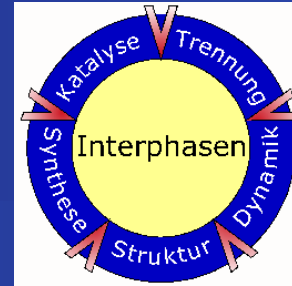


Redox-active Covalent Modifications on Spherical Non-porous Silica Nanometric Particles

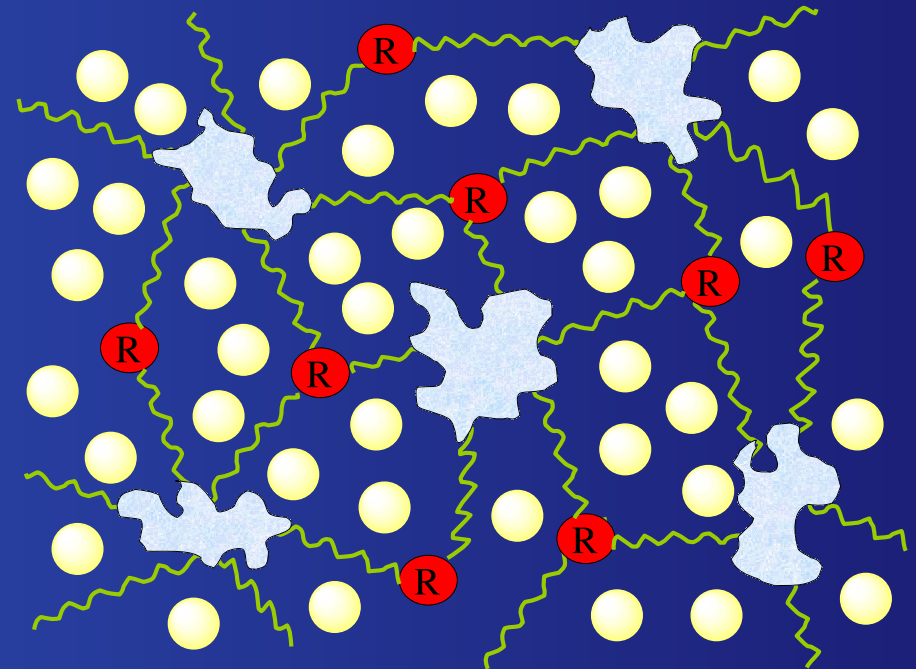
Anna Budny, Filip Novak, Nicolas Plumeré, and Bernd Speiser

Institut für Organische Chemie, Universität Tübingen

Chemistry in Interphases

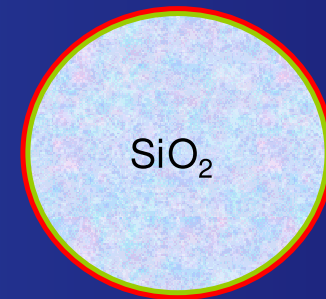


- composition
 - matrix/mobile phase
 - spacer/active centers
 - substrate
- applications
 - separation
 - catalysis
- realization
 - inorganic/organic hybrid structures
 - redox-active centers



The Redox-actively Modified Silica Particle Concept

- inert silica particles as core
- covalent bonding of redox-active molecules
- preferable conditions:
 - spherical: homogeneity
 - non-porous: accessibility
 - monodisperse: immobilization



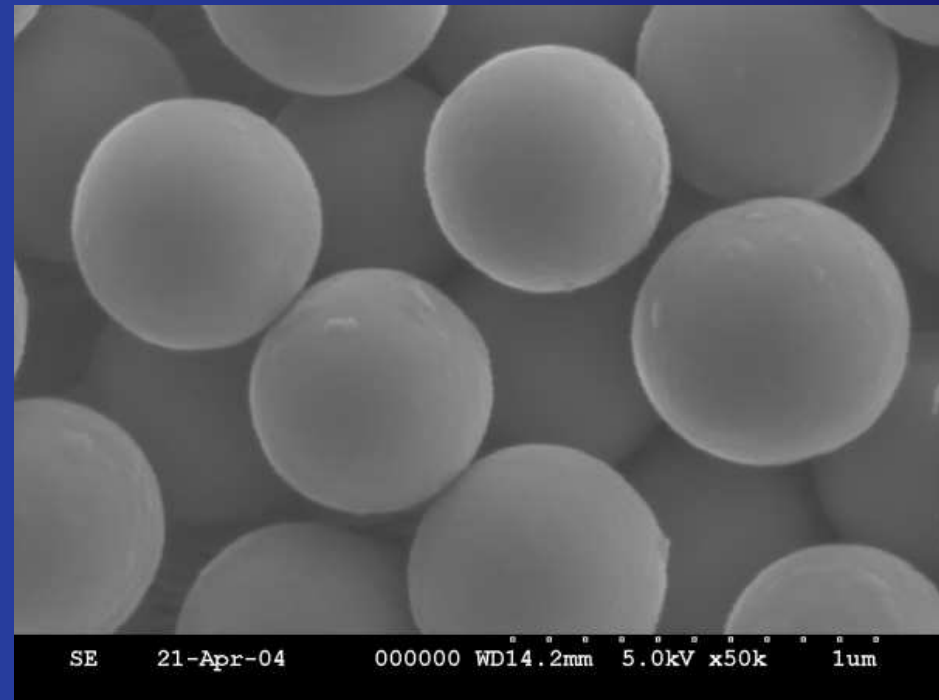
Stöber Silica Nanoparticles

- controlled hydrolysis and condensation (Stöber)



Stöber Silica Nanoparticles

- controlled hydrolysis and condensation (Stöber)
- shape and monodispersity



Stöber Silica Nanoparticles

- controlled hydrolysis and condensation (Stöber)
- shape and monodispersity
- size and porosity

| material | diameter d /nm | | specific surface area $A/m^2 g^{-1}$ | | specific concentration $\Gamma_{\max}/mol g^{-1} \times 10^4$ |
|----------|------------------|--------|---|------------|--|
| | DLS | SEM | BET | calculated | calculated |
| M1a | 150 | 140±18 | 33.1 | 19.48 | 1.74 |
| M1b | 187 | 178±10 | 24.5 | 15.32 | 1.37 |
| M1c | 252 | 252±25 | 16.0 | 10.82 | 0.967 |
| M1d | 290 | 262±19 | 16.8 | 10.41 | 0.930 |
| M1e | 639 | 592±25 | 6.4 | 4.61 | 0.411 |
| M1f | 755 | 735±23 | 4.2 | 3.71 | 0.331 |

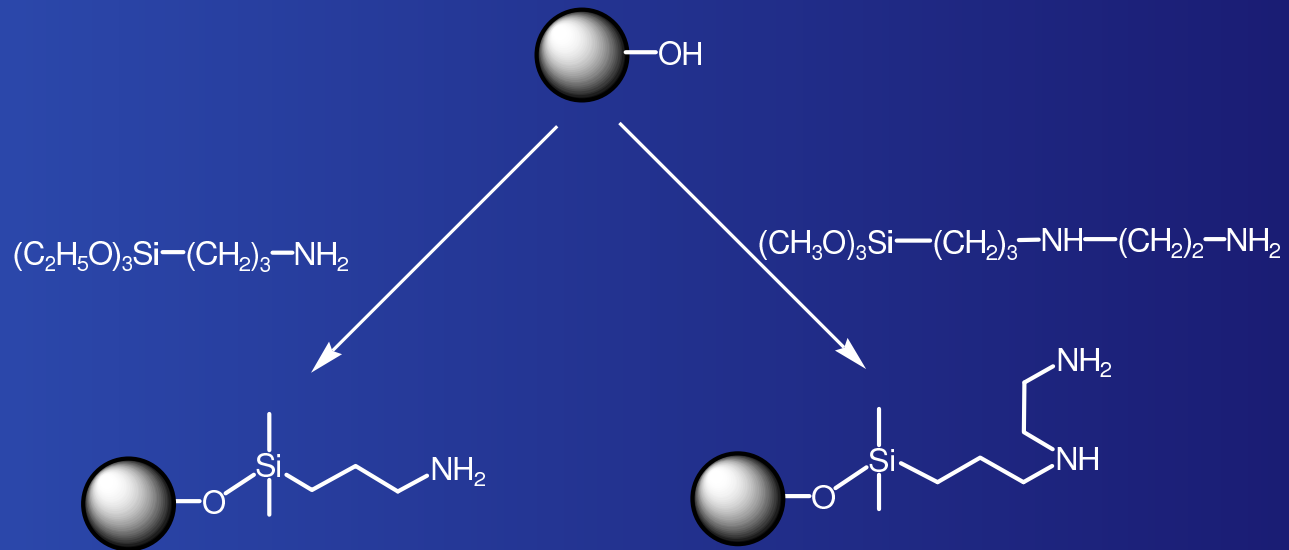
Stöber Silica Nanoparticles

- controlled hydrolysis and condensation (Stöber)
- shape and monodispersity
- size and porosity
- surface chemistry: OH

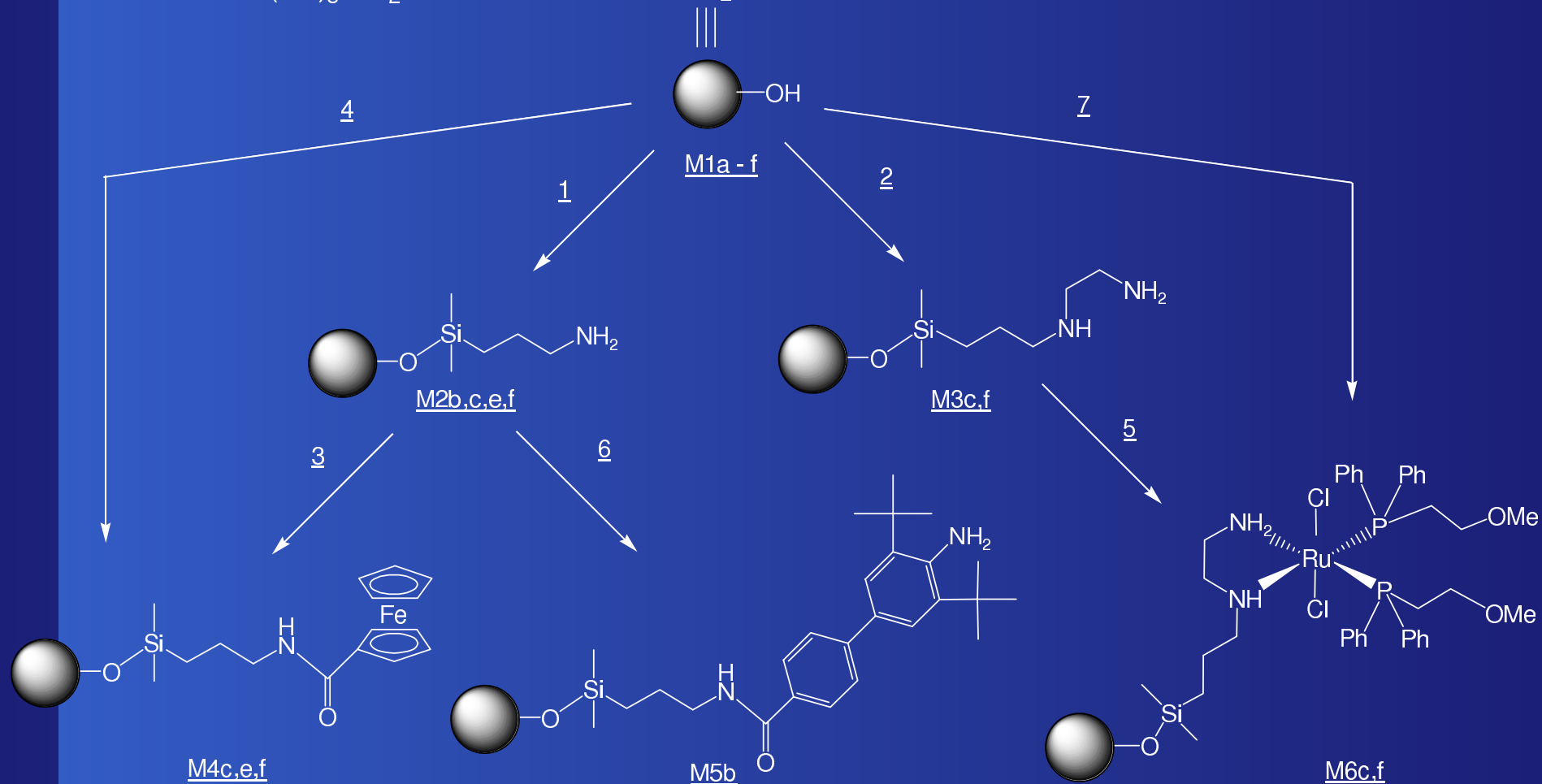
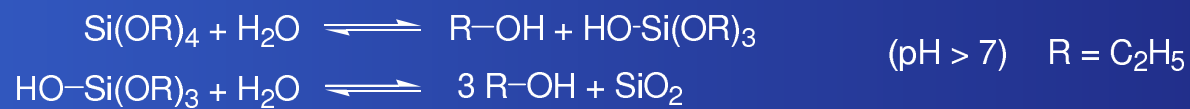
| material | diameter d /nm | | specific surface area $A/m^2 g^{-1}$ | | specific concentration $\Gamma_{\max}/mol g^{-1} \times 10^4$ |
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| M1f | 755 | 735±23 | 4.2 | 3.71 | 0.331 |

Aminopropyl Modified Silica Particles

- condensation
- mono-, diamine
- ninhydrin reaction
- ^1H suspension NMR
- ^{13}C suspension NMR

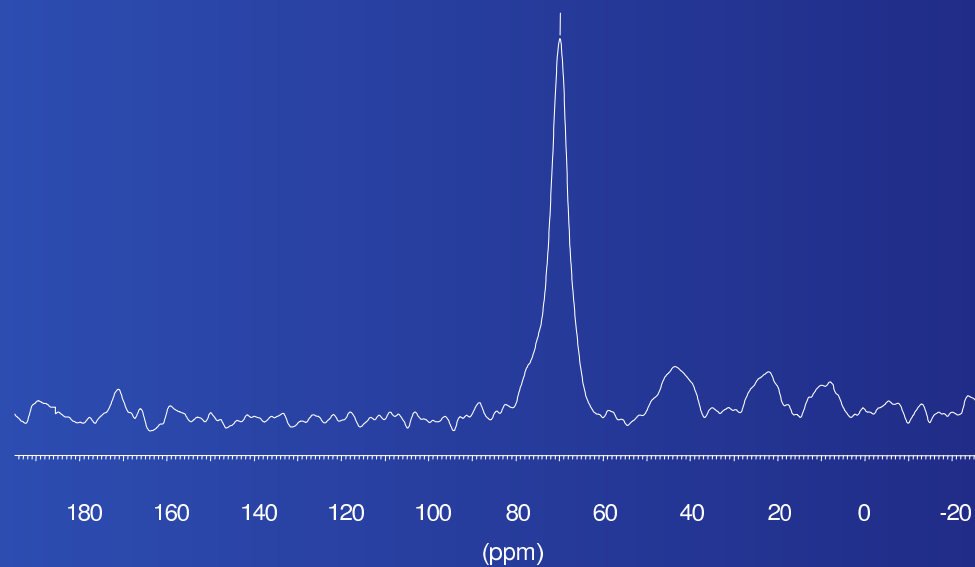


Modification Pathways



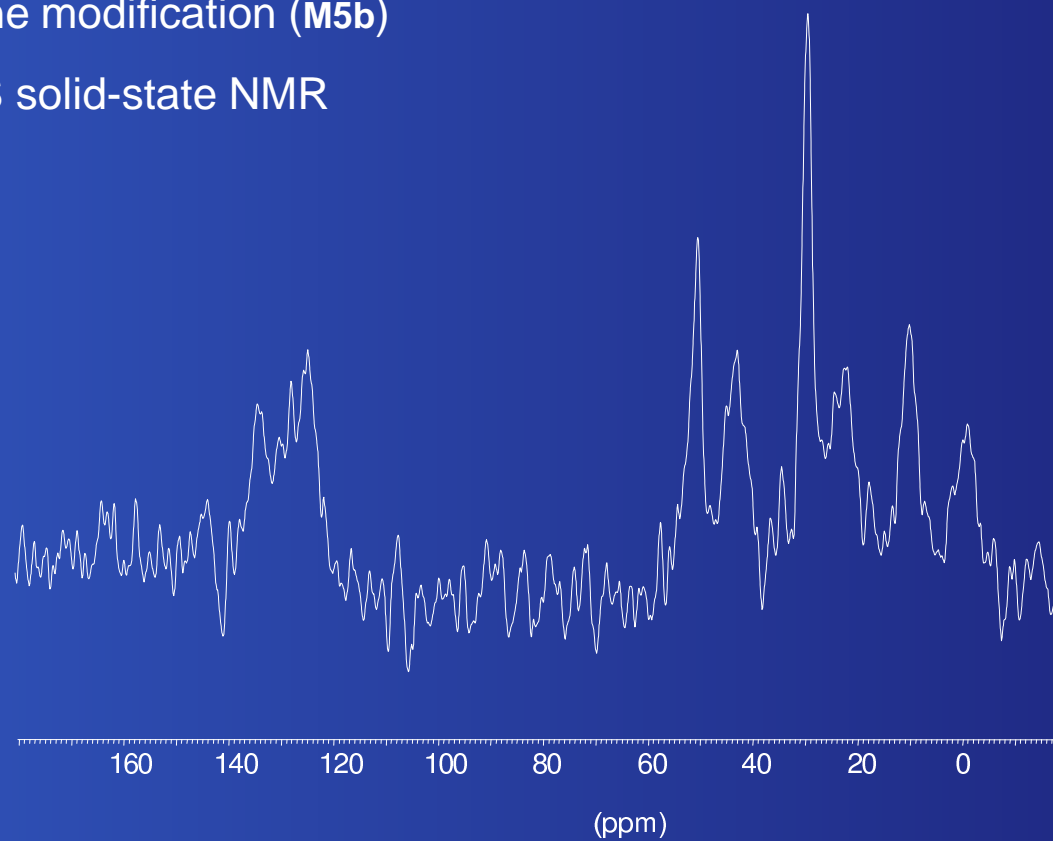
Redox-actively Modified Silica Particles

- $d = 592$ nm
- fc modification (M4e)
- ^{13}C -CP/MAS solid-state NMR



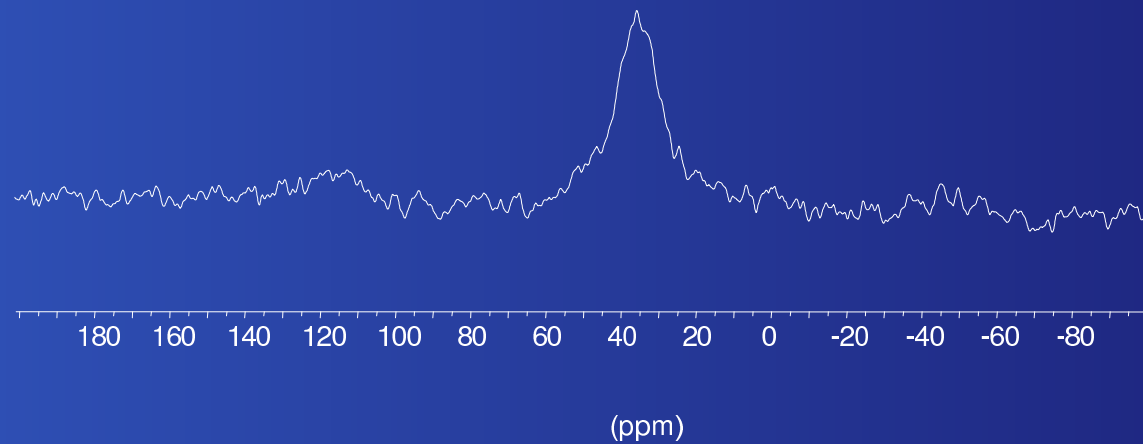
Redox-actively Modified Silica Particles

- $d = 178$ nm
- biphenylamine modification (**M5b**)
- ^{13}C -CP/MAS solid-state NMR



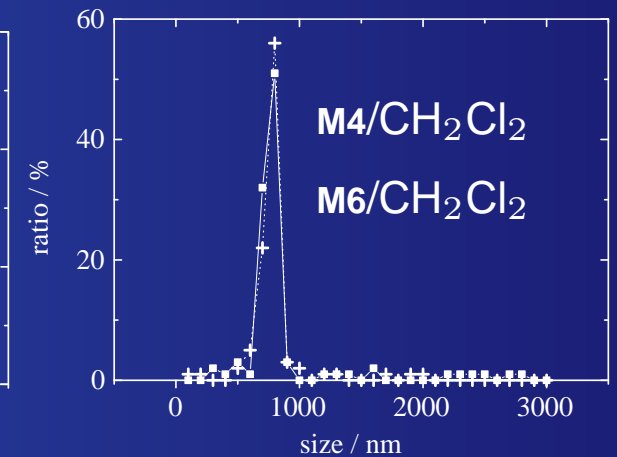
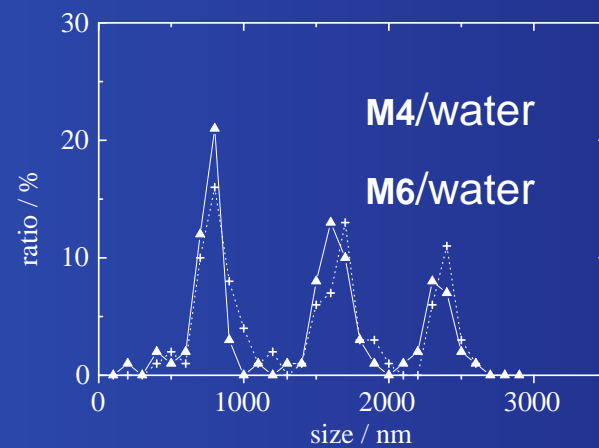
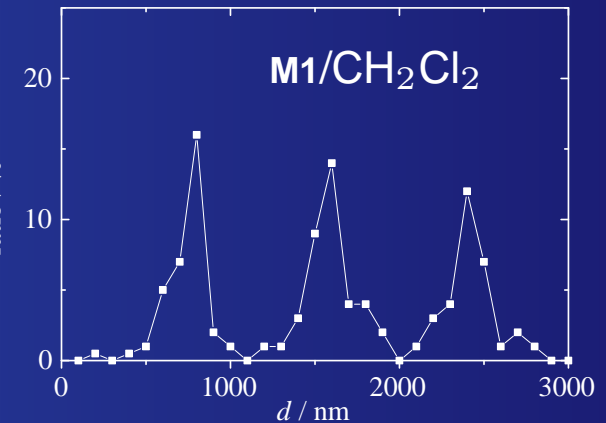
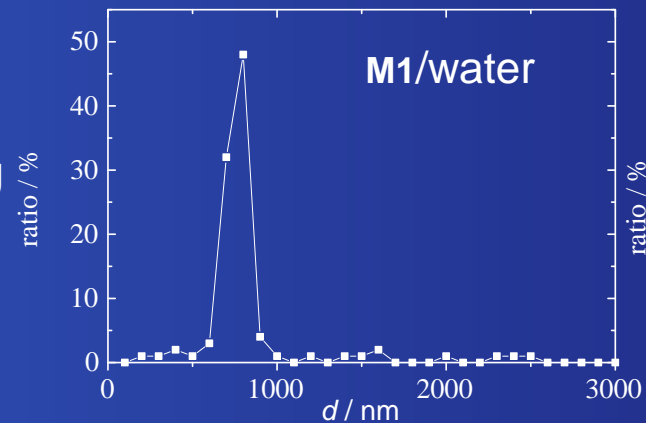
Redox-actively Modified Silica Particles

- $d = 735$ nm
- ruthenium complex modification (M6f)
- ^{31}P -VACP/MAS solid-state NMR



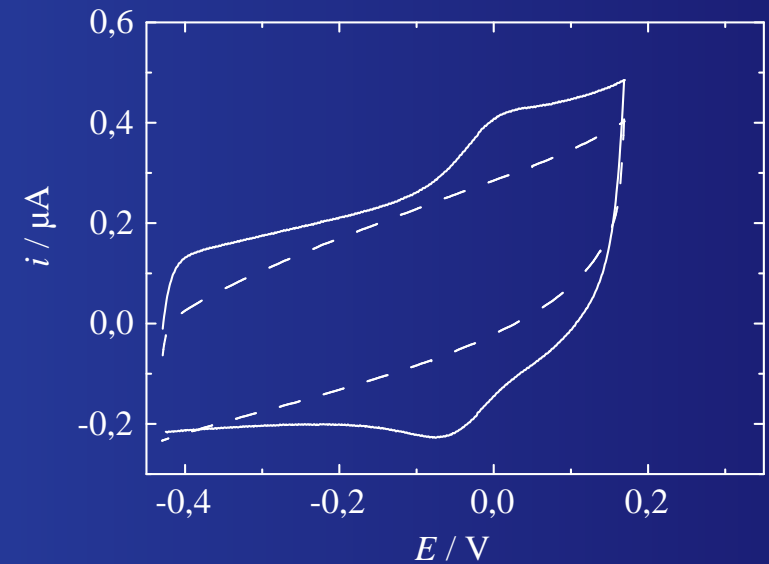
Particle Agglomeration Behavior

- $d = 735$ nm
- dynamic light scattering
- single/multiple signal(s)
- depending on solvent properties
- modified materials not agglomerated in CH_2Cl_2



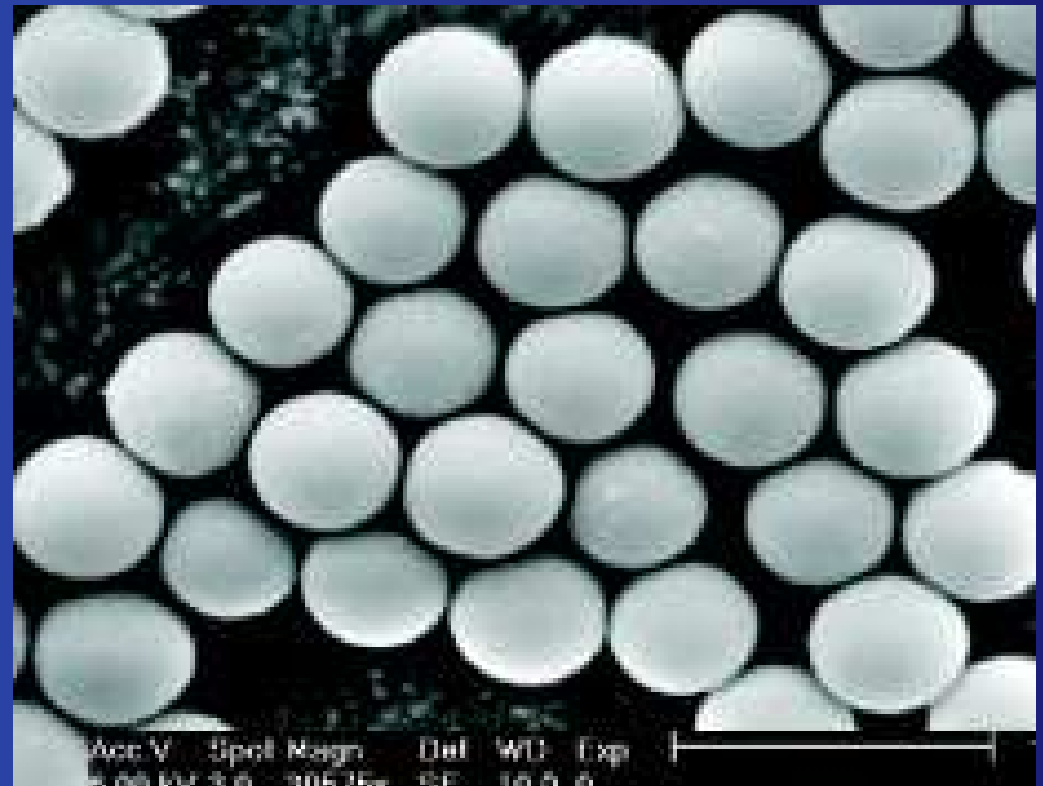
Adsorption of Modified Silica Particles on Pt Electrodes

- no immediate electrochemical response at Pt electrode in CH_2Cl_2 suspension (broken line)
- longer exposure: weak, but increasing signal in CV (full line)



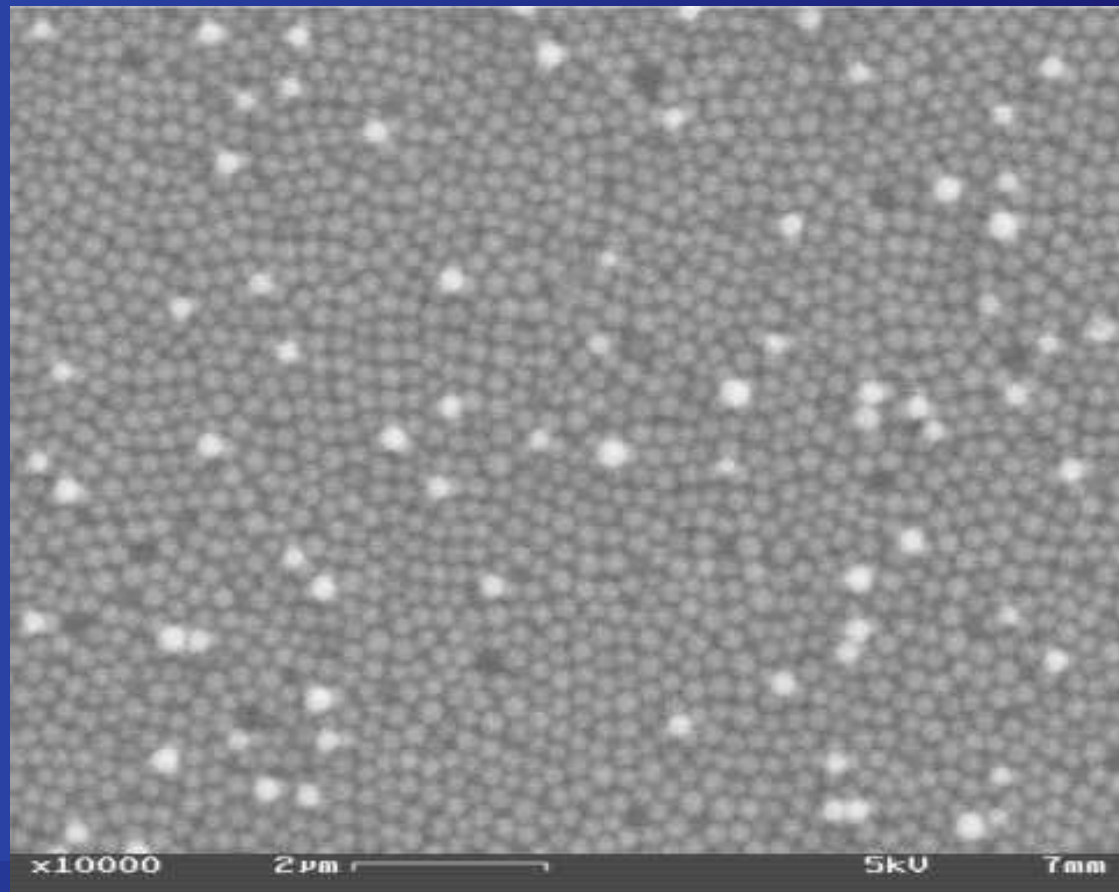
Adsorption of Modified Silica Particles on Pt Electrodes

- $d = 592 \text{ nm}$
- fc modification (M4e)
- spontaneous adsorption



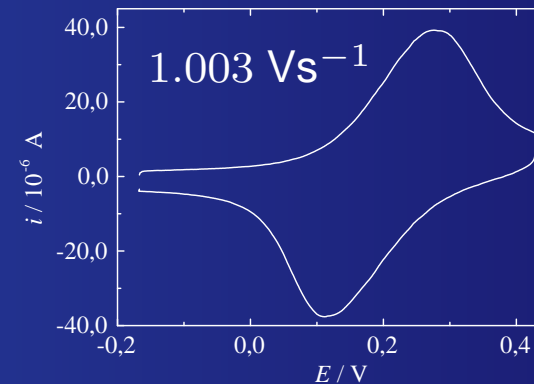
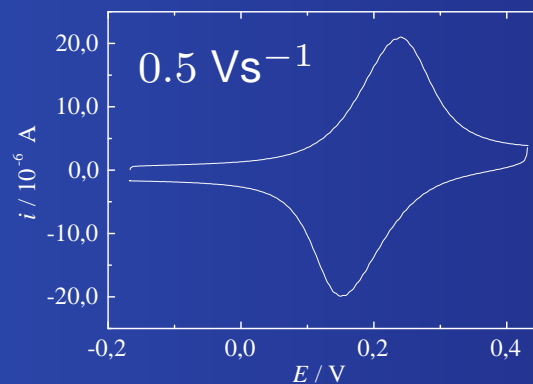
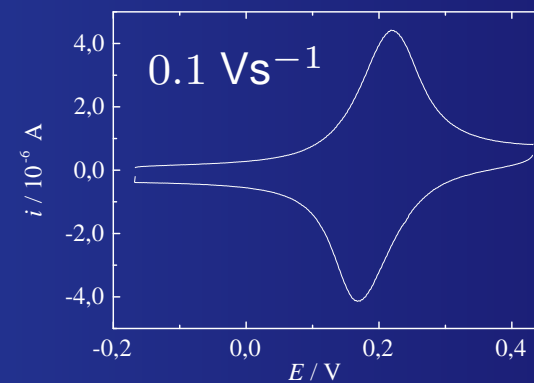
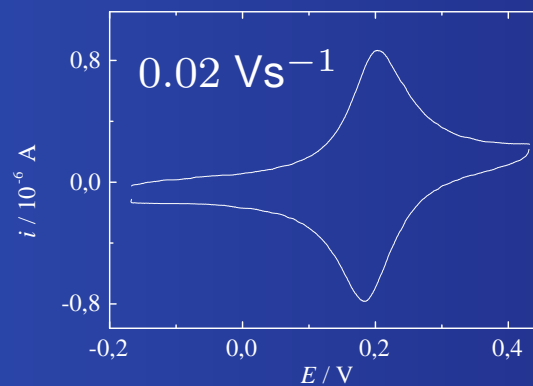
Adsorption of Modified Silica Particles on Pt Electrodes

- $d = 260 \text{ nm}$
- aminopropyl modification (M2)
- dip coating
from water/ethanol, 1:1
with controlled retraction



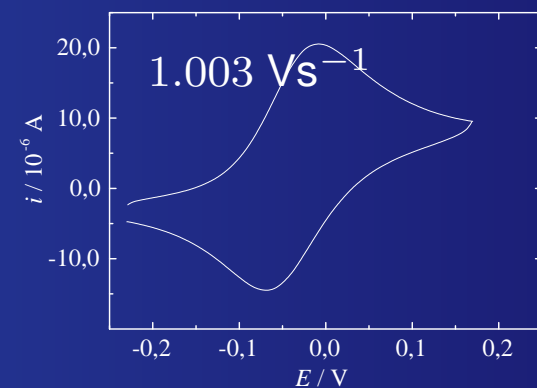
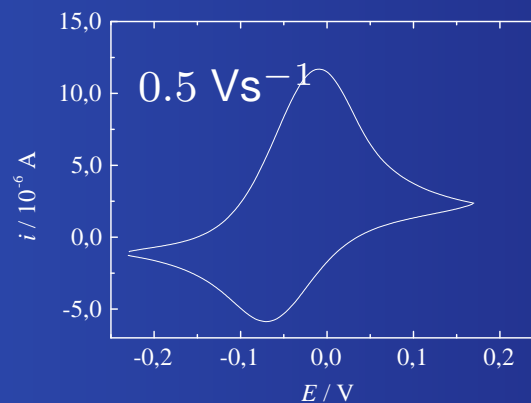
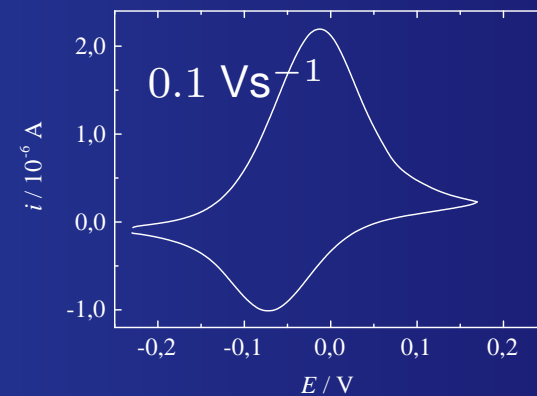
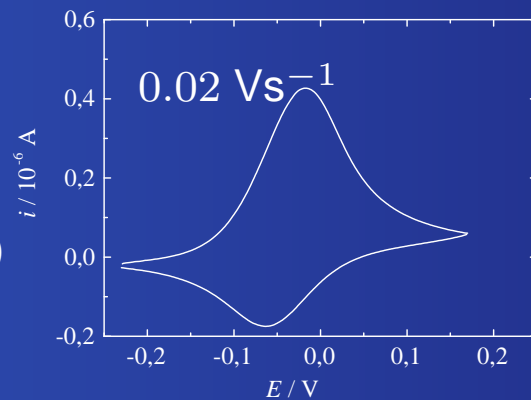
Cyclic Voltammetry of Modified Silica Particles

- time scale dependent shape of voltammograms
- fc modified particles (M4f)



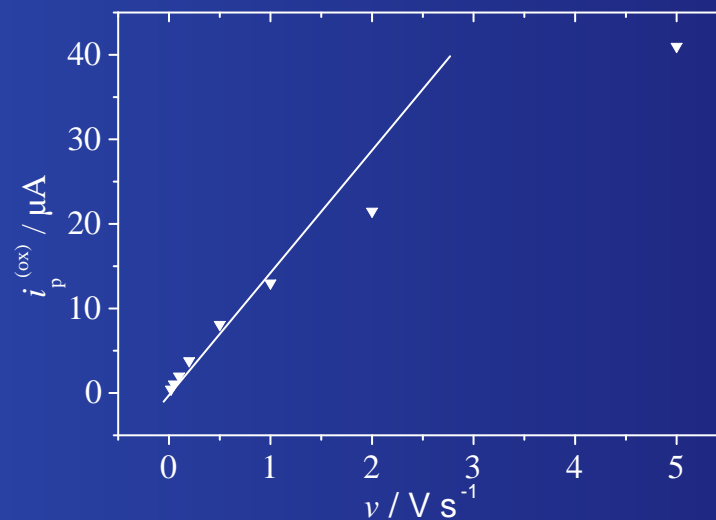
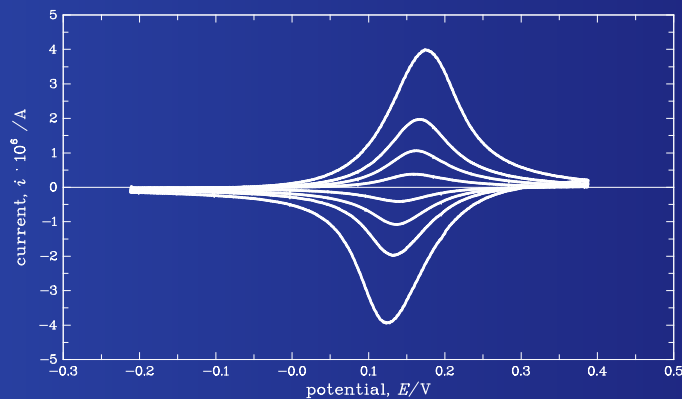
Cyclic Voltammetry of Modified Silica Particles

- time scale dependent shape of voltammograms
- Ru modified particles (M6f)

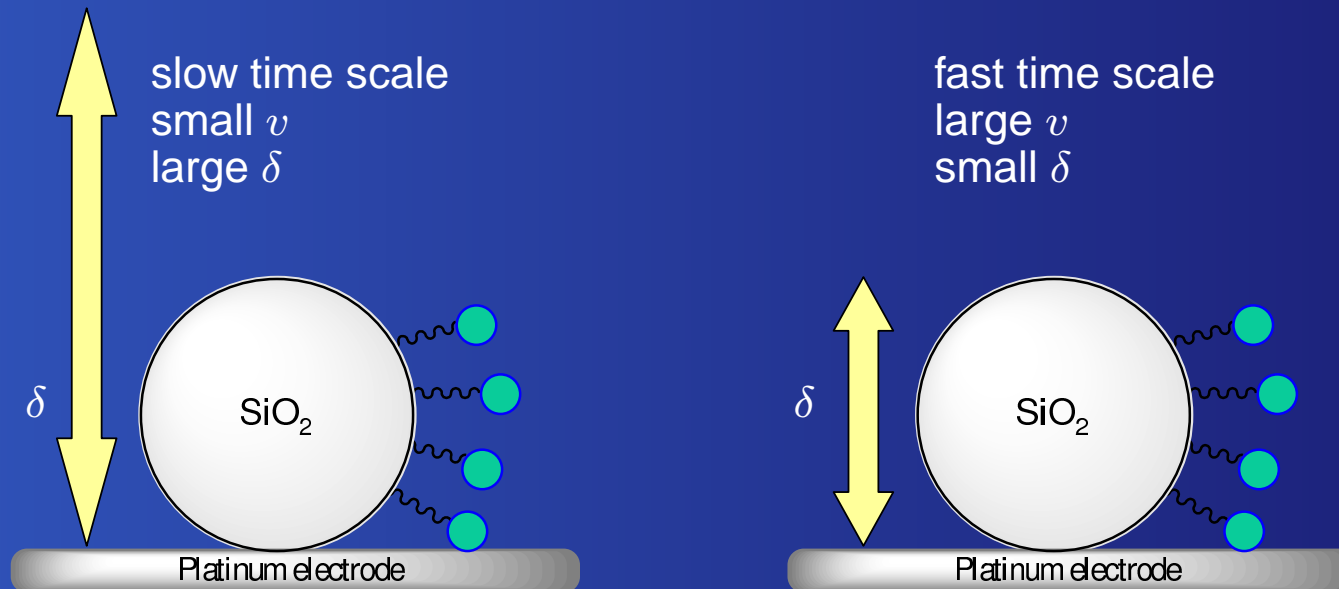


Cyclic Voltammetry of Modified Silica Particles

- deviation from linear i_p vs. v behavior
- similar to dendrimers (Amatore et al.)
- electron hopping on small objects

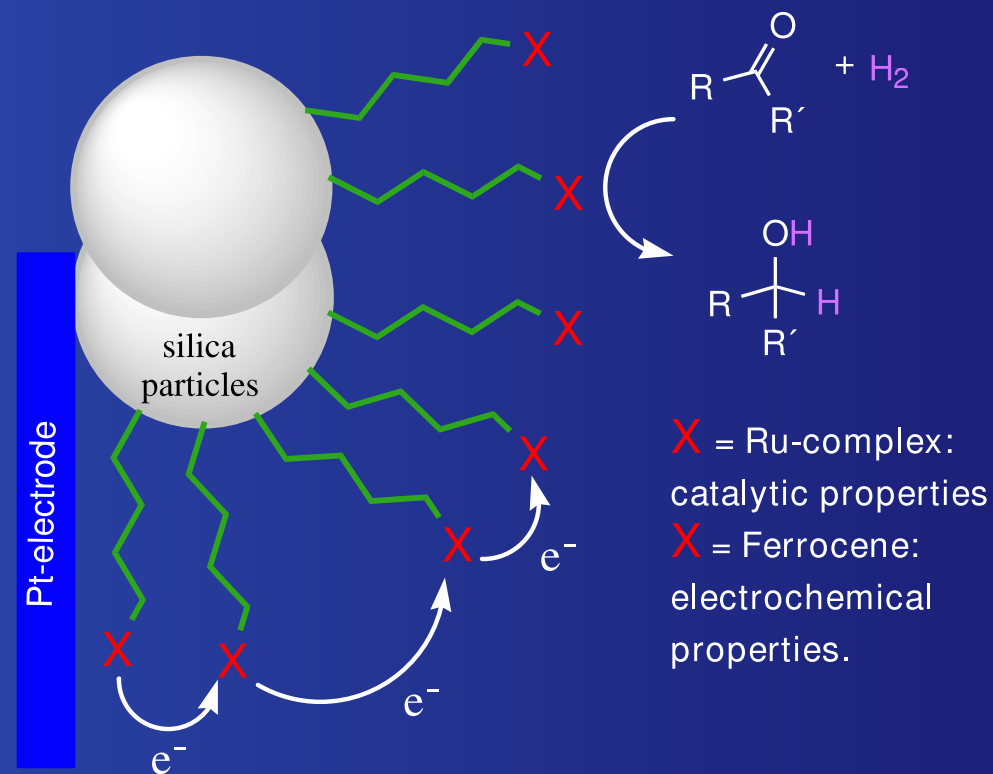


Cyclic Voltammetry of Modified Silica Particles



Catalytic Activity of Modified Silica Particles

- Ru complex: immobilized hydrogenation catalyst
- transfer hydrogenation of acetophenone



Catalytic Activity of Modified Silica Particles

● Ru complex: immobilized hydrogenation catalyst

● transfer hydrogenation of acetophenone

● activity:

● bare particles: –

● modified particles: +

● solution: –

● recovered particles: + (reduced)

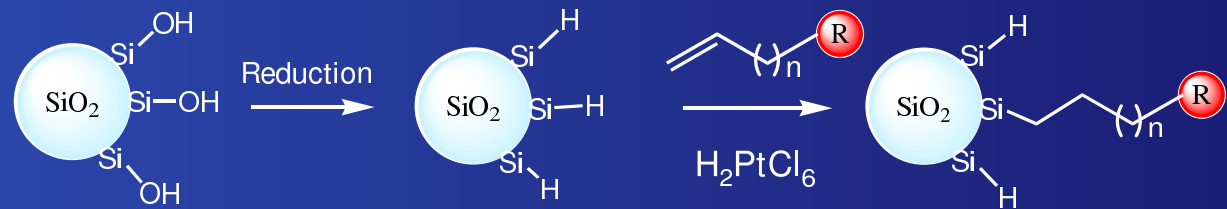
| material | duration/h | turnover/% | TOF/ h ⁻¹ |
|------------|------------|------------|----------------------|
| M1 | 20 | 0 | — |
| M6f | 14 | 100 | 6.45 |
| solution | 21 | 0 | — |
| M6f (rec.) | 91 | 56 | 0.62 |

An Alternative Immobilization Strategy for Silica Particles

- Si–O–Si bond hydrolysis?

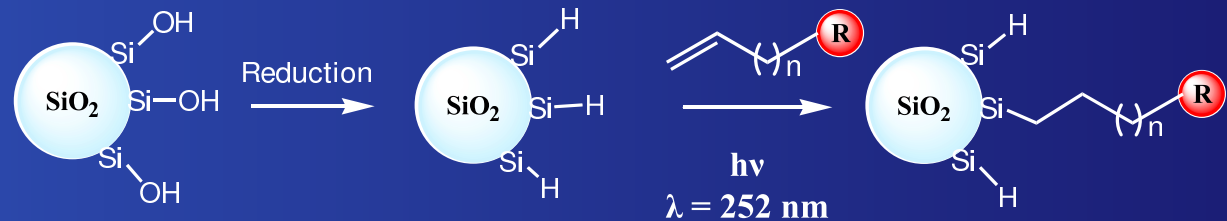
An Alternative Immobilization Strategy for Silica Particles

- Si–O–Si bond hydrolysis?
- reduction of Si–OH
- hydrosilylation
 - Pt catalysis



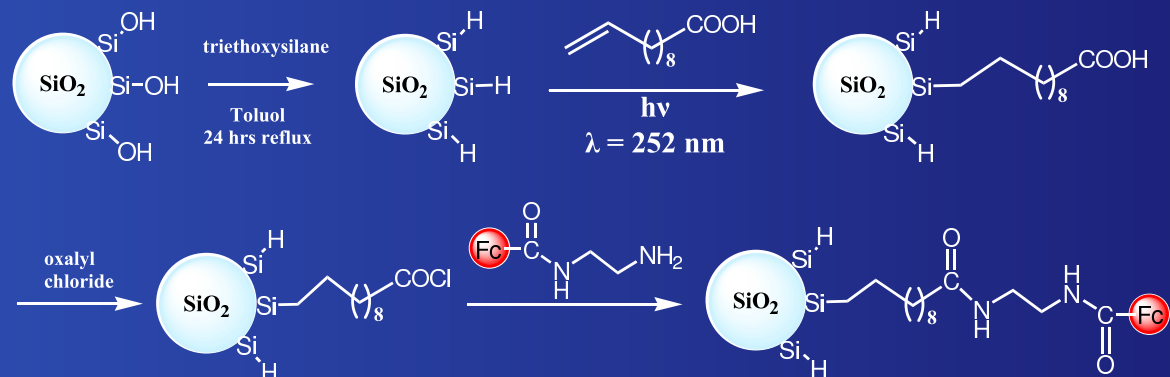
An Alternative Immobilization Strategy for Silica Particles

- Si–O–Si bond hydrolysis?
- reduction of Si–OH
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 - photochemical activation



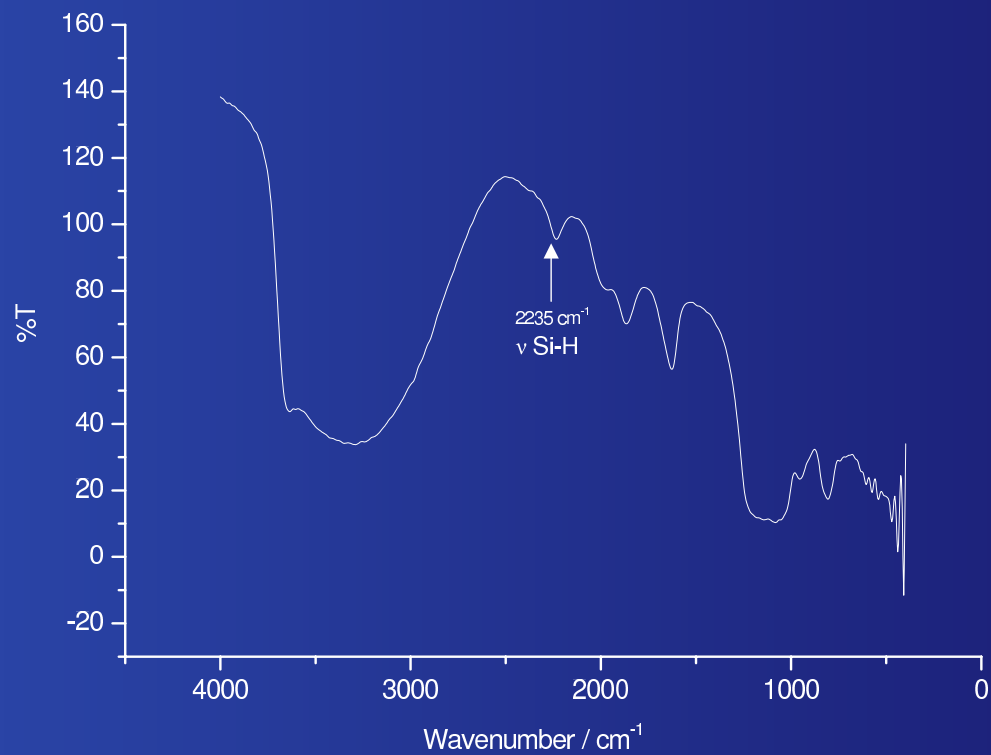
An Alternative Immobilization Strategy for Silica Particles

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 - Pt catalysis
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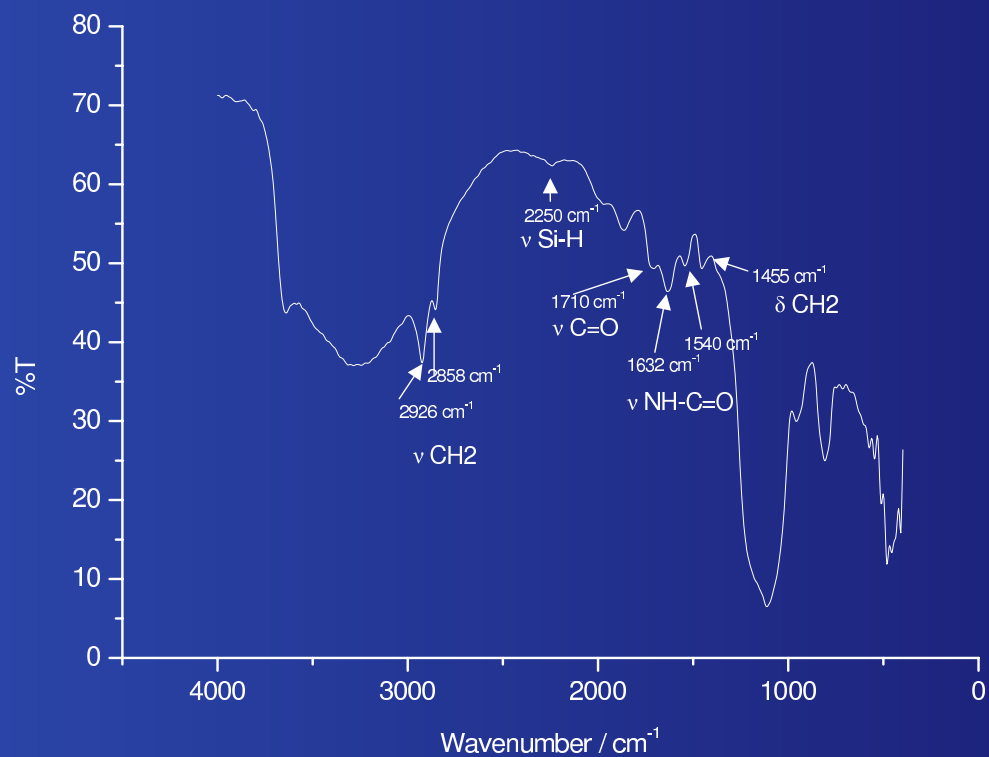
Si-C Bonded Ferrocene

- DRIFT spectrum of $\text{SiO}_2\text{-H}$



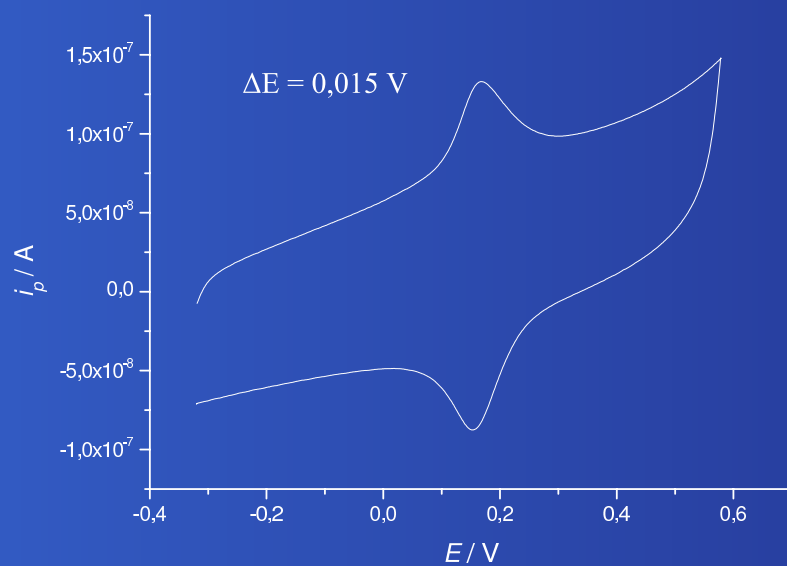
Si-C Bonded Ferrocene

● DRIFT spectrum of $\text{SiO}_2\text{-Fc}$

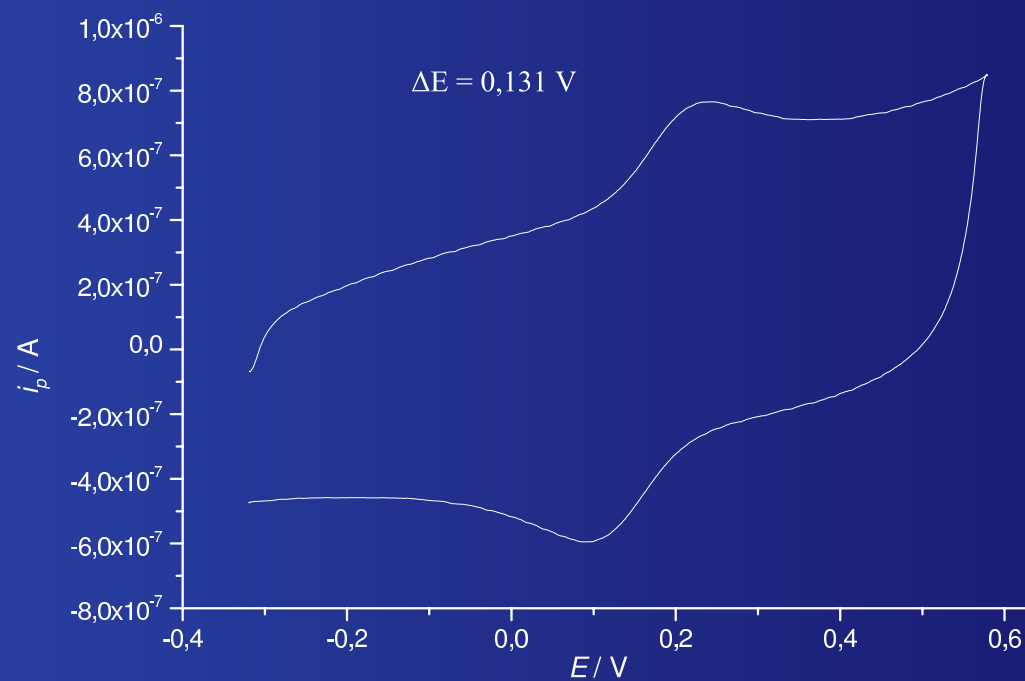


Si-C Bonded Ferrocene

- cyclic voltammetry after spontaneous adsorption, scan rate dependence



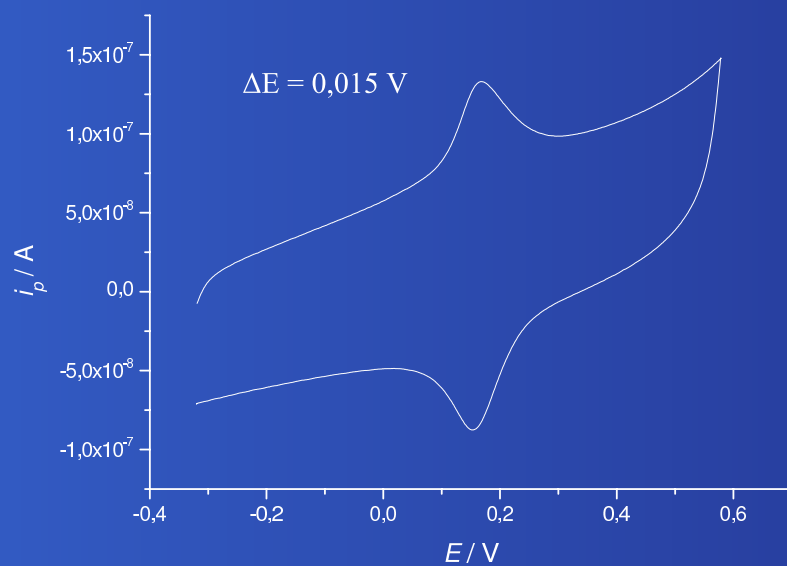
in CH_2Cl_2 , 0.1 M n-Bu₄NPF₆, 0.02 V/s, vs Fc/Fc⁺



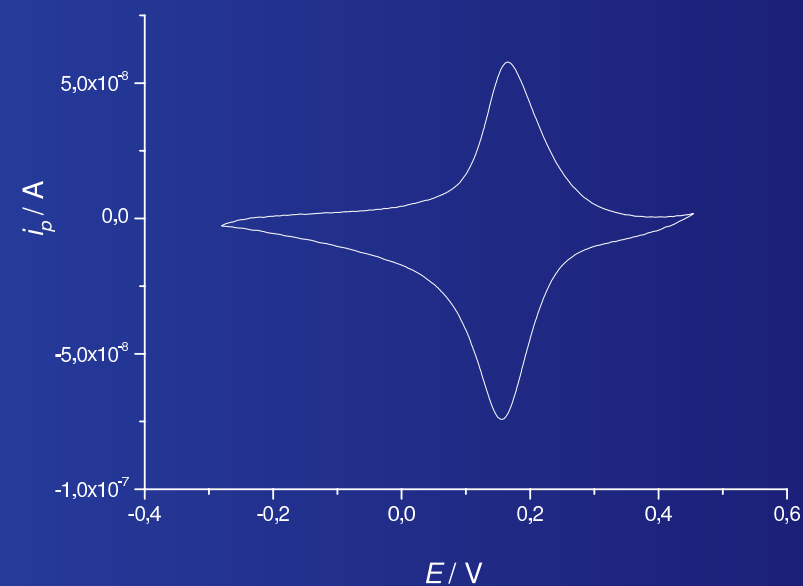
in CH_2Cl_2 , 0.1 M n-Bu₄NPF₆, 0.2 V/s, vs Fc/Fc⁺

Si-C Bonded Ferrocene

- cyclic voltammetry after spontaneous adsorption, effect of background correction



in CH_2Cl_2 , 0.1 M $n\text{-Bu}_4\text{NPF}_6$, 0.02 V/s, vs Fc/Fc^+



in CH_2Cl_2 , 0.1 M $n\text{-Bu}_4\text{NPF}_6$, 0.02 V/s, vs Fc/Fc^+
with background correction

Conclusions

- Stöber silica nanospheres as support
- unique environment for covalently bound redox-active molecules
- electrochemical activity after adsorption: electron hopping
- catalytic activity: transfer hydrogenation
- alternative immobilization strategy: Si–C bonds by photochemical hydrosilylation

Acknowledgements

- cooperation and coworkers
 - Klaus Albert, Borre Borresen, Thomas Chassé, Hans Egelhaaf, Peter Grathwohl, Ekkehard Lindner, Hermann A. Mayer
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 - Max-Buchner-Forschungstiftung
 - Marie Curie training site “SurFace”