Temperature-programmed Methods in Catalysis Research

Procedures and pitfalls of a very commonly used tool

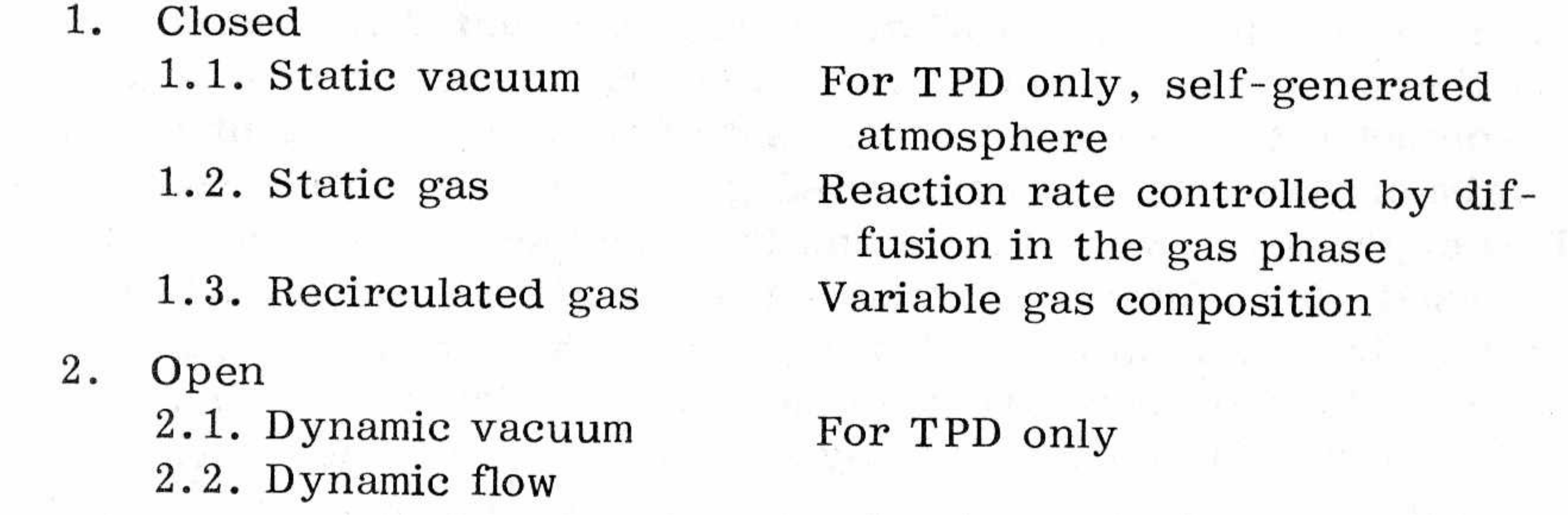
Definitions

- TPD: temperature-programmed desorption
- TPR: temperature-programmed reduction or
  - temperature programmed reaction
- TPO: temperature-programmed oxidation
- TPRS: temperature-programmed reaction spectroscopy

Methods

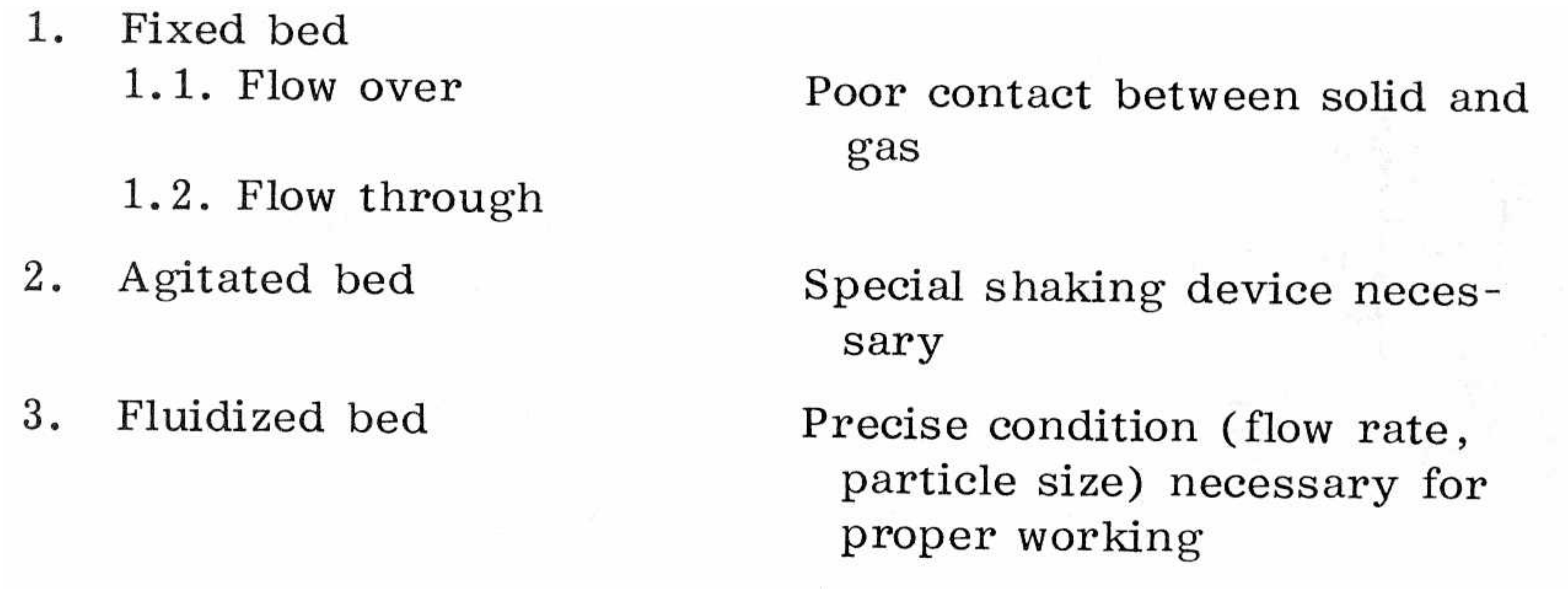
- TPD: a solid is first exposed to an adsorbate gas under well-defined conditions (wide range of pressure and temperature) and then heated under inert conditions with a temperature program:
  - parental method: Flash desorption from metal wires in UHV : G. Ehrlich, Adv. Catal., 1963
- All other methods keep solid and reactants in contact during temperatre-programmed processing
- TPD – TPRS most suitable designations

Atmospheres, Reactors and Detectors



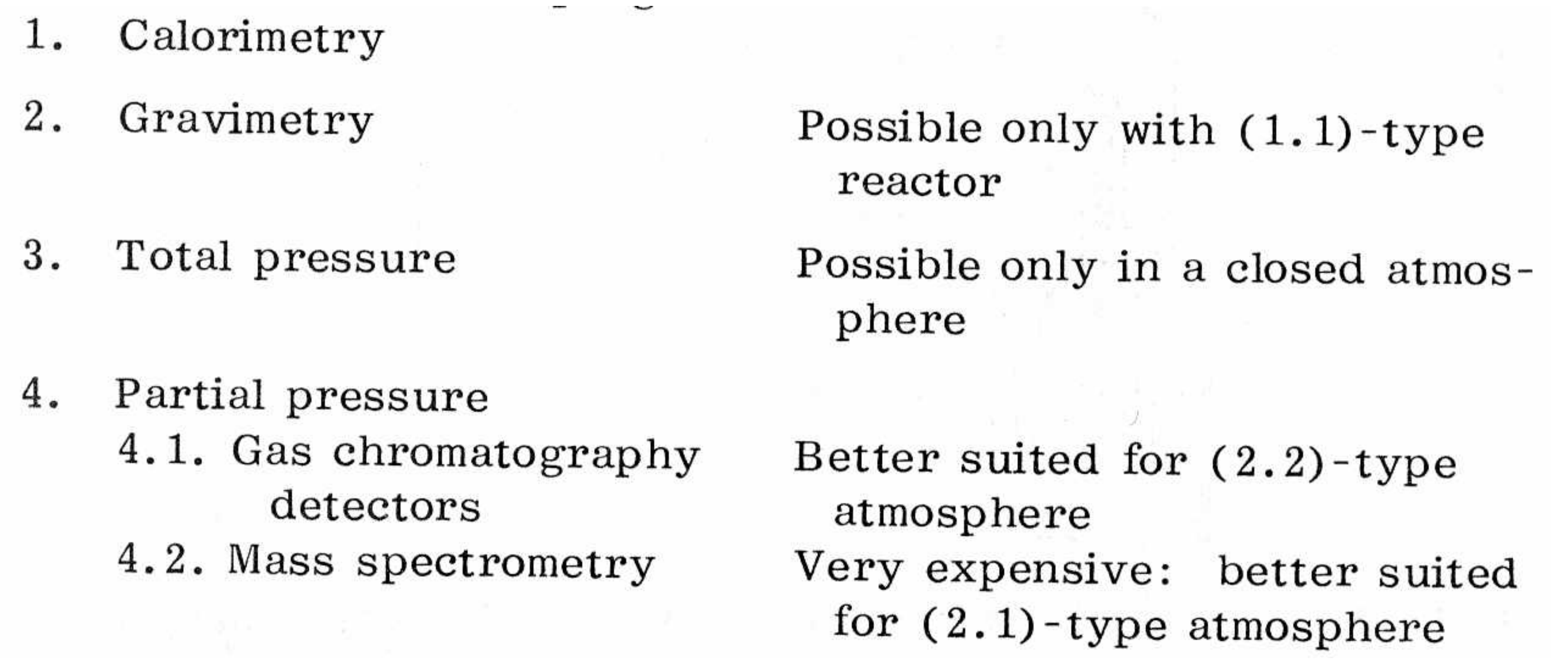
1. Closed	
1.1. Static vacuum	For TPD only, self-generated atmosphere
1.2. Static gas	Reaction rate controlled by diffusion in the gas phase
1.3. Recirculated gas	Variable gas composition
2. Open	
2.1. Dynamic vacuum	For TPD only
2.2. Dynamic flow	

Atmospheres, Reactors and Detectors



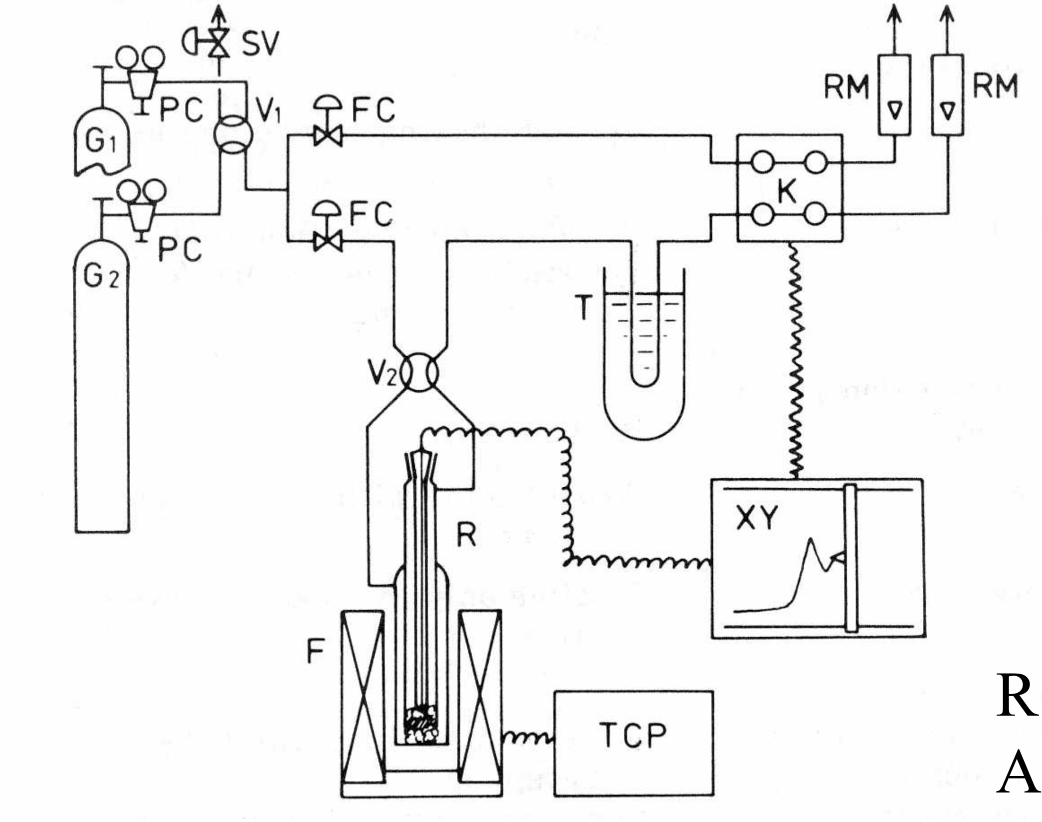
1. Fixed bed	
1.1. Flow over	Poor contact between solid and gas
1.2. Flow through	
2. Agitated bed	Special shaking device necessary
3. Fluidized bed	Precise condition (flow rate, particle size) necessary for proper working

Atmospheres, Reactors and Detectors



1. Calorimetry	
2. Gravimetry	Possible only with (1.1)-type reactor
3. Total pressure	Possible only in a closed atmosphere
4. Partial pressure	
4.1. Gas chromatography detectors	Better suited for (2.2)-type atmosphere
4.2. Mass spectrometry	Very expensive: better suited for (2.1)-type atmosphere

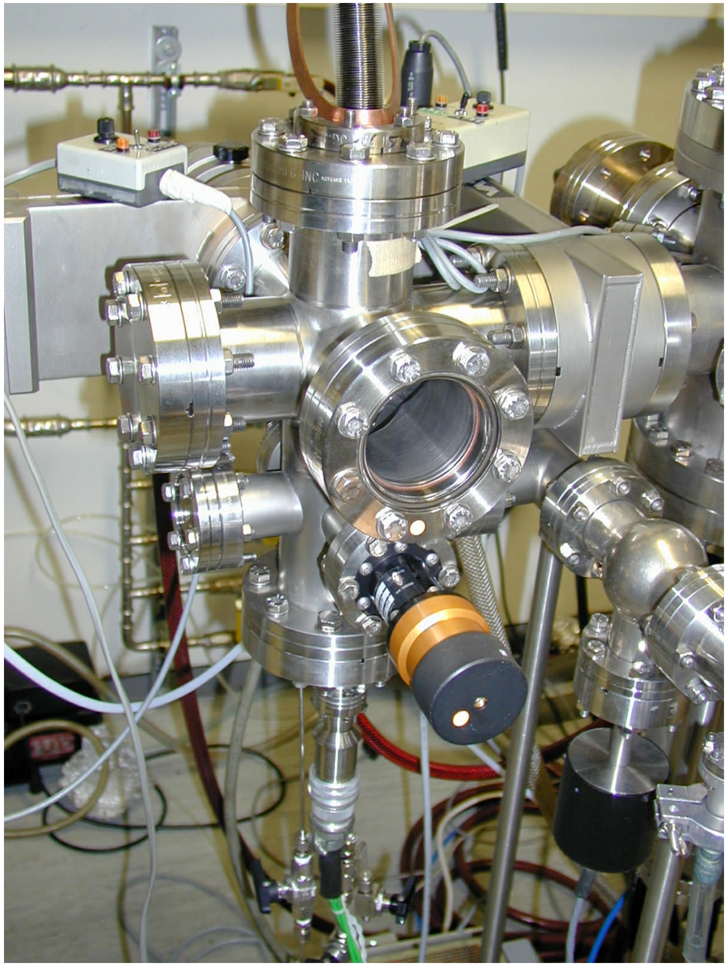
Experiment

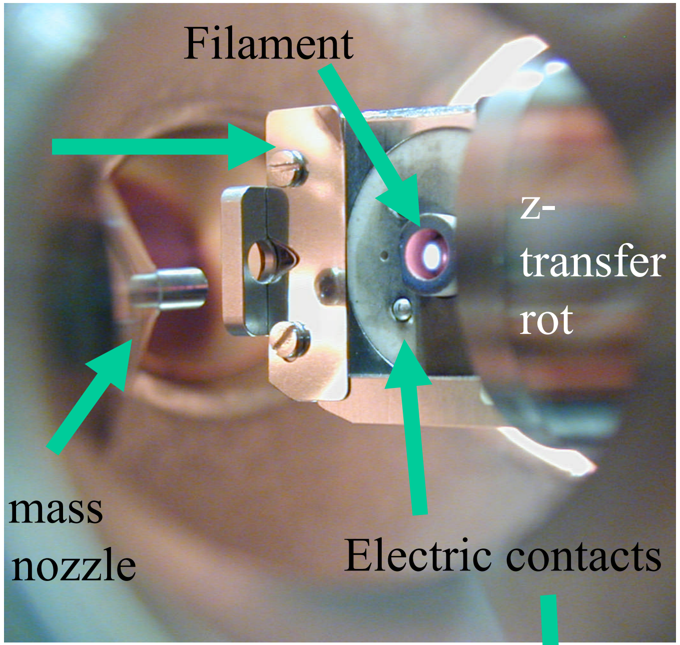


High-pressure variant with inert carrier G1 and reactant G2

R.N. Rogers,
Anal. Chem., 32, 672, (1960)

FHI-AC variable pressure TDS-reactor set-up





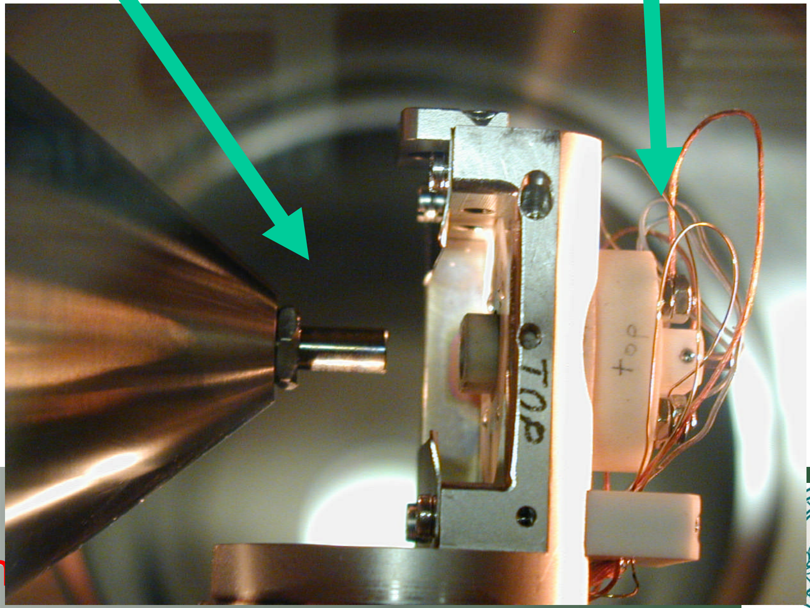
Metal clips

Filament

z-transfer rot

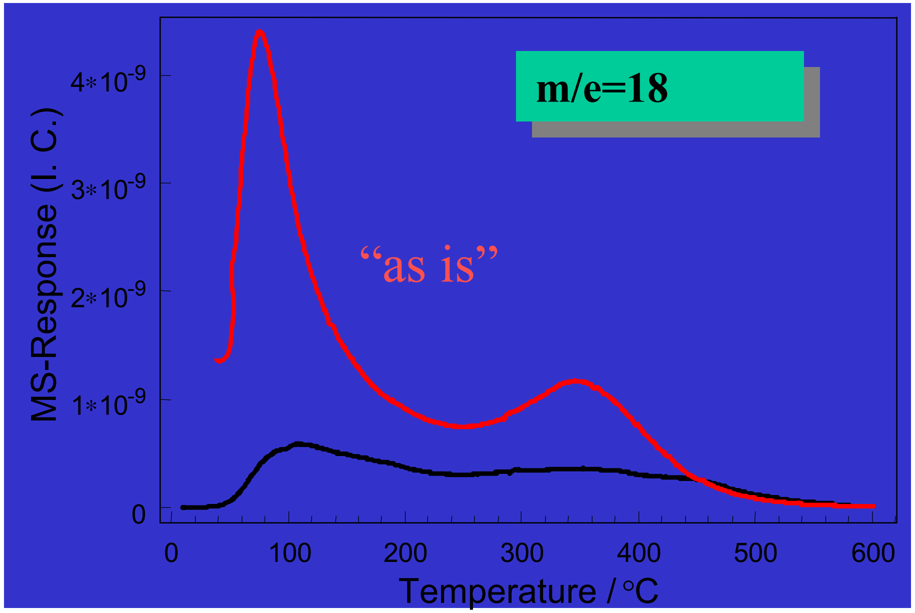
Line of sight mass spectrometer nozzle

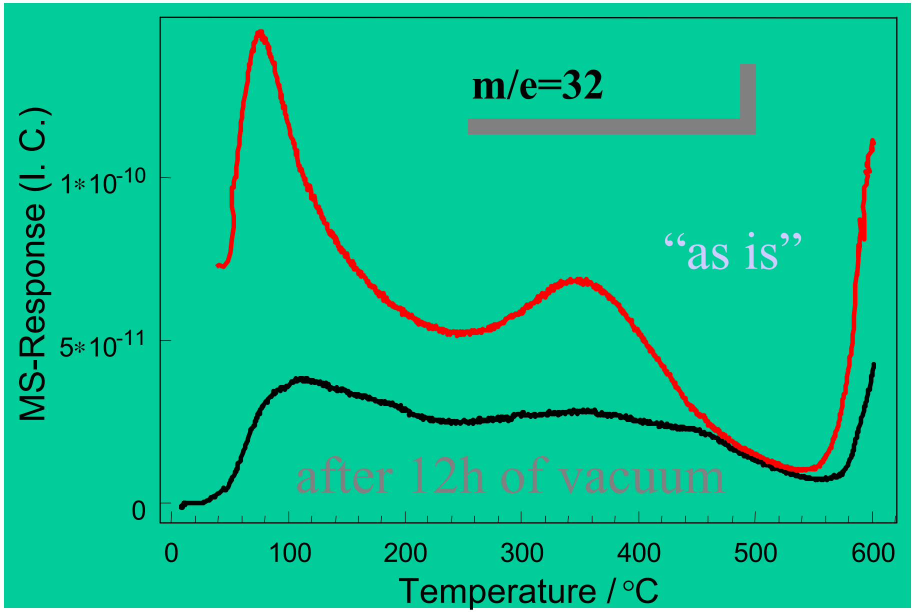
Electric contacts



Influence of Vacuum Treatment

Sample K47





Strong influence of vacuum treatment both for water and oxygen desorption traces Solid state dynamics!

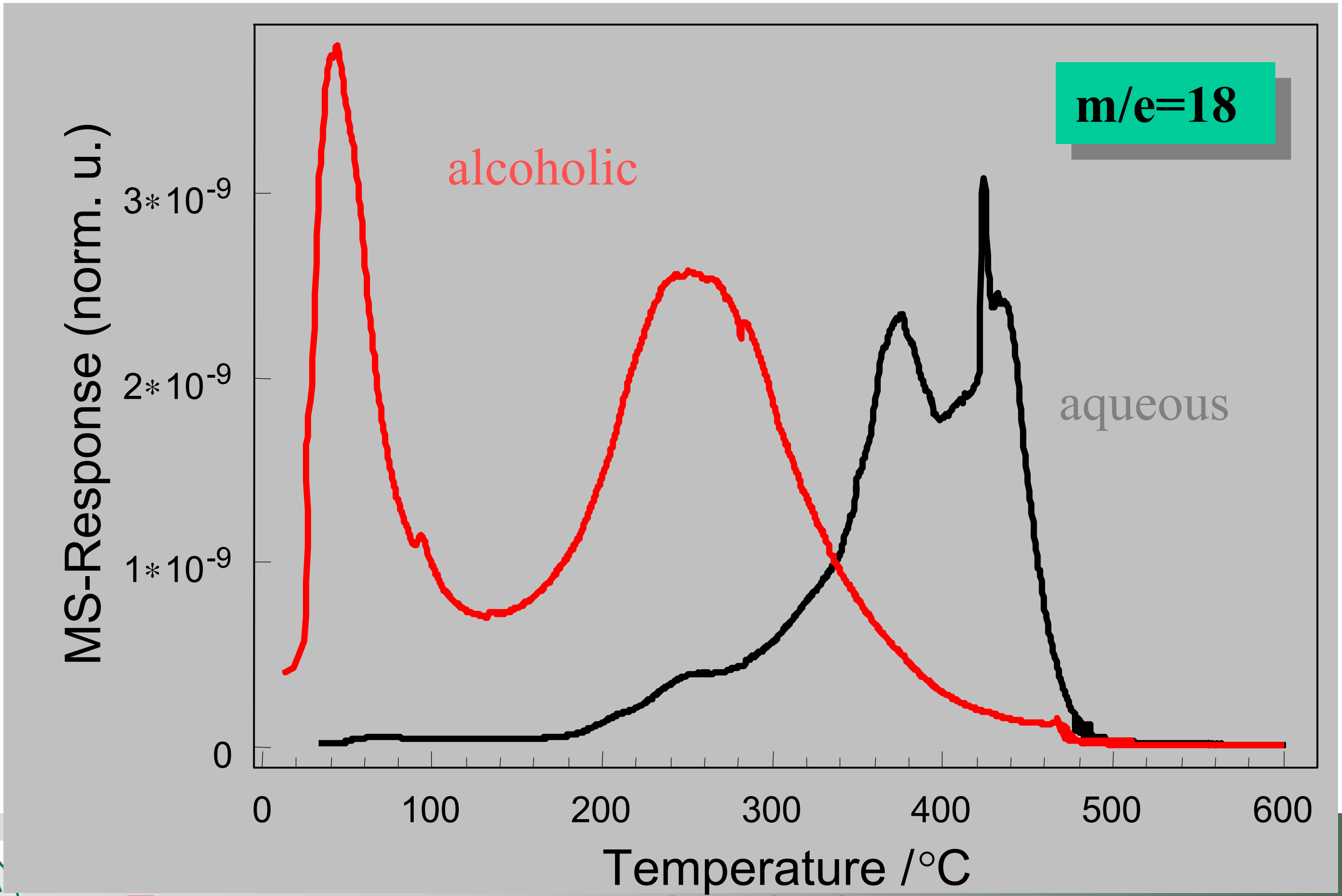
Assignment of relevant MS traces

Reaction study of sample “Partie 5010” (hemihydrate) after TDS treatment:

Molecule	**m/z fragments**
Butane	**43**, 27, 42, 41, 39
Butene	**41**, 39, 55, 27, 26
Butadiene	**39, 54, 27**
2,5-dihydro-Furan	**41, 70,** 39, 42, 27
Furan	**68, 39**
MSA	**26,** 54, 98

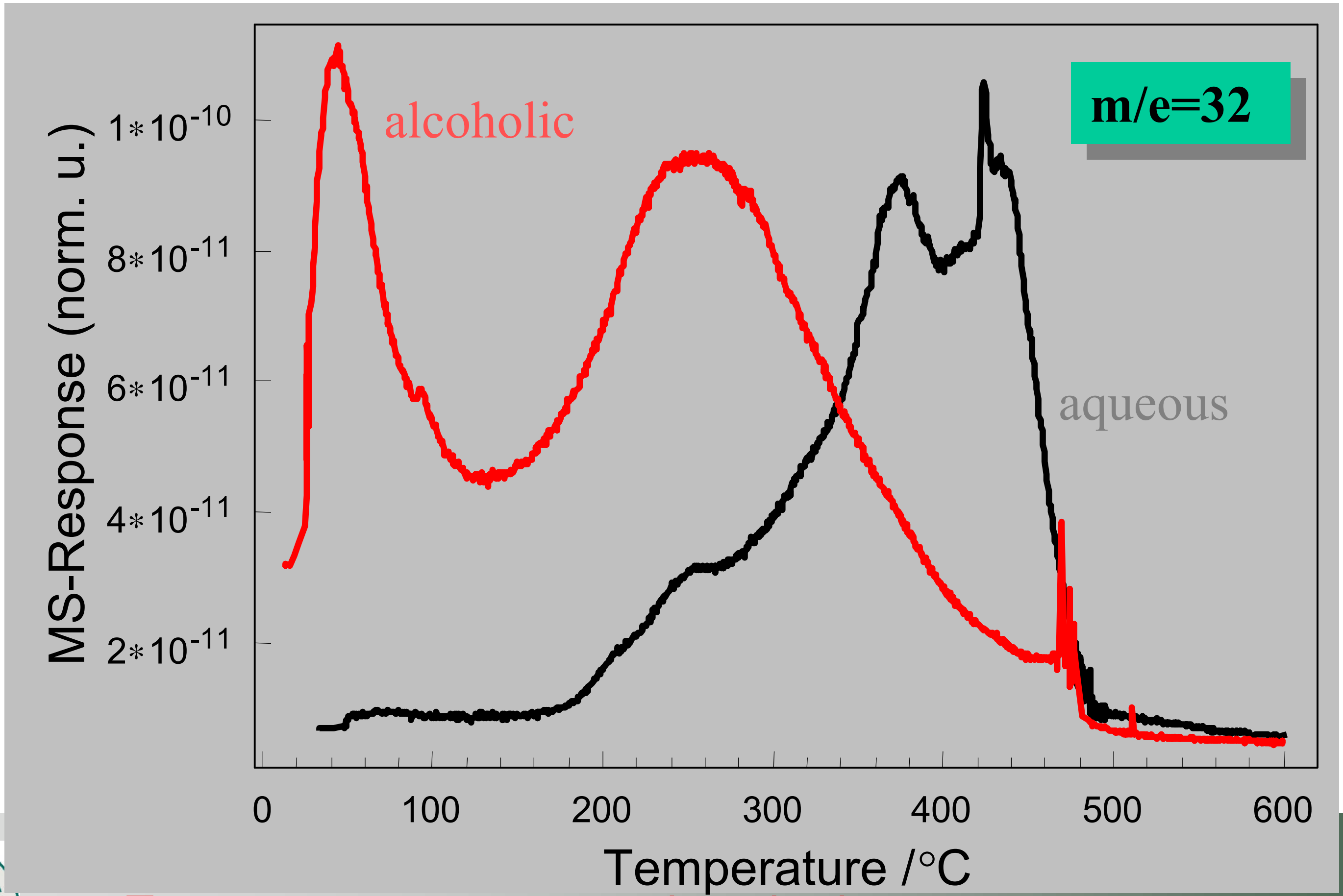
Aqueous vs Alcoholic preparation

Hemihydrate:



Aqueous vs Alcoholic preparation

Hemihydrate:



Aqueous vs Alcoholic preparation

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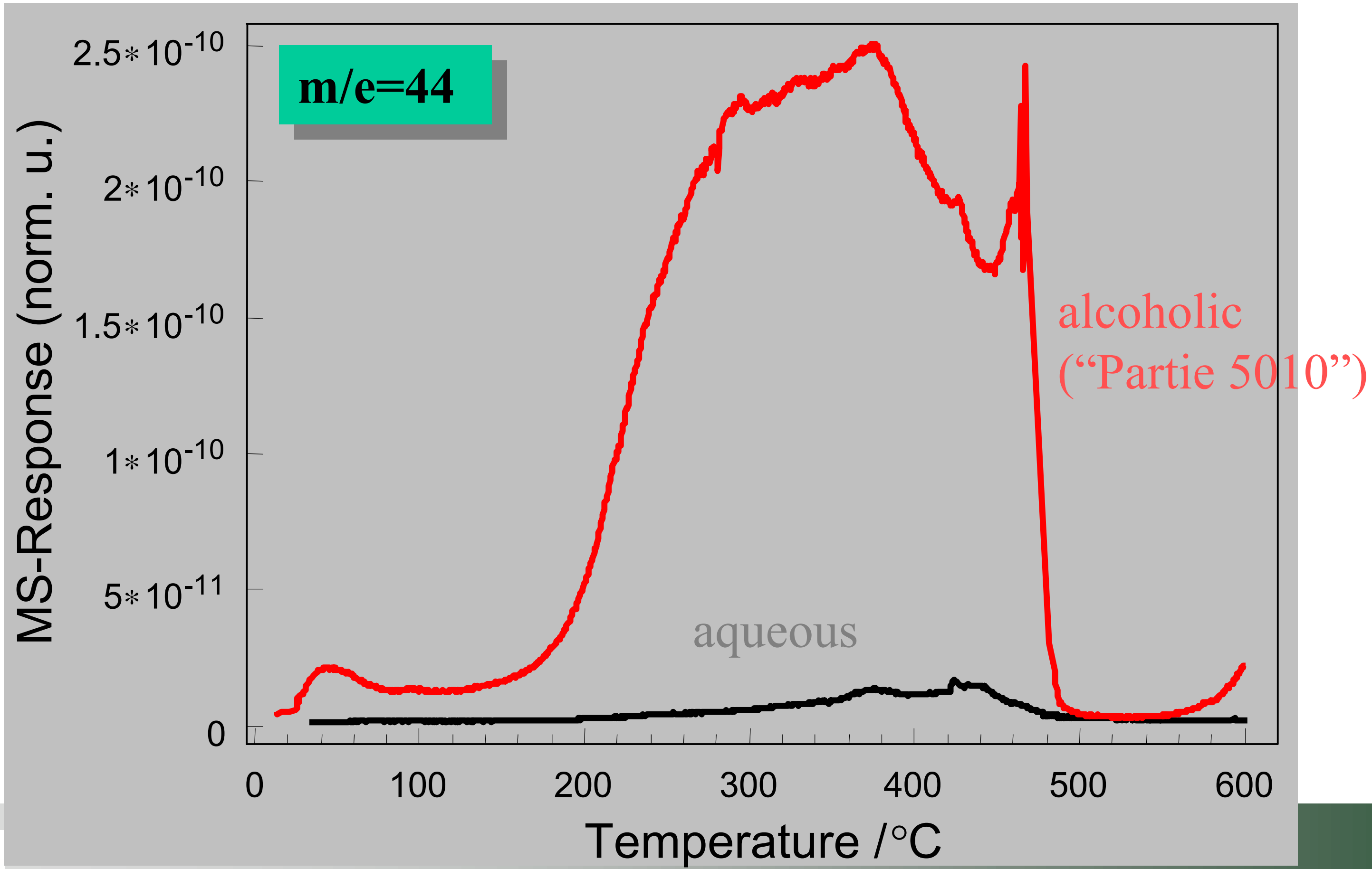
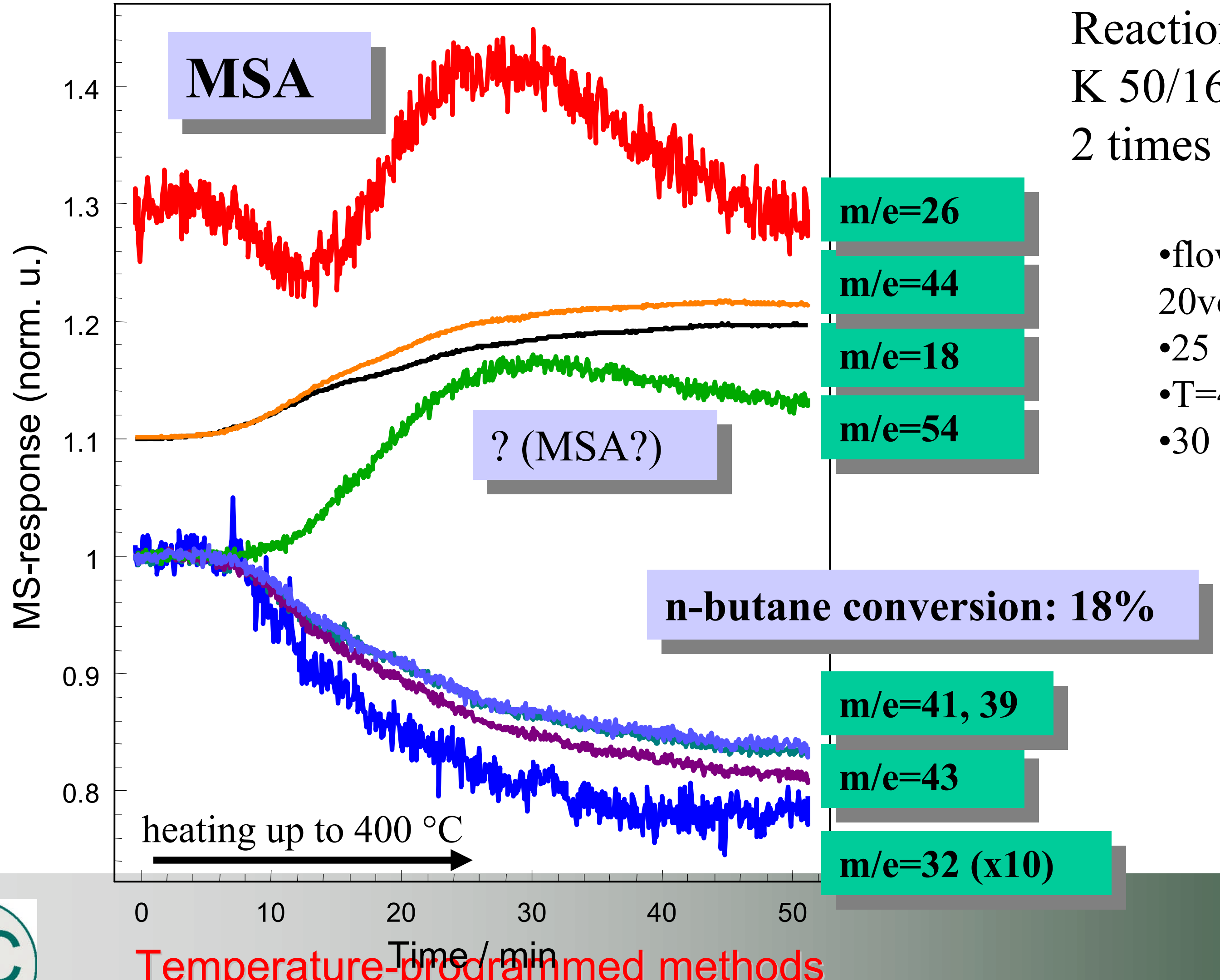


Temperature-programmed methods

Reactor Study

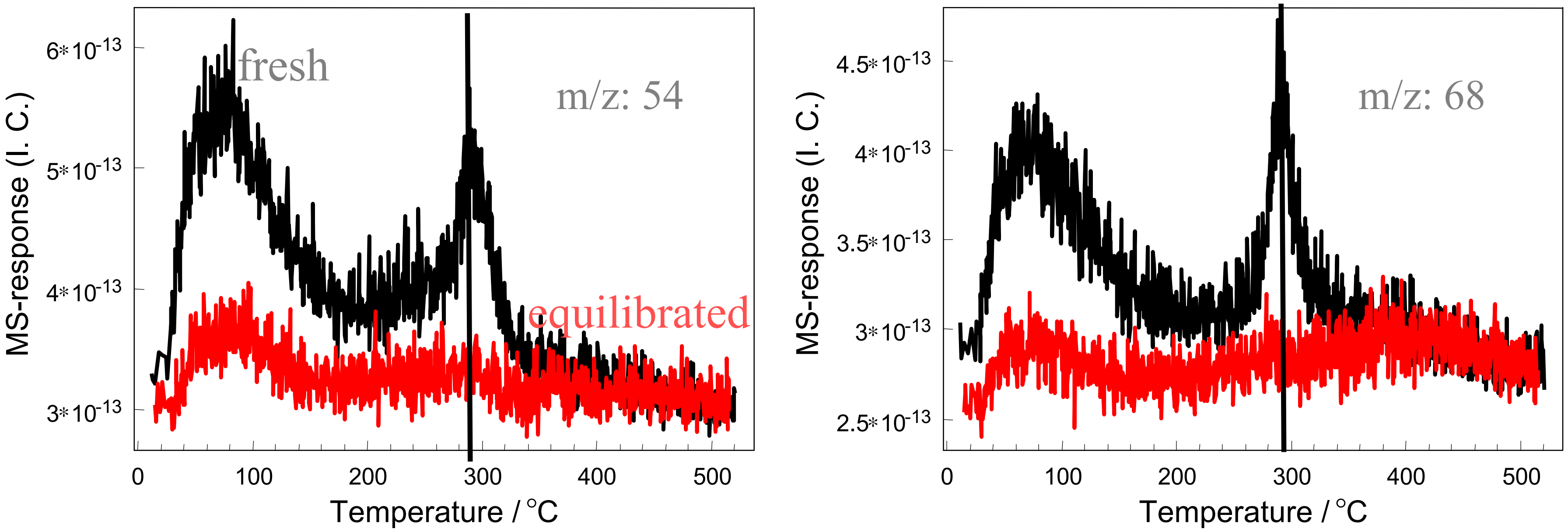


n-butane conversion: 18%

Reaction study of sample K 50/16 (fresh VPO) after 2 times TDS treatment:

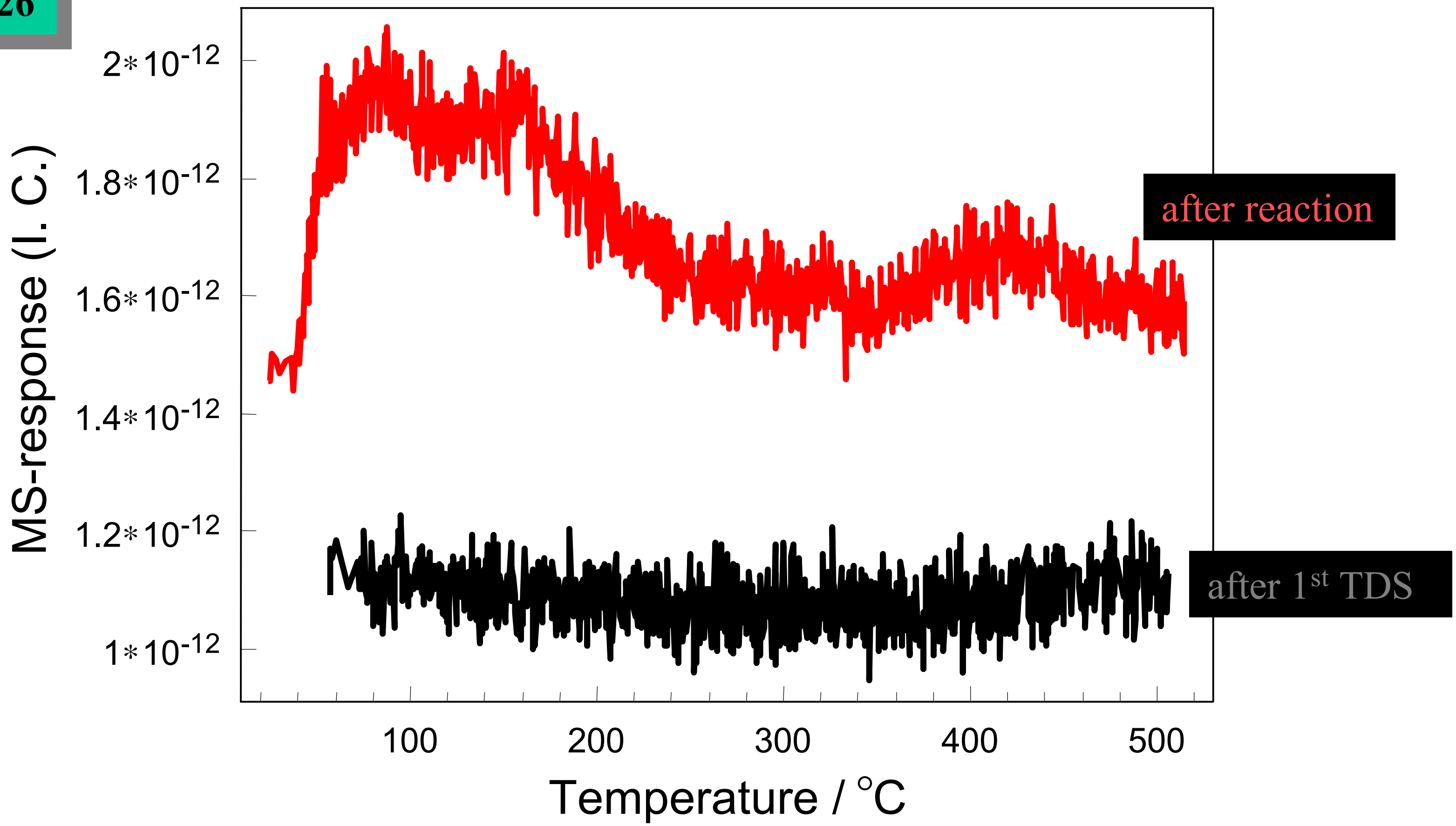
- flow of 0.7vol% n-C_4H_{10} / 20vol% O_2 / 79.3vol% He
- 25 ml/min @ 1bar
- T=400 °C
- 30 mg pellet

Comparison sample F8 “fresh” vs equilibrated

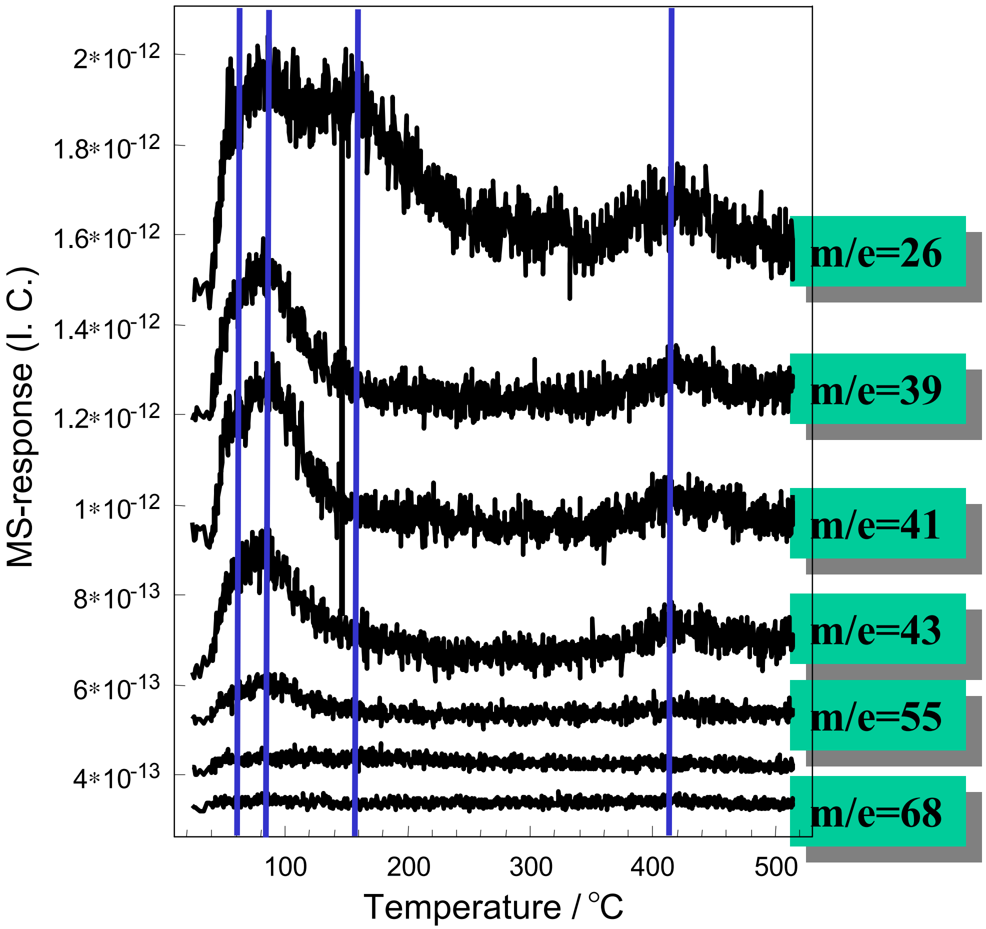


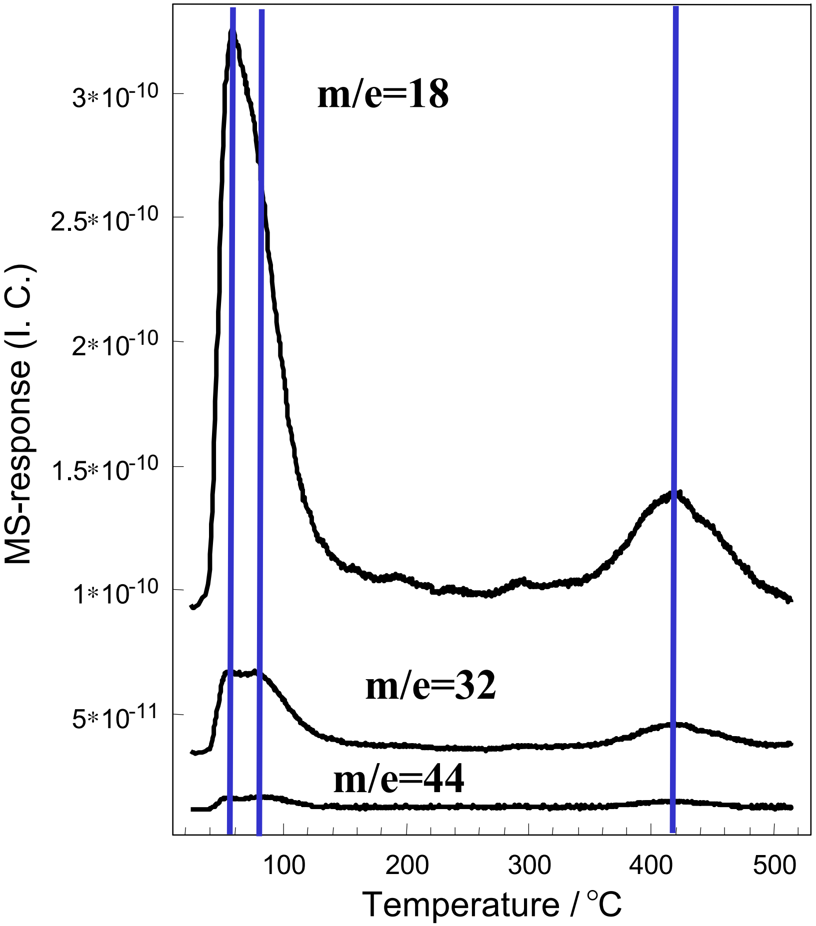
Desorption peak around 300 °C typical for non- conditioned VPO (compare to previous investigations); organics from synthesis

m/e=26



Desorption of organic fragments stemming not from synthesis after reaction (m/e=26: MSA?)





2 types of organic species: product, intermediate(s), no catalyst organics

gaps

- temperature-programmed methods are a prototype area for the existence of gaps between surface science and catalysis characterisation.
- often same methodology and data interpretation.
- but fundamental differences in boundary conditions.

TPD: a complex process

- The net rate of TPD is considered as the ration between adsorption and desorption
- in static condition: equilibrium
- in TPD: disturbance by pumping or gas flow
- boundary cases:
  - re-adsortion possible (thermodynamic control
  - re-adsortion suppresed (kinetic control) case of UHV TDS analysis

TPD and TDS: relation between surface science and catalysis charaterisation

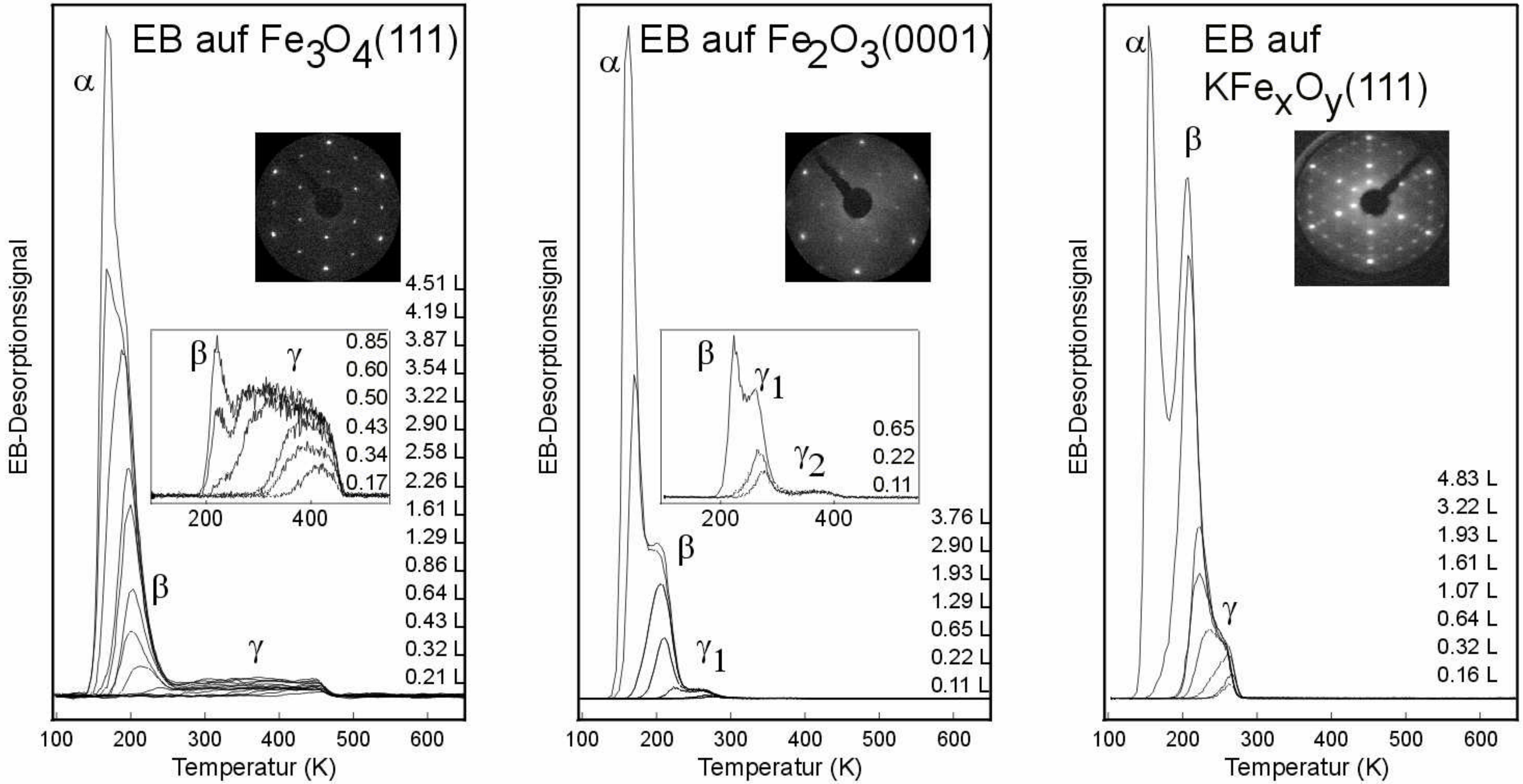
- TDS low pressure (probe situation)
- TDS: kinetic control, no re-adsorption, usually (tacitly) first order
- no clear distinction between sorptiopn and reaction
- TPD high pressure, reaction situation
- TPD: transition from kinetic to thermodynamic regime explicitely studied
- changeover in reaction process from sorption to reaction common

TDS: The method

- A pre-adsorbed species is removed from a well-defined surface by rapid heating (10 K/s) in a well-pumped UHV environment (no equilibration and re-adsorption) (caveat TMP!). (Langmuir unit!)
- Care must be taken to see only desorption from the surface!

Feulner and Menzel, J. Vac. Sci. Technol., 17, (1980), 662

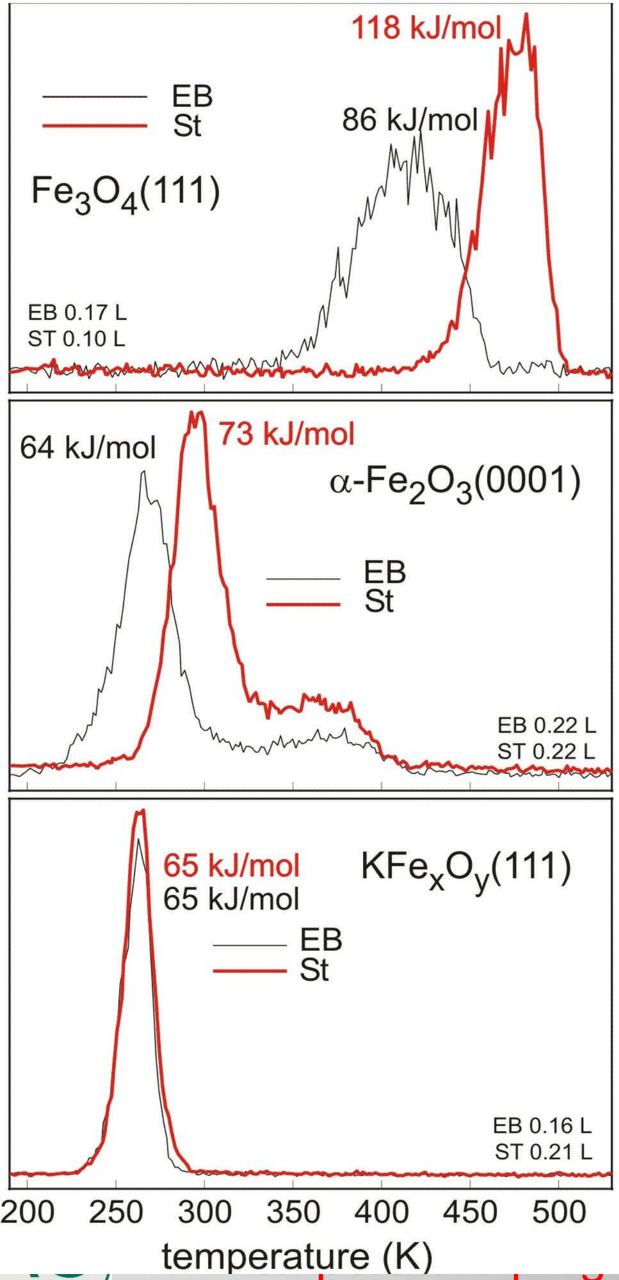
Ethylbenzol-TDS



Temperature programmed methods

Christian Kuhrs, Modellkatalyse, Abt. AC, Fritz-Haber-Institut (MPG), Berlin

Surface composition during reaction: kinetics



extrapolation to styrene synthesis conditions with Langmuir isotherms

$$\Theta(p,T) = \frac{b(T)\,p}{1-b(T)\,p} \qquad b = f(E_{des}, v, s)$$

	p=100 mbar, T=900 K		
	adsorption		coadsorption
	Θ_{EB}	Θ_{St}	$\Theta_{St} : \Theta_{EB}$
$Fe_3O_4(111)$	92%	100%	**250**
α-$Fe_2O_3(111)$	37%	29%	**0.8**
$KFe_xO_y(111)$	25%	6%	**0.2**

TDS: The observation

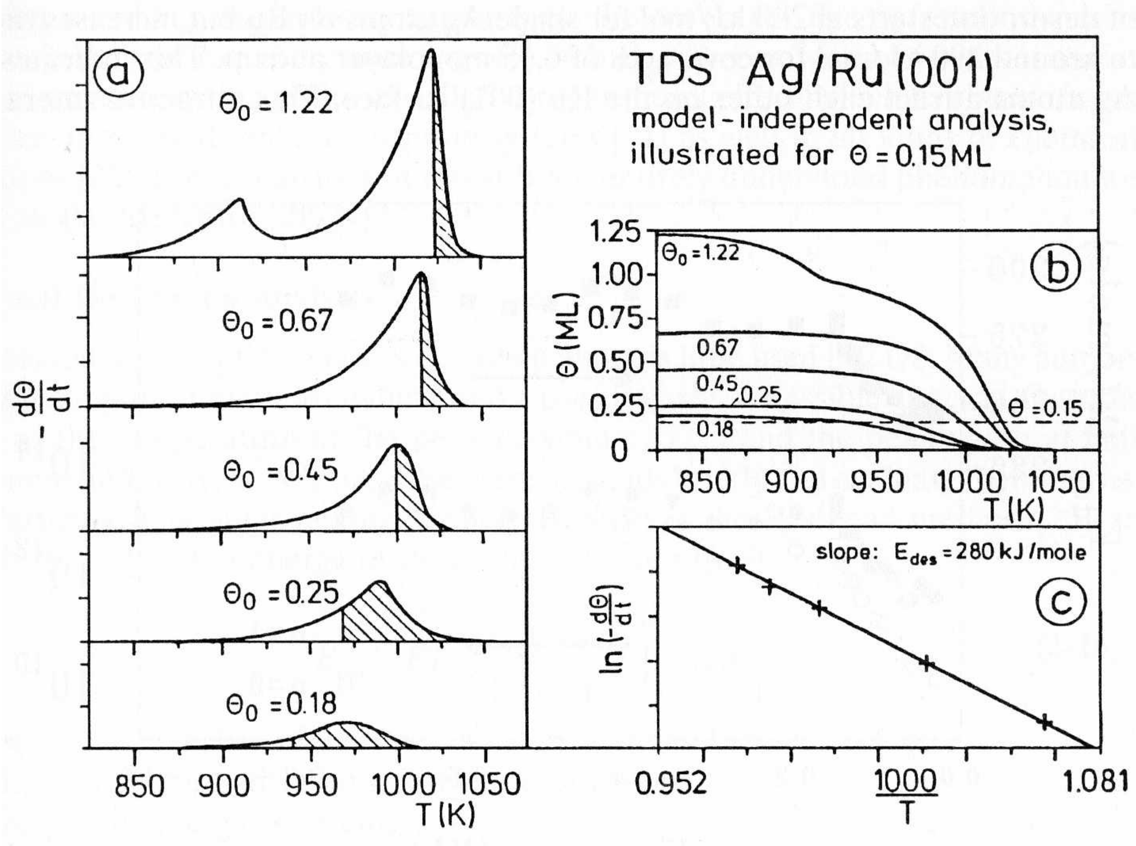
- rate of desorption:

$$r = \nu\,(\Theta)\,\Theta^{n} \exp\left[-E_{des}\,(\Theta)/RT\right]$$

r = desorption rate
n = desorption order
Θ= coverage in monolayers
ν = pre-exponential factor

ν can vary between 10^{13} and 10^{18} according to transition state

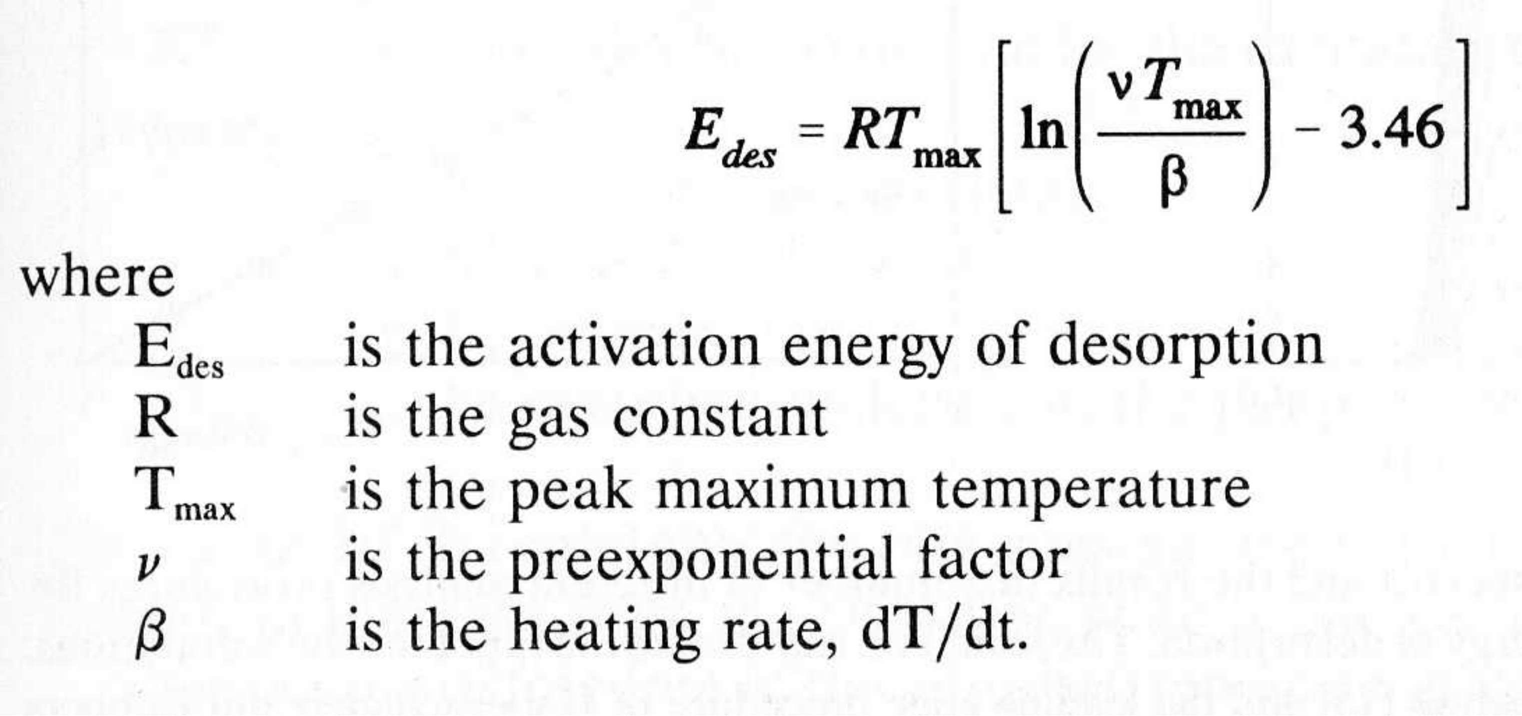
TDS: Complete analysis



Integration to chosen low desorption

Conventional analysis for activation energy

TDS: The cheap analysis



$$E_{des} = RT_{max}\left[\ln\left(\frac{\nu T_{max}}{\beta}\right) - 3.46\right]$$

where

E_{des}	is the activation energy of desorption
R	is the gas constant
T_{max}	is the peak maximum temperature
ν	is the preexponential factor
β	is the heating rate, dT/dt.

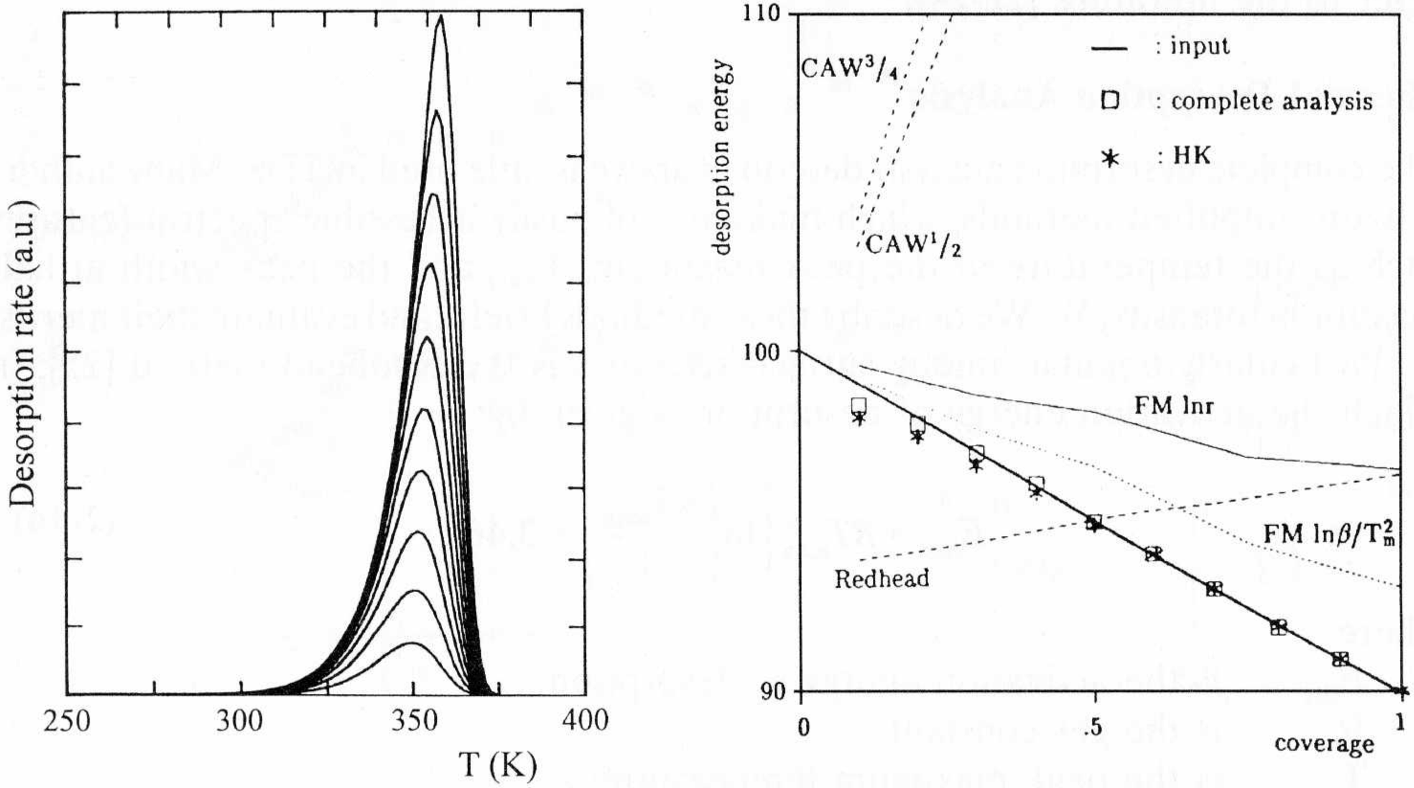
TDS: The “elaborate analysis”

$$E_{des} = RT_{max}\left[-1 + \sqrt{1 + 5.832\left(\frac{T_{max}}{W}\right)^2}\,\right] \quad for\ n = 1$$

$$\nu = \frac{E_{des}\,\beta}{RT_{max}}\, e^{E_{des}/RT^*}, \qquad T^* = 1\ K$$

Use width and peak desorption temperatures as
two parameters for finding activation energy and pre-factor

TDS: Quality of analysis



The basis of TPD

- Simplest case: A solid with adsorption sites S* gets in contact with a gas G of concentration C and populates in a first order process the vacant adsorption sites.
- Langmuir boundary conditions:
  - fixed number N of sites S* (F/cm^2)
  - constant adsorption enthalpy dH_a (and desorption enthalpy)
  - all parmetres are temperature-independent and coverage-independent

The basis of TPD

$$dN/dT = \quad p\, k\, n_a\, (N^*-N) - k_{nd}\, N$$

Langmuir model assuming the balance between competitive adsortion and desorption kinetics
as net effect: the ratio of the two kinetic constants and the adsorbate partial pressure p are the parameters.

$$k = \sigma\, (2\pi MRT)^{1/2}$$

The kinetic constant relate to the nature of the adsorbed species by
the molecular mass M (g/mol),
the specific molecular surface area (cm-²),
and the gas constant (J/Kmol)

The basis of TPD

$$p = C\,R\,T$$

The partial pressure relates to the gas concentration.

The TPD experiment requires the temperature dependencies of the sorption process: it is assumed that the process is thermally activated (not spontaneously occuring); only a fraction n_a will be adsorbed:

$$n_a \quad = A_a \exp(-E_a/RT)$$

$$k_d \quad = A_d \exp(-E_a/RT)$$ desorption process

The basis of TPD

The experiment produces a signal proportional to the change in gas concentration C with temperature

$$C = -S/F\ dN/dT$$

S denotes surface area in (cm^2/g), F the flow rate (cm^3(STP)/sg)

The experiment is time-programmed;
one obtains C as function of time t as initial observation data:

The basis of TPD

$$C(t) = \frac{S\,N\,k_d}{F + \sigma\,(RT/2\pi M)^{1/2}\,n_a\,(N^*-N)}$$

It is important to run the experiment strictly linear in temperature:

$T = T_0 + \beta T$ with β being the heating rate in (K/s)

n_a is the fraction of adsorbing molecules from the stream of species A and

Θ is the site occupancy: $\Theta = N/N^*$

Reaction rate: first order

$$C_{(T)} = \frac{S + N^* \, \Theta \, A_d \exp^{(-E_d/RT)}}{F + S \, N^* \, (1 - \Theta) \, \sigma \, (RT/2\pi M)^{1/2} \, A_a \exp^{(E_a/RT)}}$$

$$d\Theta/dT = - \frac{F}{S \, \beta \, N^*} \, C_{(T)}$$

One observes the concentration of the adsorbate C_T as function of sample temperature
and can relate this to the physically relevant change in surface coverage with temperature $d\Theta/dT$