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In Situ Vibrational Spectroscopy of Reactants and Probe Molecules on Oxide Catalysts

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CECAM WORKSHOP

**In situ atomic scale characterization of surfaces under high pressures:
recent advances in experiment and theory**

Lyon, November 4-6, 2004



Outline



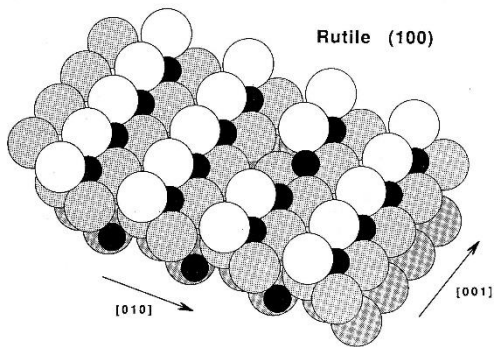
1. Introduction and classical probe molecule spectroscopy
Sites and probe molecules, vibrational spectroscopy
2. Developments
Selection of probe, band intensity, band shape
3. Reactive probing: kinetics of a model reaction
H₂ activation on Ag/SiO₂
4. In situ diffuse reflectance infrared spectroscopy (DRIFTS)
Initiation of *n*-butane isomerization on sulfated zirconia catalysts



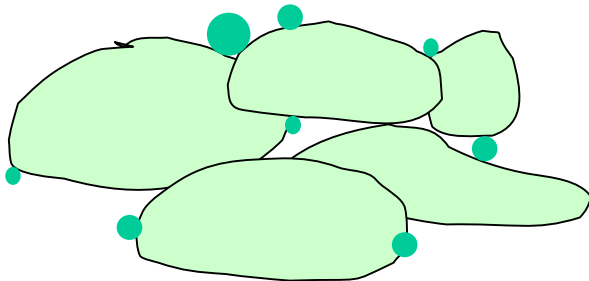
Motivation: Catalyst Active Sites



Goal: Identify nature of active surface sites and reaction mechanism



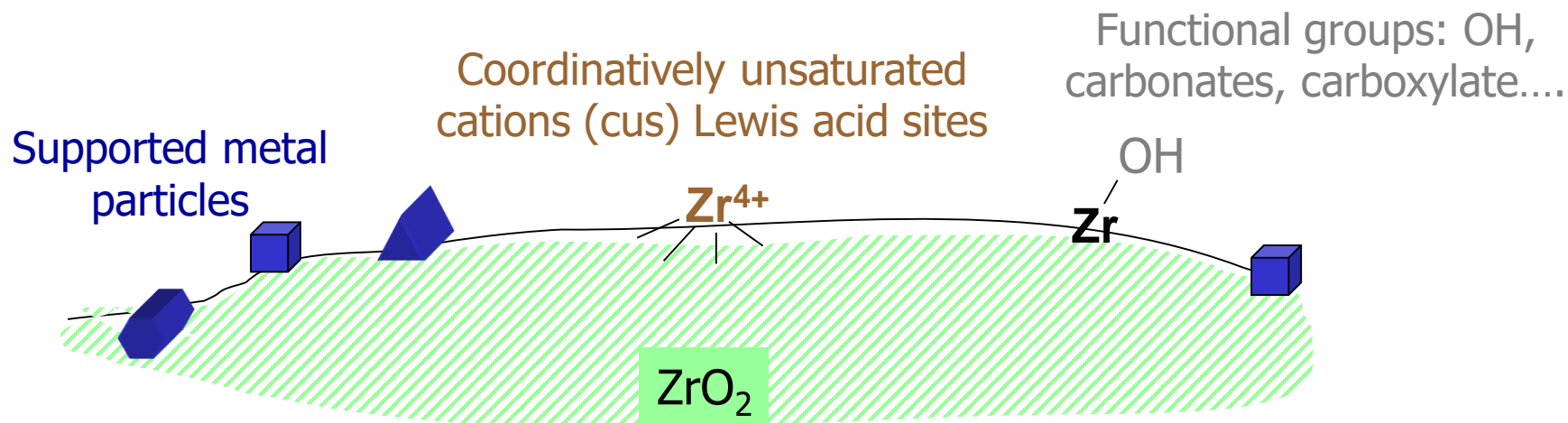
❖ structure of "ideal" surface may be analyzed under special circumstances (UHV conditions)



- ❖ structure of "real" catalyst difficult to analyze: inhomogeneous & unsuitable for many methods
- ❖ information on bulk insufficient to derive surface properties
- ❖ identify surface properties through adsorption



Surface Sites, Probe Molecules & Vibrational Spectroscopy



Select probe according to expected site properties

- ❖ acid site: basic probe (ammonia, pyridine, CO)
- ❖ basic site: acid probe (CO₂, pyrrole)
- ❖ metal: CO, H₂

Many experimental possibilities: IR, DRIFTS, ATR, IRAS, SFG, EELS, Raman

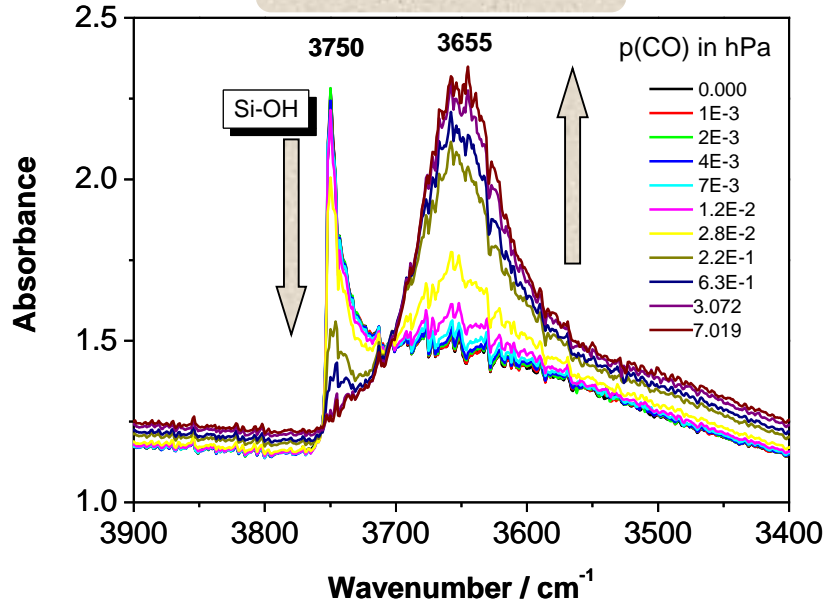
- ❖ sample form: model system (single crystal), powder
- ❖ selection rules
- ❖ wide temperature and pressure range



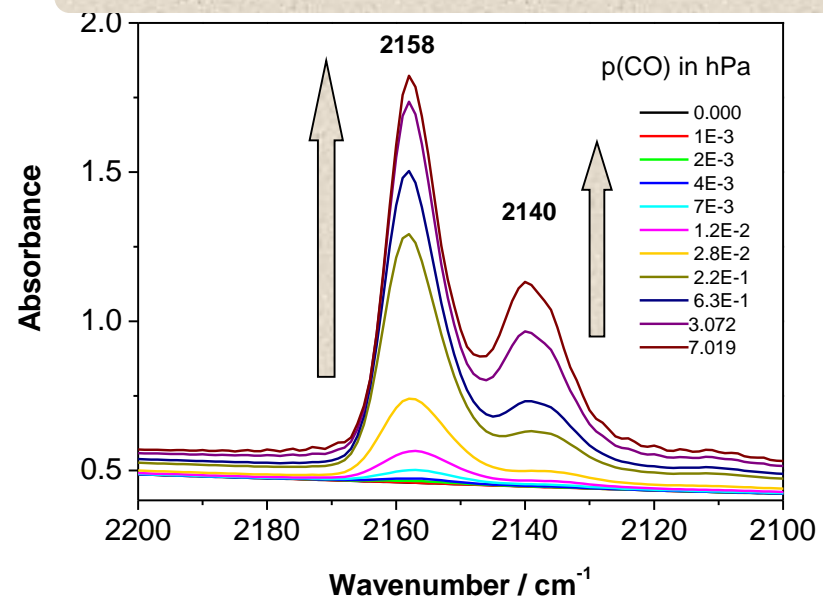
Example: CO Adsorption on SiO₂ at 77 K



OH stretching



CO stretching (free: 2143 cm⁻¹)



The ideal probe molecule...

- ❖ selective adsorption on particular site - small, non-reactive molecule
- ❖ high extinction coefficients of vibrations of interest
- ❖ large variation of vibrational frequency upon adsorption
- ❖ induce large change in vibration frequency of functional group



Shortcomings and Improvements



Band positions / shifts are analyzed...

- ❖ there is more information in an IR spectrum!
 - ➡ analyze band position, intensity, shape, and background

Selection of the probe

- ❖ we may be wrong about the nature of the "active sites"
example: sulfated zirconia is most likely not highly active in *n*-butane isomerization due to its acidic properties
- ❖ why use probe that has different chemistry than reactant?
 - ➡ "active site": reactant is the best probe

Selection of conditions

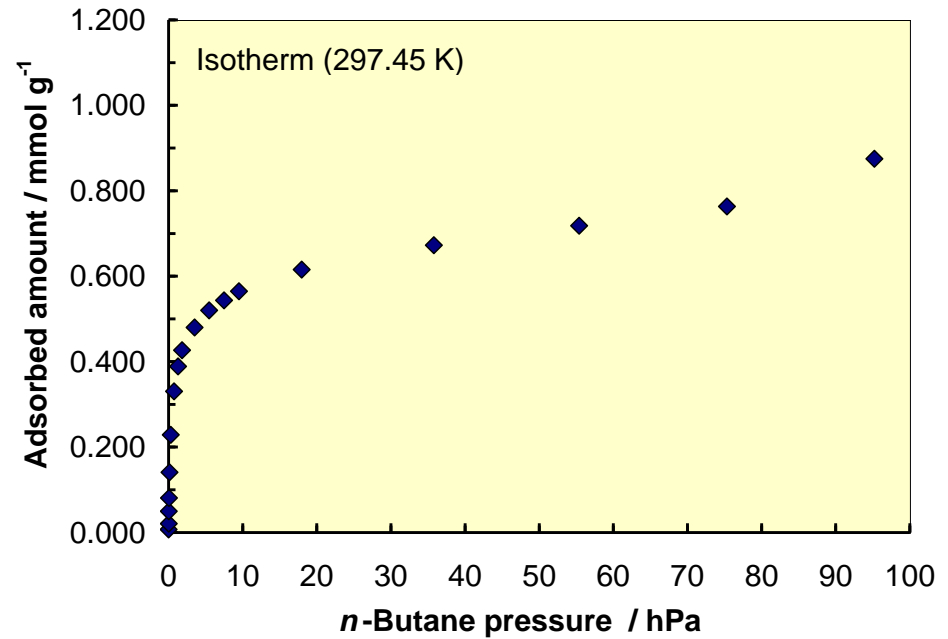
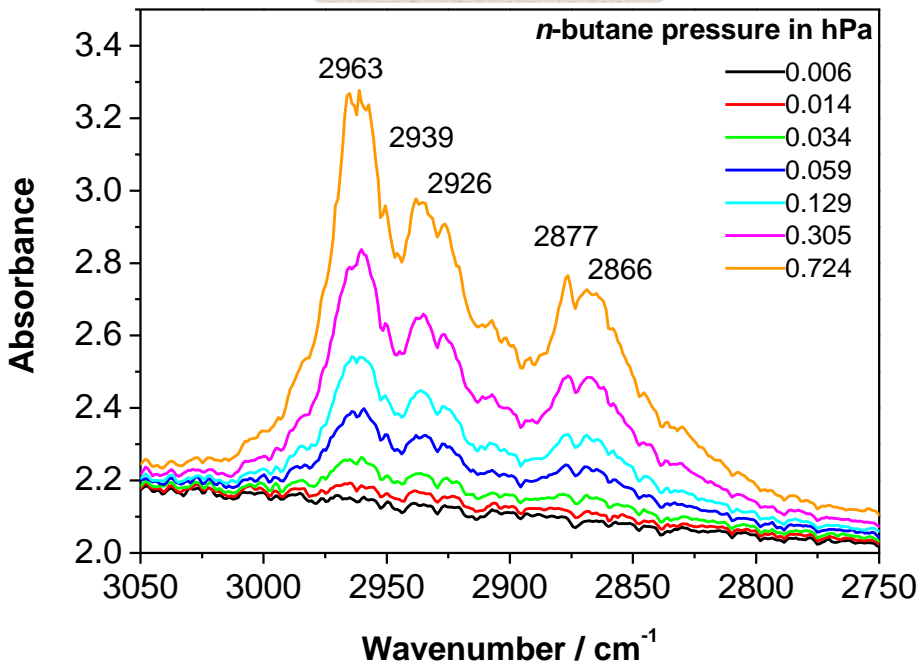
- ❖ non-reactive conditions will not inform us about mechanism
 - ➡ in situ spectroscopy



Information: Band Intensity



CH stretching

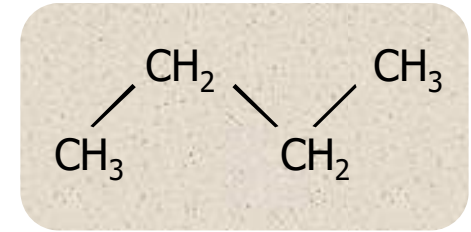
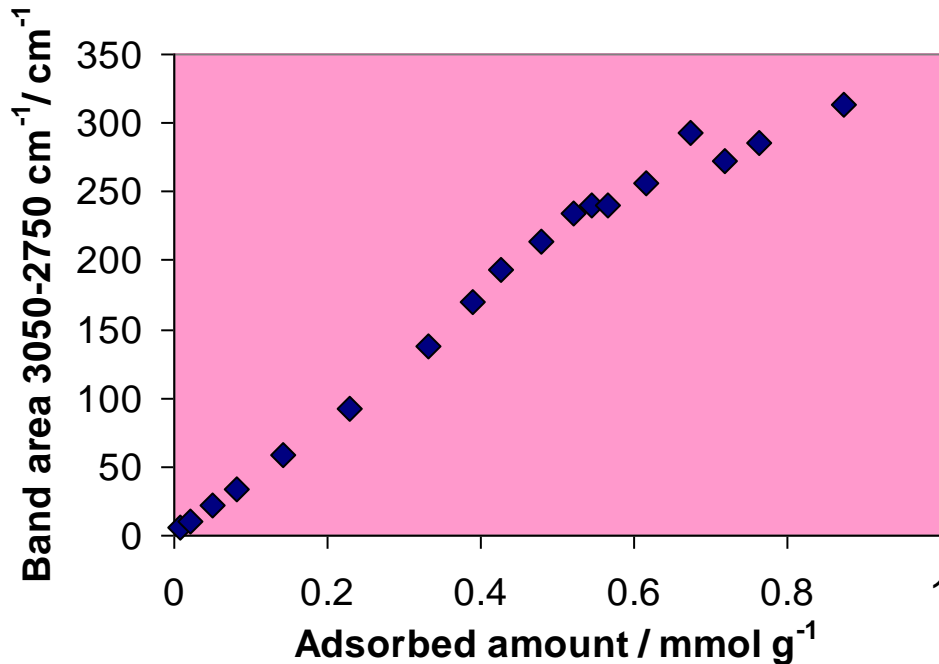


- ❖ adsorption of *n*-butane on H-Mordenite at 297 K
- ❖ simultaneous independent measurement of adsorbed amount

➡ combine information to determine extinction coefficient



Determination of Extinction Coefficients



$$I \propto \left(\frac{\partial \mu}{\partial r} \right)^2$$

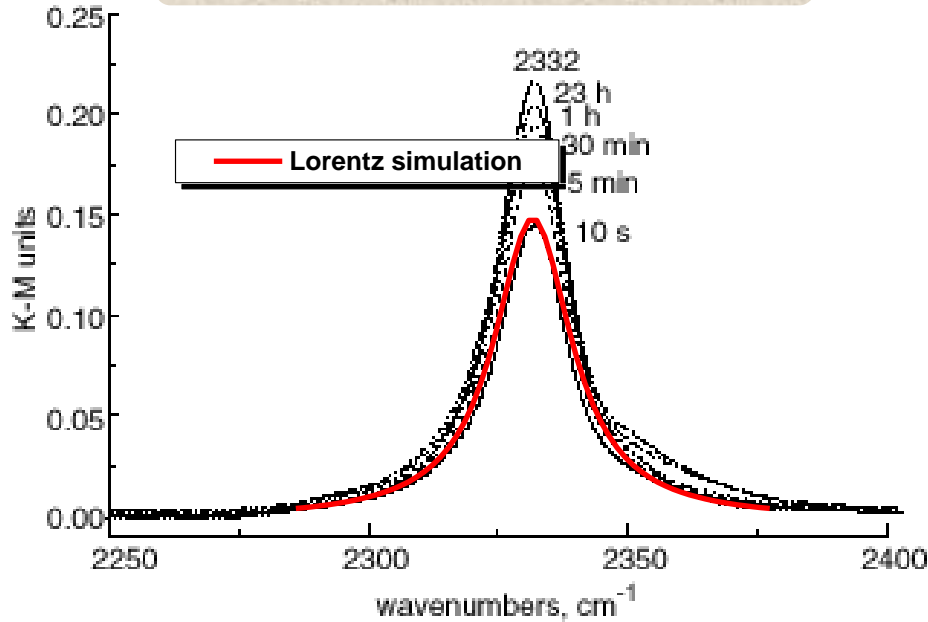
- ❖ IMEC $\approx 43.5 \text{ cm}^{-1} (\text{cm}^2 \mu\text{mol})$ for adsorbed *n*-butane
IMEC $\approx 13.1 \text{ cm}^{-1} (\text{cm}^2 \mu\text{mol})$ for gas phase *n*-butane
 - ❖ Extinction coefficients can be determined for individual stretching or deformation bands
- ➡ Information on polarization of adsorbed molecule (reaction begin!)**



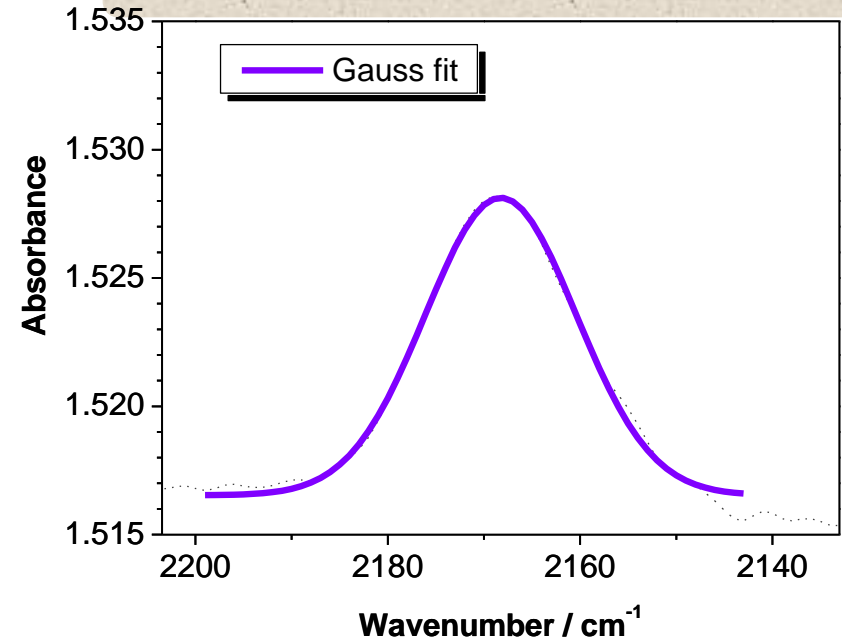
Information: Band Shape



N₂ on NaLSX-zeolite at RT



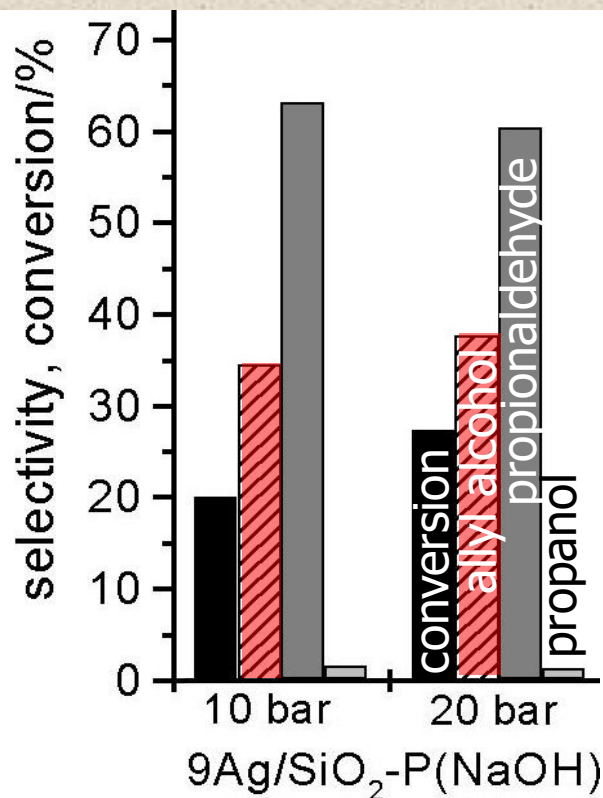
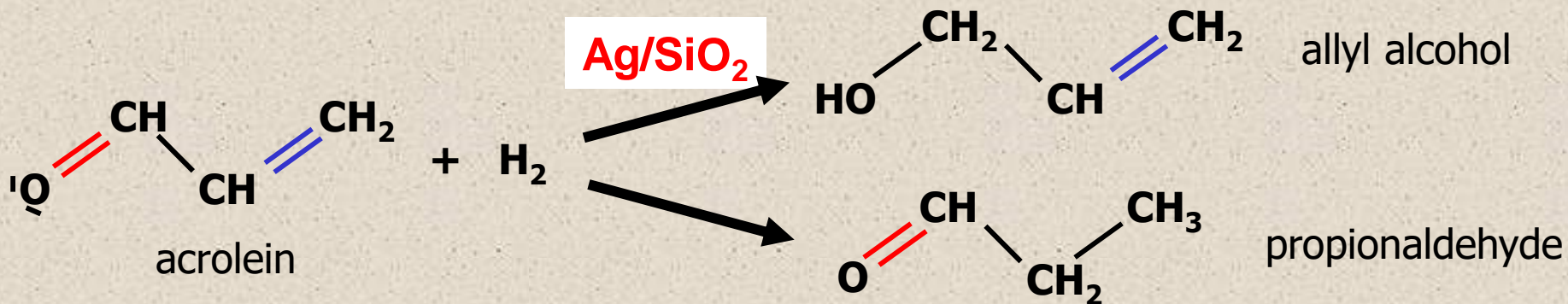
CO on sulfated zirconia at 77 K



- ❖ rarely considered (sometimes width is discussed)
- ❖ Lorentzian / Gaussian shapes



Ag/SiO₂ Catalysts: Motivation



Questions

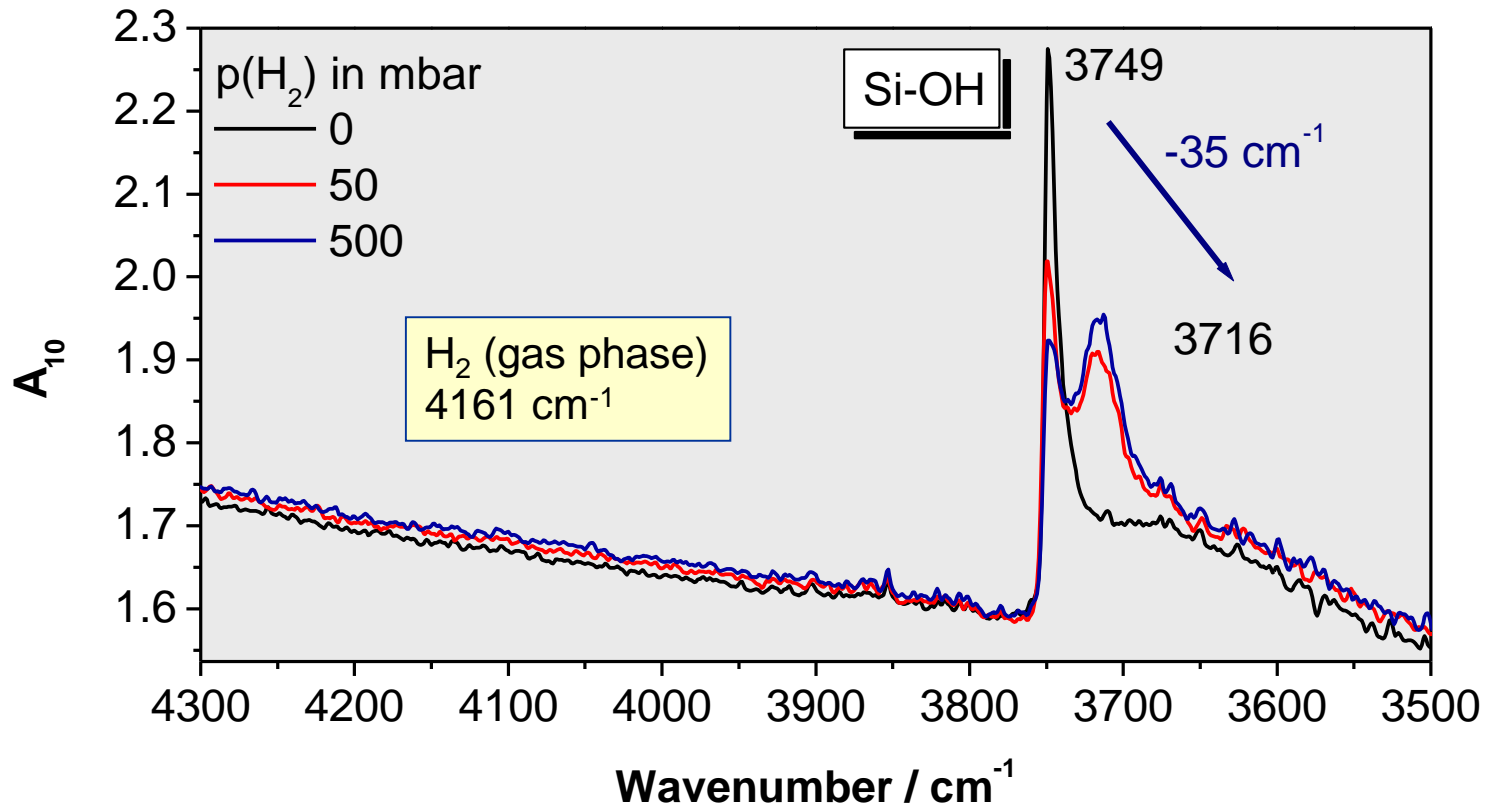
- ❖ Activation of hydrogen?
- ❖ Role of silver?

P. Claus, H. Hofmeister, J. Phys. Chem. B 103 (1999) 2766-2775.

P. Claus, P.A. Crozier, P. Druska, Fresenius J. Anal. Chem. 361 (1998) 677-679.



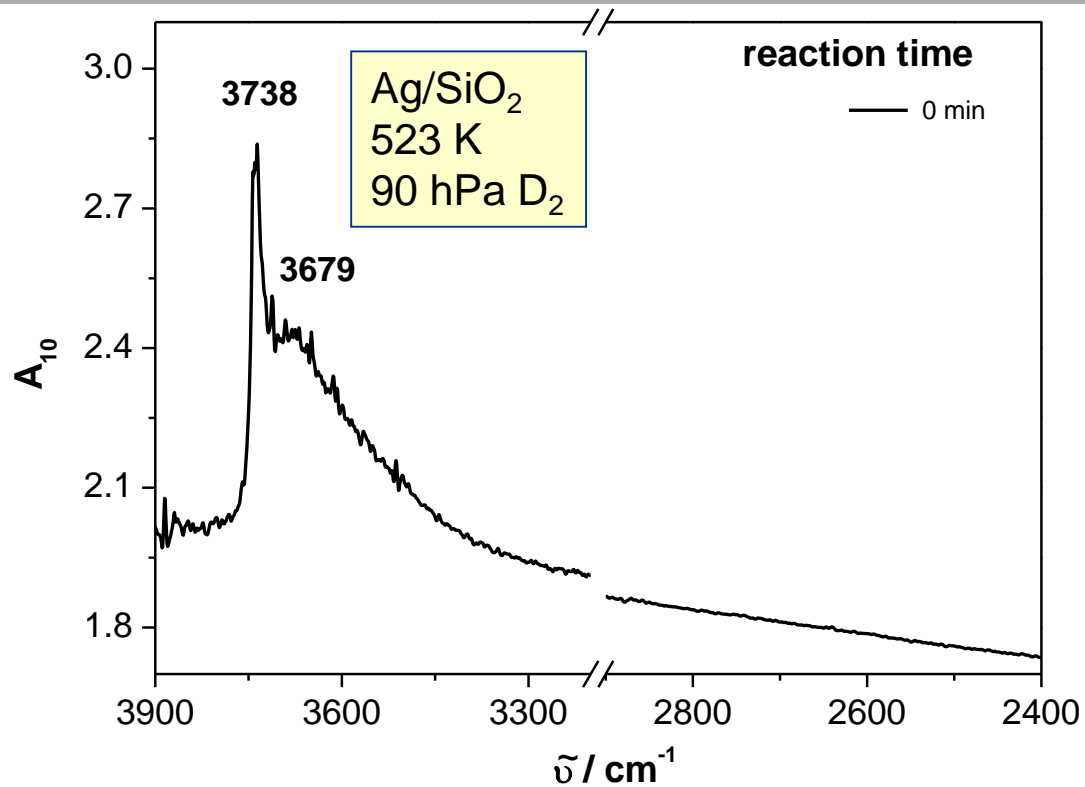
H₂-Adsorption at 77 K on SiO₂ and Ag/SiO₂



- ❖ no vibrations of adsorbed H₂ detectable in spectra
- ❖ shift of OH vibration through H₂ adsorption by ca. -35 cm^{-1}
- ❖ no difference between SiO₂ and Ag/SiO₂ (8.09 at% Ag)



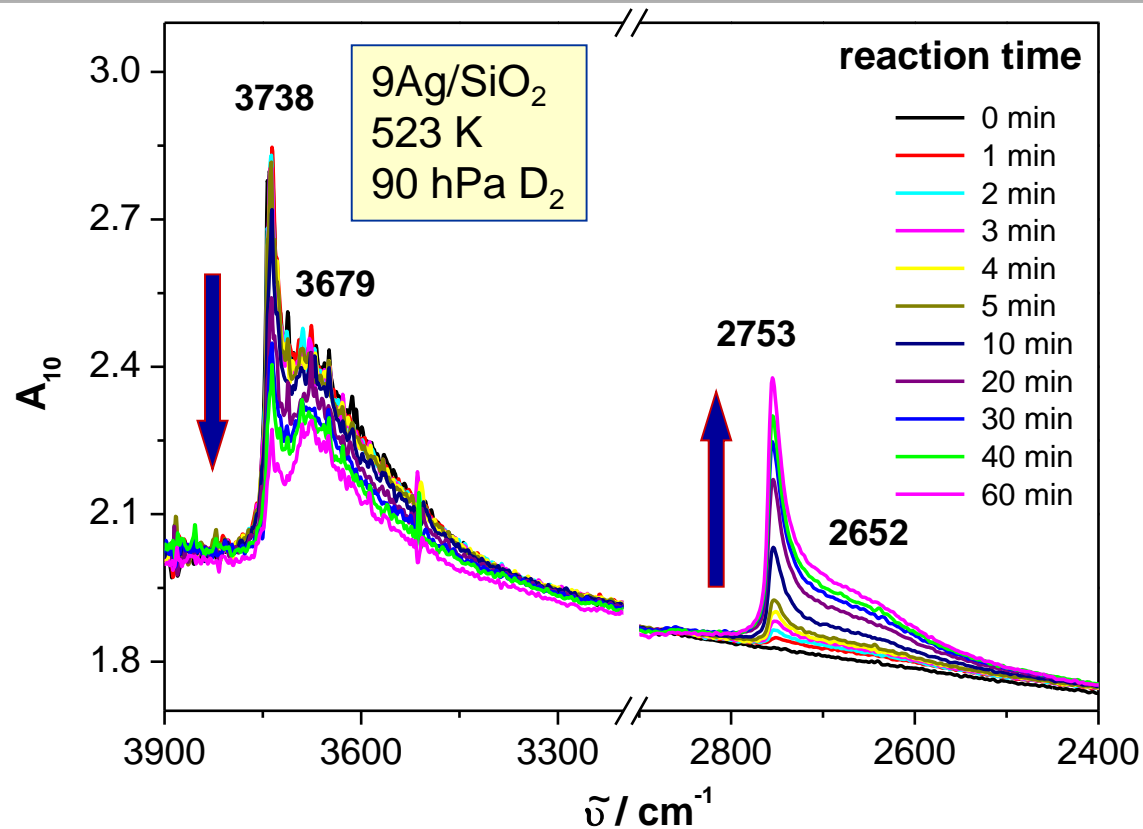
Exchange of Si-OH with D₂



❖ activation as for catalysis : 598 K, H₂



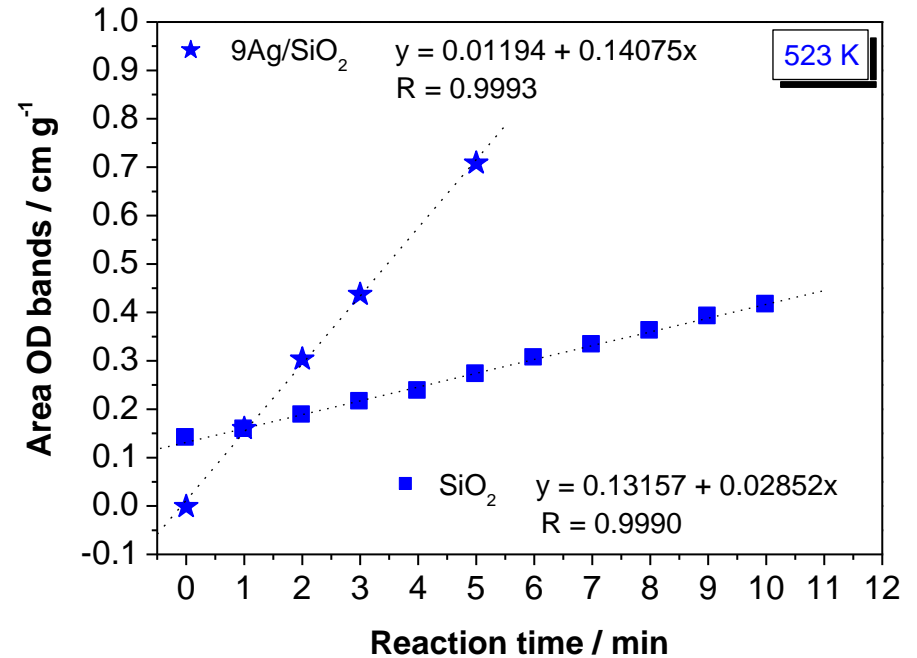
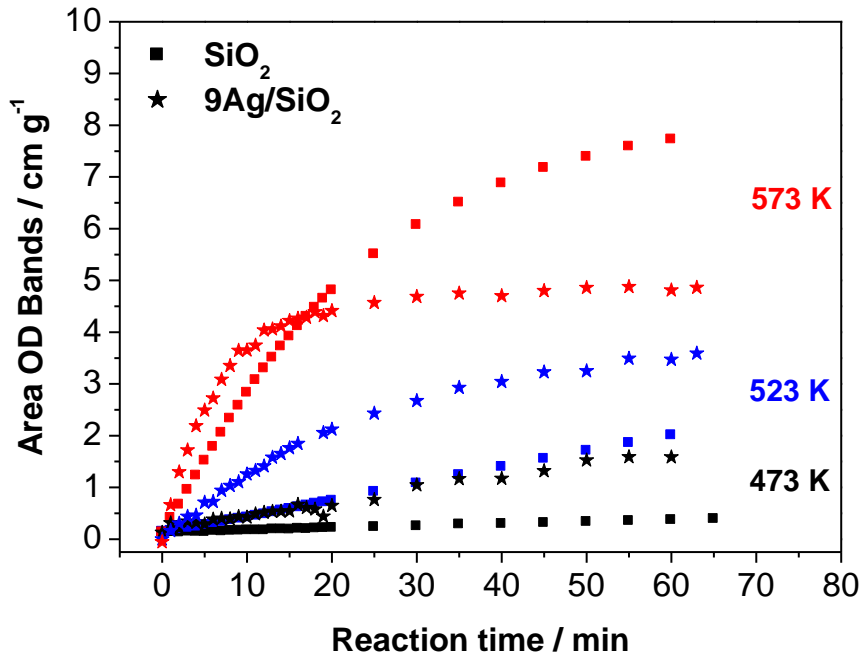
Exchange of Si-OH with D₂



- ❖ OH groups react in D₂ atmosphere to OD groups
- ❖ increase OD bands = decrease OH bands (equal ϵ ?)



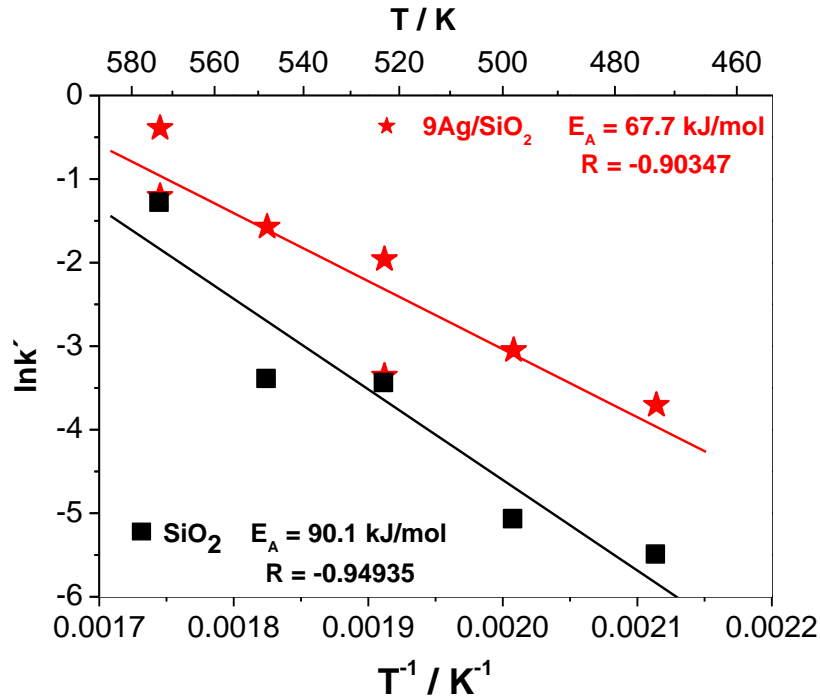
Exchange Rate



- ❖ exchange rate increases with temperature
- ❖ reaction faster for Ag/SiO₂ than SiO₂
- ❖ rate initially constant, then decrease (consumption of OH groups)



Temperature Dependence of HD Exchange



❖ Apparent activation energy E_A for HD exchange reaction

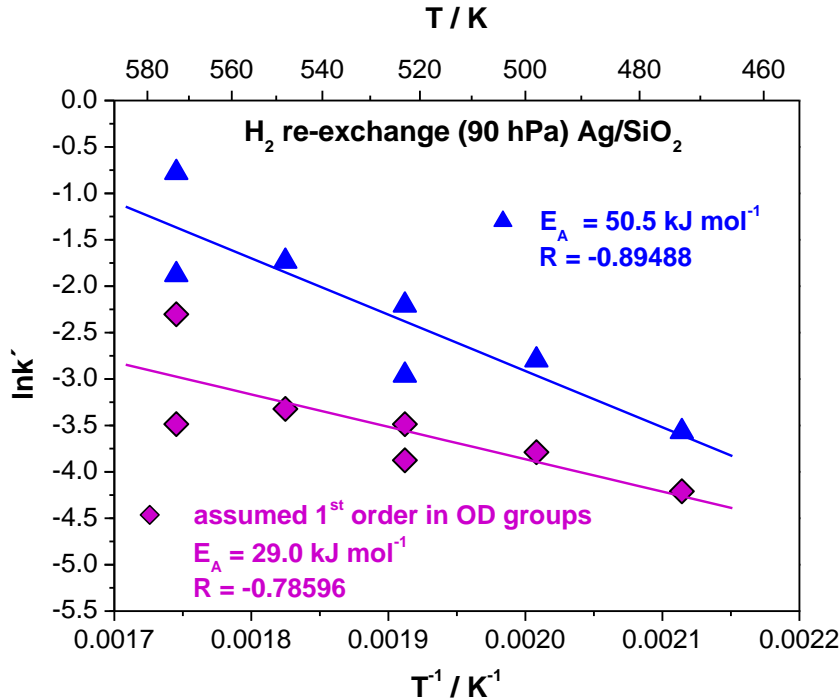
SiO_2 : 90 kJ mol⁻¹

Ag/SiO_2 : 68 kJ mol⁻¹

➡ D_2 activation on Ag



Activation of Hydrogen: DH Exchange



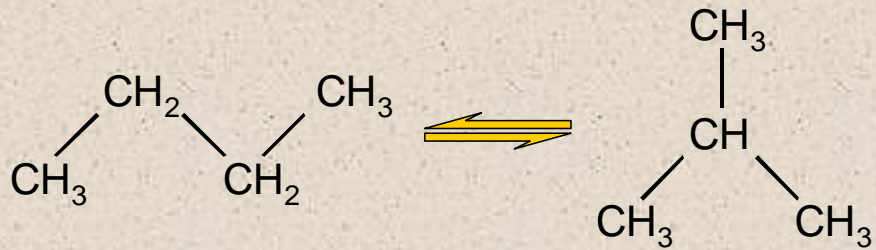
- ❖ E_A for DH exchange on Ag/SiO₂ 30 and 50 kJ mol⁻¹
- ❖ $E_A(\text{H} \rightarrow \text{D}) < E_A(\text{D} \rightarrow \text{H})$
H₂ more easily activated than D₂

- ❖ Hydrogenation of Acrolein (TU Darmstadt, Prof. Claus)
Ag/SiO₂ at 1013-2026 kPa: E_A ca. 40 kJ/mol

➡ activation of H₂ on Ag rate-determining step



Promotion of Sulfated Zirconia



equilibrium at 300 K: 71 % isobutane

❖ sulfated zirconia

Holm, Bailey 1962, US Patent 3,032,599

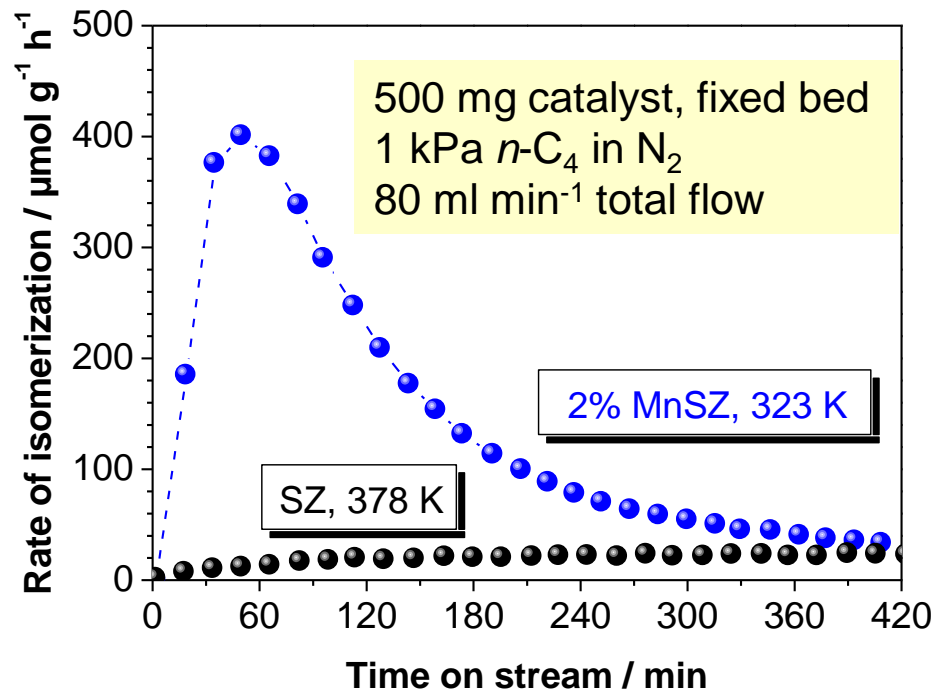
Hino, Arata, JACS 1979 & Chem. Comm. 1980

❖ Fe or Mn: promoting effect

Hollstein et al., 1990 US Patent 4,918,041;

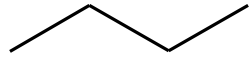
Hsu et al., Chem. Comm. 1992; Lange et al.,

Catal. Lett. 1996



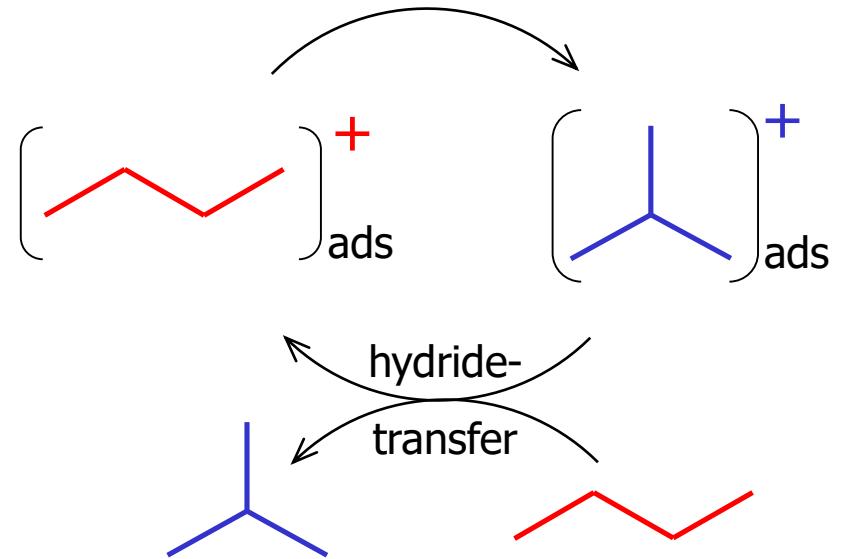


5. In situ Experiments: Mechanism



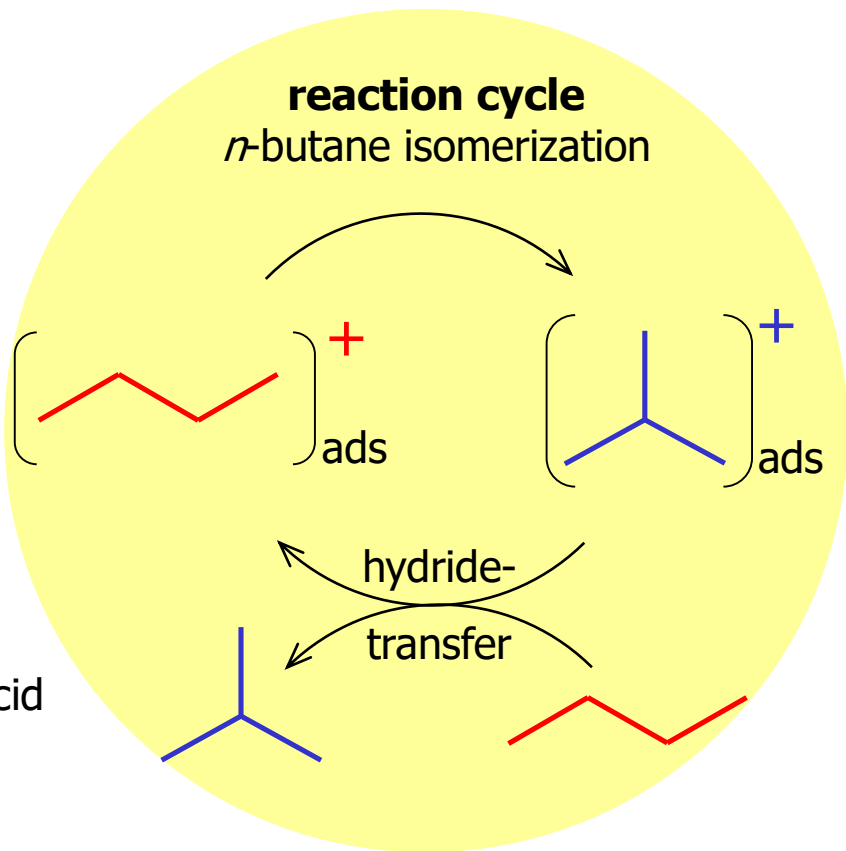
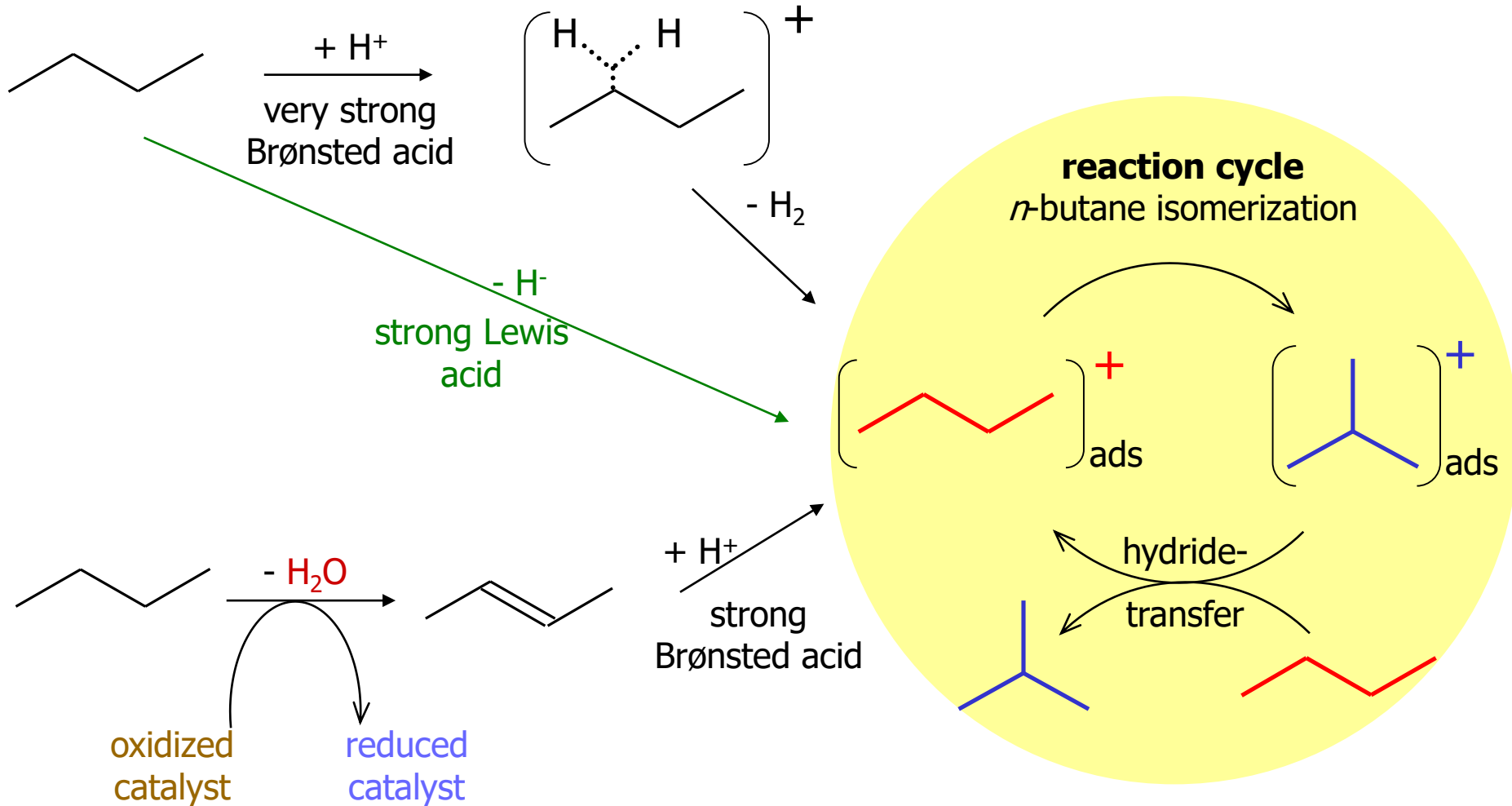
Initiation?

reaction cycle
n-butane isomerization





Possibilities for Reaction Initiation

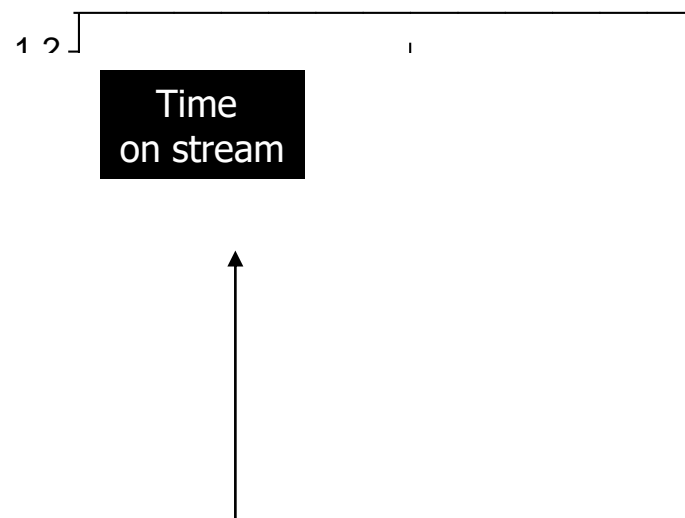
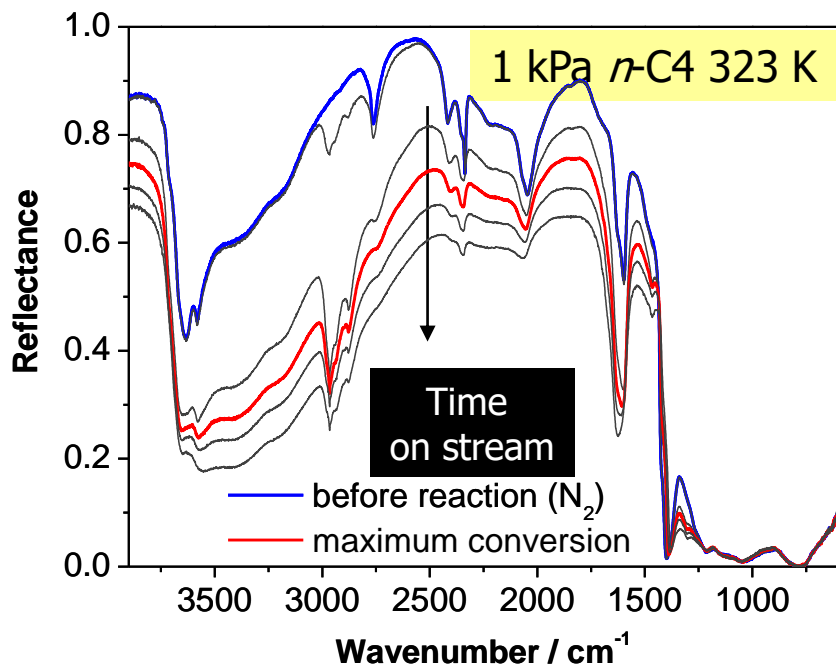


ODH (stoichiometric?)

possible oxidizing agents: S, Zr, promoters (Mn)



n-Butane Isomerization over MnSZ: In Situ DRIFTS

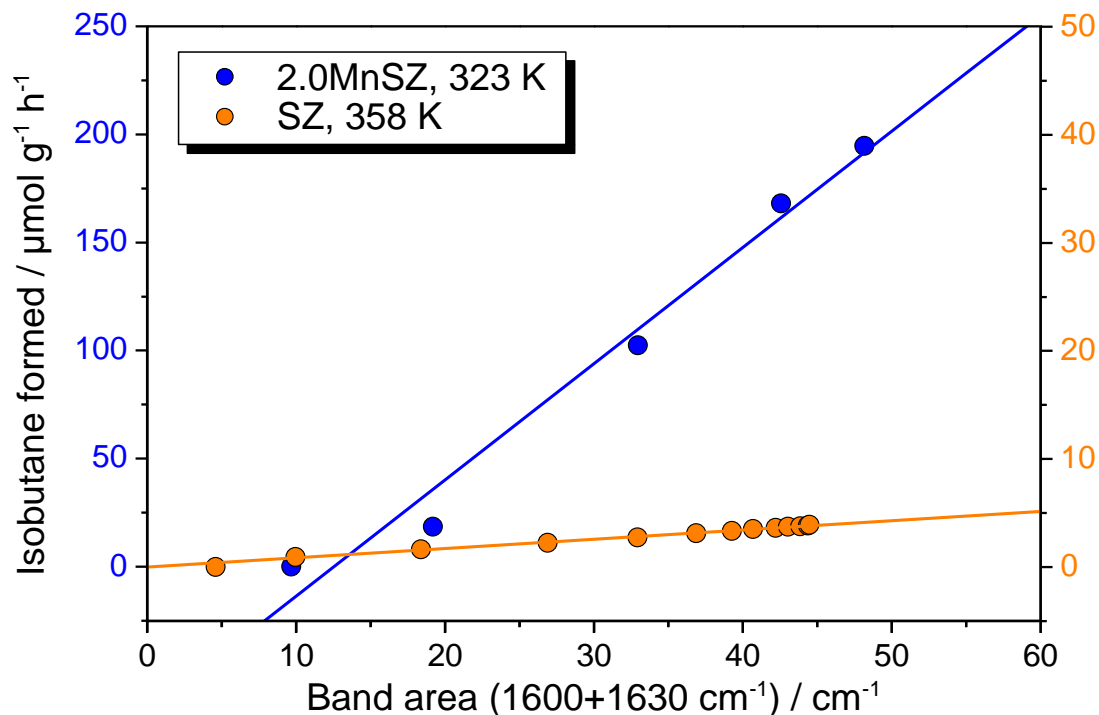


- ❖ sulfate overtones, combination modes, fundamentals (2764-2049, 1400 cm^{-1})
- ❖ butane gas phase CH-stretching and bending vibrations 2966, 2939, 2877, 1466 cm^{-1}

- ❖ bands at 1600 and 1630 cm^{-1} increase
- ❖ also range of C=C stretching vibrations, but corresponding CH vibrations not observed
- ❖ water bending vibration



Correlation of Spectral and Catalytic Information



- ❖ Rate of isomerization proportional to the amount of water formed (induction period)

X. Li, K. Nagaoka, L.J. Simon, J.A. Lercher, A. Hofmann, J. Sauer, submitted

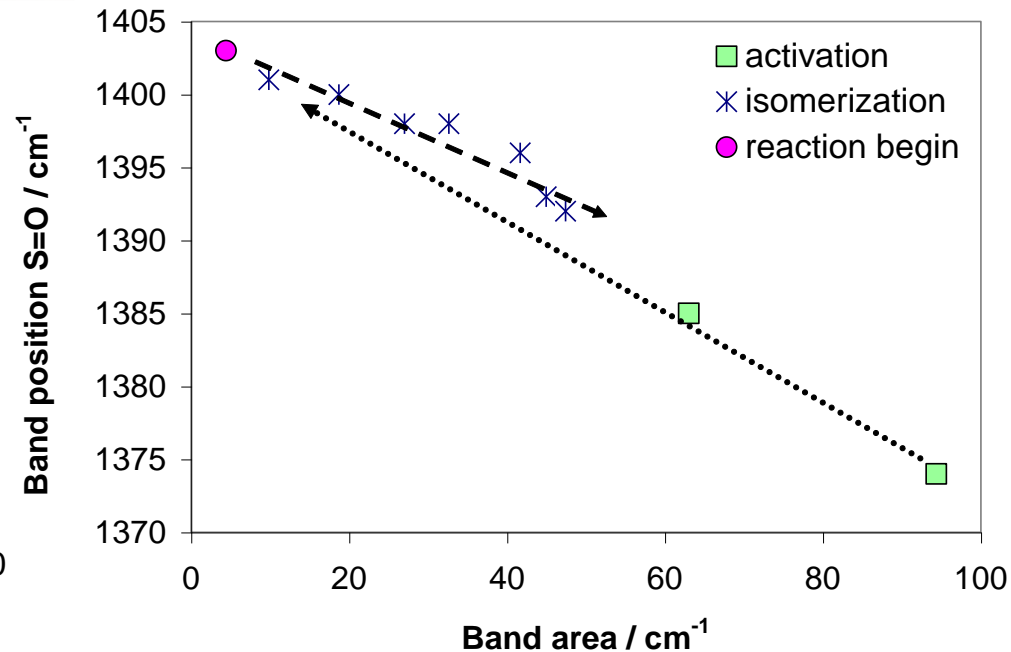
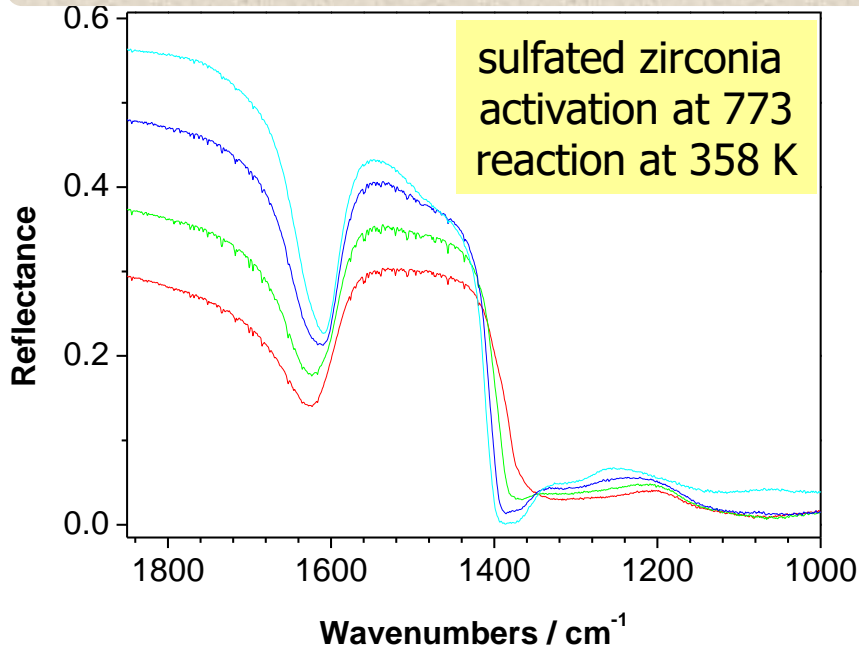
- ❖ Role of Mn is not to improve initiation reaction, in presence of Mn actual isomerization reaction is promoted



Water Adsorption and Sulfate Vibration



H₂O deformation and S=O stretching



- ❖ band positions for activated catalyst consistent with S₂O₇²⁻ according to DFT calculations
- ❖ Red shift of S=O vibration at 1400 cm⁻¹ with increasing H₂O content calculated

Hofmann, J. Sauer, J. Phys. Chem. B 108 (2004) 14652



Summary IR Spectra of Surface Species



- ❖ IR is a versatile technique, complete spectral information should be exploited
- ❖ information on local structure on any surface under wide variety of conditions (materials and pressure gap)
- ❖ extinction coefficients of individual bands inform about polarization of molecule upon adsorption: initiation of chemical transformation
- ❖ reaction kinetics (of model reactions) can be studied, determine E_A
- ❖ reaction mechanism can be revealed through in situ studies
- ❖ comparison with calculated quantities easily possible



Acknowledgements



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Humboldt Universität zu Berlin

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Joachim Sauer

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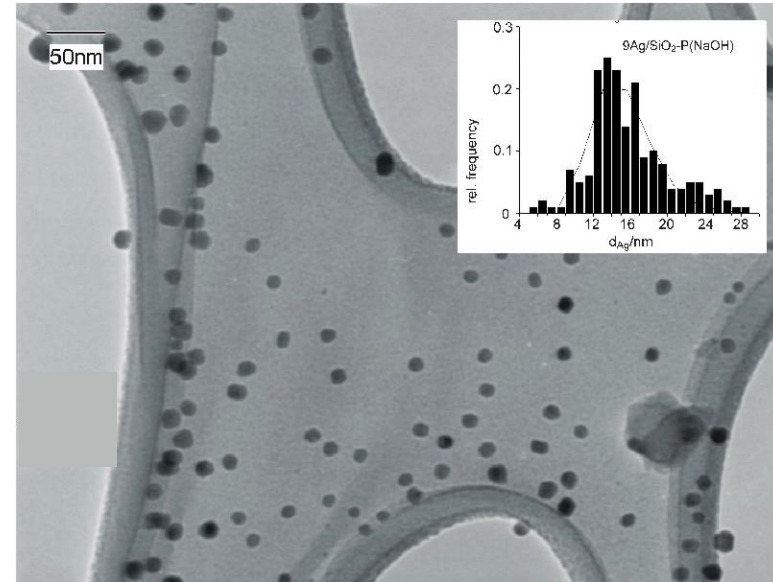


Proben und Charakterisierung (ICP, TEM, IR)

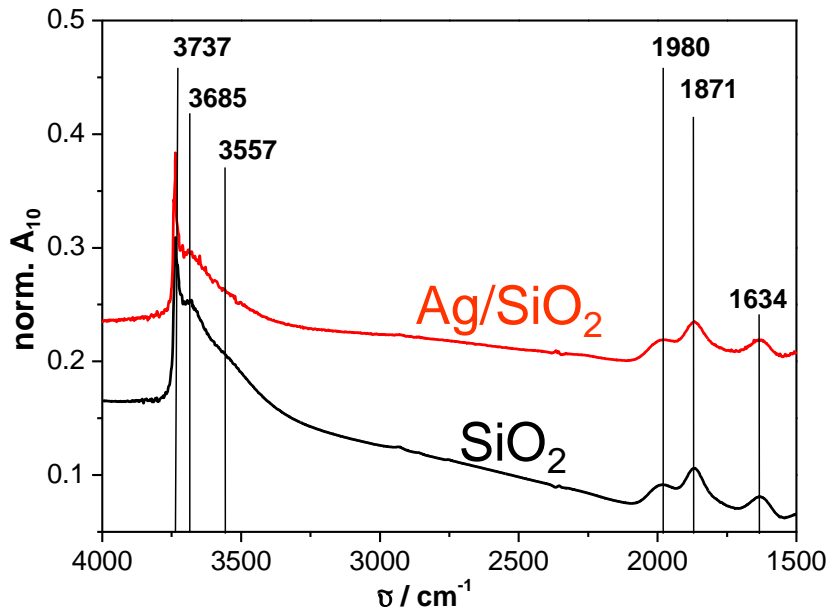


9Ag/SiO₂: AgNO₃/NaOH aufgefällt;
8.09 at% Ag; d = 15 nm

SiO₂ (Alfa): analog behandeltes SiO₂



ICP-AES, TEM: Christian Mohr,
Technische Chemie II, TU Darmstadt



Fläche OH-Banden (Si-OH + andere):

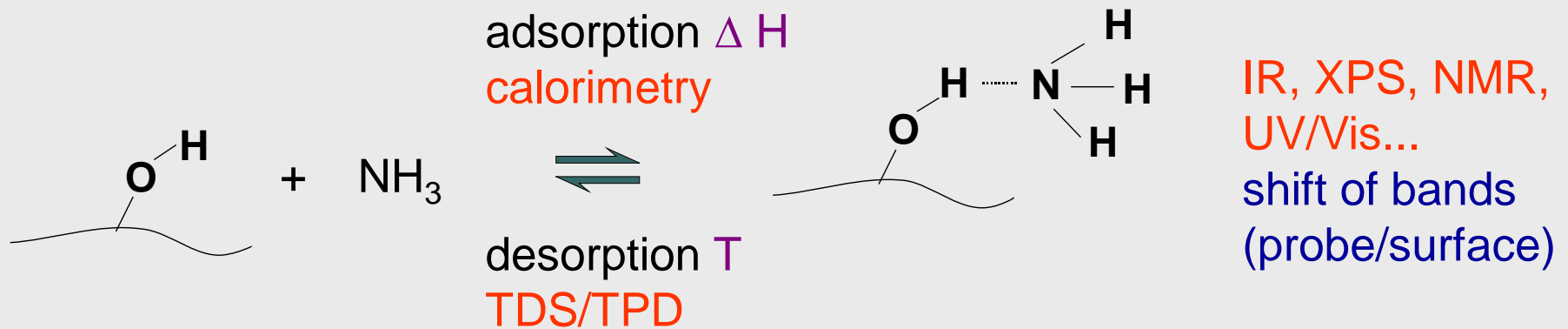
- ❖ SiO₂: 22.5 cm⁻¹ g⁻¹
- ❖ Ag/SiO₂: 12.3 cm⁻¹ g⁻¹



Adsorption of Probe Molecules



Goal: identify **type (B/L)**, **number**, **strength** of acidic sites

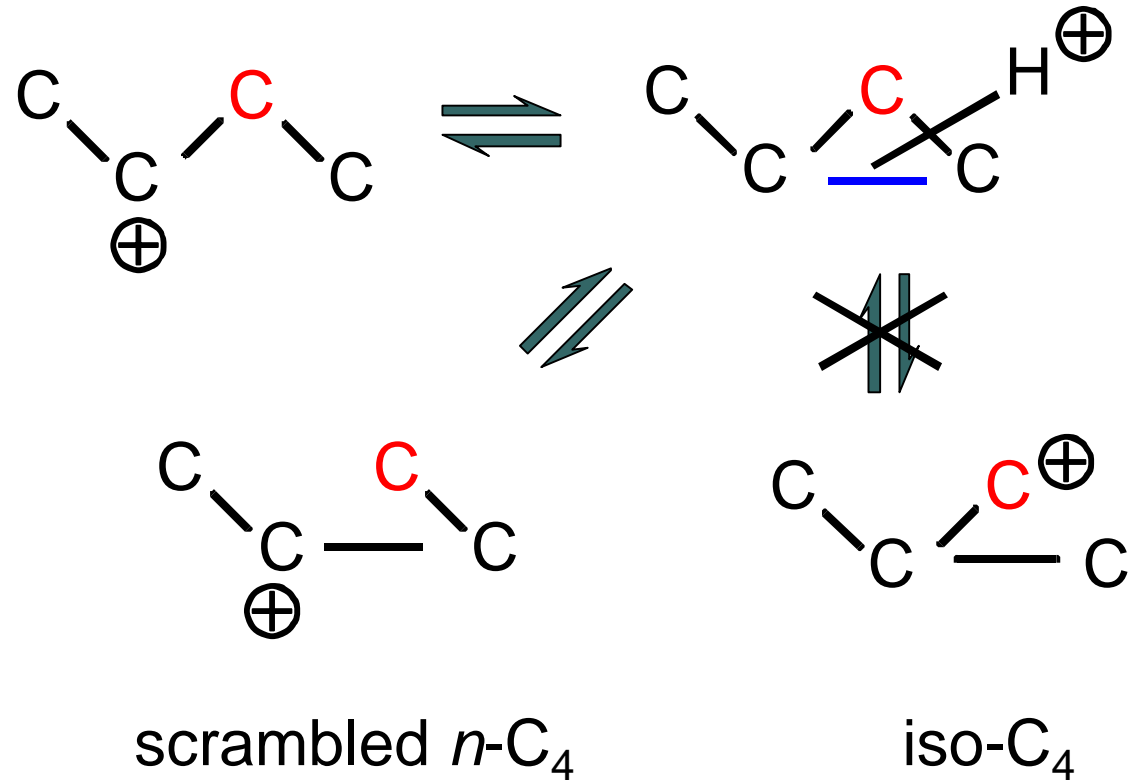


IR, NMR, calorimetry (various probes):
not superacidic, rather like strongly acidic zeolite
Kustov 1995, Adeeva 1995, Fogash 1995

 no acidic sites that explain activity

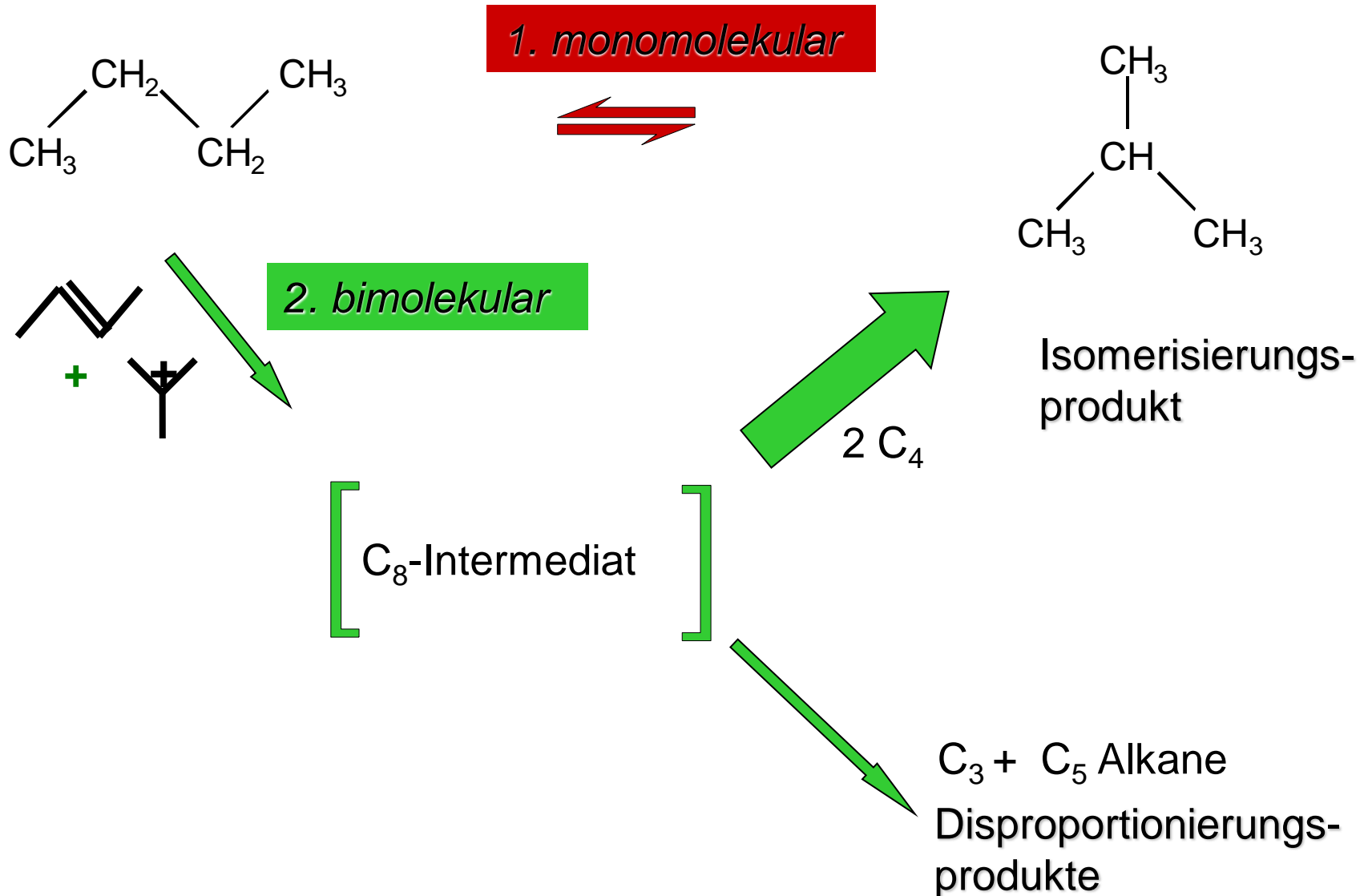


n-Butane Isomerization





Isomerisierungsmechanismen: Butan

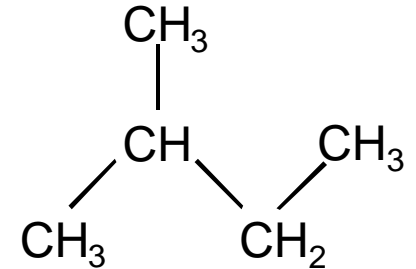
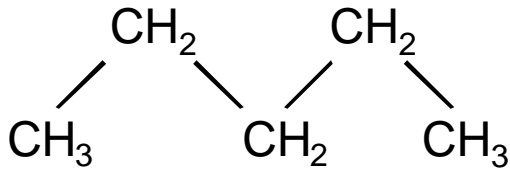




Isomerisierungsmechanismen: Pentan

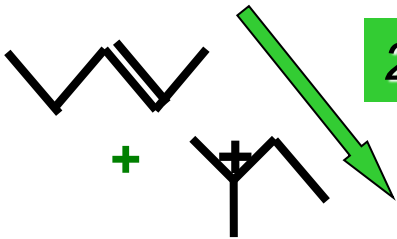


1. monomolekular



Isomerisierungs-
produkt

2. bimolekular

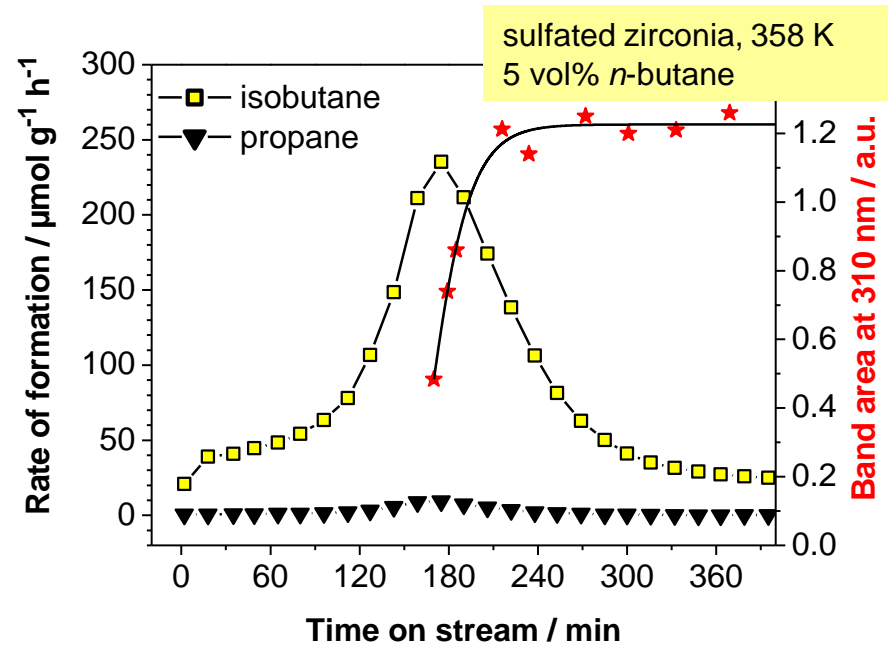
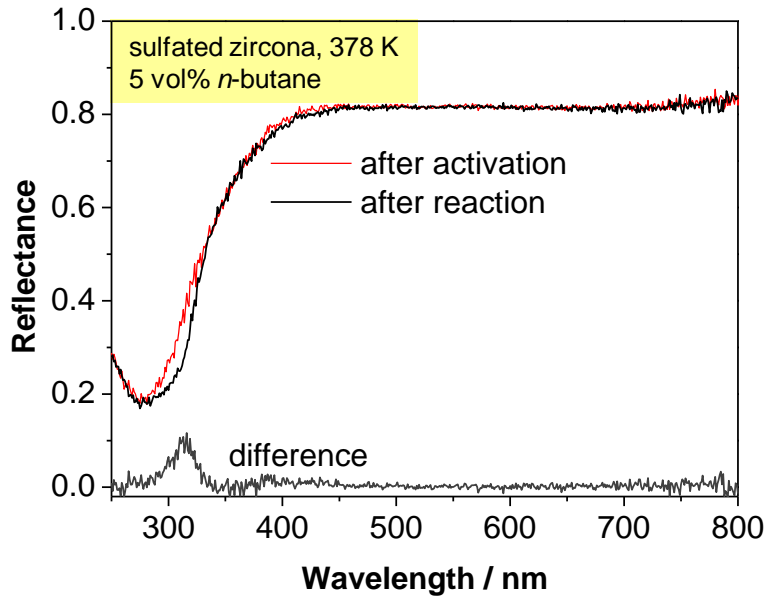


2 C₅

C₄ + (C₆) Alkane
Disproportionierungs-
produkte



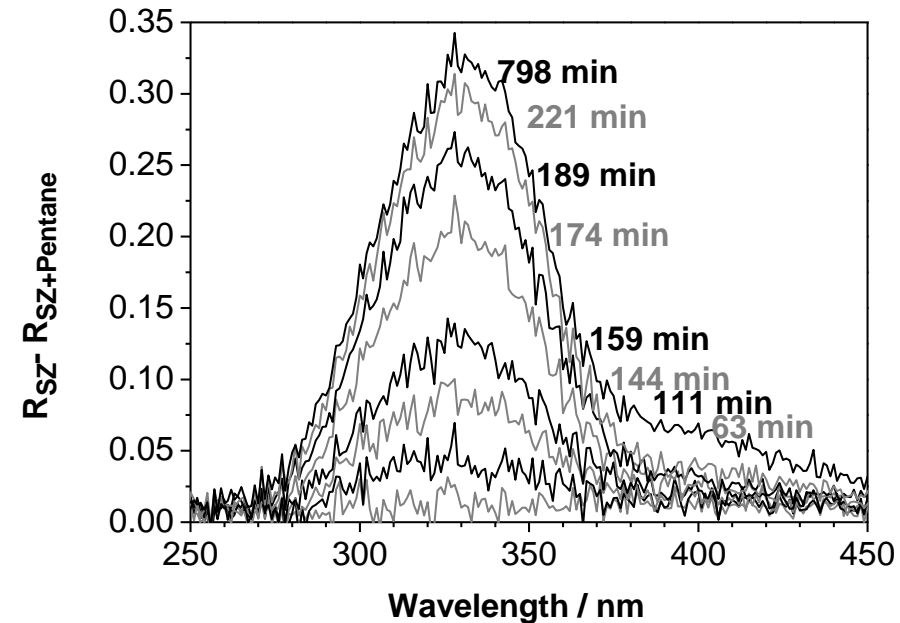
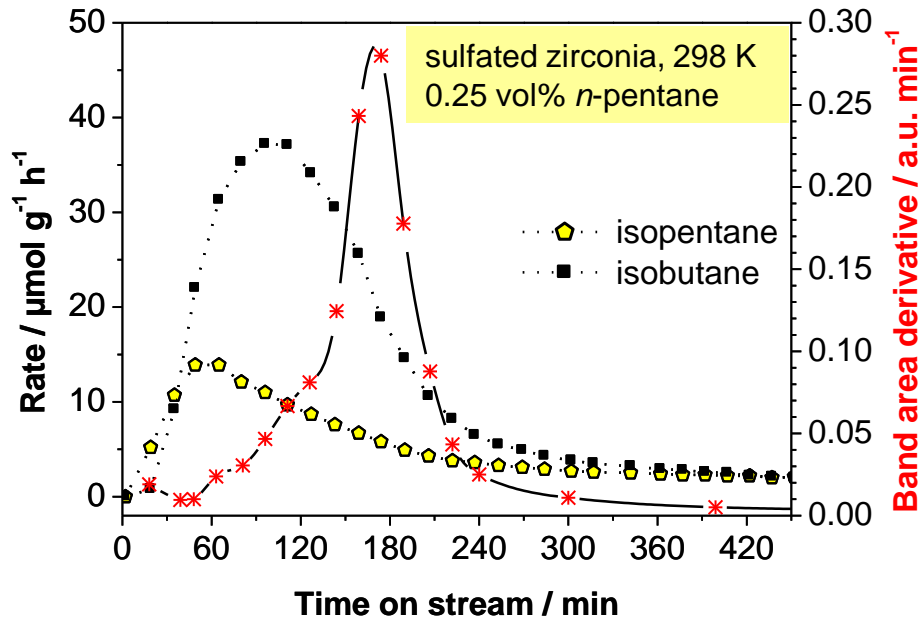
Deaktivierung: in situ UV-vis Spektroskopie



- ❖ Ausbildung von Banden im Verlauf der Reaktion bei 358-423 K
Bande bei 310 nm, Allylkationen
- ❖ Deaktivierung eine Folge der bimolekularen Isomerisierung



Pentanisomerisierung: Reaktionsprofil und „Verkokung“



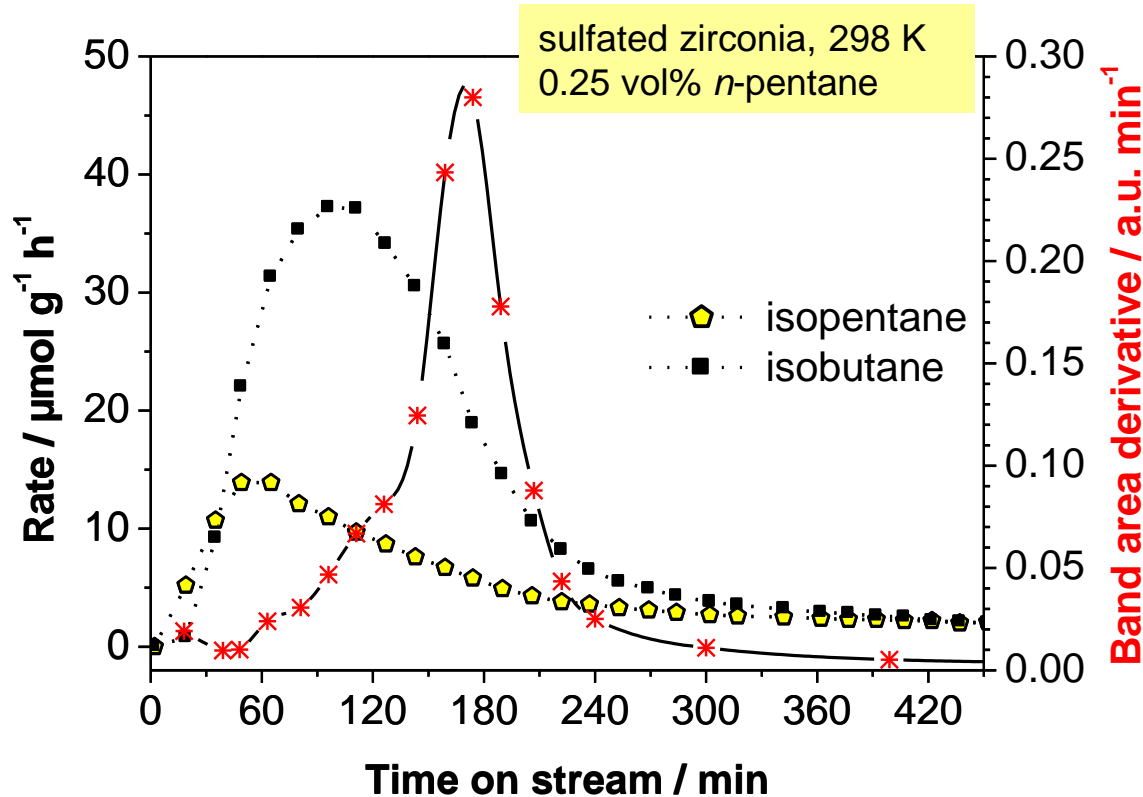
- ◆ ungesättigte Spezies sind keine Intermediate
- ◆ keine Folge der monomolekularen Isomerisierung
- ◆ Resultat des bimolekularen Mechanismus, Konkurrenzreaktion?



Reaction Profile during Pentane Isomerization



Ahmad, Jentoft et al.
J. Catal. 2003



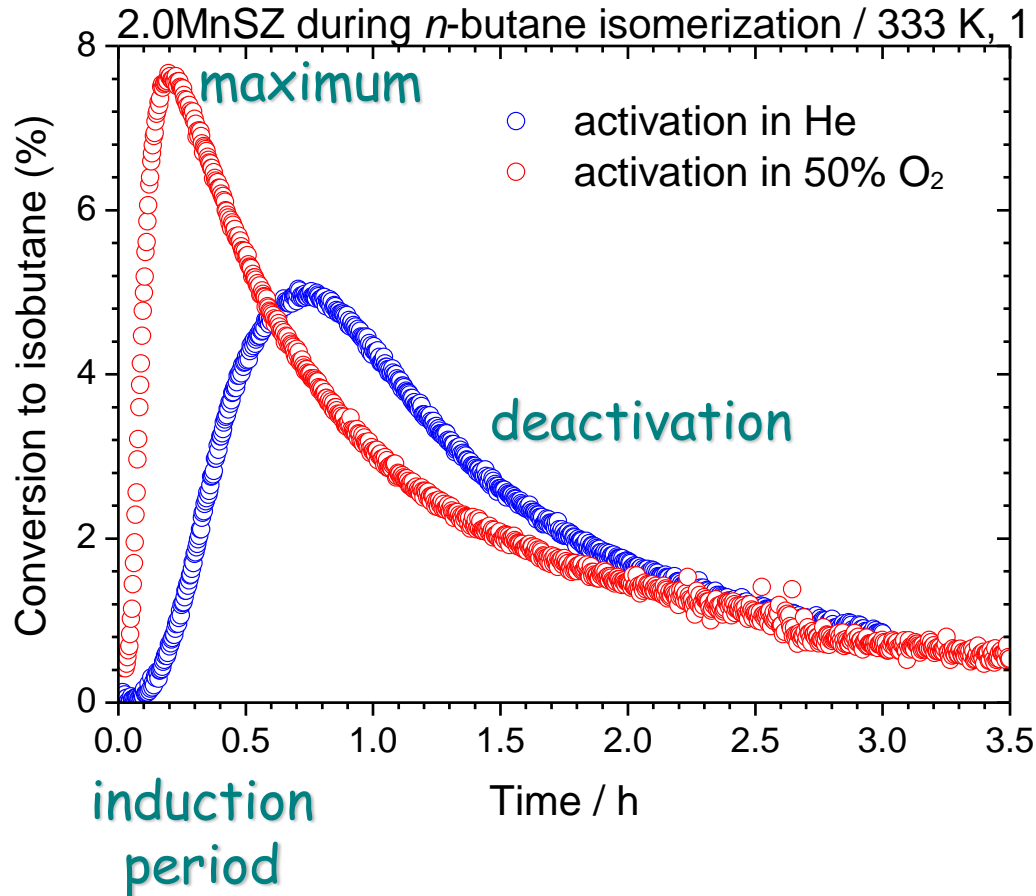
unsaturated species are not intermediates

not a result of monomolecular isomerization

result of bimolecular mechanism, competing reaction to formation of gas phase products



Activation & Catalytic Performance



He: average Mn valence after activation **2.48**

O₂: average Mn valence after activation **2.69**

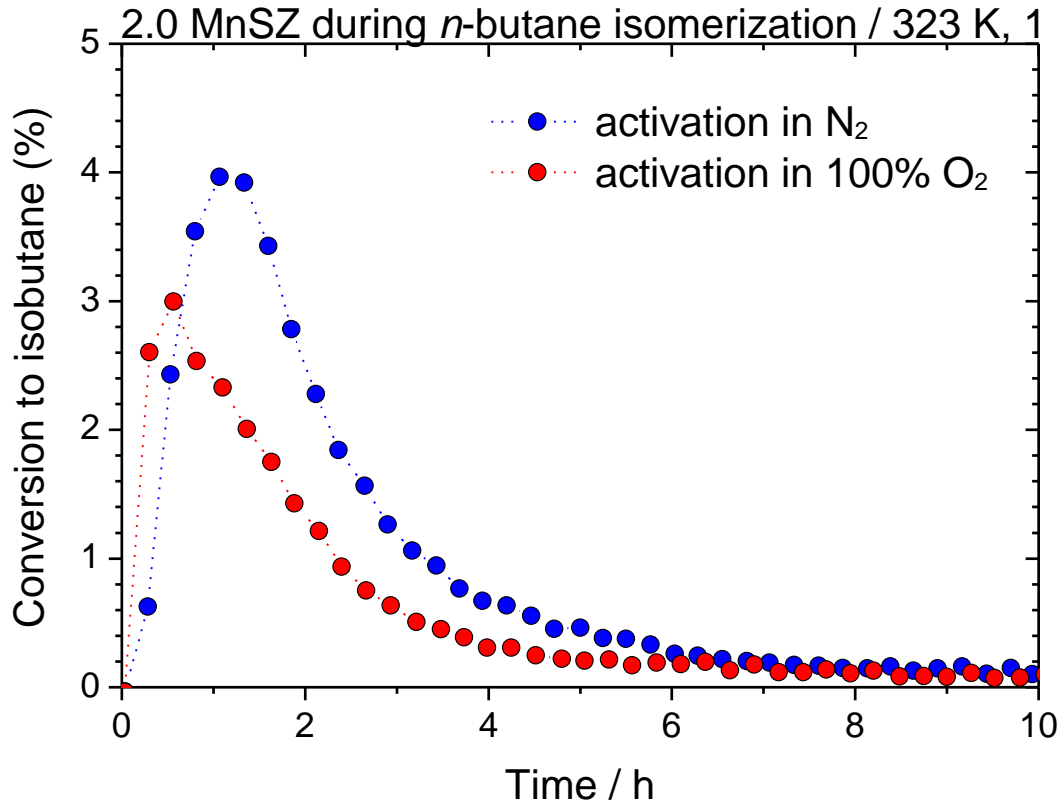
correlation between oxidation state and catalytic activity:

the higher the average Mn valence the higher the maximum isomerization rate

positive effect: **50% O₂**



Activation & Catalytic Performance



- almost identical DRIFT spectra but difference in maximum catalytic activity
- negative effect of O₂ during activation

N₂: ca. 180 μmol g⁻¹ h⁻¹

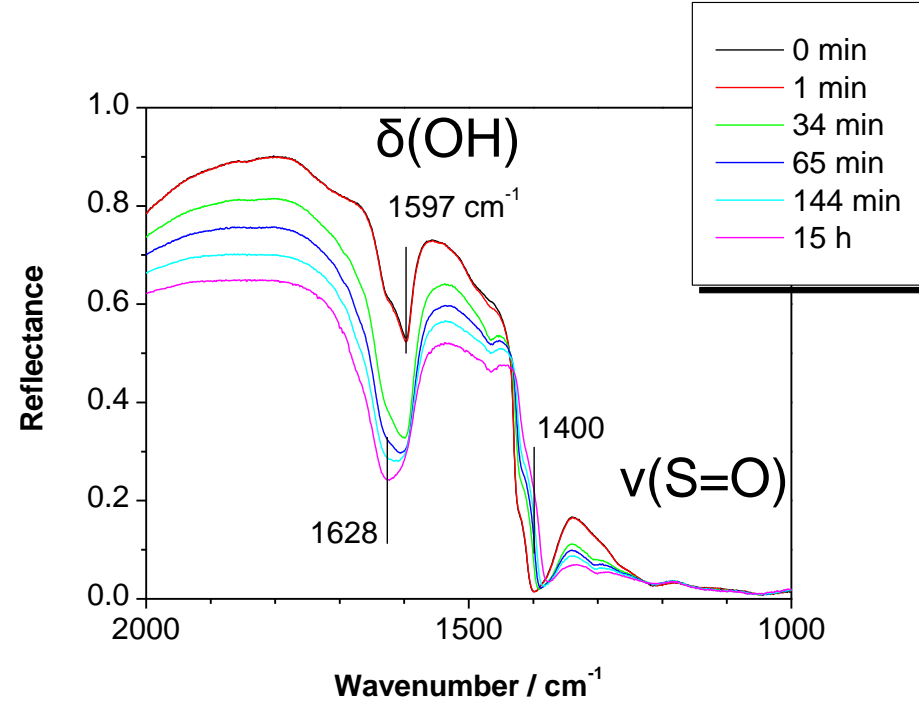
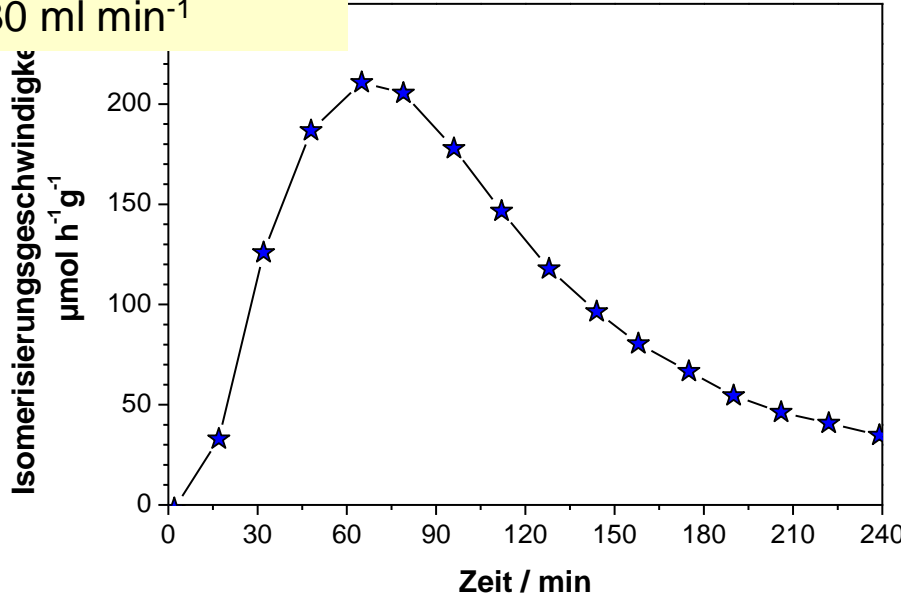
O₂: ca. 140 μmol g⁻¹ h⁻¹



In Situ DRIFT-Spektroskopie



184 mg MnSZ
1 kPa *n*-C₄, 323 K
30 ml min⁻¹

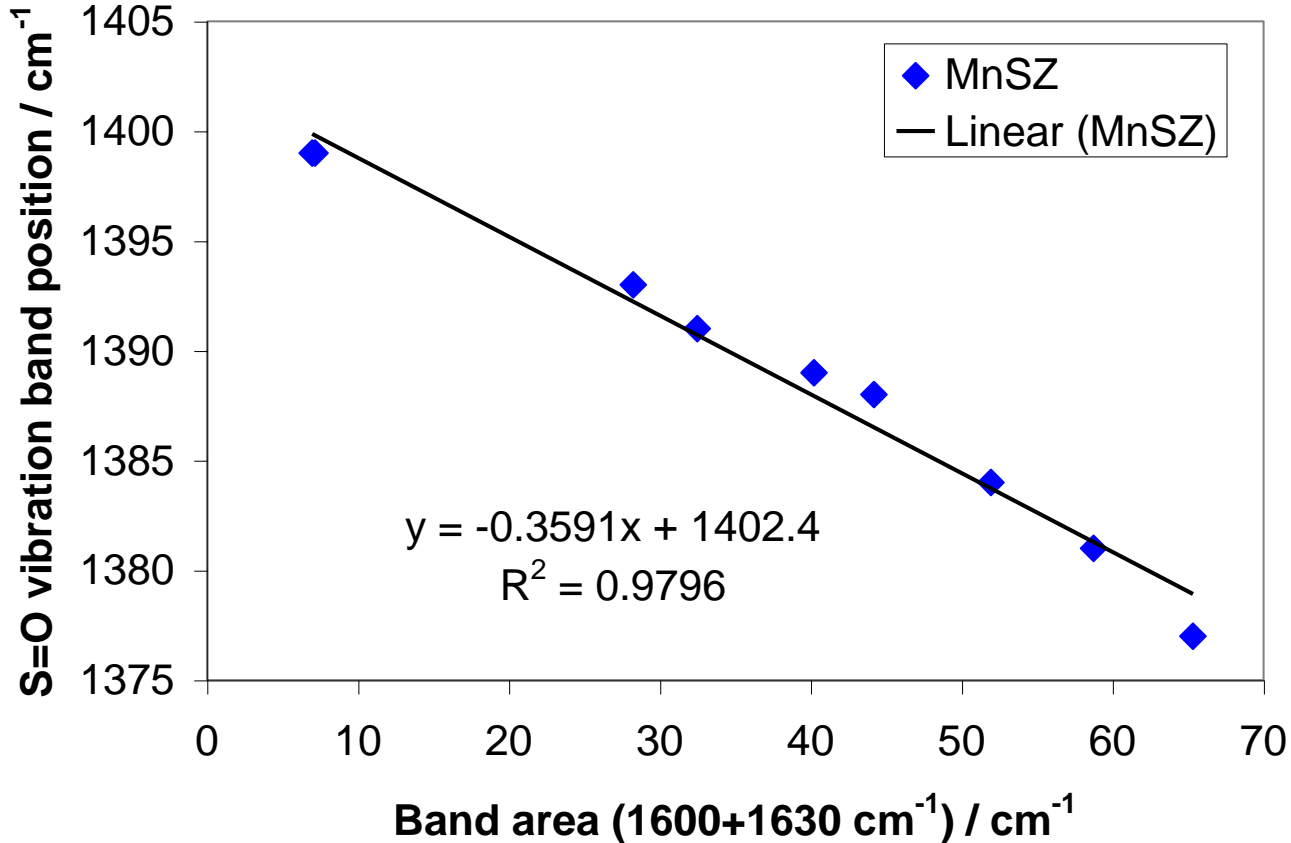


Zunahme von Bande bei 1597 cm⁻¹ bis max. Umsatz
dann Wachstum Bande bei 1628 cm⁻¹

Verschiebung S=O-Bande



In Situ DRIFT-Spektroskopie: Auswertung



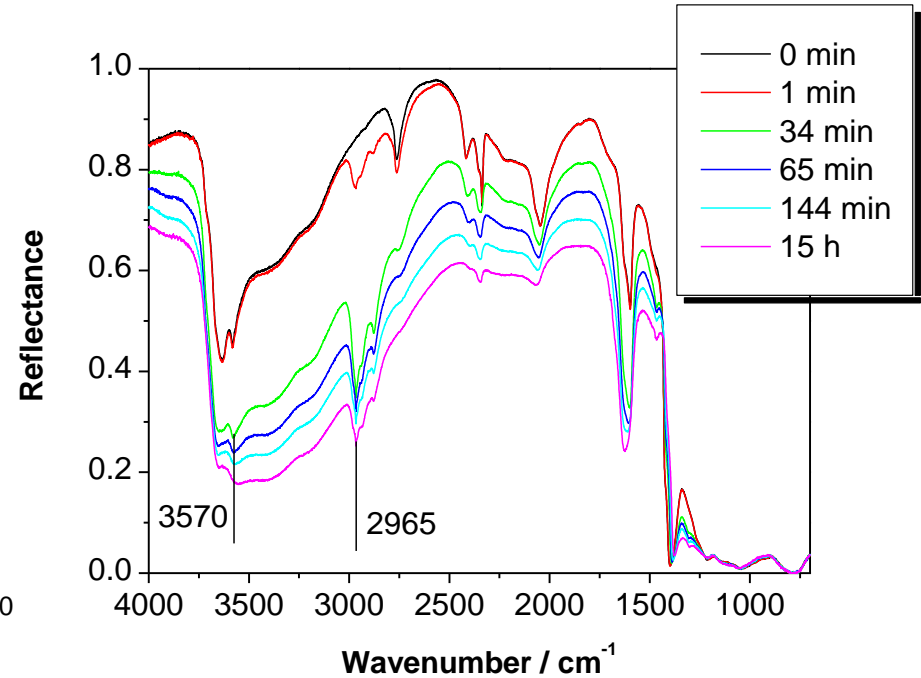
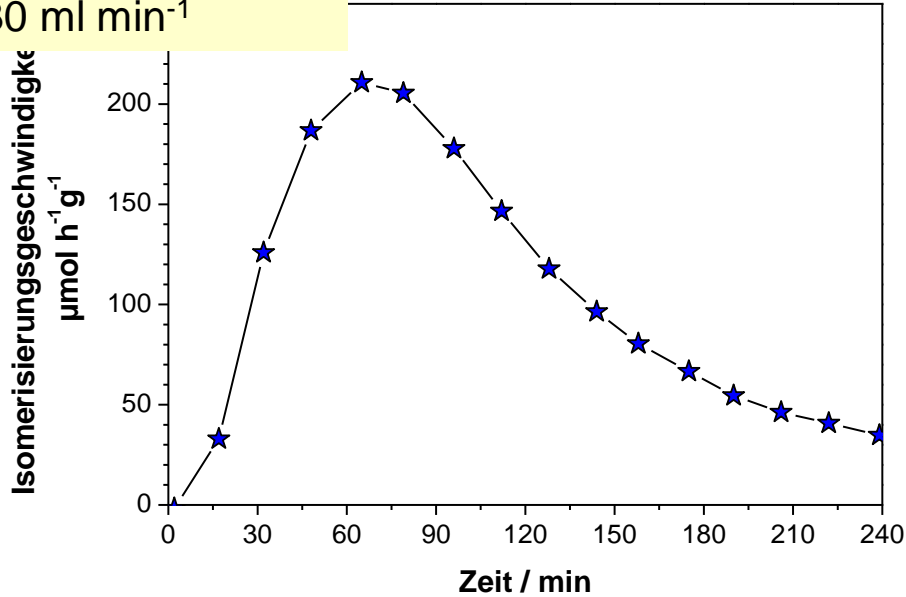
Verschiebung S=O Bande korreliert mit Fläche Banden bei 1600+1630 cm⁻¹
Wasserbildung?



In Situ DRIFT-Spektroskopie



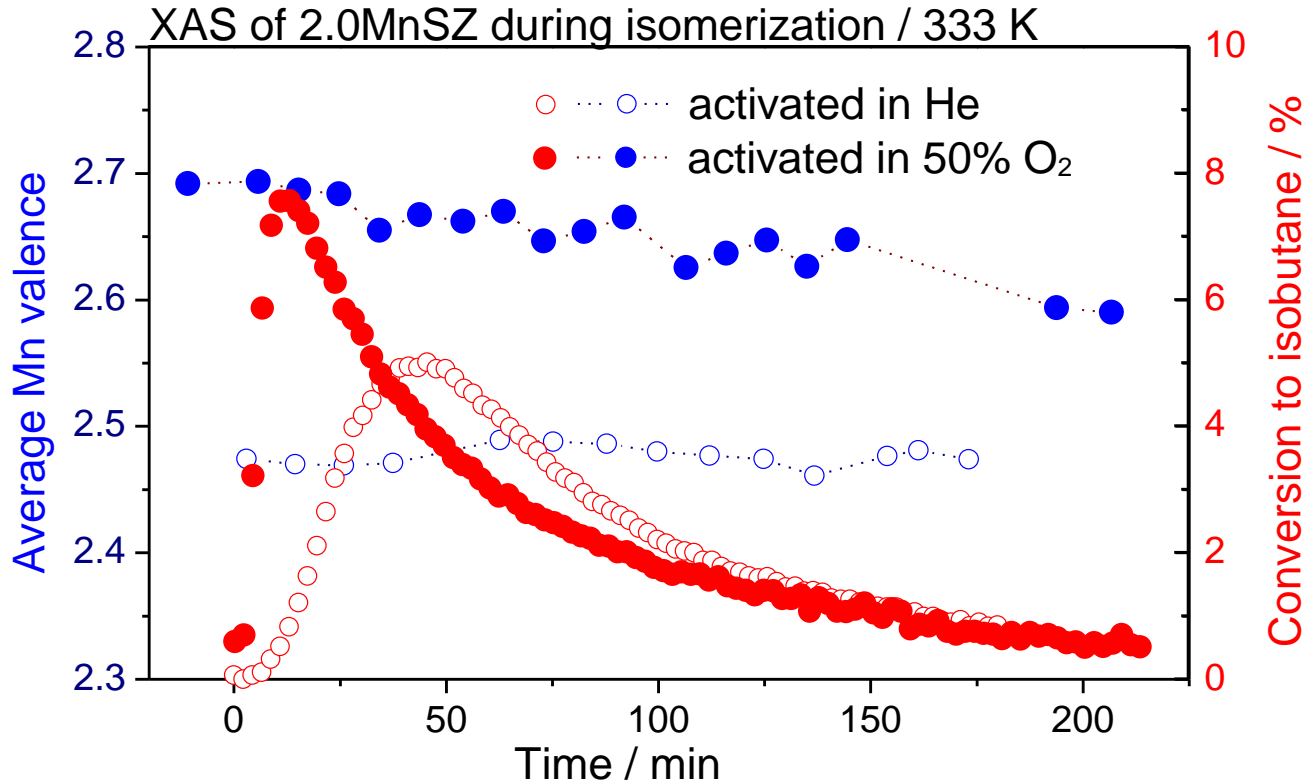
184 mg MnSZ
1 kPa *n*-C₄, 323 K
30 ml min⁻¹



Abnahme der Gesamtintensität
starke Gasphasenbeiträge im CH-Bereich



Reaction (*in situ* XAS)



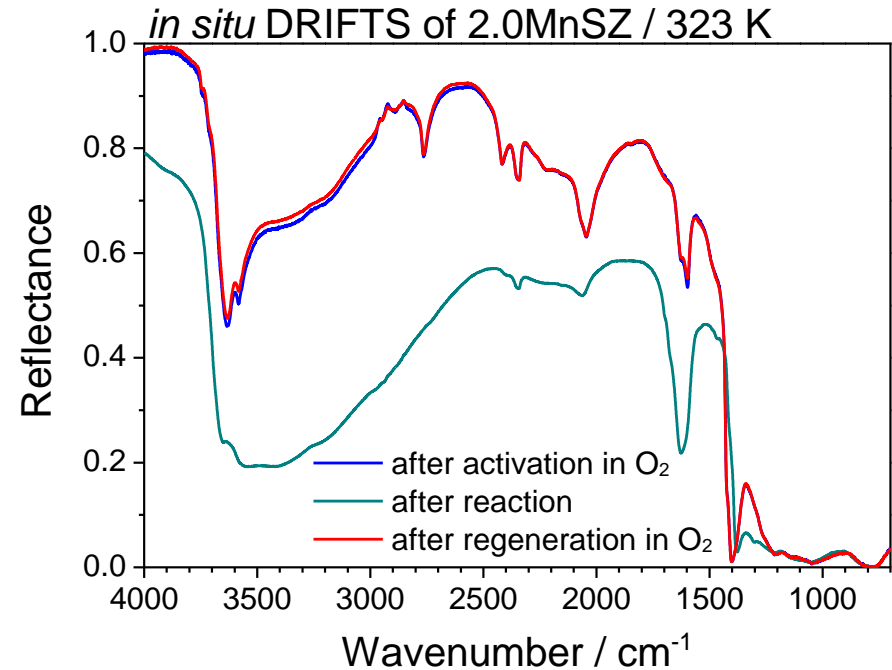
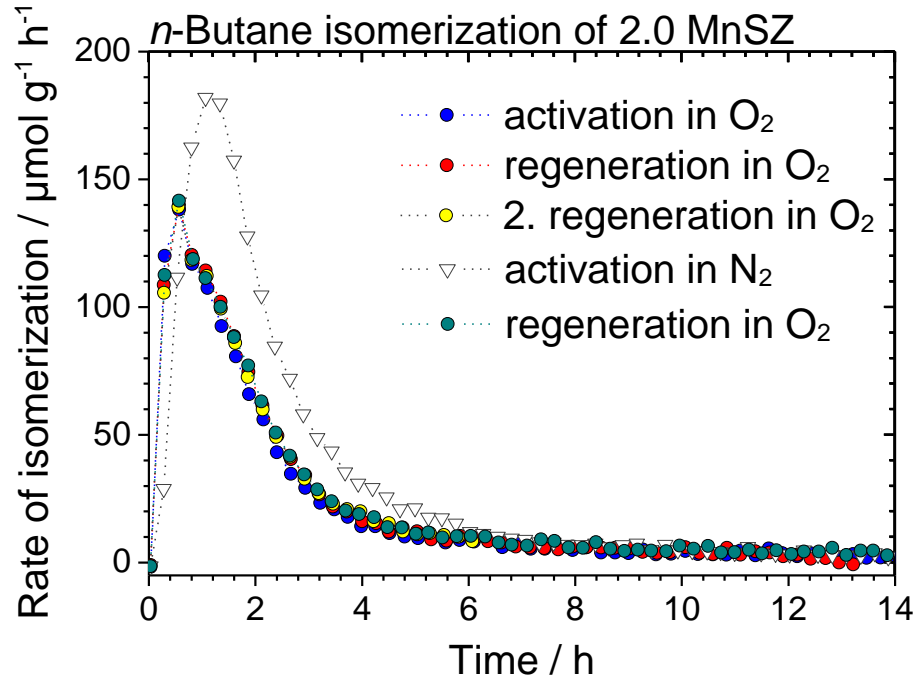
He: average Mn valence constant at **2.48**

O₂: average Mn valence decreases linearly from **2.69** to **2.59**

- no correlation of average Mn oxidation state with activity
- no evidence for oxidative dehydrogenation as non-catalytic initial reaction step



Regeneration - 100% O₂



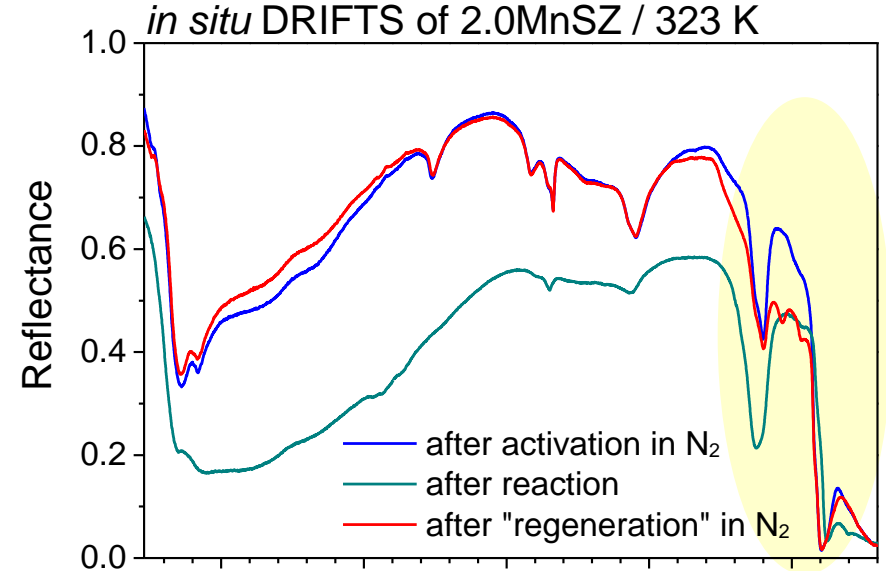
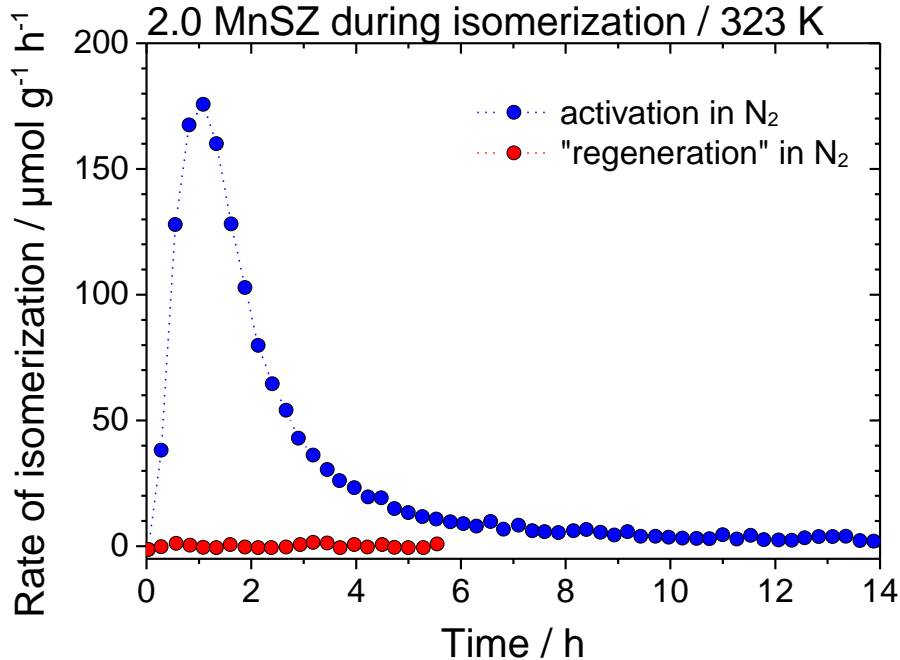
- same activity profile after regeneration in O₂
- more than one regeneration possible
- same activity after regeneration in O₂ for N₂-activated catalyst

- recovery of the original spectrum

- **regeneration in O₂ possible**
- **reproducible state of catalyst after O₂ treatment**

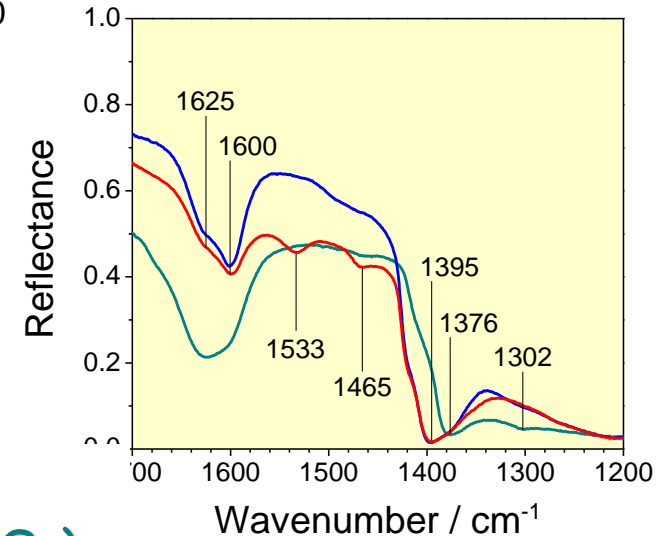


„Regeneration“ - N₂



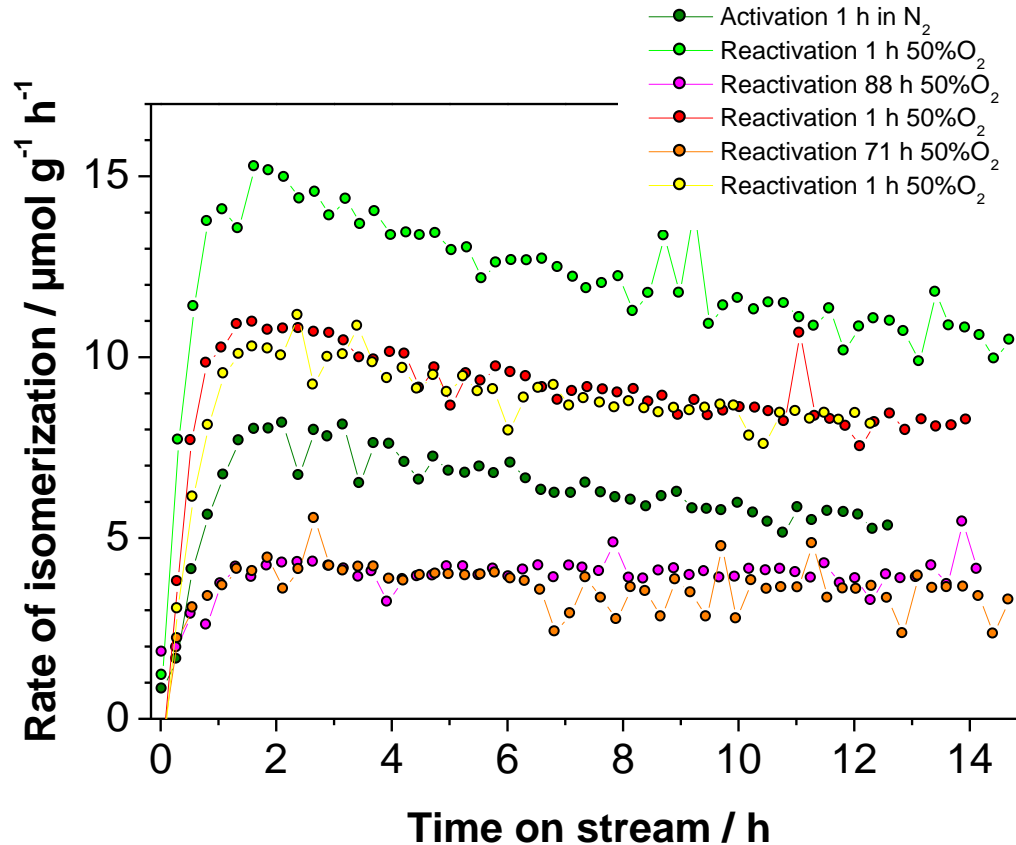
- **inactive** catalyst after regeneration procedure in N₂
- OH and sulfate groups reestablished
- two additional bands at 1533 and 1465 cm⁻¹ (conjugated C=C and CH bending)
→ dehydrogenated adsorbed hydrocarbon

- no regeneration in N₂
- surface has to be freed from deposits (→ O₂)





Regenerierung von sulf. ZrO_2



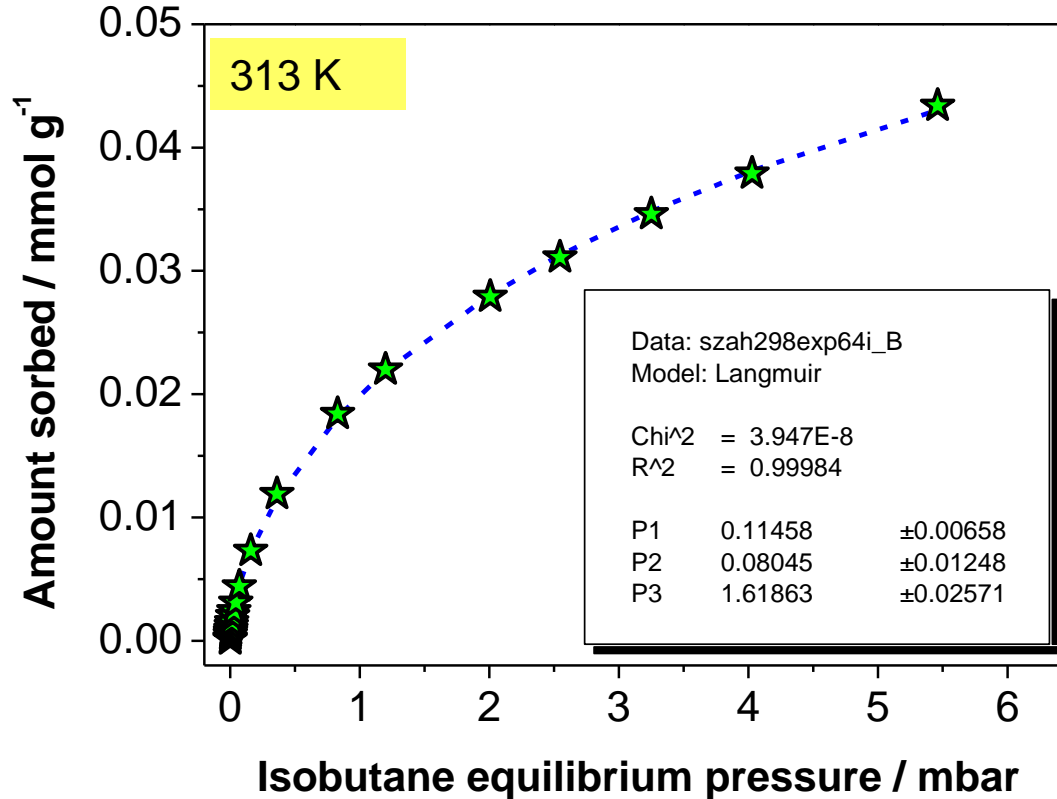
500 mg SZ, 1 kPa $n\text{-C}_4$
Reaktion bei 338 K
Reaktivierung bei 723 K

❖ „Konditionierung in O_2 “?

➔ ein Modell für sulfatiertes und promotiertes sulfatiertes ZrO_2



Zentren für Alkanadsorption an sulf. ZrO_2

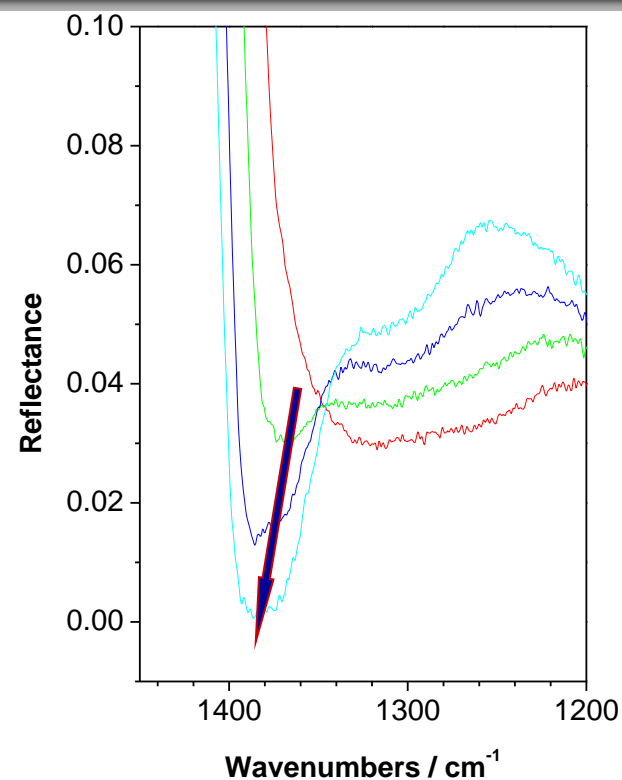
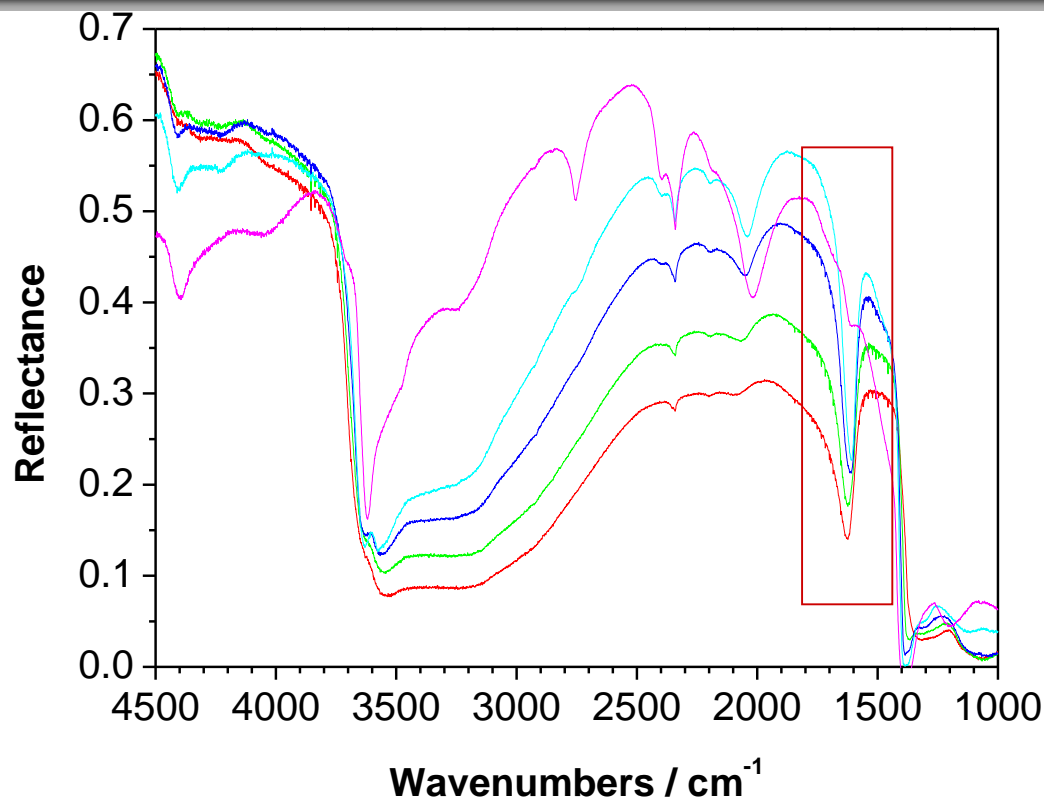


Isobutanadsorption, Anpassung mit Langmuirmodell
Monolage $\approx 80 \mu\text{mol/g}$; Sulfatgehalt $\approx 560 \mu\text{mol/g}$

➔ nur ca. 15% des Sulfat involviert in Adsorption / Reaktion



Activation of Sulfated Zirconia: In Situ DRIFTS



- ❖ adsorbed water (3700-3000, 1600 cm⁻¹) partly removed during activation at 773 K
- ❖ sulfate overtones, combination modes, fundamentals (2764-2049, 1400 cm⁻¹)
- ❖ band positions consistent with S₂O₇²⁻ according to DFT calculations
A. Hofmann, J. Sauer, J. Phys. Chem. B 108 (2004) 14652