Formaldehyde Dissociation on (111) and (0001) Metal Surfaces

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Outline

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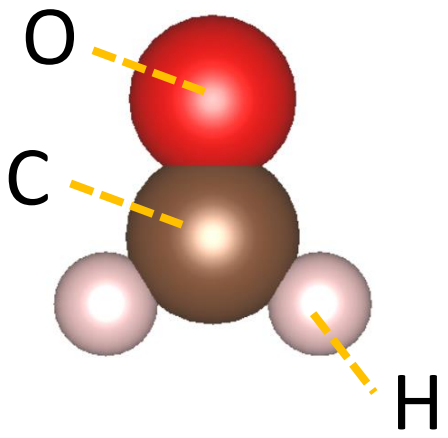
2. Formaldehyde Dissociation on Pristine Metal Surfaces
   - CH_2O (formaldehyde) and CHO (formyl) adsorptions
   - Examples: Analysis of transition states for dissociation

3. Summary and Conclusion

Introduction



What is formaldehyde?

- Formaldehyde (CH_2O) is the simplest aldehyde (R-CHO)
- Colorless gas with pungent odor at the room temperature and pressure

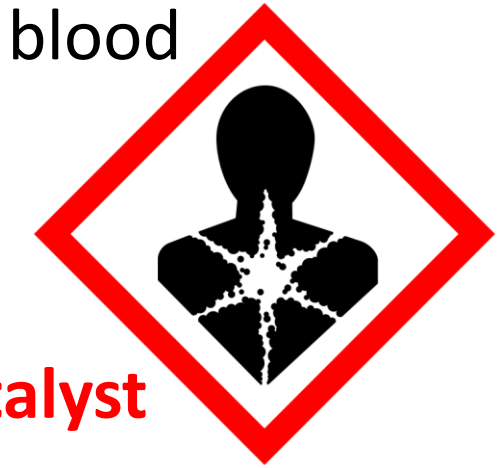
Usage

- Precursor to more complex compound, e.g., methanol
- Tissue and cells preserver
- Bacteria dispatch

[1] L. Zhang, et al., Environ. Mol. Mutagen., 51 (2010) p. 181-191

Side Effect

Formaldehyde can cause white blood cell cancer in the long term [1]



Study of Formaldehyde decomposition using metal catalyst is our current objective

Formaldehyde Dissociation on Pristine Metal Surfaces

- Experiments show that Pt is a good candidate for formaldehyde decomposition in the absence of the oxygen molecules
- Using Pt as the starting point, we extended the study to other transition metals near Pt
- Transition metals considered in this study are shown in the figure on the right (only highlighted elements are involved)

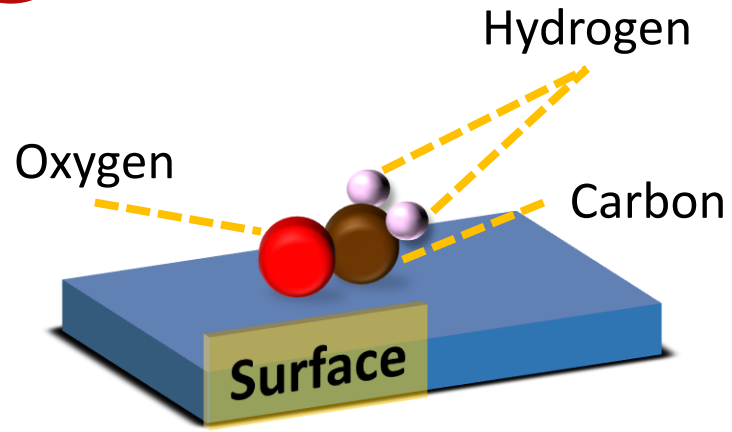
25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd
75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

Platinum group metals
Other transition metals

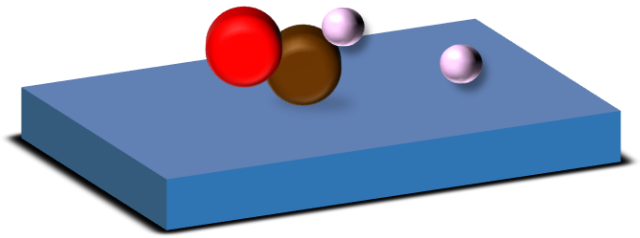
HCHO Dissociation Schematic

We considered the low coverage formaldehyde adsorption (2/9 ML in this study), as the high coverage of formaldehyde leads to the polymerization

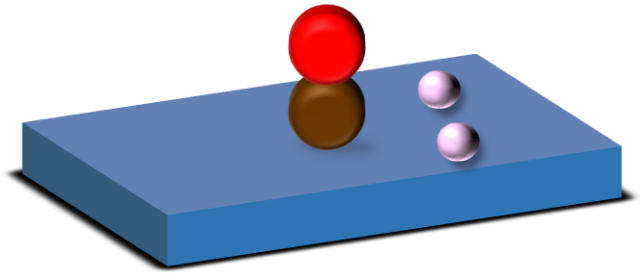
0 **CH_2O adsorption**



1 **Dissociate: CHO+H**

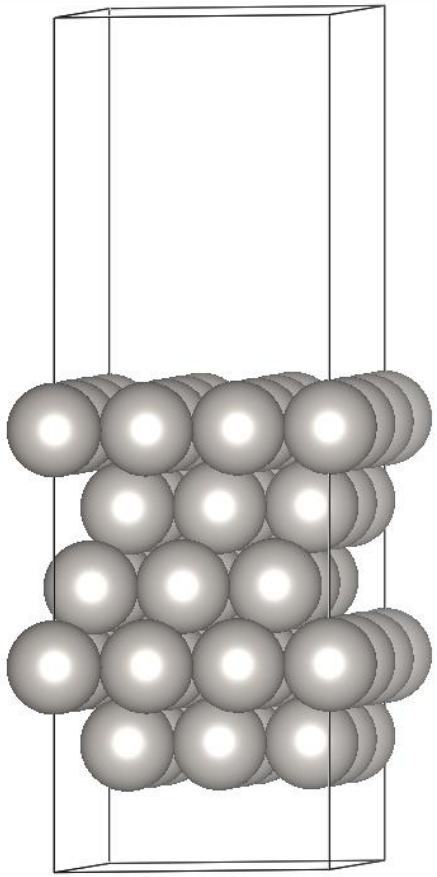


2 **Dissociate: CO+2H**

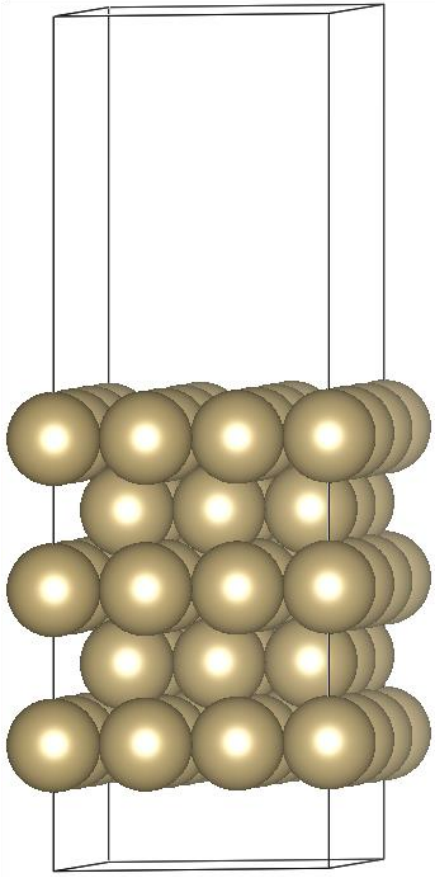


Computational Method

- First-principles approach based on density functional theory using VASP simulation package
- GGA-PBE exchange-correlation functional with vdW-DF corrections of Dion et al.
- PAW pseudopotentials
- plane-wave basis set with 400 eV cut-off energy
- $8 \times 8 \times 1$ Gamma-centered k-points
- Slab model with 9 atoms/layer, and with 5 atomic layers
- Vacuum space of ~ 14.0 Å along the direction normal to the surfaces
- CI-NEB method for transition states searching



(111) Surfaces
(Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au)



(0001) Surfaces
(Ru and Os)

Definitions: Adsorption Energies

- **For formaldehyde (CH_2O) adsorption:**

$$E_{\mathrm{ads}} = E_{\mathrm{CH_2O+surf.}} - (E_{\mathrm{CH_2O}} + E_{\mathrm{surf.}})$$

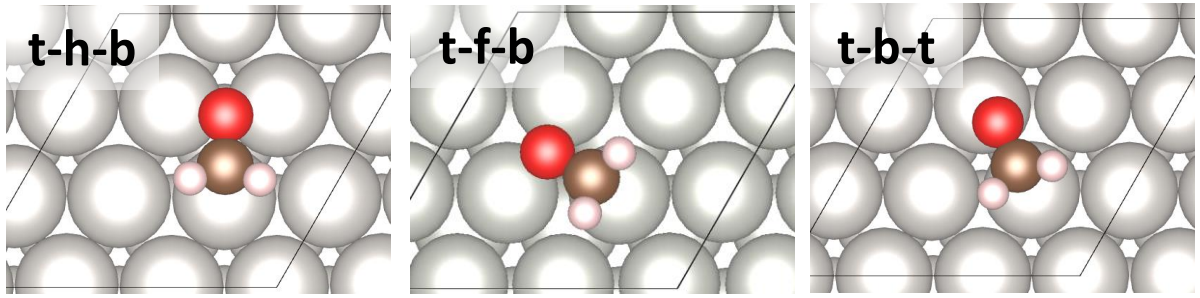
- **For formyl (CHO) adsorption:**

$$E_{\mathrm{ads}} = E_{\mathrm{CHO+surf.}} - (E_{\mathrm{CHO}} + E_{\mathrm{surf.}})$$

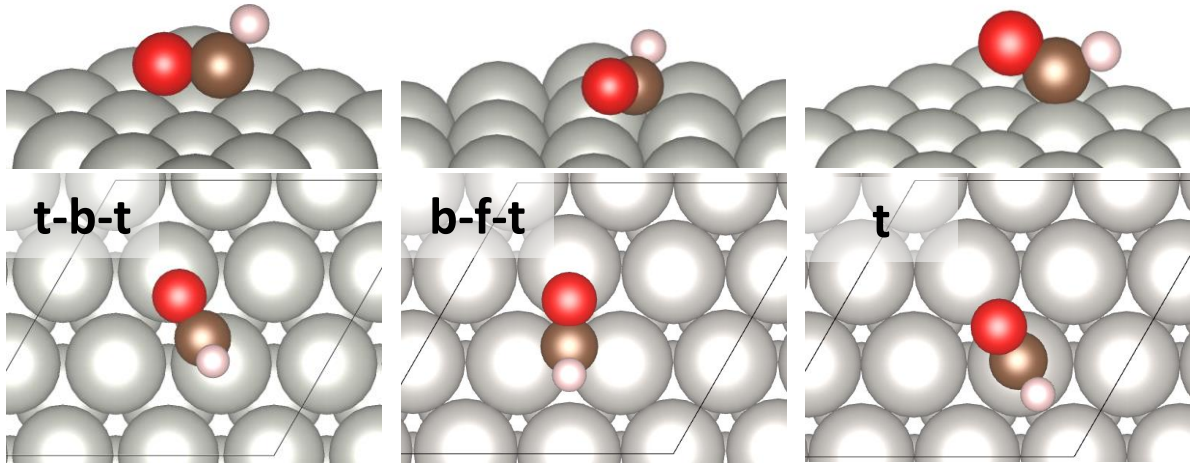
Formaldehyde and Formyl Adsorption

Adsorption Sites

Formaldehyde (CH_2O)



Formyl (CHO)



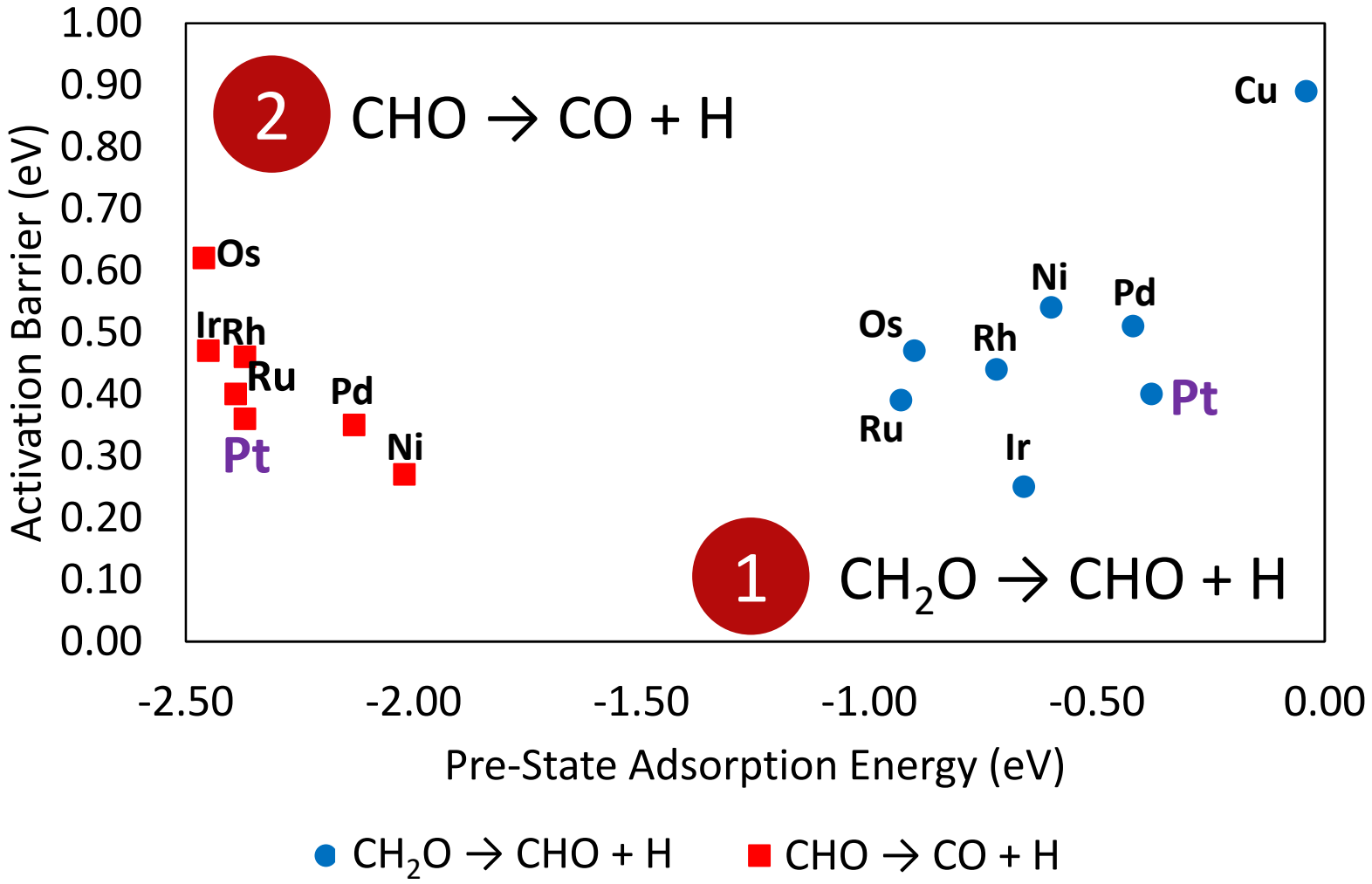
Adsorption Energies

		Formaldehyde		Formyl	
	Surface	**Site**	**E_{ads} (eV)**	**Site**	**E_{ads} (eV)**
Gr. 8	Ru(0001)	t-h-b	-0.93	t-b-t	-2.39
	Os(0001)	t-h-b	-0.90	t-b-t	-2.46
Gr. 9	Rh(111)	t-f-b	-0.72	t-b-t	-2.37
	Ir(111)	t-f-b	-0.66	t-b-t	-2.45
Group 10	Ni(111)	t-f-b	-0.60	b-f-t	-2.02
	Pd(111)	t-f-b	-0.42	b-f-t	-2.13
	Pt(111)	t-b-t	-0.38	t	-2.37
Group 11	Cu(111)	t-b-t	-0.04	t	-1.21
	Ag(111)	Desorbed	-	t	-0.89
	Au(111)	Desorbed	-	t	-1.27

t = top, b = bridge, h = hcp hollow, f = fcc hollow

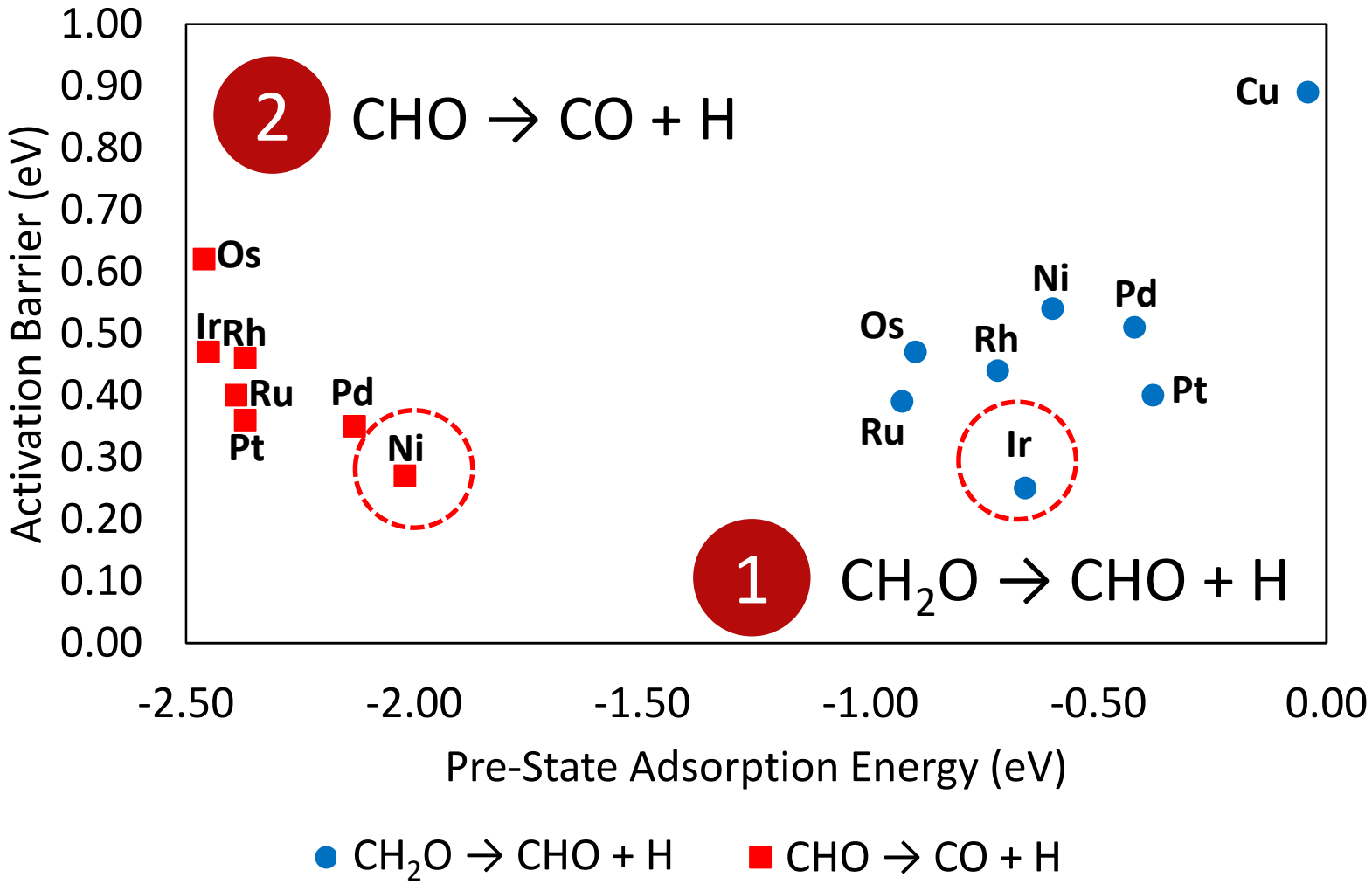
*Only the most preferable sites are reported

Activation Barriers as a Function of Pre-State Adsorption Energy



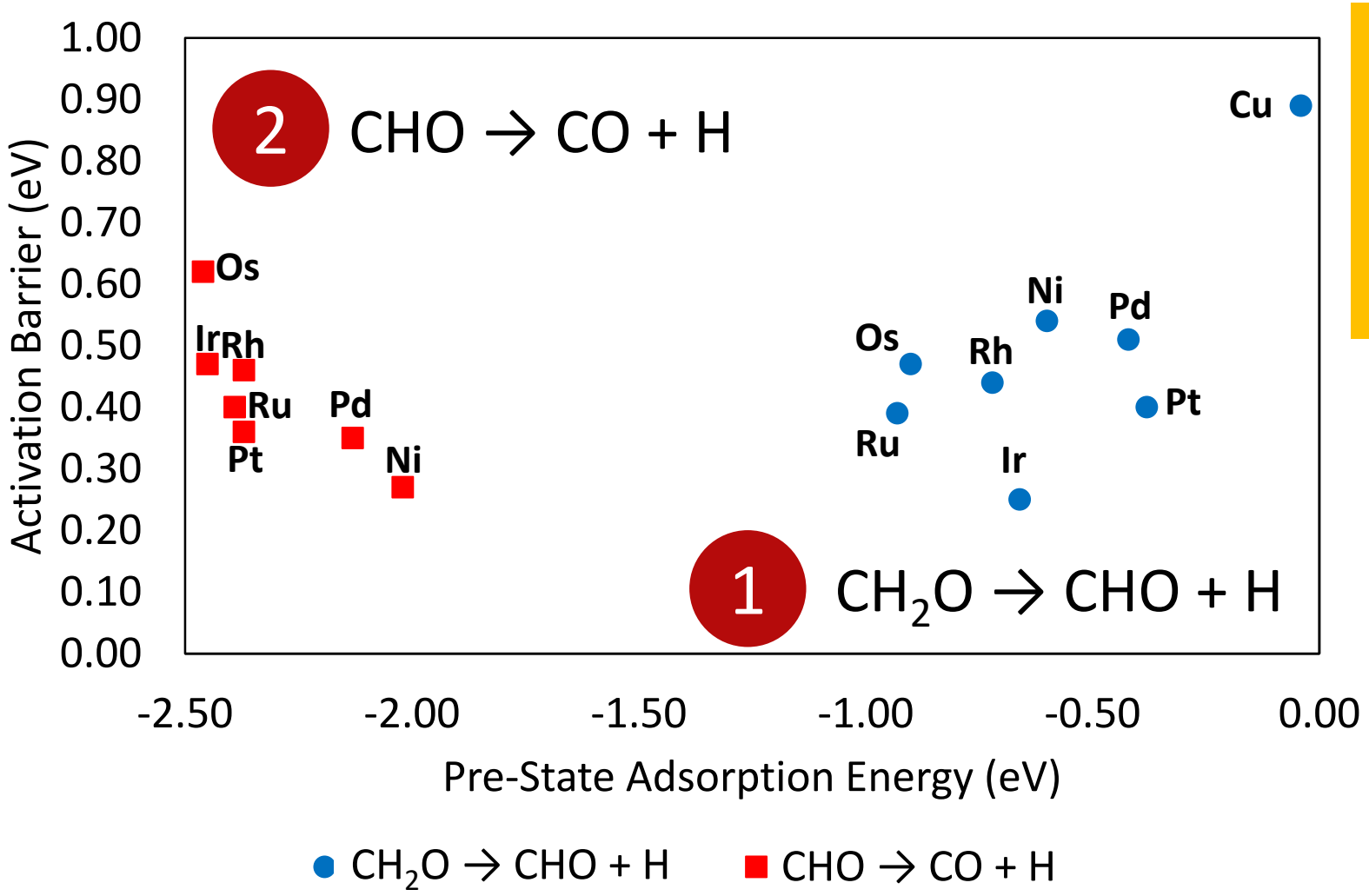
- Activation barriers of reaction $CH_2O \rightarrow CHO + H$ weakly correlate with the adsorption energy of CH_2O
- Activation barriers of reaction $CHO \rightarrow CO + H$ have correlation with the adsorption energy of CHO
- Among them, **Pt** is the best overall

Activation Barriers as a Function of Pre-State Adsorption Energy



- Ir(111) and Ni(111) are the best for the 1st and 2nd steps, respectively

Activation Barriers as a Function of Pre-State Adsorption Energy



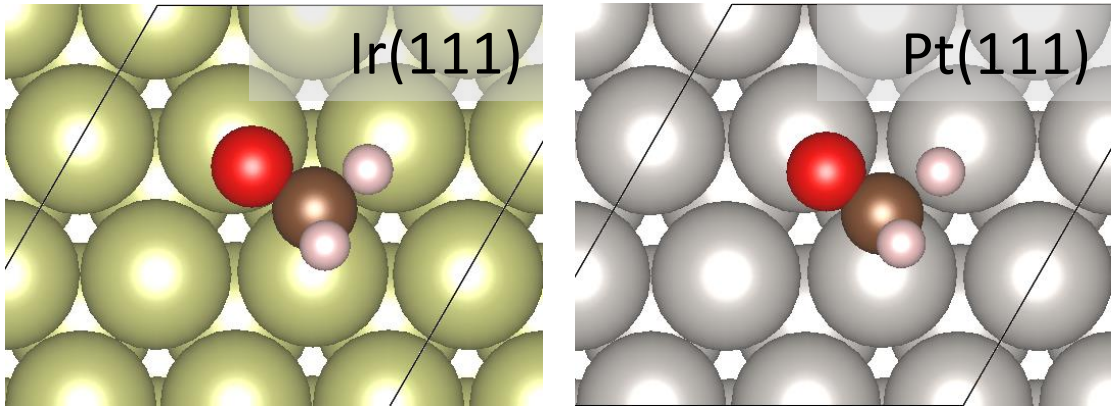
- Activation barriers of reaction $CH_2O \rightarrow CHO + H$ weakly correlate with the adsorption energy of CH_2O
- Activation barriers of reaction $CHO \rightarrow CO + H$ have correlation with the adsorption energy of CHO

1 $CH_2O \rightarrow CHO + H$ Reaction

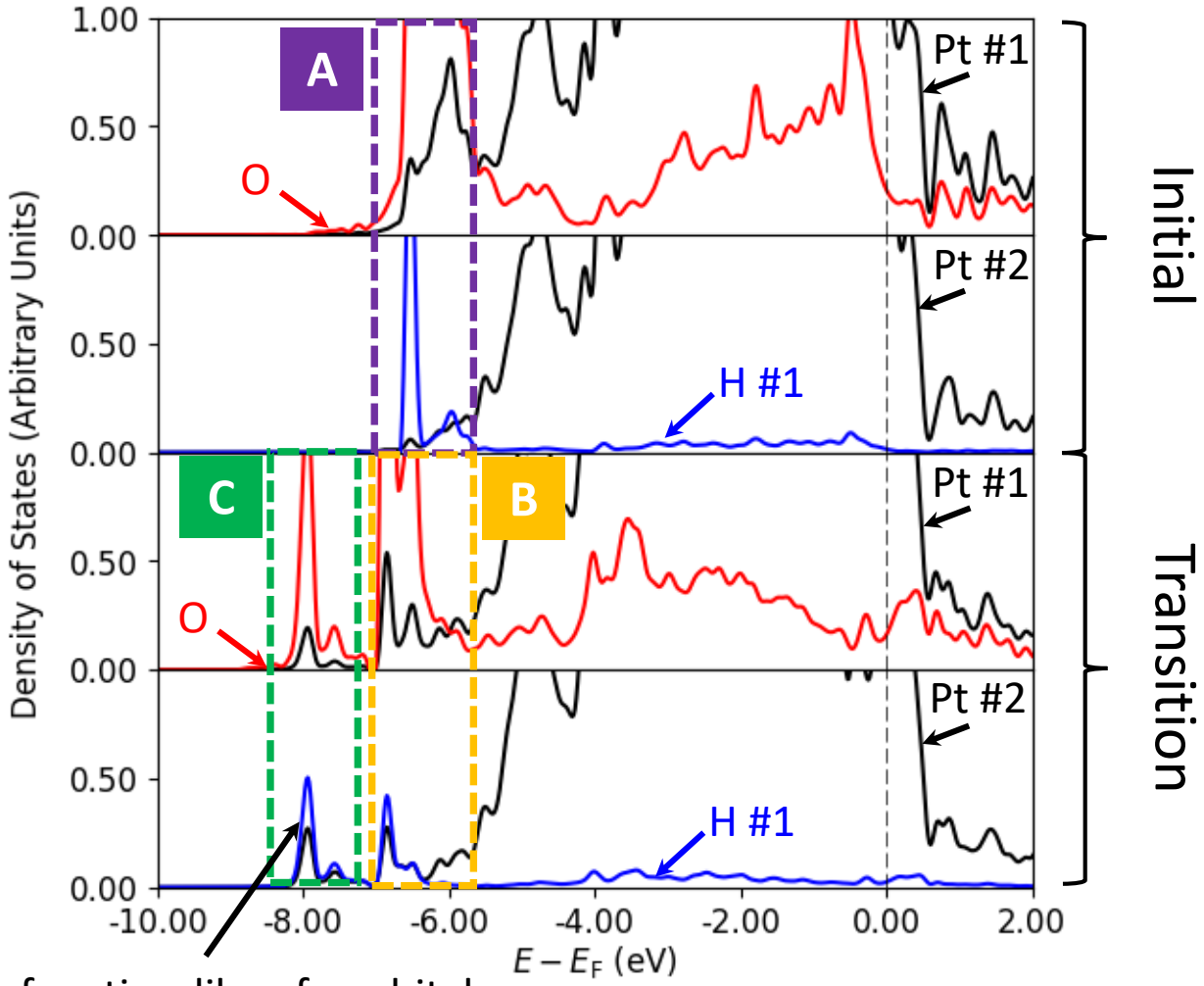
We considered the reactions on Ir(111) and Pt(111)

- Reaction on Ir(111) shows the smallest activation barrier, followed by that on Pt(111)
- They also have similar transition state configurations, simplifying the analysis

Transition state configurations

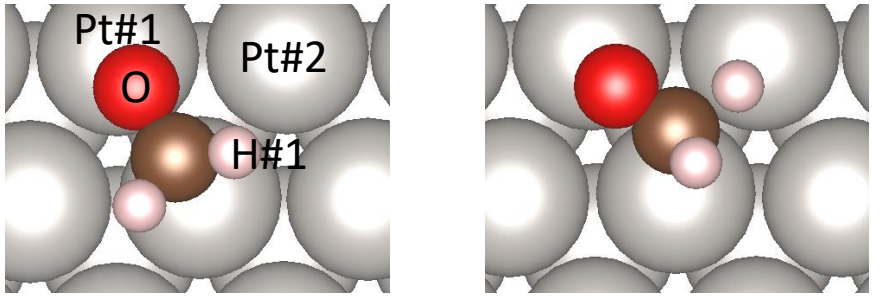


1 $CH_2O \rightarrow CHO + H$ on Pt(111)

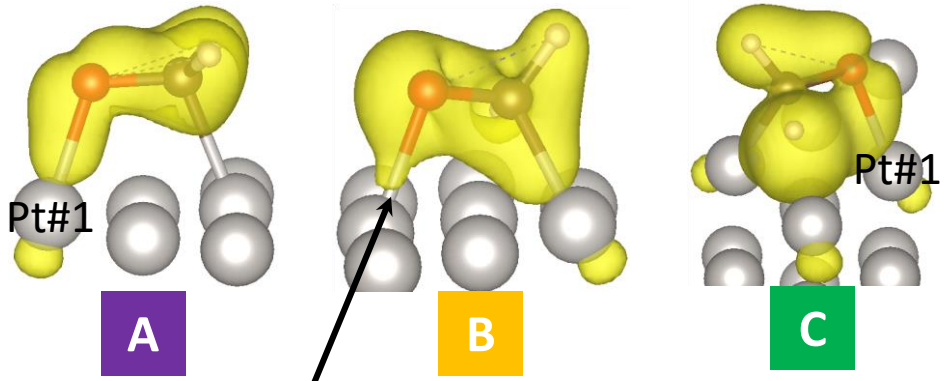


Delta function-like of *s* orbital:
H weakly interactions with Pt

HCHO Configurations

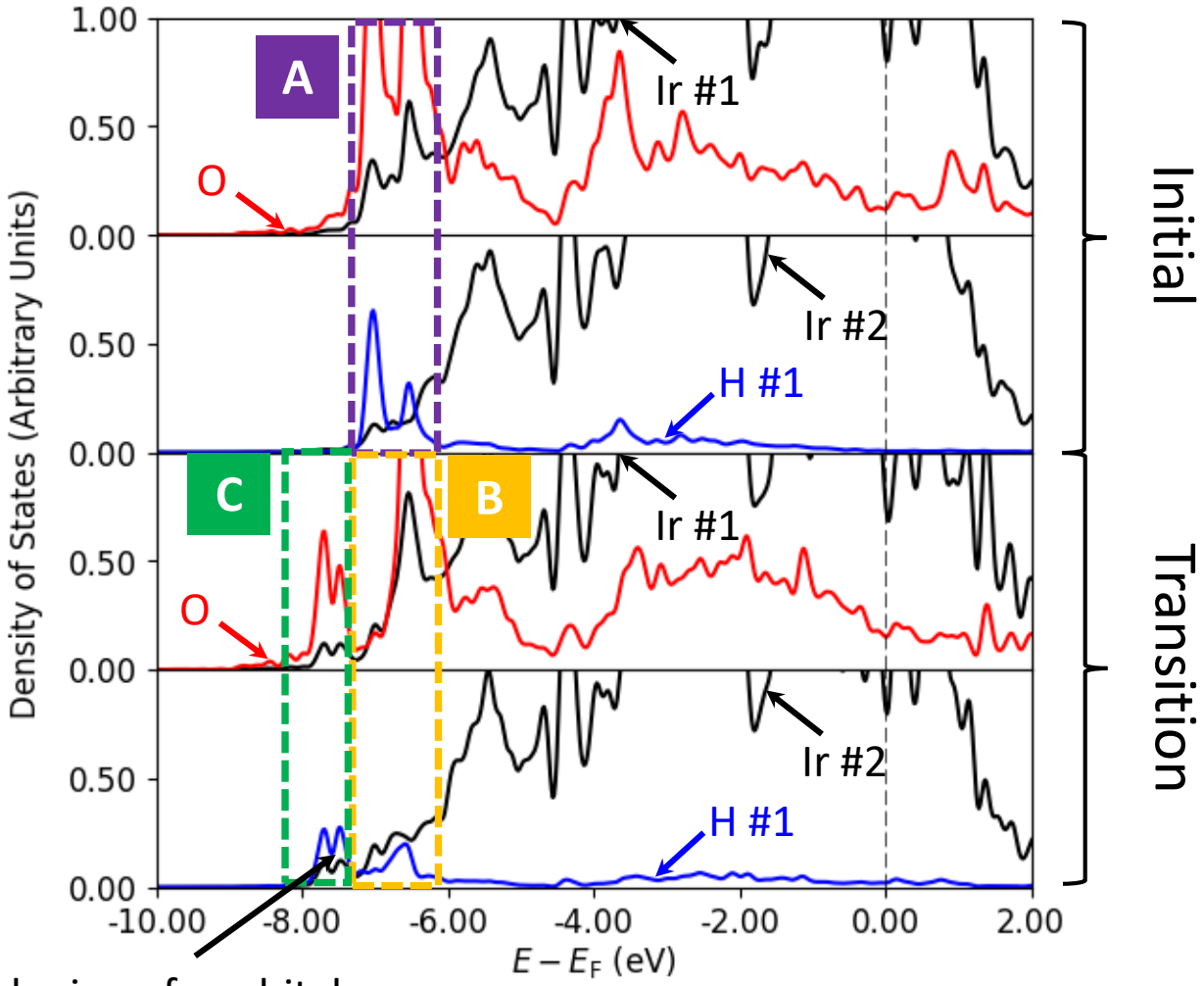


Electron density



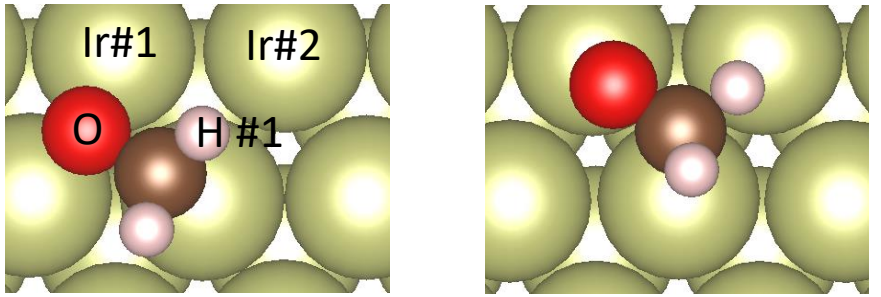
Pt-O bond has been weakened at the transition state

1 $CH_2O \rightarrow CHO + H$ on Ir(111)



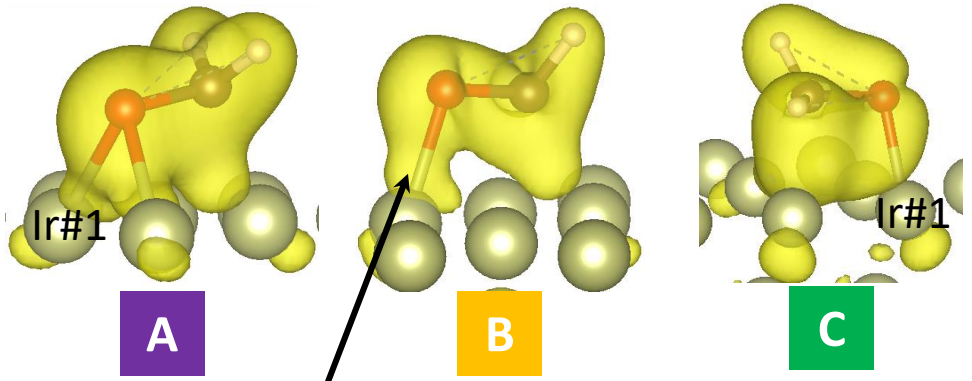
Broadening of *s* orbital:
H interacts with Ir is stronger

HCHO Configurations



Initial Transition

Electron density



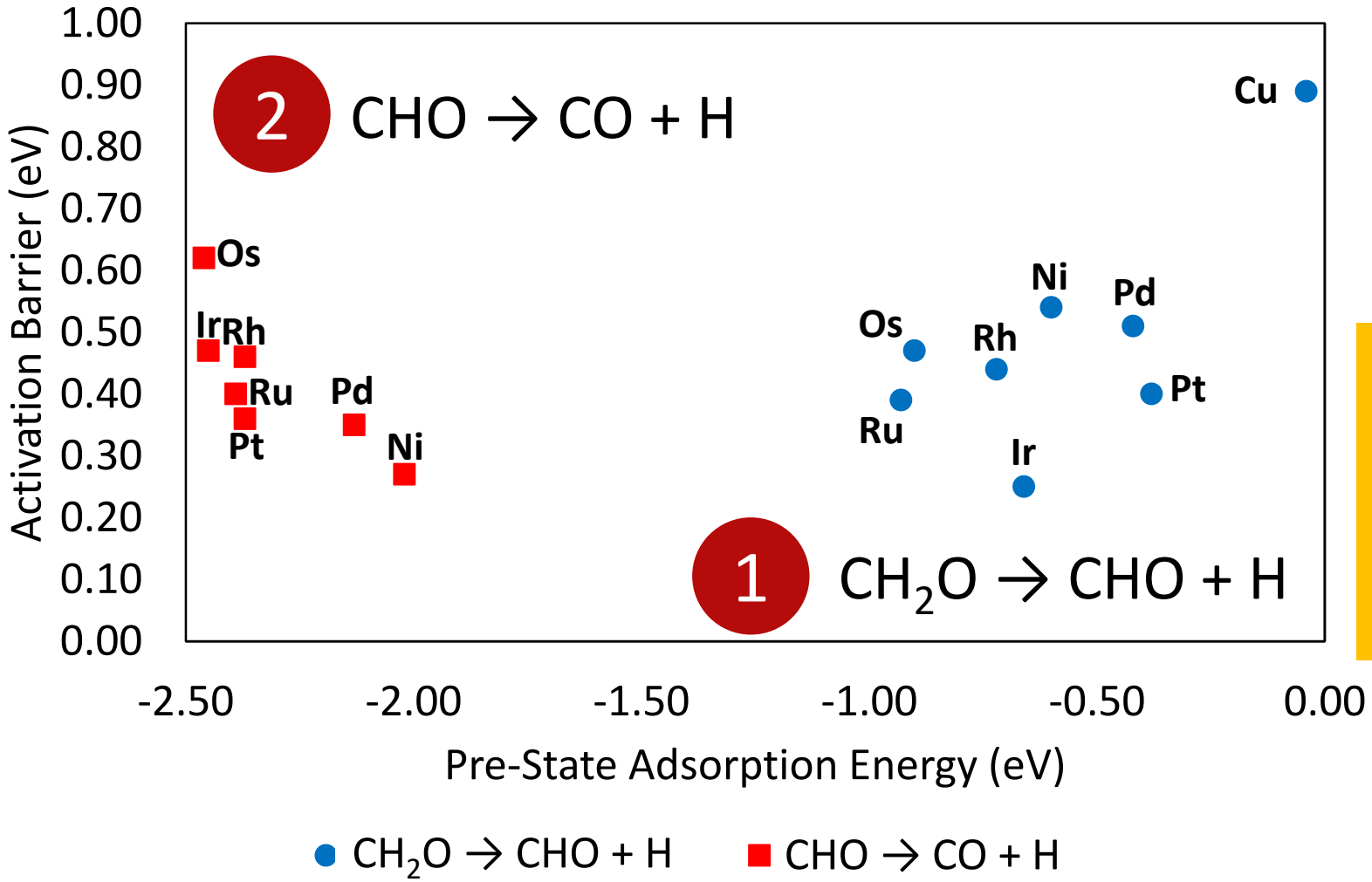
Ir-O bond has no significant change at transition state

1 $CH_2O \rightarrow CHO + H$

Two factors contribute to the lowered activation barrier of Ir(111) as compared to Pt(111)

- Hydrogen can make a stronger bond with Ir than Pt. This can be seen from the hydrogen adsorption on the top site of both surfaces
  - H adsorption on Ir(111): -0.36 eV
  - H adsorption on Pt(111): -0.27 eV
- At the transition state, oxygen (of CH_2O) bonding with Pt(111) is weakened at the transition state. On the contrary, oxygen (of CH_2O) break and form a new bond with Ir(111)

Activation Barriers as a Function of Pre-State Adsorption Energy



- Activation barriers of reaction $CH_2O \rightarrow CHO + H$ weakly correlate with the adsorption energy of CH_2O
- Activation barriers of reaction $CHO \rightarrow CO + H$ have correlation with the adsorption energy of CHO

2 $CHO \rightarrow CO + H$

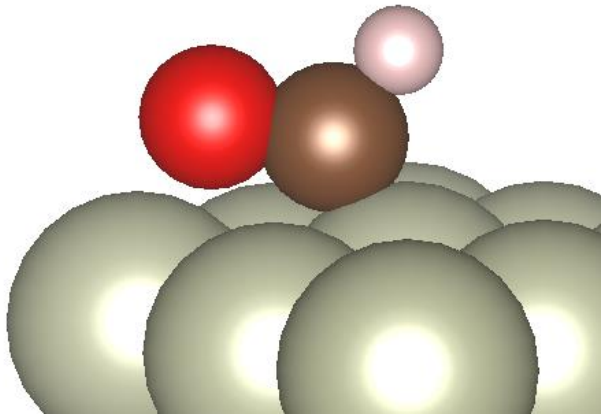
We considered the reaction on Os(0001), Ru(0001), Rh(111), and Ni(111)

- They involve the reaction with highest activation barrier [Os(0001)] and the lowest activation barrier [Ni(111)]
- The common feature of the formyl adsorption on these surfaces is that formyl's oxygen binds with the surface atom at the initial configuration

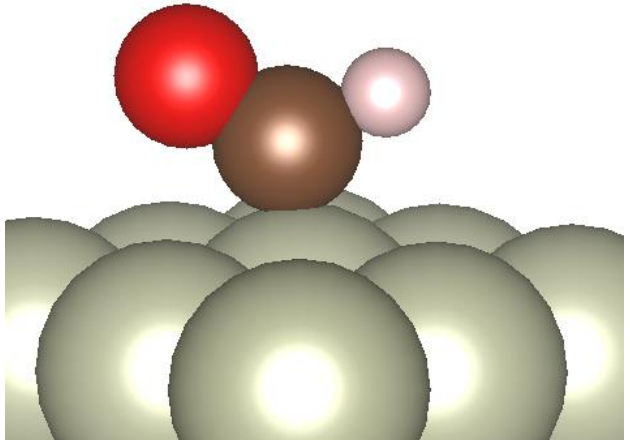
Example:

Initial and transition states of $CHO \rightarrow CO + H$ on Rh(111)

Initial

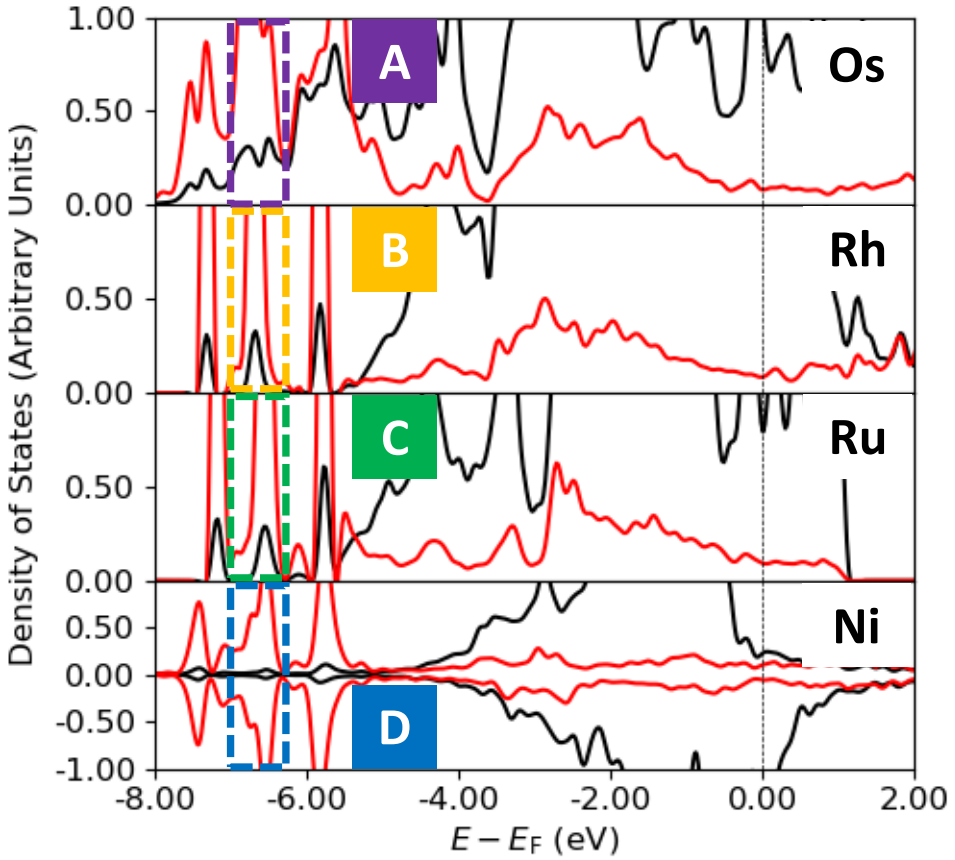


Transition

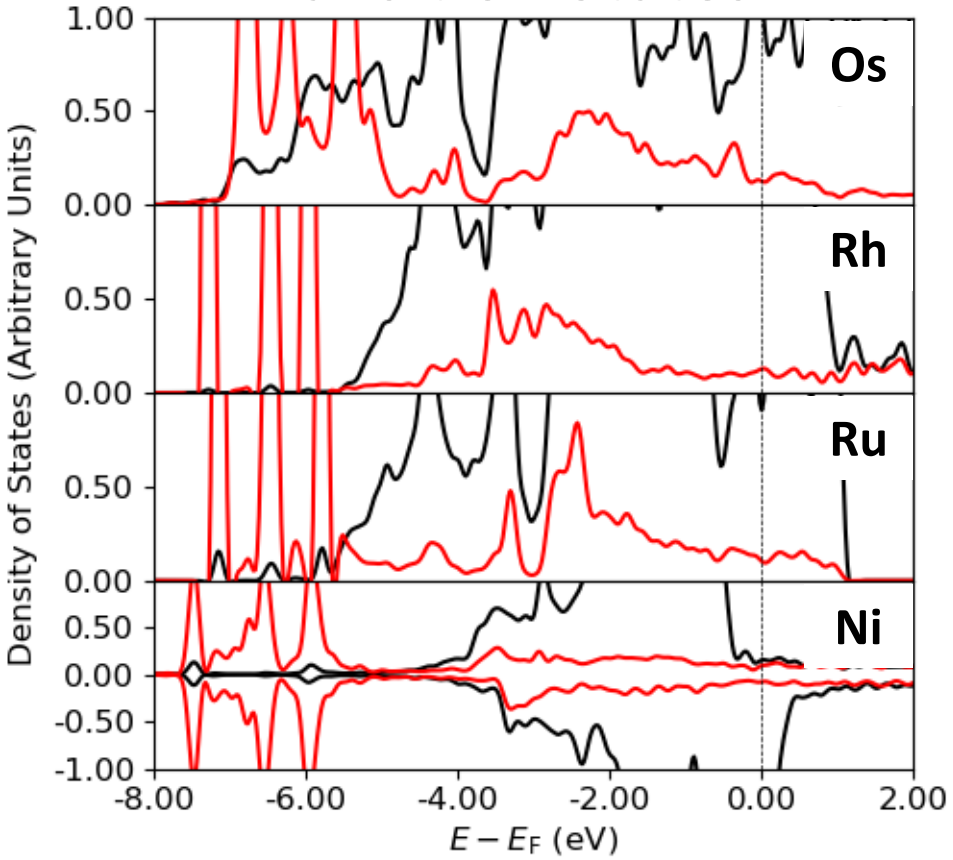


2 CHO → CO + H

Initial States



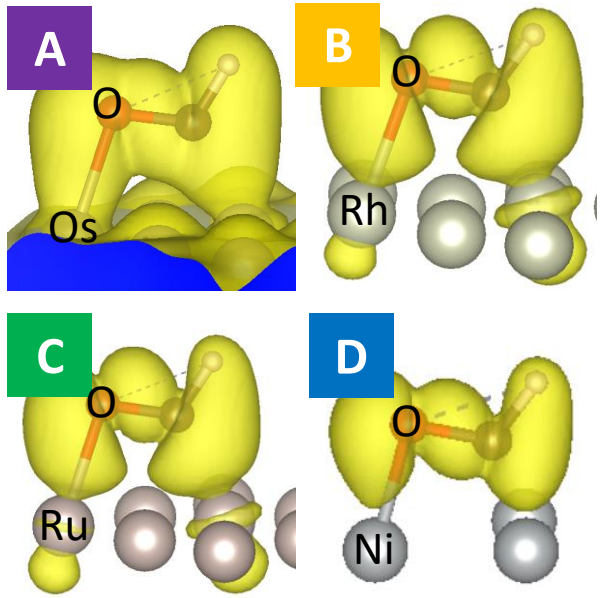
Transition States



d *p*

The *d* orbitals were projected on the metal atom under oxygen, while *p* orbitals were projected on the oxygen (of CHO)

Electron density



Since we need to break the O-metal bond, the case where O (of CHO) strongly binds with surface like Fig. A has higher activation barrier as compared to case of Fig. B, C, and D

Summary and Conclusion

CH_2O and CHO adsorption energies on pristine metal surfaces: the general trend

- CH_2O adsorption energies decrease as the metal surfaces are changed from group 8 towards group 11. Within the same group, 3*d* metals provide the strongest adsorption energies, followed by 4*d* and 5*d* metals.
- For CHO adsorption energies, 3*d* transition metals show the weakest adsorption energies, followed by 4*d* and 5*d*.

Summary and Conclusion

1 $CH_2O \rightarrow CHO + H$ reaction

- The reaction on Ir(111) has the smallest activation barrier, followed by that on Pt(111)
- Two factors contributing to the smaller activation barrier on Ir(111):
  - Hydrogen can make a stronger bond with Ir(111) than Pt(111), lowering the total energy at the transition states
  - Oxygen (of CH_2O) bond was partially broken at the transition state in the case of Pt(111), while they are retained on Ir(111)

Summary and Conclusion

2 **CHO → CO + H**

- The reaction on Ni(111) has the smallest activation barrier
- We investigated the electronic structures on Ni(111), Ru(0001), Rh(111), and Os(0001). The lowered activation barrier of the reaction on Ni(111) is due to the weak O (of CHO) bonding with the Ni(111)

Acknowledgements

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Thank you very much