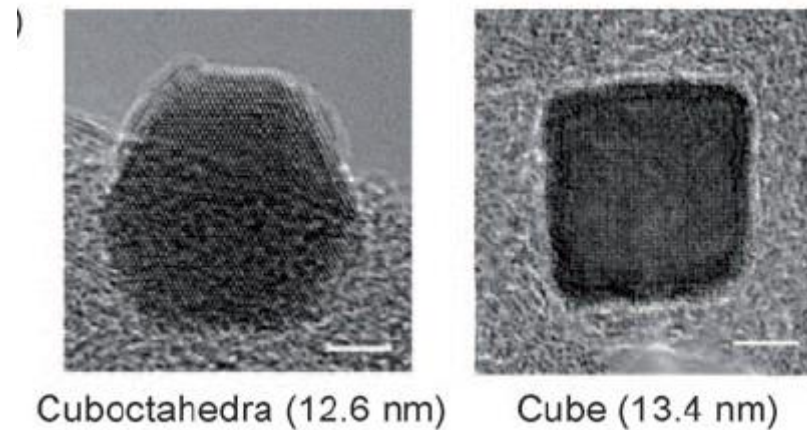
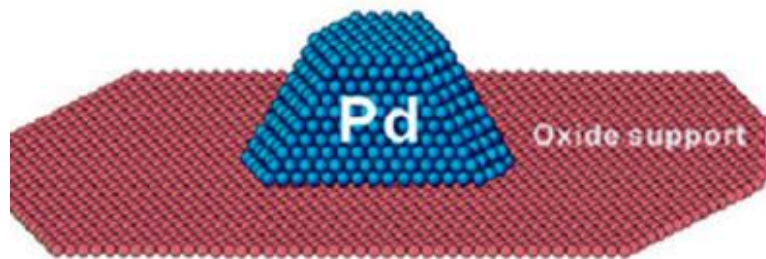


CHEMISORPTION FOR PROBING METAL SURFACE AREAS

G. PIRNGRUBER



BASIC PRINCIPLES

- Objective
 - determine number of accessible metal sites in a noble metal catalyst
- Exploit high reactivity of noble metal surface atoms
 - let them react with small molecules (H_2 , O_2 , CO , etc.)
 - count the number of molecules that have reacted
 - knowing the stoichiometry of the reaction you obtain the number of metal surface atoms
- Choice of the probe molecule
 - must be selective for reaction with metal vs. support
 - must be selective for reaction with surface atoms (not with bulk)
 - reaction must be « irreversible »

BONDING OF ATOMS TO METAL SURFACES

- Interaction of d-band of metal with orbitals of adsorbate atom generate bonding and antibonding states (with respect to the metal-adsorbate interaction)
- If the Fermi level is high both will be filled => no net bonding.
- If the Fermi level is low, the antibonding state remains empty => net bonding.

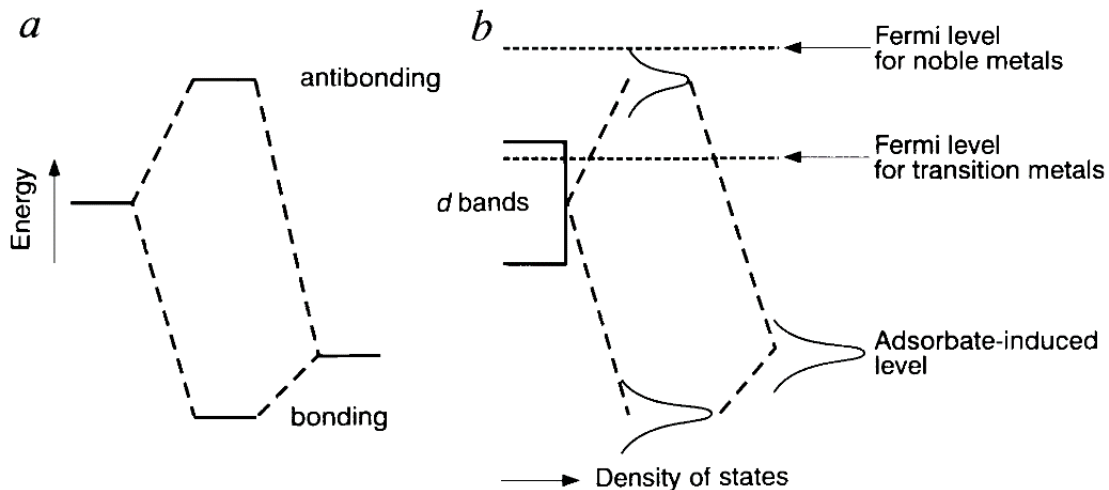
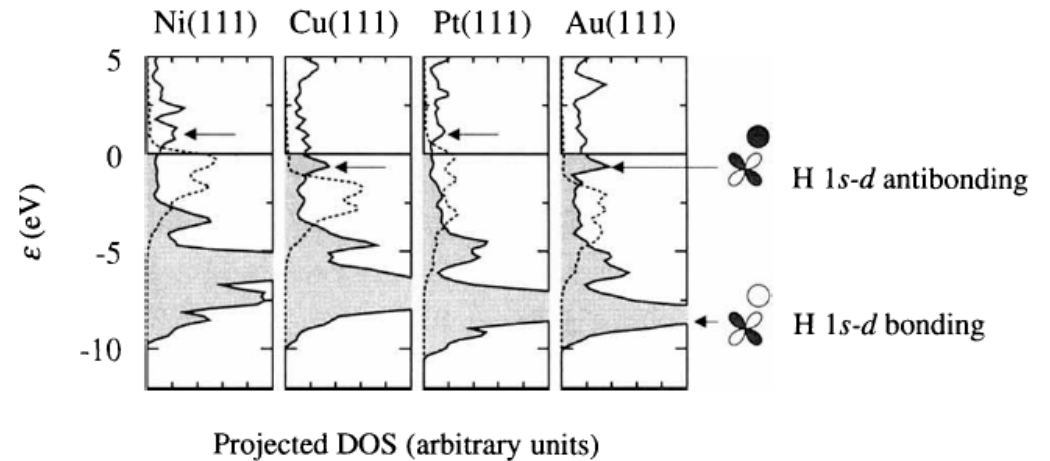


FIG. 2 Schematic illustration of the interaction between two electronic states. The down-shift of the bonding state is smaller than the up-shift of the antibonding state because the overlap of the initial states gives rise to an energy cost related to the orthogonalization of the two states. Both the energy associated with the orthogonalization, and the hybridization energy associated with the formation of bonding and antibonding states, scale with the square of the coupling matrix element. *a*, The simple case of two sharp atomic or molecular states. *b*, The interaction between a state of an adsorbate outside a metal surface, which has been broadened out to a resonance owing to the interaction with the metal *s* band, and the metal *d* bands.

NATURE · VOL 376 · 20 JULY 1995

BONDING OF MOLECULES TO METAL SURFACES

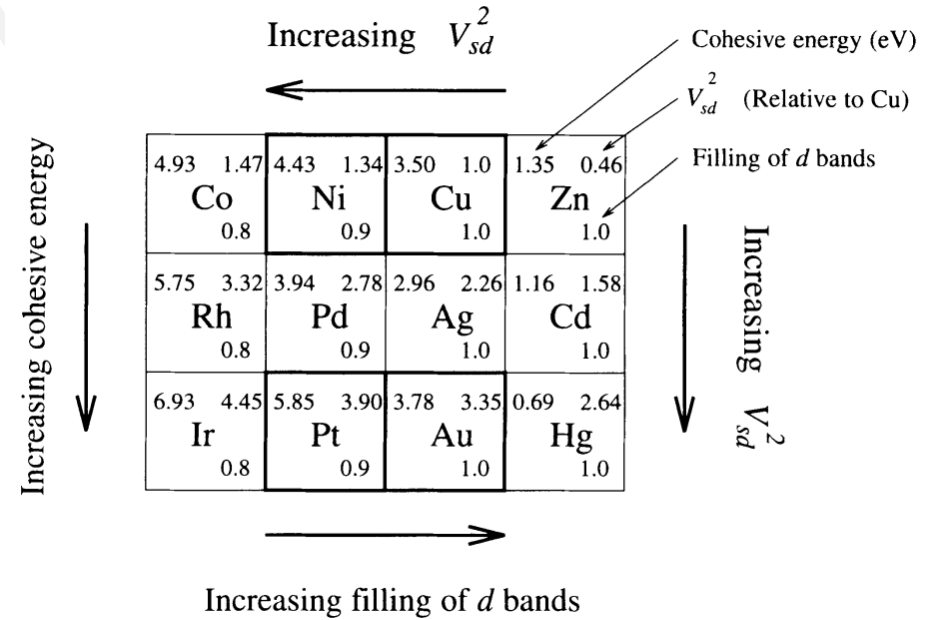
FIG. 3 The density of one-electron states (DOS) (solid lines) for H atomically chemisorbed on the (111) surface of Ni, Cu, Pt and Au. The DOS is projected onto the atomic H 1s state. The surface *d* bands DOS (dashed lines) of the four clean metal surfaces are shown for comparison. The dominant features are the H 1s–metal *d* bonding resonances at energies, ϵ , between -5 and -10 eV. Also prominent are the H 1s–metal *d* antibonding DOS peaks (indicated by arrows) directly above the metal *d* bands. These antibonding states cause repulsion on Cu and Au, where they are filled. As indicated by the grey-shading, only states below the Fermi energy (which is the energy zero in all cases) are filled.



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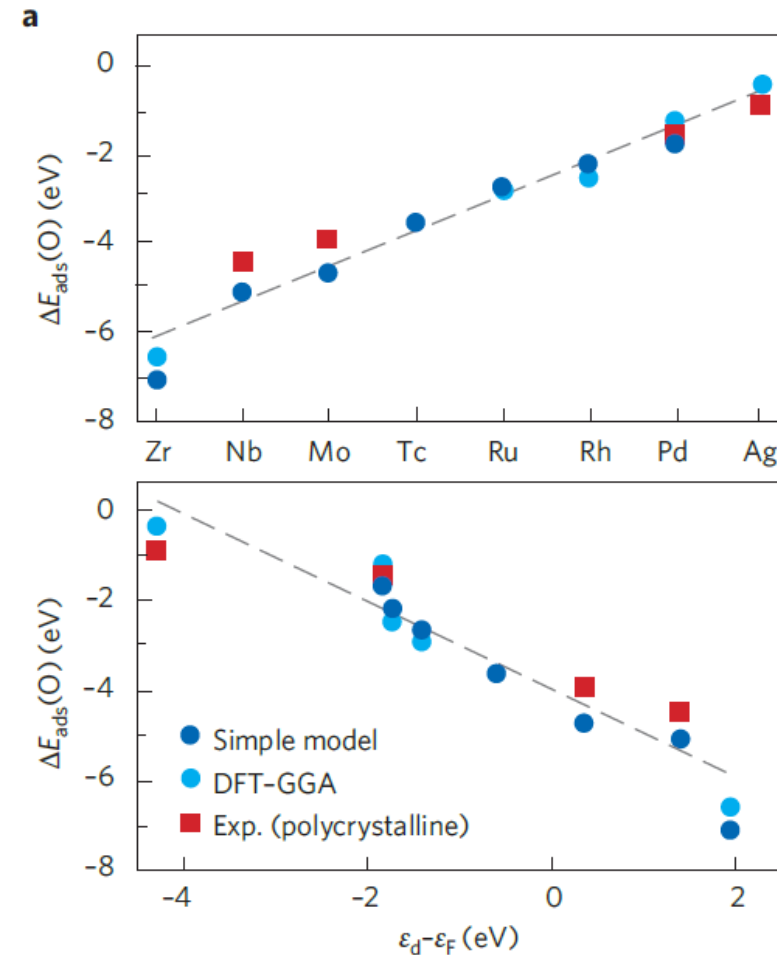
239

- Noble metals have completely filled *d*-states and high Fermi levels
- The antibonding states are also occupied => weak chemisorption



PERIODIC TRENDS IN STRENGTH OF CHEMISORPTION

- Difference between energy of center of d-band and Fermi level is a good descriptor of chemisorption energy
- Explains periodic trends in chemisorption
 - For noble metals the d-band center is much lower than the Fermi level ($\epsilon_d - \epsilon_F$ is negative)
 - For non-noble metals the d-band center may be above the Fermi level



DOI: 10.1038/NCHEM.121

ACTIVATED AND NON-ACTIVATED CHEMISORPTION

- Chemisorption is usually dissociative.
- Where do potential energy curves of adsorbed molecule and of adsorbed atoms cross?
 - Above zero => dissociation is activated
 - Below zero => spontaneous dissociation

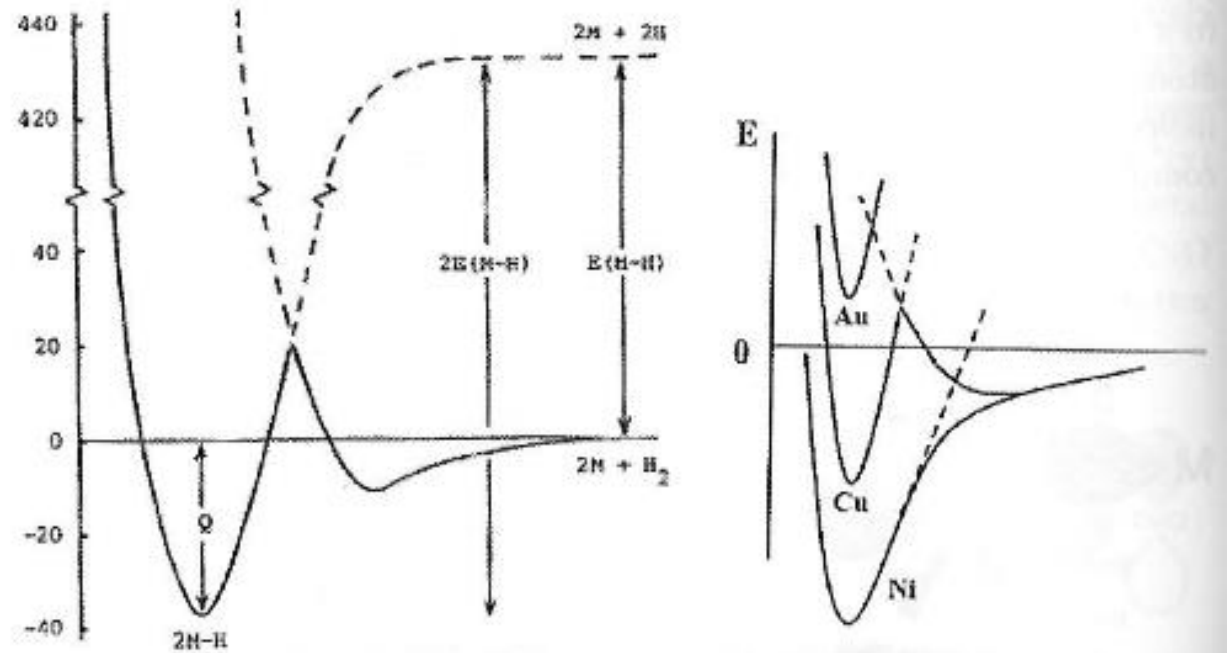


Fig. 2.16 (Left) Potential energy (in kJ/mol) of dissociative adsorption of H₂ on Cu. (Right) Potential energy along the minimum-energy reaction path for H₂ dissociation on the (111) surfaces of Ni, Cu and Au.

Prins, Introduction to Heterogeneous Catalysis

DISSOCIATION OF MOLECULES ON METAL SURFACES

- Dissociation of a molecule AB is thermodynamically favored if

$$\Delta H_{\text{bond}}(\text{A}) + \Delta H_{\text{bond}}(\text{B}) < \Delta H_{\text{bond}}(\text{AB}) + \Delta E_{\text{AB}}$$

- $\Delta H_{\text{bond}}(\text{A})$ = bonding energy of atom A to the metal surface
- $\Delta H_{\text{bond}}(\text{B})$ = bonding energy of atom B to the metal surface
- $\Delta H_{\text{bond}}(\text{AB})$ = bonding energy of molecule AB to the metal surface
- ΔE_{AB} = dissociation energy of molecule AB (in free space)

PERIODIC TRENDS IN THE DISSOCIATION OF MOLECULES

CO

Sc	Ti D	V	Cr	Mn	Fe D	Co	Ni M	Cu	3d
Y	Zr	Nb	Mo D	Tc	Ru M	Rh	Pd M	Ag	4d
La	Hf	Ta	W D+M	Re	Os	Ir M	Pt M	Au	5d

N₂

Sc	Ti (D)	V	Cr (D)	Mn	Fe D	Co	Ni	Cu	3d
Y	Zr	Nb	Mo (D)	Tc	Ru	Rh	Pd	Ag	4d
La	Hf	Ta (D)	W D	Re	Os	Ir	Pt	Au	5d

NO

Sc	Ti	V	Cr	Mn	Fe	Co	Ni D+M	Cu	3d
Y	Zr	Nb	Mo	Tc	Ru M	Rh	Pd M	Ag	4d
La	Hf	Ta	W	Re	Os	Ir D+M	Pt M	Au	5d

● D = dissociative adsorption

● M = molecular adsorption

● Metals to the top left of the periodic table tend to dissociate molecules

● CO is more difficult to dissociate than N₂ or NO





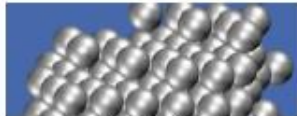
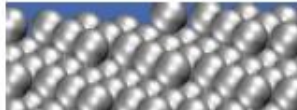
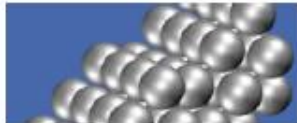
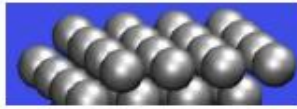
● Follows bond strength in the molecule

STEPS AND KINKS ON METAL SURFACES

- The dense Ni(111) surface has the highest activation energy for CO dissociation.
- Stepped and kinked surfaces have lower activation energy.

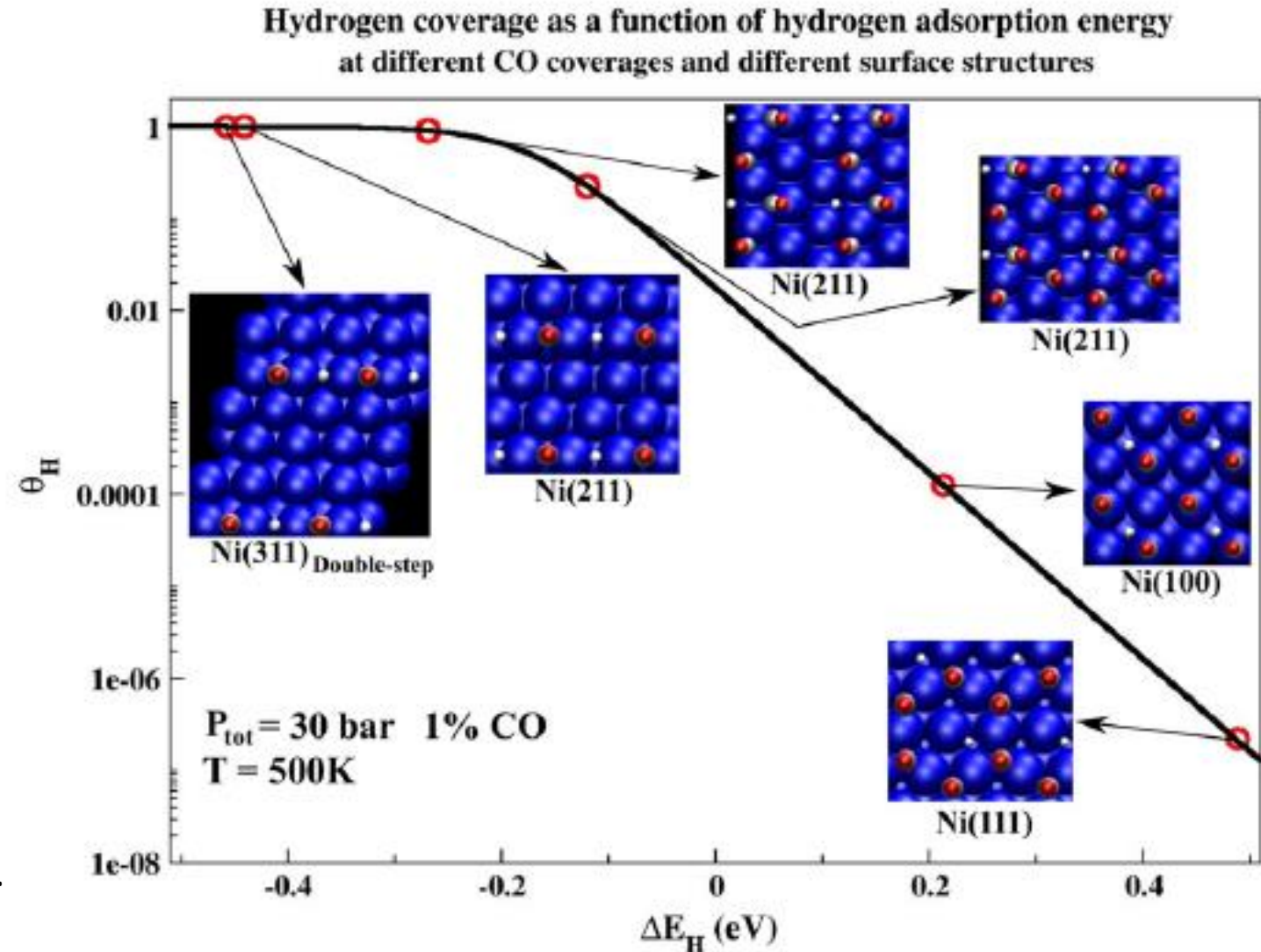
Andersson et al., J. Catal. 255 (2008) 6.

Activation energy of CO dissociation (eV)

		low θ_{CO}
A	 (111) terrace	2.85
B	 (211) step	1.94
C	 (221) step	1.91
D	 (311) double step	1.66
E	 (321) kink	1.77
F	 (431) kink	1.87
G	 (511) double step	1.68
H	 (100) terrace	1.87

STEPS AND KINKS ON METAL SURFACES

- Same tendency for adsorption of H on the Ni surface:
- On flat surfaces the chemisorption of H is weaker (positive ΔE_H), hence the H coverage is low.
- On stepped surface the H-coverage is close to 1.

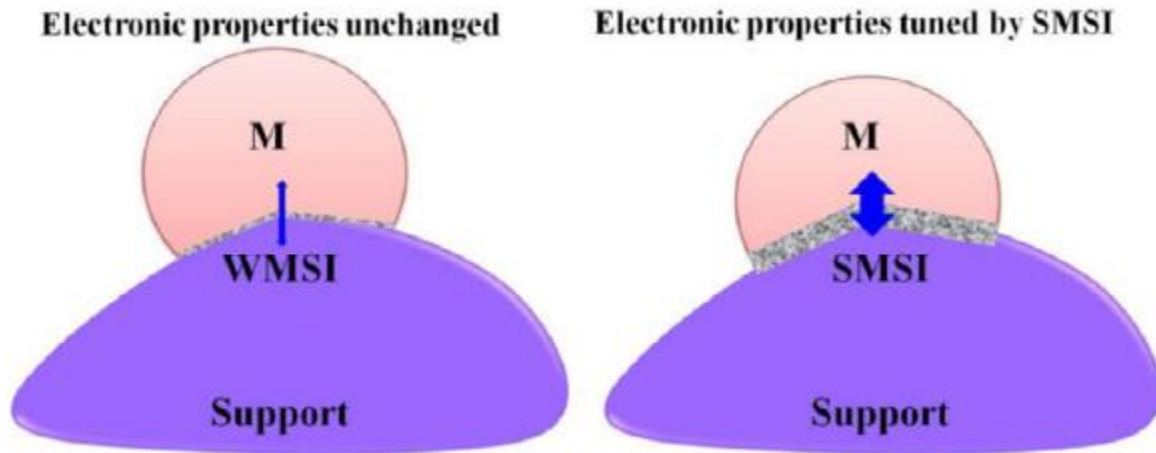


Andersson et al., J. Catal. 255 (2008) 6.

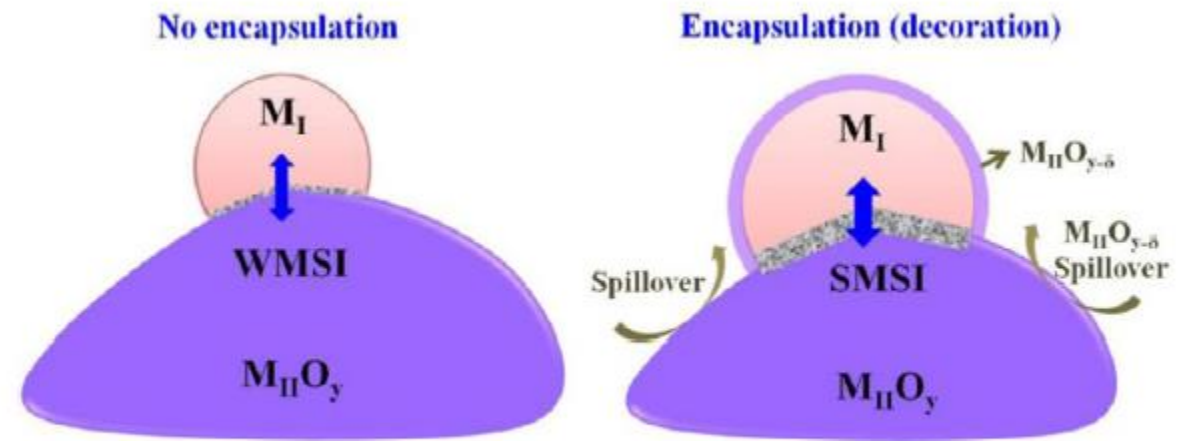
CHEMICAL PROPERTIES OF THE SUPPORT – STRONG METAL SUPPORT INTERACTIONS

- Ability of noble metals to chemisorb H_2 or CO strongly suppressed on TiO_2
 - Same phenomenon observed on other reducible supports CeO_2 , Nb_2O_5 , V_2O_5
- Oxide migrates over the metal particles and covers them.
- Small metal particles flatten out on the oxide surface.

Tauster, Acc. Chem. Res. 20 (1987) 389.



Scheme 2. Electronic effect resulting from weak metal-support interactions (WMSI) and strong metal-support interactions (SMSI).



Scheme 3. Geometric effect of encapsulation or decoration resulting from strong metal-support interactions (SMSI).

DETERMINING METAL DISPERSION

- Definition of dispersion: ratio between the quantity of metal sites that are accessible on the surface Q_{M_s} and the total quantity of metal sites Q_{M_t}

$$D \% = \frac{Q_{M_s}}{Q_{M_t}} \cdot 100 = \frac{n \cdot Q_{adsorbat}}{Q_{M_t}} \cdot 100$$

WITH

$$Q_{M_t} = \frac{\%M}{100 \cdot M_M}$$

* n = number of surface metal atoms that are occupied by the chemisorption of a gas molecule

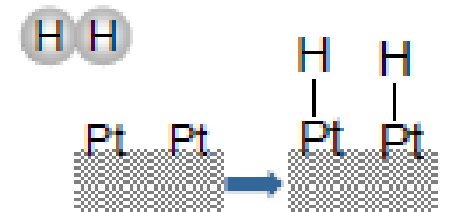
ex : H_2 on Pt : $n = 2$ because of dissociative adsorption: 1 molecule H_2 dissociates to 2 H atoms adsorbed on 2 Pt atoms

* $Q_{adsorbat e}$ = adsorbed quantity when all surface sites are occupied (mole, mmol/g, etc)

* % M = metal content of the solid (catalyst) (determined by elemental analysis, in wt %)

* M_M = molar mass of the metal (g/mol)

- In the definition of dispersion, all surface atoms are considered equivalent; is not necessarily true in terms of catalytic activity.
 - corner atoms are usually more active than atoms on the flat surfaces
 - stoichiometry of chemisorption may also change

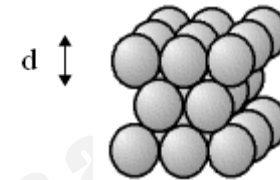


ESTIMATING THE SIZE OF THE METAL PARTICLES

■ Surface geometry (hypothesis of spherical particles)

■ for a solid with N spheres of diameter d

- Total surface area (A) = $N \cdot \pi \cdot d^2$
- Mass (M) = $\rho \cdot N \cdot \pi \cdot d^3 / 6$



$$\text{Surface (m}^2/\text{g}_{\text{metal}}) = A/M = \frac{6}{\rho \cdot d}$$

ρ = density in $\text{g}\cdot\text{cm}^{-3}$

d = diameter in μm

■ Average diameter of the spherical metal particles

$$d = \frac{6}{\rho \cdot S}$$

OR

$$S = \frac{\sigma \cdot N_A \cdot n \cdot Q_{\text{adsorbat}}}{\% M}$$

σ = surface of a metal atom (m^2/atome)

n = stoichiometry of chemisorption

N_A = Avogadro number

AND

$$D = \frac{n \cdot Q_{\text{adsorbat}} \cdot 100 M_M}{\% M}$$

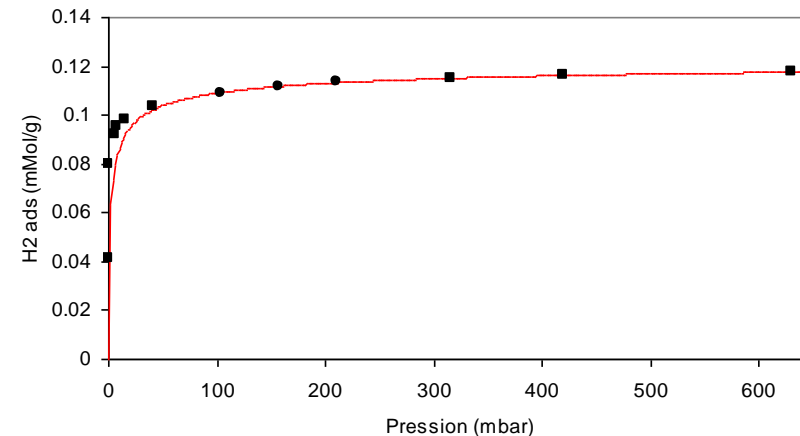
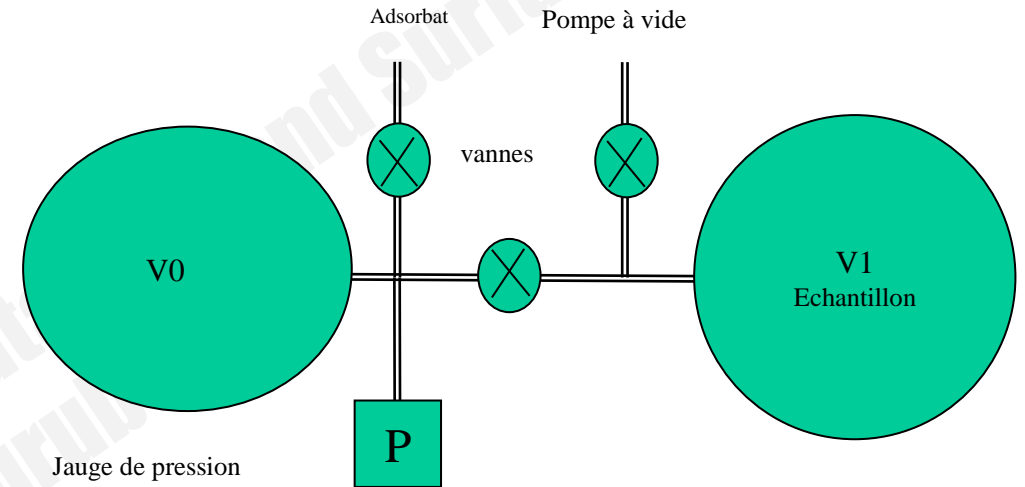


$$d = \frac{6 \cdot 100 M_M}{\rho \cdot \sigma \cdot N_A \cdot D}$$

RELATION SIZE = f (DISPERSION)

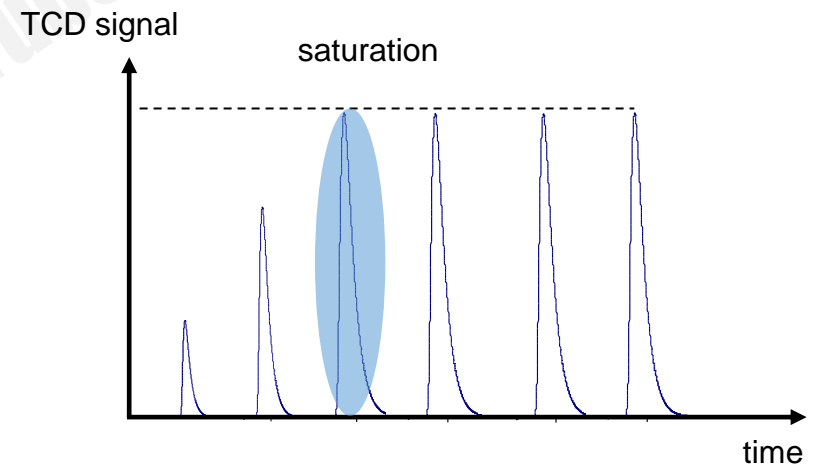
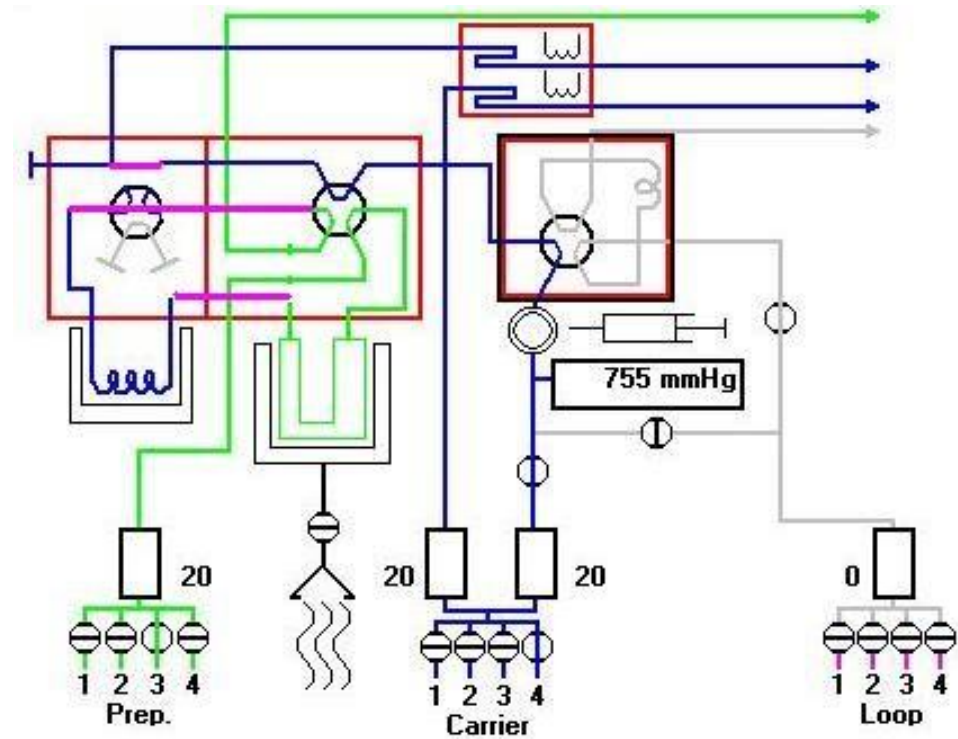
EXPERIMENTAL METHODS (1)

- Static measurement of an adsorption isotherm
 - same method as in physisorption
 - but measurement usually at room temp
- Isotherms very steep
 - chemisorption is irreversible
 - sites are saturated at very low pressure
- On top of chemisorption there may be some physisorption on the support
 - extrapolate intercept at zero
 - isotherm, evacuation, 2nd isotherm, calculate difference



EXPERIMENTAL METHODS (2)

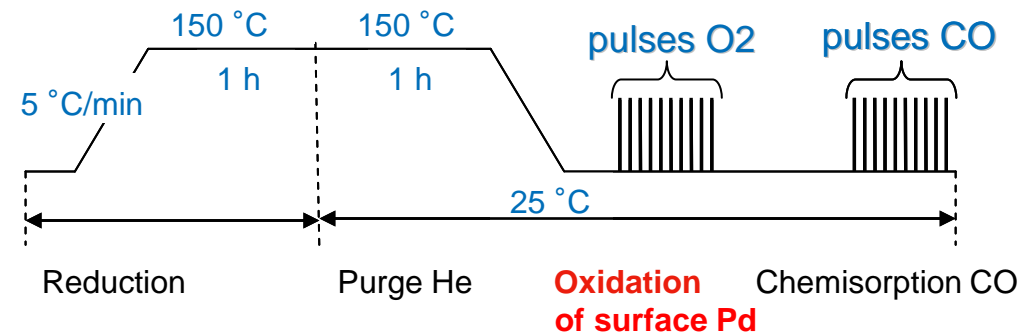
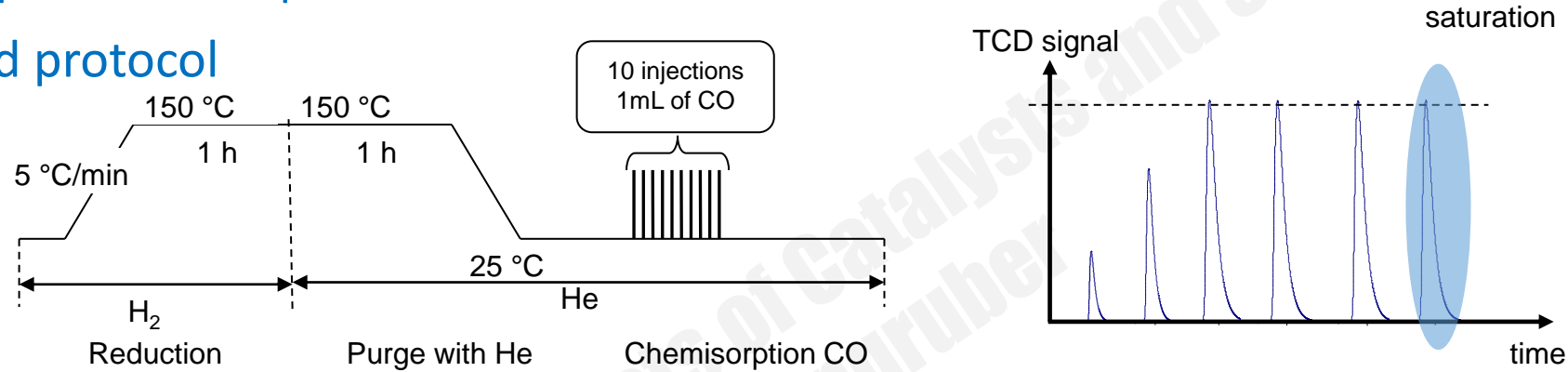
- Dynamic method – pulse method
 - send pulses of probe molecule with a carrier gas to the catalyst
 - detect consumption of probe molecule with TCD



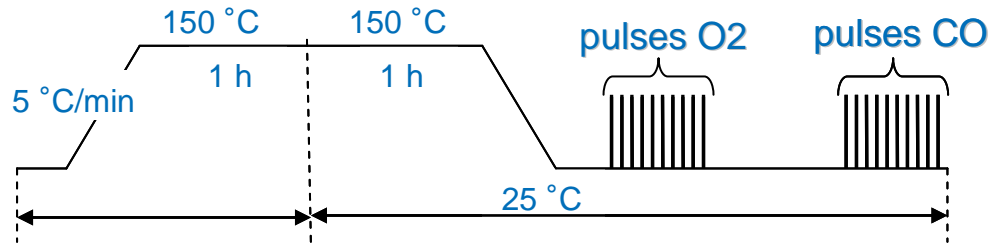
EXAMPLE – CHEMISORPTION OF CO ON Pd

- Direct titration with CO underestimates Pd dispersion
 - compared to TEM particle size

- Modified protocol



WHICH SURFACE REACTIONS ARE GOING ON?



He purge

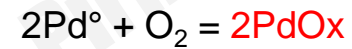
Oxidation of Pd

Reaction with CO

What is the state of Pd?
Pd[°] ou Pd-H ?

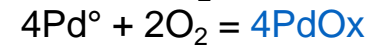
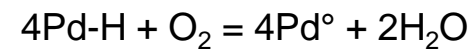
Existence of Pd[°] not probable according to literature: T > 650K, UHV

Hypothesis 1: Pd[°]

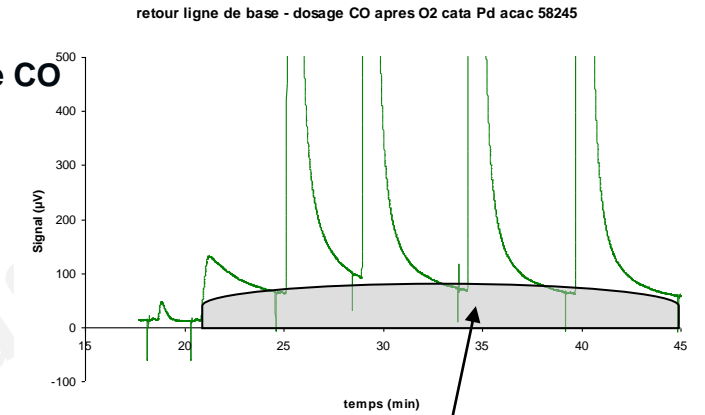


1 O₂ for 2 Pd
Stoichiometry = 2

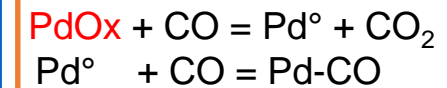
Hypothesis 2: Pd-H



3 O₂ for 4 Pd
Stoichiometry = 4/3



slow desorption CO₂ from the support material



2 CO for 1 Pd
Stoichiometry = 1/2

EXAMPLE – DISPERSION OF NI CATALYSTS

- Comparison chemisorption vs. TEM

- Chemisorption O₂ after different reduction conditions

- in dynamic mode (or static mode)

- overestimates dispersion because bulk oxidation cannot be avoided (Ni less noble than Pd, Pt)

- Chemisorption H₂

- static mode necessary because adsorption kinetics slow

- risk of underestimating dispersion if equilibrium is not reached

- values agree fairly well with TEM => best method for Ni

Catalyst	A	B	C
Dispersion O ₂ dynamic (410°C - 16 h)	26%	23 %	26%
Dispersion O ₂ static(400°C - 14 h)	27 %	32 %	/
Dispersion O ₂ dynamic (400°C - 2 h)	11.60%	7.4 %	16%
Dispersion H ₂ statique (400°C - 14 h)	9.3%	9.60%	8.00%
Dispersion TEM (410°C-16 h)	6.8%	11.1%	7.8%

EXERCISE NI DISPERSION

- An adsorption isotherm of H₂ on a Ni catalyst is recorded in static mode. The adsorbed amount extrapolated to zero is 2.53 cm³ STP/g catalyst.
- The Ni loading of the catalyst is 13.05wt% Ni.
- What is the Ni dispersion ?

- Correct answer is 10.15%.

Molecular Aspects of Catalysts and Surfaces
Pirngruber

EXAMPLE – DISPERSION OF PT CATALYSTS

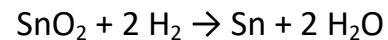
- Possible probe molecules : H₂, CO, O₂
- Method used at IFPEN
 - Reduction in H₂
 - Cooling in inert gas
 - Titration with pulses of O₂
 - $2 \text{ Pt-H} + 3/2 \text{ O}_2 \rightarrow 2 \text{ Pt-O} + \text{H}_2\text{O}$
- Other possibility
 - Reduction in H₂
 - Purge in inert gas at high temperature to remove chemisorbed H
 - Cooling
 - Chemisorption of H₂ (static or dynamic mode)

BIMETALLIC CATALYSTS

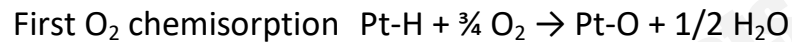
- Example PtSn/Al₂O₃ (reforming catalyst)

- exploit the fact that Sn is less noble (less reducible) than Pt
- Method to distinguish Pt and Sn

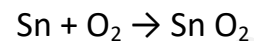
Calcination



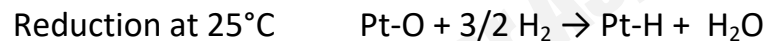
reduces Sn in contact with Pt



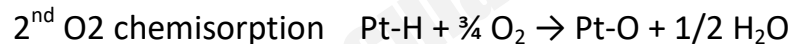
titrates Pt



and Sn that was reduced (VO₁)



reduces only Pt



titrates only Pt (VO₂)

- VO₂ measures Pt dispersion

- Ratio VO₁/VO₂ indicates amount of Sn in contact with Pt (bimetallicity index)

RECOMMENDED LITERATURE

- Prelazzi et al., *Comparison of H₂ adsorption, O₂ adsorption, H₂ titration and O₂ titration on supported Palladium catalysts*, J. Catal. 181 (1999) 73-79
 - discusses the problem of stoichiometry
 - the effect of pretreatment conditions
 - compares different methods of measuring chemisorption

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