



Synthesis and Application of LaNiO₃ Perovskite-type Nanocatalyst with Zr for Carbon Dioxide Reforming of Methane

NOOSHIN TALAIE¹, MOAYED HOSSAINI SADR^{2*},
HAMIDREZA AGHABOZORG³ and KARIM ZARE⁴

¹Department of Chemistry, Science and Research branch, Islamic Azad University, Tehran, Iran.

²Department of Chemistry, Tarbiat Moallem University of Azarbaijan, Tabriz, Iran.

³Research Institute of Petroleum Industry, Tehran, Iran.

⁴Department of Pure Chemistry, Shahid Beheshti University, Tehran, Iran.

*Corresponding author E-mail: sadr@azaruniv.edu

<http://dx.doi.org/10.13005/ojc/320546>

(Received: June 13, 2016; Accepted: August 22, 2016)

ABSTRACT

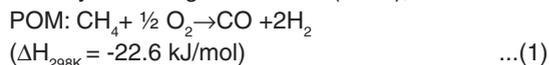
La_{1-x}Zr_xNiO₃ perovskite nanocatalysts were synthesized by citrate sol-gel method. The synthesized samples were characterized by using X-ray diffraction (XRD), temperature programmed reduction (TPR), and inductively coupled plasma (ICP) techniques. Surface areas of the compounds were measured by BET method. Morphology study of the nanocatalysts was performed using scanning electron microscopy. The XRD patterns confirmed a well-crystallized structure in doping level up to 0.2 for La_{1-x}Zr_xNiO₃. The SEM images showed that the synthesized particles were in nanoscale. The TPR analysis revealed that by increasing the amount of Zr in the prepared samples, reduction process became difficult. The catalytic activity of the nanocatalysts was studied in dry reforming of methane (DRM) with CO₂ and the H₂/CO ratio~1 when doping level was 0.1.

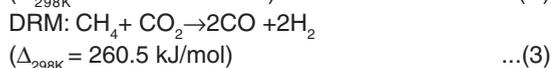
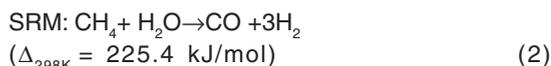
Keywords: Perovskite, Nanocatalyst, Catalytic behavior, Petrochemical technology, Dry reforming of methane (DRM).

INTRODUCTION

Synthesis gas (syngas H₂/CO) is a mixture of H₂ and CO that is an important feed used for the petrochemical industry like Fisher-Tropesh process. Generally, in syngas cycle with different ratio of H₂/CO, variety of products is obtained.

Similarly, several groups have carried out research on the production of syngas from methane. (e.g. the partial oxidation of methane (POM), reaction 1), steam reforming of methane (SRM), reaction 2) and dry reforming of methane (DRM), reaction 3¹.





Syngas economy is considered to be a good process to reduce CO₂ and CH₄ emission which are both greenhouse gases².

In recent years considerable researchers have been focused on DRM reaction to produce syngas³⁻⁵. A lower H₂/CO ratio is produced in dry reforming of methane, which favors to liquid fuel production when compared with steam reforming and partial oxidation of methane⁶⁻⁷. The reactions that take place in this process are endothermic:



Catalysts play special role in this reaction, nowadays a considerable attention is focused on the activity and stability of the catalysts.

Recently, perovskite oxide structures (ABO₃) have been studied widely as catalysts in dry reforming of methane reactions². In the perovskite-type oxides, A is (lanthanides, alkali metals and earth alkali metals) and B is (transition metals) where thermal resistance is controlled by A cations and catalytic activity is controlled with B redox cations¹. However, many researchers have doped transition metals in A-site; and lanthanides, alkali metals and alkali earth metals in B-site⁸⁻¹⁰.

There are studies reported on the beneficial effect of noble metal addition such as many studies have been carried out with the aim to synthesize complex mixed metallic oxides with the perovskite structure. A lot of papers have reported different doping level of Ni in B-site of perovskite type oxides that are successful in catalytic activity for reforming of methane¹¹⁻¹⁴.

For examples, Goldwasser *et al.* have investigated the influence of Ru partial substitution by Ni and La partial substitution by Ca in LaRuO₃ and LaRu_{0.8}Ni_{0.2}O₃, respectively, in the combined reforming of methane (CRM) with CO₂ and O₂, and DRM processes¹⁵. In another work, Jahangiri *et al.* have reported the behavior of La_{1-x}Sm_xNiO₃

and LaNi_{1-x}Co_xO₃ as catalyst precursors in CRM process¹⁶⁻¹⁷. In addition, they studied the performance of LaNi_{1-x}Fe_xO₃ perovskite-type oxides with various substitution degrees (x) in the CRM process¹⁸. In the present study, La_{1-x}Zr_xNiO₃ perovskites were synthesized with different substitution degrees(x) and characterized with conventional methods for investigating the stability and activity of them as a catalyst in the DRM process.

MATERIALS AND METHOD

In this research, La(NO₃)₃·6H₂O, (Merck, >99/9%), ZrO(NO₃)₂·6H₂O, (Aldrich, 99/99%), Ni(NO₃)₂·6H₂O (Merck, >99%), citric acid (Merck, 99/5%) and ethylene glycol (99%) were used for synthesis of La_{1-x}Zr_xNiO₃ nanocatalysts. Appropriate stoichiometric of La, Ni nitrates and Zirconium oxynitrate solution (1M) were mixed and stirred for 40 minutes, then citric acid and ethylene glycol with molar ratio of 1 were added to this solution. The mixture was stirred for 8 hours in 80 °C. The resulting gel was dried at 110 °C for 24 h and calcined in two steps: 1st at 350 °C for 0.5 h and 2nd at 800 °C for 2 h.

Equipment

The prepared samples were characterized by X-ray diffraction (using 3003 PTS diffractometer), with a copper anode (CuK_α monochromatized radiation source, λ= 1.5405 Å) to ascertain formation of the perovskite structure, phase purity and crystallite size determination. The morphology of the prepared samples was studied by scanning electron microscopy (SEM, using Philips XL30 microscope). BET method was applied for measuring the surface area of the samples using N₂ at -200°C (on a Tristar 3000 apparatus) and inductivity coupled plasma (ICP) emission spectroscopy was used (on a Perkin-Elmer ICP/5500 apparatus) for quantitative analysis of the samples. Temperature programmed reduction (TPR, on a 29000 apparatus) was performed for measuring of hydrogen consumption.

Catalytic activity evaluation

Catalytic activity of the samples was studied under 600 to 800°C. The reactants and products were analyzed by a gas chromatograph (Model 6890N, Agilent Technologies) provided with the thermal conductivity detector (TCD). The experimental tests

for the catalyst activity study were carried out using the feed gases (CH_4 , CO_2 , N_2 and H_2) with ultra-high pure grade (>99.999%) in a micro-reactor equipped with mass flow controllers (Model 5850, Brooks Instrument).

The temperature of micro-reactor was measured and controlled by two thermocouples (Ni-Cr, K-Type, 0.5 mm diameter) and two PID thermo-controllers (Model JumoiTRON08). The catalyst (0.4 g for all cases) was loaded in the middle of the reactor, and the feed gases at a total flow rate of 100 ml/min (WHSV=15 l/(h.g), $\text{CH}_4/\text{CO}_2 = 1/1$) under atmospheric pressure were introduced into the reactor as the default prior to activity measurements. Catalyst precursors were reduced in situ in a flow of 20% H_2 in N_2 (total flow rate of 50 ml/min) at 700 °C for 2 h to generate the metal phase. In all tests, the performances were evaluated by conversions. The CH_4 and CO_2 conversions, H_2/CO and H_2/CH_4 ratios are defined as follow⁷:

$$\text{CH}_4 \text{ Conversion (\%)} = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100 \quad \dots(5)$$

$$\text{CO}_2 \text{ Conversion (\%)} = \frac{\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}}}{\text{CO}_{2,\text{in}}} \times 100 \quad \dots(6)$$

$$\text{Yield of H}_2 \text{ (\%)} = \frac{\text{H}_{2,\text{out}}}{2\text{CH}_{4,\text{in}}} \times 100 \quad \dots(7)$$

$$\text{Yield of CO (\%)} = \frac{\text{CO}_{\text{out}}}{\text{CH}_{4,\text{in}}} \times 100 \quad \dots(8)$$

$$\frac{\text{H}_2}{\text{CO}} \text{ ratio} = \frac{\text{H}_{2,\text{out}}}{\text{CO}_{\text{out}}} \quad \dots(9)$$

RESULTS AND DISCUSSIONS

Crystalline structure

The XRD patterns of the synthesized samples are shown in Fig. 1. The XRD patterns

of Zr doped LaNiO_3 indicated that Zr doping level (x) in these samples were 0.2 with formation of well-crystallized perovskite structure without any impurities (JCPDS No: 33-710). For Zr doped LaNiO_3 sample, beyond x=0.2 additional peaks are presented which belongs to ZrO_2 , $\text{La}_2\text{Zr}_2\text{O}_7$ and NiO compounds.

For calibrating the position of the reflections, a quartz standard was used. Since all the prepared samples could be indexed with cubic symmetry of the ABO_3 type, the cell parameter (a) in the unit cell of these compounds was calculated using the following equation:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

The obtained results are shown in Table 1. The results indicate that by increasing the amount of Zr in the $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ samples, the cell parameter decreases.

The crystallite size of the prepared samples calculated by the Scherrer equation using the intense peak is presented in Table 2¹⁹. This table shows that the prepared particles are appeared in nanoscale.

Chemical analysis and surface area measurements

The chemical composition (wt.%) and surface area for some prepared catalysts are given in Table 2. As it is shown, the experimental data for Ni, Zr and La (wt.%) are close to the nominal values (reported in parentheses). BET surface areas of the catalysts are found in the range of 3-5 m^2/g . Since preparation of perovskite oxides by modified

Table 1: Cell parameter (a) of the prepared samples obtained from XRD data

X	$\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ Cell parameter (a)(Å)
0	3.888
0.1	3.867
0.2	3.864
0.3	3.855
0.5	3.854

citrate sol-gel method, require long exposure to high temperatures, leading to low surface area solids is not surprising. Similar behavior has also been reported by Pahlevanzadeh *et al.*¹⁷.

Morphology

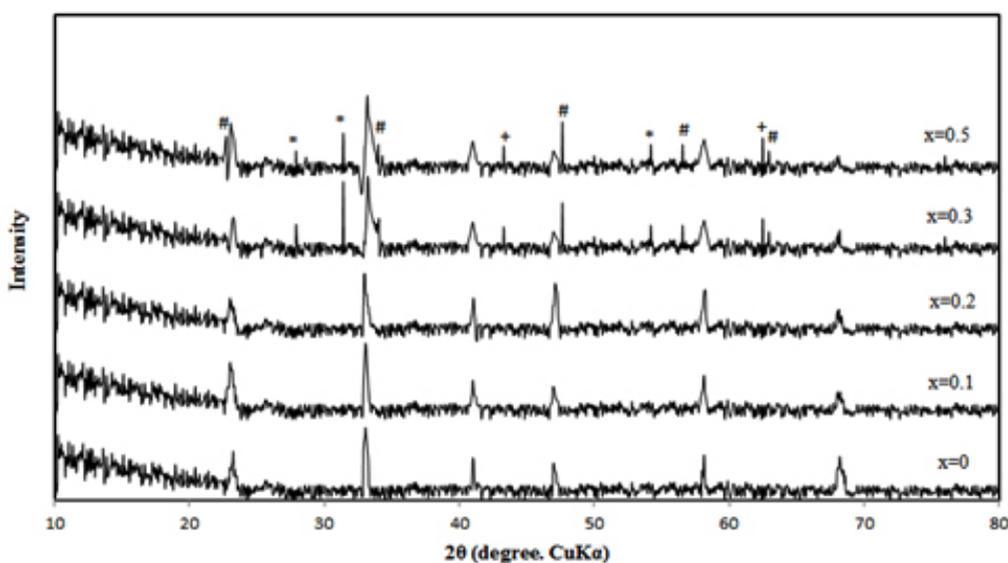
The SEM images of the samples are shown in Fig 2. These images have shown that the synthesized particles were in nanoscale which is nearly in spherical shape. For $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ samples, morphology study of the particles with doping level up to 0.2 is uniform which indicate that these samples are crystallized in mono phase perovskite.

TPR profiles of the prepared samples are shown in Fig.3. TPR study of the samples displays two main steps of hydrogen consumption. The burst one indicates the reduction of Ni^{3+} to Ni^{2+} with a maximum consumption of hydrogen in around 382°C ¹⁸. The second step can be related to Ni^{2+} to Ni^0 reduction in around 570°C ²⁰. This trend is usual for perovskite type samples and confirms that nickel is present in the B-site. In addition, for Zr doped LaNiO_3 sample, both steps shifted to higher temperatures which can be due to the presence of Ni-Zr-O system²¹. This result confirms the doping level of Zr which is obtained by XRD patterns.

Table 2: Elemental analysis*, BET surface areas and crystallite size of some calcined $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ perovskites (calculated by Scherrer equation)

X	$\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$			SA (m ² /g)	D (nm)
	La (wt.%)	Zr (wt.%)	Ni (wt.%)		
0	70.3(69.8)	0(0.0)	29.7(30.2)	3	50
0.1	65.0(64.8)	4.5(4.8)	30.5(30.4)	5	53
0.3	50.1	16.8	33.1	3	45
0.5	38.3	29.6	32.1	2	43

* Calculated by ICP** Nominal values are in parentheses



(*) ZrO_2 (JCPDS No.: 3-515)

(#) $\text{La}_2\text{Zr}_2\text{O}_7$ (17-450)

(+) NiO (JCPDS No.: 4-835)

Fig. 1: XRD patterns of $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ nanocatalysts

Catalytic activity

Catalytic activity of the prepared samples in the temperature range of 600-800 °C has been studied in DRM process. The CH₄ and CO₂ conversions and product yields in the presence of La_{1-x}Zr_xNiO₃ in different temperatures are presented in Fig. 4. These figures show that CH₄ and CO₂ conversions increase by increasing the temperature in the presence of all catalysts. However, the CH₄ conversions are lower than those of CO₂. This behavior could be due to consuming of CO₂ in reaction (4). In addition, both the H₂ and CO yields increase with increasing the reaction temperature

in the presence of the prepared catalysts, while the CO yields are higher than the H₂ yields. This effect is more notable at higher temperatures, which are in consistent with Aghabozorg *et al.* study¹⁶.

In the presence of La_{1-x}Zr_xNiO₃ samples with doping levels of x=0.3 and 0.5, there is no outstanding difference in the CH₄ and CO₂ conversions and product yields for each temperature. These results confirm that the mono phase perovskite structure shift to other metal oxide phases for doping level of x= 0.3 and 0.5 which is in consistent with XRD and TPR results.

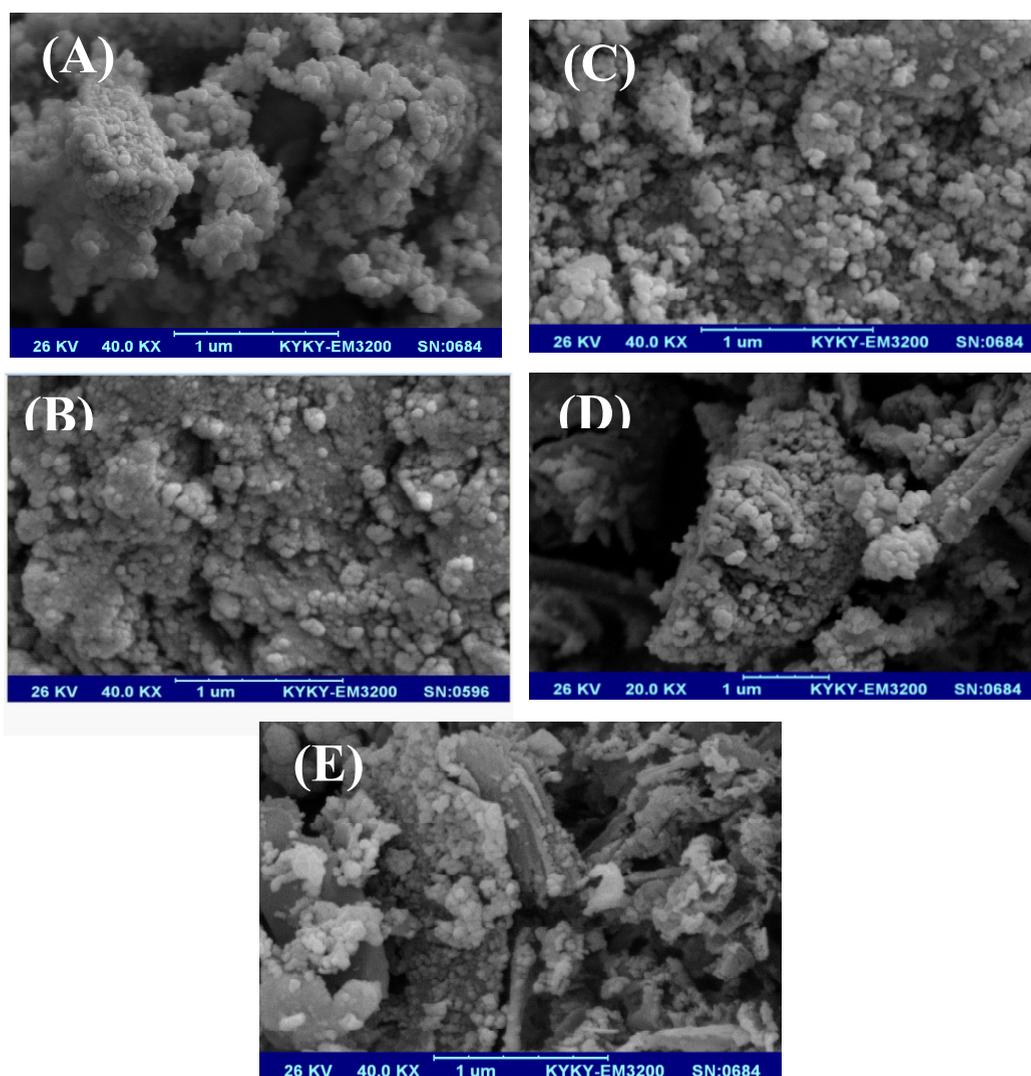


Fig. 2: SEM images of the La_{1-x}Zr_xNiO₃ (x=0 (A), x=0.1 (B), x= 0.2 (C), x=0.3 (D) and x=0.5 (E))

Catalytic activity study of the prepared samples also indicate that H_2/CO ratio in the presence of the catalyst with doping level of $x=0$ and $x=0.1$ is ~ 1 , while this ratio for upper doping level is less than 1. In other words, it can be concluded that the reactions (3) and (4) are the main occurring reactions. These results indicate that perovskite structures are favorable for producing more H_2 that is in accordance with Valderrama *et al.* research²².

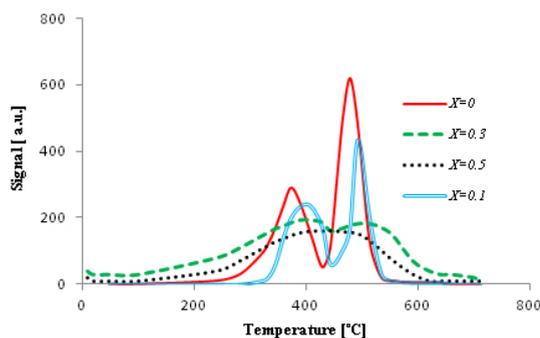


Fig. 3: TPR profiles of prepared $La_{1-x}Zr_xNiO_3$ (calcined in air at $800^\circ C$)

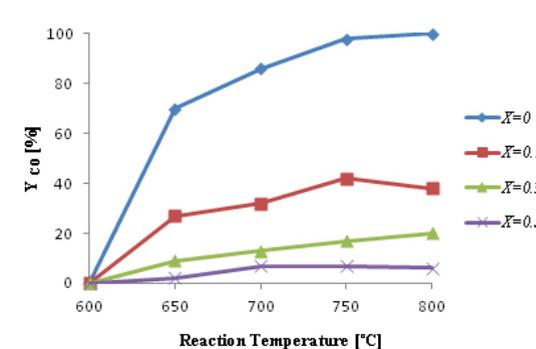
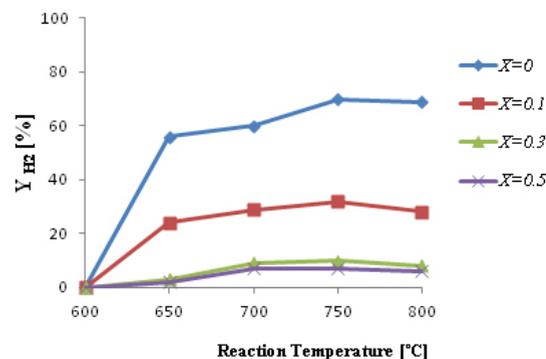
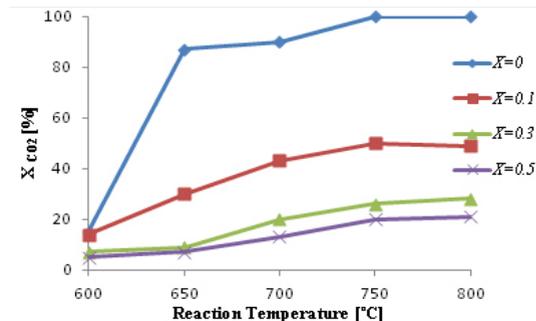
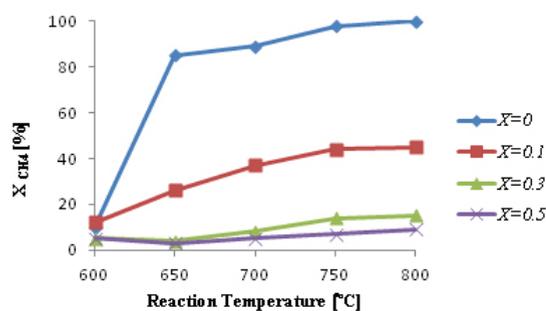


Fig. 4: CH_4 and CO_2 conversions, and H_2 and CO yields as a function of the reaction temperature for $La_{1-x}Zr_xNiO_3$ samples in DRM process ($CH_4/CO_2 = 1/1$, $WHSV = 15$ l/(h.g))

Fig. 5 indicates the CH_4 and CO_2 conversions and H_2 and CO yields versus time at $750^\circ C$ for $La_{1-x}Zr_xNiO_3$ samples. This figure shows that the CH_4 , CO_2 conversions and H_2 , CO yields in the presence of the pure perovskite are more than those of catalysts containing more than one phase. However, these parameters for $LaNiO_3$ are more observable than that of the samples containing Zr. The partial substitution of La^{3+} by Zr^{4+} in $La_{1-x}Zr_xNiO_3$ structure is undesirable for Ni reduction and leads to decreasing the mobility of the oxygen toward the surface of the solid²².

Fig. 5 (H_2 and CO yields) indicates that by letting time elapse, the yields in the presence of $La_{1-x}Zr_xNiO_3$ are decreased. However, since the extent of yield decrease roughly follows the same way for both CO and H_2 yields, the H_2/CO ratio remain constant (Fig. 6).

CONCLUSIONS

1. The XRD patterns of Zr doped $LaNiO_3$ indicated that Zr doping level (x) in these samples was 0.2 with formation of well-

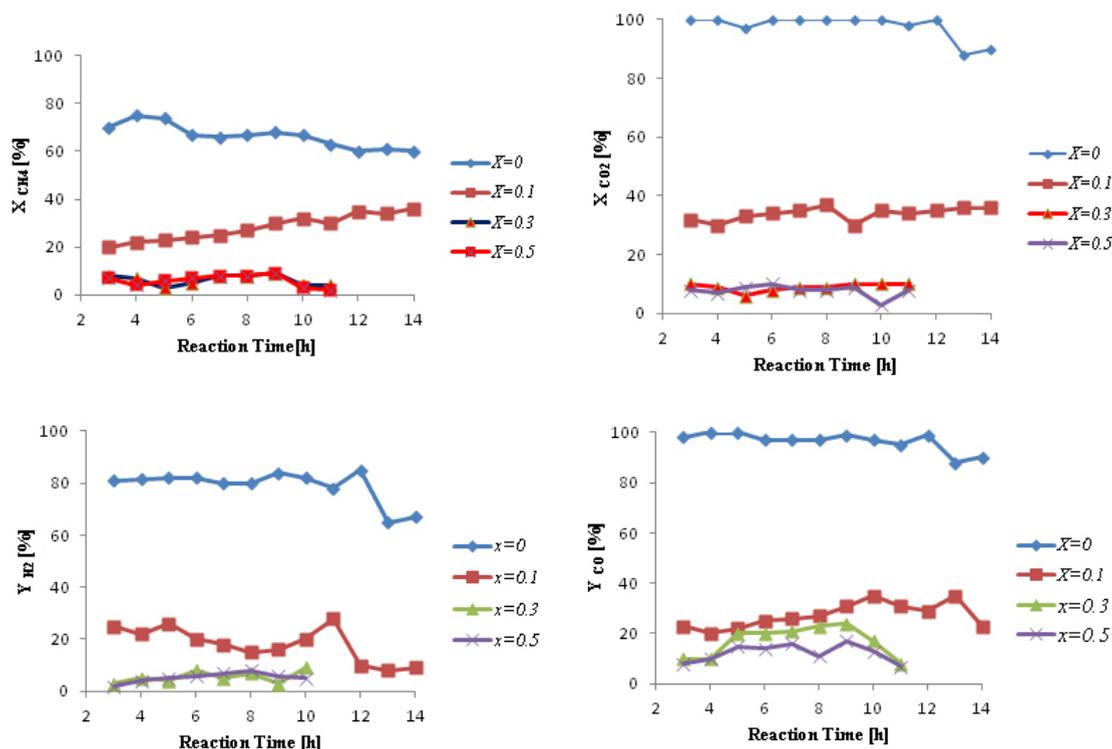


Fig. 5: CH_4 and CO_2 conversions, H_2 and CO yields as a function of the reaction time for $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ samples at 750°C in DRM process ($\text{CH}_4/\text{CO}_2 = 1/1$, $\text{WHSV} = 15 \text{ l}/(\text{h.g})$)

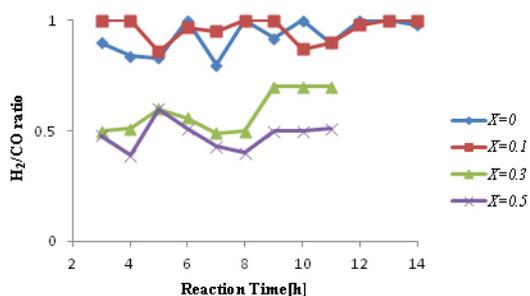


Fig. 6: H_2/CO ratios for $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ as a function of the reaction time in DRM process ($\text{CH}_4/\text{CO}_2 = 1/1$, $\text{WHSV} = 15 \text{ l}/(\text{h.g})$)

- crystallized perovskite structure in nanometer scale without any impurities.
- The cell parameter calculation obtained from XRD data showed that, by increasing the amount of Zr in the $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ samples, the cell parameter decreased.
- TPR study of the prepared samples displayed two main steps of hydrogen consumption. The burst one indicated the reduction of Ni^{3+} to

Ni^{2+} . The second step was related to Ni^{2+} to Ni^0 reduction in around 570°C . Also TPR analysis revealed that by increasing the amount of Zr in the prepared samples reduction process became difficult which could be due to presence of different forms of oxides other than perovskite type in the samples.

- CH_4 and CO_2 conversions increased by increasing the temperature in the presence of all catalysts. However, the CH_4 conversions were lower than that of CO_2 .
- The CH_4 and CO_2 conversions and H_2 and CO yields for the pure perovskite catalysts were more than those catalysts containing more than one phase.
- Global warming by greenhouse gases such as carbon dioxide (CO_2) and methane (CH_4) is one of the most important problems in all over the world. In recent years, many researches aimed to solve this problem and promote hydrogen production technology such as CO_2 reforming of methane generally called (DRM).

In this study we investigate $\text{La}_{1-x}\text{Zr}_x\text{NiO}_3$ nanostructures and its catalytic behavior in dry reforming of methane and supposed

to find out more applicable perovskite nanocatalyst in this process.

REFERENCES

- Asencios Y JO, Assaf EM. *Fuel Process Technol.* **2013**, *106*, 247-252.
- Goldwasser MR, Rivas ME, Pietri E, Perez-Zurita MS, Cubeiro ML, Gingembre L, Leclercq L, and Leclercq G. *J Mol Catal A Chem.* **2005**, *228*, 325-331.
- Ferreira-Aparicio P, Guerrero-Ruiz A, and Rodriguez-Ramos I. *Appl. Catal. Gen.* **1998**, *170* (1), 177-187.
- Khalesi A, Arandiyan H.R, and Parvari M. *Chin. J. Catal.* **2008**, *29* (10), 960-968.
- Valderrama G, Kiennemann A, and Goldwasser M.R. *J. Power Sources.* **2010**, *195*(7), 1765-1771.
- Pereniguez R, Gonzalez-Delacruz VM, Holgado J P, and Caballero A. *Appl. Catal. B.* **2010**, *93*(33), 346-353.
- Dejaidja A, Libs S, Kiennemann A, and Barama A. *Catal. Today.* **2006**, *113*(3), 194-200.
- Chendong Zuo, Doris SE, Balachandran U and Meilin Liu. *Chem. Mater.* **2006**, *18*, 4647-4650.
- Dhivya P, Prasad AK, Sridharan M. *Sensor Actuat, B: Chem.* **2016**, *222*, 987-993.
- Balamurugan C, Lee D-W. *Sensor Actuat, B: Chem.* **2015**, *221*, 857-866.
- Lima SM, Assaf JM, Pena MA, Fierro JLG. *Appl. Catal. A: Gen.* **2006**, *311*, 94-104.
- Gallego German S, Marin Jaime G, Batiot-Dupeyrat C, Barrault J, Mondragon F. *Appl. Catal. A: Gen.* **2009**, *369*, 97-103.
- Gallego German S, Mondragon F, Barrault J, Tatibouet J-M, Batiot-Dupeyrat C. *Appl. Catal. A: Gen.* **2006**, *311*, 164-171.
- Arandian HR, Li J, Lei Ma, hashemnejad SM, Mirzaei MZ, Chen J et al. *J Ind Eng Chem.* **2012**, *18*, 2103-2114.
- Goldwasser MR, Rivas ME, Pietri E, Perez-Zurita MS, Cubeiro ML, Gingembre L, Leclercq L, and Leclercq G. *Appl. Catal. Gen.* **2003**, *225*, 45-47.
- Jahangiri A, Pahlavanzadeh H, and Aghabozorg HR. *Int J Hydrogen Energy.* **2012**, *37*, 9977-9984.
- Jahangiri A, Aghabozorg HR, Pahlavanzadeh H, and Towfighi J. *Int J Chem React Eng.* **2014**, *12*, 1-10.
- Jahangiri A, Aghabozorg HR, and Pahlavanzadeh H. *Int J Hydrogen Energy.* **2013**, *38*, 10407-10416.
- Spinicci R, Marini P, De Rossi S, Faticanti M, Porta P. *J Mol Catal A Chem.* **2001**, *176*, 253-265.
- Yang Eh, Young Kim N, Noh Ys, Soo Lim S, Sun Jung J, Suk Lee J, Ju Moon D. *Int J Hydrogen Energy.* **2015**, *40*, 11831-11839.
- Barbero J, Pena M.A, Campos-Marthin J.M, Fierro J.L.G, and Arias P.L.. *Catal letters.* **2003**, *87*, 211-218.
- Valderrama G, Goldwasser MR, Navarro CU, Tatibouët JM, Barrault J, Dupeyrat CB, and Martinez F. *Catal Today.* **2005**, *107-108*, 785-791.