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Hydrogen and syn gas production via CO₂ dry reforming of methane over Mg/La promoted Co–Ni/MSU-S catalyst

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ARTICLE INFO

Article history:

Received 24 July 2015
Received in revised form
17 October 2015
Accepted 18 October 2015
Available online xxx

Keywords:

xLa/Mg yCozNi/MSU-S catalyst
O₂-TPO
H₂ and syn gas production
CH₄/CO₂ reforming
Low coking
High stability

ABSTRACT

A series of xMg/La yCozNi/MSU-S catalysts were prepared by a sol–gel method and characterized by means of N₂-physisorption, FT-IR, H₂-TPR, CO₂-TPD, H₂-TPD, XRD, HRTEM, TG/DSC and O₂-TPO techniques. The catalytic performance of the catalysts was evaluated for H₂ and syn gas production at different temperatures at atmospheric pressure. The effect of reaction temperature, catalyst composition and performance of the catalyst were investigated during CO₂ dry reforming reaction at 700–800 °C with GHSV of 2.4 × 10⁴ mL/g^{−1} h^{−1}. The results indicated that upon La, Mg and Co promotion, the Ni nanoparticles are highly dispersed on the mesoporous walls of MSU-S via strong interaction between metal ions and the HO–Si-groups of MSU-S. The presence of La₂O₃ in xLayCozNi/MSU-S results in enhancement of initial catalytic activity as compared to xMgyCozNi/MSU-S. It revealed that 3 La 2Co 7Ni/MSU-S performed the best with highest CH₄ and CO₂ conversion showing outstanding catalytic activity, greater stability and low coking for 50 h during 75 h time on stream at 750 °C.

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Introduction

Depletion of fossil fuels increased continuously with rapid industrialization and caused problems like CO₂ emission and greenhouse gas effect. Therefore, the developments of renewable and clean energy resources have been paid widespread attention globally [1]. Hydrogen is a clean energy carrier, which can be used for hydrogen engine and hydrogen-fuel cells, as it only produces water on combustion. In addition, hydrogen is used as petrochemical feedstock in petroleum industry and reduction agent in steel industries [2].

Methane reforming with CO₂ for production of hydrogen and syngas ($\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$, $\Delta H^\circ(298\text{ K}) = 247\text{ kJ mol}^{-1}$) had received considerable attention for potential usefulness in industry and environmental optimization [3]. Methane dry reforming (MDR) with CO₂ argued better than steam reforming to meet the required gas composition for Fischer-Tropsch (F-T) synthesis [4].

MDR reaction had been studied by many researchers using metal supported catalysts [5–7]. Among these, Ni-containing catalysts were investigated considerably due to cheap and abundant availability of Ni. However, the main disadvantage of DRM is the deactivation of catalyst due to the serious

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<http://dx.doi.org/10.1016/j.ijhydene.2015.10.063>

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carbon formation [8] on catalyst via CH_4 decomposition ($\text{CH}_4 \rightleftharpoons 2\text{H}_2 + \text{C}$) which is endothermic reaction [9] while the other main contributor to carbon formation is CO disproportionation ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$) Boudouard reaction [10]. In order to overcome this deactivation problem, the performance of Ni-based catalysts was improved by introduction of metals and their oxides [11]. Hou et al. [12] described that small amount of Ca could improve the dispersion of nickel and strengthen the interaction between Ni and Al_2O_3 to avoid the sintering. Liu et al. [13] suggested that the catalyst with proper ratio of La/Al showed the highest catalytic activity and stability. According to the reports of Choudhary et al. [14] and Xu et al. [15], although the modification by the CaO, MgO or by nanocrystalline ZrO_2 solid solutions can improve the stability of Ni-based catalysts due to strong interaction with metal oxides, however their catalytic performance is poor due to low surface area.

Besides, the supports such as MgO [16], La_2O_3 [17] and ZrO_2 [18] can interact with nickel to inhibit the carbon deposition of Ni-based catalysts. Especially, basic La_2O_3 can absorb CO_2 to form $\text{La}_2\text{O}_2\text{CO}_3$, which can accelerate the elimination of surface carbonaceous species [17]. The effect of Co or Mg on the catalytic activity and stability were evaluated under drastic reaction conditions [19].

In addition, the studies on $\text{La}_2\text{NiO}_4/\gamma\text{-Al}_2\text{O}_3$ [20], and the comparison among $\text{LaNiO}_3/\text{SBA-15}$, $\text{LaNiO}_3/\text{MCM-41}$ and $\text{LaNiO}_3/\text{SiO}_2$ [21], catalysts confirmed that surface area or thermal stability of the support affected CO_2 conversion. Therefore, an effective method to increase the catalytic stability and minimizing carbon deposition of Ni-based catalysts is the optimization of supports, promoters and their contents.

Furthermore, the high dispersion of the metal particles over the support can reduce the coke deposition. Up till now, perovskite [19,22–24] and other promoters [25,26] were used for CH_4/CO_2 reforming reaction but the effect of different weight ratios of La/Co/Ni and Mg/Co/Ni supported on mesoporous MSU-S has not been reported yet.

In this research, a series of 1, 3La2Co7Ni/MSU-S and 1, 3Mg2Co7Ni/MSU-S catalysts were prepared by a sol–gel method and characterized by means of N_2 adsorption, H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$), H_2 and CO_2 temperature-programmed desorption ($\text{H}_2\text{-TPD}$, $\text{CO}_2\text{-TPD}$), O_2 temperature-programmed oxidation ($\text{O}_2\text{-TPO}$), X-ray diffraction (XRD), High resolution transmission microscopy (HRTEM), UV–visible spectroscopy (UV–vis), Thermogravimetric/differential scanning calorimetry (TG/DSC) analysis and Fourier transform Infra-red (FT-IR) spectroscopy. Their catalytic performance in the CO_2 dry reforming of methane was evaluated at different temperatures.

Experimental

Material and methods

Synthesis of MSU-S

The parent MSU-S was synthesized hydrothermally according to the procedure described by Pinnavaia et al. [27]; i.e. 0.507 g of NaOH and 0.352 g of NaAlO_2 were dissolved in 10 mL deionized water (DW), then 25.578 g of sodium silicate was

added slowly to aforementioned solution under vigorous stirring at 35 °C for 4 h. The obtained clear solution was transferred into an autoclave at 110 °C for 12 h to form nanoaluminosilicate units. Subsequently, as-synthesized nanozeolite precursor was added drop-wise to the solution of cetyltrimethylammonium bromide (CTAB) at room temperature (RT). After pH was adjusted to 9–10 using H_2SO_4 solution (6 mol/L), the resultant gel was crystallized in an autoclave at 140 °C for 48 h. Finally, the precipitate was filtered, washed with DW, dried and calcined in air at 550 °C for 6 h to obtain the parent MSU-S.

Preparation of catalysts

A series of xLa_yCo_zNi/MSU-S and xMg_yCo_zNi/MSU-S catalysts were prepared by a sol–gel method [28]. Briefly, to take the preparation of 1 wt% La 2%Co 7%Ni/MSU-S and 1 wt% Mg 2%Co 7%Ni/MSU-S as example, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 25 mL of DW in separate beakers. After the addition of citric acid with molar amount 1.5 times that of total metal ions, 1 g of as-prepared MSU-S was added to the aforementioned solution to each beaker. The mixture was continuously stirred at 60 °C until the formation of gel. Next, the gel was aged at RT for 3 days. The samples were heated to 550 °C at a rate of 2 °C/min and calcined at 550 °C for 6 h. Similarly, 3 wt% La 2%Co 7%Ni/MSU-S and 3 wt% Mg 2%Co 7%Ni/MSU-S were also prepared by the same method. The obtained catalysts were denoted as 1La2Co7Ni/MSU-S, 1Mg2Co7Ni/MSU-S, 3La2Co7Ni/MSU-S and 3Mg2Co7Ni/MSU-S, respectively hereinafter. The catalysts were then pressed, and sieved through 40–60 meshes.

Characterization of catalysts

The diffraction patterns of catalysts were recorded on a PANalytical automatic diffractometer using Ni-filtered Cu K_α radiation ($\lambda = 0.154,06 \text{ nm}$) at setting of 40 kV and 50 mA. Small angle XRD patterns were performed by a Rigaku D/max X-ray Diffractometer with a scanning rate of 1 °C/min. The N_2 adsorption experiment of fresh and used xLa/Mg-yCo_zNi/MSU-S catalysts were conducted at 77 K on a self-assembled BET apparatus [28]. The catalyst was dried overnight at 120 °C and charged into the sample tube after weighed. Prior to measurement, the catalyst was degassed again in vacuum at 200 °C for 1 h. The volumes of micropores (V_{mic}) and total pore volume (V_t) were obtained by the volume of N_2 adsorbed (V_m) at $p/p_0 = 0.10$ and 0.95, respectively. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to calculate specific surface area, pore size distribution and pore volume of catalysts.

$\text{H}_2\text{-TPR}$ and $\text{O}_2\text{-TPO}$ of catalysts were conducted by gas chromatograph (GC) system [28], i.e. about 70 mg of a catalyst was charged in U-shaped quartz reactor and treated at 150 °C in the flow of N_2 or He (50 mL/min) for 30 min. After cooling to RT, the catalyst was heated to 850 °C at a rate of 10 °C/min in 5% H_2/N_2 or 5% O_2/He flow (50 mL/min). The amount of H_2 or O_2 uptake during the reaction was measured by a thermal conductivity detector (TCD).

In $\text{CO}_2\text{-TPD}$ and $\text{H}_2\text{-TPD}$ experiment, 70 mg of catalyst was charged in a quartz reactor and treated at 150 °C or 350 °C in helium (50 mL/min) for 30 min. After being cooled down to RT, the catalyst was exposed to CO_2 (50 mL/min) or H_2 (50 mL/min)

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