DICP Course - Dalian, 2012
Preparation of solid catalysts
Part 3

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Charles Kappenstein, Professor Emeritus, University of Poitiers, France

DALIAN INSTITUTE OF CHEMICAL PHYSICS, CHINESE ACADEMY OF SCIENCES

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Faculté des Sciences
Fondamentales et Appliquées
UFR SFA
Université de Poitiers

Institut de Chimie
des Milieux et Matériaux de Poitiers
IC2Mp

Outline

Introduction and general aspects

Interfacial chemistry – Electrostatic adsorption

Impregnation, drying, calcination and/or reduction

Sol-gel chemistry processing

Deposition – Precipitation – Coprecipitation

Shaping of solid catalysts – Monolith-based catalysts

Outline

<u>Zeolite-based catalysts</u>

<u>Characterization – High throughput experimentation</u>

<u>Case studies:</u>

- **Noble metal catalysts**

- **Methanol catalysts**

- **Hydrotreating catalysts**

- **……**

Outline

Impregnation, drying, calcination and/or reduction

1) Impregnation
  metal supported catalyst
  physical models
  Darcy's law, viscosity

2) Drying
  Different distributions of active phase precursor
  Precursor-support interactions
  Support dissolution and formation of mixed phase

3) Calcination
  Role of calcination atmosphere

4) Reduction
  Temperature profile
  Role of temperature

➜ **The solid support is in contact with a solution containing the active phase precursor**

Support: high surface area oxide (100 - 400 $m^2.g^{-1}$), high internal porosity (1 mL g^{-1}).

Precursor: soluble in the solvent and bonded on the surface after the impregnation.

Active phase: obtained after transformation of the precursor (activation of the catalyst).

Ex.: **Ir/Al$_2$0$_3$ catalyst for N$_2$H$_4$ decomposition, 30 to 40 wt.-% Ir**

Support: gamma alumina, specific surface area: 100-200 $m^2.g^{-1}$.

Precursor: hexachloroiridic acid H_2IrCl_6 in aqueous solution.

Impregnation procedure: wet impregnation or dry impregnation?

The procedure has to be repeated to reach the expected loading content.

American catalyst Shell-405 (now S-405): wet impregnation, procedure repeated 10 times

French catalyst CNESRO: dry impregnation, procedure repeated 3 times

Drying: fixation of the acid precursor on the basic hydroxyl groups present on the surface.

Activation, reduction in H_2, at 200 and 400 °C ➜formation of iridium crystallites

The procedure is repeated after the drying step or after the reduction step

2 phenomena

- diffusion of the solute into the pores (Fick's law)
- adsorption of solute onto the support (adsorption capacity, equilibrium constant)
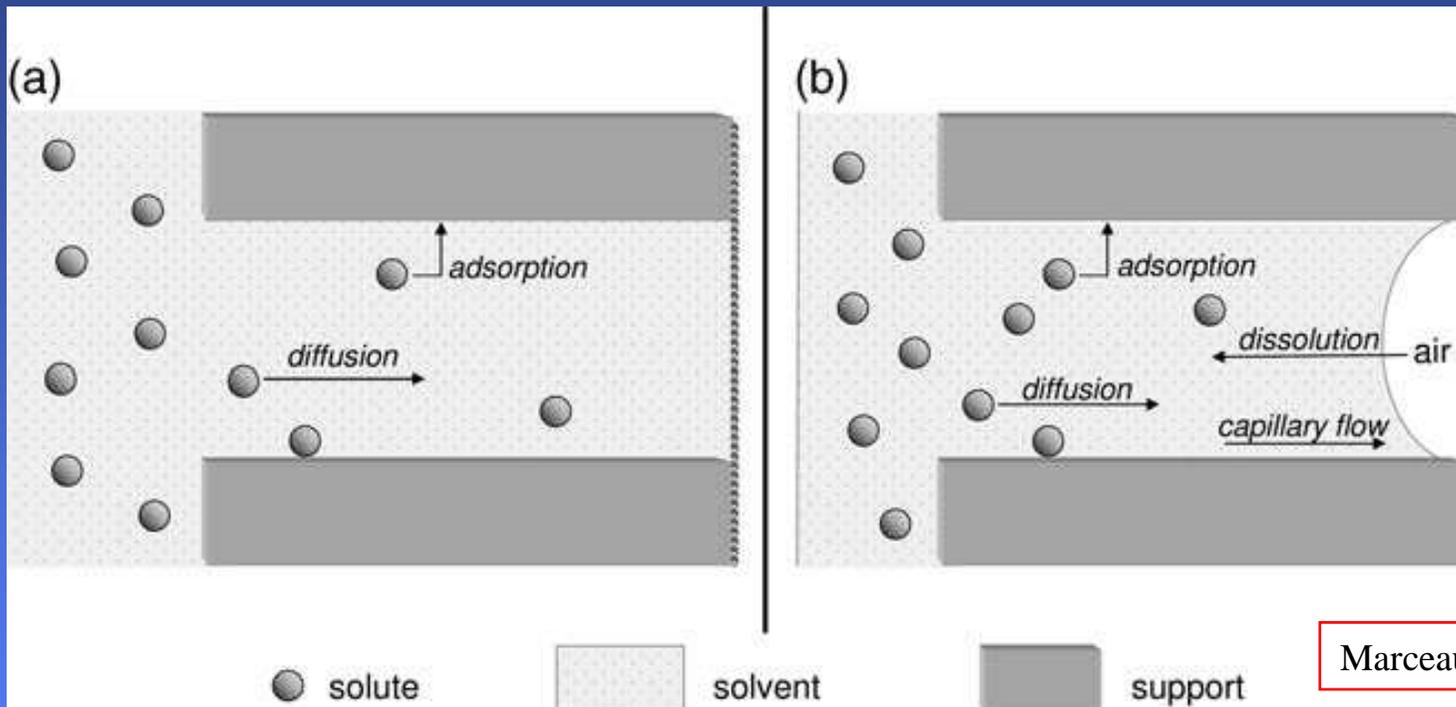
Marceau, Carrier, Che, in de Jong, 2009)

Phenomena of transport involved in (a) wet impregnation, low concentration and (b) dry impregnation, high precursor concentration
➔ **The adsorption is ruled by kinetics or by thermodynamics**
➔ **The distribution of the precursor along the pellet depends on balance between diffusion and adsorption**

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Precursor concentration ↘   ➔   diffusion ↘

Wet impregnation

Characteristic time τ to attain equilibrium in a pellet of radius R depends on R^2

Ex.: pellet size 2 mm ➔ 1 mm τ is divided by 4
     pellet size 2 mm ➔ 0.5 mm τ is divided by 16

➔ The wet impregnation can take several hours

Dry impregnation

➔ Pressure driven capillary flow inside the empty pores
➔ Depends on Darcy's law and solution viscosity

Darcy'law

Flow of a fluid in a porous medium

(analogous to Ohm's law for electrical networks, Fick's law for diffusion or Fourier's law for heat conduction
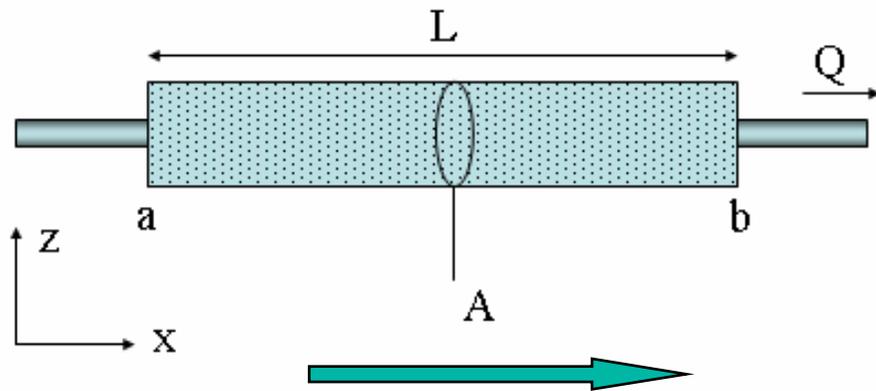
$$Q = \frac{-kA}{\mu} \frac{(P_b - P_a)}{L}$$

Q: flow (m^3 s^{-1})

k: permeability (ability of a porous medium to allow fluid to pass through) (m^2)

A: cross sectional area of the flow (m^2)

μ: viscosity (Pa s)

P_b-P_a: pressure drop (Pa)

The dynamic viscosity μ (or η) is the resistance of a fluid to flow

Ex.: water < oil < honey

Unit: Pa s

P (Poise), from Poiseuille, a French physicist);

cP (centipoise)   1 cP = 1 mPa s

Dynamic viscosity of water (20 °C): 0.001002 Pa s = 1.002 cP

Kinematic viscosity $\nu = \mu/\rho$ (m^2 s^{-1})

➔ the viscosity is an important parameter to control the impregnation:

Low viscosity ➔ uniform impregnation

High viscosity ➔ nonuniform impregnation
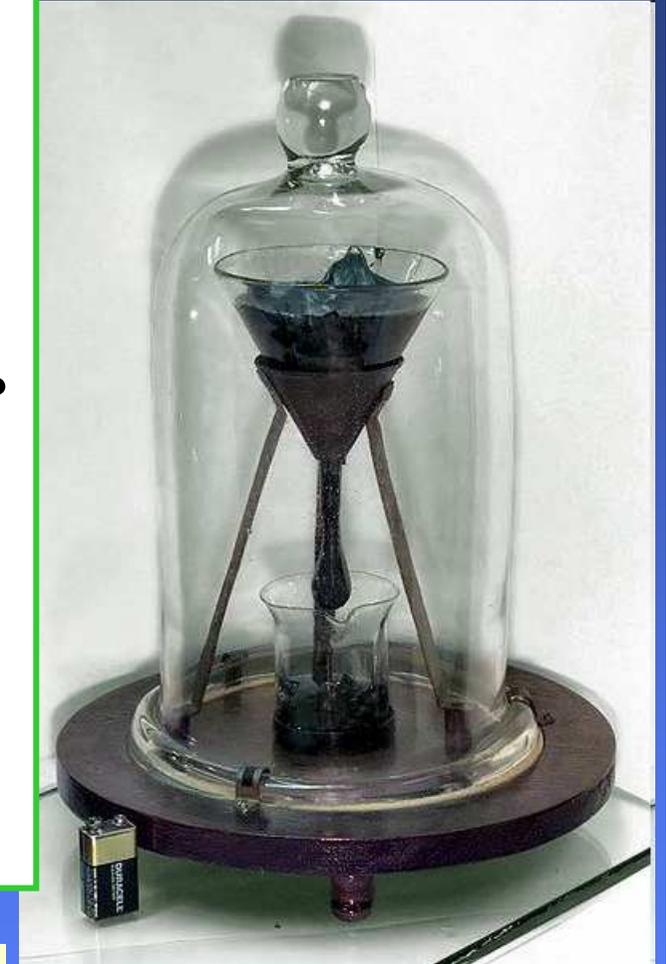
Bitumen (Pitch) drop experiment viscosity approximately 230 billion (2.3×10^{11}) times that of water!!

Different distributions of active phase precursor

Influence of the conditions of impregnation and drying

Egg-shell
Strong adsorption of the precursor during impregnation
Impregnation with a very viscous solution
Slow drying regime, in the case of solutions of low concentration and viscosity, or weakly adsorbing precursors

Uniform
Precursors and competitors equally interacting with the surface
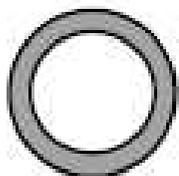Weakly interacting precursor + drying at room temperature
Drying a concentrated, viscous solution (e.g., addition of hydroxyethyl cellulose)

Egg-yolk
Competitor interacting more strongly with the surface than the precursor
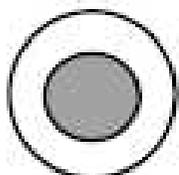Fast drying regime with predominant back-diffusion

Marceau, Carrier, Che, in de Jong, 2009)

pH adjusters: HNO_3, $R\text{-}CO_2H$, NH_3

Low concentration
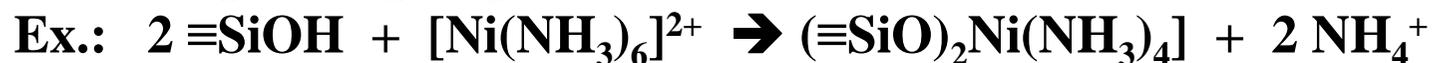The precursor-support interaction is the driving force for adsorption

High concentration
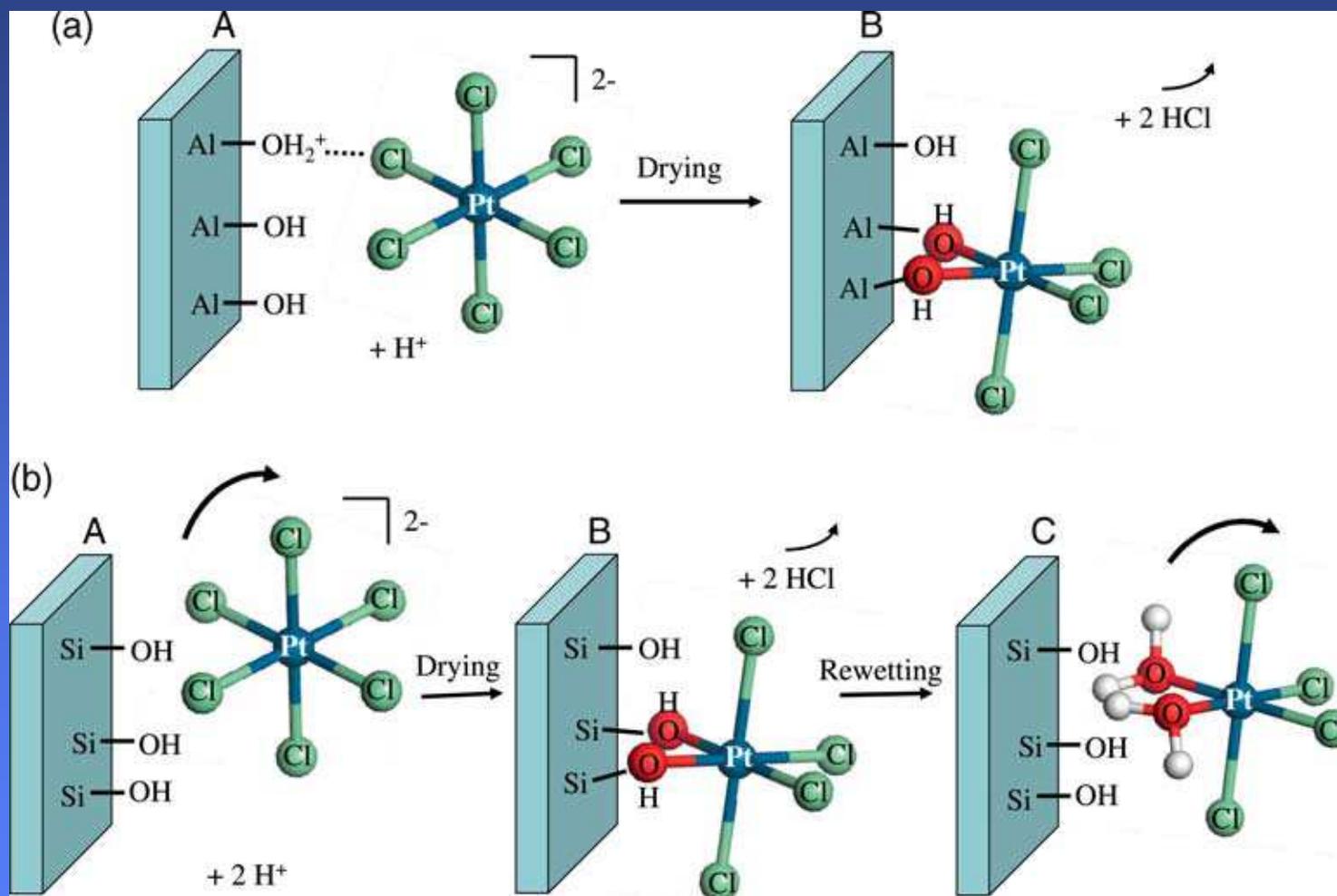The species interacting with surface act as seeds for crystallization upon drying

Two main types of interaction
- Electrostatic interaction

- Grafting through ligand substitution
Ex.: $2 \equiv SiOH + [Ni(NH_3)_6]^{2+} \rightarrow (\equiv SiO)_2Ni(NH_3)_4] + 2 NH_4^+$

Another exemple: $[PtCl_6]^{2-}$

Support dissolution and formation of mixed phase

Influence of the conditions of impregnation and drying on the formation of extended mixed phases

Support	Composition of the impregnation solution	Conditions of impregnation	Conditions of drying	Mixed phase
SiO_2	Ni(II) nitrate	IW, $t = 2$ h	$T = 90°C$, $t \geq 72$ h	Ni(II) phyllosilicate
	Ni(II) nitrate + NH_4NO_3 + NH_3	IW, $pH \geq 6.9$	$T = 80–120°C$, $t = 15$ h	Ni(II) phyllosilicate
	Mg(II) nitrate + NH_4NO_3 + NH_3	ES, $pH > 8$, $t = 15$ h	$T = 120°C$, $t = 15$ h	Mg(II) hydrous silicate

Marceau, Carrier, Che, in de Jong, 2009)

Ex.: MoO_x/Al_2O_3
To reach 10 wt.-% Mo ➔ a precursor solution 1 to 2 mol L^{-1} for dry impregnation
➔ use of a very soluble Mo-precursor: $(NH_4)_6Mo_7O_{24}$
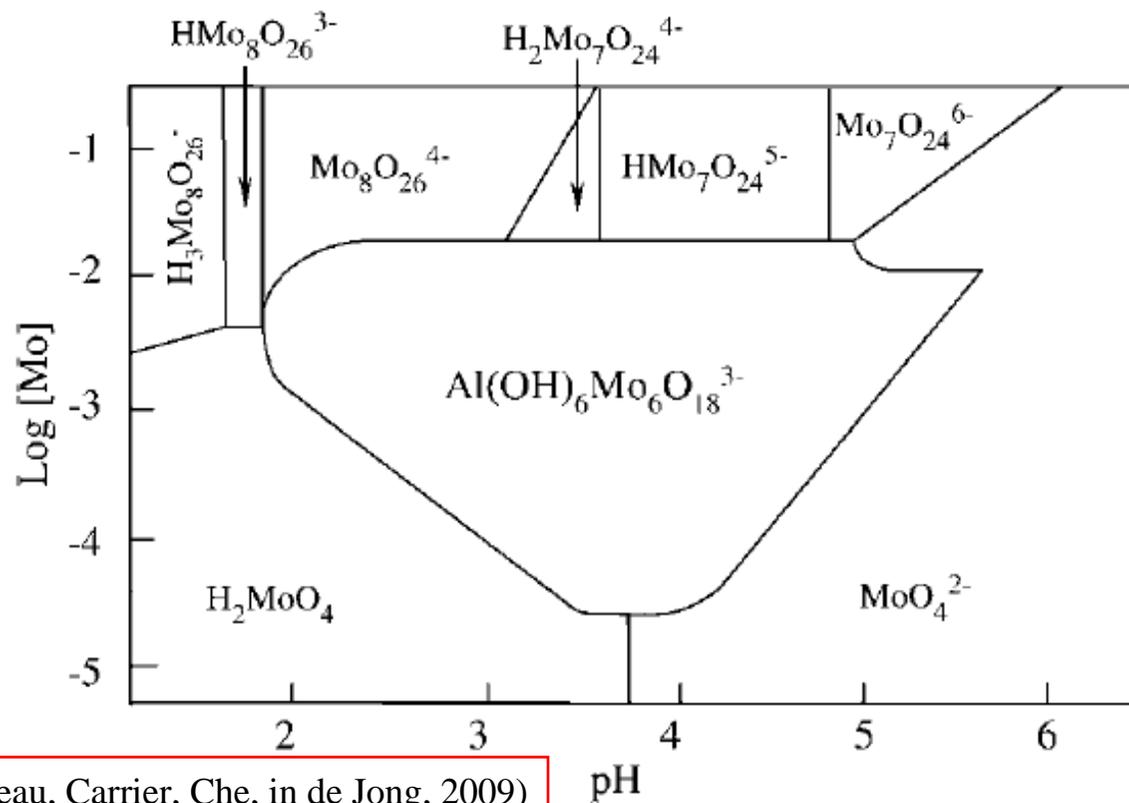
Marceau, Carrier, Che, in de Jong, 2009)

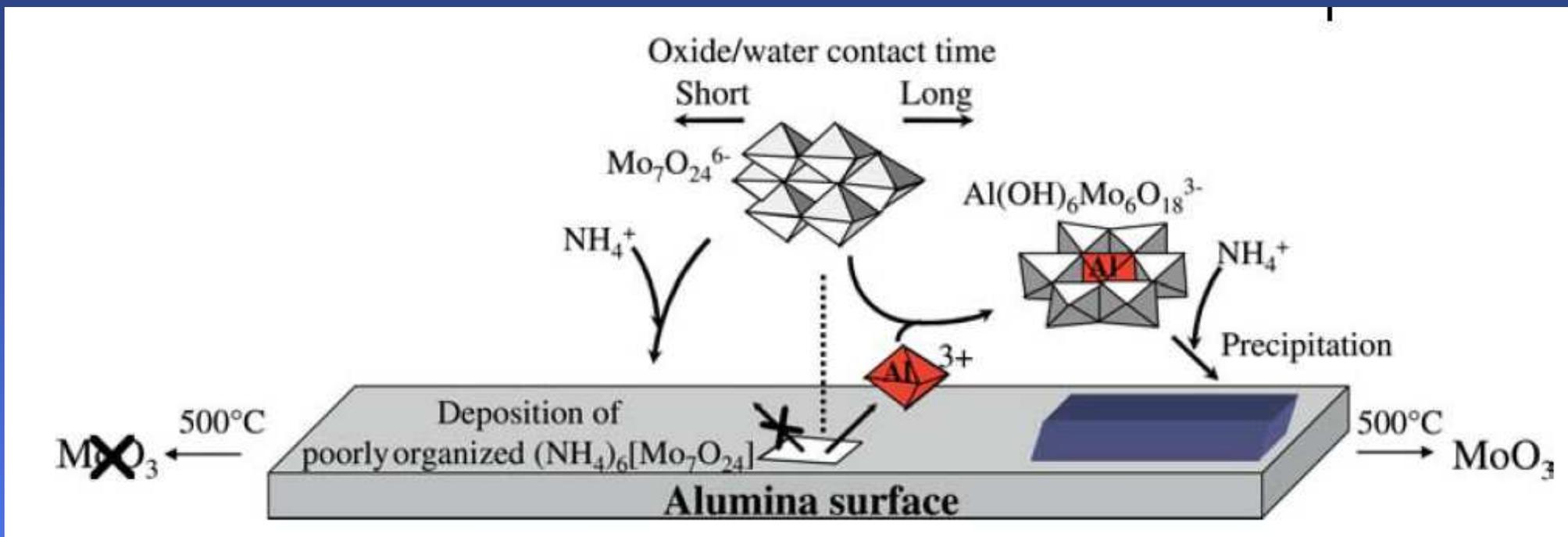**Possible formation of a mixed oxide $[Al(OH)_6Mo_6O_{18}]^{3-}$ in solution and support**

Ex.: MoO$_x$/Al$_2$O$_3$
Influence of contact time

Marceau, Carrier, Che, in de Jong, 2009)

Ex.: NiO/SBA-15   Loading 24 wt.-% NiO

Objective ➜ NiO   4 nm after calcination

SBA-15

Porous volume: 1 mL g^{-1}

Pore diameter: 9 ± 0.5 nm

Dry impregnation, solution of Ni(NO$_3$)$_2$ 4.2 mol L^{-1}

Drying 120 °C

After drying: formation of Ni$_3$(NO$_3$)$_2$(OH)$_4$ in mesopores

Calcination 450 °C

Ni$_3$(NO$_3$)$_2$(OH)$_4$(s) ➜ 3 NiO(s) + 2 NO$_2$(g) + 2 H$_2$O(g) + 1/2 O$_2$(g)

Reduction 450 °C   5 vol.-% H$_2$/He

Air calcined – N_2 physisorption

NiO/SBA-15

SBA-15

Quantity adsorbed (a.u.)

Relative pressure (p/p₀)

N_2
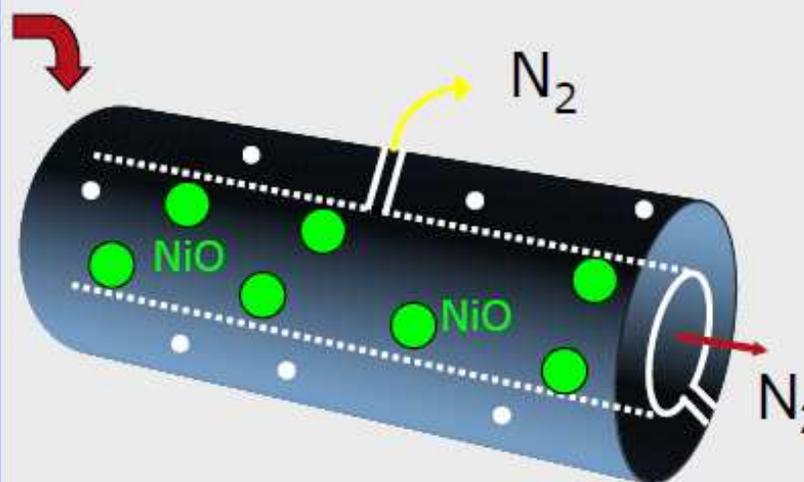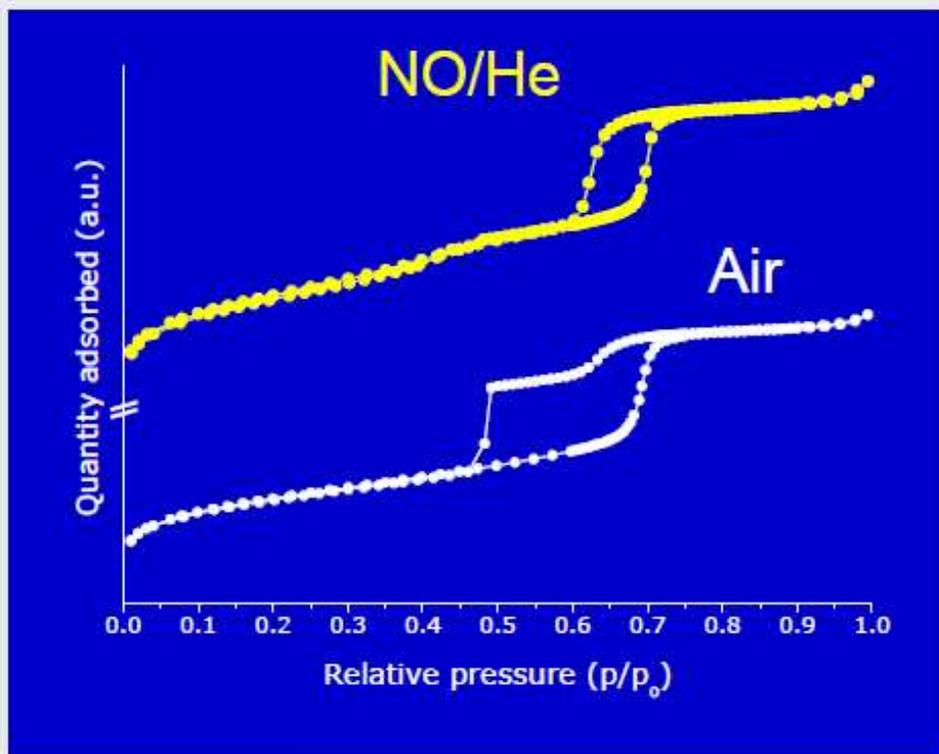
NiO

NiO
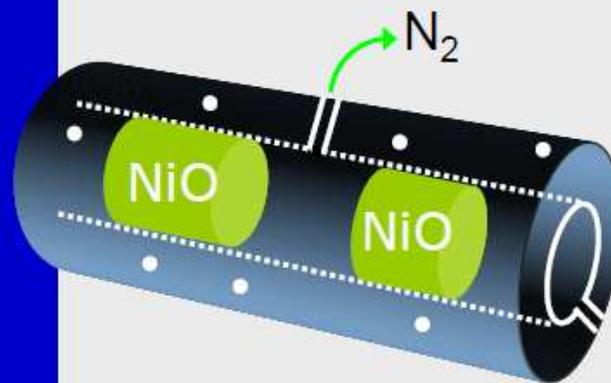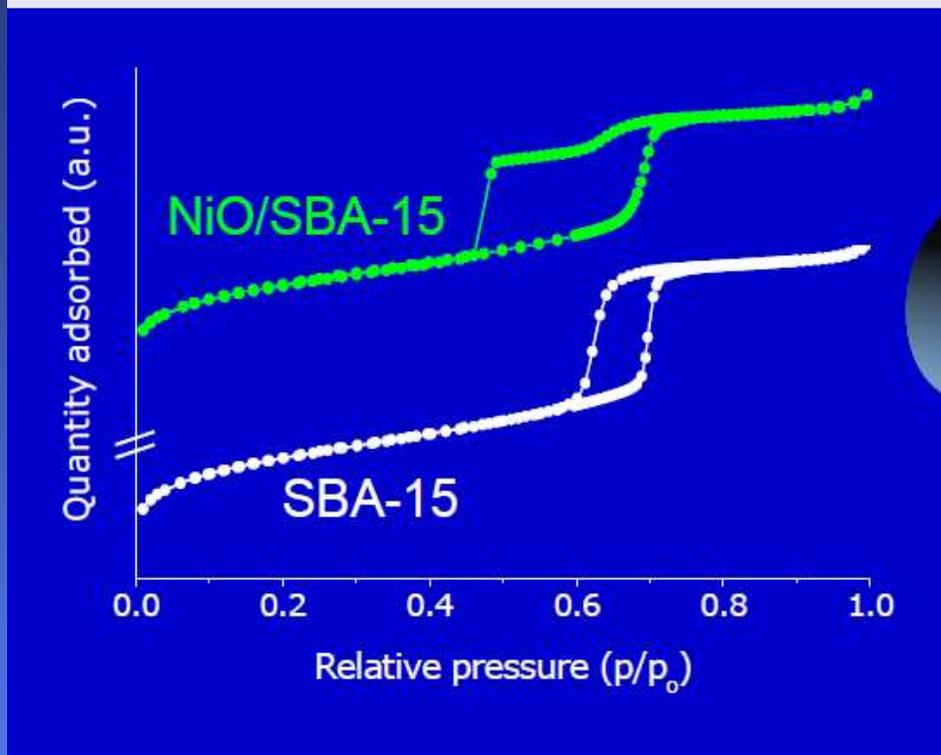
Pore blocking by NiO nanorods

24 wt% NiO/SBA-15 ex nitrate

Calcination in air ➔ NiO size 9 to 60 nm   Reduction in H2 ➔ Ni 7 to 25 nm

Detrimental ➔ pore blocking.

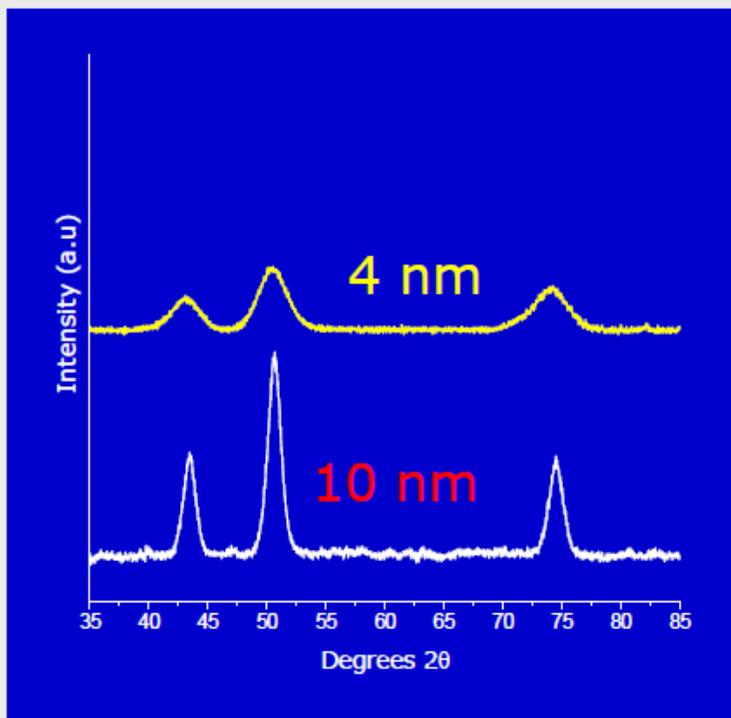**Calcination in NO/He ➜ no pore blocking**

NO/He

Air

Quantity adsorbed (a.u.)

Relative pressure (p/p$_o$)

N_2

NiO

NiO

N_2

No pore blocking by NiO nanoparticles

Sietsma et al., J. Catal. 260 (2008) 227
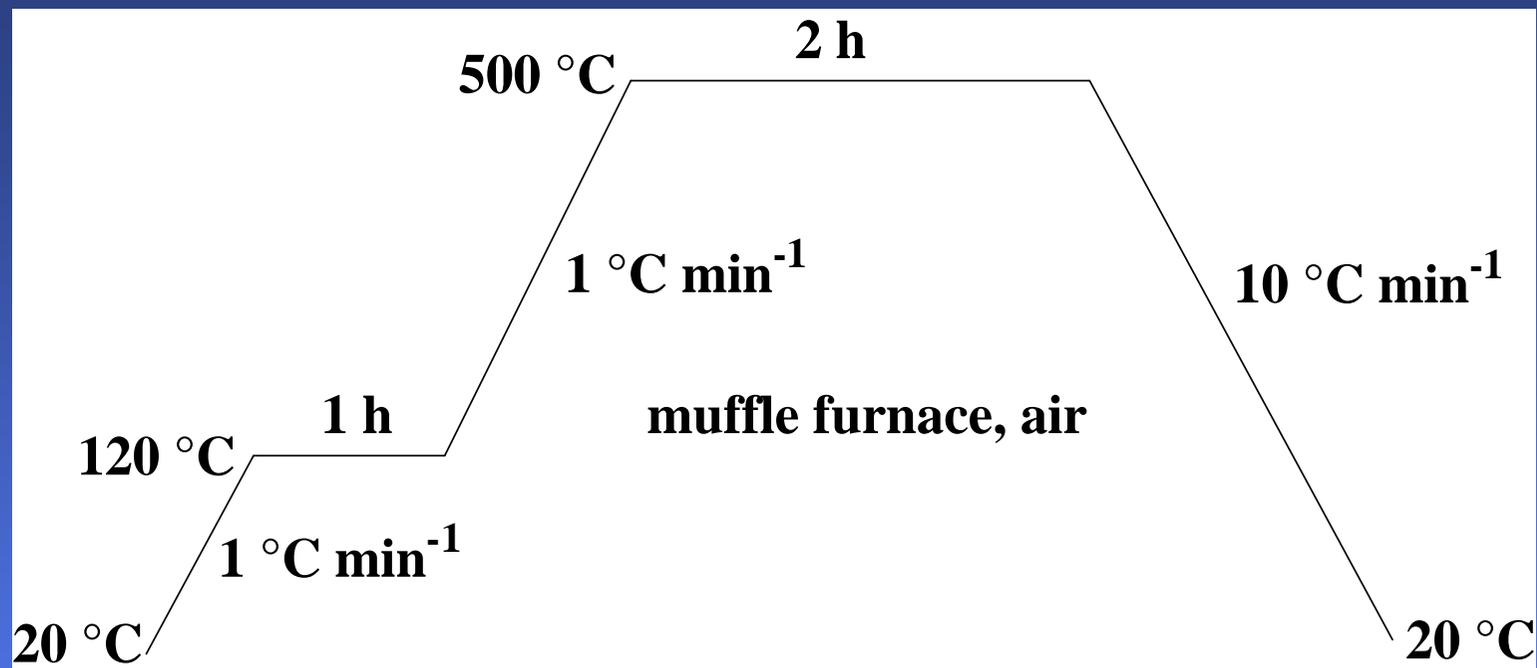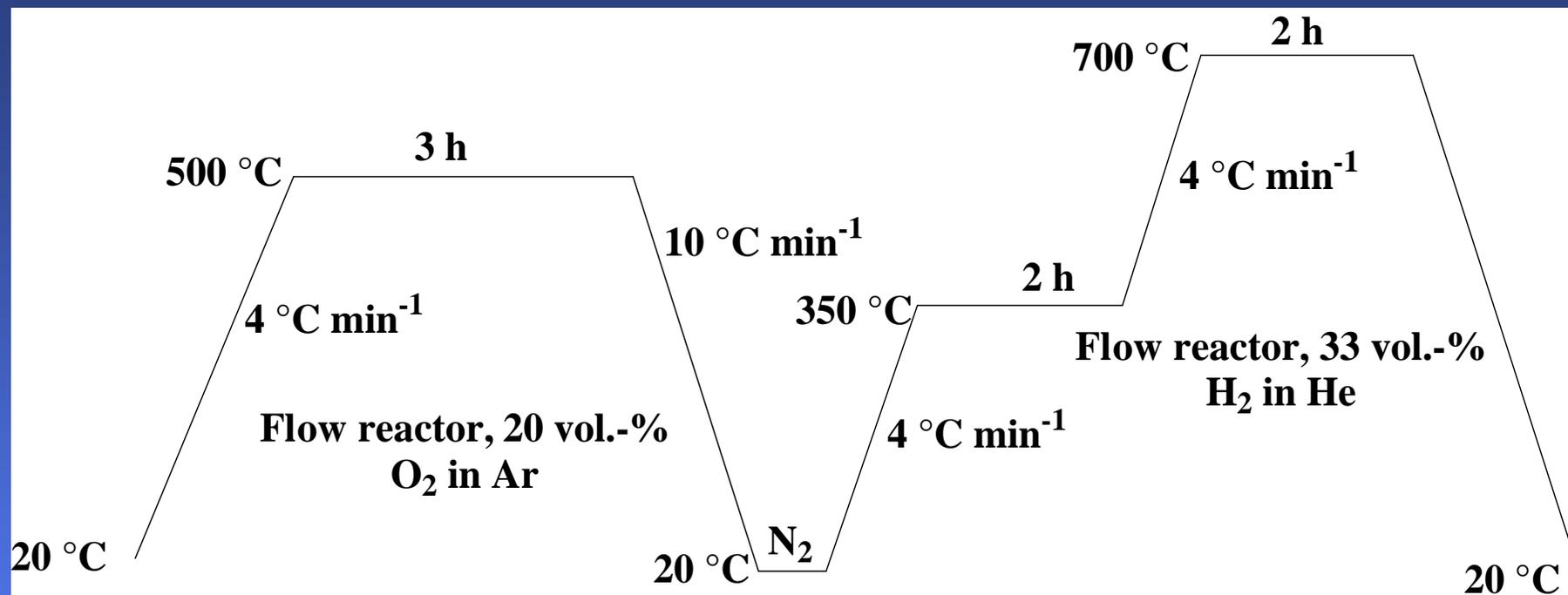
TEM confirmed by XRD

4 nm — NO/He

10 nm — Air

24 wt% NiO/SBA-15 *ex* nitrate

Calcination in air ➜ larger size than calcination in NO
This can be applied to other oxides   e.g. Co_3O_4

2 h

500 °C

1 °C min^{-1}

10 °C min^{-1}

1 h

muffle furnace, air

120 °C

1 °C min^{-1}

20 °C

20 °C

Thermal treatment of monoliths after acid washing

700 °C **2 h**

4 °C min^{-1}

500 °C **3 h**

10 °C min^{-1}

4 °C min^{-1}

350 °C **2 h**

Flow reactor, 33 vol.-%
H$_2$ in He

Flow reactor, 20 vol.-%
O$_2$ in Ar

4 °C min^{-1}

20 °C

20 °C **N$_2$**

20 °C

Role   of temperature profile
of H$_2$ %

End of part 3