Transmission Electron Microscopy Investigation on Defect Structures of Molybdenum Oxides

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Why I come here?

born in China.

Ph.D in Austria

work in Germany

look like Malay
Reduction/Oxidation of Mo Oxides

◆ XRD and XAS studies on reduction of MoO₃

\[
\begin{align*}
T & < 698K & \text{MoO}_3 + \text{H}_2 & \rightarrow & \text{MoO}_2 + \text{H}_2\text{O} \\
T & > 698K & 3\text{MoO}_3 + \text{MoO}_2 & \rightarrow & \text{Mo}_4\text{O}_{11} \\
& & \text{Mo}_4\text{O}_{11} + 3\text{H}_2 & \rightarrow & 4\text{MoO}_2 + 3\text{H}_2\text{O}
\end{align*}
\]

No Crystalline intermediates is formed

◆ XAS studies on reduction/oxidation of MoO₃₋ₓ

Presence of edge-shared octahedra with short Mo-Mo distance in MoO₃₋ₓ
(T. Ressler, etc., J. Catalysis (2000) 191, 75)

Short range order defect structure forms molybdenium suboxide?
Visualisation and detection by means of HREM and electron diffraction?
Homologous series of Mo suboxides

Shear Structures

- $\text{Mo}_n\text{O}_{3n-2}$ ($17 \leq n \leq 25$)
  $\text{Mo}_{18}\text{O}_{52}$, ... derived from $\text{MoO}_3$ (layered structure)

- $\text{Mo}_n\text{O}_{3n-1}$ ($n < 10$)
  $\text{Mo}_8\text{O}_{23}$, ... derived from $\text{ReO}_3$-type structure

Other structures

- $\text{Mo}_4\text{O}_{11}$,
- $\text{Mo}_5\text{O}_{14}$, ...
Structure Model of MoO$_3$

Space group: Pbnm

Structure type: Orthorhombic

a=3.92 Å  
b=13.94 Å  
c=3.66 Å
Structure Model of MoO$_2$

Space group: P2$_1$/c

Structure type: Monoclinic

a=5.61 Å
b=4.86 Å
c=5.63 Å
β=120.9°
Principles of Shear Operation
Structure Model of $\text{Mo}_{18}\text{O}_{52}$

- Space group: p-1
- Structure type: triclinic
- $a=8.15$ Å
- $b=11.89$ Å
- $c=21.23$ Å
- $\alpha=102.7^\circ$
- $\beta=67.8^\circ$
- $\gamma = 110.0^\circ$
Simulated EDP and HREM images of $\text{Mo}_{18}\text{O}_{52}$ on [100] projection

<table>
<thead>
<tr>
<th>Sample Thickness(Å)</th>
<th>24.4</th>
<th>73.3</th>
<th>97.7</th>
<th>146.6</th>
</tr>
</thead>
</table>

EDP

HREM Image

Defocus: -400 Å

Defocus: -600 Å
EDP and HREM of Mo$_{18}$O$_{52}$
Structural Principles of Mo$_8$O$_{23}$

Space group: P2/a

Structure type: Monoclinic

a=16.8 Å  
b=4.04 Å  
c=13.4 Å  
$\beta=106.5^\circ$
Simulated EDP and HREM images of Mo$_8$O$_{23}$ on [010] projection

Sample Thickness (Å)

| Sample Thickness (Å) | 20.2 | 60.6 | 101.0 | 141.4 |

EDP

HREM Image

Defocus: -400 Å

Defocus: -600 Å
EDP and HREM of $\text{Mo}_8\text{O}_{23}$
Structure Model of $\text{Mo}_4\text{O}_{11}$

Space group: $\text{P}2_1/\text{a}$

Structure type: Monoclinic

$a=24.54$ Å  
$b=5.44$ Å  
$c=6.70$ Å  
$\beta=94.3^\circ$
Simulated EDP and HREM images of Mo$_4$O$_{11}$ on [010] projection

<table>
<thead>
<tr>
<th>Sample Thickness(Å)</th>
<th>EDP</th>
<th>HREM Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.76</td>
<td><img src="t=21.76A" alt="EDP Image" /></td>
<td>![HREM Image](t=21.76A def=-400Å)</td>
</tr>
<tr>
<td>65.27</td>
<td><img src="t=65.27A" alt="EDP Image" /></td>
<td>![HREM Image](t=65.27A def=-400Å)</td>
</tr>
<tr>
<td>108.78</td>
<td><img src="t=108.78A" alt="EDP Image" /></td>
<td>![HREM Image](t=108.78A def=-400Å)</td>
</tr>
<tr>
<td>152.29</td>
<td><img src="t=152.29A" alt="EDP Image" /></td>
<td>![HREM Image](t=152.29A def=-400Å)</td>
</tr>
</tbody>
</table>

Defocus: -400 Å

Defocus: -600 Å
EDP and HREM of $\text{Mo}_4\text{O}_{11}$
Structure Model of $\text{Mo}_5\text{O}_{14}$

Space group: P4/mbm
Structure type: tetragonal
$a=45.99$ Å
$b=45.99$ Å
$c=3.94$ Å
Simulated EDP and HREM images of Mo$_5$O$_{14}$ on [001] projection

EDP
Thickness: 50 Å

Sample Thickness (Å)

<table>
<thead>
<tr>
<th>Sample Thickness (Å)</th>
<th>19.7</th>
<th>59.1</th>
<th>98.4</th>
<th>137.8</th>
</tr>
</thead>
</table>

HREM Image

Defocus: -400 Å

Defocus: -600 Å
Crystallographic shearing is important in understanding the oxygen diffusion and phase transition mechanism of transition metal oxides in catalytic reactions.

CS plane produces well defined satellite spots in electron diffraction pattern  

Application of TEM in the investigation of the reaction mechanism in solid state chemistry

HREM, supported by image simulation, allows the visualization of the CS structures at nanometer scale  

Opens the possibility for the in-situ HREM investigation of real catalytic reaction at atomic scale.