1. Nanotechnology: Overview of Aerosol Manufacture of Nanoparticles

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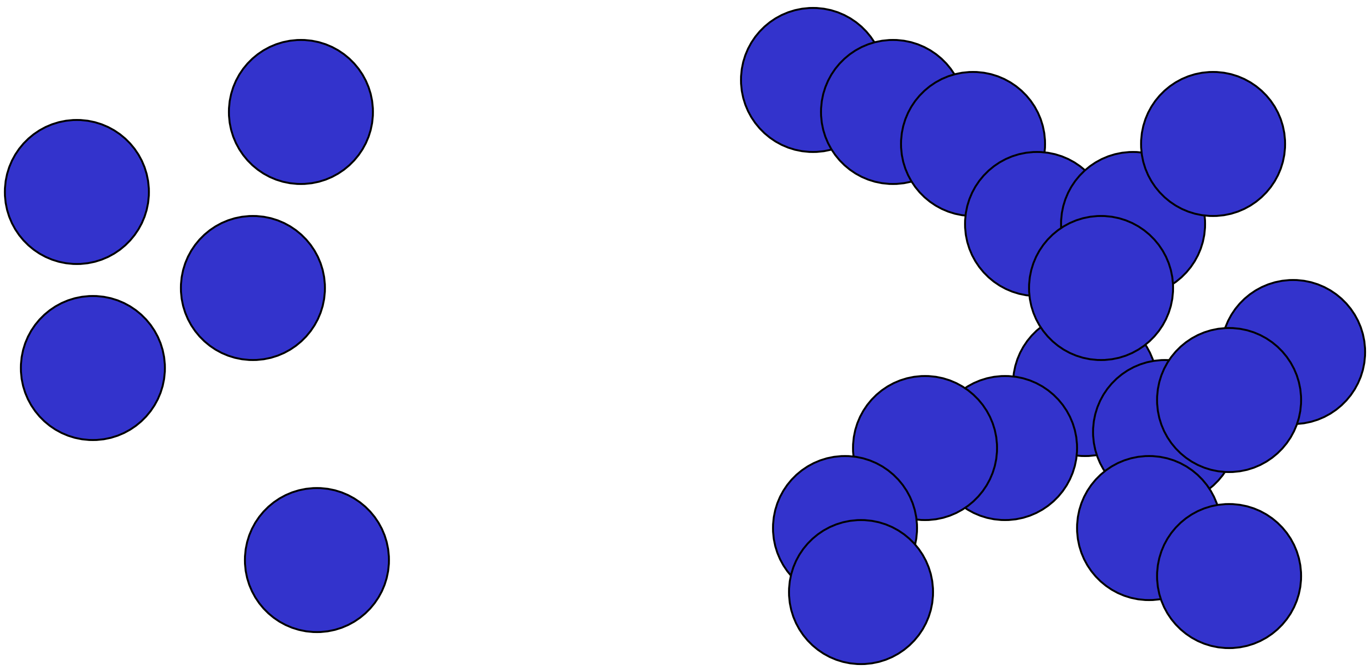
Sponsored by
Swiss National Science Foundation and
Swiss Commission for Technology and Innovation

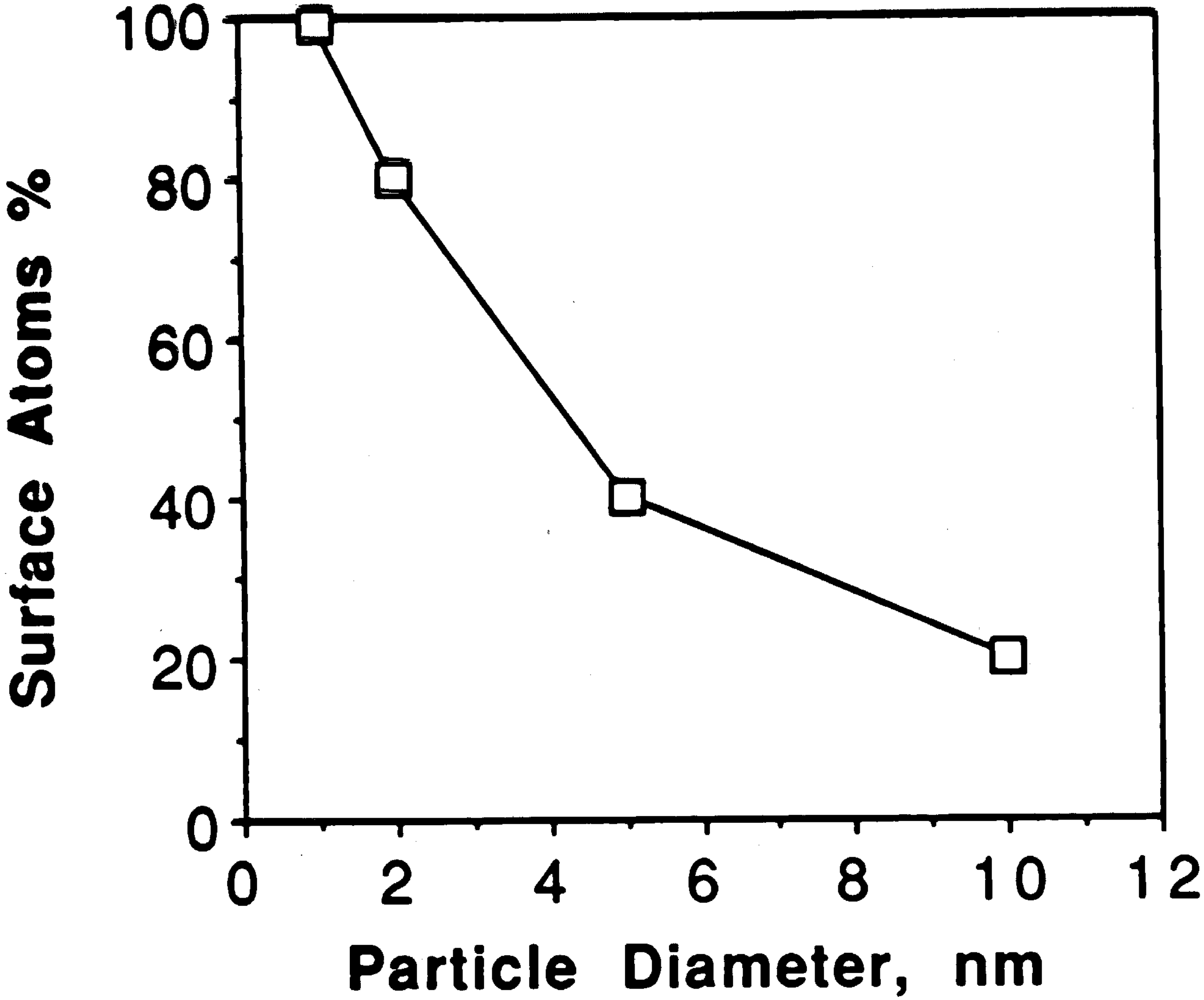
Nanoparticles

1 - 100 nm (at least into two dimensions)

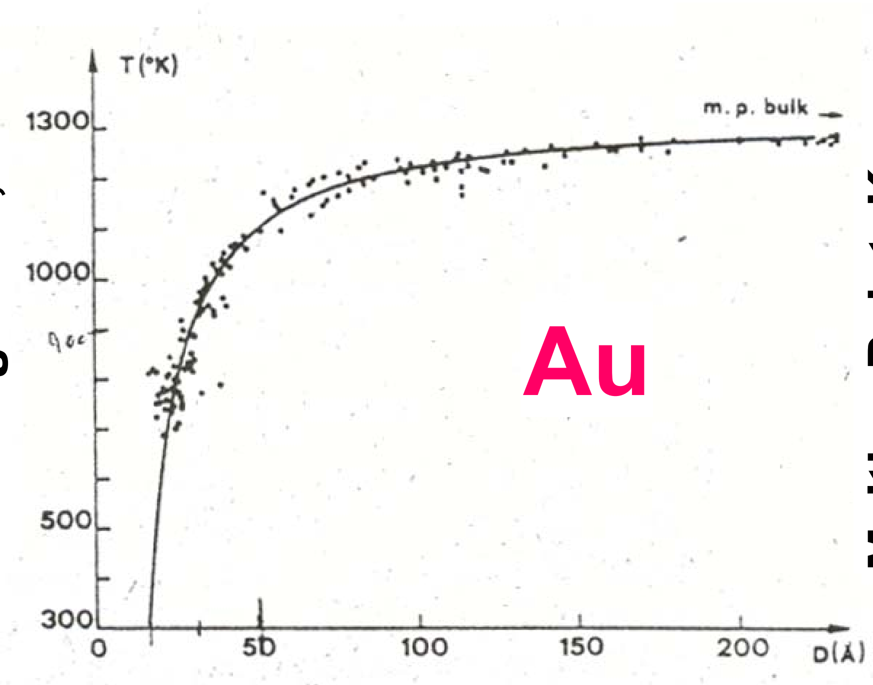


Remember, the thickness (diameter) of a human hair is 50,000 - 100,000 nm!

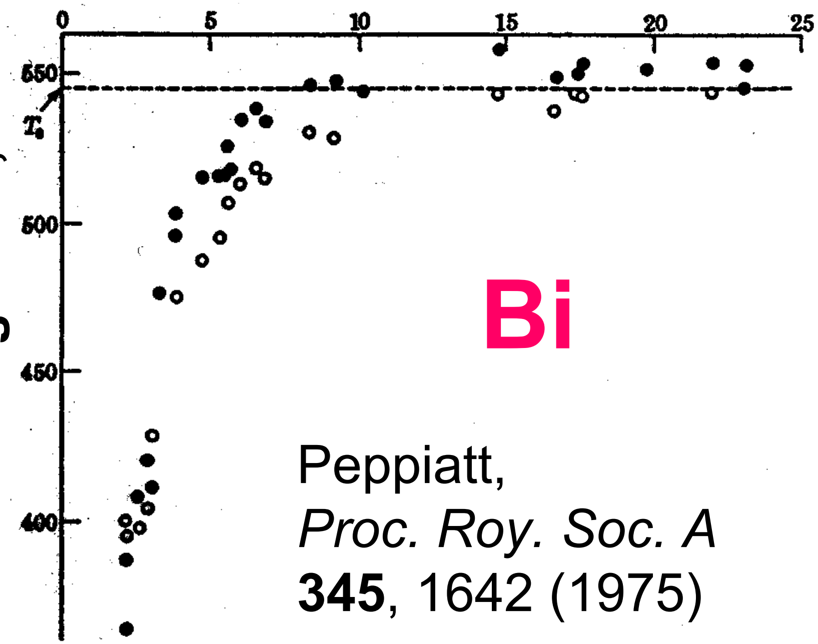
Ratio of Surface Atoms to Total Atoms in a Single Particle (Ichinose et al., 1992)



The Melting Point Decreases with Decreasing Nanoparticle Size



Buffat and Borel,
Phys. Rev. A **13**, 2287 (1976)



Peppiatt,
Proc. Roy. Soc. A
345, 1642 (1975)

Applications of Nanoparticles

- Large area per gram (adsorbents, membranes)
- Stepped surface at the atomic level (catalysts)
- Easily mix in gases and liquids (reinforcers)
- Superfine particle chains (recording media)
- Easily carried in an organism (new medicine)
- Superplasticity
- Cosmetics that last way into the night ...

Some people believe that nanoparticles are a new state of matter!

Comparison of wet- & dry-technology

Dry-technology (aerosol):

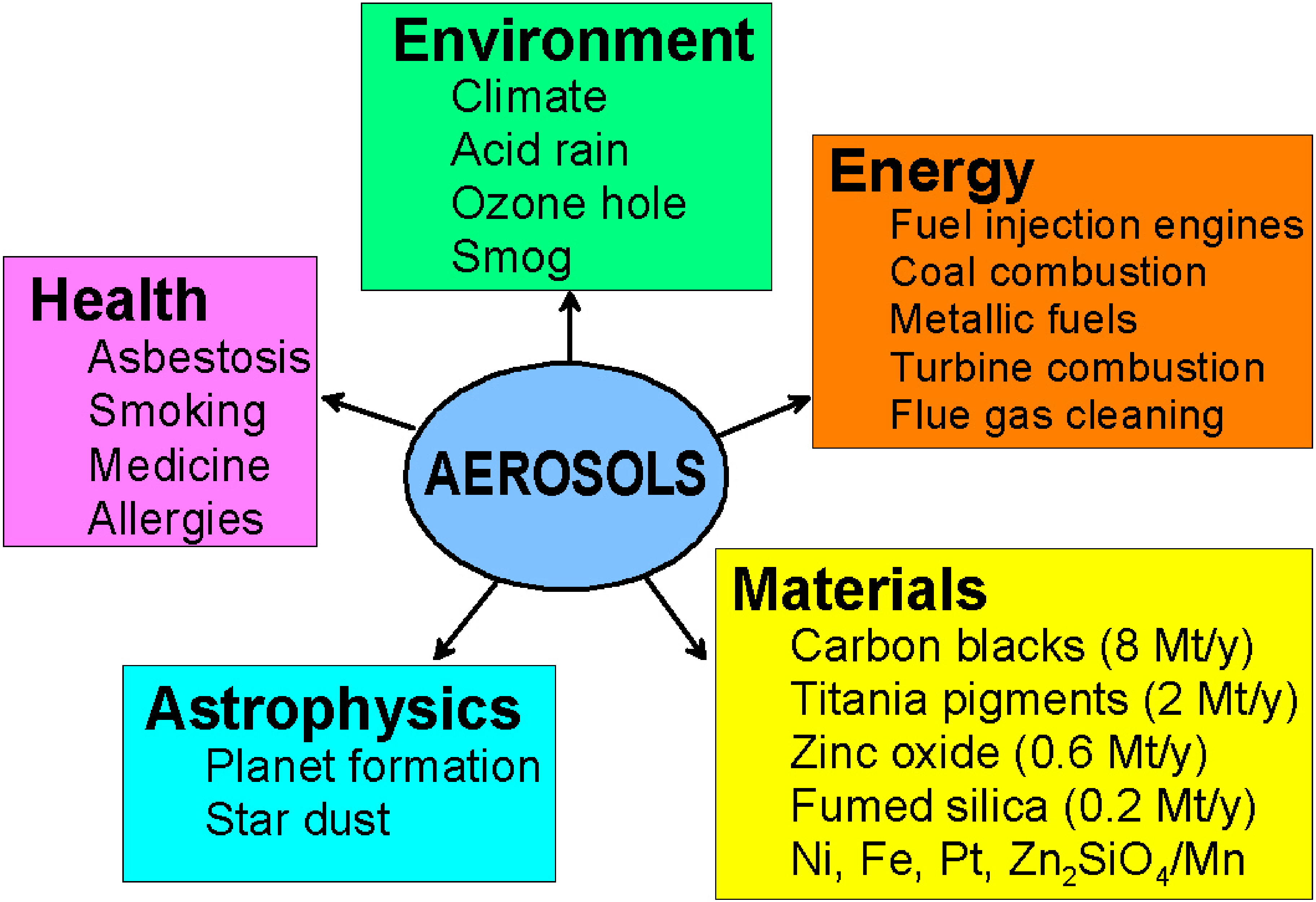
- Mix precursor
- Dry flame conversion
- Filtration
- Milling

Wet-technology:

- Dissolve
- Add precipitation agent
- Temperature/Pressure treatment
- Filtration
- Washing
- Drying
- Calcination
- Milling

Short process chains, very short process time: Reduced costs, green processes

http://www.stanfordmaterials.com/zr.html#info

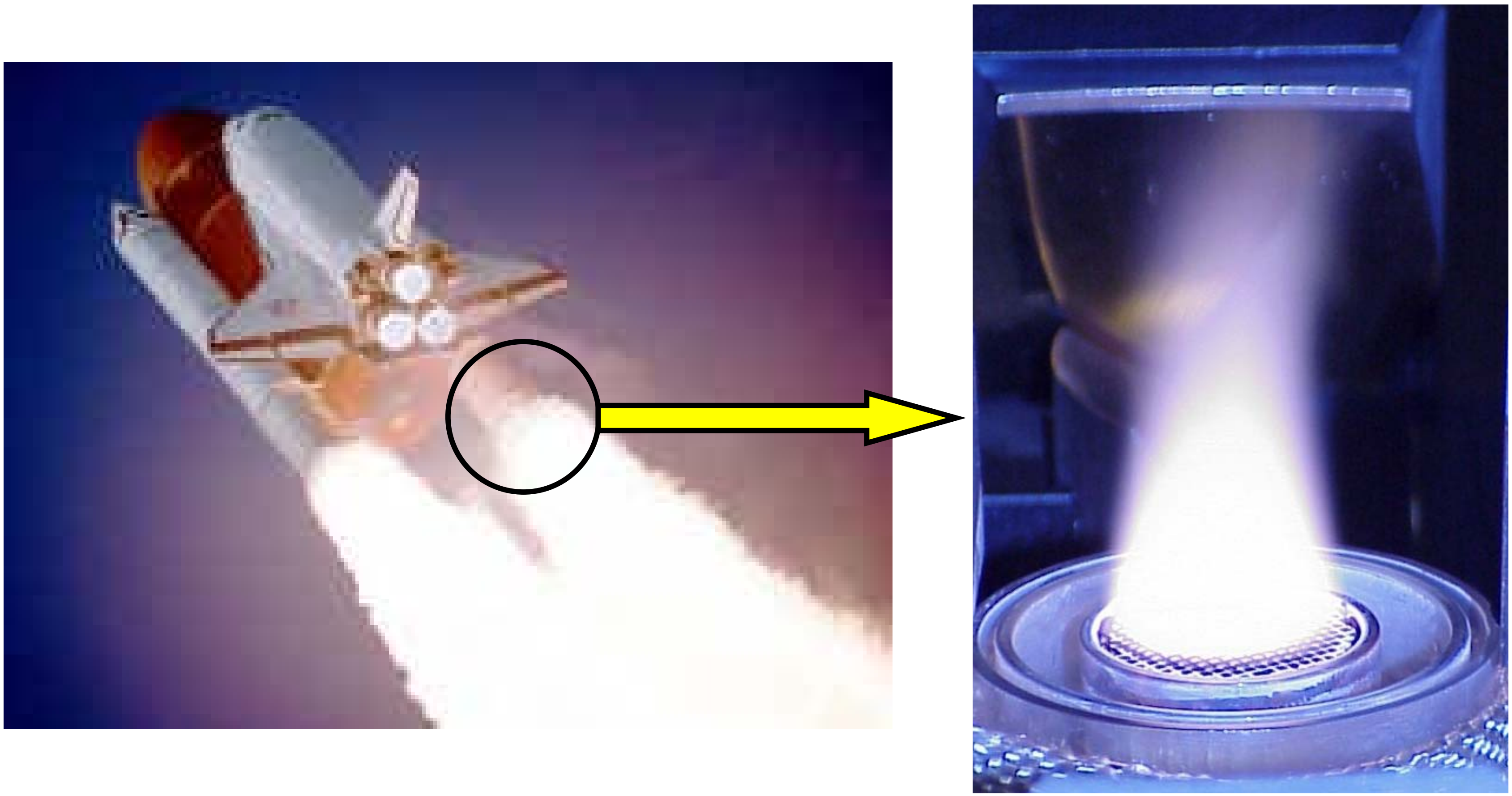

Environment
Climate
Acid rain
Ozone hole
Smog
Energy
Fuel injection engines
Coal combustion
Metallic fuels
Turbine combustion
Flue gas cleaning
Health
Asbestosis
Smoking
Medicine
Allergies
AEROSOLS
Astrophysics
Planet formation
Star dust
Materials
Carbon blacks (8 Mt/y)
Titania pigments (2 Mt/y)
Zinc oxide (0.6 Mt/y)
Fumed silica (0.2 Mt/y)
Ni, Fe, Pt, Zn_2SiO_4/Mn

AEROSOL MANUFACTURING OF NANOPARTICLES

Wegner, Pratsinis *Chem. Eng. Sci.* **58**, 4581-9 (2003).

Product Particles	Volume t/y	Value $/y	Process	Coagulation Coalescence	Surface Growth
Carbon black	**8 M**	**8 B**	**Flame, C_xH_y**	**X**	**X**
Titania	**2 M**	**4 B**	**Flame, $TiCl_4$**	**X**	**?**
Fumed Silica	**0.2 M**	**2 B**	**Flame, $SiCl_4$**	**X**	**-**
Zinc Oxide	**0.6 M**	**0.7B**	**Hot –Wall, Zn**	**X**	**X**
Filamentary Ni	**0.04M**	**~0.1B**	**Hot-Wall, $Ni(CO)_4$**	**X**	**X**
Fe, Pt, Zn_2SiO_4/Mn	**~0.02M**	**~0.3B**	**Hot-Wall, Spray…**	**X**	**X**

A rough analogy to flame aerosol reactors

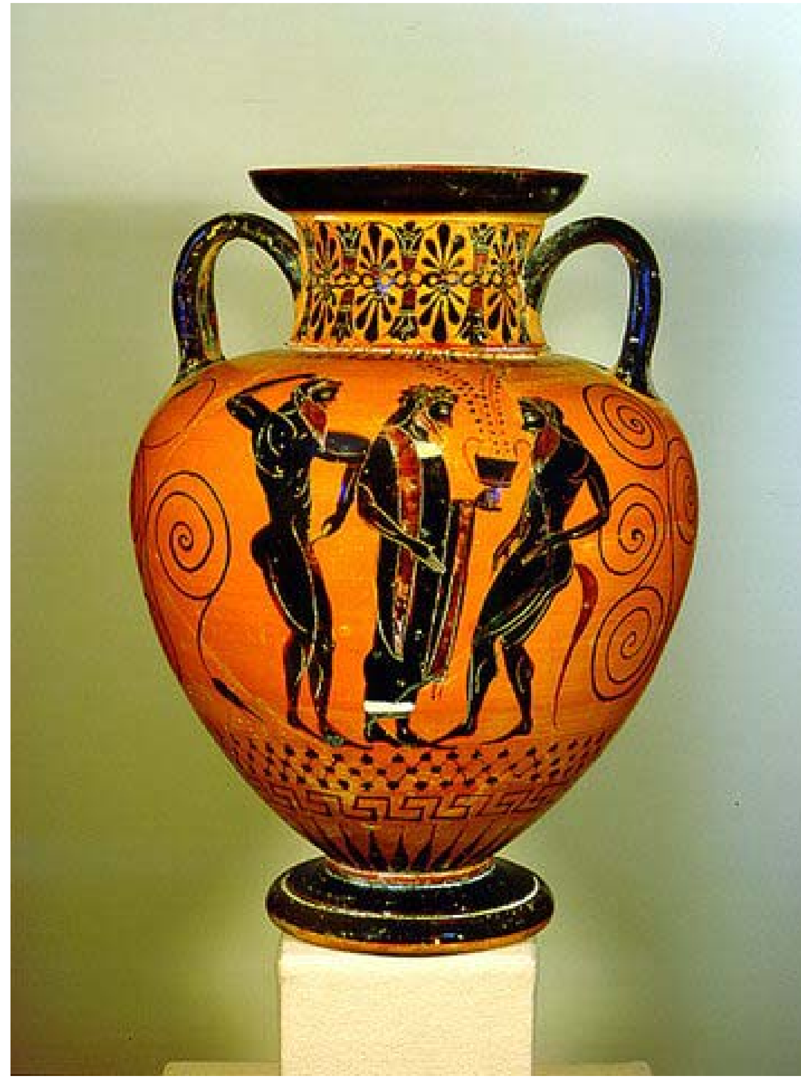


… just well attached to the ground !

Lampblack first was produced in quantity by the ancient Chinese

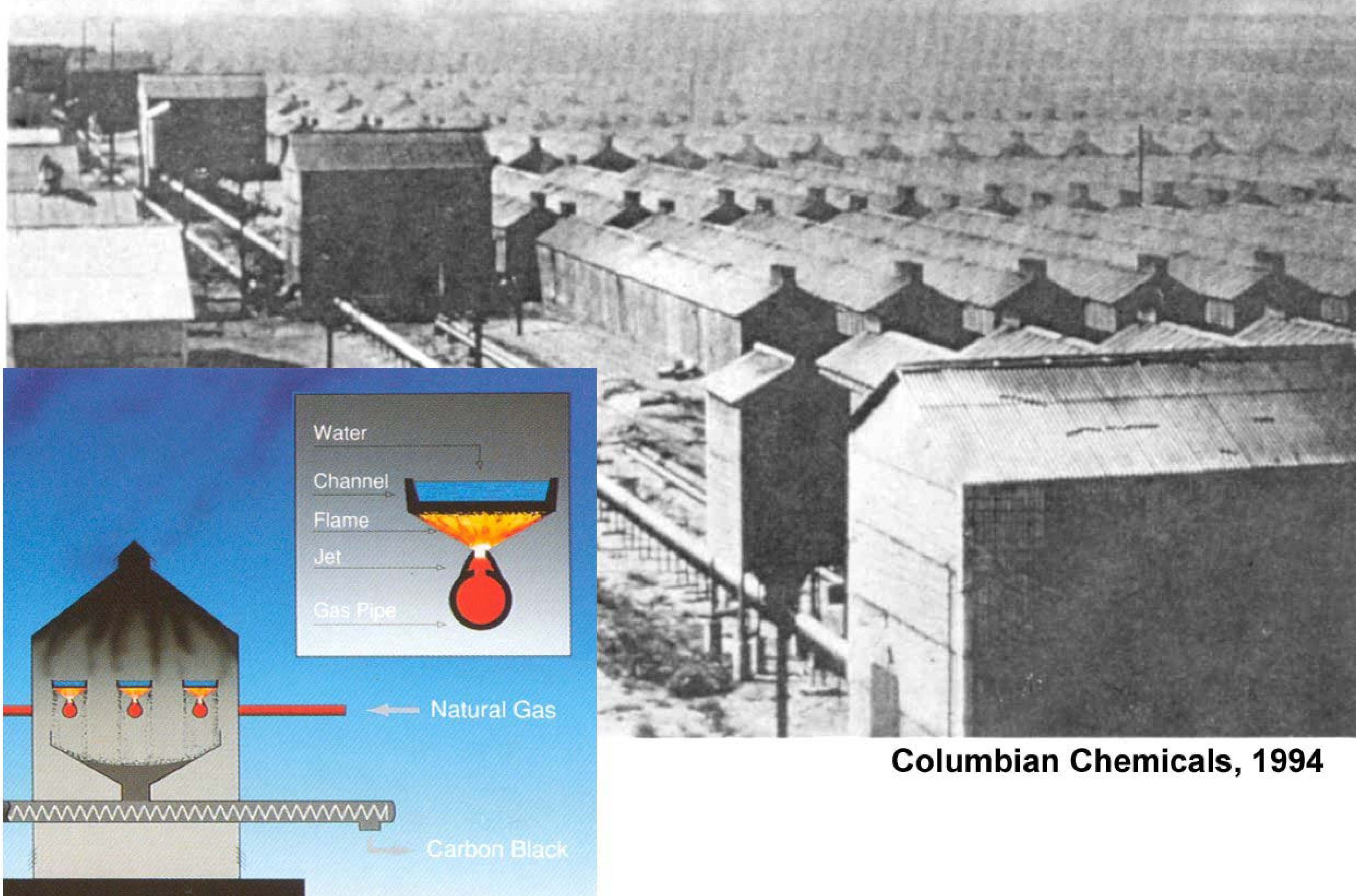
Ulrich, 1984

Attic red-figure hydria, 430-420 BC, Abdera Archeological Museum, Greece



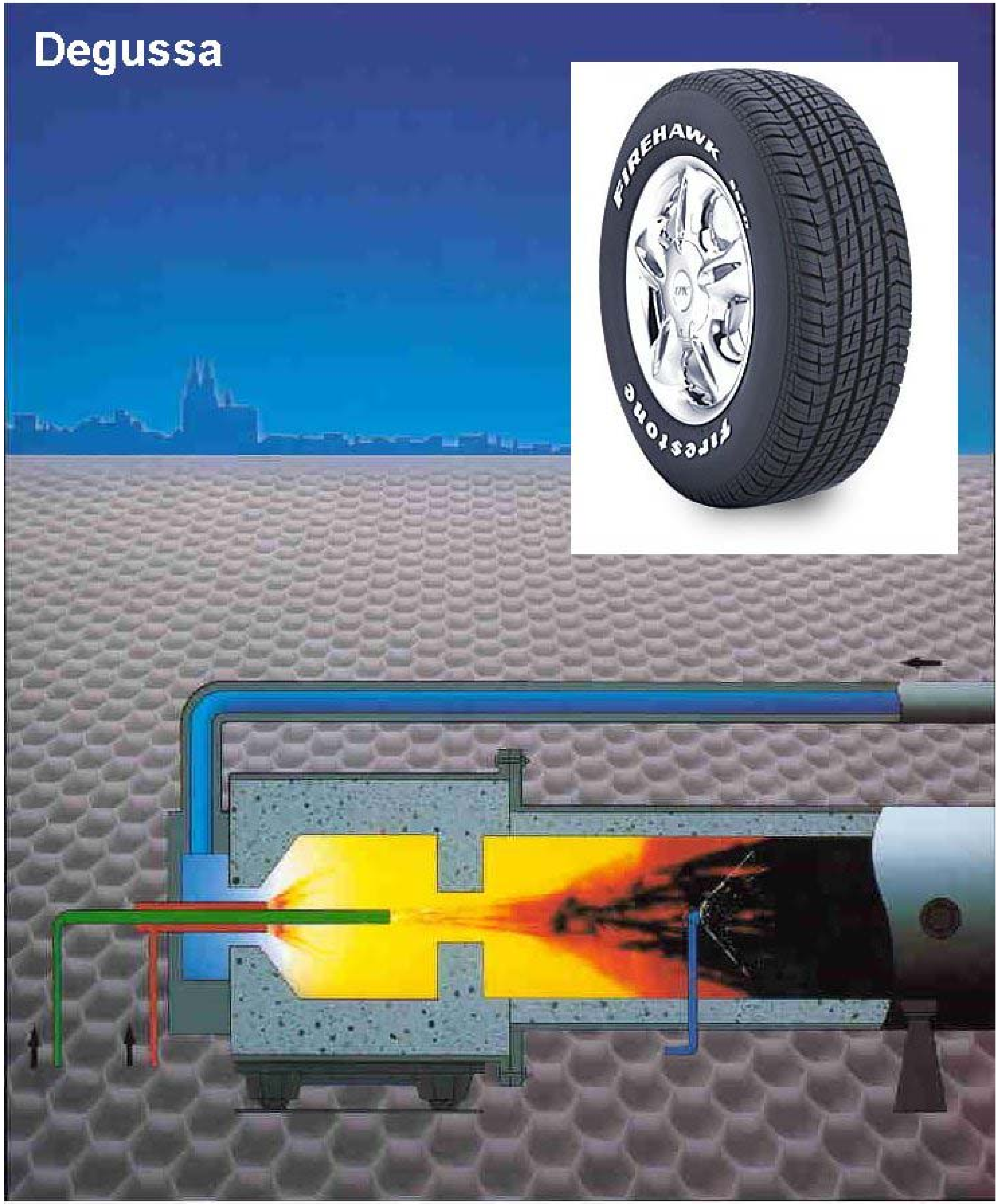
Attic black-figure amphora, 540-530 BC, Museum of Cycladic Art, Athens, Greece

Channel Plant, Texas Panhandle, 1940's



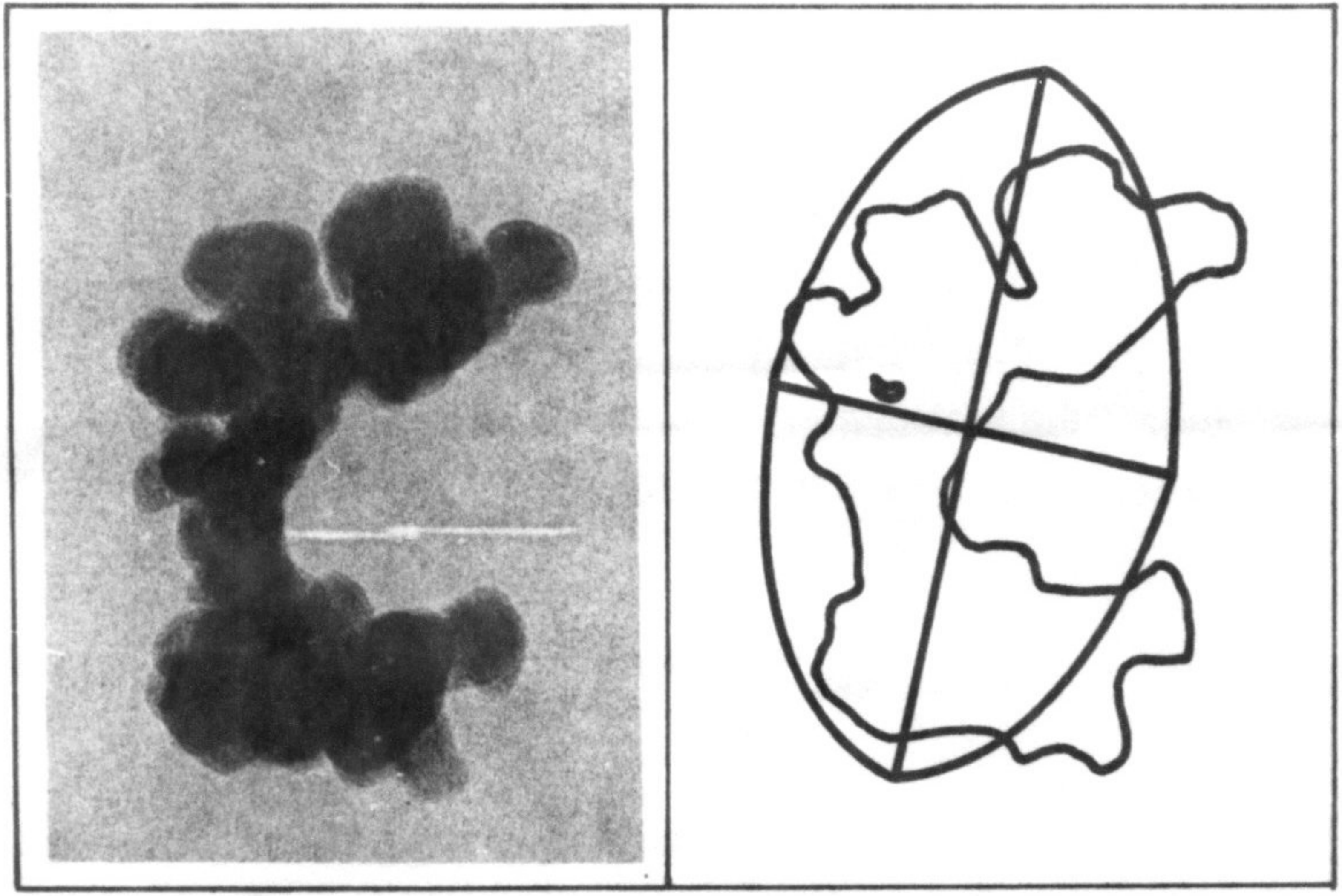
Columbian Chemicals, 1994

Degussa, 1996



Furnace Process for Carbon Black Production

Carbon Black Agglomerate

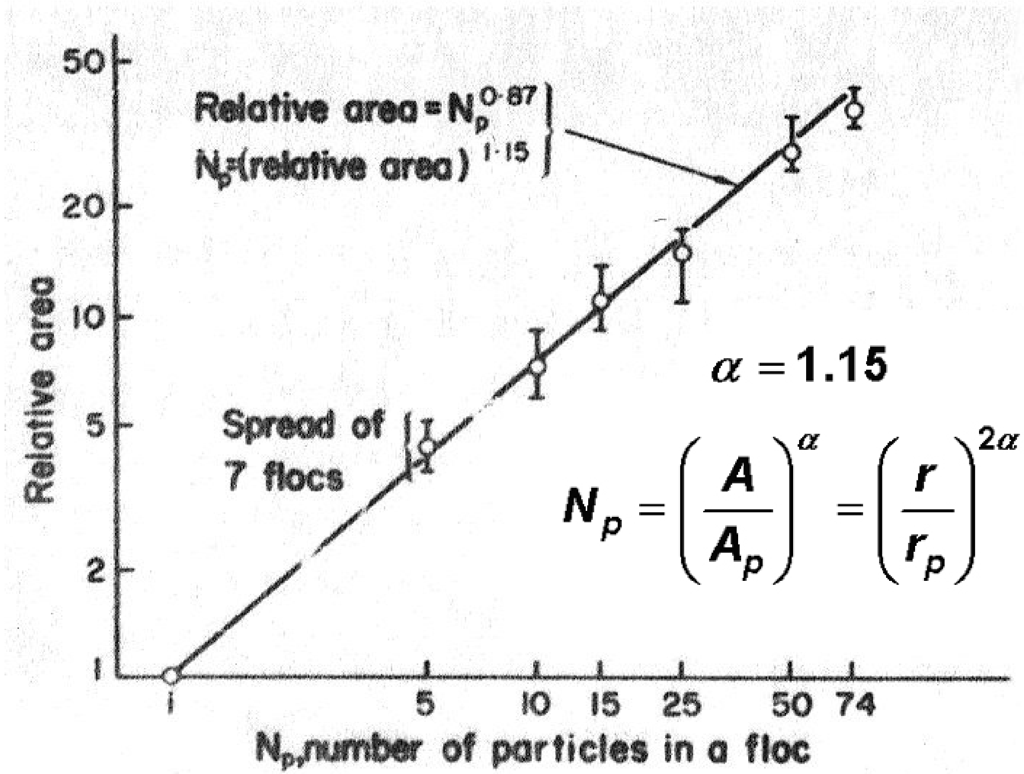


(A) (B)

Medalia & Heckman, 1967

Simulated Agglomerate Structures

Medalia & Heckman (1967)



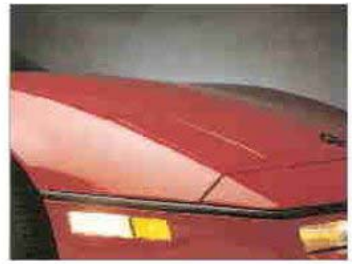
$\alpha = 1.15$

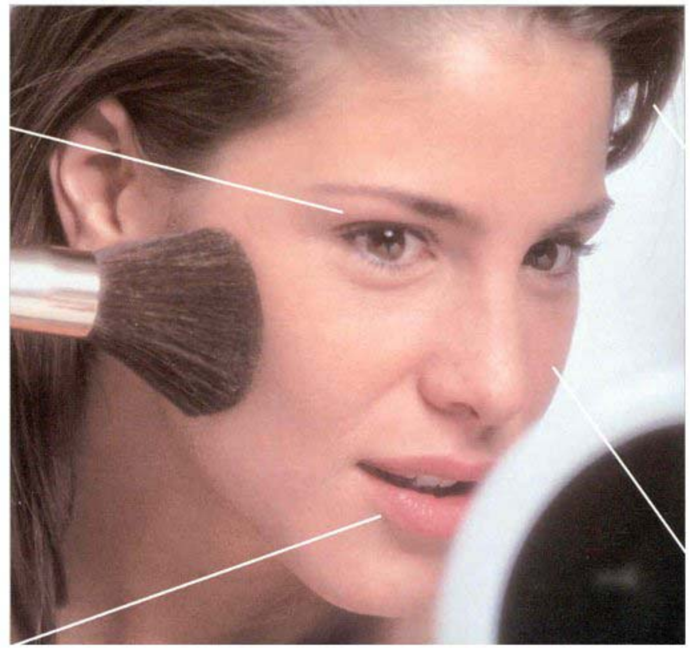
$$N_p = \left(\frac{A}{A_p}\right)^{\alpha} = \left(\frac{r}{r_p}\right)^{2\alpha}$$

Mandelbrot (1977)

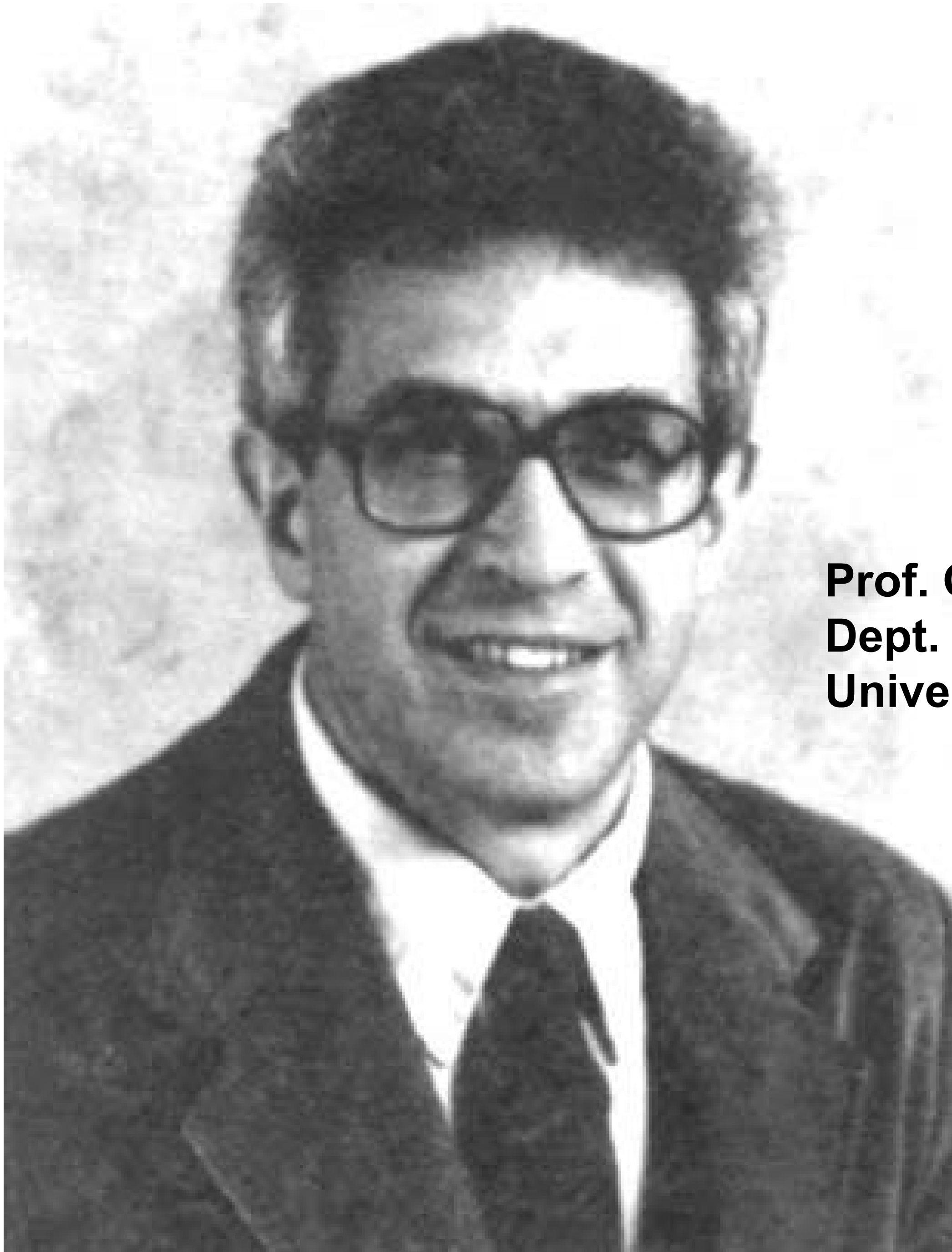
$$N_p = \left(\frac{r_c}{r_p}\right)^{D_f}$$

$$\alpha \sim \frac{D_f}{2}$$





Cabot, 1992



Prof. Gael W. Ulrich
Dept. of Chemical Engineering
University of New Hampshire

Prof. Ulrich's insightful proposals

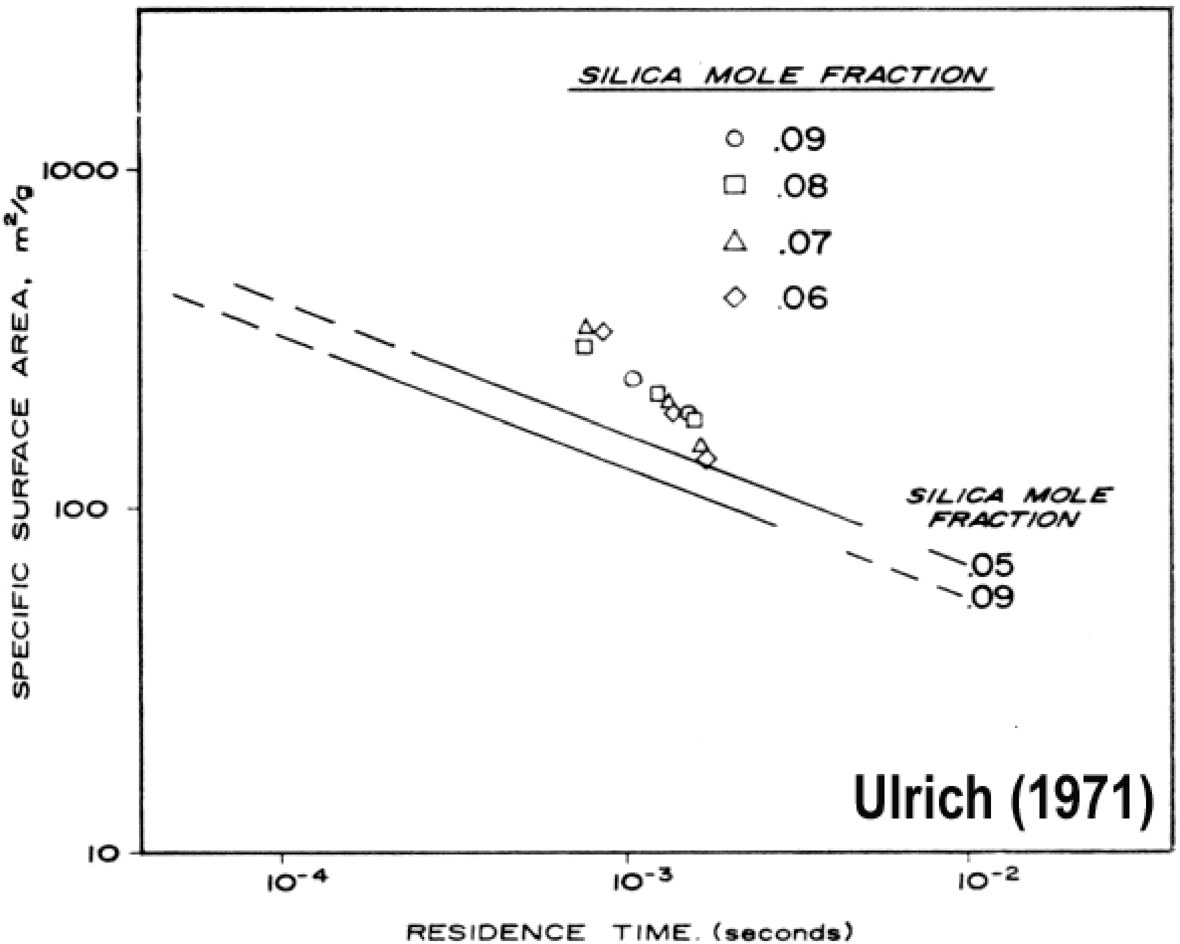
1. New particle formation (nucleation) cannot be distinguished from chemical reaction.

2. No surface growth.

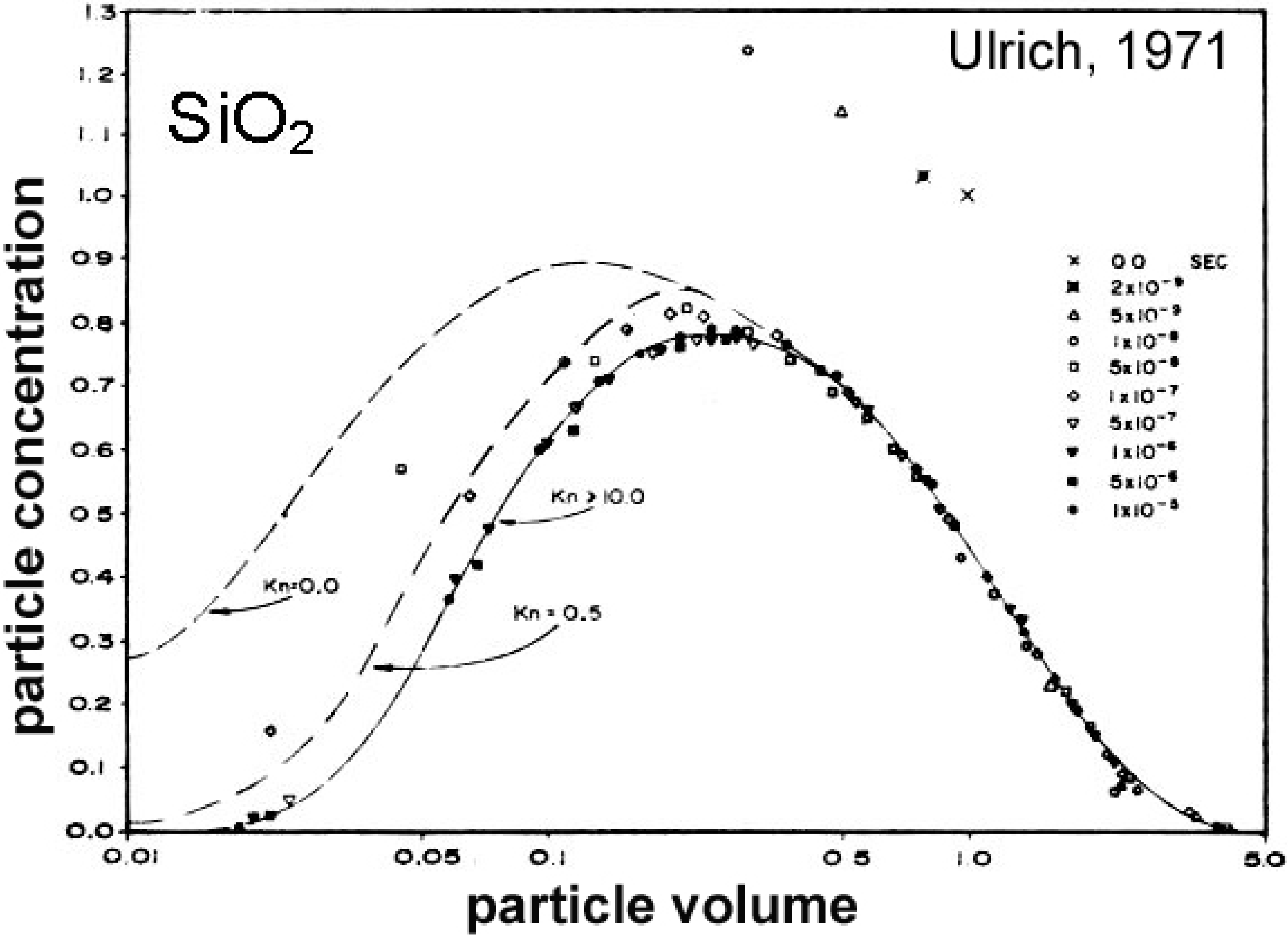
3. Turbulence does not affect particle growth.

4. Aggregates or agglomerates form when coagulation is faster than coalescence.

5. The particle size distribution is self-preserving


SILICA MOLE FRACTION
.09
.08
.07
.06
1000
100
10
SPECIFIC SURFACE AREA, m²/g
SILICA MOLE FRACTION
.05
.09
Ulrich (1971)
10⁻⁴
10⁻³
10⁻²
RESIDENCE TIME. (seconds)

$$dN_i/dt = c\left(\sum_{j=1}^{i-1}(1/2)L_{j,i-j} + (1/2)L_{ii} - \sum_{j=1}^{\infty}L_{ij}\right)$$



Applications

Paints

Niche Fields:

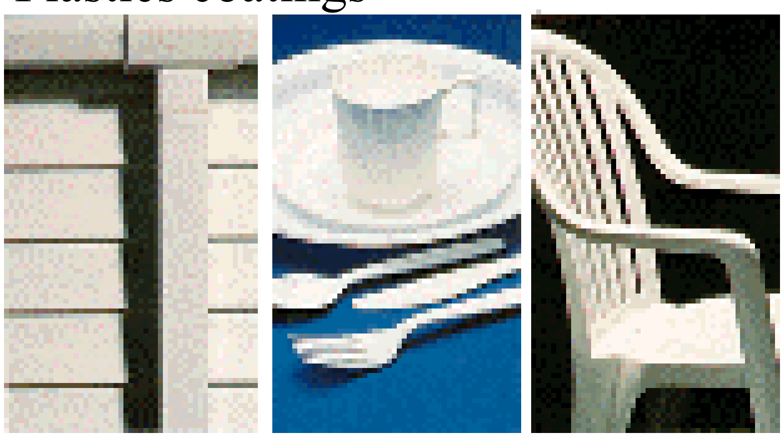
Catalysts, Sensors,

Photocatalysts,

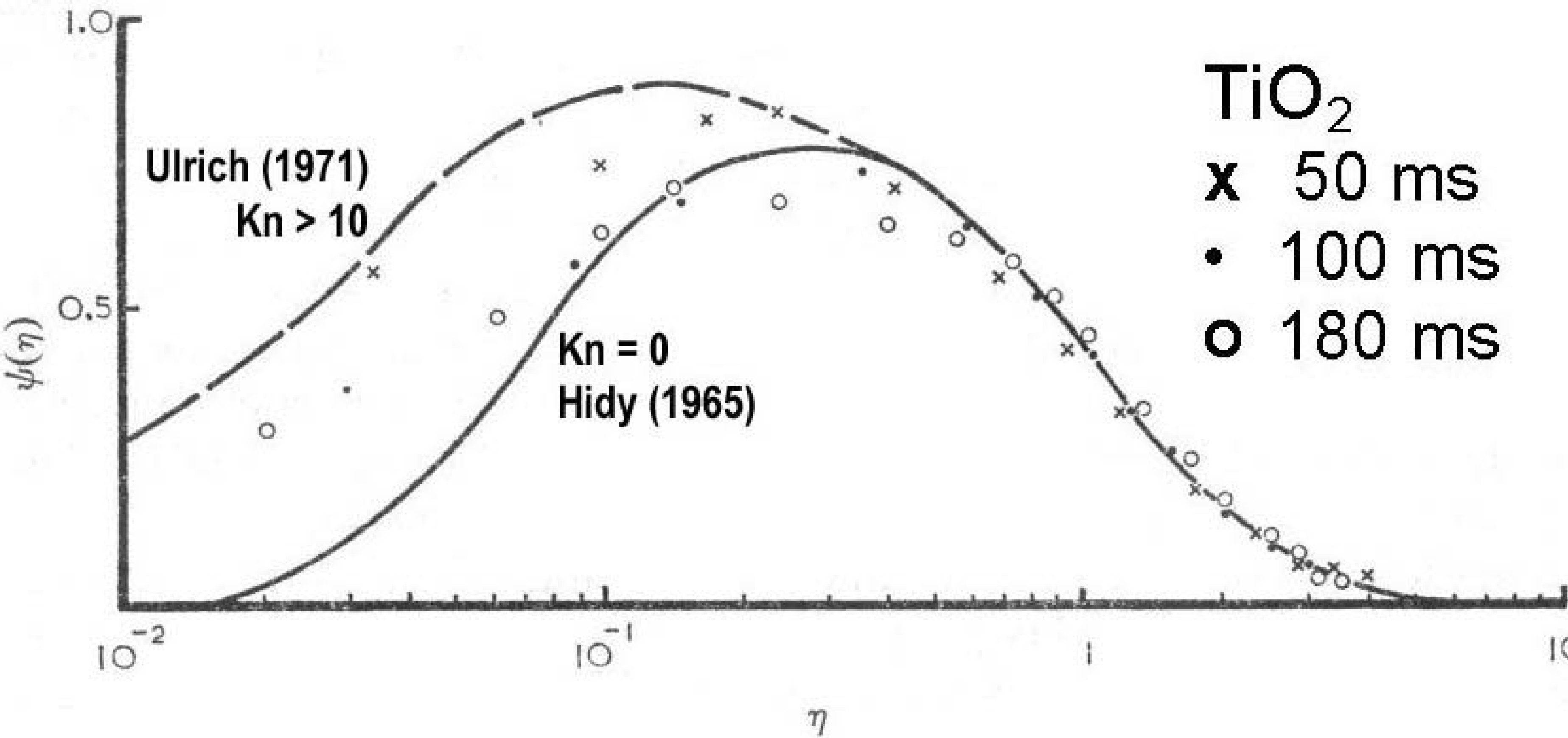
Cosmetics etc.

TiO_2 (titania)

Plastics coatings



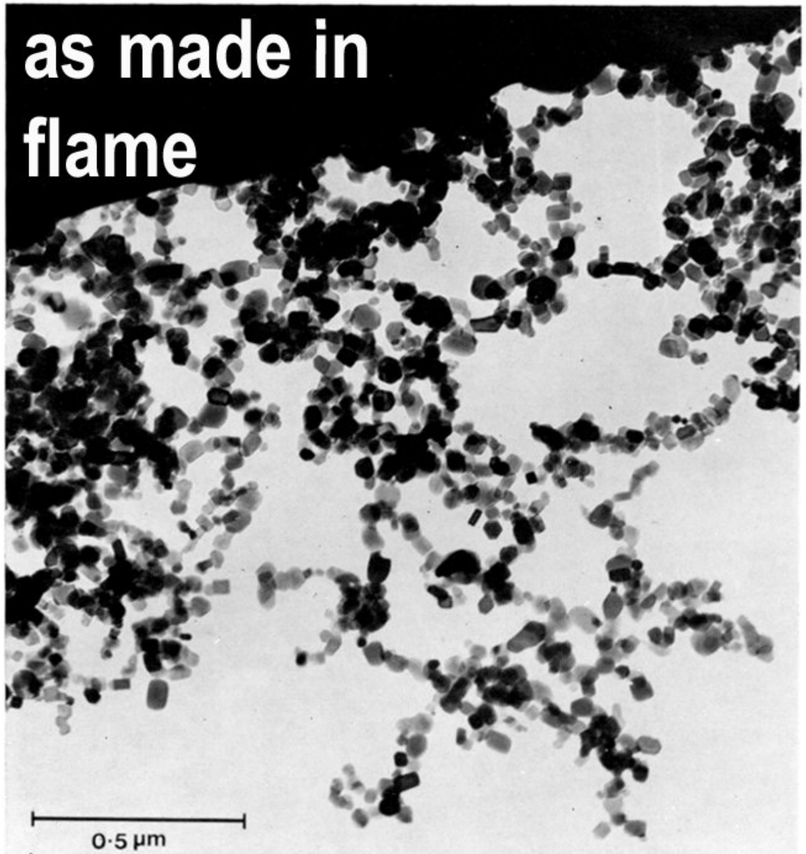
Paper coatings

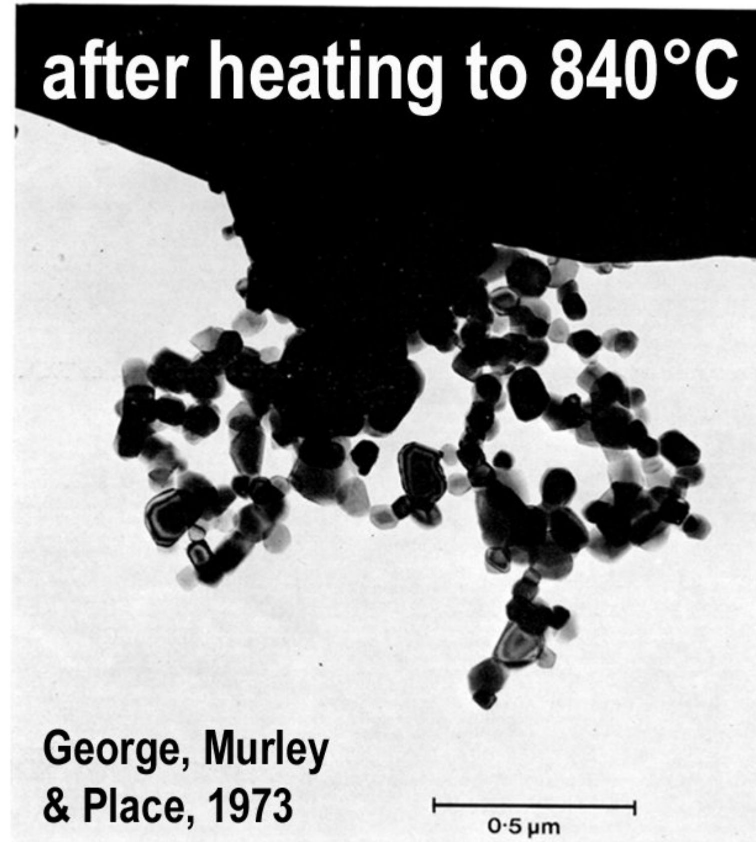


George, Murley & Place, 1973

The $\overline{d}_p$ increased 10 times

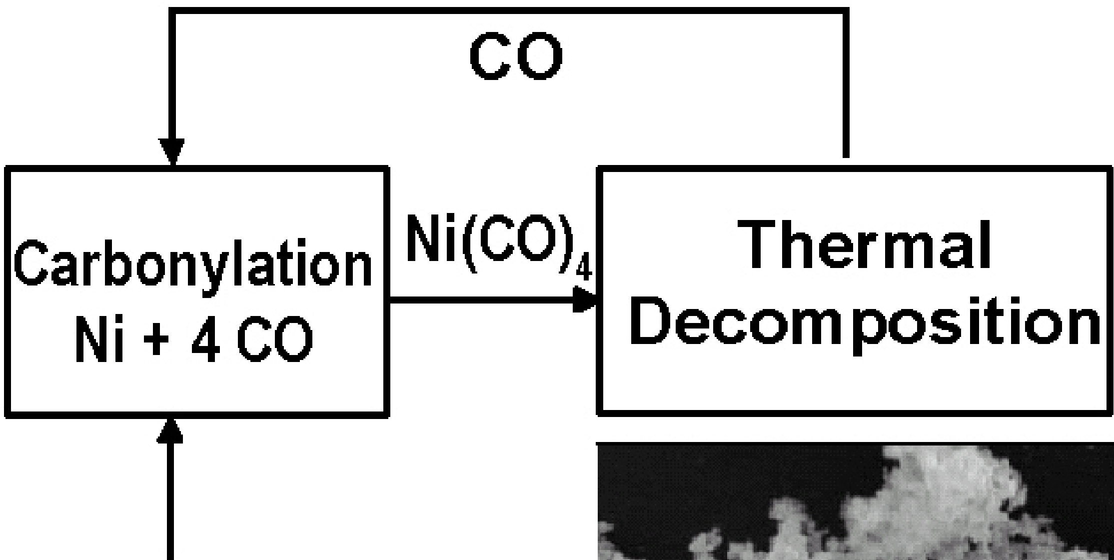
TiO_2

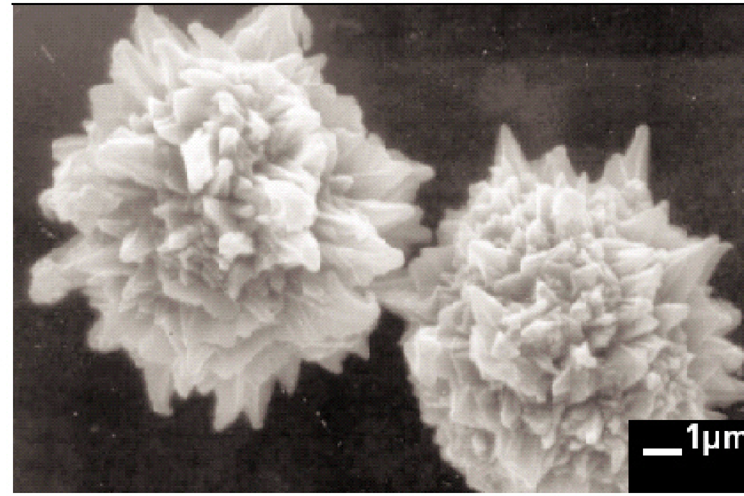




Fine particles (d_p < 63 nm) exhibit properties of the liquid state several hundred degrees below their bulk melting point (Fuchs & Sutugin, 1970)

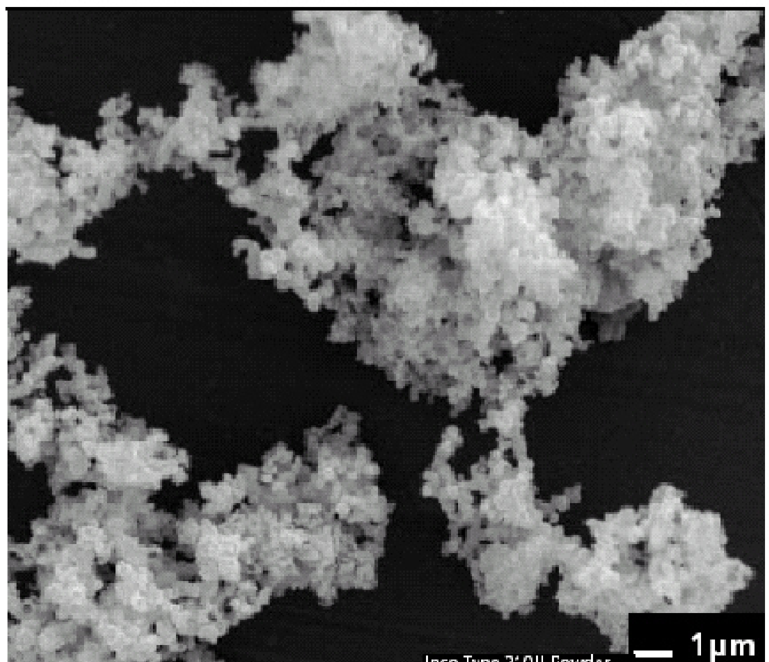
Aerosol Manufacture of Ni





Powder Metallurgy
(good sintering)

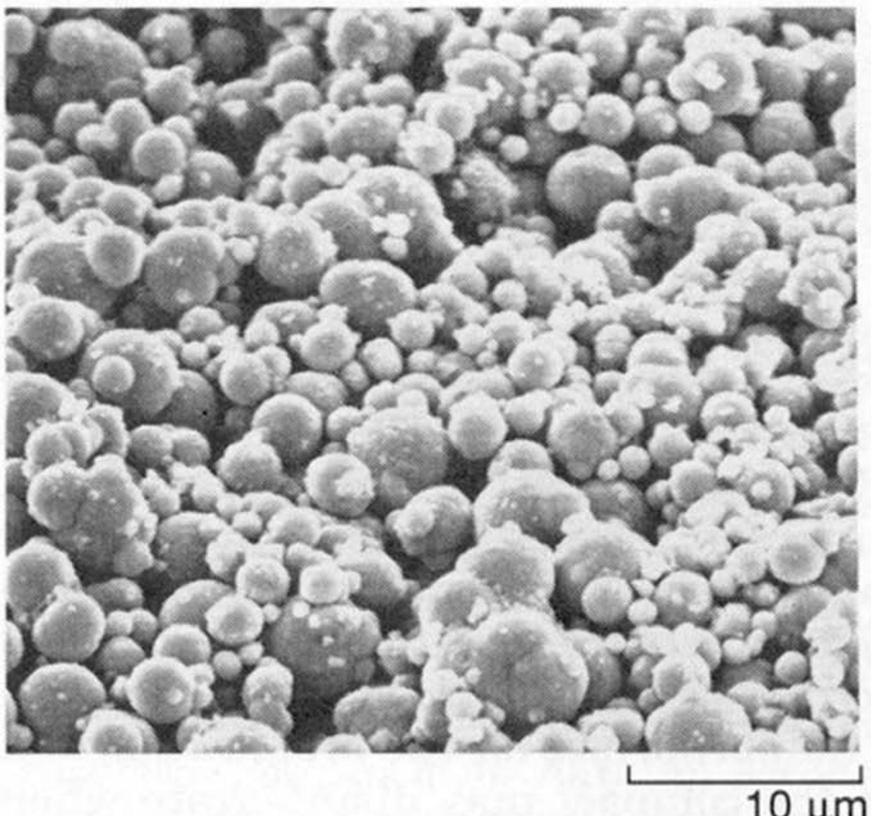
Ni pellets

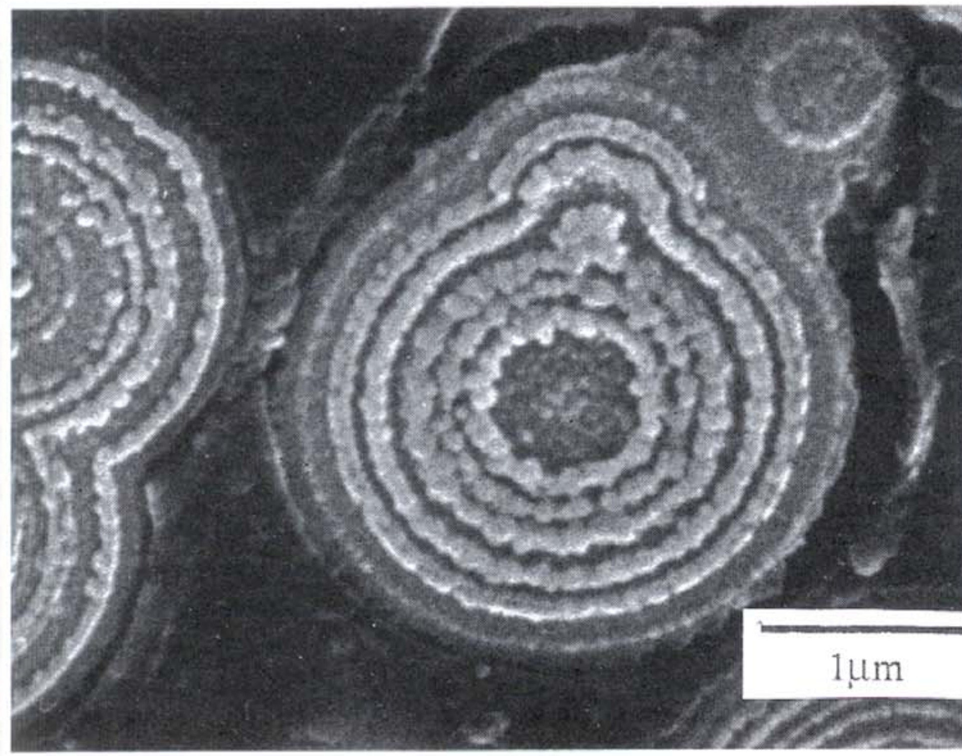


Battery electrodes
Coatings
Catalysts

www.inco.com

Microstructure of Carbonyl Iron Powder





Japka (1988,1991)

Limitations of science in the '70s

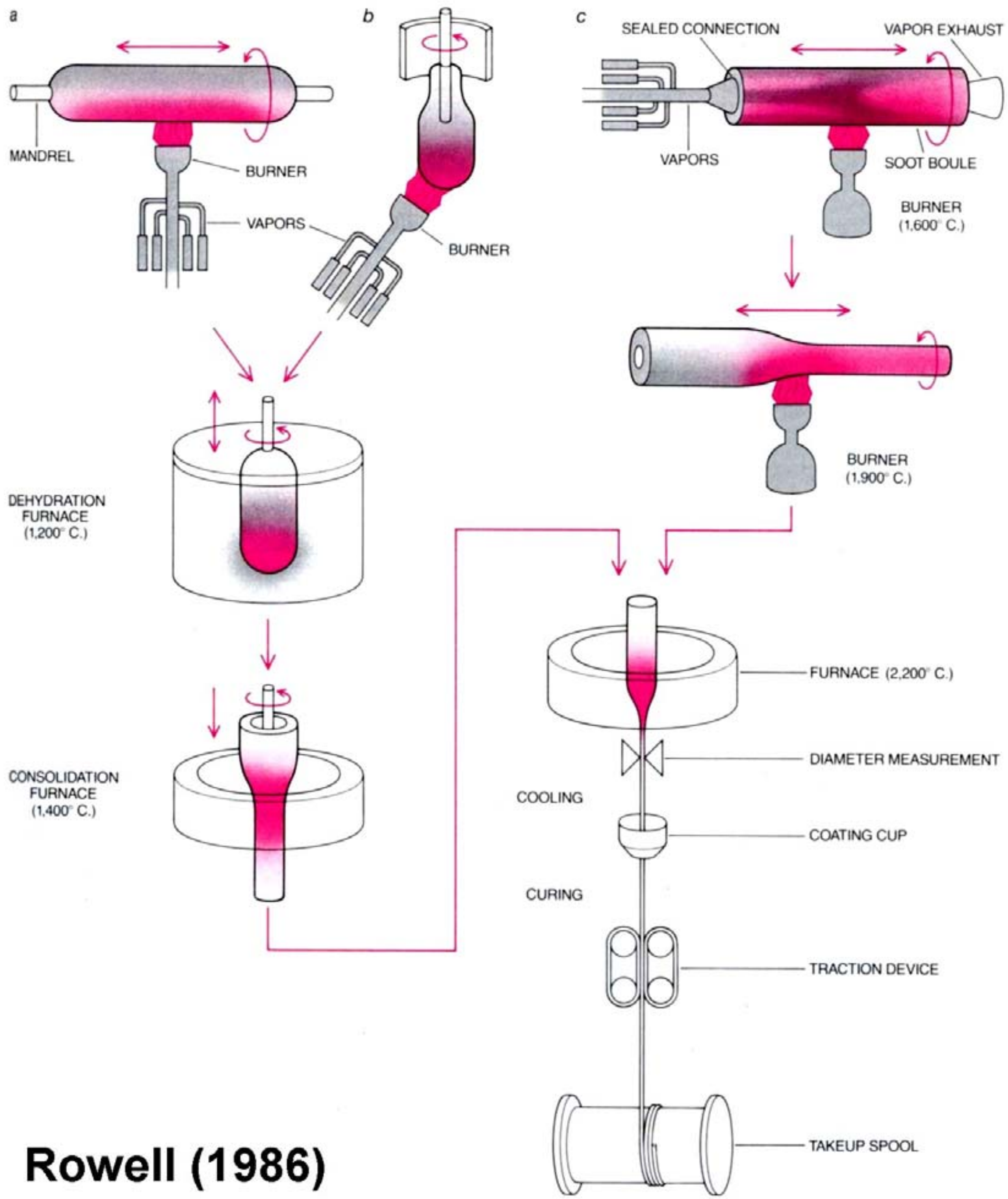
Understanding of particle formation has little impact on industrial aerosol reactor design.

Providing a plausible particle synthesis scenario alone was not enough:

1. **Probably industrial reactor data could not be duplicated in the laboratory reactors**
2. **Traditional aerosol instruments were too slow**
3. **No scale-up relationships**
4. **Too complex fluid mechanics (reactive systems).**

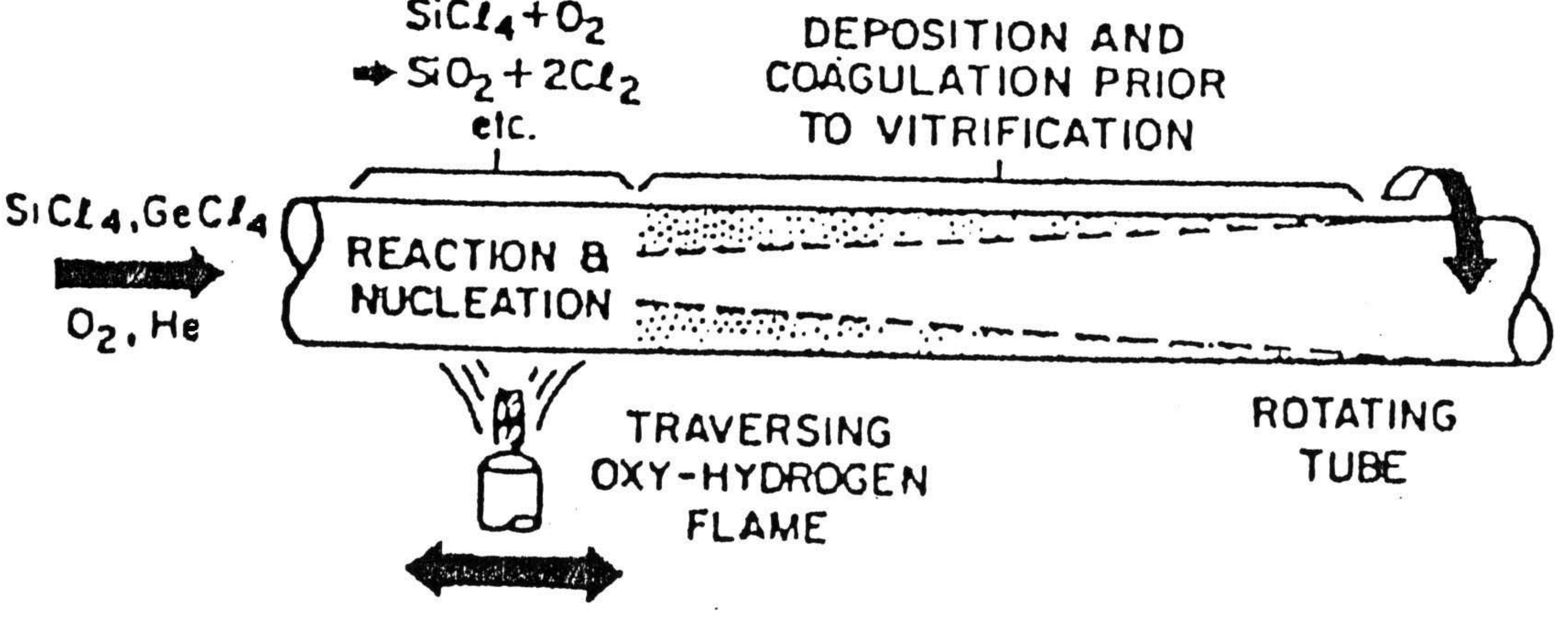
Industrial reactors were still treated as "black boxes"
Design and operation were dominated by empiricism.

Optical Fiber Production

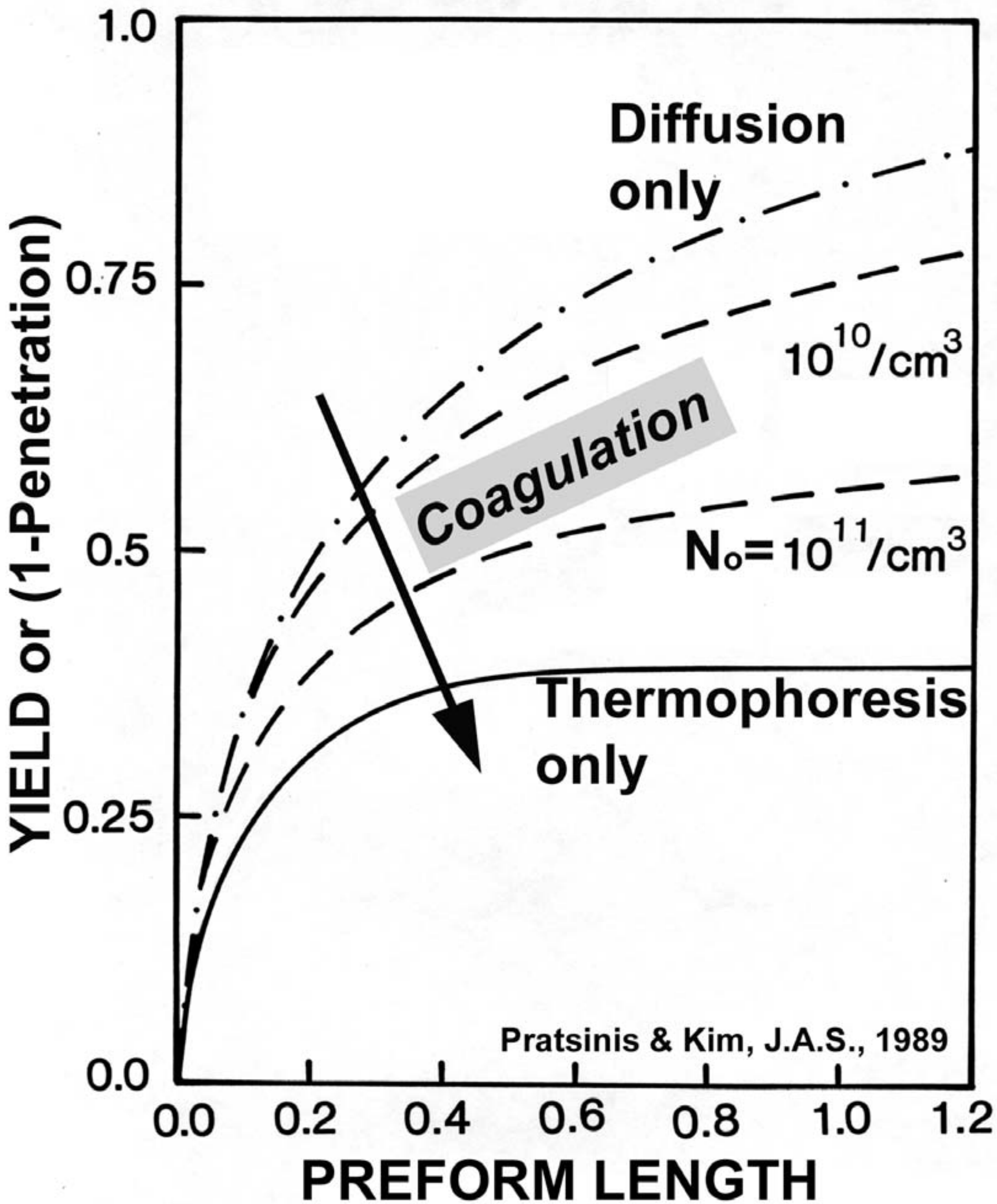


Rowell (1986)

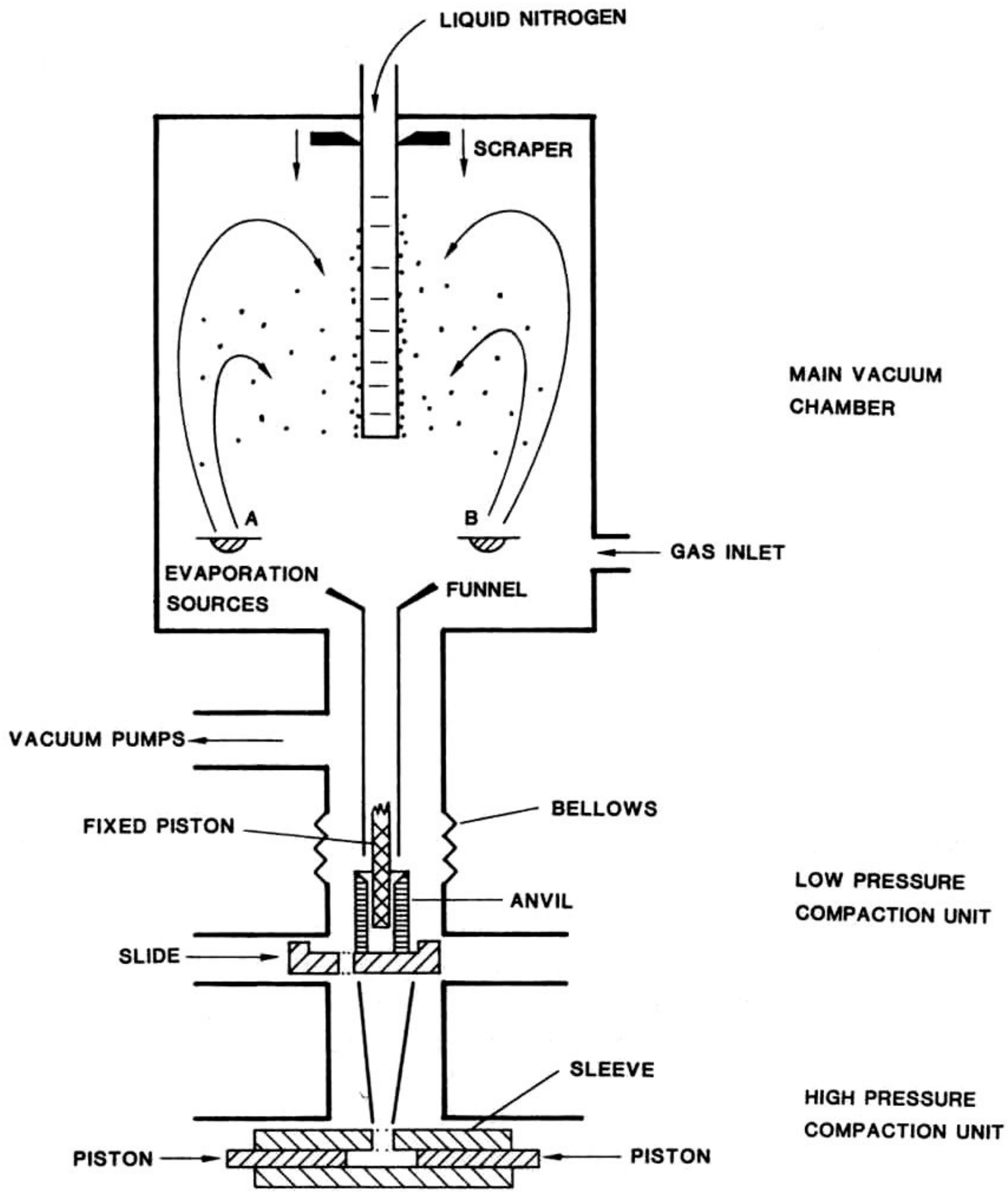
MODIFIED CHEMICAL VAPOR DEPOSITION
(McChesney et al., 1977)



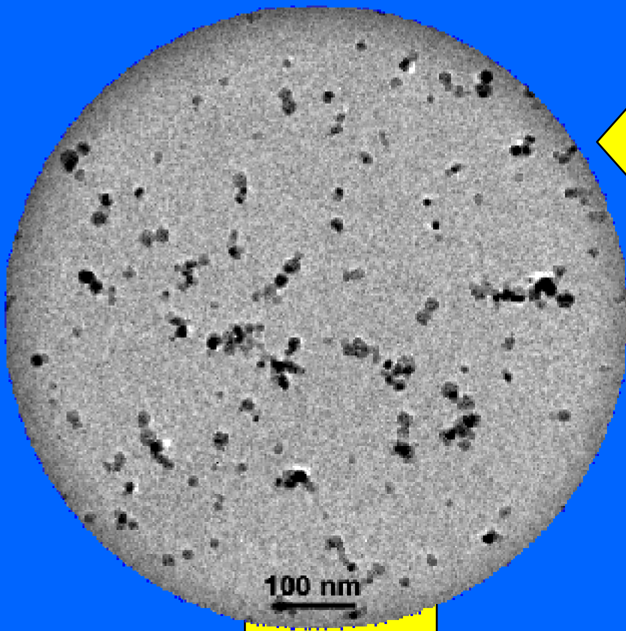
Optical Fibers by MCVD



Metal Nanoparticles by Inert Gas Condensation (Siegel, 1989)

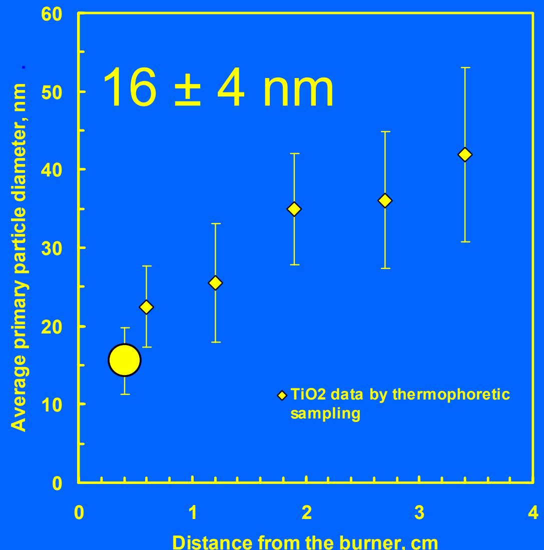


Thermophoretic Sampling (Dobbins and Megaridis, 1987))



TEM

Image Analysis

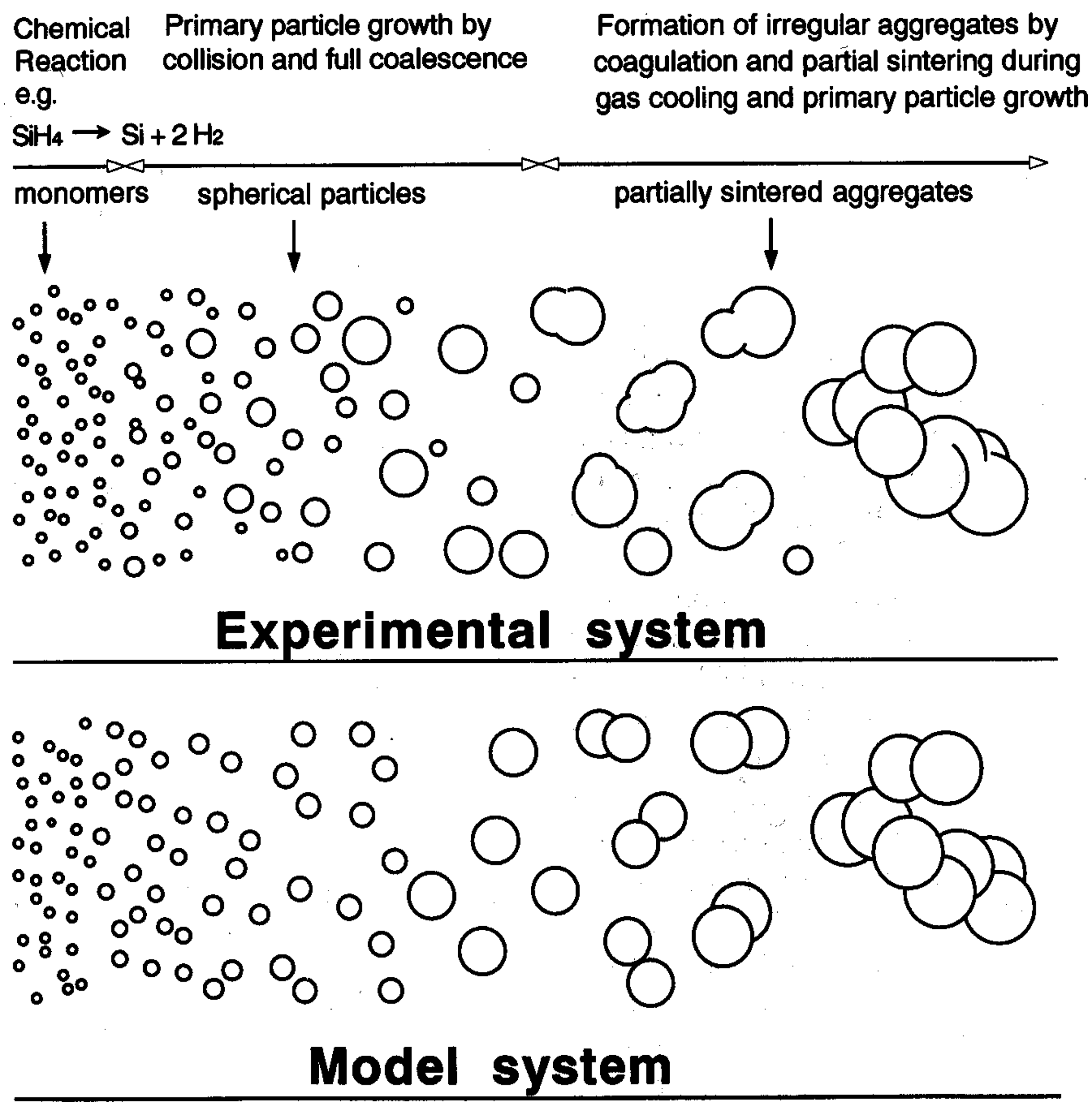


ETH Eidgenössische Technische Hochschule Zürich

Sintering rate of particle area a

$$\frac{da}{dt} = -\frac{1}{\tau}(a - a_s)$$

Koch, Friedlander, *J. Colloid Interface Sci.* **140**, 419 (1990)



Number Concentration

$$\frac{dN}{dt} = -\frac{1}{2}\beta N^2$$

Agglomerate area

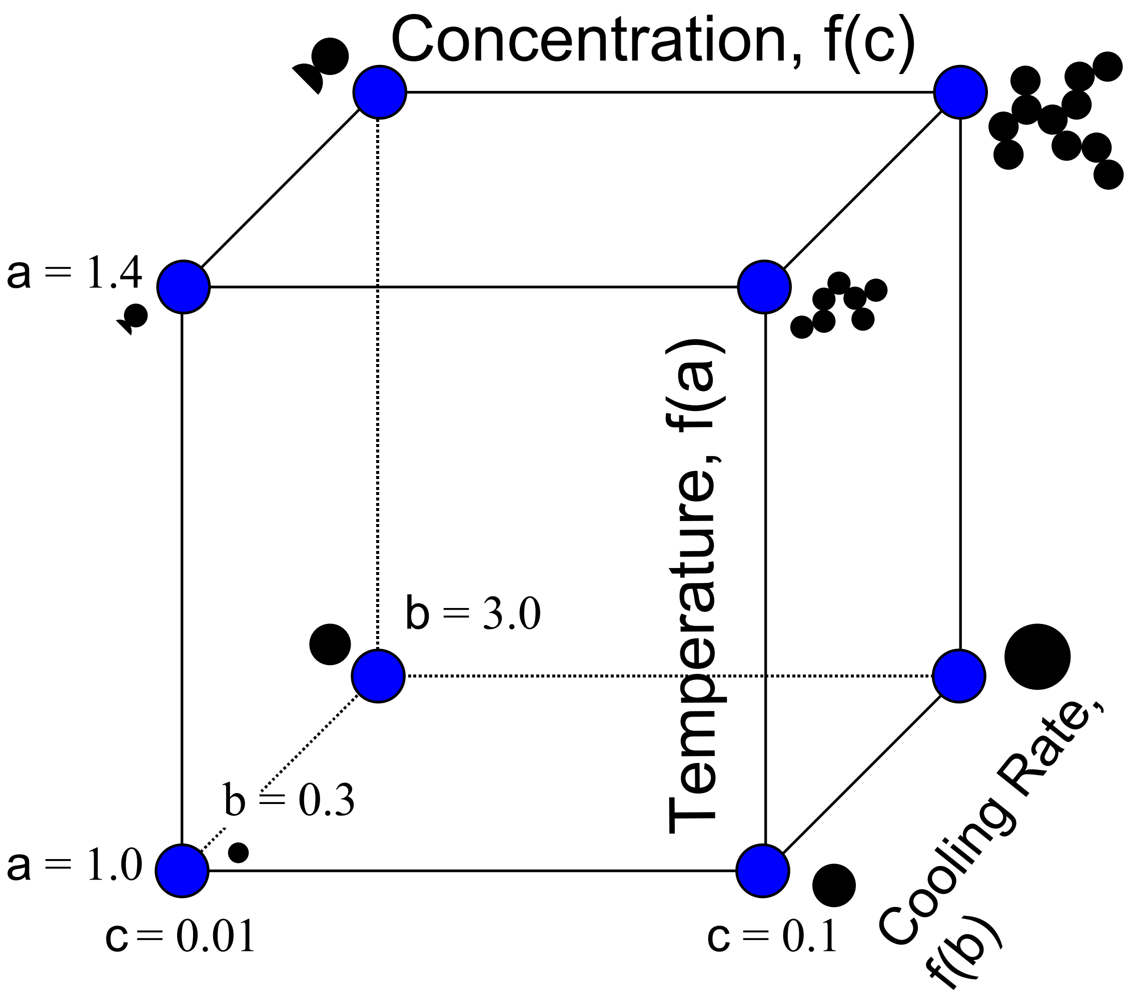
$$\frac{da}{dt} = -\frac{1}{N}\frac{dN}{dt}a - \frac{1}{\tau}(a - a_s)$$

Collision diameter

$$d_c = d_p (v / v_p)^{1/D_f}$$

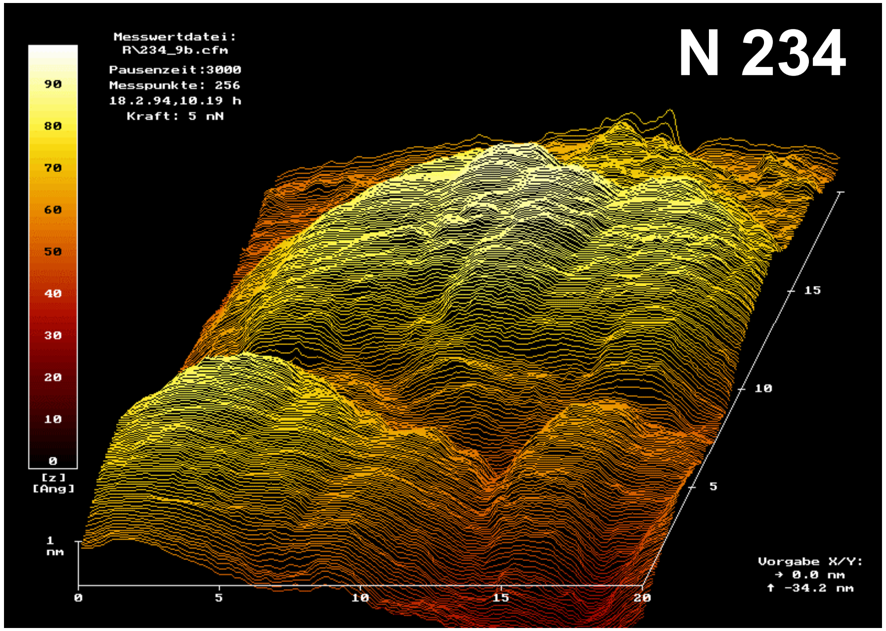
Kruis, Kusters, Pratsinis, Scarlett, *Aerosol Sci. Technol*. **19**, 514 (1993) degussa.

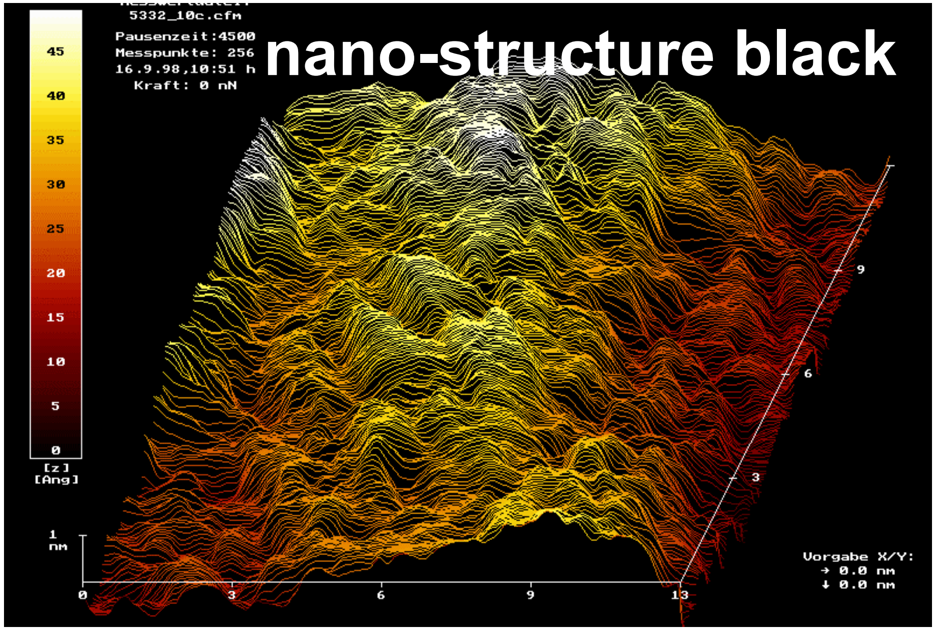
Design of Equipment



Predictions within 3% of product SSA (Gutsch, 1997)

H. Mühlenweg, A. Gutsch, A. Schild, C. Becker "Simulation for process and product optimization", *Silica 2001, 2nd International Conference on Silica*, Mulhouse, France (2001) and
G. Vargas Commercializing Chemical Technology: Realization of Complete Solutions using Chemical Nanotechnology, Lecture at Nanofair, St. Gallen, Switzerland, Sept. 11, 2003.





Niedermeier, Messer, Fröhlich (TR814.1E) degussa.

TODAY

Aerosol Scientists and Engineers lead R & D for aerosol manufacture at Degussa, DuPont, Millennium, Cabot etc.

Basic and exploratory research is needed for:

- On-line control of existing reactors for flexible manufacture of various particles
- High value functional nanoparticles with sophisticated composition and structure.
- Manufacture these nanoparticles without going through the Edisonian cycle of the past.
- Health effects of nanoparticles.

Novel Processes and Uses of Flame-made Nanoparticles

Prof. Sotiris E. Pratsinis
Particle Technology Laboratory
Department of Mechanical and Process Engineering,
ETH Zürich, Switzerland
www.ptl.ethz.ch

Sponsored by the
Swiss National Science Foundation and Swiss Commission for Technology and Innovation

Flame-made particles

Pros

High purity

Easy collection

No liquid waste

Proven scale-up

No moving parts

Challenges

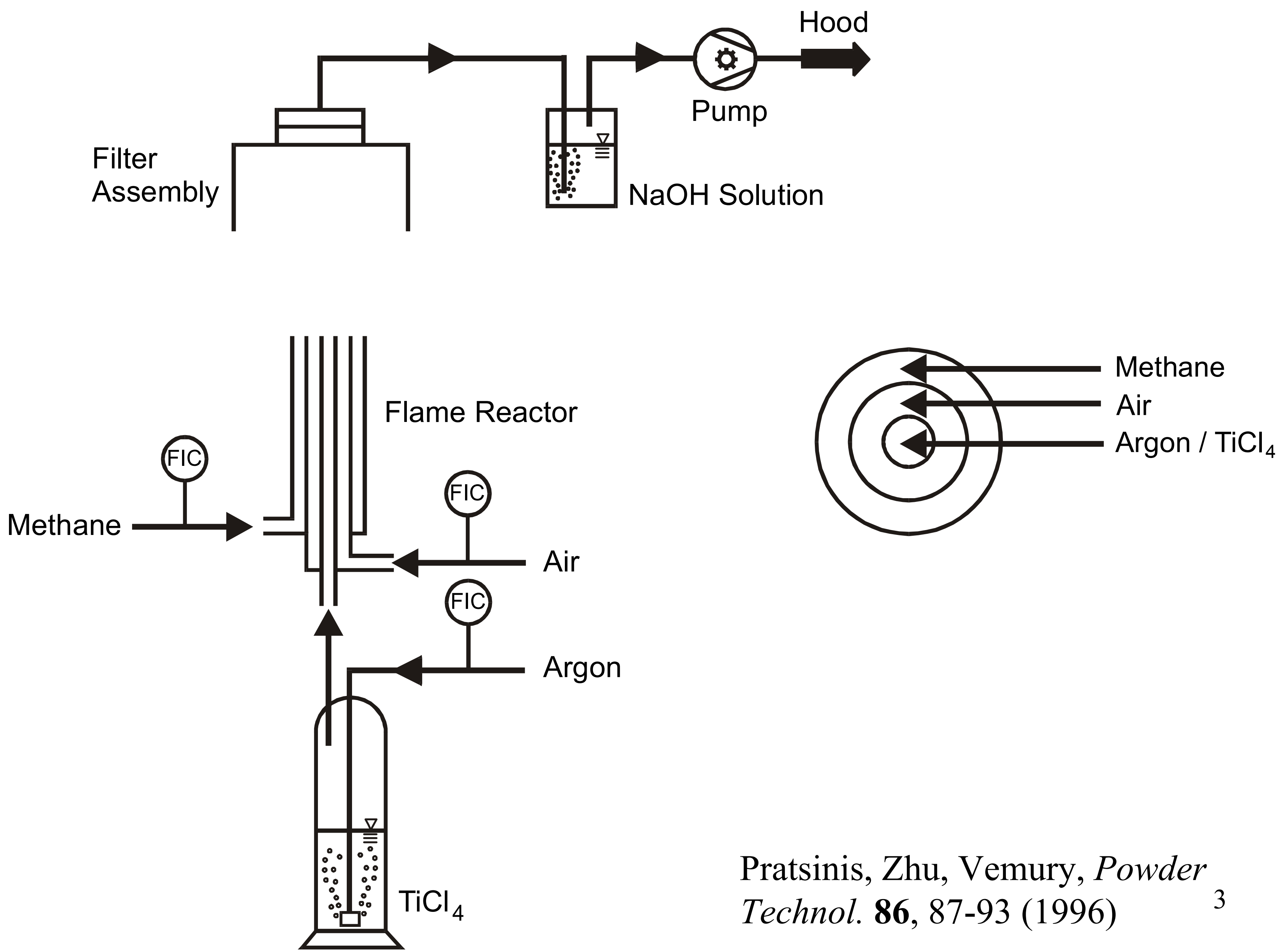
Agglomerates

Size control

Multicomponent

- ceramic/ceramic
- metal/ceramic

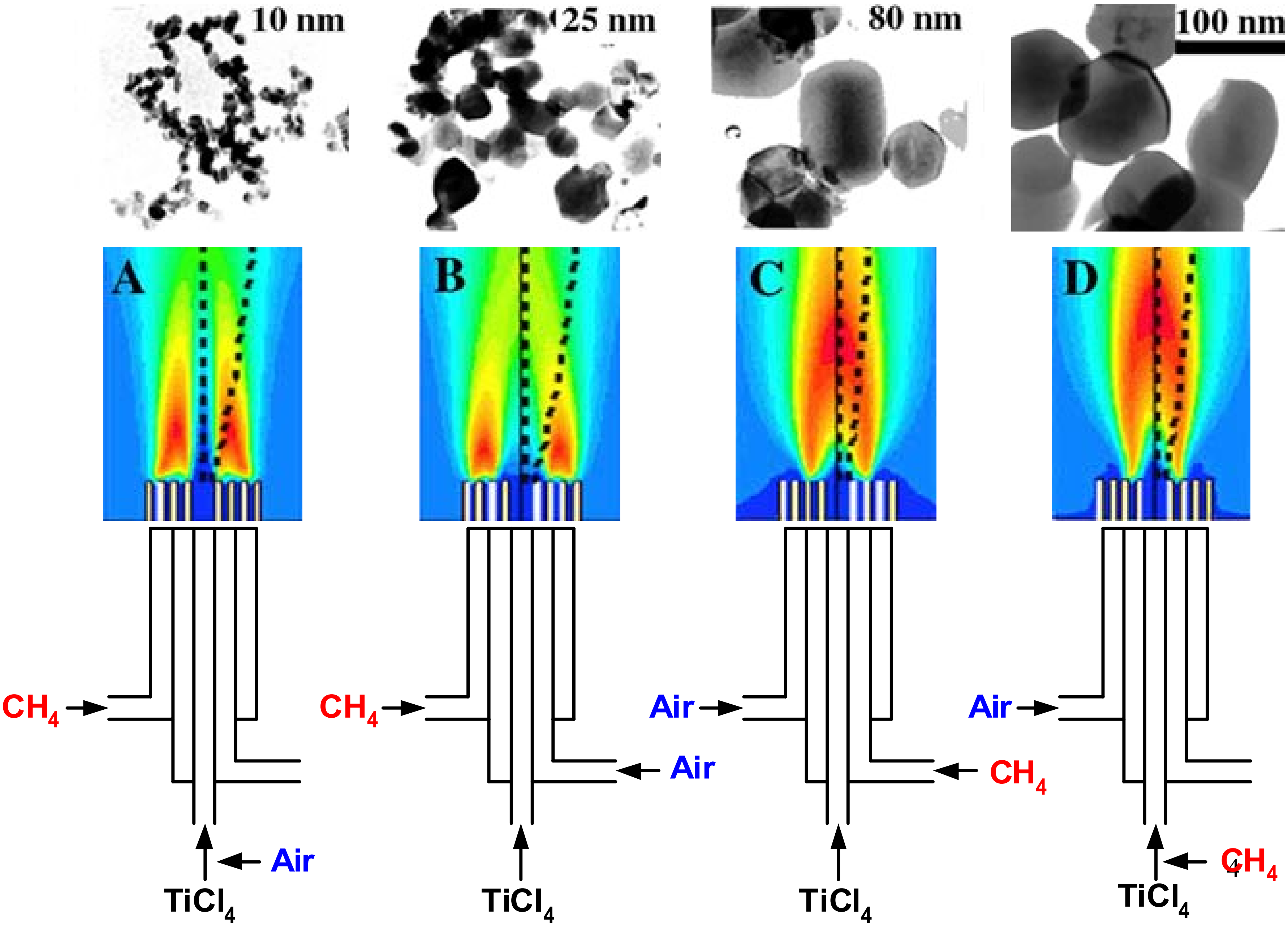
Experimental set-up for TiO_2 production



Pratsinis, Zhu, Vemury, *Powder Technol.* **86**, 87-93 (1996)

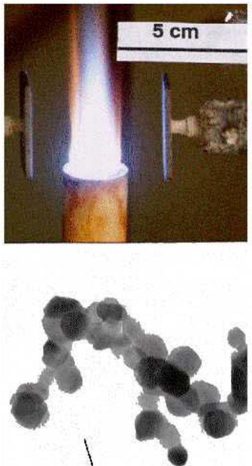
Mixing of reactant gases ==> product size-shape

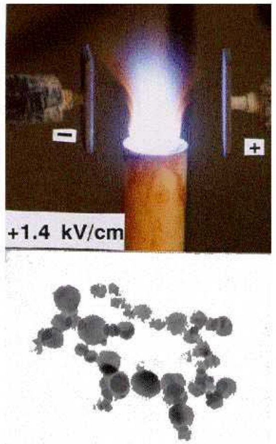
Pratsinis, Zhu, Vemury, *Powder Technol.* **86,** 87-93 (1996); Johannessen, Pratsinis, Livberg, *ibid.,* **118**, 242-250 (2001).



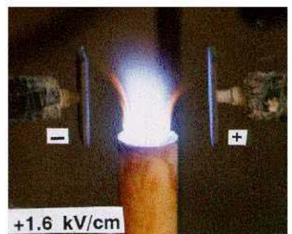
S. Vemury, S.E. Pratsinis, L. Kibbey, *J. Mater. Res.* **12**, 1031-1042 (1997).

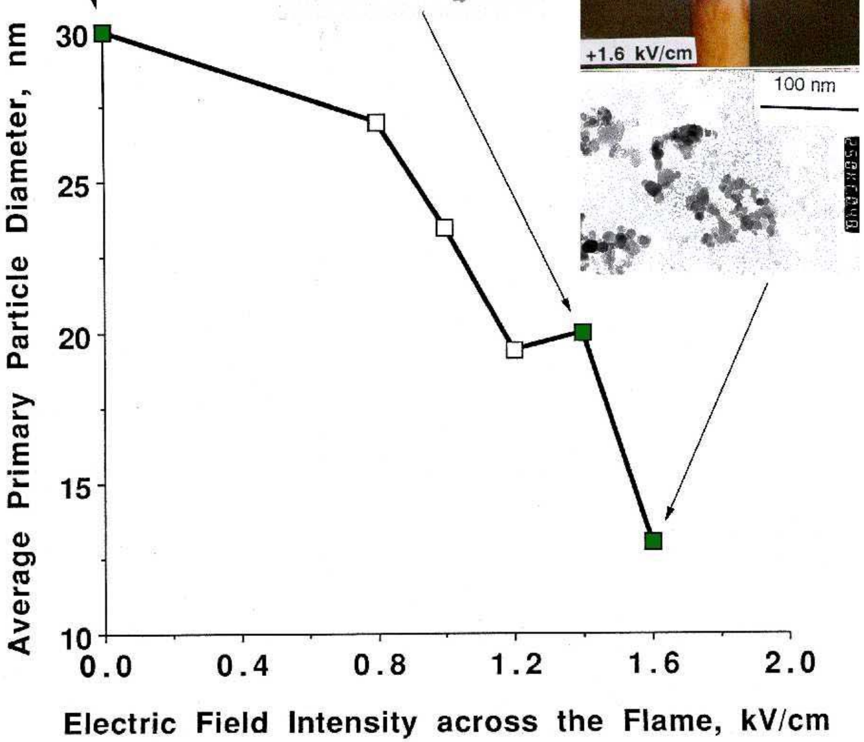
Electrically Assisted Synthesis of Nanoparticles





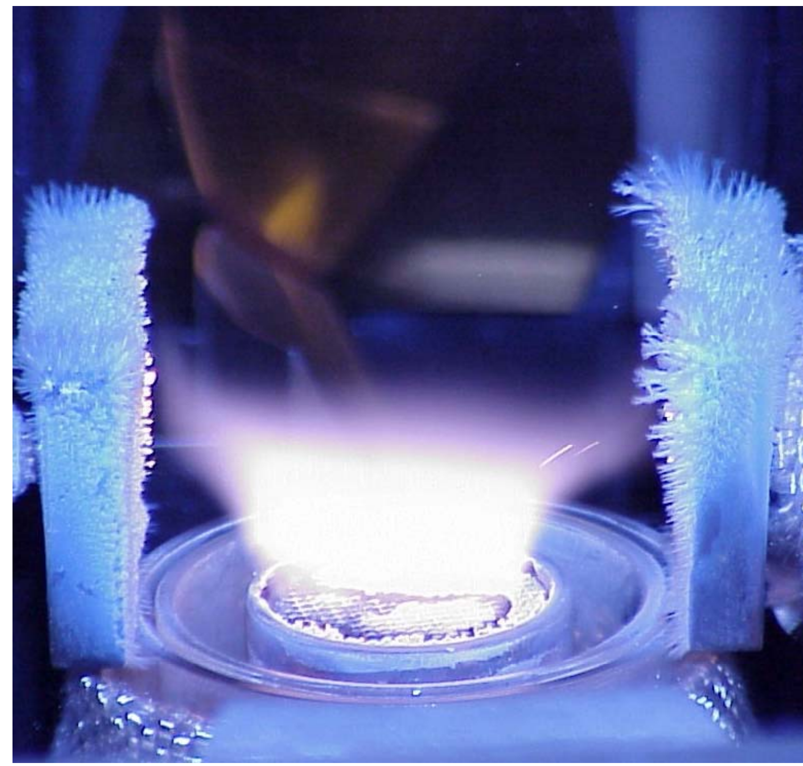
U.S. Patent 5,861,132 (1999)





Precision Size Control by Charging

Kammler, *PhD thesis, ETH #14622* (2002)



ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Evolution of TiO_2 particle growth with and w/o external electric fields

w/o electric field

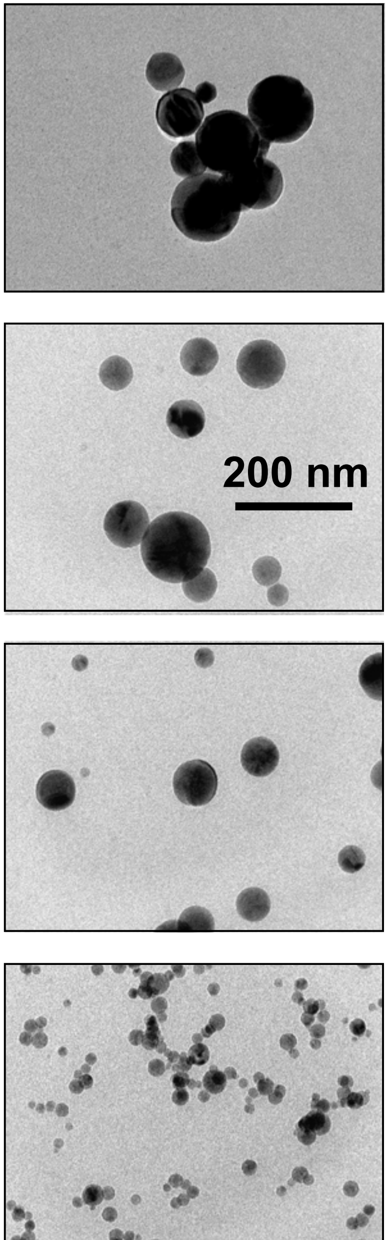
HAB

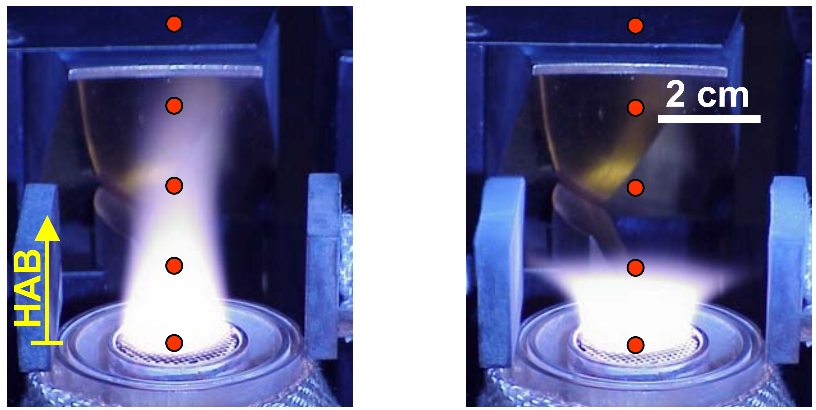
Filter
20 cm

10 cm

5 cm

0.5 cm

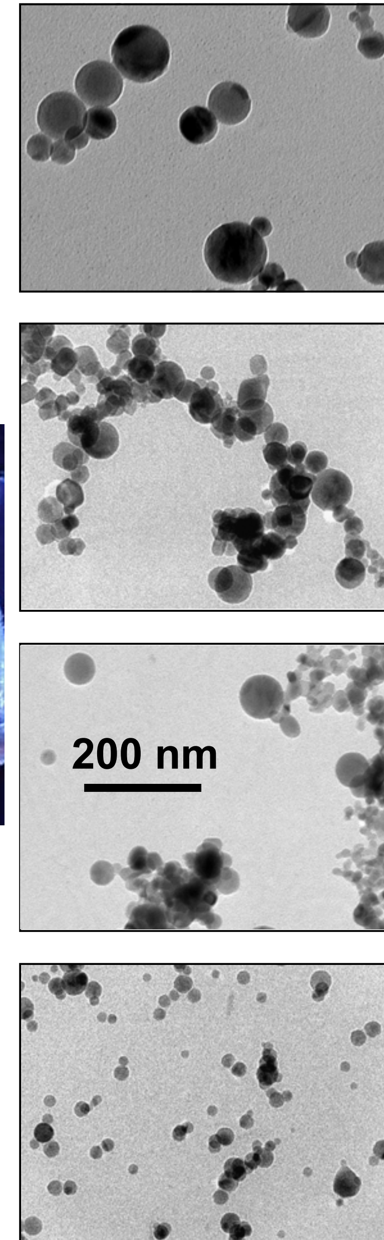




0 kV/cm

2 kV/cm

with electric field



HAB

Filter
20 cm

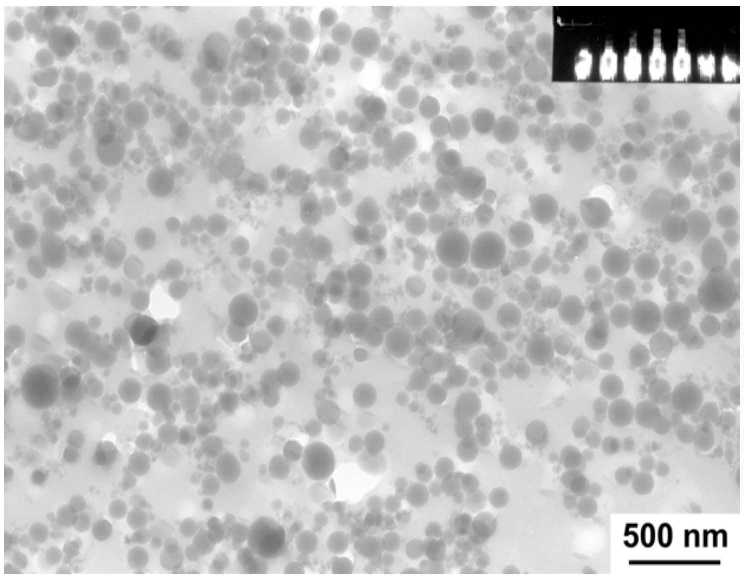
10 cm

5 cm

0.5 cm

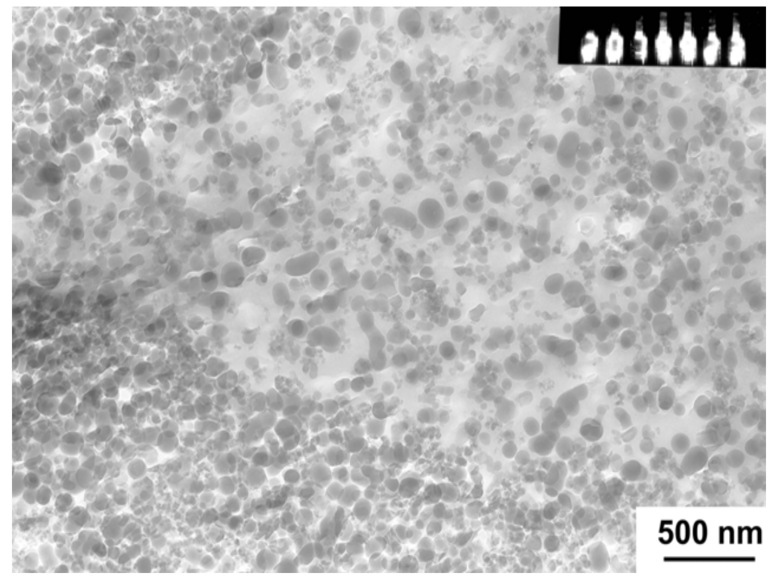
Kammler, Pratsinis, Morrison, Jr., Hemmerling, *Combust. Flame* **124**, 369 (2002)

Dental n-Composites: flame-made silicas in a dimethylacrylate matrix (50:50)



with ETH non-aggl. SiO_2

SSA = 35 m^2/g

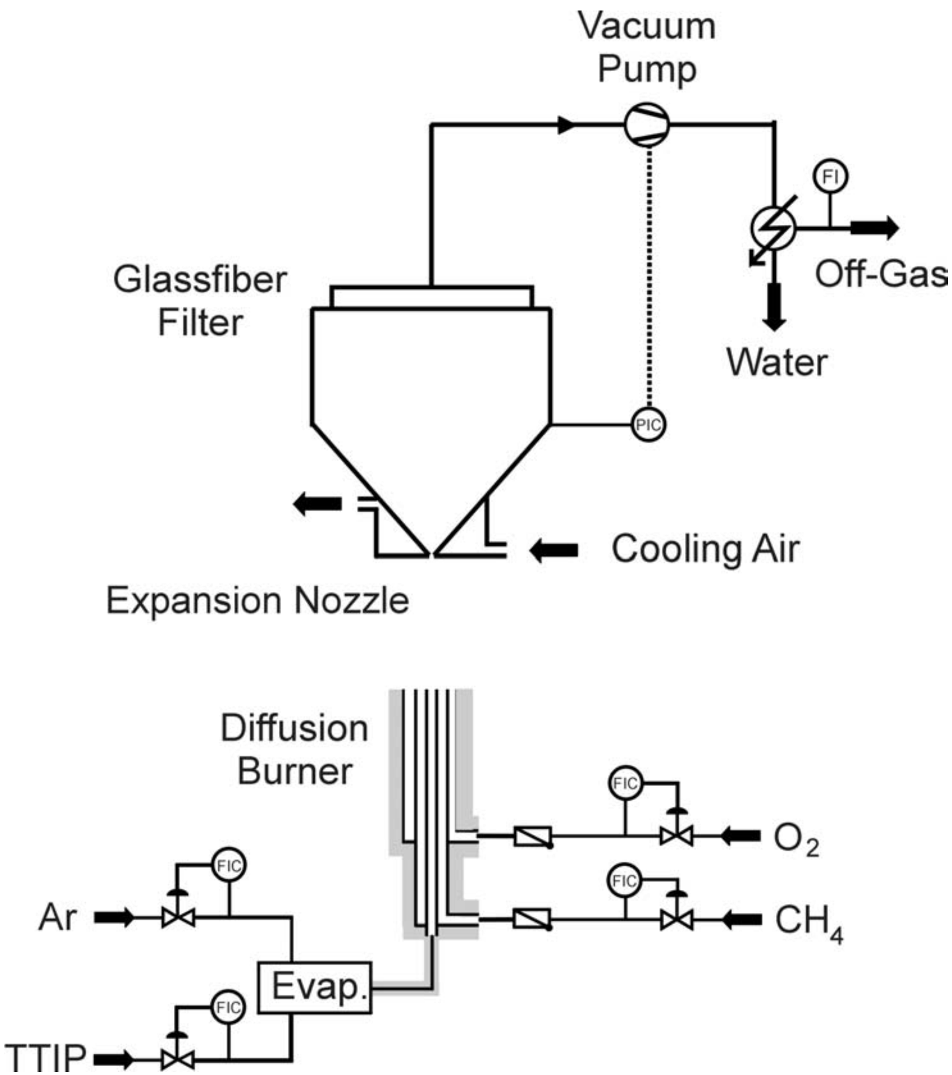


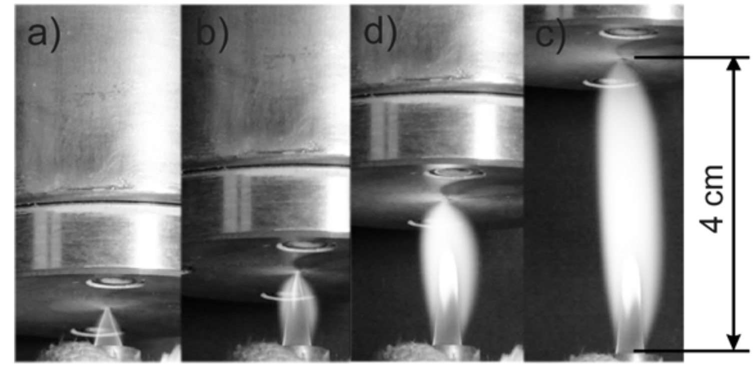
with OX50 (Degussa)

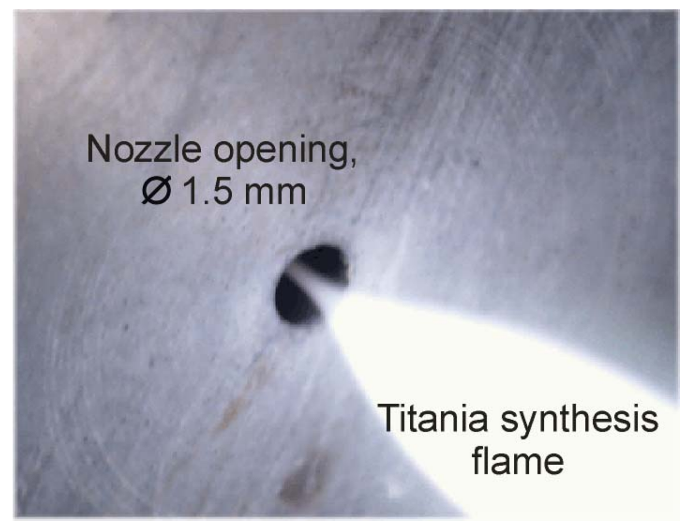
SSA = 50 m^2/g

Müller, Vital, Kammler, Pratsinis, Beaucage, Burtscher, *Powder Technol.* **140**, 40-48 (2004).

Precision Synthesis by Nozzle Quenching



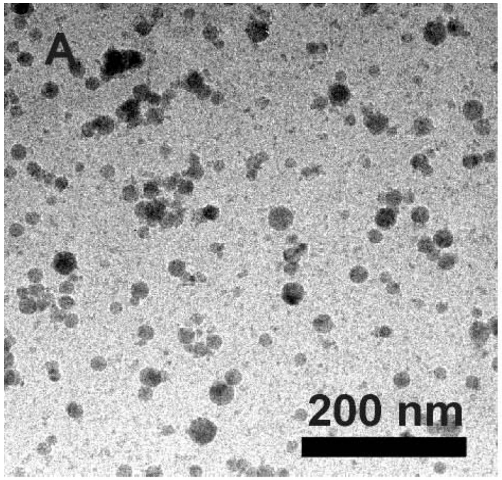




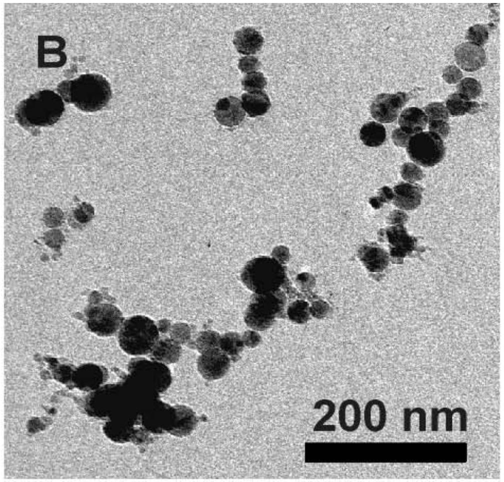
Wegner, Stark, Pratsinis, *Mater. Lett.* **55**, 318 (2002)

Reduction of Agglomeration

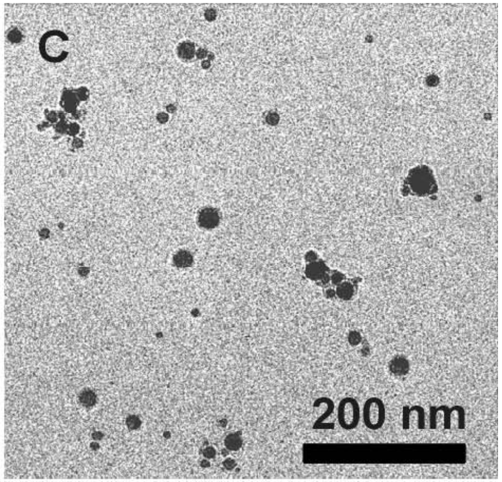
6 L/min O_2 flow rate



TS in front of nozzle
(BND = 1.5 cm)

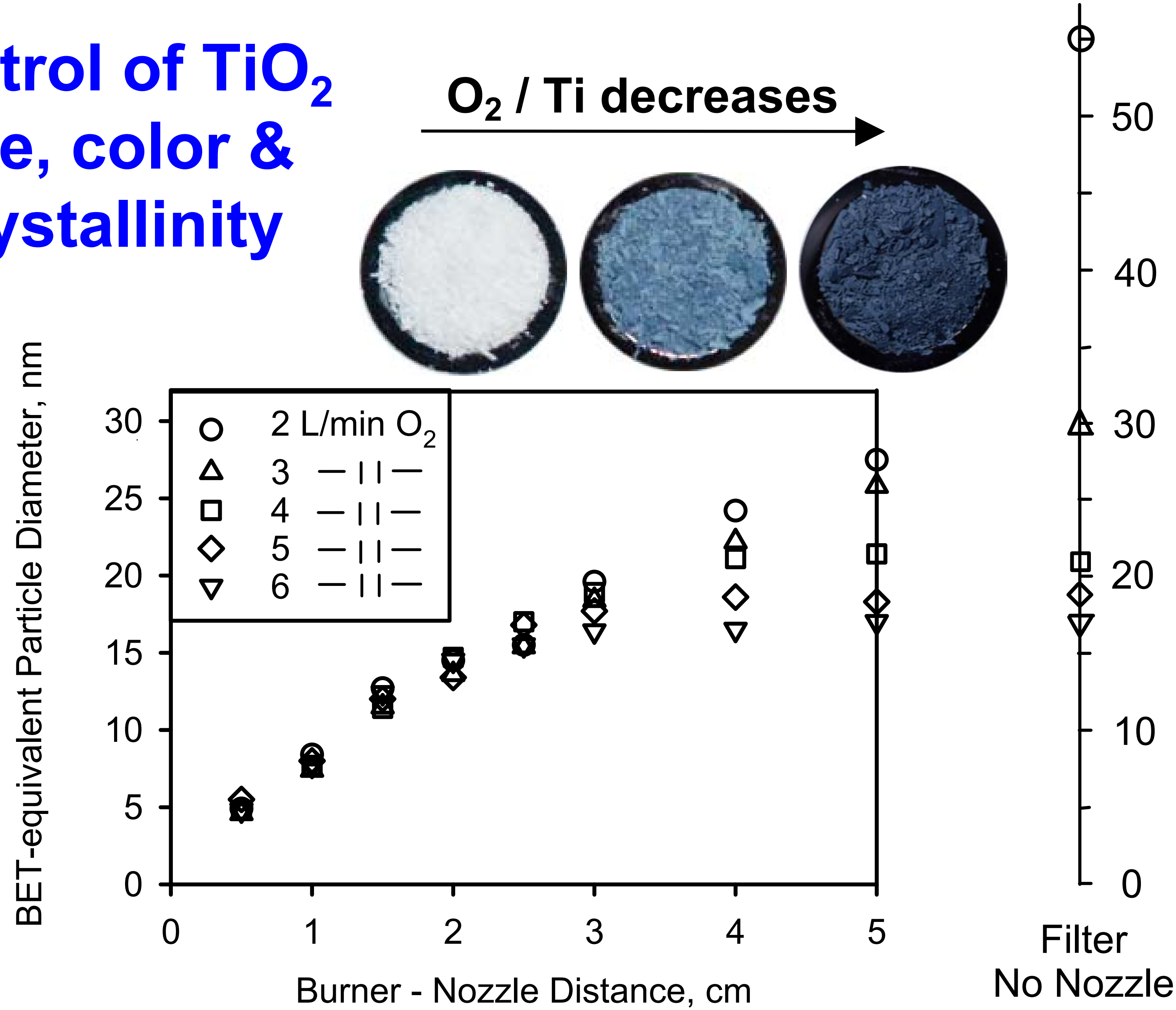


No nozzle
Product powder

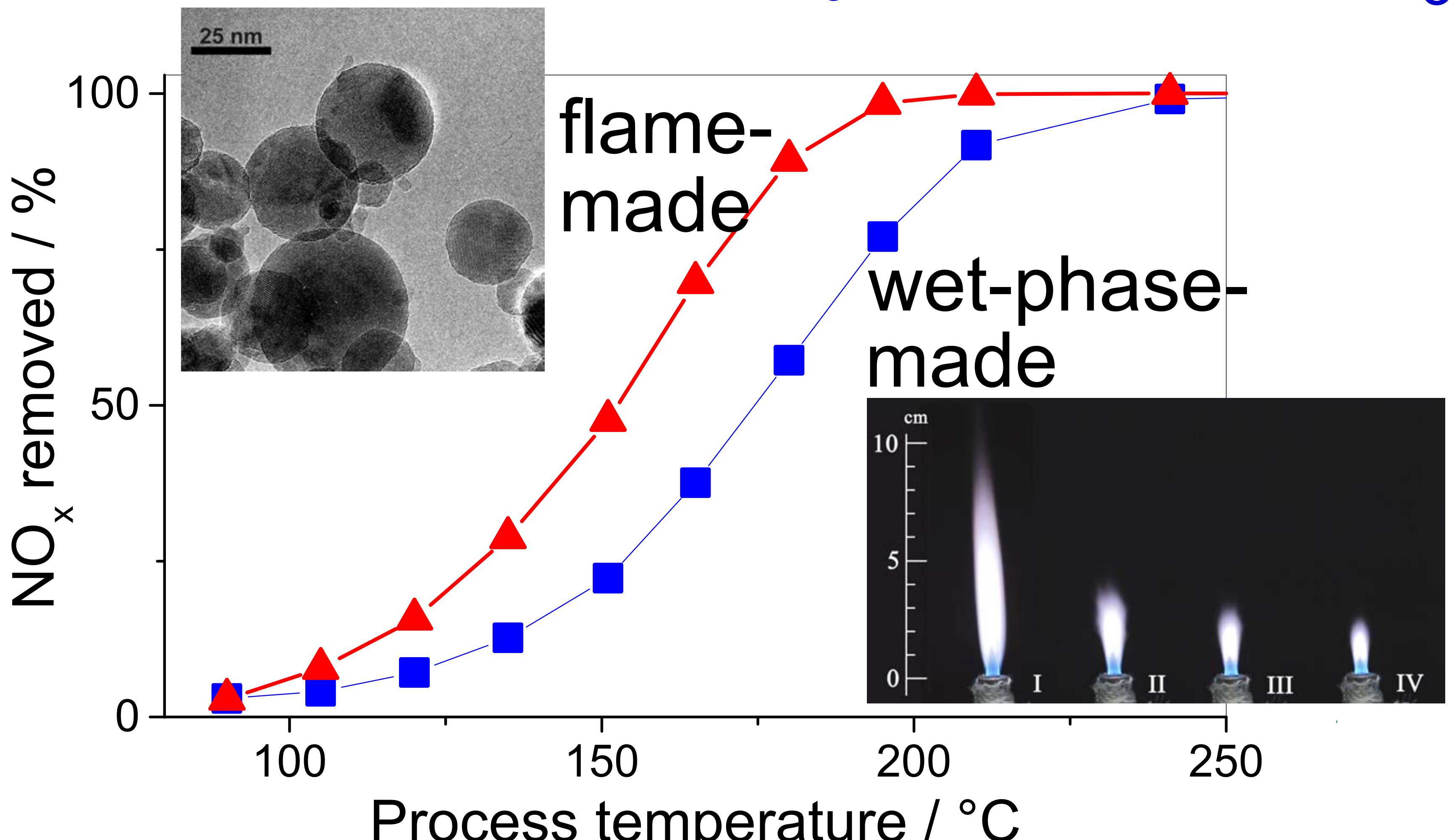


Nozzle
BND = 1.5 cm

Control of TiO_2 size, color & crystallinity



V_2O_5/TiO_2: Catalytic Removal of NO_x In Exhaust Gases by SCR with NH_3



Stark, Wegner, Pratsinis, Baiker,
J. Catal. **197**, 182 (2001)

ETH
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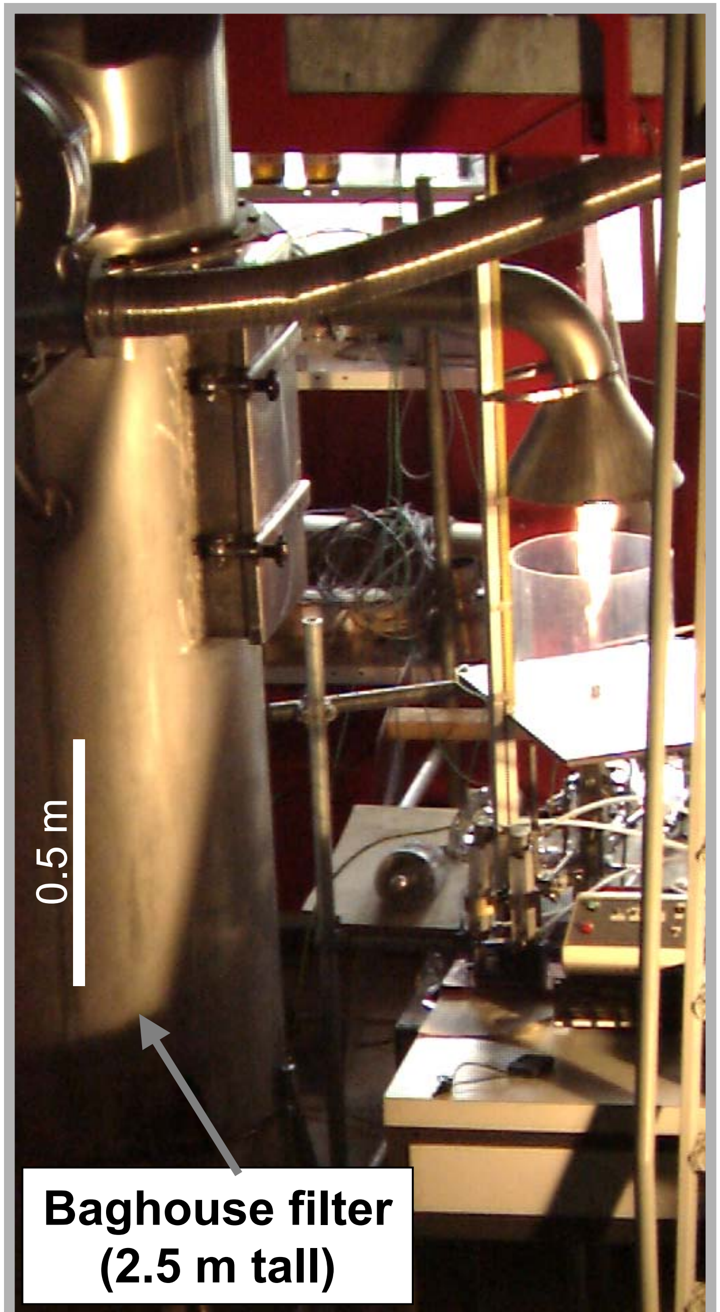
Swiss Federal Institute of Technology Zurich

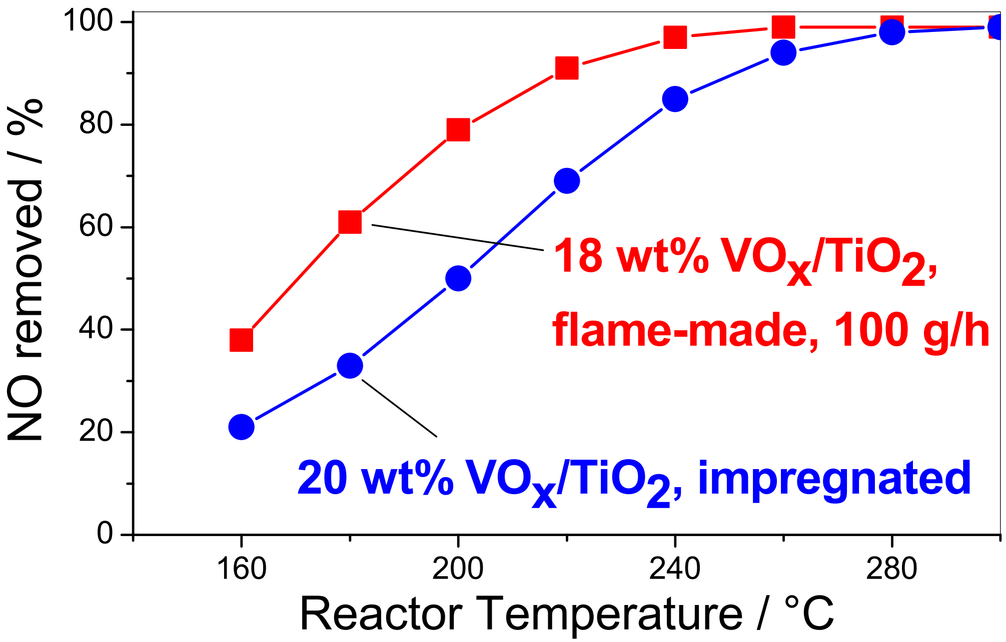


Pilot unit for flame synthesis of C/SiO_2, and now catalysts: V_2O_5/TiO_2 and TiO_2/SiO_2

Kammler, Mueller, Senn, Pratsinis,
AIChE J. **47**, 1533 (2001)

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Comparison to conventional DeNOx catalyst @ U. Essen (Prof. Cramer)



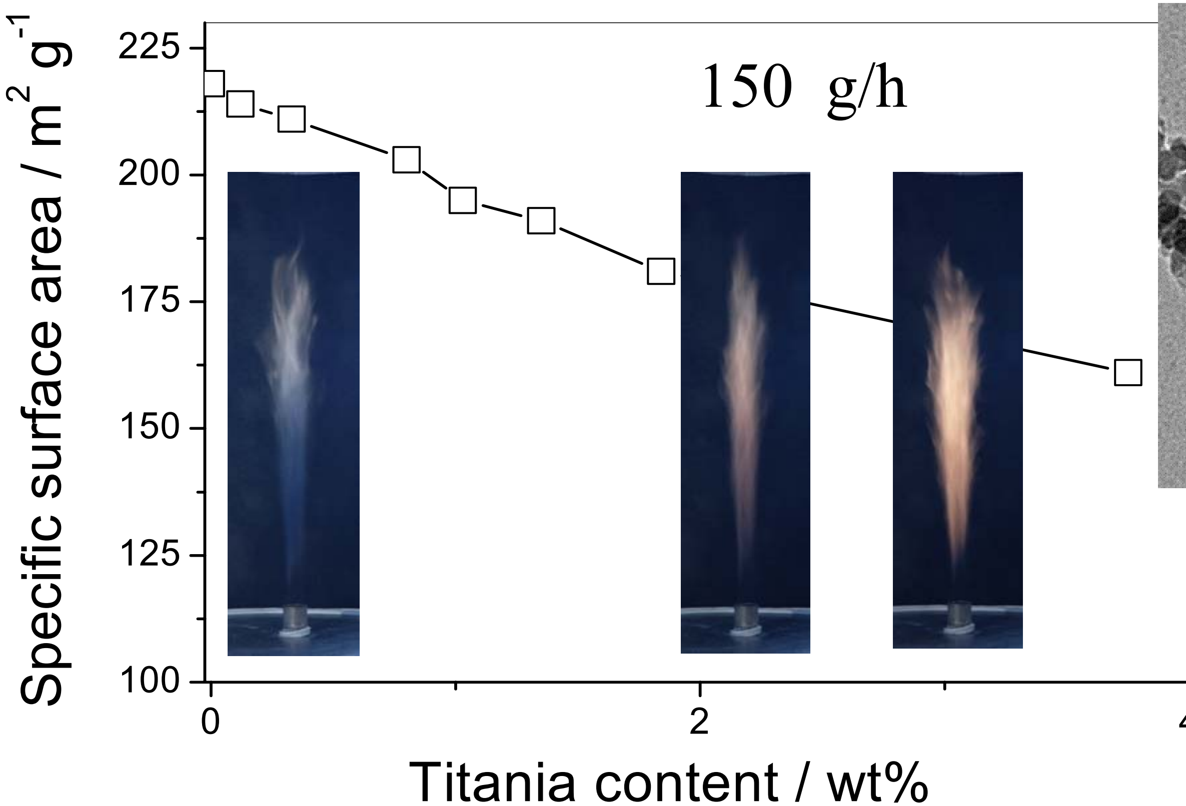
Fixed bed pilot-scale test reactor, 2.4 cm/sec

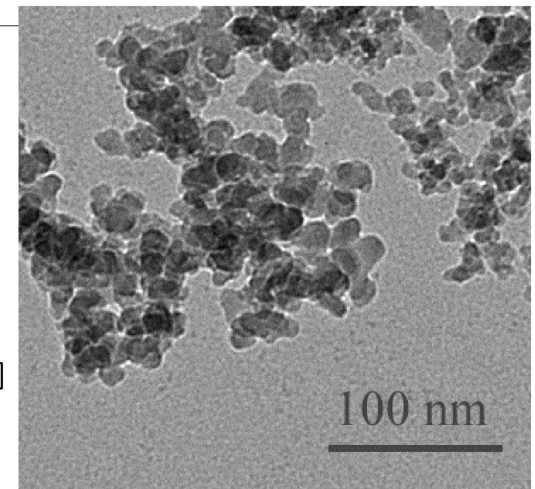
Gas composition:
-400 ppm NO
-400 ppm NH_3
-10 vol% oxygen in nitrogen

Reference:
-impregnated Degussa P 25
-same V content in both catalysts
-specific surface area: 50-55 m^2/g

•W. J. Stark, A. Baiker, S. E. Pratsinis, *Part. Part. Sys. Charact*. **19**, 306-311 (2002)

Epoxidation Catalysts: TiO_2 /SiO_2





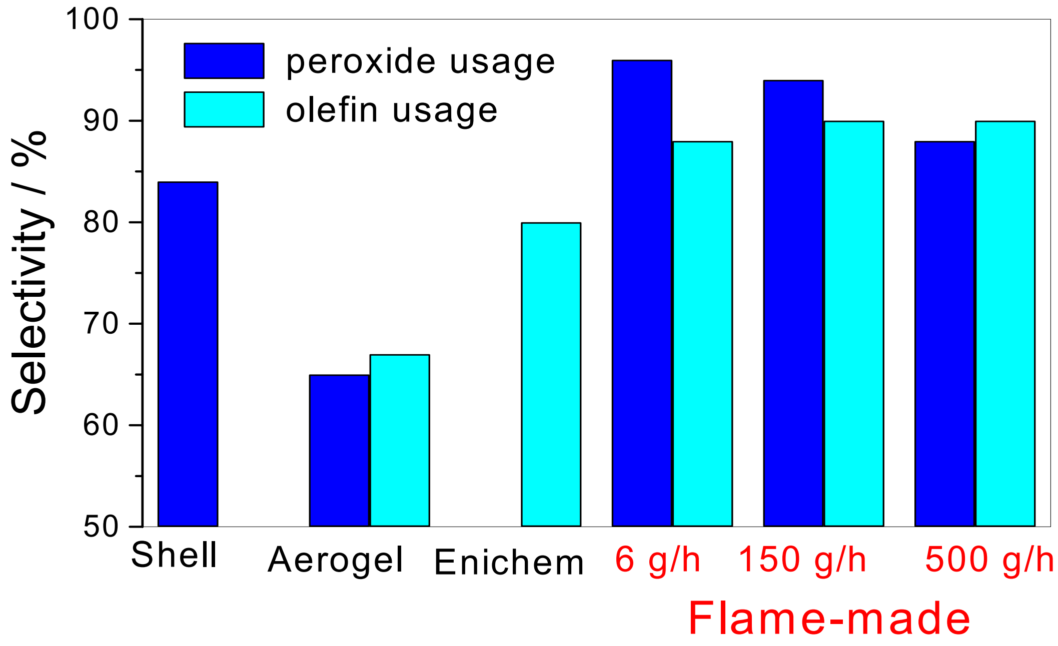
Hydrogen/air flame, burner diameter 19 mm, 0.73 m^3 H_2/h; 5.2 m^3 air/h

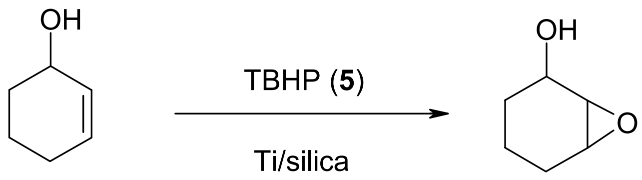
•W. J. Stark, S. E. Pratsinis, A. Baiker, *J. Catal*., **203**, 516 (2001) and *Ind. Eng. Chem. Res*., **41**, 4921 (2002)

TiO_2/SiO_2 epoxidation catalysts

Industrially (Shell, Enichem, Arco), several Mt/y :

$C_3 \Rightarrow$ *propene* $\Rightarrow$ *propene oxide* $\Rightarrow$ *polymers, surfactants*





1

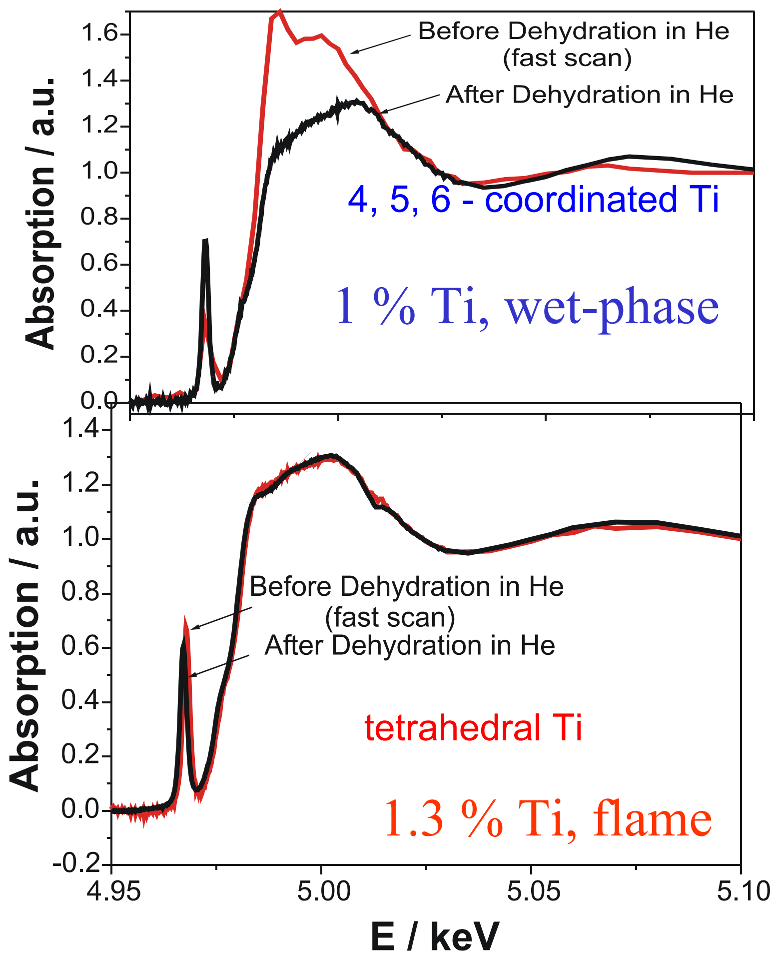
2

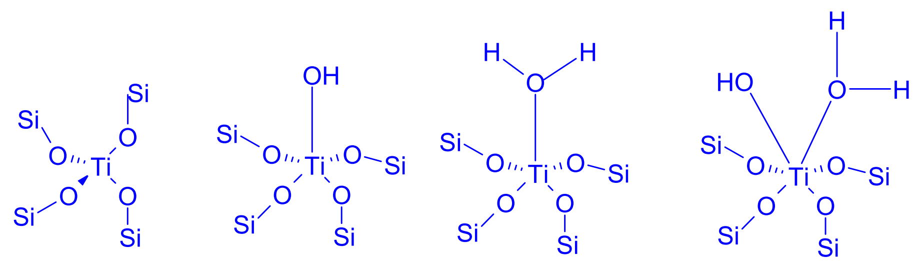
•W. J. Stark, H. K. Kammler, R. Strobel, D. Günther, A. Baiker, S. E. Pratsinis, *Ind. Eng. Chem. Res.*, **41**, 4921 (2002)

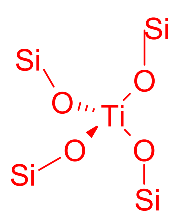
X-ray Absorption Near Edge Spectroscopy

In-situ XANES:

- -Geometry of the active site
- -Water content
- -Degree of hydration

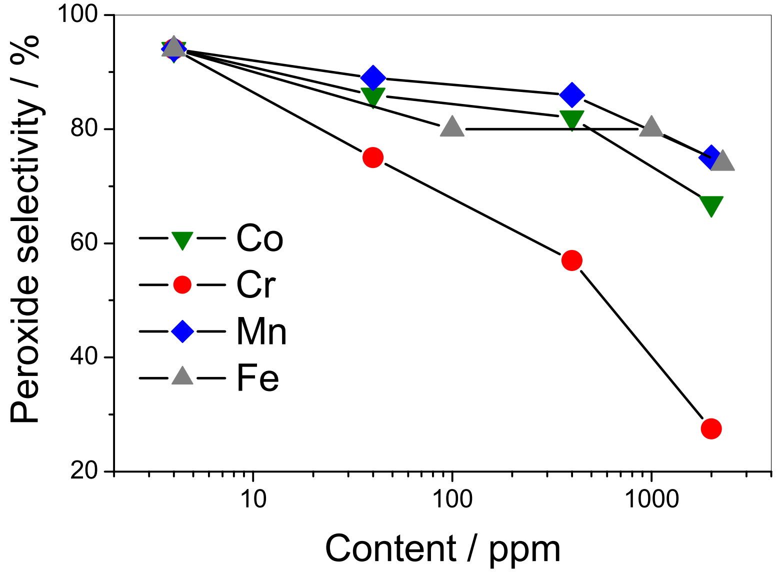


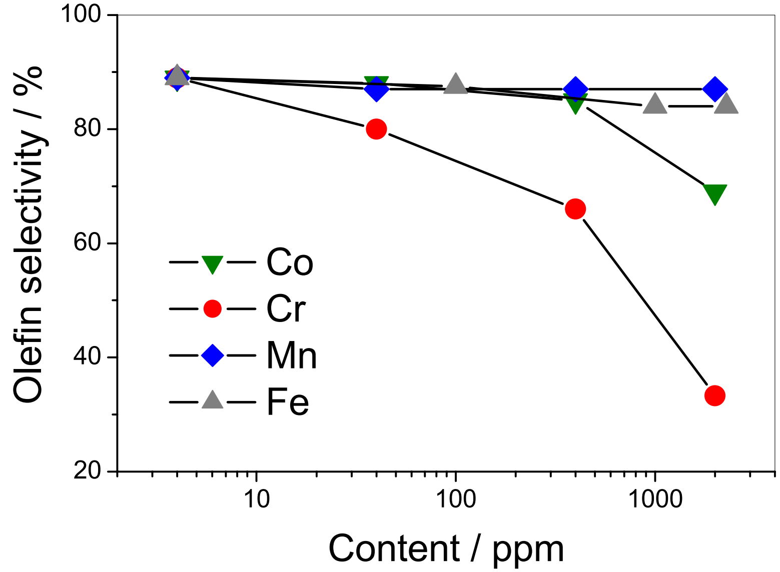




•J. D. Grunwaldt, C. Beck, W. J. Stark, A. Hagen, A. Baiker, *Phys. Chem. Chem. Phys*., **4**, 3514 (2002).

Selectivity





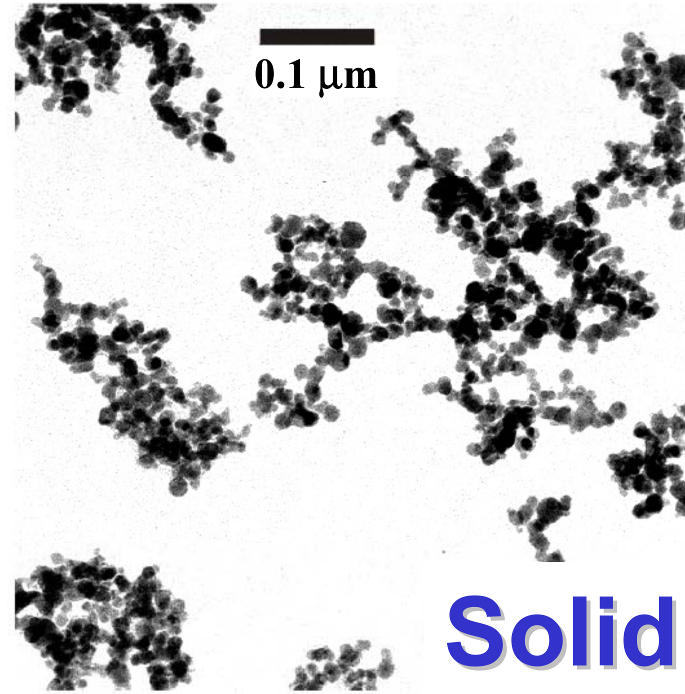
Even 40 ppm of transition metal strongly reduce selectivity

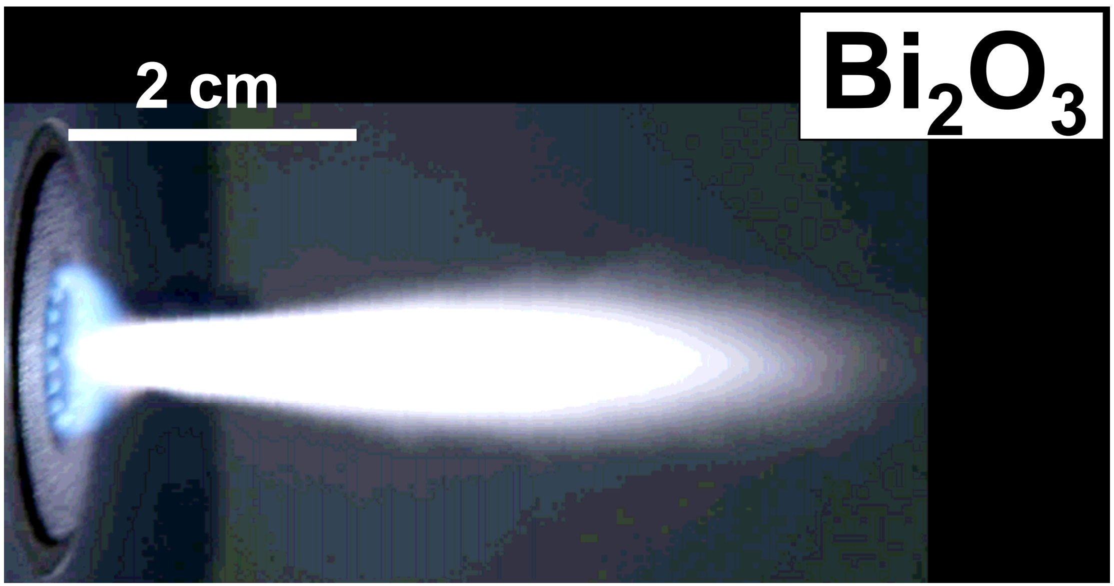
Good selectivity requires very pure catalysts.

•W. J. Stark, R. Strobel. D. Günther, S. E. Pratsinis, A. Baiker, *J. Mater. Chem*. **12**, 3620-25 (2002)

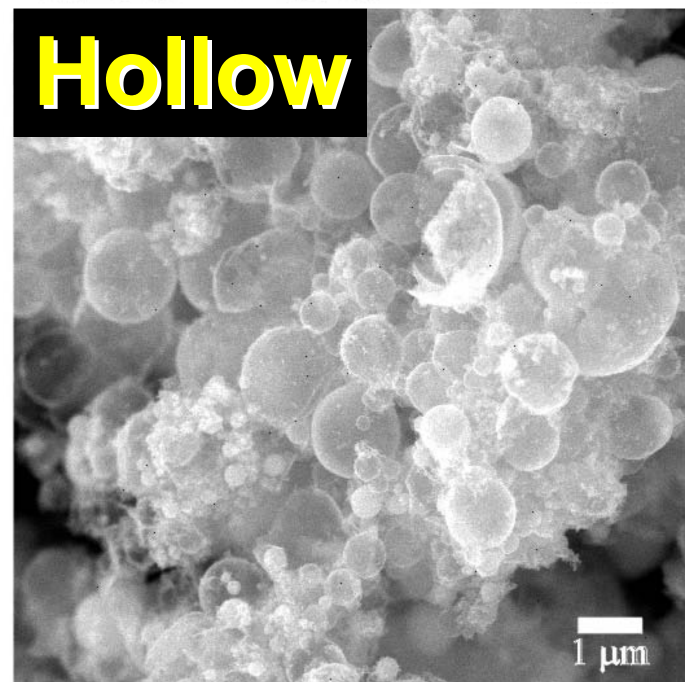
Flame Spray Pyrolysis

Al_2O_3, ZnO, CeO_2, ZrO_2
ZnO/SiO_2 , $BaTiO_3$
Au, Pt on TiO_2, SiO_2, Al_2O_3





Mädler, Pratsinis, *J.Am.Ceram.Soc*. **85,** 1713 (2002)



Varistors
Sensors
Catalysts

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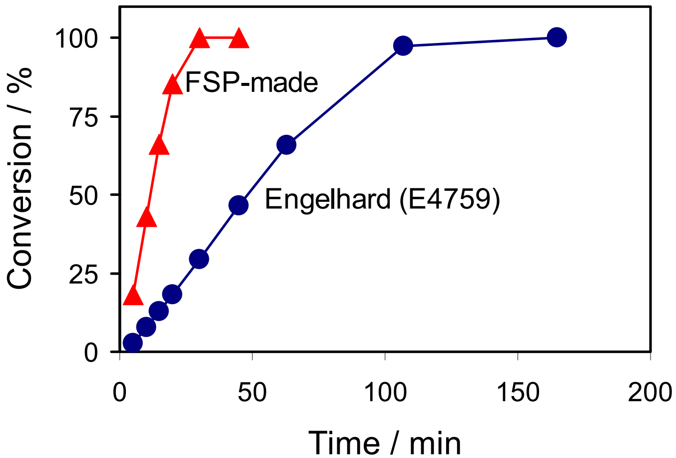
Swiss Federal Institute of Technology Zurich

Flame spray pyrolysis

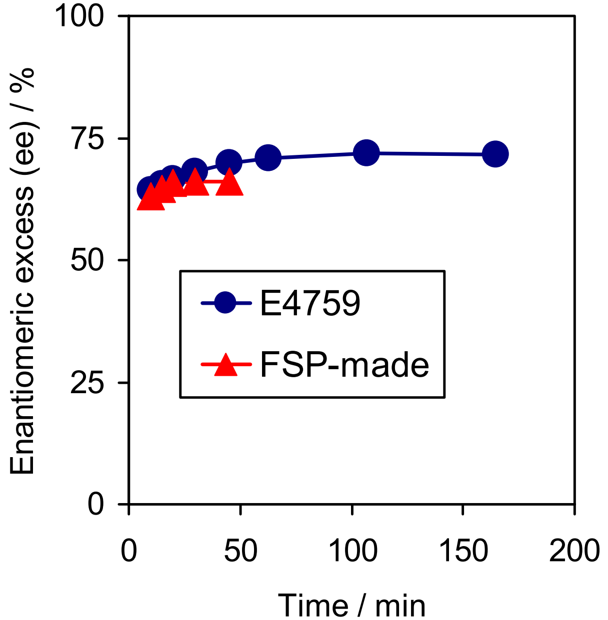
Strobel, Stark, Mädler, Pratsinis, Baiker, *J. Catal.* **213**, 296-304 (2003)

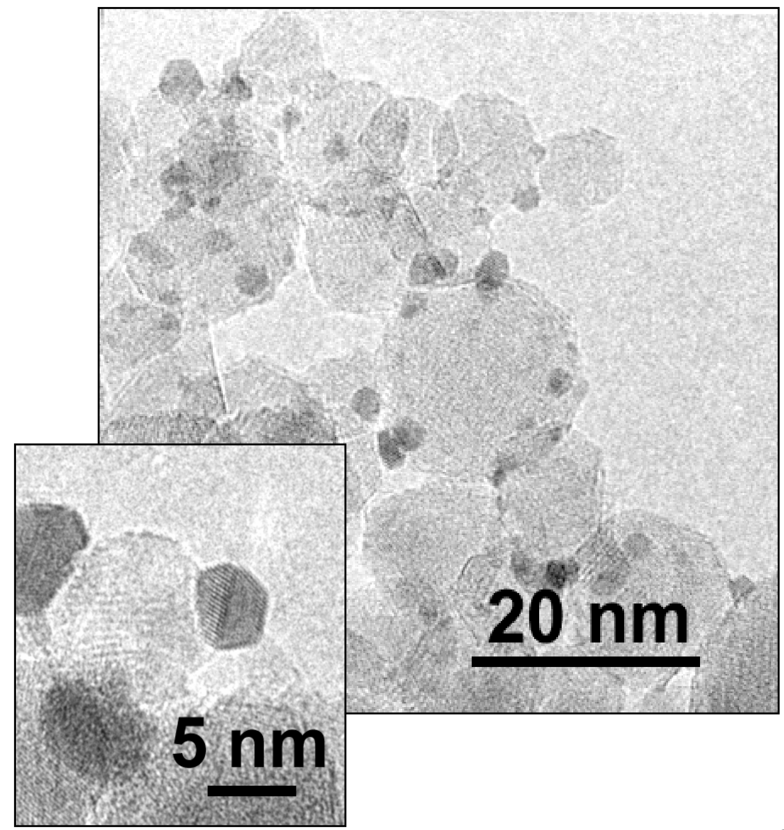
Spray flame producing Pt/Al_2O_3

Enantioselective hydrogenation of ethyl pyruvate by FSP-made Pt/Al_2O_3



Synthesis of chiral pharmaceuticals.





Strobel, Stark, Mädler, Pratsinis, Baiker, *J. Catal.* **213**, 296-304 (2003)

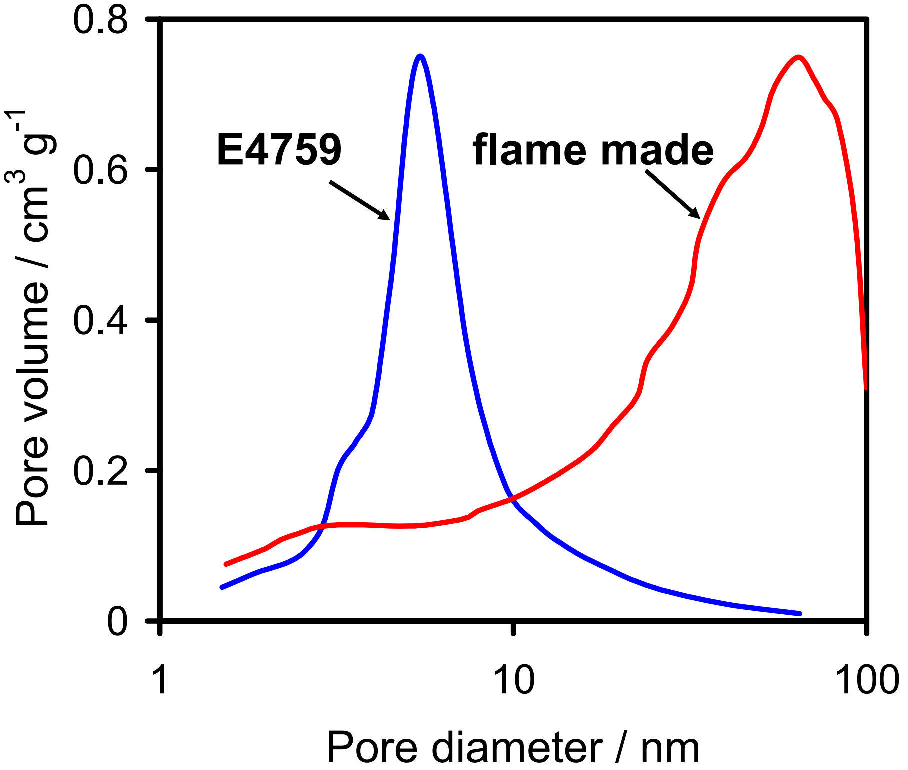
Open structure enhances activity

Nonporous, dense particles

➔ Better accessibility

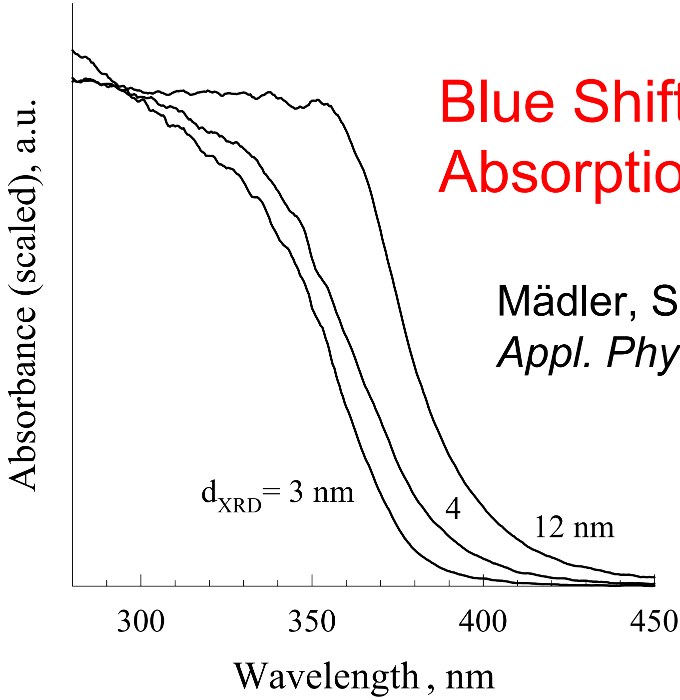
➔ High surface without trapped Pt in micropores.

➔ Maximum use of expensive platinum reduces costs



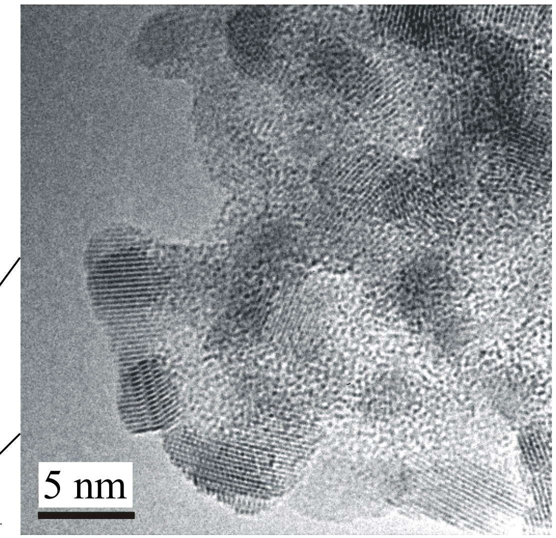
Strobel, Stark, Mädler, Pratsinis, Baiker, *J. Catal.* **213**, 296-304 (2003)

Rapid Synthesis of Stable ZnO Quantum Dots (1 - 5 nm)

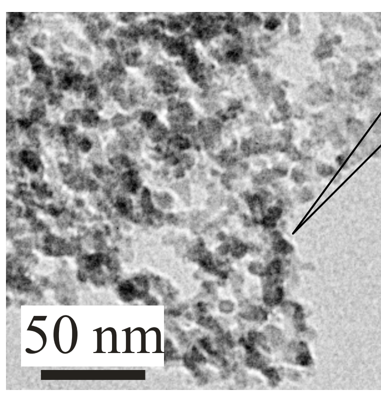


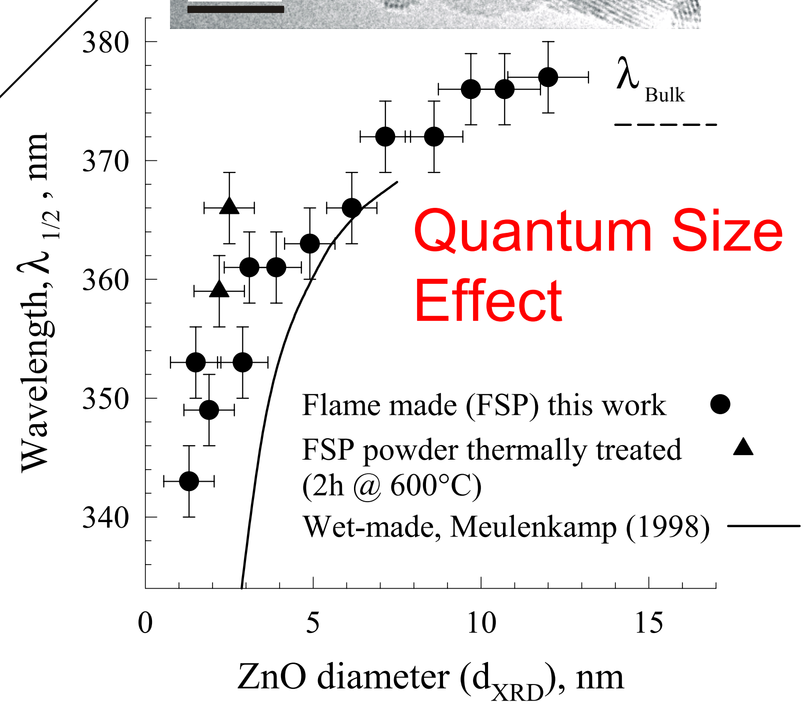
Blue Shift of Absorption Spectra

Mädler, Stark, Pratsinis, *J. Appl. Phys.* **92**, 6537-40 (2002)



Tani, Mädler, Pratsinis, *J. Mater. Sci*. **37**, 4627-4632 (2002)





Quantum Size Effect

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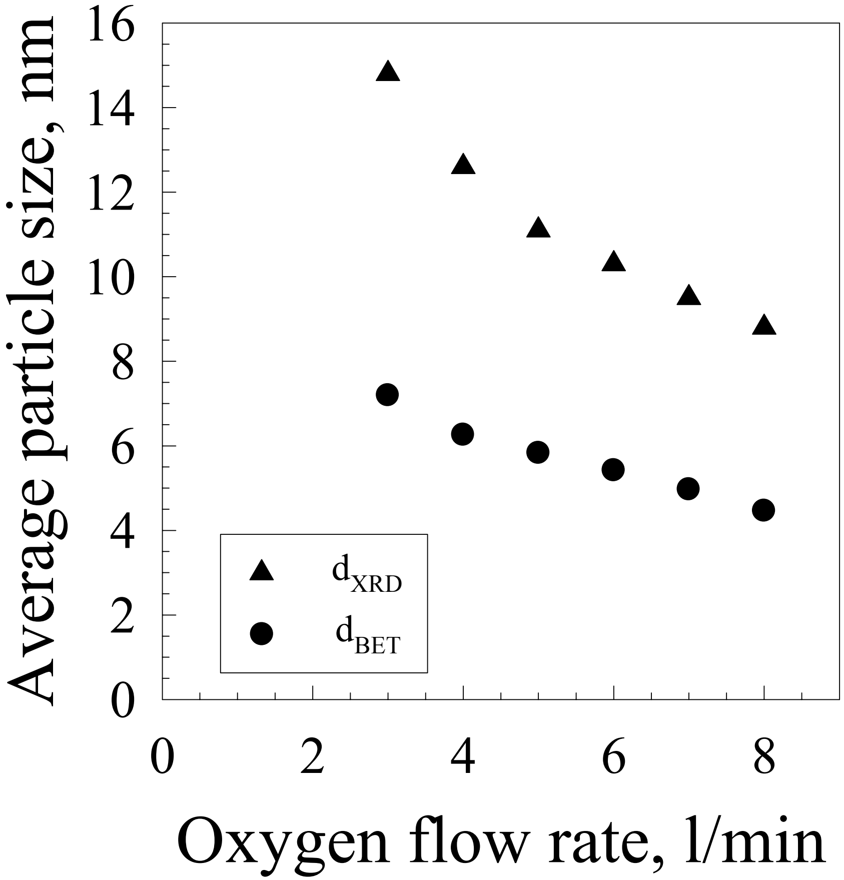
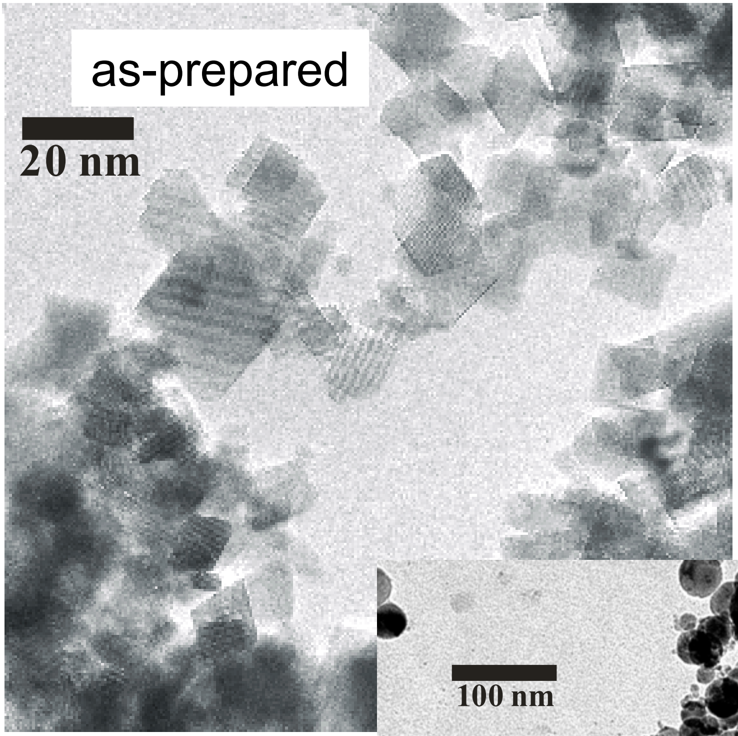
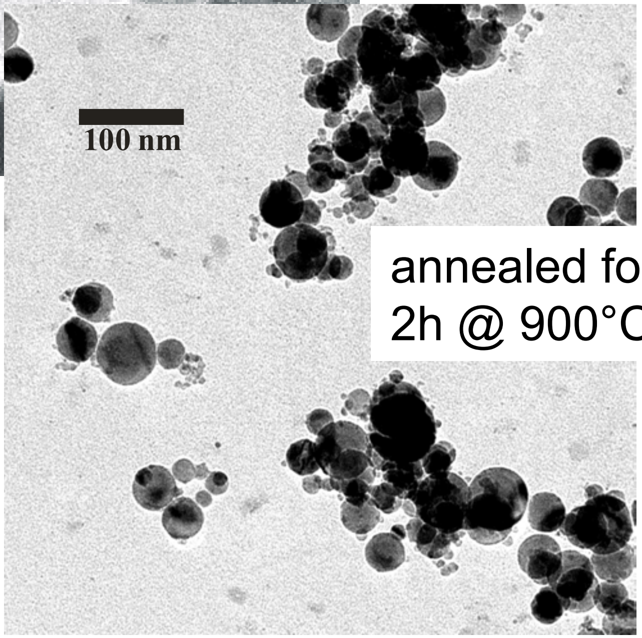
Swiss Federal Institute of Technology Zurich

Angular, rough, edgy-like n-CeO_2





Catalysts
Fuel Cells
Polishing



Mädler, Stark, Pratsinis,
J. Mater Res. **17**, 1356 (2002).

ETH
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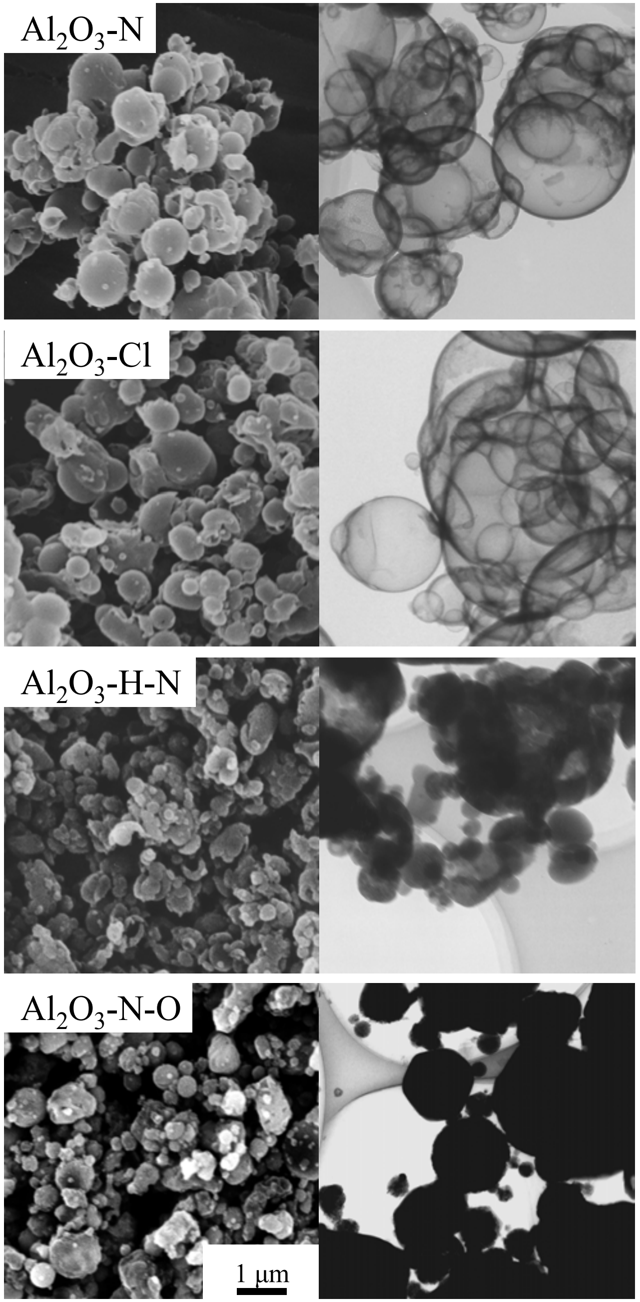
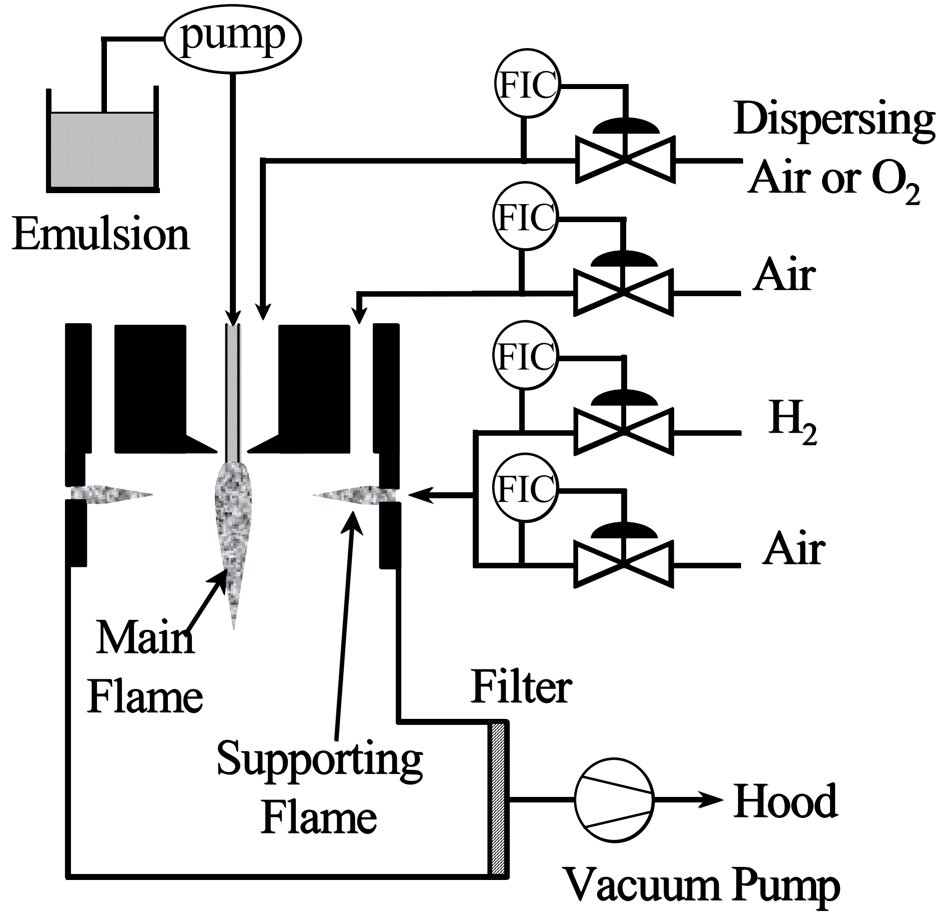
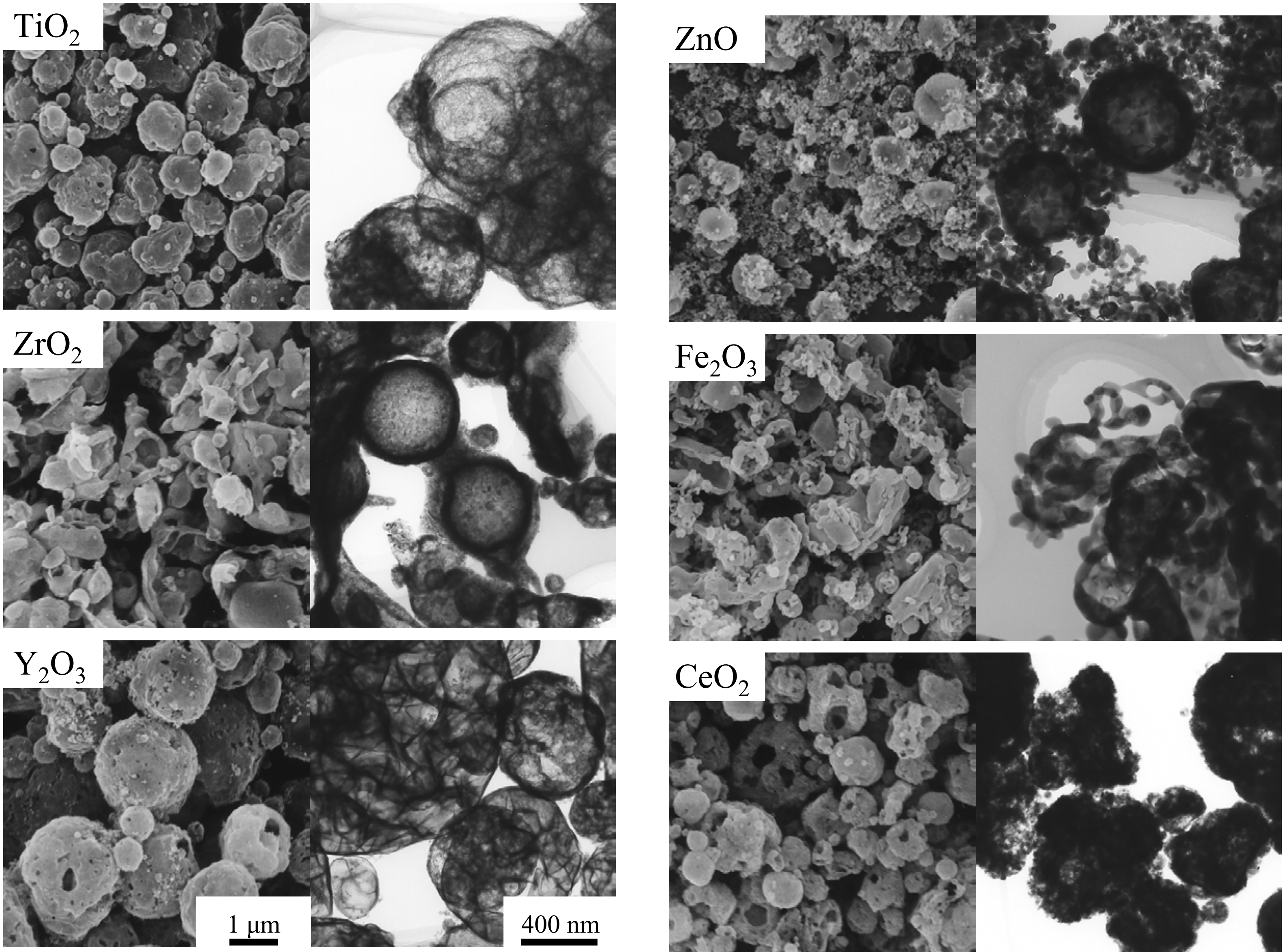
Swiss Federal Institute of Technology Zurich

Hollow particles by emulsion-fed FSP

Tani, Watanabe, Takatori and Pratsinis, *J. Am. Ceram. Soc.*, **86**, 898 (2003).







Emulsion-fed FSP.

Tani, Watanabe, Takatori and Pratsinis, *J. Am. Ceram. Soc.*, **86**, 898 (2003).

Conclusions

- V_2O_5 / TiO_2: SCR of NOx with NH_3
  – Purity improves conversion over wet-made ones
- TiO_2 / SiO_2 : Olefin epoxidation:
  – improved selectivity
  – role of transition metal dopants
  – structure of the active site
  – pilot-scale production (500 g/h)
- Pt / Al_2O_3: enantioselective hydrogenation
  – Open structure improves efficiency

Conclusions

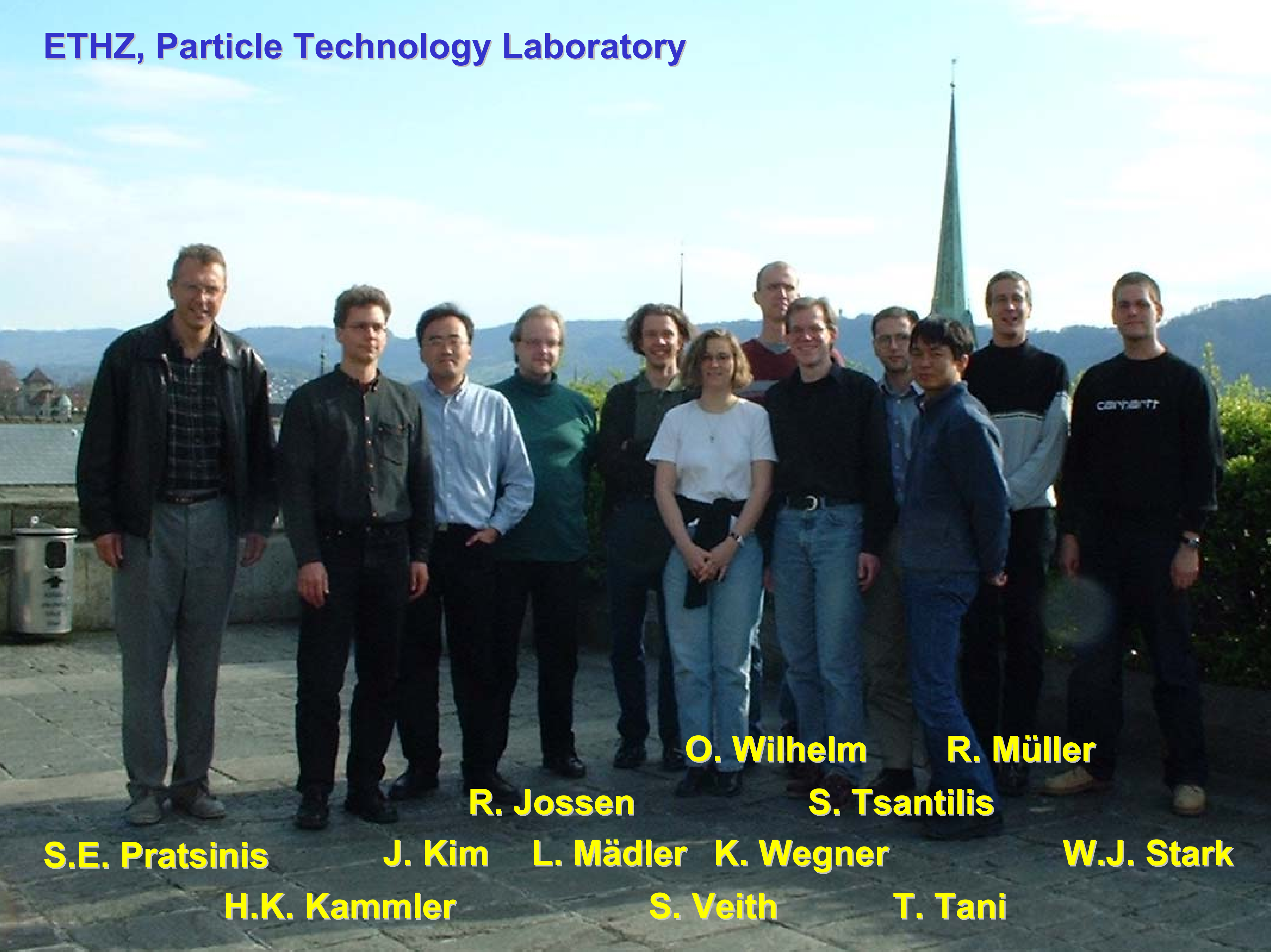
• Nanoparticle Technology is a frontier for scientific advances and even, for business opportunities (millionaires are made today!).

• Flame Processing is advantageous for particle manufacture:

Unique Structure, Crystallinity and Purity

Close control of Particle Size and Morphology

• Functional nanoparticles with tailor-made characteristics are made for catalyst, dental, battery and other materials.

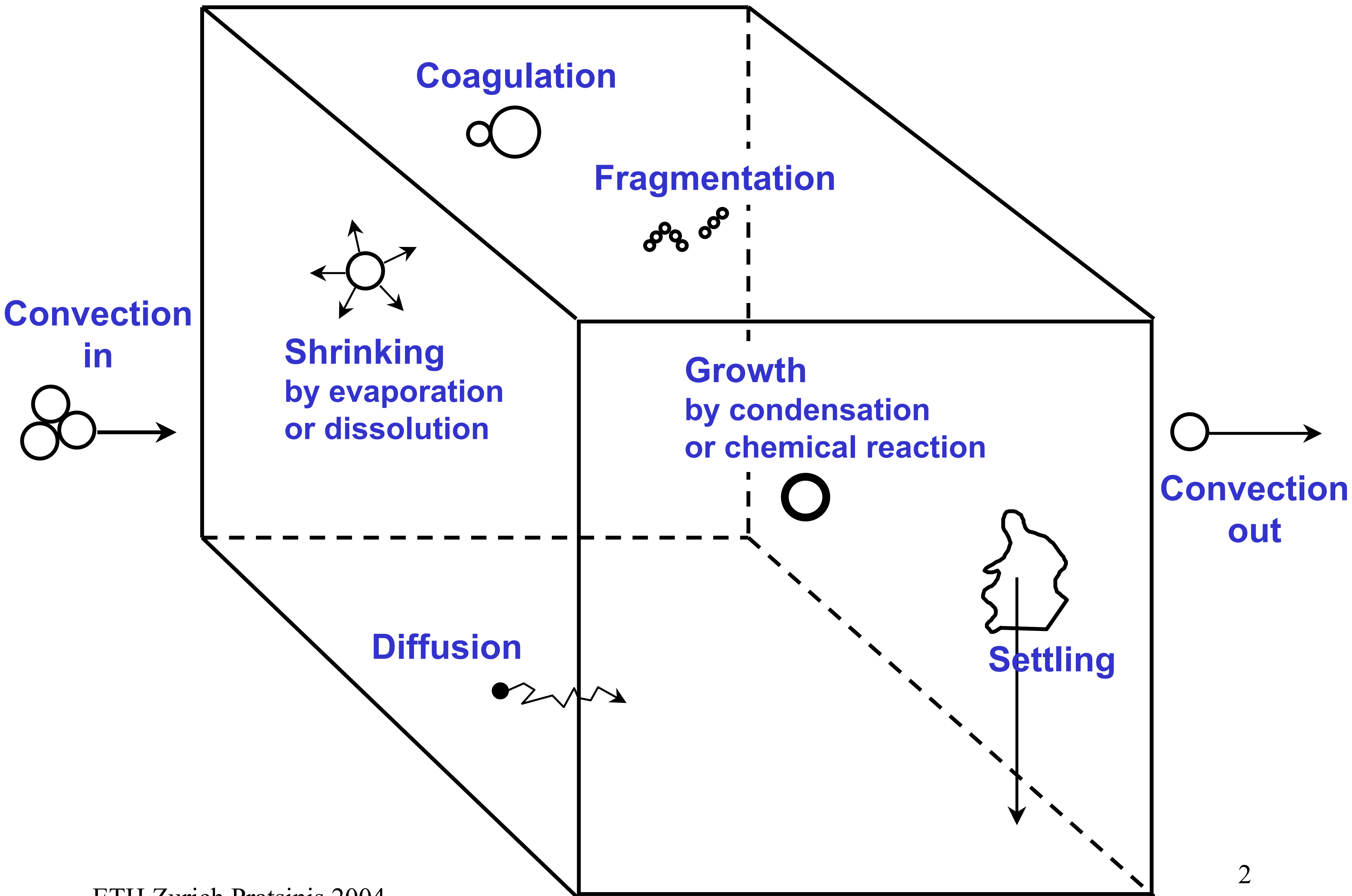

ETHZ, Particle Technology Laboratory
O. Wilhelm
R. Müller
R. Jossen
S. Tsantilis
S.E. Pratsinis
J. Kim
L. Mädler
K. Wegner
W.J. Stark
H.K. Kammler
S. Veith
T. Tani

2. Selected Fundamentals of Aerosol Formation

Prof. Sotiris E. Pratsinis
Particle Technology Laboratory
Department of Mechanical and Process Engineering,
ETH Zürich, Switzerland
www.ptl.ethz.ch

Sponsored by
Swiss National Science Foundation and
Swiss Commission for Technology and Innovation

Particle Dynamics



Theory: Population Balance Equation

$$\frac{\partial n}{\partial t} + \nabla \cdot n\,u = \nabla \cdot D \nabla n + \frac{\partial}{\partial v}\left(n \frac{dv}{dt}\right) - \nabla \cdot c\,n$$

convection diffusion growth external force

$$+\frac{1}{2}\int_0^{v} \beta(\tilde{v}, v-\tilde{v})\, n(\tilde{v})\, n(v-\tilde{v})\, d\tilde{v} - \int_0^{\infty} \beta(v,\tilde{v})\, n(v)\, n(\tilde{v})\, d\tilde{v}$$

coagulation

$$- S(v)\, n(v) + \int_v^{\infty} \gamma(v,\tilde{v})\, S n(\tilde{v})\, d\tilde{v}$$

fragmentation

u = gas velocity vector u_x, u_y, u_z $\nabla \cdot n\,u = u \nabla n + n \cdot \underbrace{\nabla u}_{0}$

continuity

D = particle diffusivity

c = velocity of particles of size v (e.g. settling)

β = coagulation rate

S = fragmentation rate

γ = fragment size distribution

2. Fundamentals of Particle Formation

2.0 Books

Smoke, Dust and Haze, S.K. Friedlander, Oxford, 2nd edition, 2000
Aerosol Processing of Materials, T.Kodas M. Hampden-Smith, Wiley, 1999
Aerosol Technology, W. Hinds, Wiley, 2nd Edition, 2000.

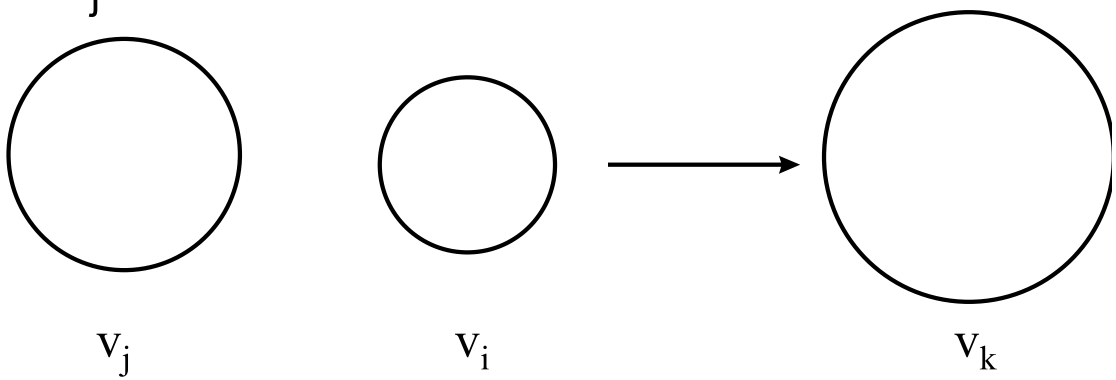
2.1 Coagulation

Atmospheric processes (air pollution, smog), Plumes, Tailpipe exhaust, Optical fibers for telecommunications, Carbon blacks for tires, Pigments, Enlargement by granulation or flocculation

The theory of coagulation is based on:
a) collision theory
b) field forces

2.1.1 Collision frequency function

Assume that collisions occur between two clouds of partices of volume v_i and v_j:



The number of collisions per unit time and unit volume is:

$$P_{ij} = \beta(v_i, v_j) n_i n_j$$

Where the collision frequency is the rate of collisions per particle per unit volume. This function depends on temperature, pressure and particle size.

The birth of particles of size k=(i+j) is given by:

$$\frac{1}{2}\sum_{i+j=k} P_{ij}$$

The factor ½ is included to correct for double counting.

The loss of particles of size k by collision with all other particles is:

$$\sum_{i=1}^{\infty} P_{ik}$$

Then the net rate of change in particle concentration is:

$$\frac{dn_k}{dt} = \frac{1}{2}\sum P_{ij} - \sum P_{ik}$$

$$= \frac{1}{2}\sum_{i+j=k} \beta(v_i, v_j) n_i n_j - n_k \sum_{i=1}^{\infty} \beta(v_i, v_k) n_i$$

This is the basic equation for coagulation that is encountered in many physical phenomena:
Granulation, Flocculation etc.

It used to be <u>very</u> intimidating 10 years ago, but not anymore.
It can be easily solved.

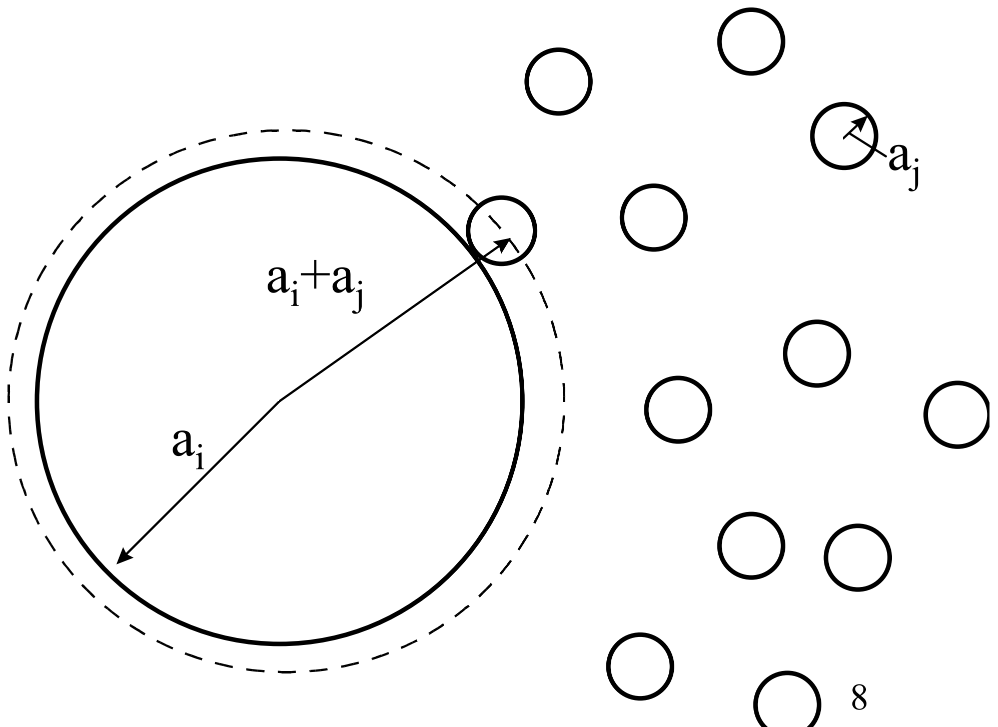
GOAL: To determine collision frequency function

2.1.2 CASE 1: Brownian Coagulation

In a stagnant gas coagulation takes place by diffusion of particles to the surface of each other.

Consider a sphere of radius a_i at a fixed point.
Particles of radius a_j are in Brownian motion and diffuse to the surface of a_i:

We would like to calculate the concentration profile n_j away from the surface of particle i so we can calculate the flux of particles j to the surface of particle i. This will give the rate of collisions of particles i and j per unit area of particle i.



Let us drop the subscript j for convenience and write a balance for particles of size a_j.
For spherical symmetry:

$$\frac{\partial n}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial n}{\partial r}\right)$$

With boundary conditions:

$$\begin{aligned} r = a_i + a_j &: \quad n = 0 \\ r \to \infty &: \quad n = n_0 \\ t = 0 &: \quad n = n_0 \quad \forall r \end{aligned}$$

The solution of this equation is:

$$n(r,t) = n_0\left[1 - \frac{a_i + a_j}{r}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\frac{r-(a_i+a_j)}{2\sqrt{Dt}}} e^{-z^2}\,dz\right)\right]$$

$$= n_0\left[1 - \frac{a_i + a_j}{r}\,\mathrm{erfc}\left(\frac{r - [a_i + a_j]}{2\sqrt{Dt}}\right)\right]$$

Now calculate the rate at which particles arrive at the surface

$$F = 4\pi\left(a_i + a_j\right)^2 J\Big|_{a_i + a_j} = 4\pi\left(a_i + a_j\right)^2 D\left(\frac{\partial n}{\partial r}\right)_{r = a_i + a_j}$$

$$= 4\pi\left(a_i + a_j\right) D n_0 \left(1 + \frac{a_i + a_j}{\sqrt{\pi D t}}\right)$$

For $t >> 0$ (d_P=1μm t>10s or d_p=0.1μm t>0.01s):

By definition $\beta = \frac{F}{n_0}$, so: $F = 4\pi\left(a_i + a_j\right) D n_0$ (1)

Now consider that the sphere a_i is in Brownian motion. Then we introduce the diffusion coefficient describing the relative motion of the two particles:

$$D = D_{ij} = \frac{\overline{\left(x_i - x_j\right)^2}}{2t} \quad \text{Einstein equation}$$

$$D_{ij} = \frac{\overline{x_i^2}}{2t} - \underbrace{\frac{\overline{2x_i x_j}}{2t}}_{\to\, 0} + \frac{\overline{x_j^2}}{2t} = D_i + D_j \qquad (2)$$

Then the collision frequency function becomes from (1) & (2):

$$\beta(v_i, v_j) = 4\pi(D_i + D_j)(a_i + a_j) \quad \text{where} \quad D = \frac{k_B T}{f}$$

$$\beta = 4\pi \frac{k_B T}{3\pi\mu}\left(\frac{1}{d_{P,i}} + \frac{1}{d_{P,j}}\right)\left(\frac{d_{P,i}}{2} + \frac{d_{P,j}}{2}\right)$$

$$= \frac{2k_B T}{3\mu}\left(\frac{1}{v_i^{1/3}} + \frac{1}{v_j^{1/3}}\right)\left(v_i^{1/3} + v_j^{1/3}\right)$$

This is the **collision frequency function** in the **continuum limit** $(d_P >> \lambda)$.

2.1.3 Coagulation of Monodisperse Particles

Assume that all particles have the same size during coagulation. This is a bold assumption but amazingly good and useful. Then, we can describe the rate of change of particle concentration as:

$$\frac{dN}{dt} = -\frac{1}{2}\beta(v_1, v_1)N^2$$

where the collision frequency function is:

$$\beta(v_1, v_1) = \frac{2k_B T}{3\mu}\left(\frac{1}{v_1^{1/3}} + \frac{1}{v_1^{1/3}}\right)\left(v_1^{1/3} + v_1^{1/3}\right) = \frac{8k_B T}{3\mu}$$

Then $\frac{dN}{dt} = -\frac{\beta}{2}N^2$ and integration gives: $N = \frac{N_0}{1 + \frac{\beta N_0}{2}t}$

This simple expression can be used to estimate the half-life of an aerosol, or the time needed for particles to grow to a certain size by coagulation, or even the significance of coagulation with respect to other processes.

For example, estimate the time needed to reduce the concentration of a monodisperse aerosol to 90%, 50% or 10% of its initial concentration 10^8 particles/cm^3, and initial diameter 100nm, cm^3/s.

For $\frac{N}{N_0} = 0.9$: $t = \frac{2\left(\frac{N_0}{N} - 1\right)}{\beta N_0} \approx 1.5$ s

For $\frac{N}{N_0} = 0.5$: $t \approx 14$ s

For $\frac{N}{N_0} = 0.1$: $t \approx 125$ s

2.1.4 CASE 2: Coagulation in the free molecule regime

In this case the concept of continuum does not exist anymore so we cannot write the Navier-Stokes equations as we did for case 1.

Instead we rely on the kinetic theory of gases (e.g. N. Davidson, Statistical Mechanics, Ch. 10, McGraw, New York, 1962).

The mean scalar velocity of N gas molecules of mass m_1 per cm^3 having a Maxwellian distribution is:

$$\bar{c} = \sqrt{\frac{8 k_B T}{\pi m_1}}$$

The total rate at which molecules strike a surface dS is

$$e(s) = \frac{1}{4} N \bar{c}\, dS$$

For a sphere of radius a_2 colliding with particles (molecules) of equivalent spherical radius a_1

$$F = e(s) = \frac{1}{4} N \bar{c} S = \frac{1}{4} N \sqrt{\frac{8kT}{\pi m_1}}\, 4\pi a^2 = \pi N \bar{c} a^2$$

where $a=a_1+a_2$ is the collision radius. Now if the sphere also moves then the number of collisions increases as:

$$F = \pi N \bar{c}_{12} a^2 = \pi N \sqrt{\bar{c}_1^2 + \bar{c}_2^2}\; a^2$$

$$F = \beta_{fm} N = \pi N \sqrt{\frac{8 k_B T}{\pi \rho_P}} \left(\frac{1}{v_1} + \frac{1}{v_2}\right)^{1/2} \left(\frac{3}{4\pi}\right)^{2/3} \left(v_1^{1/3} + v_2^{1/3}\right)^2$$

$$\beta_{fm} = \left(\frac{3}{4\pi}\right)^{1/6} \sqrt{\frac{6 k_B T}{\rho_P}} \left(\frac{1}{v_1} + \frac{1}{v_2}\right)^{1/2} \left(v_1^{1/3} + v_2^{1/3}\right)^2$$

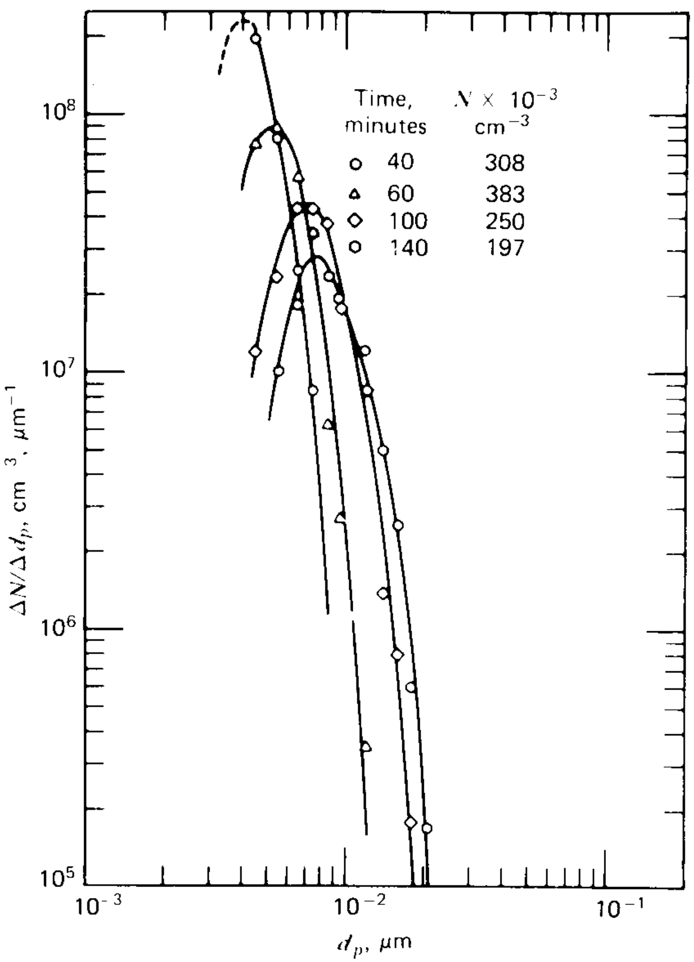
This is the **collision frequency function** for $d_P \ll \lambda$.

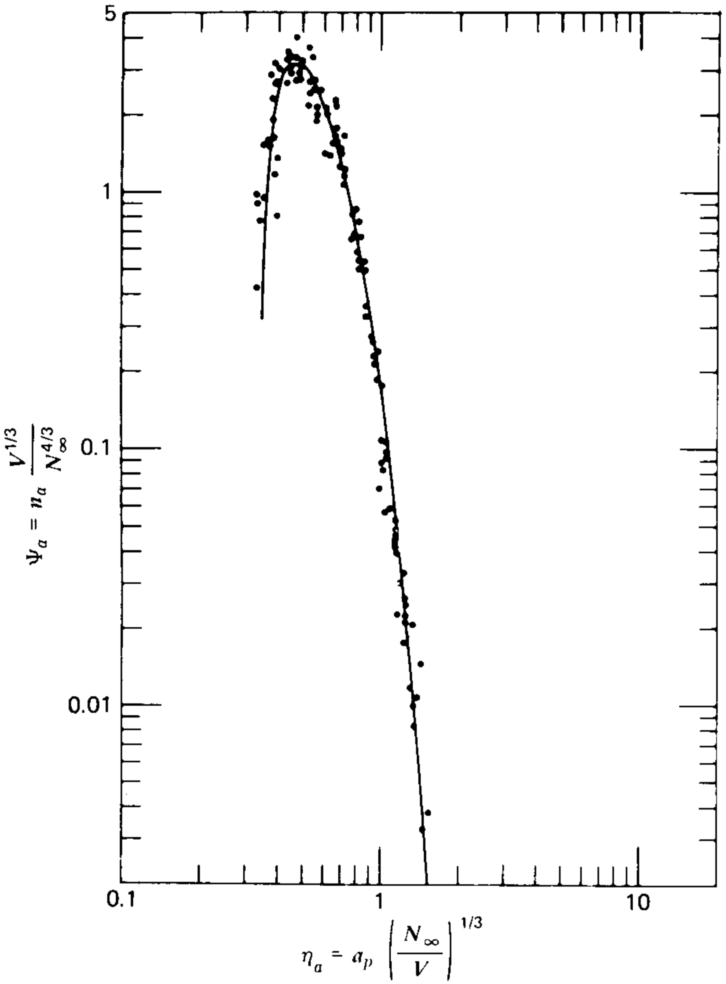
2.1.7 Self-Preserving Theory

Observation of natural particle suspensions in gases (atmospheric aerosols) undergoing coagulation indicated that after a long time the particle size distribution attains a shape that is invariant with time.

More specifically, when the size distribution is scaled by some factor (e.g. average particle size) then the distributions fall on top of each other and are called self-preserving. This was observed first experimentally

(e.g. Husar & Whitby, Environ. Sci. Technol. 7:241, 1973):





Size distribution of an aging free molecule aerosol generated by exposing filtered laboratory air in 90 m^3 polyethylene bag to solar radiation.

Size distribution as on left side, plotted in the self-preserving form. The curve is based on the data.

According to this, the particle volume v becomes non-dimensional by dividing by the average volume concentration where V is the aerosol volumetric concentration $[m_p^3/m_G^3]=[-]$ and N the number concentration respectively:

$$\eta = \frac{v}{\bar{v}} = \frac{N \cdot v}{V}$$

And the particle size distribution is defined in a non-dimensional form as:

$$\psi(\eta) = n(v)\frac{V}{N^2}$$

2.2 Particle Formation by Nucleation-Condensation

A phase transition is encountered in many industrial (e.g. crystallization, carbon black production) and environmental (e.g. smog formation) processes

The fundamental equation that describes these processes is:

$$\frac{\partial n}{\partial t} + \nabla \cdot v_i n = 0$$

With boundary conditions:

at	$d_P = d_P^*$	$n_i v_i^* = I^*$	nucleation
	$t = 0$	$n = n_0(d_P)$	initial distribution

The **goal** is to determine:

1. the critical diameter for particle formation which is dictated by thermodynamics

2. the growth rate that is determined by thermodynamics and transport

3. the nucleation rate which is determined by thermodynamics and kinetic theory by physical (e.g.cooling) or chemical (e.g. reactions) driving forces

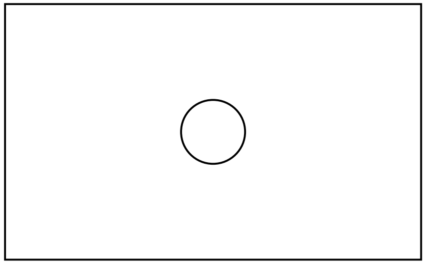
2.2.1 Critical Particle Size

Key feature: The curved interface

The goal is to derive an expression relating the concentration (vapor pressure) of species A with a particle (droplet) of radius d_P at equilibrium (Seinfeld, 1986)

If the interface was flat which is, for example, the tabulated equilibrium concentration or vapor pressure at a given temperature and pressure.

Consider the change in Gibbs free energy accompanying the formation of a single drop (embryo) of pure material A of diameter d_P containing g molecules of A:



$$\Delta G = G_{\text{embryo system}} - G_{\text{pure vapor}} \quad (1)$$

Now let's say that the number of molecules in the starting condition of pure vapor is n_T. After the embryo forms, the number of vapor molecules remaining is $n = n_T - g$. Then the above equation is written as:

$$\Delta G = nG_v + gG_l + \pi d_P^2 \sigma - n_T G_v \qquad (2)$$

where G_V and G_l are the free energies of a molecule in a liquid and vapor phases and σ is the surface energy

$$\Delta G = g(G_l - G_v) + \pi d_P^2 \sigma = \frac{\pi d_P^3}{6 v_l}(G_l - G_v) + \pi d_P^2 \sigma \quad (3)$$

Noting that $g v_l = \dfrac{\pi d_P^3}{6}$

Where v_l is the volume occupied by a molecule in the liquid phase (equivalent sphere in liquid phase).

Before we go further let's evaluate the difference in Gibbs free energy:

$dG = VdP$ then $dG = (v_l - v_v)\, dP$

But $v_l << v_v$ then $dG = - v_v\, dP$

According to ideal gas law $v_v = k_B T/P$

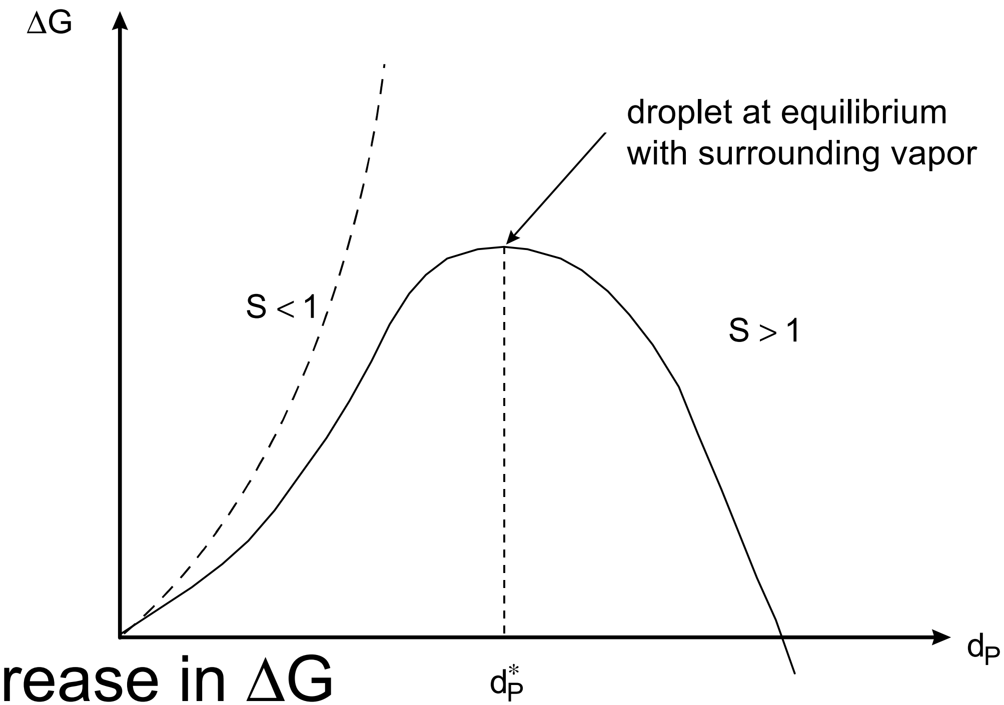
Then $$G_v - G_l = -k_B T \int_{P_{A0}}^{P_A} \frac{dP}{P} = -k_B T \ln \frac{P_A}{P_{A0}} = -k_B T \ln S$$

Where S is the saturation ratio.

Now equation 3 becomes:

$$\Delta G = -\underbrace{\frac{\pi d_P^3}{6v_l} k_B T \ln S}_{\text{volume free energy of an embryo}} + \underbrace{\pi d_P^2 \sigma}_{\text{surface free energy}}$$

Now plot ΔG as a function of d_P



S <1 monotonic increase in ΔG

S > 1 positive and negative contributions at small d_P the surface tension dominates and the behavior of ΔG as a function of d_P is close to that for S <1. For larger d_P the first term becomes important.

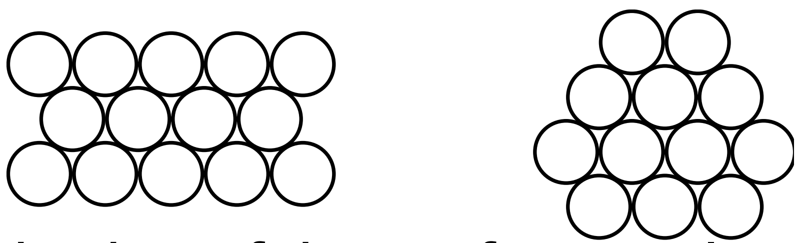
At $\dfrac{\partial \Delta G}{\partial d_P} = 0 \qquad \Rightarrow \qquad d_P^* = \dfrac{4\sigma v_l}{k_B T \ln S}$

This is the minimum possible particle size.

This equation relates the equilibrium radius of a droplet of a pure substance to the physical properties of the substance and the saturation ratio of its environment. It is called also the Kelvin equation and the critical diameter is called the Kelvin diameter.

This equation relates the equilibrium radius of a droplet of a pure substance to the physical properties of the substance and the saturation ratio of its environment. It is called also the Kelvin equation and the critical diameter is called the Kelvin diameter.

The Kelvin equation states that the vapor pressure over a curved interface always exceeds that of the same substance over a flat surface:



See the anchoring of the surface molecules on a flat and a curved surface. Surface molecules are anchored on two molecules on the layer below flat surfaces while on curved interfaces some are anchored on just one!
These can easily escape (evaporate) from the condensed (liquid or solid) phase.

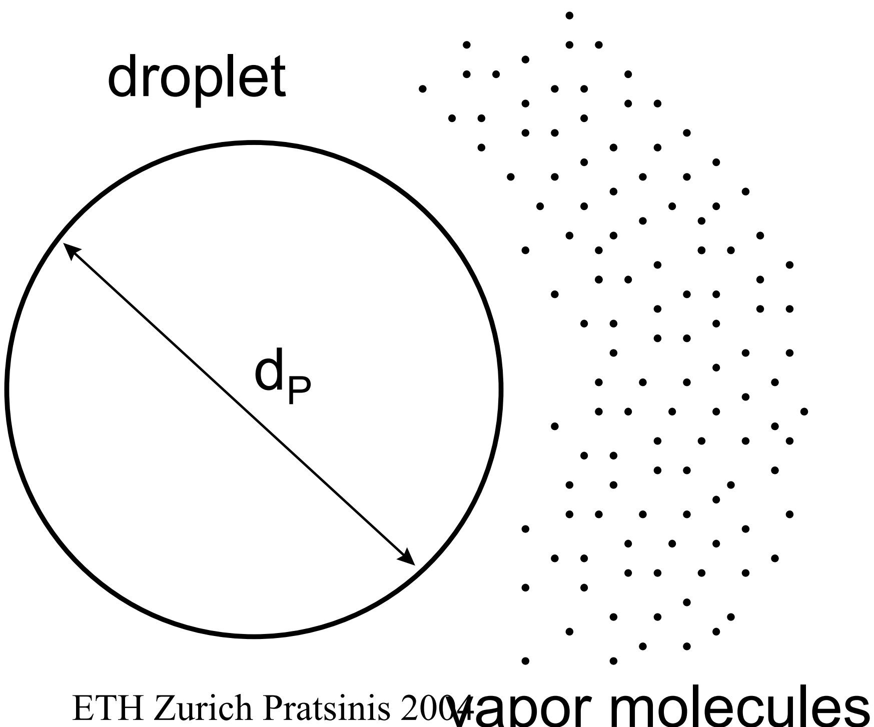
2.3 Particle Growth

The mechanism for particle growth refers to droplet or particle growth from gas (condensation), to crystal growth from solution etc..
In all cases mass should be transported to the particle surface.

In principle, two steps are required, a diffusional step followed by a surface reaction or rearrangement step.
In condensation the former is dominant while in crystallization is the latter. In many processes both can be dominant.

2.3.1 Mass transfer to a particle surface (continuum)

Consider a single droplet growing by condensation without convection at rather dilute conditions. The goal is to determine the flux of mass to its surface. For this the vapor concentration profile around the droplet is needed at steady state:



$$\frac{\partial C}{\partial t} = \frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) = 0 \qquad (1)$$

D = vapor diffusivity

C = vapor concentration (moles/cm^3)

With boundary conditions:

at $r = d_P/2$ $C = C_d$ the equilibrium concentration at the droplet surface

at $r = \infty$ $C = C_\infty$ bulk vapor concentration

Solving the above equation for C as a function of r gives:

$$\frac{C - C_d}{C_\infty - C_d} = 1 - \frac{d_P}{2r} \qquad (2)$$

Then the rate of condensation F is:

$$F = D\left(\frac{\partial C}{\partial r}\right)_{r=\frac{d_P}{2}} = D(C_\infty - C_d)\left[0 + \frac{d_P}{2(d_P/2)^2}\right]\pi d_P^2$$

$$= 2D(C_\infty - C_d)\pi d_P \qquad (3)$$

And the rate of particle volume growth is:

$$\frac{dv}{dt} = \frac{d\left(\pi d_P^3 / 6\right)}{dt} = \frac{FMW}{\rho_P} = \frac{2D(C_\infty - C_d)MW\pi d_P}{\rho_P}$$

where MW and ρ_P are the molecular weight and density of the condensing material

So the diameter growth rate is (molecules/cm^2):

$$\frac{dd_P}{dt} = \frac{4D(C_\infty - C_d)MW}{\rho_P d_P} \qquad (4)$$

2.3.2 Mass transfer to a particle surface (free molecule)

The collision rate per unit area is:

$$z = \frac{N_{AV} C \bar{c}}{4} \tag{5}$$

where c and m_1 are the molecular velocity and mass and N_{AV} the Avogadro number

so z becomes

$$z = \frac{N_{AV}(C_\infty - C_d)}{4}\left(\frac{8k_B T}{\pi m_1}\right)^{1/2} \tag{6}$$

Then the rate of condensation F to particle surface is:

$$F = z \cdot \text{area} / N_{AV} = \left(\frac{k_B T}{2\pi m_1} \right)^{1/2} \pi d_P^2 \left(C_\infty - C_d \right) \quad (7)$$

And the rate of particle volume growth is:

$$\frac{dv}{dt} = \frac{FMW}{\rho_P} = \left(\frac{k_B T}{2\pi m_1} \right)^{1/2} \pi d_P^2 \left(C_\infty - C_d \right) \frac{MW}{\rho_P} \quad (8)$$

So the diameter growth rate is:

$$\frac{dd_P}{dt} = \frac{2MW}{\rho_P} \left(\frac{k_B T}{2\pi m_1} \right)^{1/2} \left(C_\infty - C_d \right) \quad (9)$$

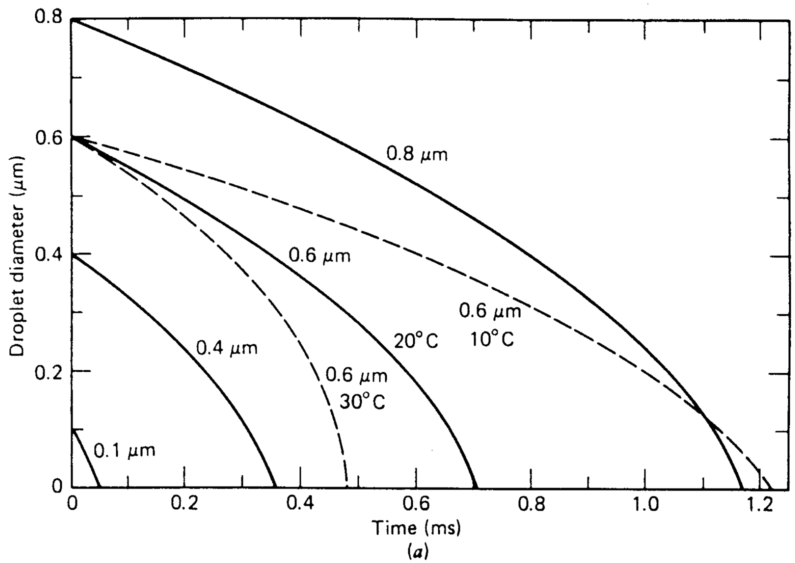
2.3.3 Mass transfer to a particle surface (entire spectrum)

For particle growth from the free molecule to continuum regime, the expression for the continuum regime is extended by an interpolation factor:

$$\frac{dd_P}{dt} = \frac{4D(C_\infty - C_d)MW}{\rho_P d_P}\left(\frac{1+Kn}{1+1.71Kn+1.33Kn^2}\right) \quad (10)$$

where the ***Knudsen number*** is Kn= $2\lambda/d_P$

This is called the **Fuchs effect**.



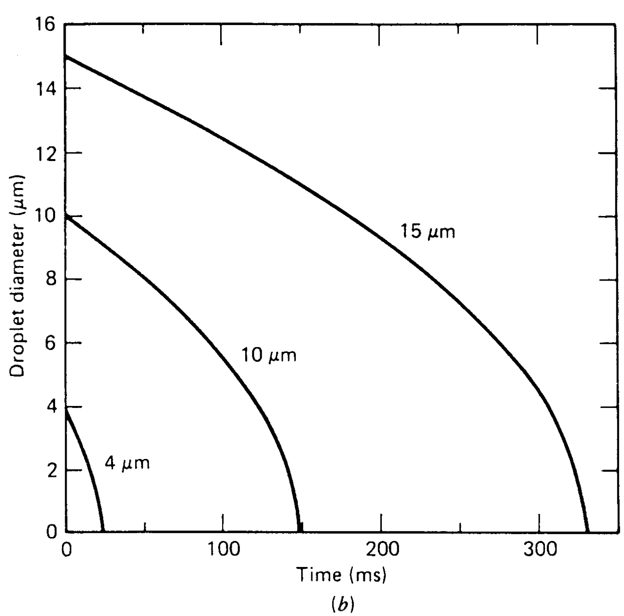


Figure 13.10 Evaporation of pure water droplets at 20°C and 50% relative humidity. (*a*) Droplet diameters 0.1–0.8 μm. Dashed lines show the effect of ambient temperature on evaporation. (*b*) Droplet diameters 4–15 μm.

The effect of of temperature depression is to reduce the partial pressure of vapor at the droplet surface and slow the rate of evaporation. Similarly a temperature enhancement slows the rate of condensation.

(adapted from Hinds (1982))

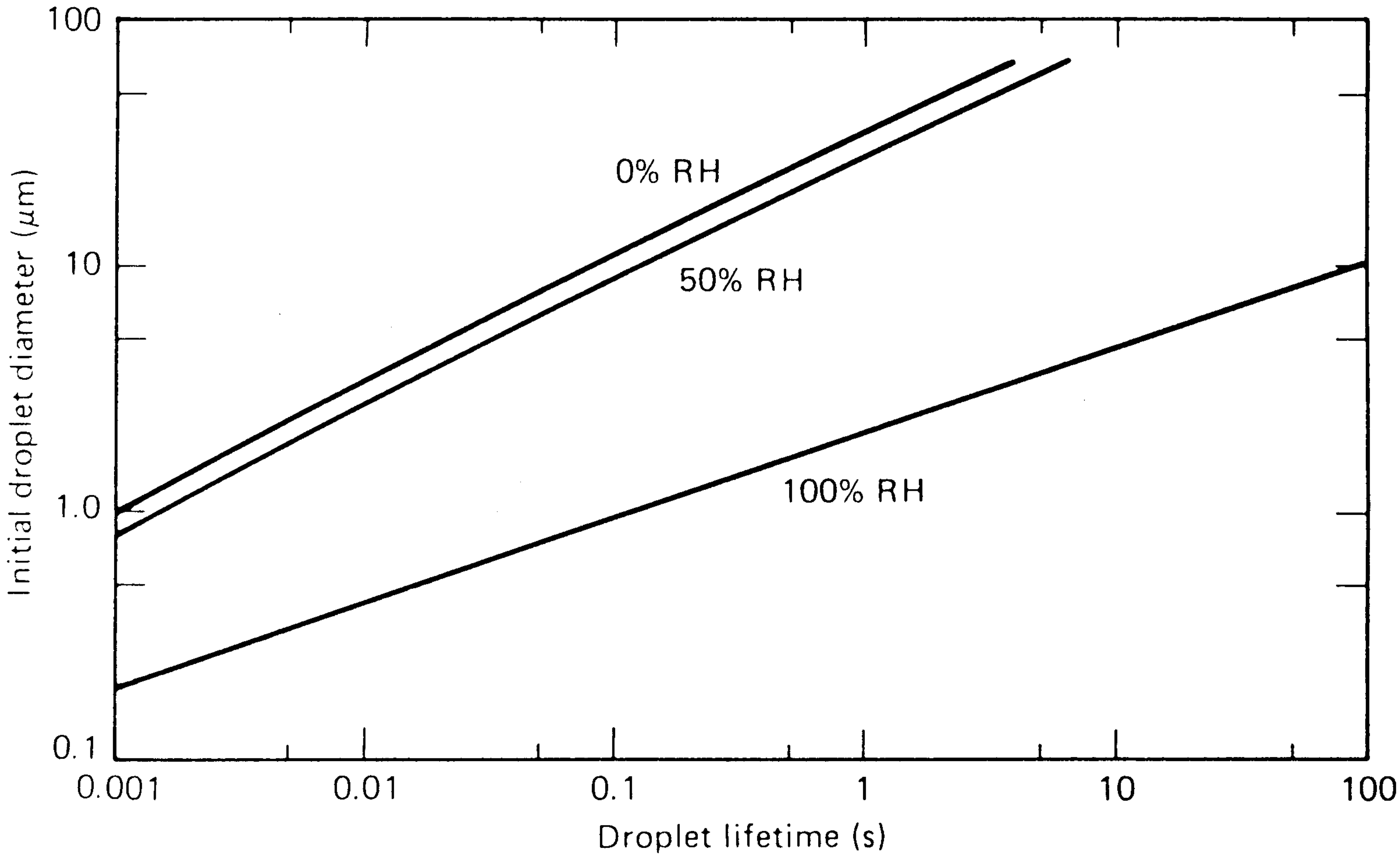


Figure 13.12 Water droplet lifetimes as function of droplet size for 0, 50, and 100% relative humidity at 20°C.

(adapted from Hinds (1982))

Table 13.2 Effect of Fuchs Effect, Kelvin Effect, and Temperature Depression Corrections on Calculated Lifetimes of Water Droplets at 20°C and 50 Percent Relative Humidity[a, b]

Droplet Diameter (μm)	Droplet Lifetime (s): Including All Corrections	Omitting Fuchs Effect Correction	Omitting Kelvin Effect Correction	Omitting Temperature Depression Correction	No Corrections (Eq. 13.18) $p_d = p_s$ $T_d = T_\infty$
0.01	1.6×10^{-6}	6.0×10^{-8}	5.0×10^{-6}	9.1×10^{-7}	6.0×10^{-8}
0.04	1.4×10^{-5}	1.7×10^{-6}	2.1×10^{-5}	6.6×10^{-6}	9.6×10^{-7}
0.1	4.7×10^{-5}	1.3×10^{-5}	5.8×10^{-5}	2.1×10^{-5}	6.0×10^{-6}
0.4	3.6×10^{-4}	2.2×10^{-4}	3.8×10^{-4}	1.5×10^{-4}	9.6×10^{-5}
1.0	1.7×10^{-3}	1.4×10^{-3}	1.8×10^{-3}	7.4×10^{-4}	6.0×10^{-4}
4.0	0.024	0.023	0.024	0.010	9.6×10^{-3}
10	0.15	0.14	0.15	0.062	0.060
40	2.3	2.3	2.3	0.97	0.96

[a] Calculated with corrections as indicated by numerical integration of Eq. 13.19.
[b] Error in calculated lifetime exceeds 20% above the line in each column.

(adapted from Hinds (1982))