Autothermal CO₂ Reforming with Methane Over Crystalline LaMn₁₋ₓNiₓO₃ Perovskite Catalysts

Annabathini Geetha Bhavani¹,²* and Jae Sung Lee³

¹Department of Chemistry, Noida International University Research Innovation Centre, Noida International University, India
²Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Republic of Korea
³School of Nano-Bioscience and Chemical Engineering, Republic of Korea

Abstract

LaMn₁₋ₓNiₓO₃ (x = 0.1-0.9) perovskite was prepared by sol-gel method in a single step. All the perovskite catalysts stability was tested over oxy thermal reforming CH₄ with CO₂ for long time-130 h on stream. The LaMn₁₋ₓNiₓO₃ perovskite catalyst shows promising catalytic activity for syngas (H₂, CO) production from autothermal reforming. XRD analysis confirms all perovskite catalysts are in single phase and crystalline. Catalysts physiochemical properties were tested by BET analysis for surface area, metallic surface area by CO chemisorption, coke content of spent catalyst by TGA analysis. Catalytic activity was compared in-terms of degree of Ni substitution in lanthanum manganite lattice. The optimal level of Ni substitution in perovskite structure increases surface area, pores volume and metallic surface area, which leads highly stable, active for long time on stream with negligible amounts of coke formation.

Keywords

LaMn₁₋ₓNiₓO₃, Ni substitution, Oxygen mobility, Autothermal CH₄ reforming with CO₂

Highlights

➢ Ni substituted lanthanum manganite LaMn₁₋ₓNiₓO₃ (x = 0.1-0.9) is in single phase perovskite structure, confirmed by XRD.
➢ Catalysts were tested extreme long run of 130 h on stream for oxy thermal reforming of CO₂ with CH₄.
➢ The high surface area and metal dispersion of catalysts shows tremendous stability and activity in syngas production.
➢ Rate of reducibility of the catalyst improved the surface oxygen, which helps to trigger deactivation of the catalysts.

Introduction

The process of converting two greenhouse gases (CH₄ with CO₂) to valuables synthesis gas (syngas), a mixture of CO and H₂ by catalytic oxy thermal reforming of methane with carbon dioxide has received significant attention in recent years [1]. Reforming process is generalized by partial oxidation of methane (exothermic reaction), carbon dioxide reforming (endothermic reaction) and oxy thermal reforming of methane with CO₂ (combined exothermic and endothermic reaction). The oxy thermal reforming catalytic process was designed to be economic as it saves energy, because the thermal energy required is generated in the partial oxidation of methane...
Oxidation of methane has been chosen as a safe and economic way for synthesis gas production in a large-scale.

Perovskite-type mixed oxides (ABO₃), are promising material for catalytic applications involving high temperatures reactions, because of their thermochromic stability and tuneable catalytic performance as oxy thermal reforming reaction requires high temperatures. The perovskite materials are reactivity is couturier by mutable substitution of A- and/or B-site cations. B site elements are partially reduced to form nano-sized metal particles, which are highly active for oxy thermal reforming reaction and resilient to carbon deposition [3,4]. Ni is successfully substituted in LaFeO₃ lattice, and reduced metallic Ni acts as a promoter for CH₄ activation [5].

Noble metal based catalysts (Pt and Ru) are well practiced for oxy thermal reforming reaction for a high activity with no carbon deposition [6] with a drawback of cost of the metals. The non-noble metal based catalysts (like Fe, Ni, Co, Mn) are practiced of their appreciable catalytic activity, good stability and low price with a drawback of metal sintering [7]. Ni-based perovskite in the form of BaZr₁₋ₓMeₓO₃ was evaluated and the results were compared the synthesis methods of sol-gel method and auto-combustion method and sol-gel found to be promising route for the use of Ni in this process with good activity can be achieved from temperature of 973 K [8].

Syngas production by CO₂ reforming of methane on La-Ni-Al₂O₃ perovskite catalysts prepared by sol-gel method with prominent bench mark results [9]. Nickel-based catalyst by impregnation and perovskites by sol gel (SG) and co precipitation (CP) method for CO₂ reforming of CH₄. Conversion of CH₄ and CO₂ were found in the order: LaNiO₃(CP) > 10% Ni/ZrO₂-Al₂O₃ > LaNiO₃(SG) > 10% Ni/K₂O-Al₂O₃ > 10% Ni/MgO-Al₂O₃ > LaCoO₃(CP) > LaCeO₃(SG) > 10% Ni/CoO-Al₂O₃ > 10% Ni/-Al₂O₃ > 5% Ni/-Al₂O₃ > 20% Ni/-Al₂O₃ > LaNiO₃(CP) gave high activity and stability due to further reduction of B-site cations which remain distributed in the structure and form well dispersed and stable metal particle catalysts which improved the stability and activity [10].

The present work to synthesize the highly crystalline porous metal catalysts and examined the activity of Mn and Ni loadings on physico-chemical properties. We aimed to develop coke resistance LaMn₃₋ₓNiₓO₃ perovskite catalysts to strong activity and stable production of syngas (H₂ and CO). By varying Ni and Mn factions like x = 0.1, 0.3, 0.5, 0.7, 0.9 respectively, by sol-gel method in order to improve its activity for oxy thermal reforming of methane and to find optimum value of bime-}

**Experimental**

**Catalyst preparation and characterization**

LaMn₃₋ₓNiₓO₃ (x = 0.1, 0.3, 0.5, 0.7, 0.9) perovskite catalysts are synthesized by sol-gel method. The stoichiometric amounts of lanthanum (NO₃)₃·4H₂O, manganese (NO₃)₂·4H₂O and nickel nitrates (NO₃)₂ are used as precursors. Citric acid and total metal ions of 1:1.5 of molar ratio was adopted to obtain the perovskite oxides materials. The various forms of polycondensation (sol) reactions to form diphasic system containing both a liquid phase and solid phase (gel). Primary powder formed by firing resulted gel at 350 °C for 5 h. After reaching to room temperature again thermally treated at 850 °C for 5 h.

The analysis of perovskite crystal phases was performed using powder X-ray diffraction (XRD) technique. The texture of the samples was characterized by the BET N₂ adsorption-desorption method at -196 °C using Micromeritics 2010 sorptometer. The BJH method was applied for determination of pore size distribution. Relative elemental composition of the prepared perovskite catalysts are analysis by atomic adsorption spectroscopy. AutoChem program in CO pulse chemisorptions analysis was used to account the metal dispersion (%) and metallic surface area (m²/g) of thermally treated catalysts. XPS analysis was used to quantify O 1s core level spectra. Spent catalysts are analyzed by thermogravimeter (Mettler Toledo, TG-SDTA 851 instrument). All the analysis procedures are detailed in our earlier report [7,11].

**Catalytic test procedure**

Tubular fixed-bed flow reactor was used for catalytic tests at atmospheric pressure. 100 mg of catalyst was preheat at 500 °C for 30 min, for reduction treatment under H₂ at 500 °C for 2 h. The mole ratio of CH₄:CO₂:O₂=1:0.8:0.2 reactant gases are fed into the reactor at gas hourly space velocity (GHSV)-243,000 h⁻¹ and gas flow rates are controlled by mass flow meters at 800 °C. After 30 min of steady-state operation of the reaction the conversion and selectivity were determined. The product mixtures were analyzed by online gas chromatograph and the calculation of products analysis shown in our earlier report [7].

**Result and Discussions**

**BET and x-ray diffraction**

Surface properties of catalysts enumerated in Table 1. All the catalyst shows comparable surface areas and compare to all the catalyst LaMn₃₋ₓNiₓO₃ catalyst shows high surface area of 9.573 m²/g and the LaMn₃₋ₓNiₓO₃ catalyst shows lowest 1.246 m²/g. These results clearly indicate that
significant Ni substitution in enhancement of surface area as well as pore volume. The perovskite materials of initial sol are well matched with elemental analysis of the prepared.

The calcined LaMn$_{1-x}$Ni$_x$O$_3$ powder XRD patterns are revealed in Figure 1, indicates all the samples are in single perovskite phase with high crystallinity. No impurity phase was found, such as NiO, MnO$_3$, Mn$_2$O$_3$. The catalyst $x = 0.7$, XRD reflection is intense compare to other $x$ ratios. Furthermore, increasing Ni substitution leads to progressive structural distortion by the lattice enlargement [12].

**Photoelectron spectroscopy (XPS)**

Table 2 shown the chemisorption measurements of LaMn$_{1-x}$Ni$_x$O$_3$ samples to determine the exposed metal surface area with CO as a probe molecule [7]. All catalysts shows significant metallic surface area and dispersion. Equate to all catalysts LaMn$_{0.3}$Ni$_{0.7}$O$_3$ shows 3.9 m$^2$/g of dispersion and 2.5% of highest metallic surface.
area and the LaMn$_{0.9}$Ni$_{0.1}$O$_3$ catalyst has lowest amount of dispersion of 0.4% and 0.7 m$^2$/g of metallic surface area. All the series results illustrates the profound influence of the Ni in amount of dispersion and metallic surface area.

Figure 2 states the XPS analysis of O 1s peaks of LaMn$_{1-x}$Ni$_x$O$_3$ various metal ratios of reduced catalysts. The binding energy of O 1s reveals two distinctive peaks for all the catalysts. The lattice oxygen O$^{2-}$ (O$_{\text{lattice}}$) peak is found at low binding energy (BE 530.0 eV) and adsorbed oxygen species (O$_{\text{adsorbed}}$) peak found at high binding energy (BE 531.4 eV) [11]. In the present case, proficiently rises the intensity of both lattice oxygen and adsorbed oxygen species by increase in Ni fractions from 0.1 to 0.3 ratios, but a further decreases the intensity of the two peaks by increase to 0.5 and 0.9 ratio. Results clearly indicates the different degrees of oxygen close to the surface due to their different surface areas.

**Oxy thermal reforming of methane with CO$_2$**

The key oxy thermal reforming reaction shown equation (1) takes place in a single chamber where partially oxidation of CH$_4$ (exothermic reaction) and CO$_2$ reforming (endothermic reaction) takes place. The combination of both reactions is a very significant triumph to obtain temperature compensation of the process. The overall reaction can be described in the following equation:

$$2\text{CH}_4 + \text{O}_2 + \text{CO}_2 \rightarrow 3\text{H}_2 + 3\text{CO} + \text{H}_2\text{O}$$

(1)

The LMN catalysts were tested for oxy thermal reforming reaction after reduction in an equimolar H$_2$/N$_2$ flow at 770 °C for 1 h. Catalytic screening results of methane and CO$_2$ conversion are shown in Figure 3A and Figure 3B and selectivity of H$_2$ and CO are shown in Figure 4A and Figure 4B, respectively at 800 °C. The spent catalysts (after 130 h of on-stream reaction) were analysed to quantify the amounts of coke formed were listed in Table 2 by TGA analysis. Catalytic performance of LaMn$_{0.9}$Ni$_{0.1}$O$_3$ catalyst is found to be stable activity with CH$_4$ and CO$_2$ conversions are around 55% and 48% with 36% of H$_2$ selectivity and left 6.48% of coke content. Increase in Ni content by 0.5% in LaMn$_{0.5}$Ni$_{0.5}$O$_3$ catalyst show highly stable performance compare to LaMn$_{0.7}$Ni$_{0.3}$O$_3$. The CH$_4$ and CO$_2$ conversions increases

![Figure 3](image-url)  
**Figure 3 (a-b):** CH$_4$ and CO$_2$ conversions over various LaMn$_{1-x}$Ni$_x$O$_3$ metal ratios at 800 °C a) x = 0.7; b) x = 0.9; c) x = 0.5; d) x = 0.3; e) x = 0.1, at CH$_4$:CO$_2$:O$_2$=1:0.8:0.2 mole ratios.

![Figure 4](image-url)  
**Figure 4 (a-b):** Product distribution of H$_2$ and CO at 800 °C over LaMn$_{1-x}$Ni$_x$O$_3$ metal ratios of catalysts are a) x = 0.7; b) x = 0.9; c) x = 0.5; d) x = 0.3; e) x = 0.1, at CH$_4$:CO$_2$:O$_2$=1:0.8:0.2 mole ratios of 800 °C.
from 60% to 84.8% and from 55% to 71%, as well as H₂ and CO selectivities, respectively. LaMn₀.₉Ni₀.₁O₃ catalyst shows a notable surge in surface area and pore diameter, this reveals that reactants are allowed to access pores for conversion and leads high and stable syngas selectivity. La₀.₉Ba₀.₁NiO₃ and LaNiO₃ perovskite catalysts [13] are studied over dry reforming of methane, where CO₂ from 39% to 51% and CH₄ conversion increased from 45% to 55% with threshold addition of Ba. By increasing 0.7% of Ni content in LaMn₀.₉Ni₀.₁O₃ catalyst revert inversible stability in performance and without a noticeable deactivation. The dissociation (reforming) of CO₂ releases the adsorbed oxygen that reacts with deposited carbon (formed by partial oxidation of methane) to form CO, thereby coke formation reduces remarkably [14]. Apart from oxygen species released by CO₂, O₂-TPD analysis reveals all the perovskite catalysts shows oxygen species are readily accessible for oxy thermal reforming reaction. Hence, the amounts of surface and lattice oxygen offered on the surface are the robust connection with activity and forceful maintenance of catalyst surface with little coke formation. In nutshells, supercilious performance of important catalyst results the highest to yield of synthesis gas with a best oxy thermal reforming performance. 

The larger Ni particle occupies enough surface area that reduces coke gasification as it needs both metallic area and surface oxygen over support. The larger metal particles leading to tend to form polymerize carbon atoms that accumulate and leads loss of activity stop the catalyst turnover. Thus, bimetallic synergy of Mn and Ni in a threshold percentages boosts the pronounced reducing property of particle sizes, and also depends the nature of the added second metal. The amount of CO₂ chemisorbs (disproportionation) is directly proportional to the surface oxygen and metal dispersion. Threshold values of metals could be the primary factor in changes of physiochemicals properties of the catalyst [17].

**Conclusion**

Ni was successfully substituted in Over LaMnO₃ lattice Ni substituted is by sol-gel process and developed the highly crystalline phase of LaMn₀.₉Ni₀.₁O₃ with chemical homogeneity. The threshold level of Ni substitution leads to high surface area, pores volume and uniformity in metallic particle dispersion. This bimetallic synergy of Ni and Mn perovskite catalyst improved reducibility leads to surface oxygen comes from bulk toward surface. Oxy thermal reforming reactions, decompositions of CH₄ occurs over metallic sites and dissociation of CO₂ occurs over metal associated with adsorbed oxygen leads outstanding syngas selectivity, and forceful maintenance of catalyst surface with little coke formation. In nutshells, supercilious performance of improved LaMn₀.₉Ni₀.₁O₃ catalysts depends on donating lattice oxygen to the catalytic cycle.

**References**

1. S Diego, L Russo, PL Maffettone, L Salemme, M Simeone,


