Electron Microscopy in Catalysis

Di Wang
Transmission electron microscope

Interaction of electron with your samples

Electron scattering

Electron gun with accelerator
Condenser elmg lenses
Selected area diffraction aperture
Objective elmg lens
Post-specimen elmg lens
Screen

Evacuated column
Condenser aperture
X-ray detector
Specimen
Objective aperture
Screen

Electron energy-loss spectrometer
Camera for recording image
Field emission gun

An FEG tip, showing the extraordinarily fine W needle

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Lens

Object plane

Back focal plane

Image plane

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Electron-sample interactions

- Incident electron beam
- Cathodoluminescence (visible light)
- Bremsstrahlung
- Characteristic x-rays
- Auger electrons
- Secondary electrons
- Backscattered electrons
- Elastically scattered electrons
- Heat
- Transmitted beam to energy-loss spectrometer
- Angle-limiting aperture
- $\beta$

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What can TEM do?

**TEM**
- Morphology
- Defects, Phases
- Defects, Interfaces, Surfaces
- Structure
- Symmetry, Strain
- Lattice parameter
- Element analysis
- Electronic structures
- Imaging the distribution of elements and even chemical states

**SEM**
- Morphology, surfaces

**STEM**
- Morphology, Z-contrast

**Bright field and dark field imaging**

**High-resolution imaging**

**Electron diffraction**

**Convergent-beam diffraction**

**Energy-dispersive X-ray spectroscopy (EDX)**

**Electron-energy loss spectroscopy (EELS)**

**Energy-filtered TEM (EFTEM)**
Image and diffraction mode

Specimen
Objective lens

Objective aperture

SAD aperture

Intermediate lens

Projector lens

Diffraction pattern

Screen

Final image

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Image contrast in TEM

I. Mass-thickness contrast

![Diagram of TEM imaging process]

- Incident beam
- Lower mass thickness
- Higher mass thickness
- Objective lens
- Objective aperture
- Image plane
- Intensity profile

Fe$_3$O$_4$

100nm

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II. Diffraction contrast

**Image contrast in TEM**

**Bright field (BF)**

- Incident beam
- Specimen
- Objective lens
- Direct beam
- Diffracted beam
- Objective aperture

**Dark field (DF)**

- Incident beam
- Specimen
- Objective lens
- Direct beam
- Diffracted beam
III. Lattice fringes in pictures
High-resolution imaging

Abbe Interpretation of imaging

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Abbe Interpretation of imaging

Incident electron wave (plain wave) → Exit wave → Electron wave before lens plane

Interaction with thin sample

Electron wave at back focal plane

Fresnel diffraction over $U$

Electron wave at image plane

Fresnel propagation over $f$

Electron wave after lens plane

Fresnel propagation over $V$

Diffraction pattern (Intensity) → Image (Intensity)

Lens
For cubic, tetragonal and orthorhombic structure,

\[ a^* = \frac{b \times c}{V}, \quad b^* = \frac{c \times a}{V}, \quad c^* = \frac{a \times b}{V} \]

\[ \mathbf{u} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \]

\[ |\mathbf{u}| = \left| h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* \right| = \frac{1}{d_{hkl}} \]
Bragg condition and Ewald sphere

\[ |\mathbf{u}| = 2|\mathbf{k}| \sin \theta = \frac{2 \sin \theta}{\lambda} \]

\[ |\mathbf{u}| = |h \mathbf{a}^* + k \mathbf{b}^* + l \mathbf{c}^*| = \frac{1}{d_{hkl}} \]

\[ 2d_{hkl} \sin \theta_{hkl} = \lambda \]
Shape factor

\[
\frac{\sin(\pi Au)}{\pi Au}
\]

Sample shape

Shape of each reciprocal lattice point
Exciting the lens strength - focus

Lenses spatially fixed, but strength changeable

Phase shift factor in back focal plane

\[
\exp\{i\pi\lambda \Delta f (u^2 + v^2)\} = \exp(i\chi_1)
\]

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The electromagnetic lenses are not perfect

Spherical aberration of lenses

\[ \Delta r_0 = C_s \theta_0^3 \]

\( C_s \) : Spherical aberration coefficient

Phase shift in back focal plane due to spherical aberration

\[ \chi_2 = \frac{1}{2} \pi C_s \lambda^3 (u^2 + v^2)^2 = \exp(i \chi_2) \]
Chromatic aberration

Faster electrons are brought to a focus beyond the Gaussian image plane.

\[ D: \text{Standard deviation of Gaussian distribution due to the chromatic aberration} \]

Envelope in back focal plane

\[ \exp(-\chi_3) \]

\[ \chi_3 = \frac{1}{2} \pi^2 \lambda^2 D^2 H^2 \]
Beam divergence

Parallel incident beam (ideal condition)
Divergence angle $\alpha \sim 0.5$ mrad (real condition)

Envelope in back focal plane

$$\chi_4 = \pi^2 \alpha^2 H^2 \left(C_s \lambda^2 H^2 + \Delta f \right)^2$$

![Graph showing envelope in back focal plane with equation $\exp(-\chi_4)$ and $\exp(-\chi_3)$ under different conditions.]
Transfer function

\[ W(H) = \exp(i\chi_I) \exp(-\chi_{II}) \]

Electron wave function and intensity in the image plane

\[
\psi_{image} = \mathcal{F}^{-1} \left\{ \mathcal{F} \left[ \psi_{exit} \right] \cdot W(H) \right\}
\]

\[ I = \psi_{image} \cdot \psi_{image}^* \]
Contrast Transfer Function (CTF)

\[
\sin(\chi_I) \exp(-\chi_{II})
\]

\(\Delta f = -430 \text{Å}\)

\(U = 200kV\)
\(C_s = 0.5mm\)
\(D_{FEG} = 38 \text{Å}\)
\(D_{LaB_6} = 100 \text{Å}\)

\(\Delta f = -750 \text{Å}\)
Phase contrast in TEM

Exit wave: \( \psi_e (\mathbf{r}) = e^{-i \sigma V_p (\mathbf{r})} \approx 1 - i \sigma V_p (\mathbf{r}) \)

Assuming weak-phase object approximation
\( V_p \) : scattering potential

Final intensity: \( I(\mathbf{r}) \approx 1 + 2 \sigma V_p (\mathbf{r}) \ast F^{-1} \{ CTF \} \)
Picturing the Contrast Transfer Function

Amorphous Thin Carbon Film

Real Space $I(\mathbf{r}) \approx 1 + 2\sigma V_p(\mathbf{r}) * F^{-1}\{CTF\}$

Reciprocal Space
Only for thin crystal (WPOA) and the focus value close to Scherzer focus, the contrast of HREM image can be interpreted as crystal structure up to point resolution. In general, the black or white dots in HREM image DO NOT correspond to atoms or atom groups.

Si [110] image with different defocus values
Simulated HRTEM images

<table>
<thead>
<tr>
<th>Thickness (Å)</th>
<th>23.04</th>
<th>46.08</th>
<th>69.12</th>
<th>92.16</th>
<th>115.20</th>
<th>138.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Defocus (Å)</td>
<td>-100</td>
<td>-300</td>
<td>-500</td>
<td>-700</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Image contrast matching

\[(\text{VO})_2\text{P}_2\text{O}_7\] \hspace{2cm} \text{Mo}_8\text{O}_{23}

2 nm
HRTEM-profile imaging
Electron diffraction

Zone axis

\[ [u, v, w] \perp (h, k, l) \]

Example: cubic structure, (100), (110), (120), (340)…… planes belong to [001] zone axis
Electron diffraction

Camera length

\[ |g_{hkl}| \frac{\lambda}{L} = \frac{1}{d_{hkl}} \]

\[ d_{hkl} = \frac{\lambda L}{D} \]

MoO₃-[010]

MoO₂-polycrystalline
Electron diffraction

Crystal tilt

\[ |k| = \frac{1}{\lambda} \]
Electron diffraction

\[ |k| = \frac{1}{\lambda} \]

FOLZ

ZOLZ

\[ hkl \]

P

G

O
Electron diffraction

Calibration by a known structure

If a $h_0k_0l_0$ diffraction from a known structure can be determined in a diffraction pattern and its distance to the center is measured as $u_0$, for any other diffraction with distance $u$ to the center, the lattice spacing $d$ is given by:

$$d = u_0 \frac{d_{h_0k_0l_0}}{u}$$
Electron diffraction

Indexing of a ring pattern
Electron diffraction

Indexing of a single crystal pattern

• Two sets of lattice planes and the angle in between

• Using extinction rules

• Using diffraction pattern on other zone axis

• Simulation

Cubic ZrO$_2$ (fluorite structure) on [110] projection

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Electron Energy Loss Spectroscopy (EELS)
- zero-loss peak
- plasmon peak
- Inner-shell ionization edges, low intensity
- Near edge structure on top of edges
- background
- Plural scattering

**EELS**

![Graph showing zero loss, plasmon peak, Inner-shell ionization edges, Near edge structure, and background.

**Energy loss (eV)**

**Zero loss**

**Electron counts (a.u.)**

**Plasmon/Outer-shell electrons**

**Background**

**Amplified**

**P L_{2,3}, B K, N K, V L_{2,3}, O K**

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ELNES of Vanadium Oxides

Correlation of peak positions of the vanadium L-edges with the oxidation states of vanadium atoms in various vanadium oxides.
EELS

Element mapping

TEM image of ZrN/ZrO$_2$

Oxygen map

Pre-edge1
Pre-edge2
Post-edge

Energy loss (eV)

450 500 550 600
SEM

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SEM

Secondary electron  Back scattered electron

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STEM

Scanning beam

ADF  BF  ADF
STEM+EDX

TiO$_2$-ZrO$_2$ after 20 min ball milling

TiO$_2$-ZrO$_2$ after 10 hours ball milling
Application in catalytic systems

**Important heterogeneous catalysts**

- Supported metal
- Transition metal oxide
- Zeolites (porous structure)
- Carbon nanofibers as support

**Information of interests**

- Particle size effects; metal-substrate interaction; structural change under chemical treatments
- Reduction behavior; defects structures
- 3D structure; intergrowth of different zeolitic structures; guest species inside a zeolitic host
- Structure and growing mechanisms

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Application in catalytic systems

Reduction of MoO$_3$ induced by electron beam irradiation
Reduction of MoO$_3$ by electron beam irradiation

Structure of MoO$_3$

Diffraction of MoO$_3$ on [010] projection
Low electron current density

Frame 1 and 2: diffractions can be attributed to MoO$_2$ on [-111] projection.
Frame 3: Diffractions can be attributed to MoO$_2$ on [-122] projection.
Low electron current density

HRTEM image showing contrast from CS structure, formed at the early stage of reduction.
Low electron current density

ELNES on O K-edge

MoO$_3$: (MoO$_6$)$^{6-}$ octahedral configuration

MoO$_2$: (MoO$_6$)$^{8-}$ octahedral configuration

t$_{2g}$ anti-bonding orbitals are partially filled by two electrons.
High electron current density

After irradiation of 10 min 40 min

$MoO \ (a = b = c = 4.08 \, \text{Å}) \text{ with NaCl structure?} \rightarrow \text{Simulation}$
High electron current density

HRTEM images for evolution of Mo oxide under electron irradiation
High electron current density

ELNES on O K-edge

MoO$_3$: $(\text{MoO}_6)^{6-}$ octahedral configuration

MoO: $(\text{MoO}_6)^{10-}$ octahedral configuration

t$_{2g}$ anti-bonding orbitals are partially filled by four electrons.
Summary

- Importance of model catalyst — simplifying complex system; facilitating analytic techniques; aware of the gap between the TEM environment and the “real” condition.

- Be sure that TEM observation on the local structure is representative to the whole catalyst.

- Distinguish electron induced effect from intrinsic features of catalyst
Literature

Reimer, Ludwig; Pfefferkorn, Gerhard.
Scanning Electron Microscopy

Reimer, Ludwig;
Transmission electron microscopy: physics of image formation and microanalysis

Williams, David B. Carter, C. Barry
Transmission electron microscopy: a textbook for materials science

Egerton, R. F.
Electron energy-loss spectroscopy in the electron microscope

Spence, John C. H.
Experimental high-resolution electron microscopy

Spence, John C. H.; Zuo, J. M.
Electron microdiffraction