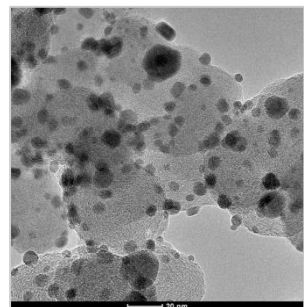


The non-innocent role of cerium oxide in heterogeneous catalysis: a theoretical perspective

M. Verónica Ganduglia-Pirovano

**Institute of Catalysis and Petrochemistry,
Spanish National Research Council -CSIC, Madrid, Spain**

Towards the rational design of catalysts



TEM image

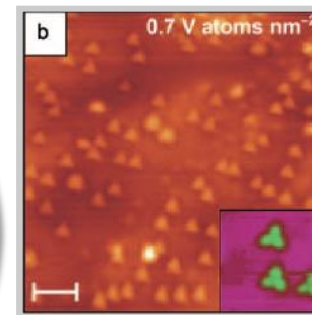
$\text{Rh}_x\text{S}_y/\text{C}$ real catalyst

Allen, R.J, Gulla, A.F.
U.S. Patent 6,967,185

**Real
Catalysts**

Pressure
&
Materials Gaps

**Exp. Model
Catalysts**



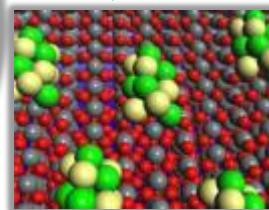
STM image

VO_x/CeO_2 model catalyst

Baron, Abbott, Bondarchuk,
Stacchiola, Uhl,
Shaikhutdinov, Freund, Popa,
Ganduglia-Pirovano, Sauer,
Angew. Chem. Int. Ed. 48,
8006 (2009)

Synergy

**Theoretical
Model Catalysts**



Understanding
Structure,
phys. & chem. properties

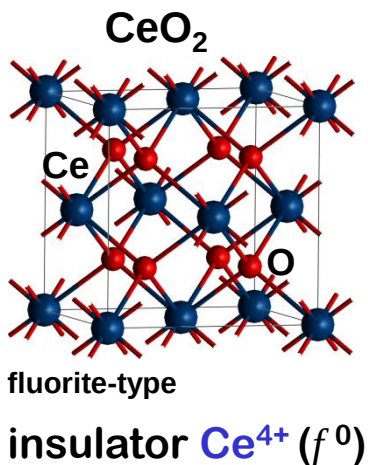


Catalytic
function



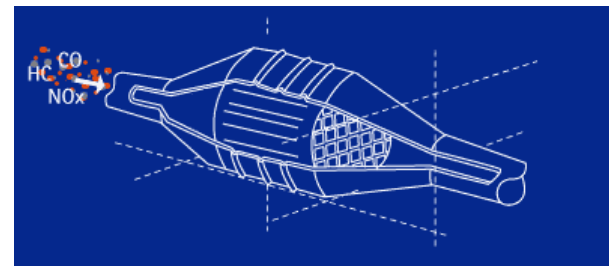
Rational design
of improved or new
catalytic systems

Cerium oxide: Reducibility and catalytic function



Use & Applications

- ☐ present as support in metal & oxide catalyst formulations
→ improved performance
- ☐ catalytic converter
→ purification of exhaust gases
- ☐ solid-fuel cell technology
→ H_2 production

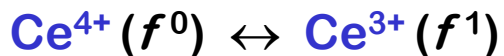


http://www.rhodia-ec.com/site_ec_us/catalysis/index_automotive.htm

Oxygen Storage Capacity

an '**oxygen-sponge**'

releasing and **storing oxygen**
according to the catalytic reaction
(oxidation or reduction)



Ceria **reducibility** is **key** to its
functionality and promoter effect

Ceria and its non-innocent role as support

□ Stand-alone catalyst

$\text{CeO}_2(111) \rightarrow$ Partial alkyne hydrogenation

Reactivity of ceria surfaces: $\text{H}_2 \rightarrow \text{H} + \text{H}$ dissociation

$\text{C}_2\text{H}_2 + n \text{H} \rightarrow \text{C}_2\text{H}_{2+n}$ ethylene hydrogenation

Collaboration: J. Pérez-Ramírez
ETH, Zurich

□ Support

$\text{V}_m\text{O}_n/\text{CeO}_2(111) \rightarrow$ ODH reactions

Structure and reactivity of supported vanadia

Collaboration: J. Sauer (HU-Berlin);
H.J. Freund (FHI-Berlin)

$\text{Ni}_n/\text{CeO}_2(111) \rightarrow$ H_2 production and CH_4 dry reforming

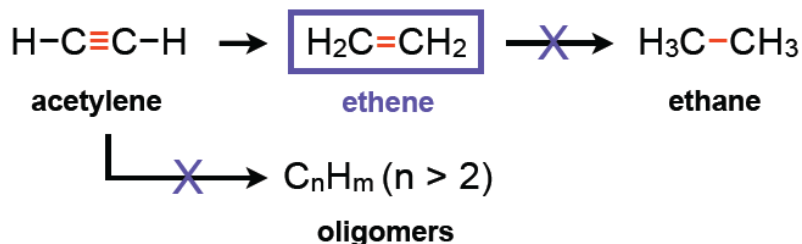
Structure and reactivity of supported nickel

Collaboration: J. A. Rodríguez
BNL, USA

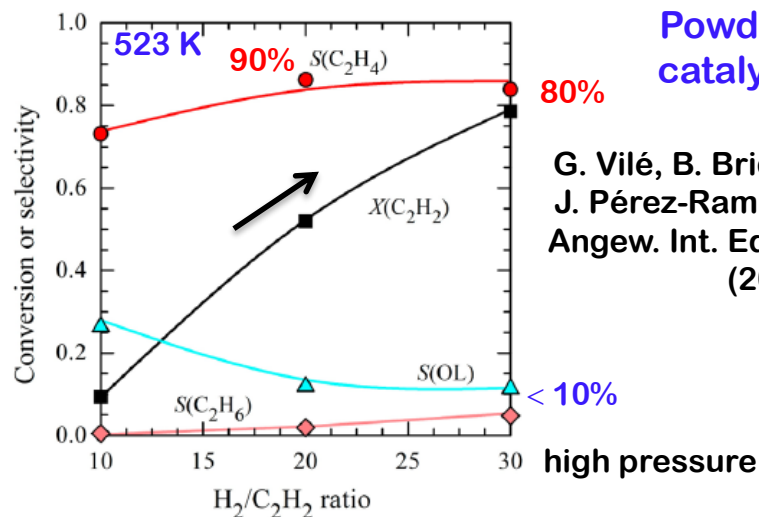
Ceria as stand-alone catalyst

□ **Partial alkyne hydrogenation**: crucial step for purification of olefin streams

□ **Conventional catalysts: Pd-based**



H₂ dissociation
crucial and rate-limiting

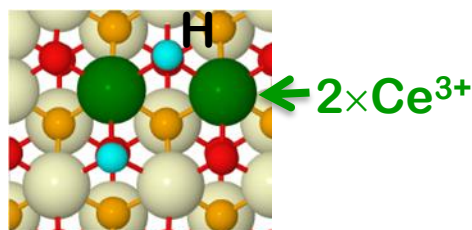


H₂ activation on CeO₂(111)

1 eV ~96 kJ/mol ~23 kcal/mol

Fernández-Torre, Carrasco, Ganduglia-Pirovano, Pérez, J. Chem. Phys. 141 (2014)

□ **H₂(gas) + CeO₂(111) → 2H /CeO₂(111)** $\Delta E = 2.4$ eV highly exothermic PBE+U(4.5)



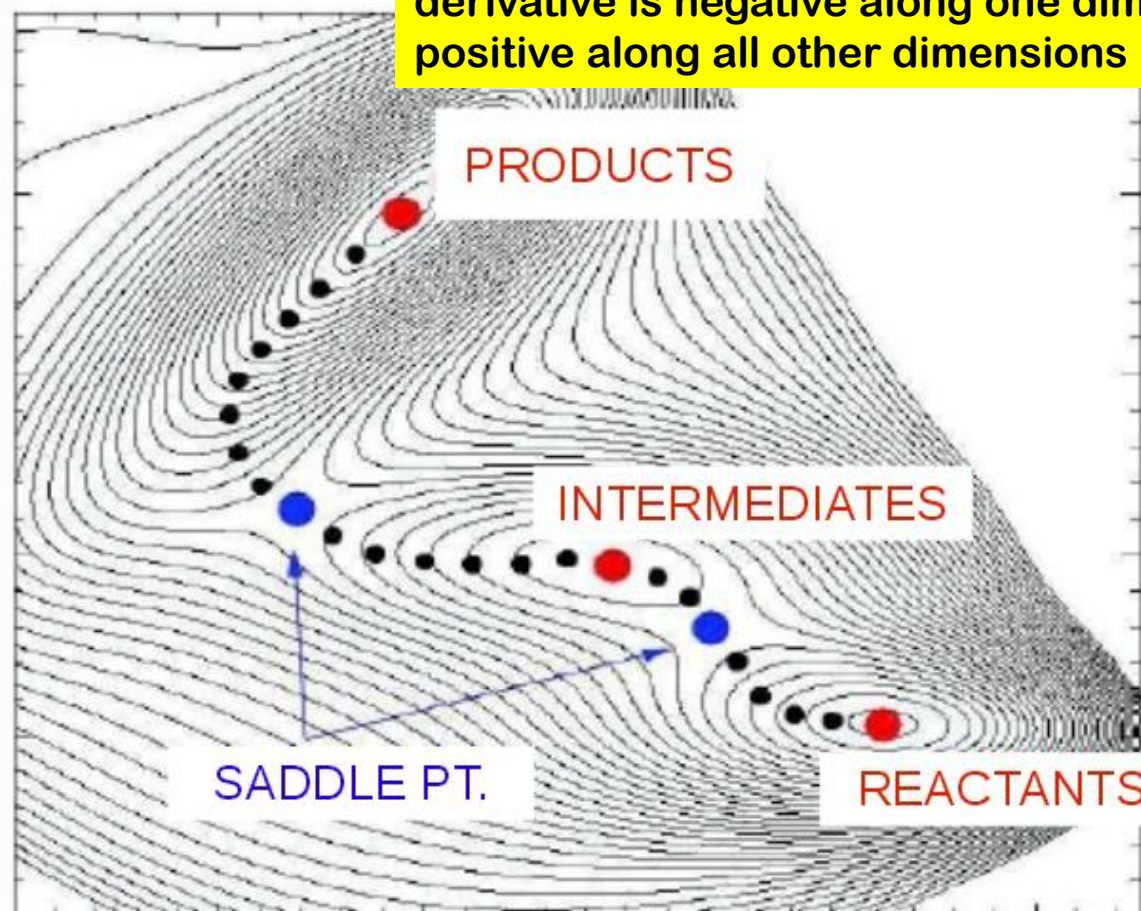
(4×4) unit cell

□ **Previous work**: too low H₂ dissociation barrier ~0.2 eV !! [(√3×1) cell, PW91+U(6.3)]

H-T Chen et al., ChemPhysChem 8, 849 (2007)

Finding a saddle point

Transition state: first derivative is zero, and second derivative is negative along one dimension and positive along all other dimensions



Minimum Energy Path (MEP): Path with highest transition probability
Components of force orthogonal to the path
is zero

$$\nabla E(\mathbf{R}_i)|_{\text{perp}} = -(\nabla E(\mathbf{R}_i) - \nabla E(\mathbf{R}_i) \cdot \boldsymbol{\tau}_i) = 0$$

The Nudged Elastic Band method

Mills, Jónsson, Schenter,
Surf. Sci. **324**, 305 (95)

□ Initial & Final configurations known

□ Distribute images (replicas) of the system connected with springs along some path between initial and final state (e.g., linear interpolation).

$R_0 \rightarrow R_1 \dots R_{P-1} \rightarrow R_P$ replicas

$$\vec{F}_i^s \equiv k_{i+1} (\vec{R}_{i+1} - \vec{R}_i) - k_i (\vec{R}_i - \vec{R}_{i-1})$$

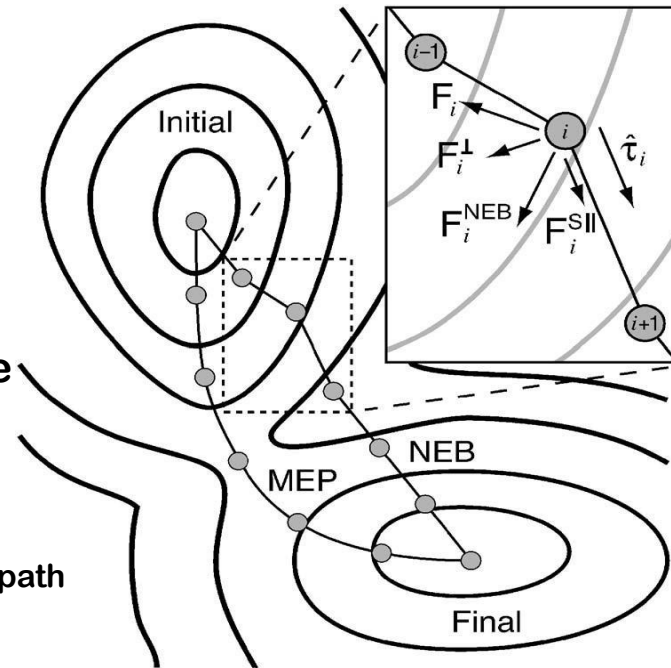
$$\vec{F}_i = -\vec{\nabla}V(\vec{R}_i) + \vec{F}_i^s$$

„Nudging“ = Force projection $\perp$ component of spring force
 $\parallel$ component of true force

$$\vec{F}_i^{nudged} = -\vec{\nabla}V(\vec{R}_i)|_{\perp} + \vec{F}_i^s \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel}$$

unit tangent along path

$$\vec{\nabla}V(\vec{R}_i)|_{\perp} = \vec{\nabla}V(\vec{R}_i) - \vec{\nabla}V(\vec{R}_i) \cdot \hat{\tau}_{\parallel} \hat{\tau}_{\parallel}$$



✓ Spring force does not interfere with the relaxation $\perp$ to the path; they distribute images along path

✓ True force does not interfere with image spacing $\parallel$ to the path; they bring the band to the MEP

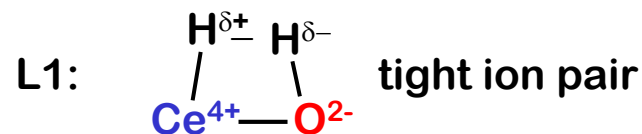
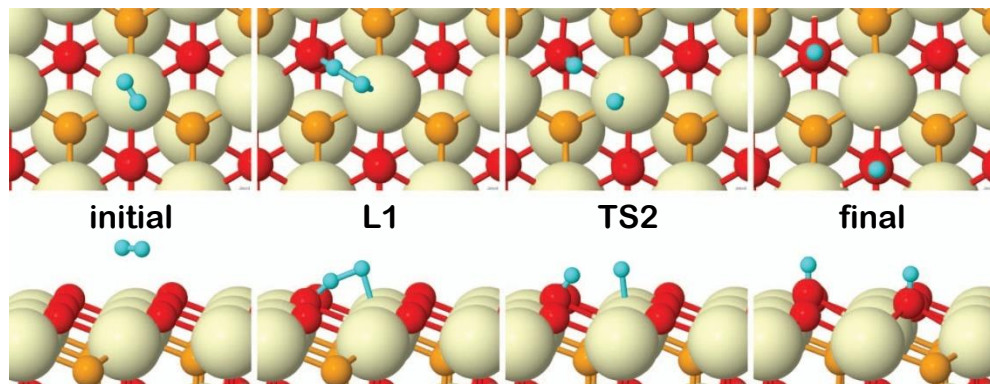
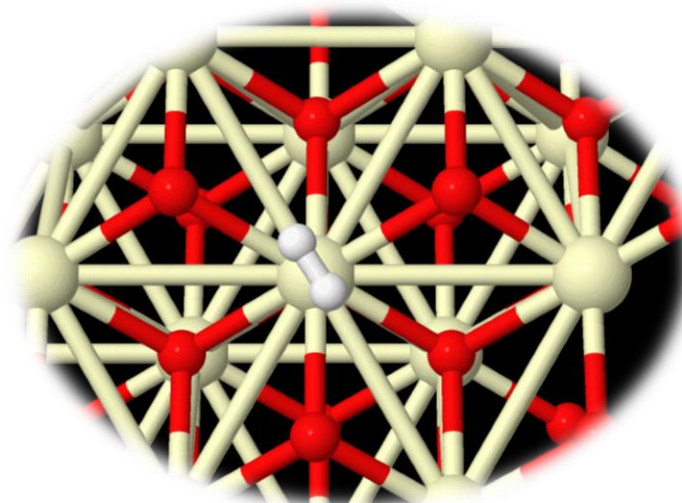
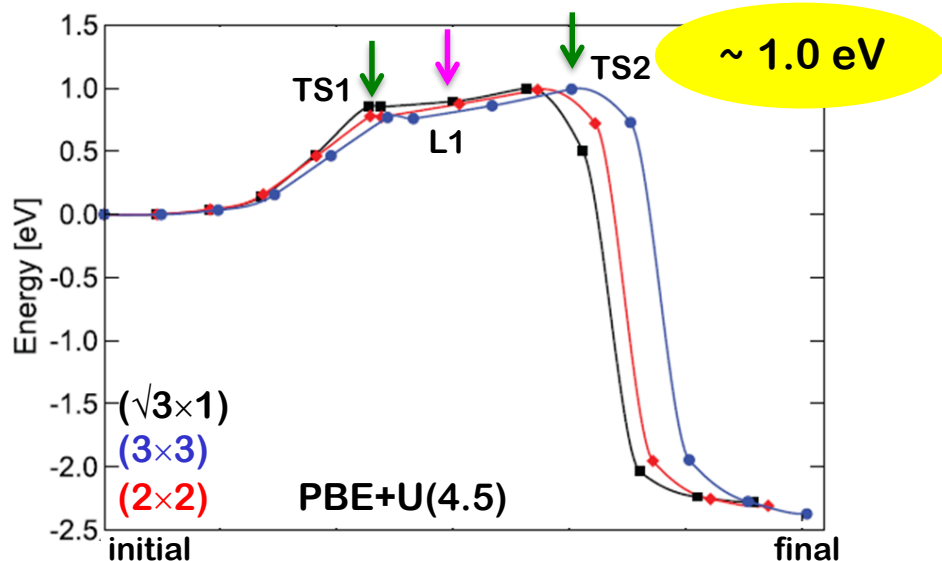
$$\vec{\nabla}V(\vec{R}_i)|_{\perp} = 0$$

H₂ on CeO₂(111): dissociation mechanism

Fernández-Torre, Carrasco, Ganduglia-Pirovano, Pérez,
J. Chem. Phys. 141, 014703 (2014)

☐ Nudged Elastic Band Method (NEB)

2×5 images

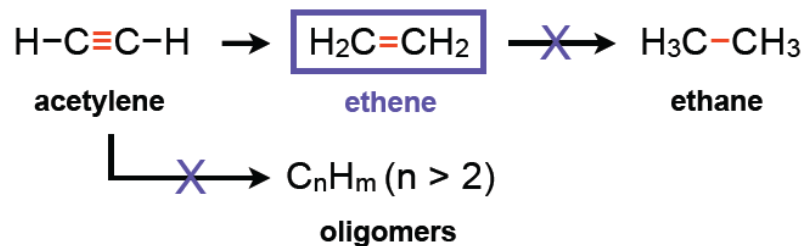


TS2: Ce–H and O–H bonds

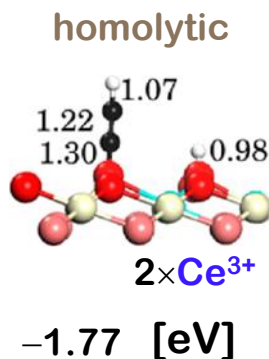
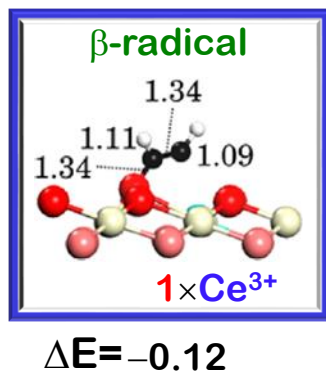
Final: 2× O–H bonds

In agreement with: García-Melchor, López,
J. Phys. Chem. C118, 10921 (2014)

Ceria as stand-alone catalyst

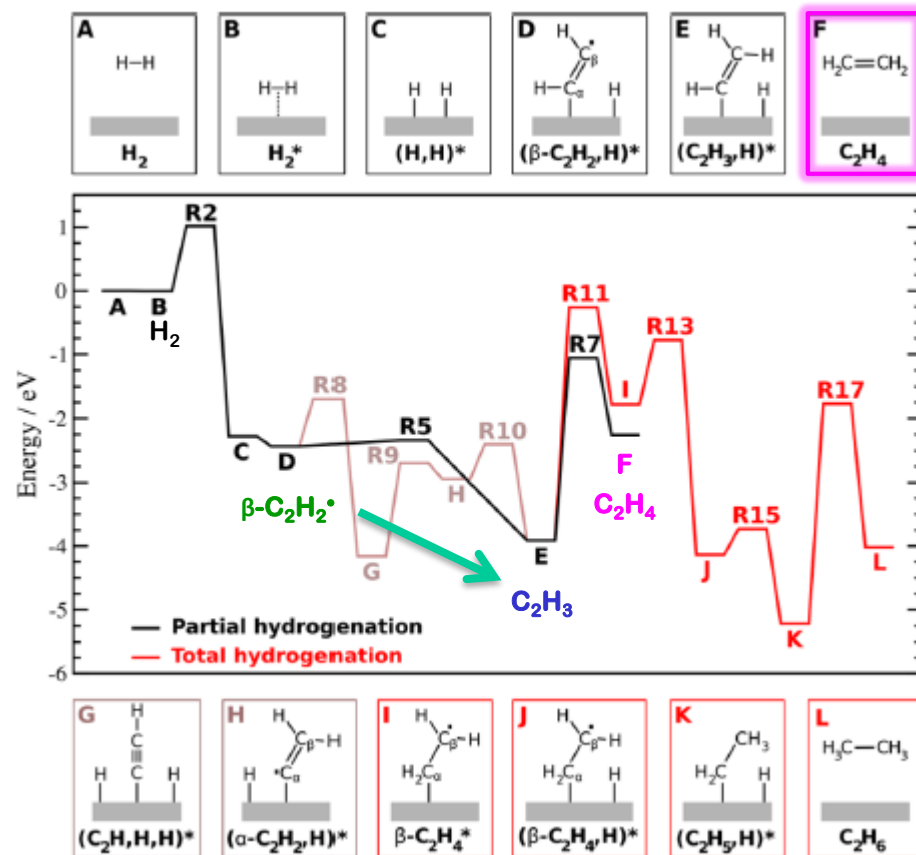


C_2H_2 activation on $\text{CeO}_2(111)$



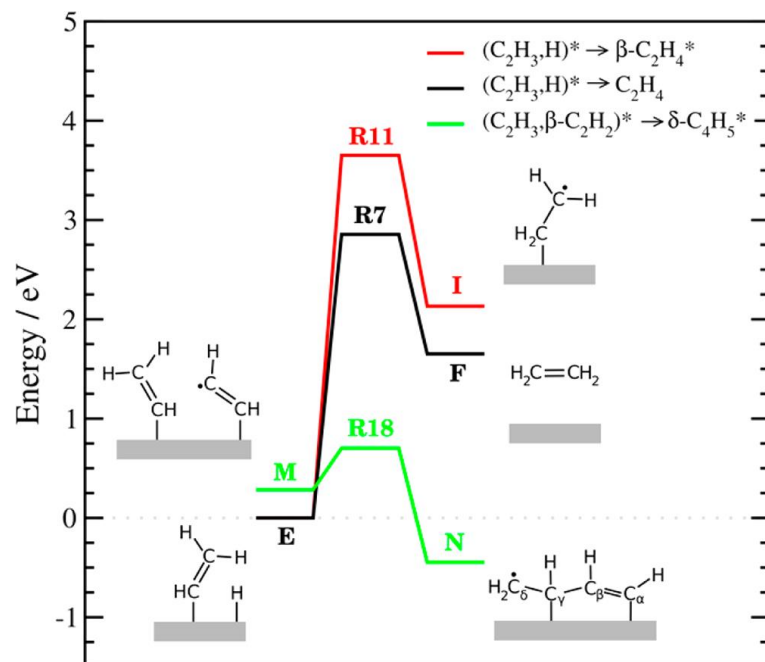
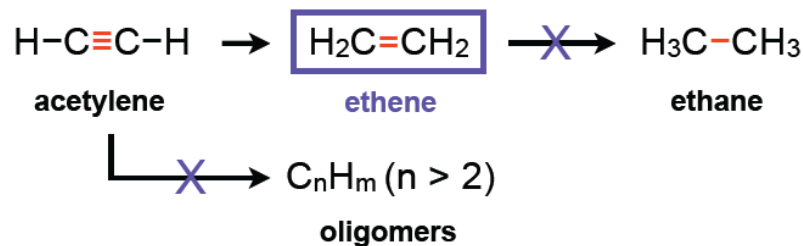
Ceria ability to stabilize reduced states: a key property

NEB Method

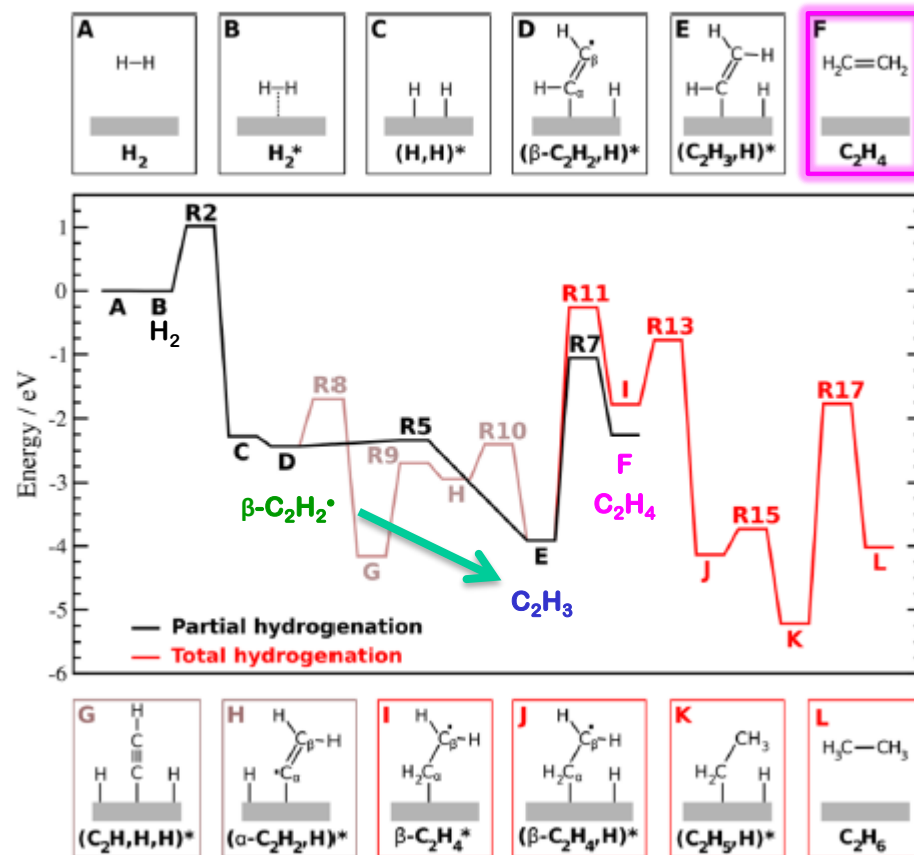


- H_2 dissociation $\rightarrow$ limiting step
- Highly reactive $\beta\text{-C}_2\text{H}_2^*$ radical species form $\text{C}_2\text{H}_3 \rightarrow$ “barrierless”
- Oligomer formation only at low $\text{H}_2/\text{C}_2\text{H}_2$ ratios; neighboring O sites not available at high ratios

Ceria as stand-alone catalyst



NEB Method



- H₂ dissociation → limiting step
- Highly reactive β-C₂H₂* radical species form C₂H₃ → “barrierless”
- Oligomer formation only at low H₂/C₂H₂ ratios; neighboring O sites not available at high ratios

Ceria as stand-alone catalyst



Molecular-Level Understanding of CeO_2 as a Catalyst for Partial Alkyne Hydrogenation

Javier Carrasco,^{*,†,‡} Gianvito Vilé,[§] Delia Fernández-Torre,^{||,⊥} Rubén Pérez,^{||,#} Javier Pérez-Ramírez,^{*,§} and M. Verónica Ganduglia-Pirovano[†]

J. Phys. Chem. C 118, 5352 (2014)

Ceria and its non-innocent role as support

□ Stand-alone catalyst

$\text{CeO}_2(111) \rightarrow$ Partial alkyne hydrogenation

Reactivity of ceria surfaces: $\text{H}_2 \rightarrow \text{H} + \text{H}$ dissociation

$\text{C}_2\text{H}_2 + n \text{H} \rightarrow \text{C}_2\text{H}_{2+n}$ ethylene hydrogenation

Collaboration: J. Pérez-Ramírez
ETH, Zurich

□ Support

$\text{V}_m\text{O}_n/\text{CeO}_2(111) \rightarrow$ ODH reactions

Structure and reactivity of supported vanadia

Collaboration: J. Sauer (HU-Berlin);
H.J. Freund (FHI-Berlin)

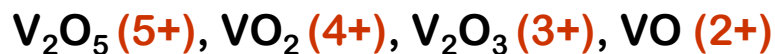
$\text{Ni}_n/\text{CeO}_2(111) \rightarrow$ H_2 production

Structure and reactivity of supported nickel

Collaboration: J. A. Rodríguez
BNL, USA

Oxide supported vanadia –VO_x– catalysts

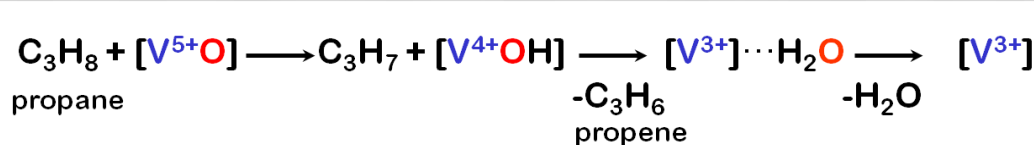
- VO_x large variety of oxidation states



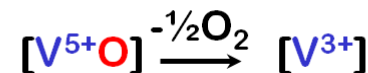
- Important catalysts in oxidation reactions

- SO₂ to SO₃ 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**



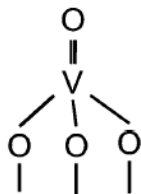
Reactivity Parameter



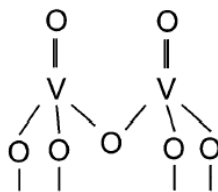
Oxygen defect formation

- The specific **support** affects the structure and catalytic performance

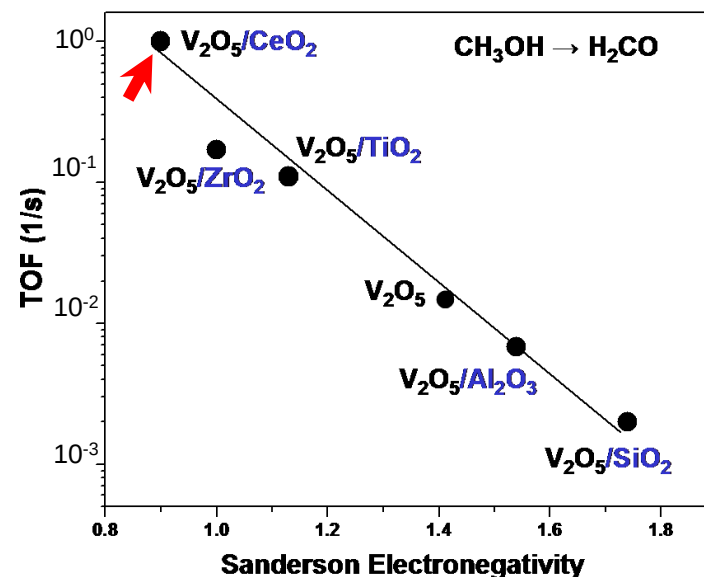
How does vanadia 'sit' on the support?



monomeric

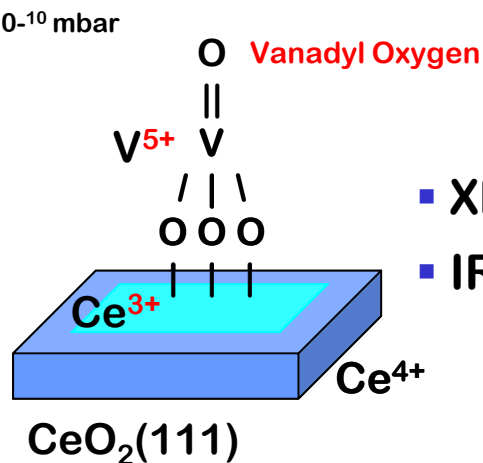


dimeric, polymeric

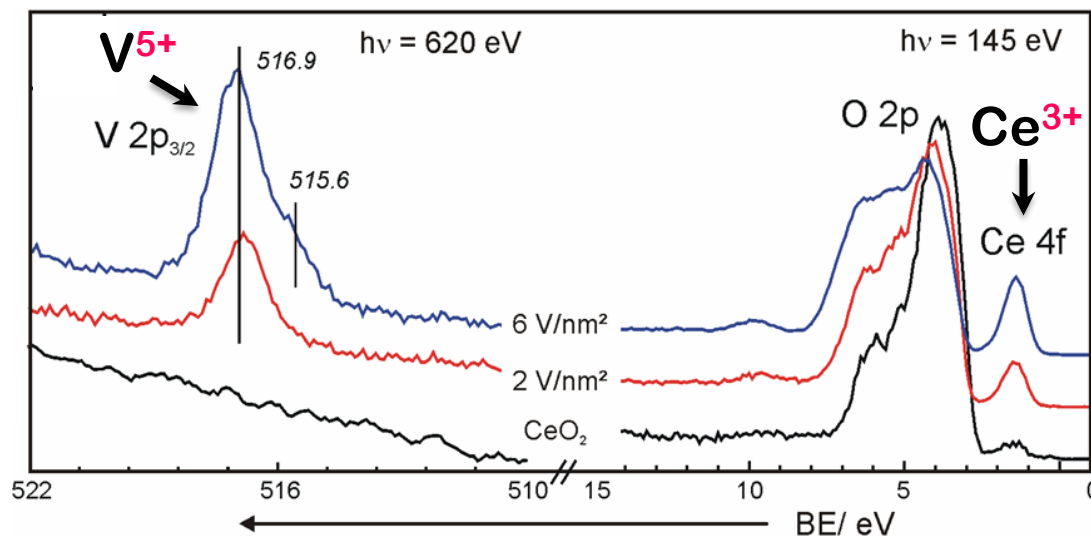


VO_x/ceria : The experimental facts

Experimental model



- XPS: Ce^{3+} and V^{5+}
- IR: $\text{V}=\text{O}$ stretch ($1000\text{--}1040\text{ cm}^{-1}$)



M. Baron, H. Abbott, O. Bondarchuk, D. Stacchiola, A. Uhl, S. Shaikhutdinov, H.-J. Freund, C. Popa, M. V. Ganduglia-Pirovano, J. Sauer, *Angew. Chem. Int. Ed.* 48, 8006 (2009)

Powder samples:

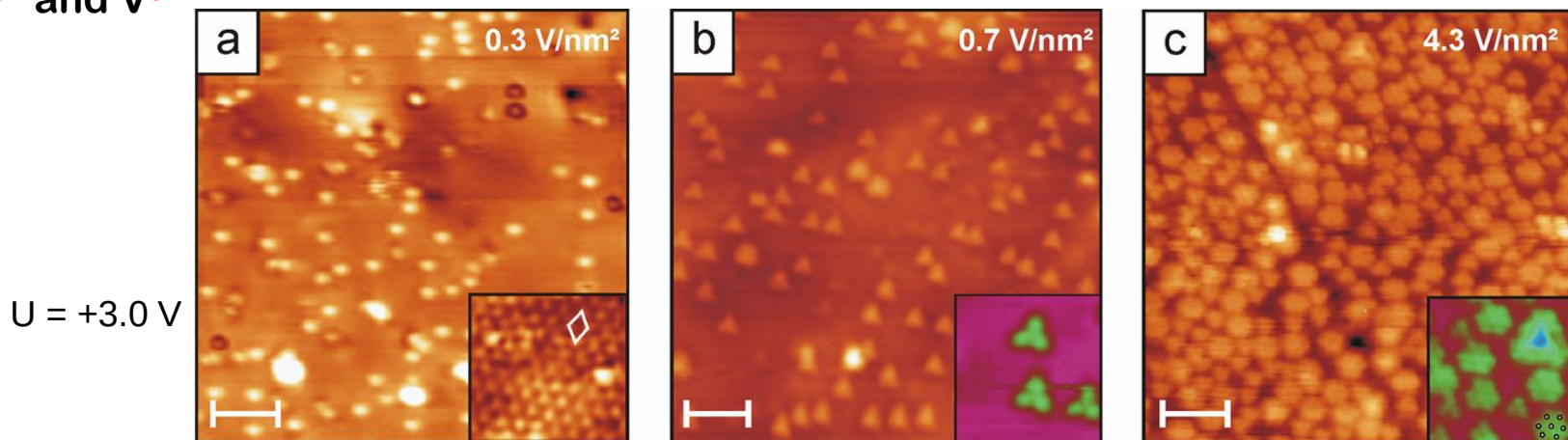
Martinez-Huerta, Deo, J L Fierro, Bañares, *JPC C* 112, 11441 (2008)

$\text{VO}_x/\text{CeO}_2(111)$: The experimental facts

- STM: **Monomers, Dimers, Trimers**

- XPS: Ce^{3+} and V^{5+}

Baron, Abbott, Bondarchuk, Stacchiola, Uhl, Shaikhutdinov, Freund, Popa, Ganduglia-Pirovano, Sauer, Angew. Chem. Int. Ed. 48, 8006 (2009)

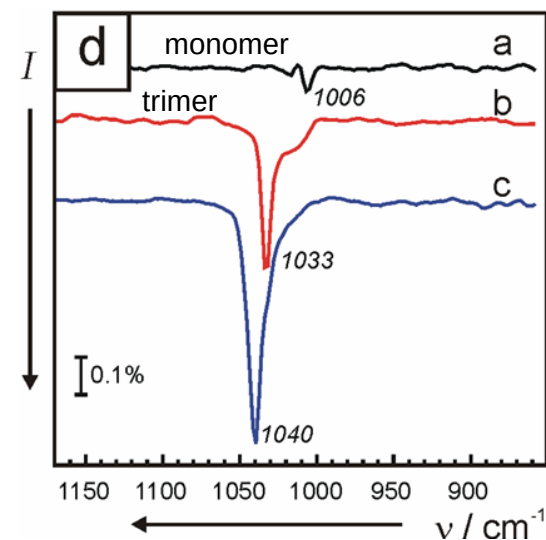


Monomers, dimers, trimers: **similar apparent height** → „**flat**“ **structures**

Trimer: **spot-spot distance** ~ CeO_2 lattice (3.9 Å)

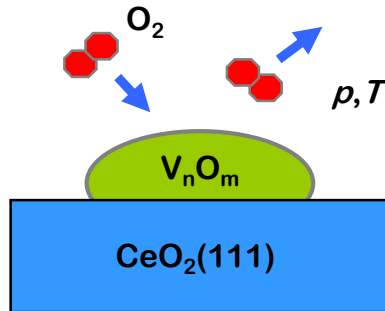
- IR: **V=O** stretch
monomer → polymeric

blue shift ~25cm⁻¹



Theoretical Models: The strategy

V_nO_m on $CeO_2(111)$

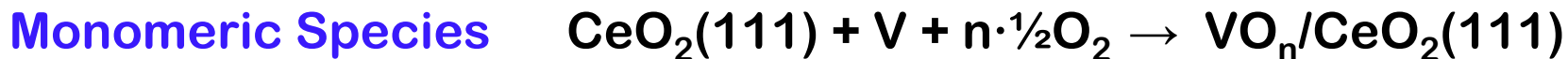


- ☐ Surface functional groups?
- ☐ Support effect ?
- ☐ Reactivity

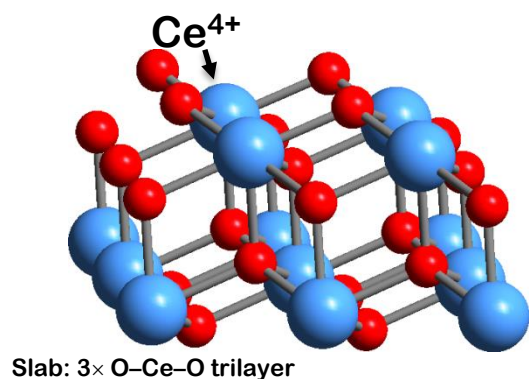
DFT+U & statistical thermodynamics $\rightarrow$ Structure

- Thermodynamic stability $\rightarrow$ surface free energy $\gamma [\mu_i(T, p_i)]$
- Electronic structure
- Vibrations (IR); diagonalization of Mass-Weighted Hessian Matrix
- Reactivity

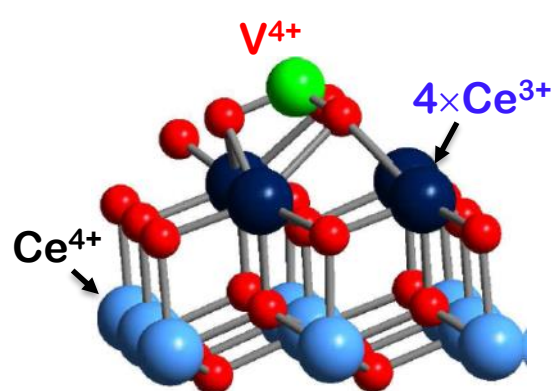
Theoretical models: $\text{VO}_x/\text{CeO}_2(111)$



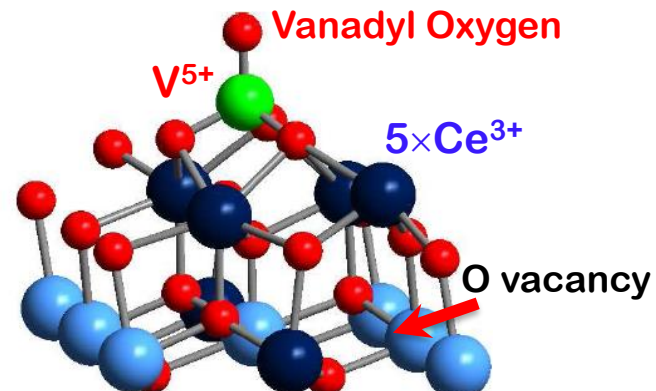
$\text{CeO}_2(111)$



$\text{V}/\text{CeO}_2(111)$

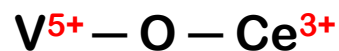


+1.48 eV



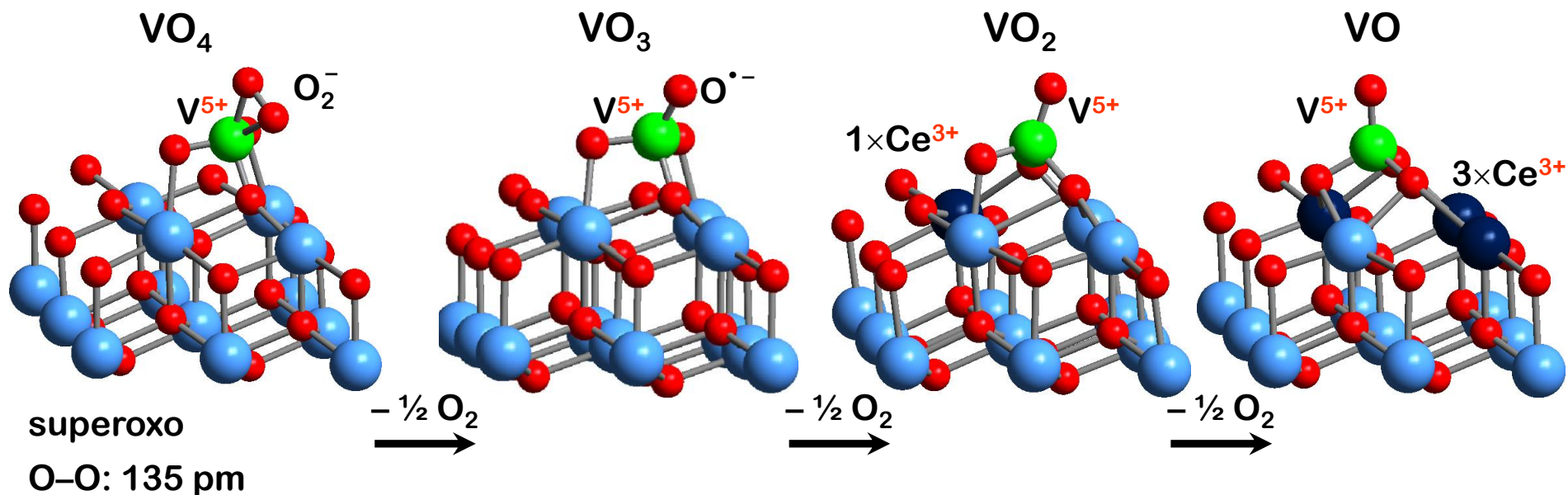
**Most stable
structure**

consistency with experiment



Theoretical models

Monomeric Species



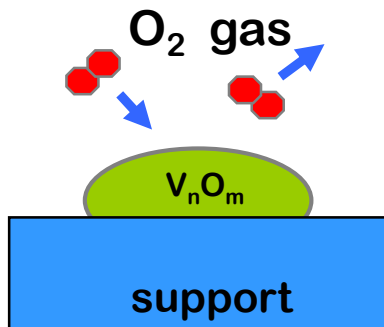
Vanadia species are **NOT** reduced!

Stability $\text{VO}_n/\text{CeO}_2(111)$



$$\Delta\gamma(T,p) = [G^{\text{V}_m\text{O}_n/\text{CeO}_2} - G^{\text{CeO}_2} - \mu_{\text{V}} - n \cdot \frac{1}{2} \mu_{\text{O}_2}(T,p)] / A$$

$$\Delta\gamma(T,p) \approx [E^{\text{V}_m\text{O}_n/\text{CeO}_2} - E^{\text{CeO}_2} - E^{\text{Vbulk}} - n \cdot \frac{1}{2} \mu_{\text{O}_2}(T,p)] / A$$

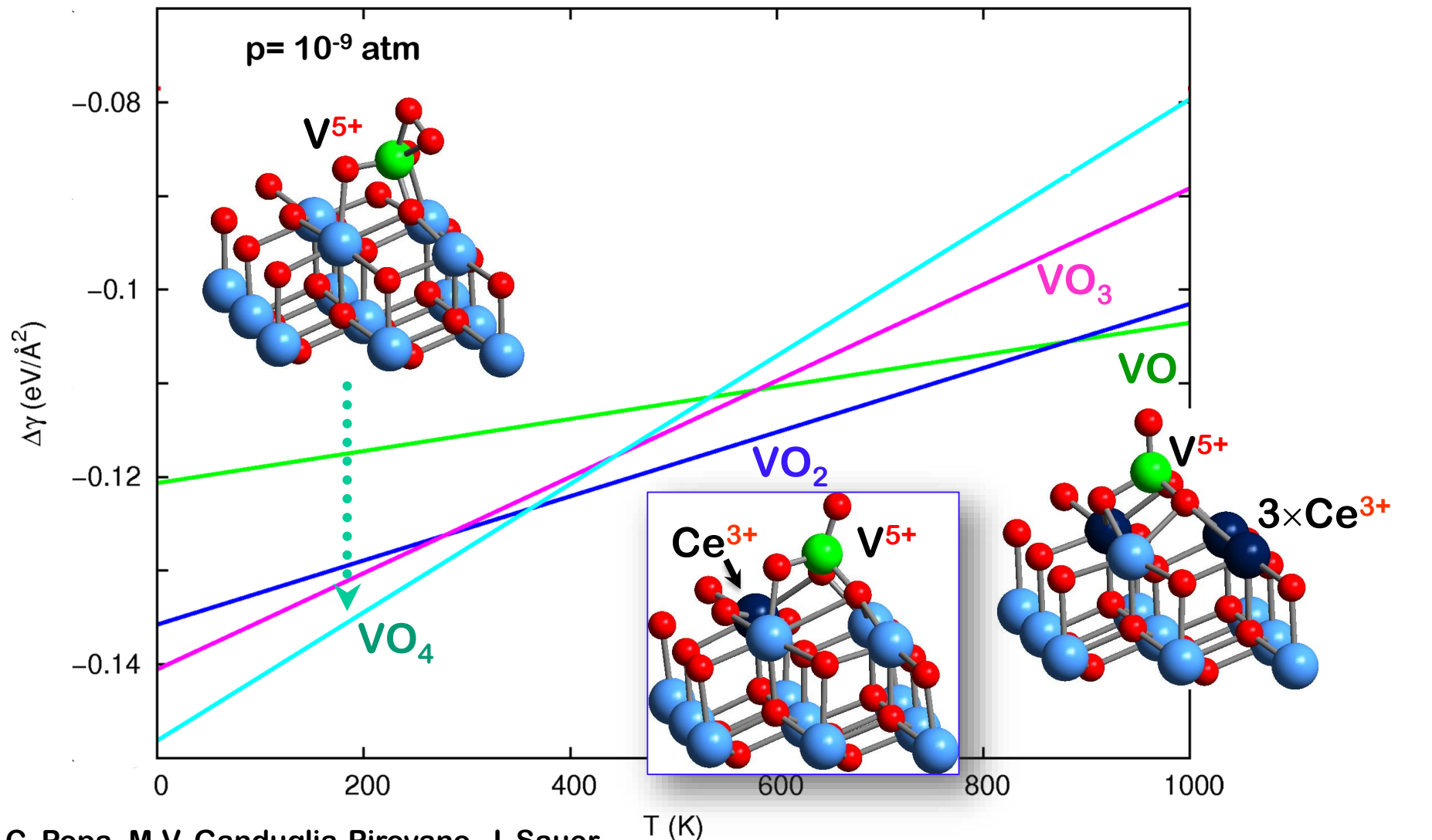


Oxygen chemical potential

$$\mu_{\text{O}_2}(T,p) = \mu_{\text{O}_2}(T,p^\circ) + RT \ln(p/p^\circ)$$

VO_n /ceria monomers: Phase diagram

Monomeric Species

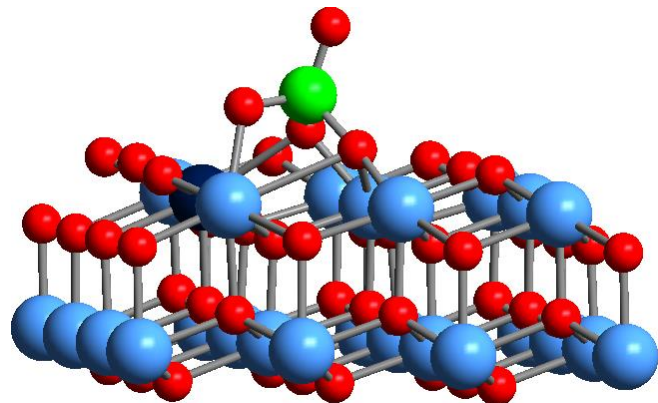


C. Popa, M.V. Ganduglia-Pirovano, J. Sauer,
J. Phys. Chem. C 115, 7399 (2011)

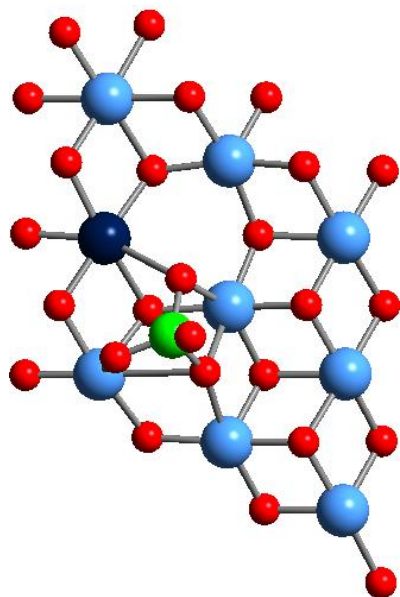
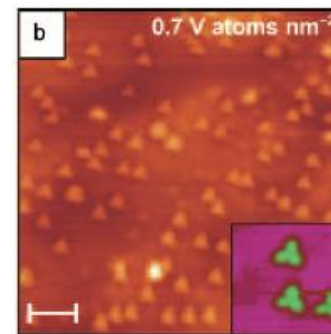
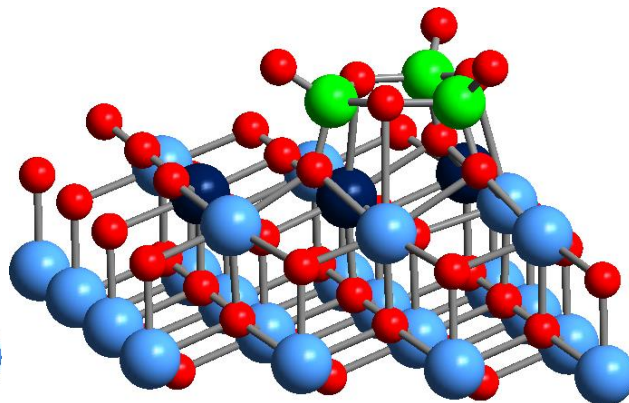
PBE+U, $U=4.5$ eV (2×2) u.cell

IR spectra and the nature of the supported species

monomer VO_2

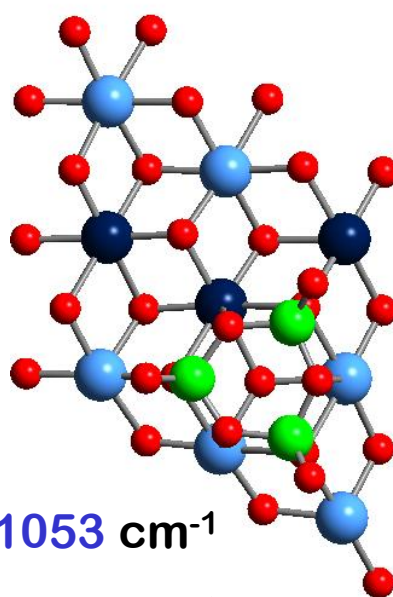


trimer 3VO_2



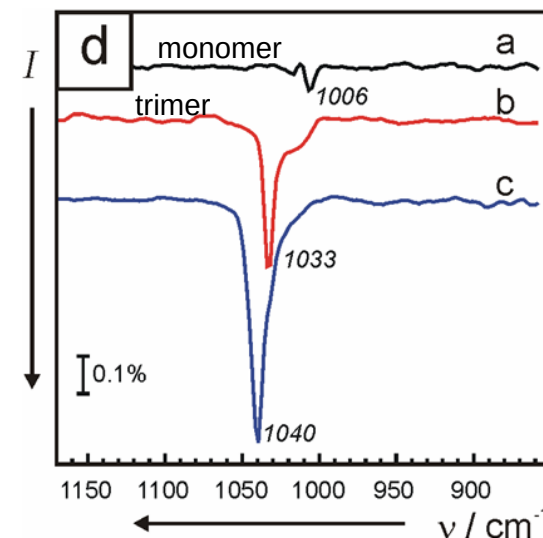
1036 cm^{-1}

blue shift $\sim 30 \text{ cm}^{-1}$



$2 \times 1053 \text{ cm}^{-1}$

1070 cm^{-1}



blue shift $\sim 25 \text{ cm}^{-1}$

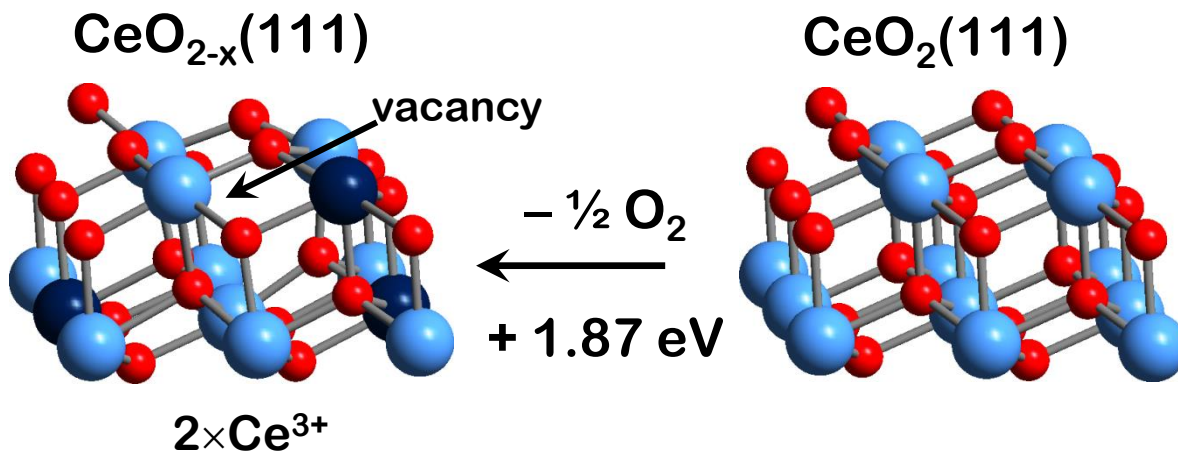
Morphology $\leftrightarrow$ Vibrations

Reactivity: The origin of the support effect

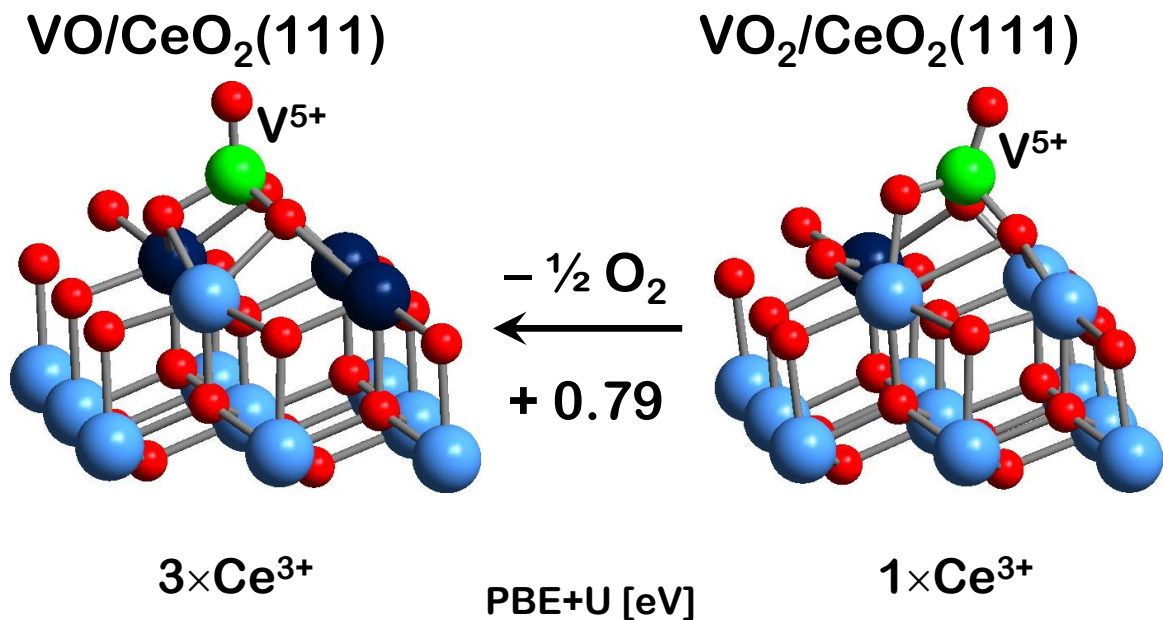
Angew. Chem. Int. Ed. 48, 8006 (2009)

JACS 132, 2345 (2010)

J. Phys. Chem. C 115, 7399 (2011)

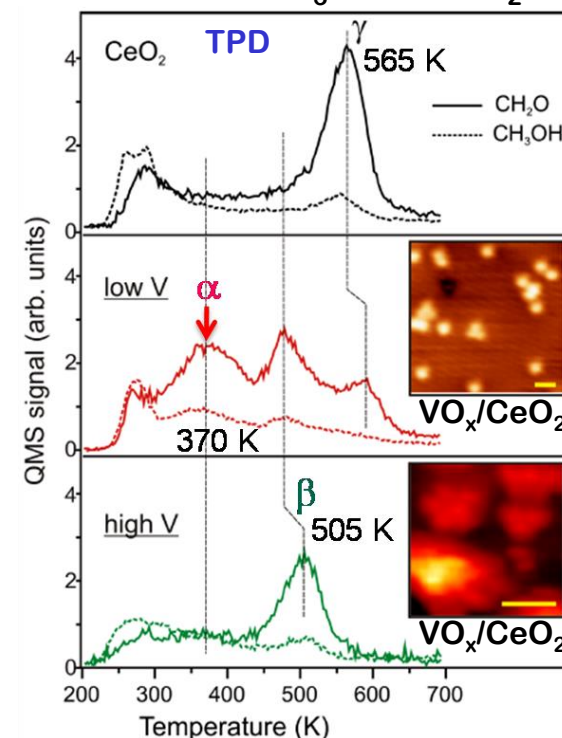


Reactivity Parameter



Reactivity

CH₃OH → CH₂O



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

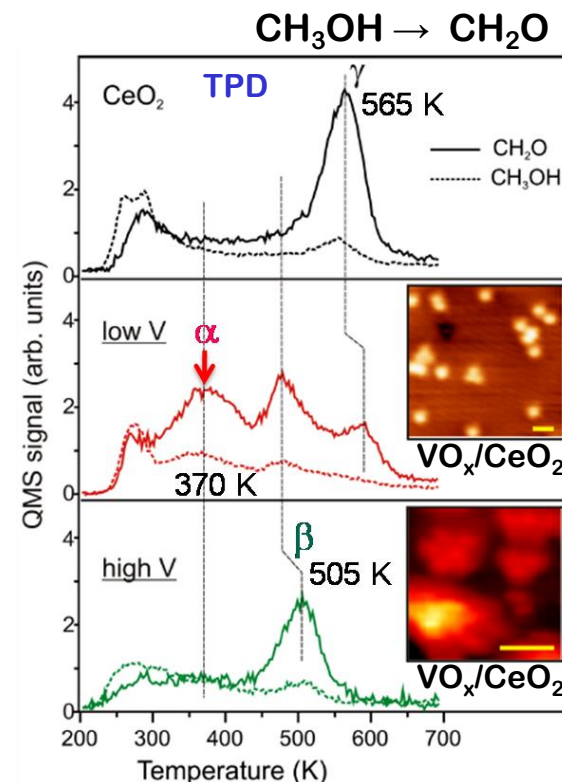
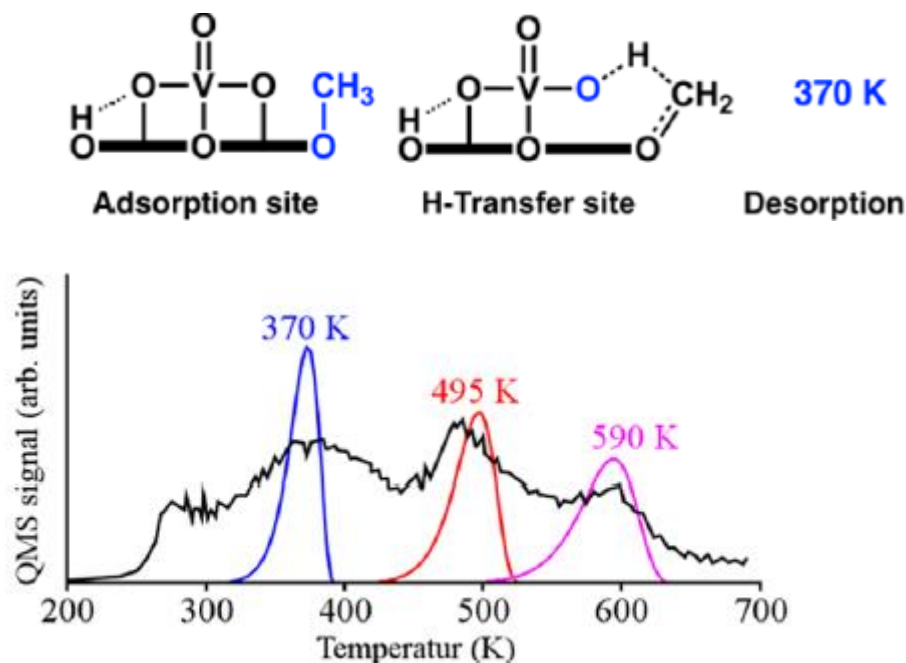
Reactivity: The origin of the support effect

Angew. Chem. Int. Ed. 48, 8006 (2009)

JACS 132, 2345 (2010)

J. Phys. Chem. C 115, 7399 (2011)

Reactivity



T. Kropp, J. Paier, J. Sauer, J. Am. Chem. Soc. 136 (2014) 14616–14625

TPD

$$-\frac{dx}{dt} = \frac{k_B T}{h} \cdot \frac{q^\ddagger}{q} \cdot \exp\left(-\frac{\Delta E_0^\ddagger}{k_B T}\right) \cdot x$$

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

Ceria and its non-innocent role as support

□ Stand-alone catalyst

$\text{CeO}_2(111) \rightarrow$ Partial alkyne hydrogenation

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Collaboration: J. Pérez-Ramírez
ETH, Zurich

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Collaboration: J. Sauer (HU-Berlin);
H.J. Freund (FHI-Berlin)

$\text{Ni}_n/\text{CeO}_2(111) \rightarrow$ H_2 production and CH_4 dryreforming

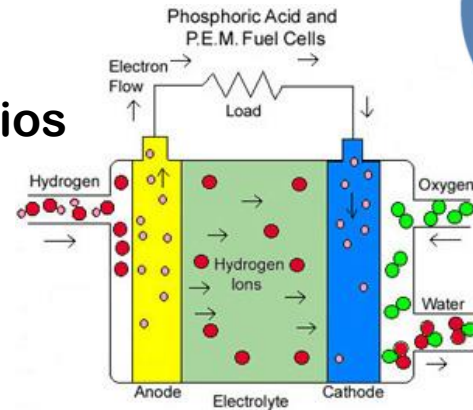
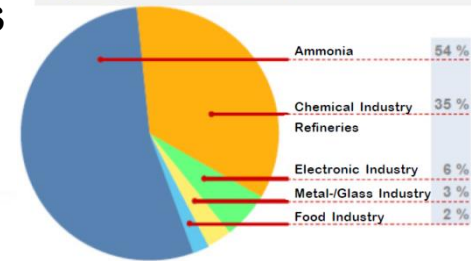
Structure and reactivity of supported nickel

Collaboration: J. A. Rodríguez
BNL, USA

Motivation: H₂ production

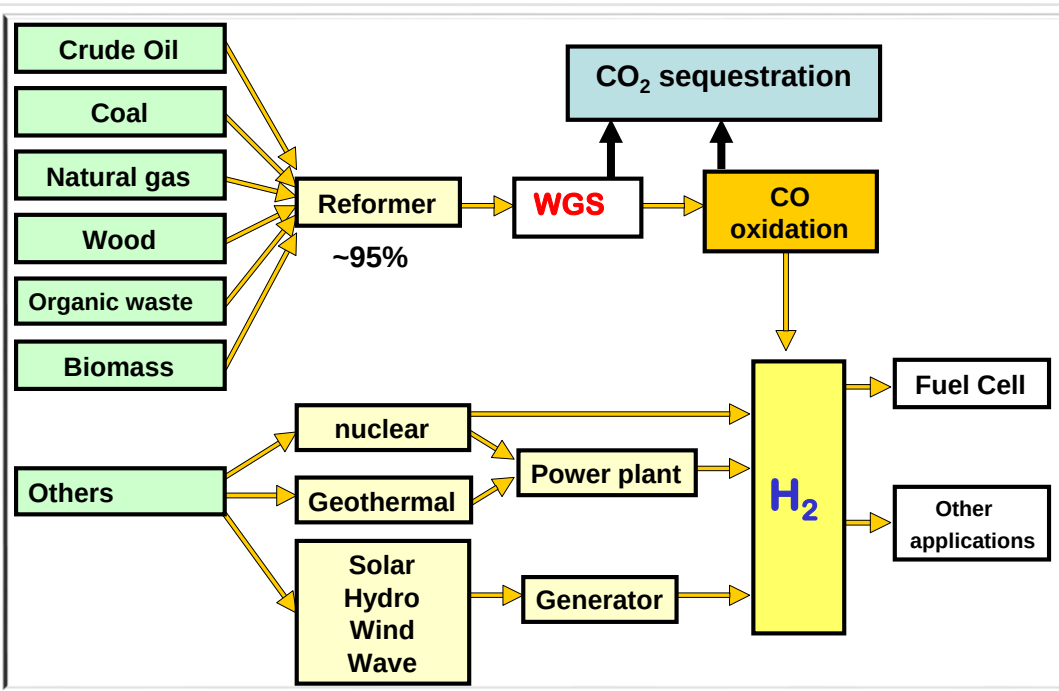
- ❑ Hydrogen is key in the production of chemicals and foods
- ❑ Hydrogen is expected to play an important role in future energy scenarios

Hydrogen Consumers:



Fuel cells
mobile and stationary
applications

H₂ production

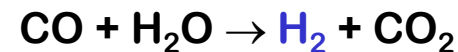


- Steam reforming of hydrocarbons:



- Fuel contains **1-10% CO**
→ Pt electrode degradation

- **Water-gas shift:**



to remove the CO

Ceria supported Ni catalysts for H₂ production

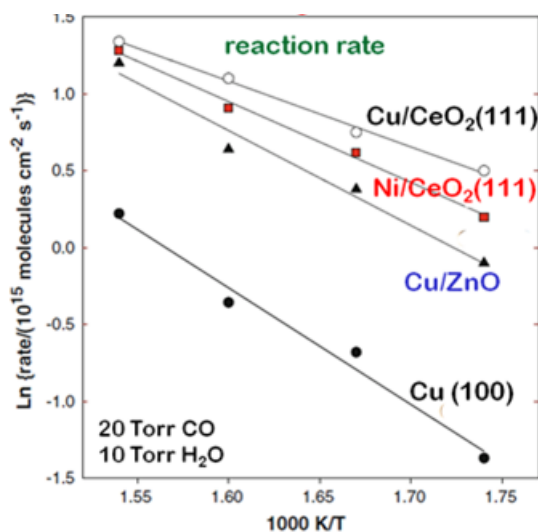
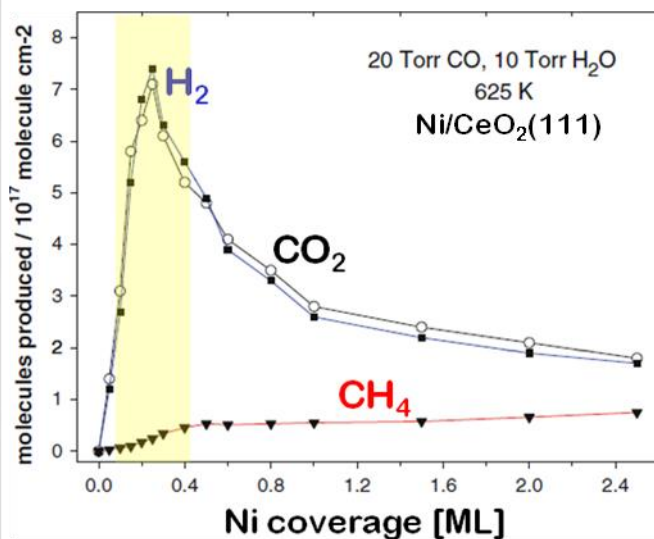
Water-gas shift $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$

- conventional catalyst: mixed Fe and Cr or Cu and Zn oxides → drawback: long preconditioning
- new catalysts: precious metal–Pt, Au–particles supported by reducible oxides–TiO₂, CeO₂



Fu et al., Science 301 (2003)

Ni/CeO₂: The alternative



low Ni loading is better!

Ni/CeO₂(111)

STM → adatoms
small 2D or 3D
particles

Ni 2p_{3/2} XPS → Ni²⁺



Support Effect

Understanding Ni/CeO₂ for WGS: The strategy



DFT Modeling
DFT(PBE)+U (4.5 eV)
VASP-code

Ni on CeO₂(111): dispersed Ni atoms
Ni₄ clusters

Geometric and Electronic Structures

Reactivity*:

H₂O
dissociation

Reactivity*:

CO and C
adsorption

*comparison
CeO₂(111) and Ni(111)

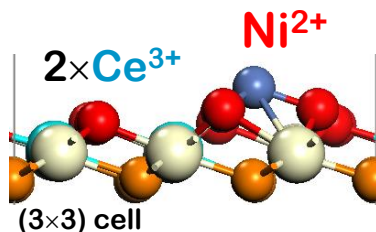
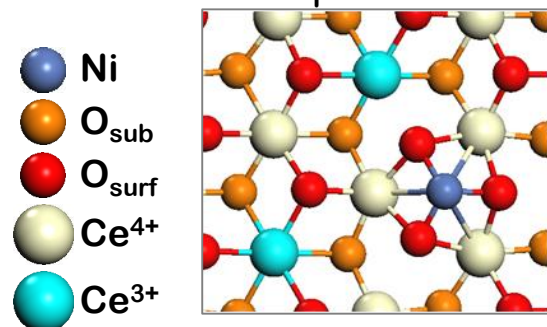


Ambient-Pressure X-ray Photoelectron Spectroscopy

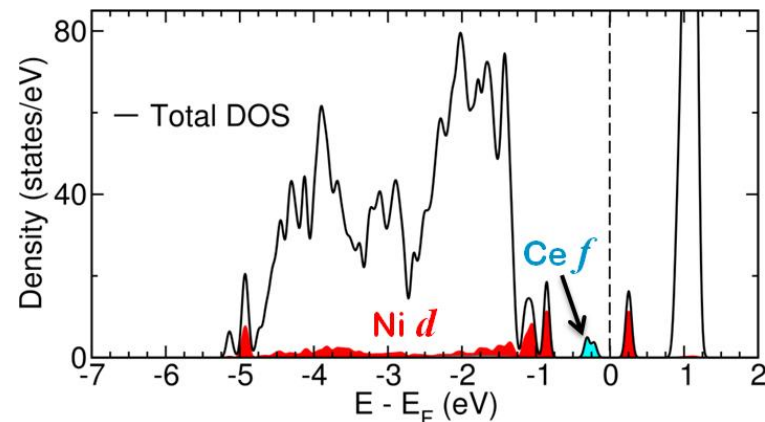
Ni/CeO₂(111) model catalyst: metal-support interaction

Carrasco et al., JPCC 117 (2013)

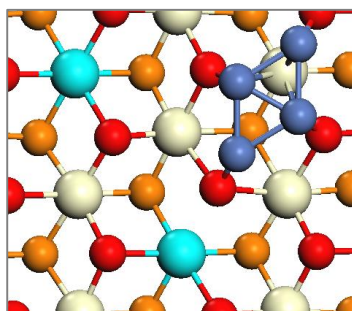
Ni₁ adatom



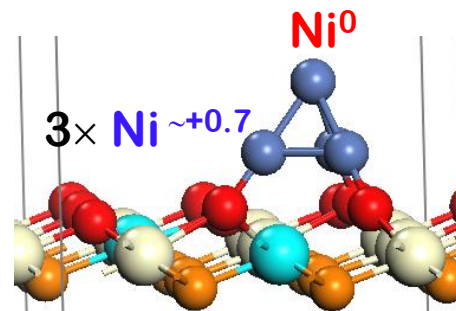
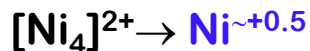
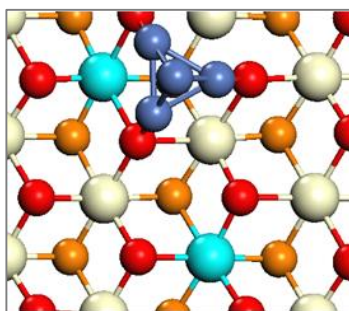
2× 4s e⁻ transferred



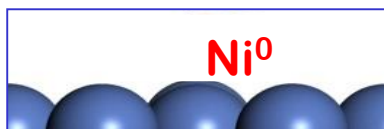
Ni₄ planar



Ni₄ pyramidal



Ni(111)



rapid weakening in the strength of the metal–oxide interactions

H₂O/ceria: Theoretical facts

D. Fernández-Torre, K. Kósmider, J. Carrasco, M.V. Ganduglia-Pirovano, R. Pérez, JPCC 112, 13584 (2012)

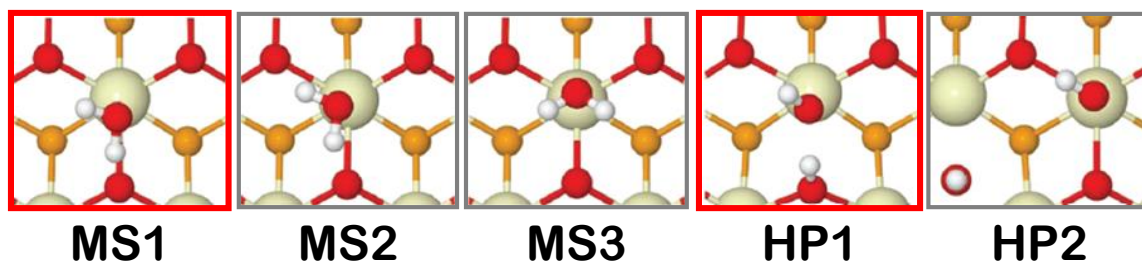
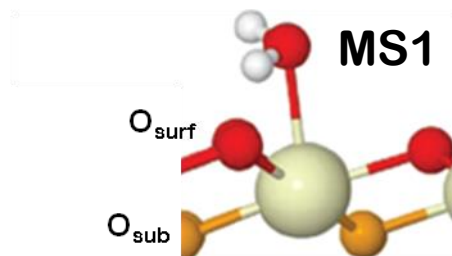
¹JCP 125, 204704 (2006)

⁴PCCP 11, 9188 (2009)

²ChemPhysChem 8, 849 (2007)

⁵JPCC 114, 14891 (2010)

³JPCC 111, 15337 (2007)



Theory:

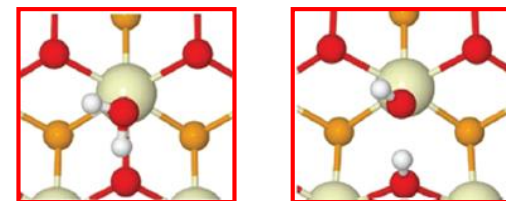
Reference	Method	Unit cell	MS1	MS2	MS3	HP1	HP2
Kumar and Scheling ¹	PW91	2x1	-0.58	-	-	-	-
Chen et al ²	PW91	√3x1	-0.49	-0.52	-	-	-
Watkins et al ³	PW91	2x√2	-	-	-0.35	-0.65	-0.15
Watkins et al ³	PW91+U(5 eV)	2x√2	-	-	-0.36	-0.66	-0.16
Fronzi et al ⁴	PBE	2x2	-	-0.49	-0.33	-0.36	-
Yang et al ⁵	PBE+U(5 eV)	2x2	-0.58	-	-	-0.55	-

Nature of the adsorption state: **molecular** or **hydroxyl pair**?

H₂O/ceria: DFT prediction

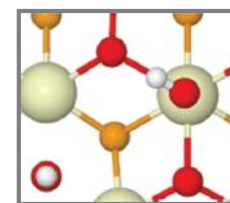
D. Fernández-Torre, K. Kósmider, J. Carrasco, M.V. Ganduglia-Pirovano, R. Pérez, JPCC 112, 13584 (2012)

Method	cell	MS1	HP1	HP2
PBE	(2×2)	-0.50	-0.45	-0.24
PBE+U	(2×2)	-0.54	-0.52	-0.24
PBE+U	(3×3)	-0.55	-0.60	-0.17
HSE06	(2×2)	-0.49	-0.47	-0.24
vdW-DF+U	(2×2)	-0.72	-0.70	—
vdW-DF+U	(3×3)	-0.73	-0.76	-0.32



MS1

HP1



HP2

vdW-DF:

$$E_{xc} = E_x^{GGA} + E_c^{LDA} + E_c^{nl}$$

OPT86b-vdW

Dion, Rydberg, Schroder, Langreth, Lundqvist, PRL 92, 246401 (2004)

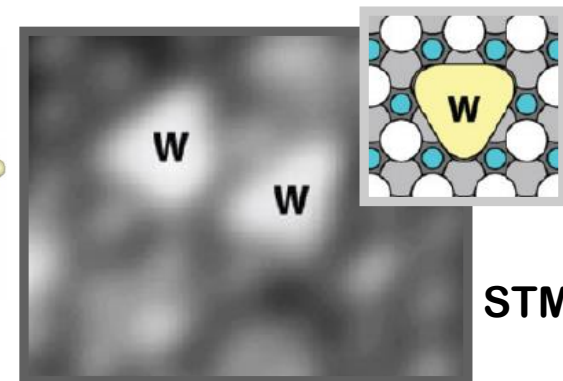
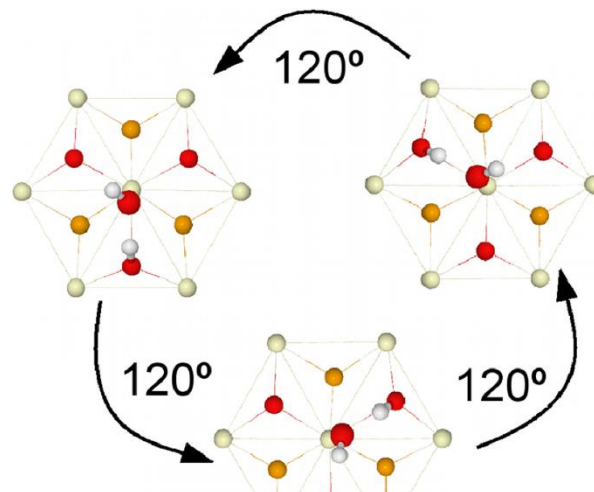
- Water dissociation → **NOT** favorable
- Molecular & hydroxyl pair → **close in energy**
- $E_{ad} \sim 0.7$ eV (exp ~ 0.9 eV)
- **vdW contribution to binding** ~ 0.18 eV

Consistency with triangular shape?

$\text{H}_2\text{O}/\text{ceria}$: DFT prediction

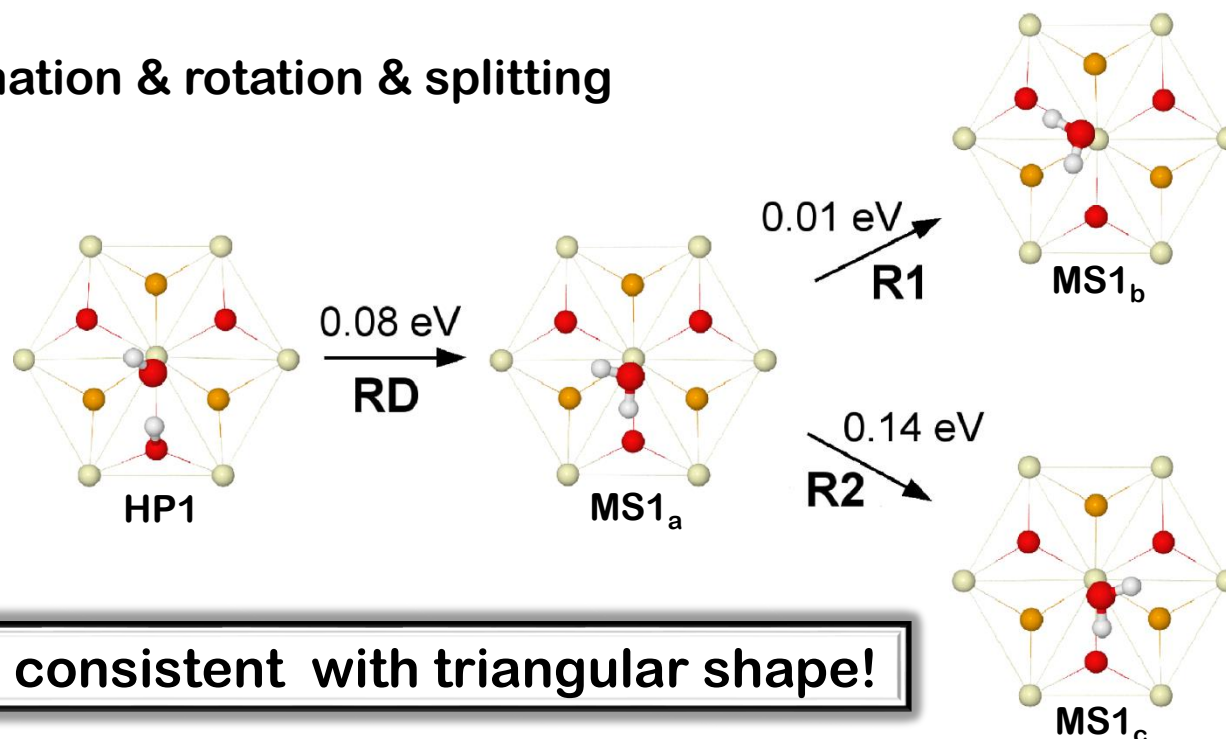
D. Fernández-Torre, K. Kósmider, J. Carrasco, M.V. Ganduglia-Pirovano, R. Pérez, JPCC 112, 13584 (2012)

- Hopping between equivalent HP1/MS1 structures $\rightarrow$ triangle



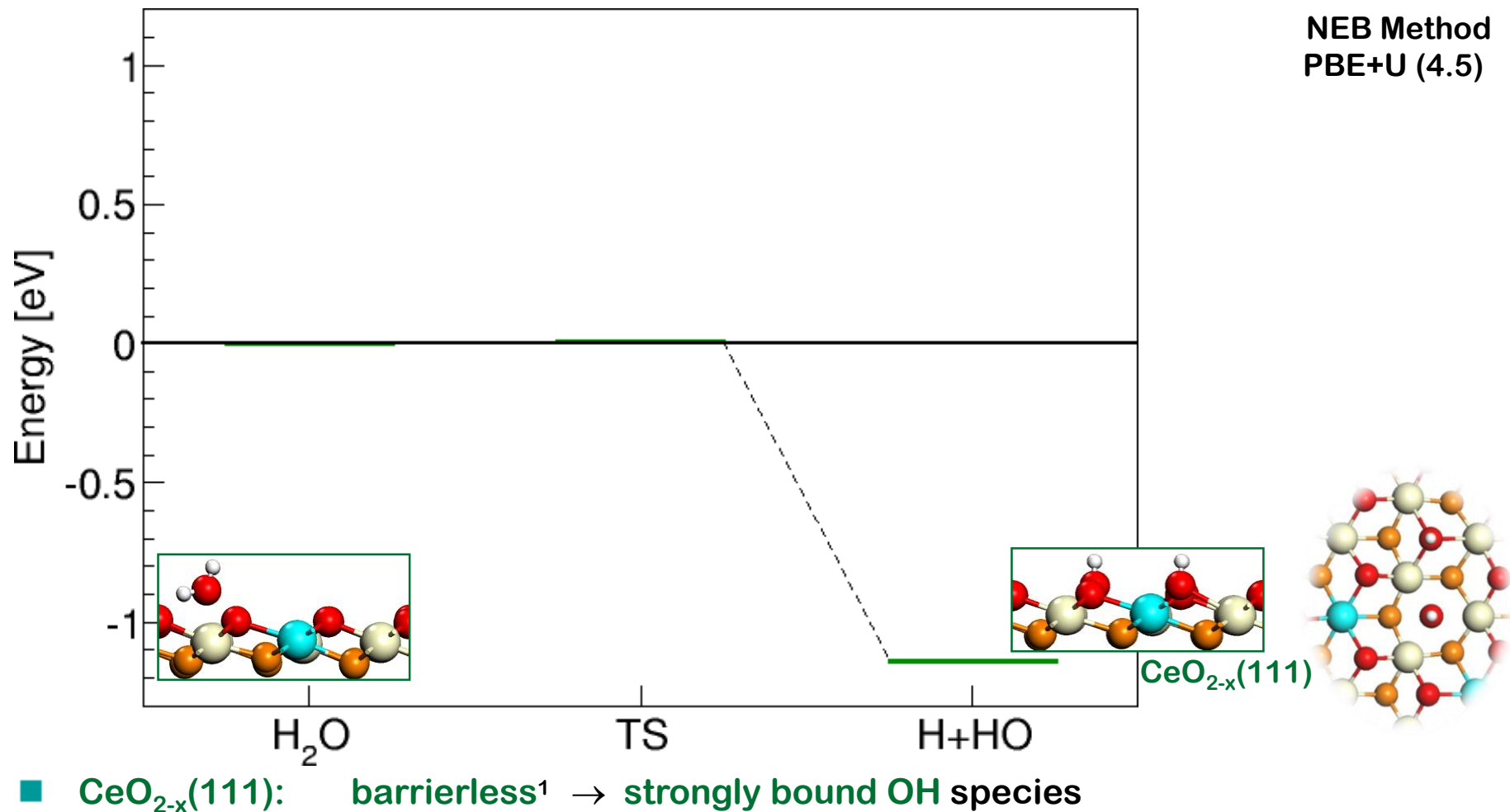
Grinter et al, JPCC 114, 17036 (2010)

- Hop via recombination & rotation & splitting with low barriers



MS1 and HP1 are consistent with triangular shape!

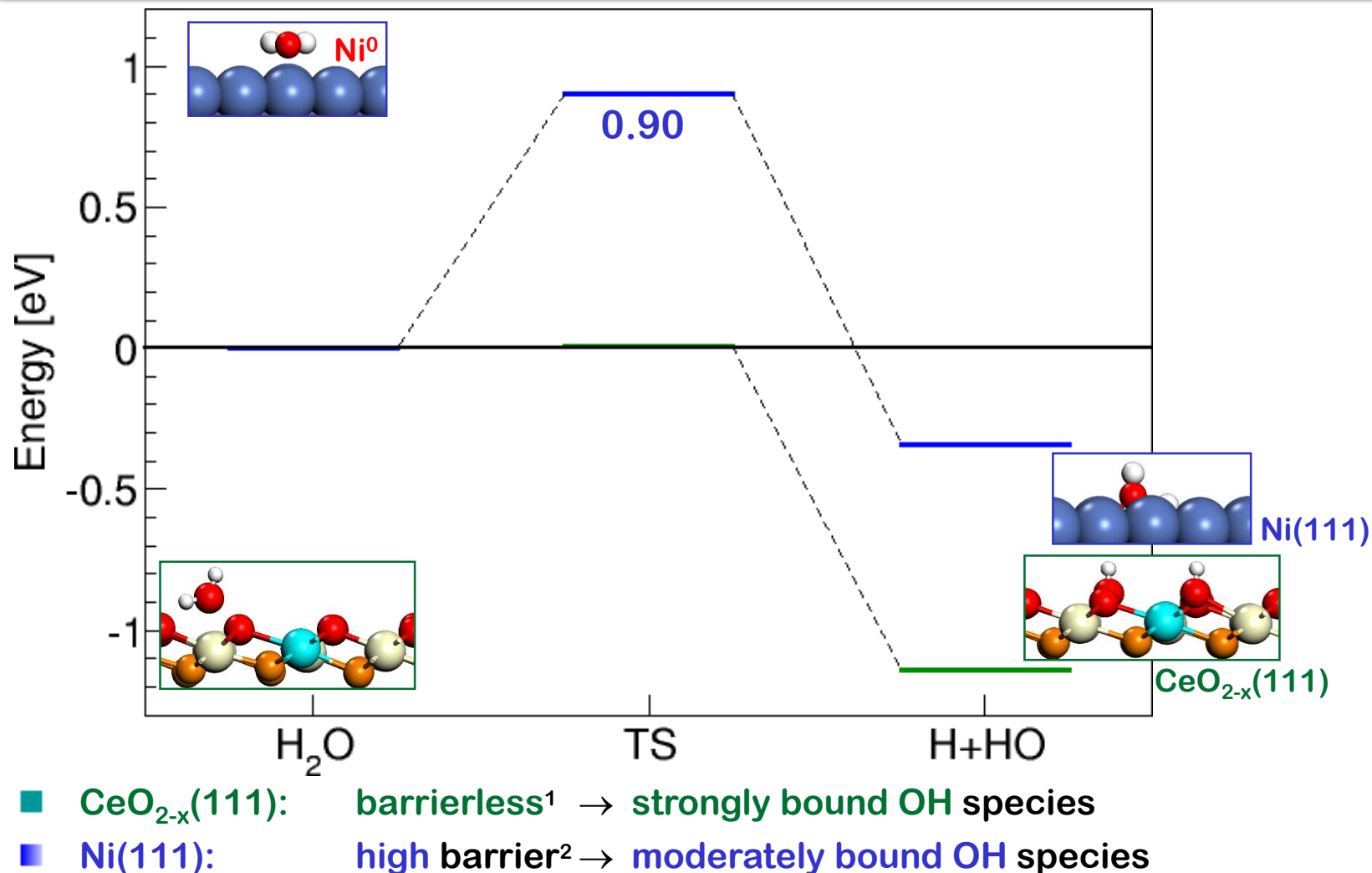
Water dissociation on Ni/CeO₂(111)



In agreement:

¹ D. Marrocchelli and B. Yildiz, J. Phys. Chem. C 116, 2411 (2011).

Water dissociation on Ni/CeO₂(111)

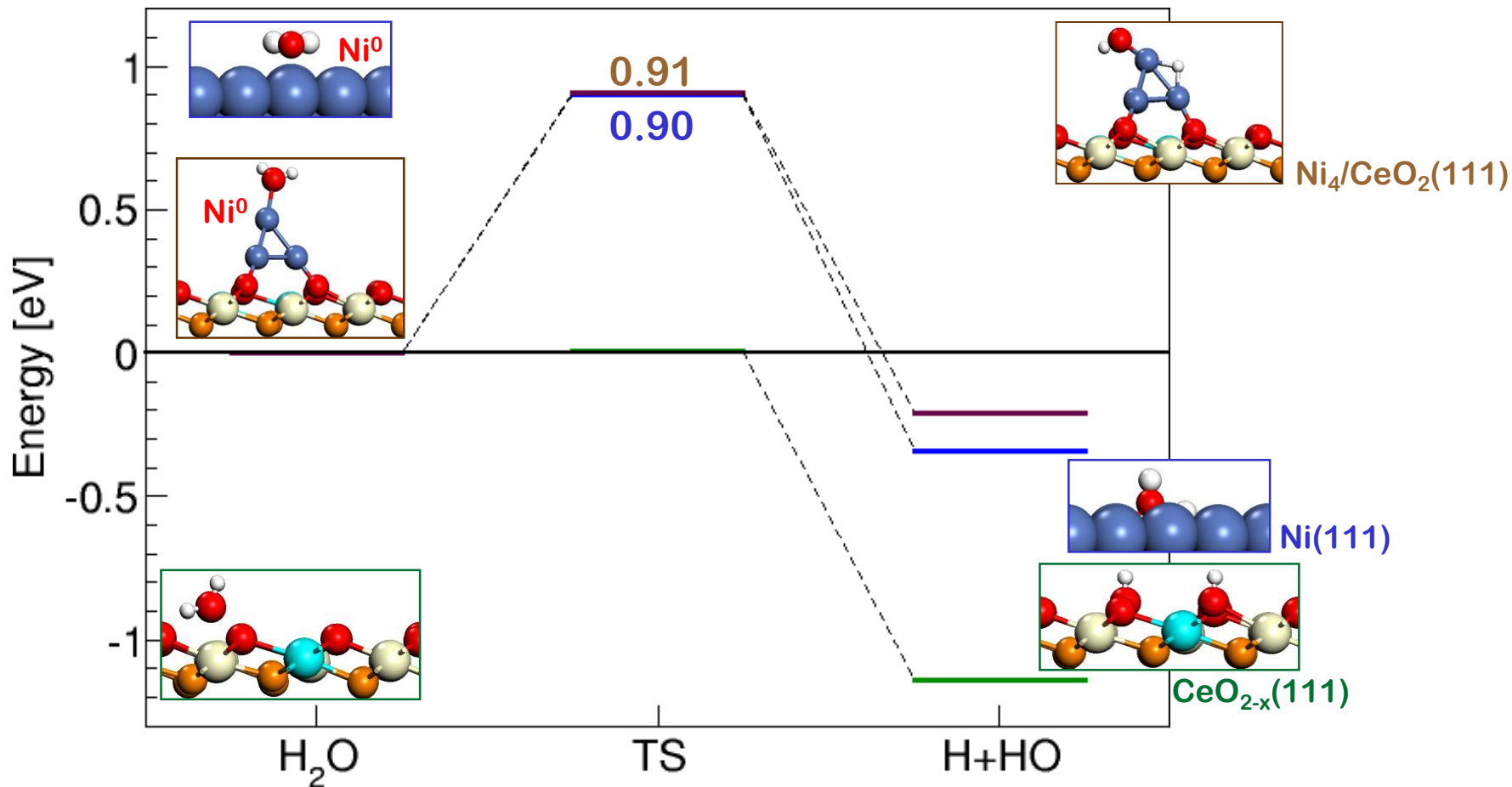


In agreement:

¹ D. Marrocchelli and B. Yildiz, J. Phys. Chem. C 116, 2411 (2011).

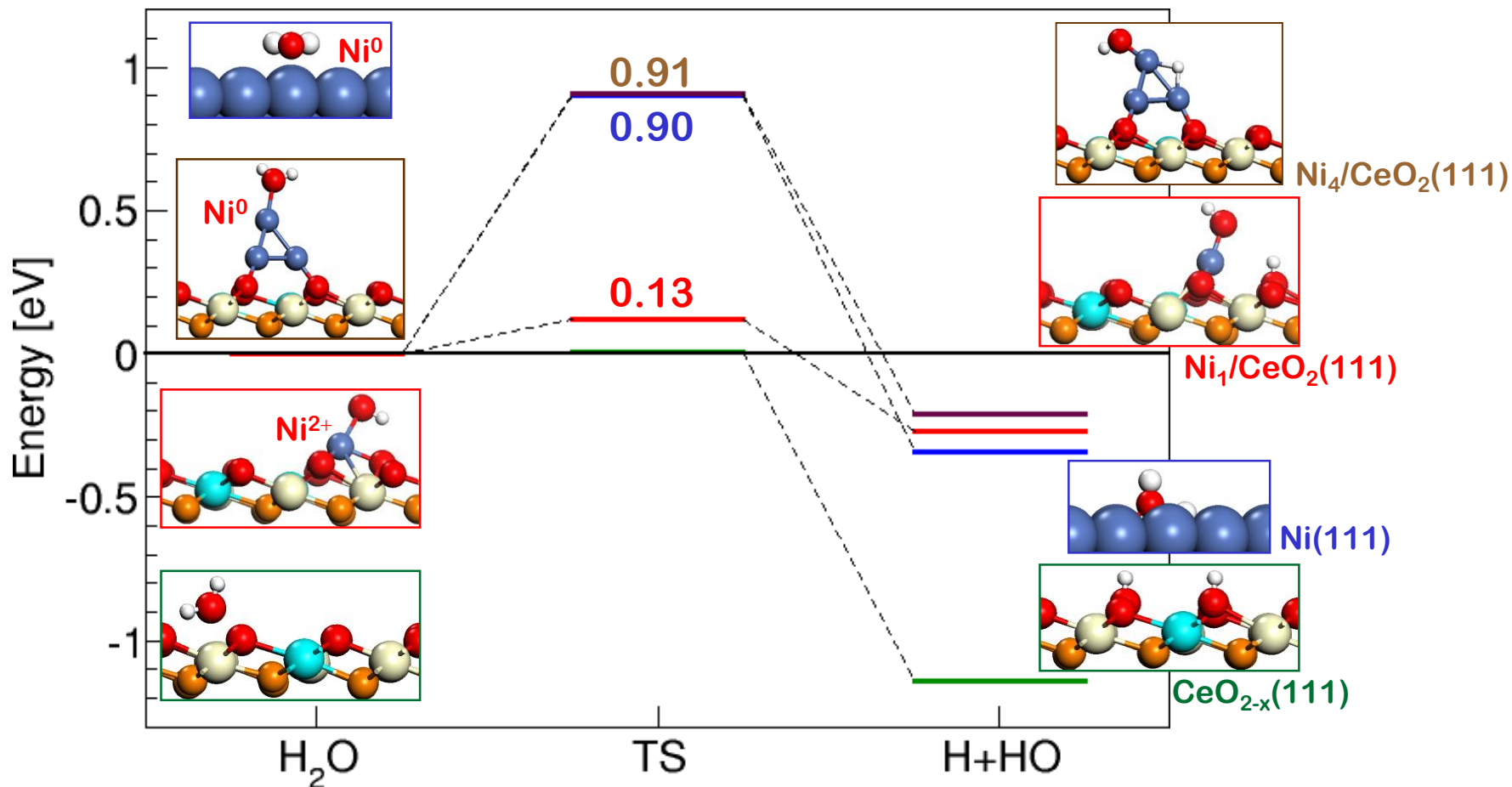
² A. A. Phatak et al., J. Phys. Chem. C 113, 7269 (2009).

Water dissociation on Ni/CeO₂(111)



- **CeO_{2-x}(111):** barrierless → strongly bound OH species
- **Ni(111):** high barrier → moderately bound OH species
- **Ni₄/CeO₂(111):** high barrier → moderately bound OH species

Water dissociation on Ni/CeO₂(111)



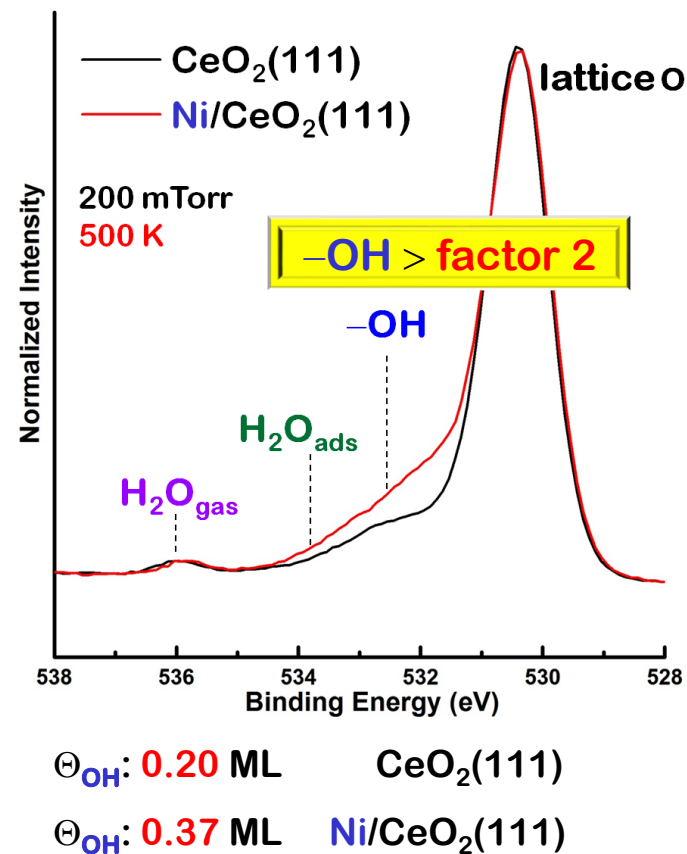
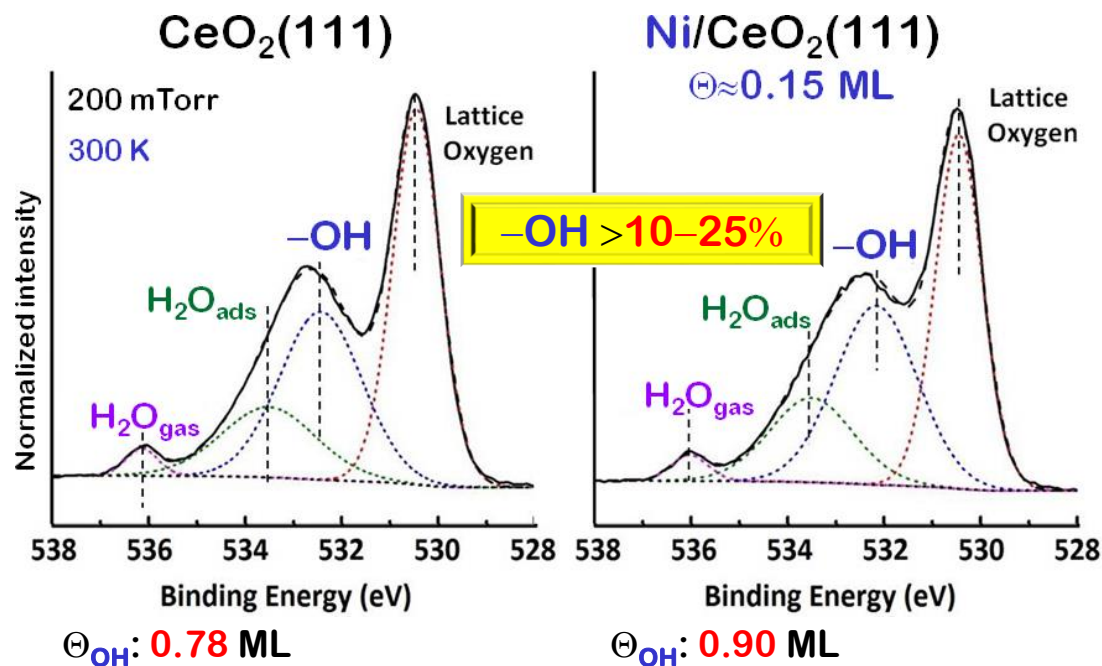
- CeO_{2-x}(111): barrierless → strongly bound OH species
- Ni(111): high barrier → moderately bound OH species
- Ni₁/CeO₂(111): low barrier → weakly bound OH species readily available for WGS

Ni²⁺ species –in direct contact with the support – are able to **fastly cleave O–H bonds**

H₂O dissociation: ambient-pressure X-ray photoelectron spectroscopy

Carrasco et al., Angew. Chem. Int. Ed. 54 (2015)

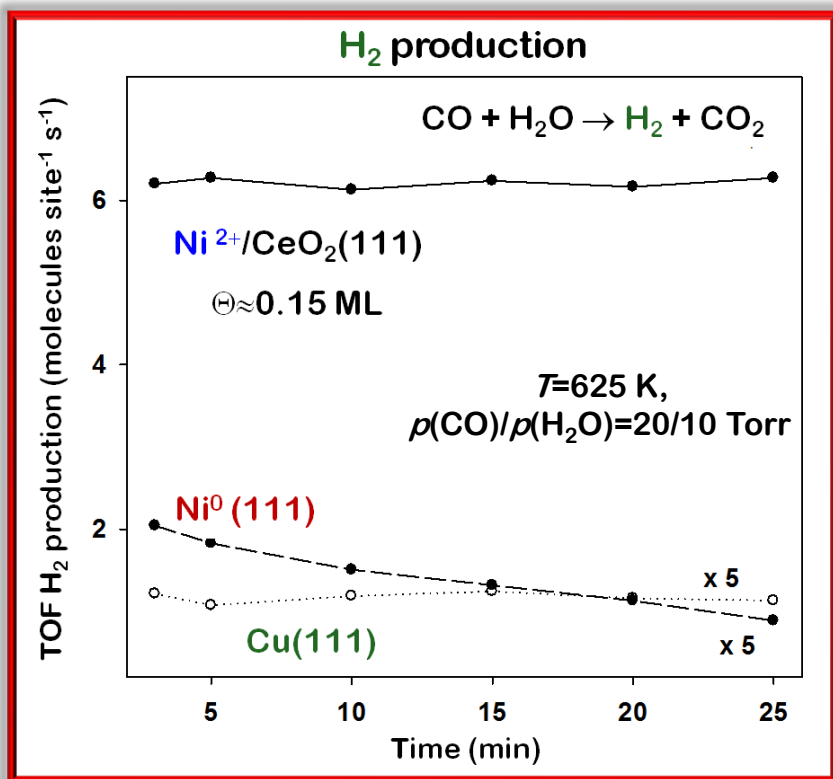
O1s XPS spectra



H₂O dissociation: ambient-pressure X-ray photoelectron spectroscopy

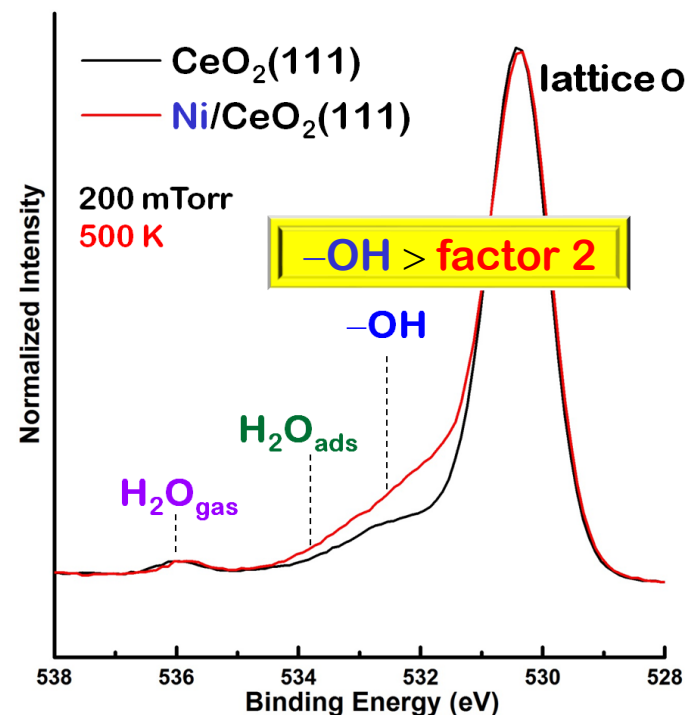
Carrasco et al., Angew. Chem. Int. Ed. 54 (2015)

Larger OH coverage on Ni/CeO₂
facilitates WGS



■ **Ni(111):** slow H₂O dissociation
deactivation $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ coke

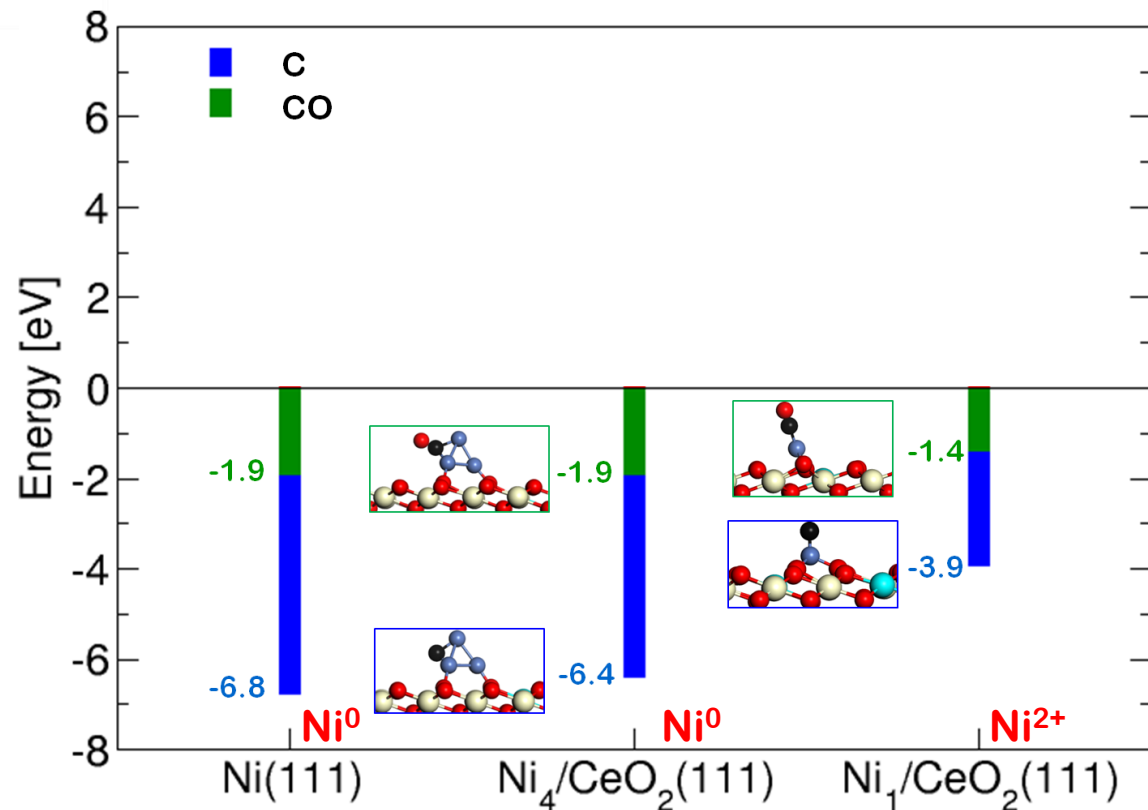
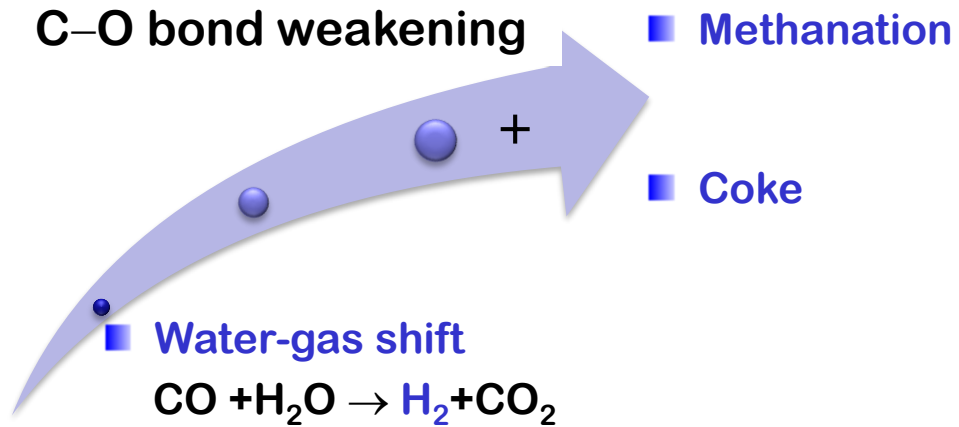
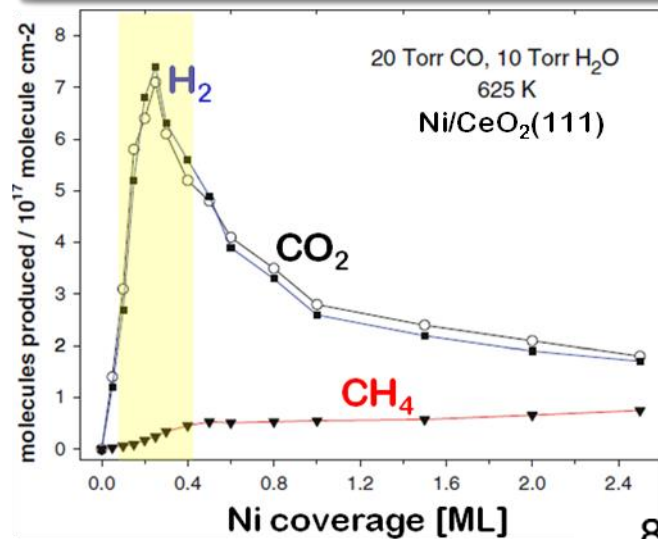
O1s XPS spectra



Θ_{OH}: **0.20** ML CeO₂(111)

Θ_{OH}: **0.37** ML Ni/CeO₂(111) Θ_{Ni}: **0.15** ML

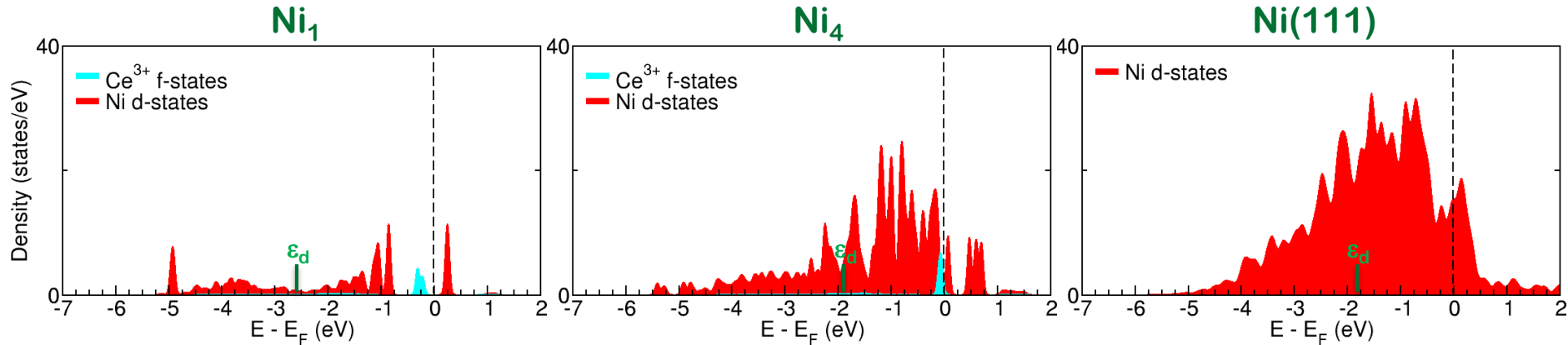
Ni/CeO₂(111): the C–O bond cleavage



C non-oxidative adsorption on Ni/CeO₂(111)

C–Ni bond:

$$\text{Ni}_1 < \text{Ni}_4 < \text{Ni}(111)$$

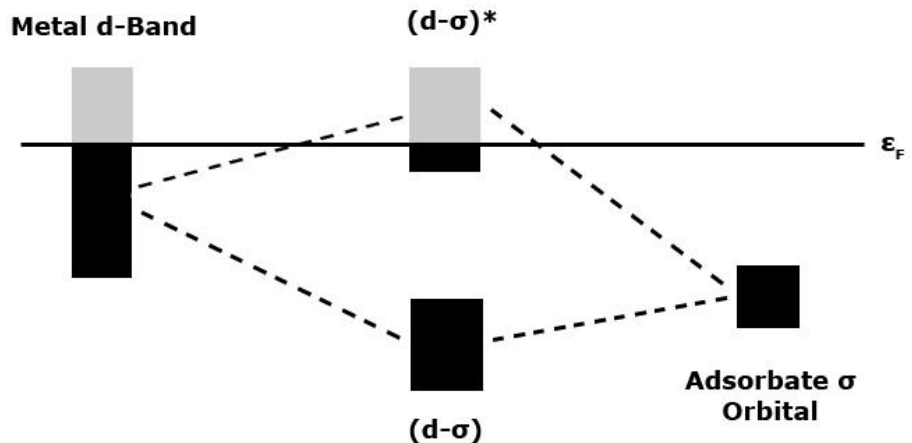


Ni₁ : lower d-band center wrt to the Fermi level → the C–Ni bond is weakest

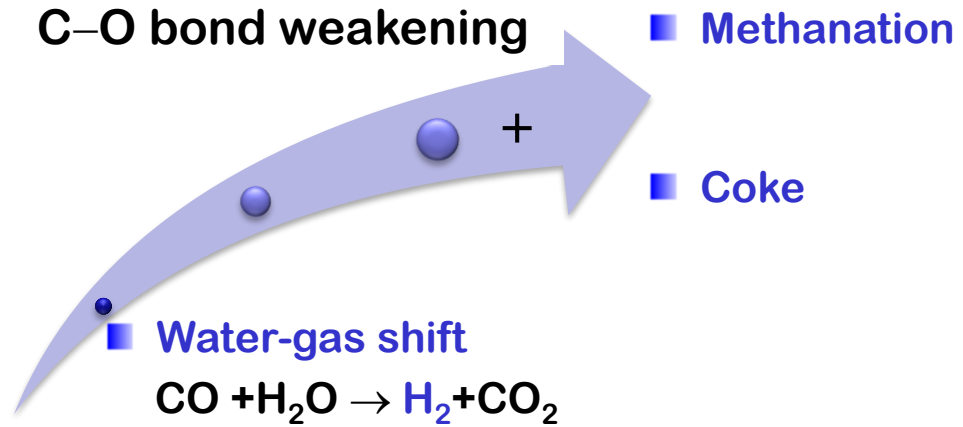
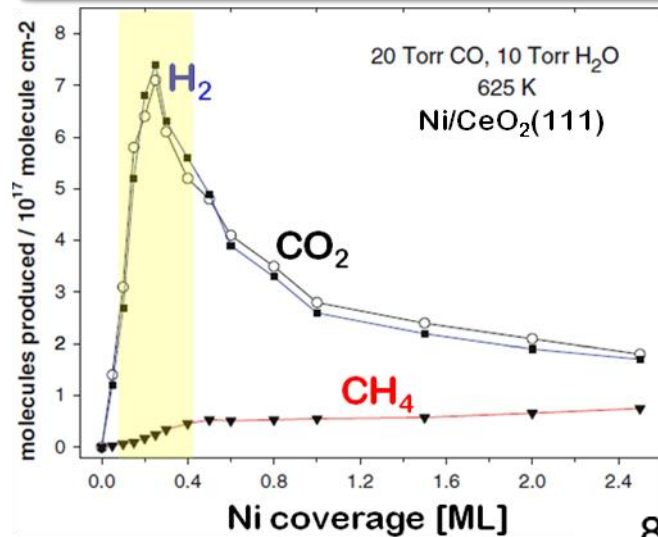
d-band model:

The higher the d states are relative to the Fermi level, the emptier the antibonding states and the stronger the adsorption bond.

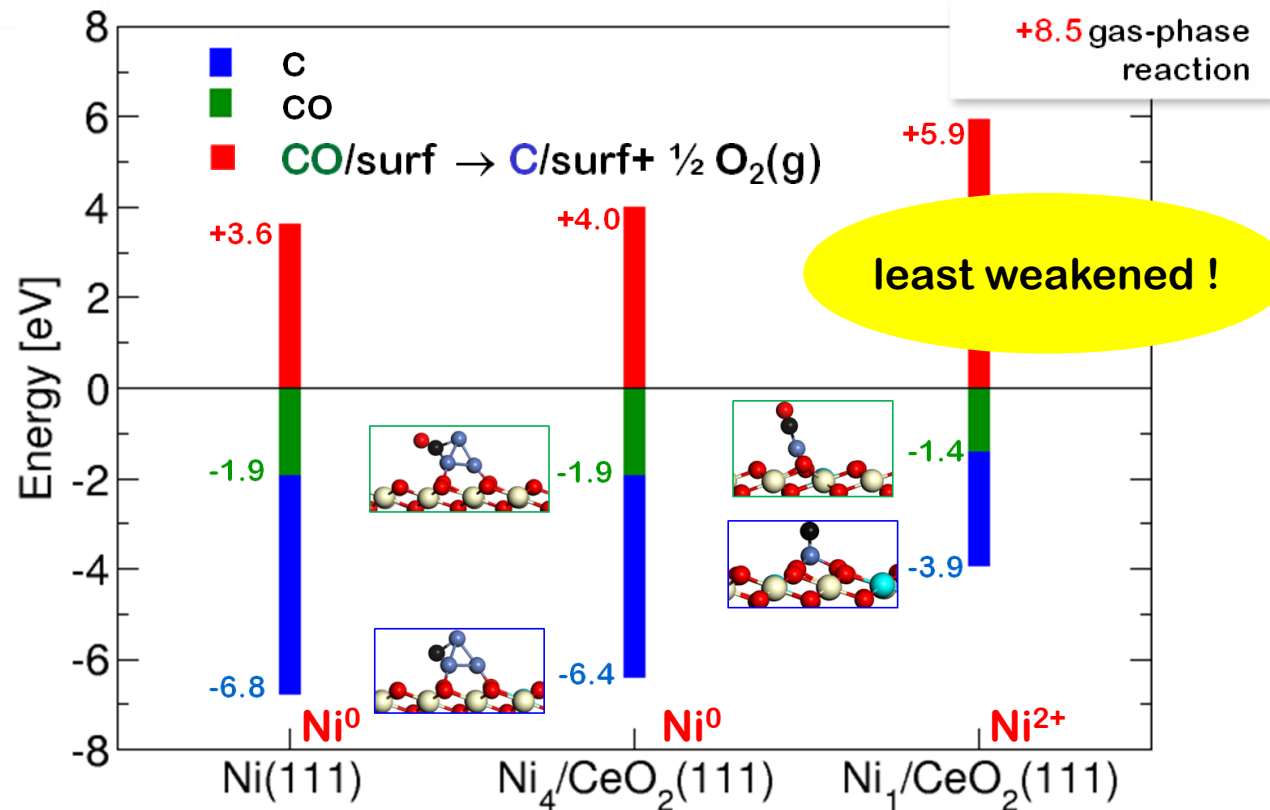
Hammer, Nørskov, Nature 376, 238 (1995)



Ni/CeO₂(111): the C–O bond cleavage



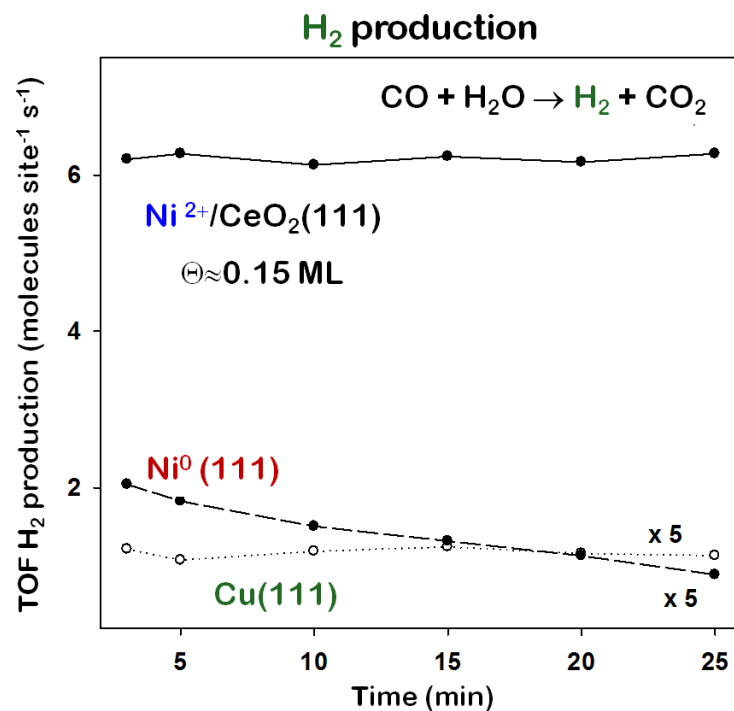
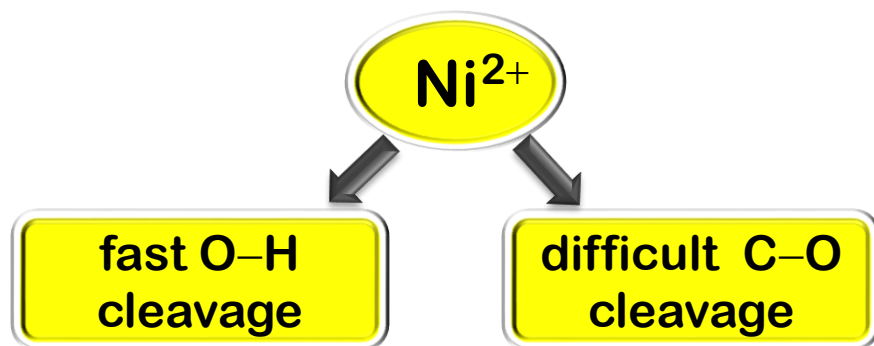
Ni²⁺ species makes more difficult to cleave C–O bonds



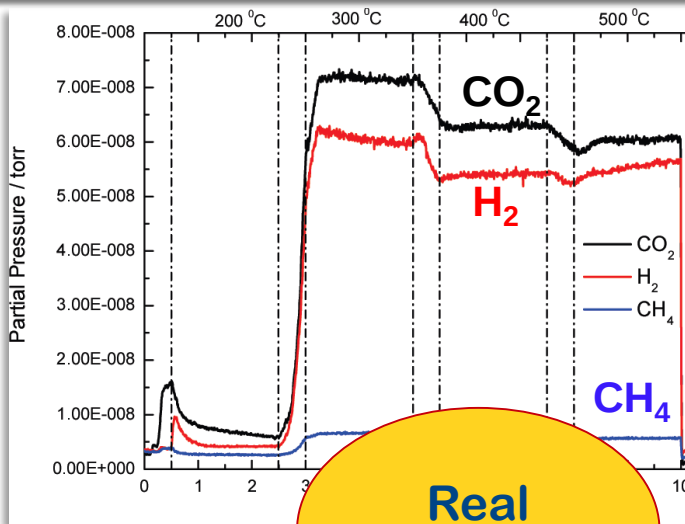
Ni/CeO₂ for H₂ production: a promising catalyst

The activity, selectivity, and stability of Ni/CeO₂ catalysts for WGS depend on strong metal–support interactions

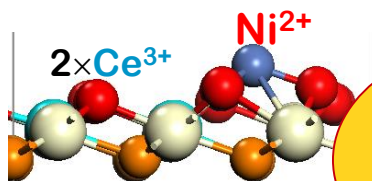
The active Ni/CeO₂ system



Towards the rational design of catalysts



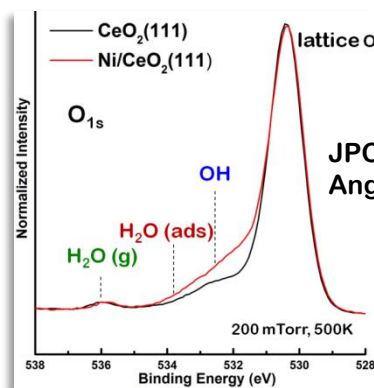
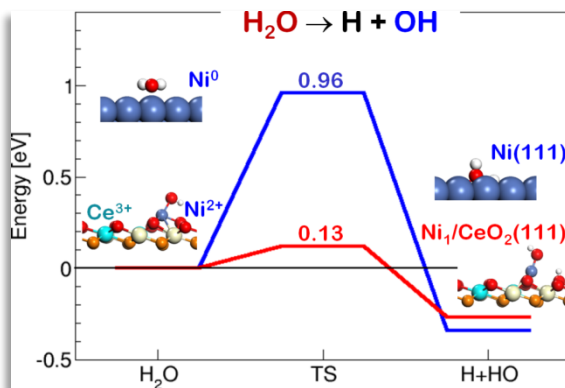
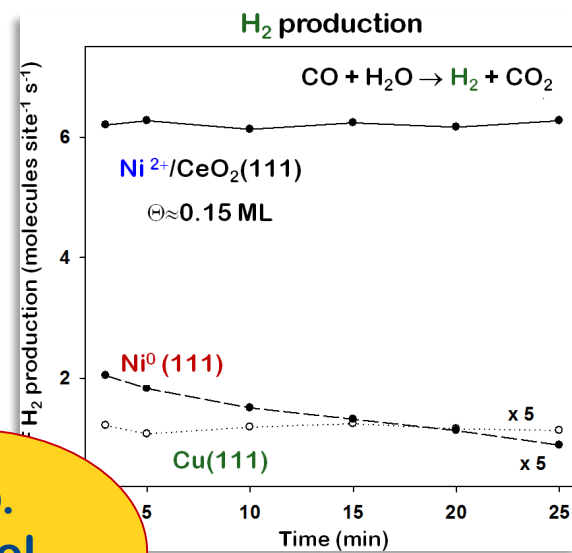
Barrio et al, JPCC 114, 12689(2010)



Theoretical
Model
Catalyst

Real
Catalyst

Exp.
Model
Catalyst



JPCC 117, 8241 (2013)
Angew. Chem. Int. Ed. 54, 3917 (2015)

Ceria supported Ni catalysts for CH₄ dry reforming

- CH₄ and CO₂ → greenhouse gases



- Natural gas (~90% CH₄)
- Landfill gas (~60% CH₄ ; ~40% CO₂)

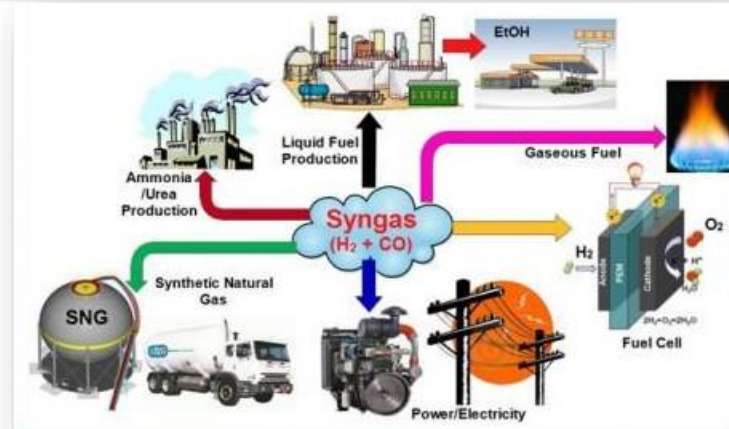


Challenges:

- Activation of CO_2 and CH_4
- High temperature (~1200 K)
- Coke formation

Catalyst:

- Pt, Rh, Ru → expensive
- Ni-Pd, Ni-Pt, Co-Pt, Co-Ru
- **Metals on an oxide support**
TiO₂, MgO, CeO₂, ...etc.

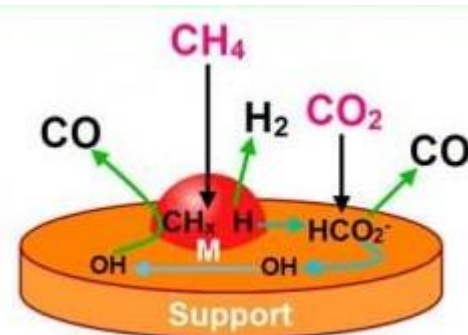


Fuel and higher value products

Rational DRM catalysts

- Active site?
- Metal-support interaction?
- Role of metal? → CH_4 dissociation
- Role of oxide? → CO_2 dissociation
- Reaction mechanism?

Pakhare et al. Chem. Soc. Rev., 2014,43, 7813-7837

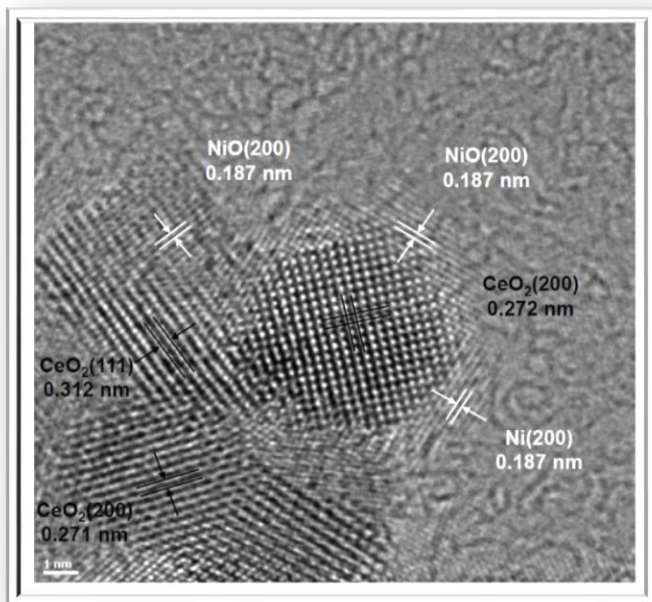


Ni/CeO₂ powder catalysts for CH₄ dry reforming

Liu et al., Angew. Chem. Int. Ed. 55 (2016)

Lustemberg et al, ACS Catal 6 (2016)

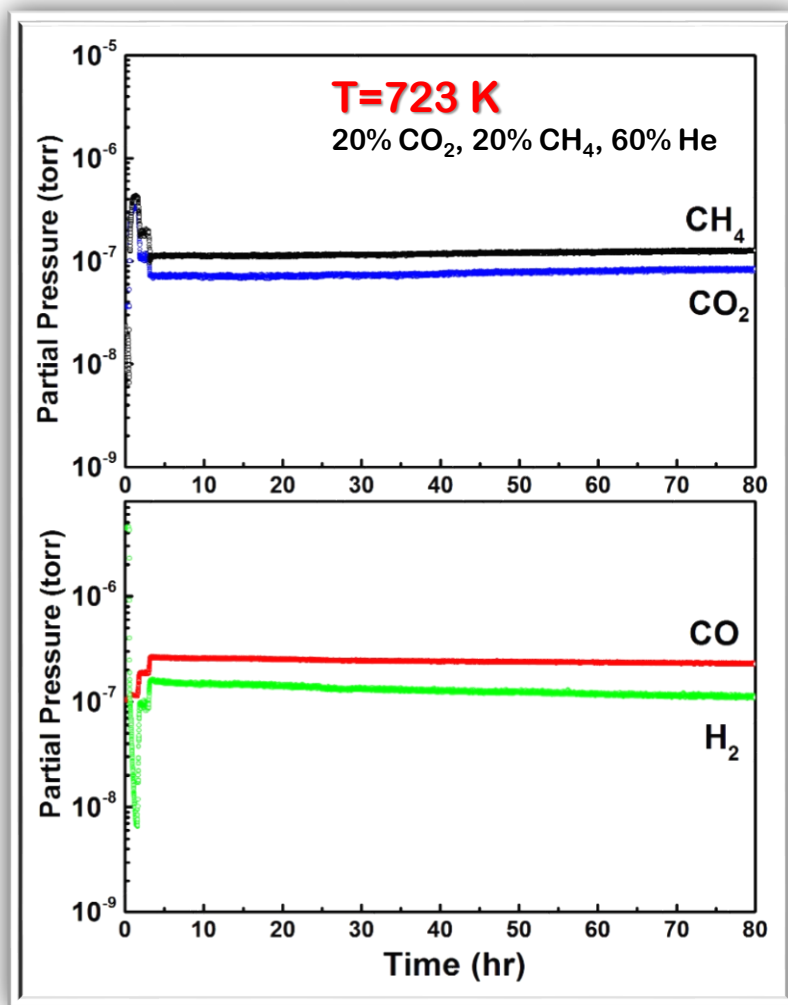
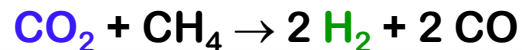
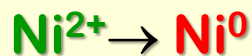
20% NiO-80%CeO₂ precursor



activation

20%H₂/He @ 723 K

In situ X-ray diffraction



Gas species derived from mass spectrum

Ni/CeO₂(111) model catalysts: CH₄ dissociation

100 mTorr CH₄

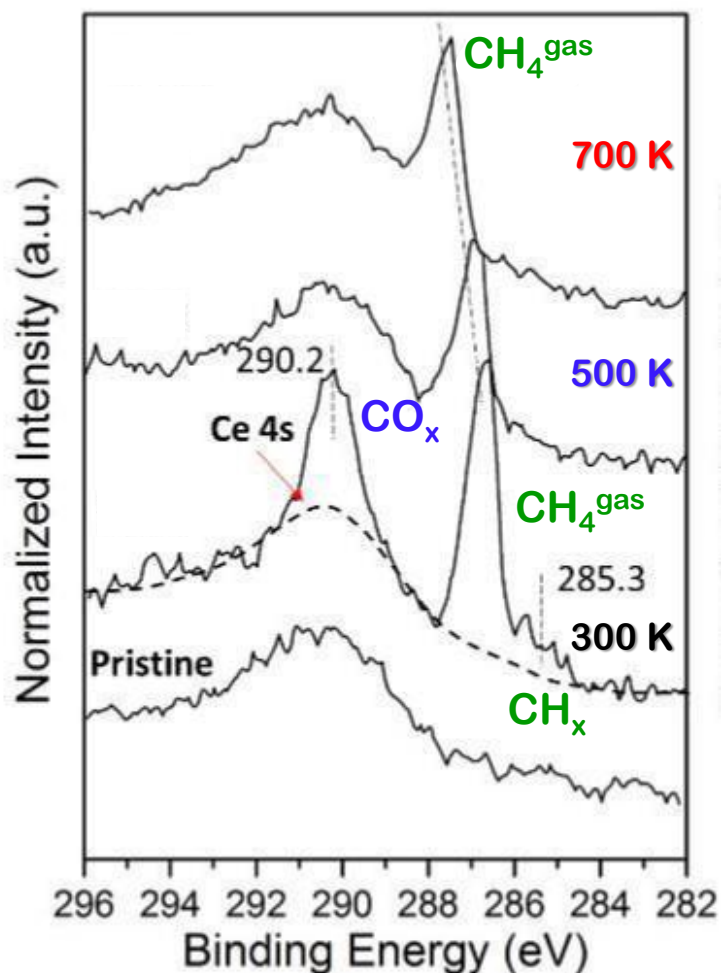


Model Catalyst @ 300K

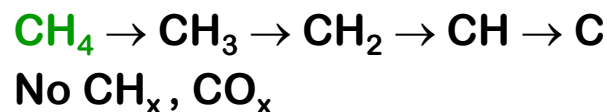
0.1 ML Ni on CeO₂(111)

Ni²⁺/CeO₂

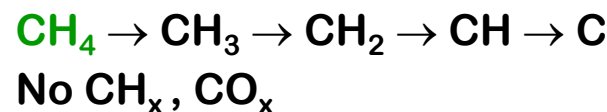
C1s XPS spectra



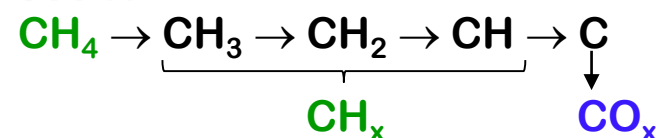
■ 700 K



■ 500 K



■ 300 K



Room T
CH₄ activation !!

Ni/CeO₂(111) model catalysts: CH₄ dissociation

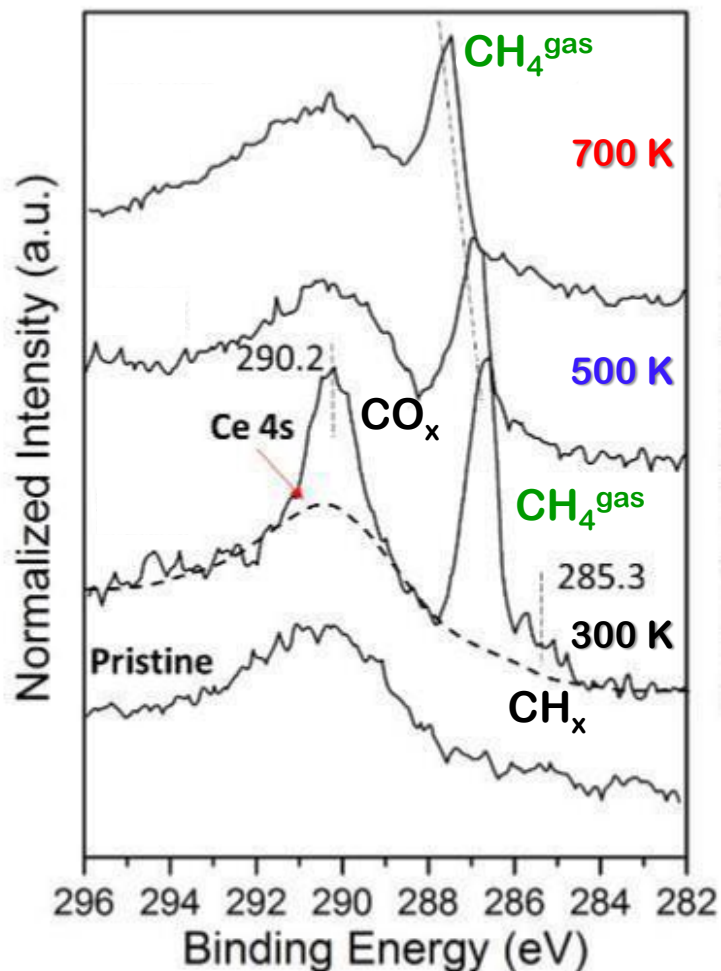
100 mTorr CH₄

Liu et al., Angew. Chem. Int. Ed. 55 (2016)

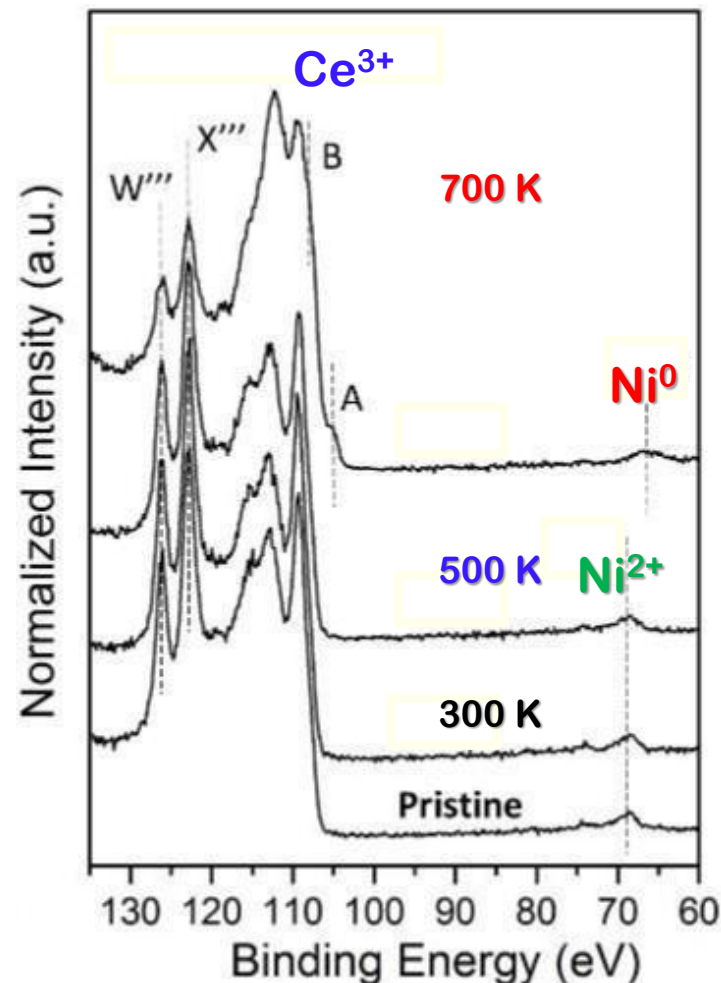
Lustemberg et al, ACS Catal 6 (2016)



C1s XPS spectra



Ce 4d + Ni 3p spectra



Ni/CeO₂(111) model catalysts: CH₄ dissociation

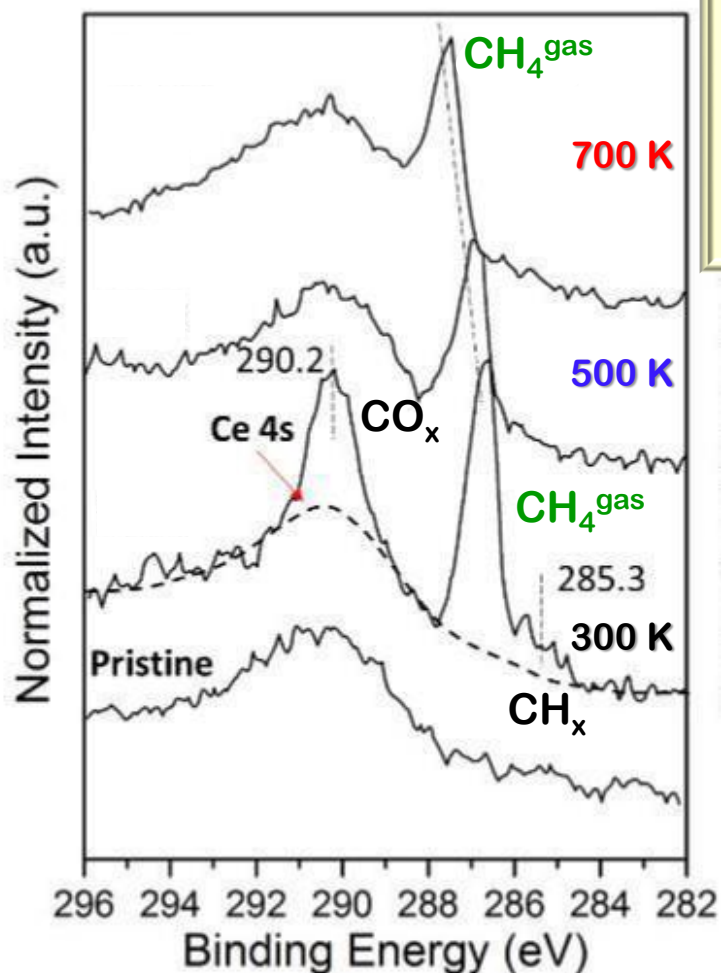
100 mTorr CH₄

Liu et al., Angew. Chem. Int. Ed. 55 (2016)

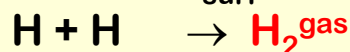
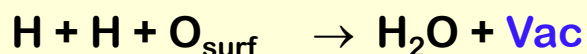
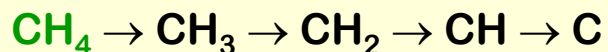
Lustemberg et al, ACS Catal 6 (2016)



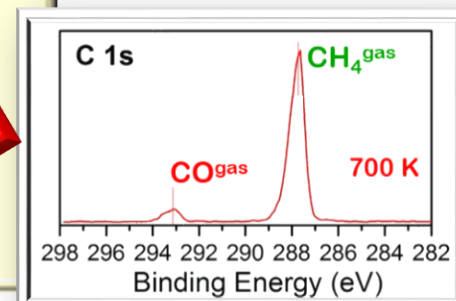
C1s XPS spectra



700 K



surface
reduction

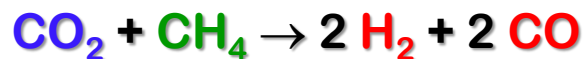


CO₂ dissociation at O-vacant sites!

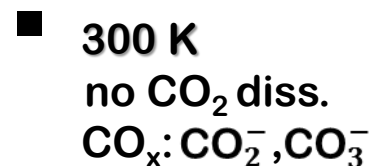
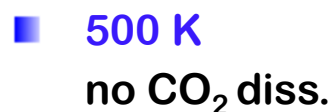
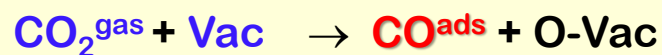
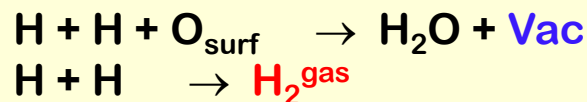
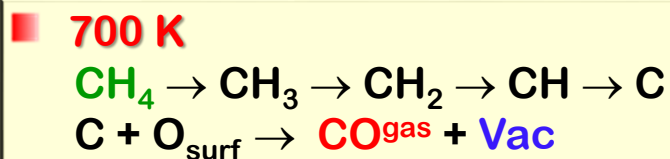
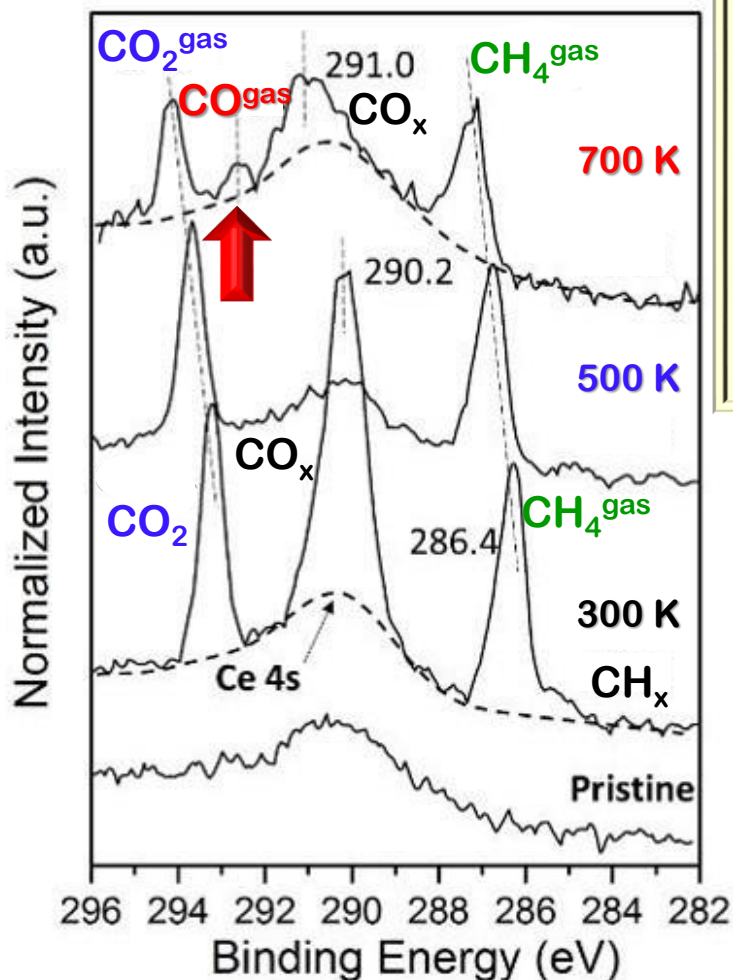
Ni/CeO₂(111) model catalysts for CH₄ dry reforming

100 mTorr CO₂
100 mTorr CH₄

Liu et al., Angew. Chem. Int. Ed. 55 (2016)
Lustemberg et al, ACS Catal 6 (2016)



C1s XPS spectra

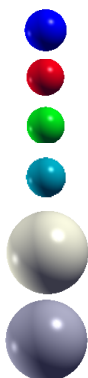


low-loaded Ni⁰/CeO_{2-x}(111):

DRM activity!! No coke !

No NiC_x!

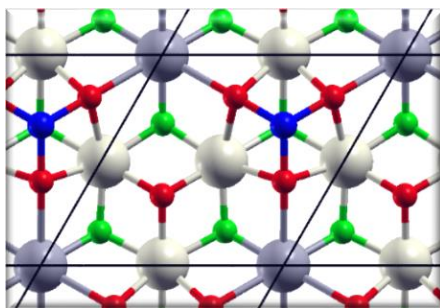
Ni/CeO_x(111) model catalyst: metal-support interaction



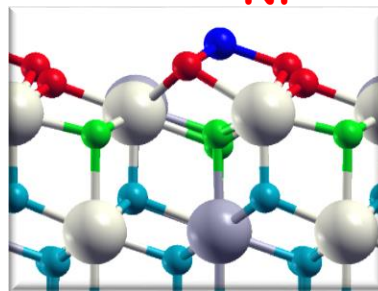
Ni
O_{surf}
O_{sub}
O_{bulk}
Ce⁴⁺
Ce³⁺

Ni₁/CeO₂(111)

Ni²⁺/CeO₂



2×Ce³⁺ (2×2) cell

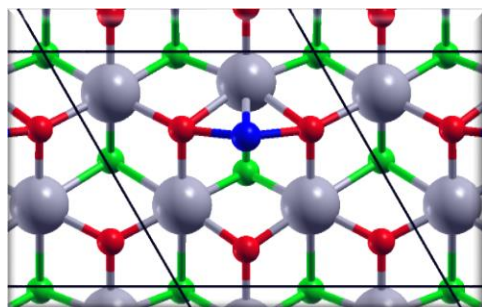


2×Ce³⁺

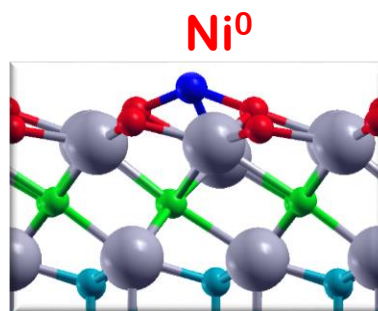
Model for CH₄ diss. @ 300 K

Ni⁰/CeO_{2-x}

Ni₁/Ce₂O₃(0001)



(2×2) cell

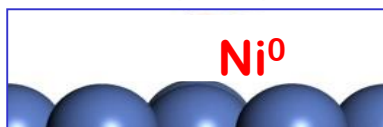


all Ce³⁺

Ce₂O₃

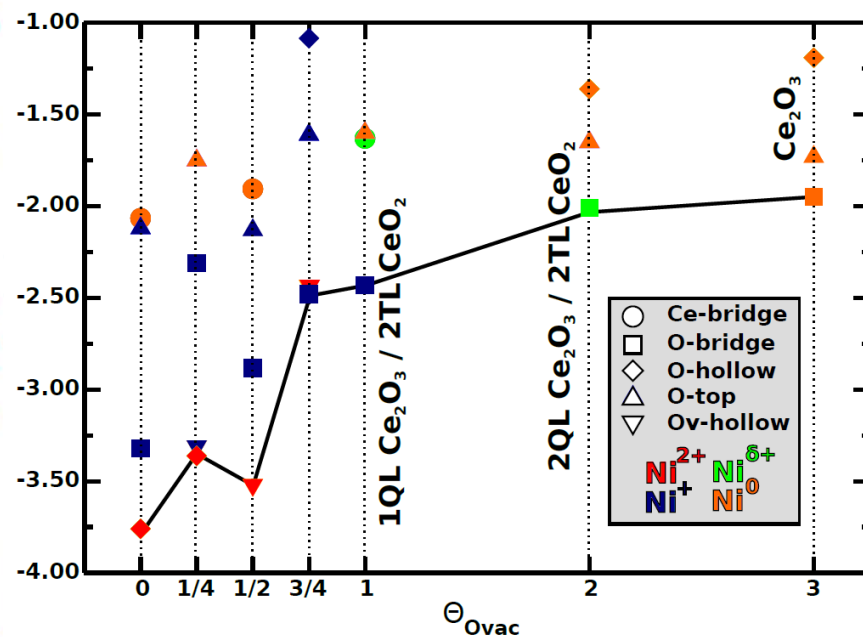
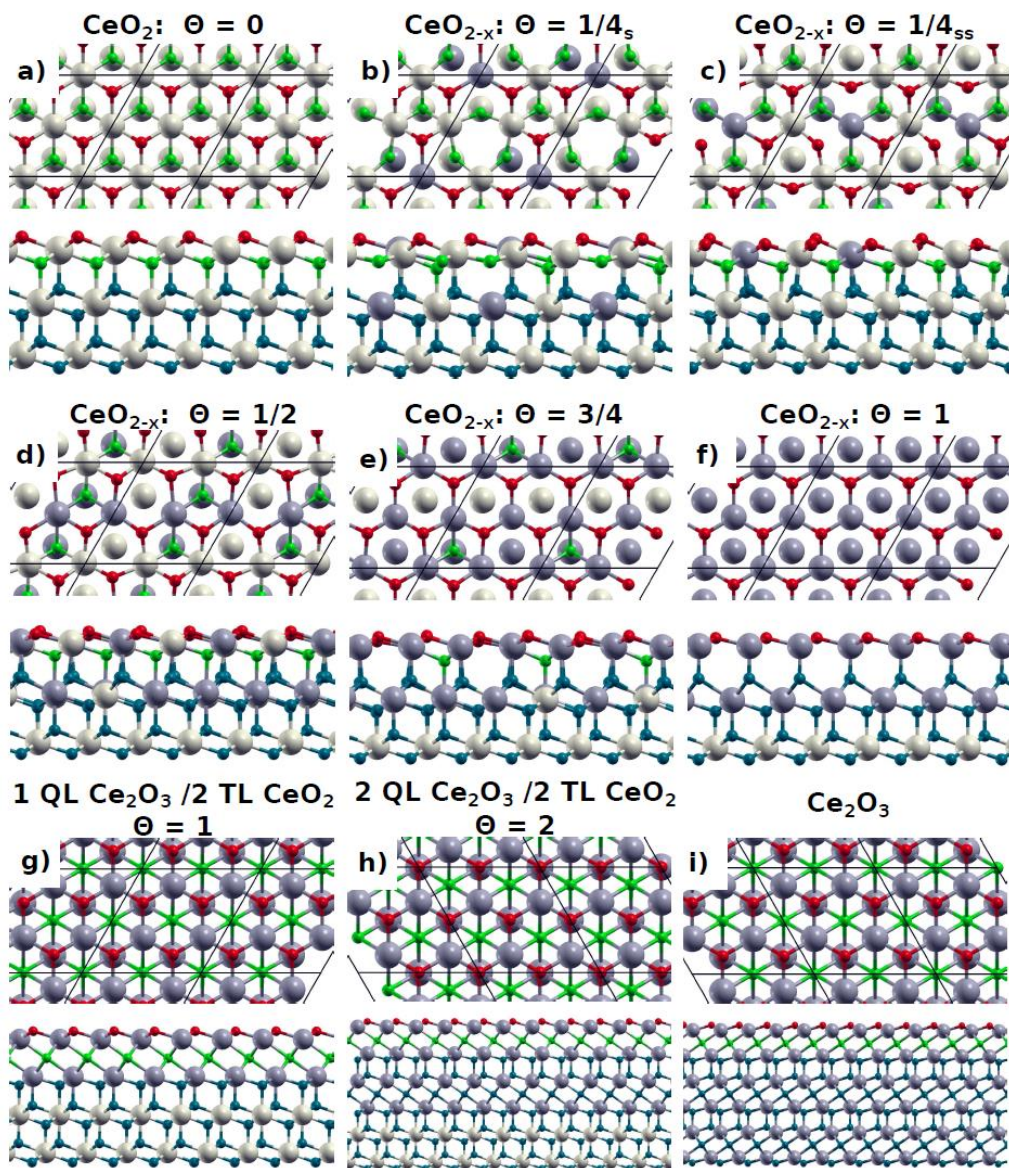
Ni(111)

Model for DRM @ 700 K



Ni/CeO_x(111) model catalyst: metal-support interaction

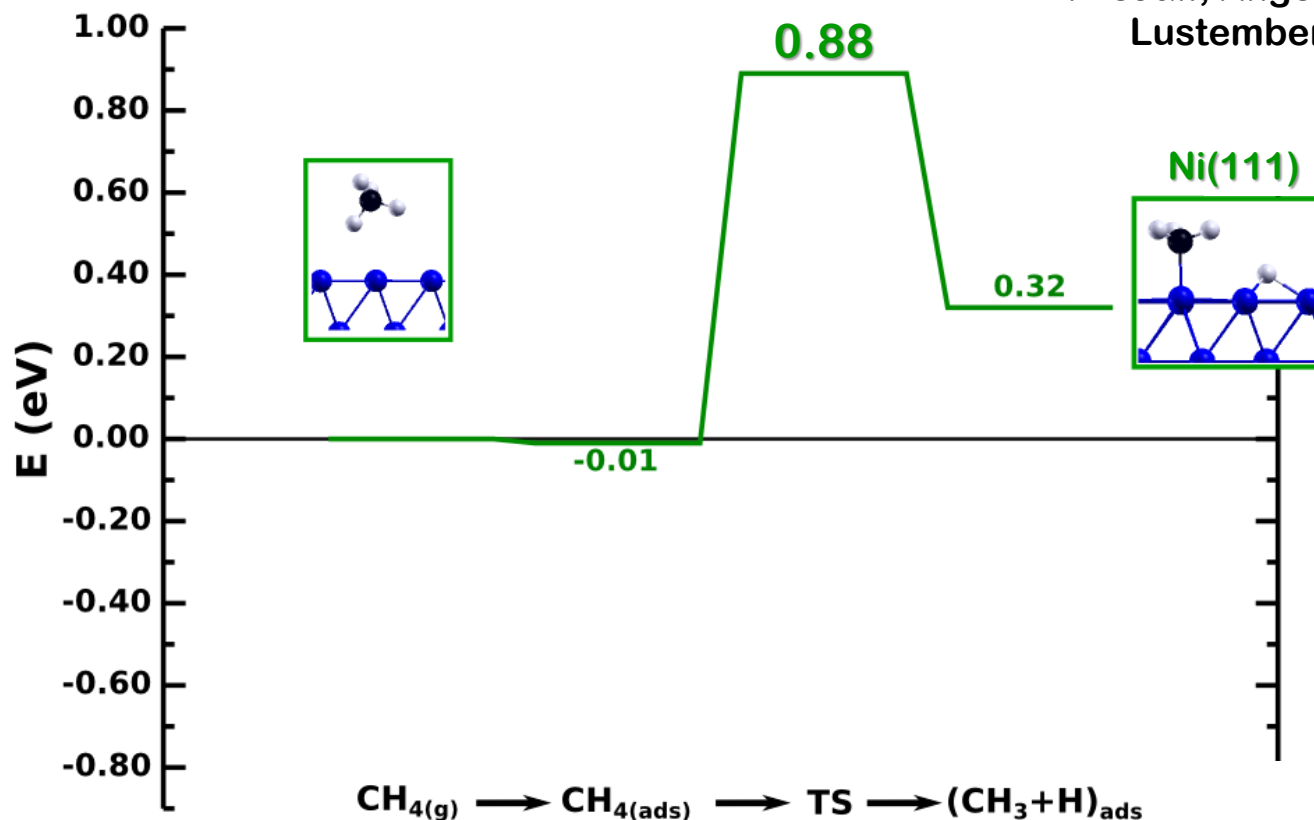
Model for DRM @ 700 K



CH₄ dissociation on Ni/CeO₂(111)

Liu et al., Angew. Chem. Int. Ed. 55 (2016)

Lustemberg et al, ACS Catal 6 (2016)



■ Ni(111): weakly bound CH₄ ; high dissociation barrier → [0.9–1.1 eV]

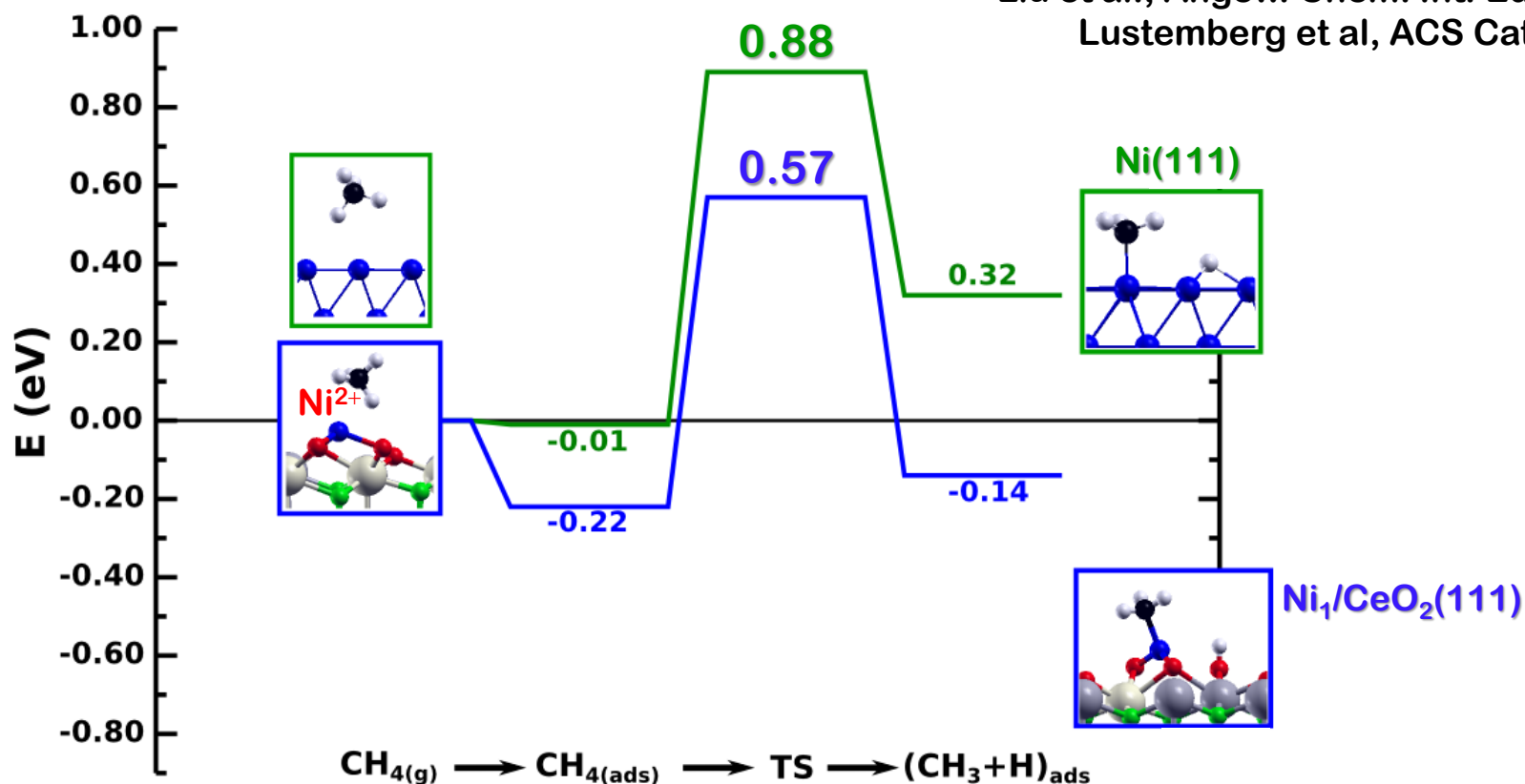
In agreement:

¹ Abild-Petersen et al. Surf. Sci. 590, 127 (2005); Li et al. Chem. Phys. Lett. 639, 205 (2015) → 1.1 eV

CH₄ dissociation on Ni/CeO₂(111)

Liu et al., Angew. Chem. Int. Ed. 55 (2016)

Lustemberg et al, ACS Catal 6 (2016)

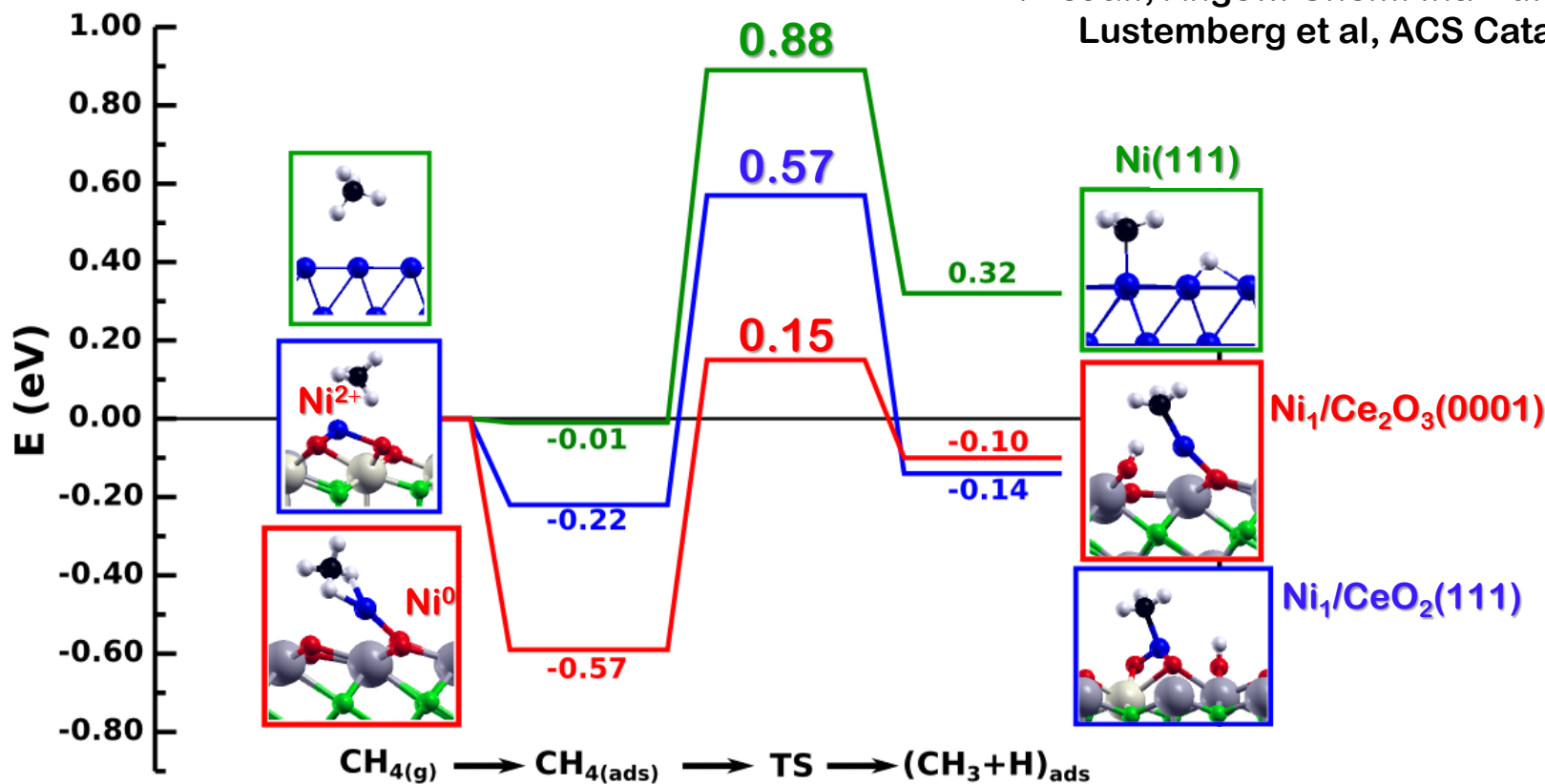


- Ni(111): weakly bound CH₄ ; high dissociation barrier → [0.9–1.1 eV]
- Ni/CeO₂(111): moderately bound CH₄ ; barrier reduction → [0.7–0.8 eV]

Ni²⁺ species enhance the reactivity of Ni to cleave C–H bonds at RT

CH₄ dissociation on Ni/CeO₂(111)

Liu et al., Angew. Chem. Int. Ed. 55 (2016)
Lustemberg et al, ACS Catal 6 (2016)



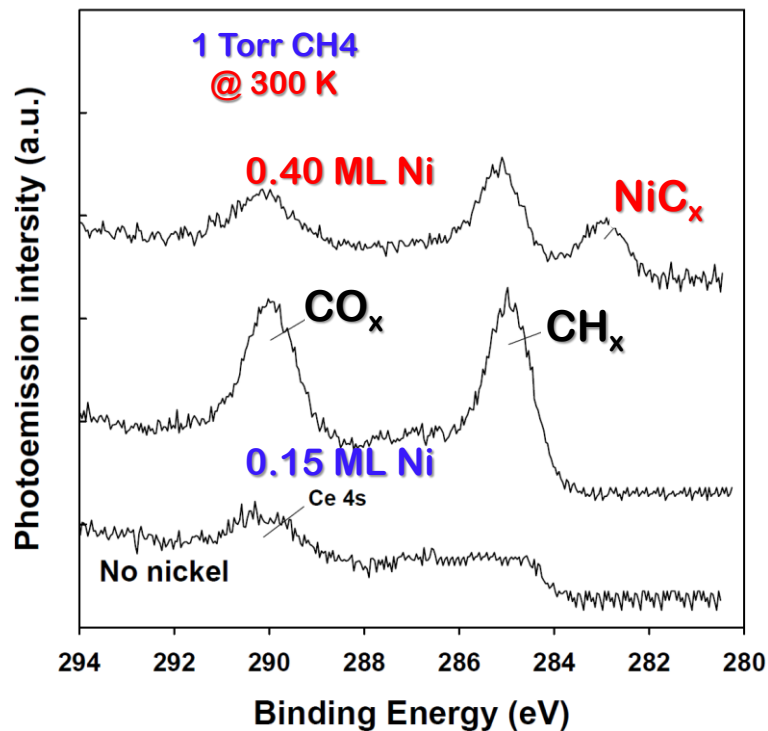
- Ni(111): weakly bound CH₄ ; high dissociation barrier
- Ni/CeO₂(111): moderately bound CH₄ ; barrier reduction
- Ni/Ce₂O₃(0001): stronger bound CH₄ ; barrier reduction

Ni⁰ species enhance the reactivity of Ni to fastly cleave C–H bonds

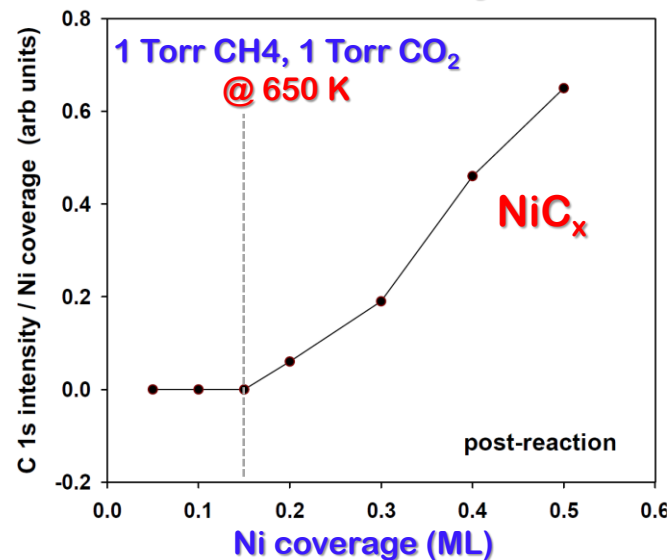
More stable CH₄ species → higher reaction probability

CH_4 dissociation on $\text{Ni/CeO}_2(111)$: The Ni coverage effect

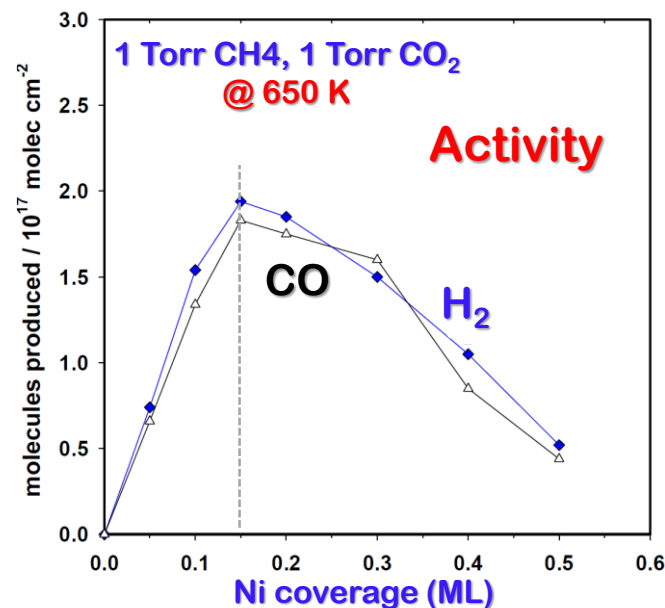
C1s XPS spectra



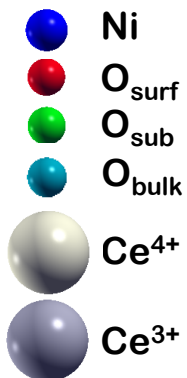
C1s intensity



Above ~ 0.15 ML $\rightarrow$ decline in the activity due to NiC_x formation

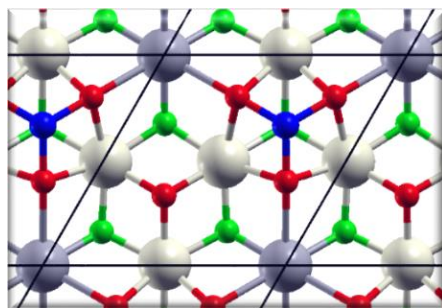


Ni/CeO_x(111) model catalyst: metal-support interaction

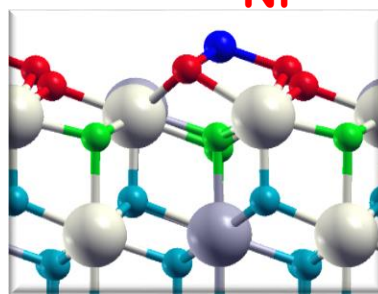


Ni₁/CeO₂(111)

Ni²⁺/CeO₂

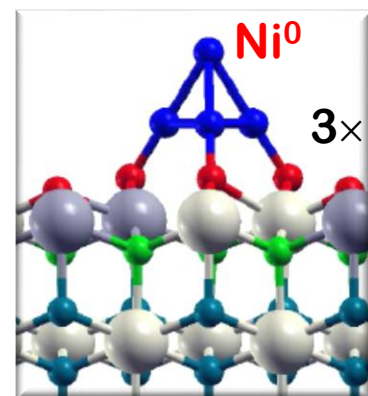


2×Ce³⁺ (2×2) cell



2×Ce³⁺

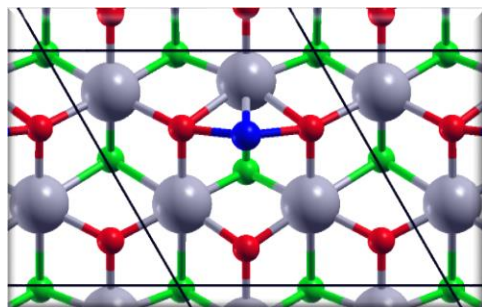
Ni₄/CeO₂(111)



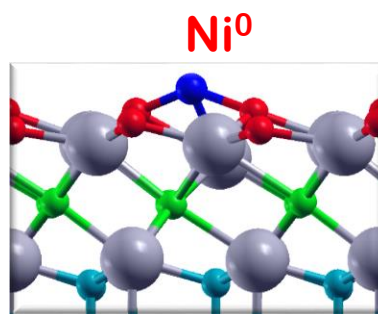
3× Ni^{~+0.7}

Ni⁰/CeO_{2-x}

Ni₁/Ce₂O₃(0001)

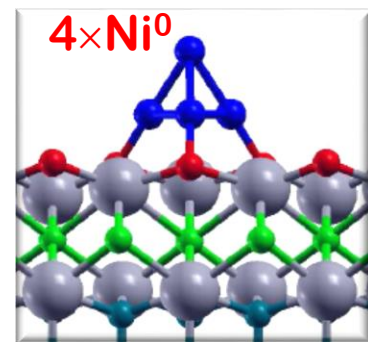


(2×2) cell



all Ce³⁺

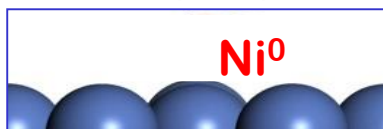
Ni₄/Ce₂O₃(0001)



Ce₂O₃

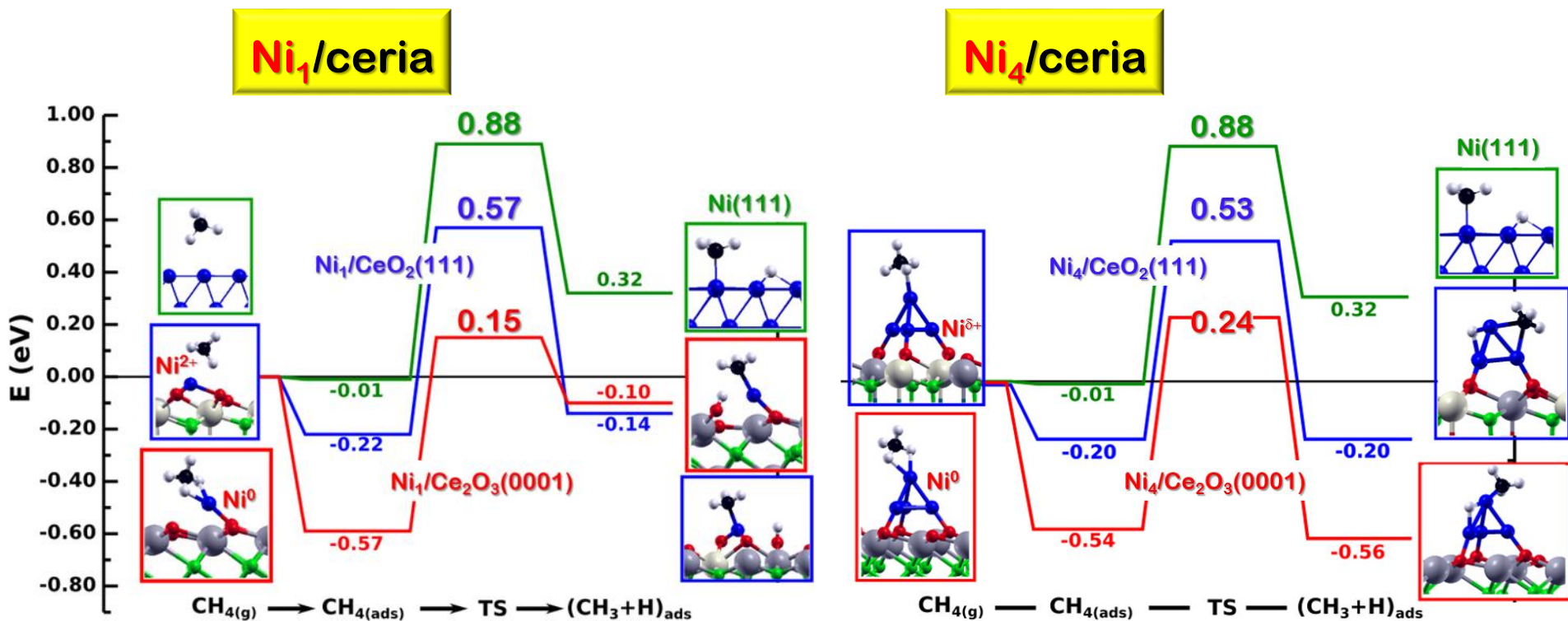
all Ce³⁺

Ni(111)

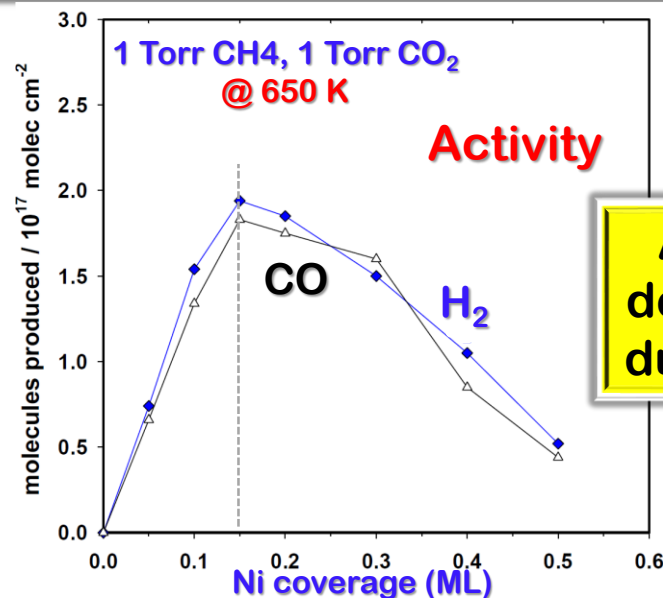
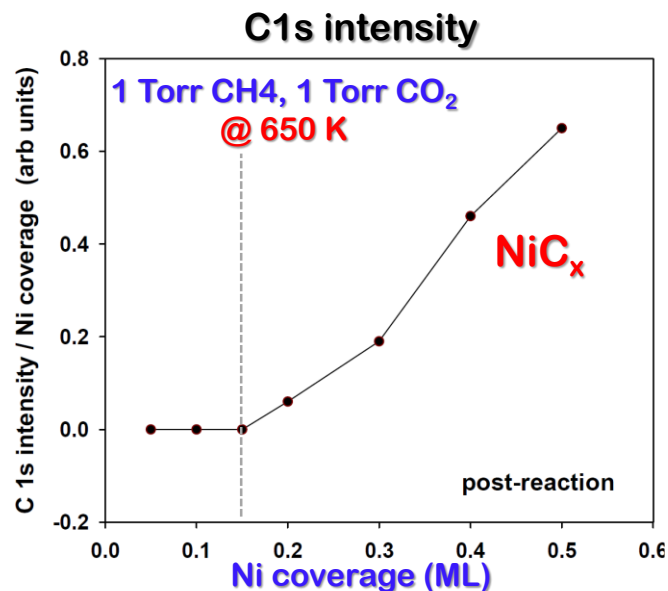


Ni⁰

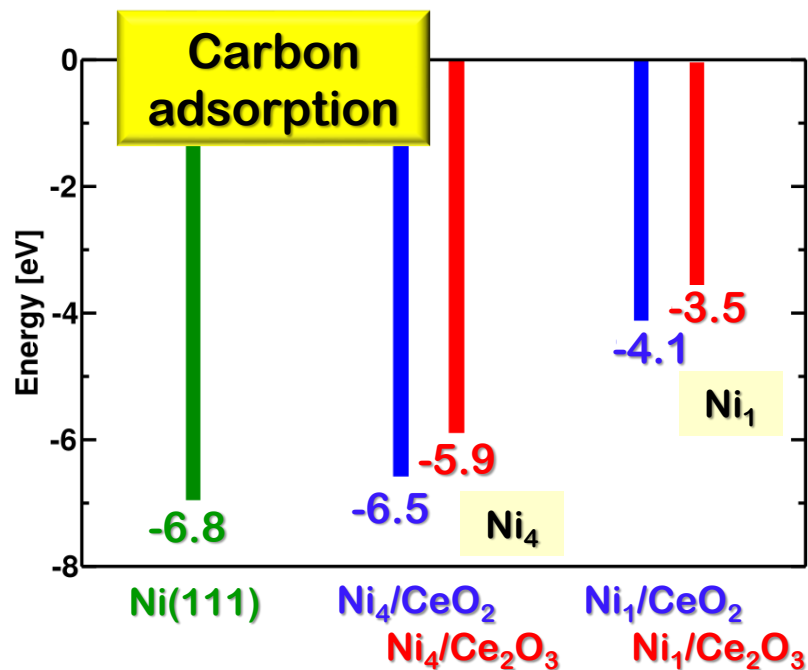
CH₄ dissociation on Ni/CeO₂(111)



CH₄ dissociation on Ni/CeO₂(111): The Ni coverage effect



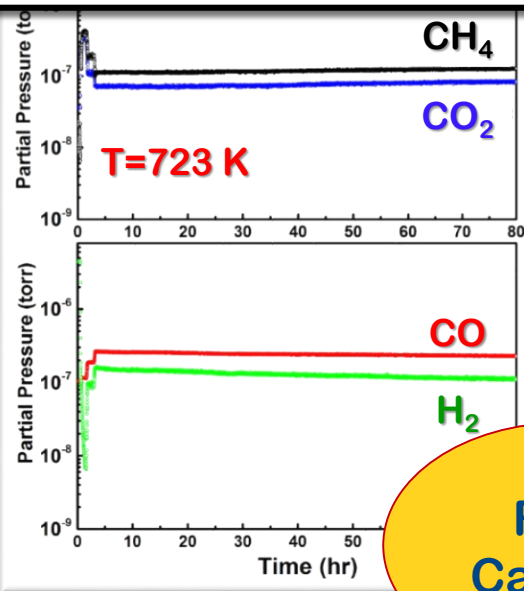
Above ~0.15 ML →
decline in the activity
due to NiC_x formation



NiC_x formation relates to
C adsorption energy trend
Ni(111) ≈ Ni₄/ceria > Ni₁/ceria

Towards the rational design of DRM catalysts

20% CO₂
20% CH₄
60% He



Ni⁰/CeO_{2-x}

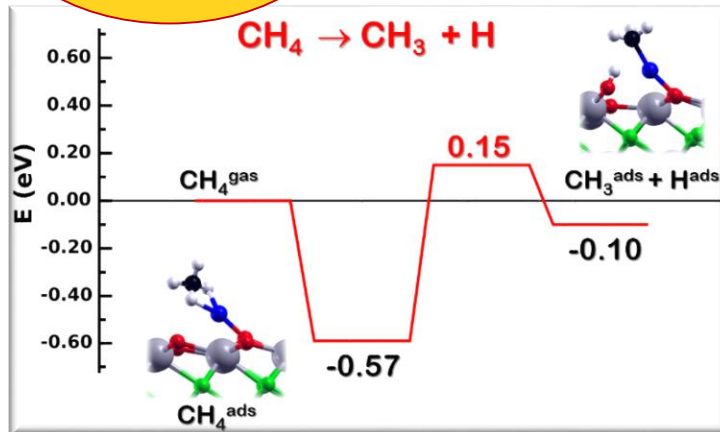
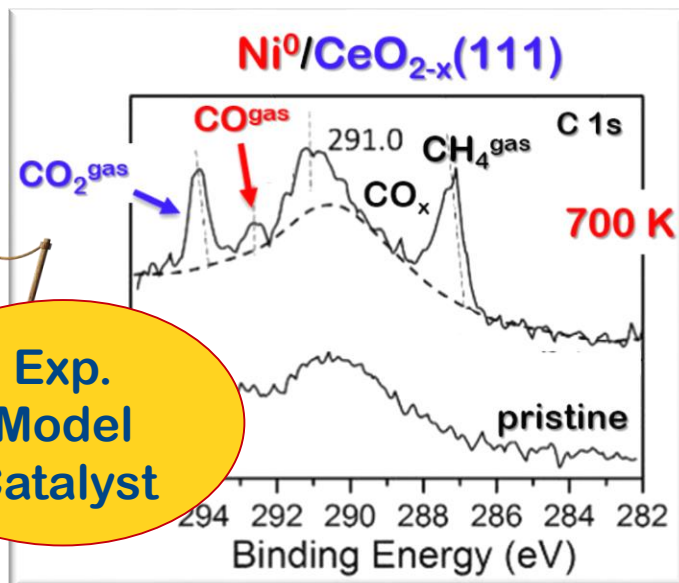
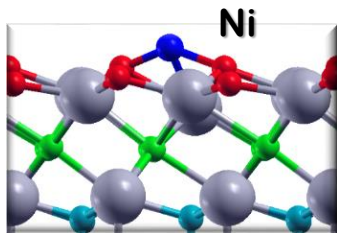
Angew. Chem. Int. Ed. 55, (2016)

Real
Catalyst

Theoretical
Model
Catalyst

Exp.
Model
Catalyst

Ni⁰/Ce₂O₃(0001)

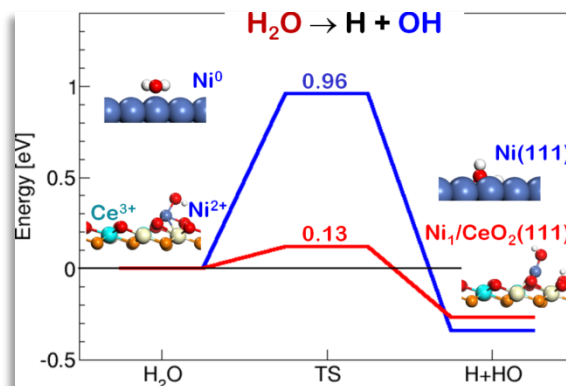
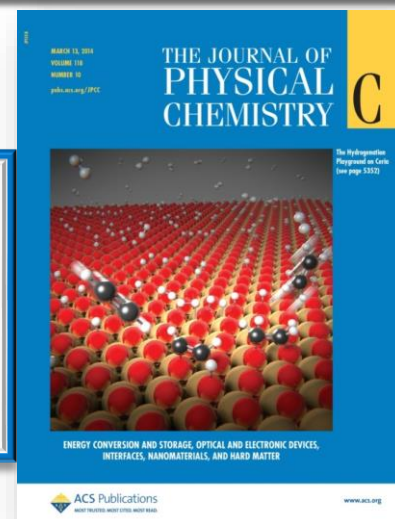
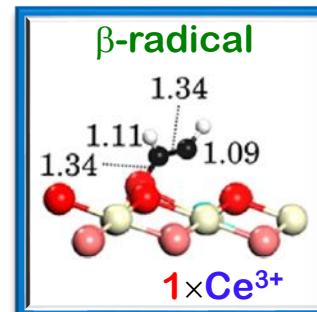


Conclusions

Partial alkyne hydrogenation

J. Phys. Chem. C 118, 5352 (2014)

Key : ability to stabilize reduced states

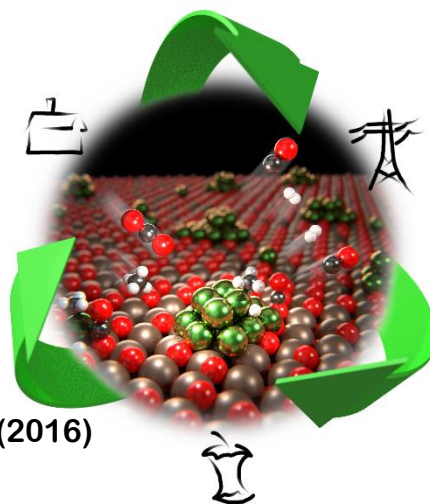


JPCA 117, 8241 (2013)

Angew. Chem. Int. Ed. 54, 3917 (2015)

Support effect

Ni/CeO₂ for DRM



Angew. Chem. Int. Ed. 55, 7455 (2016)
ACS Catal 6, 8184 (2016)

Ceria is
non-innocent

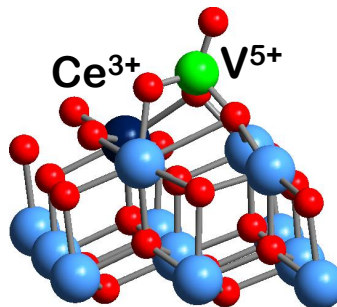


Catalysis Today 253 (2015) 20–32

Conclusions



- High catalytic activity of VO_x/ceria relates to a synergy between the ceria support and the supported oxide



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

→ **ceria –promoted by vanadia– is the active species**



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The non-innocent role of cerium oxide in heterogeneous catalysis: A theoretical perspective

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ABSTRACT

Ceria (CeO_2) is the most significant of the oxides of rare-earth elements in industrial catalysis with its reducibility being essential to its functionality in catalytic applications. The complexity of real (powder) catalysts hinders the fundamental understanding of how they work. Specifically, the role of ceria in the catalytic activity of ceria-based systems is still not fully understood. To elucidate it, well-defined ceria-based model catalysts are prepared experimentally or created theoretically and studied. The purpose of this brief review is to discuss recent results on model ceria-based catalysts using $\text{CeO}_2(111)$, $\text{VO}_x/\text{CeO}_2(111)$, and $\text{Ni}/\text{CeO}_2(111)$ as examples of catalysts for partial alkyne hydrogenation, oxidative dehydrogenation, and hydrogen production, respectively. The emphasis is here put on theoretical studies and special attention is given to the effects of ceria as catalyst support.

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**Ceria is
non-innocent**

