Y7 annual meeting of IRP $PACS_2$ @ Šmartno, 9 Nov 2021

Hydroxylation of Al surfaces: concepts and simple examples

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Motivation

Common knowledge: Al surfaces are oxidized

- **Q:** What happens when water is present (humidity, liquid water)?

  A: Water adsorbs and possibly reacts with the surface

Motivation

- Water adsorbs and possibly reacts with the surface

- Plain adsorption:

$$H_2O + * \rightarrow H_2O*$$

- Dissociative adsorption:

$$H_2O + * + O* \rightarrow 2OH*$$

and/or

$$H_2O + * \rightarrow OH* + \tfrac{1}{2}H_2$$

* ≡ free adsorption site

A* ≡ adsorbed or surface species

Motivation

- Water adsorbs and possibly reacts with the surface
- Plain adsorption:

$$H_2O + * \rightarrow H_2O*$$

- Dissociative adsorption:

$$H_2O + * + O* \rightarrow 2OH*$$

and/or

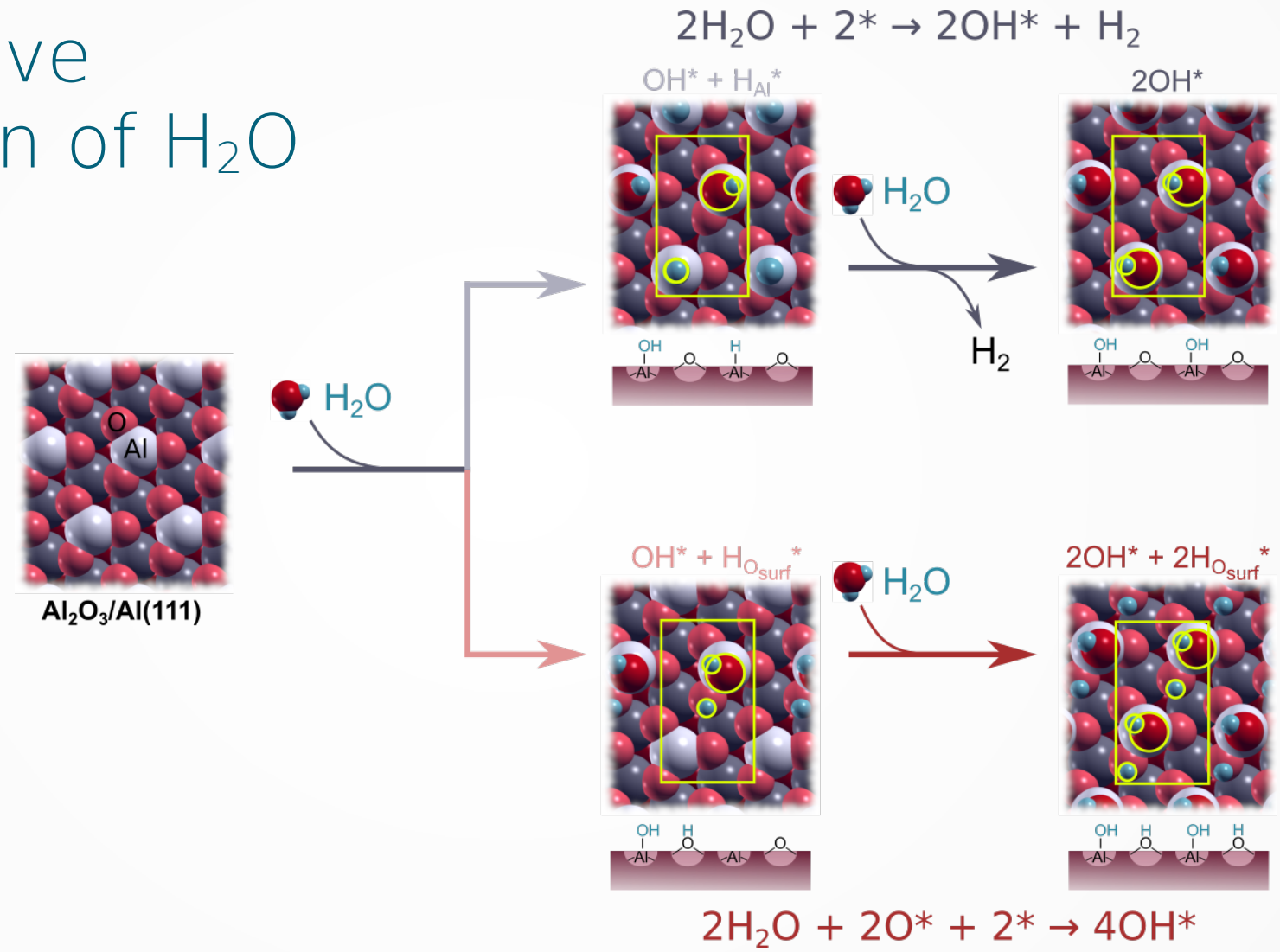
$$H_2O + * \rightarrow OH* + \tfrac{1}{2}H_2$$

preferred

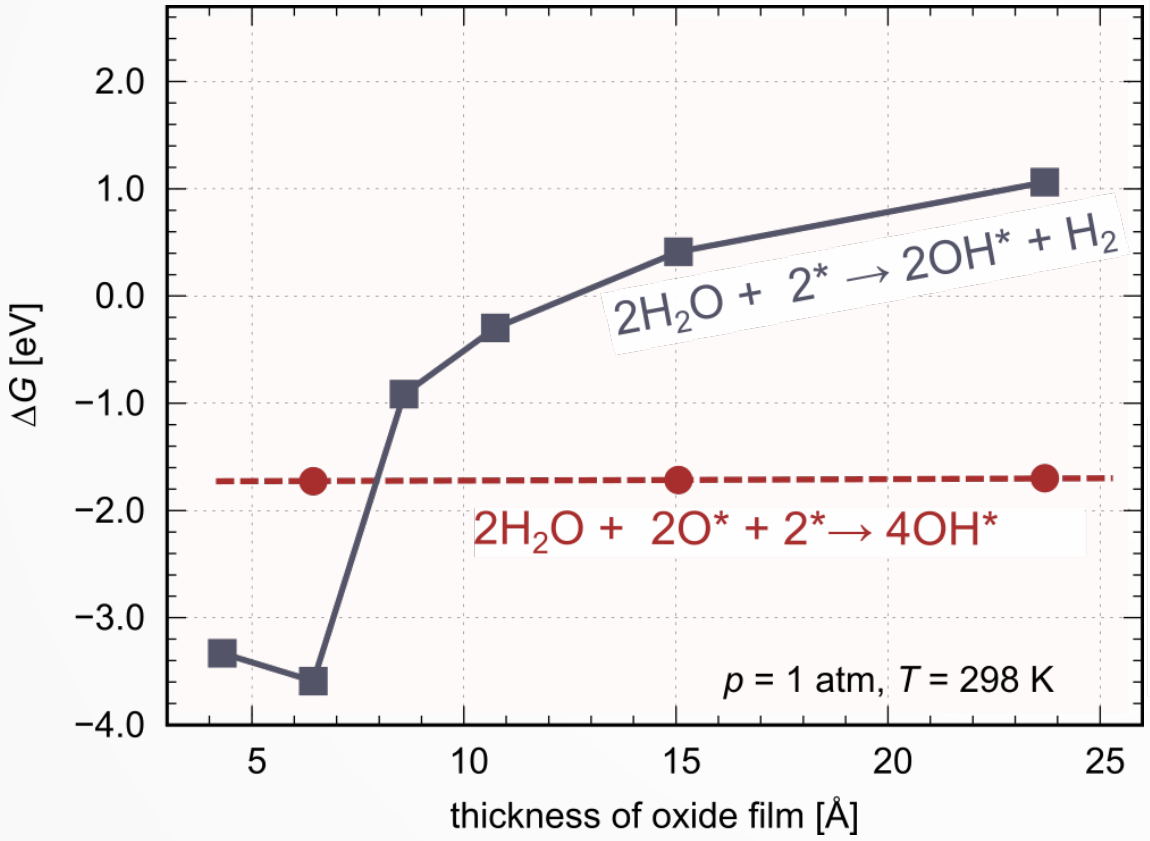
$*$ ≡ free adsorption site

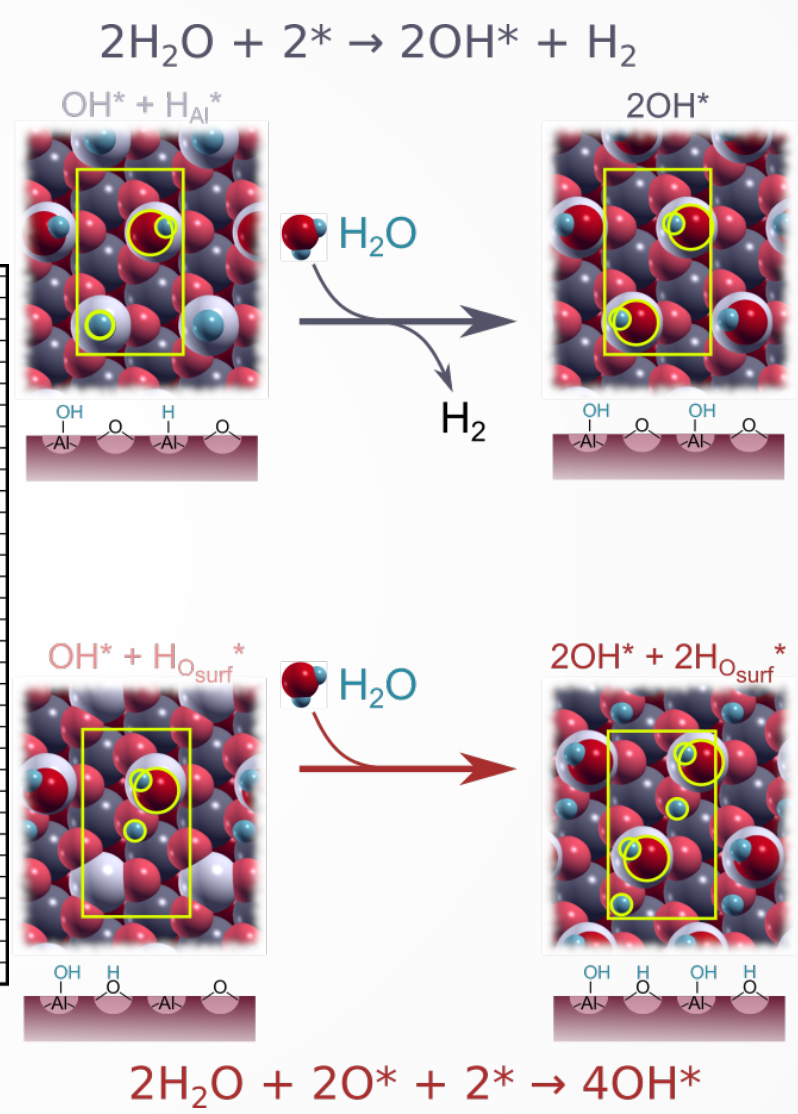
$A*$ ≡ adsorbed or surface species

Dissociative adsorption of H_2O



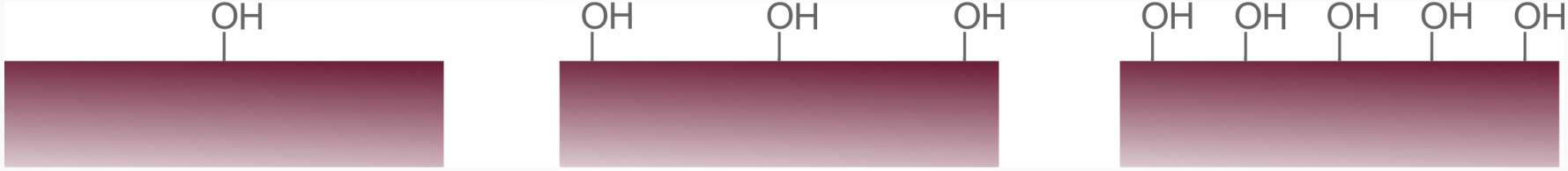
Dissociative adsorption of H_2O





Hydroxylation of Al surfaces

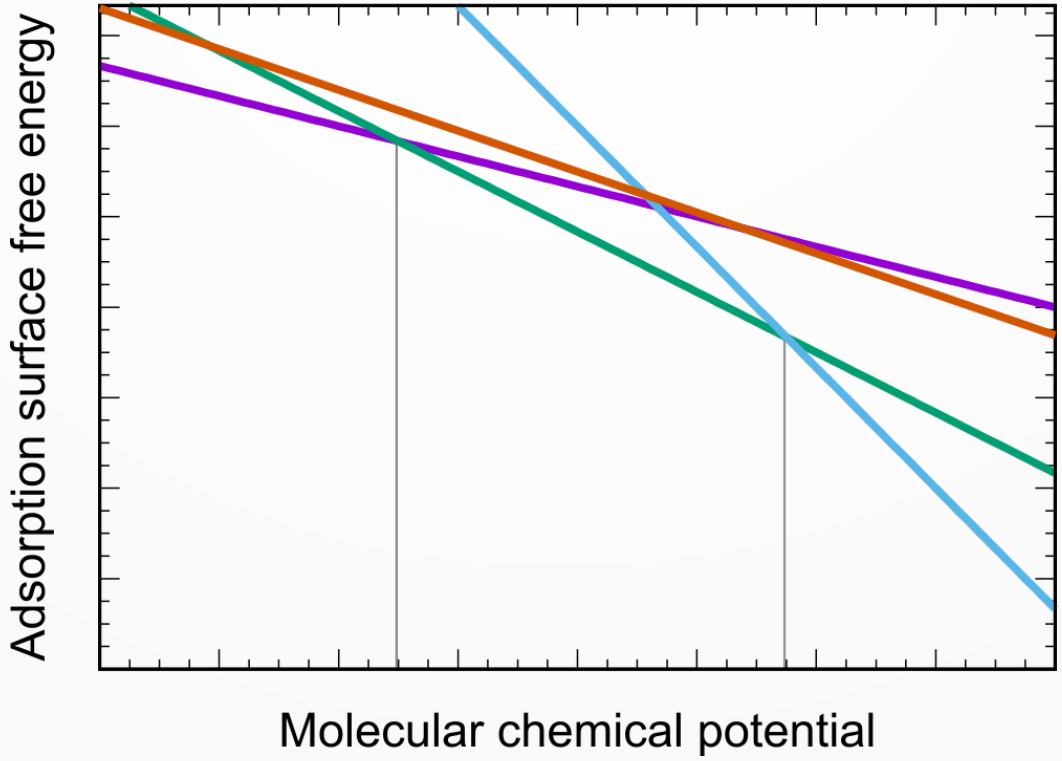
Q: What is the OH* coverage?



A: At given conditions, the structure that displays the lowest free energy is the stablest

Hydroxylation of Al surfaces

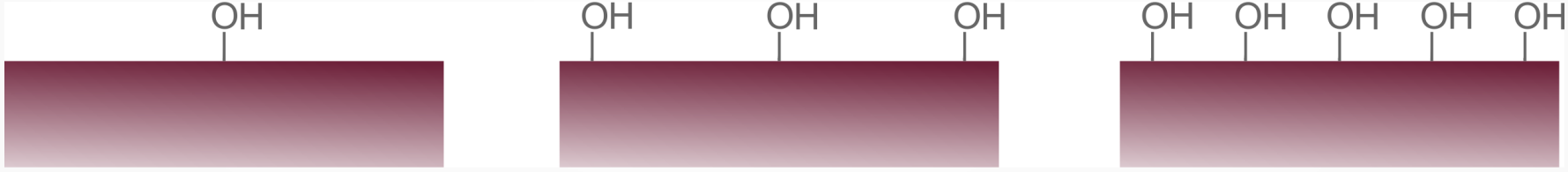
A typical answer given by a DFT practitioner:



Ab initio thermodynamics (TD)

- **Ab initio TD** (also known as “atomistic TD”) framework used in atomistic modeling

- Problem: various “coverages” display different stoichiometry → cannot be directly compared



- Solution: utilize **adsorption free energies**

Ab initio thermodynamics (TD)

standard adsorption free energy:

$$\Delta G^{\circ}_{\mathrm{ads}} = G^{\circ}_{\mathrm{ads.system}} - G^{\circ}_{\mathrm{surface}} - G^{\circ}_{\mathrm{molecule}}$$

- molecules: gas-phase (water vapor)

$$G = G_{\mathrm{translational}} + G_{\mathrm{rotational}} + G_{\mathrm{vibrational}} + \cdots$$

trivial

difficult

dependence on pressure

$$G(p,T) = G^{\circ}(1\ \mathrm{atm}, T) + RT \ln \frac{p}{1\ \mathrm{atm}}$$

Ab initio thermodynamics (TD)

standard adsorption free energy:

$$\Delta G^{\circ}_{\mathrm{ads}} = G^{\circ}_{\mathrm{ads.system}} - G^{\circ}_{\mathrm{surface}} - G^{\circ}_{\mathrm{molecule}}$$

- adsorption system: solid-phase

$$G = G_{\mathrm{vibrational}} + G_{\mathrm{configurational}} + \cdots$$

difficult

neglected

NO dependence on pressure

$$G(T) \approx G^{\circ}(T)$$

(OK for ambient or lower pressures)

Ab initio thermodynamics (TD)

adsorption free energy:

$$\Delta G_{\mathrm{ads}}(p,T) \approx G^{\circ}_{\mathrm{ads.system}}(T) - G^{\circ}_{\mathrm{surface}}(T) - G_{\mathrm{molecule}}(p,T)$$

- ideal-gas approximation: $G = N\mu \quad \leftarrow \quad \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$ (chemical potential)
- hence:

$$\Delta G_{\mathrm{ads}}(p,T) \approx G^{\circ}_{\mathrm{ads.system}}(T) - G^{\circ}_{\mathrm{surface}}(T) - N\mu_{\mathrm{molecule}}(p,T)$$

Ab initio thermodynamics (TD)

adsorption free energy:

$$\Delta G_{\mathrm{ads}}(p,T) \approx G^{\circ}_{\mathrm{ads.system}}(T) - G^{\circ}_{\mathrm{surface}}(T) - N\mu_{\mathrm{molecule}}(p,T)$$

$$\approx \Delta G^{\circ}_{\mathrm{ads}}(T) - N\left[\mu_{\mathrm{molecule}}(p,T) - \mu^{\circ}_{\mathrm{molecule}}(T)\right]$$

$$\approx \Delta G^{\circ}_{\mathrm{ads}}(T) - N\Delta\mu_{\mathrm{molecule}}(p,T)$$

- normalize to unit surface area: adsorption surface free energy

$$\gamma_{\mathrm{ads}} = \frac{\Delta G_{\mathrm{ads}}}{A} = \gamma^{\circ}_{\mathrm{ads}} - \theta\Delta\mu_{\mathrm{molecule}}$$

surface coverage, $\theta = N/A$

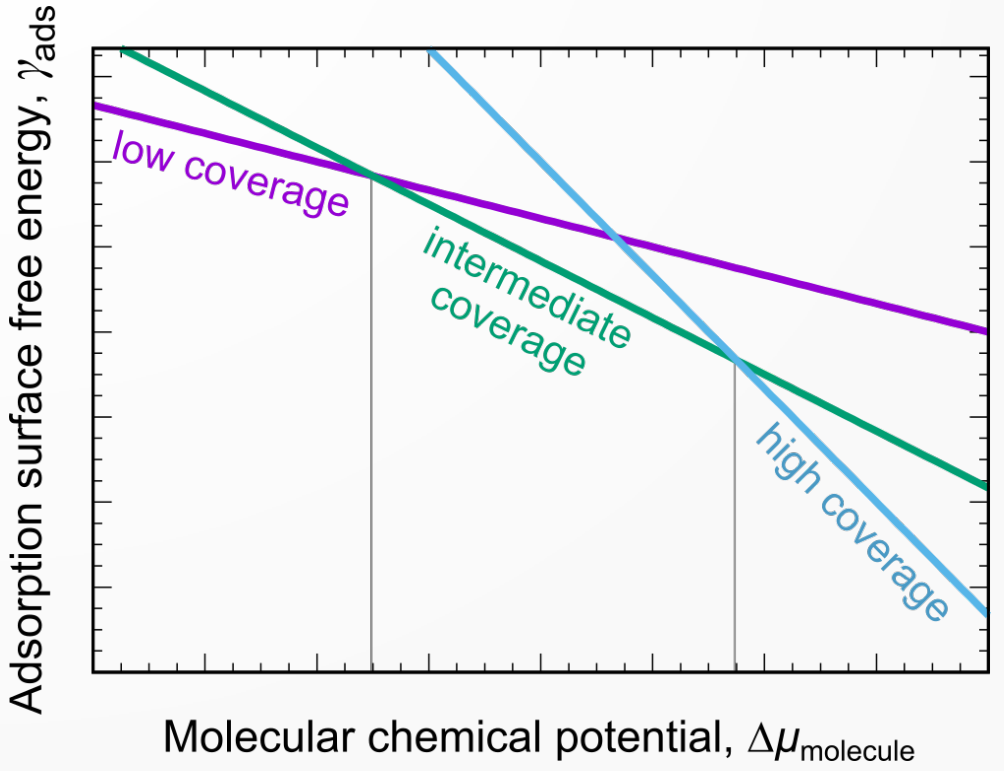
Ab initio thermodynamics (TD)

adsorption surface free energy:

$$\gamma_{\mathrm{ads}} = \gamma^{\circ}_{\mathrm{ads}} - \theta \Delta\mu_{\mathrm{molecule}}$$

specific to each adsorption structure

$$\Delta\mu_{\mathrm{molecule}}(p,T) = kT \ln \frac{p}{p^{\circ}}$$



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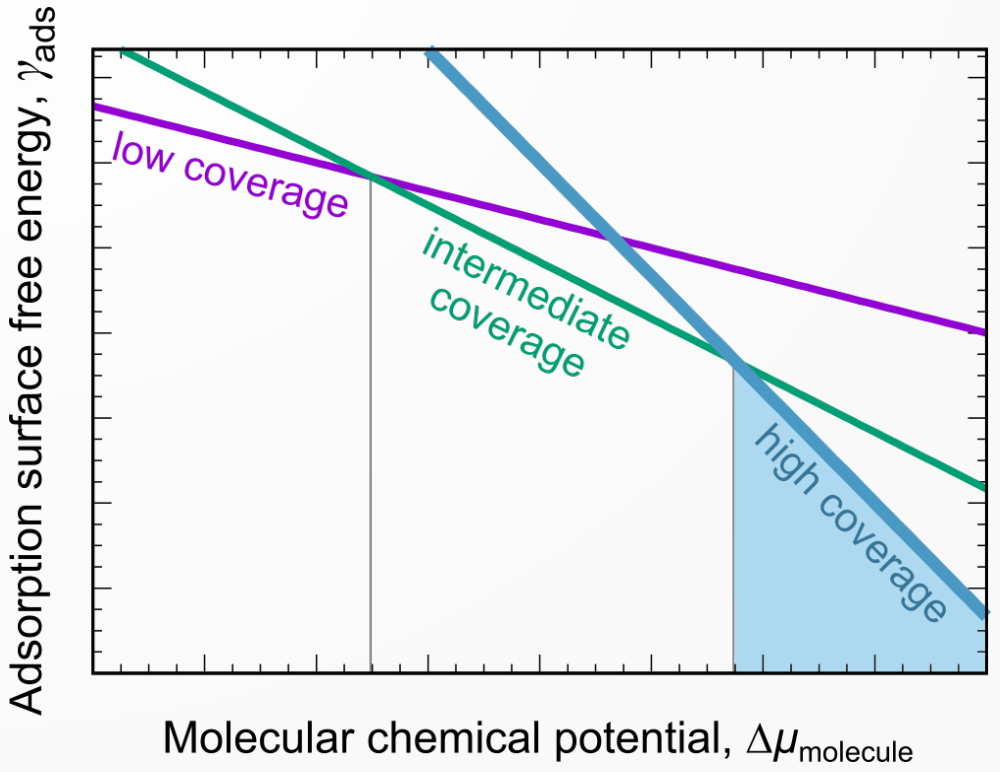

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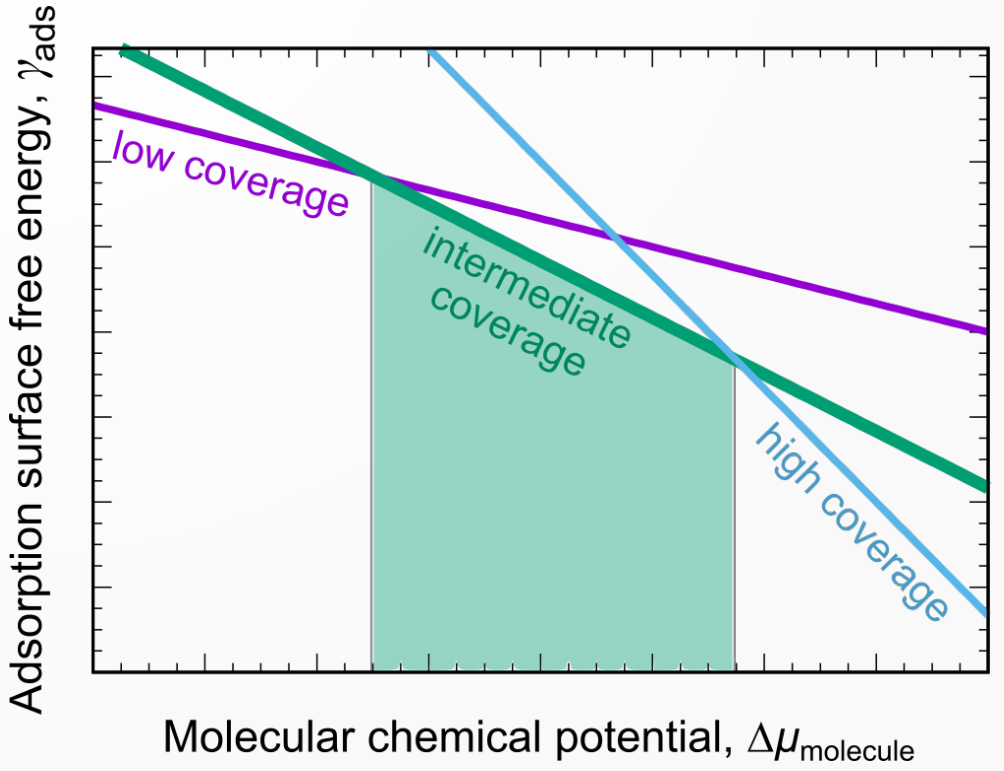

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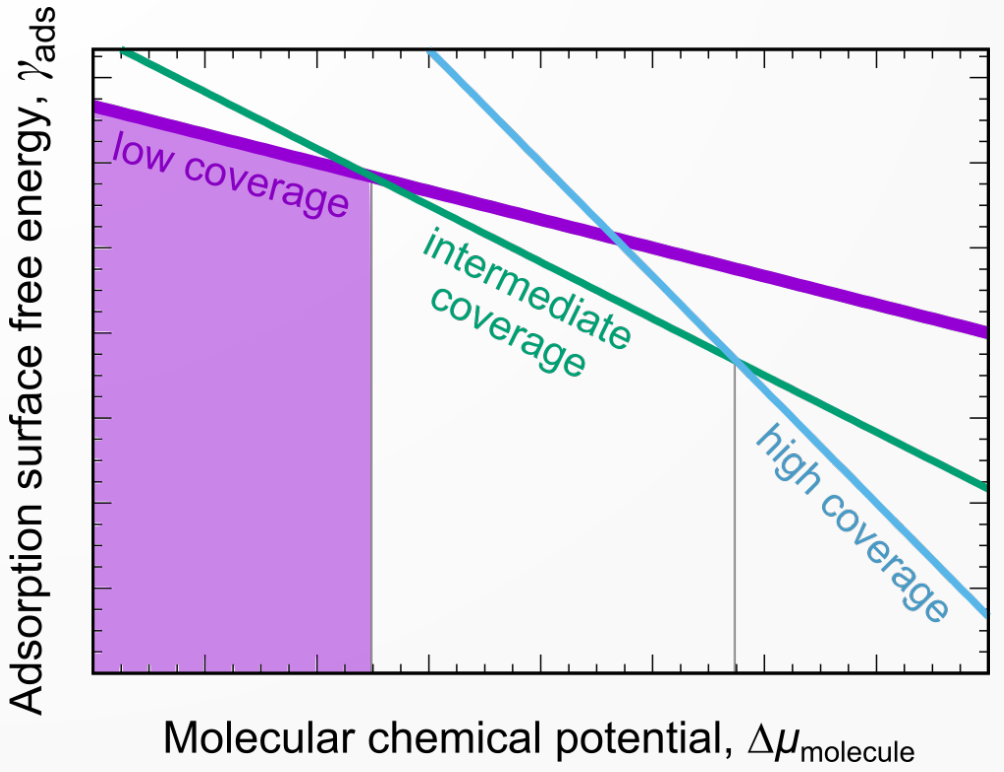

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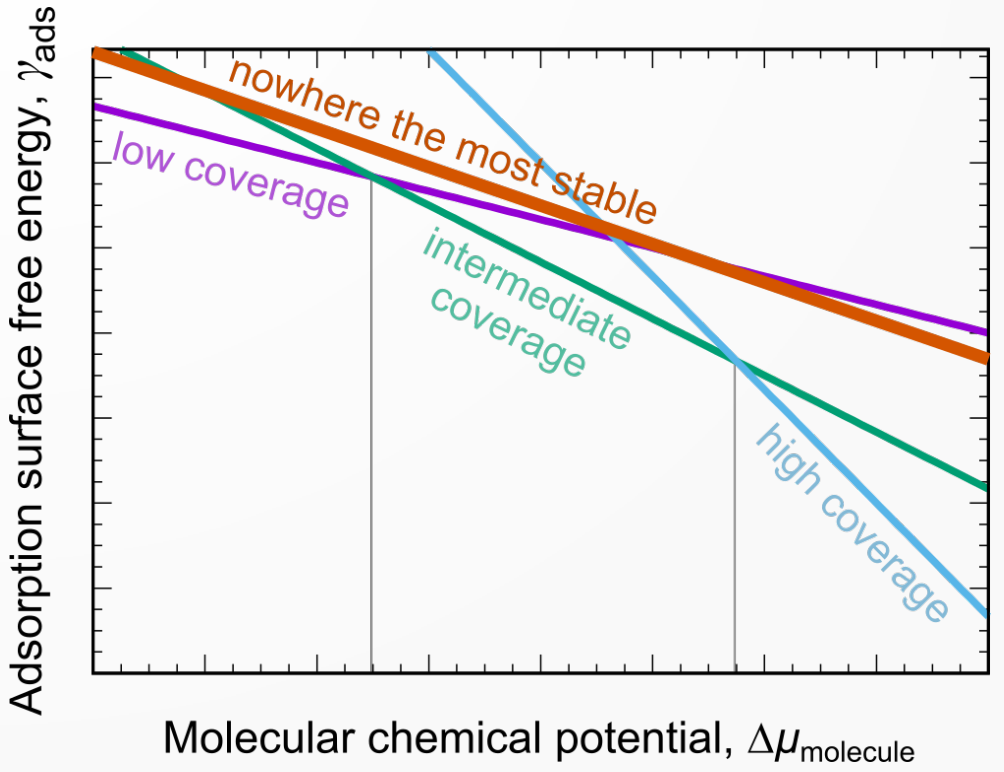
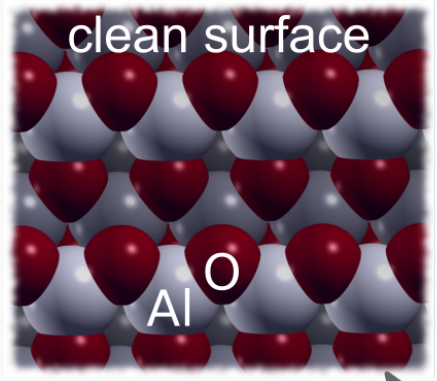
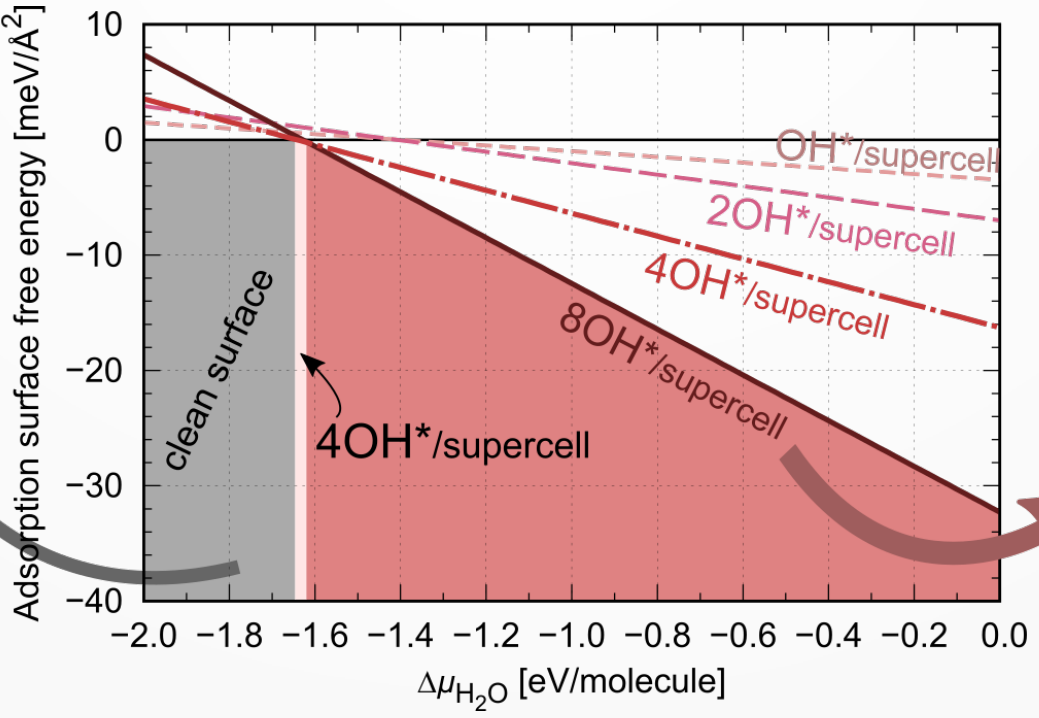


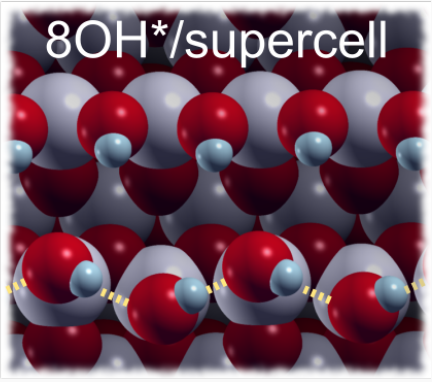
Real example

Hydroxylation of oxidized Al surface

$$\gamma_{ads} = \gamma^{\circ}_{ads} - \theta \Delta\mu_{H_2O}$$







More than one gas-phase species

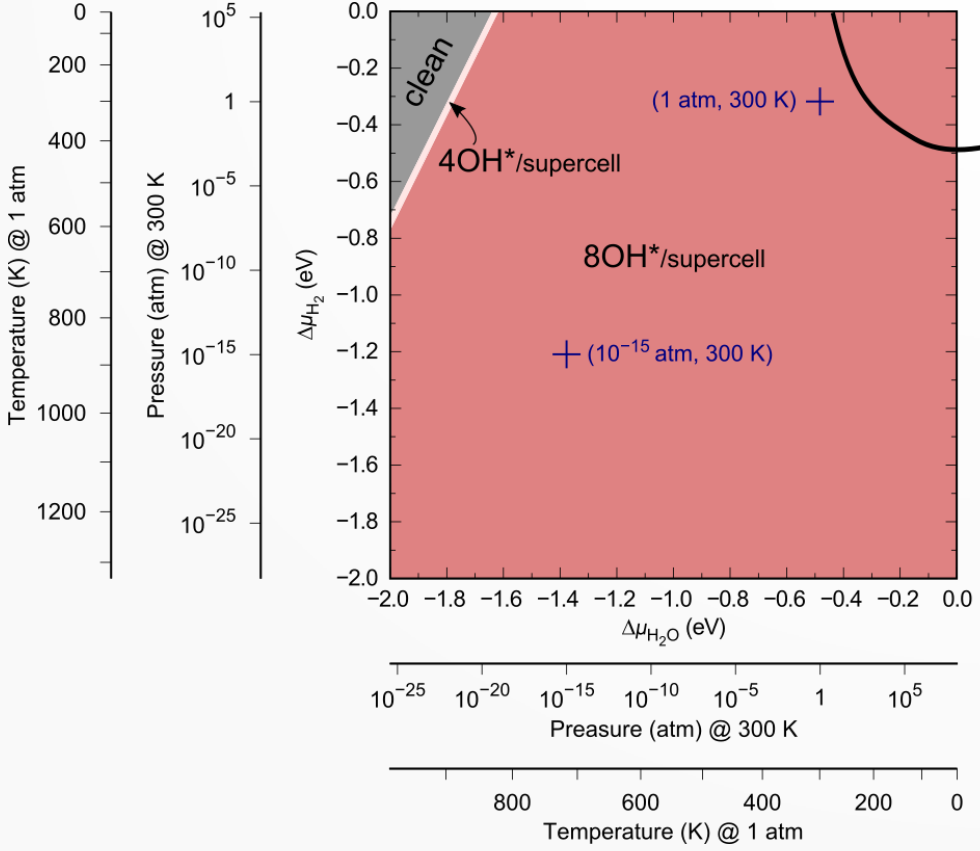
How to treat $H_2O + * \rightarrow OH^* + ½H_2$?

- gas-phase species: H_2O & H_2

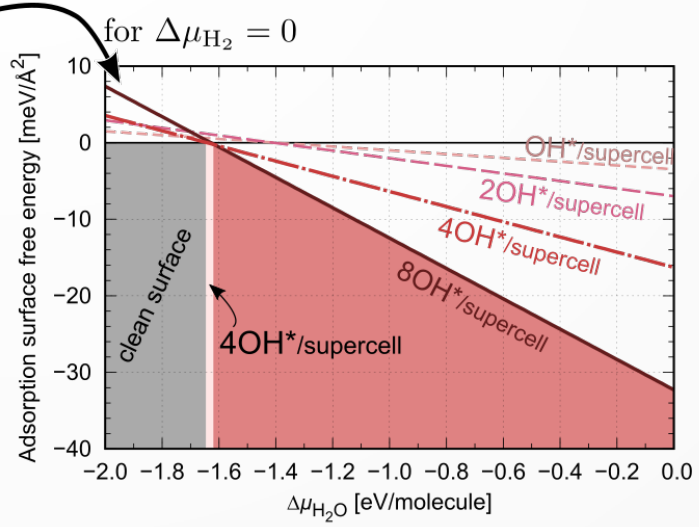
$$\gamma_{\mathrm{ads}} = \gamma^{\circ}_{\mathrm{ads}} - \theta\Delta\mu_{\mathrm{H_2O}} + \frac{1}{2}\theta\Delta\mu_{\mathrm{H_2}}$$

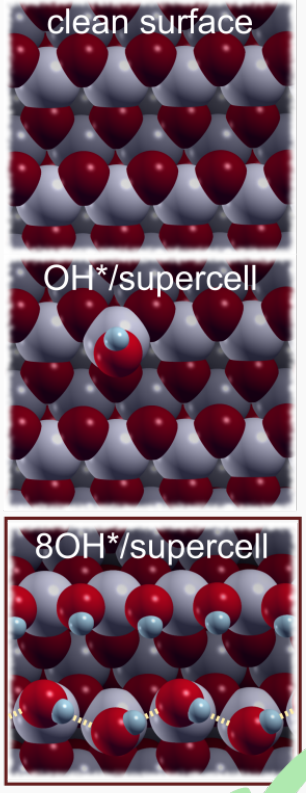
reactant product

Hydroxylation of $Al_xO/Al(111)$



$$H_2O + * \rightarrow OH* + \frac{1}{2}H_2$$





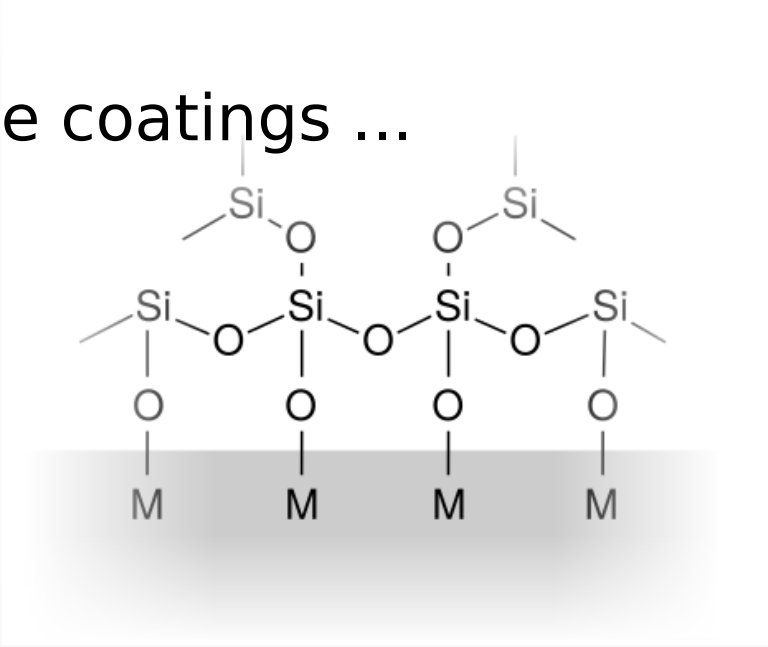
most stable surface

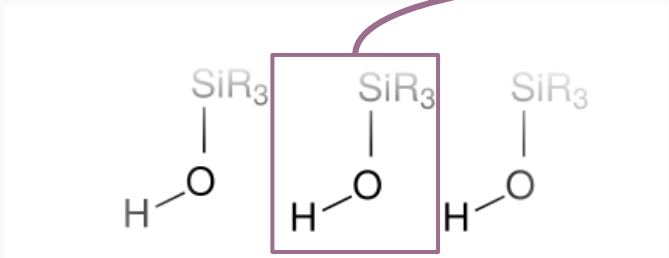
Hydroxylated oxidized Al surfaces

Premise: oxidized Al surfaces are fully hydroxylated

Applications?

... adhesion of siloxane coatings ...

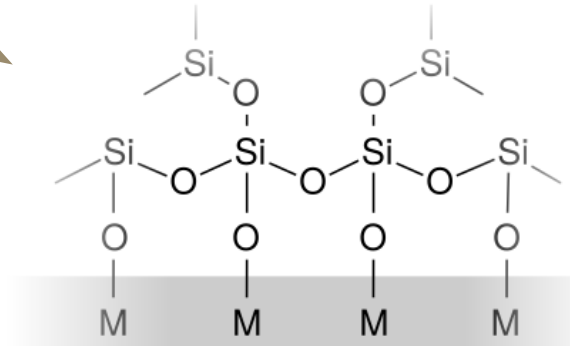




Silanol =
an alcohol where C is replace by Si

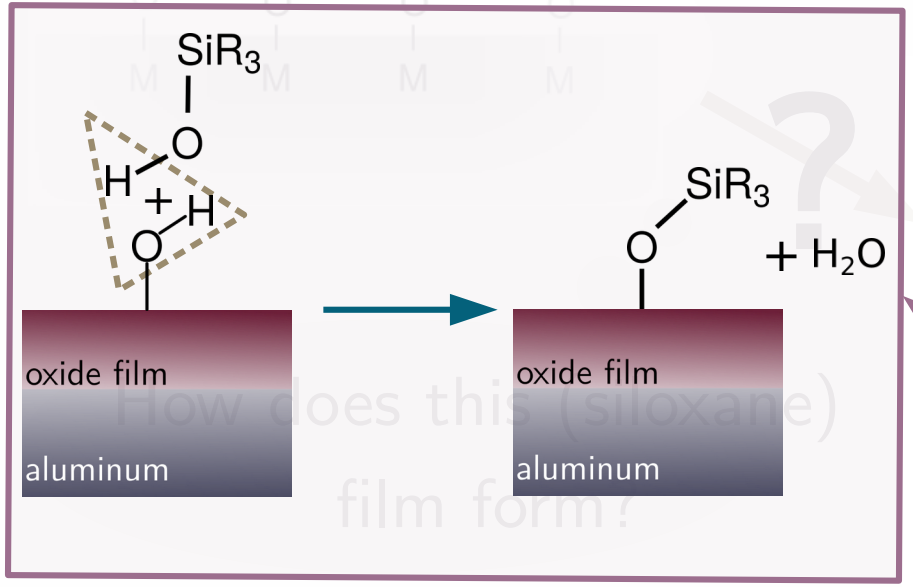
?

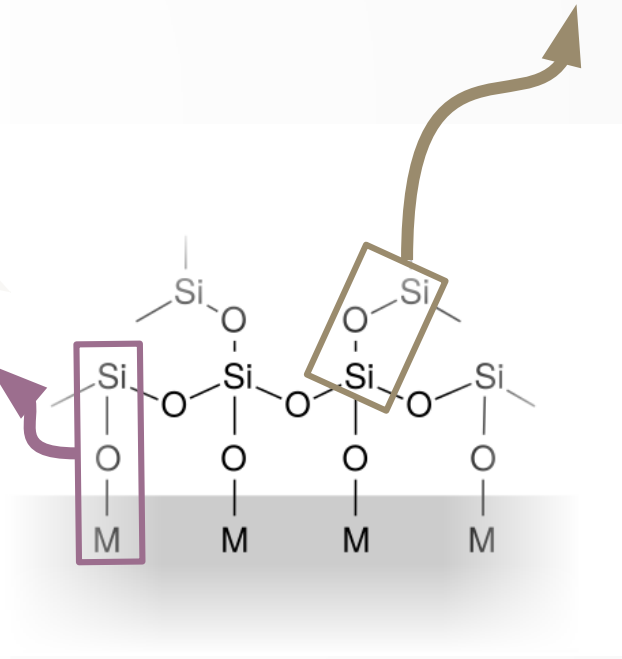
How does this (siloxane) film form?



Condensation mechanism

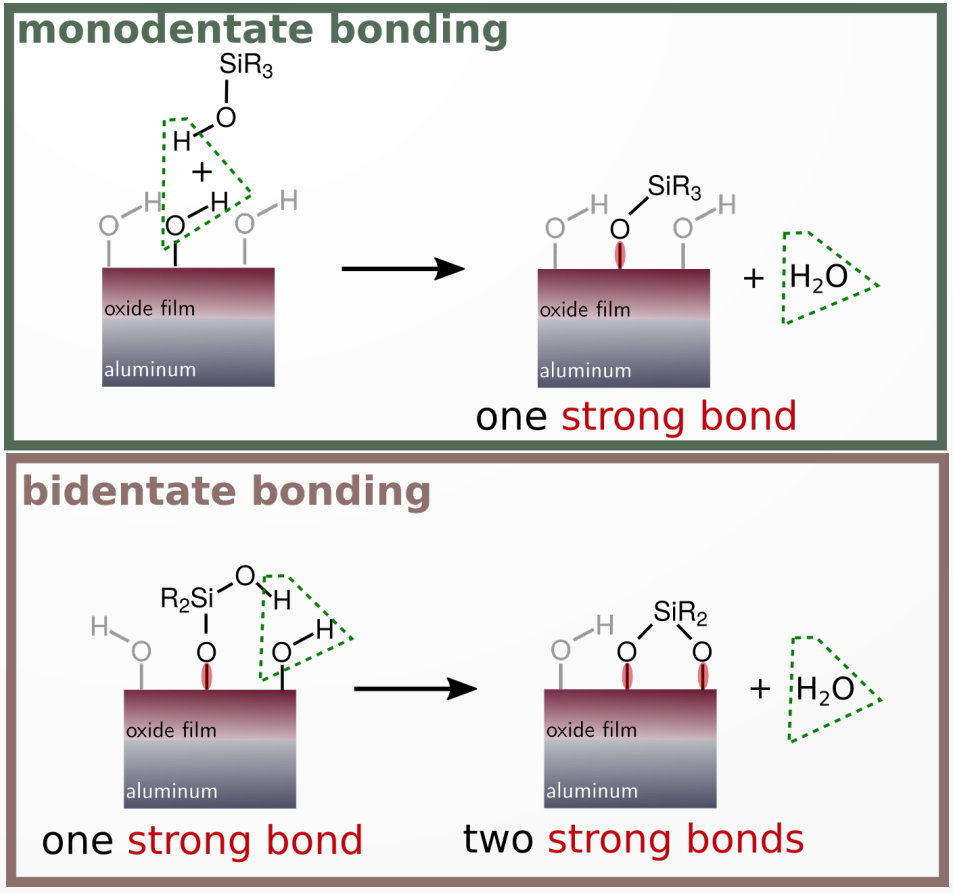
Silanols react with each other or the surface, **water** is produced





Fully hydroxylated surface

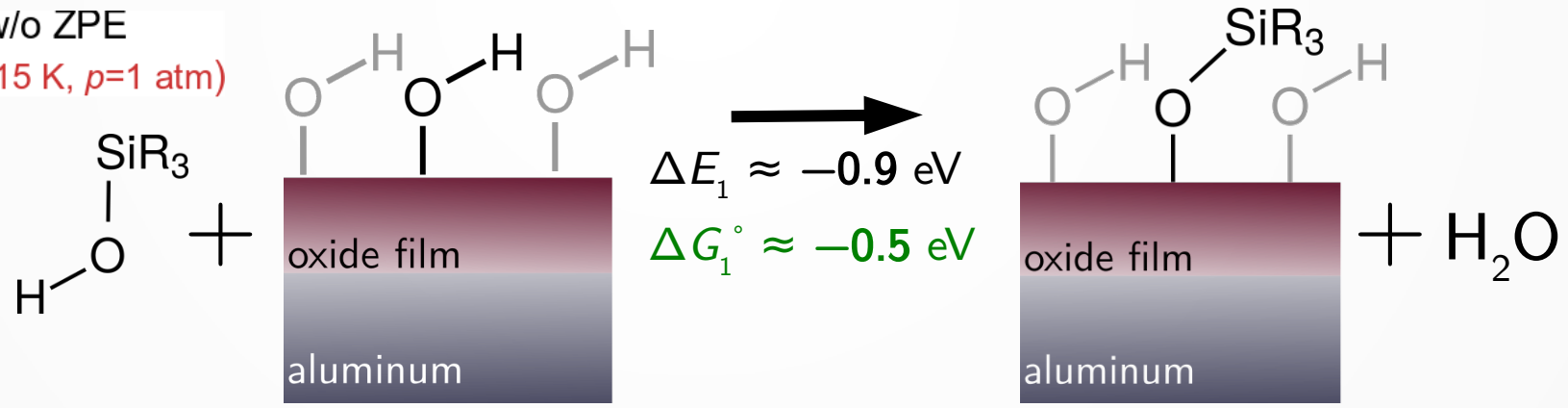
two bonding modes

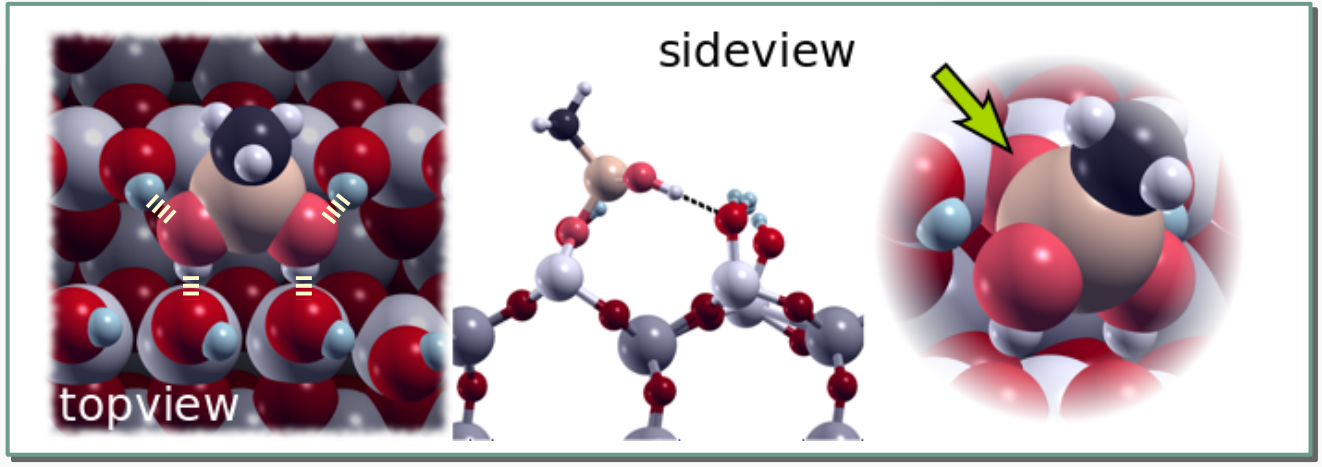


Monodentate bonding

$\Delta E \equiv \Delta E(T=0\ \text{K})$ w/o ZPE

$\Delta G \equiv \Delta G\ (T=298.15\ \text{K}, p=1\ \text{atm})$





Bidentate bonding

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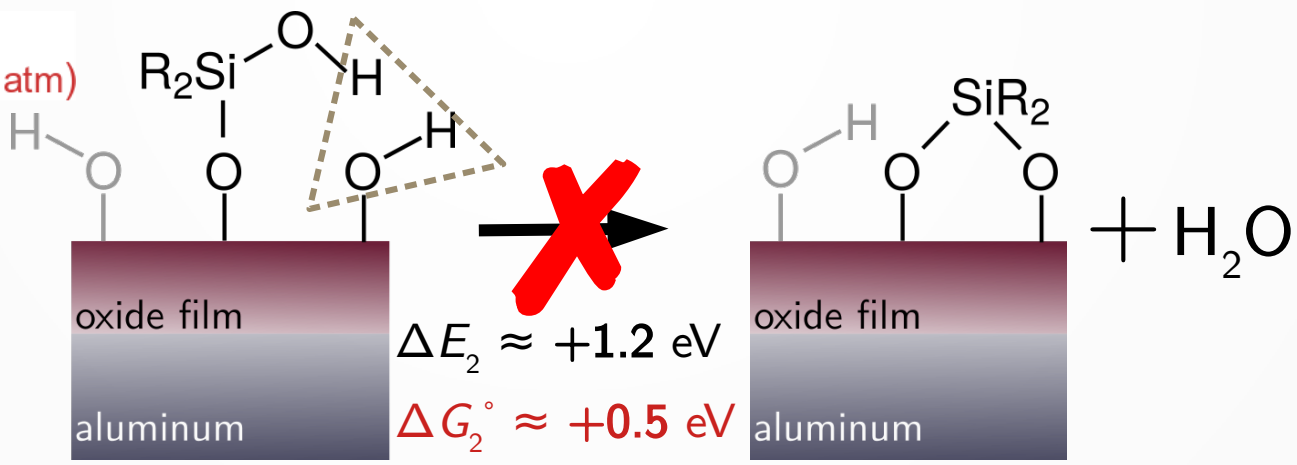

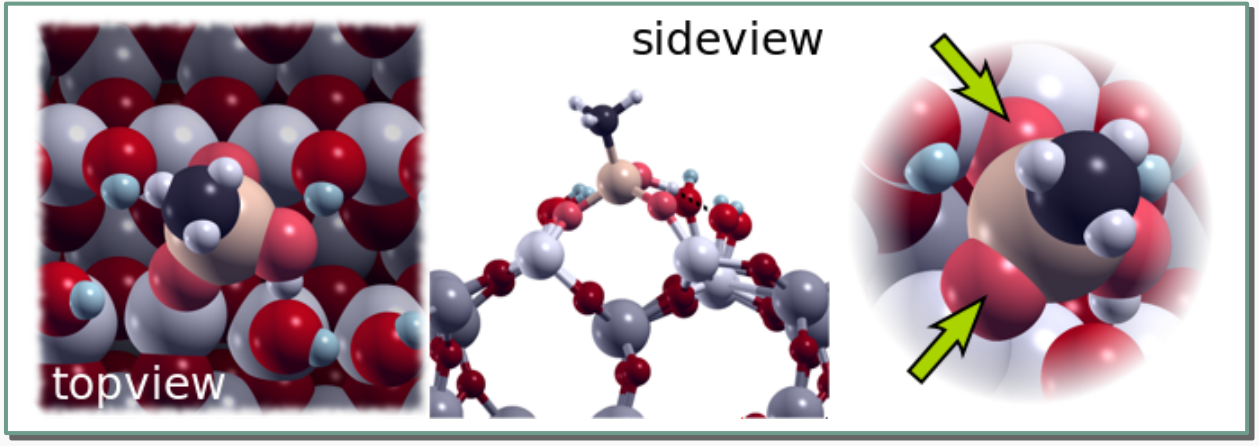

Various surface models

monodentates

vs.

bidentates

T = 298.15 K, p = 1 atm

Dimer: bidentate bonding

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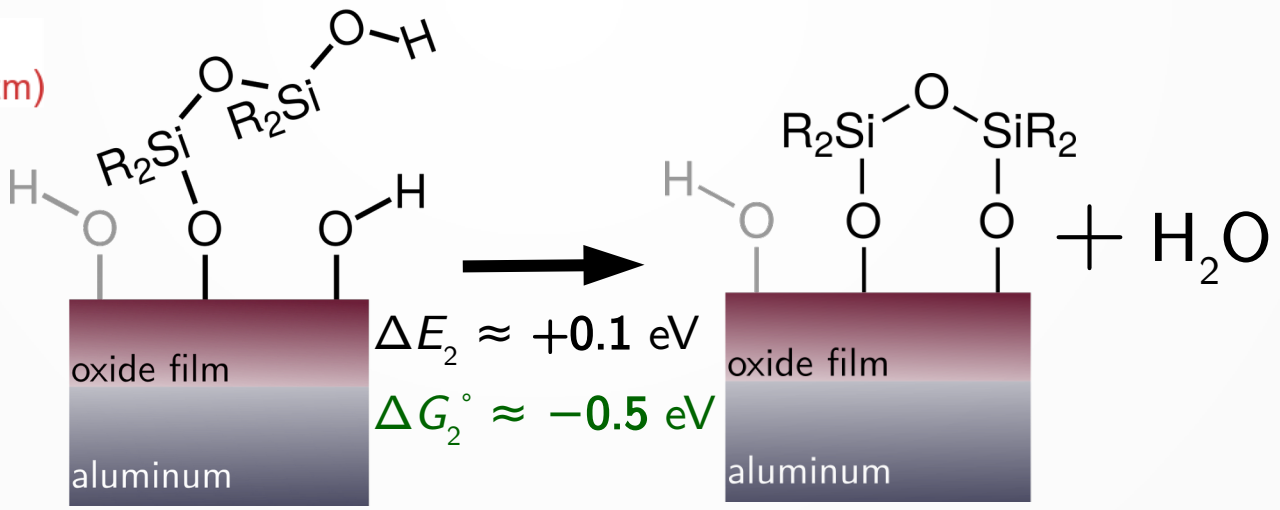

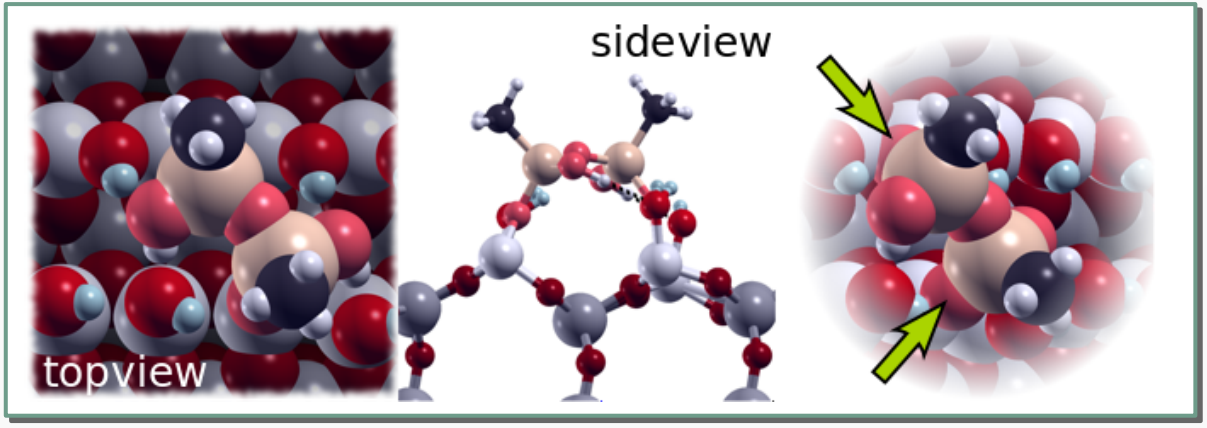

Trimer: bidentate bonding

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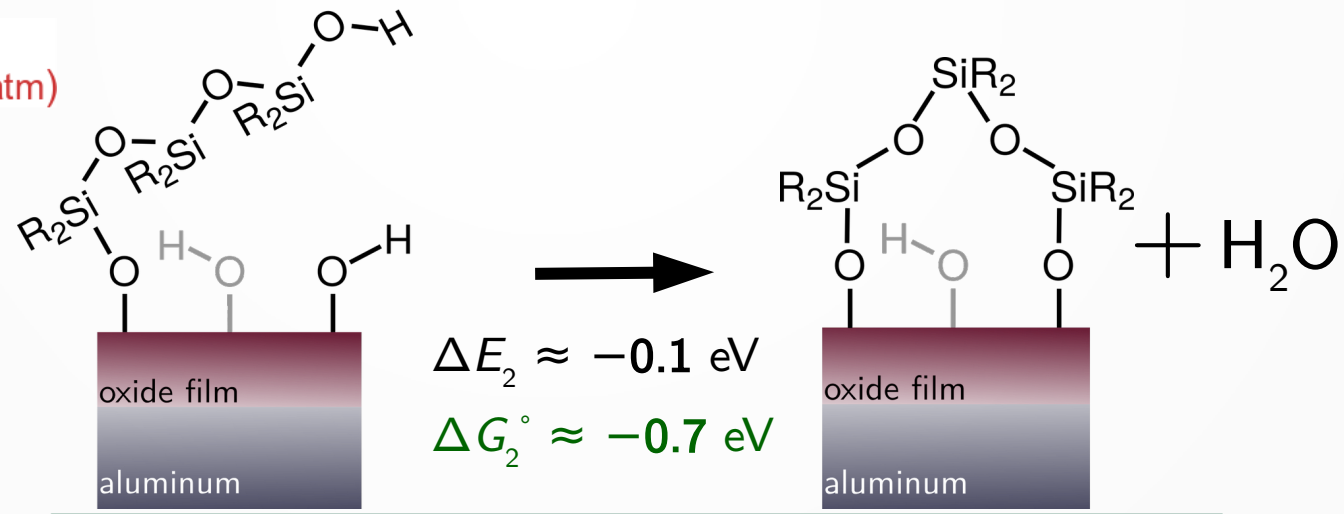
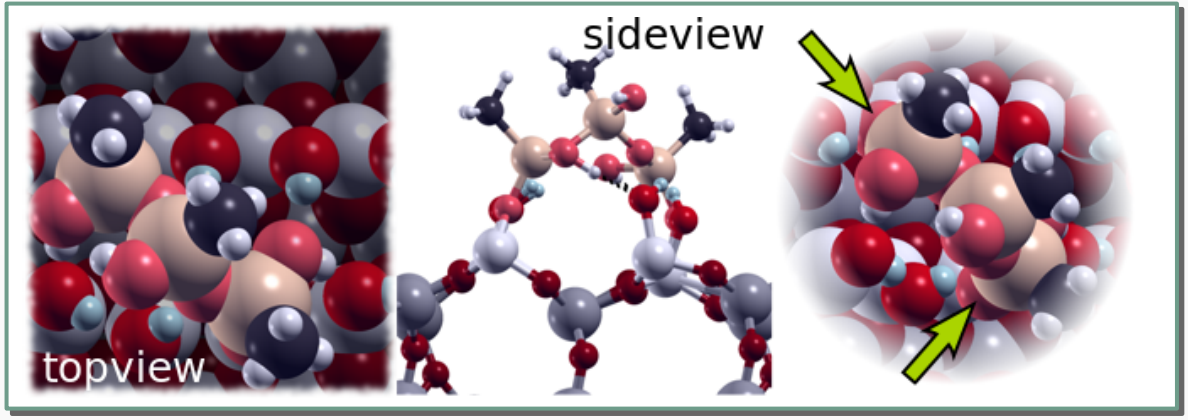
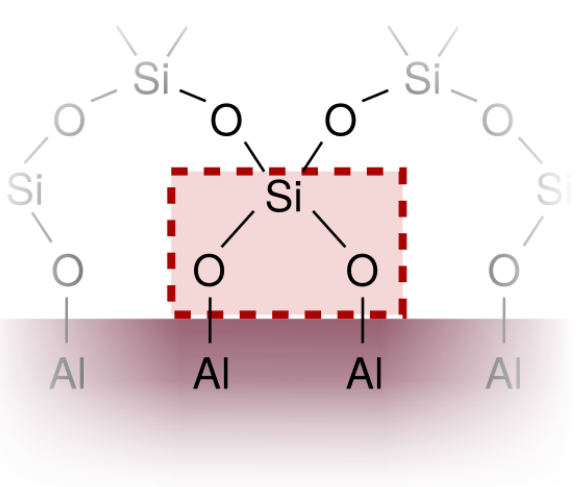




endothermic
endergonic



athermic
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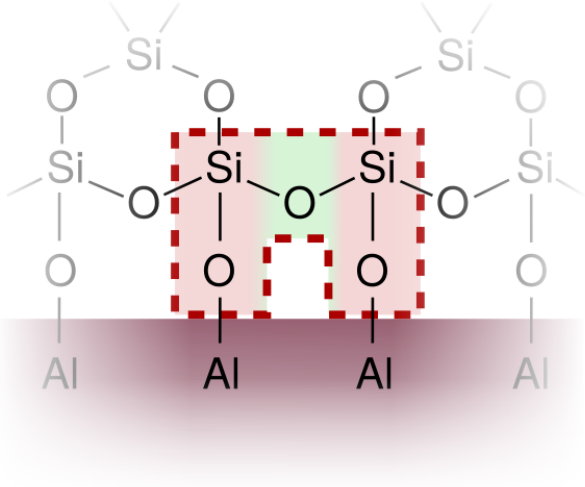

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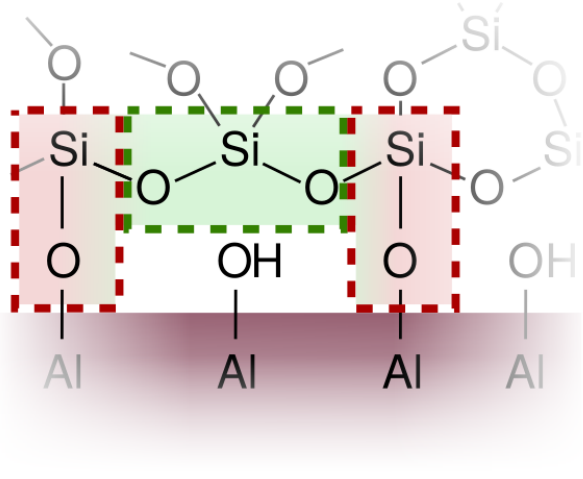

strain is reduced

Thank you for your attention!