Research note

Simple Kinetic Modeling of Selective Reduction of Nitric Oxide in Diesel Exhaust Over Cu-Zn/ZSM-5 Monolithic Catalyst

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Abstract
An integral reactor-based kinetic model for the selective reduction of nitric oxide over Cu-Zn/ZSM-5 washcoated monolithic catalysts is reported. The active component was washcoated onto a 400 cpsi ceramic monolithic substrate at a loading of 23.6 wt. % usage 2,000 ppm iso-butane was used as the reductant. High activity without significant pressure drop was achieved at a GHSV of 16,000 h^{-1}. Third order polynomial satisfactorily fitted the activity versus space time data and a low activation energy of +30.3 kJ/mol was obtained. The applicability of the model was demonstrated within 300-400 ºC and space time of 0.12-0.94 s.

Keywords: *NO, Selective Catalytic Reduction, Monolith Cu-Zn/ZSM-5, Kinetics, Integral reactor*

1- Introduction

Despite its popularity to high fuel efficiency, reliability and cheaper fuel, diesel engines produce a significant amount of NOx which causes environmental and health problems. Selective catalytic reduction (SCR) is a plausible method for NOx removal [1], but high pressure drop that can affect the performance of the engines is always a key issue [2]. Thus, monolithic catalysts are recently gaining interest for application in NOx reduction [1, 2] as the pressure drop is much lower than that caused by particulate catalysts. For this reason, the monolithic reactor should be able to handle high throughput or, in other words, the handling of higher volumetric gas flow is possible without experiencing a significant pressure drop.

The main drawback of a monolithic catalyst is low available surface area to provide a fast reaction. However, the specific surface area of the monolithic catalyst can be enhanced up to about 40 m^2/g by washcoating with suitable porous materials such as zeolites. ZSM-5-washcoated monolithic catalysts are receiving attention in the SCR of NOx applications [2, 3]. Bimetallic Cu and Zn has been demonstrated to be beneficial towards achieving improved activity and stability of

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Cu/ZSM-5 catalyst in our earlier series of study as reported in Abdullah [4]. However, the kinetic study of the SCR of NOx on monolithic catalysts, especially when operated in an integral reactor mode, is hardly reported. With the open structure of monolithic catalysts and high possible throughput of feed, an adiabatic temperature rise during the reaction could be ignored and therefore, a complicated kinetics model is deemed unnecessary. As such, this study focuses on establishing and verifying a simple, yet reliable kinetic model for an integral reactor which is applicable to a monolithic catalyst. This model should be applicable when efforts to scale up the operation are considered.

2- Experimental
2.1- Catalyst preparation method
A Cu-Zn/ZSM-5 washcoat component was prepared by impregnating Cu and Zn followed by drying and calcination using a method described by de Lucas *et al.* [3] and Nejar *et al.* [5]. The procedures resulted in a Cu-Zn/ZSM-5 catalyst with 6 wt. % and 8 wt. % of Cu and Zn, respectively. A monolithic catalyst was prepared by dip-coating a 400 cpsi, 2.0 cm diameter and 6.0 cm long ceramic monolith with 20 wt. % of washcoat in 1 wt. % of methyl cellulose in solution followed by drying and calcination. The final washcoat loading was 23.6 %. The monolithic catalyst was carefully placed in the reactor at the desired location and sandwiched by two layers of glass wool to avoid short circuiting of the feed gas.

2.2- Activity measurement
The activity measurements were carried out

in a continuous flow system as described in detail in Deeng et al. [6]. Fig. 1 shows the schematic diagram of the reactor system. It consisted of a gas feed system for each component with individual control by MKS type 1170A mass flow meters, a catalytic reactor heated with a Linberg TF 55035C tubular furnace and an exit gas flow meter equipped with a gas analysis system. The nitrogen flow was first saturated with water vapor prior to combining with other gas component streams to better simulate the diesel exhaust. The feed compositions were 900 ppm NO, 2,000 ppm iso-butane (as the reductant), 3 % oxygen and N_2 balance. The temperature of the catalyst was measured using a K-type thermocouple. The concentration of NO in the inlet and outlet gases was determined using a gas chromatograph (Shimadzu GC 8A) and a gas analyzer (KANE-MAY 900, England). This measurement was only done after a steady state condition was reached.
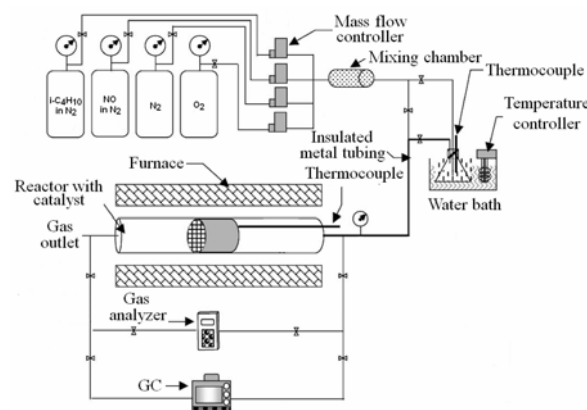

Figure 1. Schematic diagram of the reactor system

In kinetic experiments, a series of experiments were carried out at different gas hourly space velocities (GHSV) (2,000 to 16,000 h^{-1}) by varying the feed flow rate and

various reaction temperatures (300ºC to 400ºC). The corresponding space times were between 0.12 s and 0.94 s. The rate of reaction (-r_{NO}) was determined from the differentiation of concentration of NO with respect to space time (τ), which was calculated as the inverse of the GHSV. For this purpose, Polymath software was used. The porosity of the structured catalyst bed was 0.96, while the apparent volume of the structured catalyst bed was 0.816 cm³.

2.3- Kinetic study

In order to obtain the reaction rate constant (k) as a function of the reaction temperature (T) to calculate the activation energy (E_a), experimental runs were conducted at various temperatures (300ºC to 400ºC) by changing the furnace temperature. In this study, a power law model based on homogeneous kinetics was proposed. In the model for an integral reactor, the reaction order with respect to feed nitric oxide (NO) and iso-butane (HC) concentrations was widely reported to follow a first order kinetic such as that concluded recently by Tomasic *et al.* [7] and Deeng *et al.* [6]. The reaction order should also independent of O_2 concentration as O_2 was present in excess (3 v %) as compared to the concentration of NO and HC which were in ppm levels. Thus, the homogeneous model was simplified to equation (1).

$$-r_{NO} = k\, C_{NO}C_{HC} \tag{1}$$

The values of k obtained in the present study were used to obtain simulated values of NO converted, ($X_{NO\ calculation}$). The rate of reaction (-r_{NO}) is defined given by equation (2)

$$-\frac{dC_{NO}}{d\tau} = -r_{NO} \tag{2}$$

Substituting equation (1) in equation (2) gives equation (3):

$$-\frac{dC_{NO}}{d\tau} = kC_{NO}C_{HC} \tag{3}$$

In this study, the following stoichiometric reactions are considered:

$$C_4H_{10} + \frac{13}{2}NO + \frac{13}{4}O2 \longrightarrow 4CO_2 + 5H_2O + \frac{13}{4}N2 \tag{4}$$
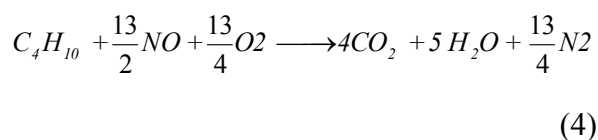
The concentration of HC (C_{HC}) can be expressed in terms of C_{NO} using equation (4) and simplified to equation (5).

$$C_{HC} = C_{NOo}\left(\theta_{HC} - \frac{X_{NO}}{6.5}\right) \tag{5}$$

where, θ_{HC} is $\dfrac{C_{HCo}}{C_{NOo}}$, thus,

$$\frac{dX_{NO}}{d\tau} = kC_{NOo}(1 - X_{NOo})(6.5\theta_{HC} - X_{NO})\frac{1}{6.5} \tag{6}$$

Integrating equation (6) gives equation (7)

$$\ln\left(\frac{6.5\theta_{HC} - X_{NO}}{1 - X_{NO}}\right) = kC_{NOo}\tau(6.5\theta_{HC} - 1) \tag{7}$$

Equation (7) was used to calculate the $X_{NOcalculation}$ once the k is evaluated from the experimental data.

3- Results and discussion

Fig. 2 shows the profiles of the NO concentration versus the space time of the feed in the reactor at different temperatures. It is noted that they are best fitted to a third order polynomial curve within the temperature range tested. It is characterized by a rapid drop in the NO conversion at very low space time (or very high GHSV) to suggest the reaction controlling phenomenon within this range. Beyond a space time of about 0.24 s to the maximum used in this study i.e., 0.94 s (corresponding to a GHSV of 16,000 h^{-1}), minimal effect was observed with decreasing flow rate (increasing space time). This was an indication of the absence of external mass transfer limitations in the reaction system at high space time [1]. This conclusion was at least valid within a temperature range of 300 to 375°C. The presence of internal mass transfer limitations within this range was unlikely as the washcoat component was in the form of a very thin layer of Cu-Zn/ZSM-5 (about 40 μm), evenly distributed over the wall of the monolithic support.
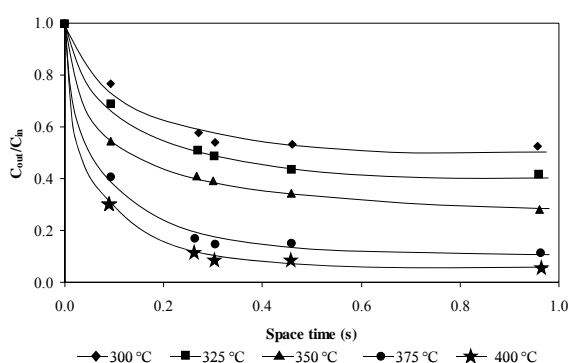
The rate constant (k) was then estimated using a non linear least square regression by means of Polymath software. The activation energy was estimated based on modified Arrhenius equation as given by equation (8).

$$ln\,k = ln\,A - \frac{E_a}{R}\left(\frac{1}{T}\right) \qquad (8)$$

Fig. 3 shows the plot of the reaction rate constant (k) versus the reciprocal of the reaction temperatures. It shows excellent fitting to a linear line with an R^2 value of 0.996, suggesting the applicability of the Arrhenius relationship in these experimental conditions. This finding also suggested that the reaction system was indeed a kinetic-controlling one and at the same time confirmed the applicability of the first order assumption of the reaction made during the development of the kinetic model. It should be mentioned that the NO reduction activity dropped when the reaction temperature exceeded 400ºC due to excessive oxidation of the HC reductant. The slope of the graph is the activation energy of the reaction and was found to be +30.3 kJ/mol. Thus, the rate constant (k) can be expressed as a function of temperature by equation (9).
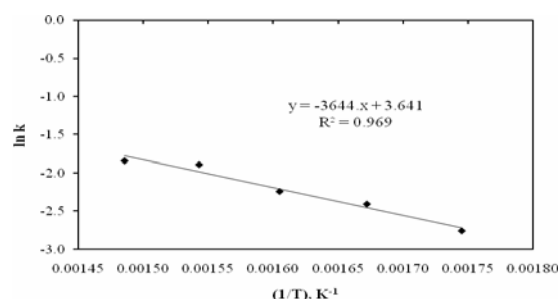

Figure 2. Normalized concentration of NO in the outlet as a function of space time at different temperatures.

Figure 3. Arrhenius plot for the determination of activation energy (E_a).

$$k = 38 \exp\left(\frac{-30.3 x\, 10^3}{RT}\right) \qquad (9)$$

The activation energy obtained in the present study was significantly lower than the activation energy for decomposing NO without the catalytic washcoat which is ~365 kJ/mol [4]. The result shows the significant role of the monolithic catalyst in promoting the selective NO reduction reaction. The activation energy calculated was also lower compared to that obtained with other catalyst for NO reduction such as 123 kJ/mol obtained with particulate Cu/ZSM-5 catalyst [7], 62 kJ/mol obtained with particulate CoOx/alumina catalyst [8] and 61 kJ/mol obtained with silver alumina catalyst [9]. The difference could partly be caused by different catalyst materials and different ranges of operating temperature window used. The presence of mass transfer limiting effects in the experiments with an unsuitable particle size of the particulate catalysts could also end up with lower than actual activation energy when the reaction is not a zero-order one [10]. In the absence of mass transfer limitations, the selective catalytic reduction is reported to be somewhere between a half to a first order reaction [11, 12].

The low activation energy for the NO reduction with the monolithic catalyst suggested that the reduction reaction was thermodynamically feasible and the activity was more superior to that of particulate catalysts. One clear advantage of the monolithic catalyst as used in this study is that the high activity was maintained up to a space time of 0.24 s or a corresponding GHSV of 16,000 h^{-1} and no pressure drop was detected. For particulate catalysts, a significant pressure drop was generally encountered above 10,000 h^{-1}, but the exact value varied with the particle size of the catalyst used. This result clearly indicated the advantage of a monolithic reactor system.

In this study, no significant adiabatic temperature rise was detected as the furnace temperature was almost similar (± 1°C) to the temperature of the catalyst bed measured by a K-type thermocouple. This was attributed to the open structure of the monolithic substrate, high heat capacity of the ceramic material and thin deposit of the zeolite washcoat layer. For a reaction with quite a narrow temperature window for high efficiency such as the SCR of NOx, adiabatic temperature rise should be avoided as it will lead to reduced efficiency. The system under investigation showed that an increase of about 50°C in the reaction temperature led to a decrease in NO removal efficiency by about 30%. In this respect, the monolithic catalyst provides an interesting advantage compared to conventional particulate catalysts. Thus, the Cu-Zn/ZSM-5 with 6 wt. % and 8 wt. % of Cu and Zn, respectively, washcoated to ceramic monolith at 23.6 wt. % as used in present study was deemed suitable for NO reduction as high efficiency was achieved at a lower temperature to translate into an energy saving operation.

It is of great interest to verify the accuracy of the kinetic model in simulating the actual experimental data for NO reduction. For this purpose, Equation (7) was then applied to calculate the NO reduction ($X_{NO\ calculation}$) using the respective kinetic constant (k) obtained. The parity plot between the experimental and the simulated results as shown in Fig. 4 prove that the homogeneous

model was sufficient to predict the values of NO reduction ($X_{NO\ calculation}$). Most of the data dropped within ± 5%, which is generally sufficient to indicate the high accuracy of the kinetic model [3]. Some deviation was attributed to experimental errors. Thus, homogeneous kinetic model as expressed in equation (7) that treated the reaction as first order to both NO concentration and HC concentration is appropriate for the SCR of NO reaction. It can be satisfactorily used in the design of the structured catalytic converter using a ceramic monolith catalyst for the reduction of NOx from diesel exhaust. The applicability of the model was demonstrated within 300-400ºC and a space time of 0.12-0.94 s. Again, the result led to the confirmation that a first order kinetic model was applicable to this kinetic-controlling reaction system.
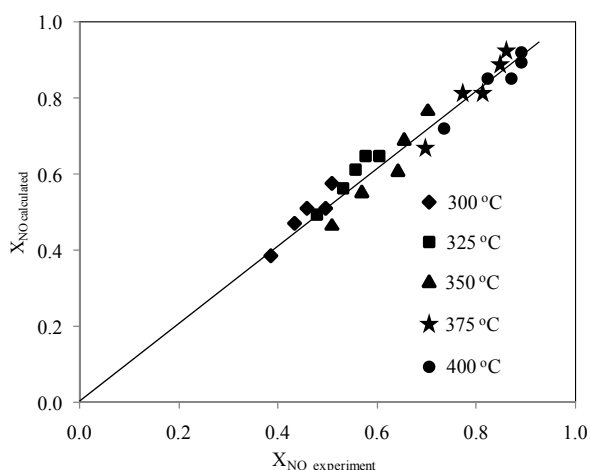

Figure 4. Comparison between simulated and experimental data for NO conversion at different temperatures.

4- Conclusions

A 23.6 wt.% Cu-Zn/ZSM-5 monolithic catalyst was successfully prepared and upon testing in the SCR of NO, a third-order

relationship between activity and space time was demonstrated and an activation energy of + 30.3 kJ/mol was obtained. This activation energy was significantly lower, compared to the reported result, to suggest the high catalytic activity of this monolithic catalyst. The homogeneous model based on an integral reactor mode satisfactorily fitted the experimental data between 300°C and 400°C and GHSV of 2,000 h^{-1} to 16,000 h^{-1} with a lower than 5% error. This result proves the applicability of the simple integral reactor-based model over various experimental conditions.

5- Acknowledgement

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