Full Length Article

Cu based catalysts for syngas production from ethanol dry reforming: Effect of oxide supports

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GRAPHICAL ABSTRACT
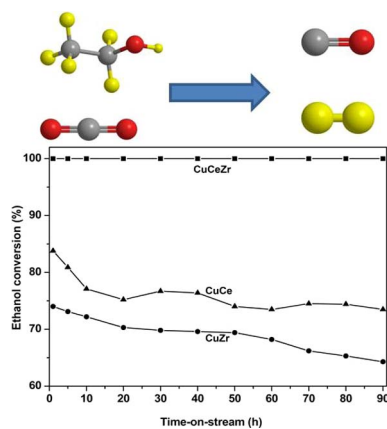
ARTICLE INFO

ABSTRACT

The Cu-based catalysts supported on different materials (CeO_2, ZrO_2, CeO_2-ZrO_2) were tested towards syngas production from CO_2 reforming of ethanol in order to determine the role of support. The physicochemical properties of the as-prepared catalysts were intensively explored by various techniques such as BET、TPR、Raman、SEM and TEM etc. Noticeably, the key features such as metal-support interaction, the reducibility and the oxygen vacancies decreased in the following order: CuCeZr > CuCe > Cu/Zr. Among the investigated catalysts, analysis of ethanol conversion as well as evaluation of the product distribution suggested CuCeZr sample as the most appropriate system for ethanol dry reforming. More precisely, CuCeZr catalyst exhibited full ethanol conversion at 700 °C and the H_2/CO ratio was close to the theoretical one (1.0). It also showed the promising stability as long as 90 h time-on-stream. In addition, the reliance of ethanol turnover frequency (TOF) on the supports was noted and CuCeZr sample still presented the highest value versus that of the others. Characterization results of the used catalysts indicated that both the smaller extent of Cu sintering and the less deactivating coke formation was observed for CuCeZr catalyst after the stability test, because of its abundant

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oxygen defects and/or sufficient metal-support interfacial area. It should be noted that the nature of carbonaceous deposits on the used CuCeZr catalysts were mainly amorphous structure. In contrast, the encapsulating coke which was detrimental for catalyst behavior was obviously detected. Herein, the present work revealed that support played an important role in ethanol dry reforming and might provide some valuable insight for the development of efficient catalysts.

1. Introduction

Recently, CO_2, a common greenhouse gas emitting from the large-scale utilization of fossil fuels, has resulted in the serious climate change [1,2]. Considering this impact, great efforts have been conducted to diminish CO_2 emission [3–6]. It mainly consisted of physical capture and/or the chemical conversion of CO_2 to liquid fuels, hydrocarbon, ester, carbonate etc. Among the various chemical routes, CO_2 reforming with methane and/or ethanol for syngas production is of great interest because this process could not only diminish CO_2 discharge but form high-valued chemicals [7–9]. Typically, syngas (a mixture of CO and H_2) was considered as a promising feedstock to generate fuels by Fischer-Tropsch approach, olefins and aromatics etc [10,11]. Compared to methane, biomass-derived ethanol seemed to be more attractive in terms of its pilot formation from the fermentation of renewable biomass, easy storage and low toxicity etc [12,13]. In addition, the development of the second generation bio-ethanol production from non edible lignocellulose made it more economic and competitive [14]. Herein, syngas production from ethanol dry reforming instead of conventional methane route is satisfactory both in energy and environment.

Up to date, only few studies have focused on CO_2 reforming of ethanol [15–18]. Thermodynamic analysis [19] suggested that both full ethanol conversion and as high as 96% yield of syngas could be obtained under optimal experimental conditions. On the other hand, Hu et al. [20] proposed that Ni/Al$_2$O$_3$ catalyst presented a promising activity and suitable H_2/CO ratio for ethanol dry reforming (EDR). Additionally, Bahari et al. [21] further studied the influence of Ce dopant for EDR process over Ni/Al$_2$O$_3$ sample and the results revealed that the Ce promoter could enhance the ethanol conversion. However, it should be noted that the investigated Ni-based catalysts normally suffered from a quick deactivation because of Ni sintering and/or coke formation during the severe reaction conditions. Hence, development of the suitable catalysts with high activity and stability is essential for the wide application of ethanol dry reforming process.

Interestingly, Cu-based catalysts have exhibited good behavior for ethanol conversion and/or CO_2 activation as pointed out in the previous literature [22–24]. Moreover, supported Cu catalysts has been in a hot research considering the less cost versus noble metals. Apart from the nature of the active metal, the types of support were also regarded as one of the critical factors for the catalyst activity and stability [25]. It was accepted that supports might control both the dispersion of active metal and the metal-support interaction, which could affect the reactant activation and coke deposition [26]. Besides stabilizing active metal sites, support might also take part in the intermediate reaction steps. Recently, numerous oxide supports such as Al$_2$O$_3$ [27], SiO$_2$ [16], SBA-15 [28], CeO$_2$ [29], ZrO$_2$ [30] and Ce$_x$Zr$_{1-x}$O$_2$ [31] etc have been investigated for dry reforming process. Among these supports, Ce$_x$Zr$_{1-x}$O$_2$ composite oxide were regarded as one of the most promising alternatives due to its high oxygen storage capacity (OSC), the good thermal properties and strong metal-support interaction which could facilitate the catalytic reaction [32,33]. Actually, the Ce/Zr molar ratio determined the catalytic behavior in the dry reforming processes. Trovarelli et al. [34] proposed that Ce$_{0.8}$Zr$_{0.2}$O$_2$ possessed the most stable composition in the investigated Ce$_x$Zr$_{1-x}$O$_2$ materials. Moreover, Potdar et al. [35] studied the influence of Ce/Zr ratio for methane dry reforming over Ni/CeO$_2$-ZrO$_2$ catalyst and reported that Ni/Ce$_{0.8}$Zr$_{0.2}$O$_2$ sample presented the best activity and the lowest deactivation rate because of the less coke deposits versus other compositions. As similarly discussed by Jun et al. [36], 15 wt%Ni/Ce$_{0.8}$Zr$_{0.2}$O$_2$ showed the high activity as a combination result of the fine dispersion of active metal and the strong metal-support contact.

In summary, the selection of a suitable support played an important role in improving the catalytic performance. So far, the development of an efficient catalyst for ethanol dry reforming is still in its infancy. Herein, the main challenge is avoiding or at least diminishing the coke deposition and/or active metal sintering during the reaction because these factors can lead to quick catalyst deactivation. A promising support might efficiently prevent carbon deposition and the sintering of active species to some extent. To the best of our knowledge, there were less or no studies about ethanol dry reforming over Cu-based catalysts.

In this work, Cu catalysts supported on different oxides such as CeO$_2$, ZrO$_2$ and Ce$_{0.8}$Zr$_{0.2}$O$_2$ were synthesized by facile co-precipitation method and tested for ethanol dry reforming under a wide reaction temperature region and long time on stream to evaluate the effect of support on ethanol conversion, product distributions as well as stability. The as-prepared catalysts were further characterized by various techniques including BET, XRD, SEM, H$_2$-TPR, and Raman etc in order to establish the relationship between the physicochemical features and the catalytic behavior.

2. Experimental

2.1. Catalyst preparation

The Cu based catalysts were synthesized by co-precipitation method with urea. (NH$_4$)$_2$Ce(NO$_3$)$_6$, Cu(NO$_3$)$_2$ and ZrOCl$_2$·8H$_2$O were selected as precursors. The nominal Cu loading was set as 15 wt% in all cases. Typically, an aqueous solution containing an appropriate amount of precursors and urea was heated to 90 °C and maintained at this temperature for 3 h under magnetic stirring. After filtration and thorough washing with hot deionized water, the precipitate was dried over night at 100 °C and finally calcined at 400 °C for 4 h in static air. The obtained catalysts were denoted as CuCe, CuZr and CuCeZr (Ce/Zr = 4.0, molar ratio), respectively.

2.2. Characterization of catalyst

The actual Cu content was determined by an inductively coupled plasma (ICP) atomic emission spectrometer (Perkin Elmer Optima 8000 equipment). Firstly, sample was dissolved into aqua regia, and then the solution was diluted with nitric acid to meet the detection limit of the apparatus. The liquid mixture was vaporized in the plasma of the monochromatic spectrophotometer and the emitted wavelengths were quantitatively analyzed.

The specific surface areas were tested using BET (Brunauer, Emmett and Teller) method. The measurements were conducted on an ASAP 2010 Micrometrics apparatus. Before analysis, the samples were pretreated by heating for 1 h at 300 °C under N$_2$ flow.

The crystalline phases of the catalyst were determined by X-ray diffraction on a Shimadzu XRD-7000S with Cu Kα radiation source operating at 40 kV and 100 mA. The crystal sizes were calculated according to the Scherrer equation [37].

The catalyst reducibility was explored by H$_2$-TPR technique [38]. Prior to test, 100 mg (40-60mesh) samples were pretreated at 300 °C for 1 h under a N$_2$ flow (50 mL/min) in order to remove the adsorbed