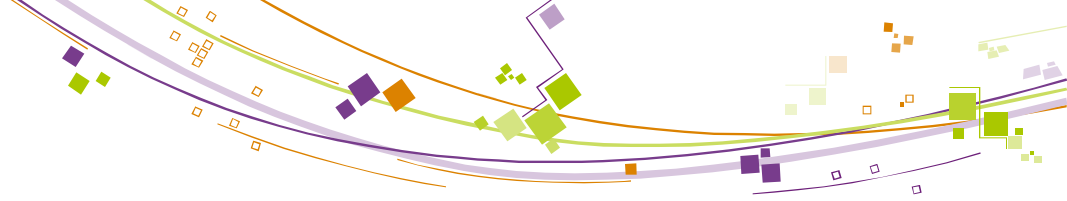# Chemisorption for probing metal surface areas

Course Surface Science and Catalysis

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 stochiometry 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 »

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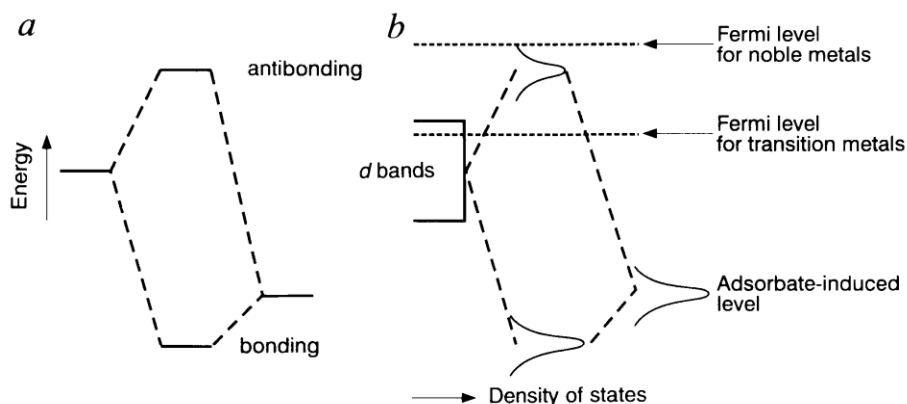
Bonding of molecules to metal surfaces

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.

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- Interaction of d-band of metal with molecular orbitals of adsorbate 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.

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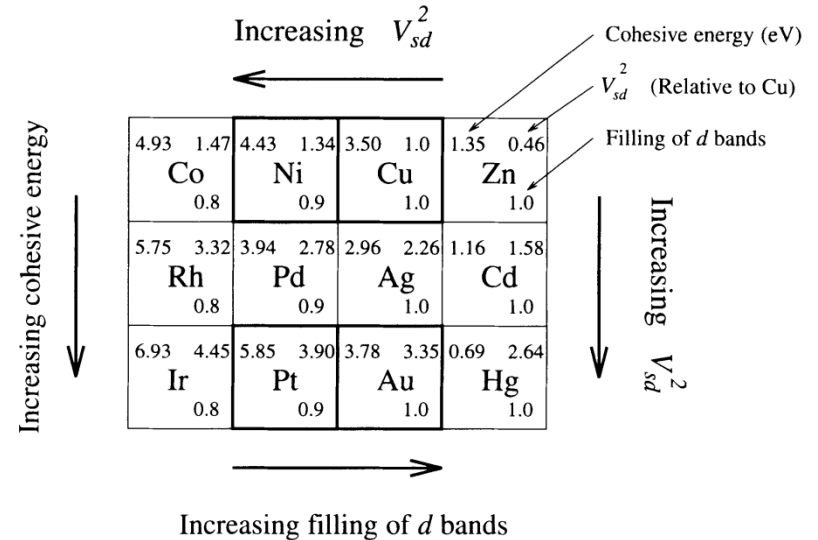
Bonding of molecules to metal surfaces

FIG. 3 The density of one-electron states (DOS) (solid lines) for H atom-ically 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 compari-son. 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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H 1s-d antibonding

H 1s-d bonding

Projected DOS (arbitrary units)
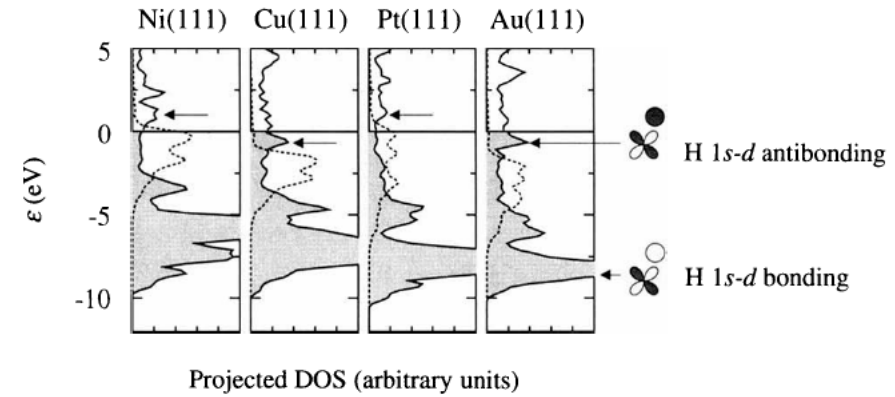
239

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

Increasing V_{sd}^2

Cohesive energy (eV)

V_{sd}^2 (Relative to Cu)

Filling of d bands

Increasing cohesive energy

Increasing V_{sd}^2

4.93 1.47 **Co** 0.8	4.43 1.34 **Ni** 0.9	3.50 1.0 **Cu** 1.0	1.35 0.46 **Zn** 1.0
5.75 3.32 **Rh** 0.8	3.94 2.78 **Pd** 0.9	2.96 2.26 **Ag** 1.0	1.16 1.58 **Cd** 1.0
6.93 4.45 **Ir** 0.8	5.85 3.90 **Pt** 0.9	3.78 3.35 **Au** 1.0	0.69 2.64 **Hg** 1.0

Increasing filling of d bands

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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 (ε_d-ε_F is negative)**

  - **For non-noble metals the d-band center may be above the Fermi level**

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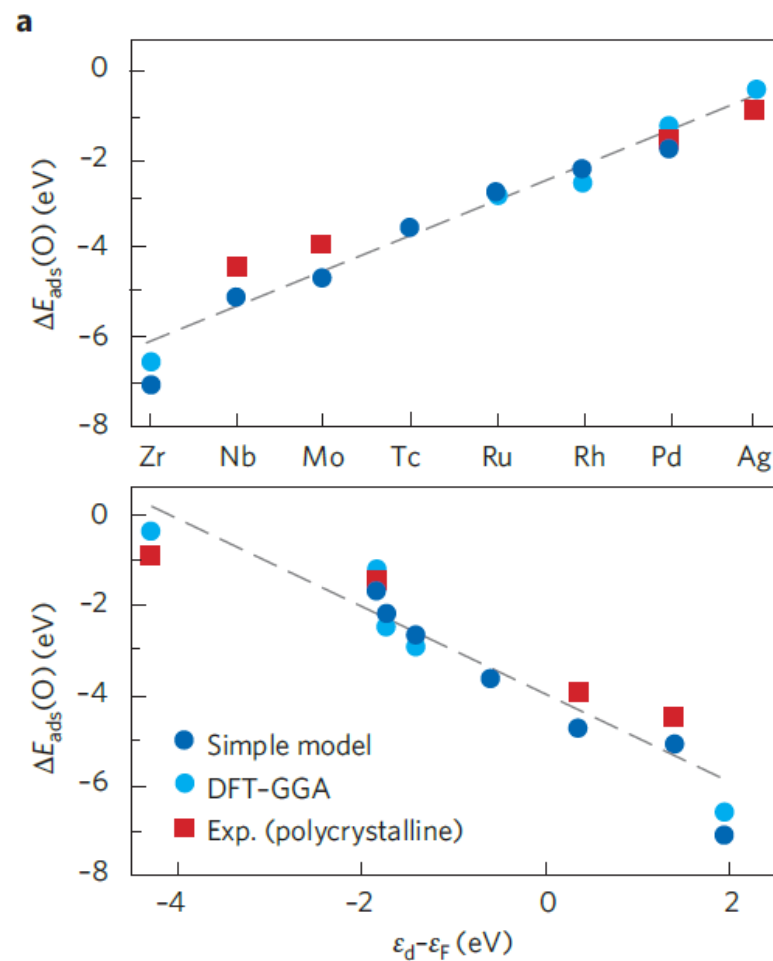
Activated and non-activated chemisorption

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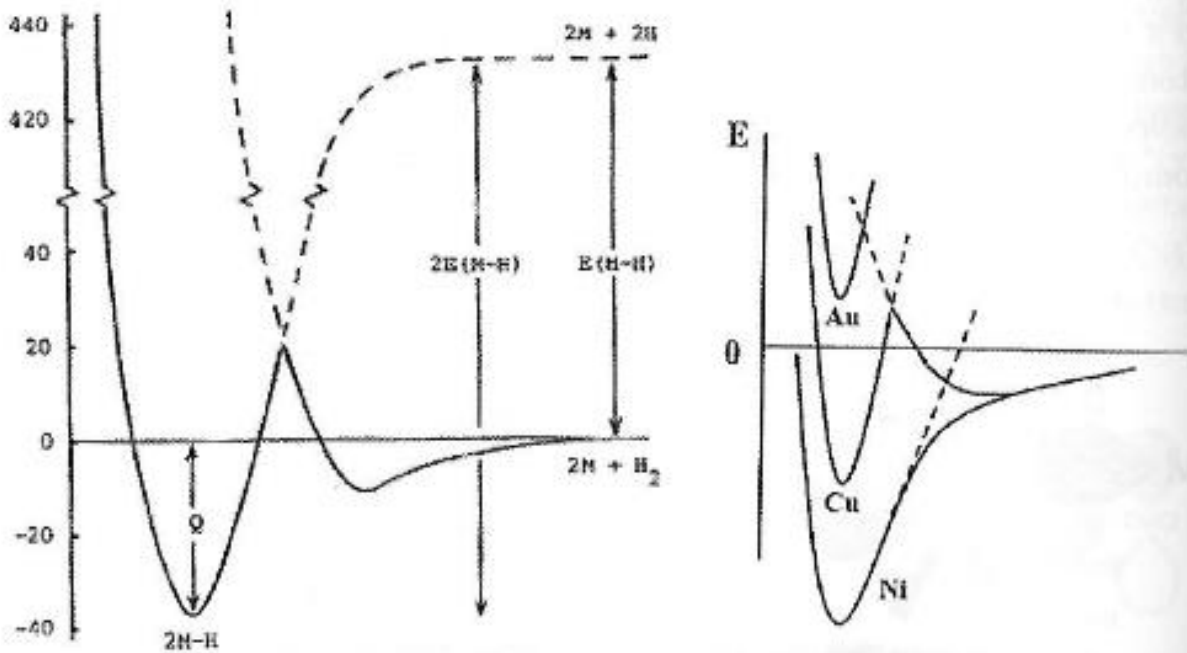
Fig. 2.16 (Left) Potential energy (in kJ/mol) of dissociative adsorption of H₂ on Cu. (Right) Potential energy along the minimum-energy reaction path for H₂ dissociation on the (111) surfaces of Ni, Cu and Au.

- **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 dissocation**

Weak chemisorption (noble metals is often activated).

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Determining metal dispersion

- **Definition of dispersion : ratio between the quantity of metal sites that are accessible on the surface QM_S and the total quantity of metal sites in the solid QM_T.**

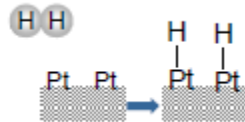$$D\ \% = \frac{Q_{M_S}}{Q_{M_T}} \cdot 100 = \frac{n.Q_{adsorbat}}{Q_{M_T}} \cdot 100 \qquad \textbf{WITH} \qquad Q_{M_T} = \frac{\%M}{100.M_M}$$

* *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
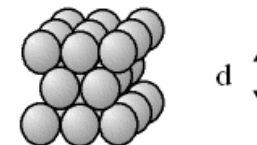   - stoichiometry of chemisorption may also change

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) = $N.\pi.d^2$

    ▪ Mass (M) = $\rho.N.\pi.d^3/6$

$$Surface \left(m^2/g_{metal}\right) = A/M = \frac{6}{\rho.\,d}$$

ρ = density in g.cm⁻³
d = diameter in μm

■ **Average diameter of the spherical metal particles**

$$d = \frac{6}{\rho.S}$$ OR $$S = \frac{\sigma.N_A \cdot n \cdot Q_{adsorbat}}{\%M}$$

σ = surface of a metal atom (m²/atome)
n = stoichiometry of chemisorption
NA = Avogado number

AND $$D = \frac{n.Q_{adsorbat} \cdot 100 M_M}{\%M}$$ → $$d = \frac{6 \cdot 100 M_M}{\rho.\sigma.N_A \cdot D}$$

RELATION SIZE = f (DISPERSION)

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Experimental methods (1)

- **Static measurement of an adsorption isotherm**
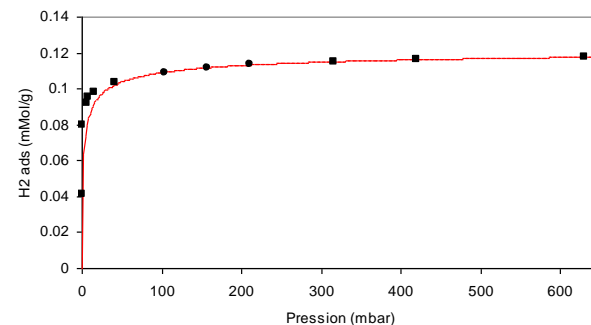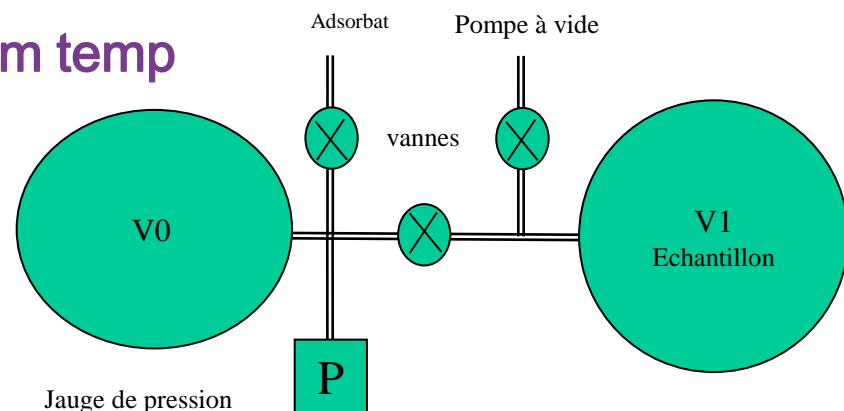 - same method as in physisorption
  - but measurment usually at room temp

- **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

Adsorbat   Pompe à vide

vannes

V0

V1
Echantillon

P

Jauge de pression

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Experimental methods (2)

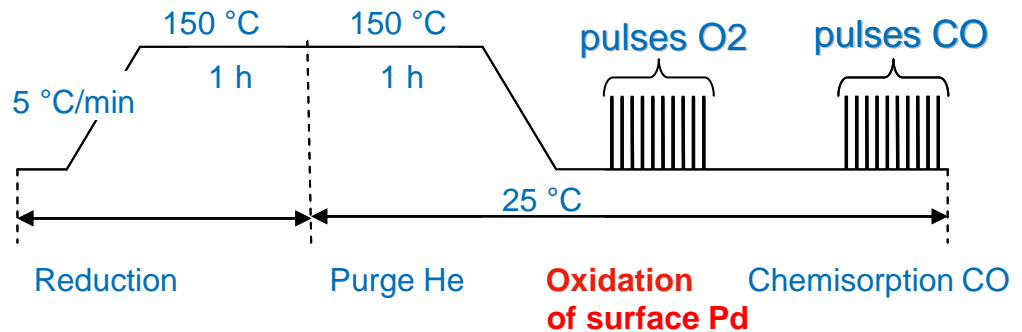- **Dynamic method – pulse method**
  - **send pulses of probe molecule with a carrier gas to the catalyst**
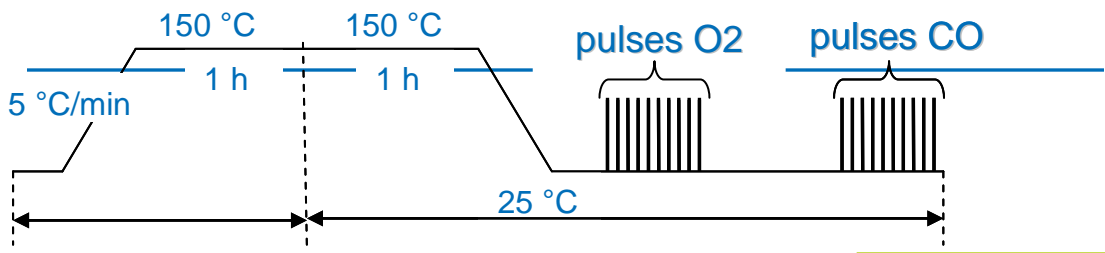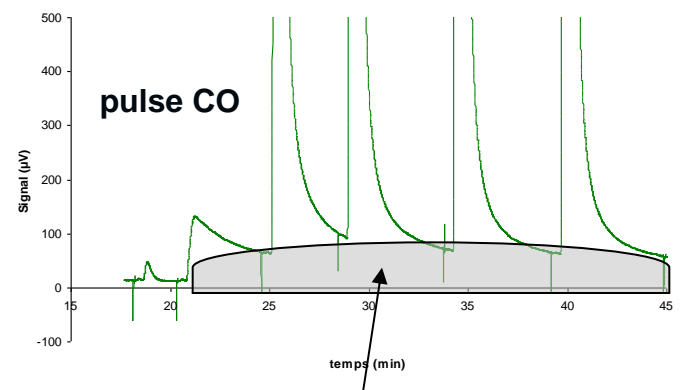 - **detect consumption of probe molecule with TCD**
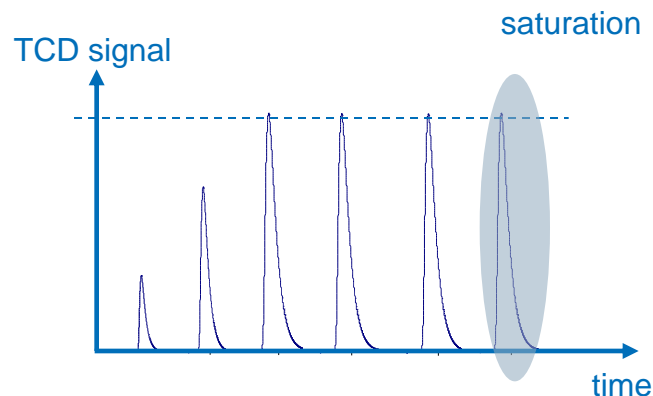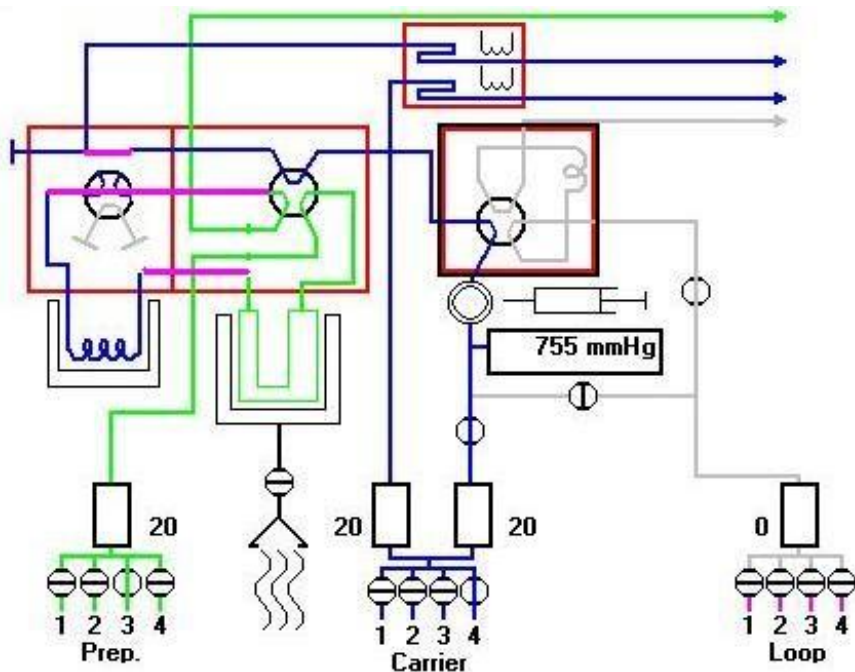
Example – Chemisorption of CO on Pd
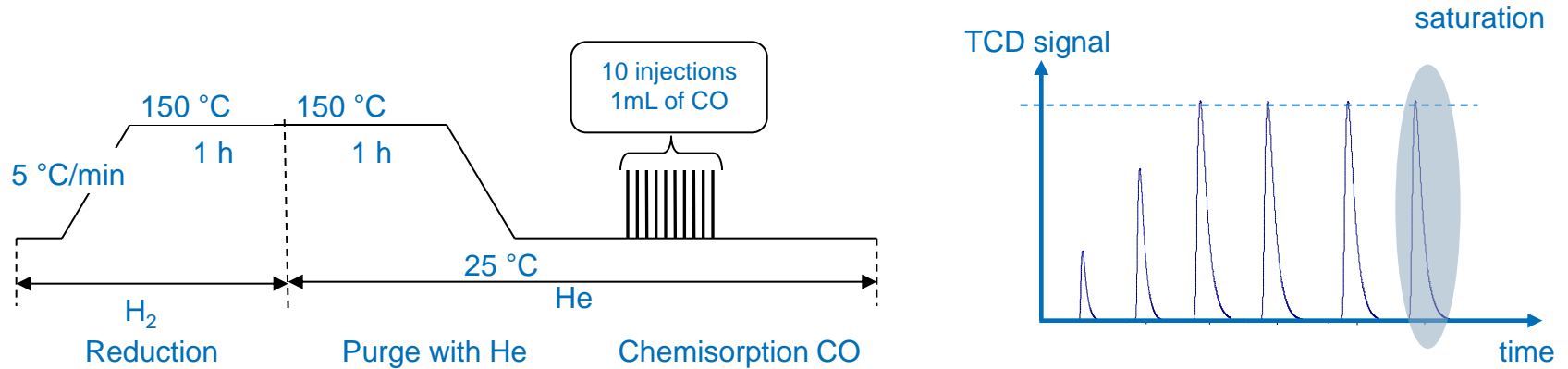
- **Direct titration with CO underestimates Pd dispersion**
  - **compared to TEM particle size**
- **Modified protocol**

Which surface reactions are going on?

pulse CO

**slow desorption CO$_2$
from the support material**

150 °C   150 °C

pulses O2   pulses CO

1 h   1 h

5 °C/min

25 °C

He purge

Oxidation
of Pd

Reaction
with CO

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

Existance of Pd° not probabale
according to literature: T>650K, UHV

Hypothesis 1: Pd°

$2Pd° + O_2 = 2PdOx$

1 O$_2$ for 2 Pd
Stoichiometry = 2

Hypothesis 2 : Pd-H

$4Pd\text{-}H + O_2 = 4Pd° + 2H_2O$
$4Pd° + 2O_2 = 4PdOx$

3 O$_2$ for 4 Pd
Stoichiometry = 4/3

$PdOx + CO = Pd° + CO_2$
$Pd° + CO = Pd\text{-}CO$

2 CO for 1 Pd
Stoichiometry = 1/2

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Example – Dispersion of Ni catalysts

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%

- **Comparison chemisorption vs. TEM**
  - **Chemisorption O_2 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 H_2**
    - 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
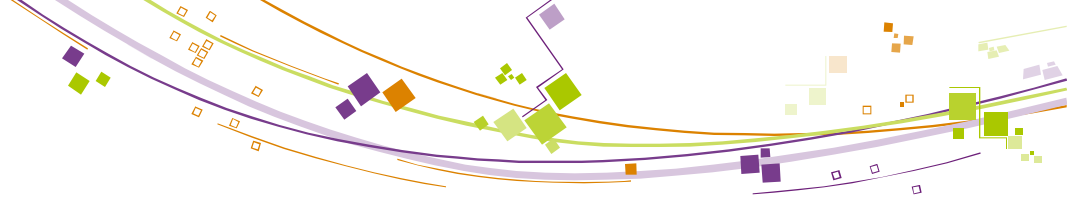
Exercise Ni dispersion

- An adsorption isotherm of H_2 on a Ni catalyst is recorded in static mode. The adsorbed amount extrapolated to zero is 2.53 cm^3 STP/g catalyst.

- The Ni loading of the catalyst is 13.05wt% Ni.

- What is the Ni dispersion ?

- Correct answer is 10.15%.
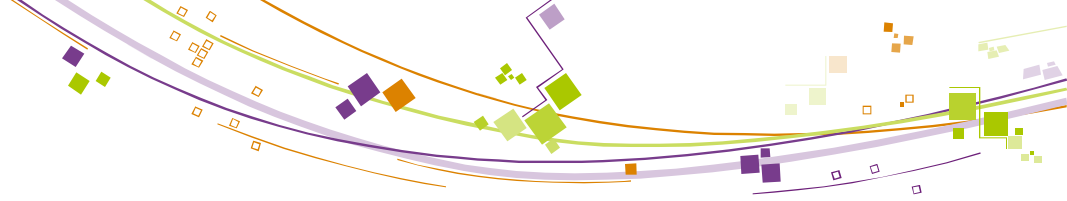
Example – Dispersion of Pt catalysts

- **Possible probe molecules : H_2, CO, O_2**

- **Method used at IFPEN**
  - **Reduction in H_2**
  - **Cooling in inert gas**
  - **Titration with pulses of O_2**
    - $2\ Pt\text{-}H + 3/2\ O_2 \rightarrow 2\ Pt\text{-}O + H_2O$

- **Other possibility**
  - **Reduction in H_2**
  - **Purge in inert gas at high temperature to remove chemisorbed H**
  - **Cooling**
  - **Chemisorption of H_2 (static or dynamic mode)**

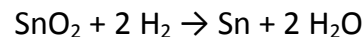Gerhard Pirngruber – Surface Science and Catalysis Course ETH
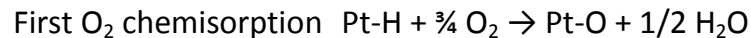
Bimetallic catalysts

- **Example PtSn/Al$_2$O$_3$ (reforming catalyst)**
  - **exploit the fact that Sn is less noble (less reducible) than Pt**
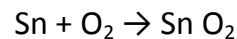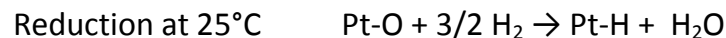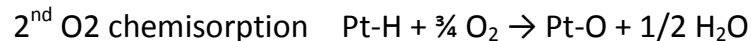 - **Method to distinguish Pt and Sn**

Calcination

Reduction at 500°C $PtO_2 + 5/2\ H_2 \rightarrow Pt\text{-}H + 2\ H_2O$

                              $SnO_2 + 2\ H_2 \rightarrow Sn + 2\ H_2O$ reduces Sn in contact with Pt

First O$_2$ chemisorption $Pt\text{-}H + ¾\ O_2 \rightarrow Pt\text{-}O + 1/2\ H_2O$ titrates Pt

                              $Sn + O_2 \rightarrow Sn\ O_2$ and Sn that was reduced (VO$_1$)

Reduction at 25°C $Pt\text{-}O + 3/2\ H_2 \rightarrow Pt\text{-}H + H_2O$ reduces only Pt

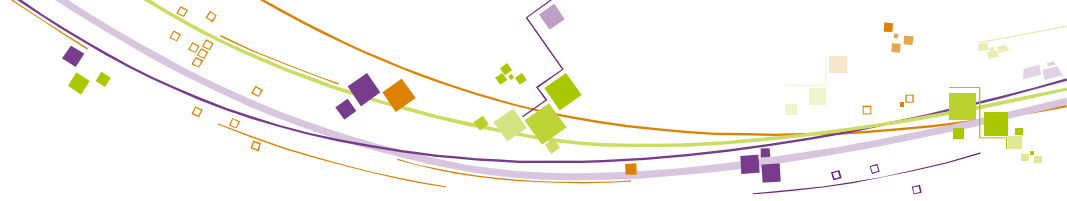2nd O2 chemisorption $Pt\text{-}H + ¾\ O_2 \rightarrow Pt\text{-}O + 1/2\ H_2O$ titrates only Pt (VO$_2$)

  - **VO$_2$ measures Pt dispersion**
  - **Ratio VO$_1$/VO$_2$ indicates amount of Sn in contact with Pt (bimetallicity index)**

G. Guryev, Applied Catalysis A, 326, 16 (2007)

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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