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ELECTRO-CATALYTIC REDUCTION OF
NITROGEN OXIDES

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BY

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ABSTRACT

ELECTRO-CATALYTIC REDUCTION OF
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Nitrogen Oxides have been linked to a broad range of air pollution problems including acid rain and the atmospheric production of photochemical ozone. Over twenty million tons of nitrogen oxides are emitted into the atmosphere each year as a result of the high temperature combustion of fossil fuels. Efforts to control nitrogen oxides emissions have lagged because of the generally low discharge concentrations of nitrogen oxides in combustion exhaust and because nitrogen oxides are more difficult to remove due to their lower reactivity.

No catalyst has yet been found that will achieve significant reduction of nitrogen oxides in an oxidizing environment. Oxygen in the exhaust stream competes with nitrogen oxides for the active catalyst sites. Also, the dissociated oxygen atoms produced by decomposition of nitrogen oxides deactivate the surface of the catalyst.

Externally applied electric fields have been used to control oxygen adsorption on metal and semi-conductor surfaces. In this investigation, a stream containing nitric oxide has been subjected to intense electric fields in the presence of catalyst materials

including steel, stainless steel, and gold plated stainless steel wools and glass wool. The electric fields have been generated using DC, AC and rectified AC potentials in the range of 0-20 KV. The effect of parameters such as inlet nitric oxide concentration, oxygen and water content, gas residence time and temperature have also been studied.

Greater than 90% nitric oxide conversion was achieved using gold plated stainless steel at an AC potential of 15 KV and a residence time of 4.5 seconds. The level of conversion was not significantly altered using steel or stainless steel wool at comparable reactor conditions. Increasing the reactor temperature from 30 to 200°C did not affect the nitric oxide removal. However, the addition of oxygen and water vapor reduced its decomposition to oxygen and nitrogen. Greater than 95% conversion was achieved using ordinary glass wool at an AC potential of 14 KV and a residence time of 2.1 seconds.

The results of this work have the potential to lay the foundation for a nitrogen oxides removal technology costing much less than the techniques currently employed.

CHAPTER I

INTRODUCTION

Nitrogen Oxides have been linked to a broad range of air pollution problems including acid deposition, the atmospheric production of photochemical ozone, health threatening nitrate particles that also limit visibility, and the formation of toxic nitrogen compounds such as nitrosamines.

Over twenty million tons of NO_x (nitric oxide and nitrogen dioxide, collectively called NO_x), are emitted to the atmosphere each year from the high temperature combustion of fossil fuels, resulting in concentrations in urban areas which are 10-100 times those found in non-urban areas. NO_x emissions from man-made sources are essentially made up in equal parts by stationary and mobile combustion sources. Because mobile sources emission standards have been relaxed, stationary source NO_x control has become the primary method of limiting NO_x discharges.

Efforts to control NO_x emissions have lagged far behind those expended to limit SO_2 discharges. This situation has been a result primarily of two factors: (1) NO_x discharge concentrations are generally much lower than those of SO_2 and (2) NO_x , approximately 95% of which is in the form of nitric oxide, is more difficult to remove from exhaust gases due to its relatively poor reactivity.

The control of NO_x emissions is being approached from two

different strategies. The first is preventing the formation of NO_x in the combustion process. Second is the post combustion removal of NO_x from exhaust gases (flue gas treatment). The goal of all combustion modification techniques being developed to prevent NO_x formation is to reduce the flame temperature and hence, the oxidation of nitrogen which is found both in the fuel and in combustion air. Techniques for achieving this include: (1) staged combustion, (2) recirculation of combustion gases, and (3) use of a boiler type that provides a relatively cool flame such as a fluidized bed. It is expected that combustion modification can lower NO_x emissions by up to 50%, a substantial reduction but not enough to meet the limit of NO_x discharges being implemented in Japan and several states in the U.S. It is clear that to meet these limits flue gas treatment must be employed.

Since no catalyst has yet been found to directly and rapidly decompose NO_x in the presence of oxygen, several other NO_x removal techniques have been developed. These processes include homogeneous (non-catalytic) reduction with ammonia (NH_3) as the reducing agent, catalytic reduction by NH_3 , sorption of NO_x with solids, absorption of NO_x followed by liquid phase oxidation or reduction, and gas phase oxidation of NO to NO_2 followed by absorption into a liquid.

In an effort to improve the economics of cleaning stack gases, NO_x removal has been combined with SO_2 removal. These processes include absorption of NO_x and SO_2 , selective catalytic reduction of NO_x by NH_3 with simultaneous sorption of SO_2 , sorption of NO_x and SO_2 , and electron beam radiation.

Selective catalytic reduction of NO_x by NH_3 is the method most preferred in Japan, where the majority of work has been done on NO_x removal due to strict emission controls. This technique requires a large capital investment due to the use of expensive catalysts, and results in high operating costs due to the need for NH_3 . The other technologies have not been developed as fully as selective catalytic reduction for various reasons. These include poor NO_x removal capability, poor NH_3 utilization, and reduced catalyst life resulting from poisoning, erosion and plugging. The combined NO_x/SO_2 removal technologies can also have the added drawbacks of increased complexity, use of high sulfur coals to favor the removal reactions, or high power requirements.

Since the current technology available for NO_x reduction is technically or economically unattractive, research is continuing to develop a NO_x removal process that is commercially feasible.

Oxygen adsorption has been a major problem in the development of an effective NO catalyst. Since stack gases commonly contain oxygen, solving this problem is necessary before catalytic decomposition of NO is a viable NO_x process. It has been shown that electric fields can be used to effectively control the adsorption of oxygen on conducting and semi-conducting surfaces.

In this investigation, a stream of nitrogen containing NO (ppm) has been subjected to high electric fields in the presence of catalysts to study the NO decomposition behavior. The catalysts tested include steel wool, stainless steel wool, gold plated stainless steel wool and glass wools. The effect of parameters such as temperature, oxygen

content, moisture content and residence time have also been studied.

The results of this work have the potential to lay the foundation for a unique NO_x removal technique utilizing electric fields and a catalyst. Since chemical reducing agents and scrubbing systems are not needed, this process may lead to much lower NO_x removal costs.

CHAPTER II

LITERATURE REVIEW

The chemical reactions for the decomposition of nitric oxide (NO) have been studied over a number of years by many investigators. These studies include homogenous reactions, heterogeneous catalytic reactions and reactions taking place in electrical discharges. Nitric oxide accounts for approximately 95% of the oxides of nitrogen emitted from a coal fired utility boiler and is found in similar ratios in most combustion exhaust streams. These oxides of nitrogen (NO_x) are pollutants which has been the main motivation behind the current interest in reactions involving NO.

Shelef and Kummer (1971) present some of the physical properties of nitric oxide as shown in Table 1. Prominent among these is the large thermodynamic instability of NO with respect to elemental nitrogen and oxygen. Shelef and Kummer (1971) in Table 2 also show the change in the equilibrium constant and equilibrium NO concentration with temperature. As can be seen from Table 2, there is no thermodynamic hindrance to the thermal decomposition of NO below 1000°K . Below approximately 700°K , thermal decomposition of NO is virtually complete to its elements.

Despite its thermodynamic instability, NO does not readily decompose at ambient temperatures. This was shown by Howard and Daniels (1958) in 1917. They sealed purified NO in glass tubes contained 1-2 grams of a catalyst made from materials such as

Table 1

Physical Properties of Nitric Oxide
(Shelef, 1971)

Molecular Properties		Thermodynamic Properties	
Bond Energy	151 Kcal/Mole	m.p.	109.49°K
Bond Length	1.15°A	ΔH fusion	549.5 cal/Mole
1st Ionization Pot.	9.5V	b.p.	121.36°K
Dipole Moment	0.16 Debye	ΔH Vaporization	3293 cal/Mole
Molar Susceptibility,		ΔH^0_f (298K)	+21,500 cal/Mole
20°K	1.43×10^{-3} cgs units	ΔF^0_f (298K)	+20,650 cal/Mole
Ground State	$^2\pi_{1/2}$	ΔS^0_f (298K)	50.35 e.u.
1st Excited State	$^2\pi_{3/2}$		
$E (^2\pi_{1/2} \rightarrow ^2\pi_{3/2})$ 352 cal/Mole (124.2 cm ⁻¹)			

Table 2

Change of the Equilibrium Constant and the Equilibrium Nitric Oxide
Concentration (at 75% N₂, 1% O₂ in the gas) with Temperature
(Shelef, 1971)

Temp. (°K)	K	Equilibrium NO Conc. (ppm)	Temp. (°K)	K	Equilibrium NO Conc. (ppm)
298	1.549×10^{15}	5.6×10^{-11}	1200	1977	43.5
400	1.413×10^{11}	6.35×10^{-7}	1300	986.3	88.0
500	6.223×10^8	1.39×10^{-4}	1400	543.3	160.0
600	1.663×10^7	5.2×10^{-3}	1500	323.6	269.0
700	1.268×10^6	6.85×10^{-2}	1600	205.6	424.0
800	1.828×10^5	4.75×10^{-1}	1700	138.0	630.0
900	4.046×10^4	2.14	1800	96.83	905.0
1000	1.208×10^4	7.23	1900	70.47	1230.2
1100	4508	19.3	2000	52.97	1640.0

transition metals, noble metals, rare earth oxides or organic polycyclic molecules. These tubes were examined every few years for evidence of NO decomposition. After forty years, less than 2% of the NO was decomposed in any tube, 2% being the minimum detectable decomposition. The extremely slow rate of thermal homogeneous decomposition was due to the high activation energy for this process which range from 63.8 kcal/mole (Kaufman and Kelso, 1955) to 82 kcal/mole (Wise and French, 1952).

Shelef and Kummer (1971) discuss the molecular orbital scheme for nitric oxide as shown in Figure 1. The eleventh electron (omitting the lone ls pairs) goes into an antibonding orbital and is the source of the molecule's paramagnetism. This electron is easily lost by the molecule as is shown by the low ionization potential ($\text{NO} \rightarrow \text{NO}^+ + \text{e}^-$). The positive nitrosonium ion (NO^+) formed when the electron is lost has a stronger N-O bond (251 kcal/mole) than the NO molecule. Forcing the NO molecule to accept an electron which would go into an antibonding orbital forming the negative nitrosyl (NO^-) ion, substantially weakens the N-O bond.

The search for an NO decomposition catalyst has been in progress for some time with no substantial success. Shelef and Kummer (1971) and Hightower and Van Leirsburg (1974) have reviewed the various catalysts tested and the problems associated with the catalytic decomposition of NO. Tables A-1 - A-3 in Appendix A show a summary of the various catalysts tested for NO activity.

Chemisorption of the NO molecule is an important step in any catalytic reaction in which this molecule participates. As noted

Figure 1. Molecular Orbital Scheme for Nitric Oxide
(Shelef, 1971)

earlier, the NO molecule can form ionic bonds leading to the formation of NO^+ and NO^- . Besides forming ionic bonds, the molecule can also bond covalently through electron sharing or coordinate as a neutral entity through one of three ways: (1) donating a lone pair of "s" electrons, (2) donating a lone pair of "s" electrons plus the odd electron or (3) accepting an electron from a metal site and forming an electron pair bond. Ionic bonding provides for the greatest changes in N-O bond strength whereas covalent or pure coordination bonding somewhat weakens the N-O bond. Ionic-coordinative bonding somewhat increases the N-O bond strength. Shelef and Kummer (1971) surmise that in most cases of bonding to a surface, the formation of NO^- ions is absent and hence no substantial weakening of the N-O bond takes place. Covalent bonding, which would slightly weaken the N-O bond is also relatively unimportant.

A second problem in the catalytic decomposition of NO is the adsorption of oxygen to the catalyst surface, which deactivates the surface. Once the surface saturates with oxygen, the low temperature catalytic activity ceases and the surface becomes inert except at high temperatures where oxygen removal may be thermally stimulated.

Shelef and Kummer (1971) propose that the best catalysts for NO decomposition are either copper chromite, cobalt oxide or copper supported on silica but that the specific decomposition rates of each of these catalysts at 500°C and 1 atm falls into the range of 1.5×10^{-9} to 1.5×10^{-8} moles $\text{m}^{-2} \text{min}^{-1}$. At this rate approximately 670 kg of catalyst would be required to achieve 90% NO conversion at 60 miles per

hour with an engine emitting 2.6g NO/mile. It is obvious that the rate of decomposition is far too low to be of practical use.

Mahaligam et al. (1981) show that zirconia supported nickel and zirconia supported cobalt achieve significant NO removal at temperatures in the vicinity of 1000°C, where the decomposition is a combination of heterogeneous and homogeneous reactions (Appendix A, Tables A-4 & A-5). The addition of oxygen to the inlet gas however, greatly reduces the rate of NO decomposition. This along with the high temperature limitation makes these catalysts of little practical importance. Hightower and Van Leirsburg (1974) conclude "we are not optimistic that a thermally stable solid catalyst will ever be found to decompose NO in an oxidizing environment at mild temperatures. Such an achievement will likely require some radical new ideas based on a fundamental understanding of chemical interactions between NO and solids."

Because of the inability to decompose NO by using only a catalyst, several other methods of removing NO_x from a combustion exhaust stream have been developed and tested. Rosenberg et al. (1980) summarize the technologies that have been developed for NO_x removal and combined NO_x and SO₂ removal in Figure 2. These processes differ in regard to considerations such as (1) wet vs. dry, (2) separate NO_x removal or simultaneous NO_x and SO₂ removal, (3) absorption vs. decomposition, and (4) catalytic vs. non-catalytic. Most of the early processes tested were of the wet type for simultaneous NO_x and SO₂ removal. This technology is the first to be developed mainly because the most common of the processes already in use for SO₂ removal have been of the wet

Figure 2. Technologies for the Removal of NOx from Stack Gases (Rosenberg, 1980)

type. Combining NO_x removal with these processes holds the promise of being economical. The main problem, however, was that NO, which is the predominant form of NO_x , is extremely unreactive and has a low solubility in H_2O .

The use of a reducing agent, with or without a catalyst, has been widely studied with CO, H_2 , CH_4 and NH_3 as the reducing agents of choice. The process most widely used in Japan, where most of the work on NO_x removal has been performed due to stringent emission requirements, is reduction with NH_3 as the reducing agent. Both catalytic and non-catalytic reduction has been used with catalytic reduction as the more favorable technique. There are several drawbacks to non-catalytic reduction with NH_3 . These include the need for a high temperature ($\sim 980^\circ\text{C}$), limited removal efficiency and poor NH_3 utilization (Slack, 1979). The conditions required with non-catalytic reduction with NH_3 must be tightly controlled to prevent NH_3 reactions with O_2 or the formation of explosive mixtures.

The more widely used technique of catalytic reduction with NH_3 also has several drawbacks including limited catalyst life, poisoning of the catalyst by constituents in the gas, catalyst erosion by dust, and air heater plugging and corrosion by ammonium bisulfate. The problems associated with the reduction of NO using NH_3 , plus the high cost of NH_3 , which has to be injected into the exhaust stream, make the development of a more economical NO removal technology highly desirable.

An alternate approach to NO_x removal has been the use of electrical techniques to overcome some of the difficulties associated

with NO catalysis or to initiate the reactions leading to the decomposition of NO. These techniques fall into three categories; (1) the use of electrostatic fields applied to NO catalysts, (2) electrical discharges to decompose NO and (3) E-beam radiation to produce active species leading to NO decomposition.

Several authors (Hoenig and Lane (1968), Devyatov et al. (1975), and Domke et al. (1968)) have shown that the application of external electric fields to semi-conducting and conducting surfaces can effectively control the absorption of oxygen to these surfaces, which is a major problem in the catalytic decomposition of NO. Wooten and Mangold (1971) in a U.S. Patent report that NO reduction can be achieved using high voltages applied to a metal catalyst. The metals tested are in the form of metal wools and include aluminum, bronze, brass, steel, stainless steel, stainless steel plated with nickel, and stainless steel plated with gold. In each case NO removal is reported when a negative potential of between 6,000 and 50,000 volts is applied to the catalysts being tested. Each catalyst is reported to have lost its NO removal capability after only a few minutes except gold plated stainless steel which is reported to have maintained a high level of NO removal (>90%) for periods up to forty hours. The gas containing NO is obtained directly from the exhaust of an automobile engine.

The Wooten and Mangold patent represents the only investigation found in the literature in which the technique of applying negative potentials to metal surfaces is used to achieve NO removal. The patent provides very few details of the experiments conducted and discussions with Mr. Wooten shed no additional light on the exact procedures used

to obtain these results. In the patent, the authors speculate that the reason for NO removal is that the metal wools are able to supply a negative charge to the gas resulting in decomposition of NO to N_2 and O_2 . An electrical discharge is not reported to be observed and the authors present no hypothesis as to how the charge is transferred to the gas.

The use of electrical discharges to initiate chemical reactions in gases have been studied over a number of years by numerous investigators. Joshi (1927, 1929a, 1929b, 1929c) studied the decomposition of nitrous oxide (N_2O) to its elements using an electrical discharge in a Siemen's ozonizer at 6,000-12,000 volts and 150 Hz. Visvanathan (1952, 1953) used procedures similar to those developed by Joshi to study the decomposition of NO. It is found that NO completely decomposed to N_2 and O_2 , with nitrogen dioxide (NO_2) as an intermediate. Bes et al. (1970) and Bes (1978) studied the decomposition of NO and NO_2 in an electric discharge. These authors report that the product of voltage and frequency is a main parameter in the kinetics of the decomposition reaction taking place. The works of Joshi, Visvanathan and Bes are reviewed in more detail in Chapter 3, Mechanism of NO Decomposition.

The use of electrical discharges to remove NO from exhaust streams has not been commercialized because of the high power needed to achieve significant NO removal. Person et al. (1985) state that in an electrical discharge there are too few electrons with high enough energy to produce the ions and radicals needed to remove NO. The authors further state that "The bulk of the energy in a gas discharge

is deposited as vibrational and rotational excitation of the flue gas molecules and has no significant effect on pollutant removal."

Two methods of more efficiently producing the active species necessary for NO removal in an electrical discharge have been tested. One is the use of a corona discharge induced by a sharp rising nanosecond pulse voltage (Masuda and Nakao (1986), Masuda and Wu (1987)). In this technique, a sharp pulse discharge is produced but the duration of the discharge is kept short enough to prevent arcing, which results in a large portion of the energy in the discharge going into heating the gas. This technique is in the early stages of development and has not been reported to be utilized on a pilot plant scale. Therefore, the possible problems associated with this method of NO removal and the economics of the process have not been resolved.

The use of electron beams is the second electrical discharge method under investigation to produce active species for NO removal. An electron beam is a stream of electrons produced by a discharge then accelerated to a very high energy level before coming into contact with the flue gas. Tokunaga et al. (1978a, 1978b, 1978c, 1978d, 1979a, 1979b, 1982), Suzuki et al. (1978, 1979, 1980a, 1980b) and Nishimura et al. (1979, 1981a, 1981b) studied the electron beam irradiation of NO_x and SO₂ in simulated flue gas. This work is further discussed in Chapter III, Mechanism of NO Removal.

The only investigation reported in the literature in which an electrical discharge in the presence of a non-conducting catalytic material is used to remove NO is reported by Henis (1976). In this investigation, several catalyst support materials (listed in Table 8)

are tested in the presence of a discharge to remove NO from an automobile engine exhaust stream. Henis reported that the removal may be due to a combination of induced discharge and surface reactions to decompose NO and adsorption of NO by the catalyst material. A review of this work is also presented in Chapter 3, Mechanism of NO Removal.

The large amount of activity in the field of NO_x removal from exhaust gases is an indication that no suitable economical process has yet been developed to solve the problem of NO_x emissions to the atmosphere. The present investigation is an attempt to combine the effects of electric fields and catalysis to achieve an economical method of treating NO_x laden exhaust gases.

CHAPTER III

MECHANISM OF NO REMOVAL

Nitric Oxide removal can be brought about in the presence of an electrical discharge in a reactor. Adding a catalytic material to the reactor enhances the rate of removal at room temperature. A description of the reaction mechanisms of the decomposition of nitric oxide (NO) with or without a catalyst in electrical discharges is presented here.

An electrical discharge is a phenomenon wherein free electrons are produced and accelerated under the influence of an electric field. The free electrons may be generated from any number of sources including cosmic rays, a source of radiation or the cold cathode emission caused by the strong electric field around the sharp point on an electrode. Electrons, once generated, can then collide with gas molecules leading to excitation and, if of enough energy, ionization and electron multiplication, which would then result in a gaseous medium with a high electrical conductivity (Fite, 1969).

Electrical discharges are known by several different names including corona, semi-corona, glow, silent luminous, Townsend, arc and plasma discharges, each carrying a specific connotation. They can be broken down into two broad categories however, glow and arc discharges. Glow discharges (including dark discharges in which there is no glow, corona, semi-corona and Townsend) are characterized by a large difference between the electron and heavy particle temperatures

whereas, in an arc the electron and heavy particle temperatures are nearly equal (Ingold, 1978). The disparity between electron and heavy particle temperatures in a glow discharge makes this system of immense chemical interest. For example, while the temperature of both the atoms and molecules present in a hydrogen discharge are very close to room temperature, the dissociation fraction present is what would be expected for hydrogen in equilibrium at 4000 °K (Fite, 1969).

Much of the early work on chemical reactions in electrical discharges has been carried out in a Siemen's Ozonizer which consists of a gas space enclosed between two concentric glass cylinders with metallic or electrolytic electrodes in contact with the cylinders. This system is considered a capacitively coupled discharge with the electrodes physically separated from the gaseous medium by a dielectric barrier. The electric field in the plasma region is caused by the oscillating electrostatic charges at the dielectric barrier surfaces covering each electrode (Flinn, 1969).

Elliott, Joshi and Lunt (1927) proposed a theory for chemical reactions in electrical discharges based on the concept of "critical activation" in which reacting molecules derived their energy of activation from collisions with the ions (electrons) possessing or exceeding a minimum amount of energy. They derived the expression:

$$K = \frac{p k i}{e^-} i e^{-\left(\frac{pkV_1}{E_2}\right)} \quad (1)$$

where: K = number of molecules reacting per second
 p = initial pressure of the gas, cm Hg.
 e^- = electronic charge, e.m. units

i = current through the gaseous medium due to the movement of ions and electrons.

V_1 = critical energy of the colliding ion, volts

E_2 = potential gradient across the annular space

k = a constant given by

$$k = \frac{I}{M p} \quad (2)$$

where: I = total current

M = mean free path of the ion at pressure p

Joshi (1927, 1929a, 1929b) investigated the decomposition of pure nitrous oxide (N_2O) in a Siemen's Ozonizer applying 6-15 KVAC (Kilovolts, alternating current) at 150 Hz. It was found that N_2O decomposed to its elements, nitrogen (N_2) and oxygen (O_2) with nitrogen dioxide (NO_2) as an intermediate. The following reactions were proposed:

It was further proposed that reaction (3a) was broken down into two simultaneous reactions:

with the NO formed in 4a immediately reacting with O_2 :

The decomposition of pure N_2O proceeded to completion, the nature of the products being independent of the initial N_2O pressure and the applied potential. It was observed however, that the rate of

decomposition changed markedly over the course of the experiment. Joshi (1929a) confirmed that the equation (1) developed by Elliott et al. (1927) held during the initial stages of the decomposition but the rate of reaction decreased substantially as the reaction proceeded. The author proposed that the decrease was due to the formation of the intermediate product, NO_2 . Nitrogen dioxide is more electronegative than N_2O , thereby having a greater affinity for the free electrons. The velocity of the electrons in the gaseous medium (U^-) is reduced by the presence of more electronegative gases, decreasing the discharge current density and the energy contained by the moving electrons, resulting in a lower rate of decomposition (Joshi, 1929b). N_2 , O_2 , and NO_2 were subsequently added to the ozonizer containing N_2O to test the electronic velocity concept. (Joshi, 1929c). The order of electronegativity of the gases considered is $\text{N}_2 < \text{N}_2\text{O} < \text{O}_2 < \text{NO}_2$. It was shown that NO_2 slowed the rate of decomposition more dramatically than O_2 which had a greater effect than N_2 .

Visvanathan (1952) studied the decomposition of NO in a silent electrical discharge, also using a Siemen's Ozonizer, at 5 KVAC, 100 Hz. The progress of the reaction was followed by constantly monitoring the system pressure and the discharge current. To account for the initial pressure decrease followed by a gradual increase to the initial value, the following mechanism was proposed.

As in N_2O decomposition, NO_2 was formed as an intermediate

product. Below initial pressures of approximately 400 mmHg, the decomposition of NO proceeded to completion. At higher pressures it was observed that the reaction ceased before complete decomposition was achieved. Continuing the discharge at the same electrical conditions for several hours resulted in no change in the product composition. These results agreed with the critical activation energy concept proposed by Joshi. The high concentration of NO_2 reduced the electronic velocity to the point that the critical activation energy required for NO_2 decomposition could not be supplied by the electrons at the applied potential difference.

Visvanathan (1953) also showed that equation (1), developed by Elliott et al., held for high initial pressures of NO (>4 mmHg) but that at low initial pressures (.1 to 4 mmHg) the equation of Brewer and Westhaver (1929, 1930), in which the rate of reaction is proportional to the current through the gas, more accurately predicted the rate of the reaction.

Bes (1970, 1977, 1978) and Lacoste and Bes (1974) studied the decomposition of NO and N_2O in an ozonizer at 0-15 KVAC, 50 to 900 Hz. The products of NO decomposition were verified to be N_2 , O_2 and NO_2 , confirming the observations of Visvanathan (1952). The rate of reaction was characterized to be proportional to the product of the applied potential, V, and the frequency, f. It was found that for $Vf < 10^6 \text{ Vs}^{-1}$, NO_2 was the intermediate product in NO decomposition. For $Vf > 10^6 \text{ Vs}^{-1}$ it was found that NO decomposed solely by reaction 6a, with no NO_2 formed.

Tokunaga et al. (1978a, 1982), Suzuki et al. (1978, 1979) and

Nishimura et al. (1979) studied the decomposition of NO, NO₂, and N₂O in N₂, using electron beam radiation. The range of initial concentration of the gases of interest was 50 - 1000 ppm.

The reactions taking place in the irradiated gaseous mixture of NO in N₂ and NO₂ in N₂ are shown in Table 3 (Tokunaga et al. 1982). Since the concentration of N₂ in the system was much greater than that of the pollutants, the whole of the energy absorbed in the mixture was taken to be absorbed into N₂. The decomposition of NO and NO₂ was then induced by attacks of active species (N₂⁺, N⁺, e⁻ and N) formed by the radiation-chemical primary reactions of N₂.

Table 3

Ion and Radical Reactions in Irradiated NO - N₂ and NO₂ - N₂ Mixtures

Radiolysis of N ₂		Radical Reactions	
N ₂	N ₂ ⁺ , e ⁻ , N	N + NO -> N ₂ + O	
		N + NO ₂ -> 2NO	
		N + NO ₂ -> N ₂ O + O	
		N + NO ₂ -> N ₂ + O ₂	
		N + NO ₂ -> N ₂ + 2O	
		N + N ₂ O -> NO + N ₂	
		N + N + N ₂ -> 2N ₂	
		O + NO + N ₂ -> NO ₂ + N ₂	
		O + NO ₂ -> NO + O ₂	
		O + O + N ₂ -> O ₂ + N ₂	
Ion Reactions			
N ₂ ⁺	+ NO -> NO ⁺ + N ₂		
N ₂ ⁺	+ e ⁻ -> 2N		
NO ⁺	+ e ⁻ -> N + O		
NO ⁺	+ e ⁻ -> NO + hv		
NO ₂ ⁺	+ e ⁻ + N ₂ -> NO ₂ ⁻ + N ₂		
NO ₂ ⁺	+ NO ₂ ⁻ -> NO + NO ₂		

Addition of O₂ to the NO - N₂ mixture sharply reduced the amount of NO decomposition in the irradiated mixture. At 3% O₂ in the inlet gas stream, NO decomposition to N₂ and O₂ dropped to 4%, compared with 60% decomposition when no O₂ was contained in the inlet gas. The bulk of the NO reacted was converted to NO₂. It is shown that for 3% O₂ a kinetic radiation equilibrium between NO and NO₂ was approached as the energy deposited in the gas was increased. The equilibrium is given

by:

$$(\text{NO}) / (\text{NO}_2)^2 = 0.027 \text{ ppm}^{-1} \quad (7)$$

This equilibrium was also approached when a mixture containing both NO (420ppm) and NO₂ (90ppm) was irradiated.

The yields of active species produced by the radiolysis of O₂ in a 3% O₂, 97% N₂ mixture were negligibly small. Therefore, all of the active species formed by the direct action of radiation can be taken as N₂⁺, N⁺ and N₂^{*}, produced by the radiolysis of N₂ as shown in Table 3. N₂⁺, N⁺ and e⁻ quickly undergo charge transfer to oxygen and react with oxygen as follows:

The O₂⁺ formed reacts easily with NO to form NO⁺ which was then neutralized by O₂⁻, leading to decomposition of a small amount of NO.

Almost all of the N atoms formed (Table 3 and eq. 8c) react rapidly with O₂ to form O atoms and NO as follows:

producing a high yield of O atoms, which can oxidize NO to NO₂ at a considerable rate. NO production from NO₂ also occurs via the O atom:

In the NO - N₂ and NO₂ - N₂ mixtures, the N atoms produced by radiolysis are largely responsible for the decomposition reactions which occurred (Table 3). In the mixtures containing 3% oxygen the N atom reacts rapidly with O₂, effectively suppressing the decomposition of NO and NO₂.

The discussion so far has focused on the gas phase reactions of NO in electrical discharges. In each of the studies mentioned the catalytic effect of the walls of the container is assumed to be negligibly small. The methods usually employed to study surface effects could not be used because they would drastically alter the electrical conditions of the discharge (Joshi, 1929a). Fite (1969) states that "our abysmally poor understanding of the adsorption of gas discharge products by discharge tube walls and the catalysis of reactions by these walls is the major blind spot in understanding of the chemistry which occurs in discharges."

Henis (1976) studied the decomposition of NO in an electrical discharge in which the discharge reactor was packed with various catalyst support materials such as alumina, magnesia, silica, and zirconium silicate. The mechanism of the reactions involved in the decomposition of NO were not completely understood but the author proposed that the mechanism involved some of the following:

Where M was any third body. The role of the surface was viewed as providing a template for adsorption of atoms and molecules and their subsequent reaction.

This review presents some of the mechanisms that may be possible for the decomposition of nitric oxide by an electric discharge in the presence of certain catalytic materials. However, no effort has been made to propose any new mechanism for the reduction of nitric oxide to nitrogen and oxygen in this investigation.

CHAPTER IV

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental set-up to investigate the electro-catalytic reduction of NO_x is shown in Figure 3. It is discussed here in four sections. The first is the gas mixing section in which the gases used in the experiments are mixed in various proportions to achieve the desired concentrations and gas flow rates. The second section discusses the reactor configurations used. The third section covers the power supply configurations and measurement of the voltages and currents. Finally, the fourth section discusses the analytical techniques used to measure the gas concentrations.

Gas Mixing Section

Cylinders of N_2 , O_2 , CO_2 and NO in N_2 provided by Matheson Gas Products, Inc., were used to obtain the desired gas concentrations. The flow rate of each of these gases was measured using Hastings Mass Flow Meters (MFM). These meters are calibrated for a specific gas and indicate the gas flow rate at standard temperature and pressure. To raise the water content of the inlet gas stream, nitrogen was passed through a bubbler containing water then mixed with the NO-N_2 stream. The tubing used in all of the piping which contained NO was either stainless steel (type 316) or teflon to minimize adsorption of NO by the tubing walls. A heat tape was wrapped around the stainless steel tubing at the inlet of the reactor to provide preheat for experiments conducted at elevated temperatures.

SCHEMATIC OF EXPERIMENTAL SETUP

Figure 3

Reactor

Two different makes of glass tubes were used as the reactor, vycor and pyrex. Vycor possesses a higher dielectric strength and volume resistivity than pyrex and was used in the bulk of the experiments including all of the experiments utilizing AC voltages. The inner diameter of both the pyrex and vycor tubes was 22mm, and the outer diameter was 25mm.

The reactor tube was placed in a three foot, three zone Lindbergh tube furnace which provided accurate temperature control for each of the three zones. A section of the reactor extending out of the furnace on the gas upstream side was wrapped with a heat tape to provide preheat capability. The heat output of this tape was adjusted so that the temperature of the gas at the inlet to the furnace, measured by a thermocouple installed in the glass tube, matched the furnace temperature as measured by a thermocouple in each of the three zones.

A thermocouple was installed in the furnace downstream of the reaction zone but had to be removed due to arcing from the inner electrode to this thermocouple.

The outer electrode was aluminum foil wrapped tightly around the reactor tube, its length coinciding with the length of the catalyst bed. The inner electrode consisted of a sealed stainless steel tube. Different diameters of tubing were used to vary the distance between the inner and outer electrodes from 10.8 to 3.9mm. A cross section of the reactor showing the electrode configuration is shown in Figure 4.

To protect the furnace from the high voltages used, sheets of 12 mil, silicon bonded, phlogopite mica paper were wrapped around the

Figure 4: Crossection of Reactor

outer electrode. A grounded metal screen was then placed outside the mica paper. The stainless steel tubing downstream of the reactor was also grounded.

Metal wools and non-conducting materials, such as glass wool, of a known mass were packed into the reactor around the center electrode. The packing material was distributed as evenly as possible throughout the reaction zone. A stainless steel tube was provided to bypass the reactor enabling the inlet gas composition to be checked throughout the experiments.

Power Supply

Three different types of voltages were used in the experiments. They consisted of DC, AC and rectified AC. The source of DC voltage was a Spellman 0 - ± 60 KV power supply. The maximum current this supply could provide was 2mA. This supply contained its own meters to monitor output voltage and current. When DC voltages were used, the outer reactor electrode was connected to ground through a Fluke digital multimeter which was used to measure the current penetrating the glass wall of the reactor.

The source of AC power was a Franceformer midpoint ground transformer. This transformer has two output terminals, each at a maximum of ± 9 KVAC but 180° out of phase with each other to provide a total voltage difference across the transformer of 18 KVAC. A variable output transformer was used to adjust the input voltage to the high voltage transformer and subsequently, the high voltage output to the reactor.

When using an AC power supply, the inner and outer electrodes were

connected to either side of the high voltage transformer. A 202 Kohm resistor was installed between the power supply and the inner electrode to ensure that a small load was placed on the system when voltage was applied, preventing the transformer's current limit from being exceeded.

The voltages applied to the inner and outer electrodes were measured using a Fluke digital multimeter with a 1000:1 voltage divider probe. Voltage and current meters were also installed on the primary side of the high voltage transformer.

The output of the high voltage transformer was rectified using a diode to produce the rectified AC used in the experiments. The electrode configurations used in these experiments are shown in Appendix C. Several configurations were tried including (1) positive or negative voltages applied to the center electrode with the outer electrode at ground, or at an AC potential, or completely removed, and (2) positive or negative potentials applied to the outer electrode with the inner electrode at an AC potential. The voltages and current were measured using the same equipment as when AC voltages were applied across the reactor.

Gas Analysis

Several instruments were obtained to analyze the gases for the compounds of interest. As mentioned earlier, a bypass around the reactor was installed so that the gases entering or exiting the reactor could be analyzed.

NO/NO_x Measurement

A Thermo Electron model 10A/R chemiluminescent NO/NO_x analyzer was

used to monitor NO and NO₂ concentrations. This instrument reacts O₃ with NO to produce excited NO₂. The light emitted by NO₂ as it returns to the ground state is measured by a photomultiplier tube. NO_x concentrations (NO and NO₂) are measured by converting the NO₂ to NO in a high temperature stainless steel chamber then subsequently measuring the NO concentration. The difference between the NO and NO_x concentrations is taken as NO₂.

Oxygen Measurement

Oxygen concentration was measured using an Infrared Industries model IR-2200 O₂ analyzer. The sensor in this instrument is a diffusion limited metal-air battery type. At the air cathode, oxygen is reduced to OH ions which in turn oxidize the metal anode. The current produced is proportional to the rate of consumption of O₂.

Water Vapor Measurement

The water vapor content of the gas was measured using a EG&G Environmental model 911 digital humidity analyzer. This analyzer uses the chilled mirror dew point condensation principle to determine the gas water vapor content.

N₂O Analysis

Nitrous oxide (N₂O) is a possible product of the reduction of NO. Its presence was checked using a Hewlett Packard 5730A gas chromatograph with thermal conductivity as the method of detection. The column used was stainless steel (9' by 1/8") packed with 50/80 mesh Poropack T packing obtained from Supelco, Inc. An analyzed span gas of 240ppm N₂O in N₂ was used as supplied and diluted to lower concentrations to determine detector response and minimum sensitivity.

Ozone Analysis

The analysis of ozone (O_3) was performed using ASTM procedure D 2912-76. In this procedure, micro amounts of ozone and other oxidants are collected by absorption in a solution of potassium iodide buffered to a pH of 6.8. The released iodide equivalent of the concentration of oxidant present in the gas stream is determined spectrophotometrically by measuring the absorption of the triiodide ion at 352nm. NO_2 gives 10% of the response of an equivalent molar concentration of ozone. The contribution of NO_2 to the total oxidant concentration was estimated by concurrent analysis for NO_2 using the NO_x analyzer.

CHAPTER V

RESULTS AND DISCUSSION

The results of this investigation of the electro-catalytic decomposition of nitric oxide to nitrogen and oxygen are presented in three sections. The first section covers experiments performed using DC and rectified AC voltages. The catalytic materials used in this part of the study are stainless steel wool (type 403), gold plated stainless steel wool, and steel wool. In the second section the results of experiments conducted using metal wool catalysts and applied AC voltages are presented and discussed. The effect of several parameters, such as the magnitude of the applied voltage, the reactor temperature, inlet gas concentrations and the catalyst materials are covered in this section. The third section presents the NO conversion and reduction achieved when AC voltages are applied in the presence of non-conducting reactor packings. The NO conversion and reduction obtained in the experiments are defined as:

$$\text{NO Conversion (\%)} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100$$

$$\text{NO Reduction (\%)} = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{x,out}}}{\text{NO}_{\text{in}}} \times 100$$

Effects of DC and Rectified AC Voltages on NO Conversion

Using Metal Wool Catalysts

DC and rectified AC voltages were applied to achieve NO decomposition in a mixture of NO and N₂ in the presence of stainless steel wool, gold plated stainless steel wool and steel wool in vycor and pyrex reactors. Results and discussion are presented as follows.

Effect of Positive DC Voltage on NO Conversion

The results of applying a positive DC potential to a vycor reactor containing gold plated stainless steel are shown in Table 4. At voltages below +20 KVDC (kilovolts, direct current) no NO conversion was obtained at temperatures of 150 and 200°C. At +20 KVDC and 200°C, some NO conversion (less than 1%) was obtained. The small conversion observed at 200°C was considered to be due to the higher current obtained (0.10 mA versus 0.03 mA at +20 KVDC, 150°C) in the circuit. This current was believed to be penetrating the vycor tube to the ground screen on the outside of the tube. To allow for a higher current through the tube, pyrex was substituted for vycor as the reactor material. Pyrex has a lower dielectric strength and volume resistivity than vycor allowing it to conduct currents at lower applied voltages.

Table 5 shows the effects of positive DC voltage on NO conversion using stainless steel wool in a pyrex tube. As expected, the pyrex material began to conduct current at the applied voltages and NO conversion was observed. The maximum NO conversion achieved was 16.5% at an applied voltage of +6.0 KVDC and a current of 1.25 mA. It is

Table 4

Effect of Positive DC Voltage on NO Conversion using Gold Plated
Stainless Steel in Vycor Tube

Run	Volt (KVDC)	Current (mA)	Temp. (°C)	Res. Time (sec)	NO _{in} (ppm)	NO _{out} (ppm)	NO Conversion (%)
1	+5	0	150	1.9	780	780	0
2	+16	.01	150	1.9	780	780	0
3	+15	.02	150	1.9	775	775	0
4	+20	.03	150	1.9	775	775	0
5	+24	.04	150	1.9	775	775	0
6	+5	0	200	1.9	765	765	0
7	+10	.01	200	1.9	765	765	0
8	+15	.03	200	1.9	765	765	0
9	+20	.10	200	1.9	765	760	0.65

Table 5

Effect of Positive DC Voltage on NO Conversion and Reduction Using
Stainless Steel Wool in a Pyrex Tube

Run	Volt (KVDC)	Current (MA)	Temp (°C)	Res. Time (sec)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conv. (%)	NO Reduct. (%)
1	0	0	150	1.0	395	395	395	0	0
2	+3.0	.04	150	1.0	395	392	392	0.8	0.8
3	+4.0	.12	150	1.0	395	385	392	2.5	0.8
4	+5.0	.25	150	1.0	395	380	385	3.8	2.5
5	+6.0	.45	150	1.0	395	363	378	8.1	4.3
6	+6.0	.73	150	1.0	395	355	370	10.1	6.3
7	+6.0	1.25	150	1.0	395	330	355	16.5	10.1
8	0	0	150	1.0	400	400	400	0	0
9	+13.0	.37	150	1.0	400	367	380	8.3	5.0
10	+13.0	.49	150	1.0	400	360	380	10.0	5.0
11	+14.0	.72	150	1.0	400	355	275	11.3	6.3

noteworthy that the NO conversion at +6.0 KVDC and 1.25 mA is higher than the conversion obtained at +14.0 KVDC and 0.72 mA for the same reactor temperatures, gas residence times, and essentially equal inlet NO concentrations. Thus, it can be concluded that the NO conversion is a function of the applied potential and current flow.

Effect of Negative DC Voltages on NO Conversion

The results obtained when negative DC potentials were applied to the reactor containing stainless steel and gold plated stainless steel wool are shown in Tables 6 and 7. The maximum NO conversion achieved was 29.1% at a voltage of -15 KVDC and a current of 0.84 mA using stainless steel wool (Table 6, S.N. 11).

Current flow through the pyrex wall could not be controlled due to heat absorbed in the reactor wall. The resistivity of pyrex decreases with temperature which caused the current flow through the wall to increase resulting in further heating of the wall and lowering of the wall's electrical resistance. This cycle continued in each case when current was made to flow through the wall until the maximum current of the power supply (1.72 mA) was reached, at which point the output voltage began to drop. This behavior can be seen in Table 6, S.N. 3 through 6, and Table 7, S.N. 4 through 7. The NO conversion appeared to be due to both the applied potential and current flow just as when positive DC voltage was used. Table 6 S.N. 4, 5 and 6 show that for a constant current the NO conversion decreased as the applied voltage dropped.

Table 6

Effect of Negative DC Voltage on NO Conversion and Reduction Using
Stainless Steel Wool in a Pyrex Tube

Run	Volt (KVDC)	Current (MA)	Temp (°C)	Res. Time (sec)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conv. (%)	NO Reduct. (%)
1	0	0	150	1.1	405	405	405	0	0
2	-5.0	.58	150	1.1	405	365	383	9.9	5.4
3	-5.0	.97	150	1.1	405	340		16.1	
4	-4.6	1.72	150	1.1	405	350		13.6	
5	-3.1	1.72	150	1.1	405	363	365	10.4	9.9
6	-3.0	1.72	150	1.1	405	363	363	10.4	10.4
7	0	0	150	1.1	395	395	395	0	0
8	-3.3	1.72	150	1.1	395	325	380	17.7	3.8
9	0	0	100	1.2	395	395	395	0	0
10	-15.0	.38	100	1.2	395	320	380	19.0	3.8
11	-15.0	.84	100	1.2	395	280	395	29.1	0

Table 7

Effect of Negative DC Voltage on NO Conversion and Reduction Using
Gold Plated Stainless Steel Wool in a Pyrex Tube

Run	Volt (KVDC)	Current (MA)	Temp (°C)	Res. Time (sec)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conv. (%)	NO Reduct. (%)
1	0	0	125	1.1	400	400	400	0	0
2	-10.0	.37	125	1.1	400	380	390	5.0	2.5
3	-10.0	1.00	125	1.1	400	370		7.5	
4	-6.5	1.72	125	1.1	400	365	375	8.8	6.2
5	-4.3	1.72	125	1.1	395	365	370	7.6	6.3
6	-4.3	1.72	125	1.1	390	340	360	12.8	7.7
7	-2.4	1.72	125	1.1	390	370		5.1	

Effects of Rectified AC Voltage and Metal Wool on NO Conversion

Experiments were conducted to study the effect of rectified AC voltages on NO conversion in the presence of stainless steel and gold plated stainless steel wools. The electrical configurations used to generate the rectified AC are shown in Appendix C. The NO conversion obtained using rectified AC was less than that obtained when DC voltages were applied in the presence of metal wool packings. Consequently, after expending much effort, these experiments were discontinued.

Experiments were also conducted to determine the effect of steel wool packing using DC and rectified AC voltages, since steel wool is an inexpensive material compared to stainless steel and gold plated stainless steel. The results, however, showed that steel wool was no more effective in these configurations than stainless steel and gold plated stainless steel.

Temperatures higher than 200°C could not be investigated using stainless steel and gold plated stainless steel. Above 200°C these metal wools became coated with the underlying impurities in the type 403 stainless steel. A search for a better quality stainless steel wool proved unsuccessful.

The NO conversions obtained in this study using DC and rectified AC voltages (29% maximum) were far below that reported in a U.S. patent by Wooten and Mangold (1971), the only information found in the literature in which a similar technique of using metallic catalysts was employed to remove NO. The patent reported that application of a negative potential in the range of -6 to -50 KV in the presence of gold

plated stainless steel wool resulted in an NO conversion of greater than 90% from the exhaust of an automobile engine. It was also reported that this level of conversion was maintained for over 40 hours. The parameters used in Wooten and Mangold's investigation such as temperature, residence time and current flow were not available, making exact duplication of their experiments not feasible.

The NO conversions obtained in this part of the study are far below that required to meet EPA emission standards. Consequently, the use of AC voltages to obtain NO conversion was investigated and is discussed in the next section.

Effect of AC Voltages and Metallic Catalytic

Materials on NO Decomposition

The NO conversion obtained in preliminary experiments with applied AC voltages was much higher than conversions obtained with DC or rectified AC voltages applied across the reactor in the presence of metal wools. To further investigate this, experiments studying the effect of catalytic material, gas residence time, reactor bed temperature and inlet NO, O₂ and H₂O concentrations were conducted using AC voltages. The reactor material for these experiments was a vycor tube, which did not show any signs of damage from the high voltages applied.

Effect of Metal Catalyst Packing on NO Conversion

Catalyst packing was considered to be one of the most important variables in this investigation. Experiments were conducted using various metal reactor packing, namely steel wool, stainless steel wool,

and gold plated stainless steel wool. Experiments without catalyst packing were also done for comparison. The reactor length in each case was 8" and the inlet gas was an NO-N₂ mixture. The results of conversion versus applied voltage are shown in Figure 5. As seen from Figure 5, gold plated stainless steel provided slightly better NO conversion than the other materials and was used in subsequent experiments. At 16 KVAC (kilovolts, alternating current) the NO conversions for gold plated stainless steel, stainless steel, steel wool and an empty bed were 58%, 51%, 44% and 33%, respectively. Another important feature was that some NO conversion was almost immediately obtained after the voltage was applied when metal wool packings were used. On the other hand, a minimum voltage of approximately 9.5 KVAC was required before any conversion of NO was observed in an empty bed. The shape of the applied voltage versus NO conversion curve for the empty bed case was also markedly different than the shapes of the curves obtained for the metal wool packings. The NO conversion initially increased much more rapidly, once the minimum voltage was reached, for small changes in applied voltage to the empty bed than in the packed beds.

Effect of Gas Residence Time on NO Conversion

A mixture of NO and N₂ was passed through a gold plated stainless steel wool packed reactor with the gas residence times varying from 1.6 to 5.3 seconds. The results for an inlet NO concentration of 385 ppm are shown in Figure 6. Figure 7 shows the results obtained when the NO inlet concentration ranged from 490 to 500 ppm. In each case, the NO conversion increased as the residence time increased. At a residence

Fig. 5: Effect of Metal Catalyst Packing Material on NO Conversion

Fig. 6: Effect of Residence Time on NO Conversion
 for Inlet NO Concentration of 385ppm

Fig. 7: Effect of Residence Time on NO Conversion
 for Inlet NO Concentration of 490-500ppm

time of 4.5 seconds and an applied potential of 16 KVAC, NO conversion of approximately 95% could be achieved.

Effect of Inlet NO Concentration on NO Conversion

Experiments were conducted with the NO concentration in the inlet NO-N₂ gas stream at 196, 495 and 700 ppm. The results are shown in Figure 8. The NO conversion increased as the inlet NO concentration decreased. At 14 KVAC, an NO conversion of 70% was achieved with 196 ppm NO in the inlet stream, compared to 52% and 37% for 495 and 700 ppm, respectively.

Effect of Inlet O₂ Concentration on NO Conversion

The effects of O₂ and H₂O on NO conversion were studied since these gases are present in stack gases. The results are discussed on the basis of NO reduction and conversion as defined earlier.

Experiments were conducted varying the inlet O₂ concentration of the NO-N₂ gas stream. The results are shown in Figures 9 and 10. Figure 9 shows that the NO conversion at 14 KVAC reduces only by 9%, from 51% to 42%, with an increase in O₂ content from 0.016% to 0.94%. However, the NO reduction to N₂ and O₂ as shown in Figure 10 changed from 44% to 25% for the same voltage and O₂ concentrations. The addition of 0.94% oxygen increased the percentage of NO converted to NO₂ from 7% to 17%, probably due to the reduced effectiveness of the metallic surface as a decomposition catalyst.

Effect of Inlet H₂O Concentration on NO Conversion

Since all fossil fuel combustion exhausts contain water vapor, the effect of H₂O on NO conversion and reduction was studied. The H₂O content of the inlet NO-N₂ gas stream was increased by bubbling N₂

Fig. 8: Effect of Inlet NO Concentration on NO Conversion

Fig. 9: Effect of Oxygen Content on NO Conversion

Fig. 10: Effect of Oxygen Content on NO Reduction

through water and then mixing it with NO. The maximum inlet water concentration that could be achieved was 1.05%. The effects of the increase in water content on NO conversion and reduction are shown in Figure 11. The NO conversion at 14 KVAC decreased from 51% to 35% when the NO-N₂ gas stream contained 1.05% H₂O. At 14 KVAC, the NO reduction dropped from 44% to 13% for the same increase in H₂O content. The addition of water changed the bulk of NO conversion from reduction of NO to oxidation of NO to NO₂, reducing the effectiveness of the process.

Stack gases from combustion exhaust contain both O₂ and H₂O therefore experiments were conducted with O₂ and H₂O added to the inlet NO-N₂ gas stream. Figure 12 shows the effect of an increase in both H₂O and O₂ content on NO conversion and reduction. The change in NO conversion was small, from 51% to 46% at 14 KVAC, when the concentration of O₂ and H₂O in the inlet gas were increased to 0.93% and 1.05%, respectively. The reduction of NO, however, dropped even more drastically when both O₂ and H₂O were included than when either O₂ or H₂O were present individually. The maximum NO reduction achieved with 1.05% H₂O and .93% O₂ was only 7% at 14 KVAC compared to 44% at 14 KVAC when only trace amounts of H₂O and O₂ were present.

Effect of Temperature on NO Conversion

The effect of temperature on NO conversion was also investigated since temperatures higher than 30°C are available in combustion exhaust streams. Experiments were conducted at reactor temperatures of 30, 100 and 200°C using an inlet NO-N₂ gas stream containing approximately 495 ppm NO in the presence of gold plated stainless steel wool. The

Fig. 11: Effect of Water Content on NO Conversion and Reduction

Fig. 12: Effect of Water and Oxygen Content on NO Conversion

results are presented in Figure 13. An increase in temperature from 30°C to 200°C increased the NO conversion from 37% to 52% at 12 KVAC.

Experiments were also conducted at 100 and 200°C in addition to 30°C to determine the effects of introducing O₂ and H₂O on NO conversion. The results of the experiments conducted at 200°C with both O₂ and H₂O present in the inlet NO-N₂ stream are presented in Figure 14. The NO conversion at 13 KVAC dropped from 58% to 34% and the NO reduction at the same voltage dropped from 53% to 13% when 1.3% O₂ and 0.90% H₂O were added. These results of adding H₂O and O₂ to the inlet gas at 200°C were about the same as when similar experiments were conducted at 30°C (see Figure 12). These results show that an increase in temperature did not significantly alter the effectiveness of the gold plated stainless steel for decomposing NO to N₂ and O₂.

The results obtained at 100°C and 200°C when H₂O and O₂ were added individually to the gas showed no significant change in NO conversion. The results are presented in Appendix B.

Similar experiments as presented in Figures 5 through 14 were also conducted using stainless steel wool as the catalyst packing. The results obtained (presented in Appendix B) show that both the gold plated stainless steel and unplated stainless steel behaved in a similar fashion when exposed to similar experimental conditions.

It became clear from the above results that the role of metallic packing on NO conversion and reduction was not what was considered earlier. It is believed that the important factor in these experiments is the electric field strength through which the NO molecules pass and not the potential difference across the two electrodes. A metal wool

Fig. 13: Effect of Temperature on NO Conversion

Fig. 14: Effect of Oxygen and Water Content on
 NO Conversion and Reduction at 200°C

packing could be approximated by a solid conductor in which all of the electronic charge resides on the outer surface. An intense electric field is established between the outer surface of the metal packing and the outer electrode when a potential is applied, but the field inside the metal wool bed is close to zero (in a solid conductor, the electrostatic field inside the conductor is exactly zero). The presence of an intense electric field only at the outer edges of the bed may explain the low NO conversions obtained in the experiments since a large percentage of the gas passes through the center of the bed and is not exposed to the high electric field.

To test the electric field concept, experiments were conducted in which the distance between the center and outer electrodes was decreased by inserting a larger diameter, solid electrode in the center of the reactor. The results of these experiments are shown in Figure 15. Reducing the distance between the electrodes from 10.8 mm to 3.9 mm allowed for a NO conversion of 88% at 14.0 KVAC without any packing material. It was noticed during these experiments that a silent electric discharge took place in the empty reactor. The discharge filled the gas space between the electrodes. A subsequent check on the metal wool packing materials also showed that a discharge was taking place but only at the outer edge of the bed. This discharge was only visible to the eye at voltages above approximately 10 KVAC. Another way to increase the electric field strength seen by the gas was to pack the reactor with a porous dielectric material. Several inexpensive materials were readily available to be used as reactor packing. The results of the experiments conducted with these materials are presented

Fig. 15: Effect of Distance (d) between Electrodes on NO Conversion in an Empty Bed

in the next section.

Effect of AC Voltages and Non-Conducting Catalytic

Materials on NO Conversion

Experiments were conducted using AC voltages in the presence of various non-conducting materials as reactor packings. The materials used were glass wool, silanized glass wool, standard kaowool, zirconium kaowool and molecular sieves. Two different makes of glass wool were used, the main difference being that the glass wool obtained from Supelco, Inc. has a much finer texture than glass wool obtained from Fisher Scientific Co. The silanized glass wool is wool obtained from Supelco which has been treated with a silane solution, replacing the OH groups on the glass wool surface with silane (SiH_4). Kaowool and zirconium kaowool are commercial insulating materials obtained from Thermal Ceramics. Standard kaowool is primarily made of silica (SiO_2 -53%) and alumina (Al_2O_3 -45%); zirconium kaowool contains 45-48% SiO_2 , 32-26% Al_2O_3 and 18-21% zirconia (ZrO_2).

The NO conversions obtained using these materials in a vycor tube and applying an AC voltage are presented in Figures 16 and 17. There was a dramatic increase in the conversions obtained with these dielectric materials compared to those obtained using metal wools. For comparable reactor size and operating conditions, an NO conversion of 52% was achieved using gold plated stainless steel at 14 KVAC (Figure 7), compared to 98% conversion using Supelco glass wool at the same voltage. NO conversions greater than 95% were routinely obtained for each of the non-conducting materials except molecular sieves which

Fig. 16: Effect of Catalyst Packing Material on NO Conversion

Fig. 17: Effect of Catalyst Packing Material on NO Conversion

provided a maximum conversion of 82%.

The important feature of the NO conversion obtained with non-conducting materials is that slight increases in the applied voltage resulted in large increases in the NO conversion. For example, using glass wool (Supelco), the NO conversion increased from 7% to 80% when applied voltage was raised from 8 to 12 KVAC. It is also seen from Figures 16 and 17 that a minimum voltage was necessary before NO conversion began to take place. These voltages range from approximately 6.5 to 9.5 KVAC for a particular electrode geometry and packing materials used. It is at these voltages that an electrical discharge began to take place.

The use of electrical discharges and non-conducting catalytic packing materials to remove NO from automobile combustion exhaust gases has been investigated by Henis (1976). The materials used in the investigation are listed in Table 8. These materials used were essentially catalyst supports, each having a high surface area to mass ratio. Out of 70 experiments reported using the materials of Table 8, greater than 90% NO removal was obtained in only three experiments. The materials used in these three experiments were zirconium silicate support, thorium oxide and acidic alumina.

Henis appears to have focused his work mainly on the surface properties of the material stating "the materials employed as surface contact material will generally have dielectric properties or be of no more than low conductivity. This is not necessarily an essential property, except to the extent necessary to avoid short circuiting when electric discharge means are utilized to produce the gaseous plasma."

In the present study, it is considered that the high NO conversions obtained by using inexpensive catalytic materials such as glass wools are due to a combination of electric and surface effects. Determining the individual magnitudes of these effects on NO conversion and the mechanism of reactions taking place is recommended as a subject for future study. However, a review of the literature discussing NO decomposition in electrical discharges is presented in Chapter III, Mechanism of NO Removal.

Table 8

Materials Tested by Henis (1976)

Neutral Alumina (72 m ² /g)	Acidic Alumina (449 m ² /g)
Magnesia Pellets	Molecular Sieve
Macroporous Silica (120 m ² /g)	Alumina Support
Aluminum Oxide balls (d=1/8")	Neutral Alumina (230 m ² /g)
Alumina catalyst support (230 m ² /g)	Cobalt Oxide
w/6" Aluminum oxide balls	Carbon
Alumina catalyst support (8x14 mesh)	Alumina
Silica gel	Thorium oxide, pellets
Silica Alumina	KOH (1%) on Silica (800
Zirconium silicate support (0.1 m ² /g)	m ² /g)
Zircon support	
(2.97% Al ₂ O ₃ , 32-33% SiO ₂ , 0.17% Fe ₂ O ₃ , 64% Zr + Hf oxides)	

CHAPTER VI

CONCLUSIONS

An investigation into the use of electric fields in the presence of catalysts to achieve the removal of nitrogen oxides from a gas stream has been conducted. The conclusions drawn from this study are presented below.

The maximum conversion achieved using DC potentials in the presence of metal wools was 29% at -15 KV, 1.2 second gas residence time and 395 ppm NO in the inlet gas. This conversion was achieved when a current of 0.84 mA was flowing through the glass reactor wall. NO conversions using DC voltages could only be attained when a current flow existed. However, this current could not be controlled and in several cases resulted in damage to the glass reactor walls.

The use of AC potentials applied to the reactor in the presence of metal wools resulted in much higher levels of NO conversion than those obtained using DC voltages. At a gas residence time of 4.5 seconds and 15 KVAC, 91% conversion and 86% reduction were achieved using gold plated stainless steel wool at a temperature of 30°C. The inlet NO, O₂, and H₂O concentrations were 500 ppm, 0.025% and 0.10%, respectively. The levels of conversion using a metal wool catalyst were also much higher than those obtained in an empty bed using AC potentials. At a 2.0-2.1 second residence time and 16 KVAC, the NO conversion in an empty bed was 33% versus 58% obtained using gold plated stainless steel.

Increasing the gas residence time or decreasing the inlet NO concentration resulted in an increase in NO conversion. At 500 ppm NO in the inlet gas, the conversion at 14 KVAC increased from 40 to 82% when the residence time was increased from 1.6 to 5.4 seconds. The NO conversion at 14 KVAC also increased, from 47 to 70% when the inlet gas NO concentration was decreased from 700 to 196 ppm at a gas residence time of 2.0-2.1 seconds.

Changing the reactor temperature did not significantly effect the levels of NO conversion achieved. NO conversion at 12 KVAC, 495-505 ppm NO, and 2.0-2.1 seconds residence time, increased from 37 to 52% when the reactor temperature was raised from 30 to 200°C.

The addition of both oxygen and water vapor, gases commonly found in combustion exhaust streams, reduced the levels of NO conversion and NO reduction achieved using AC potentials and metal wools. The NO conversion at 14 KVAC, 30°C, 2.1 second residence time and 490-495 ppm NO, dropped from 52 to 46% when the oxygen content was raised from 0.016 to 0.93% and the water vapor content was increased from 0.18 to 1.05%. At the same time, the NO reduction to N₂ and O₂ dropped from 44 to 7%. The large drop in NO reduction is an evidence that in the presence of oxygen and water vapor, the bulk of the NO converted is oxidized to NO₂.

The use of dielectric catalytic materials resulted in higher levels of NO conversion than when metal wools were used. At 15 KVAC and a residence time of 2.0-2.1 seconds, 93% conversion or better could be achieved using glass wool, silanized glass wool, kaowool, or zirconium kaowool. This is compared to 52, 47 and 40% conversion

achieved at 15 KVAC and comparable flow conditions using gold plated stainless steel, stainless steel and steel wool, respectively. The use of inexpensive dielectric catalysts reduces the residence time at 15 KVAC required for 90% conversion from approximately 4.5 seconds for metal wools to 2.0 seconds, increasing the throughput of the reactor.

The high levels of NO conversion obtained using AC potentials applied in the presence of an inexpensive catalyst material such as glass wool indicate that this electro-catalytic technique of reducing NO to nitrogen and oxygen may prove to be commercially viable.

CHAPTER VII

RECOMMENDATIONS

The use of electric fields in the presence of dielectric catalyst materials may be a feasible technology for removing nitrogen oxides from combustion exhaust streams. The high levels of NO conversion and reduction achieved in this study are encouraging but much more research work is needed before this technology can be evaluated for commercialization.

The major obstacle in the use of only electrical discharges without catalysts to remove NO_x from gas streams has been the high power consumption to achieve significant removal rates. The minimum power necessary to achieve suitable removal rates in the presence of catalysts should be investigated to determine the economic feasibility of this process.

The current effort to reduce NO_x emissions is focused on stationary sources such as utility boilers. Since the exhaust from these plants contains up to 6% oxygen and 10% water vapor, the effects of these gases on NO conversion and reduction using dielectric materials as catalysts must be studied. The effects of carbon dioxide, carbon monoxide, and sulfur dioxide on NO reduction should also be investigated.

At this time it is considered that the NO removal achieved using dielectric catalyst materials is due to both a surface effect of the material and an electric effect enhanced by the dielectric properties

of the catalyst material. To understand the reaction mechanism the nature of the catalyst surface as well as the dielectric properties of the catalyst need to be investigated. It is interesting to note that molecular sieves, with a very high surface area, did not achieve the level of NO conversion attained using glass wool in the same reactor volume and at the same conditions. Establishing the mechanism of NO removal will be a major step towards the understanding required to take full advantage of this process.

Another parameter that is of major importance in this process is the electric field strength. This is a function of many variables including the magnitude and frequency of the applied voltage, discharge current, reactor geometry, and dielectric properties of the packing material. It is recommended that the effect of these parameters must be investigated to optimize the NO reduction to N_2 and O_2 at the minimum cost.

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APPENDICES

APPENDIX A

Table A-1

Summary of the Results on the Decomposition
of Nitric Oxide on Various Catalysts

Catalyst	Pressure Range	NO Concentration Range	Temp. Range °C	Activation Energy Kcal/mole	Order of Reaction
Quartz			< 723	21.4	2
Ga ₂ O ₃	atm	10%	< 1000	19.2	0
Al ₂ O ₃	atm	10%	< 1000	31.6	0
CaO	atm	10%	< 1000	23.0	0
ZrO ₂	atm	10%	< 1000	27.8	0
Cr ₂ O ₃	atm	10%	< 1000	40-60	0
Fe ₂ O ₃	atm	10%	< 1000	16	0
ZrO ₂	atm	10%	< 1000	31.5	0
Al ₂ O ₃	atm	5-15%	700-1100	31.0	0
ZrO ₂	atm	5-15%	700-1100	24.5	0
Fe oxide*	atm	0.25%	325		
Copper					
Chromite*	atm	0.62%	320		
Supported					
Pt*	1-15atm	0.4%	430-540		2
CuO:SiO ₂	atm	900ppm	510	39	1
Al ₂ O ₃	atm	10-50%	664-807	20.0	2
CuO:Al ₂ O ₃ (1:1)	atm	720-2200ppm	304-520	31.6	0
CeO ₂ :Al ₂ O ₃ (1:1)	atm	720-2200ppm	30-520	42.2	0
Co ₃ O ₄	100-200 torr	100%	250-350	29.0	1.5-1.8
NiO	100-300 torr	100%	450-550	20.0	2
CuO-I**	not given	100%	350-700	~12.0	2
CuO-II***	not given	100%	300-450	~12.0	2
Fe ₂ O ₃	100-400 torr	100%	300-400	22.0	2
Cr ₂ O ₃	150-270 torr	100%	350-475	20.0	2
ZrO ₂	100-225 torr	100%	650-750	35.0	2

* Commercial Catalysts.

** Calcined at 700° in air.

*** Calcined at 450° in air.

Table A-2

Summary of Nitric Oxide Decomposition
Results Over Oxide Catalysts

Oxide	T (°C) ^a	E ₀ ^b	Log ₁₀ (A ₀) ^c	Pressure Dependence	E ₁ ^b	E _N ^{b,d}
MgO	590-760	37	20.66	1.0	38	35
NiO	430-600	30	20.16	1.0	45	39.5
ZnO	680-770	41	21.29	1.0	36	42
CaO	580-720	28	18.74		30	34
SrO	620-750	15	17.38		15	23
CuO	370-490	9	14.81	1.0	22	24
Al ₂ O ₃	650-750	38	20.33		45	43
Fe ₂ O ₃	520-660	16	15.00	1.0	27	22
Cr ₂ O ₃	680-780	23	16.25	1.0	38	40
Ga ₂ O ₃	610-760	29	18.09	1.0	40.5	40.5
Rh ₂ O ₃	400-560	14	16.45		10	34
GeO ₂	640-800	18	16.56		26	26
HfO ₂	730-830	18	15.71		30	30
ThO ₂	580-840	14	15.02	1.0	22	30
SnO ₂	650-790	19	16.00		27	32
TiO ₂	670-870	19	15.99		35	39
IrO ₂	330-450	16	17.91	1.0	24	30.5
Sc ₂ O ₃	540-710	31	20.43		43	46
Y ₂ O ₃	550-700	24	18.23	1.0	18.5	27.5
La ₂ O ₃	630-830	16	16.40		11	20
Nd ₂ O ₃	580-680	25	18.71		12	28
Sm ₂ O ₃	550-760	14	15.85	1.0	19	23
Eu ₂ O ₃	550-720	23	17.85		16	27.5
Gd ₂ O ₃	470-650	19	16.59		12	26.5
Dy ₂ O ₃	650-760	25	18.69		18	36
Ho ₂ O ₃	590-760	32.5	20.97	1.0	37	40
Er ₂ O ₃	570-700	28	18.49		36	39.5
Tm ₂ O ₃	630-760	28	18.89		34	32
Yb ₂ O ₃	600-720	29	18.62		30	32
Lu ₂ O ₃	540-690	26	18.59		29	35

a - Reaction Temperature Range

b - Kcal/mole

c - Molecules/cm²/s at 200 torr of NOd - Activation Energy for N₂O Decomposition

Table A-3

Summary of NO Decomposition on
Noble Metal Catalysts
(Hightower, 1974)

Surface	Temperature Range (°C)	Pressure Range (torr)	Rate Law	Activation Energy (Kcal/mole)
Pt	882-1403	100-500	$k(\text{NO})/(\text{O}_2)$	14
Pt	1210	201-479	$k(\text{NO})^2/(\text{O}_2)$	-
Pt-10%Rh	1040-1390	193-477	$k(\text{NO})^2/(\text{O}_2)$	27
Pt	860-1060	-	$k(\text{NO})/[1+b(\text{O}_2)]$	22-25
Pt/Al ₂ O ₃	386-532	760	$k(\text{NO})^{.95}$	20
Pt-Ni/Al ₂ O ₃	427-536	1-15atm	$k(\text{NO})^2/[1+b(\text{O}_2)^{.5}]^2$	variable
Pt/Al ₂ O ₃	600-700	10-150	$k(\text{NO})/[1+b(\text{O}_2)]$	18
Rh ₂ O ₃	400-560	50-400	$k(\text{NO})/[1+b(\text{O}_2)]$	14
IrO ₂	330-450	50-400	$k(\text{NO})/[1+b(\text{O}_2)]$	16

Table A-4

NO_x Removal from NO-N₂-He Mixtures
Using Supported Nickel Catalyst
(Mahaligam, 1981)

NO _x Concentration (ppm)		Percent NO _x Removal	Reactor Temp (°C)	Preheater Temp (°C)	Flow Rate of Gas Mixture ^a (m ³ /hr)	Gas Hourly Space Velocity (Hr ⁻¹)
Inlet	Exit					
1,550	550	64.5	1160	480	0.527	12,000
1,500	990	36.1	1160	510	0.903	20,400
1,500	900	40.0	1160	540	0.875	19,800
1,500	810	46.0	1160	540	0.716	16,200
1,500	800	46.7	1160	540	0.830	18,800
1,130	650	42.5	1120	480	0.932	21,100
1,070	670	37.4	1110	430	0.937	21,200
1,000	600	40.0	1110	450	0.926	21,000
890	525	41.0	1110	450	0.923	20,900
790	460	41.8	1110	430	1.107	17,300
675	395	41.5	1110	450	0.974	22,100
560	225	59.8	1110	510	0.660	15,100
480	255	46.9	1160	480	0.850	19,300
390	218	44.1	1110	450	0.966	21,900
258	158	38.8	1110	430	1.039	23,600
200	127	36.5	1110	430	1.107	25,100

^a 1 atm, 20°C

Table A-5

NO_x Removal from NO-N₂-He Mixtures
Using Supported Cobalt Catalyst
(Mahaligam, 1981)

NO _x Concentration (ppm)		Percent NO _x Removal	Reactor Temp (°C)	Preheater Temp (°C)	Flow Rate of Gas Mixture ^a (m ³ /hr)	Gas Hourly Space Velocity (Hr ⁻¹)
Inlet	Exit					
1,750	1,500	14.3	1070	480	0.912	20,600
900	790	12.2	1070	540	0.872	19,800
775	700	9.7	1070	450	1.144	25,800
750	700	6.7	1040	610	0.671	15,200
520	480	7.7	1070	470	1.274	28,800
390	365	6.4	1040	590	0.651	14,700
283	265	6.4	1040	510	0.997	22,600

^a 1 atm, 20°C

APPENDIX B

Experimental Results

Table B-1

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 99°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.038 %

Inlet H₂O: 0.12 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.08	500	400	435	20.0	13.0
8.06	500	380	400	24.0	20.0
10.02	500	330	375	34.0	25.0
12.04	500	280	335	44.0	33.0

Table B-2

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 101°C

Gas Residence Time: 2.0sec

Inlet O₂: 0.61 %

Inlet H₂O: 0.12 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	495	390	445	21.2	10.1
8.04	495	355	430	28.3	13.1
10.06	495	330	410	33.3	17.2
12.04	495	295	380	40.4	23.2

Table B-3

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 100°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.024 %

Inlet H₂O: 0.92 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.06	490	435	465	11.2	5.1
8.04	490	415	455	15.3	7.1
10.08	490	390	445	20.4	9.2
12.04	490	360	430	26.5	12.2

Table B-4

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 200°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.044 %

Inlet H₂O: 0.11 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.10	500	385	420	23.0	16.0
8.04	500	340	385	32.0	23.0
10.04	500	300	345	40.0	31.0
12.08	500	245	295	51.0	41.0

Table B-5

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 200°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.60 %

Inlet H₂O: 0.11 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	495	385	440	22.2	11.1
8.04	495	355	415	28.3	16.2
10.06	495	330	390	33.3	21.2
12.02	495	295	355	40.4	28.3

Table B-6

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 200°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.028 %

Inlet H₂O: 0.94 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.08	495	445	460	10.1	7.1
8.02	495	425	450	14.1	9.1
10.0	495	400	435	19.2	12.1
12.0	495	370	410	25.3	17.2

Table B-7

Catalyst Material: Gold Plated Stainless Steel

Reactor Temperature: 200°C

Gas Residence Time: 2.0sec

Inlet O₂: 1.27 %

Inlet H₂O: 0.88 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.10	495	400	465	19.2	6.1
8.04	495	375	455	24.2	8.1
10.06	495	355	447	28.3	9.7
12.04	493	340	440	31.0	10.8
12.94	493	327	430	33.7	12.8

Table B-8

Catalyst Material: Stainless Steel

Reactor Temperature: 24°C

Gas Residence Time: 1.6sec

Inlet O₂: 0.042 %

Inlet H₂O: 0.14 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.40	385	330	345	14.3	10.4
8.02	385	310	330	19.5	14.3
10.12	385	280	300	27.3	22.1
12.18	385	235	270	39.0	29.9
13.08	385	215	245	44.2	36.4

Table B-9

Catalyst Material: Stainless Steel

Reactor Temperature: 24°C

Gas Residence Time: 1.6sec

Inlet O₂: 3.06 %

Inlet H₂O: 0.14 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	360	300	350	16.7	2.8
8.08	360	280	340	22.2	5.6
10.04	360	260	340	27.8	5.6
12.02	360	250	330	30.6	8.3
13.02	360	240	325	33.3	9.7

Table-B10

Catalyst Material: Stainless Steel
Reactor Temperature: 24°C
Gas Residence Time: 1.6sec

Inlet O₂: 0.025 %
Inlet H₂O: 1.53 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.16	375	355	360	10.7	4.0
8.02	375	320	355	14.7	5.3
10.02	375	295	350	21.3	6.7
12.04	375	270	340	28.0	9.3
13.0	375	250	335	33.3	10.7

Table B-11

Catalyst Material: Stainless Steel
Reactor Temperature: 24°C
Gas Residence Time: 1.6sec

Inlet O₂: 3.09 %
Inlet H₂O: 1.52 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.04	360	295	345	18.1	4.2
8.14	360	270	345	25.0	4.2
10.02	360	240	340	33.3	5.6
12.02	360	215	340	40.3	5.6
13.10	360	195	340	45.8	5.6

Table B-12

Catalyst Material: Stainless Steel
Reactor Temperature: 24°C
Gas Residence Time: 1.6sec

Inlet O₂: 0.029 %
Inlet H₂O: 0.14 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	785	725	750	7.6	4.5
8.08	785	695	725	11.5	7.6
10.02	785	655	695	16.6	11.5
12.04	785	600	650	23.6	17.2
13.00	785	570	625	27.4	20.4

Table B-13

Catalyst Material: Stainless Steel
Reactor Temperature: 30°C
Gas Residence Time: 2.1sec

Inlet O₂: 0.027 %
Inlet H₂O: 0.12 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.00	500	405	440	19.0	12.0
8.02	500	365	400	27.0	20.0
10.02	500	325	360	35.0	28.0
12.02	500	280	320	44.0	36.0
14.02	500	230	260	54.0	48.0

Table B-14

Catalyst Material: Stainless Steel Wool
Reactor Temperature: 30°C
Gas Residence Time: 2.1sec

Inlet O₂: 0.016 %
Inlet H₂O: 0.17 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
2.24	195	191	194	2.1	0.5
4.14	195	162	173	16.9	11.3
6.14	195	136	146	30.3	25.1
8.08	195	107	125	45.1	35.9
10.16	195	85	100	54.6	48.7
12.04	195	61	74	68.7	62.1
14.06	195	33	43	83.1	78.0
16.00	195	17	21	91.3	89.2
18.00	195	6	10	95.9	94.9

Table B-15

Catalyst Material: Stainless Steel
Reactor Temperature: 200°C
Gas Residence Time: 0.9sec

Inlet O₂: 0.040 %
Inlet H₂O: 0.13 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	380	340	350	10.5	7.9
8.08	380	310	330	18.4	13.2
10.16	380	280	300	26.3	21.1
12.02	380	250	275	34.2	27.6
12.98	380	230	255	39.5	32.9

Table B-16

Catalyst Material: Stainless Steel
Reactor Temperature: 200°C
Gas Residence Time: 0.9sec

Inlet O₂: 2.96 %
Inlet H₂O: 0.14 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	365	320	360	12.3	1.4
8.02	365	310	355	15.1	2.7
10.08	365	300	350	17.8	4.1
12.02	365	290	340	20.6	6.9
13.02	365	285	340	21.9	6.9

Table B-17

Catalyst Material: Stainless Steel
Reactor Temperature: 200°C
Gas Residence Time: 0.9sec

Inlet O₂: 0.022 %
Inlet H₂O: 1.46 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.12	375	360	360	4.0	4.0
8.04	375	350	360	6.7	4.0
10.04	375	340	355	9.3	5.3
12.00	375	320	340	14.7	9.3
13.04	375	315	340	16.0	9.3

Table B-18

Catalyst Material: Stainless Steel
Reactor Temperature: 200°C
Gas Residence Time: 0.9sec

Inlet O₂: 2.98 %
Inlet H₂O: 1.37 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NO _x _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
6.02	360	320	360	11.1	0.0
8.02	360	300	355	16.7	1.4
10.14	360	285	355	20.8	1.4
12.08	360	270	355	25.0	1.4
13.08	360	260	350	27.8	2.8

Table B-19

Catalyst Material: Steel Wool

Reactor Temperature: 30°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.015 %

Inlet H₂O: 0.10 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
2.10	200	195	195	2.5	2.5
4.08	200	174	180	13.0	10.0
6.08	200	150	160	25.0	20.0
8.18	200	128	146	36.0	27.0
10.06	200	108	122	46.0	39.0
12.00	200	85	98	57.5	51.0
14.00	200	59	70	70.5	65.0
16.00	200	38	40	81.0	80.0

Table B-20

Catalyst Material: Steel Wool

Reactor Temperature: 30°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.017 %

Inlet H₂O: 0.12 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
2.08	495	495	495	0	0
4.14	495	465	475	6.1	4.0
6.12	495	435	455	12.1	8.1
8.06	495	410	435	17.2	12.1
10.02	495	380	410	23.2	17.2
12.06	495	355	385	28.3	22.2
14.00	495	315	350	36.7	29.3
16.00	495	280	320	43.4	35.4

Table B-21

Catalyst Material: Steel Wool

Reactor Temperature: 30°C

Gas Residence Time: 2.1sec

Inlet O₂: 0.018 %

Inlet H₂O: 0.13 %

Voltage (KVAC)	NO _{in} (ppm)	NO _{out} (ppm)	NOx _{out} (ppm)	NO Conversion (%)	NO Reduction (%)
2.08	700	700	700	0	0
4.08	700	670	680	4.3	2.9
6.08	700	640	660	8.6	5.7
8.08	700	605	640	13.6	8.6
10.04	700	580	615	17.1	12.1
12.06	700	545	590	22.1	15.7
14.06	700	505	550	27.9	21.4
16.06	700	4600	415	34.3	26.4

APPENDIX C

Electrode Configurations Tested with Rectified AC

Experiments were conducted to study the effect of rectified AC voltages on NO conversion in the presence of metal wool catalysts. The electrode configurations used are shown below. Each of the configurations was tested with the rectifying diode as shown and reversed.

(1)

(2)

(3)

(4)

{ AC Power Supply

⊢(Pyrex or Vycor Tube packed with Metal Wool Catalyst

⊢ Rectifying Diode

~ Series Load Resistor

⊙ mA Ammeter

APPENDIX D

LIST OF EQUIPMENT

Spellman Model UHR 60 PN 120/CR/MTP High Voltage DC Power Supply

Franceformer 15030P Gaseous Tube Transformer

Fluke Model 8050A Digital Multimeter

Fluke Model 80K-40 High Voltage Probe

Lindberg Type 59744-A Tube Furnace

Thermo Electron Instruments Model 10 Chemiluminescent NO-NO₂-NO_x Analyzer

Infrared Industries Inc. Model 2200 O₂ Analyzer

EG&C Environmental Equipment Model 911 Dew-All Digital Humidity Analyzer

Interscan LD-14 CO Monitoring System

Hastings Model ST Mass Flow Meters

Hastings Model PR4A Four Channel Flow Monitor

Gas Cylinders supplied by Matheson Gas Products Inc.

END

**DATE
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