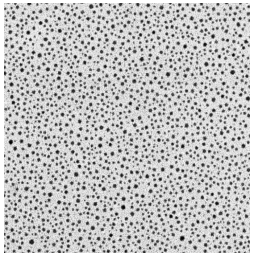
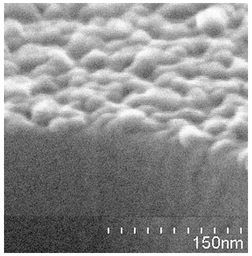
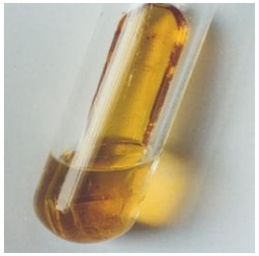
Non-Hydrolytic Sol-Gel



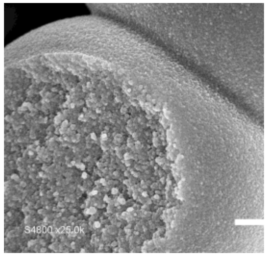
Sol



Film



Gel



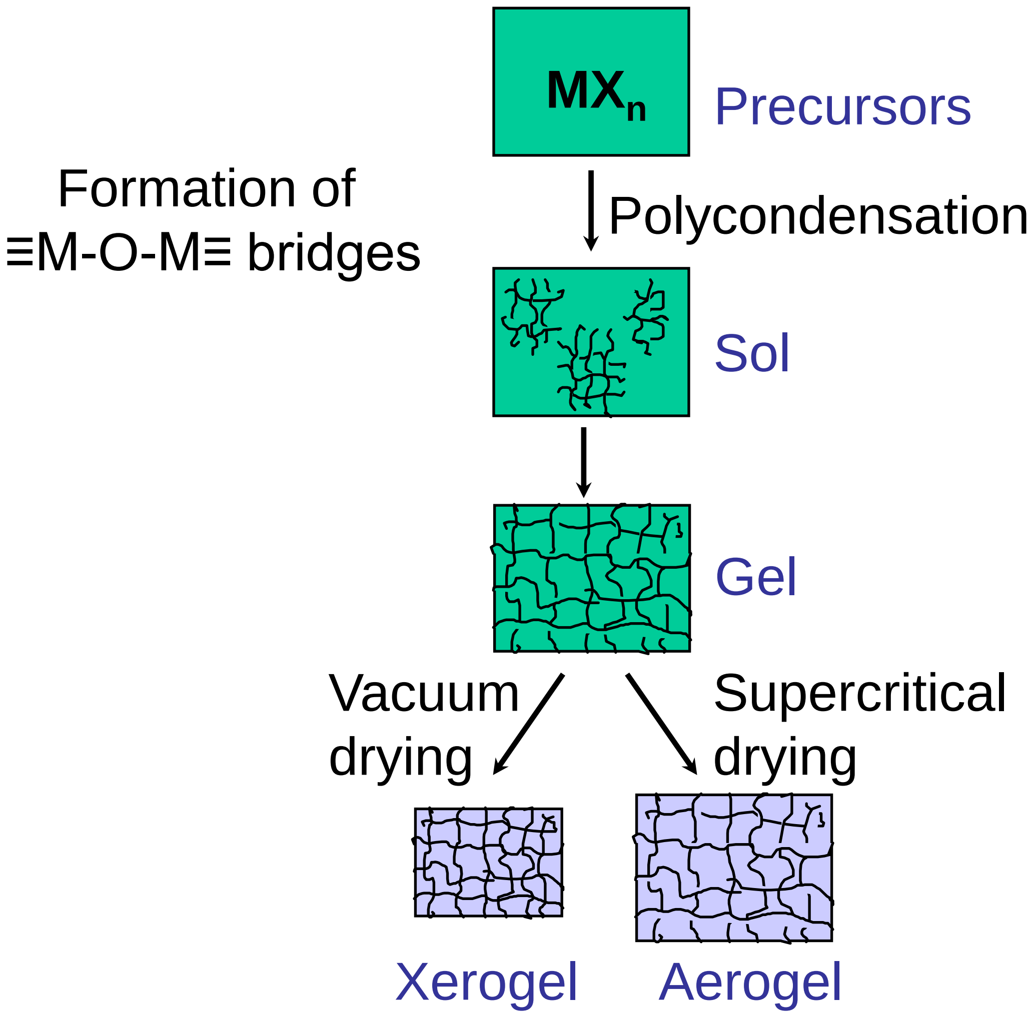
Catalyst

Today

- Principle of sol-gel process
- Non-hydrolytic sol-gel process
- Mixed oxides
- Mesoporous mixed-oxide catalysts
- Nanoparticles by NHSG

Sol-Gel Process

Low-temperature route to oxide materials

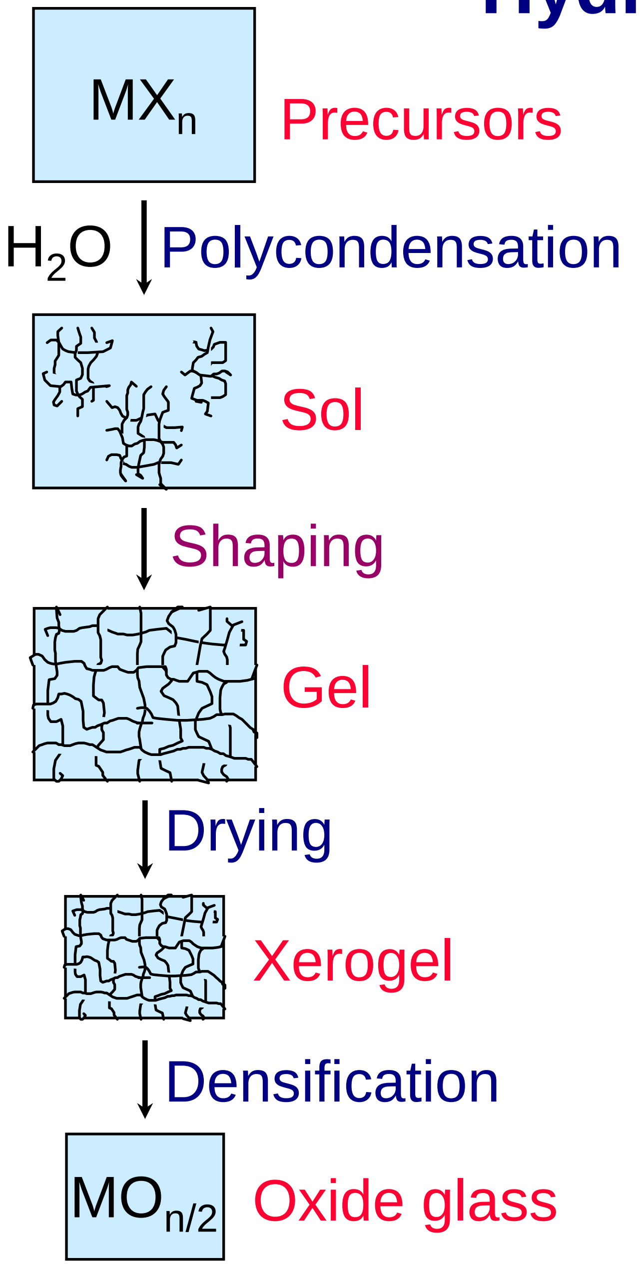


- **Oxides**
- **Mixed-oxides**
- **Organic-inorganic hybrids**

- **Porous solids:**

supports or catalysts

"Hydrolytic" Sol-Gel Process



Hydrolysis of alkoxides

$$\text{M-OR} + H_2O \longrightarrow \text{M-OH} + \text{ROH}$$

Condensation

$$\text{M-OH} + \text{M-OR} \longrightarrow \text{M-O-M} + \text{ROH}$$

$$\text{M-OH} + \text{M-OH} \longrightarrow \text{M-O-M} + H_2O$$

⇒ Oxides, Hybrid Xerogels

Porous oxide materials

Monodisperse powders

Coatings, Fibers, etc.

Dense glass

"Hydrolytic" Sol-Gel Process

SiO_2 $$Si(OEt)_4 \xrightarrow[-EtOH]{H_2O} \text{"}SiO_2\text{ gel"}$$

Silicon alkoxides: low reactivity (catalysis, H^+, OH^-, F^-), easy

⇒ Simple routes to silica and hybrid materials

Metal alkoxides: too reactive

→ Precipitates (amorphous, hydrated oxo-hydroxides)
→ Inhomogeneous mixed oxides

Reactivity modifiers

chelating ligands: carboxylic acids, β-diketonates...

Nonhydrolytic Condensations

completely different condensation reactions

Conventional Sol-Gel process

☹ **Expensive alkoxide precursors**

☹ **Disparity of hydrolysis-condensation rates:** e.g. $M(OR)n \gg Si(OR)_4$

→ Precipitates, heterogeneous mixed oxides

☹ **Low degree of condensation:**

→ Amorphous oxo-hydroxides, microporous materials

⇒ **Complicated, expensive multi-step procedures…**

- prehydrolysis, modified precursors, multi-step acid-base procedures
- templates, supercritical drying

Why not try another reaction?

Non-hydrolytic Sol-Gel process

- **Non-aqueous solvent, no water involved**
- **Based on non-hydrolytic M-Cl/M-OR condensation**

$$\text{M-O-R} + \text{Cl-M} \xrightarrow{T} \boxed{\text{M-O-M}} + \text{RCl} \qquad \text{R = Me, Et, }{}^{i}\text{Pr…}$$

M = Al, B, Fe, Ti, Zr, Nb, V, W, Mo… T = 80 - 150 °C

M = Si: very slow ⇒ catalysis by Lewis acids : $FeCl_3$, $ZrCl_4$…

Fundamentals of Non-Hydrolytic Sol-Gel

- Non-aqueous solvent, no water involved
- Based on non-hydrolytic condensations

$$\text{M-O-R} + \text{R'-CO}_2\text{-M} \longrightarrow \text{M-O-M} + \text{R'CO}_2\text{R}$$

$$\text{M-OAc} + \text{R}_2\text{N-M} \longrightarrow \text{M-O-M} + \text{AcNR}_2$$

$$\text{M-O-R} + \text{R-O-M} \longrightarrow \text{M-O-M} + \text{R}_2\text{O}$$

$$\boxed{\text{M-O-R} + \text{X-M} \longrightarrow \text{M-O-M} + \text{RX}}$$

M = Al, B, Fe, Ti, Zr, Nb, V, W, Mo… R = Me, Et, ^{i}Pr… T = 80 - 150 °C

M = Si: very slow ⇒ catalysis by Lewis acids : $FeCl_3$, $ZrCl_4$…

Non-Hydrolytic Sol-Gel Routes

- **In-situ formation of alkoxide groups:**

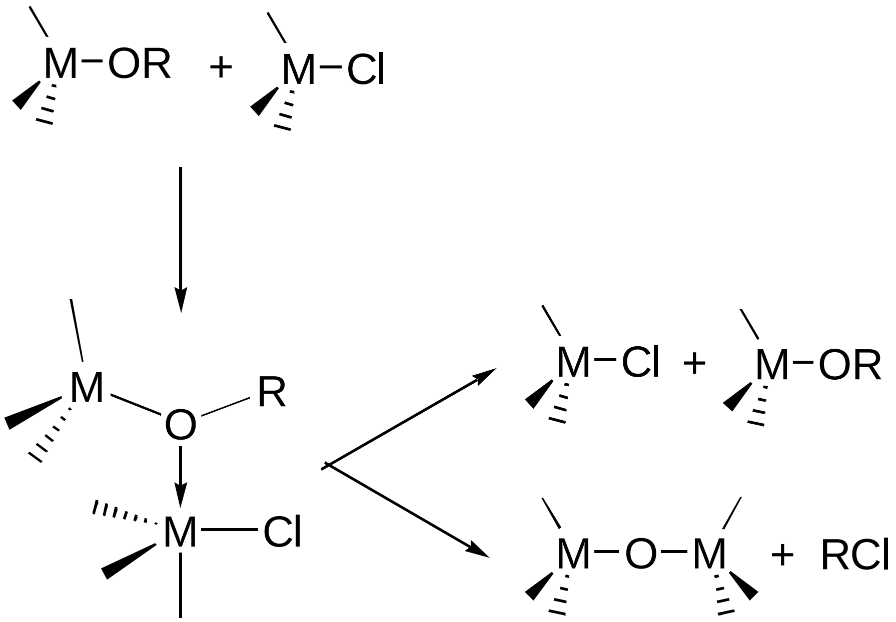
$$\text{M-Cl} + \text{R-O-R} \longrightarrow \text{M-OR} + \text{RCl}$$

$$\text{M-Cl} + \text{R-OH} \longrightarrow \text{M-OR} + \text{HCl} \quad (\text{R} = \text{Et}, {}^{i}\text{Pr})$$

$$\longrightarrow \text{M-OH} + \text{RCl} \quad (\text{R} = {}^{t}\text{Bu}, \text{Bz})$$

- **Alkoxide route** $MCl_n + M(OR)_n \xrightarrow{T} 2\,MO_{n/2} + n\,RCl$
- **Ether route** $MCl_n + n/2\,ROR \xrightarrow{T} MO_{n/2} + n\,RCl$
- **Alcohol route** $MCl_n + n/2\,ROH \xrightarrow{T} MO_{n/2} + n/2\,HCl + n/2\,RCl$

Exchange and condensation reactions



Nucleophilic attack of Cl

- **at M :** exchange (fast)
- **at R :** condensation (slow)

⇒ Precursors = mixture of chloroalkoxides

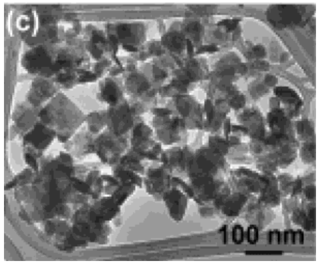
$$\mathrm{TiCl_4 + Ti(O^iPr)_4} \xrightarrow{\textbf{RT}} \mathbf{TiCl_2(O^iPr)_2} + \mathrm{TiCl_3(O^iPr) + TiCl(O^iPr)_3} \xrightarrow[-\,{}^i\mathrm{PrCl}]{\textbf{100 °C}} \mathrm{TiO_2}$$

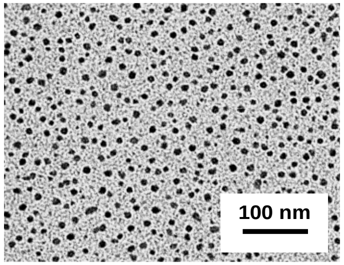
Condensation ⇒ cleavage of O-C bonds instead of O-H bonds

Oxides by Non-Hydrolytic Sol-Gel

- **Crystalline metal oxide nanoparticles:**

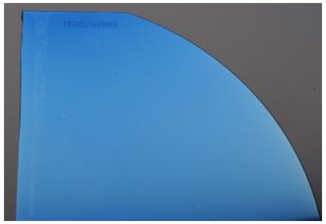
Colvin et al, *J. Am. Chem. Soc.* ***1999,*** *121,* 1613.
Niederberger et al *J. Am. Chem. Soc* ***2002,*** *124,* 13642.
Hyeon et al, *J. Am. Chem. Soc.,* ***2003,*** *125,* 6553.
Mutin et al, *Chem. Mater.* **2010**, *22,* 4519.

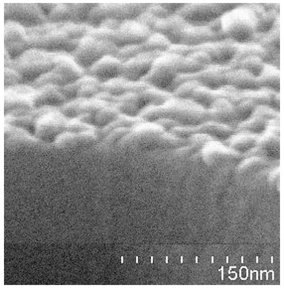




- **Metal oxide thin films:**

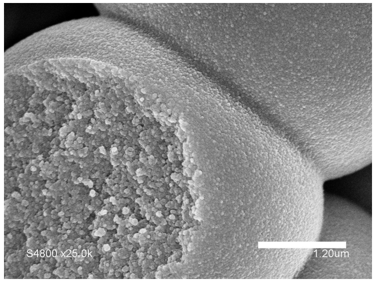
Ritala et al, *Science,* **2000**, *288,* 319.
Mutin et al, *Chem. Mater.* **2009**, *21,* 2577.

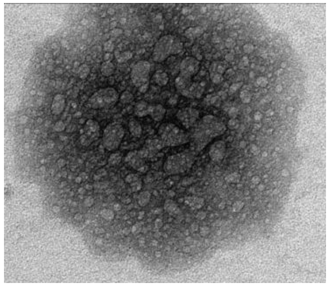




- **Mesoporous mixed oxides:**

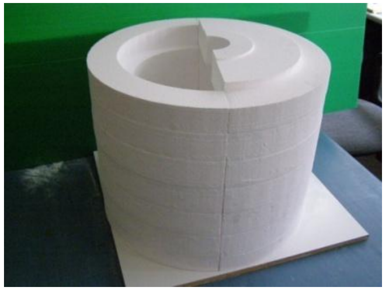
Devillers et al, *Catal. Today* **2003**, *81,* 77
Mutin et al, *Chem. Mater.* **2009,** *21,* 2817
Ricci et al, *Appl. Catal. A* ***2010,*** *389,* 147
Mutin et al, *Chem. Commun.* ***2011,*** 10728





- **Metal oxide foams:**

Grader et al. *Ceram. Trans.,* **1998**, *95,* 161.
US Patent ***2004***, Cellaris Ltd., Israel



Mixed Oxides by Non-Hydrolytic Sol-Gel

1-step reactions, no reactivity modifier:

Alkoxide route: $MCl_n + z\,M'Cl_{n'} + t\,M'(OR)_{n'} \xrightarrow[-RCl]{T} M_xO_{n/2}\,.M'_{(z+t)}O_{n'(z+t)/2}$

Ether route: $MCl_n + z\,M'Cl_{n'} + (n+n'z)/2\,ROR \xrightarrow[-RCl]{T} MO_{n/2}.z\,M'O_{n/2}$

Exchanges ⇒ mixture of chloroalkoxides $MCl_x(OR)_{n-x} + M'Cl_{x'}(OR)_{n'-x'}$

⇒ M—O—M’ + M—O—M + M’—O—M’

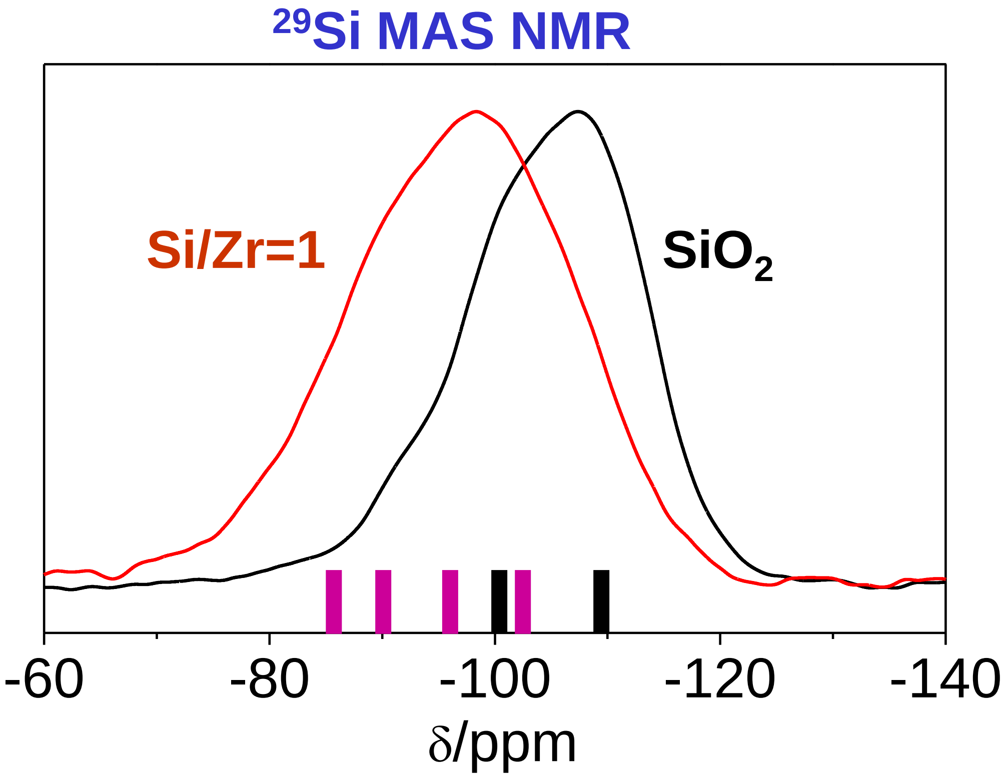
SiO_2-MO_x systems: condensations around Si catalyzed by M species:

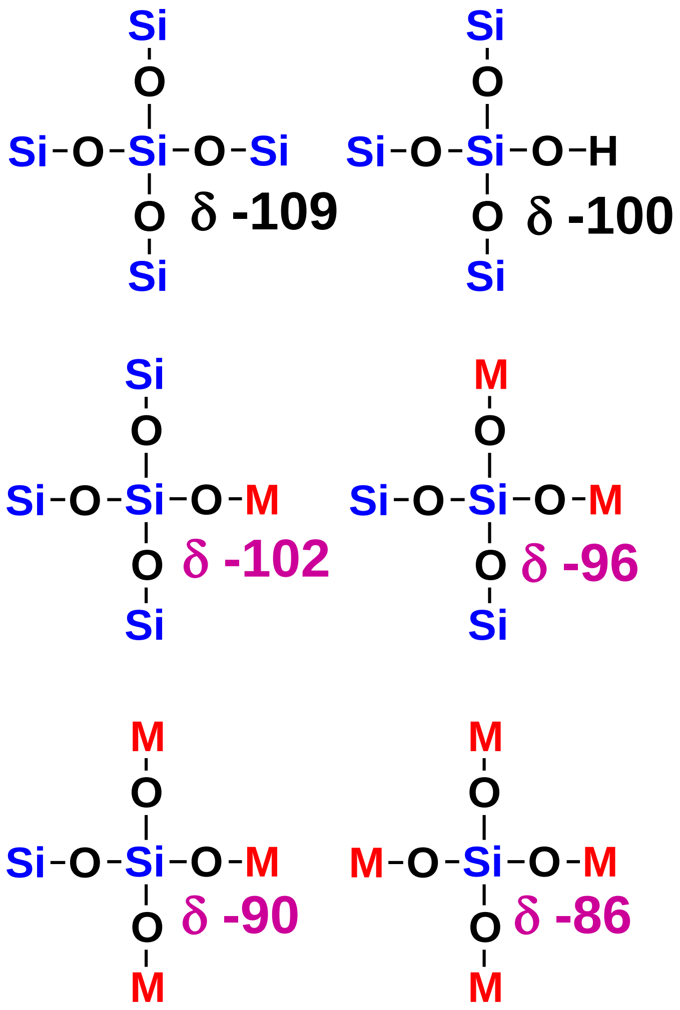
→ levelling of reactivities around Si and M

→ **Highly homogeneous xerogels**

Nonhydrolytic SiO_2 – ZrO_2

$$Si(O^iPr)_4 + ZrCl_4 \xrightarrow[CH_2Cl_2]{110°C} \xrightarrow[Air]{500°C,\ 5h}$$



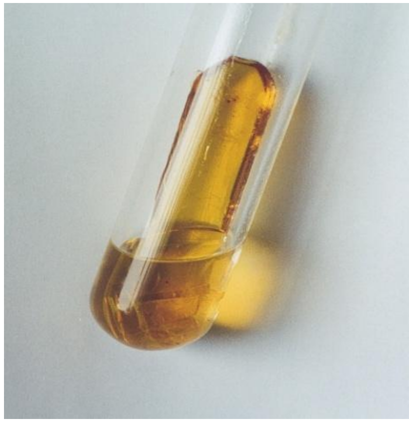


⇒ **Si-O-Zr bonds, homogeneous**

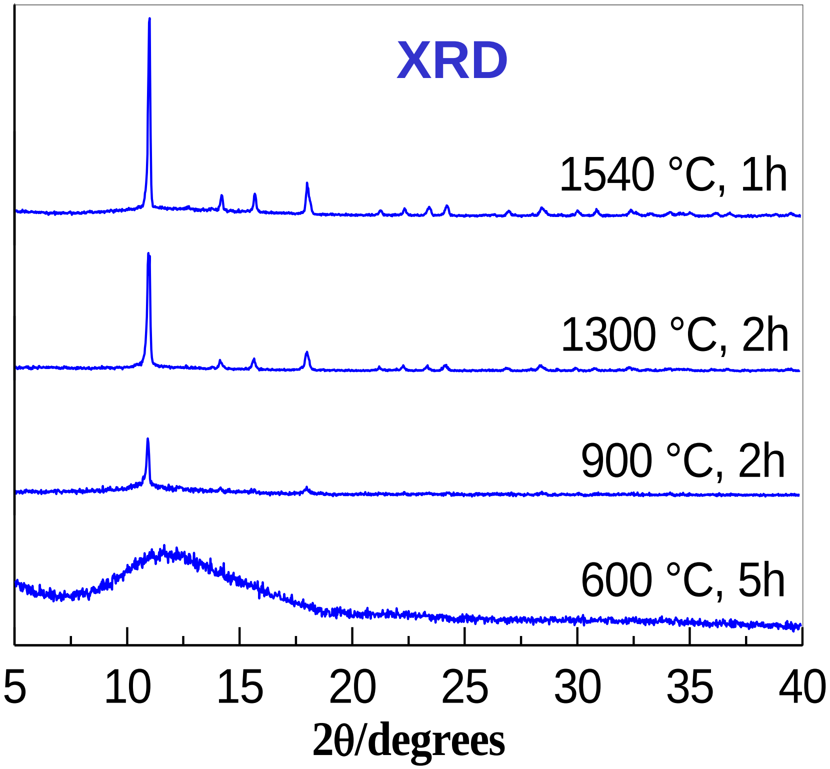
J. Mater. Chem. **1996** 6, 10

Structure of nonhydrolytic TiO_2-SiO_2

$$10\ SiCl_4 + 9\ Si(O^iPr)_4 + Ti(O^iPr)_4 \xrightarrow{110°C}$$



$$\xrightarrow{calcination}$$



Solid solution

Single phase cristobalite

Random subst. of Si by Ti

Tetragonal unit

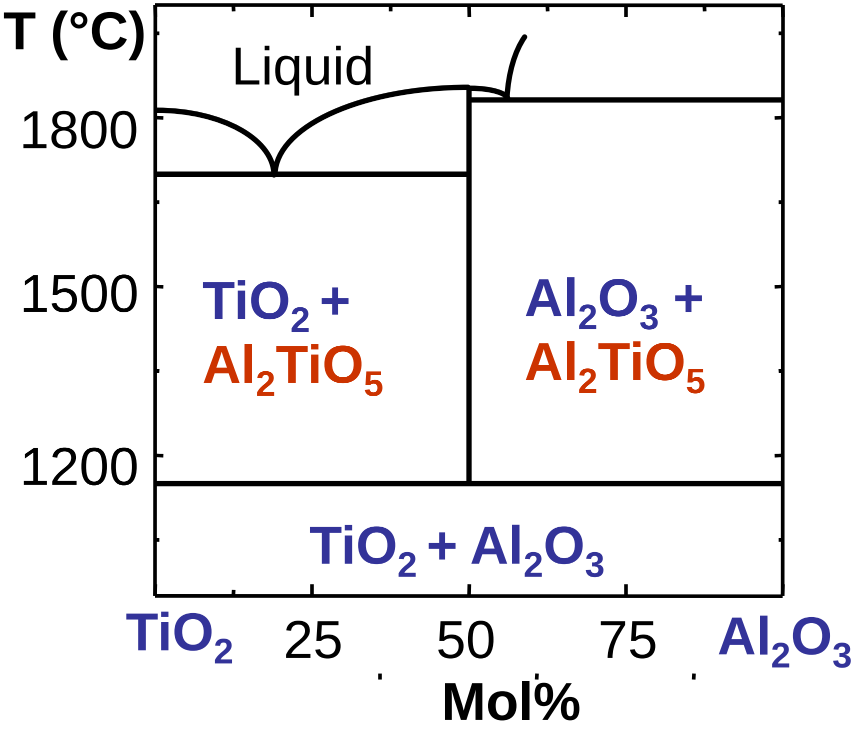
a = 5.00 Å   (SiO_2: 4.97 Å)

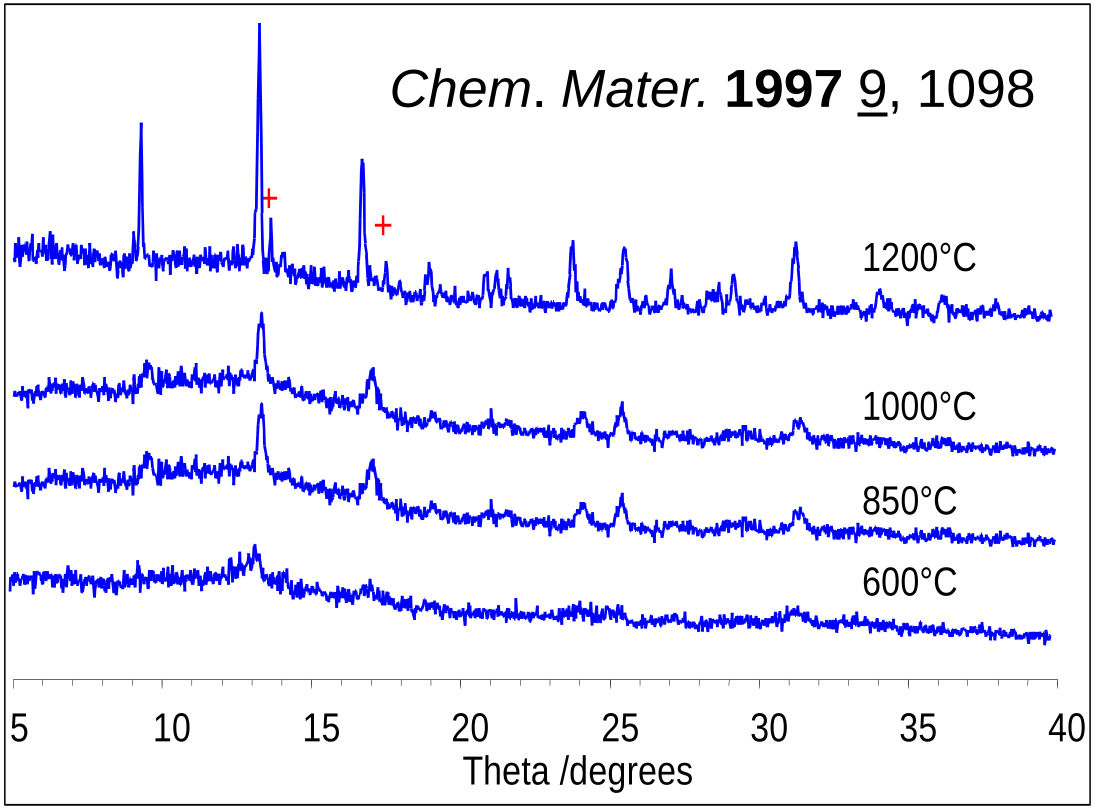
c = 6.98 Å   (SiO_2: 6.93 Å)

J. Mater. Chem. **1996** 6, 10

Al_2O_3 – TiO_2 system

$$2\ AlCl_3 + TiCl_4 + 5\ {}^iPr_2O \xrightarrow[CH_2Cl_2]{110°C} \xrightarrow[Air]{T\ °C,\ 5h}$$





Powder XRD

Chem. Mater. **1997** 9, 1098

SGNH: Direct crystn of

β-Al_2TiO_5 at 600 °C!

SiO_2-TiO_2 mild oxidation catalysts

Hydrolytic sol-gel:

simultaneous control of Ti dispersion and texture difficult

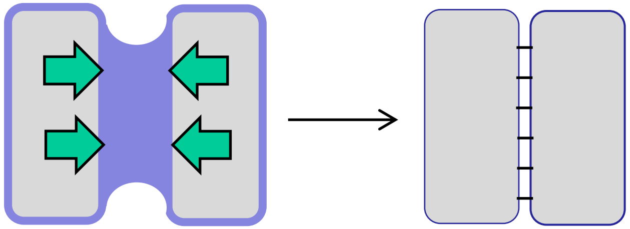
→ complicated, multi-step procedures

- **Ti dispersion**: **reaction rates around Ti >> Si**

  → *Ti precursor modification, pre-hydrolysis,* ***acidic conditions***

- **Texture:** evaporative drying

  → **high capillary pressure Pc**



acidic conditions → low degree of condensation

→ pore collapse → **microporous xerogels**

Brinker, C. J.; Scherer, G. W. *Sol-gel Science1990.*

Hutter, R.; Mallat, T.; Baiker, A. *J. Catal.* ***1995***, *157*, 665.

Klein, S.; Thorimbert, S.; Maier, W. F. *J. Catal.* ***1996, 163, 476.***

SiO_2-TiO_2 mild oxidation catalysts

- **Avoiding pore collapse**

⇒ templates, supercritical drying: *expensive...*

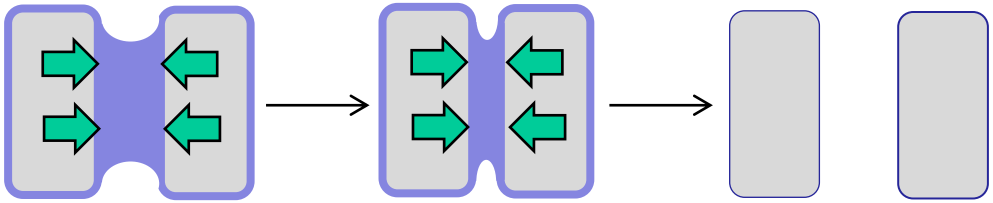
⇒ solvent exchange with **hexane** + **silylation**:

$Pc = -2\gamma\cos\theta/r$ γ : surface tension; θ: contact angle; r: pore radius

$\gamma_{\mathbf{hexane}}$ 18.4 mN/m < γ_{water} 72.8 mN/m → **decreases Pc**

silylation: OH surface groups replaced by $OSiMe_3$

→ no H-bonding, no condensation → **reversible shrinkage**



Prakash et al. *Nature* **1995**, 439

Sotelo et al. *Chem. Comm.* **1999**, 549

"Non-hydrolytic" SiO_2-TiO_2

Etherolysis:

$$\equiv M\text{-}Cl + {}^{i}Pr\text{-}O\text{-}{}^{i}Pr \longrightarrow \equiv M\text{-}O{}^{i}Pr + {}^{i}PrCl$$

Condensation:

$$\equiv M–O–{}^{i}Pr + \equiv M–Cl \longrightarrow \equiv M–O–M\equiv + {}^{i}PrCl$$

M = Ti: easily controllable kinetics, condensation at 80-150 °C

M = Si: very slow but *condensations catalyzed by Ti species*

→ **homogeneous mixed oxide xerogels even for SiO_2-MO_x systems**

no need for multi-step procedures or complicated precursors

Irreversible condensation → **very high condensation degrees** up to 90%

Chem. Mater. **2004,** 16, 5380

"Non-hydrolytic" SiO_2-TiO_2

Liquid phase: $^{i}PrCl + CH_2Cl_2$

$\gamma_{^{i}PrCl}$: 24 mN/m $\gamma_{CH_2Cl_2}$: 26.5 mN/m $<$ γ_{H_2O} : 72.8 mN/m

→ **low capillary pressure**

Surface groups: no OH, only Cl and OiPr

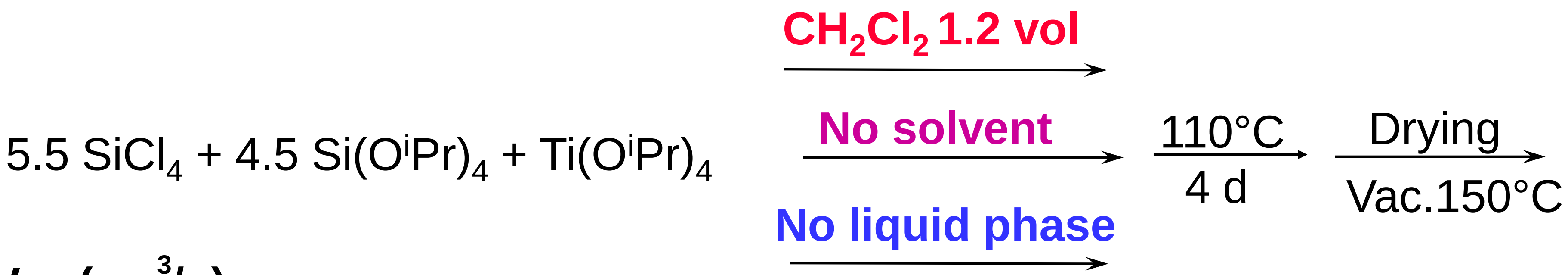
no H-bonds, no condensation at ambient T:

→ **reversible shrinkage**

No need for solvent exchange and silylation

→ **mesoporous xerogels if the degree of condensation is high enough**

NH SiO_2-TiO_2: control of texture

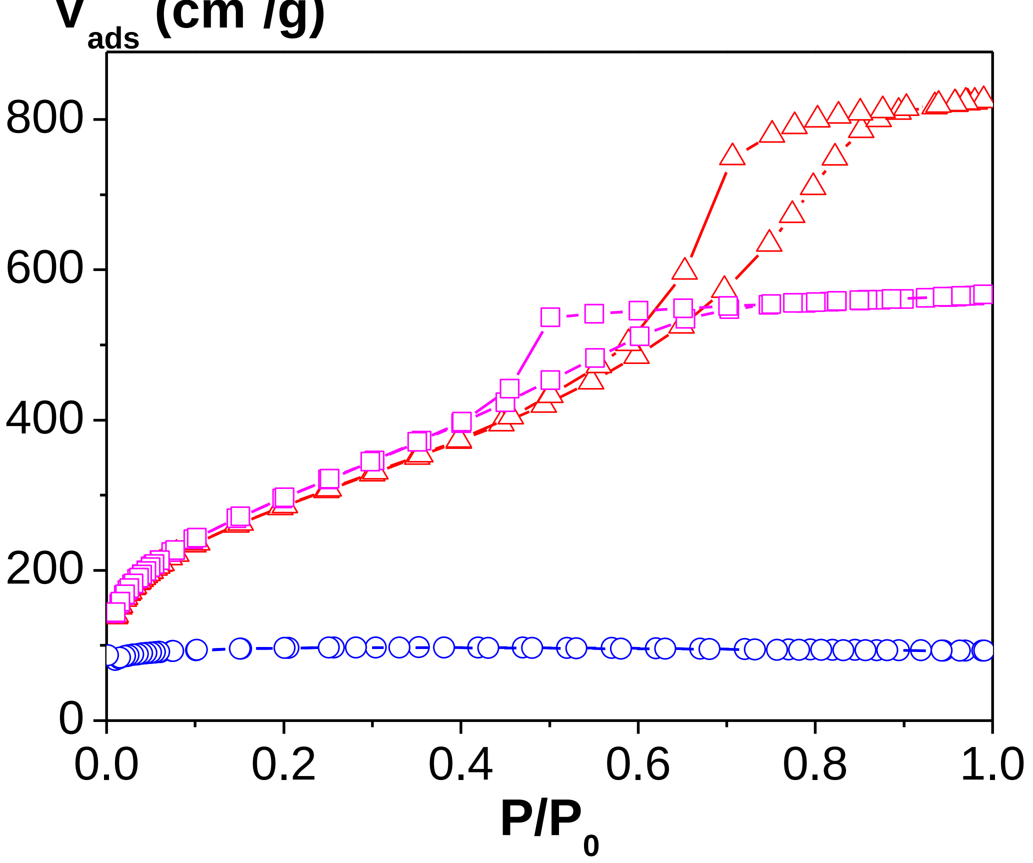


CH_2Cl_2 1.2 vol

No solvent

No liquid phase

$5.5\ SiCl_4 + 4.5\ Si(O^iPr)_4 + Ti(O^iPr)_4 \longrightarrow \xrightarrow[4\ d]{110°C} \xrightarrow[Vac.150°C]{Drying}$



S_{BET}	V_P	D_P
1030 m²/g	**1.3 cm³/g**	**50 Å**
1080 m²/g	**0.9 cm³/g**	**33 Å**
450 m²/g	**0.24 cm³/g**	**21 Å**

Chem. Mater. **2004** 16 5380

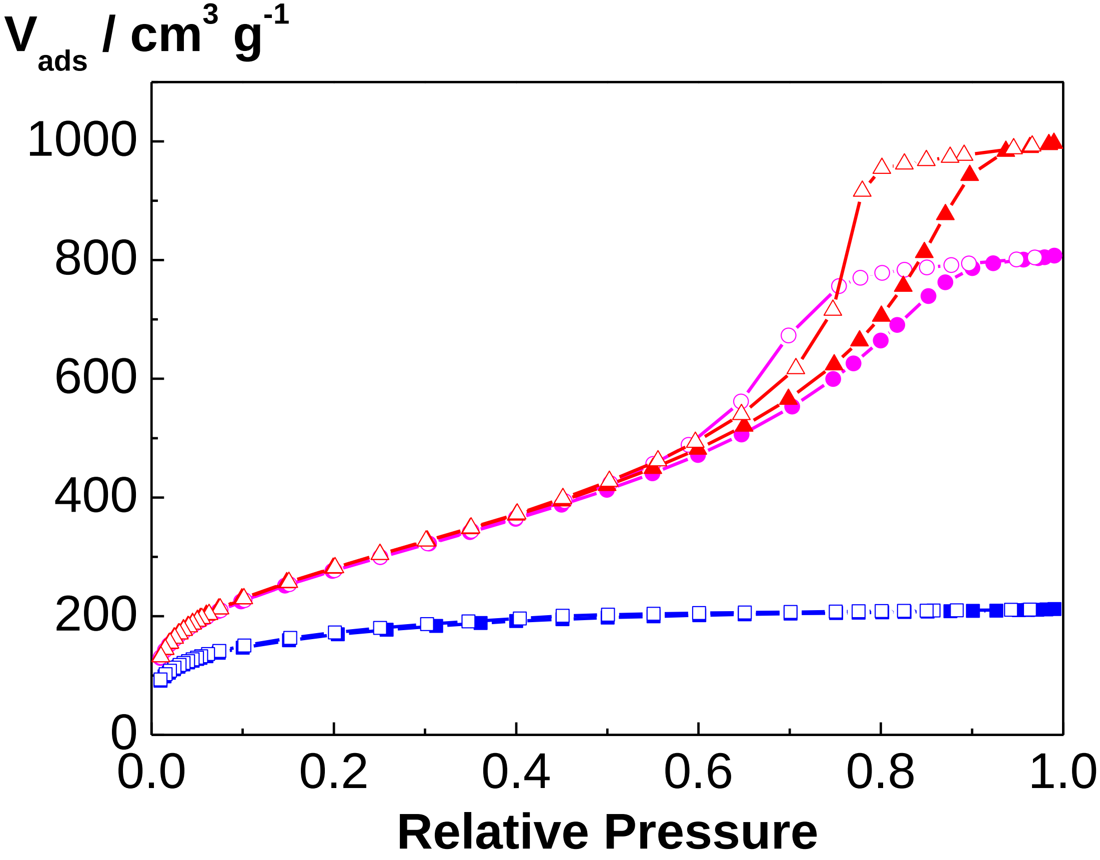
Control of texture: Si/Ti ratio and reaction temperature

Si/Ti=7.5 $7.5\ SiCl_4 + TiCl_4 + 17\ {}^iPr_2O \xrightarrow{110°C}$

Si/Ti=17 $17\ SiCl_4 + TiCl_4 + 35\ {}^iPr_2O \xrightarrow{110°C}$

Si/Ti=17 $17\ SiCl_4 + TiCl_4 + 35\ {}^iPr_2O \xrightarrow{150°C}$

$\xrightarrow[\text{Vac.150°C}]{\text{Drying}}$



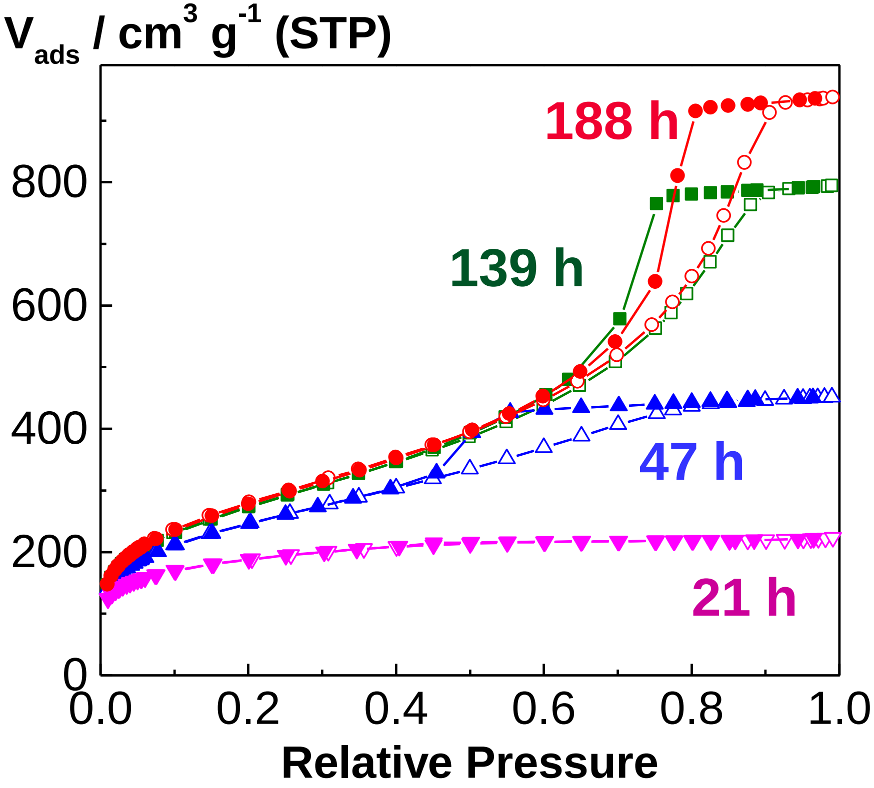
1030 m^2/g 1.5 cm^3/g 61 Å

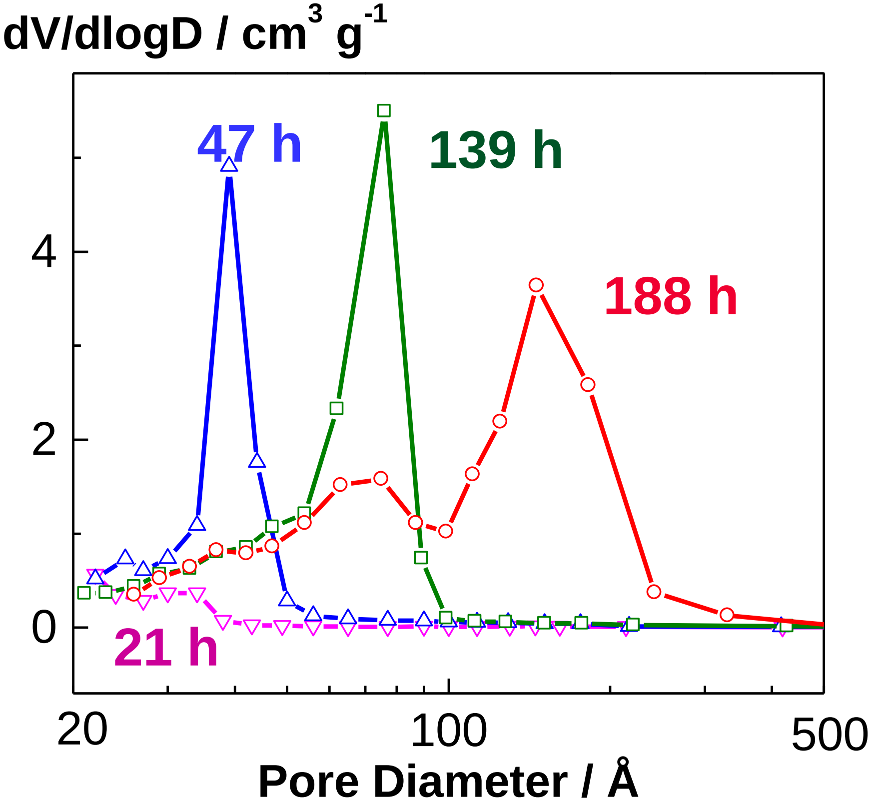
1000 m^2/g 1.3 cm^3/g 50 Å

550 m^2/g 0.3 cm^3/g 24 Å

NH SiO_2-TiO_2 : control of texture

$$10\ SiCl_4 + TiCl_4 + 22\ {}^{i}Pr_2O \xrightarrow[\text{21 to 188 h}]{\text{110°C}} \xrightarrow[\text{Vac.150°C}]{\text{Drying}}$$





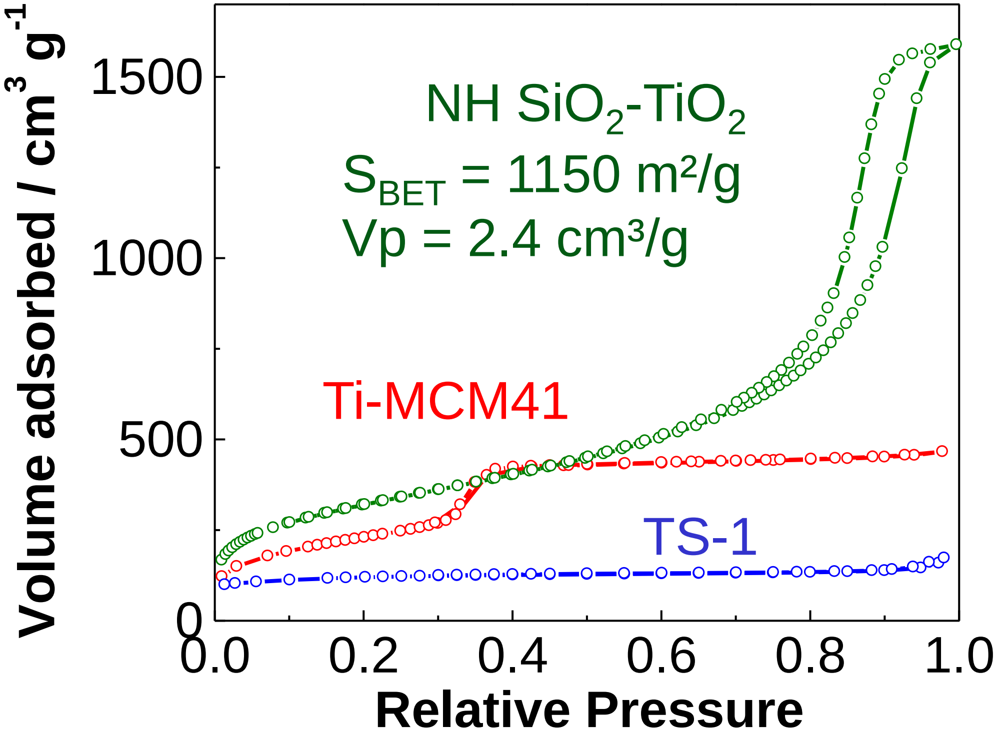
From 590 m^2/g, 0.3 cm^3/g to 980 m^2/g, 1.5 cm^3/g

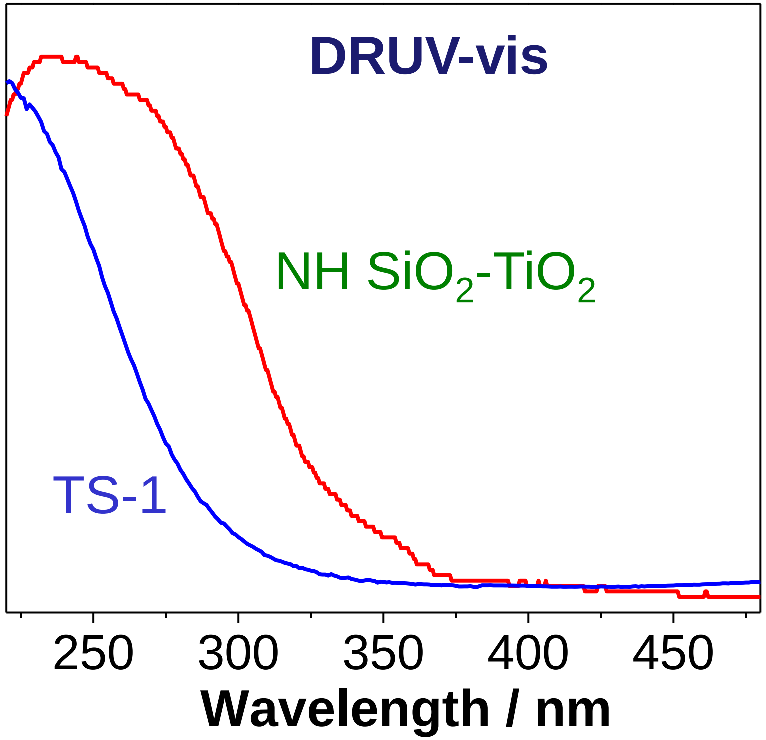
Chem. Mater. **2004** 16 5380

Application as oxidation catalysts

Collaboration Vasile Hulea (MACS-ICGM), Emil Dumitriu (Iasi, Romania)

$$16\ SiCl_4 + TiCl_4 + 34\ {}^{i}Pr_2O \xrightarrow[CH_2Cl_2]{150\ ^{\circ}C,\ 6d} \xrightarrow[150^{\circ}C,\ 3h]{\text{Vacuum drying}} \xrightarrow[\text{Air},\ 500^{\circ}C,\ 5h]{\text{Calcination}}$$



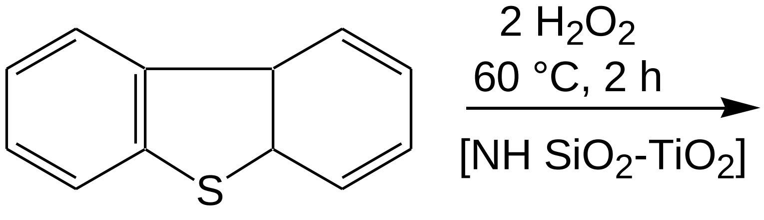


3.3 wt%Ti, outstanding texture, good Ti dispersion

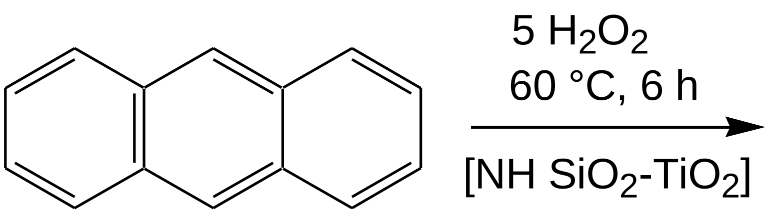
Chem. Commun., **2008**, 5357

SiO_2-TiO_2 oxidation catalysts

Oxidation of bulky compounds by aq. H_2O_2 (0.1 M)



DBTS>99 %
97% conv. in 2 h
98% H_2O_2 efficiency
TOF: 21 h^{-1} (TS1: 3 h^{-1})



AQ>95%
92% conv. in 6 h
91% H_2O_2 efficiency

- **accomodates very bulky substrates**
- **good activity, excellent H_2O_2 efficiency, reusable (>>Ti-MCM41)**

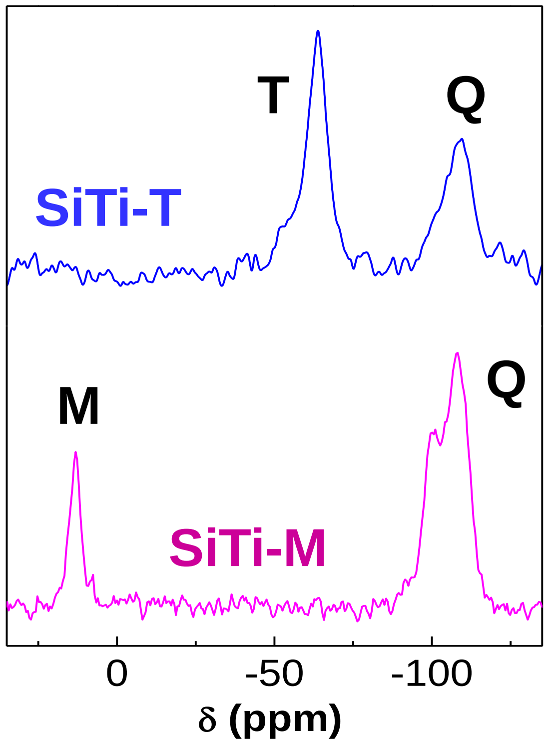
Chem. Comm. **2008**, 5357; *Appl. Catal., B* **2010**, 97, 407

Hybrid SiO_2-TiO_2 epoxidation catalysts

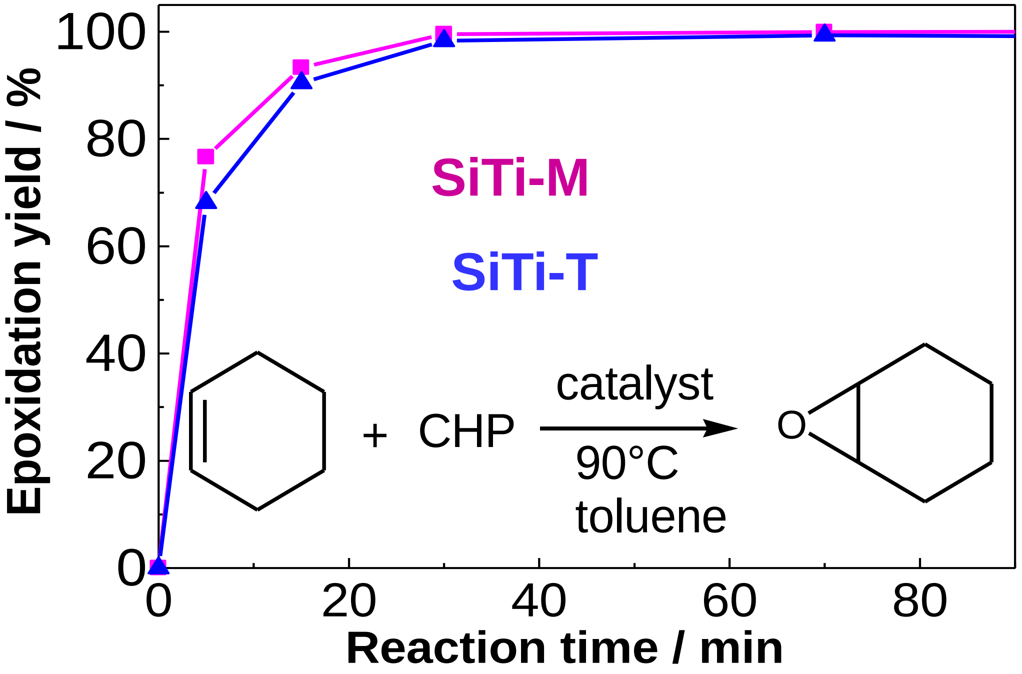
$TiCl_4 + 6\ MeSiCl_3 + 4\ SiCl_4 + 19\ {}^{i}Pr_2O \xrightarrow{110°C}$ **SiTi-T** 1060m²/g 1.3 cm³/g

$TiCl_4 + 2\ Me_3SiCl + 8\ SiCl_4 + 19\ {}^{i}Pr_2O \xrightarrow{110°C}$ **SiTi-M** 930 m²/g 0.7 cm³/g

^{29}Si MAS-NMR



Epoxidation test



Excellent activity, selectivity >99 %

WO**2005**049626; *Chem. Mater.* **2006,***18***,** 4707

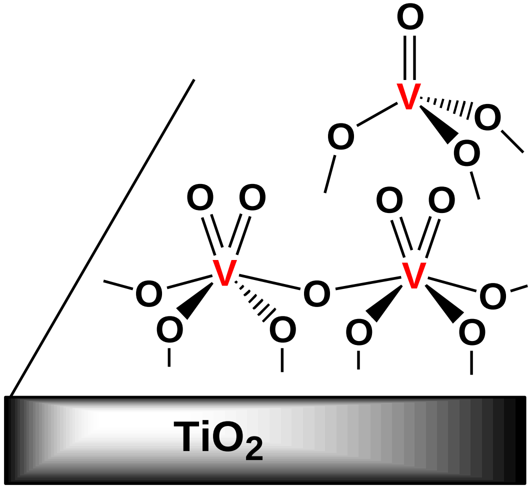
TiO_2-V_2O_5 catalysts

- Selective Catalytic Reduction of NOx by NH_3
- Selective oxidation of H_2S
- Total oxidation of Volatile Organic Compounds
- Oxidative dehydrogenation of propane

Conventional catalysts:

impregnation of TiO_2-anatase supports

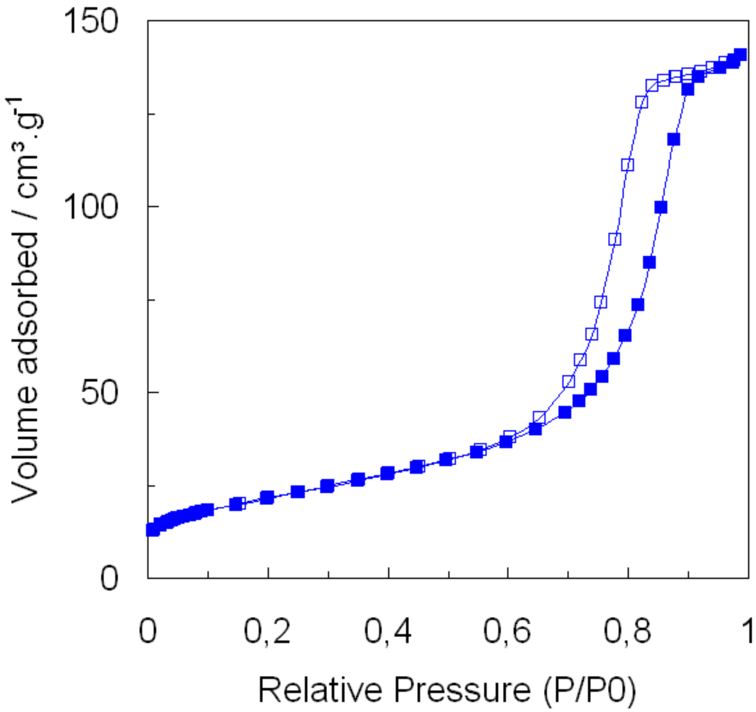
→ monolayer of vanadate species

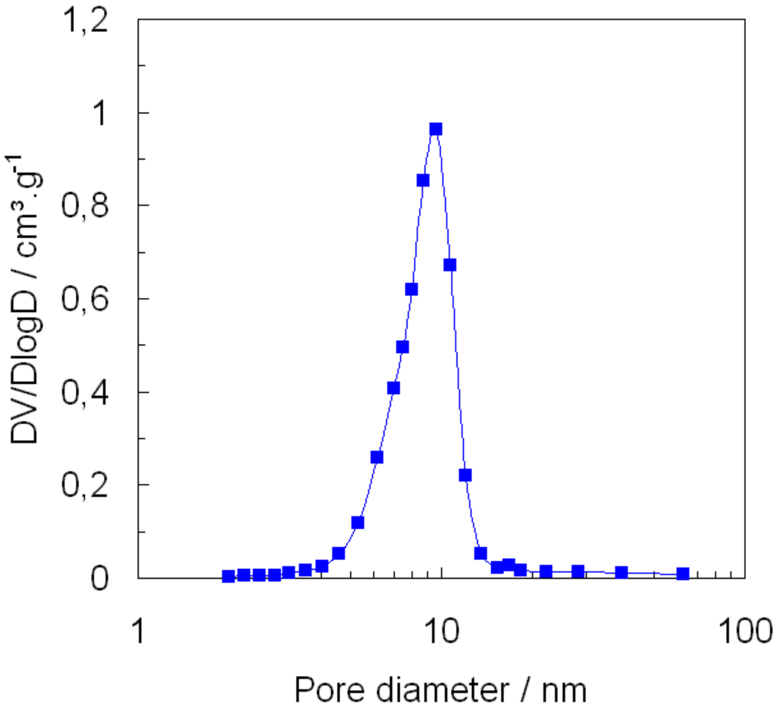


TiO_2-V_2O_5 catalysts

Nonhydrolytic synthesis: ether route, chloride and oxychloride precursors

Ex.: $10\ TiCl_4 + VOCl_3 + 21.5\ {}^iPr_2O \xrightarrow[CH_2Cl_2]{110\ °C,\ 3d} \xrightarrow[110°C,\ 3h]{Vacuum\ drying} \xrightarrow[Air,\ 500°C,\ 5h]{Calcination}$



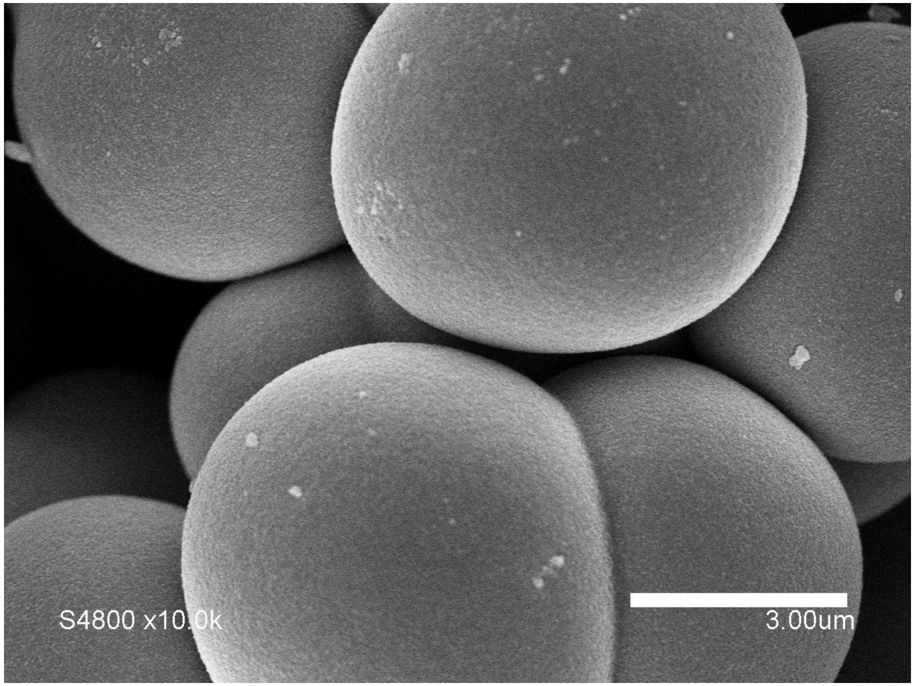


Mesoporous, ca 80 m^2/g, narrow pore size distribution

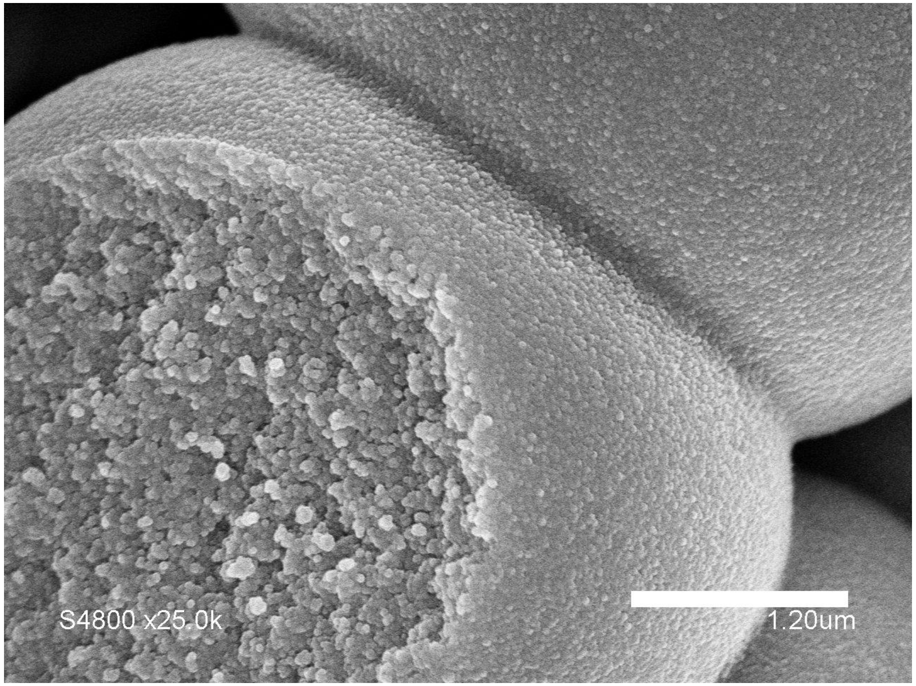
TiO_2-V_2O_5 catalysts

SEM

Aggregates of spherical particles
(2 – 7 µm)



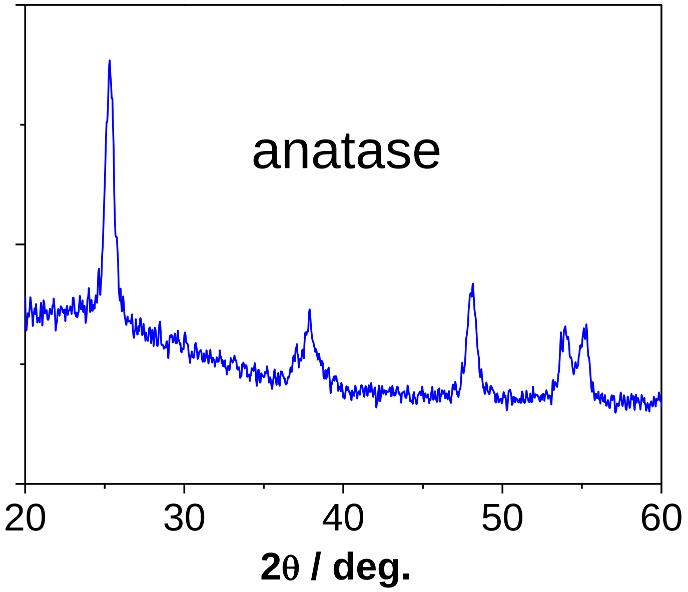
built of uniform nanoparticles
(10 – 20 nm)



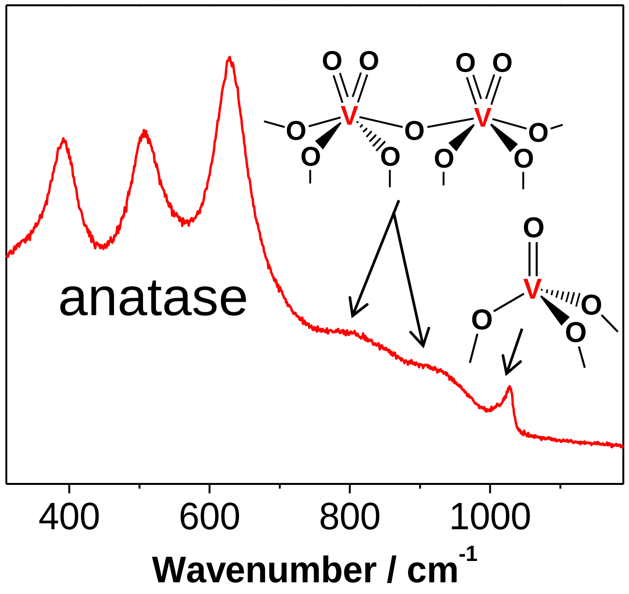
Hierarchichal texture, self-assembly of nanoparticles

TiO_2-V_2O_5 catalysts

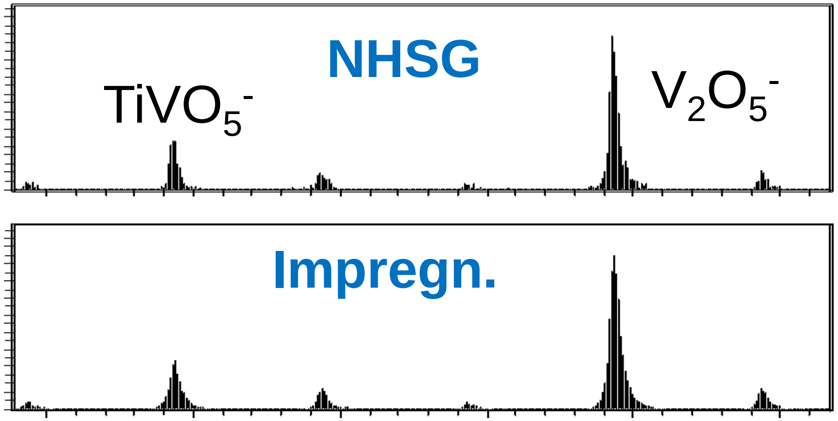
XRD



Raman



ToF-SIMS



Polymeric and monomeric V species dispersed on anatase

Surface species similar to catalysts prepared by impregnation

TiO_2-V_2O_5 catalysts

- **Selective Catalytic Reduction of NOx by NH_3 :**

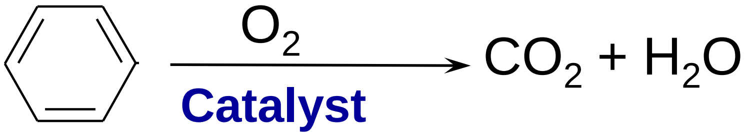
Collaboration G. Delahay, B. Coq, ICG Montpellier

$$4\ NO + 4\ NH_3 + O_2 \xrightarrow[\text{Catalyst}]{250 - 350°C} 4\ N_2 + 6\ H_2O$$

Chem. Commun. **2004**, 2214; *Appl. Catal. B* **2006**, *69*, 49.

- **Total oxidation of Volatile Organic Compounds :**

Collaboration Damien Debecker, Eric Gaigneaux, UCL



Appl. Catal. B **2010**, *94*, 38; *Catal. Today* **2010**

Activity comparable to the best conventional catalysts

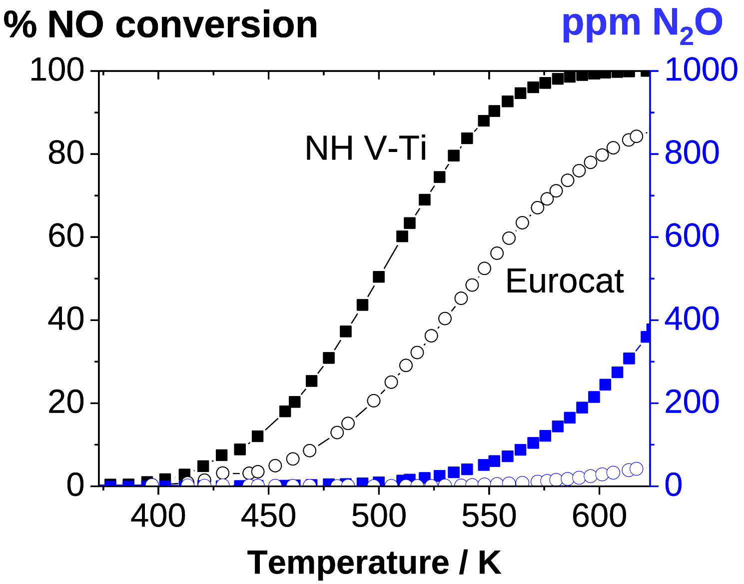
TiO_2-V_2O_5 catalysts

- **Selective Catalytic Reduction of NOx by NH_3 :**

Collaboration G. Delahay, B. Coq, ICG Montpellier

$$4\ NO + 4\ NH_3 + O_2 \xrightarrow[\textbf{Catalyst}]{250 - 350°C} 4\ N_2 + 6\ H_2O$$

Chem. Commun. **2004**, 2214; *Appl. Catal. B* **2006**, *69*, 49.



Comparison of: NH V2O5-TiO2 vs. Eurocat catalyst

Conditions:

Continuous flow, 20 mg cata., Gas flow: 138 cm3/min

Feed: 0.2 % NO, 0.2 % NH3, 3 % O2 in He

Highly active:

- at 500 K: 50 % conversion   8 ppm N2O
- No loss of activity after 100 h at 573 K.
- No SO2 poisoning (25 ppm)

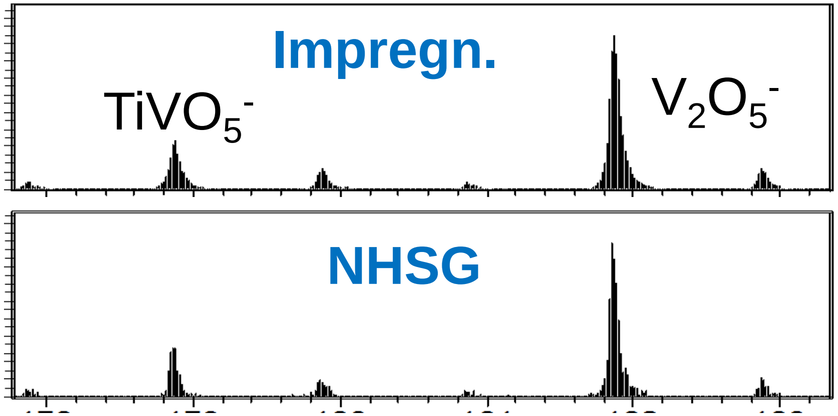
TiO_2-V_2O_5 catalysts

Collaboration D. Debecker, E. Gaigneaux, UCL

Comparison: impregnated vs. nonhydrolytic catalysts:

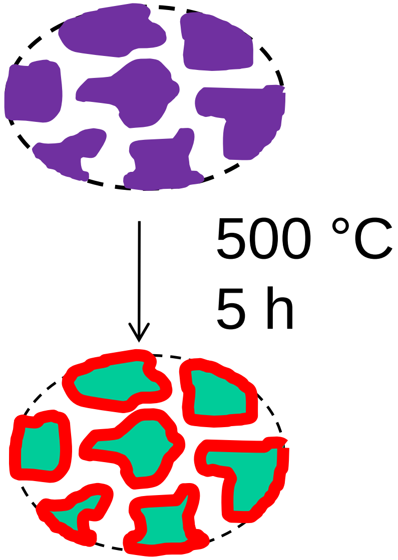
ToF-SIMS:

Similar surface species



XPS : surface composition

- xerogel: **V/Ti =0.05**
- calcined xerogel: **V/Ti =0.13**
- impregnated catalyst: **V/Ti =0.17**



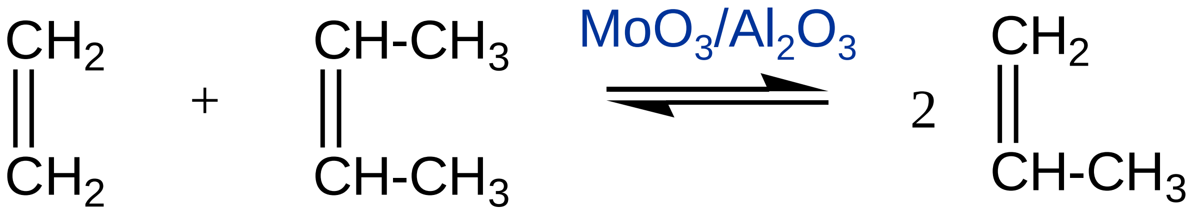
⇒ Migration of VO_x species toward the surface during calcination

Appl. Catal. B **2010**, *94*, 38.

SiO_2-Al_2O_3-MoO_3 metathesis catalysts

Collaboration: D. Debecker, E. Gaigneaux (Louvain la Neuve)
M. Stoyanova, U. Rodemerck (Rostock)

- Olefin metathesis: propene synthesis

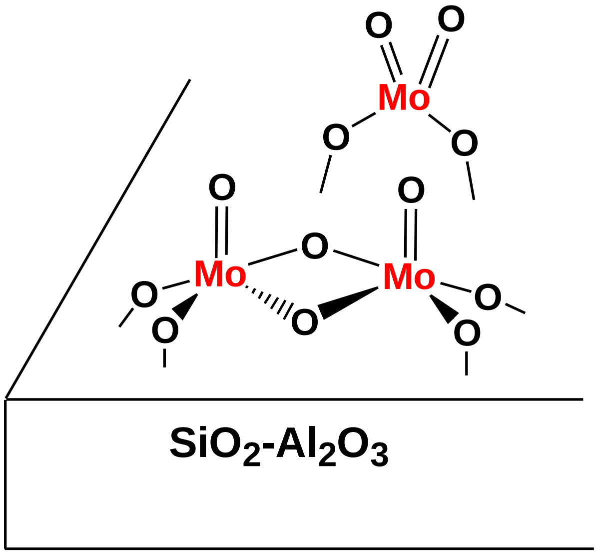


$$CH_2{=}CH_2 + CH_3{-}CH{=}CH{-}CH_3 \xrightleftharpoons{MoO_3/Al_2O_3} 2\ CH_2{=}CH{-}CH_3$$

Phillips Petroleum Co

Conventional catalysts:

- Molybdate species grafted to an alumina or **acidic silica-alumina** support
- Most active species: isolated molybdates

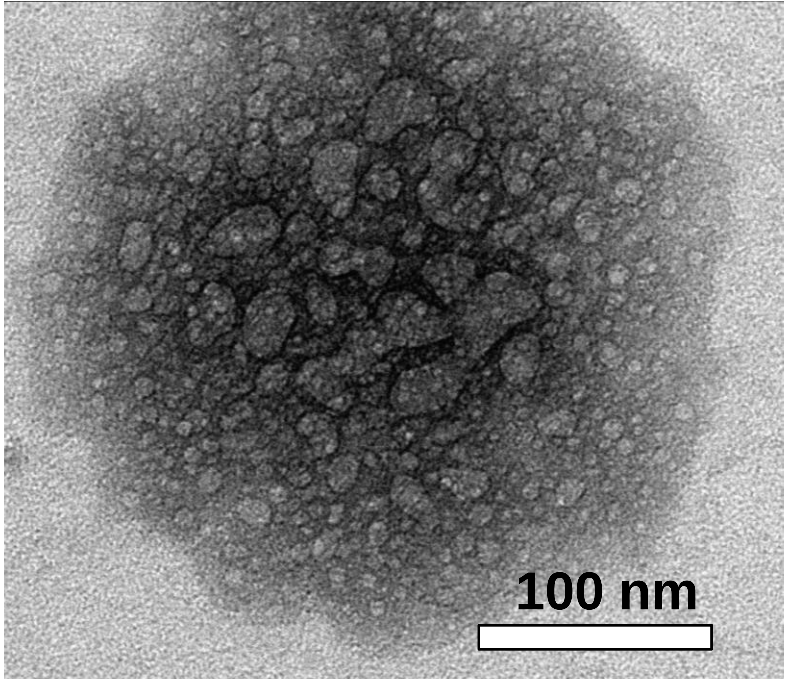


SiO_2-Al_2O_3-MoO_3 metathesis catalysts

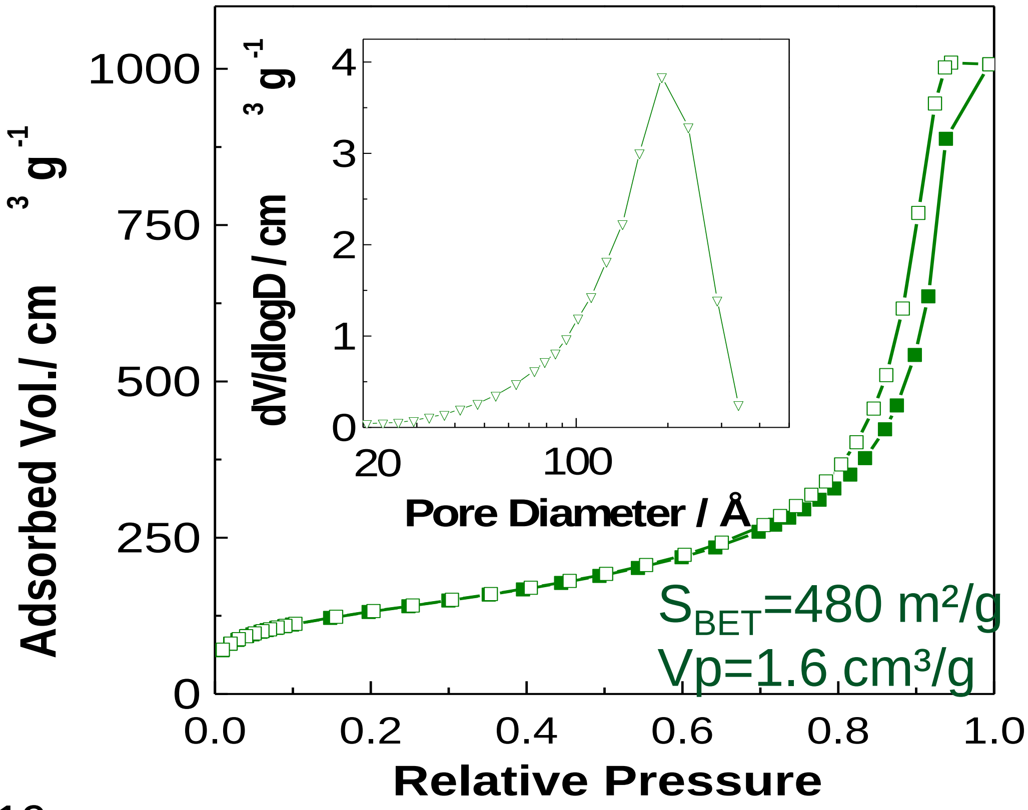
$$x\ SiCl_4 + AlCl_3 + y\ MoCl_5 \xrightarrow[\text{110 °C, 4 d}\ CH_2Cl_2]{+\ {}^iPr_2O} \xrightarrow[\text{110 °C, Vac.}]{\text{Drying}} \xrightarrow[\text{Air, 500°C, 5h}]{\text{Calcination}}$$

Si/Al = 15 ; 5-20 wt% MoO_3

TEM



NH 10% MoO_3



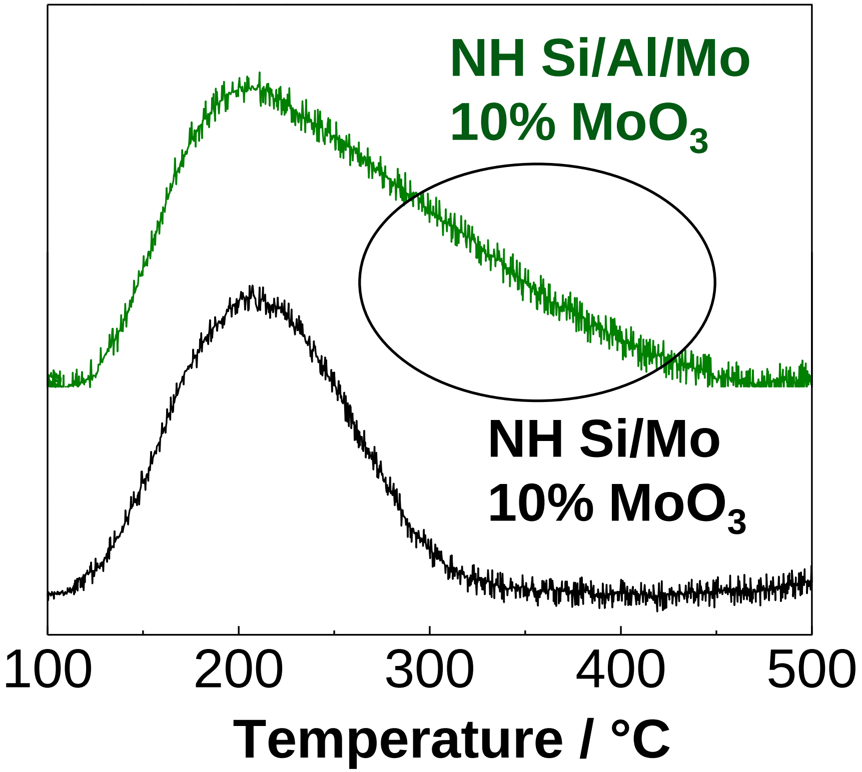
S_{BET}=480 m²/g

Vp=1.6 cm³/g

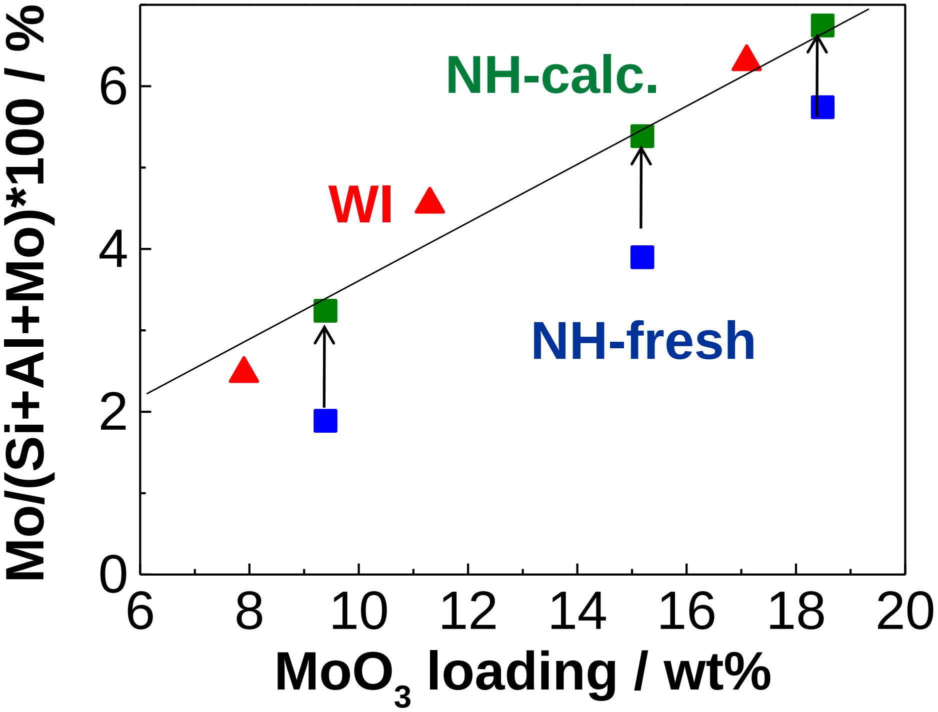
Chem. Mater. **2009**, *21*, 2819

SiO_2-Al_2O_3-MoO_3 catalysts

NH_3-TPD



XPS surface analysis



Si/Al/Mo: Acidic sites, mixed SiO_2-Al_2O_3 "support"

Calcination: Migration of MO_x species toward the surface

SiO_2-Al_2O_3-MoO_3 catalysts

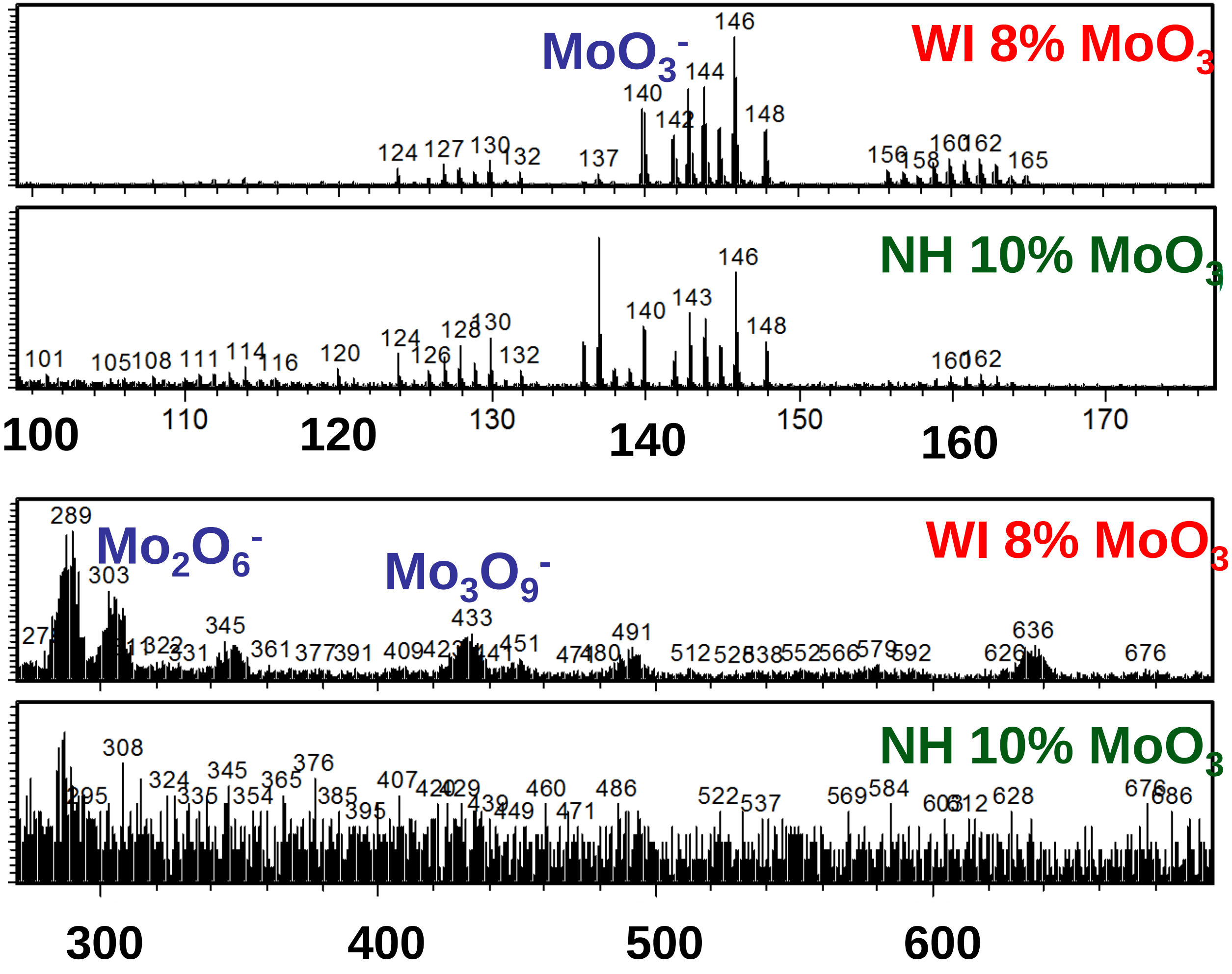
TOF-SIMS: Surface species, comparison between NHSG and Wet Impregnation

NH catalyst:

only monomeric MoO_x

species at the surface.

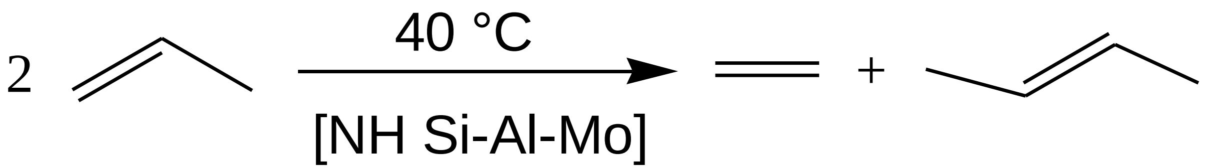
TOF-SIMS



Chem. Mater. **2009**, *21*, 2819

SiO_2-Al_2O_3-MoO_3 catalysts

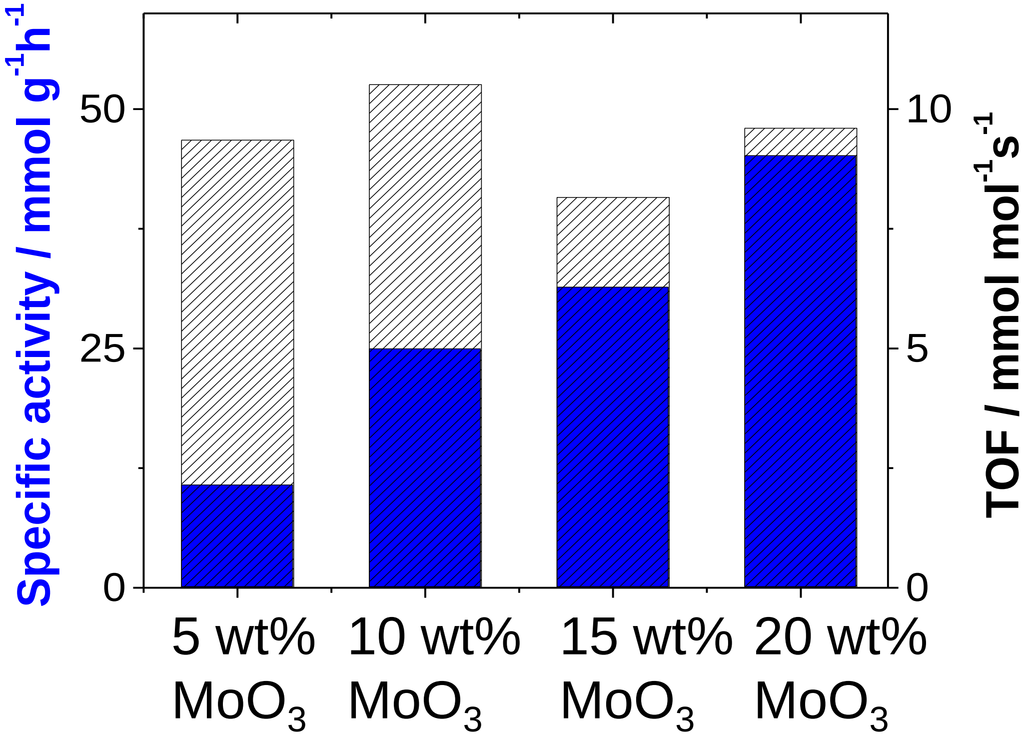
Self-metathesis of propene:



- Specific activity increases with MoO_3 loading

- TOF ≈ constant

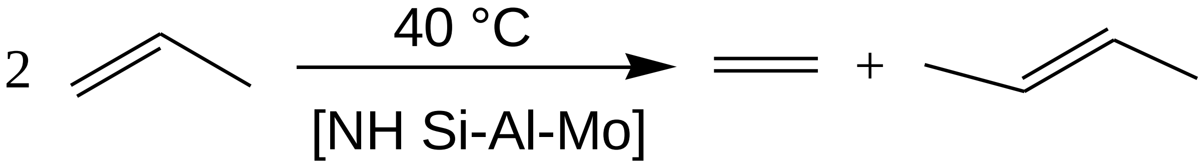
⇒ Similar active species

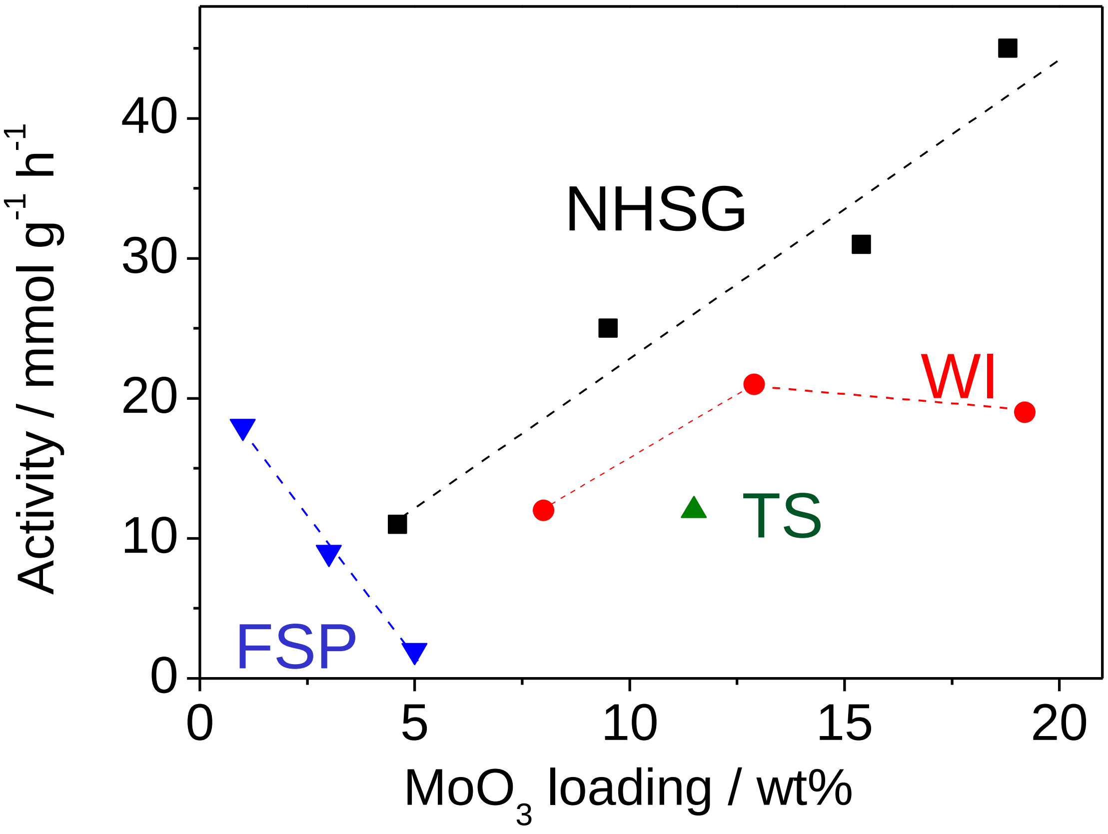


Catal. Sci. Technol. **2012**, *2*, 1157-1164

SiO_2-Al_2O_3-MoO_3 metathesis catalysts

Self-metathesis of propene (LIKAT: M. Stoyanova, U. Rodemerck)





Comparison with catalysts prepared by ≠ methods:

NHSG: up to twice higher specific activity

Non-hydrolytic routes to nanoparticles

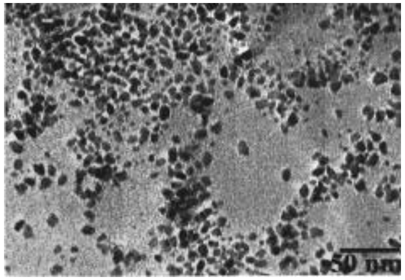
Extremely successful in the synthesis of metal oxide nanocrystals

N. Pinna, M. Niederberger, *Angew. Chem.*, ***2008,*** *47*, 5292.

- **Surfactant-assisted syntheses:**

e.g. $TiCl_4 + Ti(O^iPr)_4 \xrightarrow[\text{TOPO}]{300\ °\text{C}} \mathbf{TiO_2}$

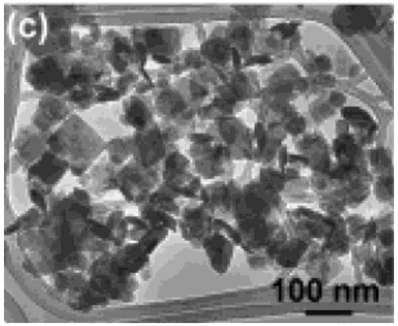
V. L. Colvin et al, *J. Am. Chem. Soc.* ***1999,*** *121*, 1613



- **Benzyl alcohol route:**

e.g. $WCl_6 \xrightarrow[\mathbf{PhCH_2OH}]{100\ °\text{C}} \mathbf{WO_3}$

M. Niederberger et al *J. Am. Chem. Soc* ***2002,*** *124*, 13642



- **Silica-based amorphous nanoparticles?**
- **Ether route? in the absence of surfactant?**

SiO_2-TiO_2 nanoparticles

Stöber synthesis:
does not lead to homogeneous SiO_2-TiO_2 nanoparticles (precipitation of TiO_2)

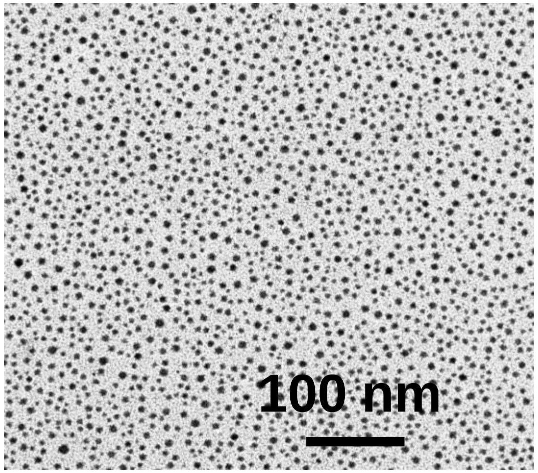
$9\ SiCl_4 + TiCl_4 + 20\ {}^{i}Pr_2O$

CH_2Cl_2
$V_{solv}/V_{prec}=15$

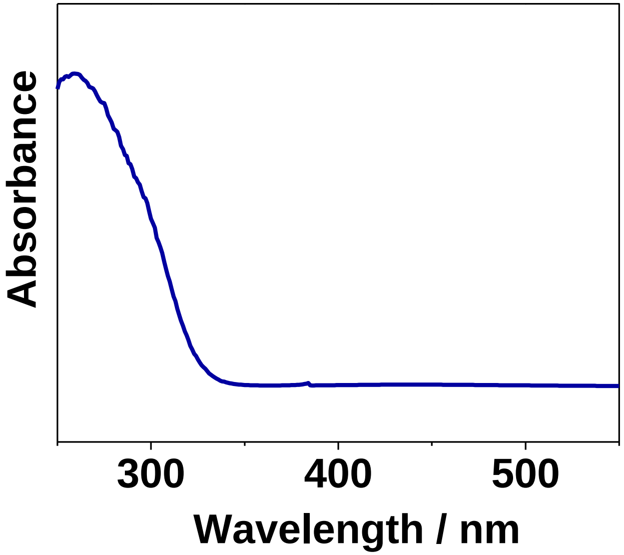
Sealed tube
110 °C, 5 d

Reaction stopped before gelation by cooling down to RT

TEM



UV-Vis



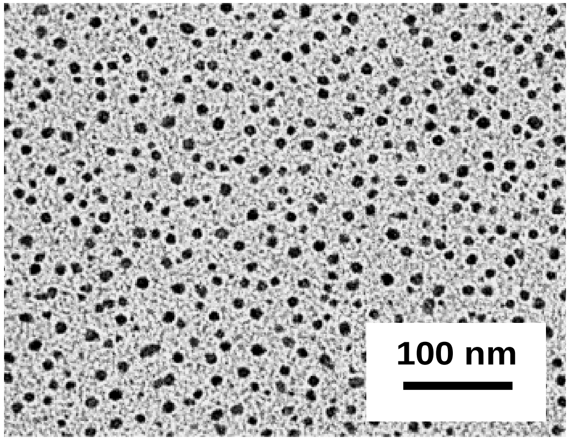
- **Homogeneous SiO_2-TiO_2 unaggregated nanoparticles**

Chem. Mater. **2009**, *21*, 2577.

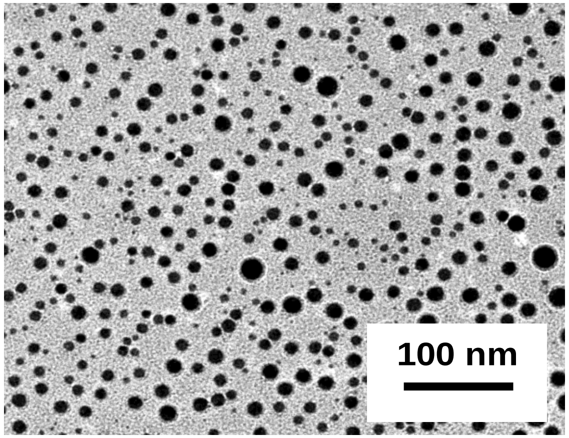
SiO_2-TiO_2 nanoparticles: influence of Si/Ti ratio

$$x\ SiCl_4 + TiCl_4\ + 2x+2\ {}^{i}Pr_2O \xrightarrow[110\ ^{\circ}C,\ 5\ d]{CH_2Cl_2} \xrightarrow{Evap.} \textbf{TEM}$$

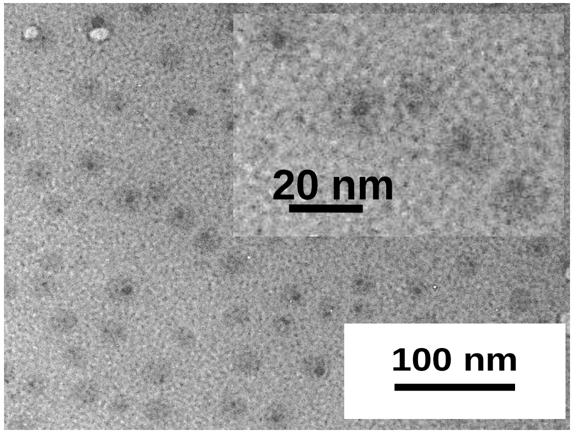
10 mol% Ti

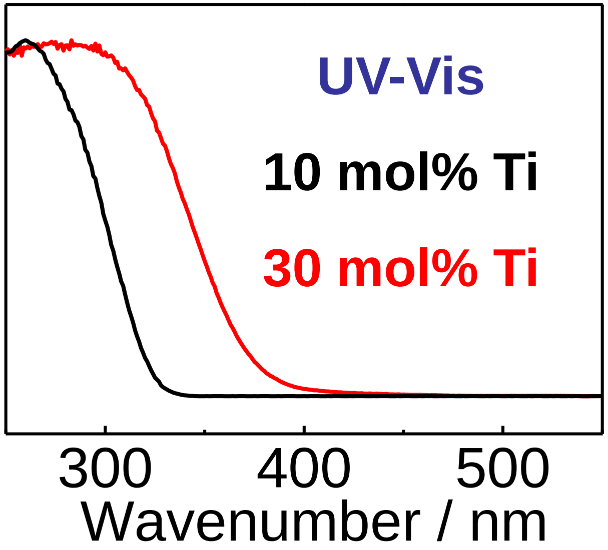


15 mol% Ti



30 mol% Ti



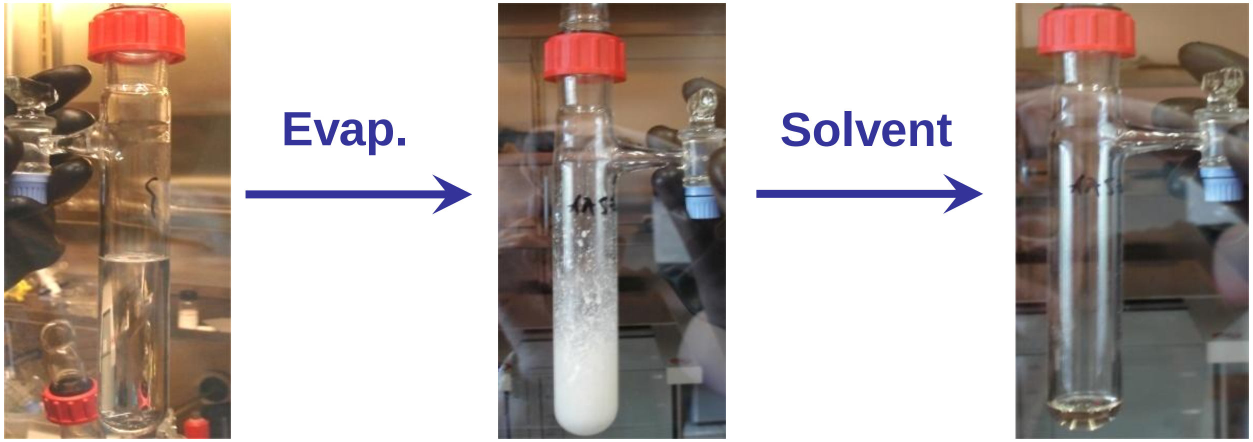


From homogeneous to core-shell

SiO_2-TiO_2 nanoparticles

Stability of SiO_2-TiO_2 sols

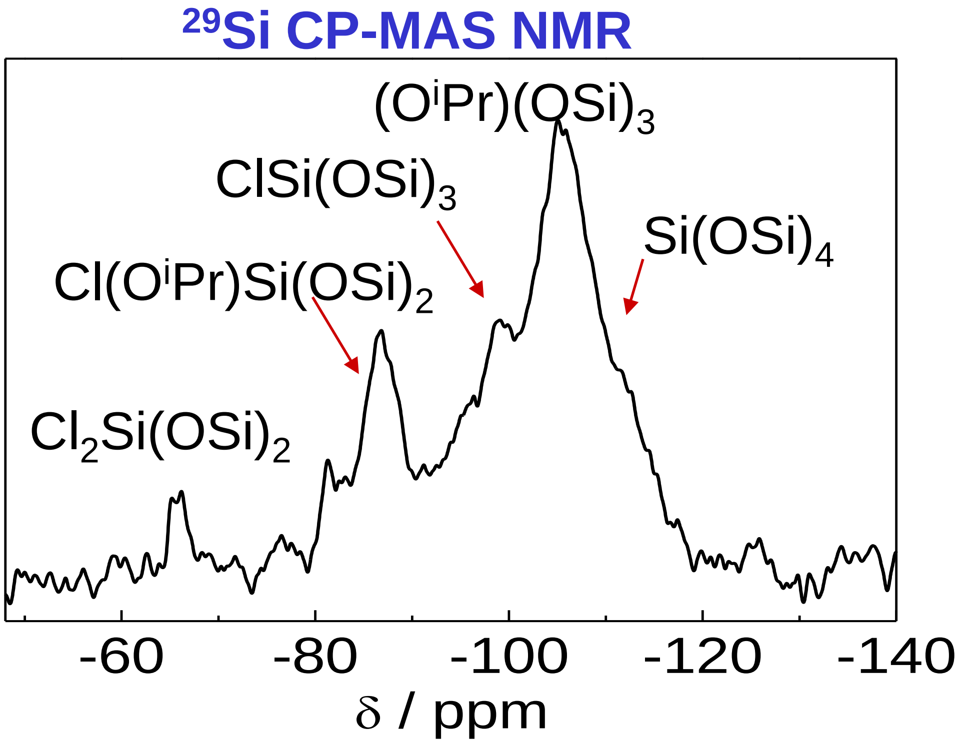
Nanoparticle sols:

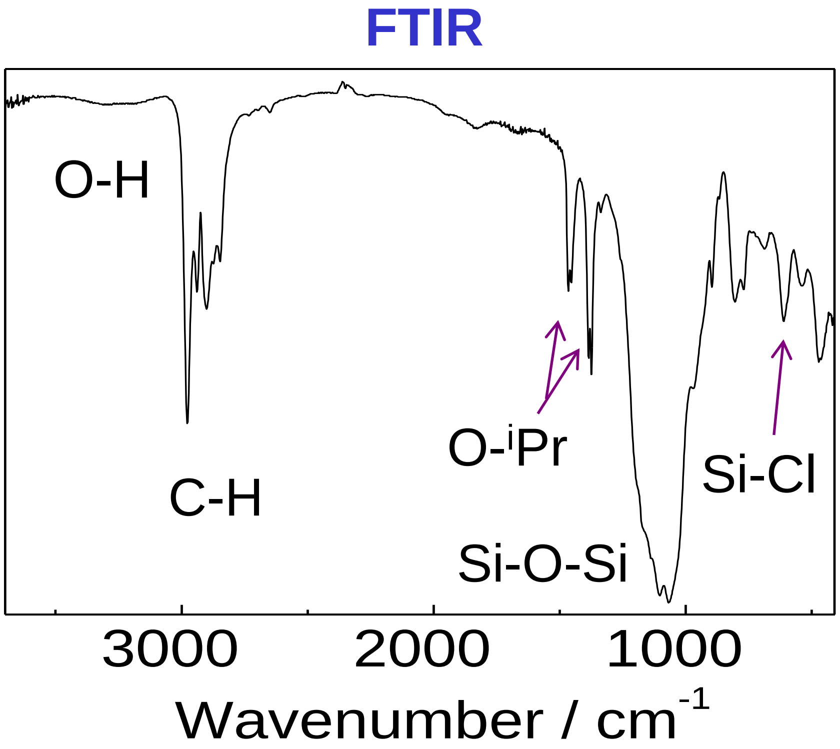


- stable at RT (in the absence of water)
- can be concentrated and redispersed in organic solvents

in the absence of surfactants or electrostatic repulsions!

Stabilization mechanism of SiO_2-TiO_2 sols



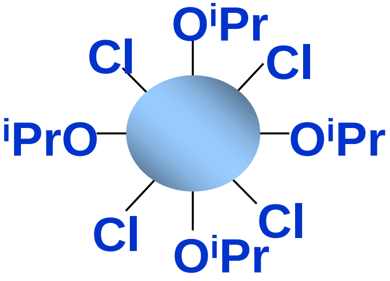


Cl and OiPr surface groups, no OH groups

Organophilic nanoparticles: solvatation

No nonhydrolytic condensation at RT

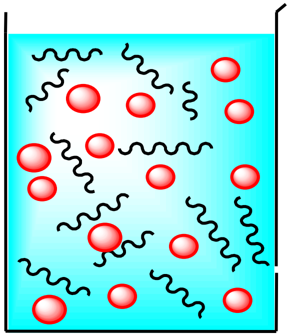
« Kinetic stabilization » of the sol



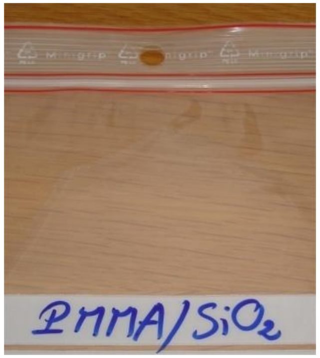
Chem. Mater. **2009**, *21*, 2577.

Application: polymer nanocomposites

Solution of NP and PMMA in CH_2Cl_2



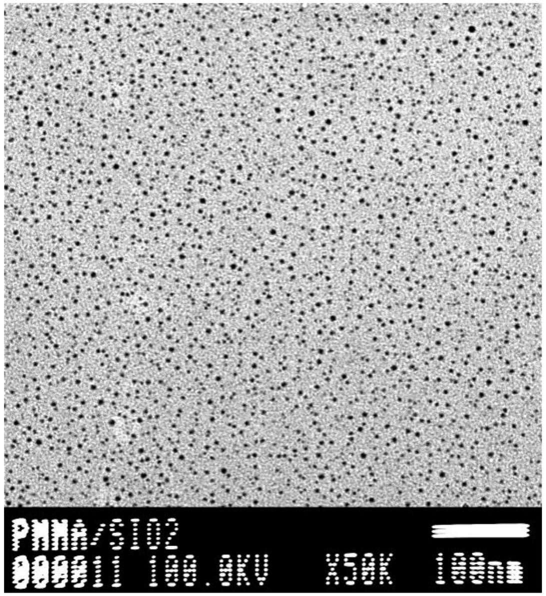
Casting



Transparent $PMMA\text{-}SiO_2$ nanocomposite

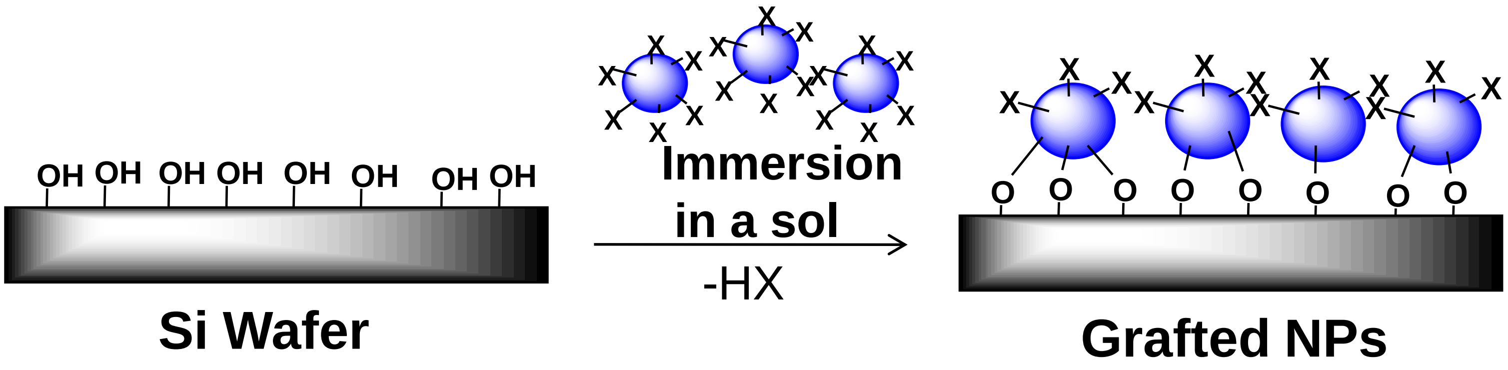
TEM image of a microtome cut: (70 nm thick)

Perfect dispersion, no need to modify the NP surface



Application: nanoparticle monolayers

No surfactant, Si-Cl and Si-OiPr surface groups ⇒ reactive surface



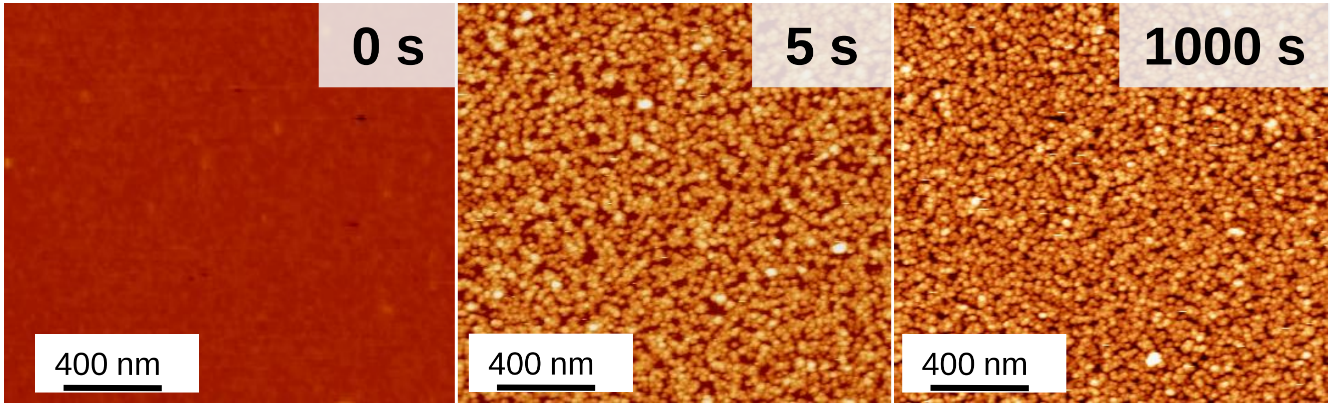
Si Wafer

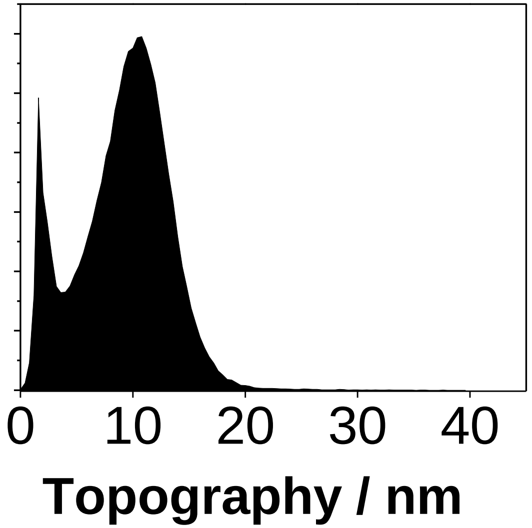
Immersion in a sol

-HX

Grafted NPs

AFM images = f(immersion time)

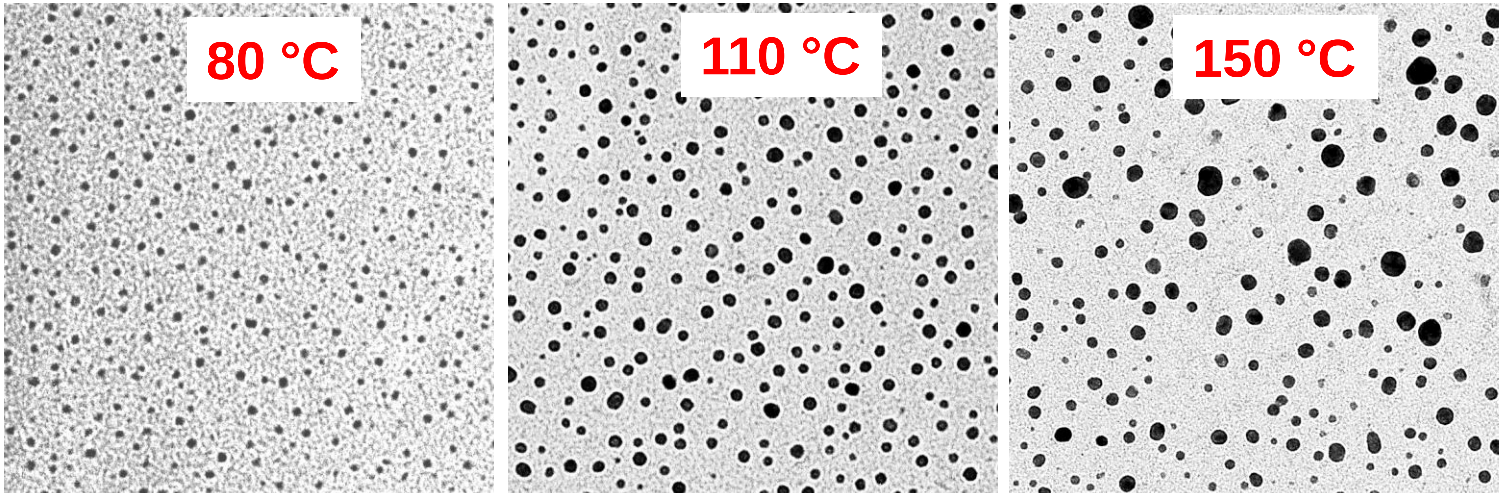


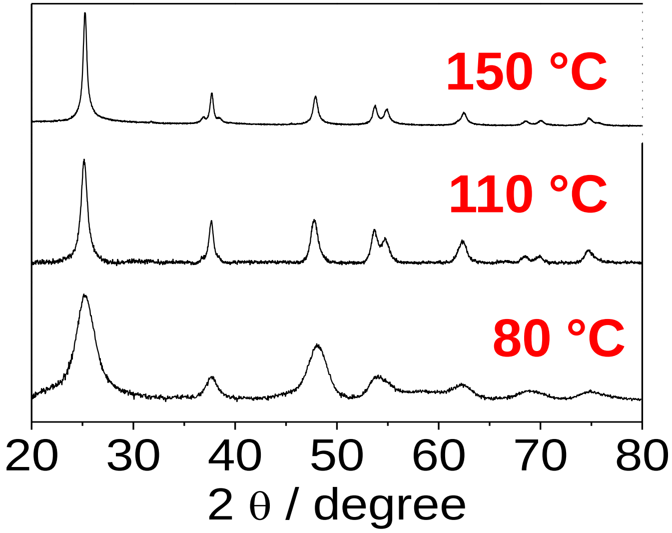


Monolayer of NP, whatever the immersion time ⇒ self-limiting grafting of NP

TiO_2 nanoparticles

$TiCl_4 + 2\ {}^{i}Pr_2O \xrightarrow[\text{T °C, 60 h}]{CH_2Cl_2} \xrightarrow{\text{Evap.}}$ **TEM**



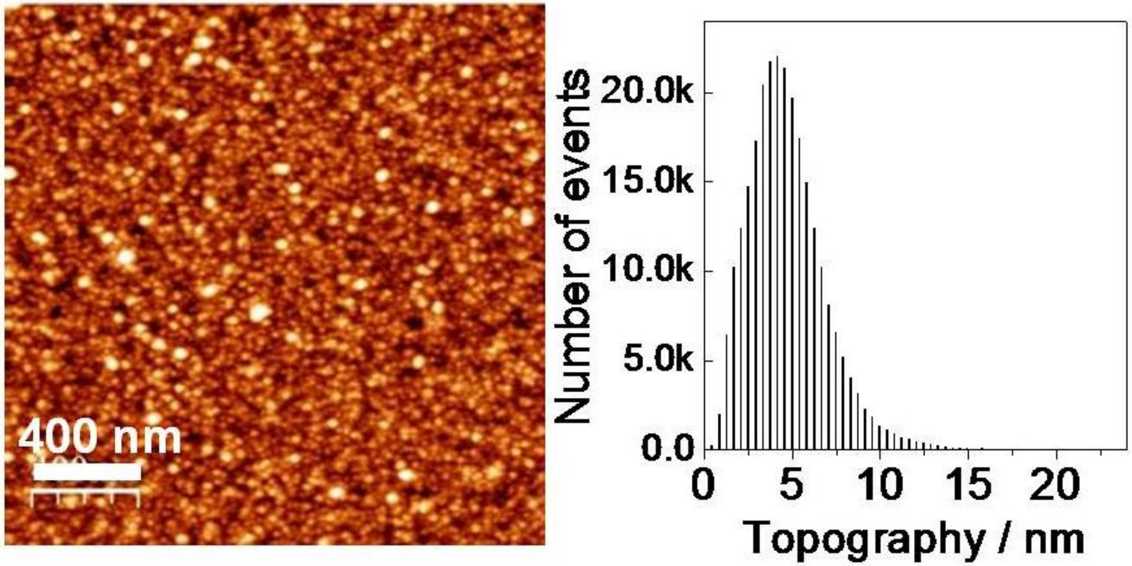


T / °C	S_{BET} (m^2g^{-1})	D_{BET} (nm)	D_{XRD} (nm)
80	430	3.6	3.8
110	170	9.1	9.5
150	105	14.7	16.3

Chem. Mater. **2010**, *22*, 4519–4521

TiO_2 nanoparticles

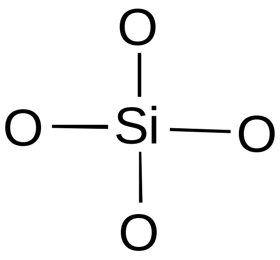
wafer immersed in a sol of $TiO_2$80 nanoparticles in THF (0.3 wt% TiO_2) for 2 hours at 25 °C



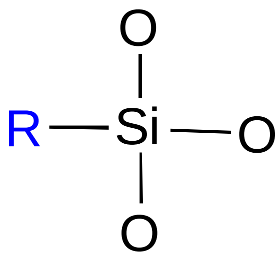
Silica and Siloxane Organic-Inorganic Hybrids by NHSG

Hydrolytic Sol-Gel: mild conditions

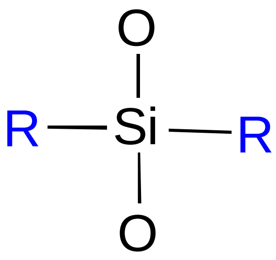
→ introduction of organic groups via Si-C bonds



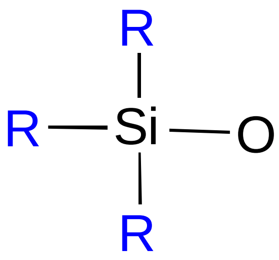
Q



T



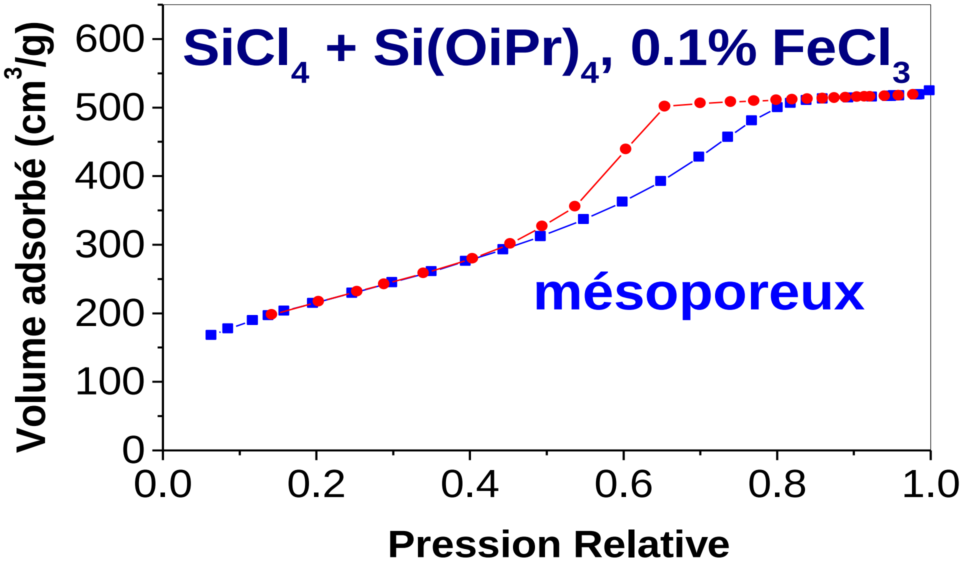
D

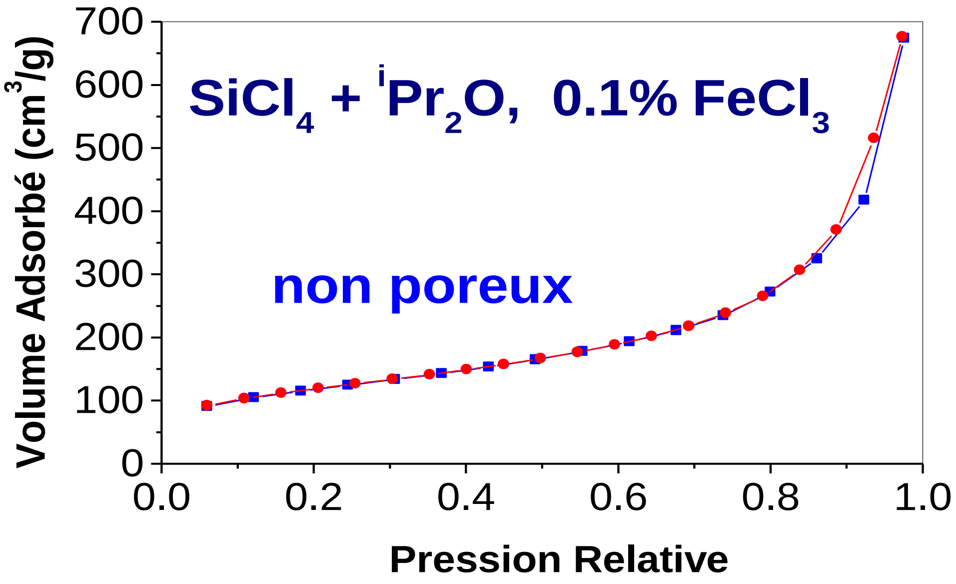


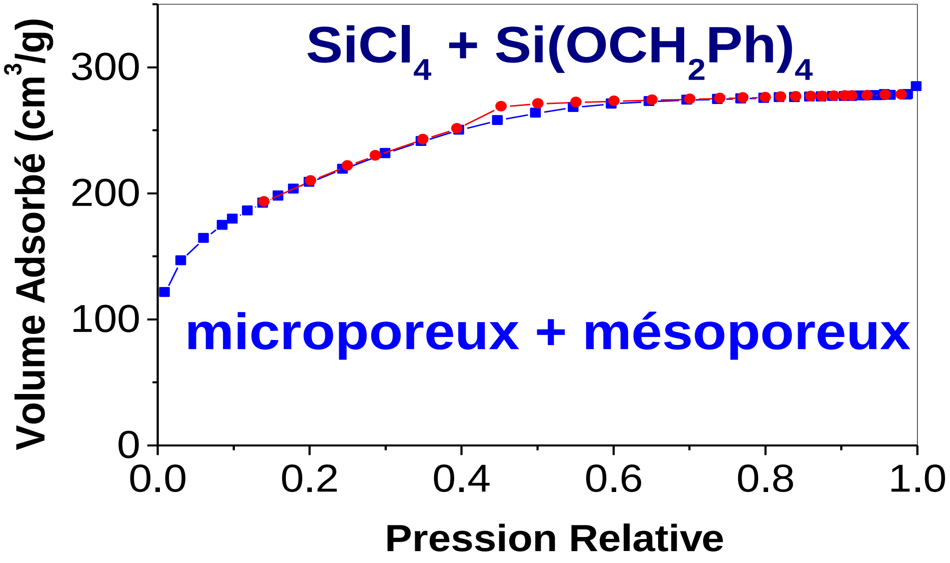
M

Applications: protective coatings, optics, electronics, catalysis, chromatography, membranes...

Silica xerogels by Non-Hydrolytic Sol-Gel







Wide range of textures depending on the conditions:

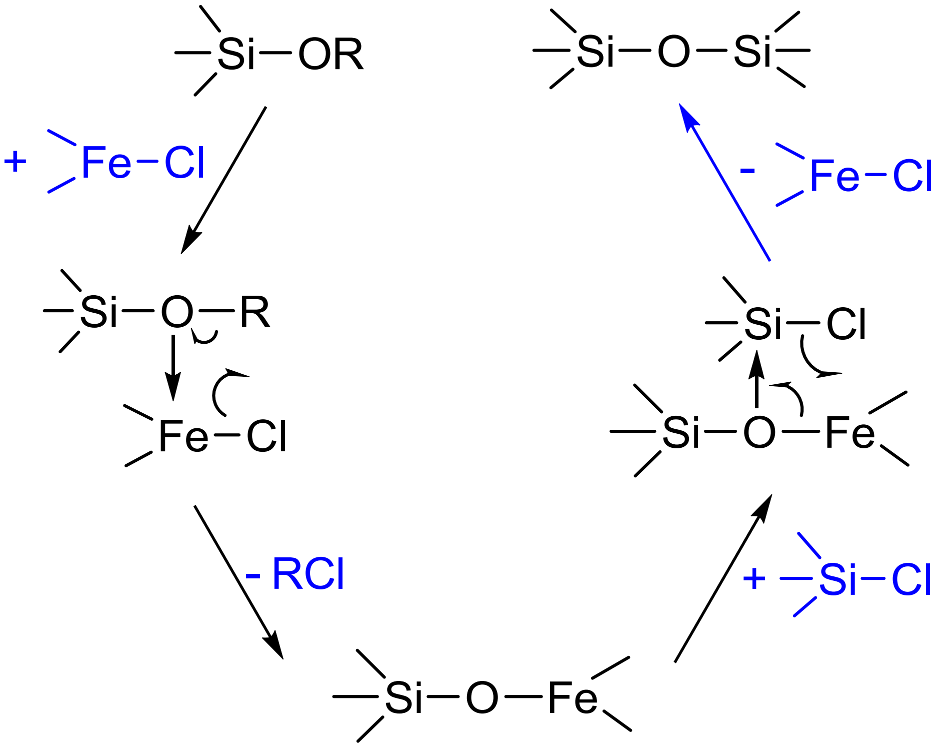
•O-donor

• time, temperature, catalyst

•liquid phase volume

Catalysis of condensations around Si

Lewis acid $FeCl_3 > ZrCl_4 > AlCl_3 > TiCl_4$



$FeCl_3$: 0.1 mol% is sufficient to form SiO_2

⇒1 $FeCl_3$ catalyzes the formation of 2000 Si-OSi bonds!

Competition between catalysis and incorporation in the SiO_2 network

Silica and siloxane hybrids by NHSG

Non-Hydrolytic Sol-Gel:

≅ 100°C, Lewis acids, alkyl chlorides   mild conditions ?

Friedel-Crafts reactions?

Exchange or cleavage of Si-C bonds?

Si-H bonds?

➡ Synthesis of model silsesquioxanes (T resins)

$R\text{-}SiO_{1.5}$ R = Me, $C_{18}H_{35}$, Vi, Ph

Silsesquioxanes by NHSG: Reaction Conditions

$$MeSiCl_3 + MeSiOEt_3 \xrightarrow[110\ °C]{1\%\ \text{Lewis acid}} 2\ MeSiO_{1.5} + 3\ Et\text{-}Cl$$

Lewis acid	$FeCl_3$ >	$ZrCl_4$ >	$AlCl_3$ >	$TiCl_4$
Gel times	0.5 h	10 h	60h	140 h

$$MeSiCl_3 + R'_2O \xrightarrow[110\ °C]{0.1\%\ FeCl_3} MeSiO_{1.5} + 3\ R'\text{-}Cl$$

Oxygen donor	$MeSi(OEt)_3$	$^iPr_2O$	Et_2O
Gel times	5 h	10 h	60 h
Condensation	>95%	>95%	90%

Silsesquioxanes by NHSG

$$R\text{-}SiCl_3 + {}^{i}Pr_2O \xrightarrow[110\ °C]{0.1\%\ FeCl_3} R\text{-}SiO_{1.5} + 3\ {}^{i}PrCl$$

R = Alkyl, Vinyl

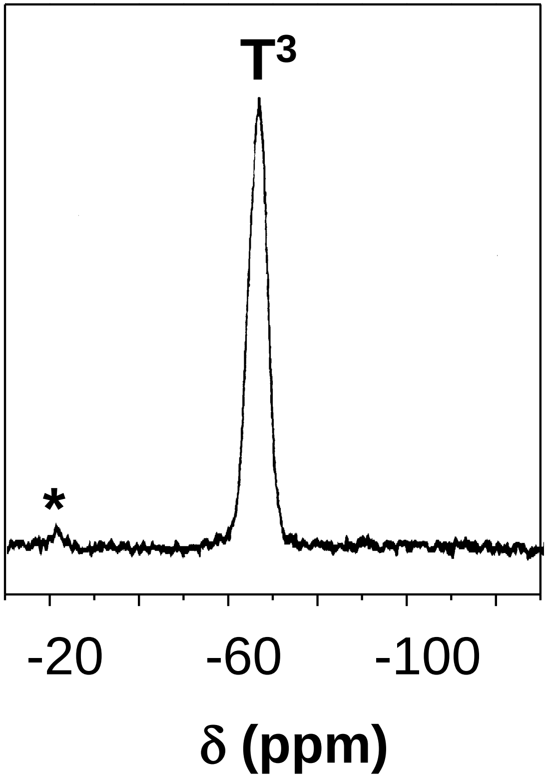
- high degree of condensation
- No Si-C redistribution
- No Si-C cleavage

R = Phenyl

- Sealed tube: cleavage of Si-Ph bonds by iPrCl
- Open system: no cleavage

J. Sol-Gel Sci. Tech. 14, 137 (1999)
J. Mater. Chem, 10, 1811 (2000)

^{29}Si CP-MAS NMR
$MeSiO_{1.5}$

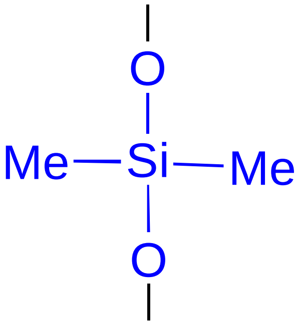


Methoxylated D/Q resins by NHSG

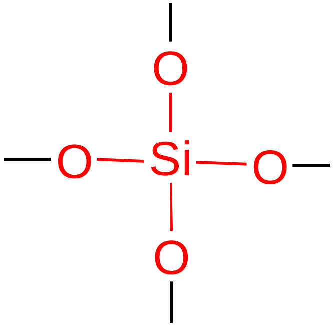
Goals:

- 1 step synthesis

- resins built of :



D units



Q units

- terminated by **Si-OMe** functions (curing by hydrolysis)

Application: adhesives for silica fibers

Hydrolytic syntheses: no control on the viscosity ⇒ NH synthesis

$$0.4\ Me_2SiCl_2 + 0.6\ Si(OMe)_4 \xrightarrow[\Delta]{\text{Cata}} (SiMe_2)_{0.4}(Si)_{0.6}O_{0.8}(OMe)_{1.6} + 0.8\ MeCl$$

No solvent, 1-step, MeCl: recycled in the synthesis of methylchlorosilanes

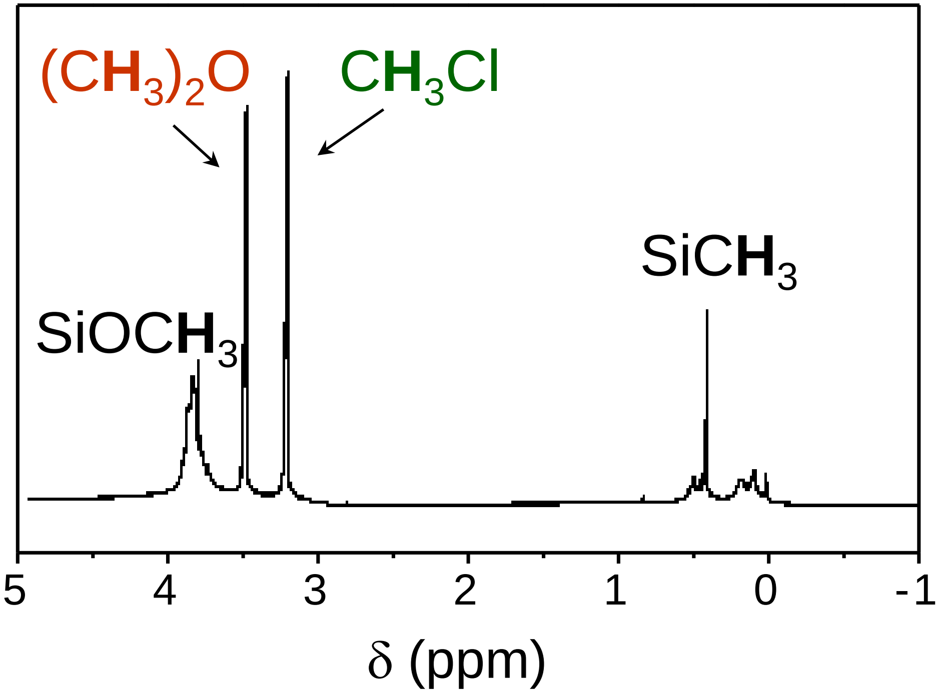
EP 728793 A1 **1996;** *J. Polym. Sci. Part A* **1998**, *36*, 2415.

D/Q^{OMe} Resins: Choice of Reaction Conditions

First try:

- **$FeCl_3$** catalyst: → **Solid!** Hydrolysis? Distillation?

⇒ Reaction in sealed NMR tubes, monitoring by **^{1}H NMR**



Formation of Me_2O

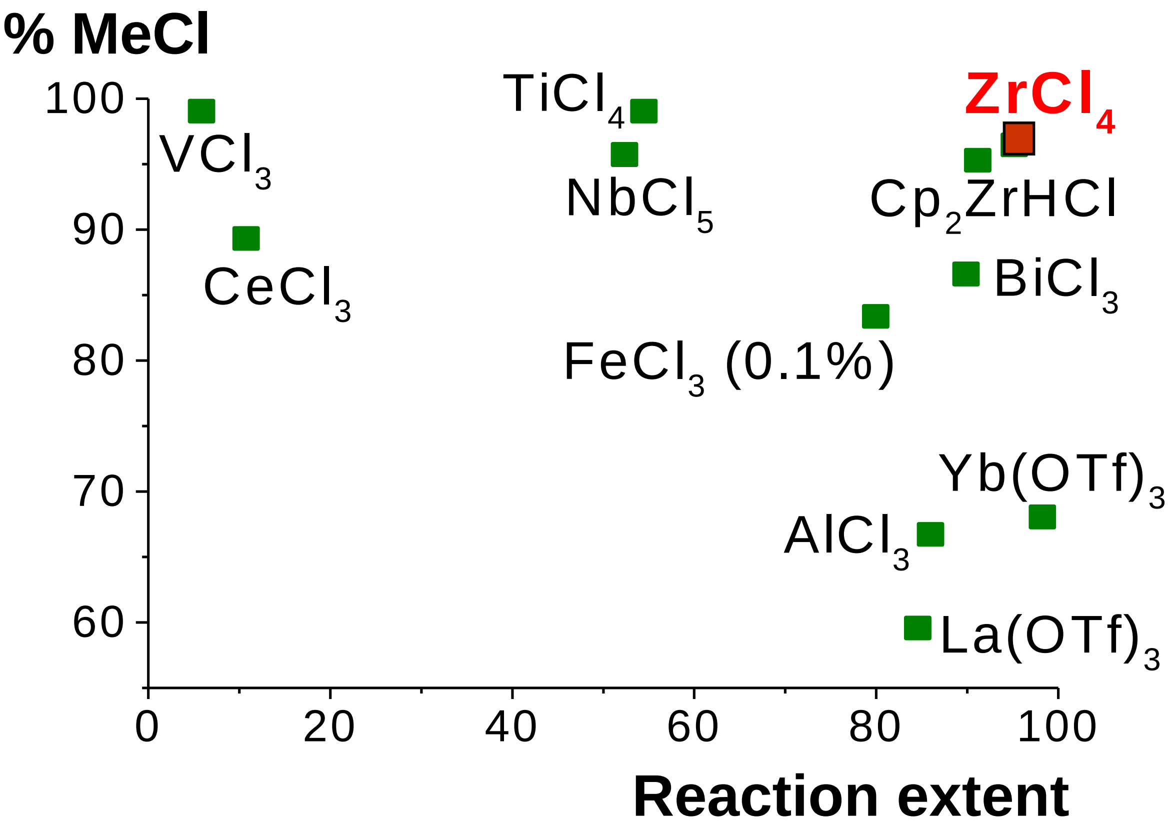
$$2\ \text{Si-OMe} \longrightarrow \text{Si-O-Si} + Me_2O$$

↑ degree of condensation (Si-O-Si)

Other catalysts???

Looking for a Selective Catalyst

Test reaction: $0.4\ Me_2SiCl_2 + 0.6\ Si(OMe)_4 \xrightarrow[\text{16h, sealed NMR tube}]{\text{130 °C, \textbf{1\% cata}}}$

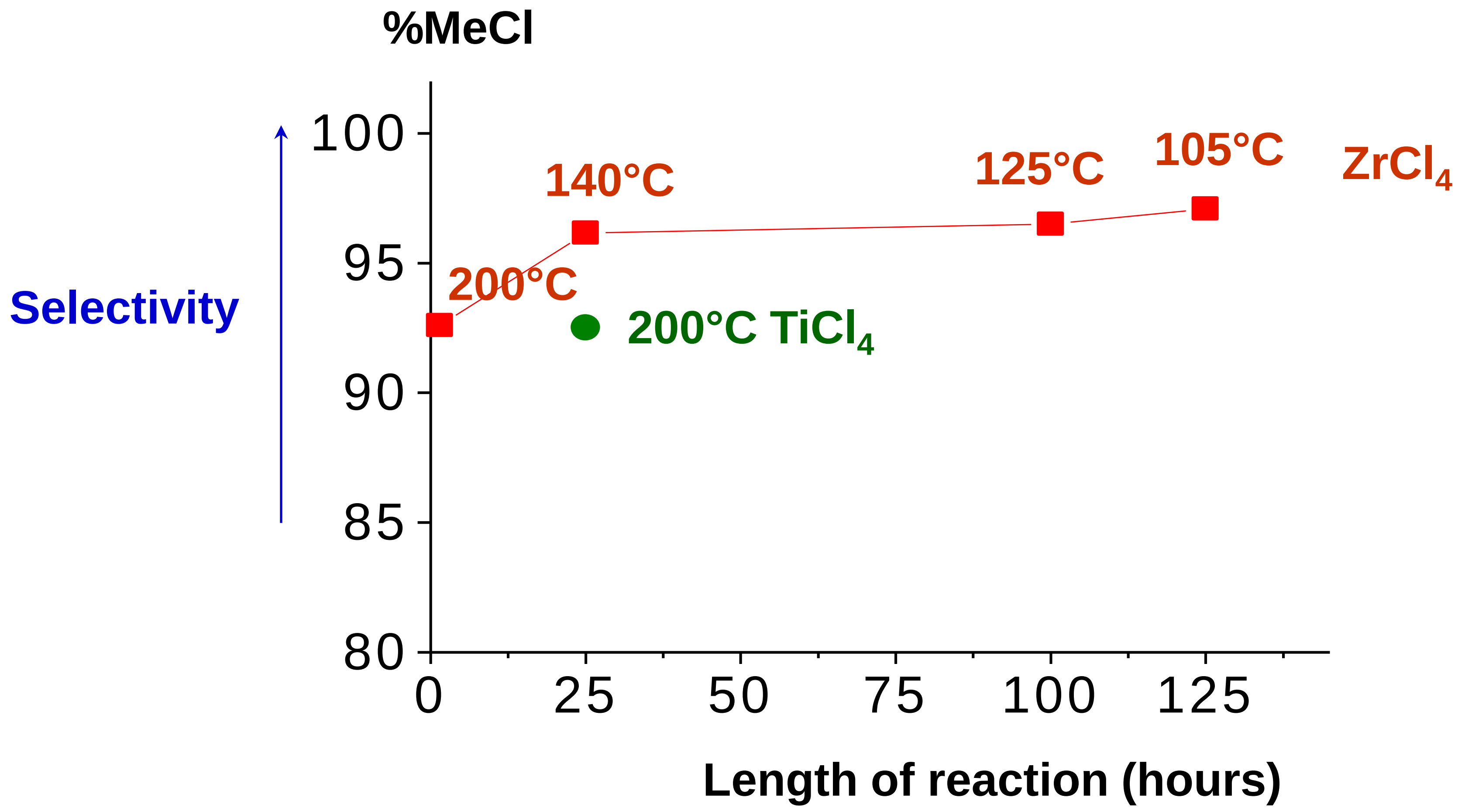


Selectivity

Reactivity

Influence of Reaction Temperature

Reaction: $0.4\ Me_2SiCl_2 + 0.6\ Si(OMe)_4 \xrightarrow[\text{sealed NMR tube}]{\textbf{T}\text{, 1\% cata}}$



Synthesis of D/Q^{OMe} Resins

Conditions:

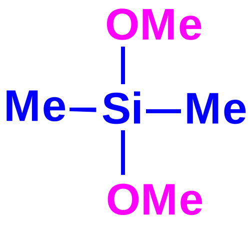
- Me_2SiCl_2 and $Si(OMe)_4$
- 1% $ZrCl_4$
- 130 to 150°C, autoclave or sealed tube

➡ Orange liquids, well-controlled viscosity

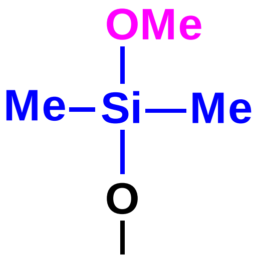
Samples	Viscosity (cP)
$0.3\ Me_2SiCl_2 + 0.7\ Si(OMe)_4 \longrightarrow$ D/Q 30/70	2.5
$0.4\ Me_2SiCl_2 + 0.6\ Si(OMe)_4 \longrightarrow$ D/Q 40/60	7.3
$0.5\ Me_2SiCl_2 + 0.5\ Si(OMe)_4 \longrightarrow$ D/Q 50/50	53

Characterization: GC/MS, ^{29}Si NMR

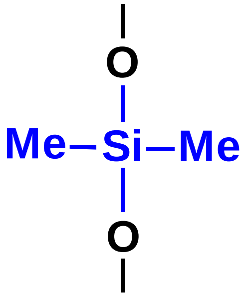
Structural units in D/Q$^{\text{OMe}}$ Resins



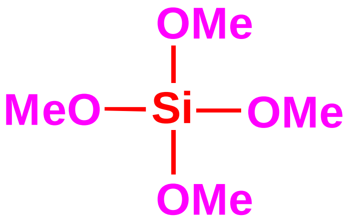
D^0



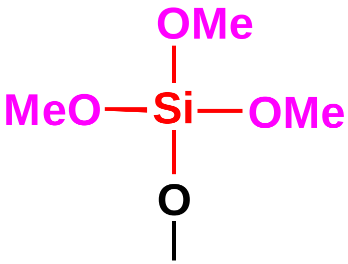
D^1



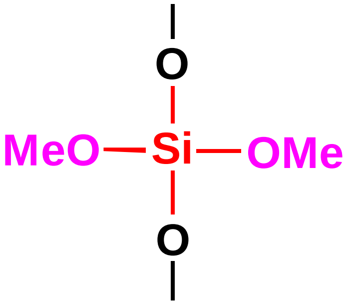
D^2



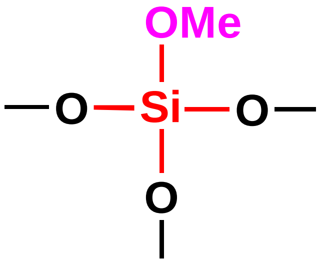
Q^0



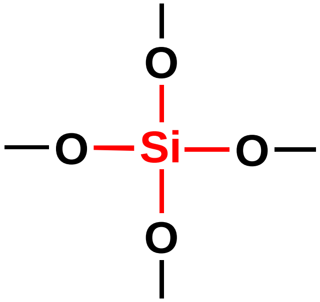
Q^1



Q^2



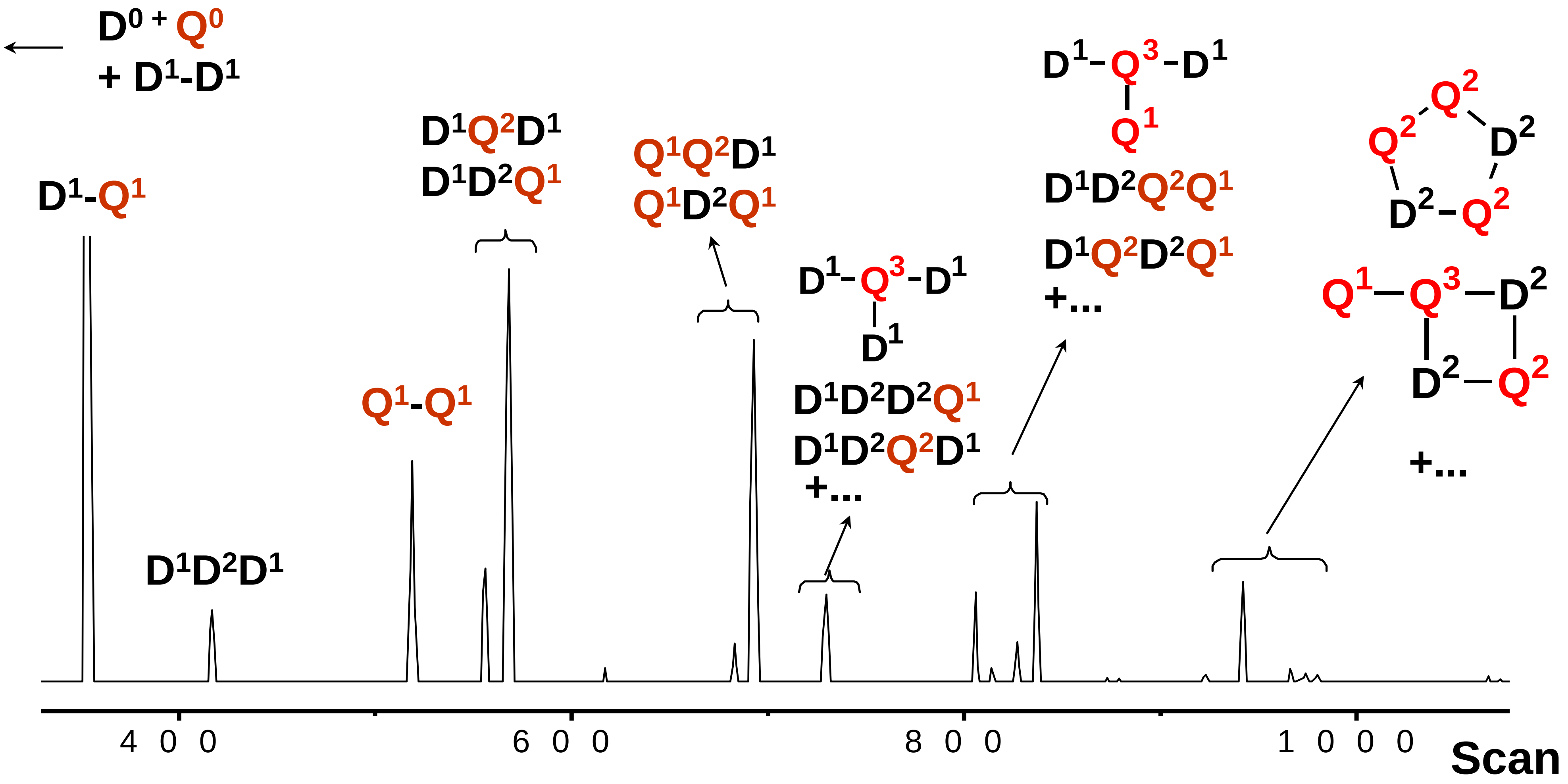
Q^3



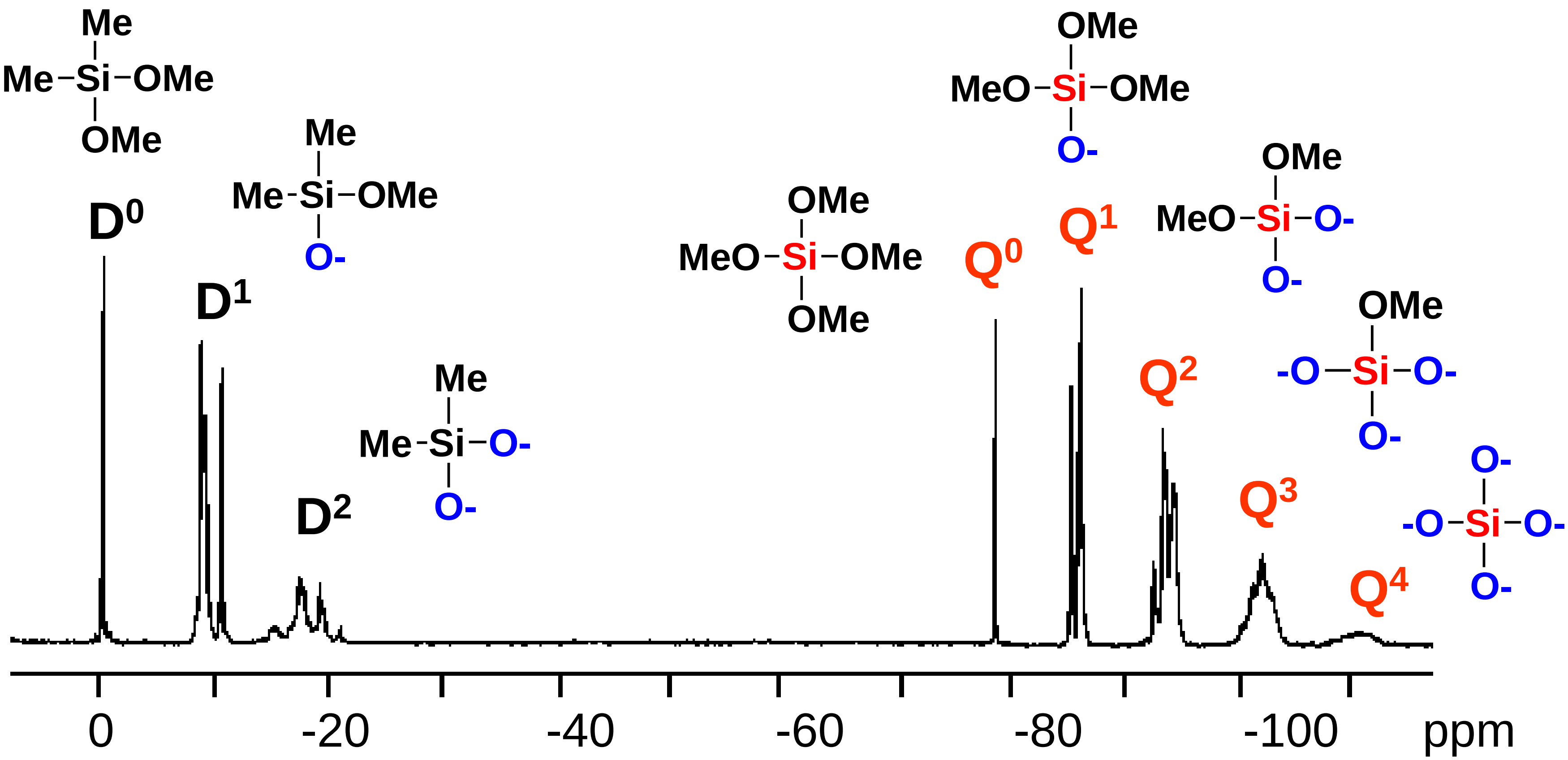
Q^4

GC/MS (D/Q 40/60)

$$0.4\ Me_2SiCl_2 + 0.6\ Si(OMe)_4 \xrightarrow[130\ °C]{1\%\ ZrCl_4}$$



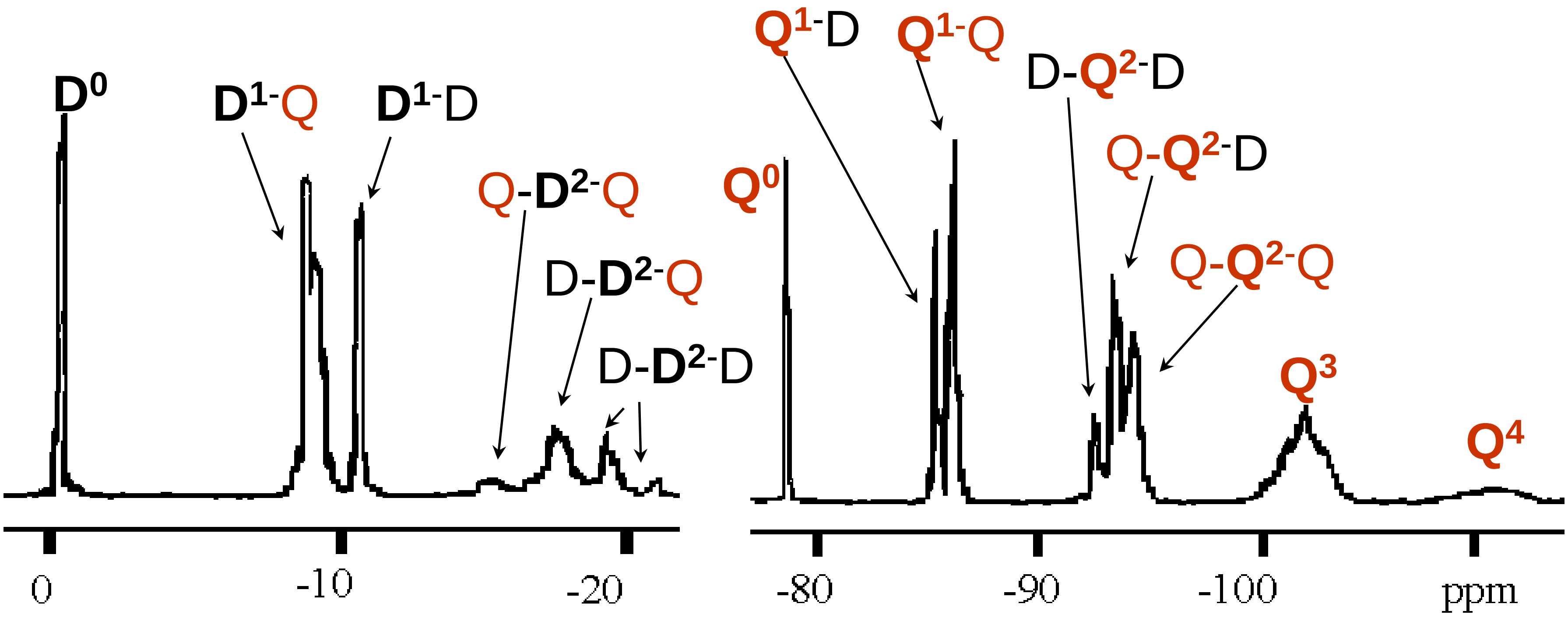
Quantitative ^{29}Si NMR (D/Q 40/60)



Good control of the composition: D/Q = 39/61 O/Si = 0.85 (th. 0.80)

⇒ Controlled viscosity of the resins

^{29}Si NMR (D/Q 40/60)



Good homogeneity: High level of D-Q bonding

Statistics: random distribution of Si-OMe and Si-OSi bonds

High T, Lewis acid: **Condensation** and **Redistribution** of Si-OX bonds

⇒ **Excellent reproducibility and stability of the resins**

Conclusions: Non-Hydrolytic Sol-Gel:

Changing reactions, changing reaction medium:

- Impacts reaction kinetics, condensation degree

- facilitates control of composition, homogeneity, texture

- Avoids using alkoxide precursors, reactivity modifiers, multi-step procedures, templating, supercritical drying…

Importance of thermal treatment of the xerogel

- Removal of residual OR and Cl groups

- Migration of the less refractory oxide species

⇒ **Attractive one-step routes to efficient mixed oxide catalysts**

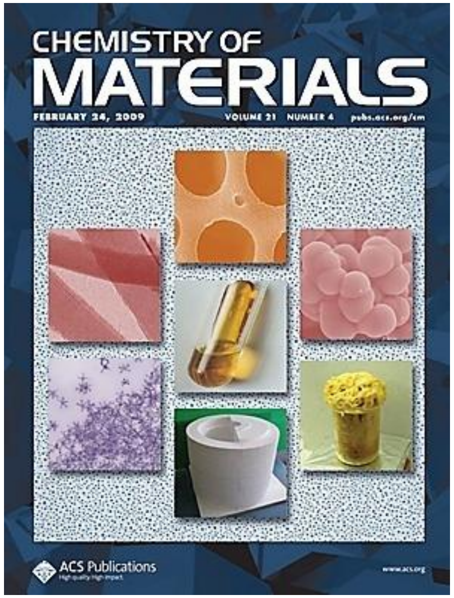
Collaborations

Damien Debecker, Eric Gaigneaux
(Louvain-la-Neuve, Belgium)

Vasile Hulea (MACS-ICGM)
Emil Dumitriu (Iasi, Romania)

Gérard Delahay, Bernard Coq (MACS-ICGM)

Uwe Rodemerck, Mariana Stoyanova (LIKAT,
Rostock, Germany)



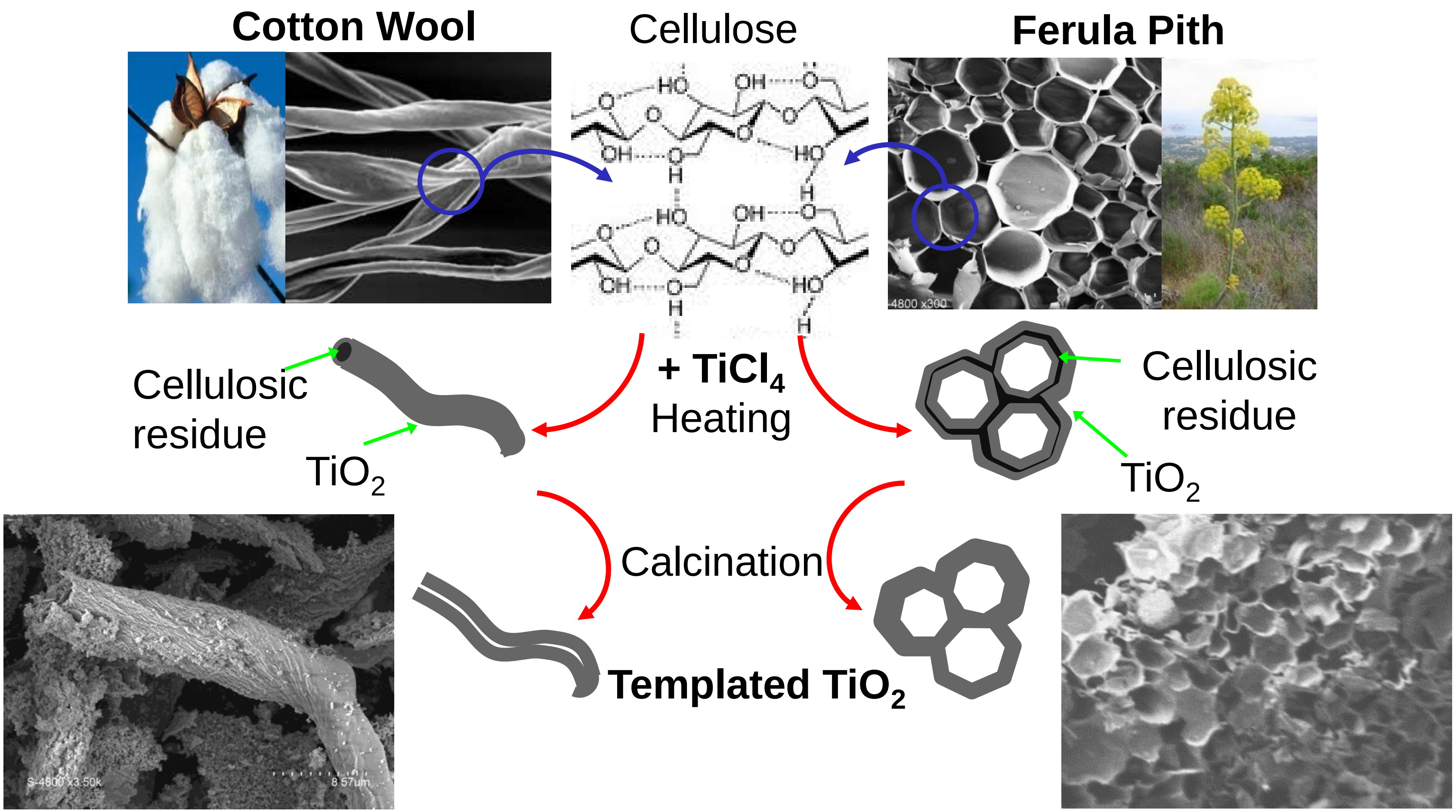
Recent reviews:

Chem. Mater. **2009**, 21, 582-596.

Chem. Soc. Rev. **2012**, 2624-2654.

Perspectives:
Hierarchical oxides using cellulosic materials

Cellulose: 50 wt% O, in alcohol and ether groups. **O-donor? template?**



Cotton Wool

Cellulose

Ferula Pith

Cellulosic residue

TiO_2

+ $TiCl_4$
Heating

Cellulosic residue

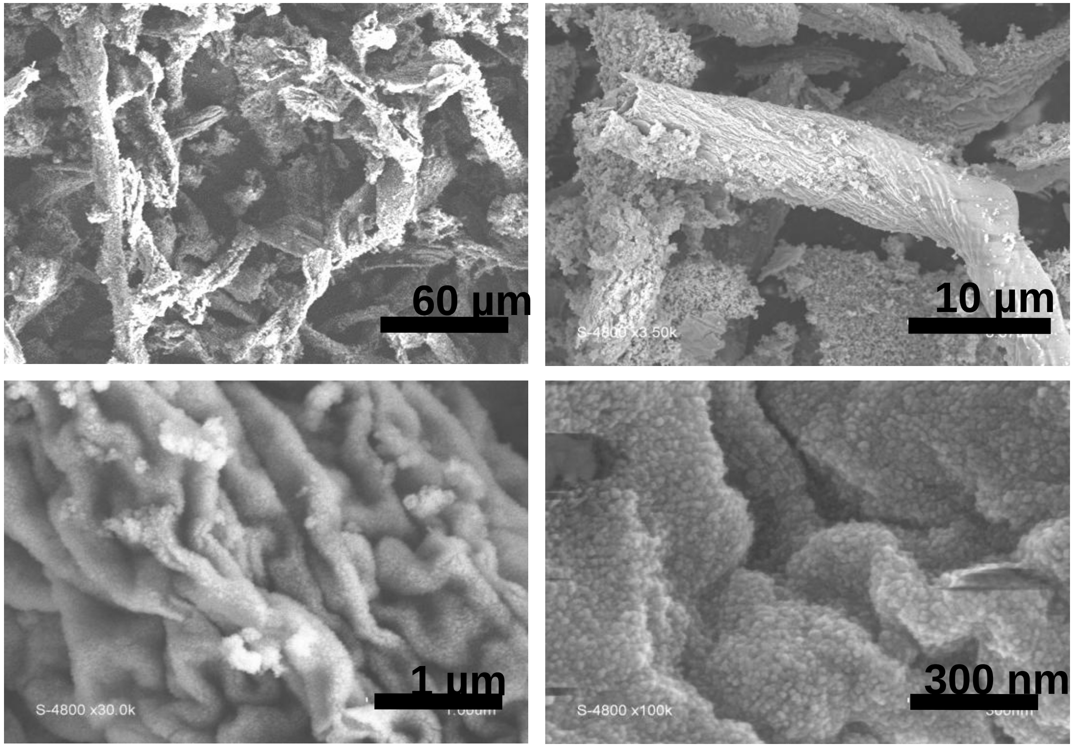
TiO_2

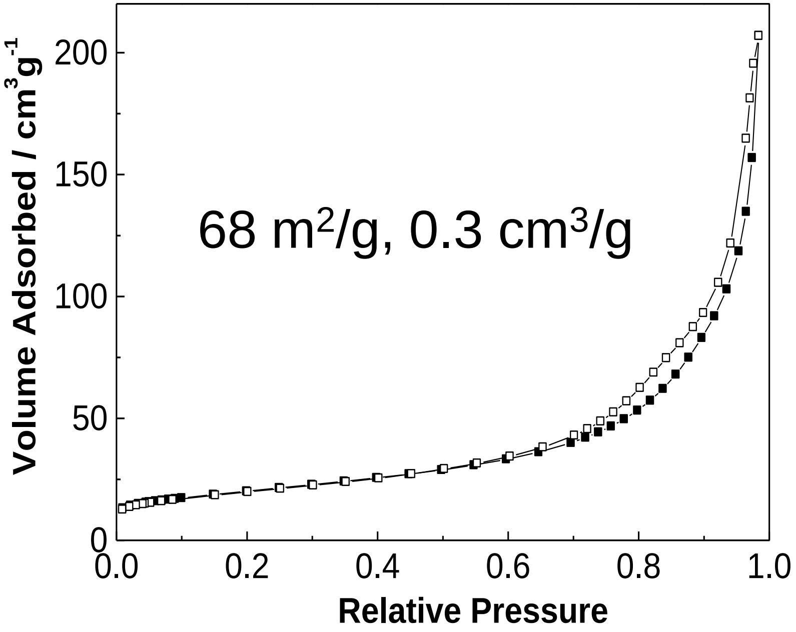
Calcination

Templated TiO_2

Titania from cotton wool

$CTiO_2$ calcined at 400 °C

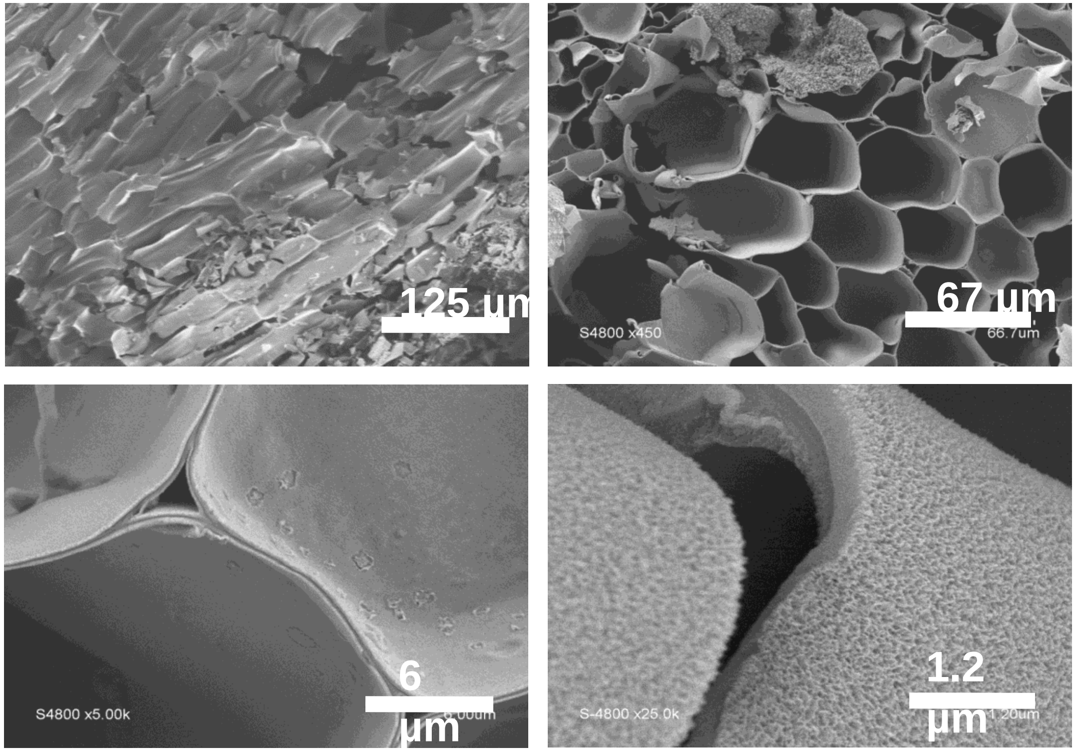


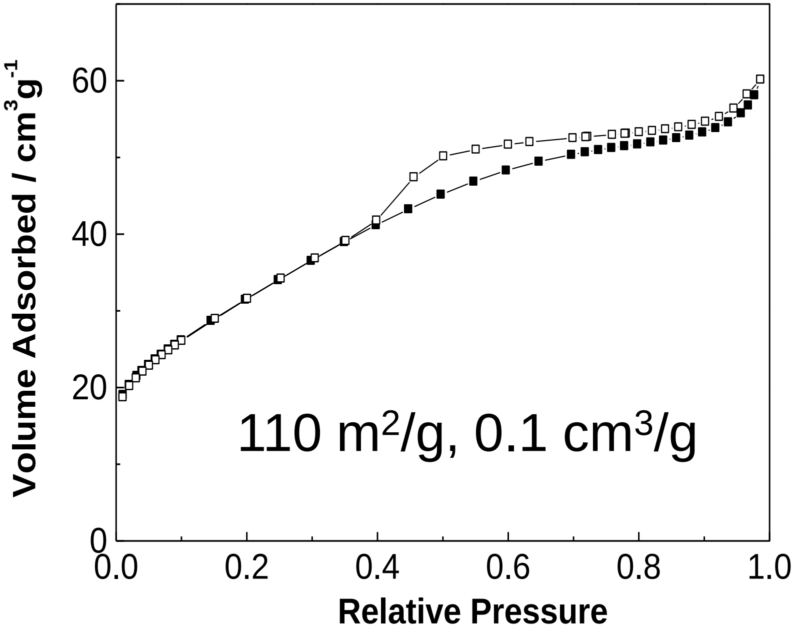

68 m²/g, 0.3 cm³/g

Nice hierarchical fibrillar structure.

Titania from ferula pith

$FTiO_2$ calcined at 400 °C





Hierarchical cellular structure.