

Syngas production in oxy-CO₂ reforming of methane over La_{1-x}Sr_xNiO₃ perovskite-type oxides

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Introduction

The demand of syngas in both academic and industrial fields has increased due to its potential in many applications such as Fischer-Tropsch process [1], in which syngas is converted into a series of liquid hydrocarbon fuels, or its direct conversion as a reactant to dimethyl ether or methanol for petrochemical industries. Syngas can be produced in many ways, such as through autothermal reforming of methane (ARM) [2], dry CO₂ reforming of methane (DRM) or partial oxidation of methane (POM) [3]. Each of the process described above shows different advantages and limitations, such as H₂/CO ratio, energy efficiency, catalytic activity and stability. Recently the development of oxy-CO₂ reforming of methane (OCM) has been investigated to produce syngas. OCM consists of both exothermic partial oxidation of methane and endothermic CO₂ reforming of methane [4], which is expected to increase the energy efficiency of the process and also to adjust the H₂/CO ratio of syngas for particular applications.

Moreover, the rapid catalyst deactivation due to coke formation is a serious concern especially for nickel metal catalyst. The use of perovskite material as the OCM catalyst could potentially overcome this problem due to its well-defined structures, which produces highly-dispersed metallic particles to promote high activity, and its oxygen storage capacity, which suppresses coke formation and enhances catalytic stability [5]. Therefore, the purpose of this study is to investigate catalyst activity, selectivity and stability using La_xSr_{1-x}NiO₃ perovskite as a catalyst precursor for oxy-CO₂ reforming of methane. The effect of the substitution of Sr (di-valent atom) with La (tri-valent atom) on catalyst activity has also been investigated as Sr could possibly form oxygen vacancies, resulting in enhancement of oxygen semi-permeability and coke reduction.

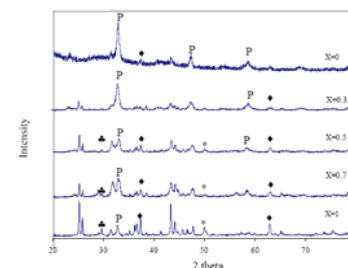
Materials and Methods

All La_{1-x}Sr_xNiO₃ catalyst precursors were prepared by a simple sol-gel process. La(NO₃)₃, Sr(NO₃)₂, Ni(NO₃)₂ were mixed and dissolved with DI water, followed by mixing citric acid to the mixture at 55°C. The mixtures were then mixed and stirred vigorously until gel was formed. The gel was then transferred to the oven for drying at 100°C for 12 h. After drying, the gel was calcined at temperatures ranging 700-1000 °C. The catalysts were using XRD (Shimadzu XRD-6000), TPR (Chembet-3000), FESEM (Jeol JSM-6700F), XPS (Shimadzu), TGA/DTA (Shimadzu DTG50) and TEM (JEOL JEM-2010). For the catalytic activity measurement, catalyst was firstly reduced under H₂/N₂ at 450°C for 30 min before the reaction was performed at atmospheric pressure with different feed mole ratio of CH₄:CO₂:O₂ and reaction temperatures between 600 – 800°C. The gas product was analyzed using a gas chromatograph (HP 6890) equipped with a Porapak Q, a molecular sieve 5A column and a TCD detector.

Results and Discussion

Figure 1 shows the XRD patterns of LSNO at different La : Sr ratio. The perovskite structure becomes less well defined with increasing Sr content. Some peaks indicating the presence of La₂SrO₆, segregated NiO phase and/or other mixed oxides are observed. The intensity of the NiO peak (labeled with “♦”) becomes higher with the increase of Sr doping, showing that Sr doping promotes the formation of NiO phase.

Figure 1. XRD patterns of La_{1-x}Sr_xNiO₃ (P) calcined at 700°C: NiO (♦), La₂SrO₆ (♣), SrO (*)



The catalytic activity results show that the conversion of CH₄ and CO₂ began to increase at around 10 h for all catalysts except for the undoped catalyst (i.e. LaNiO₃), which showed the decrease in both CH₄ and CO₂ conversion, possibly due to the accumulation of carbon deposits on the surface of this undoped catalyst, as confirmed by TG-DTA and FESEM (not shown). These results imply that doping Sr can enhance both catalytic activity and stability of the perovskite catalyst during oxy-CO₂ reforming with methane. In addition, the syngas produced by these perovskite catalysts showed good selectivity, with the H₂/CO ratio around 1.5-2 which is suitable for Fischer-Tropsch reaction.

The feed ratio of CO₂/O₂ and the space velocity have also influenced the catalytic performance. Both CH₄ and CO₂ conversion can be enhanced by increasing CO₂/O₂ feed ratio and decreased by increasing space velocity. The decrease of CO₂ conversion with the increase of space velocity was more remarkable than that in CH₄ conversion, probably due to the slower rate of DRM reaction as compared to the POM reaction.

Significance

1. The H₂/CO ratio for particular applications can be adjusted with CO₂/O₂ feed ratio.
2. Doping Sr on LaNiO₃ can enhance both catalytic activity and stability

References

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