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Preparation and characterization of ultrasound-assisted co-precipitated nanocrystalline La-, Ce-, Zr –promoted Ni-Al2O3 catalysts for dry reforming reaction

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ABSTRACT

Mesoporous nanocrystalline 25 wt.%Ni-M-Al_2O_3 (M = CeO_2, La_2O_3, and ZrO_2) powders were synthesized by the ultrasonic assisted co-precipitation method and employed in methane dry reforming. The results exhibited that the addition of 5 wt.% La_2O_3 and ZrO_2 increased the surface area and the incorporation of the same content of CeO_2 had a vice versa effect. The TPO analysis showed that the amount of deposited carbon was lower than that deposited on the surface of the unmodified catalyst. It was observed that the incorporation of promoters decreased the catalytic activity and among all the promoted catalysts, Ce-promoted sample was more effective in dry reforming reaction with a low degree of carbon formation.

1. Introduction

Increasing demand for energy and the fossil resources limitations are a cause of anxiety. On the other hand, the environmental problems such as pollution and global warming are due to use of fossil fuels [1,2]. Biogas is an attractive renewable source, which obtained from different sources such as swage, sludge, landfill or industry. Methane dry reforming ($CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$, $\Delta H^\circ = 247$ kJ/ mol) permits the utilization of CO_2 and CH_4, which are two prominent greenhouse gases. This process converts these two gases to valuable syngas (H_2 and CO mixture) with a proper ratio ($H_2/CO = 1$), which is favorable for the utilization in the Fischer-Tropsch process [3–8]. Methane dry reforming is an endothermic reaction and the main challenge of this process is catalyst deactivation because of the deposition of carbon on the surface of the catalyst [9]. Consequently, the development of a high coke resistance catalyst with high stability is one of the main issues in catalysis. Although, the noble metals are more effective and less sensitive to coke deposition, due to their high cost and limited availability the industrial usage of these metals is still a challenge [10,11]. Side reactions such as CO disproportionation (Boudouard reaction, (Eq. (1) and methane cracking (Eq. (2)) can affect the performance of the catalyst in dry reforming of methane.

$$2CO \leftrightarrow C + CO_2 \quad \Delta H^\circ = -172.4\ \text{kJ/mol} \tag{1}$$

$$CH_4 \leftrightarrow C + 2H_2 \quad \Delta H^\circ = 74.9\ \text{kJ/mol} \tag{2}$$

The Ni-based catalysts with low cost can possess acceptable catalytic performance compared to precious metals in dry reforming of methane. However, the accumulation of carbon on the surface of the catalyst results in catalyst deactivation [12–15]. The activity of the Ni-based catalyst is rapidly reduced at high temperatures, due to the existence of aggregated Ni^0 particles on the catalyst support, which are formed at high temperatures. These aggregated nickel particles favor the formation of encapsulating carbon instead of carbon nanotubes (CNTs) [16,17]. It was reported that the stability of the nickel on the Al_2O_3 carrier is much higher than on the other carriers [18]. Rostrup-Nielsen [19] reported that increasing in adsorption of steam or CO_2 can increase the carbon resistance of Ni-based catalysts due to the increasing the surface reaction rate or decreasing the methane dissociation rate. For this reason, most of the researches have been focused on the use of basic promoters such as CeO_2, SiO_2, La_2O_3,K_2O, BaO, CaO, MgO, and ZrO_2, which make the catalyst more stable [20–26]. Alipour et al. [27] studied the effects of MgO, BaO and CaO promoters on the catalytic performance of the Ni/Al_2O_3 catalyst in dry reforming. They reported that MgO was more effective for suppressing the carbon formation. Sepehri et al. [28] studied the influence of La, Ce, Zr and Sr promoters on the catalytic activity and textural characteristics of Ni/Al_2O_3 in autothermal reforming of methane and reported that just small amount of CeO_2 was effective in improving the catalytic activity. It has been stated that the CeO_2 can enhance the mobility of lattice oxygen, which improves the elimination of carbon. In addition, it has been reported that the presence of cerium oxide stabilizes alumina structure at

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high temperatures and avoids decreasing its surface area and sintering of catalyst active sites [29–33]. The basic property of La_2O_3 favors CO_2 adsorption and dissociation and results in gasification of deposited carbon, which prevents the catalyst deactivation [4,34]. Kathiraser et al. [35] reported that the increased stability of the Ni supported $LaAlO_3$-Al_2O_3 perovskite catalysts was related to the increased lattice stability and existence of $LaAlO_3$ species on the alumina support, which resulted in minimizing the aggregation of Ni particles. It has been proven that the addition of small content of ZrO_2 is able to improve the catalyst stability, which results in minimizing coke deposition in methane dry reforming [36,37]. Oemar et al. [38] showed that the surface oxygen mobility of the prepared Y_2O_3 enact significant role in enhancing the catalytic activity of the Pd-Ni/Al_2O_3 catalysts in oxy-CO_2 reforming of methane and inhibition of carbon deposition on the catalysts. Sutthiumporn et al. [39] investigated the effect of other metal ions (M = Bi, Co, Cr, Cu and Fe) into the Ni^{3+} site of $La_{0.8}Sr_{0.2}Ni_{0.8}M_{0.2}O_3$ perovskite catalysts in dry reforming of methane. They confirmed that LSN(Cu)O perovskite catalysts possessed good performance in initial activity. Also they revealed that the LSN(Fe)O perovskite catalyst exhibited higher stability due to the stronger metal-support interaction and the existence of the abundant lattice oxygen species. It has proven that co-precipitation method is a more desirable rout for the synthesis of nickel-alumina catalysts to optimize the reforming efficiency [40]. No control in size and particles growing and their tendency to agglomeration are some drawbacks of co-precipitation method [41]. Therefore, modification and improvement of the simple co-precipitation method for the production of nanoparticles are crucial. The use of high-intensity ultrasound irradiation to liquid in the sonochemical process causes acoustic cavitation, which is a physical phenomenon. Ultrasound irradiations lead to creating, grow and implosive of the bubbles in the solution mixture. Exclusive conditions such as high temperature (as high as 5000 °C) and high pressure (up to ~2000 atm) within the collapsing bubbles are the effects of bubble implosion [42]. The preparation of uniform nanocrystals with narrow size distribution and high-phase purity, reduction of phase transformation temperature, control in particle size, growth and morphology and reduction of sintering and aggregation of the as-prepared nanoparticles are some benefits of ultrasound assisted co-precipitation method [43–45].

In our previous work, the influence of the preparation conditions on the physicochemical characteristics of the catalysts prepared by the ultrasonic assisted precipitation method was studied [46]. Also we investigated the effect of Ni loading on the activity and coke formation of ultrasound-assisted co-precipitated Ni-Al_2O_3 catalyst in dry reforming of methane. The results revealed that the catalyst with 25 wt.% of Ni possessed high activity and stability in CH_4 dry reforming [47]. The aim of this study is to investigate the influence of the CeO_2, La_2O_3 and ZrO_2 promoters on the coke formation and the catalytic performance of the Ni-Al_2O_3 catalysts prepared with the ultrasonic assisted co-precipitation method in methane dry reforming.

2. Experimental

2.1. Sample preparation

The 25 wt.%Ni-MO_x-Al_2O_3 (M = Ce, La and Zr) catalysts were synthesized using a co-precipitation route with the assistance of ultrasound irradiation (US) as described in our previous article [37]. The amount of promoters (CeO_2, La_2O_3 and ZrO_2) was chosen 5 wt.% in all catalysts. In summary, an aqueous solution of metal nitrate salt precursors with desired calculated contents of the precursors was prepared and an aqueous NaOH solution (1 M) was added to the precursors solution under constant ultrasound irradiation (70 W) until pH reached 10. After this step, the slurry was vacuum filtered and thoroughly washed with distilled water. Then the filter cake was dried and calcined at 700 °C for 4 h. In addition, 25Ni-CeO_2-Al_2O_3 catalysts with different CeO_2 loadings (1, 3 and 5 wt.%) were prepared by a similar method as described above.

2.2. Characterization

X-Ray diffraction (XRD) analysis was carried out by a PANalytical X'Pert-Pro instrument. A Micromeritics chemisorb 2750 was utilized to perform the temperature programmed reduction and oxidation (TPR and TPO) analyses. The conditions of the TPR and TPO analyses were explained in details in our previous article [3]. The specific surface area, total pore volume and mean pore diameter of the prepared samples were determined using a BELSORP mini II instrument. A VEGA TESCAN microscope was used for studying the morphology of the samples.

2.3. Catalytic tests

The reaction was performed in a quartz tubular microreactor at atmospheric pressure and various temperatures. Typically, a constant weight (0.2 g) of the catalyst particles (40–60 mesh) was used and the samples were reduced with a H_2 stream (20 ml/min) at 600 °C for 2 h before the catalytic test. After that, the reactor was cooled to 550 °C and then a mixed stream of CH_4 and CO_2 was introduced into the microreactor as reactant feed. Online analysis of the outlet gas stream was done by a gas chromatograph (Varian 3400). As schematic of the catalytic evaluation system is shown in Fig. 1. The CH_4 (X_{CH_4}) and CO_2 (X_{CO_2}) conversions were determined by the following equations:

$$\mathrm{X}_{CH_4} = \frac{CH_{4(in)} - CH_{4(out)}}{CH_{4(in)}} \times 100\% \tag{3}$$

$$\mathrm{X}_{CO_2} = \frac{CO_{2(in)} - CO_{2(out)}}{CO_{2(in)}} \times 100\% \tag{4}$$

3. Results and discussion

3.1. X-Ray diffraction analysis

The XRD patterns of the promoted catalysts are illustrated in Fig. 2. The peaks corresponded to NiO, $NiAl_2O_4$, Al_2O_3, CeO_2 and ZrO_2 phases were indexed in Fig. 2. The CeO_2 and ZrO_2 characteristic peaks are attributed to the JCPDS cards No. 01-075-0076 and 01-088-1007, respectively. As can be seen, there was no diffraction peak representative of lanthanum oxide, indicating that the La_2O_3 was homogeneously dispersed on the catalyst surface [48,49]. The absence of NiO peaks in the XRD patterns could be related to the fact that the small NiO particles were highly dispersed in the catalyst structure. This effect in the case of catalyst promoted with La_2O_3 is related to the Ni-La mixed oxide formation, which leads to the formation of highly dispersed NiO particles [28]. Ce^{3+}/Ce^{4+} redox couple in the CeO_2 promoted catalyst creates the surface and oxygen bulk vacancies, which results in the M-O surface formation complexes. This increases the oxygen mobility of the catalyst, which decreases the metal-carrier interaction and improves the nickel reducibility and dispersion [50]. The average crystallite sizes of nickel aluminate at 2θ = 37°, 45° and 65° were determined by the Scherrer equation and the results are reported in Table 1.

3.2. The N_2 adsorption/desorption analysis

The textural characteristics of the prepared samples are reported in Table 1. As it is shown, the addition of 5 wt.% CeO_2 reduced the BET area from 188 to 178.1 m^2g^{-1}, but the addition of 5 wt.% ZrO_2 and La_2O_3 increased the surface area from 188 to 203.8 m^2g^{-1} and 198.3 m^2g^{-1}, respectively. Also, the addition of promoters increased the mean pore diameter and total pore volume. It is noteworthy to mention that the CeO_2 promoted catalyst possessed the highest pore