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Homogeneous precipitation synthesis of $CuO–ZrO_2–CeO_2–Al_2O_3$ nanocatalyst used in hydrogen production via methanol steam reforming for fuel cell applications

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The $CuO–ZrO_2–CeO_2–Al_2O_3$ catalysts for production of hydrogen via methanol steam reforming were prepared by the homogeneous precipitation method using urea hydrolysis, and the effect of presence of ceria and zirconia on methanol conversion was investigated. Prepared catalysts were characterized by XRD, FESEM, EDX, BET and FTIR analysis. XRD analysis showed that the addition of ceria to nanocatalysts made copper crystallites smaller. The FESEM results indicated that ceria enhanced the surface homogeneity of the samples and made particle size smaller. Catalytic performance tests proved the good practicability and high stability of synthesized catalysts via the homogeneous precipitation method for steam reforming of methanol. Furthermore, the ceria containing catalyst was the best among samples. The $CuO–CeO_2–Al_2O_3$ catalyst had better methanol conversion with low CO production. The stability test showed that this catalyst was quite stable for steam reforming of methanol. This finding is completely consistent with the characterization analysis results. Finally, a reaction pathway for steam reforming of methanol on $CuO–ZrO_2–CeO_2–Al_2O_3$ catalysts was suggested.

1. Introduction

Environmental problems arising from the use of fossil fuel, and the fear of an energy shortage crisis led to development of fuel cell technology [1–5]. Due to the limitations in hydrogen storage technologies as the most promising fuel for fuel cells, processes which produce on-board hydrogen have attracted great interest [6–10]. Among different liquid fuels, methanol has been commonly studied, due to the high H/C ratio, low boiling point, low cost and easy storage [1,7,8,11]. Methanol steam reforming (SRM) reaction has been seen as promising process for hydrogen production [12]. This process occurs at low temperatures (200–300 °C) and produces hydrogen with high concentration (up to 75%) with low CO content (1–2%) [3]. It can be described by the following chemical reactions [7,13,14]:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H^{\circ}_{298K} = +49.7(kJ/mol) \qquad (R\text{-}1)$$
$$CH_3OH \rightarrow CO + 2H_2 \qquad \Delta H^{\circ}_{298K} = +90.7(kJ/mol) \qquad (R\text{-}2)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298K} = -41.2(kJ/mol) \qquad (R\text{-}3)$$

Cu based catalysts have been widely investigated for methanol steam reforming in the literature [13,15], due to their high activity and good selectivity for hydrogen formation [13,16]. It is believed that the active sites in SRM is metallic Cu° species, then CuO should reduce to Cu° species before reaction tests [16]. The alumina is added to catalysts to increase the surface area and to reduce Cu sintering [3,17]. Compared with the Al_2O_3-surpported Cu catalysts, ZrO_2 or CeO_2 containing catalysts have shown better results [18]. The promoting effects of ceria have been attributed to increase the copper dispersion and the thermal stability [19]. The ability to adsorb and release oxygen (oxygen storage capacity) and oxygen ion conductivity is an important property of ceria which is effective on minimizing CO content in the reforming gas [20,21]. Likewise, the application of zirconia as a promoter has been found to improve the Cu dispersion and prevent the formation of $CuAl_2O_4$ spinel [18,22–24]. Moreover, high thermal and mechanical stability and redox properties makes it suitable for SRM reaction [25].

The preparation method could play an important role in the synthesis of catalysts and their activity [26–29]. Mostly Cu-based

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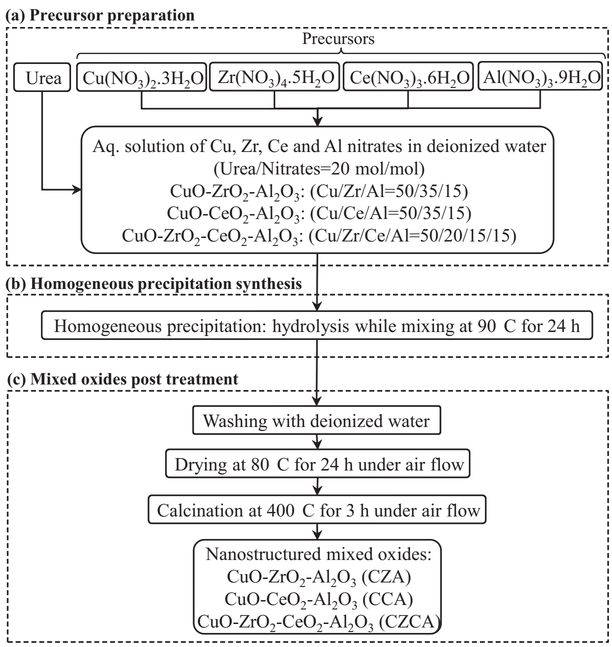

Fig. 1. Preparation steps of $CuO–ZrO_2–CeO_2–Al_2O_3$ nanocatalysts via homogeneous precipitation method.

catalysts are prepared by co-precipitation [25,30] and impregnation [6,31]. Ceria and zirconia on $CuO–Al_2O_3$ catalysts have been synthesized individually by co-precipitation method and their properties were investigated in Xinrong Zhang works [32,33] but homogeneous precipitation (HP) for the preparation of $CuO–ZrO_2–CeO_2–Al_2O_3$ (CZCA) catalysts has not been reported in the literature. According to this method, the precipitating agent is generated in a solution homogeneously by a slow chemical reaction and reacts immediately with the precursor. Homogeneity of the precipitates obtained by this method will be higher than that prepared by the direct addition of a precipitating reagent, since there is no gradient in the concentration of precipitants in the solution [34]. Then, it is conceivable that the homogeneous precipitation method may also provide an attractive alternative for fabricating new efficient catalyst system for the steam reforming of methanol.

Due to significant performance of homogeneous precipitation method for fabrication of nanocatalysts, in this paper, the SRM process over CZCA catalysts was performed which were prepared by the homogeneous precipitation synthesis method. The fabricated catalysts were analysed by XRD, BET, FESEM, FTIR and EDX techniques to understand their physicochemical properties. Moreover, because of the specific characteristics of zirconia and ceria which was studied in literature, their influence on methanol conversion and hydrogen and carbon monoxide selectivities was investigated. Furthermore, this work suggested a reaction pathway for SRM on CZCA catalysts.

2. Materials and methods

2.1. Materials

$CuO–ZrO_2–CeO_2–Al_2O_3$ precursors were prepared from copper nitrate trihydrate ($Cu(NO_3)_2·3H_2O$, Merck, extra pure), cerium

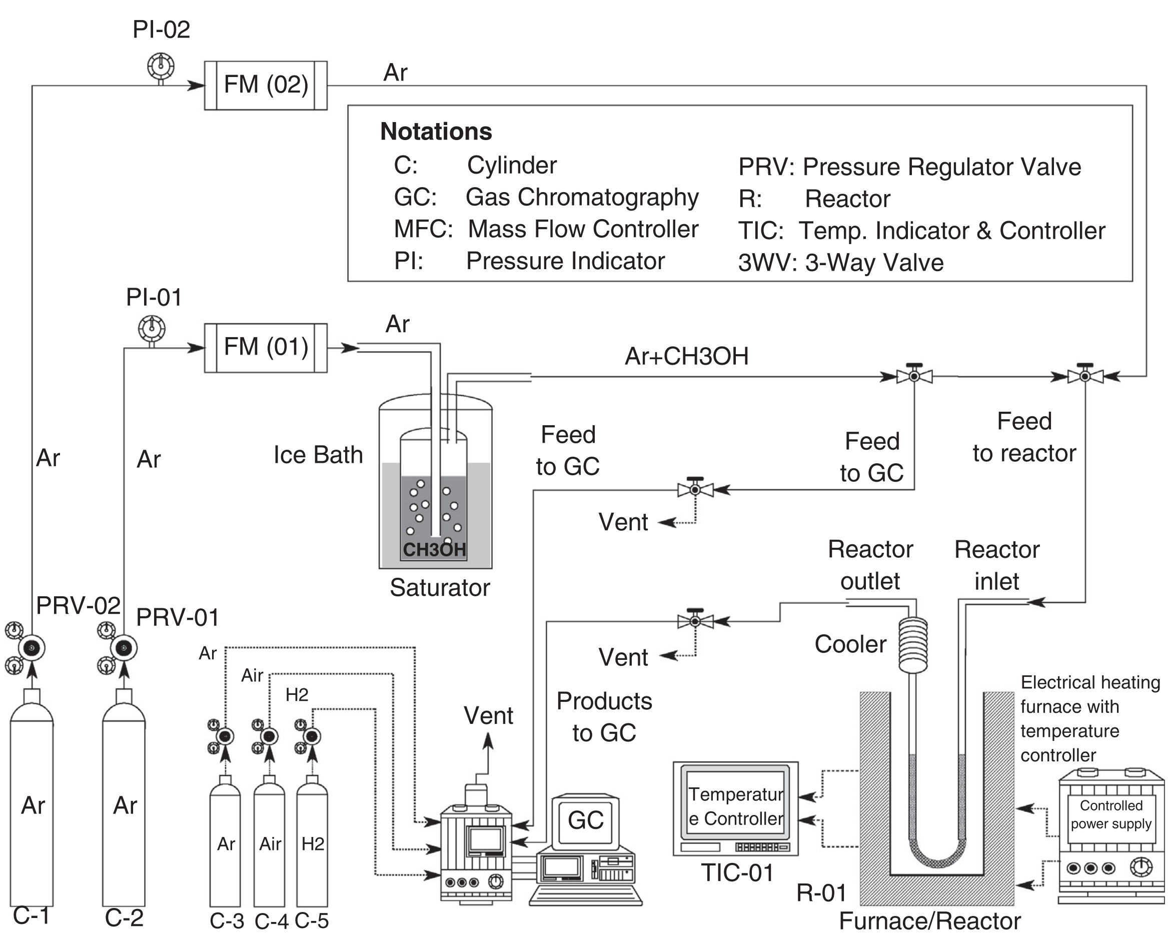

Fig. 2. Experimental setup for activity test of synthesized $CuO–ZrO_2–CeO_2–Al_2O_3$ nanocatalysts used in hydrogen production via methanol steam reforming.