



# Mechanochemical synthesis of copper manganese oxide for the ambient temperature oxidation of carbon monoxide



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## ABSTRACT

A series of copper manganese oxide catalysts have been prepared by mechanochemical grinding of carbonate precursors and tested for the low temperature oxidation of CO. It is shown that a 72 h grind time and heat treatment under oxygen is necessary to form active  $\text{CuMn}_2\text{O}_4$  for the conversion of CO to  $\text{CO}_2$  at room temperature. Energy dispersive X-ray analysis mapping indicated that the degree of mixing was improved at longer grinding times. Contraction of the  $\text{MnCO}_3$  lattice, followed by X-ray diffraction, showed that grinding times in excess of 24 h were necessary for the near complete dissolution of Cu ions into the  $\text{MnCO}_3$  framework, which in turn facilitated the formation of  $\text{CuMn}_2\text{O}_4$  upon calcination. This simple, clean and environmentally friendly synthesis shows how mixed metal oxides that are catalytically active at room temperature can be synthesized without employing aqueous precipitation techniques, which result in waste streams containing carbonate and nitrate contaminants.

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## 1. Introduction

The tenets of green chemistry include the need for one-step environmentally friendly synthesis routes using benign precursors, which generate little or no waste streams. Reactive grinding or mechanochemical synthesis of catalysts is a growing area in the field of materials chemistry and offers a simple and waste free preparative route [1]. It offers a number of advantages when compared to some traditional methods. The process is environmentally friendly and economically efficient as there are no solvents used, no waste from washing, fewer synthesis steps, and no requirement for product recovery or separation. Catalyst poisons such as  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Cl}^-$  from precipitating agents are also minimised [2]. In addition, the catalytic activity can be enhanced by virtue of the increased contact through grain boundaries [3], introduction of stacking faults [4], as well as the increase in surface area as a result of a decrease in particle size [5].

Single metal oxides are the simplest catalysts to prepare by a mechanochemical route; examples include catalysts which are highly active for the oxidation of volatile organic compounds and the degradation of pollutants. Catalysts such as  $\text{Co}_3\text{O}_4$  have been synthesised and tested for total oxidation of propane with

excellent low temperature activity, which is linked to the small particle size afforded by the grinding and rapid crystallisation [6,7]. In other examples, ZnO and  $\text{TiO}_2$  catalysts have been prepared and tested for photocatalytic reactions. ZnO was tested for the decomposition of benzene-1,3-diol and showed activity comparable to other catalysts in the literature [8]. Whereas  $\text{TiO}_2$  and carbon doped  $\text{TiO}_2$  showed improved activity for the photocatalytic generation of hydroxyl radicals and the decomposition of  $\text{NO}_x$  respectively [9,10].

Mechanochemical synthesis of mixed metal oxides can be more problematic, due to the difficulty in achieving a well mixed homogeneous distribution of the active components, although it can be achieved. Copper based catalysts for the steam reforming of methanol, such as  $\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$  [11],  $\text{Cu}/\text{Al}_2\text{O}_3$  [12] and  $\text{Cu}/\text{ZnO}$  [13–15] have received a lot of attention, possibly due to the industrial relevance of the catalyst. In many cases it was found that the activity of the catalysts was linked to the length of the grinding time, as it increased dispersion, decreased particle size and consequently increased surface area. Molybdenum zeolites have been prepared by mechanochemical methods and they are active for hydrodesulfurization [16], but they were not as active as when prepared by impregnation. Mechanochemically prepared ceria and titania supported gold catalysts have also been shown to be active for preferential oxidation of CO [17] and liquid phase oxidations [18], but again the dispersion and particle size of the active phase were difficult to control. Perovskites have been synthesised by reactive grinding and tested for alkane activation and total oxidation. It was

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found that the unprecedented high surface areas of  $>100\text{ m}^2\text{ g}^{-1}$  along with the increased defect density led to increased activity when compared to a perovskite prepared by a more traditional citrate complex method [19,20].

Mixed metal oxides of the spinel and inverse spinel type have long been synthesised by a variety of methods and investigated primarily for their catalytic, electronic, optical and magnetic properties [21,22]. An example of such a material is copper manganese oxide (Hopcalite), first investigated in the early 20th century. It is a well studied and commercially available catalyst proven to be active for a large number of oxidation reactions [23]. Commercial varieties of Hopcalite have been synthesised by a solid-state reaction between active components  $\text{MnO}_2$  and  $\text{CuO}$ , with additional binders and promoters such as  $\text{AgO}_2$  [24]. More active catalysts can be prepared by other routes such as co-precipitation [25–27], sol-gel [28] and precipitation by supercritical  $\text{CO}_2$  [29], but can be limited in their application due to the more complex preparation methods when compared to the simple solid state reaction between the metal oxides.

In this study we have investigated the preparation of Hopcalite and show how additive free mechanochemical grinding of the precursor carbonates can facilitate the preparation of Hopcalite. In particular, we were interested in the potential incorporation of  $\text{Cu}^{2+}$  ions into the  $\text{MnCO}_3$  framework in an attempt to increase the rate of copper manganese oxide formation during heat treatment. Carbonates have been used as precursors, as previously we have shown that more active materials with higher surface areas are formed by virtue of the endothermic decomposition of the carbonate precursor during calcination [30,31]. Conversely, the use of precursors that decompose exothermically can lead to phase separation and preferential reduction of one or more of the active components [32]. This effect has an important influence on the catalyst activity for low temperature carbon monoxide oxidation. In this work we have studied the relationship between the mechanochemical preparation variables, catalyst structure and activity.

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts were prepared using a planetary ball milling method. A Retsch PM100 planetary ball mill with a 10 cm zirconia grinding vessel with six 15 mm zirconia grinding balls was used. All grinding was performed at  $25^\circ\text{C}$ . Powdered  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  (Sigma Aldrich, 95%) and  $\text{MnCO}_3$  (Sigma Aldrich, 99.9%) were mixed in a 1:2 copper to manganese molar ratio. The powders were ground for varying periods of time (0.5–72 h) at 400 rpm. The resulting dry solid powders were recovered and calcined in static air ( $415^\circ\text{C}$  for 2 h with a ramp rate of  $2^\circ\text{C min}^{-1}$  from ambient temperature [26]). After calcination samples were stored in a desiccator to prevent water adsorption. Copper oxide and manganese oxides were prepared by grinding the reagents individually for 1 h by the same method. The commercial catalyst tested was stored in a desiccator to prevent water adsorption.

### 2.2. Catalyst characterisation

The catalysts were characterized by powder X-ray diffraction (XRD) using a Panalytical X'Pert diffractometer, using a Cu source operating at 40 kV and 40 mA. The phases present were confirmed by matching patterns to the ICDD database. Crystallite sizes were determined by using the Scherrer equation. Lattice parameters were determined by Reitveld analysis using Panalytical Highscore plus software. The peak profiles were fitted using pseudo-Voigt function and the parameters were refined in the order of scale

factors, zero shift, cell parameters, thermal parameters peak shape function and preferred orientation. *In situ* XRD analysis of the uncalcined catalysts was undertaken using a Panalytical X'Pert Pro diffractometer fitted with an Anton Paar 900 K *in situ* cell. An X-ray diffractogram of the precursor was taken at room temperature before heating the sample to  $600^\circ\text{C}$  at a heating rate of  $2^\circ\text{C min}^{-1}$ . Air was flowed through the sample cell at a rate of  $4\text{ mL min}^{-1}$ . The heating profile was paused every  $25^\circ\text{C}$  between  $175$  and  $600^\circ\text{C}$  to acquire diffractograms of the sample as it decomposed to form the calcined catalyst.

The surface area of the catalysts was determined using a Micromeritics Gemini 2360 analyser. The catalysts were pretreated under a flow of  $\text{N}_2$  at  $120^\circ\text{C}$  for 30 min prior to analysis. The surface area was determined by 5-point  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  and the data analysed using the BET method.

Temperature programmed reduction (TPR) analysis of the catalysts was performed using a Quantachrome ChemBET TPD/R/O apparatus. Hydrogen consumption was measured as 30 mg of the catalyst was exposed to a flow of  $10\%\text{H}_2/\text{Ar}$  at a flow rate of  $30\text{ mL min}^{-1}$  whilst heating from ambient to  $600^\circ\text{C}$  at a rate of  $15^\circ\text{C min}^{-1}$ . Thermal gravimetric analysis (TGA) was performed using a Seteram Labsys TGA/DTA apparatus. Mass loss and heat flow for the catalyst precursors were examined over a temperature range of  $30$ – $600^\circ\text{C}$  under an atmosphere of flowing air ( $30\text{ mL min}^{-1}$ ).

The morphology and elemental composition of powdered catalysts were evaluated by scanning electron microscopy (SEM) using a Jeol-6610LV equipped with an Oxford Instruments energy dispersive X-ray (EDX) analyser. Samples were gold coated using a Quorum Q150T ES sputter coater. Transmission electron microscopy (TEM) of the samples was undertaken using a JEOL 2100 microscope operating at 200 kV with a  $\text{LaB}_6$  filament. Samples were mounted on 300 mesh copper grids covered in a holey carbon film. EDX measurements were performed using an Oxford Instruments Xmax<sup>N</sup> 80T detector.

In order to obtain elemental composition data on the materials Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was performed using an Agilent 4100 MP-AES. The Cu and Mn content of each catalyst was measured using two emission lines for each metal, 324 nm and 327 nm for Cu with 403 and 404 nm used for Mn. The samples were introduced to the nitrogen plasma using a single pass spray chamber at a pressure of 240 kPa without air injection. A known amount of each catalyst precursor was dissolved in 5 mL aqua regia then diluted up to 50 mL using deionized water. A 10% aqua regia rinse solution was introduced between samples for 15 s to ensure there was no sample contamination. Each sample was run 3 times with the average result used to determine the Cu:Mn ratio.

The instrument was calibrated with standards of appropriate concentration containing both Cu and Mn in a 10% aqua regia solution along with a 10% aqua regia blank.

### 2.3. Catalyst testing

The catalysts were tested for CO oxidation using a fixed-bed microreactor. The reaction temperature was maintained isothermally at  $25^\circ\text{C}$  by immersing the U-shaped reactor tube in a thermostatically controlled water bath. 5000 vppm CO in air and a gas hourly space velocity of  $12,000\text{ h}^{-1}$  (50 mg catalyst, flow rate  $21\text{ mL min}^{-1}$ ) was used. Analysis of reactants and products was performed using on-line gas chromatography (Varian CP-3800) with a Supelco Carbosieve column ( $3\text{ m} \times 35\text{ mm}$ ) with a thermal conductivity detector. Conversion was calculated on the basis of  $\text{CO}_2$  formation and the detector was calibrated using standard gas mixtures.

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