Thermal Desorption Spectroscopy on powders

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Literature

- J.W. Niemantsverdriet, Spectroscopy in catalysis, Wiley, 2000
- Previous TDS seminars by D. Teschner, W. Ranke and D. Rosenthal

Surface Science 525 (2003) 184–196
J.M. Gottfried *, K.J. Schmidt, S.L.M. Schroeder, K. Christmann

Luis K. Ono and Beatriz Roldan Cuenya*
The idea behind TDS!

Adsorbed particles with different *binding energies* will desorb at different *temperature*.

A: Pre-adsorbed species
B: Removed from the surface by T
C: Detection of the desorbing species

**Linear heating ramp**

\[ T = T_0 + \beta_H t \]

For adsorption: \( T_0 = T_{ad} \)

**TDS signal / curve:**
Peaks can be analyzed, qualitatively and quantitatively!
Outline

1. Fundamentals of adsorption/desorption
2. Different TDS/TPD Setups
3. Curves and Evaluation methods
4. A new TDS setup: Between UHV and TPD!
5. Results and Limitations!
6. Summary
Fundamentals: Adsorption kinetics

Rate of Adsorption

\[ R_{\text{ads}} = S \times F \text{ in } 1/(m^2s) \]

Flux of incident molecules:

\[ F = \frac{P}{(2\pi mk_b T)^{1/2}} \]

Sticking probability:

\[ S = f(\theta) \cdot \exp\left(-\frac{E_a}{RT}\right) \]

Hertz-Knudsen equation:

Flux of incident molecules
Gibbs energy decreases for spontaneous processes, \( \Delta G < 0 \).

\[
\Delta G = \Delta H - T\Delta S
\]

Adsorption confines the gas to the surface: \( \Delta S < 0 \).

- for spontaneous adsorption \( \Delta H \) is negative (exothermic).
- for desorption extra energy is needed.

Reversibility: At microscopic scale depending on the energy, at macroscopic scale averaging in equilibrium.
Fundamentals: Desorption Kinetics

Polanyi-Wigner equation

\[ r_{des} = -\frac{d\Theta}{dt} = \nu_n \cdot \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \cdot \Theta^n \]

- \( E_{des} \): activation energy of desorption
- \( \Theta \): coverage
- \( \nu_{des} \): pre-exponential factor
- \( n \): order of desorption
Fundamentals: Desorption Kinetics

TPD curve represents the desorption rate

\[
r_{des} = -\frac{d\Theta}{dt} = \nu_n \cdot \exp\left(-\frac{\Delta E_{des}^{PW}}{RT}\right) \cdot \Theta^n
\]
Order of Desorption

0: rate independent of coverage; fast exchange with an “infinite” reservoir; e.g. evaporation, sublimation, surface species replenished from bulk

0.5: desorption occurs from the perimeter of i.e. a cluster/edge of a cluster

i) Zero-order kinetics:
- multilayer desorption
- unlimited supply of particles
- (no coverage dependence)
- common leading edges
Order of Desorption

1: classical molecular desorption: rate proportional to $\Theta^1$
2: associative desorption, the coverage of 2 species matters, mobility of 1 species is needed: rate proportional to $\Theta^2$

ii) First-order kinetics:
- unimolecular desorption
  $I(T) \sim$ no. of particles
  peak position independent of $\theta$
  asymmetric peak shape

iii) Second-order kinetics:
- recombinitive desorption
  $I(T) \sim$ no. of particles (no. of particles - 1) $\sim \theta^2$
  peak position shifts to lower $T$ with increasing $\theta$
  symmetric peak shape
  common trailing edges
The pre-exponential or frequency factor

Using transition state theory

\[ \nu_{\text{des}} = \kappa \frac{kT}{h} \frac{q_{\dagger}}{q_{\text{ad}}} = e\kappa \frac{kT}{h} \exp\left(\frac{\Delta S^\dagger}{R}\right) \]

\( \kappa \): transmission coefficient
\( k, h \): Boltzmann and Planck constants
\( q \): partition function of transition and adsorbed state
\( \Delta S^\dagger \): entropy of activation

If \( q_{\dagger}/q_{\text{ad}} = 1 \), \( \nu_{\text{des}} \approx 10^{13} \text{ s}^{-1} \) at RT
The pre-exponential or frequency factor

\[
\text{Molecular Desorption} \\
\begin{align*}
A^* & \rightarrow A + * \\
\text{Similar freedom for adsorbed and transition states} \\
\text{More rotational and translational freedom for transition state}
\end{align*}
\]

\[
r = A \left[ \exp \left( \frac{-E_a}{k_b T} \right) \right] \theta_A.
\]

\[
A = 10^{15}/s
\]

\[
A = 10^{16}/s
\]

\[
\text{Associative Desorption} \\
\begin{align*}
2A^* & \rightarrow A_2 + 2*
\end{align*}
\]

\[
r = A \left[ \exp \left( \frac{-E_a}{k_b T} \right) \right] (\theta_A)^2.
\]

\[
A = 10^8/s
\]

\[
A = 10^{11}/s
\]

\[
A = 10^{15}/s
\]

\[
A = 10^{16}/s
\]

Information from TPD curves

Parameters governing TDS peak $T$

- $E_{\text{des}}$
- Pre-exponential
- Coverage
- Desorption order
- Heating rate
Differential and integral methods for data analysis

Complete analysis, after King


Single TD-spectrum: Redhead’s analysis
(P.A. Redhead, Vacuum 12 (1963) 203)
Size Effects on the Desorption of O$_2$ from Au$_2$O$_3$/Au$^0$ Nanoparticles Supported on SiO$_2$: A TPD Study

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Ono and Roldan Cuenya

TABLE 1: Summary of the Kinetic Parameters [Desorption Order, Desorption Energy and Pre-exponential Factor] Obtained from Our O$_2$ TPD Measurements on ~5 nm (Sample #1) and ~1.5 nm (Sample #3) Au Nanoparticles Deposited on SiO$_2$ Using Different Analysis Methods$^a$

<table>
<thead>
<tr>
<th>sample</th>
<th>analysis method</th>
<th>desorption order (n)</th>
<th>desorption energy ($E_d$)</th>
<th>pre-exponential factor ($v_0$)</th>
<th>comments</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au NPs ~5 nm/SiO$_2$</td>
<td>Arrhenius</td>
<td>*n = 1</td>
<td>1.2 ± 0.1 eV</td>
<td>$1 \times 10^{10} \pm 1$ s$^{-1}$</td>
<td>$\theta_0 = 0.22$ ML $\beta = 0.1\sim 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.2 ± 0.1 eV</td>
<td>$4 \times 10^{10} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.22$ ML $\beta = 5$ K/s $T_{\max} = 555$ K</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redhead</td>
<td>*n = 1</td>
<td>1.5 eV</td>
<td>$1 \times 10^{13}$ s$^{-1}$</td>
<td>$\theta_0 = 0.22$ ML $\beta = 5$ K/s $T_{\max} = 555$ K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.4 eV</td>
<td>$1 \times 10^{13}$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.12$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>complete analysis</td>
<td>*n = 1</td>
<td>1.3 ± 0.1 eV</td>
<td>$1 \times 10^{11} \pm 1$ s$^{-1}$</td>
<td>$\theta_0 = 0.17$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.3 ± 0.1 eV</td>
<td>$6 \times 10^{10} \pm 1$ s$^{-1}$</td>
<td>$\theta_0 = 0.12$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HRV</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.5 ± 0.1 eV</td>
<td>$6 \times 10^{12} \pm 1$ s$^{-1}$</td>
<td>$\theta_0 = 0.04$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redhead</td>
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<td>1.3 ± 0.1 eV</td>
<td>$3 \times 10^{12} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.04$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.5 ± 0.1 eV</td>
<td>$5 \times 10^{11} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.12$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>complete analysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.5 ± 0.1 eV</td>
<td>$4 \times 10^{13} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.17$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>simulation</td>
<td>n = 1</td>
<td>1.5 eV</td>
<td>$1 \times 10^{13}$ s$^{-1}$</td>
<td>$\theta_0 = 0.22$ ML $\beta = 5$ K/s $T_{\max} = 555$ K</td>
<td></td>
</tr>
<tr>
<td>Au NPs ~1.5 nm/SiO$_2$</td>
<td>Arrhenius</td>
<td>n = 2</td>
<td>1.6 ± 0.1 eV</td>
<td>$7 \times 10^{14} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.31$ ML $\beta = 5$ K/s</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.7 ± 0.1 eV</td>
<td>$2 \times 10^{15} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.26$ ML $\beta = 0.7\sim 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redhead</td>
<td>*n = 2</td>
<td>1.5 eV</td>
<td>$1 \times 10^{13}$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.26$ ML $\beta = 5$ K/s $T_{\max} = 584$ K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.6 eV</td>
<td>$1 \times 10^{13}$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.26$ ML $\beta = 5$ K/s $T_{\max} = 584$ K</td>
<td></td>
</tr>
<tr>
<td></td>
<td>complete analysis</td>
<td>*n = 2</td>
<td>1.2 eV</td>
<td>$3 \times 10^{11} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.26$ ML $\beta = 5$ K/s $T_{\max} = 584$ K</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>1.3 eV</td>
<td>$3 \times 10^{12} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.26$ ML $\beta = 5$ K/s $T_{\max} = 584$ K</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>2.0 eV</td>
<td>$2 \times 10^{18} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.05$ ML $\beta = 5$ K/s</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>*n = 2</td>
<td>2.2 eV</td>
<td>$1 \times 10^{19} \pm 1$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.09$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>simulation</td>
<td>*n = 2</td>
<td>1.7 eV</td>
<td>$1.2 \times 10^{14}$ ML$^{-1}$ s$^{-1}$</td>
<td>$\theta_0 = 0.31$ ML $\beta = 5$ K/s</td>
<td></td>
</tr>
</tbody>
</table>

$^a$
Different **TDS/TPD** Setups!
Different TDS/TPD Setups!
Different Coverages in TPD

Graph showing time versus temperature with different coverage temperatures indicated.
Challenges for powder TDS/TPD

Powder: additional inhomogeneity from roughness: sites with different coordination to the substrate; desorption includes pore diffusion even in UHV.

During TPD with inert gas flow, pore diffusion an issue: peak form is largely affected by the rate of diffusion.
Challenges for powder TDS/TPD

1) Transport of the reactants from the fluid bulk to the boundary layer
2) Transport of the reactants to the surface
   a) through the boundary layer to the outer surface
   b) from the outer surface to the inner surface
3) Adsorption (chemisorption) of the reactant
4) Chemical reaction
5) Desorption of the product
6) Transport of the products to the fluid bulk
   a) from the inner surface to the outer surface
   b) from the outer surface through the boundary layer
7) Transport of the products from the boundary layer to the fluid bulk

Very frequently:
inner surface >> outer surface
A new TDS setup!
A new TDS setup!
A new TDS setup!

1. Sample has to be properly pre-treated: Activated / cleaned / reduced etc.
2. Adsorption process at dedicated T and t!
3. Bring from 1 bar to $2 \times 10^{-6}$ mbar!
4. Move MS to the end of the oven!
5. Start Desorption with constant heating rate!
Oxygen TDS on Ag powder

The pretreatment temperature (200-350 °C) shifts the desorption maximum to higher temperatures and new desorption events are created.
The only desorption event which is recovering belongs likely to oxygen dissolved in the Ag bulk invisible for supported samples.
Only one main de-sorption event is visible independent from the pre-treatment temperature.
High quality powder TDS data

- Ag/Al$_2$O$_3$ catalyst
- Ag powder
- Ag/SiO$_2$ nano

Graph showing the intensity of m/z 32 over temperature (T in °C) for different samples.
Adapted Polanyi-Wigner Equation

\[
\ln \left( \frac{\beta}{T_m^2} \right) = \ln \left( \frac{R A_{des} n_m^{n-1}}{E_{des}} n \Theta_m^{n-1} \right) - \frac{E_{des}}{RT_m}
\]

HRV Analysis

(Heating rate variation)
Determination of activation energy for oxygen desorption based on Polanyi-Wigner.

\[
E_{\text{des}} = 51.9 \text{ kJ/mol}
\]

Ag(111): \( E_{\text{des}} = 51.9 \text{ kJ/mol} \)

“Simple” surfaces:
Suggestive: Number of consecutively adsorbing/desorbing species. BUT!

Qualitatively: Distinction of chemisorbed, physisorbed, condensed species

Quantitative: Evaluation of coverages possible; evaluation of $E_d$, $\nu_n$ and $n$ difficult, many parameters. But still possible.

“Complex” surfaces:
Mostly only qualitative evaluation.
Summary from previous TDS lectures

“Simple” surfaces and “simple model” (Polanyi-Wigner-equation):

**Suggestive:** Number of consecutively adsorbing species

**Qualitatively:** Distinction of chemisorbed, physisorbed, condensed species

**Quantitative:**
- Evaluation of coverages possible;
- Evaluation of $E_d$, $\nu_n$ and $n$ difficult, many parameters

“Complex” surfaces and order-disorder phenomena:
- So far only qualitative evaluation or more complex model with readsoption and diffusion necessary.

See above, quantitative information are extracted!!