DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 2

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IC2MP

Outline

Introduction and general aspects

→ **Interfacial chemistry – Electrostatic adsorption**

Impregnation and drying

Sol-gel chemistry processing

Deposition – Precipitation – Coprecipitation

Shaping of solid catalysts – Monolith-based catalysts

Outline

Zeolite-based catalysts

Characterization – High throughput experimentation

Case studies:

- **Noble metal catalysts**
- **Methanol catalysts**
- **Hydrotreating catalysts**
- **……**

Outline

Interfacial chemistry – Electrostatic adsorption

1) Preparation of supported catalyst

2) Surface of oxidic support: ionization models

Point of zero charge

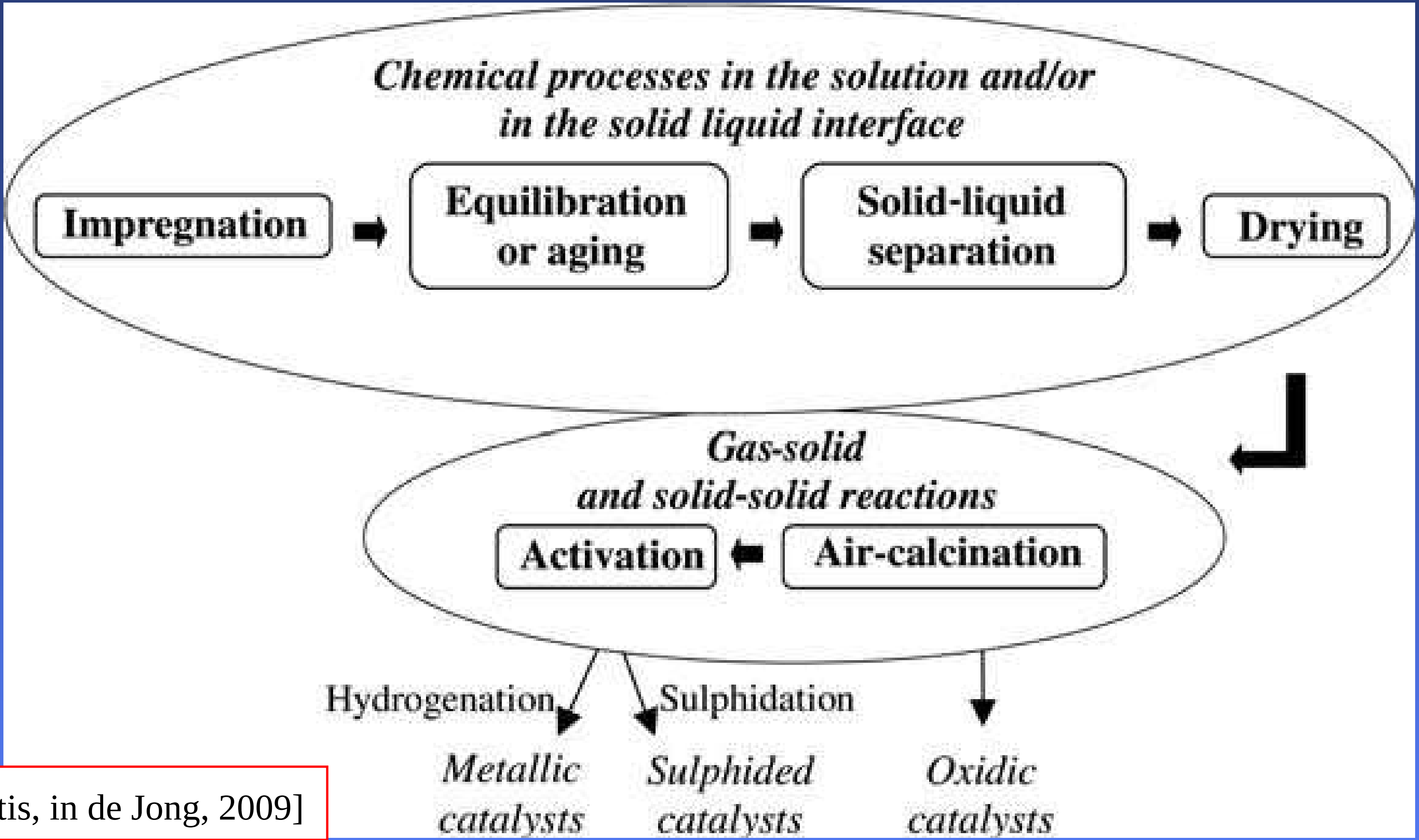
Isoelectric point

Zeta potential

3) Size and structure of interface

4) Modes of interfacial deposition

Preparation of supported catalysts: general procedure



[Lycourghiotis, in de Jong, 2009]

We want to obtain nanosized active phase particles on the surface of a support

The particles can be crystallized or amorphous

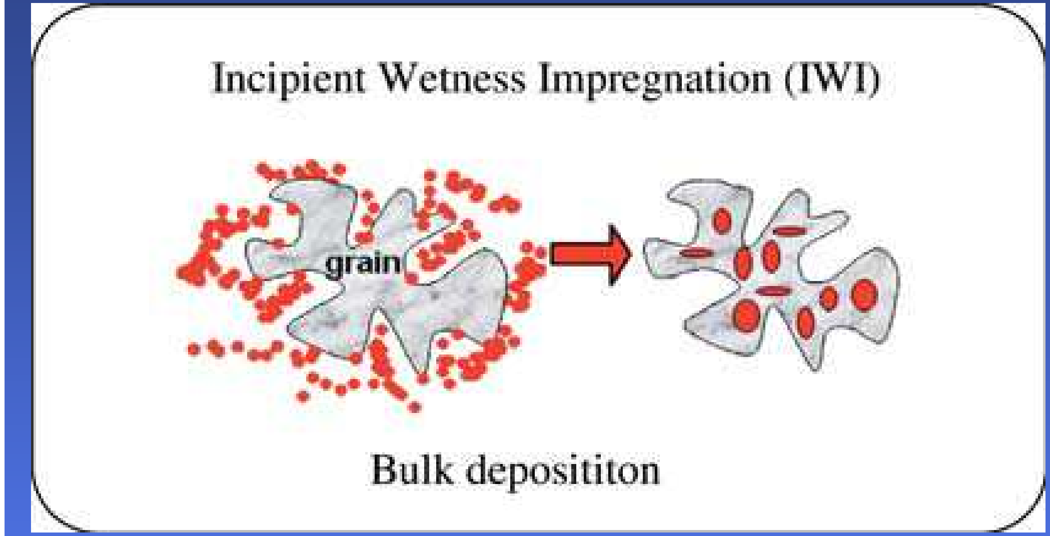
Nature of support: γ-alumina, α-Al_2O_3, SiO_2, TiO_2, carbons….

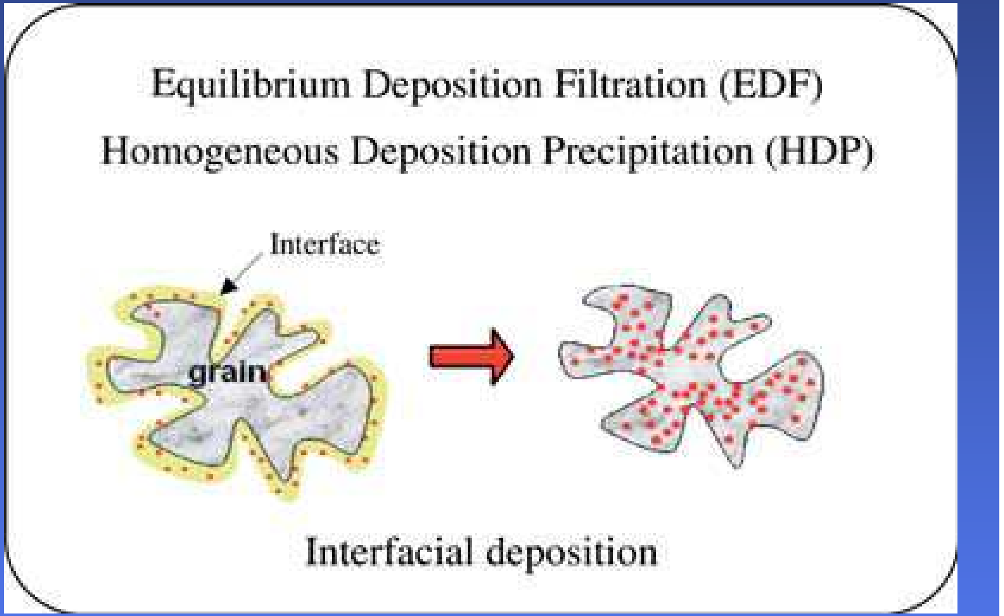
Preparation of supported catalysts

We have to choose the appropriate deposition mode of active phase precursor:

- Bulk deposition: dry deposition or incipient wetness impregnation

- Interfacial deposition: equilibrium adsorption





During drying, the active phase precursor precipitate or crystallized in the bulk solution inside the pores

Weak bonding with the support

➔Large final particles

Strong bonding with the support surface

Possibility to filtrate the remaining solution

➔ Small final nanoparticles

[Lycourghiotis, in de Jong, 2009]

Surface of oxidic support: ionization models

Point of Zero Charge (PZC) for charged surface in aqueous solution

Charge: few C m^{-2}

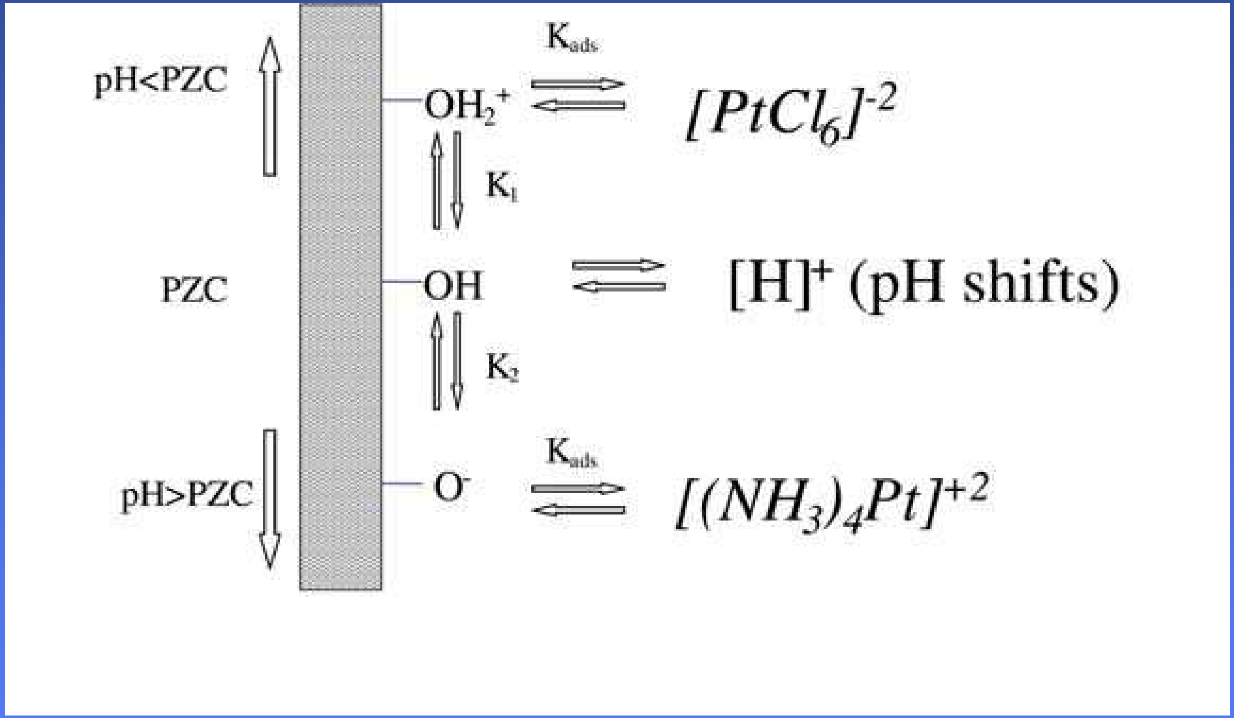
➔ Model

Support	**PZC**	**Complex**
MoO_3	<1	Cations
Nb_2O_5	2–2.5	Cations
SiO_2	4	Cations
Oxidized carbon black	2–4	Cations
Oxidized activated carbon	2–4	Cations
Graphitic carbon	4–5	Cations
TiO_2	4–6	Cations (or anions)
CeO_2	7	Cations or anions
ZrO_2	8	
Co_3O_4	7–9	Cations or anions
Al_2O_3	8.5	(Cations or) anions
Activated carbon	8–10	Anions
Carbon black	8–10	Anions

[Regalbutto, in de Jong, 2009]

Surface of oxidic support: ionization models

Point of Zero Charge (PZC) for charged surface in aqueous solution
Exemple: impregnation of platinum precursors on different oxides



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Surface of oxidic support: ionization models

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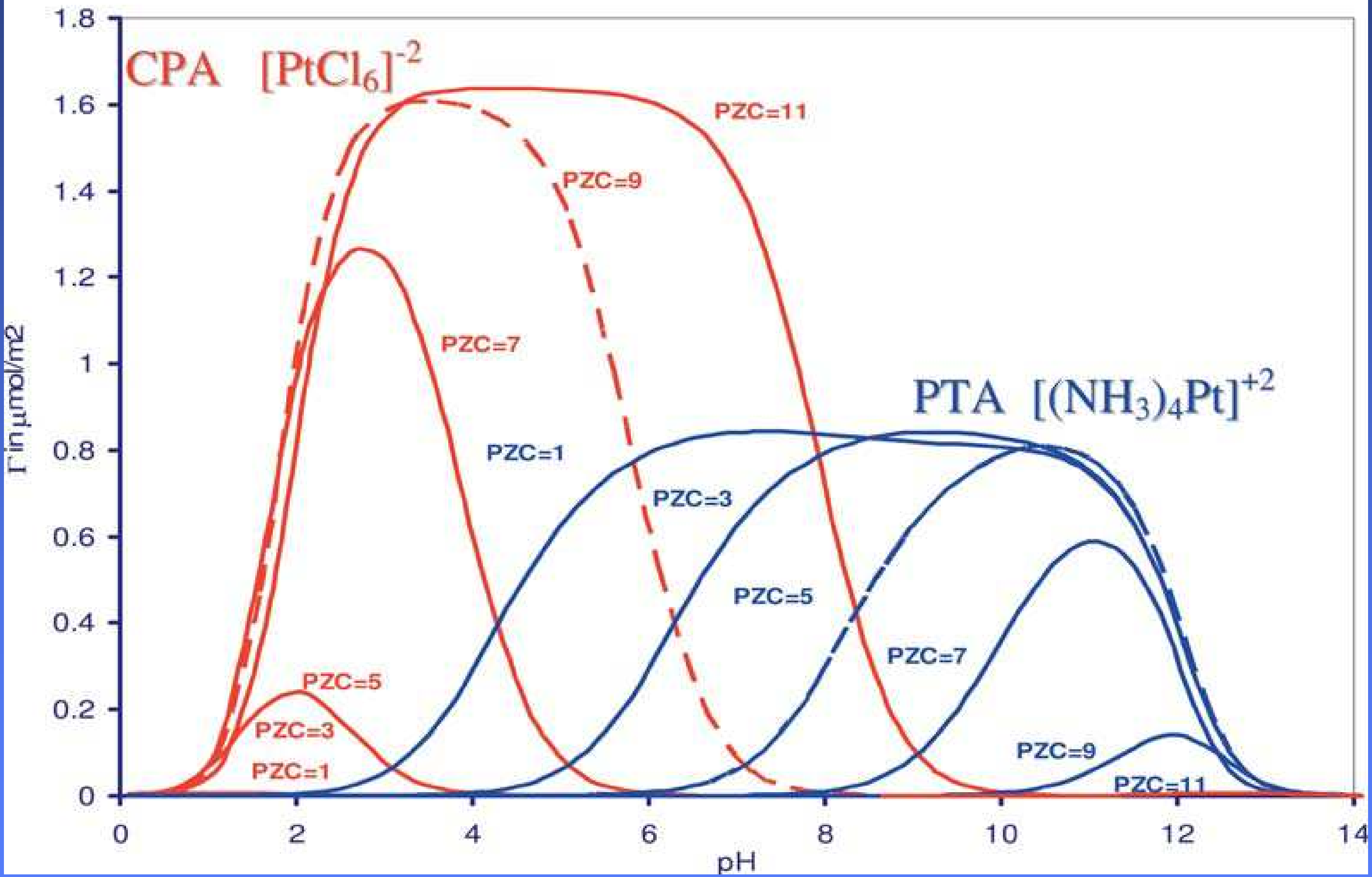
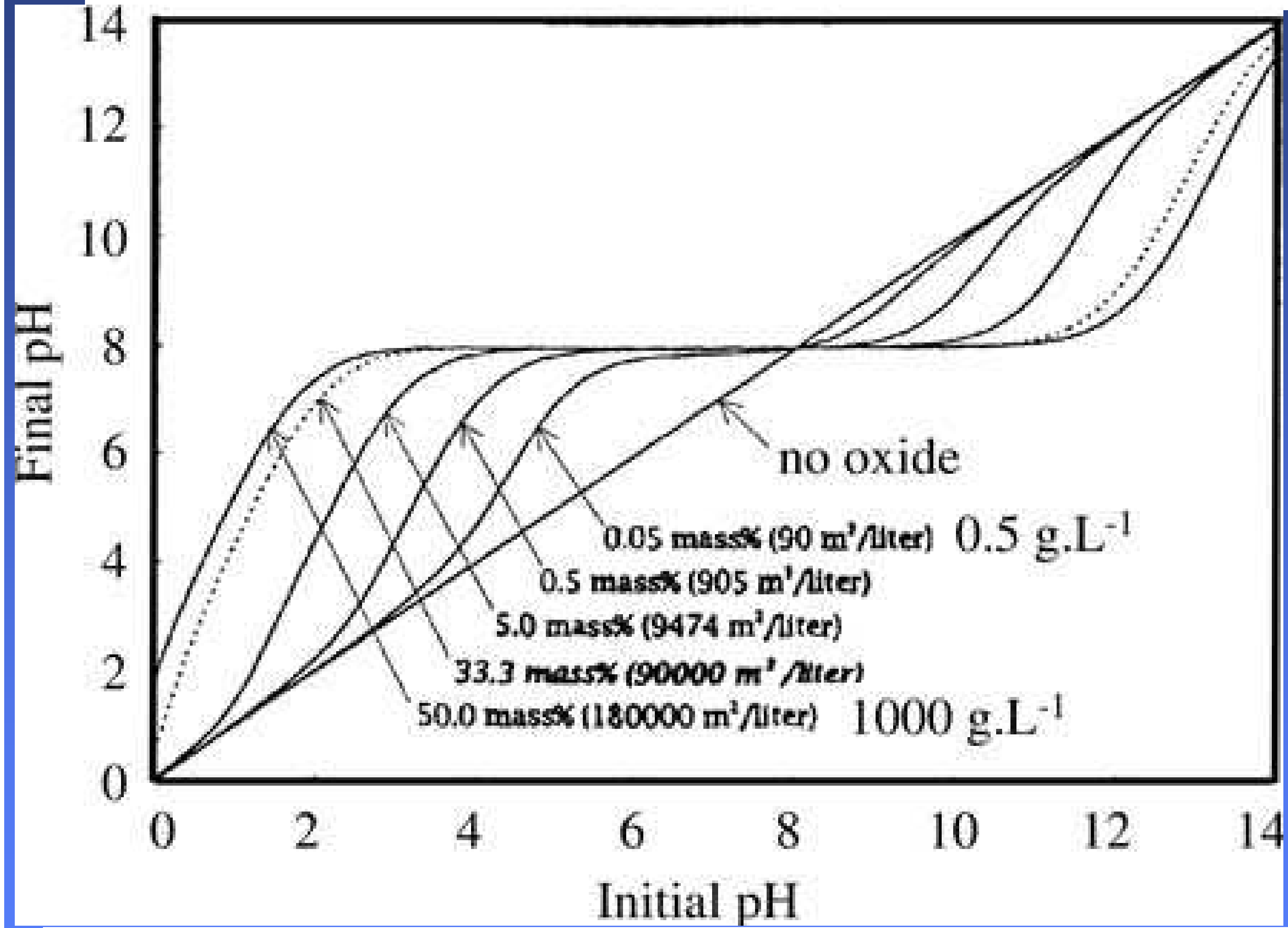


[Regalbutto, in de Jong, 2009]

Surface of oxidic support: ionization models

A key parameter: surface loading (m^2 L^{-1})

Ex. alumina, PZC = 8, Specific surface area = 180 m^2 g^{-1}



[Regalbutto, in de Jong, 2009]

pH shifts (pH final versus pH initial) as a function of surface loading

0.5 % pH = 3 ➔ pH = 4.5 5 % pH = 3 ➔ pH = 7 very limited adsorption

Surface of oxidic support: ionization models

Isoelectric point (IEP) for molecule or surface:
no global electrical charge, but possibility of local charge

Ex.: zwitterion for amino-acid: $\mathbf{pH(IEP) = (pK_1 + pK_2)/2}$

For particles: IEP = PZC in absence of specific adsorption

PZC: absence of any type of surface charge
IEP: possibility to have localized surface charge on the same surface

[Regalbutto, in de Jong, 2009]

Surface of oxidic support: ionization models

Multisite surface complexation:

M-OH

M-OH-M or M_2OH

M-OH(M)-M or M_3OH

Calculation of formal surface charge: Pauling Valence Bond

Ex. silica

Ex. γ-alumina: acidic and basic surface OH groups

Relation with infra-red spectroscopy: stretching vibration ν(OH)

Size and structure of interface

Model of charged surface: double layer (Stern-Gouy-Chapman model)

- **Stern or compact layer**
- **Diffuse layer**
- **Slipping or shear plane: limit of diffuse layer that accompanies particles**
- **Size of diffuse layer depends on ionic strength**

$$I = \Sigma c_i z_i^2$$

Variation of size with I:

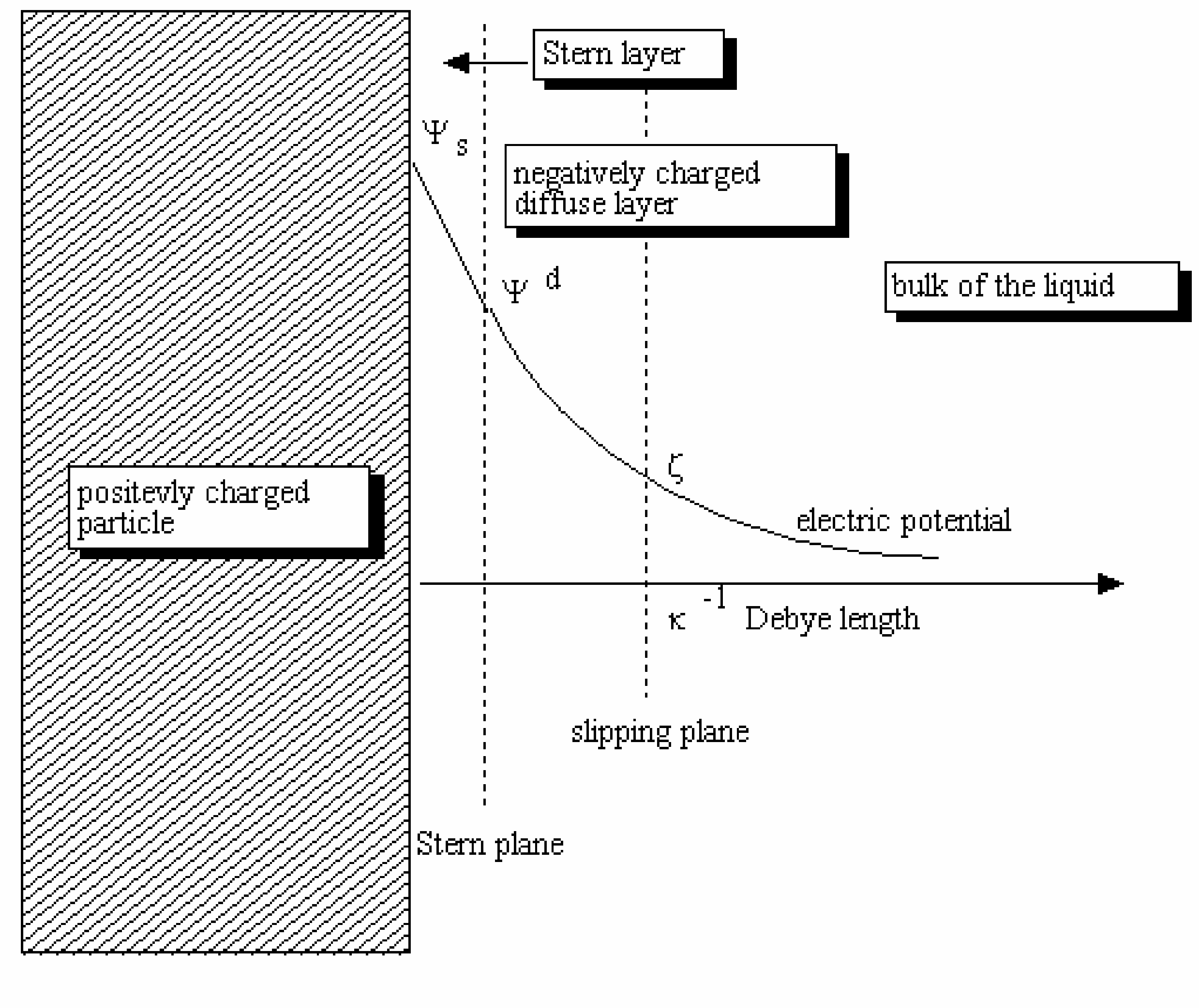
Size decreases when I increases

Variation of electric potential

Potential at the shear plane: zeta-potential or ζ-potential

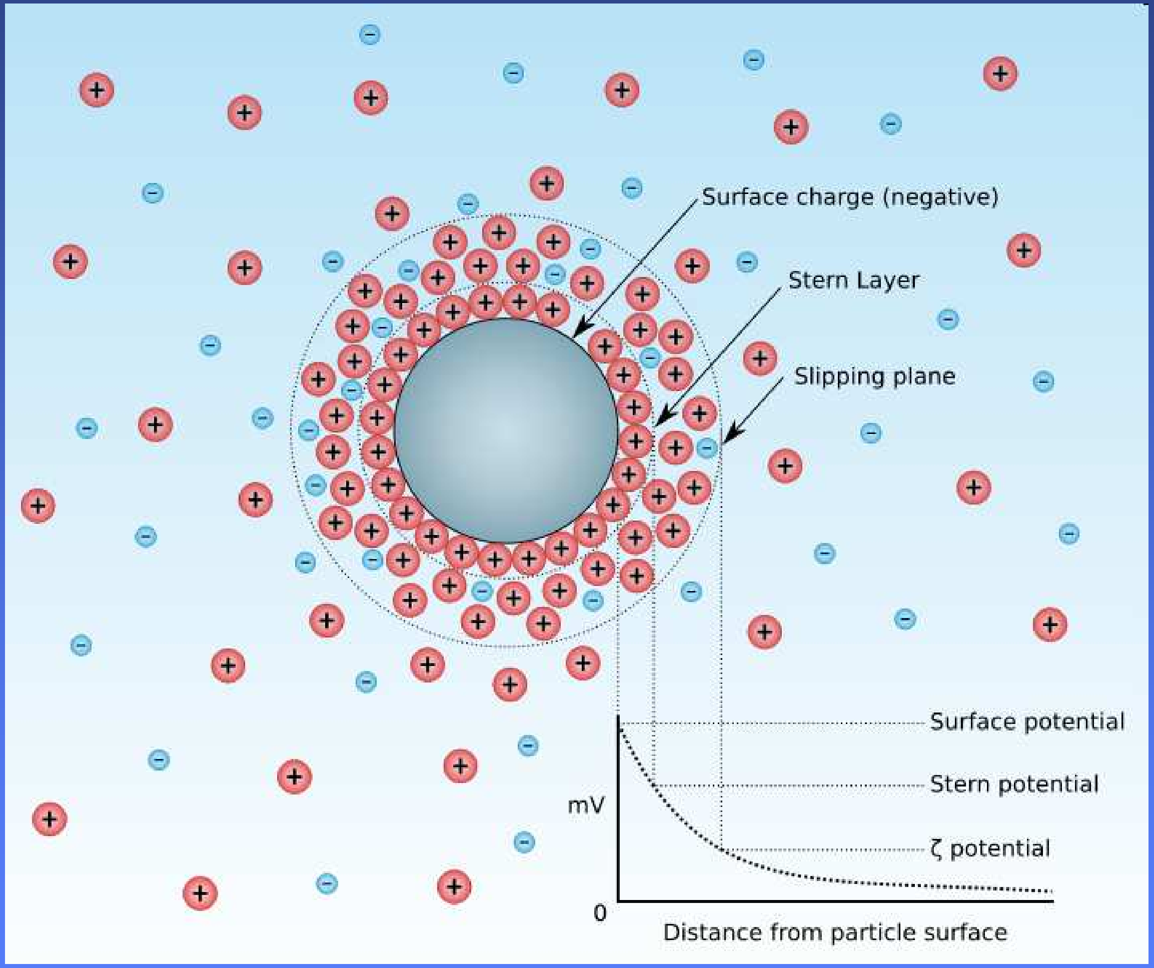
Chemical composition at which ζ-potential = 0 ➔ PZC

Size and structure of interface



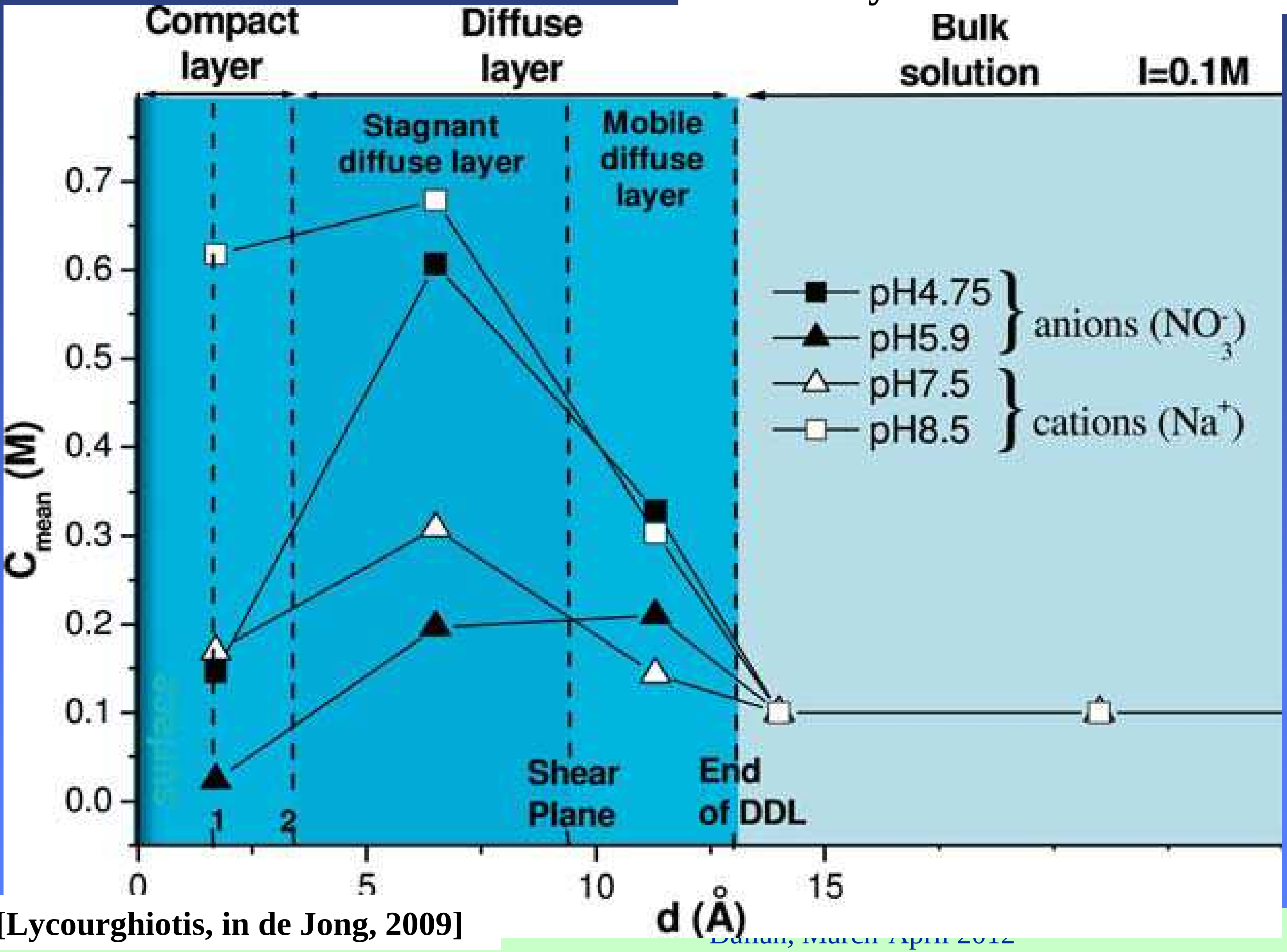
Size and structure of interface

Another view



Size and structure of interface

titania/aqueous solution interface and mean concentration of the counterions inside the various layers of the interface.



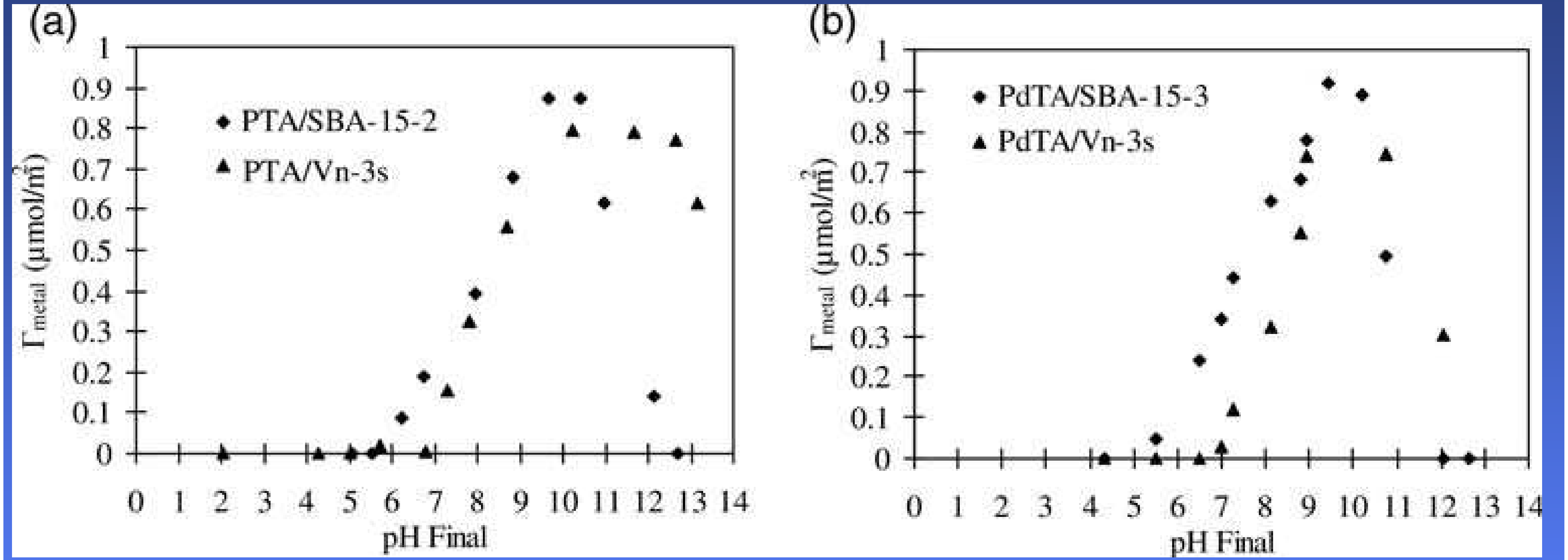
[Lycourghiotis, in de Jong, 2009]

Modes of interfacial deposition

Simple electrostatic adsorption (previous model)

Ex.: $[Pt(NH_3)_4]^{2+}$ and $[Pd(NH_3)_4]^{2+}$

[Regalbutto, in de Jong, 2009]



Pure electrostatic uptake versus pH over nonordered silica (Vn-3s, 175 $m^2 g^{-1}$) and ordered mesoporous silica (SBA-15-2, 575 $m^2 g^{-1}$, SBA-15-3, 998 $m^2 g^{-1}$).

Same surface loading (1000 $m^2 L^{-1}$)

➔ very similar curves

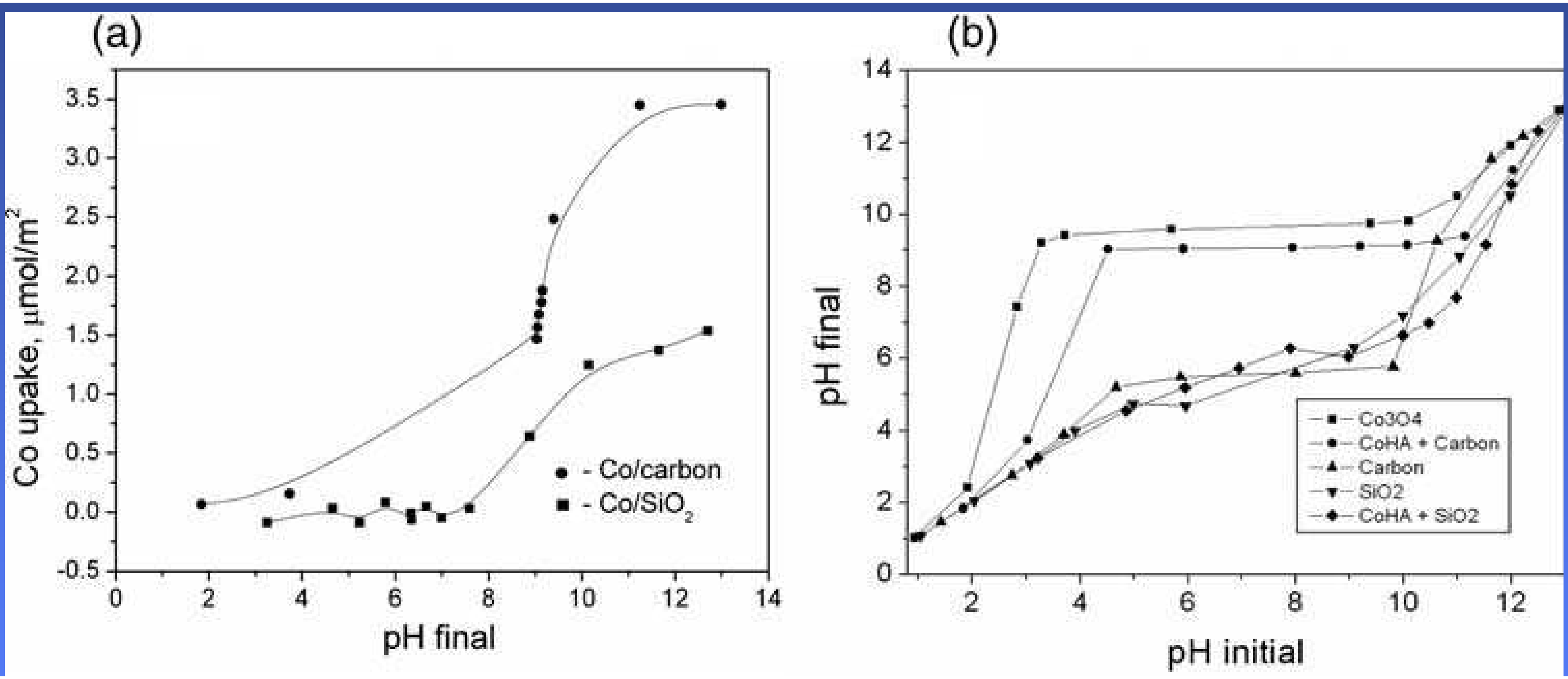
Modes of interfacial deposition

Surface reaction: possibility of ligand exchange with surface OH group

➔ formation of surface inner sphere complexes

aqua complexes: Fe, Co, Ni, Cu chloro complexes: Pt, Pd

Ex.: $[Co(NH_3)_6]^{3+}$ /C graphitic or SiO_2 PZC = 4 for both supports



Cobalt hexaammine adsorption over silica and carbon with similar PZCs (4):

(a) uptake versus pH, and (b) pH shifts

➔ over C majority of area is Co_3O_4

[Regalbutto, in de Jong, 2009]

Modes of interfacial deposition

Ex.: $[Co(H_2O)_6]^{2+}/TiO_2$

Mode of interfacial deposition?

25 °C

pH 6.0-7.5

Concentration: 10^{-3} to 2 10^{-2} mol L^{-1}

I = 0.1 mol L^{-1}

TiO_2: P25 (Evonik) contains major anatase and minor rutile

Deposition at PZC

➔ decrease of pH upon adsorption

➔ shift of PZC to lower values

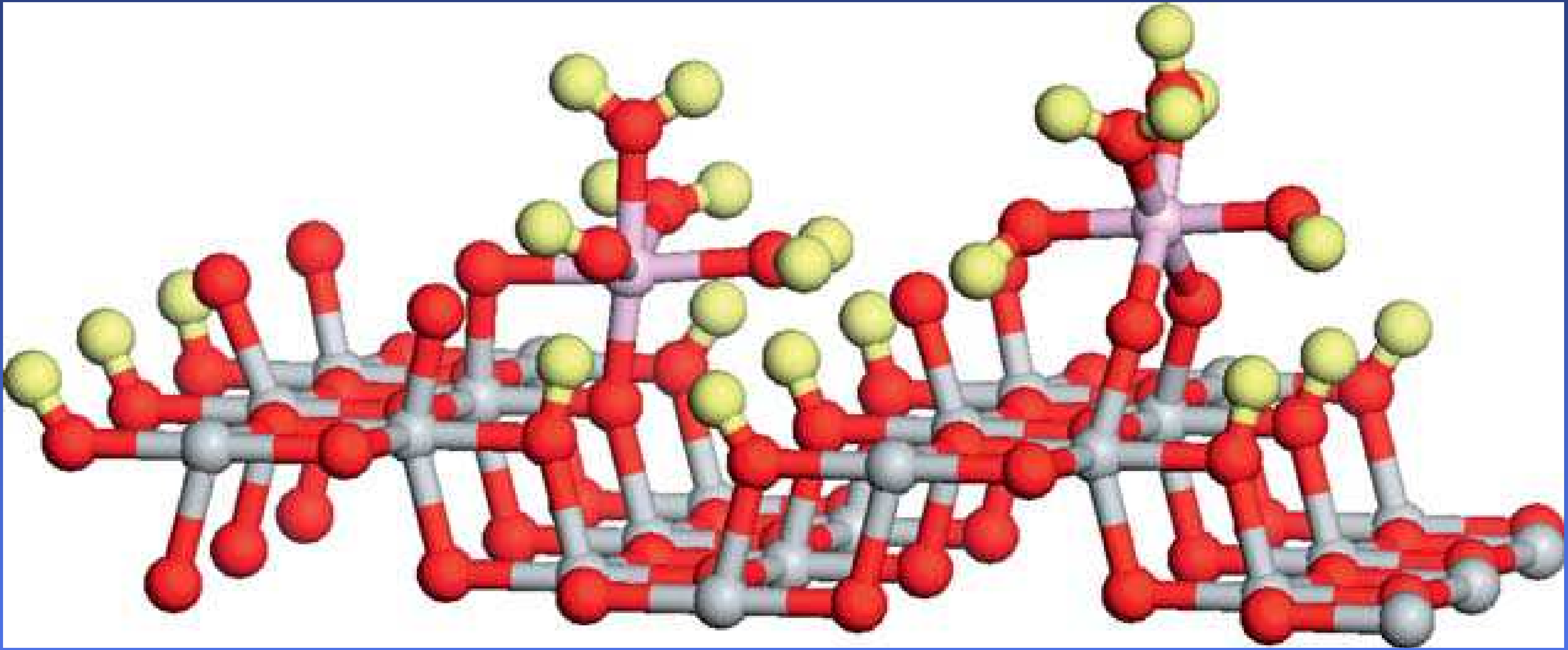
➔ increase of ζ-potential determined at different pH

➔ n(H^+ released)/n(cation adsorbed) = 2

➔ inner sphere complexes

Modes of interfacial deposition

Quantum mechanical calculations



The TO−TO (right) and BO−TO (left) configurations of the Co(II) inner-sphere complexes formed on the anatase (1 0 0) crystal face.

The O, Ti, H, and Co atoms are represented respectively by red, gray, yellow, and pink balls.

[Lycourghiotis, in de Jong, 2009]

End of part 2