

# LaNiO<sub>3</sub> perovskite catalysts modified with Sr or Zr: Catalysts for simultaneous CO<sub>2</sub> reforming and partial oxidation of methane

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## Introduction

The use of methane has been drawing increasing attention recently due to the large amount of natural gas available to be upgraded as well as the worldwide demand for low cost energy source. Recent hike in oil prices also renewed the interest for research on natural gas. While existing technologies are available to convert methane to syngas, which could be converted in Fischer-Tropsch synthesis to liquid hydrocarbons as fuels, researchers are constantly exploring techniques that are cost-reducing and efficient. Dry reforming of methane (DRM) for syngas production is of interest recently as DRM is an environmental-friendly process as it consumes the two most harmful greenhouse gases CO<sub>2</sub> and CH<sub>4</sub>. However, DRM has some major issues: rapid deactivation of catalyst due to carbon formation [1] and high energy consumption due to its highly endothermic reaction. Addition of O<sub>2</sub> as a co-reactant in DRM is believed to be able to overcome these problems by improving energy efficiency, adjusting H<sub>2</sub>/CO ratio for particular industrial applications and suppressing coke formation.

LaNiO<sub>3</sub> perovskite is a potential catalyst for simultaneous dry reforming of methane (DRM) and partial oxidation of methane (POM) reactions due to not only its well-defined structure, which produces highly-dispersed metallic Ni particles to promote high activity, but also its good oxygen storage capacity, which suppresses coke formation and enhances catalytic stability. The partial substitution of perovskite material with other metals (such as Sr or Zr) could also modify the oxidation state, mobility of oxygen lattice and redox properties, resulting in the modification of catalytic activity, selectivity and stability of perovskite catalysts [2]. Therefore, the purpose of this study is to investigate the catalytic performance of a series of LaNiO<sub>3</sub> perovskite catalysts doped with Sr or Zr for simultaneous DRM and POM reactions.

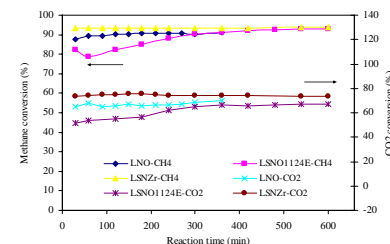
## Materials and Methods

All La<sub>1-x</sub>Sr<sub>x</sub>NiO<sub>3</sub> catalyst precursors were prepared by a simple sol-gel process. La(NO<sub>3</sub>)<sub>3</sub>, Sr(NO<sub>3</sub>)<sub>3</sub>, Ni(NO<sub>3</sub>)<sub>2</sub> and Zr(NO<sub>3</sub>)<sub>2</sub> were mixed and dissolved with DI water, followed by mixing with citric acid at 55°C. The gel formed was dried at 100°C and then calcined at temperatures ranging 700-1000°C. The catalysts were characterized by XRD, TPR, FESEM, XPS, TGA/DTA and TEM. For the catalytic activity measurement, the catalyst was reduced under H<sub>2</sub>/N<sub>2</sub> at 450°C for 30 min before the reaction was performed at atmospheric pressure with different feed mole ratio of CH<sub>4</sub>:CO<sub>2</sub>:O<sub>2</sub> and reaction temperatures between 600 – 800°C. The gas product was analyzed using a gas chromatograph equipped with a Porapak Q, a molecular sieve 5A column and a TCD detector.

## Results and Discussion

Doping Sr and Zr metal on LaNiO<sub>3</sub> has been found to influence the surface properties and catalytic performance of the modified perovskite catalysts. Partially substituting Sr with the La of LaNiO<sub>3</sub> perovskite (La<sub>0.5</sub>Sr<sub>0.5</sub>NiO<sub>3</sub>) not only shifts the H<sub>2</sub>-TPR peak to higher temperature, but also changes the intensity ratio between the first and the second reduction peak. The consumption of hydrogen at the first H<sub>2</sub>-TPR peak at around 450°C is attributed to the reduction of Ni<sup>3+</sup> to Ni<sup>2+</sup> and Ni<sup>2+</sup> to Ni<sup>0</sup> in the segregated NiO phase. Moreover, CO<sub>2</sub>

desorption from catalyst surface was performed using CO<sub>2</sub>-TPD and the surface properties of catalysts were characterized using XPS.



**Figure 1.** Effect of Sr or Zr on the catalytic performance of LaNiO<sub>3</sub> at 700 °C

Fig. 1 shows that the conversions of CH<sub>4</sub> and CO<sub>2</sub> increase with time over all perovskite catalysts doped with Sr or Zr. However, for the undoped LaNiO<sub>3</sub> catalyst, both CH<sub>4</sub> and CO<sub>2</sub> conversions decreased after 8 h 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 or Zr can enhance both catalytic activity and stability of the perovskite catalyst during oxy-CO<sub>2</sub> reforming with methane. In addition, La<sub>0.5</sub>Sr<sub>0.5</sub>Ni<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub> catalyst is found to show very high catalytic stability over 50 h, still maintaining over 94% conversion of CH<sub>4</sub> and 60% conversion of CO<sub>2</sub> at 700°C.

**Table 1.** Effect of CO<sub>2</sub>/O<sub>2</sub> feed ratio on activity and selectivity of perovskite catalyst

CO <sub>2</sub> /O <sub>2</sub> feed	Conversion of CH <sub>4</sub> (%)	Conversion of CO <sub>2</sub> (%)	H <sub>2</sub> /CO
9.0	89.2	73.8	2.2
2.3	93.2	76.0	1.6
1.5	95.0	73.3	1.5
1.0	96.4	60.4	1.4

The effect of reaction parameters, such as the feed ratio of CO<sub>2</sub>/O<sub>2</sub> and space velocity, could also influence the catalytic performance of perovskite catalyst for simultaneous DRM and POM reactions. The optimum reaction condition over La<sub>0.5</sub>Sr<sub>0.5</sub>Ni<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>3</sub> catalyst at 700°C is the CO<sub>2</sub>/O<sub>2</sub> feed ratio of 1.5 and GSHV of 12632 cm<sup>3</sup>g<sup>-1</sup>h<sup>-1</sup>, resulting in about 96% and 70% conversion of CH<sub>4</sub> and CO<sub>2</sub>, respectively. The difference of CO<sub>2</sub>/O<sub>2</sub> feed ratio is also found to influence the H<sub>2</sub>/CO values. Increasing the space velocity reduces both CH<sub>4</sub> and CO<sub>2</sub> conversion (not shown), with the decrease of CO<sub>2</sub> conversion more remarkable than the decrease of CH<sub>4</sub> conversion due to the slower rate of DRM as compared to POM reaction.

## Significance

1. Partially doping Sr or Zr on LaNiO<sub>3</sub> can enhance both catalytic activity and stability of perovskite catalyst for simultaneous DRM and POM reactions.
2. The H<sub>2</sub>/CO ratio for the syngas produced can be adjusted to a value around 1.5 with lower CO<sub>2</sub>/O<sub>2</sub> feed ratio.

## References

1. Valderrama, G., Kiennemann, A., and Goldwasser, M.R. *Catal Today*. 133-135, 142 (2008).
2. Goldwasser, M.R., Rivas, M.E., Pietri, E., Pérez-Zurita, M.J., Cubeiro, M.L., Grivobal-Constant, and Leclercq, G. *J. Mol. Catal. A*. 228, 325 (2005).