EXAFS Studies on Adsorption Desorption Mechanism of Zn at δ MnO₂-Water Interface

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Abstract: Microscopic structures of Zn(Ⅱ) surface complexes adsorbed at a δ MnO₂-water interface were studied using extended X-ray absorption fine structure (EXAFS) spectroscopy. In a 0.1 mol/L NaNO₃ solution of pH 5.50, Zn(Ⅱ) was adsorbed onto the solid surface in the form of octahedral hydroxyl Zn(Ⅱ) ions. The octahedral Zn(Ⅱ) was linked to the structural unit of octahedral MnO₆ of the δ MnO₂ surface by sharing the O atoms. The average bond length of $R_{\text{Zn-O}}$ was $(2.071 ± 0.007) \AA$ for $n = 3$ and the Zn-Mn atomic distance was $(3.528 ± 0.006) \AA$ for $n = 3$, which corresponded to a corner sharing linkage adsorption mode (weaker adsorption). Macroscopic adsorption-desorption isotherm experiments showed that, in contrast to that of Zr manganite, adsorption of Zn(Ⅱ) on δ MnO₂ was highly reversible and no apparent adsorption hysteresis was observed. EXAFS results indicated that the microscopic mechanism for the high adsorption reversibility was corresponded to the weak adsorption sites of corner sharing linkage between the adsorbate and adsorbent polyhedra.

Keywords: EXAFS; Zn; δ MnO₂; adsorption mechanism; adsorption reversibility
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1. Zn(II) / δ MnO₂ as a function of pH

![Figure 1: Adsorption of Zn(II) on δ MnO₂ as a function of pH](image)

2. Zn(II) / δ MnO₂ (T = 25.0°C, C_p = 0.4g/L, pH 5.50)

![Figure 2: Adsorption and desorption isotherms](image)

### Table 1: Experimental conditions for EXAFS samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>c_p g·L⁻¹</th>
<th>c_e mg·L⁻¹</th>
<th>δ MnO₂ / Zn adsorption data</th>
<th>1 / mg·g⁻¹</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.4</td>
<td>10</td>
<td>1.4</td>
<td>21.50</td>
<td>15.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>0.4</td>
<td>14</td>
<td>3.1</td>
<td>27.25</td>
<td>19.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>0.4</td>
<td>24</td>
<td>10.1</td>
<td>34.75</td>
<td>25.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.2 EXAFS

EXAFS Cerius3.5 EXAFS

- Fourier Transform (FT)
- Debye–Waller factor (R²)
- Zn(II) (aq)
- Mn / δ MnO₂

2.3 Zn / δ MnO₂
Fig. 3. Normalized, background-subtracted and \( \kappa \)-weighted EXAFS spectra.

Fig. 4. Radial distribution functions obtained by Fourier Transform (FT).

Fig. 5. EXAFS spectra (dashed line) and fit results (solid line) for Zn O shell.

Table 2. EXAFS results of the first shell (Zn O bond).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \kappa ) Range / Å(^{-1})</th>
<th>Window / Å</th>
<th>( N )</th>
<th>( R / Å )</th>
<th>( \sigma^2 / Å^2 )</th>
<th>( R_{\text{factor}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(^{2+}) (aq)</td>
<td>5.8</td>
<td>0.098</td>
<td>0.006</td>
<td>18.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>5.1</td>
<td>0.075</td>
<td>0.006</td>
<td>26.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>2.0 ± 1 2.2</td>
<td>5.5</td>
<td>0.008</td>
<td>19.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>5.6</td>
<td>0.063</td>
<td>0.009</td>
<td>26.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO(s)</td>
<td>4.3</td>
<td>1.97</td>
<td>0.004</td>
<td>17.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) \( \sigma \) Debye Waller factor, \( R_{\text{factor}} \) Debye Waller factor.

Table 3. EXAFS results of the second shell (Zn Mn bond).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \kappa ) Range / Å(^{-1})</th>
<th>Window / Å</th>
<th>( N )</th>
<th>( R / Å )</th>
<th>( \sigma^2 / Å^2 )</th>
<th>( R_{\text{factor}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>2.7 ± 3.7</td>
<td>4.3</td>
<td>3.531</td>
<td>0.010</td>
<td>23.03</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>2.6 ± 3.6</td>
<td>4.2</td>
<td>3.521</td>
<td>0.012</td>
<td>27.92</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>2.8 ± 3.5</td>
<td>4.3</td>
<td>3.531</td>
<td>0.013</td>
<td>28.59</td>
<td></td>
</tr>
</tbody>
</table>
EXAFS spectra (dashed line) and fit results (solid line) for Zrs Mn shell

$
\begin{align*}
\text{EXAFS} & \quad \text{Zn Mn} \quad \text{Zr Mn} \\
\text{Zn} & \quad \text{Mn} \quad \text{Zr Mn} \\
R_{\text{Zn Mn}} &= (3.528 \pm 0.006) \text{Å} \\
\delta \text{MnO}_2 & \quad \text{Zn Mn} \quad \text{Zr Mn} \\
R_{\text{Zr Mn}} &= (3.49 \sim 3.50) \text{Å} \\
\text{Zn} & \quad \text{Mn} \quad \text{O} \\
R_{\text{Zn O}} &= (2.07) \text{Å} \\
\text{Zr} & \quad \text{Mn} \quad \text{O} \\
R_{\text{Zr O}} &= (2.071) \text{Å} \\
\end{align*}$

Fig. 6

3

EXAFS spectra, pH 5.50, 0.1 mol/L NaNO$_3$, Zn(II) 0.1 mol/L MnO$_2$, Pb(II) 0.1 mol/L ZrO$_2$.
\[ \delta \text{MnO}_2 \] and \[ \text{Zn} \] ions in dilute aqueous solutions. Physica B, 1995, 208 & 209: 395 - 397.


Wadley A D. The Crystal Structure of Chalcophanite, \( \text{ZnMn}_3\text{O}_5\cdot3\text{H}_2\text{O} \). Acta Crys., 1955, 8: 165 - 172.


