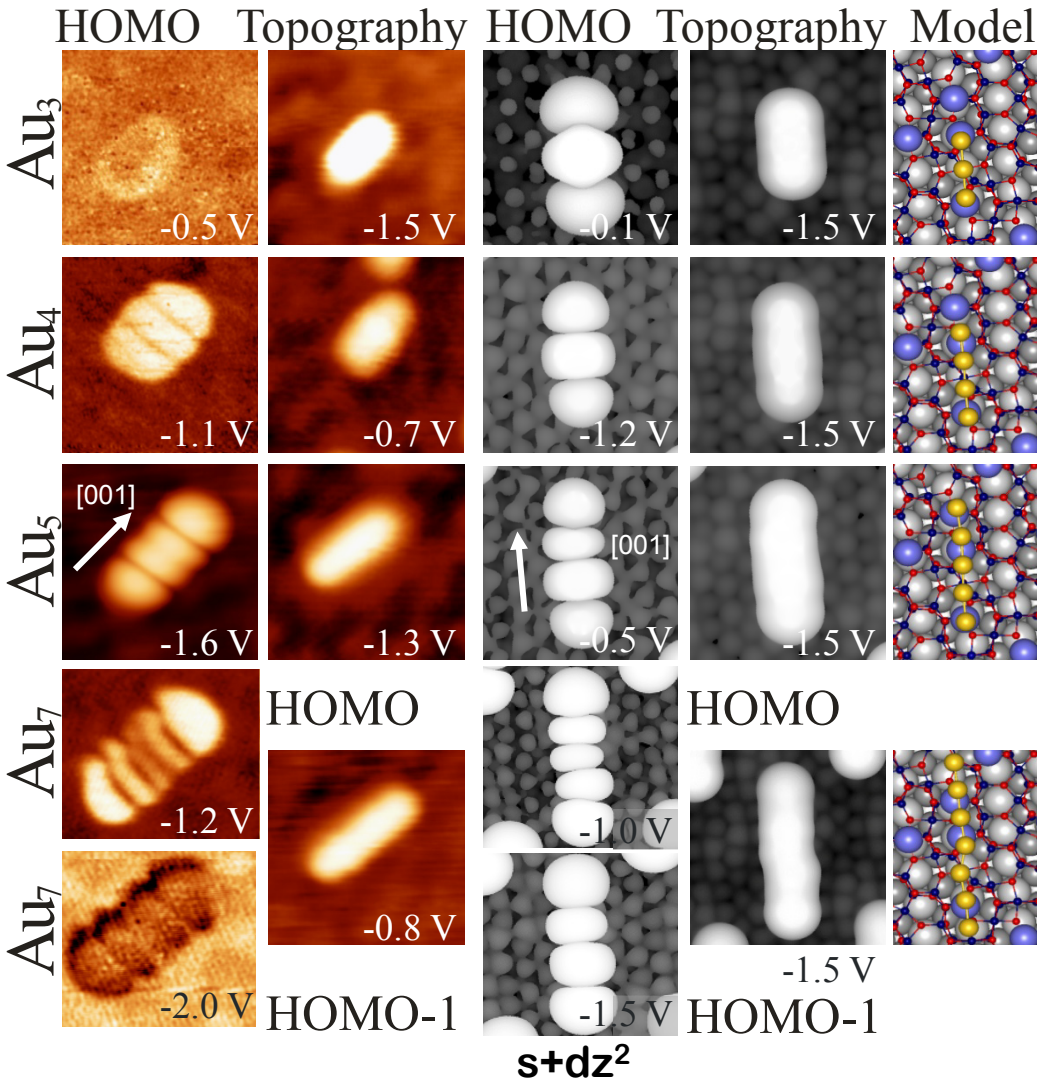
PRL 100, 096802 (2008)



Au chains

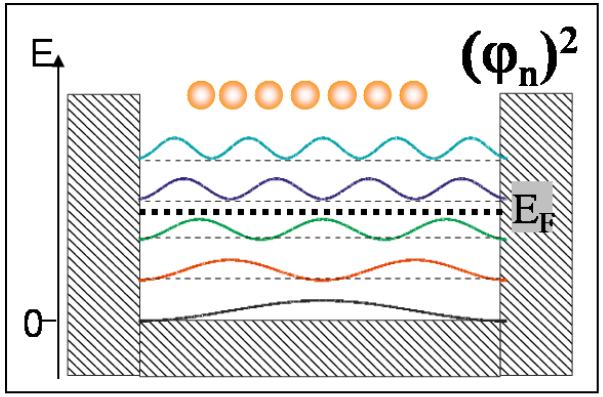
Au on a thin alumina film on NiAl: STS & STM

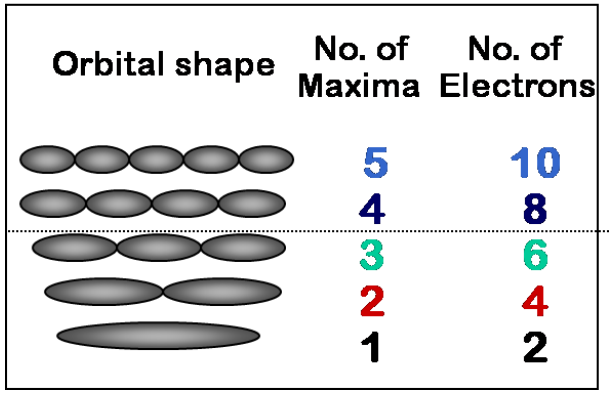
PRL 100, 096802 (2008)



quantum well states:

1 s+dz^2 state per Au atom

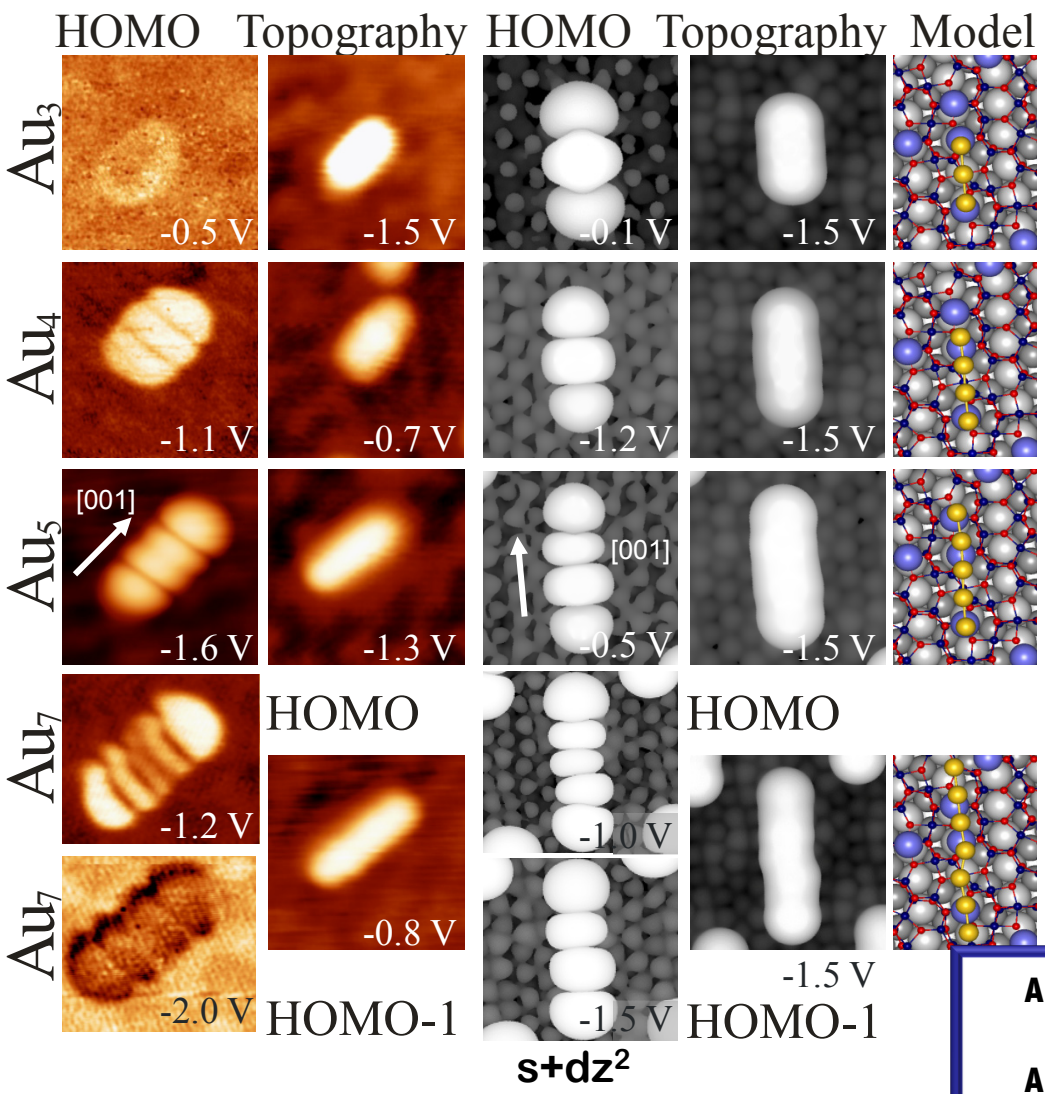




DFT-GGA

Au on a thin alumina film on NiAl: STS & STM

PRL 100, 096802 (2008)



quantum well states:

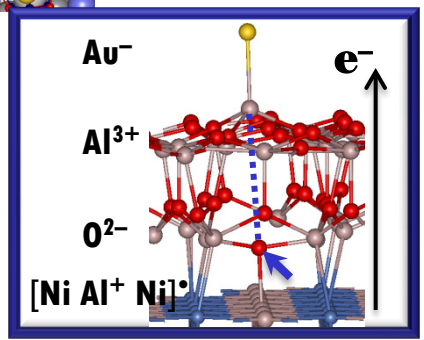
1 s+dz² state per Au atom

tetramer 4 Au
0 μ_B
2 nodes → 6 electrons
2

pentamer 5Au
1 μ_B
3 nodes → 8 electrons
3

heptamer 7Au
1 μ_B
4 nodes → 10 electrons
3

missing electrons?

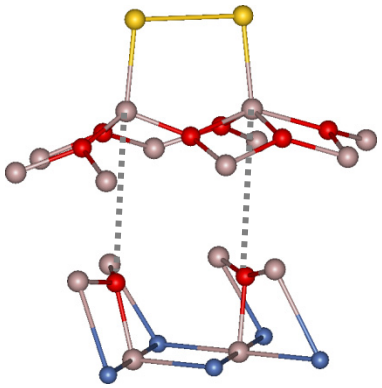


Breaking & forming of Al-O bonds

→ negative charging of Au

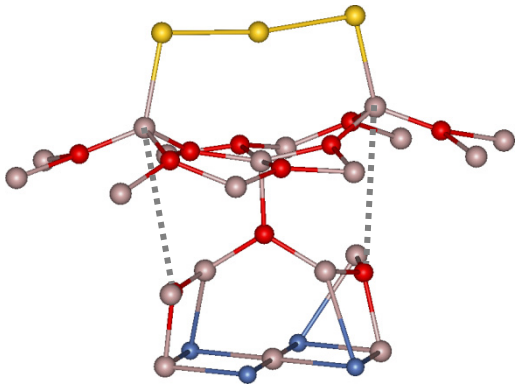
The self-assembled chains

dimer



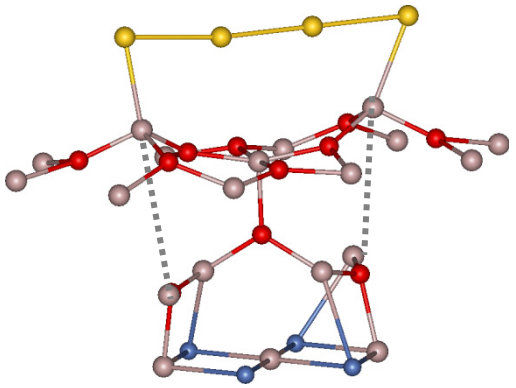
2 broken Al_{top}-O bond

trimer



2 broken Al_{top}-O bond

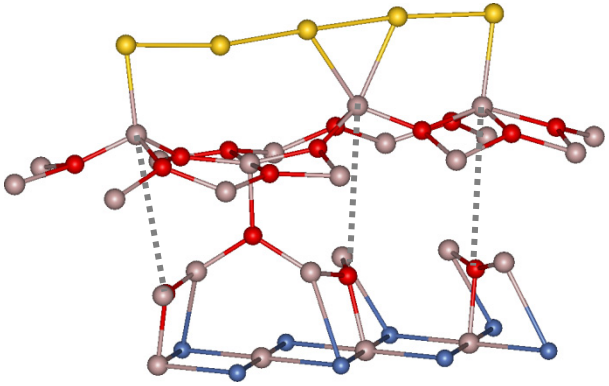
tetramer



2 broken Al_{top}-O bond

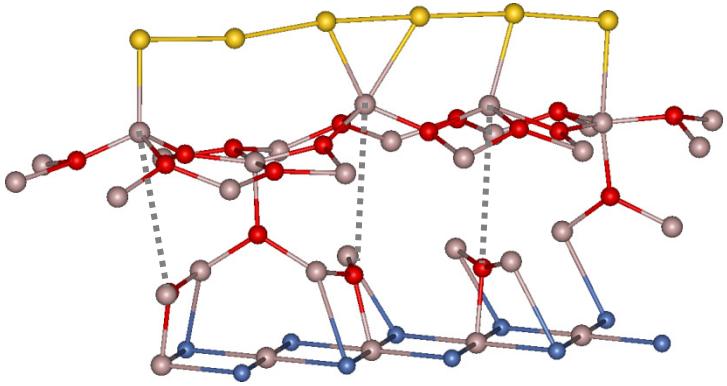
If 1 e^- per broken bond is assumed to be transferred,
the number of nodes and magnetization can be explained

pentamer



3 broken Al_{top}-O bond

hexamer



3 broken Al_{top}-O bond

PRL 100, 096802 (2008)

Oxide supported metal catalysts: Ni/CeO_2

WGS catalysts

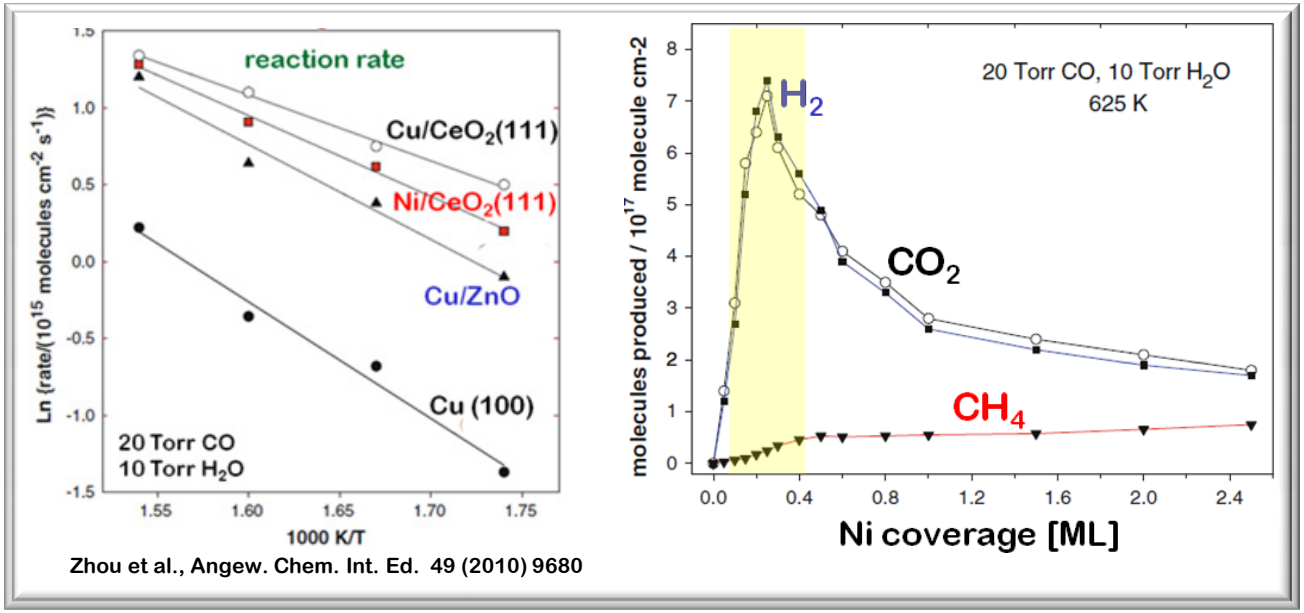
- classic catalyst formulation: mixed Fe and Cr or Cu and Zn oxides → drawback: long preconditioning

- new catalysts: metal–Pt, Au–particles supported by reducible oxides–TiO_2, CeO_2–bifunctional

Fu et al., Science 301 (2003) 935

- promising water-gas shift catalysts: Ni/ceria collaboration Brookhaven

$$CO + H_2O \rightarrow CO_2 + H_2$$



Zhou et al., Angew. Chem. Int. Ed. 49 (2010) 9680

Ni coverage dependence

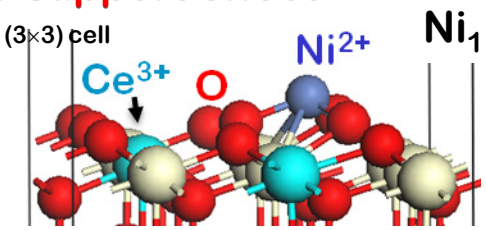
small is better!

Ni/CeO_2 model catalyst

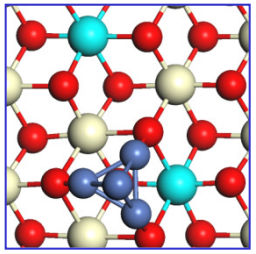
- The WGS activity depends strongly on the size of the Ni particles – the smaller the better → support effect

JPCC 117, 8241 (2013)

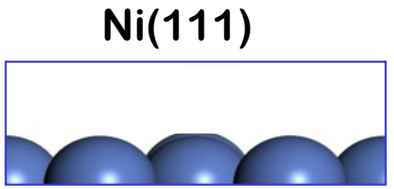
- Ni oxidation state →



$[Ni_1]^{2+} \rightarrow Ni^{2+}$

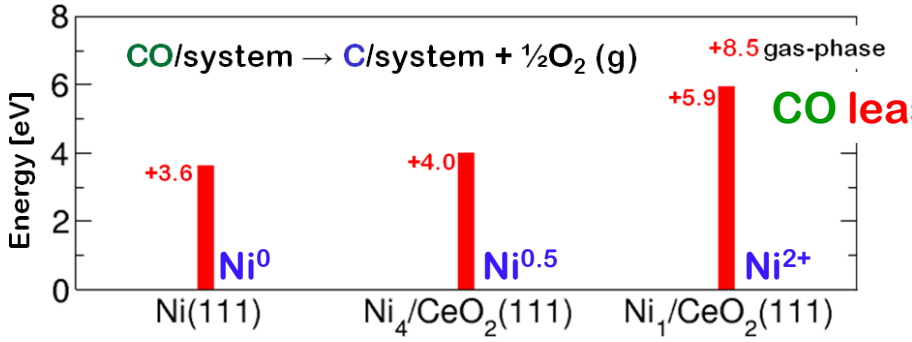


$[Ni_4]^{2+} \rightarrow Ni^{0.5}$

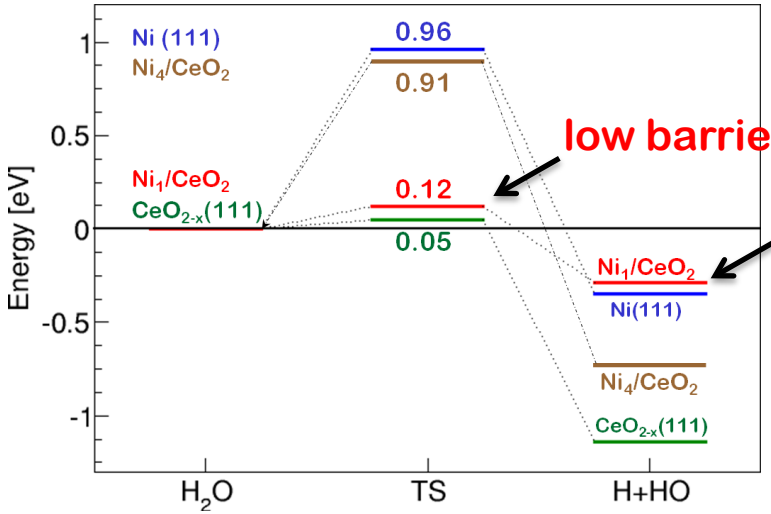


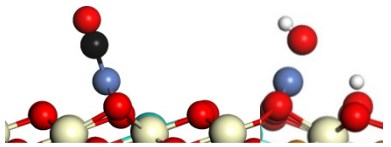
Ni^0

- C–O bond strength



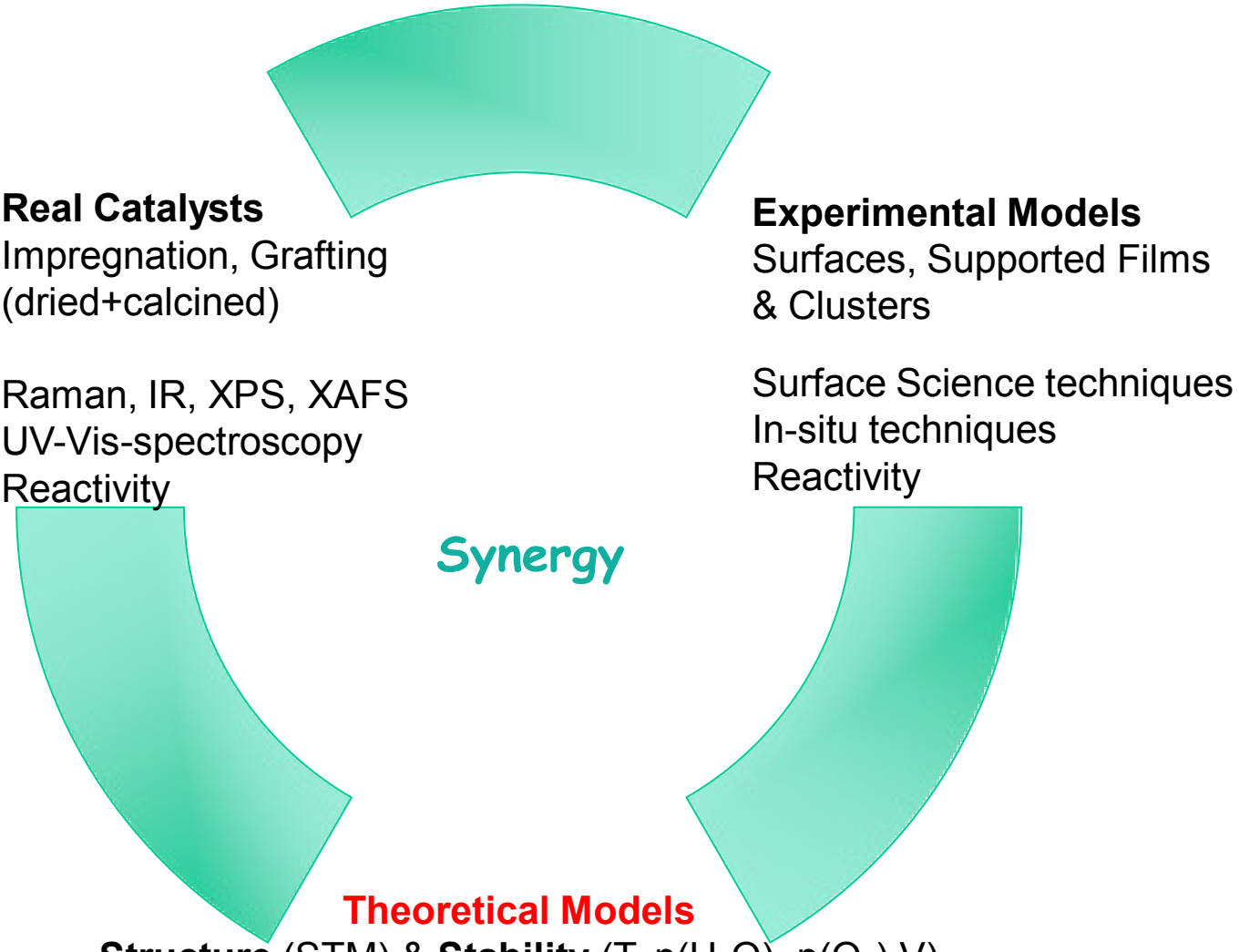
- H_2O dissociation





monofunctional

The power of synergy



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