Optical Spectroscopy

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Interaction of EM Radiation with Matter
## Comparison of Catalyst Spectroscopic Methods

<table>
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<tr>
<th>Spectroscopy</th>
<th>Temp./Pressure Limitations</th>
<th>Acquisition Time</th>
<th>Spatial Resolution</th>
<th>Molecular-level Information</th>
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<tr>
<td>LEIS</td>
<td>500°C/UHV</td>
<td>mins</td>
<td>150 nm</td>
<td>- - -</td>
</tr>
<tr>
<td>SIMS</td>
<td>500°C/UHV</td>
<td>mins</td>
<td>100 nm</td>
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<tr>
<td>AES</td>
<td>500°C/UHV</td>
<td>mins</td>
<td>100 nm</td>
<td>- - -</td>
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<tr>
<td>XPS</td>
<td>500°C/mbar</td>
<td>mins</td>
<td>1 μm</td>
<td>- - -</td>
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<tr>
<td>HR-TEM</td>
<td>925 °C/mbar</td>
<td>0.5-mins</td>
<td>0.1 nm</td>
<td>- - -</td>
</tr>
<tr>
<td>EPR</td>
<td>500 °C/1 bar</td>
<td>mins</td>
<td>None</td>
<td>YES</td>
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<tr>
<td>NMR</td>
<td>325°C/several bar</td>
<td>min-hrs</td>
<td>Some</td>
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<tr>
<td>STM</td>
<td>(conductor)/no press. limit</td>
<td>mins</td>
<td>0.1 nm</td>
<td>- - -</td>
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<tr>
<td>AFM</td>
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<td>mins</td>
<td>30 nm</td>
<td>- - -</td>
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<tr>
<td>IR</td>
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<td>msec</td>
<td>10 μm</td>
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<tr>
<td>UV/Vis</td>
<td>1500 °C/no press. limit</td>
<td>msec</td>
<td>10 μm</td>
<td>YES</td>
</tr>
<tr>
<td>Raman</td>
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<td>~1 sec</td>
<td>1 μm</td>
<td>YES</td>
</tr>
<tr>
<td>EXAFS/XANES</td>
<td>925°C/no press. limit</td>
<td>min/msec</td>
<td>mm</td>
<td>- - -</td>
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<tr>
<td>XRD</td>
<td>1500°C/no press. limit</td>
<td>min</td>
<td>mm</td>
<td>- - -</td>
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</tbody>
</table>
IR Spectroscopy

• Vibrations related to symmetry of molecule

• Only vibrations with a change in dipolar moment are IR-active (asymmetric vibrations; symmetric vibrations also present if regular symmetry is broken)

• IR is a bulk technique, but is also able to detect surface vibrations (M-OH, M=O, adsorbed molecules and surface intermediates)

• Molecular nature of IR spectroscopy makes this a very powerful technique (esp. at high T and P)
Typical IR Spectrometer
Surface Hydroxyls Present on Al$_2$O$_3$

HCOOH Adsorption on Fe$_2$O$_3$ (@ T = 100°C)

C-H Stretching Region

O-C-O Stretching Region

Absorbance (a.u.)

Wavenumber (cm$^{-1}$)

1563
1545
1596 Shoulder

1686
1727
1376
1360
1285
1210

2895
2938
2873

2980

100 torr
75 torr
50 torr
25 torr
15 torr
10 torr
4 torr
2 torr

Absorption on Fe$_2$O$_3$ (@ T = 100°C)

Bidentate

Monodentate

Molecularly Adsorbed HCOOH
Bronsted and Lewis Surface Acid Sites

Typical FTIR absorption spectrum of pyridine adsorbed on an alumina supported metal oxide catalyst.

B - Characteristic absorption bands of the pyridinium ion $\text{PyH}^+$ chemisorbed to a Bronsted acid surface site appear at: 1490, 1540, 1620, 1640 cm$^{-1}$.

L - Characteristic absorption bands for coordinatively adsorbed pyridine (a Lewis acid surface site) appear at: 1220, 1450, 1490, 1580, 1600-1630 cm$^{-1}$. 

15% MoO$_3$/Al$_2$O$_3$ at 200°C
ATR FT-IR Spectroscopy

- Uses phenomenon that occurs with light at the boundary between two media of different refractive indices.
- At an angle of incidence greater than the critical angle of the material, light is completely reflected.
- However, some energy penetrates the boundary: evanescent wave.
- The material at the boundary absorbs energy from the wave
- The absorbed energy is used to construct a spectrum.

- Multiple reflections can be used depending on crystal type and shape
- The reflections are averaged into a single spectrum
- More reflections = greater sensitivity
Surface Ti-OOH Species Form on TiO$_2$ Upon Exposure to Aqueous HOOH

• Trace of surface superoxo (O$_2^-$) species also present on TiO$_2$. 
Raman Spectroscopy

• Vibrations related to symmetry of molecule

• Only vibrations with a change in electron polarizability are Raman-active (symmetric and anti-symmetric vibrations)

• Raman is a bulk technique, but is also able to detect surface vibrations (M=O, M-OH, adsorbed molecules and surface intermediates)

• Crystalline metal oxide phases give rise to much stronger Raman bands than surface metal oxide species

• Molecular nature of Raman spectroscopy makes this a very powerful technique (esp. at high T & P)
Raman Scattering

- Discovered by Sir C.V. Raman
Raman Spectra of Aqueous Molybdenum Oxide Solution

- Raman spectra of aqueous 0.2M (NH4)6Mo7O24 solutions as a function of solution pH.

- Note, the 173 cm\textsuperscript{-1} band is from the glass dish used to hold the aqueous molybdena solution.
Raman Spectroscopy Discriminates Between Different FeOx Phases

\[ \alpha-\text{Fe}_2\text{O}_3 \]
\[ \text{Fe}_3\text{O}_4 \]

Intensity (a.u.)
Raman Shift (cm\(^{-1}\))
Bulk FeOx Phase Transforms during HT-RWGS

- Surface dioxo \((\text{O=})_2\text{CrO}_2\) species reduce during HT-WGS
Vibrational modes of Mo oxo species

Dioxo \((O=)_2\text{MoO}_2\)

- \(357\) cm\(^{-1}\) \(\delta\) \(O=\text{Mo}=O\)
- \(968\) cm\(^{-1}\) \(v_{\text{as}}\) \(\text{Mo}(=\text{O}_2)\)
- \(983\) cm\(^{-1}\) \(v_s\) \(\text{Mo}(=\text{O}_2)\)

Mono-oxo \(O=\text{MoO}_4\)

- \(1015\) cm\(^{-1}\) \(v_s\) \(\text{Mo}=\text{O}\)
Surface DIOXO \((O=)_{2}Cr(-O)_{2}\) Species Present on Fe\(_2\)O\(_3\)
UV-vis DRS

• UV-vis detects electronic transitions

• CT (M=O) transitions correspond to transition metal ions in highest oxidation state
  → MOx domain size and coordination
  → MOx dispersion

• d-d transitions correspond to reduced transition metal ions  → MOx coordination

• UV-vis generally quantitative at low transition metal ion concentrations (sensitive to low concentrations)
UV-vis DRS Integration Sphere

integration sphere (coated with MgO or BaSO₄)

sample

position for reference measurement

detector

slit monochromator

lens

mirror

Advantage: higher fraction of reflected light reaches detector
UV-vis Fiber Optic Probe

catalyst

connected to light source
connected to CCD detector
UV-vis Spectra of Vanadium Oxide Reference Compounds

CT and d-d bands shift to higher energies (lower wave length) with increasing number of d electrons.
Dependence of CT Absorption Edge Energy on Structure of V$^{5+}$

Horiba LabRam-IR High Resolution System for
Operando Raman/IR/UV-vis/TPSR Molecular Spectroscopy & Microscopy
Summary

• Optical spectroscopy provides molecular and electronic structural information.
• Can be performed at HT and HP with solids and condensed phases.
• Raman & IR $\rightarrow$ molecular structure.
• UV-vis $\rightarrow$ Domain size and oxidation state.
Raman Spectroscopy

- Single line of a continuous gas laser is focused on sample surface; measurement of inelastic light scattering yields information about vibrational frequencies of chemical bonds.
  - Penetrates bulk of solid
  - Nature of surface chemical species (especially metal oxides)
  - Sub-monolayer sensitivities
  - Types, concentrations, and strengths of chemical bonds
  - *In situ* (high temperature, high pressure)
  - Can penetrate through water

- Limitations
  - Fluorescence (signal noise)
  - Gives signals in the 10-4000 cm\(^{-1}\) range
  - Weak oxide support signals below 1000 cm\(^{-1}\)
UV-Vis (Ultraviolet-Visible) Diffuse Reflectance Spectroscopy

- UV-vis light shined on a material and inelastically scattered light contains information about electronic transitions (position and intensity)
  - bulk technique (solids & liquids)
  - sensitive at low concentrations & quantitative
  - can be performed at high T and P
  - can penetrate through water

+ charge transfer (CT) bands
  *coordination and dispersion of transition metal ions highest oxidation state
    (V$^{+5}$, Cr$^{+6}$, Re$^{+7}$, Ni$^{+2}$, etc.)

  *optical band gap or edge energy ($E_g$) related to domain size
    (monomer, dimer, polymer, cluster, bulk particle)

+ d-d transition bands
  *coordination and oxidation state of reduced transition metal ions
    (V$^{+4}$, V$^{+3}$, Cr$^{+5}$, Cr$^{+3}$, etc.)

Limitations
- d-d transitions are weak and may overlap CT and nearby d-d bands
The intensity of a beam of infrared radiation is measured before \( I_0 \) and after \( I \) it interacts with the sample as a function of light frequency. It probes vibrational motions of chemically bonded constituents.

- Penetrates bulk of solid
- Nature of surface chemical species
- Sub-monolayer sensitivity
- Types, concentrations, and strengths of chemical bonds
- \textit{In situ} (high temperature, low pressure)

Limitations
- Primarily gives signals in the 1000-4000 cm\(^{-1}\) range for practical catalysts
- Oxide supports absorb signals below 1000 cm\(^{-1}\) which obscures surface signals
- Cannot penetrate through water \( (\text{absorbed by water}) \)
UV-vis Selection Rules

- Photon energy must match energetic difference between states: $h\nu = \Delta E$
- Light absorption does not couple or decouple electron spins: $\Delta s = 0$
- Orbital angular momentum must change: $\Delta l \neq 0$
- Transitions between states of equal parity are symmetry forbidden: $u \leftrightarrow u$, $g \leftrightarrow g$, $u \leftrightarrow g$