On the solution combustion synthesis of copper based nanocatalysts for steam methanol reforming: Effect of precursor, ultrasound irradiation and urea/nitrate ratio

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ARTICLE INFO

ABSTRACT

Steam reforming of methanol over $CuO/ZnO/Al_2O_3$ nanocatalysts synthesized by ultrasound assisted urea-nitrates combustion method was investigated. Four kinds of nanocatalysts were fabricated and their characteristic properties were studied by XRD, FESEM, PSD, BET, EDX and FTIR analyses. Their physico-chemical properties proved that using boehmite instead of aluminium nitrate as the aluminium precursor leads to smaller crystallites and particles, better dispersion and more surface area and subsequently higher activity in the steam methanol reforming process. Furthermore, application of sonication for mixing of the primary gel of combustion method resulted in better dispersion of active phases, smaller and more homogeneous particles, higher methanol conversion and hydrogen production. Although enhancement of fuel/nitrates ratio increased dramatically the surface area of synthesized nanocatalysts but it had no significant effect for improving methanol conversion or hydrogen production. In a word, CZA-A-CU-UN1 had better physicochemical properties and catalytic performance for the steam methanol reforming process.

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1. Introduction

Methanol, as one of the popular chemical compounds in many large scale industries, is mainly produced from synthesis gas (mixture of CO, CO_2 and H_2) [1–3]. Its advantages such as no strong C—C bond, easy storage and transportation as well as conversion to hydrogen at low temperatures; causes to nominate as an attractive choice for production of hydrogen especially for small scale applications and automobiles [4–6]. Three common pathways are suggested to convert methanol to hydrogen including partial oxidation, decomposition and steam reforming [7–9]. Steam methanol reforming (SMR) is a promising and efficient process for conversion of methanol to the hydrogen-rich product at low temperatures [10–12]. Two kinds of catalysts are nominated for the SMR process according to their reaction temperature: Cu-based and group 8–10

metals based catalysts [13–15]. Cu-based catalysts due to their lower reaction temperature and higher activity are more desirable [16,17]. The activity of these catalysts can be influenced by preparation parameters such as promoter type, composition, synthesis method and operational parameters such as temperature, pressure, feed ratio and reactor type. Different promoters were applied to investigate their influence on activity, hydrogen and carbon monoxide selectivity and catalyst stability [18–21]. Al_2O_3 has been proved to have efficient effect on thermal and mechanical stability and enhancement of surface area. However, its excessive amounts have negative influence which should be controlled by using its optimum content [22]. ZnO increases the dispersion of Cu species and catalyst reducibility [23]. CeO_2 and ZrO_2 increase the activity of Cu-based catalysts while zirconia increases its stability, too [16,24,25].

Various synthesis methods such as co-precipitation [23,26], impregnation [27], hydrothermal [28] and homogeneous precipitation [29] has been investigated to study their influence on the catalytic performance of fabricated catalysts. Furthermore, in our previous works, the copper-based nanocatalysts were synthesized by the novel urea-nitrate combustion method [22,24]. The solution

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combustion synthesis method is a novel, fast and simple synthesis method which is applied for fabrication of different nanomaterials. In this method, a viscous solution of an oxidizer which is usually the nitrate form of precursor and an organic fuel such as urea, glycine, citric acid and etc. are prepared and heated. The solution starts to foam and burn until the final product is synthesized in a short time [30–32]. Several parameters such as pH, type of fuel, fuel/oxidizer ratio, ignition temperature and combustion environment have significant influence on the properties of resulted powders [33–36]. The fuel/oxidant ratio is known as one of the most influential parameters on properties of synthesized powders by the solution combustion method. This parameter can also influence the catalytic performance of fabricated nanocatalysts due to their effect on producing micro and nano pores which facilitates the accessibility of reactants to active sites. Also, applying proper amount of fuel can affect quantity of gaseous combustion products which can be effective on physical properties of synthesized nanocatalysts such as morphology, particle size and surface area [31,37–39]. In addition, the mixing procedure of primary solution of precursor nitrates and fuel can be effective [40].

Recently, great attention has been paid to utilization of sonication as a powerful source of energy for preparation of nanomaterials [41–43]. Smaller particle size, enhancement of surface area and increase of catalytic properties are the great advantages of ultrasound assisted catalysts [44–46]. Unfortunately, few studies were performed to investigate application of ultrasonic radiation during the solution combustion synthesis method. Therefore, in this paper, four kinds of CuO/ZnO/Al$_2$O$_3$ nanocatalysts with similar composition were synthesized by the solution combustion method. Boehmite and aluminium nitrate were applied as the aluminium precursor for fabrication of these nanocatalysts. In addition of studying the aluminium precursor effect, the influence of application of sonication and fuel/nitrate ratio on the physicochemical and catalytic properties of synthesized nanocatalysts was studied. For this purpose, various characteristic analyses such as X-ray diffraction, field emission scanning electron microscopy (FESEM), energy dispersive X-ray (EDX), Brunauer–Emmett–Teller analysis (BET), and Fourier-transformed infrared (FTIR) techniques were used. Finally, the prepared nanocatalysts were tested in a fixed bed reactor system for evaluation of their catalytic performance.

2. Materials and methods

2.1. Materials

Copper nitrate trihydrate (Cu(NO$_3$)$_2$·3H$_2$O, Merck, extra pure), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, Merck, extra pure), aluminium nitrate nonahydrate (Al(NO$_3$)$_3$· 9H$_2$O, Merck, extra pure) and Al(OH)$_3$ (Merck) were applied as the precursors for fabrication of CuO/ZnO/Al$_2$O$_3$ catalysts. All of the reagents were used without further purification. Urea as a fuel in combustion method was supplied by Merck.

2.2. Nanocatalysts preparation and procedure

Fig. 1 depicts the fabrication method which was applied for the preparation of CuO/ZnO/Al$_2$O$_3$ catalysts. This methodology is divided to three main steps: precursor preparation, synthesis via urea- nitrate combustion as well as heat treatment and catalyst forming. In the first stage, an aqueous solution of copper nitrate trihydrate and zinc nitrate hexahydrate in deionized water was prepared. Then, if the aluminium based precursor was nitrate, its precursor was added to the resulted solution. On the other hand for production of boehmite-based alumina, aluminium hydroxide heated at 400 °C for 4 h and added to the solution simultane-

ously with urea. This mixing step was performed by mechanical or ultrasound assisted mixer for 45 min. Fig. 2 illustrates the ultrasound assisted mixing apparatus. Sonication was carried out on a SONOPULS HD 3200, 130 mm diameter Ti horn, 95 W. The Ti horn was inserted 1 cm below the slurry and high intensive irradiation was applied to the solution. Two urea/nitrate ratios as 1 and 2 were considered. In the second stage, the urea-nitrate combustion synthesis was done by an open muffle furnace at 400 °C. It is worth noting that the aqueous solution was preheated over a hot plate at 80 °C to form a viscous gel before the main combustion reaction. After all in the third stage, the resulted powder catalyst was calcined at 400 °C for 3 h under air flow and later was formed to use in a laboratory reactor. Due to different methodology and aluminium precursor used for preparation of the catalysts, four different samples were achieved which are mentioned in Table 1. In this table, samples were labelled by some abbreviated names to facilitate their calling in the paper. "A" and "N" mean boehmite and nitrate as the aluminium precursor, respectively. In addition, UN1 and UN2 indicate urea/nitrate ratio of 1 and 2, respectively. The samples which were synthesized by applying ultrasound irradiation are nominated by addition of "CU" in their abbreviated names.

2.3. Nanocatalysts characterization techniques

X-ray diffraction (XRD) analysis was performed by a D5000 Siemens X-ray diffractometer using Cu Kα radiation (0.154056 nm). Its working voltage and the current were 30 kV and 40 mA, respectively. The Scherrer equation was applied to calculate the average crystallite size of samples [47]. The morphology of synthesized nanocatalysts was observed by HITACHI 4160-s field emission scanning electron microscope (FESEM). EDX and dot maps were conducted for elemental analysis (VEGA II, TESCAN). The FT-IR spectra were acquired by an Unicam 4000 FTIR spectrometer using KBr plate in the range of 400–4000 cm^{-1}. The Brunauer-Emmett-Teller (BET) surface area measurements were calculated using nitrogen adsorption at 77 K and desorption at room temperature by a Quantachrome ChemBET 3000 analyser while the samples were degassed at 200 °C for 30 min before the measurement.

2.4. Experimental setup for catalytic performance test

The prepared catalysts were tested in a laboratory catalysis system for the steam methanol reforming process. Fig. 3 illustrates schematically the laboratory catalysis setup which consists of feed gas cylinders, mass flow controllers, a saturator, a reactor and a gas chromatograph system. 400 mg of the fabricated catalyst was loaded into a U-shaped fixed bed reactor (5 mm i.d.). The reactor was set in a temperature controlled furnace. Before the main reaction performance, the catalysts were reduced under H$_2$/Ar stream at 300 °C for 3 h. Then, the feed containing water to methanol ratio of 1.5 and argon as career gas was inserted to the reactor from a saturator. The product was analysed by a gas chromatograph device (GC Chrom, Teif Gostar Faraz, Iran) which was equipped with an Agilent J&W HP-PLOT-U column to separate the gases and FID and TCD detectors for identification of components. The inner diameter of the column is 0.32 mm and has 30 m length. Its temperature limit range is −60 to 190° C. As the gaseous products (CO and CO$_2$) exit the column in 4 min at 40 °C, a temperature program was proposed to reduce the time of the methanol existence. It started from 40° C and stayed in this temperature for 5 min to ensure that CO and CO$_2$ exit completely from the column. Then, the GC temperature rise to reach 170° C and stayed in this temperature for 5 min and after existence of methanol, the temperature program ended by reducing to 40° C.