The eighth international conference on
Clean Coal Technologies
Cagliari, Italy
8–12 May 2017

A reaction mechanism study of methane and Ni-based oxygen carrier for chemical looping reforming

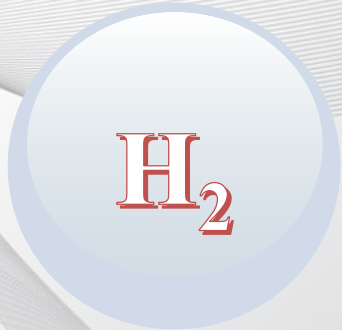
Yuchuan Feng, Xin Guo*, Chuguang Zheng

State Key Laboratory of Coal Combustion
Huazhong University of Science and Technology
Wuhan 430074, Hubei, P.R.China

Outline

- Introduction
- Computational details
- Results and discussion
- Conclusions

Introduction



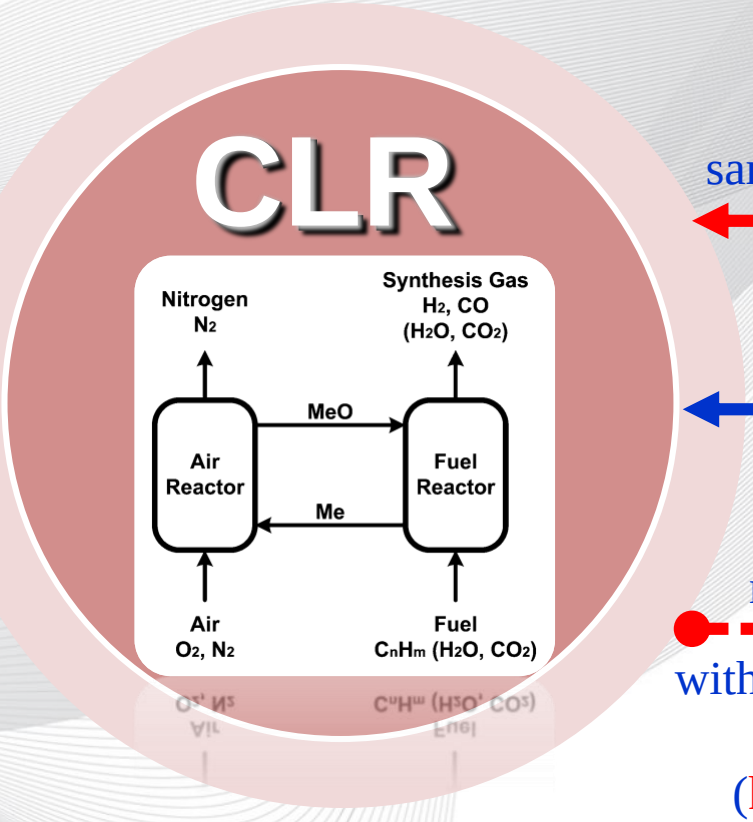
An ideal fuel

Continuously increasing demand

Transition of fossil fuels

Chemical Looping Reforming (CLR) is a promising approach for hydrogen production with environmentally friend, low-energy consumption and high hydrogen efficiency.

Introduction



same basic principles

H_2 and CO

CLC

POF

most basic form

without costly oxygen production

(heat needed for converting CH_4 to H_2)

- CLC: chemical looping combustion
- POF: partial oxidation of fuel

CLR

natural gas
laboratory reactor

Rydén M, et al. Fuel 2006;85:1631-41
de Diego LF, et al. Chemical Engineering Journal 2008;144:289-98
Silvester L, et al. International Journal of Hydrogen Energy 2015;40:7490-501.
Antzara A, et al. Catalysis Today 2016;272:32-41.

natural gas
900W_{th} circulating fluidized bed reactor

de Diego LF, et al. Journal of Power Sources 2009;192:27-34

natural gas
140kW pilot plant

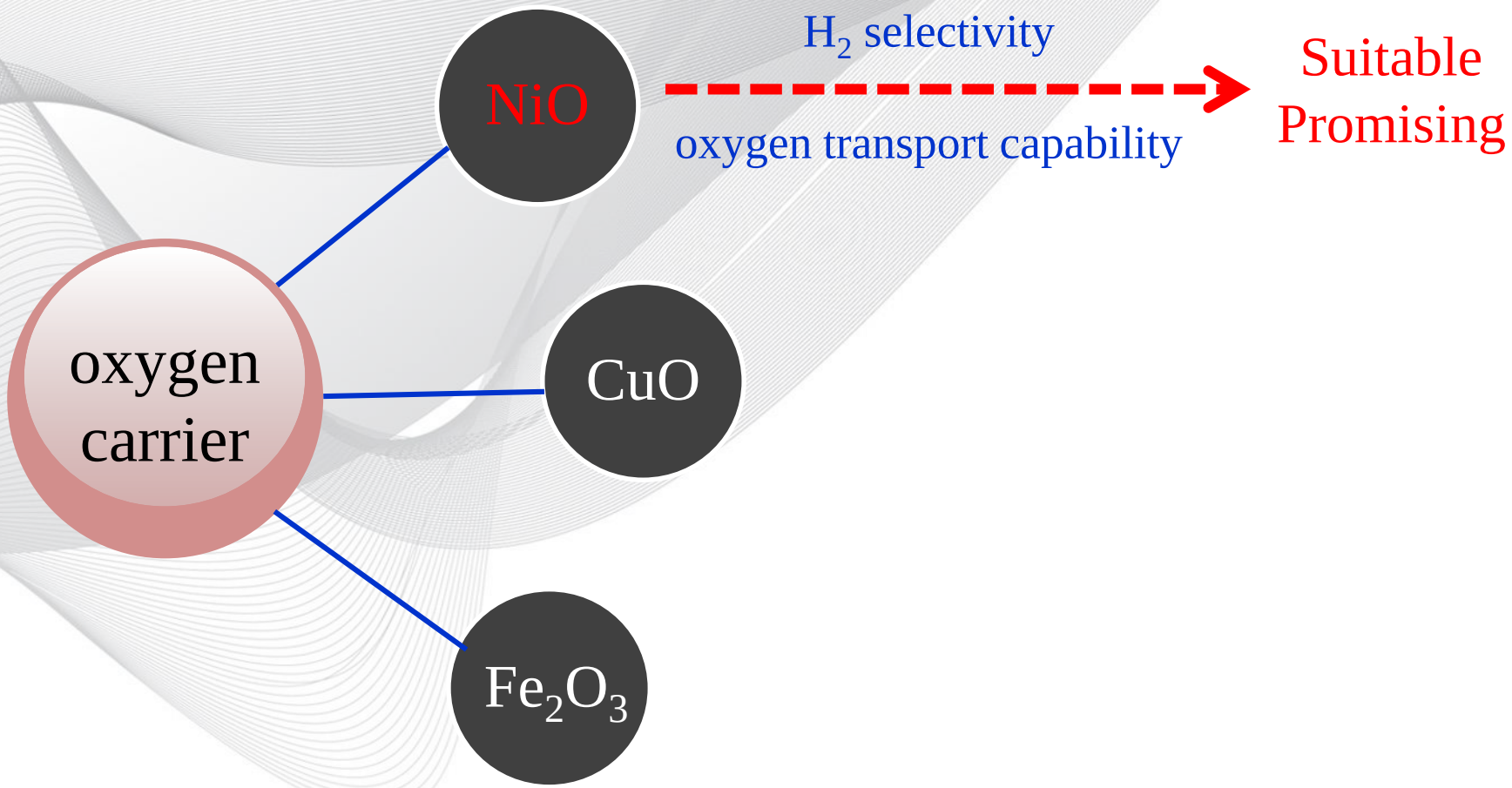
Proll T, et al. Fuel 2010;89:1249-56

ethanol
fixed-bed reactor

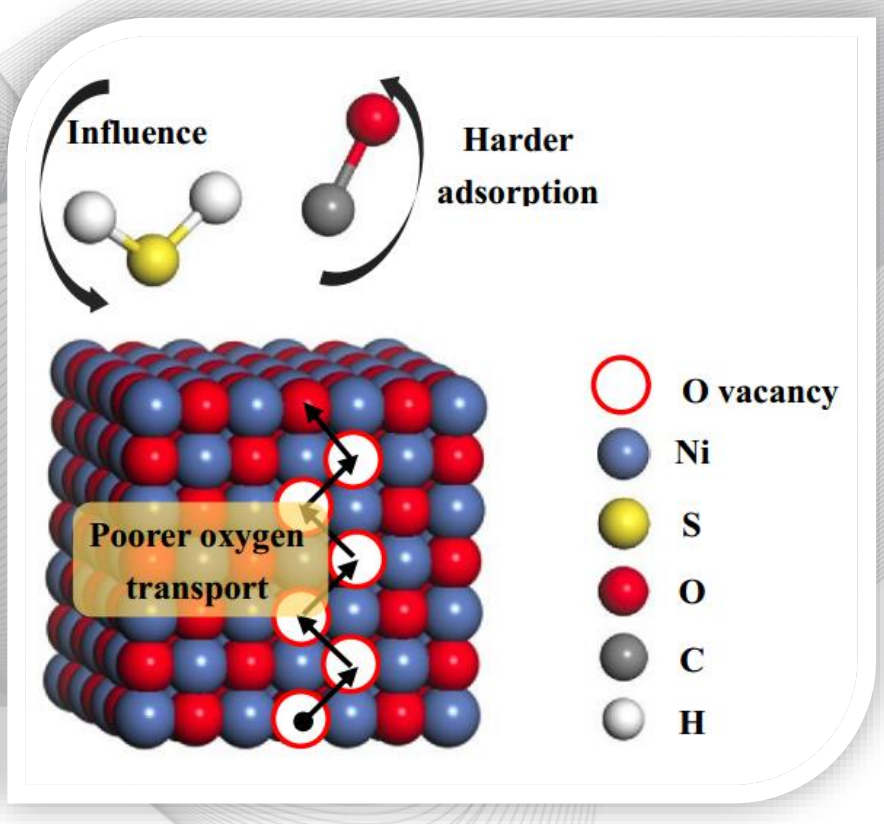
Jiang B, et al. Chemical Engineering Journal 2015;280:459-67
García-Díez E, et al. Applied Energy 2016;169:491-8.
Jiang B, et al. Chemical Engineering Journal 2016;298:96-106

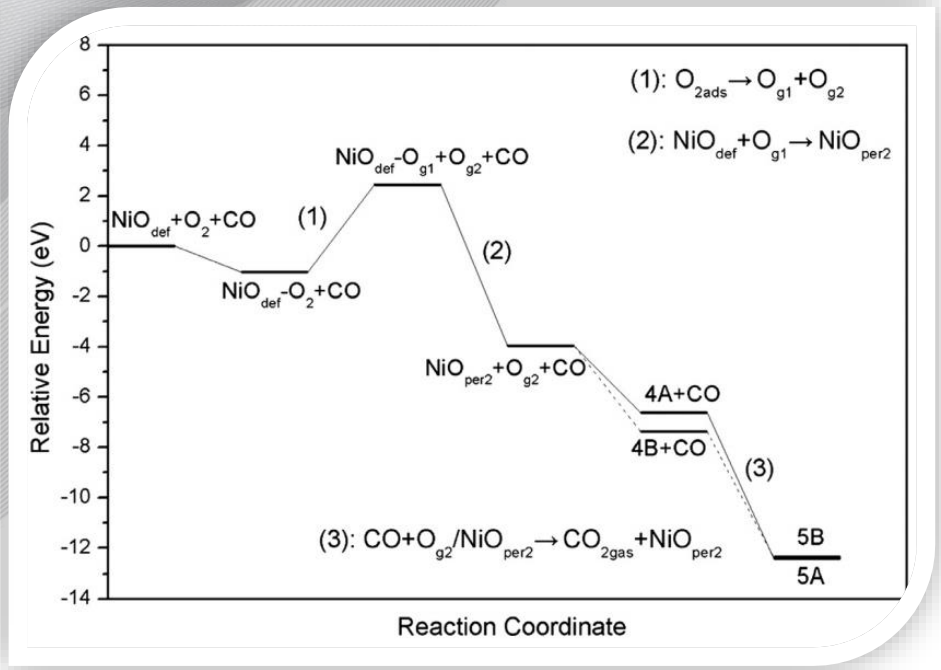
Mechanism understanding

Selection of oxygen carrier



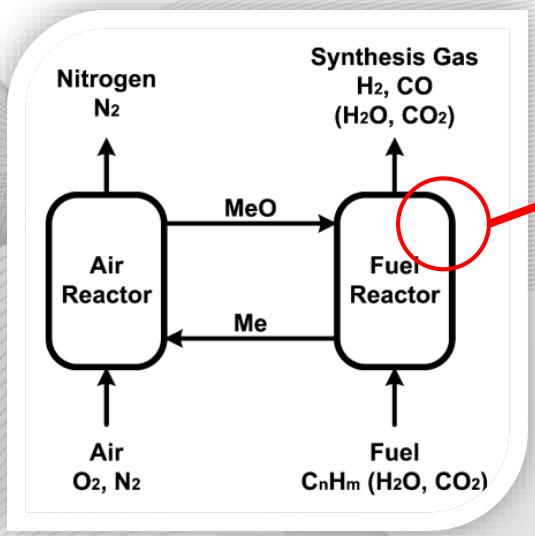
Our previous studies reported the influence mechanisms of oxygen and H_2S on the reactivity performance of Ni-based oxygen carrier.





Xin Guo, Chemical Engineering Journal 2014;244:464-72.
Yuchuan Feng, Xin Guo, Chemical Engineering Journal 2016;295:461-7.

The motivation of this work



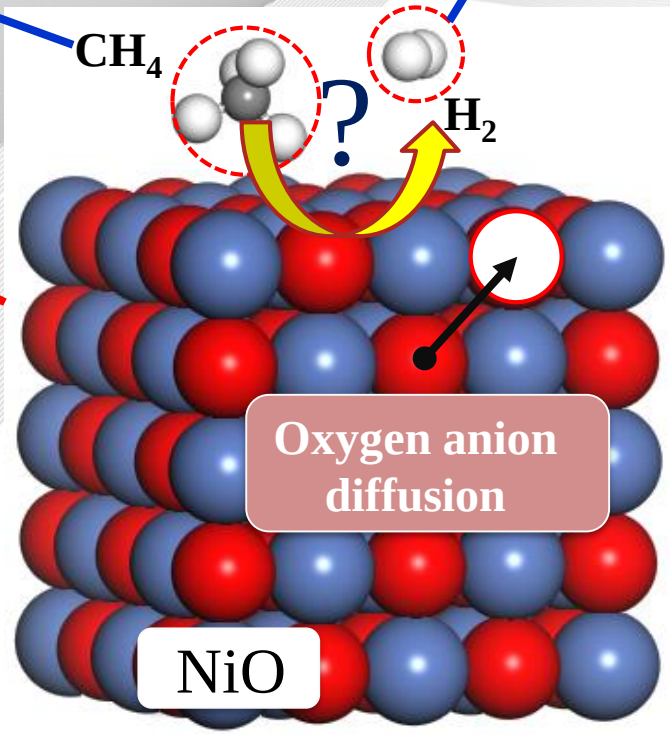
Reaction mechanism

Main reaction

$$CH_4 + NiO \longrightarrow CO + H_2$$

widely available

desirable product



C

H

O

Ni

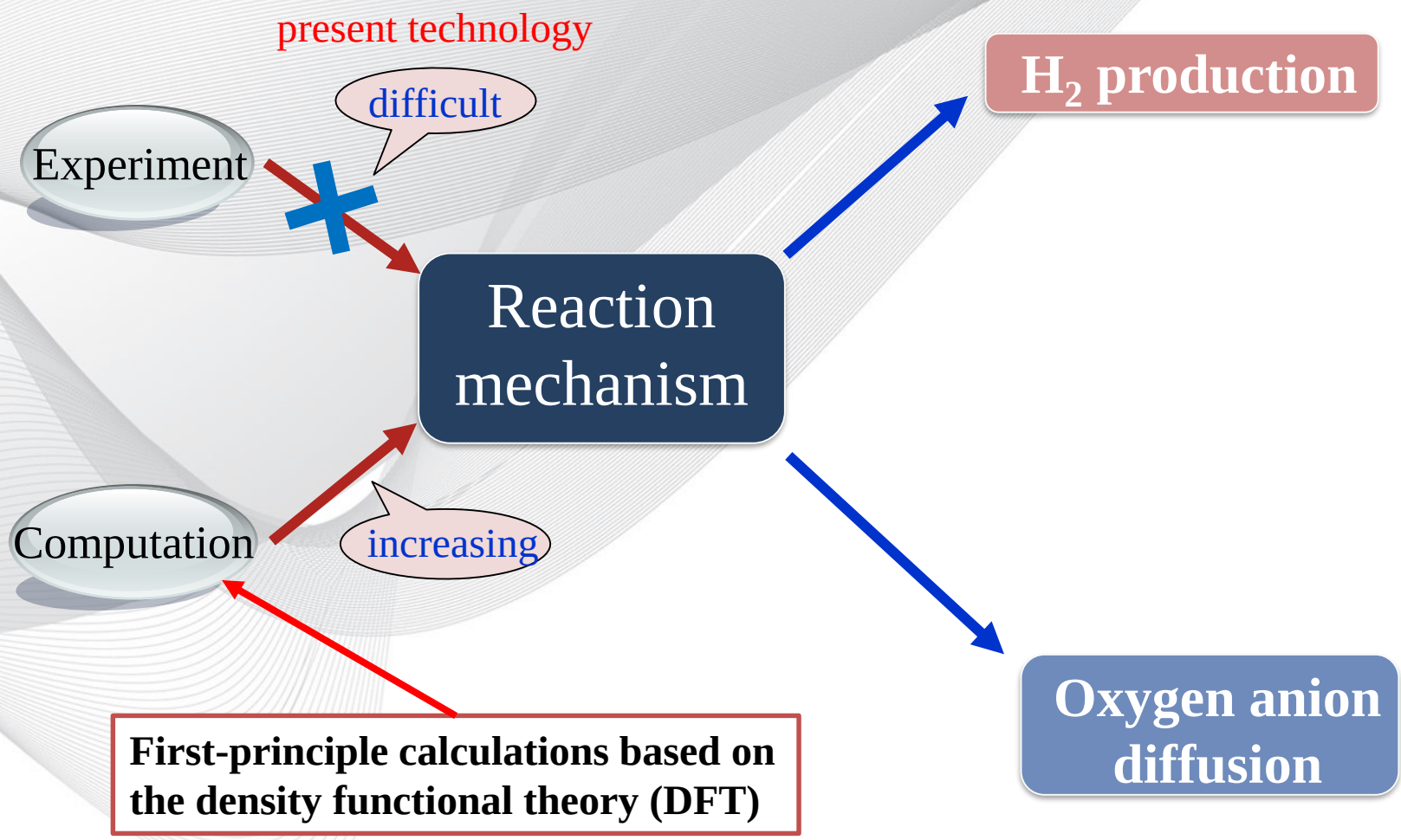
How is H_2 produced at atomic level ?

?

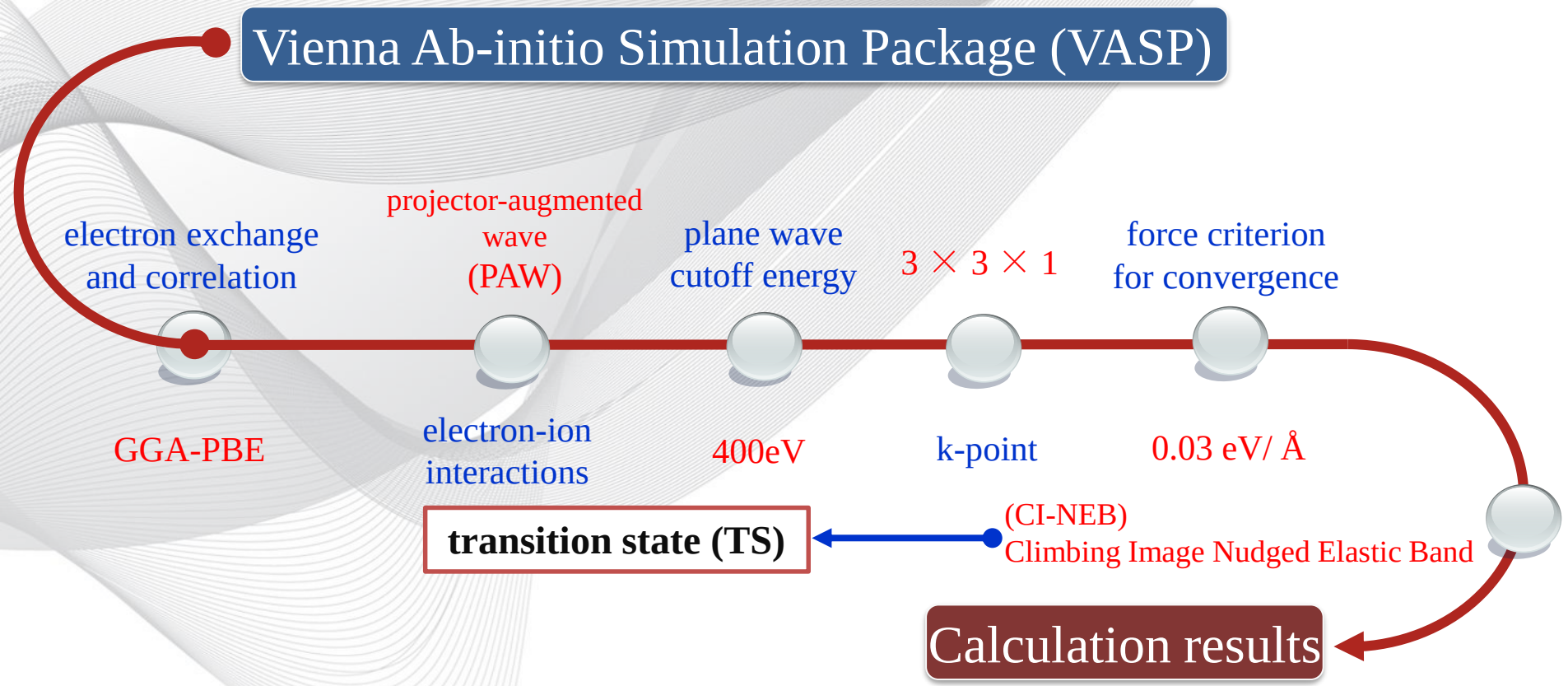
Which process limits the rate of H_2 production ?

How does the oxygen anion diffusion process affect reactivity performance of oxygen carrier ?

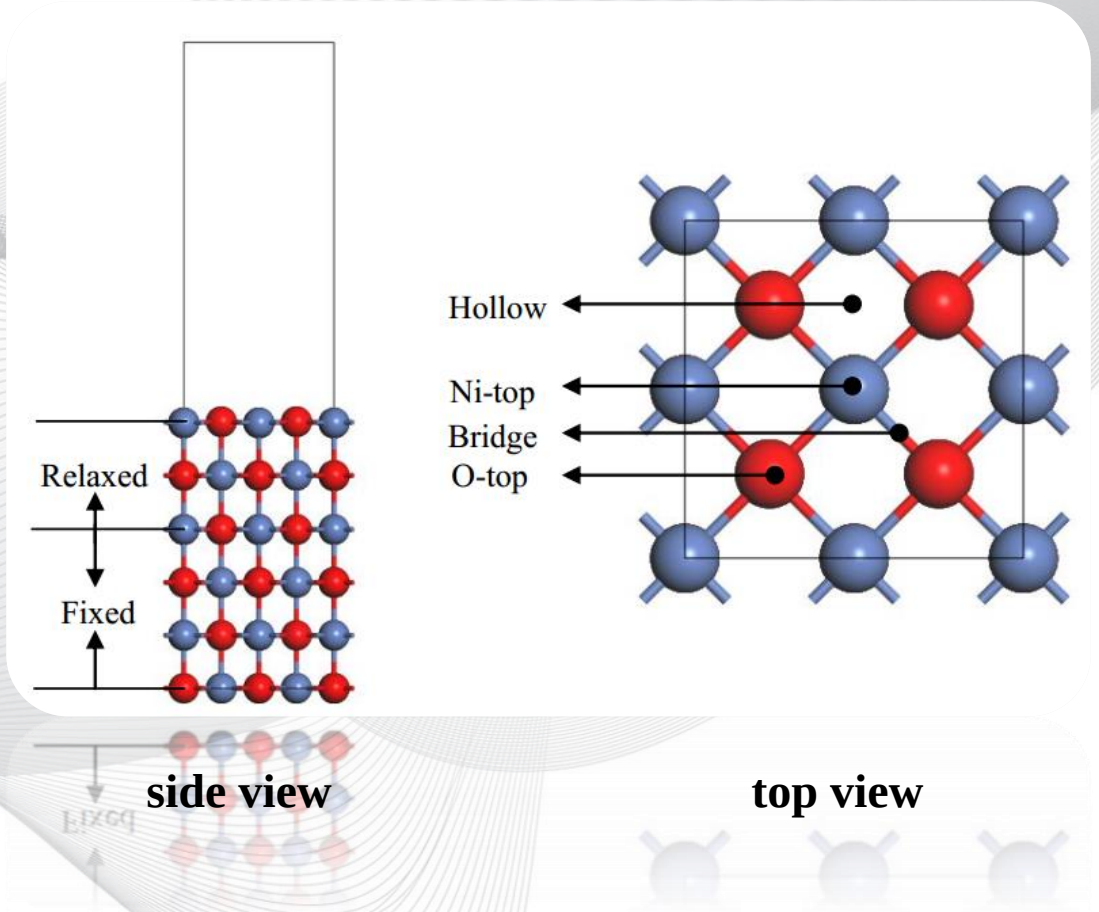
The motivation of this work



Computational details



Models



a six-layer slab with a (2 × 2) periodic supercell to model NiO(001) surface for all calculations

A 15 Å vacuum region was constructed to avoid the interaction between periodic slabs

The equilibrium configuration and adsorption sites

the total energy of the clean slab

E_{ads} (adsorption energy) equation: $E_{ads} = E_{adsorbates/slab} - (E_{slab} + E_{adsorbates})$

the total energy after adsorption

the total energy of free adsorbates

With this equation, a more negative adsorption energy suggests more favorable adsorption.

ΔH (reaction energy) and E_b (activation energy) equation:

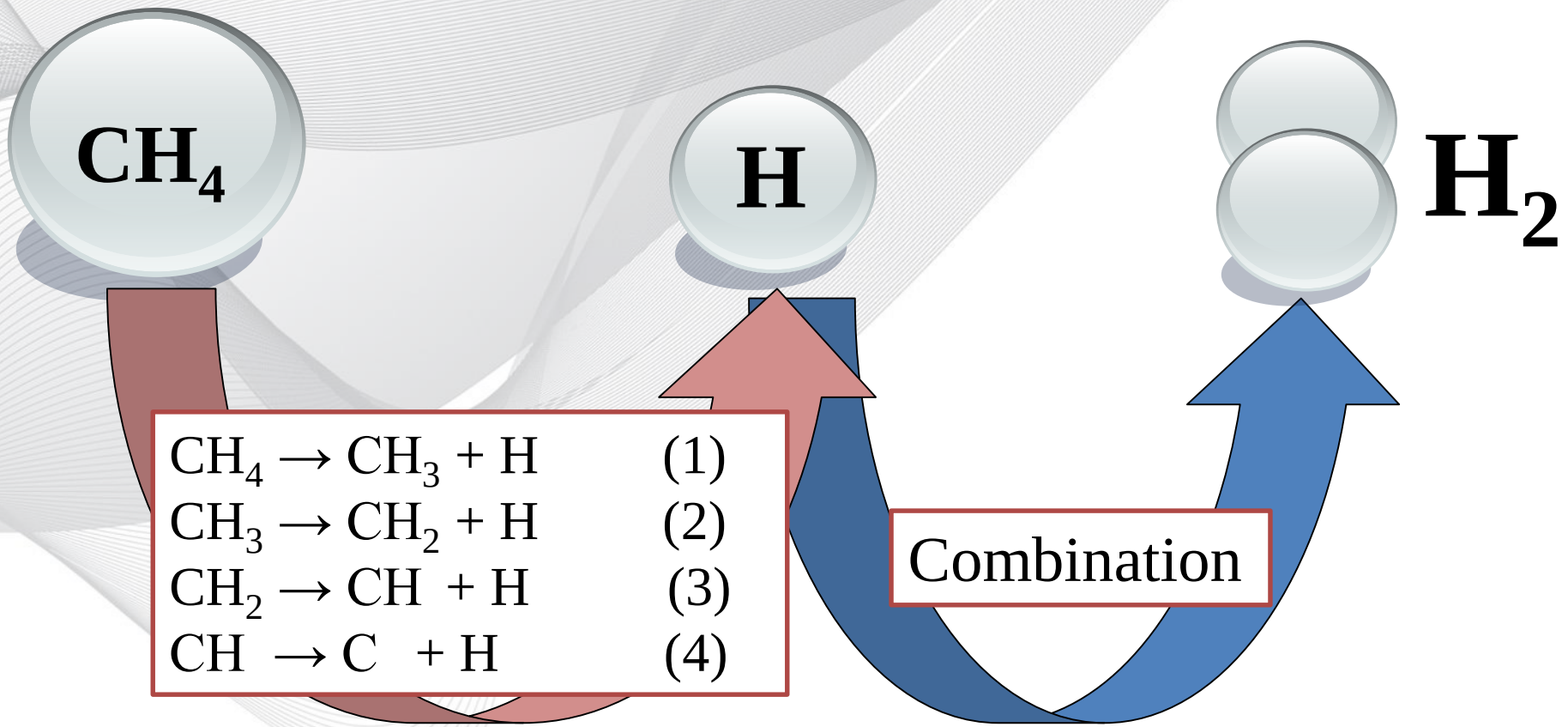
$$\Delta H = E_{FS} - E_{IS} \qquad E_b = E_{TS} - E_{IS}$$

the energy of the final state (FS)

the energy of the initial state (IS)

the energy of the transition state (TS)

How is H_2 produced at atomic level ?



Sequential dehydrogenation reaction

CH_x (x = 0-4) and H adsorption

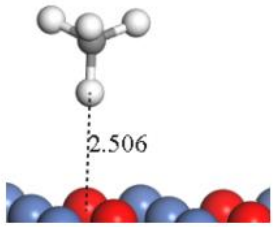
reactants and products

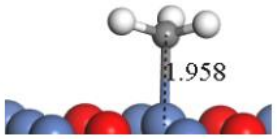
Specie	Adsorption site[a]	E_{ads} (eV)	d_N[b] (Å)	d_{C-H} (Å)
CH_4	O-top	-0.02	2.506 (H-O)	1.098
CH_3	Ni-top	-1.46	1.958 (C-Ni)	1.095
CH_2	bridge	-3.09	1.504 (C-O)	1.107
CH	bridge	-3.70	1.[illegible]	
C	bridge	-4.67	1.	
H	O-top	-1.26	0.	

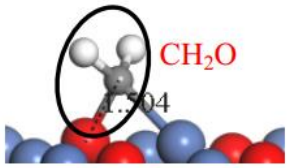
[a] The most stable adsorption site.

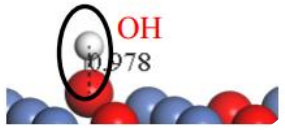
[b] The nearest distance between two atoms of adsorbate and NiO(0

increasing



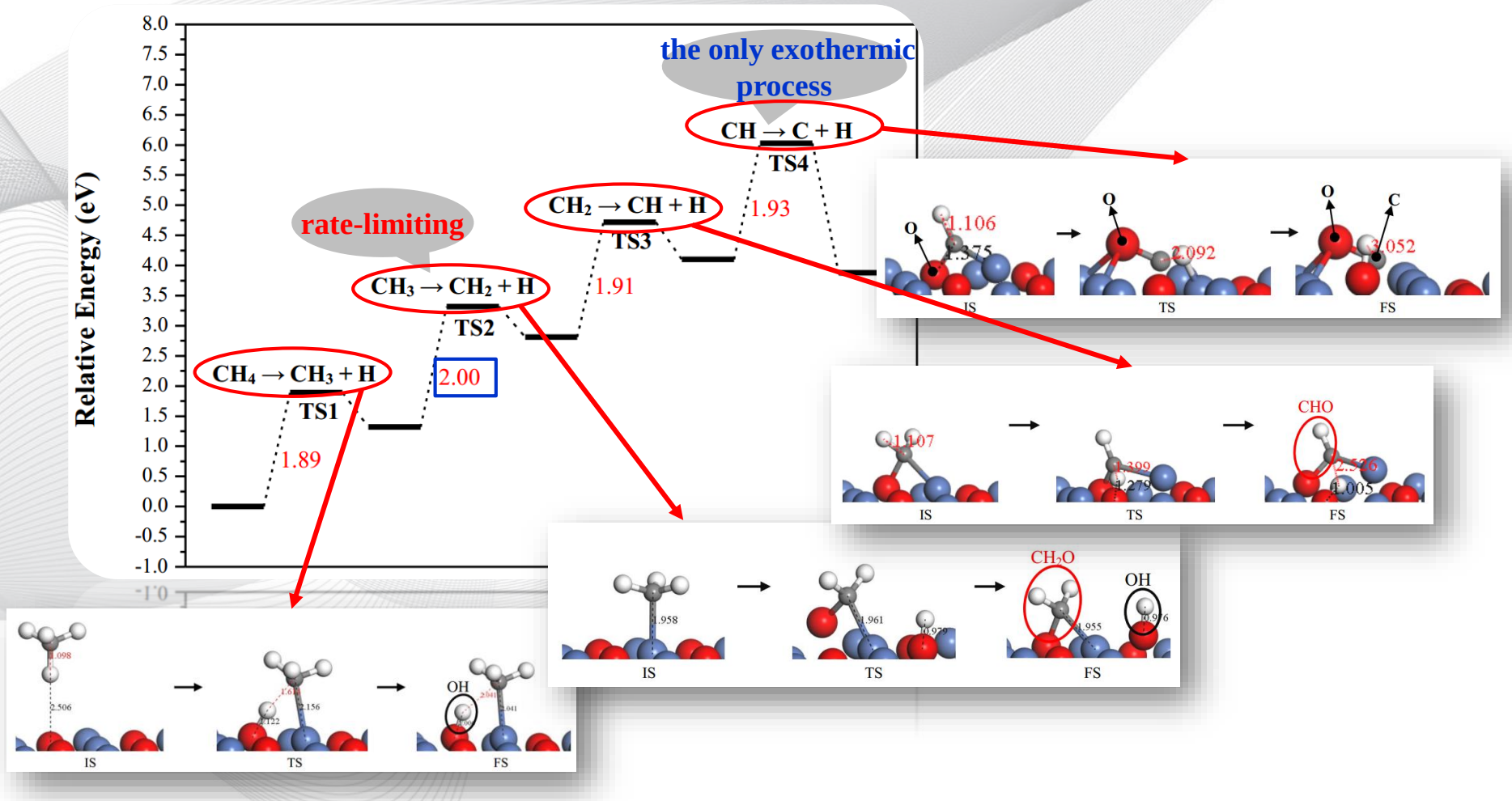




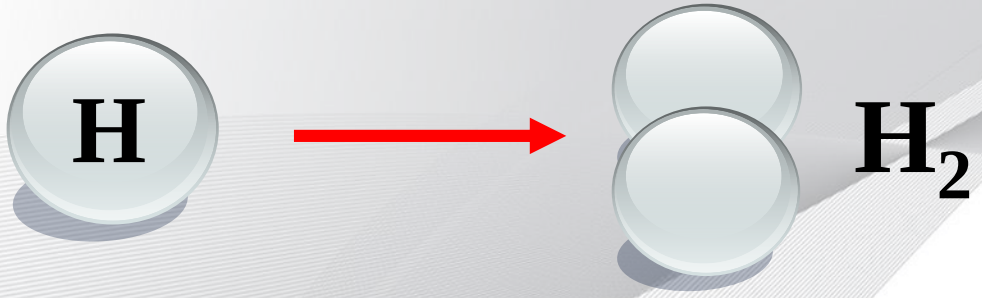


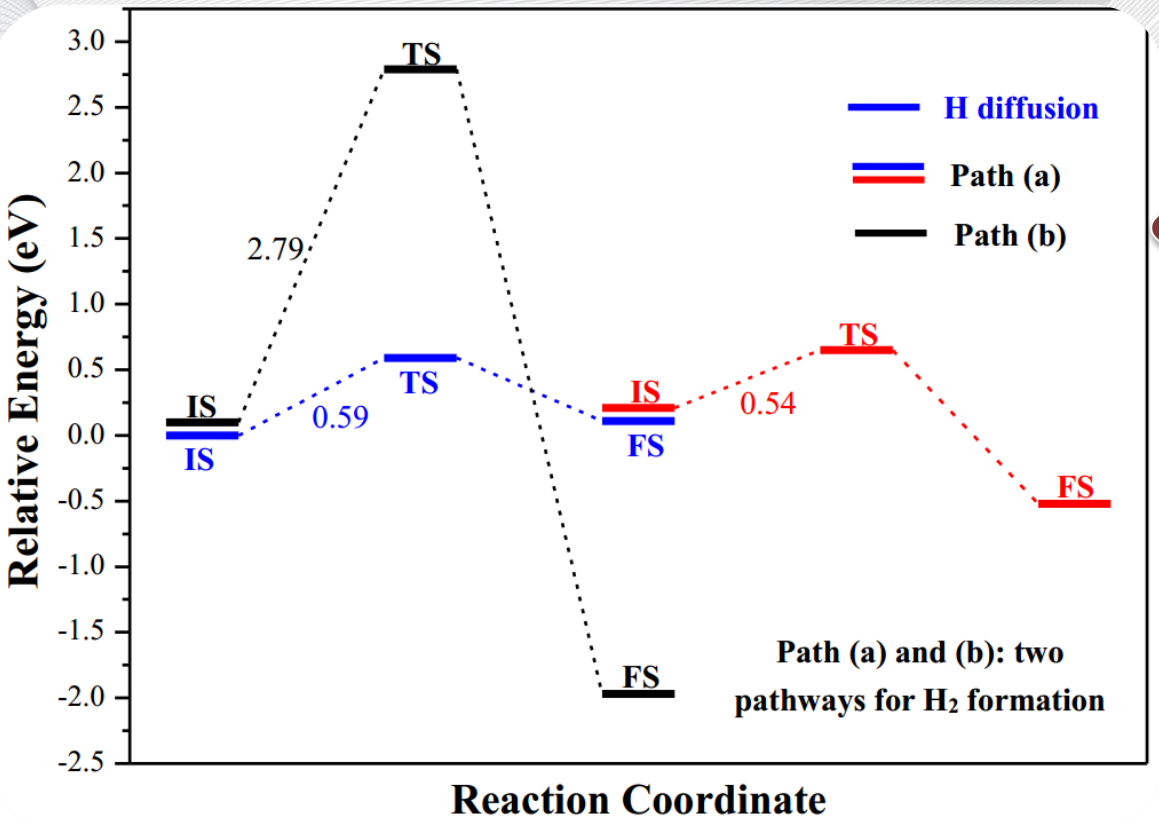
The remaining specie tends to more easily adsorb on Ni-based OC surface with the process of CH_4 sequential dehydrogenation.

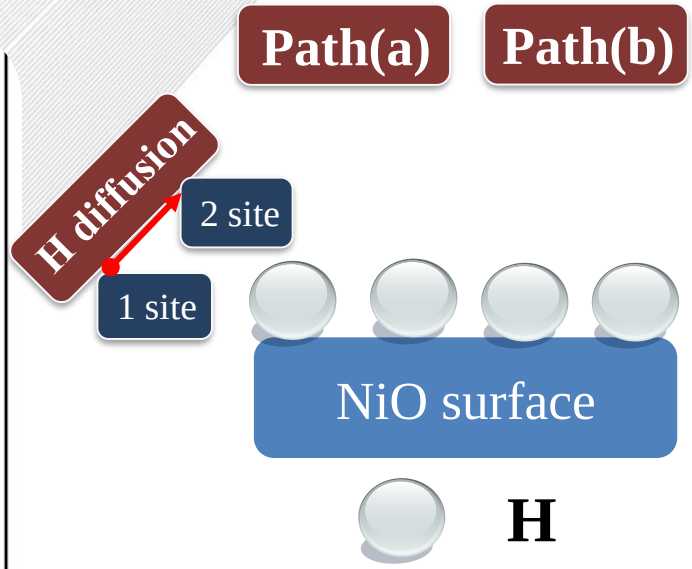
4 steps of CH_4 dehydrogenation



Overall, the activation energies for every step are high and around 1.90 eV, implying CH_4 sequential dehydrogenation process occurs at high temperatures.



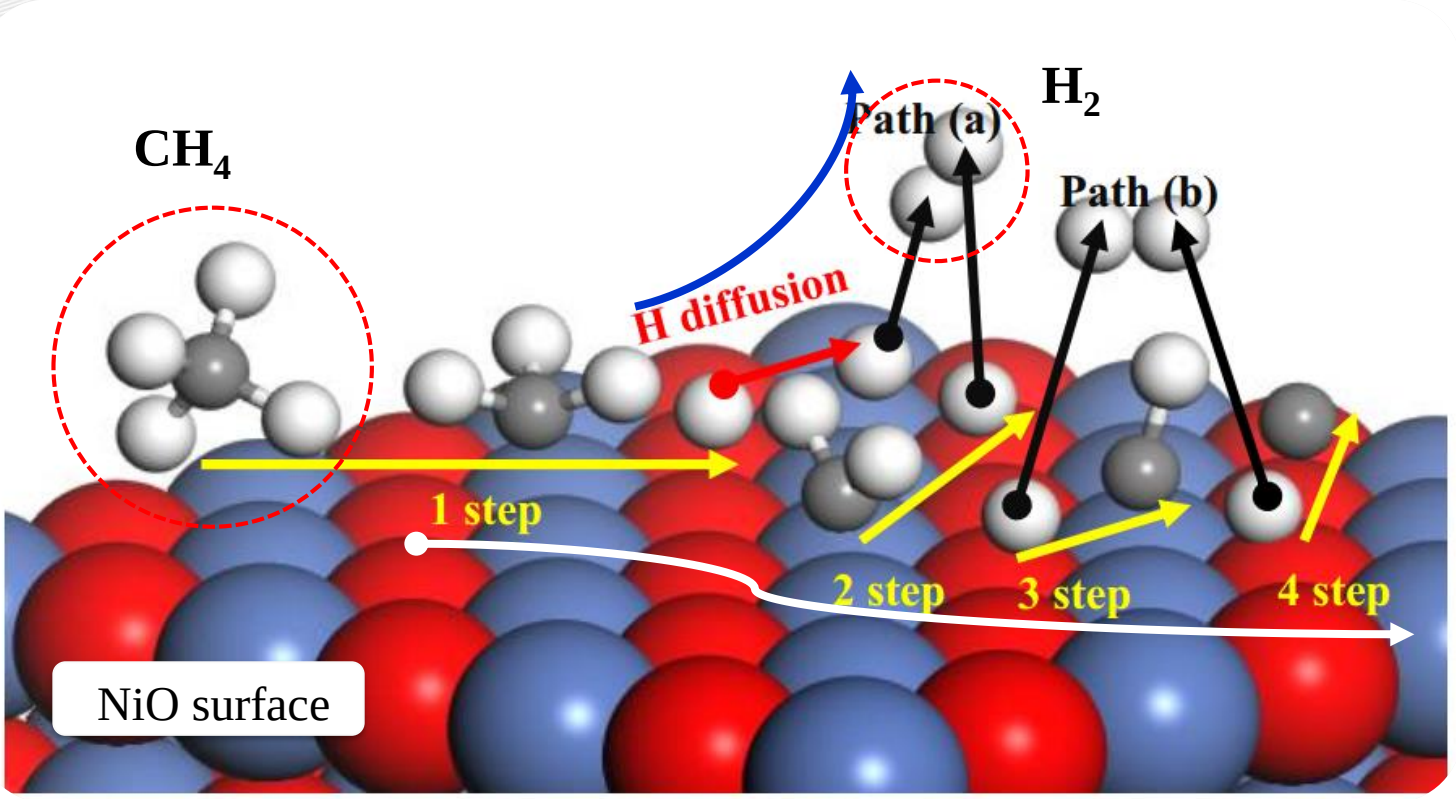




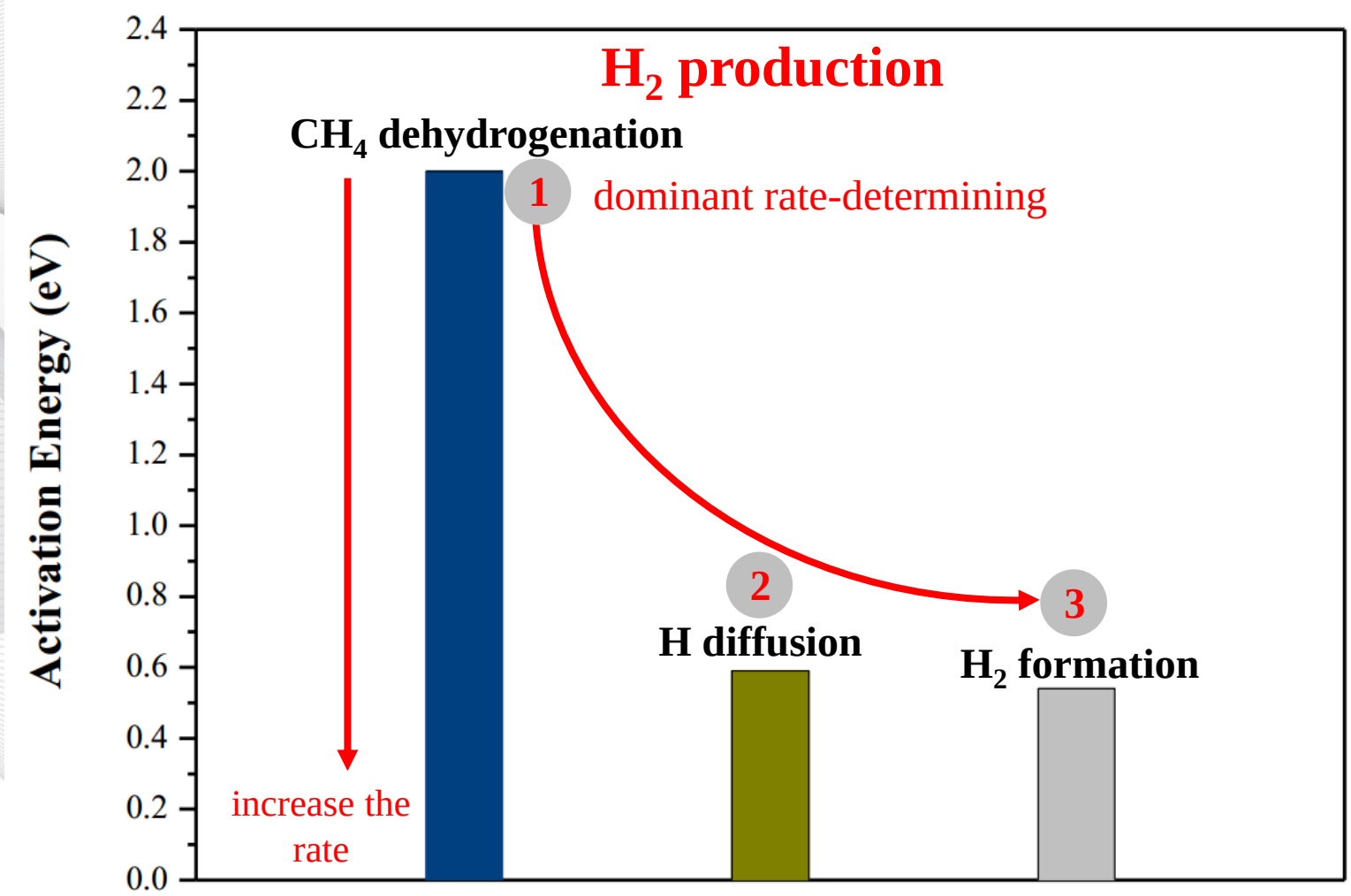
H atom on 1 site could facilely migrate to 2 site.

Path (a) is a primary pathway of H_2 formation.

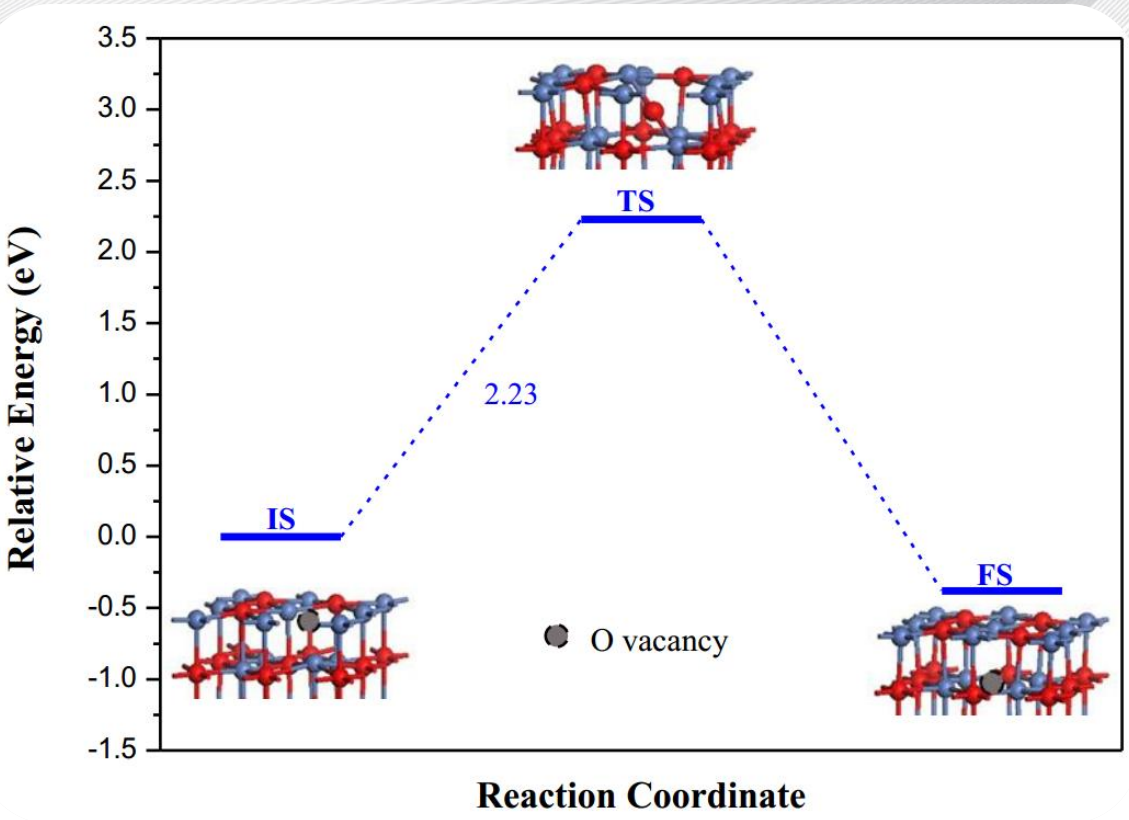
H_2 production

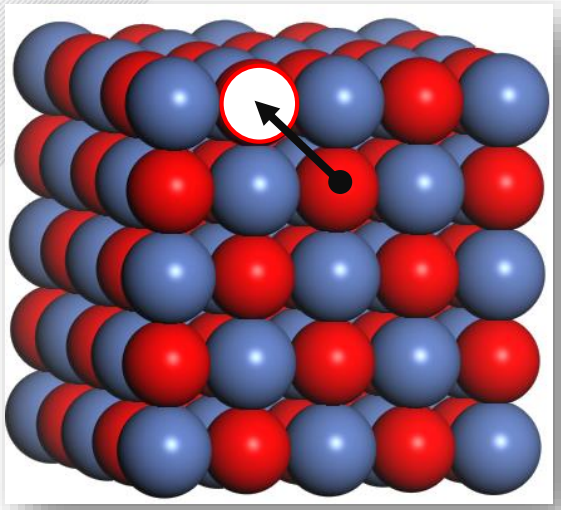


Which process limits rate of H_2 production ?



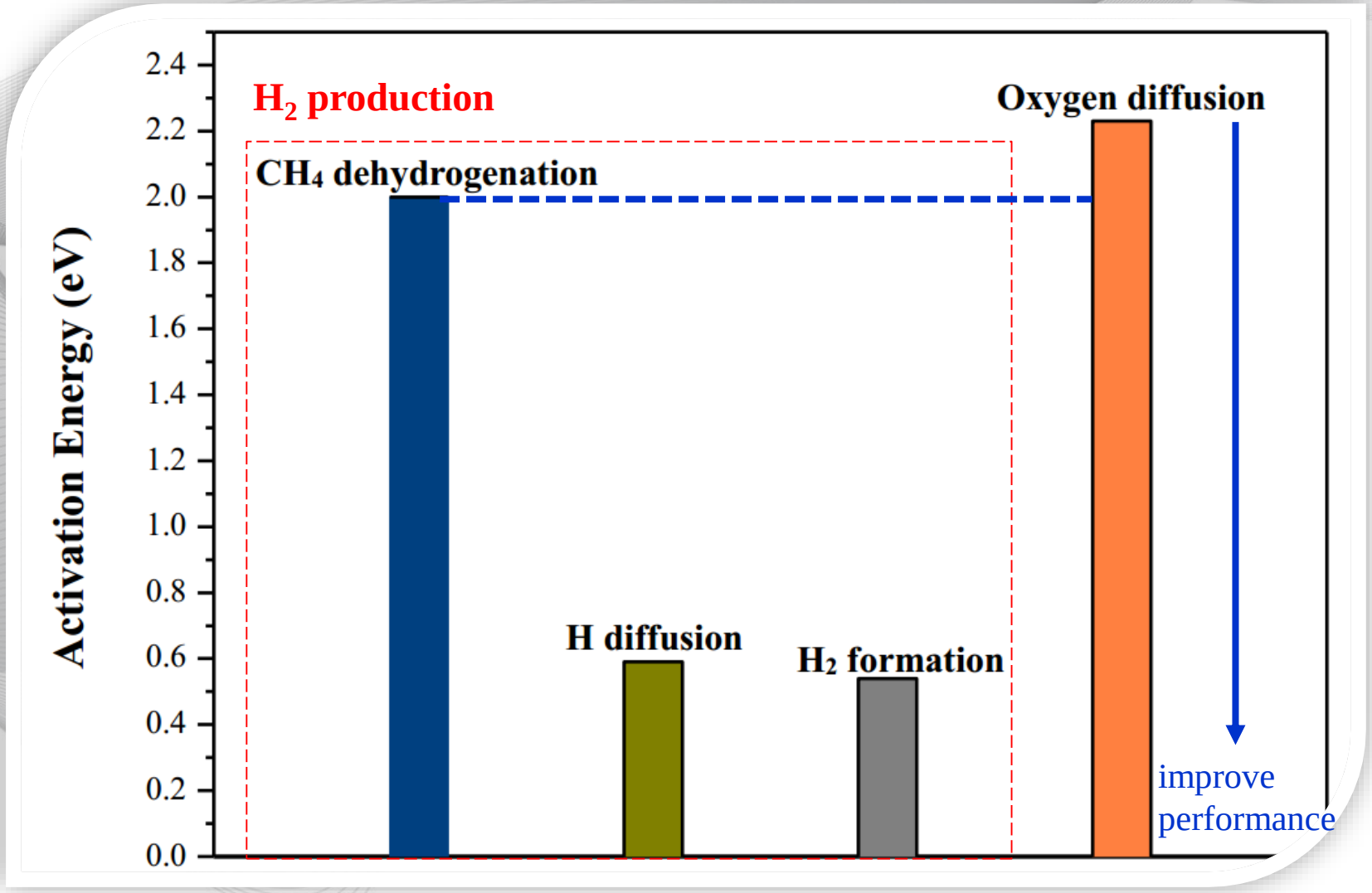
Oxygen anion diffusion





Oxygen anion migration process may proceed at high temperatures and the diffusion rate is low.

How does the oxygen anion diffusion process affect reactivity performance?



Conclusions

A comprehensive study with respect to the reaction mechanism between methane and Ni-based oxygen carrier was performed based on the DFT calculations.

We proposed two possible pathways for H_2 production process.

The CH_4 sequential dehydrogenation limits the rate of H_2 production.

The oxygen anion diffusion largely affect the reactivity performance of Ni-based oxygen carrier.

Acknowledgements

The National Natural Science Foundation of China (NSFC) (51576085)

National key R&D program of China (2016YFE0102500)