Temperature programmed methods
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:
• All other methods keep solid and reactants in contact during temperature-programmed processing
• TPD – TPRS most suitable designations
Atmospheres, Reactors and Detectors

1. Closed
   1.1. Static vacuum
   1.2. Static gas
   1.3. Recirculated gas

2. Open
   2.1. Dynamic vacuum
   2.2. Dynamic flow

For TPD only, self-generated atmosphere
Reaction rate controlled by diffusion in the gas phase
Variable gas composition

For TPD only

Temperature-programmed methods
Atmospheres, Reactors and Detectors

1. Fixed bed
   1.1. Flow over
   1.2. Flow through

2. Agitated bed

3. Fluidized bed

   Poor contact between solid and gas

   Special shaking device necessary

   Precise condition (flow rate, particle size) necessary for proper working
Atmospheres, Reactors and Detectors

1. Calorimetry
2. Gravimetry
3. Total pressure
4. Partial pressure
   4.1. Gas chromatography detectors
   4.2. Mass spectrometry

Possible only with (1.1)-type reactor
Possible only in a closed atmosphere
Better suited for (2.2)-type atmosphere
Very expensive: better suited for (2.1)-type atmosphere
Experiment

High-pressure variant with inert carrier G1 and reactant G2

R.N. Rogers,
FHI-AC variable pressure TDS-reactor set-up

Line of sight mass spectrometer nozzle

Metal clips

Filament

z-transfer rot

Electric contacts

Temperature-programmed meth
Influence of Vacuum Treatment

Sample K47

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

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M. Hävecker, Electronic Structure, Dept. Inorganic Chemistry, Fritz-Haber-Institut (MPG), Berlin, Germany
Assignment of relevant MS traces

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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>m/z fragments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>43, 27, 42, 41, 39</td>
</tr>
<tr>
<td>Butene</td>
<td>41, 39, 55, 27, 26</td>
</tr>
<tr>
<td>Butadiene</td>
<td>39, 54, 27</td>
</tr>
<tr>
<td>2,5-dihydro-Furan</td>
<td>41, 70, 39, 42, 27</td>
</tr>
<tr>
<td>Furan</td>
<td>68, 39</td>
</tr>
<tr>
<td>MSA</td>
<td>26, 54, 98</td>
</tr>
</tbody>
</table>
Hemihydrate:

Temperature-programmed methods

M. Hävecker, Electronic Structure, Dept. Inorganic Chemistry, Fritz-Haber-Institut (MPG), Berlin, Germany
Aqueous vs Alcoholic preparation

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Hemihydrate:

Temperature-programmed methods

M. Hävecker, Electronic Structure, Dept. Inorganic Chemistry, Fritz-Haber-Institut (MPG), Berlin, Germany
Reaction study of sample K 50/16 (fresh VPO) after 2 times TDS treatment:

- Flow of 0.7vol% n-C₄H₁₀ / 20vol% O₂ / 79.3vol% He
- 25 ml/min @ 1bar
- T=400 °C
- 30 mg pellet

**n-butane conversion: 18%**

**MSA**
- m/e=26
- m/e=44
- m/e=18
- m/e=54
- m/e=41, 39
- m/e=43
- m/e=32 (x10)

**MSA?**

**heating up to 400 °C**
Comparison sample F8 “fresh” vs equilibrated

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

Temperature-programmed methods

M. Hävecker, Electronic Structure, Dept. Inorganic Chemistry, Fritz-Haber-Institut (MPG), Berlin, Germany
Desorption of organic fragments stemming not from synthesis after reaction (m/e=26: MSA?)

Temperature-programmed methods
2 types of organic species: product, intermediate(s), no catalyst organics

Temperature-programmed methods
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 ratio between adsorption and desorption
- in static condition: equilibrium
- in TPD: disturbance by pumping or gas flow
- boundary cases:
  - re-adsorption possible (thermodynamic control)
  - re-adsorption suppressed (kinetic control) case of UHV
  TDS analysis
TPD and TDS: relation between surface science and catalysis characterization

- TDS low pressure (probe situation)
- TDS: kinetic control, no re-adsorption, usually (tacitly) first order
- No clear distinction between sorption and reaction
- TPD high pressure, reaction situation
- TPD: transition from kinetic to thermodynamic regime explicitly 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

 EB auf Fe$_3$O$_4$(111) 

 EB auf Fe$_2$O$_3$(0001) 

 EB auf KFe$_x$O$_y$(111) 

 Christian Kuhrs, Modellkatalyse, Abt. AC, Fritz-Haber-Institut (MPG), Berlin
Surface composition during reaction: kinetics

extrapolation to styrene synthesis conditions with Langmuir isotherms

\[ \Theta(p, T) = \frac{b(T) p}{1 - b(T) p} \]

\[ b = f(E_{des}, v, s) \]

<table>
<thead>
<tr>
<th>p=100 mbar, T=900 K</th>
<th>adsorption</th>
<th>coadsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \Theta_{EB} )</td>
<td>( \Theta_{St} )</td>
</tr>
<tr>
<td>Fe(_3)O(_4)(111)</td>
<td>92%</td>
<td>100%</td>
</tr>
<tr>
<td>( \alpha )-Fe(_2)O(_3)(111)</td>
<td>37%</td>
<td>29%</td>
</tr>
<tr>
<td>KFe(_x)O(_y)(111)</td>
<td>25%</td>
<td>6%</td>
</tr>
</tbody>
</table>
TDS: The observation

- rate of desorption:

\[ r = v \Theta^n \exp \left[-\frac{E_{\text{des}}(\Theta)}{RT}\right] \]

- \( r \) = desorption rate
- \( n \) = desorption order
- \( \Theta \) = coverage in monolayers
- \( v \) = pre-exponential factor

\( v \) 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

Temperature-programmed methods
TDS: The cheap analysis

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

where
- \( E_{\text{des}} \) is the activation energy of desorption
- \( R \) is the gas constant
- \( T_{\text{max}} \) is the peak maximum temperature
- \( \nu \) is the preexponential factor
- \( \beta \) is the heating rate, d\( T/dt \).
TDS: The “elaborate analysis”

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

\[ \nu = \frac{E_{\text{des}}}{R T_{\text{max}}} \beta e^{E_{\text{des}}/RT^*}, \quad T^* = 1 \, \text{K} \]

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/cm²)
  – constant adsorption enthalpy dHₐ (and desorption enthalpy)
  – all parameters are temperature-independent and coverage-independent
The basis of TPD

\[
dN/dT = \rho \, k \, n_a \,(N^*-N) - k_{nd} \, N
\]

Langmuir model assuming the balance between competitive adsorption and desorption kinetics
as net effect: the ratio of the two kinetic constants and the adsorbate partial pressure \(\rho\) 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 occurring); only a fraction \( n_a \) will be adsorbed:

\[ n_a = A_a \exp \left( -\frac{E_a}{RT} \right) \]

\[ k_d = A_d \exp \left( -\frac{E_a}{RT} \right) \] desorption process
The basis of TPD

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

$$C = -\frac{S}{F} \frac{dN}{dT}$$

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

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:

\[ T = T_0 + \beta T \quad \text{with } \beta \text{ being the heating rate in (K/s)} \]

\[ n_a \text{ is the fraction of adsorbing molecules from the stream of species A and} \]

\[ \Theta = N/N^* \text{ is the site occupancy:} \]

Temperature-programmed methods
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 \(d\Theta/dT\)