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Fuel cell-grade hydrogen production from methanol over sonochemical coprecipitated copper based nanocatalyst: Influence of irradiation power and time on catalytic properties and performance

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ABSTRACT

A series of ceria promoted copper based nanocatalysts were synthesized by conventional and sonochemical co-precipitation methods at different irradiation power and time. Their performance was investigated for fuel cell-grade hydrogen production from methanol. The nanocatalysts were characterized by X-ray diffraction, field emission scanning microscope, Fourier transform infrared spectroscopy, specific surface area, and energy dispersive X-ray analyses. According to crystallography analysis by increasing irradiation power and time, the copper oxide crystallinity reduced and smaller and fully dispersed crystals produced. The nanocatalyst which sonicated at 90 W for 15 min had small spherical nanoparticles which their size range varied between 1 nm to 125 nm. The performance of nanocatalysts was examined through the methanol steam reforming process at 160–260 °C and atmospheric pressure with space velocity of 10,000 cm^3/g_{cat} h in a U-shape fixed bed reactor. Among all nanocatalysts, the sample synthesized by conventional co-precipitation showed the weakest activity. But the others which synthesized by the ultrasound assisted co-precipitation method represented higher activity in terms of methanol conversion as the irradiation power and time enhanced. Complete methanol conversion achieved at 200 °C for the nanocatalyst which sonicated at 90 W for 15 min during co-precipitation which is ideal for application in fuel cell vehicles.

1. Introduction

Recently, because of environmental problems and unknown future of fossil fuel resources, hydrogen is considered as a clean and viable alternative for fossil fuels [1]. Hydrogen fuel cells as an interesting alternative for conventional vehicles motors, generate electrical power through a clean process without the production of harmful by-products. From this perspective, due to the safety limitations for the hydrogen storage technology, on-board reforming of liquid hydrocarbons attracted great interest [2]. Many alternatives were suggested for producing on-board hydrogen from liquid fuels for example, Remon et al. evaluated the possibility of application of glycerol in a aqueous phase reforming process for production of hydrogen [3]. Earlier, Duo et al. investigated using the Ni-Cu-Al catalyst for glycerol steam reforming in a continuous fixed bed reactor [4]. More interestingly, a comprehensive study was carried out on application of animal waste especially poultry tallow as the hydrocarbon source for hydrogen production [5]. But, most attention attracted to methanol because of its high H/C ratio, low coke formation and low reforming temperature (200–300 °C) [6]. Among different routes for conversion of methanol to hydrogen most of researches focused on the steam reforming of methanol (SRM) reaction as an efficient process for on-board hydrogen production [7]. It is a catalytic reaction which usually carries out on copper based catalysts [8]. The co-precipitation synthesis method is the most common pathway for fabrication of copper-based catalysts. In this method, precursors deposit at different precipitate rate, so uniform nanoparticles with narrow distribution particle size cannot be usually achieve and in most cases the particles are in micrometer scale [9]. In the co-precipitation method nucleation, growth and agglomeration occur simultaneously, therefore, much control is needed to produce particle with narrow distribution size [10]. If the nucleation process complete prior the growth step, homogeneous particle size can be achieved, otherwise a wide particle size range will be produced.

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Nomenclature

List of symbols and acronyms

GC	Gas Chromatography
FTIR	Fourier Transform Infrared Spectroscopy
BET	Brunauer Emmett Teller
XRD	X-ray Diffraction
FESEM	Field Emission Scanning Electron Microscopy
EDX	Energy Dispersive X-ray
FID	Flame Ionization Detector
TCD	Thermal Conductivity Detector
CZCA	$CuO/ZnO/CeO_2/Al_2O_3$
GHSV	Gas Hourly Space Velocity
SRM	Steam Reforming of Methanol
MFC	Mass Flow Controller

Regardless of the secondary process, such as agglomeration, anything that increase super-saturation in the solution can help to produce fine final product [11]. Hybrid methods such as plasma, microwave and ultrasound techniques can help to de-agglomerate synthesized nanomaterials and help to control the particle size [12]. Among these, ultrasound irradiation is known as an efficient complementary method for production of nanoparticles through different synthesis methods [13]. In sonochemical reactions, the fast kinetic of the process prevents the growth of the nuclei; on the other hand the growth of nucleation centers that are formed during bubble collapsing is limited by short cavity collapse time [14]. Atomic level mixing and high cooling rates after bubble collapsing create appropriate conditions for the production of nanoparticles with narrow particle size distribution and high dispersion [15]. Sonochemistry is used widely for the synthesis of nano-crystalline or nano-amorphous particle of metal oxides [16]. But, there are no reports about using the sonochemical co-precipitation method for the synthesis of the $CuO/ZnO/CeO_2/Al_2O_3$ nanocomposite for the steam reforming of methanol reaction. Some researchers study the advantages of sonochemical synthesis versus the conventional method. Awati et al. found that more uniform distribution/dispersion of nanoparticles, higher surface area, higher thermal stability along with phase purity are the advantages of the synthesis of nanocrystalline titania by the sonochemistry method [17]. Researches on the sonication process show that power and time are the most crucial parameters in the sonochemistry assisted method [18].

Therefore, the main aim of this paper was to investigate the effect of irradiation power and time on structural and catalytic properties of nanocatalysts fabricated by the novel sonochemical precipitation. For this purpose, a series of copper base nanocatalysts which were promoted by zinc oxide, ceria and alumina ($CuO/ZnO/CeO_2/Al_2O_3$) were synthesized by the sonochemical co-precipitation method at different irradiation powers and times. These samples were characterized by various analyses. Finally, the synthesized nanocatalysts were studied for their catalytic performance through the steam methanol reforming process.

2. Materials and methods

2.1. Materials

Copper nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, 99%), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$, 99%) and aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, 99%) were purchased from Aldrich (Milwaukee, WI, USA). Cerium nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99%) and sodium carbonate (Na_2CO_3, 99%) were supplied by Merck company. All of the reagents were used without further purification.

2.2. Nanocatalysts preparation and procedure

Fig. 1 shows the synthesis procedure of $CuO/ZnO/CeO_2/Al_2O_3$ nanocatalysts by conventional co-precipitation and sonochemical coprecipitation method. Schematic flow chart has three main stages, consists of precursor preparation, sonochemical coprecipitation synthesis (Fig. 2) and post treatment of nanocatalysts. At first, an aqueous solution of metal salts (1 M) was made and heated at 70 °C. A solution of sodium carbonate (1 M) was added slowly to the aqueous precursor solution while the ultrasound irradiation at different power and time glowed to resulted solution. As mentioned in Fig. 2, during this process the temperature and pH was kept constant 70–80 °C and 7–8, respectively. The precipitates were aged for 2 h at 70–80 °C, then filtered and washed three times with deionized water. The resulted slurry was dried at 110 °C for 12 h and calcined at 350 °C for 5 h. According to t different irradiation power and time of irradiation, six samples were prepared as follows: CZCA(CP), CZCA(T15-P30), CZCA(T15-P60), CZCA(T15-P90), CZCA(T5-P90) and CZCA(T10-P90). In these samples, CP refers to conventional co-precipitation method. In the samples were fabricated by sonochemical co-precipitation method, T and P refer to time and power of sonication, respectively.

2.3. Nanocatalysts characterization techniques

X-ray diffraction (XRD) analysis was performed by means of a Siemens diffractometer D5000 with a Cu Kα radiation source (0.154056 nm) with a generator voltage and current of 30 kV and 40 mA, respectively. The crystallography of samples was investigated in a scanning angle (2θ) of 10–90°. The phase identification was made with comparison to Joint Committee on Powder Diffractions Standards (JCPDSs). The microstructure properties and morphology of the nanocatalysts were investigated by field emission scanning electron microscope, FESEM (HITACHI 4160-s). Energy Dispersive X-ray (EDX) and dot maps (VEGA II, TESCAN) were used for evaluation the dispersion and elemental analysis of samples. Transmission electron microscopy (TEM) analysis was carried out using a Philips CM-200 electron microscope operated at 150 kV. Samples were ultrasonically dispersed in ethanol and then, a drop of the suspension was put on a thin carbon film-coated Cu grid. Specific surface area of nanocatalysts according to Brunauer-Emmett-Teller methodology (BET) was measured by using a Quantachrome CHEMBET-3000 device. Surface functional groups of the nanocatalysts were investigated by using Fourier Transform Infrared Spectroscopy (FTIR, UNICAM 4600) in the range of 400–4000 cm^{-1} wave number.

2.4. Experimental setup for catalytic performance test

Fig. 3 illustrates the experimental setup for catalytic performance experiments through the methanol steam reforming process. Catalytic tests were performed in the temperature range of 160–260 °C, atmospheric pressure and GHSV = 10,000 cm^3/g_{cat} h. In all experiments, 0.4 g of the shaped nanocatalyst was loaded in a U-shaped Pyrex fixed bed reactor. This setup is consisting of three main sections: the feed preparation, the methanol steam reforming reactor as well as feed and products analysis sections.