Molecular Aspects of Catalysts and Surfaces

529-0611-00L

Monday 9:45-10:30 (HCI H8.1) - Self-studies / practicals, Tuesday 15:45-17:30 (HCI H2.1)
Wednesday 8:45-10:30 (HCI D8)

Lecture Schedule (Autumn, 2020)

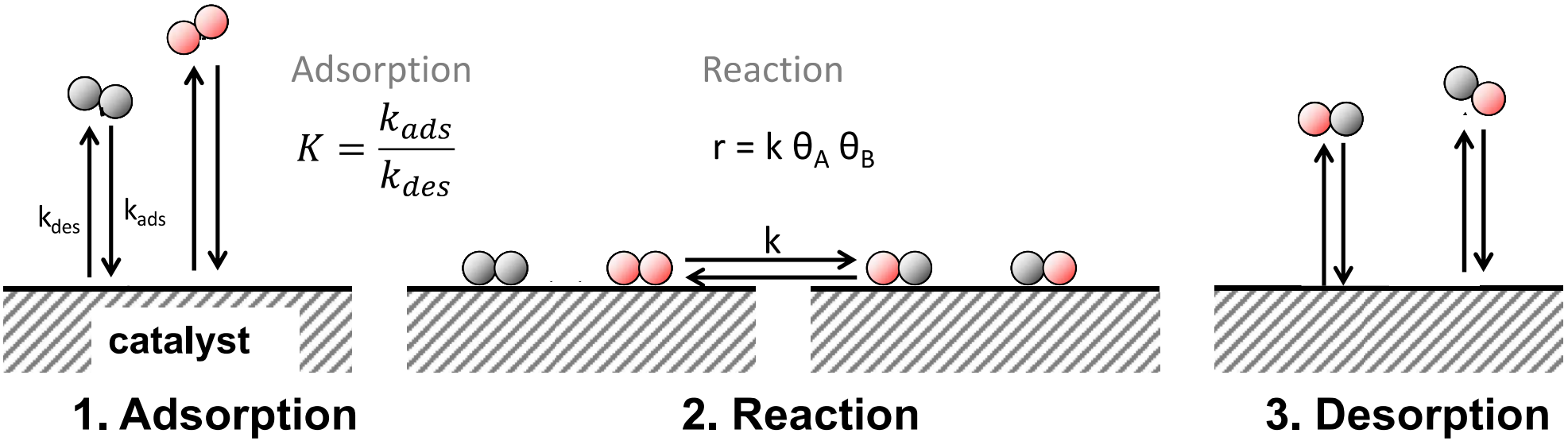
Day	Date	Hours	Lecture topic	Lecturer
Tuesday	15 Sep	2	Introduction	Prof. van Bokhoven
Wednesday	16 Sep	2	Temperature programmed techniques	Dr. Ferri
Tuesday	22 Sep	2	Physisorption, Pore Size	Dr. Pirngruber*
Wednesday	23 Sep	2	Chemisorption	Dr. Pirngruber*
Tuesday	29 Sep	2	IR	Dr. Ferri
Wednesday	30 Sep	2	IR	Dr. Ferri
Tuesday	6 Oct	2	EM	Dr. Krumeich
Wednesday	7 Oct	2	EM	Dr. Krumeich
Tuesday	13 Oct	2	ETEM	Dr. Willinger
Wednesday	14 Oct	2	Theory	Dr. Palagin
Tuesday	20 Oct	2	Theory	Dr. Palagin
Wednesday	21 Oct	2	Solid state NMR	Dr. Verel
Tuesday	27 Oct	2	Solid state NMR	Dr. Verel
Wednesday	28 Oct	2	XAS	Prof. van Bokhoven
Tuesday	3 Nov	2	XRD	Dr. Przemyslaw
Wednesday	4 Nov	2	XRD	Dr. Przemyslaw
Tuesday	10 Nov	Case study week		
Wednesday	11 Nov	Case study week		
Tuesday	17 Nov	2	XAS	Prof. van Bokhoven
Wednesday	18 Nov	2	UHV Techniques	Dr. Artiglia
Tuesday	24 Nov	2	UHV Techniques	Dr. Artiglia
Wednesday	25 Nov	2	UHV Techniques	Dr. Ferri
Tuesday	1 Dec	2	UV-vis	Dr. Ferri
Wednesday	2 Dec	2	Raman	Dr. Ferri
Tuesday	8 Dec	2	Element and isotope analysis	Dr. Hattendorf
Wednesday	9 Dec	2	In situ spectroscopy	Prof. van Bokhoven
Tuesday	15 Dec	2	Test Exam	
Wednesday	16 Dec	2	Test Exam & Questions	

* via Zoom, invitation will follow.

What does a catalyst do?

A catalyst breaks bonds ...

and makes bonds ...



What is an active site ??

Knowledge of reaction mechanism essential to appreciate characterization

TON: turnover number

TOF: turnover frequency

What does a catalyst do?

Description of surface reactions

Langmuir Hinshelwood

A → B

1. **Adsorption** A on total sites S
2. **Surface reaction** rate constant *k*
3. **Desorption**

$$A + S \rightleftharpoons AS \rightarrow \text{Products}$$

$$r = k\, C_{AS} = k\, \theta_A C_S$$

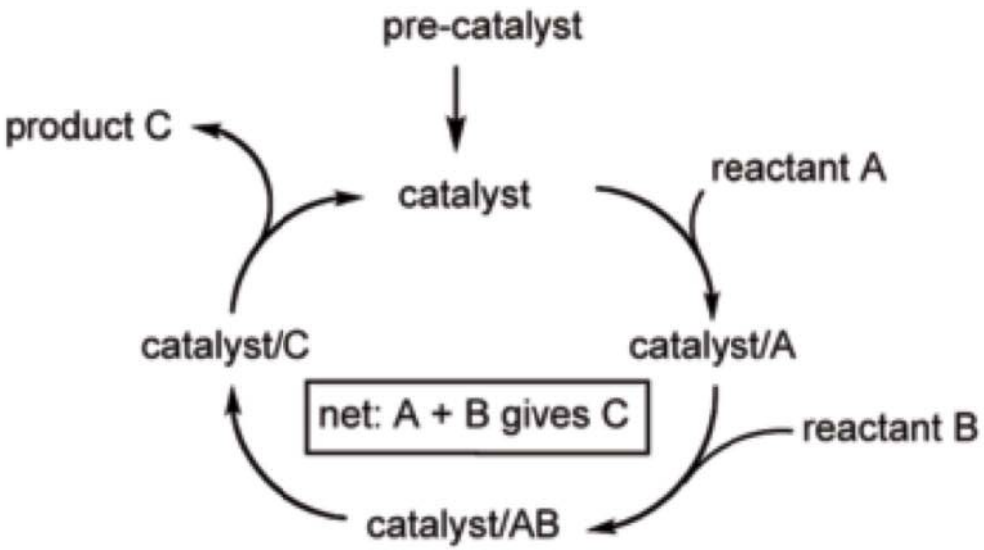
Coverage of A of total number active sites

θ is pressure dependent
Linear relation between number of sites and rate

Find linear relations between number of 'SITES' and reaction rate

Definition of an active site

The ensemble of atoms that participate in the conversion within the catalytic cycle



This is generally not a single atom….

Establishing linear relations between activity and the active site

NATURE VOL. 309 14 JUNE 1984

The active site of acidic aluminosilicate catalysts

W. O. Haag, R. M. Lago & P. B. Weisz

Mobil Research and Development Corporation, PO Box 1025 Princeton, New Jersey 08540, USA

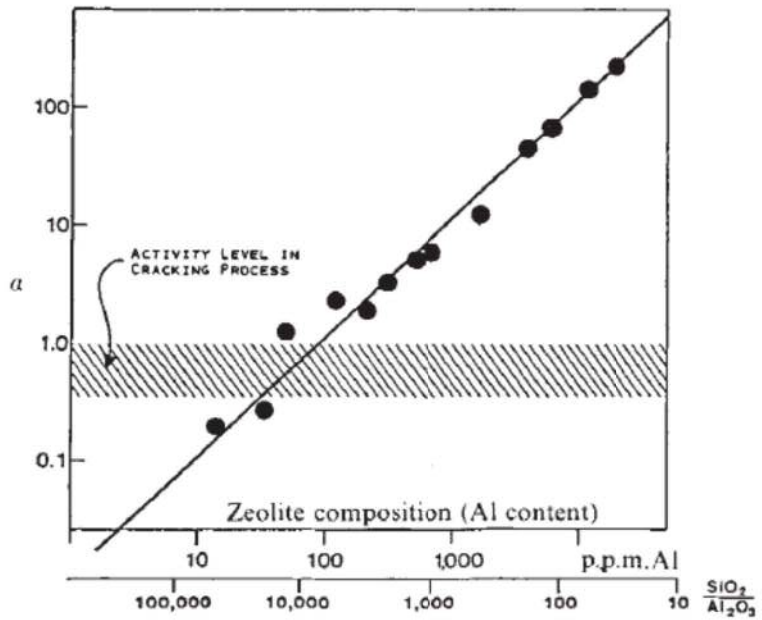


Fig. 2 The hexane cracking activity plotted against the aluminium content in HZSM-5. Shaded band indicates activities near $\alpha \simeq 1$.

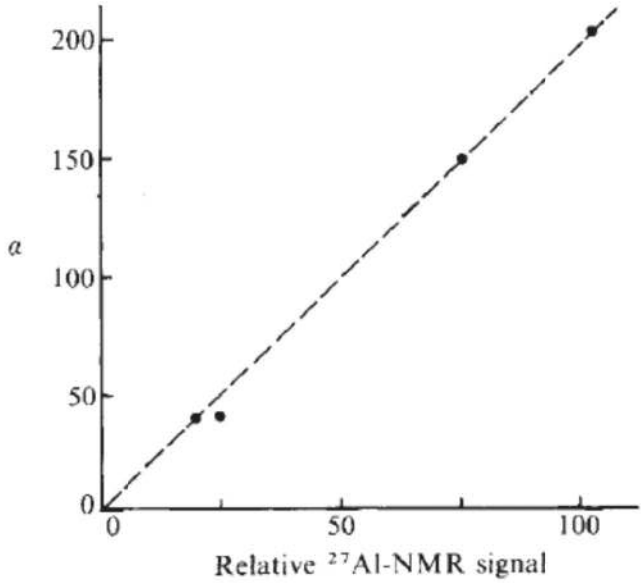
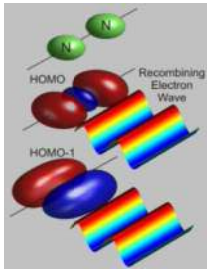
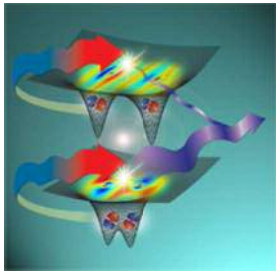


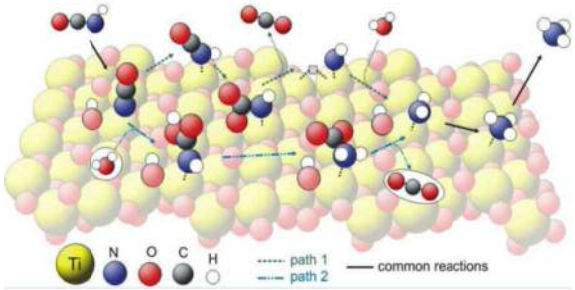
Fig. 4 The activity of HZSM-5 plotted against the tetrahedral aluminium NMR signal.

Zeolitic framework aluminum is the active site

Catalysis: time and length scales







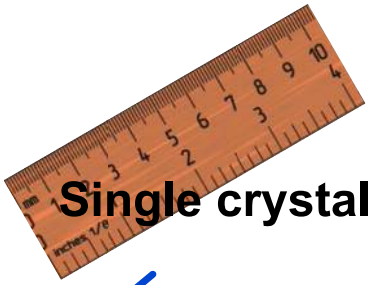
Fundamental **Applied**

10^{-18} 10^{-15} 10^{-12} 10^{-9} 10^{-6} 10^{-3} 1 10^{3} s

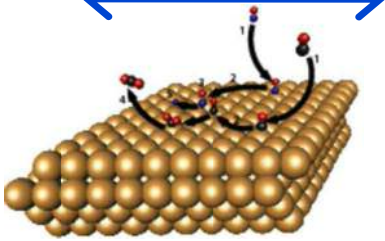
Bond breaking/ formation

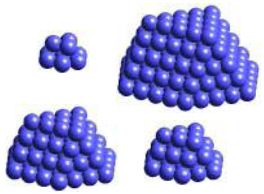
Reaction kinetics

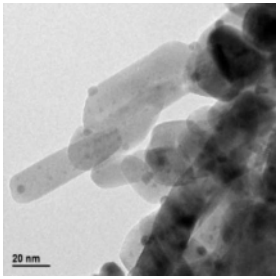
Stability, deactivation

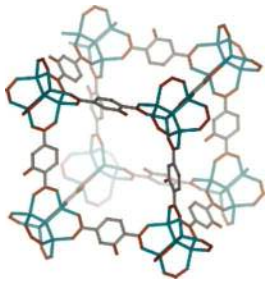


Single crystals · · · clusters · · · supported metals · · · single site catalysts · · · reactors



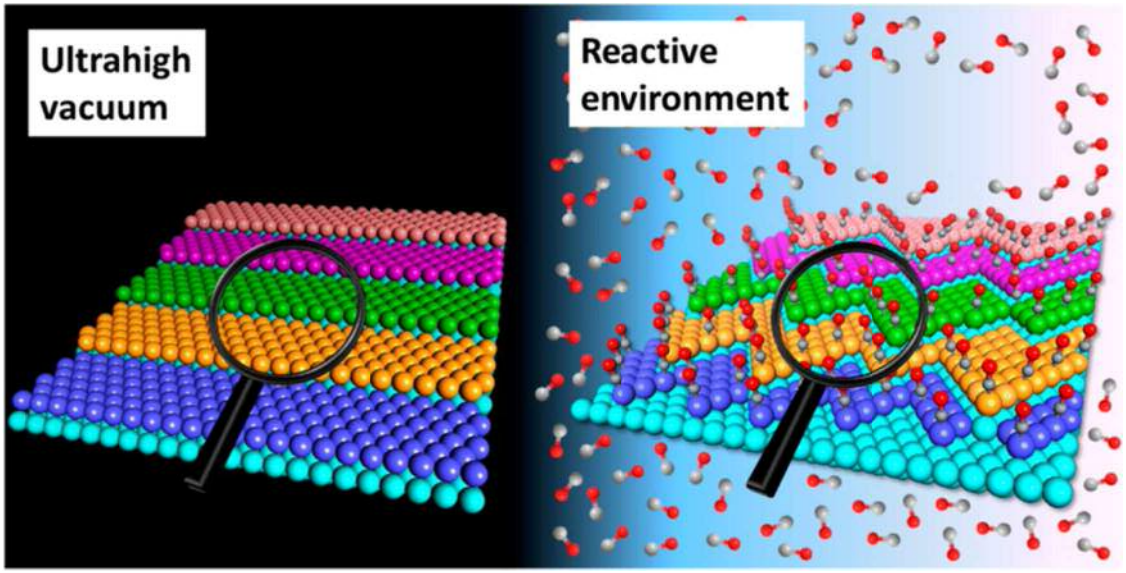






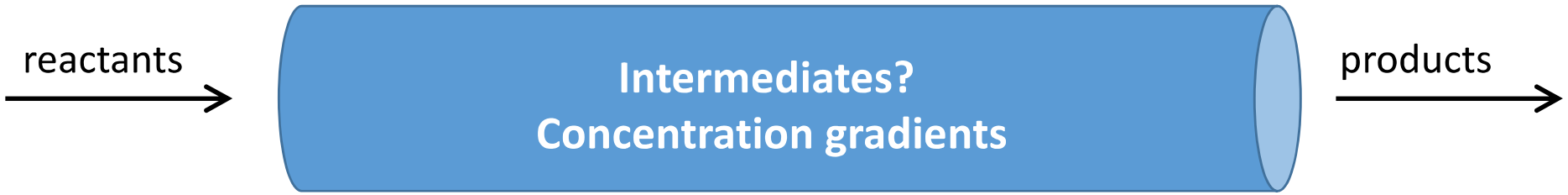
In situ spectroscopy

- Catalyst structure is a function of its environment
- Only structure measured under reaction conditions can give insight into activity
- Conversion changes the gas environment



Shiran Zhang; Luan Nguyen; Yuan Zhu; Sihui Zhan; Chia-Kuang (Frank) Tsung; Franklin (Feng) Tao; *Acc. Chem. Res.* **2013,** 46, 1731-1739.

What about a plug-flow reactor?



Catalyst structure is not necessarily the same everywhere in a reactor!!

Grundwaldt (2007) ; van Bokhoven (2010)

Catalyst characterization

- Structure of the catalyst *surface vs bulk*
- Structure of reaction intermediates

Points of care:

Spectator species *not everything one sees is active*

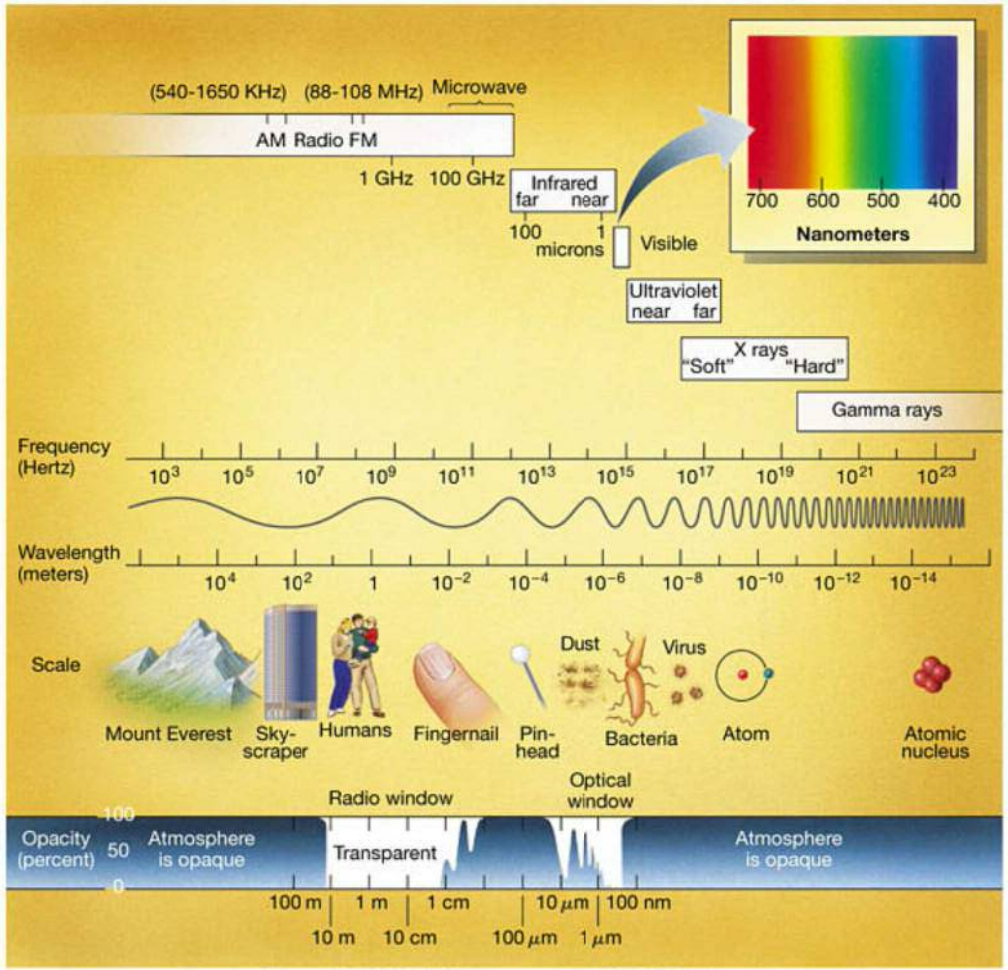
Short-lived species *the active intermediate may be short-lived*

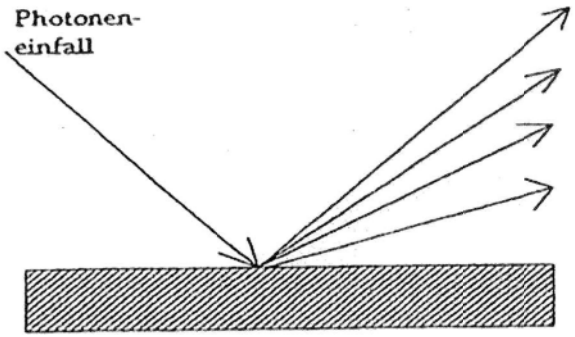
In situ / operando *catalyst structure changes with conditions*

Shining light on catalysts

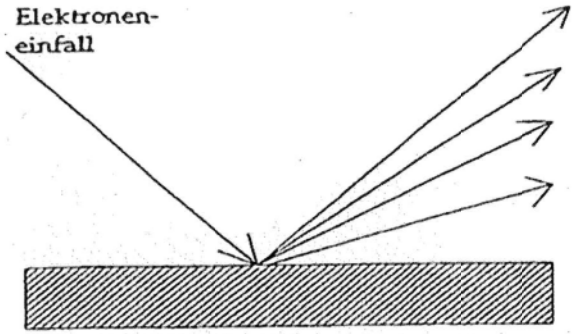
Catalyst characterization:

UVvis, infrared, XRD, TGA, TPD-MS, TPR/O, TEM, NMR, XPS, XAS, XES, … …

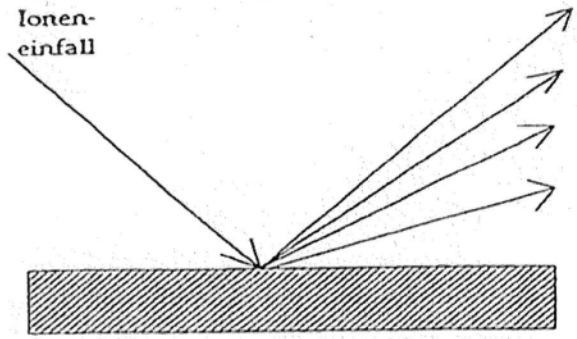




Photonen	IR-Absorption Ellipsometrie Raman-Spektroskopie XRF
Elektronen	XPS, ESCA
Ionen	
neutrale Teilchen	Photodesorption



Elektronen	LEED, HEED, RHEED, ILEED, AES, EELS
Photonen	CIS, APS, XRF
Ionen	EIID SEPSMS
neutrale Teilchen	EID SDMM



Elektronen	INS
Photonen	IIRS, PIXE
Ionen	ISS, SIMS
neutrale Teilchen	Sputtering

What is catalysis?
Why should they be characterized?
What characterization tools are needed?
Catalyst surface, bulk, adsorbates (intermediates)
The catalytic cycle: structure of the catalyst changes with gas environment
Catalytic cycle: (TON, TOF)