

# Coke-free methane steam reforming on Ni-ceria catalysts: active sites and reaction pathway

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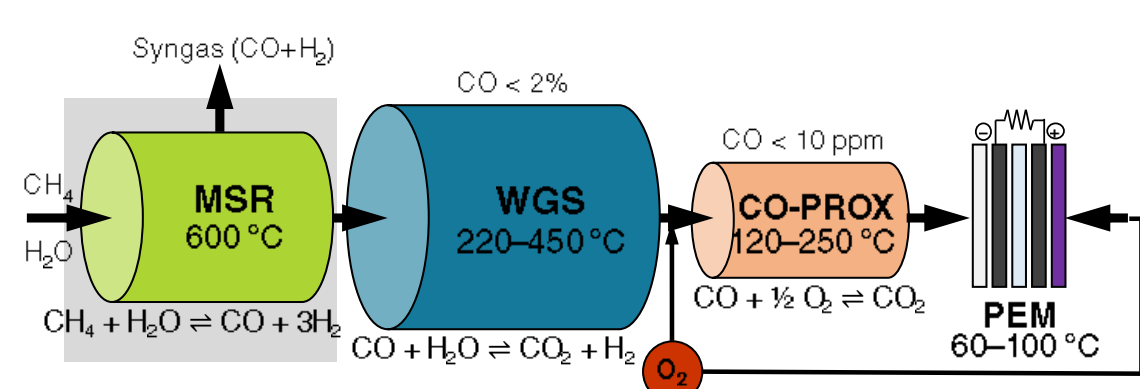
## Introduction

**Methane steam reforming (MSR)**  
 $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}$

Typical applications:

- Large-scale industrial  $\text{H}_2$  production.
- 800–1000 °C, 4–20 atm,  $\text{H}_2\text{O}/\text{CH}_4$  ratio of ~2.5.

Fuel cell applications:



- Ambient pressure operation favors reaction thermodynamics, allowing mild operating temperature and  $\text{H}_2\text{O}/\text{CH}_4$  ratio close to 1.
- Novel catalysts are required to carry out the reaction at milder conditions.

Low-loaded Ni/CeO<sub>2</sub> catalyst:

- Strong metal-support interactions.
- Room temperature  $\text{CH}_4$  activation.
- Resistance to coke poisoning.
- Excellent MSR performance at 600 °C and 1 bar.

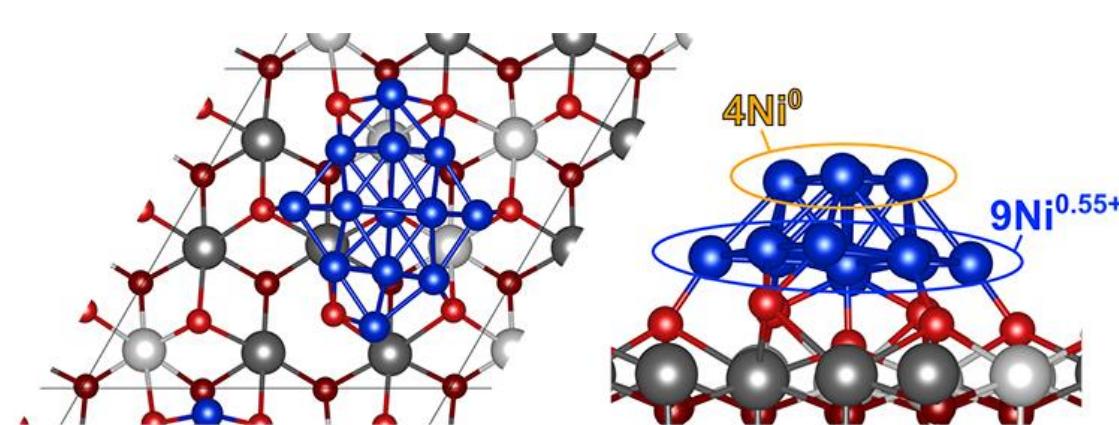
Challenge:

Deeper understanding of the reaction mechanism, to allow the rational design of enhanced Ni/CeO<sub>2</sub>-based catalysts.

Here we present a **density functional theory (DFT) study of MSR on model Ni/CeO<sub>2</sub>(111) catalysts.**

## Methods

- Model: Ni<sub>13</sub> cluster adsorbed on CeO<sub>2</sub>(111) with (3×3) periodicity.



- 2 O–Ce–O trilayers (TL), 12 Å thick vacuum-layer.
- DFT+U calculations (VASP code).
- GGA-PBE *xc* functional.
- $U_{\text{eff}} = 4.5$  eV for Ce(4f) states.
- Cutoff energy of 415 eV.
- PAW method for core electrons.
- DFT-D3(ZD) approach for long-range dispersion corrections.
- Full relaxation of the Ni cluster and the uppermost CeO<sub>2</sub> TL. Forces converged to 0.02 eV/Å.
- Transition state (TS) structures located using the climbing image NEB method.

## Acknowledgments

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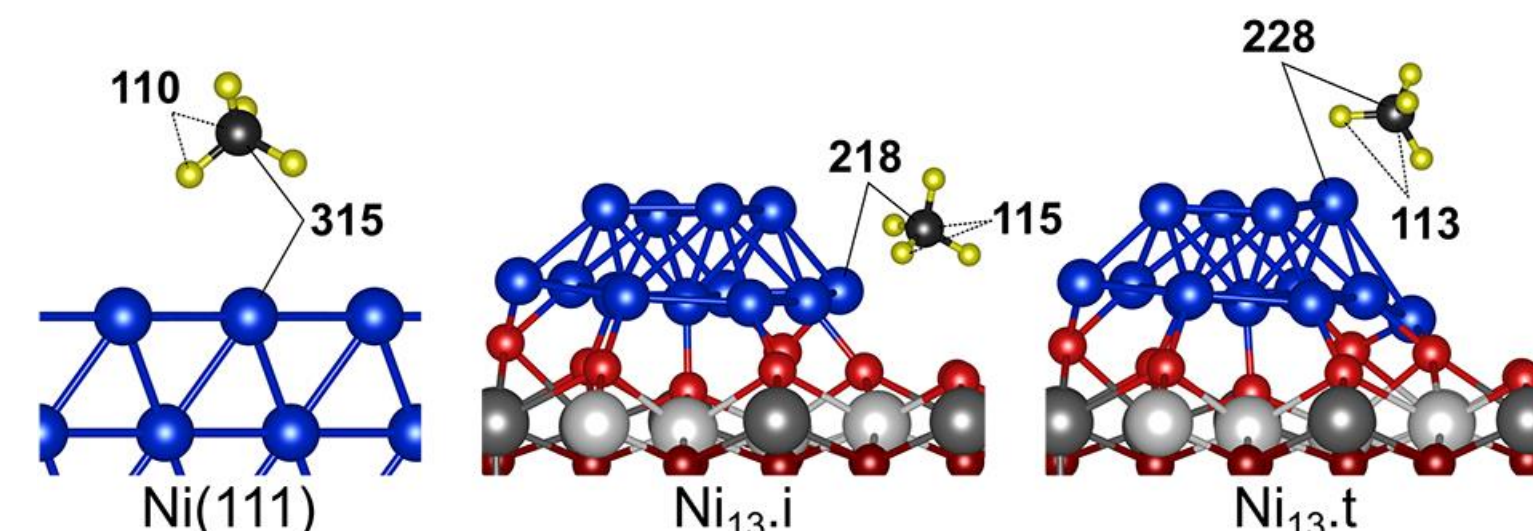
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## CH<sub>4</sub> activation and dehydrogenation

### CH<sub>4</sub> adsorption

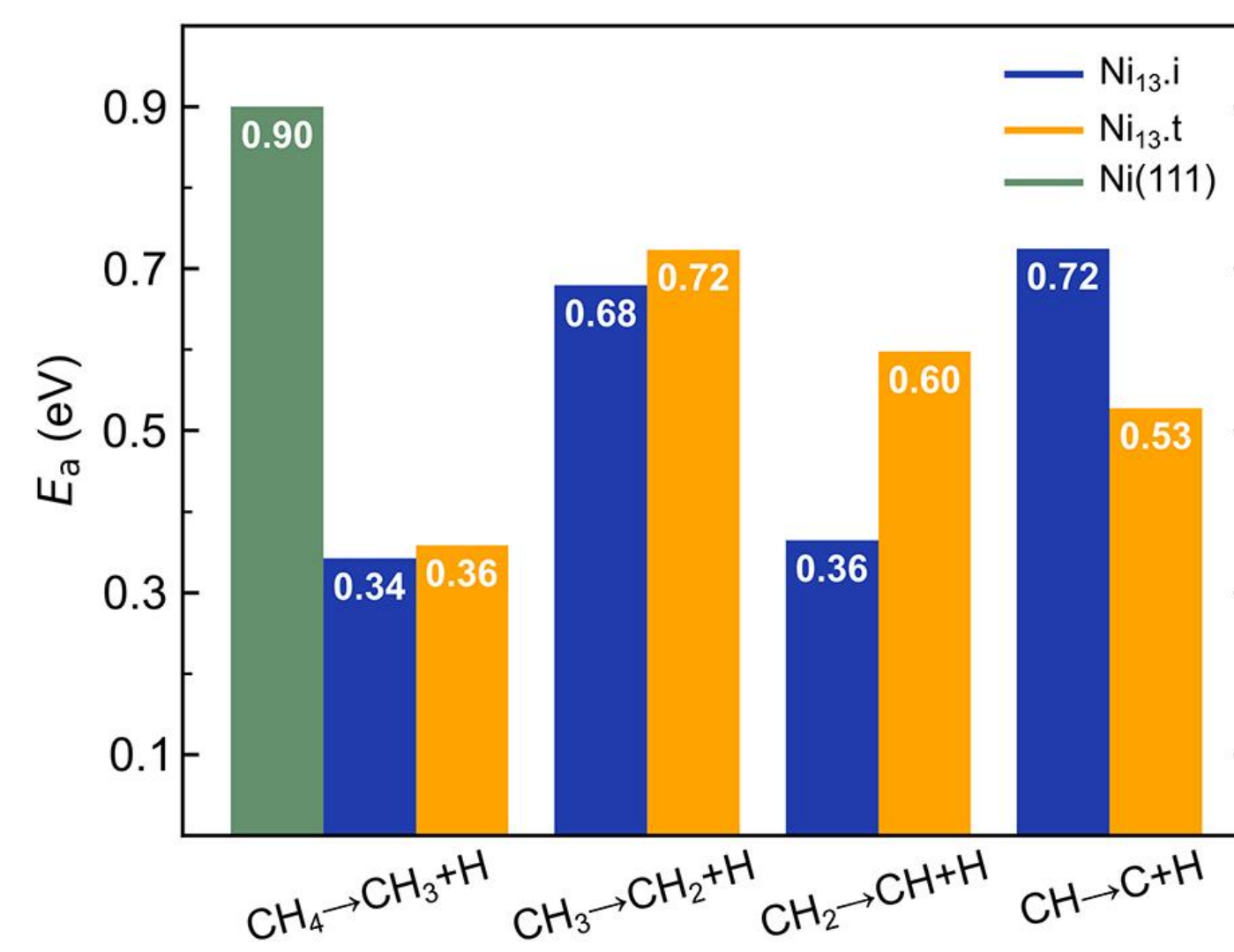
Stronger on both interfacial Ni<sub>13,i</sub> and terrace Ni<sub>13,t</sub> sites by ~0.2 eV, compared with Ni(111).



Ni(*d<sub>xz</sub>*) states of the cluster become less occupied upon adsorption on ceria:

- Reduced Pauli repulsion to methane's frontier orbital → shorter C–Ni distance.
- Pre-activation of the C–H bond pointing towards the surface, increasing its bond length.

### CH<sub>x</sub> dehydrogenation



The pre-activation of CH<sub>4</sub> lowers its first dehydrogenation barrier: 0.34 eV at Ni<sub>13,i</sub> (Ni<sup>0.55+</sup>) and 0.36 eV at Ni<sub>13,t</sub> (Ni<sup>0</sup>), compared with 0.90 eV on Ni(111).

Further dehydrogenation steps (CH<sub>3</sub> → CH<sub>2</sub> → CH → C) also show relatively low barriers.

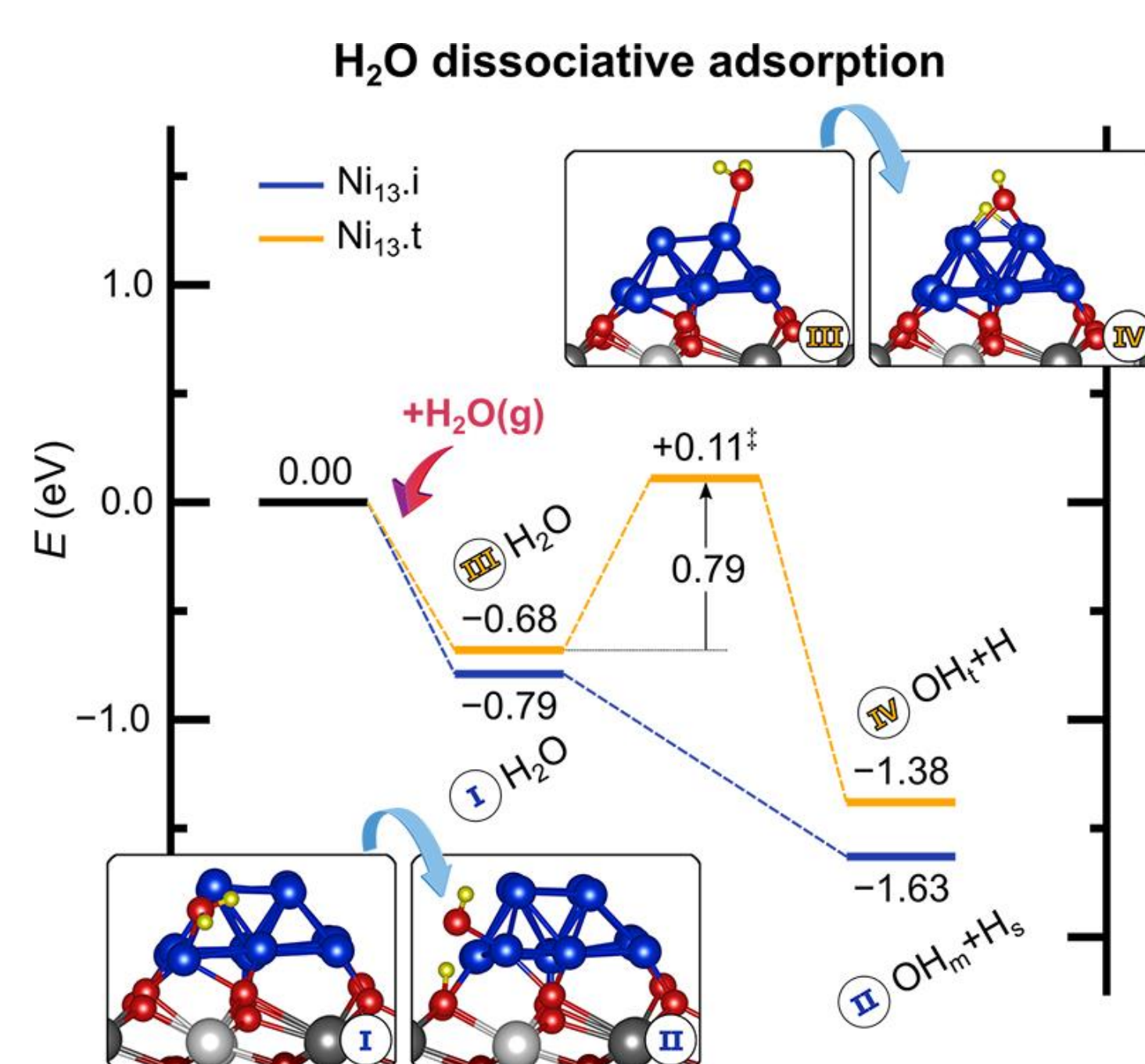
Reasons for the enhanced activity

- Metal-support interactions: change in the cluster's electronic structure.
- Higher local fluxionality: stronger CH<sub>4</sub>–Ni stabilizing interactions and lower activation barriers.

In summary: **CH<sub>4</sub> dehydrogenation to C proceeds with  $E_a \leq 0.72$  eV on the supported Ni<sub>13</sub> cluster.**

## H<sub>2</sub>O dissociative adsorption

- H<sub>2</sub>O dissociates at the Ni–CeO<sub>2</sub> interface through a virtually barrierless process:** monodentate hydroxyl (OH<sub>m</sub>) + dissociated proton on lattice oxygen (H<sub>s</sub>).
- Dissociation of H<sub>2</sub>O on Ni<sub>13,t</sub> does not involve lattice oxygen: bidentate hydroxyl (OH<sub>b</sub>) + H atom on the cluster,  $E_a = 0.79$  eV.



For comparison:

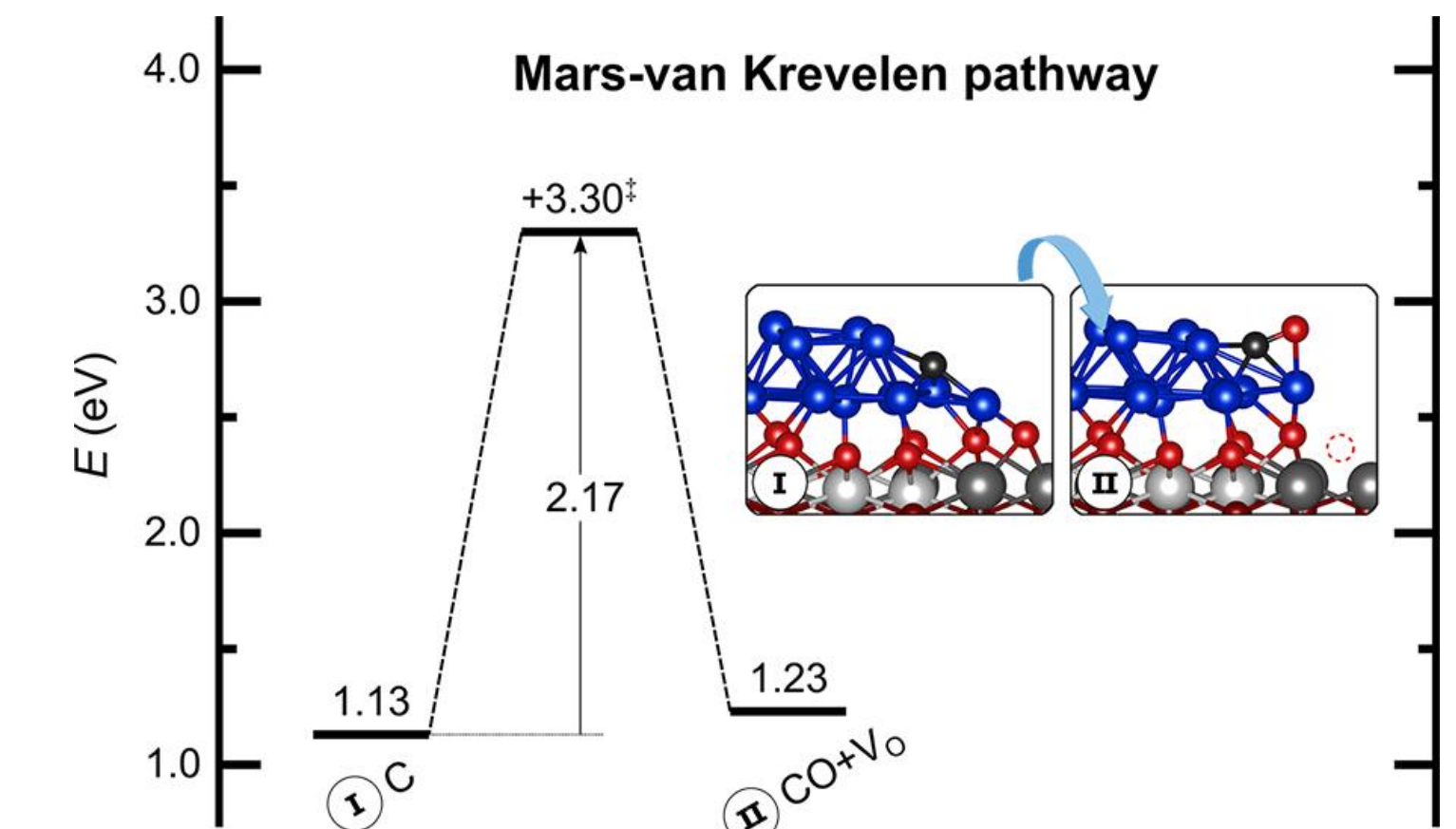
- On Ni(111):** significantly less exothermic ( $\Delta E = -0.41$  eV) and hindered by a high barrier of 0.90–1.11 eV.
- On non-defective CeO<sub>2</sub>(111):** no true dissociation occurs. The molecular state coexists with a OH-pair-like configuration that easily recombines and desorbs at reaction temperature.

In summary: **H<sub>2</sub>O will dissociate preferentially over the Ni–CeO<sub>2</sub> interface**, undergoing barrierless activation and easily producing adsorbed OH groups.

## CO formation and carbon removal

### 1) Mars-van Krevelen redox cycle

C + O<sub>s</sub> (surface lattice oxygen). **Very high barrier of 2.17 eV.**

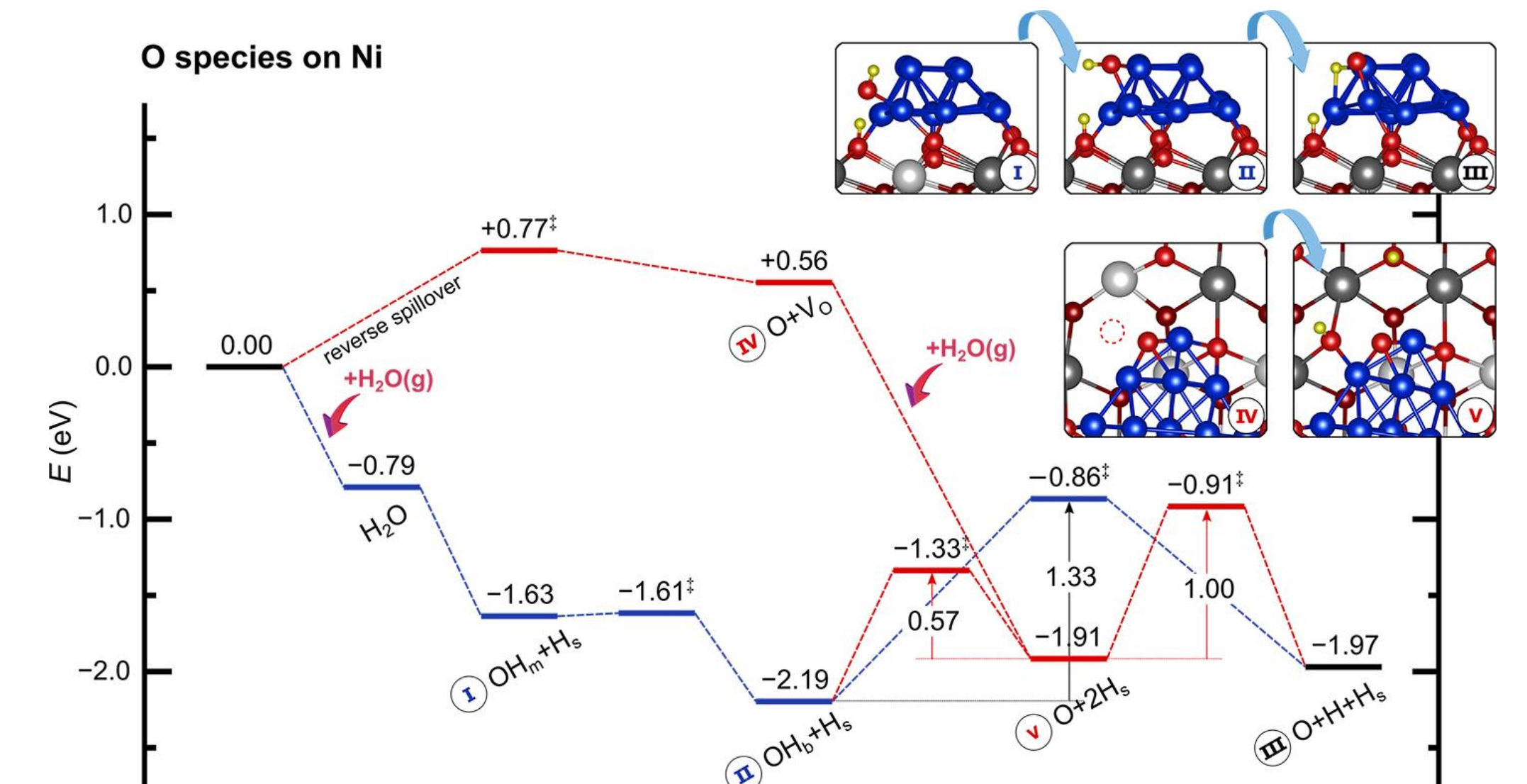


### 2) C+O chemisorbed on Ni

O species chemisorbed on Ni:

- From water (**blue pathway**): OH<sub>m</sub> migrates to a bidentate position OH<sub>b</sub> (I→II) and dissociates into O+H (II→III), with high barrier of 1.33 eV.
- Via oxygen reverse spillover (**red pathway**): O<sub>s</sub> migrates to Ni leaving behind an O vacancy on CeO<sub>2</sub> (IV), with  $E_a = 0.77$  eV. H<sub>2</sub>O is barrierlessly activated at the vacancy site, forming two H<sub>s</sub> groups (V). H<sub>s</sub> migrates to the Ni cluster to reach the O+H+H<sub>s</sub> state (V→III):  $E_a = 1.00$  eV.

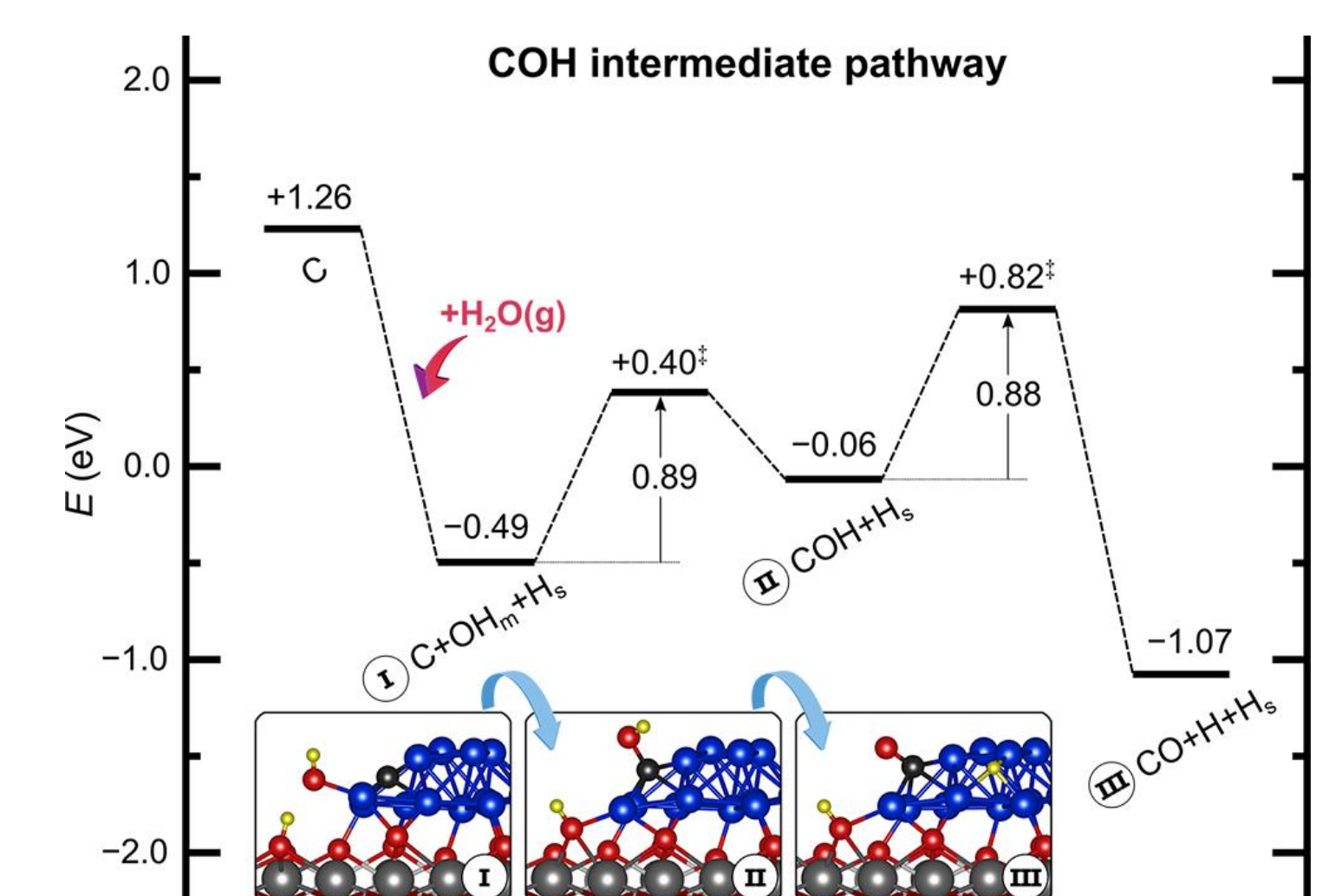
In summary: **O species chemisorbed on the Ni cluster are difficult to form and would not be easily available.**



### 2) C+OH chemisorbed on Ni

OH groups are readily available from H<sub>2</sub>O dissociation. C+OH produces the COH intermediate with  $E_a = 0.89$  eV.

These results lead us to propose a **reaction pathway to produce CO via the direct reaction of C with OH groups through a COH intermediate.**



In a final step, CO and H<sub>2</sub> must desorb to close the catalytic cycle.

- H<sub>2</sub> is easily formed from H species on Ni<sub>13</sub> ( $E_a = 0.62$  eV).
- H<sub>s</sub> species: their migration to the Ni cluster is assisted by water dissociated on Ni<sub>13,t</sub>, providing a pathway with  $E_a = 0.75$  eV.

## Conclusions

- CH<sub>4</sub> → C dehydrogenation promoted by the fluxionality and electronic structure of the cluster,  $E_a \leq 0.72$  eV.
- H<sub>2</sub>O barrierless dissociation over the Ni–CeO<sub>2</sub> interface.
- MSR reaction pathway with barriers under 0.9 eV via the formation of a COH intermediate** from chemisorbed C + OH, preventing deactivation due to carbon deposition.
- H<sub>2</sub>O facilitates the removal of H adsorbed on the support.
- Perspective:** both CH<sub>4</sub> and H<sub>2</sub>O activation steps occur very easily on low-loaded Ni/CeO<sub>2</sub>, and therefore the goal should be to modify this catalyst to lower the barriers involved in CO formation.