Nitrogen Oxides as Atmospheric Pollutants: NO_x Removal in the Presence of Oxygen with Metal Oxides

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Removal of nitrogen oxides from exhaust gases as a measure of pollution control is becoming increasingly important in the world due to the harmful effects of these oxides on the environment. The methods currently used to remove the nitrogen oxides from exhaust gases, emitted from stationary and mobile sources, are reviewed. An alternative method, by way of sorption/regeneration, is presented. Sorbents made of metal oxides, for the removal of nitric oxide in the presence of oxygen by the sorption method, are introduced. The sorbents, which have been tested and given high sorption capacities, could be regenerated by a nitrogen stream and reused.

INTRODUCTION

Oxides of nitrogen, NO_x are produced as a result of high temperature combustion of fuels and are among the common atmospheric pollutants. The principal sources of NO_x are motor vehicles and fuel combustion in chemical processes and local heating [1,2].

In combustion, NO_x results from the thermal fixation of molecular nitrogen and oxygen in combustion air or the oxidation of organically bound nitrogen in heavy fossil fuels [1]. Among the oxides of nitrogen, nitric oxide, NO, and nitrogen dioxide, NO_2, are important as air pollutants. Nitrous oxide, N_2O, is also a greenhouse gas like CO_2. Oxides of nitrogen have adverse effects on human beings, plants and animals.

In human beings, NO_x can, at high concentrations (10-30 ppm), cause nose and eye irritation, pulmonary edema (swelling), bronchitis, and even pneumonia. Fortunately, the levels even in polluted areas are not quite that high, but lower levels for an extended period of time can still contribute to pulmonary fibrosis and emphysema [3]. The effects on plants are more severe. Some broad-leafed plants can show necrosis in the 2-10 ppm range and can show growth retardation at as low as 0.5 ppm. This is important because the plants are needed to convert CO_2 to O_2 and do not do as well when inhibited in this way [3].

However, the alarming adverse effect of nitrogen oxides on the environment is through the tendency of NO_x to react with reactive organics in the atmosphere. This photochemical reaction forms what are called photochemical oxidants. Two examples of photochemical oxidants are ozone and peroxyacetal nitrate (PAN). These chemicals are very hazardous as they are severe eye, nose and throat irritants.

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Ozone in particular attacks synthetic rubber, causing it to badly crack, as well as attacking textiles, paints and other materials. Plants are especially susceptible to these chemicals, which cause discoloration and cell collapse. Vegetation can be damaged at concentrations as low as 0.05 ppm of photochemical oxidant. Eye irritation can begin at 0.10 ppm, and severe coughing will often begin by 2.0 ppm of the same chemical [3].

Nitrogen oxides can also react with oxygen and water in the atmosphere to form acids which are then washed out by rain, snow or sleet [4]. Lakes and ponds do not have much natural buffering and are therefore greatly affected by this. A pH of 4.5 can kill fish due to the deadly effect of the acid or, even more serious, the leaking of toxic metals out of the ground and into the water, which the acid promotes. Other problems include increased corrosion of steel structures, destruction of monuments and possible effects on human health [3].

The reduction of NO_x from mobile and stationary sources is becoming increasingly important. This is evidenced by regulatory legislation such as Clean Air Acts in the United States, Europe and other parts of the world. NO_x formation may be controlled by modification of combustion operating conditions and equipment and fuel switching. The mentioned modifications may not be sufficient in many cases, therefore, flue gas may be treated as well.

Stationary sources like boilers, incinerators, combustion turbines, process heaters and reciprocating engines generate exhausts with NO_x concentrations ranging from 50 ppm to 500 ppm [1]. However, some stationary sources like nitric acid and fertilizer plants may produce exhausts that have nitrogen oxide concentrations of up to 70,000 ppm. The amount of NO_x emitted by stationary sources outweighs that of automotives [1].

Current technologies to treat the flue gas, downstream of the combustion zone for stationary sources, are Selective Catalytic Reduction (SCR) and Selective Non-Catalytic Reduction (SNCR). SCR is the reduction of NO_x to nitrogen and water by injecting ammonia into a catalyst bed at a temperature range of 600° F to 750° F. NO_x and ammonia combine to form an ammonium salt, which then decomposes. SCR can typically achieve about 80% reduction [2]. If the temperature is too high, the ammonia can oxidize to either NO_x, ammonium nitrate or ammonium nitrite. Too low of an operating temperature will result in not enough energy to activate the reaction [4]. Also, the unreacted ammonia, namely ammonia slip, is a source of numerous problems. At high ammonia slip any SO_2 in the flue gas tends to be converted to SO_3 which, in turn, may react with ammonia and water to form ammonium bisulfate and ammonium sulfate. In addition to being corrosive, these compounds can deposit on the catalyst, reducing its activity and leading to a higher ammonia slip [5].

SNCR is also the reduction of NO_x to water and nitrogen, but without a catalyst. This causes the operating temperature to be significantly higher, in the range of 1600° F to 1750° F for ammonia injection [6] and as large as 1000° F to 1900° F for urea-based injection [7]. SNCR effectiveness may be in the range of 50% to 70% [6,7]. As with SCR, mixing and temperature control are very important in SNCR. If the temperature is too low, ammonia will be emitted. At a too high temperature, some ammonia may be converted to NO_x and cause loss of effectiveness.

Automotive exhaust NO_x emissions may be controlled by catalytic converters located in the exhaust system. Catalysts such as the copper-containing zeolite catalyst, called Cu/ZSM-5, have been tried in this respect, but a viable technology has not yet been developed [2].

New and improved ways of reducing nitrogen oxide emission, including improved catalysts and sorption/regeneration methods, are gaining importance. This paper includes a background to the sorption/regeneration method in removal of NO_x from exhaust gases and a review of the work done in this area by the author and colleagues since 1975.

BACKGROUND

Sorbing of nitrogen oxides in the presence of oxygen on a porous reactive solid that can be thermally regenerated was proposed by Gidaspow [8-10] as an alternative technique for NO_x control. Upon regeneration, these porous reactive solids, used as NO_x sorbents, may produce a highly concentrated mixture of nitrogen oxides and then be reused. The benefit may be twofold. First, removal of NO_x from exhaust gas and second, a concentrated stream of nitrogen oxides which may be used in the production of value-added chemicals like nitric acid. The challenge is finding a high capacity sorbent of this sort which does not lose the sorbing effectiveness after several regeneration cycles.

Onischak and Gidaspow [8] reported that ferrous sulfate that had been mixed with silica gel could be used as an adsorbent for NO_x and could be regenerated, but could only be operated at room temperature and in the absence of water vapor. Transition metal oxides, including cobalt oxide, chromium oxide, manganese oxide and coprecipitated manganese oxide on alumina base, were later tested as possible sorbents [11]. These sorbents could all sorb NO_x in the presence of oxygen, be regenerated and reused.

For all of the transition metal oxides studied, lowering the NO concentration caused the sorption capacity to increase, which was an advantage. Regeneration did not affect the sorption capacities of the oxides, except for the cobalt oxide sorbent, which displayed a drop in sorption capacity when regenerated [11]. However, the NO_x sorption capacity was not appreciable and was in the order of 0.003 to 0.007 g of NO/g of sorbent [12].

In the search for a high capacity sorbent, alumina base was replaced with cobalt oxide by Hariri [13] and a mixture of cobalt and iron oxides was prepared and tested. This led to a drastic increase in the sorption capacity [12-14], as will be described in detail in this paper.

EXPERIMENTAL SETUP AND PROCEDURE

A schematic diagram of the apparatus is shown in Figure 1. All the transmission lines were 1/4 in tubes and all fittings and valves were made of stainless steel. The concentrations of nitric oxide in the outlet and inlet gas streams were measured by an infrared analyzer with nitric oxide concentration range of 0 to 1000 ppm. The NO_x analyzer converted NO_x and 80% of the NH_3 in the gas stream into NO. The drying agent in the drying tube was Drierite, which did not sorb NO. To study the effect of moisture, a bubbler and a dew point hydrometer were used.

The sorbent in powder form was held in a quartz tube, 1.9-cm I.D. and 2.2-cm O.D., on the top of a porous quartz disc fixed in the tube. The tube was heated in a split furnace with three heating elements. Temperature control was maintained in the central zone by a three-in-one temperature controller. The central controller was adjusted by current or voltage and two end controllers were of the time-proportionating type.

The sorbent was heated in a stream of nitrogen gas to drive out the moisture before setting the reactor temperature at a desired level. The inlet gas was primarily passed through the analyzer, while by-passing the sorbent, to obtain inlet concentration data and then it was passed through the sorbent to obtain nitric oxide removal data. When the NO concentration of the outlet gas stream was 90% of the NO inlet concentration, NO removal data taking was stopped. The regeneration of the sample was carried out at 520° C by passing a stream of nitrogen through the sample. Regeneration was stopped when NO concentration in the outlet gas stream was zero.

Sorbent Preparation

A solution containing ferrous sulfate or ferric nitrate and cobalt nitrate was prepared [13]. Coprecipitation was carried out by adding an alkaline solution slowly with continuous stirring to the above solution until a desired pH was attained. The coprecipitate obtained was aged

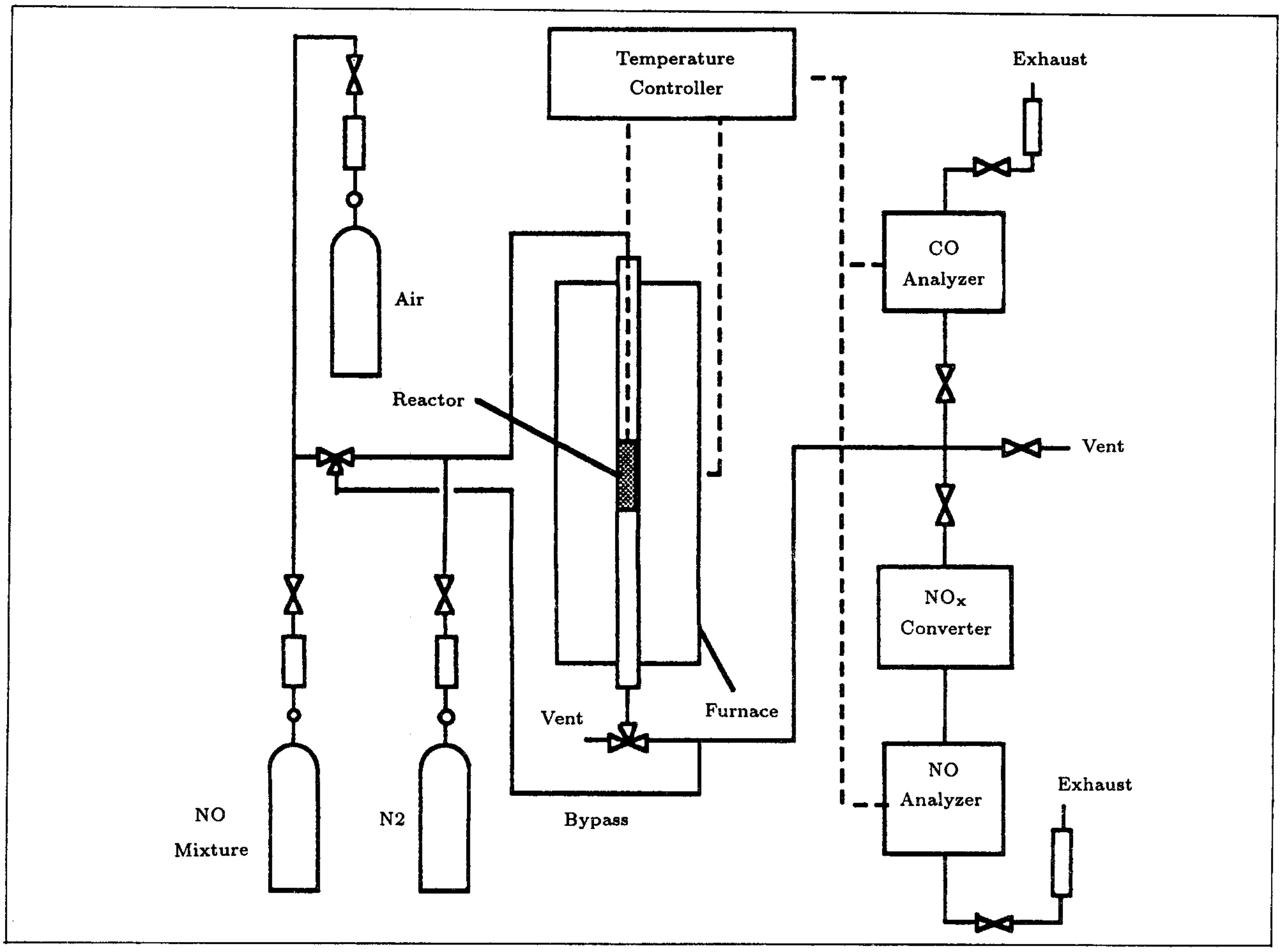

Figure 1. Experimental setup.

for three hours, filtered, washed with deionized water and dried in air at 60° C for one day. The sample was then humidity dried at a temperature of 70° C wet bulb and 90° C dry bulb for eight hours. It was finally fired in nitrogen at 650° C for eight hours.

Capacity Data Calculation

For a constant gas flow rate and inlet NO concentration, the capacity of the sorbent was calculated as:

$$\Gamma = \frac{QM_g}{W}[C_{in}t - \int_0^t C_{out}dt], \qquad (1)$$

where:

Q = volumetric flow at STP (lpm)

M_g = Molecular weight of NO

W = weight of sorbent (g)

C_{in} = inlet concentration (mol/l)

C_{out} = outlet concentration (mol/l)

Γ = capacity of sorbent (g NO/g sorbent)

SORBENTS

Two groups of sorbents, namely A and B, were prepared. For group A sorbents, the alkaline solution used was ammonium carbonate and for group B it was sodium carbonate. When ferrous sulfate was used in the preparation of the sorbents, they were named AS or BS sorbents. The sorbents prepared using ferric nitrate as iron salt were named AN or BN sorbents [13,14]. Overall, seven different sorbents were prepared using different amounts of each salt at various pH, as shown in Table 1.

Table 1. pH conditions for different sorbents [13].

Sorbent	pH
AN	7.8
AS	7.8
BN	9.7
BS1	7
BS2	8
BS3	9
BS4	9.7

RESULTS

The capacity of the sorbents for the removal of NO were determined at different temperatures and NO and oxygen concentrations in the inlet gas stream in the presence and absence of moisture. The highest capacities attained with the corresponding experimental conditions are shown in Table 2. BS3 and BS4 had appreciably higher capacities than the other sorbents.

Table 3 shows that BS3 and BS4 sorbents significantly remove NO from the gas stream before the breakthrough time. The capacity to breakthrough is 74% of the total capacity measured up to $C_{out}/C_{in} = 0.85$ for BS4 and 75% for BS3.

Effect of Operating Conditions on the Capacity of BS Sorbents

The capacities of BS sorbents generally increase with temperature, as shown in Tables 4 and 5 for BS2 sorbent. However, the improvement of the capacity, unlike the breakthrough time beyond 250° C, was not generally significant (Table 4).

Moisture did not appreciably affect the capacity of BS sorbents, as shown in Table 5, for BS2 sorbent. However, the breakthrough time was reduced significantly at high temperatures.

The high capacity of BS4 sorbent was impaired by the number of runs, as shown in Table 6. The fresh BS4 sorbent lost 25% of its total capacity in the first run and its time to breakthrough was drastically reduced. However, the effect of the number of runs on the capacity of BS4 sorbent became increasingly less pronounced as the number of runs increased. This effect may flatten out beyond twelve number of runs shown in Table 6.

NO concentration had a negligible effect on the sorption capacity of BS4 sorbent, as shown in Table 7. The variation of capacity may be basically due to run number rather than NO

Table 2. Highest capacities of NO removal by fresh sorbents at different dry conditions [13].

Sorbent	Capacity up to $\frac{C_{out}}{C_{in}} = 0.85$ gNO/gSorbent	Temperature °C	O_2 Conc. %	NO Conc. ppm
AN	0.42×10^{-2}	230	3	750
AS	0.11×10^{-2}	220	3	800
BN	1.25×10^{-2}	300	3	750
BS1	1.85×10^{-2}	300	3	750
BS2	2.92×10^{-2}	400	3	700
BS3	14.83×10^{-2}	300	3	750
BS4	16.52×10^{-2}	300	3	750

Table 3. The capacity for NO removal by fresh BS3 and BS4 sorbents up to breakthrough time [13].

Sorbent	Capacity to breakthrough, gNO/gSorbent	Breakthrough time, min.
BS3	11.19×10^{-2}	690
BS4	12.15×10^{-2}	720

300° C, 3% O_2 concentration and 750 ppm NO concentration

concentration. At zero oxygen concentration, the NO sorption capacity by BS4 sorbent was very low and appreciably increased, despite the increase in run number, when oxygen concentration increased to 0.05% (Table 8). At comparable run numbers, increase in oxygen concentration from 0.05% to 3% does not appreciably change the NO sorption capacity of BS4 sorbent (Table 8).

DISCUSSION OF THE RESULTS

Three factors contribute to the production of high capacity sorbents BS3 and BS4. Two of the factors are using iron sulfate and sodium alkaline solution in the preparation of the sorbent. The third factor is the high pH, i.e., the presence of adequate sodium alkaline solution in the production of the coprecipitate. Table 1 shows that each of the AN, AS, BN, BS1 and BS2 sorbents lacks one or more of the above factors.

It is speculated that iron sulfate may give an iron oxide which can be dissolved in sodium carbonate at high pH to produce a sodium containing complex that appreciably sorbs NO present in a gas stream in the presence of oxygen [14]. The structure of this complex probably undergoes a considerable change, as indicated by the drastic reduction of sorption capacity of fresh BS4 sorbent after the first run (Table 6). This structural change may be partly due to the regeneration procedure adopted in this work.

Rate of Reaction

A one-dimensional model [12] may be used to calculate the rate constants for the sorption reaction using the following equation:

$$ln(\frac{C_{in}}{C_{out}} - 1) = \frac{K\delta_A W_s}{M_s Q} - KC_{in}t\ . \qquad (2)$$

The values of $(\frac{C_{in}}{C_{out}} - 1)$ between $0.25 < \frac{C_{out}}{C_{in}} < 0.75$ were obtained from a breakthrough curve (Figure 2) and plotted versus time on a

Table 4. Effect of temperature on capacity of BS2 sorbent at dry conditions [13].

	Temperature °C			
	30	180	250	400
Time to breakthrough, min.	0	0.5	1	11
Capacity up to $\frac{C_{out}}{C_{in}} = 0.85$, gNO/gSorbent	0.09×10^{-2}	0.32×10^{-2}	2.38×10^{-2}	2.98×10^{-2}

O_2 concentration = 3%, average NO concentration = 700 ppm

Table 5. Effect of temperature on capacity of BS2 sorbent in the presence of moisture [13].

	Temperature °C			
	30	200	260	390
Time to breakthrough, min.	0	0	0	0.5
Capacity up to $\frac{C_{out}}{C_{in}} = 0.85$, gNO/gSorbent	0.02×10^{-2}	0.51×10^{-2}	2.75×10^{-2}	2.90×10^{-2}

O_2 concentration = 3%, average NO concentration = 700 ppm

Table 6. Effect of number of runs on the capacity and breakthrough time of BS4 sorbent at dry condition [13].

	Run number		
	1 (fresh Sorbent)	2	12
Time to breakthrough, min.	720	128	32
Capacity up to breakthrough, gNO/gSorbent	12.15×10^{-2}	2.33×10^{-2}	0.9×10^{-2}
Total capacity up to $\frac{C_{out}}{C_{in}} = 0.85$, gNO/gSorbent	16.52×10^{-2}	12.45×10^{-2}	9.41×10^{-2}
Rate constant K, liter/mole-min	124	90	96

temperature = 30° C, O_2 concentration = 3%, average NO concentration = 770 ppm

Table 7. Effect of NO concentration on the sorption capacity of BS4 sorbent [13].

	NO concentration, ppm		
	420	630	790
Run no.	4	3	2
Capacity up to breakthrough, gNO/gSorbent	1.24×10^{-2}	1.40×10^{-2}	2.33×10^{-2}
Total capacity up to, $\frac{C_{out}}{C_{in}} = 0.85$, gNO/gSorbent	11.80×10^{-2}	12.82×10^{-2}	12.45×10^{-2}

temperature = 300° C, O_2 concentration = 3%

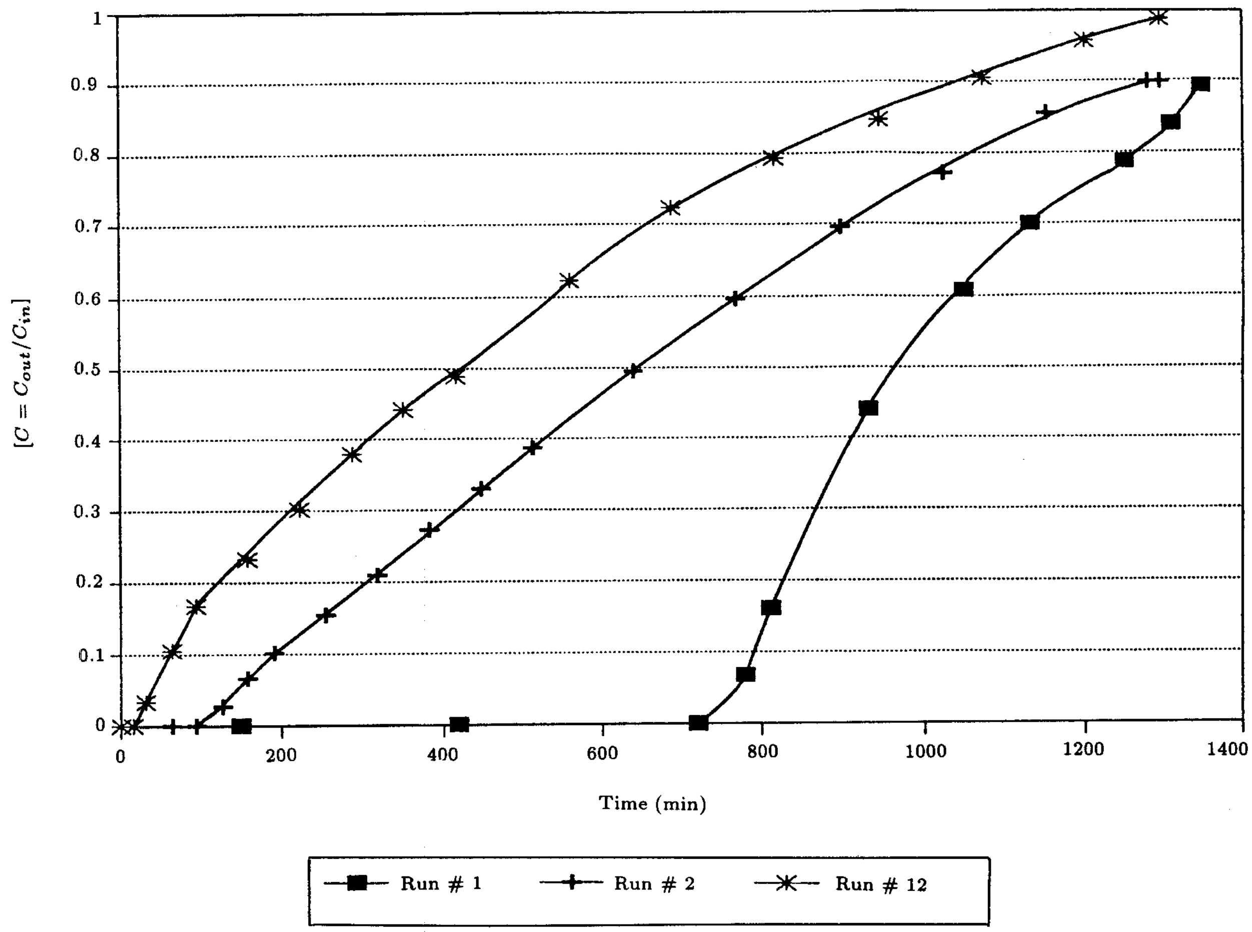

Figure 2. Concentration variation of NO with time downstream from the reactor for BS4 sorbent.

Table 8. Effect of oxygen concentration on the NO sorption capacity of BS4 sorbent [13].

	Oxygen concentration, %		
	0	**0.05**	**3**
Run no.	6	13	12
Capacity up to breakthrough, gNO/gSorbent	0	1.06×10^{-2}	0.09×10^{-2}
Total capacity up to $\frac{C_{out}}{C_{in}} = 0.85$, gNO/gSorbent	0.1×10^{-2}	9.46×10^{-2}	9.41×10^{-2}

temperature = 300° C, NO concentration = 420 ppm-790 ppm

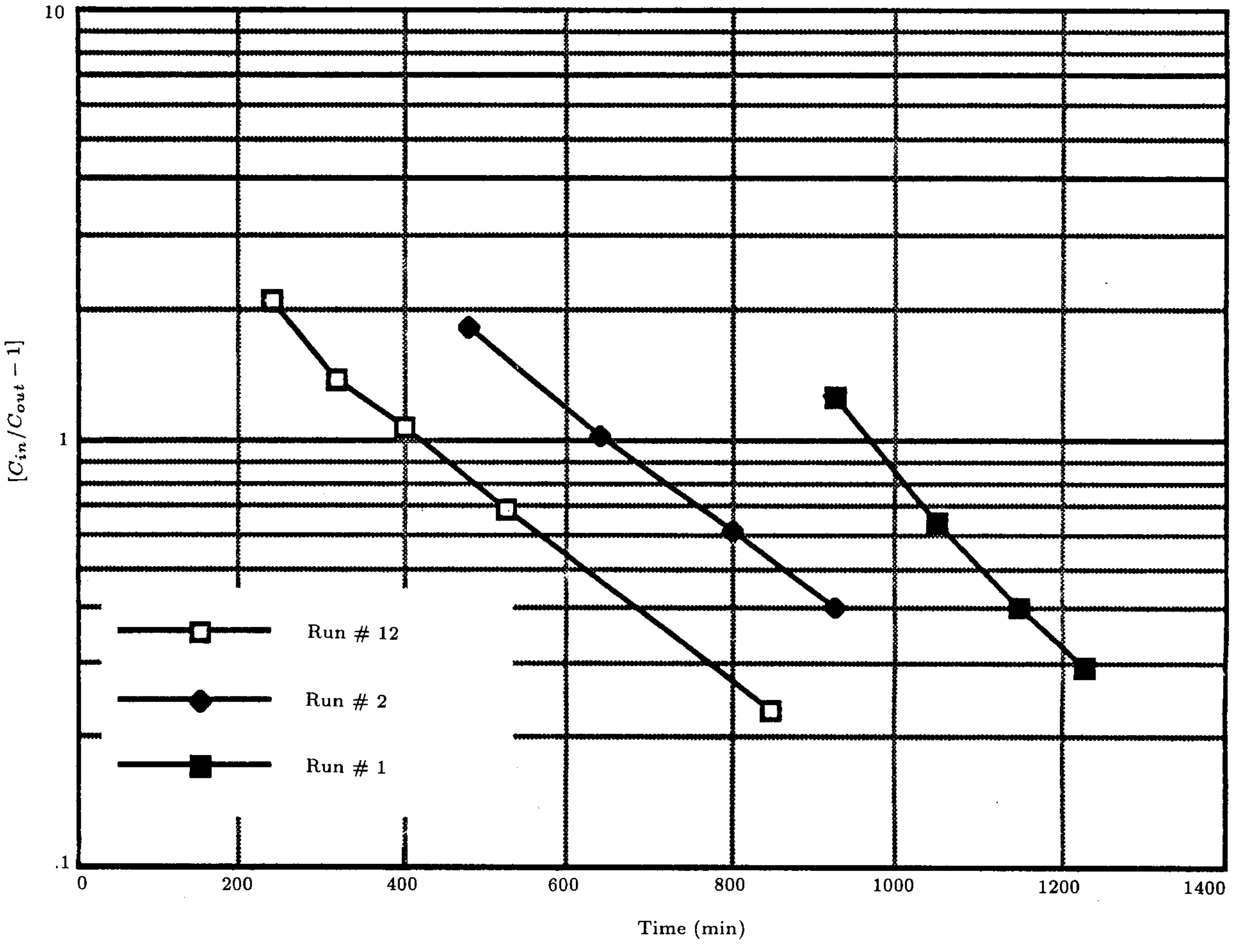

Figure 3. Rate constant of the NO sorption by BS4 sorbent.

semi-log scale as shown in Figure 3 for BS4 sorbent [13]. Straight lines are well fit to the points in Figure 3, which justifies the use of Equation 2 for calculation of the rate constant of the reaction.

The rate constants calculated from Figure 3 are presented in Table 6 and indicate an insignificant effect of run number on the rate constant. The straight lines are nearly parallel in Figure 3.

The rate constants presented in Figure 3 and Table 6 are believed to depend on diffusion of NO into the sorbent particle as well as the rate of reaction [14]. It is anticipated that the sharp drop of NO sorption capacity and breakthrough time of fresh BS4 sorbent after the first run (Table 6) is due to the structural changes and, thus, a drastic change in the rate of reaction. The sorption capacity of BS4 sorbent continues to drop after the first run at an average rate of 2% to 3%, which is believed to be mainly due to the increase in resistance to diffusion of NO into the sorbent particle.

CONCLUSION

Oxides of nitrogen, produced mainly by the combustion of fuels and emitted into the atmosphere, are of major environmental concern. Present environmental regulations require the removal of NO_x from exhaust gases. Commercial methods are presently available which convert NO_x catalytically or without using catalysts. However, these methods are costly, not very efficient and accompany some new emission problems. The sorption/regeneration technique is a new method for the removal of nitrogen oxides. Solid sorbents prepared from coprecipitating an iron salt and a cobalt salt with sodium carbonate have appreciable capacity in the removal of nitrogen oxides from exhaust gases. These sorbents may be regenerated, resulting in a stream with high NO concentration which, in turn, may be used to produce value-added chemicals like nitric acid. After regeneration, the sorbents may be reused.

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