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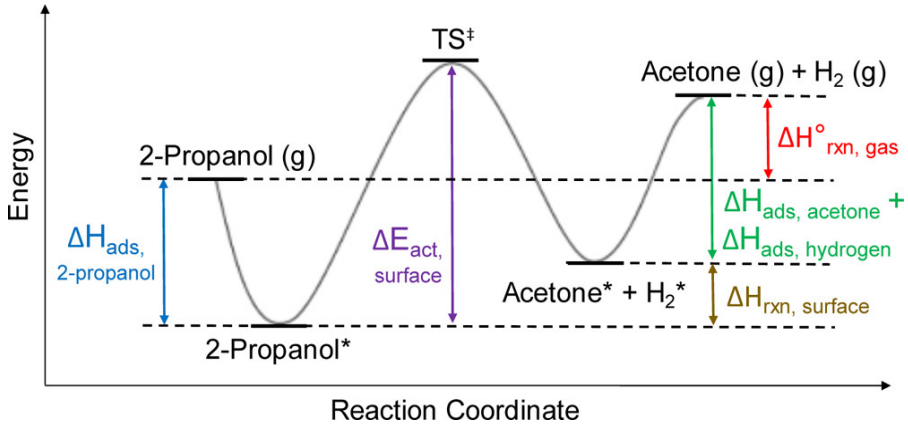
Catalytic activity of spinel ferrites in acid-base reactions

1. Chemisorption of 2-propanol surface
2. Dehydrogenation of 2-propanol to form acetone and hydrogen,
3. Desorption of acetone



Assumption of calculations:

1. Enthalpy of hydrogen adsorption ($\Delta H_{ads,hydrogen}$) is negligible for oxide surfaces.
2. The activation energy for dissociation of the hydrogen atom is negligible.
3. Heat of reaction can be approximated by:

$$\Delta H_{rxn,surface} = \Delta H_{ads,\ 2\text{-}propanol} - \Delta H_{ads,\ acetone}$$

$$\Delta H_{ads,i} = \Delta E_{surface+2\text{-}propanol/acetone} - \Delta E_{surface} - \Delta E_{2\text{-}propanol/acetone}$$

The adsorption energy of 2-propanol should be more negative than for acetone

[1] Foo et al. *ACS Catal.*, 2017, 7 (7), pp 4423–4434

Co_3O_4 (001) surface

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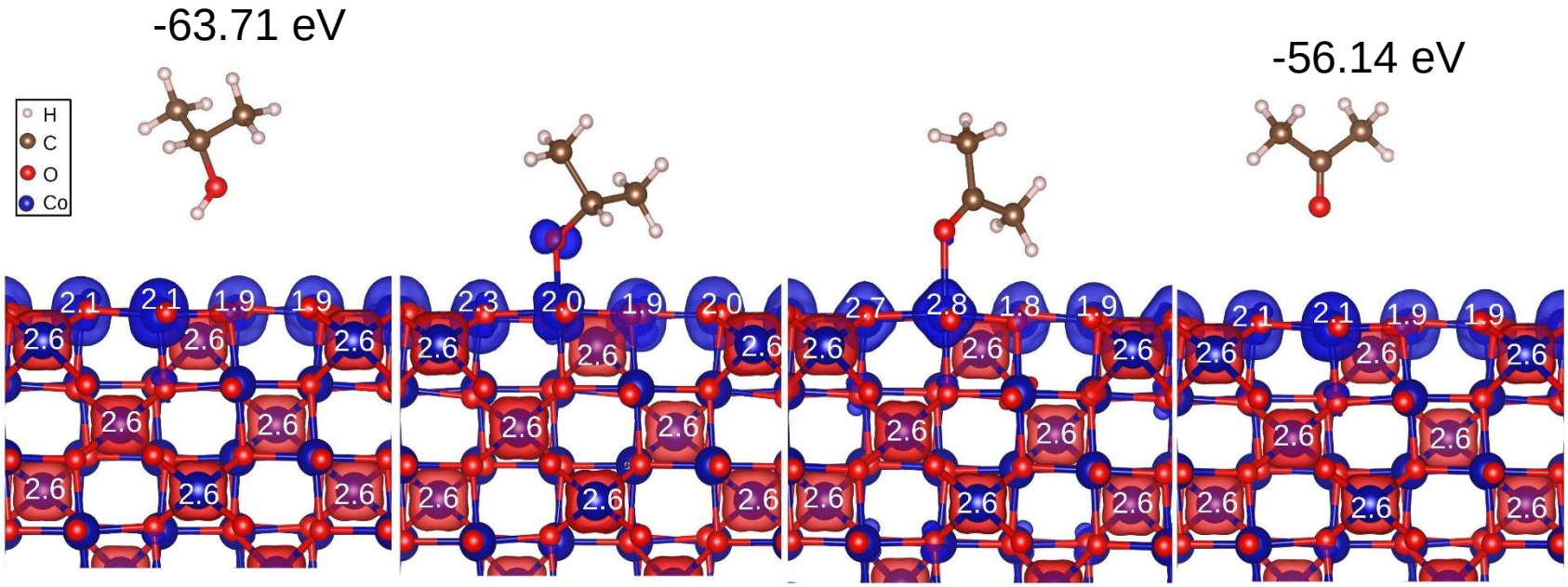

	Prop $_{isolated}$	Prop*	Acet $_{isolated}$	Acet*	Surface
Energy (eV)	-63.71	-470.46	-56.14	-462.95	-406.27

Adsorption energies: 2-propanol: -0.695 eV, Acetone: 0.04 eV

Reaction takes places on the octahedral sites

$$\Delta H_{rxn,surface} = -0.735$$

$CoFe_2O_4$ (001) surface

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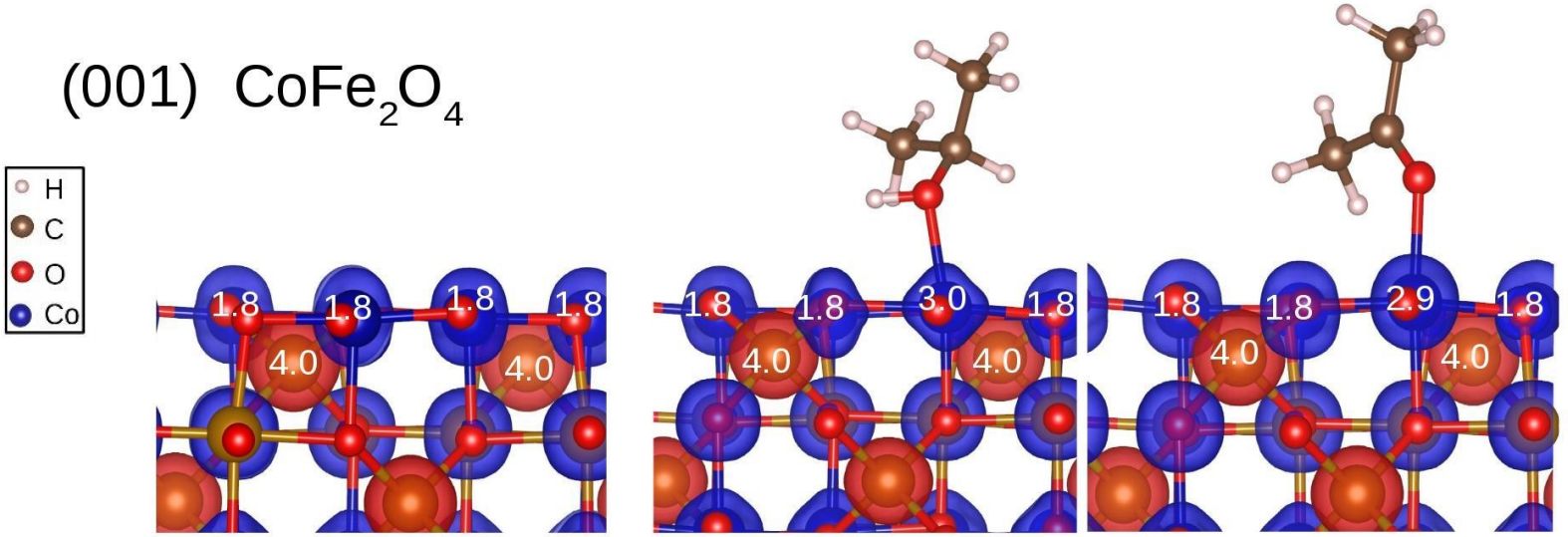

	Prop $_{isolated}$	Prop*	Acet $_{isolated}$	Acet*	Surface
Energy (eV)	-63.71	-505.322	-56.14	-497.7849	-441.3781

Adsorption energies: 2-propanol: -0.38 eV, Acetone: -0.26 eV

Reaction takes places on the octahedral sites

$$\Delta H_{rxn,surface} = -0.11$$

Co_3O_4 (110) surface

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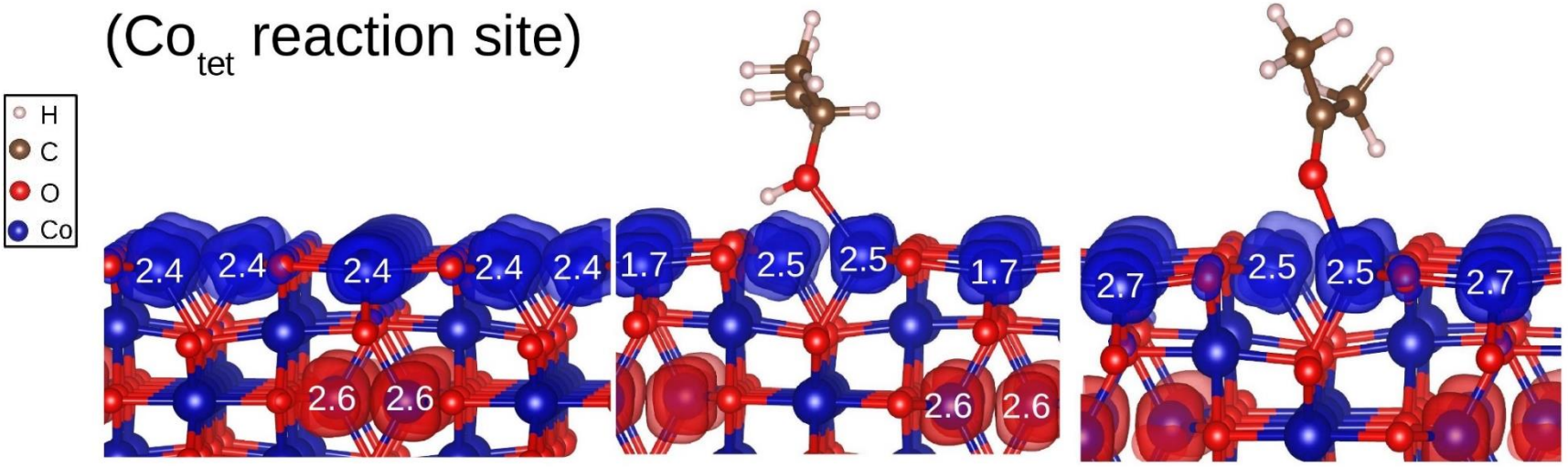

	Prop $_{isolated}$	Prop*	Acet $_{isolated}$	Acet*	Surface
Energy (eV)	-63.71	-822.60	-56.14	-814.57	-757.91

Adsorption energies: 2-propanol: -0.977 eV, Acetone : -0.51 eV

Reaction takes places on the tetrahedral sites

$$\Delta H_{rxn,surface} = -0.461$$

Co_3O_4 (110) surface

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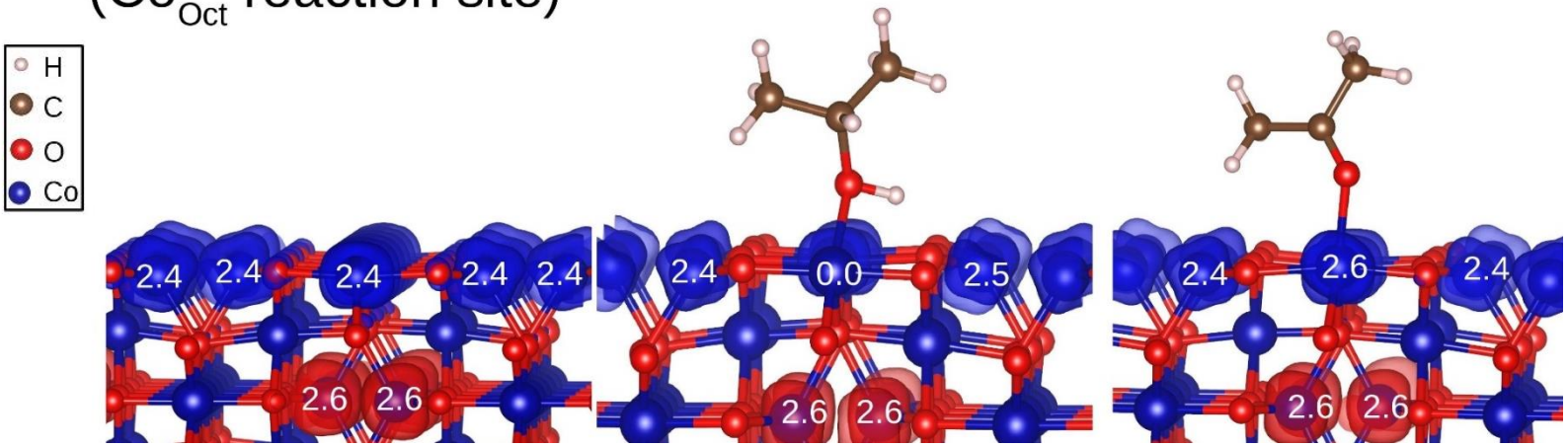
(110) Co_3O_4

(Co_{Oct} reaction site)



	Prop $_{isolated}$	Prop*	Acet $_{isolated}$	Acet*	Surface
Energy (eV)	-63.71	-822.388	-56.14	-814.3942	-757.91

Adsorption energies: 2-propanol: -0.758 eV, Acetone: -0.33 eV

Reaction takes places on the octahedral sites

$$\Delta H_{rxn,surface} = -0.419$$

Co_3O_4 (110) surface, O vacancy

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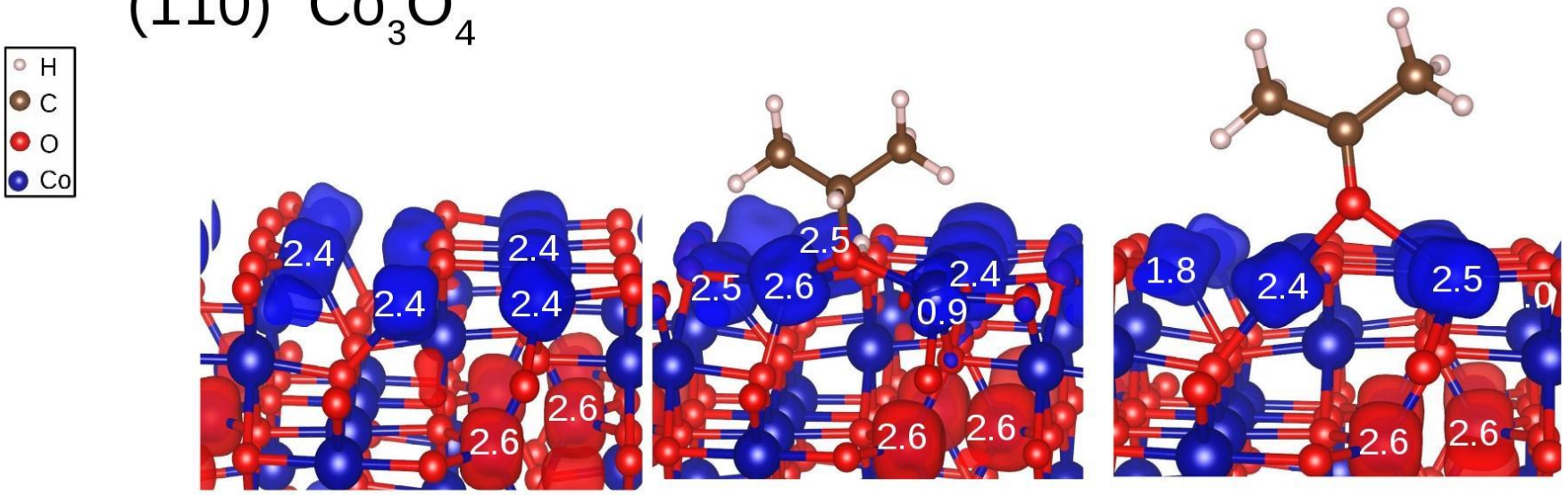
(110) Co_3O_4



	Prop $_{isolated}$	Prop*	Acet $_{isolated}$	Acet*	Surface
Energy (eV)	-63.71	-815.51	-56.14	-807.2553	-750.35

Adsorption energies: 2-propanol: -1.43 eV, Acetone: -0.68 eV

Oxygen vacancy formation: -2.67 eV

Reaction takes places on the oxygen vacancy sites

$$\Delta H_{rxn,surface} = -0.69$$

$CoFe_2O_4$ (001) surface

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Propanol and OOH group