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# Plasma-enhanced comparative hydrothermal and coprecipitation preparation of $CuO/ZnO/Al_2O_3$ nanocatalyst used in hydrogen production via methanol steam reforming

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ABSTRACT

The $CuO/ZnO/Al_2O_3$ nanocatalyst was synthesized using hydrothermal and coprecipitation methods. Then they were exposed to glow discharge plasma for 45 min at 1000 V. The performance of prepared nanocatalysts in conversion of methanol to hydrogen was investigated in steam reforming of methanol reaction. Various characterization techniques such as X-ray diffraction, field emission electron microscopy, particle size distribution, EDX-dot mapping, BET surface area and Fourier transform infrared spectroscopy were used in order to obtain physicochemical properties of synthesized nanocatalysts. XRD diffraction patterns showed that applying coprecipitation method and also glow discharge plasma, led to more dispersion of CuO (1 1 1) crystallite plate. FESEM images displayed that using non-thermal plasma assisted coprecipitation synthesis method caused to best surficial morphology and particle size distribution in $CuO/ZnO/Al_2O_3$ sample. EDX-dot mapping analysis demonstrated that the $CuO/ZnO/Al_2O_3$ sample had the most uniform dispersion of elements. Evaluation of catalytic performance indicated that plasma assisted coprecipitation synthesized $CuO/ZnO/Al_2O_3$ sample had the highest conversion of methanol and the lowest CO generation among other samples in the reaction. Stability assessment of the performance of $CuO/ZnO/Al_2O_3$ nanocatalyst represented that conversion of methanol and products selectivity were approximately constant through long term use in steam reforming of methanol reaction.



## 1. Introduction

Global environmental concerns, reduction of fossil fuels resources, growing demand to energy sources as a result of human population increase, are some of the reasons which lead to look for and develop new clean sources of energy. Electrical energy generation by proton-exchange membrane fuel cells (PEMFCs) is one of the most effective method in order to produce electrical energy with very low detrimental substances emission into environment [1–3]. Pure hydrogen gas is used as fuel in PEMFCs. Hydrogen due to its very low contamination is known as one of the most attractive energy carrier in recent years [4–6]. Earnest problems of hydrogen storage and transportation, lead to on-board production of it through simple alcohols and hydrocarbon reforming process [7–10]. Among all possible chemical compounds, methanol due to some especial advantages such as the absence of C—C bond, lower reforming temperature and high hydrogen-to-carbon ratio (4:1) can be significantly utilized in reforming process in order to produce hydrogen gas [11–14]. There are 4 different types of methanol reforming process: methanol decomposition (MD) [15,16], partial oxidation of methanol (POM) [17,18], steam reforming of methanol (SRM) [19–21] and oxidative steam reforming of methanol (OSRM) [22–24]. The highest yield of hydrogen generation and also the lowest value of carbon monoxide production are some of the advantages of steam reforming of methanol reaction [25]. There are three main reactions in SRM process [26,27]. Main reforming reaction Eq. (1), methanol decomposition, Eq. (2) and water gas shift reaction, Eq. (3) [28,29]:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H = 49.7\ \text{kj/mol} \tag{1}$$

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H = 90.2\ \text{kj/mol} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.2\ \text{kj/mol} \tag{3}$$

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As seen, in addition to hydrogen and carbon dioxide gases, carbon monoxide is also produced through SRM reaction. Because of the harmful effects of CO on the anodic catalyst and membrane of the fuel cells, the amount of this gas must be very low [30–32]. The reverse water–gas shift (RWGS) (Eq. (3)) is the most important reaction for production of carbon monoxide along steam reforming of methanol process. Forasmuch as the water gas shift reaction is strongly exothermic, the RWGS reaction cannot proceed at low temperatures, and in this way, CO production is very slight. Steam reforming of methanol is a catalytic reaction and the role of catalyst in higher activity at low temperatures in order to production of hydrogen with low concentration of carbon monoxide is very important. Also, the role of steam reforming of methanol reaction catalysts in order to provide slight selectivity toward carbon monoxide generation particularly at high temperatures is very significant. The SRM reaction catalysts are divided into two major groups: copper based and group 8–10 metals catalysts [33–40]. Copper based catalysts due to their appropriate properties such as higher activity and better selectivity toward desirable products are the most common catalysts for use in SRM reaction. The commercial catalyst for steam reforming of methanol reaction is $CuO/ZnO/Al_2O_3$. The performance of this catalyst can be improved by changing the synthesis method or applying different promoters [41–43]. The synthesis method can affect structure, surficial morphology and finally catalytic performance through sensitive variations in specific surface area, interaction between various species as well as distribution and dispersion of active phases on the catalyst. Coprecipitation, sol-gel, impregnation, homogeneous precipitation, hydrothermal and oxalate gel coprecipitation are some of the conventional synthesis methods that have been used for preparation methanol steam reforming reaction catalysts [44–49].

In addition to applying different synthesis methods, post treatment process such as different calcination conditions and plasma treatment can significantly change the performance of the catalysts. Glow discharge plasma as a kind of non-thermal plasma treatment is a novel post treatment process which is used in order to surficial treatment of the nanocatalysts before calcination process [50–53]. Positive and negative ions, electrons, atoms, free radicals and photons are some of the most important constituents of plasma. With increasing the applied voltage across the two electrodes which inserted into glass tube, the current suddenly increases sharply and if the pressure is low, on the order of a few Torrs, and also the external circuit has a large resistance to prevent a large current, a glow discharge develops. Non-thermal glow discharge plasma can significantly affect the crystallography features, surficial morphology, particles size distribution, surficial elemental dispersion and specific surface area of the catalysts. In this regard, applying glow discharge plasma, leads to higher dispersion of different metal crystallites, stronger interaction between different metal oxides, more uniform distribution of small and isomorph particles, better dispersion of various elements on the surface of catalyst and finally higher specific surface area [54–57]. With these changes in physicochemical properties, the performance of the catalysts can be significantly improved for higher conversion of methanol at low temperatures in order to generate hydrogen gas with slight concentration of carbon monoxide.

In this research we use hydrothermal and coprecipitation synthesis methods to prepare $CuO/ZnO/Al_2O_3$ nanocatalysts in order to compare the effects of synthesis method on the performance of the catalysts in SRM reaction. The effects of non-thermal glow discharge plasma treatment on the physiochemical properties and performance of the synthesized nanocatalysts by each preparation method are also investigated in this research. Different performance of the catalysts which are prepared by two various synthesis methods as well as plasma treated and non-treated samples can be attributed to different physiochemical properties of the nanocatalysts as a result of applying various preparation methods and non-thermal glow discharge plasma treatment. Physicochemical properties of the synthesized nanocatalysts are analyzed by use of XRD, FESEM, PSD, EDX spectra and dot-mapping, BET and FTIR techniques.

## 2. Materials and methods

### 2.1. Materials

In this research work, copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$) and aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were applied as copper, zinc and aluminium precursors respectively. Also, sodium hydroxide (NaOH) and sodium carbonate ($Na_2CO_3$) were used as precipitation agents. Moreover, ethanol was used as solvent for preparation of aqueous/alcoholic solution of precursors in coprecipitation synthesis method. Finally, methanol was applied for steam reforming reaction. All of materials were supplied from Merck Company. Furthermore, high purity Argon gas which was applied as plasma forming gas, was purchased from Technical Gas Service in Ajman, UAE.

### 2.2. Nanocatalysts preparation and procedure

Preparation process of $CuO/ZnO/Al_2O_3$ nanocatalyst by hydrothermal and plasma-assisted hydrothermal methods is shown in Fig. 1. Also, processing steps of preparation of $CuO/ZnO/Al_2O_3$ nanocatalyst by coprecipitation and plasma-assisted coprecipitation methods are shown in Fig. 2. As seen in Fig. 1, hydrothermal synthesis method consists of three stages. In the first stage, 1 M aqueous solution of suitable values of copper, zinc and aluminium nitrate precursors was created for preparation of $CuO/ZnO/Al_2O_3$ nanocatalyst. Copper oxide, zinc oxide and aluminium oxide weight percentages in the catalyst were 45, 45 and 10, respectively. An aqueous solution of sodium hydroxide was also created at first stage. The Amount of sodium hydroxide was three times as many as nitrate ions. In the next step, aqueous

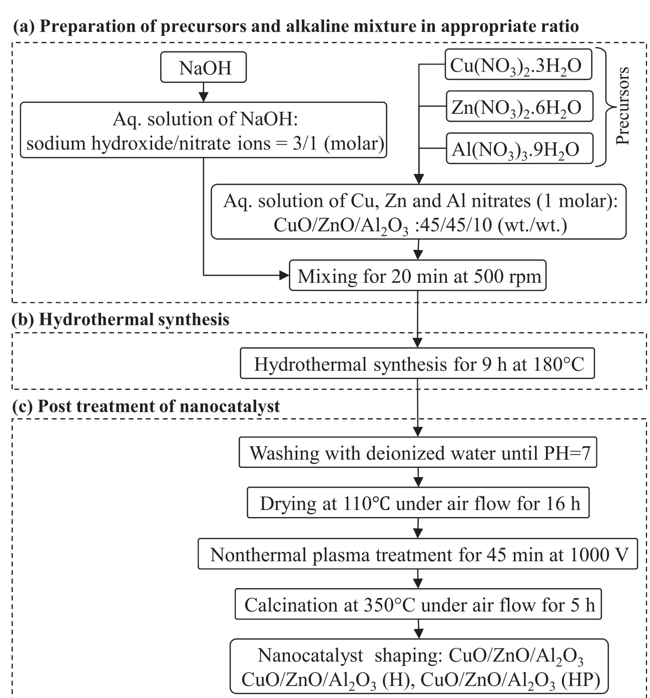


**Fig. 1.** Plasma-enhanced hydrothermal preparation of $CuO/ZnO/Al_2O_3$ nanocatalyst.