DFT study of CO_2 hydrogenation to methanol over metal nanoclusters activated on ceria interface

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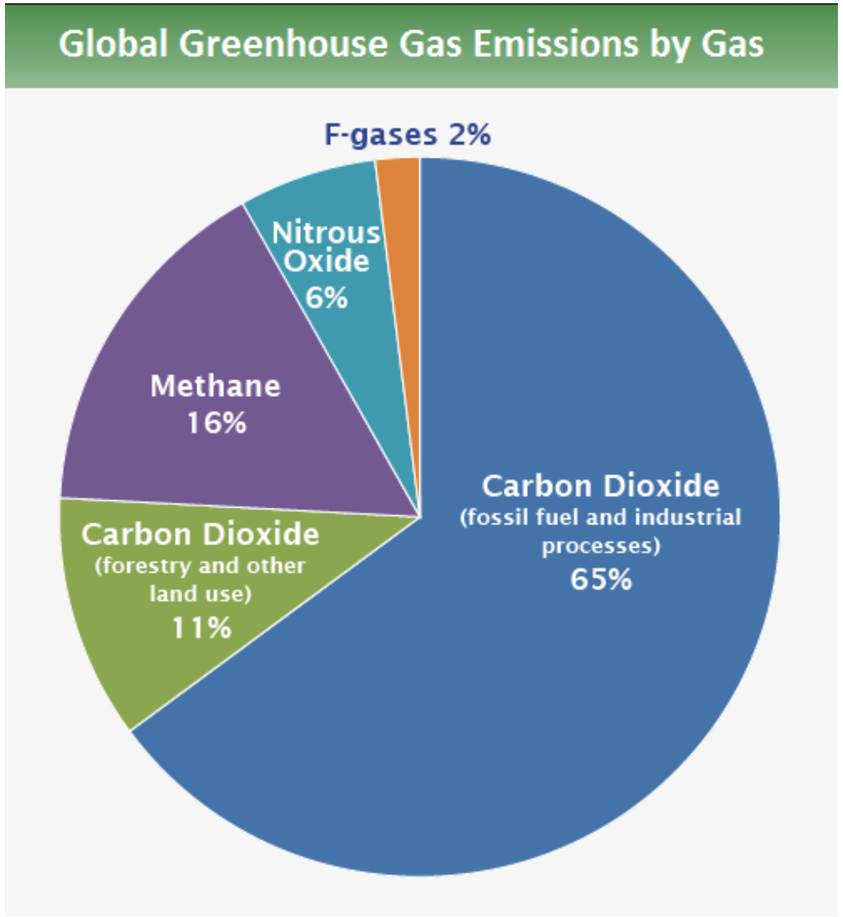
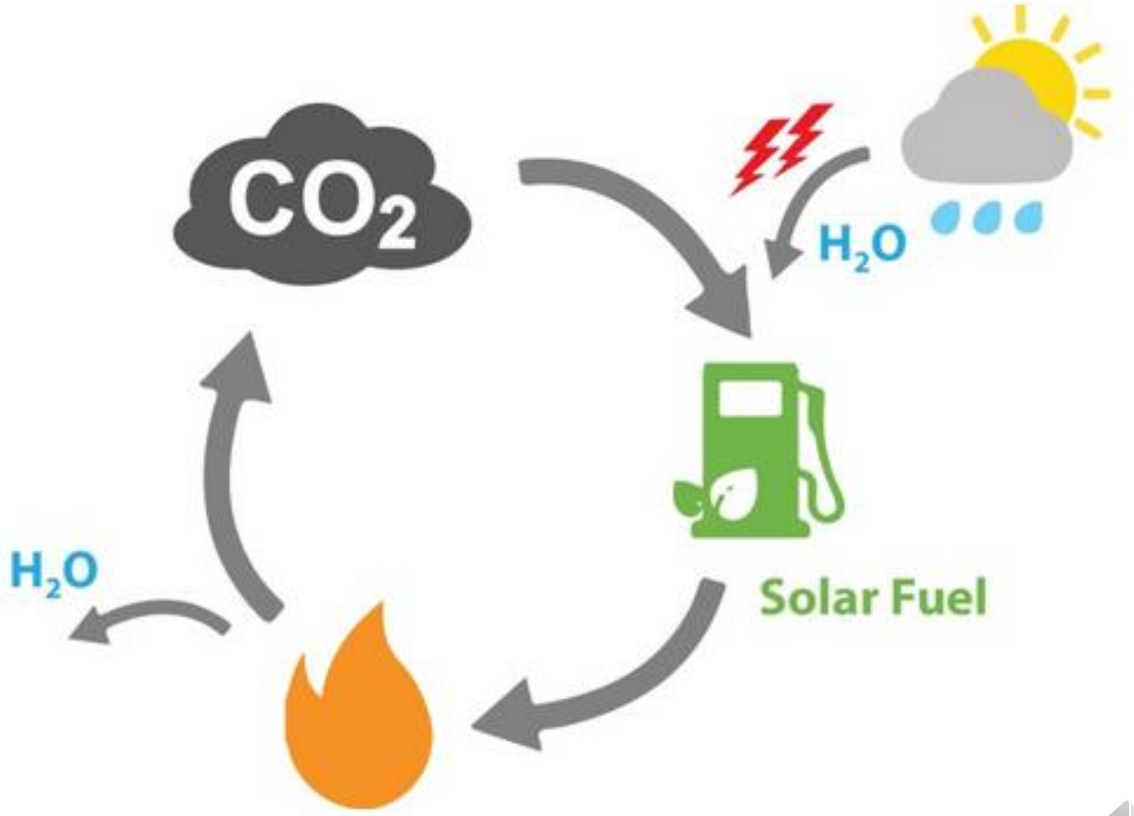
Introduction: Ecological disaster



EPA United States Environmental Protection Agency

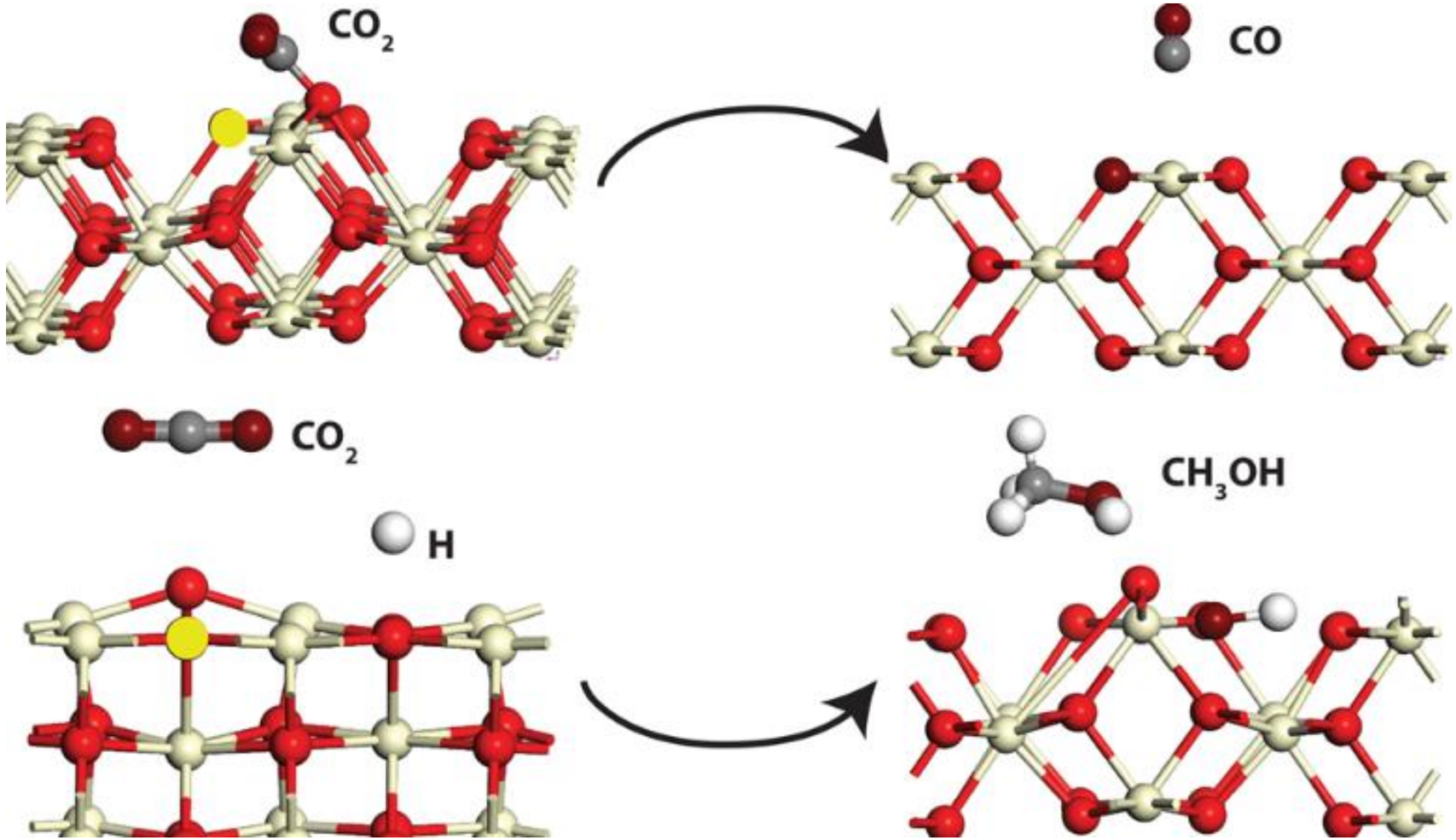
Motivation

$$H_2O + CO_2 \rightarrow C_xH_x + O_2$$



Solution

Metal-CeO_2 is a promising catalytic system for CO_2 hydrogenation



Objectives and Methods

Goal

Developing reducible metal oxide catalysts for CO_2 conversion

Objectives

1. Find the most stable metal cluster configurations on the regular and reduced ceria

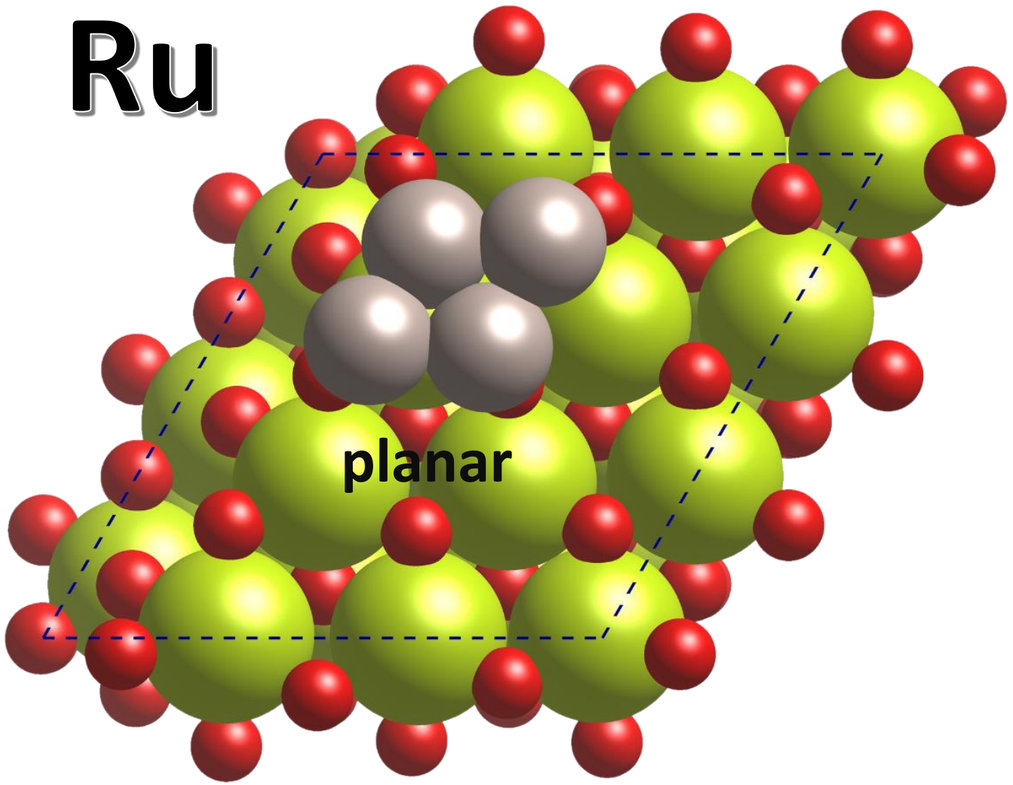
2. Calculate the possible pathways for CO_2 hydrogenation to methanol and identify the energetically favorable ones

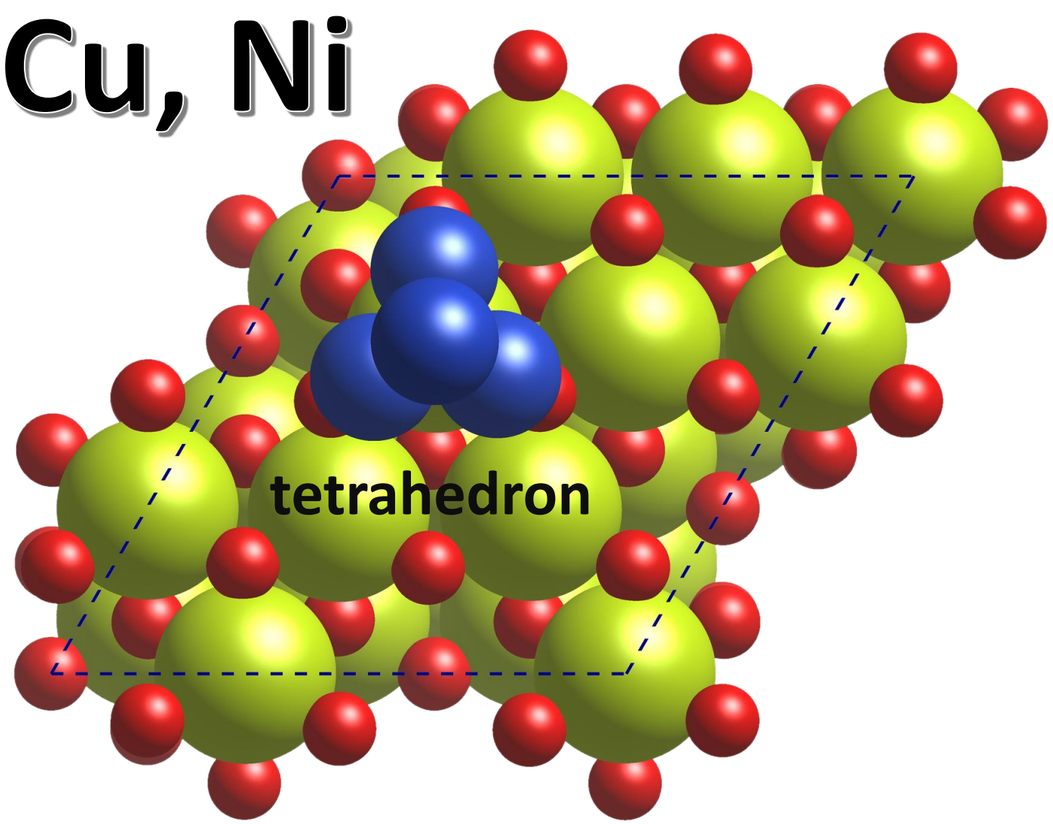
3. Based on the theoretical results, predict the promising metal nanocluster/CeO_2 system

Computational Approaches

All the DFT calculations were performed using the Vienna ab initio simulation package (VASP).

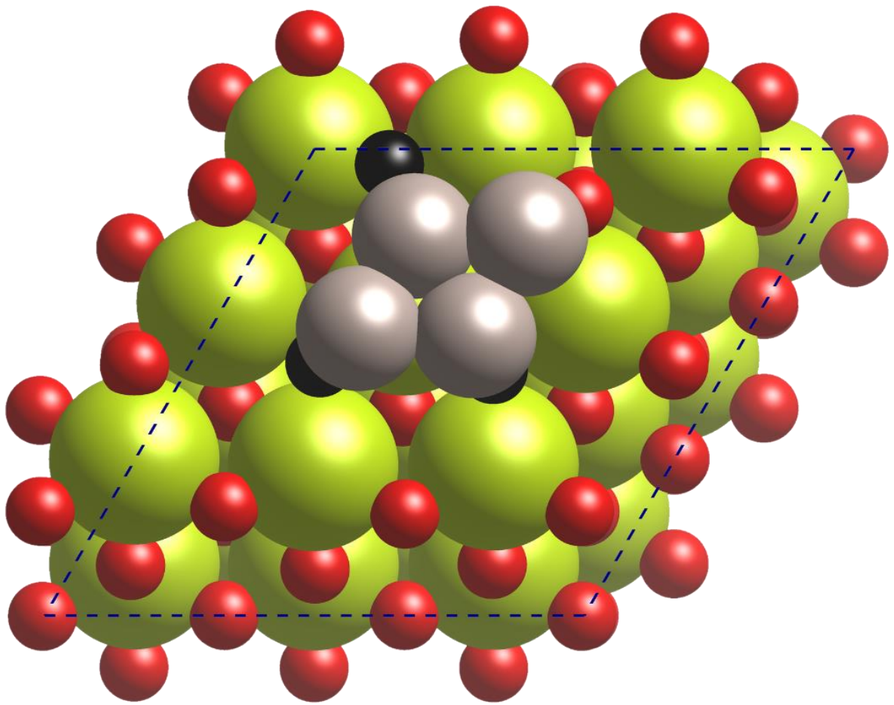
Stability of cluster configurations





Stoichiometric CeO_2: planar – Ru, tetrahedron – Cu, Ni.
Reduced CeO_2: planar.

The effect of vacancies on oxidation state



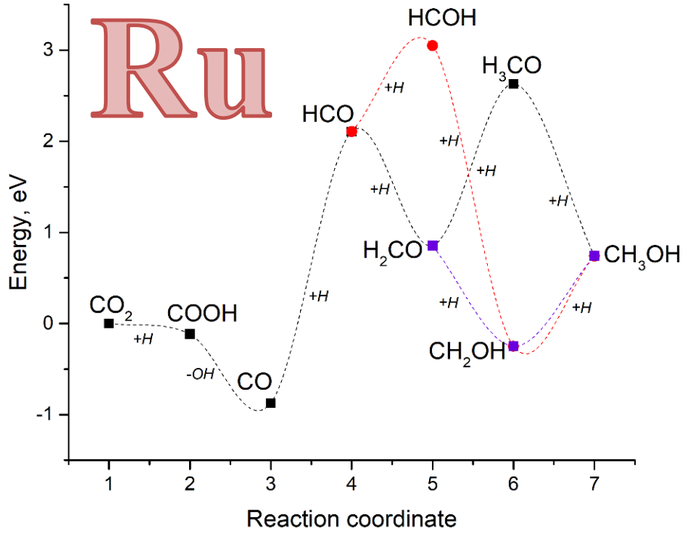
3-vac-CeO_2. Vacancy sites are highlighted in black.

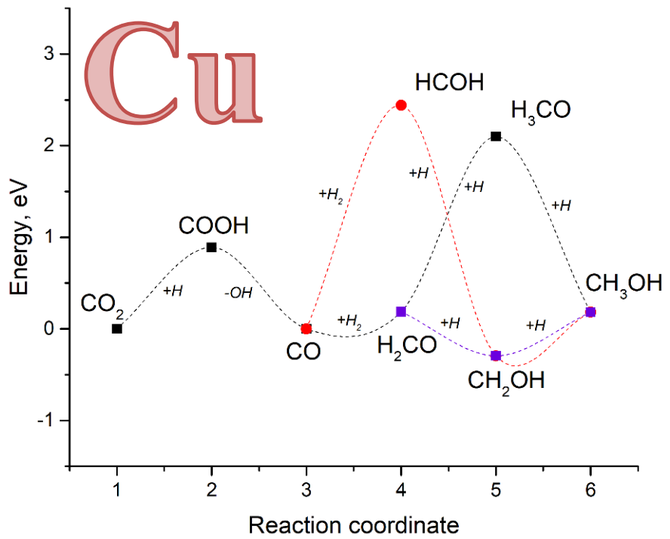
Total Bader of Me cluster	STO	3-vac
Ru	1.33	-0.60
Cu	1.05	-0.90
Ni	1.05	-0.02

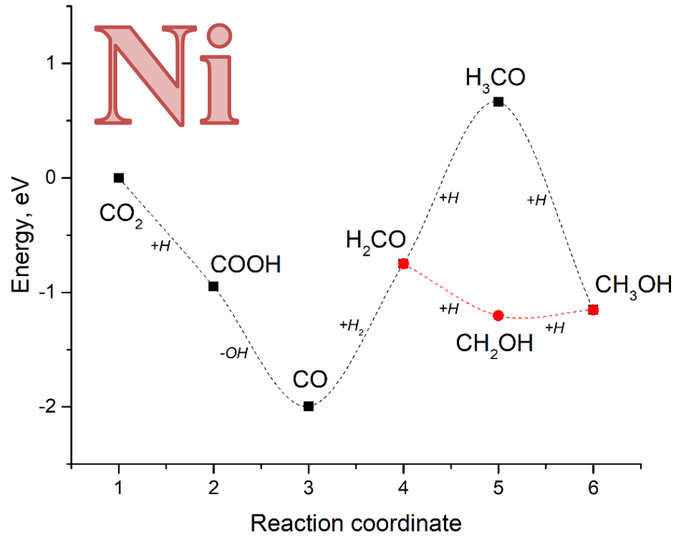
In triangularly ordered trivacancy model, three oxygen vacancies reduce the six nearest Ce^{4+} ions to Ce^{3+}.

Electron transfer between Me cluster and CeO_2-STO positively charges Me cluster, whereas electron transfer between Me cluster and CeO_2-3VAC negatively charges Me cluster.

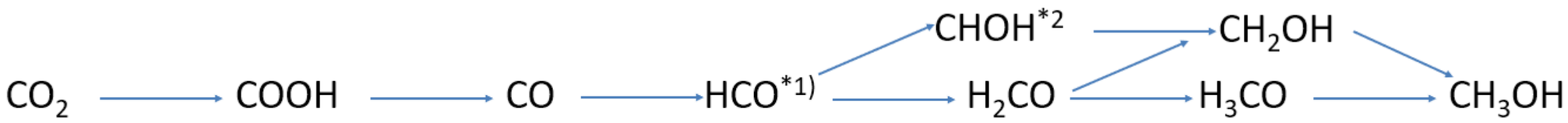
CO_2 hydrogenation to CH_3OH







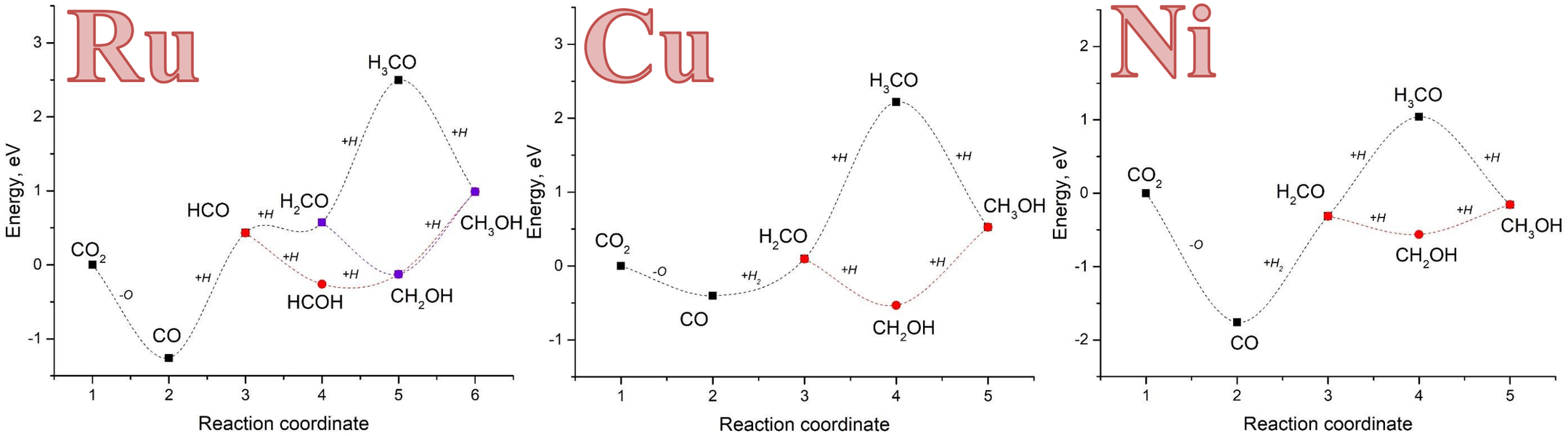
Carboxylate pathway



*1 stable only over Ru-CeO_2 , *2 not stable over Ni-CeO_2

Formate pathway

CO_2 hydrogenation to CH_3OH in the presence of O_{vac}



$CO_2 \rightarrow CO+O_{vac} \rightarrow HCO^* \rightarrow \begin{cases} CHOH^* \rightarrow CH_2OH \\ H_2CO \rightarrow H_3CO \end{cases} \rightarrow CH_3OH$

* stable only over Ru-CeO_2

Conclutions

- **Surface vacancies under the metal cluster may promote the adsorption of CO_2 due to the change of metal charge**
- **In case of the surface vacancy far from the cluster, dissociation of CO_2 accompanies with CO formation and occupation of O_{vac} site by oxygen**
- **In both cases of stoichiometric and reduced ceria formation of methanol is more favorable over Ni-CeO_2**

Acknowledgements

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THANK YOU!