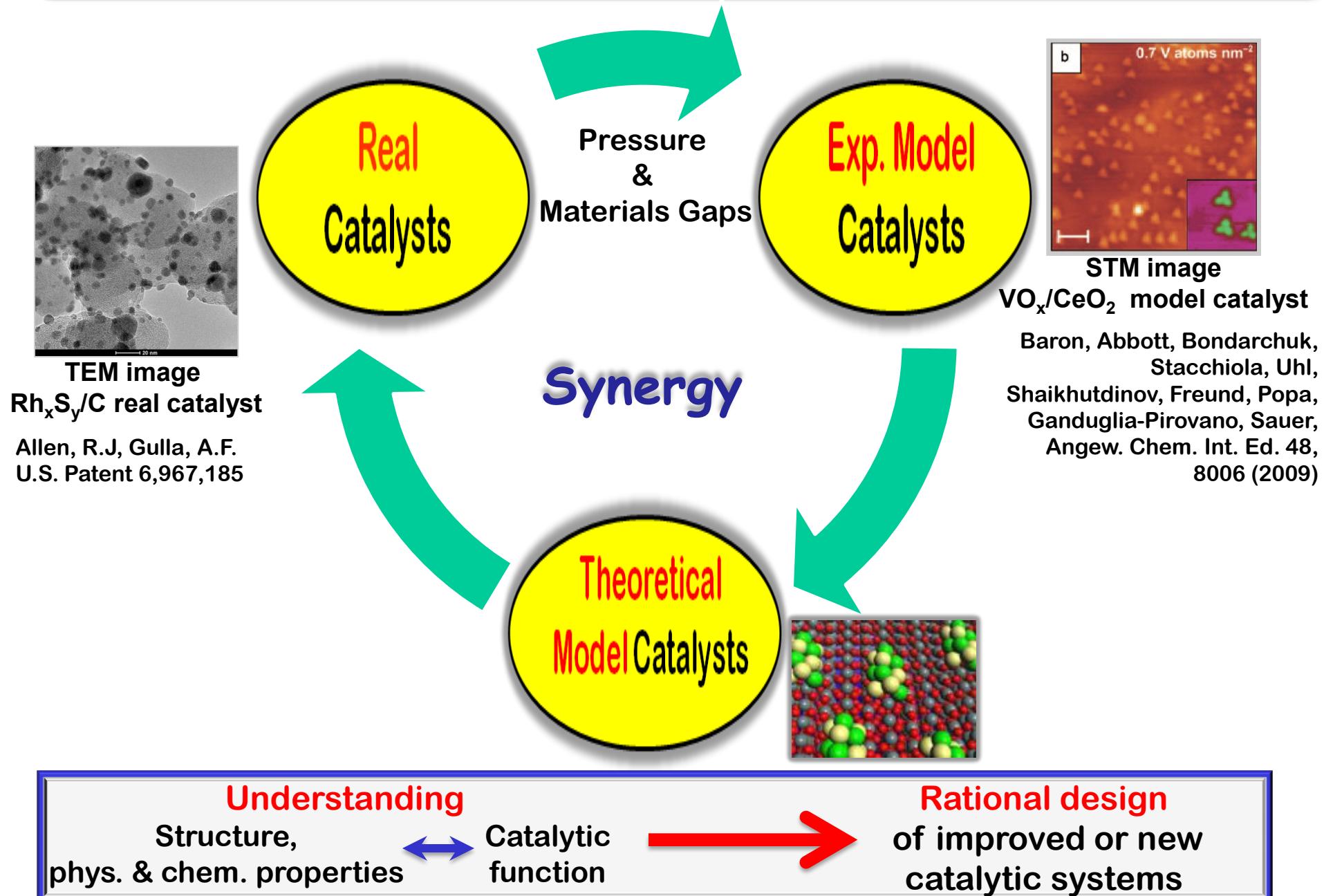


The non-innocent role of cerium oxide in heterogeneous catalysis: a theoretical perspective

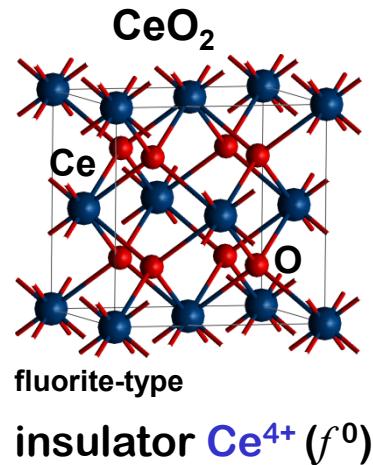
M. Verónica Ganduglia-Pirovano

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

Towards the rational design of catalysts

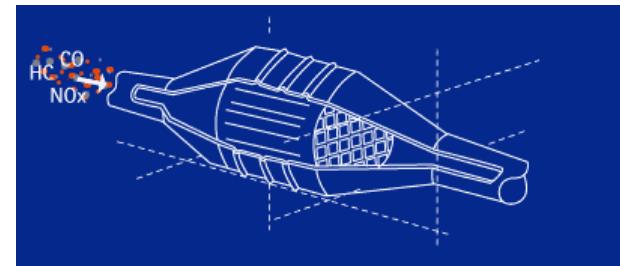


Cerium oxide: Reducibility and catalytic function



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)

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

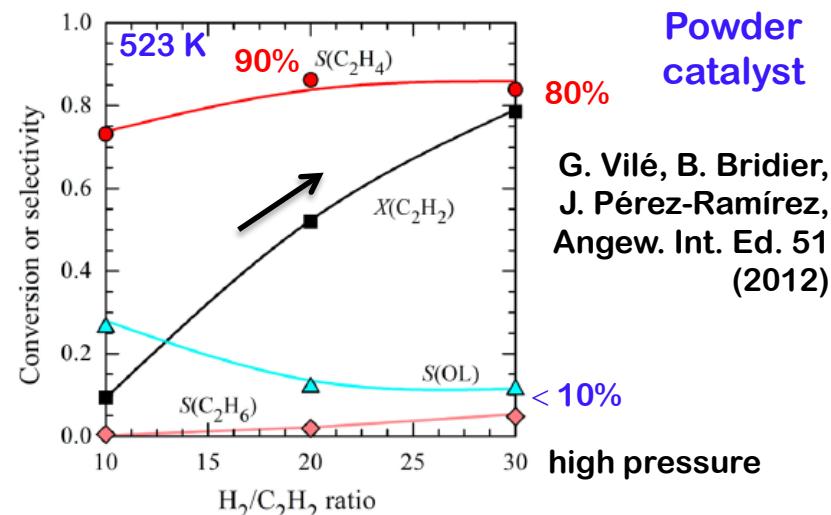
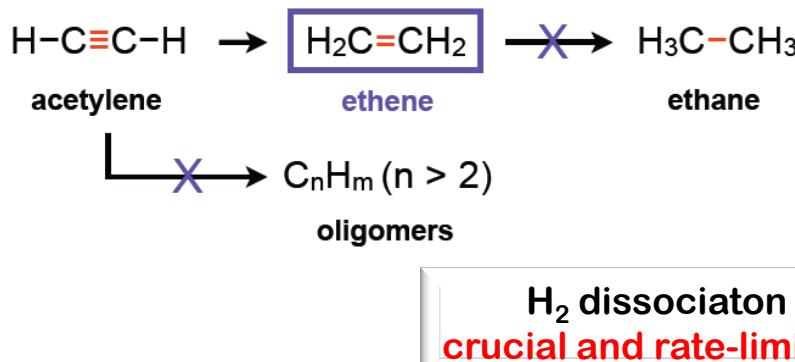
Structure and reactivity of supported nickel

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

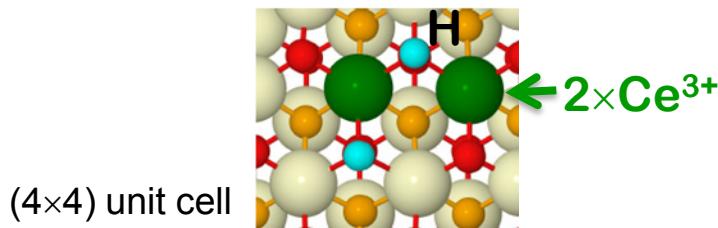


H₂ activation on CeO₂(111)

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

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

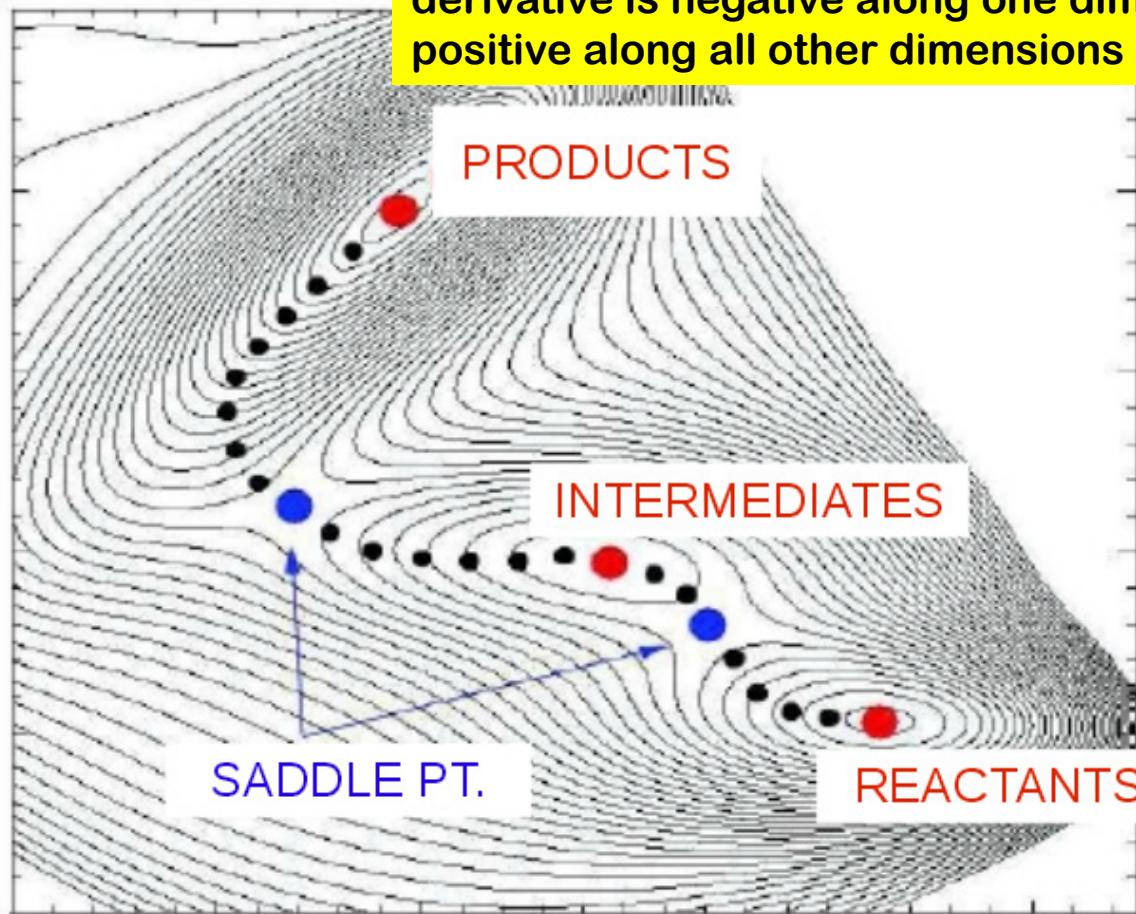
- $\text{H}_2(\text{gas}) + \text{CeO}_2(111) \rightarrow 2\text{H} / \text{CeO}_2(111)$ $\Delta E = 2.4 \text{ eV}$ highly exothermic PBE+U(4.5)



- Previous work: too low H₂ dissociation barrier ~0.2 eV !! [($\sqrt{3} \times 1$) 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

□ Initial & Final configurations known

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

□ 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

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

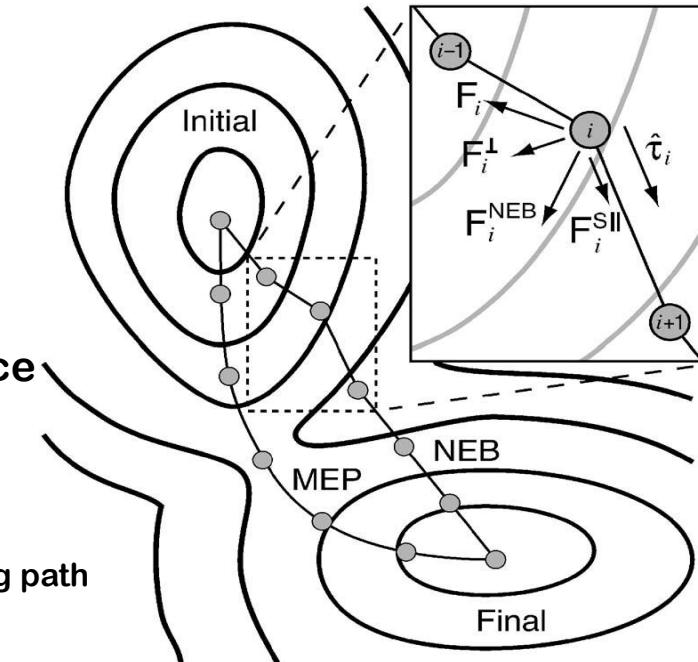
$$\vec{F}_i = -\nabla V(\vec{R}_i) + \vec{F}_i^s$$

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

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

unit tangent along path

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



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

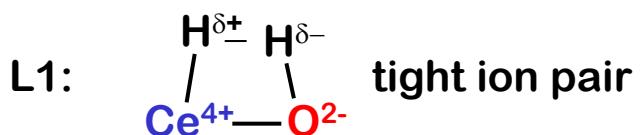
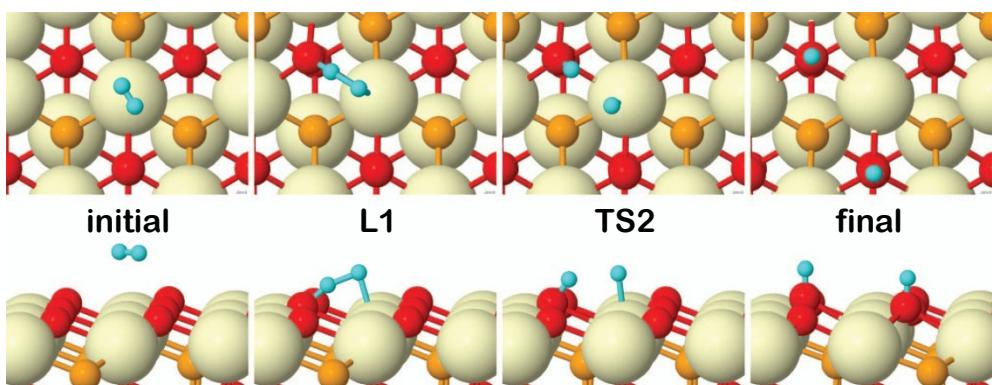
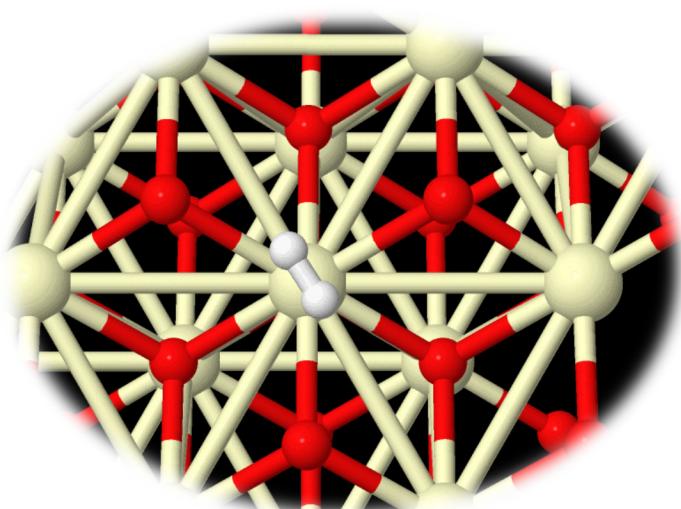
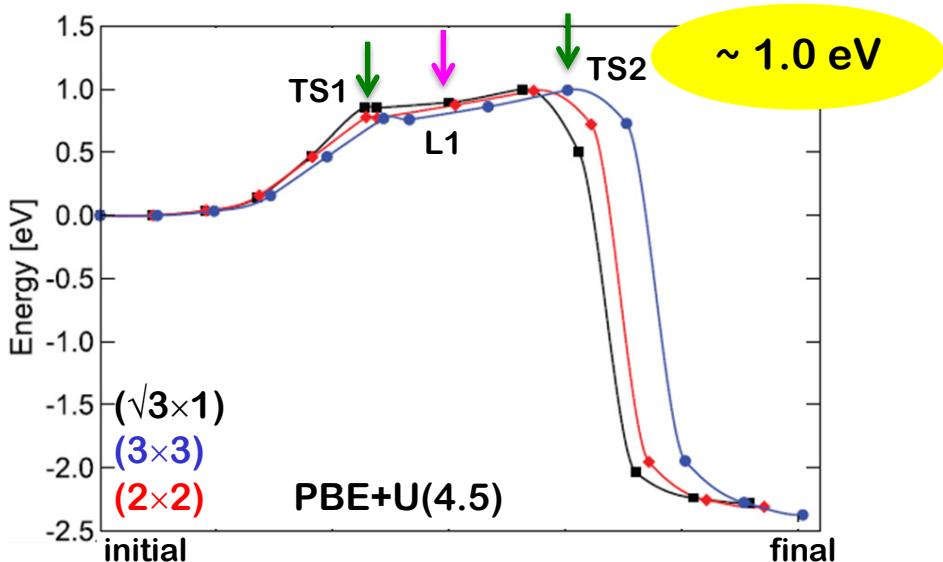
✓ True force does not interfere with image spacing \parallel to the path; they bring the band to the MEP

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

H_2 on $CeO_2(111)$: dissociation mechanism

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

- ☐ Nudged Elastic Band Method (NEB)
 2×5 images

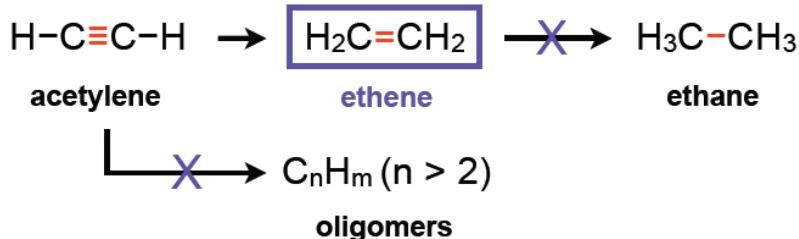


TS2: Ce–H and O–H bonds

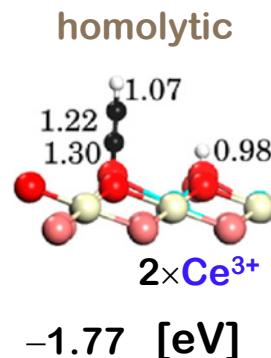
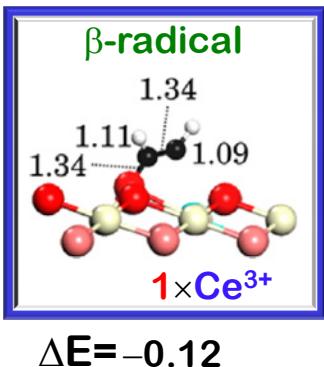
Final: $2 \times$ O–H bonds

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

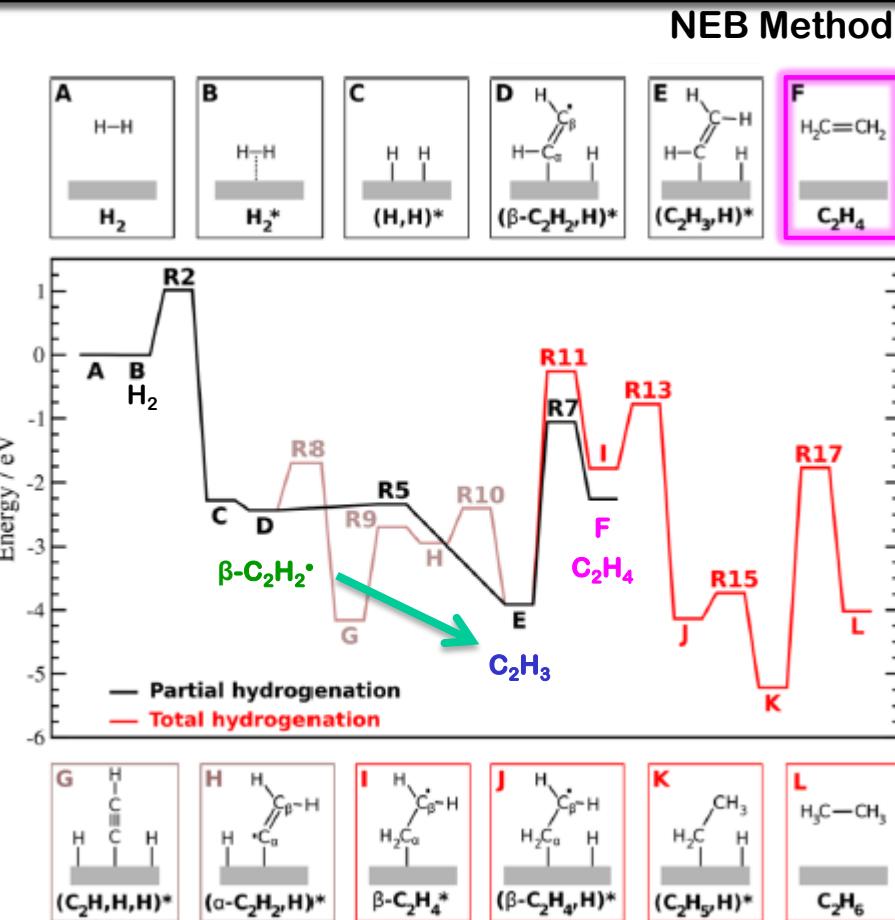
Ceria as stand-alone catalyst



H₂ activation on CeO₂(111)



Ceria ability to stabilize reduced states: a key property



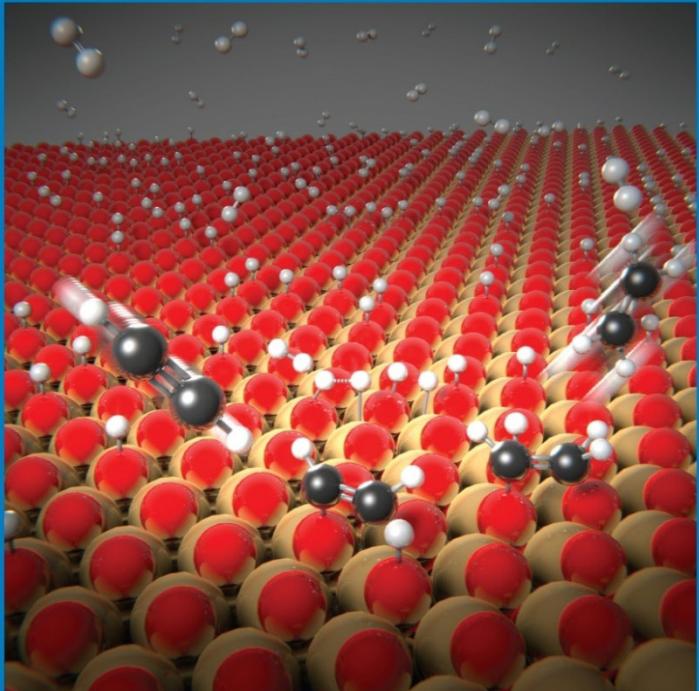
- ❑ H_2 dissociation → limiting step
 - ❑ Highly reactive $\beta\text{-C}_2\text{H}_2^{\bullet}$ radical species form C_2H_3
→ “barrierless”
 - ❑ Oligomer formation only at low $\text{H}_2/\text{C}_2\text{H}_2$ ratios;
neighboring O sites not available at high ratios

Ceria as stand-alone catalyst

JPCC

MARCH 13, 2014
VOLUME 118
NUMBER 10
pubs.acs.org/JPCC

THE JOURNAL OF PHYSICAL CHEMISTRY C



The Hydrogenation
Playground on Ceria
(see page 5352)

Molecular-Level Understanding of CeO₂ 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)

ENERGY CONVERSION AND STORAGE, OPTICAL AND ELECTRONIC DEVICES,
INTERFACES, NANOMATERIALS, AND HARD MATTER

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)

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

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

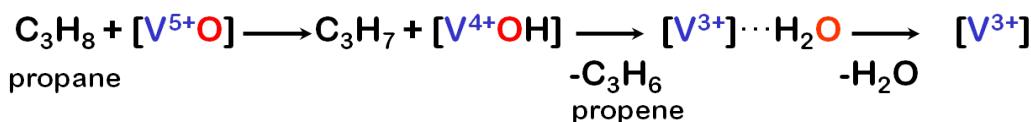


- Important catalysts in oxidation reactions

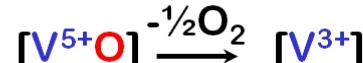
- SO_2 to SO_3 in the production of sulfuric acid
- benzene to maleic anhydride (polyester resins)
- oxidative dehydrogenation alkanes to alkenes, methanol to formaldehyde



Reducibility is key to their catalytic function



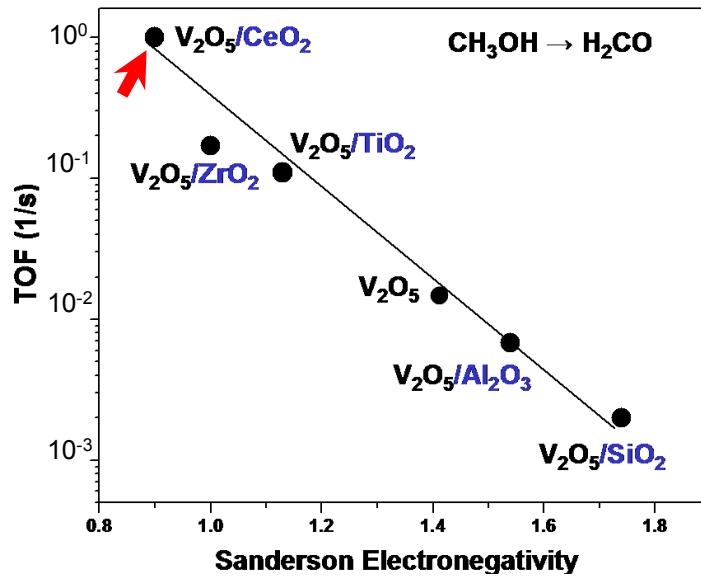
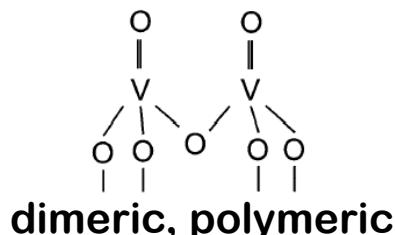
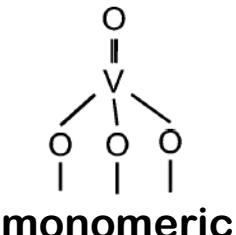
Reactivity Parameter



Oxygen defect formation

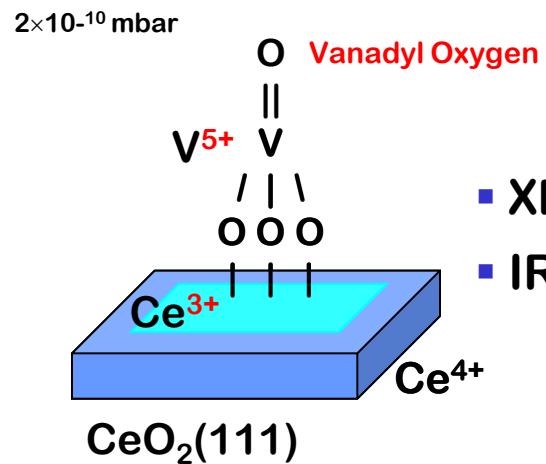
- The specific support affects the structure and catalytic performance

How does vanadia 'sit' on the support?

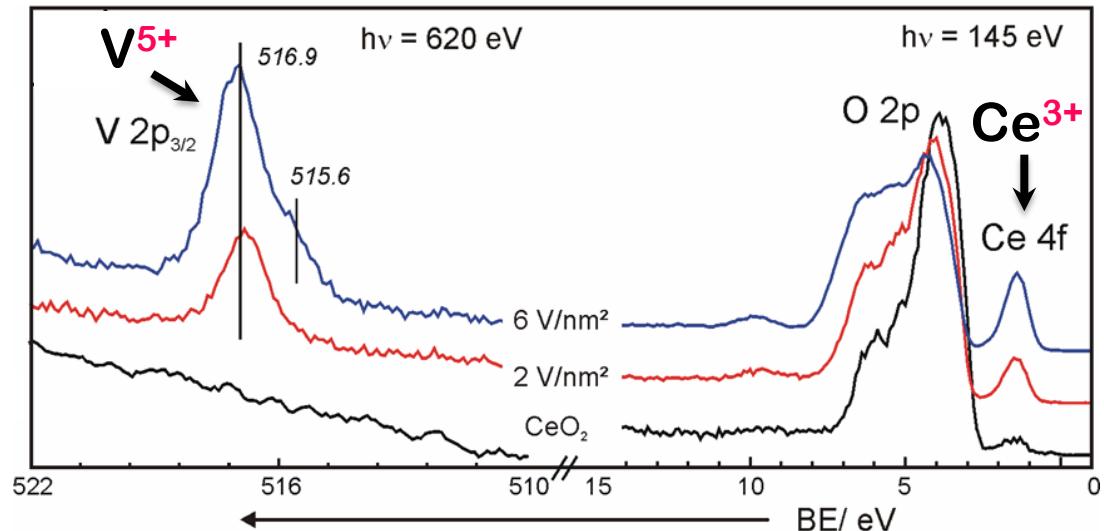


VO_x/ceria : The experimental facts

Experimental model



- XPS: Ce³⁺ and V⁵⁺
- IR: V=O stretch (1000–1040 cm⁻¹)



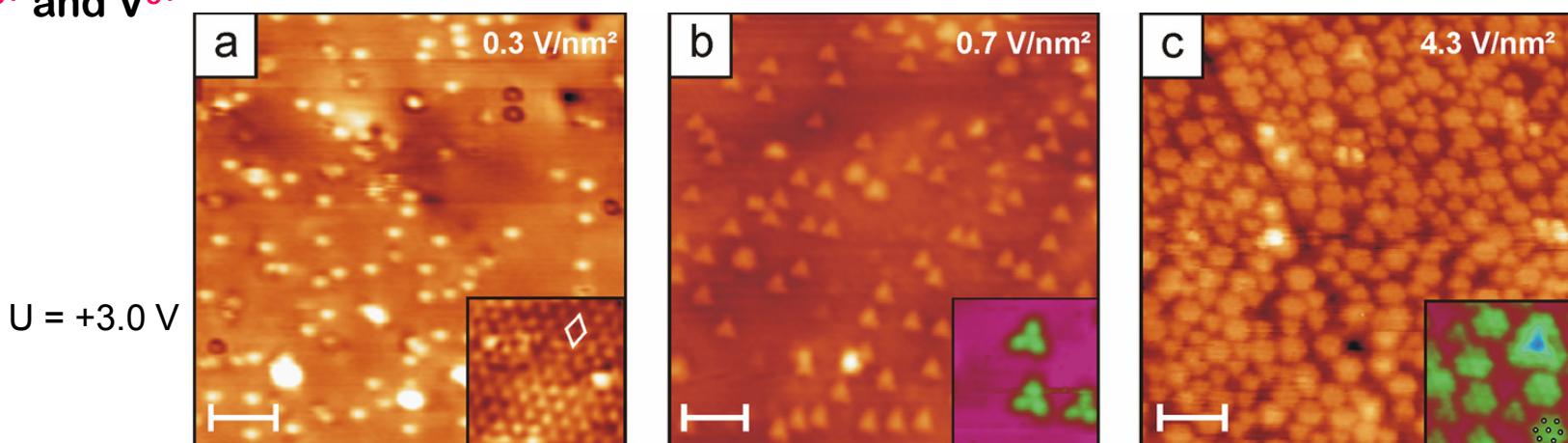
Powder samples:

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

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

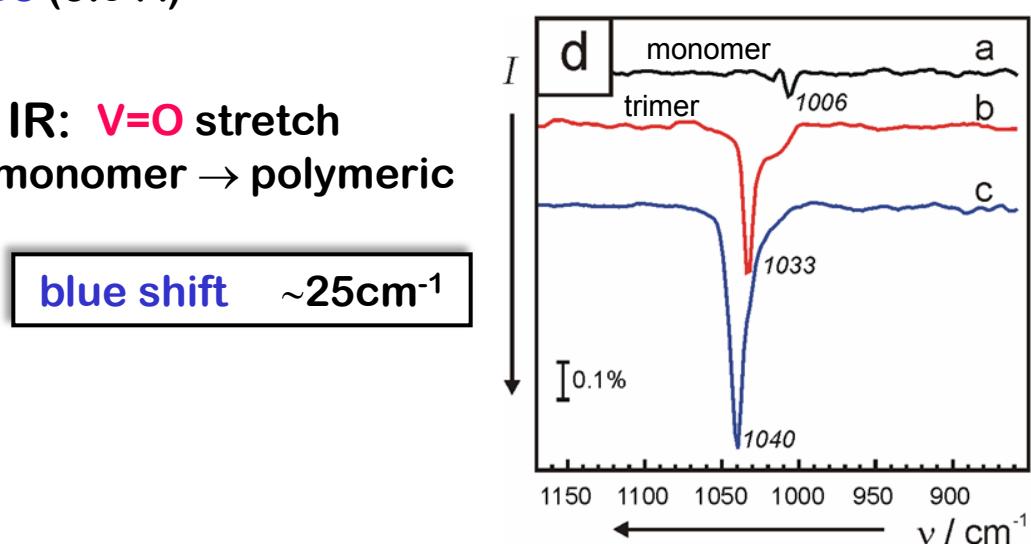


Monomers, dimers, trimers: similar apparent height → „flat“ structures

Trimer: spot-spot distance $\sim \text{CeO}_2$ lattice (3.9 Å)

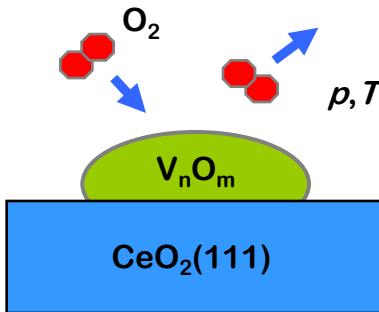
- IR: V=O stretch
monomer \rightarrow polymeric

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



Theoretical Models: The strategy

V_nO_m on $CeO_2(111)$



- Surface functional groups?
- Support effect ?
- Reactivity

DFT+U & statistical thermodynamics → Structure

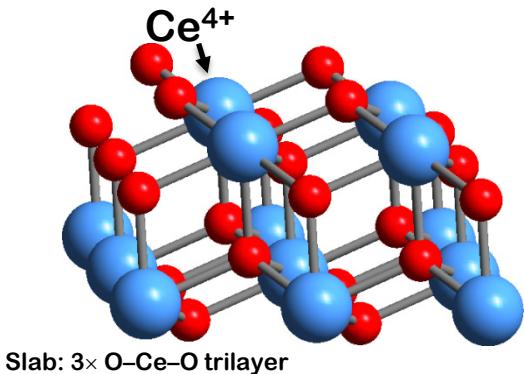
- Thermodynamic stability → surface free energy $\gamma [\mu_i(T, p_i)]$
- Electronic structure
- Vibrations (IR); diagonalization of Mass-Weighted Hessian Matrix
- Reactivity

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

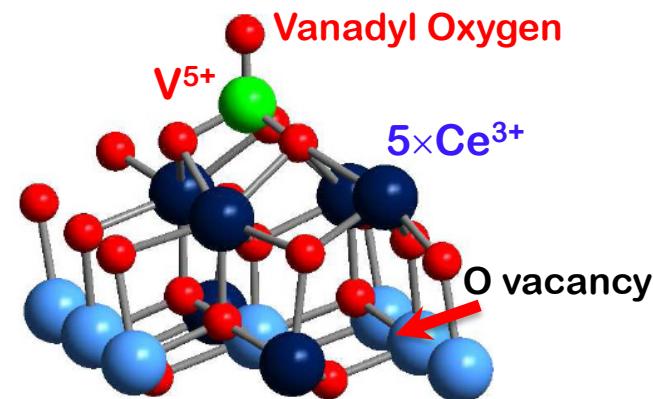
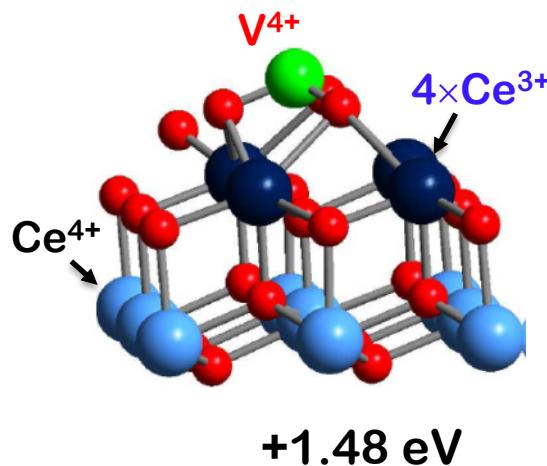
Monomeric Species



$\text{CeO}_2(111)$



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

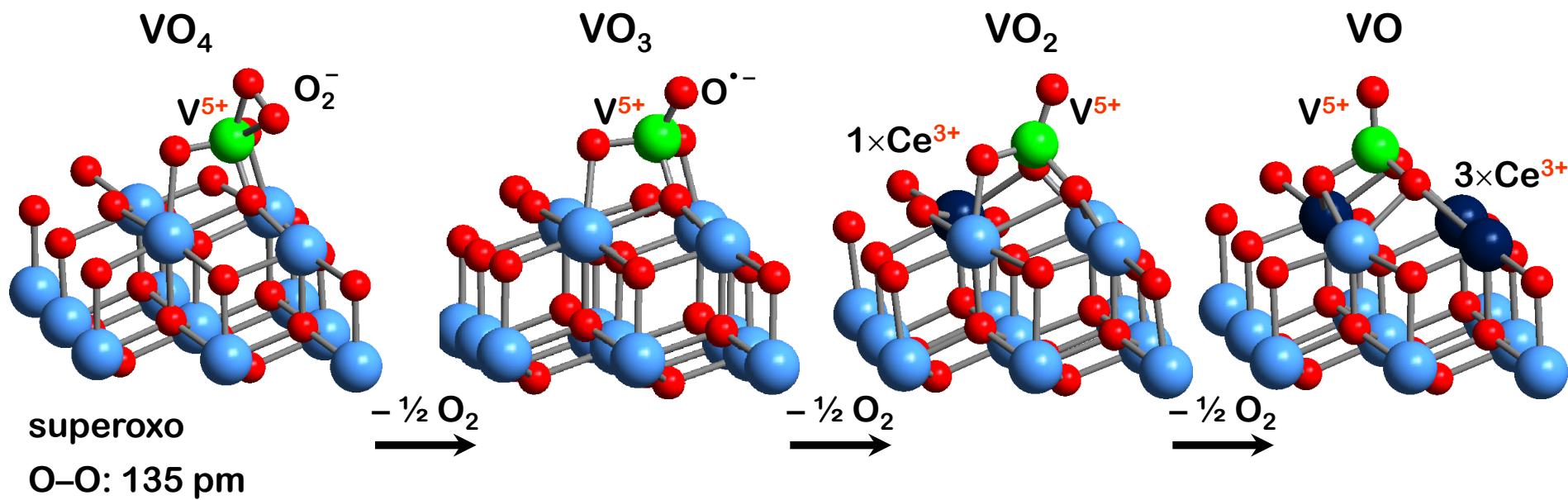


consistency with experiment



Theoretical models

Monomeric Species



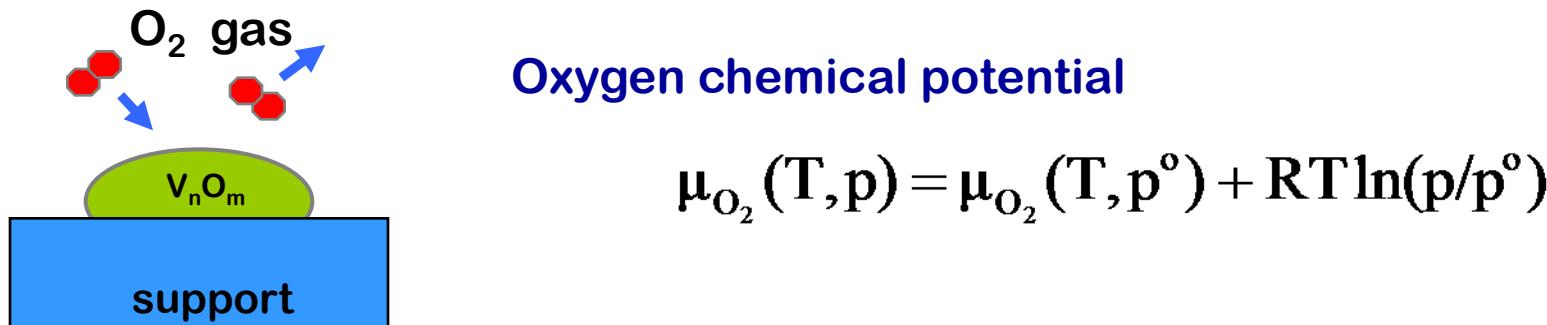
Vanadia species are **NOT** reduced!

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



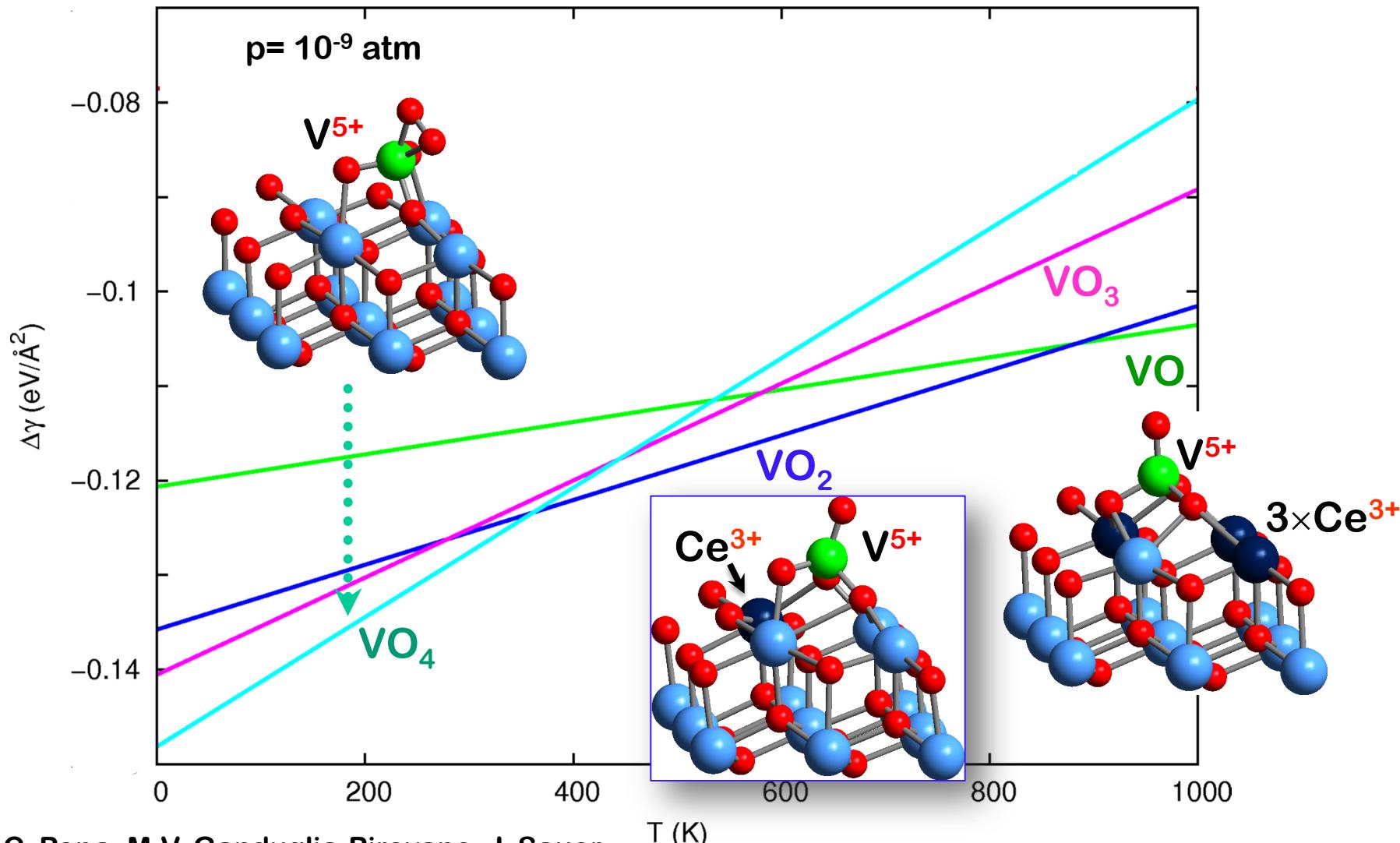
$$\Delta\gamma(T,p) = [G^{\text{V}_m\text{O}_n/\text{CeO}_2} - G^{\text{CeO}_2} - \mu_{\text{V}} - n \cdot \frac{1}{2} \mu_{\text{O}_2}(T,p)] / A$$

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



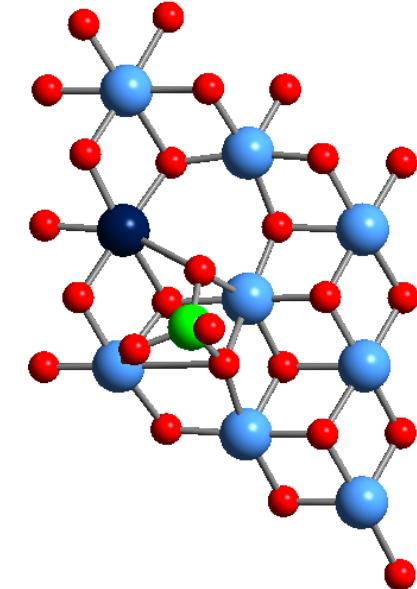
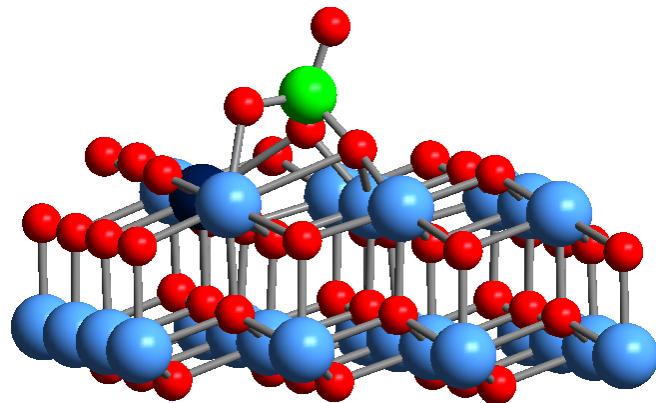
VO_n/ceria monomers: Phase diagram

Monomeric Species



IR spectra and the nature of the supported species

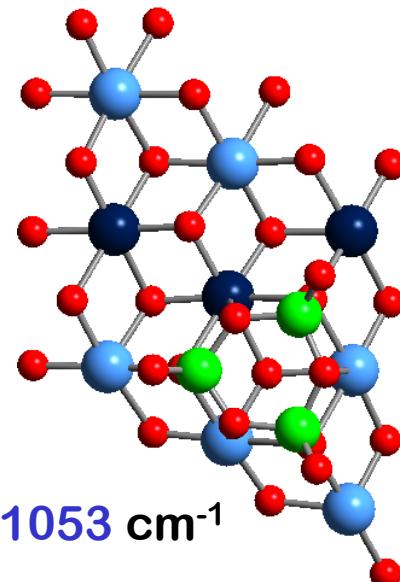
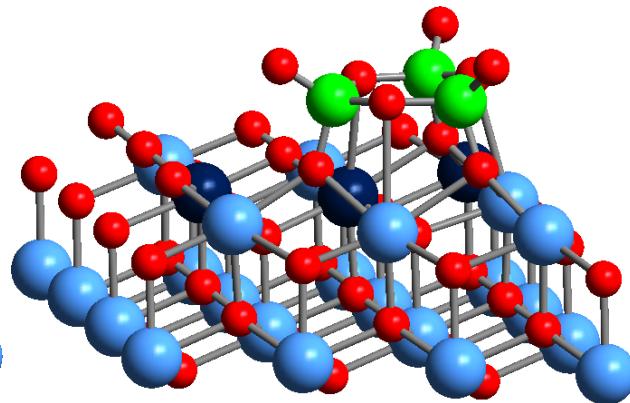
monomer VO_2



1036 cm^{-1}

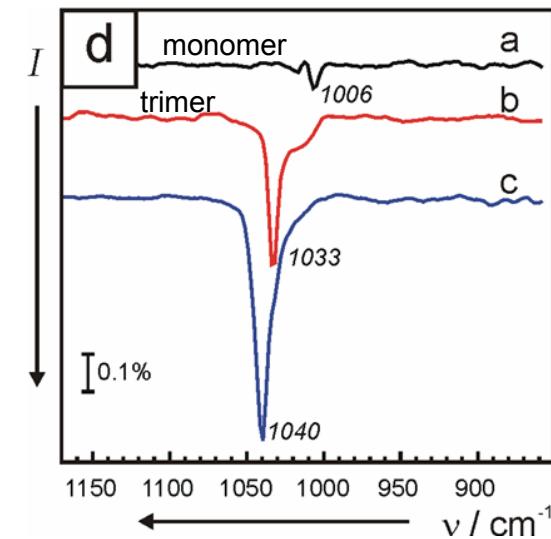
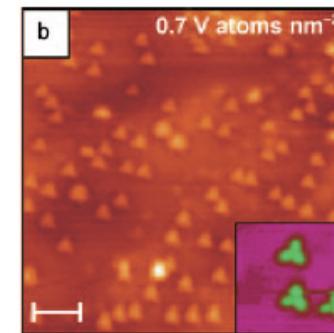
blue shift $\sim 30 \text{ cm}^{-1}$

trimer 3VO_2



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

1070 cm^{-1}

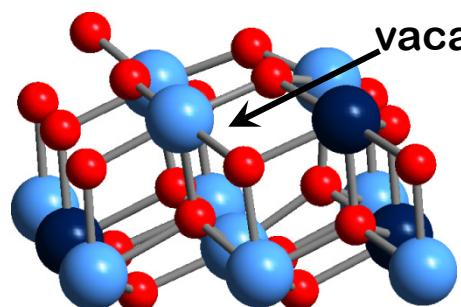


blue shift $\sim 25 \text{ cm}^{-1}$

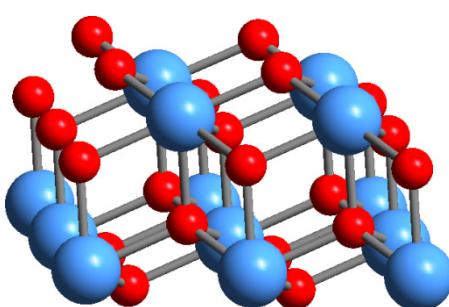
Morphology □ Vibrations

Reactivity: The origin of the support effect

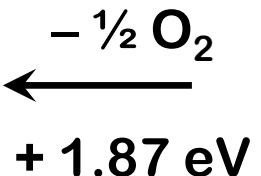
$\text{CeO}_{2-x}(111)$



$\text{CeO}_2(111)$

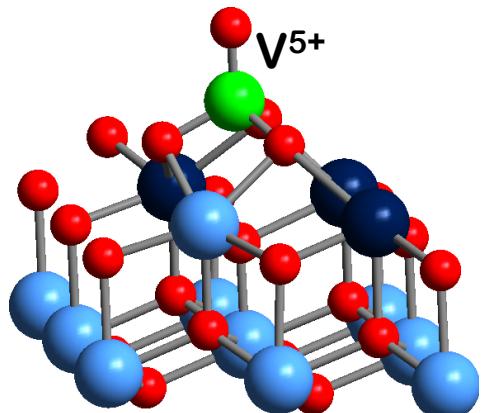


$2 \times \text{Ce}^{3+}$

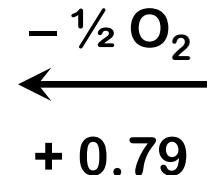


Reactivity Parameter

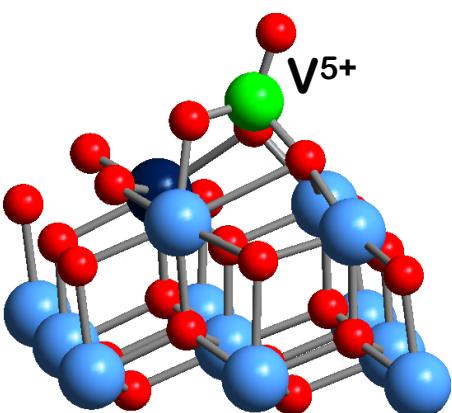
$\text{VO/CeO}_2(111)$



$3 \times \text{Ce}^{3+}$



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



$1 \times \text{Ce}^{3+}$

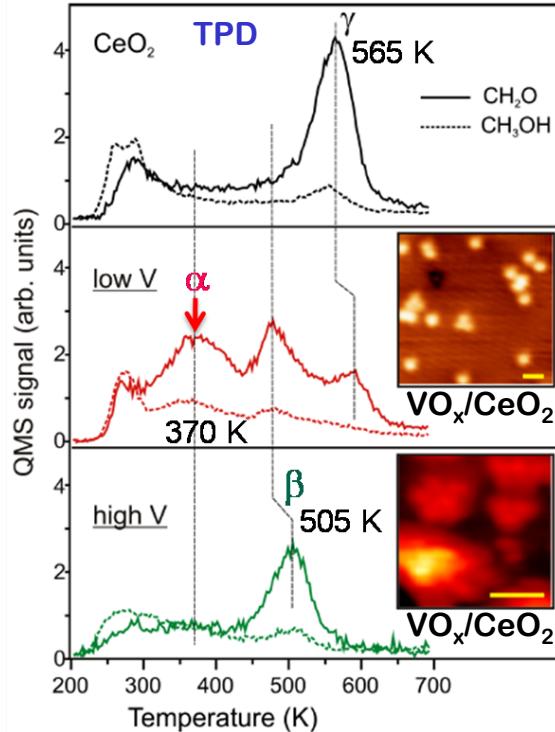
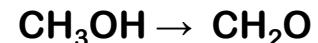
PBE+U [eV]

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

JACS 132, 2345 (2010)

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

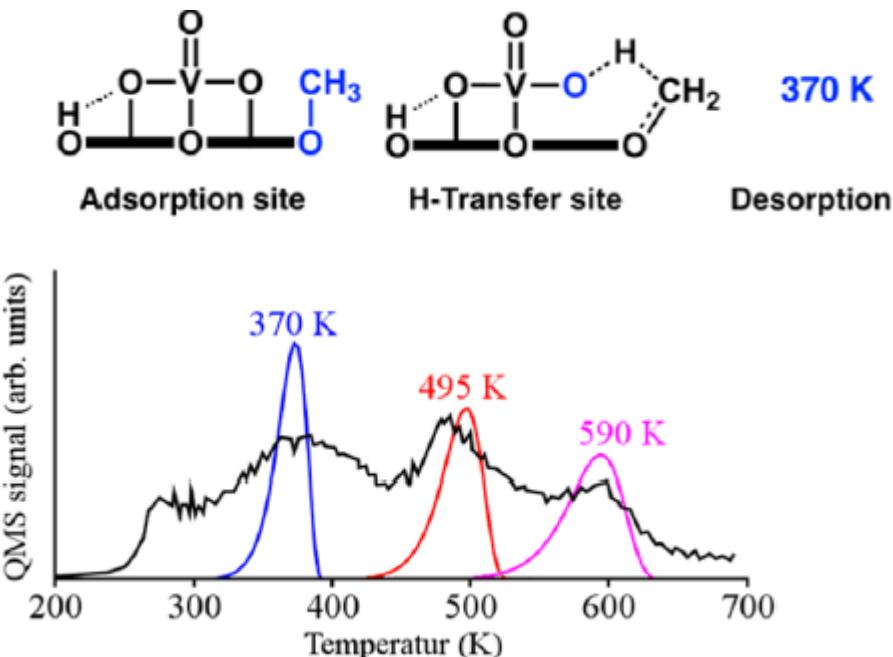
Reactivity



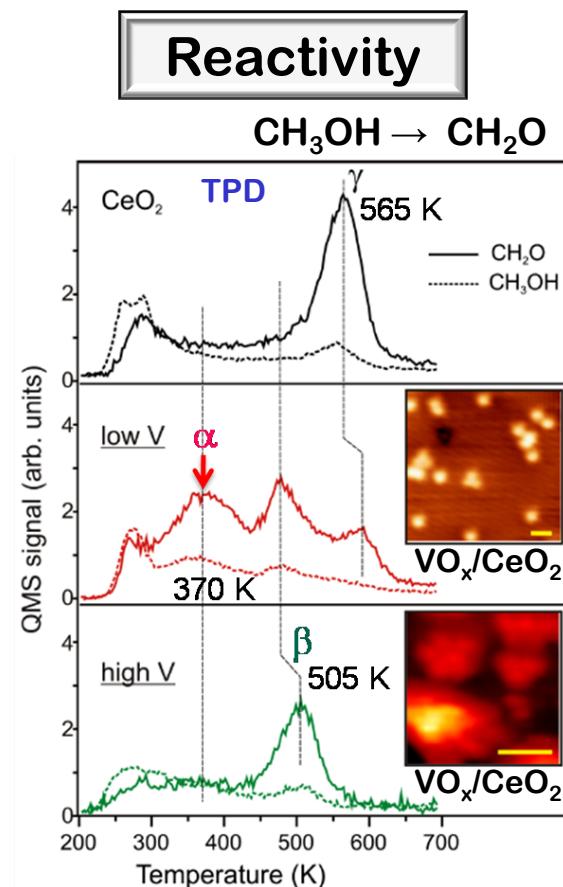
Origin of the high catalytic activity is the ability of ceria to stabilize reduced states by accommodating electrons in localized f-states, which is promoted by the vanadia species

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)



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



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

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)

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

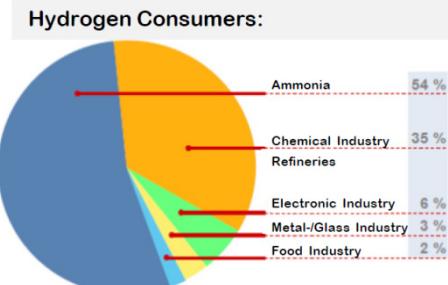
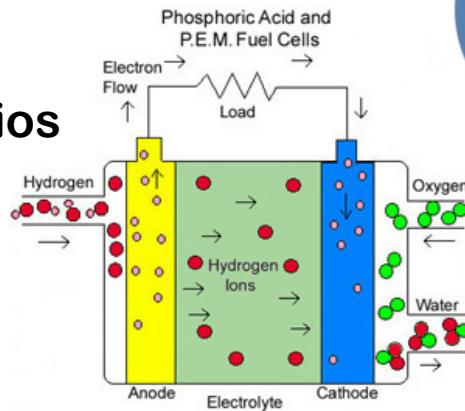
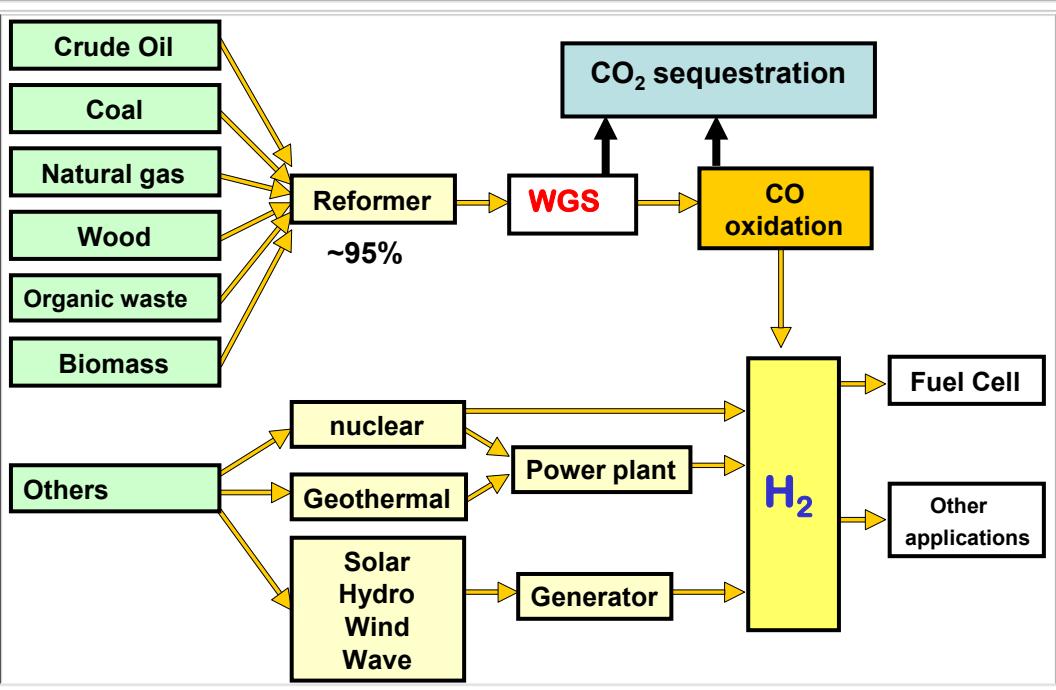
Structure and reactivity of supported nickel

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

H₂ production



Fuel cells
mobile and stationary
applications

- Steam reforming of hydrocarbons:
 $\text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightarrow n\text{CO} + (\text{n-m}/2)\text{H}_2$
- Fuel contains 1-10% CO
 \rightarrow Pt electrode degradation
- Water-gas shift:
 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$
 to remove the CO

Ceria supported Ni catalysts for H₂ production

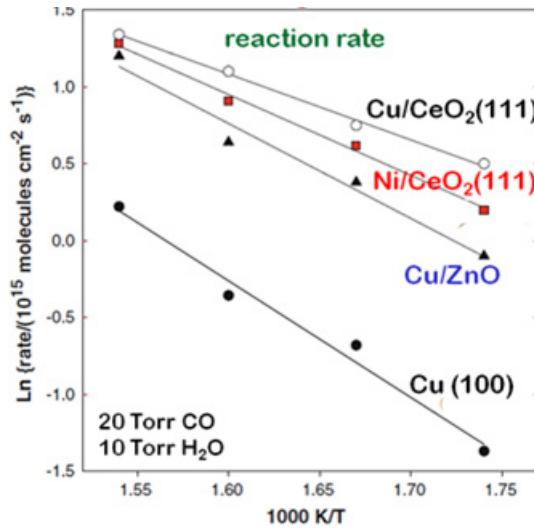
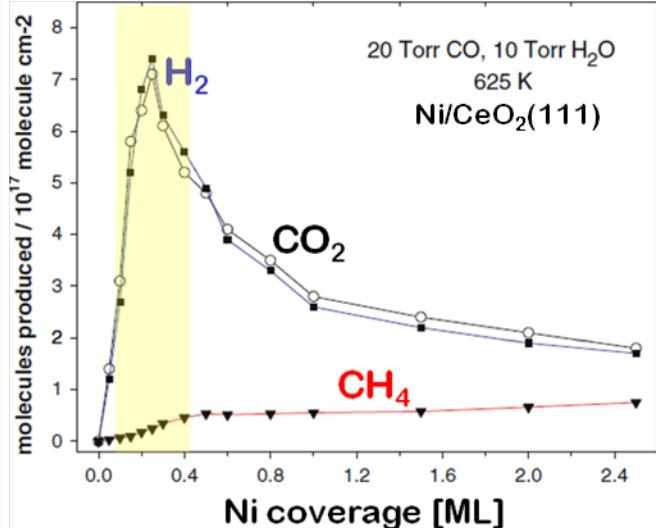


- conventional catalyst: mixed Fe and Cr or Cu and Zn oxides → drawback: long preconditioning
- new catalysts: precious metal–Pt, Au–particles supported by reducible oxides–TiO₂, CeO₂



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*:
 H_2O dissociation

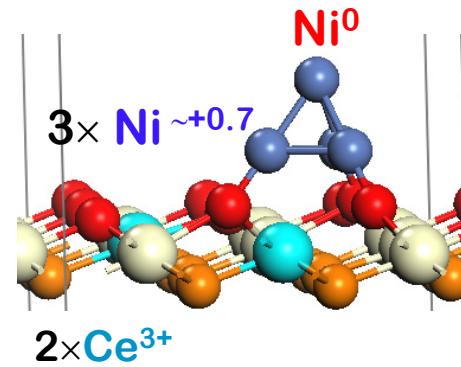
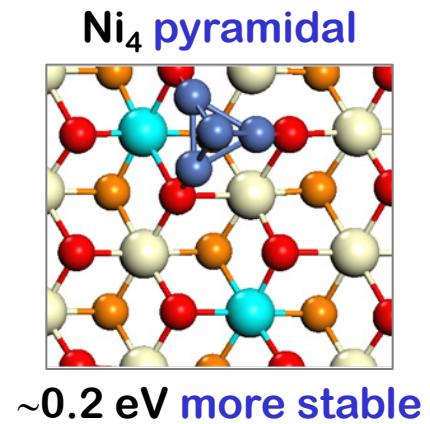
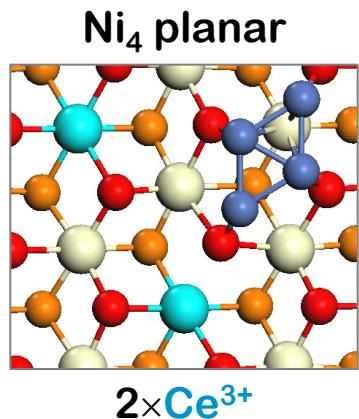
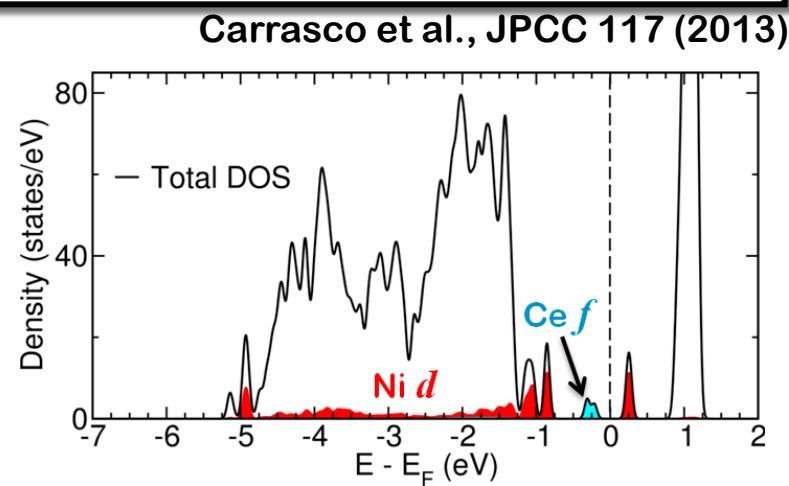
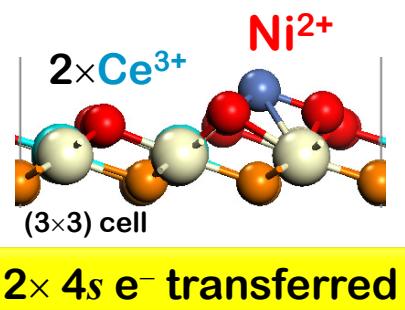
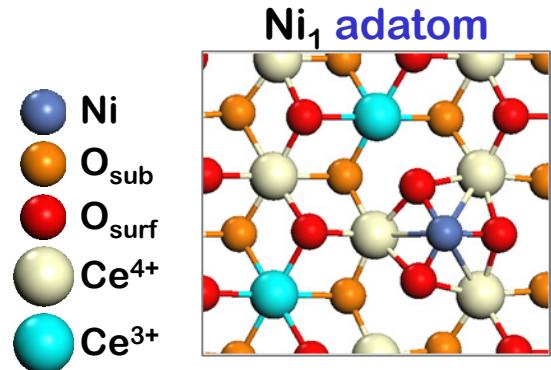
Reactivity*:
CO and C adsorption

*comparison
CeO₂(111) and Ni(111)

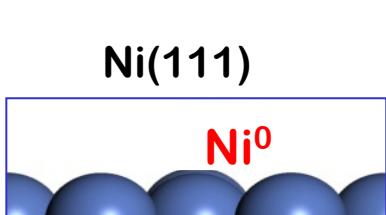
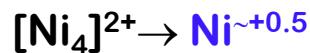


Ambient-Pressure X-ray Photoelectron Spectroscopy

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



~0.2 eV more stable



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)

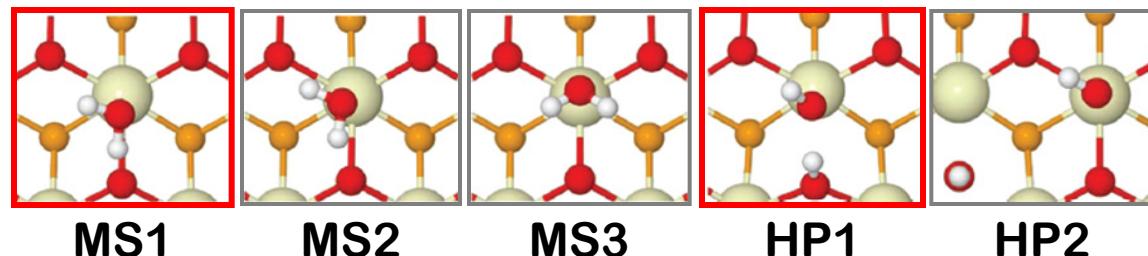
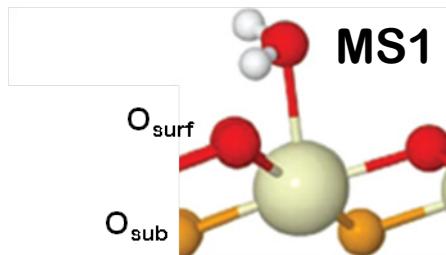
¹JCP 125, 204704 (2006)

² ChemPhysChem 8, 849 (2007)

³ JPCC 111, 15337 (2007)

⁴ PCCP 11, 9188 (2009)

⁵ JPCC 114, 14891 (2010)



Theory:

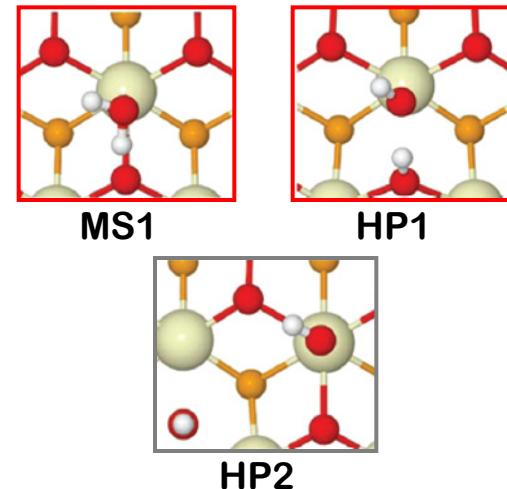
Reference	Method	Unit cell	MS1	MS2	MS3	HP1	HP2
Kumar and Scheling ¹	PW91	2x1	-0.58	-	-	-	-
Chen et al ²	PW91	$\sqrt{3} \times 1$	-0.49	-0.52	-	-	-
Watkins et al ³	PW91	$2 \times \sqrt{2}$	-	-	-0.35	-0.65	-0.15
Watkins et al ³	PW91+U(5 eV)	$2 \times \sqrt{2}$	-	-	-0.36	-0.66	-0.16
Fronzi et al ⁴	PBE	2x2	-	-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



vdW-DF:

$$E_{\text{xc}} = E_{\text{x}}^{\text{GGA}} + E_{\text{c}}^{\text{LDA}} + E_{\text{c}}^{\text{nl}}$$

OPT86b-vdW

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

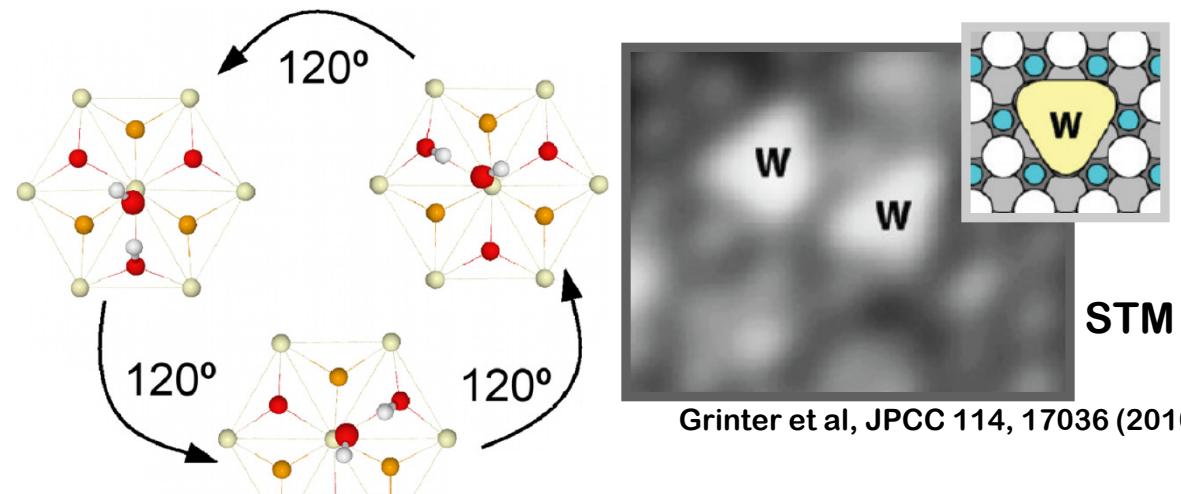
- Water dissociation → NOT favorable
- Molecular & hydroxyl pair → close in energy
- $E_{\text{ad}} \sim 0.7 \text{ eV}$ (exp ~ 0.9 eV)
- vdW contribution to binding ~ 0.18 eV

Consistency with triangular shape?

H₂O/ceria: DFT prediction

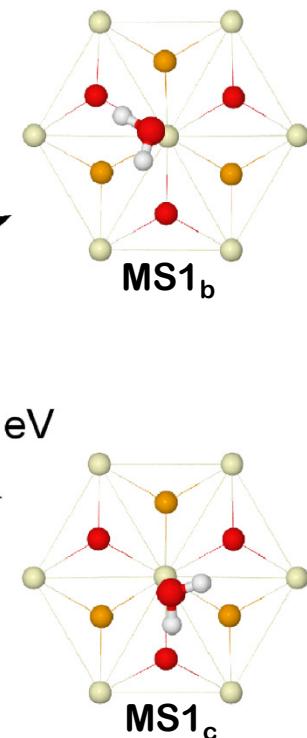
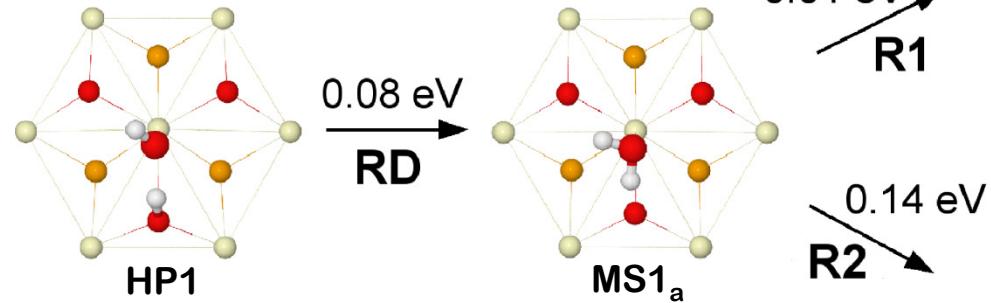
D. Fernández-Torre, K. Kósmider, J. Carrasco, M.V. Ganduglia-Pirovano, R. Pérez, JPCC 112, 13584 (2012)

- Hopping between equivalent HP1/MS1 structures → triangle



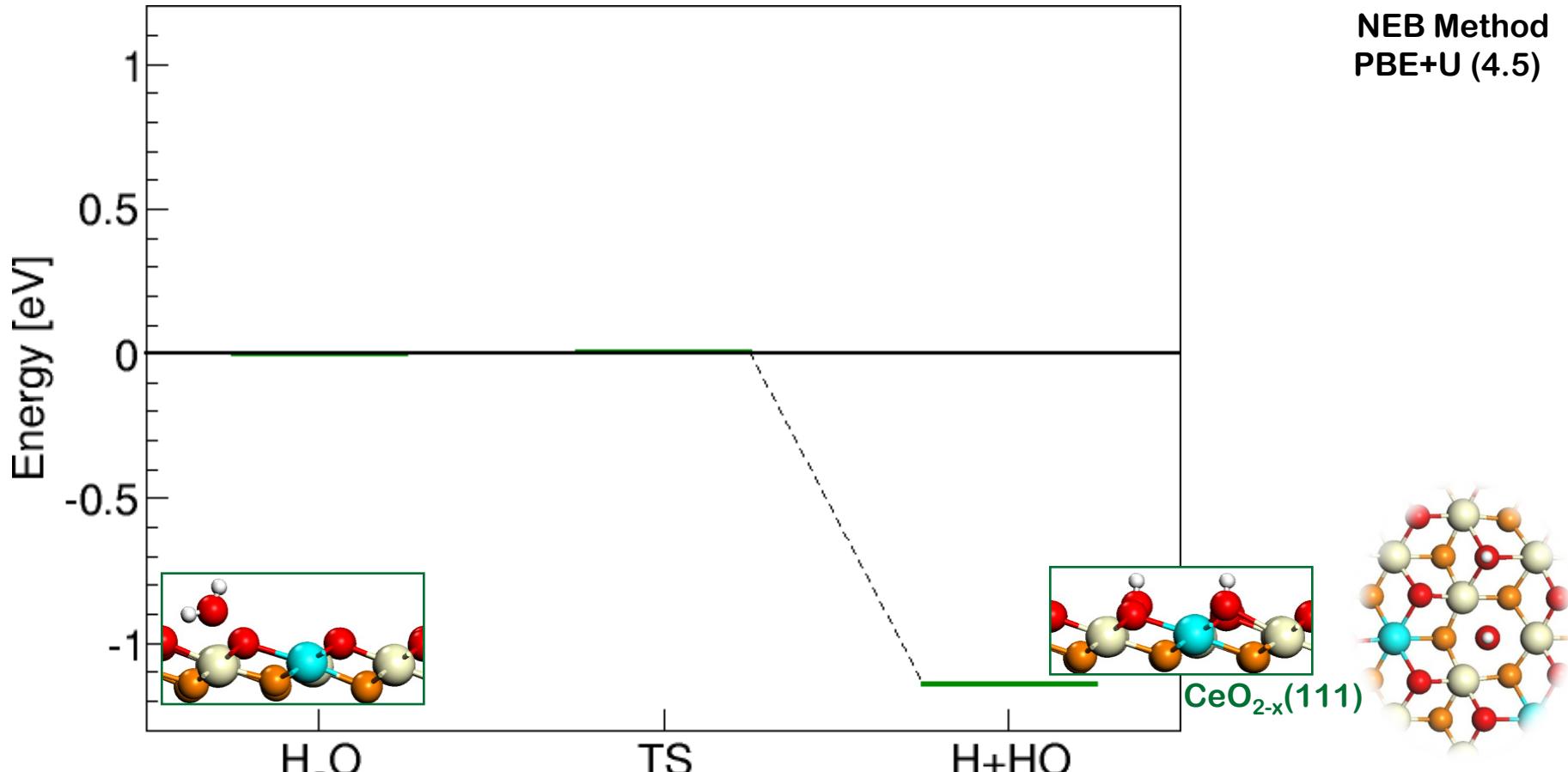
Grinter et al, JPCC 114, 17036 (2010)

- Hop via recombination & rotation & splitting with low barriers



MS1 and HP1 are consistent with triangular shape!

Water dissociation on Ni/CeO₂(111)

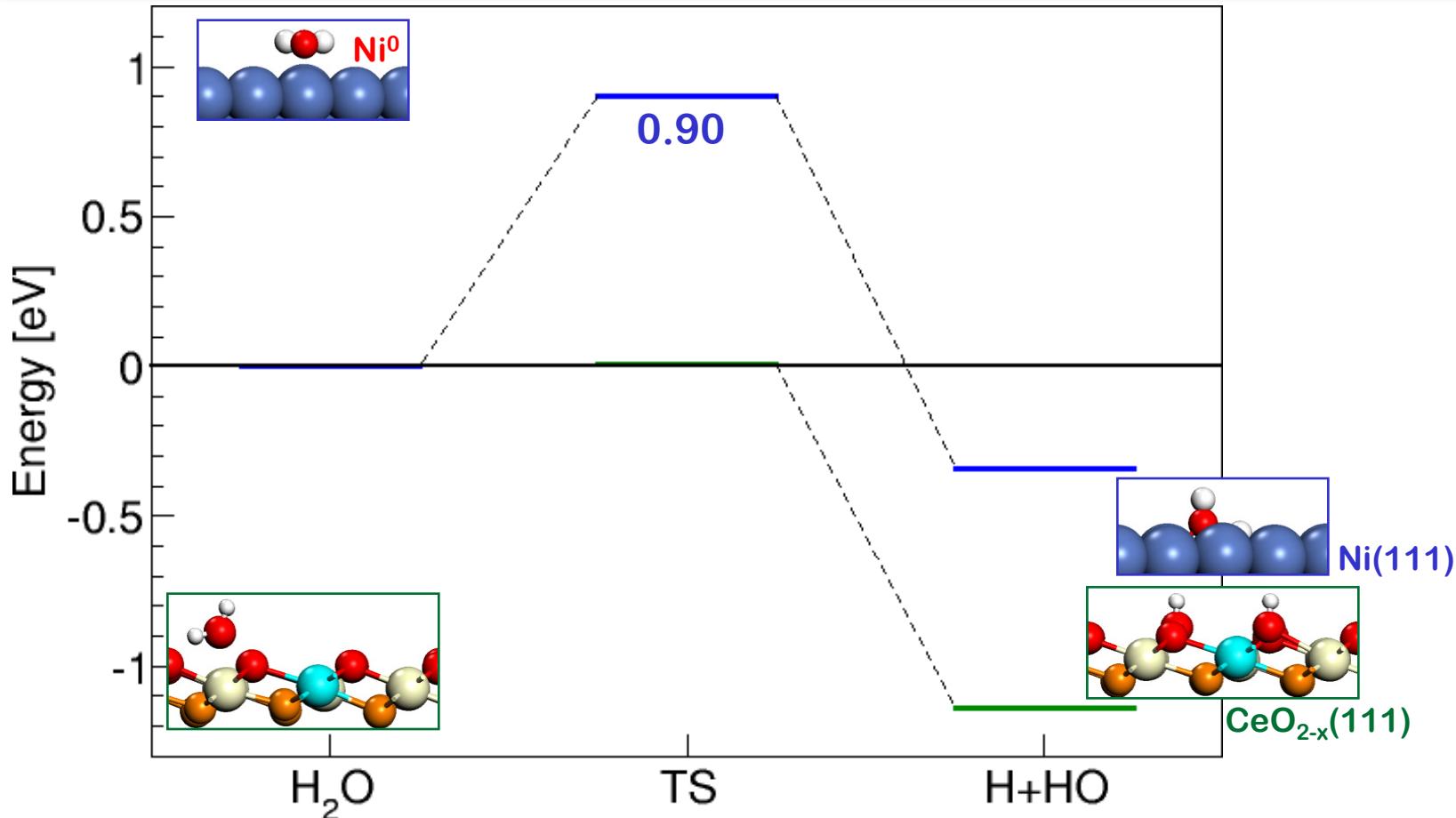


■ CeO_{2-x}(111): barrierless¹ → strongly bound OH species

In agreement:

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

Water dissociation on Ni/CeO₂(111)



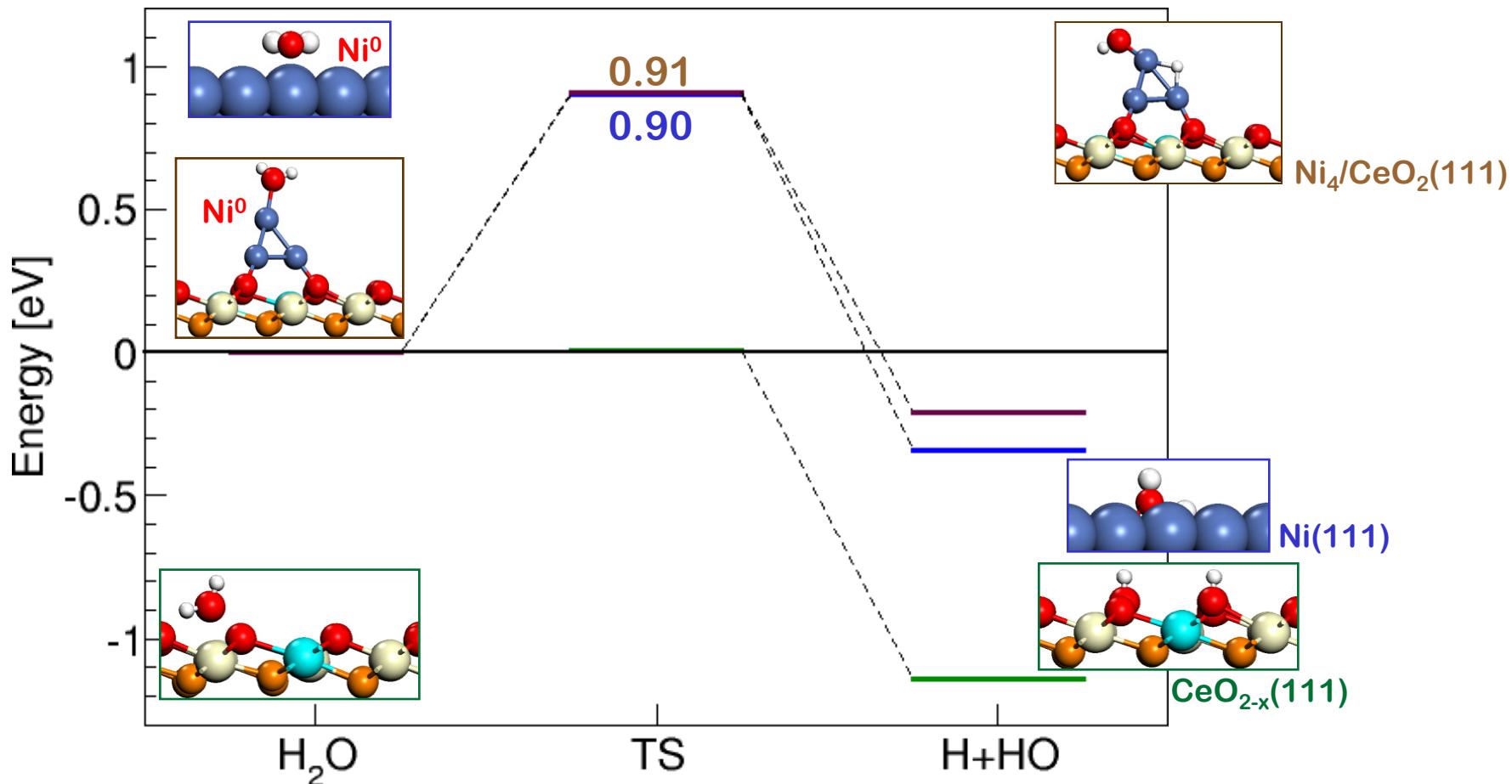
- CeO_{2-x}(111): barrierless¹ → strongly bound OH species
- Ni(111): high barrier² → moderately bound OH species

In agreement:

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

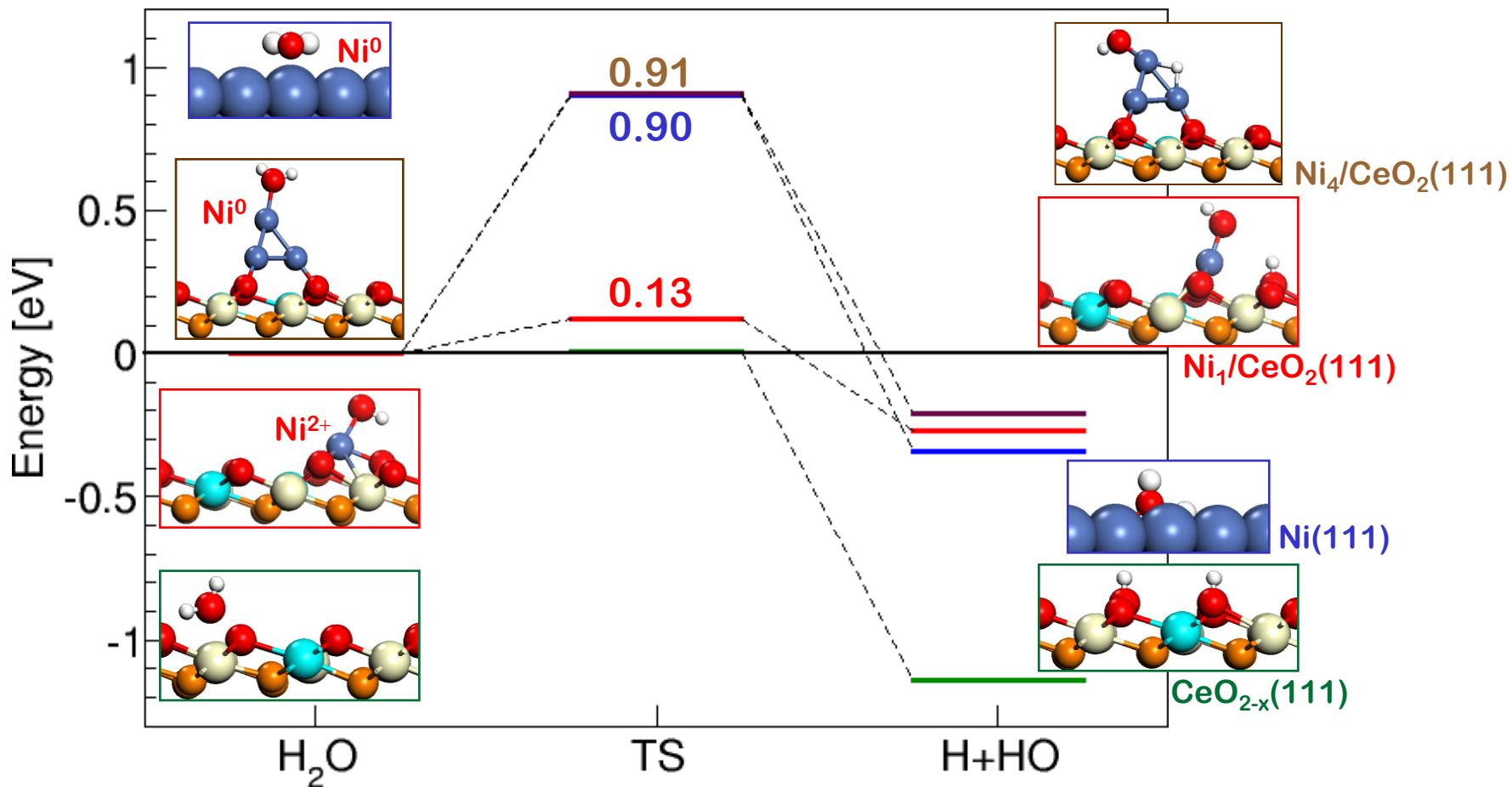
² A. A. Phatak et al., J. Phys. Chem. C 113, 7269 (2009).

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

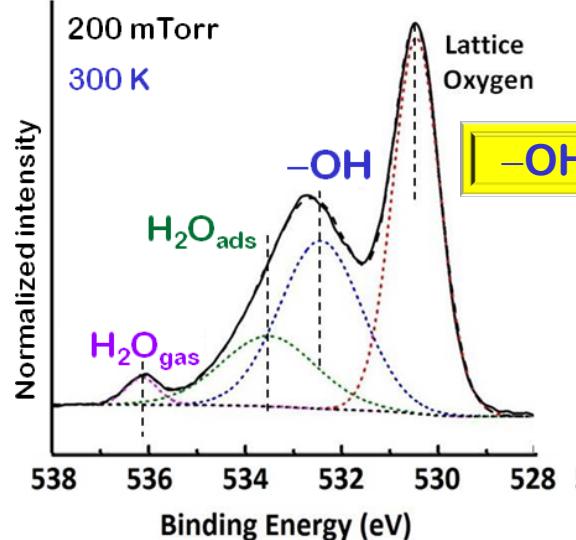
Ni²⁺ species –in direct contact with the support – are able to fastly cleave O–H bonds

H_2O dissociation: ambient-pressure X-ray photoelectron spectroscopy

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

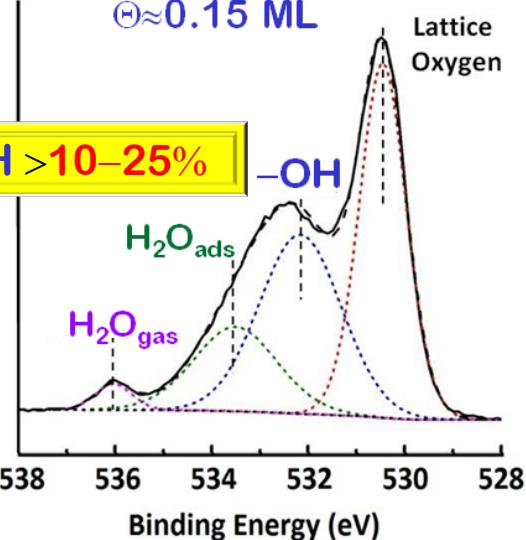
O1s XPS spectra

$\text{CeO}_2(111)$



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

$\Theta \approx 0.15 \text{ ML}$

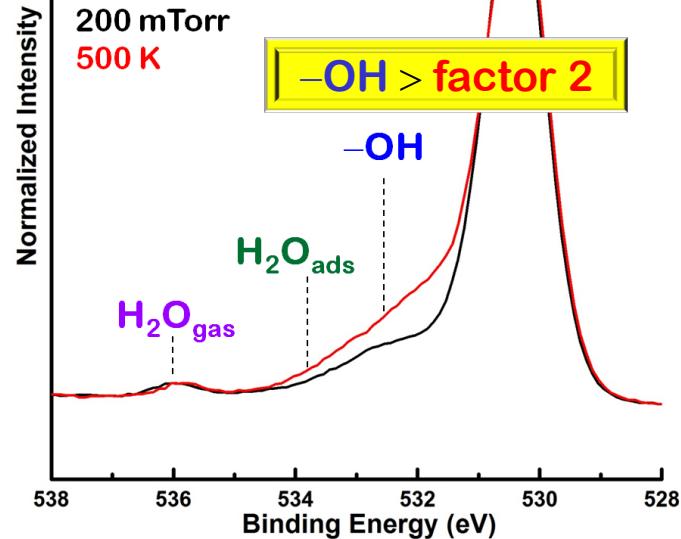


$\text{CeO}_2(111)$

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

200 mTorr

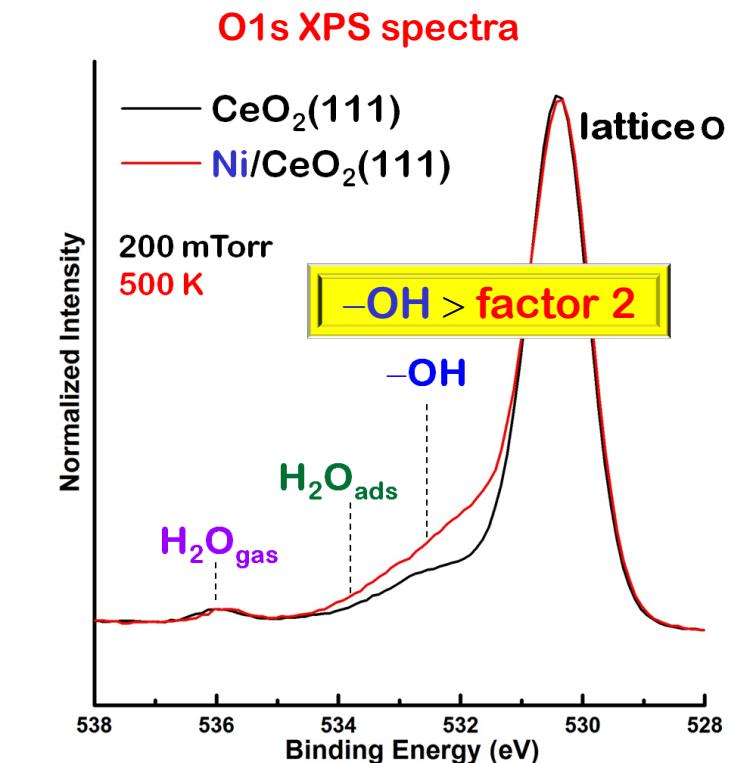
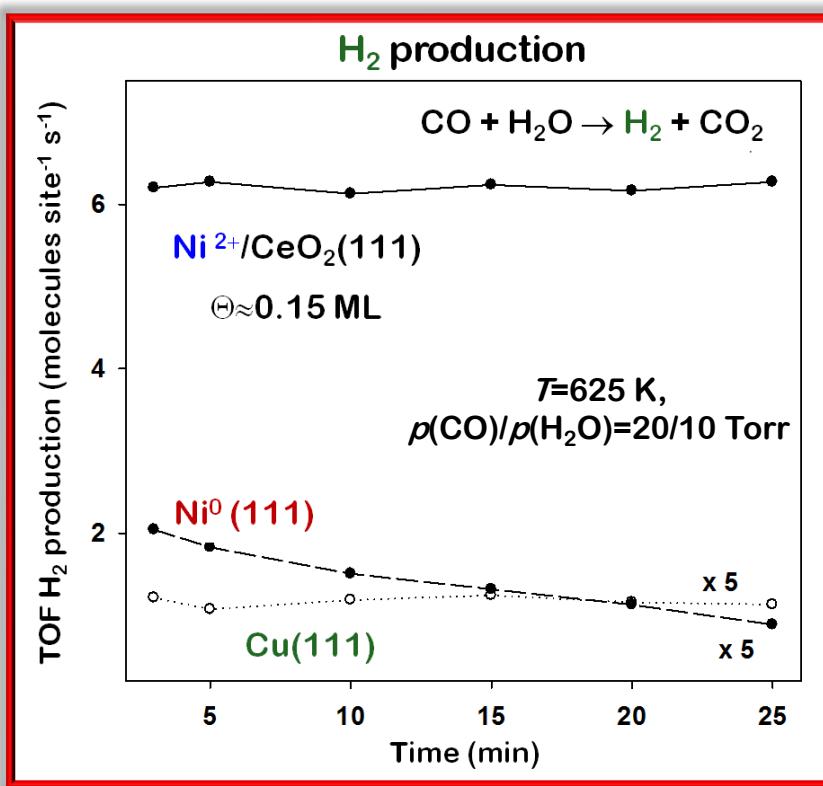
500 K



H_2O dissociation: ambient-pressure X-ray photoelectron spectroscopy

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

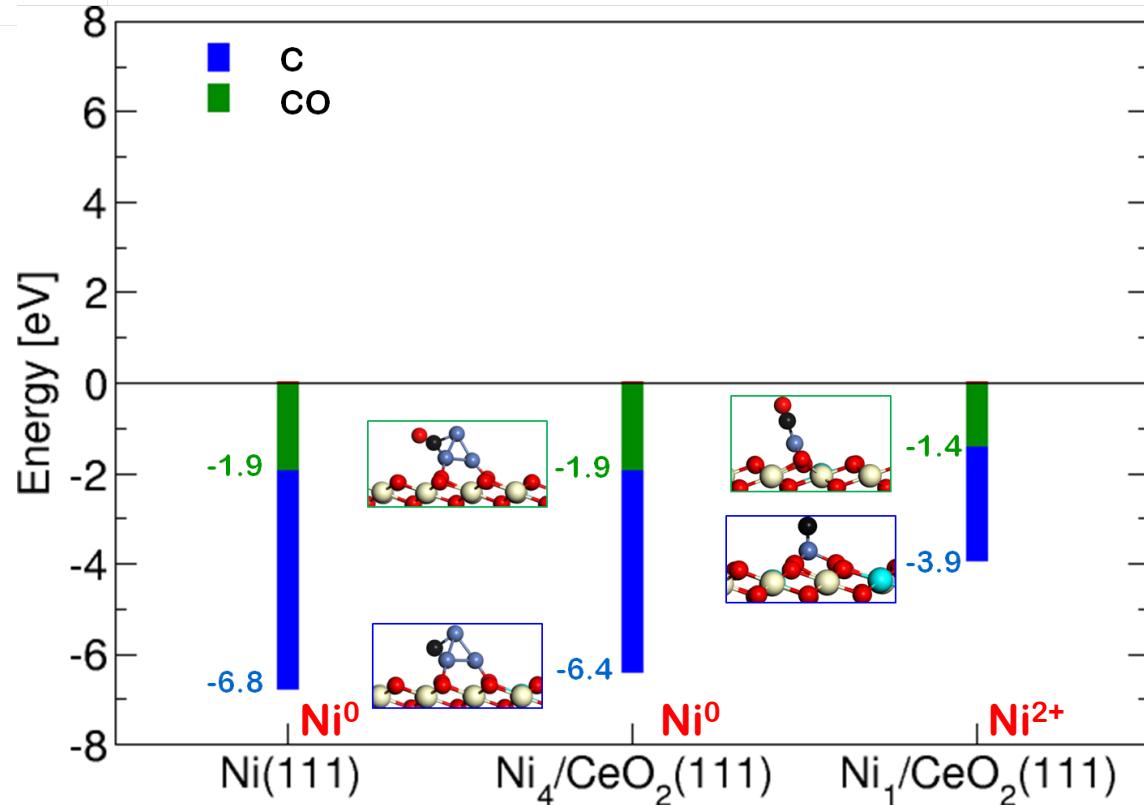
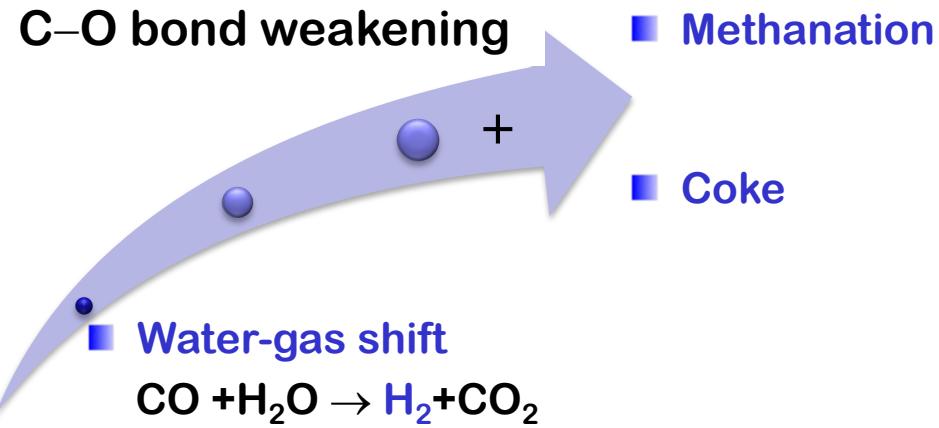
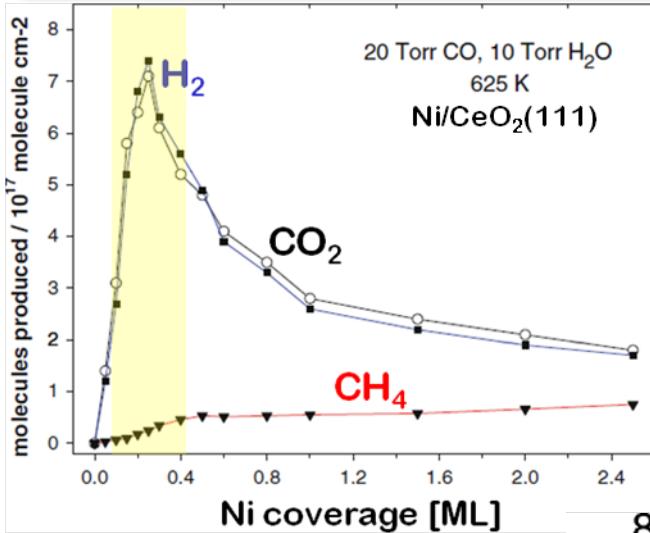
Larger OH coverage on Ni/CeO₂ facilitates WGS



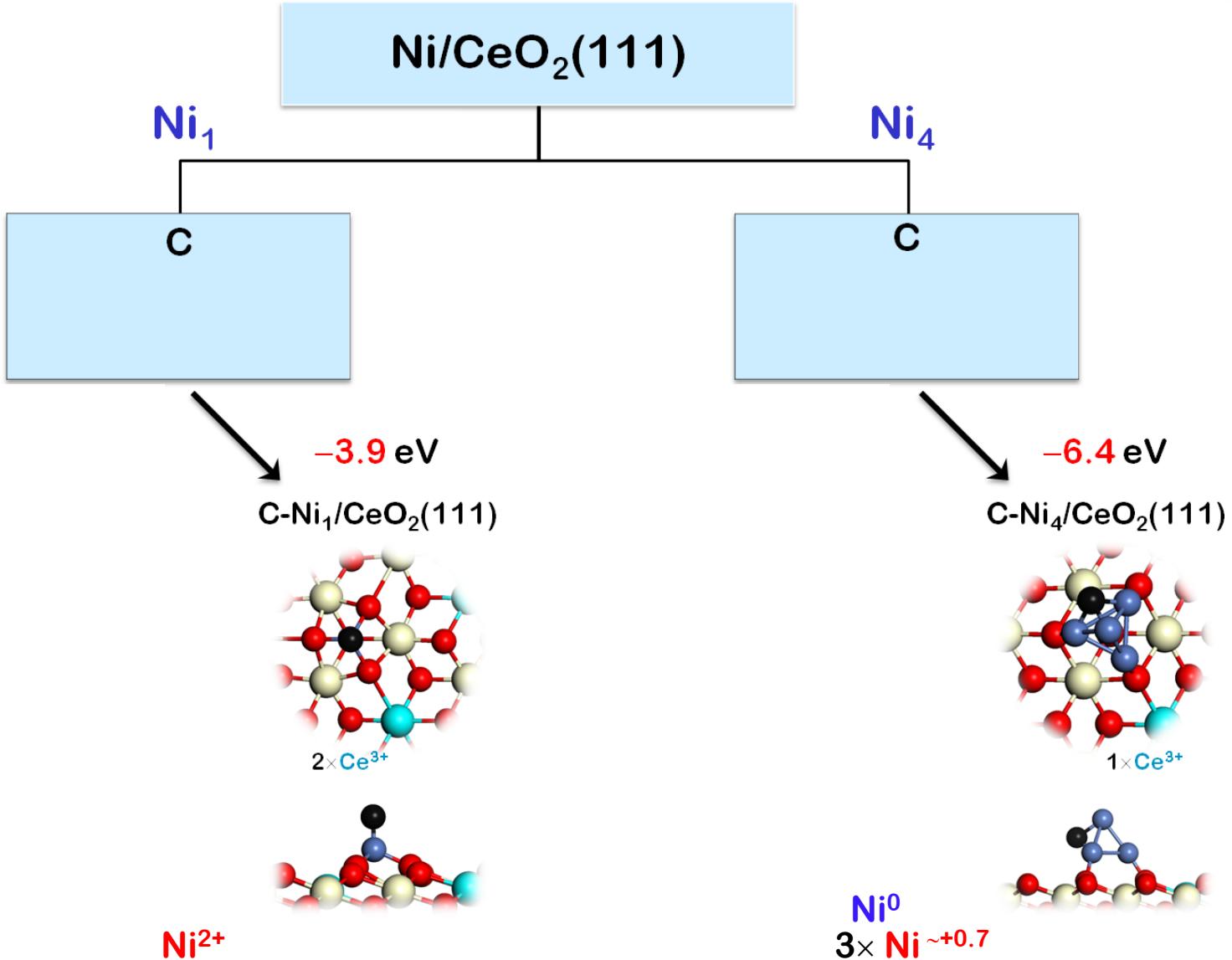
- Ni(111): slow H₂O dissociation
deactivation $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ coke

$\Theta_{\text{OH}}: 0.20 \text{ ML}$ CeO₂(111)
 $\Theta_{\text{OH}}: 0.37 \text{ ML}$ Ni/CeO₂(111) $\Theta_{\text{Ni}}: 0.15 \text{ ML}$

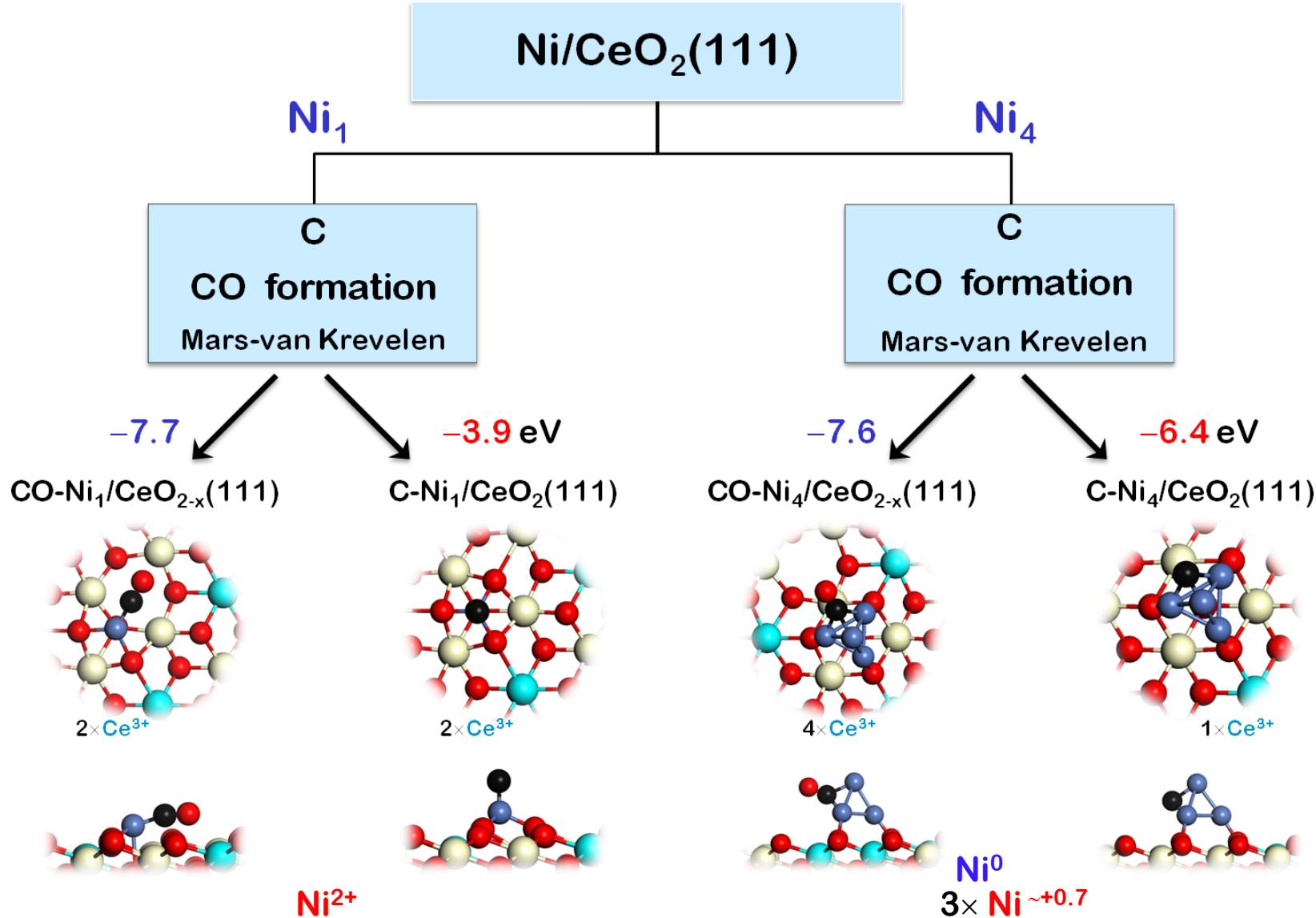
Ni/CeO₂(111): the C–O bond cleavage



C adsorption on Ni/CeO₂(111)



C adsorption on Ni/CeO₂(111)

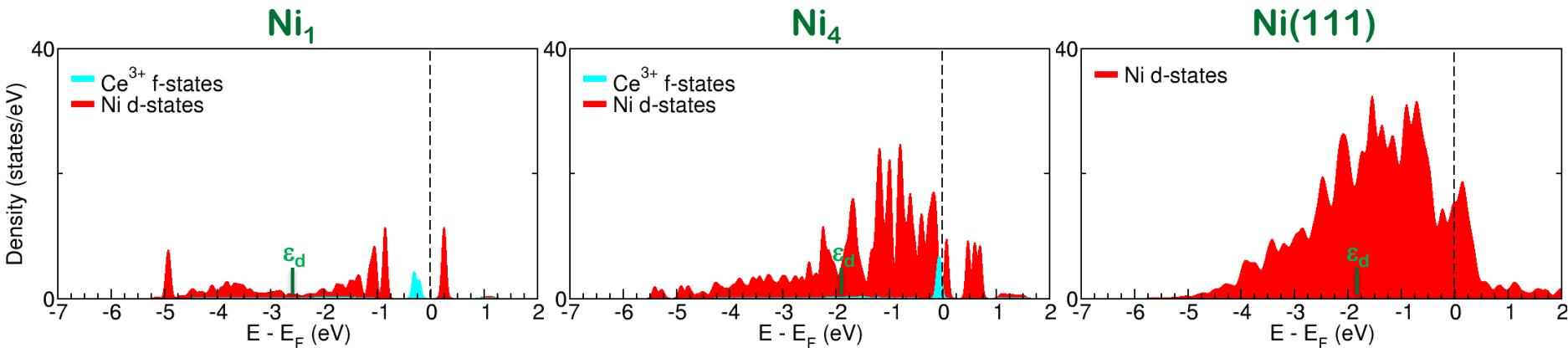


■ CO formation that remains on the surface – less coke formation → support effect

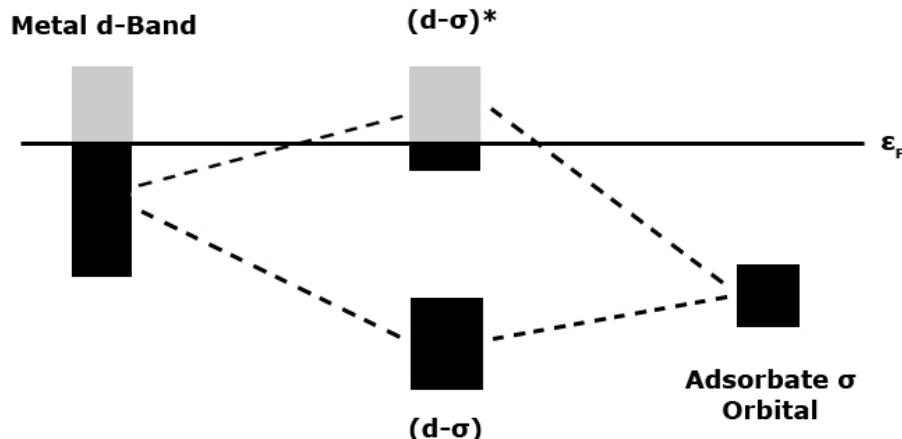
C non-oxidative adsorption on Ni/CeO₂(111)

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

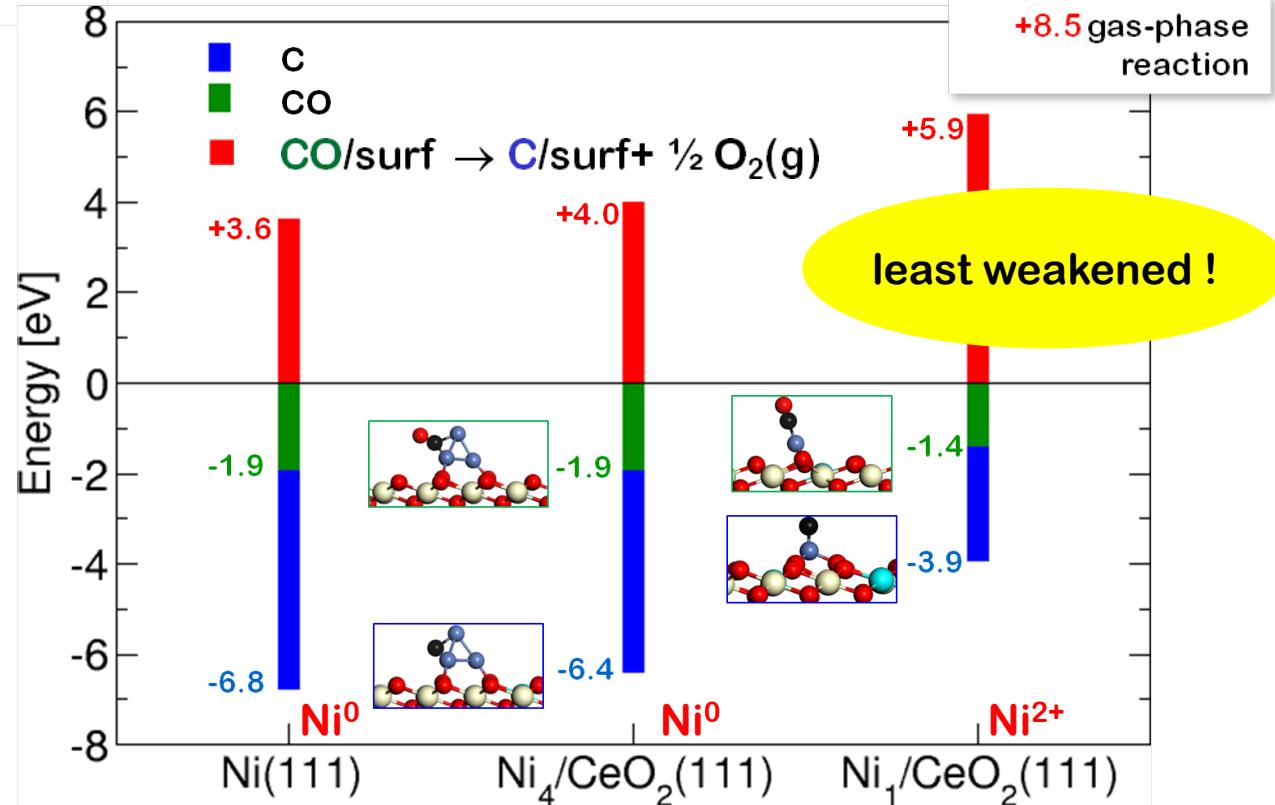
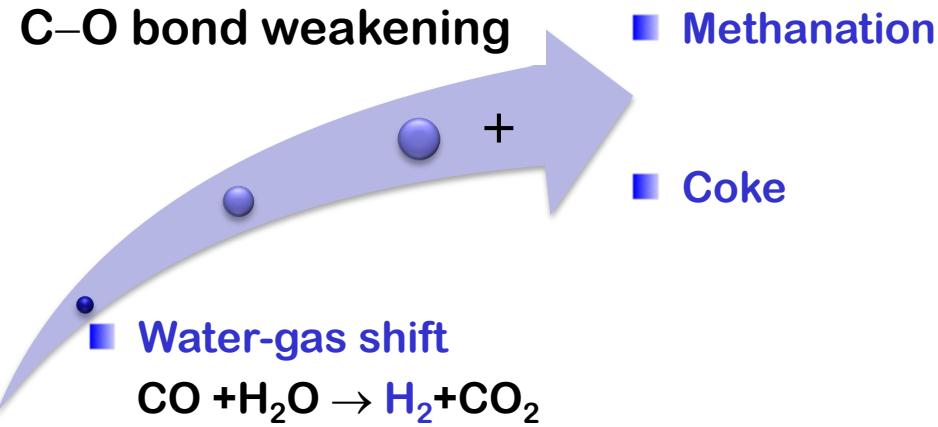
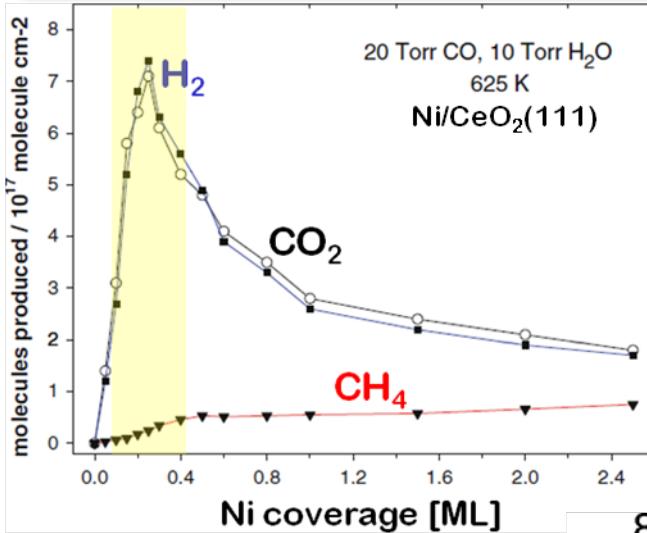


d-band model:

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

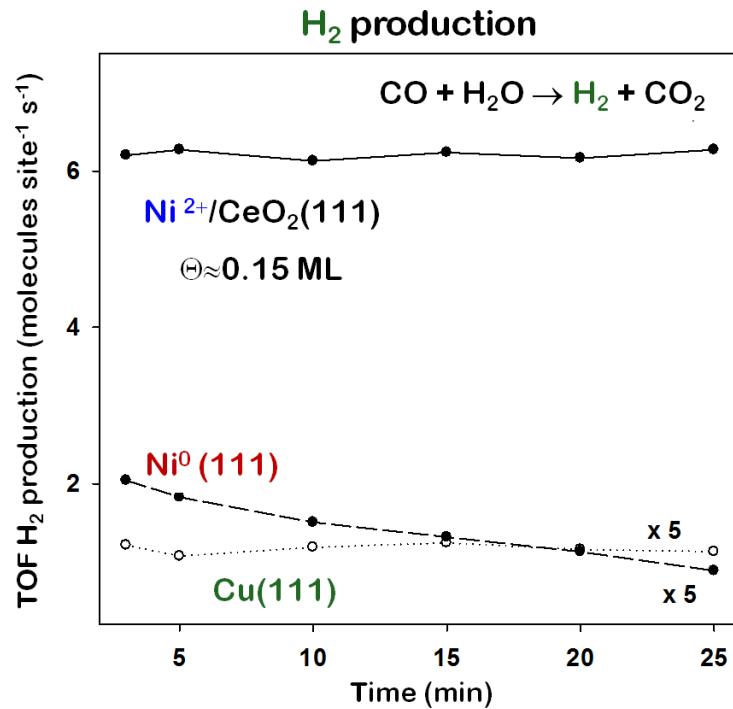
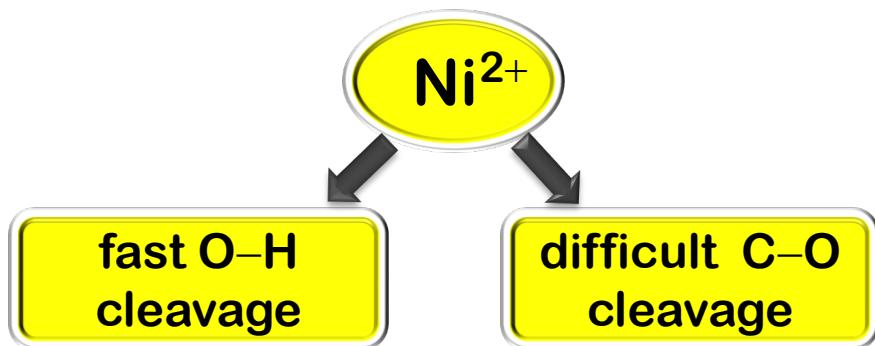


Ni²⁺ species makes more difficult to cleave C–O bonds

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

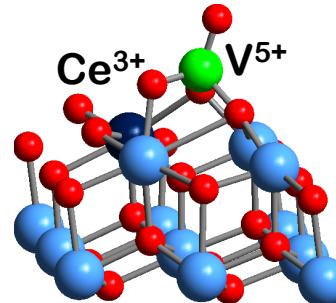


Conclusions: ceria support effect

At the origin of the –beneficial–support effect is the ability of ceria to stabilize reduced states by accommodating electrons in localized f-states.

VO_x/CeO_2

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

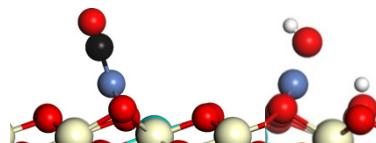


Angew. Chem. Int. Ed. 48, 8006 (2009)
JACS 132, 2345 (2010)
JPC C 115, 7399 (2011)

→ ceria –promoted by vanadia– is the active species

Ni/CeO_2

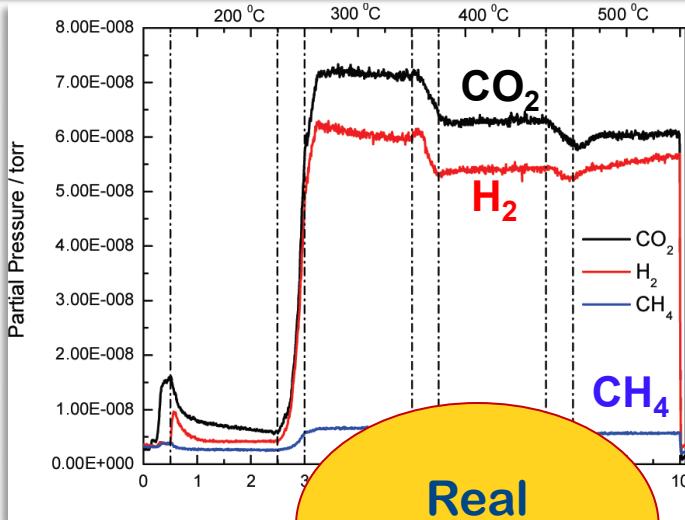
- Ni oxidation state → Ni^{2+}
- C–O bond strength → least weaken
- H_2O dissociation → Ni modified by metal-support interactions, plays a direct role



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

- The fast dissociation of water on Ni/CeO_2 has a dramatic effect on the activity and stability of this system as a catalyst for the water-gas shift reaction

Towards the rational design of catalysts



$\text{Ce}_{0.2}\text{Ni}_{0.8}\text{O}_{2-y}$

