Thermal Treatment of Catalysts

Modern Methods in Heterogeneous Catalysis Research

Friederike C. Jentoft, October 31, 2003

Outline

1. Terminology (calcination)
2. Sample vs. oven set temperature
3. Self-generated atmosphere & self-steaming of zeolites
4. Combustion
5. Glow phenomenon & zirconia catalysts
6. Crystallization
7. Loss of surface area
8. Effect of additives
9. Solid-solid wetting
10. Reductive treatments & SMSI

Steps of Catalyst Preparation

- IUPAC defines 3 steps of catalyst preparation

1. Preparation of primary solid, associating all the useful compounds
2. Processing of that primary solid to obtain the catalyst precursor for example by heat treatment
3. Activation of the precursor to give the active catalyst (reduction to metal, formation of sulfides, deammoniation of zeolites)

Heat Treatment of Intermediate Solids or Precursors

- drying
- thermal decomposition of salts (nitrates, ammonium salts)
- calcination

- product is a "reasonably inert solid" which can be stored easily

Annealing

- in a general meaning: a heating of a material over a long time span; strain and cracks in a crystalline solid can be removed

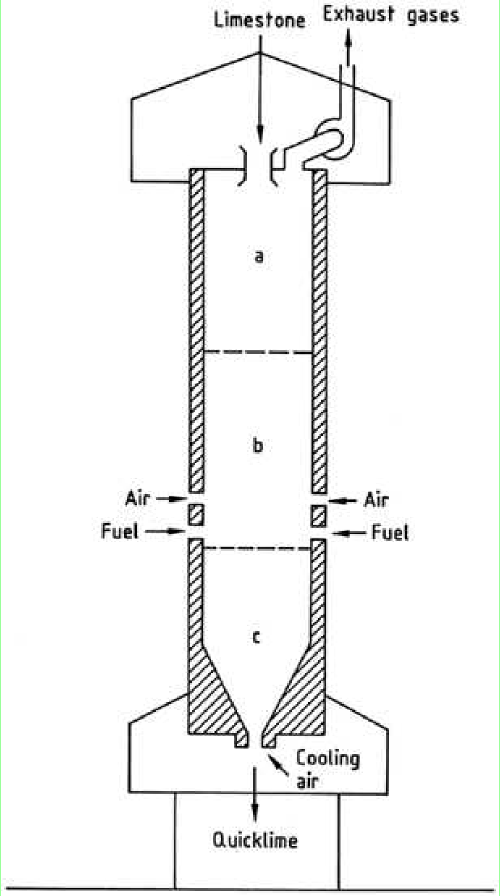
Origin of the Term "Calcination"

- latin "calx" = playstone limestone, (greek *chálix*)
- burning of calcium carbonate (limestone) to calcium oxide (quicklime)

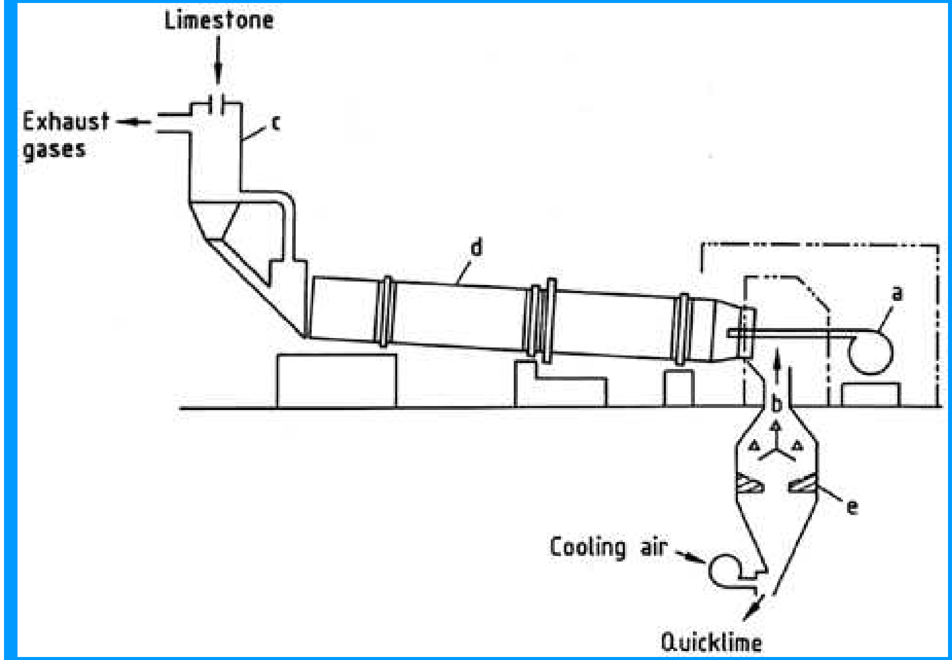
$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H(900°C)=3010\ kJ\ mol^{-1}$$

- used to construct Giza pyramids (ca. 2800 A.C.), burning of limestone ("Kalkbrennen") mentioned by Cato 184 A.C.
- performed in kilns (ovens) at 900°C
- addition of air to sustain combustion + cool product

Examples for Kilns for Calcination



- Schematic of a vertical shaft kiln.
  a) Preheating zone; b) Calcining zone;
  c) Cooling zone



- Schematic of a rotary kiln
  a) Burner; b) Combustion air;
  c) Pre-heater; d) Kiln; e) Cooler

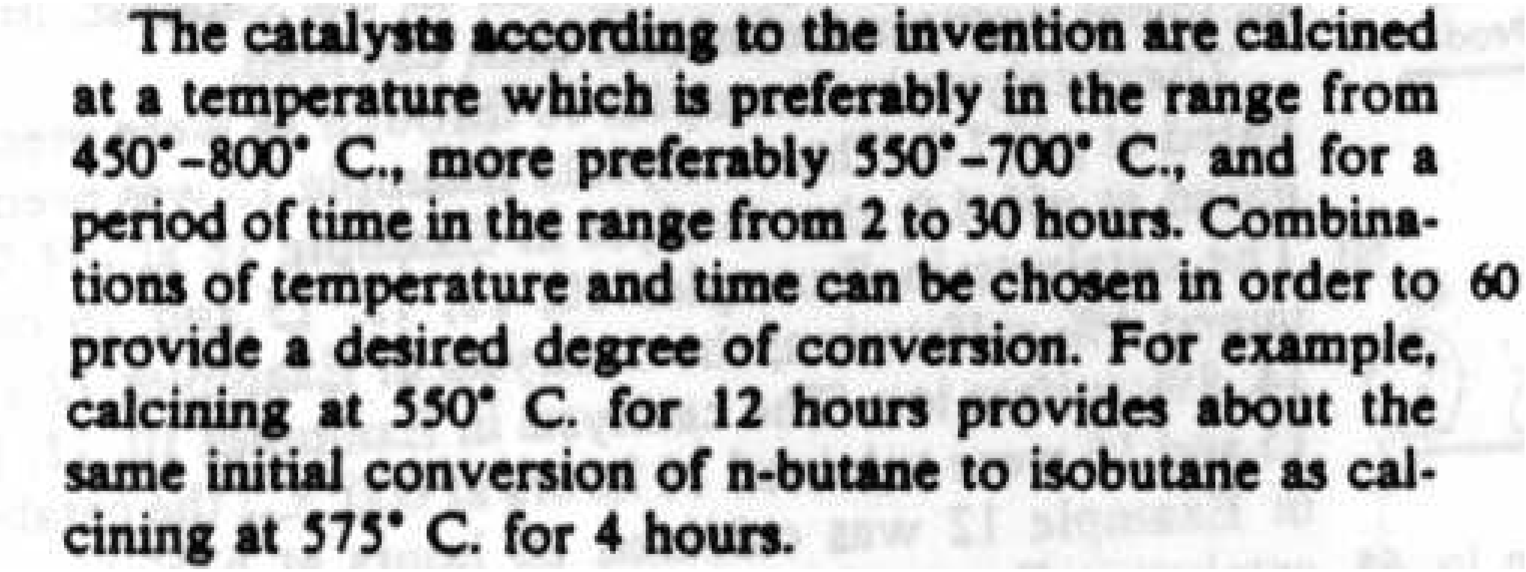
General Definition of "Calcination"

- decomposition of a substance through heating, transformation in lime-like substance – *Duden*
- to heat (as inorganic materials) to a high temperature but without fusing in order to drive off volatile matter or to effect changes (as oxidation or pulverization) – *Websters*
- heating (burning) of solids to a certain degree of decomposition, whereby with e.g. soda, gypsum the crystal water is completely or partially removed – *Römpp's Chemielexikon*
- the heating of a solid to a high temperature, below its melting point, to create a condition of thermal decomposition or phase transition other than melting or fusing – *Hüsing, Synthesis of Inorganic Materials*

Definition of "Calcination" in Catalysis Research

- thermal treatment (of a catalyst) in oxidizing atmosphere. The calcination temperature is usually slightly higher than that of the catalyst operating temperature – *Ullmann's Encyclopedia of Industrial Chemistry*
- a heat treatment of catalyst precursor in an oxidizing atmosphere for a couple of hours - *Catalysis from A to Z, Eds. Cornil et al.*
- heating in air or oxygen; the term is most likely to be applied to a step in the preparation of a catalyst - *IUPAC Compendium of Chemical Terminology*
- **often, with respect to catalysts, an oxidizing treatment is meant**
- **however, you will find statements such as "calcined in inert atmosphere"**
- **sample-generated atmosphere may be oxidative (nitrate decomposition)**

Example from Patent Literature

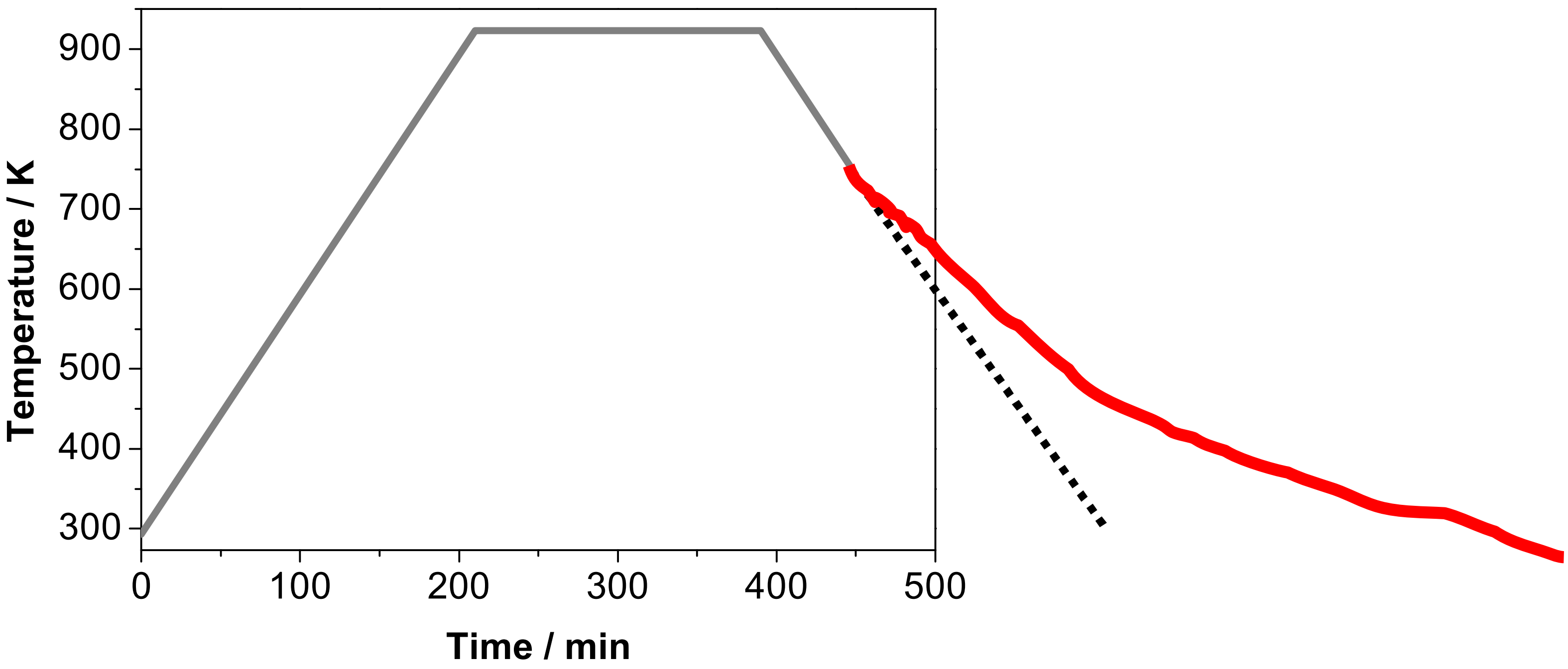


The catalysts according to the invention are calcined at a temperature which is preferably in the range from 450°-800° C., more preferably 550°-700° C., and for a period of time in the range from 2 to 30 hours. Combinations of temperature and time can be chosen in order to provide a desired degree of conversion. For example, calcining at 550° C. for 12 hours provides about the same initial conversion of n-butane to isobutane as calcining at 575° C. for 4 hours.

- ❖ extremely vague! unimportant?
- ❖ no, there is a secret to it!
- ❖ often only temperature + holding time given

E.J. Hollstein, J.T. Wei, C.-Y. Hsu, US Patent 4,918,041

Calcination Procedure: Temperature Program



- heating rate, holding time, cooling rate
- cooling usually uncontrolled below certain T, slower

Actual Temperature Program

- oven may not be able to perform selected program (lack in power): temperature lag of actual temperature behind set temperature
- poorly tuned controller may give temperature oscillations
- heat needs to be transferred from oven to sample, needs a gradient: temperature lag of sample temperature vs. oven temperature

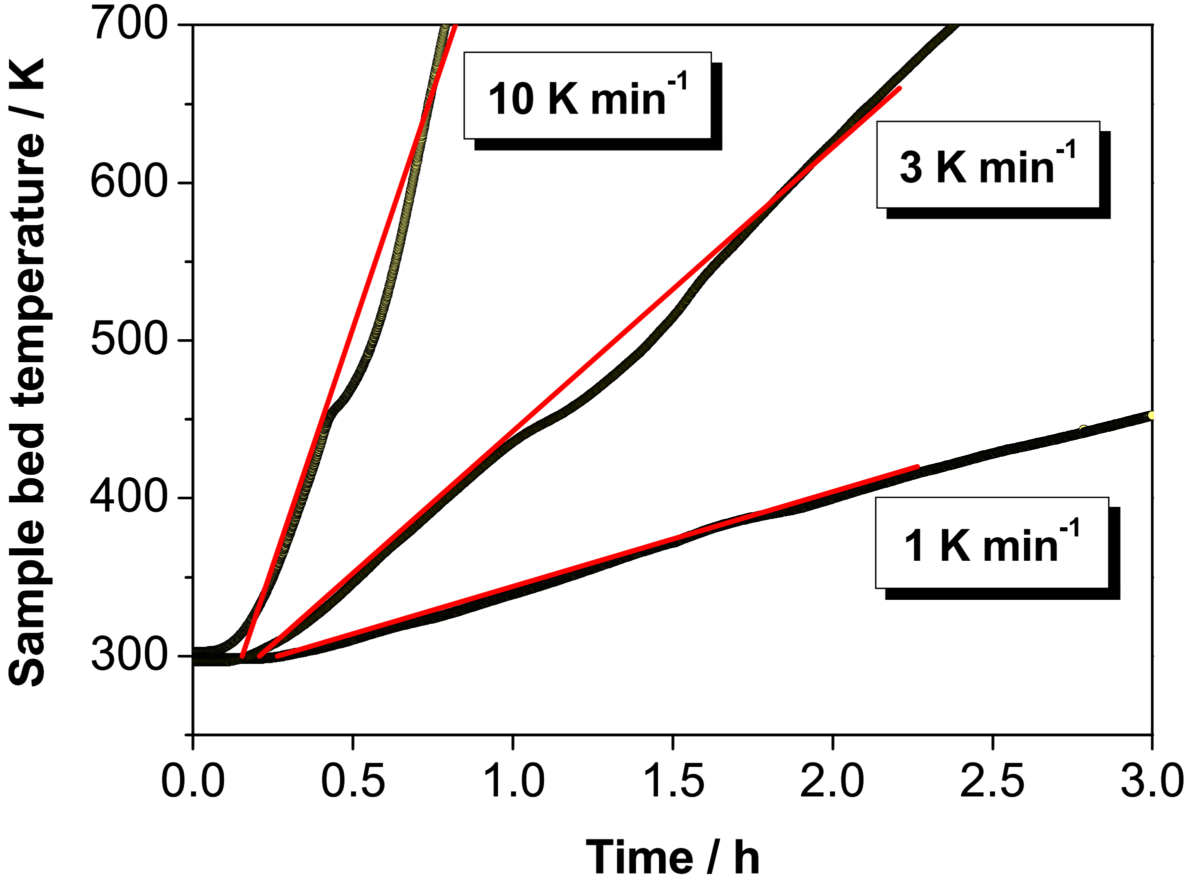
Role of Sample

- strongly endo- or exothermic events may interfere with the heating program
- endothermic events: solvent evaporation
- exothermic events: combustion of organics, crystallization

Evaporation of Water: Thermal Effects

- example: a 10 g sample containing 18 % water (0.1 mol)
- $\Delta H_{evap}(H_2O, 373\ K) = 41\ kJ\ mol^{-1}$
- to evaporate in 1 minute: ≈ 70 Watt

Example: Calcination of Zirconium Hydroxide



- ❖ with a 10 g sample, deviations can occur already at moderate heating rates

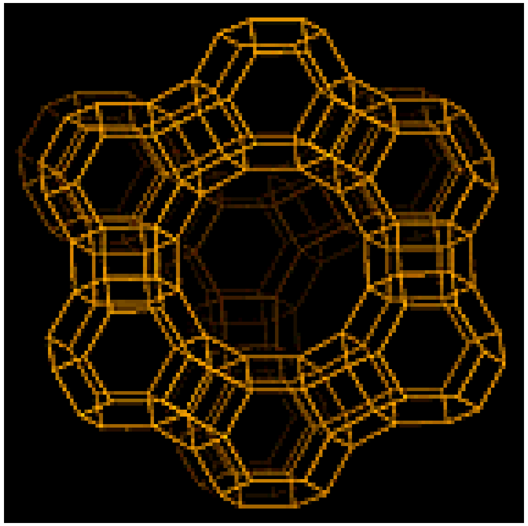
Evaporation of Water: Gas Formation

- example: a 10 g sample containing 18 % water (0.1 mol)
- at 400 K: corresponds to ≈ 3.3 l of water vapor
- depending on the
  - form of the bed
  - the type of furnace (tubular / muffle)
  - static / dynamic atmosphere (no flow / flow)

  the sample will be exposed to vapor for minutes!

Zeolite Y as a Cracking Catalyst

- zeolite Y is used as a cracking catalyst (FCC)

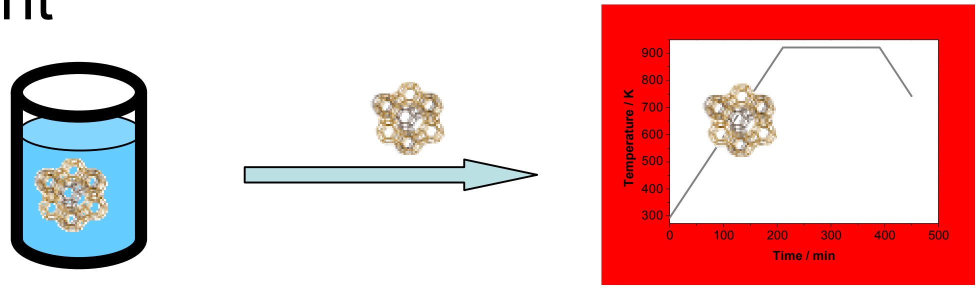


Faujasite structure

- first synthesize NaY, then exchange Na^+ by NH_4^+ (liquid phase)
- obtain active HY through thermal decomposition of NH_4Y
- regular HY not very stable

Ultrastable Y zeolite

- McDaniel and Maher 1967 report „new ultra-stable form of faujasite“
- worked with 100 g of zeolite, first exchange then heat treatment



- „keeping the elapsed time between the exchange step and the heating step at 815°C to a minimum is quite critical“

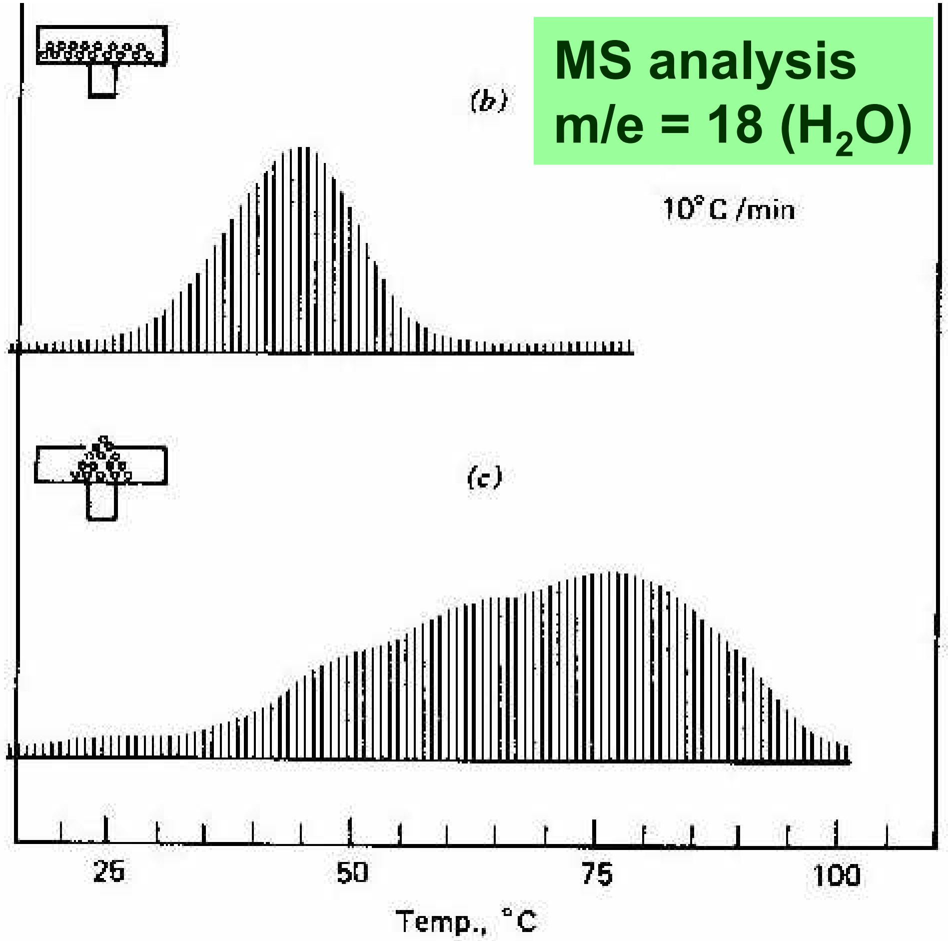
*C.V. McDaniel, P.K. Maher in Molecular Sieves, Soc. Chem. Ind. London, **1968**, p. 186*

Ultrastable Y Zeolite

- Kerr 1967: treatment of HY at 700-800°C in inert static atmosphere
- „any technique keeping this water in the system during the heating process will result in a stable product“
- published comparison of heating in „deep bed“ or „shallow bed“: deep bed produces stable product
- ascribes success of McDaniel & Maher to the large amount that they used

G.T. Kerr, J. Phys. Chem. 1967, 71, 4155 and J. Catal. 1969, 15, 200.

Influence of Packing



MS analysis
m/e = 18 (H_2O)

Figure II.13. Effect of sample packing and sample-holder geometry on the evolution of water from $CaC_2O_4 \cdot H_2O$ (43).

- Packing of a solid influences evolution of gas (water vapor)

Evaporation – Autogeneous Pressure

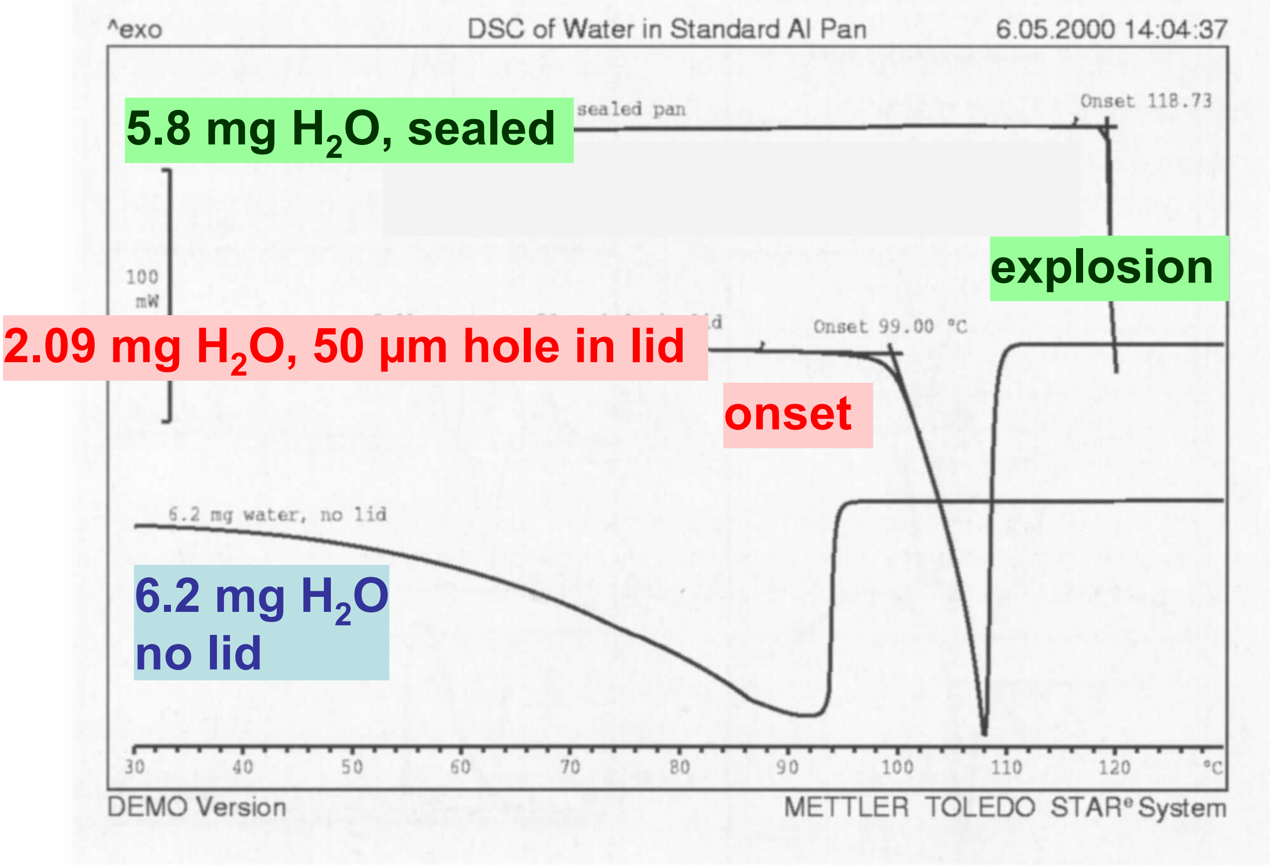


Abbildung 3: Unten: im offenen Tiegel verdunstet Wasser, bevor der Siedepunkt erreicht wird. Mitte: in selbstgenerierter Atmosphäre (50 µm Loch im Deckel) kann der Siedepunkt als Onset gemessen werden. Oben: im hermetisch verschlossenen Tiegel (bei konstantem Volumen) gibt es keinen Siedepunkt. Die DSC-Kurve verläuft geradlinig bis zur Explosion des Al-Tiegels bei ca. 119 °C. Bei starker Vergrösserung zeigt diese Kurve allerdings einen exothermen Peak (Ausschnitt), der durch Korrosion von Aluminium verursacht wird.

- boiling point of water is determined properly only in crucible with lid + hole in lid!

Stabilization Through Dealumination

- water vapor removes aluminum from zeolite framework (extra-framework aluminum)
- leads to stabilization
- today, ultrastable Y or USY is obtained through „steaming“, treatment of NH_4-Y 600-800°C in rotary kilns
- USY is used in „fluid catalytic cracking“ and „hydrocracking“ and „hydroprocessing“
- „steaming“ is a general method for dealumination of zeolites

Exothermic Reactions: Combustion

- organic matter may be present, e.g. from sol-gel process, surfactant-assisted synthesis
- will combust upon thermal treatment in oxygen-containing environment
- look at thermochemical data

  CRC Handbook of Thermophysical and Thermochemical Data
  Eds. David R. Lide, Henry V. Kehiaian, CRC Press Boca Raton New York
  1994 FHI library 50 E 55
  D'Ans Lax, Taschenbuch für Chemiker und Physiker
  Ed. C. Synowietz, Springer Verlag 1983, FHI library 50 E 54

Example: Pentane Combustion

C_5H_{12} (g) + 8 O_2 (g) → 5 CO_2 (g) + 6 H_2O (g)

$$\Delta_r H^{\Theta} = \sum_{i=1}^{L} \mathrm{n}_i \, \Delta_f H_i{}^{\circ}$$

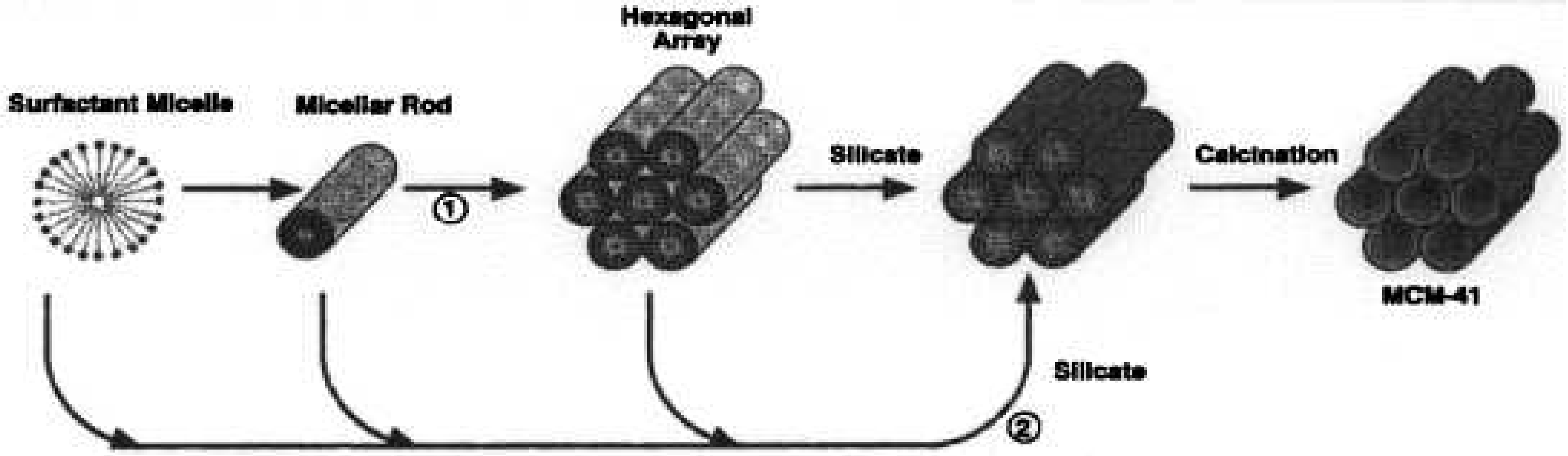
$$\Delta_r H^{\Theta} = 5\,\Delta_f H^{\circ}{}_{CO_2} + 6\,\Delta_f H^{\circ}{}_{H_2O} - 1\,\Delta_f H^{\circ}{}_{C_5H_{12}}$$

$$\Delta_r H^{\Theta} = 5\,(-393.51\,kJmol^{-1}) + 6\,(-241.82\,kJmol^{-1}) - 1\,(-146.44\,kJmol^{-1})$$

$$\Delta_r H^{\Theta} = 3272.0\,kJmol^{-1}$$

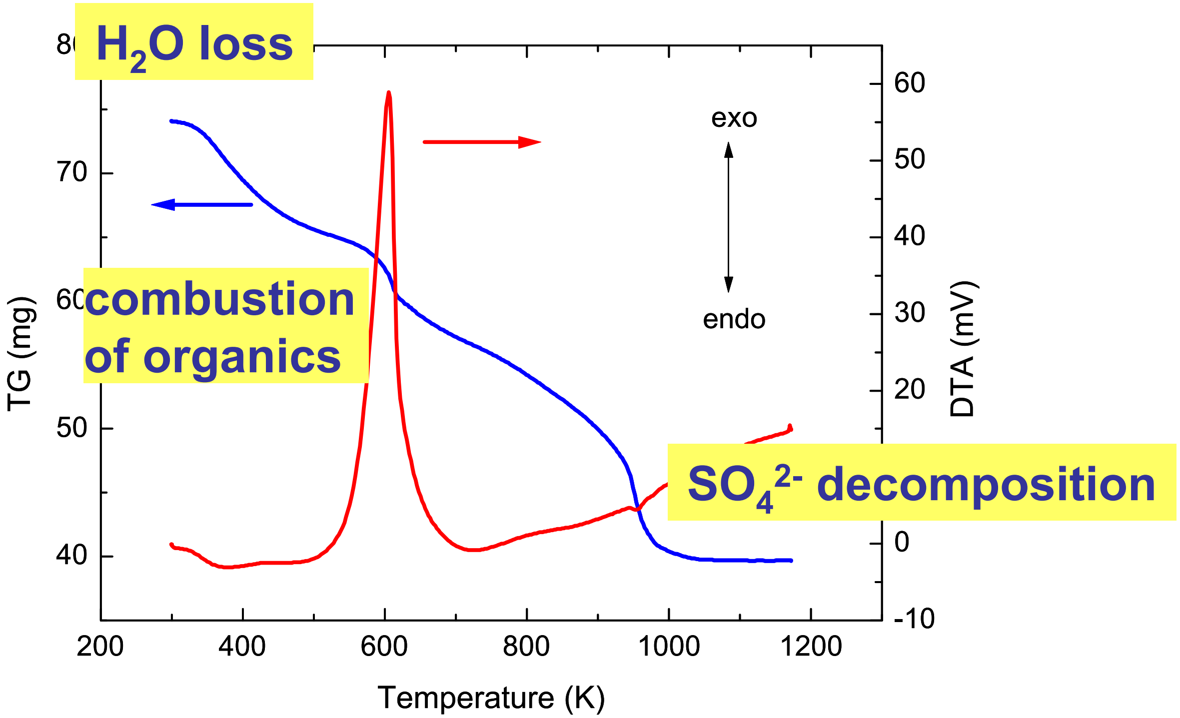
- combustion is strongly exothermic!
- oxygenates have higher enthalpies of formation, i.e. enthalpy of combustion becomes smaller

Example: Surfactant-Assisted Synthesis Mesoporous Zirconia



- surfactants (hexadecyl-trimethyl-ammonium bromide) form micelles
- inorganic matter forms around micelles

Example: TG/DTA Analysis of ZrO_2-Precursor

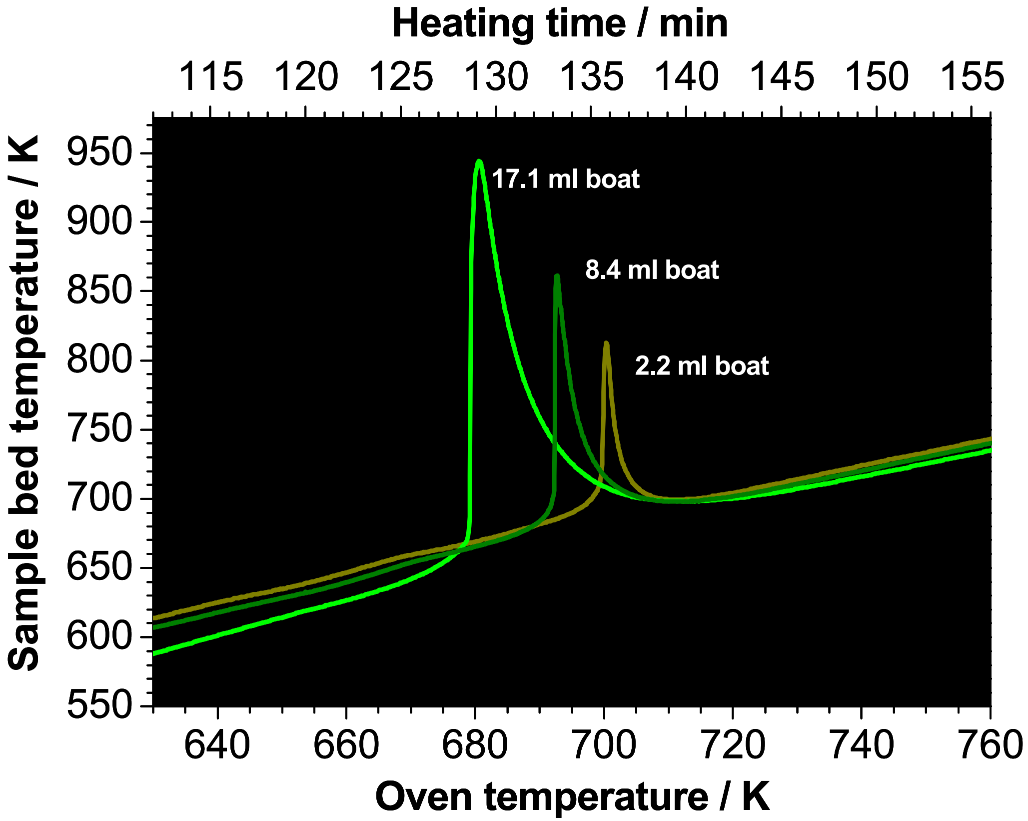


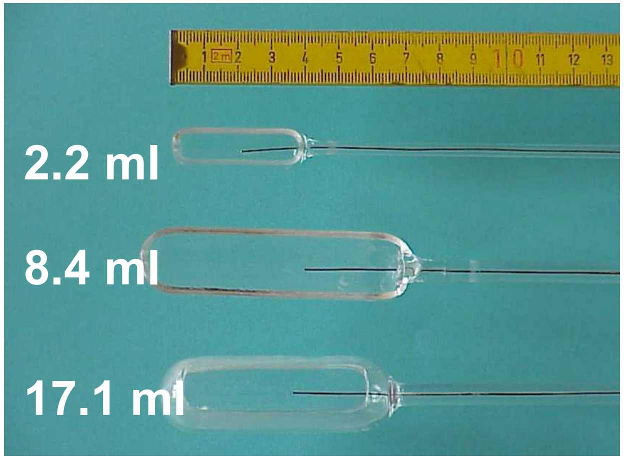
- ❖ ZrO_2/CTAB composite synthesized with $Zr(O\text{-}nPr)_4$ in the presence of sulfate ions at Zr:S:CTAB = 2:2:1, measured with 10 K/min in an air stream

Other Exothermic Reactions

- Example: calcination of X-ray amorphous zirconium hydroxide
- "ZrO_2 * 2.5 H_2O"

Heating of Zirconium Hydroxide





- strong influence of batch size / heat transfer
- rapid overheating (up to 40-50 K/s)
- overshoot of up to 300 K

History of Glow

- Overheating is so violent, it is accompanied by emission of visible light ("glow")

  Berzelius 1812 (antimonates, antimonites)

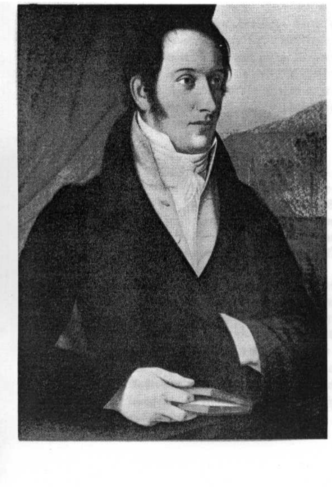
The Glow Phenomenon

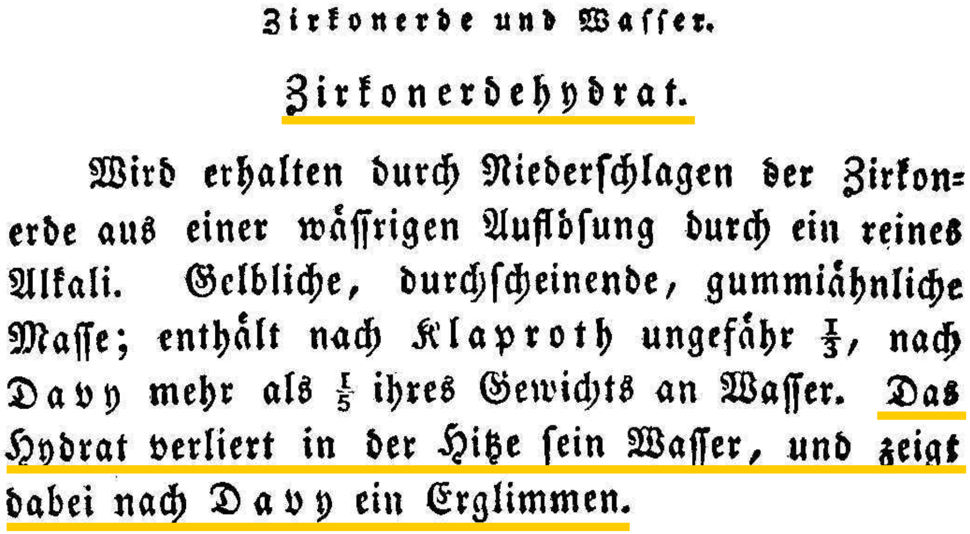
Handbuch
der
theoretiſchen Chemie

zum Behuf ſeiner Vorleſungen entworfen
von
Leopold Gmelin
Doctor der Medicin und Chirurgie; außerordentl. Profeſſor
der Chemie auf der Univerſität zu Heidelberg.

Zweiter Band
welcher die Lehre von den unorganiſchen Verbindungen der Metalle enthält.

Frankfurt am Main,
in Commiſſion bei Franz Varrentrapp.
1817.



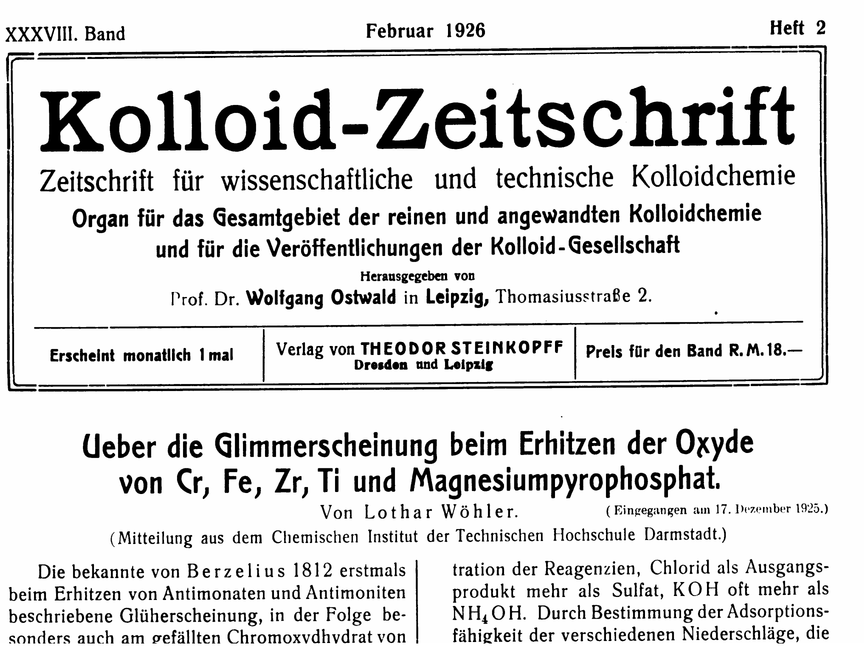


Zirkonerde und Waſſer.

Zirkonerdehydrat.

Wird erhalten durch Niederſchlagen der Zirkonerde aus einer wäſſrigen Auflöſung durch ein reines Alkali. Gelbliche, durchſcheinende, gummiähnliche Maſſe; enthält nach Klaproth ungefähr $\frac{1}{3}$, nach Davy mehr als $\frac{1}{5}$ ihres Gewichts an Waſſer. Das Hydrat verliert in der Hitze ſein Waſſer, und zeigt dabei nach Davy ein Erglimmen.

Oxides Showing a Glow



XXXVIII. Band Februar 1926 Heft 2

Kolloid-Zeitschrift

Zeitschrift für wissenschaftliche und technische Kolloidchemie

Organ für das Gesamtgebiet der reinen und angewandten Kolloidchemie und für die Veröffentlichungen der Kolloid-Gesellschaft

Herausgegeben von

Prof. Dr. **Wolfgang Ostwald** in **Leipzig,** Thomasiusstraße 2.

Erscheint monatlich 1 mal | Verlag von **THEODOR STEINKOPFF** Dresden und Leipzig | **Preis für den Band R. M. 18.—**

Ueber die Glimmerscheinung beim Erhitzen der Oxyde von Cr, Fe, Zr, Ti und Magnesiumpyrophosphat.

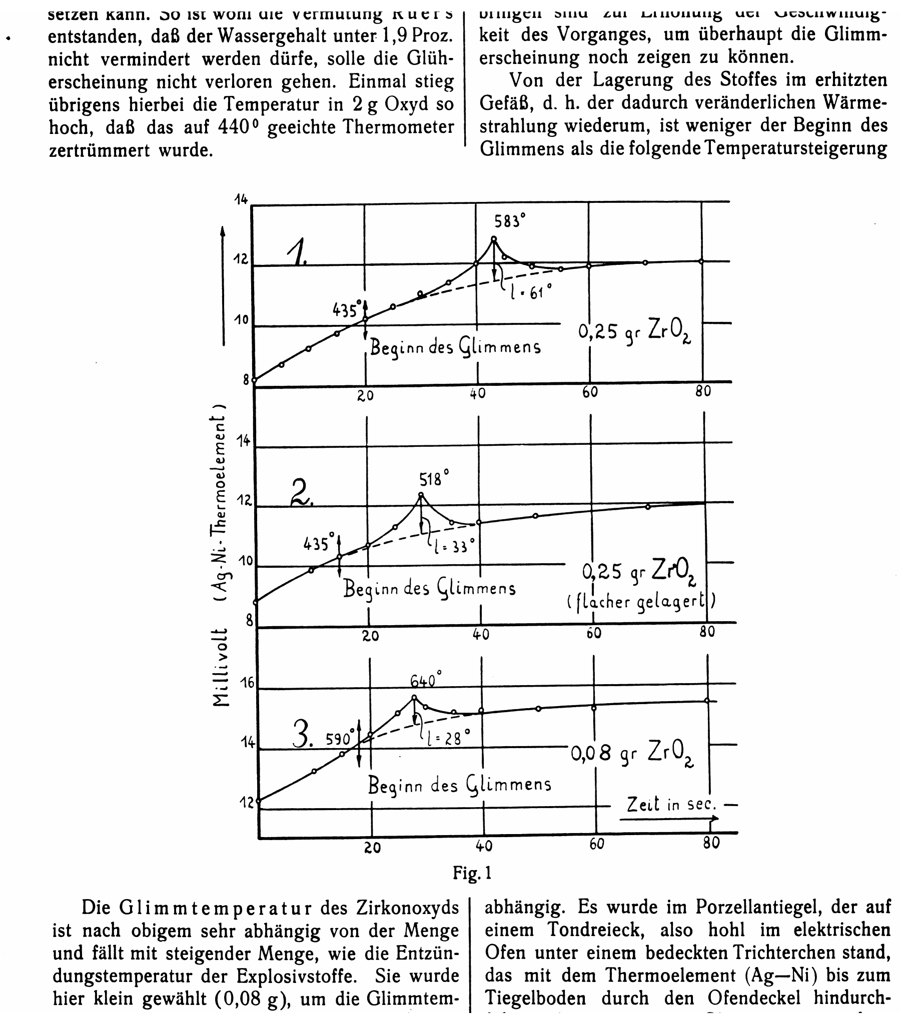
Von Lothar Wöhler.

(Eingegangen am 17. Dezember 1925.)

(Mitteilung aus dem Chemischen Institut der Technischen Hochschule Darmstadt.)

Die bekannte von Berzelius 1812 erstmals beim Erhitzen von Antimonaten und Antimoniten beschriebene Glüherscheinung, in der Folge besonders auch am gefällten Chromoxydhydrat von

tration der Reagenzien, Chlorid als Ausgangsprodukt mehr als Sulfat, KOH oft mehr als NH_4OH. Durch Bestimmung der Adsorptionsfähigkeit der verschiedenen Niederschläge, die



setzen kann. So ist wohl die Vermutung Ruers entstanden, daß der Wassergehalt unter 1,9 Proz. nicht vermindert werden dürfe, solle die Glüherscheinung nicht verloren gehen. Einmal stieg übrigens hierbei die Temperatur in 2 g Oxyd so hoch, daß das auf 440° geeichte Thermometer zertrümmert wurde.

bringen sind zur Erhöhung der Geschwindigkeit des Vorganges, um überhaupt die Glimmerscheinung noch zeigen zu können.

Von der Lagerung des Stoffes im erhitzten Gefäß, d. h. der dadurch veränderlichen Wärmestrahlung wiederum, ist weniger der Beginn des Glimmens als die folgende Temperatursteigerung

Fig. 1

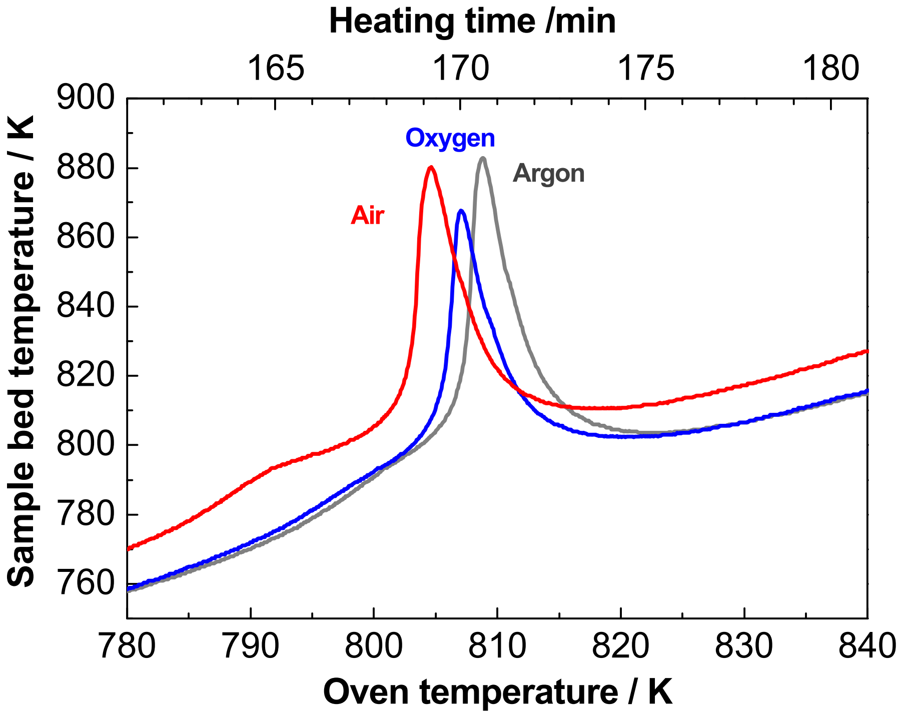
Die Glimmtemperatur des Zirkonoxyds ist nach obigem sehr abhängig von der Menge und fällt mit steigender Menge, wie die Entzündungstemperatur der Explosivstoffe. Sie wurde hier klein gewählt (0,08 g), um die Glimmtem-

abhängig. Es wurde im Porzellantiegel, der auf einem Tondreieck, also hohl im elektrischen Ofen unter einem bedeckten Trichterchen stand, das mit dem Thermoelement (Ag—Ni) bis zum Tiegelboden durch den Ofendeckel hindurch-

Origin of Glow

- combustion of organic contaminants
- heat of crystallization
- loss of surface energy through sintering

Effect of Combustion?



- ❖ atmosphere little influence on overheating effect
- ❖ heat not caused by combustion of organic contaminants

Origin of Glow

- ~~combustion of organic contaminants~~
- heat of crystallization
- loss of surface energy through formation of larger particles

Heat of Crystallization of ZrO_2 (kJ mol^{-1})

?-ZrO_2	–28.7	Keshavaraja
any ZrO_2	–23.2	Srinivas[illegible]n
t- or m-ZrO_2	–4.3 to –22.5	[illegible]
t- or m-ZrO_2	–12.9	[illegible]
t-ZrO_2	–29.3 to –3[illegible]	[illegible]
t-ZrO_2	–19.6	Mercera
t-ZrO_2	[illegible]	Haberko
t-ZrO_2	[illegible]	Molodetsky
t-ZrO_2	[illegible]	Xie
m-ZrO_2	–58.6 ± 3.3	Molodetsky

C[illegible]e energy upon a-ZrO_2 → t-ZrO_2
(a[illegible]d A_{BET} = 100 $m^2 \bullet g^{-1}$): +14.6 Molodetsky

Transition t-ZrO_2 to m-ZrO_2:	–5	Molodetsky
	–6	Xie
	–6	Coughlin

heat of crystallization of t-ZrO_2:
according to literature between -4.3 and -53.6 kJ mol^{-1}

Estimation of Temperature Rise through Crystallization

- assume a medium heat of 25 kJ mol^{-1}
- process assumed quasi-adiabatic ($\delta Q = 0$)
- molar heat of precursor / intermediate assumed similar to that of ZrO_2: 82.3 J mol^{-1} K^{-1}

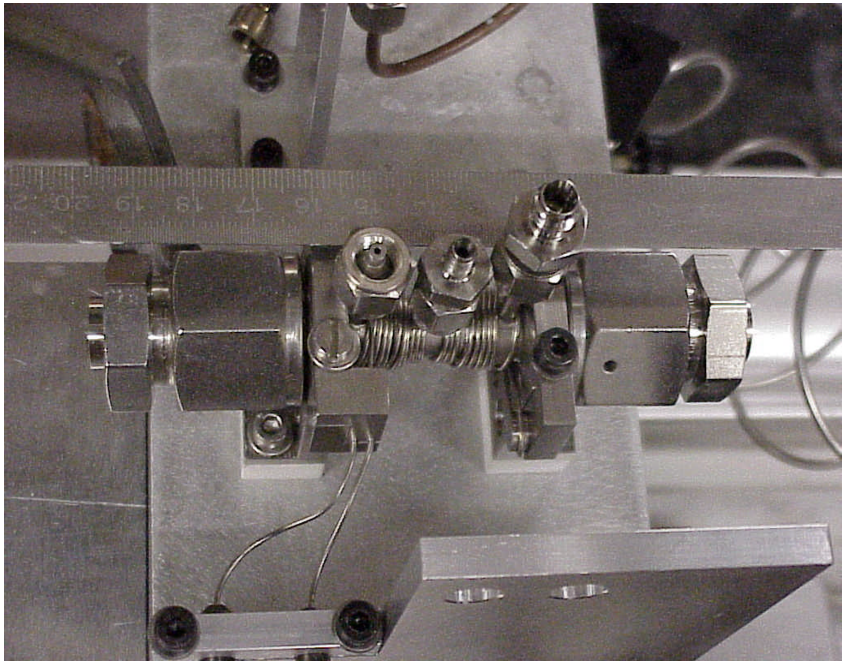
$$\Delta T = \frac{\Delta H}{c_p} \approx 300\ K$$

- corresponds approximately to observation

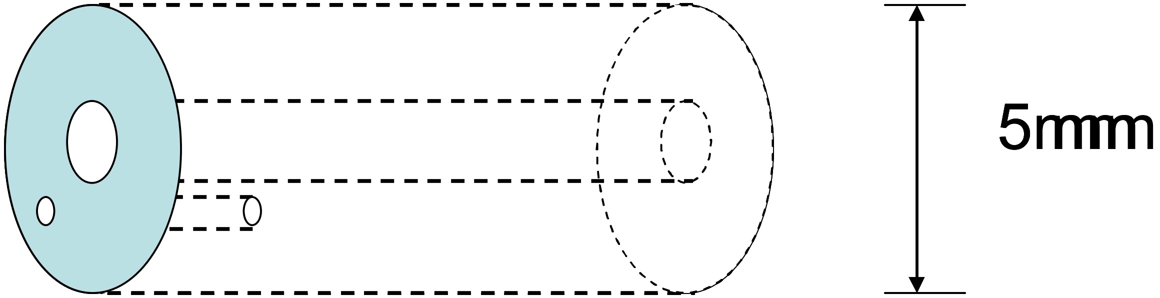
Does Crystallization Happen During Glow?

- use method that allows structure-determination and good time resolution
- X-ray absorption spectroscopy at Zr K edge at ESRF (1 spectrum per s; 10 K min^{-1} heating rate)
- allows observation of local environment around Zr^{4+} ions

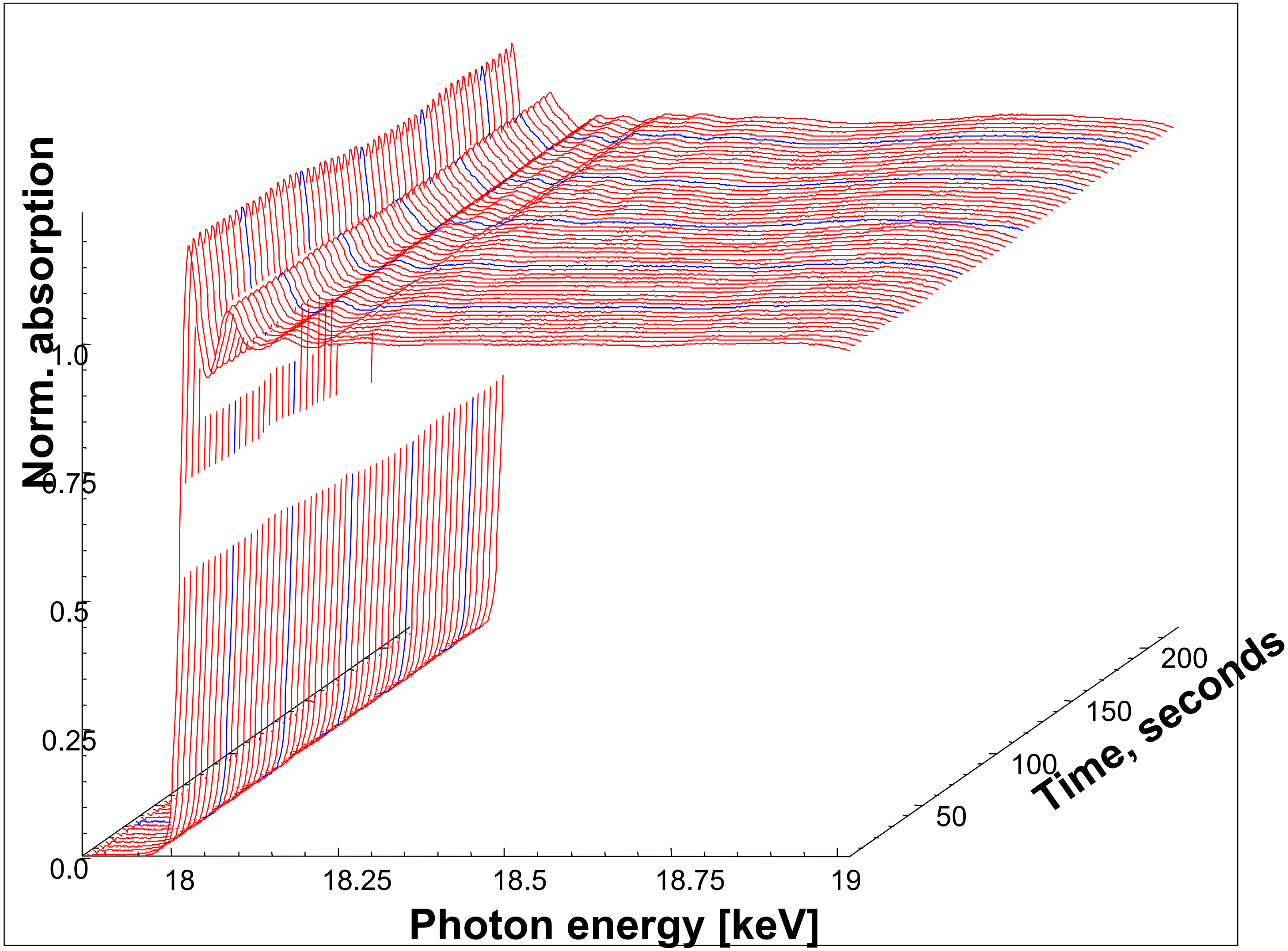
In situ X-ray Absorption Spectroscopy



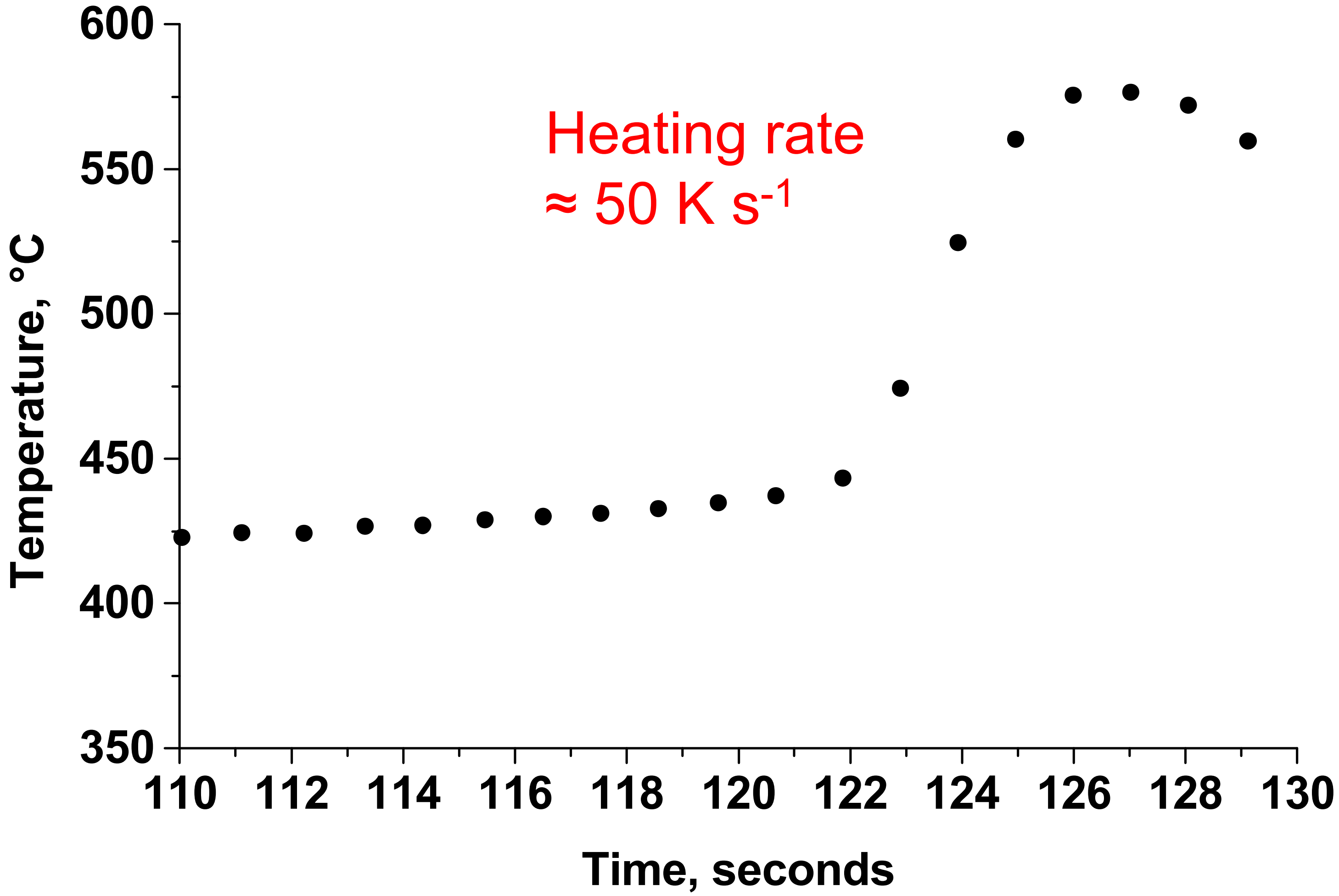
- use large pellet to create a sufficiently large glow effect
- put small pellet inside that is transparent for X-rays



XAS Spectra

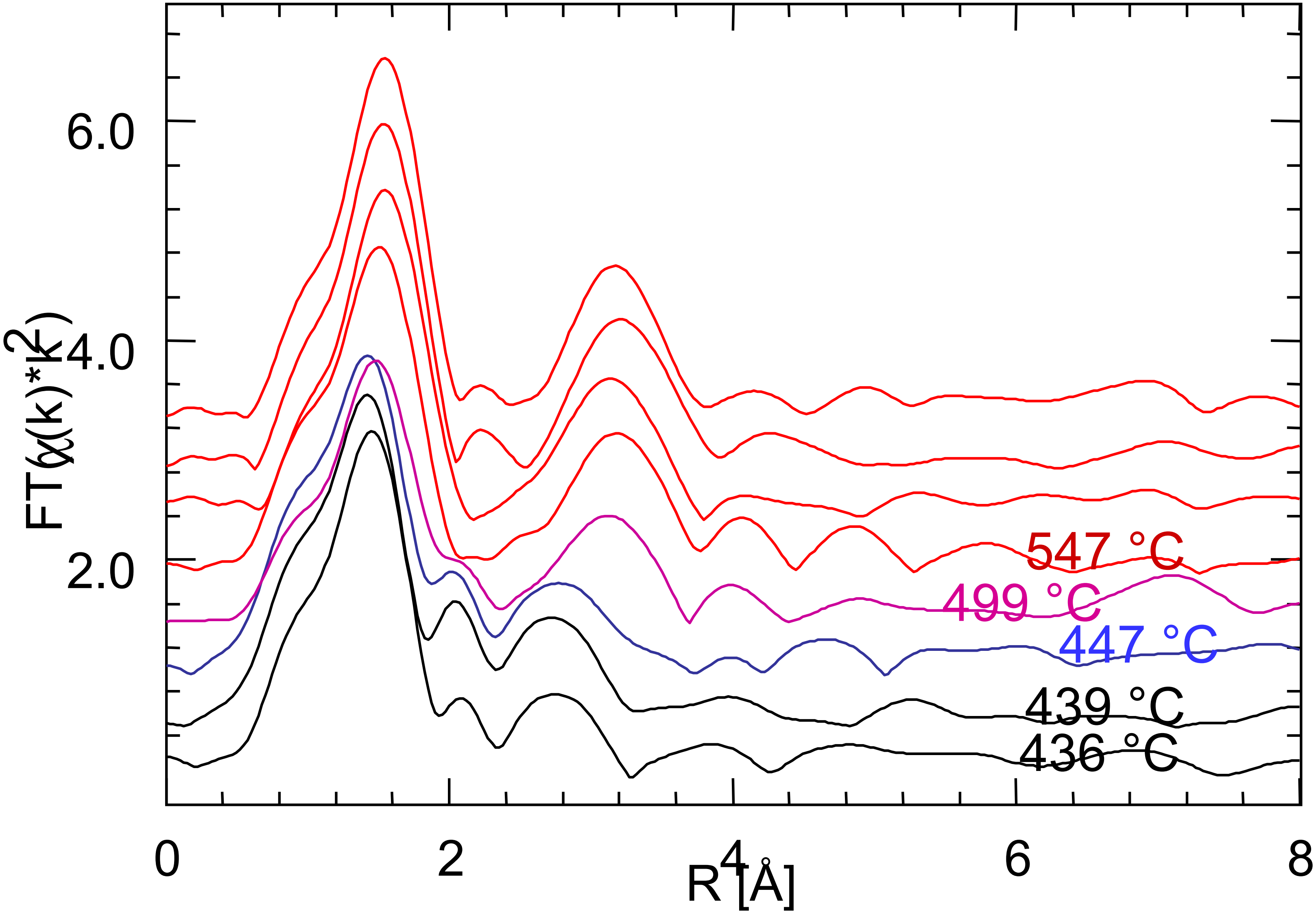

Norm. absorption
0.0
0.25
0.5
0.75
1.0
18
18.25
18.5
18.75
19
Photon energy [keV]
50
100
150
200
Time, seconds
]

Sample Temperature vs. Time



Heating rate
≈ 50 K s^{-1}

Structural Evolution



Origin of Glow

- ~~combustion of organic contaminants~~
- heat of crystallization - yes!
- loss of surface energy through formation of larger particles

Sintering

- a heat treatment at 2/3 to 3/4 of the melting point to solidify shaped bodies from pressed metal powders, occurs in 3 steps
- 1. increase of particle contacts through "sinter bridges"
  2. formation of a contiguous backbone, original particles lose their identity, shrinkage, formation of new grain boundaries
  3. rounding and elimination of pores, further shrinkage, closed pores

Tammann and Hüttig Temperature

- Tammann temperature

  temperature necessary for lattice (bulk) recrystallization

  for metal oxides $T_{Tammann} \approx 0.52\ T_F$

- Hüttig temperature

  temperature necessary for surface recrystallization

  for metal oxides $T_{Hüttig} \approx 0.26\ T_F$

with T_F the absolute melting temperature

Influence of Particle Size

- decomposition of $Al(OH)_3$, thermogravimetric analysis
- smaller particles react at lower temperature

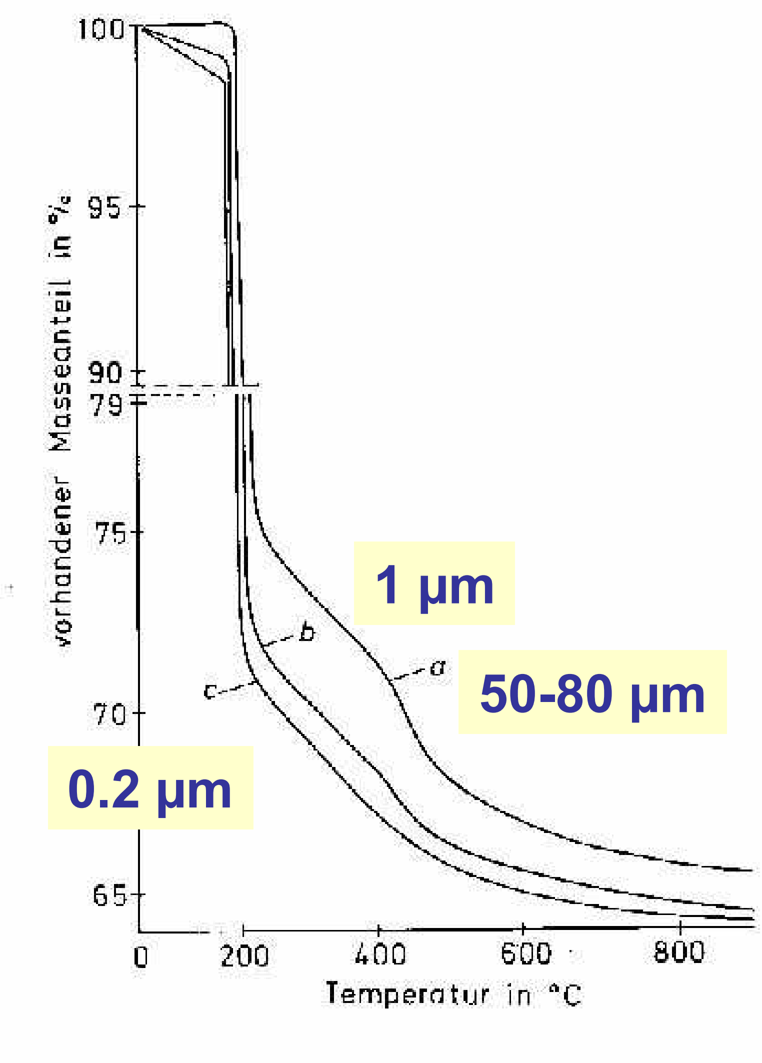


Abb. 4.19. Einfluß der Korngröße auf den Zersetzungsverlauf von $Al(OH)_3$: Druck 0,133 kPa, Zersetzungsgeschwindigkeit 11,5 mg · h^{-1} · g^{-1}. (Nach [7] aus Kap. 3).
Korngrößen: Kurve *a* 50-80µm,
Kurve *b* 1 µm,
Kurve *c* 0,2 µm

Influence of Particle Size on Melting Point of Au

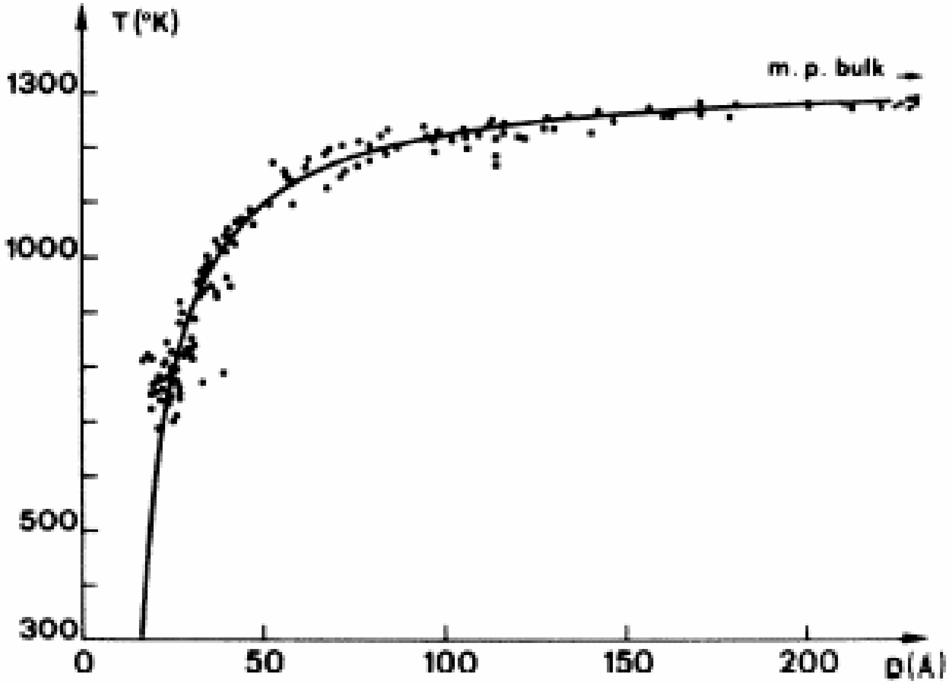
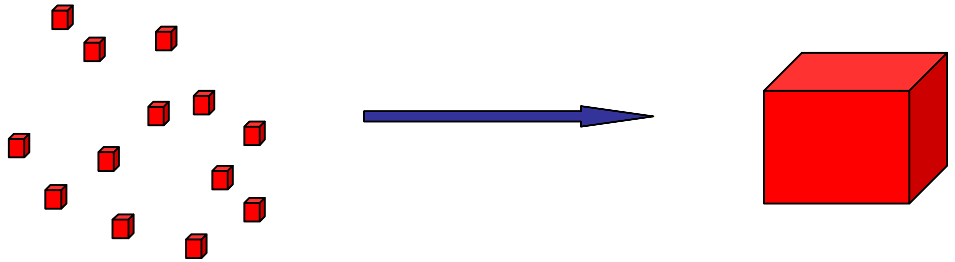


FIG. 5. Experimental and theoretical values of the melting-point temperature of gold particles : circles, present work; squares, Sambles (Ref. 28); the solid line results from a least-squares fit to the second-order relations of the first model, Eq. (13), using all the experimental data of the present work and an estimated value of the Debye-Waller factor.

- ❖ Melting point can decrease drastically with decreasing particle size!

Ph. Buffat, J. P. Borel, Phys. Rev. A 13 (1975) 2287-2298

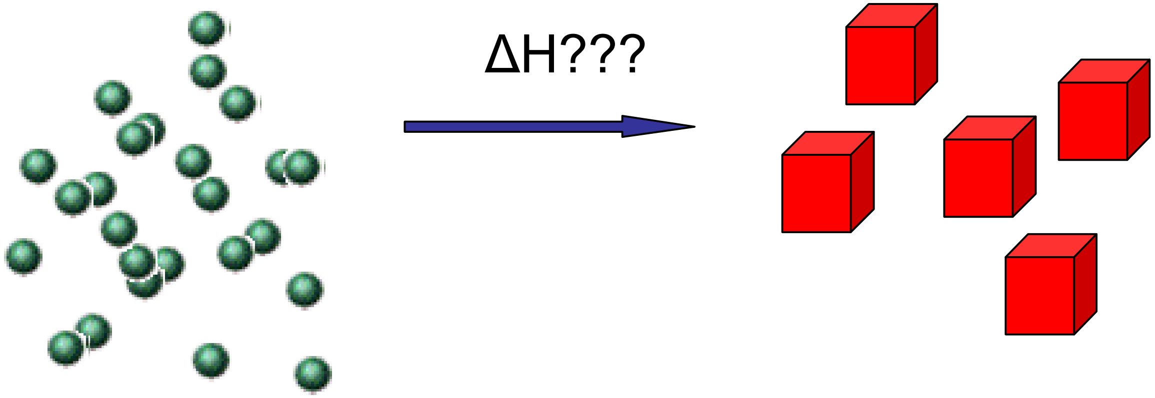
Surface Energy



- loss of surface area through formation of larger crystals

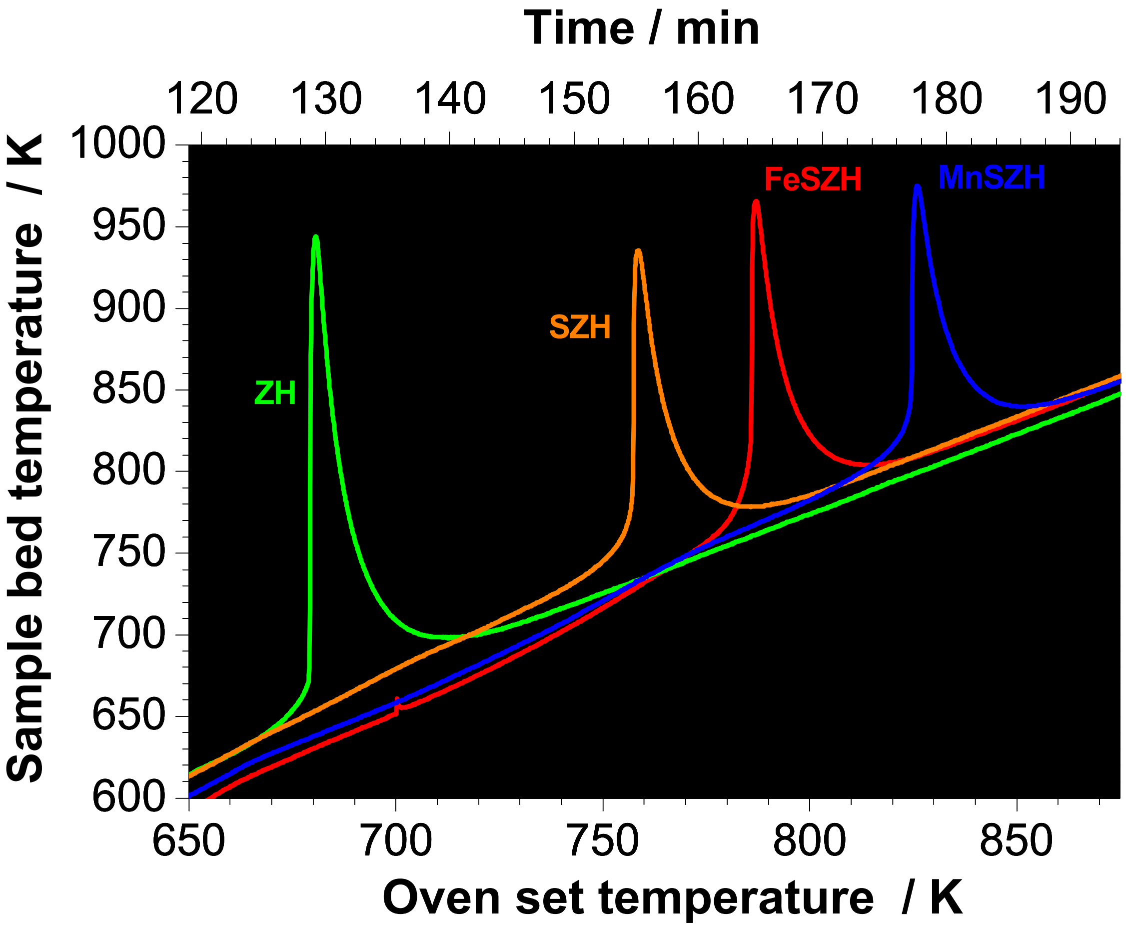
- surface energy of t-ZrO_2(101) ≈ 1.1 J m^{-2}
- surface area shrinks from 250 to 150 m^2 g^{-1} during calcination → **110 J g^{-1}** or **13.5 kJ mol^{-1}** (ZrO_2)
- is not negligible in comparison to crystallization

Formation of a Crystalline Solid from Amorphous Precursor



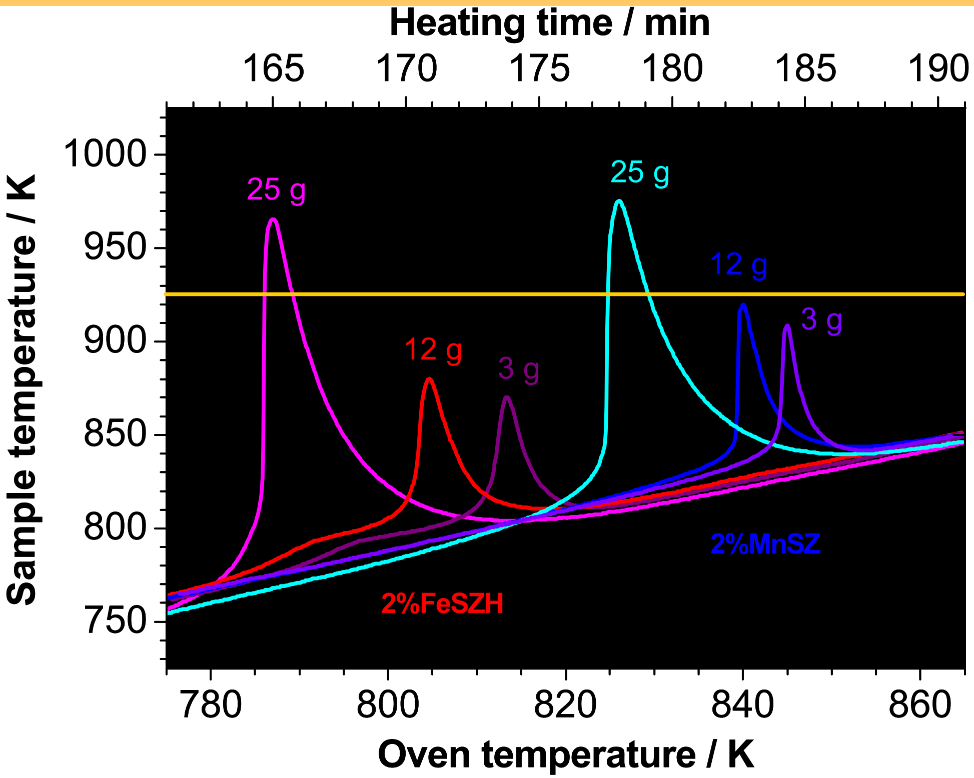
- nature of amorphous precursor usually not well-known
- ΔH depends on nature of precursor & product
- if, through variation of the treatment conditions, for the same precursor different ΔHs are obtained, the products will be different

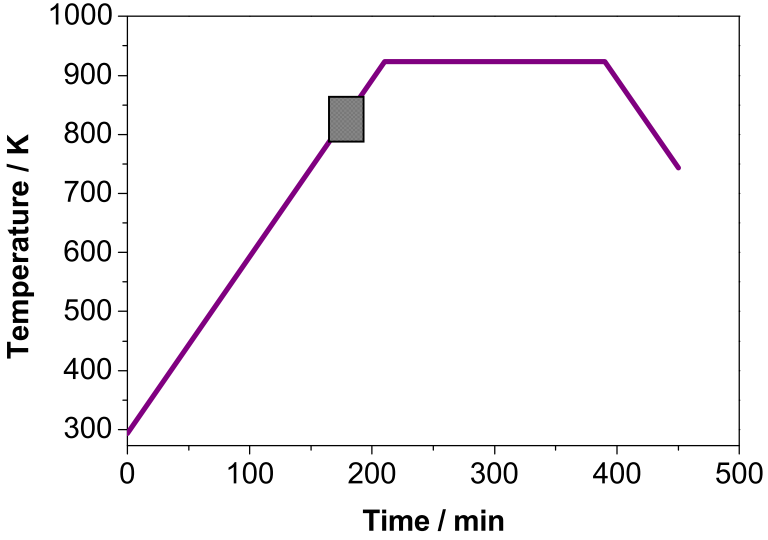
Effect of Additives



- additives shift glow to higher temperatures and reduce overshoot

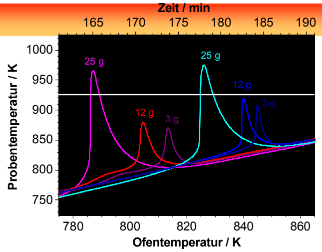
Glow Phenomenon: MnSZ and FeSZ





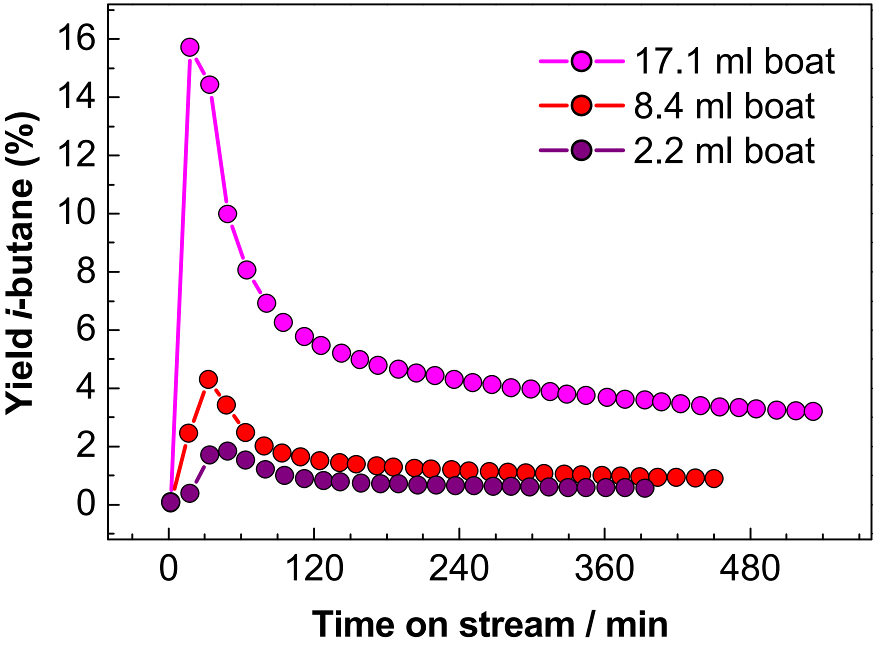
- max. calcination T may be exceeded
- promoters influence calcination chemistry (systemic), Fe and Mn different
- strong batch size dependence

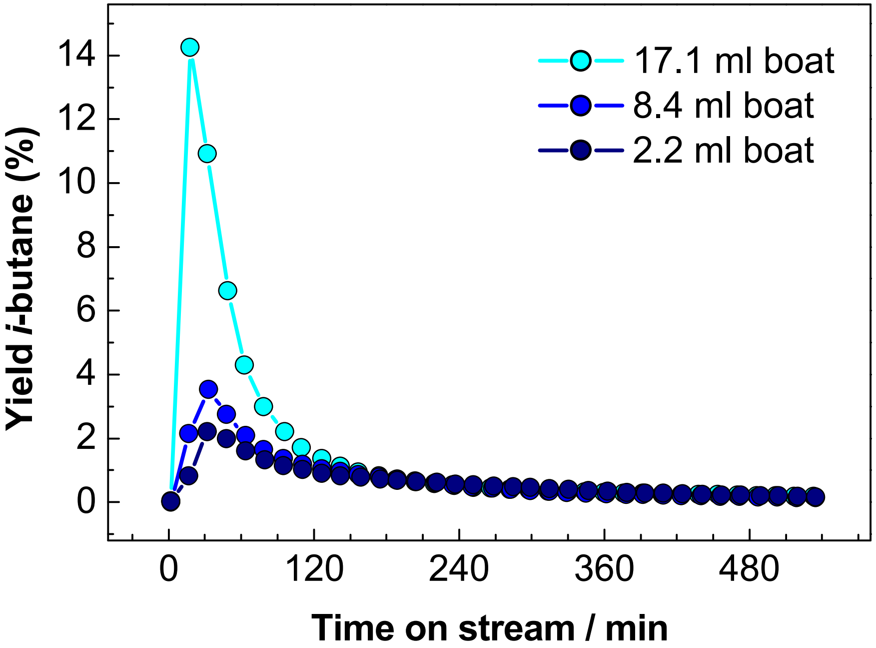
Influence on Catalytic Activity?!



2%FeSZ

2%MnSZ

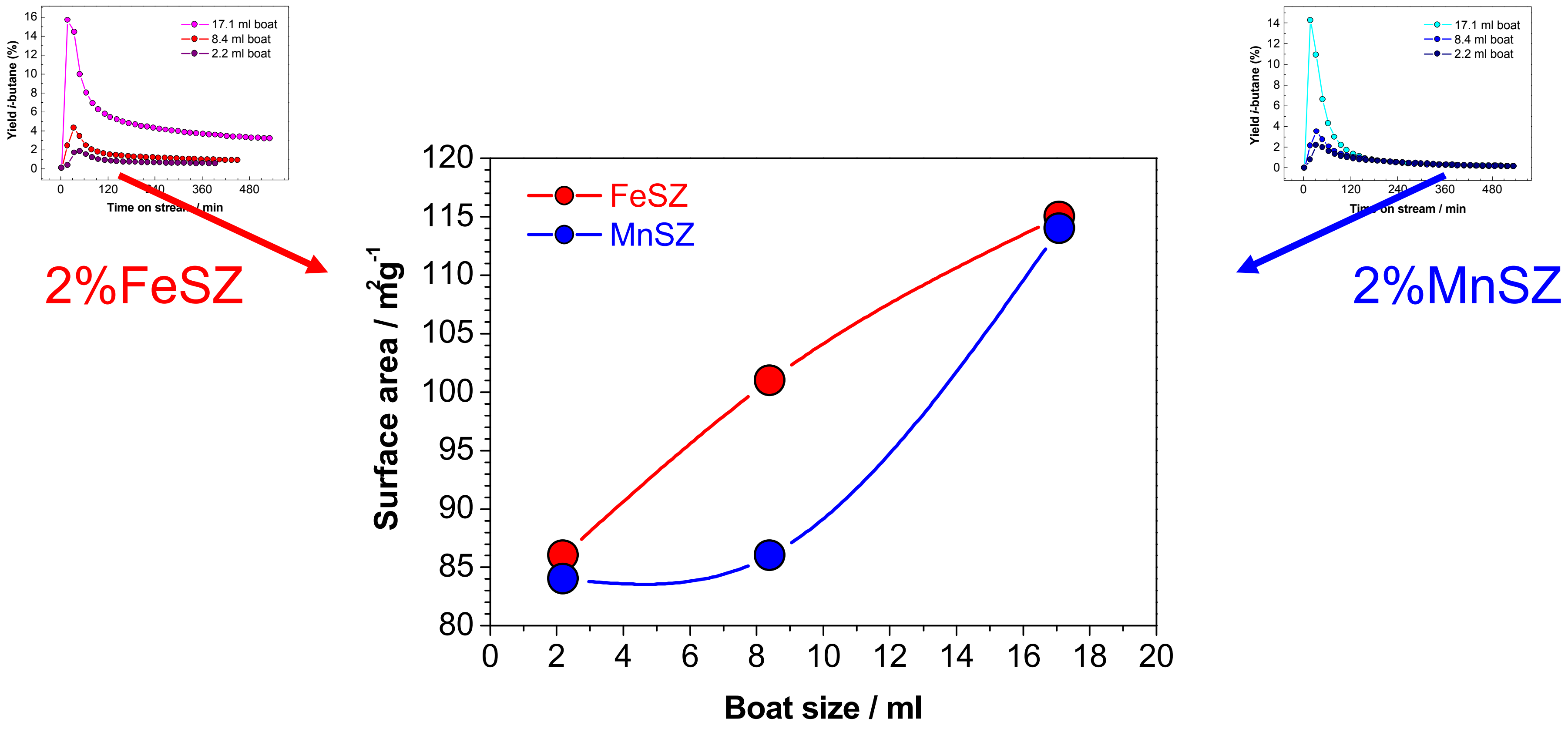




samples calcined in larger batches are more active (1 vol% *n*-butane at 338 K)

→ characterize catalysts

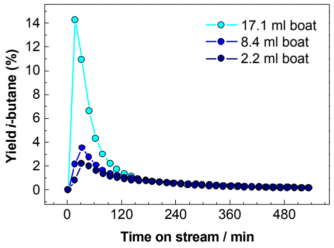
Surface Area & Calcination Batch Size

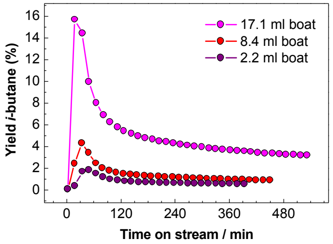


- ❖ surface area increases with calcination batch size
- ❖ differences in activity exceed differences in surface area

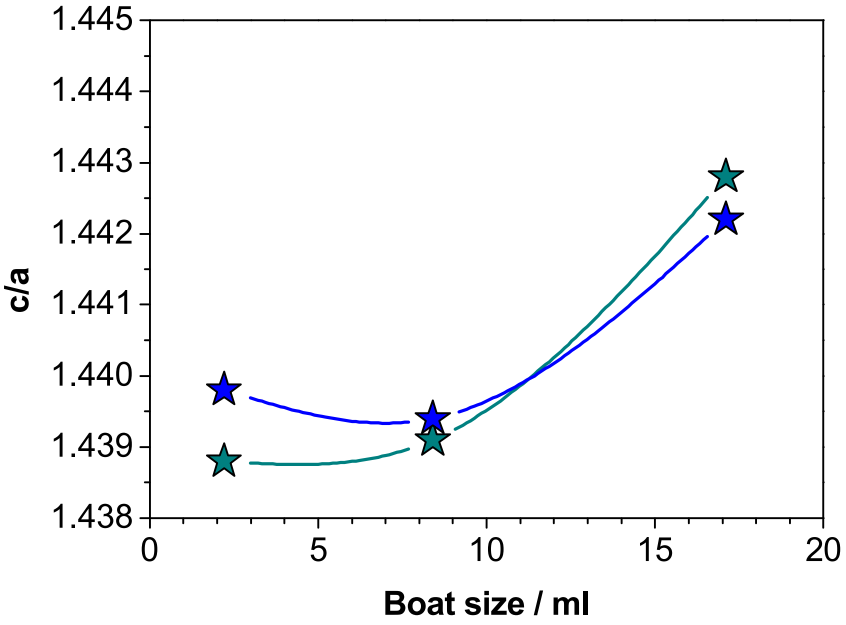
Activity and Bulk Structure

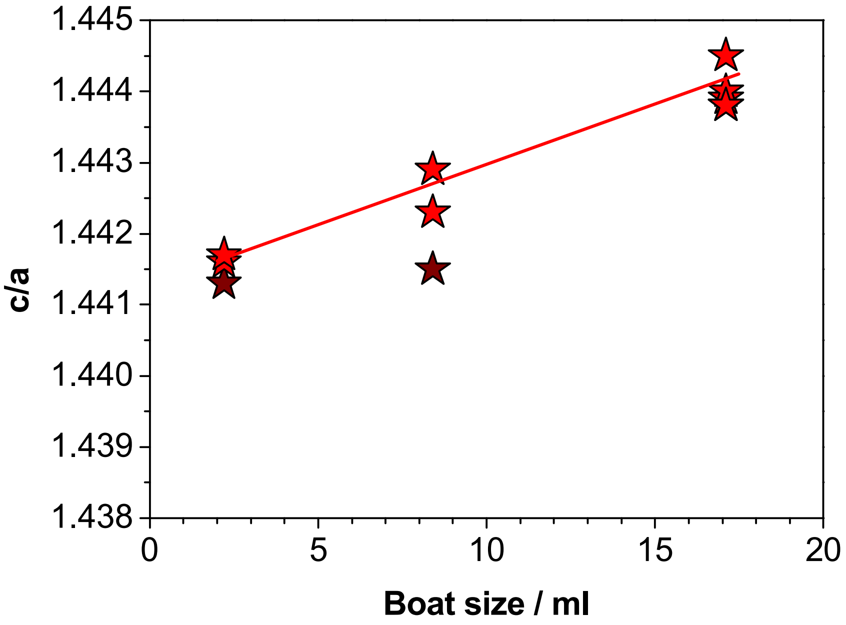
2%MnSZ





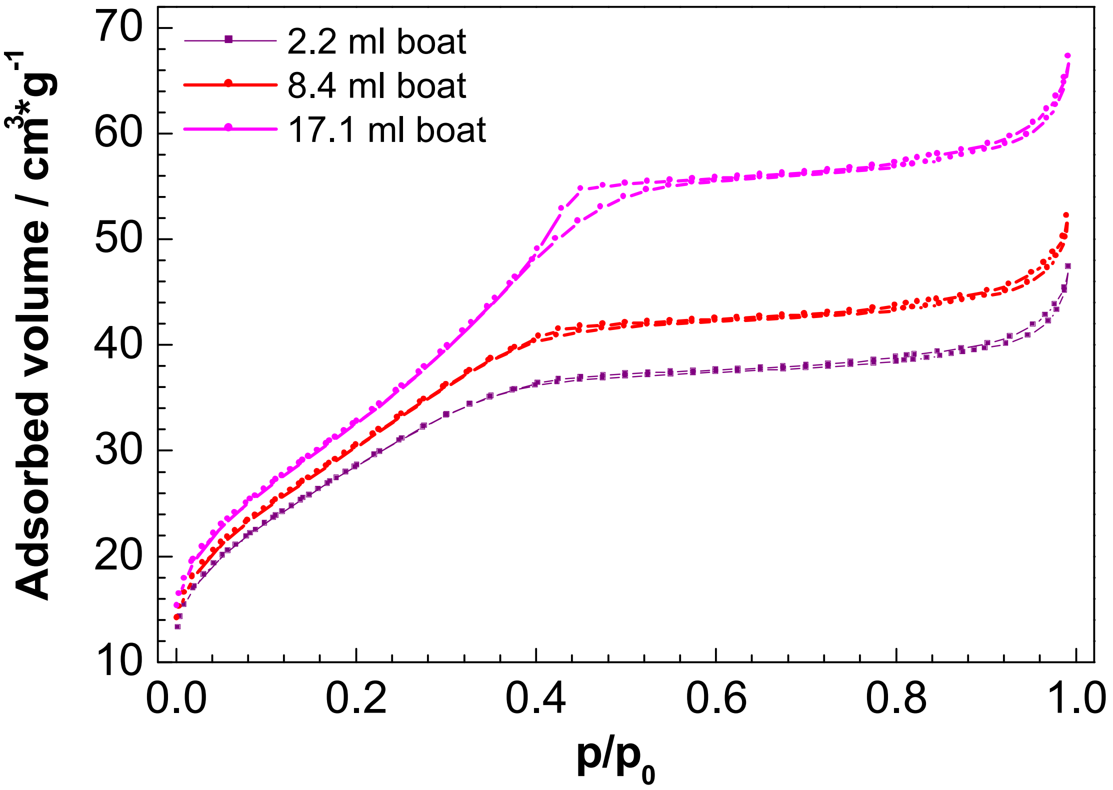
2%FeSZ





❖ lattice parameters of tetragonal ZrO_2 change

Porosity of Iron-Promoted Sulfated Zirconia



- large batch calcination: formation of mesopores, 1-4 nm

Effect of Calcination Batch Size

- samples from the same raw material (precursor) are converted into different products by variation of the batch size during calcination

Why Does Overheating Occur?

- heat is generated faster than transferred away
- look at heat transfer

Heat Transfer Modes

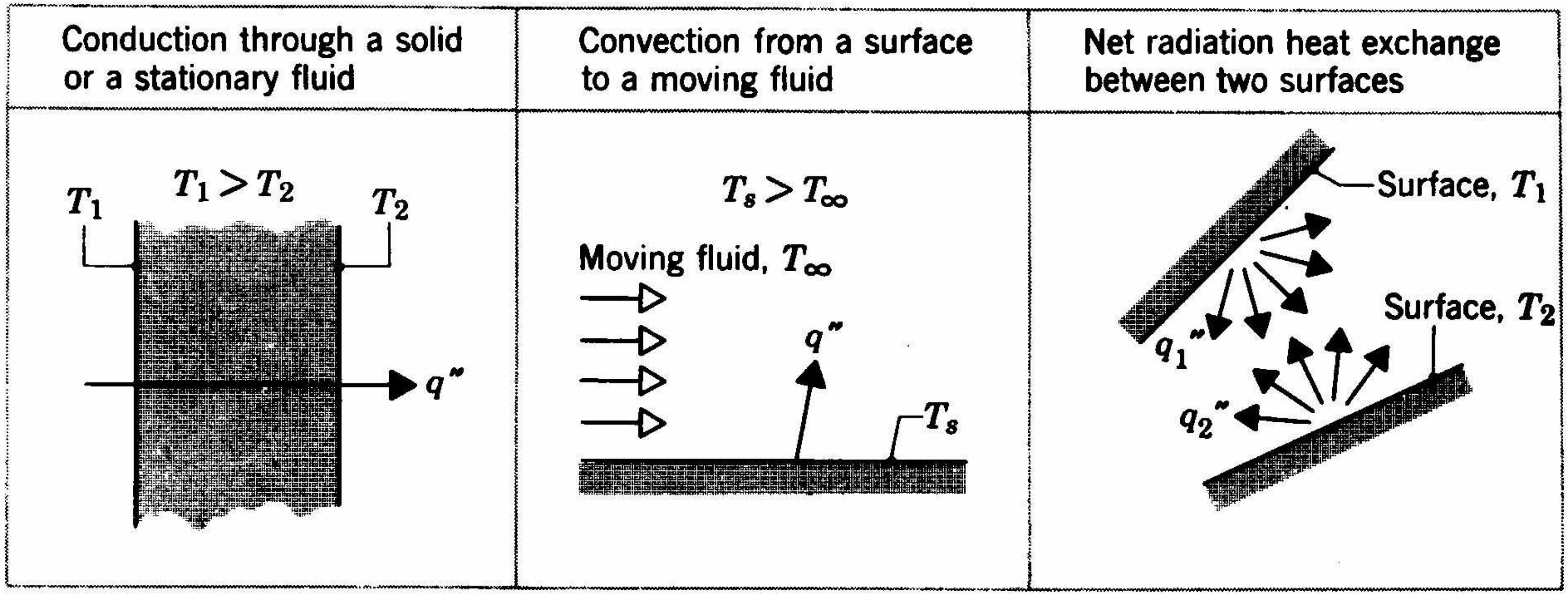


Figure 1.1 Conduction, convection, and radiation heat transfer modes.

- ❖ all of them play role during calcination
- ❖ estimations can be made!

Heat Transfer by Convection

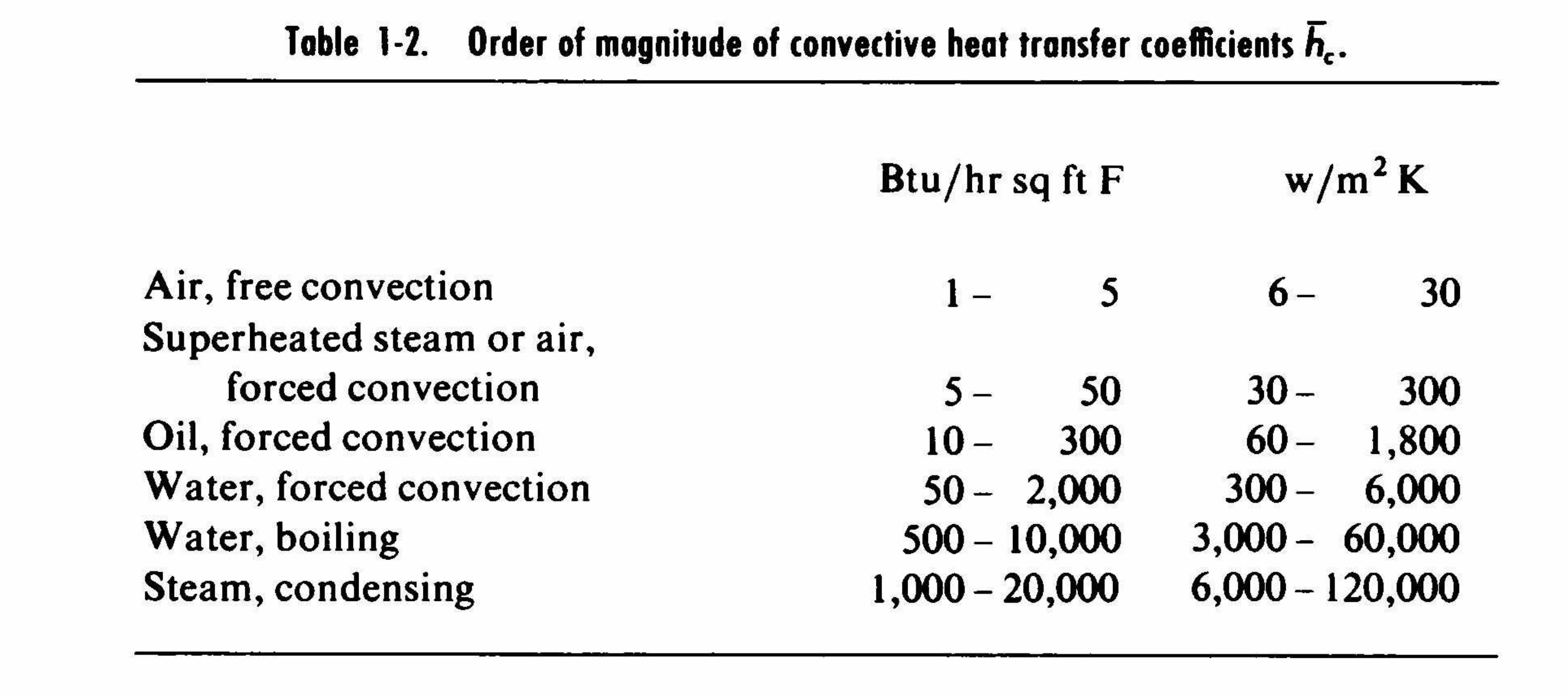
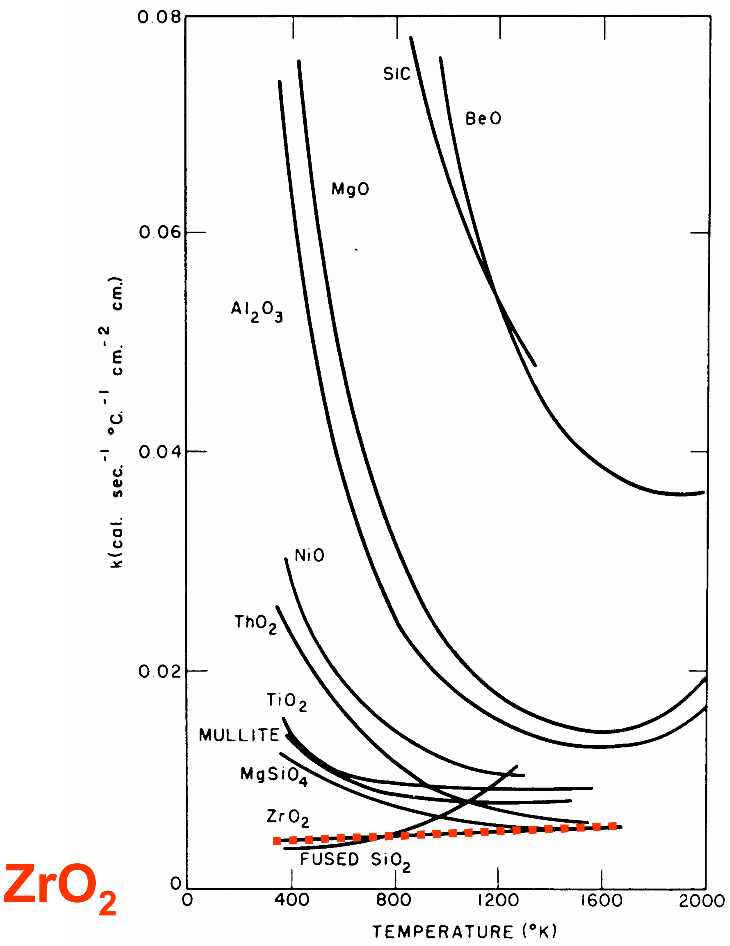


Table 1-2. Order of magnitude of convective heat transfer coefficients $\bar{h}_c$.

	Btu/hr sq ft F	w/m^2 K
Air, free convection	1 – 5	6 – 30
Superheated steam or air, forced convection	5 – 50	30 – 300
Oil, forced convection	10 – 300	60 – 1,800
Water, forced convection	50 – 2,000	300 – 6,000
Water, boiling	500 – 10,000	3,000 – 60,000
Steam, condensing	1,000 – 20,000	6,000 – 120,000

- free vs. forced convection makes a considerable difference

Thermal Conductivity



- data are for solids, conduction worse in loose powders
- exact material during calcination unknown

Kingery 1955

Radiation

- conduction and convection are proportional to difference between the temperatures (T gradient , ΔT) of the body of interest and the surrounding
- radiation is proportional to the difference between the temperatures to the forth power

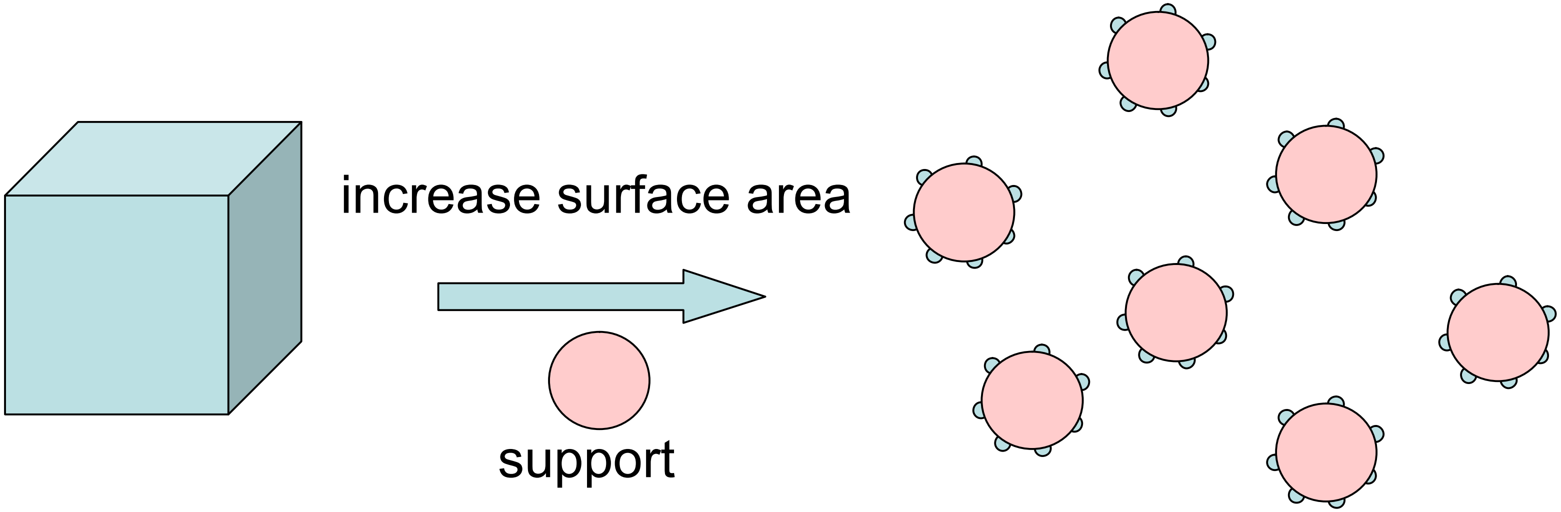
IUPAC Recommendations on Calcination

- all particles of catalyst should be subjected (..) to exactly the same (..) conditions
  only possible in moving beds (fluid beds, rotating furnaces, spray drying)
- supply a sufficient quantity of gas or liquid to the reactor to ensure complete reaction (..); special consideration should be given to mass and heat transfer

J. Haber, J.H. Block, B. Delmon, Pure & Appl. Chem. 67 (1995) 1257-1306

Preparation of Supported Catalysts

- goal: disperse an active phase on an inexpensive and inert (?) support



Interaction Between Active Phase and Support

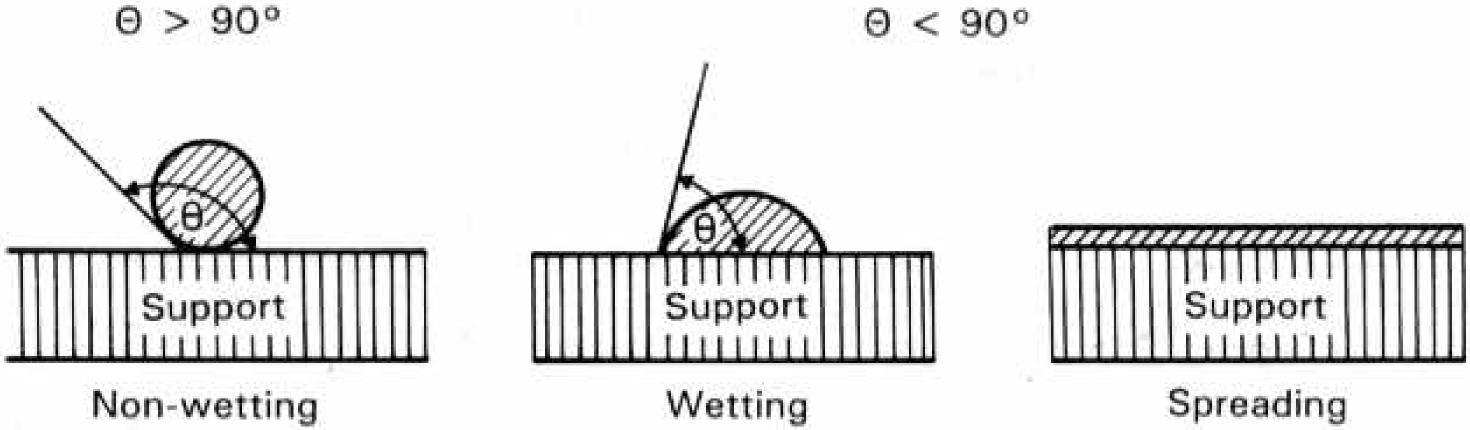


Figure 1. The solid–solid-gas interphase.

Spreading Mechanisms

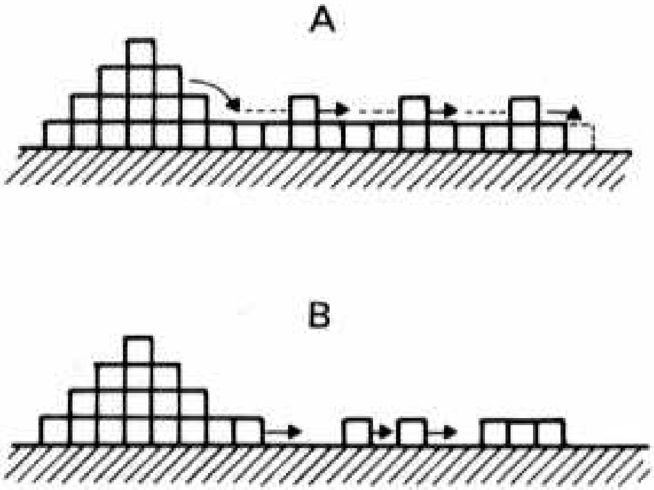
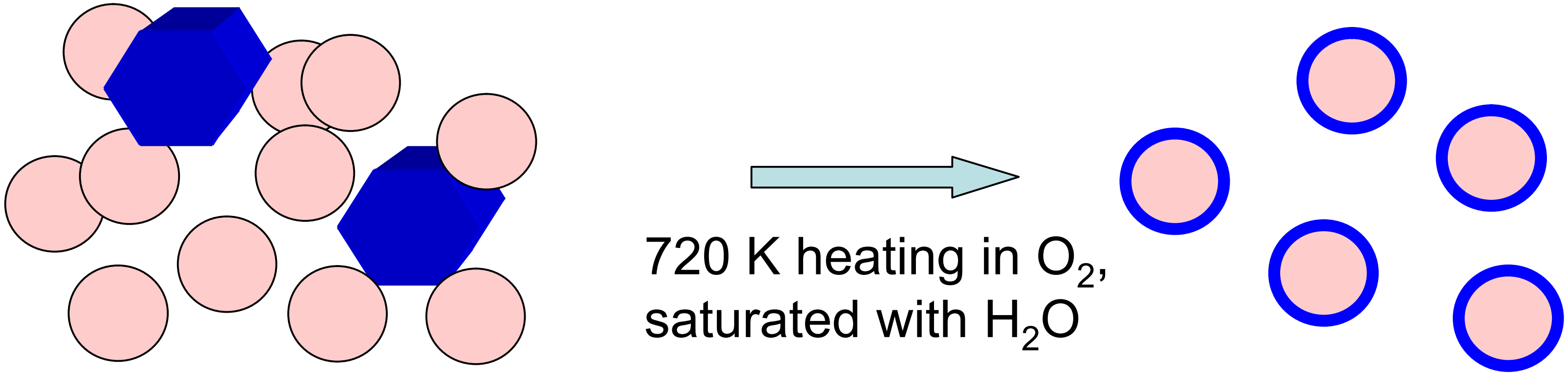


Figure 2. Schematic representation of surface transport processes: (A) unrolling-carpet mechanism; (B) transport by defect diffusion.

- transport via gas phase also possible

Preparation of SCR Catalyst by Solid-Solid-Wetting

- MoO_3/TiO_2: typical catalyst for selective catalytic reduction (reaction of NO_x with NH_3 to give N_2 and H_2O)

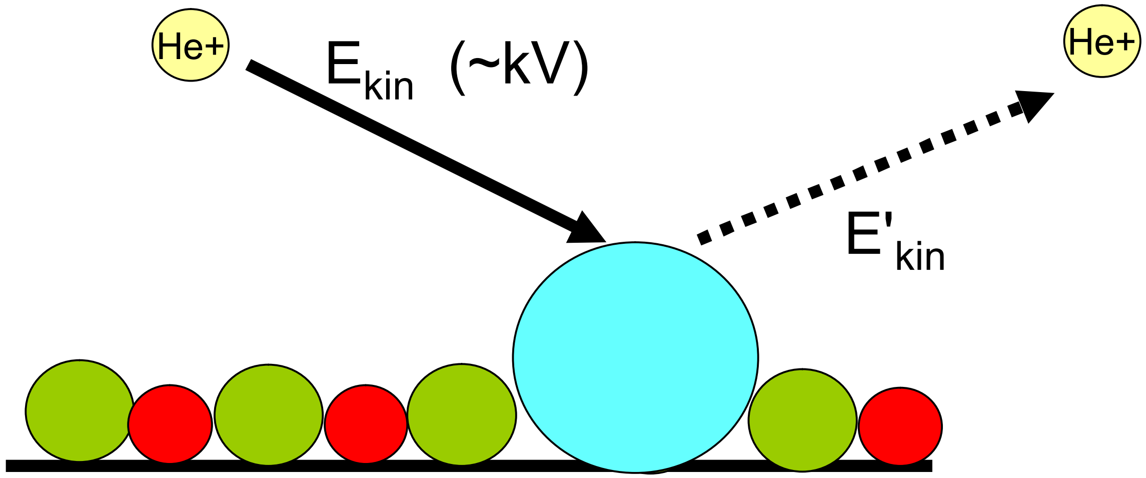


720 K heating in O_2, saturated with H_2O

- start out with physical mixture: small particles, intimate mixture
- evoke spreading through thermal treatment
- analysis of surface composition!

Ion Scattering Spectroscopy

- topmost layer of surface is probed with ion beam (He^+)



- also: LEIS = low energy ion scattering
- kinetic energy after interaction depends on mass of scattering atom
- highly surface sensitive, destructive

Spreading

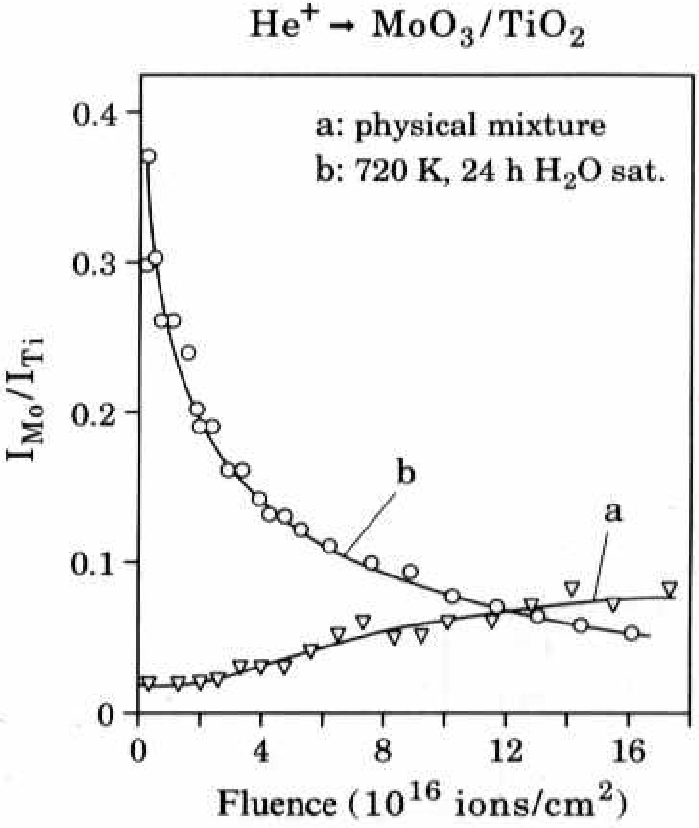


Figure 6. LEIS intensity profiles for MoO_3/TiO_2 catalyst: (a) physical mixture prior to thermal treatment; (b) after thermal treatment for 24 h at 720 K in an O_2 flow saturated with water vapor.

- Spreading of MoO_3 on TiO_2 can be achieved by thermal treatment in O_2/H_2O

Supported Metal Catalysts: Metal-Support Interaction

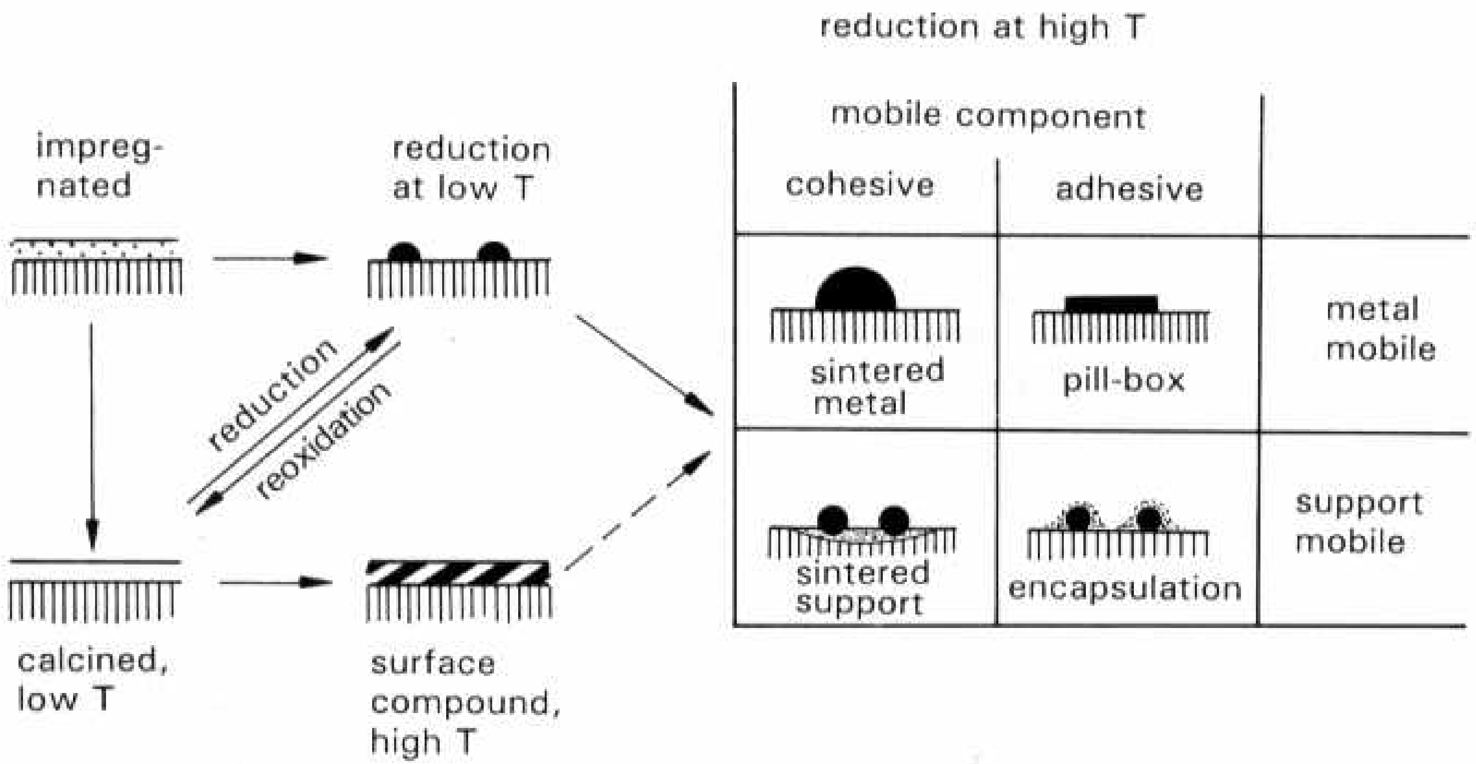


Figure 3. Schematic representation of metal–support interactions (adopted from Ref. 16).

Depth Profiling of Supported Noble Metal Catalyst

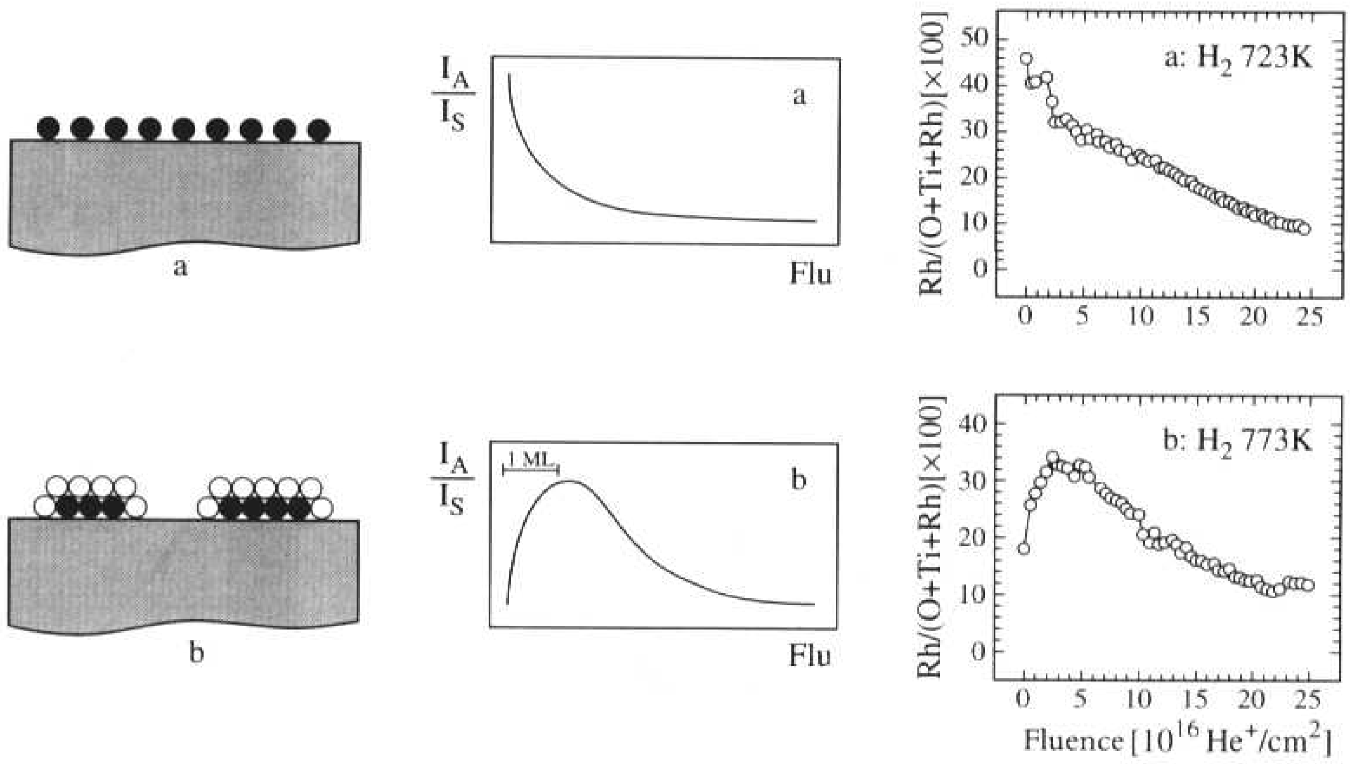


Figure 5. Low energy ion scattering on Rh/TiO_2 model catalysts: (A) structure models; (B) expected intensity profiles; (C) experimental intensity profiles (adopted from Ref. 62).

- Rh/TiO_2: a system with strong metal support interaction (SMSI)

Conclusion

- Many things can happen during a thermal treatment!