

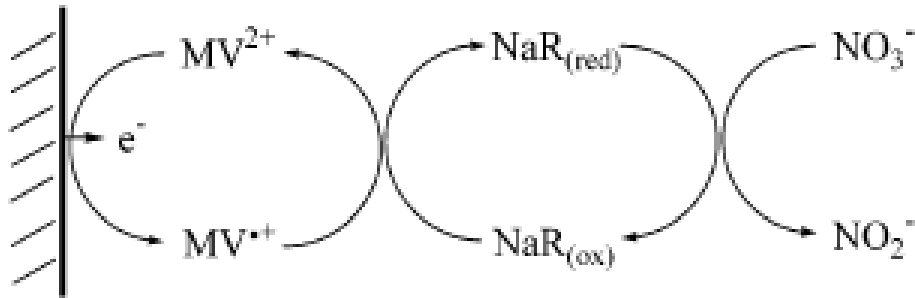
# Synthese, Charakterisierung und Elektrochemie von redox-modifizierten Kieselgelpartikeln

Nicolas Plumeré  
AK Prof. Dr. B. Speiser  
*Institut für Organische Chemie, Universität Tübingen*

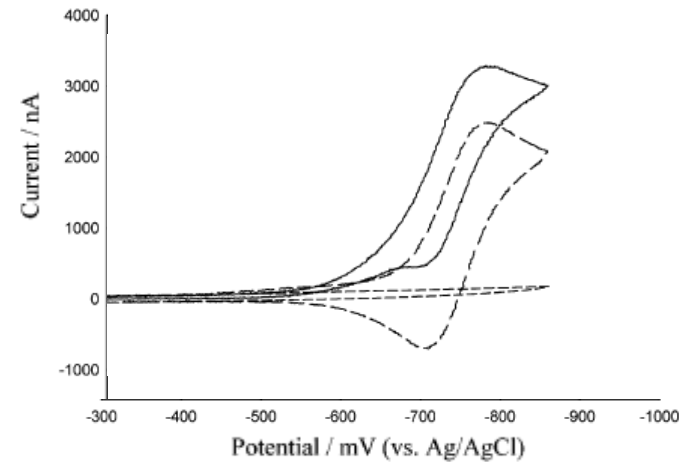
**Doktorandenseminar Biggesees Academy**

Attendorn  
Februar 9, 2006

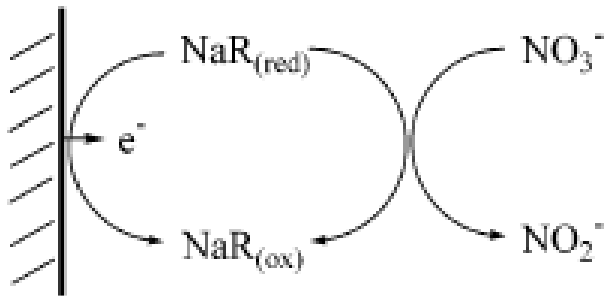
# Biosensor basiert auf Nitrat-Reductase (NaR):



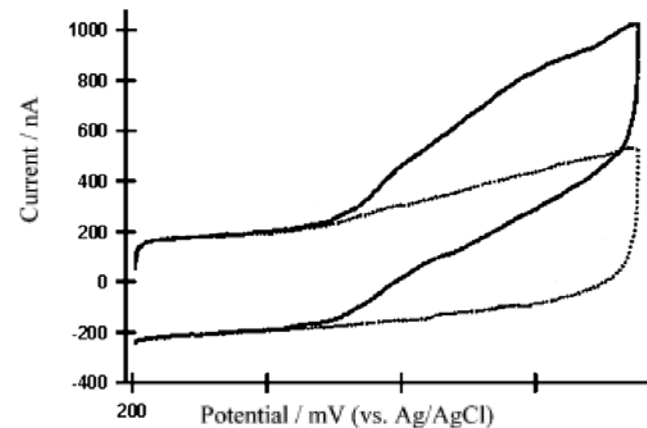
- mit Methylviologen (MV) als Mediator



D. Quan, J. H. Shim, J. D. Kim, H. S. Park, G. S. Cha, and H. Nam, *Anal. Chem.* **2005**, 77,4467-4473



- durch direkten Elektronentransfer



G. G. Barbier, R. C. Joshi, E. R. Campbell, and W. H. Campbell, *Protein Expression and Purification* **2004**, 37 61–71

# Biosensor basiert auf Nitrat-Reductase (NaR):

- Hohe Selektivität für Nitrat<sup>[1]</sup>
- Gute Aktivität <sup>[1]</sup>
- Gute Stabilität in Puffer oder als Pulver gelagert
- NaR wird in grösseren Mengen in einem Fermenter produziert
- Aktiv nur als Dimer / Deaktivierung während Immobilisierung an Elektrode
- Stabilität ist auch gering wenn immobilisiert an Elektrodenmaterial
- Die Immobilisierung in leitfähigen Polymeren führt zur totalen Deaktivierung<sup>[2]</sup>

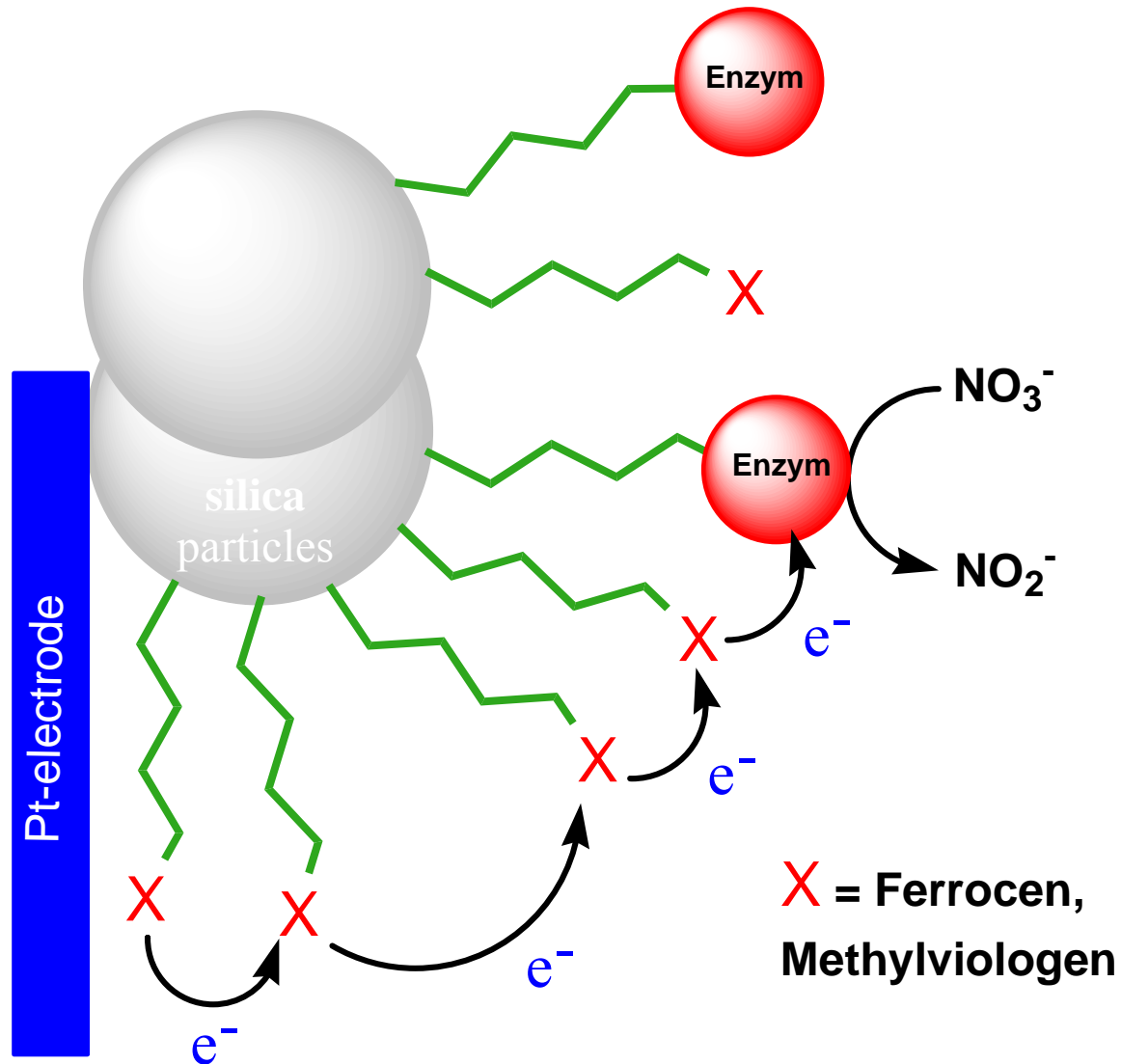


**Zurzeit gibt es keinen erfolgreichen kommerziellen Nitrat-Biosensor**

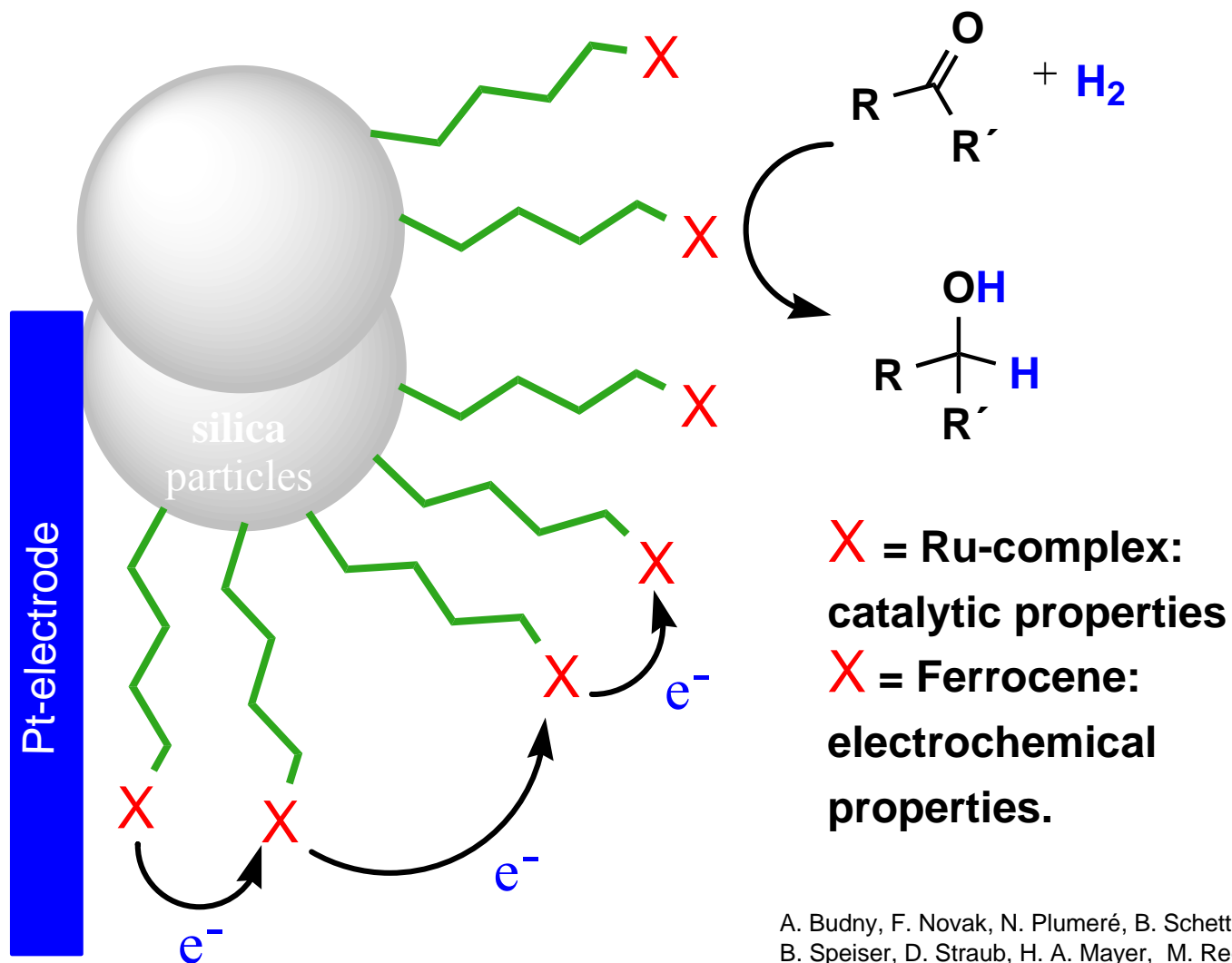
1. G. G. Barbier, R. C. Joshi, E. R. Campbell, and W. H. Campbell, Protein Expression and Purification **2004**, 37 61–71

2. G. Ramsay and S. M. Wolpert, Anal. Chem. **1999**, 71,504-506

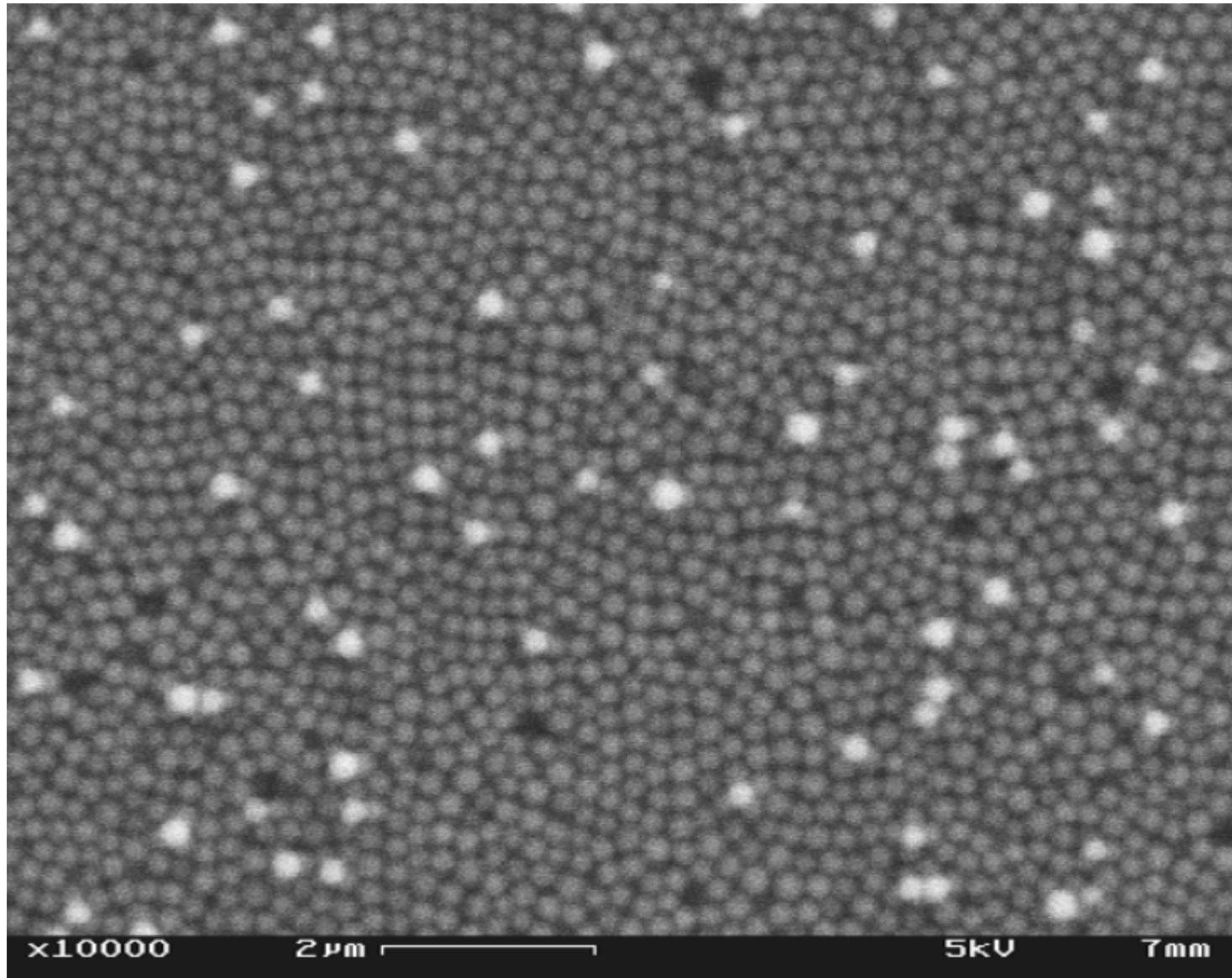
# Alternative für Enzymimmobilisierung an Elektrodenoberflächen



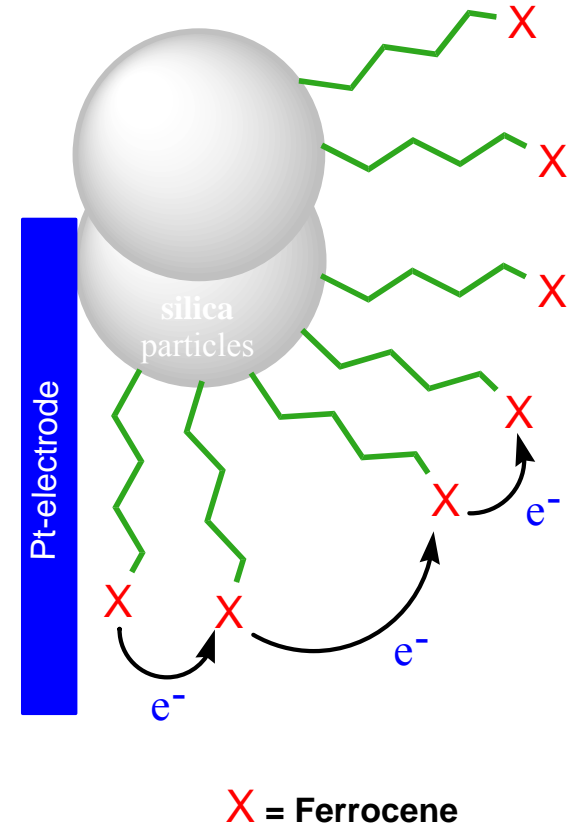
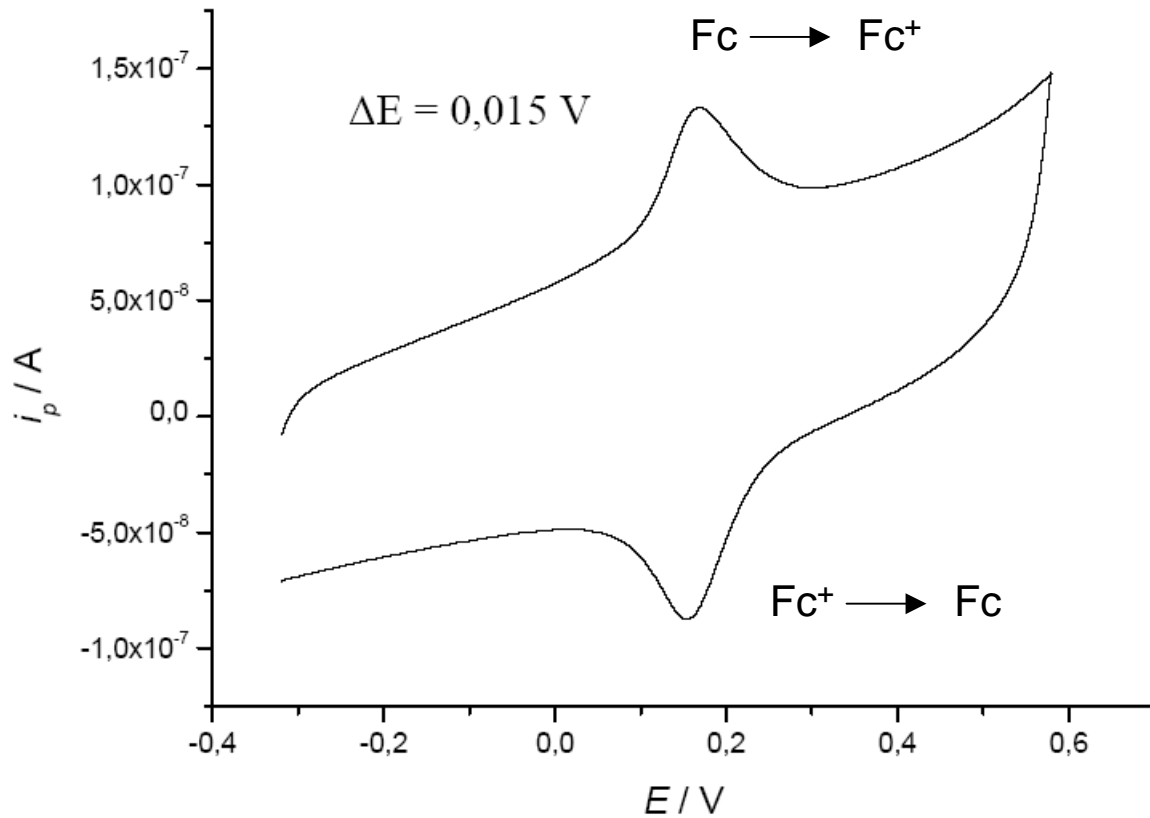
# Elektrochemie von redoxaktiven Kieselgelpartikeln



# Adsorption der redoxaktiven Kieselgelpartikel an Platin



# Cyclovoltammetrie von ferrocen-modifiziertem Kieselgel



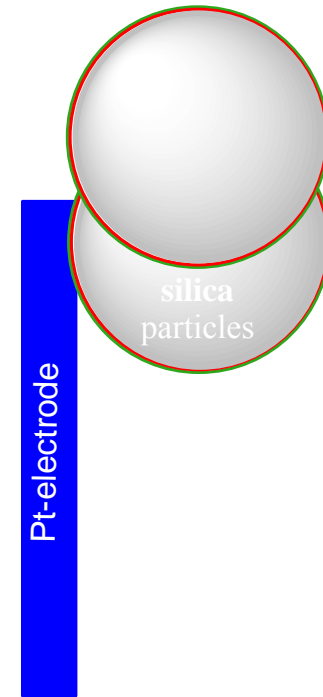
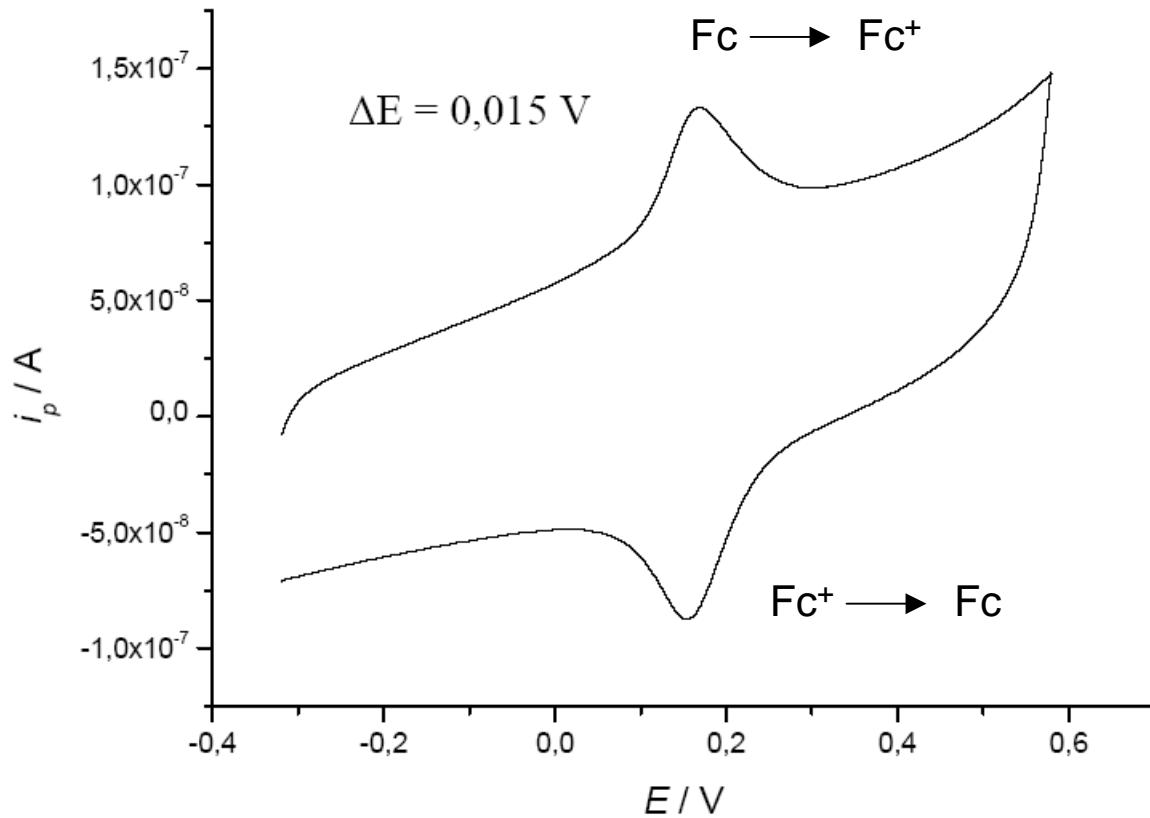
$$Fc_{AAS} = 1.96 \cdot 10^{-6} \text{ mol m}^{-2}$$



$$Fc_{CV} = 50 \% \text{ von } Fc_{AAS}$$

$$Fc_{CV} = 9.67 \cdot 10^{-7} \text{ mol m}^{-2}$$

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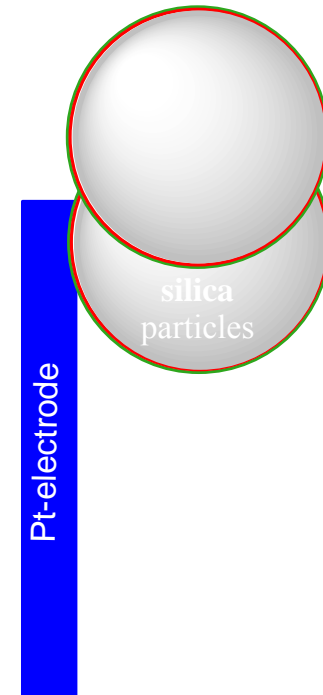
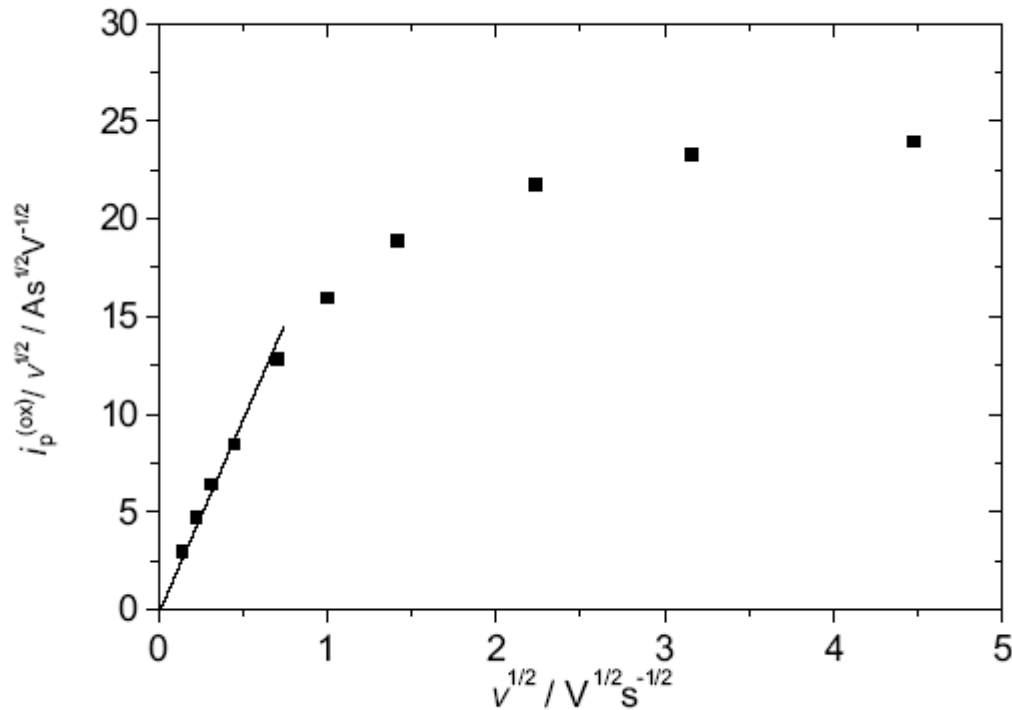
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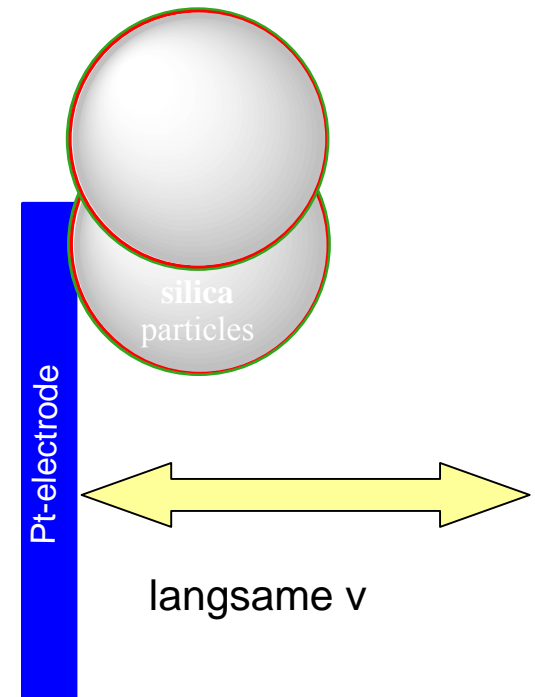
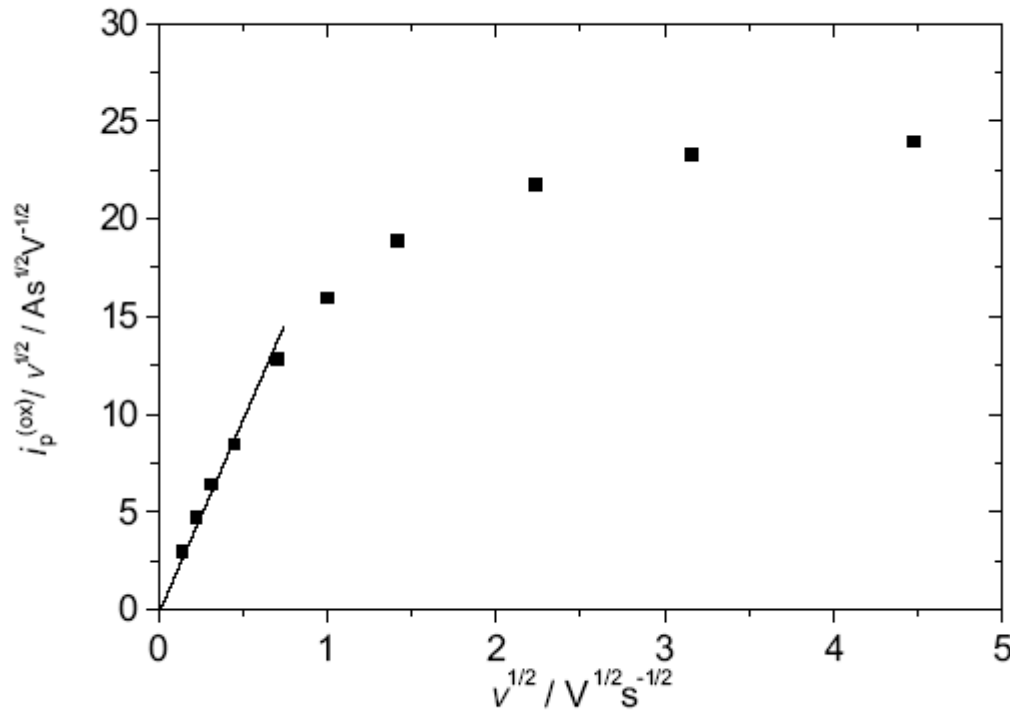
# Cyclovoltammetrie von ferrocen-modifiziertem Kieselgel



Auftragung des Stroms  $i_p$  (normalisiert) gegen die Vorschubgeschwindigkeit

- Linearität  $\Rightarrow$  Elektronentransfer hat Adsorptioncharakter
- Plateau  $\Rightarrow$  Elektronentransfer hat Diffusioncharakter.

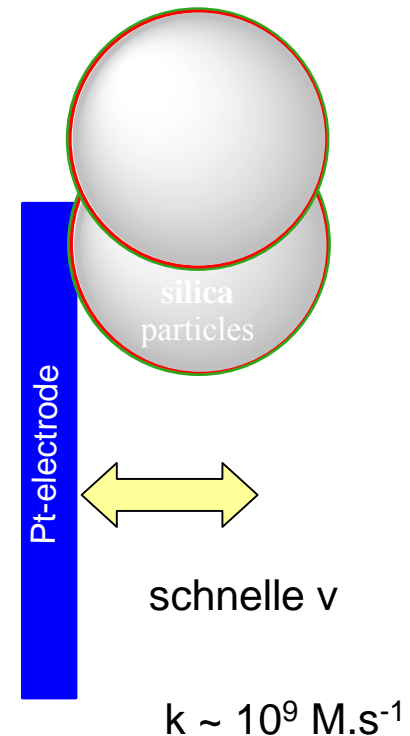
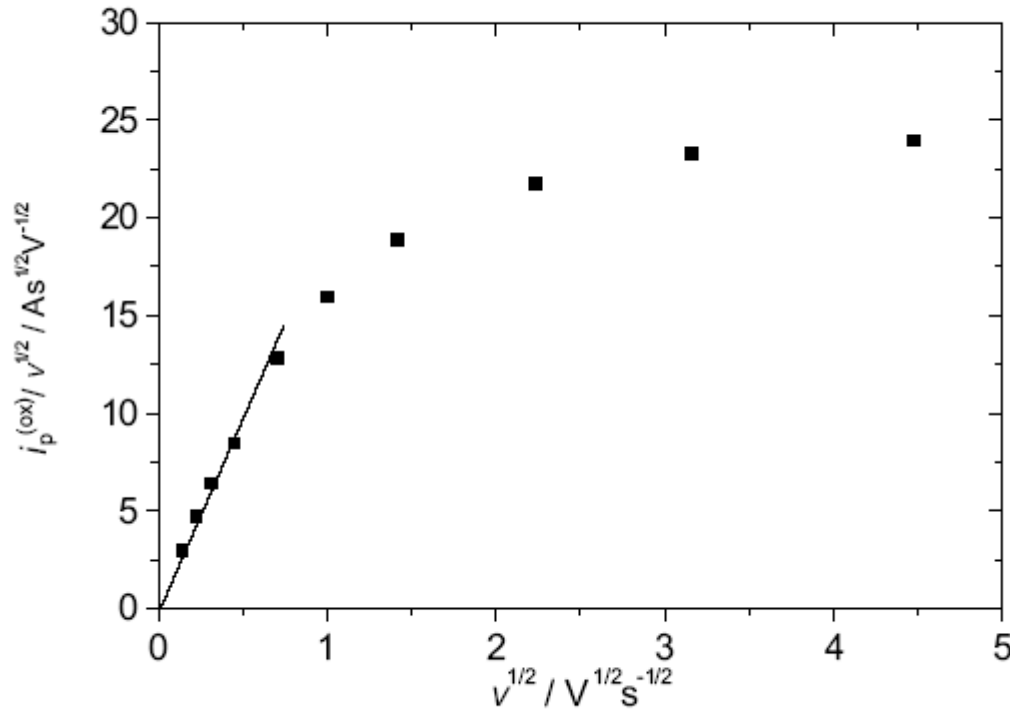
# Cyclische Voltammetrie von Ferrocen modifiziertes Kieselgel



Analyse der Strom  $i_p$  (normalisiert) für verschiedene Vorschubgeschwindigkeit ( $v$ )

- Linearität  $\Rightarrow$  Elektronentransfer hat Adsorptioncharakter
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# Cyclische Voltammetrie von Ferrocen modifiziertes Kieselgel



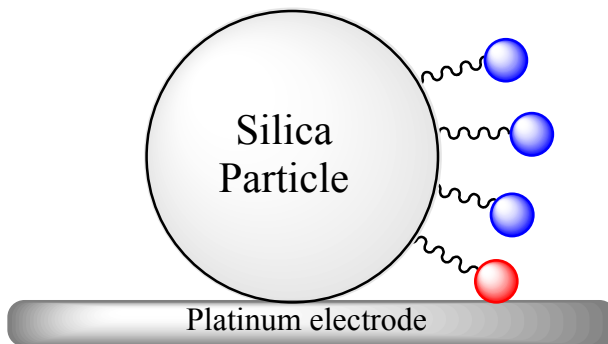
Analyse der Strom  $i_p$  (normalisiert) für verschiedene Vorschubgeschwindigkeit ( $v$ )

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## Interactions between redox centers on particle surface

Proposed mechanism:

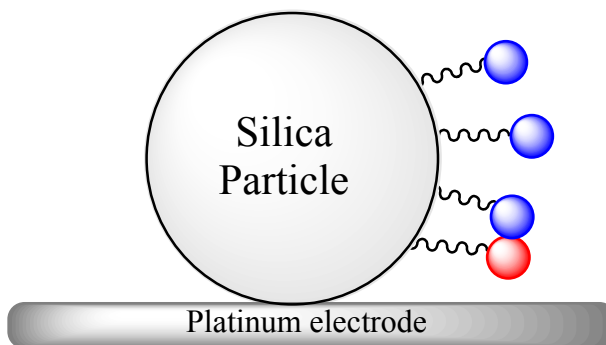
Charge transfer via electron hopping<sup>[4]</sup> between adjacent redox molecules on the particle surface.



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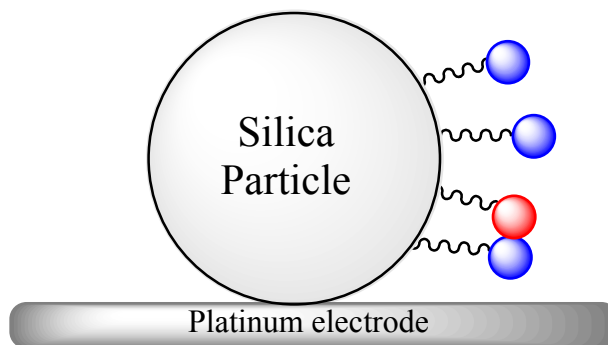
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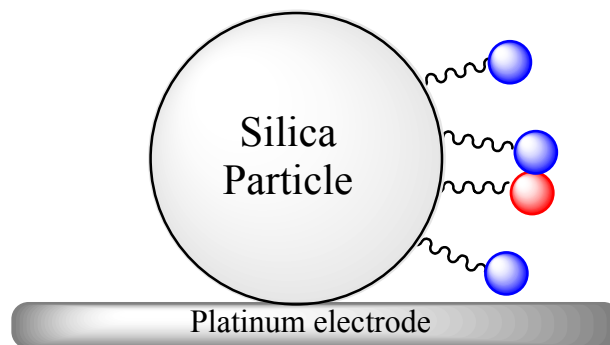
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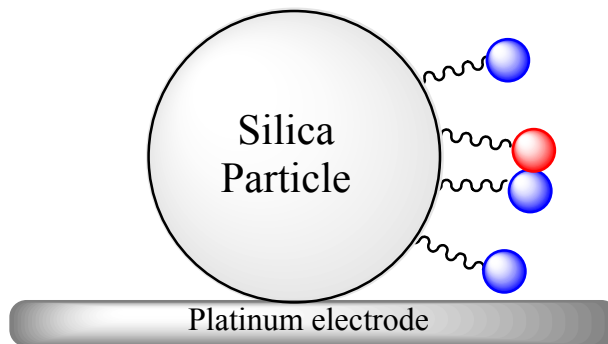
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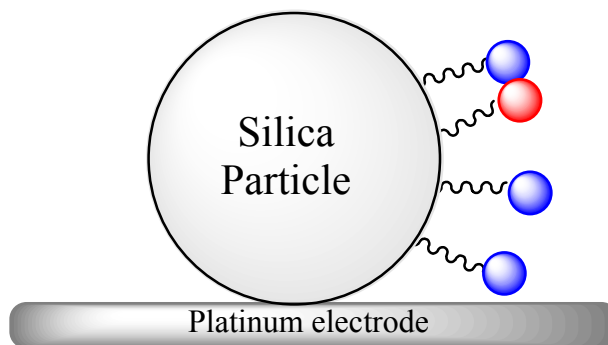




## Interactions between redox centers on particle surface

Proposed mechanism:

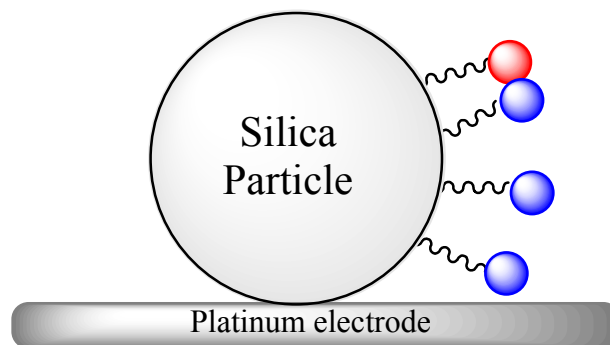
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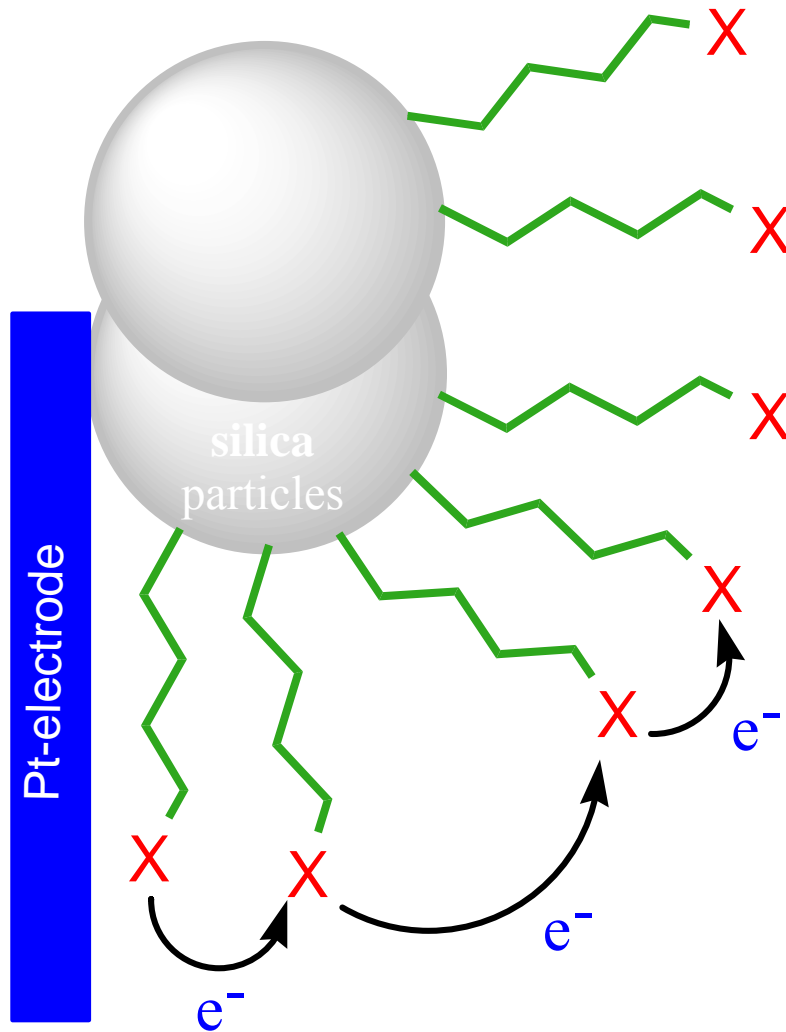
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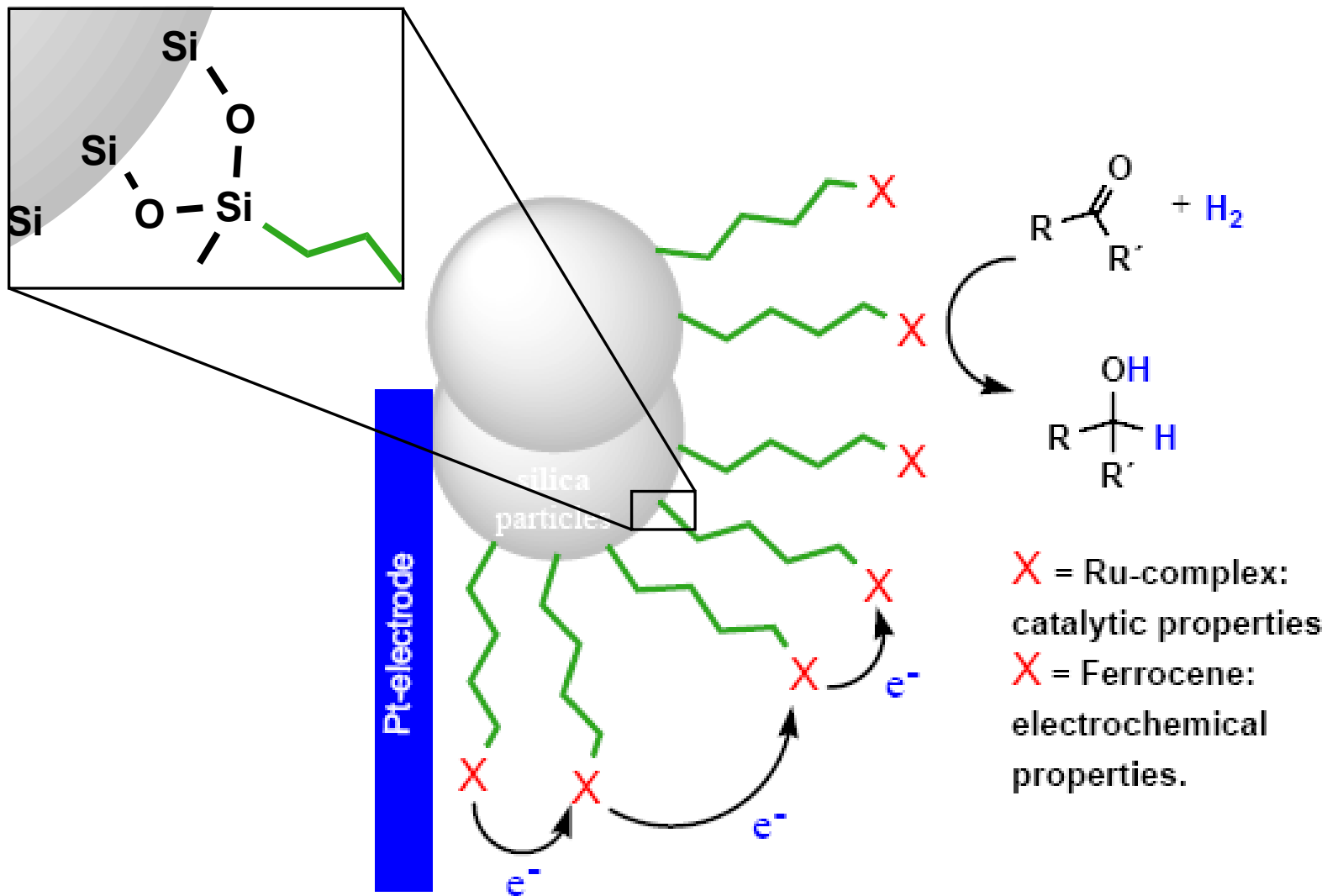
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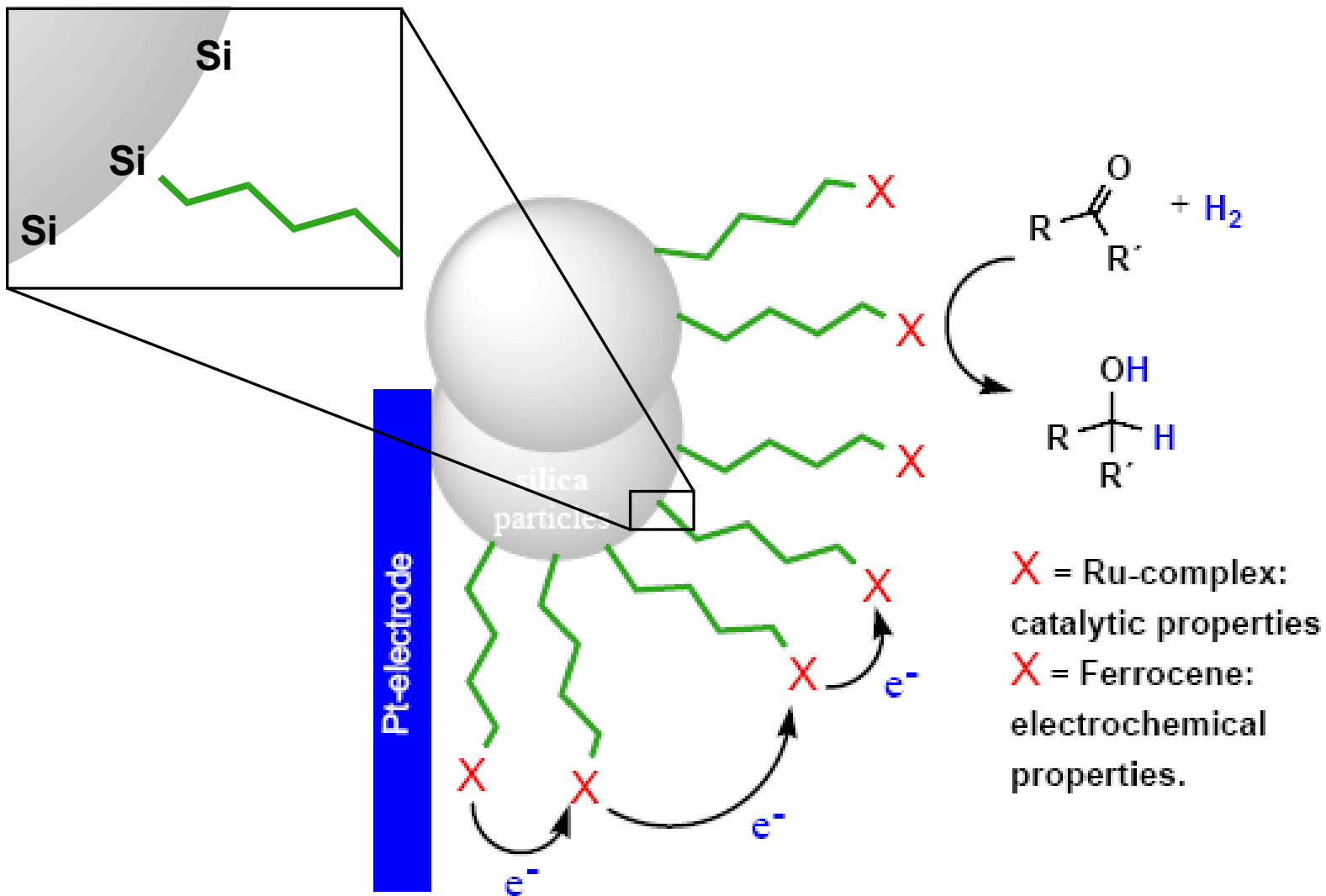
# Elektrochemie von redoxaktiven Kieselgelpartikeln



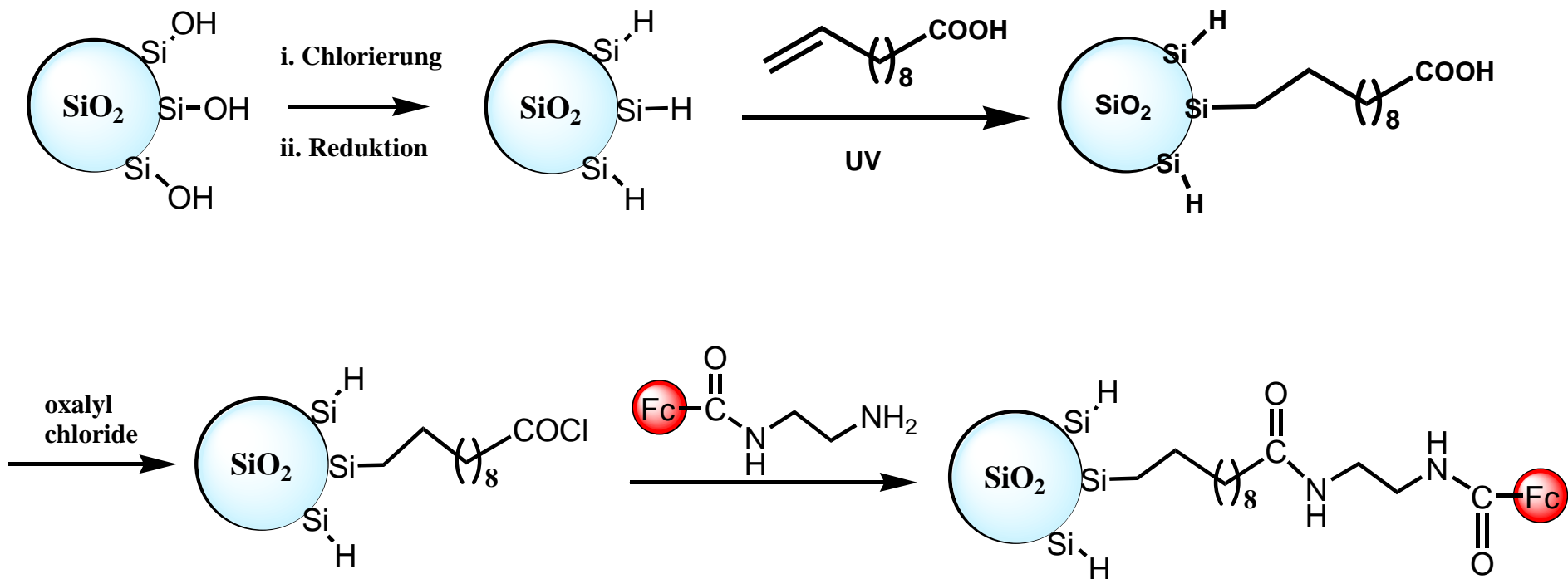
Redoxmoleküle, die nicht direkt an die Elektrodenoberfläche gebunden sind, können auch für Redoxprozesse erreichbar sein.



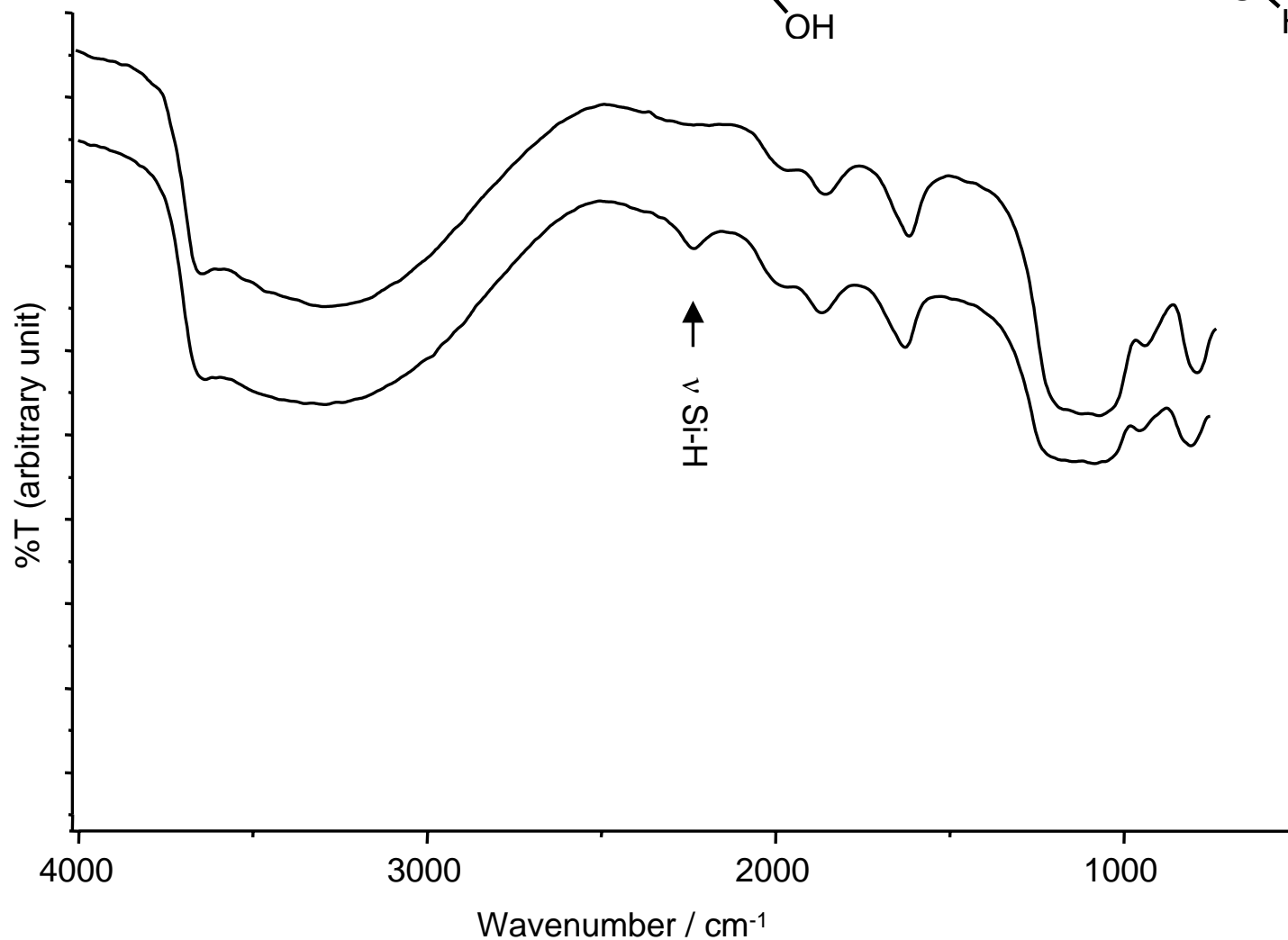
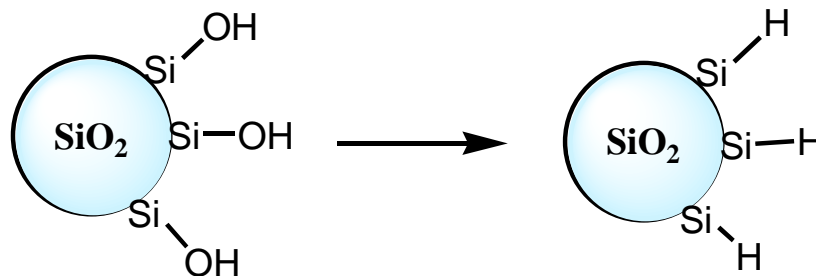
1. A. Budny, F. Novak, N. Plumeré, B. Schetter, B. Speiser, D. Straub, H. A. Mayer, M. Reginek. *Langmuir*, in press.



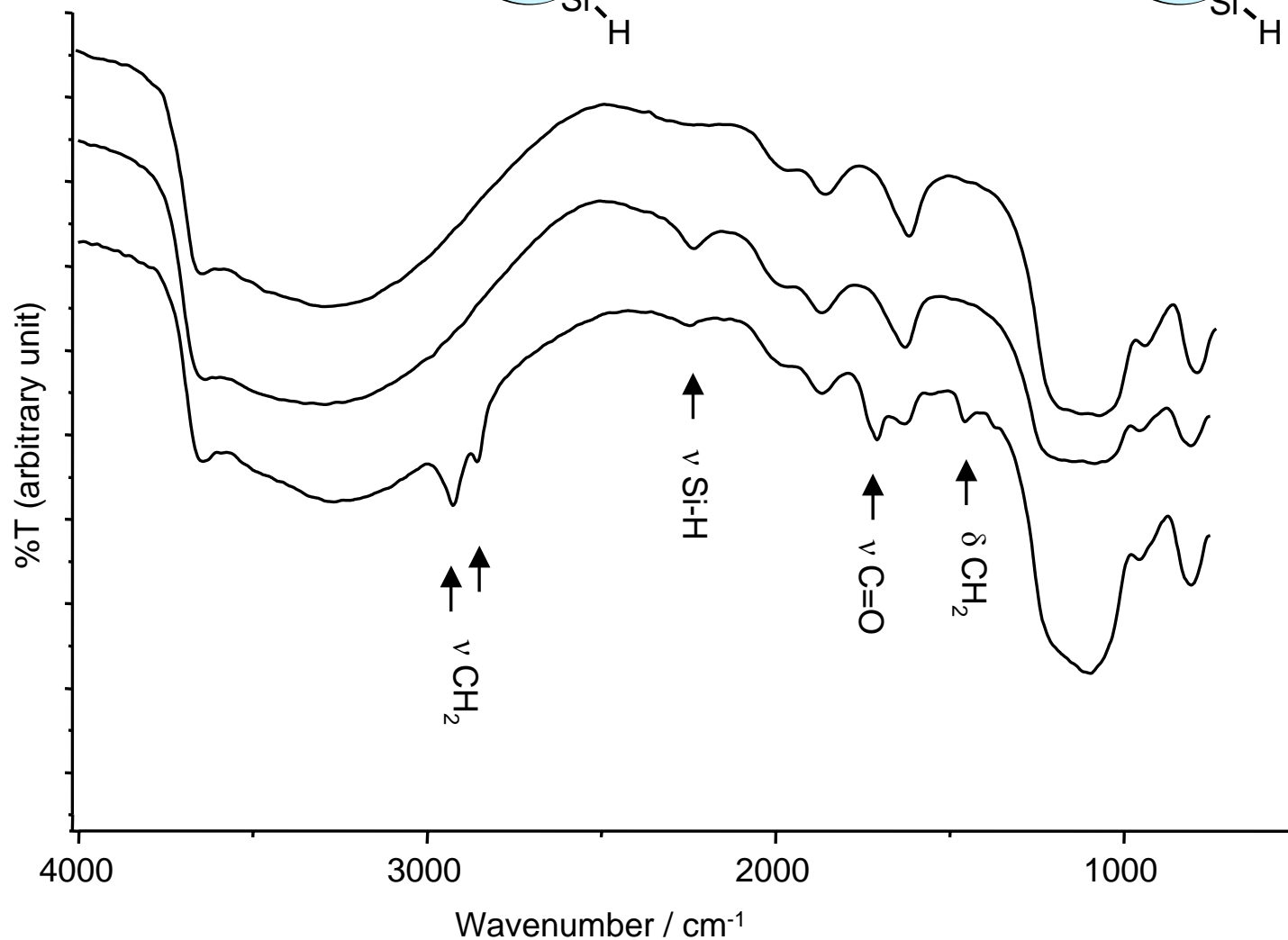
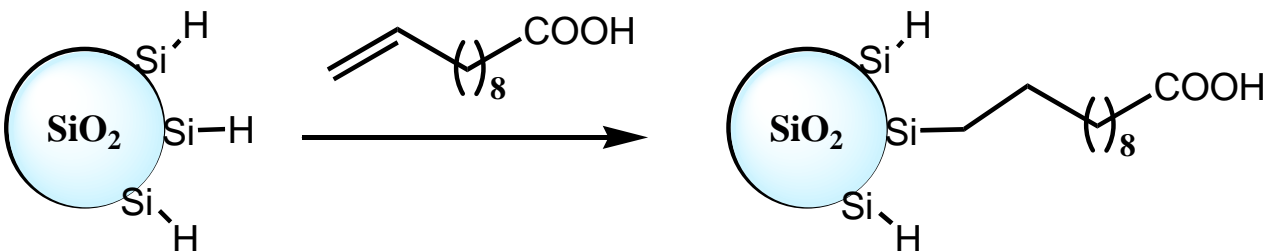
# Photochemische Hydrosilylierung :



DRIFT Spektrum von :

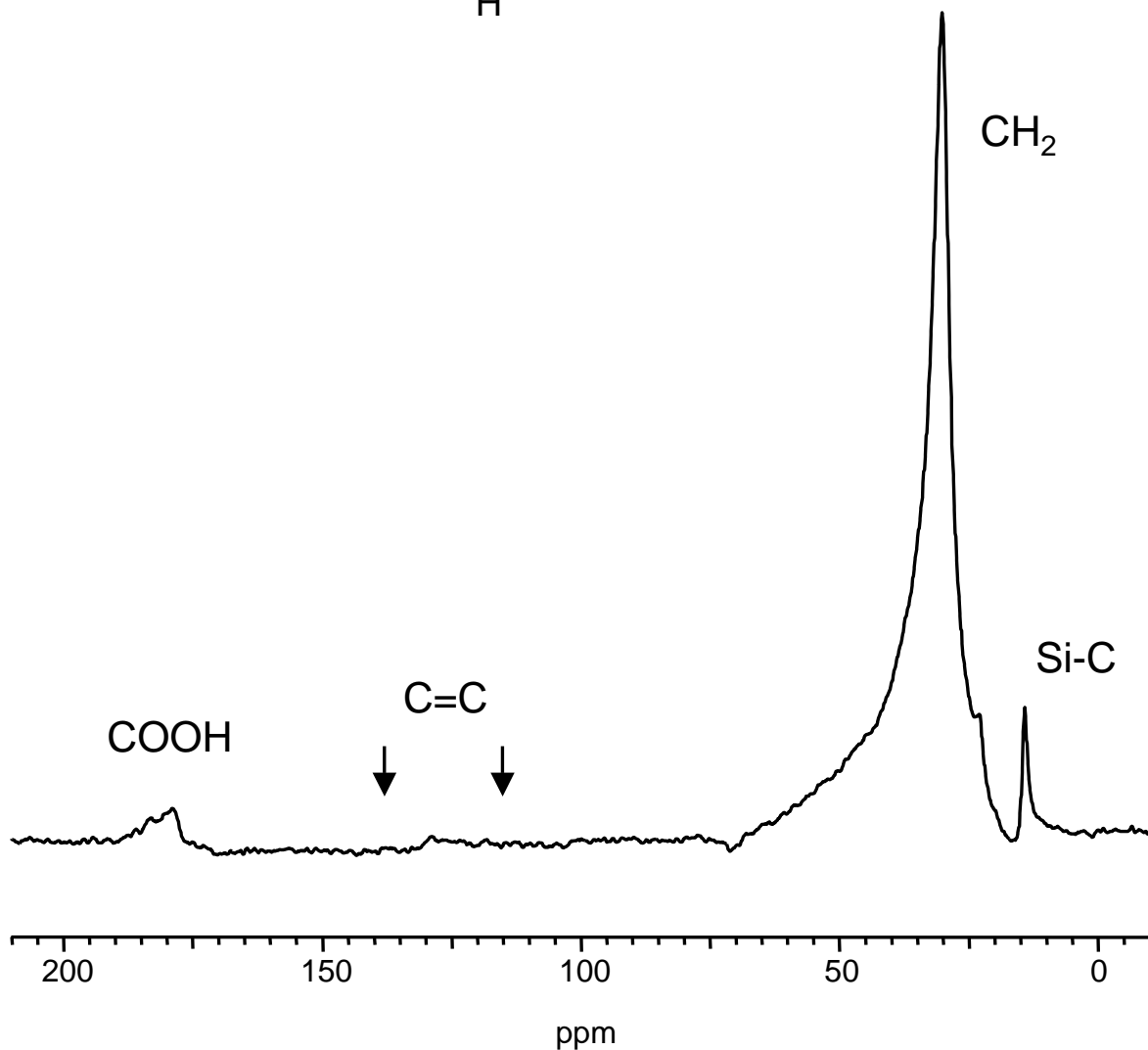
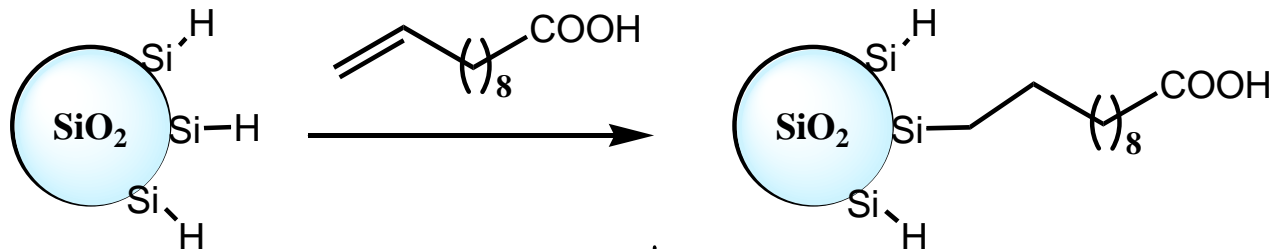


# DRIFT Spektrum von

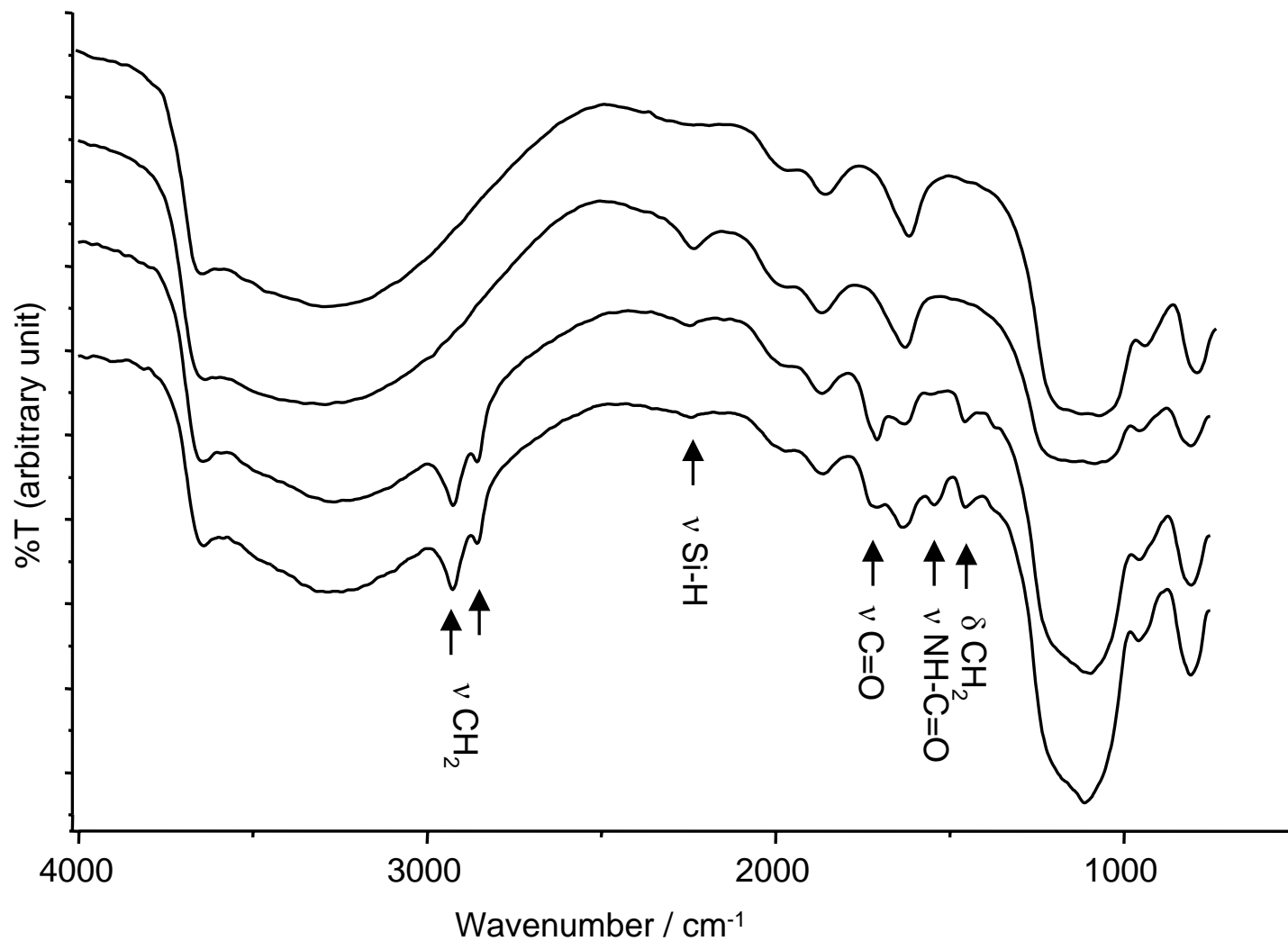
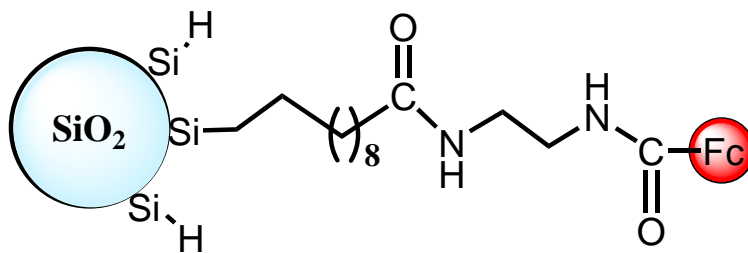




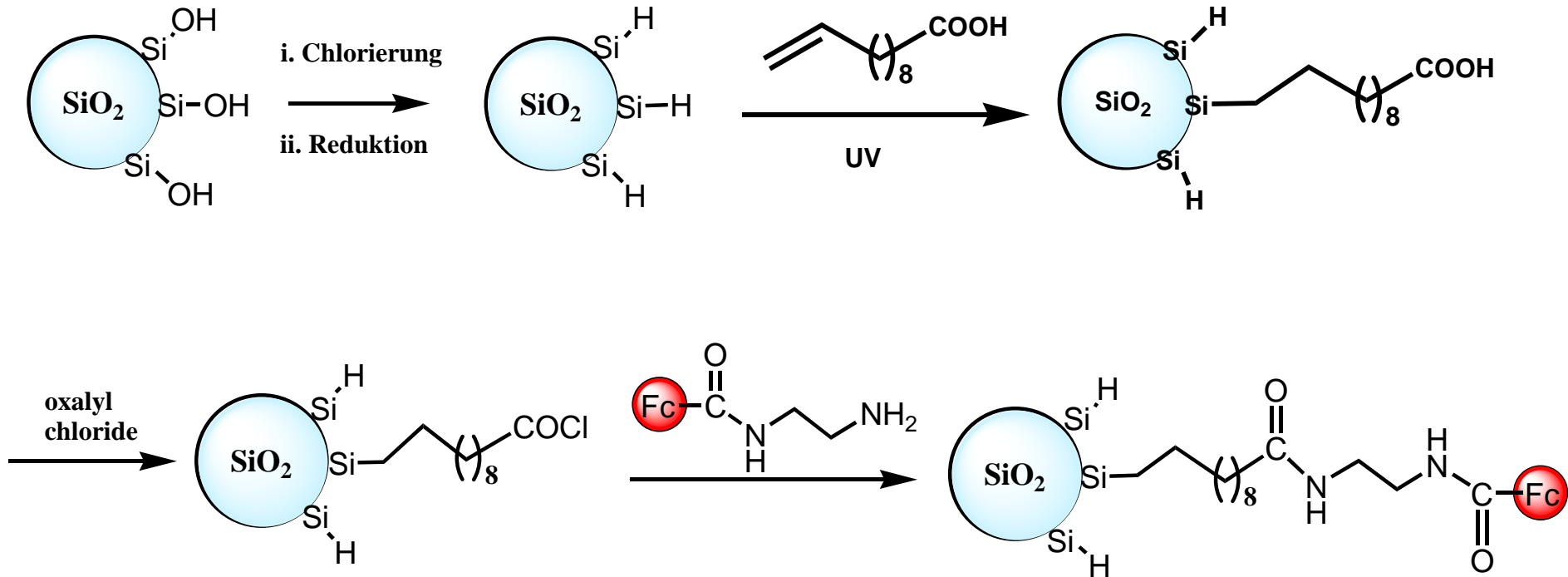
# Festkörper $^{13}\text{C}$ NMR Spektrum von:



DRIFT Spektrum von :



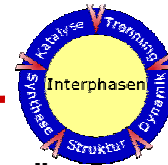
# Photochemische Hydrosilylierung :



⇒ Wasserstabile Anbindung

⇒ Einfache Methode für Elektronenmediatoranbindung





## Danksagung

- Den Mitarbeitern des Graduiertenkollegs ([www.interphasen.de](http://www.interphasen.de))
- Meinen Kollegen vom AK Speiser: Judith Schäfer, Ines Dreiling, Bernhard Sandig.
- der Deutschen Forschungsgemeinschaft