OPTIMIZATION OF Ni LOADING AND OPERATING CONDITIONS FOR CARBON DIOXIDE REFORMING OF METHANE OVER NiO/CeO₂ CATALYST USING RESPONSE SURFACE METHODOLOGY

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Abstract

Modelling and optimization of Carbon Dioxide Reforming of Methane (CORM) reaction over NiO/CeO₂ catalyst were developed using Response Surface Methodology (RSM). Relationship between responses, i.e. CH₄ conversion, H₂ and CO selectivities, and three independent variables, i.e. reactor temperature, CO₂/CH₄ ratio, and wt.% Ni in the CeO₂-supported catalyst, were presented as empirical mathematical models. The models showed a good fitting to the experimental data statistically. The NiO/CeO₂ showed a potential catalyst for the CORM process, though some coking formations were found. The catalysts exhibited a promising catalytic performance with the unity H₂/CO ratio in the product, high methane conversion, and low reverse water gas shift reaction. The reactor temperature, CO₂/CH₄ ratio, and wt.% Ni in the CeO₂-supported catalyst being 840 °C, 1, and 6.5%, respectively were suggested with respect to CH₄ conversion, H₂ and CO selectivity, and H₂/CO ratio of 75.7%, 68.5%, 54.5%, and 1.03, respectively.

Keywords: Carbon dioxide reforming of methane, NiO/CeO₂ catalyst, Response Surface Methodology

Abstrak

Permodelan dan optimisasi reaksi pembentukan kembali metana dengan karbondioksida (CORM) melalui katalis NiO/CeO₂ telah dikembangkan dengan menggunakan Response Surface Methodology (RSM). Hubungan antara respon-respon (konversi CH₄, selektifitas H₂ and CO) dengan tiga peubah tak bergantung (temperatur reaktor, rasio CO₂/CH₄, dan % berat Ni dalam katalis berpenyangga CeO₂) dinyatakan dalam model matematika empiris. Model empiris tersebut secara statistik menunjukkan korelasi yang baik terhadap data-data eksperimen. NiO/CeO₂ tersebut menunjukkan sebuah katalis yang berpotensi untuk proses CORM. Katalis tersebut menunjukkan kinerja katalitik yang menjanjikan dengan rasio H₂/CO mendekati satu dalam produk, konversi metana yang tinggi, dan reaksi reverse water gas shift yang rendah. Temperatur reaktor 840 °C, rasio CO₂/CH₄ 1, dan 6.5 wt.% Ni adalah direkomendasikan dengan konversi CH₄ 75.7%, selektifitas H₂ 68.5%, selektifitas CO 54.5%, dan rasio H₂/CO 1.03.

Kata Kunci: Pembentukan kembali metana dengan karbondioksida, Katalis NiO/CeO₂, Response Surface Methodology

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1. Introduction

Methane (CH₄) is the most important component in natural gas due to its high potential in chemical processing industries (Zaman, 1999). The methane gas is one of the greenhouse gases in addition to CO₂ and NO_x. Minimization of greenhouse gases is of great interest in recent years. Although NO_x and halogenated hydrocarbon contributed to the global warming, more than half of the greenhouse gas effects are caused by CO₂ emission. In fact, synthesis gas with unity H₂/CO ratio can be produced from methane by CO₂ reforming process. The liquid fuel reactions from synthesis gas, such as Fischer-Tropsch synthesis, methanol synthesis, and dimethyl ether synthesis, require suitable H₂/CO ratio. Therefore, the CORM is essential to produce synthesis gas with low/unity H₂/CO ratio. The effective use of CO₂ is another advantage as a carbon resource. The development of a catalyst with high activity and long life is a key research in this field.

Previous research indicated that the use of noble metals such as platinum, rhodium and palladium as a catalyst in CORM provides high stability, activity and selectivity (Chen et al., 1997; Wang and Ruckenstein, 2000). It is also known that the noble metal-based catalysts are less sensitive to coking than nickel-based catalysts, which is probably due to lower solubility of carbon in noble metals (Chen et al., 1999). Unfortunately, the noble metals are expensive. The cheap metal catalysts, such as iron, cobalt and nickel, showed a good activity but they have a rapid coking (Asami et al., 2003; Wang and Lu, 1996). The catalyst such as nickel has been more explored due to its high activity and selectivity as well as its low price. The disadvantages of nickel-based catalysts are more susceptible to the formation of carbonaceous deposition on the catalyst surface. The coking formation leads to the catalyst deactivation. The carbon deposition can be inhibited by introducing high basicity material in the catalyst (Asami et al., 2003). The interaction of support and metal plays an important role in the activity and coking resistivity in the CORM using nickel-based catalysts.

The relationships among catalyst compositions and process parameters toward the catalytic performances are very complex from the engineering and chemistry points of view. The optimal operating parameters, such as the CO₂/CH₄ ratio and reactor temperature, and the catalyst compositions, provide essential information in industrial CORM process. In the area of catalysis, only a few studies have attempted

to optimize the catalyst compositions and process parameters using response surface methodology (Wu et al., 2002; Istadi and Amin, 2005a) and multi-responses strategy (Istadi and Amin, 2005b). The study on the effect of calcinations conditions on the mechanical properties of PCoMo/Al₂O₃ hydrotreating catalyst using RSM (Wu et al., 2002) is an example of optimization study related to the catalyst preparation.

The main objective of this work is to optimize wt.% Ni loading in the CeO₂-supported catalyst and operating conditions (CO₂/CH₄ ratio and reactor temperature) of the CORM over NiO/CeO₂ catalyst. The Response Surface Methodology (RSM) technique was utilized to optimize/study the responses of CH₄ conversion, H₂ and CO selectivity corresponding to the process parameters and the wt.% Ni loading.

2. Fundamental

Carbon dioxide reforming of methane reaction proceeds stoichiometrically through Equation (1), which produces a unity H₂/CO ratio. The reverse water gas shift (RWGS) reaction is also occurred simultaneously according to Equation (2), which reduced the H₂ product during the reaction. When carbon deposition occurs, even if it proceeds through either CH₄ decomposition (Equation (3)) or disproportionation of CO formed (Equation (4)). Water formation through Equation (5), on the other hand, results in a decrease H₂/CO ratio. If the water gas shift reaction (Equation (6)) occurs successively to the water formation, the overall reaction comes to the dry reforming reaction (Equation (1)). Theoretically, carbon deposition or formation of water should not occur over NiO/CeO₂ catalyst. Actually, the carbon deposition still appears on the catalyst, which may be due to Ni species catalysis toward coking formation.

The development of a highly efficient catalyst is important, and the key to obtain a highly efficient catalyst is the catalyst design (Hattori and Kito, 1991, 1995; Hou et al., 1997; Huang et al., 2001). Conventionally, the catalyst design was based on reaction mechanism to decide the main components of catalyst and to determine the best

catalyst by several experiments. But unfortunately for most new chemical reaction, the catalytic mechanism could not be understood well. The relationships among catalyst compositions and process parameters toward the catalytic performances are very complex from engineering and chemistry points of view, but the determination of a suitable catalyst is crucial for the CORM process. Preferably, the very complex relation should be modelled at an atomic level in the catalyst design to obtain a suitable catalyst compositions and optimal operating conditions. According to the complex interaction among the catalyst compositions, the process parameters and the metal-support interaction, it is more useful for the catalyst design using empirical models especially in the optimization studies. The empirical modelling is efficient for the catalytic process optimization, but the drawback is that the model did not describe the fundamental theory or actual phenomena. Indeed, the empirical model may be more appropriate for process optimization when the kinetic mechanism is not well known.

In this paper, the empirical mathematical models of CH_4 conversion, H_2 and CO selectivity and yield are generated by the RSM method as function of independent variables. The statistical analysis was also performed to testify the adequacy of the proposed models. The research works involve several steps involved catalyst preparation, catalyst testing, design of experiment, optimization and statistical analysis.

3. Methodology

The NiO/CeO_2 catalyst was prepared by the incipient wetness impregnation method using aqueous solution of the nickel nitrate. The catalyst was prepared based on the procedures shown in Figure 1. CeO_2 (99.9% purity, ACROS) powder was used as a catalyst support, while $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, MERCK) was used as a precursor. Powdery CeO_2 was first immersed into an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 3 h at ambient temperature and was dried overnight in an oven (MEMMERT) at 393 K. Therefore, the resulted solid was calcined at 773 K in a muffle furnace (CARBOLITE) for 5 h and then crushed into the desired size. The metal loading of the catalyst was determined based on the experimental design.

Figure 1. Preparation of NiO/CeO_2 Catalyst Using Impregnation Method

Catalyst testing was conducted in a fixed-bed quartz reactor. The gas flow rates were measured and controlled by volumetric flow controllers (Alicat Scientific, Inc.). The products and unreacted gases were analyzed by an online gas chromatography (HP AGILENT 6890 series) equipped with a thermal conductivity detector (TCD), Molecular Sieve and Porapak N packed columns. The experiments were conducted at atmospheric pressure. The operating conditions of the process are determined based on the design of experiment. Reactant gases, methane (>99.999%) and carbon dioxide (>99.995%), were fed to the reactor at a total feed flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ over the catalyst weight of 1 g.

A central composite design (CCD) for three factors was employed for experimental design (Montgomery, 2001; Cornell, 1990). The value of α for orthogonality depends on the number of points in the factorial portion of the design which is given in Equation (7) (Montgomery, 2001; Cornell, 1990; Statsoft, 2001).

$$\alpha = \left(\left[(n_c + n_s + n_o)^{1/2} - n_c^{1/2} \right]^2 * n_c / 4 \right)^{1/4} \quad (7)$$

where n_c is the number of cube points in the design, n_s is the number of star points in the design, n_o is the number of center points in the design. Since there are three factors, 8 cube points, 6 star points, and 4 center points, α for orthogonality is ± 1.41 .

Three independent variables (X) or factors, namely, reactor temperature (X_1), CO₂/CH₄ ratio (X_2), and wt.% Ni loading in the CeO₂-supported catalyst (X_3), were selected. The ranges of independent variables were chosen based on the conditions from the variables screened prior to optimization and are often used in literatures (Asami et al, 2003; Wang et al., 2001). The ranges and levels of independent variables used in the experimental work are given in Table 1. In the table, X_1 denotes CO₂/CH₄ ratio, X_2 denotes reactor temperature (°C), and X_3 denotes wt.% Ni loading in the CeO₂-supported catalyst (%). In the experimental design, all variables are coded for statistical calculation according to Equation (8) (Wu et al., 2002):

$$x_i = \frac{\alpha [2X_i - (X_{\max} + X_{\min})]}{X_{\max} - X_{\min}} \quad (8)$$

where x_i is the dimensionless coded value of the i th variable, X_i is the natural value of the i th variable, $X_{\max}$ and $X_{\min}$ are the highest and the lowest limit of the i th variable (star point), respectively.

The experimental design matrix presented in Table 2 consists of 18 sets of coded conditions expressed in the natural values. The design consist

of a two-level full factorial design ($2^3=16$), six star points and four centre points. The sequence of the experiments was randomized in order to minimize the effects of uncontrolled factors.

Table 1. Experimental Ranges and Levels of Factors or Independent Variables

X	Ranges and Levels (x_i)				
	$-\alpha$	-1	0	$+1$	$+\alpha$
X_1 (°C)	808	820	850	880	892
X_2 ()	0.72	0.80	1.00	1.20	1.28
X_3 (%)	1.46	3.00	5.00	8.00	8.54

The responses and the corresponding factors are modelled and optimized using the RSM method (Montgomery, 2001; Cornell, 1990) by utilizing STATISTICA version 6 software (Statsoft, 2001). The RSM is a technique consists of: (a) designing of experiments to provide adequate and reliable measurements of the response, (b) developing a mathematical model having the best fit to the data obtained from the experimental design, and (c) determining the optimal value of the independent variables that produces a maximum or minimum response. By the RSM, a quadratic polynomial equation was

Table 2. Experimental Design Matrix in Their Natural Values

Run No	Experimental design matrix (uncoded)			Dependent variables			
	Temperature (X_1)	CO ₂ /CH ₄ ratio (X_2)	wt.% Nickel (X_3)	X CH ₄ (%)	S H ₂ (%)	S CO (%)	H ₂ /CO ratio
1	820	0.80	3	76.71	71.39	64.63	1.04
2	820	0.80	8	59.31	72.44	63.17	0.96
3	820	1.20	3	78.59	70.37	63.49	0.83
4	820	1.20	8	97.80	72.64	63.21	0.94
5	880	0.80	3	98.86	62.04	68.35	0.99
6	880	0.80	8	99.21	63.05	68.86	1.01
7	880	1.20	3	99.58	62.36	62.60	0.83
8	880	1.20	8	95.85	73.48	64.00	0.95
9	808	1.00	5	76.01	71.74	59.07	1.02
10	892	1.00	5	99.02	67.57	60.24	1.02
11	850	0.72	5	51.80	61.70	62.00	1.05
12	850	1.28	5	98.45	66.01	65.68	0.71
13	850	1.00	1.46	40.06	62.86	65.83	0.65
14	850	1.00	8.54	74.75	68.46	56.49	1.12
15	850	1.00	5	77.93	68.86	58.97	0.98
16	850	1.00	5	76.88	66.12	51.74	0.97
17	850	1.00	5	81.22	67.49	55.86	1.02
18	850	1.00	5	80.60	64.23	52.20	1.01

developed to predict the responses as a function of independent variables involving their interactions. The coefficients of the models for the three responses were estimated using multiple regression analysis technique included in the RSM. Theoretically, the steepest-ascent method is the default method in the STATISTICA software to address the optimal conditions in which each response variable achieved a maximum/minimum value. However for this case, the optimal conditions of the four responses could not be determined by using this default method. In fact, the most empirical models have no unique optimal point due to saddle-type surface profile. Therefore, the optimal response and independent variables could not be determined numerically. The suggestion of optimal conditions can be performed manually from the surface profiles by considering the relation among H_2/CO ratio, methane conversion, and selectivities of CO and H_2 . In this case, the optimal point was suggested at conditions where the H_2/CO product ratio 1.

In general, the response for the quadratic polynomials is described in Equation (9) as a function of independent variables and their interaction.

$$Y = \beta_0 + \sum_{j=1}^4 \beta_j X_j + \sum_{j=1}^4 \beta_{jj} X_j^2 + \sum_{i < j} \beta_{ij} X_i X_j \quad (9)$$

where Y is the predicted response, β_0 is the intercept term, β_i are the linear terms, β_{jj} are the squared terms, β_{ij} are the interaction terms, and X_i and X_j represent the uncoded of the independent variables.

Three-dimensional response surfaces and contour plots were used for facilitating a straightforward examination of the experimental variables influence on the responses. The individual response surface and the contour plots were created by holding two of four variables constant at their centre points. The coefficients of the models for the three responses were estimated with multiple regression analysis. The fit quality of the models was judged from their coefficients of correlation (R) and determination (R^2). The adequacy of each model was checked with the analysis of variance (ANOVA) using Fisher F-test (Montgomery, 2001; Cornell, 1990). The significance of the equation parameters for each response was assessed by p-value and Student's t-test. The significance test of regression is attempted to determine the relationship between the response variable and a subset of the independent variables.

4. Results and Discussion

A Central Composite Design was designed to estimate the coefficients of the quadratic model as presented in Equation (9). The relationship between the independent variables and the response variable was estimated using multiple regression analysis involved in the RSM technique.

The empirical mathematical model of methane conversion (CH_4) of the CORM process is presented in Equation (10). The empirical model is proposed with respect to dependent (methane conversion) and independent (reactor temperature, CO_2/CH_4 ratio, wt.% Ni loading) variables. The determination coefficient, $R^2 = 0.728$, indicates a low agreement between the observed and predicted values of the fitted model. The comparison between the observed and predicted values of the model is also demonstrated in Figure 2.

$$\begin{aligned} XCH_4 = & 6904.55 - 17.22 X_1 + 591.68 X_2 + 12.42 X_3 \\ & + 0.01 X_1^2 + 89.49 X_2^2 - 1.06 X_3^2 \\ & - 0.9 X_1 X_2 - 0.01 X_1 X_3 + 6.48 X_2 X_3 \end{aligned} \quad (10)$$

Figure 2. Comparison of The Observed and Predicted Values of CH_4 Conversion Model

The relationships between CH_4 conversion and the independent variables are depicted in Figures 3-4. Figure 3 presents three dimensional surface profiles of methane conversion over reactor temperature and wt.% Ni loading. It is shown that increasing the reactor temperature enhances the methane conversion. High reactor temperature leads to high methane conversion with low coking formation and low water formation. This fact coincides with the results by Asami et al. (2003). The similar trend is exhibited by the increasing wt.% Ni loading. In addition, the methane conversion is enhanced by increasing wt.% Ni loading in the CeO_2 -supported catalyst and it achieves maximum at 6.5%. The amount of

wt.% Ni loading higher than 6.5% does not improve the methane conversion, which may be due to increasing a coke deposition on the catalyst surface (Dong et al., 2002). The coke deposition causes pore and active sites blocking in the catalyst surface. This trend is in agreement with the result of Roh et al. (2004) that the impregnated Ni/CeO₂ catalyst gave serious coke formation in the initial stage of the reaction. They confirmed that the conventional impregnation method was not effective to prepare the catalysts having good stability in CORM. The oxygen transfer ability of CeO₂ support to Ni species should be beneficial to prevent carbon formation during CORM. Oxygen ion vacancies in the cubic CeO₂-supported catalyst have beneficial effects on the catalytic activities due to the increase in oxygen mobility. A higher rate of oxygen transfer helps to keep the Ni metal in the surface from carbon accumulation.

Figure 3. Surface Plot of CH₄ Conversion as Function of wt.% Ni Loading and Reactor Temperature Shown at Fixed CO₂/CH₄ Feed Ratio

Effect of CO₂/CH₄ ratio and wt.% Ni loading on the methane conversion is exhibited in Figure 4. It is shown that the CH₄ conversion is affected significantly by CO₂/CH₄ ratio variation at about 6.5% Ni loading. However, the variation of wt.% Ni loading exhibits a considerable effect at high CO₂/CH₄ ratio and shows a slight effect at low CO₂/CH₄ ratio. High CO₂ concentration in the feed leads to an improved C-H bond activation and coke formation reduction, which may be due to the role of active oxygen from CO₂. In fact, increasing the Ni loading higher than 6.5% lowers the methane conversion, which may be due to enhancement of coking formation at high Ni loading. Indeed, the highest activity of methane conversion is achieved at Ni loading of about 6.5% in the CeO₂-supported catalyst and is favoured at high temperature (Wang and Lu, 1996). High CH₄ and CO₂ dissociation may

be due to the role of interaction between nickel and ceria in the catalyst to form surfaces and bulk defect. Introduction of nickel to the ceria support may improve the reducibility of the ceria, which enhances the oxygen vacancy at the catalyst surface. Wang et al. (2001) also reported that the lattice oxygen may participate in the activation of both CH₄ and CO₂ at elevated temperature.

Figure 4. Contour Plot of CH₄ Conversion as Function of wt.% Ni Loading and CO₂/CH₄ Feed Ratio Shown at Fixed Reactor Temperature

In this paper, the optimal wt.% Ni loading, CO₂/CH₄ ratio and reactor temperature are also studied with respect to H₂ selectivity. An empirical mathematical model was also resulted developed by the RSM. The model addresses the H₂ selectivity as functions of reactor temperature (X_1), CO₂/CH₄ feed ratio (X_2), and wt.% Ni loading (X_3). The model is presented in Equation (11) as follow:

$$S H_2 = 2074.49 - 4.36 X_1 - 172.86 X_2 - 13.12 X_3 + 2.33E-3 X_1^2 - 20.07 X_2^2 + 0.01 X_3^2 + 0.24 X_1 X_2 + 0.01 X_1 X_3 + 2.76 X_2 X_3 \quad (11)$$

The significance of the H₂ selectivity model was checked by ANOVA as presented in Table 3. The R² value of 0.86 indicates a fairly good agreement statistically between the experimental and the predicted values. The goodness of fitting is also exhibited in the comparison between observed and predicted value of H₂ selectivity as demonstrated in Figure 5, which showed a good fitting. The results of model fitness reveal that the calculated *F*-value of 5.33 is greater than the tabulated *F*-value ($F_{0.05,9,8}=3.39$). The *F*-value of the model indicates a statistically significant regression at 5% significance level. The H₂ selectivity model shows a better fit than the CH₄ conversion model.

Table 3. ANOVA Results of H₂ Selectivity Model

Sources	SS	df	MS	F-value
S.S regression	232.67	9	25.85	5.33
S.S error	38.83	8	4.85	
S.S total	271.50	17		
R ²	0.86

Figure 5. Comparison of Experimental and Predicted Values of H₂ Selectivity Model

Table 4 presents the multiple regression results and the significance of regression coefficients of the model. The model terms are sorted according to their significance to the H₂ selectivity model indicated from both the *t*- and *p*-values. From Table 4, the linear terms of reactor temperature (X_1) have the largest effects statistically on H₂ selectivity at 95% confidence level, which is implied by the lowest *p*-value and the highest absolute *t*-values (0.02 and 2.95, respectively). The next order of significance at the same confidence level is the square term of reactor temperature (X_1^2) which have a *p*-value of 0.03. Next, the interaction between the reactor temperature and the CO₂/CH₄ feed ratio (X_1X_2) showed a low significance at 90% confidence level. However, the effects of the other terms on H₂ selectivity model are not statistically significant. In general, the significance order of the independent variables on the H₂ selectivity from high to low is reactor temperature, interaction of temperature and CO₂/CH₄ feed ratio, and interaction of CO₂/CH₄ feed ratio and wt.% Ni loading.

Figure 6 shows a three-dimensional surface plot of the estimated H₂ selectivity over CO₂/CH₄ feed ratio and reactor temperature shown at fixed wt.% Ni loading. The figure reveals that effect of the reactor temperature on the H₂ ratio

Table 4. Multiple Regression Results and Sorted Significance Effect of Regression Coefficient for H₂ Selectivity Model

Parameter	Term	Coefficient	<i>t</i> -value	<i>p</i> -value
β_0	-	2074.49	3.25	0.01
β_1	X_1	-4.36	-2.95	0.02
β_{11}	X_1^2	2.33E-3	2.69	0.03
β_{12}	X_1X_2	0.24	1.86	0.10
β_{23}	X_2X_3	2.76	1.78	0.11
β_2	X_2	-172.86	-1.47	0.18
β_3	X_3	-13.12	-1.46	0.18
β_{13}	X_1X_3	0.01	1.26	0.24
B_{22}	X_2^2	-20.07	-1.03	0.33
β_{33}	X_3^2	0.01	0.11	0.92
R ²	0.86			

selectivity is more significant than that of CO₂/CH₄ parameter. For the NiO/CeO₂ catalyst, increasing the reactor temperature (820-880 °C) gives a significant decrement effect on the H₂ selectivity particularly at low CO₂/CH₄ ratio, but it shows a significant increment of the methane conversion. It is suggested that at high temperature, methane is not converted selectively to hydrogen. In fact, the H₂ selectivity is enhanced slightly by increasing CO₂/CH₄ ratio in the range 0.8-1.2, particularly at high temperature. Effect of wt.% Ni loading on the H₂ selectivity is also shown in contour plot (Figure 7). The wt.% Ni loading affects significantly on the H₂ selectivity particularly at CO₂/CH₄ ratio higher than 0.9. The figure also shows that variation of CO₂/CH₄ ratio does not influence significantly on the H₂ selectivity. From Figures 6-7, it is shown that interaction among the independent variables has a considerable significance.

Figure 6. Surface Plot of H₂ Selectivity as Function of CO₂/CH₄ Feed Ratio and Reactor Temperature Shown at Fixed wt.% Ni Loading

Figure 7. Contour Plot of H₂ Selectivity as Function of wt.% Ni Loading and CO₂/CH₄ Feed Ratio Shown at Fixed Reactor Temperature

The low H₂ selectivity in the CORM process may be due to the reverse water gas shift (RWGS) reaction, which is indicated by higher CO₂ conversion than CH₄ conversion (Montoya et al., 2000). The CO disproportionation may be increased by increasing nickel content on the catalyst, and the carbon easily transferred from the metal to the catalyst support (Goguet et al., 2004). The NiO/CeO₂ catalyst shows a potential catalyst for the CORM, which results in the unity H₂/CO ratio in the product. The promising result pertaining to H₂/CO ratio may be due to the role of the catalyst in reducing the RWGS reaction. Therefore, although the catalyst shows a promising performance (from high methane conversion and unity ratio of H₂/CO points of view), the drawback of the catalyst in CORM reaction is still on the coke formation. Next, the modification of the catalyst is important to reduce the coking formation.

The quadratic empirical model developed by the RSM for CO selectivity as function of reactor temperature, CO₂/CH₄ feed ratio and wt.% Ni loading is demonstrated in Equation (12).

$$SCO = 2040.88 - 4.55 X_1 - 65.21 X_2 - 12.24 X_3 + 2.79e-3 X_1^2 + 115.00 X_2^2 + 0.56 X_3^2 - 0.20 X_1 X_2 + 0.01 X_1 X_3 + 0.14 X_2 X_3 \quad (12)$$

The equation is fitted to the experimental data adequately with a reasonable determination coefficient R² of 0.84. The determination coefficient indicates that the model is appropriate for CO selectivity. The ANOVA result presented in Table 5 reveals that the calculated F-value of 4.70 is greater than the tabulated F-value (F_{0.05,9,8}=3.39). The F-value indicates a

statistically significant regression at 95% confidence level. The comparison of observed and predicted CO selectivity is also exhibited in Figure 8. It is demonstrated that the experimental and predicted values of CO selectivity are correlated well.

The coefficients of the empirical model and their significance are presented in Table 6. The model terms are sorted according to their significance with respect to the CO selectivity model. The square term of CO₂/CH₄ ratio (X₂²) has the largest effects statistically on the CO selectivity at 99% confidence level which is implied by the lowest *p*-value and the highest absolute *t*-values (2.03E-3 and 4.49, respectively). The next order of significance is the square term of wt.% Ni loading (X₃²), which has a *p*-value of 0.01. Next, the square and linear terms of reactor temperature (X₁²) shows a considerable significance at 95% confidence level. However, the effects of the other terms on CO selectivity model are not statistically significant. In general, the significance order of the independent variables on the CO selectivity from high to low is CO₂/CH₄ feed ratio, wt.% Ni loading, and reactor temperature.

Table 5. ANOVA for CO Selectivity Model

Sources	SS	df	MS	F-value
S.S regression	354.12	9	39.34	4.70
S.S error	66.93	8	8.37	
S.S total	421.05	17		
R ²	0.84

Figure 8. Comparison of Observed and Predicted Values of CO Selectivity Model

Table 6. Multiple Regression Results and Sorted Significance Effect of Regression Coefficient for CO Selectivity Model

Parameter	Term	Coefficient	t-value	p-value
β_{22}	X_2^2	115.00	4.49	0.002
β_{33}	X_3^2	0.56	3.51	0.01
β_{11}	X_1^2	2.79E-3	2.45	0.04
β_0	-	2040.88	2.44	0.04
β_1	X_1	-4.55	-2.34	0.05
β_{12}	X_1X_2	-0.20	-1.16	0.28
β_3	X_3	-12.24	-1.03	0.33
β_{13}	X_1X_3	0.01	0.49	0.64
β_2	X_2	-65.21	-0.42	0.68
β_{23}	X_2X_3	0.14	0.07	0.94
R^2	0.84			

Figure 9 exhibits a three-dimensional surface plot of the predicted CO selectivity over CO_2/CH_4 feed ratio and reactor temperature, which is shown at fixed wt.% Ni loading. From the figure, it is revealed that the effect of CO_2/CH_4 variation is more significant than reactor temperature towards the CO selectivity. Increasing the reactor temperature (820-845°C) gives a considerable decrement of the CO selectivity, particularly at CO_2/CH_4 ratio of 1. The CO selectivity increased again at temperature higher than 845°C. In fact, the low CO selectivity at 845 °C and CO_2/CH_4 ratio about 1 leads to the unity H_2/CO ratio in the products. Effect of wt.% Ni loading on the CO selectivity is also presented in Figure 10. Particularly, the wt.% Ni loading affects more significantly on the CO selectivity. The figure also shows that variation of CO_2/CH_4 ratio influences the CO selectivity slightly. From Figures 9-10, it is shown that interaction among the independent variables has a considerable significance.

Figure 9. Surface Plot of CO Selectivity as Function of CO_2/CH_4 Feed Ratio and Reactor Temperature Shown at Fixed wt.% Ni Loading

Figures 11-12 demonstrate the relationship between wt.% Ni loading, reactor temperature, and CO_2/CH_4 ratio towards H_2/CO ratio in the product of CORM over NiO/CeO_2 catalyst. From the figures, it can be shown that H_2/CO ratio closes to 1 even at temperature about 840 °C. As the reactor temperature increased, the methane conversion increases and H_2/CO ratio closes to 1, which coincides with the result reported by Asami et al. (2003). From Figure 11, it is suggested that the high temperature favours the formation of CO due to the RWGS reaction. Figure 12 reveals the effect of CO_2/CH_4 ratio towards H_2/CO ratio. It is suggested that high CO_2/CH_4 ratio leads to high CO selectivity and low H_2 selectivity due to Increasing CO_2 conversion. From Figure 12, increasing the wt.% of Ni loading enhances the H_2/CO ratio in the product and the Ni loading achieves a maximum at about 6.5%. The lowering H_2/CO ratio at Ni loading higher than 6.5% may be due to the coking deposition on the surface of catalyst. The coking formation may block the active site and reduce the H_2 selectivity.

Figure 10. Contour Plot of CO Selectivity as Function of wt.% Ni Loading and CO_2/CH_4 Feed Ratio Shown at Fixed Reactor Temperature **Figure 11. Surface Plot of H_2/CO Ratio in The Product as Function of Reactor Temperature and wt.% Ni Loading Shown at Fixed CO_2/CH_4 Ratio**

Figure 12. Contour Plot of H_2/CO Ratio in The Product as Function of CO_2/CH_4 Ratio and wt.% Ni Loading Shown at Fixed Reactor Temperature

The determination of optimum H_2 selectivity should be related to CO selectivity owing to considering the H_2/CO ratio in the synthesis gas product. In this process, the unity H_2/CO ratio is expected which is suitable for feeding the Fischer-Tropsch process. With respect to the above figures and the additional criteria for optimum point determination, it can be concluded that 6.5% Ni loading, CO_2/CH_4 equal to 1, and reactor temperature about 840°C are chosen as optimum catalyst composition and operating conditions. The values of H_2 selectivity, CO selectivity, H_2/CO ratio and CH_4 conversion with respect to the optimum conditions are 68.5%, 54.5%, 1.03, and 75.7%, respectively.

5. Conclusions

The carbon dioxide reforming of methane over NiO/CeO₂ catalyst was optimized using Response Surface Methodology. The method was implemented to obtain models, statistical analysis and optimal catalyst composition and process parameters, which is suitable for the CORM process. The empirical mathematical models showed a good fitting of the experimental data. In general, the effect of the independent variables, i.e. reactor temperature, wt.% Ni loading and CO_2/CH_4 ratio, are statistically significant. The interaction between the independent variables substantially influenced the responses.

The NiO/CeO₂ catalyst showed a potential catalyst for the CORM. Accordingly, the following optimal independent variables of reactor temperature, CO_2/CH_4 ratio, and wt.% Ni in the CeO₂-supported catalyst being 840°C, 1, and 6.5%, respectively were suggested with respect to the CH_4 conversion, the H_2 and CO selectivity, and the H_2/CO ratio of 75.7%, 68.5%, 54.5%, and 1.03, respectively. The catalyst exhibited a promising

performance with the unity H_2/CO ratio in the product, high methane conversion, and low RWGS reaction. However, the coking deposition was still appeared on the catalyst. The next effort is focussed on how to reduce the coking formation during the CORM reaction by modifying the catalyst.

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