

Kinetics and Optimization of Dimethyl Carbonate Synthesis by Transesterification using Design of Experiment

Kilwoo Lee and Kye Sang Yoo[†]

Department of Chemical & Biomolecular Engineering, Seoul National University of Science & Technology, 232 Gongneung-ro, Nowon-gu, Seoul, 01811, Korea

(Received 13 November 2017; Received in revised form 8 December 2017; accepted 15 December 2017)

Abstract – A comprehensive kinetic study has been conducted on dimethyl carbonate synthesis by transesterification reaction of ethylene carbonate with methanol. An alkali base metal (KOH) was used as catalyst in the synthesis of DMC, and its catalytic ability was investigated in terms of kinetics. The experiment was performed in a batch reactor at atmospheric pressure. The reaction orders, the activation energy and the rate constants were determined for both forward and backward reactions. The reaction order for forward and backward reactions was 0.87 and 2.15, and the activation energy was 12.73 and 29.28 kJ/mol, respectively. Using the general factor analysis in the design of experiments, we analyzed the main effects and interactions according to the MeOH/EC, reaction temperature and KOH concentration. DMC yield with various reaction conditions was presented for all ranges using surface and contour plot. Furthermore, the optimal conditions for DMC yield were determined using response surface method.

Key words: Dimethyl carbonate synthesis, Transesterification reaction, design of experiment, Response surface method

1. Introduction

Dimethyl carbonate (DMC) is a versatile and nontoxic chemical substance that is an important chemical material in the current chemical industry and in the motor fuel industry. It has been proposed as a methylating agent for aromatic compounds, to replace methyl halides and dimethyl sulfate, which are both toxic and corrosive, and as an intermediate in the synthesis of polycarbonates and isocyanates, thereby avoiding the need to use phosgene. DMC is also a candidate for replacing methyl tertiary butyl ether (MTBE) as an oxygen-containing additive for gasoline because it has high oxygen content, a good blending octane, low toxicity, and quick biodegradation [1].

A number of DMC synthesis processes have been suggested and some processes have already been commercialized. The classic route to DMC involves the use of phosgene. This route is disadvantaged by the safety problem of handling highly toxic phosgene and the environmental problem of disposing of sodium chloride. Overall transesterification reaction of ethylene carbonate (EC) with methanol (MeOH) can be written as follows:

There are two kinds of transesterification for DMC synthesis: heterogeneous and homogeneous. Tatsumi et al. [2] introduced a heterogeneous catalyst and suggested that a solid base catalyst was excellent for the synthesis of DMC. Watanabe et al. [3] reported that hydrotalcite-type catalysts have good catalytic ability for DMC synthesis.

Moreover, several classes of catalysts for DMC synthesis were studied through the transesterification reaction [4,5]. The homogeneous transesterification method is featured by a high reaction rate and is most likely to be commercialized. Moreover, a cheap alkali, such as KOH, can be used as homogeneous catalyst. Accordingly, a detailed study on this method is imperative for an industrially acceptable DMC synthesis process.

Besides kinetic study, the optimization of catalytic reaction process is an essential step in developing industrial chemical plant. As the synthesis process becomes more diverse and complex, the number of experiments to find optimal synthesis conditions increases exponentially. Especially, it is difficult to find an optimal synthesis condition by using trial and error method in the case of expensive raw materials or long reaction time. To overcome this problem, there is a growing interest in research using statistical experimental design methods. In general, the experimental design method is designed to obtain maximum information at a low cost in an experiment. The experiment consists of a design step, an analysis step of the experimental data, and an optimization step [6]. In the design stage of the experiment, the selection of the experiments and the randomization, which is the order of the experiment, are determined to achieve the purpose of the experiment efficiently and practically. In the analysis stage, an appropriate model for the experimental data including screening of the key factors and the interaction effects is searched. In the optimization stage, the optimum conditions of the parameters suitable for the experimental purpose are found and the reproducibility is confirmed [7].

In this work, we proposed kinetic performance of KOH catalyst and estimated the rate constants and the reaction orders in DMC syn-

[†]To whom correspondence should be addressed.

E-mail: kyoo@seoultech.ac.kr

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

thesis, for both forward and backward reactions. Moreover, the effects of reaction conditions and their interactions on the catalytic performance were studied simultaneously on the responses using design of experiments. The obtained experimental data have been used to predict the optimum values of process parameters and their interactions for optimization by statistical approach under response surface methodology (RSM).

2. Experimental

All experiments were performed in a stainless-steel autoclave (200 ml) at atmospheric pressure. For mixing in the reaction, a magnetic stirrer was used. Reaction temperature was maintained constantly with a temperature controller. Starting materials used in this work were methanol (purity $\geq 99.5\%$) produced by Daejung Chemicals & Metals Co., and ethylene carbonate ($\geq 98\%$ from Aldrich), dimethyl carbonate ($\geq 99\%$, Acros) and ethylene glycol (EG) ($\geq 99\%$, Daejung) without further purification. The molar ratio of the initial reactants for forward reaction (MeOH:EC) was in the range of 8:1-15:1, while for backward reaction the molar ratio between DMC and EG was changed from 1:10 to 10:1. Potassium hydroxide, soluble in methanol and EG, was used as catalyst for both reactions. Catalyst concentration was 0.05~0.2 wt%. The reaction temperature was varied from 30 °C to 60 °C and from 30 °C to 80 °C for forward and backward reaction, respectively. The products were analyzed by using an on-line gas chromatograph (Agilent 6890) with FID detector. Column was installed with GS-Q (Agilent, capillary 30 m \times 0.32 mm). Minitab 17 was used to perform the statistical experimental design using experimental data.

3. Results and Discussion

The transesterification reaction as shown in Scheme 1 composed of two reactions, that are forward and backward reaction. The rate of reaction of ethylene carbonate (EC) can be expressed as follows:

$$-r_{EC} = k_{forward} C_{MeOH}^a C_{EC}^b - k_{backward} C_{DMC}^c C_{EG}^d \quad (1)$$

When only forward reaction is regarded, Equation (1) can be rearranged to Equation (2) since a high concentration of MeOH was used in the reactant for this reaction.

$$-r_{EC} = k_{forward} C_{MeOH}^a C_{EC}^b = k_{forward} C_{EC}^b \quad (2)$$

The reaction rate of EC with various initial concentrations is illustrated in Fig. 1 at different reaction temperature. The molar ratio of MeOH to EC was maintained at higher than 8 and the amount of cat-

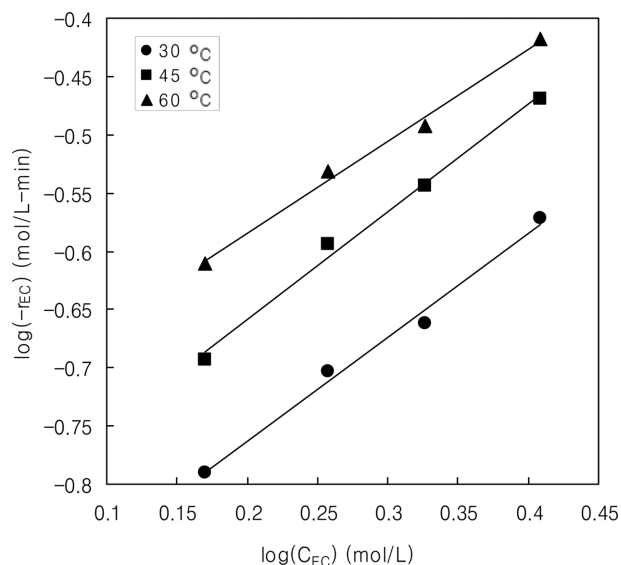


Fig. 1. The plot to determine the forward reaction order and constant in DMC synthesis.

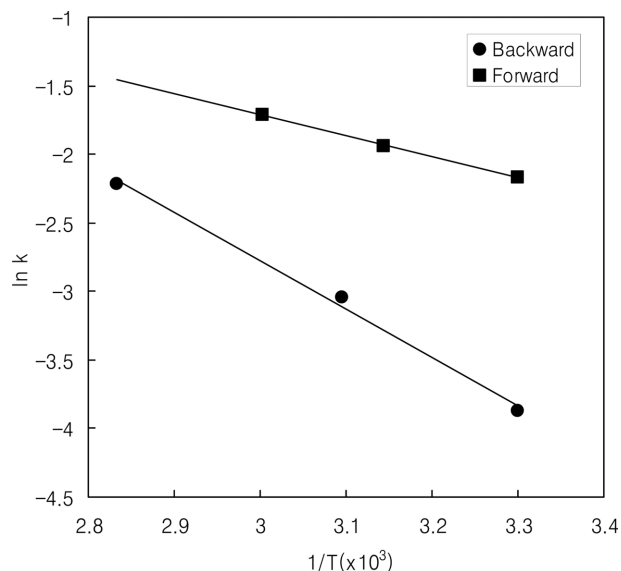
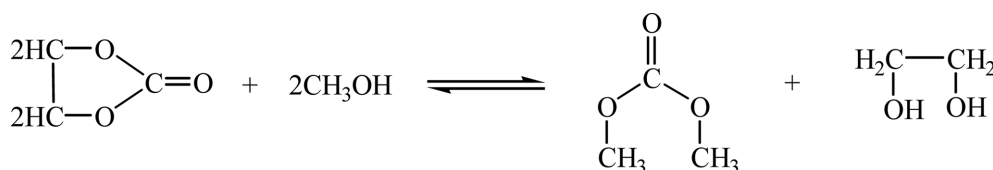


Fig. 2. Relationship of k with temperature.

alyst was 0.2 wt%. The preliminary work [5] found that there was no considerable effect of KOH more than 0.1 wt% to reaction rate of EC conversion, while below this amount the catalyst concentration had considerable effect on the reaction rate of EC conversion. So, the catalyst amount used in this work was maintained at 0.2 wt%. From the data of Fig. 2, the reaction order was determined by regression based on Equation (3) and presented in Table 1.

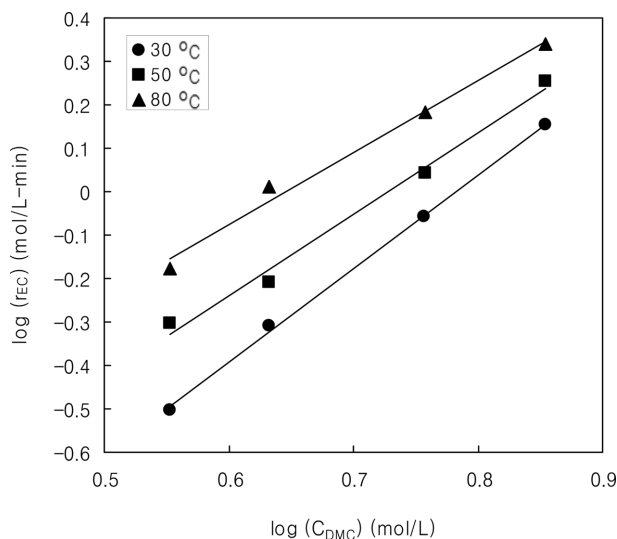
$$\log(-r_{EC}) = \log k_{forward}^* + b \log C_{EC} \quad (3)$$



Scheme 1

Table 1. Estimated value of reaction orders and rate constants

Reaction	Reaction order	Activation energy (kJ/mol)	Rate constant
Forward	b = 0.87	12.73	$18.1 e^{-12734.2/RT}$
Backward	c = 1.25, d = 0.9	29.28	$2457.5 e^{-29276.6/RT}$

**Fig. 3. The plot to determine the backward overall reaction order and rate constant in DMC synthesis.**

The effect of reaction temperature on the reaction rate of EC was investigated by various reaction temperature and the results are plotted in Fig. 2, 3. As shown in Fig. 2, the reaction rate increased with reaction temperature. The k values calculated at various temperatures were correlated by Equation (4) and shown in Fig. 3. The activation energy and rate constant were determined and illustrated in Table 1.

$$\ln k = \ln k_o - \frac{E_a}{RT} \quad (4)$$

Regarding backward reaction, Equation (1) can be rearranged to Equation (5).

$$r_{EC} = k_{backward} C_{DMC}^c C_{EG}^d \quad (5)$$

For equal concentrations of DMC and EG, Equation (5) becomes

$$-r_{EC} = k_{backward} C_{DMC}^c C_{EG}^d = k_{backward} C_{DMC}^{c+d} = k_{backward} C_{DMC}^c \quad (6)$$

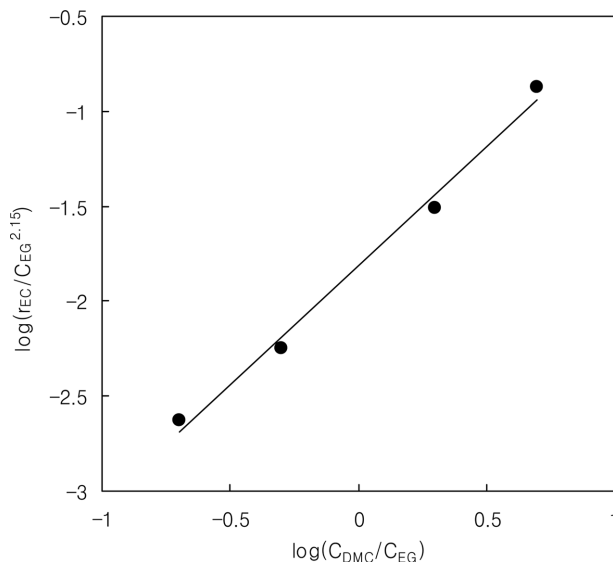
and taking logs this gives

$$\log(r_{EC}) = \log k_{backward} + n \log C_{DMC} \quad (7)$$

The overall order of backward reaction was determined by Equation (7) as shown in Fig. 4. Knowing the overall order, the reaction order with respect to each component was estimated with the following manipulation:

$$\begin{aligned} r_{EC} &= k_{backward} C_{DMC}^c C_{EG}^d = k_{backward} C_{DMC}^c C_{EG}^{n-d} \\ &= k_{backward} C_{EG}^n \left(\frac{C_{DMC}}{C_{EG}} \right)^c \end{aligned} \quad (8)$$

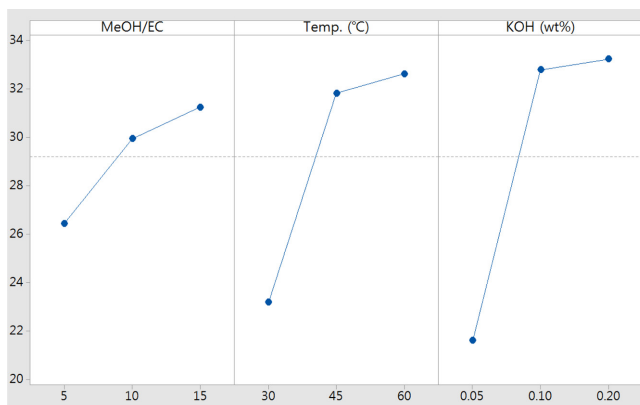
Taking logs and using the value of overall order determined, the reaction order of individual component was calculated with Equa-

**Fig. 4. The plot to determine the backward individual reaction order in DMC synthesis.**

tion (9). In Fig. 5, the correlation of experiment data to determine the reaction order was well fitted and the values calculated are illustrated in Table 1.

$$\log \frac{r_{EC}}{C_{EG}^{2.15}} = \log k_{backward} + c \log \frac{C_{DMC}}{C_{EG}} \quad (9)$$

To analyze the main effects and interactions of the reaction conditions in the synthesis of DMC, the MeOH/EC molar ratio, reaction temperature, and KOH concentration were used as experimental parameters. First, we performed Minitab 17 using the general factorial method, which is used when the level of all the factors is not 2 level. The main effect of factor level changes on DMC yield is presented in Fig. 5. All main factors show some effect to determine DMC yield. Especially, the effect of reaction temperature and KOH

**Fig. 5. Main effect plot for DMC yield (%) over various reaction conditions.**

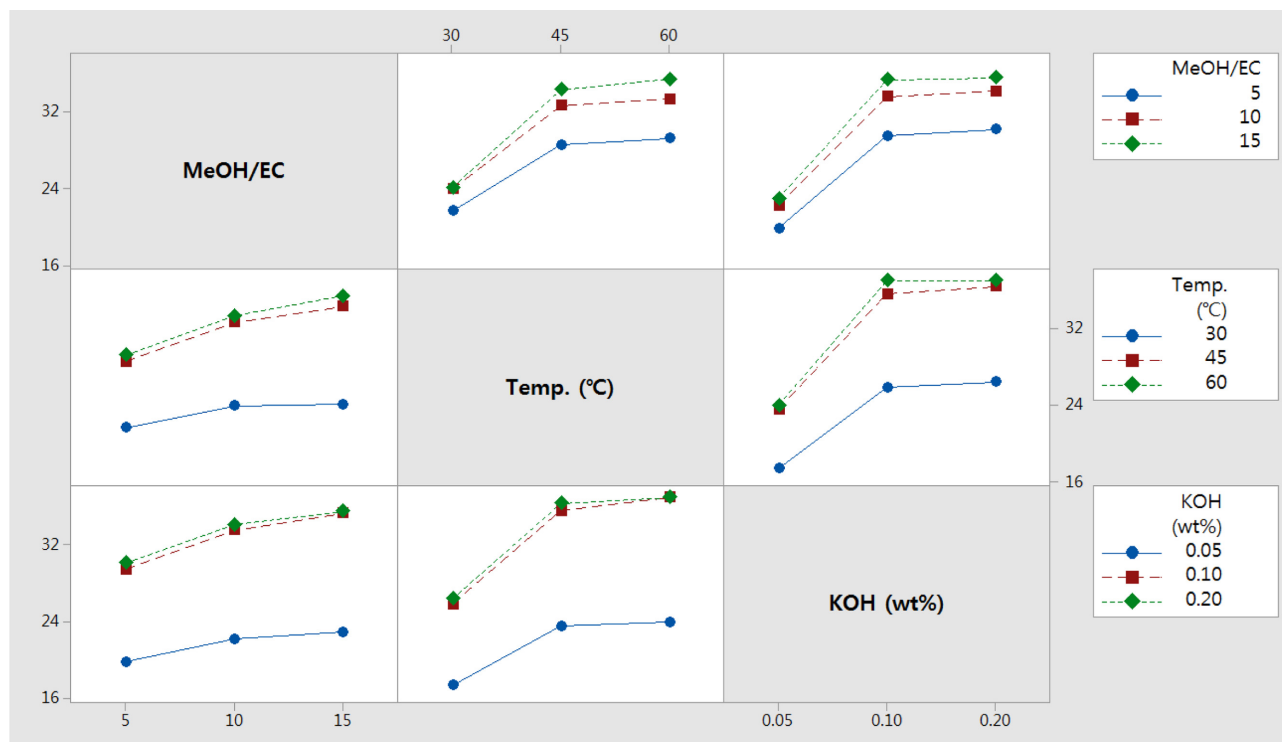


Fig. 6. Interaction plot for DMC yield (%) over various reaction conditions.

concentration on DMC yield was significant. Furthermore, the interaction which is the effect of one factor depending on the level of the other factor is illustrated in Fig. 6. The interaction effect was higher in the condition where the main effect degree of each factor was small.

The second-order polynomial equation was selected to predict the yield of DMC according to the reaction conditions. When the variable corresponding to the reaction condition was larger than the third term, the prediction result was not affected. For that reason, the equation derived here is limited to the quadratic equation. The correlation coefficient was calculated by the nonlinear regression method (using Minitab 17 program) as Equation (10).

$$Y = -41.24 + 0.662 X_1 + 1.671 X_2 + 397.0 X_3 - 0.0440 X_1^2 - 0.01741 X_2^2 - 1460.7 X_3^2 + 0.01233 X_1 X_2 + 1.229 X_1 X_3 + 0.743 X_2 X_3 \quad (10)$$

In this equation, Y is the yield of DMC, X_1 is the molar ratio of

MeOH to EC, X_2 is the reaction temperature and X_3 is the weight concentration of the catalyst, KOH. The R^2 value of the model equation derived from the analysis of variance was 0.985, which was found to be close to the experimental result.

To derive the optimal synthesis conditions for the DMC yield using second-order response surface morphology, the optimal conditions are shown using contour plots. As shown in Fig. 7, the optimal synthesis conditions for DMC yields are presented in all ranges. An experiment was then performed using the reaction conditions optimized by the design of experiment. The experimental value compares well with response surface model equation as listed in Table 2. The percentage error is only 2.2%. Therefore, the optimal synthesis condition prediction using the response surface analysis method, which is one of the statistical experimental design methods, can be regarded as a meaningful result.

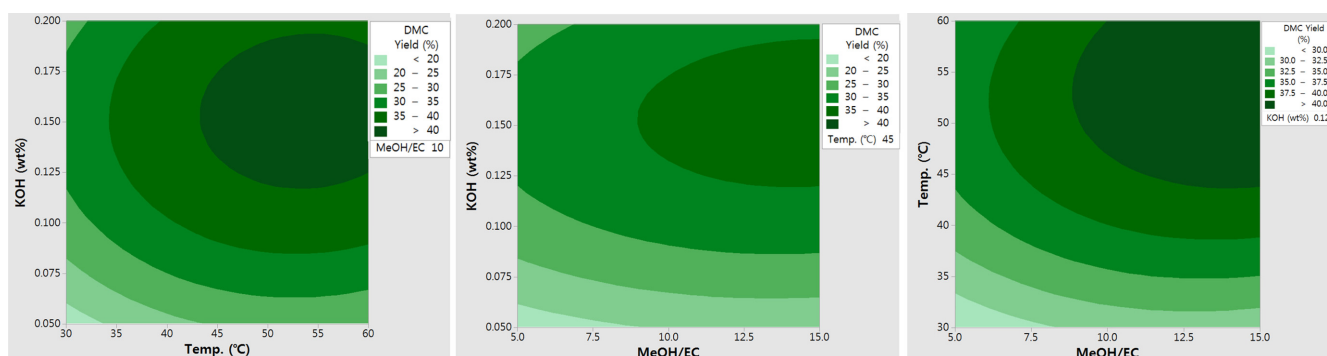


Fig. 7. Contour plots of the optimum reaction conditions with various DMC yield.

Table 2. Predicted and Experimental DMC yield at the optimum conditions for model validation

Reaction Condition			Predicted yield (%)	Experimental yield (%)	Error (%)
MeOH/EC	Temp. (°C)	KOH (wt%)			
15	55	0.15	43.8	42.8	2.2

4. Conclusion

The reaction kinetics and the experimental studies of transesterification reaction of EC with methanol were investigated. From the experimental and calculated results, the reaction order for forward and backward reactions was 0.87 and 2.15, respectively. The activation energy was 12.73 and 29.28 kJ/mol, and the rate constant was $18.1 e^{-12734.2/RT}$ and $2457.5 e^{-29276.6/RT}$ for forward and backward reactions, respectively. The results will be informative for developing the reaction process of DMC synthesis. In this study, the optimum reaction process for synthesizing DMC was proposed using experimental design method. In the analysis using general factorial experiments, MeOH / EC, reaction temperature and catalyst concentration were found to be major factors. Also, the interactions among the major factors were calculated to be large. In addition, the optimal reaction process according to the DMC yield can be presented in all ranges using the reaction surface analysis method. In this way, it is possible to optimize the synthesis process more reliably by trial and error. Especially, as the major factors participating in the synthetic reaction increase, the effect of the statistical approach will be further increased.

Acknowledgement

This study was supported by the Research Program funded by the SeoulTech (Seoul National University of Science and Technology).

References

1. Pacheco, M. A. and Marshall, C. L., "Review of Dimethyl Carbonate (DMC) Manufacture and Its Characteristics as a Fuel Additive," *Energ. Fuels*, **11**, 2-29(1997).
2. Tatsumi, T., Watanabe, Y., Koyano, K. A., "Synthesis of Dimethyl Carbonate from Ethylene Carbonate and Methanol Using TS-1 as Solid Base Catalyst," *Chem. Commun*, **19**, 2281-2282(1996).
3. Watanabe, Y., Tatsumi, T., "Hydrotalcite-type Materials as Catalysts for the Synthesis of Dimethyl Carbonate from Ethylene Carbonate and Methanol," *Micropor. Mesopor. Mater.*, **22**, 399-407(1998).
4. Knifton, J. F., Duranleau, R. G., "Ethylene Glycol-dimethyl Carbonate Cogeneration," *J. Mol. Catal.*, **67**, 389-399(1991).
5. Han, M. S., Lee, B. G., Ahn, B. S., Park, K. Y. and Hong, S. I., "Kinetics of Dimethyl Carbonate Synthesis from Ethylene Carbonate and Methanol using Alkalimetal Compounds as Catalysts," *React. Kinet. Catal. Lett.*, **73**, 33-38(2001).
6. Walpole, R. E., Ye, K. E., Raymond, H. M. and Myers, S. L., *Probability and Statistics for Engineers and Scientists*, 9th ed., 639-652, Prentice Hall, Boston, USA(2012).
7. Mason, R. L., Gunst, R. F. and Hess, J. L., *Statistical Design and Analysis of Experiments, with Applications to Engineering and Science*, 2nd ed., 568-597, Wiley-Interscience, New Jersey, USA (2003).