Dr. Thiedig

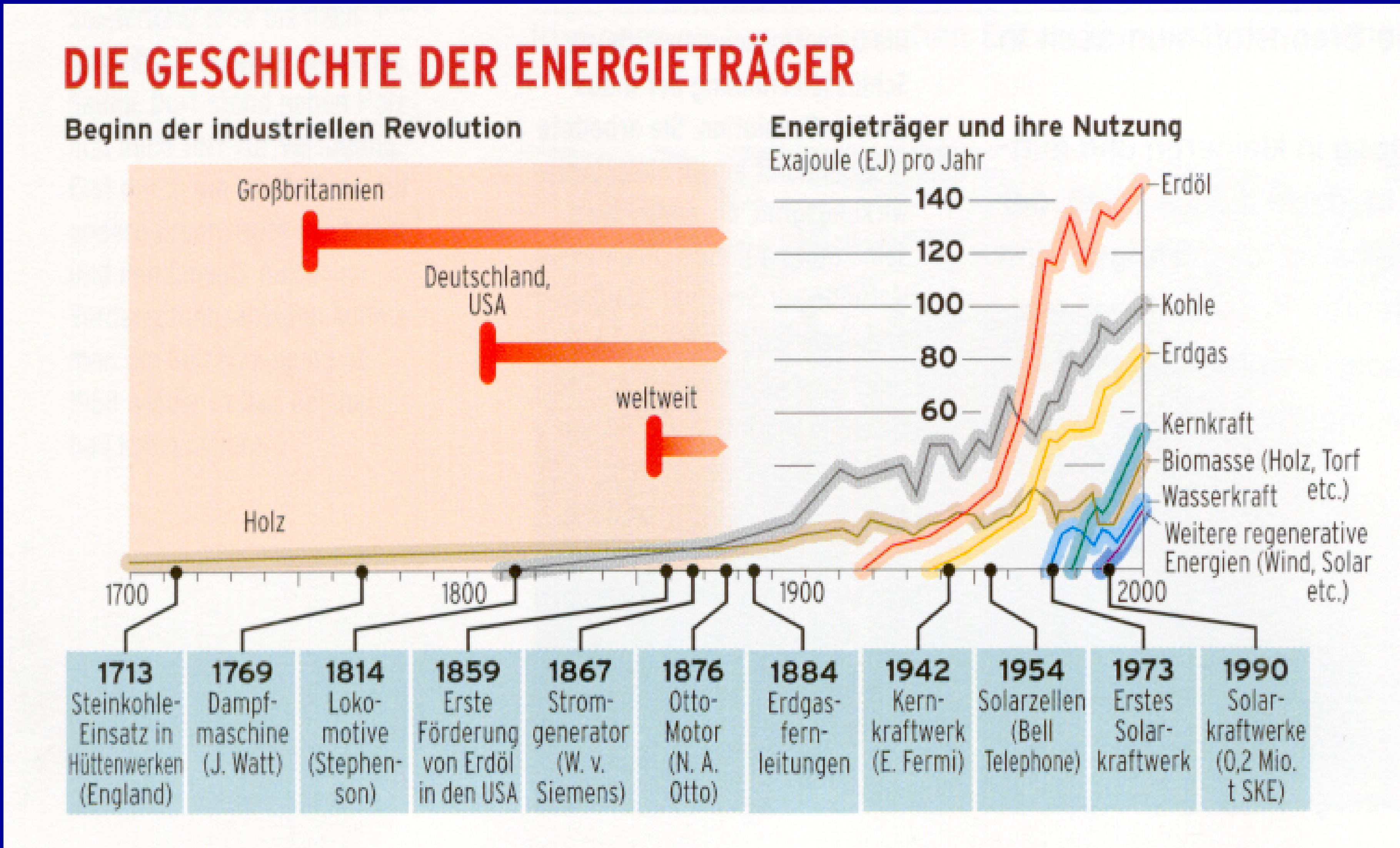
Nano-structured catalysts: Preparation from lab to technical scale

Dr. Jean Boris Stelzer

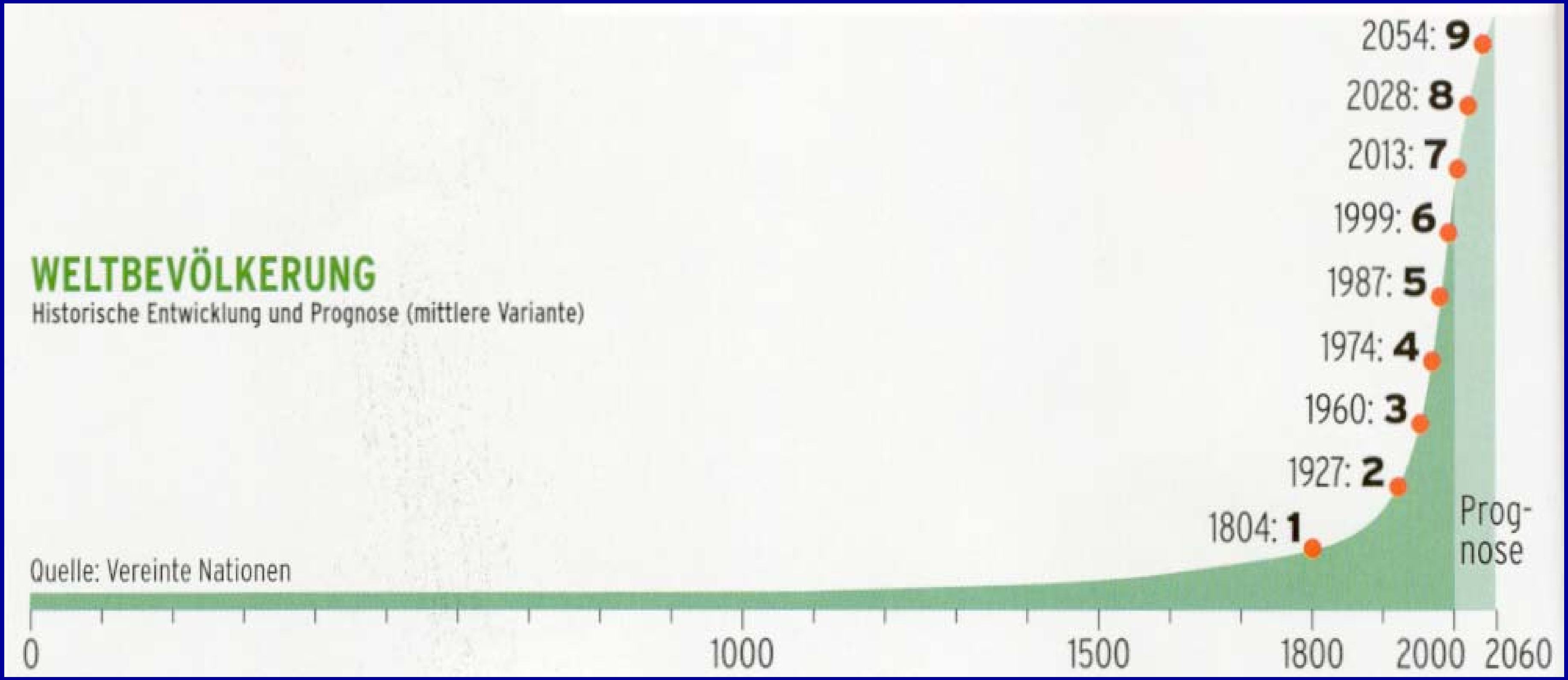
New Market – New Catalysts

SÜD-CHEMIE
Creating Performance Technology

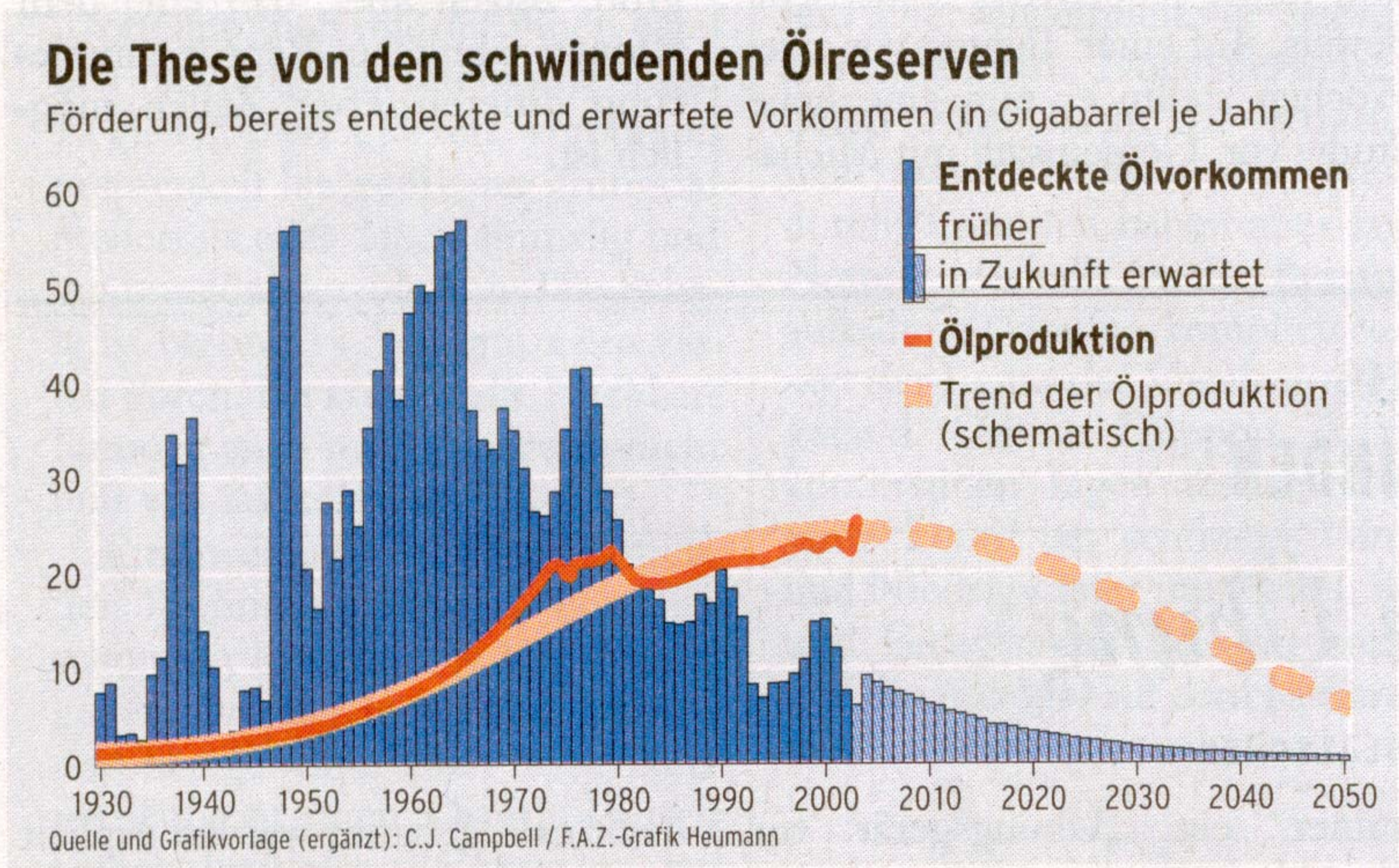
History of energy sources



World population



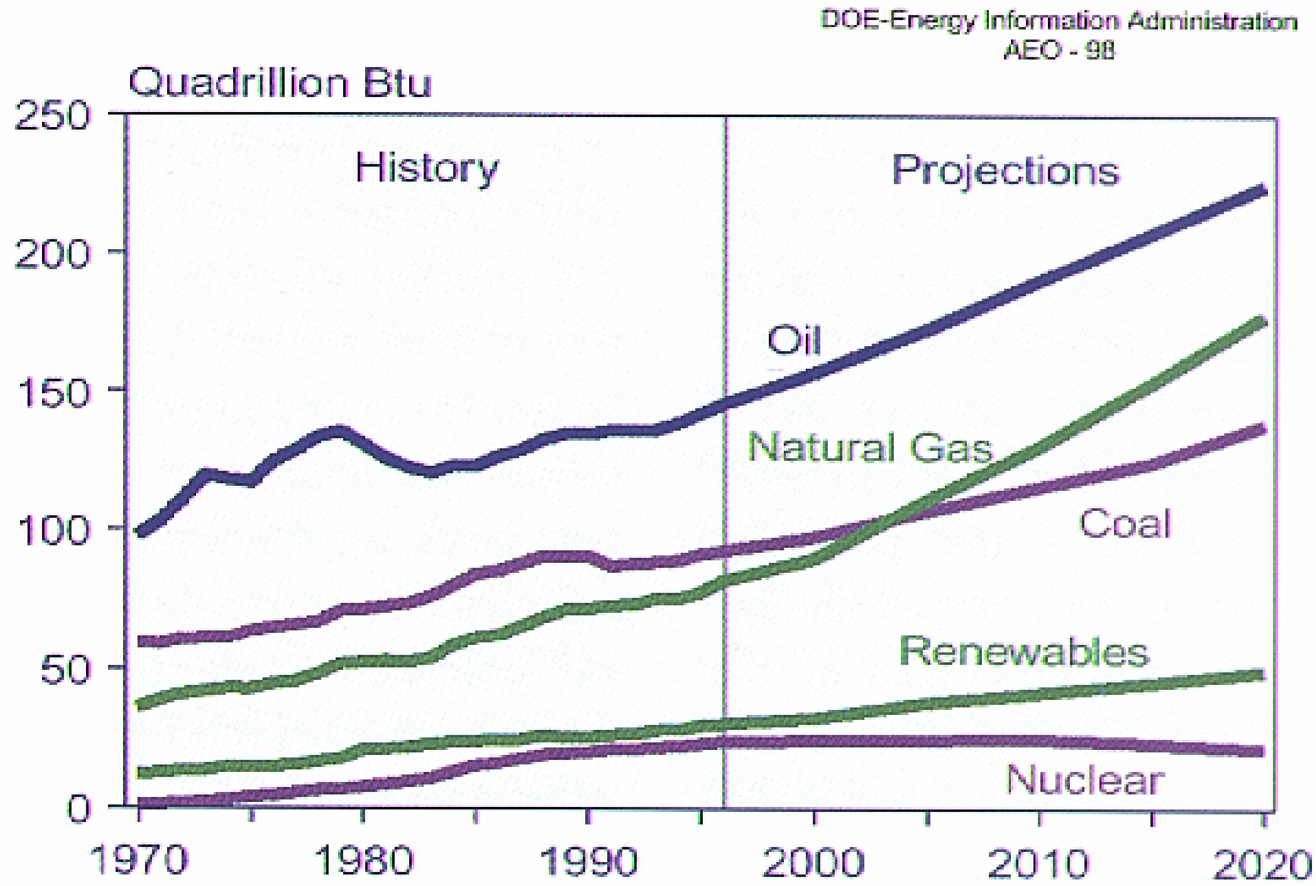
*Thesis of oil reserve and price



Die Glockenkurve *sagt voraus, daß es demnächst abwärts geht. Steigen würden nur die Preise – und damit der Anreiz, nach Alternativen zu suchen.*

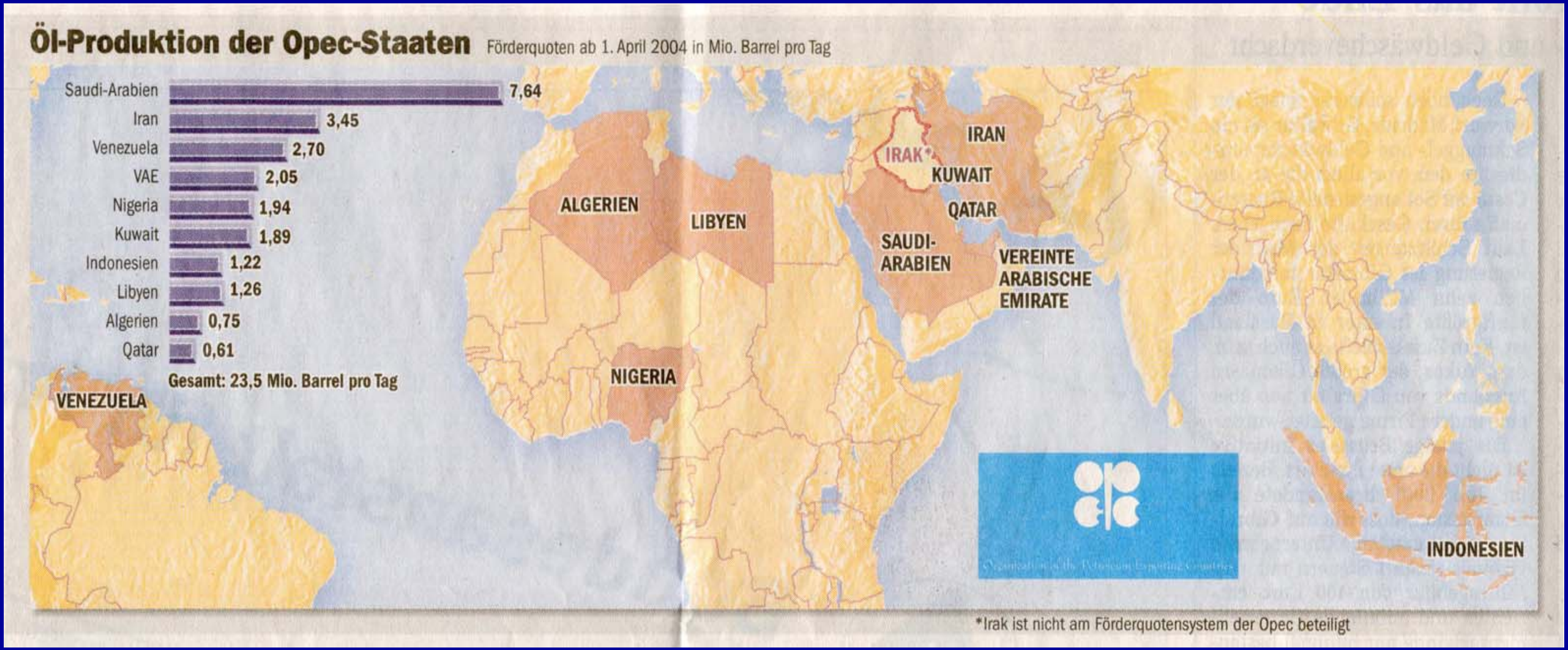
* FAZ Sonntagszeitung, 23. 5. 2004

Worldwide energy demand



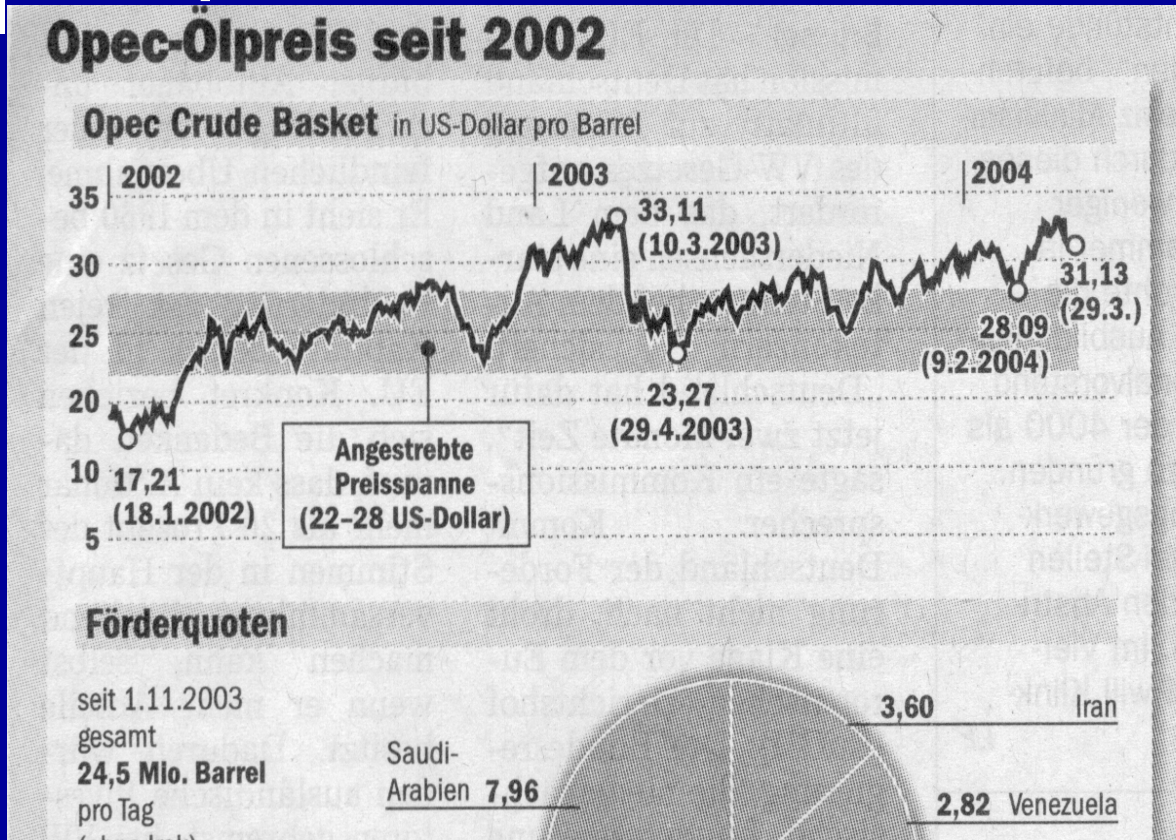
Forecast of World Energy Needs Until 2020

*Oil production of the OPEC



* Die Welt, 1. 4. 2004

*Oil price trend of the OPEC since 2002



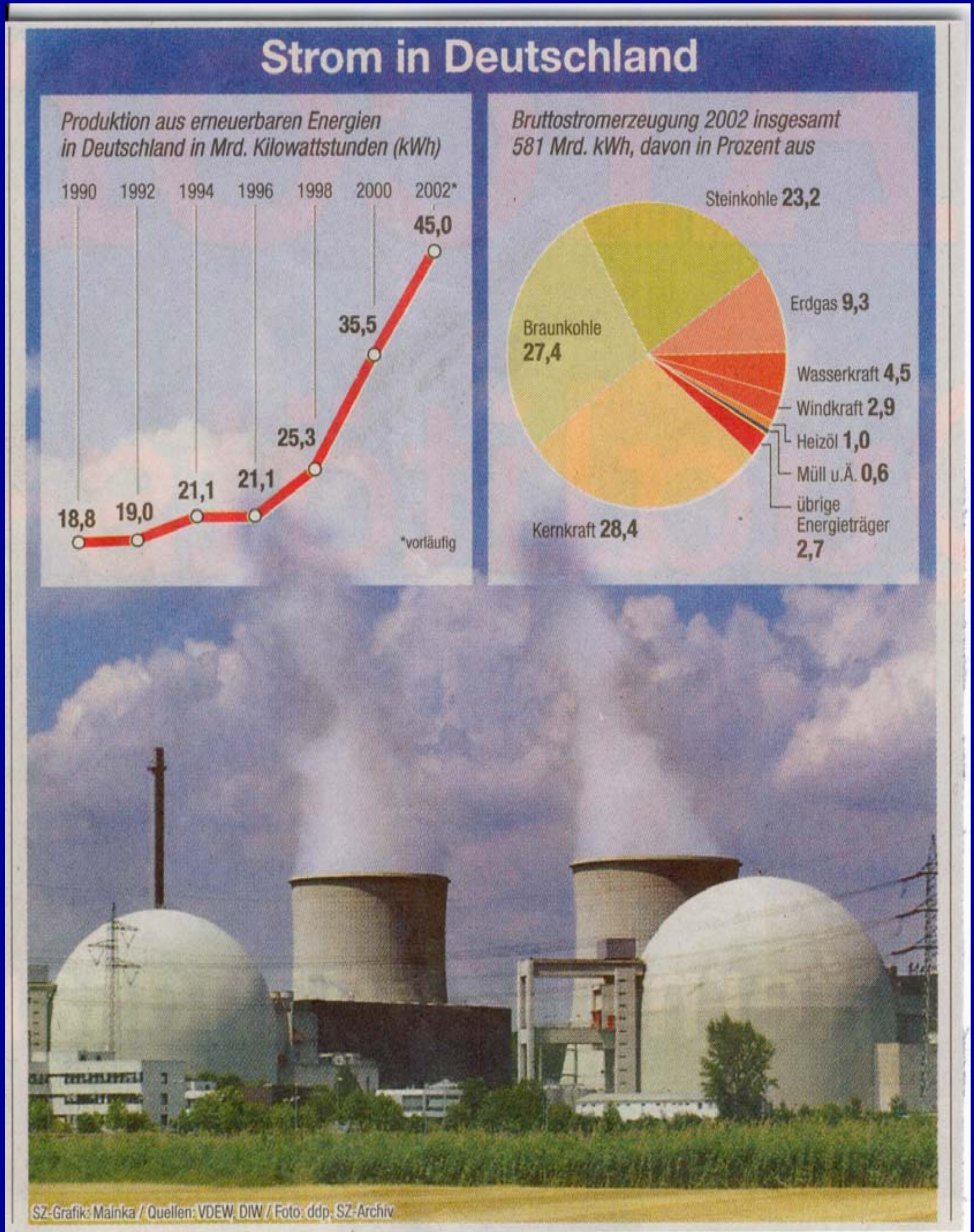
* Die Welt, 31. 3. 2004

Energy in Germany

1. Nuclear power
2. Brown coal
3. Coal
4. Natural gas
5. Hydro power
6. Wind power

Regenerative energy sources

e.g. fuel cell



Gas to Liquids - Fischer-Tropsch

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Natural gas —part. combustion→ **$CO + 2H_2$**

↕

„Synthesis gas“

What is Fischer-Tropsch ?

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Creating Performance Technology

Fe or Co catalyst

$$CO + 2H_2 \longrightarrow \text{Hydrocarbons}$$

- Paraffins
- Naphta
- Kerosene
- Diesel
- Waxes

Signs of the time

SÜD-CHEMIE
Creating Performance Technology

- Natural Gas will play a major role in the 21st century
- Competing Technologies:
  Pipeline, LNG, GTP/GTL ->
  (GTO, GTDME, GTG, Fischer-Tropsch)
- Driving Forces for GTL via FT
  - Cost of GTL plants coming down
  - **Oil price likely to increase**
    - **- Fuel consumption on the increase**
    - **- Resources are limited**
  - **Cheap Natural Gas**
    - - Qatar, Iran, Nigeria, Brasil, Bolivia Russia, Indonesia etc. are interested to monetise their gas reserves
    - - Utilisation of "Stranded Gas"

Gas to Liquids - Market

Signs of the time

- Driving Forces for GTL via FT
  - Company Strategies
    - Shell had to reduce their estimated oil reserves by 20% - compensation by NG?
    - Sasol will set the standards – others likely to follow.
  - Environmental
    - High fuel quality (sulphur < 5ppm, aromatics < 1%, lower smoke discharge)
    - Pressure to stop flaring of associated gas

- Present world capacity: 50,000 bpd
- Expected to grow to 500,000 in the next decade

Fischer-Tropsch Synthesis

The Catalysts

- **Iron Based Catalysts**

  Feed: Coal

  Product: Fuel and Chemicals (alpha-Olefins, Wax)

- **Cobald Based Catalysts**

  Feed: Natural Gas

  Product: Fuel

Introduction

- For many years, heterogeneous catalyst preparation being considered a “black art” rather than a scientific endeavour.
- Some reports* have changed this perception.
- One reason is that many industries are highly secretive concerning preparation methodology.
- This real know-how represents the true intellectual property of catalyst preparation.

* R. Schlögl, *Heterogene Katalyse - immer noch Kunst oder schon Wissenschaft,* Angew. Chem. (1993), 105, Nr. 3, 402

Important factors of catalyst preparation?

- **In general, catalysts used in industrial reactors must have the correct *texture*, *attrition resistance*, and *shape* for the application.**

- **Texture is a collective term for surface area, pore structure and bulk density.**

- **The desired texture required for the material and this must be based on a knowledge of the chemistry of the target catalysed reaction.**

Catalyst requirements

- **Partial oxidation catalysts typically have low surface area and mesopores together with macropores.**
- **Higher surface area materials would, generally, lead to non-selective oxidation due to sequential oxidation of the desired product.**
- **In contrast, catalysts for hydrocarbon formation often require high surface areas (e.g. methanol conversion to gasoline).**

Examples of solid catalyst

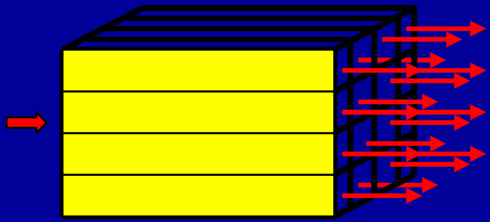
support + **active compound**

ceramic honeycombes — transition metals

or powders — Platinum, Rhodium, Palladium, Gold, Titanium, Vanadium

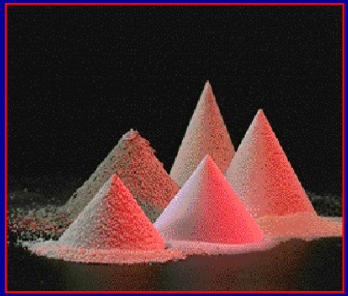
Stiff supports systems

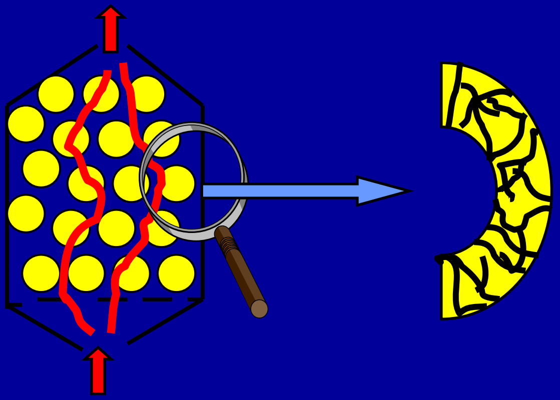
Honeycombe structures in various shapes



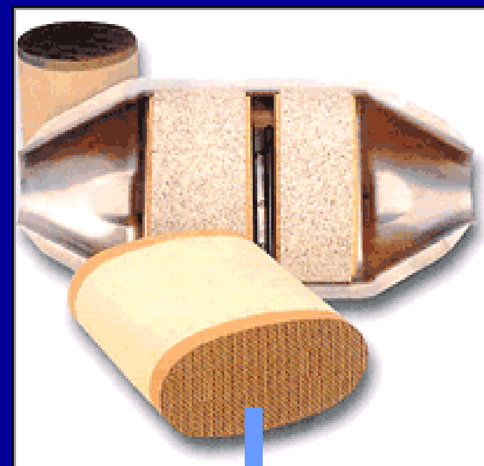
Unshaped supports:

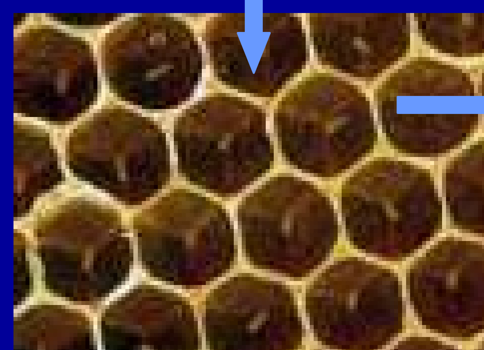
Powder Bed

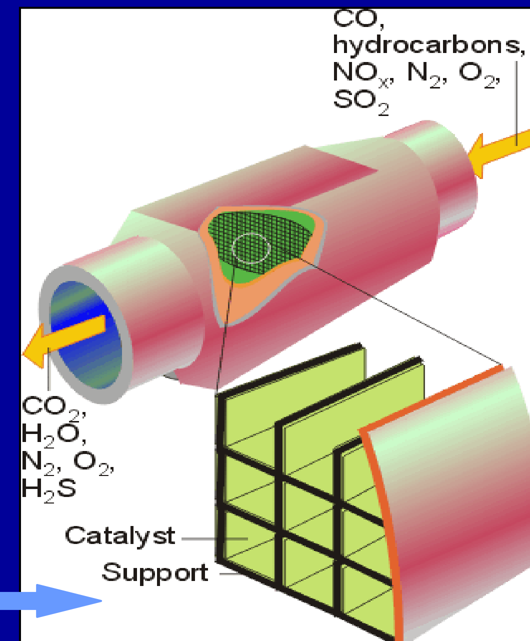




Examples of technical catalysts systems

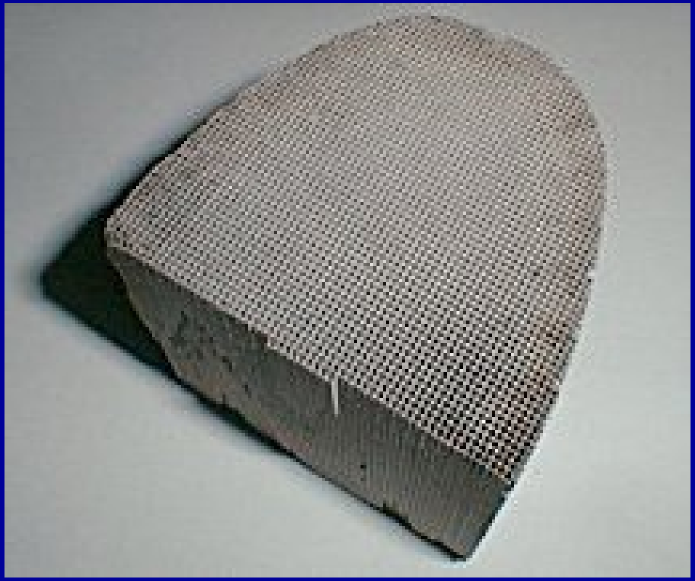


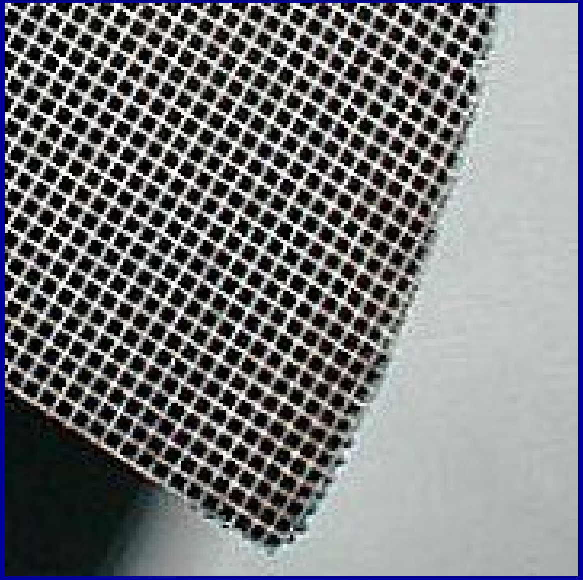




Examples of catalyst requirements

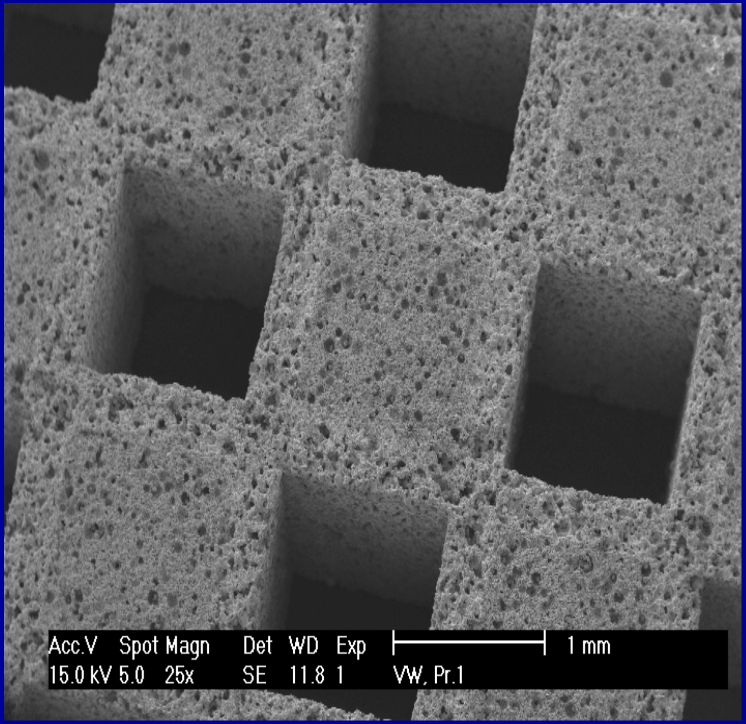
It is important to recognise whether the catalyst must withstand thermal shock, e.g. in car exhaust catalysts, or abrasion, e.g. in entrained bed reactors.

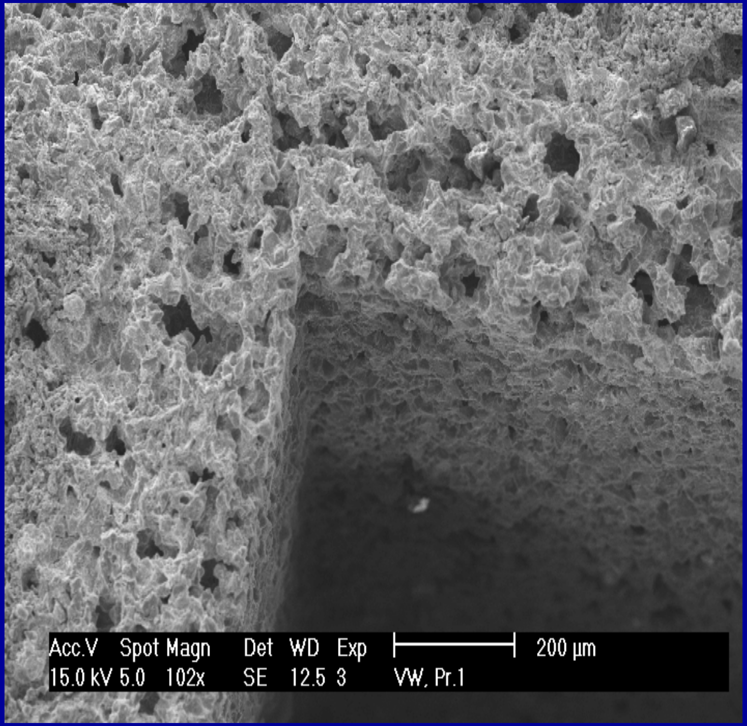




Examples of catalyst requirements

Car exhaust “diesel” from Volkswagen



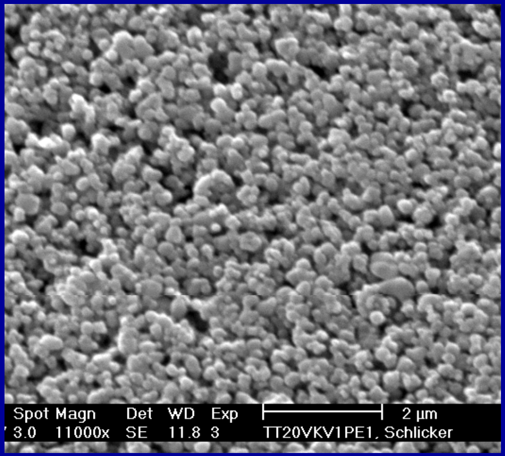


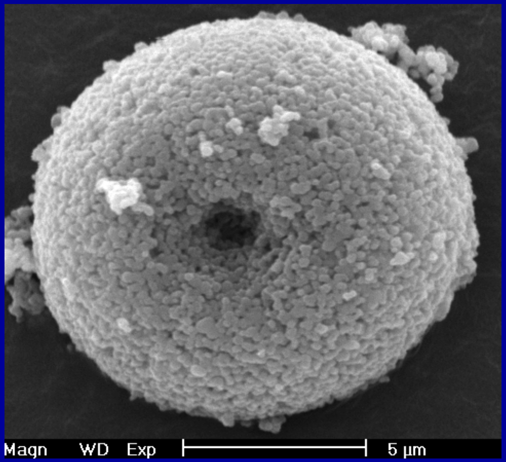
Examples of catalyst requirements

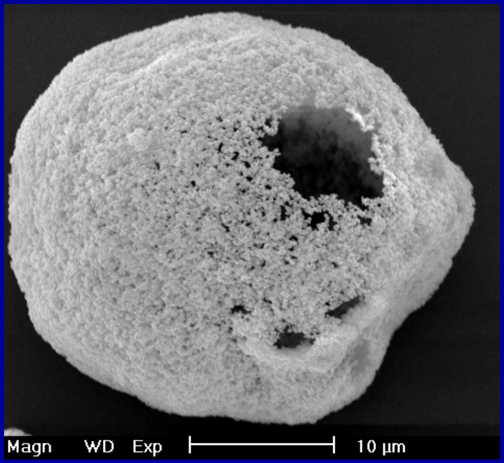
Car exhaust “diesel” from Volkswagen

Types of catalyst

- **Bulk catalysts and supports**
- **Support: Crystalline TiO_2 in anatase modification, structured by spray drying or other techniques**



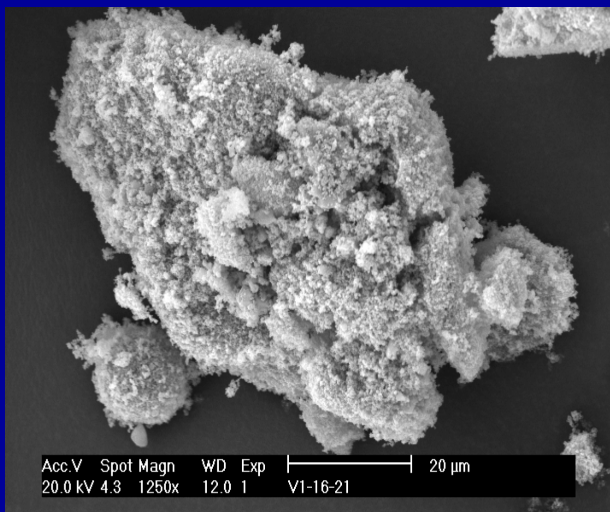




granulation: 0,5 µm up to ca. 30 µm

Types of catalyst

- **Impregnated catalysts starting from preformed supports**



V_2O_5

Impregnation

$5\ \%\ V_2O_5$

T = 500 °C

particle size

ca. 20 - 60 µm

MoO_3 crystalls

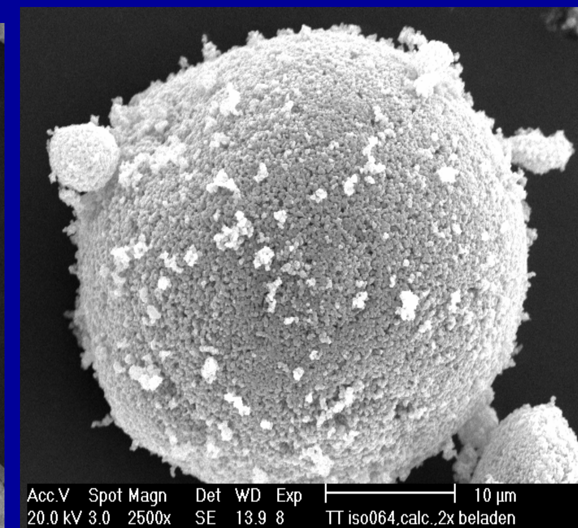
Impregnation

$5\ \%\ MoO_3$

T = 500 °C

particle size

ca. 10 - 30 µm



TiO_2

Impregnation

$5\ \%\ Ti(OC_3H_7)_4$

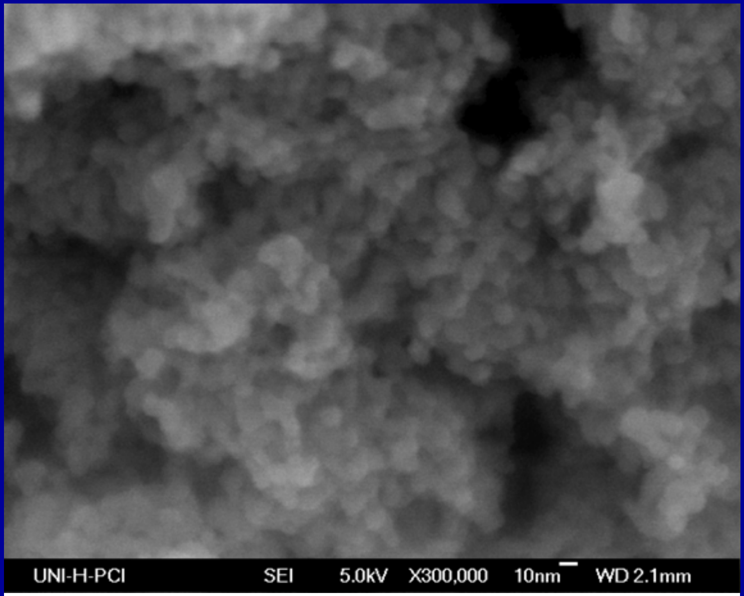
T = 500 °C

particle size

ca. 10 - 60 µm

Types of catalyst

- **Mixed-agglomerated supports**



$Ti(OC_3H_7)_4 + Sb(CH_3COO)_3$

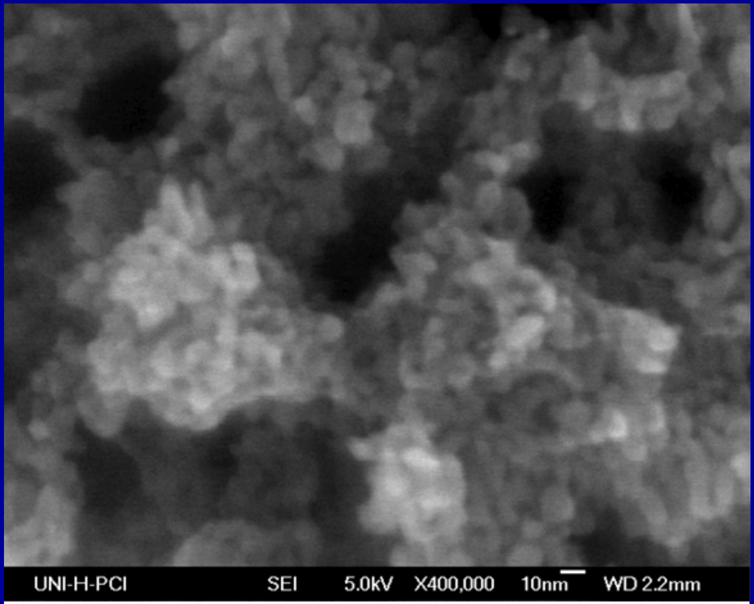
Mixed-agglomerated

5 % Sb_2O_3

T = 500 °C/air

particle size

ca. 10 nm



$Ti(OC_3H_7)_4 + Sb(CH_3COO)_3$

Mixed-agglomerated

5 % Sb_2O_3

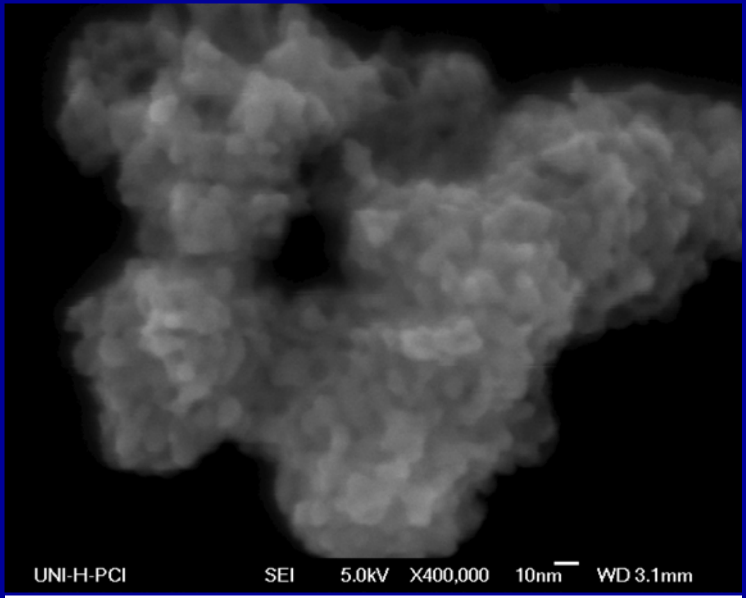
T = 500 °C/N_2

particle size

ca. 10 nm

Types of catalyst

- **Mixed-agglomerated catalysts**



$TiO_a/Sb_bO_c\text{-}VO_x$

Mixed-agglomerated supports & Impregnation

5 % Sb_2O_3 & 5 % V_{Oxa}

T = 500 °C/air

particle size

ca. 10 nm

Catalysts preparation can be schematically represented as

Chemicals	**(control impurities)**
↓	
Catalyst Precursor	**(texture)**
↓	
Form	**(texture, shape, attrition resistance)**
↓	
Final Catalyst	**(texture, attrition resistance)**

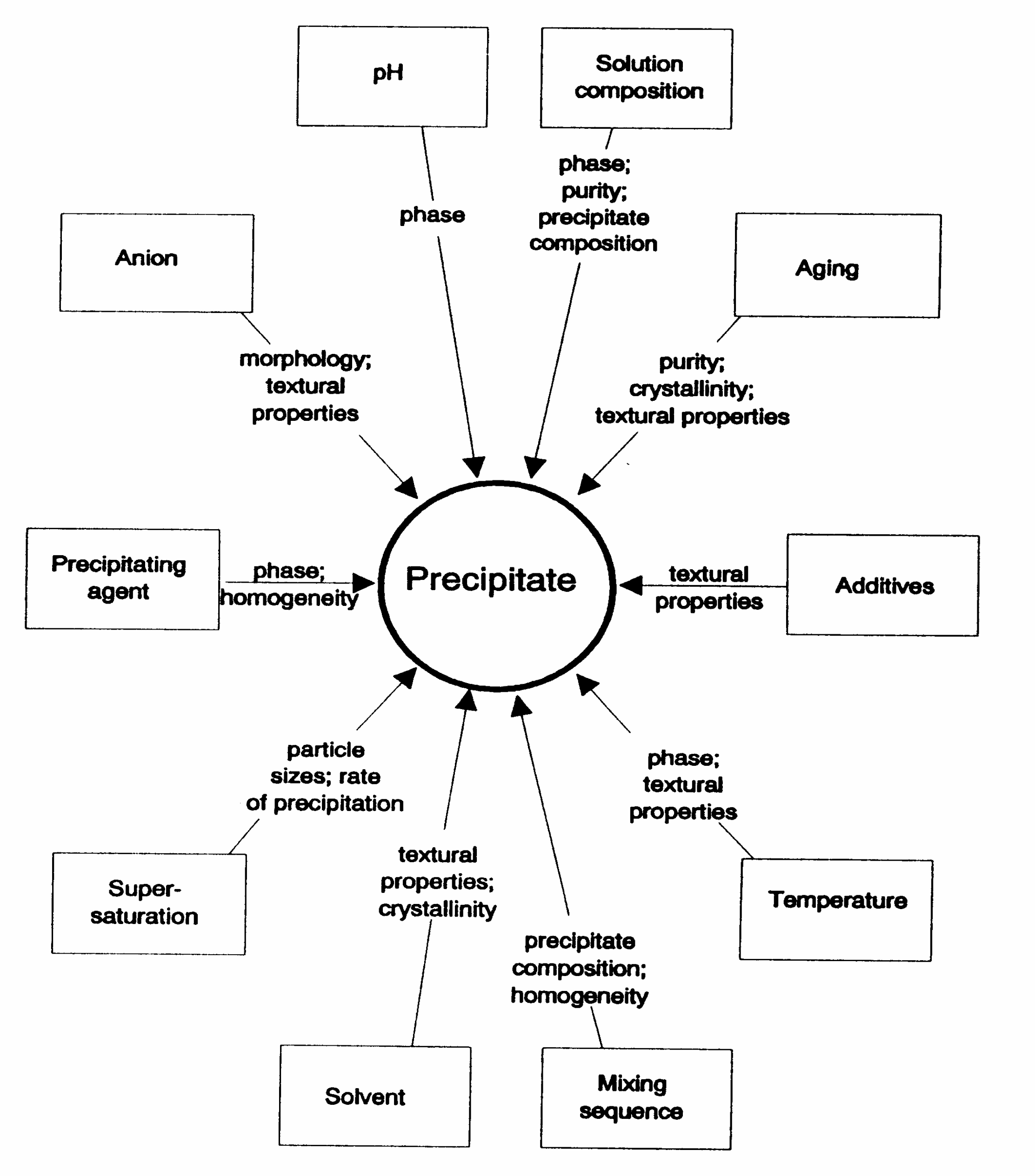
Industrial operation for manufacturing catalysts

1. **Precipitation or other synthesis process (e.g. sol-gel, solid solid, flame hydrolysis, vapour deposition)**
2. **Hydrothermal transformation**
3. **Decantation, filtration, centrifugation**
4. **Washing**
5. **Crushing and grinding**
6. **Forming and/or shaping operations**
7. **Calcination**
8. **Impregnation**
9. **Mixing**
10. **Activation, reduction**

Industrial catalysts prepared by precipitation or coprecipitation

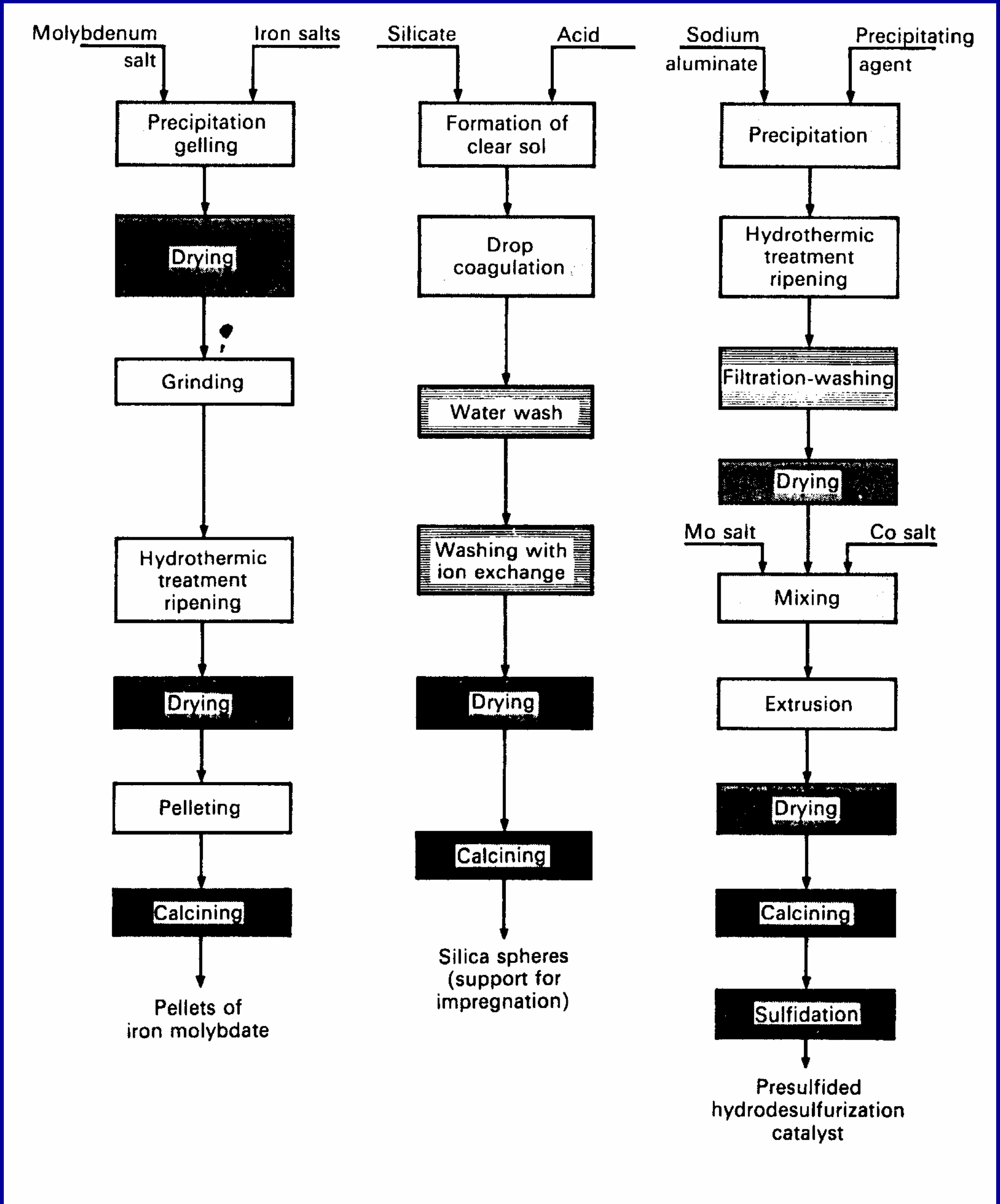
Catalysts	**Important applications**
SiO_2-Al_2O_3	acid catalysed reaction e.g. FCC isomerisation,
Fe_2O_3	Fisher Tropsch reaction, ethyl benzene to styrene
TiO_2	major component of DeNOx catalysts
ZrO_2-SO_4^{2-}	strong acid reactions
Cu-ZnO/Al_2O_3	methanol synthesis
$(VO)_2P_2O_7$	selective oxidation of butane to maleic anhydride oxidation of pentane to phtalic anhydride + maleic anhydride

*Parameters affecting the properties of final precipitate**



* G. Ertl, H. Knözinger and J. Weitkamp (ed.), *"Handbook of Heterogeneous Catalysis"*, Wiley VCH, Weinheim, 1997

Typical arrangements of unit operations for manufacturing catalyst*



* J.-F. Le Page, *"Applied Heterogeneous Catalysis, Design-manufacture-use of solid catalysts"*, Technip, Paris (1987)

Goals

Catalyst function:

Product formation with participation of oxygen from the catalyst

Study:

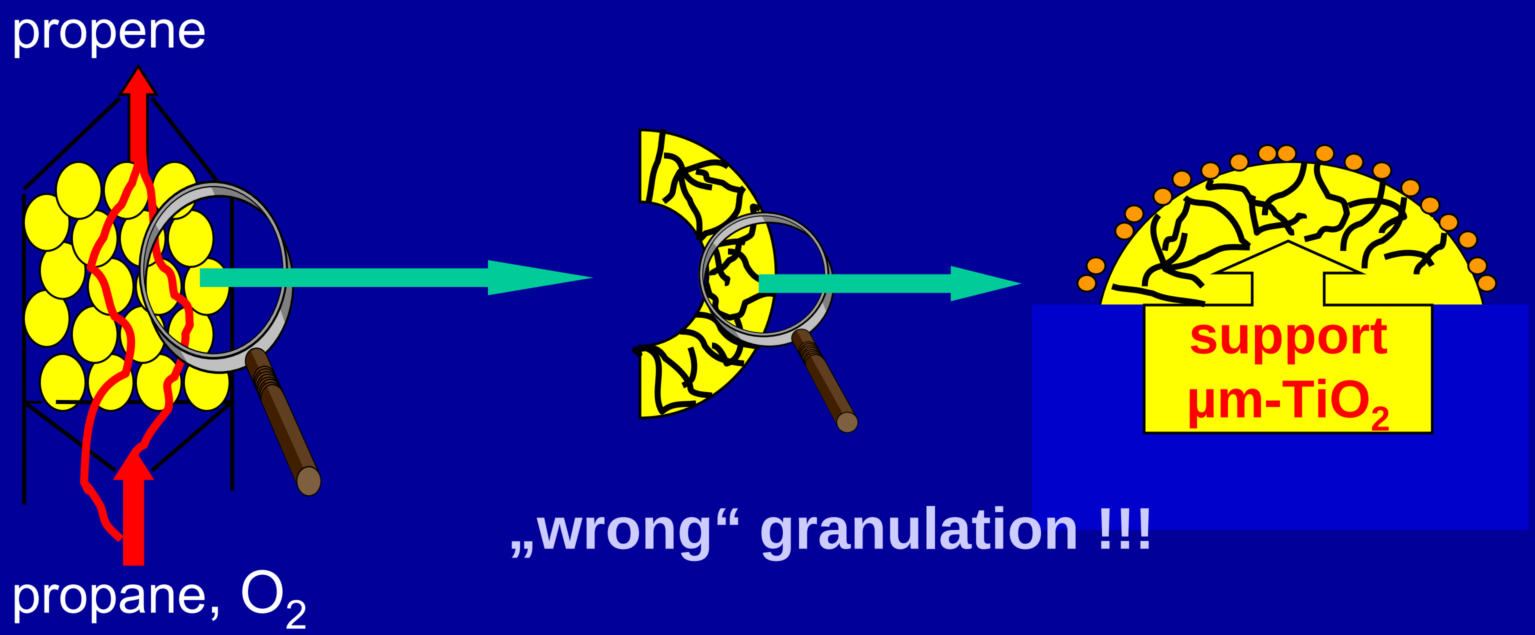
What is the effect of using two different TiO_2 supports?

Influence of nano-/ hierarchical-structure in activity and selectivity?

Challenging task:

Development of a hierarchical catalyst leading to C_3H_6 yield higher than 35 % at high selectivities and near-to- practise conditions!

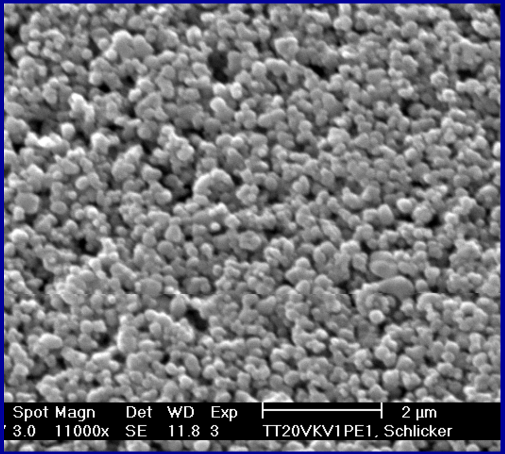
TiO_2-support

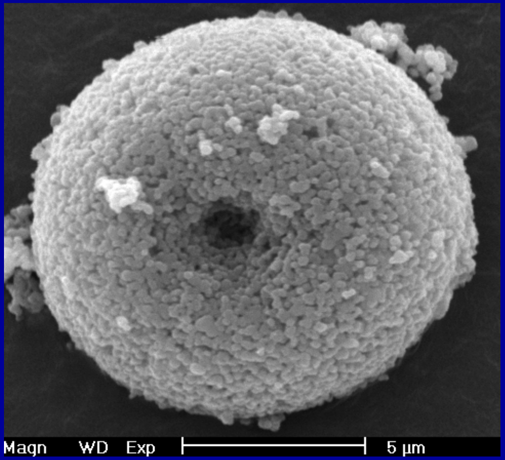


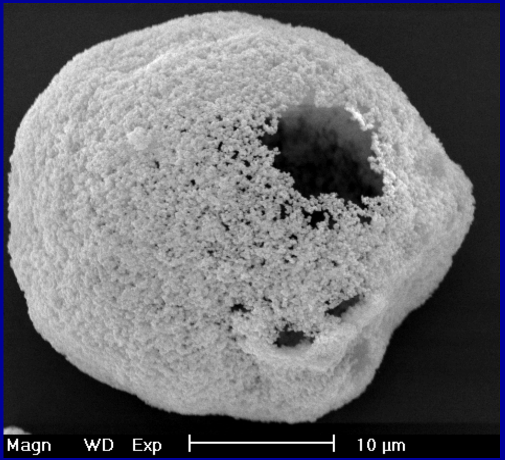
„wrong“ granulation !!!

	pressed granulate	support
granalulate-size	big	big
distribution	big distribution, high density	small distribution, big porous
morphology	full granulate	hollow granulate
wall-size	-	thin
hardness/ strength	suitable for storage, shapeable by pressing	long-run stabil, no abrasion

Spray drying technique

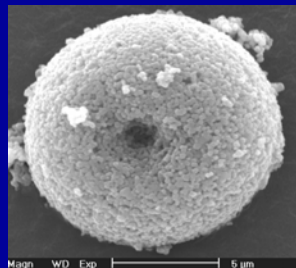
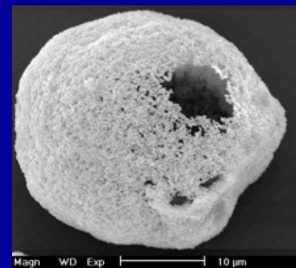
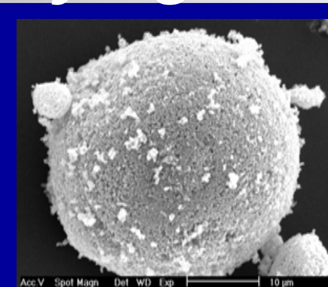
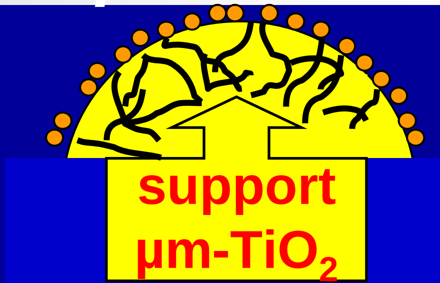






granulation: 0,6 µm up to ca. 30 µm

Outlook for spray drying technique

0 100 200 300 400 500 600 [T/°C]

Calcination (> 600 °C)

sintering of
nano particle (> 800 °C)

Bridge formation (> 900 °C)

filler
(PVA, C...)

TiO_2
Suspension → Spray-drying → Binder Cross linkage → structured support

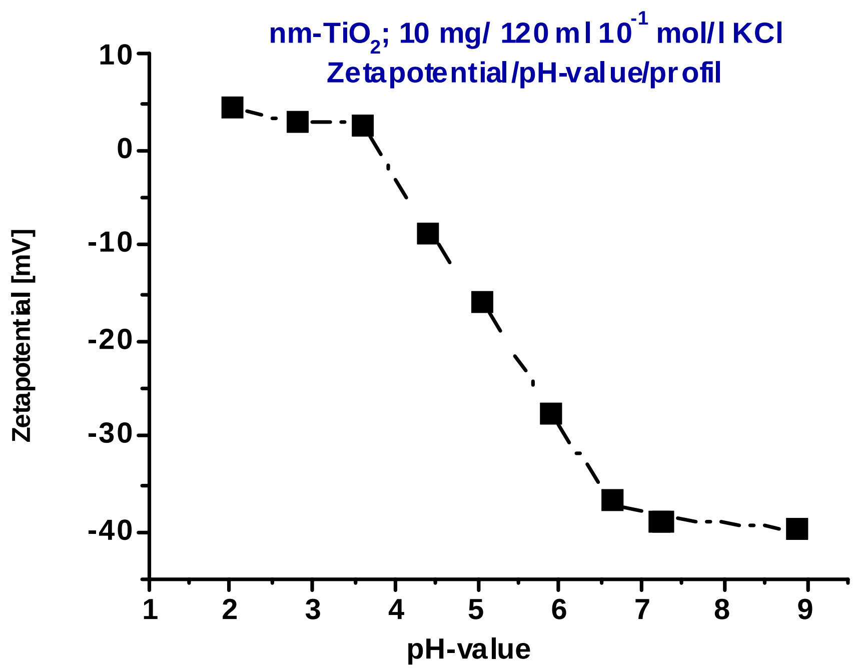
soluble
preliminary stage
(watery)

soluble
preliminary stage
(non watery) → thermolysis

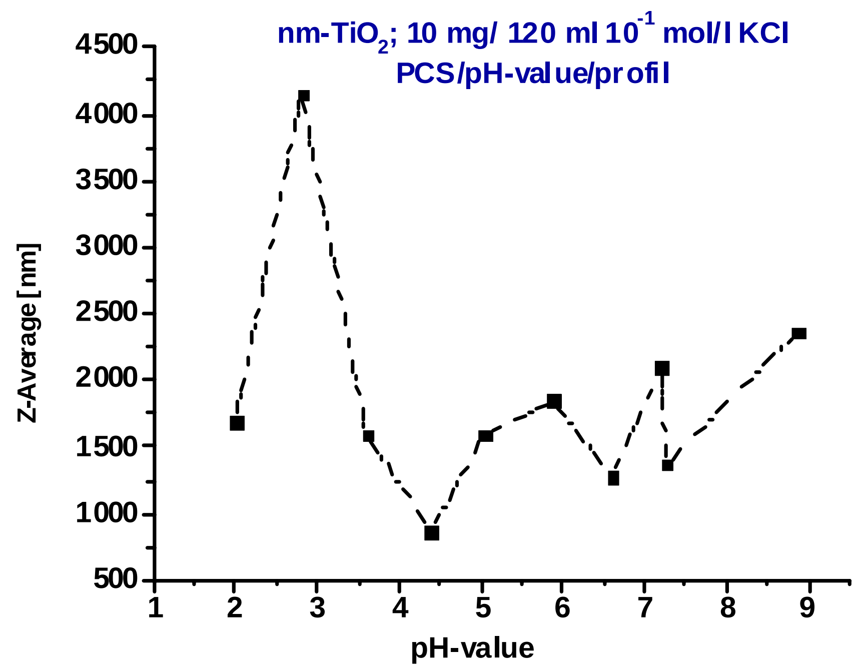
anatase
stabil
< 900°C

Characterization

Zetapotential/pH-value/profil



PCS/pH-value/profil

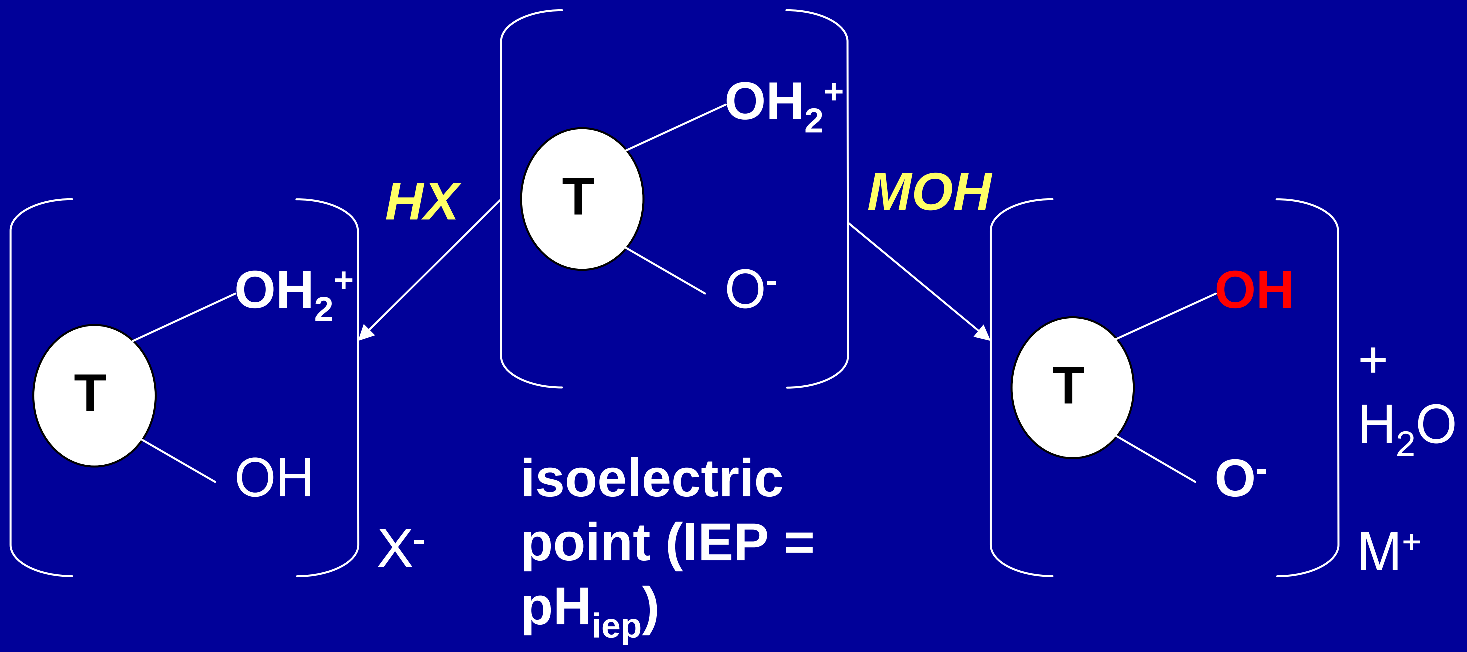


IEP pH 3.8

TiO_2 agglomeration

> 1000 nm

Preparation of Supported Catalysts



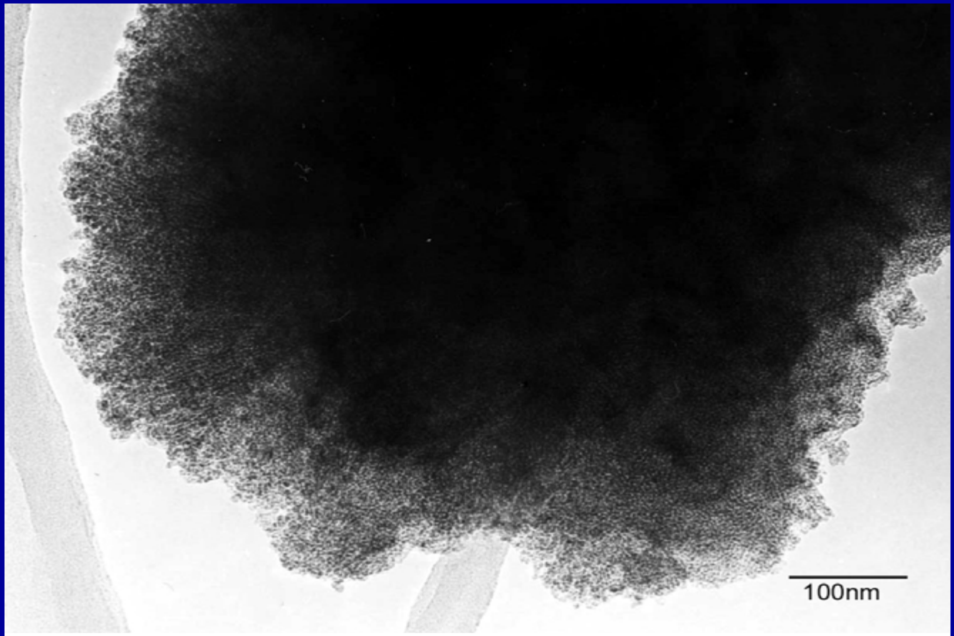
Schematic representation of a surface polarisation of an oxide particle as a function of the pH of the solution*

* J.B. Stelzer, J. Caro, R. Nitzsche, *Zeta potential measurement in catalyst preparation,* Chem. Eng. Technol. (2005) in press

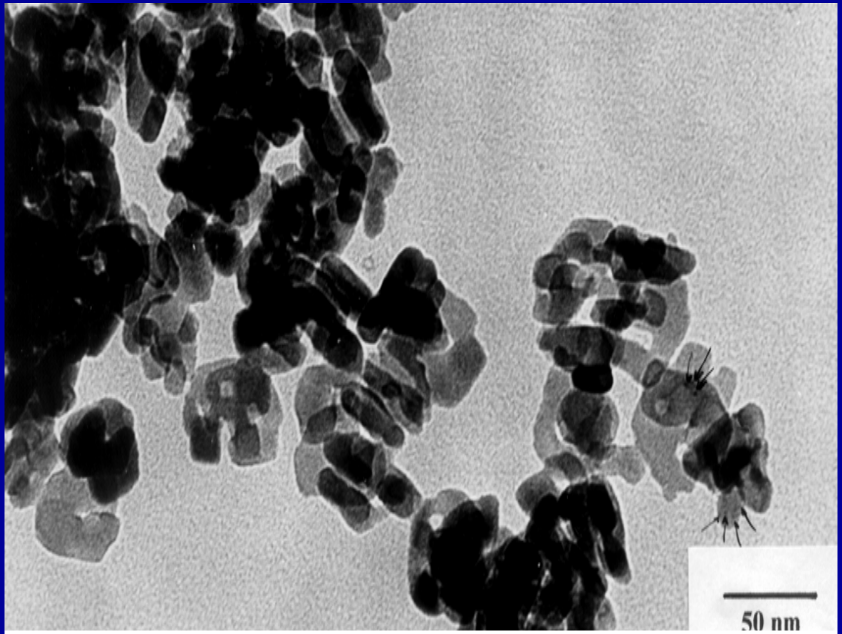
Synthesis of TiO_2

Precursor: $TiOSO_4 \cdot 2\,H_2O \cdot H_2SO_4$

→ **precipitation/hydrolysis**



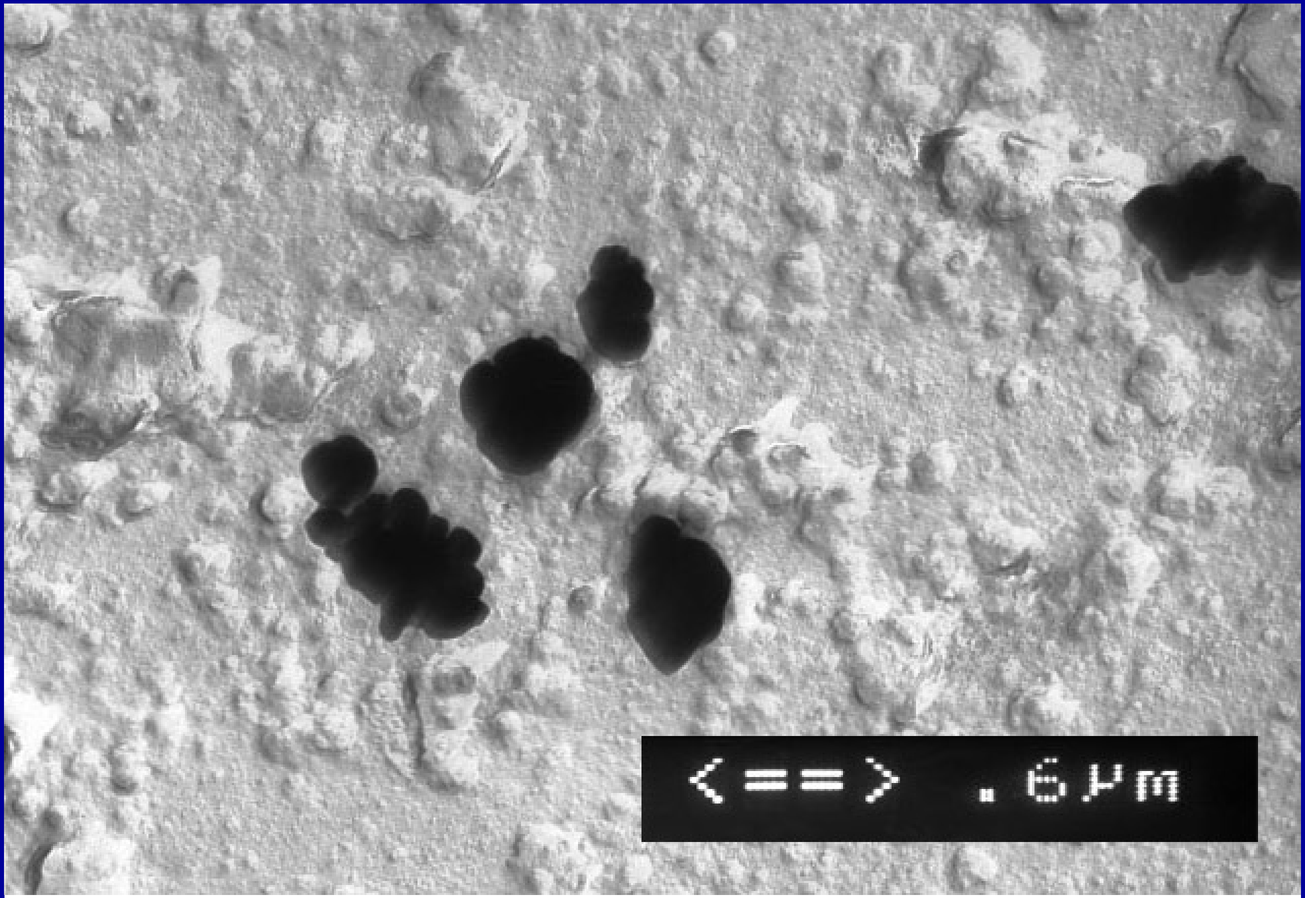
TiO_2 agglomeration
> 1000 nm



crystallit size
ca. 10 - 20 nm

* Freeze etching technique

Precursor: $TiOSO_4 \cdot 2\ H_2O \cdot H_2SO_4$ TiO_2



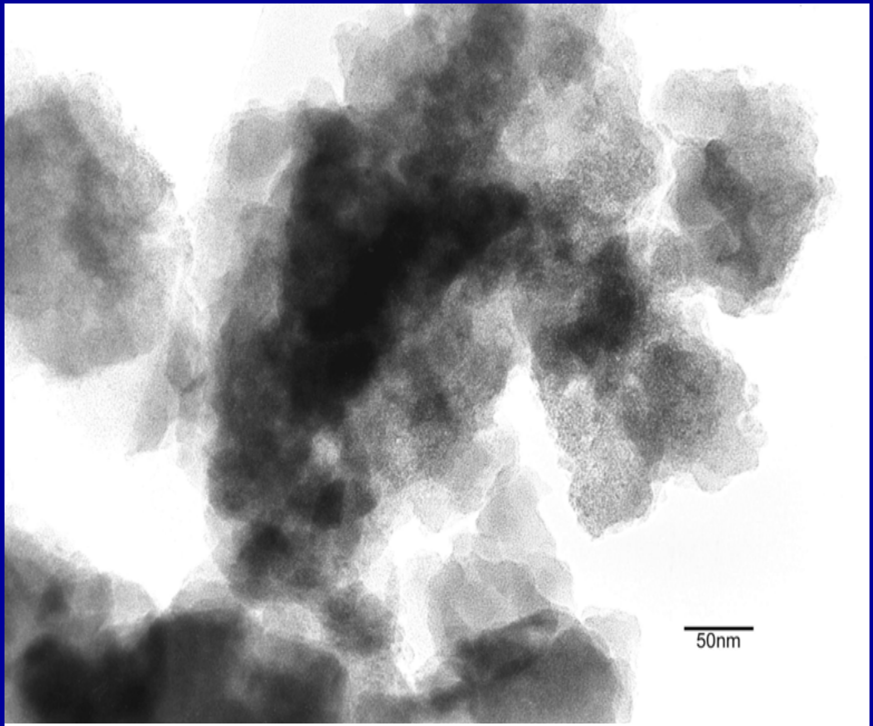
TiO_2 agglomeration!

* B. Thiersch, Universität Potsdam

* Polyol preparation of TiO_2 in DEG

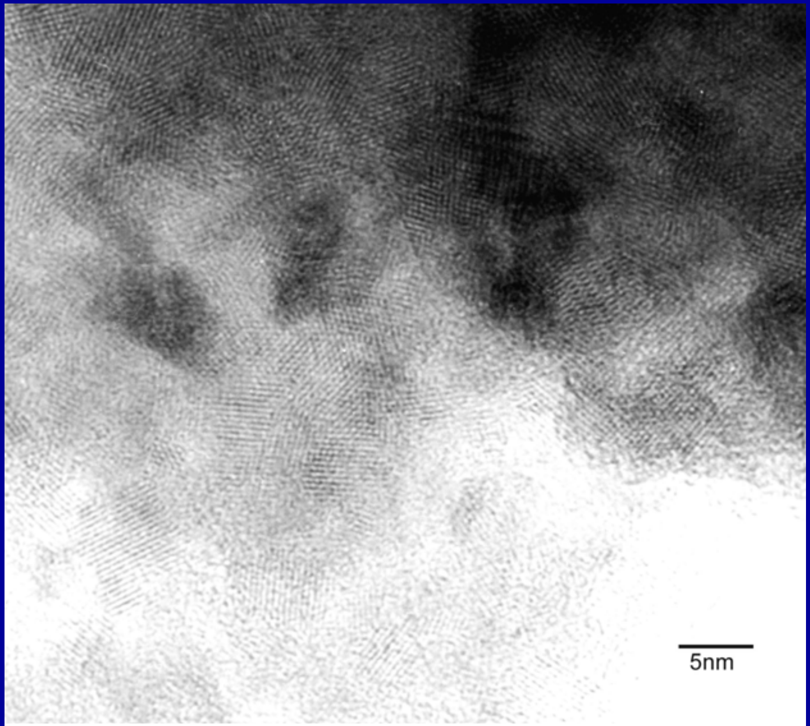
*C. Feldmann, Philips GmbH, Angew. Chem. Int. Ed. **2001**, 40, 359 -362

Precursor: $TiOSO_4 \cdot 2\ H_2O \cdot H_2SO_4$ **TiO_2**



TiO_2 agglomeration

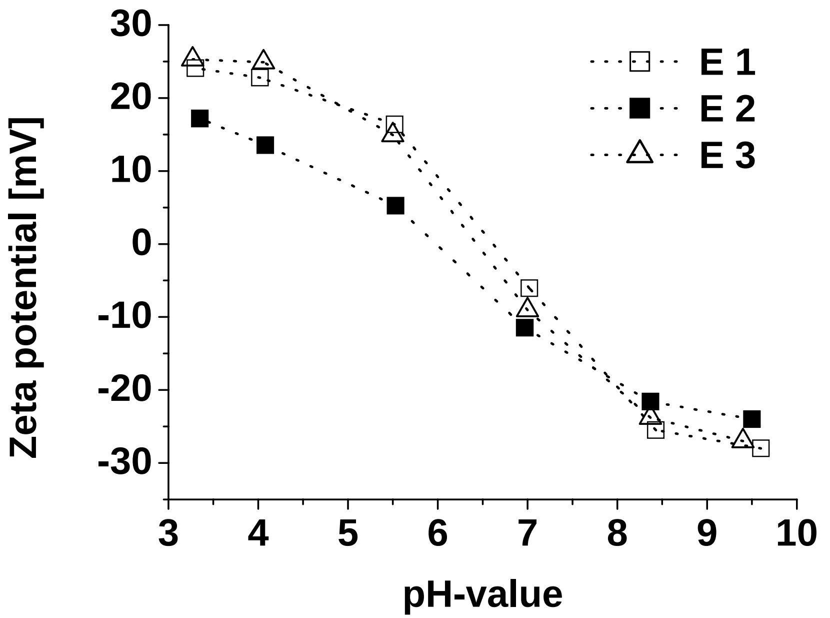
< 1000 nm

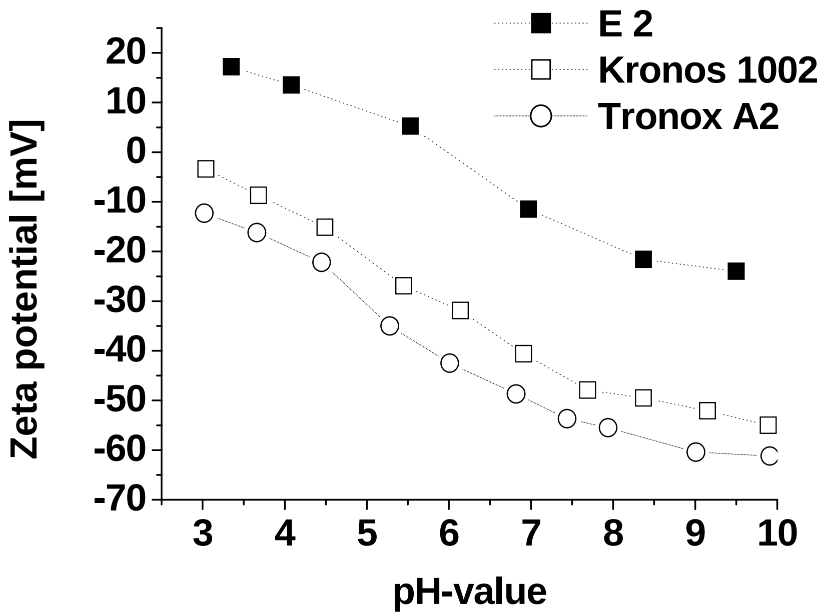


cristallit size

< 5 nm

ζ/pH-plots of TiO_2 products

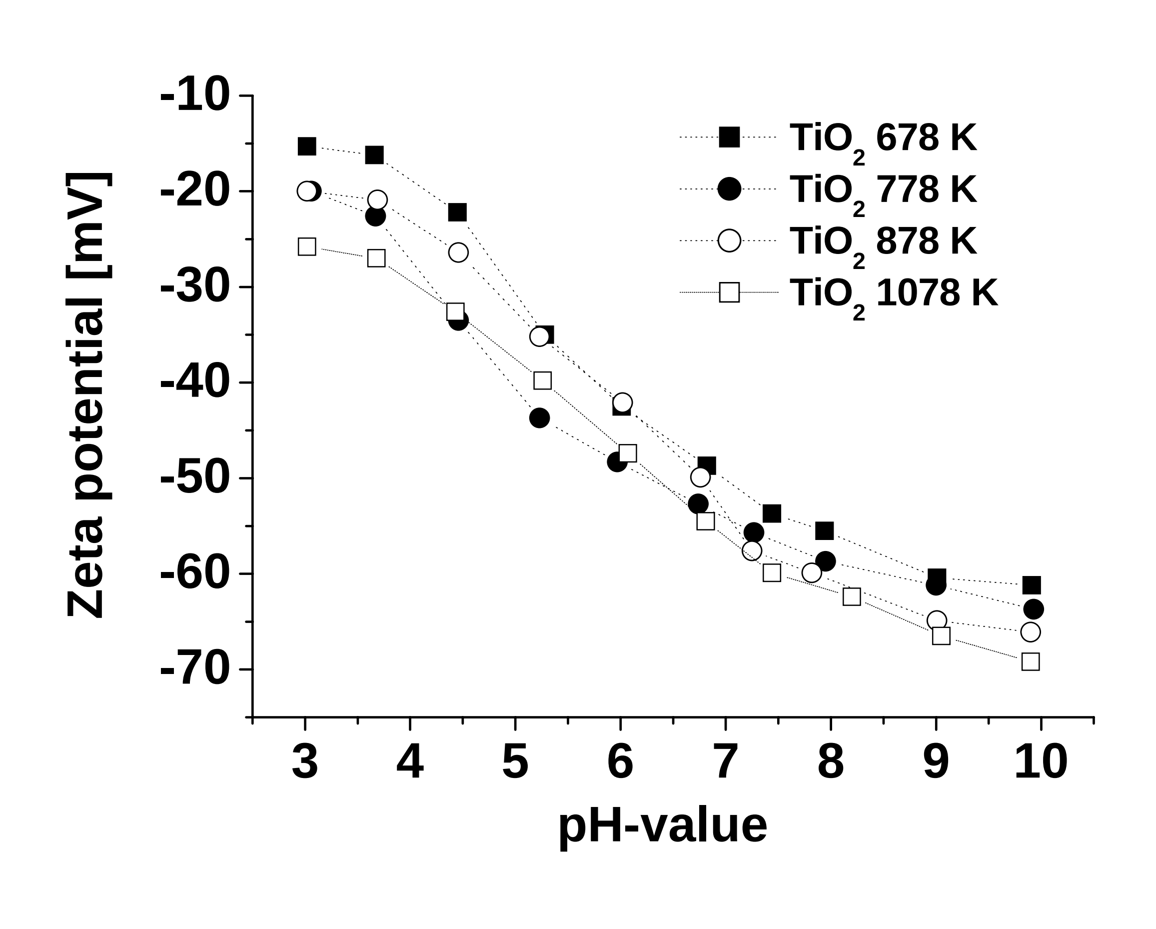




Commercial Sachtleben TiO_2 products of different sulfate content:
E1≈ E3 ≈ 0.45 wt.-% and
E2 ≈ 1.2 to 1.8 wt.-% sulfate

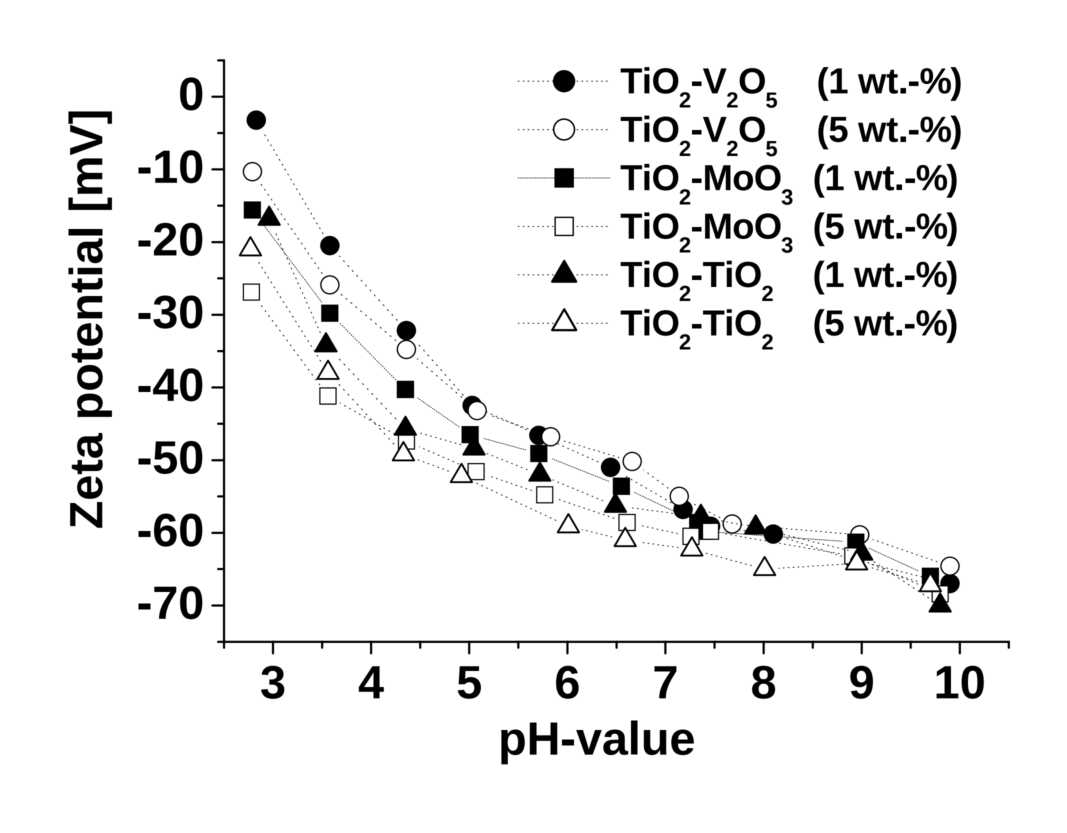
Commercial Kronos 1002,
Tronox A2
sulfate content
< 40 ppm

Influence of the calcination temperature



Tronox A2 TiO_2 on the ζ/pH-plots of suspended TiO_2

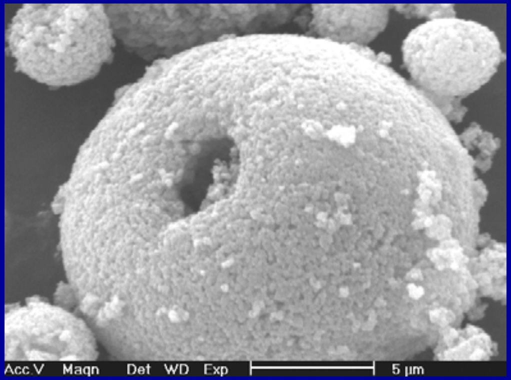
ζ/pH-plots of catalysts

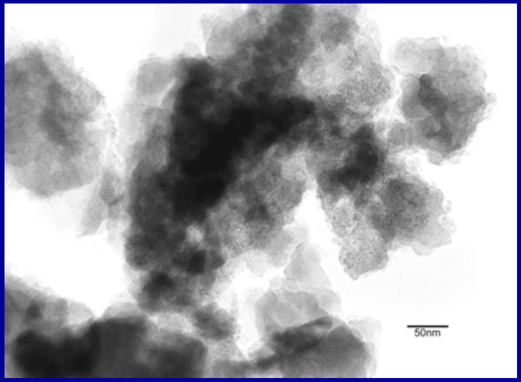


ζ/pH-plots of suspended in water catalysts which consist of the TiO_2 support (Tronox A2 spray granules) and the active components V_2O_5 and MoO_3. For comparison, the data for the intermediate TiO_2 layer is given (1 and 5 wt.-%)

TiO_2-support

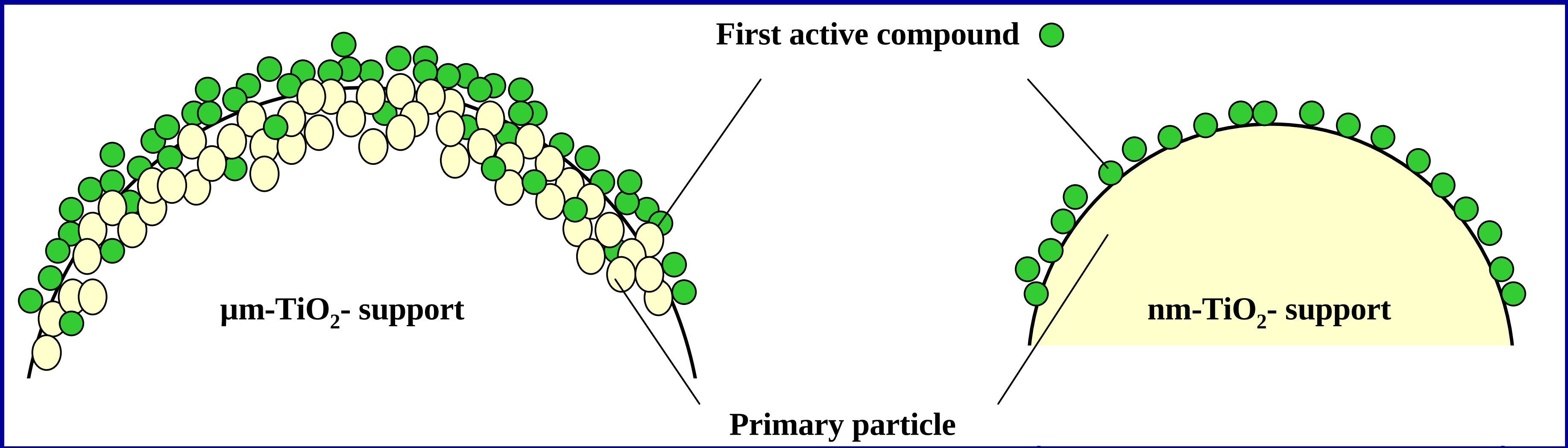
Characterization





primary particle size	**ca. 0,5 µm**	**ca. 10 nm**
isoelectric point (IEP)	**-**	**pH 3.8**
Z-Average (agglomeration)	**ca. 30 µm**	**ca. 4 - 5 µm**
S_{BET}	**< 10 m^2/g**	**140 m^2/g**
XRD	anatase	anatase
strenght	≤ 900 °C	≤ 650 °C

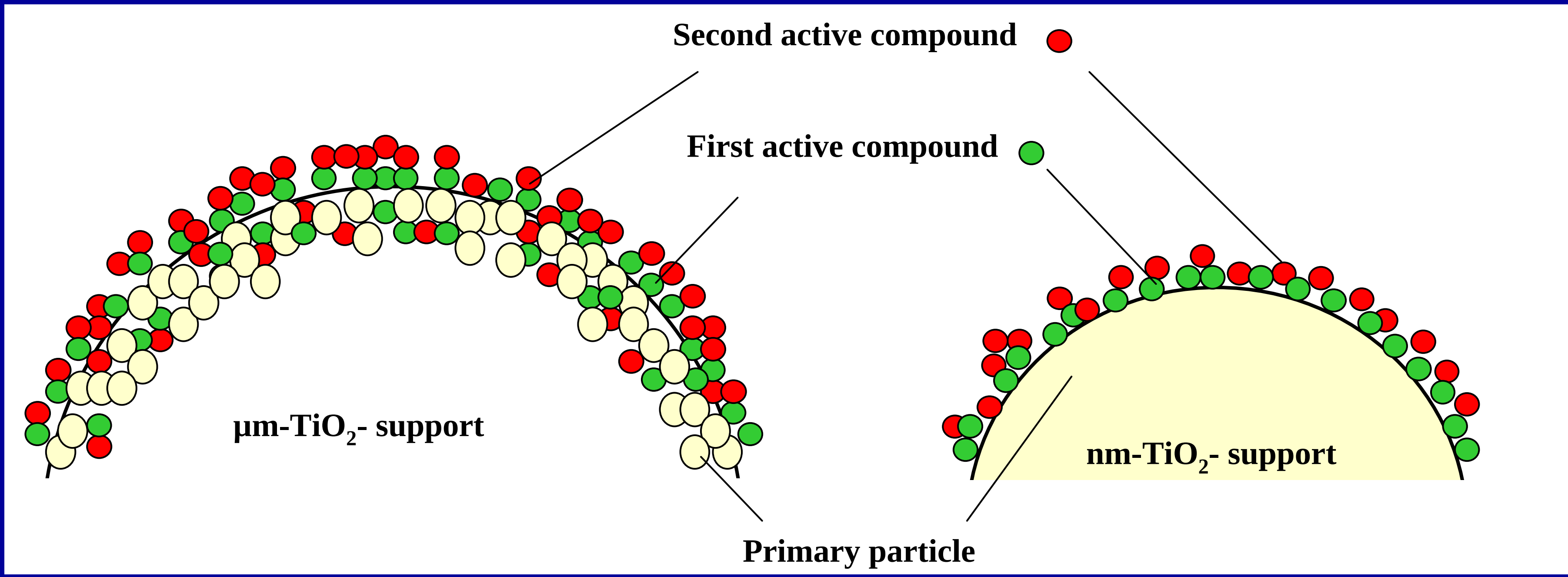
*Hierarchical model



Model of a catalyst built up from a support functionalized by one component

* J.B. Stelzer, H. Kosslick, J. Caro, D. Habel, E. Feike, H. Schubert, *Aufbau hierarchisch strukturierter Oxid-Katalysatoren Teil I*, Chem. Ing. Tech. 75 (7/2003) 872

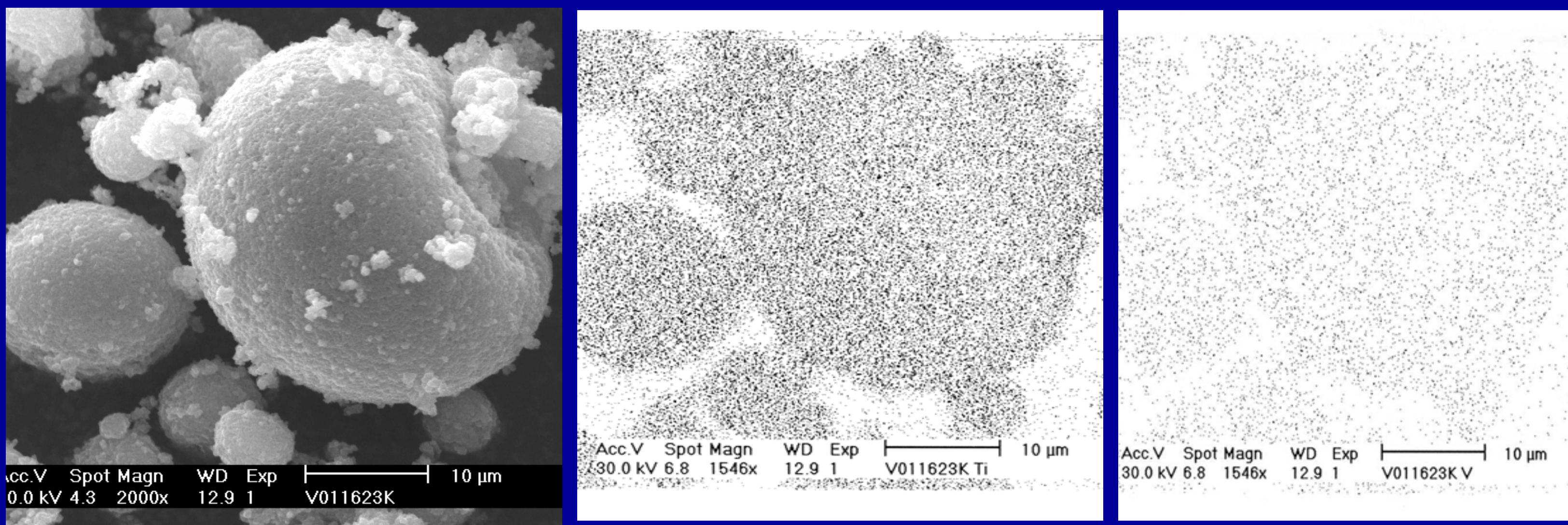
*Hierarchical model



Model of a catalyst built up from a support functionalized by two components

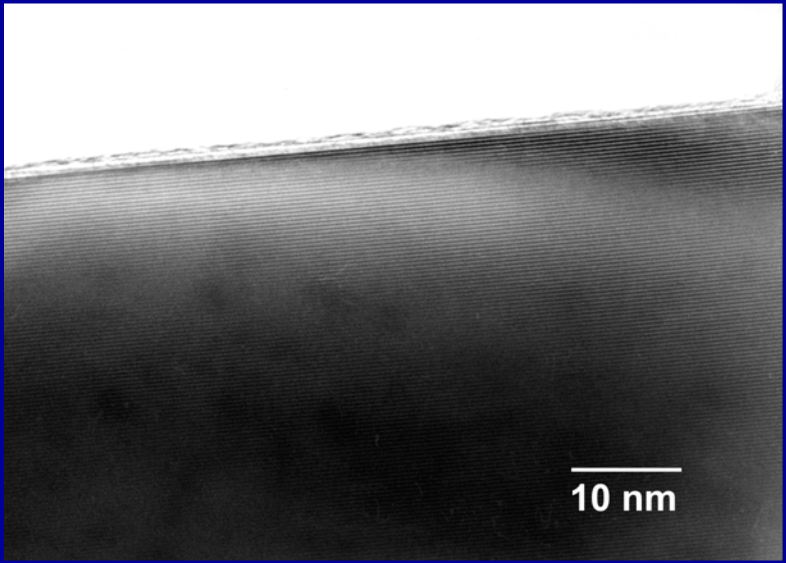
* J.B. Stelzer, H. Kosslick, M.-M. Pohl, J. Caro, D. Habel, E. Feike, H. Schubert, *Aufbau und katalytische Aktivität hierarchisch nanostruk-turierter Oxid-Katalysatoren Teil II,* Chem. Ing. Tech. 75 (11/2003) 1676

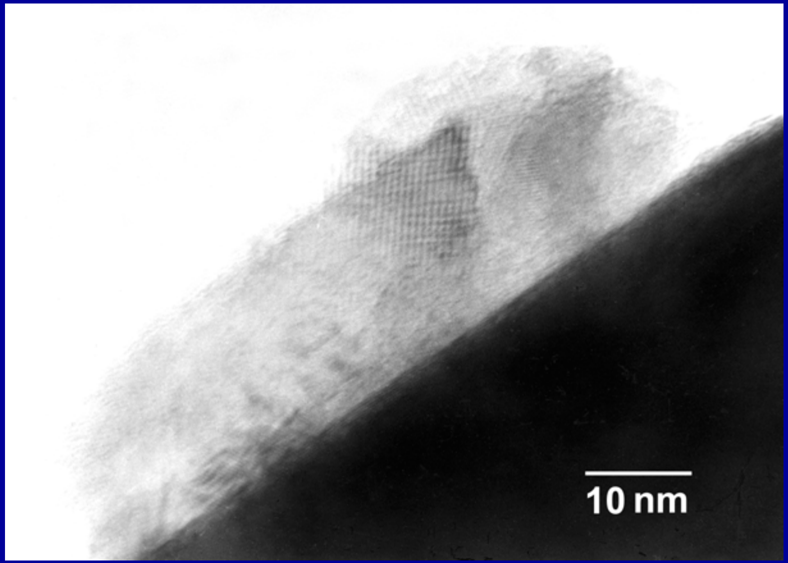
SEM & EDXS



SEM of the spray granule (left) and the EDXS element distribution of Ti (middle) and V (right) **5 %** V_2O_5

*TEM images





TEM of the pure spray granule (left) and impregnated with **10 %** V_2O_5 (right)

* M.-M. Pohl, Institut für Angewandte Chemie Berlin-Adlershof e.V.

TiO_2-support + active compound

≅ 1 monolayer

Impregnation

5 % V_2O_5

T = 500 °C

particle size

ca. 10 - 20 nm

monolayers

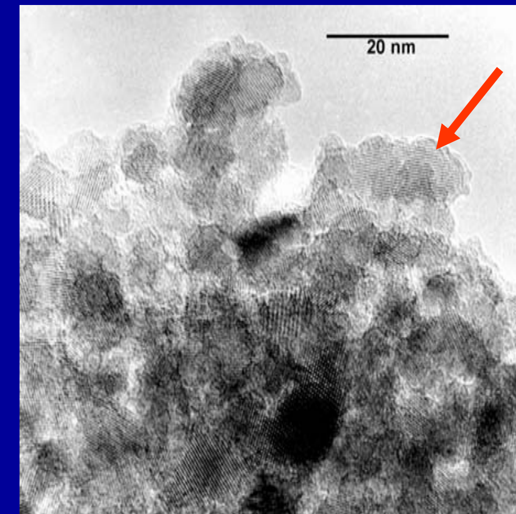
Impregnation

10 % V_2O_5

T = 500 °C

particle size

ca. 10 - 20 nm



amorphous

Impregnation

5 % MoO_3

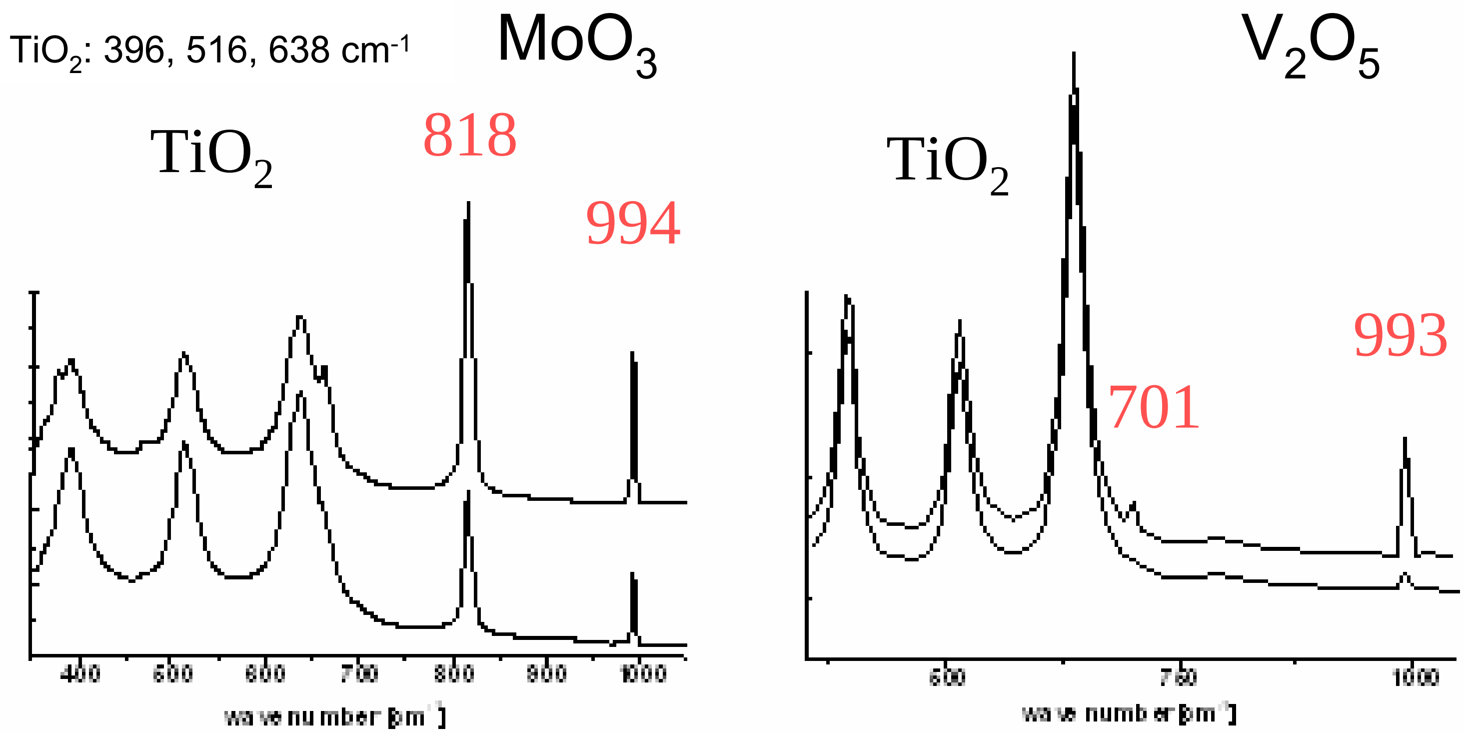
$(NH_4)_6\ [Mo_7O_{24}] \cdot 4\ H_2O$

T = 500 °C

particle size

ca. 10 - 20 nm

Raman-spectra



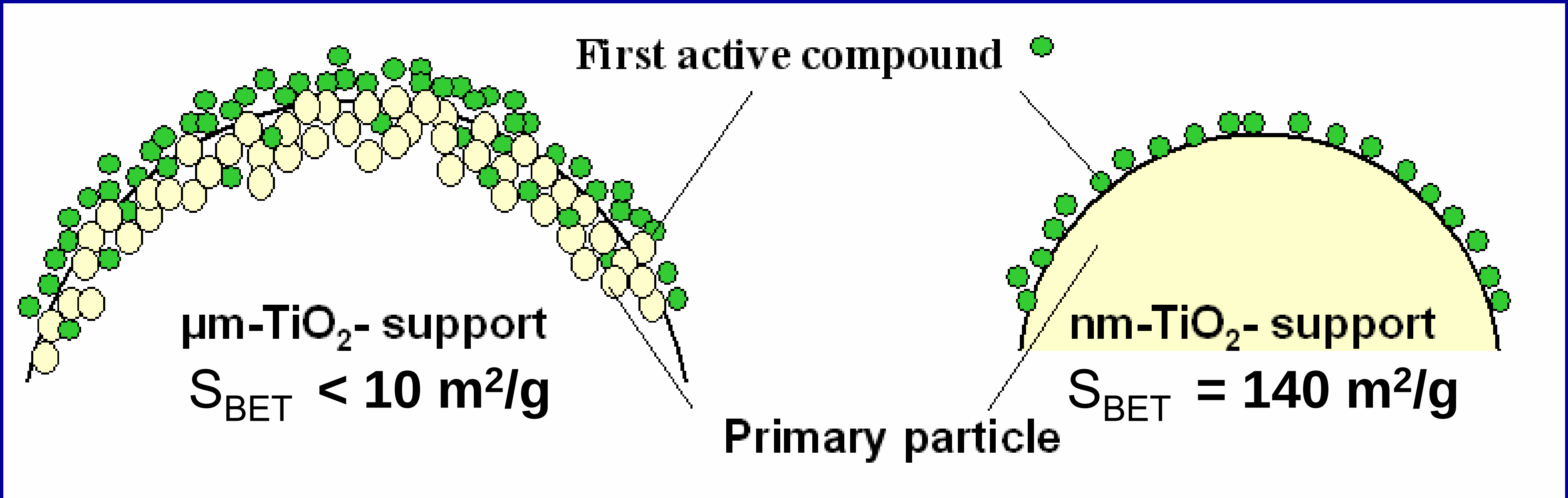
TiO_2-support + active compound
containing 1 (below) and 5 mass % (at the top)

ν (V=O) | *1040-70 cm^{-1}

*I.E. Wachs, R.Y. Saleh, S.S. Chan, C.C. Chersich, Chemtech. 15 (1985) 756

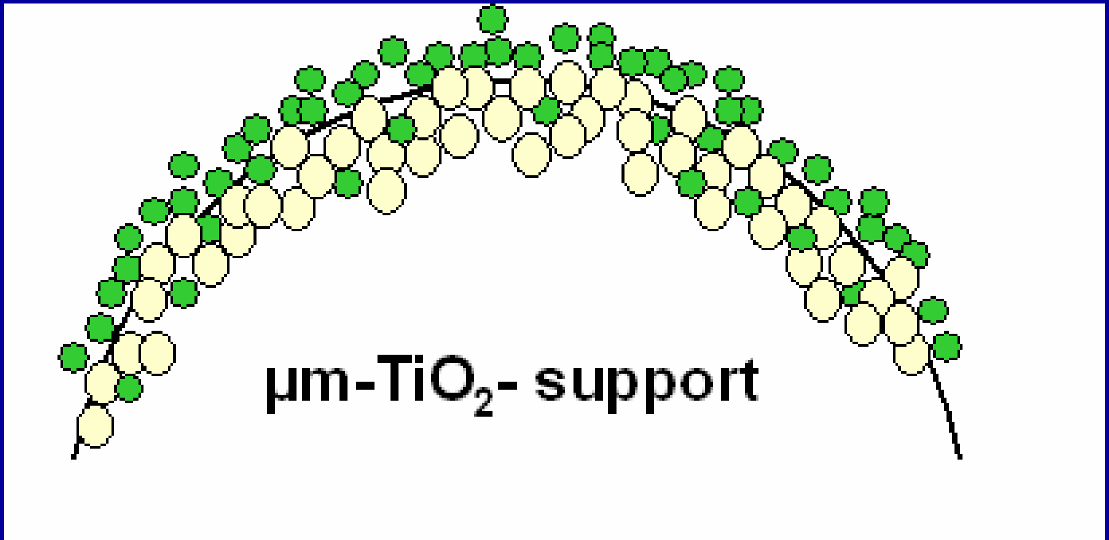
Catalysts for ODP-testing

(Feed) $C_3H_8/O_2/N_2$ = 40/20/40 $\tau \sim 0.75\ (g \cdot s \cdot ml^{-1})$



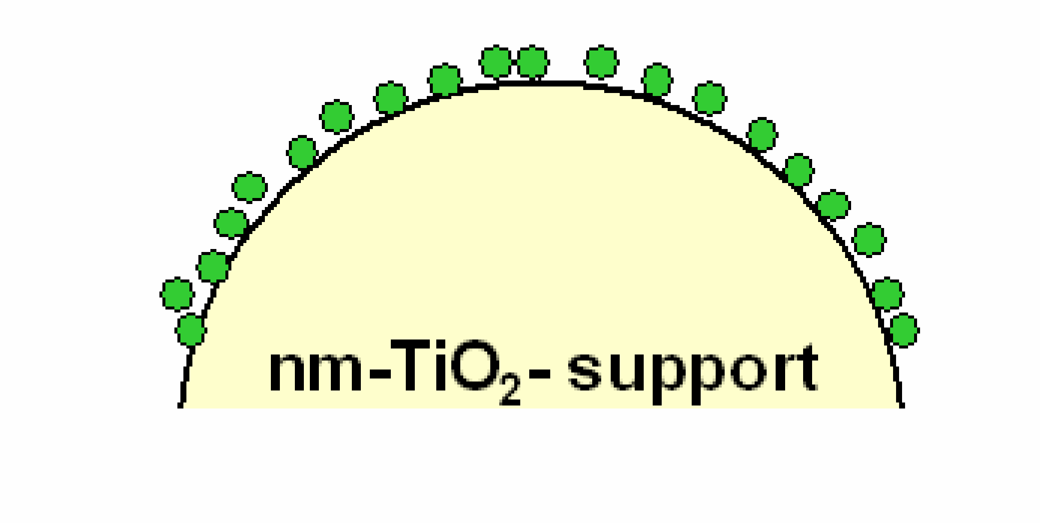
active compound	metalloxid [M %]
V_2O_5	1
V_2O_5	5

ODP ; 500 °C; τ ~ 0.75 (g·s·ml[-1])



Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
1 % V_2O_5	4.3	74.3	16.9	8.8	3.2
5 % V_2O_5	21.1	42.7	34.6	20.6	9.0

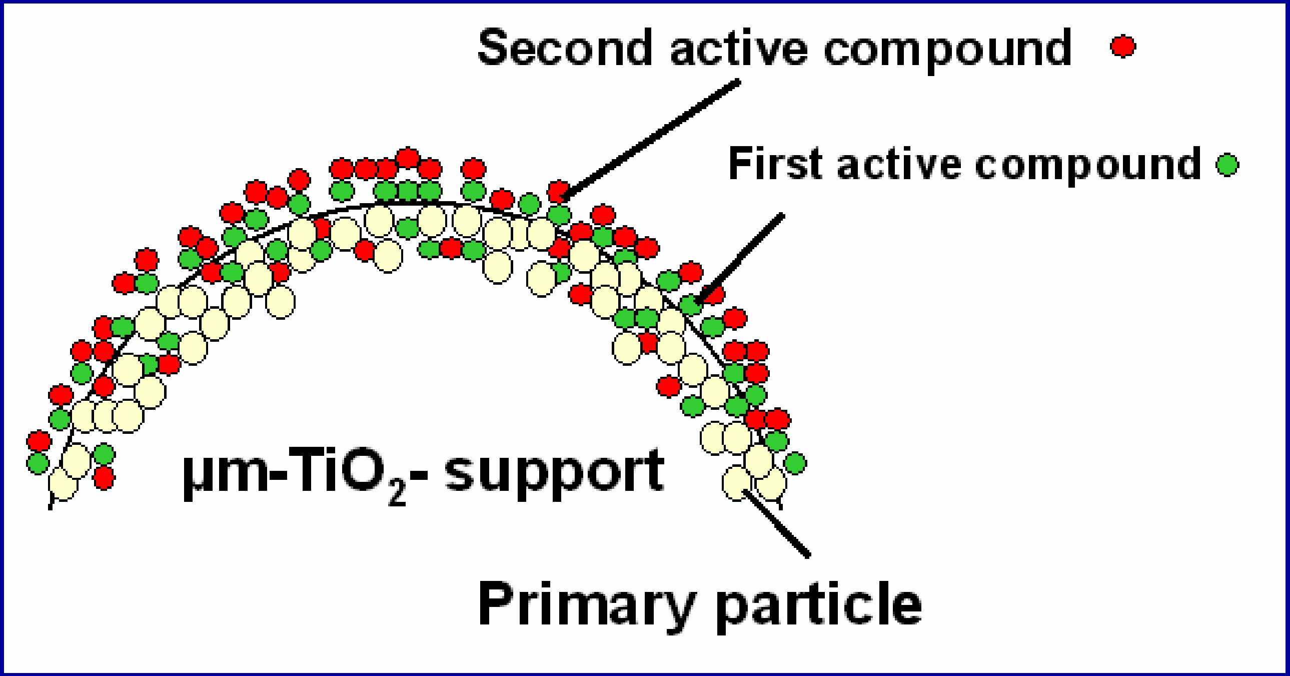
ODP ; 500 °C; $\tau \sim 0.75$ (g·s·ml^{-1})



Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
1 % V_2O_5	6.9	32.4	34.4	31.6	2.2
5 % V_2O_5	9.2	51.4	27.6	20.9	4.7

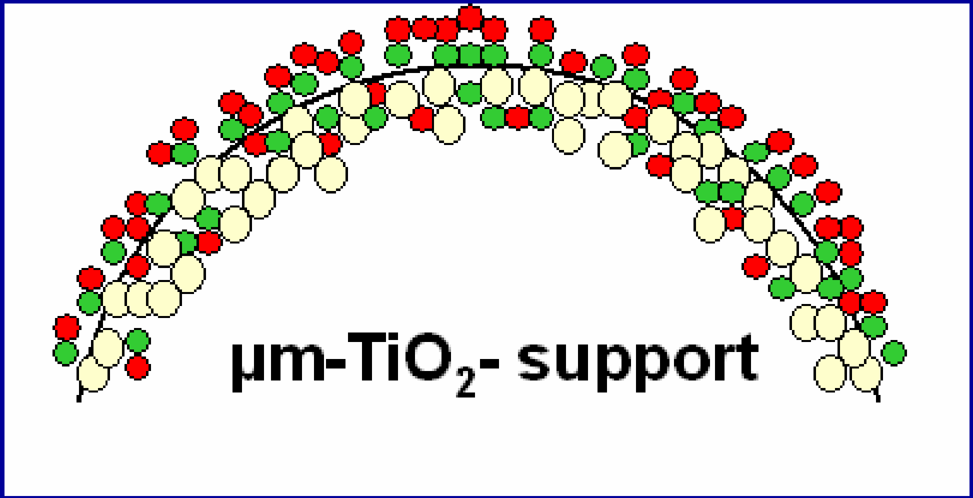
Catalysts for ODP-testing

(Feed) $C_3H_8/O_2/N_2$ = 40/20/40 $\tau \sim 0.75\ (g\cdot s\cdot ml^{-1})$



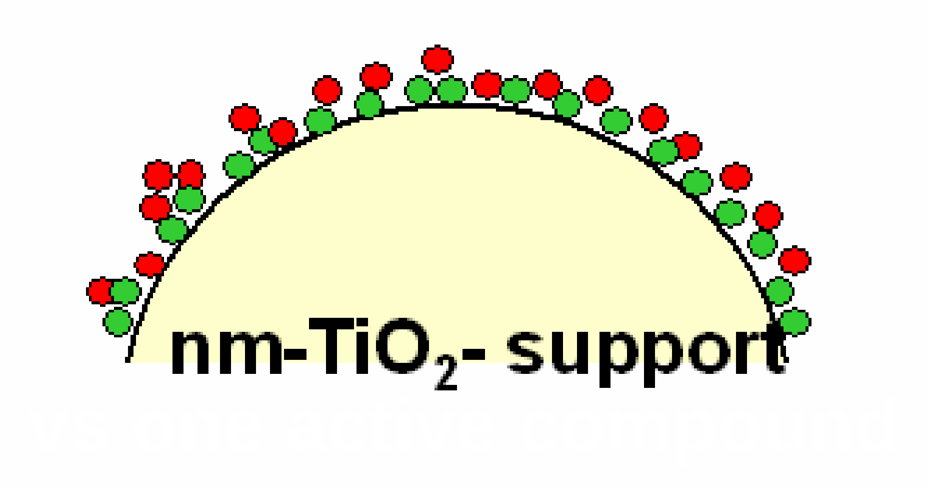
active compound	metalloxid [M %]
TiO_2/V_2O_5	0.25 / 0.25
TiO_2/V_2O_5	1.25 / 1.25

ODP ; 500 °C; $\tau \sim 0.75\ (g \cdot s \cdot ml^{-1})$



Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
TiO_2-TiO_2/V_2O_5 (0.25% /0.25%)	1.3	64.7	19.2	16.1	0.8
TiO_2-TiO_2/V_2O_5 (1.25%/1.25%)	13.2	55.6	23.4	21	7.3
vs one active compound					
TiO_2-V_2O_5 (1%)	4.3	74.3	16.9	8.8	3.2

ODP ; 500 °C; $\tau \sim 0.75$ (g·s·ml^{-1})



Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
TiO_2-TiO_2/ V_2O_5 (2.5%/2.5%)	16.4	35.9	39.7	24.4	5.9
vs one active compound					
1 % V_2O_5	6.9	32.4	34.4	31.6	2.2
5 % V_2O_5	9.2	51.4	27.6	20.9	4.7

Conclusion

- With a relative low content of 1.25 wt.-% V_2O_5, the nano structured catalyst with intermediate TiO_2 layer shows an improved selectivity at medium propane conversion in comparison with the catalyst where the active component V_2O_5 is directly deposited on the TiO_2 support.

- The propene yield of the nano structured catalyst with 1.25 wt.-% V_2O_5 becomes comparable with that of the catalyst containing 5 wt.-% V_2O_5.

Conclusion

TiO_2-VO_x

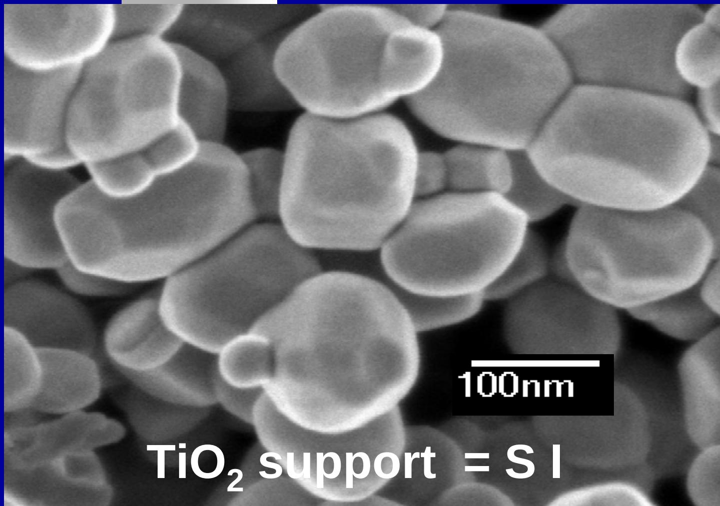
TiO_2-TiO_2/VO_x

Rate of increase

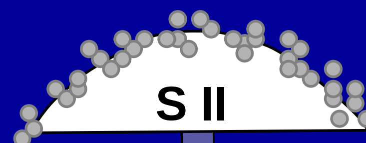
X C_3H_8	+ 75 %
Y C_3H_6	+ 50 %

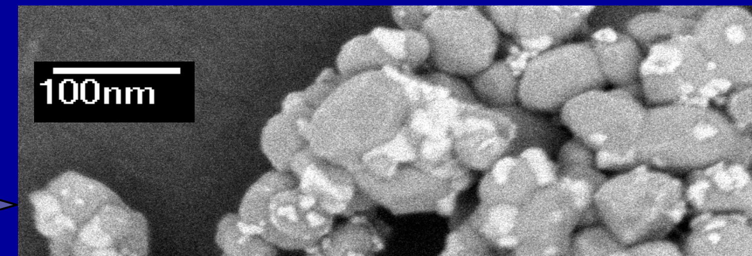
→ However, due to the higher selectivity for the olefin formation, less by products are formed in the case of the nano structured catalyst.

Outlook of preparation



+ $Sb(C_2H_3O_2)_3$



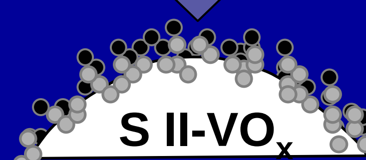


TiO$_2$-SbO$_y$ support = S II

+ Vanadium precursor

+ $VO(C_2O_4) \cdot 2\ H_2O$ | **+ $(C_6H_5NH)_4H_2V_{10}O_{28} \cdot 4\ H_2O$** | **+ NH_4VO_3**

Calcination in air or in nitrogen atmosphere at 500 °C



ODP ; 500 °C; $\tau \sim 0.15$ ($g \cdot s \cdot ml^{-1}$)

Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
TiO_2- VO_{oxa} (10 % V, N_2)	24.5	43.6	30.9	18.2	10.7
TiO_2- VO_{meta} (10 % V, N_2)	25.4	41.0	31.0	16.6	10.4
TiO_2- VO_{py} (10 % V, N_2)	25.1	42.3	27.4	15.5	10.6

Conclusion

The VO_x-catalysts from different V-precursors [($VO(C_2O_4) \cdot 2\ H_2O$, $(C_5H_5NH)_4H_2V_{10}O_{28} \cdot 4\ H_2O$ or NH_4VO_3] are similar in their activity and selectivity in the ODP.

The maximum propene yield was appr. 11 % at conversions of appr. 26 %. Catalysts which were calcined before the catalytic tests in nitrogen are more active then those calcined in air.

Outlook Processintegration

1. Period	**Goal** →	*2. Period*
raw material		raw material
milling process		milling process
spraydrying		spraydrying

1. Period

raw material
milling process
spraydrying
↓
heat treatment
preliminary stage/solvent
precipitation/hydrolysis
↓
heat treatment
disperse/immobilize
synthesis
active compounend
↓
heat treatment

spreading/disperse

heat treatment

2. Period

raw material
milling process
spraydrying

↙ ↘

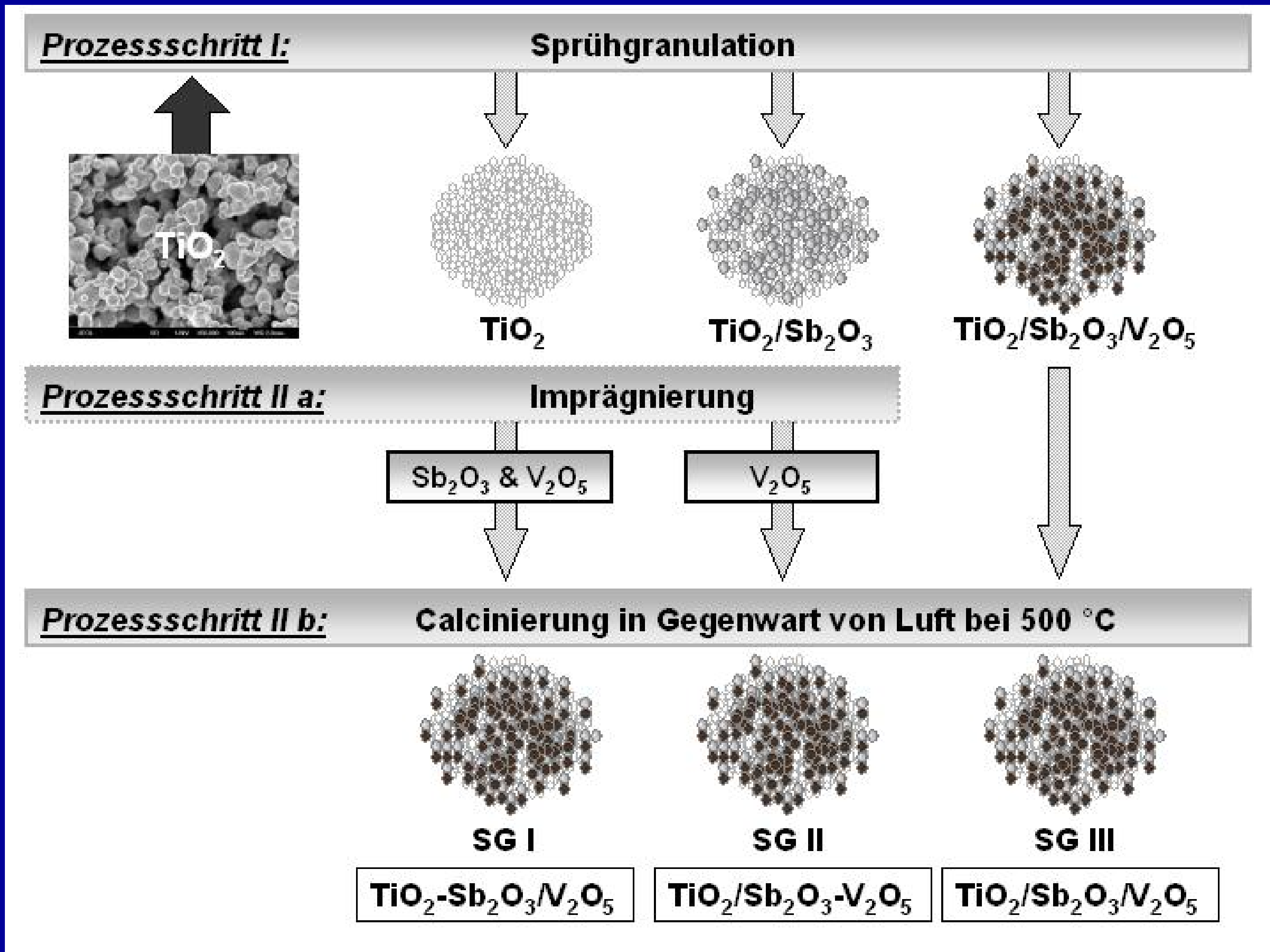
nano-structure | in situ immobilize

↘ ↙

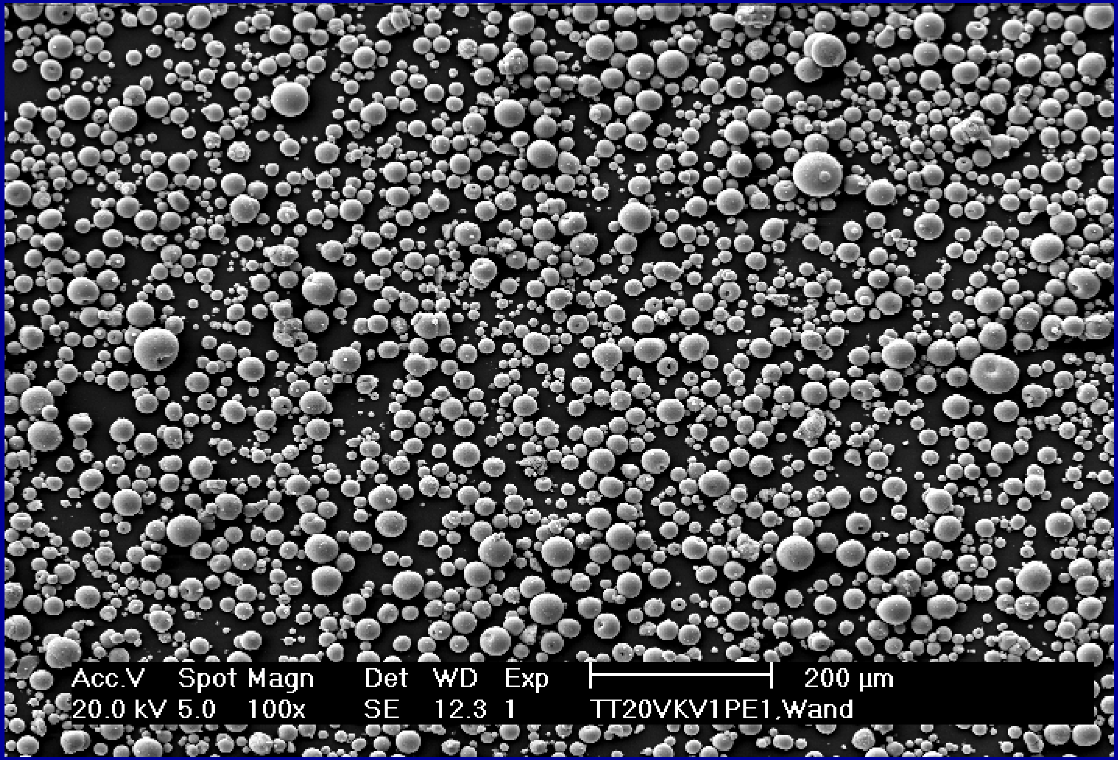
synthesis
active compounend

heat treatment

Outlook Processintegration

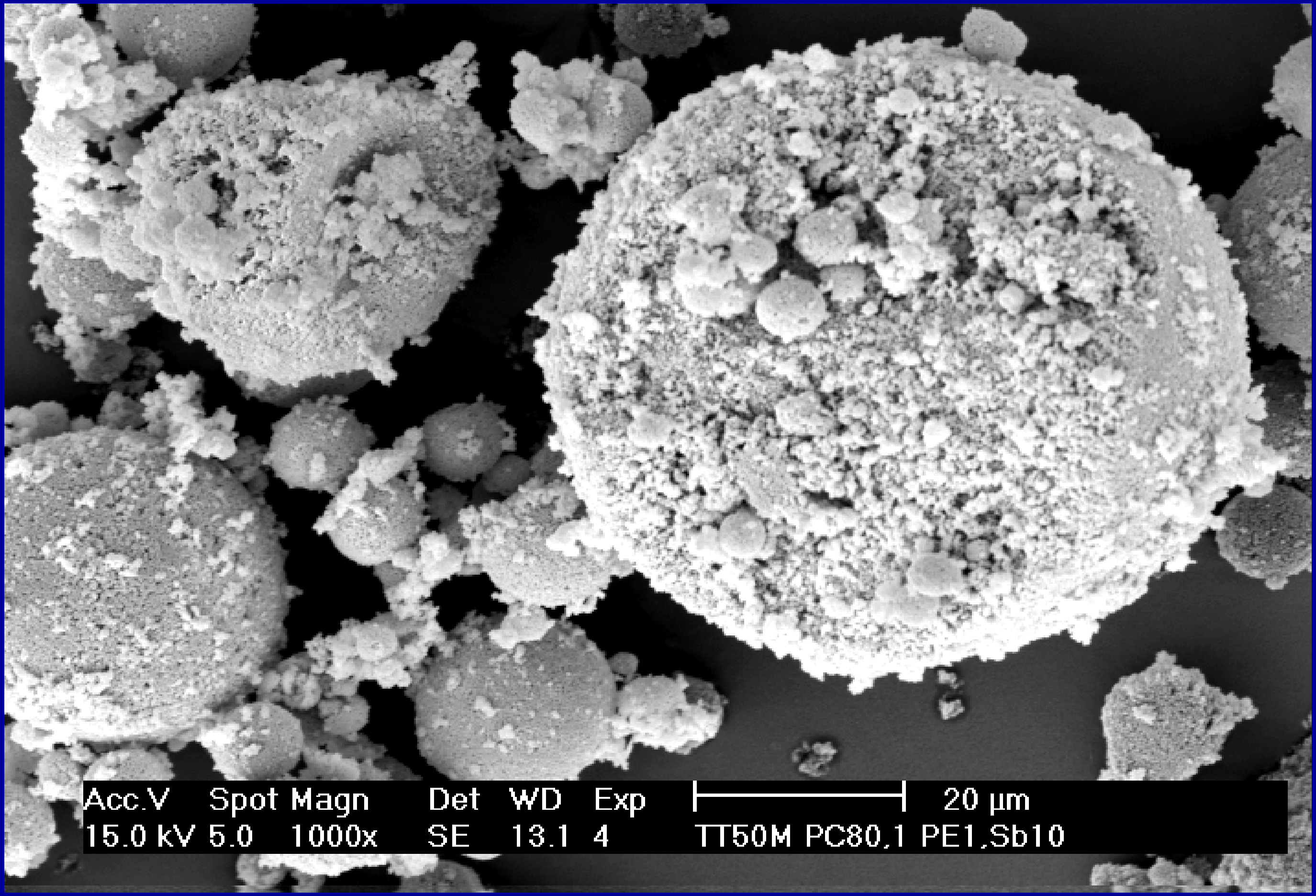


Outlook Processintegration



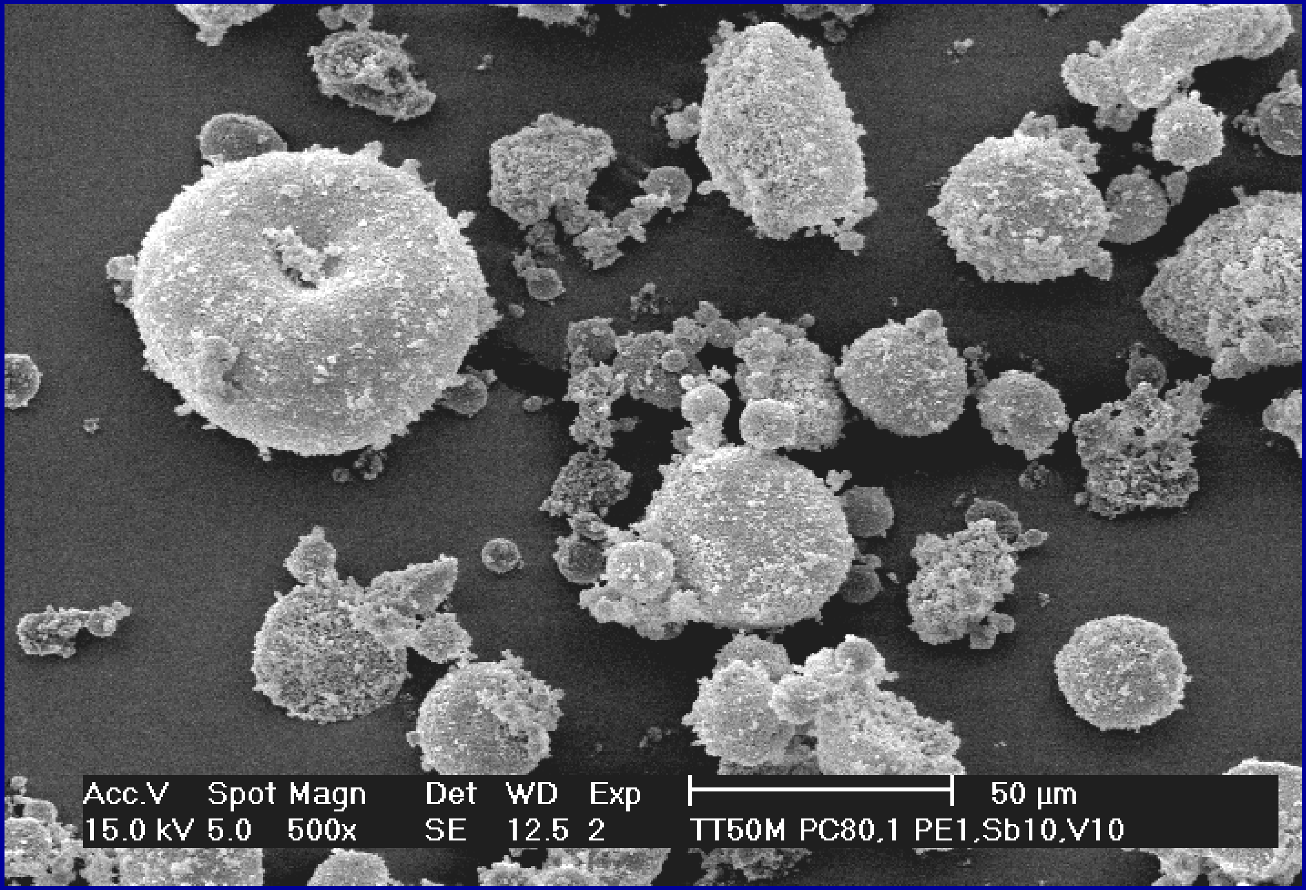
TiO_2 spray granulation: 0,6 µm up to ca. 30 µm

Outlook Processintegration



TiO_2 / Sb_2O_3 spray granule

Outlook Processintegration

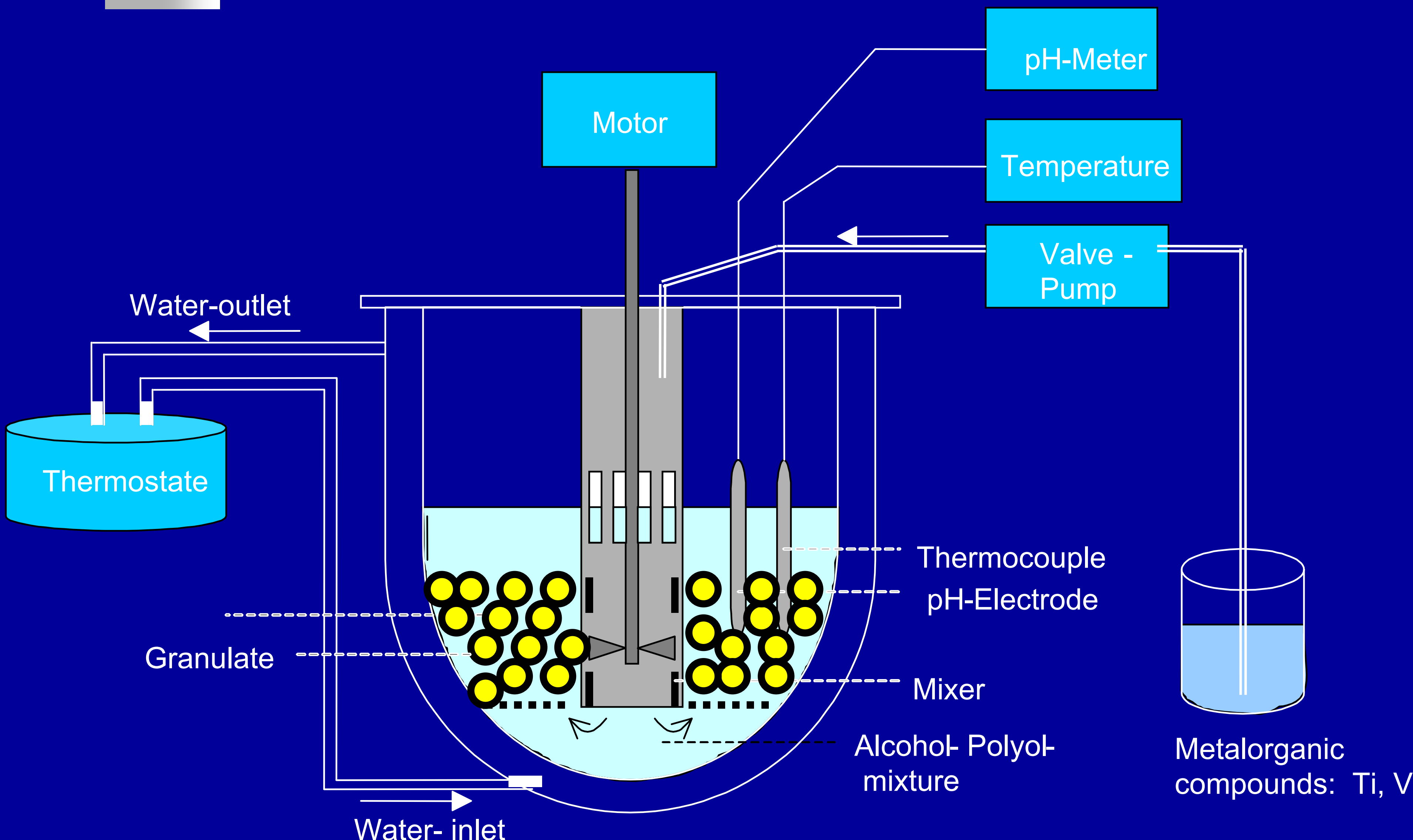


$TiO_2/Sb_2O_3/V_2O_5$ spray granule

ODP ; 500 °C; $\tau \sim 0.75$ ($g \cdot s \cdot ml^{-1}$)

Catalyst	X C_3H_8[%]	S C_3H_6[%]	S CO[%]	S CO_2[%]	Y C_3H_6[%]
Spray granule TiO_2 + impregnated with Sb_2O_3/V_2O_5					
TiO_2+ Sb_2O_3/V_2O_5 (10 % Sb/V)	18.1	35.4	38.3	24.5	6.5
Spray granule TiO_2 /Sb_2O_3 + impregnated with V_2O_5					
TiO_2/Sb_2O_3-V_2O_5 (10 % Sb/V)	16.6	35.3	38.3	19.1	5.9
Spray granule TiO_2 /Sb_2O_3 /V_2O_5					
$TiO_2/Sb_2O_3/V_2O_5$ (10 % Sb/V)	1.1	86.1	8.8	5.1	0.9

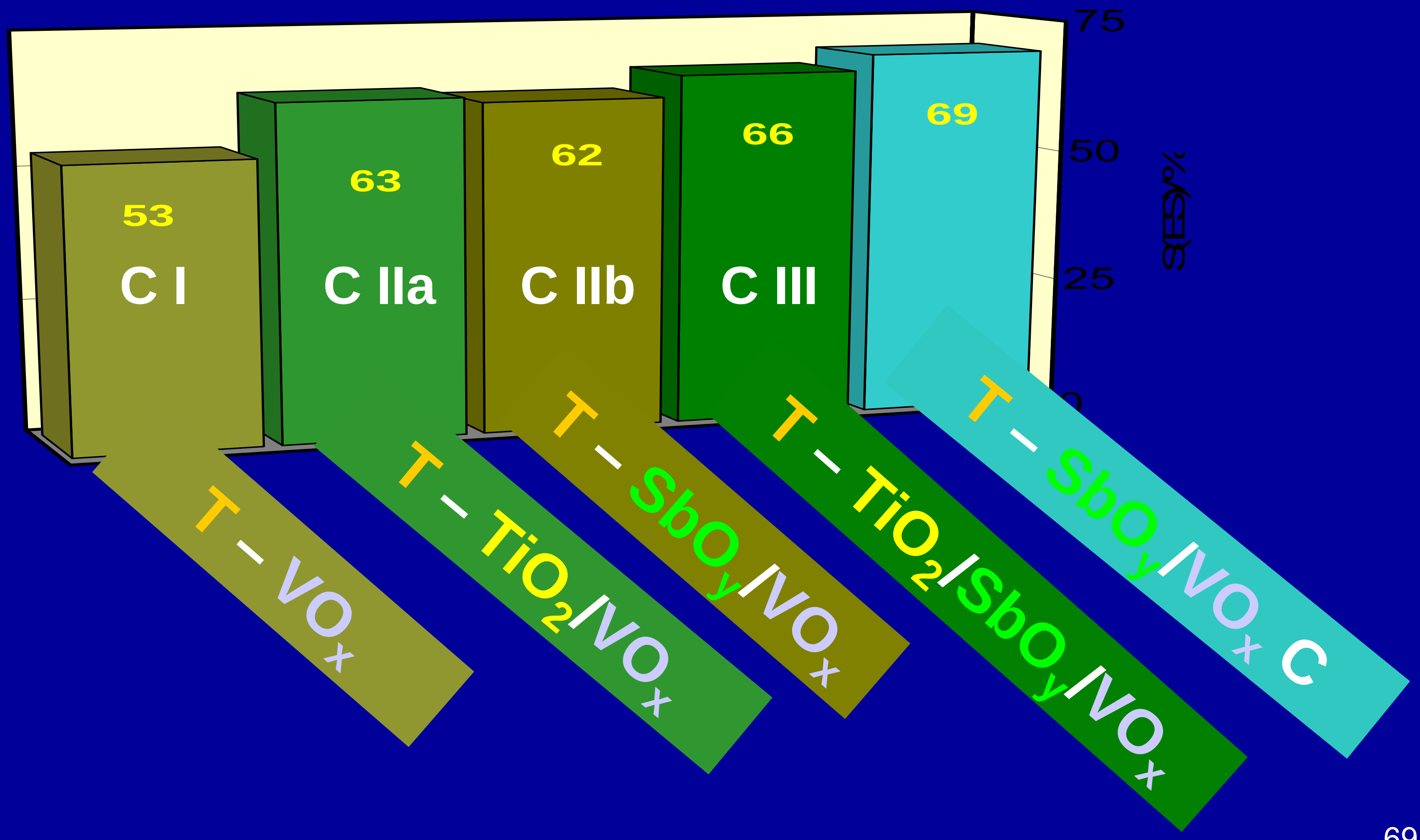
Outlook for preparation technique



Catalytic OHS-testing

T = 190 - 200 °C, p = 7 bar, t_{mod} = 0,8 g s ml $(N)^{-1}$

1,9 % C_4H_8/9,1 % O_2/24 % H_2O/N_2 $X(C_4H_8)$ = 70 %

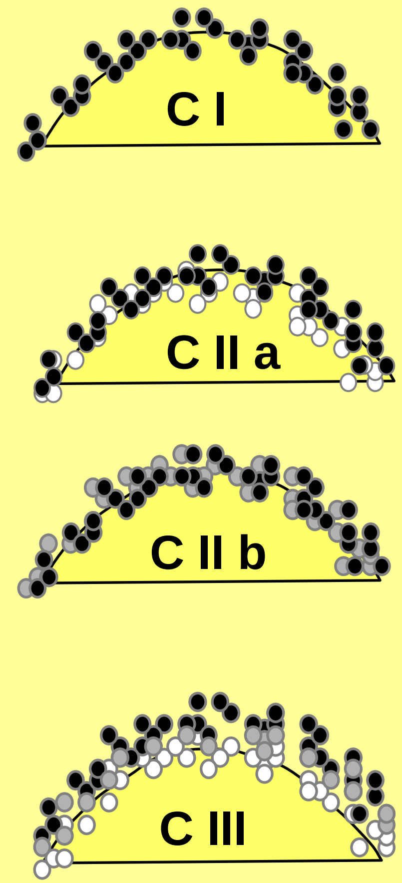


Conclusion

- The AA selectivities are noticeable enhanced by ca. 20 % for the samples C II a and C II b compared to sample C I

  S HOAc [%] + 20 %

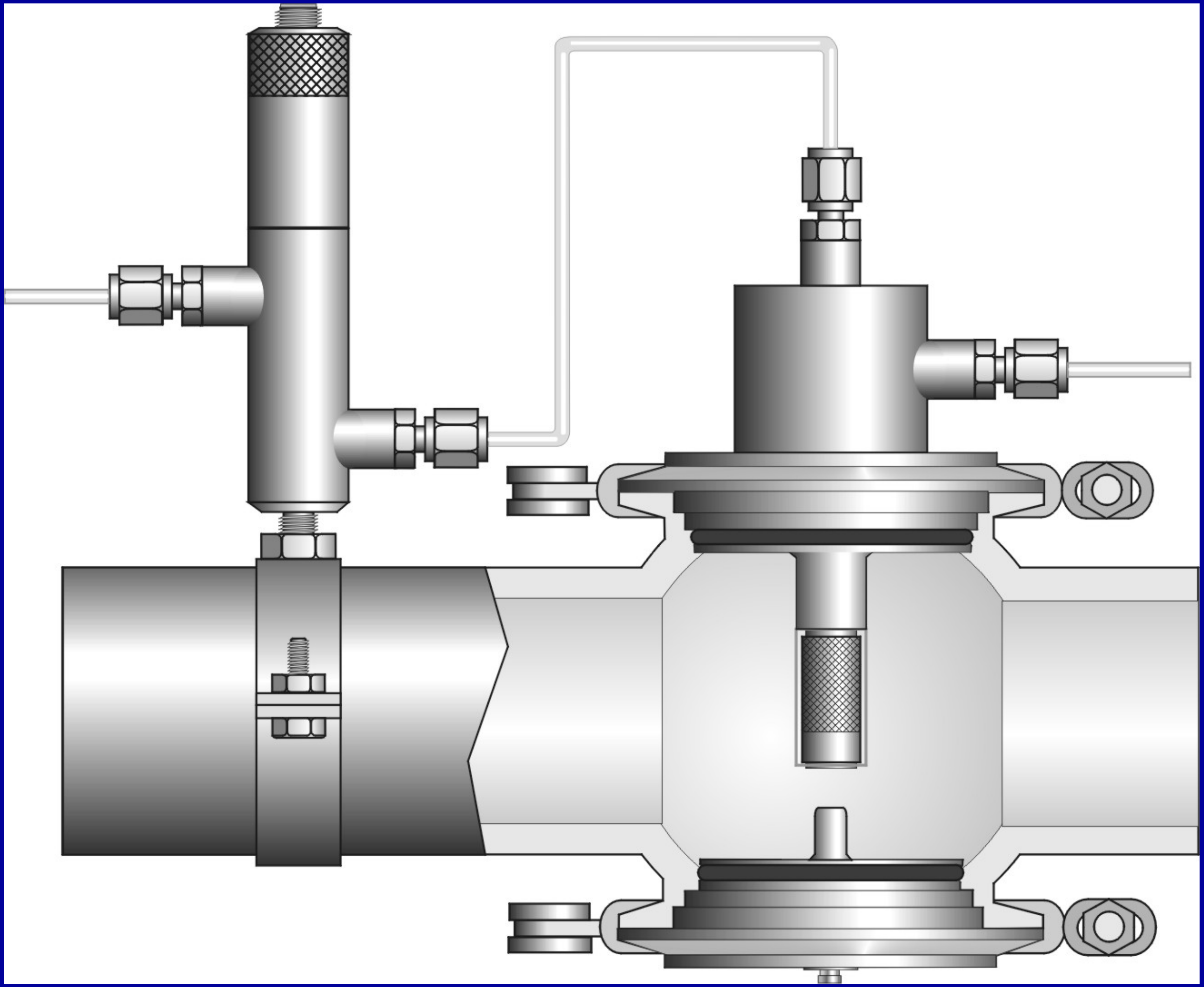
- The concept of hierarchical catalyst design combined with new synthesis strategies will open a promising route to future improvement of catalysts



Dr. Thiedig + Co

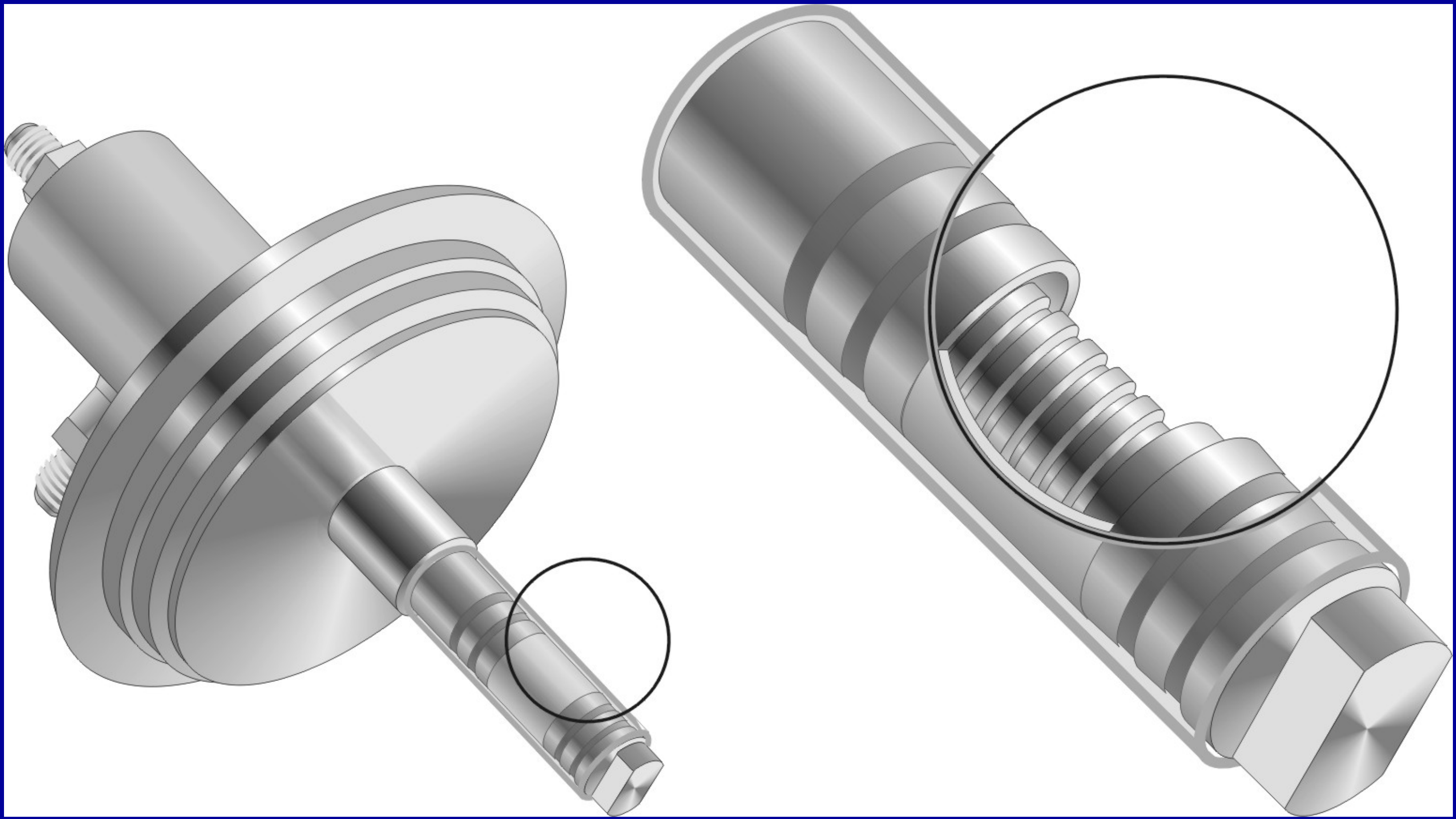
New product: DIGOX 5

Specialist O_2



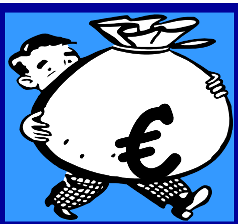
Application
for Inline-CO_2
e.g.
brewery

Cut-out of a measuring probe



Acknowledgement

Financial support of the German Research Council (DFG) (Ca 147/9-2, Schu 679/21-2 and Fe 608/1-2)



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