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Characterization of Surface Sites Using IR-Spectroscopy & Microcalorimetry

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Strasbourg, February 18, 2004

Outline

Part I - Ag/SiO_2 Catalysts

- samples & characterization by TEM, XPS
- IR spectroscopy: H/D exchange

Part II - Pt/H-Mordenite Catalysts

- sample series & catalytic performance
- characterization by XRD and TEM
- IR spectroscopy: adsorption of CO & *n*-butane
- calorimetry: adsorption of *n*-butane

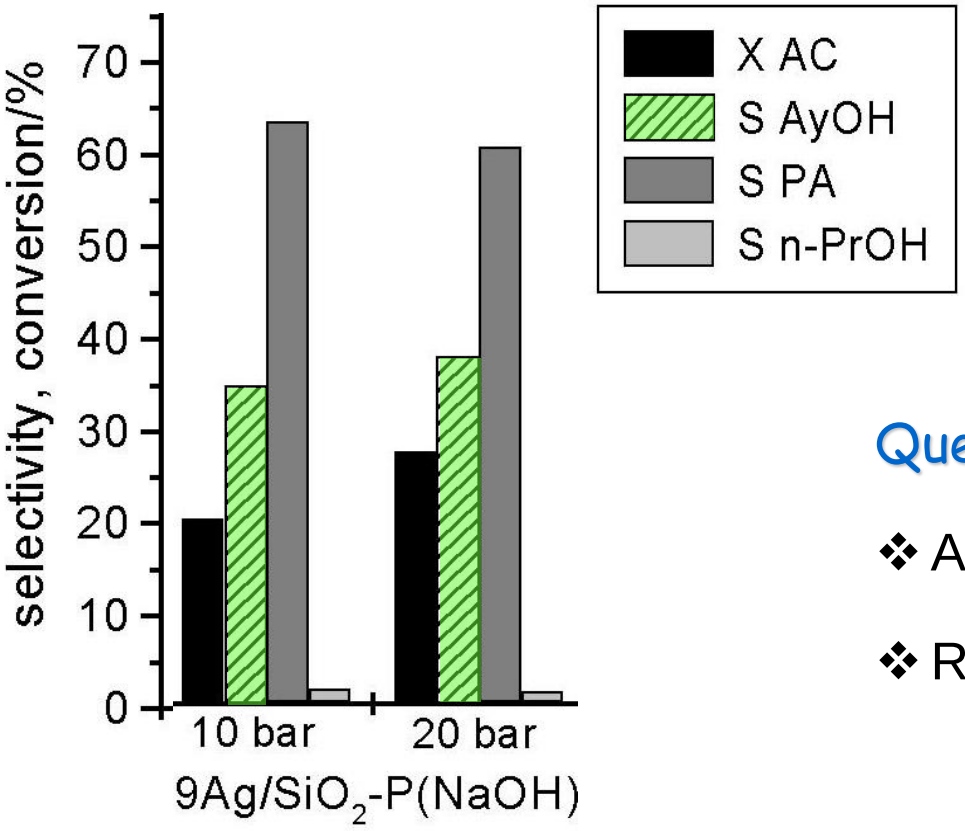
Ag/SiO_2 Catalysts: Motivation

Target Reaction: Selective Hydrogenation

- selective hydrogenation of acrolein (α,β-unsaturated aldehydes) to allyl alcohol (unsaturated alcohol)
- part of DFG priority program "Bridging the gap in heterogeneous catalysis"

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.

Ag/SiO_2 Catalysts: Motivation



Catalysis: Michael Bron and Peter Claus, Technische Chemie II, TU Darmstadt

Questions

- Activation of hydrogen?
- Role of silver?

Samples: TEM and XPS

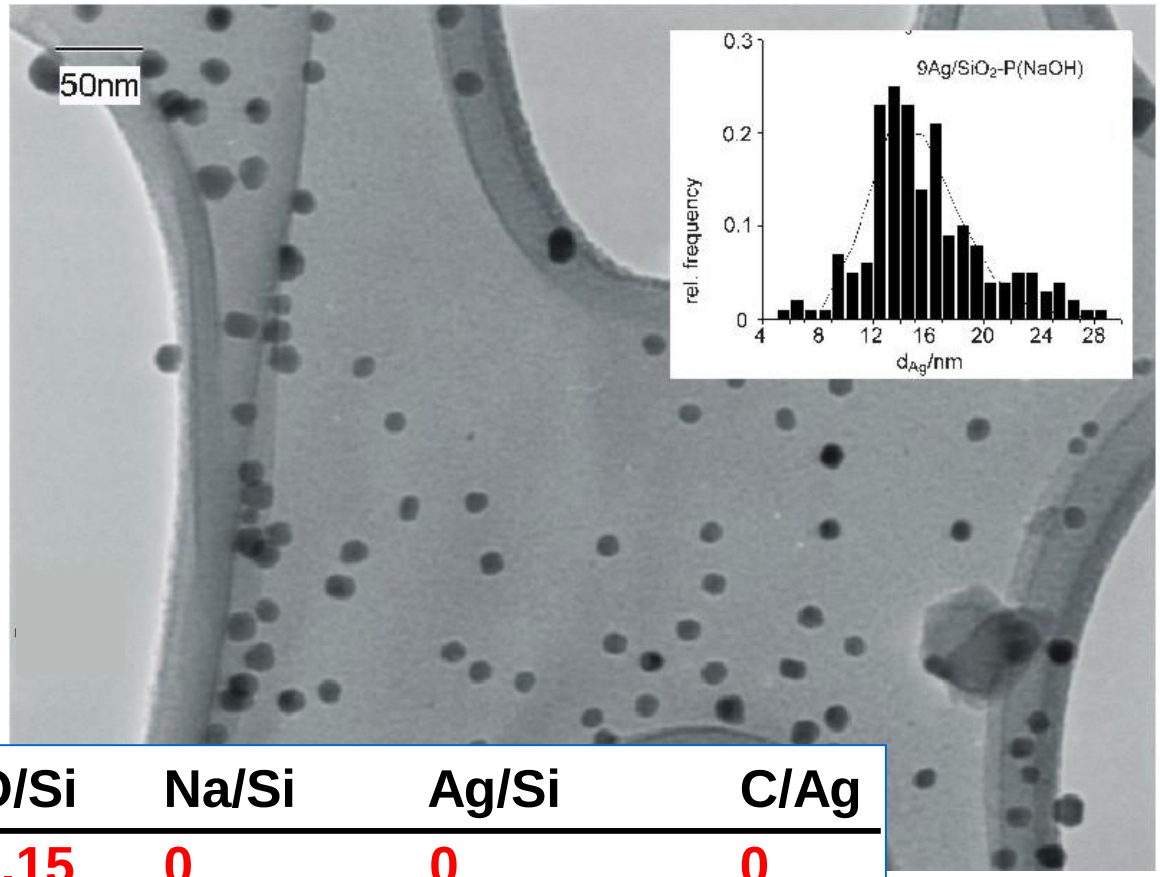
SiO_2 (Alfa)

$9Ag/SiO_2$: precipitation

$AgNO_3$ / NaOH

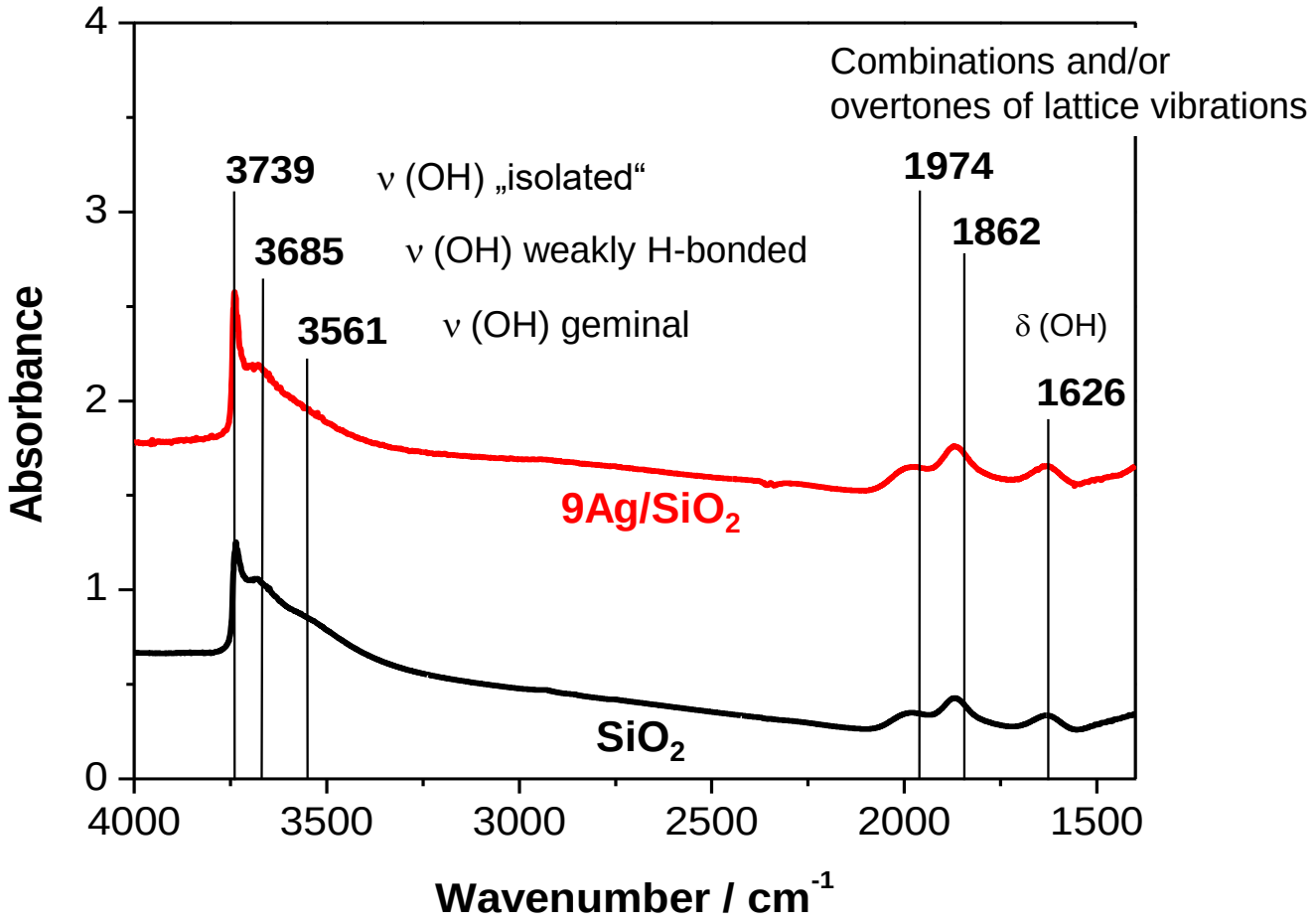
8.09 % Ag

ICP-AES, TEM: Christian Mohr, Technische Chemie II, TU Darmstadt;
XPS Andreas Scheybal, FHI



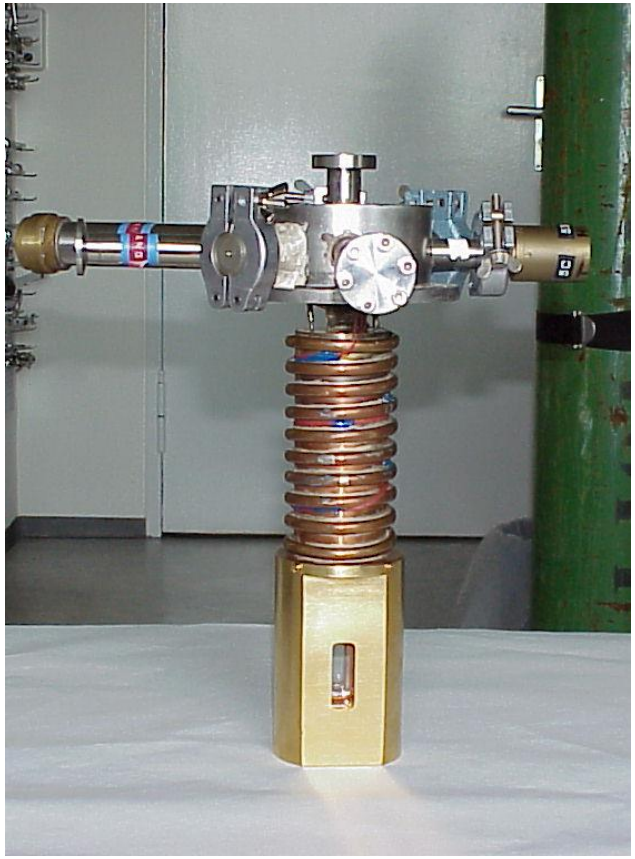
XPS	O/Si	Na/Si	Ag/Si	C/Ag
SiO_2	2.15	0	0	0
$9Ag/SiO_2$	2.10	0.0134	0.0345	0.36

IR Spectroscopy of Ag/SiO_2 Catalysts



- presence of Ag not noticeable in MIR spectra (activation at 523 K)
- first idea: investigate interaction with H_2 at low temperatures

Cell for IR Measurements at 77 K

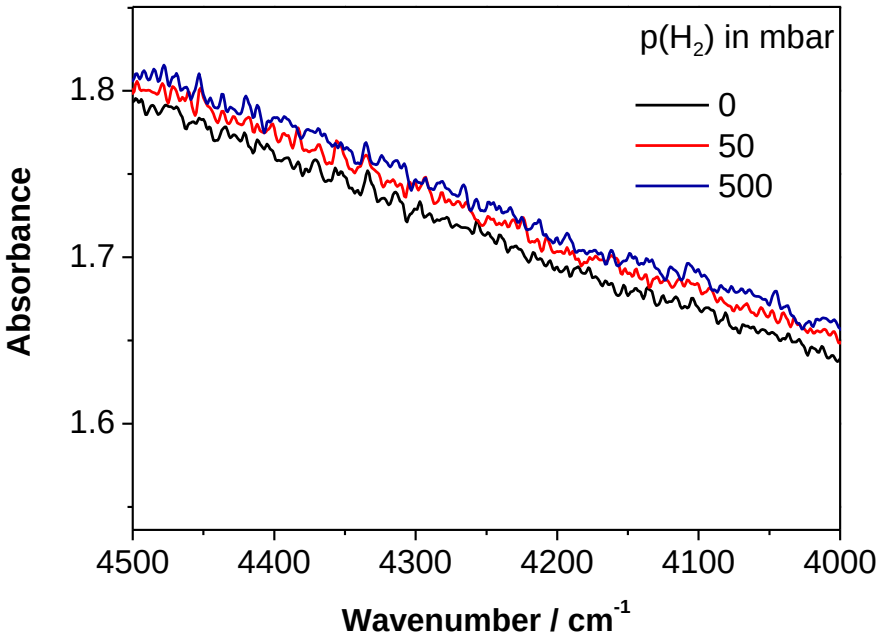


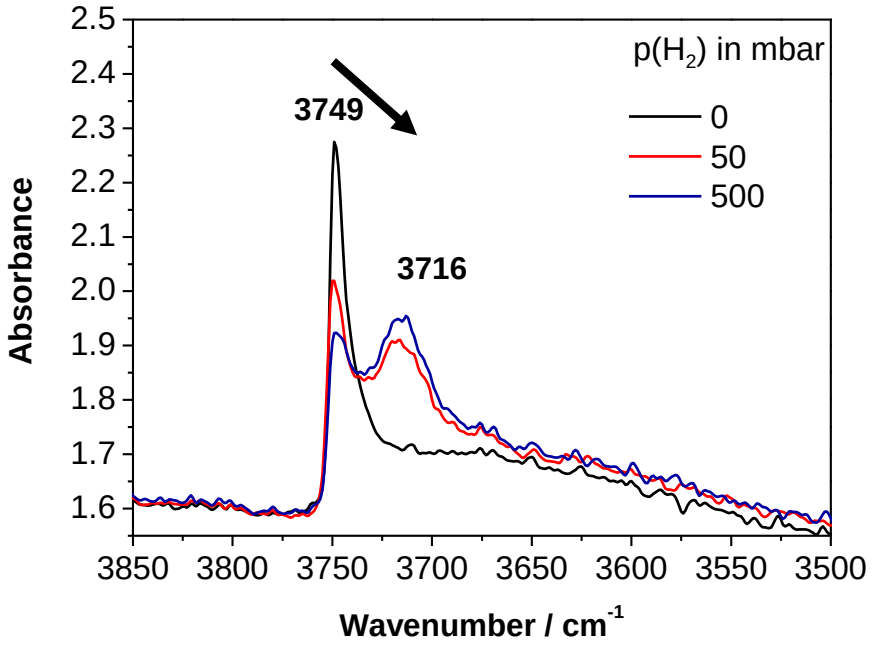
Key Features

- block with cooling coil
- double set of windows with vacuum in between

Adsorption of H_2 at 77 K on Ag/SiO_2

H_2 gas phase 4161 cm^{-1}

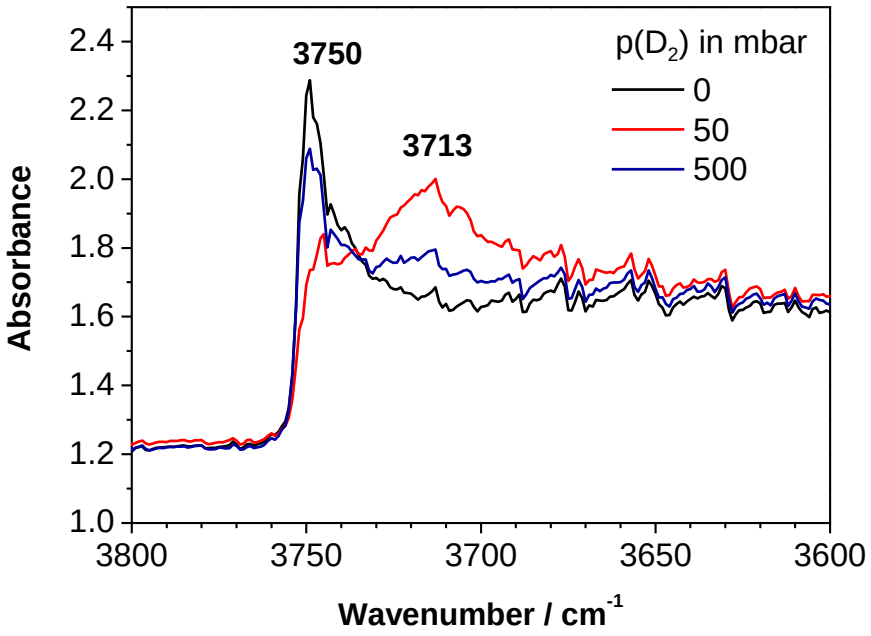


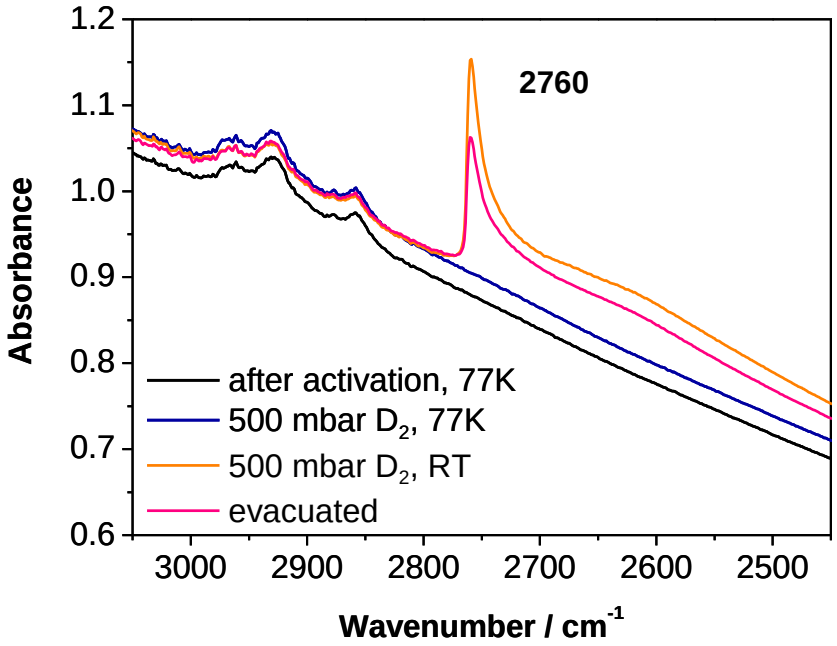


- no adsorbed H_2 visible in spectra
- shift of OH vibration through H_2 adsorption by ca. -35 cm^{-1}
- no difference between SiO_2 and Ag/SiO_2

Adsorption of D_2 at 77 K on SiO_2

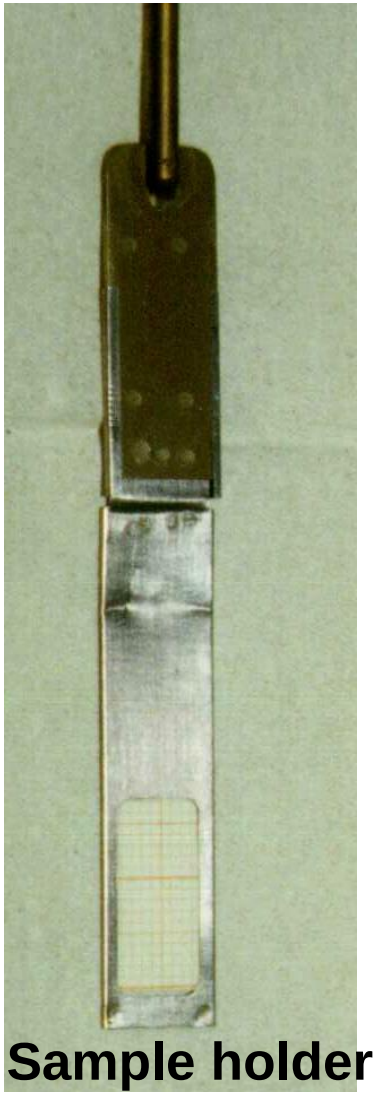
D_2 gas phase 2994 cm^{-1}



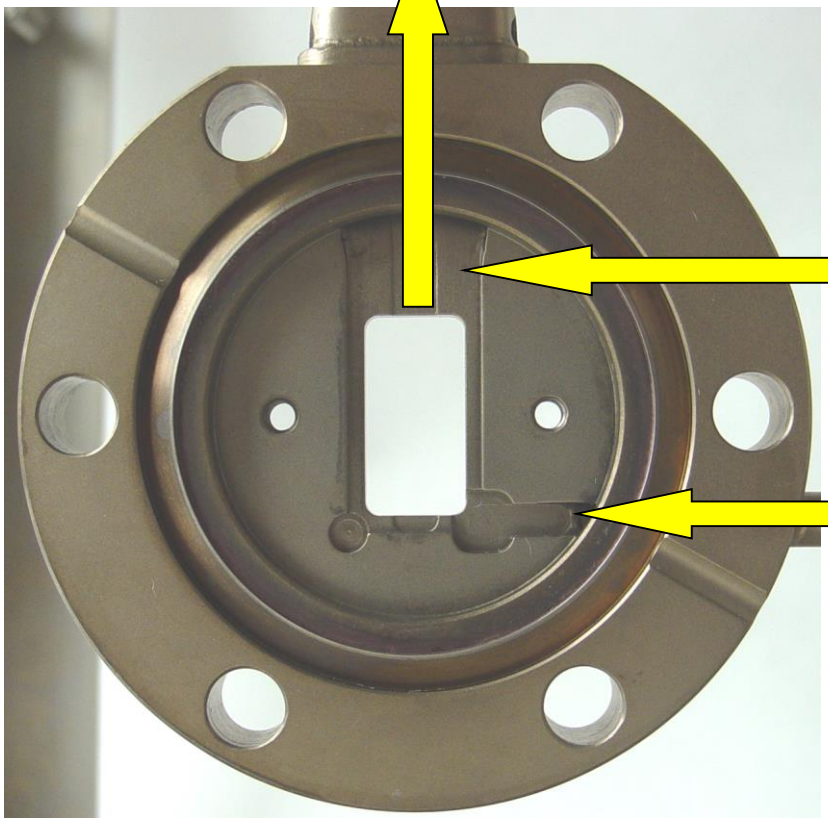


- no bands of adsorbed D_2
- shift of silanol bands
- formation of OD groups!

Sample Holder for Self-Supporting Wafers and Cell Body

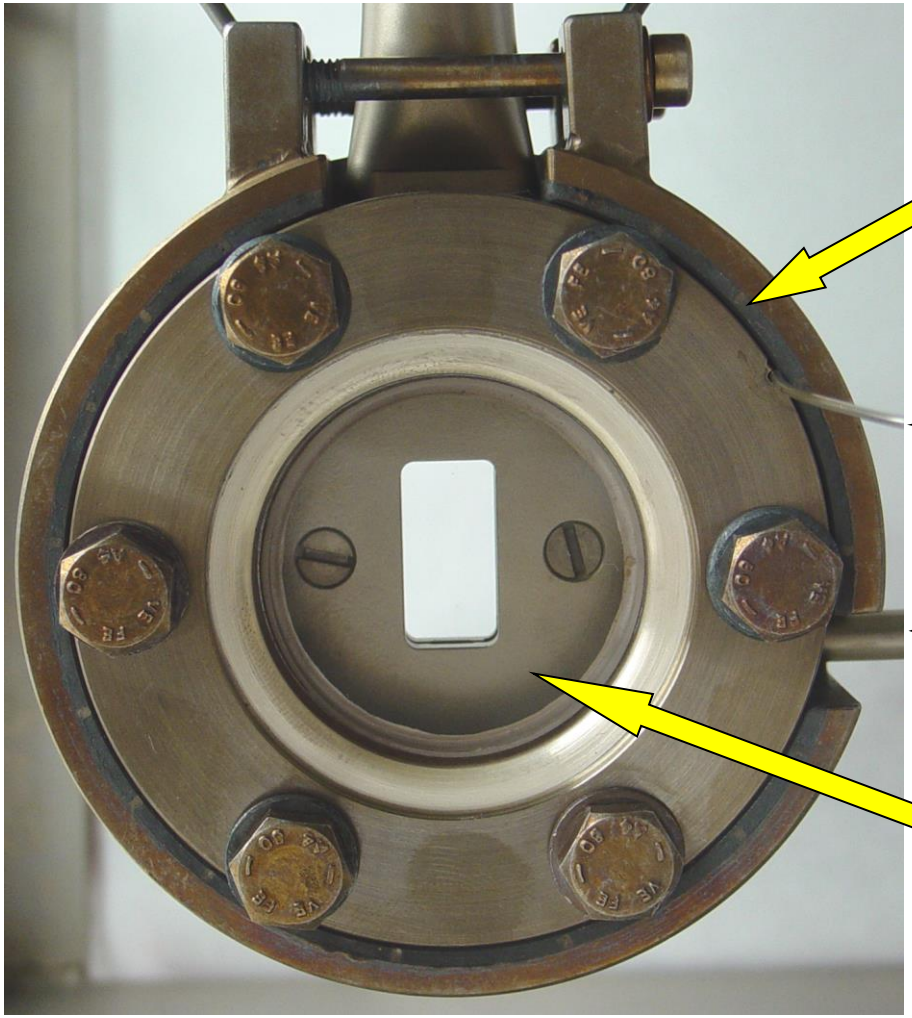


Sample holder



- 30 min activation at 598 K in flowing H_2 (5 ml/min) then 1 h in vacuum

Complete Cell body



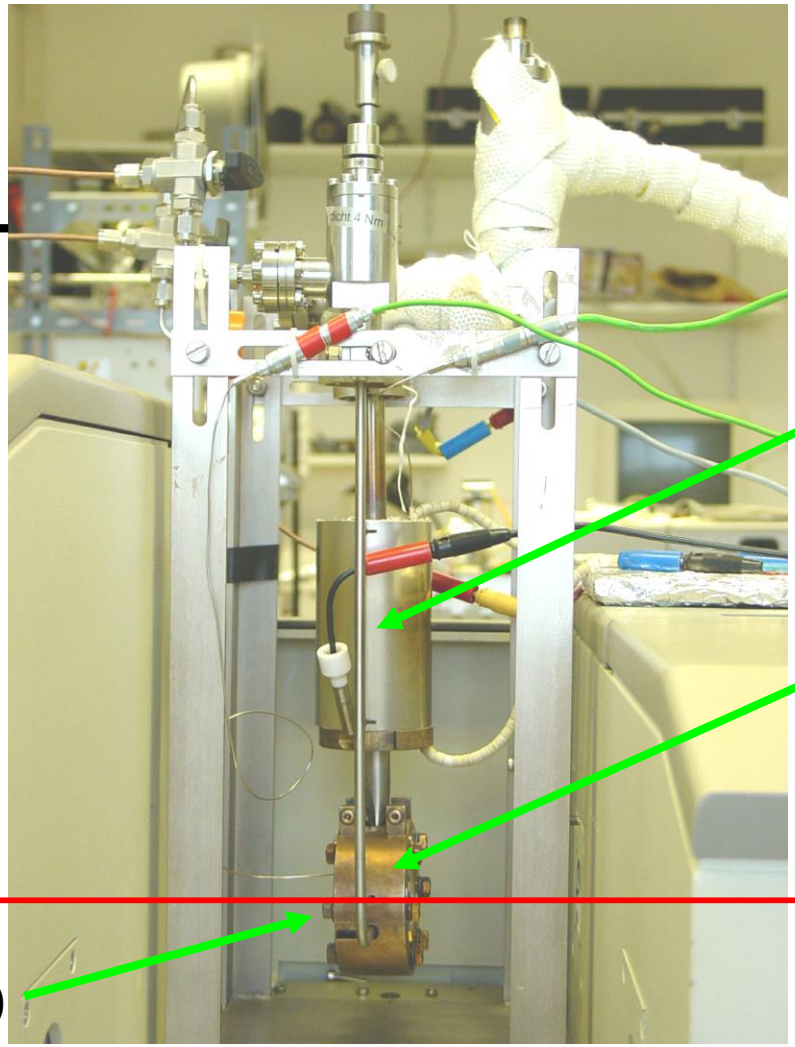
Heating mantle
T_{max} = 623 K

Thermocouple

Gas inlet

CaF_2-window in CF 35 flange

Complete Setup for Probe Molecule Adsorption and In Situ Measurements



In situ System

Gaschromatograph (Varian 3800)

Gas manifold
O_2, H_2, N_2, Feed

Gas outlet

Gas Dosing System

Dosing of gases

Pump

Activation oven (T_{max} = 550°C)

Sample: 5-30 mg/cm^2) self-supporting wafer

Cell heater (T_{max} = 350°C)

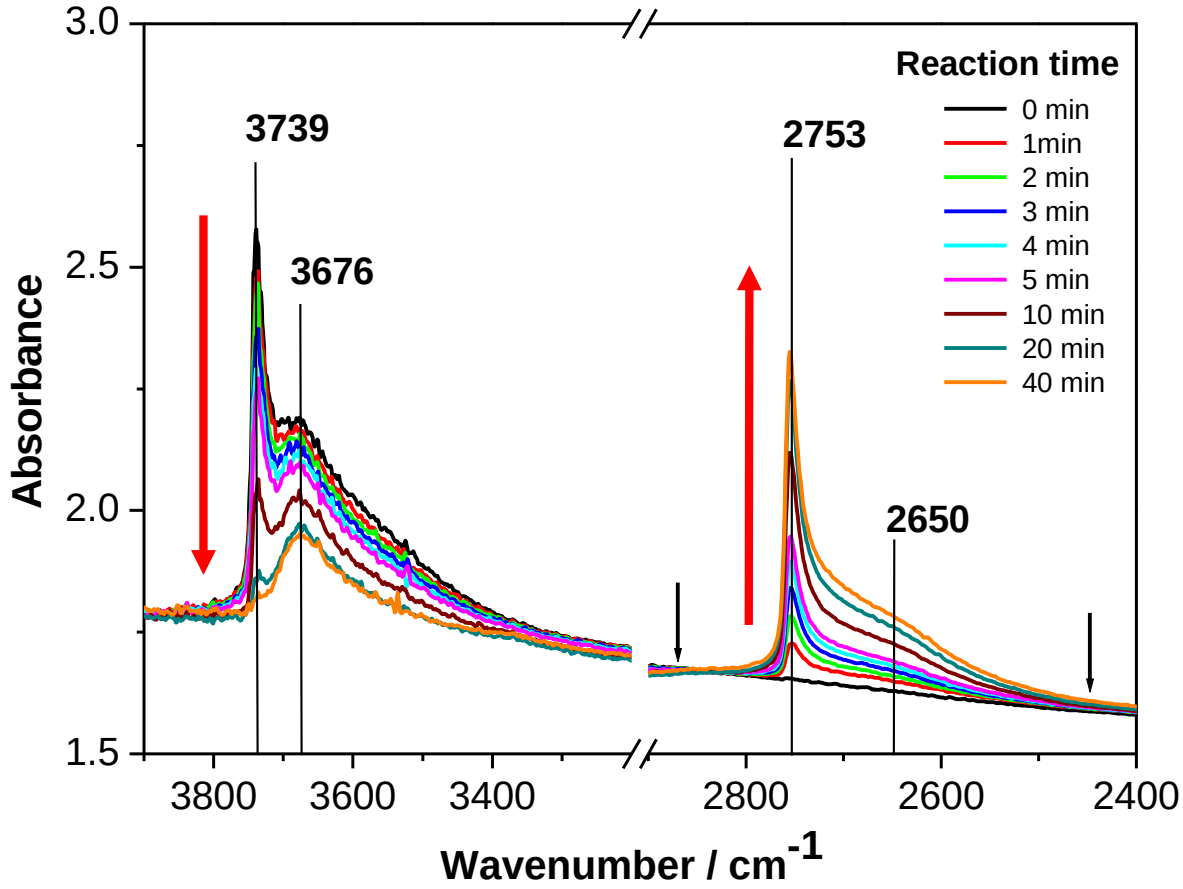
IR beam

Detector (DTGS)

CaF_2-Window (CF 35)

Spectrometer (PE 2000)

Exchange of OH groups to OD groups with D_2



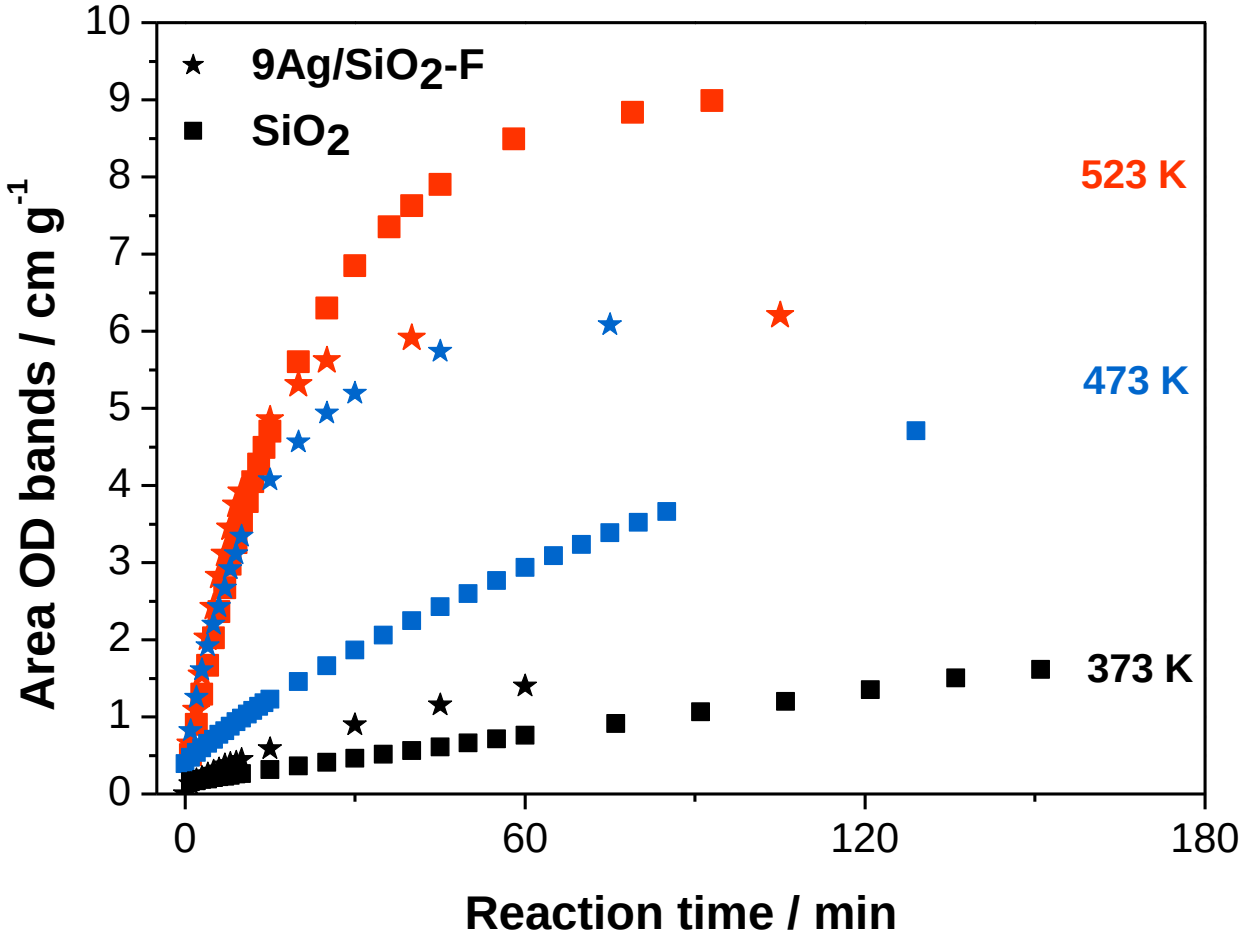
9Ag/SiO_2

523 K

100 mbar D_2

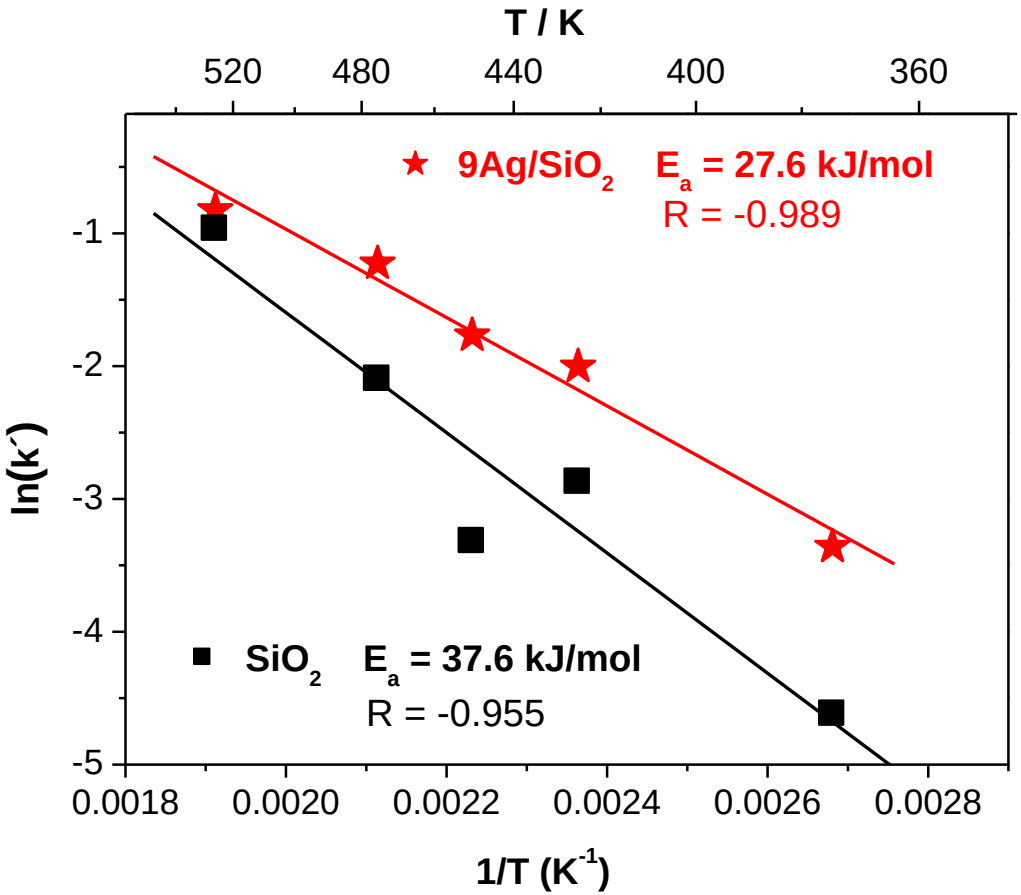
- rate of disappearance of OH bands corresponds to rate of formation of OD bands
- predominantly isolated Si-OH react

Kinetics of Exchange Reaction



❖ faster exchange with $9Ag/SiO_2$ than with pure SiO_2

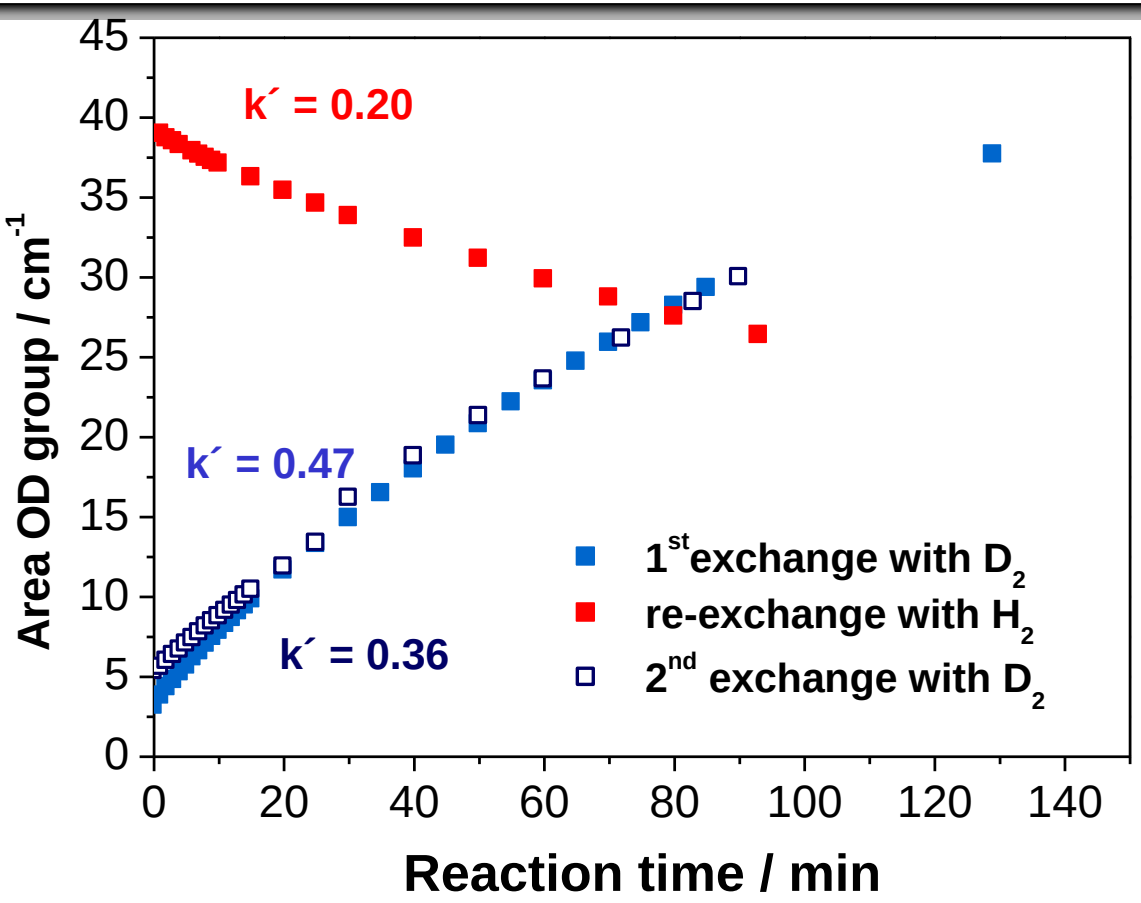
Analysis of Initial Rates: Arrhenius Plot



- $r \sim dA_{OD}/dt$
- $r = k\,[OH]^n\,[D_2]^m$
- $r_{init} = k^*$ const(s)*const = k'
- slightly lower activation energy in presence of Ag
- Ag facilitates activation of D_2

k'	9Ag/SiO$_2$-F	SiO$_2$
373 K	0.03	0.01
473 K	0.29	0.12
523 K	0.44	0.38

Kinetic Isotope Effect: SiO_2, 473 K



kinetic isotope effect:

$$\frac{k'_{OH-D_2}}{k'_{OD-H_2}} \approx 1.8 - 2.4$$

- H-D-exchange: completely reversible
- kinetic isotope effect suggests breaking of OH (OD) bond is rate determining

Summary and Outlook on Ag/SiO_2

Summary

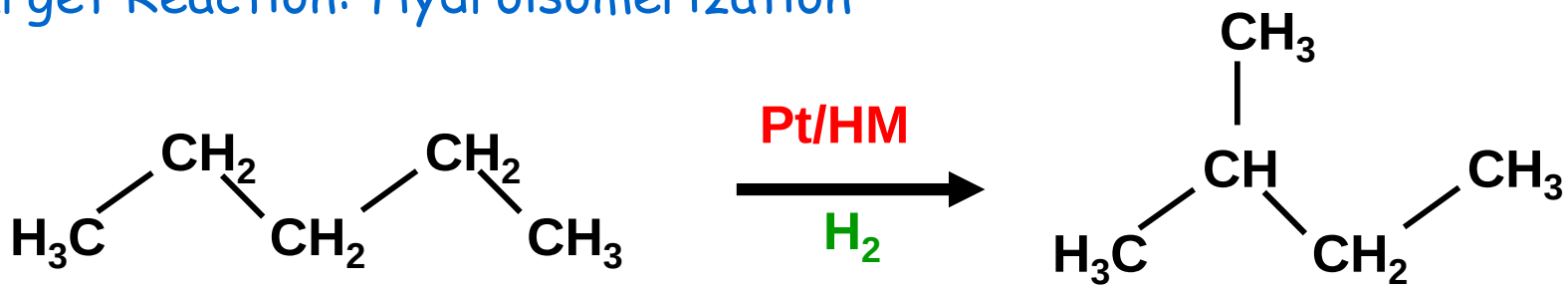
- Si-OH groups are exchanged to OD groups in D_2
- exchange reaction faster for Ag/SiO_2 than for SiO_2: Ag facilitates H_2 activation
- kinetic isotope effect

Outlook

- repeat experiment with SiO_2 after "pseudo-Ag-precipitation"
- investigate D_2 pressure dependence, compare to catalysis
- adsorb and convert acrolein

Pt/H-Mordenite Catalysts: Motivation & Strategy

Target Reaction: Hydroisomerization



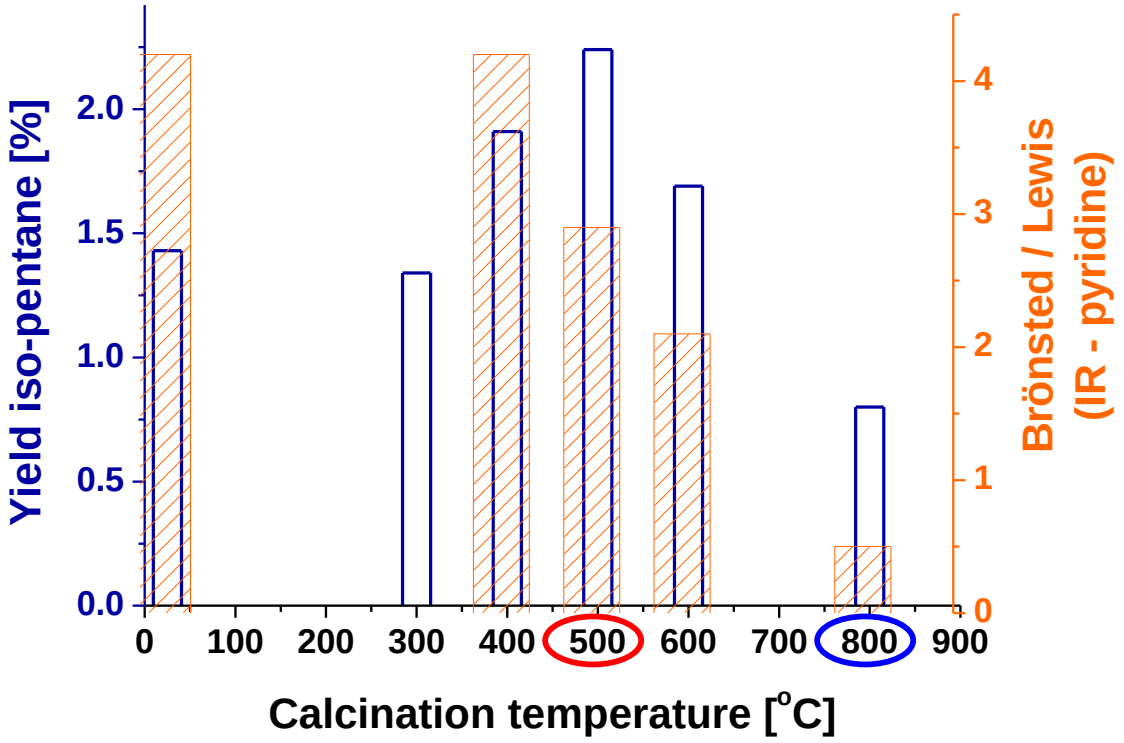
- use Pt / H-Mordenite benchmark samples to identify suitable procedures for catalyst evaluation
- part of multigroup BMBF-funded research on combinatorial catalysis
- final goal: apply identified methods in parallelized fashion

Strategy

- probe acid sites and metal sites

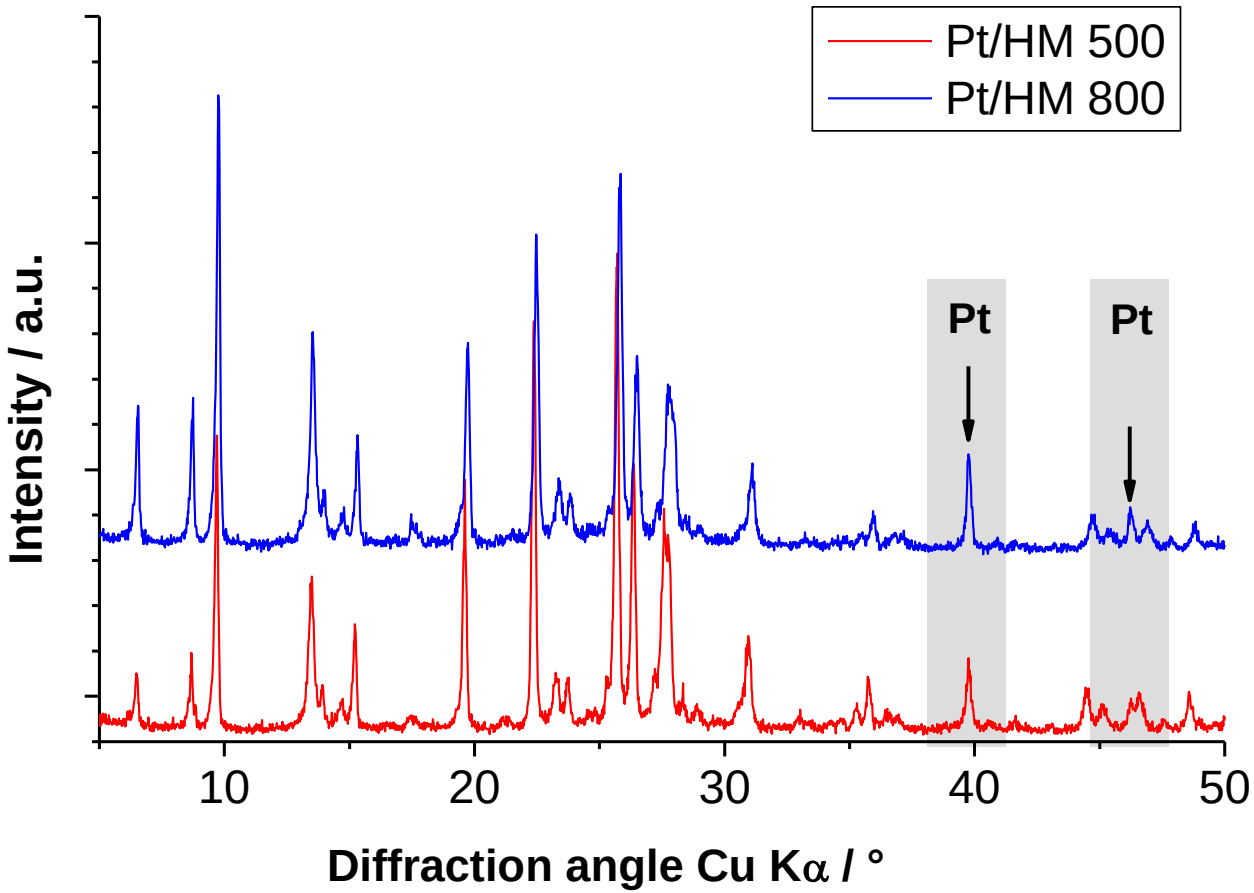
Pt/Mordenite Catalyst Sample Selection

H-Mordenite, from Na-Mordenite through ion exchange impregnated with $(NH_4)_2PtCl_6$, dried at RT, calcined



Samples: Prof. F. Schüth, Mülheim; Catalytic tests: Prof. W.A. Maier, Saarbrücken
Acidity: Prof. J.A. Lercher, München

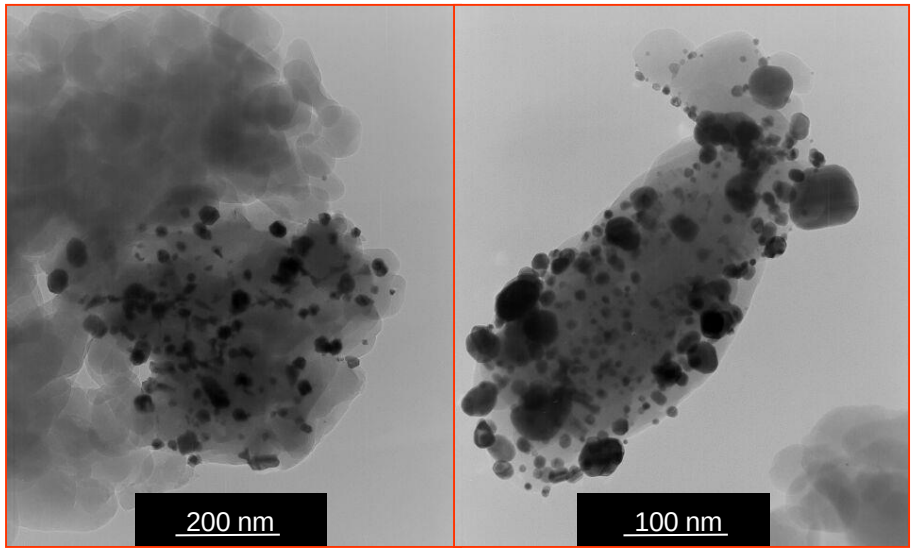
XRD: Pt/HM 500 vs. Pt/HM 800



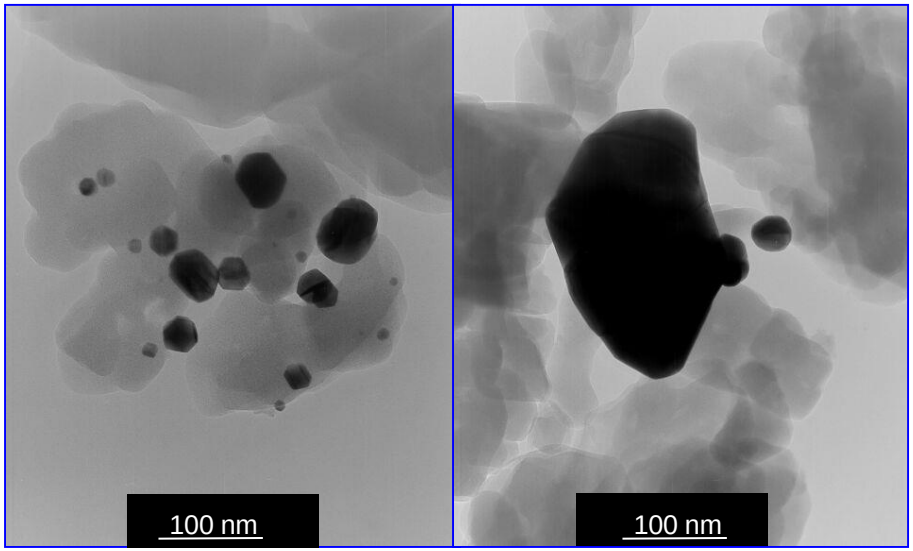
- Pt content ca. 1 wt%
- crystalline phases: Mordenite and Pt

TEM: Pt/HM 500 and Pt/HM 800

Pt/HM calcined at 500 °C



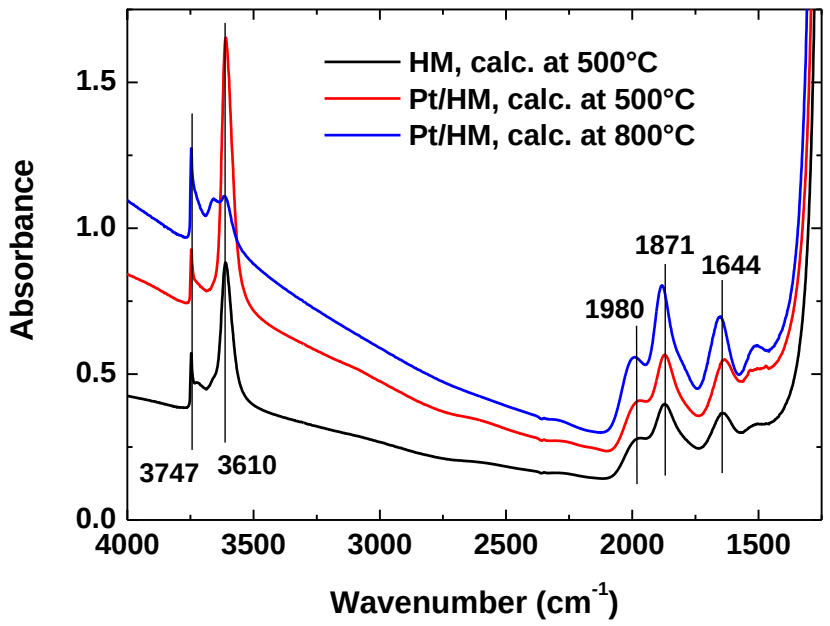
Pt/HM calcined at 800 °C

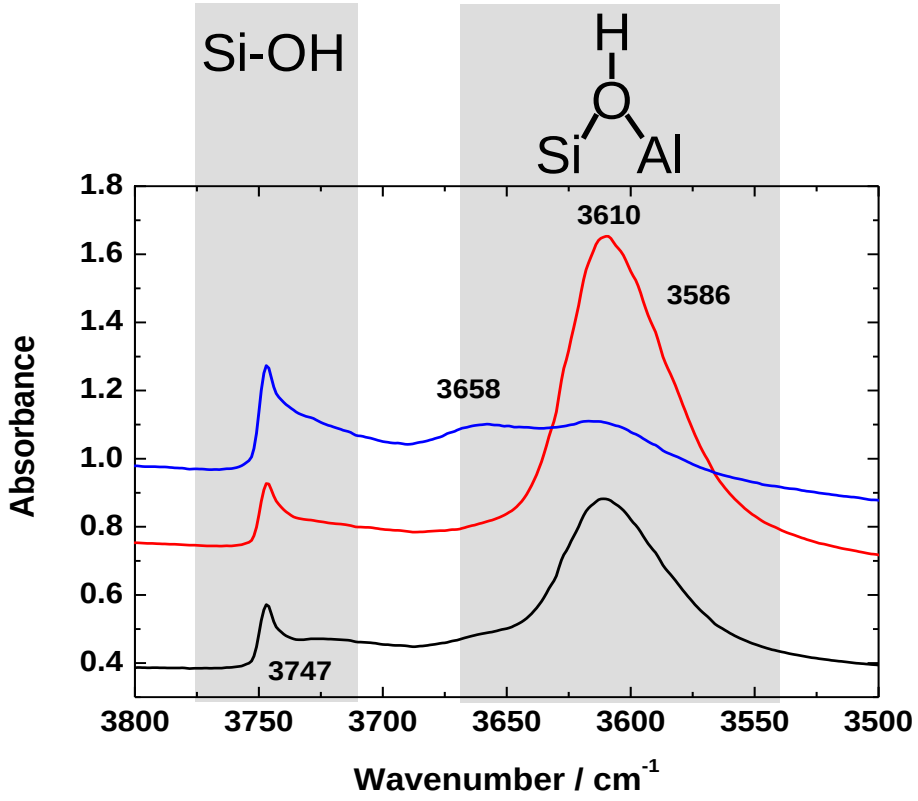


- accumulation of Pt
- large Pt particles, outside zeolite framework

IR Spectra of Pt/HM & HM

act. 450°C vacuum





- 3610 cm^{-1}: high frequency OH-group in main channel

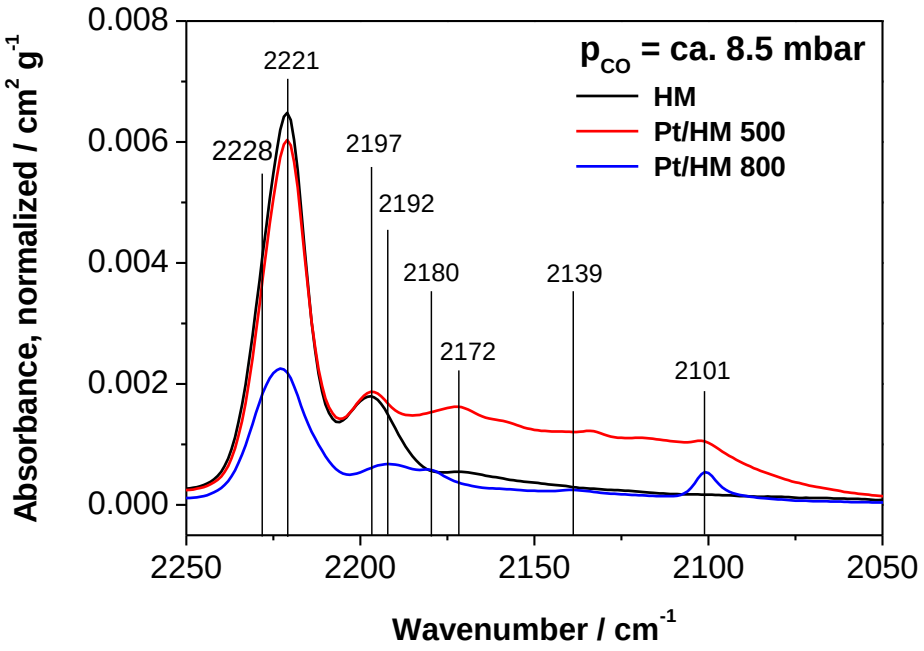
  3586 cm^{-1}: low frequency OH-group in side pocket

  Zecchina et al., Chem. Soc. Rev., (1996) 187

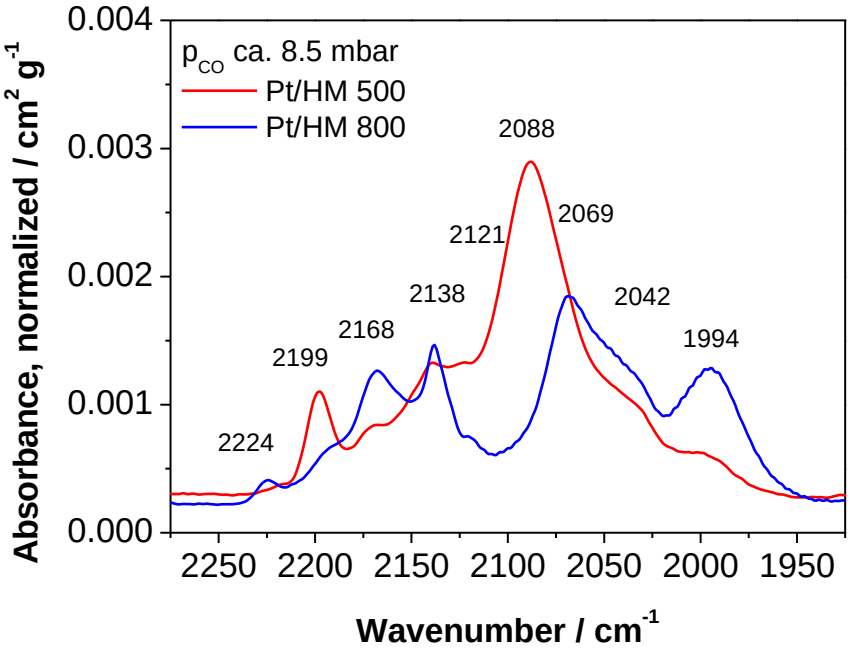
- calcination at 800°C affects OH groups

IR-Spectroscopy: Adsorption of CO at RT

act. 450°C vacuum

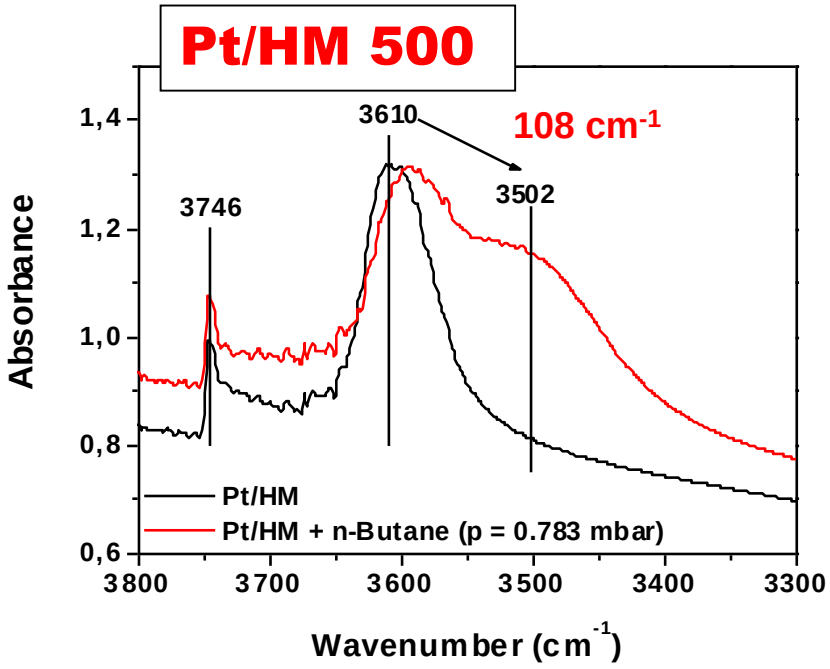


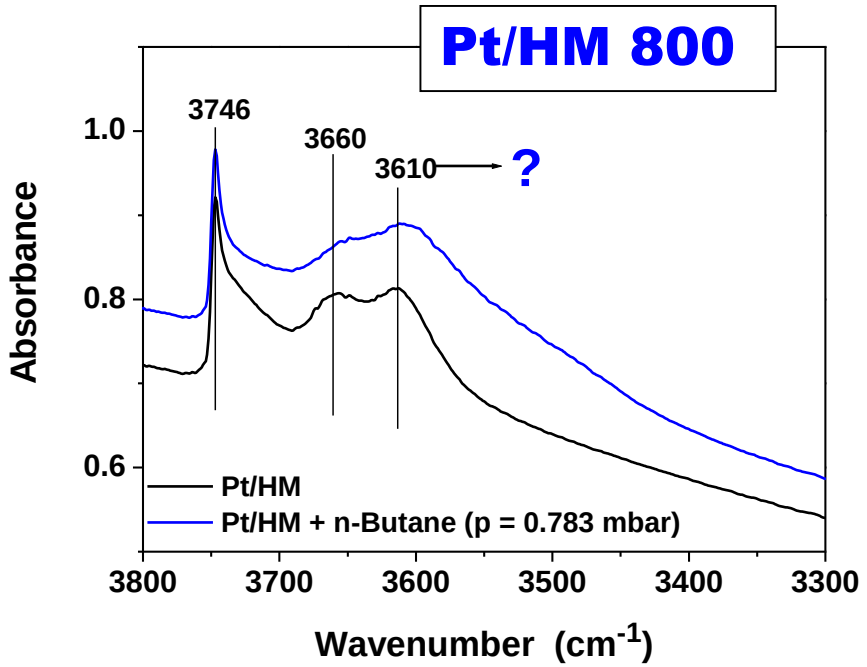
act. 375°C H_2



- 2221, 2197: Al^{3+} Lewis acid sites;
- > 2100 cm^{-1}: Pt^{n+}, below 2100 cm^{-1}: Pt^0
- 2110 cm^{-1}: Pt^{2+}-CO
- samples are different, difficult to correlate sites and activity

Adsorption of *n*-Butane at RT

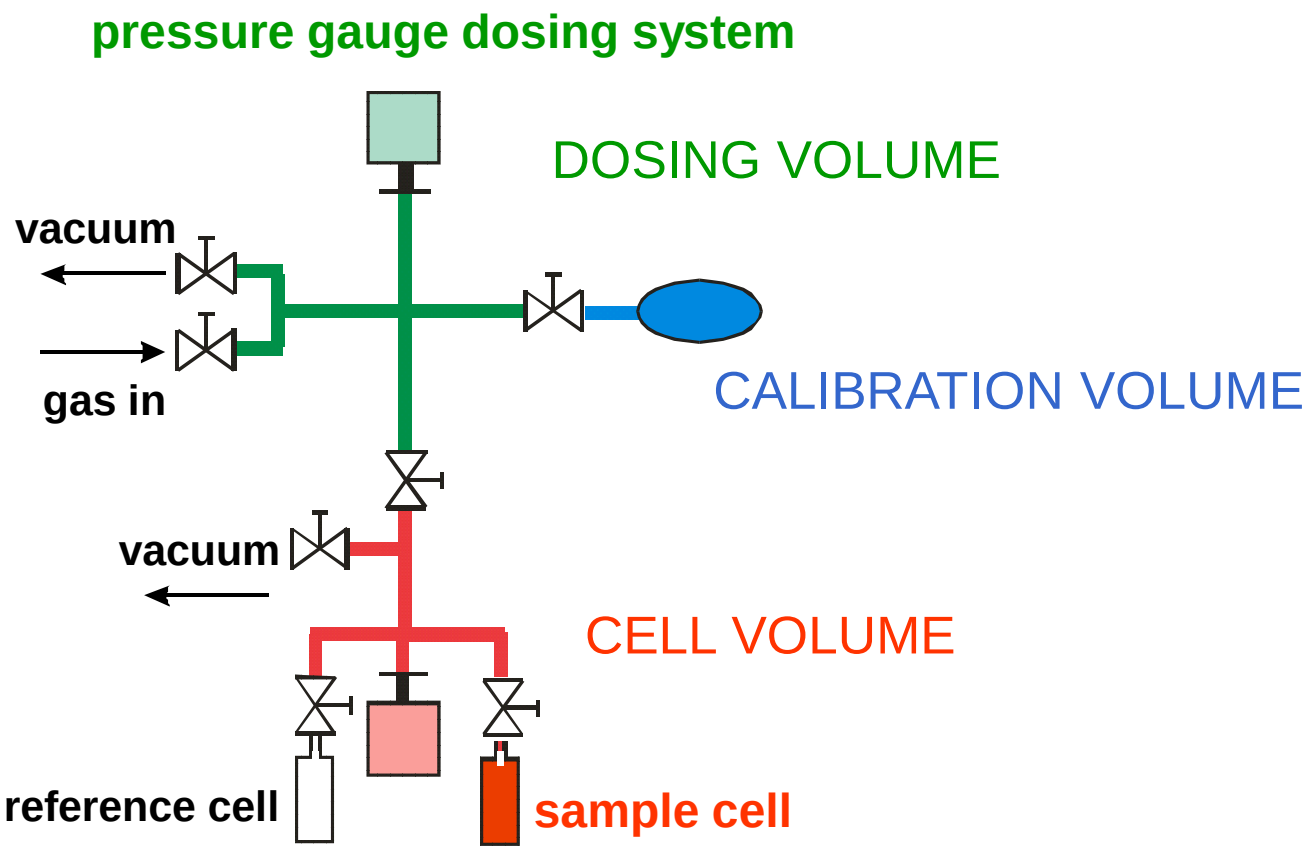




- *n*-butane (0.8 mbar) interacts with acidic OH groups
- Pt/HM 500: $\Delta\nu$(OH) ≈ -110 cm^{-1}, no measurable shift for Pt/HM 800
- shift of HM OH groups upon adsorption of CO: -294 cm^{-1}

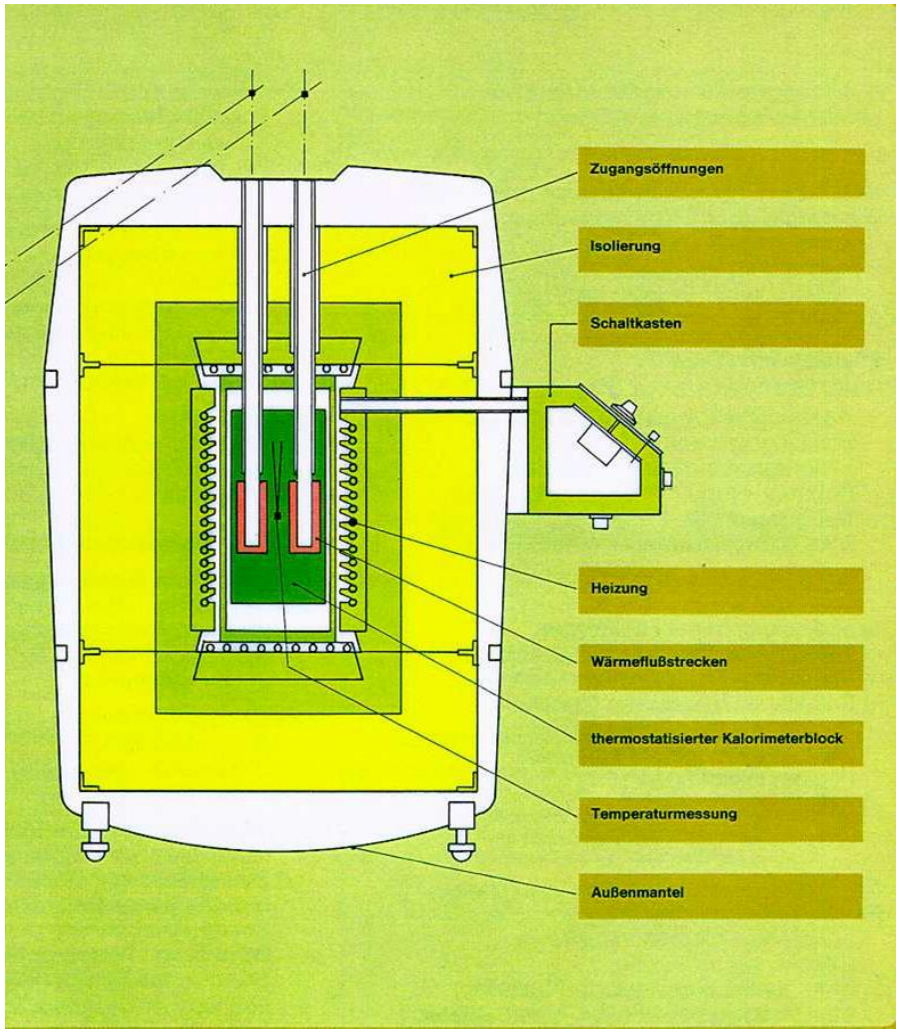
A. Zecchina, C. Otero Arean, Chem. Soc. Rev., (1996) 187

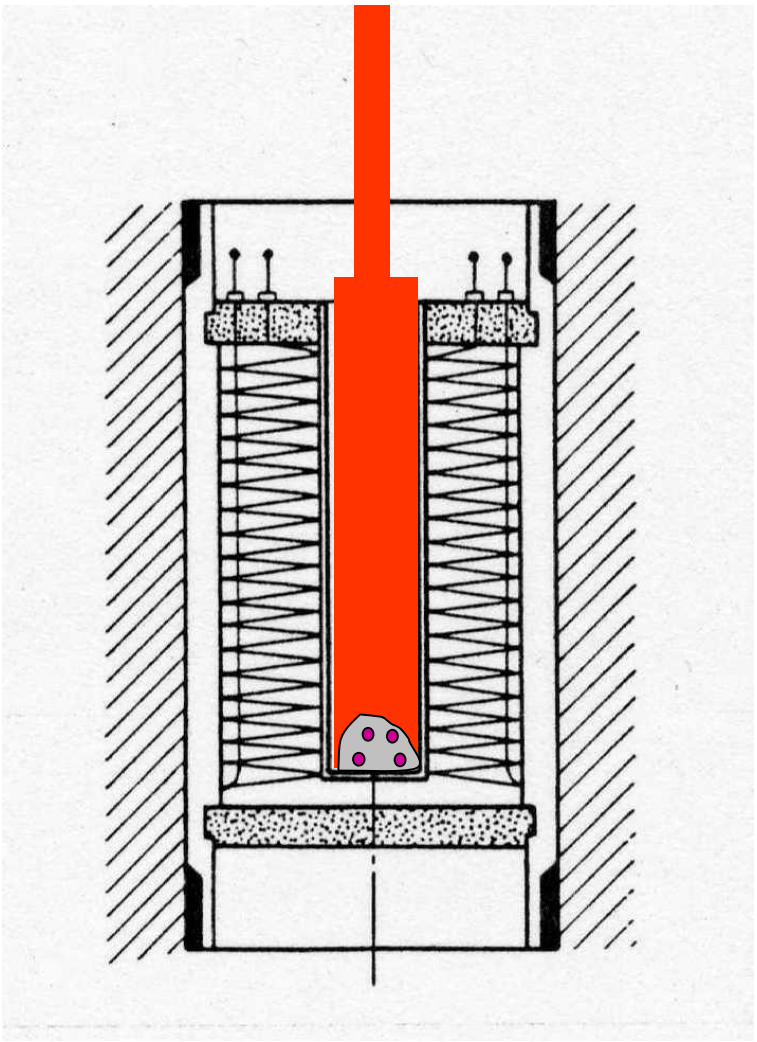
Calorimeter - Gas Dosing System



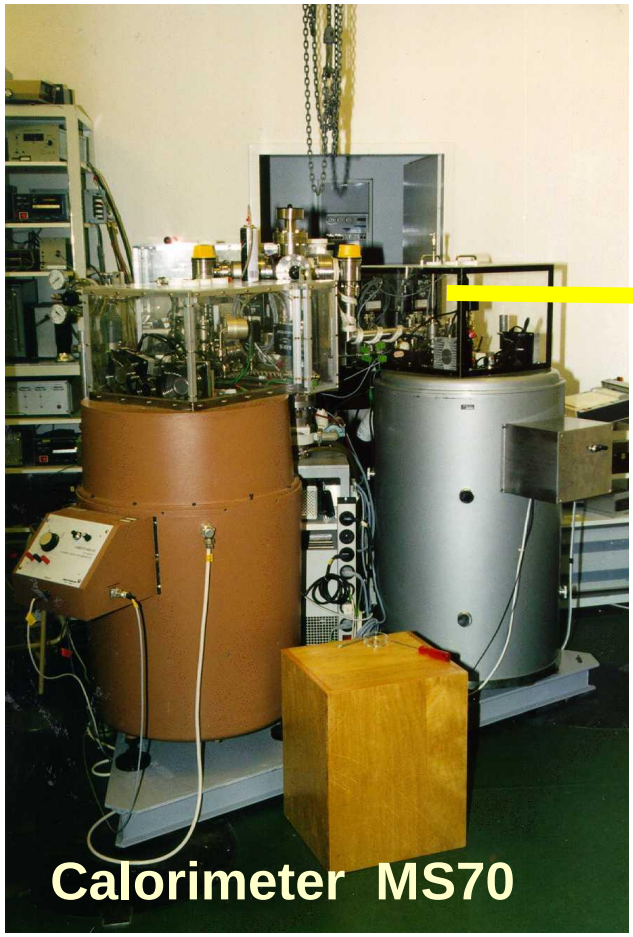
- dosing volume pressure difference gives number of molecules introduced
- measure equilibrium pressure in cell, calculate adsorbed amount

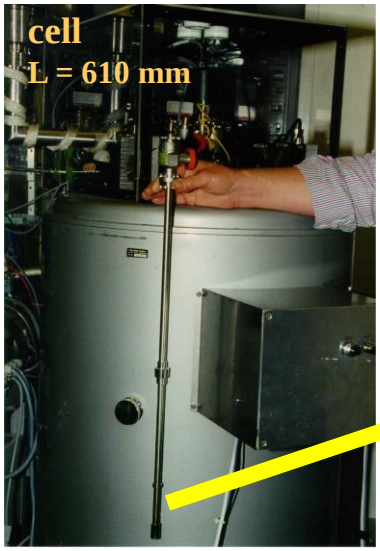
The Calvet Calorimeter



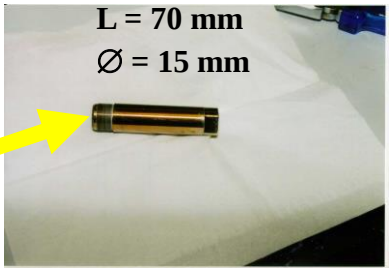


Microcalorimeter & Volumetric System



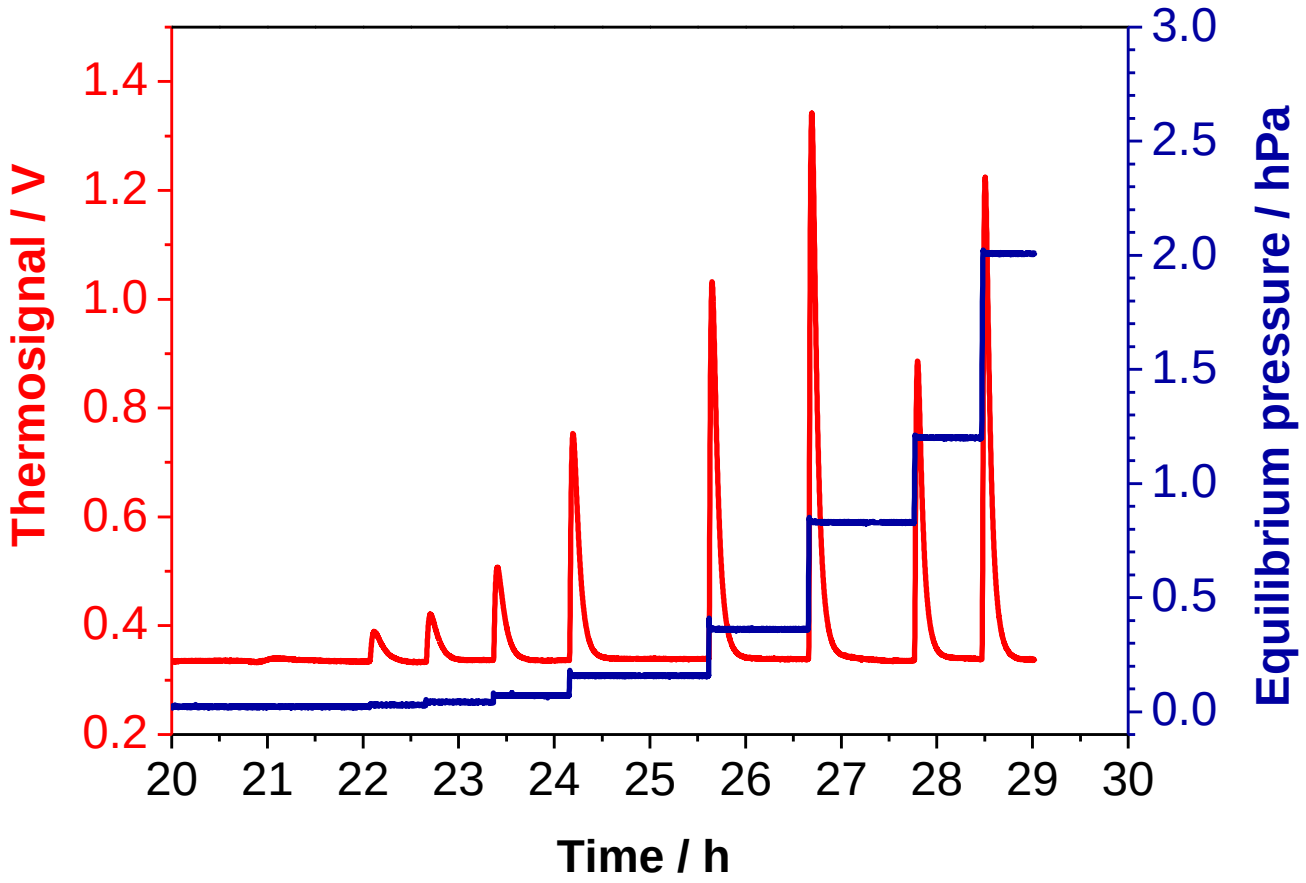


Sampleholder



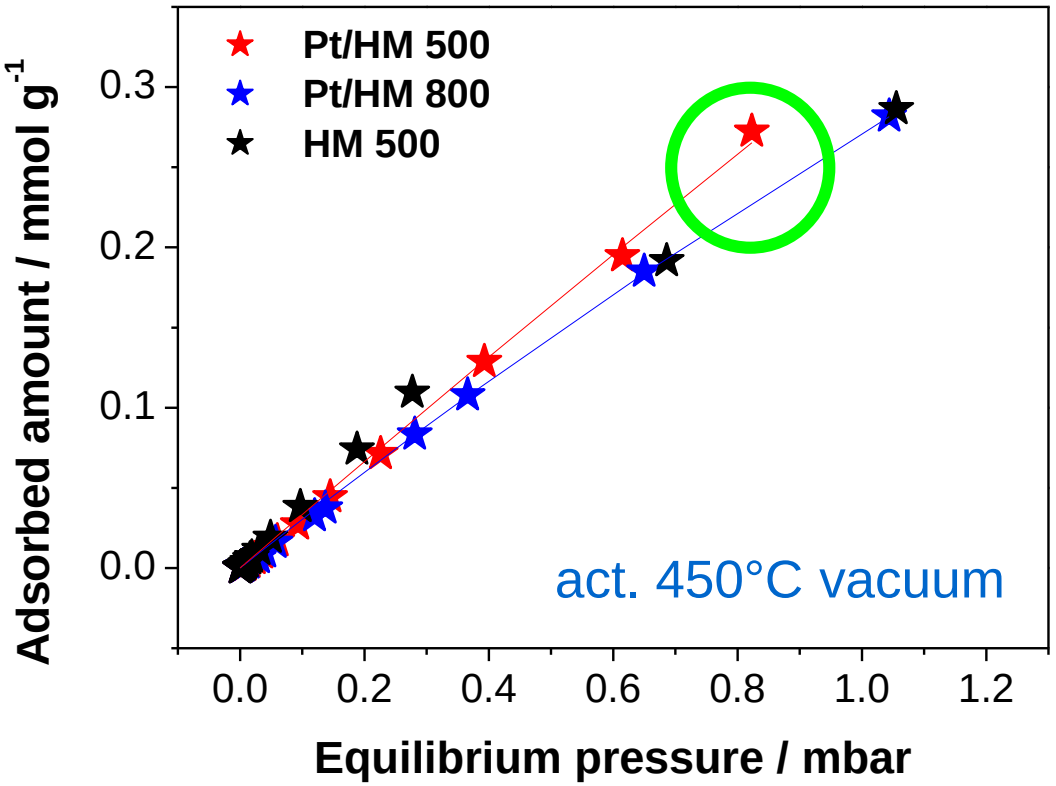
E.N. Coker, H.G. Karge,
Rev. Sci. Instrumen. 68 (1997) 4521

Adsorption Calorimetry Raw Data: Equilibrium Pressure and Thermosignal



- generation of adsorption isotherm
- differential heats of adsorption

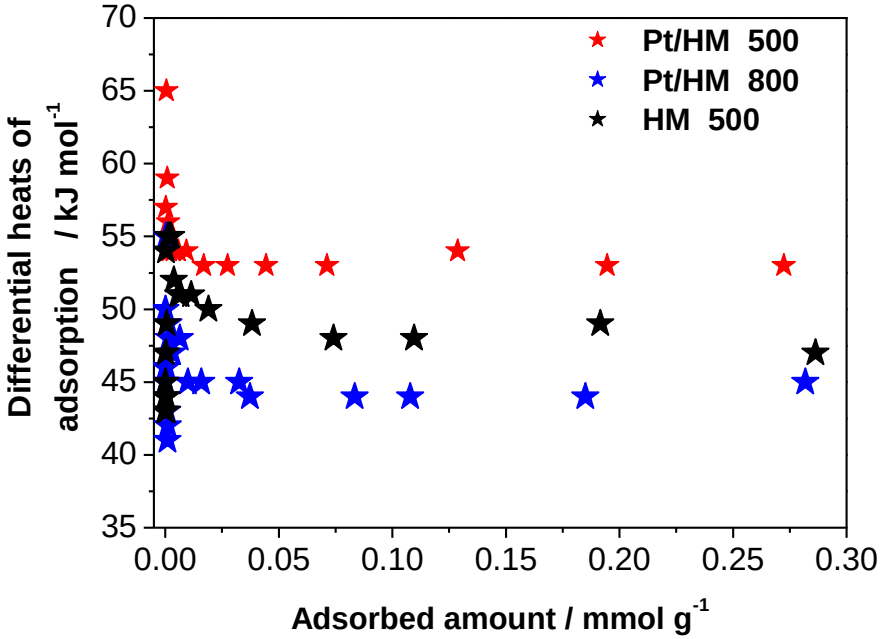
Adsorption Isotherm of *n*-Butane at 40°C

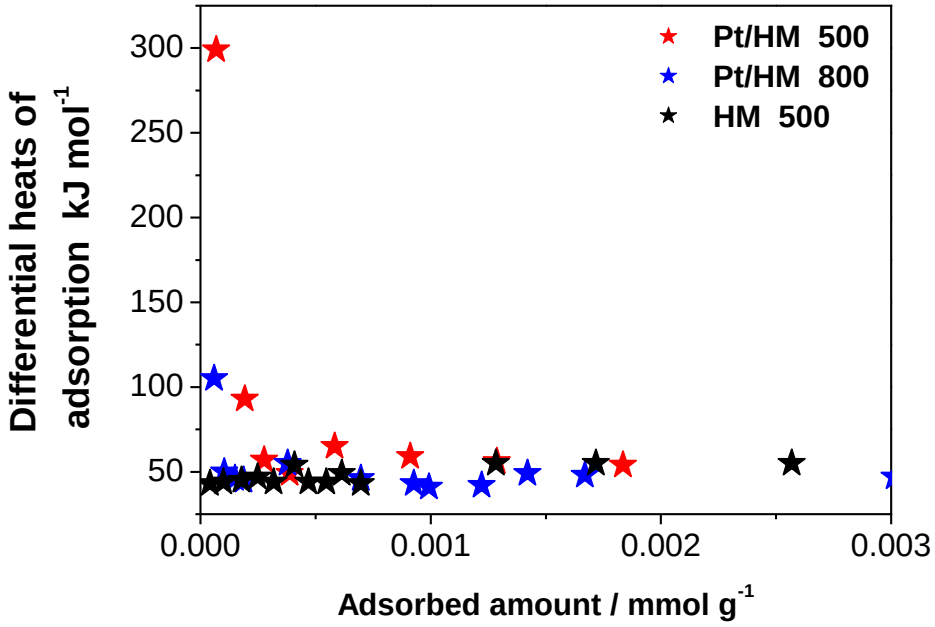


- at p =0.8 mbar Pt/HM 500 adsorbs about 40 µmol/g more *n*-butane than Pt/HM 800
- difference in number of sites is only one factor

Differential Heats of Adsorption of *n*-Butane

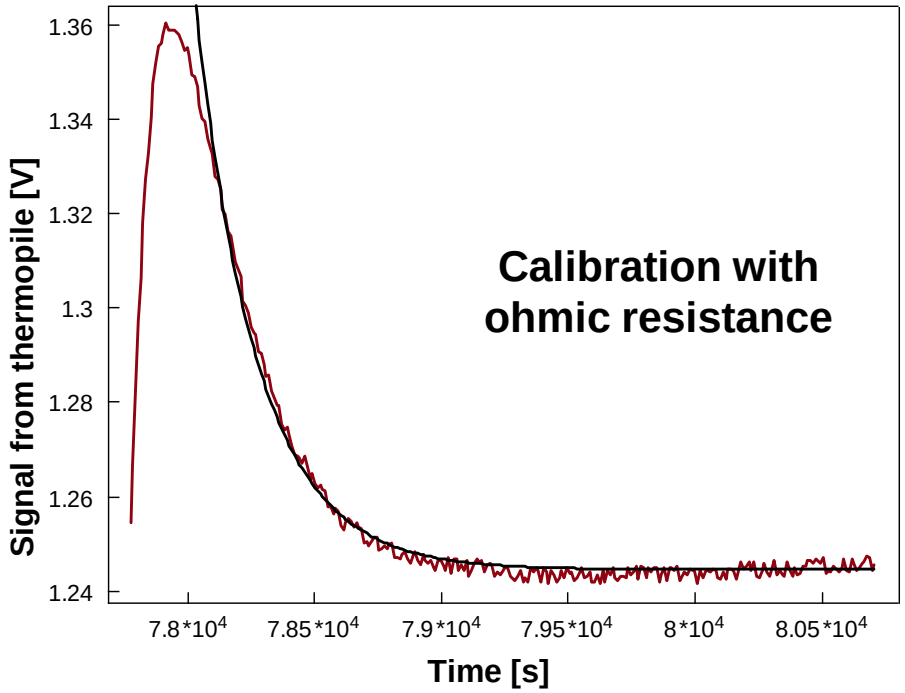
act. 450°C vacuum





- Majority of sites on individual sample equivalent (high coverage)
- Slightly higher average for Pt/HM 500 than for Pt/HM 800
- Pt containing catalyst exhibit high initial heats of adsorption (low coverage)

Calorimetry: Time Constant



Fit equation:

$$y = y_0 + A \cdot exp\left(-\frac{x - x_0}{\tau}\right)$$

y – signal from thermopile [V]

x – time [s]

y_0 – y offset, baseline height [V]

A – peak height [V]

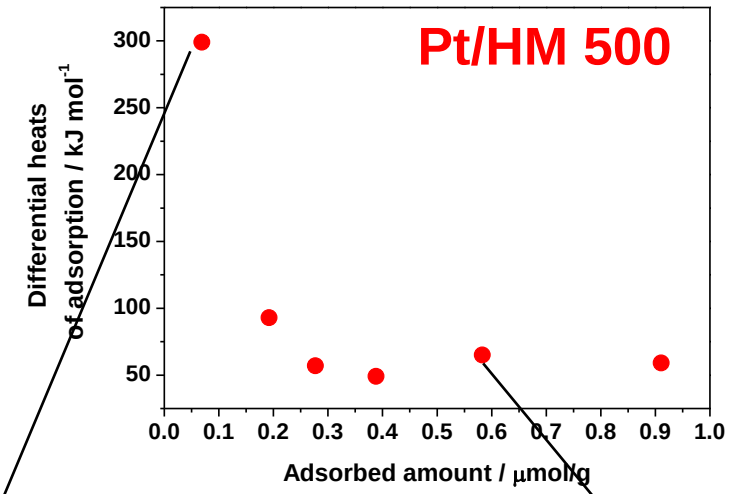
x_0 – peak position on time scale [s]

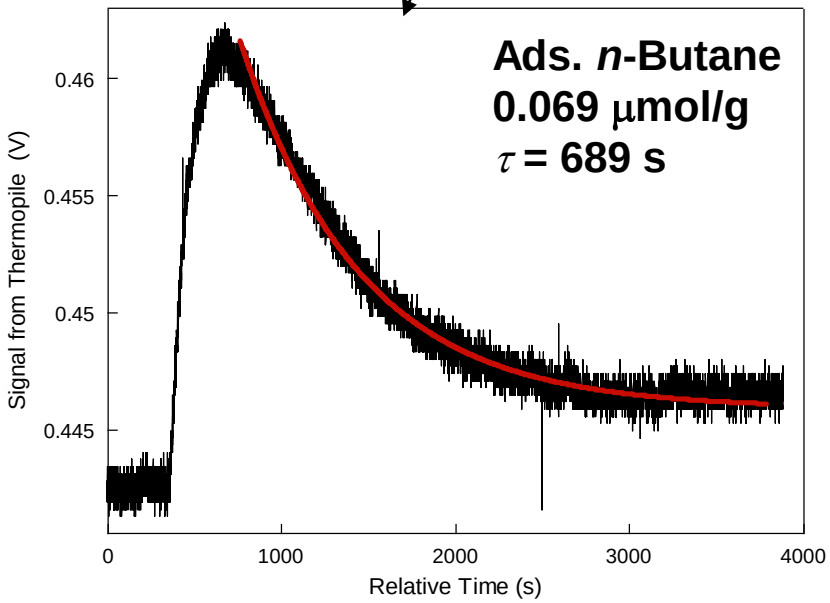
τ – time constant [s]

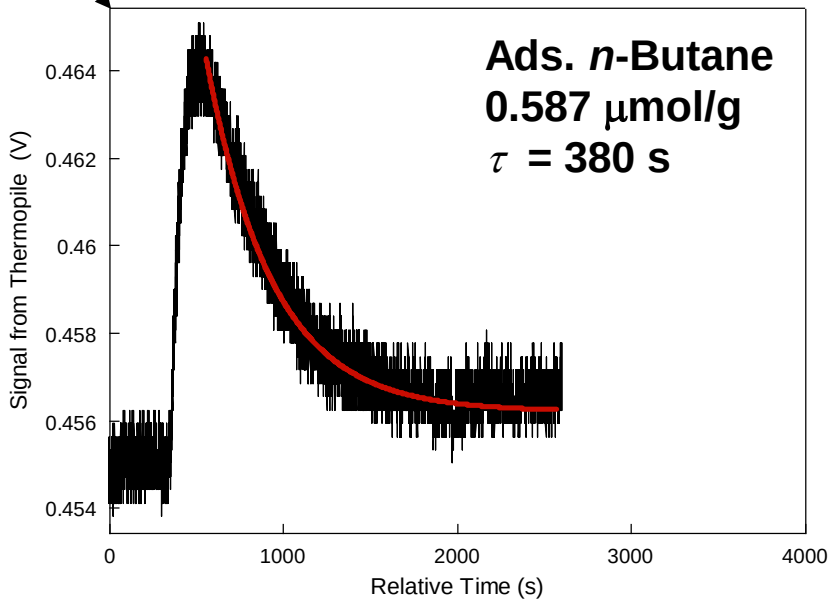
- slower or faster decay of signal indicates endo- or exothermic secondary reactions after adsorption

  C. Pluntke, G. Wedler, G. Rau, Surf. Sci. 134 (1983) 145-160

Correlation of Heats and Signal Decay for Interaction of Pt/HM 500 with *n*-Butane





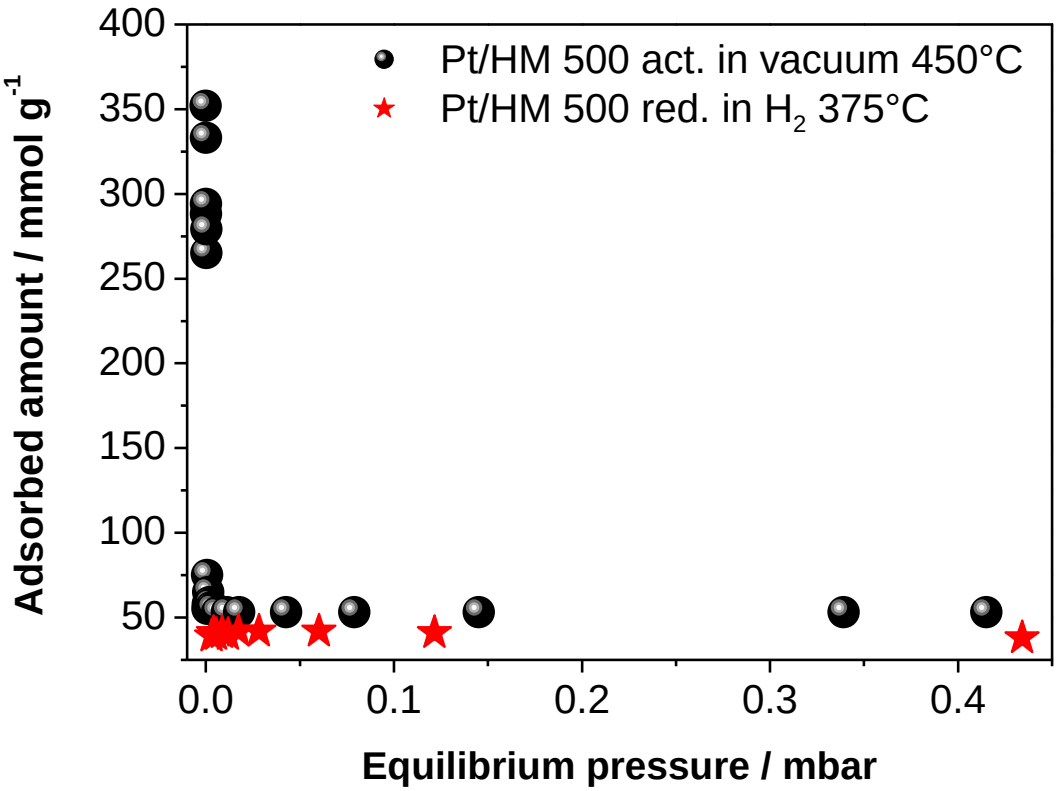


Analysis of Heat Signal Shape

Sample	Adsorbed amount n-Butane [μmol/g]	Time constant [s]
Pt/HM 500°C	0.069 0.587	689 380
Pt/HM 800°C	0.06 0.697	442 404
HM 500°C	0.099 0.469	260 288
ohmic resistance	–	245 260

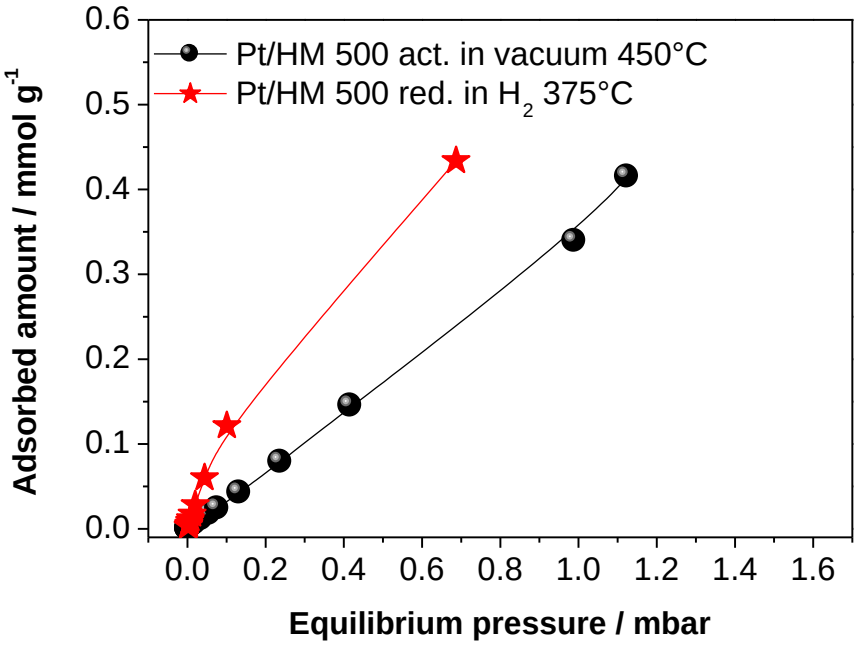
- Pt/HM catalysts produce a slow signal decay; indicating secondary reactions after the adsorption

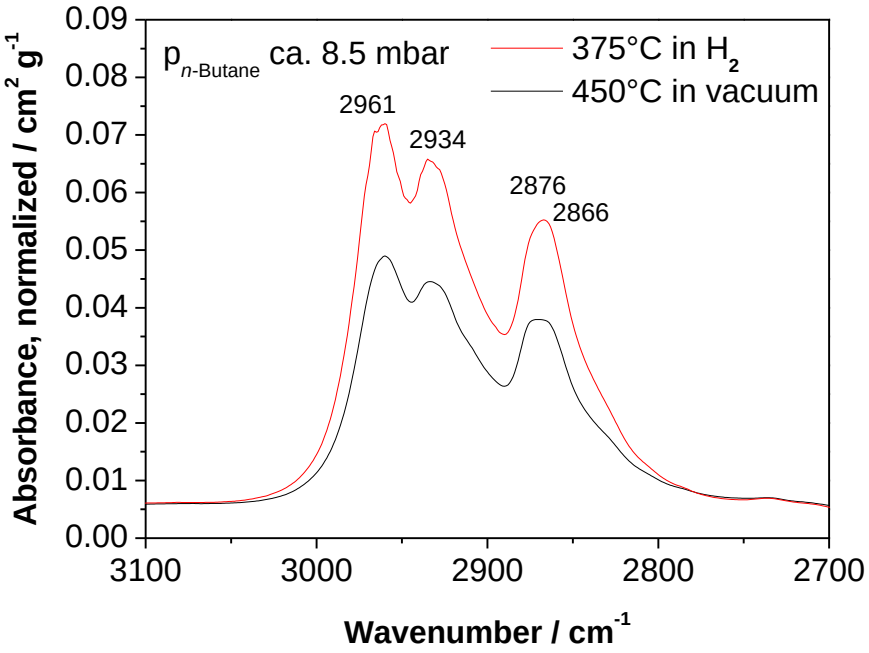
Influence of Pretreatment: Heats of Adsorption



- reduced sample: only one type of sites
- initial high heats: reduction of Pt through *n*-butane?

Influence of Pretreatment: Adsorbed Amount





- activation temperature and atmosphere determine number of sites

Conclusions

Combination of IR Spectroscopy & Calorimetry

- identification of type and strength of acid sites and valence of metal sites by using two methods and two probes (CO and *n*-butane)
- adsorption calorimetry: secondary reactions may be detected

Pt/H-Mordenite

- Pt not ideally dispersed
- partial destruction of OH-groups through 800°C calcination
- interaction with *n*-butane mostly through OH-groups, weaker for sample calcined at 800 than at 500°C
- hypothesis: *n*-butane reduces Pt^{n+} (activation in vacuum)

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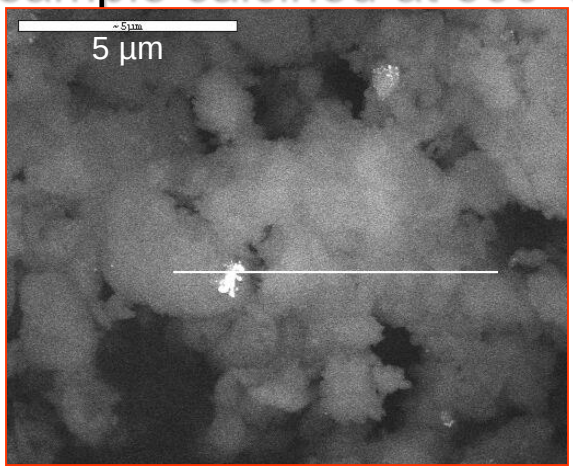
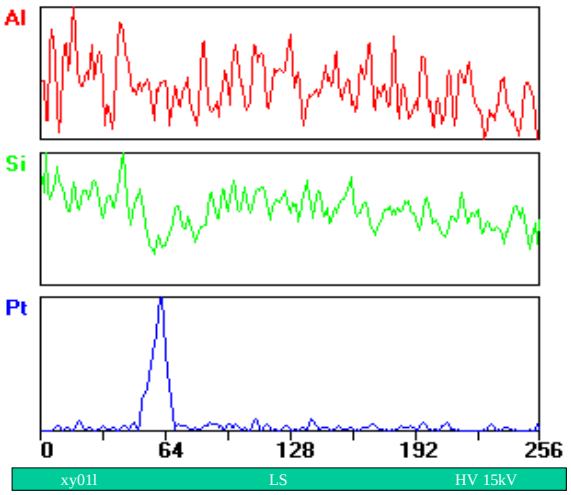
MPG

SEM/EDX: Pt/HM 500 and Pt/HM 800

sample calcined at 500°C

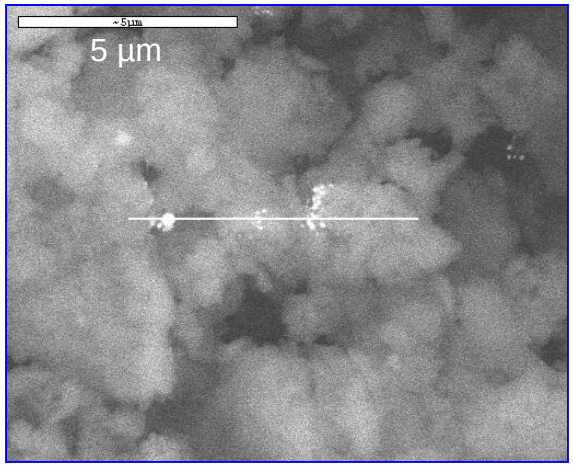


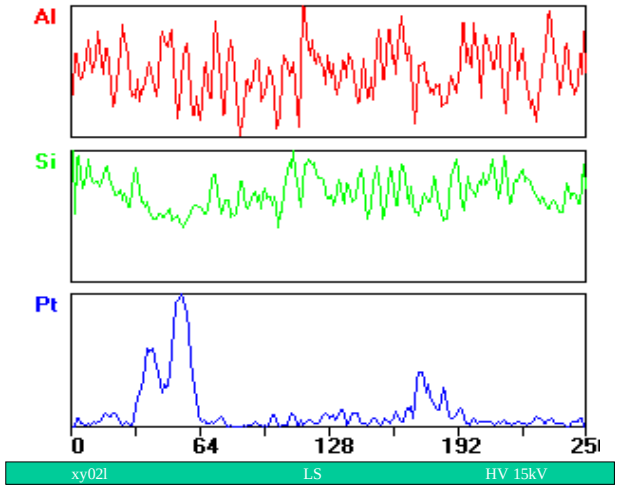


The sintered Pt particles exhibit irregular shapes and sizes (ca. 0.05 to 20 µm).

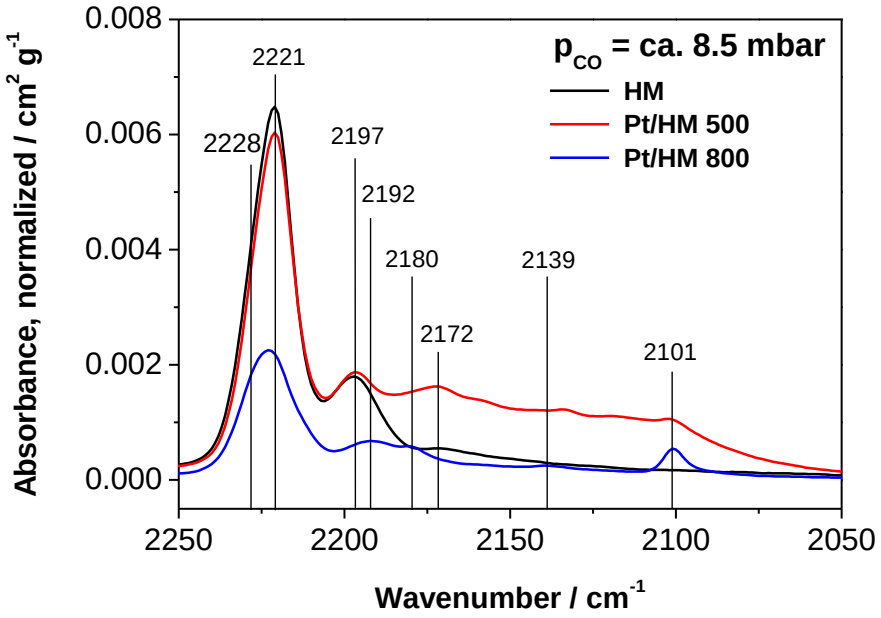
No Pt can be detected within the zeolite channels by line scan.

sample calcined at 800°C





IR-Spectroscopy: Adsorption of CO at RT



Sample	CO adsorbed on:	ν (CO) in cm^{-1}
Pt/HM 500°C	Al^{3+} oct. Al^{3+} oct. nonframework Al Pt	2171 2165 2222, 2196 2110, 2101
Pt/HM 800°C	Silanol (OH) nonframework Al Pt	2138 2222, 2192 2101
HM	Al^{3+} oct. nonframework Al	2171(slight) 2222, 2196

CO adsorption at RT
on Lewis acid and on metal (Pt) sites

Reference:
A. Zecchina, *J. Catal.*, 107 (1987) 244-247
Konigsberger et al., *Topics in Catal.*, 15 (2001) 35

Reproducibility of Adsorption Calorimetry