Oxalate precipitation synthesis of copper-manganese nanoparticles for methanol steam reforming

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Abstract. CuMn spinel nanoparticles were prepared using the oxalate precipitation synthesis technique using nitrate salts as precursors. The samples were characterized using X-ray diffractometry (XRD), and field emission – scanning electron microscopy (FE-SEM). The mixed oxalate precursor, CuMn*C2O4, was found to be single-phase and crystalline compound. H2-assisted temperature-programmed decomposition of the mixed oxalates yielded Cu1.5Mn1.5O4 spinel nanoparticles with CuO present in very minute amounts. FE-SEM analysis of the Cu1.5Mn1.5O4 spinel showed a spherical morphology of the nanoparticles. The average size of the Cu1.5Mn1.5O4 spinel nanoparticles was 11.512 nm. Thus, the nano-sized Cu1.5Mn1.5O4 spinel nanoparticles can be used as catalysts for the methanol steam reforming (MSR) reaction.

1. Introduction
In times where environmental problems pose a great threat to the society, development of cleaner and new sources of energy is of utmost concern [1]. The Fischer-Tropsch (FT) reaction was developed by Franz Fischer and Hans Tropsch in the 1920s [2]. The reaction involves the use of synthesis gas, a gaseous mixture of carbon monoxide (CO) and hydrogen (H2), to produce sulfur-free organic products at operating temperatures of 200-350°C. The synthesis gas (CO/H2), which can be harnessed from natural gas, coal, biomass or any carbonaceous source, makes the synthesis of a wide range of organic compounds such as paraffins (1), olefins (2), and oxygenates (3) is possible [3-4]. The most important reactions are summarized below:

\[
\begin{align*}
(2n + 1) \text{H}_2 + n\text{CO} & \rightarrow C_n\text{H}_{2n+2} + n\text{H}_2\text{O} \quad (1) \\
(2n) \text{H}_2 + n\text{CO} & \rightarrow C_n\text{H}_{2n} + n\text{H}_2\text{O} \quad (2) \\
(2n) \text{H}_2 + n\text{CO} & \rightarrow C_n\text{H}_{2n+1}\text{OH} + (n-1) \text{H}_2\text{O} \quad (3)
\end{align*}
\]

Hydrocarbons and alcohols can be used for reforming reactions for the in situ production of hydrogen fuel [5-6]. Although industrial production of hydrogen mainly utilizes methane as fuel, other fuels such as methanol presents several advantages compared to methane and all other fuels. Aside from being the simplest alcohol, reforming with methanol occurs at low temperatures (200-300°C) due to the absence of a strong C-C bond. Methane is reformed above 500°C [7] while ethanol, another common fuel in hydrogen production, is reformed at around 400°C [6]. Other advantages of using
methanol is its high miscibility in water, biodegradability, liquid state at atmospheric conditions, and high hydrogen to carbon ratio. The only problem with methanol is its toxicity. The methanol steam reforming (MSR) reaction is shown in equation 4:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 3\text{H}_2 \quad \Delta H = 49.7 \text{ kJ/mol} \quad (4) \]

The MSR reaction mainly produces hydrogen but other products that are formed must be taken into consideration. There are two side reactions that occur simultaneously with the MSR reaction:

\[ \text{CH}_3\text{OH} \rightleftharpoons \text{CO} + 3\text{H}_2 \quad \Delta H = 90.2 \text{ kJ/mol} \quad (5) \]
\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \quad \Delta H = -41.2 \text{ kJ/mol} \quad (6) \]

Altogether, the MSR, the methanol decomposition reaction (5) and water-gas shift (WGS) reaction (6) yields a reaction mixture composed of unreacted methanol, water, hydrogen, carbon dioxide, and minute amounts of carbon monoxide. If the hydrogen produced will be used as fuel in polymer electrolyte membrane fuel cells (PEMFC), carbon monoxide formation must be suppressed [1]. This can be achieved by tuning the performance of the catalyst. The catalyst must be highly active and highly selective to produce large amounts of hydrogen and negligible amounts of carbon monoxide. Among the catalysts for the MSR reaction, copper-based catalysts possess both high activity and high selectivity [8-9]. However, these catalysts are pyrophoric and are deactivated by thermal sintering. Addition of promoter metals further improve the activity of the Cu-based catalyst. Furthermore, method of preparation affects the overall properties of the catalyst [10].

Oxalate co-precipitation synthesis is an effective catalyst preparation technique for MSR catalysts. Copper-based catalysts that were produced via the oxalate precipitation technique have high dispersion, smaller particle and crystallite size, and high surface areas [1]. In this study, copper-manganese (CuMn) nanoparticles for the MSR reaction were synthesized via the oxalate precipitation technique. The CuMn nanoparticles were characterized using x-ray diffractometry (XRD), and field-emission scanning electron microscopy (SEM).

2. Methodology

2.1 Oxalate precipitation synthesis of copper-manganese mixed oxalates
Copper (II) nitrate hexahydrate and manganese (II) nitrate hexahydrate, with a 1:3 ratio were mixed in acetone. Accompanied with vigorous stirring, an excess of oxalic acid was added to complete the co-precipitation. After 3 hours of stirring, the wet oxalate cake was centrifuged and the excess acetone was discarded. The solid products, labeled as CuMn*\text{C}_2\text{O}_4, were grounded and then dried at 110°C for 24 hours.

2.2 H2-assisted temperature-programmed decomposition of the mixed oxalates
The temperature-programmed decomposition (TPDec) of the mixed CuC\text{2O}_4 and MnC\text{2O}_4 was performed from room temperature up to 500°C with a ramp rate of 6°C/min under a flow of 10% H\text{2} in argon. The total flow rate of the gas mixture was at 30 mL/min. After cooling to room temperature, the products were collected and labeled as CuMn.

2.3 X-ray diffractometry
Both CuMn*\text{C}_2\text{O}_4 and CuMn were characterized using a Rigaku X-ray Diffractometer (Cu K\alpha = 1.542Å) at the Lamar University. The X-ray tube was set at a voltage of 40.0 kV and a current of 30.0 mA with 2θ scan range 10° to 90°.

2.4 Field emission - scanning electron microscopy (FE-SEM)
CuMn*\text{C}_2\text{O}_4 and CuMn samples were mounted in carbon tape and were aspirated using compressed air. Morphology of the samples was studied using a Hitachi SU8230 field emission-scanning electron microscope (FE-SEM) housed at the Department of Mining, Metallurgical, and Materials Engineering.
(DMMME), University of the Philippines, Diliman. The accelerating voltage was set to 15.0 kV with probe current at 21 pA.

3. Results and discussion

3.1 Oxalate precipitation synthesis of copper-manganese mixed oxalates

Bimetallic CuMn catalysts were prepared via the oxalate precipitation route. In this technique, double-chelation of the oxalate ligands with both metals form a metal-organic framework type of structure [11]. This is indicated in Scheme 1.

Scheme 1. Copper-Manganese Mixed Oxalate Structure

The mixed oxalate products are catalytically inactive. To produce catalytically active catalysts, the oxalate ligand must be thermally stripped off [11]. The H$_2$-assisted temperature programmed-decomposition of the mixed oxalates can proceed via the two equations below:

\[ \text{MeC}_2\text{O}_4 \rightarrow \text{Me} + 2\text{CO}_2 \]  \hspace{1cm} (Eqn. 7)

\[ \text{MeC}_2\text{O}_4 \rightarrow \text{MeO} + \text{CO} + \text{CO}_2 \]  \hspace{1cm} (Eqn. 8)

Equations 7 and 8 shows us that either the metal or the metal oxide is formed depending on the gaseous products generated. The decomposition of the pure copper oxalate occurs at 265°C [11] while the pure manganese oxalate decomposes at 303°C [12]. The decomposition of the mixed oxalate occurs at around 280°C. The chemical environment during the decomposition and the nature of the metal determines whether the metal oxalate is reduced to a pure metallic phase. The thermal decomposition formed under 10% H$_2$ diluted in Ar, a reducing atmosphere, was expected to produce a pure metallic Cu phase. Meanwhile, complete reduction Mn-oxalates or oxides to pure metallic states is impossible. Thus, the expected product is a pure metallic Cu phase dispersed in a matrix of Mn oxides [13].

3.2 X-ray diffractometry

X-ray diffractometry was used to identify the identity, as well as the structure of the synthesized oxalate precursors and the thermally decomposed products. Figure 1a shows the obtained XRD pattern of copper oxalate, manganese oxalate, CuMn$^+\text{C}_2\text{O}_4$, and CuMn. The CuMn$^+\text{C}_2\text{O}_4$ XRD pattern possesses peaks from the individual oxalates, Cu$\text{C}_2\text{O}_4$ and Mn$\text{C}_2\text{O}_4$. Square symbols indicate peaks from Cu$\text{C}_2\text{O}_4$ while circular symbols indicate peaks from Mn$\text{C}_2\text{O}_4$. The appearance of these peaks suggest that the product was a single-phase mixed oxalate. The formation of the single-phase mixed oxalate might be due to the isomorphous substitution between the manganese and copper oxalate phases. The single-phase product is expected to form a well-defined CuMn spinel oxide [13].

Figure 1. (a) XRD pattern of the mixed CuMn$^+\text{C}_2\text{O}_4$, and CuMn.
XRD profile of the thermally decomposed product, CuMn, suggest that the CuMn exist as a Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel phase together with a minor CuO phase [13]. The triangular symbol denote the peak specific for the Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel while the hexagonal symbol denotes the peak for the CuO phase. The Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel is a non-stoichiometric form of CuMn$_4$O$_4$ and is commonly denoted by Cu$_{1.5}$Mn$_{1.5}$O$_4$ or Cu$_{1.5}$Mn$_{1.5}$O$_4$. It is important to note the absence of the diffraction peaks for other crystalline Mn oxides species, such as Mn$_2$O$_3$ or Mn$_3$O$_4$, from the XRD profile of CuMn. This suggests that Mn$_2$O$_3$ or Mn$_3$O$_4$ are highly dispersed in the CuMn or the oxides are amorphous in nature [14].

3.3 Field emission – scanning electron microscopy (FE-SEM)
Morphological and particle size studies of the mixed CuMn*$_4$C$_2$O$_4$ and CuMn are essential because the catalytic activity and performance are highly influenced by particle size. Figure 1b and 1c shows the FE-SEM images of the mixed CuMn*$_4$C$_2$O$_4$ and CuMn.

It can be observed from Figures 1b and 1c that the mixed oxalates are crystalline in nature but the morphology of the crystal is hard to assess. The apparent crystalline structure agrees with the XRD results. Figure 1c shows the spherical morphology of CuMn which is actually a Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel. Particle size analysis using ImageJ software revealed that the particles have an average particle size of 11.512 nm. A similar CuMn spinel has been synthesized using the water-free soft reactive grinding synthesis technique and the average size was found to be at 17 nm [13]. Thus, the synthesized Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel particles can be used as catalysts for the MSR reaction. Furthermore, the smaller sizes of the particles suggest higher active surface area and higher performance in the MSR reaction.

4. Summary
Oxalate precipitation technique was employed for the preparation of the catalytically inactive mixed oxalate CuMn*$_4$C$_2$O$_4$, and the catalytically active Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel nanoparticles. XRD profile of CuMn*$_4$C$_2$O$_4$ consists of peaks from the individual oxalates. Thus, CuMn*$_4$C$_2$O$_4$ is a crystalline single-phase mixed oxalate. FE-SEM supported the crystalline nature of the mixed oxalates. However, the morphology of the mixed oxalate was difficult to assess. XRD profile of CuMn reveals that the thermally decomposed product consists of Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel and a minor phase of CuO. This confirms that Mn oxides cannot be completely reduced to metallic Mn. The absence of Mn oxide peaks in the XRD profile suggest that the Mn oxides are highly dispersed or amorphous in nature. FE-SEM analysis of CuMn reveal the spherical morphology of the nanoparticles. The average size of the CuMn is 11.512 nm. The nano-range size of the Cu$_{1.5}$Mn$_{1.5}$O$_4$ spinel particles make them suitable catalysts for the MSR reaction.

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