MODELING AND OPTIMIZATION OF PROPANE SELECTIVE OXIDATION TO ACRYLIC ACID OVER $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_X$ CATALYST USING ARTIFICIAL NEURAL NETWORK AND BOX-BEHNKEN DESIGN

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Abstract: The prediction capability of response surface methodology (RSM) and artificial neural network (ANN) models for propane selective oxidation to acrylic acid (AA) over $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst was investigated in this work. 15 experimental runs based on the Box-Behnken design (BBD) were employed to study the effects of temperature (380 to 500 °C), superficial velocity (33.3 to 66.7 mL (min g_{cat})$^{-1}$), $(O_2)/(C_3H_8)$ ratio (1 to 3) and their interactions on propane conversion, AA selectivity and CO_x selectivity. The quadratic polynomial BBD equations and the feed-forward back propagation ANN models were developed based on the designed experimental data. Statistical analysis; coefficient of determination (R^2), mean absolute error (MAE) and analysis of variance (ANOVA) illustrated that there was acceptable adjustment between BBD and ANN predicted responses as compared to experimental data. While, the ANN model showed a clear preference and generalization capability over BBD model in the case of experimental data set which were not used to training the models. In addition the optimum conditions were found to be temperature (461.7 °C), GHSV (51.9 mL (min g_{cat})$^{-1}$) and $(O_2)/(C_3H_8)$ ratio (2.1) which were determined by desirability function approach. In these conditions, propane conversion of 15.2%, AA selectivity of 32% and CO_x selectivity of 44% which obtained experimentally were in reasonable agreement with predicted responses.

Keywords: *Catalysis, Optimization; Neural network; Box-Behnken method; Propane selective oxidation; Acrylic acid; $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$*

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1. Introduction

In the last three decades, selective oxidation of light alkanes to olefins and oxygenated products, in particular propane to acrylic acid (AA) could bring intense attention in the research areas due to the lower cost of alkanes as well as lower environmental impacts [1-3]. For propane selective oxidation to AA, the developed catalysts can be categorized in three groups: heteropolyacids, vanadyl phosphates and mixed metal oxides [4]. Among different catalysts, MoVTeNbO mixed metal oxides have been proposed as a promising catalyst for this reaction [4].

In selective oxidation of propane over MoVTeNbO catalyst, alongside AA, propylene, acrolein, CO_x, Acetone, acetic acid and propanoic acid are usually produced. Although many efforts have been carried out to enhancement the efficiency of the direct oxidation of propane to AA, commercial applications are hindered yet due to the inadequate AA yield of current catalyst formulations. Besides promotion the inherent properties of the catalyst [5, 6], different reactor technologies have also been investigated in order to improve catalytic performance and AA yield [7-10]. In addition, the product distribution and catalytic performance can be influenced significantly by reaction conditions including temperature, GHSV and feed ratio [11-13]. The optimization of operating conditions plays a key role to obtain good catalytic results. In the previous published literature [11-13], the effects of the operating variables on the catalytic performance have been investigated using traditional one-factor-at-a-time approach. This method is very costly and time-consuming, especially when the number of variables that have been considered for the study, is high. Also, the

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interaction effects of the input parameters on the output response have not been figured out with one-factor-at-a-time approach. This drawback can lead to the missing optimum process set points. Design of experiments (DoE) based on the response surface methodology and artificial neural network (ANN) provides beneficial approach to study process conditions.

DoE is a collection of statistical and mathematical methods for evaluating the effects of different factors and the interaction among them with the aim of searching optimum conditions required for desired response [14]. One of the most relevant DoE methods is response surface methodology (RSM) based on the Box-Behnken design(BBD) which has been widely employed in the literature for optimization of reaction conditions [15] as well as catalyst preparation [16, 17]. The BBD is a three levels factorial design with systematic selected points from the full three levels factorial arrangements which can be used to create a second order polynomial function. In this way the number of experimental runs can be reduced. Therefore, this method, especially in the cases where large numbers of factors are studied, is very cost effective.

Besides DoE, ANN is a useful modeling tool which has been inspired by learning process of the brain. In recent years, the popularity of ANN has grown in many areas of chemical engineering including: catalyst design [18], kinetic modeling [19], process condition [18, 20] and modeling of the reactors [21]. The main feature of the ANN is its capability for functional prediction and system modeling where the problems are not understood properly or highly complex [19]. A typical neural network composed of an input layer, one or more hidden layers and an output layer. Each layer has a certain number of neurons which are linked together by adjustable weights and biases. Complex relationships between inputs and outputs variables can be simulated using training network. Training the network is the process in which the weights and biases are determined with an iterative algorithm in such a way that the errors between the model-calculated and the actual value of the outputs are minimized. In this work, the effects of reaction conditions: temperature, GHSV and $(O_2)/(C_3H_8)$ ratio and their interactions in selective oxidation of propane over $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$were studied using BBD statistical analysis. In addition, the optimum conditions for AA production were predicted using desirability function approach. Moreover, the predictive and generalization capability of ANN to determine catalytic performance were investigated. Also the efficiency of the BBD and ANN models were compared statistically by the coefficient of determination (R^2) and mean absolute error (MAE) based on the experimental data which were not used to models development. To our knowledge, there was no attempt on BBD and ANN modeling of catalytic performance in propane selective oxidation to AA. The catalyst was synthesized by slurry method and activity tests were carried out in laboratory scale fixed bed reactor.

2. Materials and methods

2.1. Catalyst synthesis

Slurry method has been used to produce $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst [12]. Appropriate amount of ammonium monovanadate (Merck), ammonium heptamolybdate tetrahydrate (Merck), niobium oxalate hydrate (Alfa Aesar), telluric acid (Fluka) were dissolved in de-ionized water to obtain uniform slurry. The prepared slurry was stirred vigorously until its water was eliminated at a bath temperature of 60 °C. Calcination was carried out in a nitrogen flow environment at 600 °C. The furnace was heated at a rate of 5 °C/min up to 600 °C and held at that temperature for 2 h. The catalyst preparation procedure has been described in our previous work in detail [22].

2.2. Catalytic activity test

The catalytic performance of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst was evaluated in propane selective oxidation to AA using vertical, tubular quartz tube (i.e. 6 mm) at atmospheric pressure. The reactor was placed inside a vertical furnace which equipped with a PID temperature controller. The reactor temperature was measured by a K-type thermocouple placed just above the

catalyst bed. Propane, oxygen and nitrogen were fed into the reactor. Their flow rates were controlled using three mass flow controllers (Brooks). Specified flow rate of water was fed to the reactor using a syringe pump which converted to steam before entering into the reactor. The exited gases were passed through a cold trap at 0 °C and high boiling point products (water, propionic and acrylic acids) were separated. Rest of the products including CO, CO_2, propylene and un-reacted feed were analyzed by an on-line gas chromatograph equipped with TCD and FID detectors. The condensed liquid was also analyzed offline by a Lachrom HPLC, equipped with C8 column.

Propane conversion, AA selectivity and CO_x selectivity were calculated according to equations 1 to 3:

$$C_3H_8\ Conversion\,(\%) = \frac{F_{i,C_3H_8} - F_{o,C_3H_8}}{F_{i,C_3H_8}} * 100 \quad (1)$$

$$AA\ Selectivity\ (\%) = \frac{F_{o,AA}}{F_{i,C_3H_8} - F_{o,C_3H_8}} * 100 \quad (2)$$

$$CO_x\ Selectivity\ (\%) = \frac{F_{o,CO_x}}{F_{i,C_3H_8} - F_{o,C_3H_8}} * 100 \quad (3)$$

2.3. Box-Behnken design

Product distribution and catalytic performance in propane selective oxidation have been affected considerably by operating conditions: temperature, residence time and feed compositions. Based on the well-documented literature the water vapor presence in the reaction feed increases significantly the AA selectivity as compared to the reaction in the absence of water [12, 13 and 23]. But as shown by Zhu et al. [12] the steam concentration has little effects on the product distribution. The effects of steam concentration were investigated in other works [22, 23]. Obtained results were indicated that the steam reaction order in the developed Mars-Van Krevelen kinetic model was near zero [22].

In this work the effects of reaction conditions including temperature (X_1), space velocity (X_2) and O_2/C_3H_8 ratio (X_3) have been investigated on the response factors: propane conversion (Y_1), AA selectivity (Y_2) and CO_x selectivity (Y_3). In the BBD, all factors have to be set up at three levels with equally distance apart. The higher and lower values of each factor were chosen based on the literature data and experimental set-up limitations. The input variables are encoded as +1, -1 and 0 for high, low and medial levels, which are shown in table 1. The number of experimental runs designed by the BBD is specified according to the equation 4 [14].

Table 1: Input factors at three levels in the BBD

Variables	Symbol	Real value of coded levels		
		-1	0	+1
Temperature (°C)	X_1	380	440	500
Space velocity (mL min^{-1} g_{cat}^{-1})	X_2	33.3	50	66.7
$(O_2)/(C_3H_8)$	X_3	1	2	3

$$N = 2K(K-1) + C_p \quad (4)$$

Where N is the number of experimental runs, K is the number of input variables and C_p is the central point replications. At least 3 replications of central point are needed to pure error estimation of activity test. The total 15 experiments designed by BBD with their configurations and three response factors, propane conversion, AA selectivity and CO_x selectivity are shown in table 2. Reaction conditions and product distribution are depicted in supplementary data, in detail. As can be seen, the steam/C_3H_8 ratio was fixed at 7.5 in each experimental run; the main products in this work were AA, propylene and CO_x. Trace amounts of propionic acid were also produced.

In order to modeling the relationship between input variables and response factors, a quadratic polynomial equation (equation 5) was applied for fitting experimental data.

$$Y_i = \beta_0 + \sum_{j=1}^{K} \beta_j X_j + \sum_{j=1}^{K} \beta_{jj} X_j^2 + \sum \sum_{i<j}^{K} \beta_{ij} X_i X_j \quad (5)$$

Where Y_i, β_0, β_j, β_{jj}, β_{ij} and X are the response factor, the intercept, the linear effect, the square effect, the interaction effect and input variables. The analyzing and optimization procedures leading to maximum propane conversion, maximum AA selectivity, minimum CO_x selectivity, all the tables and figures were computed using Design Expert version 7.0.0 software.

Table 2: Box-Behnken design configuration with experimental responses

Run	X_1	X_2	X_3	Propane conversion (%)	AA selectivity (%)	CO_x selectivity (%)
1	500	66.7	2	26	15.2	74.8
2	380	33.3	2	4.1	32	36.9
3	440	66.7	3	7.8	31	42.9
4	440	50	2	9.8	40	32.2
5	440	33.3	1	12	21	65
6	440	66.7	1	6.2	33	40.7
7	380	50	3	4.1	32.7	25.5
8	500	50	3	35	9.2	82.9
9	440	50	2	10.5	38	33.7
10	440	33.3	3	14.9	18	70
11	500	33.3	2	36.3	5.9	88.8
12	380	50	1	2.6	30.6	23.4
13	380	66.7	2	2.4	35.6	17
14	440	50	2	9.8	40	34.5
15	500	50	1	28	12	77.7

2.4. Artificial neural network modeling

ANN is composed of input, hidden and output layers. The number of neurons in input and output layers is set equal to the input variables and output targets, respectively. The number of hidden layers as well as the number of neurons in the hidden layers had to be adjusted in order to approach the best fit of experimental data. Each input is modified by a weight. The neurons in the hidden layers will combine these weighted inputs with an activation function and use these to determine the output values. The training algorithm adjusts the weights between layers in order to minimize the errors between experimental and predicted data.

In this work, a feed forward back propagation ANN was developed. Feed forward is a type of neural network where the information moves only in forward direction through the neurons (i.e. do not form cycles like in recurrent networks) and the error between experimental and predicted data points is propagated backward through the network. The process is repeated until the error criteria are met. Temperature, GHSV and $(O_2)/(C_3H_8)$ ratio were considered as input neurons, while the output neurons were propane conversion, AA selectivity and CO_x selectivity. The BBD experimental data was used in developing ANN model (table 2). All the input and output data were normalized in the range of (-1,1) according to the equations 6 and 7 in order to prevent overflow, reducing errors as well as reducing the training time [24].

$$X_n = 2 * \frac{X - X_{\min}}{X_{\max} - X_{\min}} - 1 \quad (6)$$

$$Y_n = 2 * \frac{Y - Y_{\min}}{Y_{\max} - Y_{\min}} - 1 \quad (7)$$

Where X_n, Y_n, X and Y are the normalized value of the input, the normalized value of the target, input variable and target, respectively. The ANN in this study was trained by Levenberg-Marqurdt (LM) optimization algorithm and the performance function was mean square error (MSE) between output and target values (shown in equation 8).

$$MSE = \frac{\sum_{i=1}^{N} \left(Y_{i,e} - Y_{i,p}\right)^2}{N} \quad (8)$$

Where $Y_{i,e}$ and $Y_{i,p}$ are experimental and predicted outputs, respectively. N is the number of experimental data. MATLAB R2008a was used to implement the ANN in this study.

3. Results and discussion

3.1. Modeling by BBD

Propane conversion

The quadratic predictive BBD model of propane conversion based on the coded factors is given as equation 9. Where X_1, X_2 and X_3 are the coded input factors: temperature, space velocity and $(O_2)/(C_3H_8)$ ratio, respectively. The ANOVA was applied to figure out of the efficiency of the BBD model for propane conversion. The ANOVA results are shown in table 3.

$$C_3H_8 conversion\,(\%) = 10.03 + 14.05X_1 - 3.15X_2 + 1.63X_3 - 2.23X_1X_2 + 1.37X_1X_3 - 0.33X_2X_3 + 7.22X_1^2 + 0.021X_2^2 + 0.17X_3^2 \quad (9)$$

The model F-value was obtained 449.49 which implies that the model is significant. An R^2 of 0.9988 and highly significant p-value of the model (<0.05) further indicate the predictability of the developed BBD model. The lack of fit p-value for the model was 0.1989 indicates that lack of fit is not significant as compared to the pure error. Therefore, the model is well fitted to the experimental data and mean square of the lack of fit value is relevant to the inherent system errors. The p-value of the estimated coefficients of X_1, X_2, X_3, X_1X_2, X_1X_3 and X_1^2 are smaller than 0.05. So these model terms are significant. Other model terms with p-value greater than 0.1 are insignificant. Adeq. Precision is a signal to noise ratio. It evaluates the range of the predicted propane conversion values relative to the average prediction errors. A ratio greater than 4 is desirable. Adeq. Precision ratio of 61.109 indicates an adequate signal.

Table 3 ANOVA results for quadratic model of propane conversion by BBD

Source	Sum of squares	Degree of freedom	Mean square	F-value	p- Value
Model	1901.54	9	211.28	449.49	<0.0001
X_1	1579.22	1	1579.22	3322.34	<0.0001
X_2	79.38	1	79.38	167.00	<0.0001
X_3	21.13	1	21.13	44.44	0.0011
X_1X_2	19.80	1	19.80	41.66	0.0013
X_1X_3	7.56	1	7.56	15.91	0.0104
X_2X_3	0.42	1	0.42	0.89	0.3891
X_1^2	192.52	1	192.52	405.02	<0.0001
X_2^2	1.603E-003	1	1.603E-003	3.371E-003	0.9559
X_3^2	0.11	1	0.11	0.23	0.6541
Residual	2.38	5	0.48		
Lack of fit	2.05	3	0.68	4.18	0.1989
Pure error	0.33	2	0.16		
Total	1903.92	14			

R^2=0.9988, R^2_{adj}=0.9965, R^2_{pred}=0.9824, Std. Dev.=0.69, Mean=13.99, C.V.%=4.93, Adeq Precision=61.109

A major tool for checking whether the fit is reasonable is residual analysis using diagnostic plots. All the diagnostic plots of propane conversion BBD model have been shown in figure 1. Typically the standard deviations of residuals in a sample change significantly from one data point to another even if the standard deviations of the errors have the same value. In addition, the residuals magnitude depends on the units of the measurement. Thus making it difficult to use the residual as a way to detecting unusually predicted values without first studentizing.

Studentized residual is quotient obtained by dividing a residual on the estimate of residual standard deviation. All the observations are included in the process of estimating the variance. But it is desirable to measure the i^{th} residual when the fitted regression is based on all observations excluding the i^{th} response. If the former estimate is used the residual is said to be internally

studentized. If the latter is used, then it is used to be externally studentized [25].

The normal probability plot of residuals (shown in figure 1(a)) follows a straight line which satisfies the normal distribution of residuals. The normal distribution of the residuals suggests that the error terms are indeed normally distributed. The internally studentized residuals versus predicted values of propane conversion are shown in figure 1(b). All data points of internally studentized residuals have been dispersed in random pattern which indicates that the variance of original observations is equal for all values of response. Therefore, no apparent problems with the response were observed. Always internally and externally studentized residuals should lie in the range of -3.5 to +3.5 [26]. Unusual observations lead to studentized residuals out of the considered interval. In figures 1(b) and 1(c), the values of the internally as well as externally studentized residuals of propane conversion are within the desired range indicate the adequacy of the fitted model.

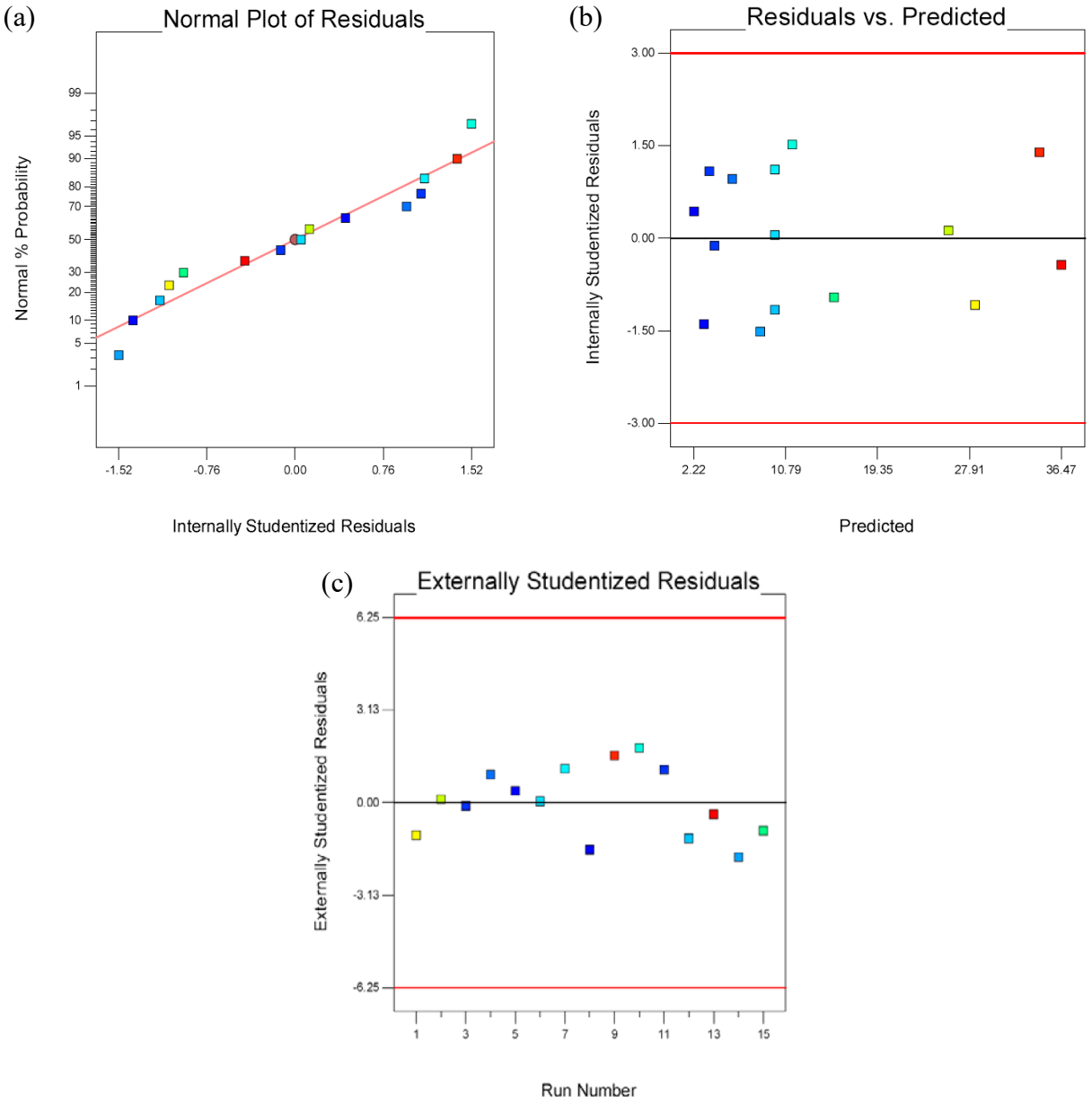


Figure 1 Diagnostic plots of propane conversion modeling using BBD

The effects of input variables; temperature, GHSV and $(O_2)/(C_3H_8)$ ratio on the propane conversion have been shown as a 3D response surface in figure 2. All of the experimental data collected in this work are consistent with the previous observations and conclusions reported in the literature [12, 27, 28]. It can be seen in figure 2 that temperature has great influence on propane conversion. The ANOVA analysis (table 3) has also shown that temperature is significant. The propane conversion increased from 4.1% at 380 °C and GHSV=33.3 mL min^{-1} g_{cat}^{-1} to 36.3% at 500 °C and GHSV=33.3 mL min^{-1} g_{cat}^{-1}. Propane is a saturated hydrocarbon and higher temperature is required for propane activation.

Thereby propane conversion increases as the reaction temperature is elevated. Increasing the GHSV leads to the reduction in the propane conversion. Since the exposure time of the propane and catalyst becomes shorter. However, space velocity is more effective at higher temperatures.

Figure 2 shows that higher oxygen concentration is desirable for propane activation and propane conversion elevates with the increasing $(O_2)/(C_3H_8)$ ratio. Similar to this work, Novakova et al. [28] and Widi et al. [27] have also reported that the effect of oxygen concentration on the propane disappearance is in the order of 0.26 and 0.24 respectively.

Acrylic acid selectivity

The quadratic predictive BBD model of the acrylic acid selectivity based on the coded factor is given as equation 10. Where X_1, X_2 and X_3 are the coded input factors: temperature, space velocity and $(O_2)/(C_3H_8)$ ratio, respectively. The ANOVA results are also shown in table 4.

$$\text{AA selectivity}\,(\%) = 39.33 - 11.07X_1 + 4.74X_2 - 0.71X_3 + 1.42X_1X_2 - 1.23X_1X_3 + 0.25X_2X_3 - 10.89X_1^2 - 6.27X_2^2 - 7.32X_3^2 \quad (10)$$

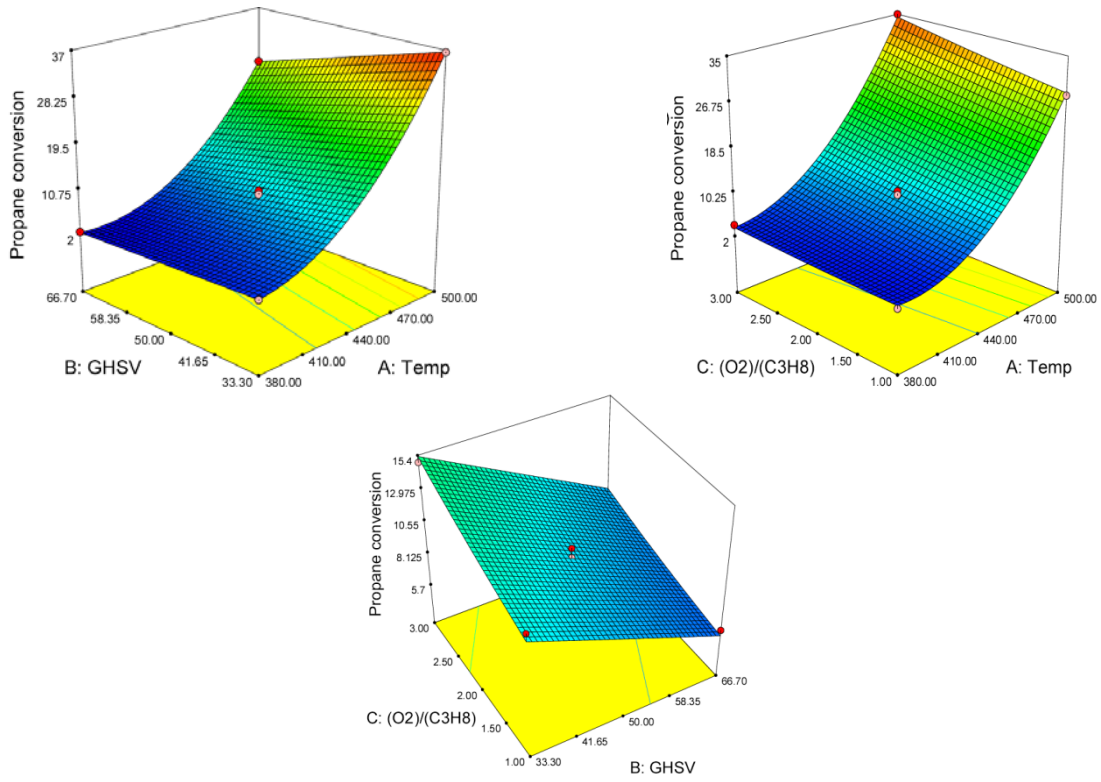


Figure 2 The effects of interaction between input variables on propane conversion as 3D response surface

Table 4 ANOVA results for quadratic model of AA selectivity by BBD

Source	Sum of squares	Degree of freedom	Mean square	F-value	p- Value
Model	1865.22	9	207.25	40.32	0.0004
X_1	981.25	1	981.25	190.91	<0.0001
X_2	179.55	1	179.55	34.93	0.0020
X_3	4.06	1	4.06	0.79	0.4148
X_1X_2	8.12	1	8.12	1.58	0.2642
X_1X_3	6.00	1	6.00	1.17	0.3292
X_2X_3	0.25	1	0.25	0.049	0.8342
X_1^2	438.01	1	438.01	85.22	0.0003
X_2^2	145.00	1	145.00	28.21	0.0032
X_3^2	197.66	1	197.66	38.46	0.0016
Residual	25.70	5	5.14		
Lack of fit	23.03	3	7.68	5.76	0.1515
Pure error	2.67	2	1.33		
Total	1890.92	14			

R^2=0.9864, R^2_{adj}=0.9619, R^2_{pred}=0.8019, Std. Dev.=2.17, Mean=26.28, C.V.%=8.63, Adeq Precision=18.581

The highly significant p-value of the model indicates the adequacy of the BBD model for acrylic acid selectivity. The lack of fit p-value of the model was 0.1515. There is a 15.15% chance that a "lack of fit F-value" this large could happen due to the noise. Therefore, the model predictions are well fitted to the experimental data. The R^2_{pred} of 0.8019 is in reasonable agreement with R^2_{adj} of 0.9619. Adeq. Precision was obtained 18.581 which is greater than 4 required to support statistical prediction fitness. The p-value of the estimated coefficients of X_1, X_2, X_1^2, X_2^2 and X_3^2 are smaller than 0.05. So these model terms are significant. Other model terms are insignificant.

All the diagnostic plots of acrylic acid selectivity BBD model have been shown in figure 3 to evaluate the validation of the regression. The normal distribution of the response has been checked by normal probability plot versus studentized residuals (figure 3(a)). It can be seen that all the normal probability of residuals was near the straight line suggest that no problems with the normality of experimental data were existed. Random dispersion of studentized residuals vs. predicted acrylic acid selectivity has been demonstrated in figure 3(b). Also internally as well as externally studentized residuals fall into the desired range of -3.5 to 3.5 (figures 3(b) and 3(c)).

The effects of input variables; temperature, GHSV and $(O_2)/(C_3H_8)$ ratio on the acrylic acid selectivity have been shown as a 3D response surface in figure 4. As the temperature is elevated, the acrylic acid selectivity attains a slight maximum value and then reduces strongly by further increasing in the reaction temperature. Oh et al. [11] have also reported a maximum in acrylic acid selectivity at 400°C as temperature is increasing from 370 to 520°C. Acrylic acid is more reactive component than propane. Therefore, increasing reaction temperature would accelerate the deep oxidation of acrylic acid to CO_x.

It can be seen that semi-spherical response surface of acrylic acid selectivity, interestingly, passes through a maximum as GHSV increases from 33.3 mL $min^{-1}g_{cat}^{-1}$ to 66.7 mL $min^{-1}g_{cat}^{-1}$. Reaction pathway in the selective oxidation of propane over different catalysts has been investigated widely [27, 28, 29-31]. A reaction network for propane oxidation over MoVSbNbO catalyst has been proposed by Novakova et al. [28] and shown in scheme 1. It can be seen that first propane is dehydrogenated to propylene which is oxidized to acrylic acid through acrole in as intermediate. Decline acrylic acid selectivity with increase in GHSV from 50 mL $min^{-1}g_{cat}^{-1}$ to 66.7 mL $min^{-1}g_{cat}^{-1}$ (figure 4) also confirms that acrylic acid is not a primary product. With decreasing contact time of the components with catalyst, part of the propylene leaves the reactor without chance of being oxidized to acrylic acid. So selectivity to acrylic acid decreases when GHSV is in the range of 50 mL $min^{-1}g_{cat}^{-1}$ to 66.7 mL $min^{-1}g_{cat}^{-1}$.

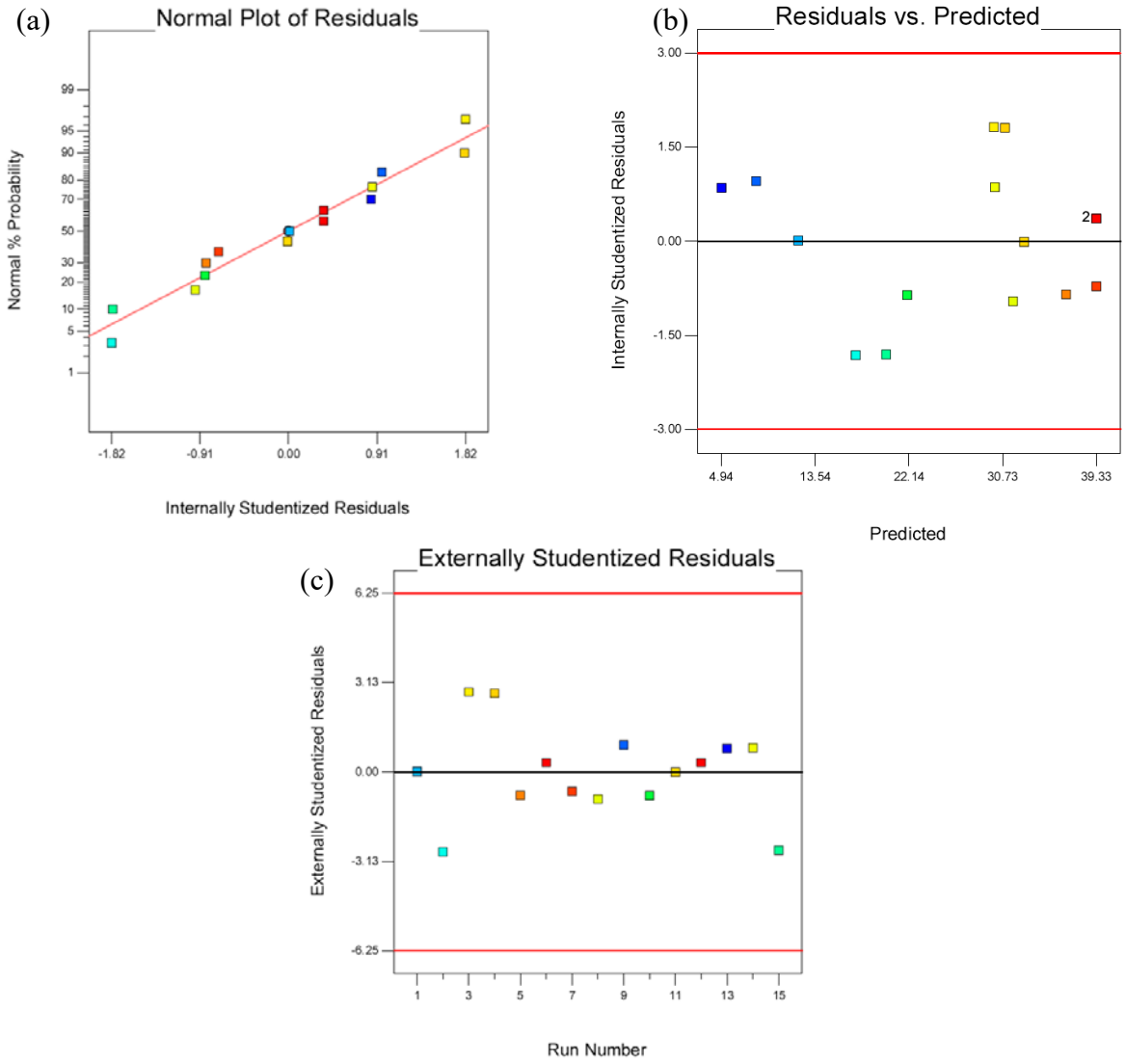


Figure 3 Diagnostic plots of acrylic acid selectivity modeling using BBD

ANOVA analysis shown in table 4 indicates that $(O_2)/(C_3H_8)$ ratio is not a significant variable in acrylic acid selectivity. Based on the well documented literature [22, 32, 33], the selective oxidation of propane is believed to proceed through Mars-Van Krevelen (MVK) mechanism. In the MVK mechanism, hydrocarbon reacts with lattice oxygen to form products followed by re-oxidation of reduced sites by gas phase oxygen. Grasselli et al. [33] have suggested that re-oxidation of reduced sites is a fast reaction as compared to their reduction by hydrocarbons conversions. So lattice oxygen is always available and oxygen concentration has negligible effects on acrylic acid selectivity.

CO_x selectivity

The quadratic predictive BBD model of the CO_x selectivity based on the coded factor is given as equation 11. Where X_1, X_2 and X_3 are the coded input factors: temperature, space velocity and $(O_2)/(C_3H_8)$ ratio, respectively. The ANOVA results are also shown in table 5.

$$CO_x\ Selectivity(\%) = 33.47 + 27.67X_1 - 10.66X_2 + 1.81X_3 + 1.48X_1X_2 + 0.78X_1X_3 - 0.7X_2X_3 + 9.32X_1^2 + 11.59X_2^2 + 9.59X_3^2 \quad (11)$$

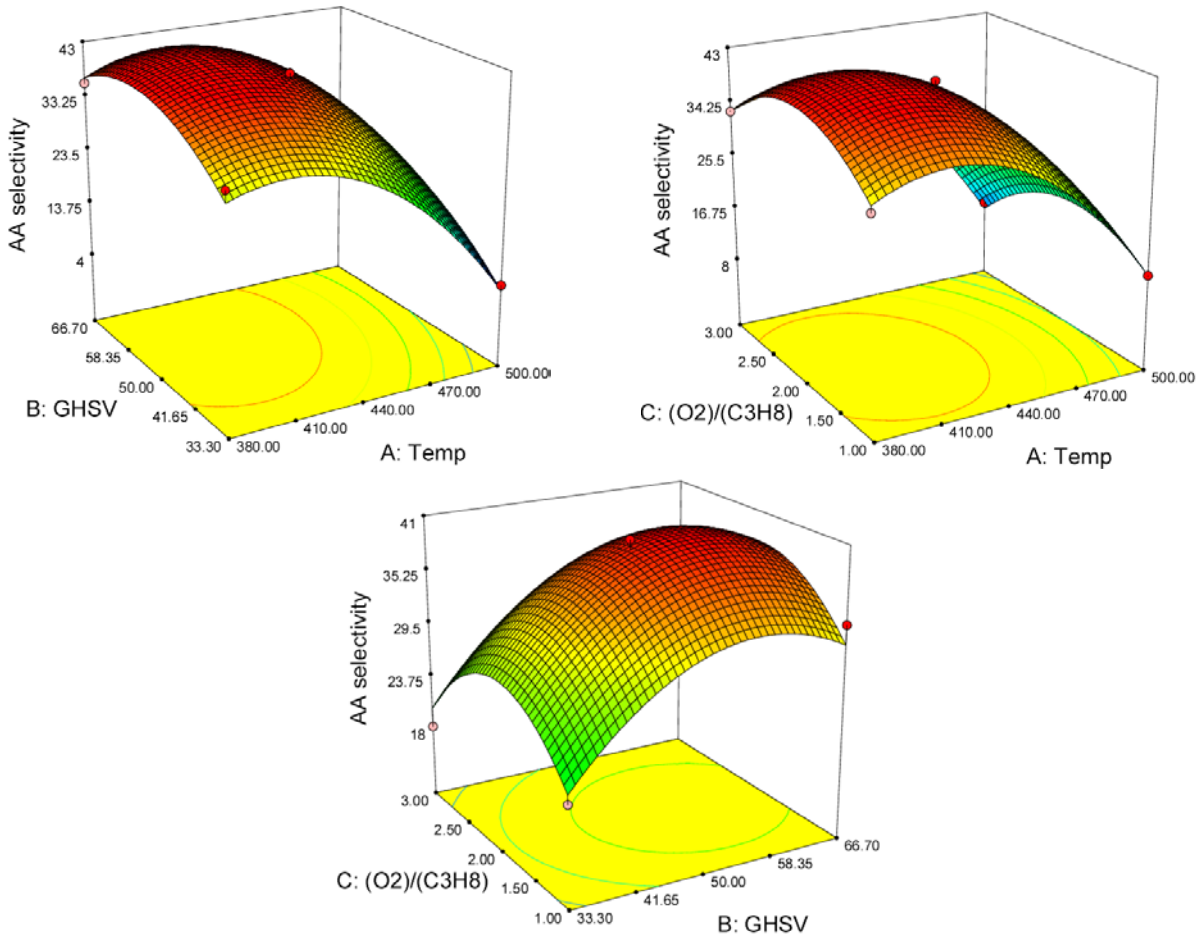
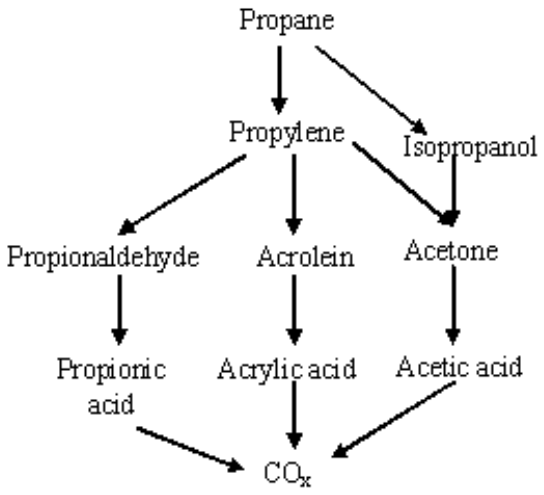


Figure 4 The effects of interaction between input variables on acrylic acid selectivity as 3D response surface



Scheme 1 Proposed reaction networks for propane oxidation over MoVSbNbO catalysts [18]

Table 5ANOVA results for quadratic model of CO_x selectivity by BBD

Source	Sum of squares	Degree of freedom	Mean square	F-value	p- Value
Model	8080.70	9	897.86	108.15	<0.0001
X_1	6127.24	1	6127.24	738.06	<0.0001
X_2	909.51	1	909.51	109.56	0.0001
X_3	26.28	1	26.28	3.17	0.1353
X_1X_2	8.70	1	8.70	1.05	0.3529
X_1X_3	2.40	1	2.40	0.29	0.6137
X_2X_3	1.96	1	1.96	0.24	0.6476
X_1^2	320.49	1	320.49	38.61	0.0016
X_2^2	496.12	1	496.12	59.76	0.0006
X_3^2	339.69	1	339.69	40.92	0.0014
Residual	41.51	5	8.30		
Lack of fit	38.78	3	12.93	9.48	0.0969
Pure error	2.73	2	1.36		
Total	8122.21	14			

R^2=0.9949, R^2_{adj}=0.9857, R^2_{pred}=0.9228, Std. Dev.=2.88, Mean=49.73, C.V.%=5.79, Adeq Precision=32.592

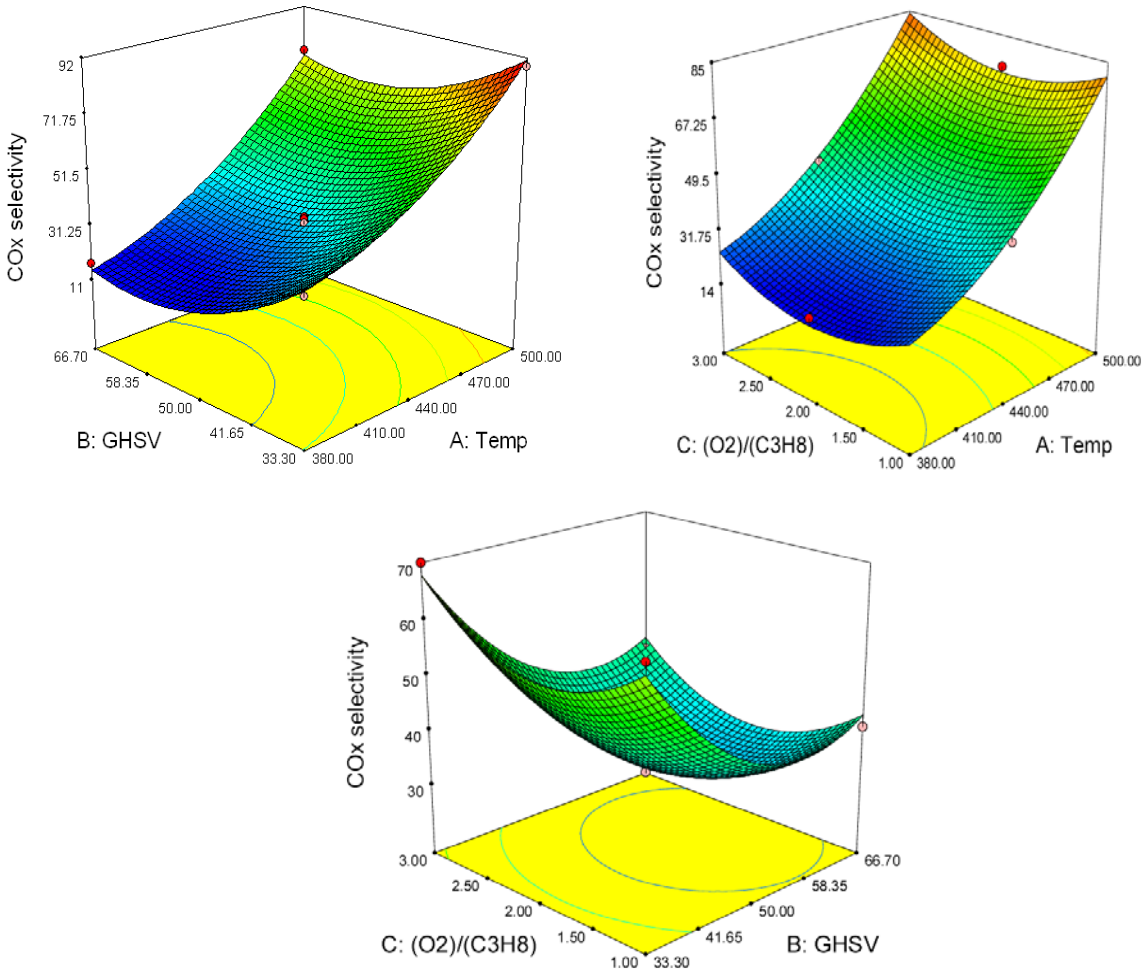


Figure 5 The effects of interaction between input variables on CO_x selectivity as 3D response surface

The model p-value of <0.0001 indicates that the model is highly significant. The R^2 value was obtained 0.9949 which implies the prediction capability of developed BBD model for CO_x

selectivity. Adeq. Precision was found greater than 4. Therefore the experimental data can support the statistical analysis to evaluate the prediction range of CO_x selectivity function in relation to different errors. The lack of fit p-value was found to be 0.0969 (not significant). So the mean square of the lack of fit is due to the random inherent system errors and the developed BBD model is well fitted to the experimental data. X_1, X_2, X_1^2, $X_2^2$and X_3^2terms are significant. Other model terms are insignificant.

All the diagnostic plots of CO_x selectivity BBD model have been shown in supplementary data in order to validate the developed model. All the criteria about the residuals have been met e.g. the residuals were normally distributed, the internally as well as externally studentized residuals were randomly dispersed and also limited in the desired range. So it can be concluded that the developed model for CO_x selectivity were fitted to the experimental data reasonably.

The effects of input variables; temperature, GHSV and $(O_2)/(C_3H_8)$ ratio on the acrylic acid selectivity have been shown in figure 5 as a 3D response surface. Figure 5 shows that temperature has great effect on CO_x selectivity. As the temperature elevates from 380°C to 500°C, the CO_x selectivity increases severely. Propane, propylene, AA and other intermediates have more activity at higher temperatures, so increasing temperature would accelerate the over-oxidation.

Elevating space velocity from 33.3 mL $min^{-1}g_{cat}^{-1}$ to.50 mL $min^{-1}g_{cat}^{-1}$ which is accompanied by shortening contact time leaded to decreasing CO_x selectivity (figure 5). However by increasing further in GHSV level to greater extent than 50 mL $min^{-1}g_{cat}^{-1}$, CO_x selectivity does not change much.

Acrylic acid selectivity response surface shows (figure 4) an increasing trend with increase in $(O_2)/(C_3H_8)$ ratio from 1 to stoichiometric ratio of 2. With further increase in oxygen concentration, acrylic acid selectivity declines. Figure 5 illustrates that higher oxygen concentration promotes the deep oxidation of materials which accompanied by increasing CO_x selectivity. Widi et al. [27] and Ramos et al. [32] have also reported that oxygen reaction order in propane selective oxidation to AA and acrolein is close to zero. While, the oxygen reaction order in total oxidation (non-selective reaction) is obtained greater. All of these observations confirm that lower oxygen concentration conducts the reaction in the desired selective path.

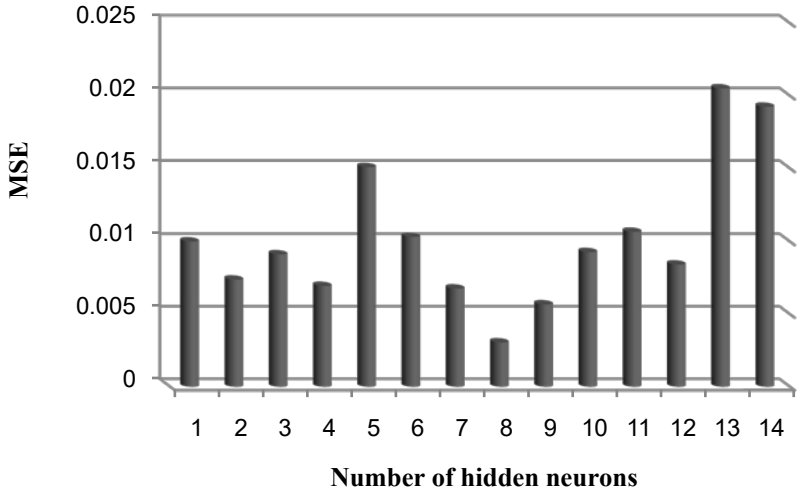


Figure 6 Selection of appropriate hidden neurons at the least MSE

3.2. Proposed ANN model

The normalized experimental data were arranged into an input matrix [P] and a target matrix [T]. In order to avoid over-fitting, the experimental data were divided randomly in to three data sets for training, testing and validation [19]. From 15 experimental data, 80%, 10% and 10% were used for training, testing and validation, respectively. A multilayer feed forward back propagation ANN with tangent sigmoid transfer function (tansig) at the hidden layer and a linear transfer function (purelin) at the output layer was implemented. There are a number of different parameters that impact on the ANN prediction capability and must be decided in the designing phase. The number of hidden layers, the number of neurons per layer and the learning rate are among these parameters. Based on the well documented literature [19], network performance is stable with 0.01 learning rate. Too many hidden neurons can lead to the system that is over-specified and unable for generalization. In addition with increase in hidden neurons, ANN complexity and time required for training increase [34]. On the other hand, too few hidden neurons can reduce the accuracy of ANN. The optimum number of hidden layers as well as the optimum number of hidden neurons was determined based on the minimum value of the obtained MSE of the validation set.

In this work, one hidden layer configuration with different number of neurons between 1 and 14 was applied for training of the network and the MSE between the normalized predicted and experimental value of propane conversion, AA and CO_x selectivities were computed. Obtained MSE in the training process as a function of the hidden neurons has been shown in figure 6.

Figure 6 indicates that the lowest MSE (0.00304) occurred when 8 hidden neurons were selected. Therefore, the ANN model with 1 hidden layer and 8 hidden neurons was chosen as the most suitable model to predict experimental data. In this design, the test set MSE and the validation set MSE had similar features. Therefore over-fitting had not been happened. Figure 7 illustrates the architecture of the proposed ANN and transfer function type between the input-hidden layer and that between hidden-output layer. In the figure 8, the normalized experimental values of propane conversion, AA and CO_x selectivities have been compared with its corresponding predicted values using the proposed ANN model. Figure 8 shows that high values of R were obtained for the training, validation, test and all predicted sets (0.9937, 0.9991, 0.9996 and 0.9938, respectively). These high values of R suggest that the proposed ANN model can well predict catalytic performance in propane selective oxidation over $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$. The weight and bias matrices for the proposed ANN model obtained after training are shown in equations 12 to 15. Where W_1 is the connection weights between input and hidden layer neurons, W_2 is the connection weights between hidden and output layer, B_1 is the bias for the hidden layer and B_2 is the bias for the output layer.

3.3. BBD Model validation using optimum condition

The numerical optimization analysis was performed by desirability approach function. The optimization criteria were selected at the range option for all input variables (temperature, GHSV and $(O_2)/(C_3H_8)$ ratio), maximum, maximum and minimum for propane conversion, AA selectivity and CO_x selectivity, respectively. The optimum values of the operating conditions were subjected to the developed BBD model and the outputs were calculated using equations 9 to 11. To evaluate the prediction, an experiment was carried out at the optimum conditions. The experimental values and the BBD optimum results have been compared in table 6. It can be seen in table 6 that there is good agreement between experimental and BBD predicted results. Therefore the validity of the BBD model in determining the optimum conditions for propane selective oxidation to AA over $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst has been confirmed.

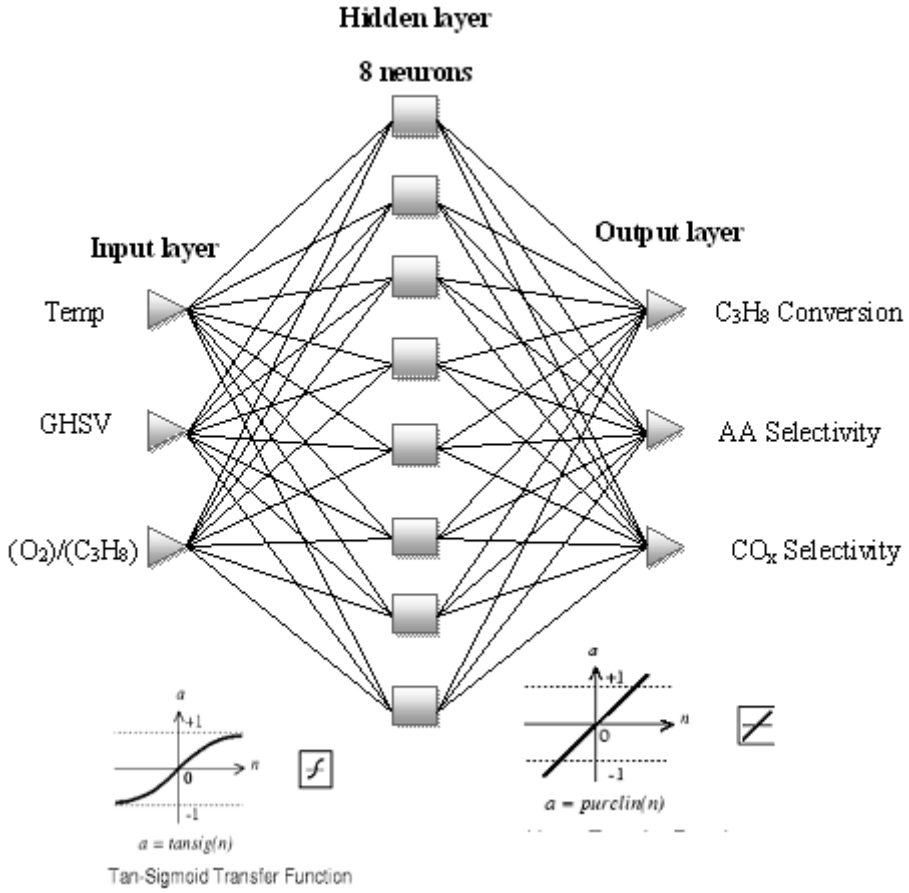


Figure 7 Proposed ANN architecture

$$W_1 = \begin{bmatrix} -1.4248 & -0.0042 & -3.2619 \\ 1.1958 & -0.3724 & -0.2603 \\ 1.5647 & -0.3642 & 2.2269 \\ 3.3317 & -0.6732 & 0.3280 \\ -0.5756 & 2.2427 & -2.4832 \\ -3.0267 & -0.0078 & -0.4499 \\ 0.5851 & 3.3780 & -1.0052 \\ -0.2392 & 2.0236 & -0.1151 \end{bmatrix} \tag{12}$$

$$W_2 = \begin{bmatrix} 0.2365 & 0.9736 & 0.3017 & 0.2884 & 0.0471 & 0.3157 & -0.0345 & 0.0240 \\ -0.4875 & -1.2305 & -0.5192 & -0.1805 & 0.0329 & -0.5419 & -0.0659 & 0.7481 \\ 0.4585 & 0.7469 & 0.2184 & 0.2947 & -0.0940 & 0.0963 & 0.1177 & -0.3933 \end{bmatrix}$$

(13)

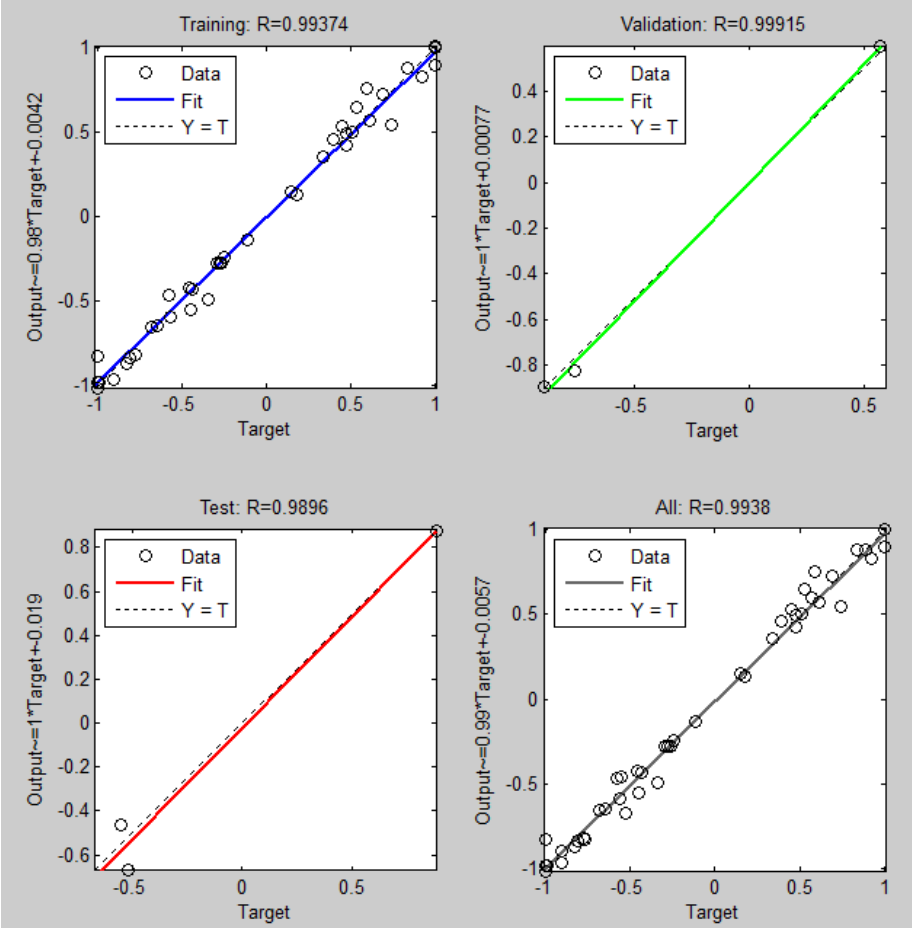


Figure 8 Correlation between ANN predicted outputs and target values of normalized propane conversion, AA selectivity and COx selectivity

Table 6 BBD model validation using optimum condition

Run	Temp (°C)	GHSV (mL/(ming$_{cat}$))	(O_2)/(C_3H_8)	Propane conversion (%)			AA selectivity (%)			CO_x selectivity (%)		
				Exp	BBD	Error	Exp	BBD	Error	Exp	BBD	Error
1	461.7	51.9	2.1	15.2	15.51	-0.02	32	34.4	-0.07	44	42.8	0.03

$$B_1 = \begin{bmatrix} -2.4531 \\ -0.4000 \\ 2.9526 \\ -0.4387 \\ -0.4375 \\ -0.7818 \\ -0.3804 \\ 2.7164 \end{bmatrix} \quad (14) \qquad B_2 = \begin{bmatrix} -0.1549 \\ -0.7848 \\ 0.5893 \end{bmatrix} \quad (15)$$

3.4. Comparison between BBD and ANN models

In this section, the capability of the BBD and ANN models to predict experimental data is evaluated for two data sets: 1) The experimental data that were used for development of the models (DoE data). 2) The experimental data did not exist in the training process of the models (Unseen data). The

performance of ANN and BBD models in response predictions were compared based on (R^2) and MAE demonstrated in equations 16 and 17.

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(Y_{i,e} - Y_{i,p}\right)^2}{\sum_{i=1}^{N}\left(Y_{i,p} - Y_e\right)^2} \quad (16)$$

$$MAE = \frac{1}{N}\sum_{i=1}^{N}\left|Y_{i,e} - Y_{i,p}\right| \quad (17)$$

Where $Y_{i,e}$, $Y_{i,p}$, Y_e and N are experimental data, corresponding predicted data, mean value of experimental data and total number of experimental data, respectively.

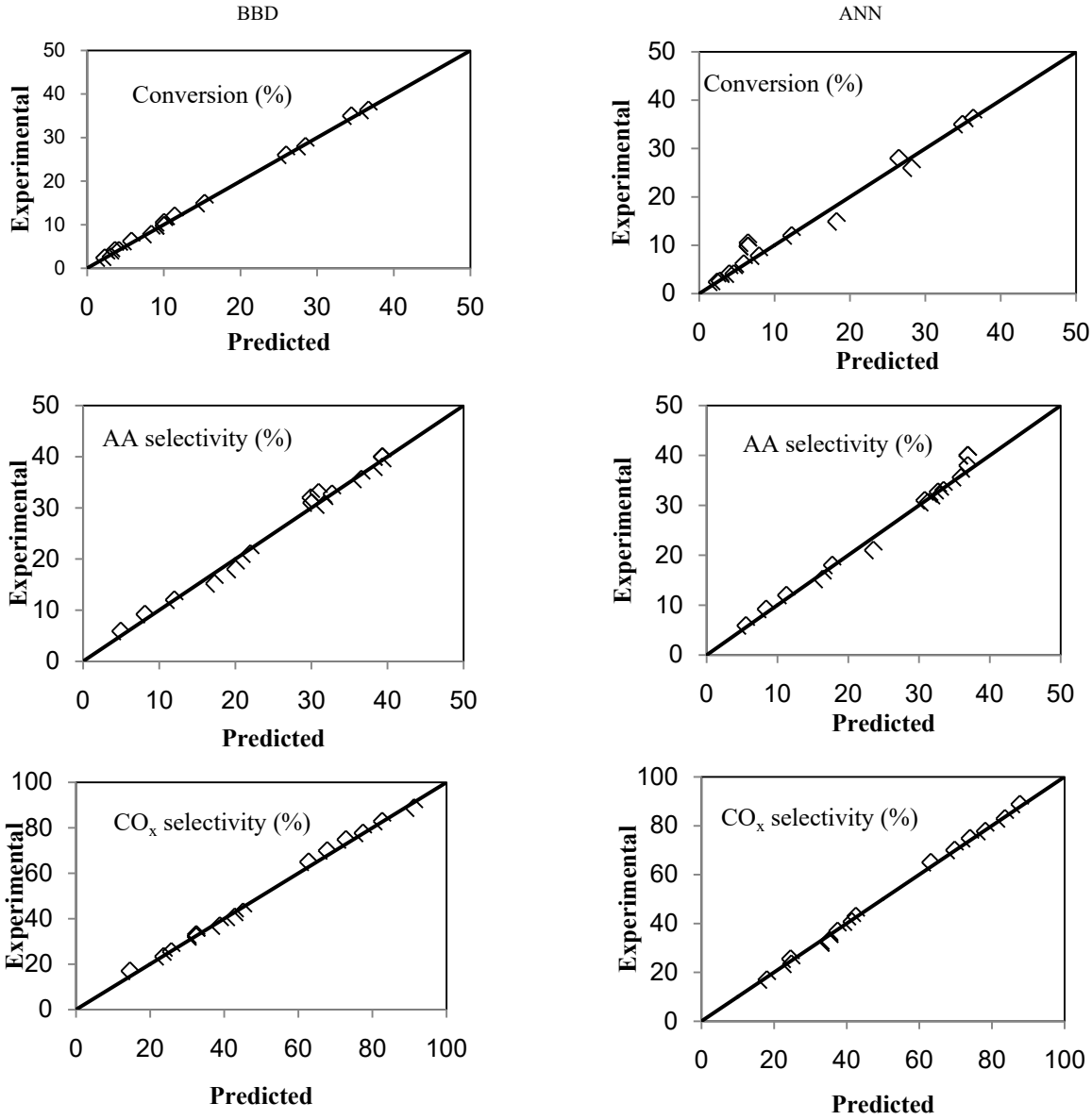


Figure 9 Comparison between experimental and predicted values by BBD and ANN for DoE data set

The obtained values of R^2 and MAE for DoE data set are shown in table 7. The results of table 7 indicate the predictability of both models due to the values of R^2, which are very close to 1, and small values of MAE. However BBD model is more efficient in predicting propane conversion, the developed ANN model showed a clear preference over BBD in AA and CO_x selectivity predictions. In addition, the parity plots for ANN and BBD predicted against experimental values of DoE data set are shown in figure 9. It can be seen in figure9 that there is good agreement between experimental and predicted data. The DoE data points are distributed around the diagonal line very

closely. In the case of unseen data set, the separate experimental data (7 runs), which were not used to train the models, were selected. The operating conditions of each run (temperature, GHSV and $(O_2)/(C_3H_8)$ ratio) were subjected to the developed ANN and BBD models in order to obtain predicted propane conversion, AA and CO_x selectivity. The operating conditions, predicted and actual value of responses, R^2 and MAE for unseen data are given in table 8. According to table 8 the developed ANN model has more predictive capability as compared to BBD. This has confirmed the distinct generalization capacity of ANN over RSM. The better performance of ANN is related to its ability to correlate the nonlinearity of the systems. While the RSM is limited to provide a second order polynomial.

Table 7 Unseen data set for developed models with statistical analysis

Run	Temp (°C)	GHSV (mL/(ming$_{cat}$)	$(O_2)/(C_3H_8)$	Propane conversion (%)			AA selectivity (%)			CO_x selectivity (%)		
				exp	ANN	BBD	exp	ANN	BBD	exp	ANN	BBD
1	380	66.7	1	2	1.82	2.54	32.3	32.17	28.47	21.7	21.95	24.33
2	440	50	3	8.9	11.20	11.8	28	29.77	31.3	41	41.65	44.37
3	500	50	2	30	31.04	31.3	12.5	11.74	17.37	78.7	81.60	69.96
4	380	33.3	1	3.8	4.2	3.72	30	30.08	22.33	37.9	38.45	47.21
5	380	33.3	3	5.2	4.8	4.90	31.5	30.51	22.87	44.5	43.78	50.67
6	440	33.3	2	14	14.58	13.20	23	22.89	28.32	63.5	62.83	55.22
7	440	50	1	9	4.78	8.57	33.2	35.82	32.72	42.9	39.77	40.75
R^2					0.957	0.980		0.972	0.346		0.990	0.788
MAE					1.366	0.877		0.944	5.026		1.420	6.686

4. Conclusion

The aim of this study is investigation the possibility of developing BBD and ANN models for prediction the catalytic performance of $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_x$ catalyst in propane selective oxidation to AA. For this purpose, 15 experimental runs were designed based on the BBD to determine the effects of three variables; i.e. temperature, space velocity and $(O_2)/(C_3H_8)$ ratio on the three responses; i.e. propane conversion, AA selectivity and CO_x selectivity. Three quadratic regression equations were developed in order to demonstrate the relationship between input variables on the responses. The significance of each factor and their interactions on the responses were examined by ANOVA. In addition an ANN model was also developed and

trained using the designed experimental data. R^2 of 0.9987 and 0.9722 for propane conversion, 0.9862 and 0.9821 for AA selectivity, 0.9952 and 0.9960 for CO_x selectivity obtained by developed BBD and ANN models respectively implied the acceptable adjustment of the both models. The prediction capability of developed BBD and ANN models were also examined by a new data set in which the ANN priority is prominent in comparison with BBD. The optimum conditions; temperature of 461.7 °C, GHSV of 51.9 mL(min $g_{cat})^{-1}$, $(O_2)/(C_3H_8)$ ratio of 2.1, with the aim of maximizing propane conversion, maximizing AA selectivity and minimizing CO_x selectivity, were specified. Catalytic performance obtained experimentally under optimal conditions was in close agreement by that of BBD model predicted.

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