Modifying perovskite-type oxide catalyst LaNiO$_3$ with Ce for carbon dioxide reforming of methane

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ABSTRACT

Perovskite-type oxide catalysts LaNiO$_3$ and La$_{1-x}$Ce$_x$NiO$_3$ ($x \leq 0.5$) were prepared by the Pechini method and used as catalysts for carbon dioxide reforming of methane to form synthesis gas (H$_2$ + CO). The gaseous reactants consisted of CO$_2$ and CH$_4$ in a molar ratio of 1:1. At a GHSV of 10,000 hr^{-1}, CH$_4$ conversion over LaNiO$_3$ catalyst increased from 66% at 600 °C to 94% at 800 °C, while CO$_2$ conversion increased from 51% to 92%. The achieved selectivities of CO and H$_2$ were 33% and 57%, respectively, at 600 °C. To prevent the deposition of carbon and the sintering nickel species, some of the Ni in perovskite-type oxide catalyst was substituted by Ce. Ce provided lattice oxygen vacancies, which activated C—H bonds, and increased the selectivity of H$_2$ to 61% at 600 °C. XRD analysis indicates that the catalyst exhibited a typical perovskite spinel structure and formed La$_2$O$_2$CO$_3$ phases after CO$_2$ reforming. The FE-SEM results reveal carbon whisker of the LaNiO$_3$ catalyst and the BET analysis indicates that the specific surface area increases after the reforming reaction. The H$_2$-TPR results confirm that Ce metals can store and provide oxygen.

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1. Introduction

Global warming, caused by the emission of greenhouse gases, is an issue of greater public concern. The effective reduction of the emissions of greenhouse gases (GHG) has become an important issue worldwide. Major greenhouse gases include carbon dioxide (CO$_2$), nitrous oxide (N$_2$O), methane (CH$_4$), chlorofluorocarbons, hydrochlorofluorocarbons (CFCs, HFCs, HCFCs), perfluorocarbons (PFCs) and sulfur hexafluoride (SF$_6$). More than 80% of global GHG emissions in the industrial sector are CO$_2$. Therefore, the primary greenhouse gas reduction focus on CO$_2$. Major CO$_2$-emitting sources include the energy
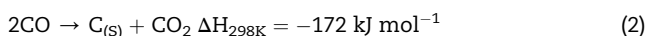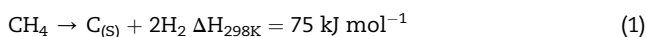
supply industry, the chemical industry and the transportation sector, which use fossil fuels to provide energy. New forms of energy, such as hydrogen, which is more efficient, cleaner, of higher energy density and can be easily converted into electrical and thermal energy as a pollution-free primary energy carrier, should be applied to reduce their environmental impact. In recent years, much research has focused on hydrogen production technology such as CO$_2$ reforming with methane (CO$_2$ + CH$_4$ → 2CO + 2H$_2$, ΔH$_{298K}$ = 247 kJ mol^{-1}), commonly called the dry reforming of methane (DRM) [1]. This reaction is strongly endothermic and utilizes greenhouse gases including CH$_4$ and CO$_2$ to produce synthesis gas (H$_2$ + CO) [1–3], which can be used in chemical energy transmission systems.

These systems are utilized in Fisher–Tropsch synthesis to produce liquid hydrocarbons or methanol [4].

Several catalytic systems for CO_2 reforming with methane, including ion-exchanged zeolites, noble metals and metal oxide catalysts, have been investigated [3,5–7]. However, the high cost of the noble metals limits their application in the reforming reaction despite their excellent catalytic performance. Nickel-based catalysts have been intensively investigated because of their low cost and relatively high activity in the reforming process [8]. However, the deactivation of nickel-based catalyst due to carbon deposition remains a serious problem for the reforming reactions. The carbon deposition is mainly resulted from CH_4 decomposition (Eq. (1)) and Boudouard (Eq. (2)) reaction at high temperature [8,9].

$$CH_4 \rightarrow C_{(S)} + 2H_2 \; \Delta H_{298K} = 75 \text{ kJ mol}^{-1} \tag{1}$$

$$2CO \rightarrow C_{(S)} + CO_2 \; \Delta H_{298K} = -172 \text{ kJ mol}^{-1} \tag{2}$$

Therefore, the development of effective and efficient DRM catalysts has become an important challenge.

Perovskite-type oxide with a general formula of ABO_3 or A_2BO_4 has been considered to be a potential auto-exhaust catalysts, where A is an alkaline metal or an alkaline earth metal and B is a transition metal [10,11]. Perovskite-type oxides with different physical properties can be synthesized by substituting different metals at the A and B sites and by varying the chemical compositions [12]. Sutthiumporn et al. (2012) reported that the A-site substituted perovskite-type oxide shows substantial electronic and ionic conductivity at elevated temperatures. Additionally, partial substitution at the 'B-site' improves structural stability and catalytic behavior [13]. Elements A or B can be partially substituted by other metal elements to modify the structure or nature of the oxide to enhance its catalytic activity. Perovskite-type oxide catalysts are active for CO_2 reforming with methane. Catherine et al. (2005) reported [4] that 75% CO_2 conversion efficiency of gaseous $CH_4/CO_2/He = 10/10/80$ at 700 °C can be achieved with 50 mg $LaNiO_3$ catalyst, with a gas flow rate of 100 mL min^{-1}. Previous studies have investigated the possibility of adding basic or noble metals to promote La substitution to form $La_{1-x}M_xNiO_3$ (with for example M = Pt [11], Ce [10,12,14,15], Sr [9,16], Mg [17]). The resulting compound exhibits high resistance to carbon deposition because of the existence of an optimal Ni crystallite size and a large number of oxygen vacancies. Ce-promoted catalysts have recently attracted increasing attention for their high oxygen storage capacity and high lattice oxygen mobility [15]. Structural defects of the perovskite oxides can be formed by adding other metallic elements to increase its catalytic activity.

The aim of this study is to investigate the activity of the perovskite-type oxide catalyst, $LaNiO_3$, for CO_2 reforming with methane at different reaction temperatures and space velocities. Additionally, the activity of $La_{1-x}Ce_xNiO_3$ for CO_2 reforming with methane is also evaluated. The objective is to achieve a high conversion of reaction gases (CO_2, CH_4) and high selectivities of the products (H_2, CO) at a low reaction temperature. The catalyst must also exhibit a good resistance to carbon deposition. The catalytic performances were compared and the physical–chemical properties of the catalysts were characterized by XRD, SEM, BET and H_2-TPR.

2. Experimental

2.1. Preparation of catalysts

Samples of $LaNiO_3$ and $La_{1-x}Ce_xNiO_3$ ($x \leq 0.5$) were prepared by the Pechini method, following the procedures that are presented in Fig. 1. The corresponding metal nitrates were utilized as the starting materials for generating an aqueous solution with the appropriate stoichiometry. Citric acid was added to the mixed aqueous solution of metal nitrates in a designated proportion so that the molar ratio of citric acid to the total metal cations is 4:1. Ethylene glycol was then added to the mixed aqueous solution to control the molar ratio of citric acid to ethylene glycol at 1:1. The mixed aqueous solution was then heated and stirred in a water bath to start the process of sol formation and the transformation of sol into gel. A green gel was eventually formed. It was dried at 110 °C for 24 h, and then heat treated at 350 °C for 0.5 h in air, and finally calcined in air at 700 °C for 2 h. The synthesized particles were then pulverized to a 100 mesh size for use.

2.2. Characterization of catalysts

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) (JEOL, JSM-6700F) were used to determine the structures and the composition of the prepared catalysts. The Brunauere–Emmette–Teller (BET) surface areas of the catalysts were measured by N_2 adsorption at 77 K using a Micromeritics ASAP 2010. Powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer (BRUKER, D8AXRD) over the temperature range $5° \leqq 2\theta \leqq 80°$, operated at 40 kV and 10 mA, using Cu Kα radiation with a nickel filter. Temperature-programmed reduction (TPR) was
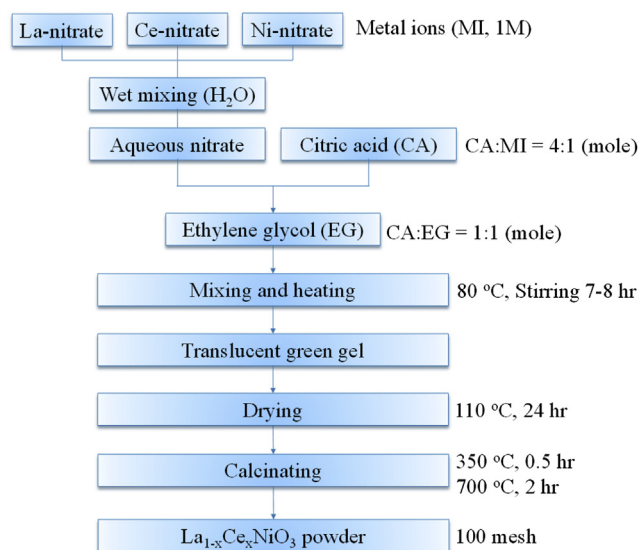

Fig. 1 – Procedures for perovskite-type oxide catalyst preparation.