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Process optimization studies of structured Cu–ZSM-5 zeolite catalyst for the removal of NO using design of experiments (DOE)

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Abstract

There has been growing interest in structured catalytic reactors because of their several advantages over conventional fixed-bed catalytic reactor. The structured bed having open macrostructure allows high flow rates with a low-pressure drop. In the present study, the structured catalyst made of ZSM-5 zeolite coatings on stainless steel wire mesh with copper being incorporated in the ZSM-5 was used. The catalytic activity of Cu–ZSM-5 structured catalyst for the selective catalytic reduction (SCR) of NO with iso-butane as reducing agent was studied using design of experiments (DOE). The response surface methodology (RSM) coupled with center composite design (CCD) was used to obtain the optimum process conditions. The optimum conditions were 1730 ppm of NO, 1280 ppm of iso-butane and 375 °C reaction temperature with 94% reduction of NO and 4.6% SCR-HC selectivity. The NO reduction was also studied in the presence of 5–20 vol% of water vapor and 50–200 ppm of sulfur dioxide (SO_2). Water vapor caused reversible deactivation, whereas SO_2 resulted in permanent deactivation of the catalyst. The catalyst was also tested for its stability subject to time on stream study. No structural changes were found in the catalyst after 48 h of continuous operation.

Keywords: Structured catalyst; Copper-ZSM-5; Design of experiments (DOE); Optimization; Selective catalytic reduction (SCR); NO removal

1. Introduction

The selective catalytic reduction (SCR) of NOx of the oxygen rich stream of diesel exhaust emissions using hydrocarbon as reducing agent has attracted a lot of interest [1]. Most of these studies reported in the literature using conventional packed bed reactors [2]. The main disadvantages of packed bed are high-pressure drop during the gas passage through the catalytic bed, flow maldistribution causing loss of selectivity and high susceptibility to fouling by diesel particulate [3]. A simple way to circumvent the pressure drop versus pore diffusion trade-off is to make use of thin films of zeolite crystals coated on structured support materials, such as monoliths, stainless steel wire mesh and alumina foam. These novel materials are called structured zeolite catalysts [4]. Usually, structured catalytic bed reactors have large void fraction ranging from 0.7 to more than 0.9, compared to 0.5 in packed bed reactors. The path of the fluid follows in structured reactors is less twisty as compared to the conventional packed bed reactors. Finally, the structured catalysts are operated in a different hydrodynamic regime. In single-phase flow, the regime is laminar, and flow characteristics of packed bed reactor are absent. The pressure drop in structured catalysts is significantly lower than the randomly packed bed of particles [3].

The macrostructure of the support material ensures a low-pressure drop, whereas the thin catalytic coating ensures high efficiency and selectivity [5]. Zeolite coatings are prepared by in situ synthesis on the support [6]. The main advantage of in situ hydrothermal synthesis is that the support acts as a base for nucleation and a chemical bonding between crystals and outer support layer is formed [7]. This method utilized zeolite material more efficiently than a gel-coating method, since zeolite crystals are fully exposed on the support surface without dilution by any other material [4].

Iwatomo et al. [8] reported the selective catalytic reduction of NOx with hydrocarbons over Cu–ZSM-5 for the elimination of NOx in the exhaust gases under excess oxygen conditions. Cu–ZSM-5 is reported to be an effective catalyst for the reduction of NOx emission when applied to the exhaust of real lean burn engines, such as diesel engine exhaust. It was found that the main reaction controlling was the reduction of NO by hydrocarbons present in the emission gases. NO is one of the major component present in NOx.

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The objective of the present work is to synthesize structured zeolite catalyst (ZSM-5 coating) using in situ hydrothermal method. ZSM-5 coating was exchanged with copper metal ions resulting in Cu–ZSM-5 catalyst. The selective catalytic reduction of NO over Cu–ZSM-5 structured catalyst was studied using design of experiments (DOE). The center composite design (CCD) coupled with response surface methodology (RSM) was used to obtain the optimum values of process parameters for selective catalytic reduction of NO using iso-butane as reducing gas. The NO reduction was also studied in the presence of 5–20 vol% water vapor and 50–200 ppm sulfur dioxide (SO_2).

2. Experimental

2.1. Catalyst preparation

The catalyst support was subjected to acid-pretreatment process before the synthesis [7,9]. The zeolite synthesis mixture was prepared by adding sodium chloride (99.5%, Merck), sodium aluminate (52.5 wt.% $NaAlO_2$, Riedel-de Haën), and tetra-propyl-ammonium hydroxide (0.1 M in water, Merck-Schurchardt) in the demineralised water at room temperature. Tetraethyl ortho-silicate (98%, Merck-Schurchardt) was added in the mixture under vigorous stirring. The mixture was aged and homogenized for 5 h. After the ageing process, the mixture was poured in a Teflon-lined autoclave containing the vertically positioned catalytic support packing. The temperature of the autoclave was increased to 160 °C. The treatment was carried for 48 h under autogenously pressure in order for zeolite synthesis to take place on the support. The synthesis procedure was repeated three times with a fresh solution each time to enhance the weight of zeolite coating. Finally, the structured packing was kept in an ultrasonic bath (50 kHz) for 30 min to remove loosely attached zeolite crystals and dried overnight at 130 °C. The whole support packing containing zeolite coating was calcined overnight in air at 500 °C. The MFI structure was obtained in the sodium form. The zeolite coating was exchanged three times with ammonium nitrate, NH_4NO_3 at room temperature. Subsequently, it was exchanged three times with copper acetate, $Cu(CH_3COO)\cdot H_2O$ and calcined at 500 °C for 10 h in air resulting in Cu–ZSM-5. The coverage of coating was determined by dividing the mass of zeolite on the packing by the packing surface area.

2.2. Characterization

The BET surface area of the structured catalyst was determined by nitrogen adsorption (77K) employing Autosorb-I instrument (Quanta Chrome). The crystal structure and morphology of a zeolite coating were studied using scanning electron microscope (SEM; Leica Cambridge S-360 apparatus, 15 kV of accelerating voltage). X-ray diffraction (XRD) was performed on a Philips PW 1820 system with Cu Kα monochromatic radiation ($\lambda = 1.5406$ Å) to obtain information about the zeolite structure deposited over the wire mesh. Si/Al molar ratio of the crystals was determined by the energy dispersive X-ray (EDX) analysis.

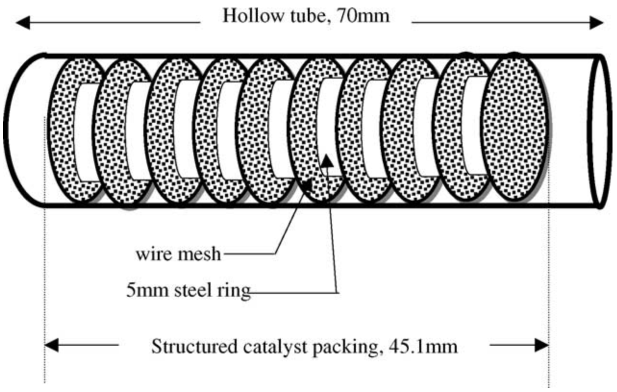

Fig. 1. Schematic diagram of structured catalyst packing.

2.3. Structured catalyst

The structured catalyst packing was arranged by a superposition of 10 stainless steel wire mesh (21 mm in diameter) circular discs, separated from each other by steel rings of 5 mm length and packed into 21.5 mm stainless steel hollow tube as illustrated in Fig. 1. The total length of the catalyst packing was 70 mm while the length of the structured catalyst bed was 45.1 mm. The reactor was designed as cross sectional detachable-type with a center joint, where the catalyst packing can be mounted and removed easily from the reactor. The gasket lined supporting jig at both end were used to support the structured catalyst packing and prevent the flow maldistribution and channeling problem. The multi-channel digital temperature scanner (Cole-Parmer-92000-05) connected to thermocouple-type K (Cole-Parmer-88500-10) with its tip touching the structured catalyst packing was used to measure the temperature. The reactor was enclosed in a horizontal mini tube. The temperature controller (Lindbergh -TF 55035C) was used to control the furnace temperature in the range of 300–400 °C. There was a difference of about ±1 °C between the set temperature and that measured by temperature scanner. There was a negligible pressure drop across the reactor under the normal operating conditions.

2.4. Experimental set up

Fig. 2 shows the experimental set up for the catalytic activity measurements. The experimental rig was consisted of three major parts: (1) synthetic exhaust gas preparation and gas flow system, (2) catalytic reactor, and (3) gas analysis system. The synthetic exhaust gas was made up of nitrogen (N_2), nitric oxide (NO), iso-butane ($i\text{-}C_4H_{10}$), SO_2 and oxygen (O_2). Mass flow controllers (Model MKS type

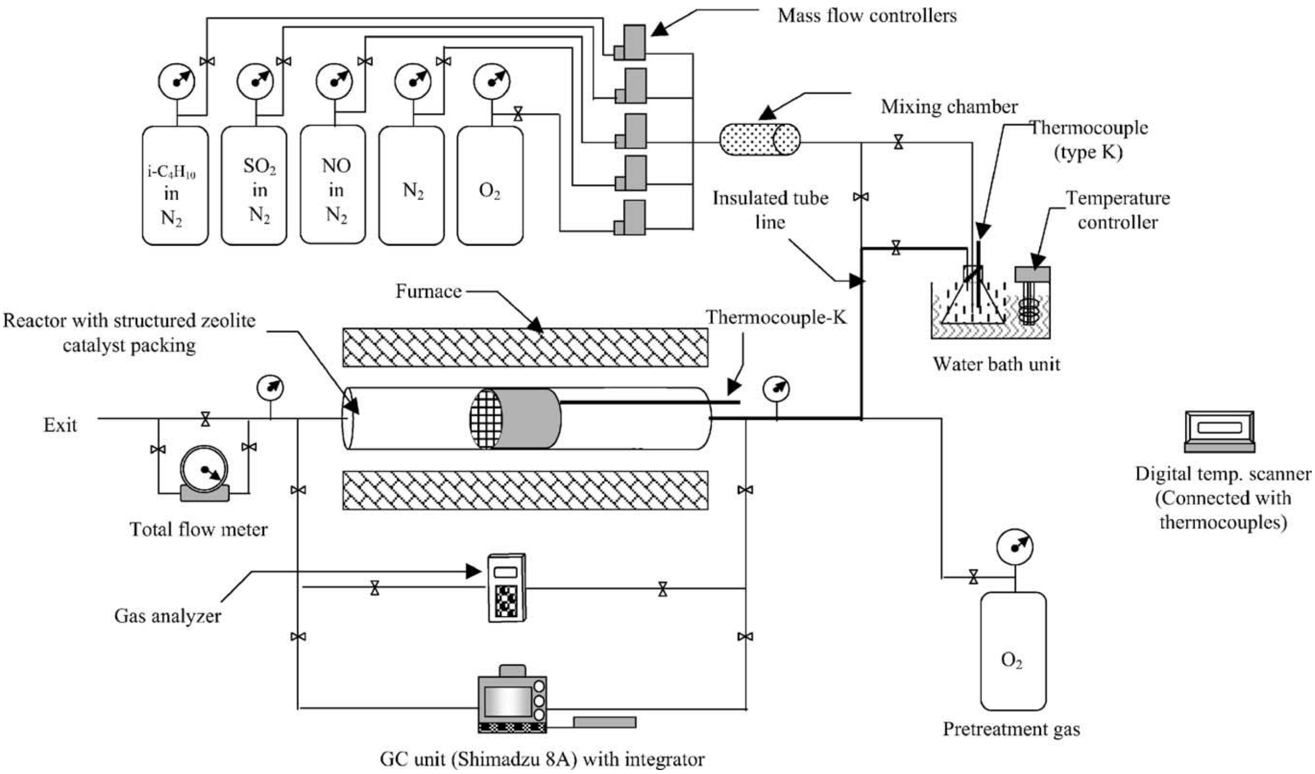

Fig. 2. Experimental set up for catalytic activity measurement (not drawn to scale).

1179A series) were used to obtain the required feed gas composition assuming ideal gas mixture in the mixing chamber. The structured catalyst packing containing about 0.1 g of Cu/ZSM-5 coating was mounted at the center of the catalytic reactor, placed horizontally in the tubular furnace.

The in situ pretreatment of the catalyst was carried out in flowing O_2 with 100 ml/min at 450 °C for 2 h in order to remove possible organic impurities [10]. The furnace was allowed to cool down and the tubing system was flushed with nitrogen for about 30 min to remove excess oxygen. The feed gas mixture of known composition was fed into the system at 50 ml/min and the reactor was heated to desired reaction temperature. The feed gas mixture was allowed to flow about 30 min at the reaction temperature before reaching steady state. The concentration of gases at the reactor outlet was determined using GC unit (Shimadzu 8A, Japan) equipped with thermal conductivity detector (TCD) and gas analyzer (KANE-MAY 900, England). The molecular sieve 5 Å column (2m × 3mm) was used for separating O_2, N_2, and i-C_4H_{10}. CO_2 analysis was done on Porapak Q (2 m × 3 mm) column using gas chromatograph. The following stoichiometric reactions are considered for the selective catalytic reduction of NO using hydrocarbon, i-C_4H_{10} [11].

$$C_4H_{10} + \tfrac{13}{2}NO + \tfrac{13}{4}O_2 \rightarrow 4CO_2 + 5H_2O + \tfrac{13}{4}N_2 \qquad (1)$$

$$C_4H_{10} + \tfrac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O \qquad (2)$$

The percentage of NO reduction was calculated from the difference between the inlet concentration $(C_{NO})_{in}$ and outlet concentration of NO $(C_{NO})_{out}$ using the Eq. (3).

$$\text{NO reduction}\,(\%) = \frac{(C_{NO})_{in} - (C_{NO})_{out}}{(C_{NO})_{in}} \times 100 \qquad (3)$$

The conversion of iso-butane into carbon dioxide was calculated as the difference between the concentration of iso-butane at the reactor outlet $(C_{CH})_{out}$ and that at the reactor inlet $(C_{CH})_{in}$ as:

$$\text{Conversion of } i\text{-}C_4H_{10}\,(\%) = \frac{(C_{HC})_{in} - (C_{HC})_{out}}{(C_{HC})_{in}} \times 100 \qquad (4)$$

The selectivity of SCR-HC was calculated as the ratio of the moles of nitrogen formed at the reactor outlet (C_{N_2}) to the moles of carbon dioxide formed (i.e. equivalent to moles of iso-butane reacted). From Eq. (1) the amount of NO consumed is equal to twice of the N_2 produced. Hence the selectivity of SCR-HC, $S_{SCR\text{-}HC}$ is defined as:

$$S_{SCR\text{-}HC}\,(\%) = \frac{\frac{1}{13}(C_{N_2})\text{ formation}}{C_{CO_2}\text{ formation}} \times 100 \qquad (5)$$

3. Results and discussion

3.1. Characterization

A total coverage of about 140 g ZSM-5 m^{-2} of grid was obtained after three times repeated synthesis and the SEM

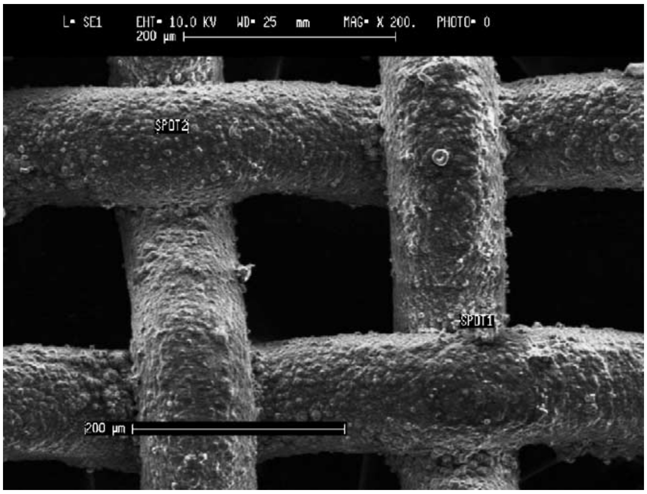

Fig. 3. SEM micrograph of zeolite coatings on the surface of wire mesh (three times coating).

micrograph is shown in Fig. 3. It was found that after three times repeated synthesis no part of the wire mesh was left without zeolite coating. The thickness of zeolite coating was estimated as about 4 μm. A further coating was not found reasonable for the grid geometry used in this study, since the void fraction would decrease and could result in a high-pressure drop during the passage of gas through the catalytic bed. The copper was exchanged with ZSM-5 coating and 5.7 wt.% copper was loaded in ZSM-5. Since copper was loaded using ion exchange, therefore copper loading was limited to 5.7 wt.%. The XRD zeolite coating shows 90% crystallinity as compare to commercial H-ZSM-5 sample. The Si/Al ratio of zeolite coating was 25 and BET surface area of the zeolite coating was 322 m^2/g ZSM-5 with a total pore volume of 0.1768 cc/g ZSM-5.

3.2. Catalyst activity measurements

The catalyst activity of Cu–ZSM-5 structured catalyst was measured at various gas hourly space velocities, GHSV (10,000–27,000 h^{-1}) and different reaction temperatures. The feed was composed of 1000 ppm NO, 1500 ppm i-C_4H_{10}, 3 vol% O_2 and balance N_2 with total gas flow rate of 50 ml/min. The reaction temperature was in the range of 300–400 °C which was the optimum temperature window of Cu–ZSM-5 catalyst for selective catalytic reduction of NO with hydrocarbon as reducing agent (SCR-HC) reported in the literature [12,13]. Fig. 4 shows that the NO reduction increased with the increase in reaction temperature and decreased with the increase of GHSV. The experiments were carried out at GHSV of 13,000 h^{-1} to determine the NO reduction profile for wider operating temperature window (i.e. 100–650 °C). Fig. 5 shows the NO reduction profile in the temperature range of 100–650 °C at GHSV of 13,000 h^{-1} over Cu–ZSM-5 structured catalyst. The results show that the NO reduction dropped at higher temperature. The optimum NO reduction was observed at a reaction temperature of 375 °C. The decline at higher temperature was primarily attributed to the direct oxidation of i-C_4H_{10} by the excess oxygen [14] as reflected by the formation of CO_2 that was detected.

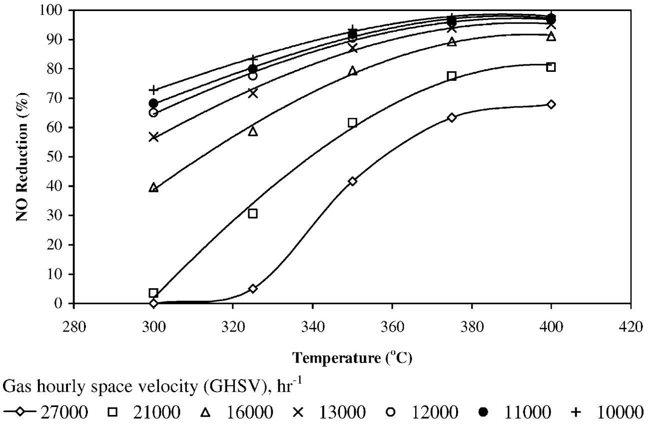

Fig. 4. NO reduction profile in the temperature range of 300–400 °C at various GHSV (10,000–27,000 h^{-1}) over Cu/ZSM-5 structured catalyst.

Fig. 6 shows the concentration of i-C_4H_{10} in percentage (relative to i-C_4H_{10} initial concentration) and CO_2 formation at different reaction temperatures. The CO_2 yield was calculated based on the relative ratio of the area under the CO_2 chromatogram at a reaction temperature and the area under the CO_2 chromatogram at complete conversion of i-butane at temperatures higher than 400 °C. It shows that at temperature above 400 °C, all of the i-C_4H_{10} was converted to CO_2 (i.e. CO_2 yield was 100%). This suggested that at higher temperature, the oxidation of hydrocarbon becomes dominant resulting in the drop of NO reduction. Fig. 7 shows the experimental data of N_2 formation and NO converted at space velocity of 13,000 h^{-1} for different reaction temperatures. In the present study, only nitrogen was detected as the product from selective catalytic reduction of NO over Cu–ZSM-5 structured catalyst. The formation of NO_2 or N_2O_4 was not detected during the reaction as reported for Pt-ZSM-5 catalyst in the literature [15,16]. Refer to Eq. (1),

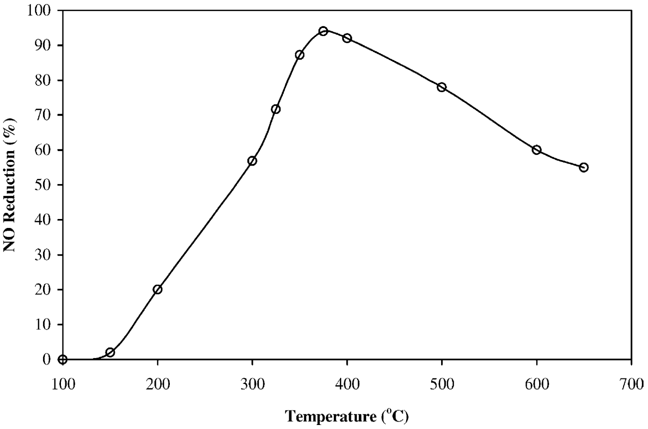

Fig. 5. NO reduction profile in the temperature range of 100–650 °C at GHSV of 13,000 h^{-1} over Cu/ZSM-5 structured catalyst.

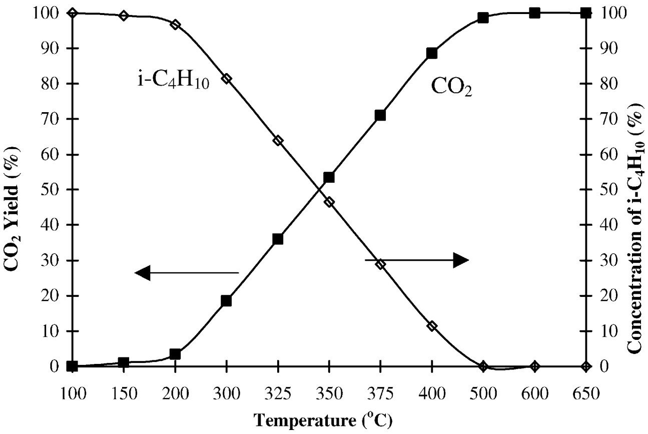

Fig. 6. Concentration of i-C_4H_{10} (relative to i-C_4H_{10} initial concentration) and CO_2 formation during selective catalytic reduction of NO process over Cu/ZSM-5 structured catalyst at different reaction temperatures.

the amount of NO consumed is equal to twice the amount of N_2 produced. The 100% selectivity of nitrogen implied that only N_2 was in the selective catalytic reduction of NO.

The gas hourly space velocity (GHSV) is another important operating parameter in assessing the performance of potential catalysts for reduction of NO. It represents the engine load speed (rpm), which indirectly controls the exhaust gas flow rate. The maximum reduction of NO dropped about 30% once the GHSV increased from 10,000 to 27,000 h^{-1}. It was found that the mass transfer limitations in Cu–ZSM-5 structured catalyst have minor influence in the NO reduction.

3.3. Process parameters studies using design of experiments

Design of experiments was used to obtain the optimum value of important variables in the selective catalytic reduction of nitric oxide (NO) with iso-butane as the reducing agent. The RSM was used to obtain the optimum conditions (i.e. NO concentration, iso-butane concentration and reaction temperature) at fixed amount of catalyst (0.1 g Cu/ZSM-5 coated on structured catalyst packing) and space velocity of 13000 h^{-1}. A central composite is designed to estimate the coefficients of a quadratic model presented in Eq. (6).

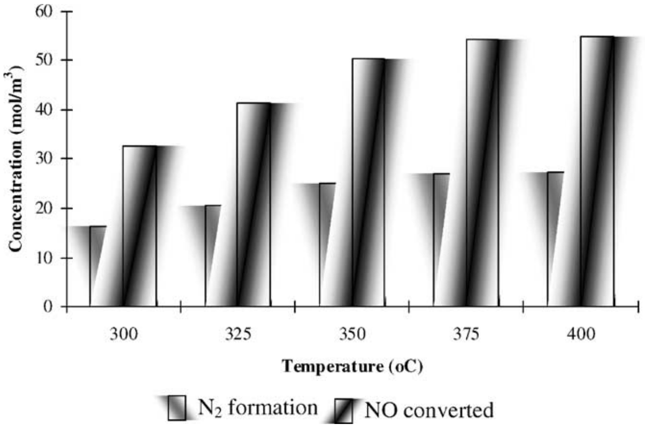

Fig. 7. Concentration of N_2 formation and NO converted at space velocity of 13,000 h^{-1} for different reaction temperatures over Cu/ZSM-5 structured catalyst.

Table 1
Independent variables: coded and real value in center composite design

Factor	Factor code	Unit	Low level (−1)	High level (+1)
Feed NO concentration (C_{NO})	A	ppm	900	2000
Feed Iso-butane concentration (C_{HC})	B	ppm	900	2000
Temperature (*T*)	C	°C	300	400

$$y = \beta_o + \sum_{i=1}^{k}\beta_i x_i + \sum_{i=1}^{k}\beta_{ii} x_i^2 + \sum\sum_{i<j}\beta_{ij} x_i x_j + \varepsilon \qquad (6)$$

where, y is the measured response, β_o is the intercept term, β_i, β_{ii} and β_{ij} are the measures of the effects of variables x_i, $x_i x_j$ and x_i^2, respectively. The variable $x_i x_j$ represents the first order interaction between x_i and x_j ($i < j$) and ε is error.

The analysis of variance (ANOVA) for quadratic model was carried out to establish its significance. In the statistical study, the variables identified were the reaction temperature (*T*), feed concentration of nitric oxide (C_{NO}) and feed concentration of iso-butane (C_{HC}). Since the relationship between the independent variables and response variable was unknown, it was estimated by using regression analysis program (Design Expert 6.0.6 Software). The factors were studied at two levels, low level coded (−1), and high level coded (+1) as presented in Table 1. The 2^3 center composite design matrix of 16 experiments covering full design of three level factors used to build a quadratic model and the experimental data of the three observed responses is shown in Table 2. Three experiments (run 17, 18 and 19) were repeated to check the reproducibility and to estimate an experimental error. All three responses gave a reproducible result where the deviation of each run was found small and within an experimental error (i.e. ± 0.35 for NO reduction, ±0.15 for i-C_4H_{10} conversion and ±0.23 for selectivity SCR-HC).

3.3.1. NO reduction

Table 3 shows the ANOVA for 2^3 full CCD of the NO reduction. A quadratic model was proposed in terms of independent and dependent variables. The quadratic model for the NO reduction in terms of coded factors is presented in Eq. (7) as:

$$\begin{aligned}\text{NO reduction (\%)} = {} & 93.15 - 2.90A + 3.32B + 22.95C \\ & - 2.00A^2 - 2.42B^2 - 14.87C^2 \\ & + 0.30AB + 0.55AC + 0.87BC \qquad (7)\end{aligned}$$

The model *F*-value of 38.18 implies that the model is significant under 95% level of confidence. Values of “*P* > *F*”

Table 2
Experiment matrix of 2^3 center composite design

Run	Factors			Responses		
	NO concentration (ppm)	HC concentration (ppm)	Reaction temperature (°C)	NO reduction (%)	$i\text{-}C_4H_{10}$ conversion (%)	Selectivity HC-SCR (%)
1	2380	1450	350	79	51.1	4.7
2	900	900	300	55.6	19.6	5.3
3	2000	900	400	91.5	85.7	4.4
4	1450	1450	434	93.9	100	1.7
5	900	2000	300	56.1	16.3	2.9
6	1450	1450	266	6.9	1.4	9.0
7	1450	1450	350	92.4	51.1	3.4
8	1450	520	350	75.9	50.9	7.6
9	2000	2000	400	96.8	87.4	2.1
10	520	1450	350	94.3	51.4	1.2
11	2000	900	300	50	17.4	11.9
12	1450	1450	350	94.1	42	4.2
13	900	900	400	94.1	85.7	2.0
14	2000	2000	300	52.5	15.8	6.2
15	1450	2380	350	95	51.9	2.1
16	900	2000	400	98.9	86.4	1.0
Repeated experiments						
17	2000	900	300	50.3	17.3	12.0
18	2000	900	300	49.8	17.6	11.7
19	2000	900	300	50.5	17.5	12.1

less than 0.0500 indicate that the model terms are significant. In this case C and C^2 were found as significant model term for NO reduction. The lack of fit was calculated from the experimental error (pure error) and residuals. The lack of fit is the ratio between the residuals and pure error. "Lack of fit F-value" of 22.79 implied the lack of fit was not significant relative to the pure error due to noise. Therefore, the suggested model for NO reduction in Eq. (7) is valid for the present study. Fig. 8 compares experimental values of NO reduction with the predicted model value of NO reduction obtained from the Eq. (7). The value of correlation coefficient, R^2 was found high (i.e. close to unity) confirming the accuracy of the model. The suggested model is also shown graphically in Fig. 9. The figure shows the variation of the NO reduction with the NO concentration and $i\text{-}C_4H_{10}$ concentration.

Table 3
Analysis of variance (ANOVA) for 2^3 full center composite design (CCD) for NO reduction

Source	Sum of squares	DF	Mean square	F-value	$P > F$
Model	9784.62	9	1087.18	38.18	0.0001[a]
A	115.34	1	115.34	4.05	0.0908
B	150.93	1	150.93	5.30	0.0609
C	7188.46	1	7188.46	252.43	<0.0001
A^2	37.70	1	37.70	1.32	0.2937
B^2	55.01	1	55.01	1.93	0.2140
C^2	2033.60	1	2033.60	71.41	0.0001
AB	0.73	1	0.73	0.03	0.8780
AC	2.44	1	2.44	0.09	0.7797
BC	6.08	1	6.08	0.21	0.6604
Residual	170.86	6	28.48		
Lack of fit	169.38	5	33.88	22.79	0.16[b]
Pure error	1.49	1	1.49		
Cor total	9955.48	15			

[a] Significant under 95% level of confidence.
[b] Not significant relative to the pure error due to noise.

3.3.2. Iso-butane conversion

The linear model for the $i\text{-}C_4H_{10}$ conversion in terms of coded factors is represented as:

$$i\text{-}C_4H_{10}\ \text{conversion}\ (\%) = 50.88 - 0.17A - 0.054B + 32.36C \qquad (8)$$

The model is shown graphically in Fig. 10. The figure shows the variation of the $i\text{-}C_4H_{10}$ conversion with the NO concentration and $i\text{-}C_4H_{10}$ concentration.

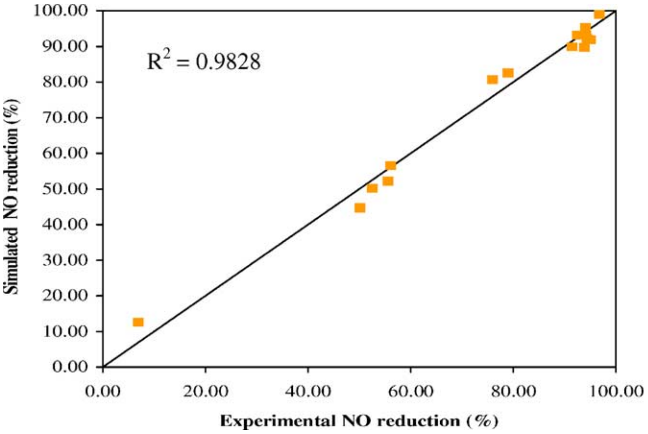

Fig. 8. Parity plot for the actual NO reduction and the NO reduction value predicted from Eq. (7).

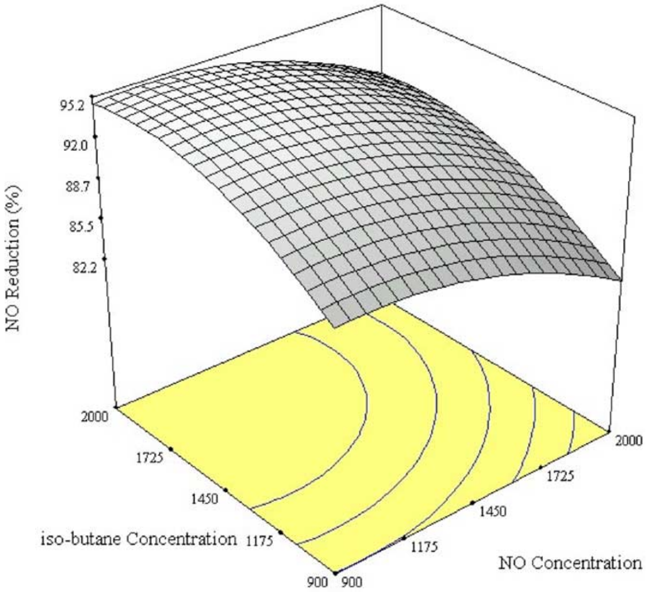

Fig. 9. Effect of NO concentration and i-C_4H_{10} concentration on the NO reduction.

3.3.3. Selectivity of SCR-HC

A quadratic model was proposed in terms of independent and dependent variables. The quadratic model for the selectivity SCR-HC in terms of coded and actual factors is presented in Eq. (9) given by:

$$\begin{aligned}\text{Selectivity SCR-HC} = {} & 3.77 + 1.41A - 1.53B - 2.12C \\ & - 0.27A^2 + 0.39B^2 + 0.58C^2 \\ & -0.58AB - 0.81AC + 0.58BC \qquad (9)\end{aligned}$$

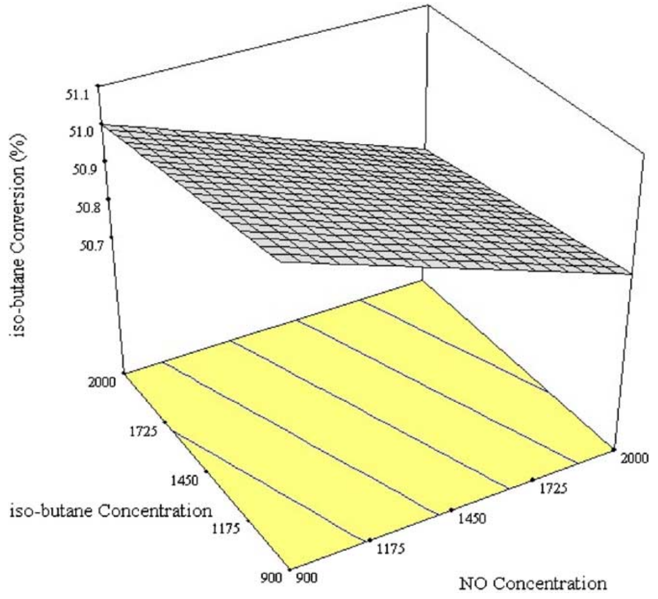

Fig. 10. Effect of NO concentration and i-C_4H_{10} concentration on the i-C_4H_{10} conversion.

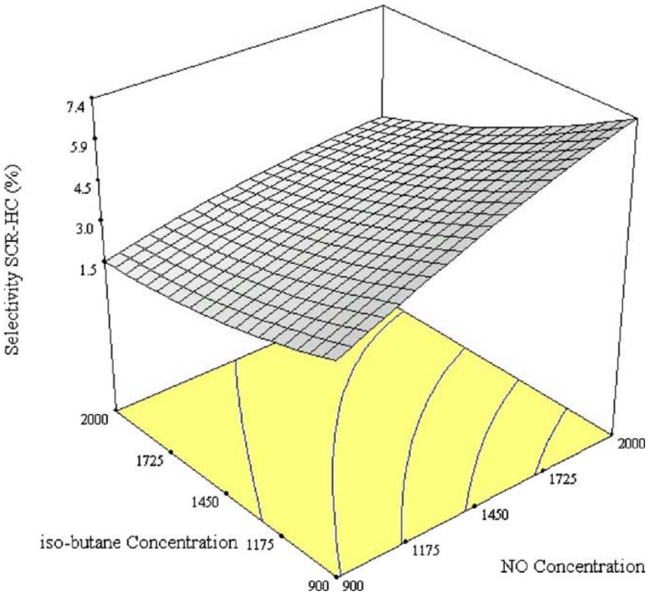

Fig. 11. Effect of NO concentration and i-C_4H_{10} concentration on the selectivity SCR-HC.

The model is presented graphically in Fig. 11. The figure shows the variation of the selectivity SCR-HC with the NO concentration and i-C_4H_{10} concentration.

3.4. Optimization using RSM

The optimum conditions for three independent variables, i.e. NO concentration, iso-butane concentration and reaction temperature for Cu/ZSM-5 coated structured catalyst in selective catalytic reduction of NO with iso-butane as reducing agent were obtained by using numerical optimization feature of Design Expert 6.0.6 Software. The optimization module in Design-Expert searches for a combination of factor levels that simultaneously satisfy the requirements placed on each of the responses and factors. The goal was set to optimize the NO reduction, i-C_4H_{10} conversion and selectivity of SCR-HC. Table 4 presents the two solutions found by DOE for the selective catalytic reduction of NO with i-C_4H_{10} as reducing agent over Cu–ZSM-5 structured catalyst. By default, the solutions are sorted from best to worst, thus the optimum condition in solution 1 was chosen for further process studies. Fig. 12 shows the desirability for each factor and each response individually for solution 1 where the desirability for combined effects was found as 0.72.

The additional 10 experiments were carried out at 375 °C with total feed gas flow rate of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2, and balance N_2) over Cu–ZSM-5 structured catalyst out to check the accuracy of the optimum conditions obtained from DOE experiments. Table 5 shows the results of the 10 experiments conducted at the optimum conditions. The NO reduction obtained from the experiment was compared with the value predicted by DOE. There was an error of ±0.56% for NO reduction value under 95% confidence level (i.e. 94 ± 0.52%).

Table 4
Optimum conditions obtained from DOE for the selective catalytic reduction of NO with i-C_4H_{10} as reducing agent over Cu/ZSM-5 structured catalyst

NO concentration	i-C_4H_{10} concentration	Temperature (°C)	NO reduction (%)	i-C_4H_{10} conversion (%)	Selectivity SCR-HC (%)
1731	1283	375	94.00	71.11	4.6
1708	1266	375	94.00	71.11	4.4

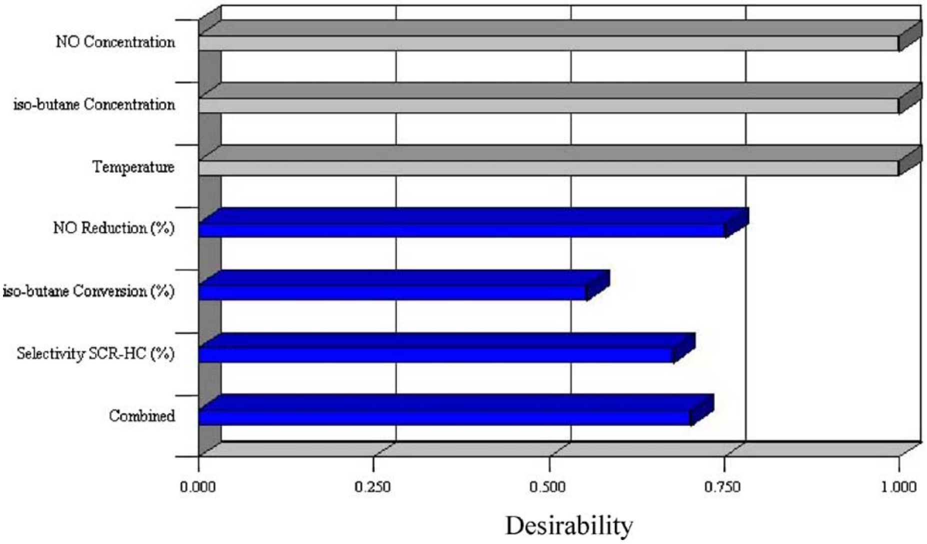

Fig. 12. Desirability of optimum conditions.

3.5. Durability study

The durability of Cu/ZSM-5 structured catalyst was carried out with feed gas stream of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2 and balance N_2) and results are shown in Fig. 13. The reaction temperature used were 300, 350 and 375 °C, which were in the optimum range (i.e. 300–400 °C) for Cu/ZSM-5 catalyst for selective catalytic reduction of NO reported in the literature [12,13]. The results showed that the structured catalyst was able to maintain its activity for NO reduction for 48 h of continuous operation without any structural changes.

Table 5
Verification experiments at optimum conditions over Cu/ZSM-5 structured catalyst

Run	NO concentration (ppm)		NO reduction (%)		[a]Error
	$(C_{NO})_{in}$	$(C_{NO})_{out}$	$(X_{NO})_{exp}$	$(X_{NO})_{DOE}$	
1	1730	130	92.5	94	−1.5
2	1730	118	93.2	94	−0.8
3	1730	111	93.6	94	−0.4
4	1730	102	94.1	94	0.1
5	1730	112	93.5	94	−0.5
6	1730	107	93.8	94	−0.2
7	1730	142	91.8	94	−2.2
8	1730	107	93.8	94	−0.2
9	1730	107	93.8	94	−0.2
10	1730	131	92.4	94	−1.6
Mean error	−0.75				
[b]Standard deviation (σ)	0.761				
[c]95% confidence level	0.4713				

[a] Error: $(X_{NO})_{exp} - (X_{NO})_{DOE}$.
[b] $\sigma = \sqrt{(n\sum x^2 - (\sum x)^2)/n(n-1)}$.
[c] Confidence level $= \pm 1.96(\sigma\sqrt{n})$ where n represents the sample size.

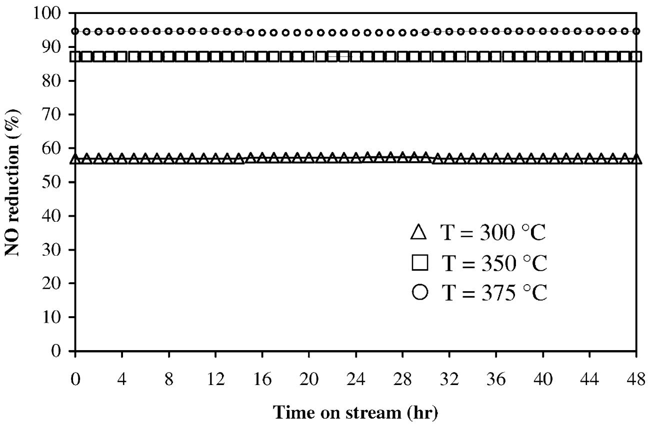

Fig. 13. Durability study of Cu/ZSM-5 structured catalyst for 48 h.

3.6. Effect of water vapor

The optimum conditions obtained from the design of experiments were used to study the effect of water vapor (0, 5, 10, 15 and 20%) in the NO reduction. Experiments were carried out with feed gas stream of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2, 0, 5, 10, 15 and 20% of water vapor and balance N_2). Water vapor is one of the component generally present in diesel exhaust and it is important that a potential catalyst for the reduction of NO should be able tolerant to its presence [12]. Water vapor as high as 10% in diesel exhaust composition appeared to deactivate many of the proposed catalysts for the removal of NOx. Fig. 14 shows the percentage NO reduction achieved when 0, 5, 10, 15 and 20% of water vapor was introduced into the feed gas stream. In the absence of water vapor, NO reduction was 93.5%, close to the value predicted from the DOE. However, the percentage of maximum NO reduction dropped drastically to about 52% when 5, 10, 15 and 20% of water vapor were introduced. The drop in the catalytic activity of Cu–ZSM-5 catalyst in the presence of water vapor could be due to framework degradation [17]. The presence of water vapor promoted dissociation of water due to the hydrophilic nature of the zeolite, to balance the net negative charged of the zeolite framework [18]. The durability test was conducted on a fresh Cu–ZSM-5 catalyst with 10% of water feed for 55 h at 375 °C as shown in Fig. 15. Reversible effect of water vapor on Cu–ZSM-5 structured catalyst was observed. This was in agreement with the work of Oh et al. [19] who reported that when 10% of water vapor was eliminated from the feed gas stream, Cu–ZSM-5 showed higher NO conversion in comparison to test under wet conditions.

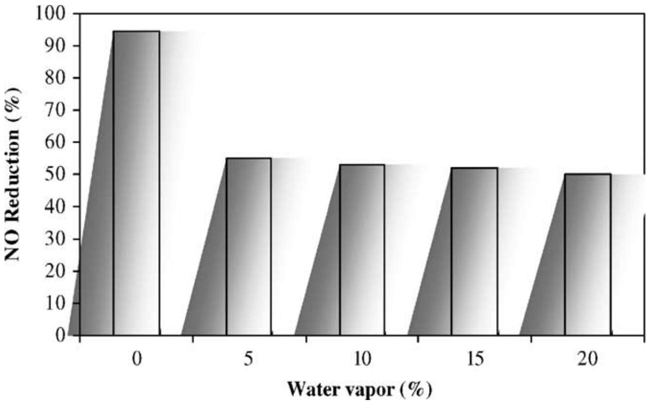

Fig. 14. Maximum NO reduction achieved at 0, 5, 10, 15 and 20% of water vapor for feed gas stream of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2 and balance N_2) over Cu/ZSM-5 structured catalyst.

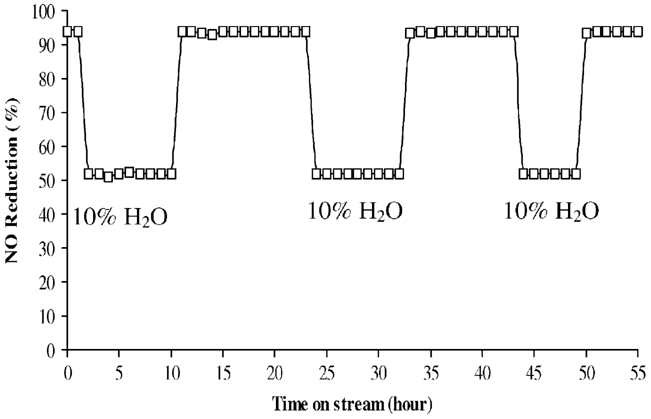

Fig. 15. Time on stream test of Cu/ZSM-5 structured catalyst with alternate feed of 10% water vapor.

3.7. Effect of sulfur dioxide

Diesel engine emission contains 10–150 ppm and SO_2 is generated from the sulfur present in the diesel fuel that generally contains 0.01–0.4 wt.% of sulfur depending upon source and different regulations [20]. Many proposed catalyst in the literature for removal of NOx from diesel exhaust emission exhibited severe deactivation in the presence of [12]. The optimum conditions obtained from DOE were used to study the effect of sulfur dioxide on the NO reduction. Experiments were carried out with feed gas stream of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2, 0, 50, 10, 150, 200 ppm of sulfur dioxide and balance N_2) over Cu–ZSM-5 structured catalyst. Fig. 16 shows the maximum NO reduction achieved when 0, 50, 100, 150 and 200 ppm of sulfur dioxide were introduced into the feed gas stream. In the absence of sulfur dioxide, NO reduction was 94.1%, close to the value predicted from the DOE. However, percentage of maximum NO reduction dropped drastically to about 25% when 50, 100 and 150 ppm of sulfur dioxide were introduced. The NO reduction further dropped to about 20% when Cu–ZSM-5 structured catalyst was exposed to 200 ppm of sulfur dioxide. Although the exposure of sulfur dioxide was terminated at tenth hour of the experiment as shown in Fig. 17, Cu–ZSM-5 structured catalyst was not able to recover back to its initial activity. This result suggested that sulfur dioxide remained as a severe poisoning component where its presence of 50 ppm in the feed gas stream was

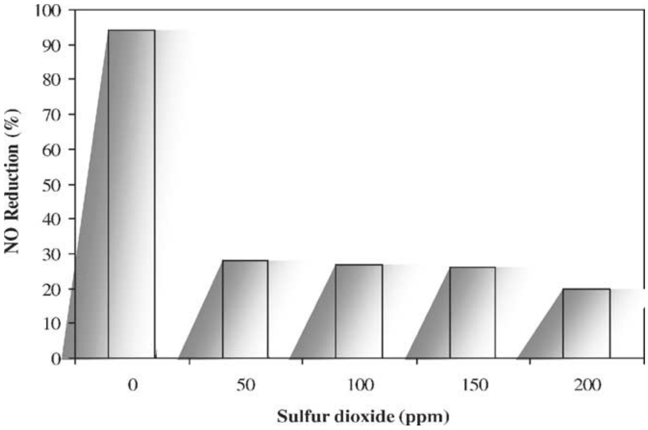

Fig. 16. Maximum NO reduction achieved at 0, 50, 100, 150 and 200 ppm of sulfur dioxide for feed gas stream of 50 ml/min (1730 ppm NO, 1280 ppm i-C_4H_{10}, 3 vol% O_2 and balance N_2) over Cu/ZSM-5 structured catalyst.

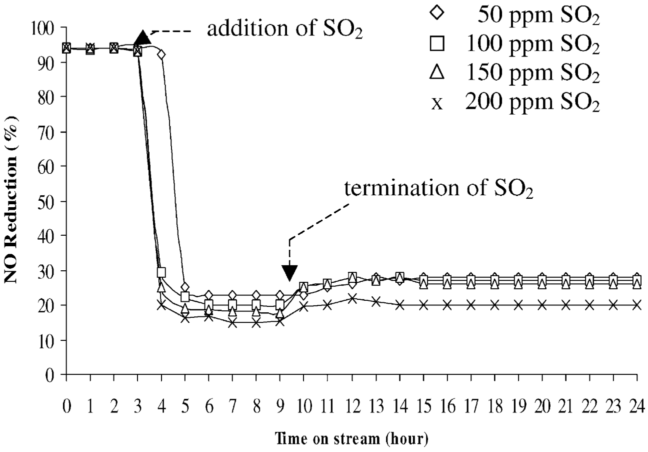

Fig. 17. Effect of sulfur dioxide on the catalytic test of Cu/ZSM-5 structured catalyst.

enough to cause deactivation. Oxidation of sulfur dioxide produces sulfur trioxide (SO_3) and sulfur tetra-oxide (SO_4). It was suggested from EDX analysis that these two species (i.e. SO_3 and SO_4) are the components that blocked the active site of the catalyst from adsorption of reactant molecules [21,22]. These sulfur species have strong adsorption on the catalyst surface with high heat of adsorption of 225 kJ/mol [22].

4. Conclusions

Structured zeolite catalyst was successfully produced by in situ hydrothermal synthesis method. Scanning electron microscope results showed uniform dense zeolite coating onto stainless steel wire mesh. The total coverage after three times repeated coating process was found about 140 g ZSM-5 m^{-2} of grid and the thickness of coating was 4 μm. The BET surface area of zeolite was 322 m^2/g after three times repeated coating. Copper was exchanged with the ZSM-5 zeolite coating and 5.7 wt.% of copper was loaded. Design of experiments was applied in the process parameters studies of Cu–ZSM-5 structured zeolite catalyst. Response surface methodology coupled with DOE was used to obtain the optimum values of NO concentration, iso-butane concentration and reaction temperature for a fixed amount of catalyst and constant space velocity for selective catalytic reduction of NO with iso-butane as reducing agent. The optimum conditions were 1730 ppm of NO concentration, 1280 ppm of iso-butane concentration and 375 °C reaction temperature with 94% reduction of NO and 4.6% SCR-HC selectivity. The presence of water vapor and sulfur dioxide was studied over NO reduction. The water vapor caused reversible deactivation whereas sulfur dioxide caused permanent deactivation of the structured Cu–ZSM-5 catalyst.

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