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Optimization of La-Ce/HZSM-5 catalyst for thermal catalytic cracking of naphtha to light olefins to save energy and reduce CO_2 emission

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ABSTRACT

Thermal cracking of hydrocarbons at 850-900 degree centigrade is the governing technology worldwide for light olefins production. But the most disadvantages of this route is large energy consumption and air pollution because of flue gas emission containing CO_2 and NOx. To overcome these drawbacks catalytic cracking is an important and new field for research. So, in this work the effects of temperature and loadings of cerium and lanthanum over HZSM-5 catalyst for thermal catalytic cracking of naphtha were investigated using response surface methodology. In these experiments, the temperature, Ce, and La loadings were varied from 600 to 700 °C, 4 to 12wt.%, and 0.8 to 3wt%, respectively. The Box-Behnken design was utilized and a set of experiments were designed to obtain the optimum catalyst for maximizing the yield of ethylene and propylene. The analysis of variance (ANOVA) was carried out to identify the statistical significance of independent factors and their interactions. The results showed that temperature and Ce loading had the highest effects on the yields of ethylene and propylene, respectively. Based on the multi-objective optimization, the maximum yields of ethylene and propylene (17 and 33wt%, respectively) were obtained at cerium loading of 12 wt.%, lanthanum loading of 1.2 wt.%, and temperature of 700 °C.

1. Introduction

Light olefins such as ethylene and propylene are building blocks of the petrochemical industry and have been extensively used to produce plastics, fibers, and other chemicals [1,2]. They are traditionally produced by thermal cracking process. This method has some drawbacks such as high reaction temperature, which makes it one of the most energy-consuming processes in the petrochemical industry by consuming nearly 40% of the total energy [3-5]. Catalytic cracking is an effective way for the production of light olefins at moderate temperatures [6]. Several effective

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catalysts such as HZSM-5 [7-10], ZSM-5 [11,12], SAPO-34 [13,14], and carbon nanotubes (CNT) [15,16] have been studied for the catalytic cracking of hydrocarbons. Among these catalysts, HZSM-5 has been widely used for cracking due to its hydrothermal stability, acidity, and shape selectivity [17]. In addition, modifications with rare earth and transition metals were applied to improve the zeolite performance [18-20].

The effects of rare earth metals addition to HZSM-5 on the catalytic cracking of butane to light olefins were studied in a fixed bed reactor. It was found that the total olefins yield increases with rare earth metals loadings and the addition of Ce and Nd gave the highest total olefin yield (57.2 wt.%) and propane yield (25.9 wt.%) at 600 °C, respectively [18]. La2O3/P/ZSM-5 catalysts were used in catalytic cracking for the production of light olefins by Yoshimura et al. [19]. The results showed that the yield of ethylene and propylene (60%) at 650 °C was 10% percent higher than the steam cracking method at 820 °C. Wei et al. studied the catalytic cracking of naphtha over modified ZSM-5 at 650 °C [11]. Among the catalysts, modification of ZSM-5 with Cu, Fe, and La tended to produce more aromatics. However, the modified ZSM-5 with P and Mg produced more light olefins. The P-La/ZSM-5 catalyst had a better catalytic performance for the production of light olefins in which higher yields of olefins and better catalyst stability were obtained. To optimize the yield of ethylene and propylene, Alyani et al. used the Box-Behnken method to investigate the effective parameters on the production of light olefins using the HZSM-5 catalyst [8]. The maximum yield of ethylene and propylene (42 wt.%) was obtained at 670 °C, WHSV 44 h−1, and 6wt% Fe loading. Keyvanloo et al. used the central composite design (CCD) methodology to study the optimum amount of La_2O_3–MoO_3 and CeO_2–MoO_3 mixed oxides supported on HZSM-5 [21]. The proper amount of cerium, lanthanide, and molybdenum tends to increase the yield of light olefins. However, the high loadings of La and Ce decrease the olefin yield. The optimal range of La_2O_3 loading and CeO_2 loading was found to be 7.2 wt.% and 8.8 wt.%, respectively. Taj synthesized and used IM-5 zeolite in naphtha catalytic cracking to produce light olefins. The results showed that this catalyst is more selective to light olefins in comparison to other zeolite type catalysts [30]. Li et al. investigated the synthesis and application of ZSM-12 nanocrystals in catalytic cracking of n-hexadecane and showed that the coke formation rate is reduced [31]. Sanhoob et al. synthesized La-Ce/ZSM-12 for catalytic cracking of n-hexane and they showed that the catalyst is still active after 240 min. [32]. As can be inferred from the literature, the catalytic cracking of naphtha for the production of ethylene and propylene over the Ce/La-HZSM-5 catalyst has not been fully understood. Therefore, the overall objective of this study is to investigate the effects of temperature and loading of cerium and lanthanum over the HZSM-5 catalyst in the catalytic cracking of naphtha for light olefin production. The Box-Behnken experimental design was used to develop a polynomial expression for predicting olefin production as a function of Ce and La loading and temperature and optimal values of the parameters were reported. The analysis of variance (ANOVA) was also applied to investigate the significance of the variables and their interactions. Catalytic Cracking of naphtha to produce light olefins is not commercial, so in this work we tried to introduce a novel catalyst and new operating conditions to reduce the operating temperature from 850○C in thermal cracking to 700 °C for catalytic cracking and produce more propylene (33%) in comparison to 16% in thermal cracking of naphtha. In terms of energy saving, catalytic cracking is generally considered to be more efficient than thermal cracking. According to a report by U.S Department of Energy, catalytic cracking requires about 20% less energy than thermal cracking to produce the same amount of light olefins [33]. Another study found that the selectivity of catalytic cracking for light olefins can be as high as 90%, while thermal cracking typically has a selectivity of around 50% [34].

2. Materials and methods

2.1. Catalyst preparation

The HZSM-5 zeolite (Si/Al=100) with a surface area of 414.7 $\mathrm{m^2 g^{-1}}$ and pore volume of 0.13 $\mathrm{cm^3 g^{-1}}$ was used as a support, supplied by ZEOCHEM, Switzerland. The HZSM-5 zeolite was impregnated by certain concentrations of La $(NO_3)_3.9H_2O$ and Ce $(NO_3)_3.9H_2O$ solutions with an incipientwetness impregnation method. In the experimental design, the ranges of cerium and lanthanum contents were varied from 4 to 12 and 0.8 to 3 wt.%, respectively. The prepared samples were then kept at room temperature for 10 h, dried at 120℃ in an oven for 24 h, followed by calcination in air at 550℃ for 4 h. The samples were then crushed and sieved to a mesh size of 10-20 μm for catalytic cracking runs and XRD characterization. The samples were then characterized using X-ray diffraction (XRD). The XRD patterns were performed on a D5000 diffractometer that uses Cu Kα radiation at 40 kV, 40 mA with a scanning rate of 0.05 °/s. The data were recorded from $2\theta = 5^{\circ}$ to $2\theta = 80^{\circ}$.

2.2. Reactor tests

The catalytic reactions were performed in a fixed bed flow reactor under atmospheric pressure at 600-700 °C. Using the GC facilities in Research Institute of Petroleum Industries, the properties and compositions of naphtha feed are presented in Table 1. The reactor consists of a stainless-steel tube with 45 cm in length and 1.35 cm in diameter. An appropriate amount of steam was added to the reactor to prevent or reduce coke formation. Steam and naphtha were pumped into two preheaters and then mixed into the reactor. The effluent from the reactor was quenched in an ice bath followed by two water-cooled condensers placed in series. The gas-phase components were then analyzed by online gas chromatography (Hewlett Packard 5890 GC). The experimental apparatus was shown elsewhere [15]. The testing conditions for catalytic cracking of naphtha were as follows: steam to naphtha ratio = 0.5 g/g, weight hourly space velocity (WHSV) = 80 h^{-1}, and weight of catalyst = 1 g.

Table1. Properties and composition of naphtha

Physical Properties				
Specific gravity (g/cm^3)				0.655
Initial boiling point (˚C)				60.7
Final boiling point (˚C)				120.3
Chemical composition (wt.%) %				
Carbon no.	n-	i-Paraffin	Naphthene	Aromatics
C_4	2.16	0.12	0	0
C_5	27.34	21.38	3.58	0
C_6	10.19	12.29	3.84	1.58
C_7	3.29	3.82	4.34	1.57
C_8	1.04	1.2	0.92	0.55
C_9	0.26	0.5	0	0.03
Sum	44.28	39.31	12.68	3.73

2.3. Experimental design (response surface methodology)

Response surface methodology (RSM) is a collection of statistical and mathematical techniques that can be used to model and optimize processes. The various process factors are optimized using one of the response surface methods. RSM computes the relationship between the convenient input factors and the response surfaces achieved [22,23]. The Box-Behnken experimental design can save time and effort by reducing the number of experiments rather than other conventional factorial design methods. The number of experiments is calculated by:

$$N=2k\ (k-1) + C_0 \tag{1}$$

where k is the number of factors, C0 is the replicate number of the central point and N is the total number of experiments [24]. Independent variables (A: temperature, B: Ce loading, and C: La loading) and their levels for the Box–Behnken design used in this study are shown in Table 2. The coded values of the process parameters were determined as follows:

$$x_i = \frac{X_i - X_0}{\Delta x} \tag{2}$$

where x_i is the coded value of the i^{th} factor, X_i is the uncoded factor value, X_0 is the uncoded factor value at the center point, and Δx is the uncoded value of the factor-variation interval [25]. Three important factors were included in the Box-Behnken experimental design to determine the influence of each factor and obtain optimal loadings and temperature to achieve high production of light olefins. The optimum values of the selected variables were obtained by solving the polynomial equation to maximize the yields of light olefins as the optimization criteria [26].

Table 2. The levels of different factors for the Box–Behnken experimental design.

Factors		level		
		-1	0	1
A	Loading Ce (wt.%)	4	8	12
B	Loading La (wt.%)	0.8	1.9	3
C	Temperature (℃)	600	650	700

3. Results and discussion

3.1. Catalyst characterization

XRD patterns of the fresh and modified HZSM-5(10%Ce 2%Le/HZSM-5) are shown in Figure. 1. Upon the addition of Ce and La, some new peaks can be observed, which proved the existence of these two elements. After modifying the HZSM-5 catalyst with Ce and La, the crystallinity of the HZSM-5 catalyst was slightly evident by the lower intensity of the XRD spectra for modified HZSM-5.

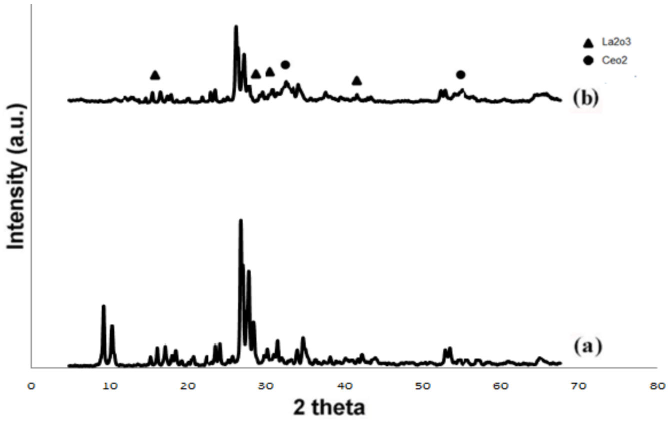

Fig. 1. XRD patterns of HZSM-5 (a), Ce-La-HZSM-5 (b).

3.2. Analysis of data

The experimental results for the yields of ethylene and propylene are presented in Table 3. Regression analysis by considering linear, quadratic, 2FI, and cubic models were performed on the two responses for ethylene and propylene yields. Furthermore, the ANOVA was performed for each derived model to investigate whether the equation can satisfactorily represent the actual relationship between the response and the significant variables [27]. The adequacy of the models for ethylene and propylene yields was also studied using a sum of squares (SS), p-value, F value, and adjusted determination coefficient (R^2).

Table 3. Box-Behnken design matrix and the response of the ethylene and propylene yield.

Run	Factors			Yield (%)	
	Temperature	La (wt. %)	Ce (wt. %)	Ethylene	Propylene
1	600	0.8	8	13.7	25.1
2	650	1.9	8	15.2	35.6
3	650	0.8	4	13.2	25.9
4	700	1.9	4	14.1	31.4
5	600	1.9	12	15.8	27.2
6	600	3	8	14.5	29.9
7	700	0.8	8	15.3	33.9
8	700	3	8	15.1	33.7
9	650	1.9	8	15.3	36
10	650	3	4	14.3	30.6
11	650	3	12	16.6	28.1
12	700	1.9	12	17.4	32.6
13	600	1.9	4	13.4	23. 8
14	650	1.9	8	14.9	35.2
15	650	0.8	12	16.7	32
16	650	1.9	8	15	35.4
17	650	1.9	8	14.7	34.7

The F value is determined using the following equation 3:

$$F\ value = MSF/MSE \qquad (3)$$

where MSF is the mean squares of parameters or interactions and MSE is the mean squares of errors. The parameters that have greater F value were considered more significant. Furthermore, p-values less than 0.05 show the significance of the model or parameters. From Tables 4, it can be concluded that the linear model is adequate for predicting ethylene yield with F-value of 46 and P-value of < 0.0001, while propylene yield with a quadratic model gives the best result. These results clearly show that considering some parameters in the model for the interaction of the variables significantly improves the model.

Table 4. F-value and P-value of different models for the ethylene and propylene responses.

	Ethylene		Propylene		
Source	**F value**	**Prob>F**	**F value**	**Prob>F**	**Remark**
Linear	46.16	< 0.0001	2.57	0.0993	
2FI	2.43	0.1261	0.65	0.5985	
Quadratic	7.05	0.0161	105.09	< 0.0001	Suggested
Cubic	0.08	0.9673	3.14	0.1491	Aliased

From Table 5, as it is obvious, the R^2 values increase with using higher order models including more parameters from linear to cubic. The R^2 value increases from 0.91 to 0.99 by using linear or cubic models, respectively for the ethylene yield. Although the R^2 value increases from linear to cubic model, the improvement in the model is marginal compared to the parameters added to the model (3 parameters for linear equation compare to 9 parameters for quadratic). Therefore, the F value for the linear equation (ethylene yield) is higher than higher-order models such as quadratic or cubic. However, this is not the case for propylene response; the R^2 suddenly increased from 0.37 to 0.99 for linear and quadratic models, respectively.

Table 5. Statistics of different models for the ethylene and propylene responses.

	Source	Std. Dev.	R^2	PRESS	Remark
Ethylene	Linear	0.38	0.9142	3.62	
	2FI	0.33	0.9503	4.47	
	Quadratic	0.19	0.9876	0.63	Suggested
	Cubic	0.25	0.9883		Aliased
Propylene	Linear	3.49	0.3721	247.84	
	2FI	3.64	0.4751	332.94	
	Quadratic	0.64	0.9886	33.6	Suggested
	Cubic	0.46	0.9966		Aliased

The ANOVA calculation on the yields of ethylene and propylene to investigate the significance of independent variables (temperature, La loading, and Ce loading) is listed in Table 6 and Table 7, respectively. The results obtained by the ANOVA test indicate that factors A (temperature), B (La loading), C (Ce loading), and interactions A×B, B×C, and C^2 had statistically main effects on the yield of ethylene. Among the parameters, A and C have a huge effect on the response evidenced by the low p-values. Based on the ANOVA results for propylene, the most important parameters affecting the yield of propylene were A, B, C, A×B, B×C, A^2, B^2 and C^2. The F values of the interactions (A×B and B×C) for ethylene is ranging from 6 to 9 and for propylene, it is between 15 and 45 showing that the interactions become very important for the propylene response. It is even more pronounced for A^2, B^2, and C^2 parameters. It is consistent with what we found that the optimum model for propylene is quadratic (includes interactions) and for ethylene is linear (does not have interactions).

Table 6. Analysis of variance for the yield of ethylene from the experimental design.

Factor	df	SS	MS	F	P
A-T	1	2.6	2.6	68.49	< 0.0001
B-loading La	1	0.34	0.34	8.89	0.0205
C-loading Ce	1	16.70	16.70	440.54	< 0.0001
AB	1	0.25	0.25	6.46	0.0385
AC	1	0.19	0.19	4.97	0.0611
BC	1	0.34	0.34	9.05	0.0197
A^2	1	0.18	0.18	4.64	0.0683
B^2	1	0.15	0.15	3.98	0.0864
C^2	1	0.52	0.52	13.63	0.0077
Error	4	0.25	0.063		
Total	16	21.48			

Table 7. Analysis of variance for the yield of propylene from the experimental design.

Factor	df	SS	MS	F	P
A-T	1	81.92	81.92	199.58	< 0.0001
B-loading La	1	3.46	3.46	8.43	0.0229
C-loading Ce	1	8.41	8.41	20.48	0.0027
AB	1	6.30	6.30	15.35	0.0058
AC	1	1.17	1.17	2.84	0.1357
BC	1	18.49	18.49	45.05	0.0003
A^2	1	27.7	27.7	67.47	< 0.0001
B^2	1	19.64	19.64	47.85	0.0002
C^2	1	69.74	69.74	169.89	< 0.0001
Error	4	0.86	0.21		
Total	16	252.03			

The relationship between the response and independent variables was obtained from the following second-order polynomial equations:

$$\text{Ethylene yield (wt.\%)} = -30.24 + 11.75 \times 10^{-2}\,X_A + 4.24\,X_B - 5.68 \times 10^{-1}X_C - 4.5 \times 10^{-3}X_AX_B - 1.08 \times 10^{-3}X_AX_C - 6.66 \times 10^{-2}X_BX_C - 8.17 \times 10^{-5}X_A^2 - 15.64 \times 10^{-2}X_B^2 + 2.18 \times 10^{-2}\,X_C^2 \quad (4)$$

$$\text{Propylene yield (wt.\%)} = -515.21 + 1.46X_A + 26.12X_B + 7X_C - 2.28 \times 10^{-2}X_AX_B - 48.86 \times 10^{-2}X_BX_C - 2.7 \times 10^{-3}X_AX_C - 1.02 \times 10^{-3}X_A^2 - 1.78X_B^2 - 25.44 \times 10^{-2}X_C^2 \quad (5)$$

in which X_A, X_B, and X_C denote the actual variables of temperature, La loading, and Ce loading, respectively. The determination coefficient for Eq. (4) was calculated as 0.987, which reveals that the predicted data has good agreement with experimental results. R^2 of 0.986 in Eq. (5) also shows fitting with high precision for the achieved experimental results of propylene yield. The main effects of factors (A, B, C) and statistically significant two-factor interaction effects (A×B, A×C, B×C) for ethylene and propylene are shown in Figure 2 and Figure 3, respectively. According to Figure 2a, the yield of ethylene increases as the reaction temperature and the Ce loading increase. However, an increase in the La loading did not produce significant changes in the yield. Figure 2b shows the effect of interactions for two variables. As seen in this figure, the effect of the La loading was negligible when the reaction temperature (A) was set at a high level (700 °C); however, at a low level for temperature, increasing the La loading slightly increases the ethylene yield. At a high level of temperature, as depicted in the middle of Figure 2b, the increase in the yield of ethylene by Ce loading (C) is more pronounced (14.1 to 17.4%) than at a low level of temperature. The same explanation can be given in Figure. 3. As observed from Figure 3a, the yield of propylene increases by an increase in the reaction temperature and Ce loading. It is interesting to note that at a high level of temperature, the effects of Ce and La loading were negligible (Figure 3b). Increasing the La loading at two extremes of Ce loading has an opposite effect on the yield of propylene. At a low level of Ce loading, increasing the La loading increases the yield while at a high level of Ce loading, increasing the La loading decreases the yield. This practice demonstrates that some parameters can be highly correlated and their effects cannot be simply investigated by constant-a-time experimental design.

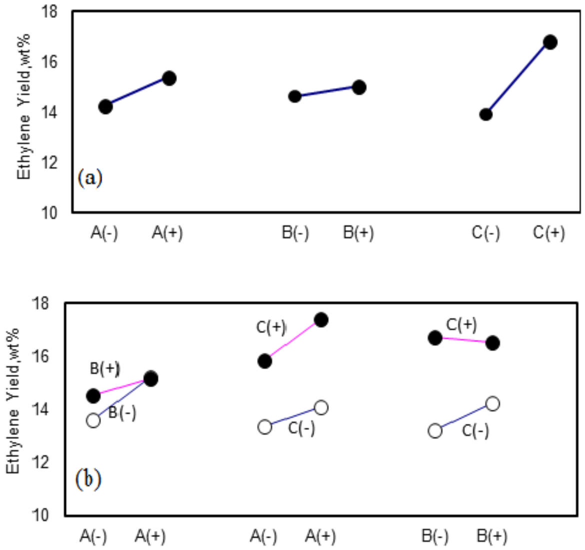

Fig.2. The main effects of factors A, B, and C on the yield of ethylene (a). Interaction effects of A×B, A×C, B×C on the yield of ethylene (b) where + and - indicate the high and low levels of each variable, respectively.

3.3. *Contour plots*

The relationships between the dependent and independent variables were further clarified by using contour plots. Since the regression model has three independent variables, one variable was held at the constant value at the center level for each plot, resulting in three contour plots [28]. Equations (4) and (5) were used to construct the contour plots for the yields of ethylene and propylene against temperature as well as Ce and La loading as shown in Figure 4 and Figure 5. These contour plots facilitate the comparison of the dependency of the yields on the process variables. From Figure 4a, the yield of ethylene is significantly increased with the simultaneous increase of temperature and Ce loading. Figure 4b demonstrates that the yield of ethylene initially increases, reaching a maximum, and then decreases by increasing the La loading. The variation of the propylene yield with temperature and Ce and La loading is presented in Figure 5. The yield of propylene is significantly increased with increasing the temperature up to 680 °C and afterward shows a slight decrease. It can also be deducted that with an increase in Ce loading, the yield of propylene initially increases, reaching a maximum, and then decreases. The most significant parameter affecting the ethylene yield is Ce loading. The F values of temperature, La, and Ce loading for ethylene are 68.49, 8.89, and 440.54, respectively, indicating that La loading and temperature are less significant in ethylene production (Table 6). Temperature is the most significant factor in the propylene yield albeit Ce and La loading is statistically important. For propylene, as depicted in Table 7, the F value of temperature is 199.58 which is much larger than that of the Ce (F = 8.43) and La (F = 20.48).

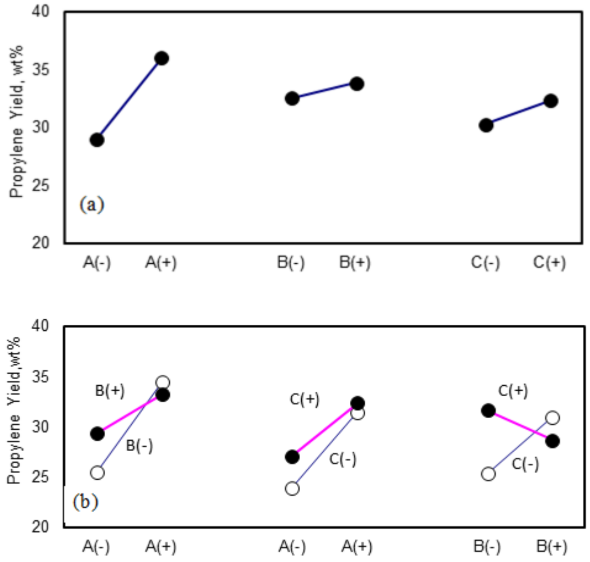

Fig. 3. The main effects of factors A, B, and C on the yield of ethylene (a). Interaction effects of A×B, A×C, B×C on the yield of propylene (b) where + and - indicate the high and low levels of each variable, respectively.

3.4. *Multi-objective optimization*

The optimum value for ethylene and propylene yields can be calculated using Eqs. (4) and (5), respectively. The steam catalytic cracking was optimized to maximize the yields of ethylene and propylene simultaneously. This procedure was reported elsewhere [29]. As shown in Table 8 an optimum set of variables that can maximize both ethylene and propylene yield was found at T=700℃, La loading = 1.2 wt.%, and Ce loading = 11.8 wt.%. The optimized responses for ethylene yield and propylene yield were obtained as 17.4 and 33.7 wt.%, respectively. The optimum point which only maximizes ethylene yield was very close to the optimum point for multi-objective optimization; however, the optimum point for maximizing only the propylene yield was obtained at T=700℃, La loading = 1.8 wt% and Ce loading = 9.6 wt% with ethylene and propylene yield of 16 wt.% and 36.1 wt.%, respectively. To confirm the accuracy of the obtained results, the validation test was carried out under optimum conditions. Table 8 presents the experimental values for the ethylene and propylene yields corresponding to multi-objective optimization as 17.7 wt.% and 34 wt.%, respectively, very close to the predicted value from the response surface methodology. The differences between the predicted and achieved values are satisfactory and confirm the prediction capability of the Box-Behnken method.

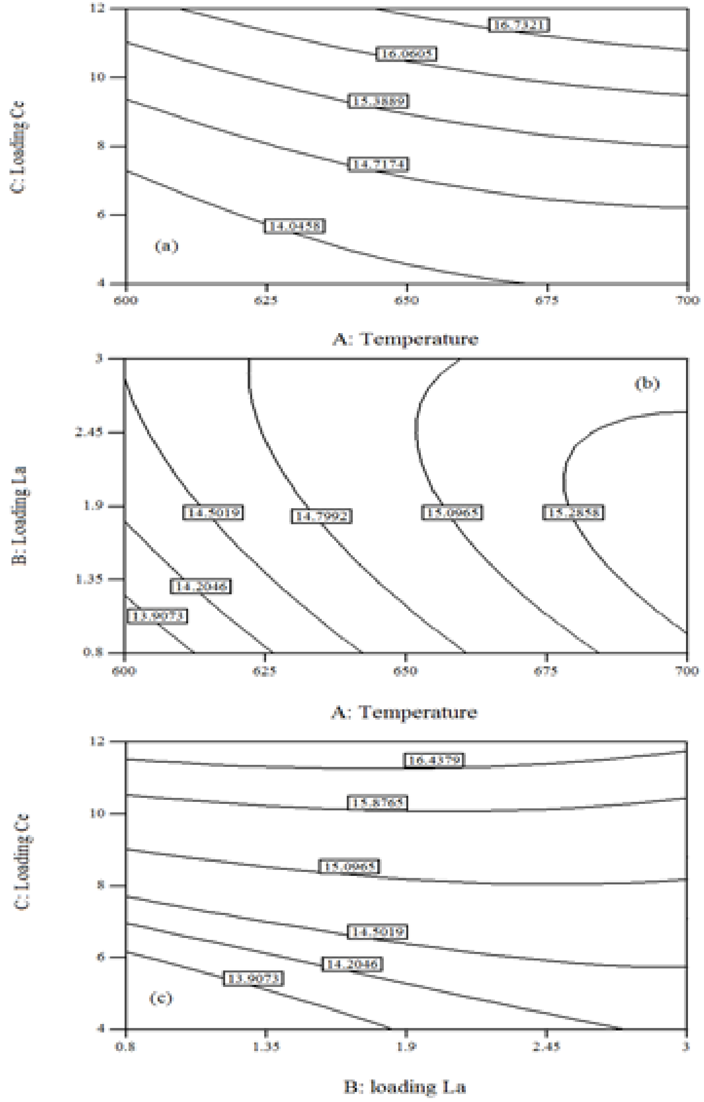

Fig. 4. Contour plots describing the response surfaces for ethylene as a function of temperature vs. loading Ce (a), temperature vs. loading La (b), and loading La vs. loading Ce (c).

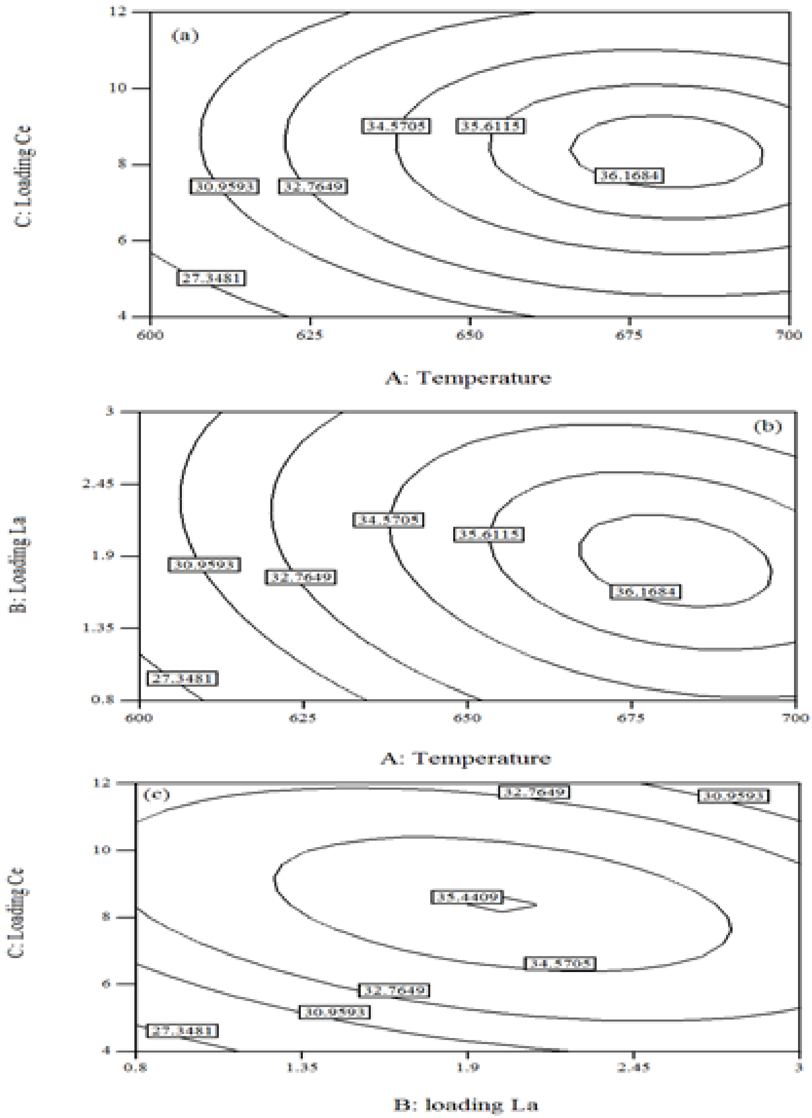

Fig. 5. Contour plots describing the response surfaces for propylene as a function of temperature vs. loading Ce (a), temperature vs. loading La (b), and loading La vs. loading Ce (c).

Table 8. Validation of the optimal point in the optimization of ethylene and propylene.

parameter	Temperature	La(wt.%)	Ce(wt.%)	Desirability	Yield (wt.%)			
					Experimental		Predicted	
					Ethylene	Propylene	Ethylene	Propylene
Ethylene	700	1.6	12	0.75	17.6	34	17.4	33.2
Propylene	700	1.8	9.6	0.78	16.35	36.2	16	36.1
Ethylene + Propylene	700	1.2	11.8	0.89	17.7	34	17.4	33.7

4. Conclusions

The effect of three parameters (temperature, Ce, and La loadings) was determined and an experimental design was used based on the Box-Behnken method to obtain the optimum catalyst for maximizing the yield of ethylene and propylene production. It was found that the most effective parameters in the yields of propylene and ethylene are temperature and loading of Ce, respectively. Apart from these factors, ANOVA indicated that interactions between temperature and La loading as well as interactions between La and Ce loadings are statistically significant in the yields of ethylene.

In the case of propylene yield, interactions between (temperature and Ce loading) and (temperature and La loading) are the most important variables. In general, the significance of interactions for a yield of propylene was much higher than those of interactions for ethylene yield. Therefore, the quadratic model was found to be statistically significant for predicting the yield of propylene while the linear model was good enough for ethylene yield. The goodness of fit analysis indicates excellent agreement between experimental observations and model outputs. At moderate loading of Ce, we can achieve the highest yield of propylene. In addition, high temperature increases the yields of both ethylene and propylene.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that would influence this paper.

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