Heterogeneous catalysis

Lecture 3

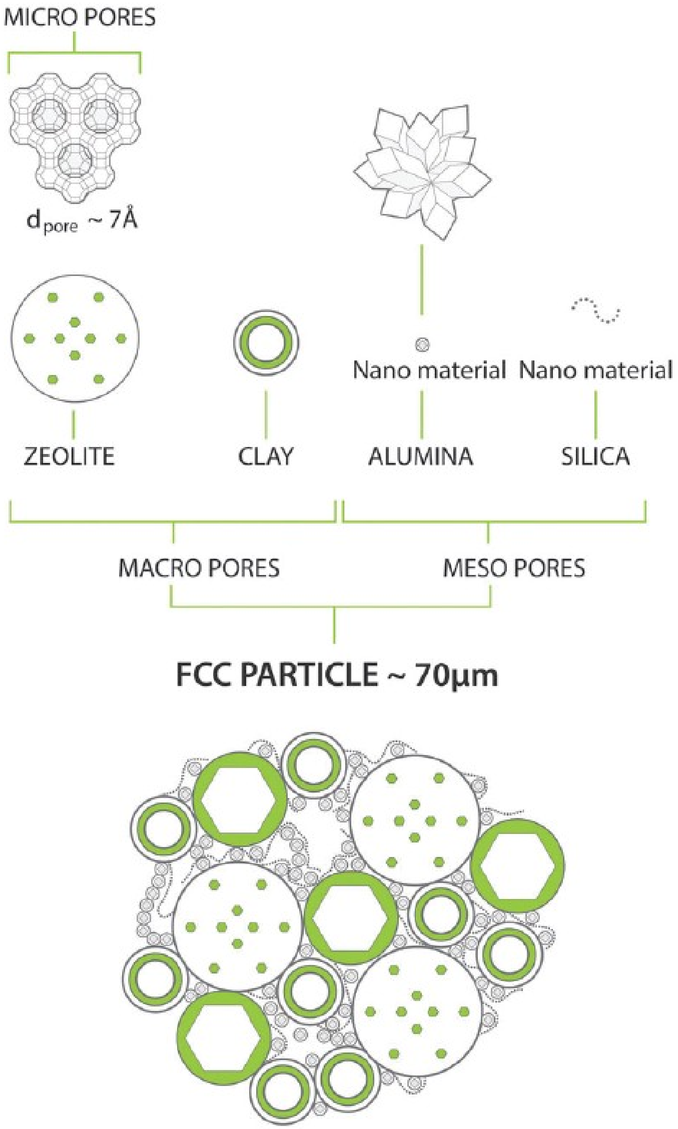
Catalysts preparation

Types of catalysts

- Bulk catalysts
- Supported catalysts
- Malaxed-agglomerated catalysts

Types of catalysts

- Bulk catalysts
- Supported catalysts
- **Malaxed-agglomerated catalysts**
  - Intermediate category
  - Catalysts obtained by mixing active species with support (powders+precursors)
  - Ill defined catalysts – broad application in industry



Chem. Soc. Rev., 2015, **44**, 7342–7370

Types of catalysts

- **Bulk catalysts**
- Supported catalysts
- Malaxed-agglomerated catalysts

Preparation of bulk catalysts

- The whole body of the catalyst is made of one active substance
- = It must be cheap, thermally, mechanically, and chemically stable, porous,…!
  - Silica-alumina (cracking)
  - Raney nickel, Co molybdate (hydrogenation)
  - Catalyst supports: silica, alumina, silica-alumina, zeolites, TiO_2, MgO, carbon

Preparation of bulk catalysts

- Ceramic route (heat and beat)
  - e.g. Molybdates $Bi_2O_3 + MoO_3 \rightarrow Bi_2MoO_6$
  - Used as selective oxidation catalysts (propylene to acrolein)
  - Homogeneity, time, temperature
- (Co-)Precipitation
  - E.g. $NH_4VO_3 + Al(NO_3)_3 \rightarrow$ V-Al oxynitride (used in propene ammoxidation to acrylonitrile)
  - change of pH leads to precipitation
- Sol-gel method
- Combustion synthesis
- Solvothermal method
  - e.g. zeolites

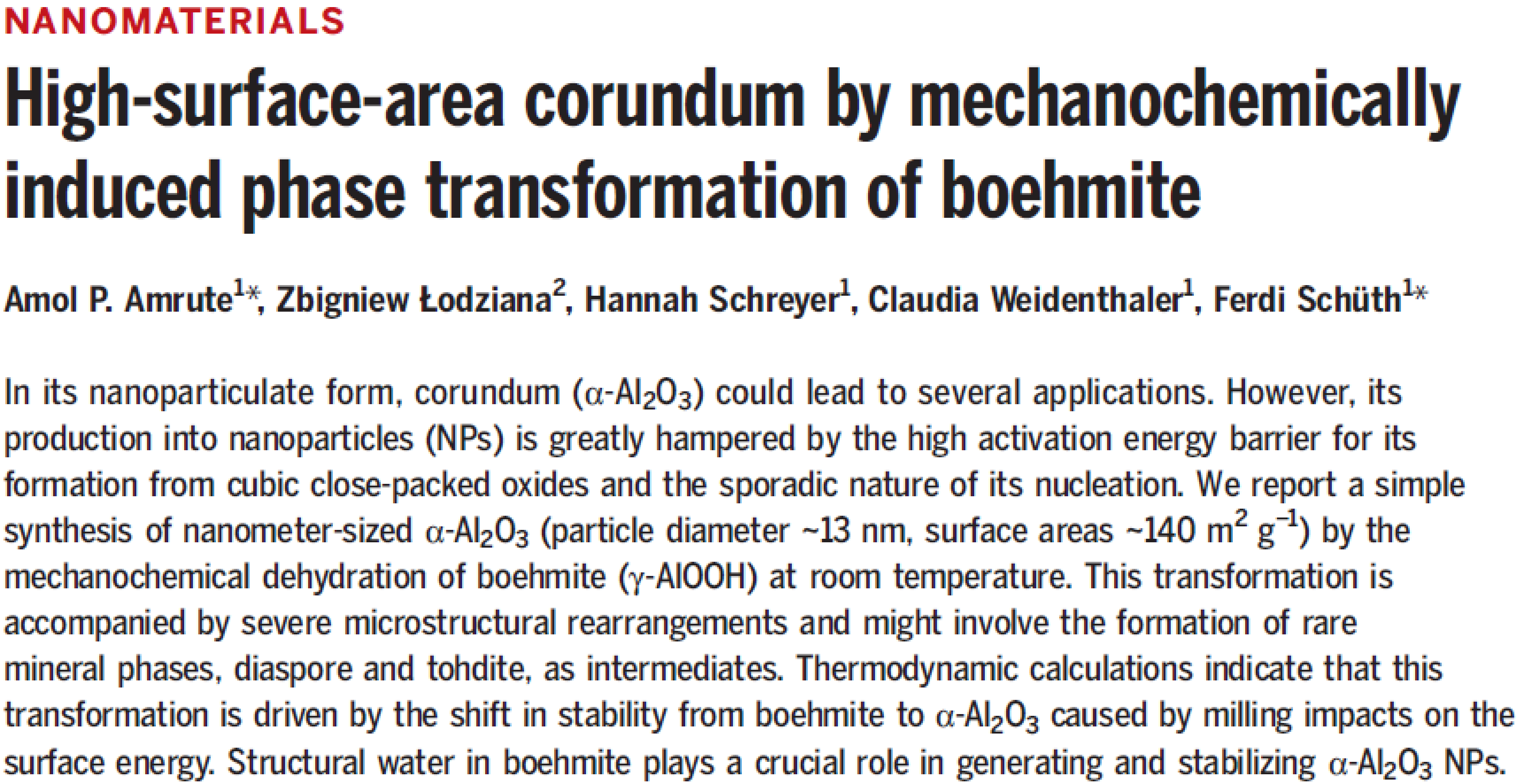
Preparation of bulk catalysts

- Ceramic route, (co-)precipitation, sol-gel method, combustion synthesis, and solvothermal method: #InorgMatChem
- Heat and beat quickly and effectively?
- Sol-gel continuously???

Ball milling!

Aerosol assisted sol-gel process!

Preparation of bulk catalysts



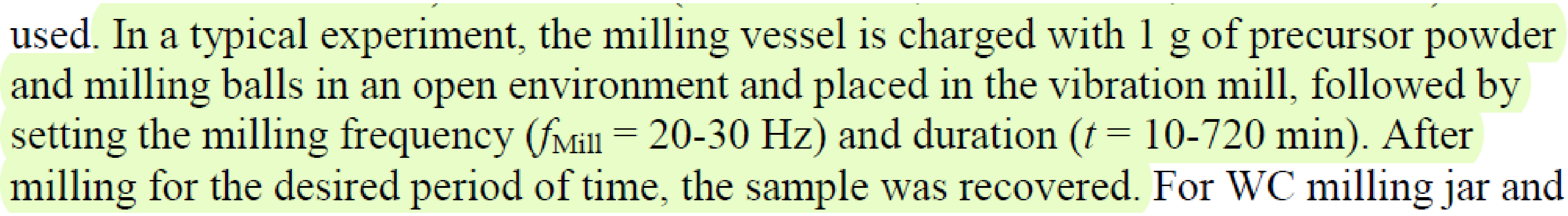
NANOMATERIALS

High-surface-area corundum by mechanochemically induced phase transformation of boehmite

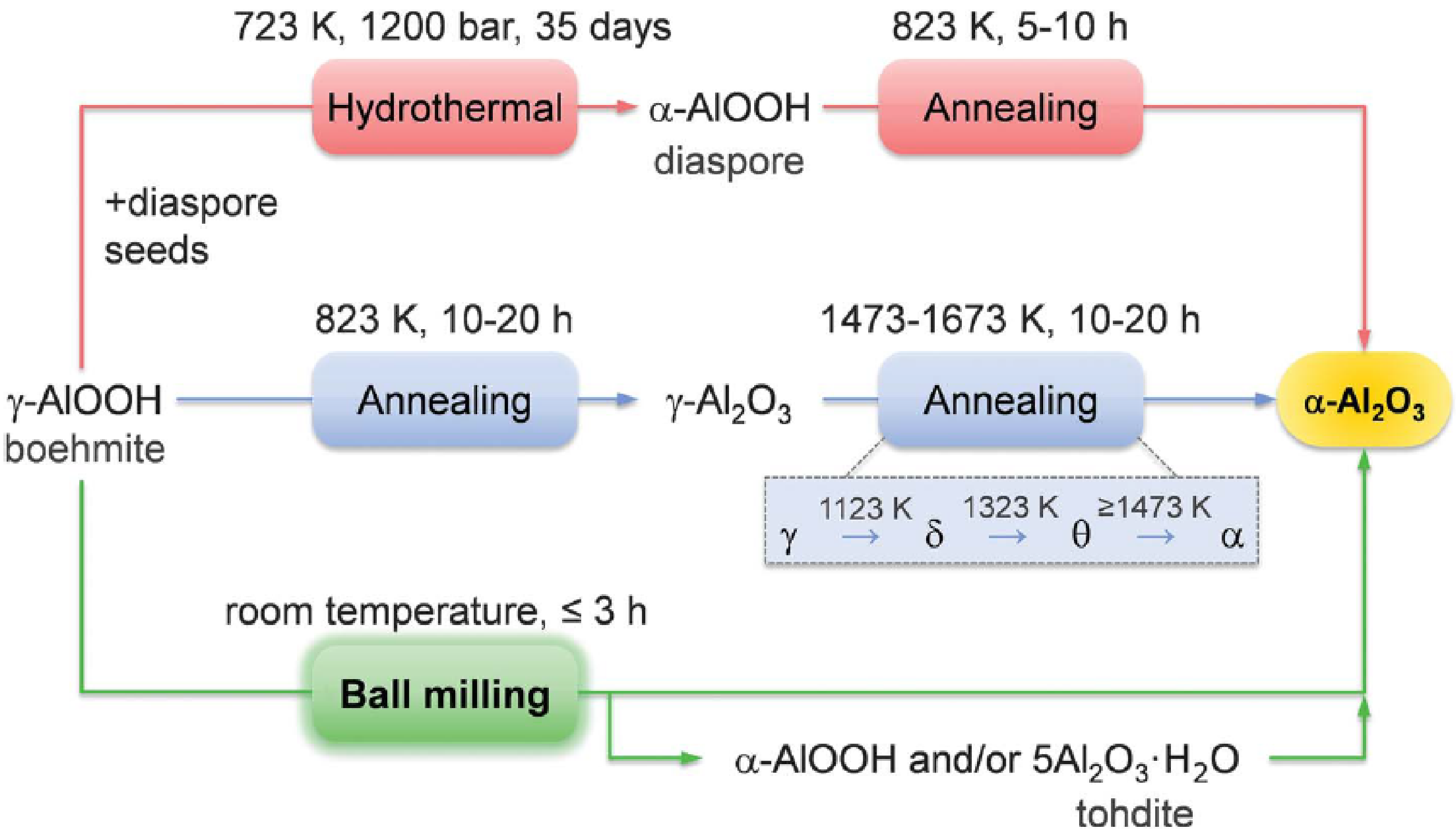
Amol P. Amrute[1*], Zbigniew Łodziana[2], Hannah Schreyer[1], Claudia Weidenthaler[1], Ferdi Schüth[1*]

In its nanoparticulate form, corundum (α-Al_2O_3) could lead to several applications. However, its production into nanoparticles (NPs) is greatly hampered by the high activation energy barrier for its formation from cubic close-packed oxides and the sporadic nature of its nucleation. We report a simple synthesis of nanometer-sized α-Al_2O_3 (particle diameter ~13 nm, surface areas ~140 $m^2\ g^{-1}$) by the mechanochemical dehydration of boehmite (γ-AlOOH) at room temperature. This transformation is accompanied by severe microstructural rearrangements and might involve the formation of rare mineral phases, diaspore and tohdite, as intermediates. Thermodynamic calculations indicate that this transformation is driven by the shift in stability from boehmite to α-Al_2O_3 caused by milling impacts on the surface energy. Structural water in boehmite plays a crucial role in generating and stabilizing α-Al_2O_3 NPs.

Preparation of bulk catalysts



used. In a typical experiment, the milling vessel is charged with 1 g of precursor powder and milling balls in an open environment and placed in the vibration mill, followed by setting the milling frequency (f_{Mill} = 20-30 Hz) and duration (t = 10-720 min). After milling for the desired period of time, the sample was recovered. For WC milling jar and



723 K, 1200 bar, 35 days

Hydrothermal

α-AlOOH diaspore

823 K, 5-10 h

Annealing

+diaspore seeds

γ-AlOOH boehmite

823 K, 10-20 h

Annealing

γ-Al_2O_3

1473-1673 K, 10-20 h

Annealing

α-Al_2O_3

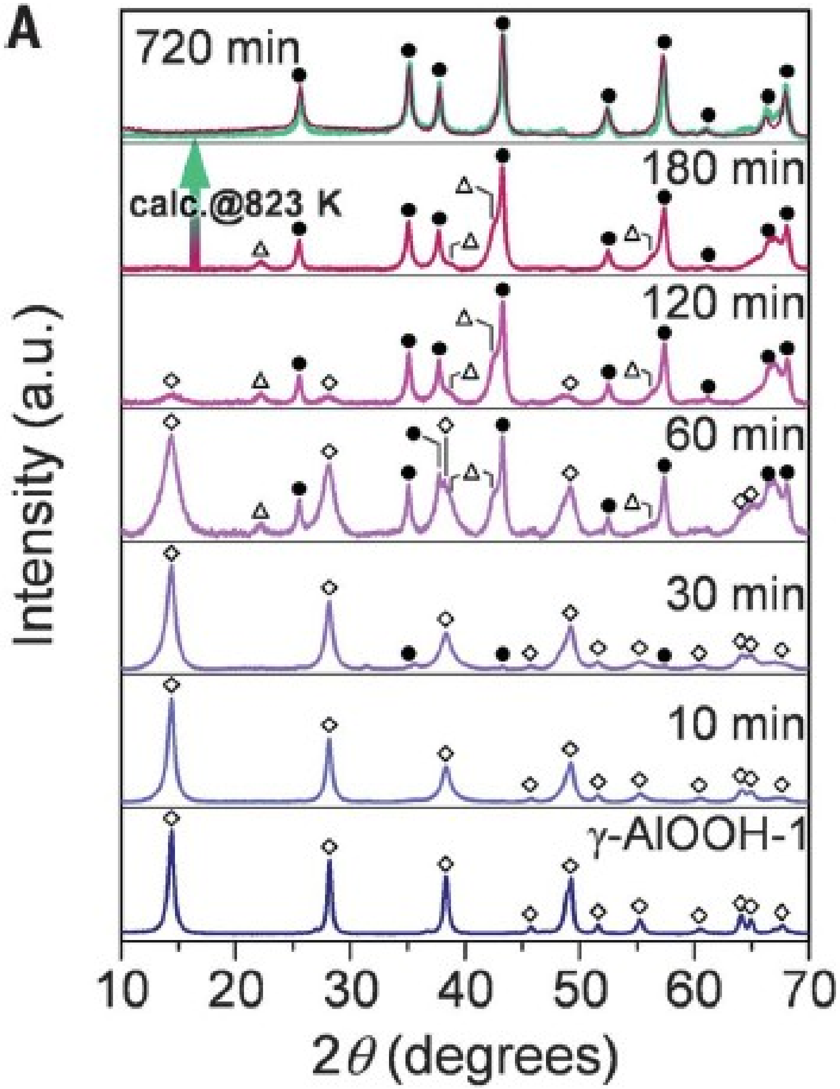
$\gamma \xrightarrow{1123\ K} \delta \xrightarrow{1323\ K} \theta \xrightarrow{\geq 1473\ K} \alpha$

room temperature, ≤ 3 h

Ball milling

α-AlOOH and/or $5Al_2O_3 \cdot H_2O$ tohdite

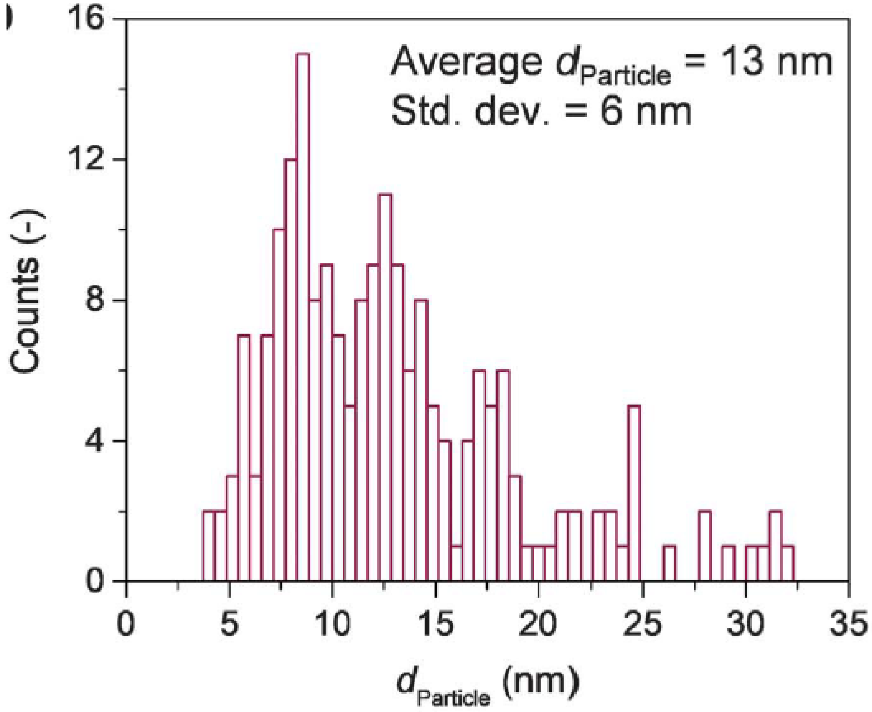
Preparation of bulk catalysts



◊ γ-AlOOH

● α-Al_2O_3

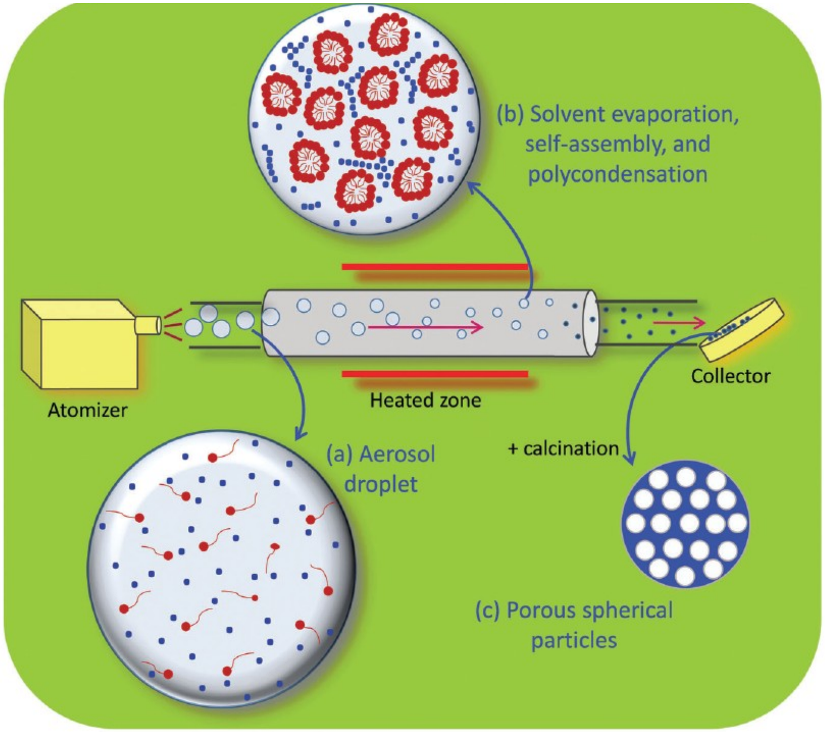
Δ α-AlOOH

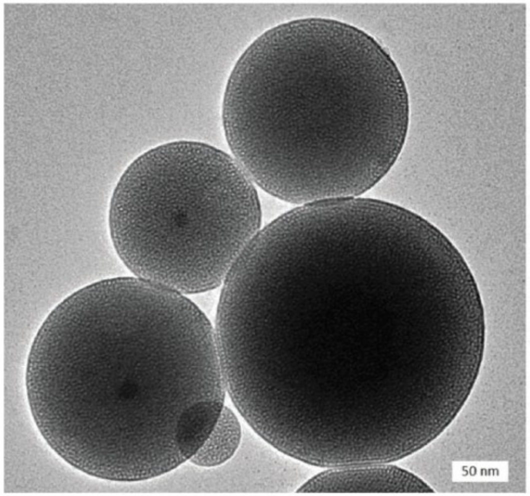


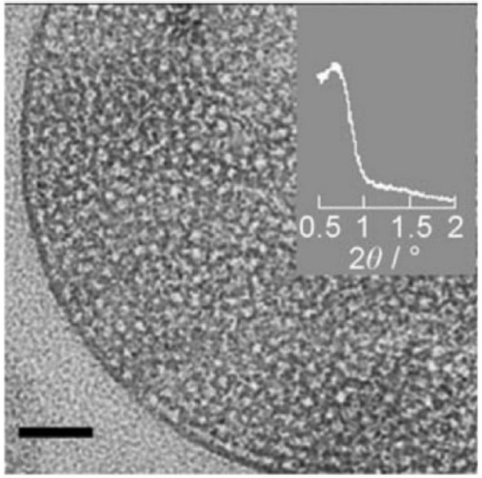
Preparation of bulk catalysts

Aerosol processing: a wind of innovation in the field of advanced heterogeneous catalysts

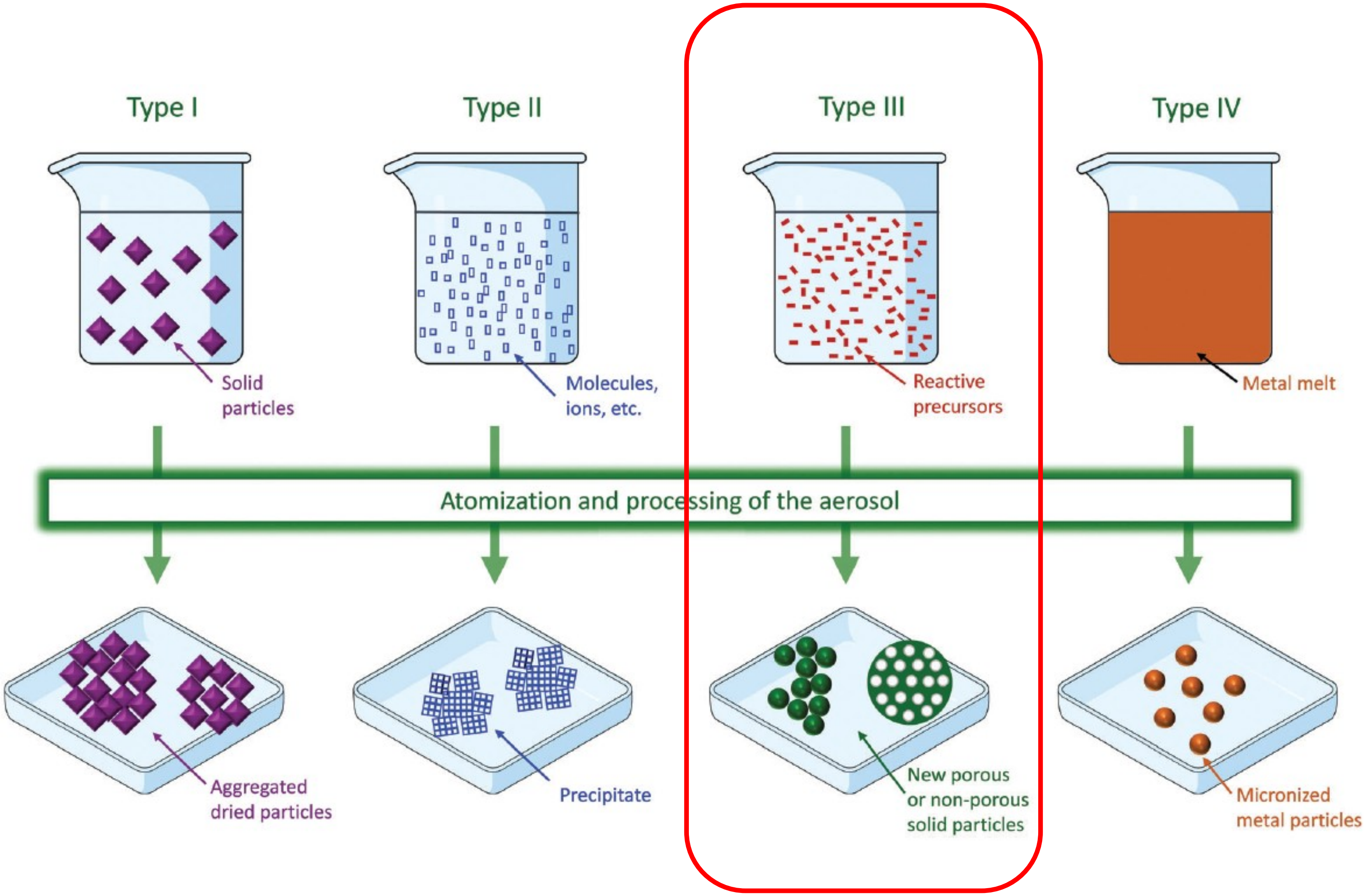
Damien P. Debecker, *[a] Solène Le Bras, [a] Cédric Boissière, [b]
Alexandra Chaumonnot[c] and Clément Sanchez *[b]







Preparation of bulk catalysts



Types of catalysts

- Bulk catalysts
- **Supported catalysts**
- Malaxed-agglomerated catalysts

Preparation of supported catalysts

- Properties of catalyst supports
  - Cheap
  - Porous
  - Thermally, mechanically, and chemically stable
  - …
- Role of catalyst supports (non-innocent)
  - Porosity/hydrophobicity vs. Activity/selectivity
  - O, H, N,…bank (MvK mechanism)
  - Electron donor/acceptor (Haber-Bosch)
  - …

Preparation of supported catalysts

- Three types of interaction between support and active phase
  - Weak
  - Electrostatic
  - Covalent

Preparation of supported catalysts

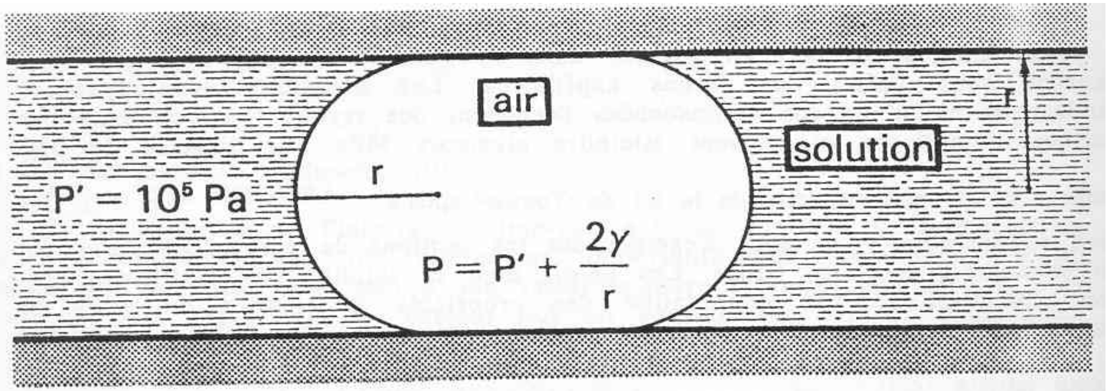
- Weak interaction = **Impregnation methods**
  - Wet impregnation
    - Suspension of support (e.g. SiO_2 in water)
    - Solution of metal salt (e.g. $Cu(NO_3)_2$ in water)
    - Mixed together (suspension)
    - Cu^{2+} cations diffuse into the pores of SiO_2 support (=we need to wait for enough **long** time, Fick laws)
    - Drying, calcination (= formation of Cu_2O NPs on SiO_2), (reduction of Cu_2O to Cu NPs)
    - Disadvantages: Time, homogeneity.

Preparation of supported catalysts

- Weak interaction = Impregnation methods
  - Dry impregnation (Incipient wetness impregnation)
    - Dry support, pores full of gas (e.g. SiO_2 in ambient air)
    - Solution of metal salt, V = pore volume (e.g. $Cu(NO_3)_2$ in water)
    - Mixed together (paste)
    - Capillary elevation (**fast**) brings Cu^{2+} solution directly into the pores (concentration gradients might occur – pore size!)
    - Drying, calcination (= formation of Cu_2O NPs on SiO_2), (reduction of Cu_2O to Cu NPs)
    - Solubility limits!

Preparation of supported catalysts

- Weak interaction = Impregnation methods
  - – Dry impregnation (Incipient wetness impregnation)
    - Big issue: Gas trapped inside the pores



- Laplace law : $\boxed{\Delta P = P - P' = \frac{2\gamma}{r}}$
- $\underline{d = 50\ \text{nm}}$, $\gamma = 7.10^{-2}\ \text{N.m}^{-1} \longrightarrow P = P' + 5.6\ 10^6\ \text{Pa}$

$\boxed{P = 57.10^5\ \text{Pa (57 atm.)}}$

Pore collapse
Mechanical degradation
Attrition
…

Preparation of supported catalysts

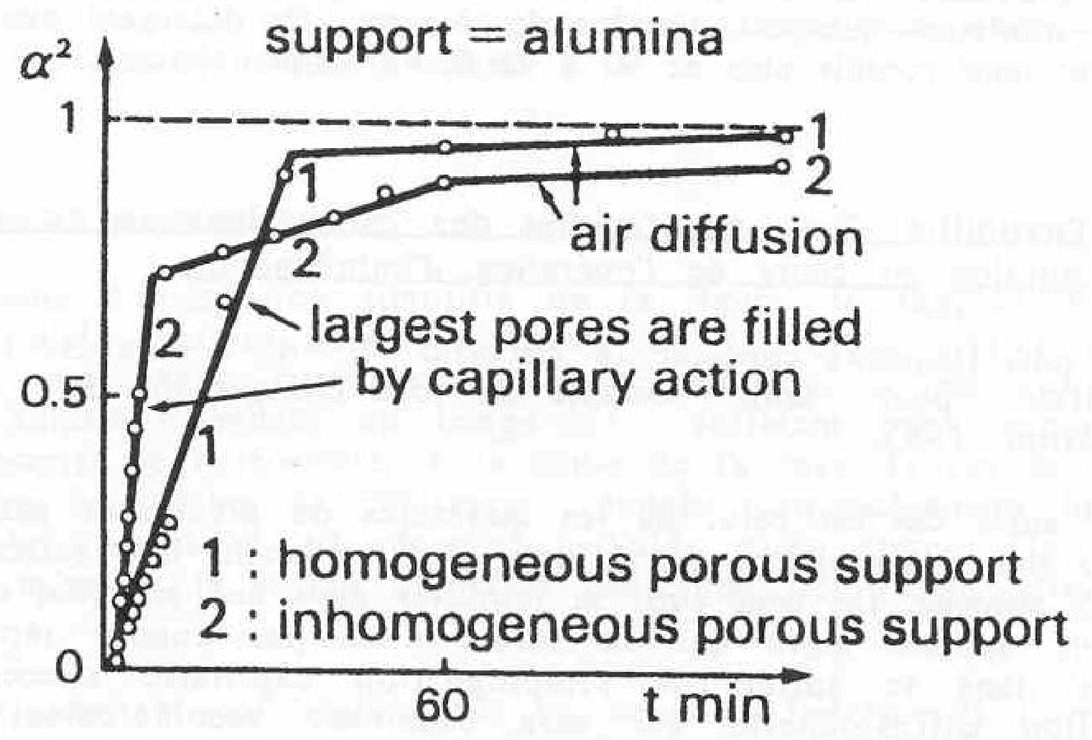
- Weak interaction = Impregnation methods
  - Dry impregnation (Incipient wetness impregnation)
    - Big issue: Gas trapped inside the pores

Possible solutions:

- No gas (impregnation under **vacuum**)
- Lower surface tension (addition of a **surfactant**)
- **Wait** until gas dissappears and impregnation is completed (either gas dissolves in solution or bubbles move out from the pores)

Preparation of supported catalysts

- Weak interaction = Impregnation methods
  - – Dry impregnation (Incipient wetness impregnation)
    - Big issue: Gas trapped inside the pores



Preparation of supported catalysts

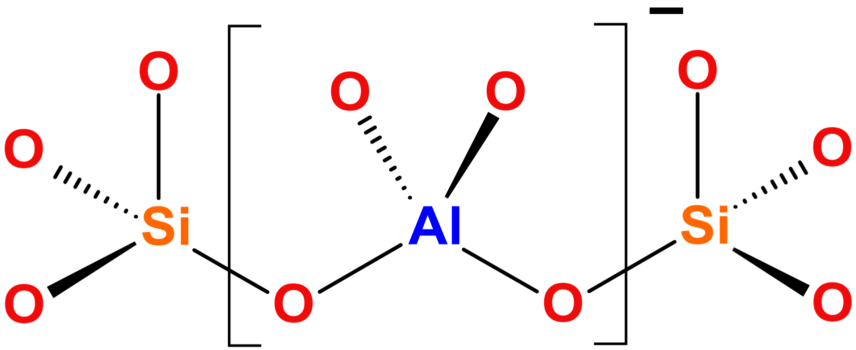
- Three types of interaction between support and active phase
  - Weak
  - **Electrostatic**
  - Covalent

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Classic ion exchangers: clays, layered hydroxides, **zeolites**
  - Oxides with the help of pH

Preparation of supported catalysts

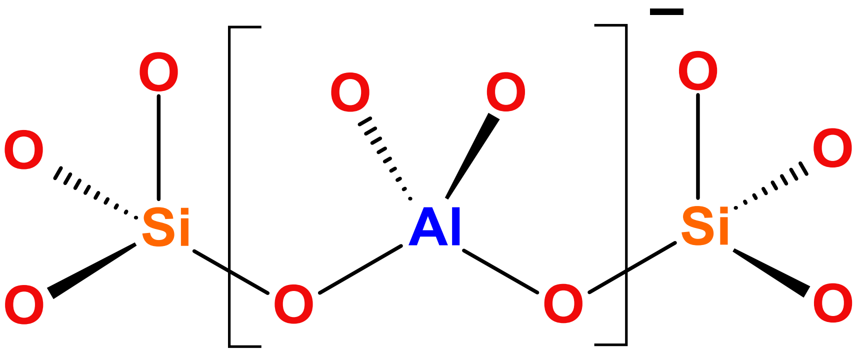
- Electrostatic interaction = **Ion exchange**
  - Zeolites, how does it work?



  - Cation compensating the negative charge?
  - Na^+ from the synthetic step

Preparation of supported catalysts

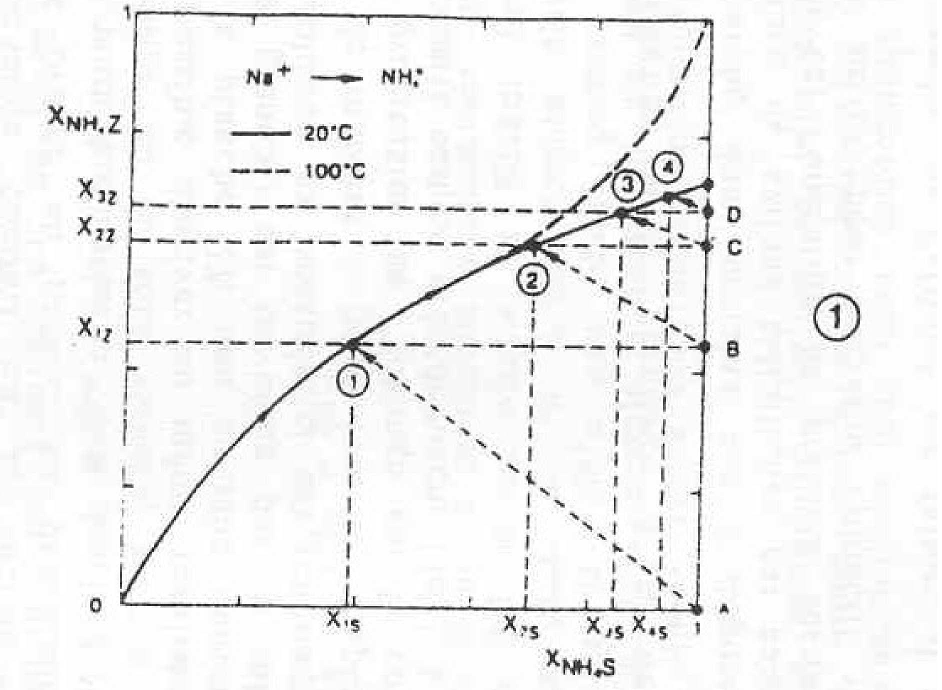
- Electrostatic interaction = **Ion exchange**
  - – Zeolites, how does it work?
  - – $Na^+ \rightarrow H^+$ directly?
  - – $Na^+ \rightarrow ??? \rightarrow H^+$



Preparation of supported catalysts

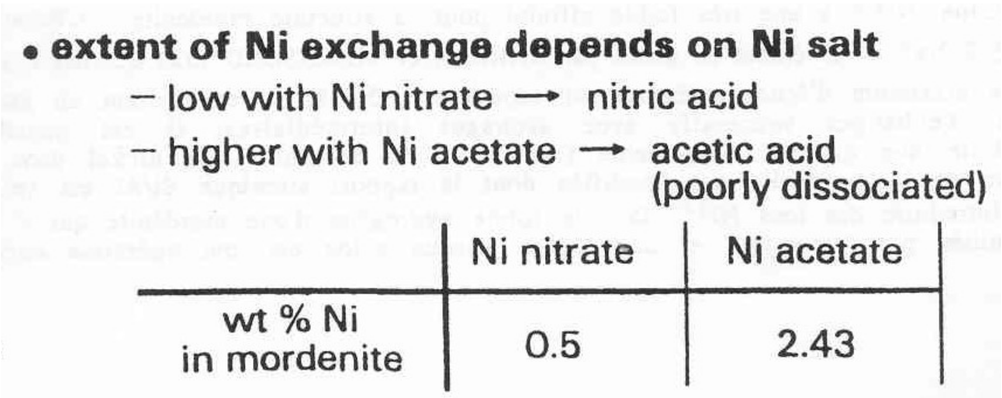
- Electrostatic interaction = **Ion exchange**
  - Zeolites, how does it work?
  - $Na^+ \rightarrow NH_4^+ \overset{\Delta T}{\rightarrow} H^+$
  - Zeolite NaY
  - Up to 73 % of Na^+ can be exchanged at R.T.
  - 4 consecutive steps
    or
    continuous ion exch.

NaY dans solution de NO_3NH_4 (M<1 mole/l)



Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Enhancement…trap for leaving ion (shifting equilibrium)!
  - e.g. Exchange of Ni^{2+} for H^+ in zeolite mordenite
  - $Ni(NO_3)_2$ vs. $Ni(OAc)_2$

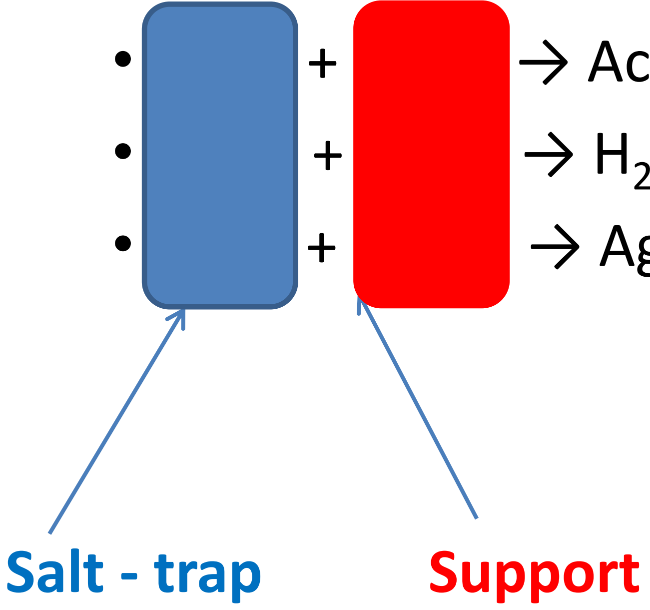


- **extent of Ni exchange depends on Ni salt**
  - low with Ni nitrate → nitric acid
  - higher with Ni acetate → acetic acid (poorly dissociated)

	Ni nitrate	Ni acetate
wt % Ni in mordenite	0.5	2.43

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Trap



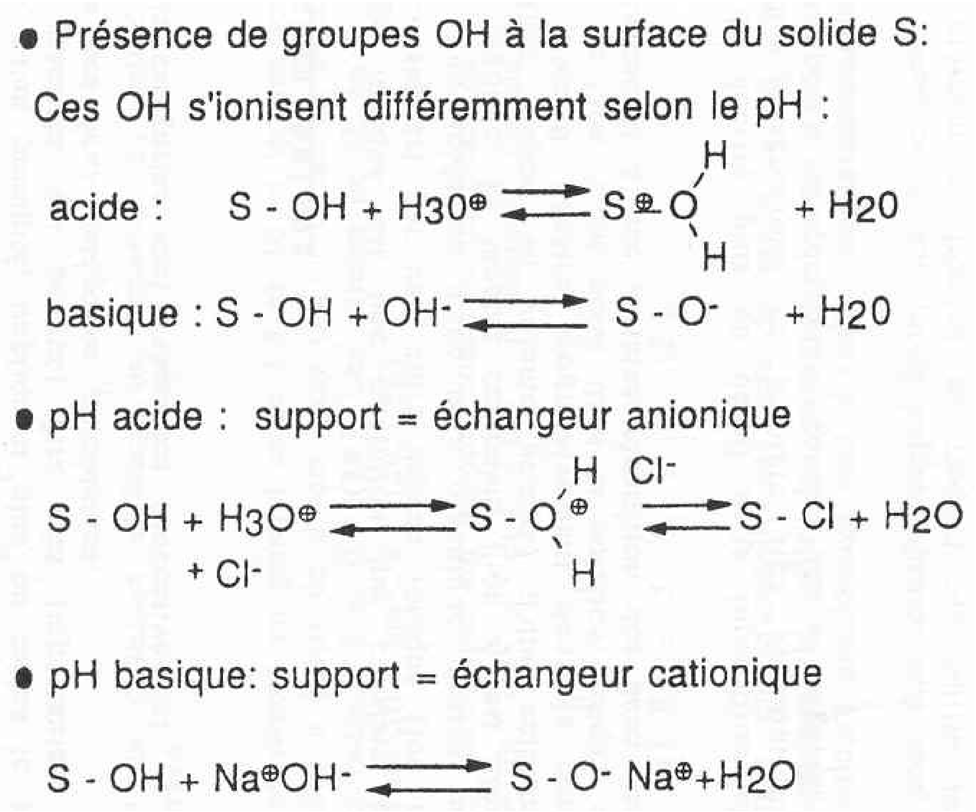
    - + → AcOH (rarely dissociated)
    - + → H_2O (rarely dissociated)
    - + → AgSCN (rarely dissociated)

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Classic ion exchangers: clays, layered hydroxides, zeolites
  - **Oxides with the help of pH**

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - **Oxides with the help of pH**



- Présence de groupes OH à la surface du solide S:

Ces OH s'ionisent différemment selon le pH :

acide : $\mathrm{S - OH + H_3O^{\oplus} \rightleftharpoons S^{\oplus}\!-\!\overset{H}{\underset{H}{O}} \quad + H_2O}$

basique : $\mathrm{S - OH + OH^- \rightleftharpoons S - O^- \quad + H_2O}$

- pH acide : support = échangeur anionique

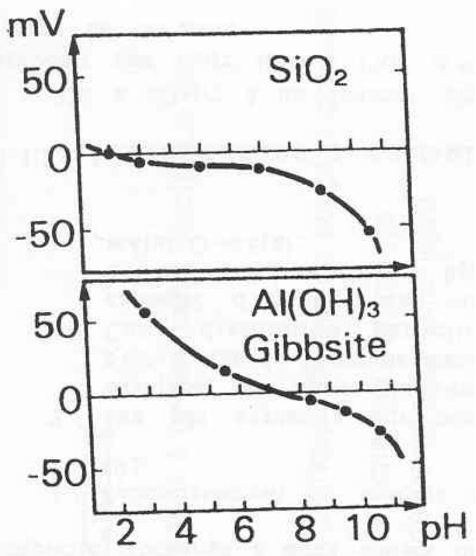
$$\mathrm{S - OH + \underset{+\,Cl^-}{H_3O^{\oplus}} \rightleftharpoons S - \overset{H}{\underset{H}{O}}{}^{\oplus}\ Cl^- \rightleftharpoons S - Cl + H_2O}$$

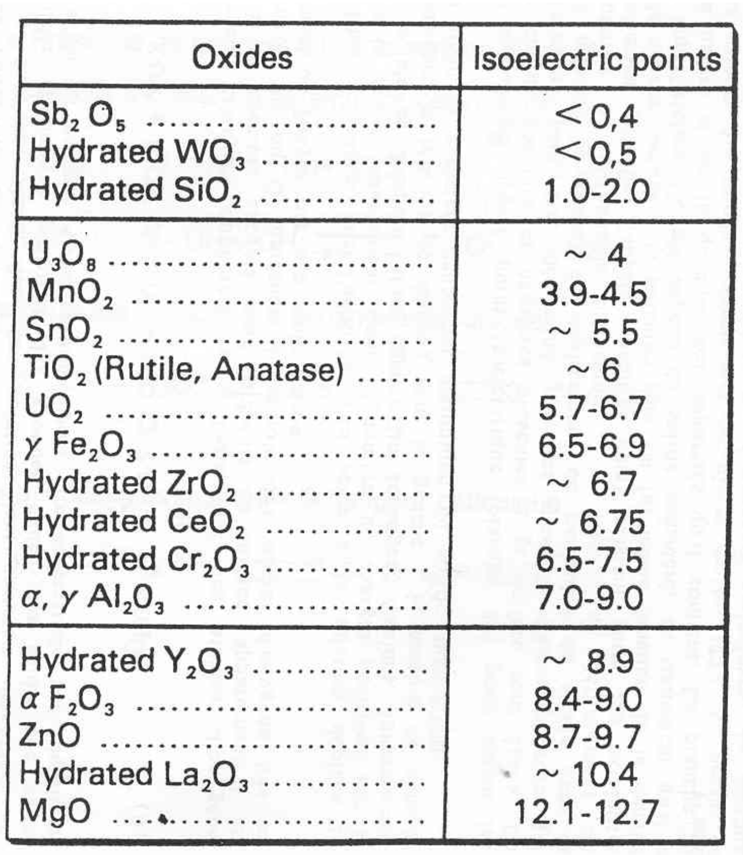
- pH basique: support = échangeur cationique

$$\mathrm{S - OH + Na^{\oplus}OH^- \rightleftharpoons S - O^- \, Na^{\oplus} + H_2O}$$

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Isoelectric point

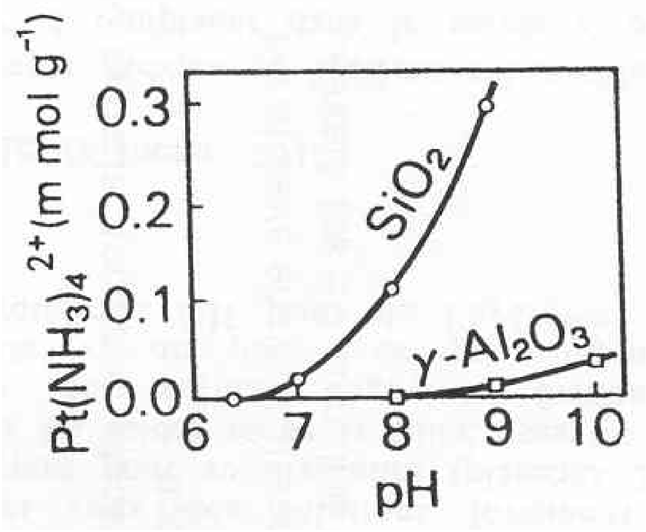




Oxides	Isoelectric points
Sb_2O_5	< 0,4
Hydrated WO_3	< 0,5
Hydrated SiO_2	1.0-2.0
U_3O_8	~ 4
MnO_2	3.9-4.5
SnO_2	~ 5.5
TiO_2 (Rutile, Anatase)	~ 6
UO_2	5.7-6.7
γ Fe_2O_3	6.5-6.9
Hydrated ZrO_2	~ 6.7
Hydrated CeO_2	~ 6.75
Hydrated Cr_2O_3	6.5-7.5
α, γ Al_2O_3	7.0-9.0
Hydrated Y_2O_3	~ 8.9
α F_2O_3	8.4-9.0
ZnO	8.7-9.7
Hydrated La_2O_3	~ 10.4
MgO	12.1-12.7

Preparation of supported catalysts

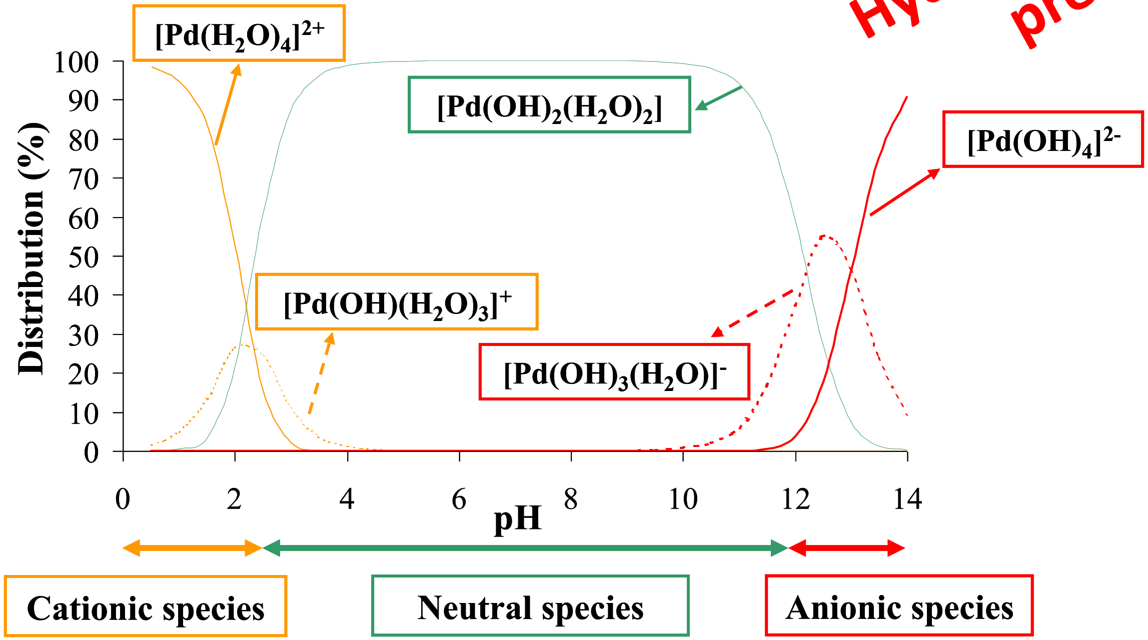
- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Exchange capacity: the farther you are from isoelectric point, the higher the exchange capacity.



Preparation of supported catalysts

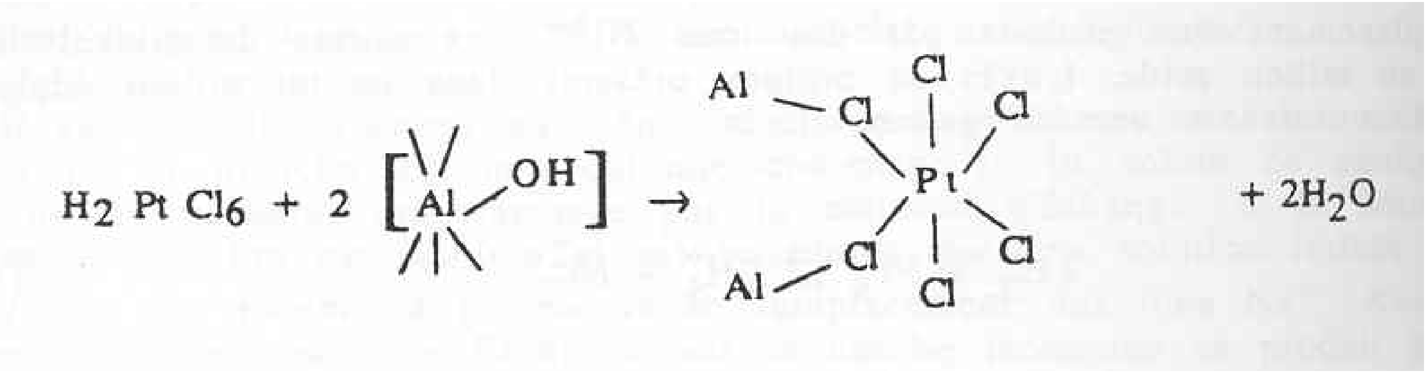
- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Stability of support at different pH!
    - Precursor stability at different pH!

Hydrolysis, condensation, precipitation…!



Preparation of supported catalysts

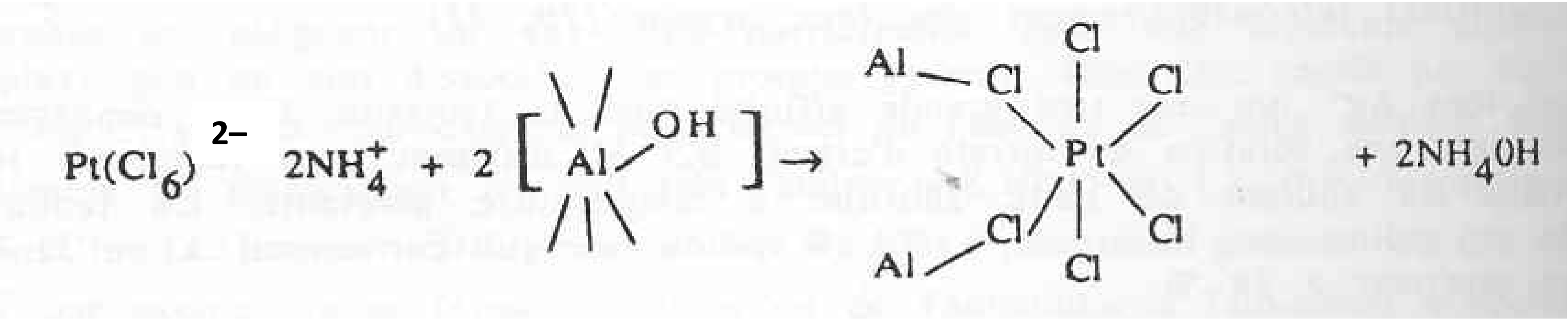
- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Competitive ion exchange



- Example: very high affinity between Al_2O_3 and Pt
- Result: heterogeneous distribution of Pt (only outer surface)

Preparation of supported catalysts

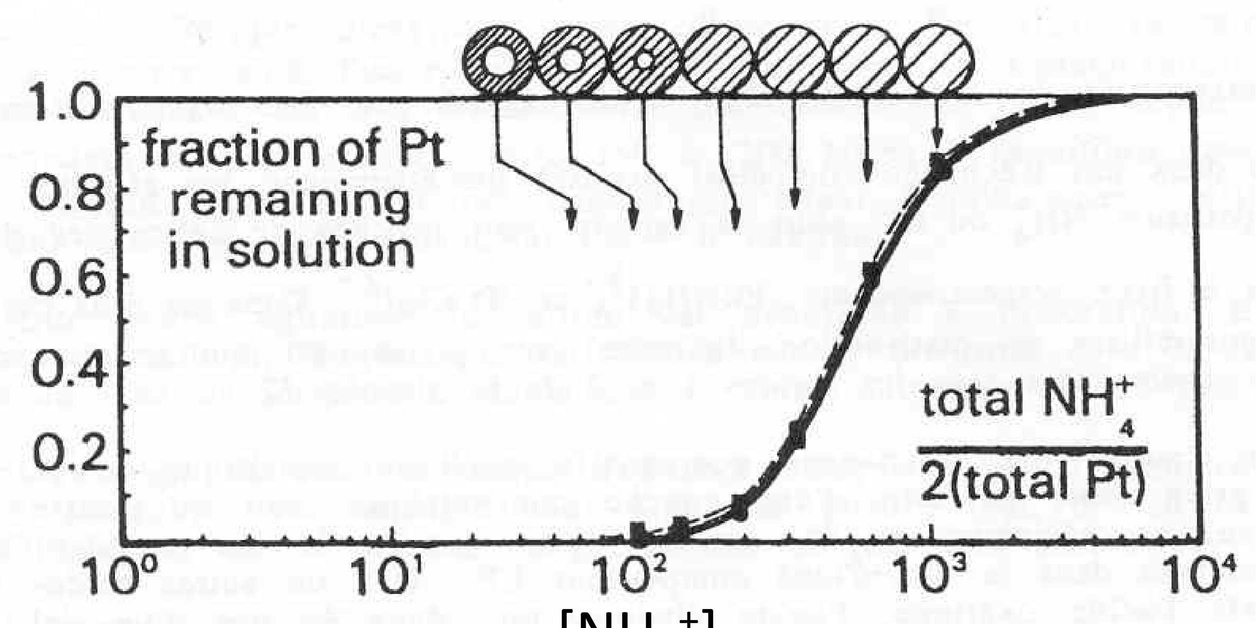
- Electrostatic interaction = **Ion exchange**
  - – Oxides with the help of pH
    - Competitive ion exchange



- NH_4OH dissociates readily, NH_4^+ competes with Pt for sites (= inverse to trap)
- Result: homogeneous distribution of Pt through the support

Preparation of supported catalysts

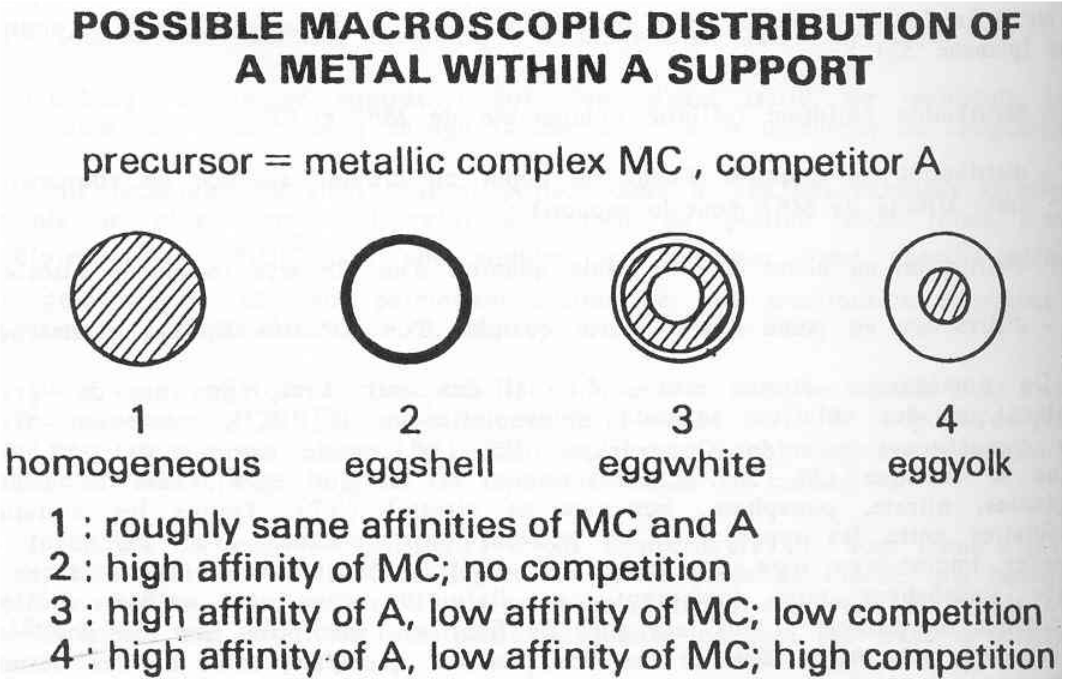
- Electrostatic interaction = **Ion exchange**
  - – Oxides with the help of pH
    - Competitive ion exchange



$[NH_4^+]$

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Competitive ion exchange



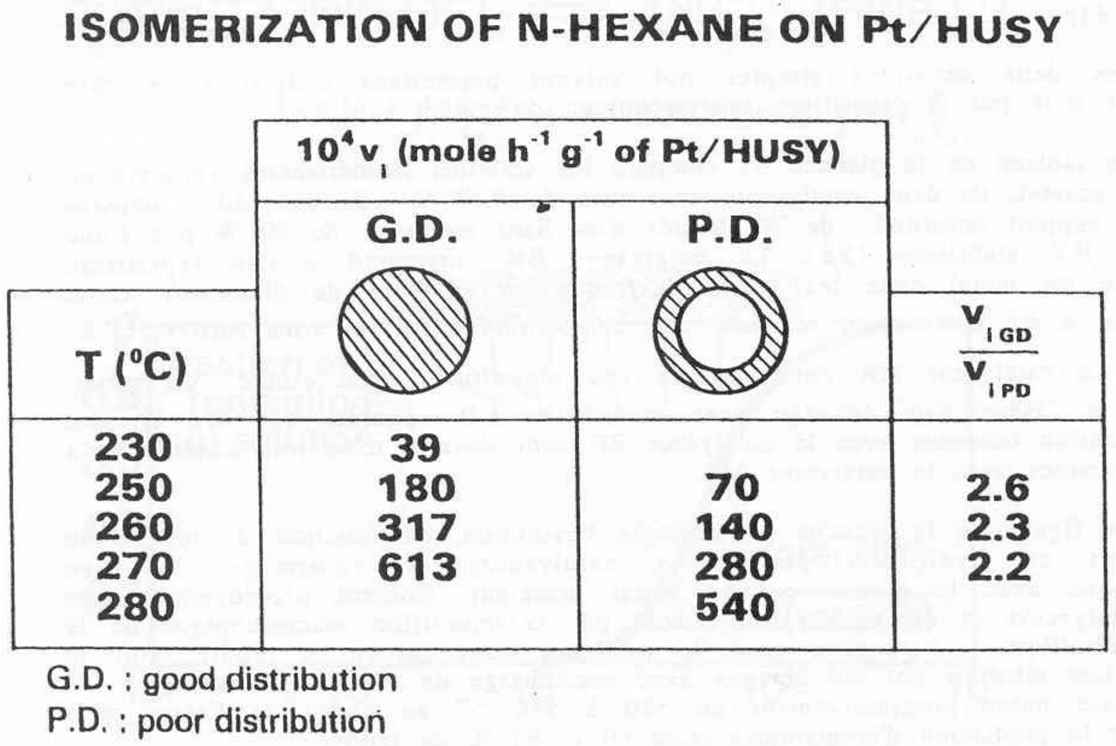
POSSIBLE MACROSCOPIC DISTRIBUTION OF A METAL WITHIN A SUPPORT

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 competition
4 : high affinity of A, low affinity of MC; high competition

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - – Oxides with the help of pH
    - Competitive ion exchange



ISOMERIZATION OF N-HEXANE ON Pt/HUSY

T (°C)	$10^4 v_i$ (mole h^{-1} g^{-1} of Pt/HUSY) G.D.	 P.D.	$\frac{V_{iGD}}{V_{iPD}}$
230	39		
250	180	70	2.6
260	317	140	2.3
270	613	280	2.2
280		540	

G.D. : good distribution
P.D. : poor distribution

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Competitive ion exchange: Note
    - We say homogeneous Pt distribution…
    - But how homogeneous???
    - Latest research from de Jong group (University Utrecht, HR-TEM, perfect control of Pt deposition on atomic scale) shows that uniform Pt homogeneity is not ideal for hexane isomerization!

Preparation of supported catalysts

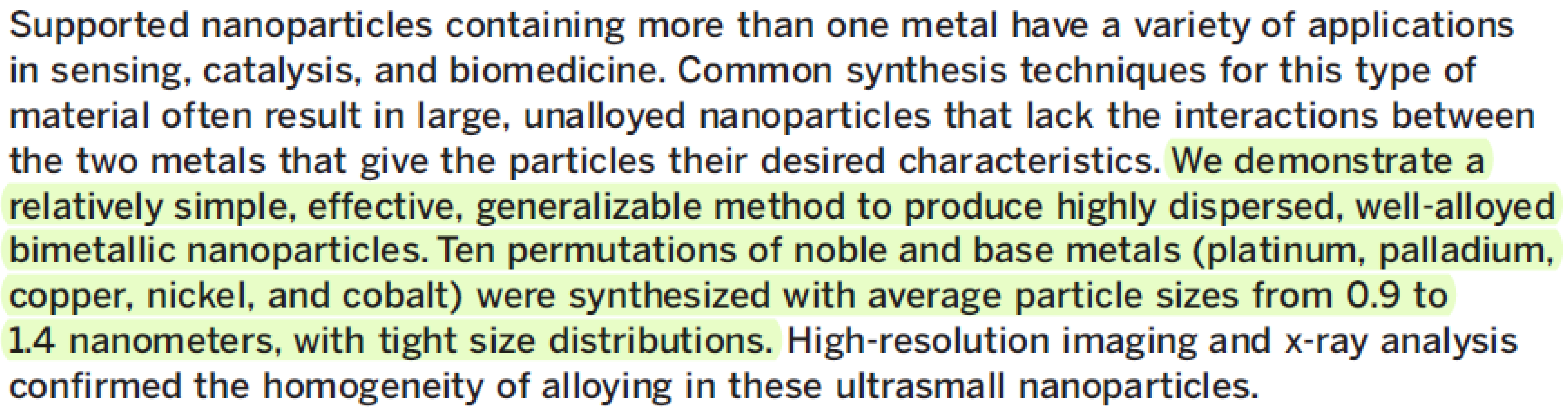
- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Detailed knowledge of isoelectric point, precursor behavior, control over pH:

Synthesis of ultrasmall, homogeneously alloyed, bimetallic nanoparticles on silica supports

A. Wong,[1] Q. Liu,[1] S. Griffin,[1] A. Nicholls,[2] J. R. Regalbuto[1]*

Preparation of supported catalysts

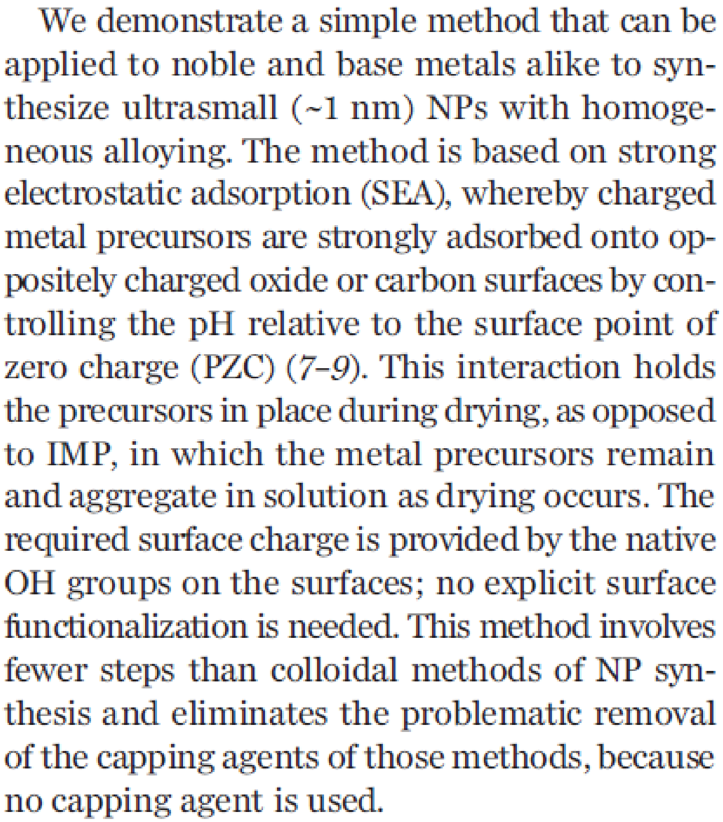
- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH
    - Detailed knowledge of isoelectric point, precursor behavior, control over pH:



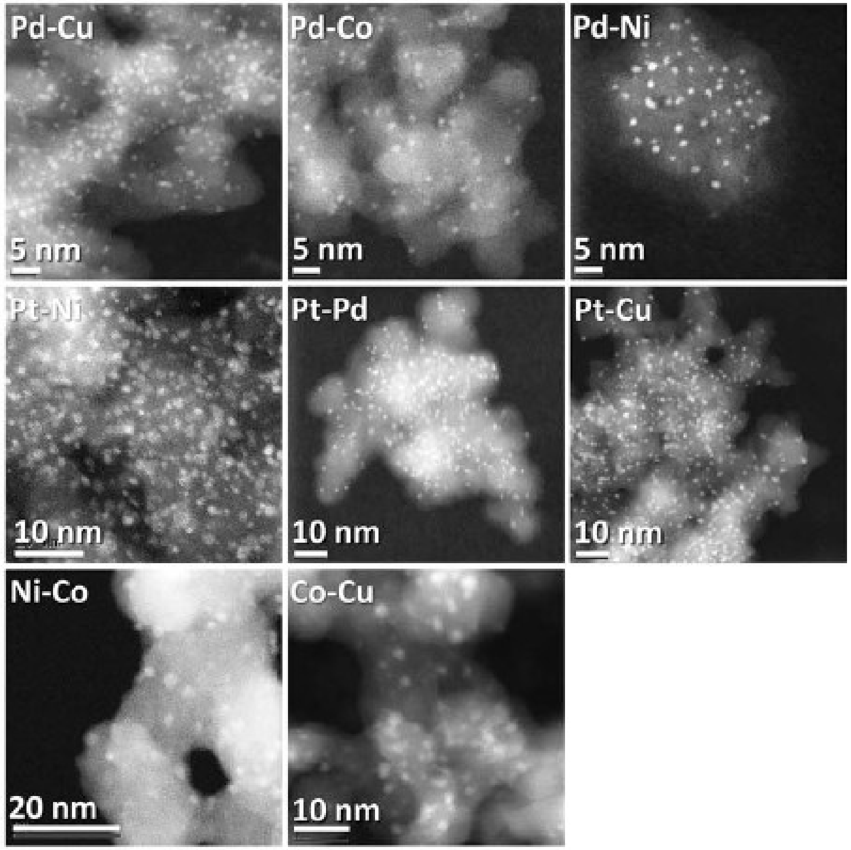
Supported nanoparticles containing more than one metal have a variety of applications in sensing, catalysis, and biomedicine. Common synthesis techniques for this type of material often result in large, unalloyed nanoparticles that lack the interactions between the two metals that give the particles their desired characteristics. We demonstrate a relatively simple, effective, generalizable method to produce highly dispersed, well-alloyed bimetallic nanoparticles. Ten permutations of noble and base metals (platinum, palladium, copper, nickel, and cobalt) were synthesized with average particle sizes from 0.9 to 1.4 nanometers, with tight size distributions. High-resolution imaging and x-ray analysis confirmed the homogeneity of alloying in these ultrasmall nanoparticles.

Preparation of supported catalysts

- Electrostatic interaction = **Ion exchange**
  - Oxides with the help of pH



We demonstrate a simple method that can be applied to noble and base metals alike to synthesize ultrasmall (~1 nm) NPs with homogeneous alloying. The method is based on strong electrostatic adsorption (SEA), whereby charged metal precursors are strongly adsorbed onto oppositely charged oxide or carbon surfaces by controlling the pH relative to the surface point of zero charge (PZC) (*7–9*). This interaction holds the precursors in place during drying, as opposed to IMP, in which the metal precursors remain and aggregate in solution as drying occurs. The required surface charge is provided by the native OH groups on the surfaces; no explicit surface functionalization is needed. This method involves fewer steps than colloidal methods of NP synthesis and eliminates the problematic removal of the capping agents of those methods, because no capping agent is used.

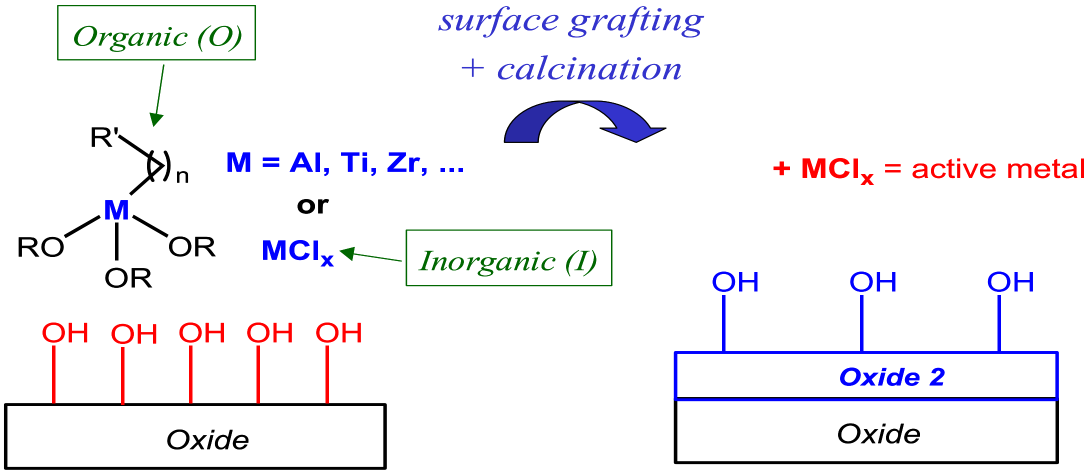


Preparation of supported catalysts

- Three types of interaction between support and active phase
  - Weak
  - Electrostatic
  - **Covalent**

Preparation of supported catalysts

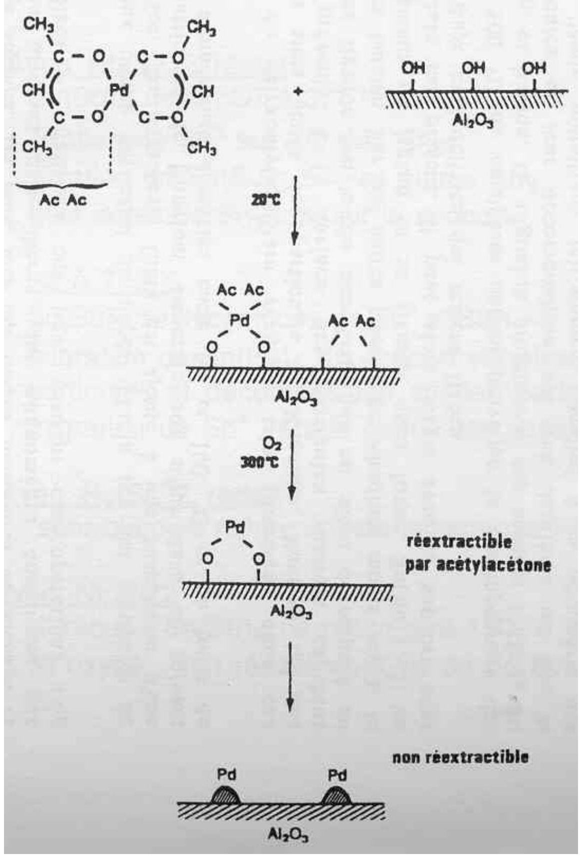
- Covalent bonds = **grafting**
  - Formation of metal oxide on top of catalyst support



  - Is calcination necessary? More in lecture on single site catalysts…

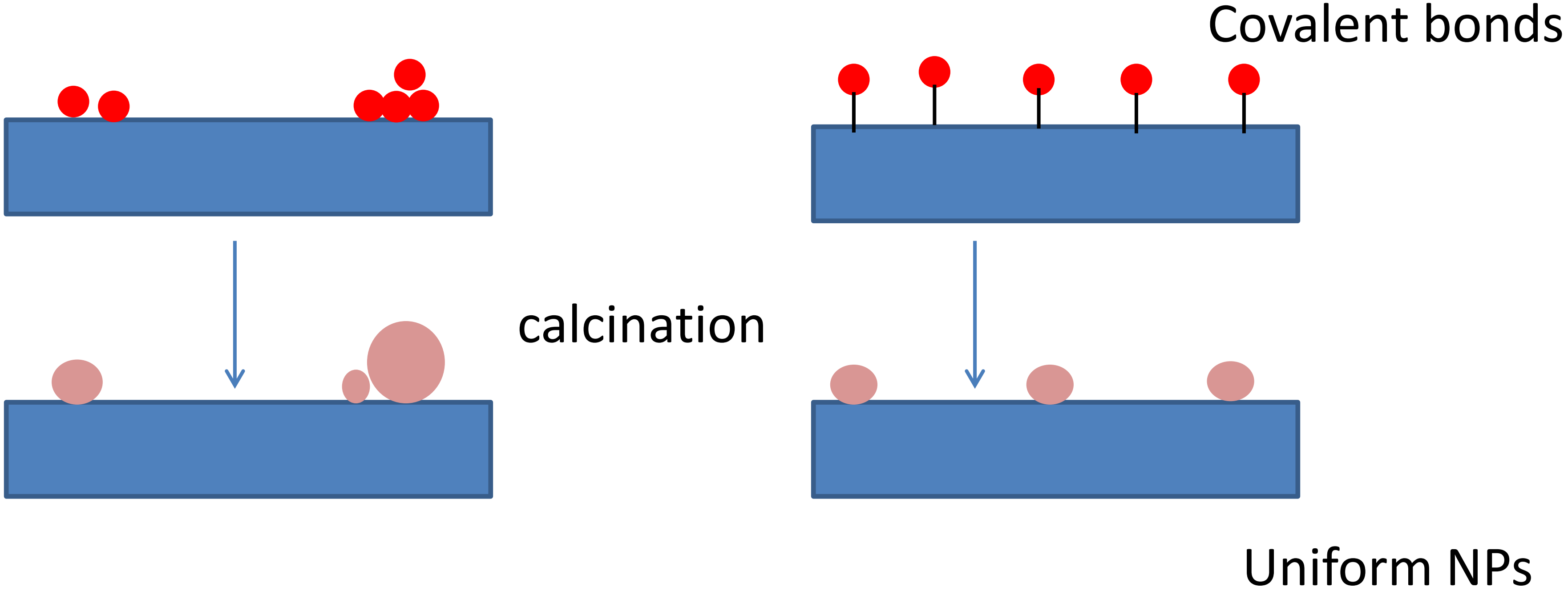
Preparation of supported catalysts

- Covalent bonds = **grafting**
  - Formation of metal NPs on top of catalyst support



Preparation of supported catalysts

- Covalent bonds = **grafting**
  - NPs by impregnation vs. grafting



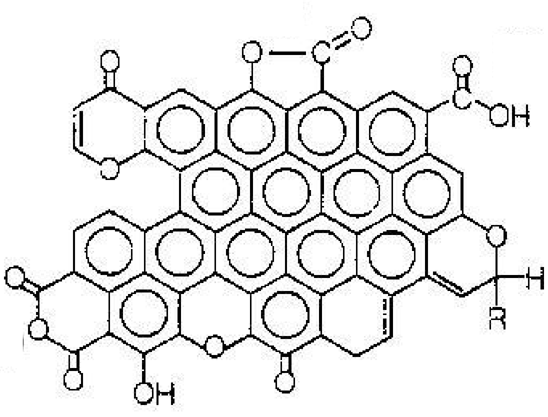
Covalent bonds

calcination

Uniform NPs

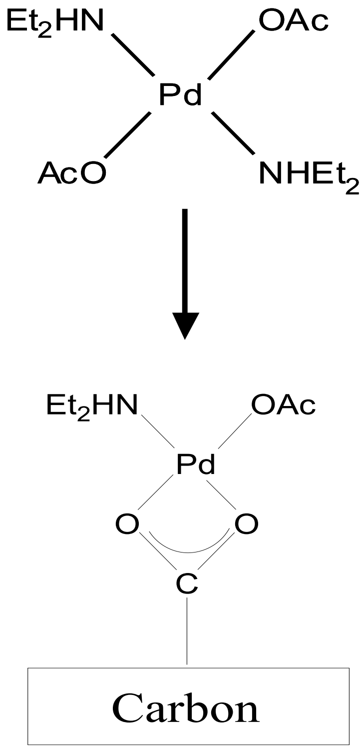
Preparation of supported catalysts

- Covalent bonds = **grafting**
  - Formation of metal NPs on top of graphene oxide



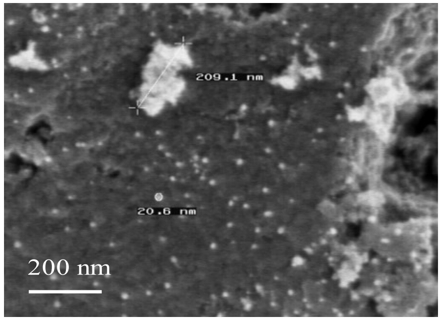
Content of COOH groups increased by oxidation (HNO_3, H_2O_2,O_3,…)

complex [$Pd(OAc)_2(Et_2NH)_2$]

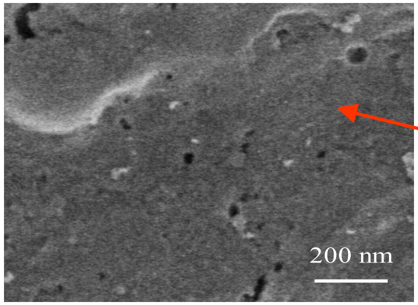


Preparation of supported catalysts

- Covalent bonds = **grafting**
  - – Formation of metal NPs on top of graphene oxide
  - – Last step: Pd reduction



Without functionalization by oxidation (thus almost no grafting)



With functionalization by oxidation (thus grafted Pd complexes)

no visible metal aggregates!

Preparation of supported catalysts

- Covalent bonds = **Deposition/precipitation**
  - Starts as a dry impregnation
  - Metal salt is then selectively precipitated at the catalyst surface
  - Precipitation mainly by pH change – hydrolysis/condensation