

# 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<sup>1</sup>. This generates significant nitrate waste along with poisoning the catalyst with sodium that must be washed out, generating further waste<sup>2</sup>. 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 1cm 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 21mLmin<sup>-1</sup>. Evolved CO<sub>2</sub> analysis was undertaken using a TCD attached to a Varian 3400 GC. XRD was performed using a panalytical pro xpert diffractometer.

## Results and Discussion

XRD studies suggest that Cu<sup>2+</sup> is being incorporated into the MnCO<sub>3</sub> 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 Cu<sup>2+</sup> incorporation into the MnCO<sub>3</sub> lattice as has previously been remarked upon by Porta et al<sup>3</sup>

Table 1: Physical properties of the catalyst precursors prepared by mechanochemical milling determined by XRD

Grinding Time/h	2θ shift/° (104)	Crystallite Size /nm	Unit Cell Volume/ Å <sup>3</sup>	Calcined Surface area/ m <sup>2</sup> g <sup>-1</sup>	Temperature of thermal decomposition/°C
0.5	0	35	312.380	65	300, 495
1	0.034	27	312.367	35	307, 483
12	0.119	15	307.629	50	480
24	0.171	14	306.954	21	475
72	0.211	14	306.451	78	438

The incorporation of Cu<sup>2+</sup> into the MnCO<sub>3</sub> to form a Cu<sub>x</sub>Mn<sub>1-x</sub>CO<sub>3</sub> species removes the barrier of atomic diffusion that must be overcome, easing the formation of the CuMn<sub>2</sub>O<sub>4</sub> phase. A direct consequence of this is the lowering of the temperature of thermal decomposition as a function of grinding time. In situ XRD was used to investigate this and found that the onset of CuMn<sub>2</sub>O<sub>4</sub> formation was 50°C lower in the sample ground for 72h compared to the sample ground for 1h.

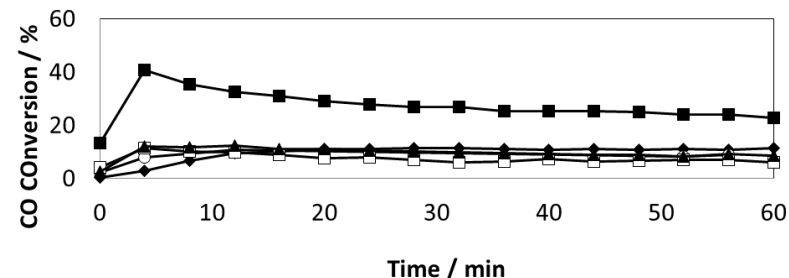


Figure 1. Time online CO Oxidation activity of catalysts produced by mechanochemical

milling, M6 (30min): ◆ M7 (1h): ○ M8 (12h): □ M9 (24h): ▲ M10 (72h): ■ (25°C, GHSV, 5000ppm CO in synthetic air)

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 CuMn<sub>2</sub>O<sub>4</sub> 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 Cu<sup>2+</sup> into the lattice of the MnCO<sub>3</sub> precursor serves to lower the temperature of CuMn<sub>2</sub>O<sub>4</sub> formation allowing for formation of the active phase.

## References

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