



Full Length Article

Facile one-step synthesis of mesoporous Ni-Mg-Al catalyst for syngas production using coupled methane reforming process



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ARTICLE INFO

Keywords:

Dry reforming of methane
 Partial oxidation of methane
 Al_2O_3
 Nickel catalyst
 Syngas

ABSTRACT

Mesoporous Ni-Mg-Al and Ni-Al catalysts were facilely synthesized via evaporation-induced self-assembly (EISA) method and employed for coupled reforming reaction consisting of dry reforming of methane (DRM) and partial oxidation of methane (POM) to produce syngas ($\text{H}_2 + \text{CO}$). The Ni-Mg-Al and Ni-Al catalysts with encapsulated nickel nanoparticles were directly synthesized in one-pot way. For comparison, Ni/ Al_2O_3 as reference catalyst was also prepared by general impregnation method. Characterization by BET, XRD and H_2 -chemisorption revealed that the Ni-Mg-Al catalyst owned larger surface area and higher Ni dispersion as well as smaller metallic Ni particles size compared to Ni-Al and Ni/ Al_2O_3 catalysts. CO_2 -TPD demonstrated that the Ni-Mg-Al catalyst presented stronger basicity due to Mg incorporation. H_2 -TPR confirmed that the reduction of Ni-based species to Ni^0 was performed in high temperature due to the formed NiAl_2O_4 phase. Activity tests indicated that this Ni-Mg-Al catalyst, due to its excellent physicochemical property, exhibited higher CH_4 conversion, H_2 selectivity, and H_2/CO ratio in the coupled DRM-POM reaction. XRD, SEM and TG-DTA analyses of the used catalysts disclosed that the Mg-modified Ni-Mg-Al catalyst for syngas production using coupled DRM-POM reaction exhibited robust resistance to coke deposition. Consequently, by the synergistic cooperation between the coupled DRM-POM reaction and Mg-modified Ni-Mg-Al catalyst, high catalytic activity and stability could be accomplished to produce syngas.

1. Introduction

Synthesis gas ($\text{CO}_2 + \text{H}_2$), as a crucial chemical feedstock, was primarily used for downstream liquid fuels production by gas-to-liquid technologies, such as Fischer–Tropsch synthesis (FTS), methanol synthesis etc [1–3]. Syngas can be produced from various reforming methods, including dry reforming of methane (DRM), steam reforming of methane (SRM) and partial oxidation of methane (POM) [4–7]. As known, methane (CH_4) and carbon dioxide (CO_2) are important carbon resources, which can serve as raw materials for high-value chemicals production. In addition, with increasing requirement of energy, large numbers of CO_2 and CH_4 (greenhouses) are emitted into air, which leads to global climate warming and environment destruction. Dry reforming of methane to syngas is considered as an important production process because it converts two kinds of greenhouse gases ($\text{CH}_4 + \text{CO}_2$)

simultaneously to valuable syngas [8,9]. However, catalysts used in dry reforming of methane easily deactivate due to extreme coke deposition on catalyst as well as catalyst sintering, thereby lowering catalytic activity and catalyst lifetime. Given that the easy deactivation of catalyst in DRM reaction, designing robust catalyst that makes effective resistance to high temperature sintering and coke deposition presents a big challenge [10].

In the past researches, numerous catalysts for DRM reaction had been prepared and investigated. As a result, noble metals-based catalysts, such as Rh, Ru, Pt, Pd, Ir, etc., exhibited excellent catalytic activities and stabilities, at the same time increasing the use-cost [11–14]. Furthermore, Ni-based catalysts had also shown high catalytic activity in DRM reaction [15,16], while rapid deactivation of Ni-based catalysts caused by coke deposition limited their extensive application [17,18]. Although Ni-based catalysts showed easy deactivation in comparison

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with noble metals catalysts, they, due to low cost, still attract broad interest in the research of methane reforming to syngas. Many studies had confirmed that the formation of Lewis basic sites on catalysts could be effective to suppress coke deposition, consequently enhancing catalytic activity and prolonging catalyst lifetime. This was due to a fact that basic sites could reduce the coke deposition rate by accelerating CO₂ chemisorption to catalyst surface, through which adsorbed CO₂ reacted with deposited coke to generate CO (CO₂ + C ⇌ 2CO). Taken with this strategy, the presence of basic modifier plays an important role in inhibiting coke deposition and improving catalytic activity. Wang et al. employed MgO-modified SBA-15 supported nickel catalyst for DRM reaction, and the result indicated that the MgO-modified Ni/SBA-15 catalyst showed higher catalytic activity and stronger resistance to coke deposition compared to that of SBA-15 directly supported nickel catalyst [19]. A Ni_xMg_{1-x}O catalyst showed excellent catalytic stability in DRM reaction, with only active coke species that was irresponsible for deactivation being found over spent catalyst [20].

Until now, mesoporous alumina has been extensively used as catalyst support because of low cost and excellent physicochemical properties. However, different preparation methods could affect textural properties of alumina such as surface area, pore size, as well as thermal stability. Since a reproducible and feasible preparation method for mesoporous alumina synthesis was first reported by Yuan et al., improved procedures had been used for one-step nickel-aluminum oxides synthesis [21,22]. On the basis of this method, metallic Ni nanoparticles could be directly encapsulated inside pore channels, effectively improving the thermal stability of Ni species to increase catalytic activity [23–25]. In addition, with this one-step synthesis method, the metallic Ni nanoparticles loaded on Al₂O₃ were smaller compared with that prepared by general impregnation method, which was due to the confined effect of Al₂O₃ pore channel. Most importantly, the small metallic Ni nanoparticles became more effective to inhibit the nucleation and growth of coke species, thereby restraining coke deposition on catalyst [26,27].

In this work, we synthesized Ni-Mg-Al catalyst via one-step synthesis route by using solvent evaporation-induced self-assembly method (EISA). The prepared Ni-Mg-Al catalyst exhibited excellent textural properties, like high specific surface area, uniform pore size and small metallic Ni nanoparticles. Mg as basicity modifier was used to dope alumina, which could effectively enhance the CO₂ absorption ability to retard the coke deposition. Additionally, the introduction of Mg could help to disperse active Ni species. The metallic Ni nanoparticles directly loaded and confined on alumina had smaller particle size, which could contribute to higher catalytic performance.

For dry reforming of methane to syngas, coke easily deposited on the surface of catalyst and led to catalyst deactivation. It is noteworthy that coupling dry reforming of methane with partial oxidation of methane (DRM-POM) could be regarded as more effective process for syngas production compared to single DRM process. It was attributed to two main advantages: (1) the exothermic POM can in situ transfer heat to endothermic DRM and then realize homogeneous catalyst bed temperature; (2) POM, due to the existing oxygen, can apparently remove coke deposition and increase catalytic activity. The prepared Ni-Mg-Al catalyst was used for syngas production by employing a coupled DRM-POM process [6]. Activity tests indicated that the Ni-Mg-Al catalyst showed excellent catalytic activity, stability and strong coke suppression.

2. Experimental

2.1. Catalyst preparation

Mesoporous Ni-Mg-Al catalyst was prepared via one-step evaporation-induced self-assembly method (EISA) referenced to previous reports [21,28]. Typically, 1 g of triblock copolymer PEO₂₀-PPO₇₀-PEO₂₀ (Pluronic P123, Molecular weight = 5800, Sigma-Aldrich) was

dissolved in 20 ml of anhydrous ethanol. Then, 1.6 ml nitric acid and 2.04 g aluminum isopropoxide as well as a certain amount of nickel nitrate hexahydrate and magnesium nitrate were added to above solution with vigorous stirring at room temperature for 6 h, where the 10 M% of Mg/(Mg + Al) was designed. Then, the mixture solution was put in a drying oven at 60 °C with 48 h, in which ethanol slowly evaporated. After that, a green xerogel was obtained and then calcined at 700 °C for 4 h in air atmosphere with a heating rate of 5 °C/min. Finally, the obtained sample was named as Ni-Mg-Al. Mesoporous Ni-Al catalyst without Mg modifier was also synthesized, based on this similar preparation process of Ni-Mg-Al catalyst. For comparison, Al₂O₃ supported Ni catalyst (denoted as Ni/Al₂O₃), as reference catalyst, was also prepared by incipient wet impregnation method. Nickel loading amount for all catalysts was theoretically designed at 10 wt%.

2.2. Catalyst characterization

The crystalline structure of the prepared catalysts was detected by a Rigaku RINT2000 diffractometer with Cu-Kα radiation under an operating condition of 40 kV and 20 mA. The pore structure properties of catalysts were measured by N₂ physisorption method using an automated Quantachrome Nova 2200e apparatus. Prior to tests, all samples were degassed in vacuum at 200 °C for 4 h. The surface area and pore size distribution were obtained by BET method and BJH method respectively.

The surface morphologies of catalysts were observed by using a scanning electron microscope (JEOL JSM-6360 LV) equipped with an energy dispersive spectroscopy (EDS, JED-2300). The elemental valence states of catalysts were decided by using X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi spectrometer. Before operation, samples were pressed into wafers and placed on the holders. These obtained spectra were calibrated with C1s peak at binding energy of 284.5 eV.

In order to illustrate the reduction behaviors of the as-made catalysts, H₂ temperature-programmed reduction (H₂-TPR) was performed using a BELCAT-B analyzer (BEL, Japan). Before measurements, all catalysts were degassed and purged in He flow (30 ml/min) at 200 °C for 1 h. H₂-TPR was carried out in H₂/Ar flow (10% H₂, 30 ml/min) by heating temperature from 50 °C to 900 °C with a ramping rate of 10 °C/min. The basic properties of catalysts were characterized using CO₂ temperature-programmed desorption (CO₂-TPD). Prior to tests, catalyst pretreatments were carried out in Ar flow (30 ml/min) at 200 °C for 1 h and subsequently decreased to 50 °C. Then CO₂ was introduced for chemisorption at 50 °C with 30 min. CO₂-TPD test was performed by heating temperature from 50 °C to 900 °C with a ramping rate of 10 °C/min in He gas flow. H₂ chemisorption was carried out with a pulse injection way. Catalysts were firstly degassed at 200 °C with 2 h, followed by being reduced in 10% H₂/Ar flow (30 ml/min) at 750 °C with 2 h. After that, the catalyst temperature was cooled to 50 °C in vacuum, and then H₂ chemisorption was conducted under this temperature.

For methane reforming to syngas, coke easily deposits on catalyst, decreasing the catalytic performance and catalyst lifetime. The amounts of coke deposition at the used catalysts were determined by a Shimadzu DTG-60 thermogravimetric analyzer. The used catalysts were ramped to 800 °C in air atmosphere with a heating rate of 10 °C/min in a platinum sample cell.

2.3. Catalytic reaction

Catalytic reactions were measured in a fixed-bed quartz tube reactor (6 mm i.d.) at ambient pressure. 100 mg of catalyst (30–50 mesh) and 400 mg quartz sand were mixed and then loaded into the center position of quartz tube. The catalyst was heated up to 750 °C in N₂ flow, followed by being in situ reduced for 2 h under 5% H₂/Ar flow (100 ml/min). After reduction, reactant gases consisting of 90% CH₄/Ar, CO₂ and O₂ were introduced to the reactor, in which Ar was used as internal

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