

[ENE06] Optimization of ethylene yield in oxidative coupling of methane over Li/MgO catalyst

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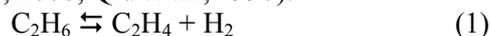
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Introduction

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 direct transformation of methane to more valuable products has attracted many research efforts in order to provide alternative routes over the traditional syngas-based processes. Among the numerous attempts for direct conversion, the oxidative coupling of methane (OCM) to C₂ hydrocarbons still remains one of the potential routes.

In the OCM reaction, the selectivity to ethane is usually higher than ethylene, but ethylene is more reactive and is also an important feed stock to the chemical industry. One possible method to improve the ethylene yield is by recirculating unreacted methane after a selective adsorptive separation (Machocki, 1996). 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 (Pak *et al.*, 2000; Qiu *et al.*, 1997). However, ethane still remains in the recycle stream along with unreacted methane and an additional step to dehydrogenate ethane is needed.

Previous studies showed that the dehydrogenation of ethane to ethylene can be carried out thermally without catalyst (Pak *et al.*, 2000; Qiu *et al.*, 1997):



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 (Kiyoharu *et al.*, 2001) i.e. 50–100°C higher than the optimal operating temperature for C₂₊ 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 (Choudhary *et al.*, 1997; Hoogendam *et al.*, 1994; Ito and Lunsford, 1985; Karasuda and Aika, 1997; Lunsford *et al.*, 1994; Lunsford, 1999; Mallens *et al.*, 1996; Marco *et al.*, 1997; Nibbelke *et al.*, 1995;) 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 C₂ yield beyond 25% and a selectivity of C₂ higher than 80% in a single-pass mode (Lunsford, 2000).

As mentioned earlier, the OCM process can be modified by adding a second reactor in order to obtain a high C₂₊ yield. In this paper, catalytic performances of Li/MgO catalysts for the OCM reaction are studied and central composite design (CCD) is used to predict the optimum conditions for maximum ethylene production by applying response surface methodology (RSM). The operating temperature, inlet O₂ 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 95% confidence level. The results from the optimum exercise will be useful for studying the two-step methane conversion process in our future work.

Experimental

Catalyst Preparation

The lithium promoted magnesium oxide catalyst (Li/MgO, with Li/Mg weight ratio = 0.1) was prepared by the wet impregnation method. Magnesium oxide (supplied by GCE with purity >98%) was used as catalyst support. The aqueous solution was prepared by dissolving a proper amount of lithium nitrate (LiNO₃, 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 for six hours at 750°C.

Catalytic Performance Tests

The OCM catalytic reaction was carried out 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 carried out in the following range: operating temperature = 737-913°C, F/W = 7309-35720 ml/g-hr, and inlet O₂ concentration = 6-24 vol%. The feed was a mixture of pure methane and oxygen. The reactions were performed for four hours 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).

Results and Discussion

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.

Accordingly, Box-Wilson central composite experimental design was chosen to optimize the ethylene yield. Along with central composite design, the total number of experiment is $2^k + 2k + n_0$, where k is the number of independent variables and n_0 is the number of experiments repeated at the center point. In this case, $n_0 = 2$ and $k = 3$, and as a result, a total of 16 runs were needed.

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

$$Y_u = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$

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 O₂ concentration and F/W, respectively. The term β_0 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 95% degree of confidence. The experimental design and ANOVA analysis was obtained from the "Statistica" software version 6.0 and the experimental results are shown in Table 1.

TABLE 1 Central composite design and experimental results.

Run ^a	X ₁		X ₂		X ₃		C ₂ H ₄ Yield (%)
	Temp. (°C)	Level ^b	O ₂ conc. (vol%)	Level ^b	F/W (ml/g-hr)	Level ^b	
O1	775	-1	10	-1	15000	-1	4.6
O2	775	-1	10	-1	30000	+1	3.7
O3	775	-1	20	+1	15000	-1	6.5
O4	775	-1	20	+1	30000	+1	7.0
O5	875	+1	10	-1	15000	-1	5.7
O6	875	+1	10	-1	30000	+1	6.1
O7	875	+1	20	+1	15000	-1	7.0
O8	875	+1	20	+1	30000	+1	6.9
S1	737	-α	15	0	22500	0	0.7
S2	913	+α	15	0	22500	0	6.8
S3	825	0	6	-α	22500	0	4.2
S4	825	0	24	+α	22500	0	7.6
S5	825	0	15	0	9280	-α	7.9
S6	825	0	15	0	35720	+α	6.5
C1	825	0	15	0	22500	0	7.6
C2	825	0	15	0	22500	0	7.6

^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

ANOVA

An empirical relationship between ethylene yield and the test variable in coded unit is given in equation (3):

$$Y_{C_2H_4} = -355.66 + (8.2799 \times 10^{-1})X_1 + 1.9735X_2 - (2.3681 \times 10^{-4})X_3 - (4.7944 \times 10^{-4})X_1^2 - (2.0014 \times 10^{-2})X_2^2 - (1.6507 \times 10^{-9})X_3^2 - (1.5275 \times 10^{-3})X_1X_2 + (2.8952 \times 10^{-7})X_1X_3 + (3.2107 \times 10^{-6})X_2X_3 \quad (3)$$

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

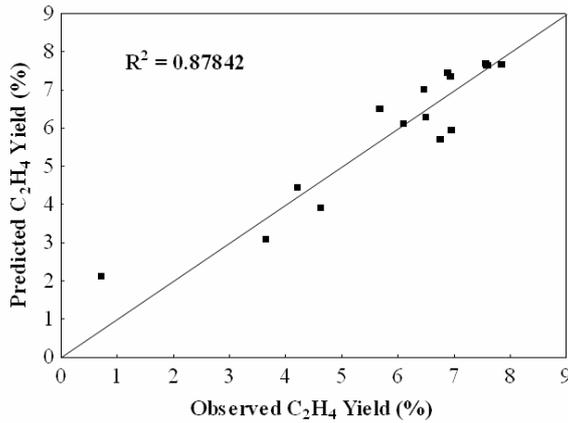


FIGURE 1 Parity plot for the observed and the predicted C_2H_4 yield

The parity plot for the observed and predicted C_2H_4 yield is shown in Fig. 1. The R^2 is bigger than 0.75, implies that most of the variation is fitted to the model (Haaland, 1989). The ANOVA for the response is shown in Table 2. The F-value of 4.81 (>3.37) in the table further confirms the accuracy of the model under 95% level of confidence. The significance of each coefficient is shown in Fig. 2. The p-value serves as a tool to check the significance of each coefficient. 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 .

TABLE 2 ANOVA for C_2H_4 yield.

Sources	Regression	Error	Total
Sum of Squares	46.60	6.46	53.06
Degree of Freedom	9	6	15
Mean Squares	5.18	1.08	
F value	4.81		
Tabulated $F_{0.05}$	3.37 (Lee, 1997)		

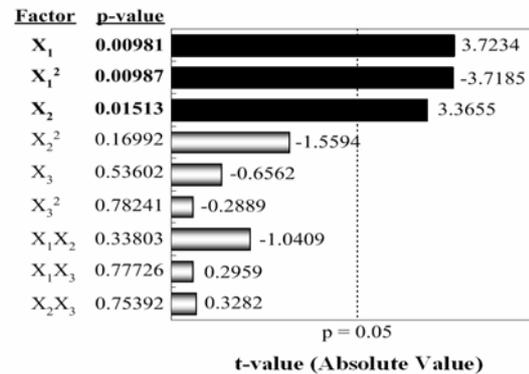


FIGURE 2 Pareto chart and p-values of the C_2H_4 yield

The ethylene yield model is shown graphically in Figs 3. It is interesting to note that the optimum points could be found within the experimental region in Figs 3. Thus, 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 study.

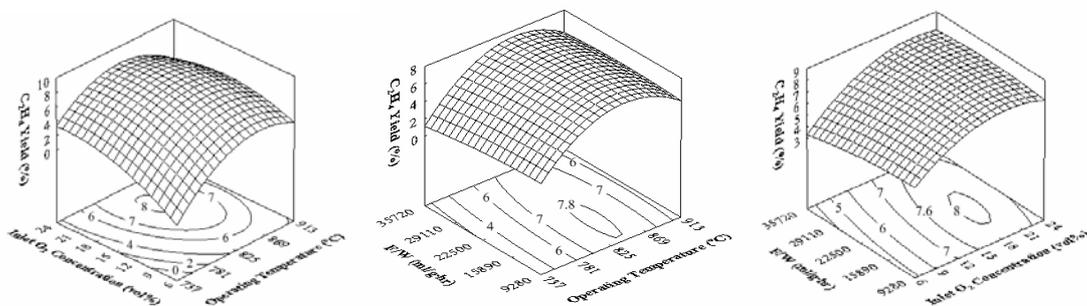


FIGURE 3 The response surface plot of C_2H_4 yield as the function of operating temperature, inlet O_2 concentration and F/W

Optimization of C₂H₄ Yield using Response Surface Methodology

The response surface analysis by using Statistica 6.0 software indicated that the predicted maximum ethylene yield is 8.14% at operating temperature = 839.51°C, inlet O₂ concentration = 18.89% and F/W = 20,264.34ml/g·hr. 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 Table 3. The ethylene selectivity and the methane conversion at the same condition were also predicted and compared to the observed value and include in the same table. As illustrated, the experimental values are 8.32%, 34.91% and 23.83% for the C₂H₄ yield and selectivity, and CH₄ conversion respectively. At this condition, no residue O₂ was detected, indicating that O₂ conversion was 100%. C₂H₄/C₂H₆ achieved was as high as 3.04 and the overall C₂₊ yield (including ≈ 1% C₃ and C₄ hydrocarbons yield) of 12.07% could be achieved.

TABLE 3 Comparison between predicted and observed responses at the optimum condition obtained from RSM.

Catalytic Activities	Predicted (%)	Observed (%)	Error (%)
C₂H₄ yield	8.14	8.32	2.21
C₂H₄ sel.	33.69	34.91	3.62
CH₄ conv.	25.01	23.83	4.72

Meanwhile the differences between the predicted and observed results are 2.21%, 3.62% and 4.72% for C₂H₄ yield, C₂H₄ selectivity and CH₄ conversion respectively. The errors can be considered small as the observed value are within the 95% confidence intervals. The confidence intervals were calculated based on the ANOVA error term of each equation. This observation clearly indicates that the statistical model is useful in the accurate prediction and optimization of the process.

Conclusion

The Central Composite Design and the response surface method were effective to determine the optimum C₂H₄ yield for OCM over Li/MgO (Li/Mg = 0.1). The second order polynomial equation models were derived to

estimate the values of C₂H₄ yield, C₂H₄ selectivity and CH₄ 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 have good estimation of the methane conversion and ethylene yield, but less significant for ethylene selectivity. Operating temperature and inlet O₂ concentration were to affect 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 O₂ concentration and 20,264.34ml/g·hr for the F/W with maximum ethylene yield being 8.14%. The reliability of the optimization results is confirmed by mean of additional experiments.

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References

- Choudhary, V.R., Rane, V.H., Pandit, M.Y. (1997). Comparison of Alkali Metal Promoted MgO Catalysts for Their Surface Acidity/Basicity and Catalytic Activity/Selectivity in the Oxidative Coupling of Methane. *Journal of Chemistry Technology and Biotechnology* 68: 177-186.
- Haaland, P.D. (1989). *Experimental Design in Biotechnology*, New York and Basel: Marcel Dekker Inc.
- Hoogendam, G.C., Seshan, K., van Ommen, J. G., Ross, J. R. H. (1994). Oxidative coupling of methane over doped Li/MgO catalyst. *Catalysis Today* 21: 333-340.
- Ito, T., Lunsford, J.H. (1985). Oxidative Dimerization of Methane Over a Lithium-promoted Magnesium Oxide Catalyst. *Journal of American Chemical Society* 107: 5062-5068.
- Karasuda, T., Aika K. (1997). Isotopic Oxygen Exchange between Dioxygen and

- MgO Catalysts for Oxidative Coupling of Methane. *Journal of Catalysis* 171: 439-448.
- Kiyoharu N., Chiaki K., Kimito O., Na-oki I., Mikka N., Toshihiro A., Tetsuhiko K., Toshimitsu S. (2001). Role of Carbon Dioxide in the Dehydrogenation of Ethane over Gallium-Loaded Catalysts. *Journal of Catalysis* 203: 87-93.
- Lee, M.H. (1997). *Jadual Statistik untuk Kejuruteraan dan Sains*, Skudai: Universiti Teknologi Malaysia.
- Lunsford J. H., Hinson, P.G., Rosynek, M.P., Shi, C.L., Xu, M.T., Yang, X.M. (1994). The Effect of Chloride Ions on a Li⁺-MgO Catalyst for the Oxidative Coupling of Methane. *Journal of Catalysis* 147: 301-310.
- Lunsford, J.H. (1999). Oxidative Coupling of Methane and Related Reactions, in: Jansen, F.J.J.G., and van Santen R.A. (Eds.), *Environmental Catalyst*, London: Imperial College Press, pp 87-102.
- Lunsford, J.H. (2000). Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catalysis Today* 67: 165-174.
- Machocki, A. (1996). Methane oxidative coupling in an undiluted reaction mixture in a reactor-adsorber system with gas recirculation. *Applied Catalysis A: General* 146: 391-400.
- Mallens, E.P.J., Hoebink, J. H. B. J., Marin, G. B. (1996). An Investigation of the Oxygen Pathways in the Oxidative Coupling of Methane over MgO-Based Catalysts. *Journal of Catalysis* 160: 222-234.
- Marco, E., Santos, A., Menéndez, M., Santamaría, J. (1997). Fluidization of agglomerating particles: influence of the gas temperature and composition on the fluidization of a Li/MgO catalyst. *Powder Technology* 92: 47-52.
- Nibbelke R. H., Scheerova, J., Decroon, M.H.J.K., Marin, G.B. (1995). The Oxidative Coupling of Methane over MgO-Based Catalysts: A Steady-State Isotope Transient Kinetic Analysis. *Journal of Catalysis* 156, 106-119.
- Pak, S., Rades T., Rosynek, M.P., Lunsford, J.H. (2000). Steady-state Conversion of Methane to C₄₊ Aliphatic Products in High Yields Using an Intergrated Recycle Reactor System. *Catalysis Letters* 66, 1-4.
- Qiu, P., Lunsford, J.H., Rosynek, M.P. (1997). Steady-state Conversion of Methane to Aromatics in High Yields Using an Integrated Recycle Reaction System. *Catalysis Letters* 48, 11-15.