Characterization of solid catalysts

2. TPR and TPO

Prof dr J W (Hans) Niemantsverdriet
Schuit Institute of Catalysis
How often are techniques used

- XRD: 18.4%
- Adsorption: 17.4%
- XPS: 10.0%
- TP Techniques: 9.2%
- Infrared: 7.3%
- TEM: 6.9%
- SEM: 4.3%
- UV-vis: 4.3%
- NMR: 3.6%
- Raman: 3.2%
- ESR: 2.0%
- EXAFS: 1.9%
- XANES: 1.5%
- EDX: 1.2%
- Mossbauer: 0.8%
- Calorimetry: 0.4%
- ISS / LEIS: <0.1%
- Neutron Scattering: <0.1%
- SIMS: <0.1%

Journals:
- Applied Catalysis A & B
- Catalysis Letters
- Journal of Catalysis
- Jan 2002 and Oct 2006

Total Number of Articles: 8112
Temperature Programmed Techniques

- TPR: Reduction
- TPO: Oxidation
- TPS: Sulfidation
- TPD: Desorption
- TPRS: Reaction Spectroscopy
- TP-SIMS, TP-IR, etc.
measures $H_2$ consumption by the catalyst as a function of temperature

TPR set up
(based on thermal conductivity detector)

charged with unreduced catalyst

measures $H_2$ in

measures $H_2$ out

removes $H_2O$
mass spectrometer measures composition of the gas leaving the reactor as a function of temperature
Thermodynamics of Reduction

\[ MO_n + nH_2 \rightarrow M + nH_2O \]

\[ \Delta G = \Delta G^o + nRT \ln \left( \frac{p_{H_2O}}{p_{H_2}} \right) \]

\[ \Delta G = nRT \ln \left[ \frac{p_{H_2O}}{p_{H_2}} \right] \left( \frac{p_{H_2O}}{p_{H_2}^{eq}} \right) \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxide</th>
<th>((p(H_2O)/p(H_2)))_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>TiO₂</td>
<td>4.10⁻¹⁶</td>
</tr>
<tr>
<td></td>
<td>TiO</td>
<td>2.10⁻¹⁹</td>
</tr>
<tr>
<td>V</td>
<td>V₂O₅</td>
<td>6.10⁻⁴</td>
</tr>
<tr>
<td></td>
<td>VO</td>
<td>2.10⁻¹¹</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe₂O₃</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>FeO</td>
<td>0.1</td>
</tr>
<tr>
<td>Co</td>
<td>CoO</td>
<td>50</td>
</tr>
<tr>
<td>Ni</td>
<td>NiO</td>
<td>500</td>
</tr>
<tr>
<td>Cu</td>
<td>CuO</td>
<td>2.10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>Cu₂O</td>
<td>2.10⁻⁶</td>
</tr>
<tr>
<td>Mo</td>
<td>MoO₃</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>MoO₂</td>
<td>0.02</td>
</tr>
<tr>
<td>Rh</td>
<td>RhO</td>
<td>10¹³</td>
</tr>
<tr>
<td>Pd</td>
<td>PdO</td>
<td>10¹⁴</td>
</tr>
<tr>
<td>Ag</td>
<td>Ag₂O</td>
<td>3.10¹⁷</td>
</tr>
</tbody>
</table>

Careful removal of water is a key factor in the successful reduction of catalysts at 400 °C.
Metal Oxide Reduction

Nucleation: reduction by $\text{H}_2$
- slow for non-noble metals;
- fast(er) for noble metals

Growth: reduction by $\text{H}$
(fast)

- PtOx
- Pt
- Ni
- NiO
Metal Oxide Reduction

Degree of reduction, $\alpha$

Time

---

Degree of reduction, $f(\alpha)$

Contracting sphere

Nucleation and growth

Metal Oxide

Shrinking core

nucleation

Contracting sphere

Nucleation and growth
Example: TPR of supported catalysts

**Full reduction:**

Rh₂O₃ + 3 H₂ = 2 Rh + 3 H₂O
H₂/Rh = 1.5

Fe₂O₃ + 3 H₂ = 2 Fe + 3 H₂O
H₂/Fe = 1.5

Fe₃O₄ + 4 H₂ = 3 Fe + 4 H₂O
H₂/Fe = 1.33

FeO + H₂ = Fe + H₂O
H₂/Fe = 1.0

**Reduction promotion:**

- Noble metal Rh assists in the reduction of the less noble Fe
- Rh metal nucleates fast; this enables H₂ dissociation; H-atoms reduce the iron oxide
TPR: Effect of Heating Rate - CrO$_x$ / Al$_2$O$_3$

heating rate $\beta$:

$\beta = 17$ K/min

$\beta = 11$ K/min

$\beta = 6$ K/min

$\frac{dM}{dt} = \frac{dM}{dT} \frac{dT}{dt} = \beta \frac{dM}{dT}$

TPR: Effect of Particle Size

Small nano particles: almost intrinsic rate of reduction

Large particles: TPR broadened by mass transport limitations

Supported nanoparticles of copper oxide

Unsupported, large, copper oxide particles

Fig. 3. Temperature-programmed reduction of unsupported and silica-supported copper oxide.
TPR: Effect of Support Interaction

Unsupported NiO nanoparticles:

Supported nanoparticles with strong support interaction:

Fig. 2. Temperature-programmed reduction of unsupported and silica-supported nickel oxide.

Temperature Programmed Techniques

TPR  Reduction
TPO  Oxidation
TPS  Sulfidation
TPD  Desorption
TPRS Reaction Spectroscopy
TPO of coke on catalysts

Coke on Pt/SiO₂

Coke on Al₂O₃

Active phase in hydrotreating catalysts:

sulfides (e.g. MoS$_2$)

Catalysts are prepared by sulfiding oxides with H$_2$S / H$_2$ mixtures
Temperature Programmed Sulfidation

TPS of MoO$_3$/Al$_2$O$_3$

H$_2$
H$_2$S
H$_2$O

MoO$_3$
MoO$_x$S + MoS$_3$
MoS$_2$

Temperature Programmed Techniques

TPR  Reduction
TPO  Oxidation
TPS  Sulfidation

information on
• reaction temperature
• extent of reaction (degree of reduction)
• reaction mechanism
Download the handout for this lecture from www.catalysiscourse.com

Read more about temperature-programmed techniques in Chapter 2 of Spectroscopy in Catalysis: An Introduction, Third Edition

J. W. Niemantsverdriet

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gives many examples and references to the literature

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