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Editor's choice paper

Sequential impregnation vs. sol-gel synthesized Ni/Al_2O_3-CeO_2 nanocatalyst for dry reforming of methane: Effect of synthesis method and support promotion

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ABSTRACT

The effects of CeO_2 addition (10 wt.%) as a support promoter on the catalytic performances of Ni catalysts supported over Al_2O_3 were studied in the dry reforming of methane (DRM). Ni/Al_2O_3-CeO_2 nanocatalyst was prepared with sequential impregnation and sol-gel methods using low cost metal nitrate precursors to explore the effect of preparation method. The obtained materials were characterized by XRD, FESEM, BET and FTIR techniques. Catalytic activity and time-on-stream catalytic performance have been explored at different feed ratios, gas hourly space velocities and reaction temperatures. The results showed that CeO_2 addition as a support modifier to the Ni/Al_2O_3 catalysts improved catalytic activity and stability. High dispersion of active phase in sol-gel synthesized catalyst was achieved in comparison with the impregnation synthesized one. FESEM images display smaller particle size (100% below 100 nm) and a narrow particle size distribution for sol-gel synthesized sample, also this sample showed higher activity in the reforming reactions.

1. Introduction

Steam reforming of methane to syngas is industrially practiced over the world [1–3]. During recent decades dry reforming of methane (DRM) attracts much attention from both environmental and industrial concerns too [4–6]. Reactions involving DRM produce highly valuable syngas (mixture of CO and H_2) through utilization of two harmful greenhouse gases (CO_2 and CH_4) [7–10]. The main reaction in DRM process is shown as Eq. (1):

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \Delta H^0_{298} = 247 \text{ kJ/mol} \quad (1)$$

Simultaneously the reverse water-gas shift (RWGS) reaction (Eq. (2)), methane decomposition (Eq. (3)) and CO disproportionation also known as Boudouard reaction (Eq. (4)) can be involved in the whole reaction network [11,12] as described below:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \Delta H^0_{298} = 41.17 \text{ kJ/mol} \quad (2)$$

$$CH_4 \leftrightarrow C(s) + 2H_2 \Delta H^0_{298} = 74.85 \text{ kJ/mol} \quad (3)$$

$$2CO \leftrightarrow C(s) + CO_2 \Delta H^0_{298} = -173.46 \text{ kJ/mol} \quad (4)$$

One of the obstacles encountered in the application of this process is the rapid deactivation of the catalyst which is mainly due to coke accumulation and sintering of both support and active metal particles [13–15]. Both noble metals (Ru, Rh, Pt, etc.) and group VIII (Fe, Co, Ni) metals have shown to be active in catalysing DRM reactions [16,17]. Despite the fact that noble metals are insensitive to coke formation, Ni is widely used in industry due to the high activity, wide-availability and low-price [18–21]. Thus, Ni was chosen as active component to meet the discussed properties [22–24]. The main technical issue arisen by Ni catalyst is the strong propensity to carbon deposition [25–27]. Introducing catalyst support into the reaction system is a good measure to resolve this issue, since the catalyst support allows better dispersion of active metals on its surface. Ni has been supported on different carriers such as MgO, Al_2O_3, ZrO_2, SBA-15, MSU-S and TiO_2 [28–31]. In this work Al_2O_3 was chosen as catalyst support due to its higher surface area. Also, to improve the performance of Ni/Al_2O_3 catalyst several modification methods such as adding metal oxide promoters (MgO, CeO_2, La_2O_3, etc.) to influence the support basic-

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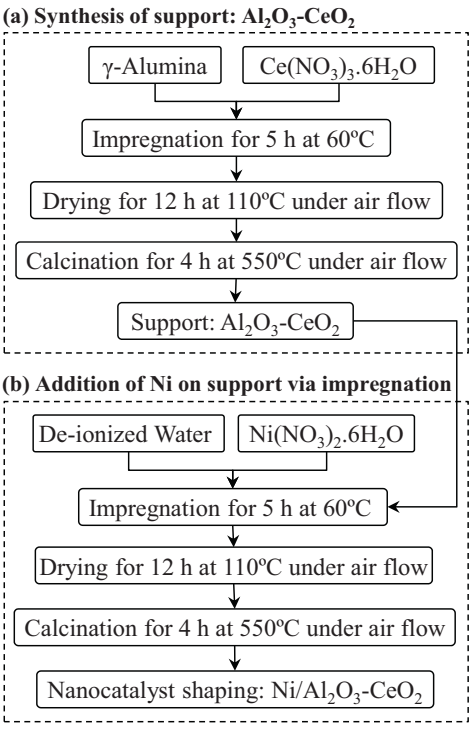

Fig. 1. Schematic flow chart for the preparation steps of Ni/Al2O3-CeO2 nanocatalyst via impregnation method.

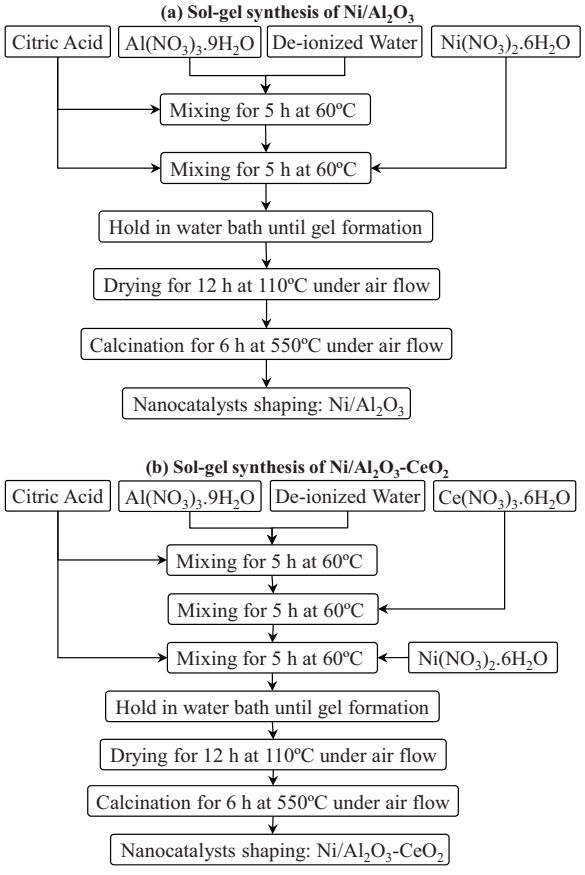

Fig. 2. Schematic flow chart for the preparation steps of (a) Ni/Al2O3 and (b) Ni/Al2O3-CeO2 nanocatalysts via sol-gel method.

ity have been studied [32–34]. Among these promoters Ceria has the excellent thermal and mechanical resistance and due to its unique property of storing and releasing oxygen (redox property) helping the thermal resistance of the supports, the better dispersion of active metal and resultantly the decrease in coke formation on the catalyst surface [35]. However, CeO_2 based supports generally suffer from the drawbacks of high cost and relatively low surface areas. Keep those mentioned above in mind and this that DRM is normally performed at high temperatures (700–900 °C) to achieve high conversions considering the endothermic nature of the reaction, a mixed framework of Al_2O_3–CeO_2 is proposed with the consideration of making use of high thermal stability of CeO_2 and the high specific surface area of Al_2O_3. Effect of Ceria addition and other rare earth metals was investigated before. Nabgan, W., et al. synthesized bimetallic Nickel-Cobalt (Ni-Co) catalyst supported on different ratios of Lanthanum (III) Oxide (La_2O_3) and gamma-aluminum oxide (γ −Al2O3) and they found out that La_2O_3 enhanced the metal-support interaction resulted in reduction of coke [36]. Wang, C.-y., et al. published their research regarding alumina-supported nickel catalysts with or without La_2O_3 or CeO_2. Rare earth oxides enhanced the activity of nickel catalysts [37]. Furthermore, CeO_2 implemented as an active metal in steam reforming of methane by Yang, X., et al. [38]. They investigated the addition of small amount of cerium and resulted in improvement of the nickel dispersion leading to inhibition of carbon deposition, but more amount of cerium addition was not favorable for nickel dispersion due to the blocking of active sites. Furthermore, modification by the rare earth elements (Ce, La, Sm, Pr) was reported by Xu, L., et al. [39]. They claimed that rare earth metals played crucial roles in promoting the catalytic activities and reducing the carbon deposition. Apart from catalyst compositions, catalyst preparation methods can have considerable influences on the catalytic performance [40]. Parameters such as morphology, particle size, dispersion of active metal and metal-support interaction through selection of different synthesis methods can alternate which is going to affect the performance of the DRM process. Among different synthesis methods sol-gel method because of its ability to produce uniform and reproducible nanoparticles, homogeneous dispersion and low synthesis temperature in comparison with traditional methods has gained much attentions [41–43].

In this work, we explore the promoting role of CeO_2 in Ni/Al_2O_3 catalyst for the DRM reaction. Also performance of Ni/Al_2O_3-CeO_2 catalyst prepared by sol-gel and sequential impregnation method was investigated. To the best of our knowledge, CH_4–CO_2 reforming reaction over Ni/Al_2O_3–CeO_2 catalysts differing in preparation method has been seldom reported previously. This report contains the synthesis of nanocatalysts, physicochemical characterization of the samples by XRD, FESEM, BET, and FTIR techniques and then performance tests to investigate the influence of different GHSVs, CH_4/CO_2 ratios and temperatures on the catalyst activity. Furthermore the stability test was conducted for 10 h.

2. Materials and Methods

2.1. Materials

Synthesis of the nanocatalysts was carried out using raw materials namely γ-alumina, Ce $(NO_3)_3.6H_2O$, Ni $(NO_3)_3.6H_2O$, Al $(NO_3)_3.9H_2O$ and citric acid as gelling agent in sol-gel method. All the chemicals were purchased from Merck Company and employed without further purification. De-ionized water was used during all of the preparation steps.