Simple mechanochemical synthesis of a copper manganese oxide catalyst for CO oxidation.

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Introduction
Copper manganese oxide (Hopcalite) is a well-known and popular CO oxidation catalyst and is used in a wide range of industrial situations. In recent years much study has been undertaken on the preparation of Hopcalite from nitrate reagents by co-precipitating a carbonate precursor using sodium carbonate, which is then calcined to form the active catalyst. This generates significant nitrate waste along with poisoning the catalyst with sodium that must be washed out, generating further waste. We have investigated a simple, waste free, mechanochemical synthesis of Hopcalite using carbonates as precursors. We aim to demonstrate that this facile synthesis method can produce Hopcalite that is suitable for use as a CO oxidation catalyst.

Materials and Methods
The catalyst were prepared by grinding copper hydroxycarbonate and manganese carbonate in a 1:2 ratio using a Retch PM100 planetary ball mill. The precursors were ground for varying lengths of time at 400RPM in a zirconia vessel with 7 cm zirconia grinding balls. Catalyst testing was undertaken in a glass micro reactor filled with 50mg of catalyst with 5000ppm CO flowing through the bed at 21mL min⁻¹. Evolved CO₂ analysis was undertaken using a TCD attached to a Varian 3400 GC. XRD was performed using a panalytical pro expert diffractometer.

Results and Discussion
XRD studies suggest that Cu²⁺ is being incorporated into the MnCO₃ lattice of the precursor during the milling process. A shift in the reflection position was observed, this led to determination of the unit cell volume of the precursor by Rietvelt refinement. The refinement showed a contraction in the unit cell that was concurrent with Cu²⁺ incorporation into the MnCO₃ lattice as has previously been remarked upon by Porta et al. Table 1: Physical properties of the catalyst precursors prepared by mechanochemical milling determined by XRD

<table>
<thead>
<tr>
<th>Grinding Time/h</th>
<th>2θ shift° (104)</th>
<th>Crystallite Size /nm</th>
<th>Unit Cell Volume/ Å³</th>
<th>Calced Surface area/ m²/g</th>
<th>Temperature of thermal decomposition/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0</td>
<td>35</td>
<td>312.380</td>
<td>65</td>
<td>300, 495</td>
</tr>
<tr>
<td>1</td>
<td>0.034</td>
<td>27</td>
<td>312.367</td>
<td>35</td>
<td>307,483</td>
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<tr>
<td>12</td>
<td>0.119</td>
<td>15</td>
<td>307.629</td>
<td>50</td>
<td>480</td>
</tr>
<tr>
<td>24</td>
<td>0.171</td>
<td>14</td>
<td>306.954</td>
<td>21</td>
<td>475</td>
</tr>
<tr>
<td>72</td>
<td>0.211</td>
<td>14</td>
<td>306.451</td>
<td>78</td>
<td>438</td>
</tr>
</tbody>
</table>

The incorporation of Cu²⁺ into the MnCO₃ to form a CuₓMnₓ-CO₂ species removes the barrier of atomic diffusion that must be overcome, easing the formation of the CuMnO₂ phase. A direct consequence of this is the lowering of the temperature of thermal decomposition as a function of grinding time. Insitu XRD was used to investigate this and found that the onset of CuMnO₂ formation was 50°C lower in the sample ground for 72h compared to the sample ground for 1h.

Figure 1 shows the time online CO oxidation activity of the prepared copper manganese oxides calcined at 415°C. Activity for the majority of the materials is low, however after grinding for 72h a large increase in activity is observed. This is rationalized as due to the formation of the active amorphous CuMnO₂ phase.

Significance
A simple mechanochemical milling has been used to prepare copper manganese oxides that are active for CO oxidation without the need for the creation of environmentally damaging nitrate waste streams and competitive in activity with commercial catalysts. It has been demonstrated that the incorporation of Cu²⁺ into the lattice of the MnCO₃ precursor serves to lower the temperature of CuMnO₂ formation allowing for formation of the active phase.

References