Optimization of Calcination Conditions for Cu/ZnO/Al$_2$O$_3$-ZrO$_2$ Catalyst

Nur Insyirah Zulkifli $^1$, Nor Hafizah Berahim $^1$, Noor Aswamati Mohd Zabidi $^1$,* and Sara Faiz Hanna Tasfy $^2$

1 Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS, Seri Iskandar 32610, Malaysia; nur_19000323@utp.edu.my (N.I.Z.); nor_19001638@utp.edu.my (N.H.B.)  
2 Department of Chemical and Petroleum Engineering, American University of Ras Al Khaimah, Ras Al Khaimah 10021, United Arab Emirates; sara.tasfy@aurak.ac.ae  
* Correspondence: noorasmawati_mzabidi@utp.edu.my; Tel.: +60-5-368-7675

Abstract: Promoted Cu/ZnO catalyst was synthesized on Al$_2$O$_3$-ZrO$_2$ support. Effects of calcination conditions on the catalytic performance in a CO$_2$ hydrogenation reaction were studied systematically using the response surface methodology (RSM). The application of RSM with rotatable central composite design (RCCD) for optimization on the influence of catalyst’s calcination variables on the CO$_2$ conversion and methanol selectivity is presented. The calcination variables studied include temperature, $A$ (181–518 °C), ramping rate, $B$ (1–30 °C/min), and duration, $C$ (1–7 h). From the RSM-generated model, the optimum calcination condition for this catalyst was 350 °C with 17.5 °C/min ramping rate for a 4 h duration. At the optimum calcination condition, the catalyst exhibited a Brunauer–Emmett–Teller (BET) surface area of 147 m$^2$/g, a pore volume of 0.31 cm$^3$/g, and a pore diameter of 8.1 nm.

Keywords: RSM; CO$_2$ hydrogenation; methanol synthesis; calcination condition; Cu-based catalyst

1. Introduction

The hydrogenation of CO$_2$ into value-added products such as methanol and dimethyl ether (DME) is one of the attractive options to mitigate the rise in CO$_2$ concentration in the atmosphere [1–5]. Cu-based catalysts have been recognized as efficient catalysts for the industrial methanol production that uses syngas as the feedstock. Methanol production based on CO$_2$ feedstock is yet to be applied at industrial scale, despite the extensive research conducted in this field. Some of the issues on the CO$_2$ hydrogenation process relates to the co-production of H$_2$O with methanol which would have detrimental effects on the conventional Cu-based catalyst. It was reported by [6–8] that the Cu/ZnO catalyst was deactivated due to accelerated crystallization of Cu and ZnO by water produced from CO$_2$-rich feedstock used in the methanol synthesis. Thus, intense efforts on catalyst design for methanol synthesis via CO$_2$ hydrogenation route have been carried out by many researchers around the world [9–13]. Some of the catalyst design approach include introduction of multicompontent system which has the capability to activate the very stable CO$_2$ molecule and dissociate H$_2$ molecule, and to minimize the effects of H$_2$O on the physicochemical properties of the catalyst [6].

Methanol synthesis is a structure-sensitive reaction, thus the efficiency of the catalyst is significantly influenced by the method of preparation of the catalyst, their pre-treatment conditions, active metals component, and choice of support and promoters. The preparation methods for the methanol synthesis catalysts include impregnation, co-precipitation, combustion, and sol–gel [7]. The industrial methanol catalyst is typically prepared using the co-precipitation method. Fujita et al. [14] investigated the effects of calcination and reduction conditions on the physicochemical properties of Cu/ZnO catalyst prepared by the co-precipitation method. They reported that the crystallite size of CuO for a catalyst prepared from aurichalcite precursor was significantly affected by the ramping rate during
the calcination process. The crystallite size of CuO was found to increase from 3.9 nm to 8.5 nm when the ramping rate was increased from 5 K/min to 100 K/min. The increase in the ramping rate during the calcination process resulted in a decrease in Cu dispersion and a corresponding decrease in the rate of methanol formation.

The commonly used $\gamma$-Al$_2$O$_3$ catalyst support is hydrophilic but ZrO$_2$ is weakly hydrophilic and the usage of ZrO$_2$ as a co-support will be beneficial for the desorption of produced H$_2$O from the CO$_2$ hydrogenation reaction [6]. Zhang et al. [15] reported that addition of up to 15 wt% ZrO$_2$ into $\gamma$-Al$_2$O$_3$ improved the dispersion of CuO species and enhanced the catalytic performance in the CO$_2$ hydrogenation reaction.

In the present study, we report the synthesis of Cu/ZnO on mixed oxide support comprising Al$_2$O$_3$ and ZrO$_2$ using the impregnation method. To the best of our knowledge, the effects of calcination conditions on the catalytic performance for CO$_2$ hydrogenation reaction over Cu/ZnO catalyst supported on Al$_2$O$_3$-ZrO$_2$ has not been reported. In the present contribution, the influence of calcination conditions of the promoted Cu/ZnO/Al$_2$O$_3$-ZrO$_2$ catalyst on their catalytic activity in CO$_2$ hydrogenation is systematically studied via response surface methodology (RSM) with rotatable central composite design (CCD).

2. Results and Discussion
2.1. Model Fitting

Three independent variables for the calcination process (temperature, ramping rate, and duration) at different levels were investigated in this study. An experimental design was constructed and analyzed using Design Expert Version 10 (Stat Ease, Minneapolis, MN, USA) in order to find the optimum point of the calcination condition for the synthesized catalyst (MNCZAZ). Optimization of the calcination conditions (calcination temperature, ramping rate, and duration) were carried out with rotational central composite design (CCD), which is the best DOE that applies RSM [16]. CCD is the experimental design introduced by Box and Wilson in 1951. CCD is one of the best experimental designs used in RSM. However, this design requires selection of the correct type of CCD. The CCD types include spherical (SCCD), rotatable (RCCD), orthogonal (OCCD), and face-centered (FCCD) central composite. In this study, the RCCD approach was used to determine the interaction between the process variables and the process response. According to previous research, the common type of CCD is either face-centered or rotatable [17]. One of the reasons for choosing rotatable CCD is the ability to perform extreme analysis in DOE compared to face-centered CCD. Therefore, the studied range would be much wider and more reliable to observe the trends.

The number of tests needed for RCCD includes the standard $2^k$ factorial with the origin at the center, $2k$ points fixed axially at a distance, say $\theta$, from the center to generate the quadratic terms, and retests at the center; where $k$ is the number of variables [18]. The axial points are chosen to be rotatable, which ensures that the variance of the model prediction is constant at all points equidistant from the design center. Repeats of the test at the center are very important as they provide an independent estimate of the experimental error [19]. For three variables, the recommended number of trials at the center is six. Therefore, the total number of trials required for these three independent variables is $2^3 + (2 \times 3) + 6 = 20$ [19,20]. Once the desired ranges of values of the variables are defined, they are coded to be $\pm 1$ for the factorial points, 0 for the midpoints, and $\pm \alpha$ for the axial points. The codes are computed as functions of the range of interest of each factor, as shown in Table 1. Table 2 shows the design matrix for the study on calcination conditions and the measured responses (CO$_2$ conversion, methanol selectivity, and methanol yield).
Table 1. Independent variables in Experimental Design.

| Variables            | Unit     | Levels          |
|----------------------|----------|-----------------|
| A: Calcination temp  | °C       | 181 250 350 450 518 |
| B: Ramping rate      | °C/min   | 1 5 17.5 30 40  |
| C: Duration (h)      | h        | 1 2 4 6 7       |

Table 2. Experimental design matrix for MNCZAZ calcination condition.

| Run | A    | B    | C   | Response 1: $X_{CO_2}$ | Response 2: $S_{MEOH}$ | Yield$_{MEOH}$ |
|-----|------|------|-----|-------------------------|------------------------|----------------|
| 1   | 350  | 17.5 | 4   | 16.02                   | 75.86                  | 12.15          |
| 2   | 518  | 17.5 | 4   | 7.19                    | 58.35                  | 4.19           |
| 3   | 450  | 5    | 6   | 3.35                    | 52.39                  | 1.75           |
| 4   | 250  | 30   | 6   | 5.55                    | 25.43                  | 1.41           |
| 5   | 250  | 5    | 2   | 8.17                    | 20.91                  | 1.70           |
| 6   | 250  | 30   | 2   | 7.97                    | 47.59                  | 3.79           |
| 7   | 450  | 30   | 2   | 7.43                    | 63.83                  | 4.74           |
| 8   | 350  | 17.5 | 1   | 5.55                    | 47.76                  | 2.65           |
| 9   | 250  | 5    | 6   | 7.87                    | 5.57                   | 0.43           |
| 10  | 350  | 1    | 4   | 15.81                   | 68.77                  | 10.87          |
| 11  | 350  | 17.5 | 4   | 13.6                    | 63.1                   | 8.58           |
| 12  | 350  | 17.5 | 4   | 15.9                    | 74                     | 11.76          |
| 13  | 350  | 17.5 | 4   | 16.01                   | 75                     | 12.00          |
| 14  | 350  | 40   | 4   | 9.63                    | 52.54                  | 5.05           |
| 15  | 350  | 17.5 | 4   | 16.04                   | 76.1                   | 12.2           |
| 16  | 450  | 30   | 6   | 11.28                   | 37.34                  | 4.21           |
| 17  | 350  | 17.5 | 4   | 16.1                    | 75.1                   | 12.09          |
| 18  | 181  | 17.5 | 4   | 6.47                    | 19.52                  | 1.26           |
| 19  | 350  | 17.5 | 7   | 7.91                    | 24.63                  | 1.94           |
| 20  | 450  | 5    | 2   | 5.75                    | 42.46                  | 2.44           |

The CO$_2$ conversion, $X_{CO_2}$, and methanol selectivity, $S_{MEOH}$, were taken as the response variables of the designed experiments. The design of experiment was tabulated in Table 2 and the experimental data were then modeled using polynomial Equation (1) (CO$_2$ conversion) and Equation (2) (methanol selectivity).

\[
X_{CO_2} = 15.84 - 0.052A + 0.38B + 0.18C + 1.52AB + 0.52AC - 3.10A^2 - 1.80B^2 - 3.92C^2 \]  
(1)

\[
S_{MEOH} = 74.09 + 11.79A + 4.92B - 7.10C - 5.03AB + 2.62BC - 5.40BC - 12.25 A^2 - 8.45B^2 - 16.67C^2 \]  
(2)

2.2. Regression Model Equation and Analysis of Variance (ANOVA)

To determine the best model for both responses, the proposed model should be considered as a favorable beginning [21]. The proposed model by the software is the quadratic model, which shows that both models are adequately sufficient to describe the calcination condition within the experimental range.

As shown in Table 3 for first response parameter, $X_{CO_2}$, the quadratic model is suggested with high significance at a 5% confidence level as indicated by low p-value < 0.0001. On the other hand, the insignificant lack of fit (LOF) value (0.0711), of this study indicates that the model is a good representation of the response as the probability for lack of fit describes the variation of the data around the fitted model. The determination coefficient ($R^2$) values which measures the fitness of the data with the model is at 93%, suggesting that the model is significant with $R^2$ value and adjusted $R^2$ of 0.93 and 0.87, respectively. The value is acceptable because it is very close to unity. The $R^2$ value illustrate the closeness of the selected model to the experimental data points. Meanwhile, the adjusted $R^2$ describes the
amount of variation about the mean explained by the model [21]. Furthermore, adequate precision values of the model also show a value higher than 4, which is desirable for the design with value of 15.31.

For a second response, \( S_{\text{MEOH}} \), the model is also proved to be significant with \( R^2 \) value up to 0.96 and LOF of 0.2813.

### Table 3. Analysis of variance (ANOVA) for the calcination study of MNCZAZ.

| Source       | \( X_{\text{CO}_2} \) | \( S_{\text{MEOH}} \) |
|--------------|------------------|------------------|
| Standard deviation | 1.59             | 5.84             |
| \( R^2 \)       | 0.93             | 0.96             |
| Adjusted \( R^2 \) | 0.87             | 0.93             |
| Adequate precision | 9.75             | 15.36            |
| \( p \)-value | <0.0001          | <0.0001          |
| F-value       | 15.31            | 28.86            |
| LOF           | 0.0711           | 0.2813           |

Multiple regression coefficient of a second order polynomial model describing the effect of catalyst (MNCZAZ) calcination conditions on the values of \( X_{\text{CO}_2} \) and \( S_{\text{MEOH}} \) are summarized in Tables 4 and 5, respectively. The significance of each coefficient was determined by \( F \)-value and \( p \)-value. The \( p \)-value is considered as significant if the value is less than 0.05. For the calcination condition effect of the catalyst (MNCZAZ) on \( X_{\text{CO}_2} \), the interaction between first order effect of A (temperature) and B (ramping rate) are significant at \( p \) value of 0.0224 while the other interactions are not significant (\( p > 0.05 \)). Furthermore, the second order effect of A (temperature) and C (duration) are also significant with \( p \)-value of <0.0001. The same trend is also observed with second order effect of B (ramping rate) with \( p \)-value = 0.0044. The coefficient estimate values of the regression model are \( A = 0.052 \) (temperature), \( B = 0.38 \) (ramping rate), and \( C = 0.18 \) (duration). Therefore, ramping rate has the highest effect on the response \( X_{\text{CO}_2} \), followed by duration and temperature, summarized as \( B > C > A \).

### Table 4. Coefficient of regression model and their significance for first response, \( X_{\text{CO}_2} \).

| Source | Coefficient Estimate | \( F \)-Value | Prob. > \( F \) | Remarks |
|--------|----------------------|--------------|----------------|---------|
| Quadratic model |                      | 15.31        | <0.0001        | significant |
| A      | -0.052               | 0.015        | 0.9063         | insignificant |
| B      | 0.38                 | 0.61         | 0.4545         | insignificant |
| C      | 0.18                 | 0.16         | 0.6949         | insignificant |
| AB     | 1.52                 | 7.27         | 0.0224         | significant |
| AC     | 0.52                 | 0.86         | 0.3758         | insignificant |
| BC     | 0.52                 | 0.84         | 0.3802         | insignificant |
| \( A^2 \)    | -3.10                | 55.75        | <0.0001        | significant |
| \( B^2 \)   | -1.80                | 13.41        | 0.0044         | significant |
| \( C^2 \)   | -3.90                | 62.38        | <0.0001        | significant |

Effects of catalyst (MNCZAZ) calcination conditions on the second response, \( S_{\text{MEOH}} \), are shown in Table 5. All three first order effects of A (temperature), B (heating ramp), and C (heating duration) are significant with \( p \)-value of <0.0001, 0.0208, and 0.0016, respectively. The interaction between the first order effect of AB and BC are also significant with \( p \)-value of 0.0352 and 0.0257, respectively. In addition, the second order effect of A, B, and C are also significant with \( p \)-values \leq 0.0009. The coefficient estimate values of the \( S_{\text{MEOH}} \) regression model are \( A = 11.79 \) (temperature), \( C = 7.10 \) (duration), and \( B = 4.92 \) (ramping rate).

Based on the corresponding \( p \)-value, the first order effect of B is least significant amongst the variables studied as it has lowest coefficient estimation Therefore, temperature
has the highest effect to the response $S_{\text{MEOH}}$, followed by duration and ramping rate, summarized as $A > C > B$.

**Table 5.** Coefficient of regression model and their significance for second response, $S_{\text{MEOH}}$.

| Source       | Coefficient Estimate | F-Value | Prob. > F | Remarks     |
|--------------|----------------------|---------|-----------|-------------|
| Quadratic model | 28.86                | <0.0001 | significant |
| A            | 11.79                | 55.74   | <0.0001   | significant |
| B            | 4.92                 | 7.51    | 0.0208    | significant |
| C            | -7.10                | 18.48   | 0.0016    | significant |
| AB           | -5.03                | 5.93    | 0.0352    | significant |
| AC           | 2.62                 | 1.61    | 0.2336    | insignificant |
| BC           | -5.40                | 6.85    | 0.0257    | significant |
| $A^2$        | -12.25               | 64.72   | <0.0001   | significant |
| $B^2$        | -8.45                | 21.84   | 0.0009    | significant |
| $C^2$        | -16.67               | 83.45   | <0.0001   | significant |

2.3. Interaction Effect of Calcination Condition of Catalyst (MNCZAZ)

The optimum response and the relationship between significant model terms are illustrated in Figures 1–6 which exhibit the 3-D curvature and its respective contour plots for:

1. temperature and ramping rate (AB)
2. temperature and duration (AC)
3. ramping rate and duration (BC)

These are the three possible two-factor combination interactions for studying the effects of catalyst (MNCZAZ) calcination conditions on the values of $X_{\text{CO}_2}$ and $S_{\text{MEOH}}$.

Figure 1 shows the simultaneous effects of A and B variables which have the most significant influence on the CO$_2$ conversion ($X_{\text{CO}_2}$). The values of $X_{\text{CO}_2}$ increased when A and B were increased from 181–350 (°C) and 5–17.5 (°C/min), respectively. Increasing the calcination temperature further to 450 and 518 (°C) caused $X_{\text{CO}_2}$ to decrease significantly by 10–13% from that of the highest value (16.01%). The same trend was observed when the calcination temperature was decreased from 250 to 181 (°C).

![Figure 1. Interaction effects of AB on CO$_2$ conversion.](image-url)
Interaction effects of AB and AC on methanol selectivity are depicted in Figures 4 and 5, respectively. Figure 6 shows the simultaneous effects of B and C, which exhibit the most significant influence on methanol selectivity, \( S_{\text{MEOH}} \) study. The selectivity to methanol was maximized when B was at the center point at 17.5 °C/min and C was increased from 1–4 (h). Increasing or decreasing the ramping rate of 17.5 (°C/min) and duration longer than 4 h caused the \( S_{\text{MEOH}} \) to decrease significantly by 70–90% from the highest value of 75.86%.
Figure 4. Interaction Effect of AB for methanol selectivity.

Figure 5. Interaction Effect of AC for methanol selectivity.
2.4. Diagnostic Plots of the Calcination Parameters to $X_{\text{CO}_2}$ and $S_{\text{MEOH}}$ Responses

Residual analysis was applied to both models for adequacy inspection to avoid any inadequate fit of the approximating model. The normal probability plots shown in Figures 7 and 8a implied that the experimental data fitted well to the straight lines. These trends indicated normal distribution of the data, thus confirming the normality of the experimental data. The qualification of fit data plots, shown in Figures 7 and 8b, further confirmed good representation of the established polynomial model. The statement was validated as the actual data points fell near the straight line within acceptable variance range, when compared to the calculated value [22]. Based on this analysis, the optimal calcination condition for the catalyst (MNCZAZ) was then calculated using Equation (1) for $X_{\text{CO}_2}$ and Equation (2) for $S_{\text{MEOH}}$ experiments. To summarize, the analysis agreed with the experimental data where the difference between the calculated and experimental optimal point for $X_{\text{CO}_2}$ and $S_{\text{MEOH}}$ was only 4.32 and 2.81%, respectively (Table 6).

Table 6. Optimum conditions for the synthesized catalyst (MNCZAZ).

| Variables                     | Units       | Optimum Conditions |
|-------------------------------|-------------|--------------------|
| A                             | °C          | 342                |
| B                             | °C/min      | 17.9               |
| C                             | h           | 4                  |
| $X_{\text{CO}_2}$, activity, calculated | %           | 16.2               |
| $X_{\text{CO}_2}$, activity, experimental | %           | 15.5               |
| Percentage error, $X_{\text{CO}_2}$ | %           | 4.32               |
| $S_{\text{MEOH}}$ activity, calculated | %           | 74.7               |
| $S_{\text{MEOH}}$ activity, experimental | %           | 72.6               |
| Percentage error, $S_{\text{MEOH}}$ | %           | 2.81               |
| Standard deviation            | %           | 1.01               |
2.5. RSM Optimizations of Calcination Parameters

The main objective of RSM is to determine the optimum condition for the process. From the analysis, the optimum calcination parameters for CO$_2$ hydrogenation activity of the synthesized catalyst (MNCZAZ) are summarized in Table 6. The selected optimum conditions were based on the maximum $X_{CO_2}$ and $S_{MEOH}$ and its desirability, which is 1.000. Using the same experimental method, three confirmation runs were conducted to validate the results. The calculated $X_{CO_2}$ and $S_{MEOH}$ activity differences with experimental...
values were approximately 0.7% to 2.1%, respectively. The percentage errors difference between the calculated and experimental values were within the acceptable value of 5%. Thus, these repeated optimized runs further confirmed the reliability of the regression equation model.

2.6. Textural and Morphological Properties

Figure 9 shows the field-emission scanning electron microscopy (FESEM) image and the elemental maps of the Cu, Zn, Al, Zr of the MNCZAZ catalyst. This elemental map shows that both CuO and ZnO were dispersed on the Al$_2$O$_3$-ZrO$_2$ support with slight agglomeration on the surface (represented by the scattered green and yellow spots).

![Figure 9. (a) FESEM image (b) Elemental mapping of MNCZAZ catalyst obtained by energy dispersive X-ray (FESEM/EDX).](image)

Table 7 shows the impregnated elemental composition of the catalyst, as determined by X-Ray fluorescence (XRF) technique. The compositions of Cu and Zn as well the Mn and Nb promoters were found to be in good agreement with the theoretical values.

| Weight (%) | Cu    | Zn    | Mn    | Nb    |
|------------|-------|-------|-------|-------|
|            | 11.27 | 3.72  | 0.05  | 0.04  |

Table 8 shows the textural properties of some of the catalysts which were calcined under various conditions. The data were arranged from the highest to the lowest calcination temperature. The results of ANOVA indicated that calcination temperature had the highest effect to the methanol selectivity. The BET surface areas and pore diameters of the catalyst were found to be influenced by the calcination temperature. The BET surface area increased from 137 m$^2$/g to 167 m$^2$/g as the calcination temperature decreased from 518 °C to 181 °C at the same condition of 17.5 °C/min ramping rate and 4 h duration. An opposite trend was observed for the pore diameter which decreased from 8.9 nm to 7.4 nm when the calcination temperature decreased from 518 to 181 °C. Near the optimum calcination condition, the catalyst exhibited a BET surface area of 147 m$^2$/g, a pore volume of 0.31 cm$^3$/g, and a pore diameter of 8.1 nm, which resulted in the highest methanol selectivity.
Table 8. Textural properties of catalysts calcined under different conditions.

| Temperature (°C) | Ramping Rate (°C/min) | Duration (h) | \(S_{\text{BET}}\) (m²/g) | \(V_p\) (cm³/g) | \(D_{\text{BJH}}\) (nm) | \(X_{\text{CO}_2}\) (%) | \(S_{\text{MeOH}}\) (%) |
|----------------|----------------------|--------------|-----------------|----------------|----------------|----------------|----------------|
| 518            | 17.5                 | 4            | 137             | 0.31           | 8.9            | 7.19           | 58.35          |
| 450            | 5                    | 6            | 143             | 0.31           | 8.6            | 3.35           | 52.39          |
| 350            | 10                   | 4            | 140             | 0.31           | 6.2            | 15.81          | 68.77          |
| 350            | 17.5                 | 4            | 147             | 0.31           | 8.1            | 16.02          | 75.86          |
| 250            | 5                    | 6            | 123             | 0.24           | 7.6            | 7.87           | 5.57           |
| 181            | 17.5                 | 4            | 167             | 0.31           | 7.4            | 6.47           | 19.52          |

\(S_{\text{BET}}\) is BET surface area; \(V_p\) is pore volume; and \(D_{\text{BJH}}\) is the BJH pore diameter.

3. Materials and Methods

3.1. Experimental Design

A standard response surface methodology (RSM) design, also known as central composite design (CCD), was used to study the calcination parameters of the synthesized Cu-based catalyst (MNCZAZ) for CO₂ hydrogenation reaction. The calcination parameters investigated were the temperature, ramping rate, and duration. An empirical model was developed to correlate the response \(X_{\text{CO}_2}\) and \(S_{\text{MeOH}}\) to the three respective parameters affecting the CO₂ hydrogenation process in methanol synthesis by using a second-degree polynomial equation, as given by the following equation.

\[
\gamma = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_12 A + \beta_13 AC + \beta_23 BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \tag{3}
\]

where \(\gamma\) is the predicted response; \(\beta_0\) is the constant coefficient; \(\beta_1, \beta_2\) and \(\beta_3\) are the linear coefficients; \(\beta_12, \beta_13,\) and \(\beta_23\) are the interaction coefficients; \(\beta_{11}, \beta_{22},\) and \(\beta_{33}\) are the quadratic coefficients; and \(A, B, C\) are the coded values of independent input parameters.

To correlate between all responses and analyze the experimental condition with the highest desirability, Design Expert Version 10 (Stat Ease, Minneapolis, MN, USA) was utilized. Analysis of variance (ANOVA) explained every variation in the statistically obtained model and illustrates the importance of each model parameter. The F-test for a confidence level of 95% as well as the lack of fit (LOF) test was used to evaluate the significance of the model. Typically, the model is classified as more significant when it shows greater F-value and smaller \(p\)-value.

3.2. Preparation and Characterization of MNCZAZ Catalyst

To synthesize 10 g MNCZAZ catalyst, 0.021 g of Mn(NO₃)₂·4H₂O [Merck, Subang Jaya, Malaysia], 0.014 g of C₄H₄NNbO₉ [Merck, Malaysia], 3.995 g of Cu(NO₃)₂ [Merck, Malaysia], and 1.644 g of Zn(NO₃)₂ [Sigma Aldrich, Malaysia], were stirred for 1 h in deionized water then added drop wisely onto the Al₂O₃-ZrO₂ [SASOL, Hamburg, Germany] powder. The composition of the mixed support was 80 wt% Al₂O₃ and 20 wt% ZrO₂. The slurry was continuously stirred for 24 h at pH 7 using 10% ammonia solution, NH₄OH [Merck, Malaysia] to maintain the pH. The mixture was filtered and dried at 120 °C for 12 h and then calcined in air under the calcination conditions listed in Table 2.

The surface morphology of the synthesized samples was observed on a Hitachi-8020 field-emission scanning electron microscope (FESEM/EDX) (Hitachi High-Technologies Corporation, Tokyo, Japan) The textural properties were obtained via nitrogen adsorption-desorption isotherms measured on a Micromeritics ASAP 2020 adsorption analyzer (Micromeritics Instrument Corporation, Norcross, GA, USA) Metal contents were determined by X-ray fluorescence using a Bruker S8 Tiger X-ray Spectrometer (Bruker, Wissembourg, France).
3.3. Catalytic Performance Evaluation of MNCZAZ Catalyst

Catalytic activity evaluation was performed in a stainless-steel fixed-bed reactor (Microactivity Reference, PID Eng Tech, Norcross, GA, USA). A 0.2 g sample was reduced in situ by pure H2 flowing at 20 mL min\(^{-1}\) for 2 h prior to the hydrogenation process. Then, CO\(_2\) hydrogenation reaction was performed on the reduced catalyst at 22.5 bar, 250 °C, and CO\(_2\): H\(_2\) (1:3) with a total flow rate of 36 mL/min for 5 h. The reaction condition was fixed for all the catalysts synthesized according to the design matrix (Table 2). A gas chromatograph (Agilent 7890A) equipped with a TCD detector for H\(_2\) and CO\(_2\) analysis, and an FID detector for analysis of alcohols and other hydrocarbons, were used to analyze the reactor effluents [23]. CO\(_2\) conversion, methanol selectivity, and methanol yield were calculated using Equations (4)–(6), respectively.

\[
\text{CO}_2 \text{ conversion}\% = \frac{\text{Mole of CO}_2 \text{ in} - \text{Mole of CO}_2 \text{ out}}{\text{Mole of CO}_2 \text{ in}} \times 100 \quad (4)
\]

\[
\text{Methanol selectivity}\% = \frac{\text{mole of methanol produced}}{\text{total mole of product}} \times 100 \quad (5)
\]

\[
\text{Methanol yield}\% = \frac{\text{CO}_2 \text{ conversion}\%}{100} \times \text{Methanol selectivity}\% \quad (6)
\]

4. Conclusions

In conclusion, the calcination conditions of Cu-based catalysts for methanol synthesis through CO\(_2\) hydrogenation process was optimized using RCCD of RSM. Quadratic model was proposed to correlate the experimental variables for both CO\(_2\) conversion (\(X_{\text{CO}_2}\)) and methanol selectivity (\(S_{\text{MEOH}}\)) responses. It was found that the model was able to predict the experimental data to high accuracy for \(X_{\text{CO}_2}\) and \(S_{\text{MEOH}}\) with \(R^2\) of 0.93 and 0.96, respectively. The interactions among the calcination temperature, A, and ramping rate, B, were found to have the most significant effect on the CO\(_2\) conversion; meanwhile, the calcination’s ramping rate and duration (B and C) had a significant effect on the methanol selectivity. The optimization of calcination conditions was studied and the computed values by the models were found to be in good agreement with the experimental values. The optimum calcination condition for a Mn/Nb-promoted Cu/ZnO/Al\(_2\)O\(_3\)-ZrO\(_2\) catalyst (MNCZAZ) for a CO\(_2\) hydrogenation reaction to produce methanol is at 342 °C, with a ramping rate of 17.9 °C per min for 4 h. Confirmatory experiments were conducted to evaluate the accuracy of the optimized conditions and the findings show that the range of deviation was 1.01%.

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