

Reduction of NO_x Gases Using Copper Zeolite Catalyst

Abdallah M. Hasna

Abstract— Energy demand and production have raised vast amounts of pollutants such as NO_x and other harmful components. These are emitted daily from various industrial processes including stationary and non-stationary sources, i.e. automotive engines, industrial boilers and power plants. This article reports on an experimental investigation of the conversion levels for NO decomposition over Cu-ZSM5(158) catalyst using electrical heating element reactor. This was achieved by passing a stream containing 1% NO and 99% He, through the reactor, and then measuring the concentration of the stream exiting the reactor. The purpose of this paper is to illustrate the conversion calculation process at various temperatures and contact times. This included the applicability of first order kinetics, i.e. whether the system followed the Arrhenius temperature relationship by calculating and plotting the equilibrium constants at each reaction temperature.

Index Terms—Copper Zeolite, Arrhenius temperature relationship, oxidation.

I. INTRODUCTION

Nearly all pollution is related to the burning of fossil fuels. Gasoline is the primary fuel utilised in the internal combustion engine and approximately 600 million tonnes is consumed by the OECD countries. Of this total, 57% is used by the US alone, with Western Europe using 26% and Japan 8%. The rest of the world (excluding the ex-Soviet block) accounts for about 130 million tonnes, [1]. Oxides of nitrogen (NO_x) reduction using metal/zeolite type catalysts has been the subject of much research [2] [3] [4] [5] [6] [5] [7] [8] [9] [10] [11] [12] [13] [14]. The dominant impact of NO_x emissions on the climate is through the formation of tropospheric ozone, the third largest single contributor to positive radiation forcing, [15]. NO_x has been linked with urban smog formation, acid rain and the growing global problem of oxides, which play a major role in the photochemistry of the atmosphere, [16] [17]. Approximately half of all the hydrocarbons (HC), carbon monoxides (CO) and nitrogen oxides (NO_x) emitted are associated primarily to the burning of fossil fuels, particularly those produced by gasoline and diesel engines. Several car manufacturers have investigated different engine operational parameters in order to reduce HC, CO and NO_x emissions [18]. In light of their

findings, car manufacturers perceived HC and CO to be more harmful environmentally than NO_x and therefore designed their cars accordingly. However, these eventually lead to unacceptable increases in NO_x concentration in the atmosphere, which consequently increased the need for more efficient NO_x conversion processes [19]. The focus of this article is concerned with the elimination of NO_x, which arises from the fixing of atmospheric nitrogen due to the high temperatures which exist in engines. Thus, vehicle emissions can be derived either directly from the fuel, or from the interaction between the fuel and the engine. However Mobile sources of emissions, such as automobiles, operate at much lower temperatures and as a result catalytic decomposition is extremely difficult. Consequently, NO_x removal from exhaust gases of mobile sources is best treated by “Three-Way” catalyst technology. the EPA 2000 signed emission standards for model year 2007 and later heavy-duty highway engines. The rule includes two components: (1) emission standards and (2) diesel fuel regulations. The first component of the regulation introduces new, very stringent emission 2010 standards are as follows: NO_x – 0.20 g/bhp-hr.

Stationary sources of emissions, such as stacks, operate at very high temperatures, usually at or above 1000 °C. At such temperatures, nitric oxide is thermodynamically unstable with respect to its molecular elements, and hence catalytic decomposition of NO to N₂ and O₂ is the simplest method for NO removal from exhaust streams. Initially the operational control method consisted of a direct catalytic decomposition unit using noble metal catalysts. However, there were several problems associated with this initial design, in that the catalytic activity was low, the lifetime short and the catalyst easily poisoned by oxygen. Recent research in the development of new catalysts for this purpose has shown that zeolite supported metal catalysts have resulted in far better decomposition of nitrogen oxides. This is a favorable characteristic of zeolite since it tends to be resistant to oxygen and sulfur poisoning. As for an economical scale, current zeolite market prices indicate a competitive edge over most of the more common noble metal based catalyst. These findings have attracted the attention from many researchers around the world to develop a new technology for the decomposition of NO_x for combustion systems. Nitrogen oxides are usually a mixture containing 95% nitrogen monoxide (NO) and 5% nitrogen dioxide (NO₂). They are formed from combustion processes by the conversion of nitrogen and fuel containing nitrogen. These combustion processes can be represented by the following reactions:



On release to the atmosphere, nitrogen oxides pose serious environmental hazards. This is because NO_x can be

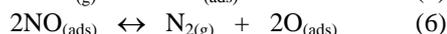
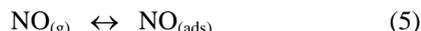
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oxidised by ozone, OH or HNO_2 radicals to form amongst other things, photochemical smog and acid rain. This is summarised below in reactions 3 and 4 respectively:



As mentioned previously, the low catalytic activity is a result of self-poisoning of the catalyst, which occurs when the oxygen atom produced by NO decomposition remains strongly absorbed to the catalyst. Several studies have shown that zeolites ($ZSM-5$) in general have higher catalytic activity than the traditional catalysts, for mechanism of NO decomposition refer to [20]. In particular, the $Cu-ZSM-5$ catalyst has been found to be the most active and most effective in the decomposition of NO . The decomposition reactions are illustrated below:



Research has shown that there was significant activity in the initial stages of the decomposition, however this began to decrease as the reaction progressed. This decline in activity was caused by oxygen production, which began to accumulate amongst the catalyst sites. However, the effectiveness of the catalyst was restored to its original state by heating the catalyst above $350\text{ }^\circ\text{C}$, and maximum activity was observed at around $450\text{ }^\circ\text{C}$. Upon heating the catalyst, it was discovered that the oxygen atoms and water vapour produced did not poison the catalyst further. It was also found that the decomposition of NO into N_2 and O_2 was increased with an increase in contact time.

II. EXPERIMENTAL

A basic diagram of the experimental rig used in this investigation is illustrated in figure-1. The five inlet streams to the reactor consisted of a NO/He mixture (1% NO - 99% He by volume), two pure He streams and two O_2 streams. The pure He cylinder was used in order to dilute the NO/He mixture to the desired experimental conditions. These streams were connected to rotameters and mass flow controllers, which were mounted on a front panel where the gas flowrate could be measured. The experiments were carried out in a $5\text{ mm} \times 200\text{ mm}$ flow reactor made of quartz, which is shown in detail in figure-2. As a microreactor was used, it was not possible to build a sintered ceramic disc within the reactor.

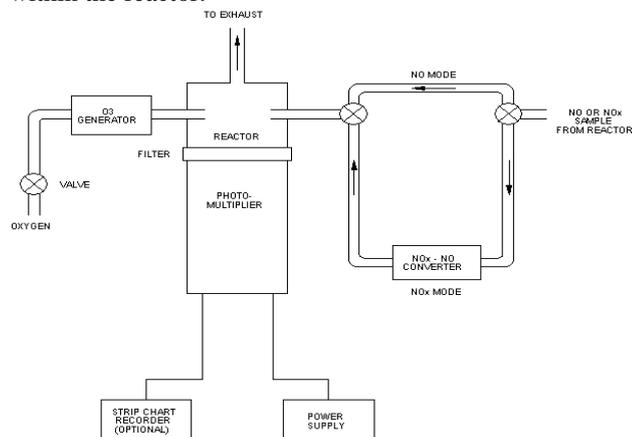


Fig. 1: schematic representation of experimental rig

Thus, ceramic wool was used to keep the zeolite catalyst in place from top and bottom. The reactor was then placed inside a chamber equipped with heating elements in order to control the reaction temperature. Once the NO/He mixture had passed through the reactor, the effluent from the reaction was routed through stainless steel tubing to the NO/NO_x analyser where the stream compositions were analysed.

To measure NO_x concentrations, the sample gas flows through an NO_2 to NO converter and then to the reactor. The analyser used in this experiment was a Thermo Electron Corporation Model 44 Chemiluminescent analyser. The emissions were then linearly proportional to the NO_x concentration entering the instrument. As the gas sample blends with ozone in the reactor, the reaction of NO and O_3 provides the basis for measurement of NO_x conversion. Specifically:



Although $Cu-ZSM-5$ was proven to have very high activity for the decomposition of NO , researchers have not yet been able to find a practical catalyst which operates at lower temperatures. As the temperature of an automobile catalytic converter is approximately below $500\text{ }^\circ\text{C}$, the catalyst is not practical for its required application - to control automobile emissions. The catalyst used in this investigation was Cu -Zeolites, $Cu-ZSM-5(158)$.

The catalyst naming system was denoted as metal ion, zeolite type and degree of exchange. Thus, $Cu-ZSM-5(158)$ indicates that Cu was the metal ion, $ZSM-5$ was the type of zeolite and (158) was the degree of exchange. It was prepared from A.R. grade chemicals by ion-exchange in aqueous solution and solid-state ion-exchange.

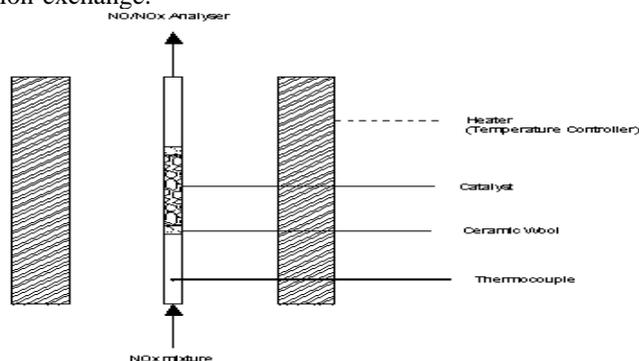


Fig. 2: cross section conventional microreactor

In order to avoid concentration and heat gradients in the catalyst bed during experiments, very small amounts of catalyst samples (10 mg) were used. When heating up the catalyst, extra precautions were taken to ensure that the catalyst was not heated up too quickly, hence preventing the possibility of it being overheated. The reaction temperature was measured using an iron-constantan thermocouple and a potentiometer accurate to 0.02 millivolts. Constant temperature was required throughout the experiment, and was supplied by an on-off controller. This was obtained by stabilising the main power supply line. For each run, the reaction temperature was kept constant within $\pm 5\text{ }^\circ\text{C}$.

III. RESULTS AND DISCUSSIONS

Part of measuring the conversion of NO to N_2 using a copper zeolite catalyst contact time was crucial variable to this experiment. The results obtained are plotted for each reaction temperature in Fig. 3. At each reaction temperature, the conversion increases with increasing contact time, but levels off at higher contact times. This was due to the oxidation of active sites on the catalyst surface. A mass of 0.1 g of catalyst was used. Furthermore, the conversion also increased with increasing reaction temperature. At 350 °C, the maximum conversion was found to be 60.60 %, whereas at 400 °C it was 62.03 % and at 450 °C it was 64.32 %. The plots also showed good correlation existed between the fitted data as all graphs had R-squared values well above 90%. However, it has been reported that if the temperature were to be increased above a certain temperature (approximately 600 °C), the conversion would decline as the reaction temperature increases further. This is important if the catalysts are to be used for automotive engine exhaust clean up, which generally operate at temperatures below 500 °C.

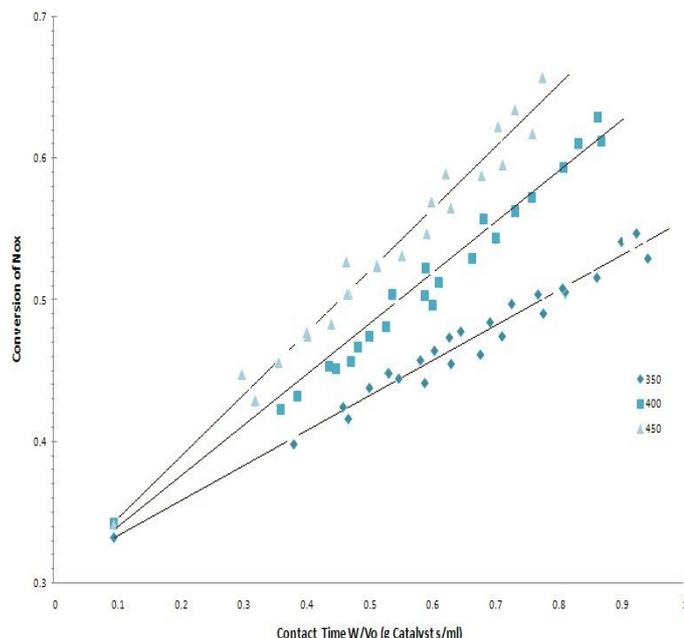


Fig. 3: Conversion of NO_x at 350, 400 and 450 °C

Fig. 4 show plots of $\ln(1/1-X)$ versus $(W/V_o)(T_o/T)$. From this plot the linear relationships, is evidence that first order rate kinetics exists since each plot produced straight line. This is justified by the relatively high R-squared values for each plot, which are all greater than 95 %. First order kinetics was then used to evaluate the equilibrium constants at each of the reaction temperatures, using the slope of the line. This is displayed in table-1.

Temperature (°C)	Temperature (K)	Equilibrium Constant, k (cm ³ /g cat. s)
350	623.15	2.2761
400	673.15	2.5550
450	723.15	2.8369

Table 1: Equilibrium Constants

Furthermore, from Fig. 5 , it is evident that the data was consistent and followed an Arrhenius temperature

relationship, since the resultant data produced a straight line. This can be verified by the extremely high R-squared value of 99.98 %. However, since the experimental data was recorded over a relatively small temperature range (100 °C), the plot may not be as accurate as the data suggests. This plot was then used to determine the activation energy (E_a) and the pre-exponential factor (k_o). These were calculated to be 119.304 J/mol and 11.1719 cm³/g catalyst s respectively.

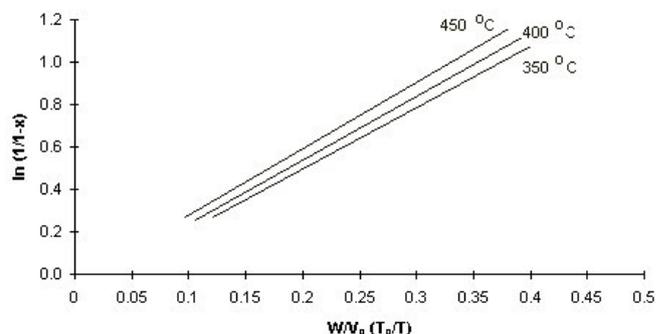


Fig. 4: First order kinetics - Conversion of NO_x at 350 °C

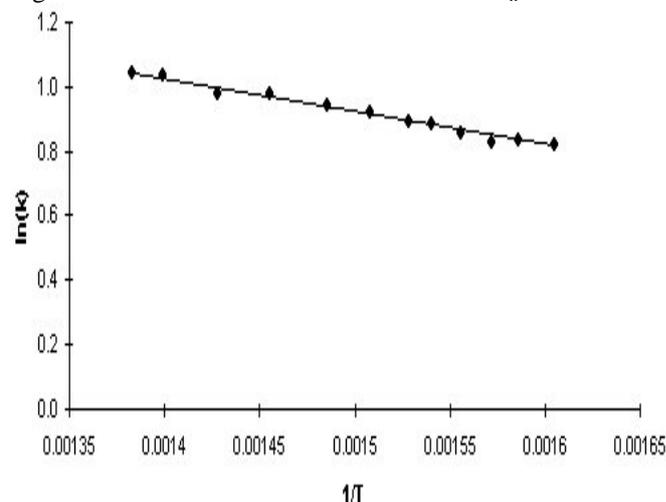


Fig. 5 : Determination of k_o and E_a

IV. LIMITATIONS

Although the experimental data appears to be consistent, there is still undoubtedly room for error. The main source of error would be temperature measurement. Firstly, the recorder temperature did not necessarily correspond to the reaction temperature. The exact location of the thermocouple used to measure the temperature outside the reactor, and thus the measurement recorded by the thermocouple may not have corresponded to the reaction temperature. Furthermore, there may have been significant fluctuations in the temperature within the reactor, since the on-off temperature controller used in the experiment was not performing sufficiently. As a result of the temperature controller not performing sufficiently, another source of error may have been introduced, in that the catalyst may have been over heated. This effectively would have reduced the activity of the catalyst, and hence the conversion of NO to N_2 . The experiment was also conducted under the assumption that the flow was adiabatic, i.e. that the change in temperature was zero. This could not be justified since there was no thermocouple in the outlet stream, and thus the outlet temperature was unknown.

V. CONCLUSION

The results obtained showed that maximum conversion of 64.32 % was obtained at the highest contact time and the highest temperature. It was found that the data did follow first order kinetics since a straight line was obtained from a plot of $\ln(1/1-X)$ versus $(W/V_o)(T_o/T)$. The data also followed the Arrhenius temperature relationship since an Arrhenius plot also produced a straight line. Using the data obtained from this plot, the Arrhenius equation was calculated to be $k = 11.1719e^{-119.304/RT}$. Hence the rate equation is $r = 11.1719e^{-119.304/RT} C_{NO}$. The results obtained from this experiment illustrate a consistent source data for the reduction of NO_x in a microreactor for the copper zeolite catalyst, Cu-ZSM5 (158), at temperatures of 350, 400 and 450 °C. Finally based on the data deduced from this experiment of conversion of NO to N_2 using Cu-ZSM-5 (158) catalyst, the Conversion increased with both increasing contact time and reaction temperature over the experimental temperature range. The maximum conversion of 64.32% was obtained at 450°C. The results were consistent with that of first order rate kinetics. An Arrhenius temperature relationship was found to exist, having the relationship $k = 11.1719e^{-119.304/RT}$.

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APPENDIX A

Sample Calculation

Temperature = 350 °C
 Mass of catalyst, W = 0.1 g
 Rotameter reading = 4
 Off rotameter conversion $V_o = 0.11 \text{ cm}^3/\text{s}$
 Initial NO concentration (blank) = 9390 ppm
 Final NO concentration = 3700 ppm
 Therefore conversion,

$$X = \frac{\text{Initial NO concentration} - \text{Final NO concentration}}{\text{Initial NO concentration}}$$

$$X = \frac{9390 - 3700}{9390}$$

$$X = 0.6060$$

Contact time, $\tau = W/V_o$

$$\tau = 0.1 \text{ g} / 0.11 \text{ cm}^3/\text{s}$$

$$\tau = 0.9091 \text{ g s} / \text{cm}^3$$

After graph of $\ln(1/1-X)$ versus $(W/V_o)(T_o/T)$ was plotted, the equilibrium constant k, was then determined from slope of straight line:

$$k = 2.2761 \text{ cm}^3/\text{g cat. s}$$

Using k values obtained from each temperature, Arrhenius plot was constructed by plotting $\ln(k)$ versus $1/T$. The pre-exponential constant k_o , was determined from the intercept of the Arrhenius plot:

$$k_o = 11.1719 \text{ cm}^3/\text{g cat. s}$$

The activation energy was calculated from the slope of the Arrhenius plot:

$$\text{slope} = -E_a/R$$

$$-991.9 = -E_a / 8.314 \text{ J/mol K}$$

$$\therefore E_a = 119.304 \text{ J/mol}$$

APPENDIX B

Rate equation is used to assist in the design equation for a plug flow reactor

$$W = F_{NO} \int \frac{dX}{r_{NO}} \quad (1)$$

where W = mass of catalyst, mg

F_{NO} = molar feed rate of NO_x , cm^3/s

r_{NO} = rate of reaction of NO_x , mol/g catalyst s

For a first order rate equation:

$$r_{NO} = kC_{NO} \quad (2)$$

$$r_{NO} = kC_{NO,0}(1 - X)$$

$$F_{NO,0} = V_O C_{NO,0}$$

Where $V_O C_{NO}$ is measured at room temperature, $C_{NO,0}$ is measured at reaction temperature.

$$W = V_O, C_{NO,0} \int_0^{X_f} \frac{dX}{kC_{NO,0}(1 - X)} \quad (3)$$

At T_o = room temperature, the equation becomes:

$$\frac{W}{V_o} = \frac{C_{NO}(T_o)}{C_{NO}(T)} \frac{1}{k} \int_0^X \frac{dX}{(1 - X)}$$

$$\frac{W}{V_o} = \left(\frac{Y_{NO,0} P}{R T_o} \right) \frac{1}{\left(\frac{Y_{NO,0} P}{R T} \right) k} \ln \left(\frac{1}{1 - X} \right)$$

Rearranging:

$$\ln \left(\frac{1}{1 - X} \right) = k \left(\frac{T_o}{T} \right) \left(\frac{W}{V_o} \right) \quad (4)$$

A plot of $\ln \left(\frac{1}{1 - X} \right)$ against $\left(\frac{W}{V_o} \right) \left(\frac{T_o}{T} \right)$ should produce

a straight line of slope k if the data follows first order rate kinetics. Once the equilibrium constant k, had been determined for each temperature, an Arrhenius plot was developed in order to determine whether an Arrhenius temperature relationship existed. As stated previously in equation (2):

$$r_{NO} = kC_{NO}$$

For an Arrhenius temperature relationship:

$$k = k_o e^{-E_a/RT} \quad (5)$$

$$\ln(k) = \ln(k_o) - \left(\frac{E_a}{R} \right) \left(\frac{1}{T} \right) \quad (6)$$

In order for an Arrhenius relationship to exist, a plot of $\ln(k)$ against $\left(\frac{1}{T} \right)$ should produce a straight line of slope

$\left(-\frac{E_a}{R} \right)$ and intercept $\ln(k_o)$. For further assistance on reactor design refer to [21]