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Influence of process variables and optimization of ethylene yield in oxidative coupling of methane over Li/MgO catalyst

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Abstract

The effects of operating temperature, inlet oxygen concentration, and F/W on ethylene production by oxidative coupling of methane (OCM) were studied over Li/MgO (Li/Mg = 0.1) catalyst. Central composite experimental design (CCD) and response surface methodology (RSM) were utilized to determine the best operating condition for maximum ethylene production. The design led to three surface responses describing the dependence of methane conversion, ethylene yield, and ethylene selectivity on operating temperature (737–913 °C), inlet oxygen concentration (6.2–23.8 vol.%) and F/W (9280–35,720 ml/g h). The equation models were tested with analysis of variance with 5% level of significance. The results of the analysis revealed that the equation models fitted well with the experimental results for methane conversion and ethylene yield. Numerical results indicated the maximum ethylene yield was 8.14% at optimum operating temperature = 839.51 °C, inlet oxygen concentration = 18.89 vol.% and F/W = 20264.34 ml/g h. Additional experiments were carried out at the optimum condition for verification.

Keywords: Ethylene production; OCM; Li/MgO; Response surface methodology; Central composite design; Optimization

1. Introduction

Due to the large natural gas reserves worldwide, methane appears to be the cheapest and most available carbon source for the gas-based petrochemical industry. The development of a simple and commercially advantageous process for the direct conversion of natural gas to more easily transportable products was desired. Keller and Bhasin [1] suggested that catalytic reaction for the direct conversion of natural gas to ethane and ethylene offered a new route for ethylene production. Among the numerous attempts for direct conversion, the oxidative coupling of methane (OCM) to C_2 hydrocarbons still remains one of the potential routes.

Innumerable catalysts were investigated and were found to be promising in this complex heterogeneous–homogeneous process. It has also been reported that a part of the surface oxygen becomes active at high temperatures, reacting with methane even on irreducible oxides such as MgO. The special oxygen structure such as O^-, has been proposed as the active species. Thus, it can be seen that the OCM reaction occurs on MgO only at high temperatures, usually in the range of 873–1073 K. If O^- is the active species, O^- or the surface structure accepting O^- must be generated only at high temperature on MgO catalytic systems. Furthermore, O^- (stable at high temperature) has been reported to be produced by doping with alkali metal ions [2]. The Li^+O^- center in MgO has been detected by EPR and proposed as the active center of the OCM reaction [3]. The Li^+O^- centers are formed by the substitution of Li for Mg in the MgO lattice which is possible since the respective ionic radii of Li^+ and Mg^{2+} are nearly equivalent.

In another development, Lunsford et al. [4] proposed a mechanism for the oxidative coupling of methane reaction in which the active sites are Li^+O^- species at the surface of the catalyst. It was proposed that methane is activated by hydrogen abstraction on the active sites for the simultaneous formation of methyl radicals. Ethane and ethylene are subsequently formed by the coupling of methyl radicals in the gas phase. In addition to coupling, nonselective reactions are catalyzed by the surface and gas phase radicals reaction may lead to the formation of CO_x.

In the OCM reaction, the selectivity to ethane is usually higher than ethylene, but ethylene is more reactive and is also

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an important feed stock to the chemical industry. One possible method to improve the ethylene yield is by adding an adsorbent for continuous removal of olefinic products, which were subsequently recovered by thermal treatment. The unreacted methane is recycled after the selective adsorptive separation. By using this system, Machocki [5] obtained a C_2 selectivity of 70% (consisting of 92% ethylene) at a total CH_4 conversion of 94%.

Another alternative method would be adding one more reactor after the OCM process so that the dilute ethylene present in the OCM product stream could be converted to less volatile aromatics or gasoline products [6,7]. However, ethane still remains in the recycle stream along with unreacted methane and an additional step to dehydrogenate ethane is needed.

Previous studies have shown that the dehydrogenation of ethane to ethylene can be carried out thermally without catalyst [6,7]:

$$C_2H_6 \leftrightarrows C_2H_4 + H_2 \tag{1}$$

For that reason, reaction (1) can take place in the same reactor with OCM reaction. However, one major problem with the dehydrogenation of ethane is that high temperature (800–900 °C) is required [8], i.e. 50–100 °C higher than the optimal operating temperature for C_{2+} hydrocarbons in the OCM reaction. Hence, it is important to determine the optimal operating condition to achieve maximum ethylene yield in the OCM reaction.

The Li/MgO catalyst is one of the most extensively studied catalysts in literatures [2,9–16] for the OCM reaction as it shows high catalytic activity in the low temperature range. However, Li/MgO and many other catalysts still could not achieve a C_2 yield beyond 25% and a selectivity of C_2 higher than 80% in a single-pass mode [17].

In this paper, central composite design (CCD) is used to predict the optimum conditions for maximum ethylene production by applying response surface methodology (RSM) in evaluating the catalytic performances of Li/MgO catalysts for the OCM reaction. RSM is a collection of mathematical and statistical techniques for empirical model building. By careful design of experiments, the objective is to optimize a response (output variable) which is influenced by several independent variables (input variables). The operating temperature, inlet O_2 concentration and F/W are the three variables pertaining to operating conditions. The estimated mathematical model was examined with the analysis of variance (ANOVA) at 5% level of significance. The results from the optimum exercise will be useful for studying the two-step methane conversion process in our future work.

2. Experimental

2.1. Catalyst preparation

The lithium promoted magnesium oxide (MgO supplied by GCE with purity >98%) catalyst was prepared by the wet impregnation method (Li/MgO, with Li/Mg weight ratio = 0.1). The aqueous solution was prepared by dissolving the desired amount of lithium nitrate ($LiNO_3$, supplied by Merck with purity 99.995%) in distilled water. MgO was added slowly into the solution under constant stirring. The paste formed was dried overnight in the oven at 110 °C. The dried material was then crushed into powder and calcined in a furnace at 750 °C for 6 h.

2.2. Catalytic performance tests

The OCM catalytic reaction was performed in a continuous flow quartz reactor (i.d. 9 mm). The catalysts were preheated in situ in a flow of nitrogen at the reaction temperature for an hour. Activity testing was conducted in the following range: operating temperature = 737–913 °C, F/W = 7309–35,720 ml/g h, and inlet O_2 concentration = 6–24 vol.%. The feed was a mixture of pure methane and oxygen. The reactions were performed for 4 h and 0.2–0.3 g of catalyst was used for each test. The reactor effluent gases were analyzed by an on-line Hewlett Packard Agilent 6890N gas chromatograph equipped with TCD and four series columns (UCW 982, DC 200, Porapak Q and Molecular Sieve 13A).

3. Results and discussion

3.1. Influence of process variables

The catalytic activity of Li/MgO catalyst was optimized based on the “one-variable-at-a-time” approach. The maximum ethylene yield is 7.86% at operating temperature = 850 °C, F/W = 21,915 ml/g h and inlet O_2 concentration = 14.29% ($CH_4/O_2 = 7$). The “one-variable-at-a-time” technique of optimization has some major flaws because the experimental space is not explored very well and the solution may be missed if there are interactions among the variables [18]. However, the experimental data provided some interesting information about the influence of each process variables, as described in the following section.

3.1.1. Effect of operating temperature

Fig. 1(a) shows the variations of methane conversion and the product yields at different operating temperature, while the other variables remained constant. Initially, the methane conversion, ethylene yield and C_{3+} hydrocarbons (propane, propylene, butane and butylenes) yield increased with operating temperature, but the products decreased as the temperature exceeded 850 °C. In contrast, both the CO_2 yield and CO yield increased whilst ethane yield decreased with operating temperature.

On the other hand, Galuszka [19] reported that a substantial amount of available lithium was converted to a less active and stable carbonate ($LiOCO_2$ and/or $Mg(Li)O_2CO$) which could not be decomposed easily even at 800 °C during OCM. Therefore, low OCM activity at operating temperature lower than 800 °C can be attributed to the carbonate. However, at operating temperature higher than 800 °C, these carbonates most likely decomposed and the active centers of Li/MgO were recovered. The increment in the methane conversion and hydrocarbons yield are evidence that the catalytic activity improved, but the effect is only temporarily as the conversion and yield started to decline again at 900 °C. For example, methane conversion and ethylene yield decreased from 14.6 and 6.3%, respectively, at

850 °C to 11.1 and 4.1%, respectively, at 900 °C. The decline in the catalytic activity at a temperature higher than 900 °C imply that the optimum operating temperature of Li/MgO catalyst for OCM reaction should be in the range of 800–900 °C.

It should also be noted that the conversion of O_2 was not 100% all the time in this study. The increment of CO_x products indicated that hydrocarbons oxidation activity over Li/MgO catalyst is favored at high temperature. As a result, the hydrocarbons selectivity reduced with temperature, as shown in Fig. 1(b). The increase in the C_2H_4/C_2H_6 ratio with temperature, suggests that the dehydrogenation of ethane to ethylene is favored at higher temperature. The trend may be attributed to the increase in the rate of the thermal and gas phase oxidative dehydrogenation of ethane to ethylene at higher temperature [13].

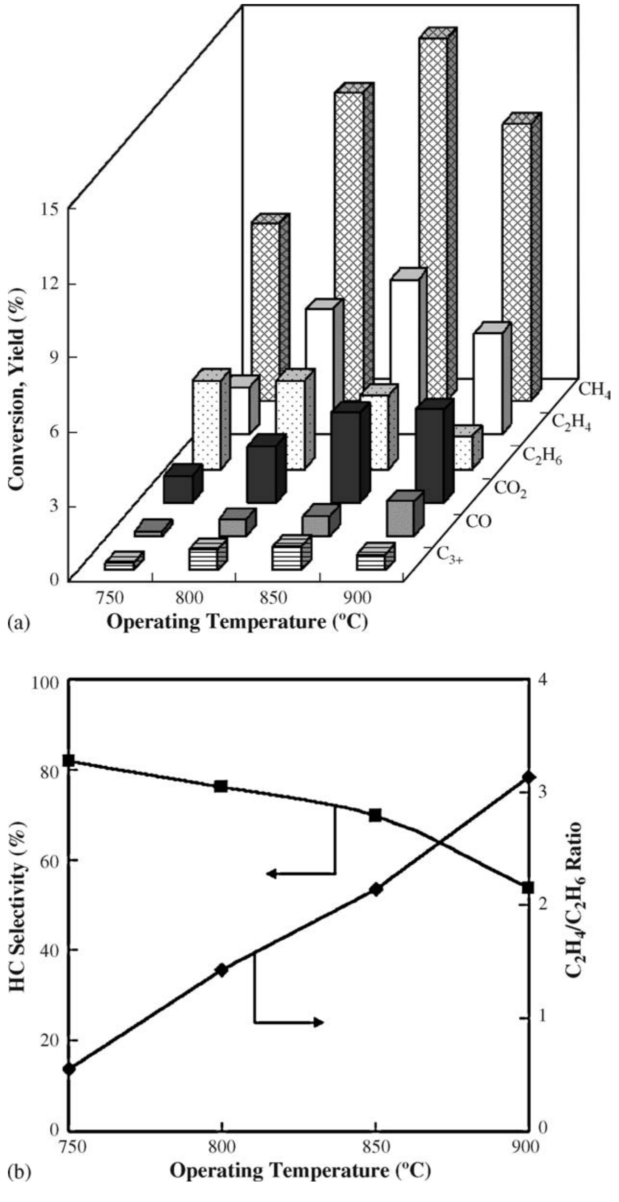

Fig. 1. Effect of operating temperature on (a) methane conversion and products yield; (b) hydrocarbons selectivity and C_2H_4/C_2H_6 ratio. F/W = 7305 ml/g h, inlet O_2 concentration = 11.1%.

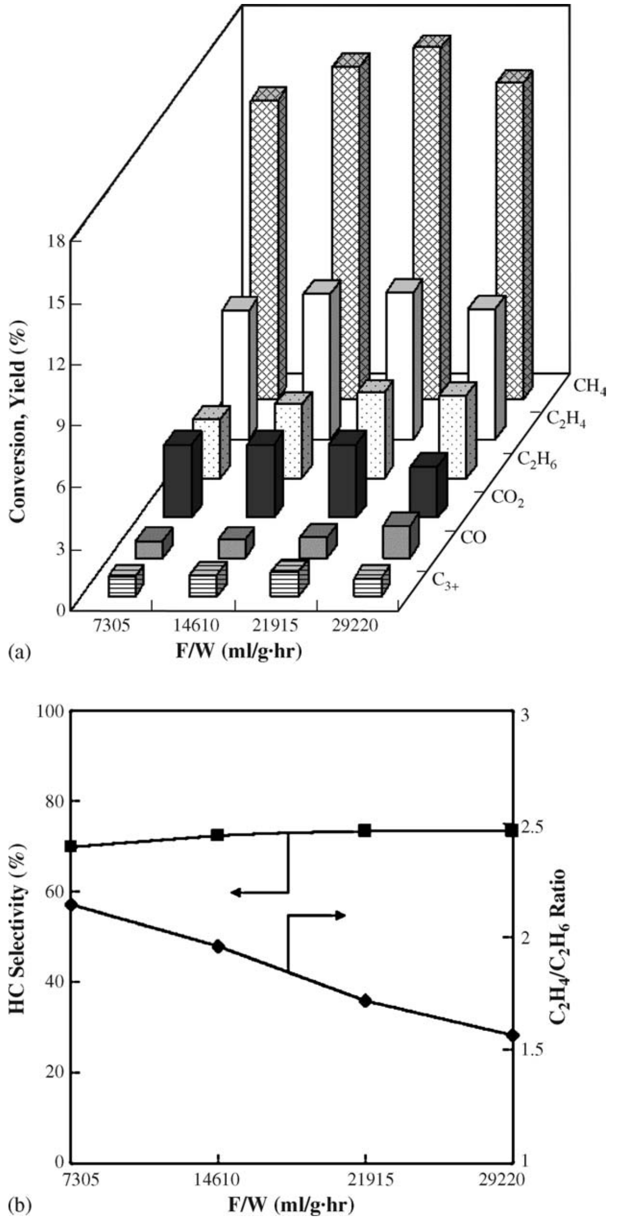

Fig. 2. Effect of F/W on (a) CH_4 conversion and products yield; (b) hydrocarbons selectivity and C_2H_4/C_2H_6 ratio. Operating temperature = 850 °C, inlet O_2 concentration = 11.1%.

3.1.2. Effect of F/W

The effect of F/W on the methane conversion and product yields at constant operating temperature and inlet oxygen concentration is demonstrated in Fig. 2(a). As can be seen, the effect of F/W on the catalytic activity is not very significant even over the broad range of F/W between 7305 and 29,220 ml/g h. At F/W = 21,915 ml/g h, the methane conversion, C_2H_4, C_2H_6 and C_{3+} yields improved initially, reaching maximum values of 17.2, 7.2, 4.2 and 1.2, respectively. However, the values dropped to 15.4, 6.4, 4.1 and 0.9%, respectively. At the same time, the CO_x yield was kept almost constant at lower F/W, but the CO_2 yield decreased and CO yield increased when the F/W exceeded 21,915 ml/g h.

The effect of F/W on the catalytic activity is quite complex. Nevertheless, it can be clearly seen that a suitable F/W is desired to create sufficient residence time for the $CH_3^\bullet$ formation and sweep the radicals away out of the reaction zone, allowing them to couple in gas phase [4]. In addition, the increment of CO yield and decrement of CO_2 yield at low contact time with the catalyst (i.e. high F/W) implied that ethane and ethylene were oxidized to form CO first, and then further oxidized to CO_2, which is consistent with the reaction network proposed by Mallens et al. [2].

As shown in Fig. 2(b), no effect of F/W on hydrocarbons selectivity was observed. However, the C_2H_4/C_2H_6 ratio increased with a decrease of F/W. The result is in agreement with the previous studies on supported MgO catalysts [13,20] suggesting that ethylene is formed in a consecutive reaction: $CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4$.

3.1.3. Effect of inlet O_2 concentration

The CH_4 conversion and C_2H_4/C_2H_6 ratio increased but the hydrocarbons selectivity decreased with an increase in the inlet O_2 concentration, as shown in Fig. 3(a) and (b). The trend observed is similar to earlier studies on OCM over alkali metal promoted MgO [13], rare earth promoted MgO [20] and other catalysts [21].

The increase of C_2H_4 yield (up to 14.3 vol.% of O_2 concentration) and C_2H_4/C_2H_6 appear to be a consequence of increasing availability of O_2 necessary for the following reactions [12]:

$$O_2 + 2^* \leftrightarrows 2O^* \quad (1)$$

$$CH_4 + O^* \leftrightarrows CH_3^\bullet + OH^* \quad (2)$$

$$CH_3^\bullet + CH_3^\bullet \leftrightarrows C_2H_6 \quad (3)$$

$$C_2H_6 + O^* \leftrightarrows C_2H_5^\bullet + OH^* \quad (4)$$

$$C_2H_5^\bullet + O^* \leftrightarrows C_2H_4 + OH^* \quad (5)$$

where * indicates the active sites on the catalyst surface.

However, the oxidation of methane, ethylene and other intermediate products were intensely induced at higher oxygen concentration. From Fig. 3(b), it can be clearly seen that the hydrocarbons selectivity shows a sharp diminution as the inlet oxygen concentration increased. As expected, both the CO and CO_2 yield increased significantly at the same condition, thus, reducing the hydrocarbon selectivity.

3.2. Process variable study using central composite design

Optimization of process condition using statistical approach involved three major steps: selection of design of experiment, estimation of coefficient based on mathematical model and response prediction, and finally confirmation of model adequacy check. Table 1 presents the independent variables with the operating range of each variable.

Box–Wilson central composite design with three process variables was chosen to obtain optimum process condition for ethylene production. According to the CCD, the total number of experiments conducted is 16 with 2^3 two-level factorial design, two central points and six star points. Each variable consists of three different levels from low (−1), to medium (0) and to high (1). Table 2 shows the experimental design and the results of the three observed responses.

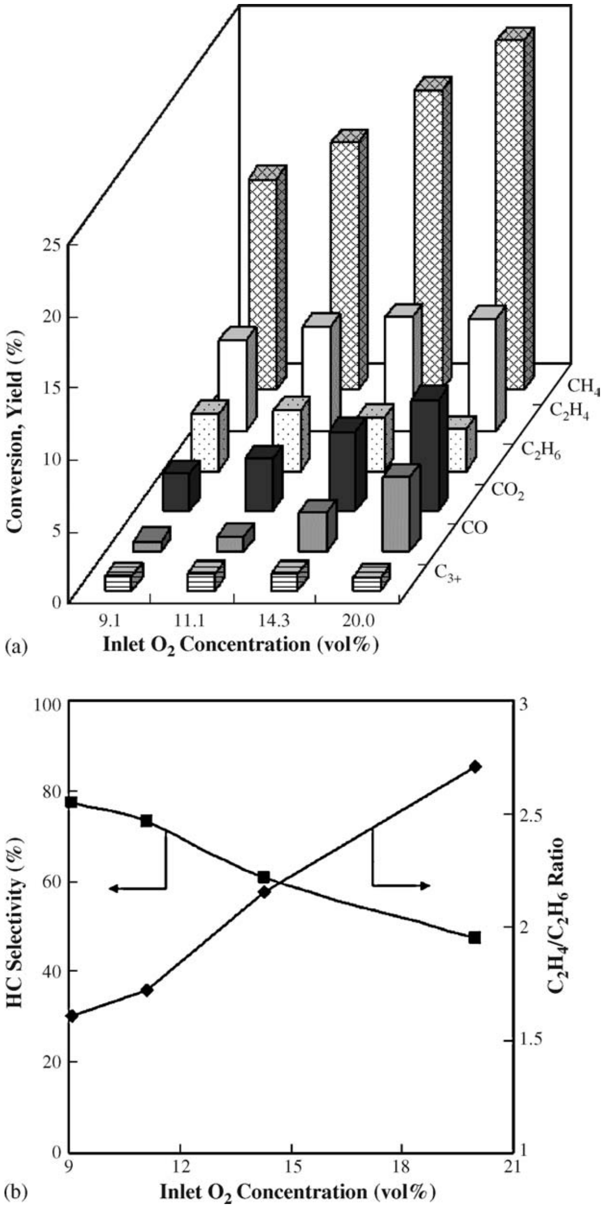

Fig. 3. Effect of inlet O_2 concentration on (a) methane conversion and products yield; (b) hydrocarbons selectivity and C_2H_4/C_2H_6 ratio. F/W = 21,915 ml/g h, operating temperature = 850 °C.

Table 1
Independent variables and their coded and actual values used for optimization

Independent variable	Symbol	Coded levels		
		−1	0	+1
Operating temperature (°C)	X_1	775	825	875
Inlet O_2 concentration (vol.%)	X_2	10	15	20
F/W (ml/g h)	X_3	15000	22500	30000

Table 2
Central composite design and experimental results

Run[a]	Manipulated variables						Responses		
	X_1		X_2		X_3		C_2H_4 yield (%)	C_2H_4 selectivity (%)	CH_4 conversion (%)
	Operating temperature (°C)	Level[b]	Inlet O_2 concentration (vol.%)	Level[b]	F/W (ml/g h)	Level[b]			
O1	775	−1	10	−1	15000	−1	4.6	35.8	12.9
O2	775	−1	10	−1	30000	+1	3.7	33.7	10.9
O3	775	−1	20	+1	15000	−1	6.5	35.5	18.3
O4	775	−1	20	+1	30000	+1	7.0	36.4	19.1
O5	875	+1	10	−1	15000	−1	5.7	39.1	14.6
O6	875	+1	10	−1	30000	+1	6.1	41.7	14.6
O7	875	+1	20	+1	15000	−1	7.0	25.5	27.3
O8	875	+1	20	+1	30000	+1	6.9	28.0	24.7
S1	737	$-\alpha$	15	0	22500	0	0.7	14.6	5.1
S2	913	$+\alpha$	15	0	22500	0	6.8	31.3	21.6
S3	825	0	6	$-\alpha$	22500	0	4.2	39.4	10.7
S4	825	0	24	$+\alpha$	22500	0	7.6	27.9	27.1
S5	825	0	15	0	9280	$-\alpha$	7.9	38.0	20.7
S6	825	0	15	0	35720	$+\alpha$	6.5	38.5	16.8
C1	825	0	15	0	22500	0	7.6	37.4	20.3
C2	825	0	15	0	22500	0	7.6	37.5	20.2

[a] O = orthogonal design points, C = center points, S = star or axial points.

[b] −1 = low value, 0 = center value, +1 = high value, +/−α = star point value.

The full quadratic models were established by using the method of least squares:

$$Y_u = \beta_o + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \qquad (6)$$

with Y_u being the predicted response u whilst X_1, X_2 and X_3 are the coded forms of input variables for operating temperature, inlet O_2 concentration and F/W, respectively. The term β_o is the offset term, β_1, β_2 and β_3 the linear terms, β_{11}, β_{22} and β_{33} the squared terms, and β_{12}, β_{13} and β_{23} the interaction terms. The equation model was tested with the ANOVA analysis with 5% level of significance.

The analysis of variance (ANOVA) is used for checking the significance of the second-order models. The statistical significance of the second-order model equation is determined by F-value. In general, the calculated F-value should be greater than the tabulated F-value, if the model is good predictor of the experimental results [22]. The F-value is a measurement of variance of data about the mean, based on the ratio of mean square of group variance due to error [23]. The calculated F-value is defined as $MS_{regression}/MS_{residual}$, where $MS_{regression}$ and $MS_{residual}$ are obtained by dividing SSR/DF and SSE/DF, respectively. $F_{(p-1,N-p,\alpha)}$ is the tabulated of the F distribution based on the value of $p-1$ and $N-p$ which are DF for regression and for residual, respectively, at a specified level of significance, α-value.

3.2.1. Methane conversion

The quadratic model for the methane conversion is presented in Eq. (7) as

$$C_{C1} = -583.16 + 1.4114 X_1 - 2.5590 X_2 - (8.4978 \times 10^{-4}) X_1^2 \qquad (7)$$

where C_{C1} is the predicted percentage of methane conversion. Fig. 4 compares the observed experimental methane conversion with the predicted methane conversion obtained from Eq. (7). A practical rule of thumb for evaluating the determinant coefficient, R^2 is that it should be at least 0.75 or greater [18]. The value for R^2 for the predicted methane conversion model is 0.95821, indicating that the empirical model is adequate to explain most of the variability in the assay reading.

The F-value is a measurement of variance of data about the mean, based on the ratio of mean square of group variance due to error [23]. In general, if the model is a good prediction of

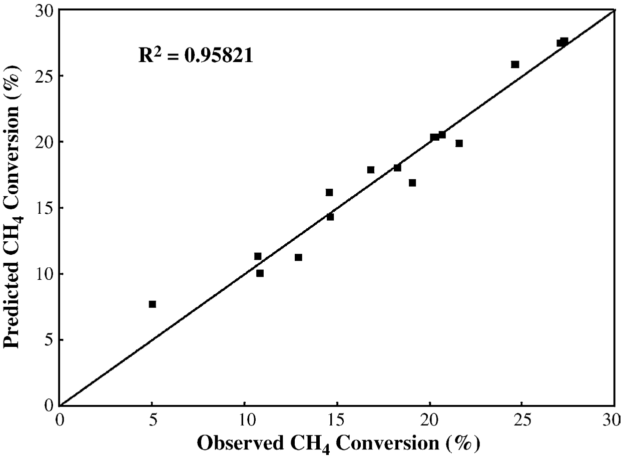

Fig. 4. Parity plot for the observed and the predicted CH_4 conversion.

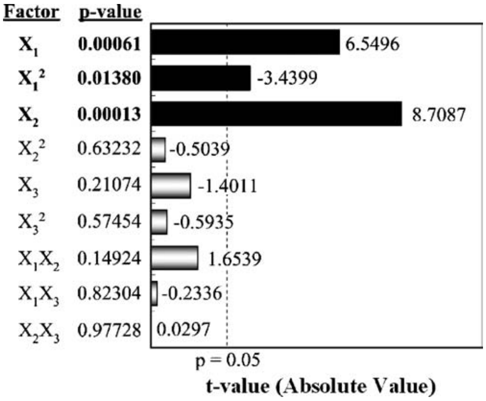

Fig. 5. Pareto chart and *p*-values of CH_4 conversion.

the experimental results and the estimated factor effects are real, the calculated *F*-value should be several times larger than the tabulated value. In this study, the computed *F*-value for methane conversion model is larger than the tabulated *F*-value ($F_{0.05} = 3.37$) at $\alpha = 0.05$ in the statistic table. It can be concluded that Eq. (7) gives good prediction of the methane conversion and the model was significant at a high confidence level.

Fig. 5 shows the Student's *t*-distribution values in a Pareto chart and the corresponding *p*-values of the variables in Eq. (7). The *p*-value serves as a tool to check the significance of each coefficient. The smaller the *p*-value or the greater the magnitude of *t*-value the more significant is the corresponding coefficient. Generally, we specify a 5% level of significance. As illustrated, X_2, the inlet O_2 concentration (linear) has the largest effect on methane conversion, having a *p*-value of 0.00013. X_1, operating temperature (linear) and X_1^2, operating temperature (quadratic) could also be regarded as significant factors in affecting the methane conversion. The rest of the variables could be considered less significant to affect the methane conversion as their *p*-values are greater than 0.05.

3.2.2. *C_2H_4 yield*

An empirical relationship between ethylene yield and the test variable in coded unit is given in Eq. (8):

$$Y_{C2=} = -355.66 + (8.2799 \times 10^{-1})X_1 + 1.9735X_2 - (4.7944 \times 10^{-4})X_1^2 \quad (8)$$

where $Y_{C2=}$ is the predicted percentage of C_2H_4 yield.

The parity plot for the observed and predicted C_2H_4 yield is shown in Fig. 6. The R^2 of 0.87842 implies that most of the variation is fitted to the model. The *F*-value of 4.81 in Table 3 further confirms the accuracy at 5% level of significance. The significance of each coefficient is shown in Fig. 7. It can be seen that the variable with the largest effect was the linear term of operating temperature, X_1, followed by the quadratic term of operating temperature, X_1^2, and the linear term of inlet O_2 concentration, X_2.

The effects of operating temperature, inlet O_2 concentration, and F/W on ethylene yield are depicted in the three-dimensional contour plots in Figs. 8–10. It is interesting to note that the optimum points can be found within the experimental region in Figs. 8–10. For that reason, one can conclude that all experiments were conducted in the optimal region, and the optimum C_2H_4 yield should not lie beyond the experimental range considered in the present studies.

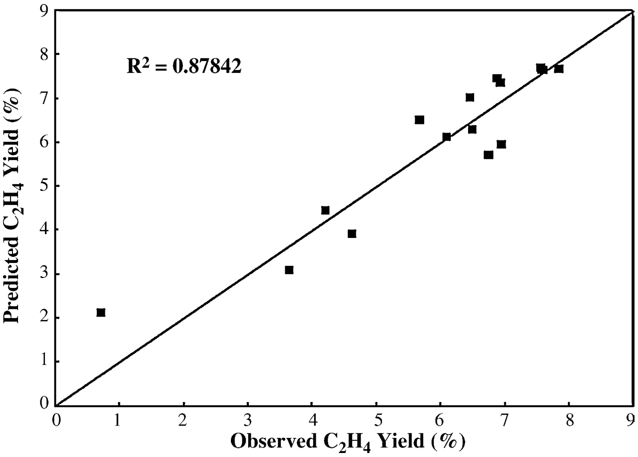

Fig. 6. Parity plot for the observed and the predicted C_2H_4 yield.

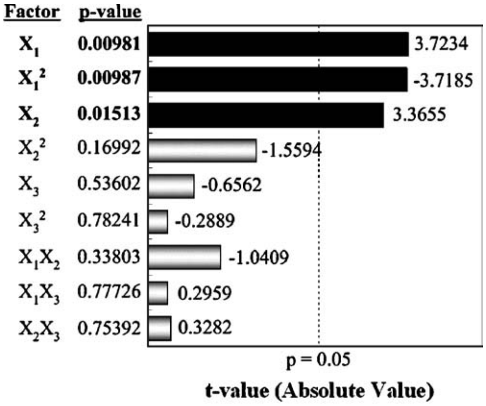

Fig. 7. Pareto chart and *p*-values of the C_2H_4 yield.

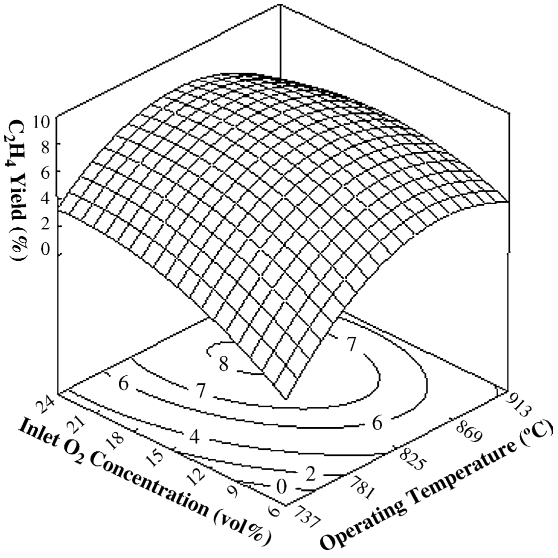

Fig. 8. The response surface plot of C_2H_4 yield as the function of operating temperature and inlet O_2 concentration at F/W = 22,500 ml/g h.

Table 3
ANOVA for CH_4 conversion, C_2H_4 yield and C_2H_4 selectivity models

Sources	Sum of squares (SS)	Degrees of freedom (d.f.)	Mean square (MS)	F-value	$F_{0.05}$
CH_4 conversion model					
Regression (SSR)	521.92	3	173.97	47.42	>3.37
Error (SSE)	44.03	12	3.67		
Total (SST)	565.95	15			
C_2H_4 yield model					
Regression (SSR)	42.52	3	14.17	14.94	>3.37
Error (SSE)	11.39	12	0.95		
Total (SST)	53.91	15			
C_2H_4 selectivity model					
Regression (SSR)	402.51	2	201.26	8.40	>3.37
Error (SSE)	311.60	13	23.97		
Total (SST)	714.11	15			

3.2.3. C_2H_4 selectivity

The quadratic model for the C_2H_4 selectivity in terms of coded factors is presented in Eq. (9):

$$S_{C2=} = -1278.6 + 3.0113X_1 + 12.295X_2 \qquad (9)$$

where $S_{C2=}$ is the predicted percentage of C_2H_4 selectivity.

The determinant of coefficient $R^2 = 0.8$ (Fig. 11) indicates that this model is sufficient to explain most of the variation. From the ANOVA analysis in Table 3, the computed F-value of 8.40 for ethylene selectivity model is larger than the tabulated F-value of 3.37, presenting that this model is significant at the chosen level of significance. In Fig. 12, only operating temperature (quadratic), X_1^2, and inlet O_2 concentration (linear), X_2 were indicated as significant model term for ethylene selectivity with the p-values of 0.03001 and 0.04806, respectively.

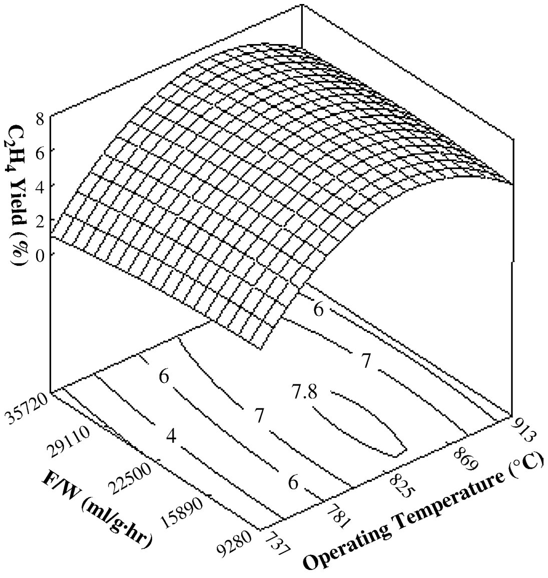

Fig. 9. The response surface plot of C_2H_4 yield as the function of operating temperature and F/W at inlet O_2 concentration = 15 vol.%.

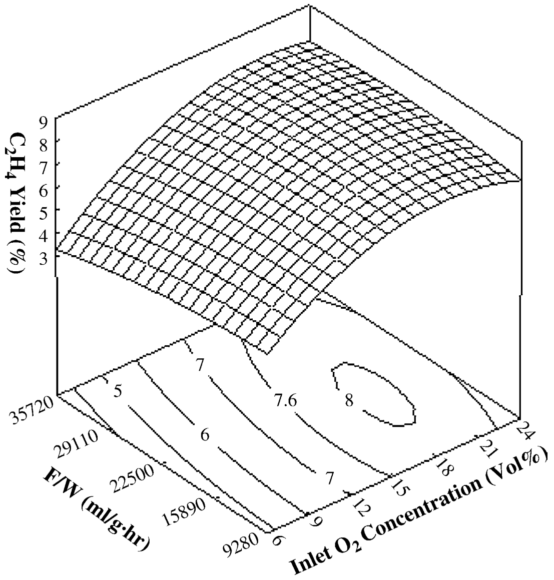

Fig. 10. The response surface plot of C_2H_4 yield as the function of inlet O_2 concentration and F/W at operating temperature = 825 °C.

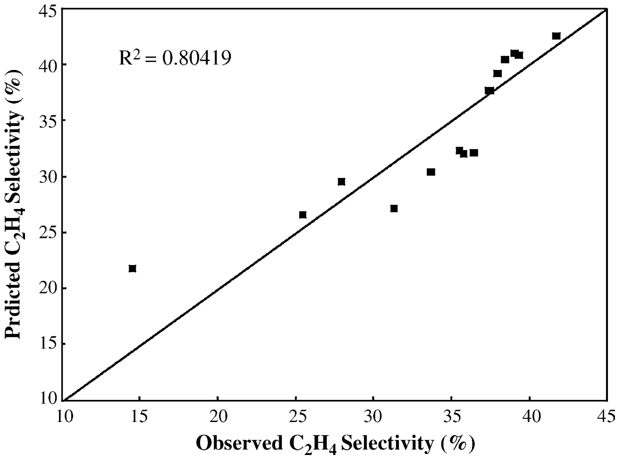

Fig. 11. Parity plot for the observed and the predicted C_2H_4 selectivity.

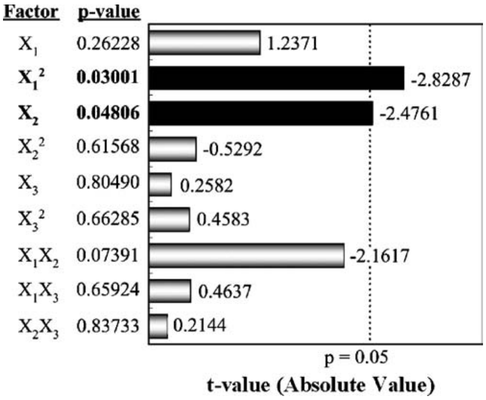

Fig. 12. Pareto chart and *p*-values of C_2H_4 selectivity.

3.3. *Optimization of C_2H_4 yield using response surface methodology*

In this paper only the ethylene yield is optimized since the value for the yield is the product of the ethylene selectivity and methane conversion. The response surface analysis using Statistica 6.0 software indicated that the predicted maximum ethylene yield is 8.14% at operating temperature = 839.51 °C, inlet O_2 concentration = 18.89% and F/W = 20264.34 ml/g h. Additional experiment was carried out to validate the optimization result obtained by the response surface analysis.

The comparison between the experimental and predicted ethylene yield at optimum condition is shown in Table 4. The ethylene selectivity and the methane conversion at the same condition are also predicted and compared with the observed value and are included in the same table. The experimental values are reported as 8.32, 34.91 and 23.83% for the C_2H_4 yield, selectivity, and CH_4 conversion, respectively. At this condition, no residue O_2 was detected, indicating that O_2 conversion was 100%. C_2H_4/C_2H_6 achieved was as high as 3.04 and the overall C_{2+} yield (including ≈ 1% C_3 and C_4 hydrocarbons yield) of 12.07% could be achieved.

Meanwhile, the differences between the predicted and observed values are 2.21, 3.62 and 4.72% for C_2H_4 yield, C_2H_4 selectivity and CH_4 conversion, respectively. The errors can be considered small as the observed values are within the 5% level of significance. The standard deviation obtained from the ANOVA table is used to derive the confidence intervals. In addition, the optimization of C_2H_4 yield with RSM (8.32%) was more efficient than the "one-variable-at-a-time" approach (7.86%) indicating that the statistical model is useful in the accurate prediction and optimization of the process.

Table 4
Comparison between predicted and observed responses at the optimum condition obtained from RSM

	Predicted value (%)	Observed value (%)	Error (%)
C_2H_4 yield	8.14	8.32	2.21
C_2H_4 selectivity	33.69	34.91	3.62
CH_4 conversion	25.01	23.83	4.72

4. Conclusion

The central composite design and the response surface method were effective to determine the optimum C_2H_4 yield for OCM over Li/MgO (Li/Mg = 0.1). The second-order polynomial equation models were derived to estimate the values of C_2H_4 yield, C_2H_4 selectivity and CH_4 conversion based on the experimental data. The adequacies of these models were evaluated via the analysis of variance (ANOVA) and the results showed that these models gave good estimation of the methane conversion, ethylene yield and ethylene selectivity. Operating temperature and inlet O_2 concentration affected the catalytic activities more significantly than F/W. The optimum conditions were estimated to be 839.51 °C for the operating temperature, 18.89 vol.% for the inlet O_2 concentration and 20264.34 ml/g h for the F/W with maximum ethylene yield being 8.14%. The reliability of the optimization results is confirmed by means of additional experiments.

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