Heterogeneous catalysis

Lecture 6

Catalysts characterization - continuation

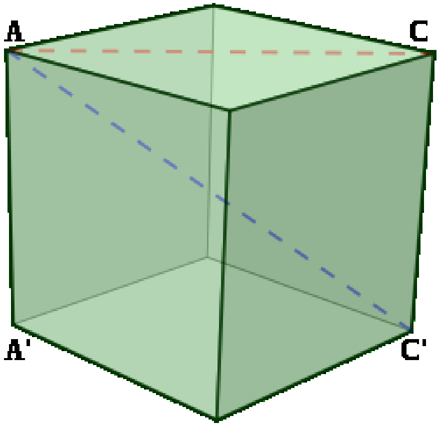
Catalyst characterization

- Outline
  - Solid state NMR techniques
  - **Hydrophilicity vs. Hydrophobicity meas**
    - **Water sorption**
    - **Dynamic water sorption**
    - **Inverse gas chromatography**
    - **Microcallorimetry**
    - **Quartz crystal microbalance**
  - In situ and operando techniques

Solid state NMR techniques

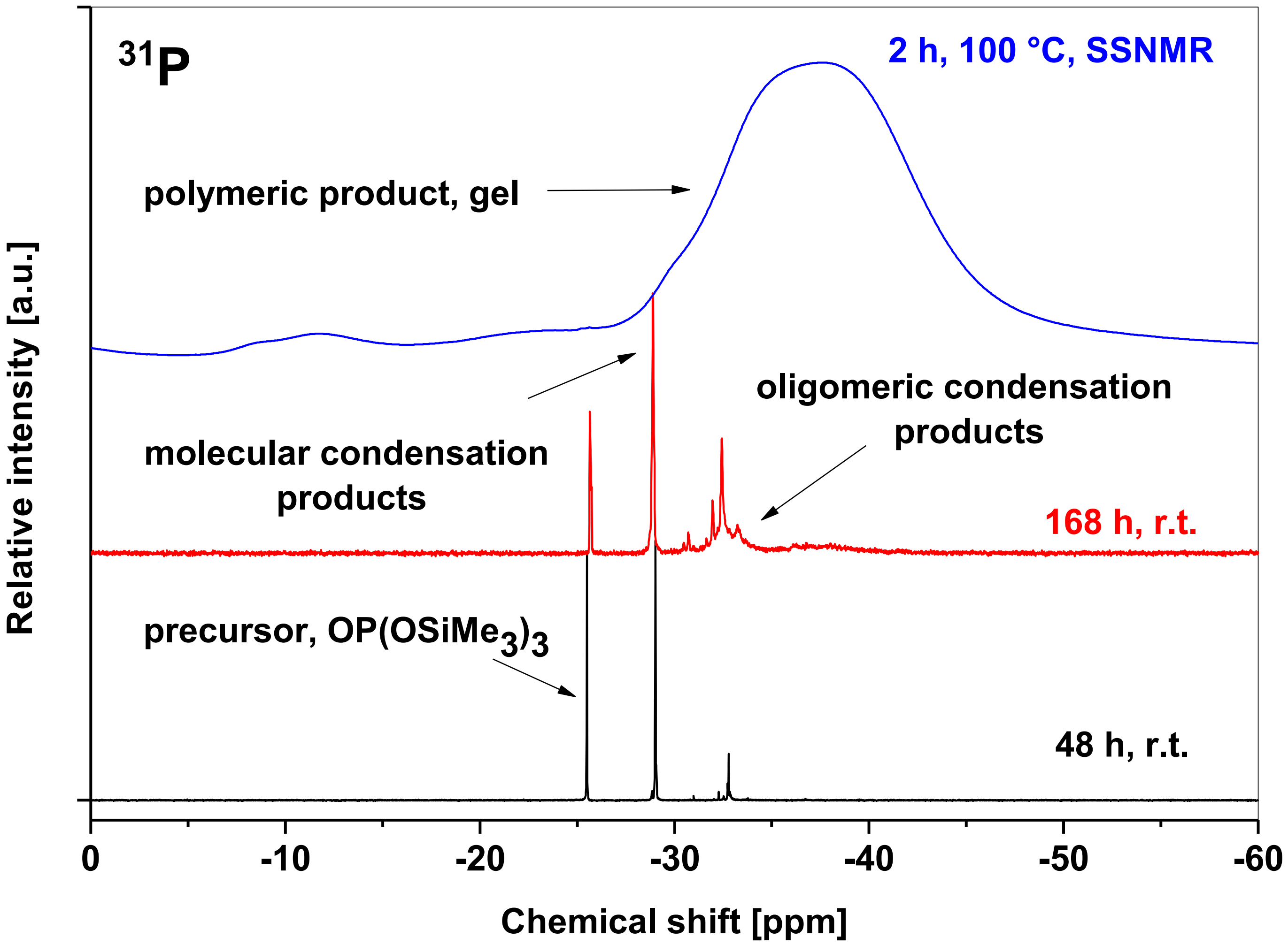
- Magic angle spinning (MAS)
- Multiple quantum experiments (MQ)
- Dynamic nuclear polarization (DNP)

Solid state NMR techniques

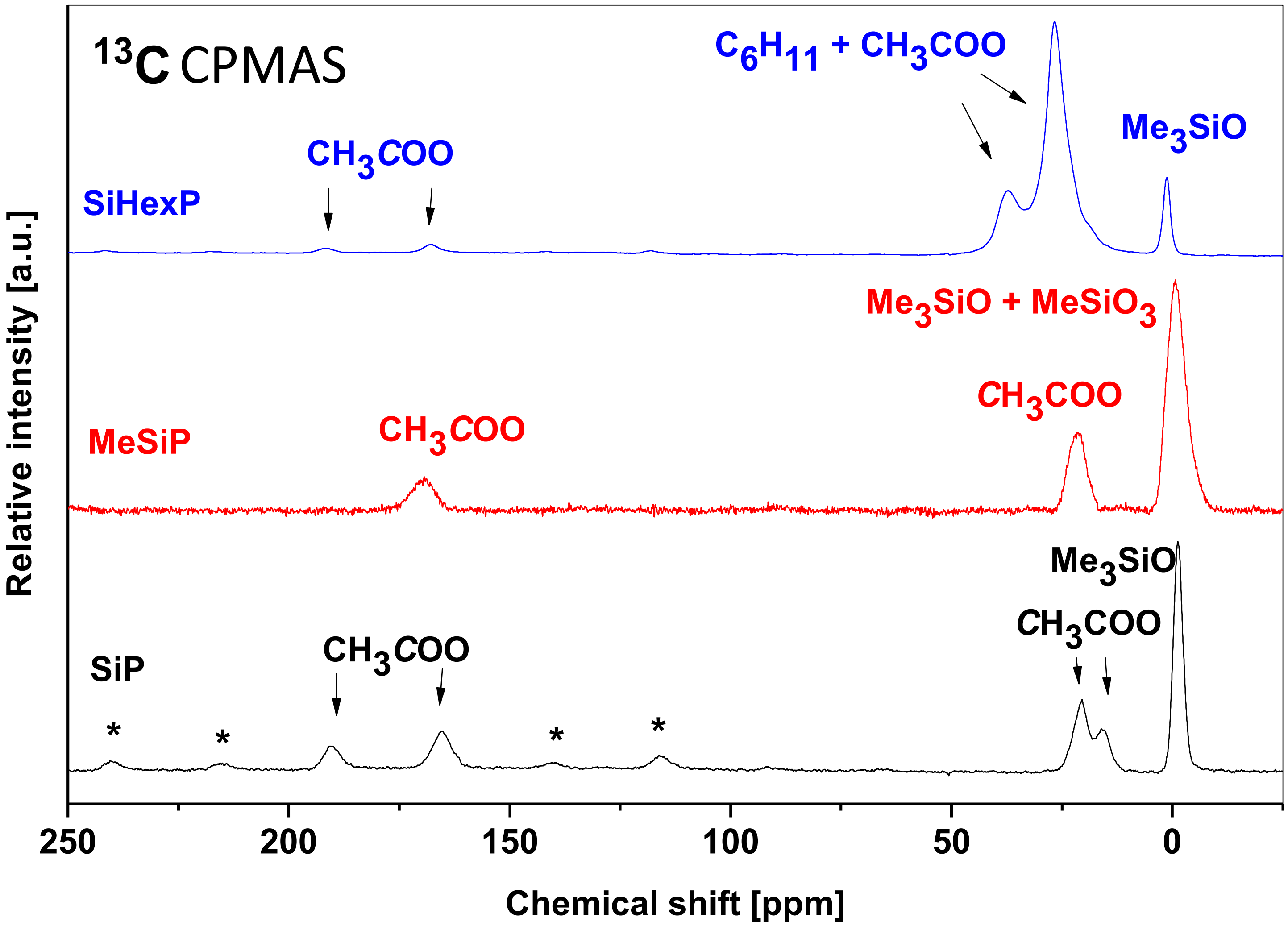


- Magic angle spinning (MAS)
  - 54.74 °
  - Spinning averages dipolar interaction, chemical shift anisotropy, and quadrupolar interaction
  - "Residues" of these interactions are observed as spinning sidebands
  - Static and double rotation NMR possible

Solid state NMR techniques

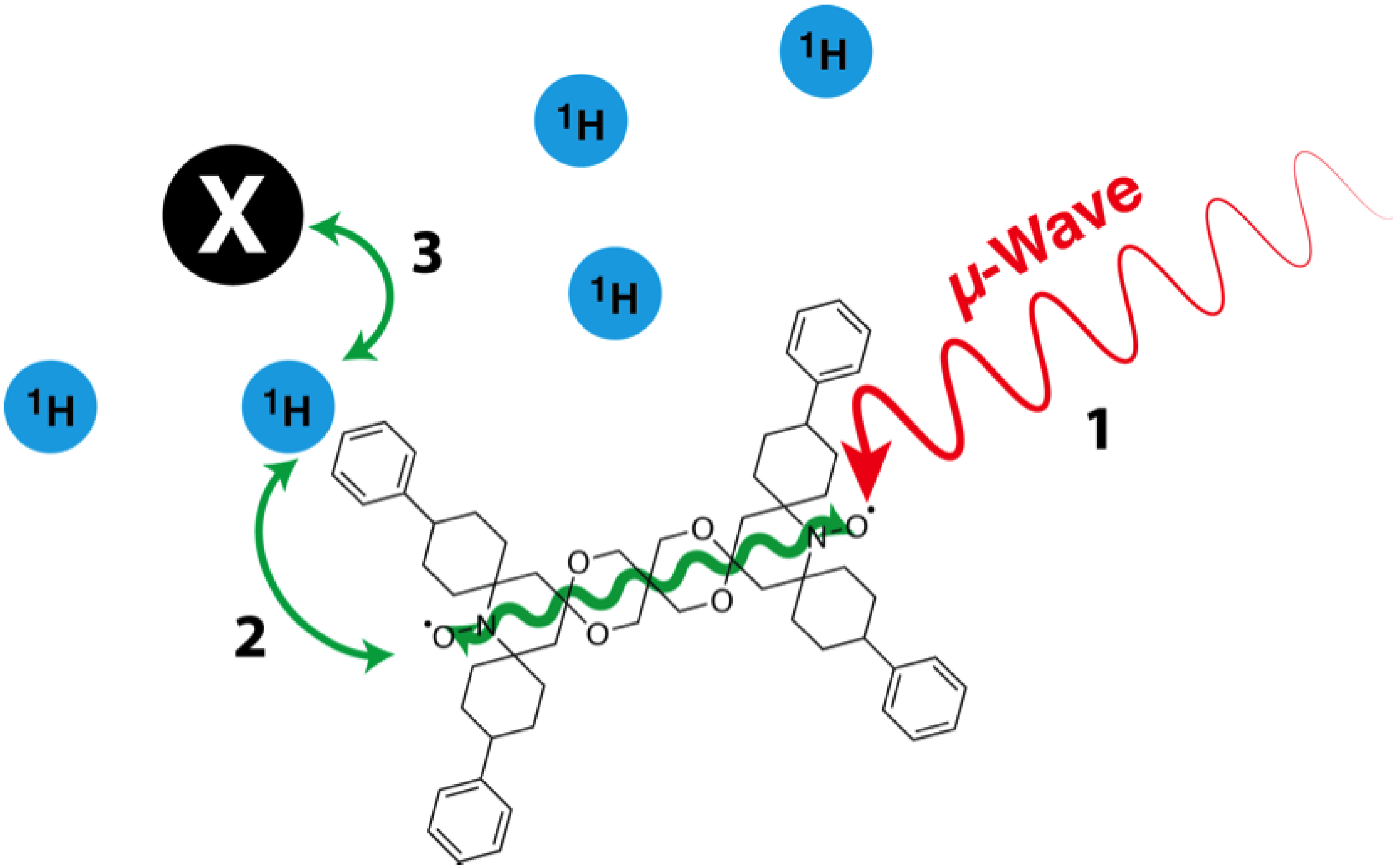


Solid state NMR techniques



Solid state NMR techniques

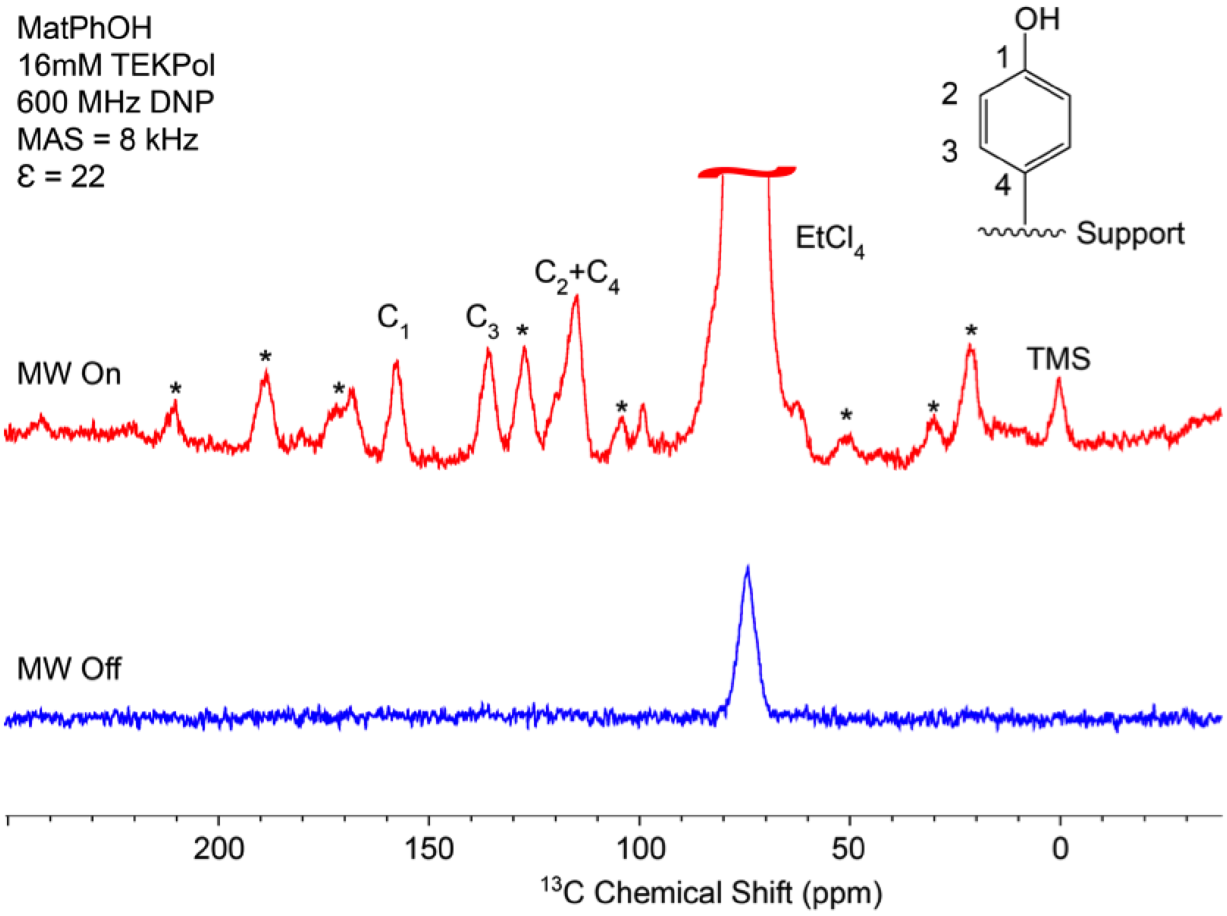
- Dynamic nuclear polarization (DNP)



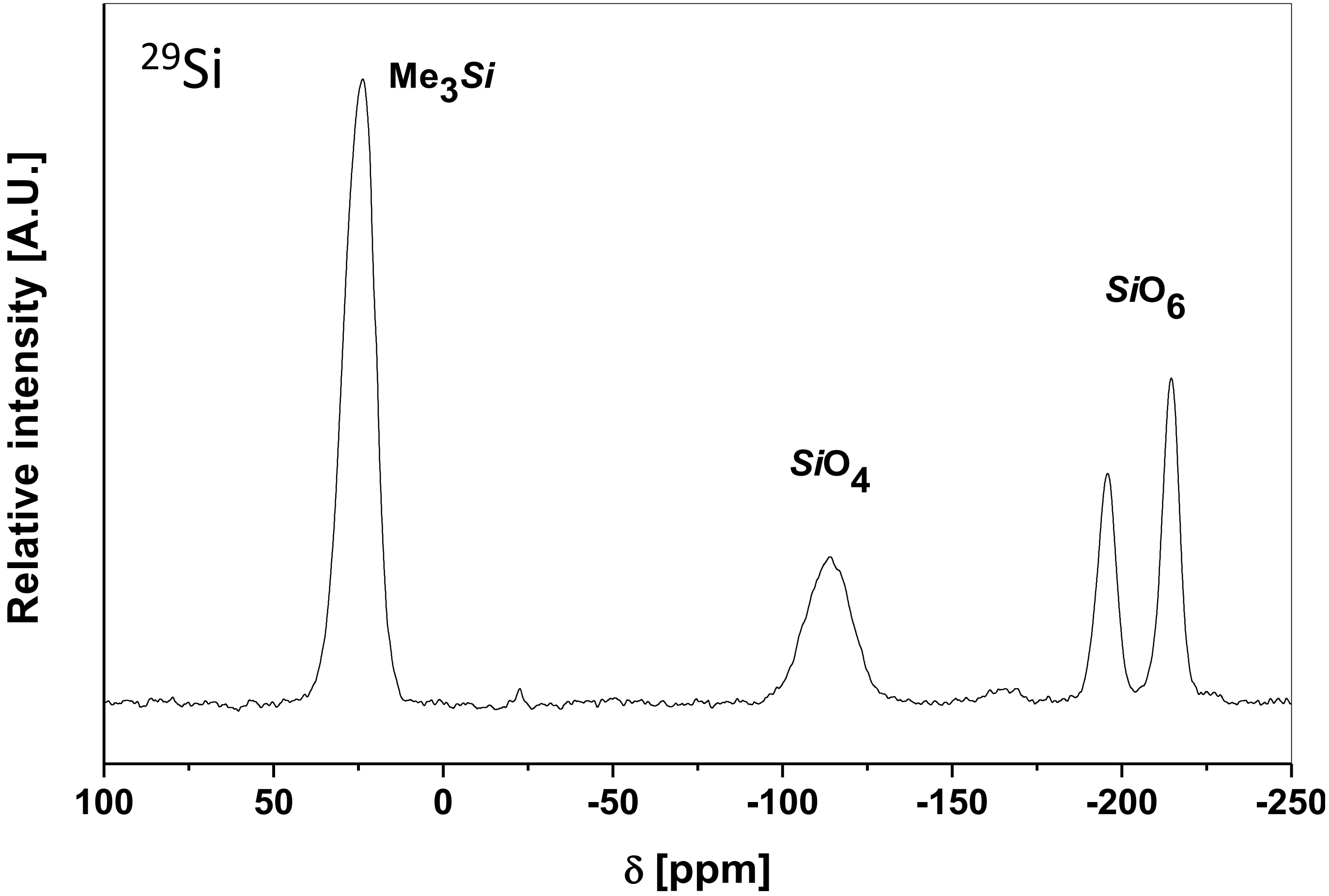
Solid state NMR techniques

- Dynamic nuclear polarization (DNP)

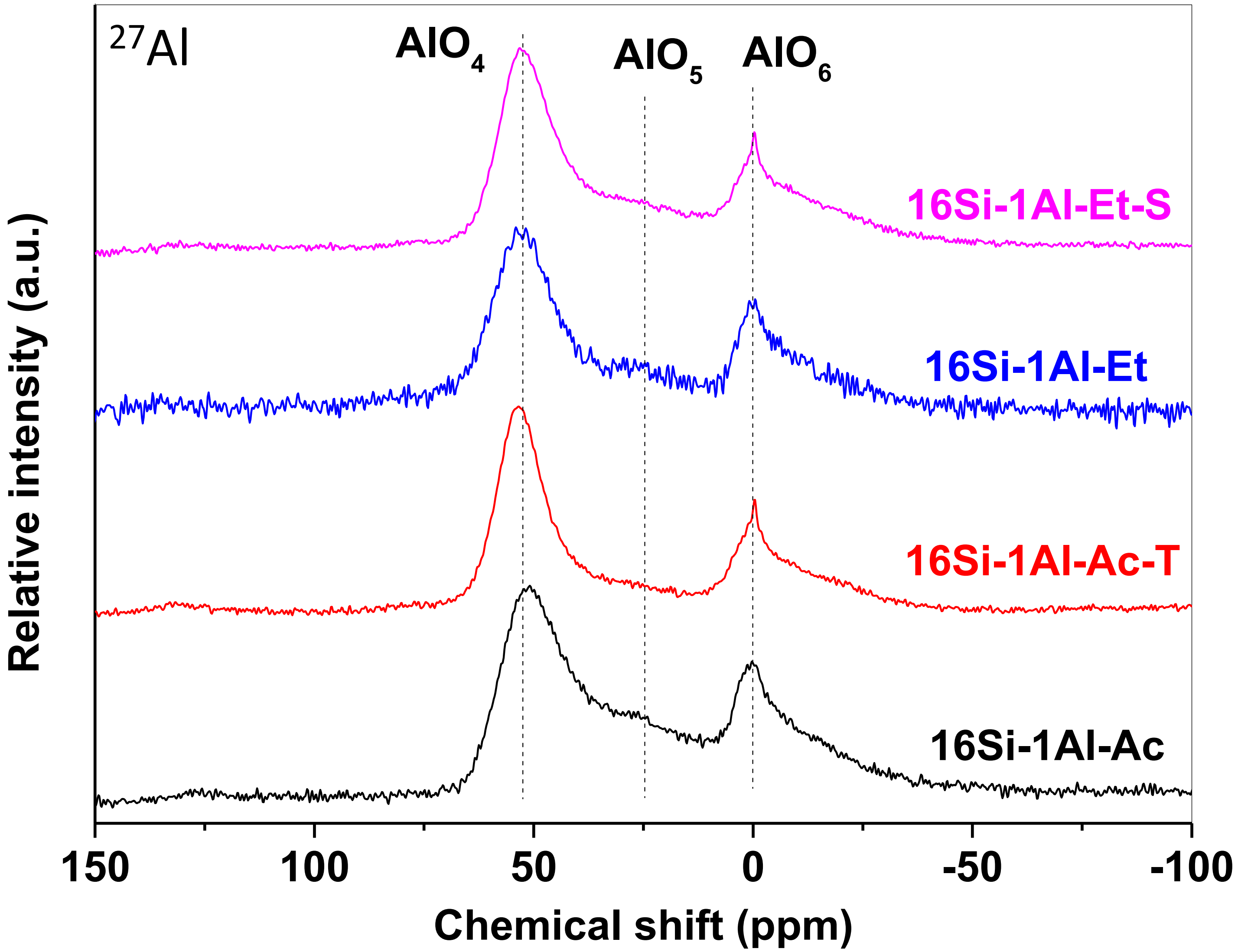
^{13}C



Solid state NMR techniques



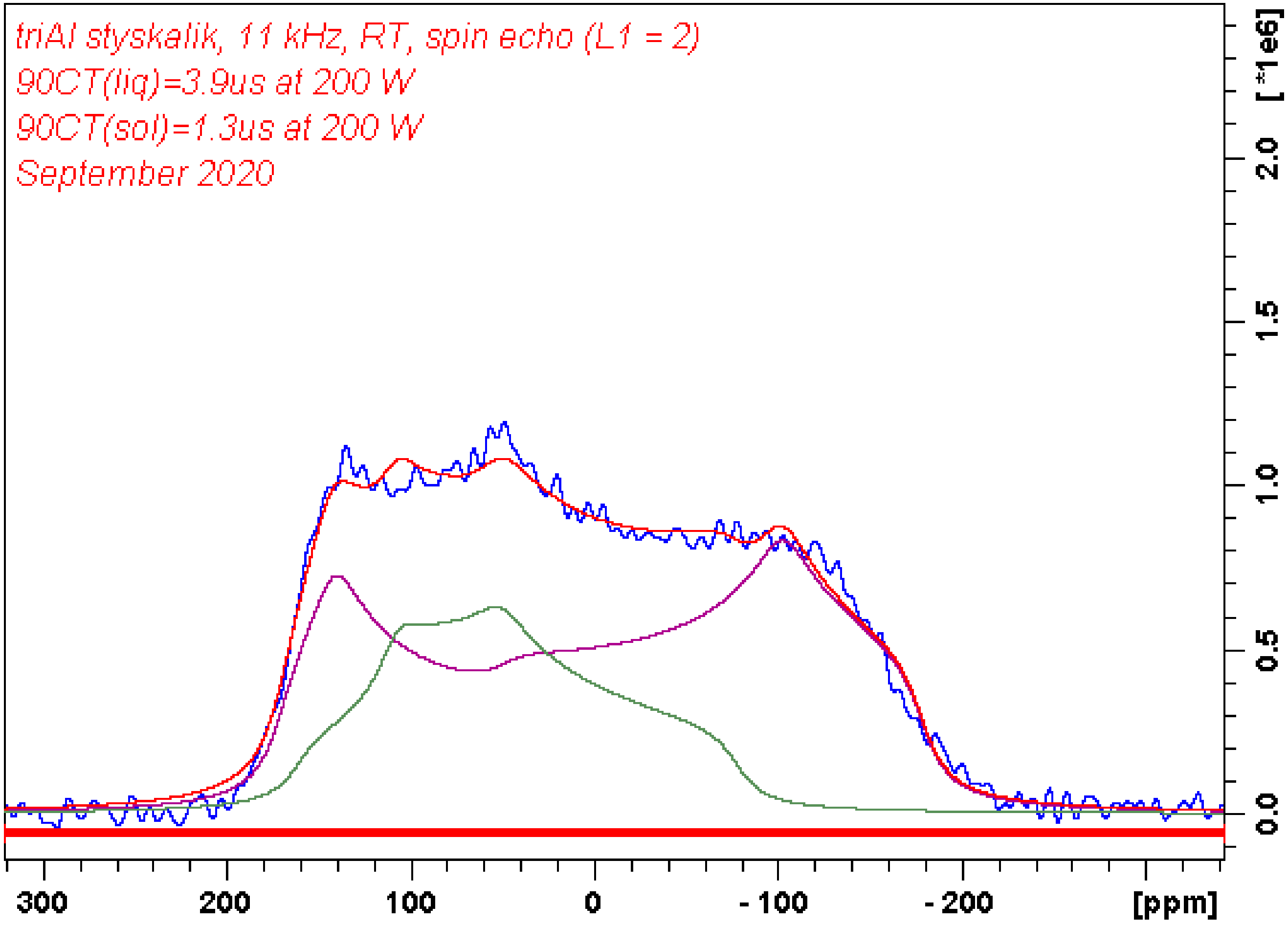
Solid state NMR techniques



Solid state NMR techniques

- Static NMR (=no spinning)

^{27}Al

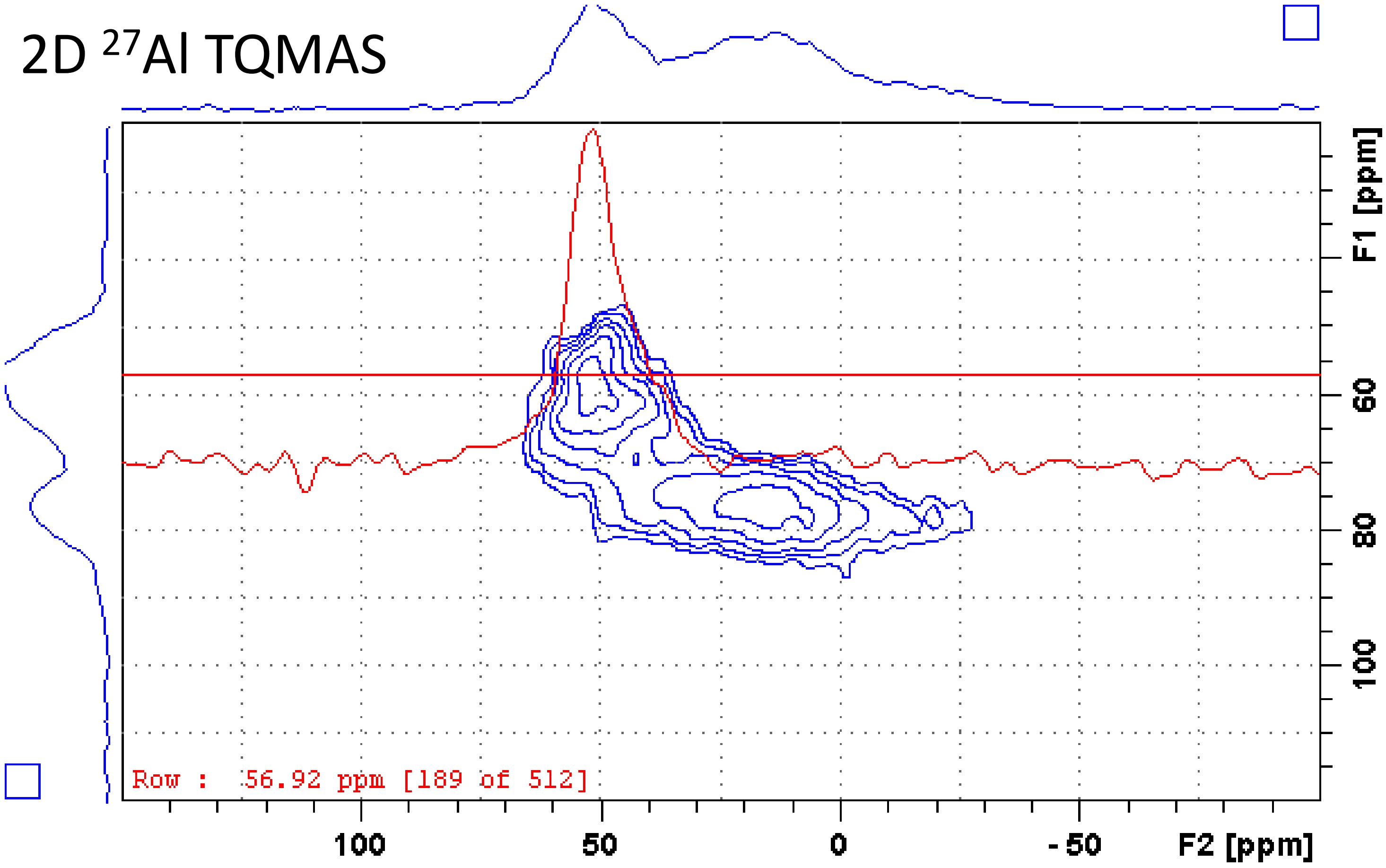


triAl styskalik, 11 kHz, RT, spin echo (L1 = 2)
90CT(liq)=3.9us at 200 W
90CT(sol)=1.3us at 200 W
September 2020

Solid state NMR techniques

- Multiple quantum MAS (MQMAS)

2D ^{27}Al TQMAS



Hydrophilicity vs. Hydrophobicity

- Why?
  - Remember: Adsorption/desorption step in cata as important as cata rxn itself (@Lecture 1)
  - Moreover: strong efforts nowadays put forward bio-sources instead of fossil fuels
  - Compare
    - Oil – long hydrocarbon chains (hydrophobic)
    - Wood – cellulose, lignin = sugar based materials = a lot of oxygen, OH groups (hydrophilic)

Hydrophilicity vs. Hydrophobicity

- Possibilities:
  - Water sorption
  - Dynamic vapor sorption/Quartz crystal microbalance
  - Inverse gas chromatography
  - Microcallorimetry

Hydrophilicity vs. Hydrophobicity

- Problems:
  - What is a measure of hydrophobicity?
    - A material can have high/low affinity to both water and organic molecules (i.e. if a sample is hydrophilic, it does not necessarily mean it is hydrophobic!)
      - % of pore volume filled with water at certain p/p_0
      - Hydrophobic index (water/toluene competitive sorption)
      - Heat of adsorption, heat of immersion
      - …
  - Chemisorption: Do chemisorbed molecules account for hydrophobicity/philicity?

Hydrophilicity vs. Hydrophobicity

- Water sorption
  - Similar to N_2 physisorption
  - Known volume and pressure in the cell, known mass of the sample

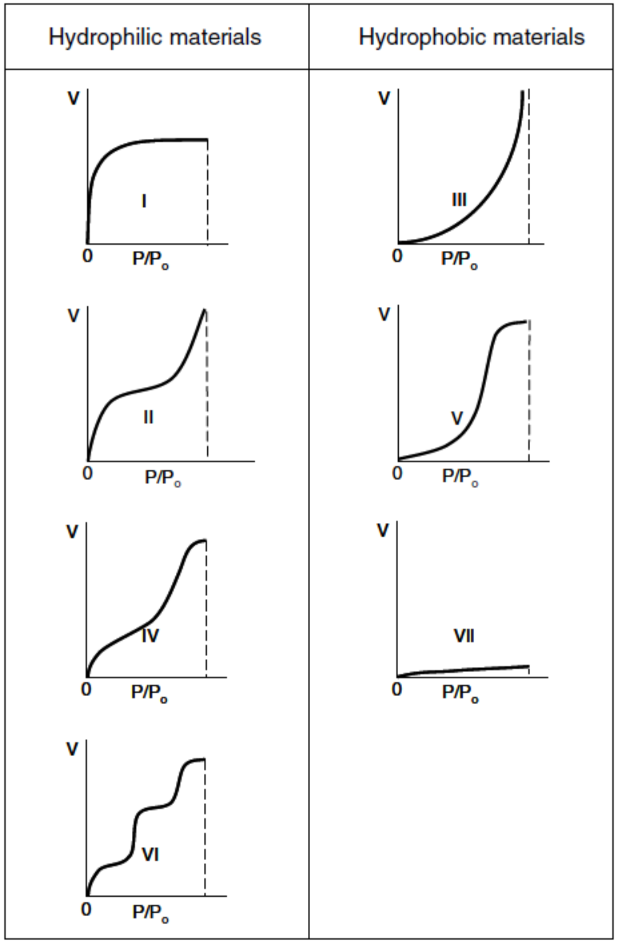
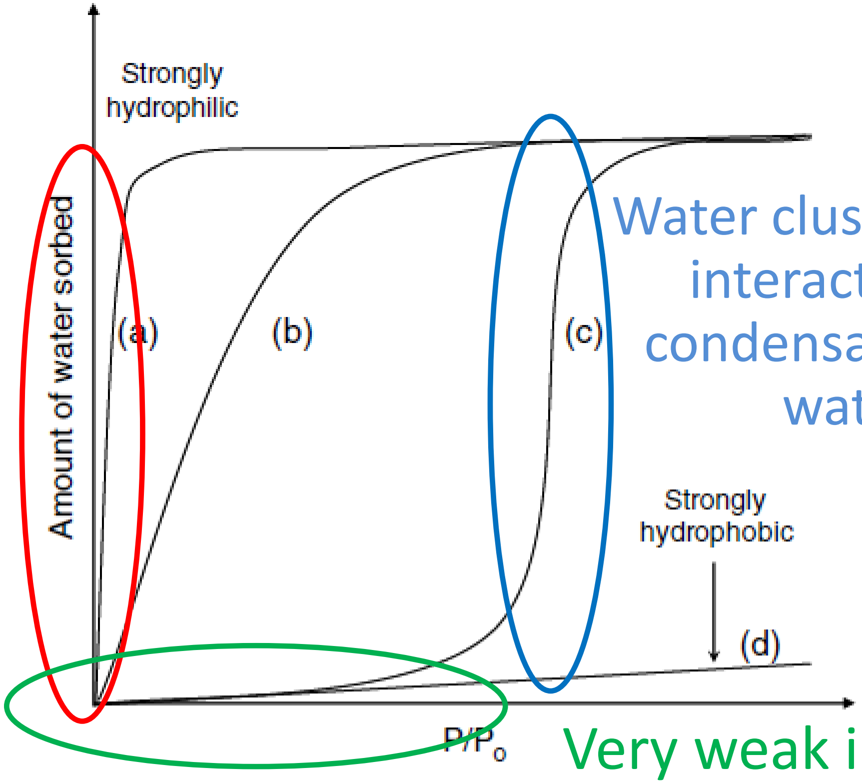


Fig. 1. Adsorption isotherms classified according to IUPAC: type I: very hydrophilic material, type II: hydrophilic material, type III: hydrophobic/low hydrophilic material with weak sorbent–water interactions, type IV: hydrophilic material, type V: hydrophobic/low hydrophilic material with weak sorbent–water interactions, type VI: hydrophilic material with multiple sorbent–water interactions and stepwise sorption, type VII: very hydrophobic material.

Hydrophilicity vs. Hydrophobicity

- Water sorption



Very strong interaction water-adsorbent

Water clustering = water-water interaction (liquefaction, condensation) stronger than water-adsorbent

Very weak interaction water-adsorbent

E.-P. Ng, S. Mintova / Microporous and Mesoporous Materials 114 (2008) 1–26

Hydrophilicity vs. Hydrophobicity

- Water sorption
  - Plotting *ln p* against *1/T* at constant adsorption uptake gives a straight line with a slope equal to H_{iso}/R
  - H_{iso} = isosteric heat of adsorption
  - Isotherms at multiple temperatures needed!

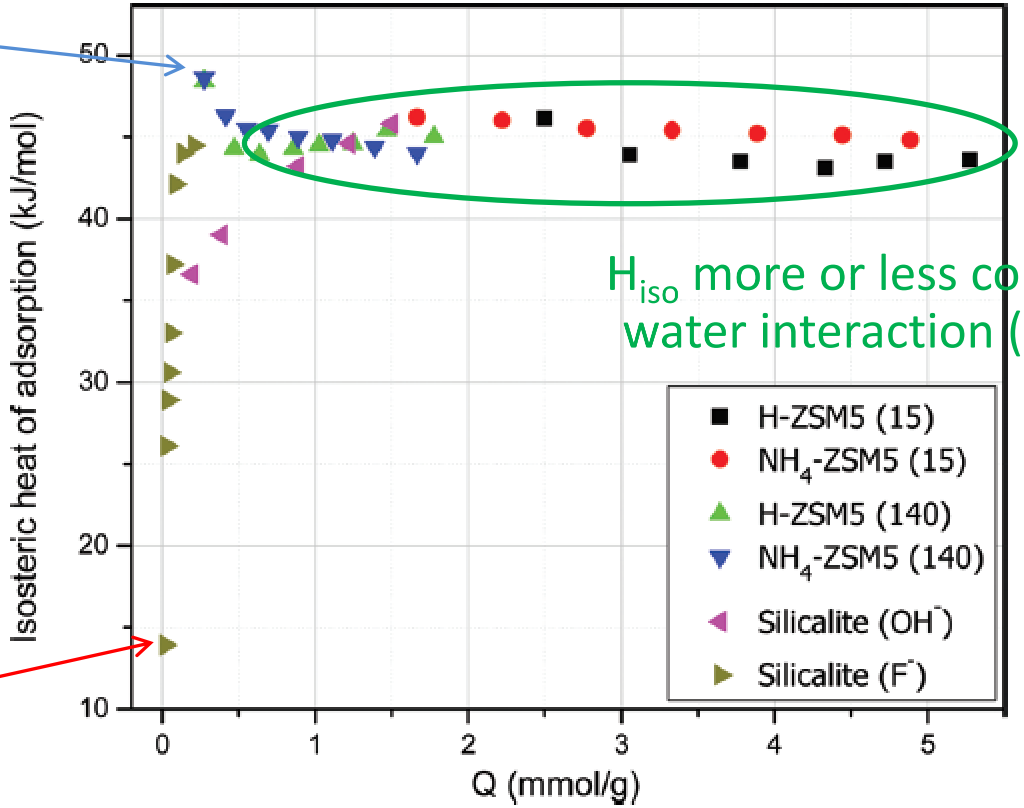
J. Phys. Chem. C 2012, 116, 18816−18823

Hydrophilicity vs. Hydrophobicity

- Water sorption
  - H_{iso} = isosteric heat of adsorption

Hydrophilic material = very high H_{iso} = strong interaction water-adsorbent

Hydrophobic material = very low H_{iso} = negligible interaction water-adsorbent



H_{iso} more or less constant = water-water interaction (condensation)

Hydrophilicity vs. Hydrophobicity

- Dynamic vapor sorption/Quartz crystal microbalance
  - You deposit your material on an accurate microbalance
  - You expose it to vapors of different gases/liquids (water, alcohols, hydrocarbons,…)
  - You follow the uptake by changes of mass
  - If we can control/follow pressure, then isotherms can be obtained similar to a classic physisorption

Hydrophilicity vs. Hydrophobicity

- Inverse gas chromatography
  - You pack column (≈ 50 cm) with the material you want to test (≈ 0.5 g)
  - You inject series of gases/liquids (e.g. methane, ethane,…hexane, heptane; methanol, ethanol,…; benzene, toluene, xylene…)
  - You follow retention time (you directly see „affinity“ of your material to selected liquids)
  - Models (math) can give surface energy,…

Hydrophilicity vs. Hydrophobicity

- Immersion microcalorimetry
  - Evacuated sample sealed in a bulb with brittle end
  - Bulb immersed in a testing liquid, sealed
  - Bulb broken (rod pushed down)
  - Liquid gets into the bulb, adsorbs, heat of immersion released and measured

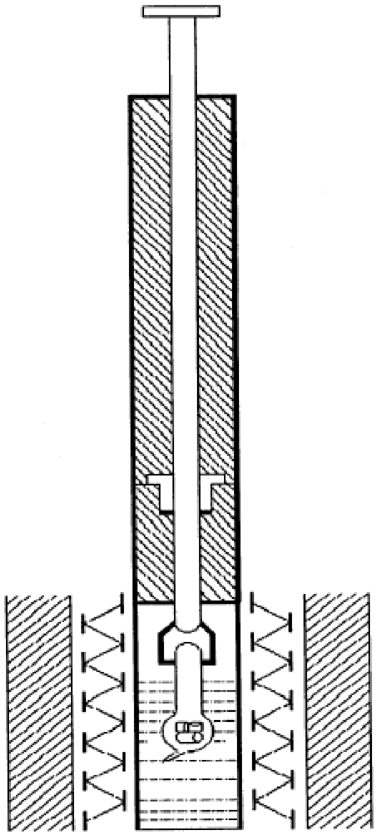


Fig. 1. Set-up for immersion calorimetry.

Hydrophilicity vs. Hydrophobicity

- Immersion microcalorimetry
  - Ti-MCM-41, pure inorganic vs. increasing degree of surface silylation (increasing carbon content)

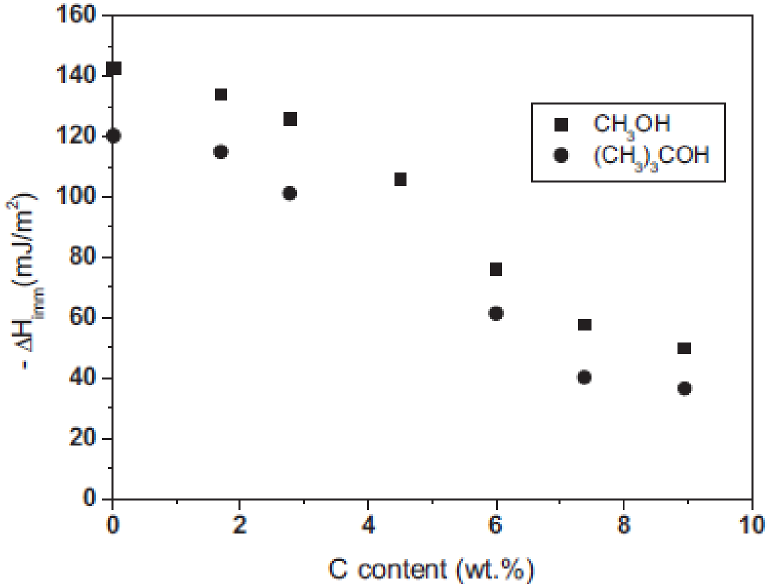


Fig. 7. Evolution of the areal enthalpy of immersion (mJ/m^2) in methanol and 2-methyl-2-propanol as a function of carbon content for the different silylated Ti-MCM-41 samples.

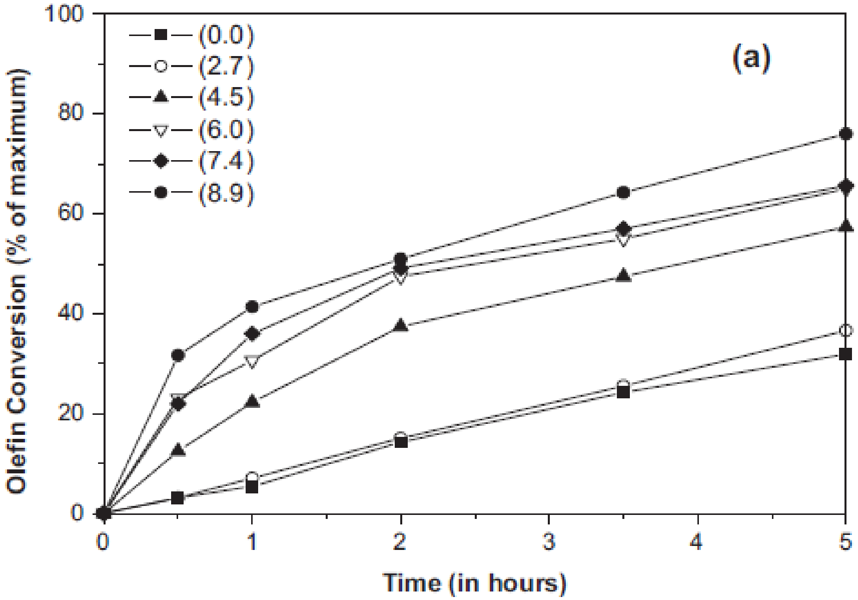


Fig. 8. Catalytic activity of Ti-MCM-41 materials with different silylation degrees in the cyclohexene epoxidation with TBHP (and 0.5 wt% of catalyst) at 333 K during 5 h. (a) Cyclohexene Conversion (%Mol.); (b) Epoxide Selectivity (%Mol.).

J. Silvestre-Alberó et al. / Applied Catalysis A: General 507 (2015) 14–25

In situ and operando techniques

- In situ = online analysis of a working catalyst
- Operando = online analysis of a working catalyst at relevant conditions (p, T, WHSV)

	Technique	Information	Suitable to *operando* charac.
ν → ν	**IR spectroscopy** (FTIR/DRIFTS/ATR/IRAS)	Adsorbate nature, adsorption site	✓
	Raman spectroscopy (SERS/TERS)	Solid structure, adsorbate nature	✓
	XAS (EXAFS/XANES/QXAS)	Local environment, oxidation state	✓
	SAXS (GISAXS)	NP size and morphology	✓
	XRD (PXRD/SXRD/HEXRD)	Crystal phase and dimension	✓
ν → e-	**XPS** (NAP-XPS)	Chemical composition, oxidation state	Low pressure, large volume
e- → e-	**TEM** (Environmental TEM) (*In situ* TEM)	Atomic structure, chemical distribution	Low pressure, large volume Low catalyst amount
	SPM (STM, AFM…)	Surface structure	Planar model catalysts

In situ and operando techniques

- We already know these techniques, let‘s look at the examples!
  - Low energy electron diffraction (LEED, gives similar results to x-ray diffraction = analysis of crystal structures)
  - X-ray absorption near edge structure (XANES)
  - Diffusive reflectance infrared Fourier transform spectroscopy (DRIFTS)

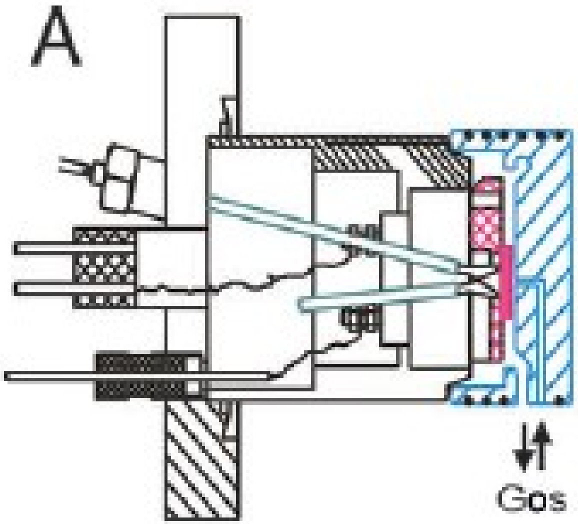
In situ and operando techniques

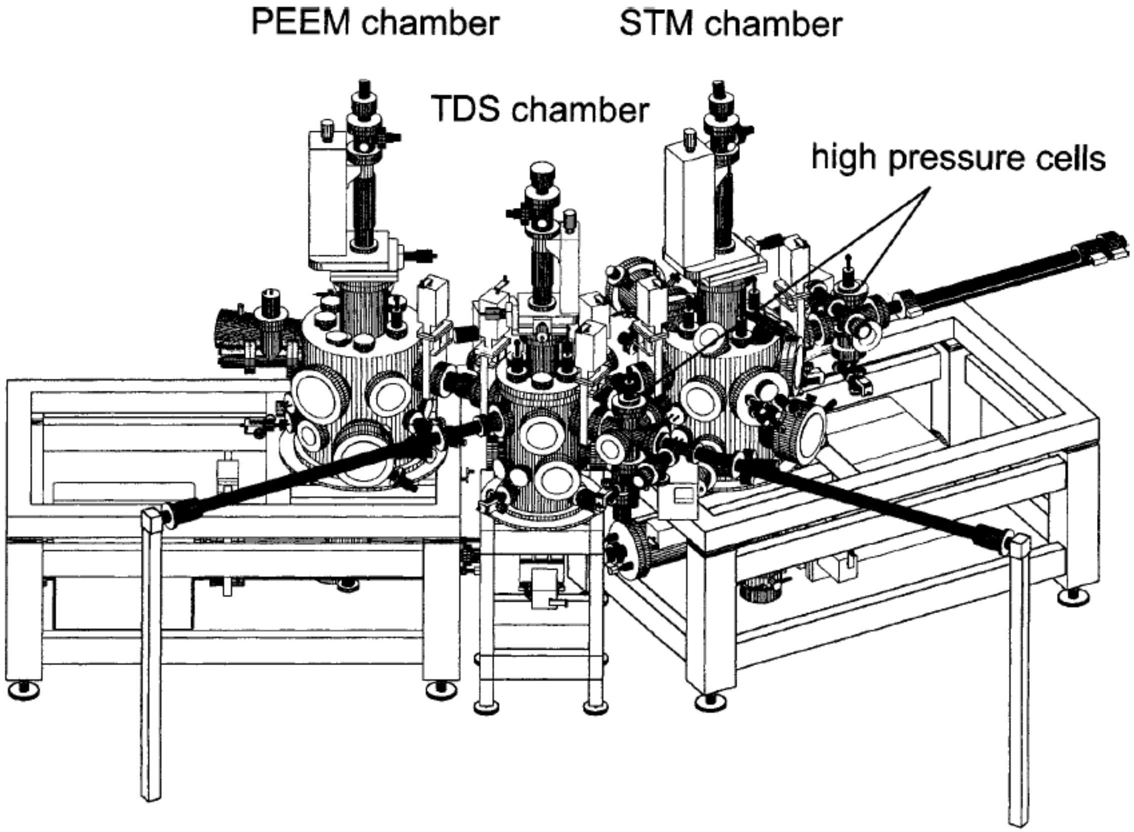
- Example: LEED – low energy electron diffraction
- Ethylbenzene dehydrogenation to styrene
  - 600 °C, 1 atm, 10-fold excess water vapor
  - Over Fe_2O_3 epitaxially grown on Pt(111)
- Flow reactor located in a high pressure cell
  - Heated by lasers
  - GC-MS analysis of catalytic products
  - LEED analysis enabled by gate valve (high pressure/ultra high vacuum) and sapphire window

W. Weiss, R. Schlögl / An integrated surface science approach towards metal oxide catalysis

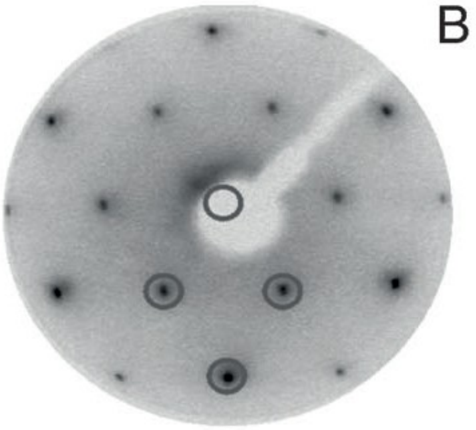
In situ and operando techniques

- Example: LEED – low energy electron diffraction



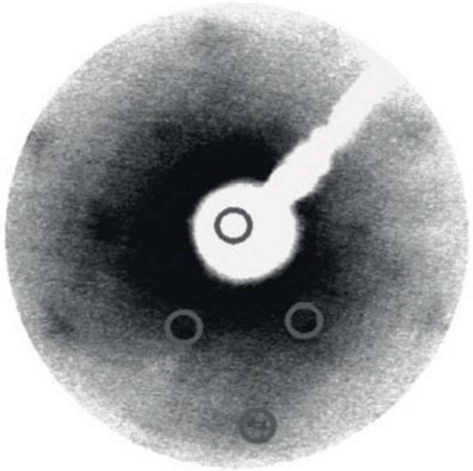


Before catalytic reaction

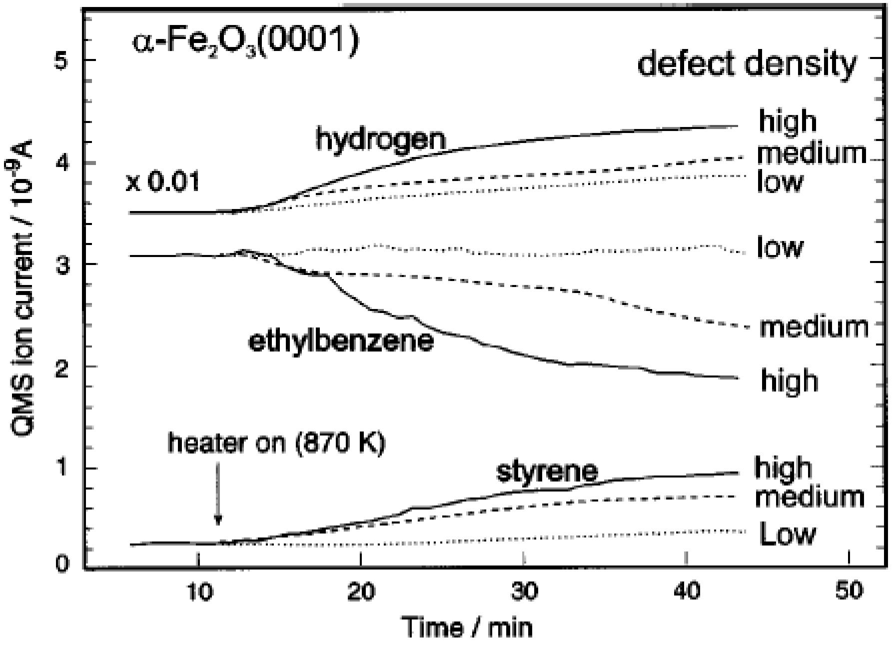


Initial period, no catalytic activity

After catalytic reaction

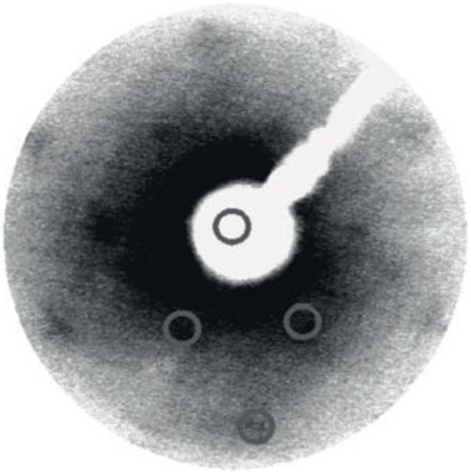


Working catalyst



In situ and operando techniques

- Example: LEED – low energy electron diffraction



Active catalyst

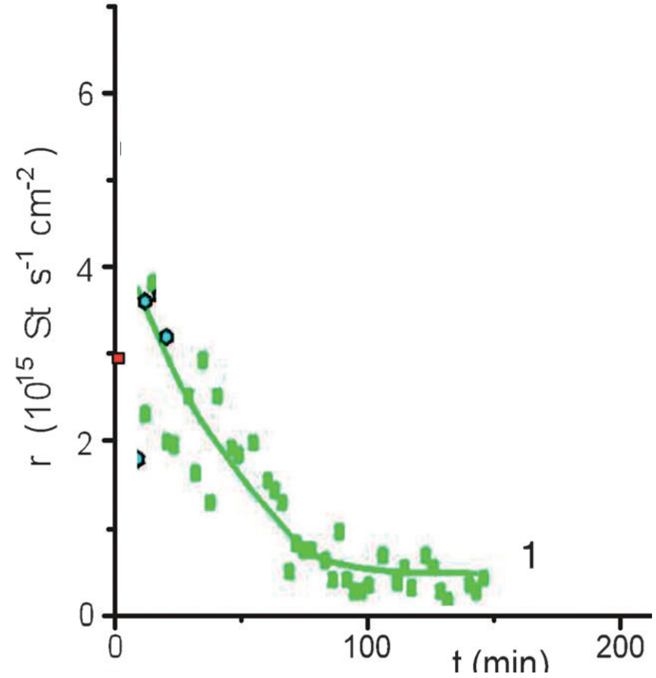
Non-crystalline Fe_2O_3

Metastable (Reduction!)

Carbon deposition (Styrene!)

Loss of catalytic activity

0.5 eq O_2 addition



In situ and operando techniques

- Example: XANES – x-ray absorption near edge structure
- Methanol oxidation to formaldehyde over Cu
  - 25–450 °C, 1 mbar
  - Cu in the form of polycrystalline foil

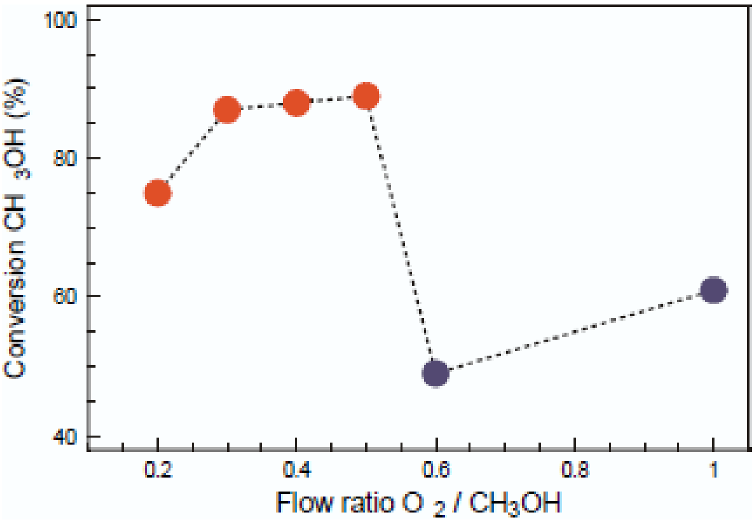
$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$

In situ and operando techniques

- Example: XANES – x-ray absorption near edge structure

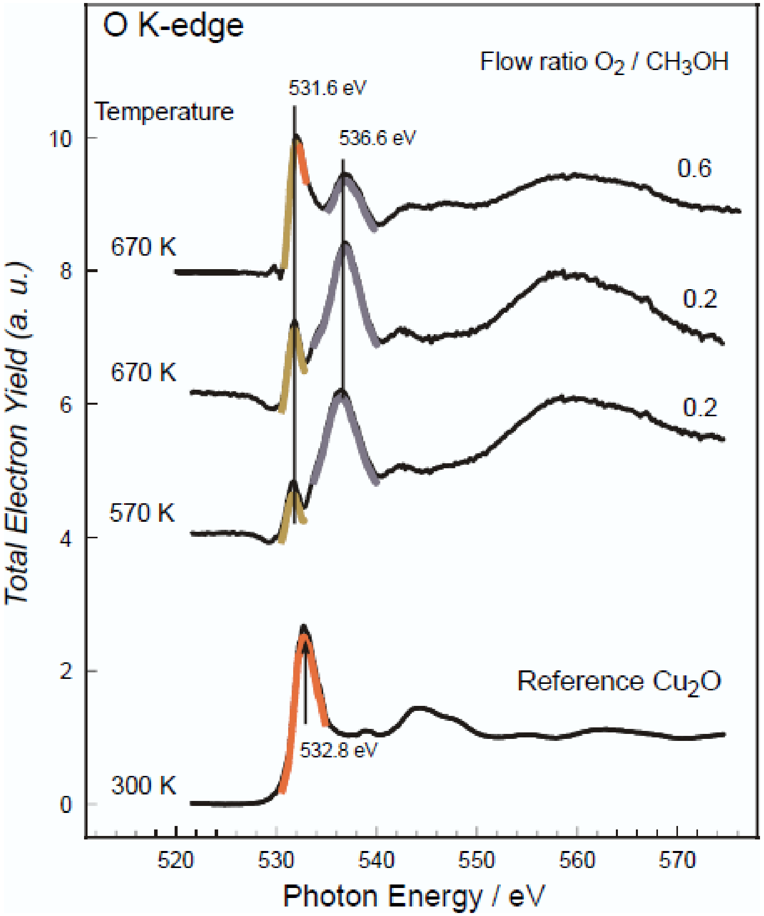
$$2\ CH_3OH + O_2 \rightarrow 2\ CH_2O + 2\ H_2O$$

Catalytic Activity



In situ and operando techniques

- Example: XANES – x-ray absorption near edge structure



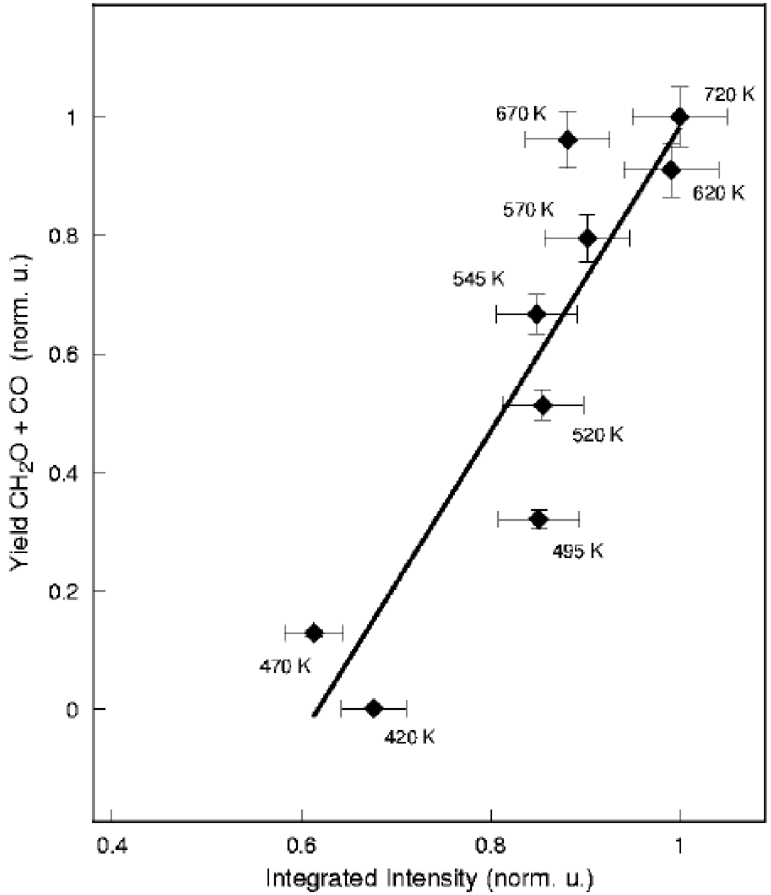
less active

very active

2 oxide and 1 suboxide species

In situ and operando techniques

- Example: XANES – x-ray absorption near edge structure



- Positive correlation between catalytic activity and Cu suboxide species
- Explanation/idea/description of active species: Subsurface oxygen cover by a strained layer of copper atoms
- Results confirmed by near ambient pressure XPS (NAP XPS)

In situ and operando techniques

- Example: DRIFTS – diffuse reflectance infrared Fourier transform spectroscopy
- Coupling of ethanol and acetaldehyde to 1,3-butadiene over Ta doped zeolite
  - 300 °C, 1 atm
  - Well dispersed (virtually isolated) Ta sites

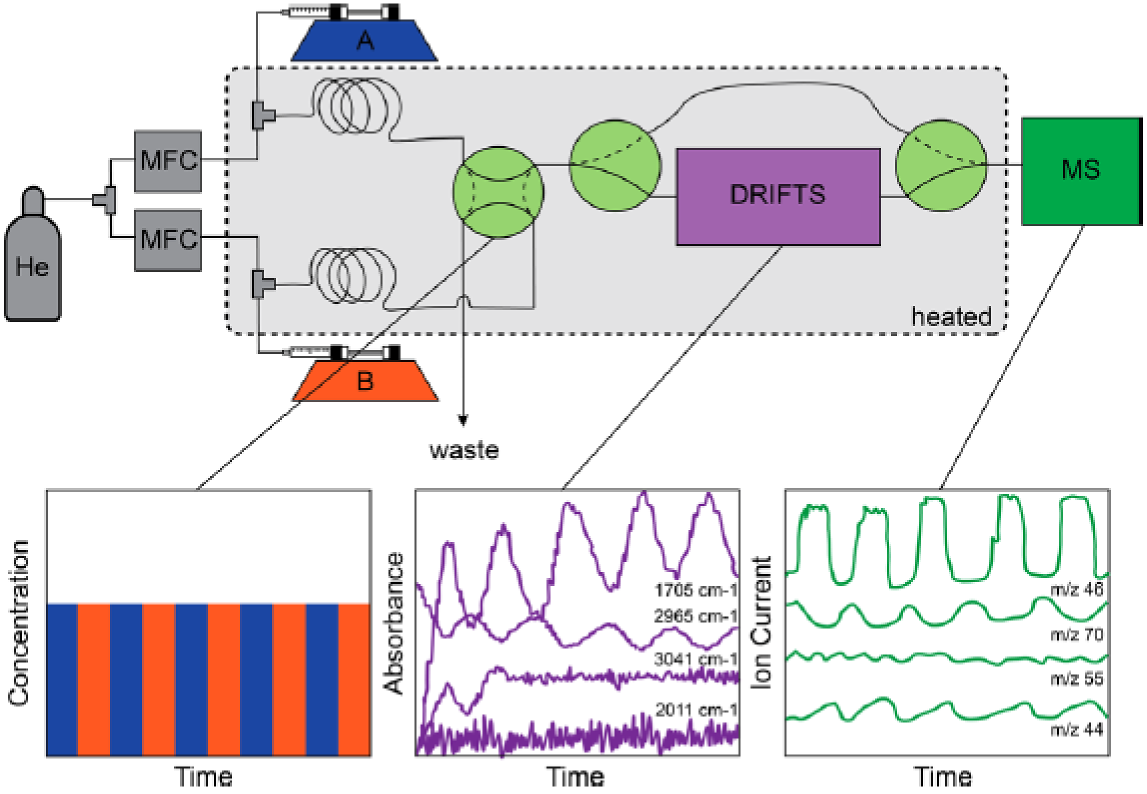
$$2\ C_2H_5OH + CH_3CHO \rightarrow C_4H_6 + 2\ H_2O$$

DOI: 10.1021/acscatal.6b01642
ACS Catal. 2016, 6, 6823–6832

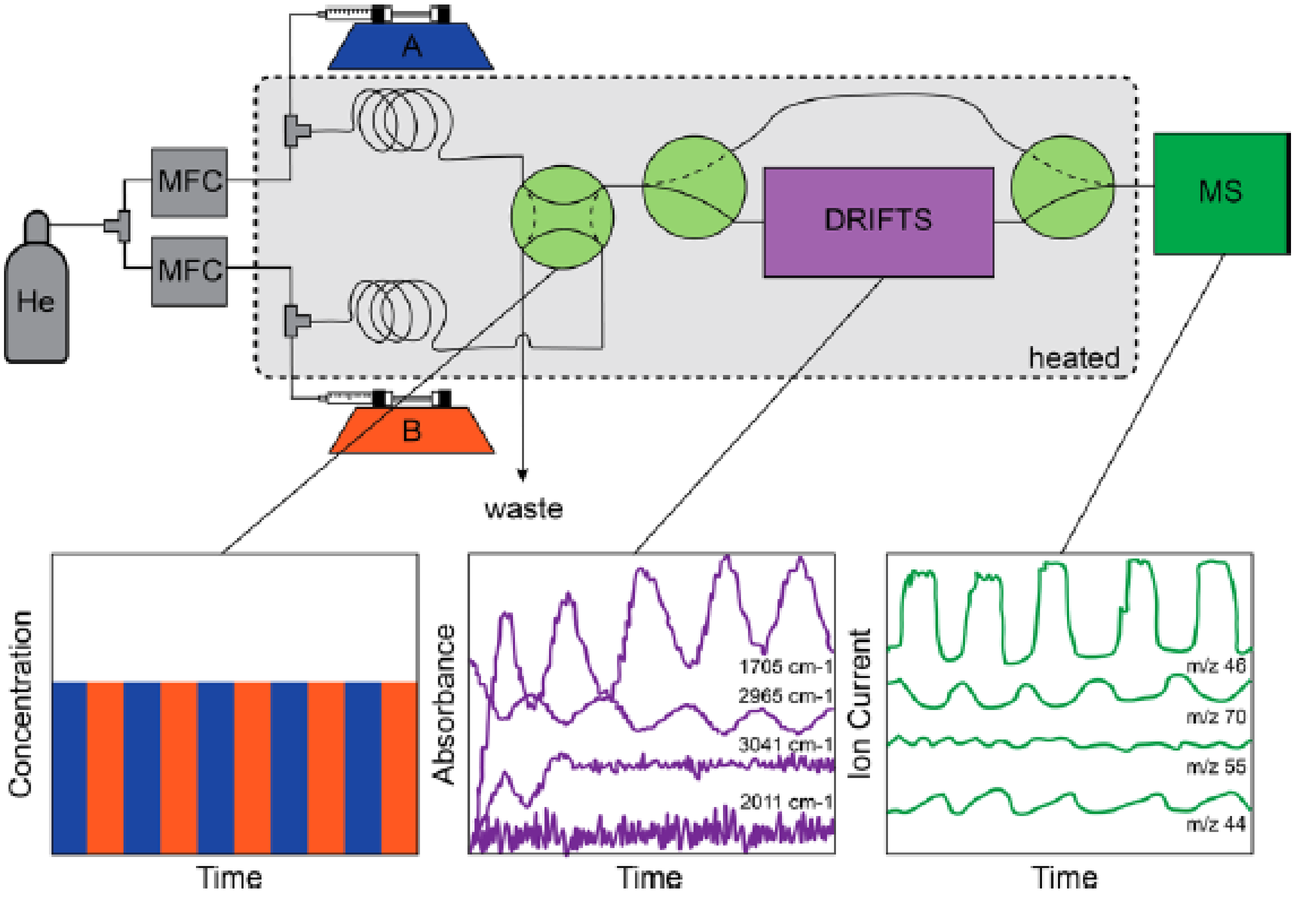
In situ and operando techniques

- Example: DRIFTS – diffuse reflectance infrared Fourier transform spectroscopy

Scheme 2. Schematic Overview of the DRIFTS-MS Setup[a]



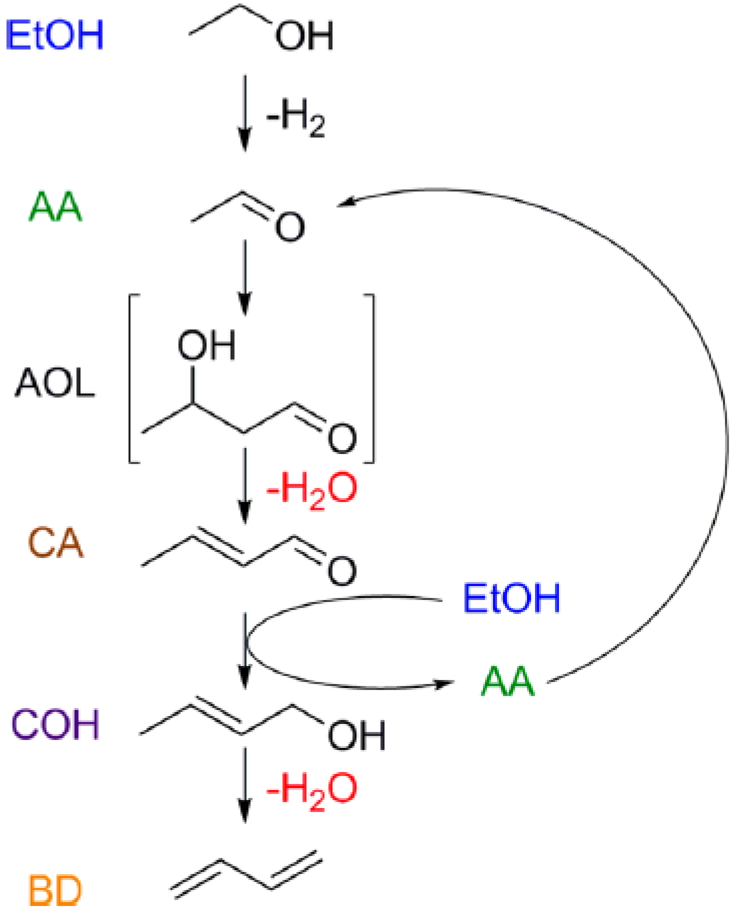
Scheme 2. Schematic Overview of the DRIFTS-MS Setup[a]



[a] By using two syringe pumps and heated coils that enter a two-position–four-way valve, the gas-phase composition can be modulated between substrates A and B. Depending on the chosen position, either flow A or B flows through the DRIFTS accessory followed by the online mass spectrometer. In addition, two three-way valves allow the substrates to bypass the DRIFTS accessory to ensure steady gas-phase concentrations prior to measurements.

In situ and operando techniques

- Example: DRIFTS



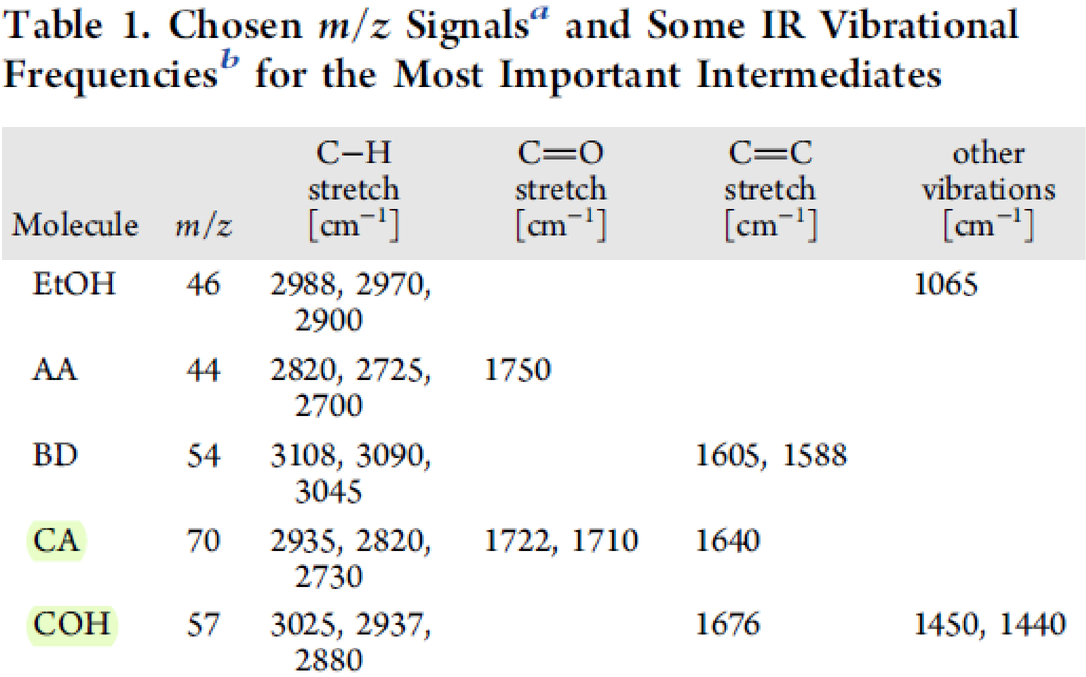


Table 1. Chosen *m/z* Signals[a] and Some IR Vibrational Frequencies[b] for the Most Important Intermediates

Molecule	*m/z*	C–H stretch [cm^{-1}]	C=O stretch [cm^{-1}]	C=C stretch [cm^{-1}]	other vibrations [cm^{-1}]
EtOH	46	2988, 2970, 2900			1065
AA	44	2820, 2725, 2700	1750		
BD	54	3108, 3090, 3045		1605, 1588	
CA	70	2935, 2820, 2730	1722, 1710	1640	
COH	57	3025, 2937, 2880		1676	1450, 1440

In situ and operando techniques

- Example: DRIFTS – diffuse reflectance infrared Fourier transform spectroscopy