DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 5

Supported by the Chinese Academy of Sciences

Charles Kappenstein, Professor Emeritus, University of Poitiers, France

DALIAN INSTITUTE OF CHEMICAL PHYSICS,
CHINESE ACADEMY OF SCIENCES

1431
Université de Poitiers

中國科學院
CHINESE ACADEMY OF SCIENCES

cnrs
dépasser les frontières

Faculté des Sciences Fondamentales et Appliquées
UFR SFA
Université de Poitiers

Institut de Chimie des Milieux et Matériaux de Poitiers
IC2MP

Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation, drying, calcination and/or reduction

Sol-gel chemistry processing

➡ **Deposition – Precipitation and 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

Deposition – Precipitation and Coprecipitation

→ 1) Introduction

2) Backgrounds: thermodynamics

3) Molecular details

4) Case studies

Introduction

Use of metal compound with low solubility
The precipitation takes place at the surface of the support
The support (powder, µm-sized, or pellets, mm-sized) is in suspension in the solution

Ex.: $Ni^{2+}(aq) + 2\ OH^{-}(aq) \rightarrow Ni(OH)_2(s)$

How to introduce the hydroxyl groups?

- injection of an alkaline solution
  but difficult to control, high local pH change
- hydrolysis of urea

$$CO(NH_2)_2(aq) + 2\ H_2O(l) \rightarrow HCO_3^{-}(aq) + NH_4^{+}(aq) + NH_3(aq)$$

pH of the resulting solution?
→ see predominance diagram versus pH

General methods to bring about precipitation

- pH change
- reduction
- ligand removal

Outline

Deposition – Precipitation and Coprecipitation

1) Introduction

2) Backgrounds: thermodynamics

3) Molecular details

4) Case studies

Background: thermodynamics

solute ➔ solid

Conditions for the formation of nanoparticles on the support?

➔ compare energy of solute and energy of solid

But unfavorable high surface energy of small particles

Balanced factors of bulk and surface free energy

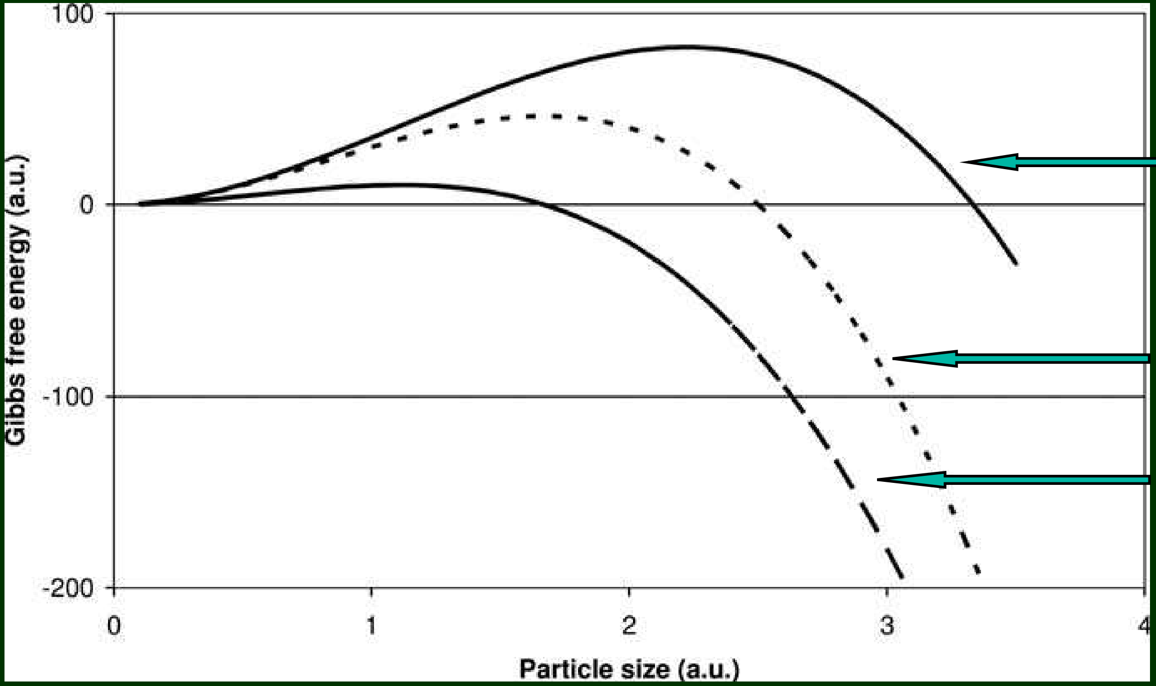
➔ overall Gibbs free energy change

$$\Delta G_{tot} = ¾\, \pi\, r^3 .\ \Delta\mu_{sl} + 4\pi\, r^2 . \gamma$$

r = **radius of the particle**
$\Delta\mu_{sl}$ = **difference in thermodynamic potential of solid and solute (negative)**
γ = **surface free energy of the solid in contact with solution or support.**

➔ See figure explanations

Background: thermodynamics



high solubility –high surface energy

low solubility – high surface energy

high solubility – low surface energy

The facilitated nucleation by the presence of the support plays a key role

But nucleation in the bulk liquid may take place in the vicinity of the injection point

Challenge ➔ restrict concentration gradients

- double-walled thermostatted vessel (fine control of temperature
- stirrer: vigorous stirring
- pH-electrode
- two or three injections point (liquid and gas)
- prevent evaporation of solvent

Outline

Deposition – Precipitation and Coprecipitation

1) Introduction

2) Backgrounds: thermodynamics

➡ 3) Molecular details

4) Case studies

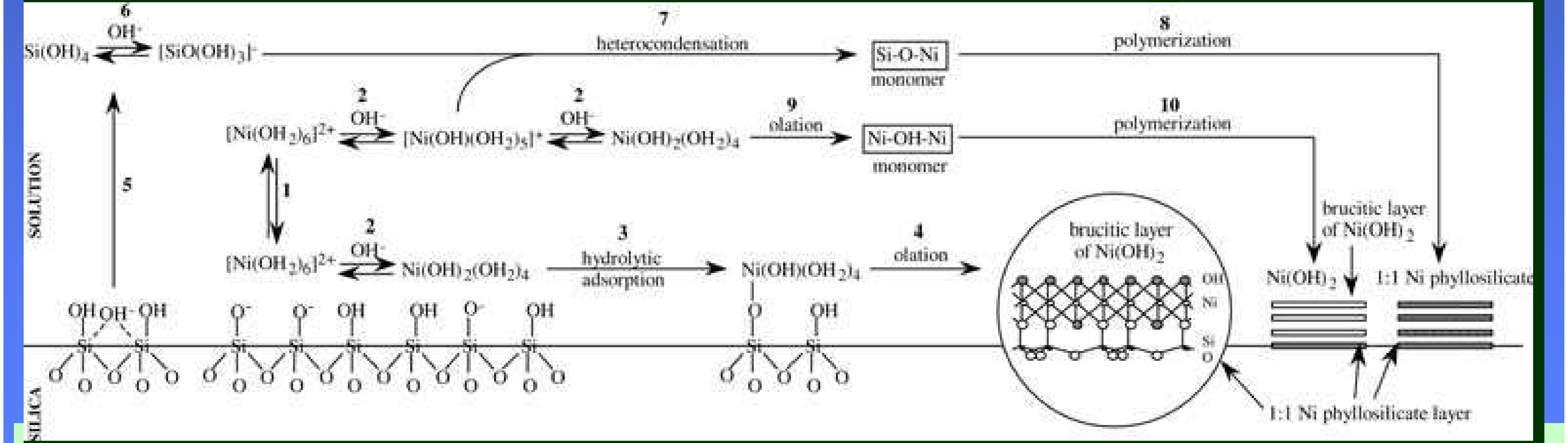
Molecular details: Ni/SiO_2

1. Electrostatic adsorption of $[Ni(OH_2)_6]^{2+}$ onto silica

2. With increasing pH, $[Ni(OH_2)_6]^{2+}$ is hydrolyzed to form $[Ni(OH)(OH_2)_5]^+$ and $[Ni(OH)_2(OH_2)_4]$

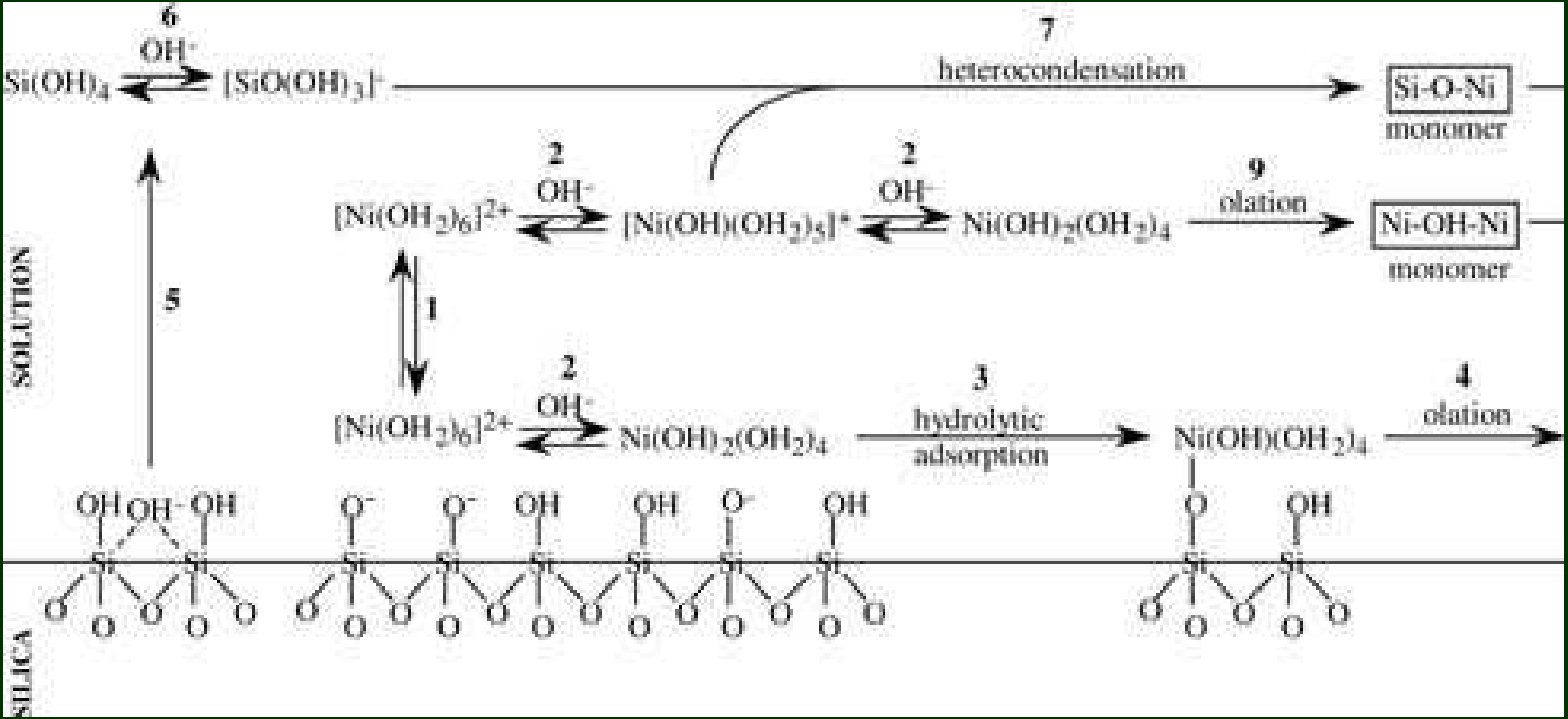
3. Adsorption of all of these species onto silica
Ex.: $[Ni(OH)(OH_2)_5]^+ + \equiv Si\text{-}OH \rightarrow \equiv Si\text{-}O\text{-}Ni(OH_2)_5^+ + H_2O$

4. Several routes from solution and from surface reactions to form nickel hydroxide and nickel phyllosilicate



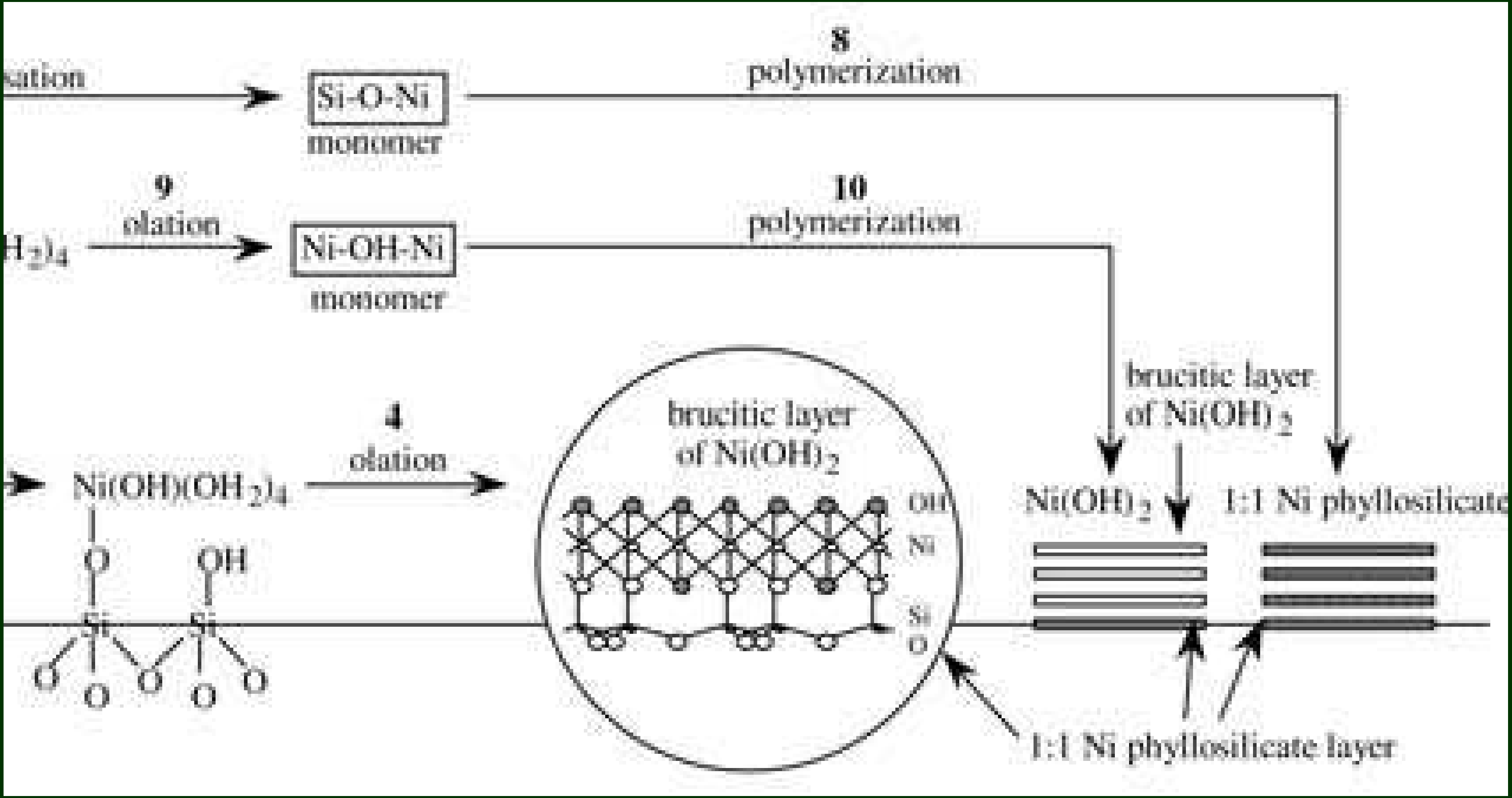
Molecular details: Ni/SiO_2

Enlargement



Molecular details: Ni/SiO$_2$

Enlargement



Outline

Deposition – Precipitation and Coprecipitation

1) Introduction

2) Backgrounds: thermodynamics

3) Molecular details

➡ 4) Case studies

Case studies

Ex. 1: La_2O_3/SiO_2

$La(NO_3)_3(aq) + NH_3(aq)$ ➔ formation of lanthanum hydroxide

pH from 4 to 10

then interaction between $La(OH)_3$ and SiO_2

Formation of an amorphous phase

Write the balanced equation of the reaction

$$La^{3+}(aq) + 3\ NO_3^-(aq) + 3\ NH_3(aq) + 3\ H_2O(l) \rightarrow La(OH)_3(s) + 3\ NH_4^+(aq) + 3\ NO_3^-(aq)$$

Ex.2: $FeCu/SiO_2$

- **Cu^{2+} deposited onto silica using urea**
- **Redispersion of the solid in a iron(III) nitrate solution**
- **Injection of $NH_3(aq)$ ➔ precipitation of iron hydroxide onto the copper loaded silica**

Case studies – reduction deposition precipitation

The support is suspended in a solution of the metal precursor and a reducing agent is added (formaldehyde, hydrazine…) to deposit the metal.

Ex.: Ag/SiO_2

deposition of silver from the diamminesilver complex and formaldehyde

Temperature 5 °C to avoid premature reaction, then increase to 50 °C

Write the equation of the reaction

$$2\,[Ag(NH_3)_2]^+(aq) + 2\,NO_3^-(aq) + HCHO(aq) + 3\,OH^-(aq)$$
$$\rightarrow 2\,Ag(s) + 4\,NH_3(aq) + HCOO^-(aq) + 2\,H_2O(l) + 2\,NO_3^-(aq)$$

Case studies – reduction deposition precipitation

Ex.: Mo_2O_3/SiO_2

Deposition of molybdenum(III) oxide onto silica spheres 1.5 mm diameter

Reactants: ammonium molybdate, hydrazine
pH 8.7
Temperature 0 to 60 °C
Loading 1 to 20 wt.-% Mo

Write the equation of the reaction

$$4\,MoO_4^{2-}(aq) + 8\,NH_4^+(aq) + 3\,N_2H_4(aq) \rightarrow 4\,Mo(OH)_3(s) + 3\,N_2(g) + 8\,NH_3(aq) + 4\,H_2O(l)$$

Case studies – reduction deposition precipitation

Ex.: Mo_2O_3/SiO_2

At low Mo loading, short reaction time ➔ deposition at the center of the sphere

At more elevated Mo loading ➔ progressive enrichment up to the surface of the sphere

Technique to control this characteristics?

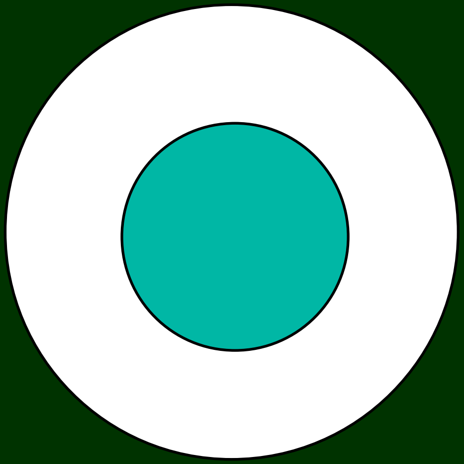
EDX coupled with SEM

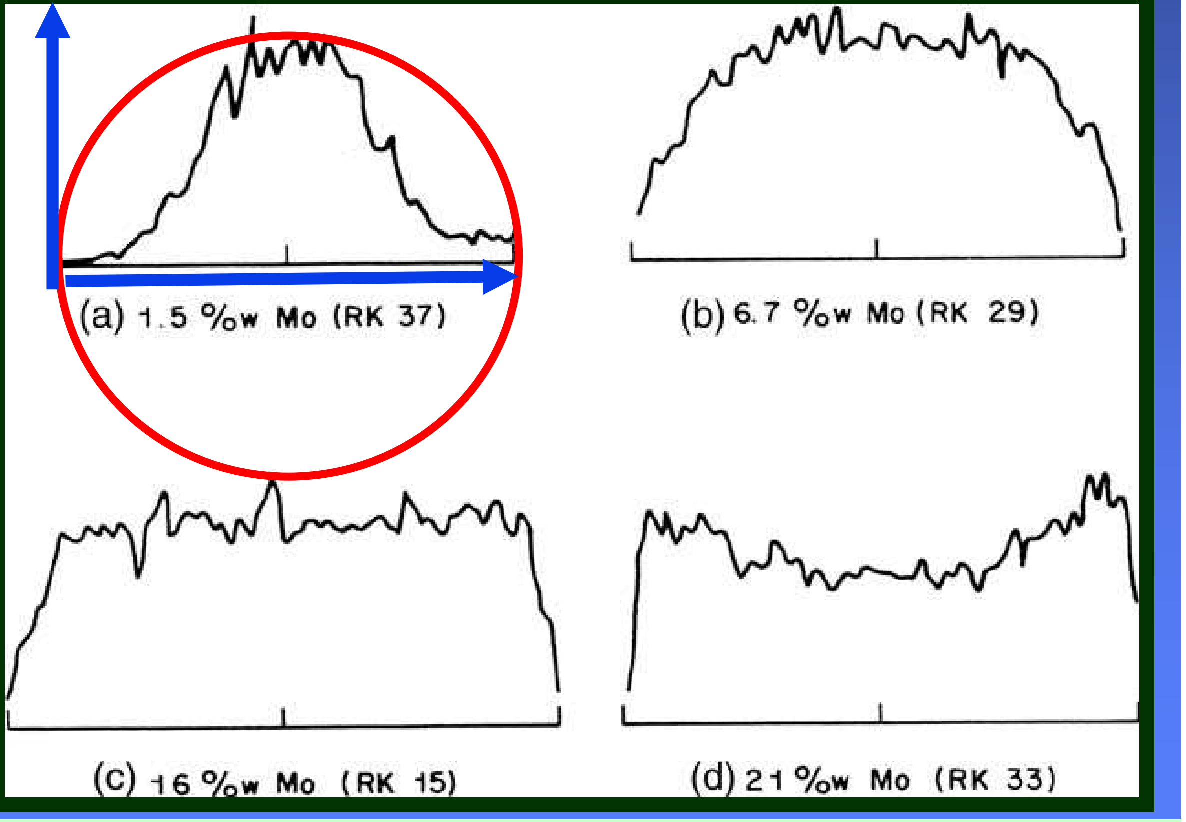
(Energy Dispersive X-ray analysis)

(Scanning Electron Microscopy)

EDX line scans for Mo concentration versus position

➔ egg yolk distribution





Case studies – reduction deposition precipitation

Ex.: MoS_2/Al_2O_3

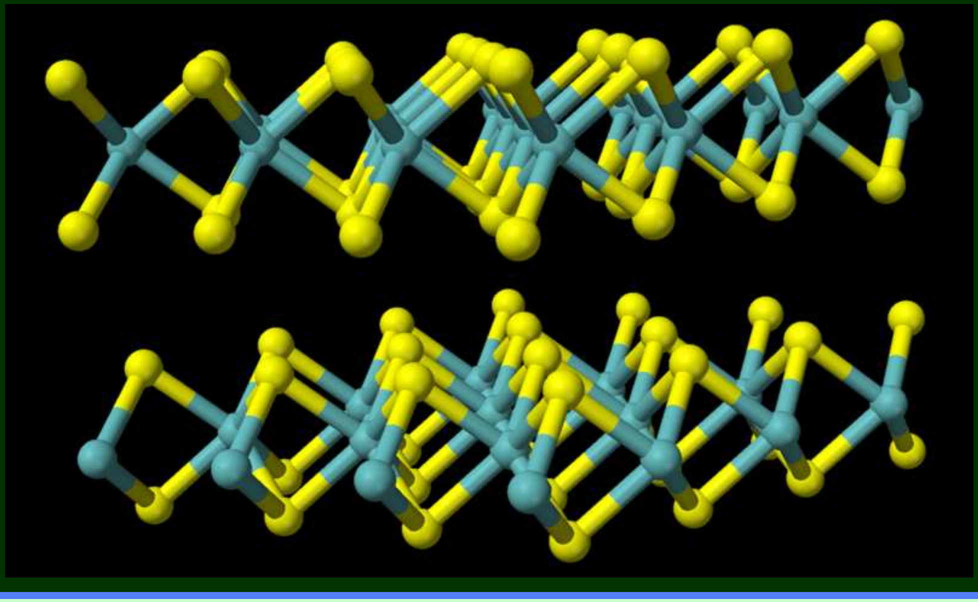
Ammonium tetrathiomolybdate (VI) + hydrazine in aqueous solution

Write the balanced equation of the reaction

$4\ NH_4^+(aq) + 2\ MoS_4^{2-}(aq) + N_2H_4(aq) \rightarrow 2\ MoS_2(s) + N_2(g) + 4\ NH_4^+(aq) + 4\ HS^-(aq)$

➔ Formation of nanocrystals with an average stacking number of 3 and an average length along the basal planes of 3 nm

Structure of MoS_2?
Mo: CN 6
S: CN 3
CN = coordination number



Case studies – reduction deposition precipitation

Formation of bimetallic active phase

Ex.: AgPt/SiO_2

1) form nanoparticles of Pt (2 nm)

2) use reduction of diamminesilver complex by formaldehyde

3) under carefully chosen conditions ➔ deposition of Ag on Pt particles (3 nm)

Ex.: PtPd/Al_2O_3

1) form nanoparticles of Pd

2) adsorb hydrogen of the Pd particles

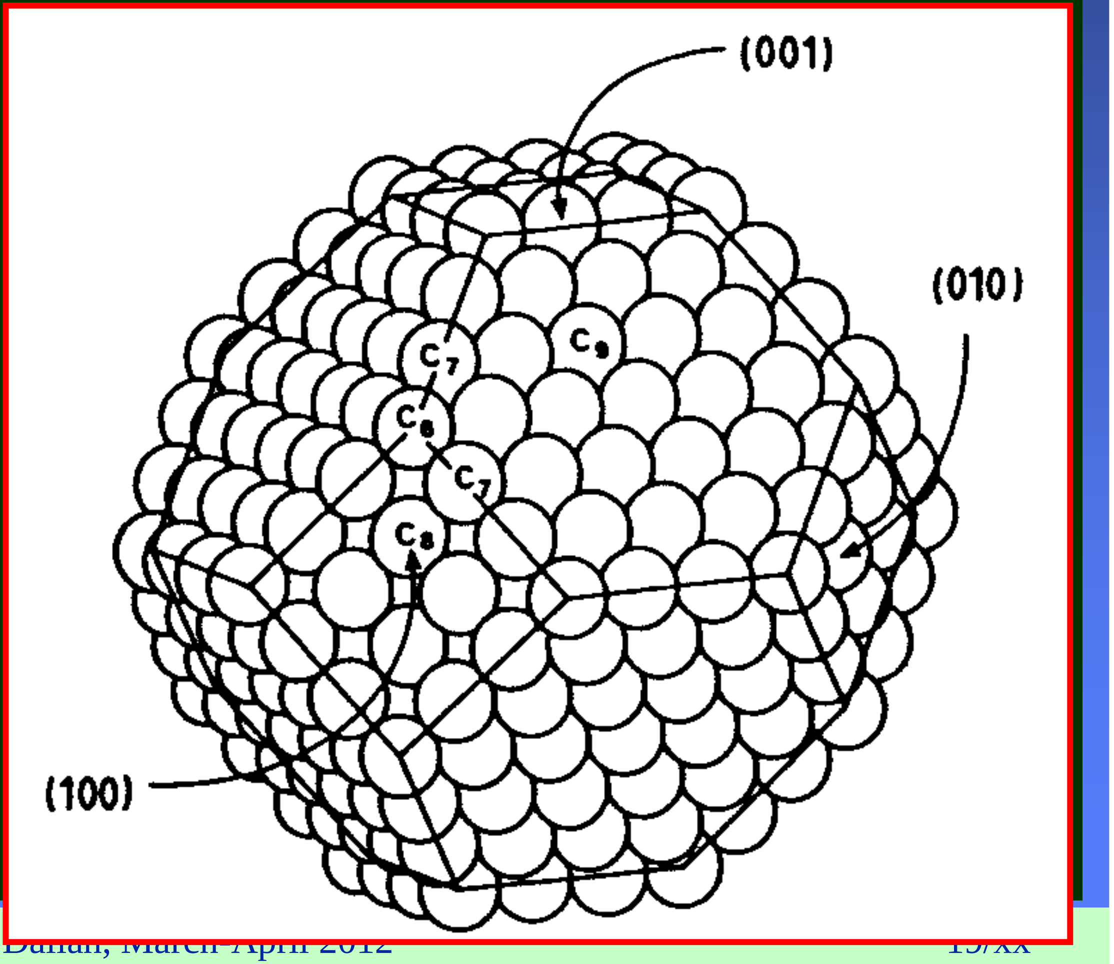
3) add Pt^{2+} ions in acetone

➔ Pt^{2+} is reduced by H-adsorbed atoms

Pt^{2+}(acetone) + 2 H-Pd(s)

➔ 2 Pt-Pd + 2 H^+(acetone)

➔ Pt atoms are preferentially deposited on low-coordination sites of Pd particles (remember cuboctahedron)



Case studies – reduction deposition precipitation

Deposition of metal oxides (columns 4, 5, 6) - how to prepare V_2O_5/SiO_2 ?

VO_4^{3-} does not interact with silica surface (why?)

➔ possible reduction of the oxoanions? ➔ see the E-pH diagram

Reactants Ammonium metavanadate + Formic acid

$NH_4VO_3(s) + H_2O(l) \rightarrow NH_4^+(aq) + H_2VO_4^-(aq)$

E^0 $CO_2(g)/HCOOH(aq) = 0.11$ V

Possible reduction up to $V^{3+}(aq)$

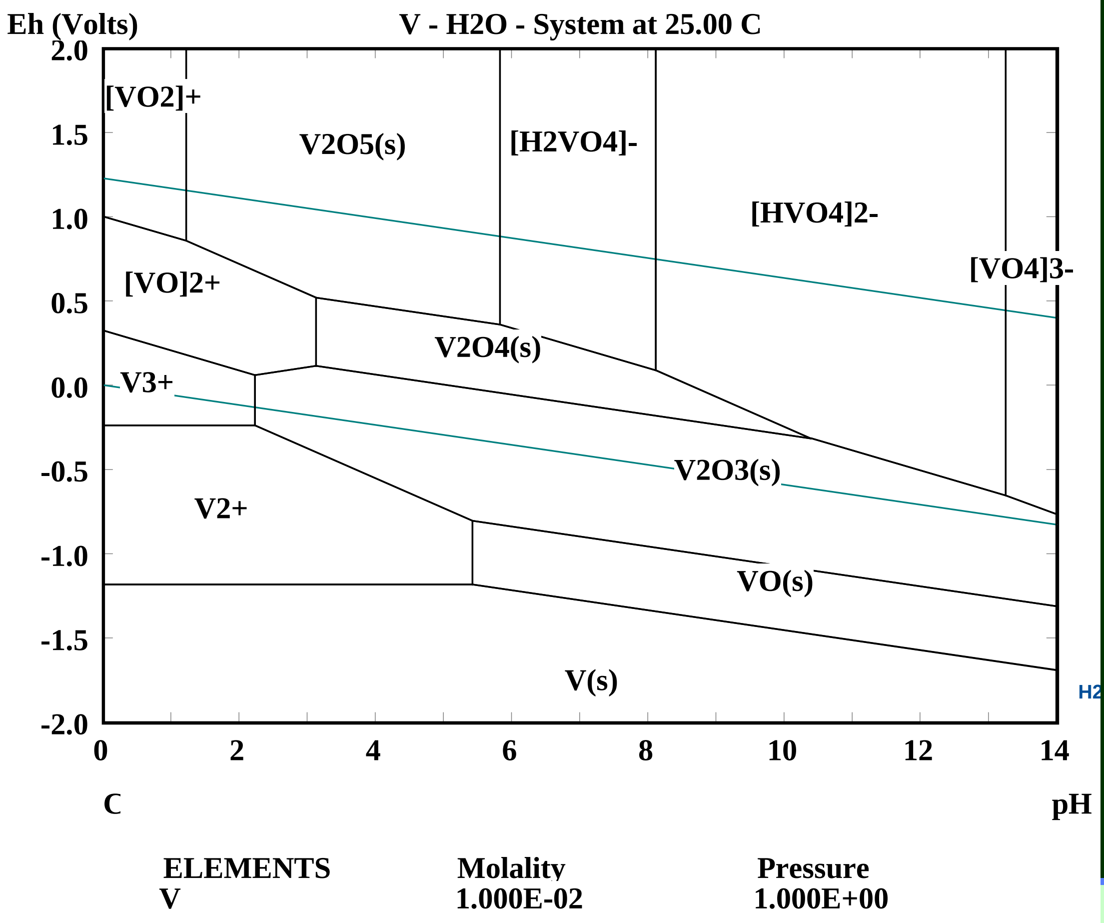
SiO_2 is suspended in the solution at pH 2.3 (why?)

Under N_2, NaOH is added at 25 °C up to pH 6

➔ highly dispersed V_2O_3

After filtration, drying and calcination

➔ V_2O_5/SiO_2, 1.5 nm



Outline

Deposition – Precipitation and Coprecipitation

1) Introduction

2) Backgrounds: thermodynamics

3) Molecular details

4) Case studies

→ **5) Coprecipitation**

Basic principles of precipitation and nucleation

One or more metals are precipitated together with the support or its precursor

It is easy to obtain a precipitate

Ex.: $Fe^{3+}(aq) + 3\ NO_3^-(aq) + 3\ Na^+(aq) + 3\ HO^-(aq)$

$\rightarrow Fe(OH)_3(s) + 3\ NO_3^-(aq) + 3\ Na^+(aq)$

But it is not easy to control

- the exact phase: $Fe_2O_3(s)$, $Fe_2O_3 \cdot nH_2O$, $Fe(OH)_3$, $FeO(OH)$…..
- the size and size-distribution of the crystallites
- the shape of the crystallites
- the agglomeration of the crystallites into grains

Generally, we observe the formation of complex mixtures

Precipitation is a complex phenomenon comprising:

- liquid mixing
- nucleation
- nucleus growth to primary particles
- aging (Ostwald ripening): small particles ↓, large particles become larger
- aggregation of the primary particles
- coagulation and finally precipitation

Basic principles of precipitation and nucleation

Nucleation and growth to primary particles

➔ classical model

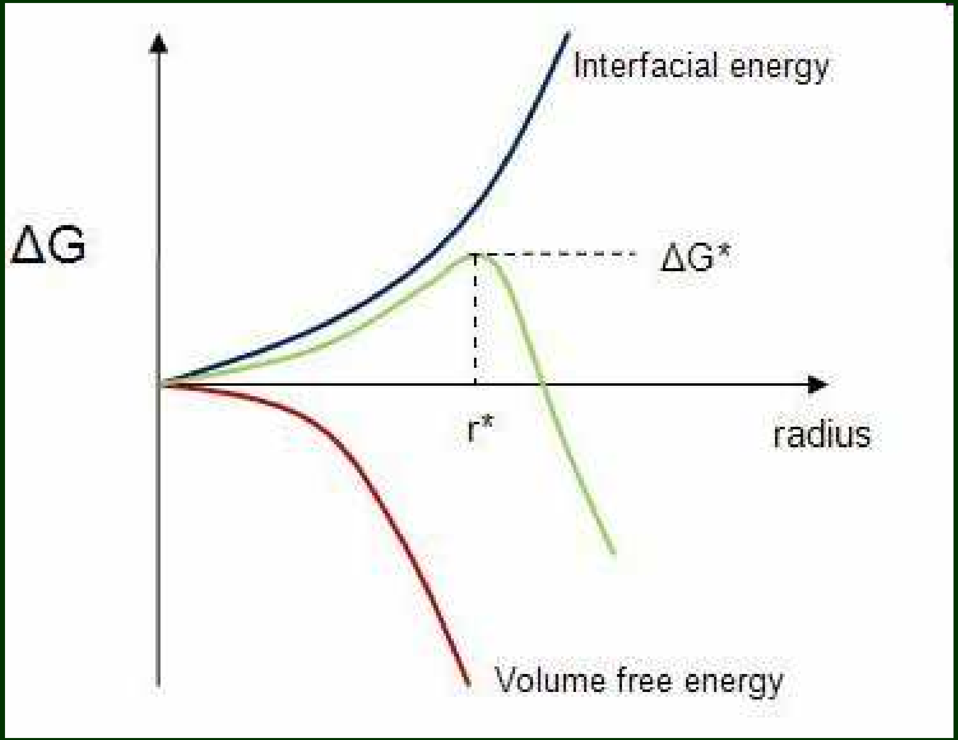
➔ a critical size is necessary for the growth process; nucleus smaller than this size tend to redissolve, while larger nucleus will continue to grow

How can we obtain uniform crystallites?

➔ separation between nucleation step and growth step

➔ Free energy of activation ΔG^*

If ΔG^* is important



➔ supersaturated solution

➔ video: supersaturated solution of $NaCH_3CO_2\cdot3H_2O$

Basic principles of precipitation and nucleation

Nucleation depends on concentration and temperature

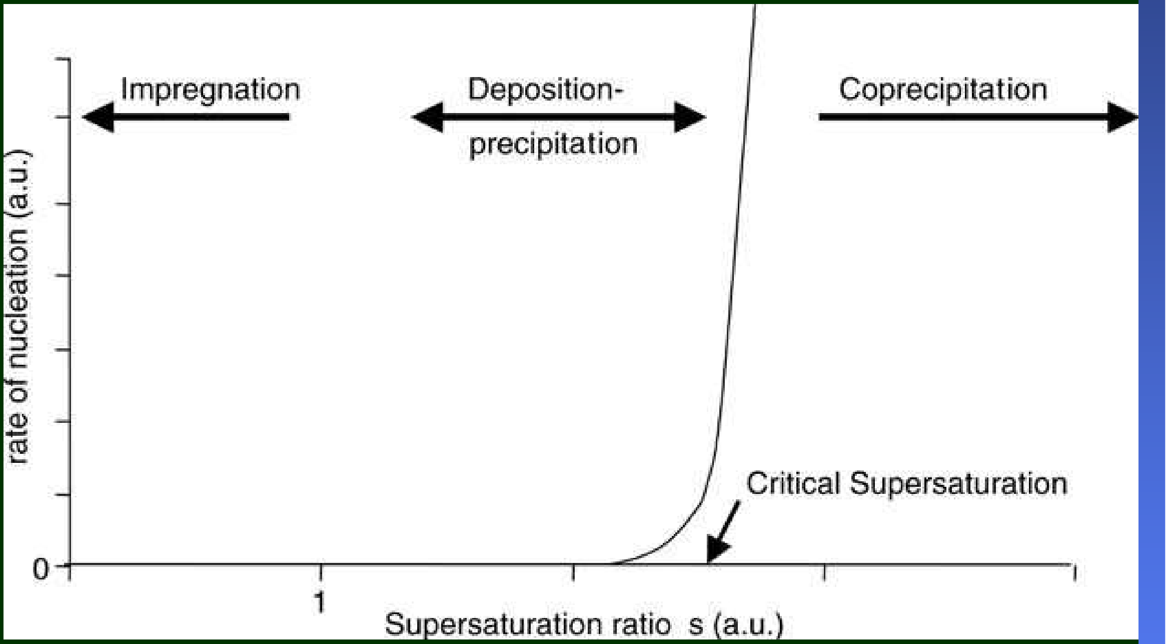
Relation between nucleation rate (nuclei per ml/s) versus degree of supersaturation *s*

***s* = (actual concentration)/solubility**

➔ critical supersaturation concentration

below: very slow nucleation

above: very fast nucleation



For multicomponent systems

➔ high supersaturation level

➔ solubility product of all products is simultaneously exceeded

(otherwise a possibly undesired sequential precipitation may occur)

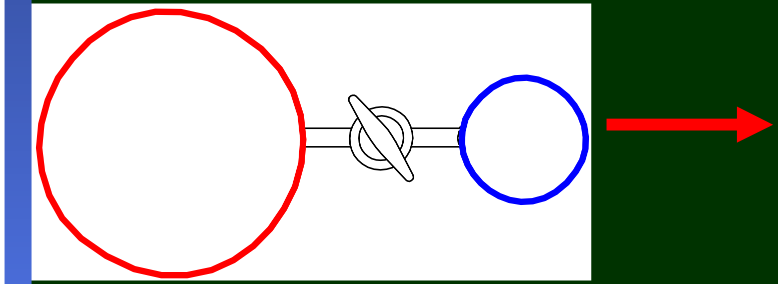
➔ high supersaturation level promote nucleation rather than crystal growth and favor precipitation of highly dispersed materials.

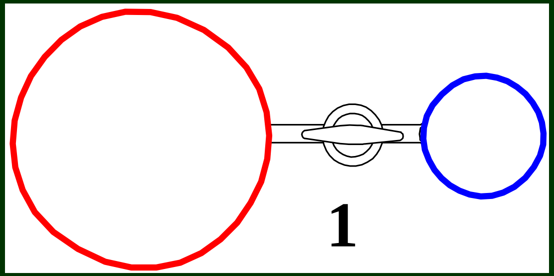
(precipitation from more dilute solutions tends to produce fewer, but larger crystals)

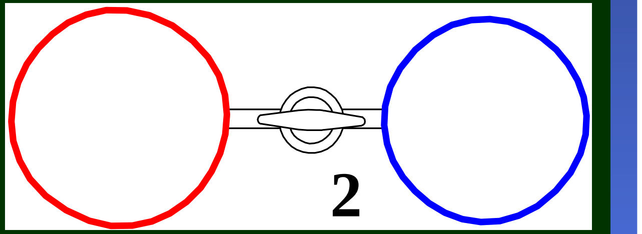
Basic principles of precipitation and nucleation

What about Ostwald ripening?
Surfaces and interfaces are key parameters:
surface energy and surface thermodynamics

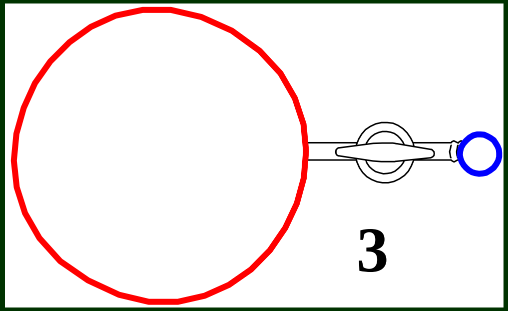
➔An experiment with balloons: pressure versus curvature radius

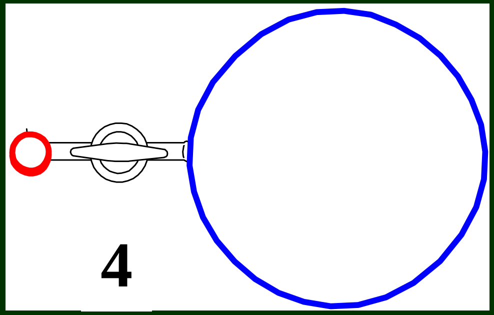






What is the right answer?





Precipitation conditions

Hydroxides or carbonates are suitable due to their very low solubility

Formation of hydroxides by pH variation

Ex.: $Fe^{3+}(aq) + HO^{-}(aq) \rightarrow Fe_2O_3(s), Fe_2O_3 \cdot nH_2O, Fe(OH)_3, FeO(OH)$

How to control nature, shape, size and agglomeration of crystallites?

➔ concentration

➔ nature of reactant: NaOH, Na_2CO_3, $NH_3(aq)$…

➔ key parameter: rate of pH variation

- **difficult to control by adding the second reactant: large local increase of pH**
- **use of a neutral reactant which will transform slowly into a basic species**

➔ urea NH_2CONH_2

$$NH_2CONH_2(aq) + 2\ H_2O(l) \rightarrow NH_4^{+}(aq) + NH_3(aq) + HCO_3^{-}(aq)$$

Slow hydrolysis controlled by temperature and concentration

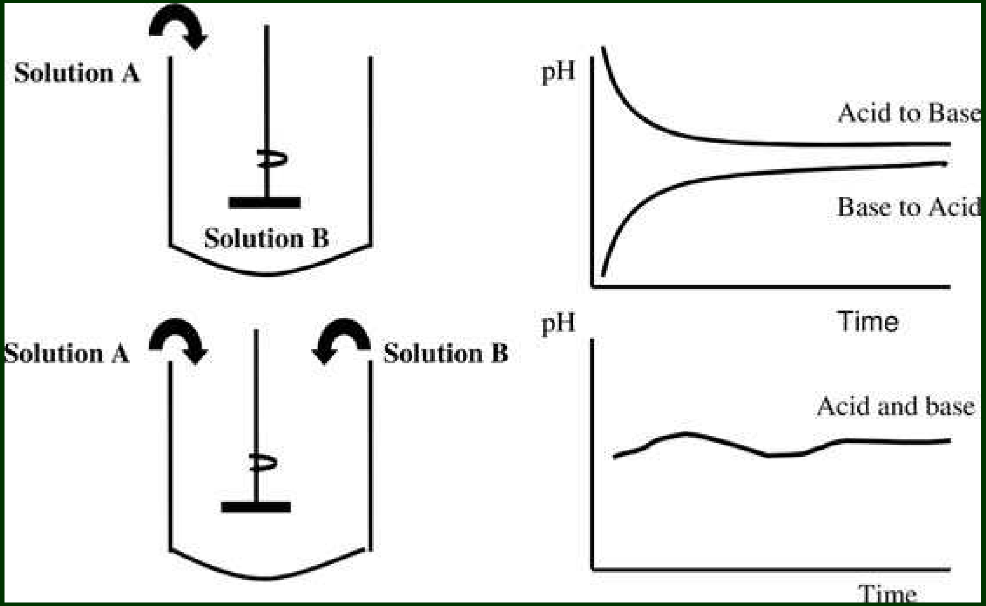
Final pH controlled mainly by $NH_4^{+}(aq)/NH_3(aq)$ acid-base couple: ➔ pH ~ 9

Precipitation conditions

Formation of hydroxides by pH variation

Precipitation processing routes:

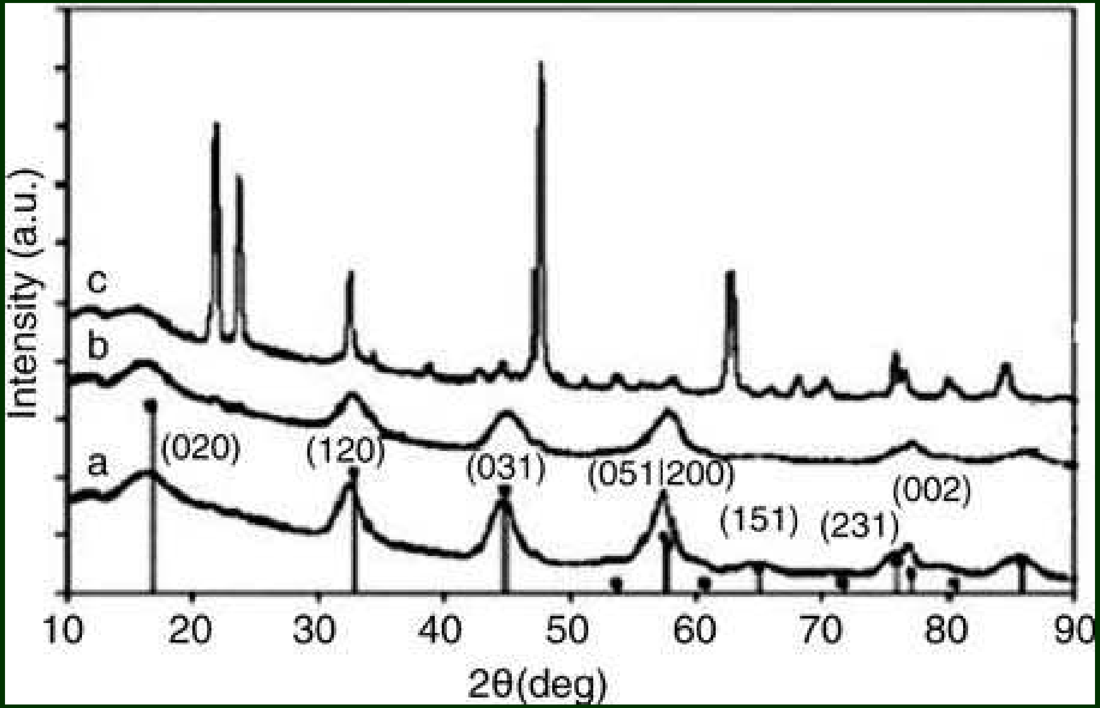
- **forward precipitation (base to acid)**
- **reverse precipitation (acid to base),**
- **continuous precipitation, and corresponding pH profiles.**



Precipitation conditions

Formation of hydroxides by pH variation

Effect of order of addition on alumina composition;
XRD patterns of alumina obtained by
(a) continuous precipitation at constant pH ➔ formation of boehmite AlO(OH)·xH_2O
(b) acid to base addition ➔ formation of boehmite
(c) base to acid addition ➔ bayerite $Al(OH)_3$



Precipitation conditions

Formation of carbonate or hydroxocarbonate by pH variation
Addition of sodium carbonate or ammonium carbonate

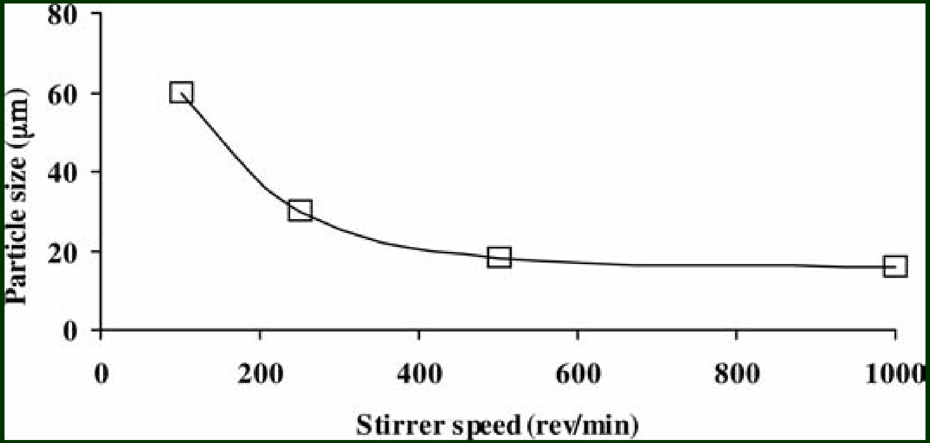
balance the equation: formation of copper hydroxycarbonate

$$Cu^{2+}(aq) + NO_3^-(aq) + Na^+(aq) + CO_3^{2-}(aq) \rightarrow Cu_2(OH)_2CO_3(s)$$

Basic principles of precipitation and nucleation

Ex.: formation of hydroxides by pH variation

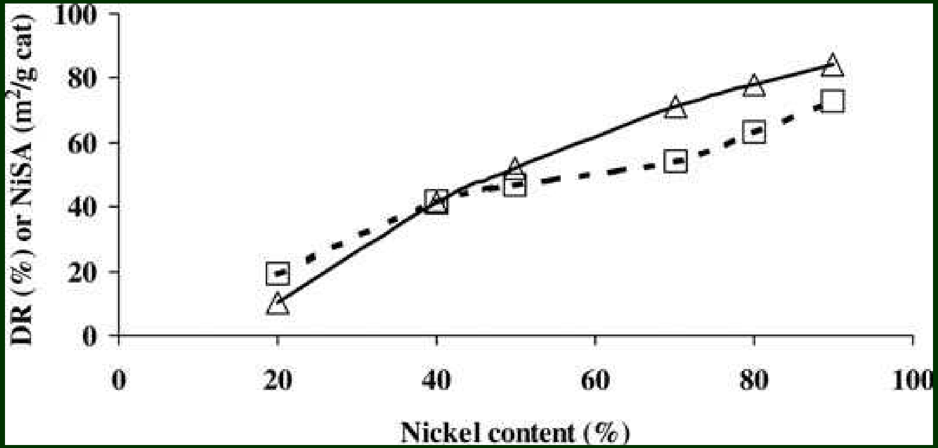
Relation particle size and stirring speed for nickel/guhr catalysts.



Basic principles of precipitation and nucleation

Ex.: formation of hydroxides by pH variation

Coprecipitated nickel-alumina catalysts: Nickel surface area (NiSA, triangles) and degree of reduction (DR, squares) as a function of nickel content. (After [26].)



End of part 5