Preparation of Supported Catalysts

Lecture Series „Modern Methods in Heterogeneous Catalysis Research“

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1. Introduction, classification, overview
2. Traditional Procedures of catalyst preparation and catalyst forming (overview)
3. Bulk catalysts and supports (classification only: precipitation/co-precipitation; sol-gel; flame hydrolysis; spreading/wetting, melting/metallurgy; Raney alloys)
4. Supported catalysts
    - solid-liquid interfacial chemistry (oxide surfaces; surface acidity and charge)
    - impregnation
    - ion exchange and equilibrium adsorption
    - grafting
    - chemical vapour deposition (CVD)
    - immobilization of metal particles and clusters
    - deposition-precipitation
    - spreading and wetting
    - heterogenisation of homogeneous catalysts (anchoring)
5. Final thermal treatment (calcination, reduction, activation)
6. Literature

Preparation of heterogeneous Catalysts

Starting point: desired chemical and physical properties of the catalyst

⇓

Task: choice of a suitable preparative method

⇓

high activity and selectivity

Different approach and aim:

Academic research:

Synthesis of well defined structures

Systems, which can be well characterized

highlights for publications/originality

Industrial demands:

Life time, stability against heat, poinsoning, variation of process parameters

Mechanical properties: hardness, pressure resistance, attrition

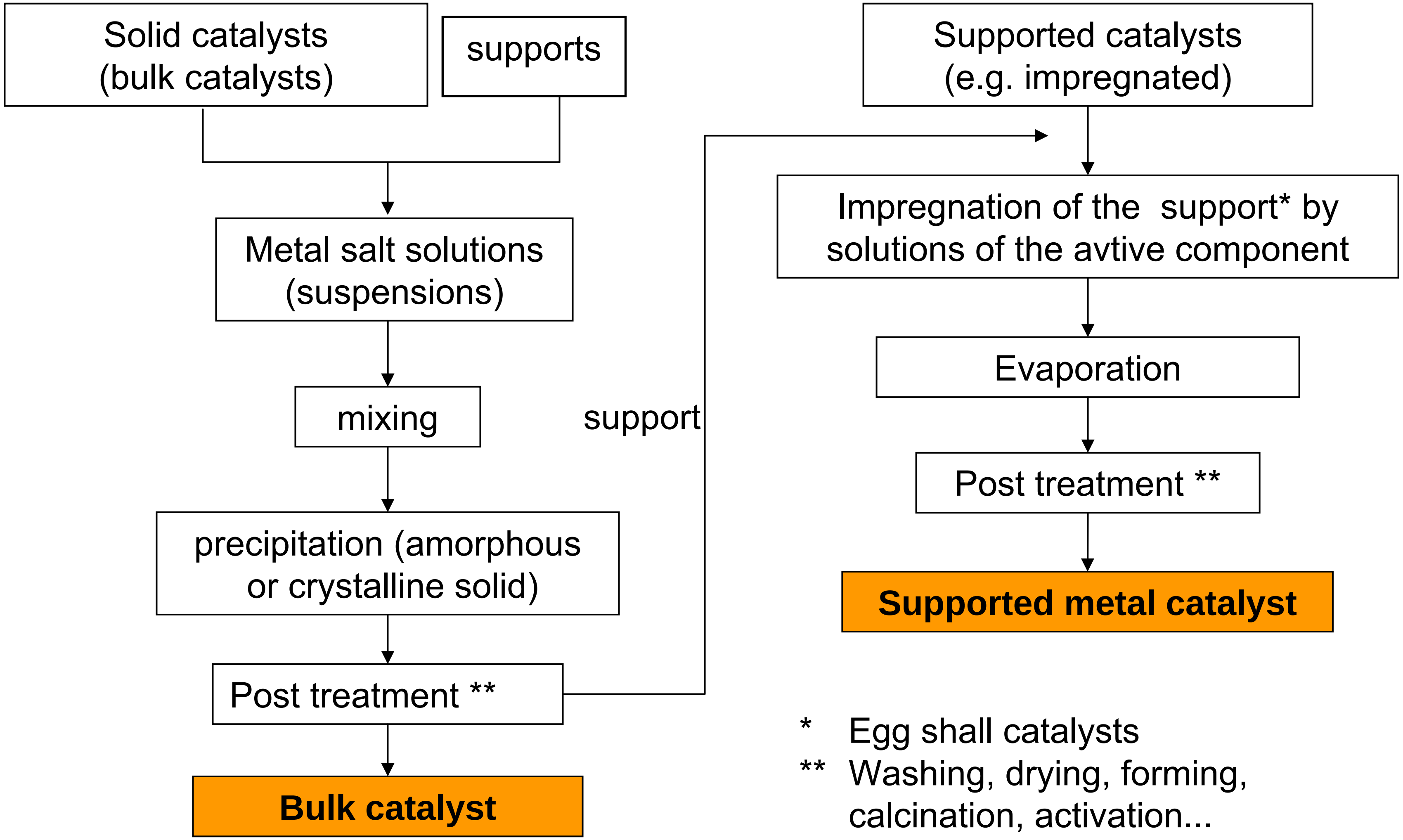
Morphology (external shape, grain size); porosity

Thermal properties (thermal conductivity)

Regenerability; reproducibility

Patent situation, costs

Traditional preparation methods of industrial heterogeneous (solid) catalysts (engineering aspects, typical examples)



Solid catalysts
(bulk catalysts)

supports

Metal salt solutions
(suspensions)

mixing

precipitation (amorphous
or crystalline solid)

Post treatment **

Bulk catalyst

support

Supported catalysts
(e.g. impregnated)

Impregnation of the support* by
solutions of the avtive component

Evaporation

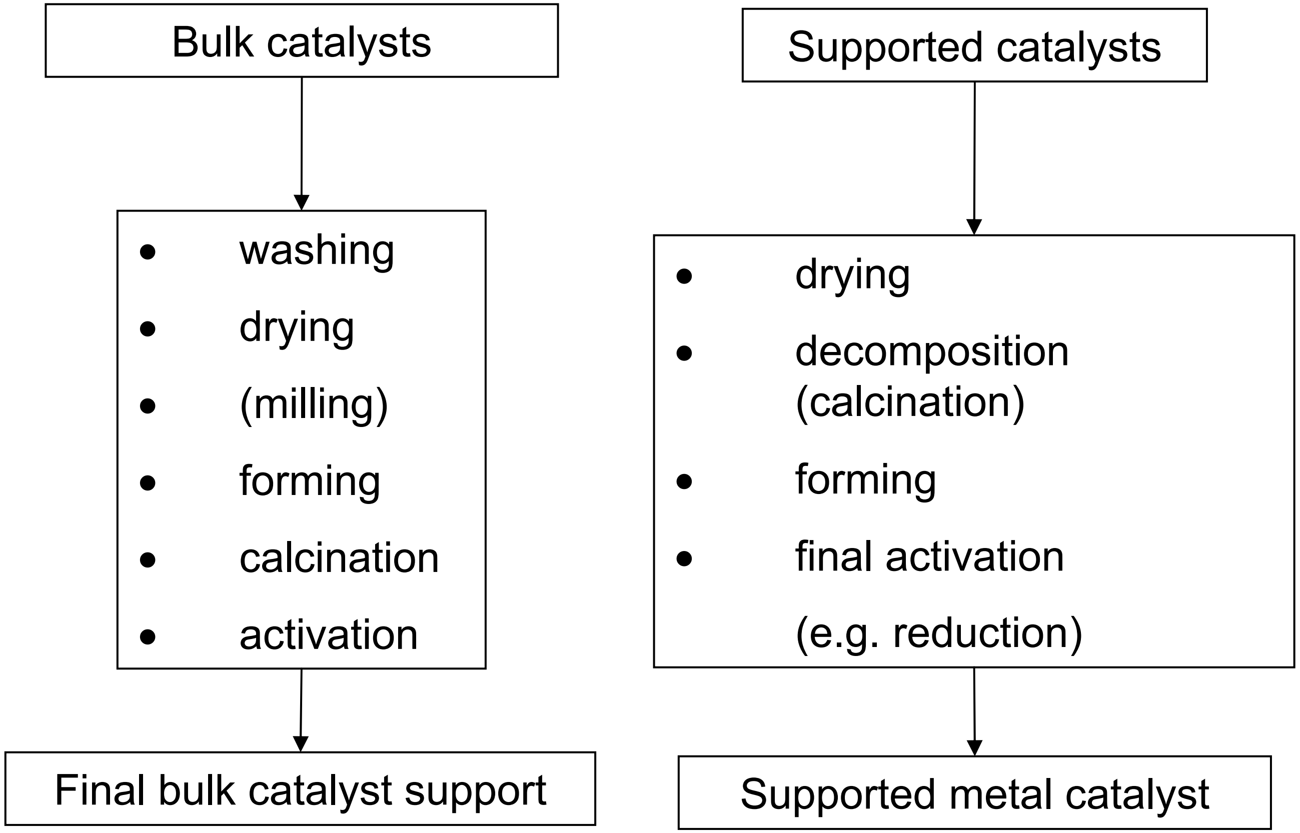
Post treatment **

Supported metal catalyst

* Egg shall catalysts

** Washing, drying, forming,
calcination, activation...

Post-treatment of heterogeneous catalysts



Bulk catalysts

- washing
- drying
- (milling)
- forming
- calcination
- activation

Final bulk catalyst support

Supported catalysts

- drying
- decomposition (calcination)
- forming
- final activation

  (e.g. reduction)

Supported metal catalyst

Honeycumb (monoliths), egg-shell catalysts: first preparation of skeleton / shape support materials, then deposition/coating of the supported powder catalyst (washcoat) or of the active component

Definitions associated with porous solids

- ***Pore***:	Cavity or channel, which is deeper than wide.
- ***Open Pore***:	Pore, which has access to the surface.
- ***Interconnected pores***:	Pores, which communicate with other pores.
- ***Closed pore***:	Pore, which is not connected to the surface.
- ***Pore size***:	Internal (minimal) diameter of a pore.
- ***Pore volume***:	Volume of the pores per unit mass of solid.
- ***Porosity***:	Ratio of pore volume to geometrical (apparent) volume of the particles.
- ***Specific surface area***:	Surface area per unit mass of solid.
- ***Internal surface area***:	Surface area of pore walls.
- ***External surface area***:	Surface area outside the pores, geometrical surface area.

Forming of Catalysts

Mircogranules

- **Spray-dryer** (spraying of microdrops into a hot gas stream, 7-700 μm)

Particular shapes and techniques, e.g.:
- honeycumb (some cm - 1 m)
- metal networks, wires

„Millimeter“-Granules

- **Extrusion** (various shapes):
  - press extruders (viscous)
  - screw extruders (thixotropic)
- **Granulation** (humidified powder in a rotating pan, broad size Distribution, 1-20 mm)
- **Pelletizing** (pellets of few mm)
- **Oil-drop coagulation** (spheres, few mm)

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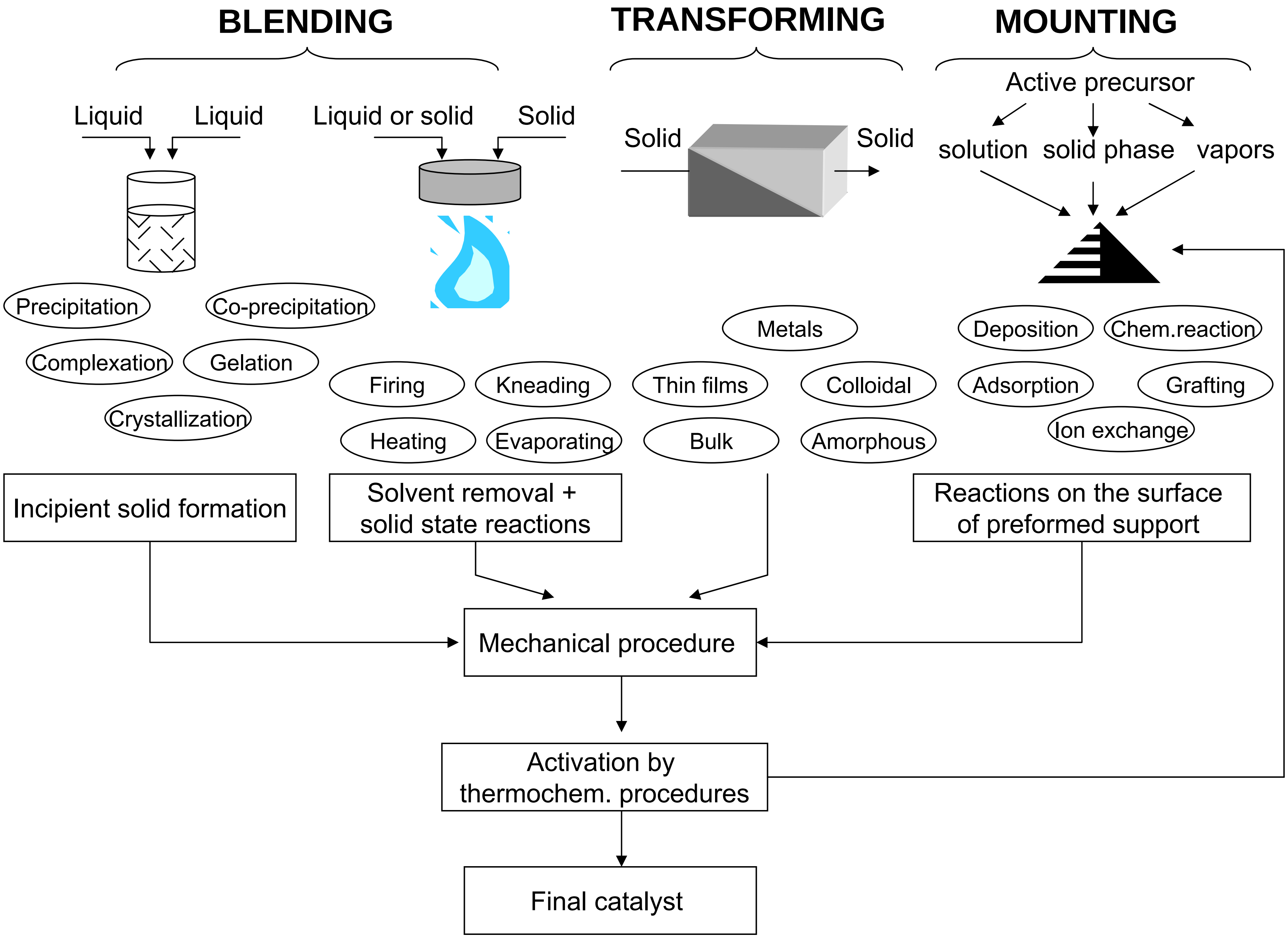
BLENDING
TRANSFORMING
MOUNTING
Liquid
Liquid
Liquid or solid
Solid
Solid
Solid
Active precursor
solution
solid phase
vapors
Precipitation
Co-precipitation
Complexation
Gelation
Crystallization
Firing
Kneading
Heating
Evaporating
Metals
Thin films
Colloidal
Bulk
Amorphous
Deposition
Chem.reaction
Adsorption
Grafting
Ion exchange
Incipient solid formation
Solvent removal + solid state reactions
Reactions on the surface of preformed support
Mechanical procedure
Activation by thermochem. procedures
Final catalyst

Supported catalysts

⇒ Catalytically active component(s) bound to a(n) (inert) support with large specific surface area

Motivation:
- stabilization of high/ optimal dispersion of active component(s) (e.g. of noble metal particles) against sintering
- reduction of costs
- utilization of important mechanical and morphological properties of the support

General procedure:
- depostition of the precursor onto the support surface
- transformation of the precursors into the required active compound (oxide, sulfide, metal)

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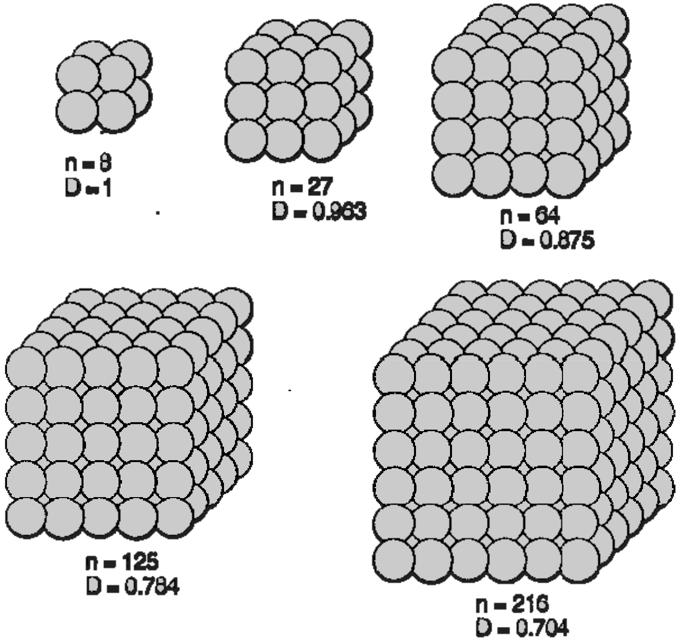
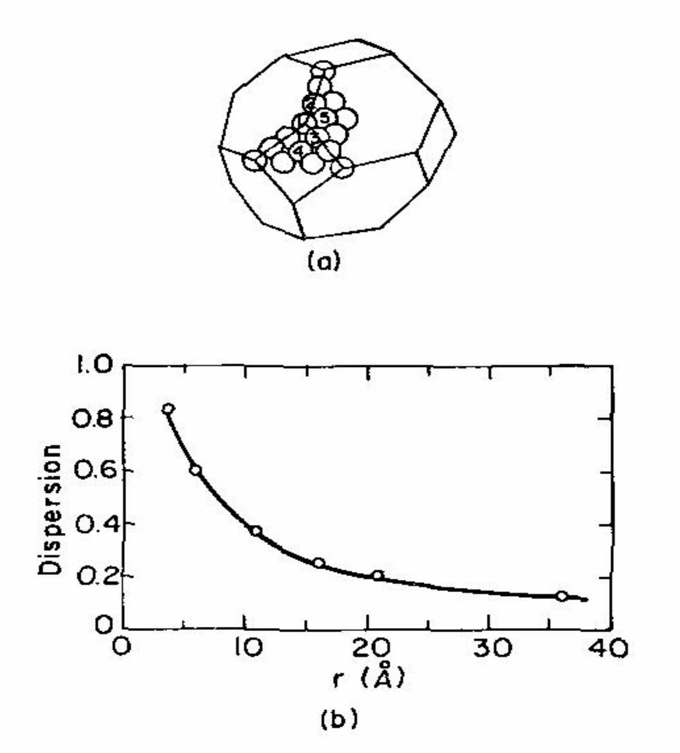
Dispersion = n(s) / N

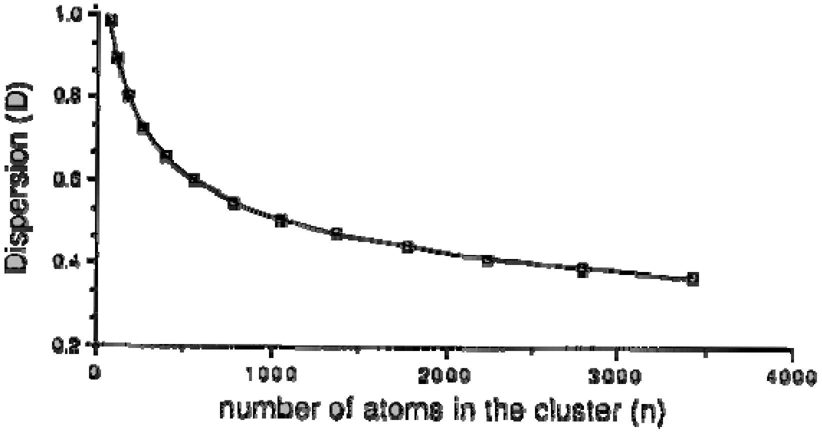


n(s) = Number of surface atoms

N = total number of atoms in the „cluster“/particle

D = f (particle shape)





Preparation methods for supported catalysts

→ Impregnation

→ Ion exchange / equilibrium adsorption

→ Grafting

→ Anchoring / heterogenization of homogeneous catalysts

→ Deposition-precipitation

→ Spreading and Wetting

→ Immobilization of metal particles and clusters

→ Chemical vapor depostion (CVD)

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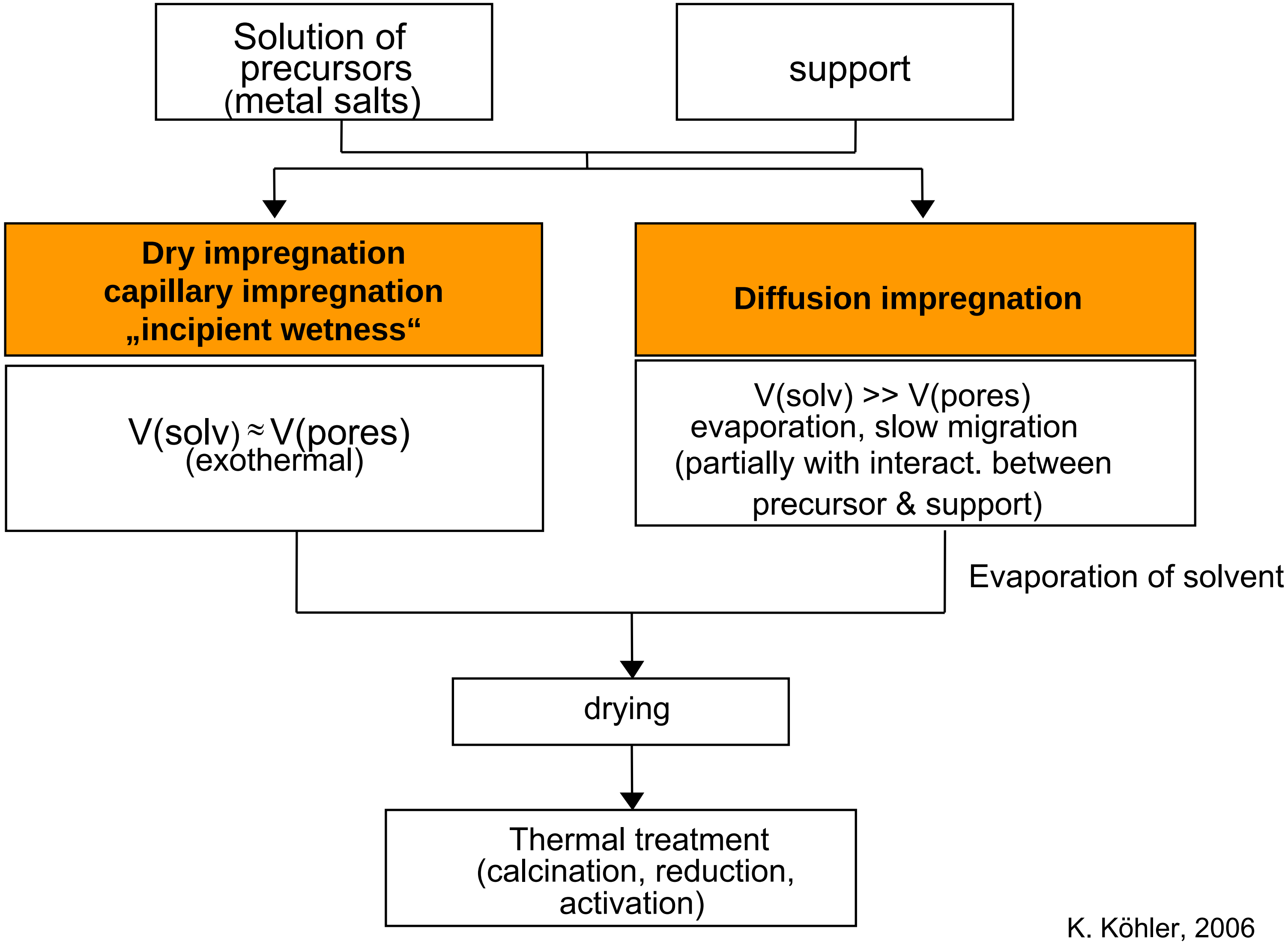
Impregnation
(without precursor- support interactions)



Solution of precursors (metal salts)

support

Dry impregnation
capillary impregnation
„incipient wetness“

$V(solv) \approx V(pores)$
(exothermal)

Diffusion impregnation

V(solv) >> V(pores)
evaporation, slow migration
(partially with interact. between precursor & support)

Evaporation of solvent

drying

Thermal treatment (calcination, reduction, activation)

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Excursus: Solid-Liquid Interfaces – Interfacial Coordination Chemistry (ICC)

Oxide surfaces in aqueous suspension

Analogy to electrochemistry of surfaces of electrodes: multilayer model of the environment of a solid surface (e.g. Gouy-Chapman-Stern):

1. Monomolecular layer of water or OH-groups chemically bound to the surface,
2. At least one additional layer near to the surface with properties different from the bulk solvent.

→ melting and boiling point and dielectric constant different from bulk water;
→ unmixing / separation in water containing organic solvents
→ formation of a thin aqueous layer at the solid surface (or filling of micropores)
→ application: SLP (SAP)-catalysts: Supported Liquid (Aqueous) Phase catalysts.

Surface acidity and surface charge

Water coordinated to metal ions (e.g. in first layer of the above multi layer model) represents a stronger Brønsted-acid than free water, similar as in aqua complexes. For chemisorbed water, the following **acid-base equilibria** are resulting:

$$\equiv M\text{-}OH_2^+ \quad \rightarrow \quad \equiv M\text{-}OH + H^+ \qquad (K_{a1})$$

$$\equiv M\text{-}OH \quad \rightarrow \quad \equiv M\text{-}O^- + H^+ \qquad (K_{a2})$$

Acid constants*:*

$$K_{a1} = \{\equiv M\text{-}OH\}[H^+] / \{\equiv M\text{-}OH_2^+\} ; \quad K_{a2} = \{\equiv M\text{-}O^-\}[H^+] / \{\equiv M\text{-}OH\} ;$$

Depending on the pH region, surface OH groups react as Brønsted-acids or -bases.

The ***acidity of surface OH groups (K_{a1}, K_{a2})*** depends upon the

- nature of the cations in the crystal lattice,
- degree of protonation (charge density) at the surface and
- neighbouring medium (solvent, gas).

The ***surface charge*** originates from:

- substitution of metal ions in the crystal lattice by other ions of different charge (permanent charge),
- acid-base equilibria at the surface ($\equiv$M-OH_2^+ oder $\equiv$M-O^-) or
- chemical bonding of charged metal complexes or compounds (chemisorption).

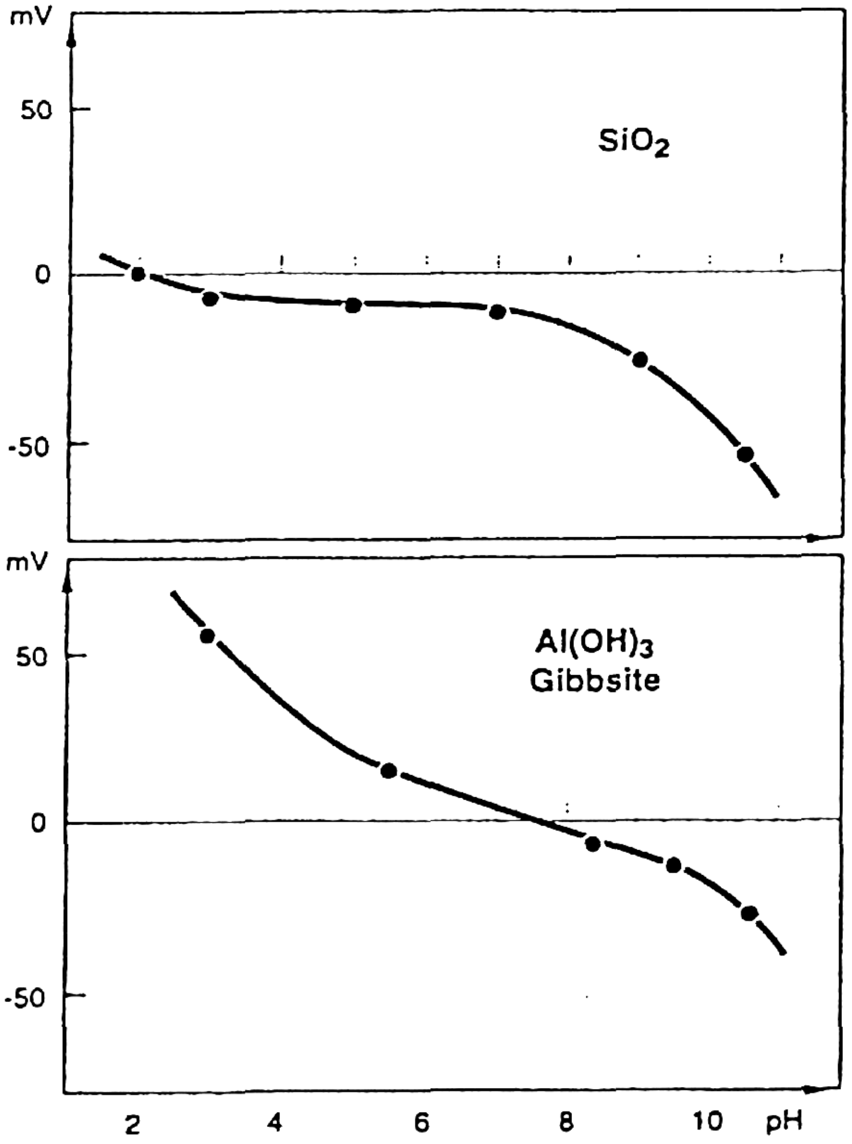
In aqueous solution (suspension), the surface charge is pH dependent. The point, at which the surface is uncharged (M-OH) or at which the number of positive ($\equiv$M-OH_2^+) and negative ($\equiv$M-O^-) charges is equal, is called

isoelectric point, pH_{pzc} (pzc = point of zero charge)

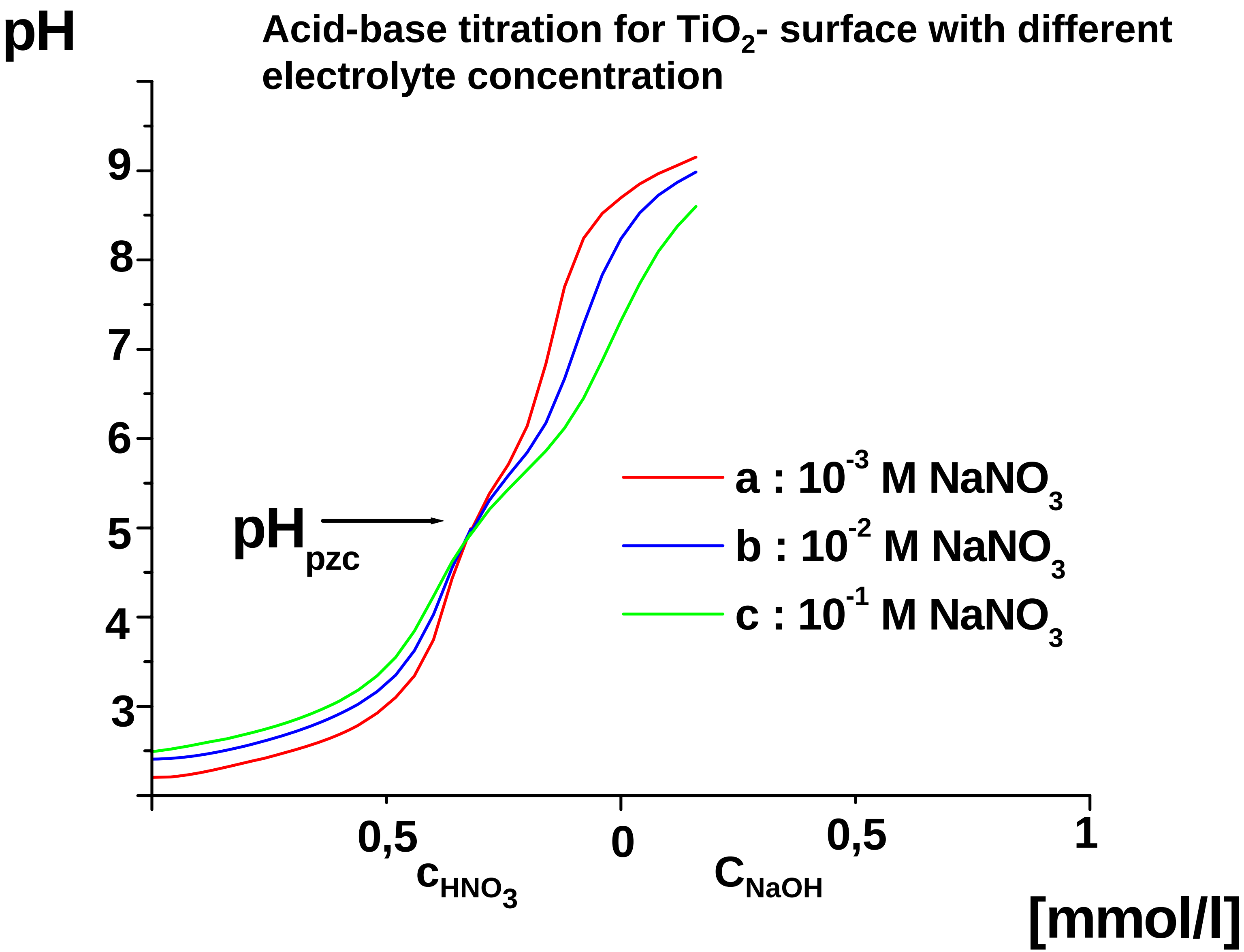
Determination:

- electrophoresis (migration of charged oxide particles in an electric field), or
- acid-base titration of oxidic suspensions with different ionic strength.

Determination of isoelectric points and surface charge by electrophoresis (migration of charged particles in an electric field)



Acid-base titration for TiO_2- surface with different electrolyte concentration



Isoelectric points of chosen oxides:

Oxidic material	pH_{pzc}
α-Al_2O_3	9,1
α-$Al(OH)_3$	5,0
γ-AlOOH	8,2
CuO	9,5
Fe_3O_4	6,5
α-FeOOH	7,8
γ-Fe_2O_3	6,7
MgO	12,4
δ-MnO_2	2,8
β-MnO_2	7,2
SiO_2	2,0
$ZrSiO_4$	5
kaolinite	4,6
montmorillionite	2,5

The ***oxide surface*** is a ***polyelectrolyte*** ⇒ ion exchange:
Ion exchange capacity and selectivity are dependen upon
- Size (dimansions) and charge of the adsorbing ions,
- Concentration relations.

Often, chemical interactions are superimposed to the electrostatic ones.

The oxide surface as ligand

The oxide surface can act as „supramolecular“ Ligand: surface oxygen ions can bind (coordinate) to adsorbed metal ions forming surface complexes.

Surface complex formation (surface/interfacial coordination chemistry):
- „outer spere“ (second sphere) complexes,
- „inner sphere“ complexes (surface as mono-, bi- oder tri-dentate ligand).

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Ion exchange

⇒ Exchange of Ions at the surface of the support (solid electrolyte) by different ions

⇒ Basis: electrostatic interactions + concentration gradient

<u>Ion exchanger</u>:

(a) natural or artificial
(pillared clays, hydrotalcite, zeolites)

(b) anion-exchanger (e.g. $-NR_4^+$)
cation-exchanger (O^-: zeolites, oxides, polymers: $-SO_3^-$, $-CO_2^-$)

Origin of the charge of the solid electrolyte:

	Lattice substitution (e.g. Al^{3+} for Si^{4+})	Surface species (e.g. protonation)
Exchange capacity	not pH-dependent	Strongly pH-dependent
Examples	zeolites, silicates, clays	Oxides

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Experiment: mixing (stepwise addition of the metal salt)
stirring (equilibrium reached within several hours)
separation (eventually multiple exchange ⇒ higher loadings)
calcination, reduction, activation

Example: Na^+ (9,9 wt.-%) in NaY-zeolite substituted by NH_4^+
- maximum exchange 73 % in one step
- (more) complete exchange by repeated (discontinuous) exchange or continuous procedures (zeolite fixed bed)

⇒ high dispersion achievable (however: no strong bonding to the surface!)

⇒ maximum loading is strongly dependent on the support (on oxides ev. < 1 wt.-%, whereas $[Pt(NH_3)_4]^{2+}$ can be exchanged up to 25 wt.-% relative to the water free zeolite)

superposition of electrostatic and chemical interactions

(formation of surface complexes)

Equilibrium adsorption

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(Equilibrium-)Adsorption of metal ions at oxide surfaces from (aqueous) solution – relevant parameter

- pH value: surface charge (acid-base eq.), structure and charge of the complex molecule (precursor) in solution, possibility of H-bonding

- solvent: solubility, equilibrium ⇒ dispersion, relevance of electrostatic interactions

- nature of the metal ion: oxidation state/ charge, kinetic stability

- ligands: charge, size, H-bonding to the surface, entropy effects, dissolution of the support, (volatility/decomposition), competing adsorption

- nature of the Oxide: „lattice“ charge (doping, mixed oxides), IEP/ pH_{pzc}, specific surface area, pore structure

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Example: reforming catalyst: Pt/ Al_2O_3
(+ promotors Cl^- or Re)

- Precursor: H_2PtCl_6
- maximum loading on Al_2O_3: 2-4 wt.-%
- industrially applied: 0,2-0,6 wt.-%

- $[PtCl_6]^{2-}$: positive surface charge necessary: $pH < pH_{pzc} = 9$

- homogeneous Pt distribution by additional competing adsorption of Cl^- (simultaneously promotor und stabilizer of the coordination sphere)

- $[PtCl_6]^{2-}$:partial hydrolysis ati pH = 5-7 (aqua complexes: modified coordination sphere and charge!)

- pH = 3-4.

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Example: supported rhodium catalysts (I)

Task/aim:

Preparation: **1.0 mass-% *highly dispersed* rhodium metal at SiO_2**

Ways:

- impregnation (“incipient wetness”-~, diffusion-~)
- ion exchange / equilibrium adsorption
- grafting

Variables (selection):

- Rh starting compound (precursor)
- starting concentration of the precursor ($\Rightarrow$ desired loading)
- method of immobilization
- thermal treatment (calcination, reduction, ev. passivation; temperature (-ramp), duration of the treatment, amount of catalyst)

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Example: supported rhodium catalysts (II)

Selected literature for preparation of Rh/SiO_2 catalysts:

Lit. 1 (J. P. Candy et al.): “The rhodium is deposited by exchange of the acidic sites of the support by $RhCl(NH_3)_5^{2+}$, with ammonium as competitor ions:

$$\equiv Si\text{-}OH + NH_4OH \rightarrow \equiv Si\text{-}O\text{-}NH_4 + H_2O$$

$$[RhCl(NH_3)_5]^{2+} + 2Cl^- + 2 \equiv Si\text{-}O\text{-}NH_4 \rightarrow 2[\equiv Si\text{-}O\text{-}]\text{-}[RhCl(NH_3)_5]^{2+} + 2NH_4Cl$$

In both cases, after 24 h of contact between the solution and the solid, the solid is filtered and air dried at 383 K. It is then calcined at 673 K in flowing dry air, and reduced at the same temperature in flowing hydrogen. The amount of rhodium thus deposited is respectively 1.0 and 1.3 wt% Rh/SiO_2 **A** and **B**.”

Lit. 2 (B. Didillon et al.): “Rhodium was grafted onto silica (Aerosil 200 m^2/g, Degussa) by cationic exchange between $[RhCl(NH_3)_5]^{2+}$ ions and surface groups. The surface complex obtained was decomposed by calcination at 673 K in flowing nitrogen/oxygen (5/1), reduced in flowing hydrogen at 673 K, and then “passivated” at 298 K under dry air. The Rh and Cl loadings were 1.1% and 0.06 % by weight, respectively.”

Lit. 3 (EP 0 422 968 B1): “... fixation du rhodium par imprégnation de chlorure de rhodium chloropentammine en solution ammoniacale sur une silice dont la surface spécifique est égale à 280 m^2 par gramme ..., suivie d’une filtration, d’un séchage à 110 °C, d’une calcination sous air à 450 °C et d’une réduction sous hydrogène à 450 °C ...”

Example: supported rhodium catalysts (III)

Working steps	**Result**
- Literature	- missing data (in partic. c_A)
- Precursor (choice)	- $[RhCl(NH_3)_5]Cl_2$
- Impregnation	- D $\approx$ 0,02 – 0,5 (d $\approx$ 3-600 nm)
- Adsorption isotherms: f(t, c, pH, washing)	- c_A=1,5 ma.-% $\Rightarrow$ c_E=1,0 ma.-% pH: NH_3 solution (25%)
- Opt. Working procedure:	- 24 h, 2 x washing (NH_3 solution)
- Thermal Treatment/ activation (Lit./Opt.)	- Ar/O_2 (5:1) 80ml/min//5K/min//673K//1h - H_2 (1:0) 20ml/min//5K/min//673K//1h
- Analytics:	
Elemental analysis	- 1,0 ma.-% Rh rel. SiO_2
Chemisorption	- D = 0,88, (d$\leq$ 1-2 nm).

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Grafting

IUPAC:

Formation of strong (covalent) bonds between support (polymer or inorganic solid) and metal complexes (in the very first step of immobilization)

Chemical reaction between functional groups (e.g. OH) of the surface and the precursor compound

Typical precursors:

(a) Metal halides and oxyhalides

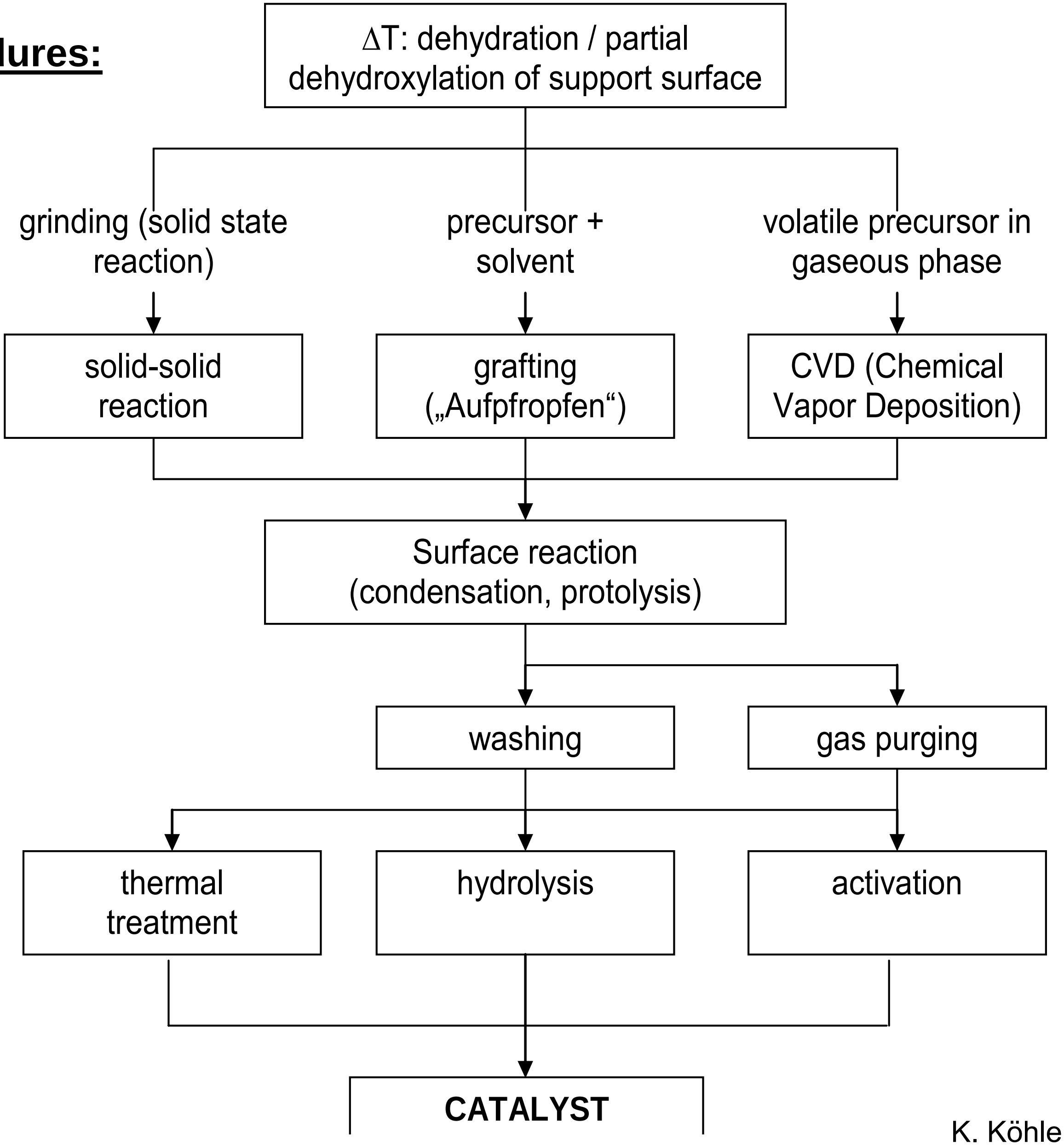
(b) Metal alkoxides and amides

(c) Metalorganic compounds (e.g. alkyl-, allyl complexes) or metal carbonyles

Advantages:

- highly dispersed metal ions at a (previously) dehydrated and partially dehydroxylated (oxide) surface
- hindering of migration, agglomeration and sintering during subsequent thermal treatment
- control of (metal) loading (by degree of dehydroxylation, multiple grafting)

Grafting procedures:



ΔT: dehydration / partial dehydroxylation of support surface

grinding (solid state reaction)

precursor + solvent

volatile precursor in gaseous phase

solid-solid reaction

grafting („Aufpfropfen“)

CVD (Chemical Vapor Deposition)

Surface reaction (condensation, protolysis)

washing

gas purging

thermal treatment

hydrolysis

activation

CATALYST

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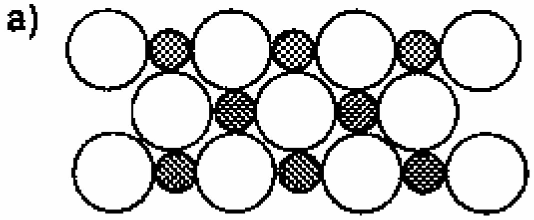
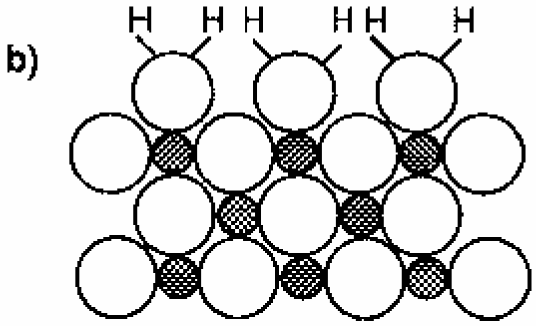
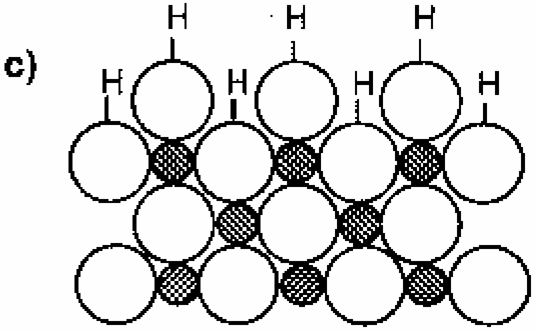
Formation of a hydrated / hydroxylated oxide surface



cut through a single crystal (thought experiment, UHV): coordinative unsaturated metal ions

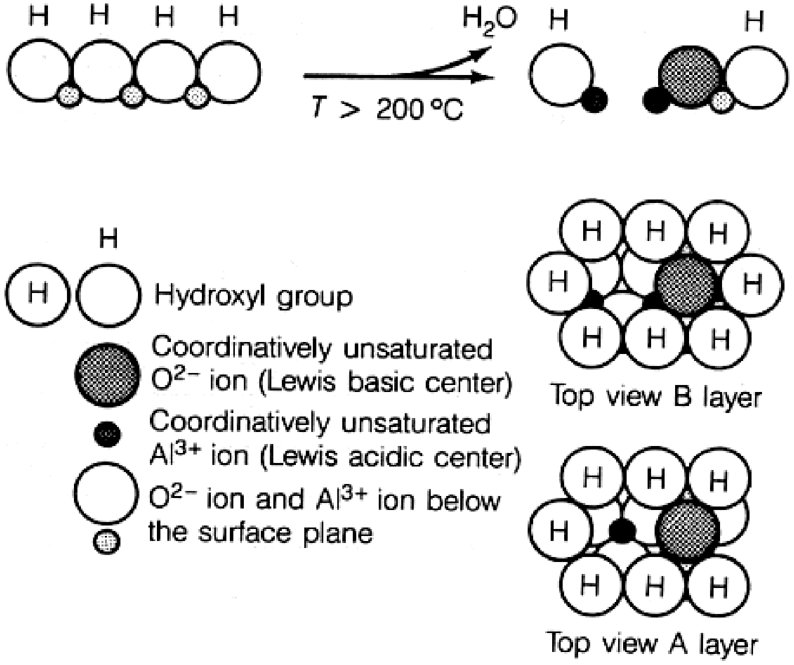


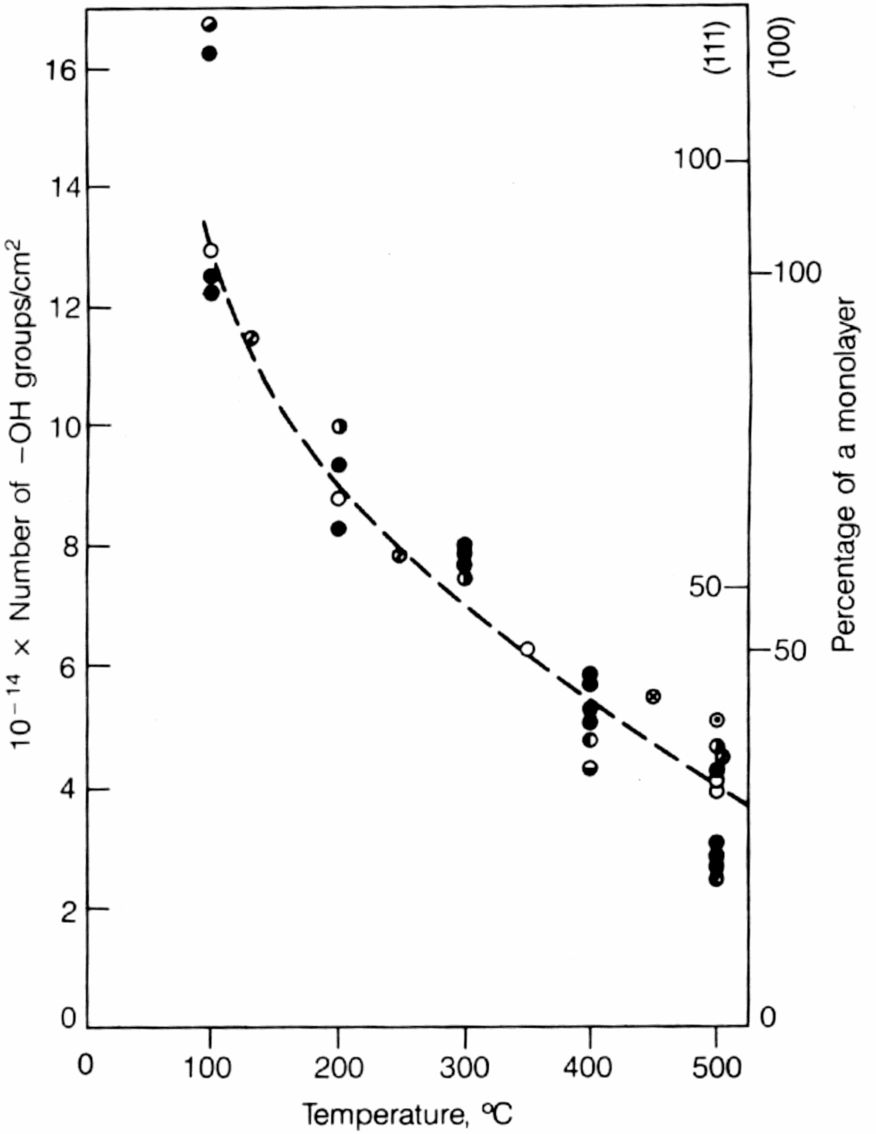
molecular adsorption of water



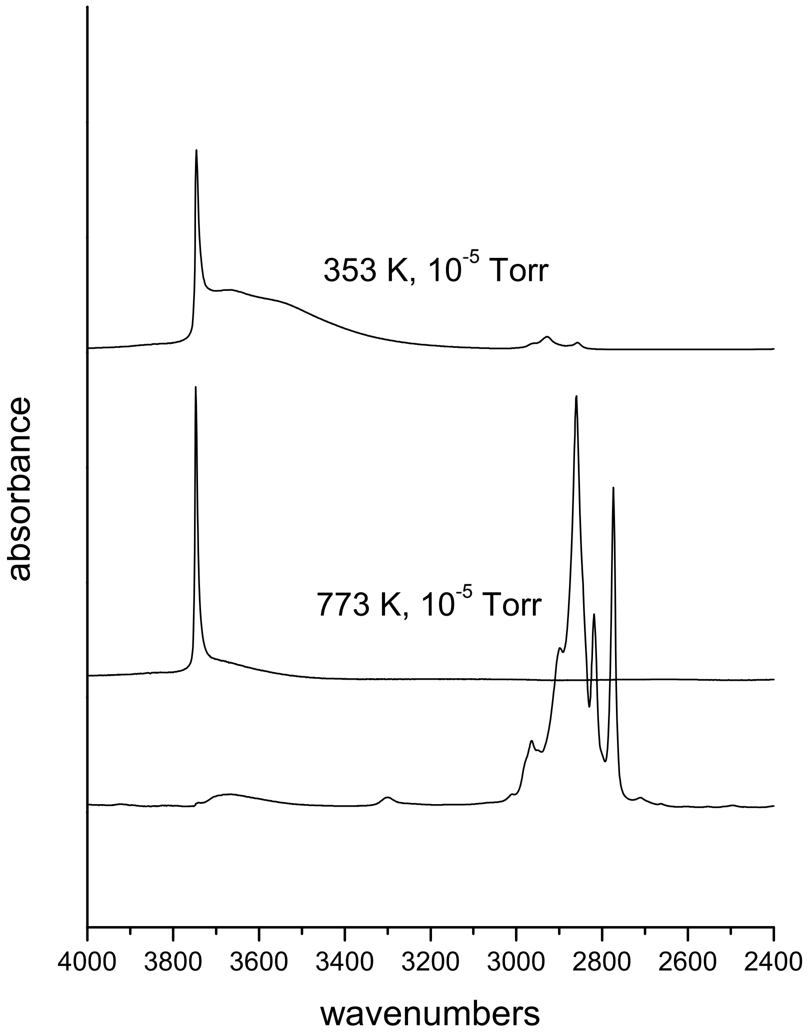
OH-groups by dissociation of surface water and proton shift

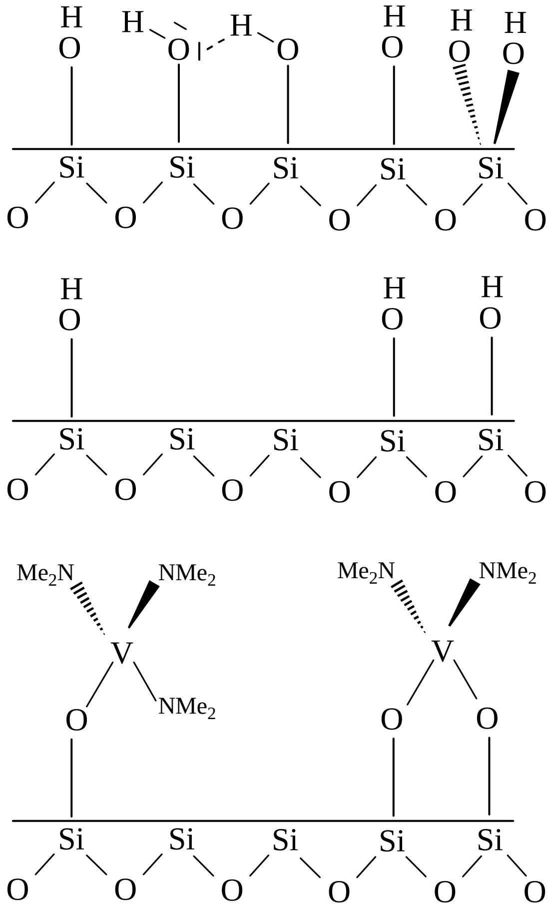
Surface structure and dehydration/ dehydroxylation of γ-alumina (γ-Al_2O_3)





Grafting of $V[N(CH_3)_4]$ onto SiO_2 surfaces





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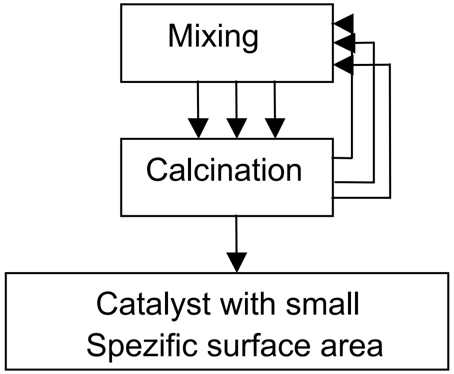
Preparation of supported heterogeneous catalysts by physical mixing of solids (precursor + support) – solid state reactions (spreading und wetting)

Preparation of supported oxides by the „dry method“:

Mixing of solid components (dry or moist mass): mortar, ball mill

e.g. easily decomposable salts (formates, carbonates, nitrates, oxalates, ...)



Mixing

Calcination

Catalyst with small Spezific surface area

Atomic mobility of solids is limited, but can be initiated at catalytically relevant T (solid-solid interfaces) :

<u>Important for:</u> Sintering,
Redispersion, → Thermal treatment (calcination, activation)
Covering of a metal particle by an oxide (SMSI),
Solid ion exchange

e.g. KOH + chromium und iron oxides: styrene process)

Tamman temperature: T, where lattice atoms become mobile: $T_T \approx 0.5 \times T_{melt}$ [K]

Hüttig temperature: T, where surface atoms become mobile: $0,3 \times T_{melt}$ [K]

(metals become mobile already at $0.3 \times T_{melt}$: Cu, Ag, Au: $T_{melt} \approx 1300$ K, i.e. > 450 K. ⇒ applied always supported or using structural promotors).

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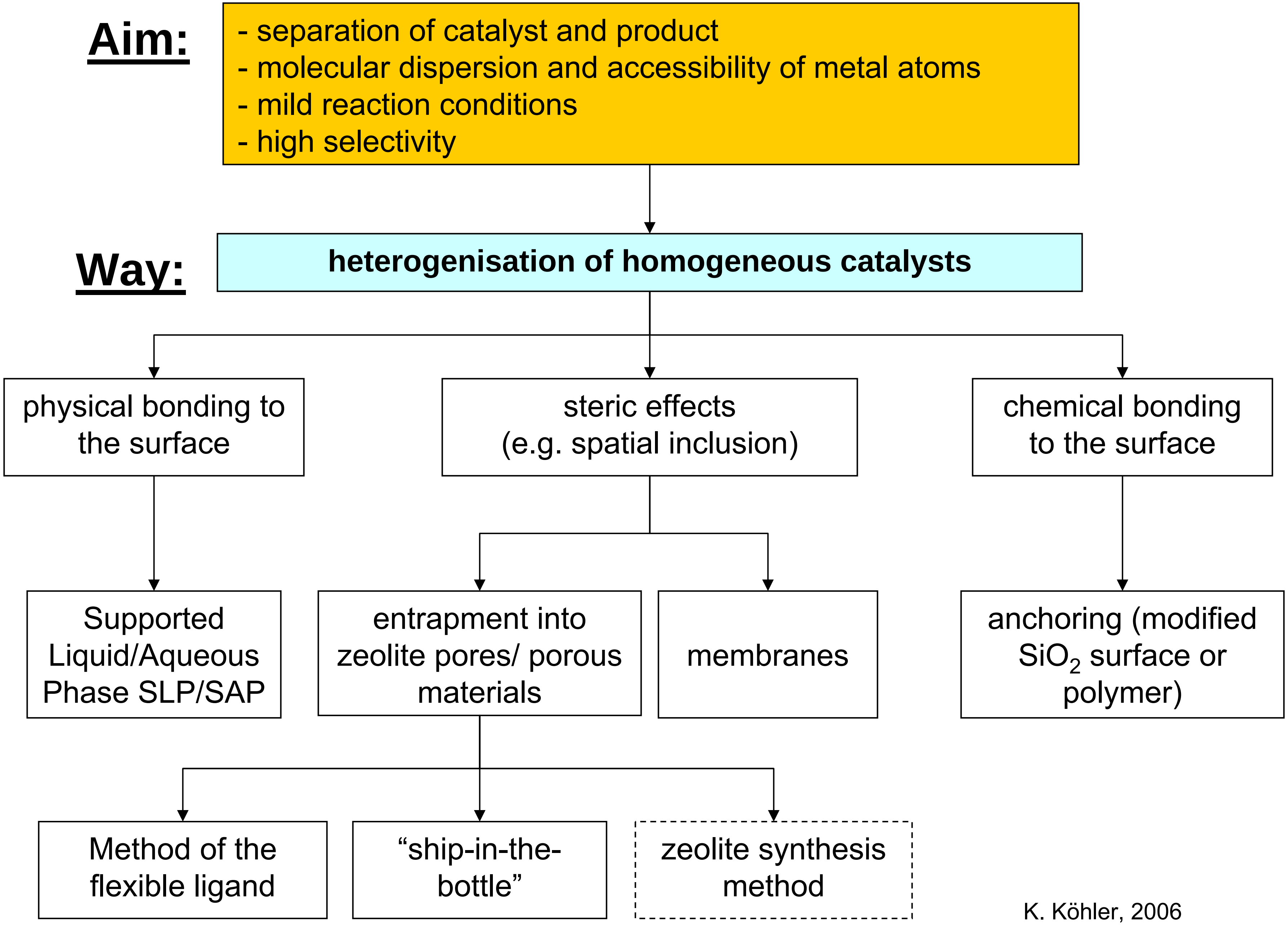

Aim:

- separation of catalyst and product
- molecular dispersion and accessibility of metal atoms
- mild reaction conditions
- high selectivity

Way:

heterogenisation of homogeneous catalysts

physical bonding to the surface

steric effects (e.g. spatial inclusion)

chemical bonding to the surface

Supported Liquid/Aqueous Phase SLP/SAP

entrapment into zeolite pores/ porous materials

membranes

anchoring (modified SiO_2 surface or polymer)

Method of the flexible ligand

“ship-in-the-bottle”

zeolite synthesis method

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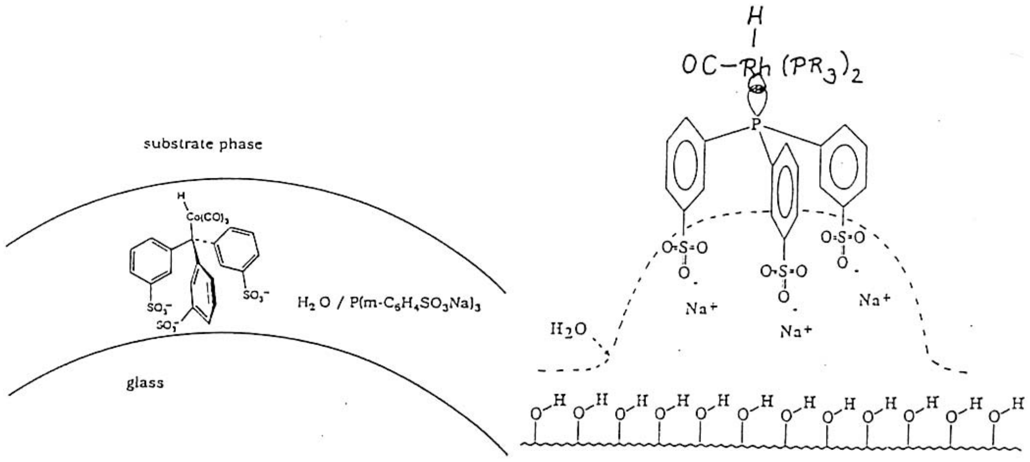
Adsorption and formation of water layers on metal oxide surfaces – practical applications

⇒ Drying or organic solvents: Al_2O_3, SiO_2, zeolites

⇒ Supported Aqueous Phase (SAP) catalysts



⇒ chromatography (mobile phase: organic solvent, stationary phase: interlayer/water.

Formation of the final, catalytically active species: *calcination and activation*

Activation (IUPAC): Transformation of precursor(s) into the catalytically active phase

- decomposition, desorption of volatile components
- chemical bonding to the support
- chemical transformation (solid state chemistry) ⇒ new phases (thermal treatment under inert, oxidizing, reducing, sulfur-containing or reaction gas atmosphere: calcination, reduction, sulfidation, …)

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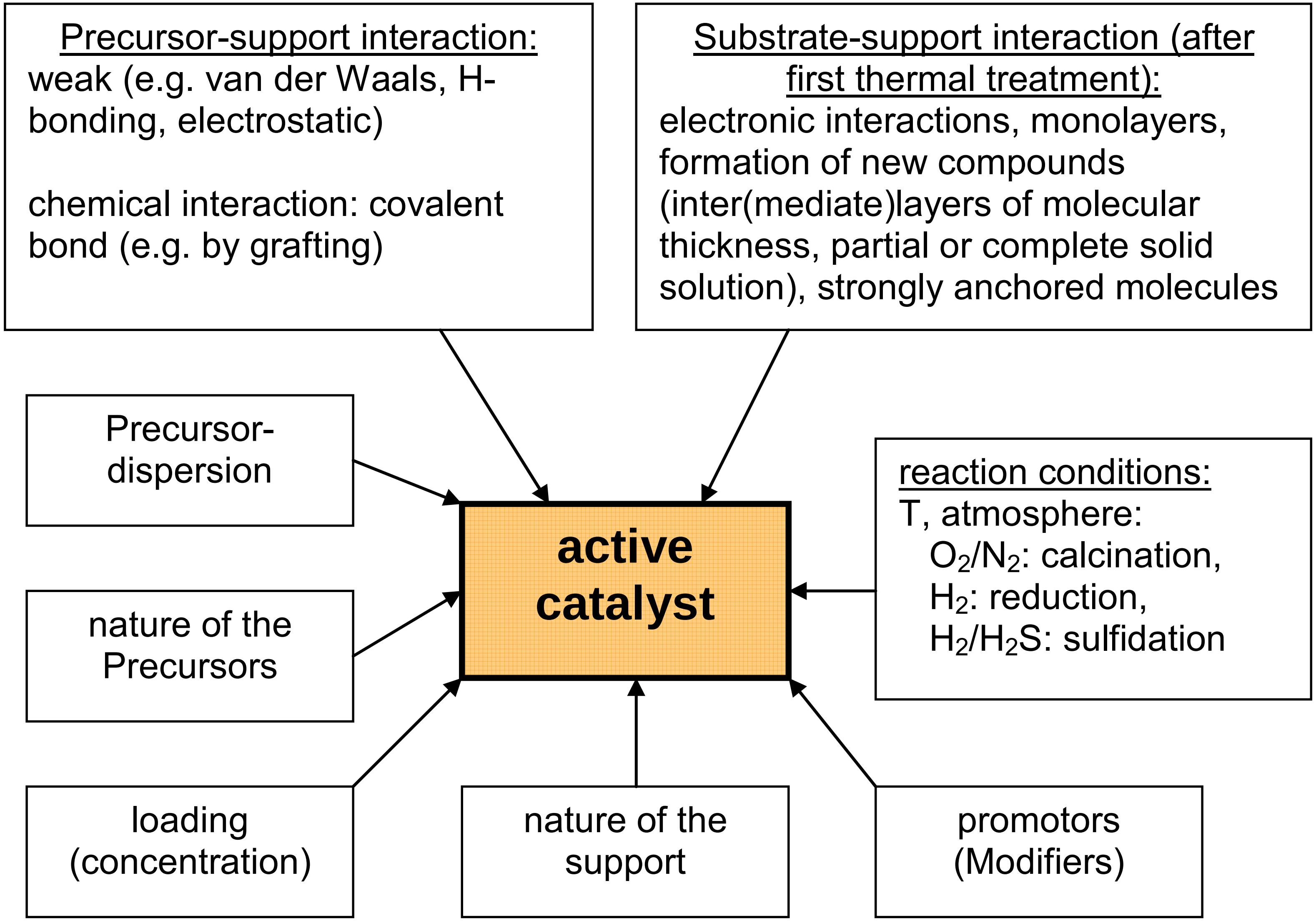
Parameters for Activation



Precursor-support interaction:
weak (e.g. van der Waals, H-bonding, electrostatic)

chemical interaction: covalent bond (e.g. by grafting)

Substrate-support interaction (after first thermal treatment):
electronic interactions, monolayers, formation of new compounds (inter(mediate)layers of molecular thickness, partial or complete solid solution), strongly anchored molecules

Precursor-dispersion

active catalyst

reaction conditions:
T, atmosphere:
O_2/N_2: calcination,
H_2: reduction,
H_2/H_2S: sulfidation

nature of the Precursors

loading (concentration)

nature of the support

promotors (Modifiers)

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Literature

Introducing and review literature on preparation of heterogeneous catalysts

Text books:

J. Hagen, *Technische Katalyse: eine Einführung*, VCH Weinheim, 1996.

J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis,* VCH Weinheim, 1997 (chapter 5.: important classes of inorganic compounds for solid catalysts).

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