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Methanol steam reforming in a microchannel reactor by Zn-, Ce- and Zr- modified mesoporous Cu/SBA-15 nanocatalyst

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ABSTRACT

Hydrogen production by steam reforming of methanol was studied over several Cu/SAB-15-based nanocatalysts in a parallel-type microchannel reactor. The catalysts were prepared through impregnation method and XRD, BET, FT-IR, FE-SEM, TEM, H_2-TPR and TGA techniques were used to characterize surface and structural properties of the synthesized catalysts. The effects of reaction temperature, WHSV and S/C molar ratio on the methanol conversion and selectivities of the gaseous products were studied. Then, effects of the metallic promoters were investigated to improve performance of the catalysts. It was revealed that ZnO and CeO_2 promoters have positive effects on decreasing CO selectivity and ZrO_2 promotes methanol conversion. Furthermore, ZrO_2 and CeO_2 were declared to improve stability of the catalyst. Among the evaluated catalysts, $Cu/ZnO/CeO_2/ZrO_2/SBA$-15 can provide optimal methanol conversion with low CO concentration in the gaseous products. For this catalyst, the methanol conversion and hydrogen selectivity reached 95.2% and 94.6%, respectively.

Introduction

Due to limited fossil fuel resources and climate change, efforts should orient towards full replacement of fossil fuels with renewable energy sources. Among different renewable energy resources, hydrogen is recognized as an ideal energy carrier since it provides the lowest level of pollution and it can be employed in fuel cells to generate electricity [1,2]. Recently, hydrogen required for on-board fuel cells has been supplied through two main methods. In the first method, hydrogen is directly provided by storing it in the form of a pressurized gas, chemical hydrides, a cryogenic liquid or a solid fuel. In the case of solid fuels, metal hydrides or carbon nanotubes are used, which have adsorbed a considerable amount of hydrogen molecules. In the second method, hydrogen is produced on-site by reforming liquid hydrocarbons, such as methanol and ethanol [3,4]. With respect to the second method, reforming of liquid hydrocarbons is a favorite option to respond hydrogen demand of small-scale reactors due to possibility of modifying and reconstructing the available energy networks for liquid fuel transportation with a low cost. One of the most commonly used liquid hydrocarbons is methanol. Methanol can be reformed through three important approaches of steam reforming (STR), autothermal reforming (ATR) and partial oxidation (POX) [3]. However, methanol

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steam reforming (MSR) has gained more interest due to its associated low reaction temperature, noticeable water miscibility, low CO and high hydrogen concentrations in the reformate gas [5]. The main reactions involved in MSR process are [6]:

Steam reforming of methanol (SMR):

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \quad \Delta H^0_{298} = +49.4 \text{ kJ mol}^{-1} \tag{1}$$

Methanol decomposition:

$$CH_3OH \leftrightarrow 2H_2 + CO \quad \Delta H^0_{298} = +92.0 \text{ kJ mol}^{-1} \tag{2}$$

Water-gas shift reaction (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41.1 \text{ kJ mol}^{-1} \tag{3}$$

An appropriate reactor candidate for MSR based portable electronics is microchannel reactor coated with catalyst. In this way, structure of the fuel processor would be compact enough and the system would exhibit some advantages corresponding to behavior transience, heat and mass transport and hydrodynamics [7,8]. On the other hand, conventional reforming reactors, i.e. packed-bed, which contain a packed-bed filled with the catalyst particles, suffer from needing high pumping power consumption and heat transfer restrictions [9,10]. Since the efficiency of heat transfer is an important issue due to endothermicity of the MSR process, metallic microreactors have been adopted as alternatives to packed-bed reformers. Microreactors are structures including channels with a dimension below 1 mm [10]. They improve heat and mass transfer, provide higher surface area to volume ratio and cause control of reaction temperature within flammable regions with high accuracy, which reduces number of hot spots [11]. Zeng et al. [3] evaluated MSR catalytic activity of $Cu/ZnO/ZrO_2/Al_2O_3$ in cube-post microreactor. The $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst synthesized via co-precipitation and coated on the reactor plate through wash-coating method. They achieved maximum methanol conversion of 70.3%, at 280 °C and almost 74.4% H_2 and 1% CO concentrations in the reformate gas. The low level of methanol conversion obtained in this study is attributed to the microreactor structure while with modification of microchannels dimensions could reach 95% [12].

MSR by Cu-based catalysts has been studied widely due to their high activity for MSR and low-cost. Despite the mentioned advantages, Cu-based catalysts are high selective for CO production and unstable during long-term MSR process. Cu-based catalysts with high activity for H_2 production and low selectivity towards CO, can be prepared with addition of promoters or changing the synthesis method. Both these approaches are suggested to enhance metal dispersion, increase surface area and reduce particle size of the catalysts [13]. ZnO, CeO_2 and ZrO_2 are the most commonly used promoters for Cu-based catalysts [14]. ZnO addition enhances Cu dispersion and CuO reducibility of Cu-based catalysts that led to good performance of Cu-Zn-based catalysts in MSR process [15]. Also, the excellent activity of Cu-Zn-based catalysts may be attributed to enhancement of methanol adsorption [16], the spill-over of both H_2 from Cu to ZnO [17] and O_2 from ZnO to Cu sites [18]. CeO_2 promoter can improve Cu dispersion and suppresses coke formation due to its oxygen storage characteristic [19]. In more detail, CeO_2 has fluorite structure, in which the oxygen atoms are all co-planar, allowing for rapid oxygen atoms diffusion through the lattice [20]. Also, CeO_2 can promote catalytic activity, H_2 selectivity and thermal stability of catalysts, effectively. CeO_2 provides all these advantages by lowering CO content of the reformate gas through suppressing reverse water-gas shift (WGS) reactions and methanol decomposition [21,22]. The other common promoter, ZrO_2, enhances dispersion of Cu on catalyst surfaces to give higher catalytic activity and promotes catalyst reducibility and stability [23]. Agrell et al. [15] approved reducibility improvement of Zr-containing catalysts by investigating reduction–oxidation cycles. Also, ZrO_2 addition to Cu-based catalysts prevents Cu sintering and amorphous phase formation during MSR process [24].

Notably, the choice of an appropriate support with a high surface area is important issue to enhance dispersion of the catalytically active metals over the support surface and, consequently, improve catalytic activity. γ-Al_2O_3, ZSM-5, SiO_2, MCM-41 and SBA-15 have been widely applied as catalyst supports [25]. Specifically, SBA-15 has been selected by many researchers since it is a mesoporous material and possesses larger pores (3–30 nm) compared to microporous catalysts (pore size <2 nm) [26]. As SBA-15 pores are large, conversion of larger molecules is possible whereas traditional microporous catalysts cannot convert large molecules, such as tars. Furthermore, SBA-15 is thermally and hydrothermally stable, which makes it a promising support for different catalysts [27,28]. It should be mentioned that SBA-15 has illustrated excellent properties as a MSR catalyst support. Eswaramoorthi and Dalai [29] investigated SBA-15 supported Pd-Zn catalysts with various Pd and Zn contents to produce H_2 from methanol via STR and POX reactions. They reported that the best H_2 selectivity and a low level of CO generation obtained with the catalyst containing 4.5%Pd and 6.7% Zn. Yao et al. [30] studied MSR process for H_2 generation using SBA-15, as an effective novel structural promoter, to obtain SiO_2-modified Cu/ZnO/Al_2O_3 catalysts. They concluded that application of SBA-15 modified catalyst can provide superior catalytic activity with methanol conversion enhancement and reduction of CO formation. Also, they suggested that intrinsic nature of SBA-15 can modify the catalyst to achievement higher Cu dispersion.

In this study, SBA-15 mesoporous material was synthesized by hydrothermal method and was employed as a support for several Zn, Ce and Zr promoted Cu-based catalysts. The Cu/SBA-15-based nanocatalysts were prepared through impregnation method and characterized by XRD, BET, FT-IR, FE-SEM, TEM, H_2-TPR and TGA techniques. MSR performances of the nanocatalysts were evaluated in a microchannel reactor and influence of the promoters on activity of the Cu/SBA-15 catalysts was investigated in detail. Finally, a continuous MSR process was carried out at 300 °C, WHSV of 43.68 h^{-1} and the S/C molar ratio of 2, to evaluate stability of the nanocatalysts.

Experimental

Materials

Triblock copolymer (Pluronic P-123), hydroxypropyl cellulose (HPC), copper nitrate ($Cu(NO_3)_2 \cdot 3H_2O$, purity ≥ 99%), zinc

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