EPFL
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SuNMiL
Supramolecular NanoMaterials and Interfaces Laboratory

Catalysis on Surfaces
Lesson 14

MSE 304

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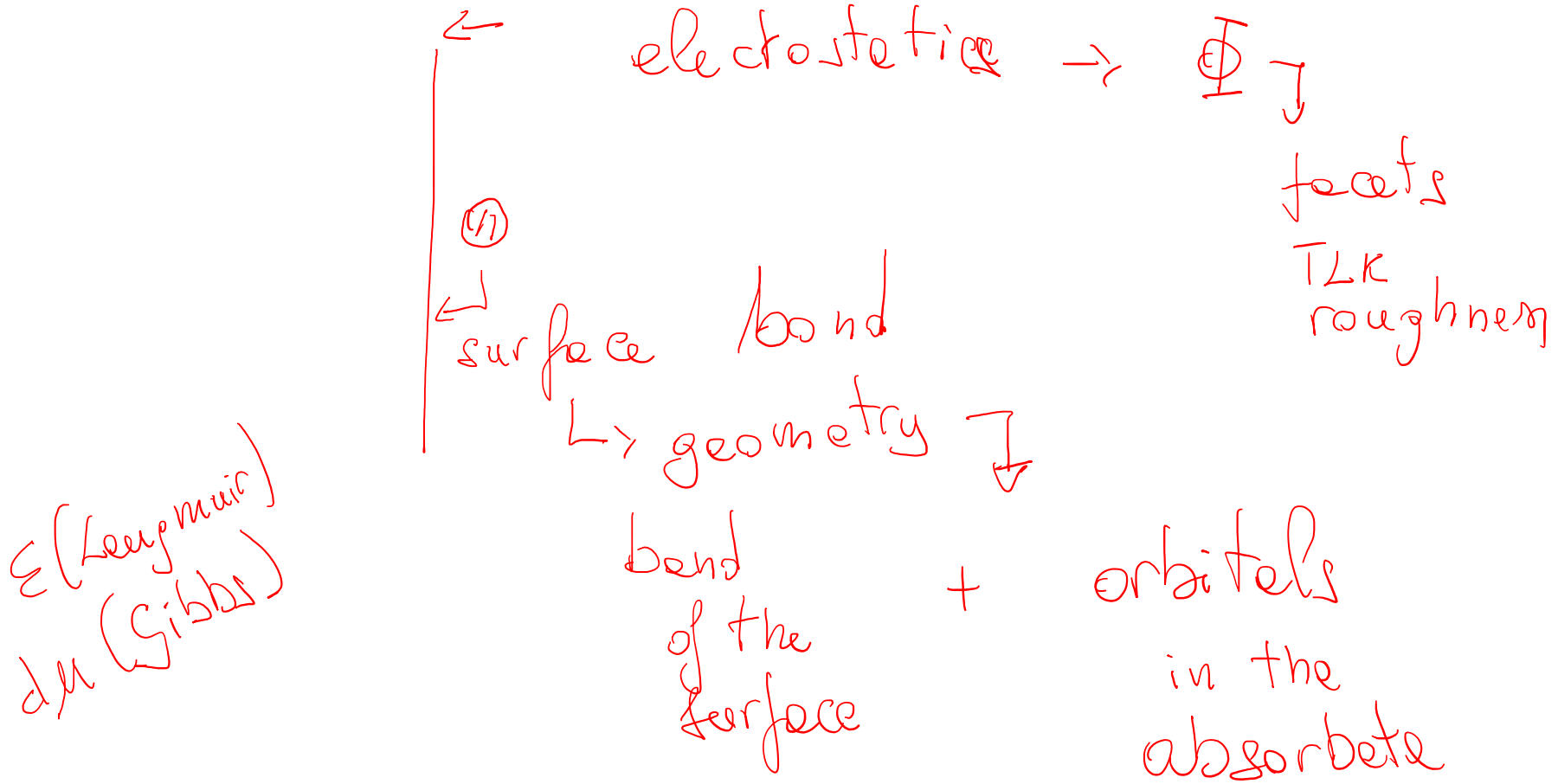
Reading for this Class

Reviews by Nørskov

Chapter 7 Semorjai's book

Key Topics from the Previous Class



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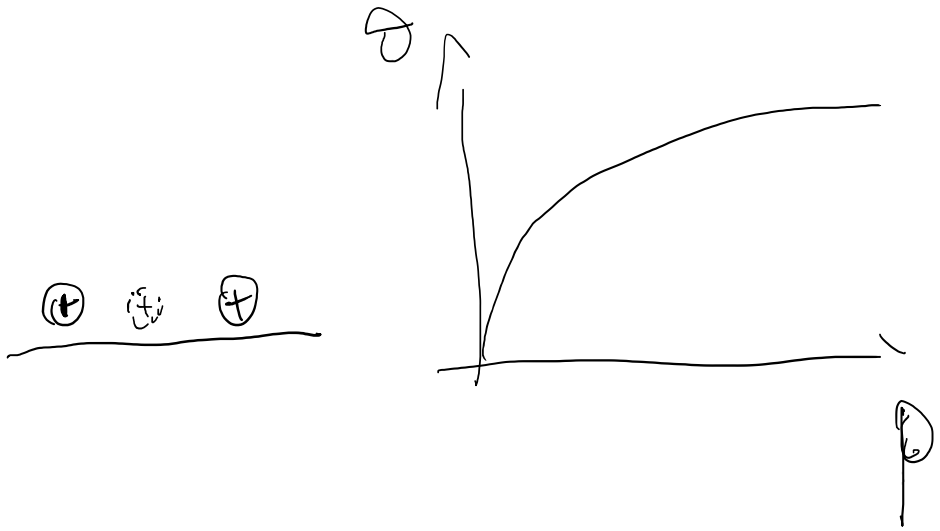
Absorption at Interfaces

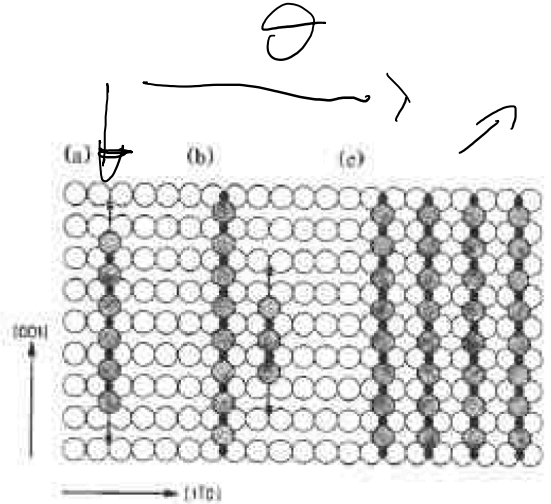


interaction between adsorbate surface depends on coverage (θ)

→ electrostatic interaction between adsorbates

→ direct adsorbates interact

Absorption at Interfaces – Effect of Surface Coverage



(2x1)-O/Cu(110)

θ → (2×1)

absorbates tend to acquire at least locally ordered structures on surfaces

→ some crystallographic conventions than surface reconstructions

Absorption at Interfaces – Surface "Softness"

induced reconstructing

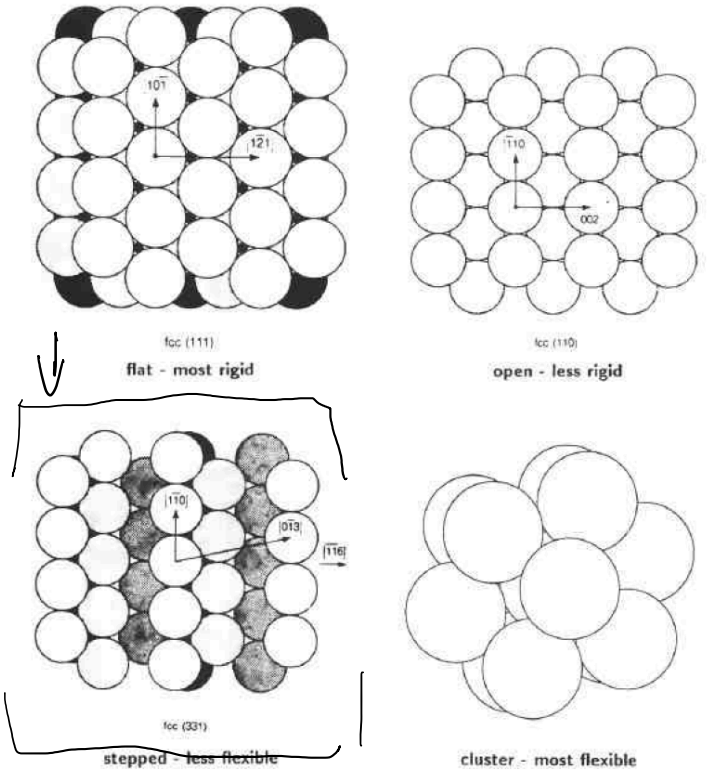
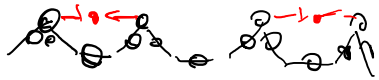
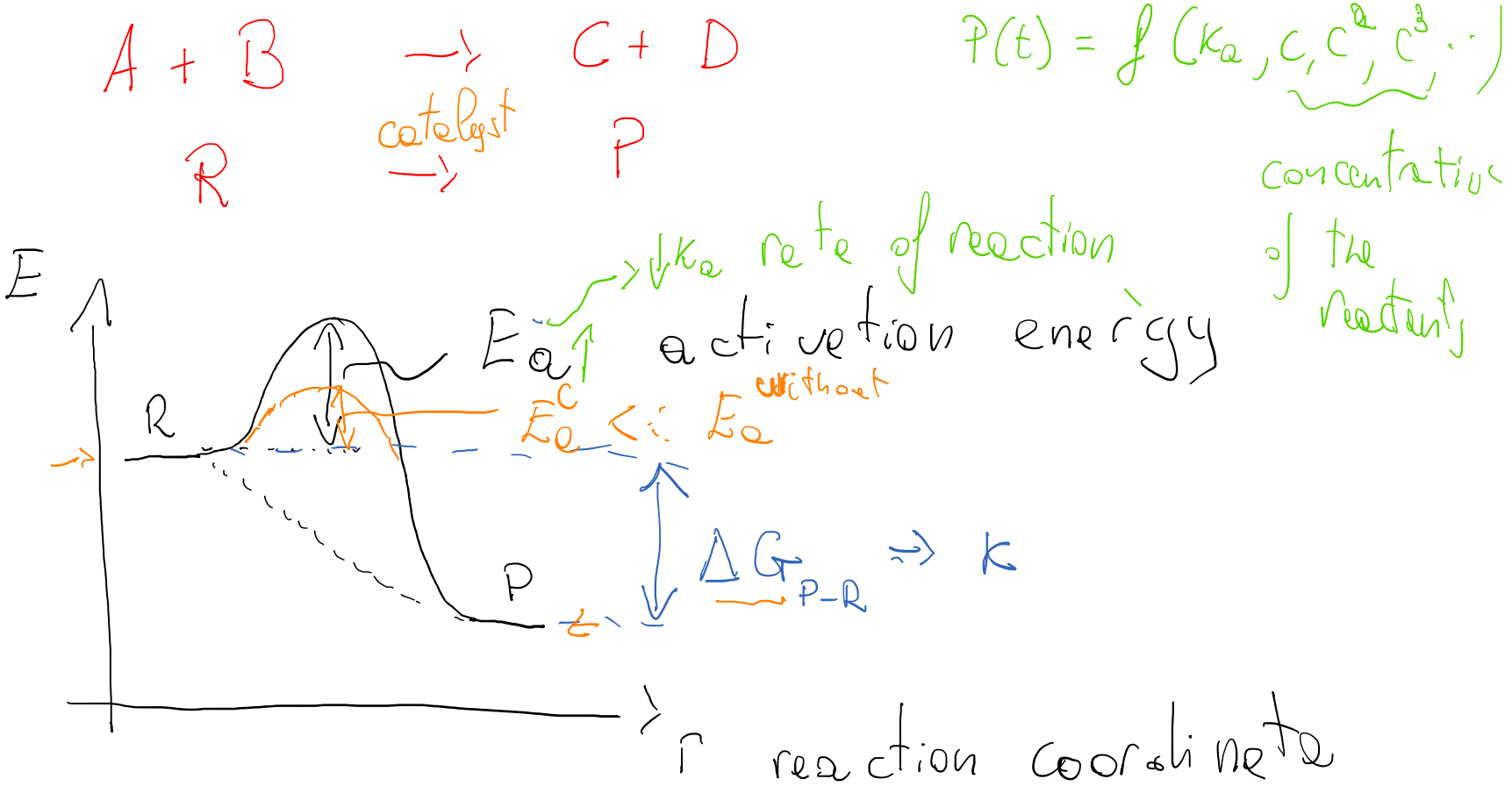


Figure 6.12. Models of surfaces divided according to their atom coordination. Atoms in the close-packed (111) surfaces of fcc metals have the highest coordination, their relaxation is small, and chemisorption-induced restructuring is most difficult. These we call *rigid surfaces*. Clusters have the lowest coordination accompanied by large relaxation and thermodynamically favorable chemisorption-induced restructuring; these are the most flexible. The more open fcc (110) surface and stepped surfaces show intermediate flexibility [29].



change the surface bond structure of the material

What is Catalysis?



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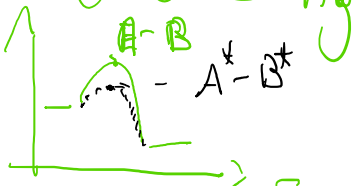
Why Surfaces can be Catalysts?

1) locally enhance the concentration of reactants

example $P(t) = K_R \cdot C_R$

$C_R^* \gg C_R^{solution}$

2) surface bond can change the energy landscape of the reaction lowering E_a



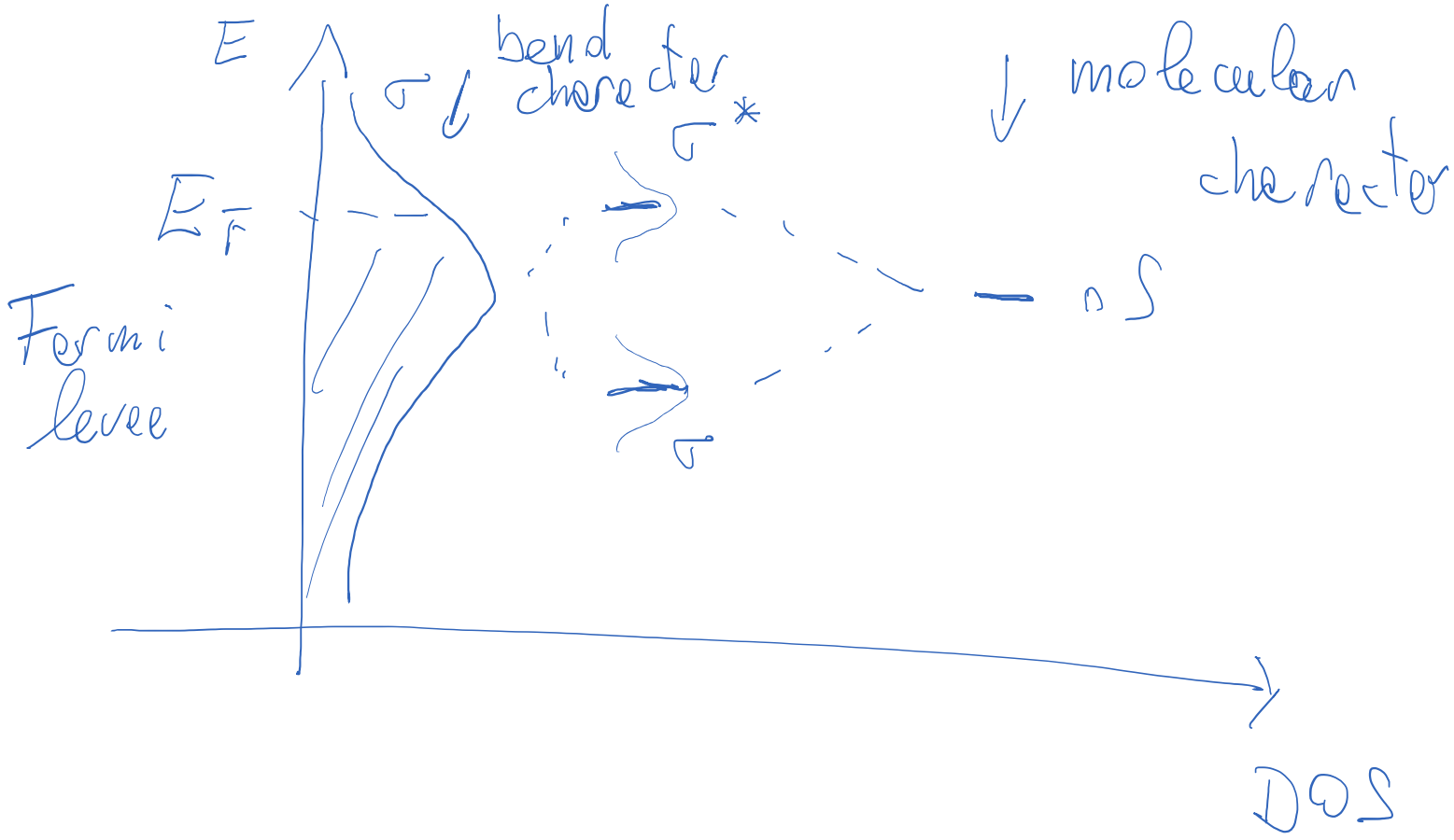
$A + B \xrightarrow{A-B} C$

$b(A^*-B^*) < b(A-B)^{solution}$

A^*-B^* adsorbed stably on the surface

3) induce one step of the reaction

The Molecular Orbital Theory



Bonding at Surfaces

s band will be very wide

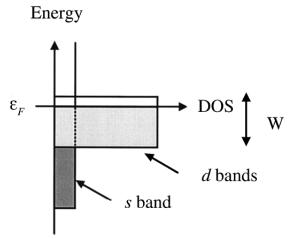


FIG. 2. Schematic illustration of the density of states of a transition metal, showing the broad *s* band and the narrow *d* bands (width *W*) around the Fermi level, ε_F.

d bands narrow

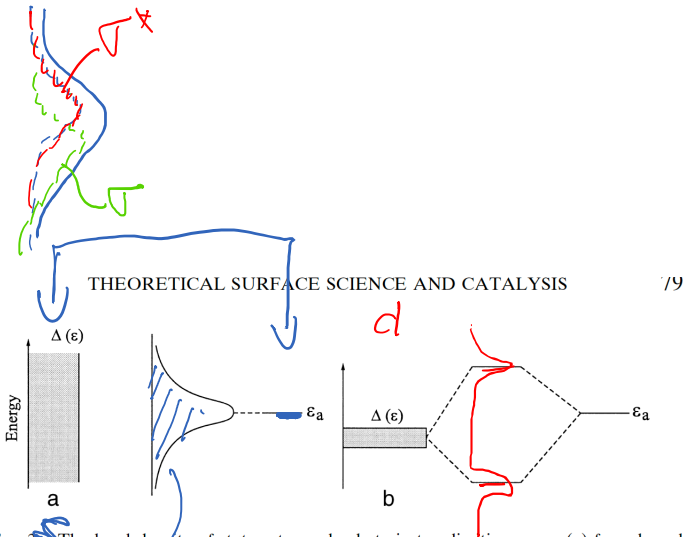


FIG. 3. The local density of states at an adsorbate in two limiting cases: (a) for a broad surface band; (b) for a narrow metal band. Case a corresponds to the interaction with a metal *s* band and case b is representative of the interaction with a transition metal *d* band.

→ broad bond character

Bonding at Surfaces – Strength of Bonding

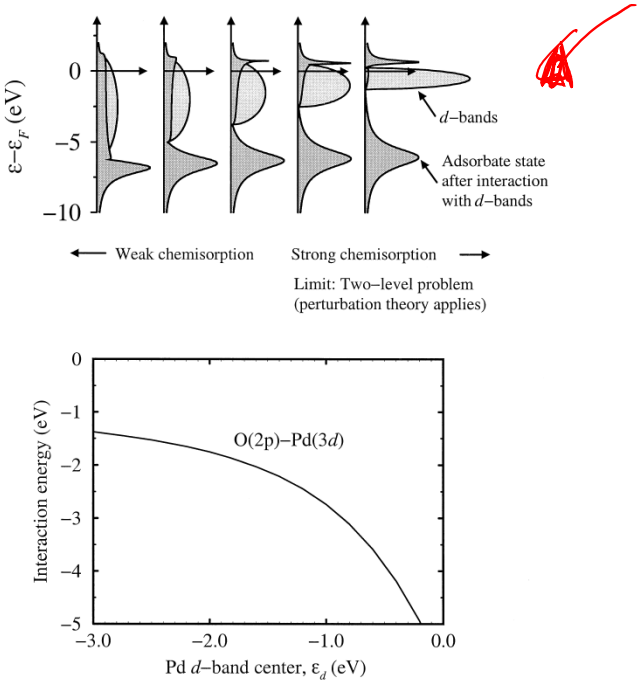
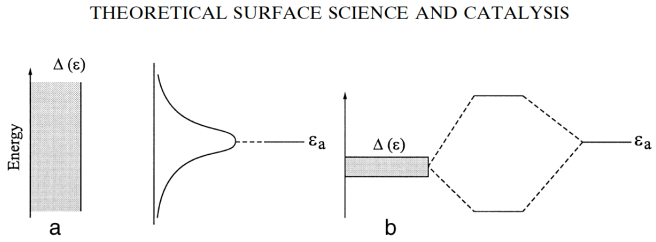


FIG. 4. The local density of states projected onto an adsorbate state interacting with the d bands at a surface. The strength of the adsorbate–surface coupling matrix element V is kept fixed as the center of the d bands ε_d is shifted up toward the Fermi energy ($\varepsilon_F = 0$) and the width W of the d bands is decreased to keep the number of electrons in the bands constant. As ε_d shifts up, the antibonding states are emptied above ε_F and the bond becomes stronger (bottom). The calculation was done by using the Newns–Anderson model (*37*). Adapted from Hammer (*38*).



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O in a p(2X2) layer on Pt(111)

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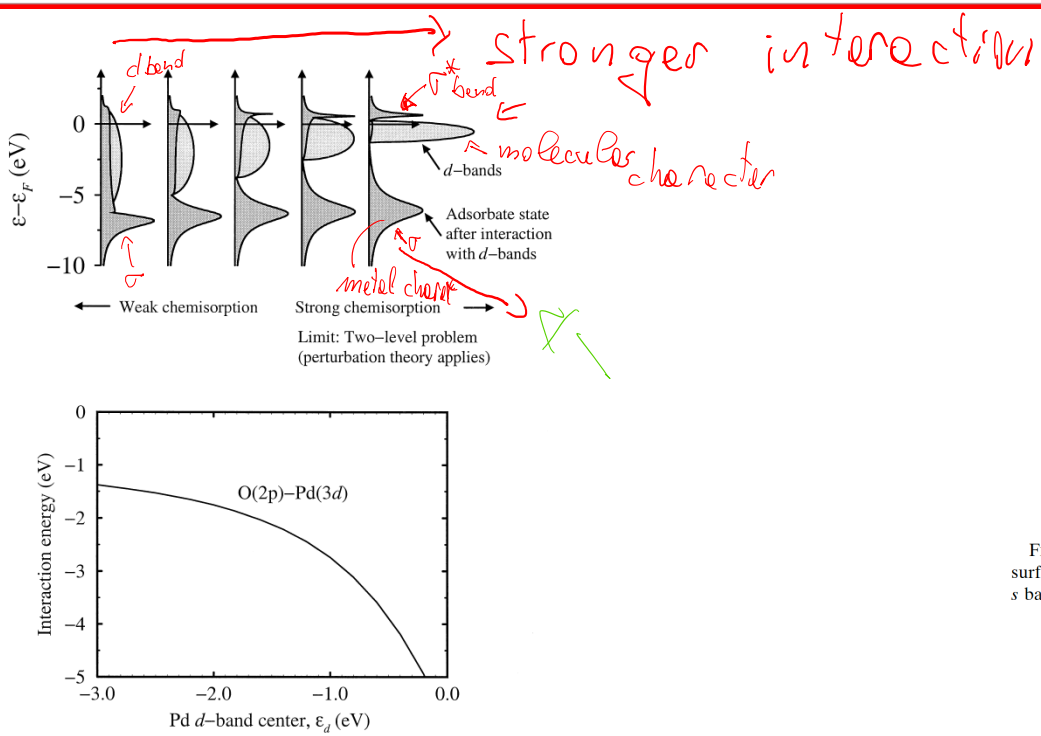
Bonding at Surfaces – Strength of Bonding



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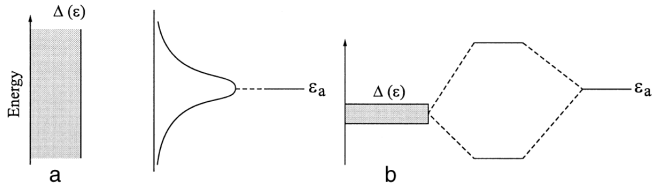

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Bonding at Surfaces – The Antibonding Molecular States

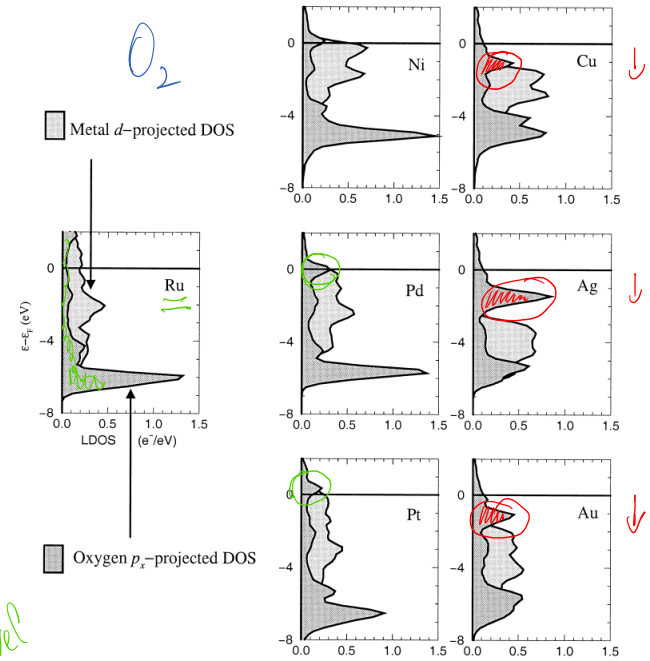

FIG. 7. Local density of states projected onto the oxygen $2p_x$ state (dark-shaded area) for atomic oxygen 1.3 Å above close-packed surfaces of late transition metals (cf. Fig. 6). The light-shaded areas give the metal *d*-projected DOS for the respective metal surfaces before the oxygen chemisorption. From Hammer and Nørskov (*40*).

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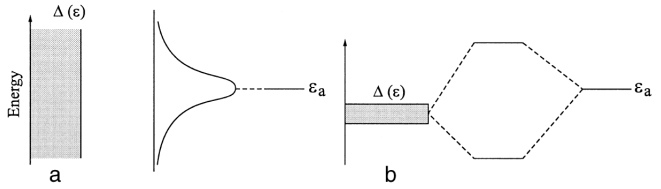

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The Chemical Bond

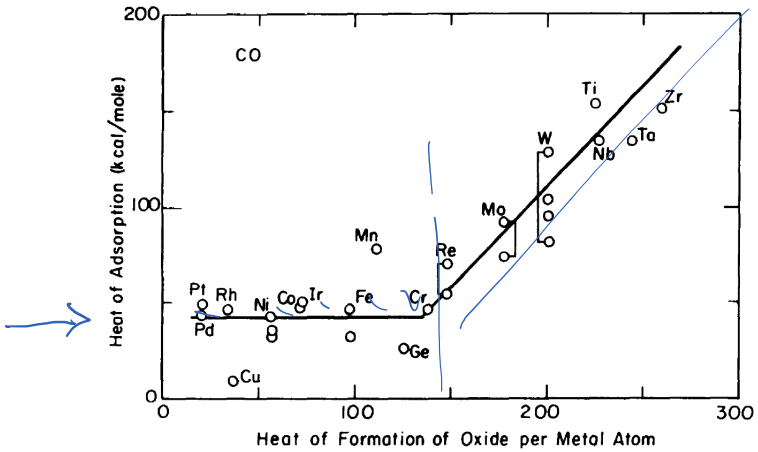

Figure 6.3. Heats of adsorption of CO on various transition metals as a function of the heats of formation of the corresponding oxides (per metal atom) [2].

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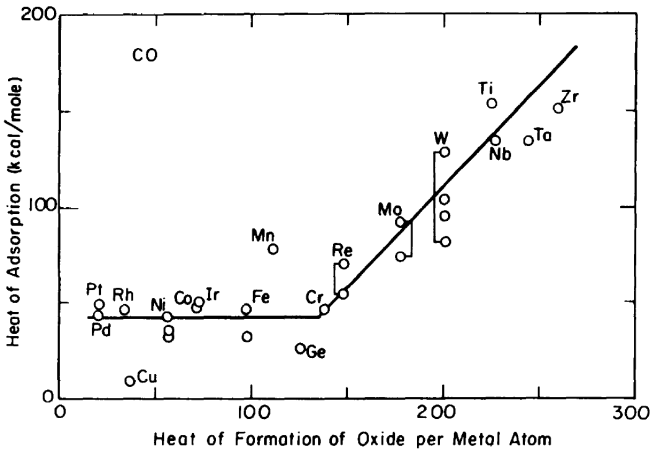

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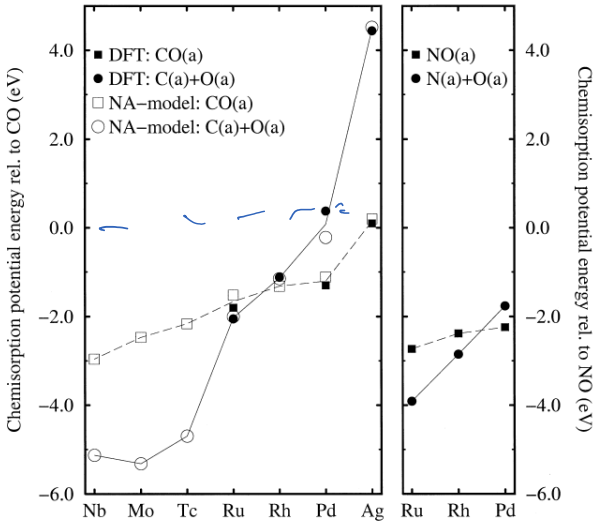

FIG. 13. (Left) Calculated (PW91) and model estimates of the variation in the adsorption energy of molecular CO compared to atomically adsorbed C and O for the most close-packed surface of the 4d transition metals. (Right) Calculated (PW91) molecular and dissociative chemisorption of NO. Solid symbols are DFT calculations; open symbols are Newns–Anderson model calculations. For CO, dissociative chemisorption appears to the left of rhodium. For NO, dissociative chemisorption appears farther to the right, i.e., also on rhodium.

Dissociative Absorption at Surfaces

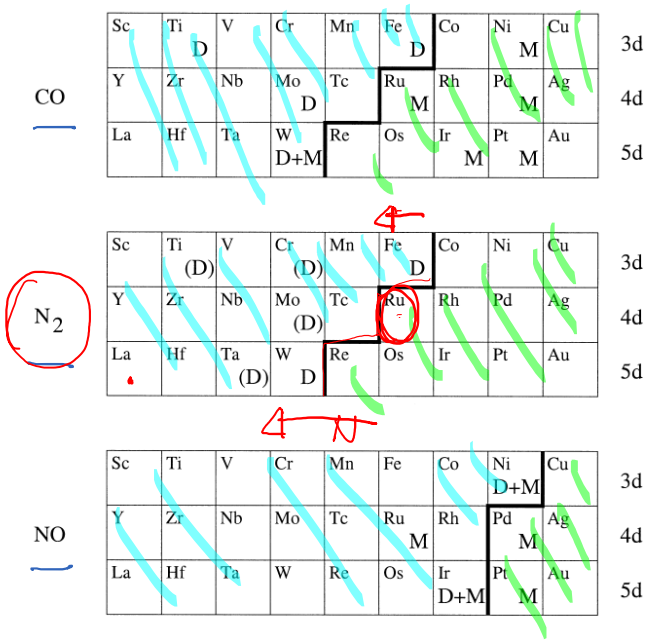

FIG. 14. Compilation of experimental data for the ability of transition metals to adsorb and dissociate CO, N_2, and NO molecules. M, molecular adsorption; D, dissociative adsorption. Adapted from Broden *et al.* (57).

- dissociated molecule
- molecule as such

antibonding orbital of the surface bond relative to the surface Fermi level

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Catalysis at Surfaces

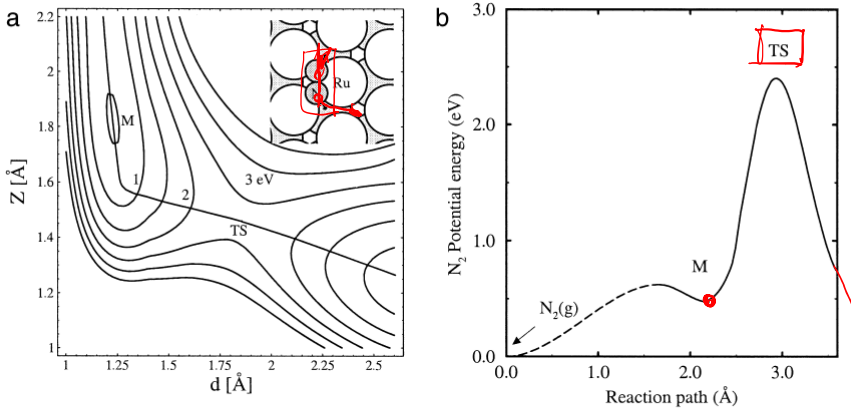


FIG. 19. (a) The potential energy surface (RPBE) for N_2 dissociating on a Ru(0001) surface. The energy zero is a molecule far from the surface. The adsorption geometry is shown in the inset. The distance of the center of mass of the molecule above the surface, Z, and the N–N bond length, d, are varied. The minimum energy path is indicated, and in (b) the energy along the path is shown. Note that here only two degrees of freedom have been included. When the rest are included, the minimum energy path has a lower energy barrier (Fig. 34). Adapted from Murphy *et al.* (*71*).

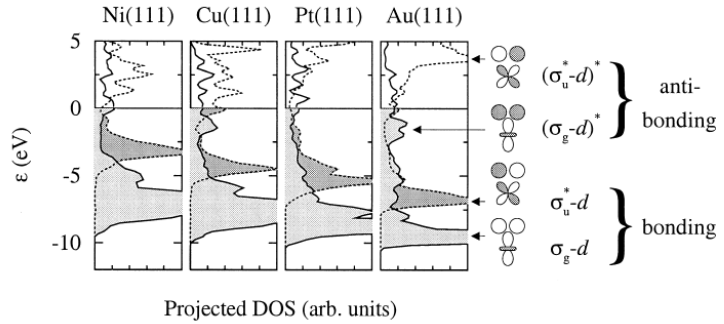
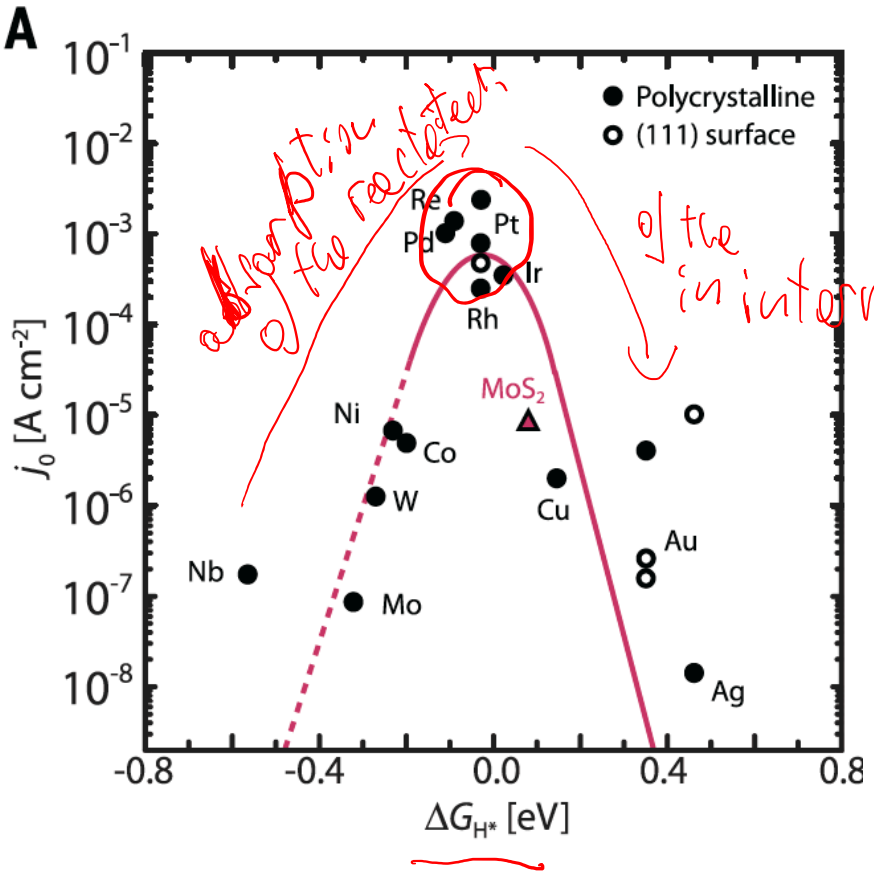


FIG. 21. The DOS projected onto σ_g and σ_u^* for H_2 in the dissociation transition state on Cu(111), Ni(111), and Au(111), and Pt(111) surfaces. From Hammer and Nørskov (*40*).

The Sabatier Principle

Volcano Plot



adsorption of the reactants

of the intermediate product

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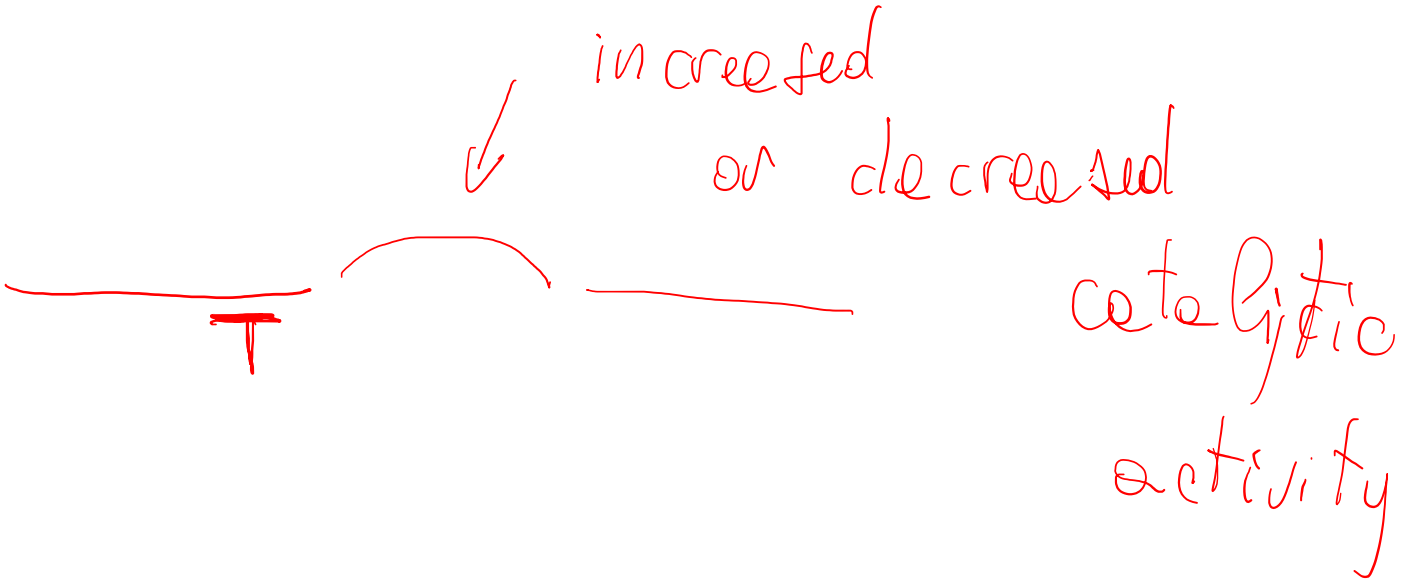
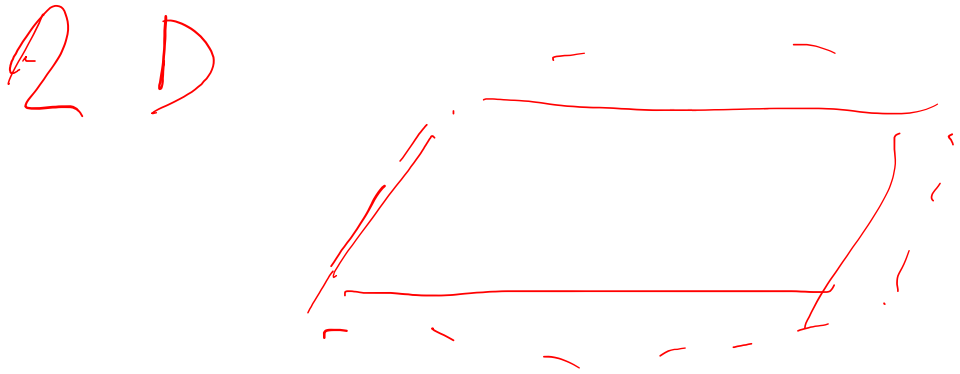
Real Surfaces: Strain

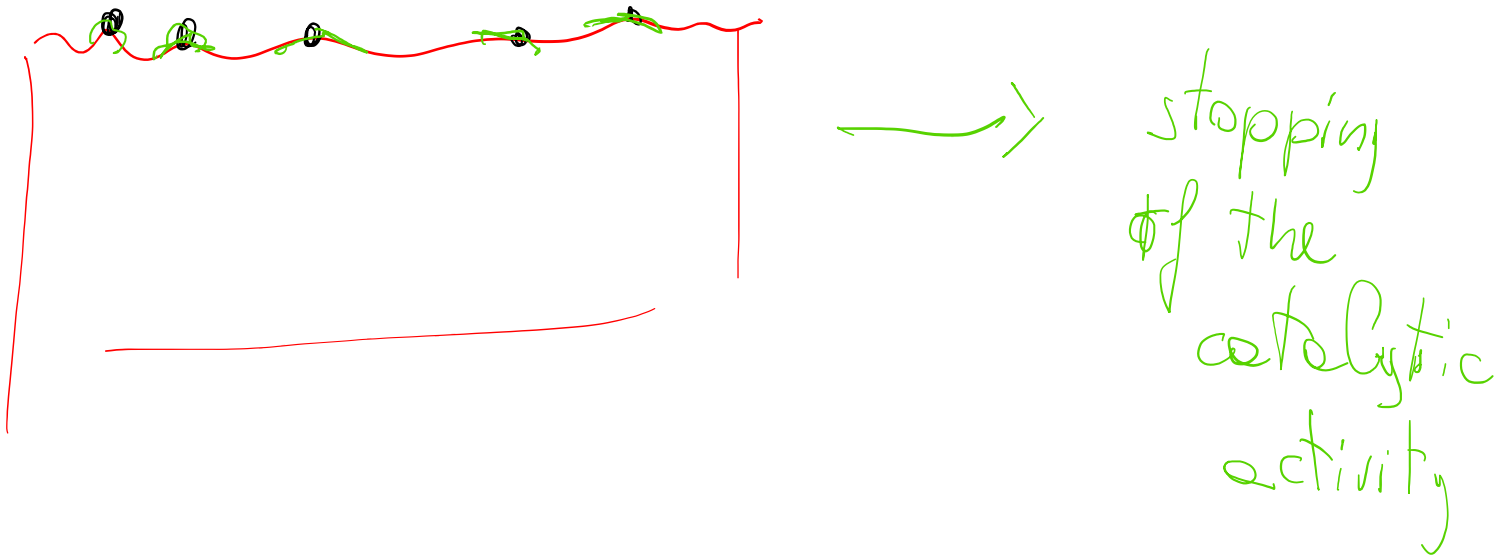


Real Surfaces: TLK

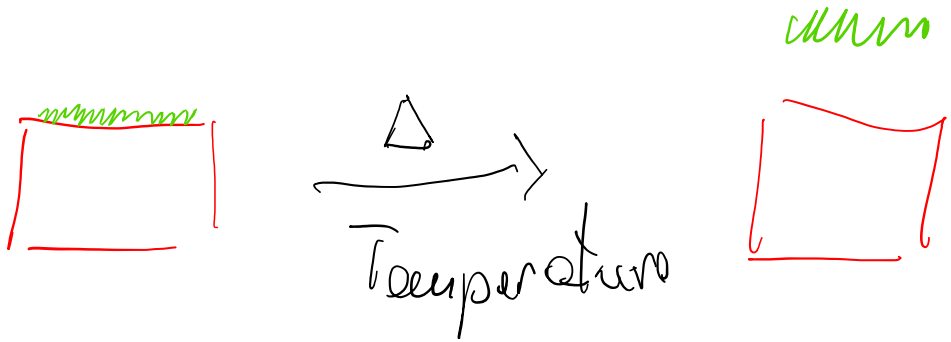
Real Surfaces: Edges



Catalyst Poisoning



Catalyst Regeneration



Real Surfaces: Frontier Research

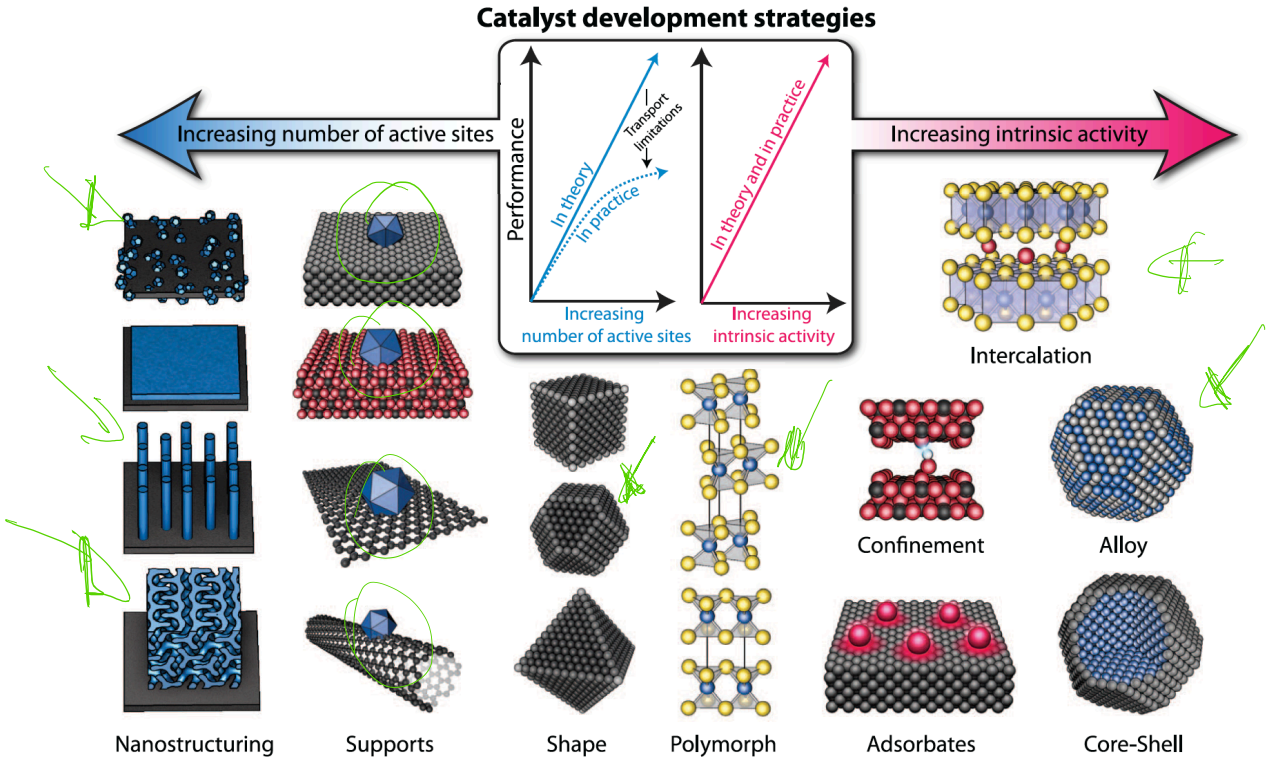


Fig. 2. Catalyst development strategies. Schematic of various catalyst development strategies, which aim to increase the number of active sites and/or increase the intrinsic activity of each active site.

Why is this Important

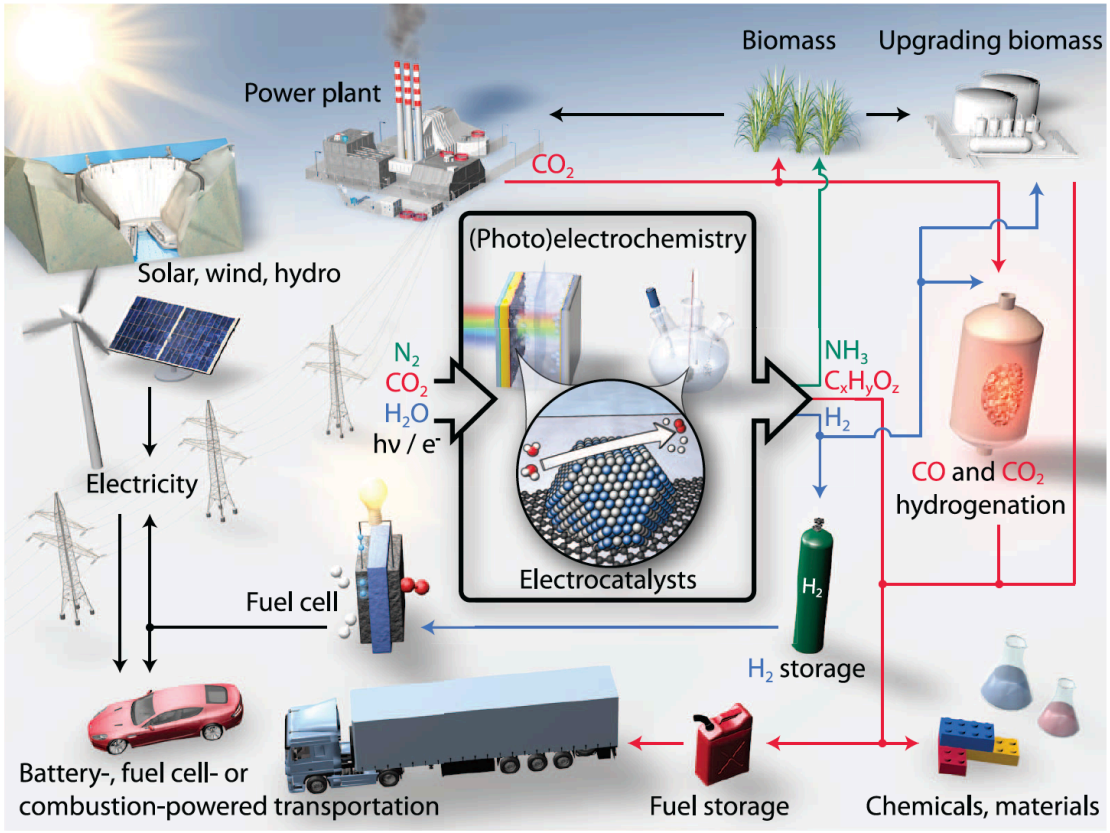


Fig. 1. Sustainable energy future. Schematic of a sustainable energy landscape based on electrocatalysis.

Selective Catalysts

→ selectively absorb a molecule

→ efficient catalyst

selective catalyst

$R \rightarrow P_1 + P_2$

$R \xrightarrow{C_1} P_1$ lowering $\bar{E}_a^{P_1}$ leaving $\bar{E}_a^{P_2}$

Conclusions

Surface are key in catalysis

heterogeneous

↓

c*, pathway

help with molecular

dissociation