CHEMISORPTION FOR PROBING METAL SURFACE AREAS

G. PIRNGRUBER

Cuboctahedra (12.6 nm)   Cube (13.4 nm)
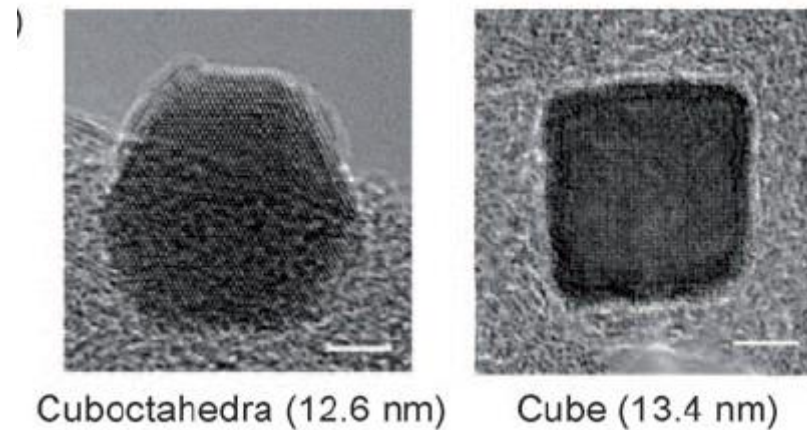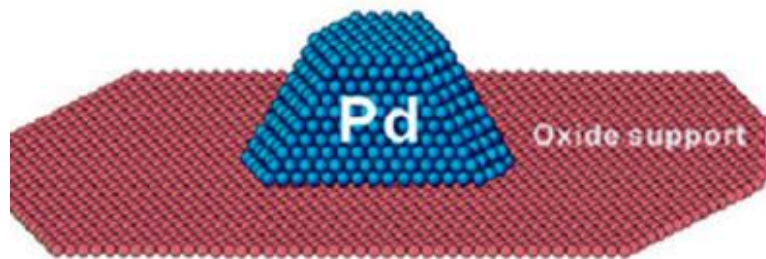
BASIC PRINCIPLES

- 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 »

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.

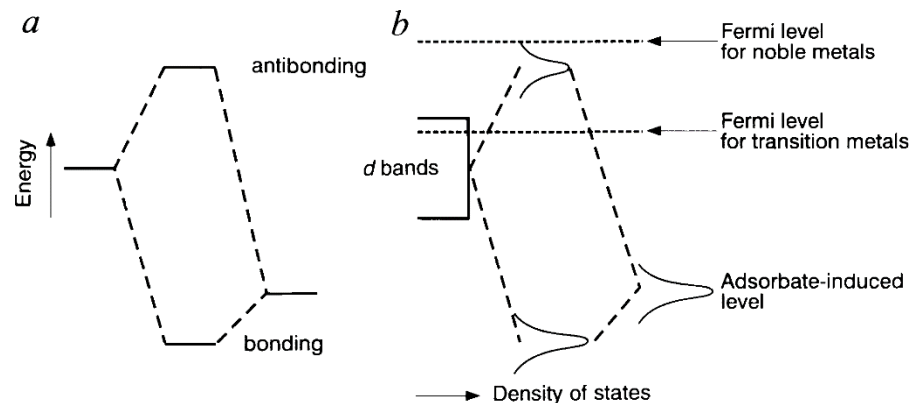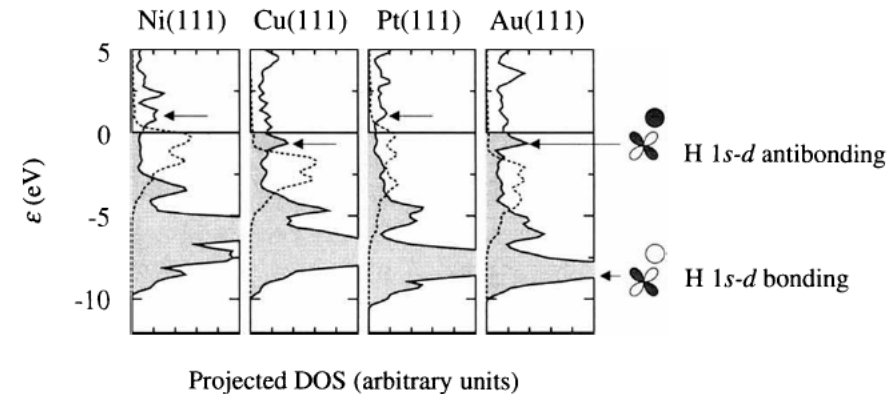- If the Fermi level is low, the antibonding state remains empty => net bonding.

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 ove NATURE · VOL 376 · 20 JULY 1995 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.

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.

- Noble metals have completely filled d-states and high Fermi levels
- The antibonding states are also occupied => weak chemisorption
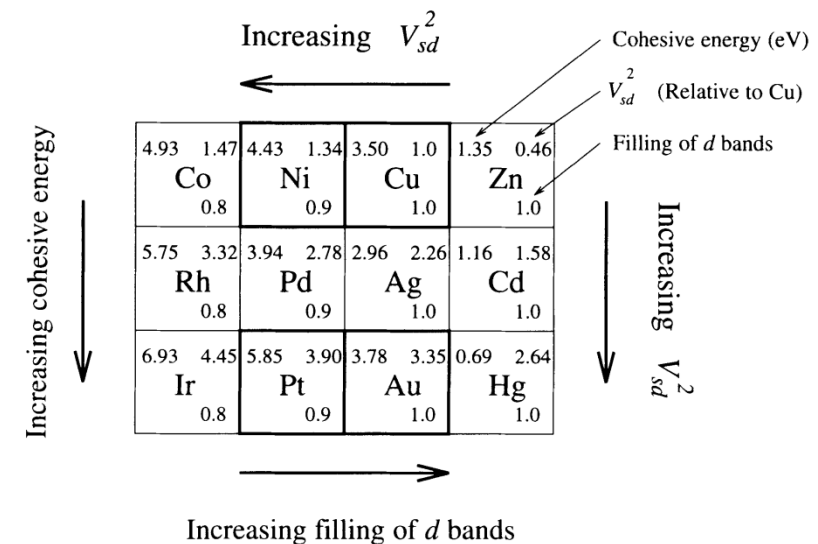
PERIODIC TRENDS IN STRENGTH OF CHEMISORPTION

- 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 ($\varepsilon_d - \varepsilon_F$ is negative)
  - For non-noble metals the d-band center may be above the Fermi level
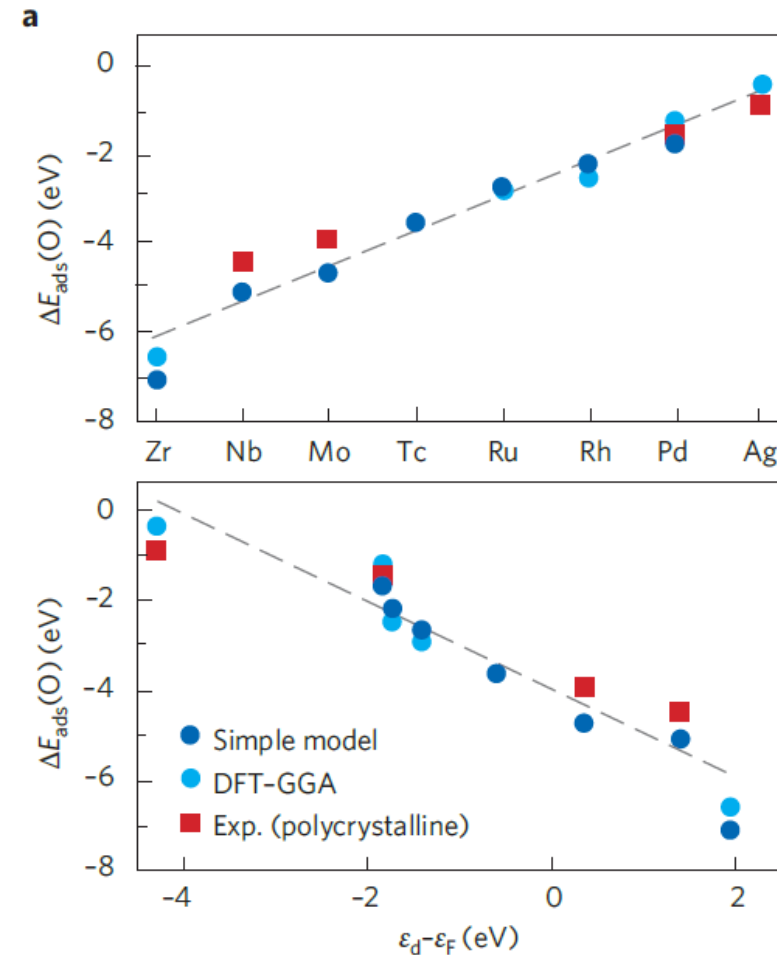
ACTIVATED AND NON-ACTIVATED CHEMISORPTION

- Chemisorption is usually dissociative.

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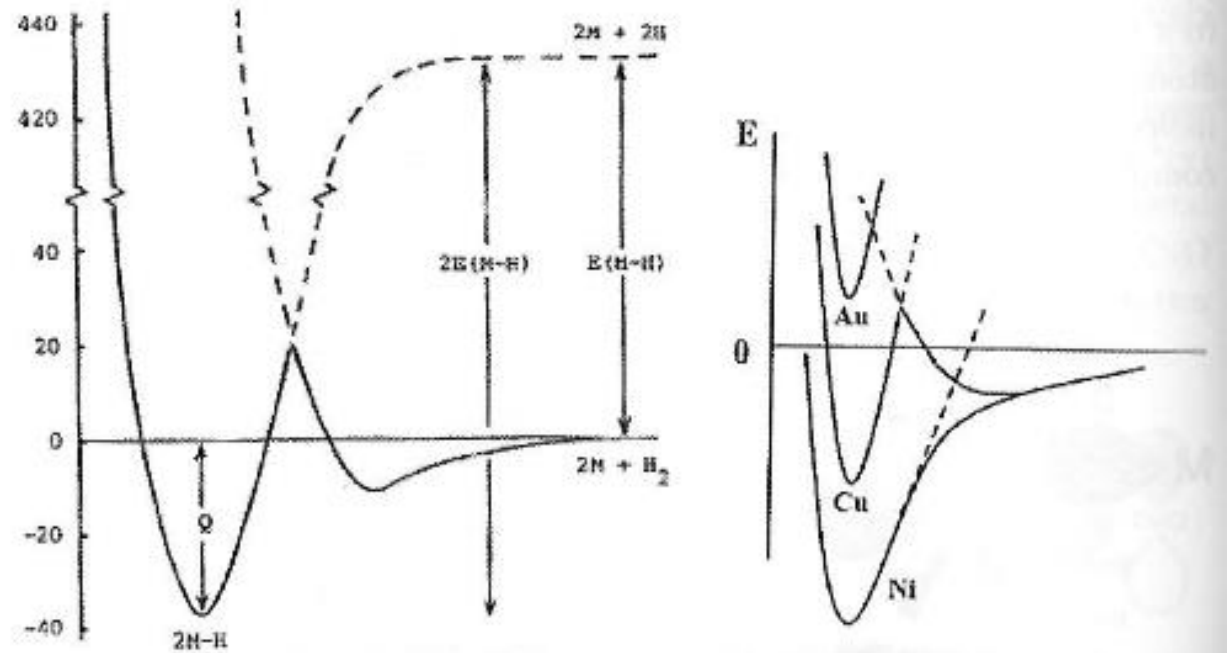 - Below zero => spontaneous dissocation

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

- Dissocation of a molecule AB is thermodynamically favored if

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

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

CO

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

N_2

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

NO

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

- D = dissocative adsorption
- M = molecular adsorption

- Metals to the top left of the periodic table tend to dissociate molecules
- CO is more difficult to dissociate than N_2 or NO
  - Follows bond strength in the molecule
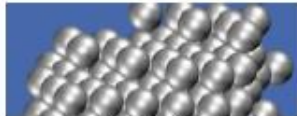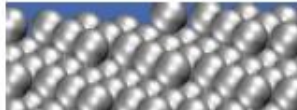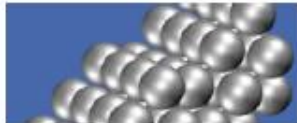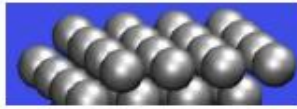
Hammer, Noskov, Adv Catal 2000

STEPS AND KINKS ON METAL SURFACES

- The dense (111) surface has the highest activation energy for CO dissociation.

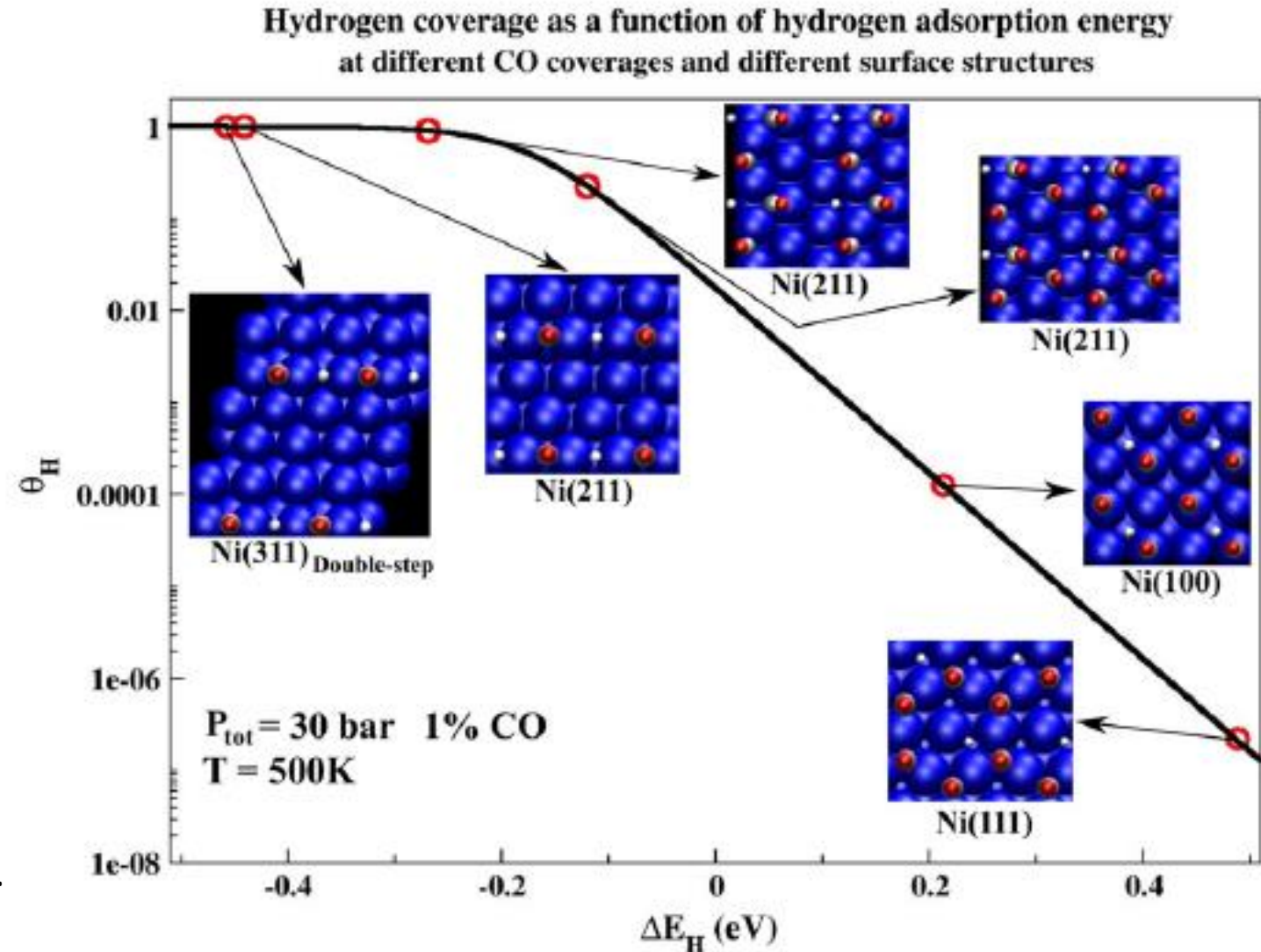- Stepped and kinked surfaces have lower activation energy.

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.

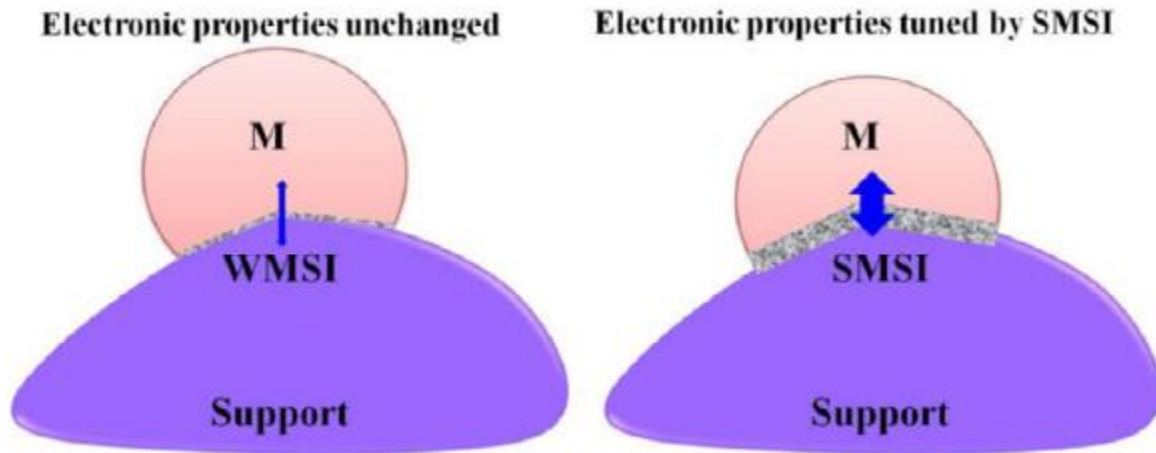- On stepped surface the H-coverage is close to 1.

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

Hydrogen coverage as a function of hydrogen adsorption energy at different CO coverages and different surface structures

P_{tot} = 30 bar   1% CO
T = 500K

θ_H

ΔE_H (eV)

Ni(311) Double-step
Ni(211)
Ni(211)
Ni(211)
Ni(100)
Ni(111)

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.

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

- Small metal particles flatten out on the oxide surface.

Electronic properties unchanged

M
WMSI
Support

Electronic properties tuned by SMSI

M
SMSI
Support

No encapsulation

M_I
WMSI
$M_{II}O_y$

Encapsulation (decoration)

M_I
$M_{II}O_{y-\delta}$
Spillover
SMSI
$M_{II}O_{y-\delta}$
Spillover
$M_{II}O_y$

Scheme 2. Electronic effect resulting from weak metal-support interactions (WMSI) and strong metal-support interactions (SMSI).
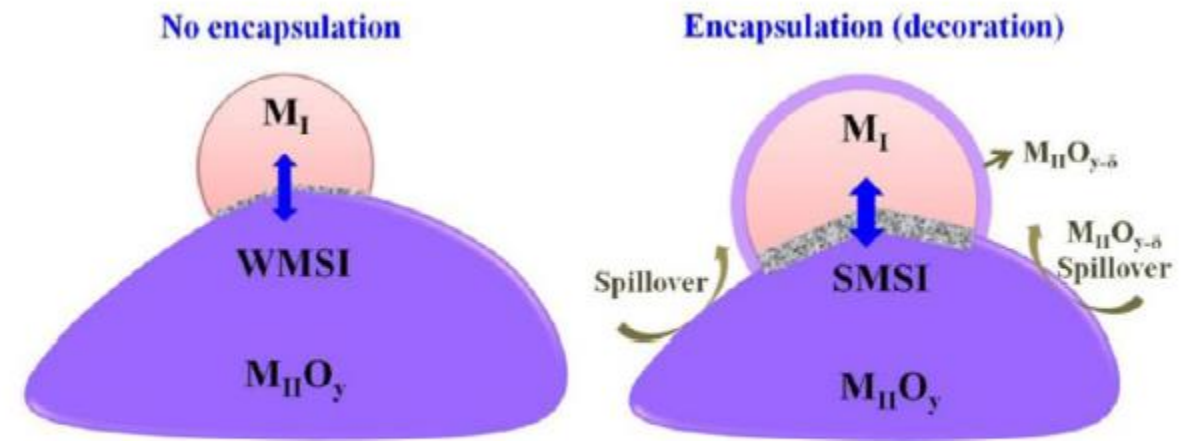
Scheme 3. Geometric effect of encapsulation or decoration resulting from strong metal-support interactions (SMSI).

Pan et al., J. Taiwan Int Chem Eng 74 (2017) 154.

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 QM$_t$

$$D \% = \frac{Q_{M_S}}{Q_{M_T}} \cdot 100 = \frac{n.Q_{adsorbat}}{Q_{M_T}} \cdot 100$$

WITH

$$Q_{M_T} = \frac{\%M}{100.M_M}$$

* 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)
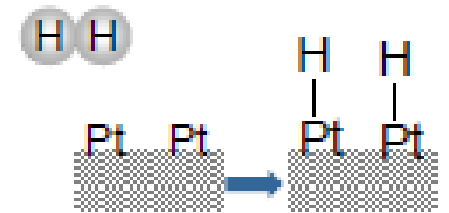
■ <u>In the definition of dispersion,</u> all surface atoms are considered equivalent; is not necessarily true in terms of catalytic activity.

   ■ corner atoms are usually more active than atoms on the flat surfaces

   ■ stoichiometry of chemisorption may also change

- **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) = $\rho.N.\pi.d^3/6$
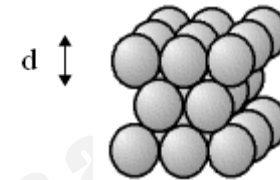
$$Surface\left(m^2/g_{metal}\right) = A/M = \frac{6}{\rho.\,d}$$

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 (m^2/atome)

n = stoichiometry of chemisorption

NA = Avogado number

AND

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

$$\Longrightarrow$$

$$d = \frac{6 \cdot 100M_M}{\rho.\sigma.N_A \cdot D}$$
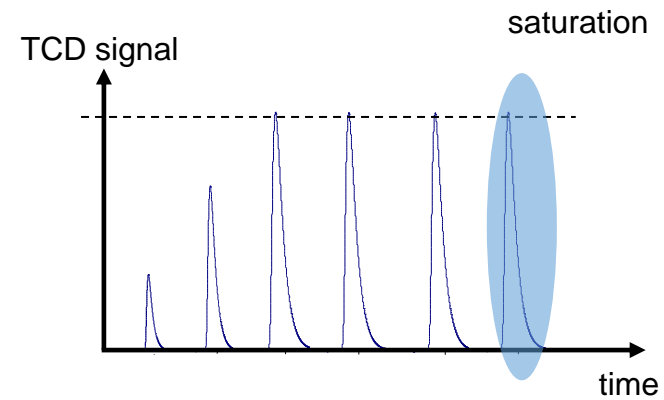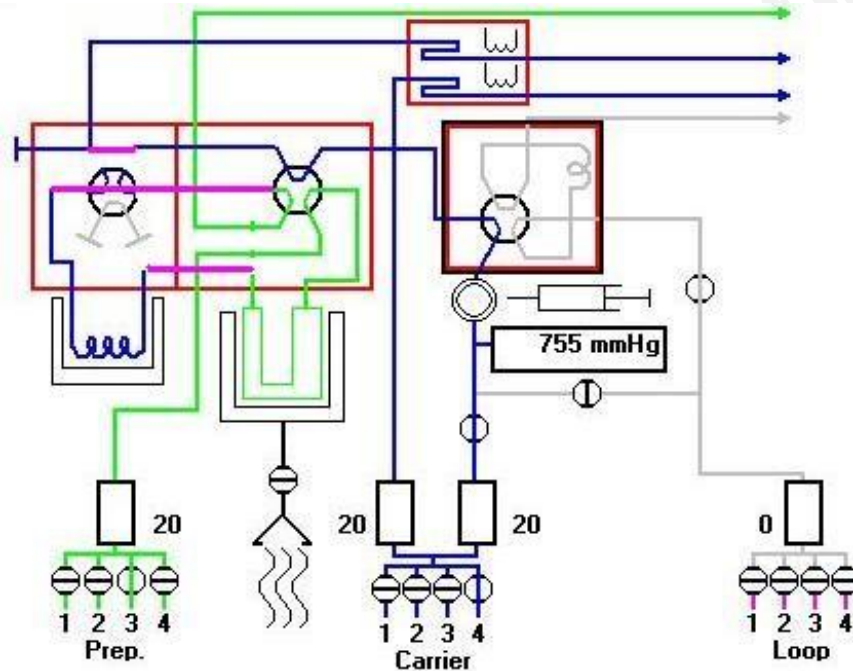
RELATION SIZE = f (DISPERSION)

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

Adsorbat   Pompe à vide
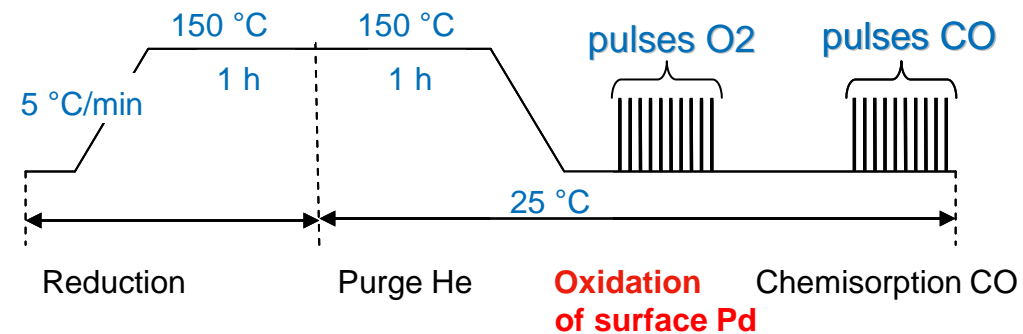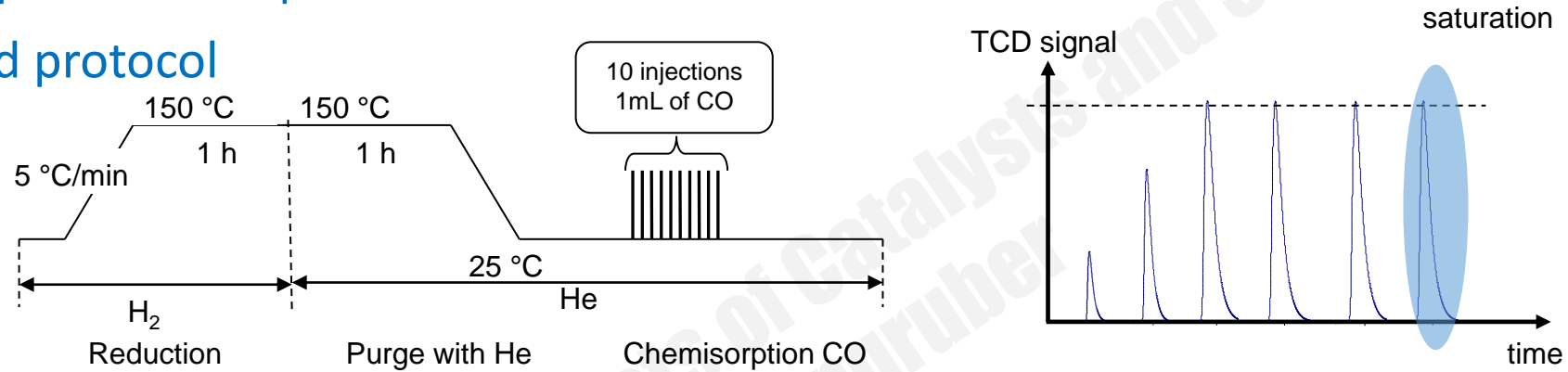
vannes

V0

V1
Echantillon

P

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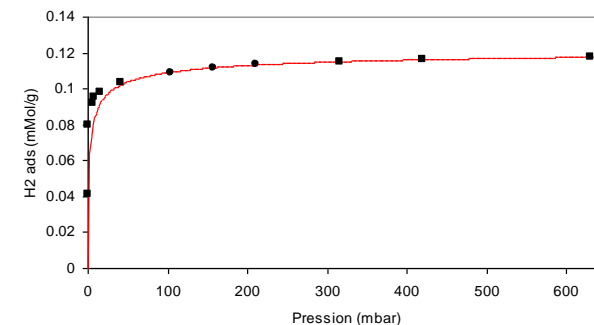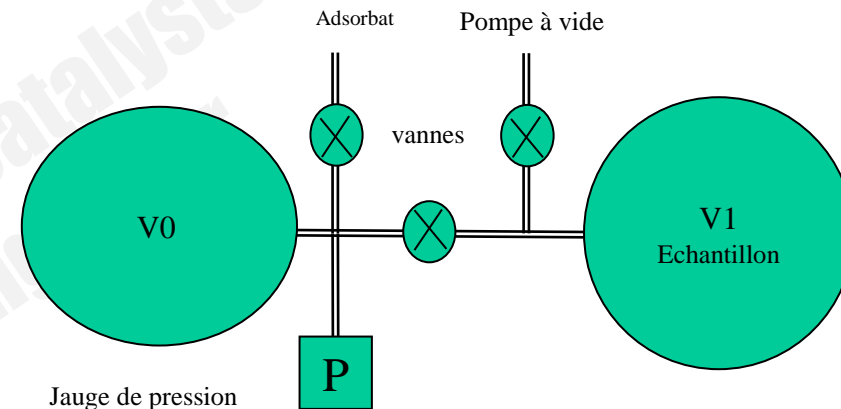
- Dynamic method – pulse method
  - send pulses of probe molecule with a carrier gas to the catalyst
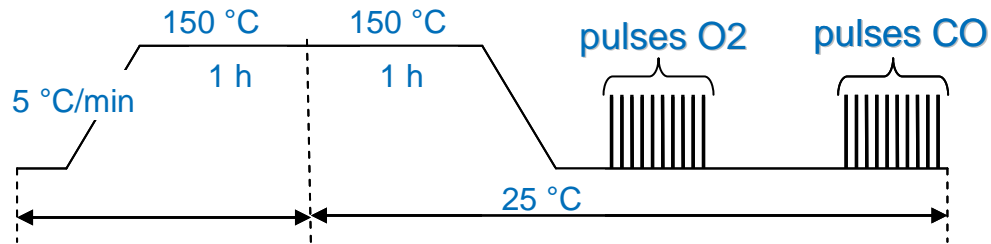 - detect consumption of probe molecule with TCD

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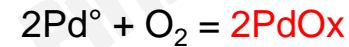- Modified protocol

WHICH SURFACE REACTIONS ARE GOING ON?

pulse CO

5 °C/min

150 °C
1 h

150 °C
1 h

pulses O2   pulses CO

25 °C

He purge

Oxidation of Pd

Reaction with CO

slow desorption CO_2 from the support material

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

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

Hypothesis 1: Pd°
$2Pd° + O_2 = 2PdOx$
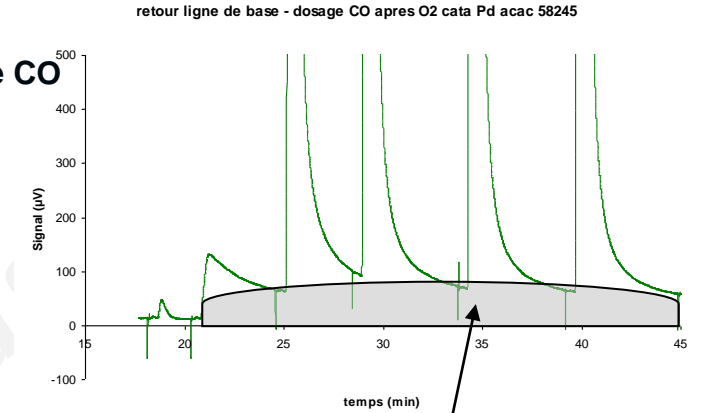
1 O_2 for 2 Pd
Stoichiometry = 2

Hypothesis 2 : Pd-H
$4Pd\text{-}H + O_2 = 4Pd° + 2H_2O$
$4Pd° + 2O_2 = 4PdOx$
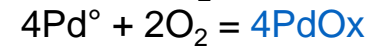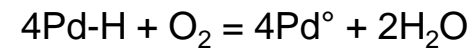
3 O_2 for 4 Pd
Stoichiometry = 4/3

$PdOx + CO = Pd° + CO_2$
$Pd° + CO = Pd\text{-}CO$
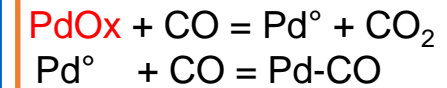
2 CO for 1 Pd
Stoichiometry = 1/2

- 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

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 H_2 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
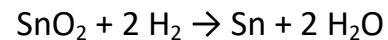
- Possible probe molecules : H_2, CO, O_2

- Method used at IFPEN
  - Reduction in H_2
  - Cooling in inert gas
  - Titration with pulses of O_2
    - $2 \text{ Pt-H} + 3/2 \text{ O}_2 \rightarrow 2 \text{ Pt-O} + H_2O$

- 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)

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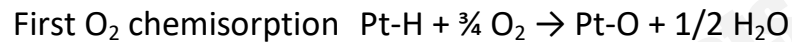
- Example PtSn/Al$_2$O$_3$ (reforming catalyst)
  - exploit the fact that Sn is less noble (less reducible) than Pt
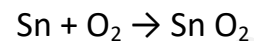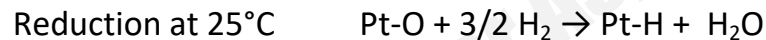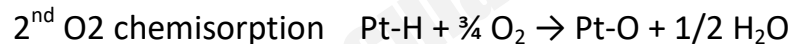 - Method to distinguish Pt and Sn

Calcination

Reduction at 500°C	PtO$_2$ + 5/2 H$_2$ → Pt-H + 2 H$_2$O	
	SnO$_2$ + 2 H$_2$ → Sn + 2 H$_2$O	reduces Sn in contact with Pt
First O$_2$ chemisorption	Pt-H + ¾ O$_2$ → Pt-O + 1/2 H$_2$O	titrates Pt
	Sn + O$_2$ → Sn O$_2$	and Sn that was reduced (VO$_1$)
Reduction at 25°C	Pt-O + 3/2 H$_2$ → Pt-H + H$_2$O	reduces only Pt
2nd O2 chemisorption	Pt-H + ¾ O$_2$ → Pt-O + 1/2 H$_2$O	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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