New Insights from LEIS about Anomalous Surface Compositions of Stoichiometric Mixed Oxide Compounds*

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Heterogeneous Catalysis

- Catalysts accelerate chemical reactions and control relative activity of reaction pathways giving rise to enhanced selectivity.

- Heterogeneous catalysis involves chemical reactions between gaseous or condensed molecules and solid surfaces of catalysts.

- Molecules can **not** diffuse into bulk lattice of solid catalysts unless solids are porous (e.g., zeolites).

- Heterogeneous catalysis models for mixed oxides have traditionally **assume** that the catalyst surfaces are just truncations of the bulk lattice.
Modern Surface Analysis Techniques

X-ray Photoelectron Spectroscopy (XPS): Provides composition and oxidation states, BUT averaged over 10–20 atomic layers (1-3 nm)

Low Energy Ion Scattering (LEIS) Spectroscopy: Provides composition of outermost surface layer (0.2 nm), BUT no information about oxidation state

Combination of LEIS + Chemical Titration: Provides both composition and oxidation state information of the outer surface atoms
Consequences of Monolayer Sensitivity

LEIS 0.2 nm depth resolution: observes

XPS 1-3 nm depth resolution: observes

&
## XPS “Surface” Analysis of Stoichiometric Oxides

<table>
<thead>
<tr>
<th>Oxide (Me = …)</th>
<th>XPS lines used</th>
<th>Stoichiometry Mo/Me (V/Me)</th>
<th>XPS “Surface” Mo/Me (V/Me)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrV₂O₇ (Me = Zr)</td>
<td>V 2p(_{3/2}) // Zr 3d</td>
<td>2</td>
<td>2.0</td>
</tr>
<tr>
<td>AlVO₄ (Me = Al)</td>
<td>V 2p(_{3/2}) // Al 2p</td>
<td>1</td>
<td>0.63</td>
</tr>
<tr>
<td>Ce₈Mo₁₂O₄₉ (Me = Ce)</td>
<td>Mo 3d // Ce 3d</td>
<td>1.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Fe₂(MoO₄)₃ (Me = Fe)</td>
<td>Mo 3d // Fe 2p</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>(\alpha)-Bi₂Mo₃O₁₂(K) (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>1.5</td>
<td>1.7 (K : Bi = 0.09)</td>
</tr>
<tr>
<td>(\alpha)-Bi₂Mo₂O₉(K) (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>1</td>
<td>1.4 (K : Bi = 0.10)</td>
</tr>
<tr>
<td>(\gamma)(H)-Bi₂MoO₆(K) (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>0.5</td>
<td>0.33 (K : Bi = 0.10)</td>
</tr>
<tr>
<td>Bi₆Mo₂O₁₅(K) (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>0.33</td>
<td>0.24 (K : Bi = 0.07)</td>
</tr>
<tr>
<td>Bi₃₈Mo₇O₇₈(K) (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>0.18</td>
<td>0.19 (K : Bi = 0.22)</td>
</tr>
<tr>
<td>(\gamma)(H)-Bi₂MoO₆ (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>0.5</td>
<td>0.86</td>
</tr>
<tr>
<td>(\gamma)(L)-Bi₂MoO₆ (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>0.5</td>
<td>0.43</td>
</tr>
<tr>
<td>(\alpha)-Bi₂Mo₃O₁₂ (Me = Bi)</td>
<td>Mo 3d // Bi 4f</td>
<td>1.5</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Surface VOx Monolayer Present on ZrV$_2$O$_7$!

![Graph](image.png)

1. ZrV$_2$O$_7$

2. V/Zr intensity ratio

3. $V_2O_5/ZrO_2$

4. Kinetic Energy, eV

5. Intensity, cps

6. Scan No.

7. (every 5th scan)
Surface VOx Monolayer Present on AlVO₄!
Surface MoOx Monolayer Present on Ce₈Mo₁₂O₄₉!
Surface MoOx Monolayer Present on Fe$_2$(MoO$_4$)$_3$!
Surface of Bulk Bi-Mo-O Catalyst Does Not Possess Bi and Contaminated with K!

![XPS spectra](https://via.placeholder.com/150)

- **K / Bi = 0.04**
- **C 1s**
- **K 2p**

![Bi$_2$MoO$_6$ binding energy spectrum](https://via.placeholder.com/150)

- Intensity, a. u.
- Binding energy, eV
- K / Bi = 0.04
- XPS
- **Bi$_2$MoO$_6$**
- E / $E_0$
Conclusions

• Only LEIS provides true surface compositions of stoichiometric oxides

• Stoichiometric mixed oxide surfaces enriched in MoOx and VOx due to their low surface energy & surface diffusion (low Tammann Temperatures)
RETHINK EVERYTHING