



# Particle size measurement

03/11/2006 A. Trunschke

## Further reading

T. Allen, Particle Size Measurement, Volume 1, Powder sampling and particle size measurement methods, Chapman & Hall, London 1997.

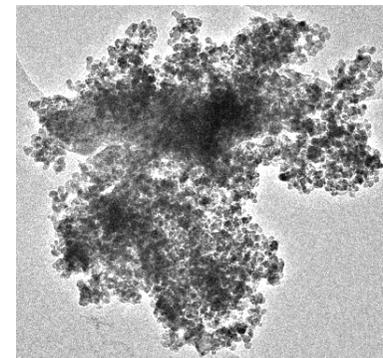
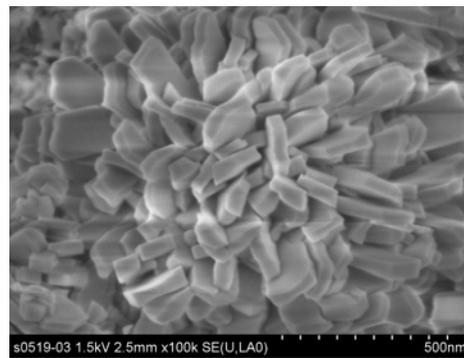
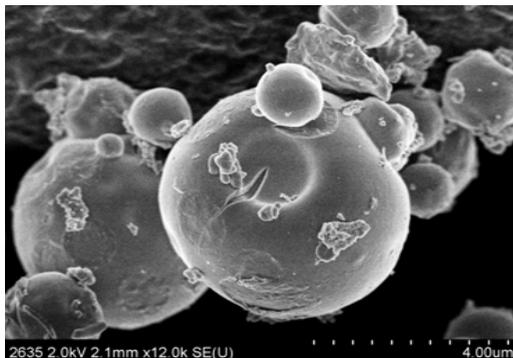
C. Bernhardt, Particle Size Analysis, Classification and Sedimentation methods, Chapman & Hall, London 1994.

J.P.M. Syvitski (Ed.), Principles, methods, and application of particle size analysis, Cambridge University Press, Cambridge 1991.

J.B.J. Berne, R. Pecora, Dynamic Light Scattering, John Wiley & Sons, Inc. NY, 1976.

H.-D. Dörfler, Grenzflächen- und Kolloidchemie, VCH, Weinheim, 1994.

G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997.



## Outline

1. Definitions
2. Classification of methods
3. Particles of an active phase – supported metal particles
  - 3.1. Chemisorption
  - 3.2. LBA
  - 3.3. EM
4. Dispersions, colloids, bulk catalysts
  - 4.1. Sieving
  - 4.2. Sedimentation
  - 4.3. Light scattering
  - 4.4. Acoustic methods
  - 4.5. SAXS
5. General remarks and recommendations

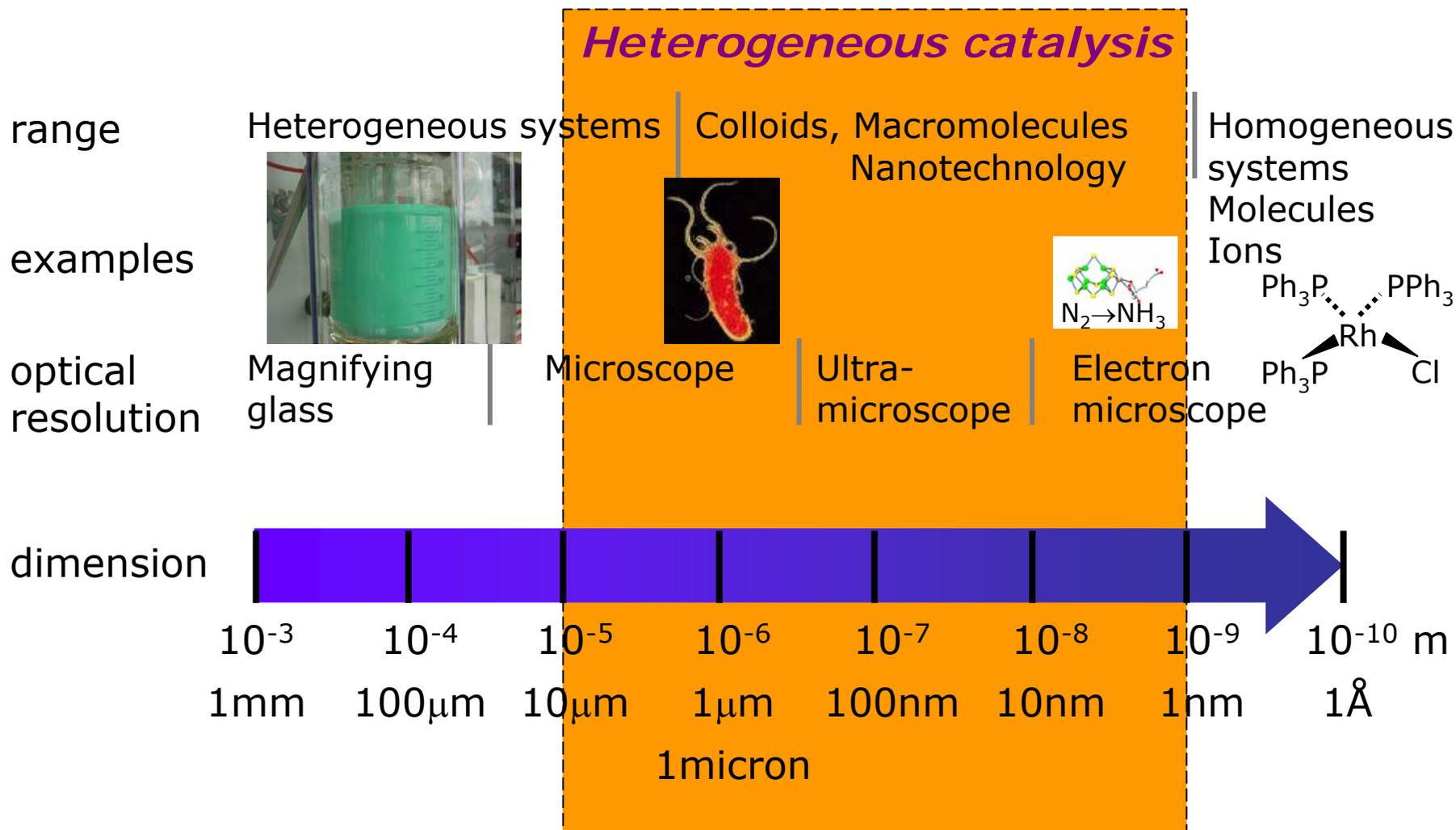
## Particle

small object of any size from the macroscopic scale ( $10^{-3}$  m) to the atomic scale ( $10^{-10}$  m)

Continuous phase	Disperse phase	Denomination	Examples / applications
Gaseous	Solid	Aerosol	Synthesis of oxides
Liquid	Liquid	Emulsion	Extraction
Liquid	Solid	Suspension Sol Gel	Precipitation Sol-gel chemistry Colloidal metals
Solid	Gaseous	Xerogel, Aerogel, Foam	Supports, bulk catalysts (zeolites)
Solid	Solid	Alloy Dispersed metals	Pt-Rh gauze for $\text{NH}_3$ oxidation Pt-Sn/ $\text{Al}_2\text{O}_3$

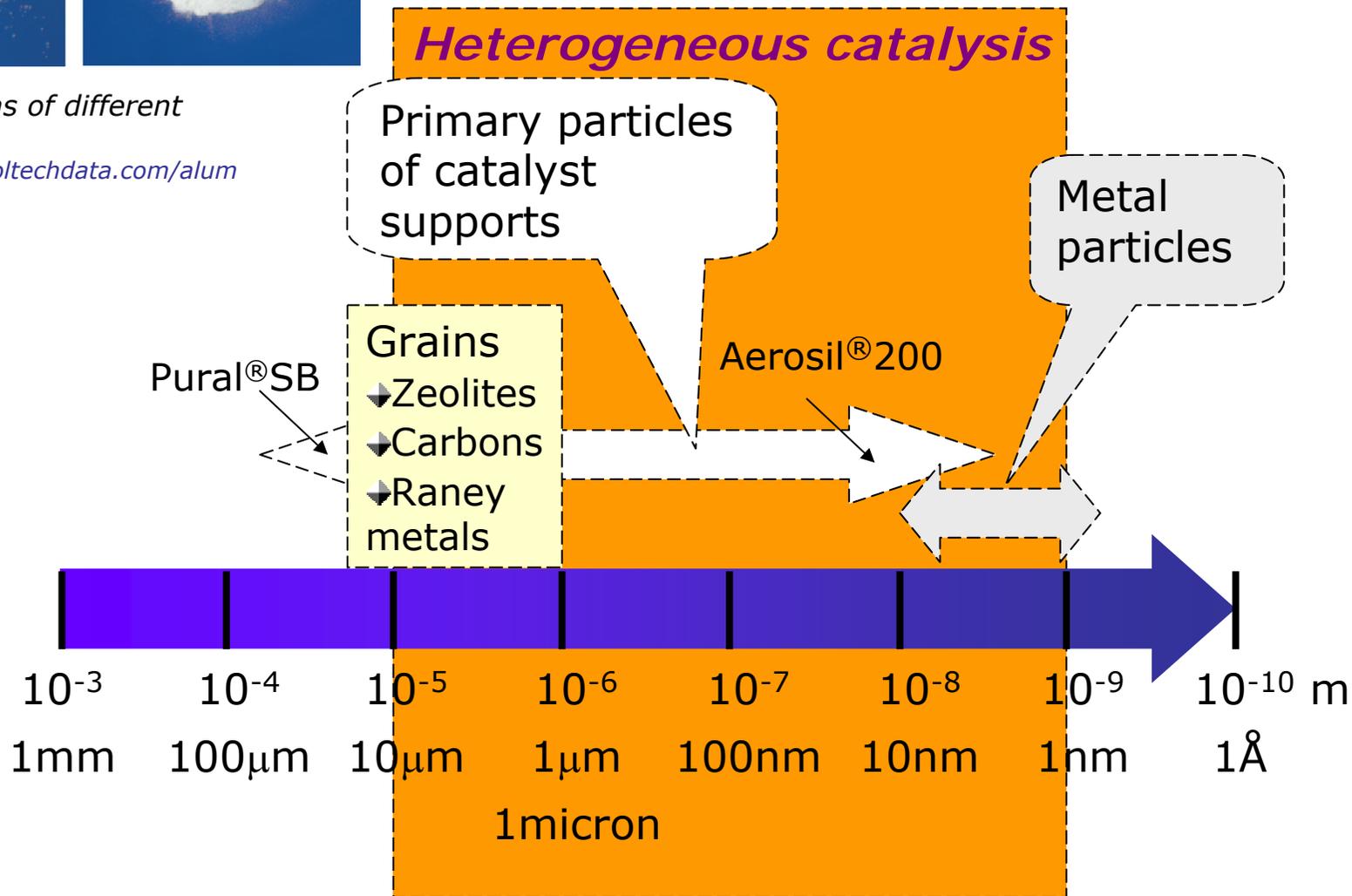
**Particle**

small object of any size from the macroscopic scale ( $10^{-3}$  m) to the atomic scale ( $10^{-10}$  m)



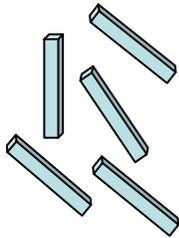


Sasol aluminas of different particle size  
[http://www.sasoltechdata.com/alumina\\_group.asp](http://www.sasoltechdata.com/alumina_group.asp)

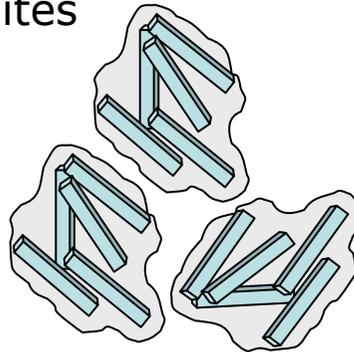


**Crystallite**

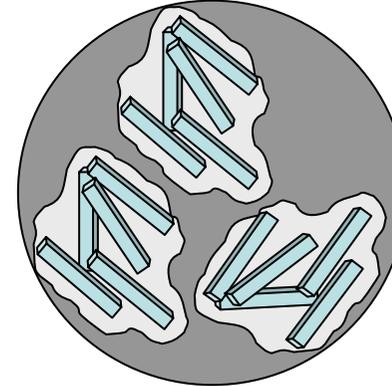
small single crystal  
primary catalyst particles could be formed by one or more crystallites



Primary particles



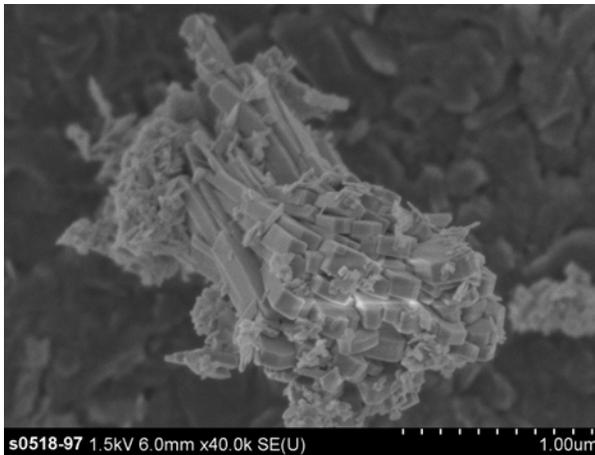
Secondary



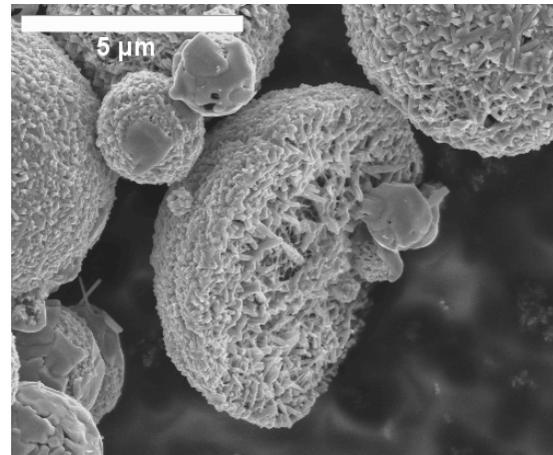
Agglomerated

Grains, shaped catalysts

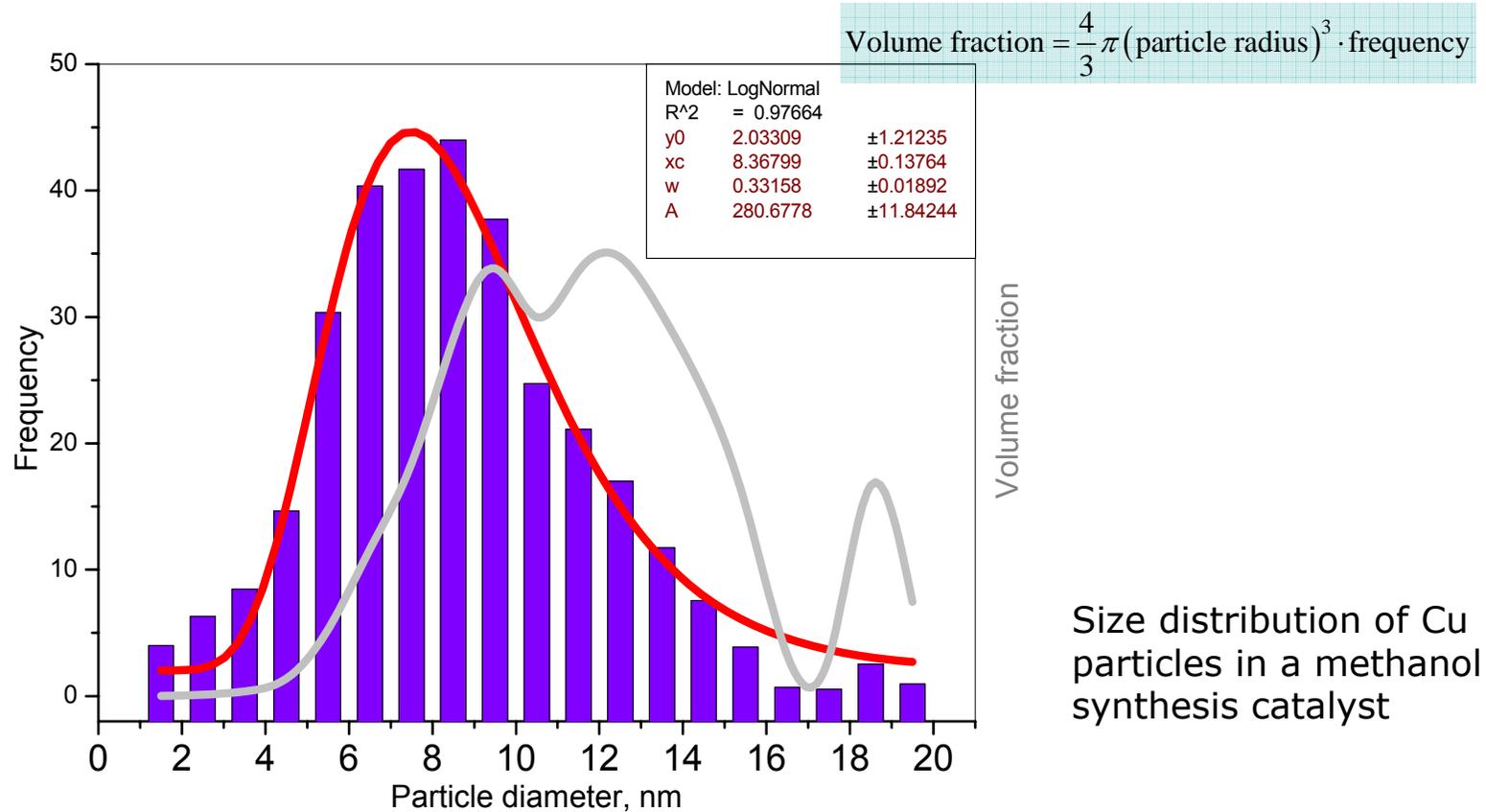
CuZn hydroxycarbonate precipitated



Agglomerates of MoVTeNbO<sub>x</sub> crystals (M1) spray-dried



**Particle size** catalyst particles present a **size distribution**



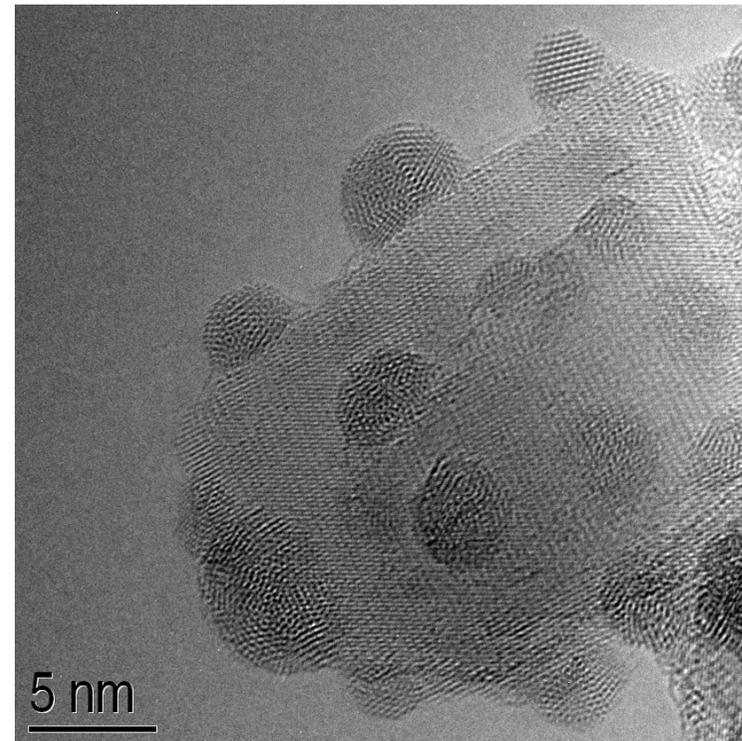
Size distribution of Cu particles in a methanol synthesis catalyst

**Complications**

- ➡ Shape is not spherical
- ➡ Shape is not homogeneous

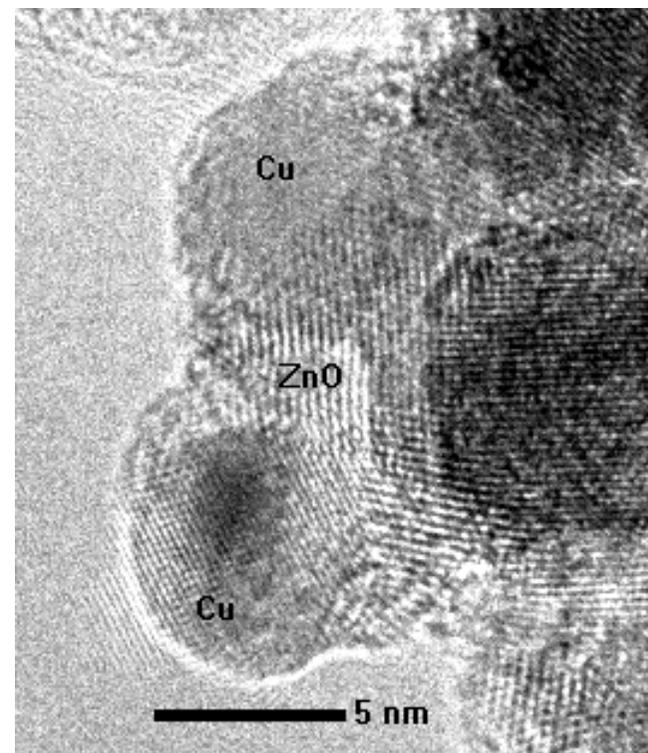
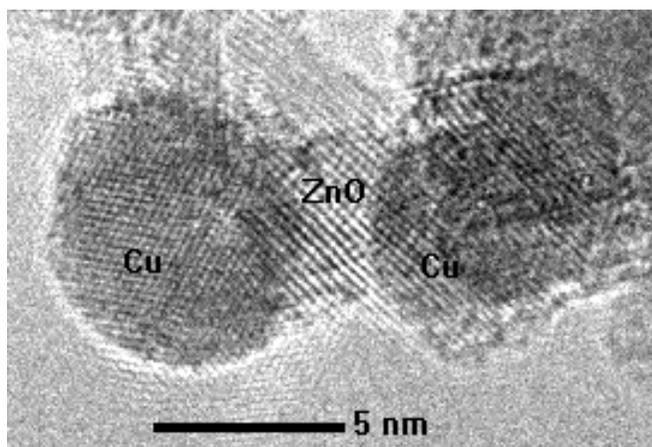
Nanoparticles

Very small particles (1 – 20 nm) of an active component dispersed on high-surface-area solids

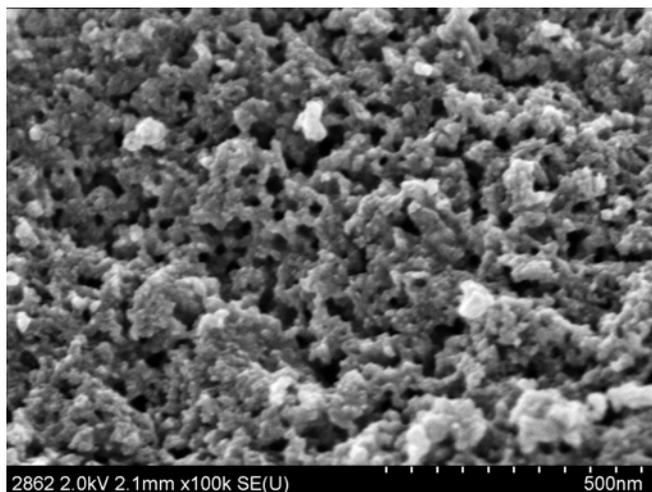
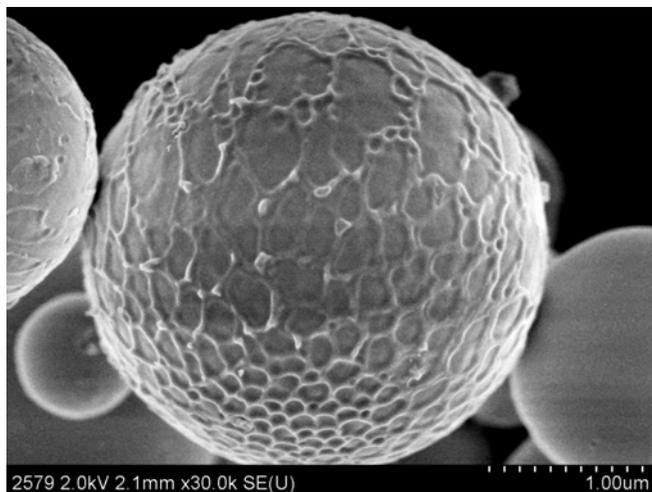


Ag-TiO<sub>2</sub>-40

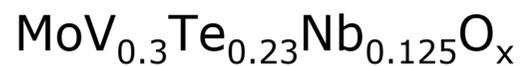
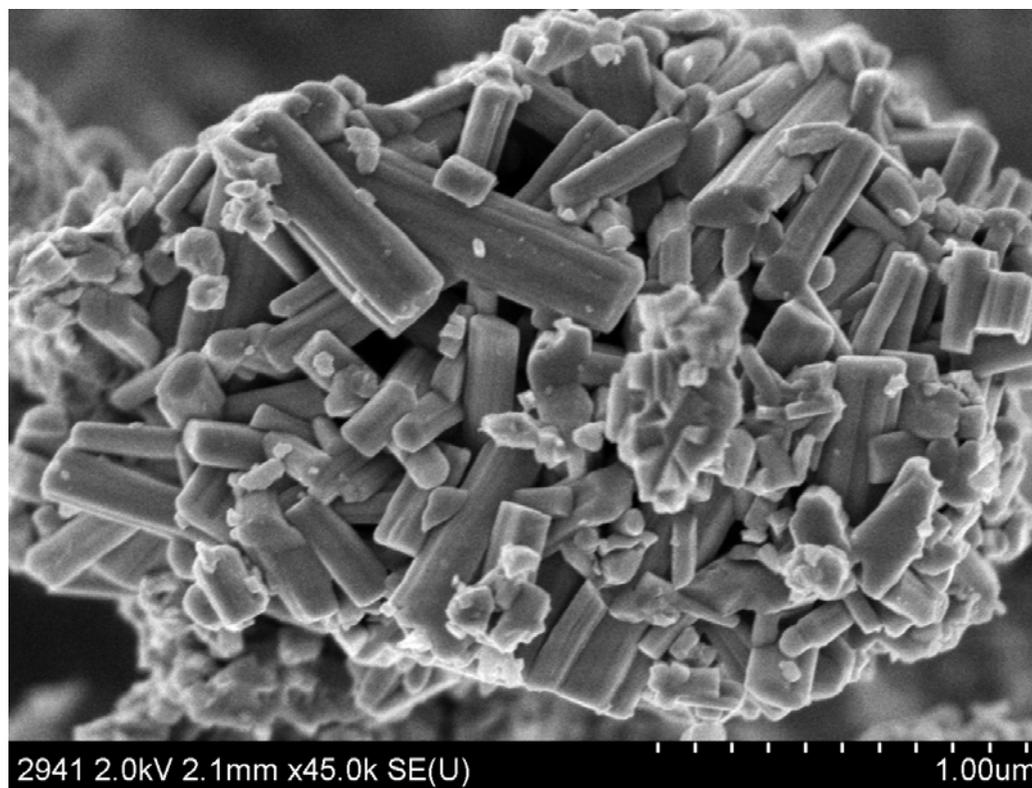
Embedded Cu particles in catalysts for methanol synthesis



Bulk catalyst precursor



Bulk catalysts



## 1. Materials chemistry, catalyst preparation

↳ Precipitation

↳ Nucleation

↳ Crystal growth

↳ Recrystallization



↳ Dispersions

↳ Colloids

↳ Impregnation/incipient wetness

↳ Surface charge

## 2. Catalyst

Particle size is related to

- Active surface area
- Electronic properties
- Exposed crystal faces
- Metal-support interaction
- Deactivation
  - Sintering
  - Coverage



➤ Solid state

Particle shape is related to

- Exposed active planes (structure sensitive catalytic reactions)
- Particle shape and morphology determine the relative amount of edge and corner atoms

Examples from literature

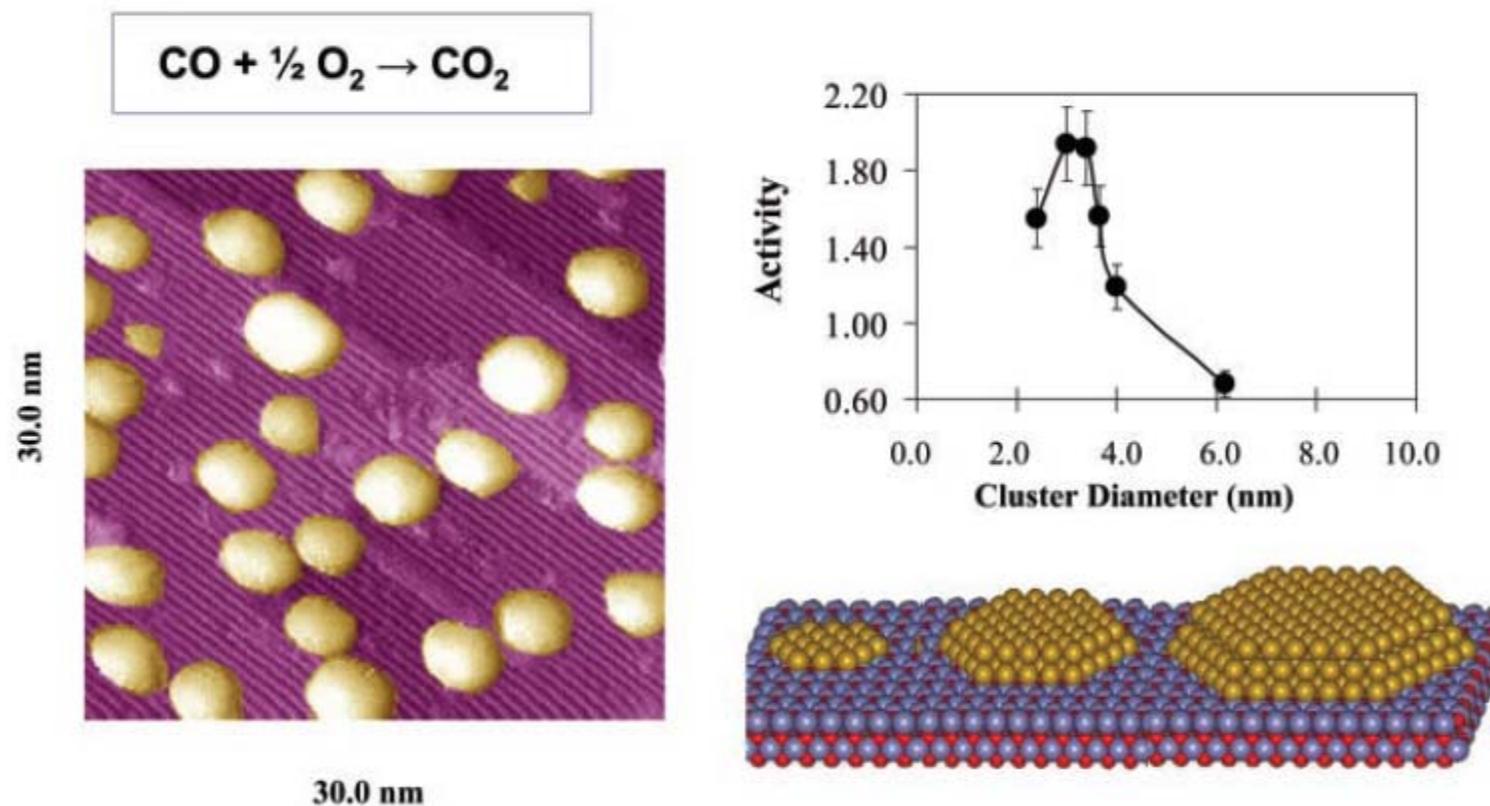


Fig. 2. Effects of particle size on the activity of titania-supported Au for the oxidation of CO (5).

M. Valden, X. Lai, D. W. Goodman, *Science* **281**, 1647 (1998).

## Examples from literature

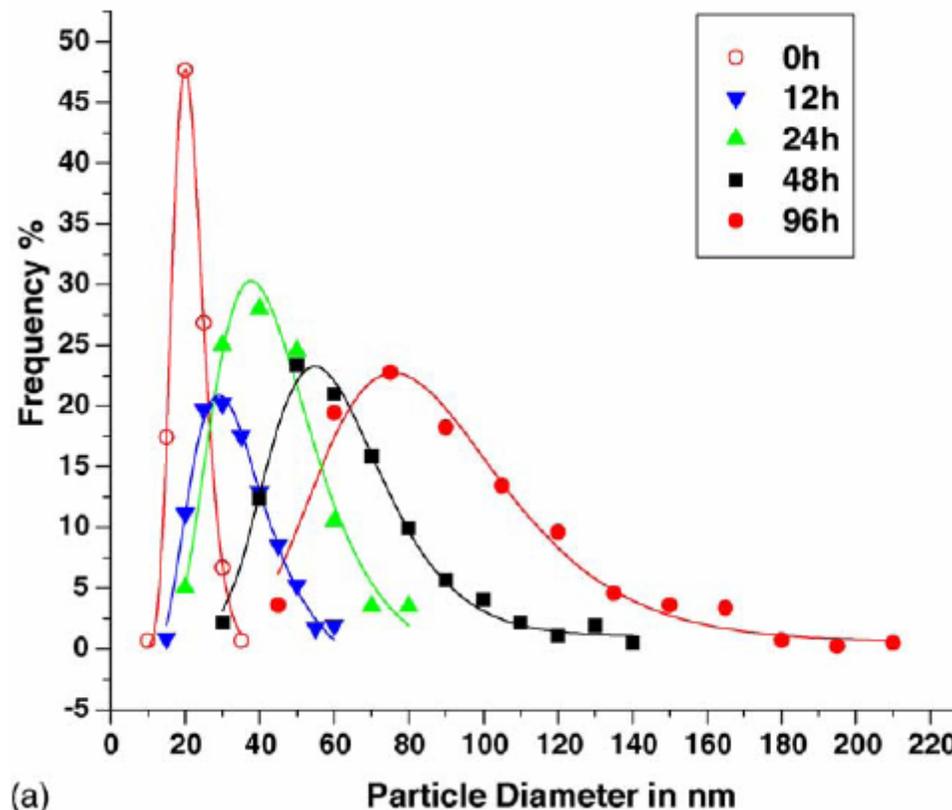
Problem of sintering for catalysts operating at high temperature, e.g., catalysts for

- catalytic combustion of methane
- close-coupled automotive exhaust catalysts
- steam reforming of methane



Investigation of the sintering mechanism

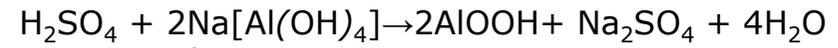
A.K. Datye et al., *Catalysis Today* 111 (2006) 59–67.



(a)

Particle size distributions after sintering at 900°C for differing lengths of time. All data have been fitted using a log normal distribution: 7 wt.% Pd/alumina

## Examples from literature



starting solutions:

Educt A:  $\text{Na}[\text{Al}(\text{OH})_4]$  + NaOH in  $\text{H}_2\text{O}$  (pH 13.5)

Educt B:  $\text{H}_2\text{SO}_4$  (0.5 mol/l)

The precipitation temperature 65°C, pH 9, solid concentration of boehmite of about 1.5% by weight

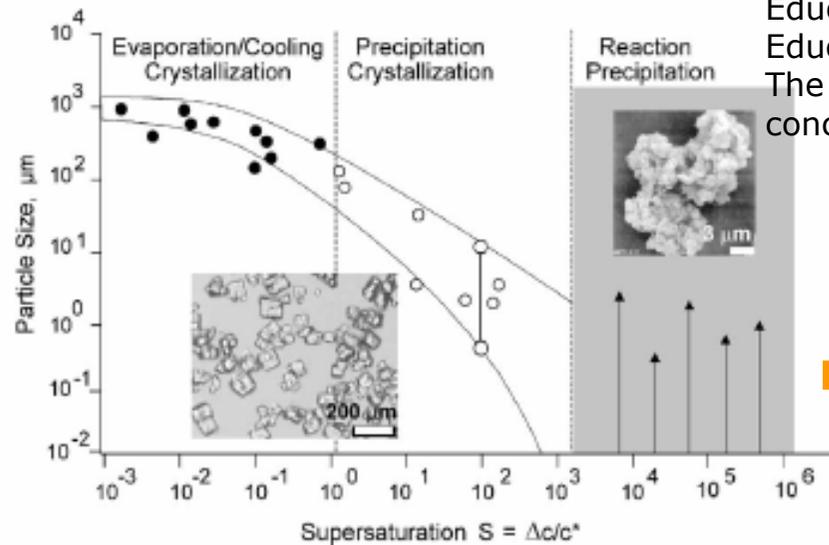
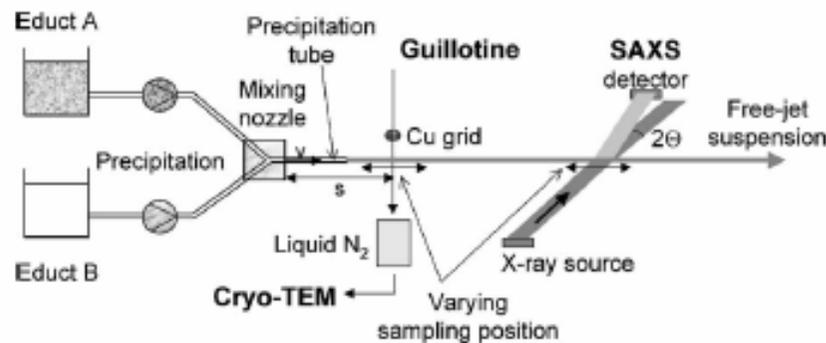


Fig. 1. Grain size as a function of supersaturation/solubility.

Investigation of the particle formation process during precipitation



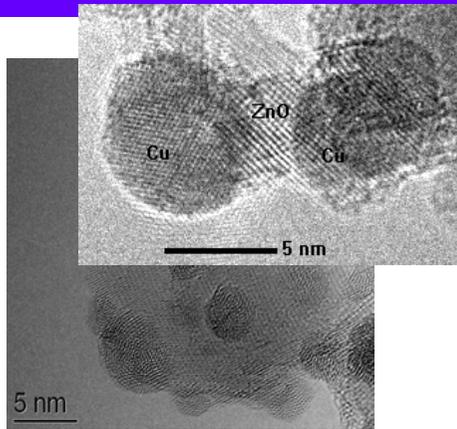
free-jet SAXS measurements were taken at a distance of 11.5 and 56.5 cm from the mixing point, which corresponds to residence times of 40 and 200 ms

Fig. 2. Design for time-resolved measurements on free-jet suspensions. Online SAXS and cryo-TEM experiments for studying precipitation reactions at time  $t_r = s/v$ .

H. Haberkorn et al., *Journal of Colloid and Interface Science* 259 (2003) 112.

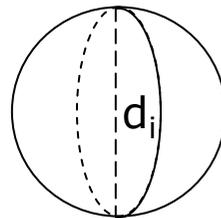
<i>Active phase</i>	<i>Bulk materials / colloids</i>
<ul style="list-style-type: none"> <li>➤ Chemisorption (essentially restricted to metal particles)</li> <li>➤ X-ray diffraction – Line broadening analysis (crystallite size)</li> <li>➤ Small-angle X-ray scattering (SAXS) (particle size)</li> <li>➤ Electron microscopy</li> </ul>	<ul style="list-style-type: none"> <li>➤ Sieving</li> <li>➤ Sedimentation</li> <li>➤ Light scattering</li> <li>➤ Acoustic methods</li> <li>➤ Time-of flight techniques</li> <li>➤ Small-angle X-ray scattering</li> <li>➤ X-ray diffraction – Line broadening analysis (crystallite size)</li> <li>➤ Electron microscopy</li> </ul>

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**Assumptions, if microstructural analysis is not available:**

collection of  $n_i$  particles  
 particles are **spherical**



Surface area of the spheres

$$A_i = \pi d_i^2$$

Volume of the spheres

$$V_i = \pi d_i^3 / 6$$

Two **mean particle sizes** are usually considered:

*length-number*

$$d_{LN} = \frac{\sum n_i d_i}{\sum n_i}$$

*volume-area*

$$d_{VA} = \frac{6(\sum n_i V_i)}{\sum n_i A_i}$$

$$= \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

**Dispersion**

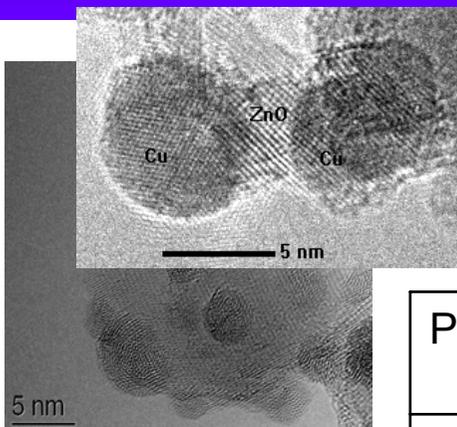
*(fraction of surface atoms)*

$$D(\%) = \frac{(N_s/N_t)100}{1}$$

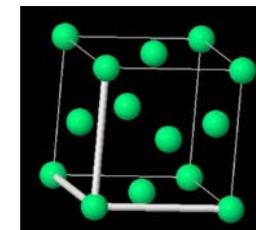
$N_s$  number of surface atoms

$N_t$  total number of atoms

(bulk and surface)



Number of atoms per unit surface area in the three low index planes of **copper**  
(fcc structure with  $a=3.615 \times 10^{-10}$  m)



Plane	Surface cell	Area	Area / m <sup>2</sup>	Atoms per cell	Atoms per m <sup>2</sup>
(111)	triangular	$(a^2\sqrt{3})/2$	$11.32 \times 10^{-20}$	2	$1.77 \times 10^{19}$
(100)	square	$a^2$	$13.07 \times 10^{-20}$	2	$1.53 \times 10^{19}$
(110)	rectangular	$a^2\sqrt{2}$	$18.48 \times 10^{-20}$	2	$1.08 \times 10^{19}$
<b>Mean number of atoms per unit area <math>n_s</math></b>					$1.46 \times 10^{19}$

M atomic mass  
(63.55 g mol<sup>-1</sup>)  
 ρ density  
(8.92 g cm<sup>-3</sup>)  
 N<sub>A</sub> 6.022 × 10<sup>23</sup> mol<sup>-1</sup>

Surface area occupied by a Cu atom

$$a_{Cu} = 1/n_s = 6.85 \times 10^{-20} \text{ m}^2$$

Volume occupied by a Cu atom

$$v_{Cu} = M/\rho N_A = 1.183 \times 10^{-29} \text{ m}^3$$

Specific surface area

$$S_{sp} = a_m(N_A/M)D = \sum n_i V_i / \rho \sum n_i A_i$$

$$= 6/(\rho d_{VA})$$

If  $d_{VA} = 5$  nm,

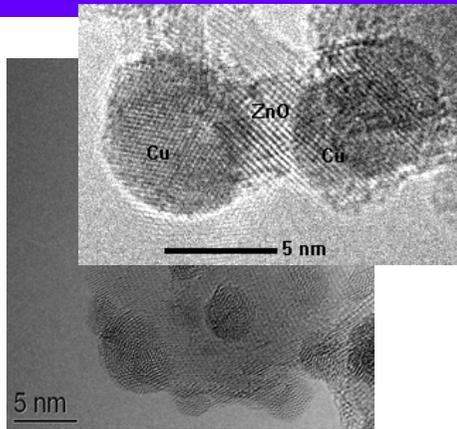
$$S_{sp} = 134.5 \text{ m}^2\text{g}^{-1}$$

Dispersion

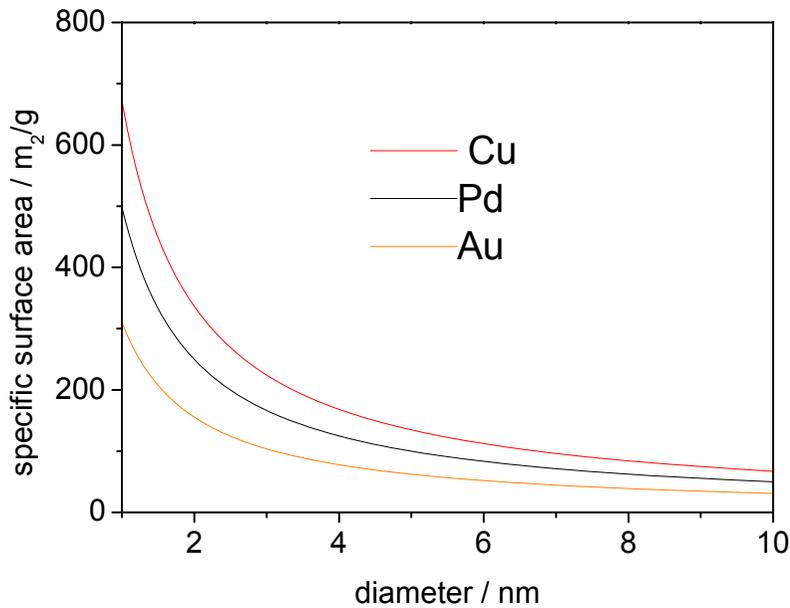
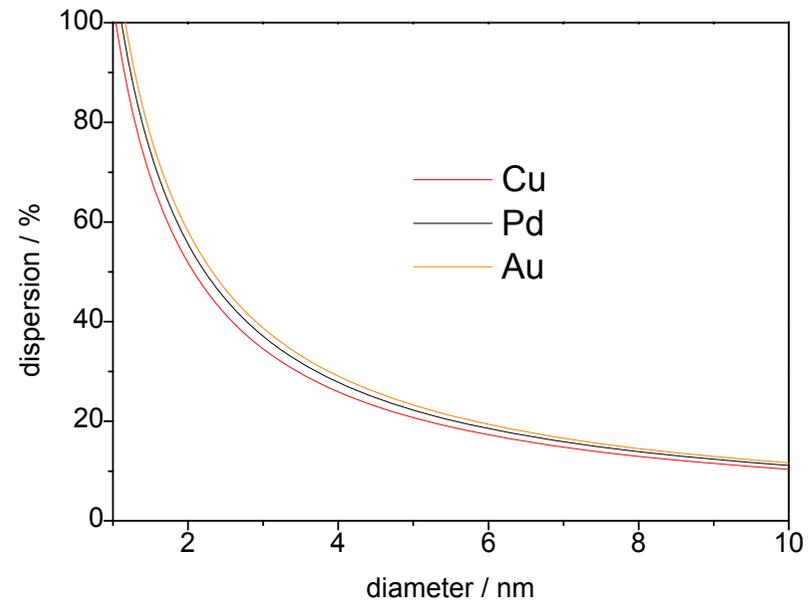
$$D = 6(v_m/a_m)/d_{VA}$$

If  $d_{VA} = 5$  nm

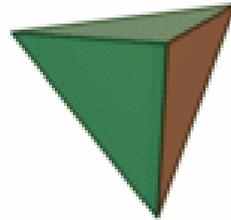
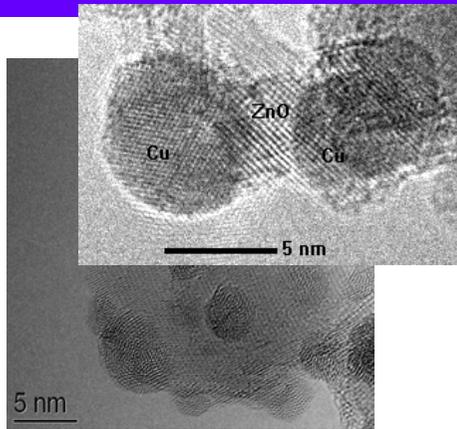
$$D = 21\%$$



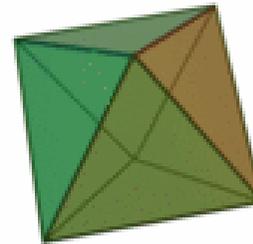
Plot of dispersion  $D$  as a function of mean diameter  $d_{VA}$  for copper, palladium and gold.



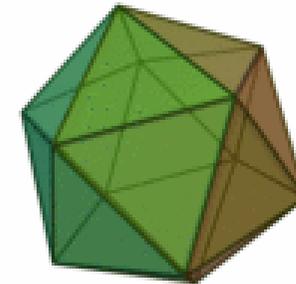
Plot of specific surface area  $S_{sp}$  as a function of mean diameter  $d_{VA}$  for copper, palladium and gold



$$A_O = \sqrt{3} a^2 \approx 1,73 a^2$$

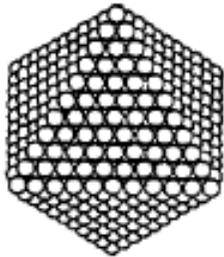


$$A_O = 2\sqrt{3} a^2 \approx 3,46 a^2$$

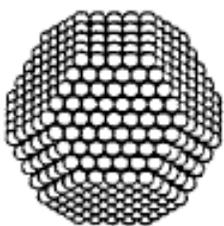


$$A_O = 5\sqrt{3} a^2 \approx 8,66 a^2$$

Clusters of cubic metals



891 atom octahedron



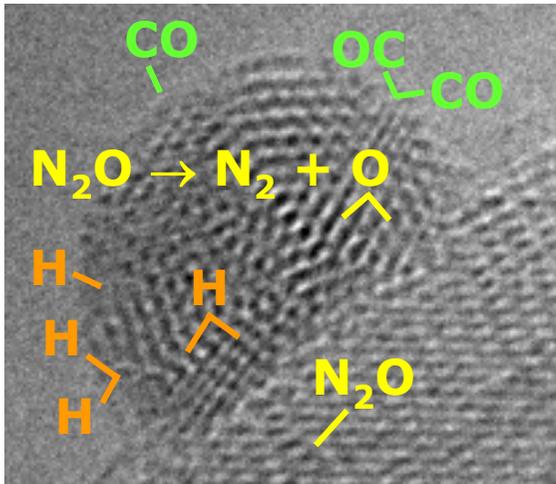
1289 atom Wulff polyhedron  
(minimum energy shape)

- ▶ Spherical geometry should **not** be used for particles smaller than **ca. 1.2 nm**
- ▶ For smaller particles, geometrical models should be considered

*Metal particle size measurements*

- Chemisorption
- X-ray diffraction – Line broadening analysis (crystallite size)
- Small-angle X-ray scattering (SAXS) (particle size)
- Electron microscopy

Exposed surface area (esp. of metals)



Other probes

$O_2$ , NO,  $N_2$ ,  $H_2S$ ,  
 $CS_2$ ,  $C_6H_6$ , ...

*Principle*

Formation of an irreversibly, selectively adsorbed monolayer

Stoichiometry of the chemisorption reaction is known

*Measurement of the amount adsorbed*

➤ Static methods

➤ Volumetry

➤ Gravimetry

➤ Dynamic methods

➤ Continuous flow

➤ Pulse adsorption

➤ Temperature-programmed desorption / MS

$$S_{sp} (\text{m}^2\text{g}^{-1} \text{ metal}) = (V_m/22414)N_A n(1/m)a_m(100/\text{wt})$$

$$D (\%) = (V_m n/22414 \text{ m})/(\text{wt}/100 \text{ M})$$

$V_m$  volume of chemisorbed gas required to form a monolayer ( $\text{cm}^3$ )

$a_m$  surface area occupied by a metal atom ( $\text{m}^2$ )

$n$  chemisorption stoichiometry

$m$  mass of catalyst (g)

$\text{wt}$  metal loading (%)

### Complications

- ↘ Equilibrium coverage increases with adsorption pressure
- ↘ Non-selective chemisorption (chemisorption on the support, spillover)
- ↘ Reversible chemisorption

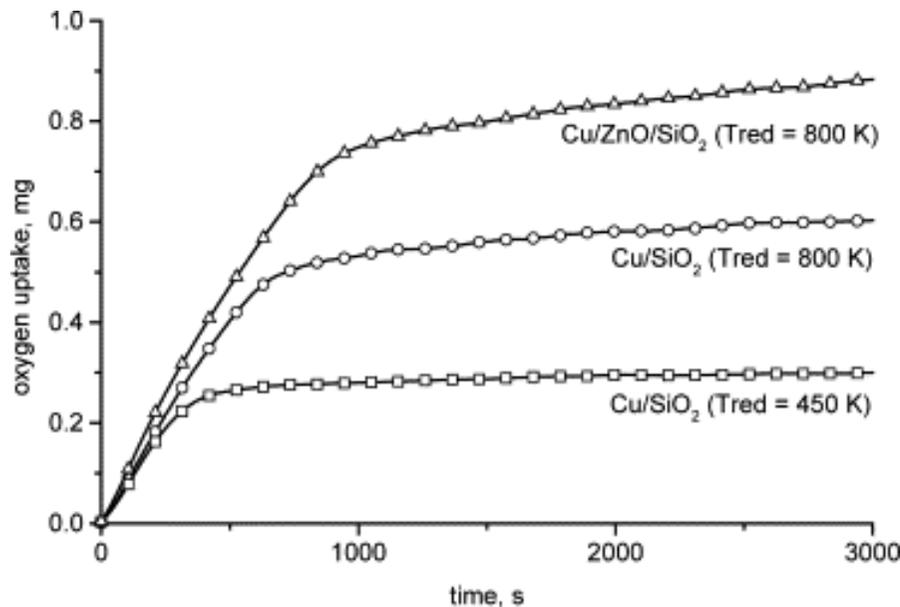


G.C. Chinchen *et al.*,  
J. Catal. 103 (1987) 79.

E.D. Batyrev *et al.*, J. Catal. 229 (1) (2005) 136.

M.J. Luys *et al.*, Appl. Catal. 46 (1989) 161.

- ▶ Chemisorption: Flow of 2 cm<sup>3</sup>/s 1% N<sub>2</sub>O/99% Ar at 363 K during 50 min
- ▶ Amount of oxygen consumed was determined from the weight gain of the sample
- ▶ Linear extrapolation of the subsurface contribution to  $t=0$
- ▶ Assumptions:  $\text{Cu}_{\text{s}}/\text{O}_{\text{ads}}=2$ ,  $1.46 \times 10^{19}$  Cu<sub>s</sub> atoms/m<sup>2</sup>



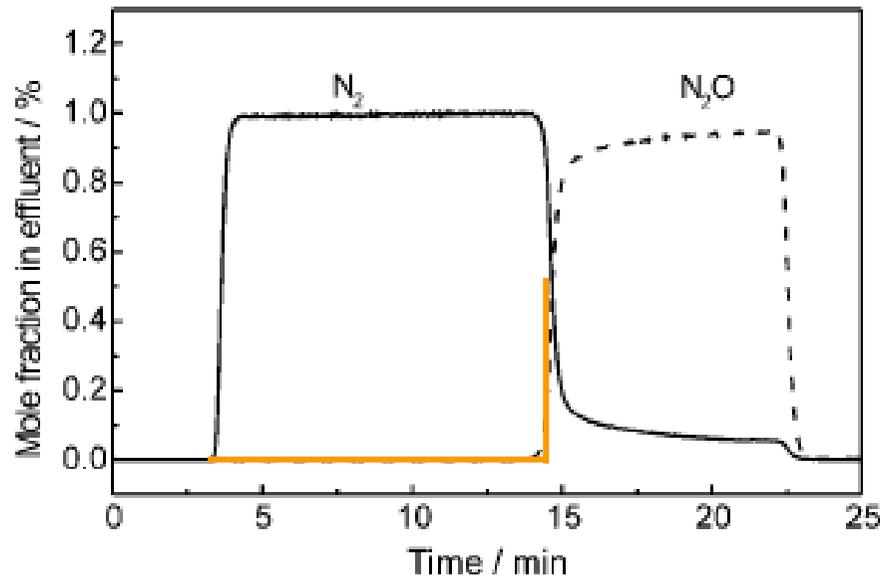
- ▶ Increasing the N<sub>2</sub>O concentration, surface oxidation but not subsurface oxidation is increased
- ▶ Subsurface oxidation rate increases with temperature (local T during N<sub>2</sub>O chemisorption depends on Cu dispersion as well as thermal properties of the system!)

## Continuous flow technique (frontal sorption method)



$$\Delta_{\text{R}}H = 317 \text{ kJ/mol}$$

(N<sub>2</sub>O, Cu/ZnO)

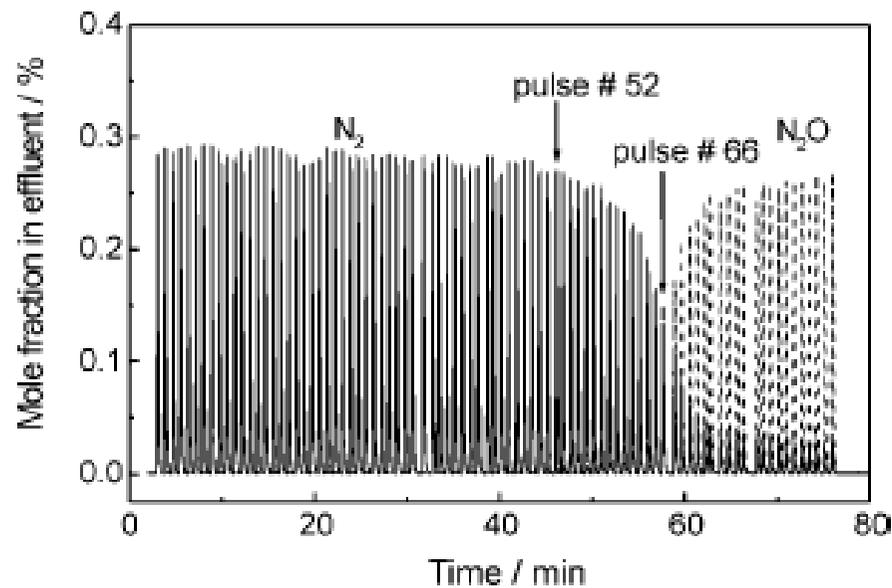


Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst

↘ Flow of 10 Nml/min  
 1% N<sub>2</sub>O/He at 300 K,  
 p=0.1 MPa, m<sub>cat</sub>=0.2 g  
 bed height=20 mm  
 contact time = 1.4 s  
**ΔT approx. 1 K**

↘ Determination of N<sub>2</sub>  
 formed as product of  
 molar flow and peak area

*O. Hinrichsen, T. Genger, and M. Muhler, Chem. Eng. Technol. 23 (2000) 11.*

*Pulse technique (pulse sorption method)*

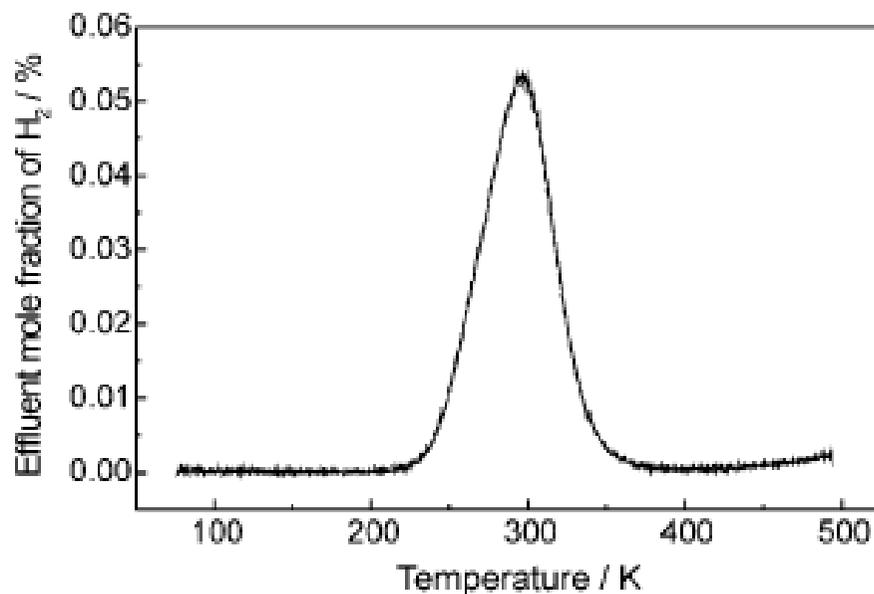
Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst

Injection of successive small pulses of known volume into the flow of an inert gas

➤ Flow of 20 Nml/min He  
V = 1.0 ml N<sub>2</sub>O  
T = 300 K  
p = 0.1 MPa

➤ #66 = 125 μmol/g N<sub>2</sub>

*O. Hinrichsen, T. Genger, and M. Muhler, Chem. Eng. Technol. 23 (2000) 11.*



↘ Saturation with H<sub>2</sub> at 1.5 MPa, T=240K, cooling down in H<sub>2</sub> flow to 78K, purging with He

↘ TPD:  
 Flow He 100 Nml/min  
 heating rate 6 K/min

Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst

*M. Muhler et al., Catal. Lett. 14 (1992) 241.*

*O. Hinrichsen, T. Genger, and M. Muhler  
 Chem. Eng. Technol. 23 (2000) 11.*

Sequence of experiment	Amount of desorbed N <sub>2</sub> or H <sub>2</sub> (μmol/g)	Specific Cu metal surface area (m <sup>2</sup> /g)
H <sub>2</sub> TPD	115	18.8
1% N <sub>2</sub> O RFC	217	17.8
H <sub>2</sub> TPD	115	18.8

- ✦ Convenient method for routine measurements
- ✦ Chemisorption probes the exposed surface = surface relevant for catalysis
- ✦ Measured surface areas depend on the catalyst pretreatment
- ✦ Absolute value of particle size involves many assumptions

### Recommendations

- ✦ Minimization of
  - ✦ Reversible chemisorption
  - ✦ Chemisorption at the support
  - ✦ Reactive chemisorption

By application of proper operating conditions, established by other methods (TPD, FTIR)
- ✦ Chemisorption of different probe molecules
- ✦ Investigation of the catalyst with additional/complementary methods helps to avoid misinterpretation of the chemisorption results

**Crystallite size** (from 1.5-2 nm to 100 nm)

Breadth of a X-ray reflection depends upon

- Size of the crystallite
- Defects in the lattice (microstrains or stacking faults)
- Instrumental factors (slit width, sample size, penetration of the beam,...)

### *The Scherrer Formula*

$$L_{hkl} = k\lambda/(\beta \cos\theta_0)$$

$L_{hkl}$	thickness of the crystallite in the direction perpendicular to the diffracting planes ( $hkl$ )
$k$	shape factor; $k=1$ (integral); (0.9 for $\beta_{1/2}$ )
$\lambda$	wavelength of the diffraction line
$\beta$	breadth of the diffraction profile in radians
$\theta_0$	angular position of the peak maximum

### *Complete Line Profile Analysis*

1. Correction for the effects of instrumental broadening
2. Separation between size and strain broadening
3. Derivation of size parameters

For further information, see X-ray diffraction lecture, F. Girgsdies, 20/10/06

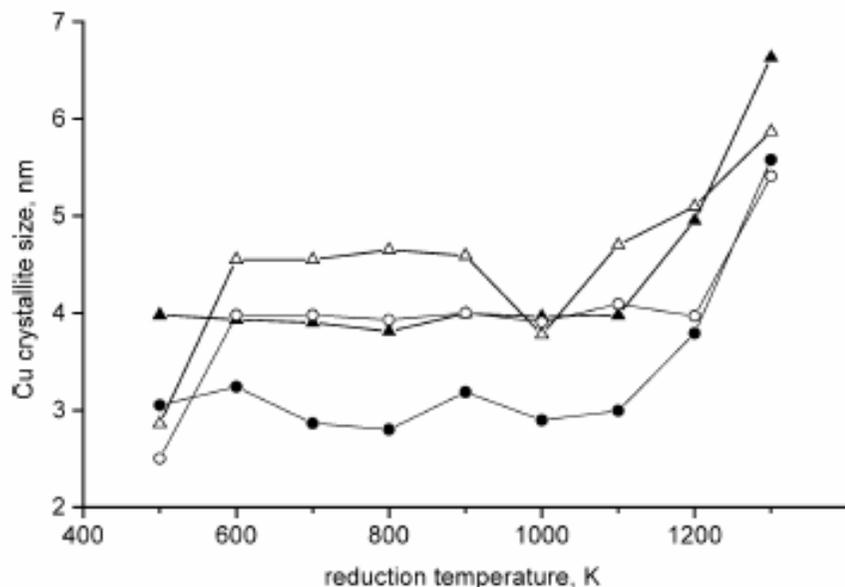
### *Limitations of LBA*

- Overlap of different diffraction lines (e.g., reflections from different phases, neighboring reflections of fcc metals are overlapping when the crystals become very small)
- Lack of contrast between the intensity of reflections and that of overall scattering, particularly for metals with low atomic number
- Upper limit: Broadening of the signal due to crystallite size becomes too small with respect to the instrumental broadening
- Crystallite size is not necessarily particle size
- LBA is a bulk analysis !

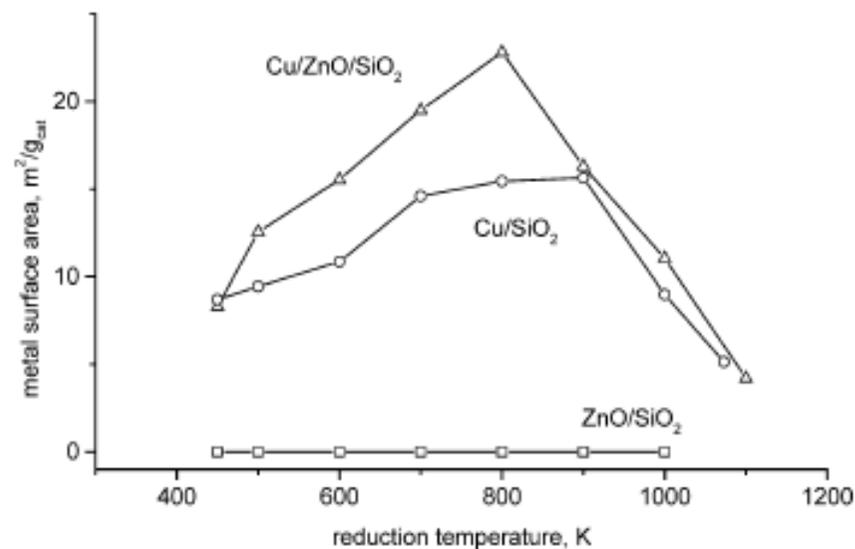
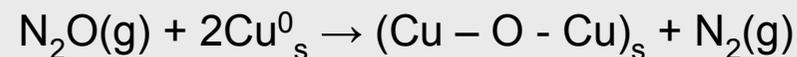
	<b>S<sub>Cu-RFC</sub></b> <b>[m<sup>2</sup>/g<sub>cat</sub>]</b>	<b>S<sub>Cu-XRD</sub></b> <b>[m<sup>2</sup>/g<sub>cat</sub>]</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-1</b>	<b>17,53 +/- 1,47</b>	<b>17,2</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-2</b>	<b>5,26</b>	<b>20,1</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-3</b>	<b>8,27</b>	<b>16,3</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-4</b>	<b>5,72</b>	<b>14,4</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-5</b>	<b>8,02</b>	<b>17,9</b>
<b>Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>-6</b>	<b>4,78</b>	<b>14,2</b>
<b>Cu/ZnO-1</b>	<b>13,13</b>	<b>30,5</b>
<b>Cu/ZnO-2</b>	<b>22,07</b>	<b>22,9</b>

RFC: 1 vol-% N<sub>2</sub>O (He), flow: 10 ml/min, temperature:  
30 °C, sample: m<sub>cat</sub> = 12 mg + 100 mg BN

## Cu crystallite size



Size of Cu (111) and Cu (200) crystal planes from the XRD spectra of Cu/SiO<sub>2</sub> (solid symbols) and Cu/ZnO/SiO<sub>2</sub> (open symbols) catalysts at increasing reduction temperature. Assignment: triangles for Cu (111), circles for Cu (200).



Equivalent metal surface area of the ZnO-promoted catalyst (triangles) and unpromoted catalyst (circles) as a function of the reduction temperature. The ZnO/SiO<sub>2</sub> reference is also included (squares).

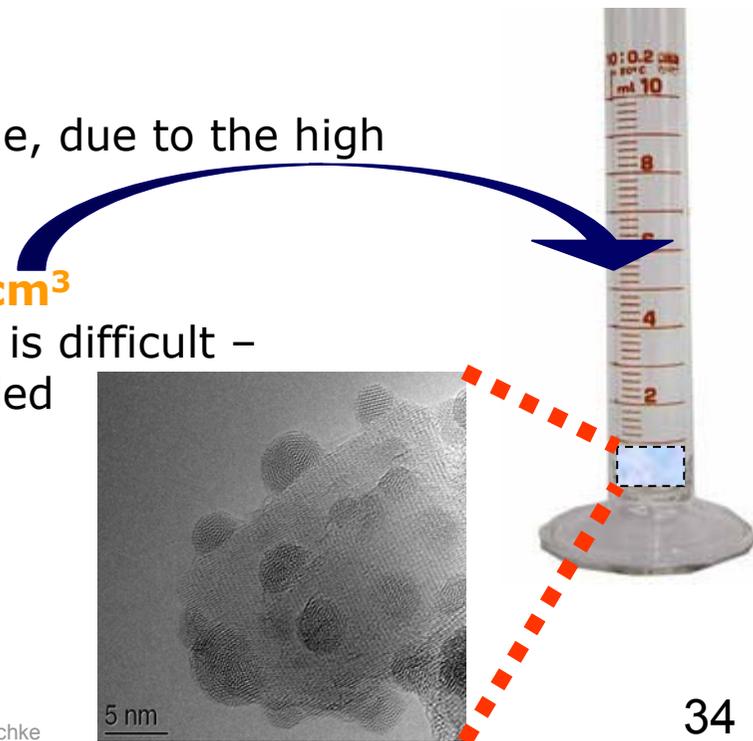
E.D. Batyrev *et al.*, *J. Catal.* 229 (1) (2005) 136.

- Powerful technique for understanding the properties of heterogeneous catalysts
- Practical industrial catalysts can be directly examined in an electron microscope
  - Atomic resolution images (exposed faces, structural defects, surface atomic structure)
  - Diffraction patterns from nanometer regions
  - Nanometer-scale spectroscopy – elemental composition, electronic structure, oxidation state (EELS, XEDS, AES, ...)

## Limitations

- Results generally have poor statistical value, due to the high spatial resolution
  - Supported metal catalyst:  
approx.  **$1 \times 10^9$  metal particles per  $\text{cm}^3$**
- Accurate determination of size distribution is difficult – high-throughput image analyzers are needed
- Sample preparation
- UHV / beam damage

For further information, see EM lectures, R.Tesche, 19/01/07 D.S.Su, 26/01/07



## Combination of methods for characterization of Cu catalysts

	Cu lattice spacing [Å]	Cu lattice strain [%]	$D_v$ Cu <sup>0</sup> [nm]	Cu-S <sub>o</sub> [m <sup>2</sup> /g] - XRD -	Cu S <sub>o</sub> [m <sup>2</sup> /g] - TEM -	RFC [m <sup>2</sup> /g]
Cat-1	3.619	0.0123	5.2	31.0	24.0	-
Cat-2	3.618	0.0110	5.8	26.9	-	
Cat-3	3.618	0.0110	5.8	26.9	24.5	32
Cat-4	3.618	0.0137	3.8	41.4	23.2	-
Cat-5	3.616	0.0150	4.2	37.1	26.7	-
Cat-6	3.618	0.0152	4.3	36.8	27.1	-
Cat-7	3.618	0.0128	5.0	31.4	24.7	-

## Classification of methods

<i>Active phase</i>	<i>Bulk materials / colloids</i>
<ul style="list-style-type: none"><li>➤ Chemisorption (essentially restricted to metal particles)</li><li>➤ X-ray diffraction – Line broadening analysis (crystallite size)</li><li>➤ Small-angle X-ray scattering (SAXS) (particle size)</li><li>➤ Electron microscopy</li></ul>	<ul style="list-style-type: none"><li>◆ Sieving</li><li>◆ Sedimentation</li><li>◆ Light scattering</li><li>◆ Acoustic methods</li><li>◆ Time-of flight techniques</li><li>◆ Small-angle X-ray scattering</li><li>◆ X-ray diffraction – Line broadening analysis (crystallite size)</li><li>◆ Electron microscopy</li></ul>

„Sieving is the Cinderella (Aschenputtel) of particle size analyzing methods.“

H. Heywood, Proc. Particle size Anal. Conf., Bradford, Soc. Anal. Chem, 186 (1970) 1.

Mesh size = number of wires per linear inch



sieve designation standard	sieve designation alternate "mesh"	nominal sieve opening (in.)	nominal wire diameter (mm)
125 mm	5	5	8
75 mm	3	3	6.3
63 mm	2 1/2	2.5	5.6
53 mm	2.12	2.12	5
50 mm	2	2	5
2 mm	No. 10	0.0787	0.9
1 mm	No. 18	0.0394	0.56
850 $\mu\text{m}$	No. 20	0.0331	0.5
500 $\mu\text{m}$	No. 35	0.0197	0.315
150 $\mu\text{m}$	No. 100	0.0059	0.1
53 $\mu\text{m}$	No. 270	0.0021	0.036
20 $\mu\text{m}$	No. 635	0.0008	0.02

- ▶ Hard work, but simple and inexpensive
- ▶ Important for accuracy and reproducibility
  - ▶ Calibration with a calibration powder
  - ▶ Standard operating procedures should be adopted



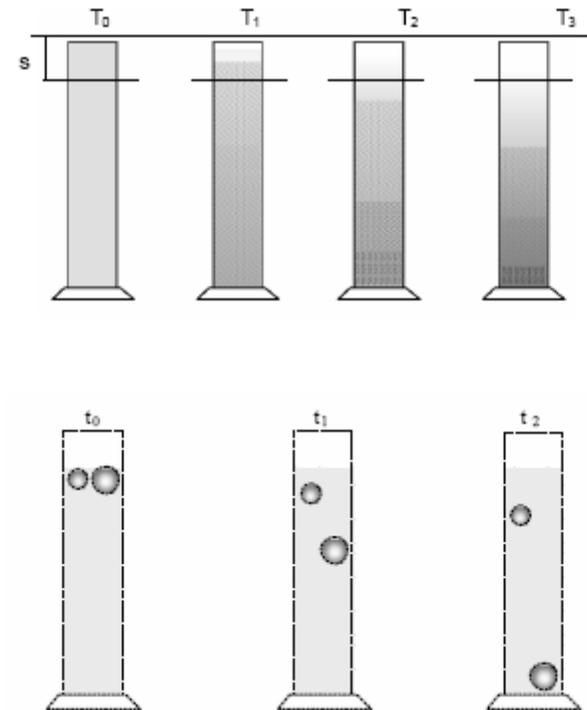
T. Allen, Particle Size Measurement, Volume 1, Powder sampling and particle size measurement methods, Chapman & Hall, London 1997.

ASTM standards - examples

## Particle sizing by measurement of settling velocity

### Classification

- I. According to the position of the particles at the beginning of the measurement
  - a) Homogeneous methods
  - b) Line-start methods
- II. Place of quantity measurement
  - a) Incremental methods (thin layer)
  - b) Cumulative methods
- III. Force field
  - a) Gravitational methods
  - b) Centrifugal methods ( $d < 1\mu\text{m}$ )
- IV. Measurement principle
  - a) Gravimetric
  - b) Absorption of electromagnetic radiation
  - c) Suspension density



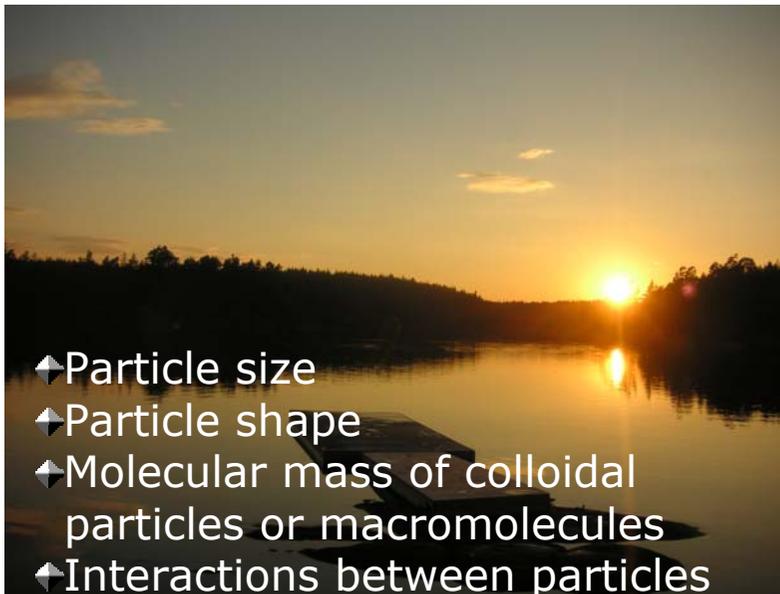
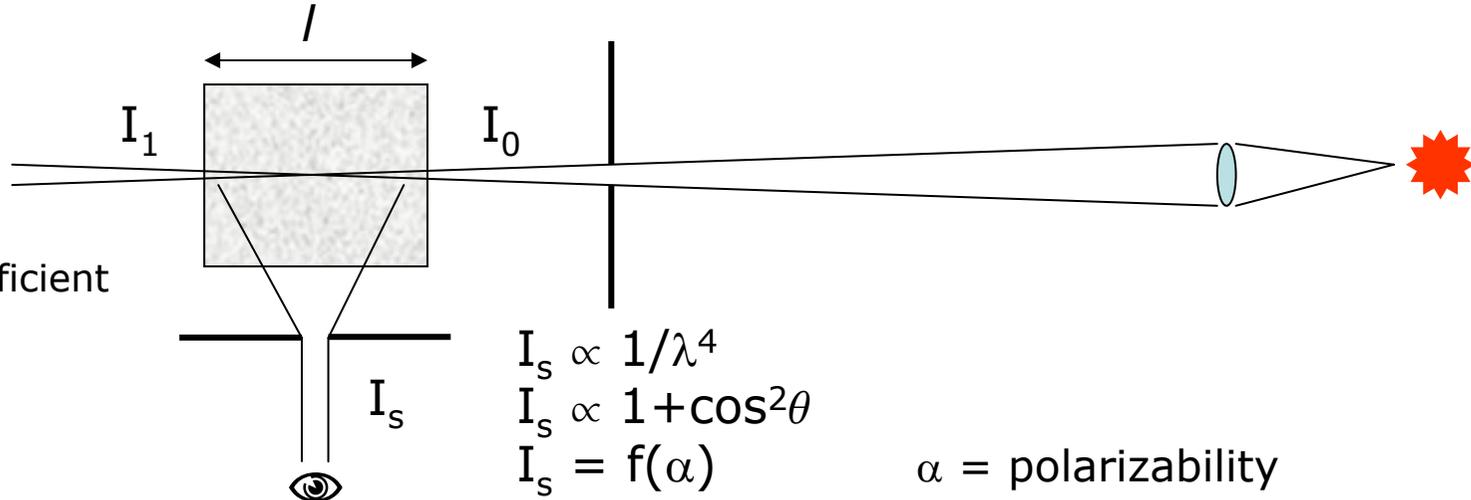
Paul A. Webb Micromeritics, January 04

C. Bernhardt, Particle Size Analysis, Classification and Sedimentation methods, Chapman & Hall, London 1994.

Turbidity

$$I_1 = I_0 e^{-\tau l}$$

$\tau$  turbidity coefficient



- ◆ Particle size
- ◆ Particle shape
- ◆ Molecular mass of colloidal particles or macromolecules
- ◆ Interactions between particles and between particles and continuum (solvent)

**Static light scattering (Laser diffraction)**

Measurement of time-averaged intensity of scattered light

◆ Rayleigh scattering  $d < \lambda/20$

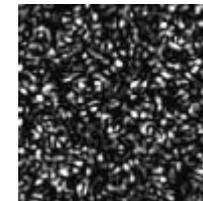
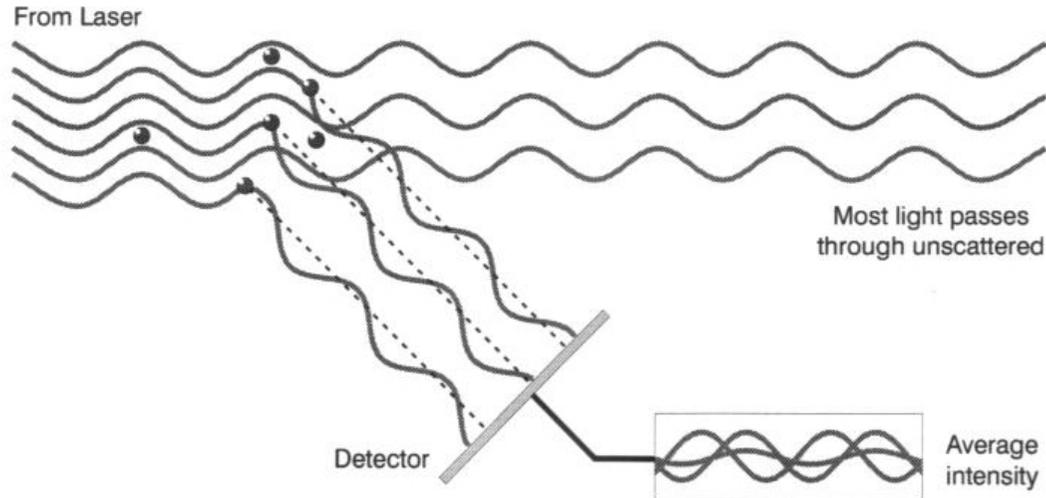
$$I_s = (8/3)\pi I_0 (2\pi/\lambda_0)^4 \alpha^2$$

◆ Mie scattering  $d \geq \lambda/20$

Multiple photon scattering at the particle → interference → angular dependence of the sample scattering intensity

**Dynamic light scattering**

Measures Brownian motion and relates this to the size of the particles



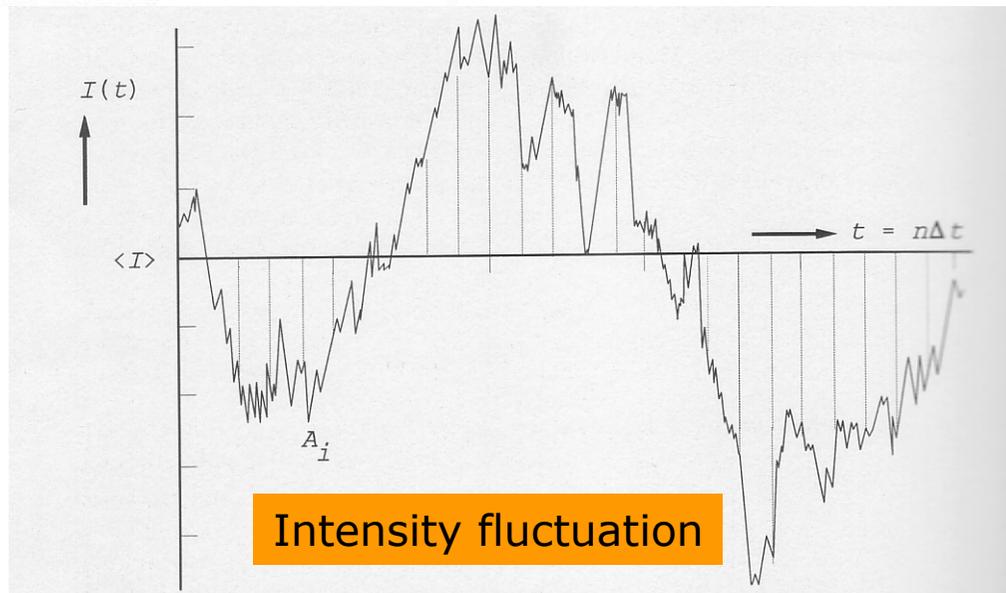
Speckle pattern

The scattered light falling on the detector.

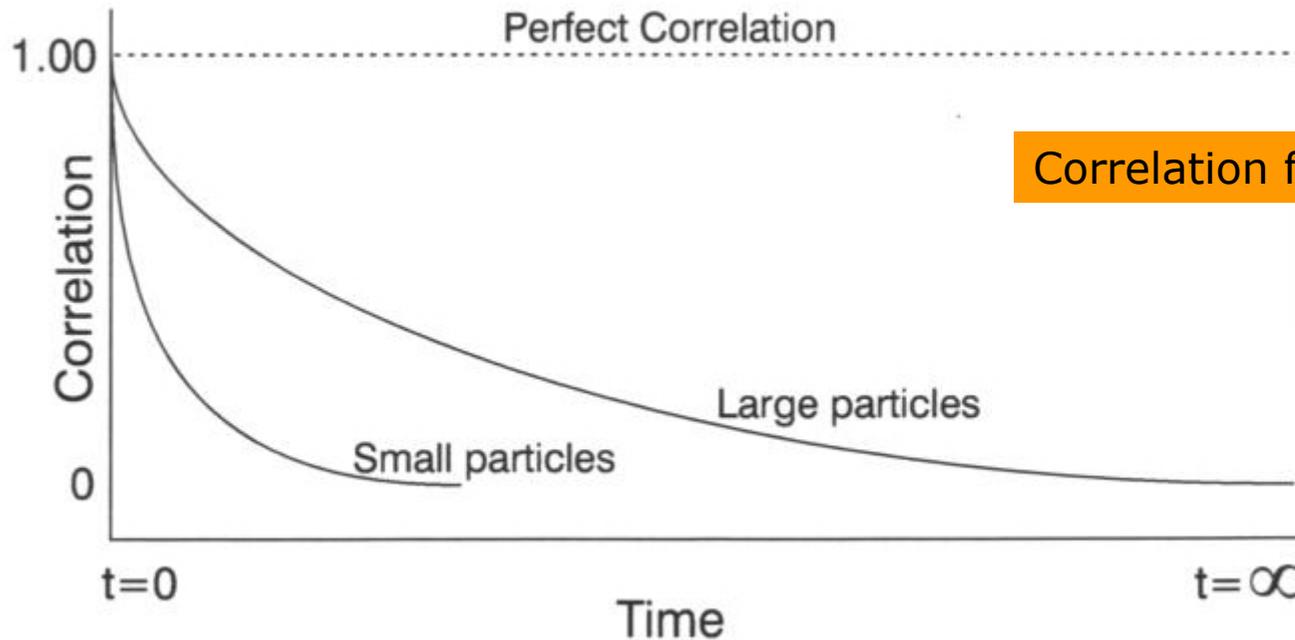
The particles are moving due to Brownian motion

The correlation is reducing with time

Time scale: nanoseconds or microseconds



Correlation = degree of similarity between the intensity at  $t$  and  $(t+\delta t)$



$$g_1(Q, t) = e^{-DQ^2t} = e^{-\frac{t}{\tau}}$$

$Q$  = scattering vector

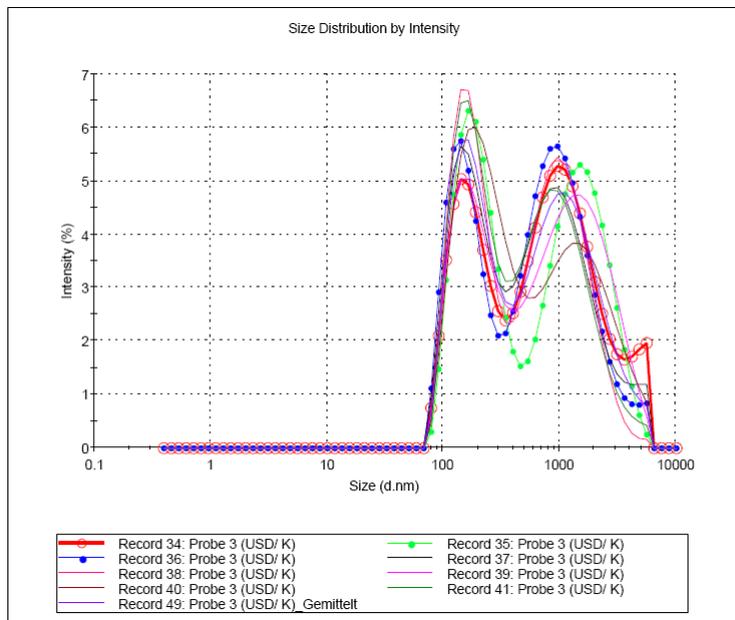
$$Q = \frac{4\pi n_M}{\lambda} * \sin(\theta)$$

The relationship between the size of a particle and its speed due to Brownian motion is given by the Stokes-Einstein equation

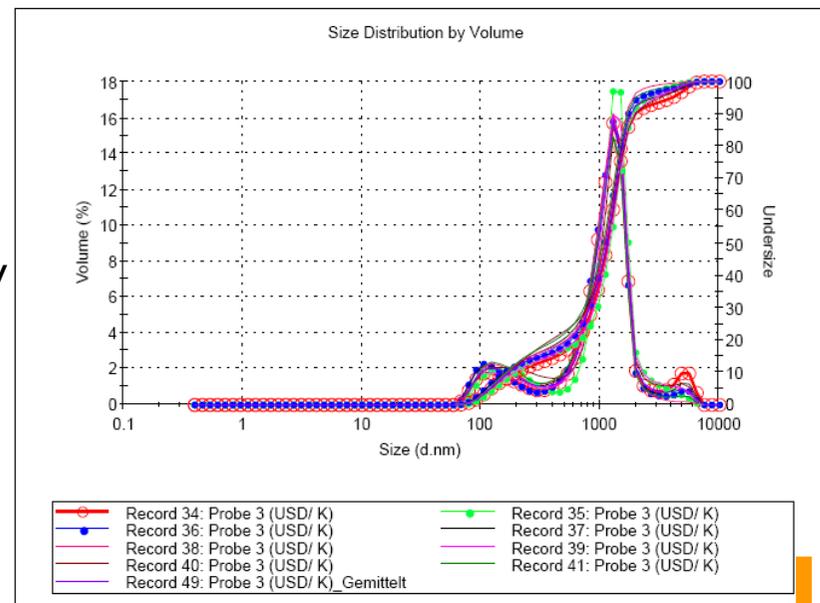
$$D_0 = \frac{kT}{6\pi\eta R}$$

$D$  = Diffusion coefficient  
 $k$  = Boltzmann constant  
 $T$  = absolute temperature  
 $\eta$  = dynamic viscosity of the solvent  
 $R$  = radius of the particle

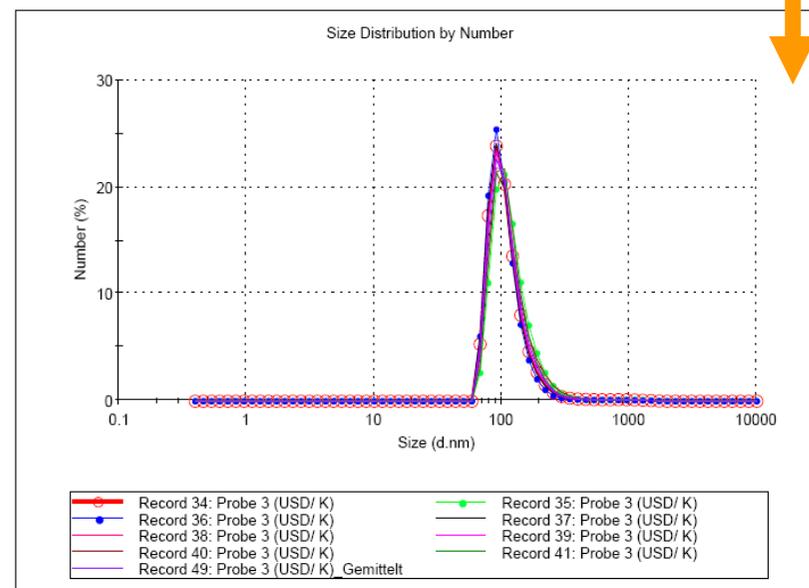
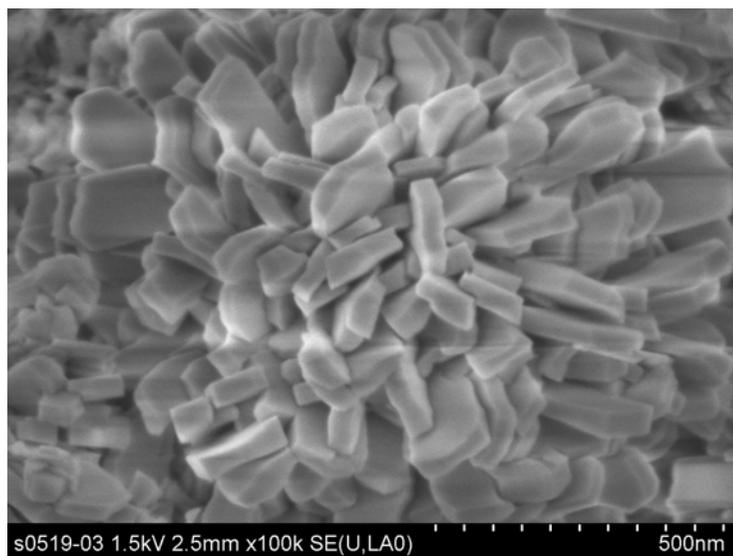
The rate of decay for the correlation function is related to the particle size



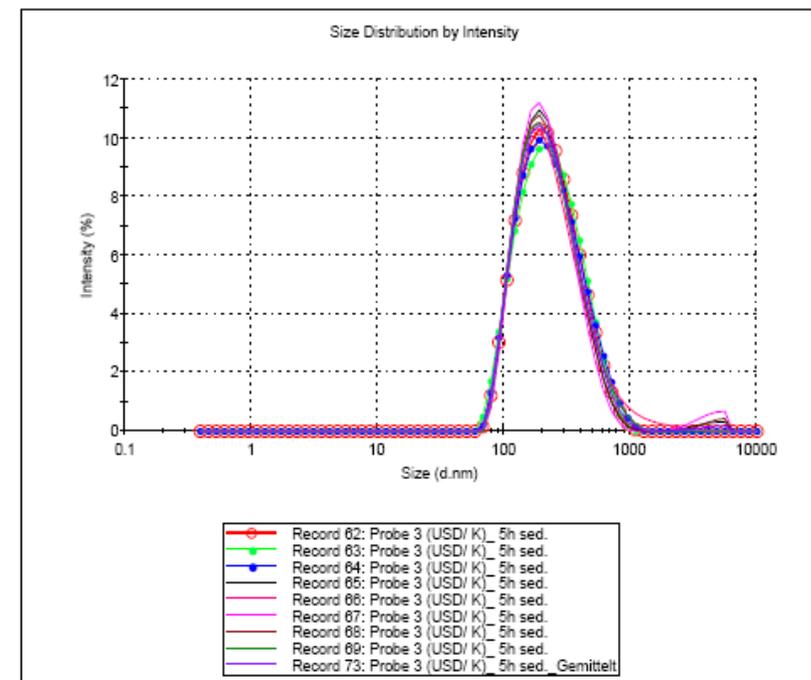
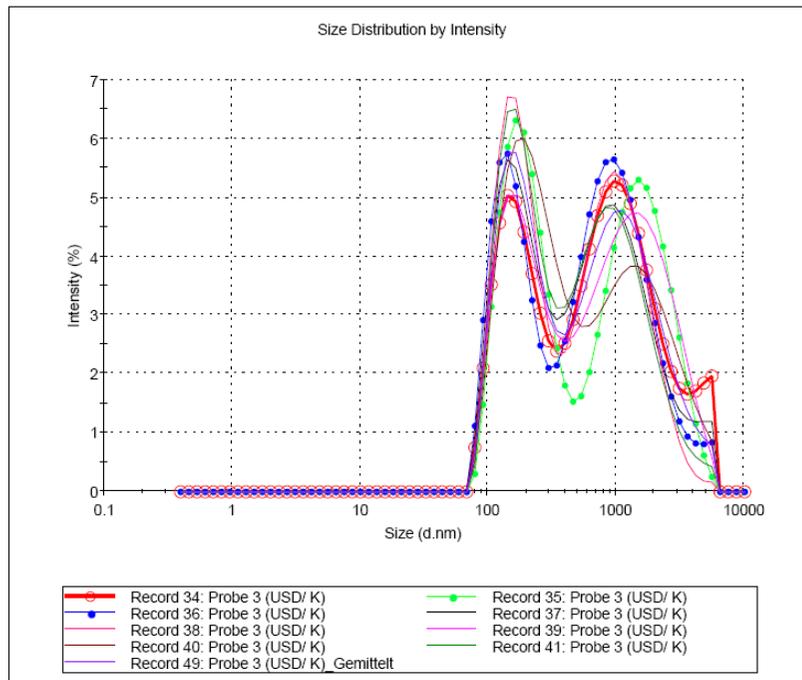
Mie theory



$n = 1.59$

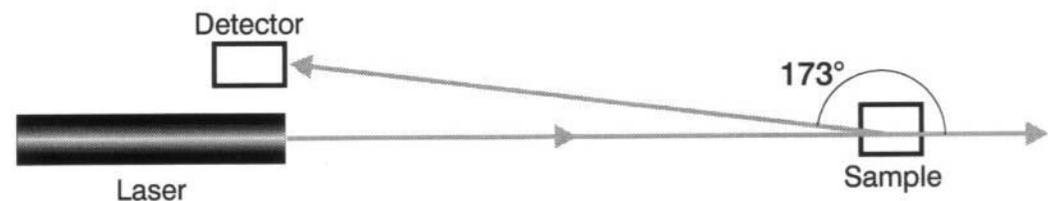


## 5h sedimentation

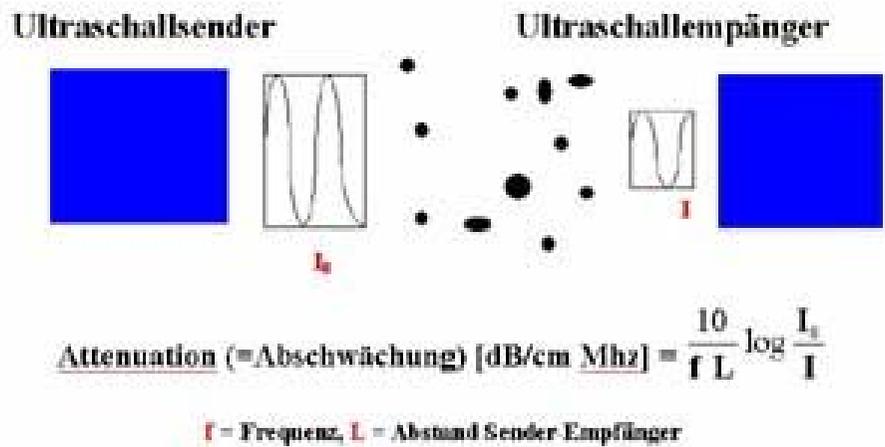


## Limitations

- Only diluted suspensions can be measured to prevent multiple scattering of the light after scattered off the particle
  - 173° detection optics – backscatter detection (Zetasizer Nano ZS) reduces multiple scattering



- Implementation of Diffusing Wave Spectroscopy (DWS) – analysis of autocorrelation functions from multiply scattered light
  - Analysis of concentrated suspensions using fiber-optic probes
- Discremination between primary particles and agglomerates not possible

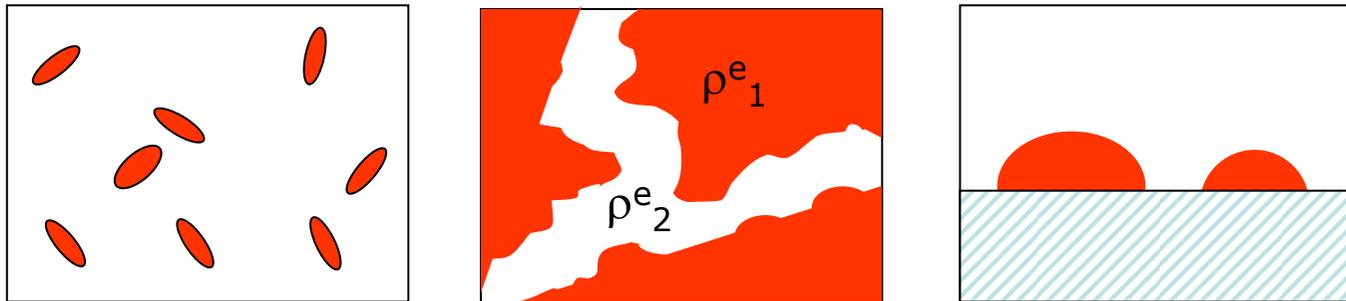


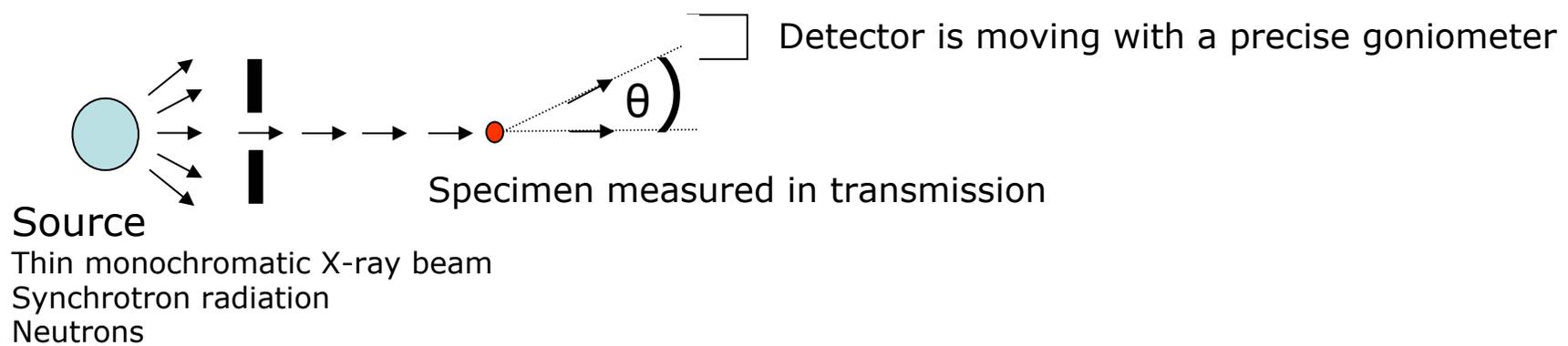
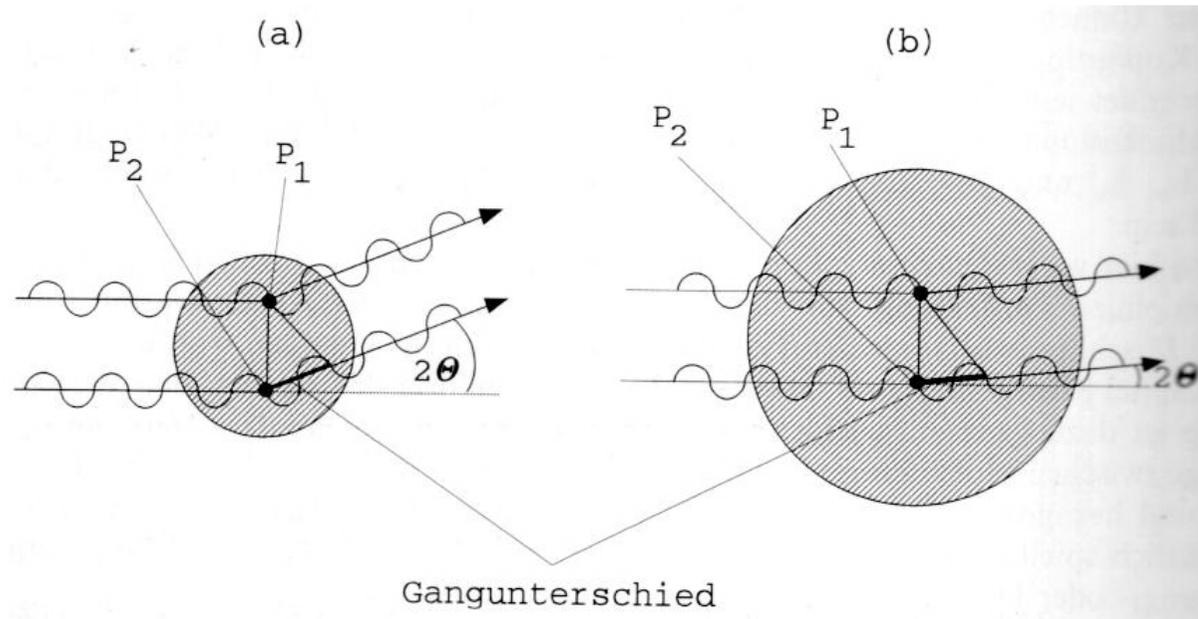
[http://www.quantachrome.de/messmethoden/index\\_partikelgroessenbestimmung.html](http://www.quantachrome.de/messmethoden/index_partikelgroessenbestimmung.html)

Mean particle size (from 1 nm to 100 nm), specific surface area and particle shape

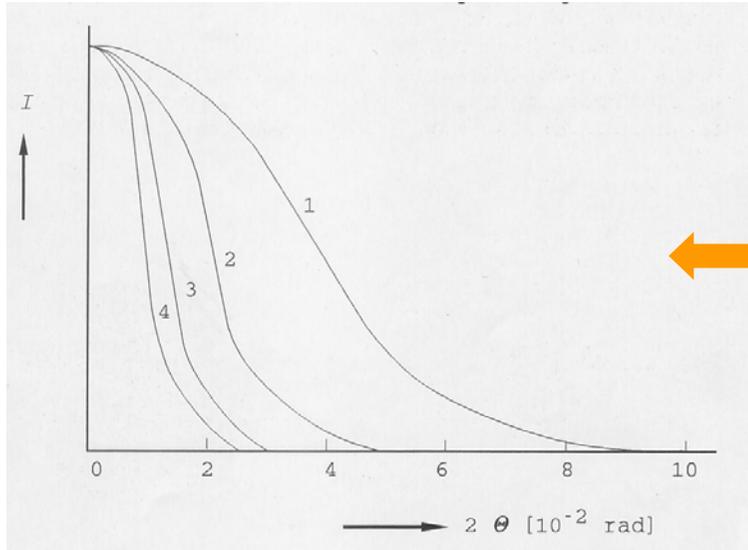
Principle:

Scattering of X-rays by small domains of uniform matter (crystalline or amorphous), for which the electron density  $\rho^e$  is different from the continuous medium





H.-D. Dörfler, Grenzflächen- und Kolloidchemie, VCH, Weinheim, 1994.

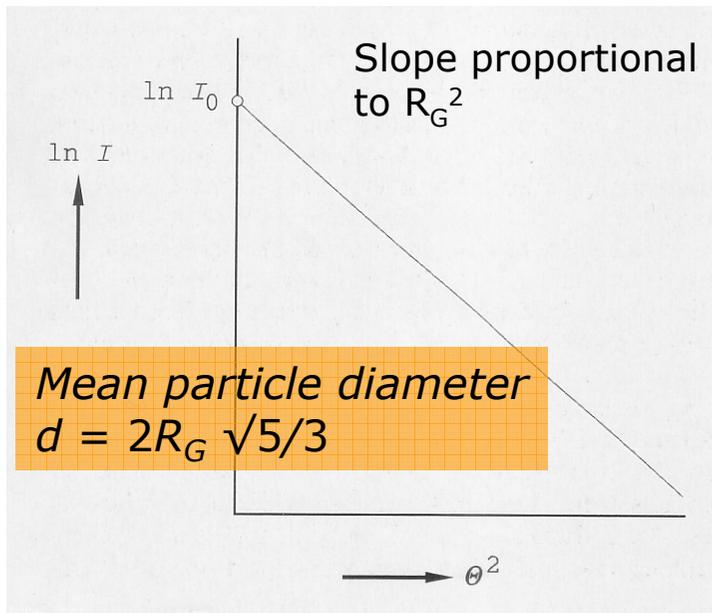


The central peak scattered intensity gets broader as the domain size (particles, voids) decreases



SAXS parameters (mean size / size distribution / specific surface area) are derived from analysis of the profile of the SAXS curve

$I(s)$  scattered intensity  
 $s$  scattering vector  $s = (2 \sin \theta) / \lambda \approx 2\theta / \lambda$



### Guinier

In case of dilute system and identical particle shape the SAXS curve can be represented by an exponential approximation:

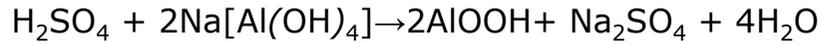
$$I(s) = (\rho^e_1 - \rho^e_2)^2 V^2 \exp(-4\pi^2 s^2 R_G^2 / 3)$$

$R_G$  radius of gyration = radius of a hypothetical sphere around the center of symmetry

$V$  volume of the domain

Relation between  $R_G$  and the dimension of regular solids:  $R_G^2 = (3/5)R^2$

$R$  radius of a sphere



starting solutions:

Educt A:  $\text{Na}[\text{Al}(\text{OH})_4] + \text{NaOH}$  in  $\text{H}_2\text{O}$  (pH 13.5)

Educt B:  $\text{H}_2\text{SO}_4$  (0.5 mol/l)

T = 65°C, pH 9, solid concentration of boehmite of about 1.5% by weight

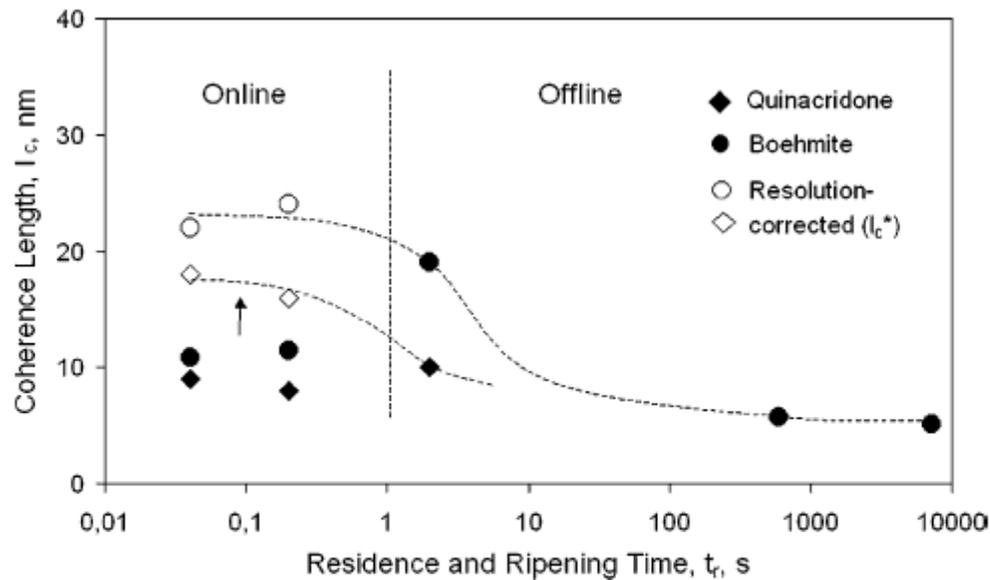


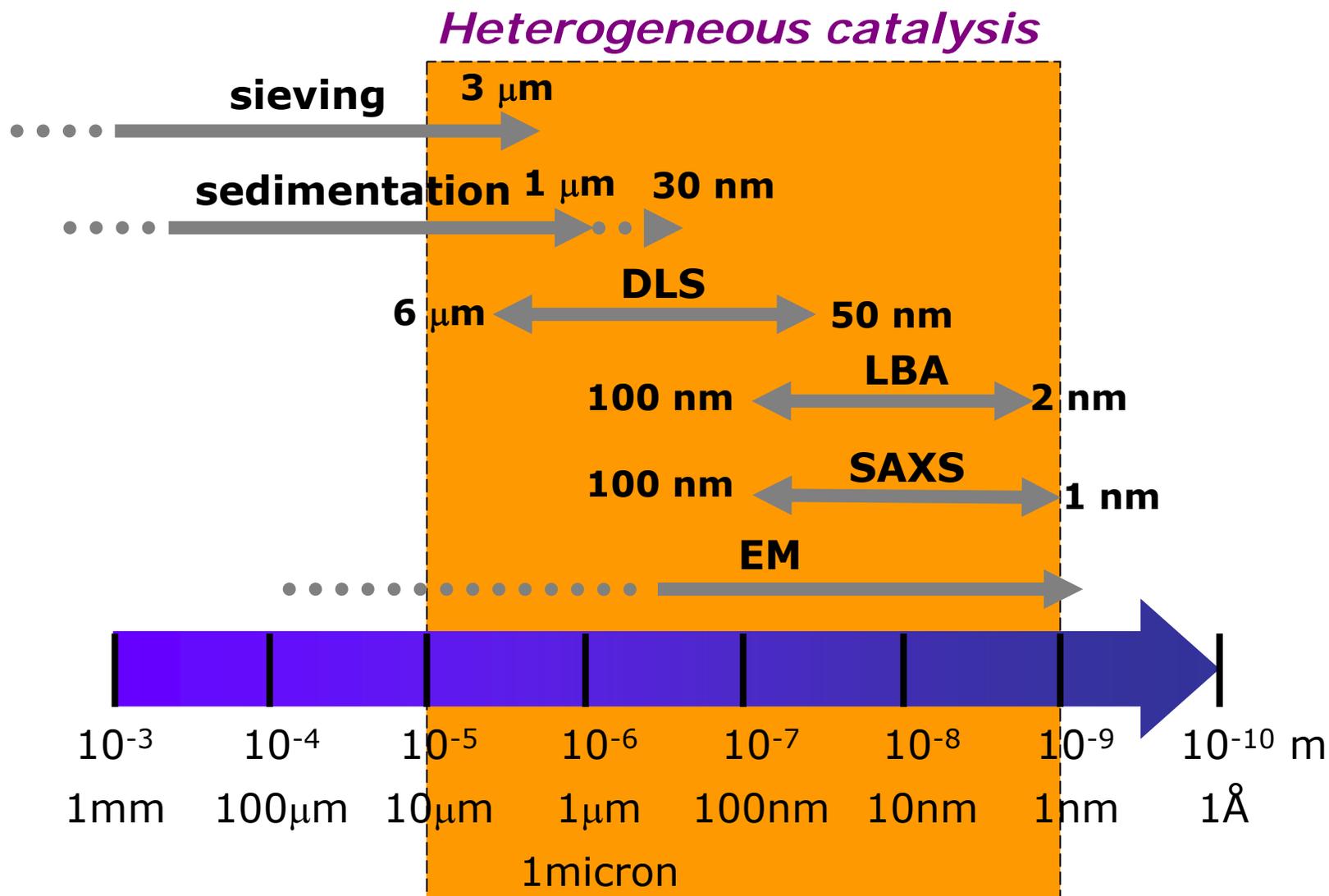
Fig. 17. Online and offline SAXS results on free-jet and on ripened suspensions. Effect of the residence and ripening time  $t_r$  on the coherence lengths  $l_c$  and  $l_c^*$  (standard precipitation conditions).

H. Haberkorn et al., Journal of Colloid and Interface Science 259 (2003) 112.

### *Advantages of SAXS*

- The method can be used for analysis of powders in either dry state or when suspended in a dispersing medium
- Little interference due to multiple scattering in dispersions with high solids concentrations
- Sensitive to the presence of agglomerates, hence, the technique can be used to distinguish primary particles from agglomerates and in some cases the morphology of the agglomerates
- Complementary to LBA

No routine analysis!

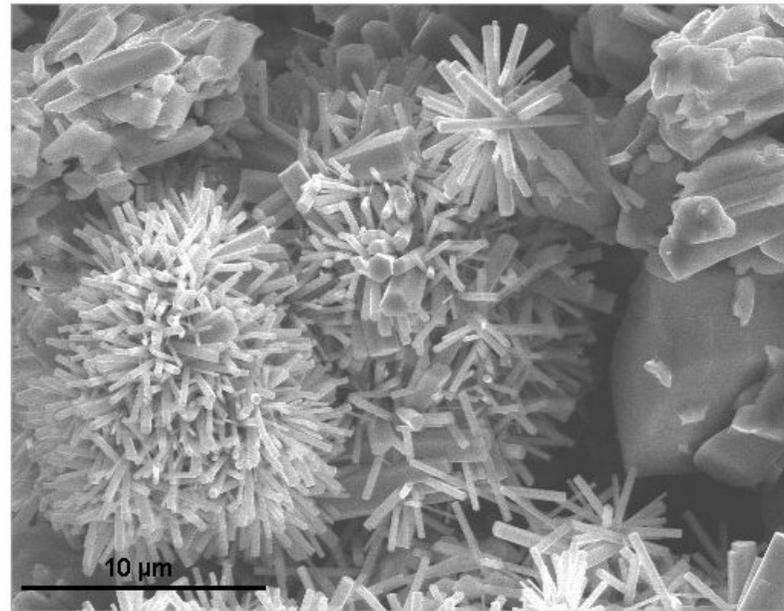


- The diversity of particles sizes (from mm to nm) and states of aggregation (solid, liquid, gaseous) account for a large variety of particle size measurement methods.
- A combination of two or more methods would be necessary to obtain an unambiguous evaluation of particle size.
- Size distribution,
- Spatial distribution (accessibility/ phase interaction) and
- Particle shape / microstructure  
are more critical for the performance of a catalysts than the mean particle size.

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