Lead Adsorption and Arsenite Oxidation by Cobalt Doped Birnessite

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Abstract: In order to study the effects of transition metal ions on the physico-chemical properties of manganese dioxides as environmental friendly materials, three-dimensional nano-micromesh cobalt-doped birnessite was synthesized by reduction of potassium permanganate by mixtures of concentrated hydrochloride and cobalt (II) chloride. Powder X-ray diffraction, chemical analysis, N2 physical adsorption, field emission scanning electron microscopy (FE-SEM) and X-ray photoelectron spectra (XPS) were used to characterize the crystal structure, chemical composition and micro-morphologies of products. In the range of molar ratios from 0.05 to 0.20, birnessite was fabricated exclusively. It was observed that cobalt incorporated into the layers of birnessite and had little effect on the crystal structure and micromorphology, but crystallinity decreased after cobalt doping. Both chemical analysis and XPS results showed that manganese average oxidation state decreased after cobalt doping, and the percentage of Mn3+ increased. Co(III)OOH existed mainly in the structure. With the increase of cobalt, hydroxide oxygen percentage in molar increased from 12.79% for undoped birnessite to 13.05%, 17.69% and 17.79% for doped samples respectively. Adsorption capacity for lead and oxidation of arsenite of birnessite were enhanced by cobalt doping. The maximum capacity of Pb2+ adsorption increased in the order HB (2.538 mmol/kg) < CoB5 (2.798 mmol/kg) < CoB10 (3.932 mmol/kg) < CoB20 (3.146 mmol/kg). Oxidation percentage of arsenite in simulated waste water by undoped birnessite was 76.5%, those of doped ones increased by 2.0%, 12.8% and 18.9% respectively. Partial of Co3+ substitution for Mn3+ results in the increase of negative charge of the layer and the content of hydroxyl group, which could account for the improved adsorption capacity of Pb2+. After substitution of manganese by cobalt, oxidation capacity of arsenite by birnessite increases likely due to the higher standard redox potential of Co3+/Co2+ than those of Mn3+/Mn4+. Therefore, Co-doped birnessite is more applicable for the remediation of water polluted with heavy metal ions, implying new methods of modification of manganese dioxides in practice.

Key words: manganese dioxide; birnessite; cobalt doping; lead adsorption; arsenite oxidation; X-ray photoelectron spectroscopy
筛理化特性的常用方法

率和选择性

影响锰氧八面体分子筛催化氧化乙醇脱氢反应的转化

料

矿

原能力和电荷数量的改变

这些研究多集中在掺杂锰氧八面体分子筛合成

杂不同金属离子的锰钾矿比表面积和孔体积增大

锰矿

热稳定性减弱

用

入到锰氧化物结构中

态存在

(1 30)

锰替代与电荷

电极材料

%((n

B

*)

U A

A

W R

层间存在水分子

掺钨锰钾矿电阻

*, 0

将氯化钴与浓盐酸一起缓

流反应

本研究在浓盐酸

锰元素呈混合价

比表面积大

化学性质如比表面积大

吸附

B

LN ON P

锰氧化物结构中

F 4

盐酸羟胺

E( F 3

将矿物粉末压片

8B

E( I-

用原子吸收光谱仪

射线衍射

衍射几何

样品于锥形瓶中

F 7 ; P 4

样品溶解

加入

硫酸

(180)

高锰酸钾返滴定

1.2.2

Bragg-Brentano

LynxEye

Ni

CuKa

λ

0, 154 06 nm

40 kV,

40 mA,

0.02°,

1 (°) /min.

1.2.3

Sherwood Model 410

K

( manganese average oxidation state, Mn AOS)

(Quantachrome Autosorb-1, JEDL-6390/LV).

1 5 h

1.0000 g

5 mL

H2C2O4

(0.5000 mol/L)

10 mL

H2SO4 (1 mol/L)

75°C

K

3

1.2.3

specific surface area, SSA)

0.100 0 – 0.200 0 g

110°C

3 h.
N₂

1.2.4

( field emission-scanning electron microscopy, FE-SEM )

JEOL-JSM6700F (Japan).

1.3

(X-ray photoelectron spectroscopy, XPS)

VG Multilab2000 X

AlKα (1486 eV),

Cu 2p3/2 Cu 3p

857.5 eV ± 0.1 eV.)

100 eV, φ = 1.0 eV; 25 eV, φ = 0.1 eV. 1 s (284.62 eV).

Thermo Advantage

Shirley

(FWHM)

O 1s

20: 80 Lorentzian; Gaussian.

1.4

5 g/L, 0.1 mol/L

HNO₃ 0.1 mol/L NaOH pH = 5.00,

24 h pH ± 0.05,

15 mmol/L

Pb(NO₃)₂ ( pH = 5 ± 0.05,

15 mol/L NaNO₃

50 mL

10 mL

5 mL

1.67 g/L, Pb²⁺

1 mol/L NaNO₃

0.1 mol/L NaCl,

1.67 mol/L

(25 ± 1)°C,

250 r/min

24 h.

pH = 5.00 ± 0.05.

12 000 r/min,

10 min.

(Varian AAS240FS)

Pb²⁺, Mn²⁺, Co²⁺,

( Sherwood Model 410 )

K⁺. 3 [17].

1.5

(25°C)

0.125 g

150 mL 0.1 mol/L NaNO₃ 12 h,

Fig. 1 Powder XRD patterns of Cobalt-doped birnessites
2.4  表 1  元素分析、SSA和Mn AOS的

<table>
<thead>
<tr>
<th></th>
<th>钴含量</th>
<th>Mn含量</th>
<th>SSA / m²/g</th>
<th>Mn AOS / %</th>
<th>(Co) Mn/AOS / %</th>
<th>n(Co) / Mn²⁺</th>
<th>SSA / m²/g</th>
<th>Mn AOS / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>52.7</td>
<td>0</td>
<td>8.36</td>
<td>3.78</td>
<td>19.3</td>
<td>0</td>
<td>19.2</td>
<td>3.76</td>
</tr>
<tr>
<td>CoB5</td>
<td>51.3</td>
<td>3.46</td>
<td>8.25</td>
<td>3.78</td>
<td>19.3</td>
<td>0</td>
<td>19.2</td>
<td>3.76</td>
</tr>
<tr>
<td>CoR10</td>
<td>48.9</td>
<td>6.23</td>
<td>8.20</td>
<td>3.78</td>
<td>17.2</td>
<td>0</td>
<td>17.2</td>
<td>3.74</td>
</tr>
<tr>
<td>CoB20</td>
<td>45.7</td>
<td>10.7</td>
<td>7.98</td>
<td>3.74</td>
<td>10.3</td>
<td>0</td>
<td>10.3</td>
<td>3.71</td>
</tr>
</tbody>
</table>

2.5  (FE-SEM)

2.6  (XPS)
图 2 FE-SEM images of cobalt-doped bimessites

图 3 XPS broadscans of bimessite and cobalt-doped bimessites

图 2 中，Co 2p

图 3 中，Co 2p , K 2p , C 1s

随着钴锰摩尔比逐渐增加，Mn 2p 的含量逐渐减小，Mn 3p 的含量逐渐增多。
Table 2  Binding energy values for Mn 2p, Mn 3p, Co 2p and O 1s/eV

<table>
<thead>
<tr>
<th></th>
<th>Mn 2p$_{1/2}$</th>
<th>Mn 2p$_{3/2}$</th>
<th>Mn 3p</th>
<th>Co 2p$_{1/2}$</th>
<th>Co 2p$_{3/2}$</th>
<th>ΔBE (Co 2p$<em>{1/2}$ - 2p$</em>{3/2}$)</th>
<th>O 1s</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>653.93</td>
<td>642.32</td>
<td>49.97</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>529.76</td>
</tr>
<tr>
<td>CoB5</td>
<td>653.66</td>
<td>641.68</td>
<td>49.47</td>
<td>780.09</td>
<td>14.92</td>
<td>529.34</td>
<td></td>
</tr>
<tr>
<td>CoB10</td>
<td>653.55</td>
<td>641.77</td>
<td>49.46</td>
<td>779.86</td>
<td>15.14</td>
<td>529.29</td>
<td></td>
</tr>
<tr>
<td>CoB20</td>
<td>653.49</td>
<td>641.59</td>
<td>49.56</td>
<td>779.58</td>
<td>15.38</td>
<td>529.21</td>
<td></td>
</tr>
<tr>
<td>CoOOH$^{[23]}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>780.20</td>
<td>15.10</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Co(OH)$_2^{[23]}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>781.0</td>
<td>15.90</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 4  Mn 2p$_{3/2}$ spectrum of cobalt-doped birnessites
Table 3 Mn 2p\textsubscript{3/2} peak fitting parameters

<table>
<thead>
<tr>
<th>Mn\textsuperscript{2+} 2p\textsubscript{3/2}</th>
<th>BE/eV</th>
<th>FWHM/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>639.75</td>
<td>1.25</td>
</tr>
<tr>
<td>Mn\textsuperscript{3+}</td>
<td>640.05</td>
<td>1.25</td>
</tr>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>641.75</td>
<td>1.25</td>
</tr>
<tr>
<td>Mn\textsuperscript{3+}</td>
<td>642.65</td>
<td>1.25</td>
</tr>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>644.15</td>
<td>1.25</td>
</tr>
<tr>
<td>Mn\textsuperscript{3+}</td>
<td>646.75</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 4 Results of composition of Mn of fits of the spectra of Mn 2p\textsubscript{3/2}

<table>
<thead>
<tr>
<th></th>
<th>Mn\textsuperscript{2+}/%</th>
<th>Mn\textsuperscript{3+}/%</th>
<th>Mn\textsuperscript{4+}/%</th>
<th>Mn AOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>1.20</td>
<td>16.07</td>
<td>82.74</td>
<td>3.82</td>
</tr>
<tr>
<td>CoB5</td>
<td>1.52</td>
<td>21.75</td>
<td>76.73</td>
<td>3.75</td>
</tr>
<tr>
<td>CoB10</td>
<td>2.17</td>
<td>29.1</td>
<td>69.73</td>
<td>3.71</td>
</tr>
<tr>
<td>CoB20</td>
<td>2.92</td>
<td>35.71</td>
<td>61.37</td>
<td>3.58</td>
</tr>
</tbody>
</table>

Fig. 5 Co 2p spectra of cobalt-doped birnessites

Co\textsuperscript{3+} and Mn\textsuperscript{3+} (HS, \( \chi = 1.675 \))  
Co\textsuperscript{3+} (LS, \( \chi = 1.791 \))  
Co\textsuperscript{3+} (HS, \( \chi = 1.923 \))  
Co\textsuperscript{3+} (LS, \( \chi = 2.331 \))  

2.7 Langmuir

2.8

Portier [28]. Mn\textsuperscript{3+} in O 1s, Co\textsuperscript{3+} in Mn AOS, Co\textsuperscript{3+} in Mn AOS.
掺钴水钠锰矿对铅的吸附及对砷的氧化

图

上方圆圈为实验谱，粗实线为最佳拟合谱，下方点划线（划线分别为实线（划线）分别为O^2-，OH^-，H_2O）

图

表

表

Table 5 Fitting parameters and Results of O 1s of cobalt-doped biremminites

<table>
<thead>
<tr>
<th>样品</th>
<th>O^2-</th>
<th>OH^-</th>
<th>H_2O</th>
<th>O^2-</th>
<th>OH^-</th>
<th>H_2O</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>529.76</td>
<td>1.65</td>
<td>73.22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoB5</td>
<td>531.24</td>
<td>1.65</td>
<td>12.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoB10</td>
<td>532.56</td>
<td>2.20</td>
<td>13.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoB20</td>
<td>529.34</td>
<td>1.65</td>
<td>67.59</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) 原子百分比

图

Fig. 6  O 1s spectrum of cobalt-doped biremminites

图

Table 6 Langmuir parameters for adsorption of Pb^{2+} and Maximum amounts of Mn^{2+}，H^+，K^+ released

<table>
<thead>
<tr>
<th>样品</th>
<th>0.1 mmol·kg^{-1}</th>
<th>K</th>
<th>R^2</th>
<th>Co^{2+}</th>
<th>Mn^{2+}</th>
<th>H^+</th>
<th>K^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB</td>
<td>2.538</td>
<td>17.70</td>
<td>0.998</td>
<td>2.778</td>
<td>0</td>
<td>1283</td>
<td></td>
</tr>
<tr>
<td>CoB5</td>
<td>2.798</td>
<td>1.018</td>
<td>0.999</td>
<td>14.6</td>
<td>0</td>
<td>1396</td>
<td></td>
</tr>
<tr>
<td>CoB10</td>
<td>2.932</td>
<td>413.9</td>
<td>0.999</td>
<td>17.0</td>
<td>0</td>
<td>1545</td>
<td></td>
</tr>
<tr>
<td>CoB20</td>
<td>3.146</td>
<td>294.9</td>
<td>0.999</td>
<td>24.5</td>
<td>0</td>
<td>1710</td>
<td></td>
</tr>
</tbody>
</table>
**Fig. 8** Curves of the oxidation rate of As(III) by cobalt-doped birnessites

CoB5 > HB. BNW, CoB5, CoB10, CoB20 BNW, BNW 2.0%, 12.8%, 18.9%.

Co<sup>3+</sup>/Co<sup>2+</sup> (E° = 1.92 V) BNW, MnO2/Mn<sup>2+</sup> (E° = 1.224 V) MNW, Mn<sup>3+</sup>/Mn<sup>2+</sup> (E° = 1.542 V) BNW.

Lee BNW [10].

3

(1) BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

(2) BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

(3) XPS BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

(4) BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

(5) BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

---


[3] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

---

[4] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

[5] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

[6] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

[7] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

[8] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.

[9] BNW, Co(III) OOH BNW, BNW, Mn AOS, Co (III) OH BNW, BNW.


