Modern Methods in Heterogeneous Catalysis Research

Thermal analysis methods

Rolf Jentoft

03.11.06
Outline

• Definition and overview
• Thermal Gravimetric analysis
• Evolved gas analysis (calibration)
• Differential Thermal Analysis/DSC
• Kinetics introduction
• Data analysis examples
Definition

Thermal analysis:
the measurement of some physical parameter of a system as a function of temperature.

Usually measured as a dynamic function of temperature.
Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods
Thermogravimetric

Developed by Honda in 1915

- Oven
- Sample
- Balance

Oven heated at controlled rate
Temperature and Weight are recorded
Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods
First introduced by Le Chatelier in 1887, perfected by Roberts-Austen 1899

**DTA/DSC**

Sample    Reference

Oven heated at controlled rate

Temperature and temperature difference are recorded
Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods
Dilometry (DIL)

Dilometry: change in length with temperature
DIL of “Green” and Sintered Yttria-stabilized Zirconia
TMA and DMA

Dynamic mechanical analysis:
change in mechanical properties with temperature while under dynamic stress
Glass transition starts at 75°C. The storage modulus decreased from approx. 4,200 MPa to 200 MPa.

$E'$ is storage modulus
$E''$ is loss modulus
$\delta$ is the phase lag
Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods
Dielectric analysis

Change in conductivity with temperature
Types of thermal analysis

- TG (Thermogravimetric) analysis: weight
- DTA (Differential Thermal Analysis): temperature
- DSC (Differential Scanning Calorimetry): temperature
- DIL (Dilatometry): length
- TMA (Thermo Mechanical Analysis): length (with strain)
- DMA (Dynamic-Mechanical Analysis): length (dynamic)
- DEA (Dielectric Analysis): conductivity
- Thermo Microscopy: image
- Combined methods
Sintering of W 1600-2700 °C
TGA with Optical Window

FIG. 2. Detail showing the TGA furnace, its side tube, and the optical window that allows direct observation of reacting particles placed in the sample pan.

FIG. 7. Sequence of digital images showing the size and shape changes of two pyrolyzing coal particles at several reactor temperatures. The particles are separated on the pan by a platinum wire mesh.

Matzakos and Zygourakisa Rev. Sci. Instrum. 64 (6), June 1993, 1541-48
TG analysis

Thermolysis curve
Pyrolysis curve
Thermogram
Thermogravimetric curve
Thermogravigram
Thermogravimetric analysis curve
TG curve

\[ A \text{ (Solid)} \rightarrow B \text{ (Solid)} + C \text{ (Gas)} \]

Information obtained depends on procedure
Not fundamental property
TG analysis: uses

1) Thermal decomposition of substances (calcination and heat treatment and polymer stability)
2) Corrosion of metals
3) Determination of moisture, volatiles, and ash content
4) Evaporation rates and sublimation
5) Distillation and evaporation of liquids
6) Reaction kinetics studies
7) Compound identification
8) Heats of vaporization and vapor pressure determinations
TG curve: Instrumental effects

Furnace heating rate

Slower heating = better resolution

Usually,
Higher heating rate = shift to higher temperature

Figure II.2. Effect of heating rate on the TG curves of Ca₃C₂O₄·H₂O (15). Sample 14.8 mg; dynamic He atmosphere at 150 ml/min.
TG curve: Instrumental effects
Furnace gas atmosphere

\[
\begin{align*}
A \text{ (solid)} & \rightarrow B \text{ (solid)} + C \text{ (gas)} \\
A \text{ (solid)} & \leftrightarrow B \text{ (solid)} + C \text{ (gas)} \\
A \text{ (solid)} + B \text{ (gas)} & \rightarrow C \text{ (solid)} \\
A \text{ (solid)} + B \text{ (gas)} & \leftrightarrow C \text{ (solid)} \\
A \text{ (solid)} + B \text{ (gas)} & \rightarrow C \text{ (solid)} + D \text{ (gas)} \\
A \text{ (solid)} + B \text{ (gas)} & \leftrightarrow C \text{ (solid)} + D \text{ (gas)}
\end{align*}
\]

\[
\begin{align*}
\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \text{ (s)} & \leftrightarrow \text{CaC}_2\text{O}_4 \text{ (s)} + \text{H}_2\text{O} \text{ (g)} \\
\text{CaC}_2\text{O}_4 \text{ (s)} & \rightarrow \text{CaCO}_3 \text{ (s)} + \text{CO} \text{ (g)} \text{ (in N}_2\text{)} \\
\text{CaC}_2\text{O}_4 \text{ (s)} + \frac{1}{2} \text{O}_2 \text{ (g)} & \rightarrow \text{CaCO}_3 \text{ (s)} + \text{CO}_2 \text{ (g)} \text{ (in O}_2\text{)} \\
\text{CaCO}_3 \text{ (s)} & \leftrightarrow \text{CaO} + \text{CO}_2 \text{ (g)}
\end{align*}
\]

Solid line in nitrogen, dashed line in oxygen
TG curve: Instrumental effects
Furnace gas atmosphere

\[
\begin{align*}
\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O} \ (s) & \leftrightarrow \text{CaC}_2\text{O}_4 \ (s) + \text{H}_2\text{O} \ (g) \\
\text{CaC}_2\text{O}_4 \ (s) & \rightarrow \text{CaCO}_3 \ (s) + \text{CO} \ (g) \ (\text{in } \text{N}_2) \\
\text{CaC}_2\text{O}_4 \ (s) + \frac{1}{2} \text{O}_2 \ (g) & \rightarrow \text{CaCO}_3 \ (s) + \text{CO}_2 \ (g) \ (\text{in } \text{O}_2) \\
\text{CaCO}_3 \ (s) & \leftrightarrow \text{CaO} + \text{CO}_2 \ (g)
\end{align*}
\]
TG curve: Instrumental effects
Furnace configuration

Dehydration of CaC$_2$O$_4$.H$_2$O, (dashed line, single crystal)
TG curve: Instrumental effects

Measurements may have a significant change in weight due to changes in gas density and viscosity.
TG curve: Sample effects

Crucible type

Mass transport by flow ($\Delta P$) and diffusion ($\Delta C$)

\[
\begin{align*}
A \text{ (solid)} & \rightarrow B \text{ (solid)} + C \text{ (gas)} \\
A \text{ (solid)} + B \text{ (gas)} & \rightarrow C \text{ (solid)} \\
A \text{ (solid)} + B \text{ (gas)} & \rightarrow C \text{ (solid)} + D \text{ (gas)}
\end{align*}
\]

- Thin layer vs. Large amount of sample
- Detection limit vs. Diffusion limitation
- Self generated atmosphere
TG curve: Sample effects
Thermal conductivity and particle size

Large particles and low thermal conductivity can effect results

<table>
<thead>
<tr>
<th>Material</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure metals</td>
<td>30–400</td>
</tr>
<tr>
<td>Alloys</td>
<td>14–160</td>
</tr>
<tr>
<td>Al₂O₃ (sintered)</td>
<td>25–35</td>
</tr>
<tr>
<td>Powders</td>
<td>0.1–0.8</td>
</tr>
<tr>
<td>(Particle size: 0.1–0.4 mm)</td>
<td></td>
</tr>
<tr>
<td>Glasses</td>
<td>0.7–1.4</td>
</tr>
<tr>
<td>Pyrex glass</td>
<td>1.12</td>
</tr>
<tr>
<td>Plastics</td>
<td>0.15–0.35</td>
</tr>
<tr>
<td>Liquids</td>
<td>0.1–0.6</td>
</tr>
<tr>
<td>Water</td>
<td>0.6</td>
</tr>
<tr>
<td>Gases (inorganic)</td>
<td>0.01–0.17</td>
</tr>
<tr>
<td>Air</td>
<td>0.02</td>
</tr>
</tbody>
</table>
TG curve: Sample effects
Diffusion limitation
Evolved gas analysis

• Single thermal analysis method may not be sufficient to understand changes in sample

• Control of gas phase requires analysis of gas phase

• Mass spectrometry and Infra-red analysis

• Transfer of gas to analytical instrument

• Calibration of the gas analysis technique
Evolved gas analysis: Pulse Calibration

Inject known volume of gas into TG under measurement conditions
Integrate peak in MS
Response factor is moles gas divided by area of peak
Thermal analysis: crucibles

The best type of crucibles are disposable crucibles.

Crucible selection criteria (size and material):

- Temperature range
- Chemical compatibility
- Detection limits
- Gas exchange characteristics

Crucible cleaning

Mechanical cleaning not recommended.
## Thermal analysis: crucibles

<table>
<thead>
<tr>
<th>Calibration substance</th>
<th>Cyclopentane</th>
<th>Water</th>
<th>Gallium</th>
<th>Indium</th>
<th>Tin</th>
<th>Lead</th>
<th>Zinc</th>
<th>Lithium sulfate</th>
<th>Aluminum</th>
<th>Silver</th>
<th>Gold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corundum, Al₂O₃</td>
<td>☐</td>
<td>☐</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Boron nitride, BN</td>
<td>☐</td>
<td>☐</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Graphite, C</td>
<td>☐</td>
<td>☐</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Silicate glass</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Quartz glass, SiO₂</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>?</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Aluminum, Al</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Aluminum, oxidized</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Silver, Ag</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Gold, Au</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Nickel, Ni</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Iron, Fe</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Stainless steel</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Platinum, Pt</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Molybdenum, Mo</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tantalum, Ta</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tungsten, W</td>
<td>☐</td>
<td>☐</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

+ : No solubility and influence on melting temperature to be expected.
- : Melt dissolves crucible material, greater change of melting temperature.
• : Partial solution processes possible with negligible change of melting temperature.
× : Crucible melts.
? : Compatibility unknown.
☐: Combination cannot be realized.
DTA/DSC

DTA

Measure temperature difference between sample and reference while they are being heated.

DSC

Measure difference in heat flow to sample and reference while they are being heated.
DSC

Heat flux DSC

- Heat flows through disk
- Temperature of disk measured
- Heat transfer through disk greater than through gas phase

Power compensating DSC

- Each sample has own heater
- Temperature of samples controlled independently
- Less power required with endotherm
DSC
DTA/DSC : Reference

Reference should have same physical properties as sample

Reference should not have any transformations during heating

Reference for sample which looses weight?

Commonly used, SiC, Al$_2$O$_3$, empty crucible
DTA/DSC: Temperatures

Temperature of oven, reference and sample during measurement
Heat integration

Curing a epoxy resin,
Simple linear baseline
Heat integration

Re-heat cured resin to measure baseline (heat capacity) at end of reaction
TG analysis: combined methods

Thermal analysis methods are more powerful when combined
Analysis Methodology

- VxOy Characterization
V\textsubscript{x}O\textsubscript{y} Nanoparticles

- Model catalyst for partial oxidation of butane
  - Alkoxide/benzyl alcohol route*
- Catalytic properties
  - At 473 K mainly acetic acid
    (C-C bond cleavage)
  - At 573 and 673 K mainly malaic anhydride
    (oxidation)
- Previous knowledge
  - From EELS and XPS V oxidized from mix of V\textsuperscript{+3} and V\textsuperscript{+4} to V\textsuperscript{+4} and V\textsuperscript{+5}

$V_xO_y$ Nanoparticles

- From TEM, EELS, and XPS vanadium is oxidized from $V^{+3}$ and $V^{+4}$ to $V^{+4}$ and $V^{+5}$

- What causes the change in selectivity?

- What can TGMS tell us about the material?

- Only several milligrams of material available!
TGMS of $V_xO_y$ particles

Conditions: 21% oxygen, 5 K/min to 773K
TGMS of $V_xO_y$ particles

- Calibrate MS:
  - $H_2O$ ($CuSO_4\cdot4H_2O$)
  - $CO_2$ (pulse valve)
- First M/e 18: 0.94mg
- Dehydration and combustion (assume C:H = 1:1) = 1.92 mg
- Weight loss of only 1.77mg suggests simultaneous re-oxidation
- Prolonged re-oxidation produces $V_2O_5$: basis for valence calculation of 4.5 at 340°C.


Acknowledgement for Examples

Fritz-Haber-Institute of the MPG, Department of Inorganic Chemistry

Robert Schlögl
Annette Trunschke
Michael Hävecker
Dangsheng Su
Di Wang
Klaus Weiss
Ute Wild
Juan Delgado (diffusion limited combustion example)

Max Planck Institute for Colloids and Interfaces

Markus Antonietti
Matthijs Groenewolt
Nicola Pinna
Markus Niederberger
Ice Calorimeter by Lavoisier