Catalyst Synthesis

FHI-AC Lecture Series on Modern Methods in Heterogeneous Catalysis

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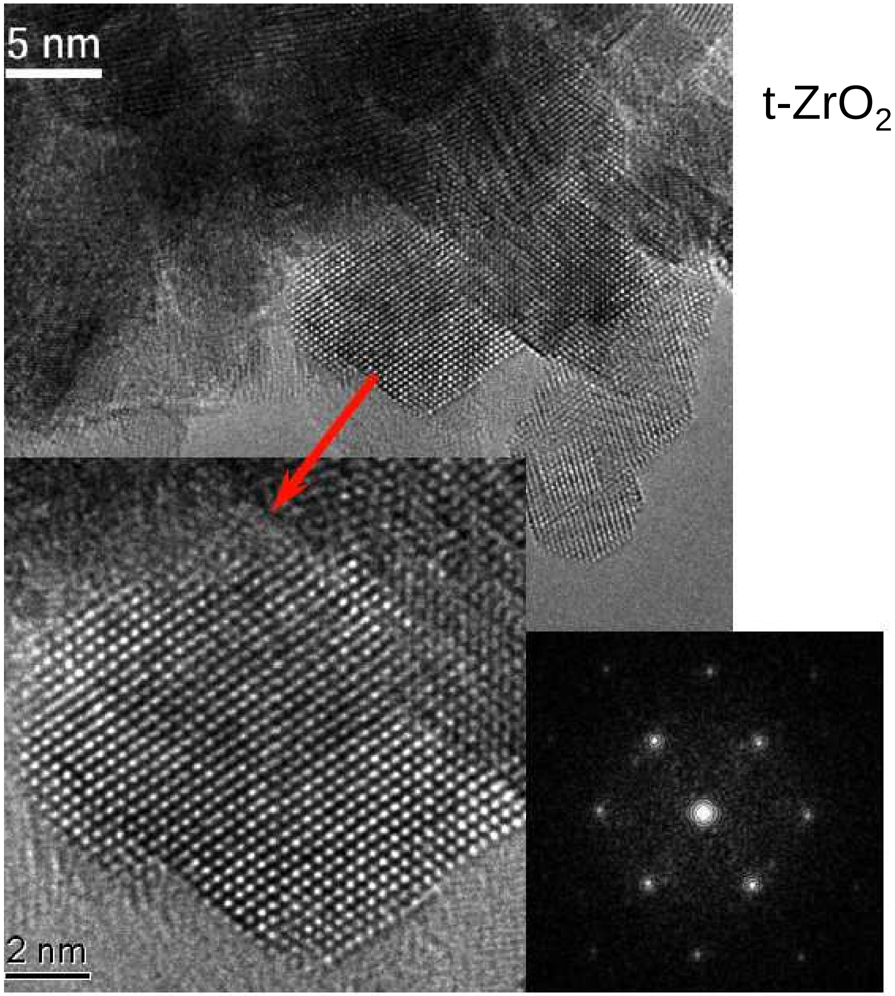
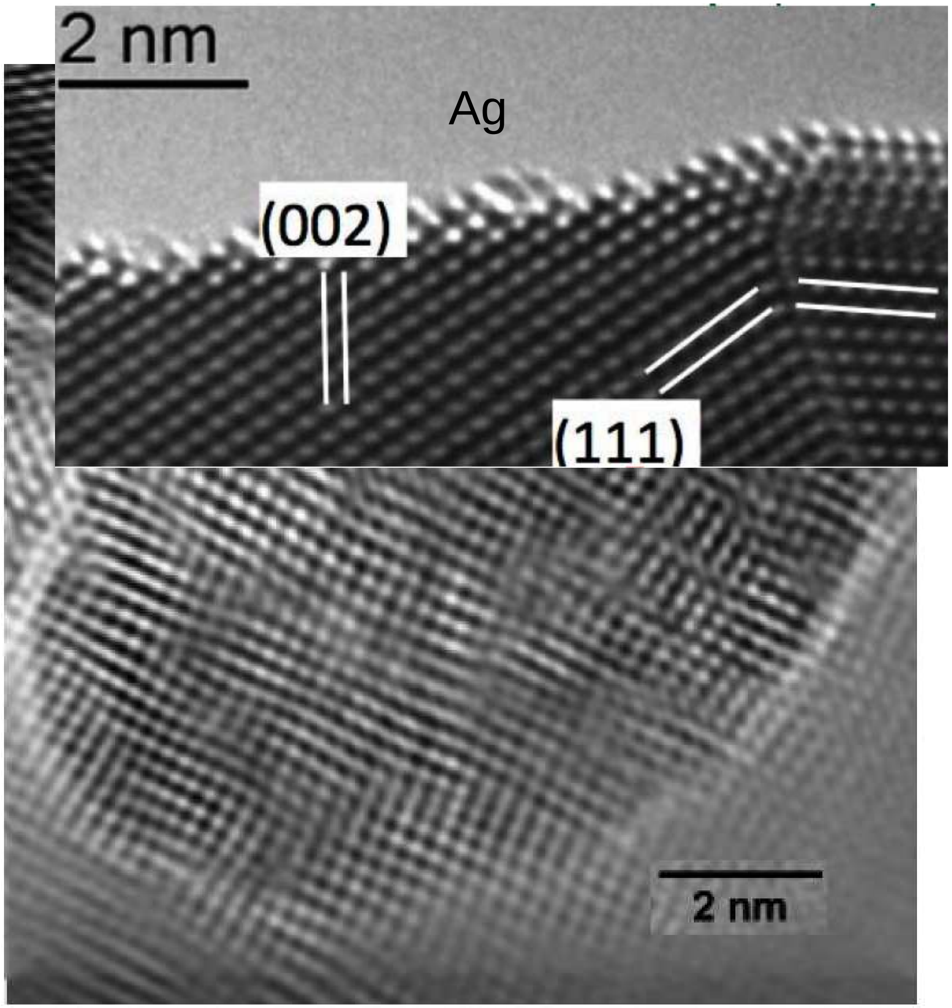
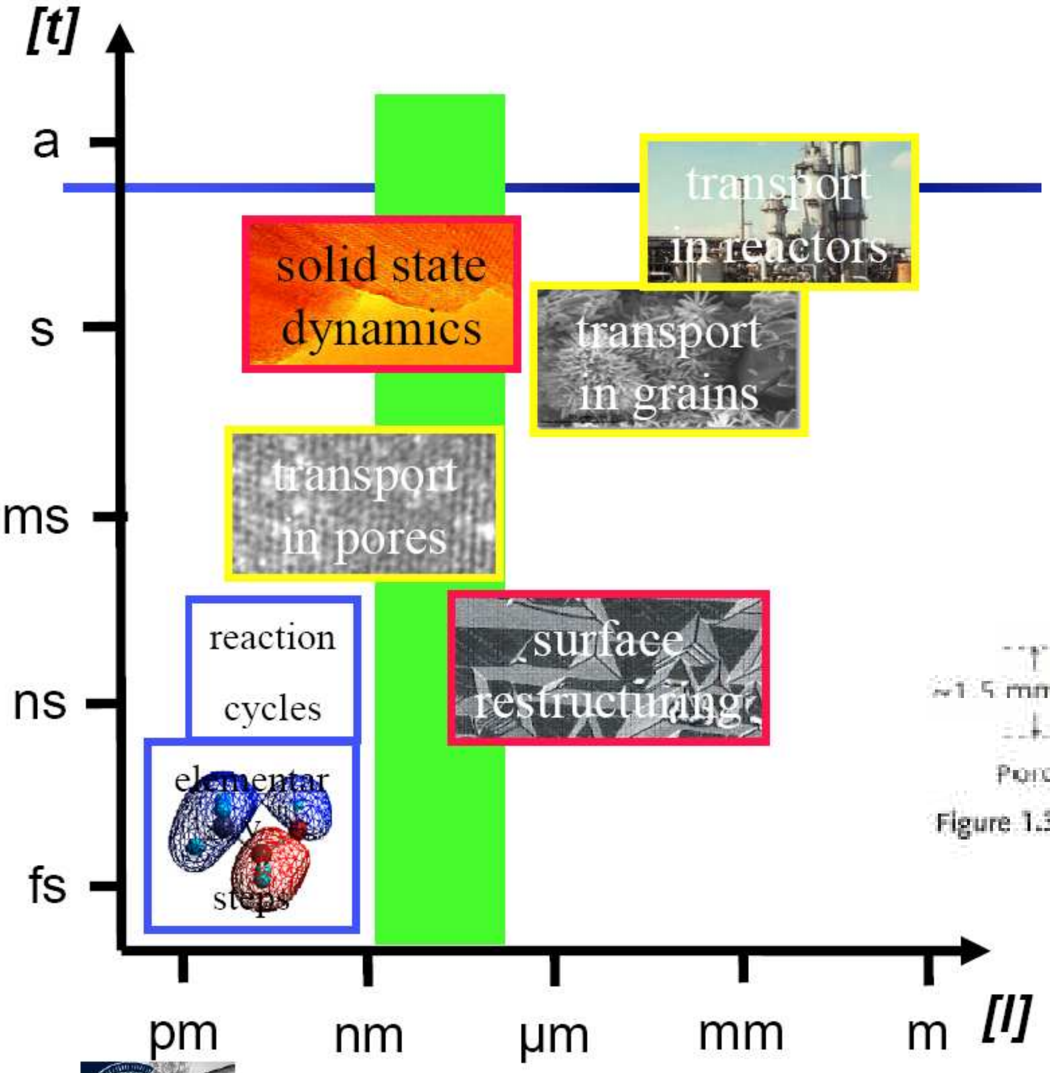
Active microstructures



t-ZrO_2



Dimensions of catalyst preparation



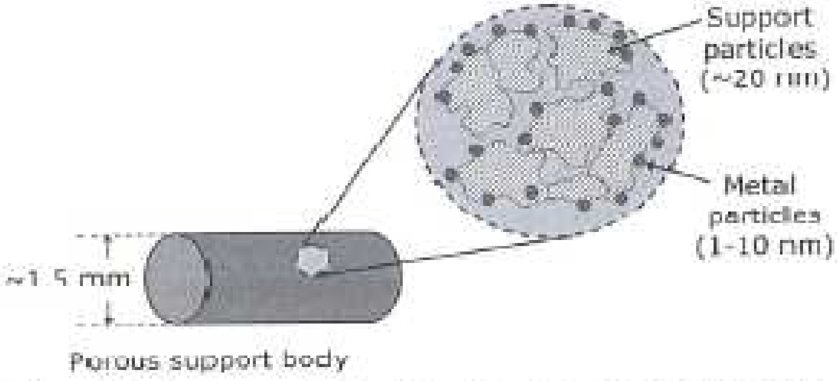


Figure 1.3 Structure at different length scales of catalyst extrudate.

Catalyst preparation

- Target configuration (active sites) often unknown
- Material and pressure gap in heterogeneous catalysis
- High surface area material are desired (“porous” / “nano”)
- Defects play a role
- Homogeneity is an issue

- Mostly empirical (trail & error) optimization
- Application requires reproducibility, scalability and economic / environmental feasibility

Progress of catalyst synthesis

Table 1.2 Survey of selected catalysts with their main applications.

Catalyst	Applications
Ni/SiO_2	Hydrogenation
$K_2O/Al_2O_3/Fe$	Ammonia synthesis
$Ag/\alpha\text{-}Al_2O_3$	Epoxidation
CrO_x/SiO_2	Polymerization
$CoMoS_2/\gamma\text{-}Al_2O_3$	Hydrotreating
Co/SiO_2	Fischer–Tropsch synthesis
$Cu/ZnO/Al_2O_3$	Methanol synthesis
Zeolite Y composite	Catalytic cracking
Pt/Mordenite	Hydroisomerization of light alkanes
V_2O_5/TiO_2	NO_x abatement
Pt/C	Hydrogenation; fuel cell

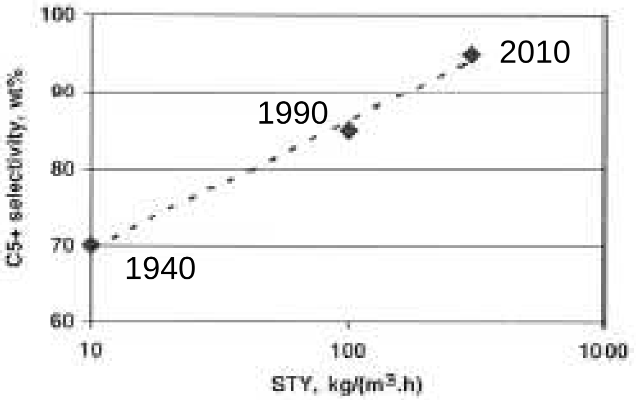


Figure 1.1 Development of cobalt-based Fischer–Tropsch synthesis in terms of both activity (STY = space time yield) and selectivity to hydrocarbons of five or more C-atoms. Data from 1940 to 2010 with data points from left to right at years 1940, 1990, and 2010, respectively.

Triggered by law

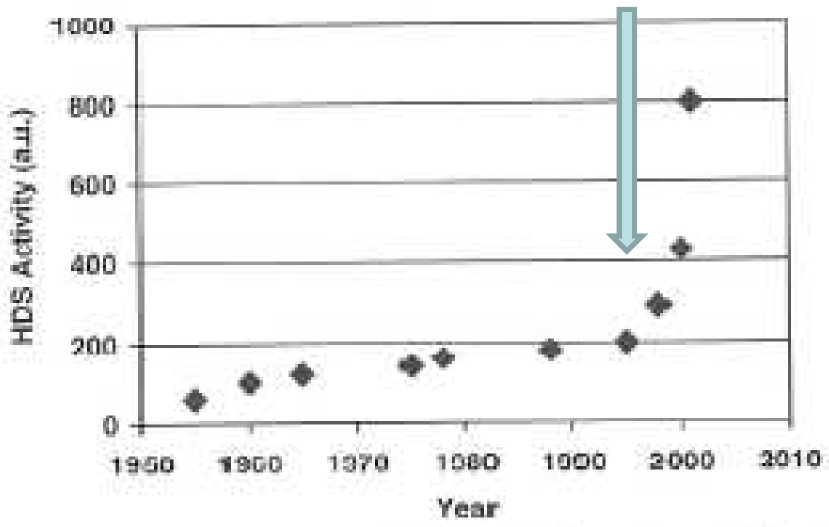
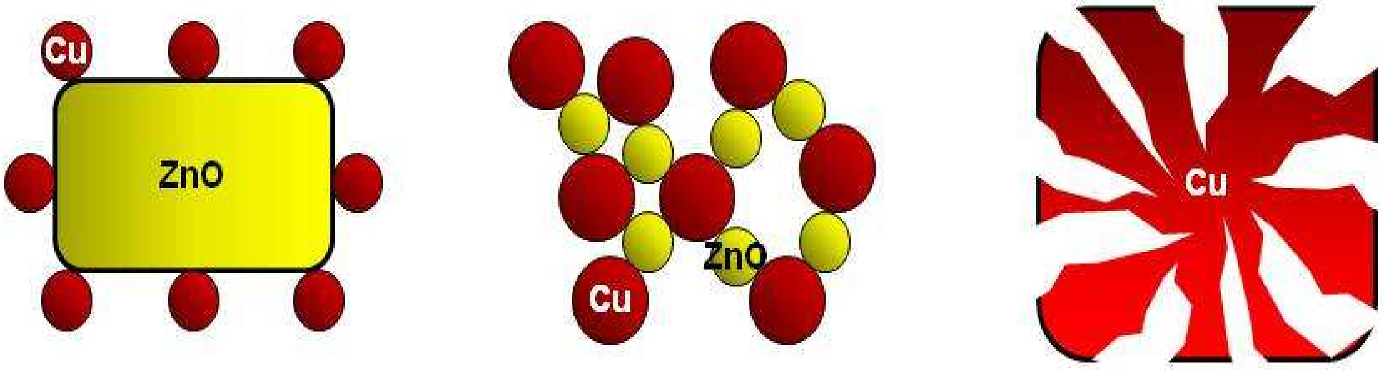


Figure 1.2 Development of hydrodesulfurization (HDS) catalyst activity over the years [6].

Krijn P. de Jong (ed): Synthesis of solid catalysts, Wiley 2009

Catalyst Microstructures



a) Supported catalyst

b) Porous bulk catalyst

c) Skeletal catalyst

Distribute a liquid precursor *uniformly* on a pre-formed support

Form acitve phase and stabilizer by thermal treatment of a *homogeneous* solid precursor

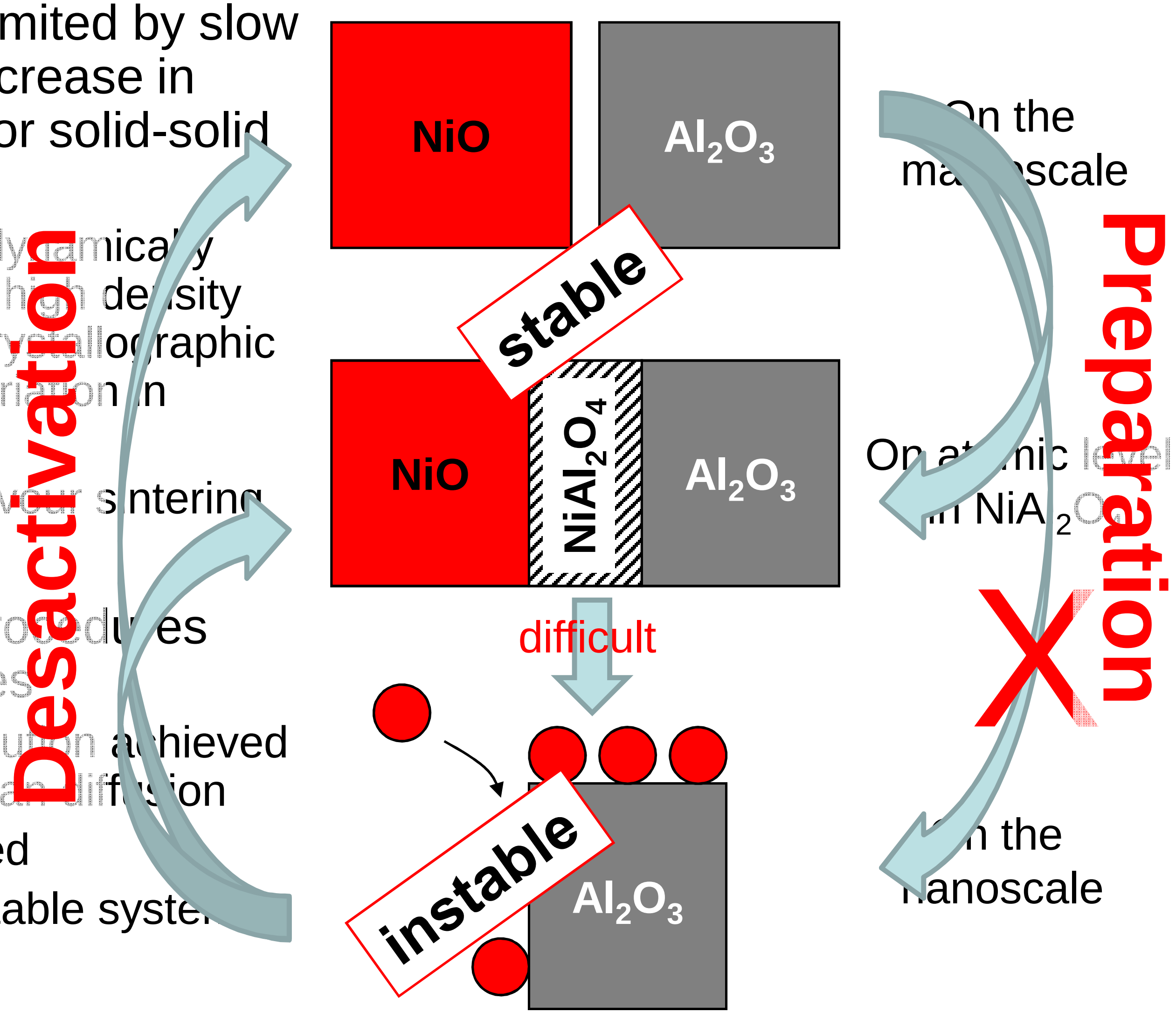
Leach pores into a previously *homogenous* alloy

Aspects of solid state chemistry

- Reactivity of solids is limited by slow diffusion processes: Increase in temperature required for solid-solid reactions (T > 600℃)
  - Formation of thermodynamically stable compounds of high density (low porosity), high crystallographic symmetry and low variation in building blocks
  - High temperatures favour sintering

- Catalyst preparation procedures avoid high temperatures
  - Homogeneous distribution achieved by other measures than diffusion
  - Liquid phases involved
  - Catalysts are meta-stable systems

Ni-Al distribution



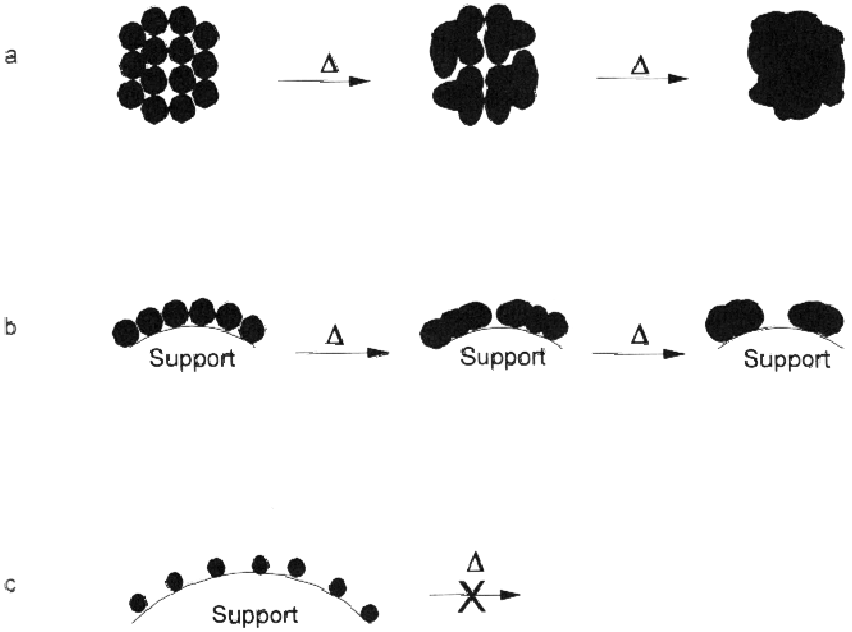
Outline

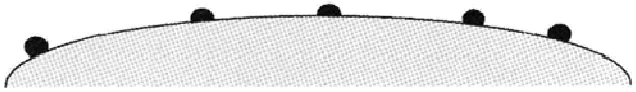
- Impregnation
  - Support materials
  - Key experimental parameters
  - Example: 3-way catalyst
- Co-precipitation
  - Precursor chemistry
  - Example: Methanol synthesis catalyst
- Skeletal catalysts
  - Leaching of alloys
  - Example: Raney nickel
- Hydrothermal synthesis
  - Principles of hydrothermal synthesis
  - Example: Zeolites
- Summary

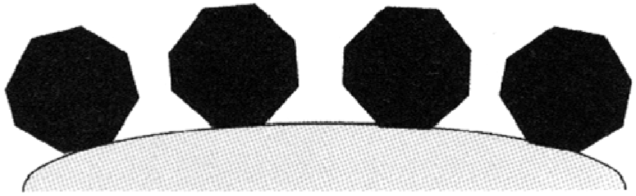
Impregnation: Role of supports

- Why (most) catalysts need to be supported: Sintering
- Support:
  - carries the active components
  - provides surface area (porosity)
  - keeps high dispersion of active component
  - is thermostable and chemically inert (?)

- Maximum active surface area of the active component desired
  - per unit weight (expensive precious metals, typical loading ~ 1 wt.-%)
  - per unit volume (base metals, oxides, typical loadings ~20 wt.-%)




Supported Precious Metal Catalyst


Supported Base Metal Catalyst

Preparation of supported catalysts

- Deposition of a precursor of the active phase onto the surface of the support
  - At the solid-liquid (wet) interface
    - Impregnation
    - Deposition precipitation
  - At the solid-gas (dry) interface
    - Vapor deposition
- Transformation of the precursor into the active phase

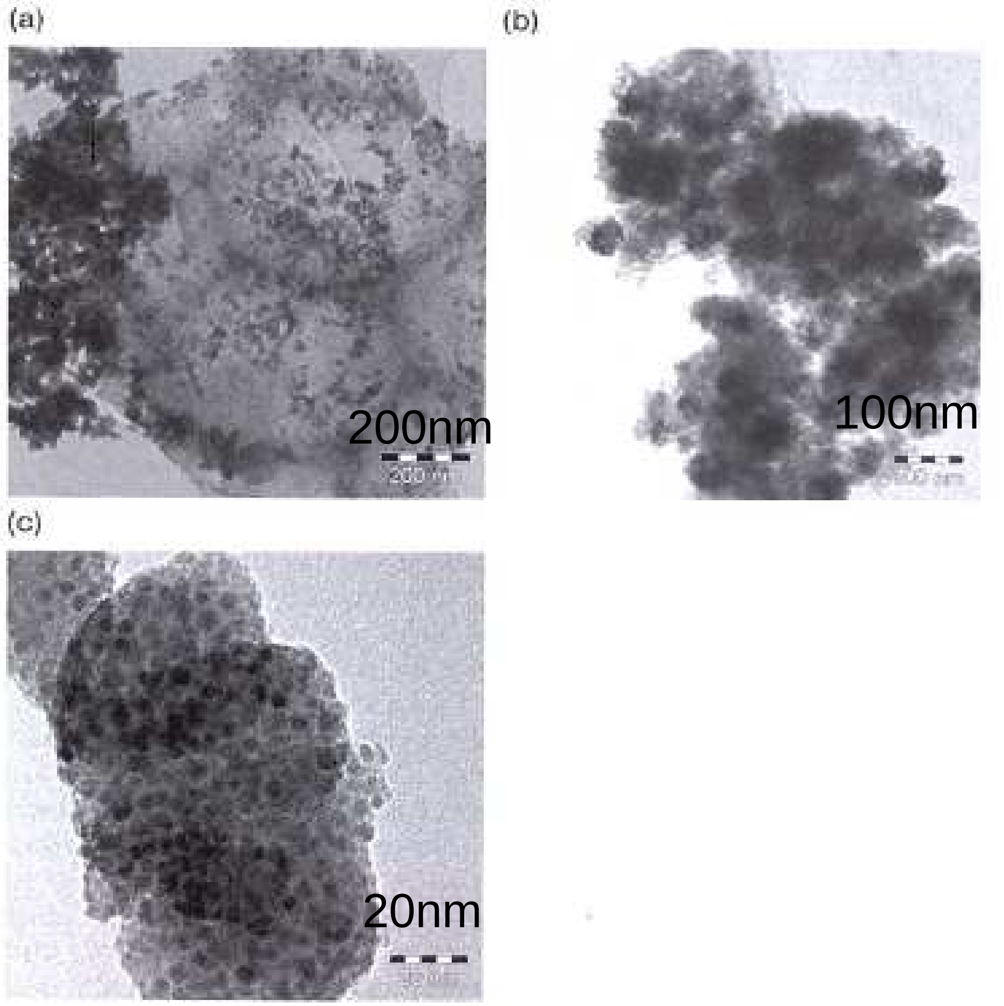
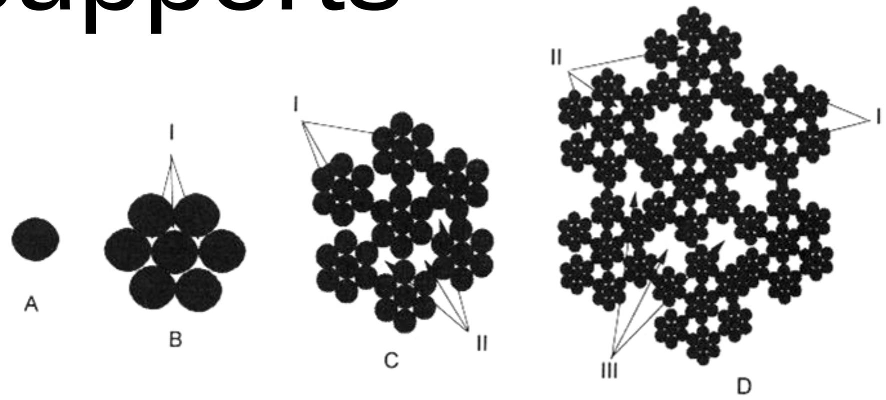
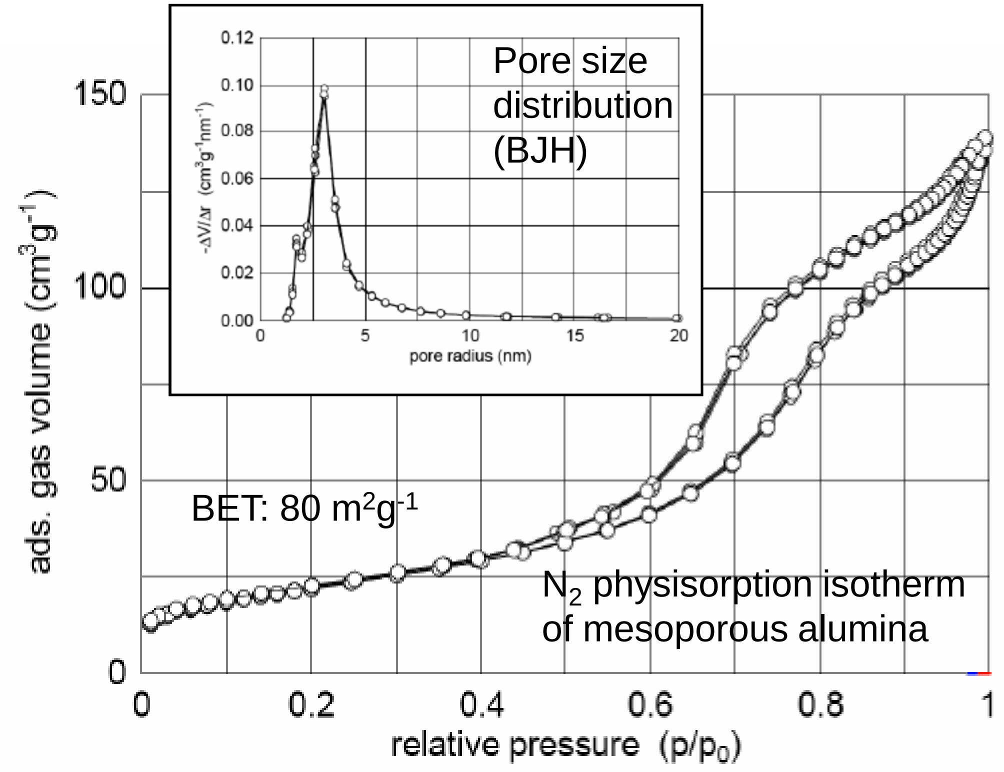


Figure 1.5 Three generations of silica-supported cobalt catalyst. (a) 50 wt% Co/kieselguhr prepared by precipitation; (b) 18 wt% Co on silica gel obtained by calcination in air flow; and (c) 18 wt% Co on silica gel obtained by calcination in NO/He flow.

Typical supports

- Alumina
  - mostly γ-phase
  - SA up to 400 m^2g^{-1}
- Silica
  - amorphous
  - SA up to 1000 m^2g^{-1}
- Carbon
  - amorphous, unstable in oxidative environment
  - SA up to 1000 m^2g^{-1}
- Zeolites / ordered mesoporous materials
  - highly defined pore system
- also: TiO_2, MgO, …





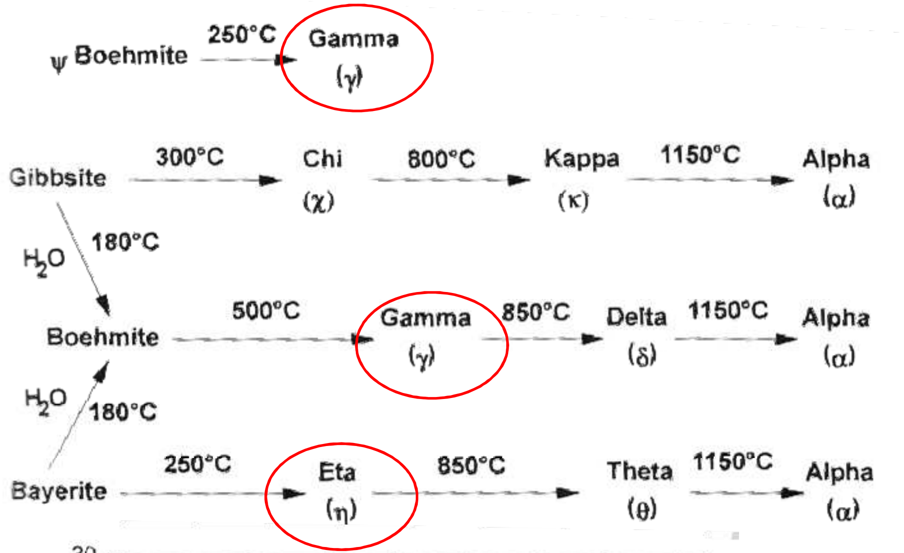
Pore size distribution (BJH)

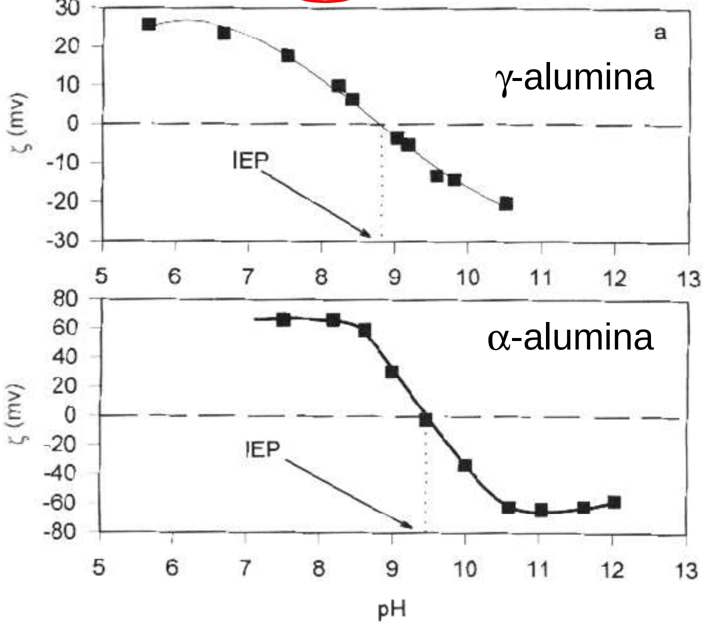
BET: 80 m^2g^{-1}

N_2 physisorption isotherm of mesoporous alumina

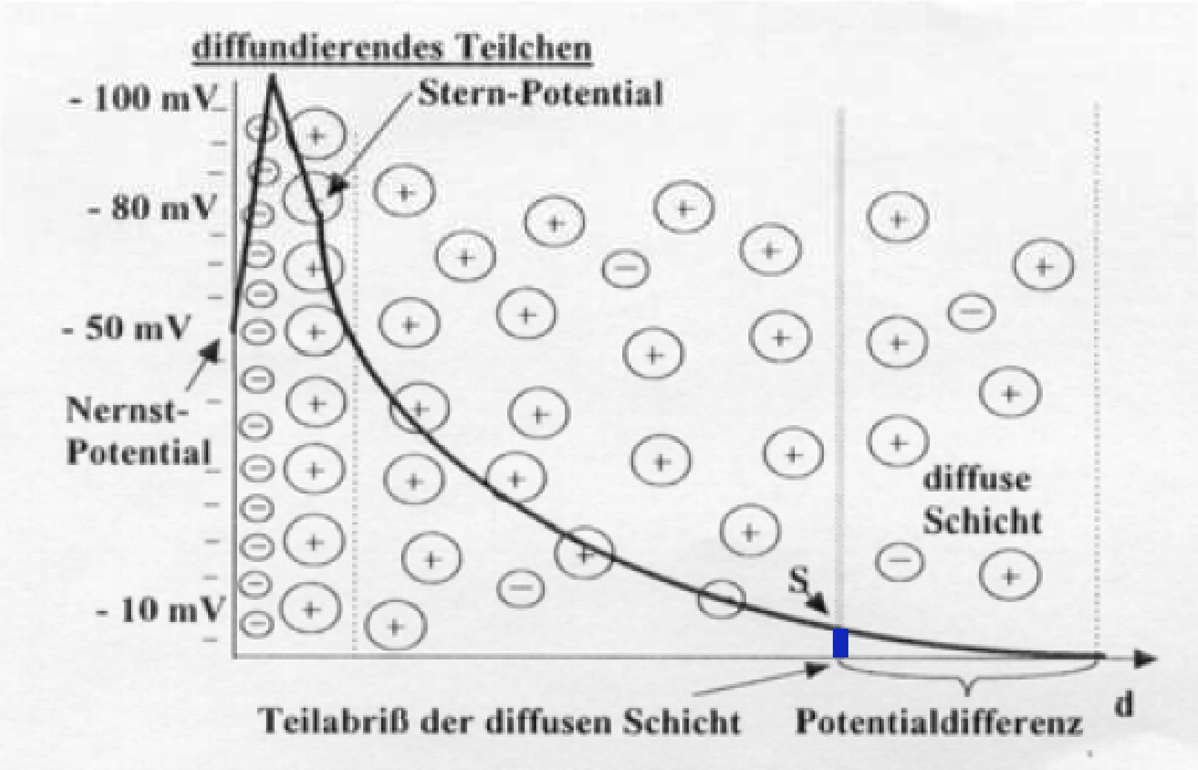
Synthesis of supports: Alumina

- Porous aluminas are obtained by controlled dehydration of $Al(OH)_3$ (Gibbsite, Bayerite) or $AlO(OH)$ ((Pseudo-)Boehmite)
  - transition aluminas: $Al_2O_3 \cdot x\ H_2O$
  - active aluminas: γ and η
  - full dehydration: non-porous α-Al_2O_3 (corundum)
- The non-porous hydroxides can be precipitated from Al salt solutions by increasing pH
  - Bayerite: high T and pH
  - (Pseudo-)Boehmite: low pH
- High purity aluminas are prepared by hydrolysis of Al-alcoholates

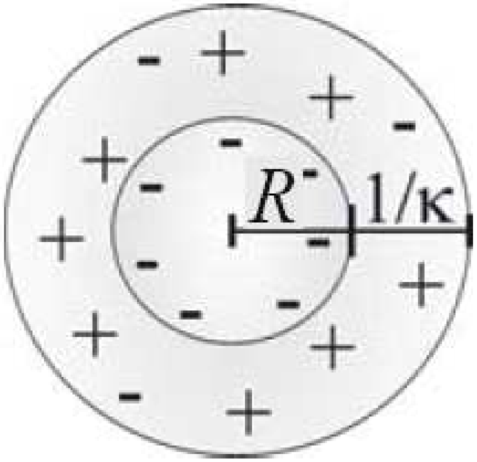




Surface charge and Zeta potential



Potential an der Scherebene S = Zetapotential (ZP)
(= Potentialdifferenz)

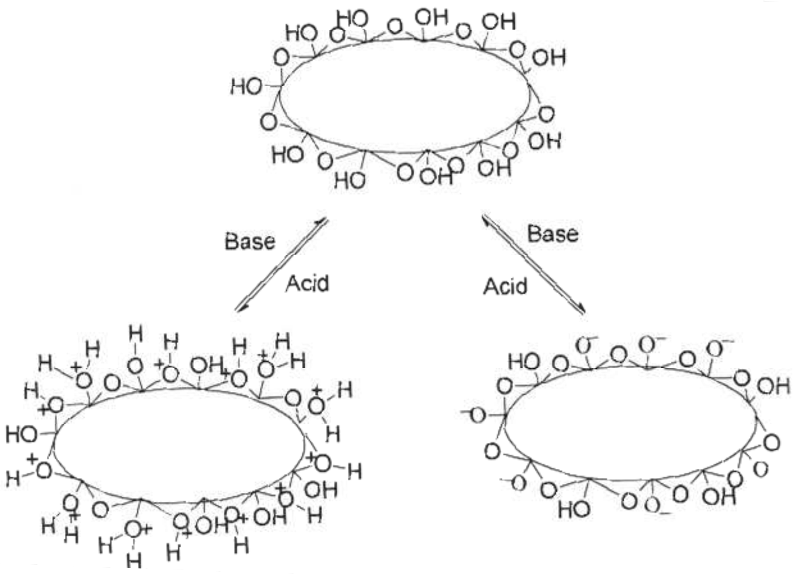


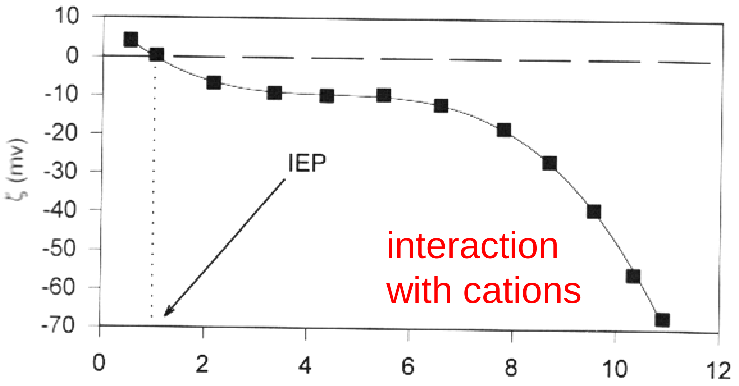
R: Partikelradius

κ^{-1}: rezipr. Debyesche Abschirmlänge

Surface charge of oxide supports

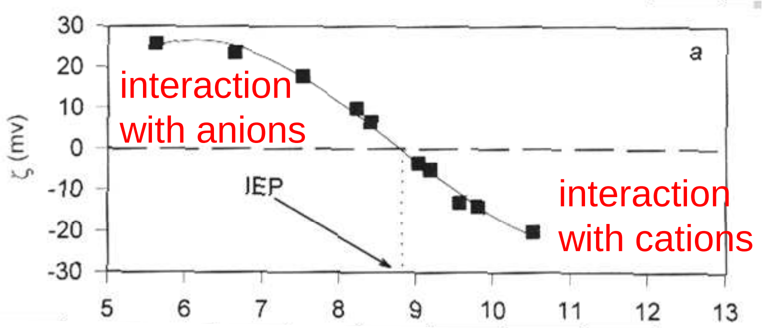
- In contact with water hydroxyl groups are formed on the oxide surface (M-OH)
- M-OH may behave as Brønstedt acids or bases
    - $M\text{-}OH + OH^- \rightarrow M\text{-}O^- + H_2O$
    - $M\text{-}OH + H^+ \rightarrow M\text{-}OH_2^+$
- Surface charge depends on solution pH
- Zeta (ζ-) potential is an estimation of surface charge





interaction with cations

silica

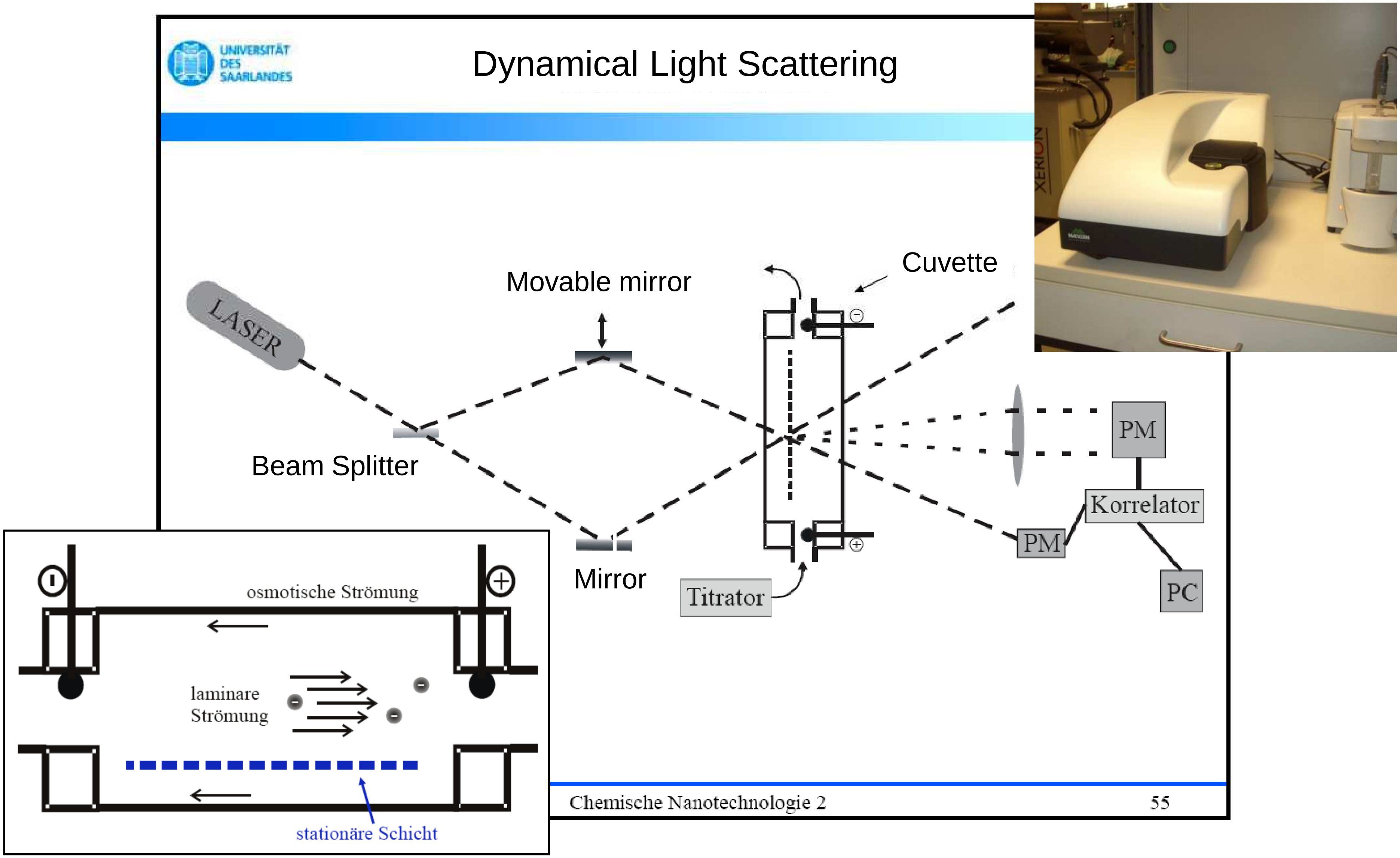


interaction with anions

interaction with cations

γ-alumina

Zeta potential measurement



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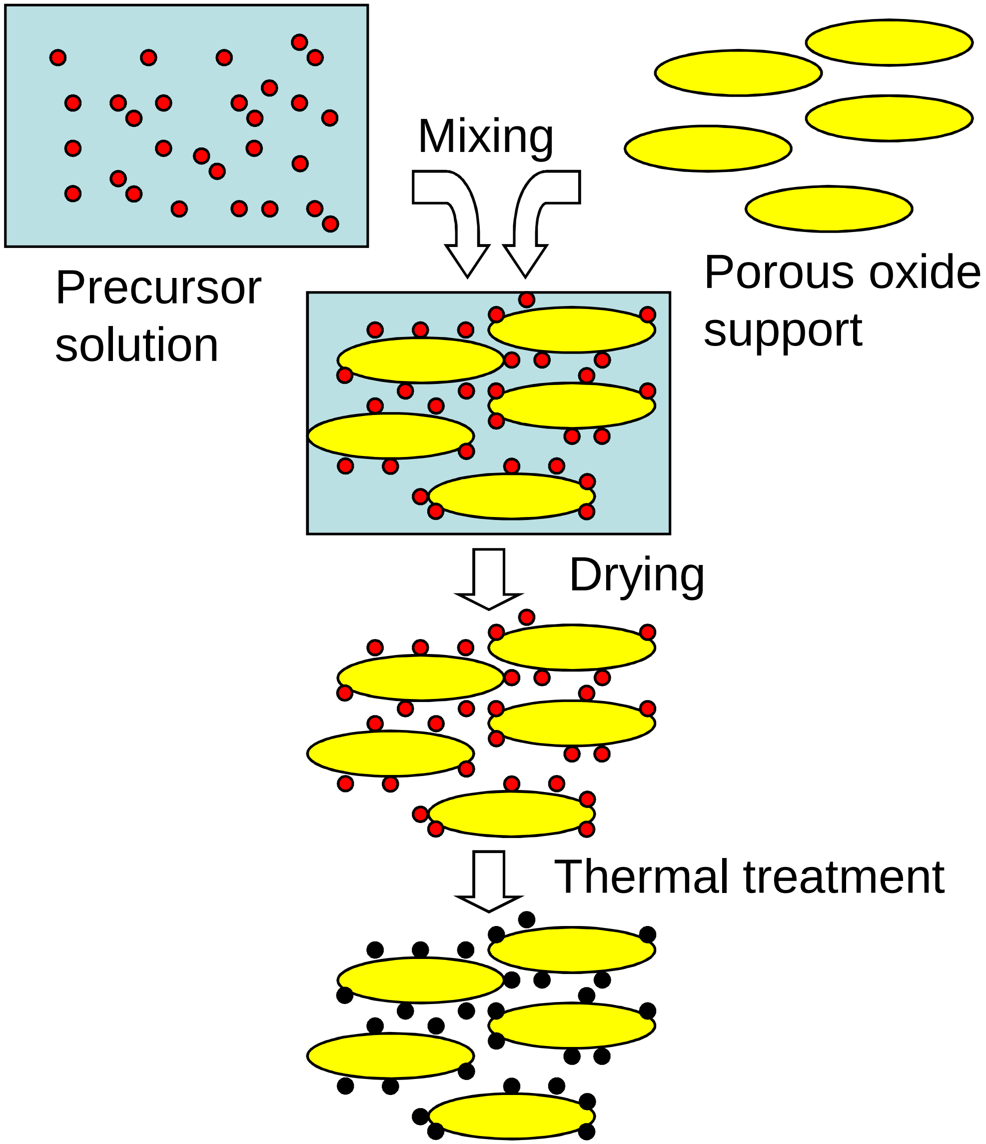
Dynamical Light Scattering

Chemische Nanotechnologie 2

55

Impregnation

- Low volume of precursor solution (usually a transition metal salt) is mixed with the support and the mixture is dried
- The whole precursor is expected to retain on the support (no washing)
- Precursor solution contains decomposable counter ions and ligands (NH_4^+, NO_3^-, $C_2O_4^{2-}$, …)
- Two types
  - Pores of the support are initially filled with air: Capillary impregnation
  - Pores of the support are initially filled with liquid: Diffusional impregnation



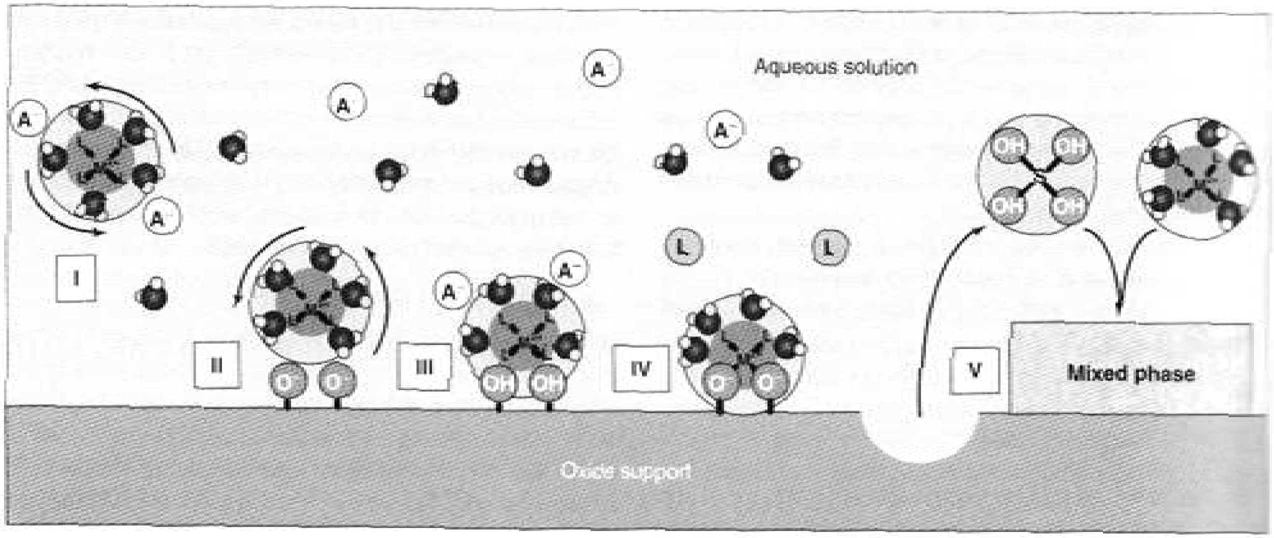
Capillary vs. diffusional impregnation

Support of pore volume V_p is in contact with the precursor solution of volume V

- $V_p = V$: dry or incipient wetness impregnation
- exothermal process, increase in T
  - Pre-treatment with super-heated steam
- air bubbles are trapped as the solution is sucked into the pores by capillary forces and may burst the support particles lowering the mechanical strength
  - Operation in vacuum, usage of surfactants
- filling of pores theoretically finished in seconds, but trapped air leads to delay of the process and possibly inhomogeneous distribution of the active component

- $V_p < V$: wet impregnation
- Pores of the support are pre-filled with pure solvent
- Solvent-saturated support is immersed into the precursor solution
- Concentration gradient between external precursor solution and pores leads to migration of precursor salt into the pores
- non-exothermic, but longer process

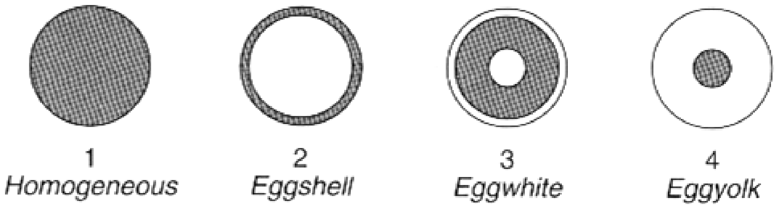
Distribution of the active phase



- Homogeneous distribution on the macroscale is not always desired
- Distribution of the active phase is determined by the interaction of the precursor and the support surface (adsorption)

- If interaction is too high strong adsorption on the edge sites is observed
  - precursor concentration is locally decreased, no concentration gradient between inner particle and outer shell, migration of precursor is hindered → eggshell distribution

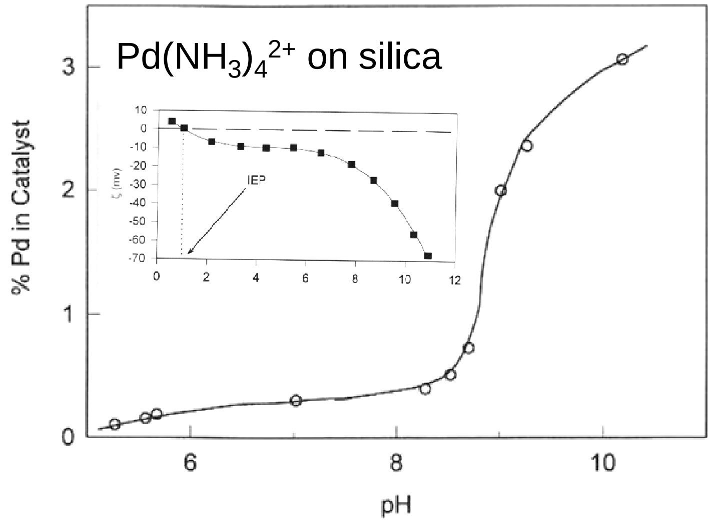
Precursor = metallic complex (MC), competitor (A)



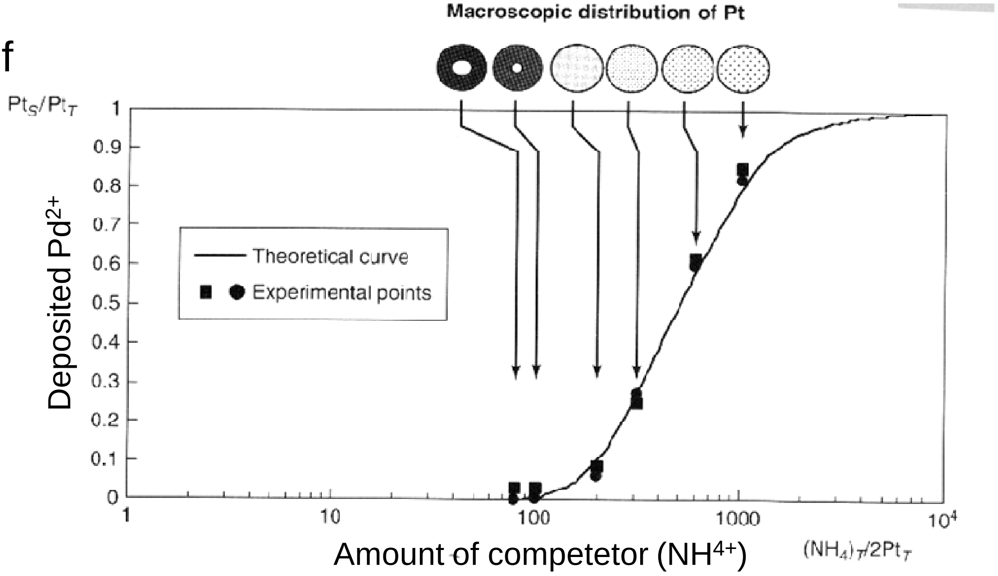
1: roughly same affinities of MC and A
2: high affinity of MC; no competition
3: high affinity of A, low affinity of MC; low A/MC ratio
4: high affinity of A, low affinity of MC; high A/MC ratio

Key experimental parameters I

- IEP (alumina: pH ~9, silica: pH ~2)
  - electrostatic interaction of solid oxide surface and precursor complex (anions adsorbed for pH < 9, cations for pH > 9)
  - can be regulated by varying T (IEP at higher pH at higher T), selective adsorbates (Na^+: abrupt increase of pzc/IEP, F^-: decrease of pzc/IEP)
- pH
  - determines the surface charge of the solid oxide
  - determines the solution species of the precursor complex (NH_3- or H_2O-complexes, monomers or oligomers, …)
- Type of ligands
  - charge, bulkiness, stability, …
- Competitive ions
  - blocking of edge sites forcing precursor complexes further into the pores of the support particle



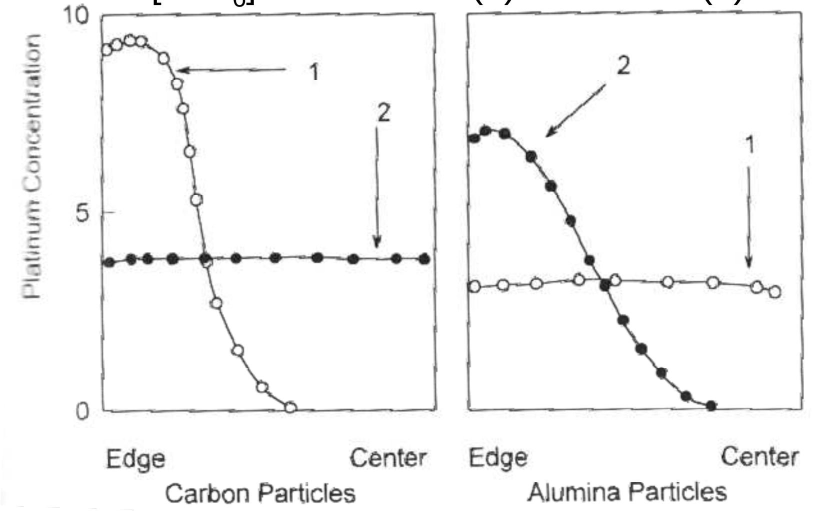
(for $[PtCl_6]^{2-}$ on alumina: acidic environment required)

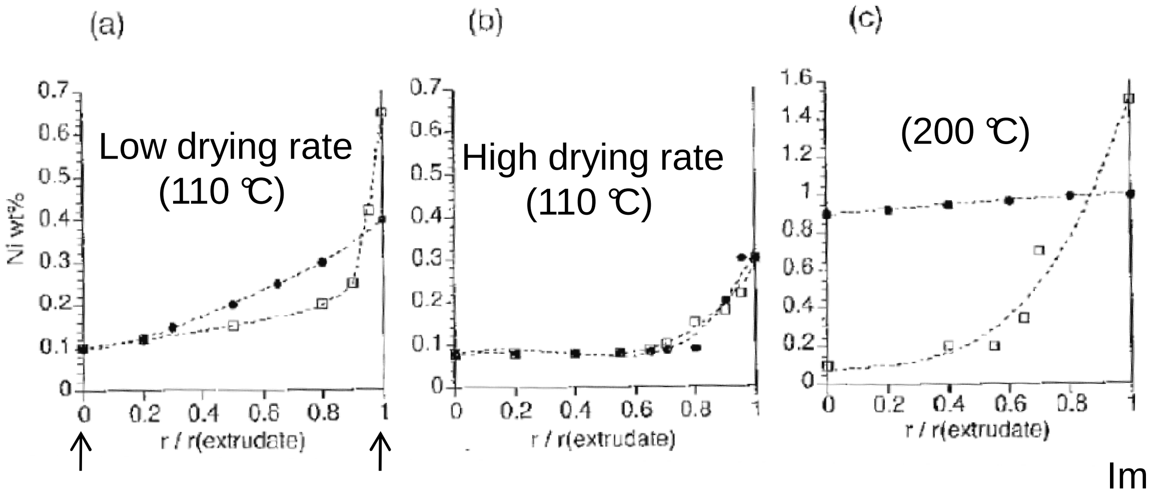


Key experimental parameters II

- Solvent
  - influences the interaction of solvated complex and surface of support
- Kinetics
- Drying
  - if interaction of precursor and oxide surface is too low, precursor species may migrate out again as the liquid leaves the pores

$[PtCl_6]^{2-}$ in acetone (1) and water (2)





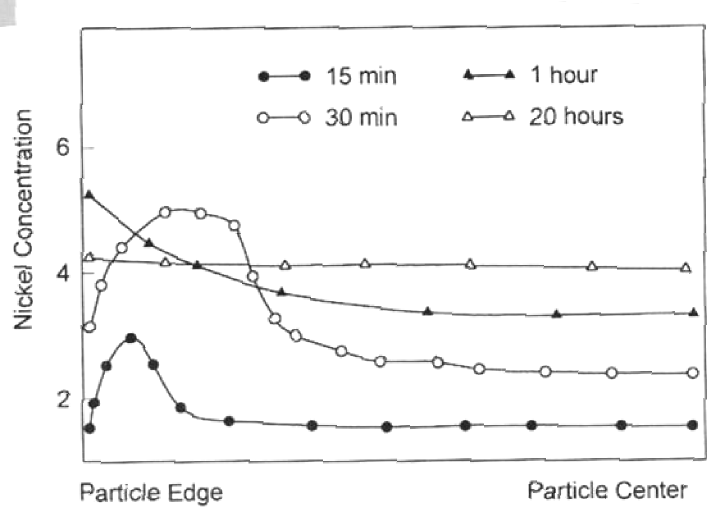
Low drying rate (110 ℃)

High drying rate (110 ℃)

(200 ℃)

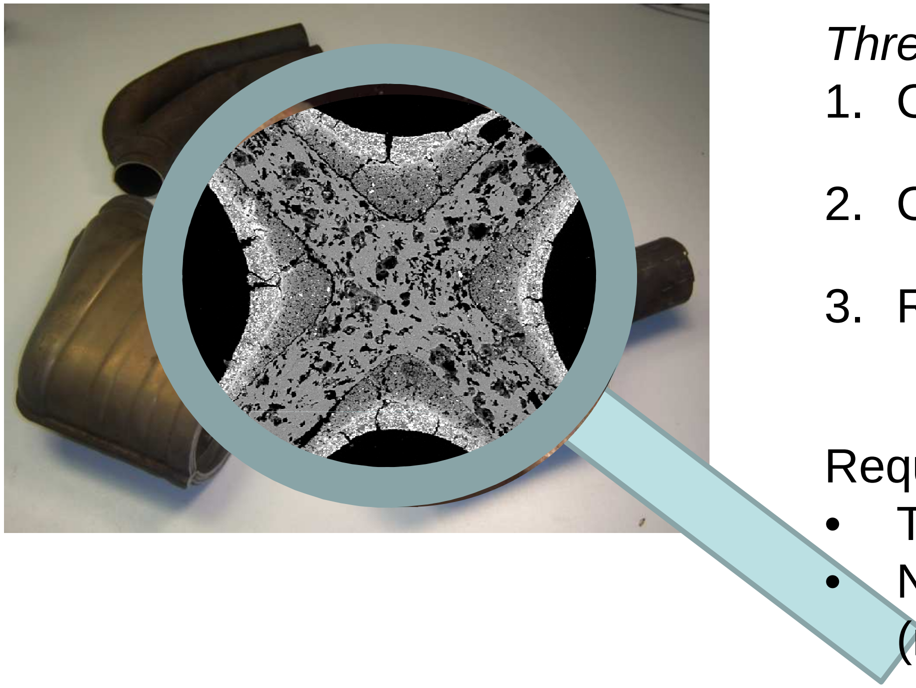
Center

Edge



Impregnation of alumina with aqueous $Ni(NO_3)_2$

Three-way-catalyst



Three modes of operation:

1. Oxidizes unburnt fuel:

   $C_xH_{2x+2} + [(3x+1)/2]\ O_2 \rightarrow x\ CO_2 + (x+1)\ H_2O$
2. Oxidizes CO:

   $2\ CO + O_2 \rightarrow 2\ CO_2$
3. Reduces NO_x:

   $2\ NO_x \rightarrow x\ O_2 + N_2$

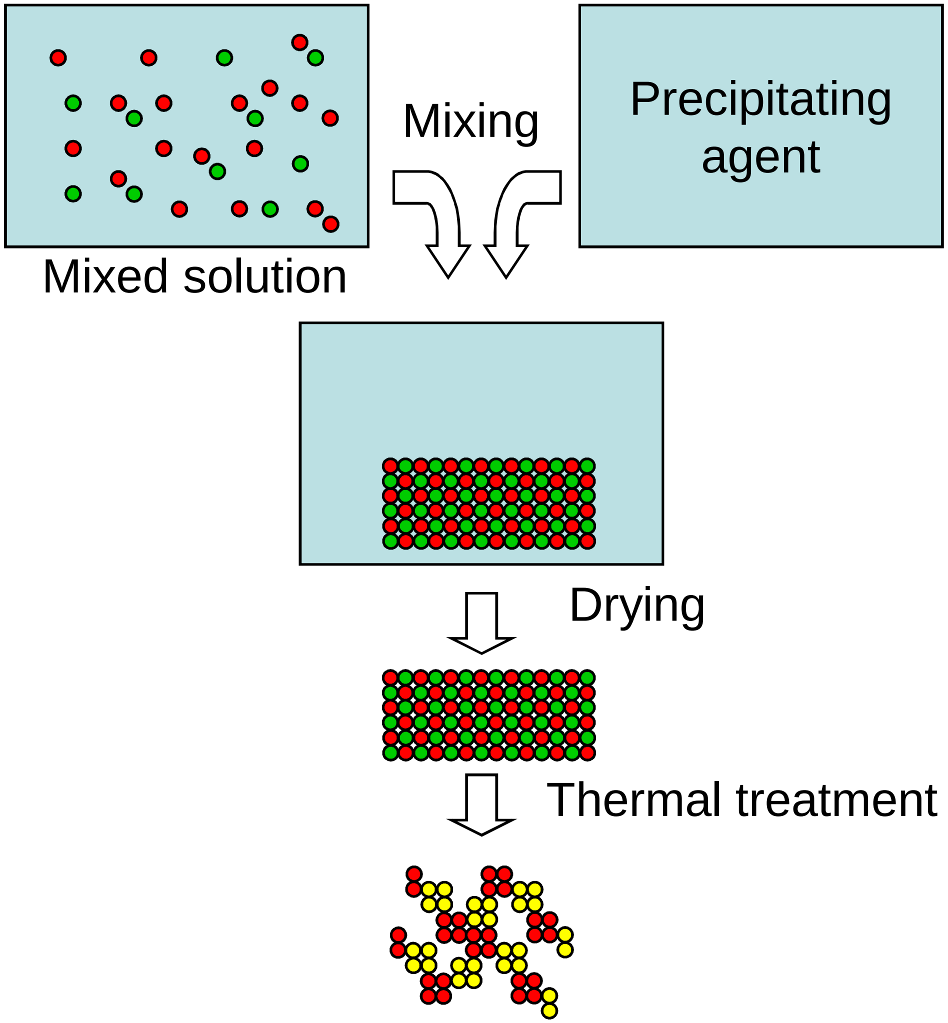
Requires optimal fuel/air ratio:

- Too much O_2: NO_x residues (lean mixture)
- Not enough O_2: C_xH_{2x+2}/CO residues (rich mixture)

Example: $Pd/Zr_{(1-x)}Ce_xO_2/\ Al_2O_3/Mg_2Al_3(Si_5AlO_{18})$ (Cordierite)

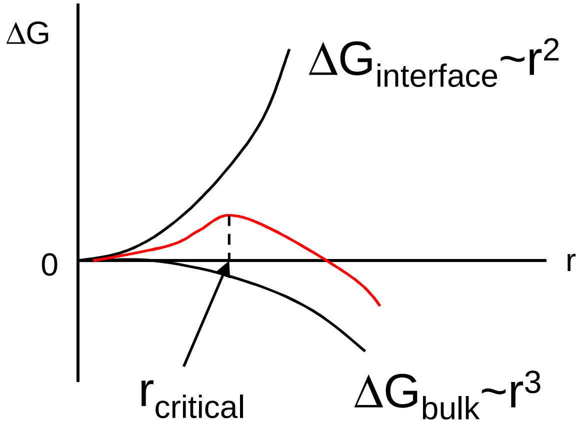
Co-precipitation

- Precipitation of a mixed solution to form a precursor containing several species in a homogeneous distribution (preferably within a single phase)
- Thermal decomposition of counter ions by calcination (NO_3^-, CO_3^{2-}, NH_4^+, $C_2O_4^{2-}$,…),
- Sometimes further thermal treatment (activation)



Precipitation – Nucleation & growth

- Homogeneous nucleation
  - $\Delta G = \Delta G_{bulk} + \Delta G_{interface}$ (+ ΔG_{others})
  - $r_{critical}$: size of the nucleus
  - nucleus: smallest solid-phase aggregate of atoms, which is capable of spontaneous growth
  - The more nucleation is favoured compared to growth, the smaller the particles will be
  - Nucleation is temperature-dependent



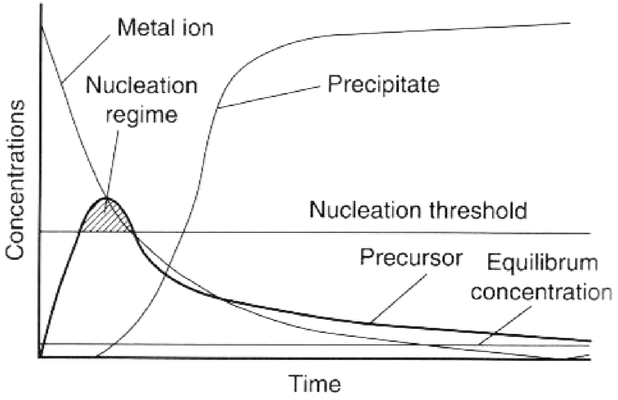
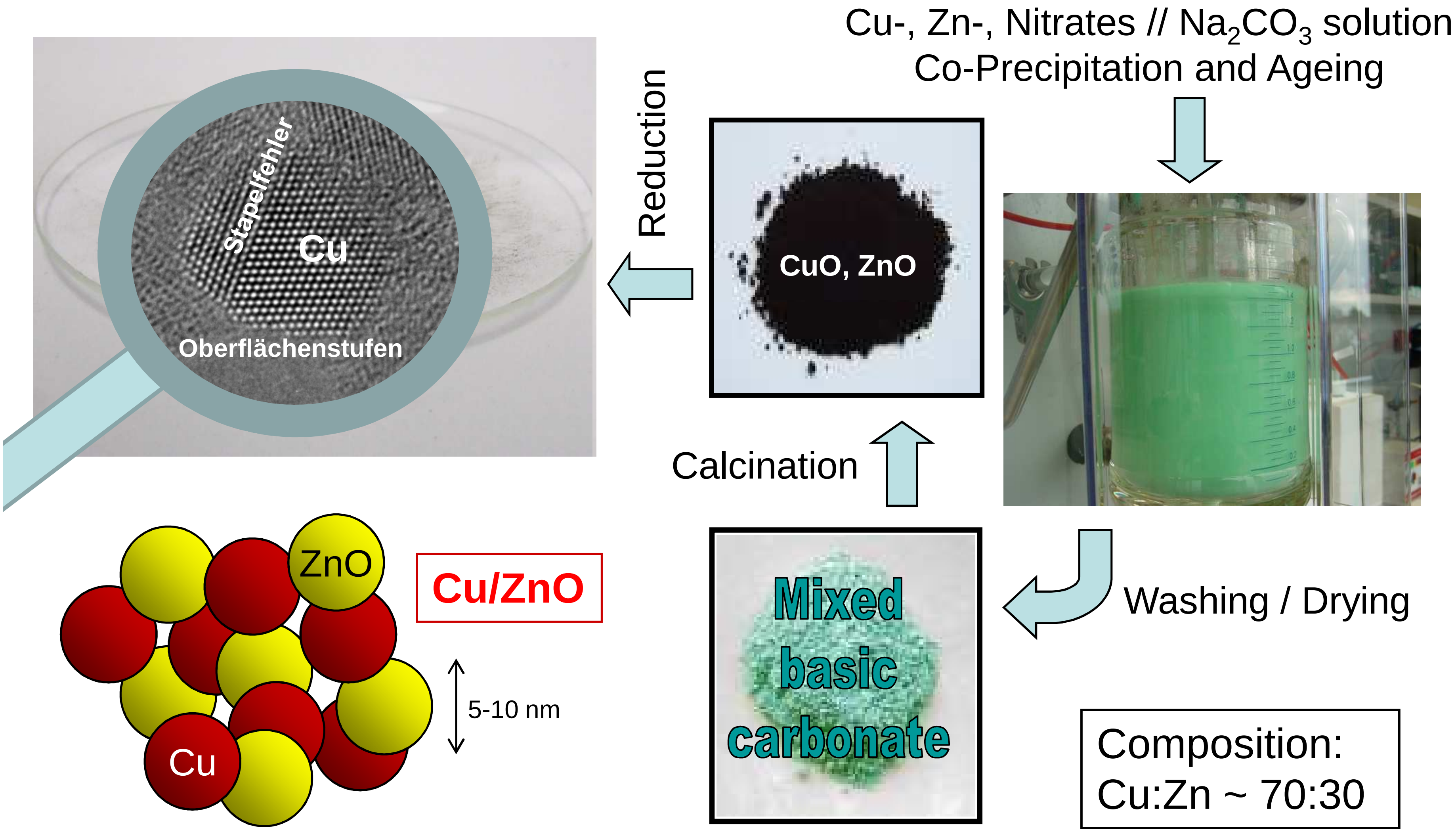


Fig. 2 Simplified scheme for the formation of a solid product from solution. From the metal ions a precursor species is formed, for example by hydrolysis or raising the pH. When the concentration of the precursor species exceeds the nucleation threshold, precipitation of the product begins, consuming the precursor by nucleation and growth. New nuclei are formed only in the shaded area.

Cu/ZnO methanol synthesis catalysts



Cu-, Zn-, Nitrates // Na_2CO_3 solution
Co-Precipitation and Ageing

Washing / Drying

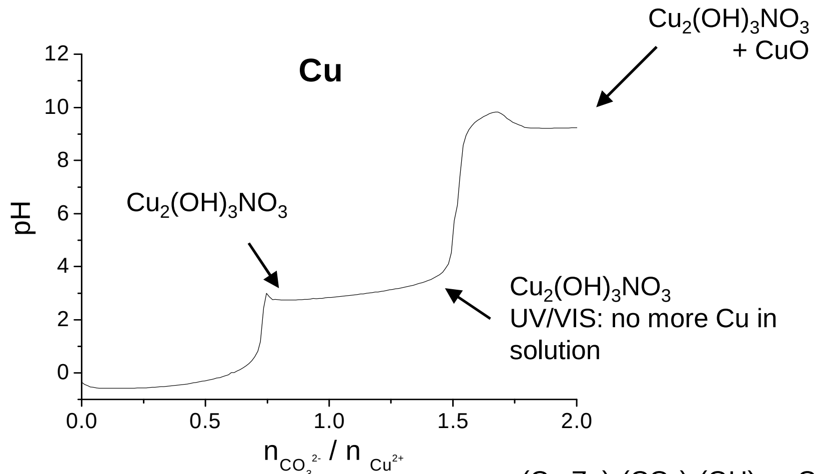
Calcination

Reduction

Composition:
Cu:Zn ~ 70:30

Cu/ZnO

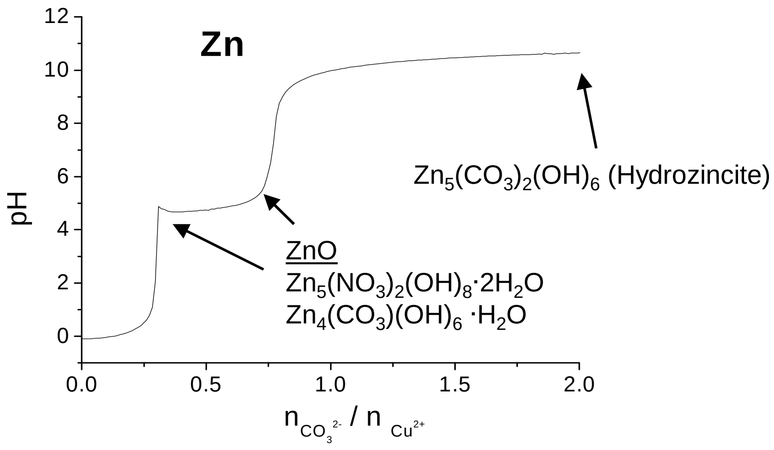
Cation hydrolysis



$Cu_2(OH)_3NO_3$ + CuO

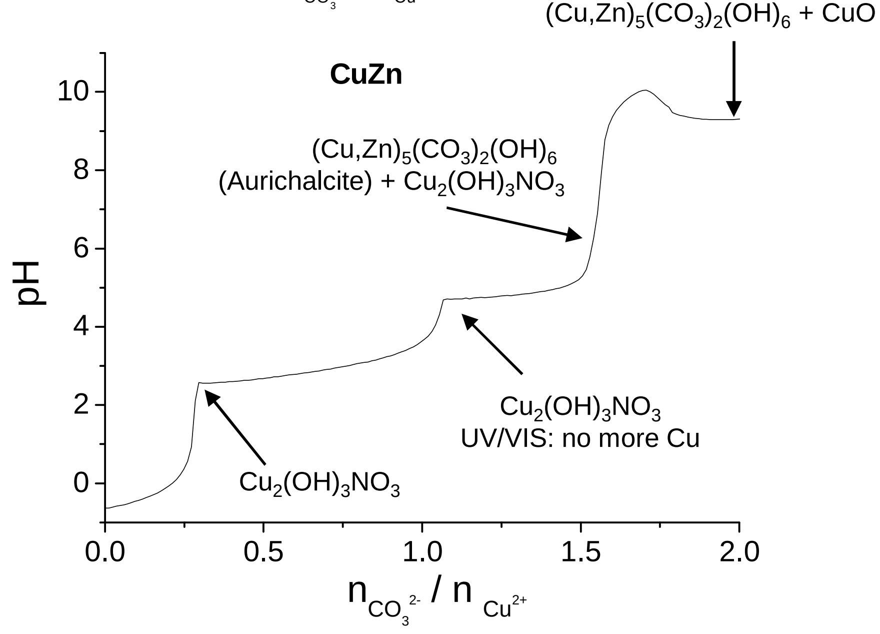
$Cu_2(OH)_3NO_3$

$Cu_2(OH)_3NO_3$
UV/VIS: no more Cu in solution



$Zn_5(CO_3)_2(OH)_6$ (Hydrozincite)

ZnO
$Zn_5(NO_3)_2(OH)_8 \cdot 2H_2O$
$Zn_4(CO_3)(OH)_6 \cdot H_2O$



$(Cu,Zn)_5(CO_3)_2(OH)_6$ + CuO

$(Cu,Zn)_5(CO_3)_2(OH)_6$
(Aurichalcite) + $Cu_2(OH)_3NO_3$

$Cu_2(OH)_3NO_3$
UV/VIS: no more Cu

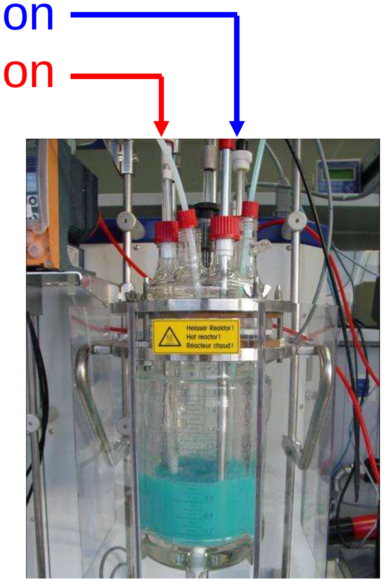
$Cu_2(OH)_3NO_3$

- Titration curve of the binary system is composed from the curves of the single systems
- No real co-precipitation under increasing pH conditions

Constant pH co-precipitation

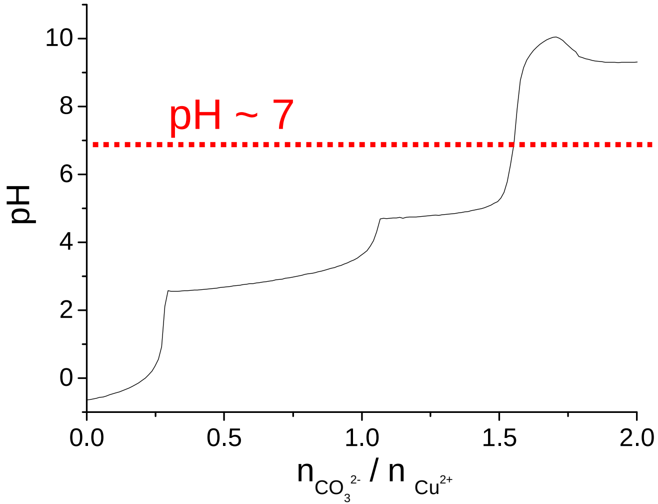
CuZn solution

Na_2CO_3 solution



constant pH 7
T = 65 °C

automatic
reactor



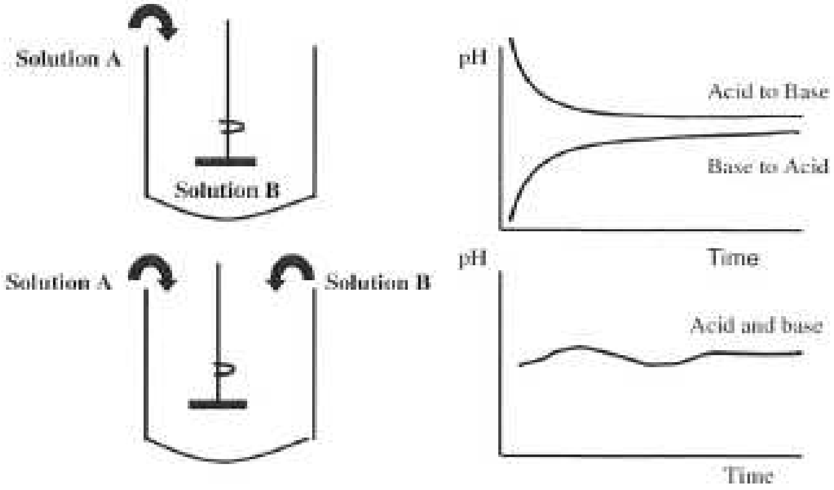
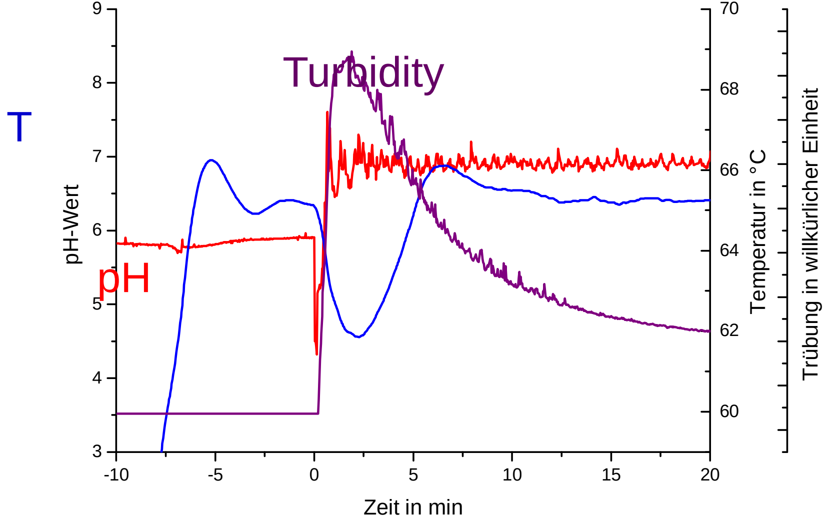
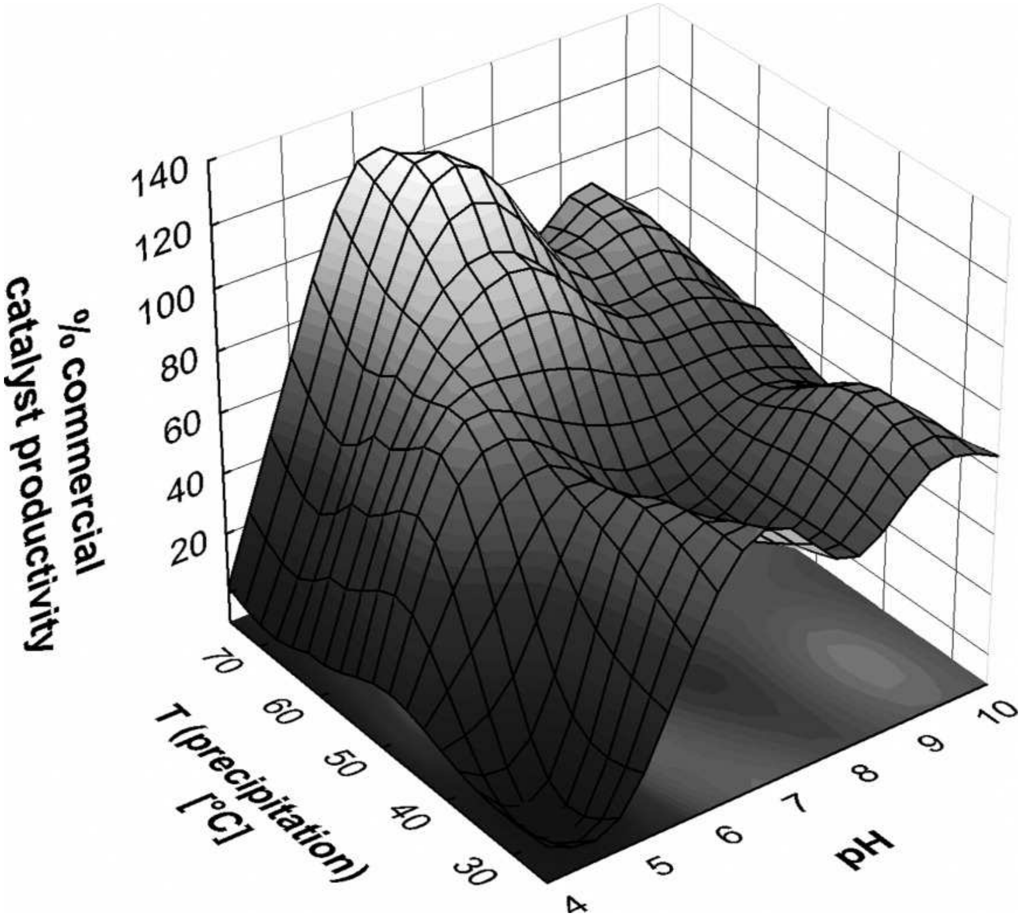


Figure 7.3 Precipitation processing routes: forward (base to acid) and reverse (acid to base) precipitation, continuous precipitation, and corresponding pH profiles.



Parameters for $Cu/ZnO/(Al_2O_3)$ preparation

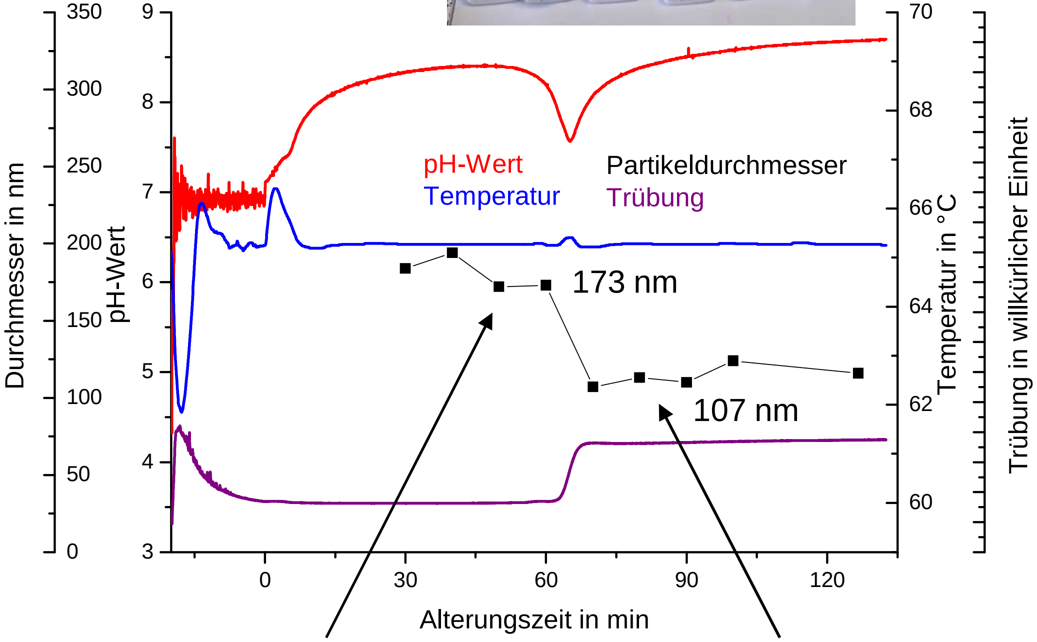


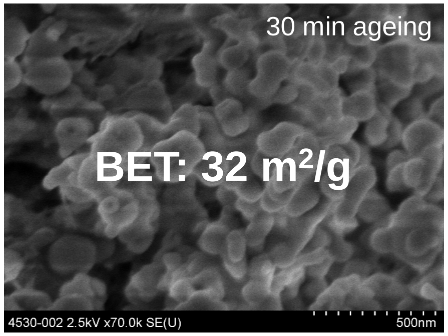
"Chemical memory"

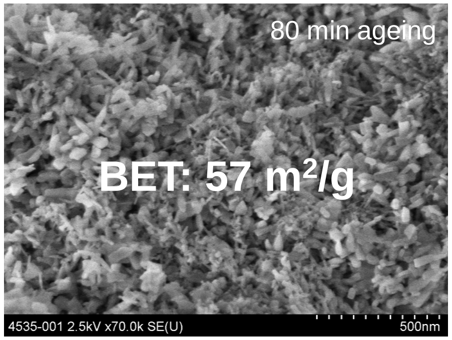
C. Baltes, S. Vukojević, F. Schüth, J. Catal. 258 (2008) 334,

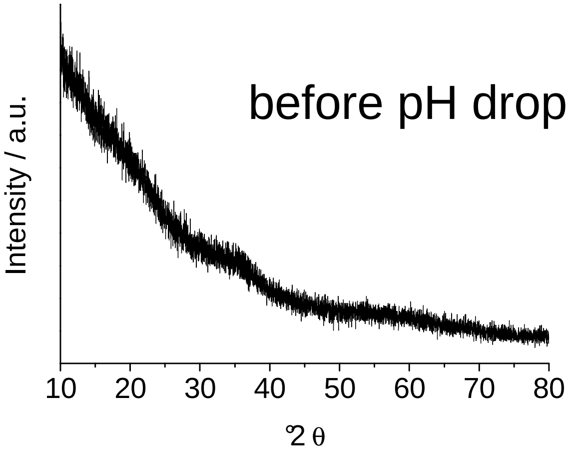
Effects of ageing

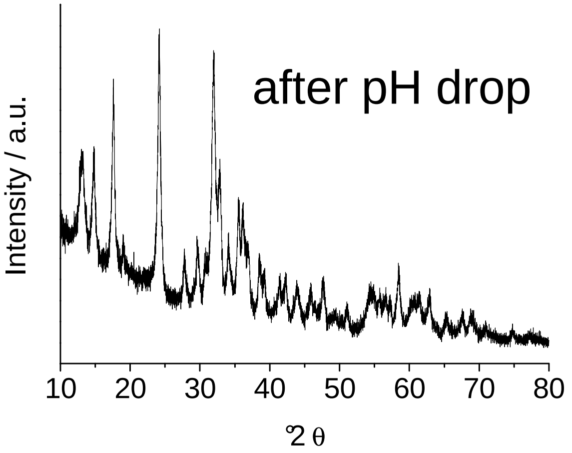
CuZn co-precipitation









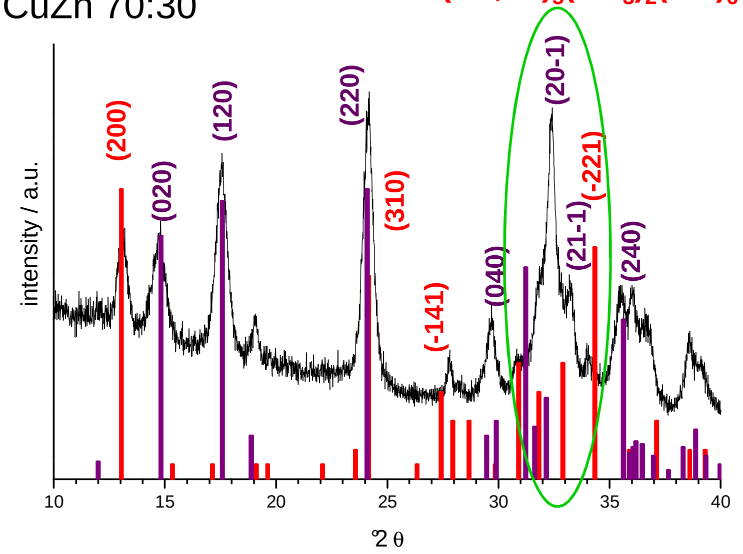


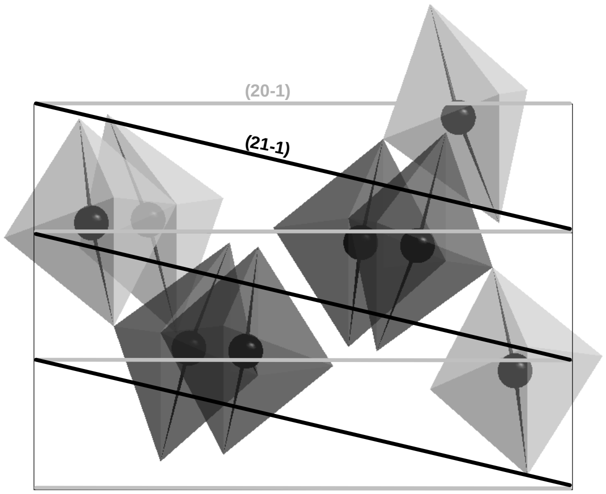
The importance of precursor chemistry

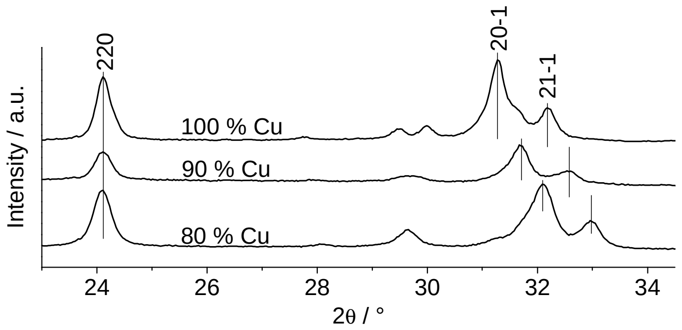
CuZn 70:30

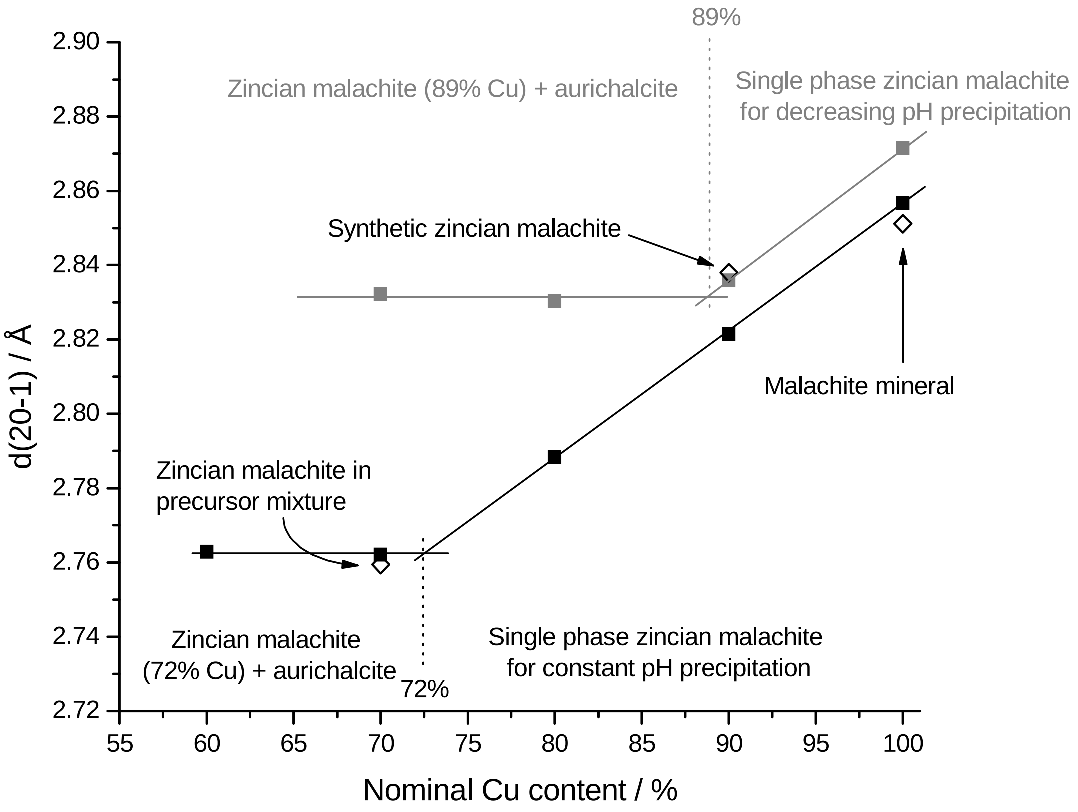
Malachit $Cu_2(OH)_2CO_3$

Aurichalcit $(Cu,Zn)_5(CO_3)_2(OH)_6$

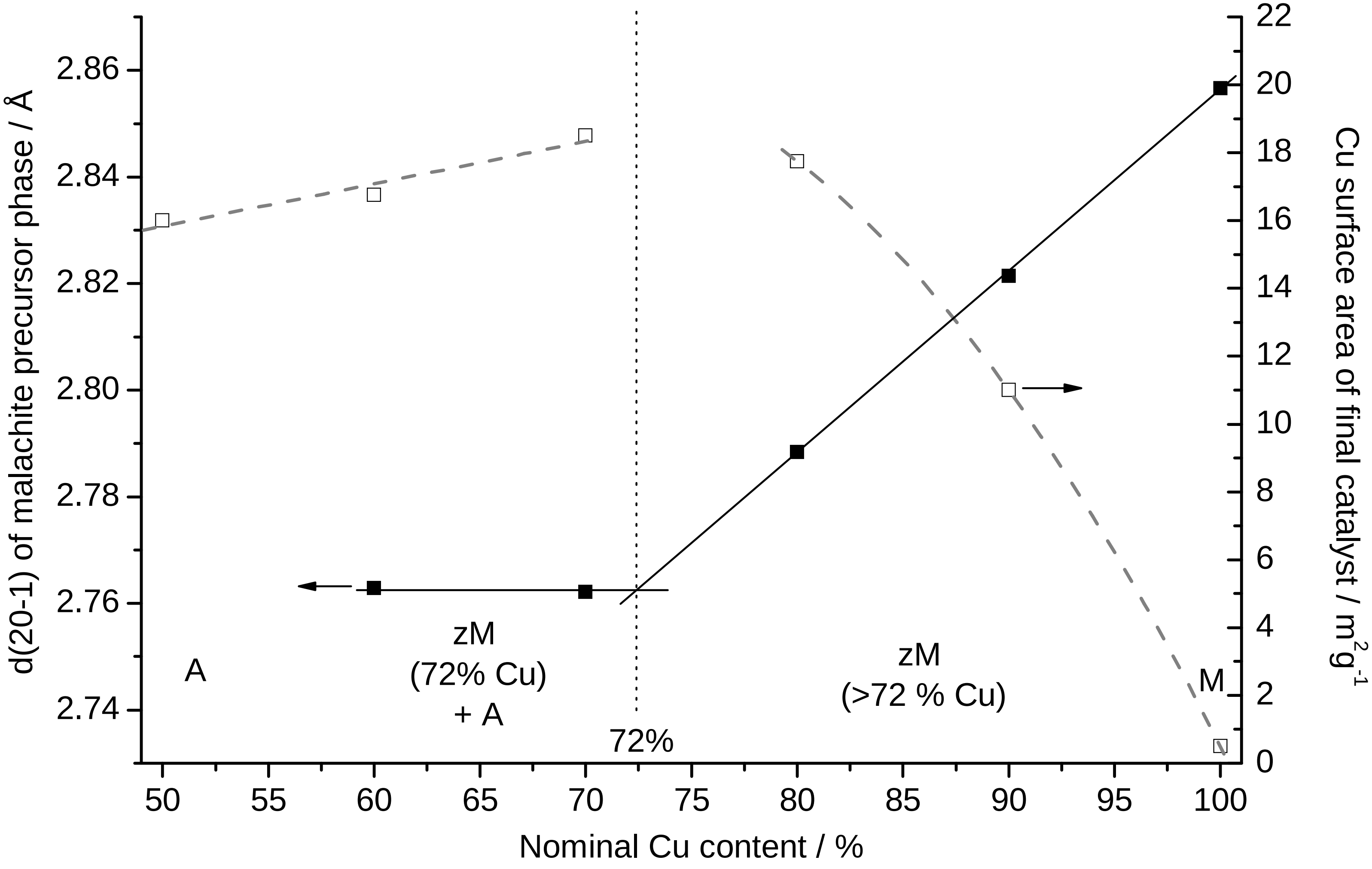




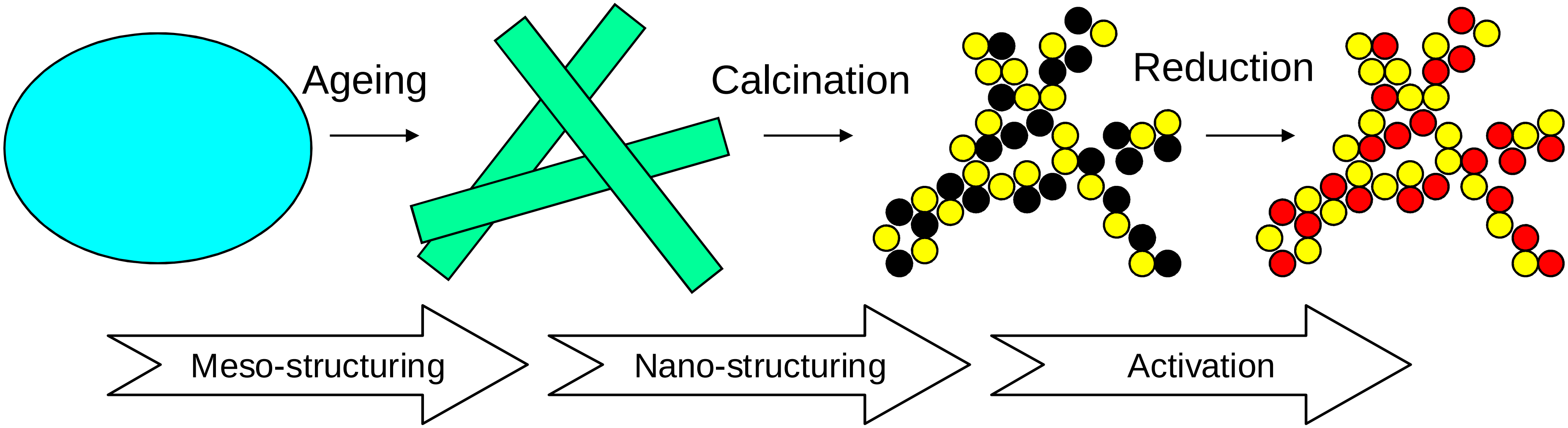




The right precursor composition



Structuring of the Cu/ZnO catalysts



Ageing → Calcination → Reduction →

Meso-structuring

Nano-structuring

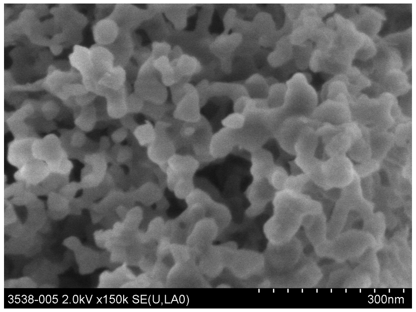
Activation

Initial precipitate
Zincian georgeite

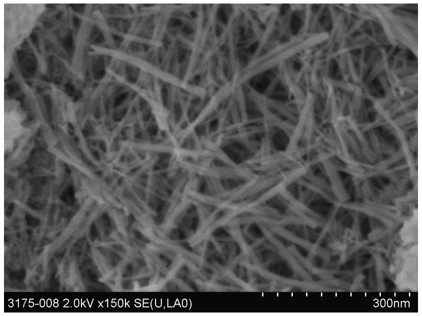
Aged precipitate
Zincian malachite

Calcination product
CuO / ZnO

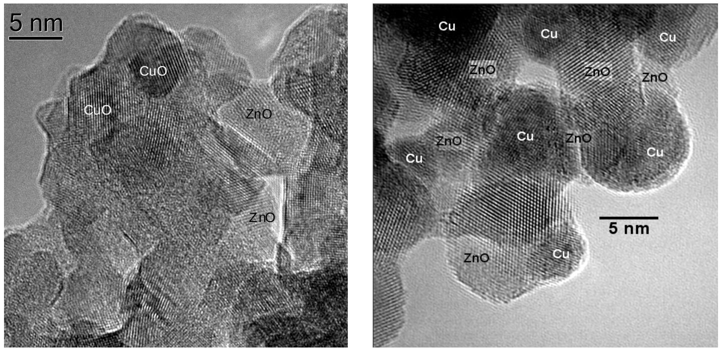
Active catalyst
Cu / ZnO



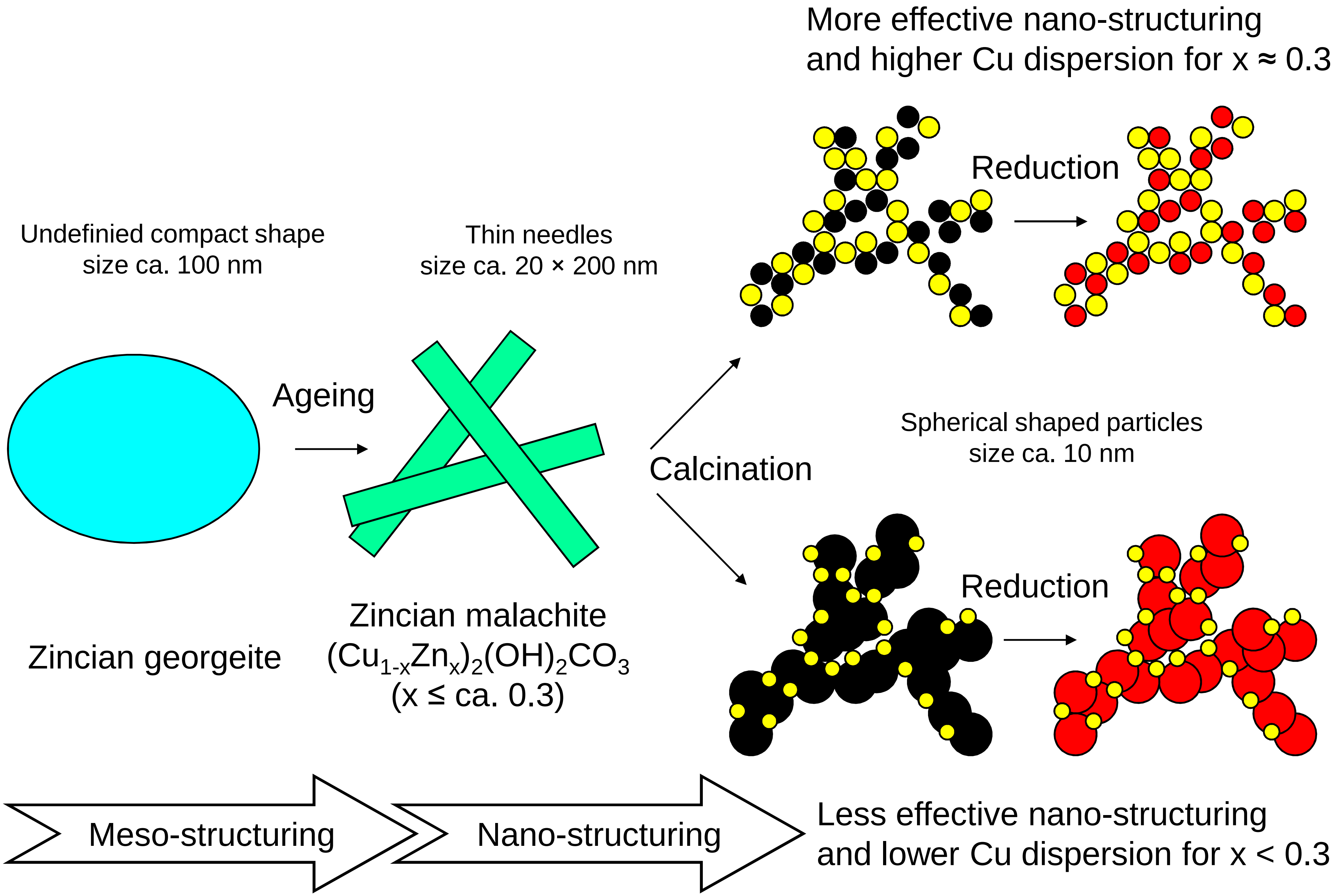
undefined compact shape
size ca. 100 nm



thin needles
size ca. 20 × 200 nm



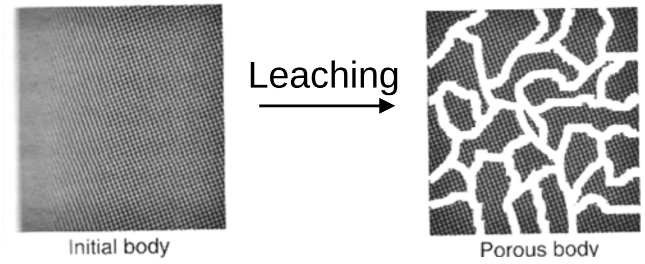
spherical particles
size ca. 10 nm

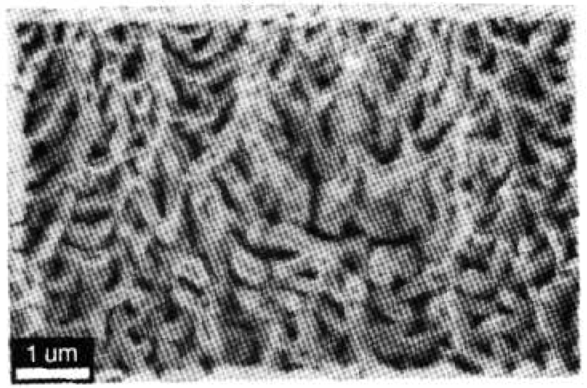

More effective nano-structuring
and higher Cu dispersion for x ≈ 0.3
Reduction
Undefinied compact shape
size ca. 100 nm
Thin needles
size ca. 20 × 200 nm
Ageing
Spherical shaped particles
size ca. 10 nm
Calcination
Reduction
Zincian malachite
$(Cu_{1-x}Zn_x)_2(OH)_2CO_3$
($x \leq$ ca. 0.3)
Zincian georgeite
Meso-structuring
Nano-structuring
Less effective nano-structuring
and lower Cu dispersion for x < 0.3

Skeletal catalysts

- Skeletal catalysts are prepared from an M-Al alloy (M: Ni, Cu, …) by leaching of Al with sodium hydroxide (20-40 wt.-%)
- Alloys are prepared by melting the active metal and Al, quenching and crushing
- Porosity can be controlled by composition of the alloy, T of leaching
- No activation necessary

$$\begin{gathered} 2\ \mathrm{M\text{-}Al}_{(s)} + 2\ \mathrm{OH}^- + 6\ \mathrm{H_2O} \\ \downarrow \\ 2\ \mathrm{M}_{(s)} + 2\ [\mathrm{Al(OH)_4}]^- + 3\ \mathrm{H}_{2(g)} \end{gathered}$$

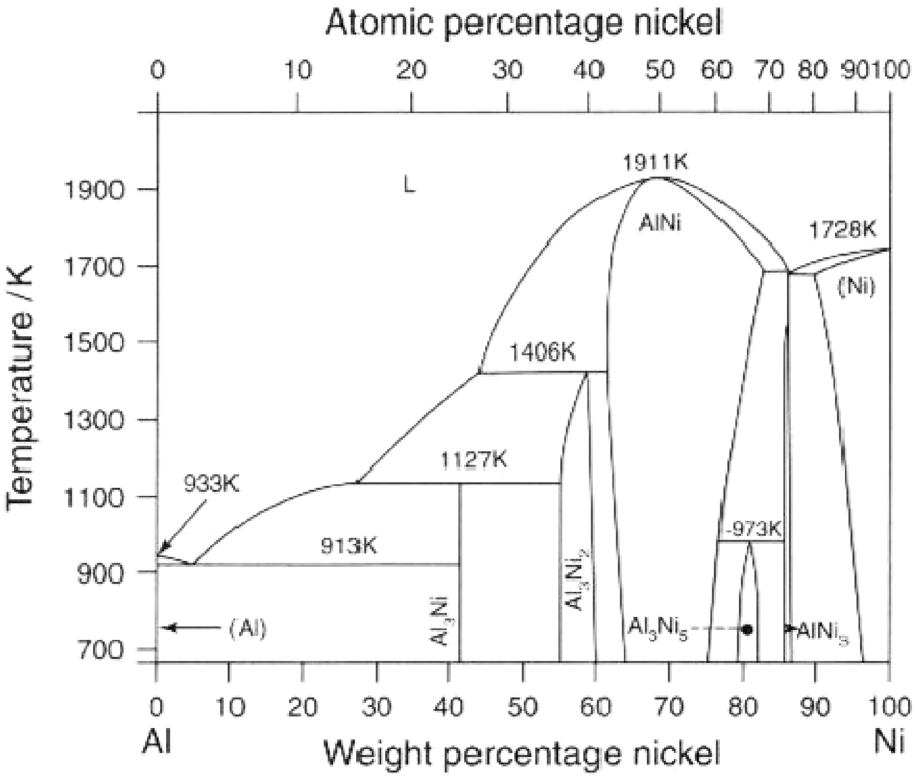




Skeletal Cu catalysts prepared from a 50 wt.-% Cu-Al alloy

Raney nickel

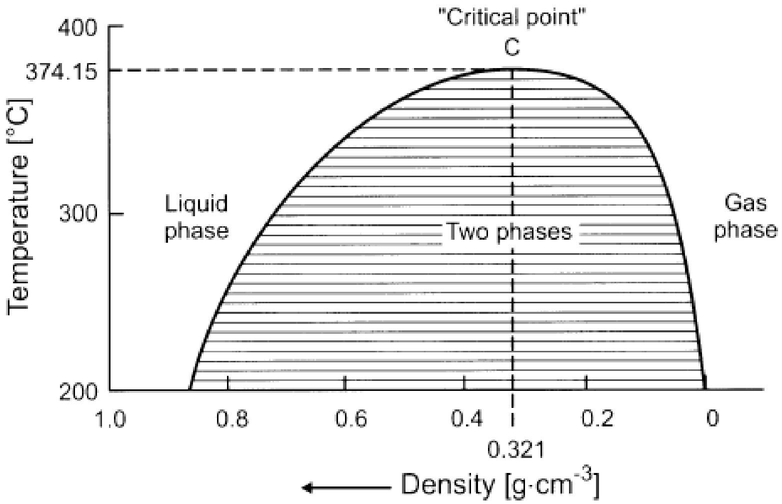
- Used for hydrogenation reactions and as electrocatalyst
- 5 times more active than supported Ni catalyst used before (M. Raney, 1925)
- Ni-Al alloys (40-50% Ni) produced by dissolution of Ni in molten Al and quenching
- Phases: Ni_2Al_3, $NiAl_3$
- $NiAl_3$ is leached more rapidly → smaller crystallite, but mechanically weak
- Ni_2Al_3 is more difficult to leach → strong residual material

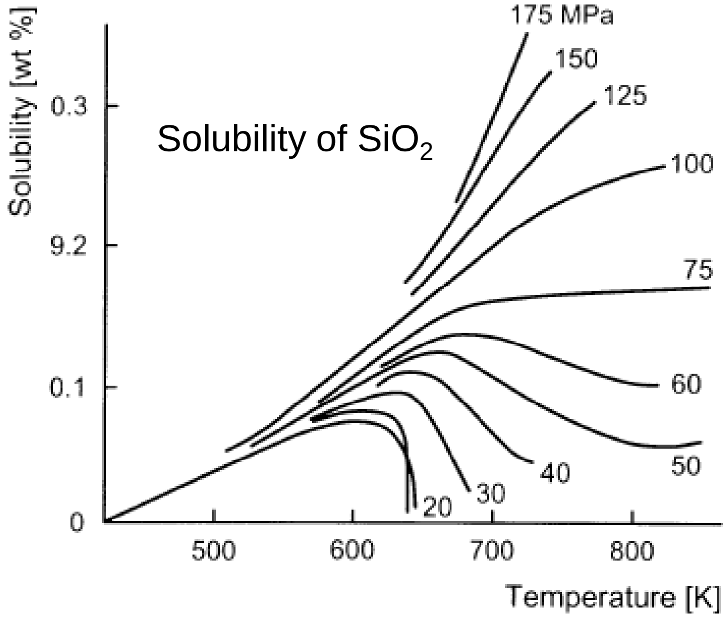


- BET SA 50-100 m^2g^{-1}
- crystallite size and pore diameter: 2 – 6 nm
- highly pyrophoric, has to be stored under liquid (water pH~9)

Hydrothermal synthesis

- Educts and solvent (water) are heated in a close reaction vessel (autoclave)
- At T > 100℃ an autogeneous pressure builds up and the properties of water change
  - viscosity decreases → higher mobility of ions
  - water self dissociation increases → hydrolysis favoured
- If 2-5 % of educts dissolve (sometimes mineralizer required) → rearrangement of building blocks (SBUs) to form new structures
- Conditions mild enough to allow crystallization of open framework structures

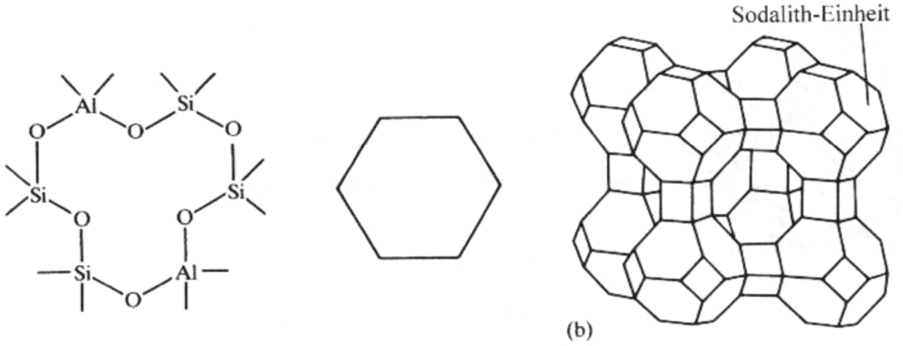



Solubility of SiO_2

Zeolites

- General composition $M_{x/n}(Al_xSi_yO_{2(x+y)})\cdot z\ H_2O$
  - M: cation of charge n
  - M: H^+, group 1 or 2 or organic cation
- Si/Al varies between 1 and ∞
- Zeolite type obtained is determined by synthesis parameters

Zeolite A: $Na_2[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27\ H_2O$

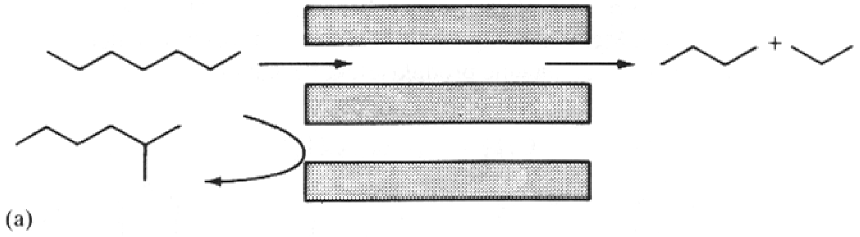


cage diameter: 1140 pm
window diameter: 410 pm

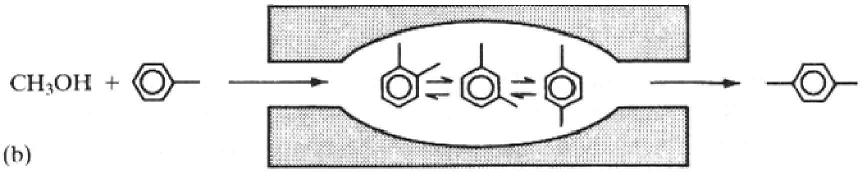
Properties of zeolites

- highly defined pore structure
- application as molecular sieves
- inner surface accessible for catalysis
- ion exchange possible
- proton exchanged zeolites: solid state acids
- after heating: Lewis acids
- shape selective catalysts
- used for catalytic cracking

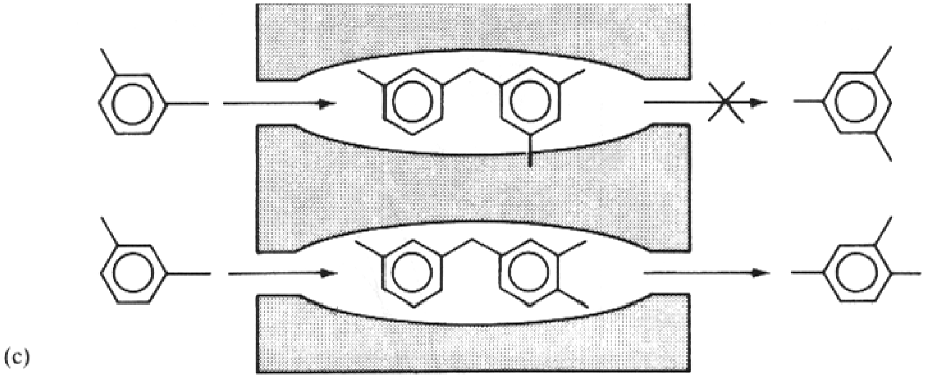
selective towards reactants



selective towards products

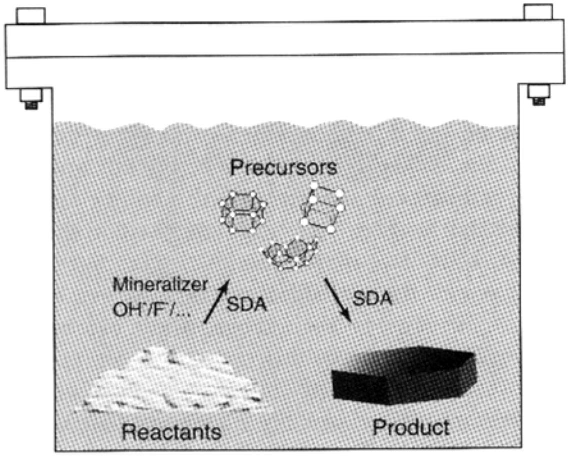


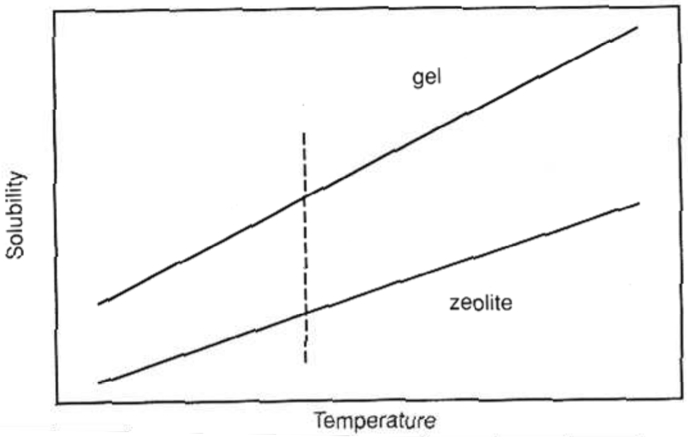
selective towards transition states



Hydrothermal synthesis of zeolites

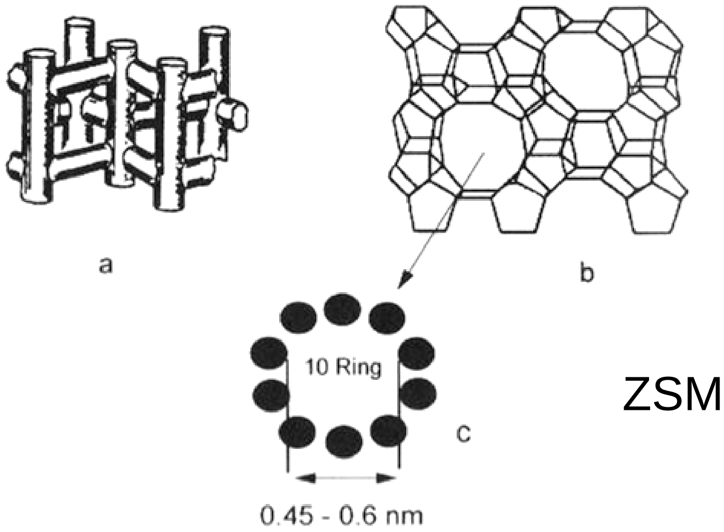
- Si- and Al-sources form a mixed hydrogel
- OH^- as mineralizer (pH 9-13)
- Formation of polyanionic species in solution
- Nucleation and growth
  - by addition of preassembled elementary units
  - by aggregation



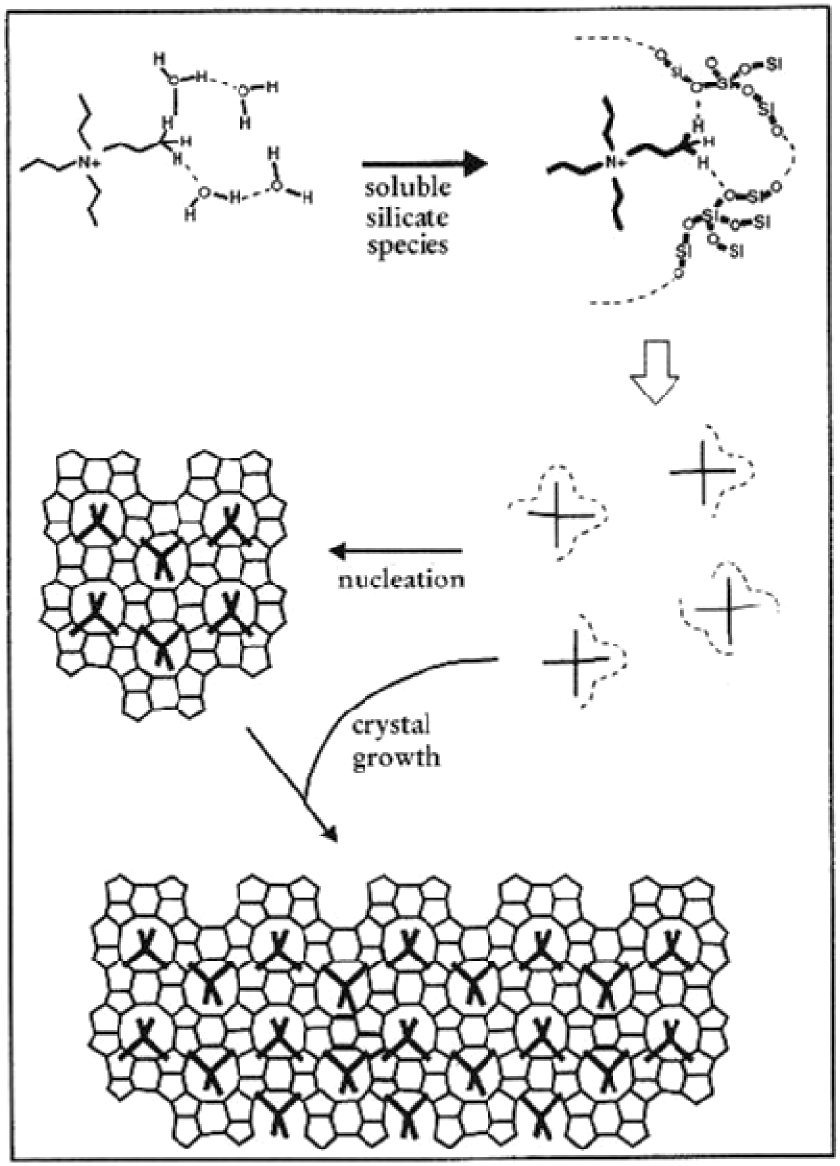


Template assisted synthesis

- Building blocks present in solution arrange around a structure-directing agent
- SDA acts as a template for the pore structure
- SDA can be removed by heating



ZSM-5



Summary

- Supported catalysts can be prepared by impregnation
  - The interaction of the support surface and the precursor species in solution is the key factor for a homogeneous distribution
- Co-precipitation may provide intimate porous mixtures of active and refractory components
  - Properties of the precipitate pre-determine the final catalyst’s properties, complex processes
- Skeletal catalysts exhibit high metal surface areas
  - Leaching process parameters control porosity
- Hydrothermal synthesis yields crystalline porous framework materials
  - Template assisted synthesis can lead to ordered and well defined pore structure
- (Other important preparation methods for catalysts are deposition precipitation, sol-gel processes, chemical vapour deposition, mechnano-chemical routes, solid state reactions, …)

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