Fun With Cobalt

By Nathan Buch ’10
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Spinels

\[ \text{AB}_2\text{O}_4 \text{ spinel} \]

The red cubes are also contained in the back half of the unit cell.

(A) \( (8 \cdot \frac{1}{8}) + (6 \cdot \frac{1}{2}) + 4 = 8 \)
(B) \( 4 \times 4 = 16 \)
(O) \( 4 \times 8 = 32 \)

\[ \text{AB}_2\text{O}_4 \]
$\text{Co}_3\text{O}_4$

Three synthesis methods of spinel structure:

(1) By embedding in mesoporous silica template$^1$

\begin{itemize}
  \item 8 nm rod diameter
  \item 130 nm average rod length
  \item average 48 rods per bundle
\end{itemize}

(b) SBA-15/Co$_3$O$_4$ 8\% loading; (c) Co$_3$O$_4$ nanocluster after removal of silica by etching

\begin{align*}
\text{Estimated TOF} &= 1170 \text{ s}^{-1} \\
&\text{(per nanocluster)}
\end{align*}
(2) Controlled growth of nanocubes²

(b) Aging time = 6 h

(c) Aging time = 12 h

![Graph showing the relationship between aging time and average particle size.](image)

- Sodium Nitrate = 150 g
- Sodium Nitrate = 90 g
(3) Ultrasonication

Cobalt acetate + tetramethylammonium hydroxide (TMAH)

Also performed with manganese

Works by causing local high temperatures and pressures; characterized by high pitched squealing
GC Peak Integrator

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**GC O2 & N2 Peak Integration**

**Oxygen Area:** 81.84

**Nitrogen Area:** 142.12

**RATIO [O2/N2]:** 0.5759

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**Raw Data**

**Oxygen Peak**

**Nitrogen Peak**
Gas Chromatography

Method (1): mesoporous silica impregnation

Closely replicates results found in original paper

Majority of O2 generation occurs in first 10 min

Leveling presumed to be due to limited persulfate in solution
Method (3): Ultrasonication

Increases in O₂ content continue beyond initial 10 min
Clark Electrode: Continuous O2 Monitoring

![Graph showing O2 Generation with and without Nitrate](Image)
Clark Electrode Analysis

<table>
<thead>
<tr>
<th>Time (min) (after catalyst addition)</th>
<th>mmol O₂/g catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
<td>10</td>
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<tr>
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<tr>
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<tr>
<td>24</td>
<td>0.85</td>
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</tbody>
</table>

Conversion: 0.28887 µmol O₂/mL @ 20°C

But what exactly is ultrasonication producing?
Sonicated Mn: produces clear XRD pattern...

...while sonicated Co produces mush.
Sonicated Co w/o Nitrate IR spectrum

Purified Co w/o Nitrate IR spectrum
Co Nanocubes IR spectrum

Co Nanocubes XRD pattern

Purified sonicated Co XRD pattern is mush, again.

Purified Sonicated Co IR spectrum
Something in here produces $O_2$, but what?
We’ve extracted the wrong component.
References


