

# Sol-Gel-Processes

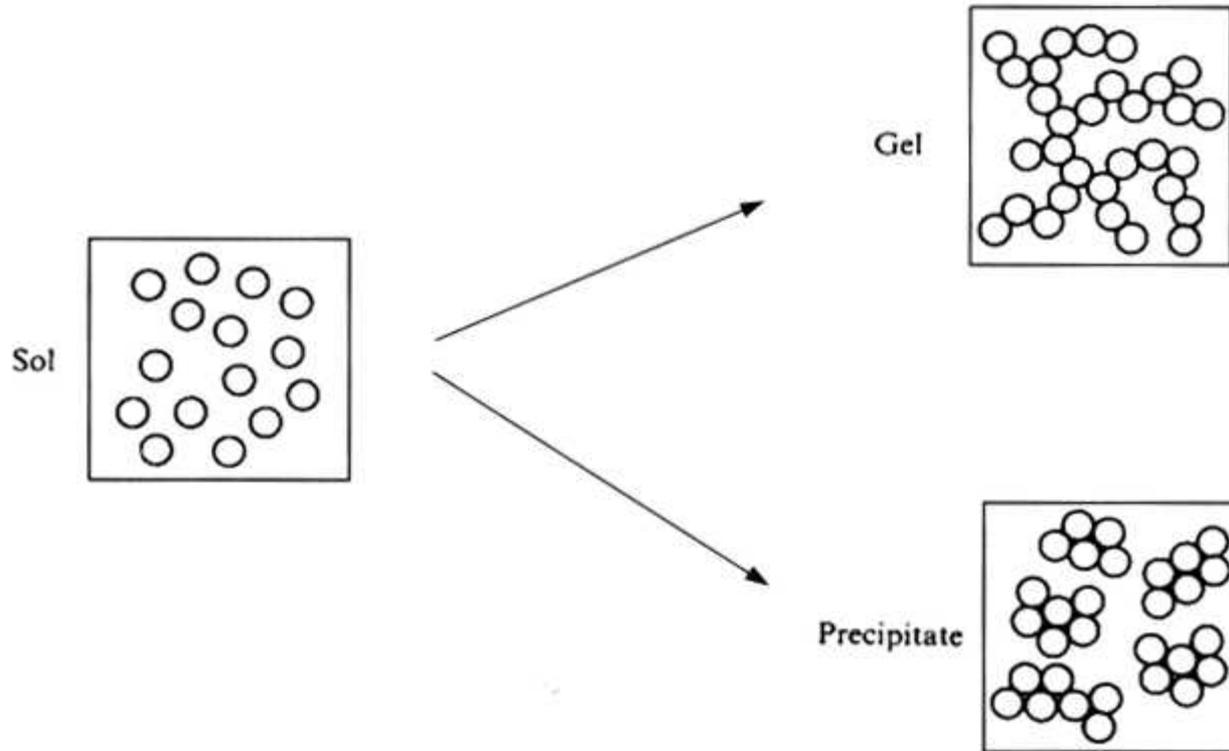


Illustration of gel formation and precipitation (flocculation) from a sol.

# The Sol-Gel-Process

**Gel:** low mechanical stability, at least two phasic,

consists of a net work structure in which the „interspaces“ are filled up by a liquide or a gas → **Hydrogels , Alkogels, Xerogels/Aerogels**

characterized by a certain transparence (low light diffraction)  $\emptyset < 100\text{nm}$

Although mainly applied to inorganic systems, also organic polymers may form the network of Gels (Organogel)

**Sol** colloidal solution in which particles or macro-molecules are dispersed in a liquide in such a way that no or just low interaction among them exists.

**Particle size** → nm-range → no Rayleigh scattering

→ „nano-particle dispersion“

# Background

## i) Synthesis of Silicagels

(adsorption.....chromatography)

stabilisation of a gel due to  $H^+$  or  $OH^-$  which form a charged surface layer  charge at the surface

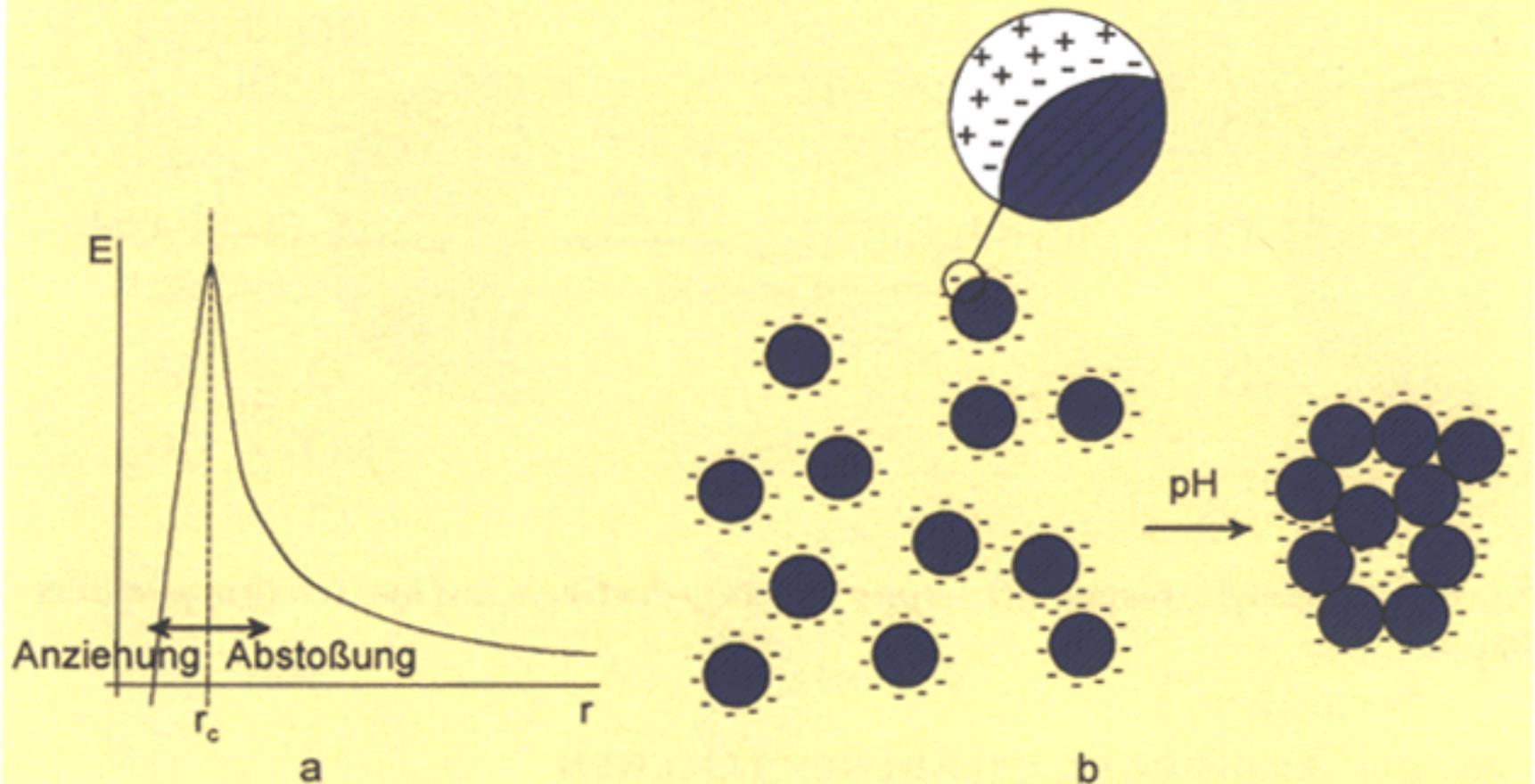
prevents the agglomeration (particles up to 50 -100 nm may be stabilized)

solid content is limited up to 10% only!

destabilisation also due to pH-variation

 reduction of the surface charge up to 0

## GELBILDUNG DURCH DESTABILISIERUNG DES SOLS

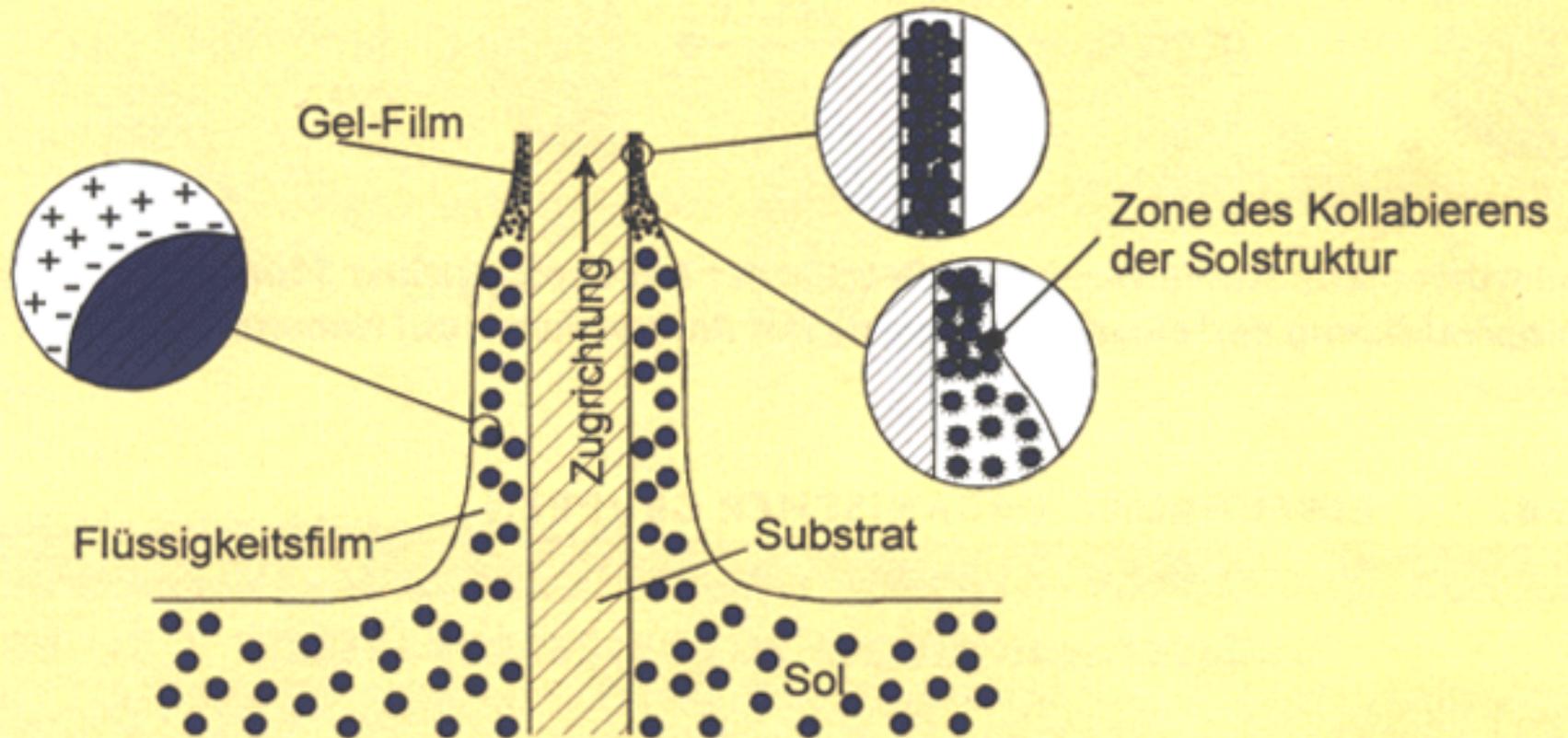


**a: Stern-Potential und elektrostatische Stabilisierung; b: und Destabilisierung mit anschließender Gelbildung;  $r_c$  = kritischer Radius;  $E$  = freie Enthalpie des Systems.**

ii) inorganic, transparent coatings

destabilisation due to change from repulsion to attraction (Stern potential)

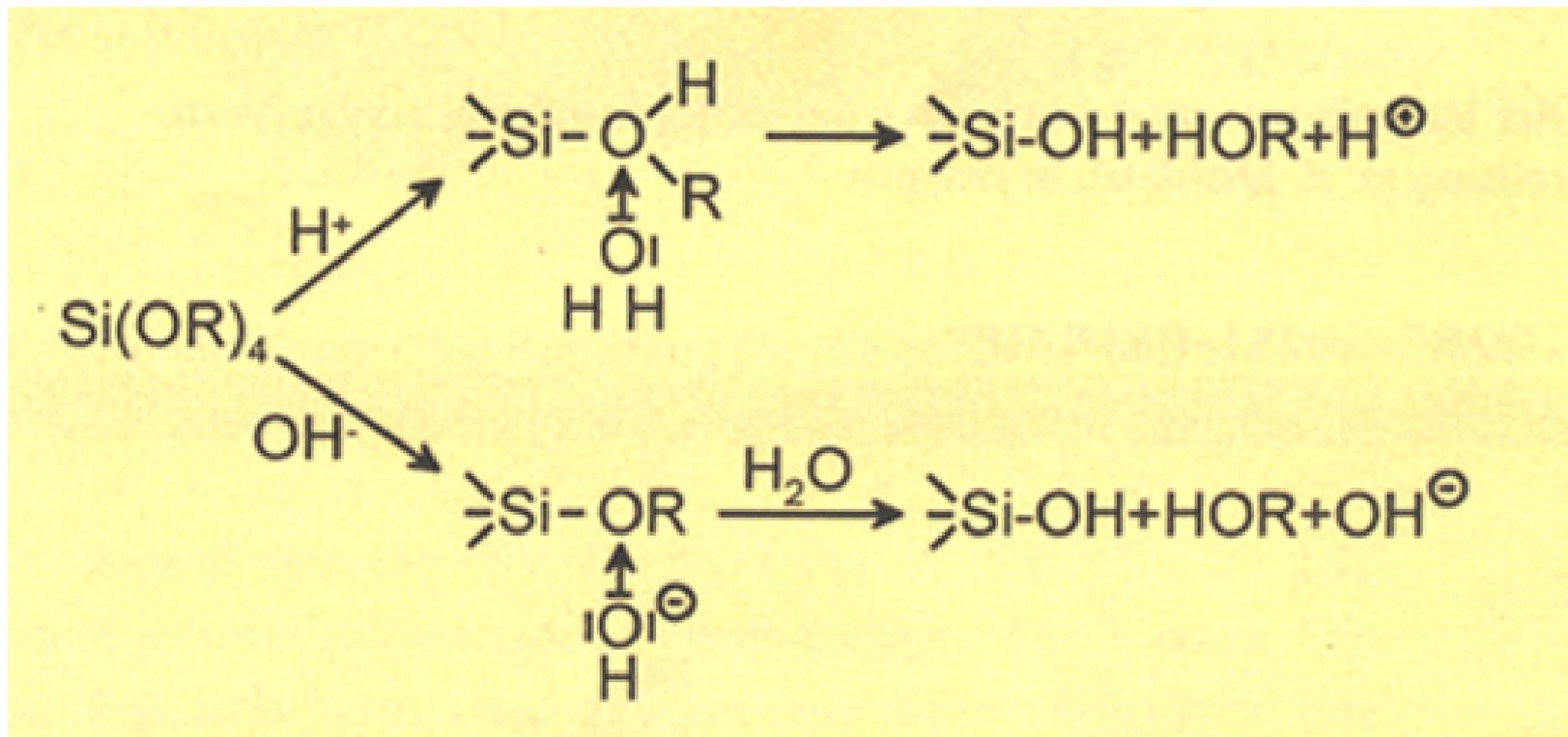
# GELBILDUNG DURCH VERDAMPFEN DES LÖSUNGSMITTELS



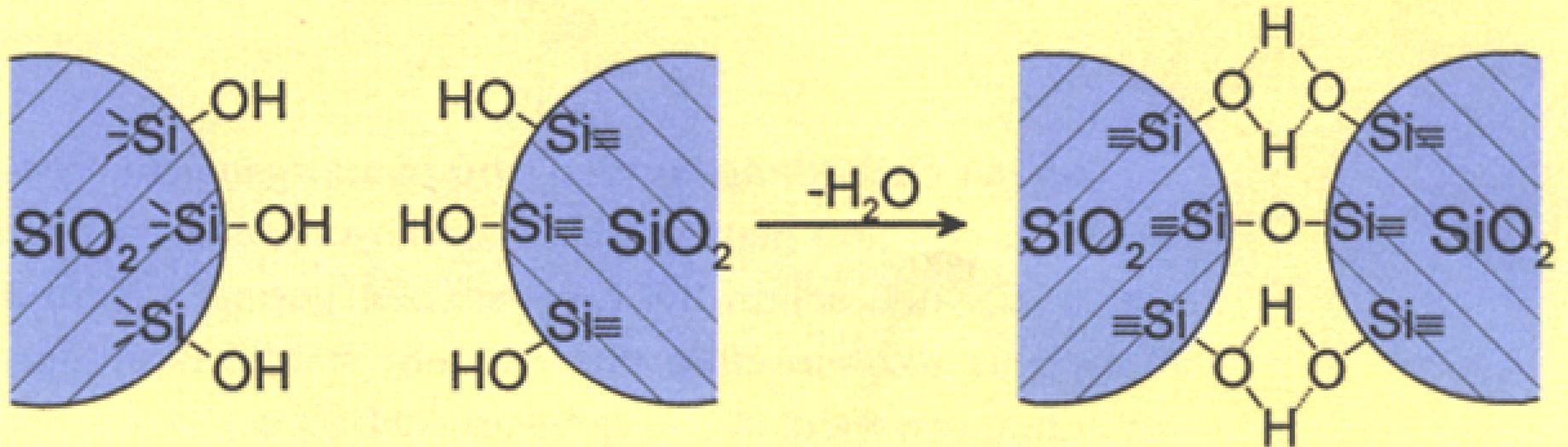
**Gelbildung bei der Entstehung von Schichten über „Austrocknen“ des Sols.**

During Gel-formation, creation of very stable bonds between the Sol-particles occurs

☞ simplest method: hydrolysis followed by condensation of metal alkoxides



## KONDENSATIONSPROZESSE

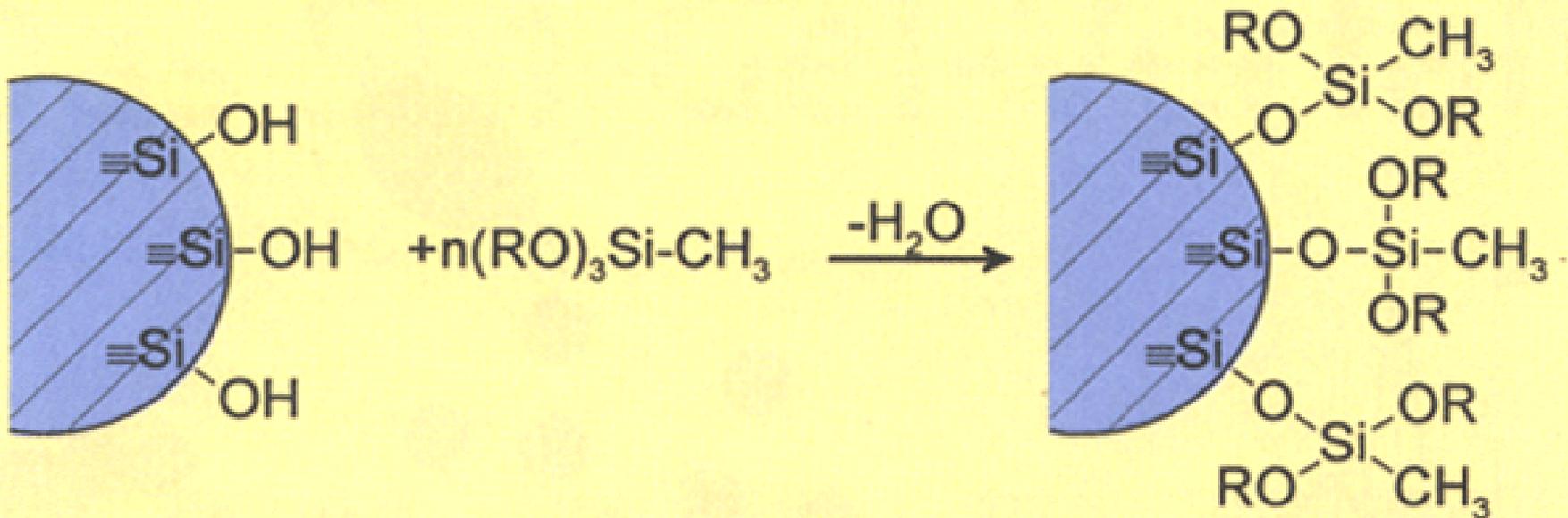


***Bildung von Sauerstoff-Metall-Bindungen durch Kondensationsprozesse bei der Gelbildung sowie die Ausbildung von Wasserstoffbrücken zwischen Sol-Partikeln.***

Alternative methods try to overcome the electrostatic stabilisation approach by chemical modification of the surface

Sols with concentrations up to 50%!

## MODIFIZIERUNG VON SOL-TEILCHEN



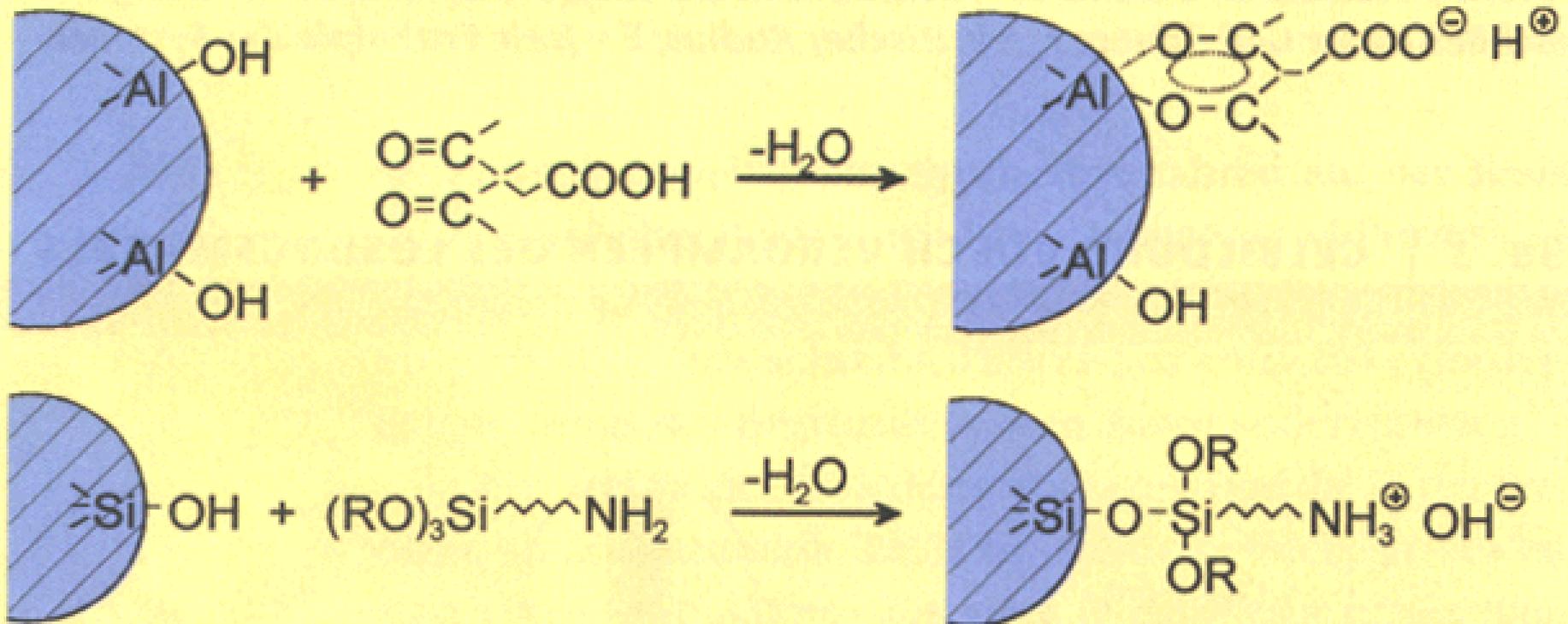
**Prinzip der Oberflächenmodifizierung von  $\text{SiO}_2$ -Partikeln mit inerten Gruppen über Silanisierung.**

Alternatively: electrostatic stabilisation, however, without irreversible network formation

e.g., modification of  $\text{SiO}_2$  particles by  $\gamma$ -aminopropyltriethoxysilane

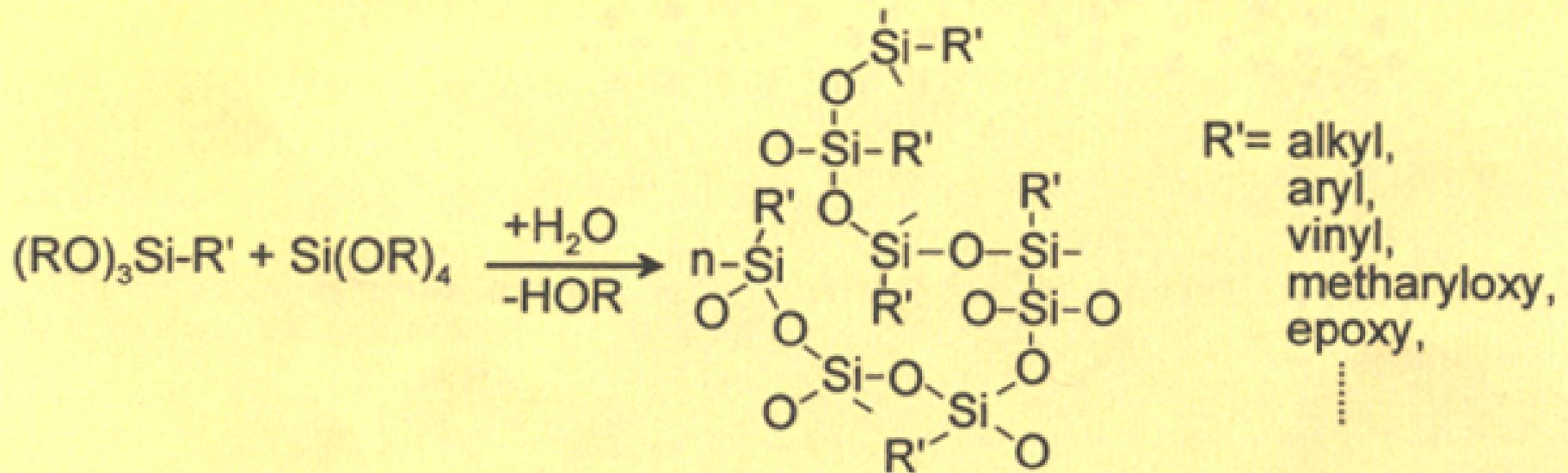
Via the amino group, now surface charges may be created which, in contrast to Si-OH-groups, do not irreversibly react

## ANBINDUNG GELADENER TEILCHEN



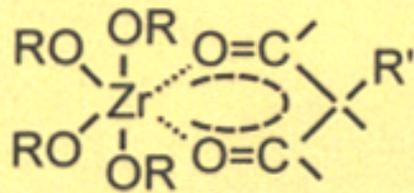
**Elektrosterische Stabilisierung am Beispiel der Ankopplung einer Säuregruppe über Komplexbildung und einer Silanisierung mit Ammosilanen auf Nanopartikeloberflächen.**

## EINFÜHRUNG ORGANISCHER GRUPPEN

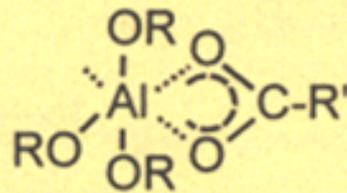


*Prinzip der Herstellung von organisch modifizierten Sol-Gel-Kondensaten.*

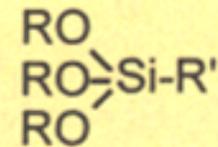
## ORGANISCHER PRECURSOR UND SOLE



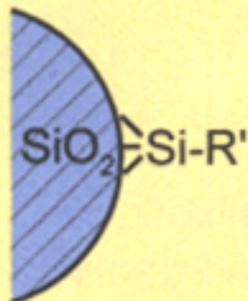
$\beta$ -Diketonate  
(Komplexbildung)



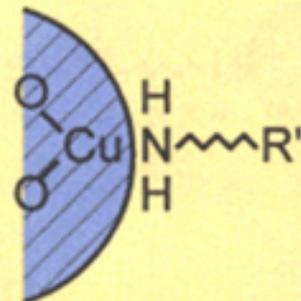
Acetate und  
andere organische  
Säuren



Silane



Silanmodifizierung



Komplexbildung

R' = inerte und  
funktionelle  
Gruppen

**Beispiele für die organische Modifizierung von anorganischen Ausgangsmolekülen bzw. Solen.**

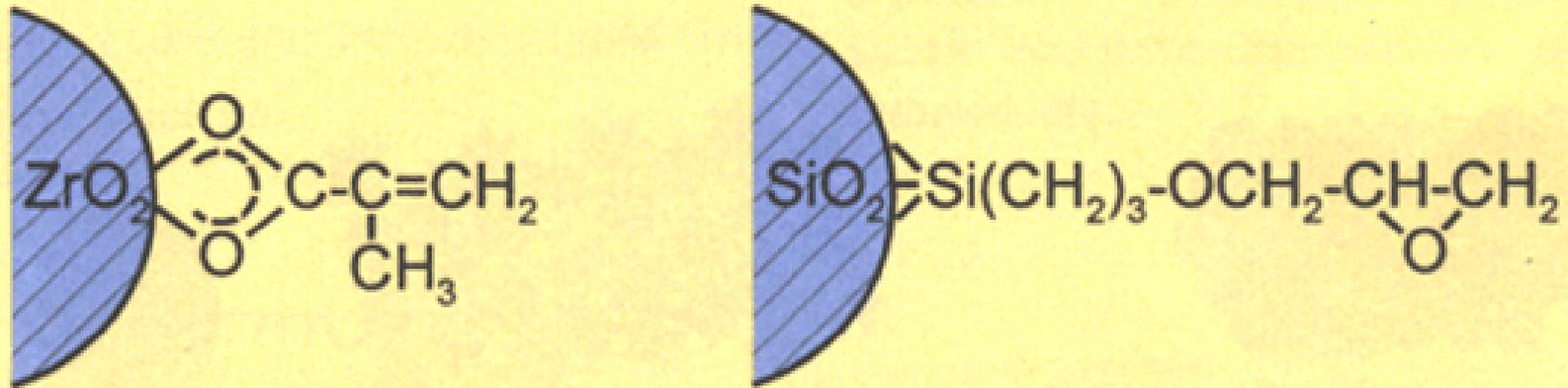
According to this idea, many Sol-types with varying compositions may be produced.

Hence, the inorganic Sol-Gel process may be adapted to create „organic modified“ systems

Condition is, the bond must survive the next steps like gel formation (hydrolysis resistant), calcination etc.

With reactive ligands like epoxides or methacrylates, Sols may be formed which can undergo polymerisation or polyaddition, respectively.

## POLYMERISIERBARE SOLE



*Kolloide mit reaktiven Oberflächen.*

# Reaction principles

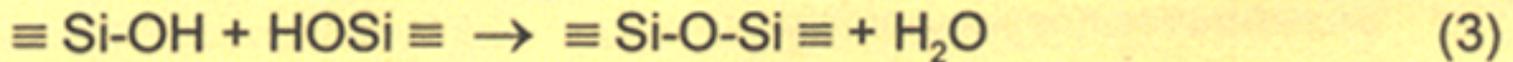
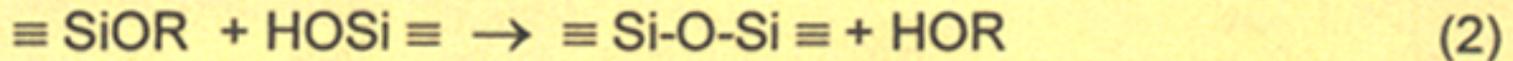
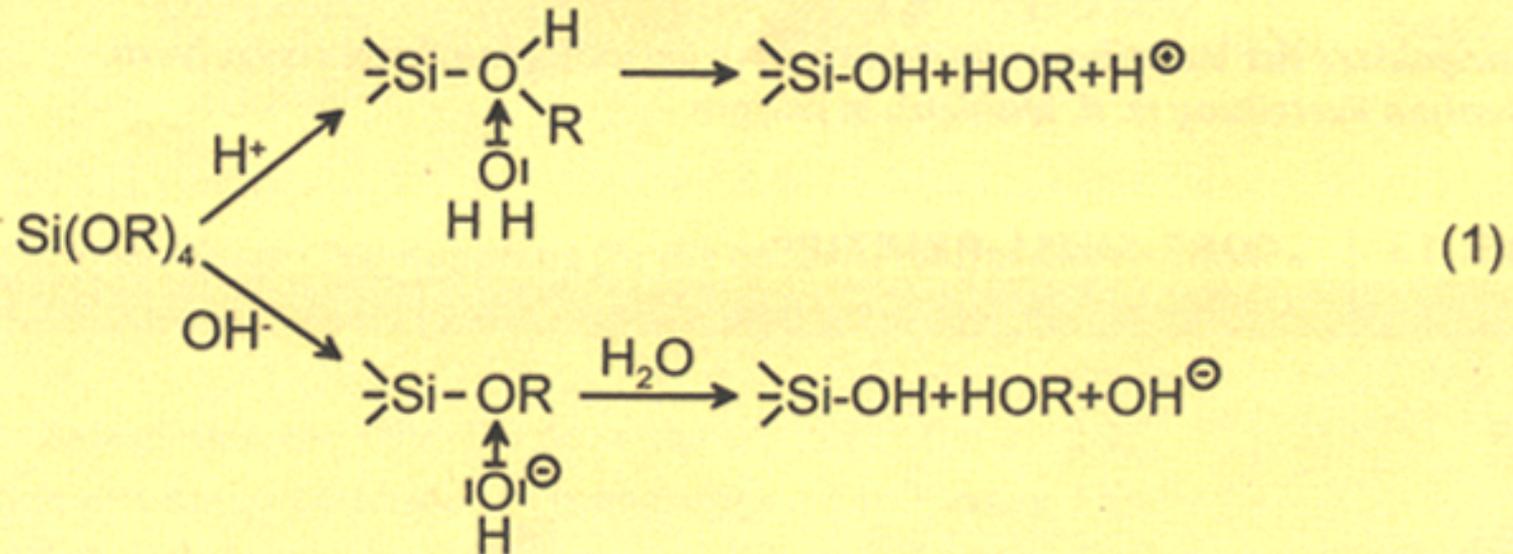
## Methods for Sol-Precursor Generation

### \* Comparison with amorphous silica

#### i) addition of an acid to a silicate solution



## ii) Hydrolysis of reactive metal alkoxylates



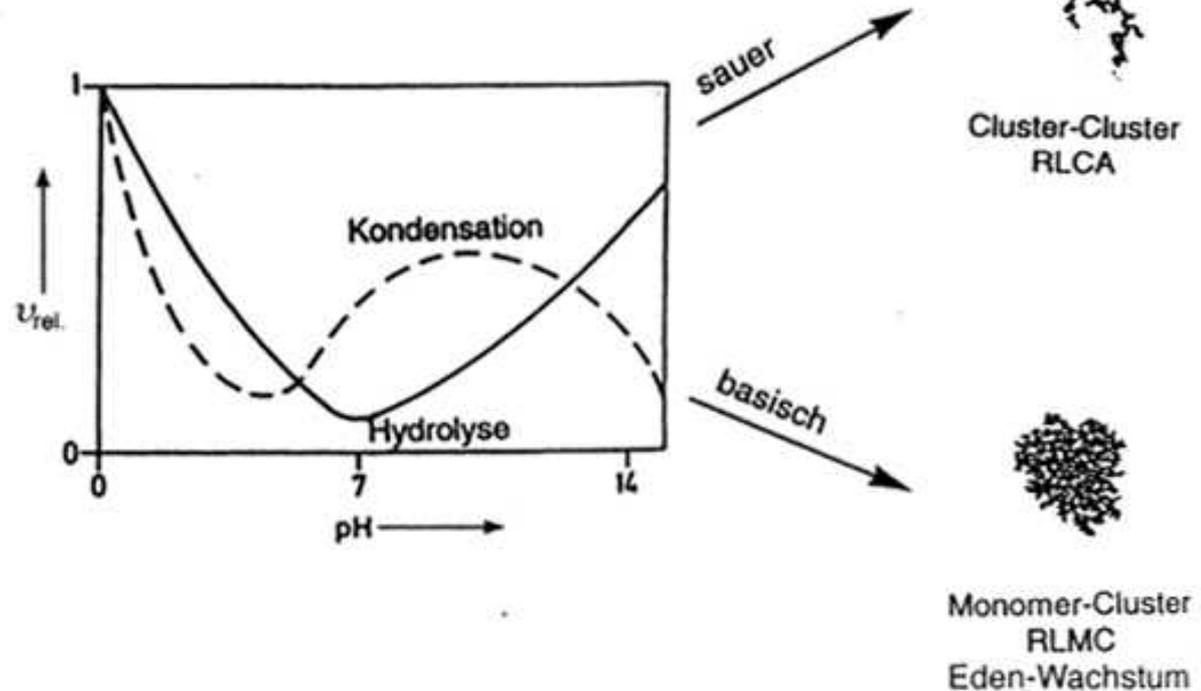
**Reaktionsmechanismen der Hydrolyse von Kieselsäureestern.**

# Influence of pH on the gel formation

pH < 2 : globular primary structures

pH = 2-6: chain-like, also branched Gels with positive charge

pH > 7 : spheric particles of few up to 300 nm size



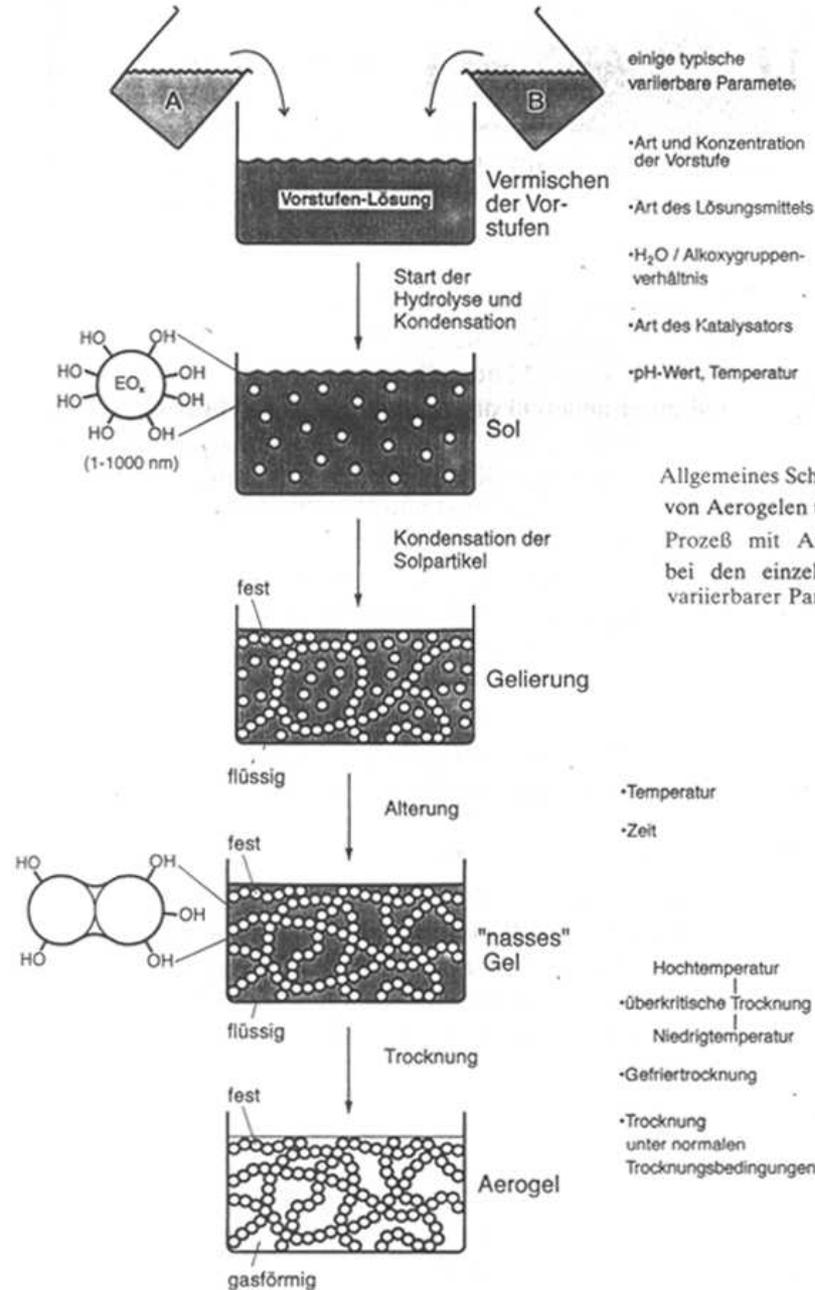
Abhängigkeit der Hydrolyse- und Kondensationsreaktionen vom pH-Wert und daraus abgeleitete kinetische Wachstumsmodelle für Gelstrukturen, die durch RLCA und RLMC (Eden-Wachstum) gebildet werden (nach Lit.<sup>[7, 35]</sup>).  $v_{rel.}$  = relative Reaktionsgeschwindigkeit.

# Steps during the Sol-Gel-synthesis

General scheme for the synthesis of aerogels via the Sol-Gel process

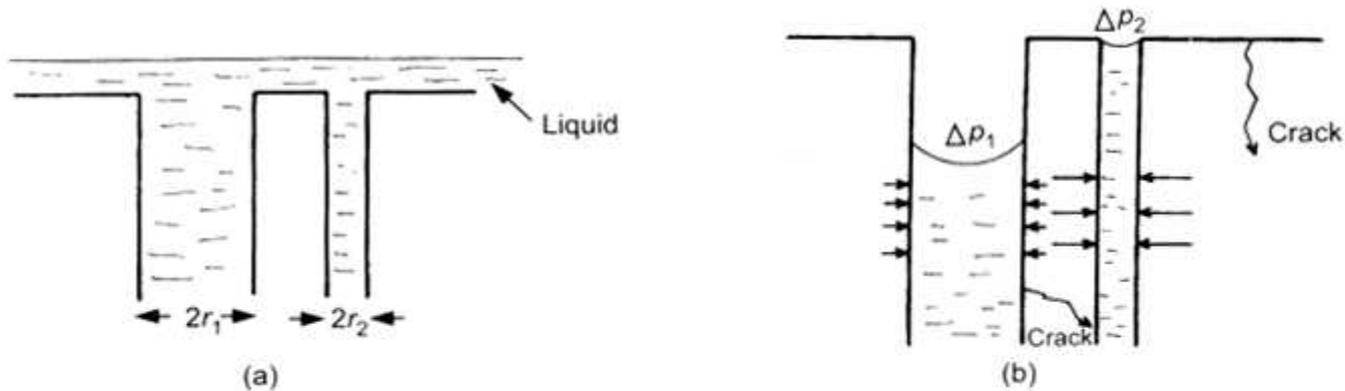


typical steps and parameters influencing the pathway



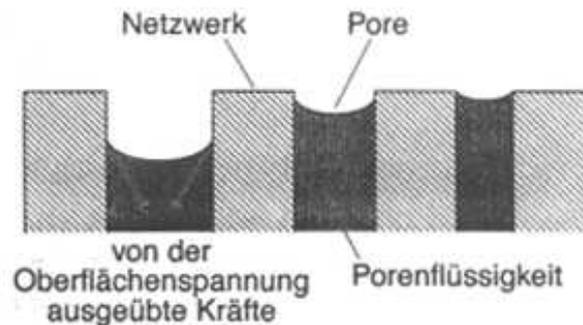
Allgemeines Schema für die Herstellung von Aerogelen über den Sol-Gel-Prozeß mit Angabe einiger typischer bei den einzelnen Verfahrensschritten variierbarer Parameter.

# Drying of Gels

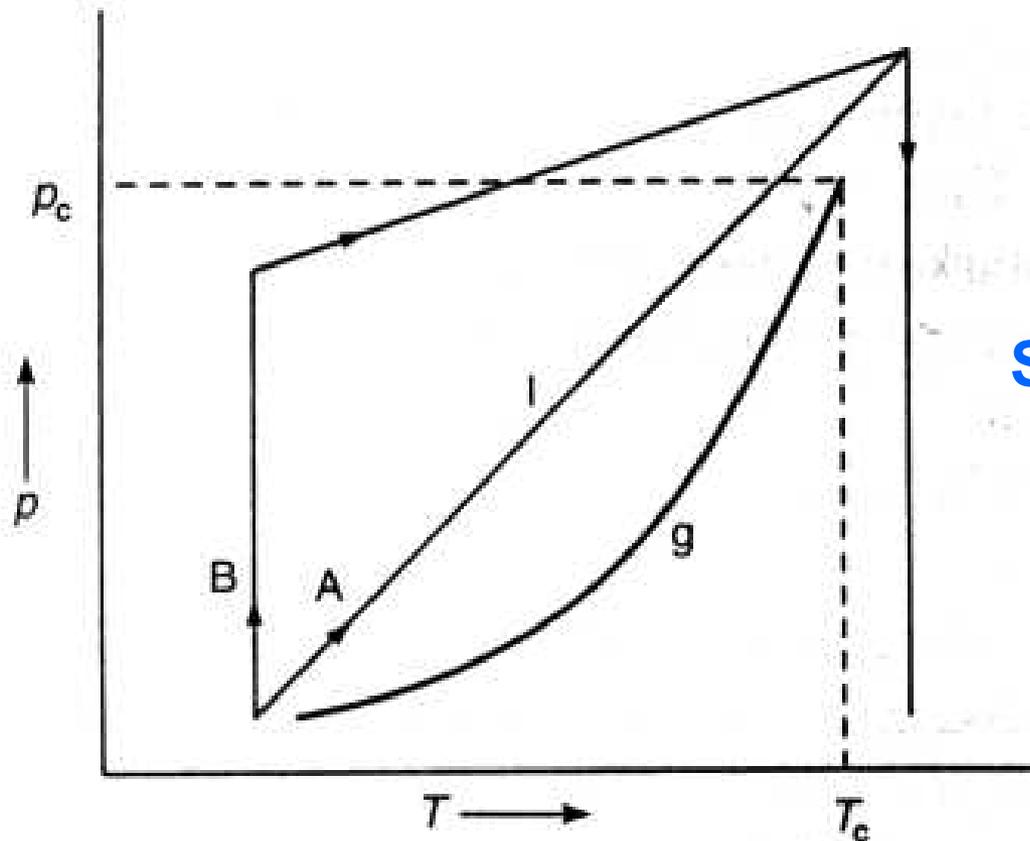


Two pores in a gel in: (a) the 'wet' state, where the pores are completely filled with sol liquid; (b) a partially dried gel, where pressure differences across the menisci are different,  $\Delta p_2 > \Delta p_1$ , for pores with different radii,  $r_2 < r_1$ . The associated differential stresses can cause the gel to crack.

## Trocknungsverfahren



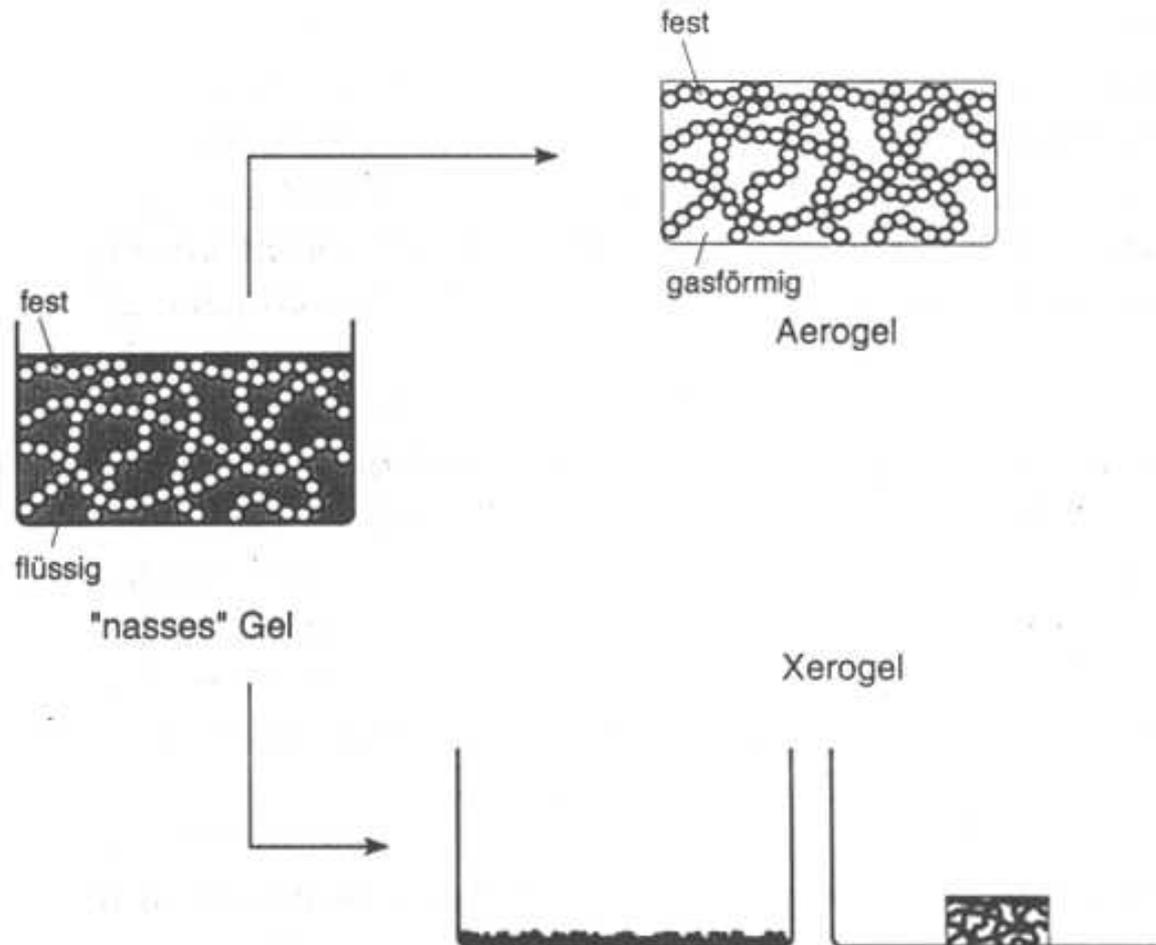
Darstellung der kontraktiven Oberflächenkräfte während einer Trocknung in Poren unterschiedlicher Größe. Bei gleichem Druck ist die Krümmung der Menisken in den Poren gleich. Aus diesem Grund entleeren sich größere Poren zuerst



## Supercritical drying

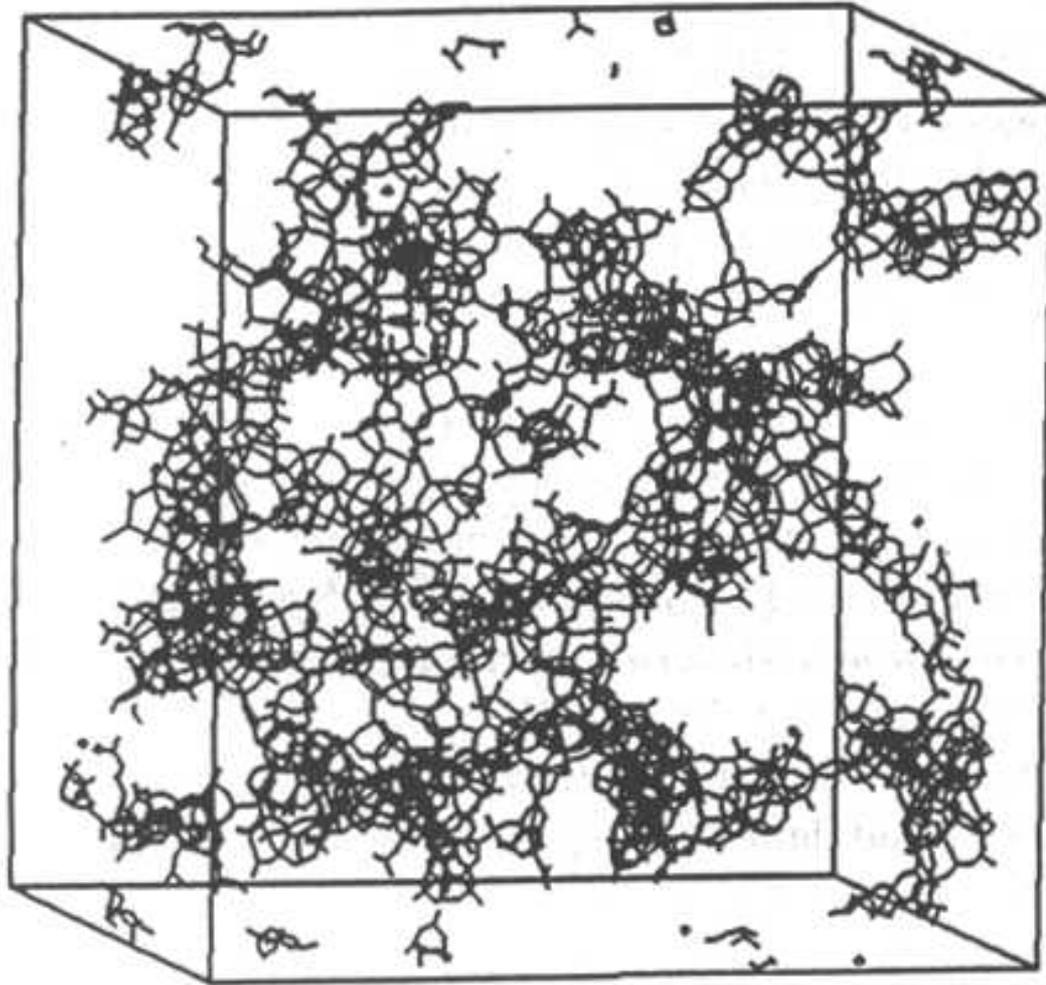
Schematische Darstellung des Prinzips der überkritischen Trocknung. Am kritischen Punkt ( $T_c$ ,  $p_c$ ) sind die Dichten der Flüssigkeit (l) und des Gases (g) dieselben. Die überkritische Trocknung kann wahlweise auf Weg A oder B durchgeführt werden.

# Xerogeles und Aerogeles



Trocknung eines nassen Gel-Formkörpers unter Vermeidung der Schrumpfung zum Aerogel (oben) und zum Xerogel (unten) als Pulver (links) bzw. Monolith (rechts).

# Aerogel structure



Schematische Beschreibung der SiO<sub>2</sub>-Aerogel-Struktur

# Characterisation of porous solids

Begriffe, die zur Charakterisierung poröser Feststoffe dienen.

Begriff	Erläuterung
Porosität	Verhältnis des Porenvolumens zum Volumen, das die Partikel (Pulverkörner) einnehmen
Porenform	flaschenhals-, zylinder-, trichter- oder schlitzförmig
Zugänglichkeit der Poren	offene oder geschlossene Poren
Porengröße, <sup>[5]</sup> dominierende Transportmechanismen	<i>Mikroporen</i> : < 2 nm, aktivierter Transport <i>Mesoporen</i> : 2 – 50 nm, Knudsen-Diffusion, Diffusion entlang der Porenwandungen, Kapillartransport <i>Makroporen</i> : > 50 nm, molekulare Diffusion
Dichte	Skelettdichte: Dichte des festen Netzwerks Bulkdichte: Menge an Feststoff pro Volumeneinheit (Volumen = feste Phase + geschlossene Poren + offene Poren)

## PE Beaker

Formation of the alkoxide-gel



### Autoclave

Supercritical drying

$$T > T_{c, ROH}$$

wet gel

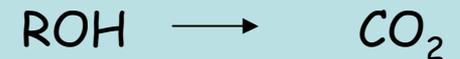
### Oven

Calcination

HT-Aerogel

### Autoclave

Solvent exchange



Supercritical drying

$$T > T_{c, CO_2}$$

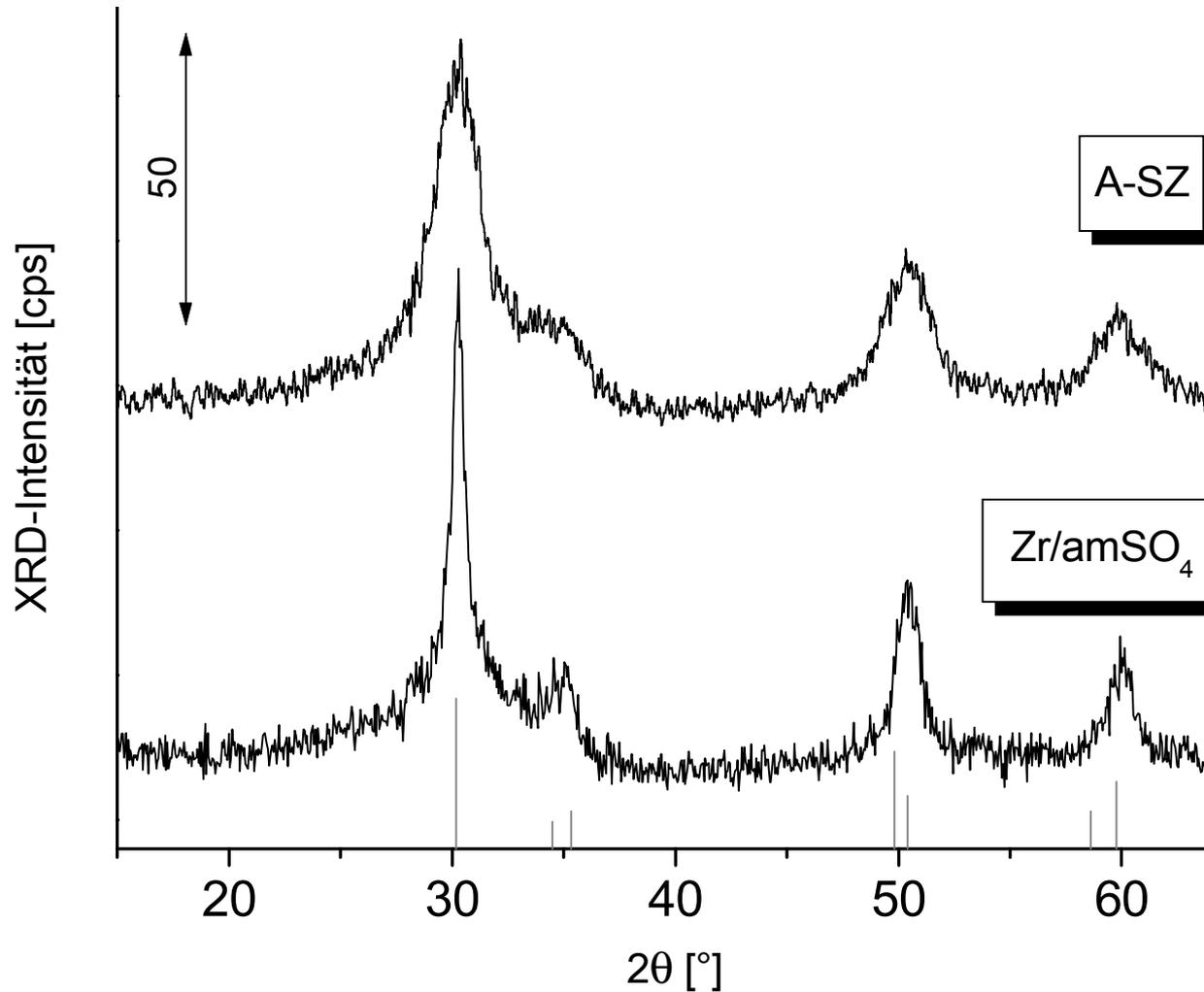
row gel

### Oven

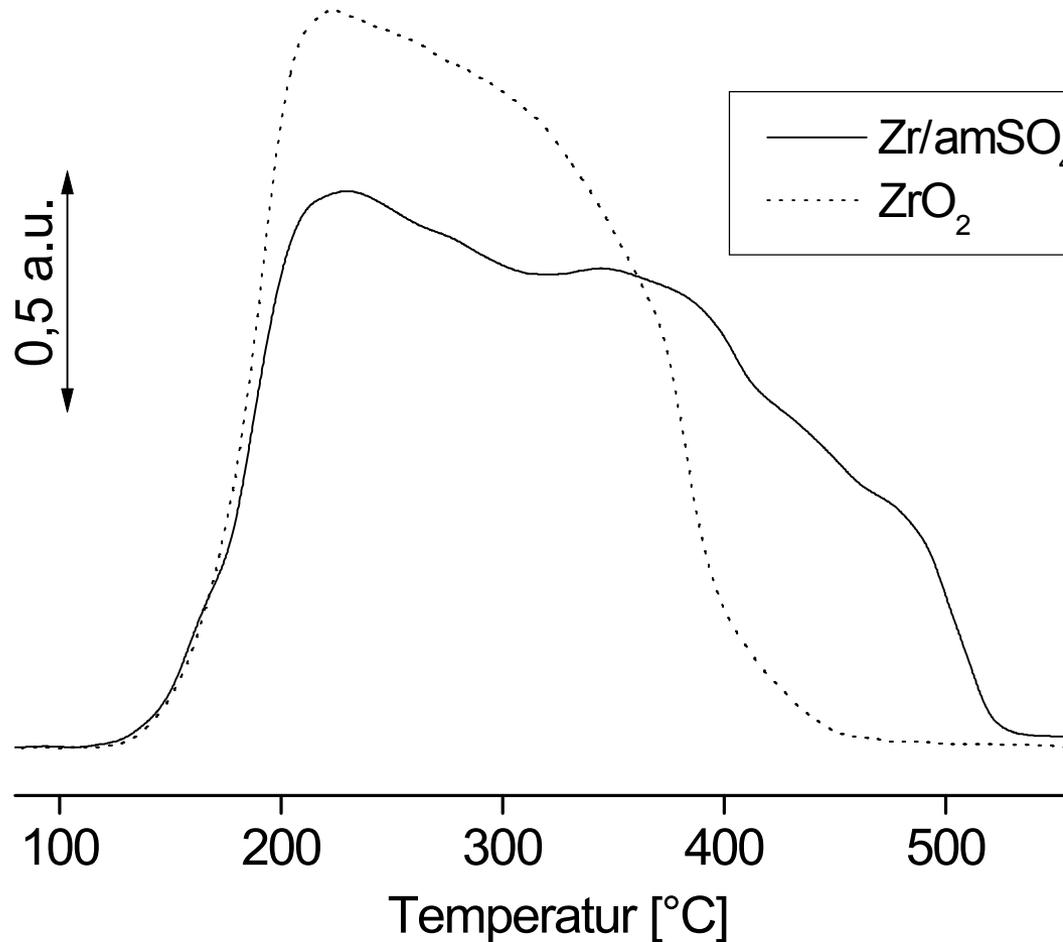
Calcination

LT-Aerogel

X-ray powder diffraction of  $Zr/amSO_4$  and SZ-Aerogel, A-SZ.  
additional reflexes of the tetragonal  $ZrO_2$ -modification are indicated

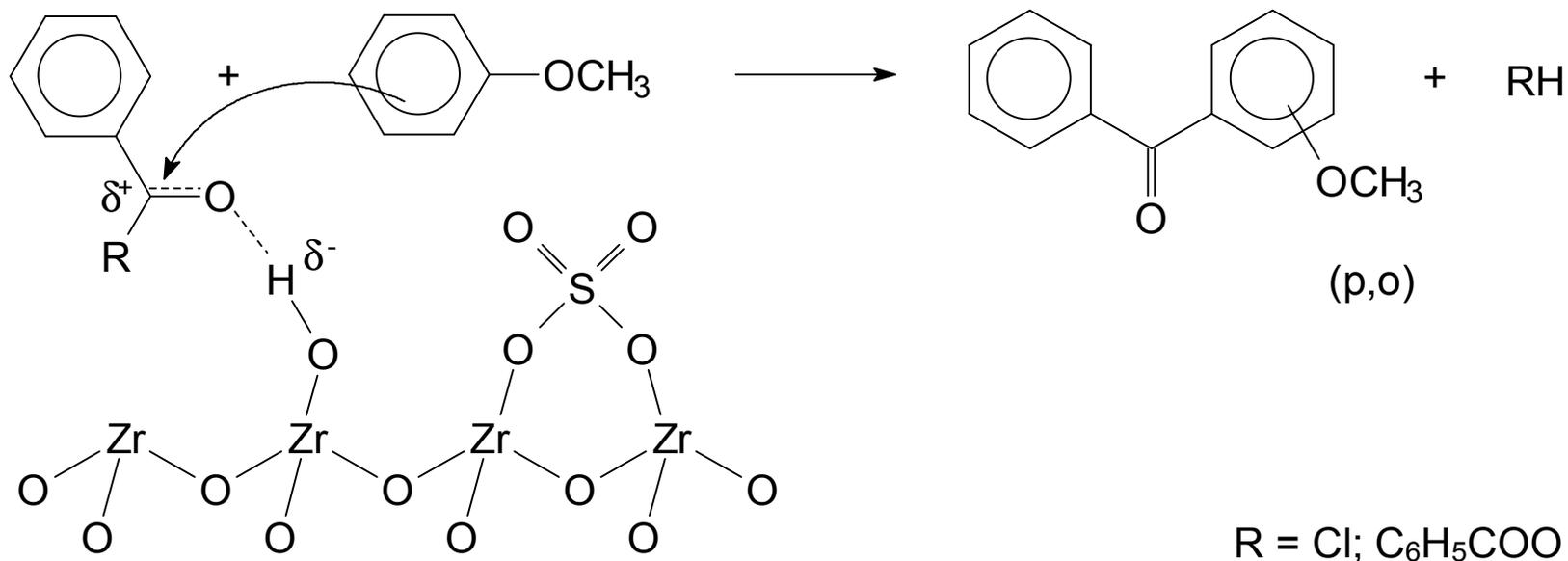


# Profiles of temperature programmed desorption of ammonia on sulfated zirconia and the unmodified sample



The square below the curve corresponds to the detected concentration of acid sites

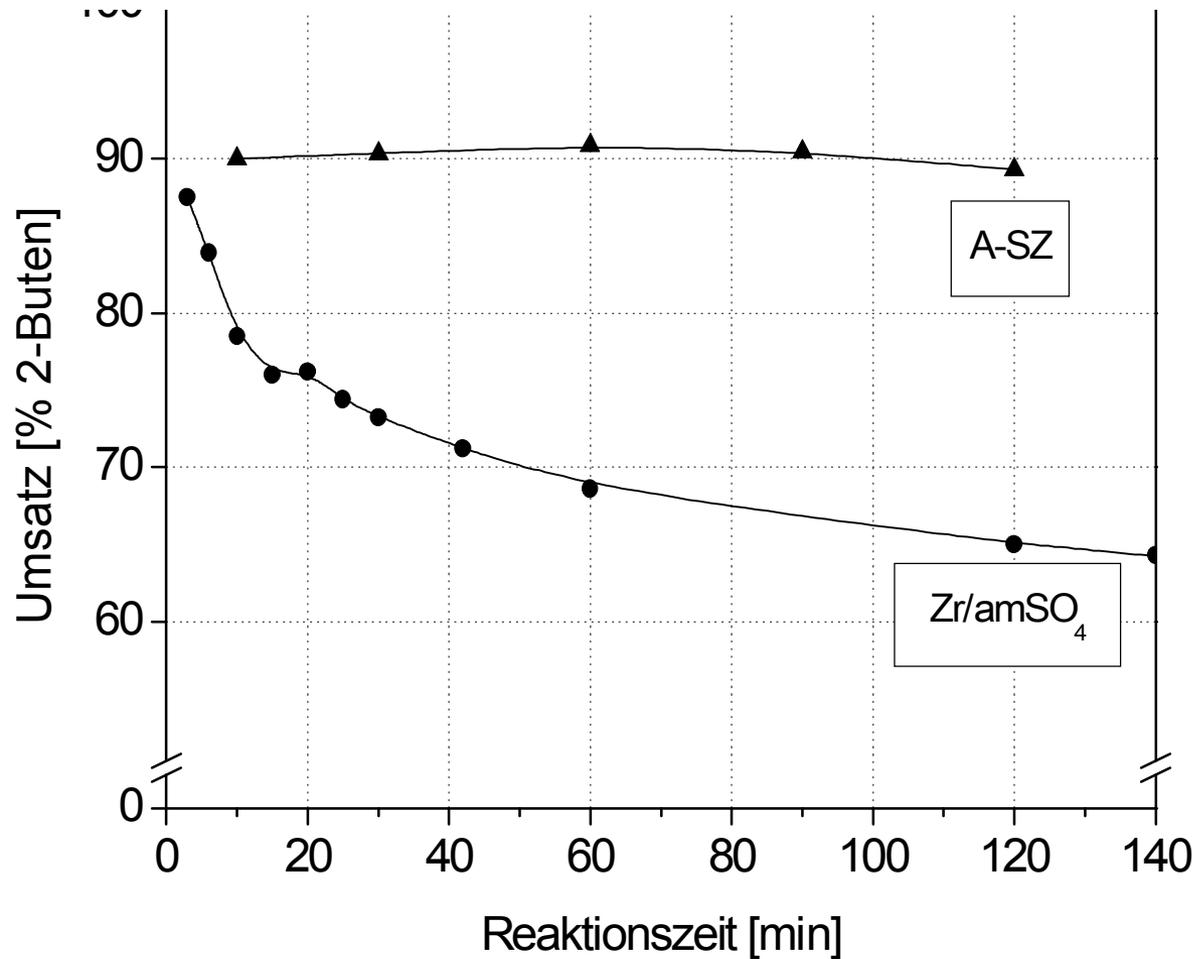
# The Friedel-Crafts-Acylation



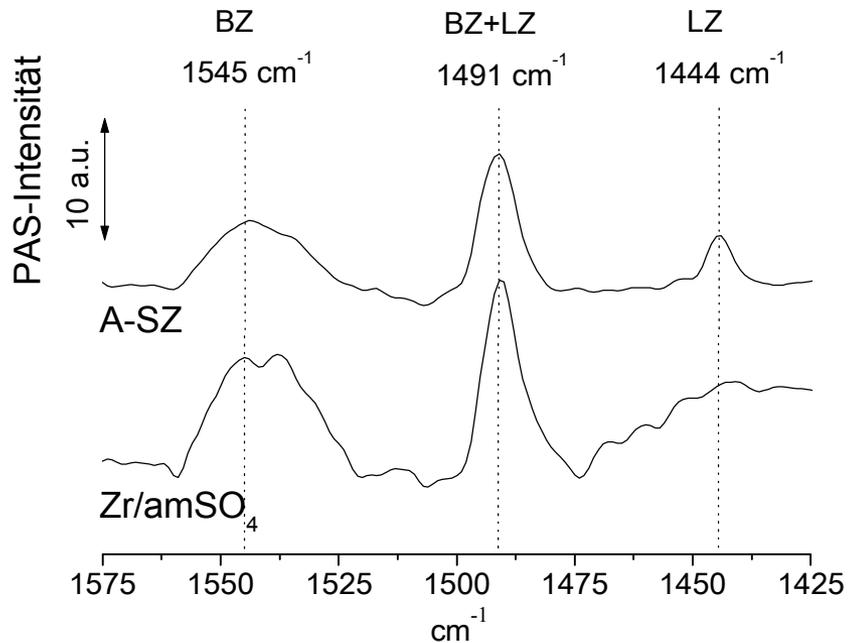
The interaction of the benzoylation reagent with a Brønsted-acid site increases the electrophilicity of the acylation reagent and, hence, promotes the reaction with the (electron rich) aromatic compound, anisole.

# Duble bond isomerisation of 1-buten on differently synthesized SZ-phases

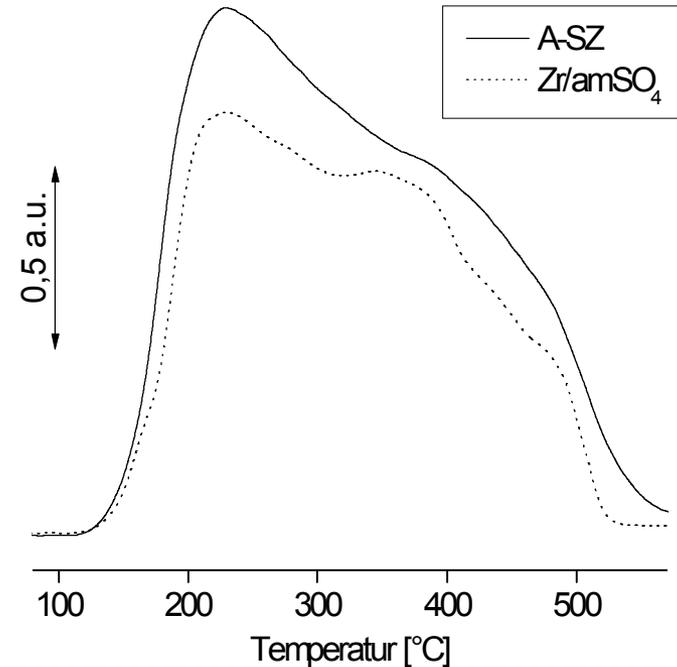
(A-SZ: Aerogel, Zr/amSO<sub>4</sub>: standard sample, T: 100 °C, t<sub>r</sub>:1,2 s.



# SZ: synthesised via different methods methodes

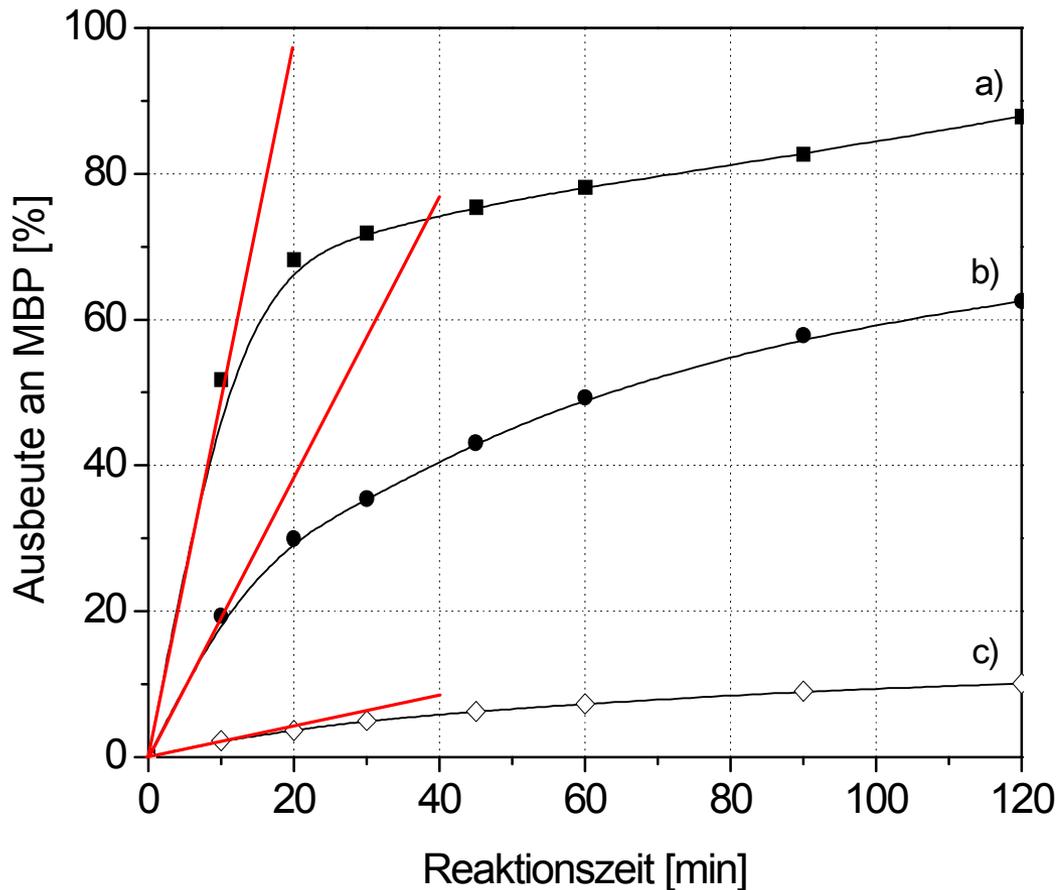
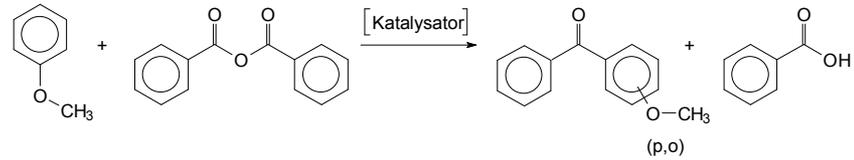


Photoacoustic spectra of Pyridine-adsorbat complexes of differently synthesized SZ-samples  
 (A-SZ: Aerogel  
 Zr/amSO<sub>4</sub>: Standard sample)



NH<sub>3</sub>-TPD-profiles of SZ-phases A-SZ and Zr/amSO<sub>4</sub>. the squares below the curves correspond to desorbed amounts of ammonia being 0,30 or 0,37 mmol/g), respectively.

# Comparison of SZ with the most powerful zeolit, H- $\beta$

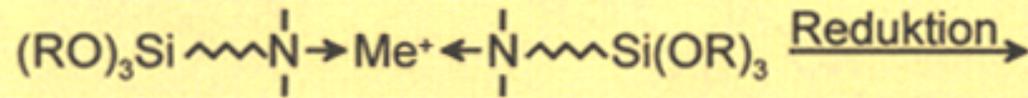
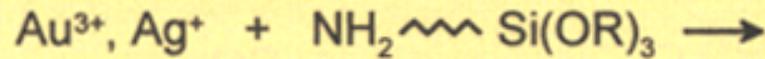


Kinetic investigations of the reaction between anisole and benzoic acid anhydrid at 50 °C on different catalysts:  
a) A-SZ, b) Zr/amSO<sub>4</sub>, c) Zeolit H- $\beta$ .

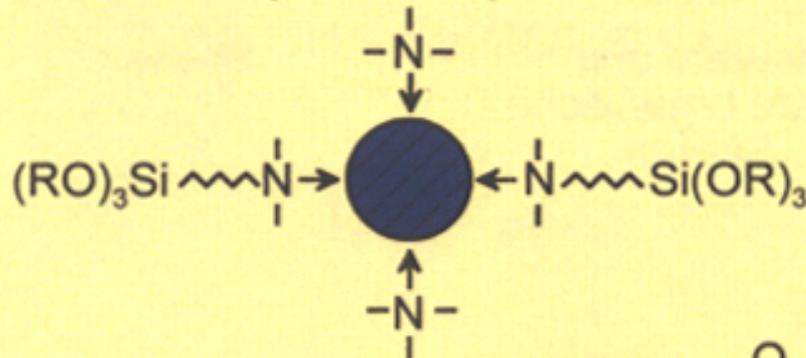
Applications

besides catalysis

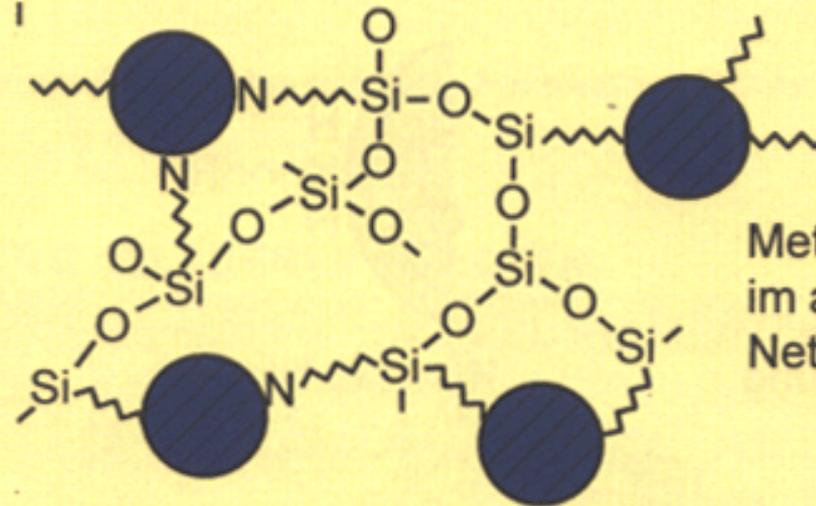
# FARBIGE GLASSCHICHTEN DURCH METALLKOLLOIDE



Addition of metal colloids → coatings of different colours



$\xrightarrow[\text{Kondensation}]{\text{H}_2\text{O/Hydrolyse}}$



Metallkolloide  
im anorganischen  
Netzwerk

**Herstellungsschema von Metallkolloiden in anorganischen Netzwerken**

## Manufacturing of ceramics

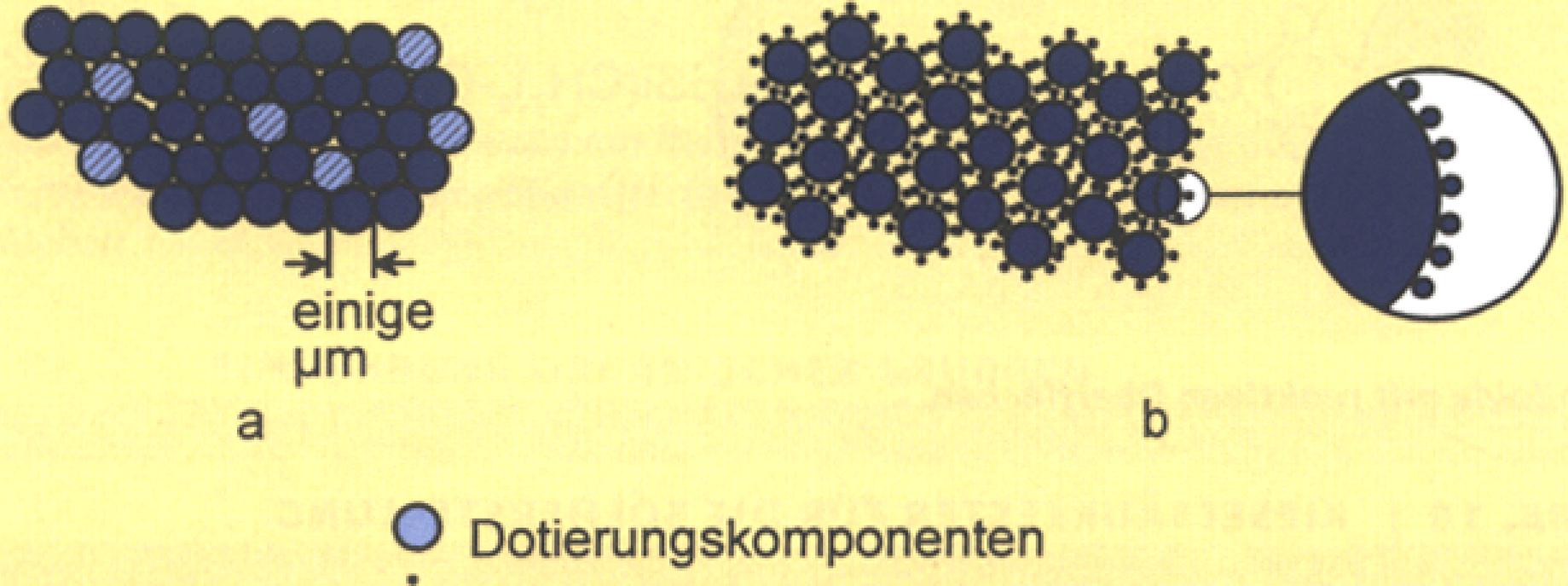
Ordinary procedure: cointering of small particles (role of defects, stability etc.)

Sintering temperature is a function of the particle size.

However, small particles exhibit high surface area → adsorption of other components.

Homogeneous distribution of sinter additives by milling is very difficult:

## VERTEILUNG VON DOTIERUNGSKOMPONENTEN



**Prinzipische Verteilung von Additiven in keramischen Ausgangspulvern.**  
**a:  $\mu\text{m}/\mu\text{m}$  Verteilung (z. B. Mahlen); b:  $\mu\text{m}/\text{nm}$ .**

# Sol-Gel precursors for the manufacture of ceramics

For the deposition of dopands on surfaces, Sol-Gel is a powerful technique.

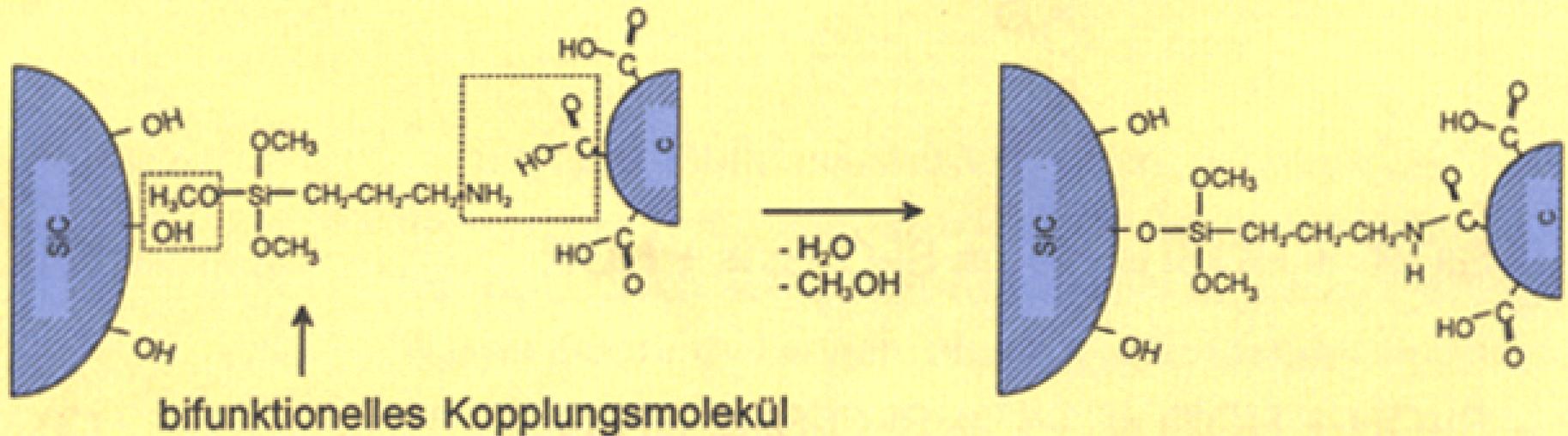
## Deposition of dopands:

i) coating by adsorption

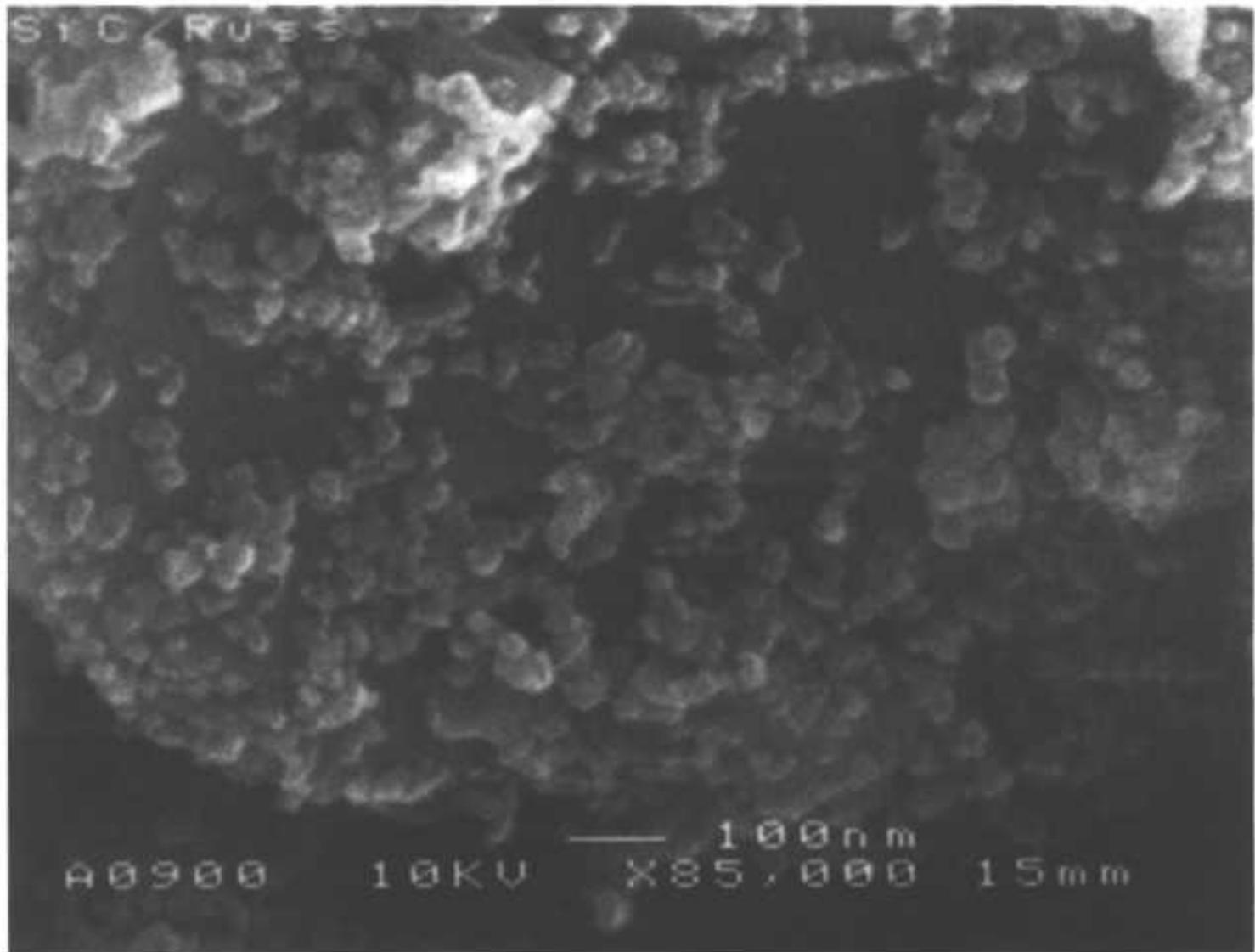
ii) molecular reaction

E.g., SiC coated by carbon (necessary to reduce  $\text{SiO}_2$  formed during sintering)

## „CORE-SHELL-PRINZIP“



**Prinzip der Kopplung von Ruß-Nanopartikeln an SiC-Oberflächen.**

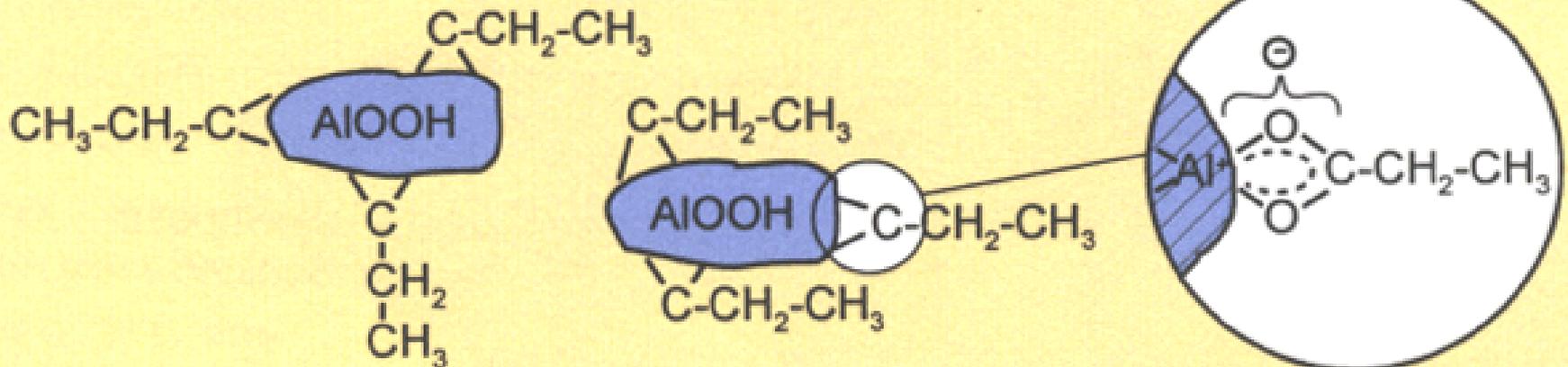


***Beschichtung von SiC-Partikeln mit nanoskaligem Ruß-Sol über chemische Reaktionen an die Oberflächen von SiC.***

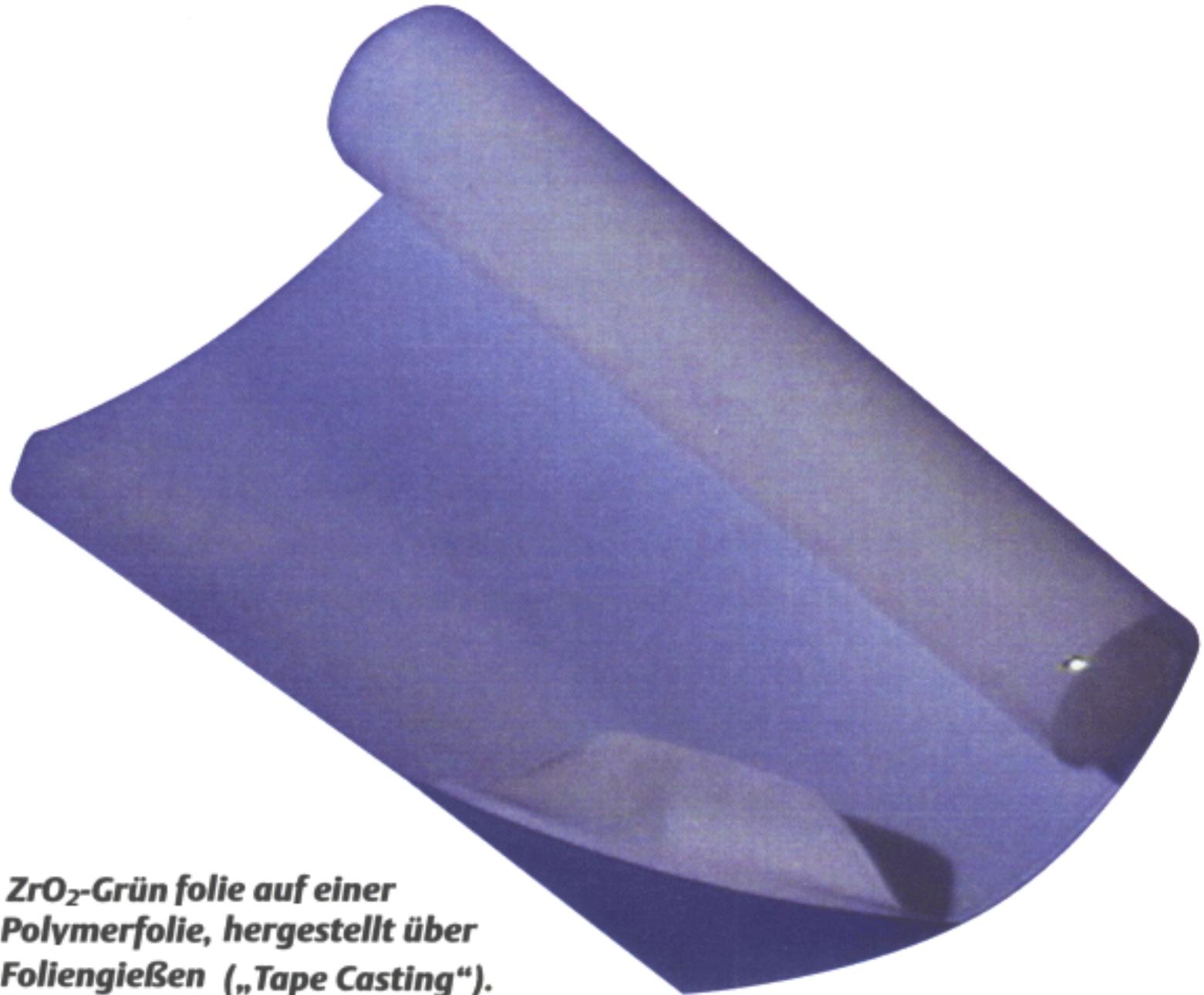
Prevention of agglomeration during sintering by introduction of protecting surface groups.

Nanotechnology  $\rightarrow$  wet forming becomes possible and lower sintering temperatures

## SCHUTZGRUPPEN ZUR AGGLOMERATIONSKONTROLLE



**Belegen von AlOOH-Sol-Partikeln mit Schutzgruppen (hier mit Propionsäure).**



**ZrO<sub>2</sub>-Grün folie auf einer  
Polymerfolie, hergestellt über  
Foliengießen („Tape Casting“).**

# Inorganic-organic nanocomposites

1976 developed and named **Ormosiles** and **Ormoceres**

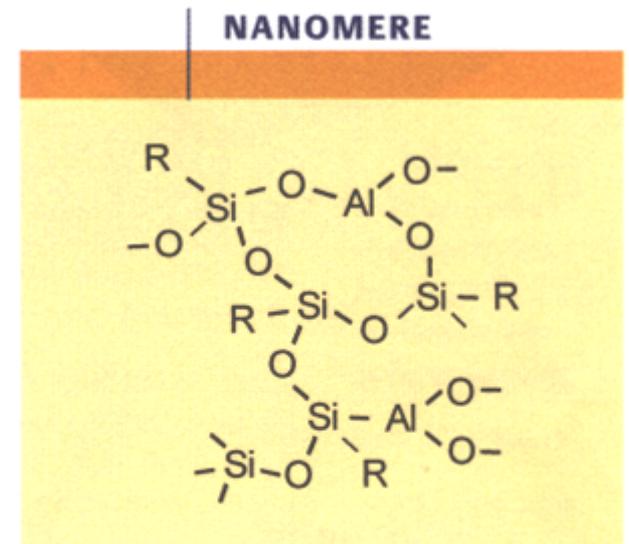
Organics are linked to the inorganic network via Si-C-bonds (e.g., hardened plastic lenses)

The inorganic network determines the structure

Since the particles are very small, these materials are mostly transparent

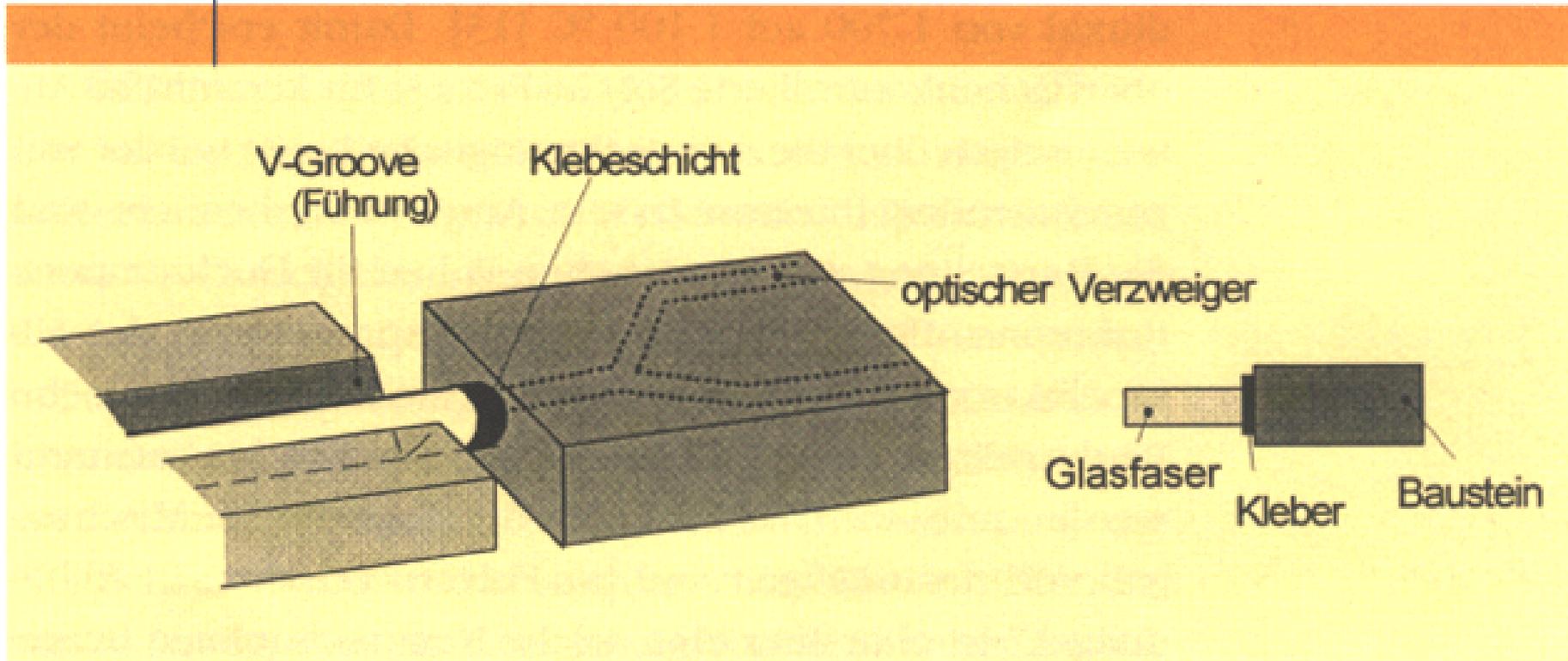
☞ mainly used as transparent coatings

(as a rule: if  $\varnothing < 1/20$  of the wave length of the light, Rayleigh diffraction is small)



**Hybridstruktur von Ormosilen und Ormoceren; R = Alkyl, Aryl, organische Säure- und Base-Gruppen, Doppelbindungen, etc.**

# LICHTLEITFASER

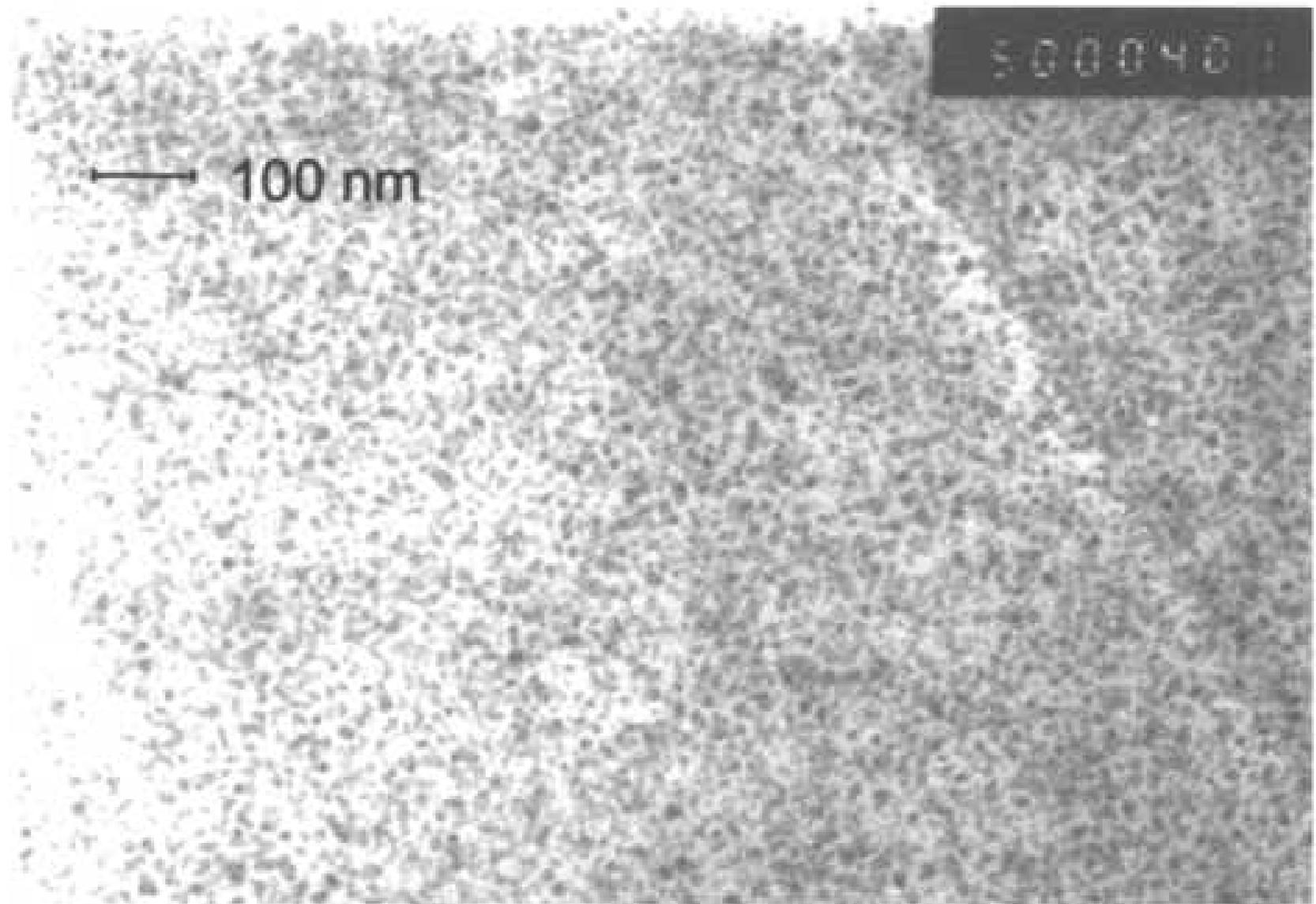


## **Prinzip der Faser-Chip-Kopplung für die optische Nachrichtentechnik**

Classical PMMA-epoxy-copolymeres exhibit several disadvantages:

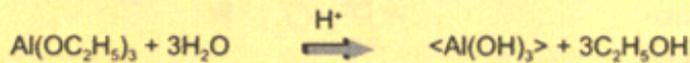
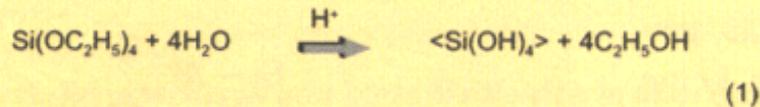
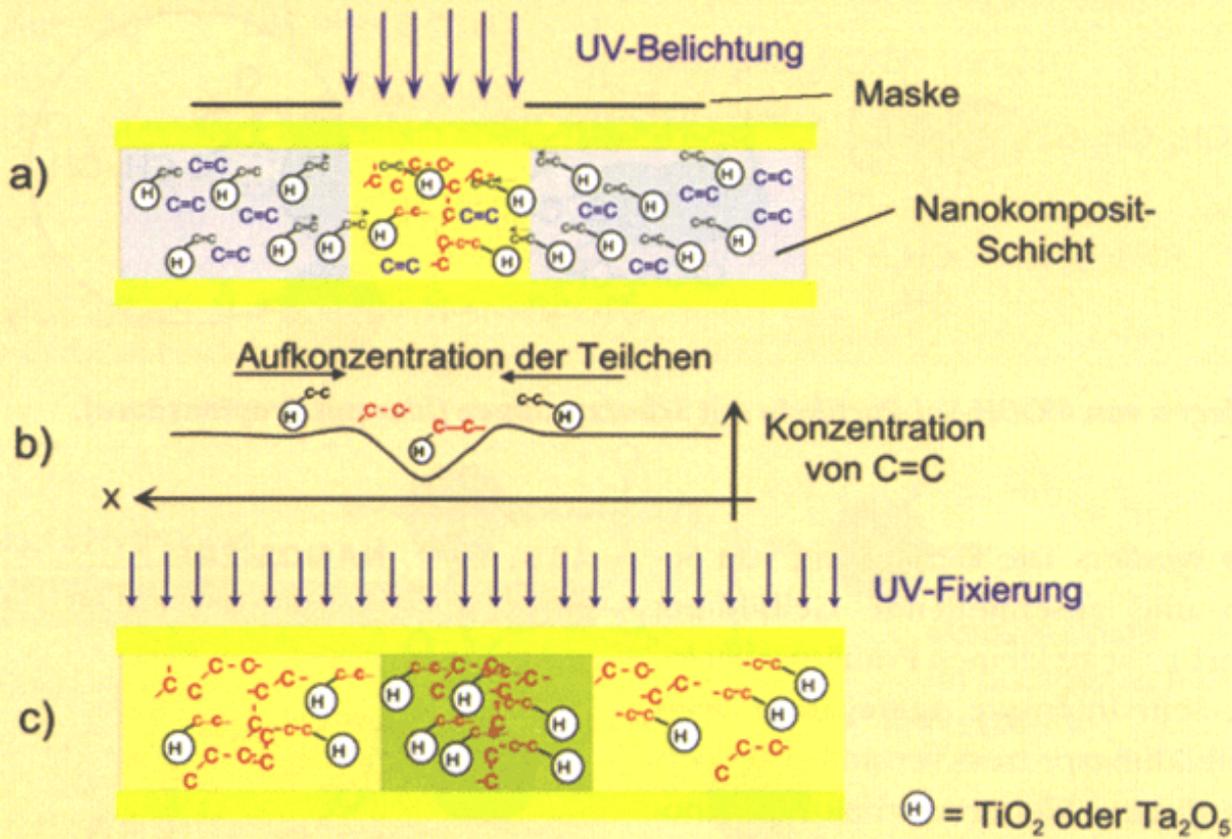
de-justification due to melting,

thermal expansion coefficient is high (expansion during calcination and shrinking during cooling)



**TEM- Aufnahme eines Nanokomposit klebers auf PM-MA-Epoxy copolymerbasis.**

# HOLOGRAMMHHERSTELLUNG



Nanoparticles are coated by polymerisable (epoxy-, methacryloxy-) groups which prevent agglomeration.

Photo-catalyst and radiation induce linking.

If a mask is used, this can be locally controlled  $\rightarrow$  diffusion increases  $\rightarrow$  concentration at these places

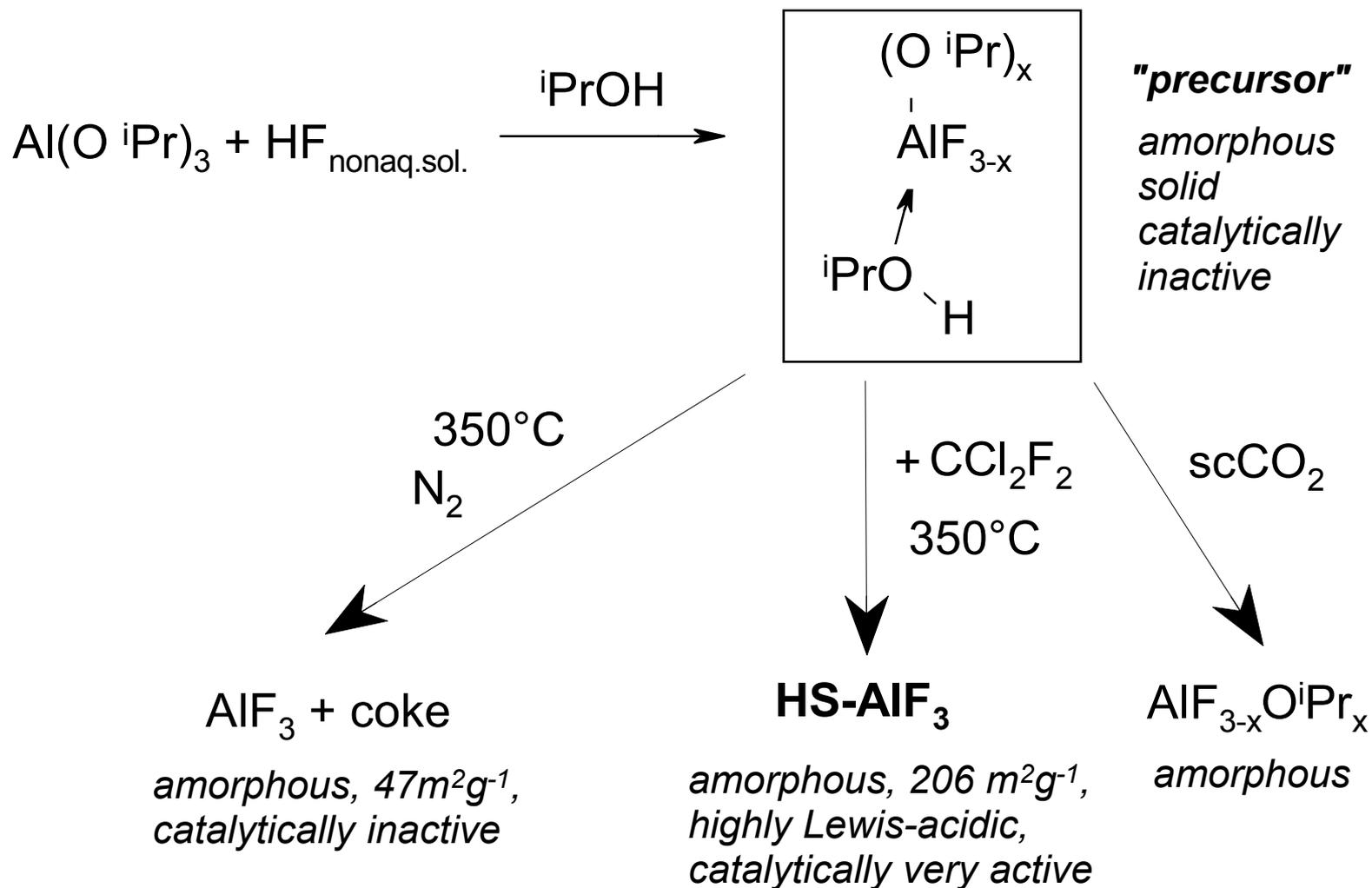
If the materials show different refractions, optical information will be obtained (stored).

**Prinzip der photolithographischen Herstellung von Gittern und Hologrammen über Aufkonzentration von Nanopartikeln.**

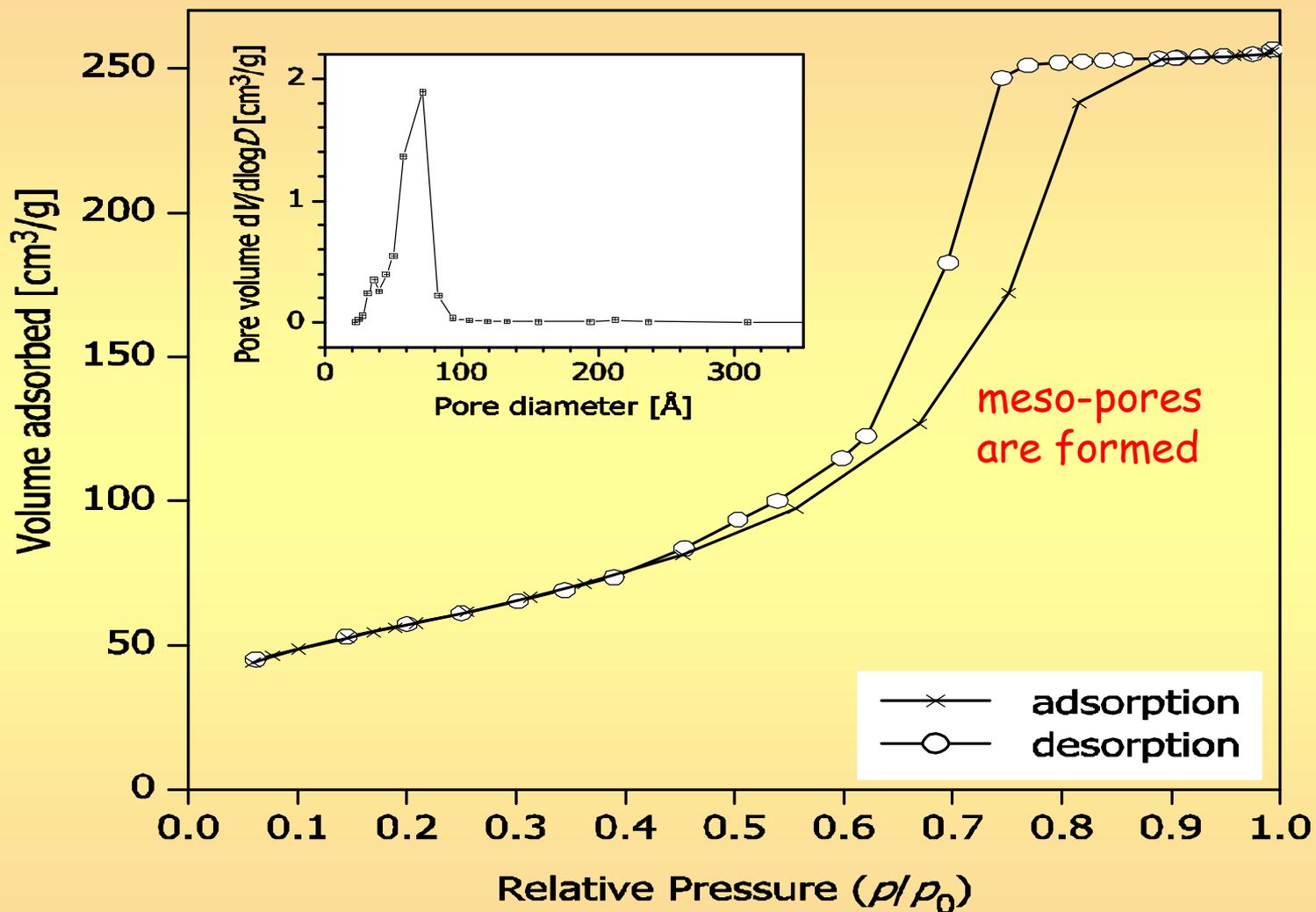
The first example of a non-oxidic Sol-Gel

Metal fluorides with exciting properties

# A new, exciting $\text{AlF}_3$ : High Surface area $\text{AlF}_3$ ( $\text{HS-AlF}_3$ )



# HS-AlF<sub>3</sub>: high specific surface area (ca. 200 m<sup>2</sup>/g)



# HS- $\text{AlF}_3$ : Some properties

Easy to prepare

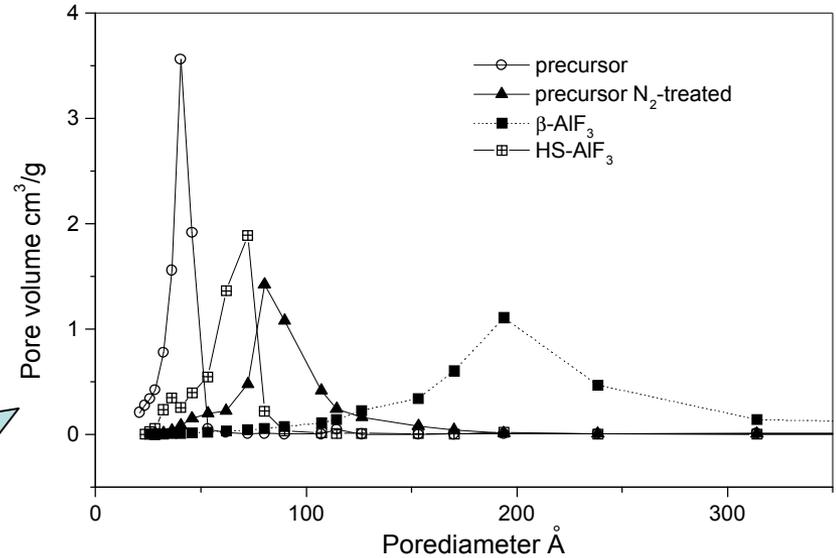
X-ray amorphous

BET- $S_g$ : 200 to 300  $\text{m}^2/\text{g}$

Narrow pore size distribution

XPS: pure  $\text{AlF}_3$  ( $BE_{\text{Al}2p} = 76,3\text{eV}$ ,  $BE_{\text{F}1s} = 686,7\text{eV}$ )

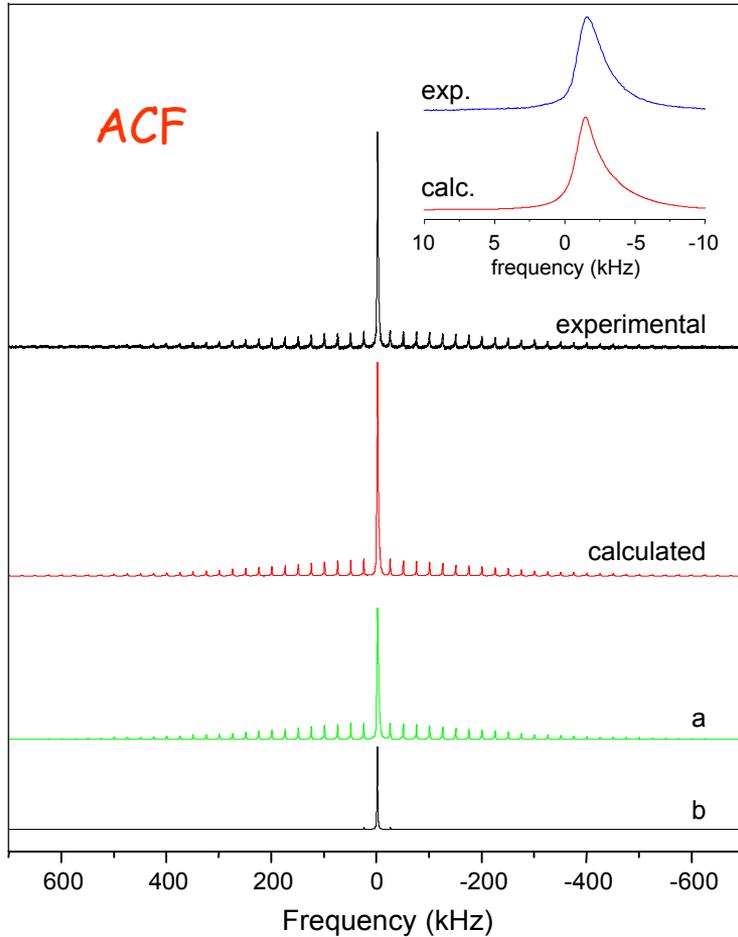
EDX: phase pure (traces of O, ads.  $\text{H}_2\text{O}$ )



Can be stored and handled at open air

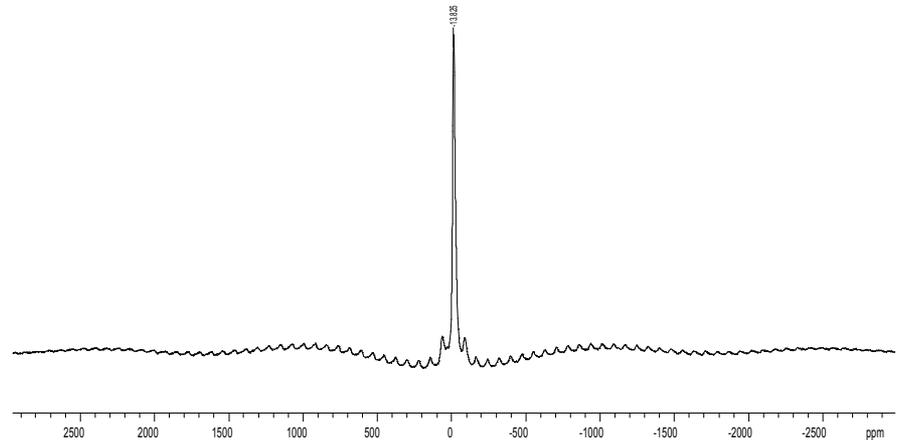
Synthesis can be applied to other metal fluorides

# $^{27}\text{Al}$ MAS-NMR spectra



HS- $\text{AlF}_3$

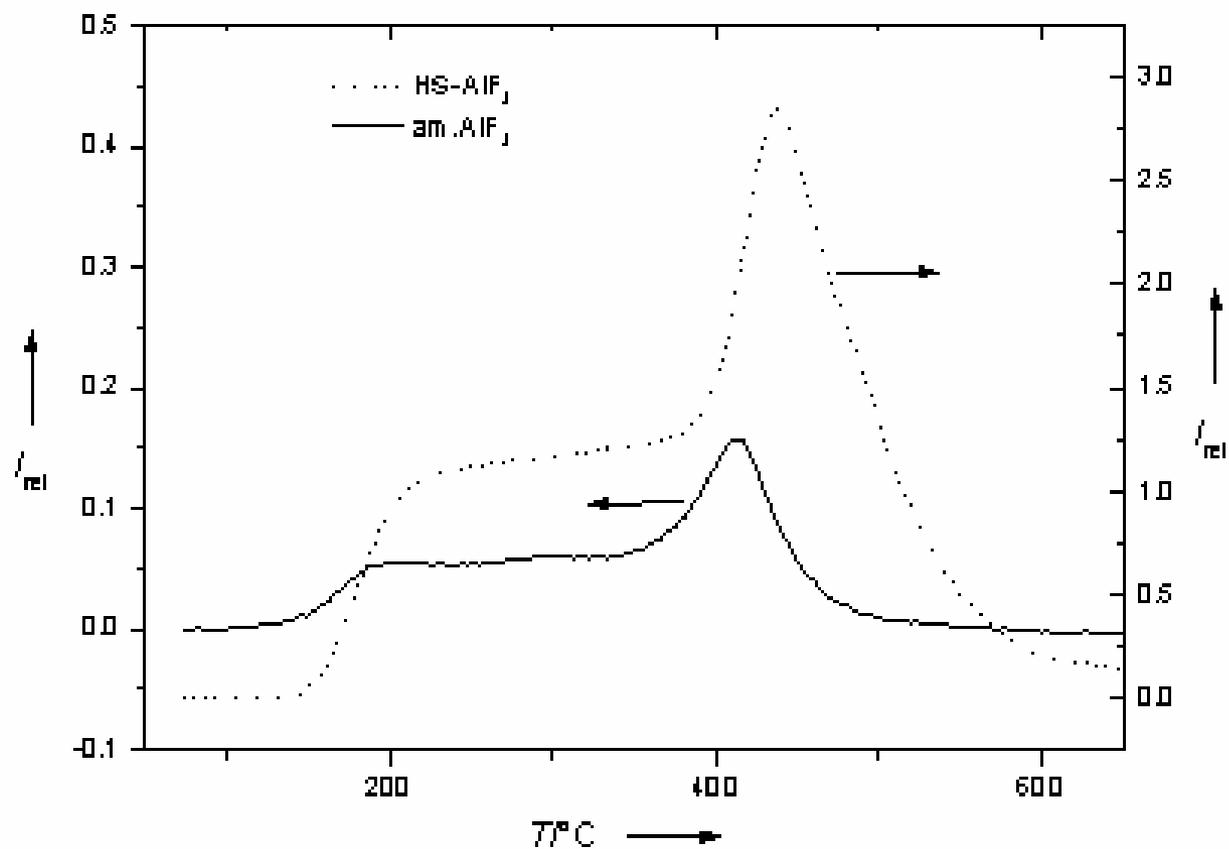
Quadrupolar coupling constant:  $c_Q \sim 1,5$  MHz



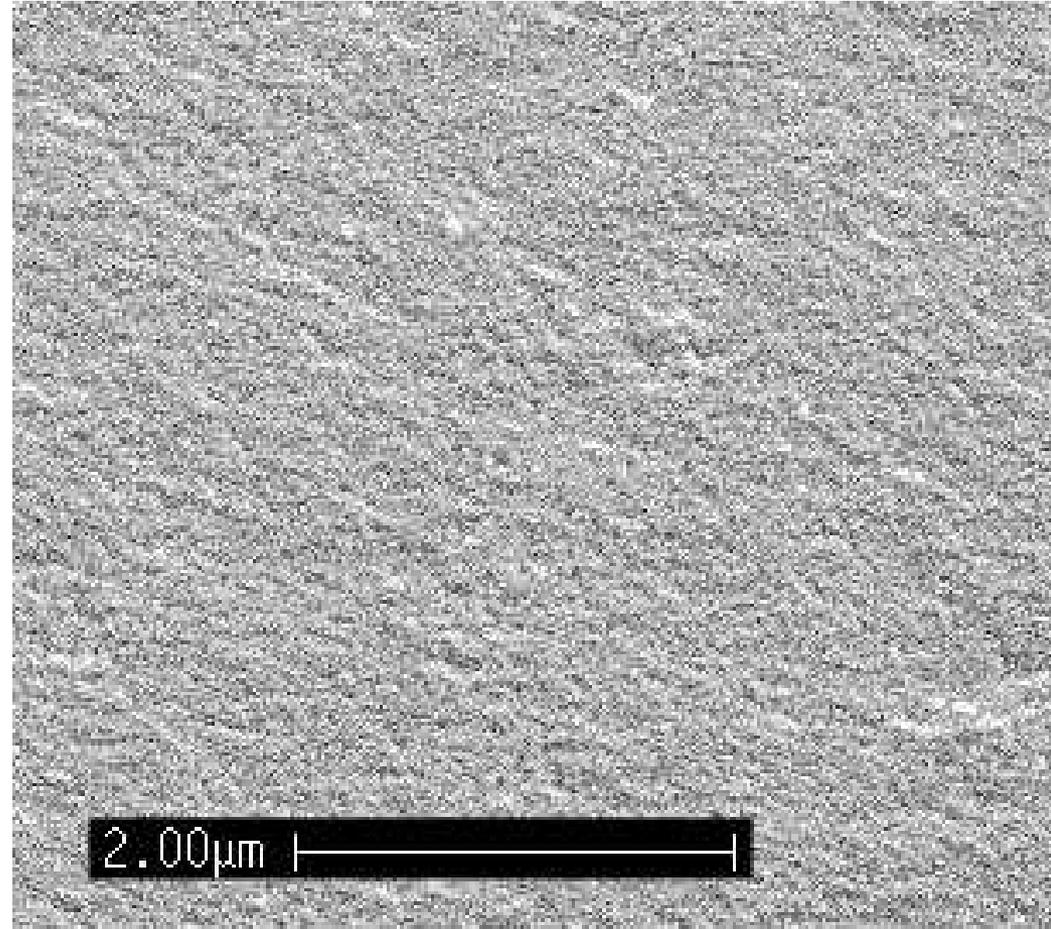
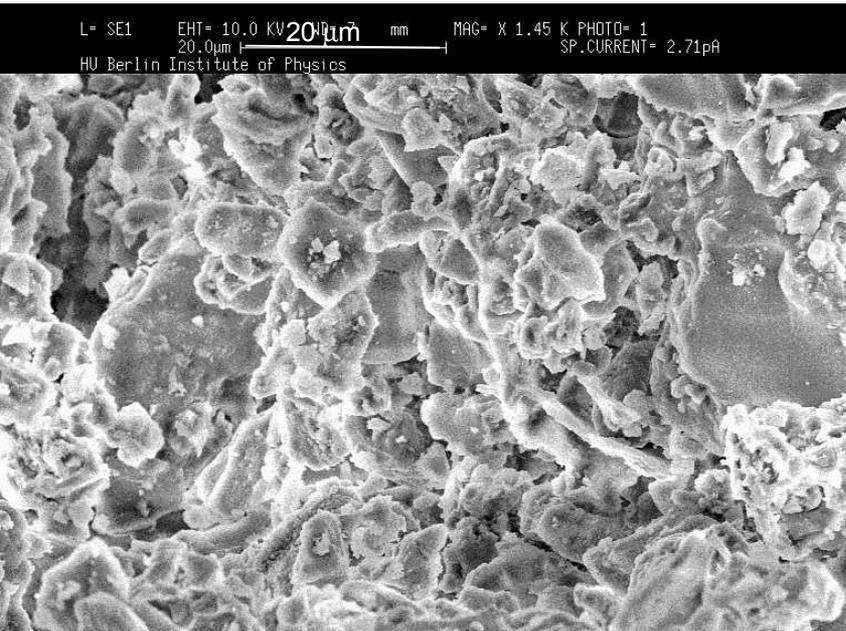
Catalytically highly active (comparable with ACF!)

IR and NMR spectra indicate similar high disordering as in ACF

# HS- $\text{AlF}_3$ : Lewis acidity proved by $\text{NH}_3$ -TPD

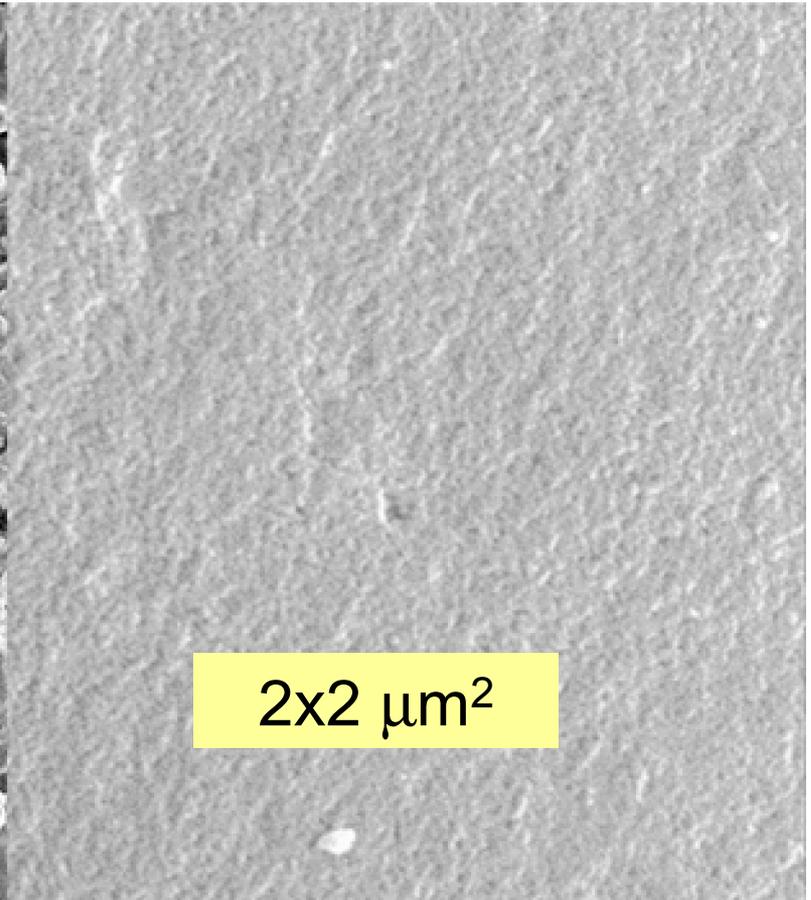
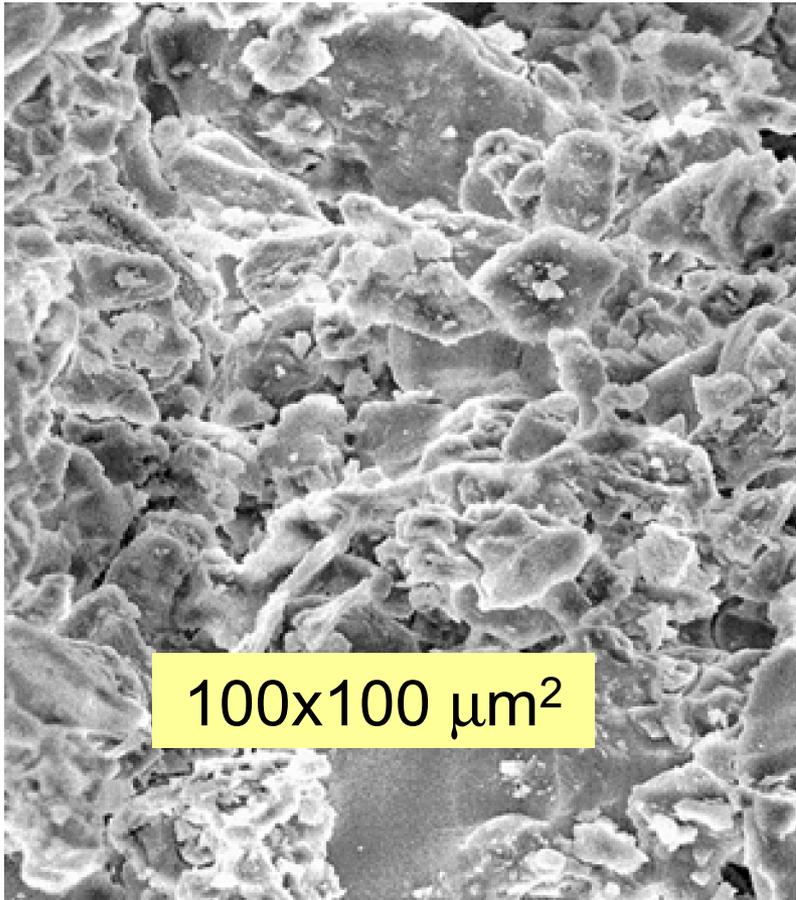


# SEM-scan of HS- $\text{AlF}_3$ (high resolution)



# HS-AlF<sub>3</sub>: Surface morphology

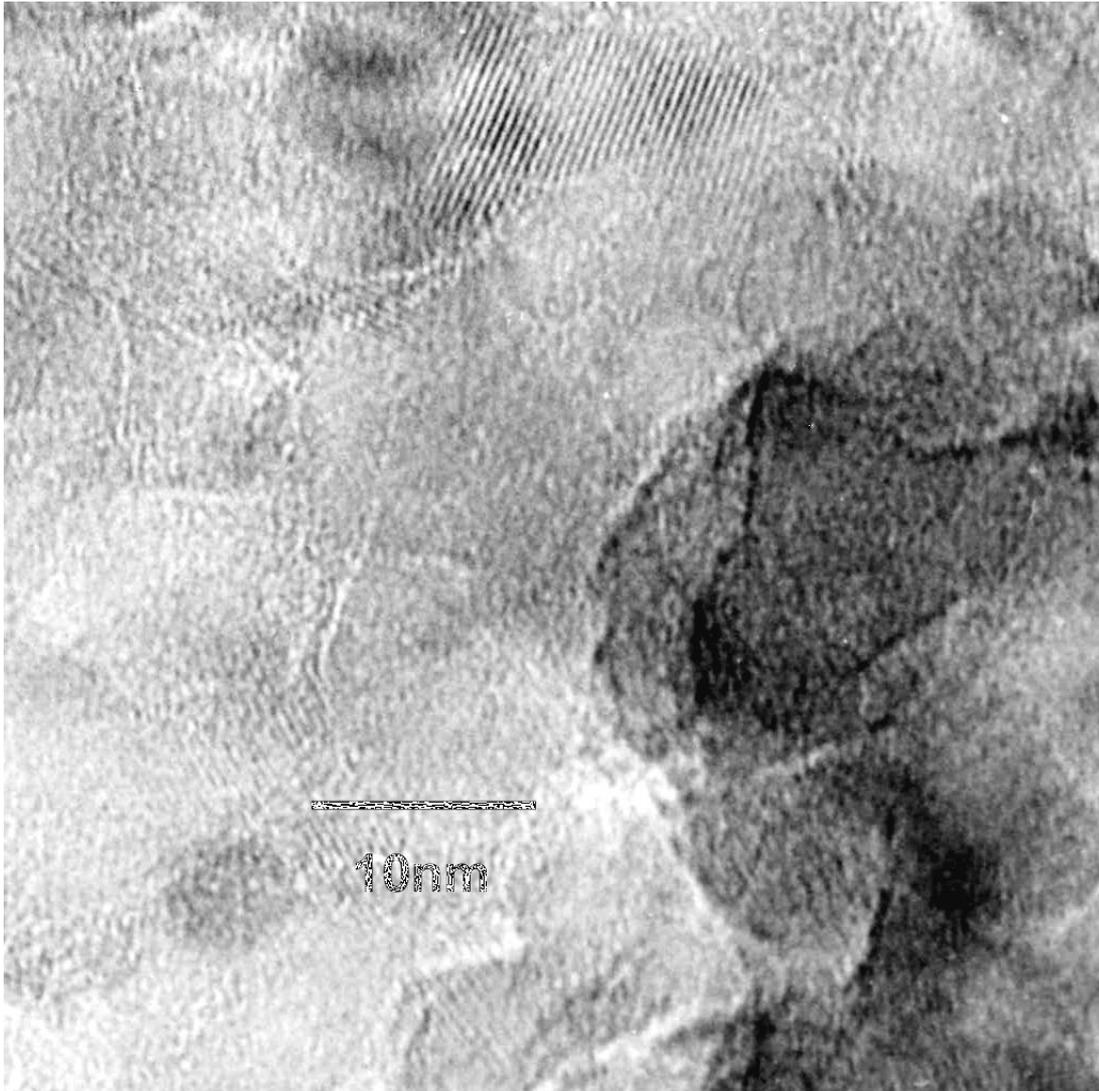
SEM micrographs - high resolution



# Micrograph of HS-AlF<sub>3</sub> obtained by Transmission Electron Microscopy (TEM)

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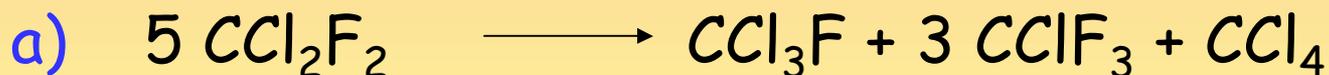
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$d = 3,6 \text{ \AA}$

## HS-AlF<sub>3</sub>: Highly catalytically active

Test reactions used: (a) Dismutation and (b) isomerization



flow system: ca. 0.5 g of catalyst in a Ni tube of 0.5 cm i.d.,  
CCl<sub>2</sub>F<sub>2</sub> flow 2 mL/min, contact time ca. 2 s, on-line GC analysis



(according to V. A. Petrov et al.; reaction proceeds with the strongest known Lewis acids only: SbF<sub>5</sub> and ACF)

batch reaction at room temperature, <sup>19</sup>F-NMR analysis

## HS- $\text{AlF}_3$ : Results of test reactions

### Catalytic activity of selected aluminum fluorides

Sample	$\text{CCl}_2\text{F}_2$ Dismutation [%]				$\text{C}_3\text{Br}_2\text{F}_6$ Isomerization [%]	
Temp[°C]	300	250	200	150	100	25
Precursor	0		0		0	0
<b>HS-<math>\text{AlF}_3</math></b>	<b>96</b>	<b>96</b>	<b>87</b>	<b>59</b>	<b>22</b>	<b>&gt;90</b>
b- $\text{AlF}_3$	93		47			0
$\text{AlF}_3$ *	96	90	55	20	8	5

\*Prepared conventionally, but additionally treated with  $\text{CCl}_2\text{F}_2$  at 350°C