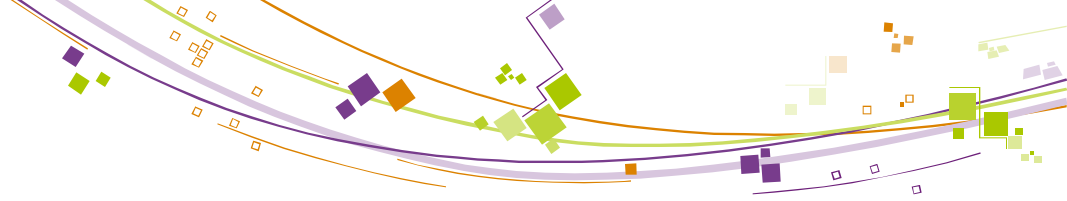


Chemisorption for probing metal surface areas

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 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 »

Experimental methods (1)

■ Static measurement of an adsorption isotherm

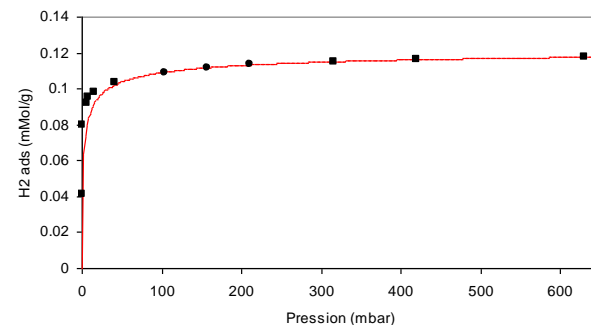
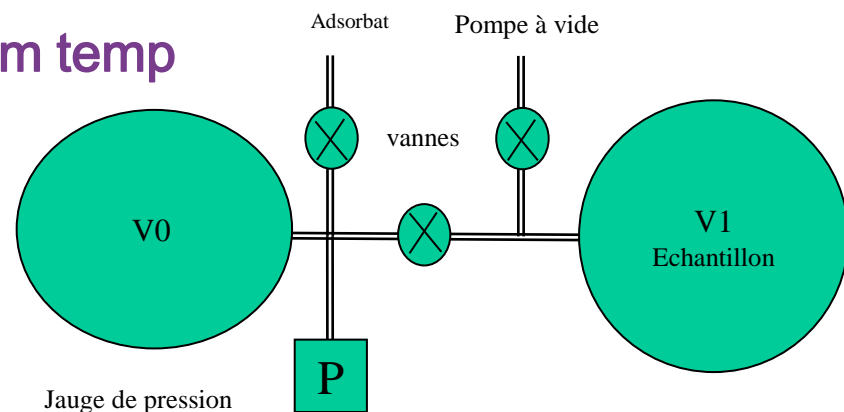
- same method as in physisorption
- but measurement usually at room temp

■ 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

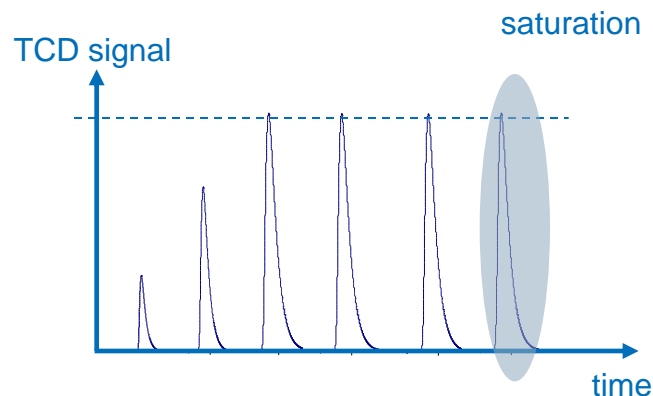
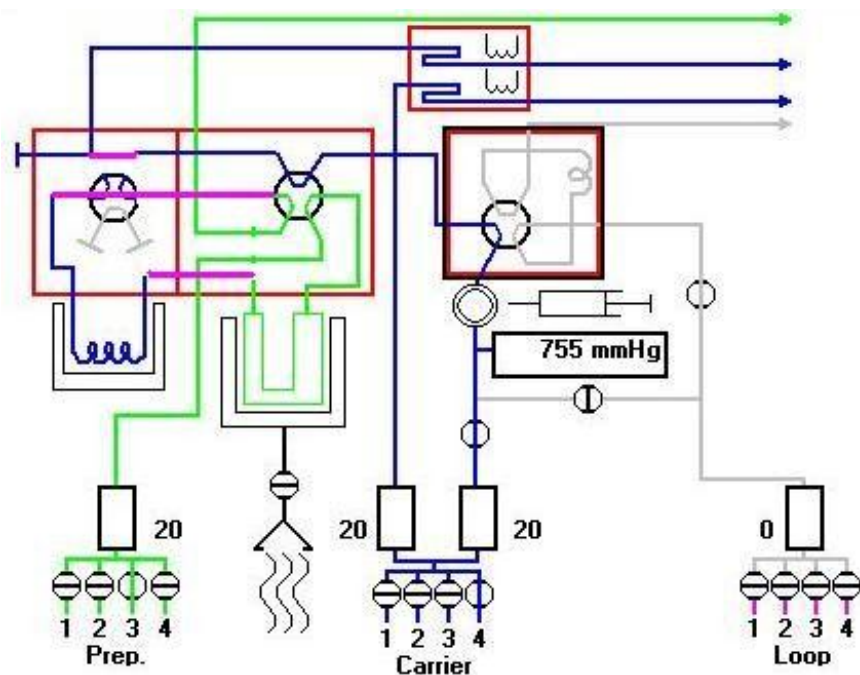
- extrapolate intercept at zero
- isotherm, evacuation, 2nd isotherm, calculate difference



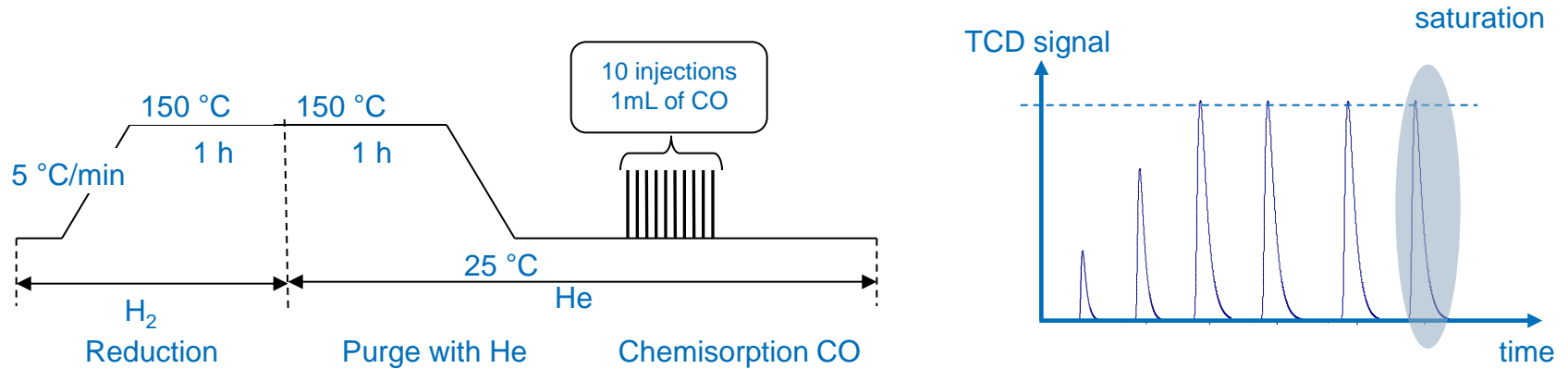
Experimental methods (2)

■ Dynamic method – pulse method

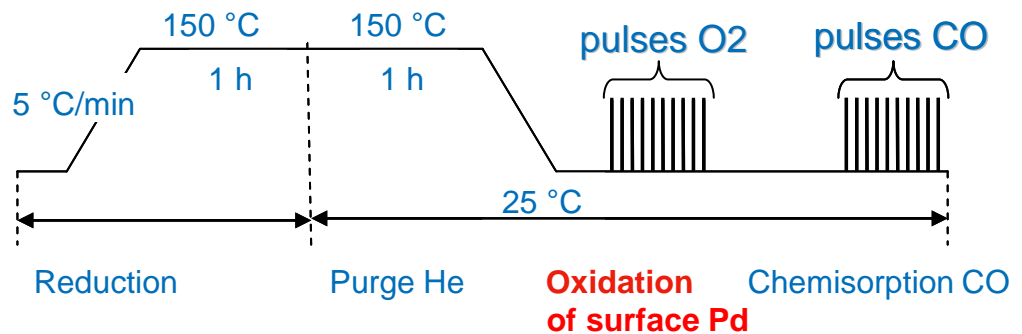
- send pulses of probe molecule with a carrier gas to the catalyst
- detect consumption of probe molecule with TCD



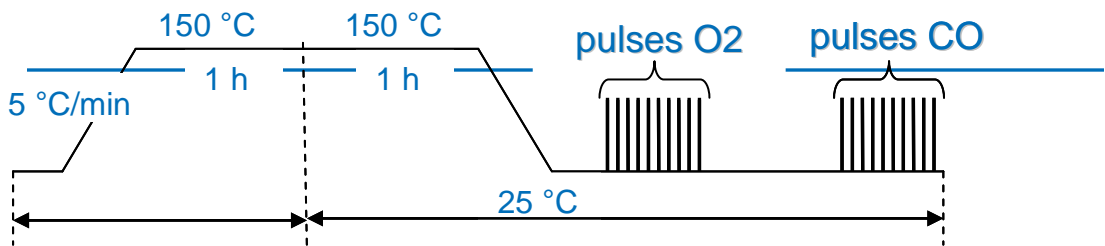
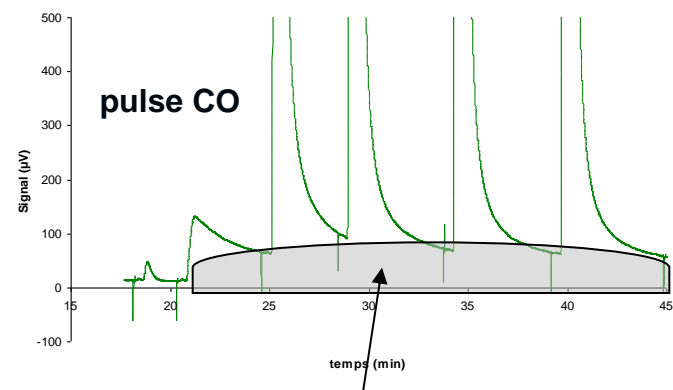
Example – Chemisorption of CO on Pd



- **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°
 $2Pd^\circ + O_2 = 2PdOx$
 1 O₂ for 2 Pd
 Stoichiometry = 2

Hypothesis 2: Pd-H
 $4Pd-H + O_2 = 4Pd^\circ + 2H_2O$
 $4Pd^\circ + 2O_2 = 4PdOx$
 3 O₂ for 4 Pd
 Stoichiometry = 4/3

$PdOx + CO = Pd^\circ + CO_2$
 $Pd^\circ + CO = Pd-CO$
 2 CO for 1 Pd
 Stoichiometry = 1/2

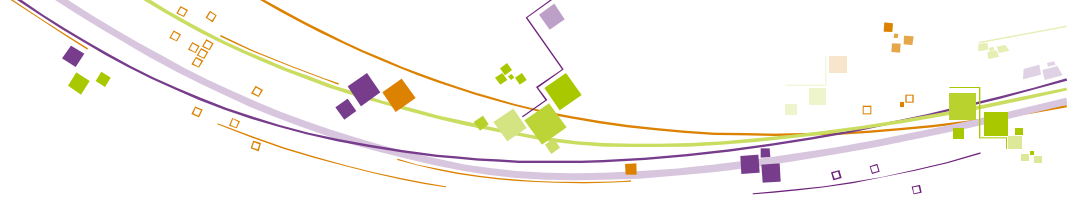


Example – Dispersion of Ni catalysts

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

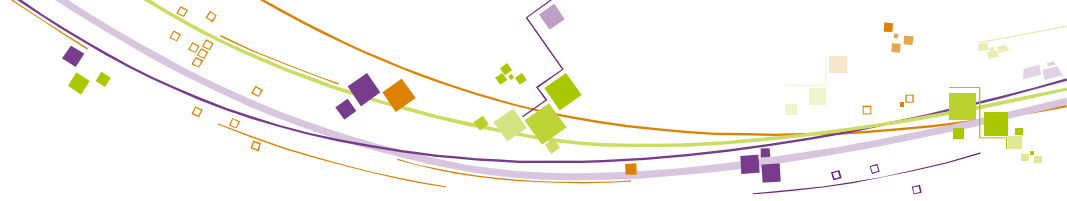
- Chemisorption O₂ after different reduction conditions
 - in dynamic mode (or static mode)
 - overestimates dispersion because bulk oxidation cannot be avoided (Ni less noble than Pd, Pt)
- Chemisorption H₂
 - static mode necessary because adsorption kinetics slow
 - risk of underestimating dispersion if equilibrium is not reached
 - values agree fairly well with TEM => best method for Ni



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%.



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)

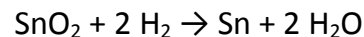


Bimetallic catalysts

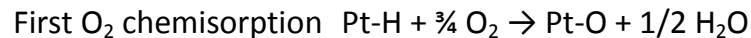
■ Example PtSn/Al₂O₃ (reforming catalyst)

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

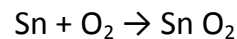
Calcination



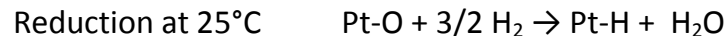
reduces Sn in contact with Pt



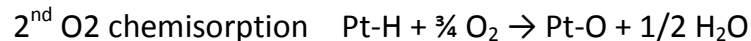
titrates Pt



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)

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