OPTIMIZATION OF THE SELECTIVE CATALYTIC REDUCTION OF NO IN DIESEL EXHAUST OVER CU-ZN/ZSM-5 CATALYST USING CENTRAL COMPOSITE DESIGN

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ABSTRACT **:** The optimization of the operating conditions in nitric oxide (NO) selective catalytic reduction (SCR) process over Cu-Zn/ZSM-5 bimetallic catalyst using combined Response Surface Methodology (RSM) and Central Composite Design (CCD) is reported. A bimetallic catalyst containing 6 wt. % Cu and 8 wt. % Zn was prepared through a combined impregnation and ion-exchange process. The process conditions investigated were temperature (300 - 400 °C), NO concentration (900-2,000 ppm) and iso-butane (reductant) concentration (900 - 2,000 ppm). The weight hourly space velocity (WHSV) was fixed at 13,000 h^{-1}. Cu-Zn/ZSM-5 catalyst proved its potential for the SCR process. Statistical analyses showed that the NO reduction was affected by all the operating conditions with the temperature as the most dominant one. Based on the experimental design, a second order mathematical model was successfully developed and satisfactory fitting to the experimental data was demonstrated. Interactions between variables were also analyzed at 99.99 % confidence level. The optimum conditions obtained were 624 ppm for the NO concentration, 2,440 ppm for the iso-butane concentration and 389 °C for the reaction temperature to give a corresponding NO reduction of 96.13 %.

KEYWORDS: *SCR; gases; catalysis; zeolite; Central Composite Design; optimization.*

5. INTRODUCTION

Diesel-powered engines always offer better fuel economy than stoichiometric gasoline engines because of the lean-burn conditions at high pressure that yield higher combustion temperatures [1-3]. However, diesel engine exhaust has many adverse environmental effects, particularly due to the emission of nitrogen oxides (NOx). NOx directly involve in the formation of irritating ground level ozone. Their reactions with other chemicals present in the air also lead to the formation of other toxic chemicals such as nitrate particles and acid aerosols [4]. The lean-burn conditions also produce an exhaust containing high concentration of oxygen. Such an oxidative environment complicates conventional approaches to chemically reduce NOx to environmentally benign nitrogen gas [5].

The pioneering works by Iwamoto *et al.* [5, 6] prove the plausibility of selective catalytic reduction (SCR) technique with hydrocarbons as the reducing agents for the removal of NOx. In this method, the unburned hydrocarbons in the exhaust in combination with added ones are used to reduce NOx by means of a suitable catalyst. Many catalysts have been investigated and zeolites-based catalysts produced very convincing results [3, 4, 7]. In this respect, ZSM-5 recently gained attention in environmental catalysis, especially in reduction of NOx emission [3, 8, 9]. Witzel *et al.* [1] reported that three-dimensional structure of ZSM-5 zeolite enabled reactant molecules to detour via adjacent channels whenever one of the channels was completely filled up by the reactant gases. This material was also found to be resistant to soot that is usually encountered in diesel exhaust [10].

Among metals studied as the active components of the catalysts are Cu [4, 5, 7], Pt [11], Pd [12] and Co [2, 4]. By reviewing the results, Cu should have the advantage on the basis of sufficiently high activity, high stability, low toxicity and low cost. Therefore, it was used in this study. Recently, bimetallic catalysts have created particular interest due to the promotional effects between metal species [11]. The second metal should allow the first metal in the active state. However, when one of the metals is easily reduced, the other should stay in a low oxidation state [13, 14]. The bimetallic catalysts generally have higher resistance towards metal sintering that will usually lead to the loss of contact between the metal and the support. The second metal could also prevent active metal migration in the supports and improve metal dispersion [13, 14]. In this respect, Zn is reported to improve the activity of Rh/TiO_2 catalysts [15] and Co/ZSM-5 [2]. The desired chemical effect was mainly attributed to the retardation of the oxidation of reluctant in the exhaust during the SCR process.

Besides focusing on the catalyst itself, the optimum operating conditions in a NOx reduction process are also critical in order to minimize the operating costs while ensuring highest possible removal efficiency. Usually, a reaction temperature of between 300 and 400 °C is needed to achieve sufficiently high catalytic activity. This range occurs within the normal operating temperature of most diesel engine exhausts. Lower and higher temperature would result in low reaction rate and excessive oxidation of the reductant, respectively. Excessive addition of hydrocarbons may lead to a decrease in the NOx reduction because the exothermic reaction could raise the temperature to exceed the optimum value for NOx reduction [7]. Apart from that, the ratio of NOx and hydrocarbon is also critical. While the reductant is required for the SCR reaction, too high concentration of NOx in the mixture would prevents the adsorption and activation of hydrocarbon. Consequently, the overall reaction rate is adversely affected. This has been proven by Bueno-Lopez *et al.* [16] who observed that for a constant NO concentration, an increase in C_3H_6 concentration increased the maximum NO reduction only up to a C_3H_6 concentration of 2,500 ppm.

Meanwhile, an increase in the NOx concentration usually has a negative effect on the NOx conversion. Therefore, the process variables should be optimized for the sake of obtaining the most efficient SCR process. It is always advisable that a certain design of experiment (DOE) to be employed to achieve the objective as limited number of experimental runs would be needed. However conclusions with high statistical significance could still be generated. Besides, interactions between the critical process variables could be simultaneously analyzed.

In the present work, a bimetallic Cu-Zn/ZSM-5 catalyst was used for the SCR of nitric oxide (NO) in a synthetic diesel exhaust. The preparation method for the catalyst had been optimized through a series of studies [17]. NO was used as the model NOx compound while iso-butane (i-C_4H_{10}) was used as the reductant. This reductant was successfully used for SCR reaction in our earlier works [7, 11]. The main objective of this work was to achieve the maximum NO reduction at optimum conditions consisting of the reaction temperature, the NO and iso-butane concentrations. For this purpose, combined Response Surface Methodology (RSM) with Central Composite Design (CCD) was employed to simultaneously study the effects of the three reaction variables on the NO reduction. A mathematical model was developed to correlate the NO reduction with the reaction conditions and the possible interactions between the variables demonstrated and analyzed. Whereas the exhaust conditions are dictated by many external factors such as speed, the way the engine is driven etc., the result in this study would be of great assistance if a catalytic NOx abatement system were to be optimally designed and operated. In addition, highly stable catalytic activity was observed throughout the study.

2. MATERIALS AND METHODS

2.1 Bimetallic Catalyst Preparation

NH_4-ZSM-5 (Zeolyst International, USA, Si/Al=40) was first converted to its H-ZSM-5 form by calcination at 600 °C for 5 h. The first active metal (Cu) was then loaded into the H-ZSM-5 using a conventional impregnation method. It was performed by mixing a 2.0 M Cu $(NO_3)_2$ solution with H-ZSM-5. The amount of aqueous solution per gram of zeolite used was as reported by Nejar and Gomez [18] to produce a Cu loading of 6 wt. % in the catalyst. The slurry was then placed in a rotary evaporator until it was free flowing. It was subsequently dried at 105 ºC for 24 h and then calcined at 600 ºC. Then, it was kept under vacuum at 100 ºC for 2 h until the slurry became completely dry and free flowing.

Zn as the second metal was incorporated into the Cu/ZSM-5 catalyst using an ion-exchange method. It was performed by mixing the Cu/ZSM-5 catalyst with 2.0 M of Zn $(NO_3)_2$ solution whereby the amount of aqueous solution used per gram of zeolite used was as reported by de Lucas *et al.* [4]. The mixture was then continuously stirred at room temperature for 24 h. Subsequently, the suspension was filtered and dried at 100 ºC for 24 h, followed by calcination at 600 ºC for 2 h. The ion-exchange process was repeated until the catalyst contained 8 wt. % of Zn. The Cu-Zn/ZSM-5 catalyst in powder form was then pelletized, crushed and sieved to produce particles in a size range between 250 and 350 μm. The catalysts were characterized using a Micromeritic ASAP 2000 surface analyzer.

2.2 Catalytic Activity Study

The NO reduction experiments were carried out in a continuous flow system. The same system as used by Deeng *et al.* [7] was used in this study. In brief, the set-up consisted of a gas feed system for each component with individual flow control by mass flow meters, a catalytic reactor heated by a tubular furnace and an exit gas flow meter equipped with gas analysis system. The reactor was packed with 0.2 g of the catalyst. In this study, catalyst particles in the size range of 250 and 350 μm were used as our previous

study showed that the system would operate in a reaction-controlling regime with the catalyst in this size range under the experimental conditions used [11].

To better simulate the conditions in the diesel engine exhaust, the nitrogen gas was saturated with water vapor prior to mixing with other gas components. The feed gas at a total flow rate of 150 ml/min with a corresponding weight hourly space velocity (WHSV) of 13,000 h^{-1} was allowed to flow into the reactor containing the catalyst for about 30 min at the reaction temperature. The concentration of inlet and outlet gases was determined by means of a chemiluminescence gas analyzer (KANE-MAY 900, England). The temperature of the catalyst bed which was measured using a K-type thermocouple installed in contact with the catalyst bed was taken as the reaction temperature.

2.3 Design of Experiment

A design of experiment was used to evaluate the effects of significant parameters and to obtain the optimum value of important variables in the selective catalytic reduction of NO with iso-butane as the reducing agent. For this purpose, Response Surface Methodology (RSM) was used to obtain the optimum conditions (NO concentration, iso-butane concentration and reaction temperature). RSM is a collection of mathematical and statistical techniques which is useful for modeling and problem analysis purposes. The highest NO reduction was targeted in this optimization study.

The effects of three input variables i.e. reaction temperature, feed NO and feed iso-butane concentrations towards NO reduction were investigated according to a Central Composite Design (CCD) experiment. The optimization of NO conversion was carried out by three chosen independent process variables using 2^3 factorial experiments design with six star points (α=2) and 6 replicates at center points. Table 1 lists the ranges and levels of the three independent variables studied. The design led to 20 sets of experiment as given in Table 2. These parameter ranges were used based on a reported result by Deeng *et al.* [7]. All variables at zero level were used as the center points while the variables at the lowest (-2.0) or highest (+2.0) level formed the axial points. The experimental runs were conducted in a random order to minimize the effects of the uncontrolled factors.

Table 1: Levels of the reaction variables used in this study.

Reaction Variable	Code	Unit	Level				
			-2	-1	0	1	2
Temperature	A	ºC	250	300	350	400	450
Feed NO	B	ppm	350	900	1,450	2,000	2,550
Feed i-C_4H_{10}	C	ppm	350	900	1,450	2,000	2,550

Table 2: Matrix of the experimental design.

Run	Point type	Variables			Response
		A	B	C	R1
		Temperature (ºC)	NO concentration (ppm)	Iso-butane concentration (ppm)	NO conversion (%)
1	Fact	300.00	900.00	900.00	30.0
2	Fact	400.00	900.00	900.00	87.5
3	Fact	300.00	2000.00	900.00	29.0
4	Fact	400.00	2000.00	900.00	70.6
5	Fact	300.00	900.00	2000.00	70.0
6	Fact	400.00	900.00	2000.00	95.0
7	Fact	300.00	2000.00	2000.00	55.0
8	Fact	400.00	2000.00	2000.00	72.4
9	Axial	250.00	1450.00	1450.00	10.0
10	Axial	450.00	1450.00	1450.00	69.0
11	Axial	350.00	350.00	1450.00	93.0
12	Axial	350.00	2550.00	1450.00	46.8
13	Axial	350.00	1450.00	350.00	50.0
14	Axial	350.00	1450.00	2550.00	76.6
15	Center	350.00	1450.00	1450.00	70.0
16	Center	350.00	1450.00	1450.00	76.2
17	Center	350.00	1450.00	1450.00	69.1
18	Center	350.00	1450.00	1450.00	65.1
19	Center	350.00	1450.00	1450.00	71.0
20	Center	350.00	1450.00	1450.00	69.3

The predictive effects of the factors influencing the NO reduction and iso-butane conversion were to be obtained through a quadratic model shown by Equation (1).

$$Y= \beta_0 + \beta_1 A+ \beta_2 B+ \beta_3 C+ \beta_{11} A^2+ \beta_{22} B^2+ \beta_{33} C^2+ \beta_{12} AB + \beta_{13} AC+ \beta_{23} BC \qquad (1)$$

where, Y is the response calculated by the model while A, B, C are the coded variables corresponding to the reaction temperature, NO concentration and iso-butane concentration, respectively. The constant β_0 refers to the intercept coefficient and $\beta_1, \beta_2, \beta_3$ are the terms for the single variable effects. The $\beta_{11}, \beta_{22}, \beta_{33}$ coefficients predict the double actions of the each factor while the β_{12} β_{13} β_{23} coefficients indicate the extent of interactions between the variables studied.

The regression data obtained in this study was analyzed by the RSM. The evaluation of a second order model equation was then performed using a Fisher's test and the proportion of variance in the model was evaluated on the basis of the multiple coefficient of determination (R^2). The graphical and numerical analyses provided by a software (Design-Expert 6.0.7, USA) were employed to predict the optimum conditions for the NO reduction.

3. RESULTS AND DISCUSSION

3.1 Characteristics of the Bimetallic Catalyst

Table 3 shows the surface characteristics of Cu-Zn/ZSM-5 catalyst as compared to its H-ZSM-5 support. The support had a BET surface area of 402 m^2/g and more than half of this was contributed by micropores. Despite being theoretically microporous material, meso- and macropores contributed significantly to the overall surface area of the Cu-Zn/ZSM-5 catalyst. They were ascribed to the interstices between the zeolite particles, between the extra-framework species as well as that formed between the metal crystallites. It was found that the catalyst preparation procedure unsed in this study resulted in about 13 % and 15 % loss in BET surface area and micropores, respectively. A surface area of 348 m^2/g with a pore volume of 0.27 ml/g were generally sufficient for an effective heterogeneous catalyst.

Table 3: Characteristics of Cu-Zn/ZSM-5 catalyst as compared to the H-ZSM-5 support.

Characteristics	H-ZSM-5	Cu-Zn/ZSM-5
BET surface area (m^2/g)	402	348
Micropore area (m^2/g)	215	182
Total pore volume (ml/g)	0.26	0.27
Cu loading (wt. %)	-	6
Zn loading (wt. %)	-	8

3.2 Regression Models

The NO conversions obtained in Table 2 were correlated with the three variables studied by means of a multiple regression analysis. At first, the suggested model was in a quadratic form. However, the model was modified by excluding the insignificant terms which were identified by Fisher's Test to assure the significant level of the model. The test results were analyzed by comparing the calculated *F* and theoretical *F* values based on 99.99 % confidence level for the first order of all variables and second Order of Term a (Temperature). The other model term remained showed acceptable level of significance (99.70 %). The calculated *F* values should be higher than the theoretical values to make the term significant or in other words, the null-hypothesis should be rejected. The final model (significant level> 99.99%) in terms of coded value after excluding the insignificant terms (identified using Fisher's Test) is given in Equation (2). The significance of each coefficient in the Eq. 2 was determined by Student's *t*-test and *p*-values. The *t*-test is a statistical hypothesis test in which the test statistic follows a Student's *t*-distribution if the null hypothesis is true. Meanwhile, the p-value is the probability of obtaining a test statistic at least as extreme as the one that was actually observed, assuming that the null hypothesis is true.

$$NO\ conversion\ (R1) = 69.51 + 16.22\ A - 9.24\ B + 8.03\ C - 7.17\ A^2 - 7.09\ A\ C \quad (2)$$

The positive sign in front of the terms indicates a synergic effect, while the negative sign indicates an antagonistic effect [7]. The quality of the model developed could be evaluated from their coefficients of correlation. The value of R^2 for Equation (2) is 0.9504. It implies that 95.04 % of the total variation in the NO conversion was attributed to the experimental variables studied. The remaining (4.96 % of NO conversion) was therefore, explicated by the residues. On the other hand, the value of R^2 which is very close to 1 suggests that the predicted data from the model are comparable with experimental data with sufficient degree of accuracy (as shown in Fig. 1).

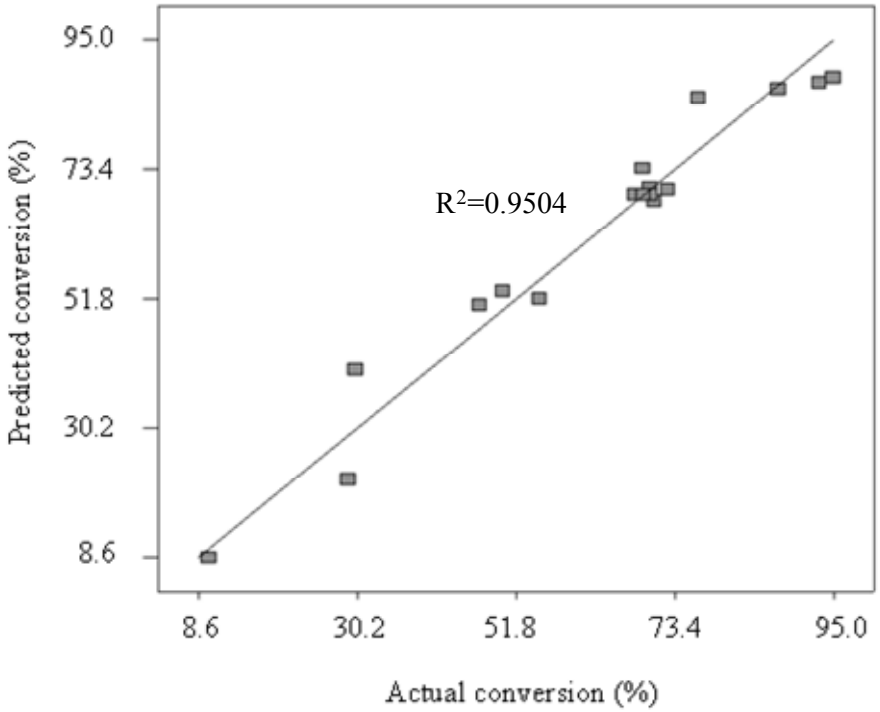

Fig. 1: Parity plot between the predicted and actual data for the NO reduction reaction.

As suggested by Eq. 2, the coefficient value for A is the highest, indicating the dominant effect of this variable in the SCR of NO. But the effect on the NO conversion was in a quadratic pattern. Next, it was the reductant concentration to be influencial while NO concentration between 900 and 2,000 ppm was not so influencial on the NO removal percentage. An increase in NO concentration in the feed between 900 to 2,000 ppm as used in the present study was detrimental to the fraction of NO removal. On the other hand, increasing iso-butane concentration generally increased the NO removal. Interaction between the temperature (A) and reductant concentration (C) was also detected in this reaction system. This interaction suggests the differrent patterns of NO removal when moving from the lower limit to the higher limit of these variables. Whereas this interaction is deemed to have minimal effect on the variable A, the significance impact on variable C could result.

3.3 Model Adequacy

In order to check for the adequacy of the model developed to represent the reaction system, an analysis of variance (ANOVA) was performed and the results are shown in Table 4. The ANOVA was basically required to test the significance and adequacy of the model at the confidence level of 95 %. The ANOVA of the model developed demonstrates that the model is highly significant (99.99 %) for NO conversion as the computed *F* value (53.66) is much higher than the theoretical $F_{0.05}$ (5, 14) value. Apart from that, each term in the model is also found to be significant at a >99.7 % confidence level as the the computed *F* value for each term is higher than the theoritical $F_{0.05}$ (1, 14) value. Values of Prob > F less than 0.0500 indicate model terms are significant. In this case terms A, B, C, A^2, AC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. The "Lack of Fit F-value" of 3.21 implies the Lack of Fit is not significant relative to the pure error. There is a 10.59 % chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good. The "Pred R-Squared" of 0.8750 is in reasonable agreement with the "Adj R-Squared" of 0.9327. "Adeq Precision" measures the signal to noise ratio. According to the software manual a ratio greater than 4 is desirable. The ratio of 26.207 indicates an adequate signal.

Table 4: Analysis of variance (ANOVA) for the 2^3 full CCD of the NO reduction process.

Source	Sum of Squares	DF[a]	Mean Square	F-Value	Prob > F	
Model	8407.484	5	1681.497	53.66467	< 0.0001	significant
Residual	438.6677	14	31.33341	-	-	-
Lack of Fit	373.9994	9	41.55548	3.21297	0.1059	not significant
Pure Error	64.66833	5	12.93367	-	-	-
Corr. Total	8846.152	19	-	-	-	-

R^2= 0.9504, CV[b]=8.78 %
[a]Degree of Freedom
[b]Coefficient of variance

From these statistical tests, it was found that the model was adequate for predicting the NO conversion within the range of the variables studied. Therefore, the model developed for NO conversion in equation (2) is valid for present study. In agreement with discussion in Section 3.2, the reaction temperature (A) had the largest effect on the NO conversion with the highest F value followed by the NO concentration (B) and reductant concentration (C). The descrepancy between this result and that given in the Equation (2) with respect to the significance order of variable B and C is attributed to the AC interaction. The quadratic term (A^2) also significantly affects the NO conversion as compared to the interaction between variables (AC).

The interaction between the reaction temperature and the reductant concentration was associated with the selectivity of the reductant to undergo oxidation in the presence of oxygen and NO. The reaction between iso-butane and oxygen led to the formation of carbon dioxide while that between iso-butane and NO led to the formation of nitrogen (or in other words, the reduction of NO was achieved). The preference for these two reactions differed at different temperature and the reactions could either occur in the gas phase or on the surface of the catalyst. Low temperature was found to favor NO reduction while higher than optimum temperature accelerated the mineralization of the organic [11]. This was based on the fact that the combustion of iso-butane involves the breaking of many C-C bonds while the reduction of NO only requires the extraction of oxygen atom from the single nitrogen atom. The high enthalpy of combustion for the iso-butane (ΔH_c = -2,869 kJ/mol) reflects the stability of the hydrocarbon to render higher preference towards NO reduction.

3.4 Effects of Process Variables

The result in Table 2 shows that the process variables have great effect on the NO conversion. As the model developed in this work showed no maximum NO conversion within the experimental domain examined, the optimum conditions were defined as those that resulted in the highest NO conversion. Thus, the model developed was used to construct response surfaces to facilitate a straight forward examination of the effects by the process variables on the NO conversion. Response surfaces can also be visualized as two-dimensional plots that present the response as a function of two variables, while keeping the third one constant.

Figure 2 demonstrates the response surface for the effect of interactions between every two of the process variables i.e. temperature, NO concentration and iso-butane concentration, respectively. Figure 2 (a) shows the effects of temperature and feed NO on NO conversion. It can be seen that with an increase in reaction temperature up to approximately 390 °C the NO conversion increases while a slight drop is seen afterwards. The iso-butane concentration was fixed at 1,450 ppm at the center point. It is noted that at lower temperature, a relatively more rapid increase in the conversion is observed and then it stabilizes at higher temperature. A linear moderate decrease could be observed by the increase in NO feed which can be also observed clearly in Fig. 2 (c). From Fig. 2 (a) it can be noticed that high feed of NO (> 2000 ppm) at low temperatures (<260 ^{o}C) no conversion happens. Figure 2 (b) demonstrates the response surface of NO conversion with varying temperature and i-C_4H_{10} concentration. The NO feed was fixed at 1450 ppm at its center point. NO conversion decreased with an increase in iso-butane concentration obvious in Fig. 2 (c) as well. In Fig. (c) The increase or decrease trend follows a relatively linear pattern as compared to that observed in Fig. 2 (a) and (b). A higher concentration of NO in the mixture prevented the adsorption and activation of hydrocarbon and, consequently, the overall reaction rate was adversely affected [16]. A similar trend for all parameters was achieved by Deeng *et al.* [7] in their study using a structured catalyst. Thus, similar mechanism could be assumed regardless of the type of catalyst used.

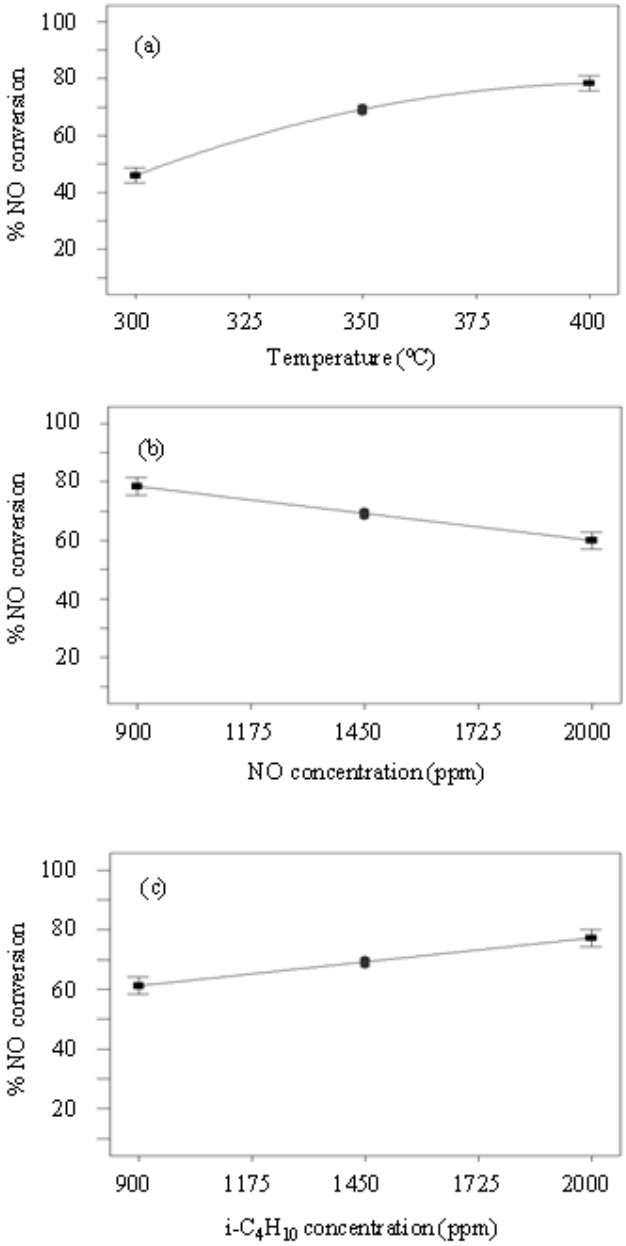

Fig. 2: Influences of (a) reaction temperature (b) NO concentration and (c) iso-butane (i-C_4H_{10}) concentration on the NO conversion (Other variables were set at their respective center points).

Meanwhile, the increase in the iso-butane concentration was proven to be beneficial to the SCR of NO as it acted at the reductant to this highly polluting oxide.

Figure 3 shows the changes in NO conversion with varying temperature at 900 ppm and 2,000 ppm of iso-butane concentration. NO concentration in the feed was kept constant at 1,450 ppm. At low temperature, a significantly lower conversion of NO was

achieved when the iso-butane concentration was 900 ppm as compared to that observed with 2000 ppm of iso-butane. However, it increased more rapidly with an increase in the temperature until it ended up with almost the same conversion at 400 ºC. Thus, the benefit of having higher reductant concentration was only enjoyed at lower temperature. It is also noted in the figure that the NO conversion decreased if the reaction temperature was increased beyond 400 °C. The loss of the activity at high temperature was associated with the onset of the oxidation of iso-butane by oxygen as reported by Guzman-Vargas *et al.* [8] and de Lucas *et al.* [4]. Furthermore, Cu has been found to be sufficiently active in the oxidation of organics at high temperature [19].

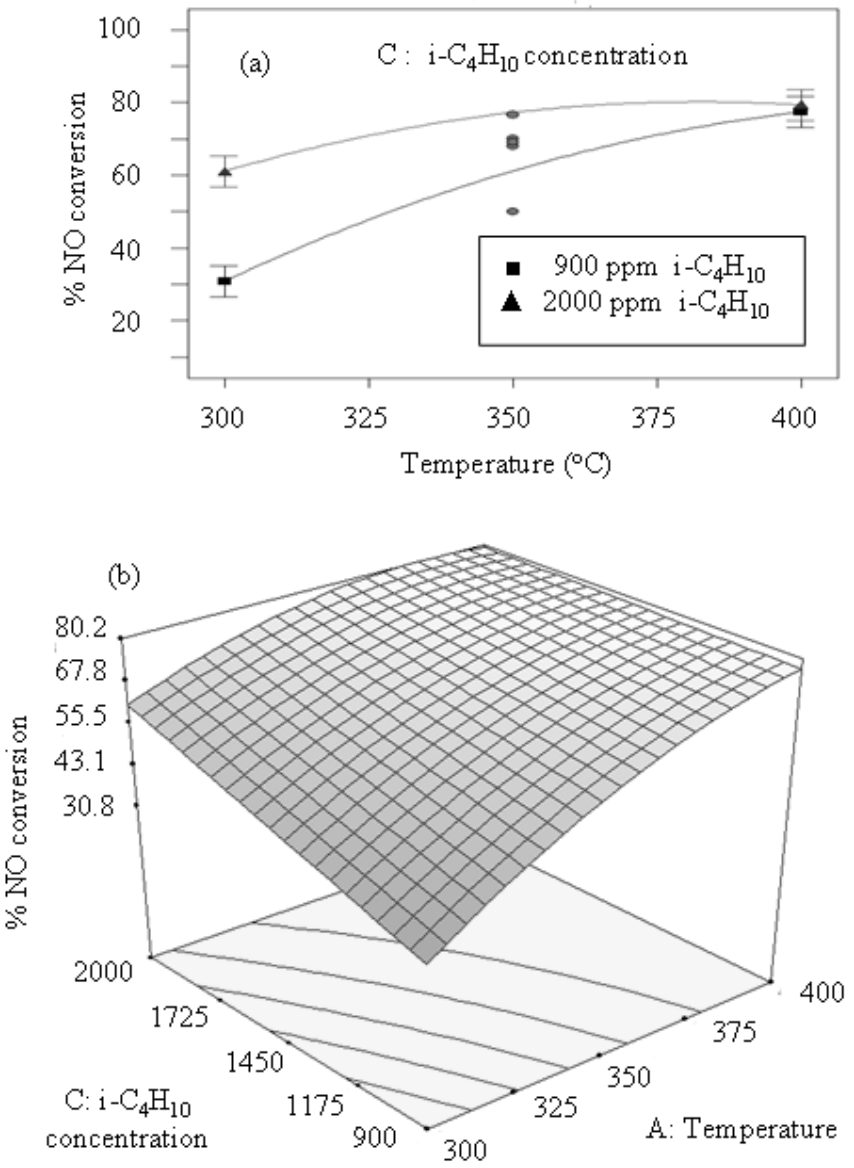

Fig. 3: Effects of iso-butane ($i\text{-}C_4H_{10}$) concentration and temperature on NO conversion shown in an interaction plot

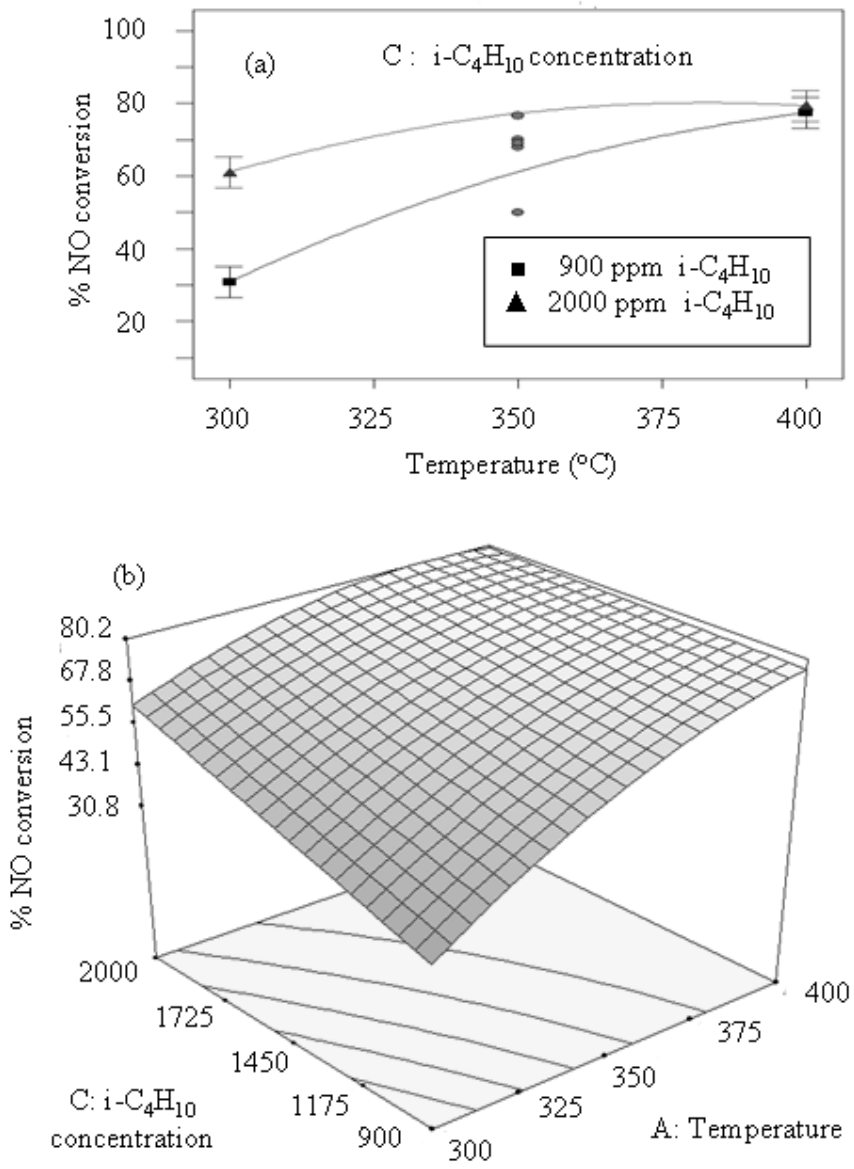

Fig. 3: Effects of iso-butane (i-C_4H_{10}) concentration and temperature on NO conversion shown in an interaction plot

Figure 2(b) shows the three-dimension response surface plot of the effect of iso-butane concentration and temperature on NO conversion. It is clearly noted that at high temperature, the NO conversion is high in the range of reductant concentration tested. This observation shows that increasing iso-butane concentration did not significantly influence the NO conversion at high reaction temperature. The promotional effect was only significant at lower temperature. Thus, over usage of the reductant could be avoided if the concentration of the reductant could be set at the optimum level base on the reaction temperature used.

3.5 Optimization Analysis

As the exact optimum conditions could not be obtained within the range of process variables studied, the optimization was then attempted using numerical optimization feature of Design Expert 6.0.7 software. The primary objective was to search for a combination of factors that could simultaneously satisfy the requirements placed on each of the process variable and response. Table 5 shows the constraints used to obtain the optimum value for process variables. The goal was set to maximize the NO reduction while the temperature should be in the range between 2500 and 450 °C while NO and i-C_4H_{10} concentrations should be in the range of 350 to 2,550 ppm.

Table 5: Constraints used to obtain the optimum conditions for the reaction.

Name	Goal	Lower limit	Upper limit
Temperature	in range	250	450
NO concentration	in range	350	2550
i-C_4H_{10} concentration	in range	350	2550
NO reduction	maximize	10	95

Table 6: Selected optimum conditions generated by the DOE.

Temperature (°C)	NO concentration (ppm)	i-C_4H_{10} concentration (ppm)	NO reduction (%)
389	624	2,440	96.13

The DOE result proposed 10 possible sets of solution. By default, the solutions are sorted from the best to the worst. Thus, the first set of solution which is given in Table 6 was taken as the best solution to be used for further confirmatory process studies. For that, 5 additional experimental runs were carried out in the laboratory to determine the accuracy of the optimum conditions obtained from DOE. These experiments were carried out at 389 ºC with a total feed gas flow rate of 150 ml/min (624 ppm NO, 2,440 ppm iso-butane, 3 v/v % O_2 and balance N_2). The purpose was to evaluate the applicability of the model in predicting the optimum conditions of the SCR of NO process on the basis of statistics.

Table 7 shows the results from the 3 experiments conducted at the optimum conditions. The values of NO reduction obtained from experiment were compared with the one predicted by the DOE. The average NO reduction efficiency obtained was 95.2 % which was 0.93 % lower as compared to the simulated value of 96.13 %. There is an error of ± 0.06 % for the NO reduction value. Thus, the null hypothesis saying that there is no significant difference between the two mean values should be accepted. It means, the proposed statistical model is adequately accurate and reliable in predicting the NO reduction for the reaction system. In this study, only the activity of fresh catalyst was

Table 7: Results of verification experiments conducted at optimum conditions as obtained from DOE.

Run	NO Conc. (ppm)		NO Reduction (%)		[a]Error	Mean Error	[b]Standard Deviation
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	$(X_{NO})_{exp}$	$(X_{NO})_{DOE}$			
1	624	32	94.9	96.13	-1.23		
2	624	23	96.31	96.13	0.18	0.606	0.588
3	624	29	95.35	96.13	-0.77		

a= Error = $(X_{NO})_{exp} - (X_{NO})_{DOE}$
b= $\sigma = \sqrt{(n\Sigma x^2 - (\Sigma x)^2)/n(n-1)}$

evaluated and modeled. It is of great interest to learn whether the same model can also be used to represent the performance of the deactivated catalyst after few hours on stream. Similarly, the use of other type of catalyst or reductant is also expected to cause some degree of deviation from the values predicted by the statistical model. All these topics should be properly addressed to prove the robustness of the statistical model to accurately predict the behavior of the process under various conditions.

4. CONCLUSION

Cu-Zn/ZSM-5 bimetallic catalyst was successfully synthesized and it demonstrated high activity for the SCR of NO in diesel exhaust. Through combined application of Response Surface Methodology (RSM) and Central Composite Design (CCD), the optimization of the operating conditions in the NO selective catalytic reduction (SCR) process over the catalyst was successfully performed. Based on analysis of variance (ANOVA), NO reduction was significantly affected by all the operating conditions but the effect of temperature was the most dominant. A second order mathematical model was successfully developed and satisfactory fitting to the experimental data was demonstrated. Interaction between the reaction temperature and iso-butane concentration were also detected at 99.99 % confidence level. The optimum process were achieved with 624 ppm of the NO concentration, 2,440 ppm of the iso-butane concentration and a reaction temperature of 389 °C to give a corresponding NO reduction of 96.13 %.

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NOMENCLATURE

Symbol	Definition	Unit
WHSV	Weight hourly space velocity	h^{-1}
α	Central composite design factor value	Dimensionless
β_o	Constant coefficient	Dimensionless
B_i	Coefficients for the linear effects	Dimensionless
B_{ii}	Coefficients for the quadratics effects	Dimensionless
B_{ij}	Coefficients for the interactions effects	Dimensionless
Y	The response calculated by the model	%