Strategies targeted to synthesis of meso- and nanostructured oxides with catalytic functions

21.10.2005 / A. Trunschke

- Preparation of Solid Catalysts, Edited by G. Ertl, H. Knözinger, J. Weitkamp, WILEY-VCH, Weinheim, 1999.

- J.-P. Jolivet, Metal Oxide Chemistry and Synthesis – From Solution to Solid State, John Wiley & Sons Ltd., Chichester, 2000.

- M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer-Verlag, Heidelberg, 1983.

- G.J. de A.A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, Chem. Rev. 102 (2002) 4093-4138.

- A. Taguchi, F. Schüth, Micropor. Mesopor. Mater. 77 (2005) 1-45.

Catalytic functions– highly dispersed active species

- Strong acidity
    - cracking and hydrocracking reactions
- Mild acid-base properties
    - fine chemical synthesis
- Redox properties
    - selective oxidation or oxidative dehydrogenation
- Supported nanoparticles
    - hydrogenation
    - hydrocracking
    - hydrotreatment (HDS, HDN)
- Anchored and grafted active species
    - immobilization of molecular catalysts including chiral/non-chiral organometallic complexes and enzymes

Unit operations in catalyst preparation

1. Precipitation
2. Gelation
3. Hydrothermal transformation
4. Decantation, filtration, centrifugation
5. Washing
6. Drying
7. Calcination
8. Forming operation
9. Impregnation
10. Crushing and grinding
11. Mixing
12. Activation

Some or even all operations are involved in most catalyst formulations.

Prepartion methods of oxide-based catalysts

Bulk oxides and supports	Supported catalysts

Bulk oxides and supports

- Precipitation and Coprecipitation
- Hydrothermal synthesis
- Sol-Gel-techniques
- Solid state reactions
- Flame hydrolysis

Supported catalysts

- Impregnation and ion exchange
- Deposition precipitation
- Anchoring of organometallic complexes
- Heterogenization of complexes and enzymes
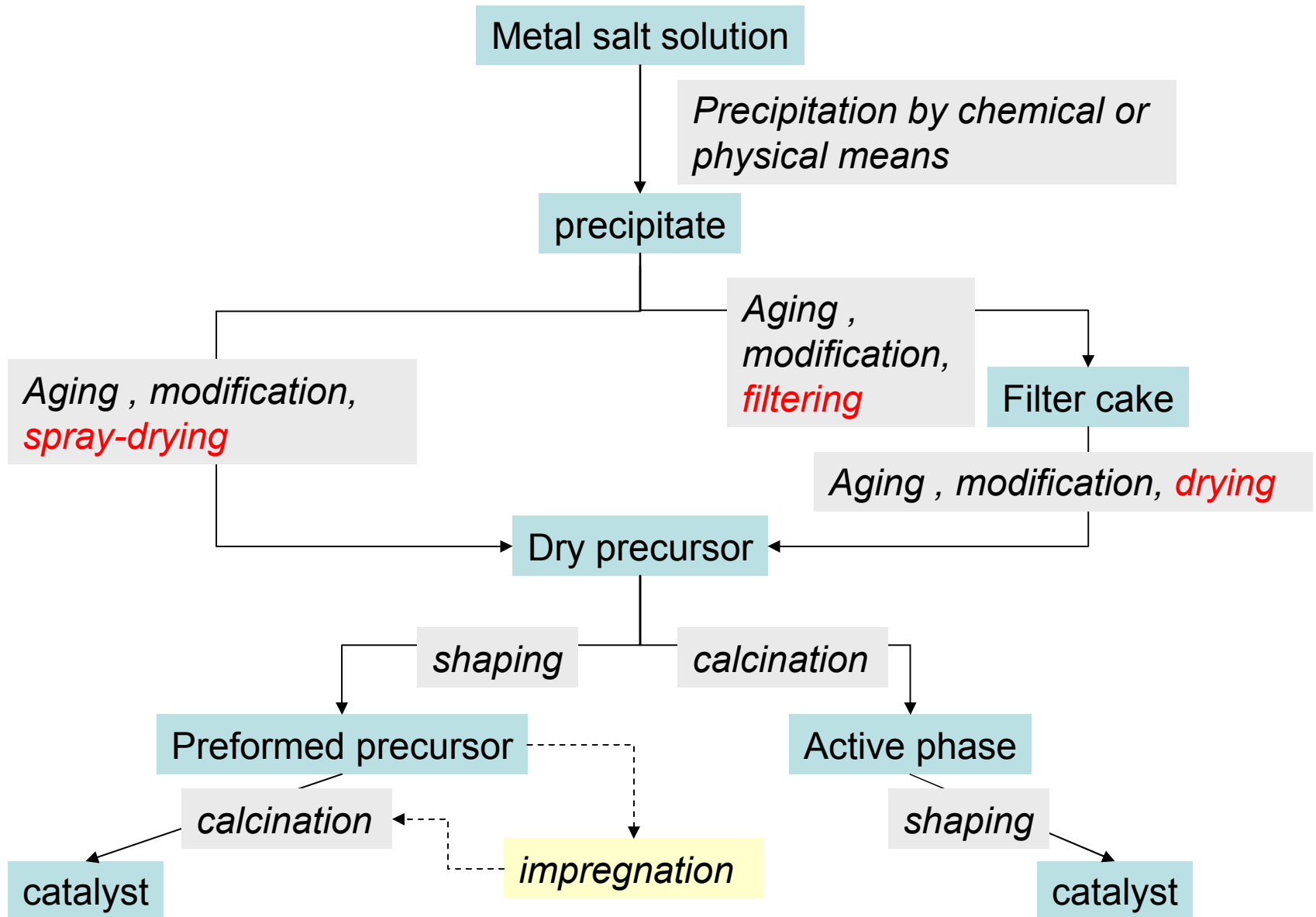- Ship-in-bottle synthesis
- Chemical vapor deposition

Precipitation – more an art than a science

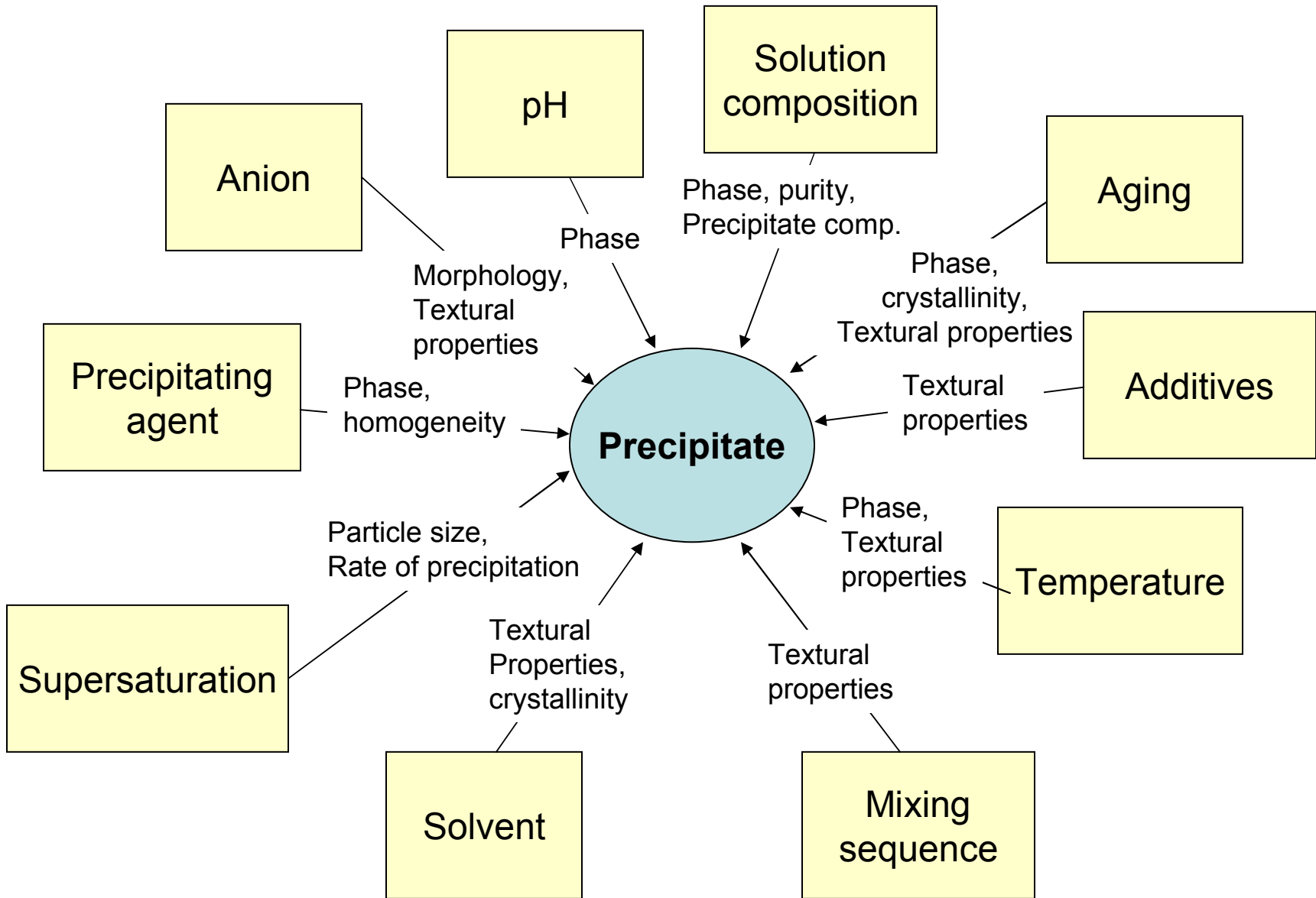| Material	Use	Important examples
Al_2O_3 (mostly γ, in special cases α or η)	support, catalyst	Claus process, dehydration of alcohols to alkenes and ethers, support of hydrotreating catalysts, support for three-way catalyst
SiO_2	support	noble metal/SiO_2 for hydrogenation reactions, Ni/SiO_2 for hydrogenation reactions, V_2O_5/SiO_2 for sulfuric acid production
Al_2O_3/SiO_2	catalyst	acid-catalyzed reactions such as isomerizations
Fe_2O_3	catalyst, catalyst component	Fischer–Tropsch reactions, major component of catalyst for ethylbenzene reaction to styrene
TiO_2	support, catalyst, catalyst component	major component of DeNOx catalyst
ZrO_2	catalyst	acid catalyst after sulfate modification
Cu/ZnO	catalyst	methanol synthesis
$(VO)_2P_2O_7$	catalyst	selective oxidation – for instance butane to maleic anhydride
Cu–Cr oxides	catalyst	combustion reactions, hydrogenations
$AlPO_4$	support, catalyst	polymerization, acid-catalyzed reactions
Sn–Sb oxide	catalyst	selective oxidation – for instance isobutene to methacrolein
Bi molybdates	catalyst	selective oxidation – for instance propene to acrolein (mostly supported)

Technically very important and demanding, because:

• Necessity of product separation after precipitation

• Large volumes of salt-containing solutions generated in the precipitation process

F. Schüth, K. Unger in Preparation of Solid Catalysts, p. 62.

Preparation scheme for precipitated materials

Metal salt solution

Precipitation by chemical or physical means

precipitate

Aging , modification, spray-drying

Aging , modification, filtering

Filter cake

Aging , modification, drying

Dry precursor

shaping   *calcination*

Preformed precursor

Active phase

calcination

impregnation

shaping

catalyst

catalyst

F. Schüth, K. Unger in Preparation of Solid Catalysts, p. 63.

6

Precipitation parameters – frequently empirically optimized

Anion — Morphology, Textural properties → Precipitate

pH — Phase → Precipitate

Solution composition — Phase, purity, Precipitate comp. → Precipitate

Aging — Phase, crystallinity, Textural properties → Precipitate

Additives — Textural properties → Precipitate

Precipitating agent — Phase, homogeneity → Precipitate

Supersaturation — Particle size, Rate of precipitation → Precipitate

Solvent — Textural Properties, crystallinity → Precipitate

Mixing sequence — Textural properties → Precipitate

Temperature — Phase, Textural properties → Precipitate

F. Schüth, K. Unger in Preparation of Solid Catalysts, p. 69.

7

Precipitation parameters

Precipitation of MoO_3 with HNO_3 from aqueous $(NH_4)_6Mo_7O_{24} * 4\ H_2O$, Na_2MoO_4, Li_2MoO_4, or K_2MoO_4 solutions
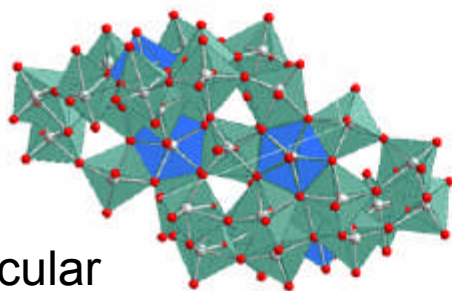
Supramolecular $Mo_{36}O_{128}$
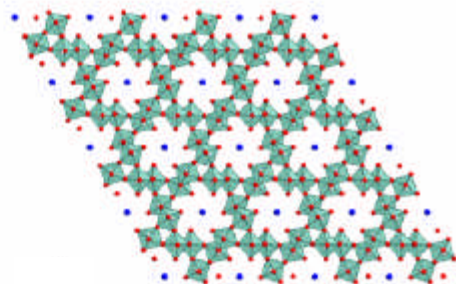
Hexagonal MoO_3
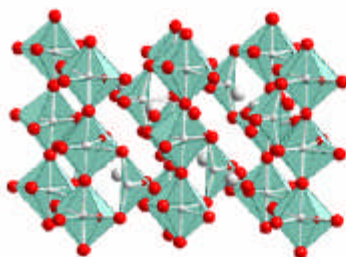
Trimolybdate
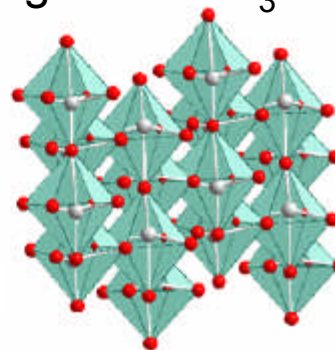
Orthorhombic MoO_3

Depending on temperature, molybdenum concentration, acid concentration and the choice of starting material and counter ion such as Li^+, Na^+, K^+, and NH^{4+}, four different families of products were obtained by precipitation

Condensation reactions

Hydrolysis equilibria of cations in aqueous solution

$$[M(OH_2)]^{z+} \xrightleftharpoons{H_2O} [M(OH)]^{(z-1)+} + H^+_{aq} \xrightleftharpoons{H_2O} [M\text{-}O]^{(z-2)+} + 2\,H^+_{aq}$$

aquo   hydroxo   oxo
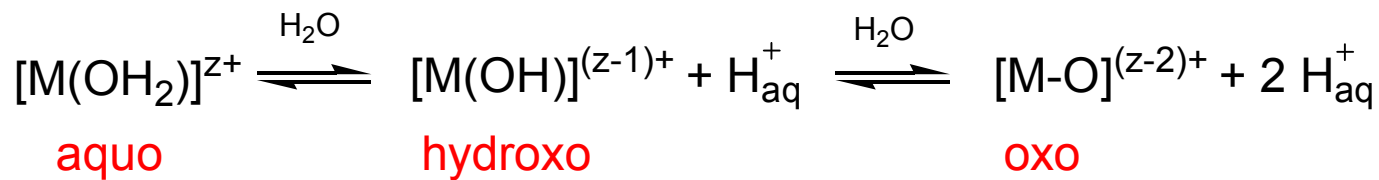
pH<7, $z \leq 4$ pH>7, $z \leq 4$ $z > 4$

•Formal charge, size, nature of the element

Initiation (hydroxylation)

$$[M\text{-}O]^- + H_3O^+ \longrightarrow M\text{-}OH + H_2O \longleftarrow [M\text{-}OH_2]^+ + HO^-$$

precursor
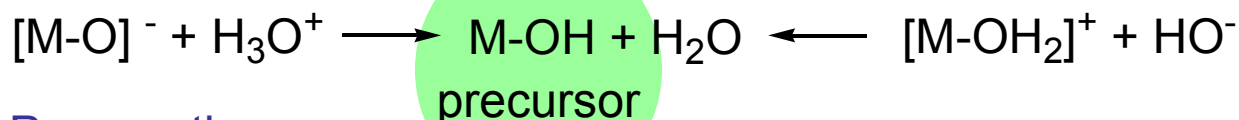
Propagation
Olation   Oxolation

$$M\text{-}OH + M\text{-}OH_2 \longrightarrow M\text{-}OH\text{-}M + H_2O$$

$$M\text{-}OH + M\text{-}OH \longrightarrow M\overset{\overset{\textstyle H}{|}}{-}O\text{-}M\text{-}OH \longrightarrow M\text{-}O\text{-}M + H_2O$$
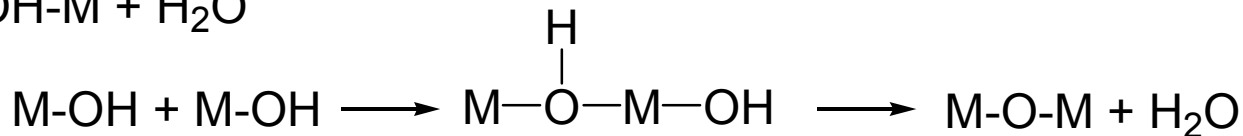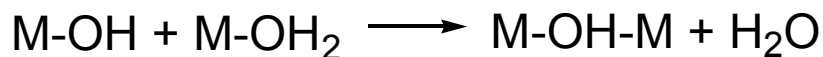
Termination

•Condensation of cationic or anionic hydroxylated complexes leads to polycations and polyanions, respectively.
•The formation of a solid requires the presence of zero-charge complexes

9

Spontaneous precipitation
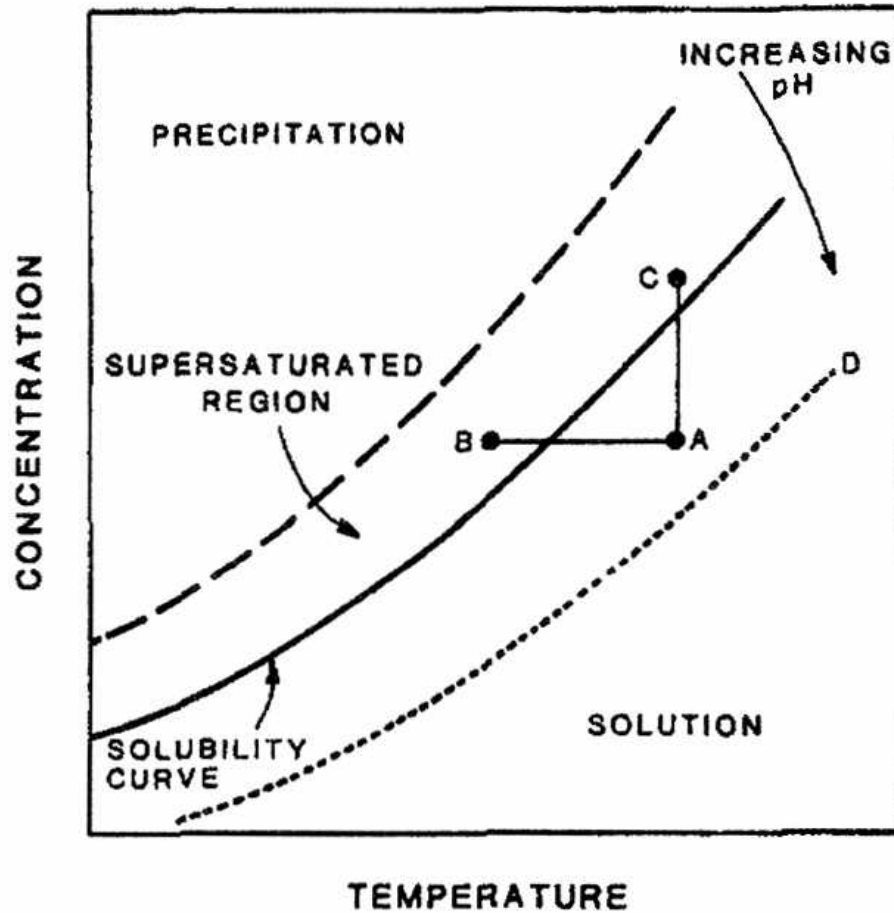
Supersaturation dependence on T, and pH

C. Perego, P. Villa, Catal. Today 34 (1997) 281.

Steps of formation of a solid

1. Formation of a precursor (e.g. the hydrolysis product of a metal ion in solution), which is able to condense and to form a solid phase

2. Creation of nuclei through condensation

Nucleus
„smallest solid-phase aggregate of atoms, molecules or ions, which is formed during a precipitation and which is capable of spontaneous growth"

3. Growth of the nuclei through the addition of matter, until the primary particle stage is reached
   - Growth and nucleation could occur simultaneously
   - The size distribution of the primary particles is linked to the relative nucleation and growth rates
4. Aging of the particles in suspension
   - „Ostwald ripening" – increase in the average particle size and aggregation
   - Changes in morphology
   - Changes in crystal type
   - Crystallization of amorphous particles

Nucleation curve
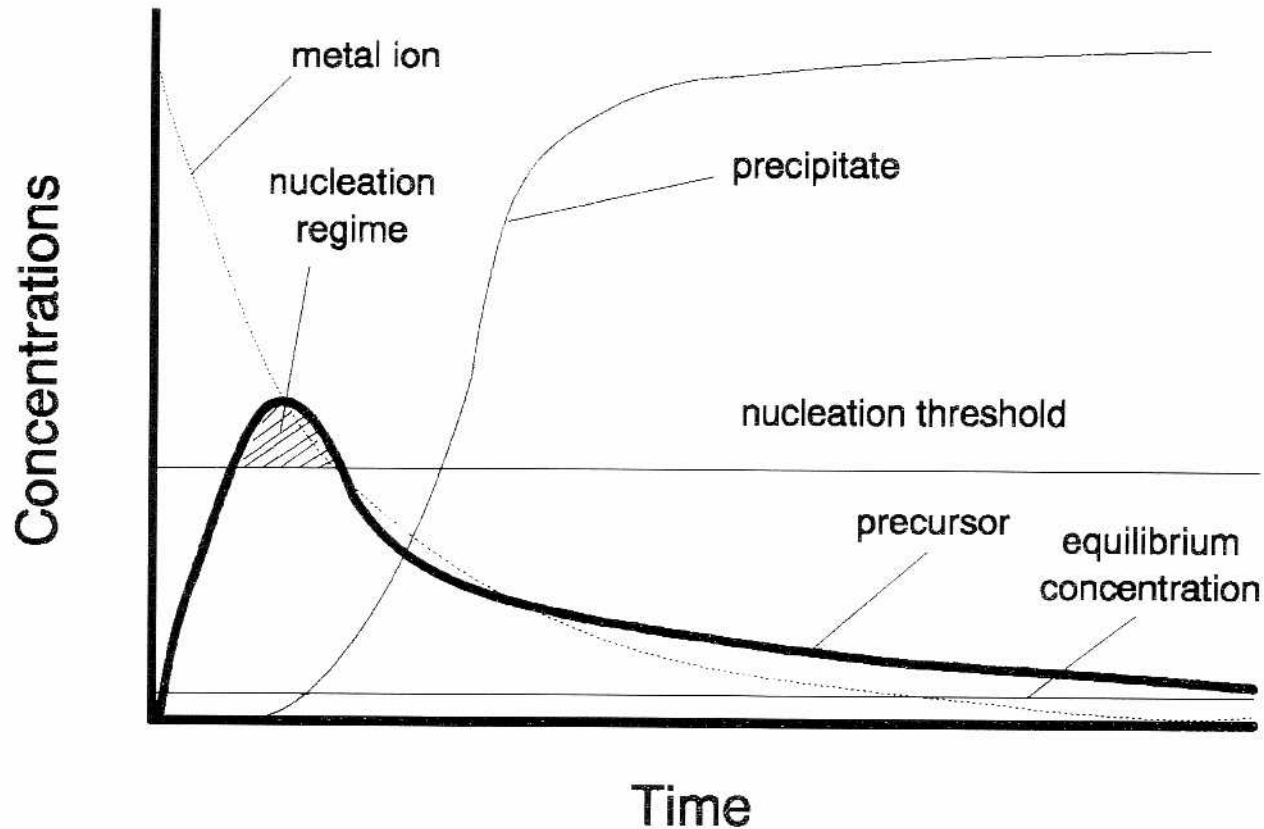
The size distribution of the particles finally formed is dependent on the shadowed section:

•Short nucleation period – monodispersed particles
•Long nucleation period – wide particle size distribution

F. Schüth, K. Unger in Preparation of Solid Catalysts, p. 64.

12

Nucleation from n precursors – key step

$$\Delta G = \Delta G_{bulk} + \Delta G_{interface} + \Delta G_{others}$$

ΔG total free energy change due to agglomeration
ΔG_{bulk} difference of the free energy between solution species and solid species
$\Delta G_{interface}$ free energy change related to the formation of the interface
ΔG_{others} strain, impurities
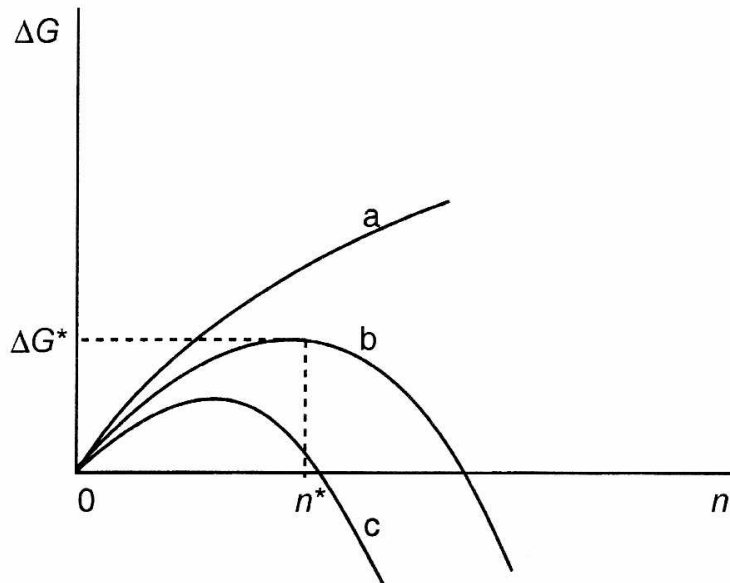
S supersaturation ratio of the solution $S = c_L/c_S$

a S<1
b S>1
c S>>1

c_L precursor concentation
c_S solubility of the solid phase

J.-P. Jolivet, p. 40.

Variation in the free enthalpy of formation of a nuclei as the function of the number of precursor molecules n associated in the nucleus

13

Radius of the critical nucleus

Gibbs-Kelvin equation

$$r^* = (3n^*v/4\pi)^{1/3} = \frac{2\gamma v}{2kT\ln S}$$

r^*	radius of the critical nucleus formed from n precursors
v	molecular volume of the precursor
γ	Interfacial energy
S	supersaturation ratio of the solution $S = c_L/c_S$
c_L	precursor concentation
c_S	solubility of the solid phase

Particle size of oxides can be controlled by physico-chemical conditions of the medium:

• pH of the solution

• Nature and concentration of electrolytes (ionic strength)
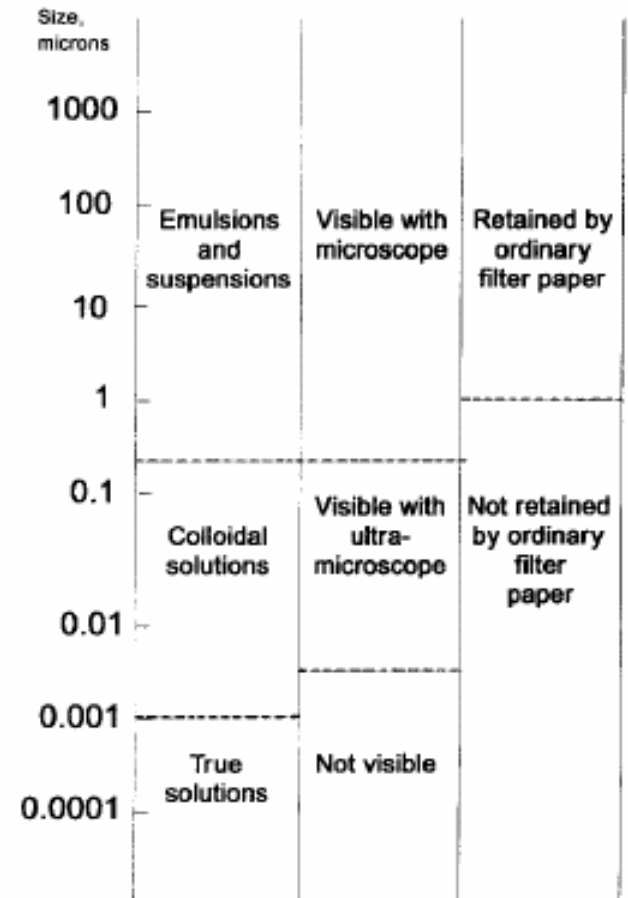
Properties of colloidal particles,
C. Perego, P. Villa, Catal. Today 34 (1997) 281.

14

Precipitation of Magnetite Fe_3O_4
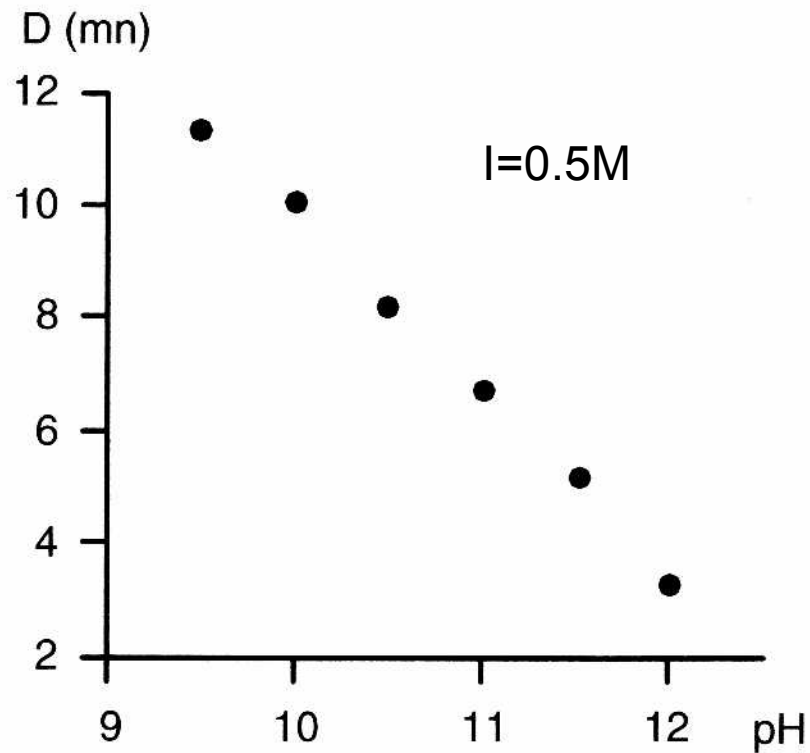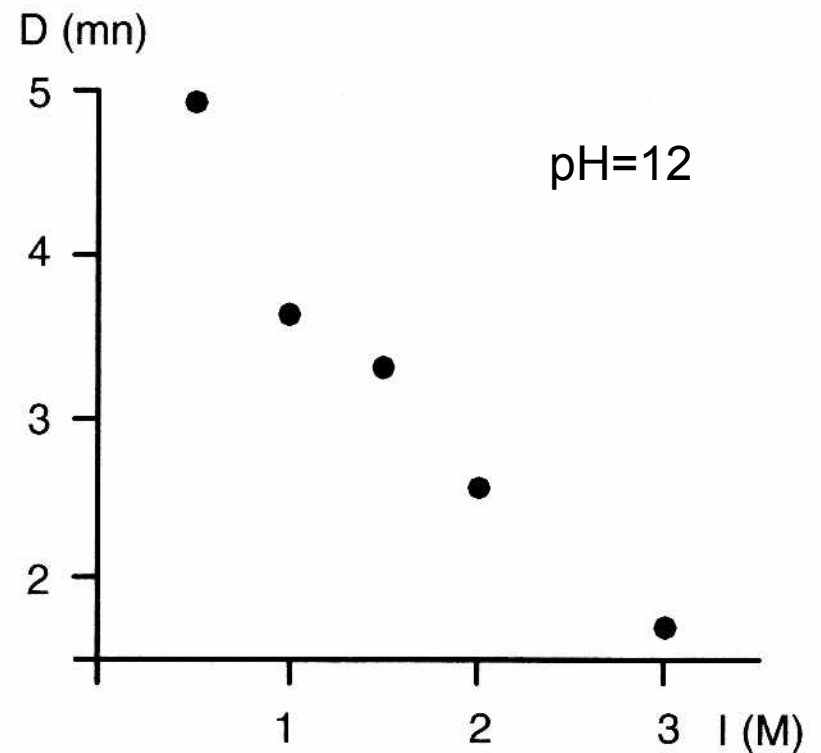
Average size of Fe_3O_4 particles formed from $FeCl_3$ + 0.5 $FeCl_2$ after 8 days of aging

J.-P. Jolivet, p. 280.

Nucleation rate

$$J = J_0 \exp\left[\frac{-\Delta G_N}{kT}\right]$$

$$J = J_0 \exp\left[\frac{\Delta G^* + \Delta G^R}{kT}\right]$$

$$J = J'_0 \exp\left[\frac{16\pi\gamma^3 v^2}{3(kT)^3(\ln S)^2}\right] \qquad J'_0 = J_0 \exp(-\Delta G^R/kT)$$

J_0 frequency of collisions between precursor molecules

ΔG_N nucleation activation energy

ΔG^* height of the energy barrier, required for the formation of a nucleus

ΔG^R related to the type of chemical reaction involved in the process (olation and/or oxolation), usually 35 kJ mol^{-1}

Nucleation rate of an oxide at 300 K: 10^5 nuclei per 1 cm^3 s^{-1}

for γ = 100 mJ m^{-2}, v = 2 x 10^{-5} m^3 mol^{-1}, J'_0 = 10^{30} cm^{-3} s^{-1}, S =100

S=10:   formation of 1 nucleus every 10^{70} seconds

Nucleation is sharply accelerated by seeds (heterogeneous nucleation):

•Seeding allows nucleation at small supersaturation levels
•Coating of oxides
•Heterogeneous nucleation can be avoided by ultrafiltration

Growth

Incorporation of precursor molecules into the particle during and after nucleation stage

Average particle size
= f (number of nuclei, amount of matter available)

Particle size distribution
= f (mechanism of nuclei growth)

Diffusion-limited growth

- Fast incorporation
- Sharp particle size distributions seldom

AFM microscopy. Regular growth of terraces observed on the [010] face of a silicalite-1 crystal

C.S. Cundy, P.A. Cox, Chem. Rev. 103 (2003) 663.
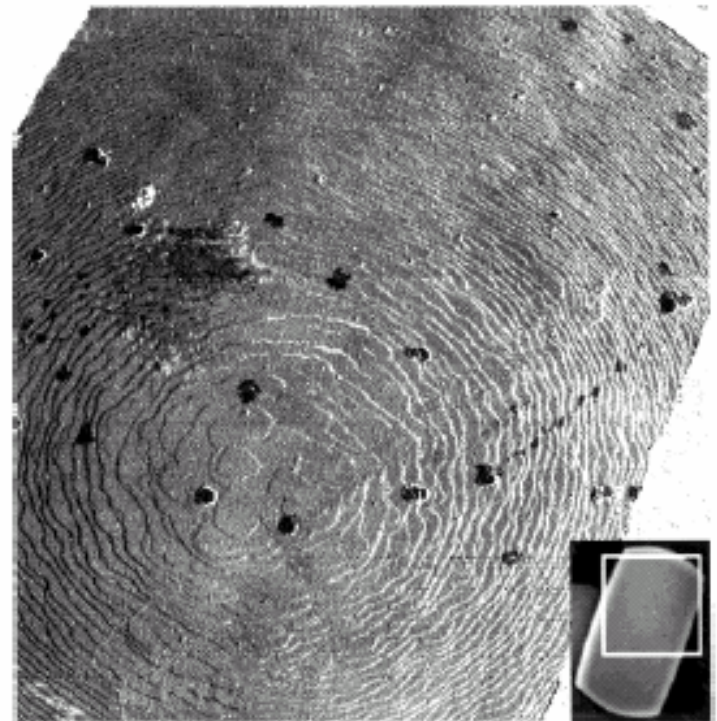
Aging

Aging allows the system to tend towards or to reach thermodynamic stability

Aging phenomena:

(i) Increase in particle size
  - Dissolution-crystallization
  - Aggregation (favored by physicochemical conditions of the medium (pH, ionic strength) which minimize the surface electrical charge of the particles)

(ii) Change in crystal type
  TiO_2: anatase -> rutile
  Amorphous $Al(OH)_3xH_2O$ ->boehmite ->bayerite

(iii) Changes in morphology
  - Small particles are often spherical
  - Anisotropy develops during growth (structural and chemical reasons)

Aging

Intensity [a.u.]

2 θ

pH

B.Bems, Dissertation 2003
B. Kniep, Dissertation 2005

Aging 120 min

Precipitation
Cu/Zn ratio
70/30 mol%
pH=7

Influence on Cu microstrucure in Cu/ZnO catalysts

aurichalcite

$(Cu_xZn_{1-x})_5(OH)_6(CO_3)_2$

rosasite

$(Cu_xZn_{1-x})_2(OH)_2CO_3$

$$CH_3OH + H_2O \longrightarrow 3\ H_2 + CO_2$$

Conversion CH$_3$OH

Ageing [min]

19

Olation – Polycations and solid phases

$$M\text{-}OH + M\text{-}OH_2 \longrightarrow M\text{-}OH\text{-}M + H_2O$$

$[Cu(OH)_2(OH_2)_4]0$

Olation

Olation

$Cu(OH)_2$

(a)

CuO

(b)

PdO, PtO
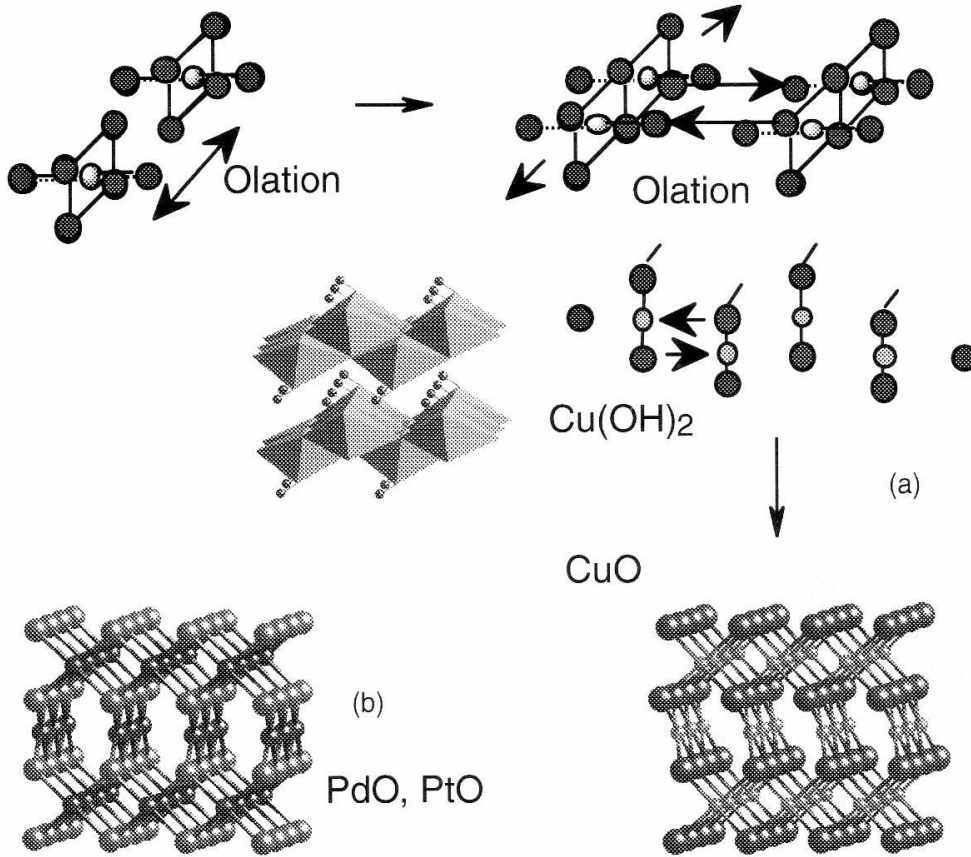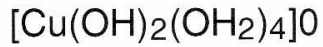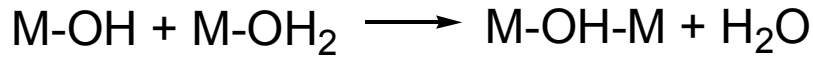
Possible reaction mechanism of the formation of copper hydroxide

$Cu(OH)_2$ isostructural to boehmite

Precursor : $[Cu(OH)_2(OH_2)_4]_n^0$ chains formed by neutralization of linear polycations

H. Jaggi, H.R. Ostwald, Acta Cryst. 14 (1961) 1041.

J.-P. Jolivet, p. 80.

Coprecipitation

Coprecipitation (hydroxides, carbonates) is the simultaneous precipitation of more than one component
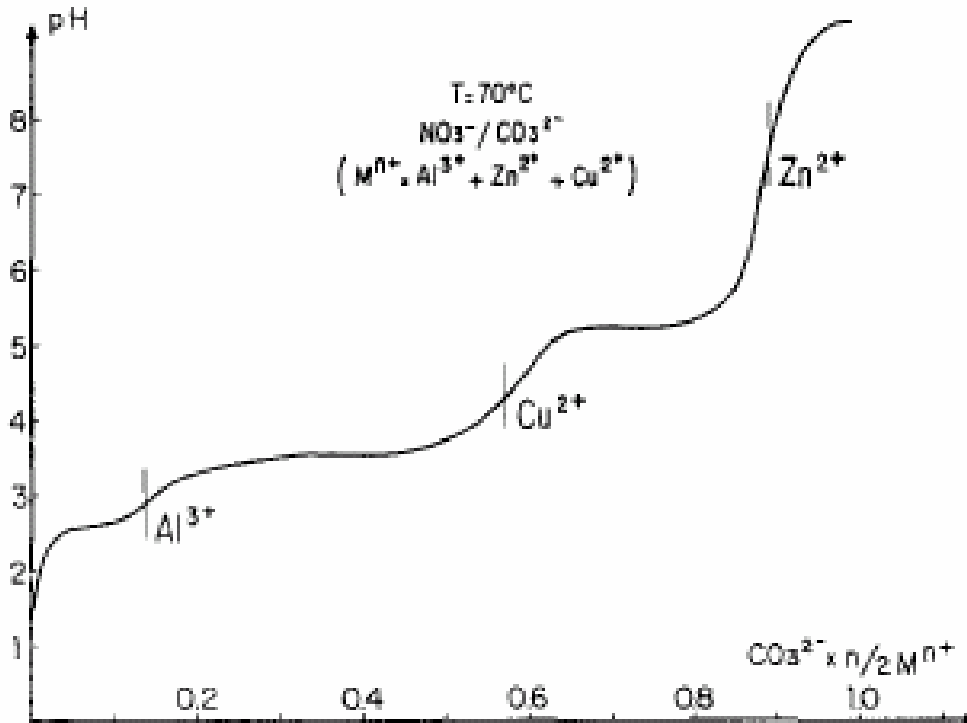
Composition of the solution may determine the composition of the final product

Consecutive precipitation must be avoided by operation at constant pH

Neutralization of Cu^{2+} Zn^{2+} Al^{3+} nitrate solution (0.35 M) with a Na_2CO_3 solution (0.4 M)
pH vs. Na_2CO_3 equivalents

C. Perego, P. Villa, Catal. Today 34 (1997) 281.

Precipitation process

a) Variation of batch composition

Inhomogeneities possible

b) Concentration of ions not precipitated changes

Different residence times of the precipitates

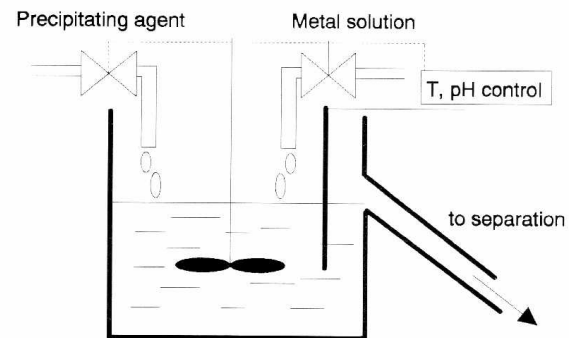c) All parameters (T,c,pH,t) constant

Higher demands on the process control

P.Corty, C. Marcilly, Stud. Surf. Sci. Catal. 16 (1983) 485.

a: Batchwise operation
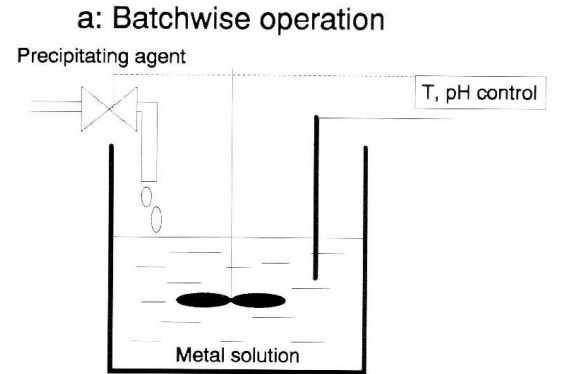
b: Batchwise operation, constant pH
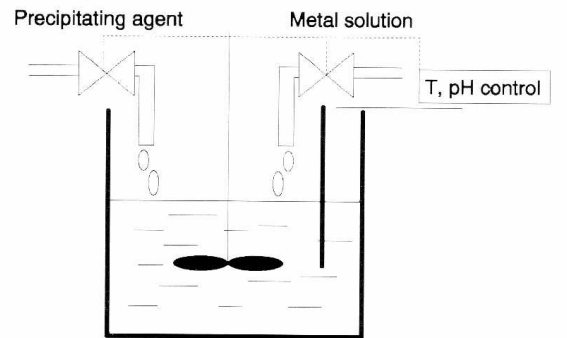
c: Continuous operation

Parameters that influence the properties of the final product

Precursor concentration (supersaturation level)

- Higher degree of supersaturation leads to faster precipitation
- Smaller particle sizes and higher surface areas are achieved at higher concentrations
- To obtain narrow particle size distributions supersaturation should be maintained as low as possible after nucleation in order to prevent simultaneous nucleation and growth

Temperature

- Nucleation rates strongly depend on the temperature
- The optimum precipitation temperature has to be determined experimentally

pH

- The pH directly controls the degree of supersaturation
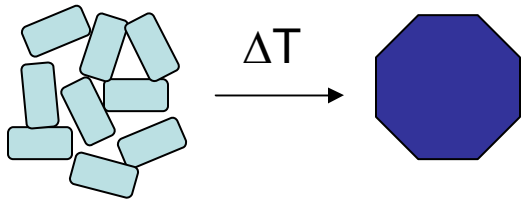- Moreover: Complex influence that depends on the system

Additives

- Organic molecules may be added to control the pore structure

ZrO$_2$ 100 nm

TiO$_2$ 40 nm

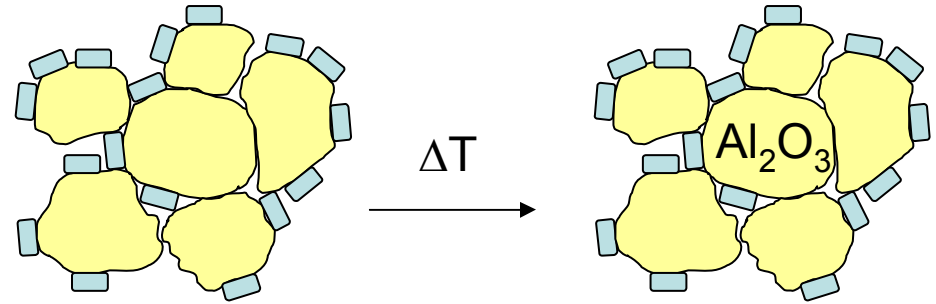SnO$_2$ 20 nm

Block copolymer templated oxides
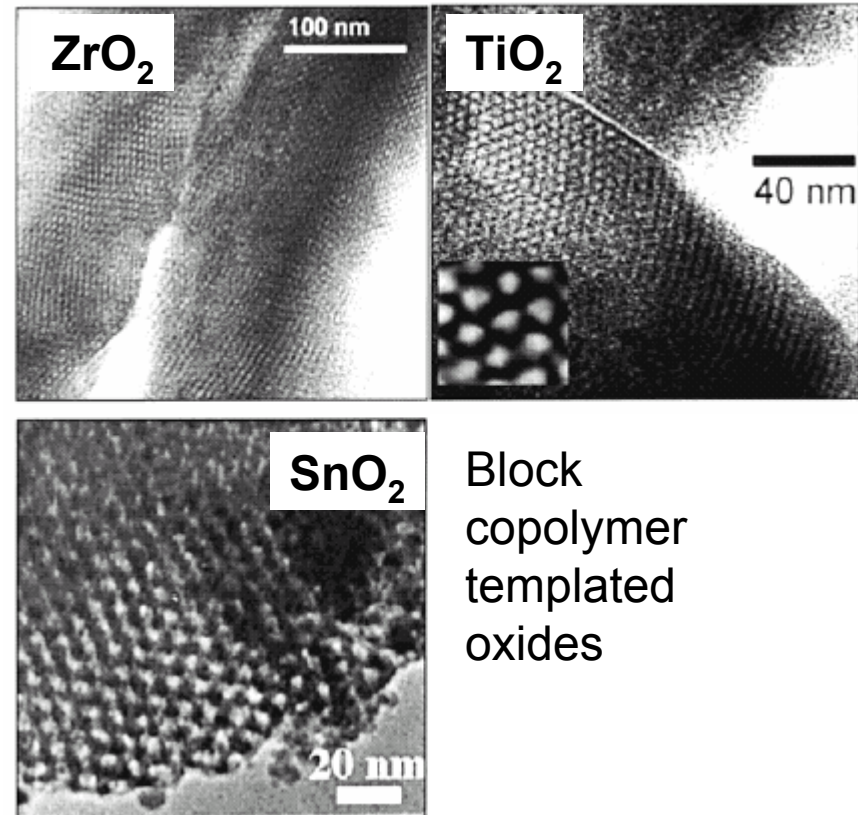
G.J.de A.A. Soler-Illia et al., Chem. Rev. 102 (2002) 4093.
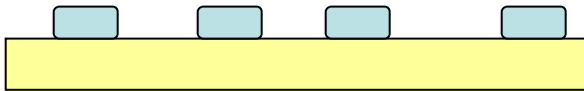
Deposition precipitation

Sintering of unsupported
active particles

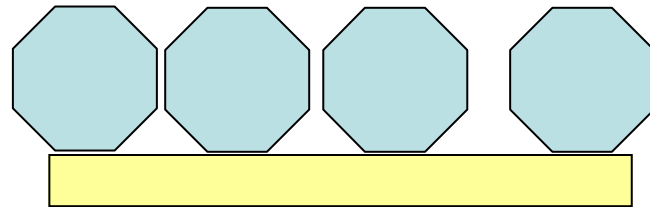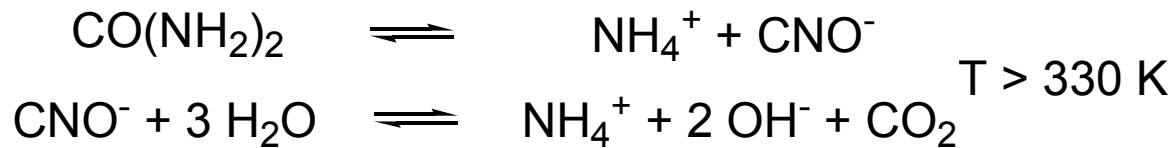Supported thermostable active material

Impreganation

Deposition precipitation

Low loadings

Loadings > 10-20%
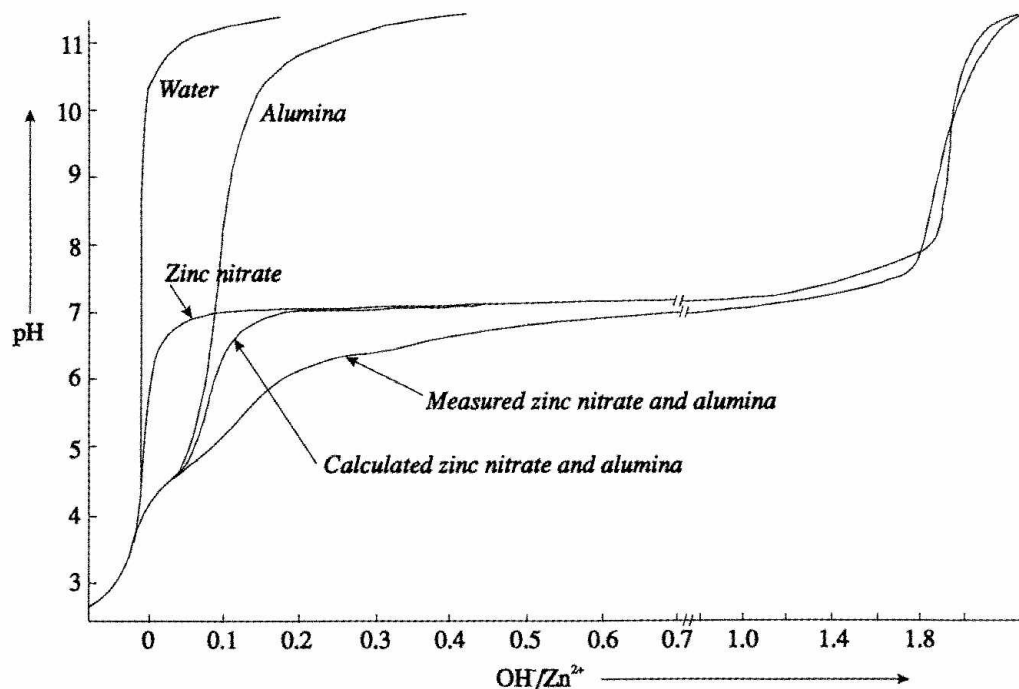
Deposition precipitation

Change of pH level

$$CO(NH_2)_2 \rightleftharpoons NH_4^+ + CNO^-$$

$$CNO^- + 3\,H_2O \rightleftharpoons NH_4^+ + 2\,OH^- + CO_2$$

T > 330 K

Ammonia-free procedure (anaerobic!)

$$3\,NO_2^- + H_2O \rightleftharpoons 2\,NO + NO_3^- + 2\,OH^-$$

☹
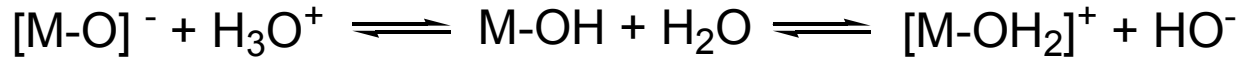- waste water containing chemically bonded nitrogen
- NO_x emissions

Interaction with the support – prerequisite to achieve the coverage the surface of the support

Electrostatic/chemical

Precipitation of Zn(II) by injection of NaOH at 293K

J.W. Geus, A.J. van Dillen in Preparation of Solid Catalysts, p. 473-4.

pH vs OH^-/Zn^{2+} — curves labeled: Water, Alumina, Zinc nitrate, Measured zinc nitrate and alumina, Calculated zinc nitrate and alumina.

25

Oxide-Solution interface

$$[M\text{-}O]^- + H_3O^+ \rightleftharpoons M\text{-}OH + H_2O \rightleftharpoons [M\text{-}OH_2]^+ + HO^-$$

Surface charge density 0.2-0.4 C/m²

$\sigma_0 = (F/A)([M\text{-}OH_2^+]\text{-}[M\text{-}O^-])$

A   surface area of particles (m²/l

F   Faraday constant (96500 C/mol)

oxide	PZC
MgO	~12.5
ZnO	9-10
$\alpha\text{-}Fe_2O_3$	5.5-9
$\alpha\text{-}Al_2O_3$	6.5-10
TiO_2	3.5-6.5
SiO_2	2-4
WO_3	~0.4

Point of zero charge (PZC) of a surface depends on

• Chemical nature (polarizaton of the surface groups by the cation)

• Crystal structure and particle morphology

• Heat treatment and physicochemical history of the oxide

J.-P. Jolivet, p. 213.

26

Determination of the PZC
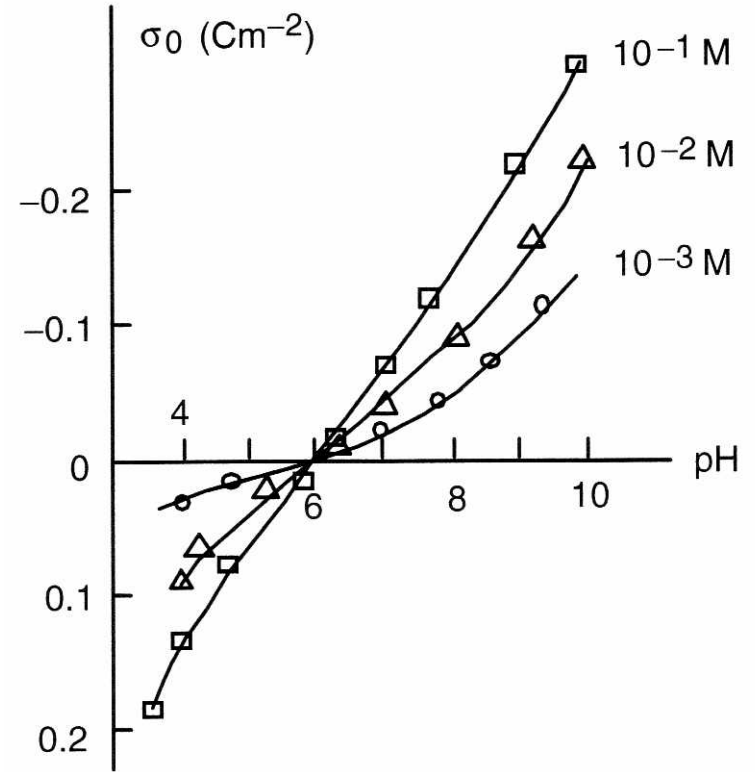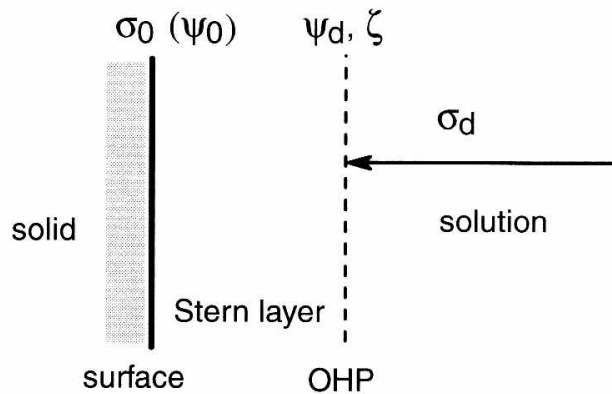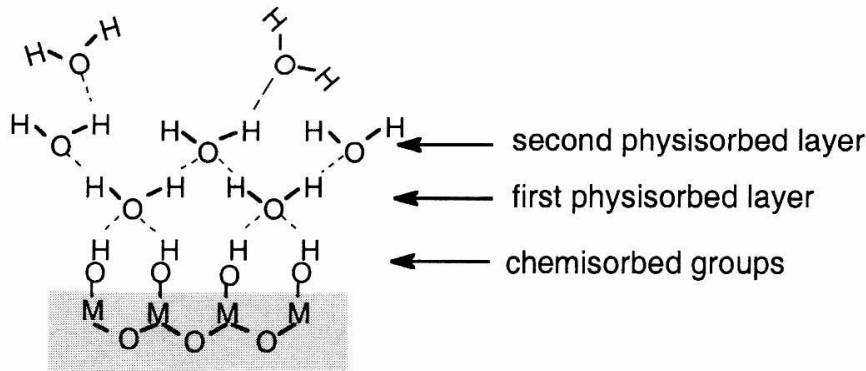
Variation of the surface charge of TiO_2 anatase as a function of the pH of NaCl solutions for several concentrations
J.-P. Jolivet, p. 218.

PZC   absence of positive or negative charges (M-OH)
IEP   equal amount of positive and negative charges $[M-OH_2^+] = [M-O^-]$
        determination by zeta potential measurements
        (measurement of the electrophoretic mobility by light scattering)

Chemical complexation methods

Oxalates, tartrates, and citrates of various metals can form well-crystallized complex salts which decompose to mixed oxides, e.g.
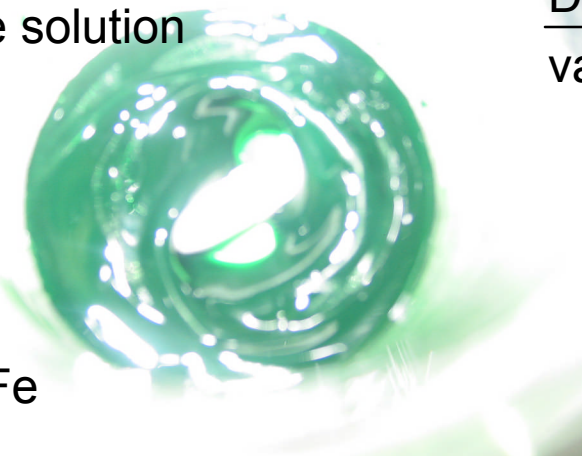
$Ca_2Cu(C_6H_5O_7)_2 x9H_2O$
$CuK_{10}(C_6H_4O_7)_3 x12H_2O$
$ZnNa_2(C_6H_4O_7)$
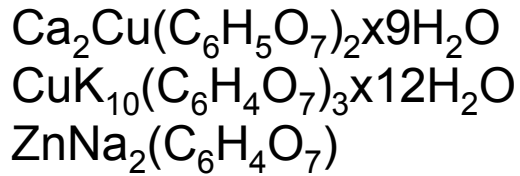
Amorphous precursor citrate method

Metals in form of nitates or ammonium salts + citric acid (1g/g metal)
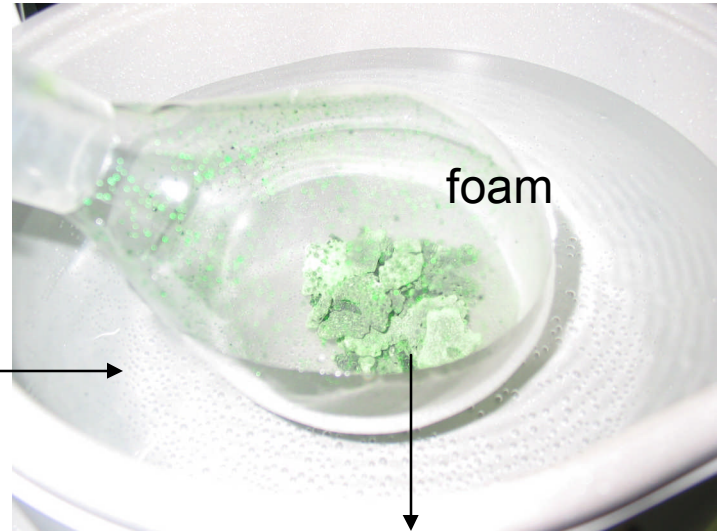
foam

Viscouse solution

Dehydration
vacuum 350 K

Sol

CuFe

Thermal decomposition

Fine powder, high surface area

Chemical complexation methods

Preparation of perovskite-type catalysts

a) Calcination of solid mixtures of constituent metal oxides (ceramic method): surface area of $LaCoO_3$ = 1.7 m^2g^{-1}

b) Evacuation of aqueous solutions of the constituent metal nitrates or acetates followed by calcination

Sample	Citrate process		Acetate process	
	Calcination temp. (K)	Surface area $(m^2\,g^{-1})$	Calcination temp. (K)	Surface area $(m^2\,g^{-1})$
$LaMnO_3$	923	44.8	1123	7.3
$LaCoO_3$	873	11.3	1123	2.2
$LaCo_{0.4}Fe_{0.6}O_3$	823	22.7	1123	3.3
$LaMn_{0.6}Cu_{0.4}O_3$	873	33.0	1123	7.5
$La_{0.8}Sr_{0.2}MnO_3$	873	36.4	1123	8.2
$LaCo_{0.8}Cu_{0.2}O_3$	823	24.7	–	–
$La_{0.6}Ca_{0.4}MnO_3$	873	33.0	–	–
$La_{0.4}Ca_{0.6}CoO_3$	873	14.3	–	–

P.G. Menon, B. Delmon in Preparation of Solid Catalysts, p. 131.

29

Hydrothermal transformations

Modification of precipitates, gels or flocculates, under aging or ripening at **T>100°C, p>1bar** in an aqueous medium or steam

- Small crystals or amorphous particles -> large crystals or amorphous particles
- Amorphous material -> crystalline material
- Crystal 1 -> crystal 2
- Aging of a gel
- Metastable, more complex structures are favoured involving smaller enthalpy and entropy changes than standard conditions

Nature: Formation of minerals in
            geological processes

Realization in the lab: Autoclaves, T=150-400°C

Autoclave/Parr

Water under hydrothermal conditions

•The dielectric constant of water decreases with increasing temperature and increases as pressure increases – electrolytes form ion pairs

•The viscosity of water decreases with increasing temperature – increased mobility of dissolved species

•The ionic product of water (dissociation) increases strongly with the temperature – strength of acids and bases is modified
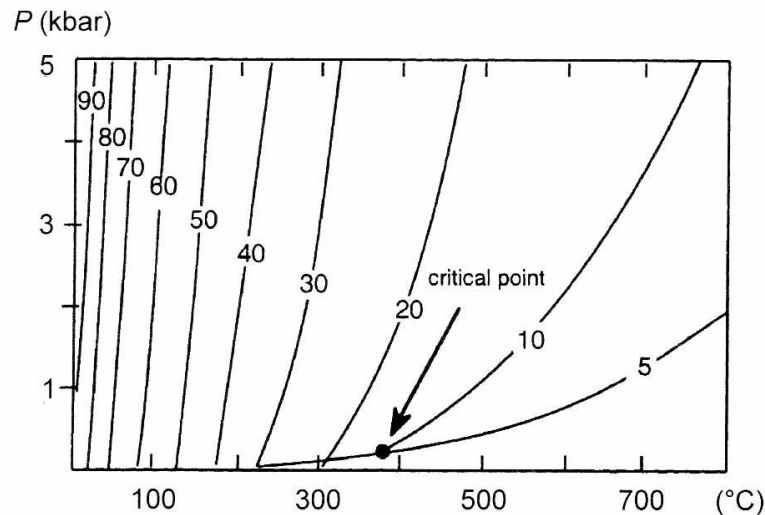
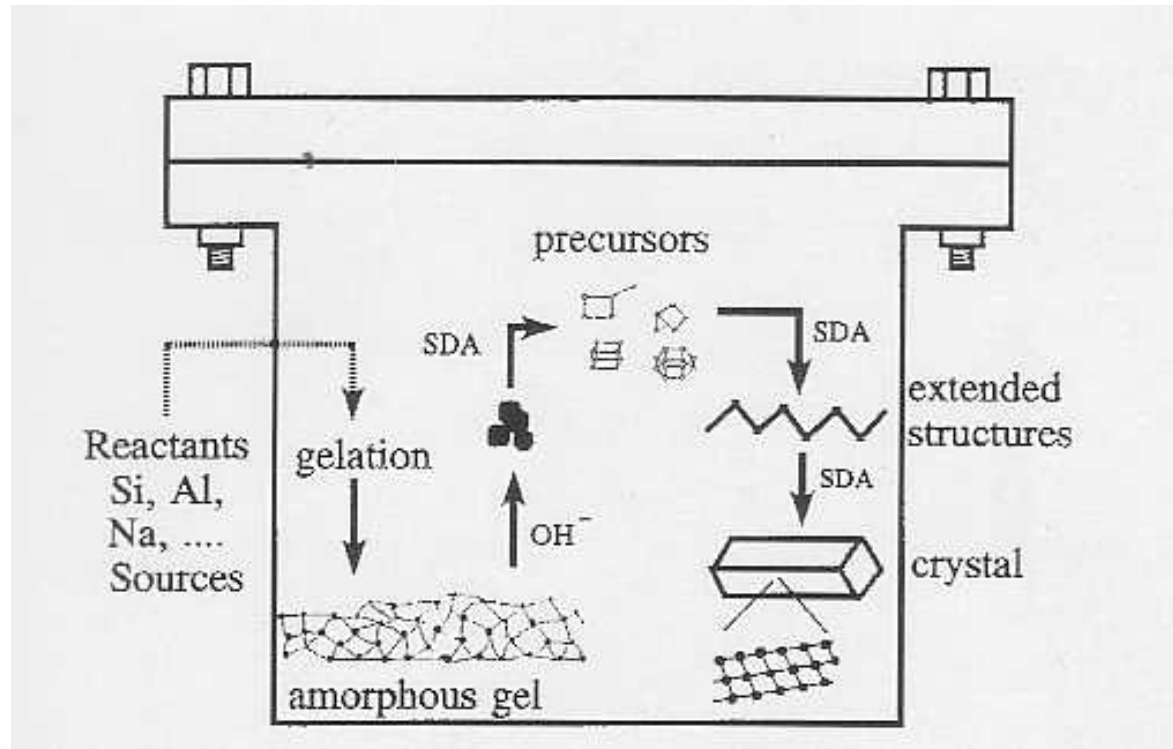Change in the dielectric constant of water as a function of T and p
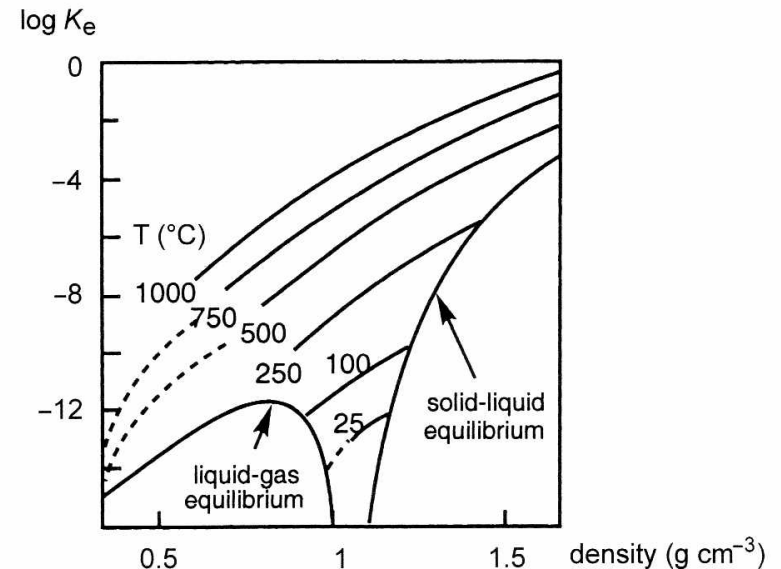
Ionic product of water as a function of T and density of the liquid

A. Rabenau, Angew. Chem. 97 (1985) 1017.   *J.-P. Jolivet, p. 21-2.*

Hydrothermal zeolithe synthesis

Colloidal silica
Waterglass
Silicon alkoxides
(TEOS)

Gibbsite
Pseudo-boehmite
Aluminate salts

Mineralizing agent

Schematic representation of the zeolite formation process , SDA= structural directing agent

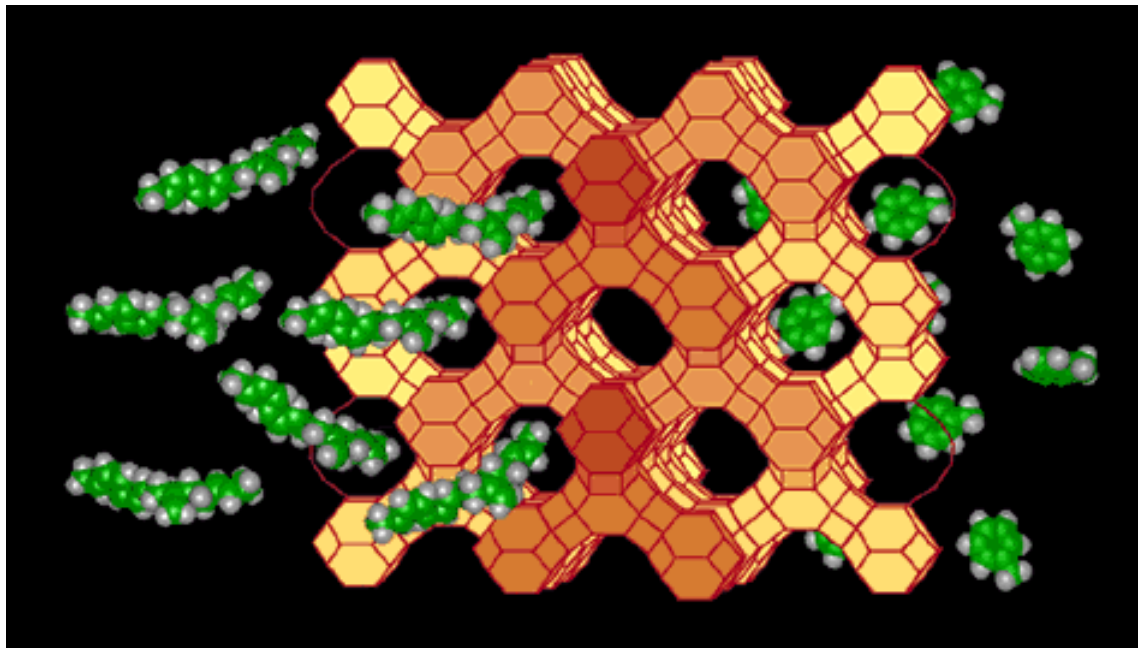*E.J.P. Feijen, J.A. Martens, P.A.Jacobs, Catalyst preparation, p. 263.*

Depending on reaction conditions (composition, acidity, T, p, ..., many different compounds are formed.

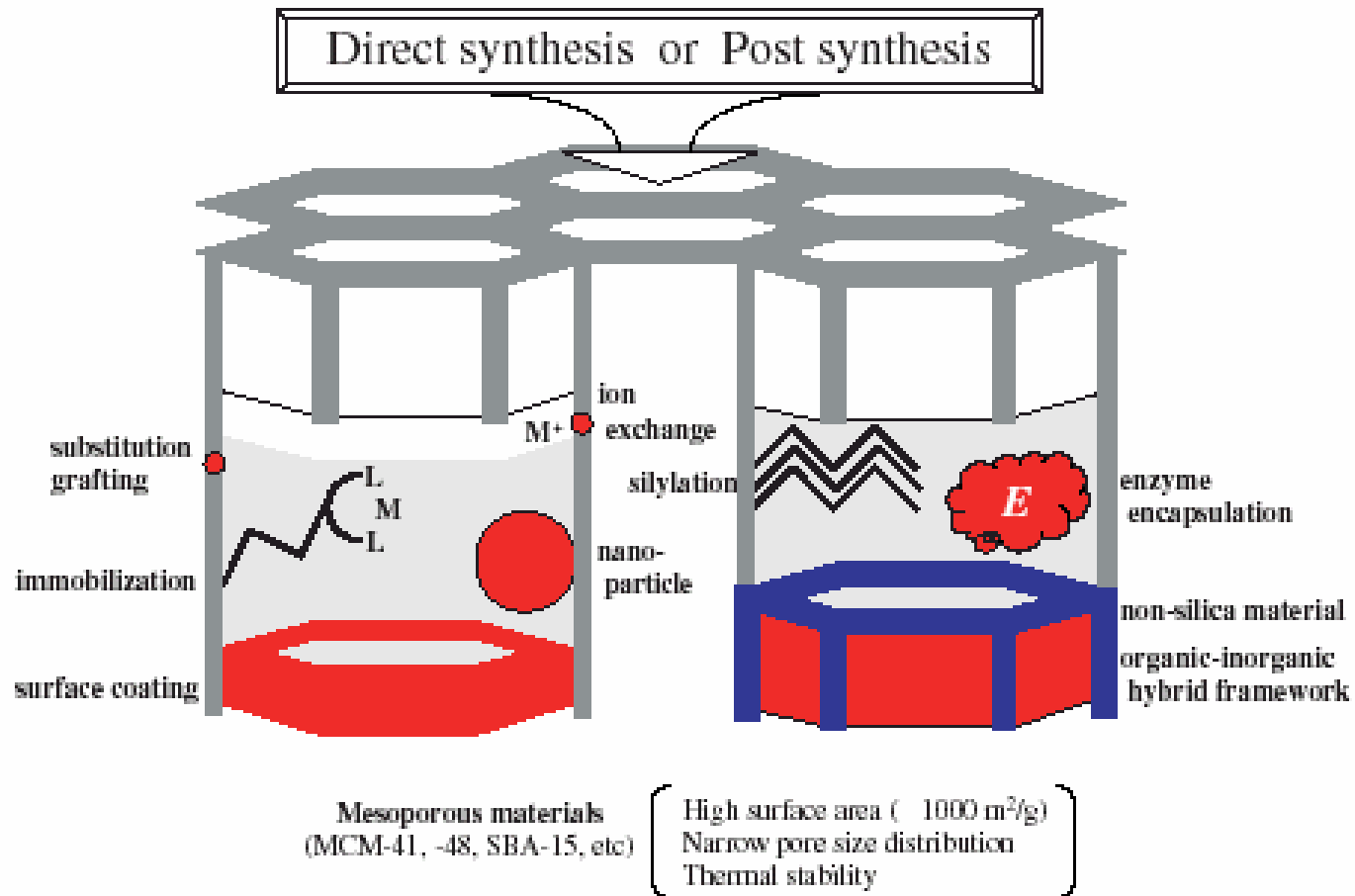# Hydrothermal zeolithe synthesis

Tetramethylammonium cations occluded into the sodalite cage

G.J. de A.A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, Chem. Rev. 102 (2002) 4093.
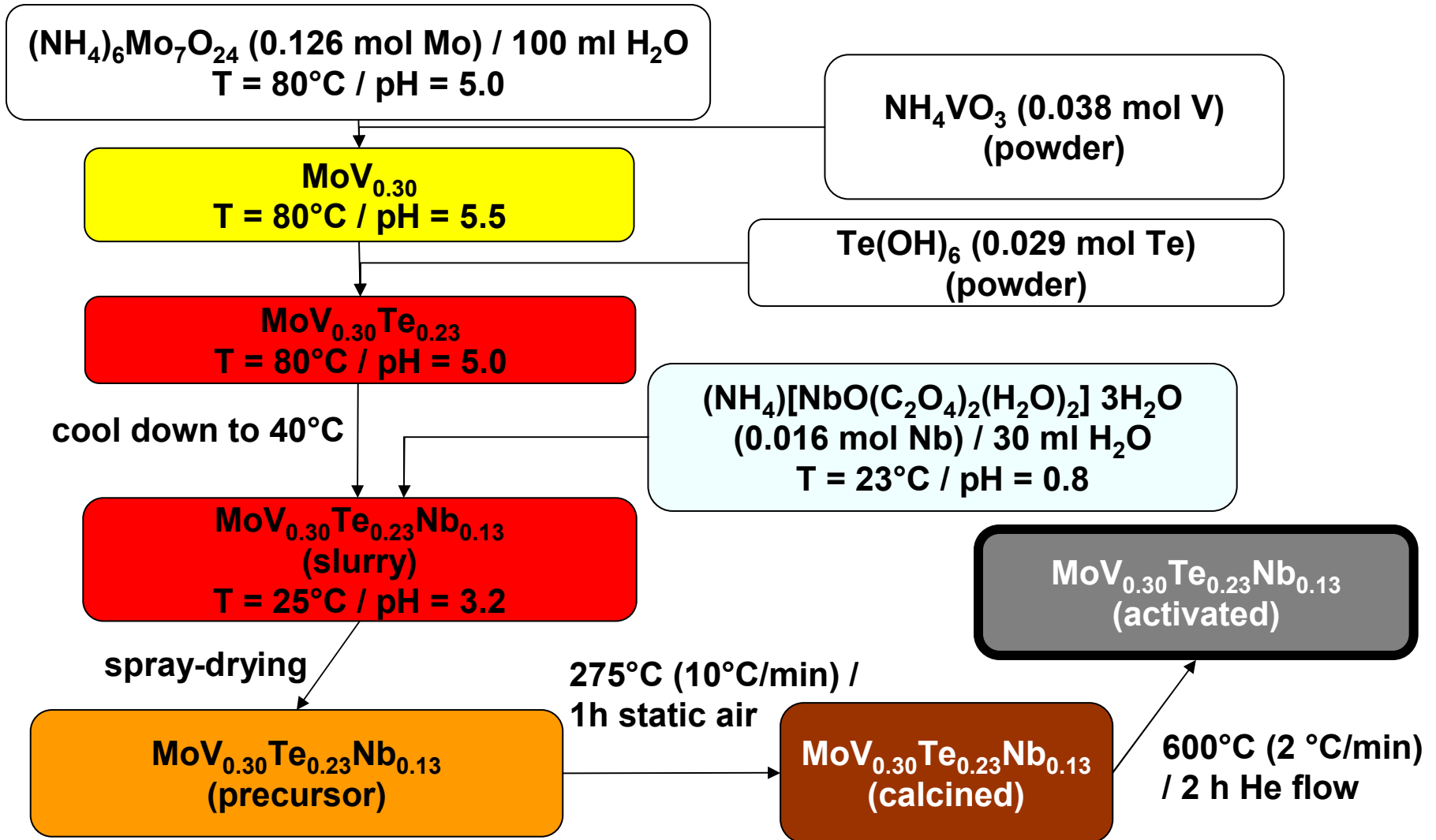
Hydrothermal zeolithe synthesis

Direct synthesis or Post synthesis

substitution grafting · ion exchange · silylation · enzyme encapsulation · immobilization · nano-particle · non-silica material · organic-inorganic hybrid framework · surface coating

Mesoporous materials (MCM-41, -48, SBA-15, etc) — High surface area (1000 m²/g) · Narrow pore size distribution · Thermal stability
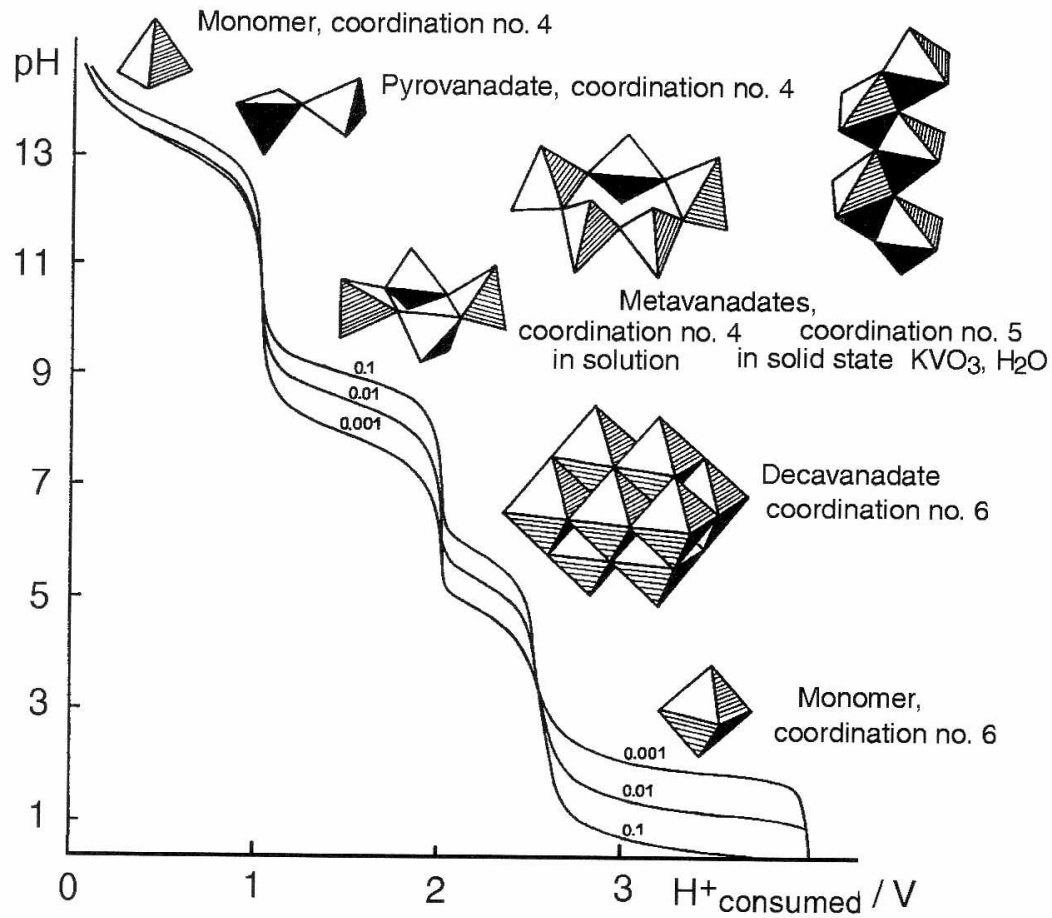
Schematic sketch of the various methods for the functionalization of mesoporous material - There are many possible strategies and pathways to introduce novel functions in mesoporous materials

A. Taguchi, F. Schüth, Micropor. Mesopor. Mater. 77 (2005) 1.

Preparation of $Mo_1V_{0.3}Te_{0.23}Nb_{0.125}O_x$ by the „slurry method"

$(NH_4)_6Mo_7O_{24}$ (0.126 mol Mo) / 100 ml H_2O
T = 80°C / pH = 5.0

NH_4VO_3 (0.038 mol V)
(powder)

$MoV_{0.30}$
T = 80°C / pH = 5.5

$Te(OH)_6$ (0.029 mol Te)
(powder)

$MoV_{0.30}Te_{0.23}$
T = 80°C / pH = 5.0

$(NH_4)[NbO(C_2O_4)_2(H_2O)_2]$ $3H_2O$
(0.016 mol Nb) / 30 ml H_2O
T = 23°C / pH = 0.8

cool down to 40°C

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(slurry)
T = 25°C / pH = 3.2

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(activated)

spray-drying

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(precursor)

275°C (10°C/min) /
1h static air

$MoV_{0.30}Te_{0.23}Nb_{0.13}$
(calcined)

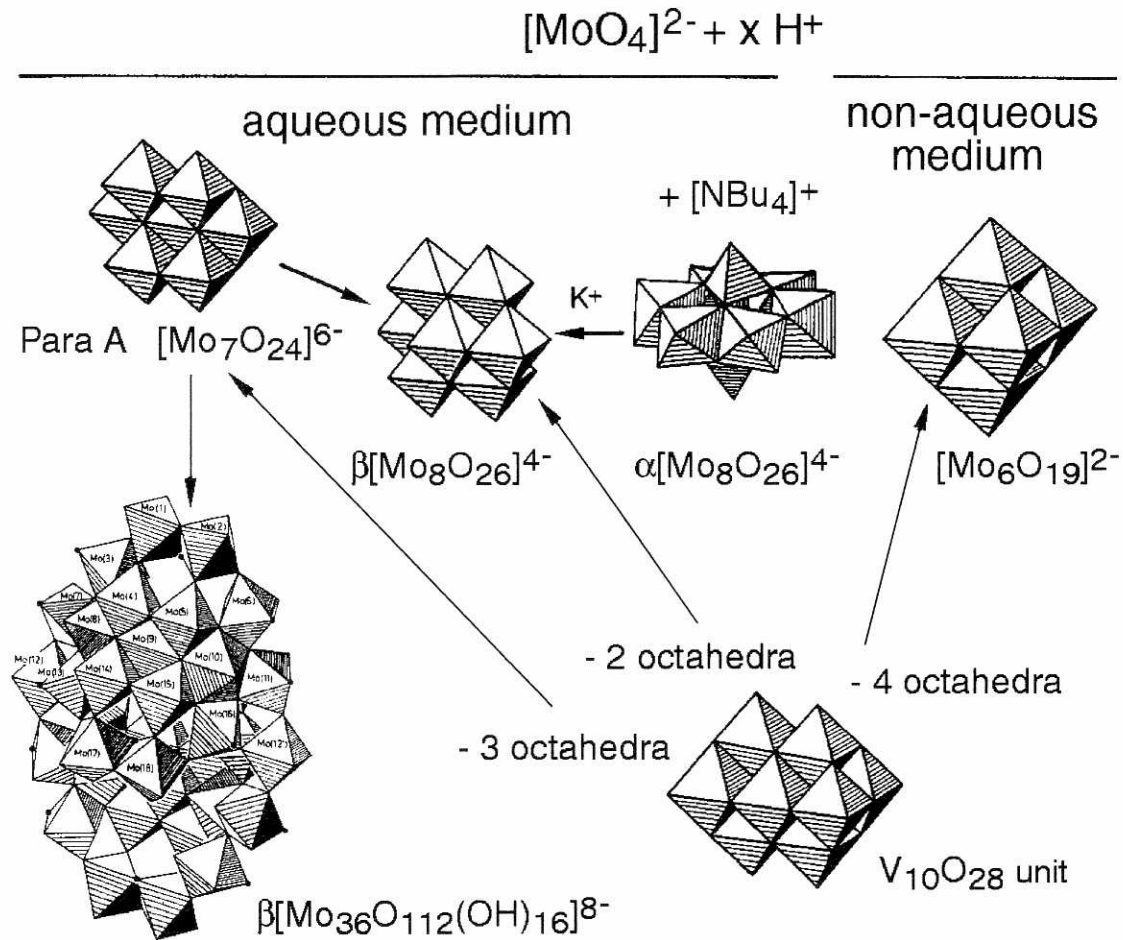600°C (2 °C/min)
/ 2 h He flow

35

Oxolation – condensation of tansition metals

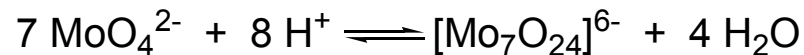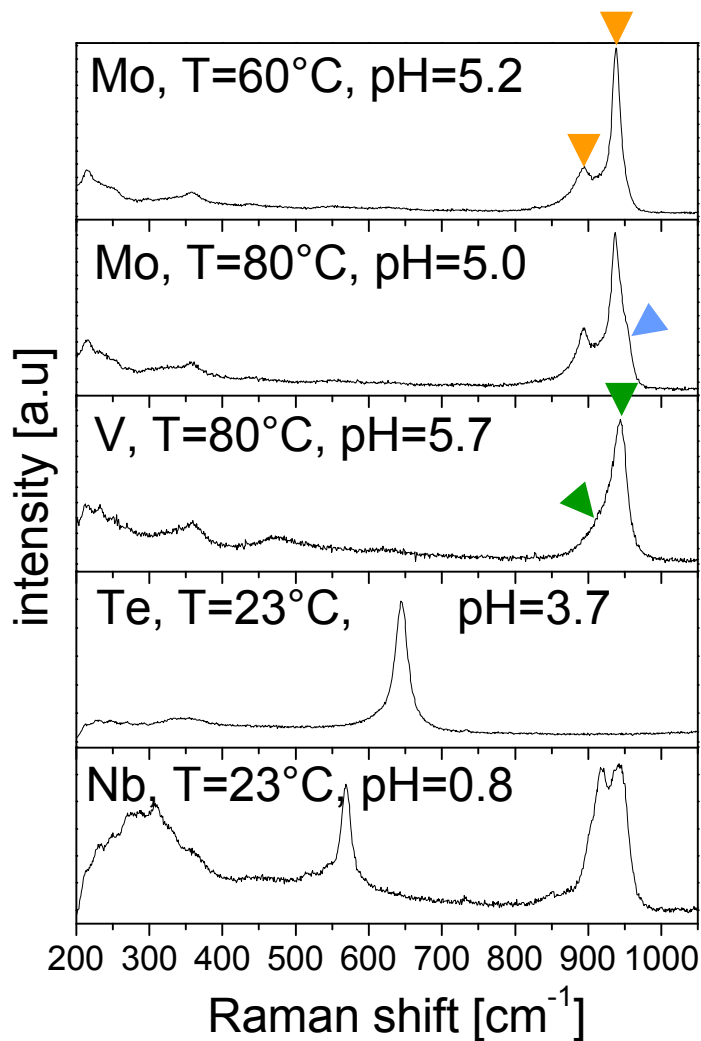Titration curves of vanadate solutions for various vanadium concentrations

J.-P. Jolivet, p. 115
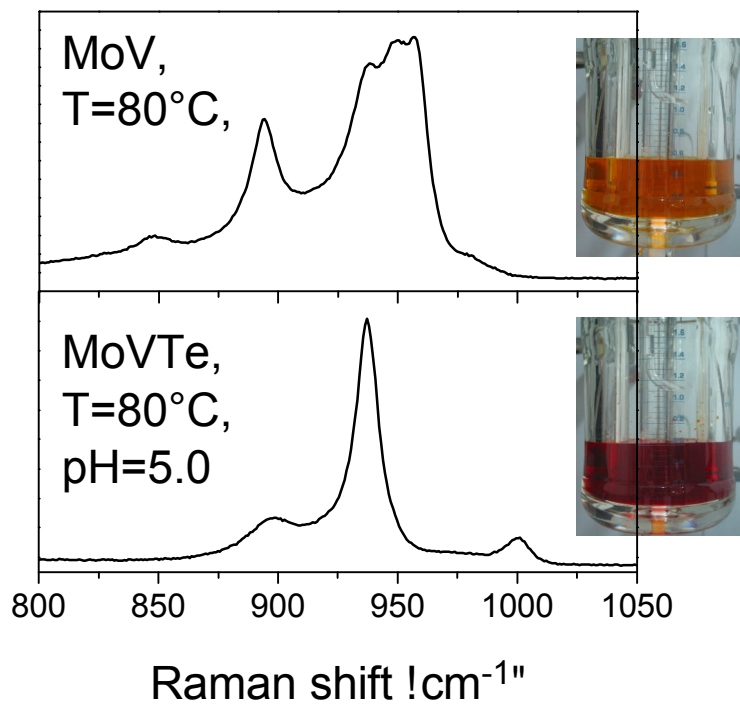
Oxolation – condensation of tansition metals

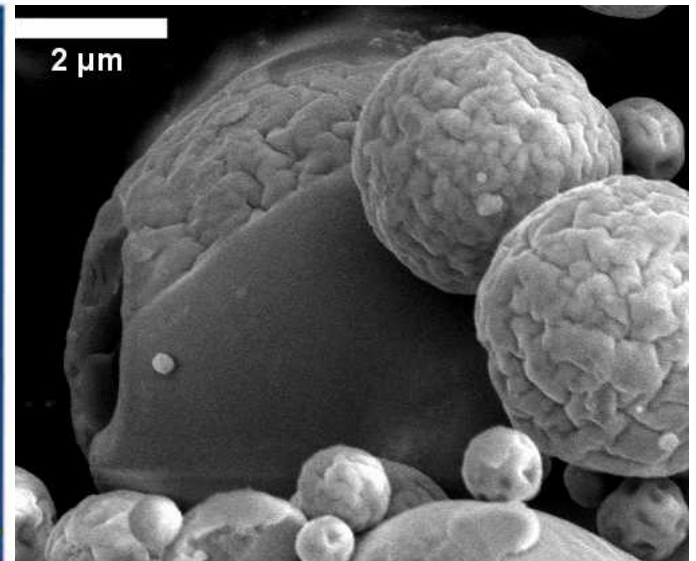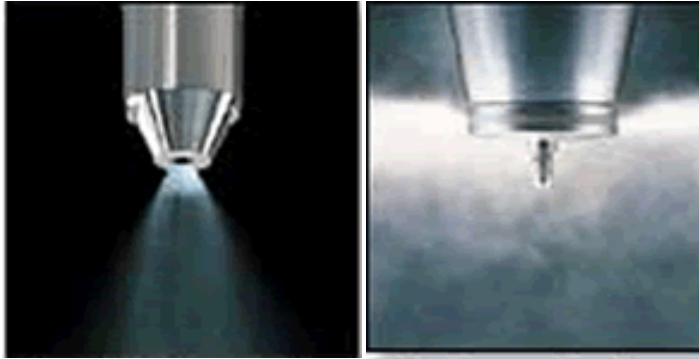Structure of a few molybdic ions

Raman spectroscopy on initial solutions

$$7\ MoO_4^{2-}\ +\ 8\ H^+ \rightleftharpoons [Mo_7O_{24}]^{6-}\ +\ 4\ H_2O$$

$$8\ MoO_4^{2-}\ +\ 12\ H^+ \rightleftharpoons [Mo_8O_{26}]^{4-}\ +\ 6\ H_2O$$

ν [cm^{-1}]	assignment
937 (s) 893 (m)	ν (Mo=O) $Mo_7O_{24}^{6-}$
955 (sh)	n (Mo=O) $Mo_8O_{26}^{4-}$
944 (s) 900 (sh)	ν (V=O) $[VO_3]_n^{n-}$
644 (s)	ν (Te-O)
570 (m) 942 (s) 919 (s)	ν (Nb-O) ν (Nb=O)

*M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer Verlag, Berlin 1983.*

MoV,
T=80°C,

MoVTe,
T=80°C,
pH=5.0

Raman shift $!cm^{-1}"$

Spray drying

1	Feed pump, peristaltic
2	Rotary atomizer
3	Two-fluid nozzle, co-current
4	Two-fluid nozzle, fountain
5	Pre-filter, EU4
6	Heater, 7.5 kW
7	Drying chamber, Ø800 mm x 620 mm
8	Cyclone, Ø140 mm
9	Cartridge filter (optional)
10	Cartridge filter, in-line
11	Exhaust fan, 0.75 kW
12	Supply fan, 0.75 kW
13	HEPA filter
14	Laminar air flow box
15	Tube/shell condenser
16	Nitrogen compressor (optional)
17	Oxygen analyser

Morphology of spray-dried $MoVTeNbO_x$
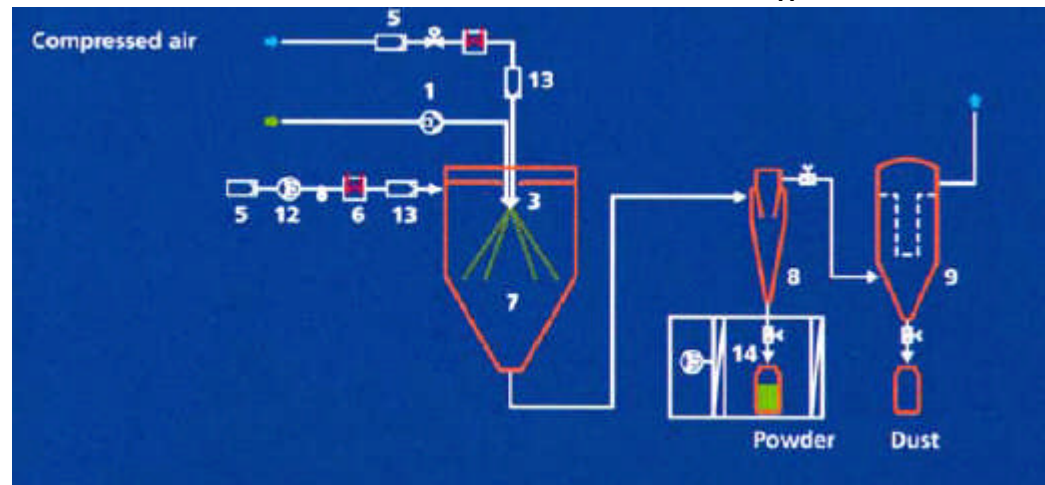
Raman spectra of spray-dried materials