



Effects of sonication on co-precipitation synthesis and activity of copper manganese oxide catalyst to remove methane and sulphur dioxide gases



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ABSTRACT

The utilisation of ultrasound in chemical preparation has been the focus of intense study in various fields, including materials science and engineering. This paper presents a novel method of synthesising the copper-manganese oxide (Hopcalite) catalyst that is used for the removal of volatile organic compounds and greenhouse gases like carbon monoxide. Several samples prepared under different conditions, with and without ultrasound, were subjected to a series of characterisation tests such as XRD, BET, FE-SEM, EDX, TPR-H₂, TGA and FT-IR in order to establish their chemical and physical properties. A series of catalytic tests using a micro-reactor were subsequently performed on the samples in order to substantiate the aforementioned properties by analysing their ability to oxidise compressed natural gas (CNG), containing methane and sulphur dioxide. Results showed that ultrasonic irradiation of the catalyst led to observable alterations in its morphology: surfaces of the particles were noticeably smoothed and an increased in amorphicity was detected. Furthermore, ultrasonic irradiation has shown to enhance the catalytic activity of Hopcalite, achieving a higher conversion of methane relative to non-sonicated samples. Varying the ultrasonic intensity also produced appreciable effects, whereby an increase in intensity results in a higher conversion rate. The catalyst sonicated at the highest intensity of 29.7 W/cm² has a methane conversion rate of 13.5% at 400 °C, which was the highest among all the samples tested.

1. Introduction

Methane, being a Volatile Organic Compound (VOC), is found to be 20–30 times more potent than carbon dioxide in contributing to global warming [1]. Despite being a greenhouse gas (GHG), most of the focus on GHG emission centers around the removal of carbon monoxide and other more hazardous gases such as hydrogen sulphide. Most commonly, there is no legislation in controlling the emission of methane gas to the atmosphere. Hence, this alarms the need to have a better treatment on methane gas from being emitted to the atmosphere.

Several methods have been developed to treat VOCs in order to prevent their emission to the environment, namely, thermal incineration, physical filtration with adsorbents and catalytic combustion [2]. Ultimately, the latter has demonstrated to be the most superior method and can be vindicated by its omnipresence in automobile catalytic converters. Among the catalysts, copper-manganese oxide, or more commonly known as Hopcalite, was discovered to be one of the best and widely used catalysts for the oxidation of CO and VOCs due to its

excellent oxidising properties, and is commonly used in air filtration systems and air regulators (e.g. respiratory masks for scuba diving and fire-fighting) [3].

Hopcalite was originally developed as a mixture of 50% MnO₂, 30% CuO, 15% Co₂O₃ and 5% Ag₂O [4]. It was prepared by separating the precipitations followed by intimately mixing the Mn, Cu and Co oxides. Subsequently the silver species was precipitated into the mixture. Within a short time span, a second formulation was developed and it comprised of 60% MnO₂ and 40% CuO, which was synthesised by the thermal decomposition of copper carbonate precipitated onto the MnO₂, however, it is good to note that the presence of water vapour will greatly deactivate the catalysts. This have resulted in many on-going researches attempting to improvise the utility of Hopcalite. Hopcalite was initially determined by XRD to possess a structure that resembles an analogue of the cubic spinel with a mixed metal oxide phase of CuMn₂O₄ [4]. Albeit widely recognised as the active structure of the Hopcalite catalyst, the presence of the CuMn₂O₄ phase was notably refuted by several dissenting studies. Amongst, some claim that a

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mixture of $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$ and Mn_2O_3 is present instead of the CuMn_2O_4 phase [5–8].

It is known that heterogeneous catalysts might necessitate rare and extremely expensive metals in particular cases. Sonication has emerged to be a promising technique by activating less costly metals that are not as catalytically active. For example, hydrogenation experiments with sonically prepared Nickel (Ni) catalysts have shown tremendously enhanced results [9]. Besides Ni, sonically prepared Iron-Cobalt (Fe-Co) alloys also showed high catalytic activity for the dehydrogenation of cyclohexane to benzene, with 1:1 ratio Fe-Co alloys having selectivities as high as 100% [10], which is highly contributed by the inter-particle collisions caused by the cavitation-induced shockwaves when ultrasound passed through the materials.

Although the synthesis of Hopcalite had been extensively studied, they were mostly centered on the removal of CO at ambient temperatures [11–16]. Conventionally, precious metals such as Platinum and Palladium were employed on the catalysts used for the oxidation of CH_4 [17,18]. While these catalysts have shown positive removal of CH_4 , they were rather expensive, therefore are not economically feasible at large scale. This has gathered attention from several researchers to study on the potential uses of Hopcalite to remove CH_4 as a cheaper alternative. Amongst, Machej and co workers discovered that synthesising Hopcalite using a typical co-precipitation method at Cu:Mn ratio of 1:2 resulted in approximately 16% of CH_4 conversion, and upon addition of Aluminium to the catalyst at a specific ratio have resulted in significant enhancement in the catalytic activity [19], while others have also shown significant improvement in CH_4 conversion upon the addition of other metals such as Zinc, Magnesium and Aluminium onto the existing metal oxide mixture [20]. While these literatures have found improvements in CH_4 conversion, they were highly relied on the addition of other metals into the system, and were only conducted under pure CH_4 conditions. Lately, Zhao and co workers [21] attempted to evaluate the catalytic activity of Cu-Mn oxides in diesel soot, which contained hydrocarbons and nitrogen oxides, in order to simulate the catalytic performance in a real environment. They found that the ratio of Cu:Mn played a crucial role in enhancing a specific catalytic reaction, and for the case of diesel soot, contrary to the commonly used Cu:Mn ratio of 1:2, they found that the ratio of 1:1 produced the best catalytic performance.

With no previous studies for the preparation of Hopcalite via the ultrasound technique, this research initiates to explore the possibilities of improving its catalytic activity. Further to this, to appraise the performance of Hopcalite synthesised, the catalyst have been investigated by conducting several reaction tests using a mixture of gases containing methane (CH_4) and sulphur dioxide (SO_2) to carbon dioxide (CO_2) and water (H_2O) in a packed bed laboratory micro-reactor, in order to simulate the catalytic activity in the presence of gaseous mixtures.

2. Experimental

All the chemicals utilised were of analytical grade, purchased from R & M Chemicals Malaysia, and used without further purification. The ultrasonic probe used in this experiment was a 20 kHz with a diameter of ca. 1 cm (Sonics and Materials, VCX750, 750 W).

2.1. Catalyst synthesis

The preparation of hopcalite catalysts closely follow a recipe developed by Hutchings et al. [12], with slight modification. In detail, 4.83 g of copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and 2.509 g of manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) were dissolved in deionised water (50 mL) separately. 0.8 M of Na_2CO_3 solution was added drop-wise to the nitrate solution upon heated to 45 °C and stirred at 350 rpm until a pH of 8.3 was reached and a suspension was formed. The resultant suspension was left at room temperature (25 °C) to age for 30 min, followed by filtering the precipitate using a 125 mm filter paper. The resulting

Table 1

Cu:Mn molar ratios of the catalyst samples and their respective ultrasonic conditions.

Sample	A	B	C	D	E (Benchmark)
Cu:Mn	2:1	2:1	2:1	2:1	1:2
Ultrasonic amplitude (%)	–	20	30	40	–

precipitate was then thoroughly rinsed for 5 times with deionised water. The precipitate was then dried in an oven at 120 °C for 16 h and finally calcined at 410 °C for 2 h.

For comparison, several other samples were synthesised by altering their preparation parameters (i.e. Cu:Mn molar ratio, and the usage of ultrasound as well as its amplitude during aging). All synthesised samples with their respective preparation conditions are listed in Table 1. Samples incorporating the usage of ultrasound (B, C and D) were aged under the influence of a sonicator for the same duration of 30 min. The ultrasonic probe was set at amplitudes ranging from 20 to 40%, which corresponds to ultrasonic intensities of 11.5–29.7 W/cm^2 [22] and its probe was immersed into the suspension while it was being aged for 30 min. Sample E, with Cu:Mn molar ratio of 1:2, was also synthesised and used as a benchmark to compare with the literature.

2.2. Catalyst characterisation

The structure and characteristics of the catalysts synthesised were determined through the conduction of several characterisation tests, in which the techniques are described below.

2.2.1. X-Ray powder diffraction (XRD)

X-ray diffraction patterns were acquired using a PANalytical X'Pert-PRO diffractometer in order to determine the crystalline phase structure and the chemical composition of the samples. The wavelength of the Cu-K α X-ray radiation applied was 1.54060 Å while the beam current and voltage were 40 mA and 45 kV, respectively. Crystallite size was determined using the Scherrer's equation: Particle size = $(0.9 \times \lambda)/(\text{d} \cos \theta)$.

2.2.2. Field emission scanning electron microscopy (FE-SEM) and scanning transmission electron microscopy (STEM)

SEM and STEM images were obtained using a field emission scanning electron microscopy (FE-SEM, Fei Quanta 400F). The micrographs were taken using a Fei Quanta 400 F microscope at a beam current of 1 μA and an accelerating voltage of 20 kV.

Image analyses on the particle sizes were performed using ImageJ software, where the surface particle size distributions (PSD) of the synthesised catalysts were determined.

2.2.3. Energy dispersive X-ray (EDX) analysis

The elemental composition of the samples was acquired using a same field emission scanning electron microscope (FESEM) equipped with an Oxford Instruments X-MAX energy dispersive X-ray (EDX) analyser at an accelerating voltage of 20.0 kV and an acquisition live-time of 45 s.

2.2.4. Brunauer-Emmett-Teller (BET) analysis

The specific surface areas (S_{BET}) and the porosities of the samples were obtained using a Micromeritics ASAP 2020 Surface Area and Porosity Analyser by employing the Brunauer-Emmett-Teller (BET) method. The adsorption and desorption experiments were executed at -195.681 °C (77 K) using nitrogen (N_2). Prior to the analysis, the samples were pre-treated by degassing at 120 °C overnight.

2.2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was conducted on a Perkin Elmer STA 6000 simultaneous thermal analyser under an air

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