

# HPC applied to Methane dissociation and conversion and HCl interaction on CeO<sub>2</sub> based catalyst

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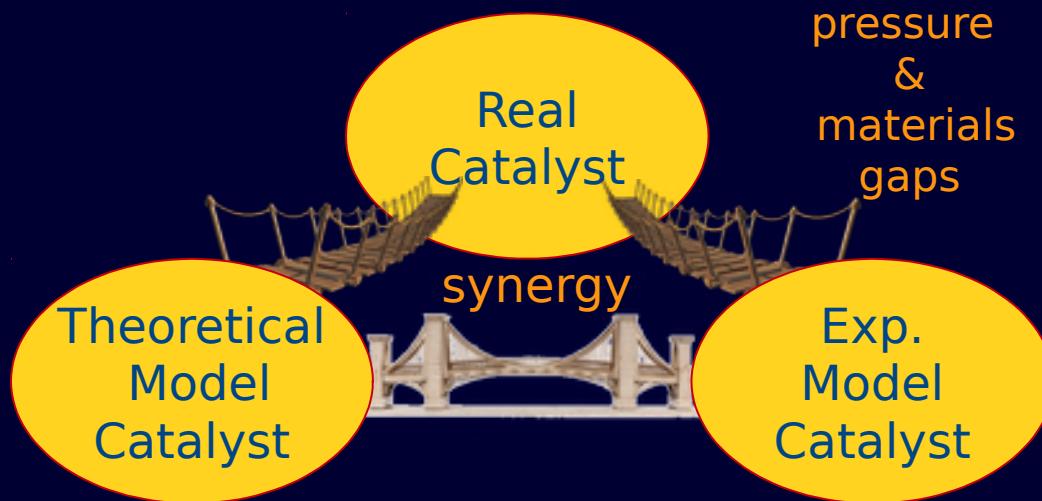
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Special Thanks: Javier Carrasco (CIC-Energiegune, Spain)  
Fabio H. Busnengo (IFIR-Rosario, Argentina)  
John J. Carey (University of York., UK)  
Michael Nolan (Tyndall Natl. Inst., Ireland)



# Towards the rational design of catalysts



Rational design of  
improved or new  
catalytic systems



Understanding  
Structure, phys. &  
chem. properties  $\leftrightarrow$  Catalytic  
function

# Reactivity of ceria-supported metal nanoparticles

■  $\text{Ni}_n/\text{ceria}$ ,  $\text{Co}_n/\text{ceria}$  &  $\text{Cu}_n/\text{ceria} \rightarrow \text{CO}_2$  reforming of  $\text{CH}_4$



■  $\text{Ni}_n/\text{ceria} \rightarrow \text{Methanol production}$   $\text{CH}_4 + \frac{1}{2} \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH}$

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□  $\text{CH}_4 \rightarrow$  greenhouse gas

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## ■ ***$\text{CO}_2$ reforming of $\text{CH}_4$***

Challenges:

- Activation of  $\text{CO}_2$  and  $\text{CH}_4$
- High temperature ( $\sim 1200$  K)
- Coke formation

Catalyst:

- Pt, Rh, Ru → expensive
- Ni-Pd, Ni-Pt, Co-Pt, Co-Ru
- Metals on an oxide support  
 $\text{TiO}_2$ ,  $\text{MgO}$ ,  $\text{CeO}_2$ , ...etc.

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

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## ■ ***$\text{CO}_2$ reforming of***

### ***$\text{CH}_4$***

Challenges:

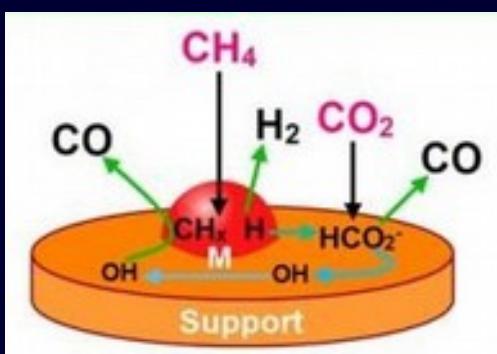
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DRM catalysts

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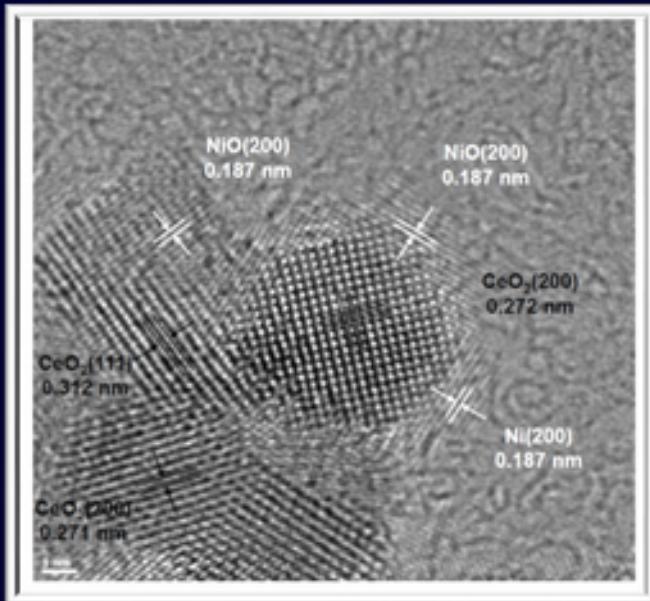
Pakhare et al. Chem. Soc. Rev., 2014, 43, 7813-7837



- Active site?
- Role of metal?  $\text{CH}_4 \rightarrow \text{CH}_x + x\text{H}$
- Role of oxide?  $\text{CO}_2 \rightarrow \text{CO} + \text{O}$
- Reaction mechanism?

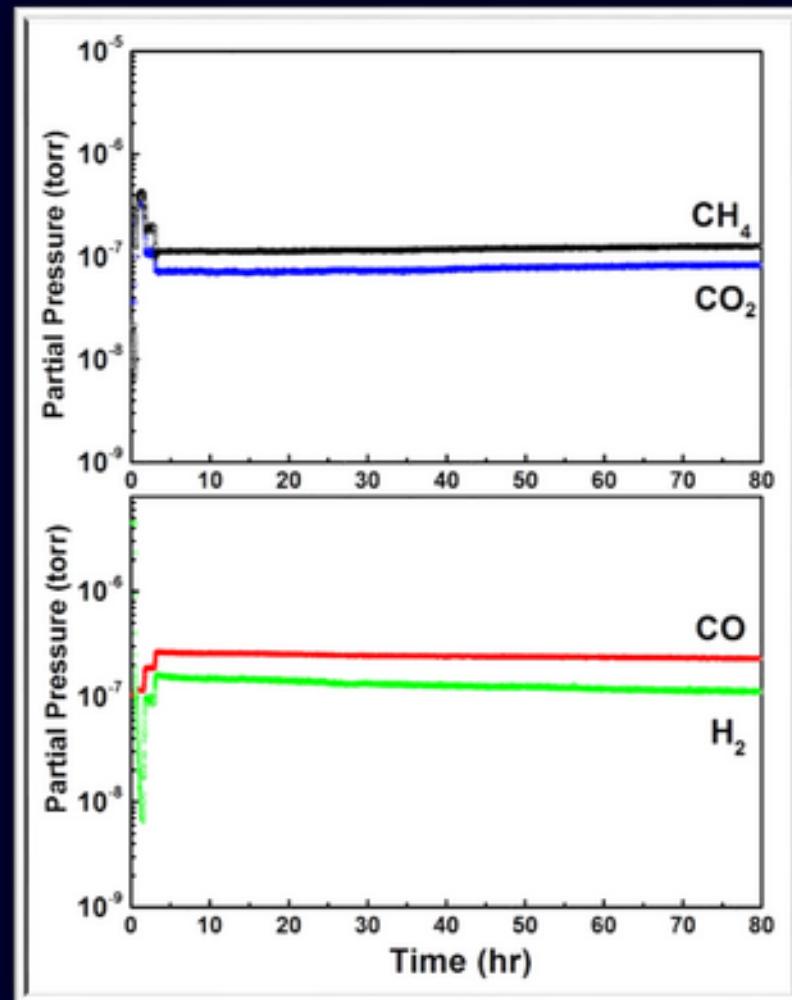
# Ni/CeO<sub>2</sub> real catalyst

NiO/CeO<sub>2</sub> precursor



↓ activation  
20%H<sub>2</sub>/He @ 723 K

In situ X-ray diffraction  
 $\text{NiO} \rightarrow \text{Ni}^0$   
↓  
 $\text{Ni}^0/\text{CeO}_{2-x}$



Gas species derived from mass spectrum

# Ni/CeO<sub>2</sub>(111) model catalysts: CH<sub>4</sub> dissociation

100 mTorr CH<sub>4</sub>

Model Catalyst @ 300K

0.1 ML Ni on CeO<sub>2</sub>(111)

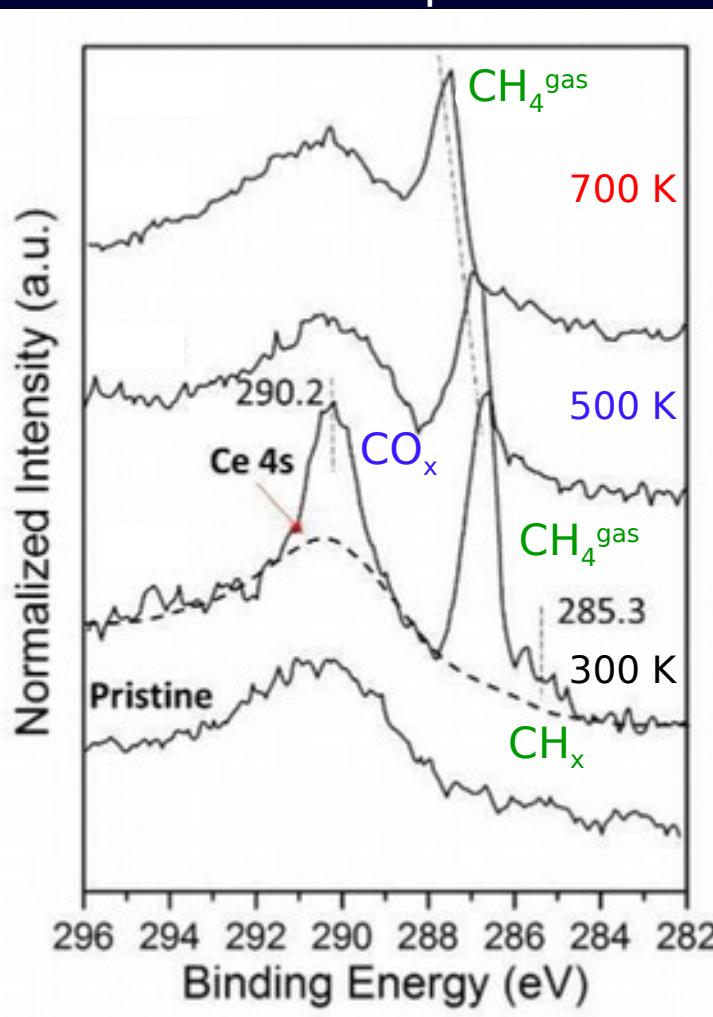
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100 mTorr CH<sub>4</sub>



Model Catalyst @ 300K  
0.1 ML Ni on CeO<sub>2</sub>(111)

C1s XPS spectra



- 700 K  
 $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{C}$   
No CH<sub>x</sub>, CO<sub>x</sub>
- 500 K  
 $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{C}$   
No CH<sub>x</sub>, CO<sub>x</sub>
- 300 K  
 $\text{CH}_4 \rightarrow \text{CH}_3 \rightarrow \text{CH}_2 \rightarrow \text{CH} \rightarrow \text{C}$   
 $\text{CH}_x^{\bullet}$       CO<sub>x</sub>

Room T  
CH<sub>4</sub>  
activation !!

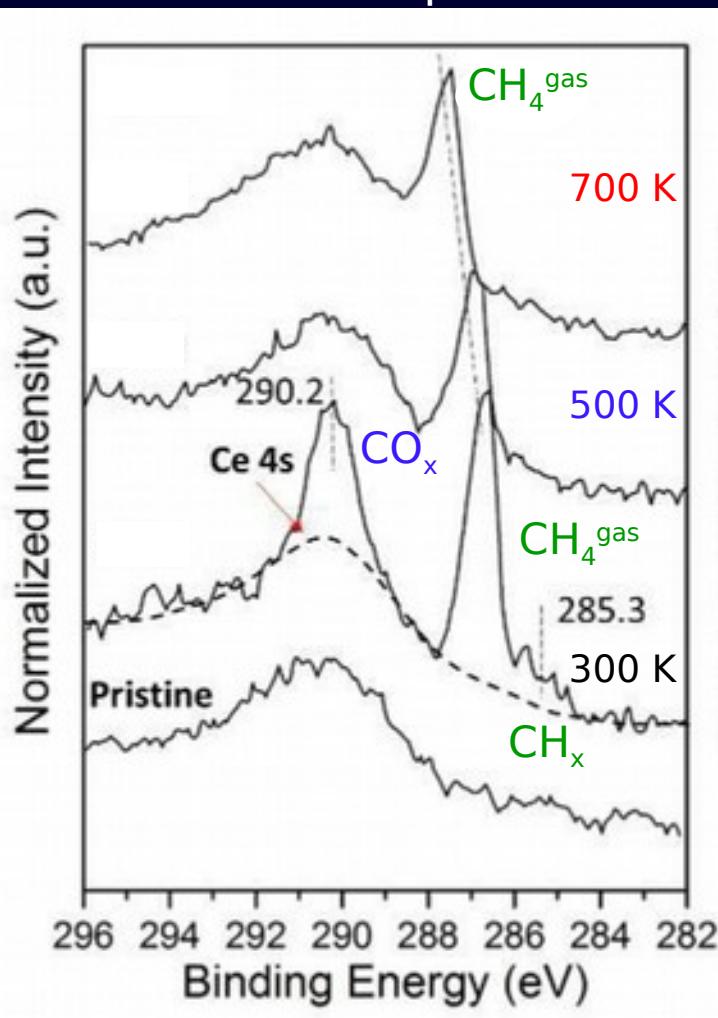
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Liu et al., Angew. Chem. Int. Ed. 55 (2016)  
Lustemberg et al, ACS Catal 6 (2016)

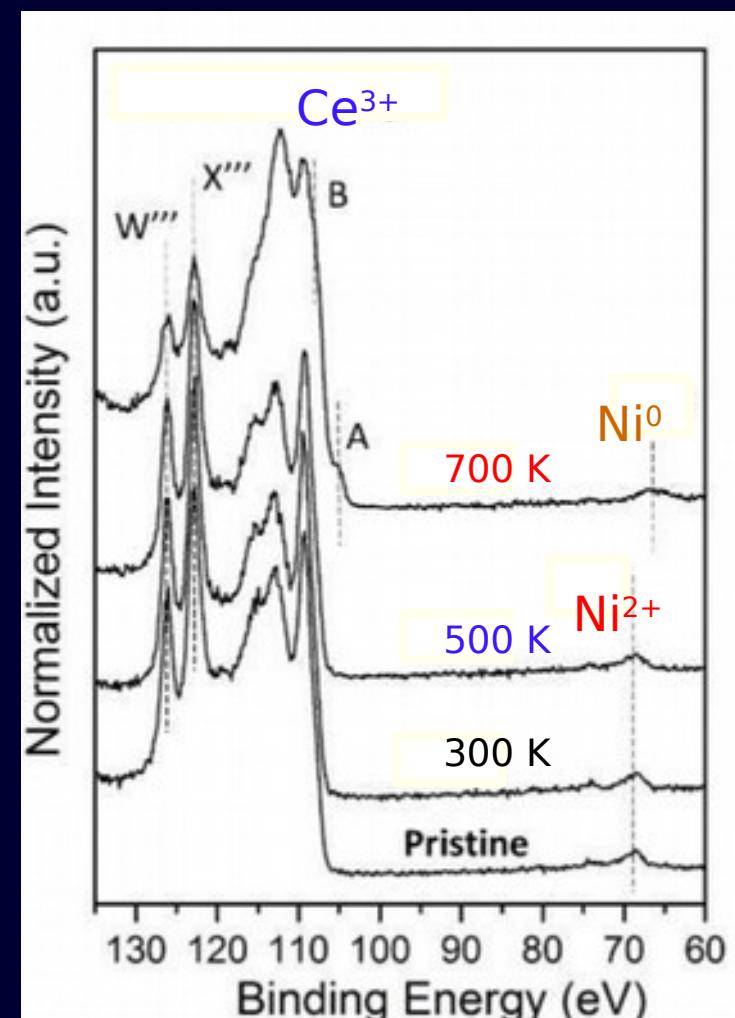
100 mTorr CH<sub>4</sub>



C1s XPS spectra



Ce 4d + Ni 3p spectra



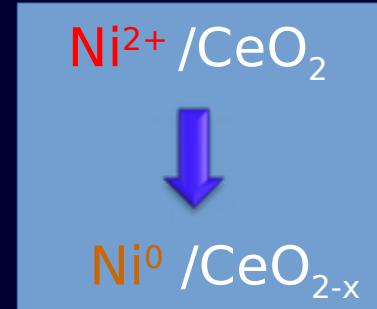
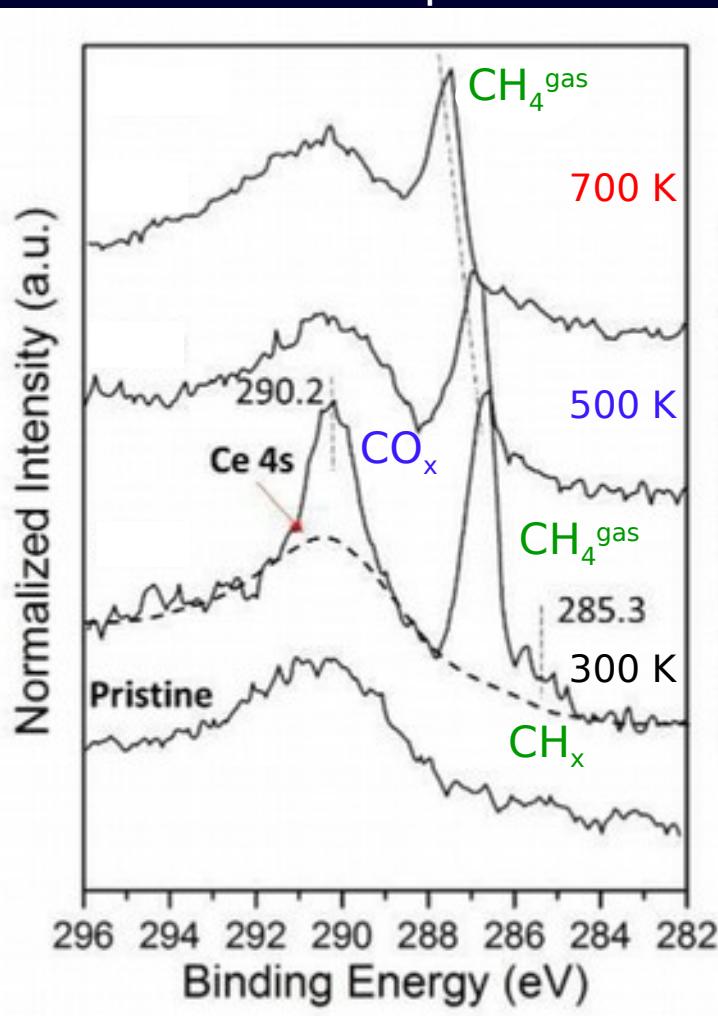
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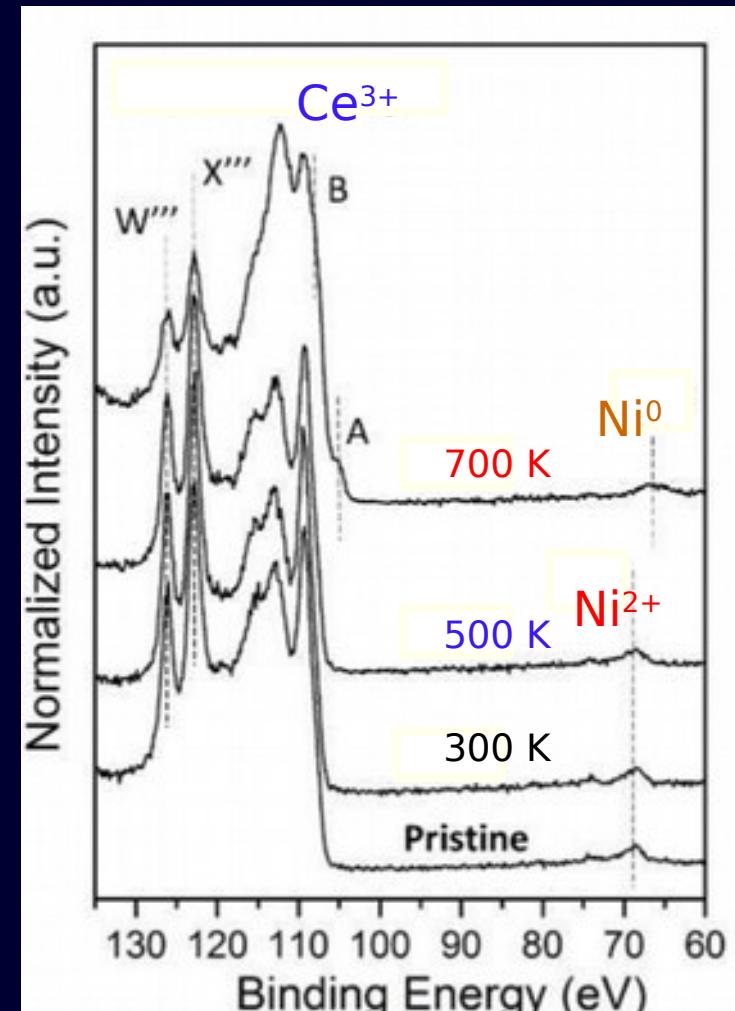
100 mTorr CH<sub>4</sub>



C1s XPS spectra

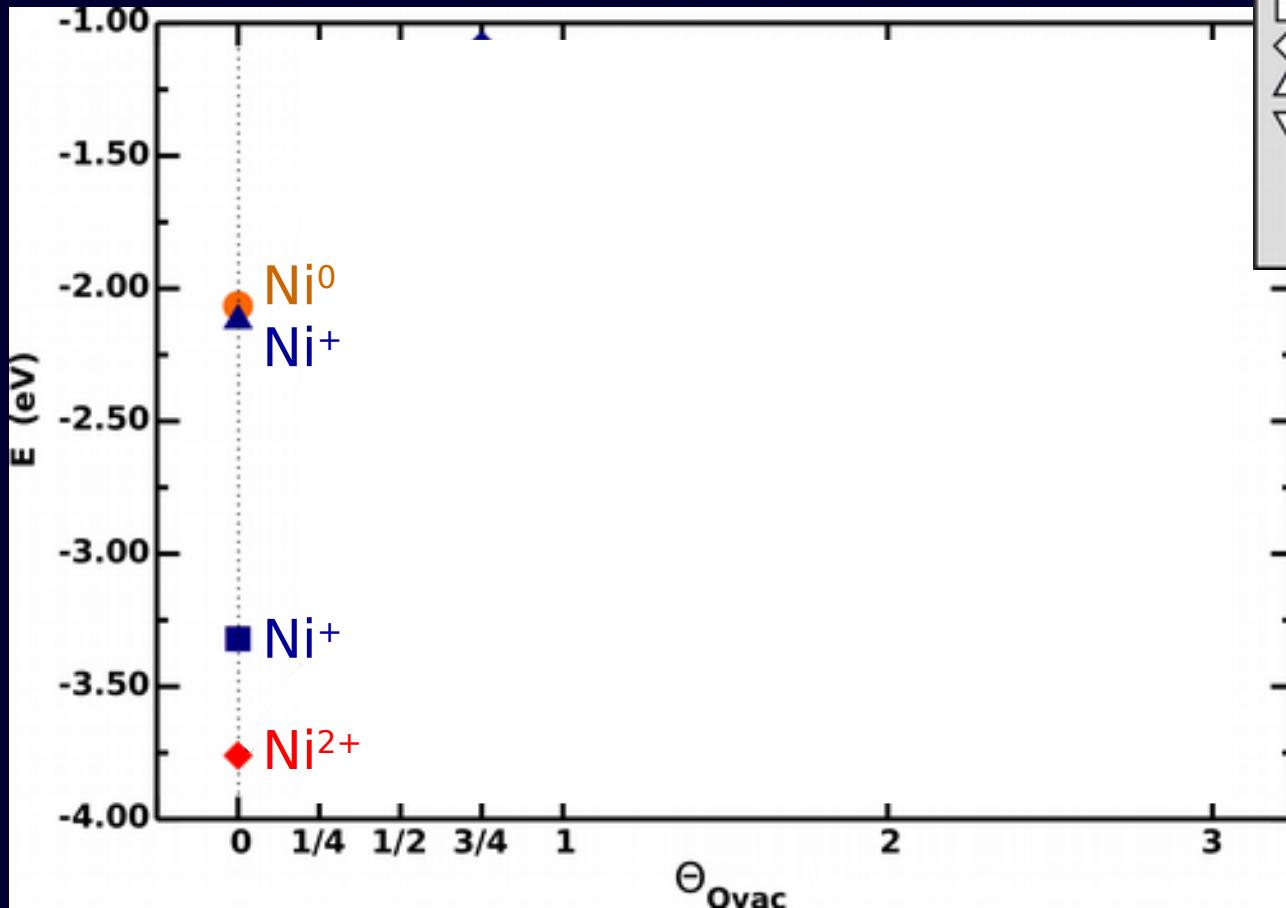


Ce 4d + Ni 3p spectra

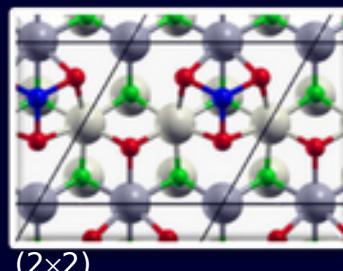


# Effect of metal-support interactions on oxidation states

## The example of atomic Ni on CeO<sub>2</sub>(111)



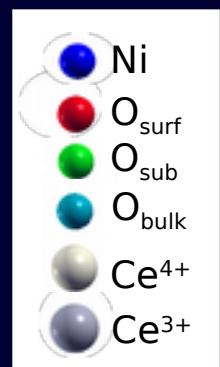
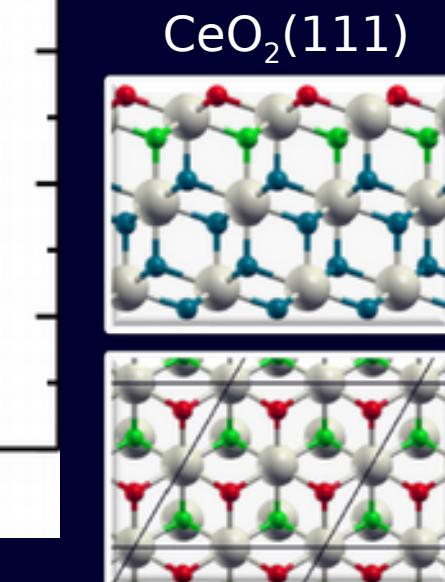
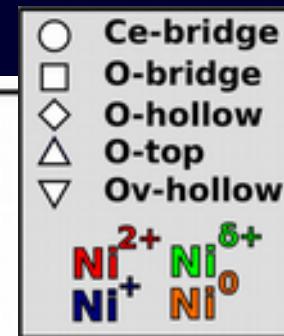
Ni<sup>2+</sup> @ O-hollow



2x Ce<sup>3+</sup>

**strong support  
effect**

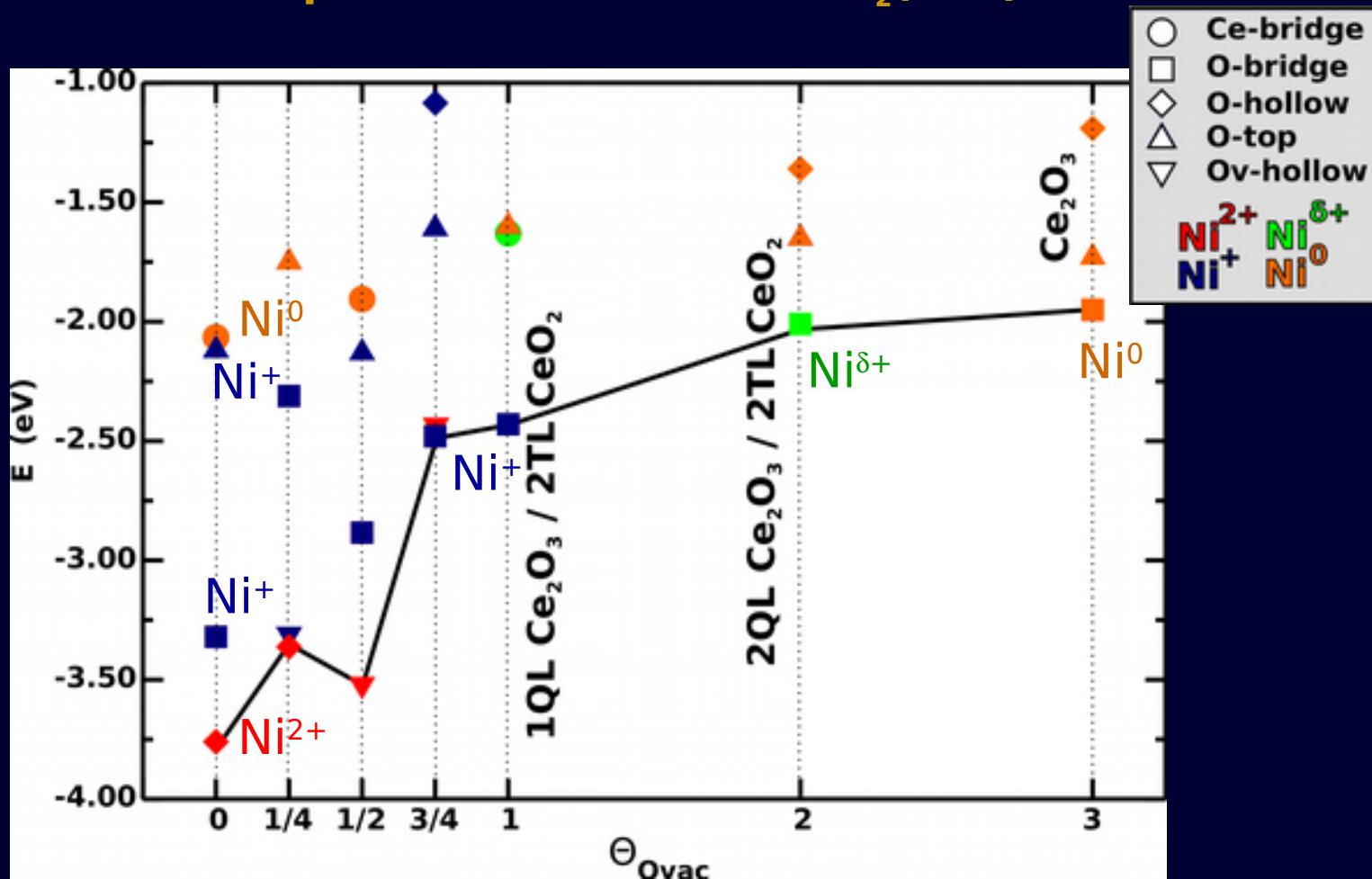
J. Phys. Chem. C 117, 8241 (2013)  
ACS Catal 6, 8184 (2016)



PBE+U  
(4.5 eV)

# Effect of metal-support interactions on oxidation states

The example of atomic Ni on  $\text{CeO}_2(111)$



PBE+U  
(4.5 eV)

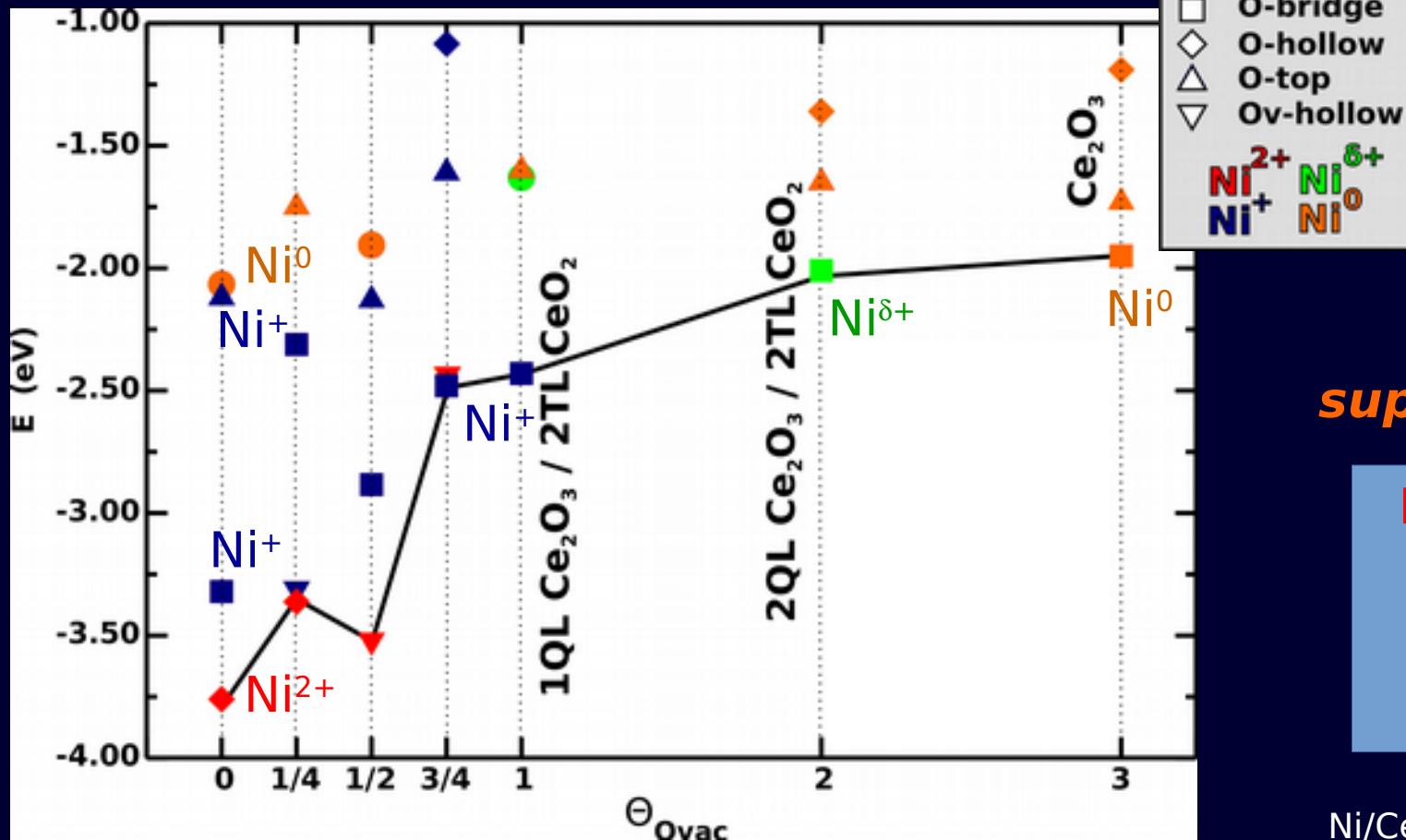
HPC

1 state  $\rightarrow$  64 processors  $\times$  72 hs = 4.6 TH

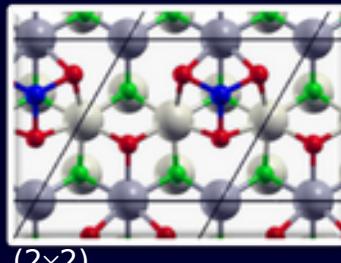
150 state  $\sim$  690 TH

# Effect of metal-support interactions on oxidation states

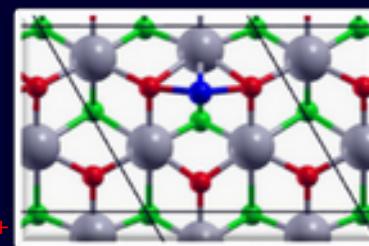
The example of atomic Ni on  $\text{CeO}_2(111)$



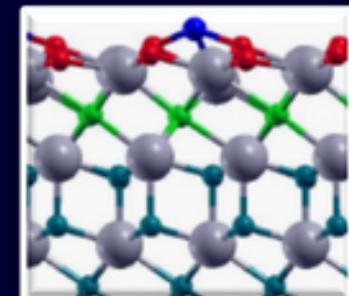
$\text{Ni}^{2+}$  @ O-hollow



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



$\text{Ni}/\text{Ce}_2\text{O}_3(0001)$

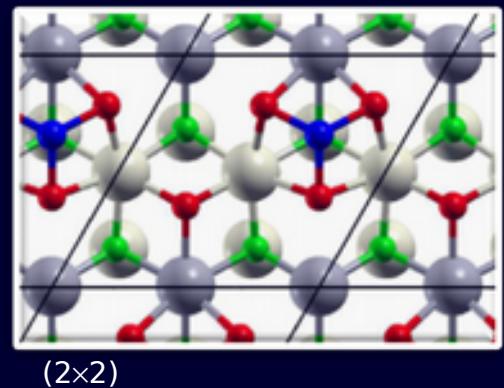


# Effect of metal-support interactions on oxidation states

## The example of Ni on CeO<sub>2</sub>(111)

J. Phys. Chem. C 117, 8241 (2013)  
ACS Catal 6, 8184 (2016)

Ni<sub>1</sub> / CeO<sub>2</sub>(111)



Ni<sup>2+</sup>

2× Ce<sup>3+</sup>

2× 4s e<sup>-</sup> transferred

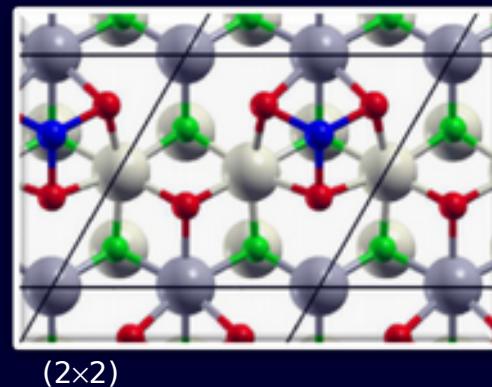
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Ni<sub>1</sub> / CeO<sub>2</sub>(111)



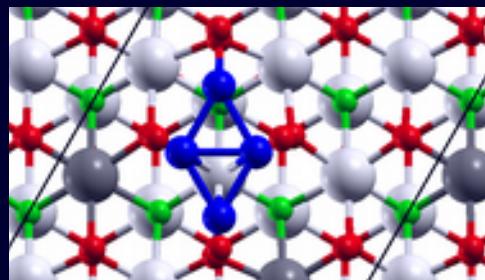
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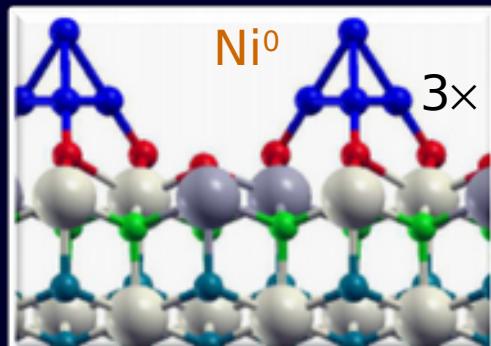
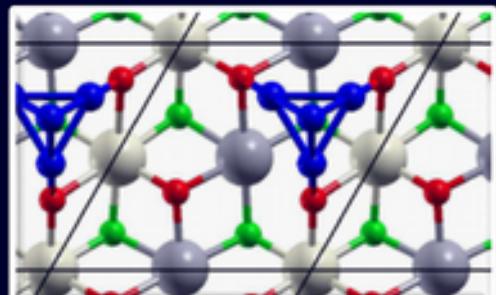
Ni<sub>4</sub> / CeO<sub>2</sub>(111)

Flat



4 × Ni ~+0.5

Pyramid



Ni<sup>0</sup>

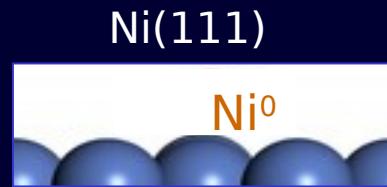
3× Ni ~+0.7

2× Ce<sup>3+</sup>

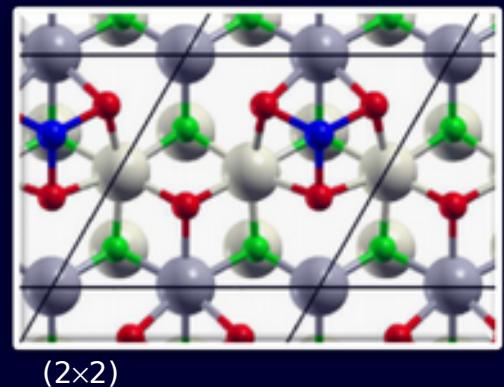
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## The example of Ni on CeO<sub>2</sub>(111)

J. Phys. Chem. C 117, 8241 (2013)  
ACS Catal 6, 8184 (2016)



Ni<sub>1</sub> / CeO<sub>2</sub>(111)

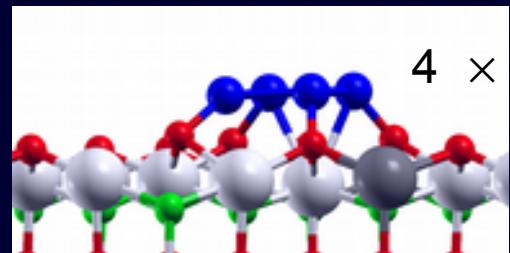
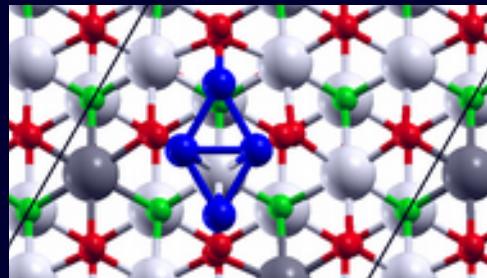


Ni<sup>2+</sup>

2× 4s e<sup>-</sup> transferred

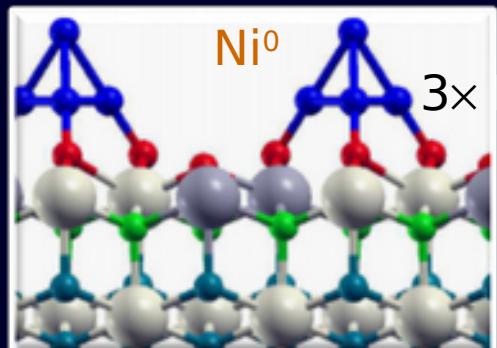
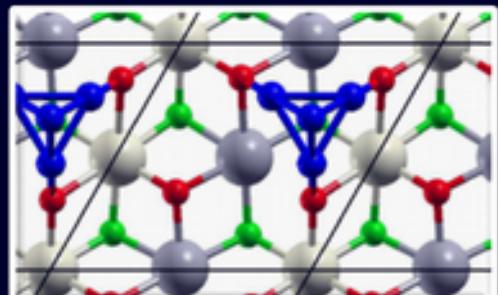
2× Ce<sup>3+</sup>

Ni<sub>4</sub> / CeO<sub>2</sub>(111)



4 × Ni<sup>~+0.5</sup>

Pyramid



Ni<sup>0</sup>

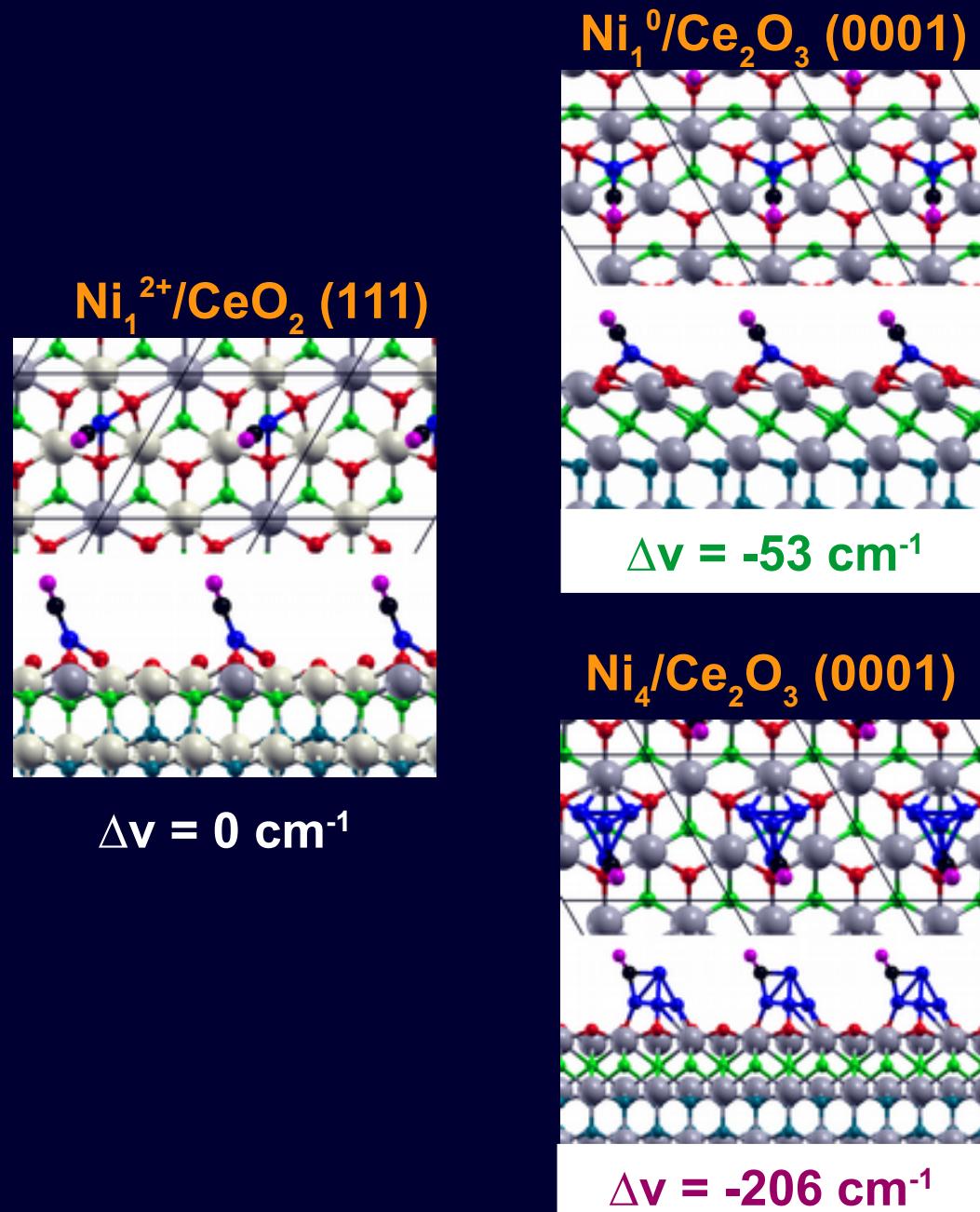
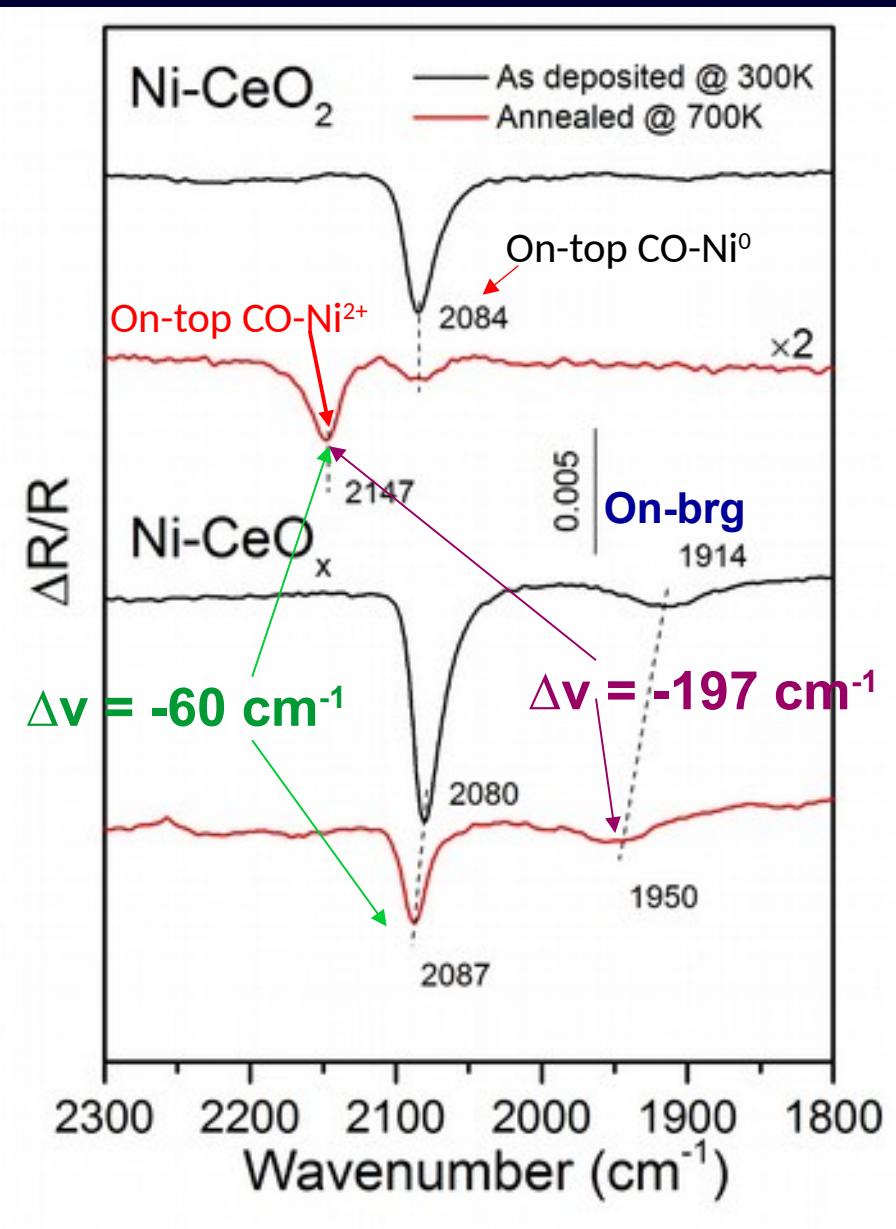
3× Ni<sup>~+0.7</sup>

2× Ce<sup>3+</sup>

rapid weakening of  
metal–oxide  
interactions

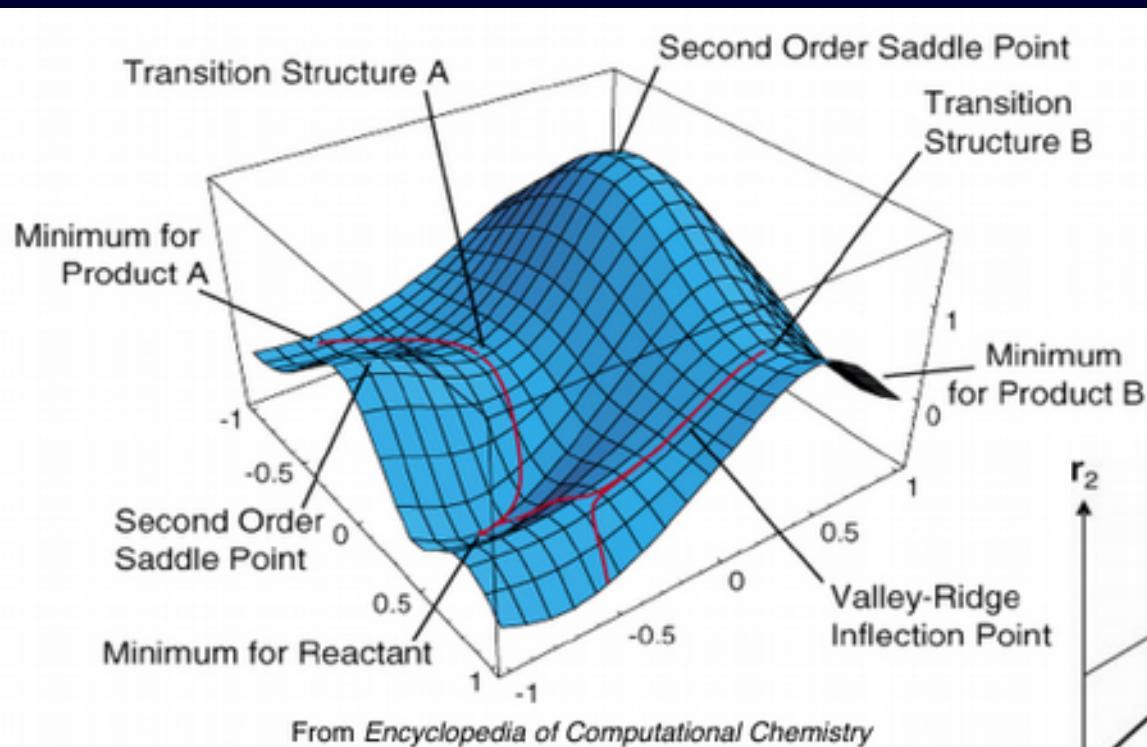
# Models Validation

## IRRAS CO adsorption at 100K



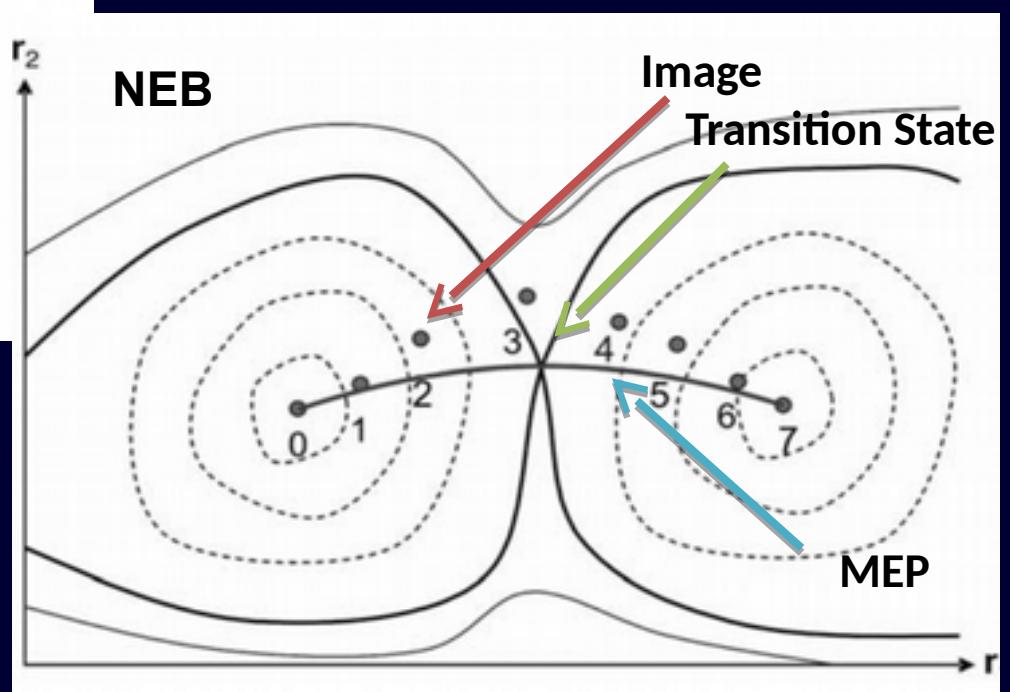
# $\text{CH}_4$ dissociation on Ni/CeO<sub>2</sub> (111)

## Minimum Energy Path



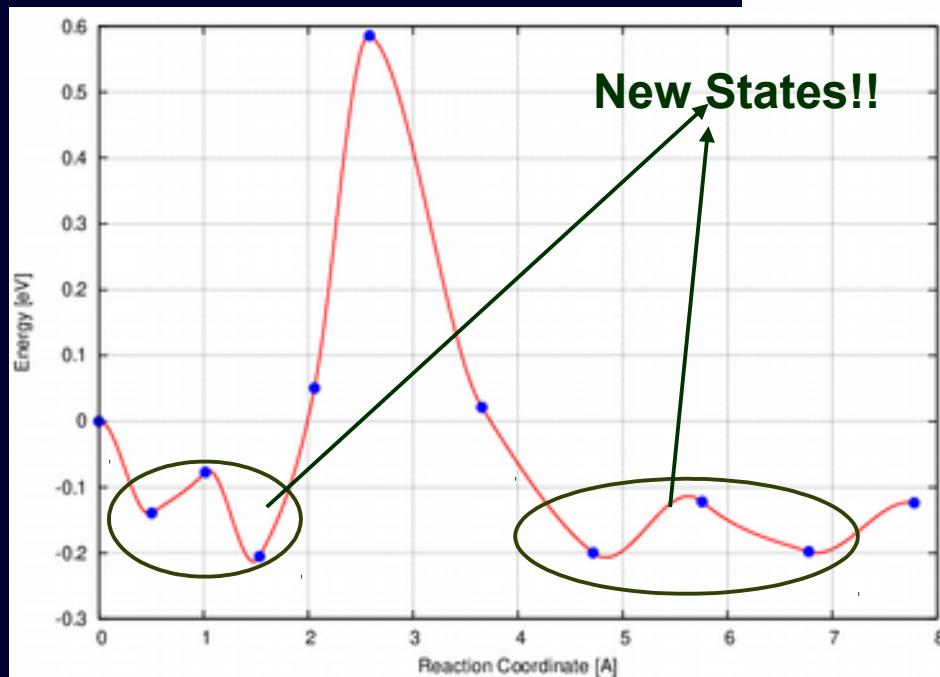
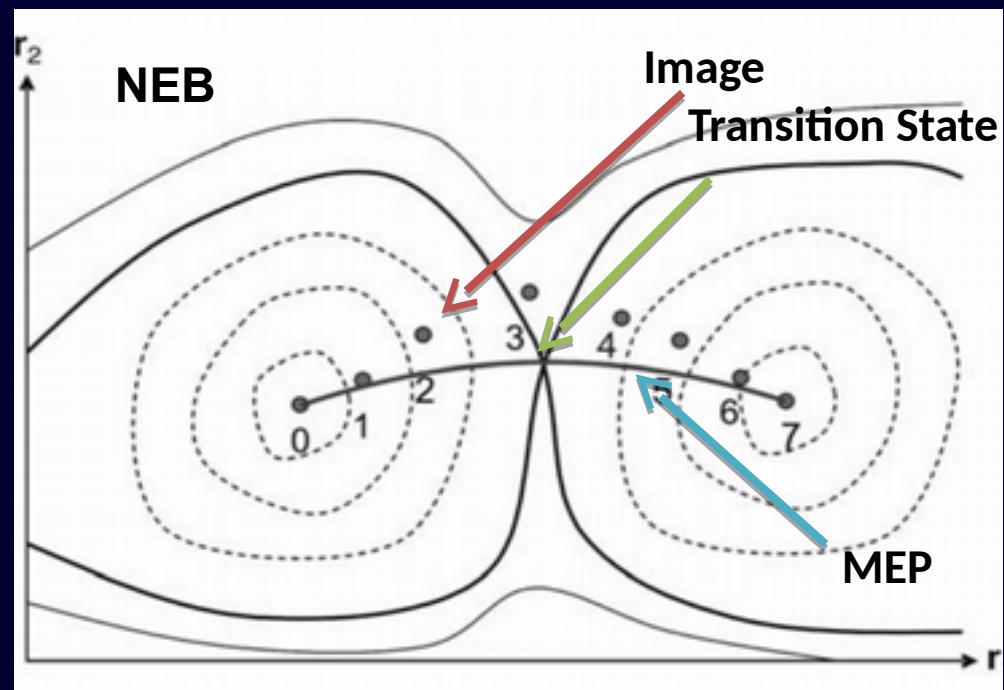
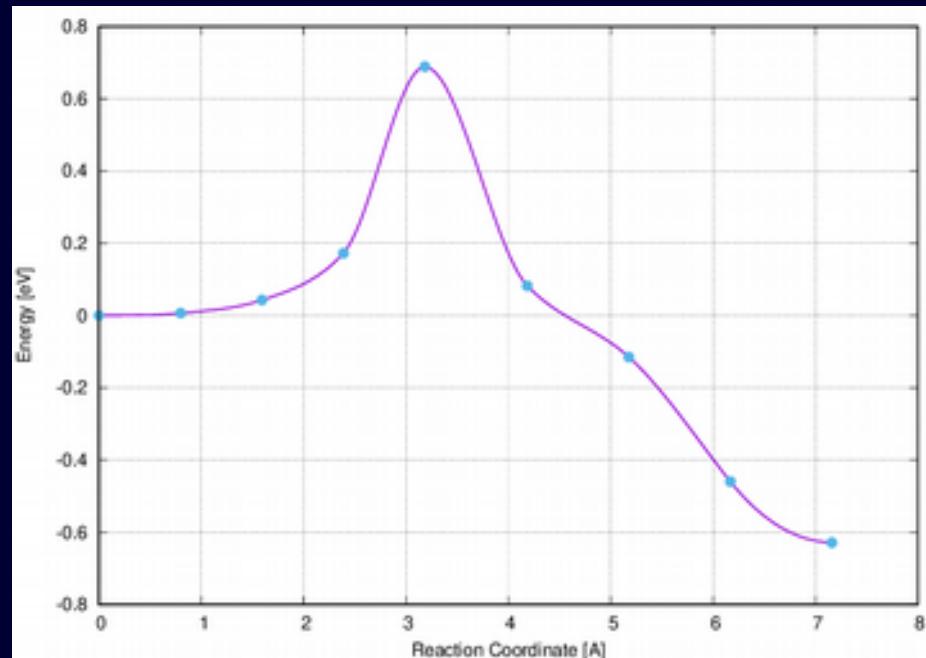
A path is an MEP only if the forces defined by any image along the path are oriented directly along the path

Landscape of potential energy surface for a catalytic reaction can be very complicated!!!



NEB method @Vasp

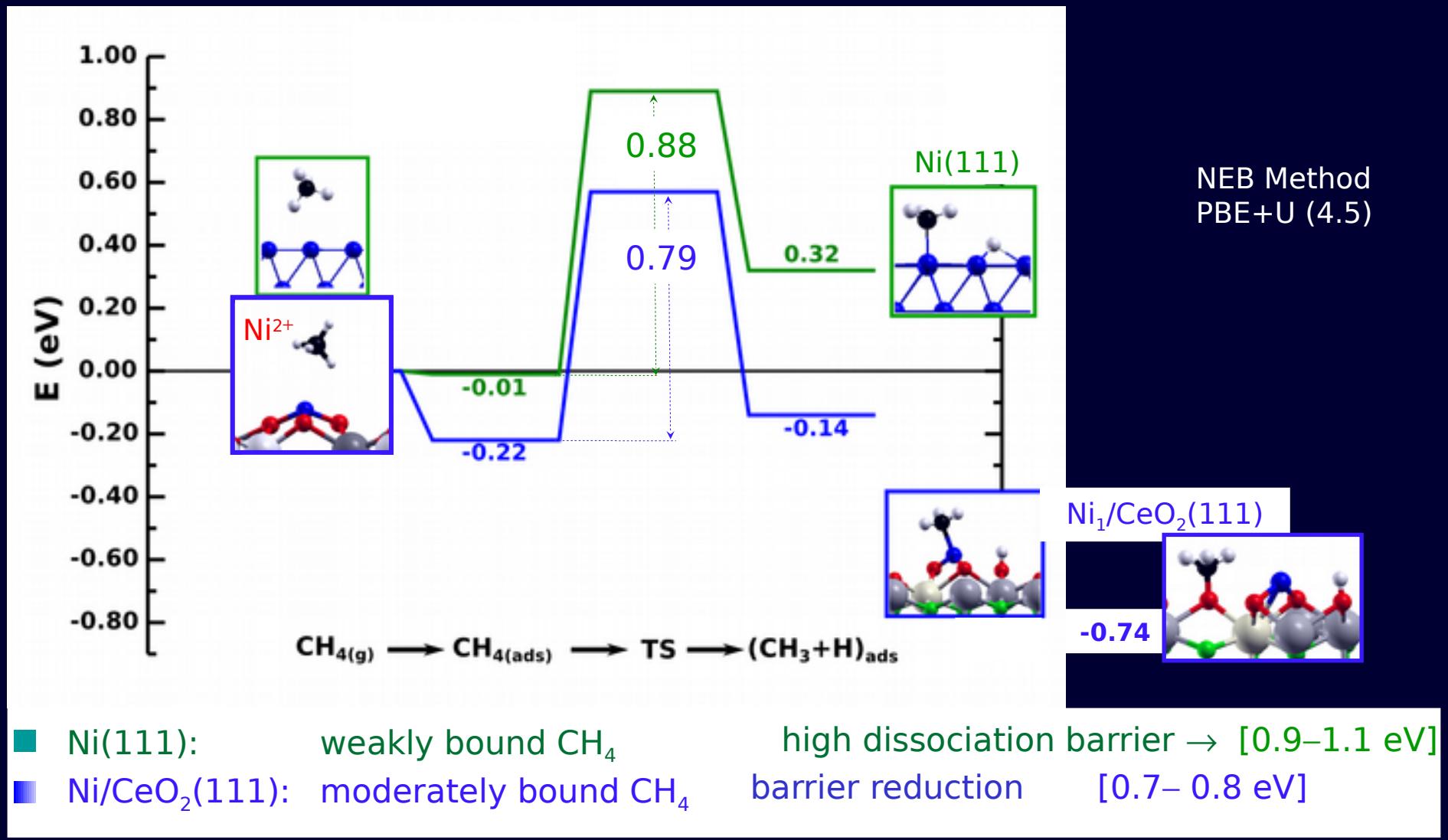
# CI-NEB



9 Images x 96 cpu each image = 864 proc  
100 iterations in MN4 ~ 1 day ~ **21 TH**

# $\text{CH}_4$ dissociation on Ni/CeO<sub>2</sub> (111)

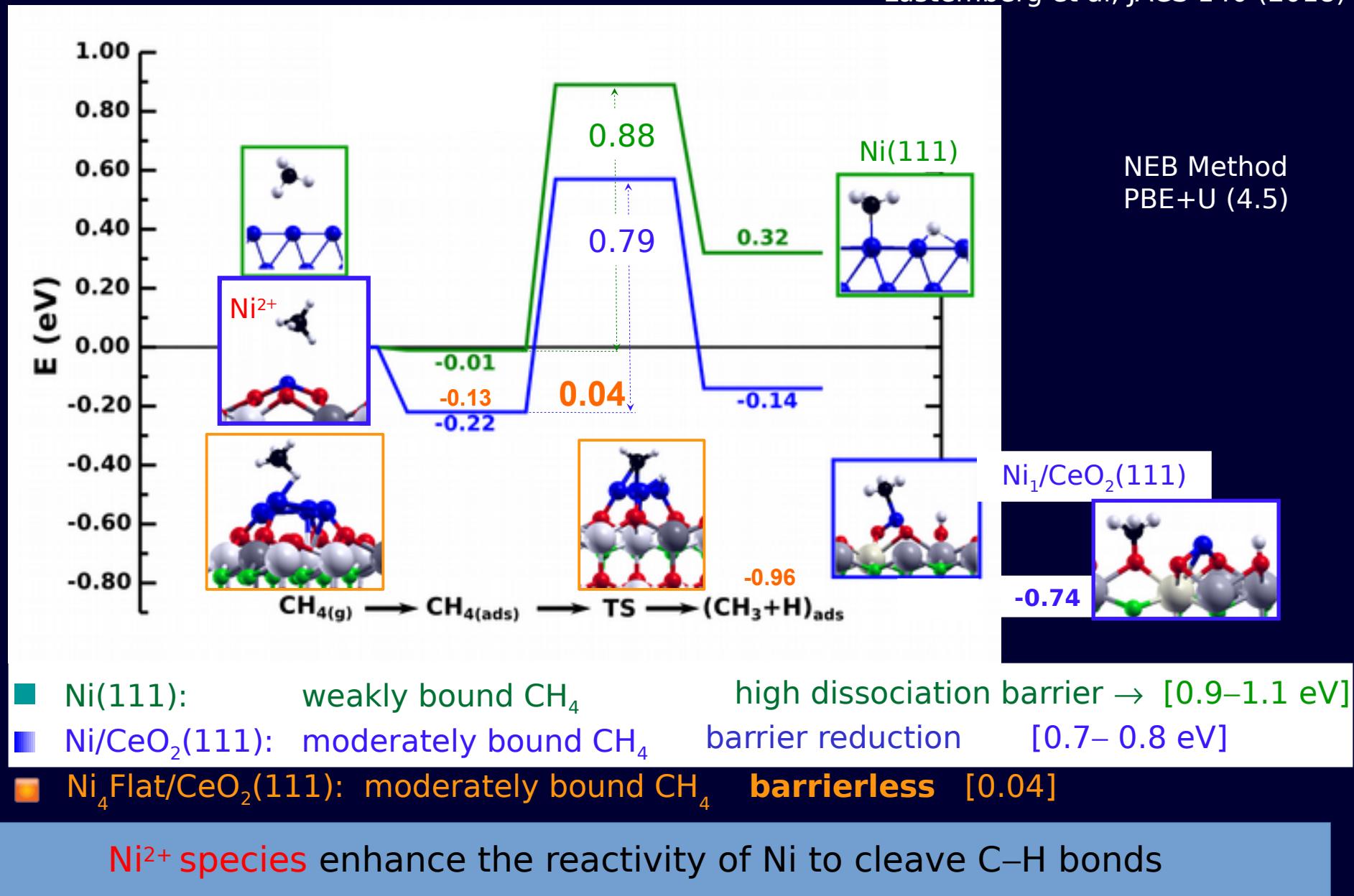
Liu et al., Angew. Chem. Int. Ed. 55 (2016)  
Lustemberg et al, ACS Catal 6 (2016)



Ni<sup>2+</sup> species enhance the reactivity of Ni to cleave C–H bonds

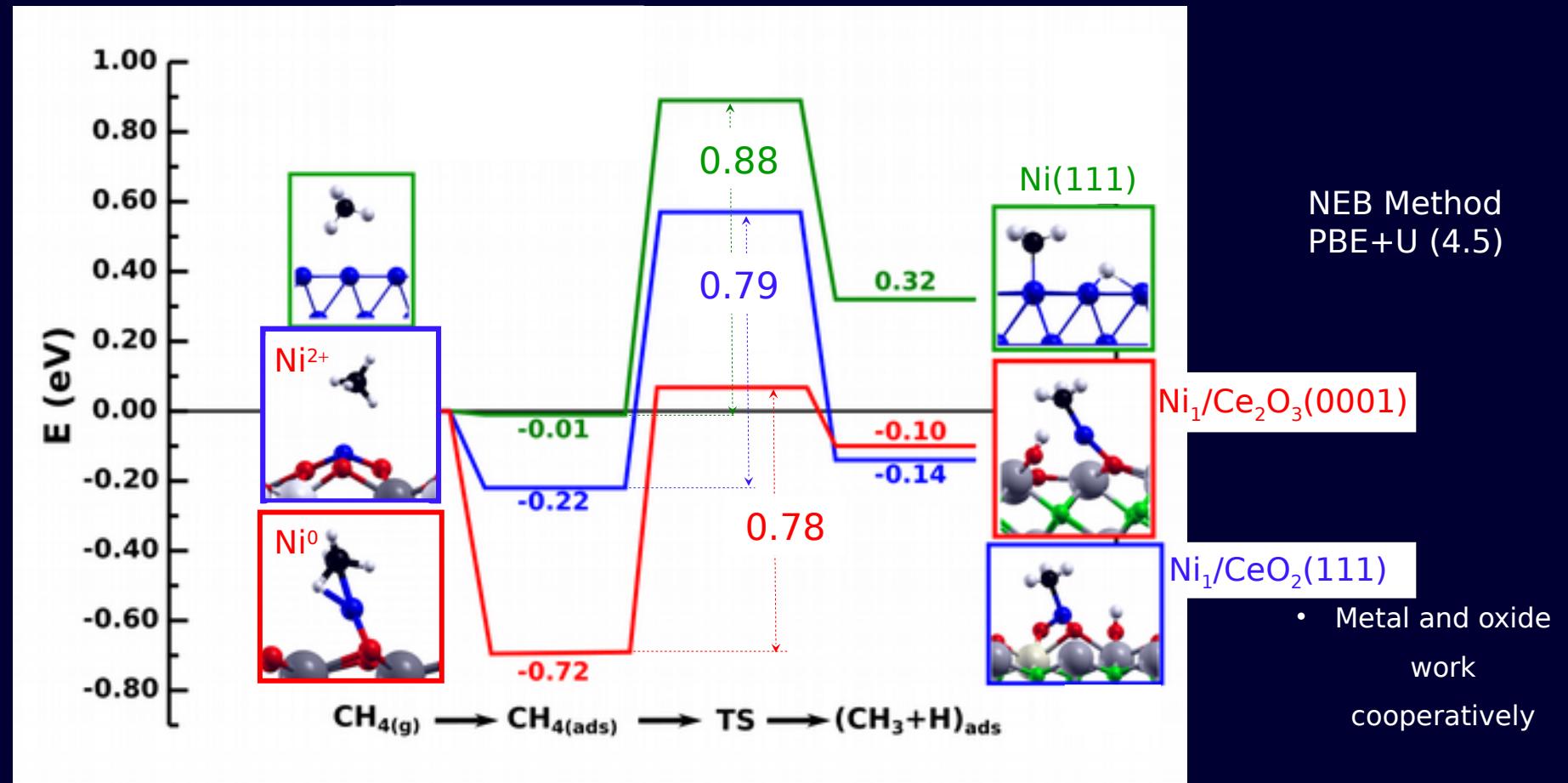
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Lustemberg et al, ACS Catal 6 (2016)  
Lustemberg et al, JACS 140 (2018)



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



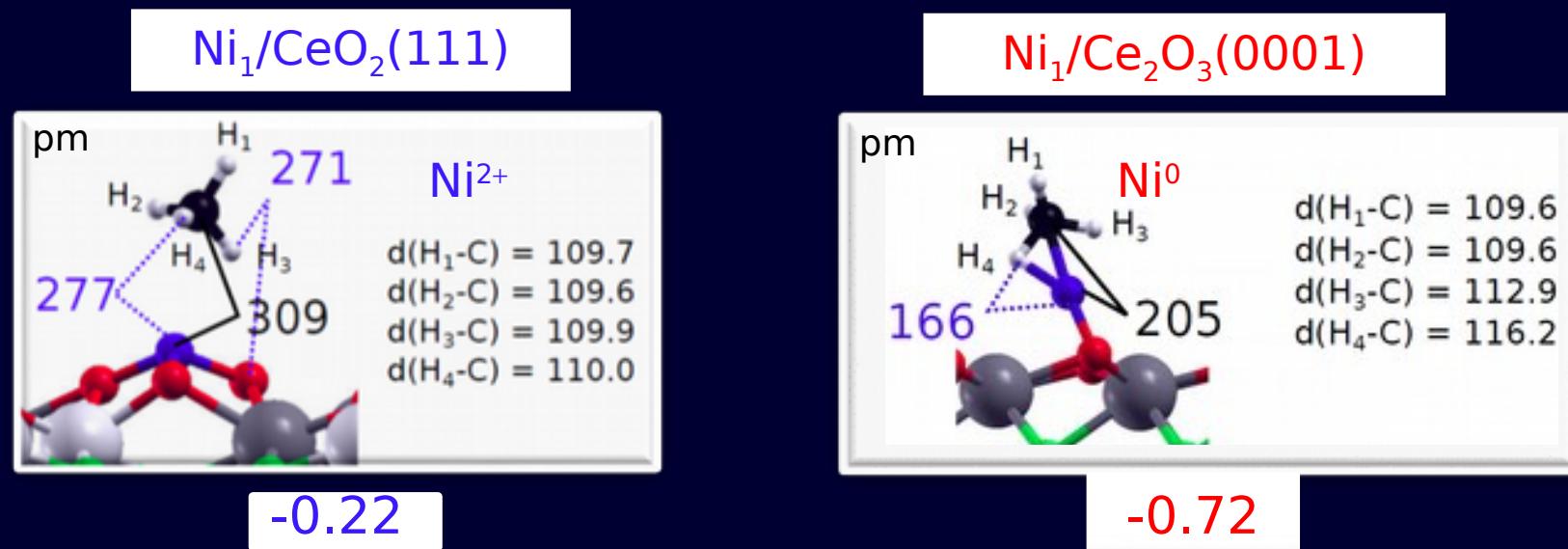
- |   |   |
|---|---|
| <ul style="list-style-type: none"> <li>Ni(111): weakly bound <math>\text{CH}_4</math></li> <li>Ni/CeO<sub>2</sub>(111): moderately bound <math>\text{CH}_4</math></li> <li>Ni/Ce<sub>2</sub>O<sub>3</sub>(0001): stronger bound <math>\text{CH}_4</math></li> </ul> | <ul style="list-style-type: none"> <li>high dissociation barrier → [0.9–1.1 eV]</li> <li>barrier reduction [0.7–0.8 eV]</li> <li>barrier reduction</li> </ul> |
|---|---|

Ni<sup>0</sup> species enhance the reactivity of Ni to fastly cleave C–H bonds

# $\text{CH}_4$ adsorption on Ni/Ceria

DFT+U (4.5)

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



C–Ni distance reduced by  $\sim 1 \text{ \AA}$

CH<sub>4</sub> adsorption on the M<sup>0</sup>/Ce<sub>2</sub>O<sub>3</sub>(0001) surfaces is aided by substantial **hydrogen-metal interactions**

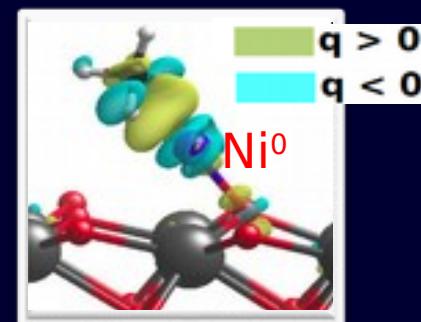
Closer approach



increased charge transfer

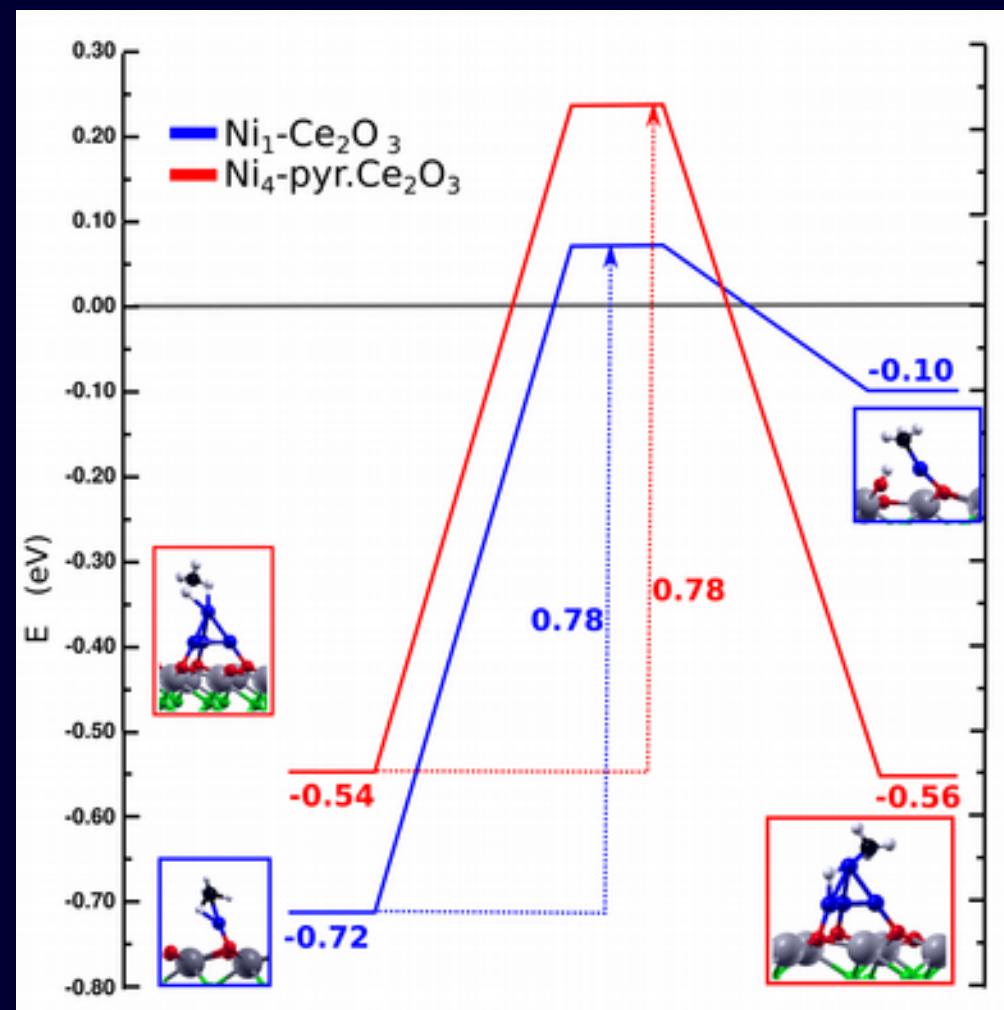
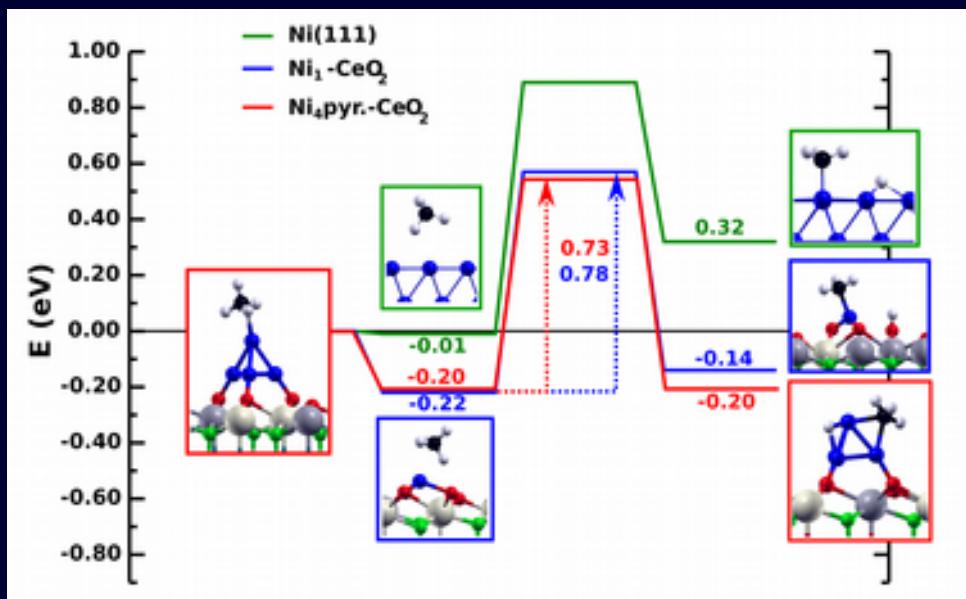
Bader  $\Delta q_C$  wrt CH<sub>4</sub><sup>gas</sup>

Ni <sup>2+</sup>	Ni <sup>0</sup>
-0.09 e <sup>-</sup>	+0.15 e <sup>-</sup>



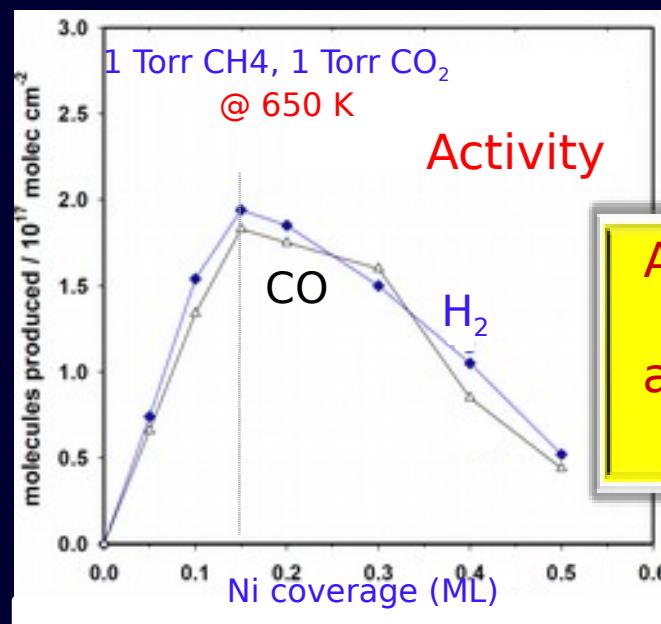
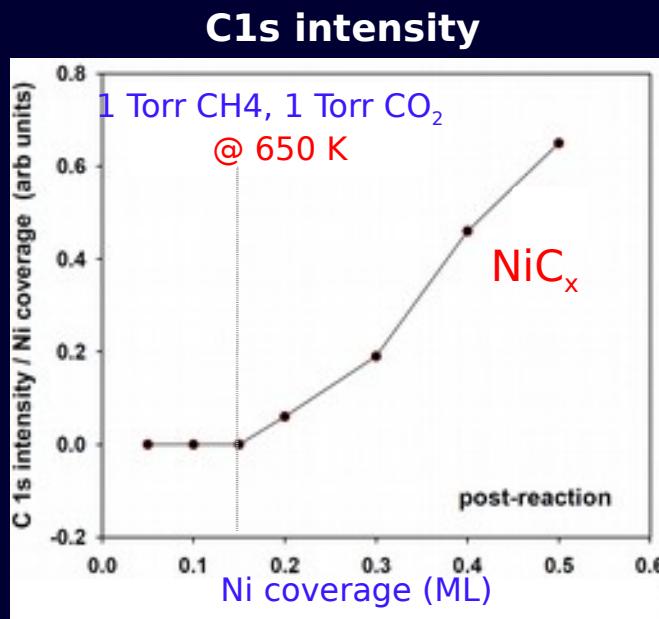
Ni<sub>1</sub>/Ce<sub>2</sub>O<sub>3</sub>(0001)

# $\text{CH}_4$ dissociation on $\text{Ni}_4\text{-pyr}/\text{CeO}_2$ (111)

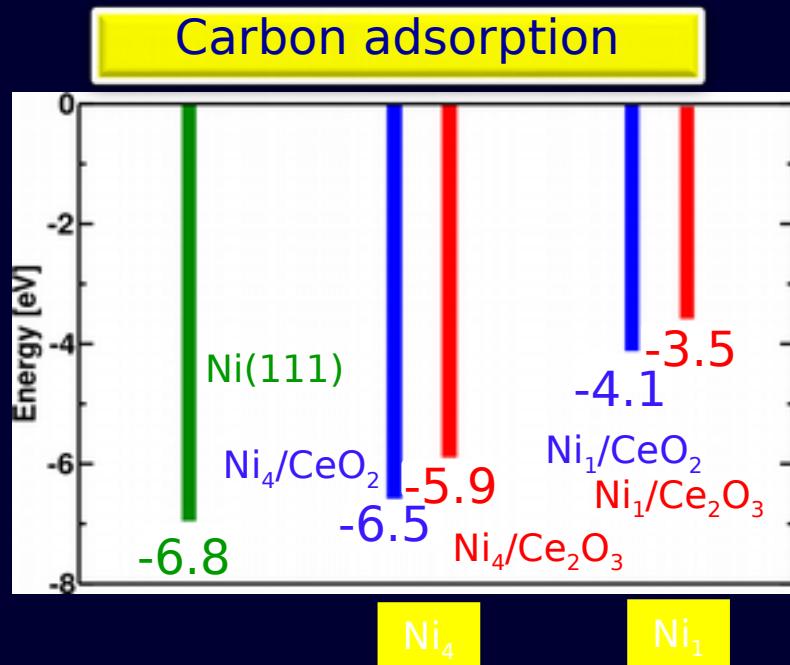


Same Trend!!!

# $\text{CH}_4$ dissociation on Ni/CeO<sub>2</sub> (111): The Ni coverage effect



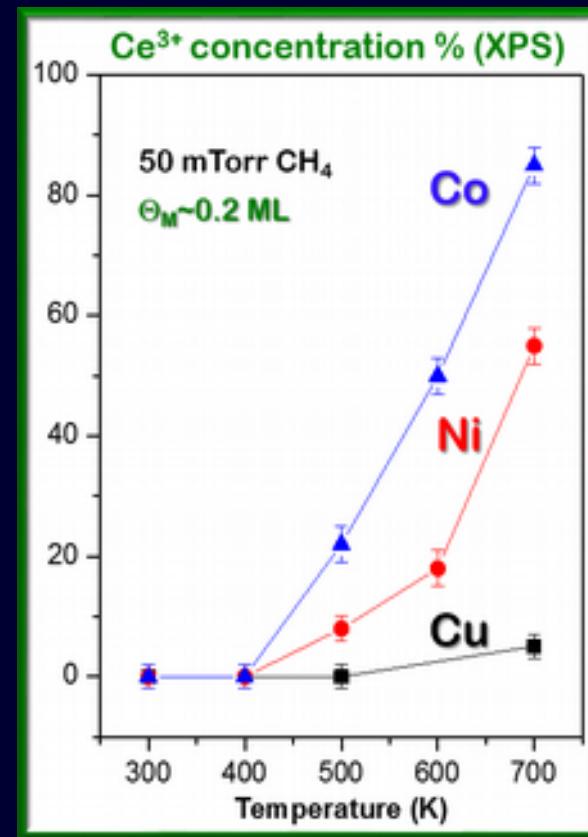
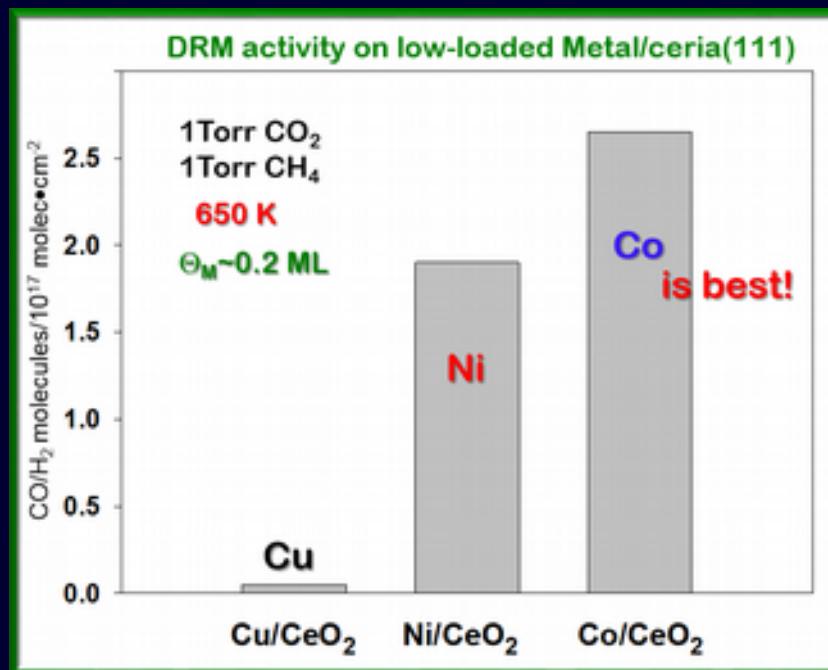
Above  $\sim 0.15$  ML  $\rightarrow$  decline in the activity due to NiC<sub>x</sub> formation



NiC<sub>x</sub> formation relates to C adsorption energy trend  
 $\text{Ni}(111) \approx \text{Ni}_4/\text{ceria} > \text{Ni}_1/\text{ceria}$

# How unique is Ni/ceria for DRM? The examples of Cu & Co

Liu et al. Angew. Chem. Int. Ed. 56, 13041 (2017)

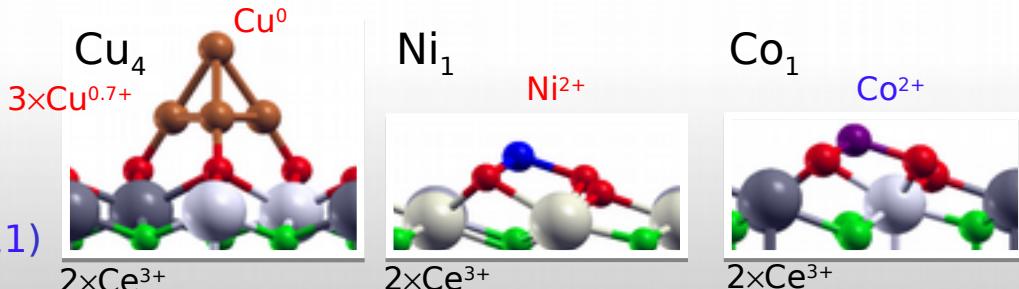


T	Cu	Ni	Co
300 K $\text{CH}_4$ dissociation	$\text{Cu}^{1+} \text{ atoms} \rightarrow \text{Cu}^0 \text{ particles}$ ✗	$\text{Ni}^{2+}/\text{CeO}_2$ ✓	$\text{Co}^{2+}/\text{CeO}_2$ ✓
~700 K DRM activity	✗	$\text{Ni}^0/\text{CeO}_{2-x}$ ✓	$\text{Co}^0/\text{CeO}_{2-x}$ ✓

$\text{M}^{2+}/\text{CeO}_2 \rightarrow \text{M}^0/\text{CeO}_{2-x}$



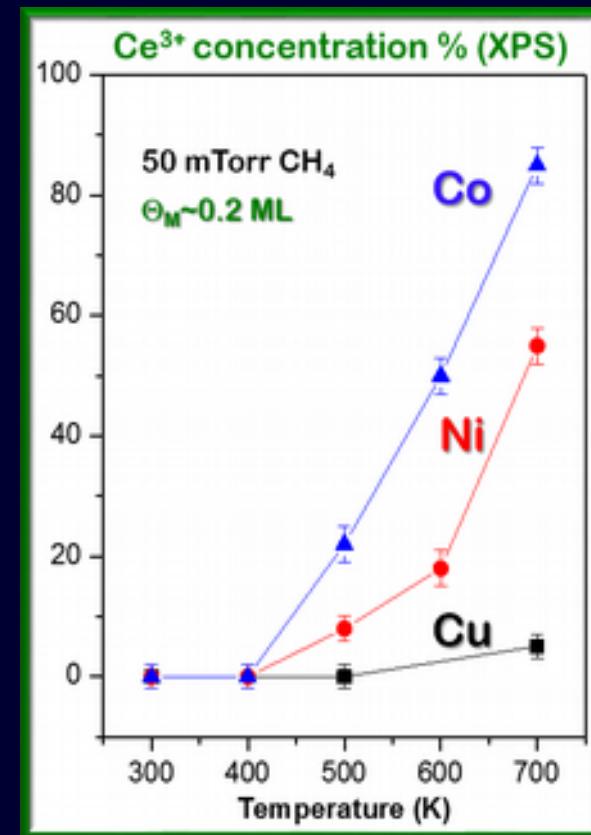
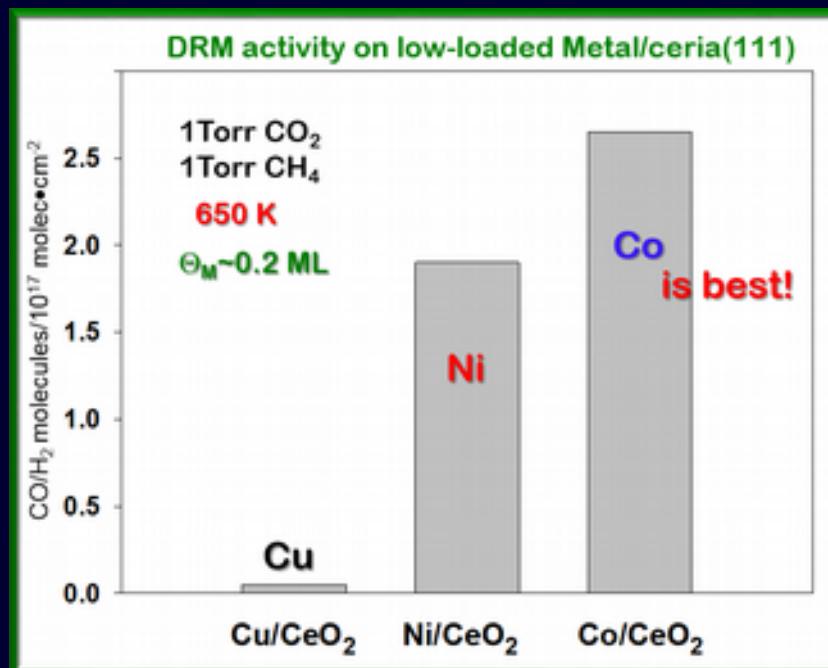
## Models



- $\text{CH}_4$  produces vacancies, i.e.,  $\text{Ce}^{3+}$
- Very high reaction with  $\text{Co}^0/\text{CeO}_{2-x}$
- Poor reaction with  $\text{Cu}^0/\text{CeO}_{2-x}$

# How unique is Ni/ceria for DRM? The examples of Cu & Co

Liu et al. Angew. Chem. Int. Ed. 56, 13041 (2017)

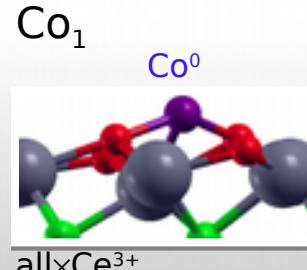
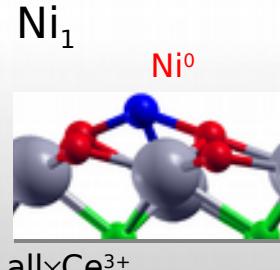


T	Cu	Ni	Co
300 K CH <sub>4</sub> dissociation	$\text{Cu}^{1+} \text{ atoms} \rightarrow \text{Cu}^0 \text{ particles}$ ✗	$\text{Ni}^{2+}/\text{CeO}_2$ ✓	$\text{Co}^{2+}/\text{CeO}_2$ ✓
~700 K DRM activity	✗	$\text{Ni}^0/\text{CeO}_{2-x}$ ✓	$\text{Co}^0/\text{CeO}_{2-x}$ ✓

$\text{M}^{2+}/\text{CeO}_2 \rightarrow \text{M}^0/\text{CeO}_{2-x}$

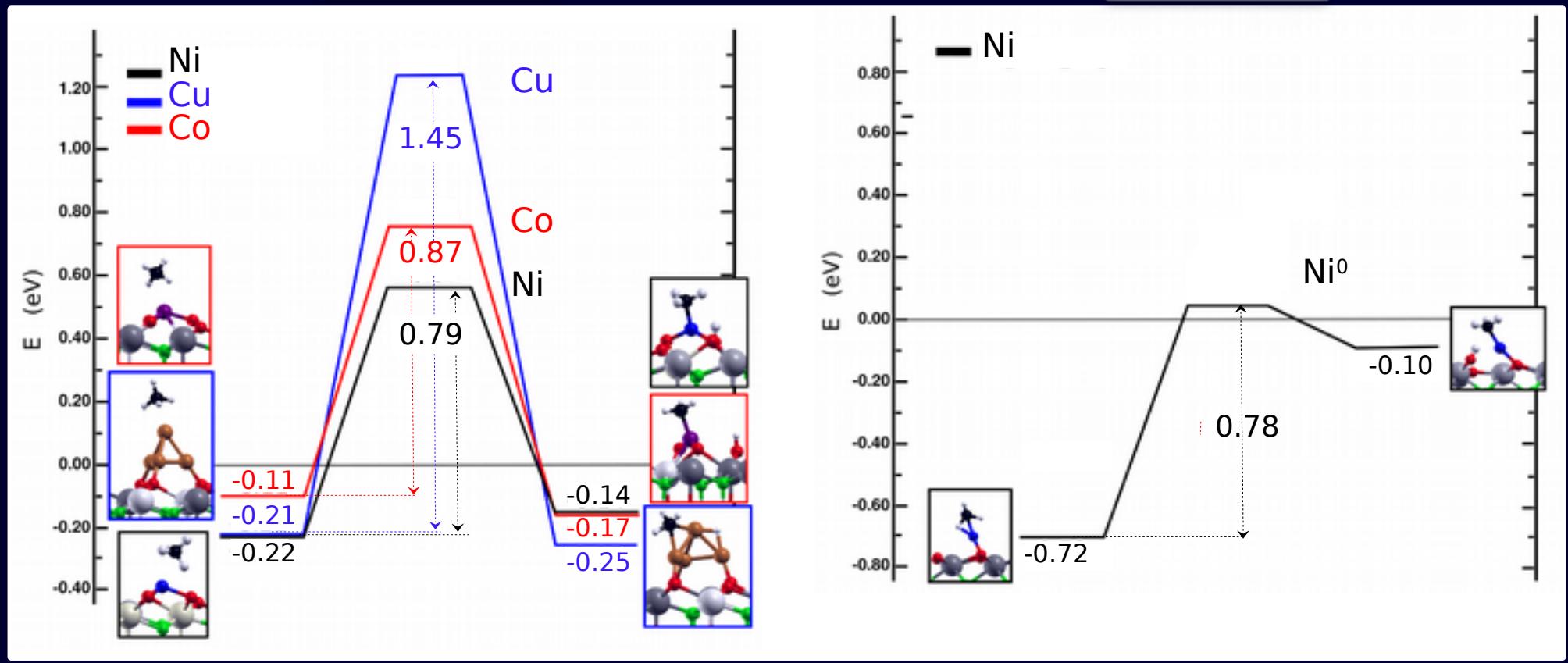


## Models



- CH<sub>4</sub> produces vacancies, i.e., Ce<sup>3+</sup>
- Very high reaction with Co<sup>0</sup>/CeO<sub>2-x</sub>
- Poor reaction with Cu<sup>0</sup>/CeO<sub>2-x</sub>

# CH<sub>4</sub> dissociation on Metal/Ceria (111)



□ Cu<sup>0</sup>: large energy barrier → negligible dissociation

□ Ni<sup>0</sup>: Ni<sup>0</sup>/CeO<sub>2-x</sub> and Ni<sup>2+</sup>/CeO<sub>2</sub> → similar barriers  
more strongly bound CH<sub>4</sub> → enhanced reactivity

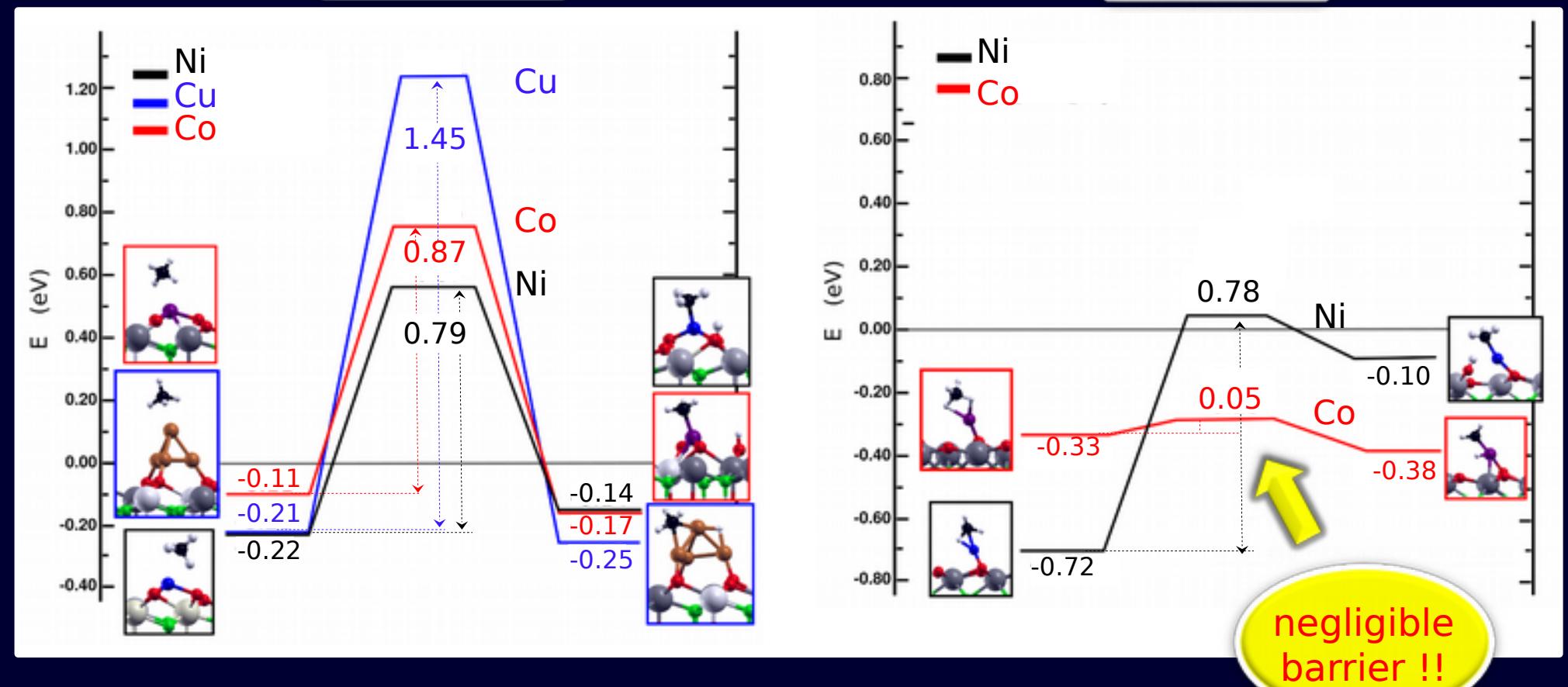
□ Co<sup>2+</sup>/Ni<sup>2+</sup>: barrier reduction wrt. extended metals (~0.2 eV)  
CH<sub>4</sub> → CH<sub>3</sub>+H    accessible at lower T

Cu(111): 1.64

Co(0001): 1.07

Ni(111): 0.9

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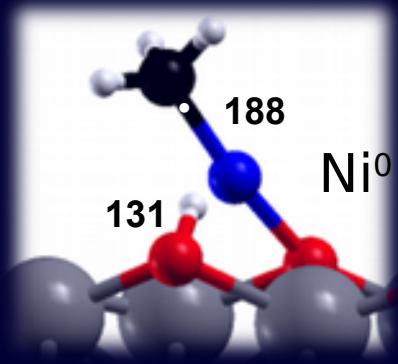
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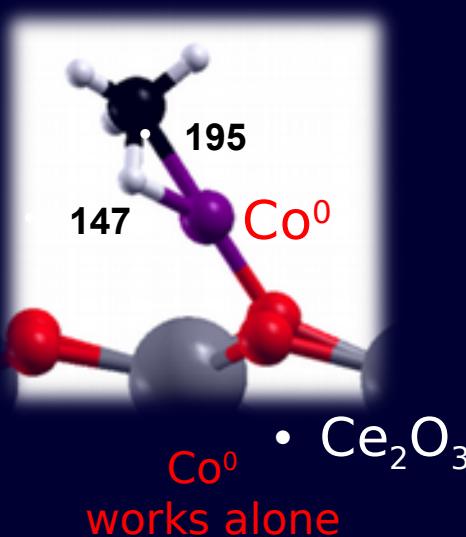
# $\text{CH}_4$ dissociation on Metal/Ceria (111)

$\text{M}^0/\text{Ce}_2\text{O}_3$

- TS



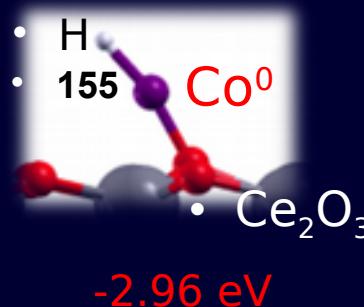
- $\text{Ni}^0$  and Osurf work cooperatively



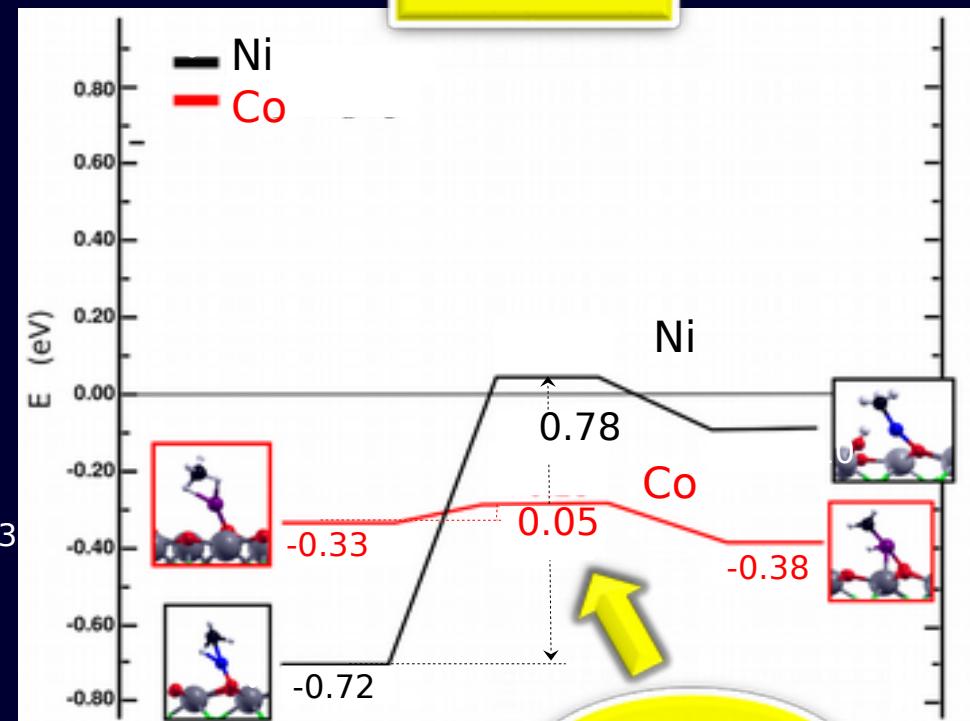
$\text{Co}^0$  forms stronger Metal-H bonds



- -2.24 eV
- wrt.  $\frac{1}{2} \text{H}_2$



-2.96 eV

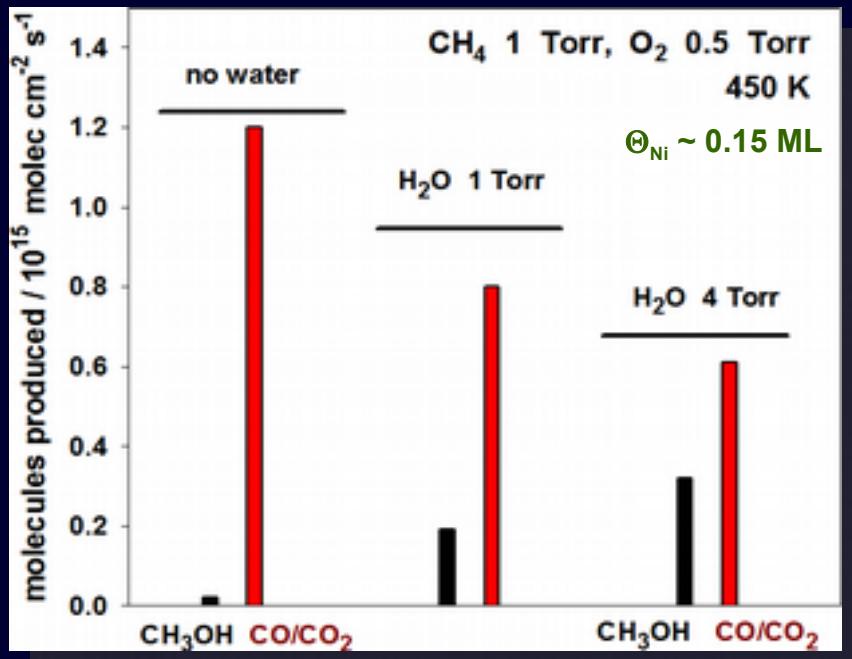


negligible  
barrier !!

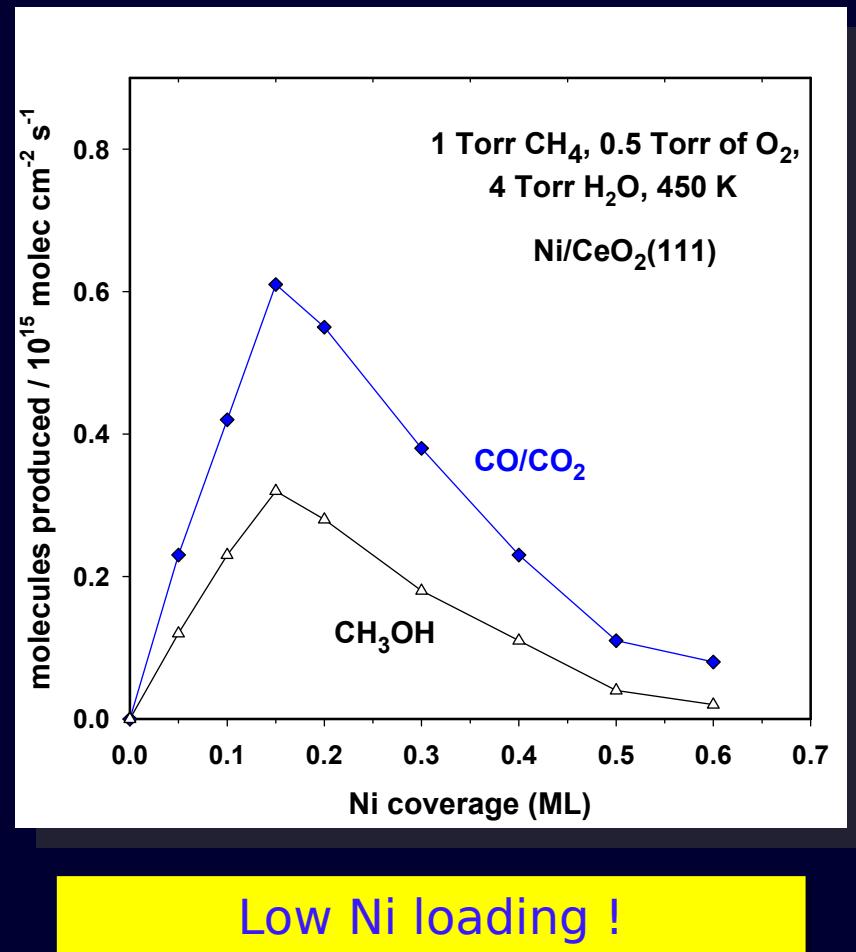
$\text{Co}^0/\text{CeO}_{2-x}$

- C–H more easily cleaved
  - ↓
- more  $\text{Ce}^{3+}$ ; more  $\text{O}_{\text{vac}}$

# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2(111)$



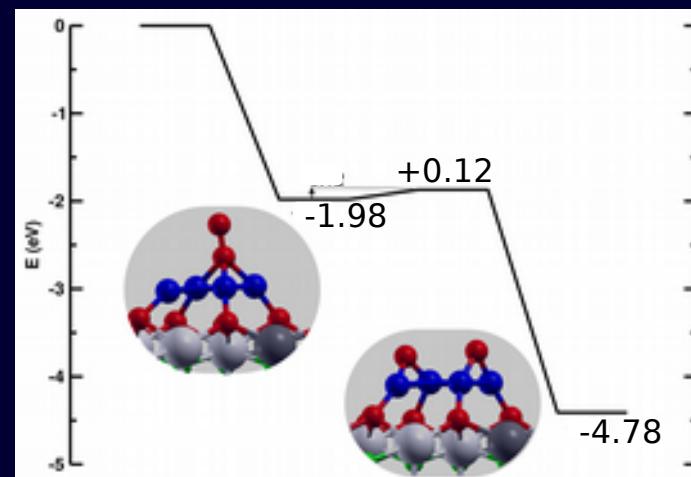
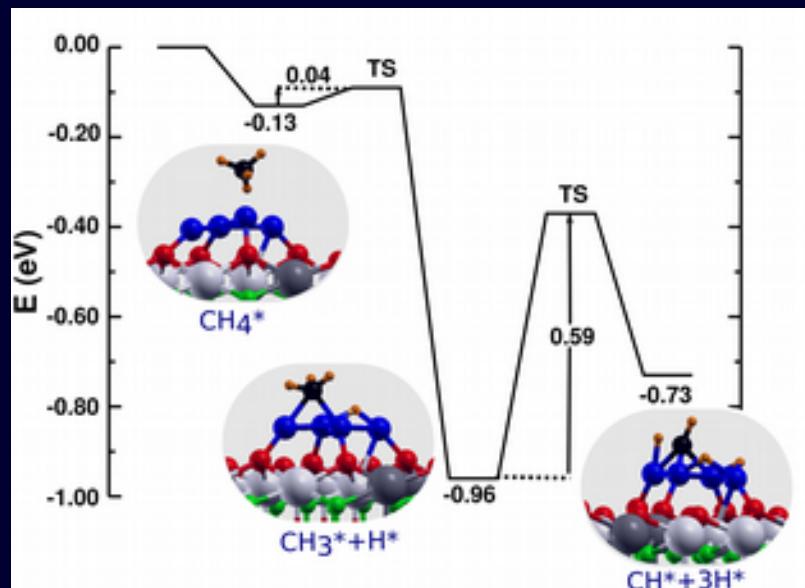
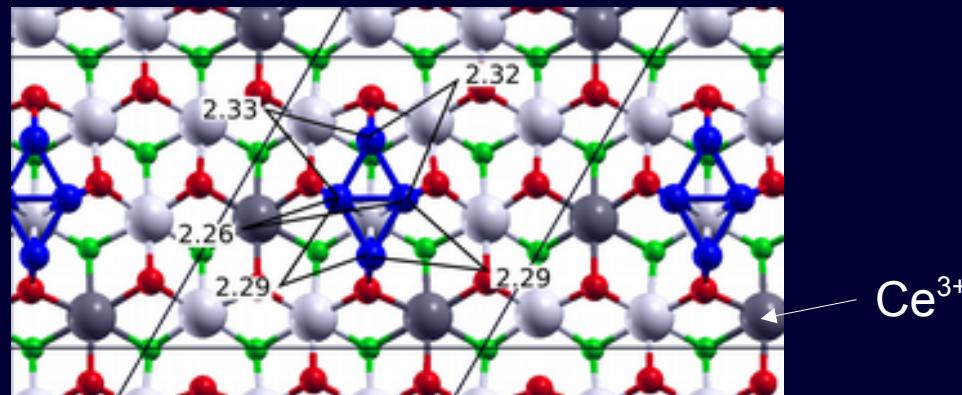
$\text{H}_2\text{O}$  rich environment helps!



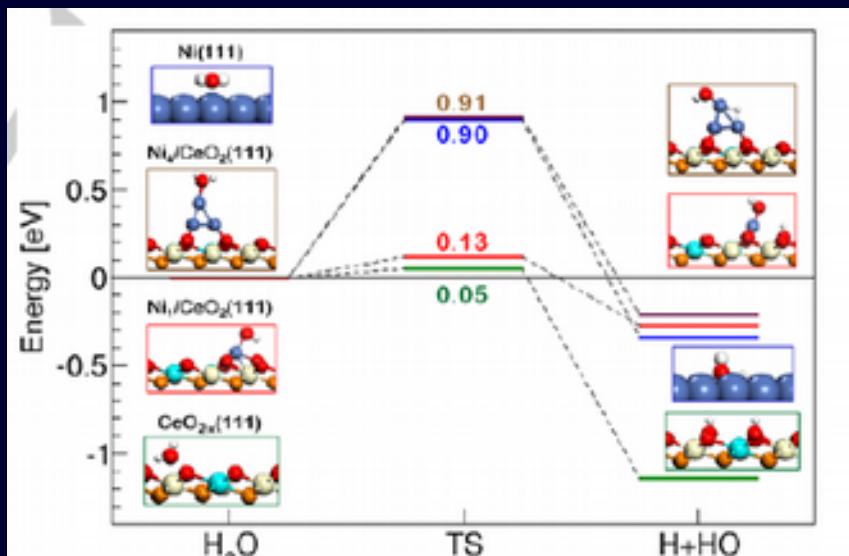
Low Ni loading !

# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2$ (111)

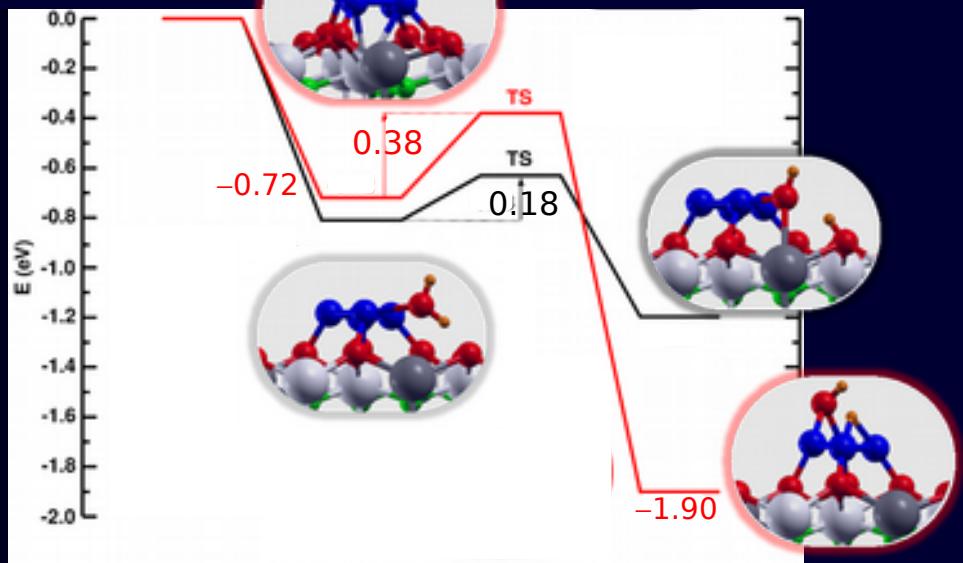
## $\text{Ni}_{\frac{1}{4}}\text{Flat}/\text{CeO}_2$ Model



# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2(111)$

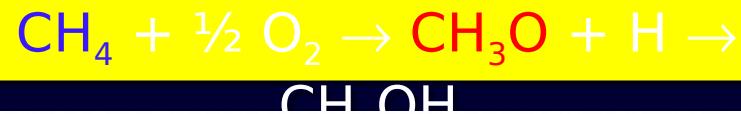


Angew. Chem. Int. Ed. 54, 3917 (2015)

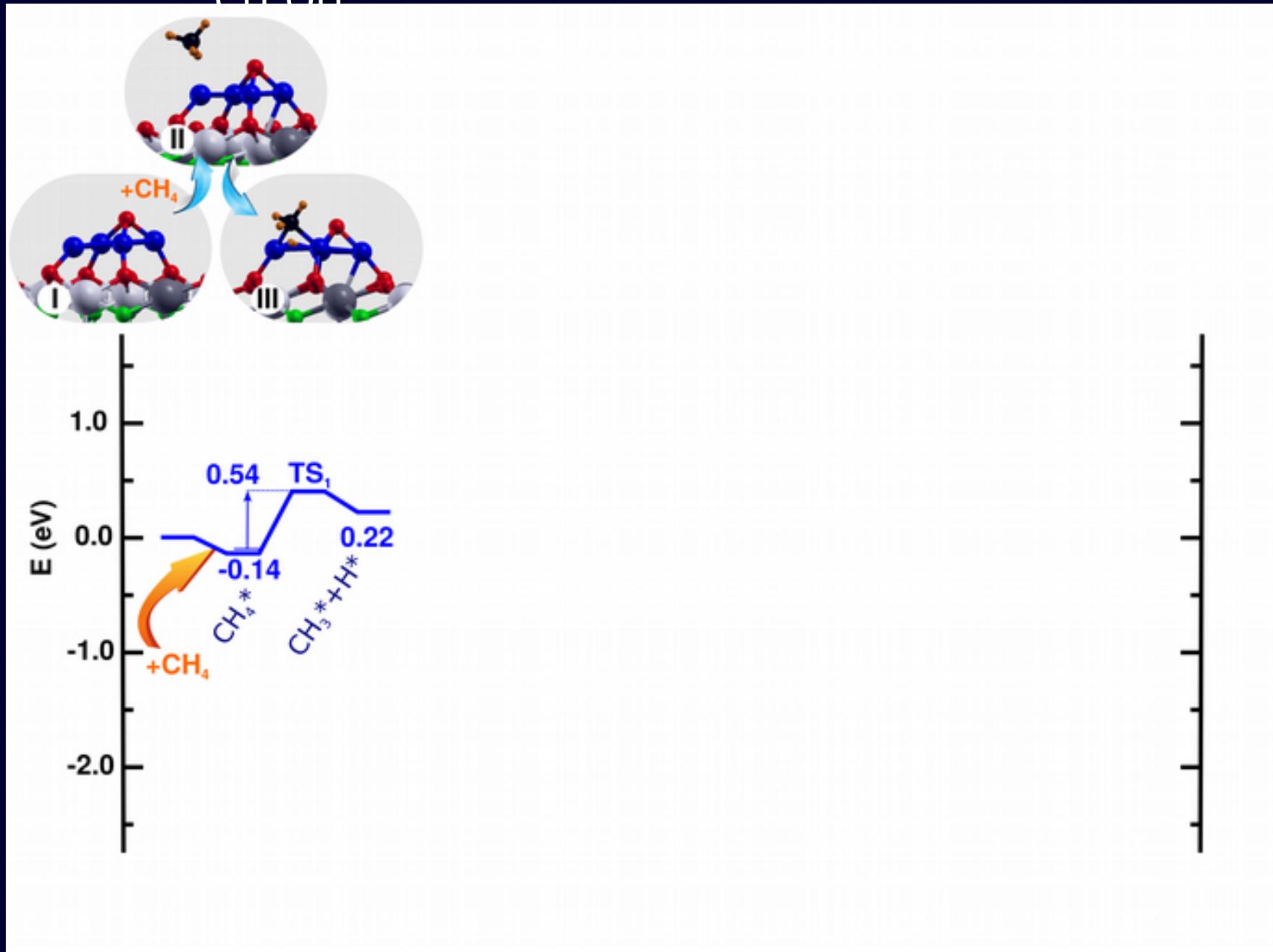


- How does  $\text{CH}_3\text{O}$  form?
- How does  $\text{H}_2\text{O}$  help?

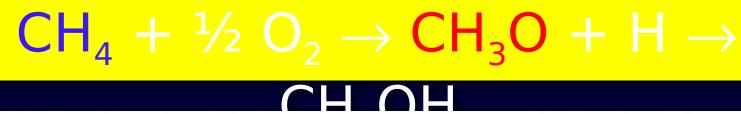
# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2$ (111)



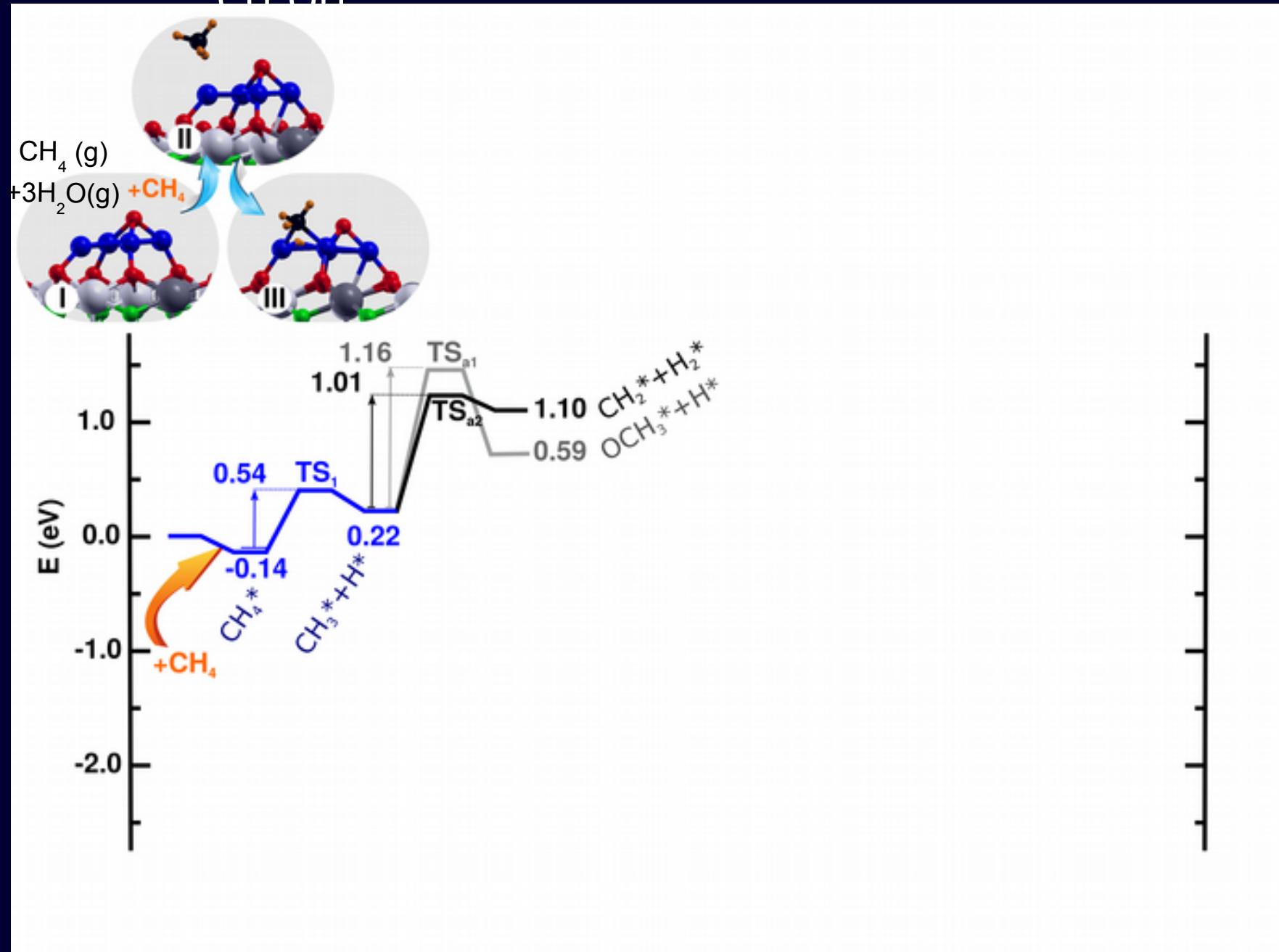
Lustemberg et al. JACS 140 (2018)



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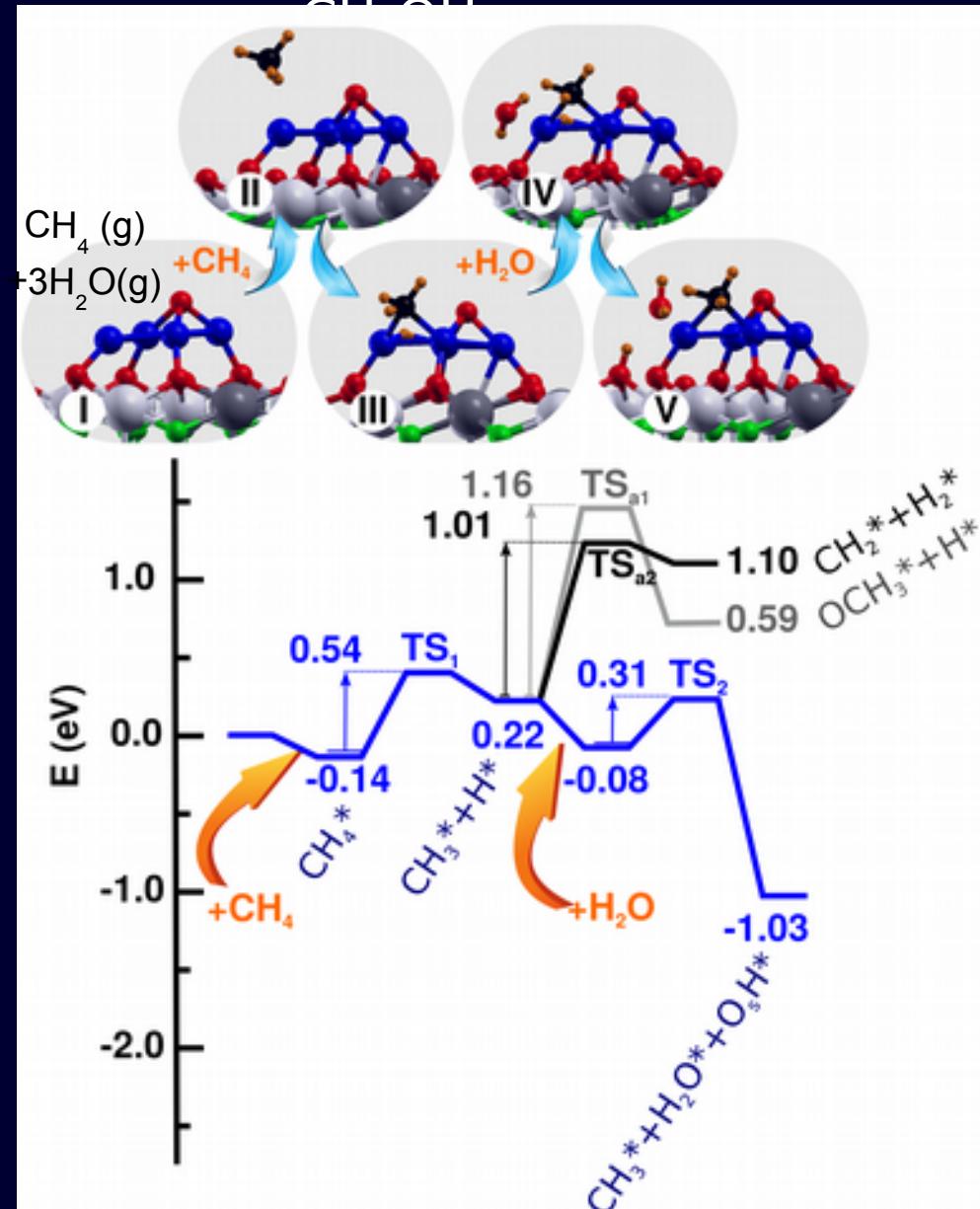
Lustemberg et al. JACS 140 (2018)



# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2$ (111)



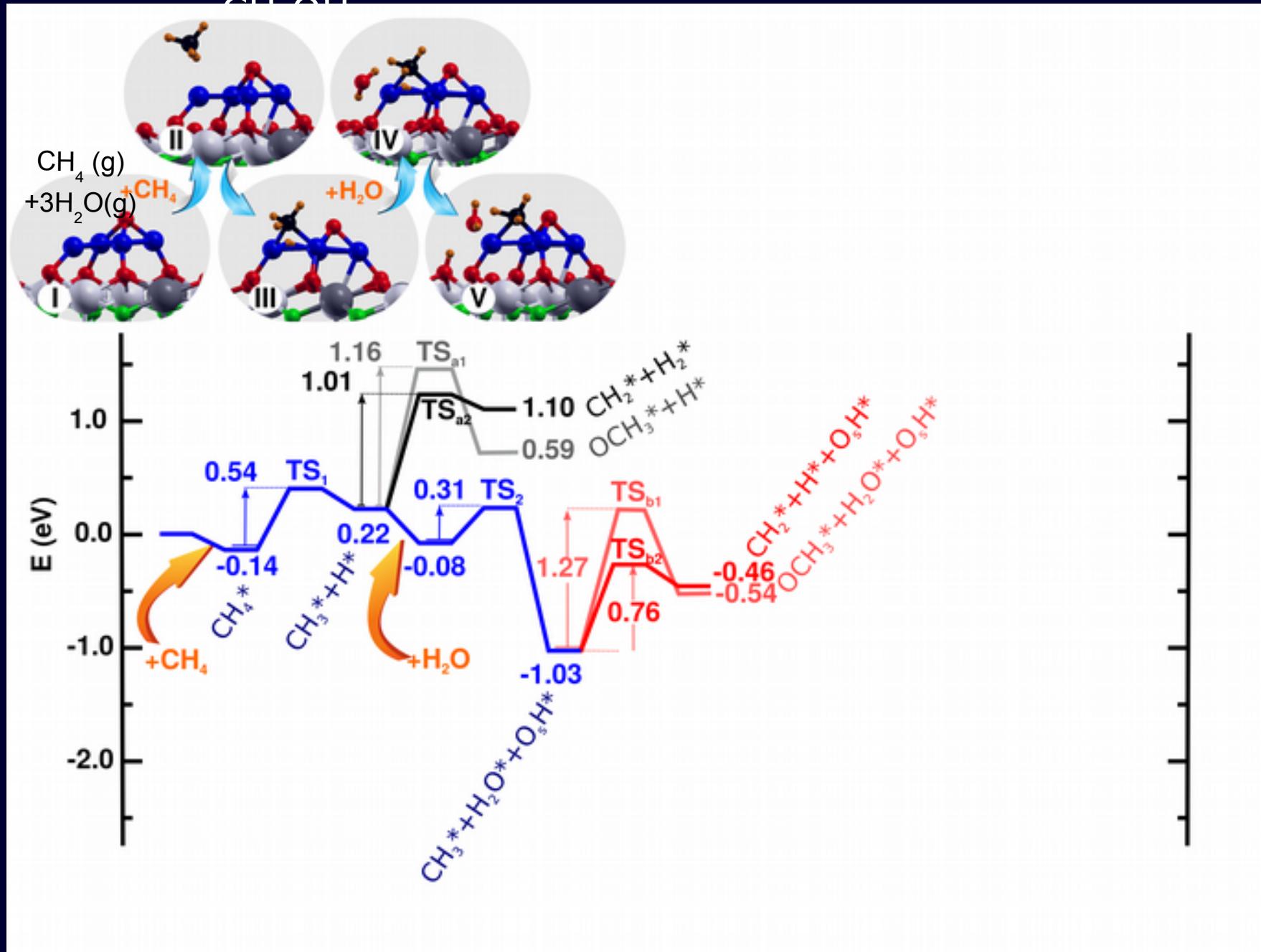
Lustemberg et al. JACS 140 (2018)



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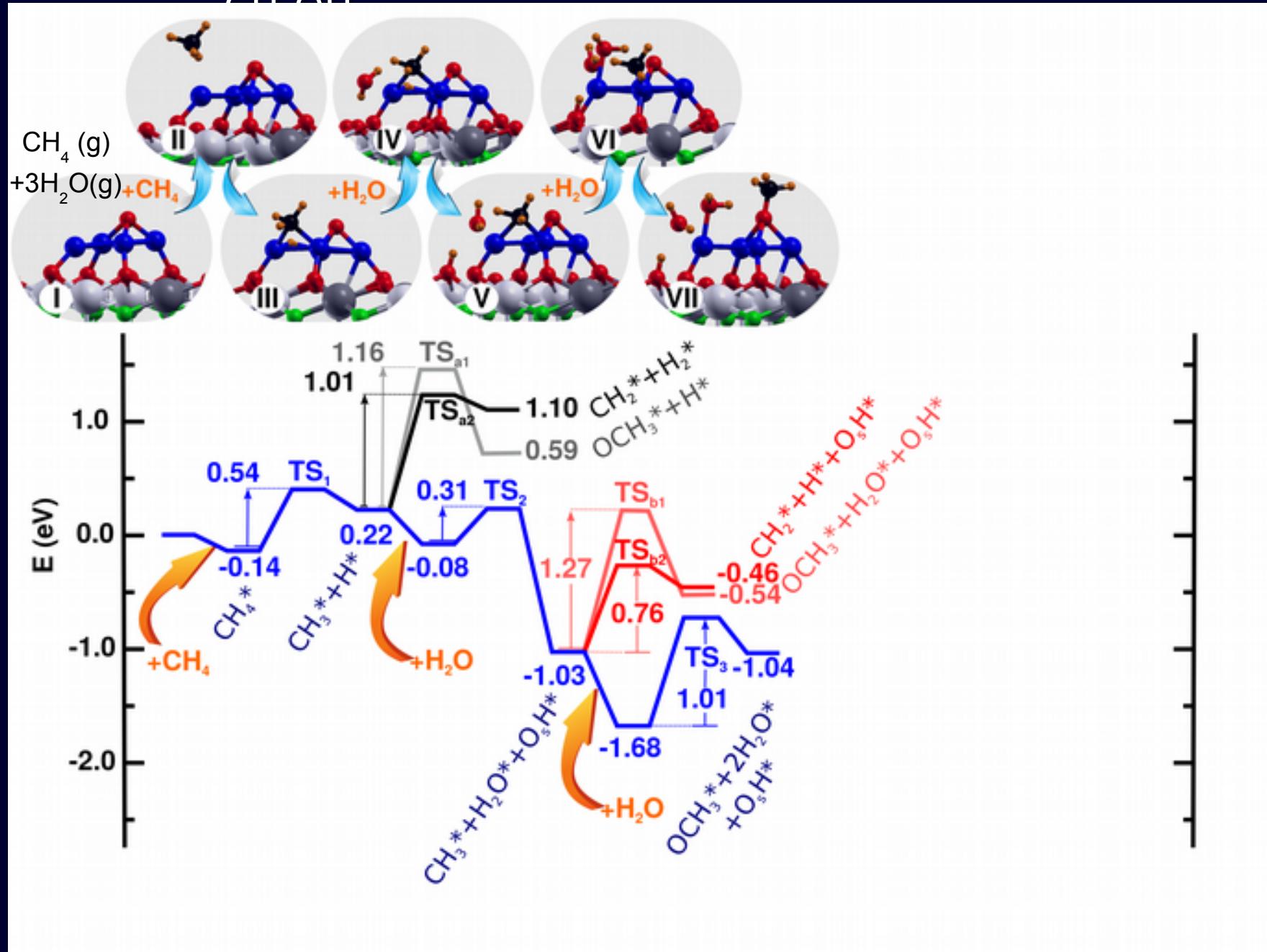
Lustemberg et al. JACS 140 (2018)



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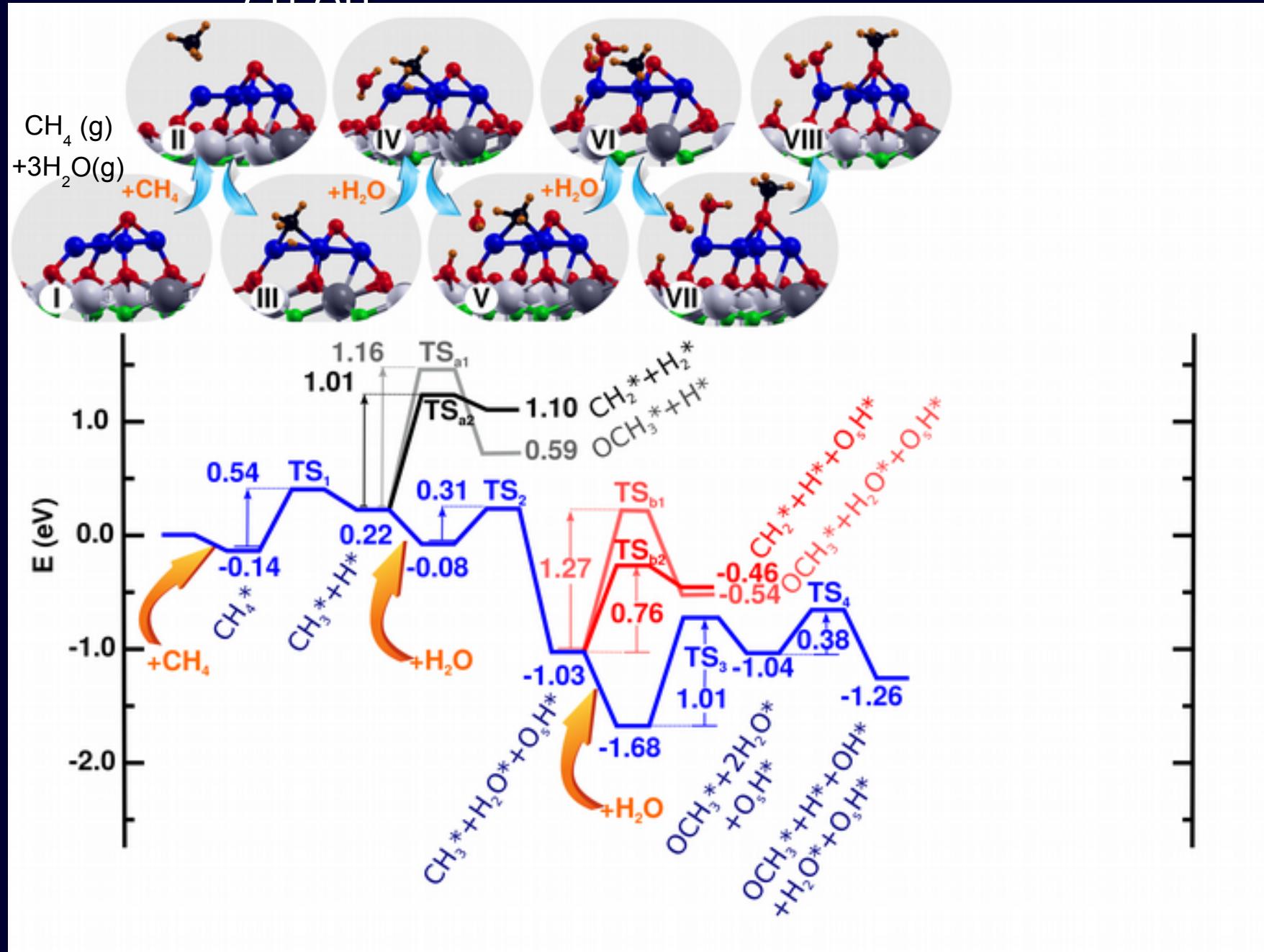
Lustemberg et al. JACS 140 (2018)



# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2$ (111)



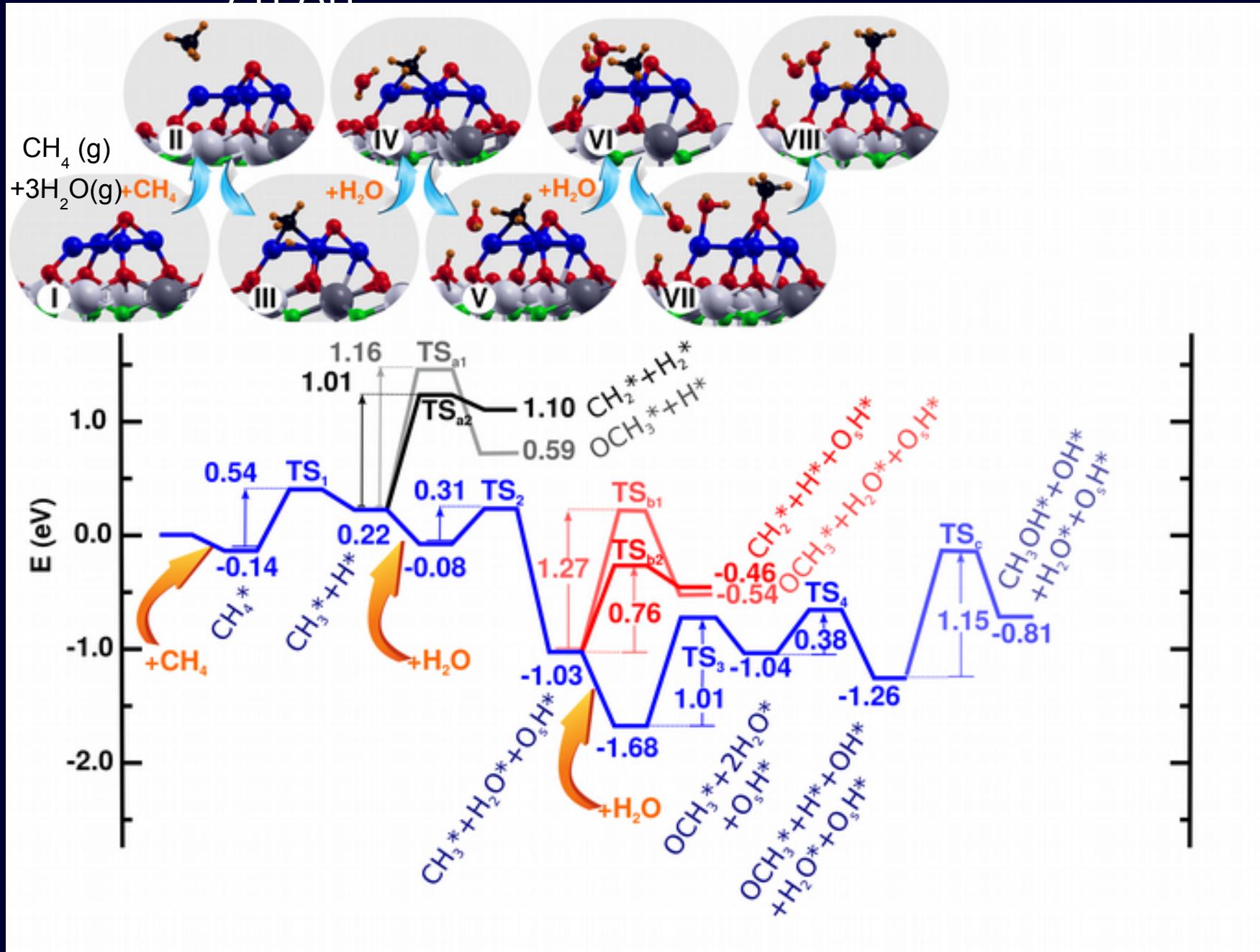
Lustemberg et al. JACS 140 (2018)



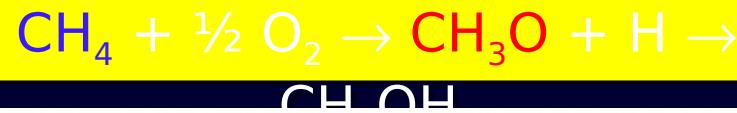
# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2(111)$



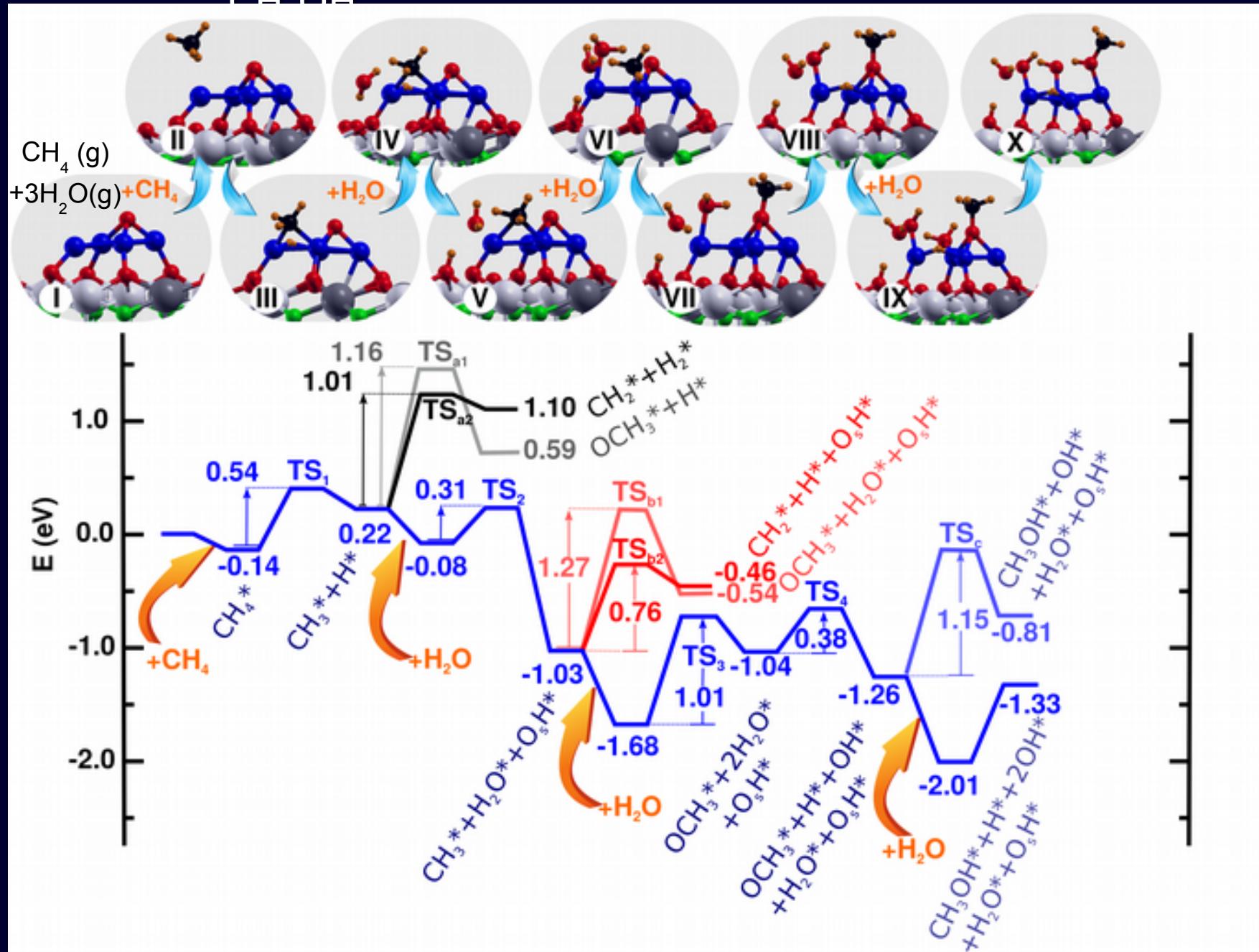
Lustemberg et al. JACS 140 (2018)



# Direct conversion of $\text{CH}_4$ to $\text{CH}_3\text{OH}$ on $\text{Ni}/\text{CeO}_2$ (111)



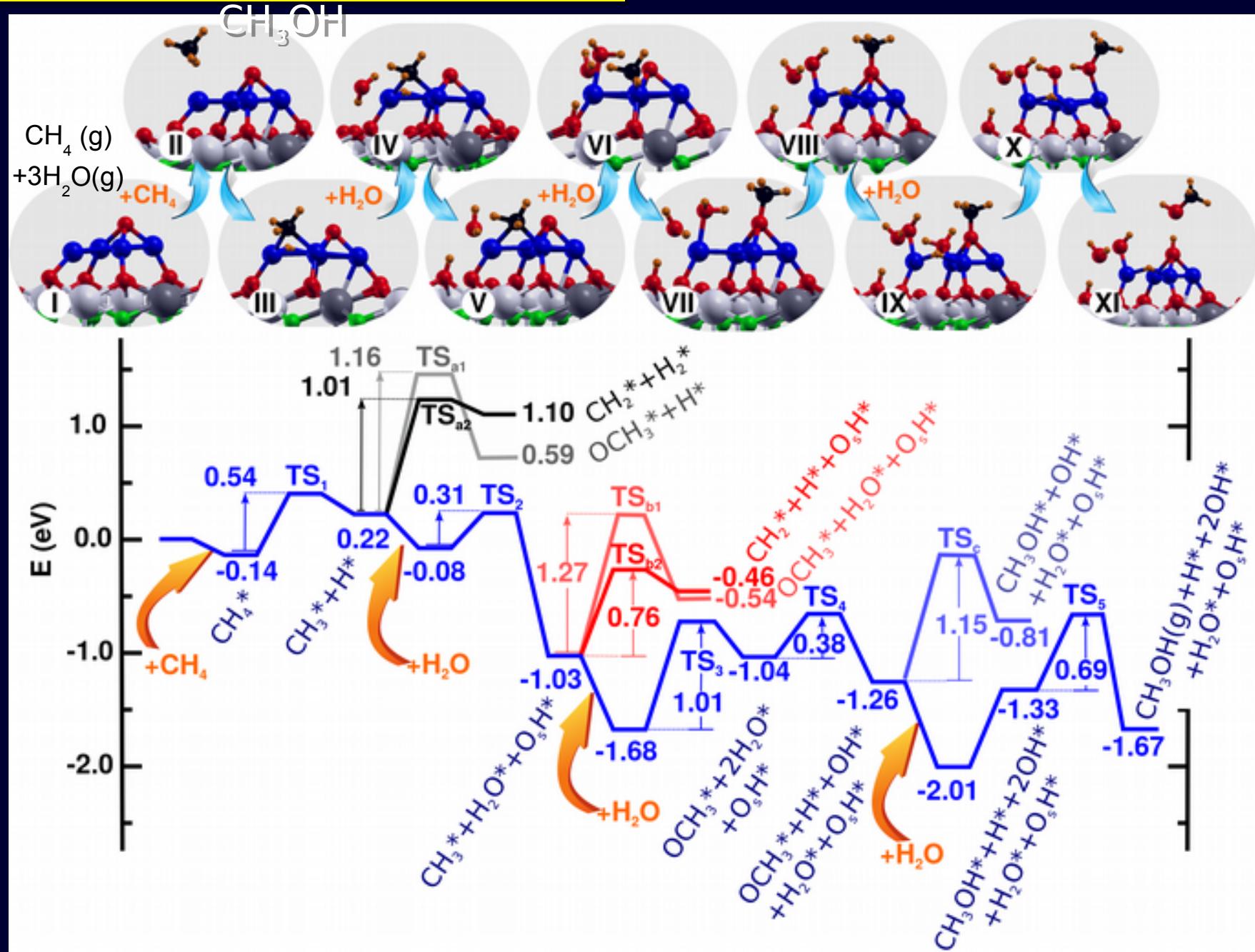
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Lustemberg et al. JACS 140 (2018)



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Lustemberg et al. JACS 140 (2018)



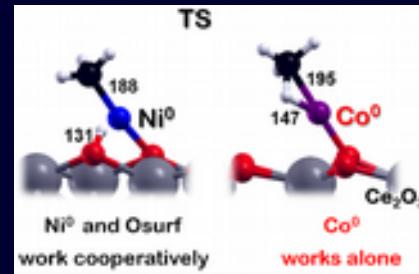
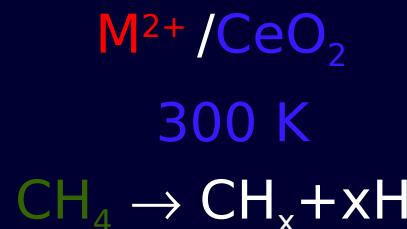
- ✓ changes the path
- ✓ blocks sites for  $\text{CH}_3$  dissociation
- ✓ provides OH + H:  $\text{Ni}-\text{OH} + \text{CH}_3\text{OH}_{(g)}$

# Summary

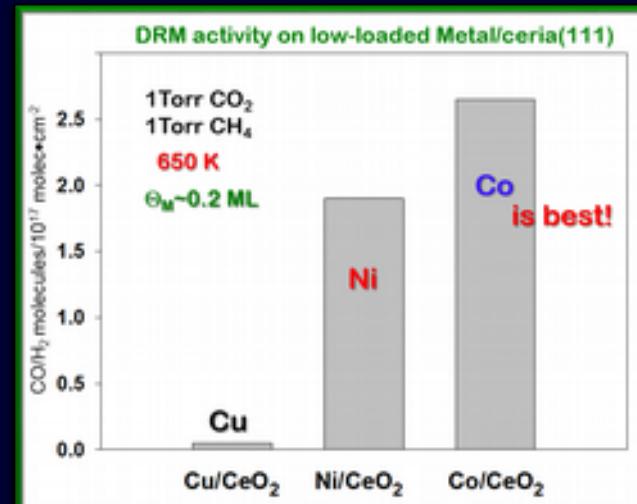
- Support effect

- “right” metal-oxide
- metal loading

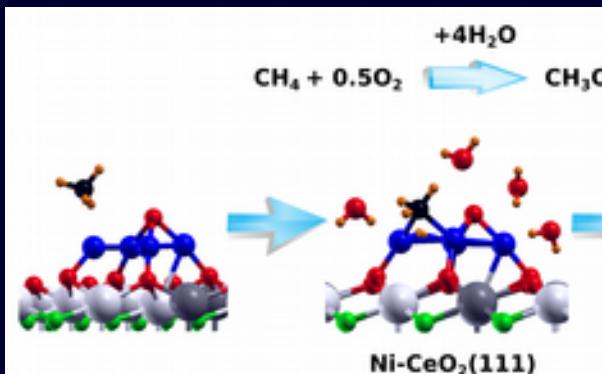
## Ni/Co/ceria for DRM



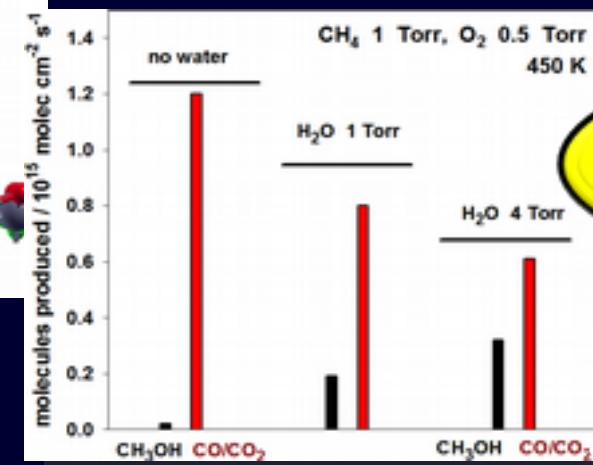
- Angew. Chem. Int. Ed. 55, 7455 (2016)
- ACS Catal 6, 8184 (2016)
- Angew. Chem. Int. Ed. 56, 13041 (2017)



## Ni<sub>n</sub>/ceria → Methanol production



Lustemberg et al. JACS (2018) in press



- Ceria is
- non-innocent



# Interaction of HCl with CeO<sub>2</sub> (111)

Sack et al., J. Phys. Chem. C 122 (2018)

## Deacon Reaction

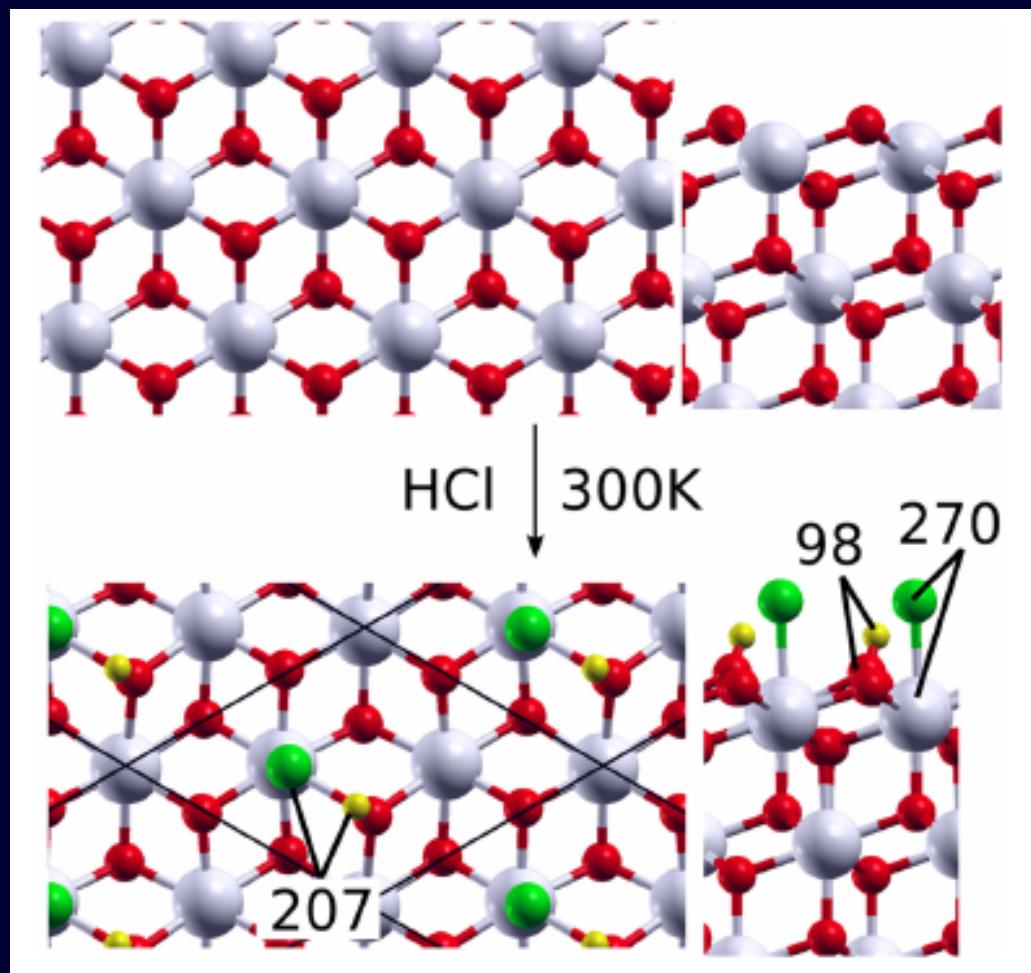
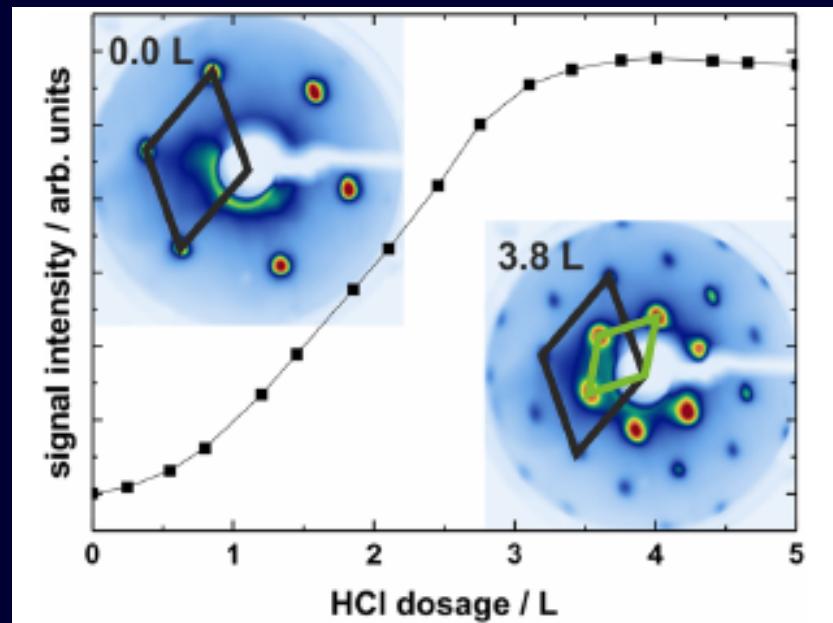


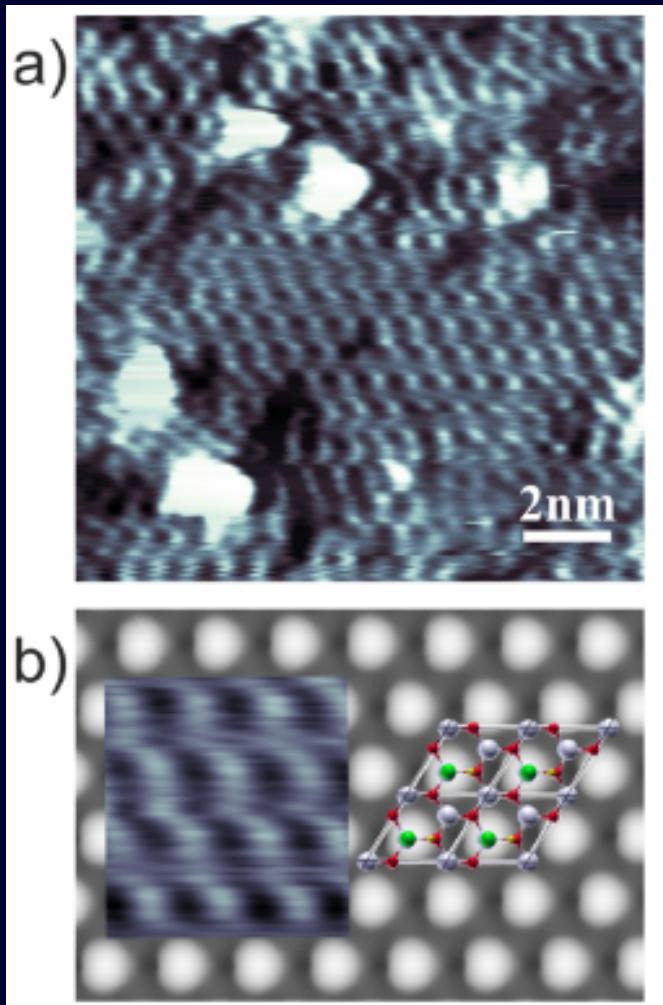
Figure LEED patterns (49 eV) of the CeO<sub>2</sub>(111) layer and after exposure of 3.8 L of HCl to CeO<sub>2</sub>(111) at 300 K. The (1 × 1) unit cell is shown in black and the ( $\sqrt{3} \times \sqrt{3}$ )R30° unit cell in green. The graph shows the integrated intensity of the first order overlayer diffraction spot as a function of HCl exposure at 300 K, 49 eV.

- dissociative adsorption of HCl

# Interaction of HCl with CeO<sub>2</sub> (111)

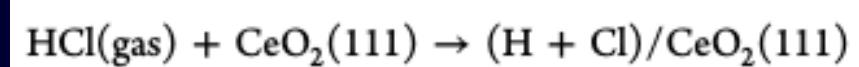
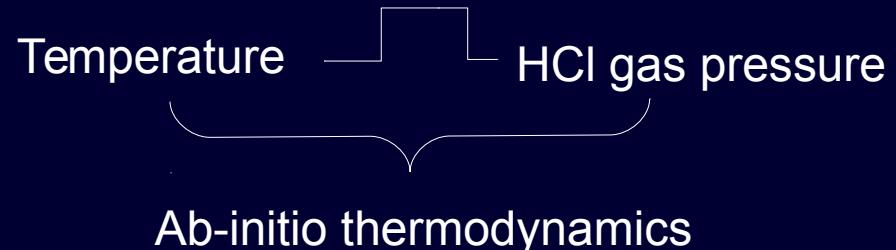
STM

Sack et al., J. Phys. Chem. C 122 (2018)



**Figure .** STM image of the CeO<sub>2</sub>(111) ( $\sqrt{3} \times \sqrt{3}$ )R30° structure after exposing the CeO<sub>2</sub>(111) surface to 5 L of HCl at 300 K. (a) 13 × 13 nm<sup>2</sup>,  $U = 3.7$  V, and  $I = 0.15$  nA. (b) DFT simulations of empty-state STM images (0–1.8 eV) of the ( $\sqrt{3} \times \sqrt{3}$ )R30° – Cl + H surface compared to a small section of (a). The calculated structure is superimposed where H and Cl species and the outermost O and Ce ions are depicted as yellow, green, red, and gray spheres, respectively.

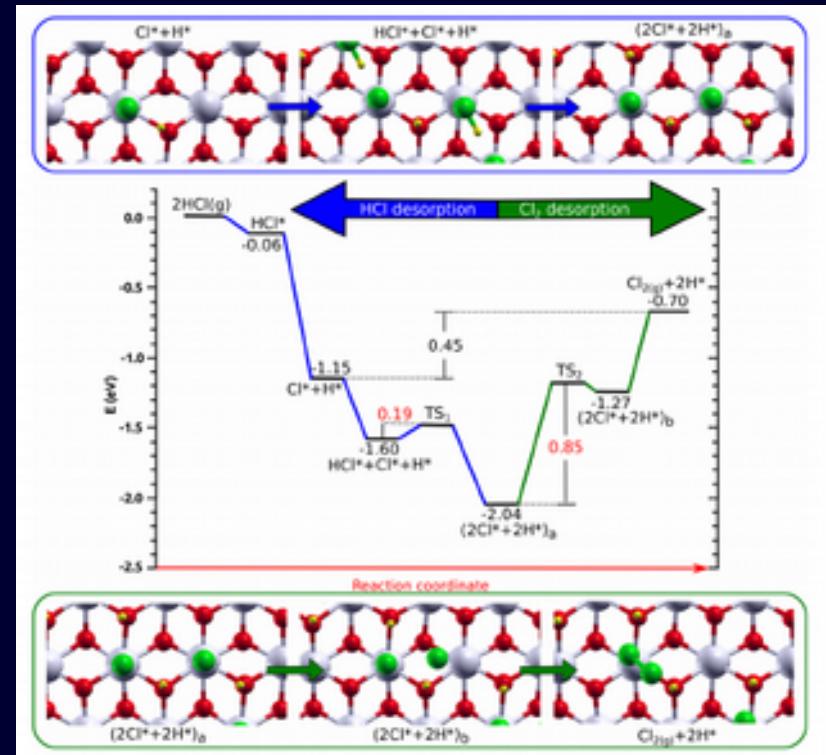
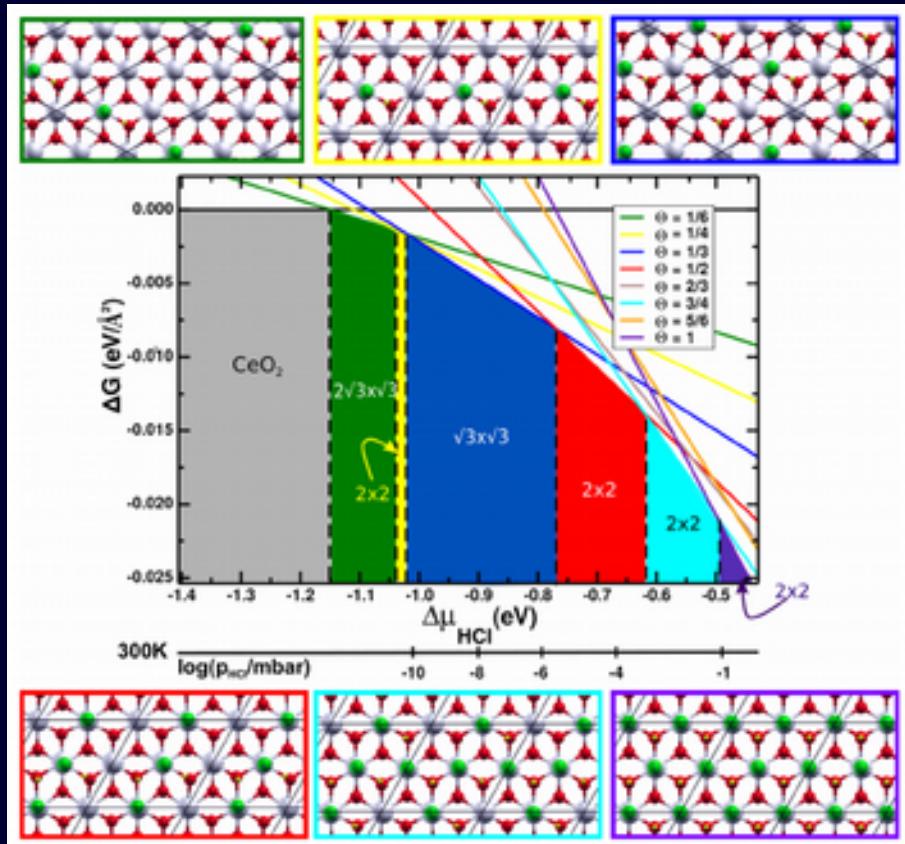
## HCl/CeO<sub>2</sub> (111) surface structure



$$\Delta G \cong \frac{N}{A} \left[ \frac{E_{\text{H+Cl/CeO}_2(111)} - E_{\text{HCl(gas)}} - E_{\text{CeO}_2(111)}}{N} - \Delta \mu_{\text{HCl}} \right]$$

$$\Delta \mu_{\text{HCl}}(T, p) = [H(T, p^0) - H(0 \text{ K}, p^0)] - TS(T, p^0) + RT \ln \left( \frac{p}{p^0} \right)$$

# Interaction of HCl with $\text{CeO}_2$ (111)



Associative desorption of HCl is much more favorable than the recombinative Cl<sub>2</sub> desorption

# Acknowledgments

Diamond Light Source

## Theory Team



M. Verónica  
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Busnengo  
• IFIR  
Argentina



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Vitoria, Spain

• David  
Grinter  
Diamond Light Source



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Tyndall Ireland



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Laramie, Wyoming, USA

## Experimental Team - CH<sub>4</sub>



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Rodriguez



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Senanajake



• Zongyuan  
Liu



• Si Luo



• Thuyduong  
Nguyen-Phan  
• Ping  
Liu



• Iradwikanari  
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Upton, New York, USA



• Robert M.  
Palomino  
• Dario  
Stacchiola



• Yinghui  
Zhou  
University of Wyoming  
Laramie, Wyoming, USA

# Acknowledgments

Special Thanks to:



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Special Thanks to:

Computer Time

Memento

RES

24/26 Granted Projects

PRACE

MareNostrum (3 & 4)

Archer

BEM

La Palma

Tirant

Pirineus

Calendula

FinisTerrae

Picasso

PRL; 2x Angew; 2x JPCC;  
ACS Catal; JACS

Marie S. Curie Fellowship

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Thank you very much for your attention!!

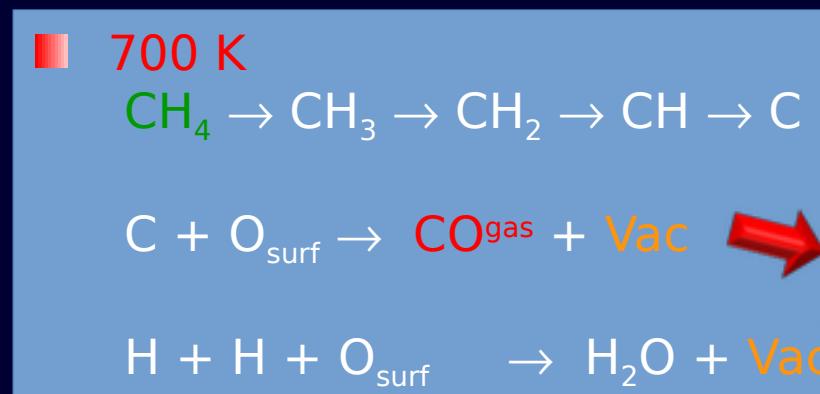
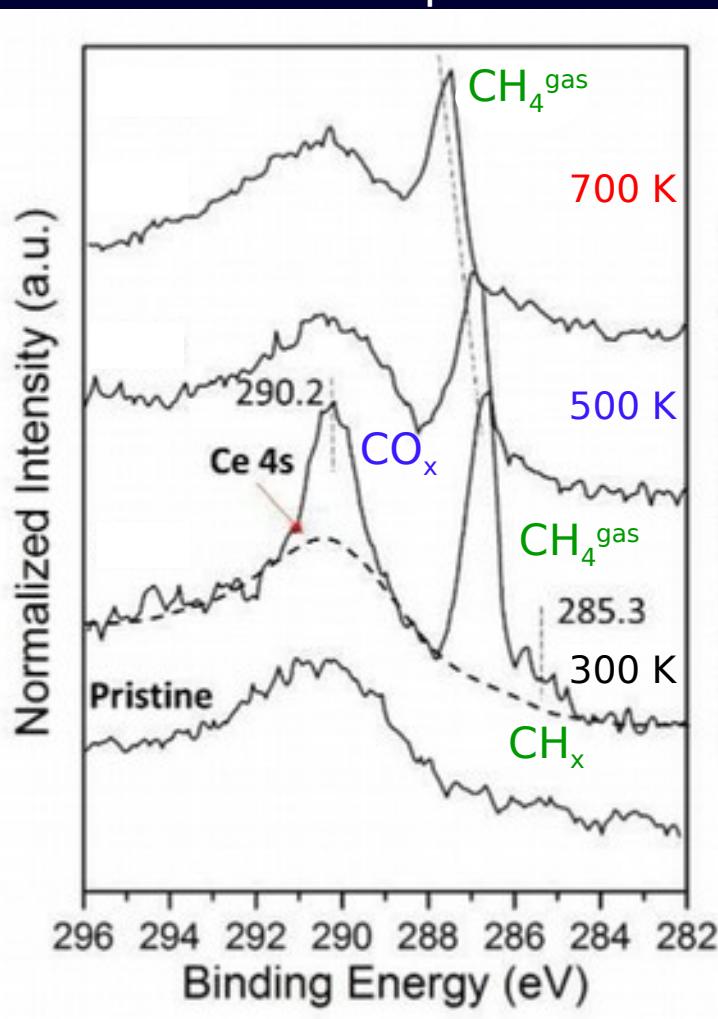
# Ni/CeO<sub>2</sub>(111) model catalysts: CH<sub>4</sub> dissociation

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

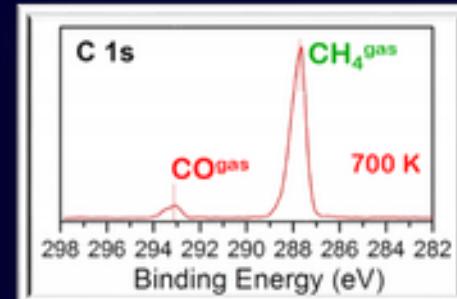
100 mTorr CH<sub>4</sub>



C1s XPS spectra



surface reduction



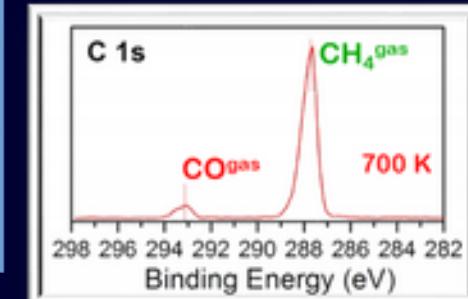
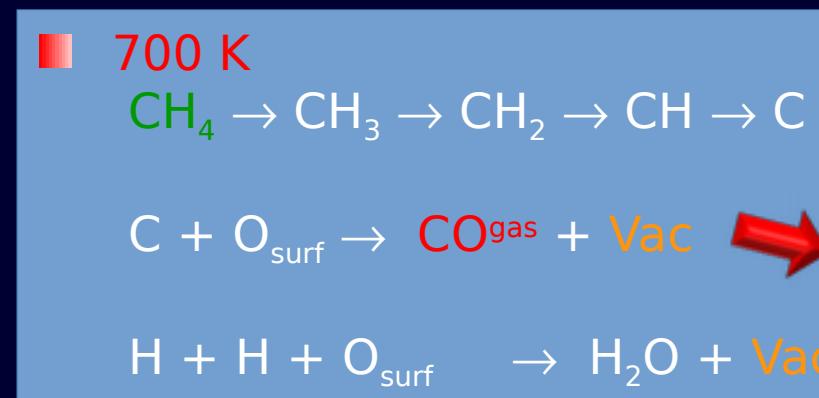
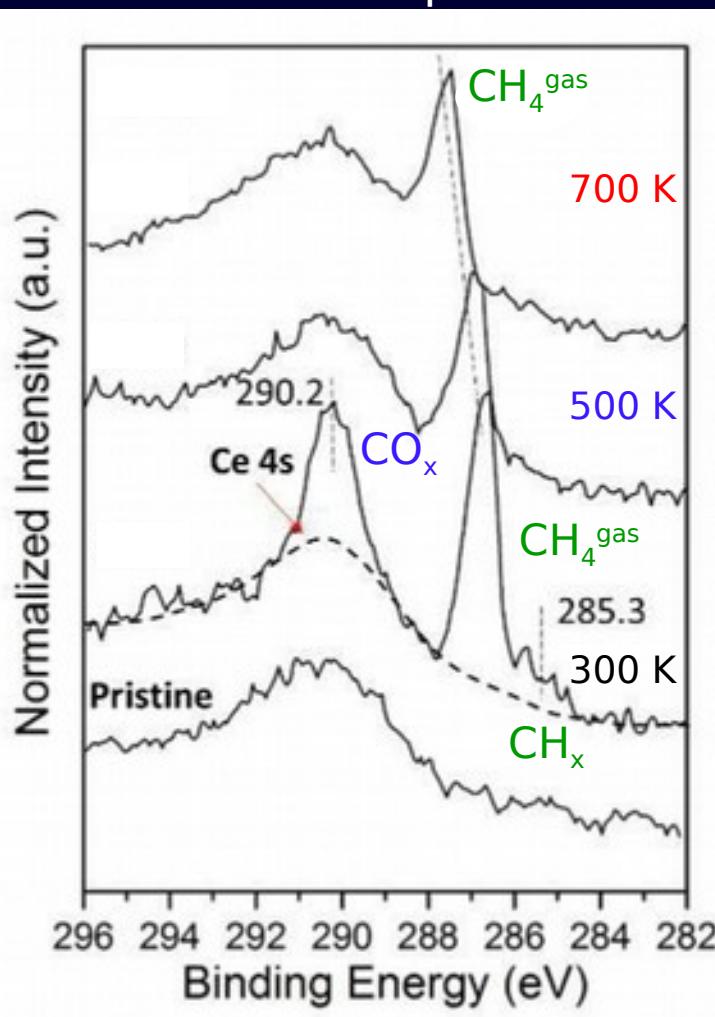
# Ni/CeO<sub>2</sub>(111) model catalysts: CH<sub>4</sub> dissociation

Liu et al., Angew. Chem. Int. Ed. 55 (2016)  
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100 mTorr CH<sub>4</sub>



C1s XPS spectra



surface reduction

CO<sub>2</sub> dissociation at O-vacant sites!

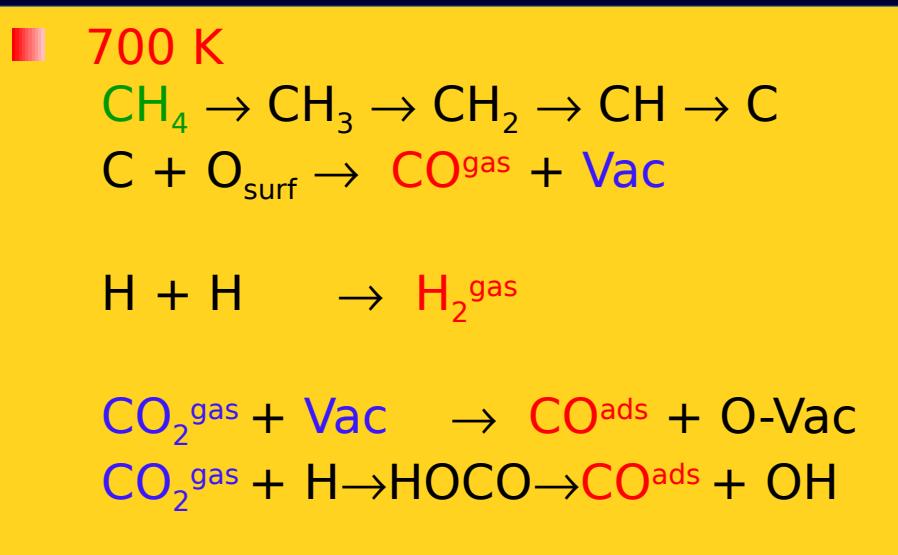
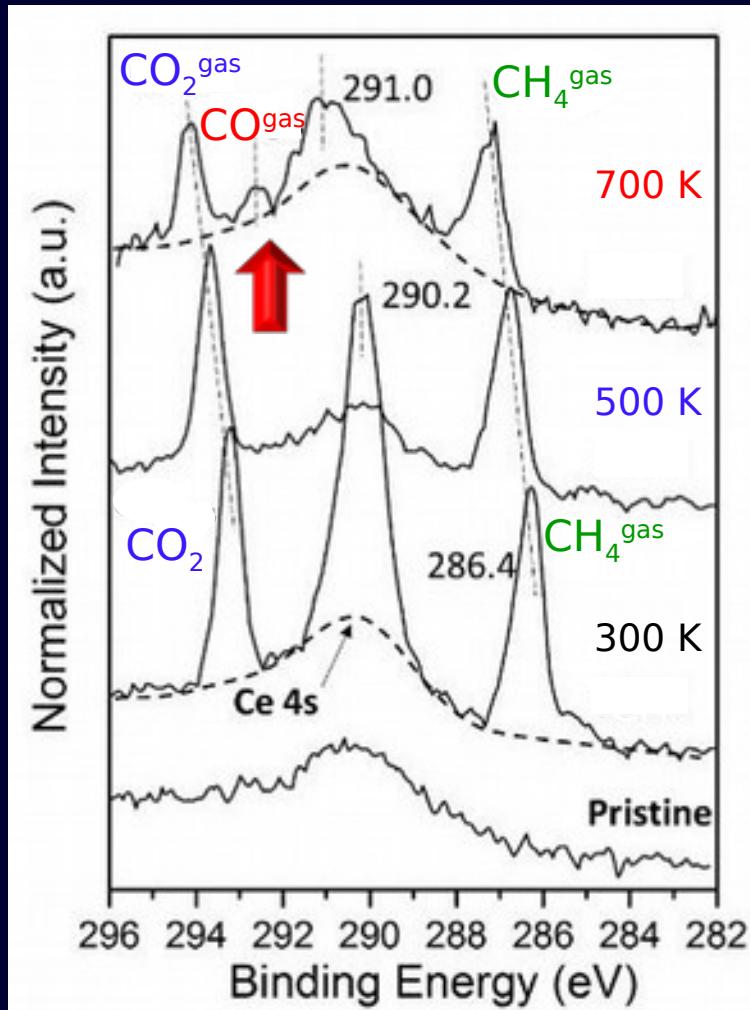
# Ni/CeO<sub>2</sub>(111) model catalysts: CH<sub>4</sub> dissociation

100 mTorr CO<sub>2</sub>  
100 mTorr CH<sub>4</sub>

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



C1s XPS spectra



■ 500 K  
no CO<sub>2</sub> diss.

■ 300 K  
no CO<sub>2</sub> diss.  
CO<sub>x</sub>: CO<sub>2</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>

low-loaded Ni<sup>0</sup>/CeO<sub>2-x</sub>(111):  
DRM activity!!  
No coke ! No NiC<sub>x</sub> !