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Evaluating the Catalytic Performance of $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ Nanostructure Perovskites in the Carbon Dioxide Reforming of Methane

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Abstract

In this research nanostructure perovskites $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ were prepared by sol-gel auto-combustion method and their application were evaluated for methane reforming with carbon dioxide and syngas production. Catalysts were designed by Response Surface Method (RSM) based on central composite design (CCD) with three factors of catalyst characteristics, x, y and Tc. The prepared catalysts were examined in methane reforming process at 750 ˚C temperature and atmospheric pressure. Analysis of variance (ANOVA) showed that parameters don't have any linear effect on catalytic activity and their effect is proportional to square form. Among this investigated parameters, Ni content effect is considerable and calcination temperature (Tc) has a partial effect. In this research R2 value was 94.88%. The optimum catalyst which determined by RSM was $La_{0.60}Ce_{0.40}Ni_{0.81}Zn_{0.19}O_3$ in 747 ˚C calcination temperature that corresponds to empirical result. The XRD characterization of optimum catalyst showed that perovskite catalyst was formed in rhombohedra phase with nanostructure crystals and the SEM of optimum catalyst confirmed the nano scale of prepared particles.

Keywords: Nanoparticle; Dry reforming; Mixed metal oxide; RSM.

1. Introduction

In the beginnings of the third millennium, the natural gas is glimpsed as the fuel of the future, Valderrama et al. (2008). The combustion of fossil fuels is widely considered as a leading cause for CO_2 emissions, which is the main

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contributor to global warming effect, Tang et al. (2015). The imminent danger of global warming has driven both the scientific and industrial communities to search for environment-friendly energy sources, Valderrama et al. (2013). Dry reforming of methane (DRM) ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$), has gained a growing interest in recent years, because of great potential in converting CH_4 and CO_2 (major greenhouse gases) into synthesis gas, Al–Fatish et al. (2009). The demand of syngas in industrial fields has increased due to its potential in Fischer-Tropsch process and convert into a liquid hydrocarbon fuels or methanol for petrochemical industries, Chawla et al. (2013). DRM yielded a lower syngas ratio ($H_2/CO=1$), which is suitable for the synthesis of oxygenated chemicals and hydrocarbons from Fischer-Tropsch synthesis, Usman et al. (2015). Supported Ni catalysts have been used for the industrial reforming processes because of their inherent availability and lower cost in comparison to noble metal-based catalysts, Al–Fatish et al. (2009). An attractive alternative catalyst for methane dry reforming is a perovskite-type oxide. These oxides have the general formula of $ABO3$, in which the cation A is responsible for the thermal resistance, while the cation B is associated with the catalytic activity, Stojanović et al. (1997). The perovskite lattice can accommodate multiple cation substitutions with only small changes in the average structure, Araujo et al. (2008).

In the present work, perovskite-type oxides $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ were studied with the aim of developing suitable catalysts with optimum values of x and y and calcination temperature, which can be active in the methane reforming with carbon dioxide.

2. Experimental

2.1. Catalysts preparation

The $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ samples were prepared by self-combustion sol-gel. The initial composition of the solution was lanthanum nitrate [$La(NO_3)_3$-6H_2O], cerium nitrate [$Ce(NO_3)_3$-6H_2O], nickel nitrate [$Ni(NO_3)_2$-6H_2O], zinc nitrate [$Zn(NO_3)_2$ -6H_2O] dissolved in water. This solution was heated to 70 ˚C on a stirring plate and then the fuel (citric acid) [$C_6H_8O_7$] was added and evaporated to dryness at 80 ˚C to eliminate the excess of water. Afterward the temperature was increased to 200 ˚C until complete drying. The solid solution was calcinated at 600-800 ˚C for 5h at air. The amount of materials and the calcination temperatures was determined by response surface method (RSM).

2.2. Catalyst characterization

The perovskite structure of all catalysts was confirmed by powder X-ray diffraction (XRD) using a Siemens D-500 Siemense diffractometer with CuKα radiation. The diffraction patterns were recorded in the range of 2θ=4–70˚ and counting time of 1s per step. The morphology of the catalyst was observed by scanning electron microscopy (SEM) LEO44oi England.

2.3. Catalytic performance

Activity evaluation studies were carried out in a continuous flow fixed-bed tubular reactor (8 mm I.D.) under atmospheric pressure and 750 ˚C temperature. Set temperature is maintained by means of a programmable electric furnace (Exciton). In typical run, 200 mg of powder catalyst used to form a catalyst bed. The pre-mixed gases composed of 100:100:20 vol. % of CH_4:CO_2: Ar was fed at a constant feed rate of 220 mL/min. The Ar gas in the feed was used as an internal standard for mass balance measurements. The products were analyzed by GC equipped with HP Molesieve column and TCD detector. The CH_4 conversion was calculated according to the equation (1):

$$X_{CH_4}(\%) = \left(\frac{x_{Ar_{out}} x_{CH_{4in}} - x_{Ar_{in}} x_{CH_{4out}}}{x_{Ar_{out}} x_{CH_{4in}}} \right) \tag{1}$$

2.4. Catalyst design

The reaction parameters were optimized using a technique called the response surface methodology (RSM), Kusworo et al. (1997). This usually leads to an experiment designed to investigate these factors with a view toward eliminating the unimportant ones, Myers et al. (2009). A central composite design was employed in this study. Using the central composite design (CCD) model of RSM method, the optimum level for each factor is determined, Park et al. (2008). Three independent experimental variables, namely, lanthanum mol fraction (X_1), Ni mol fraction (X_2) and calcination temperature (X_3) were selected as controlled factors. Their experimental range and levels used in this work are given in Table 1. Table 2 shows the experimental conditions which are determined by RSM and the influence of factors on the response and optimum experimental conditions. Minitab software (Version 16) was used for analysis of the results.

Table 1. The levels of variables chosen for trials.

	-α	-1	0	1	+α
X_{La}	0.60	0.68	0.80	0.91	1.00
X_{Ni}	0.60	0.68	0.80	0.91	1.00
T_c	600	640.53	700	759.46	800

Table 2. Operating conditions of experimental runs.

Run No.	1	2	3	4	5	6	7	8	9	10
X_1	0.68	1	0.91	0.91	0.80	0.80	0.80	0.80	0.80	0.91
X_2	0.91	0.80	0.91	0.68	0.80	0.80	1.00	0.80	0.80	0.91
X_3	759.46	700.00	640.54	759.46	600.00	700.00	700.00	700.00	700.00	759.46
No.	11	12	13	14	15	16	17	18	19	20
X_1	0.68	0.80	0.80	0.80	0.68	0.60	0.91	0.68	0.80	0.80
X_2	0.91	0.80	0.60	0.80	0.68	0.80	0.68	0.68	0.80	0.80
X_3	640.54	700.00	700.00	800.00	640.54	700.00	640.54	759.46	700.00	700.00

3. Results and discussion

3.1. Statistical Analysis

Twenty sets of experiments with one replicates were conducted to explore the effect of X1, X2 and X3 on the methane conversion in the DRM process. The mean values of the obtained results, as well as the standard deviations are presented in Table 3 These results were then analyzed by ANOVA to evaluate the "goodness of fit" to the predicted models. The analysis equations generated by the first test were reduced by removing the terms that were not statistically significant (p-value < 0.05) which indicates that the variable in the model is significant Table 3 shows the regression coefficients and other statistical parameters for the reduced and non-reduced models.

Table 3. The results data for the independent variables obtained from the designed experiments.

Run Order	1	2	3	4	5	6[c]	7	8[c]	9[c]	10
Pt type	1	-1	1	1	-1	0	-1	0	0	1
Y	83.84	58.55	82.23	32.06	59.70	76.91	888.31	77.81	76.37	75.13
Y_p	87.09	58.3	79.42	32.90	67.38	76.95	84.93	76.95	76.95	81.21
Run Order	11	12[c]	13	14	15	16	17	18	19[c]	20[c]
Pt type	1	0	-1	-1	1	-1	1	1	0	0

| Y | 77.30 | 76.81 | 36.62 | 77.71 | 77.37 | 88.50 | 43.60 | 69.81 | 77.36 | 76.45 |
| Y_P | 76.49 | 76.95 | 39.96 | 70.00 | 71.32 | 88.98 | 40.39 | 72.64 | 76.95 | 76.95 |

Y. methane conversion, Y_p. Predicted value for Y, c. centre point

For the reduced models, data obtained in this table confirmed that the reduced full quadratic models were the most significant with p-values < 0.05. In addition to the p-value, the determination coefficient R2 is also a good tool for judging the significance of the mathematical model by determining the goodness of fit between the model and the experimental data.

Table 4. Full model and reduced model coefficient parameters for both responses.

Regression coefficient	Symbol	Full model		Reduced model	
		Parameter estimate	*p*-value	Parameter estimate	*p*-value
		Methane conversion(Y_1)	Methane conversion (Y_1)	Methane conversion (Y_1)	Methane conversion (Y_1)
Linear	X_1	-200.373	0.447	-556.323	0.00
	X_2	-15.687	0.952	200.152	0.0419
	X_3	1.157	0.083	1.122	0.060
Quadratic	X_1^2	-86.148	0.381	–	–
	X_2^2	-362.723	0.003	-354.169	0.003
	X_3^2	-0.001	0.053	-0.001	0.043
Interaction	X_1X_2	598.680	0.001	598.680	0.001
	X_1X_3	-0.312	0.245	–	
	X_2X_3	0.328	0.223	–	–
R^2		94.88%		92.81%	
R^2 adjusted		90.28%		89.50%	

3.2. Effects of investigated parameters on methane conversion

For the methane conversion response, the ANOVA results shown in Table 4 indicate that the X2 and X3 have effects on response. The relationship between the variables and the methane conversion is explained by the response surface plots shown in

Fig. 1. The general trends of these plots indicate that the reciprocal interaction between the X1 and X2, X1 and X3, X2 and X3 have an effect on the methane conversion. The feature of using response surface plots as a function of two variables at a time is that it can describe the effects of both the main and the interaction factors. According to Fig. 1a it can be understood that the interaction between the lanthanum mol fraction and nickel mol fraction is negligible. Fig. 1b shows that in any calcination temperature the conversion of methane is contrary related with lanthanum mol fraction. Fig. 1c shows that the conversion of methane in any calcination temperature is directly related with nickel mol fraction.
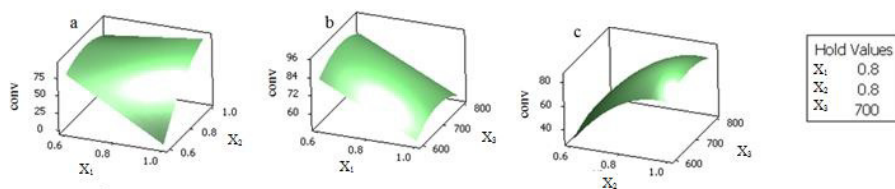

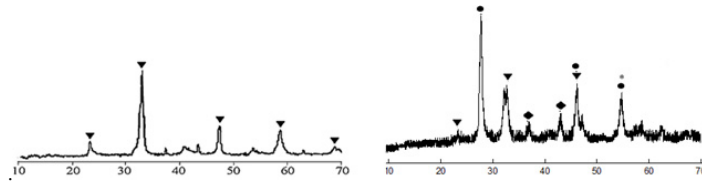Fig. 1. The interaction effectof process variables on methane conversion: (a) X_1 and X_2; (b) X_1 and X_3; (c) X_2 and X_3.

Fig. 2. XRD profiles of calcined perovskites. (a) $LaNiO_3$; (b) $La_{0.60}Ce_{0.40}Ni_{0.81}Zn_{0.19}O_3$.($\blacktriangledown$: $LaNiO_3$, $\bullet$:La_2O_3, $\blacklozenge$:NiO, *:CeO_2, □:ZnO).
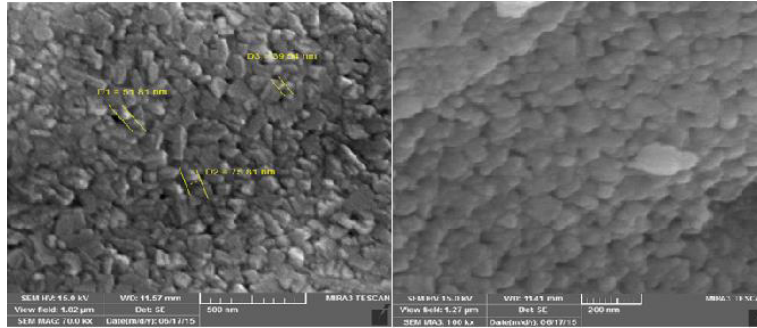

Fig. 3. SEM images of the optimum catalyst $La_{0.60}Ce_{0.40}Ni_{0.81}Zn_{0.19}O_3$.

4. Conclusions

In this work, the DRM reaction was performed over $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ catalysts. To maximize methane conversion, a statistical method was effectively employed to analyse the variation effects of the process variables. Three process parameters, including the calcination temperature, the lanthanum and nickel mol fraction were investigated using RSM. The ANOVA results demonstrated that the X2 and X3 had effects on the response. A second-order regression equation was obtained for the response. The response optimizer revealed that the optimum values of the studied variables were X1 of 0.6, X2 of 0.81 and X3 of 747 ˚C. Verification experiment was performed at the optimum conditions and the experimental value (89.62%) closely agreed with predicted value (90.47%). This indicated that RSM is an applicable method to optimize the catalyst preparation parameters.

Acknowledgements

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