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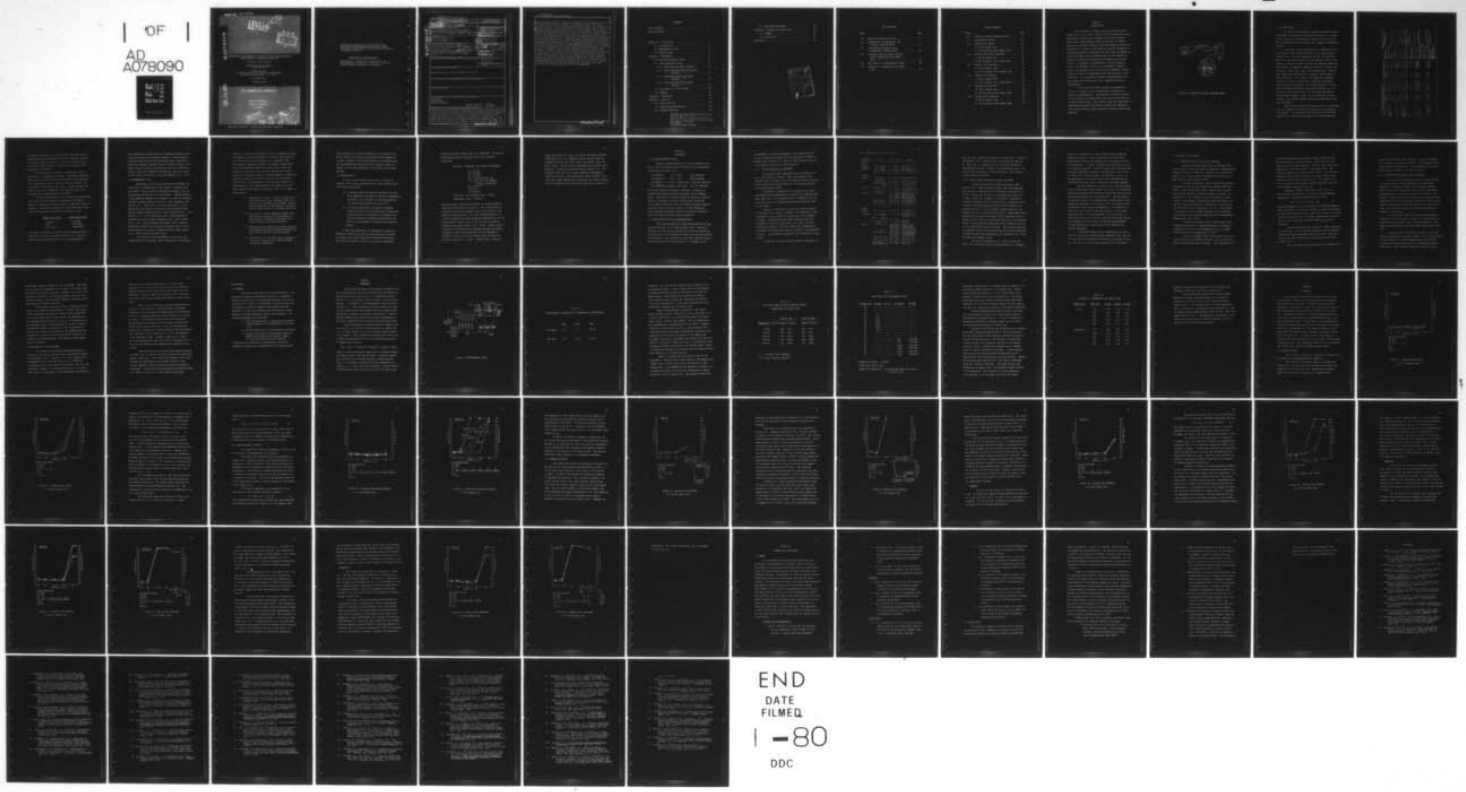

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EXPERIMENTAL ASSESSMENT OF NITROGEN OXIDES TRANSFORMATIONS WHILE SAMPLING COMBUSTION PRODUCTS

Ronald Clinton Benson

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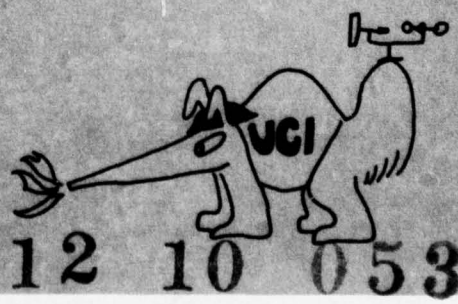

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Analysis of combustion products is performed by conveying the exhaust effluents to instrumentation by means of a sample probe and sampling line. Frequently, the selection of sampling materials does not consider potential chemical transformations that can occur in the sample line and probe. Nitrogen oxides are combustion products that are especially vulnerable to transformations. Nitric oxide (NO) and nitrogen dioxide (NO_2) are the primary components of NO_x. The ratio of NO/NO_2 emissions from combustion sources is not well established (due

Unclassified

to the potential reduction of NO_2 to NO in sample probes and sample lines) and the total emission of NO_X is subject to uncertainty in some cases (due to potential removal of NO_X in sample probes and sample lines). The objective of the present study is to investigate the extent of transformations of NO_X in the presence of oxidizing and reducing species. Stainless steel and silica were the two sampling tube materials used in this investigation. Simulated combustion products of 500 ppm NO, 75 ppm NO_2, 12% CO_2 bal N_2 at 25°C were common to all tests. The oxidizing species and concentrations considered included 1 and 5% O_2. Various concentrations of carbon monoxide, hydrogen, and hydrocarbons were used for the reducing species. Temperature and pressure effects were evaluated in this particular study. The results indicated that transformation was more pronounced in stainless steel than silica. Reduction of NO_2 to NO, and removal of NO_2 and NO were the dominant transformation types observed. In the presence of reactive reducing species (e.g. hydrogen, propylene, and ethylene), reduction of NO_2 to NO occurred as low as 200°C in stainless steel, at 300°C in the presence of hydrogen in silica, and at 400°C in the presence of ethylene or propylene in silica. Removal of NO_X by both hydrogen and propylene was observed in the absence of oxygen at 300°C in stainless steel, and removal of NO_X by ethylene was observed at 400°C. In the presence of less reactive reducing species (e.g. methane and carbon monoxide), either higher concentrations or higher temperatures were required to reduce NO_2 to NO. The presence of oxygen suppressed but did not prevent the reduction of NO_2 to NO. Neither methane nor carbon monoxide were active in removing NO_X. The present data were collected in the pressure range of 1.0 and 1.15 atmospheres.

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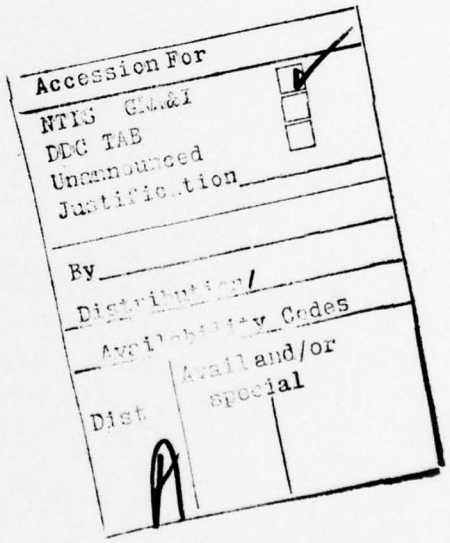

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Chapter 1

INTRODUCTION

The analysis of exhaust gases from anthropogenic sources such as the spark ignited internal combustion engine, compression ignited diesel engines, gas turbine engines, power plants, and package boilers is critical in terms of monitoring pollutant emission levels and measuring operating efficiency. In order to undertake an accurate assessment of pollutant emissions, a sampling line and probe are needed to convey the gases from the exhaust plane of the combustion source to analytical instruments for subsequent analysis. Figure 1-1 illustrates schematically a typical sampling train. An important criterion for selecting a sampling train is to maintain the integrity of the chemical species between the point of measurement and the analytical instrumentation. Any significant chemical transformations occurring within the sampling line will compromise emission measurements.

Of all the significant products of combustion, oxides of nitrogen (NO_x) are especially suspectible to chemical transformations. The species of primary interest in the oxides of nitrogen family are nitric oxide (NO) and nitrogen dioxide (NO_2). The present study was undertaken to experimentally assess the extent to which and conditions under which nitrogen oxides experience chemical change when sampling.

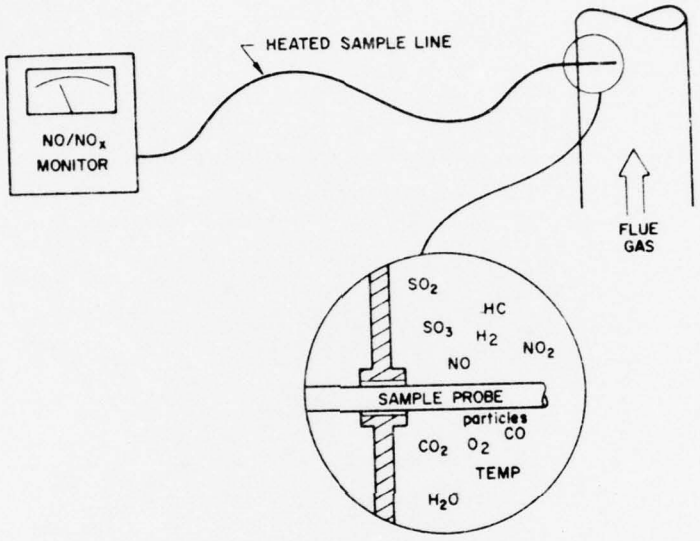


FIGURE 1-1 COMBUSTION PRODUCT SAMPLING TRAIN

1.1 NO_x EMISSIONS

The variety of combustion sources from which oxides of nitrogen are emitted is presented in Table 1-1. A broad range of effluent concentrations, mixture ratios, and sampling temperatures are identified for a number of combustion systems.

The amount of NO_x measured from a combustion source will depend on the combustion device, fuel, and fuel/air mixture ratio. For any combustion process, the stoichiometric or chemically correct fuel/air mixture ratio is the amount of fuel/air by mass required for complete combustion. The products of complete combustion consist of carbon dioxide (CO_2), water vapor (H_2O), and nitrogen (N_2). However, most combustion processes are incomplete and/or operate with excess air. As a result, the combustion products coexist in either an oxidizing or reducing environment. For oxidizing environments, the oxygen available is sufficient to oxidize the remaining reducing species (e.g. CO, H_2, HC's) given enough time. For reducing environments the available oxygen, if any, is not sufficient to fully oxidize the reducing species remaining regardless of the time available.

The electric generating steam boiler is a good example of a combustion source that operates in an oxidizing environment. The operating conditions of the boiler are conducive to oxidizing hydrocarbons and carbon monoxide.

Table 1-1 Sampling conditions for nitrogen oxides.

Reference: Samuelsen and Harman 1975

Source	Typical NO_x ppm	Sampling Point	Typical Sampling Environment Temperature °C	Atmosphere	References Examples of NOx probing	Prior Studies Relevant to NOx Changes
Internal Combustion Engine	500-4000	Combustion Zone	1300-2400	Reducing	Zuonow et al. 1967 Alperstein and Bradow 1965	- - - - - - - -
	500-1000	Engine Exhaust	200-500	Reducing	EPA 1974a EPA 1975	Halstead et al. 1972
Diesel Engine	1000-7000	Combustion Zone	700-2500	Reducing & Oxidizing	Bennethum et al. 1975	- - - - - - - -
	700-2500	Engine Exhaust	200-500	Oxidizing	EPA 1974b	Halstead et al. 1972
Residential Oil Burners	20-100	Flue Gas	100-300	Oxidizing	Barrett 1973	Halstead et al. 1972
Boilers	200-1000	Combustion Zone	100-1600	Reducing & Oxidizing	Muzio and Wilson 1973 Krumwiede et al. 1975	England et al. 1973 Schefer et al. 1973 Allen 1975
	25-800	Flue Gas	100-300	Oxidizing	EPA 1976 Bartok et al. 1971 Cato and Robinson 1974	Halstead et al. 1972
Gas Turbine	1000-8000	Combustion Zone	1300-2700	Reducing & Oxidizing	Tuttle et al. 1973	- - - - - - - -
	25-200	Engine Exhaust	400-1500	Oxidizing	Few et al. 1977 Davidson and Domal 1972 Blazowski and Henderson 1972 Elwood and Dieck 1974 Grossman et al. 1974	Tuttle et al. 1973 Halstead et al. 1972
Flame Research	10-8000	Within Flame	700-2500	Reducing & Oxidizing	Cernansky and Sawyer 1975 Merryman and Levy 1975 Fenimore 1971 Fenimore 1975 Pompei and Heywood 1972 Malte and Pratt 1973	England et al. 1973 Schefer et al. 1973 Allen 1975

The amount of excess air and sufficient residence times at maintained temperatures enable virtually complete oxidation of reducing species to occur. Flue gas emissions of NO_X from boilers will typically vary from 25-800 ppm at temperatures of 100-300°C.

The automobile is typical of combustion sources operating in a reducing environment. Incomplete combustion under actual operating conditions produces carbon monoxide (CO), hydrocarbons (HC's), particulates and hydrogen (H_2) in addition to nitrogen oxides (NO_X). Engine exhaust emissions of NO_X from automobiles will typically vary from 500-1000 ppm at temperatures of 200-500°C.

Although NO_X sampling of flue gases from automobiles and boilers involves moderate temperatures (25-600°C), sampling temperatures do vary widely in flame and combustion research. Three major temperature groups have been identified for NO_X sampling (Samuelsen and Harman, 1975):

Temperature Group	Temperature Range
moderate	25-600°C
high	600-1200°C
very high	1200-2500°C

The moderate temperature range is most frequently found in sampling flue gases from mobile sources (e.g. the automobile) and stationary sources (e.g. package boilers).

High temperature probing occurs in combustion research while very high temperature probing is common in flame research. Although flame research has historically been conducted in laboratory systems (premixed flames, diffusion flames, shock tubes, stirred reactors and plug flow reactors) combustion zones in practical combustion systems are now being probed as well (Muzio and Wilson, 1973 and Krumweide et al., 1975).

1.2 MEASUREMENT OF NO_X

Measurement of total NO_X emissions from flames and combustors are compromised by NO_X removal in sample lines and probes. NO_X are reactive combustion products, and precaution must be employed to avoid removal. General reviews of NO_X sampling problems are available to assist in designing sampling systems (Halstead and Munro, 1971; Halstead, 1971; Tuttle et al., 1973; Allen, 1973; and Allen et al., 1974). Additional information is available from specialized combustion studies (Halstead et al., 1972; England et al., 1973; Schefer et al., 1973; and Allen, 1975), chemiluminescent analyzer converter studies (Hodgeson et al., 1971; Sigsby et al., 1973; and Breitenbach and Shelef, 1973), studies conducted to explore the catalytic oxidation of CO in automobile exhaust by O_2 and NO (Baker and Doerr, 1965; Shelef et al., 1968; and Ayen and Ng, 1966).

In addition to the measurement of total NO_X, the determination of the NO/NO_2 ratio is becoming of increasing

interest. Although the NO/NO_2 ratio from combustion sources is uncertain, typical estimates of 90-95% NO and 5-10% NO_2 have been made in the literature (e.g. Seinfeld, 1975). The emission standards, currently proposed or promulgated by the Environmental Protection Agency (EPA), limit the emission of NO_x but do not, as yet, address the relative amounts of NO and NO_2 allowed. Current emission inventories specify NO and NO_2 in terms of total NO_x for both mobile sources (e.g. the automobile) and stationary sources (e.g. power plants). The significance of the NO/NO_2 ratio has been reported by Samuelsen and Harman (1975) for a number of applications:

(1) Assessment of local air quality impact due to nitrogen dioxide (NO_2) emissions from line sources (e.g. roadways and highways) requires the determination of the amount of nitrogen dioxide (NO_2) emitted as a primary pollutant.

(2) Assessment of plume visibility impact from power plants requires the determination of the amount of nitrogen dioxide and nitric oxide emitted as primary pollutants.

(3) Regional oxidant modeling requires a spatial and temporal geocoded emissions inventory for both nitric oxide and nitrogen dioxide.

(4) Measurement of the NO/NO_2 ratio in flames is required to identify the chemical kinetic mechanisms responsible.

These applications require knowledge of the proportion of nitric oxide to nitrogen dioxide emitted from combustion sources. However, without knowledge of the possible chemical transformations occurring within sampling lines and probes, an accurate assessment of the NO/NO_2 ratio cannot be made.

1.3 PRESENT STUDY

To more clearly establish the role of probes and sampling lines in NO_x transformations, the following objectives were established:

(1) To examine probe and sampling materials for sampling combustion effluents at moderate temperatures (25-400°C) in the presence of oxidizing species (O_2) and reducing species (CO, H_2, HC's)

(2) To provide preliminary information regarding sources of error, if any, while using conventional stainless and silica materials for sampling combustion effluents at moderate temperatures (25-400°C) in the presence of oxidizing and reducing species

To meet the objectives, an experimental system was designed to explore NO_2 and NO transformations in probes and sample lines under controlled laboratory conditions. Concentration changes of NO and NO_2 across isothermally

maintained 2 meter sample tubes were monitored. NO_2 and NO transformations were investigated for the following conditions:

mixtures: simulated, dry combustion products

O_2: 0,1,5%
NO: 500 ppm
NO_x: 575 ppm
CO: 0,100,1000,2500 ppm
HC: 0,500,1000 ppm (methane ethylene, propylene)
H_2: 0,.5%,3%
CO_2: 12%
N_2: balance

materials: 316 stainless steel, silica

temperature range: 25-400°C

The experimental system was designed to simulate sampling conditions encountered in practice. The concentration of oxidizing and reducing species cover a wide range of combustion effluent levels. The lower concentrations of CO and HC's simulate fuel lean emissions characteristic of the package boiler (Cato et al., 1975) and the gas turbine engine during cruise (Jones et al., 1974). Higher concentrations of CO and HC's with unburned hydrogen are representative of fuel rich emissions from the automobile (Seinfeld, 1975) and the gas turbine engine during idle and taxi (Jones et al., 1974). Methane (CH_4), ethylene

(C_2H_4) and propylene (C_3H_6), the three hydrocarbon species investigated, are all prominent species emitted from the automobile (Olson Labs, 1977; Black and Braden, 1975; and Black, 1976). The NO and NO_2 concentrations simulate those observed in combustion source effluents (Table 1-1). 316 stainless steel and silica glass represent conventional sampling materials. The temperature range (25-400°C) coincides with those temperatures associated with engine exhaust from the automobile and flue gases from boilers (Table 1-1).

Chapter 2

BACKGROUND

2.1 NO_X TRANSFORMATION TYPES

Chemical transformations of nitrogen oxides in sampling lines and probes may be divided into four categories (Samuelsen and Harman, 1977):

NO OXIDATION	$NO \longrightarrow NO_2$	NO_X conserved
NO_2 REDUCTION	$NO_2 \longrightarrow NO$	NO_X conserved
NO_X REMOVAL	$NO, NO_2 \longrightarrow N_2, NH_3, HCN..$	NO_X not conserved
NO_X FORMATION	$C_WN_XH_Y \longrightarrow NO, NO_2$	NO_X not conserved

The fourth chemical mechanism, formation, involves the oxidation of nitrogen containing species such as ammonia (NH_3). Formation of nitrogen oxides in probes and sampling lines are generally limited to specialized conditions (e.g. sample extraction from flue gases into which ammonia has been injected for NO_X control, or from flames into which nitrogen containing compounds have been injected to study fuel bound nitrogen oxides formation).

2.2 INVESTIGATIONS OF NO_X TRANSFORMATIONS

The following sections review investigations of NO_X studies pertinent to the experimental study. Studies of catalytic and gas phase reactions with mixtures containing NO and/or NO_2 in the presence of oxygen and reducing species are described. The methods of conventional sampling versus optical techniques are also reported. A summary of the

transformation reactions proposed in the literature to be active in probes and sample lines is presented in Table 2-1. Whether these reactions or others in addition may be active is the object of continuing investigation.

2.3.1 OXYGEN(NO_2/NO/O_2/N_2) MIXTURES

Investigators have observed catalytic reduction of NO_2 in the absence of oxygen. White and Beddows (1973) observed that a two meter long 321 stainless steel converter totally reduced an initial mixture of 25 ppm NO_2, balance N_2 at approximately 200°C.

Furthermore, Halstead (1971) reported that stainless steel probes catalytically reduced NO_2 at temperatures above 300°C for a gas concentration of 30 ppm NO_2, bal N_2. A six foot length of unspecified stainless steel was used for the study.

Catalytic reduction of NO_2 has also been observed in the presence of oxygen. However, the reduction is less pronounced in the presence of oxygen than in the absence of oxygen. Wikstrom and Nobe (1965) observed that the conversion to N_2 and O_2 was less in air than in N_2 for a CuO-alumina catalyst. For the initial NO_2 concentration (1260 ppm) and temperature range (304-520°C), 55% conversion of NO_X in $_2$ was observed compared to 47% conversion of NO_X in air.

Oxygen may not only inhibit catalytic reduction of

Table 2-1 Homogeneous, Heterogeneous, and Catalytic NO_x Reactions

Transformation (Reaction Type)	Reaction	Temp(°C)	Study	Reference
NO OXIDATION				
Homogeneous	$2NO + O_2 \longrightarrow 2NO_2$	25	Gas Phase	Halstead and Munro (1971)
Heterogeneous	$NO + O \xrightarrow[wall]{} NO_2$	- - - -	Flame	Allen (1975)
Catalyst	$2NO + O_2 \longrightarrow 2NO_2$	- - - -	Combustion	Halstead and Munro (1971)
	$Cr_2O_3 + NO \longrightarrow 2CrO_2 + NO_2$	400-600	Combustion	Hilliard and Wheeler (1977)
NO_2 REDUCTION				
Homogeneous	$2NO_2 \longrightarrow 2NO + O_2$	130-620	Gas Phase	Latimer and Hildebrand (1964)
	$NO_2 + O \longrightarrow NO + O_2$	- - - -	Flame	Allen (1975)
	$H_2 + NO_2 \longrightarrow H_2O + NO$	400	Gas Phase	Ashmore and Levitt (1956,1957)
	$CH_4 + NO_2 \longrightarrow CO, CO_2, CH_4, \ldots$	350-400	Gas Phase	Bromberg and Taylor (1955)
	$CO, CO_2, NO, \ldots$	300-400	Gas Phase	Gagarina and Emanuel (1959)
Heterogeneous	$NO_2 + \text{metal} \xrightarrow[wall]{} \text{metal oxide} + NO$	25-400	Combustion	White and Beddows (1973)
		400	Converter	Breitenbach and Shelef (1973)
	$NO_2 + C \xrightarrow[wall]{} CO + NO$	750	Converter	Breitenbach and Shelef (1973)
Catalyst	$2NO_2 \longrightarrow 2NO + O_2$	300	Combustion	Halstead (1971)
		475-750	Converter	Breitenbach and Shelef (1973)
		25-600	Converter	Hodgeson et al. (1971)
		750	Converter	Sigsby et al. (1973)
		200-400	Combustion	White and Beddows (1973)
		304-520	Catalyst	Wikstrom and Nobe (1965)
	$NO_2 + CO \longrightarrow NO + CO_2$	180-250	Catalyst	Ayen and Yonebayashi (1967)
	$NO_2 + CO \longrightarrow products$	25-400	Combustion	White and Beddows (1973)
	$2NO_2 \longrightarrow 2NO + O_2$	304-520	Catalyst	Wikstrom and Nobe (1965)
NO_x REMOVAL				
Homogeneous	$NO + HC \longrightarrow CHO + N$	823-1423	Gas Phase	Myerson and Blair (1975)
				Myerson (1975)
Heterogeneous	$NO_2 + \text{wall} \longrightarrow \text{absorbed}$	- - - -	Combustion	Halstead and Munro (1971)
	adsorbed			Allen (1975)
				Halstead et al. (1972)
	$NO(NO_2) + \text{metal} \xrightarrow[wall]{} \text{metal oxide} + N_2$	500-750	Converter	Siewert (1975)
	$NO_2 \xrightarrow[condensate]{} \text{absorbed}$	- - - -	Combustion	Allen (1975)
				McNulty (1974)
Catalyst	$NO + CO \longrightarrow CO_2 + 1/2N_2$	25-1700	Combustion	Halstead et al. (1972)
		100-600	Catalyst	Shelef et al. (1968)
		160-240	Catalyst	Ayen and Ng (1965)
		115-270	Catalyst	Baker and Doerr (1972)
		320-510	Catalyst	Shelef and Gandhi (1972)
	$H_2 + NO \longrightarrow NH_3, \ldots$	100-750	Catalyst	Shelef and Gandhi (1972)
	$5H_2 + NO \longrightarrow 2NH_3 + 2H_2O$	370-600	Catalyst	Klimisch and Barnes (1972)
		347-502	Catalyst	Lamb and Tolleson (1975)
		375-425	Catalyst	Ayen and Peters (1962)
	$NO + H_2 \longrightarrow H_2O + 1/2N_2$	375-425	Catalyst	Ayen and Peters (1962)
	$2NO + H_2 \longrightarrow H_2O + N_2O$	150-300	Catalyst	Peterson et al. (1972)
	$NO + H_2 \longrightarrow N_2 + \text{products}$	480	Catalyst	Peterson et al. (1972)
	$C_3H_6 + NO \longrightarrow NH_3, \ldots$	420-550	Catalyst	Shelef and Gandhi (1974)
	$C_3H_6 + NO \longrightarrow 2HCN + 3H_2O + 1/2N_2$	520	Catalyst	Germain (1969)

NO_2 but also promote the oxidation of NO to NO_2. Hilliard and Wheeler (1977) observed that for mixtures of 1000 ppm NO, 5%O_2, bal N_2, oxidation of NO to NO_2 was observed at temperatures of 400°C to 600°C in 316 stainless steel. The results were attributed to the activation of the chromium oxide transition at 400°C.

2.3.2 CARBON MONOXIDE(NO_2/NO/O_2/N_2/CO) MIXTURES

Several investigators (Baker and Doerr, 1965; Shelef et al., 1968; and Ayen and Ng, 1966) have explored the catalytic oxidation of CO in automobile exhaust by O_2 and NO. Oxygen was observed to preferentially oxidize CO to CO_2 at 500°C for a number of catalysts. Furthermore, Stricker and Meinel (1977) observed that a stainless steel converter operating between 500°C and 700°C promotes the oxidation of CO to CO_2 by residual oxygen present in the exhaust gas from a spark-ignition engine. Experimental data obtained by Hilliard and Wheeler (1977) supported the oxidation of NO to NO_2 by the chromium content in 316 stainless steel. Carbon monoxide inhibited the NO oxidation but only at CO concentrations above 1000 ppm. The catalytic activity of stainless steel while sampling NO_x and CO from combustion systems has also been investigated by Halstead et al. (1972) and White and Beddows (1973).

The work by Halstead et al. (1972) is the most definitive regarding potential transformations of nitrogen

oxides in the presence of carbon monoxide while sampling combustion products. Actual combustion products from a Tunnel Mixing Burner were sampled under both lean and fuel rich conditions. A supply of natural gas with air was used as the burning mixture. Stainless steel and silica were the two probe materials evaluated (stainless steel 210 cm long by 6 mm i.d. and silica tubing, 210 cm long by 6 mm i.d.). The temperature at the probe inlet varied between 800 and 1700^{o}C and the probe outlet temperature was about ambient.

Halstead observed no change in NO_X readings between silica and stainless steel probes under lean fire conditions. Conflicting readings were observed between the stainless and silica probes under rich fire conditions. NO_X was removed in excess of 90% in the stainless steel probe while no NO_X removal was observed in the silica probe. Halstead's work demonstrated that reducing atmospheres in the presence of stainless steel probes affect NO_X readings. The unknown concentrations of reducing species (e.g. CO,H_2,HC's) at which the reduction and removal reactions occur and temperature gradient along the probe length prevent assessment of the conditions for activation of the reduction and removal mechanism.

White and Beddows (1973) investigated NO_2 reduction by CO in a 321 stainless steel sampling line. The initial gas mixture consisted of 25 ppm NO_2 and 450 ppm CO bal N_2. The loss of NO_2 was more pronounced in the presence

of CO than in its absence.

2.3.3 HYDROGEN(NO_2/NO/O_2/N_2/CO/H_2) MIXTURES

Reactions between NO and NO_2 and hydrogen have been studied in both gas phase and catalytic investigations. Ashmore and Levitt (1956,1957) observed the reduction of NO_2 by H_2 to be essentially homogeneous with high H_2 to NO_2 ratios at approximately 400°C.

Several investigators have explored the catalytic reduction of NO by H_2 at temperatures between 200°C and 500°C. Lamb and Tolleson (1975) observed that a solid alloy monel catalyst, containing copper and nickel, is effective for the reduction of NO by hydrogen in high velocity gas streams containing low concentrations of NO and O_2. The H_2 concentration ranged from .06-2.50% and the NO concentration ranged from .22-.31%. Specifically, the proportion of NO removed increased with decreasing inlet oxygen and increasing hydrogen partial pressures at temperatures above 350°C.

Klimisch and Barnes (1972) reported that gases containing hydrogen or compounds producing hydrogen can reduce nitric oxide in the presence of Cr_2O_3 or copper oxide catalysts at temperatures of 375°C.

Shelef and Gandhi (1972) investigated the role of general catalysts in ammonia formation from a mixture of nitric oxide and molecular hydrogen. The temperature for

90% NO conversion was determined in NO-H_2, NO-H_2-CO, and NO-CO systems with copper chromite, copper oxide, nickel oxide, and iron oxide catalysts. The inlet gas composition consisted of 1000-1200 ppm NO, 1.4%H_2 and 1.4%CO. The catalyst temperatures ranged from 210-510°C. All catalysts examined except nickel oxide and iron oxide showed higher conversion of NO with H_2 than with CO. The effect of NO with a H_2 and CO mixture was a higher conversion than with either reducing species singularly.

Peterson, Landau, and Saucedo (1974) observed nitrous oxide as a product of the nitric oxide-hydrogen reaction on a stainless steel catalyst at 340°C:

$$2NO + H_2 \longrightarrow N_2O + H_2O \qquad (1)$$

N_2O was measured as a gas intermediate at moderate temperatures (150-300°C) and was not present at higher temperatures in most heterogeneous catalytic reactions of NO on a reduced stainless steel surface. At higher temperatures, the reaction of nitric oxide and hydrogen formed N_2 and other products.

Further studies by Ayen and Peters (1962) validated the importance of more than one reaction from the catalytic interaction between hydrogen and nitric oxide. Reduction to N_2 or NH_3 was observed for the stainless steel flow reactor used.

The investigations reported show that hydrogen can

reduce nitric oxides over a number of catalytic surfaces for a temperature range of 200-500°C. The products depend on the reaction temperature. Hydrogen appears to be more reactive with NO than CO for most catalysts.

2.3.4 HYDROCARBON(NO_2/NO/O_2/N_2/HC) MIXTURES

The reaction of hydrocarbons with nitrogen oxides has been observed for both catalytic and homogeneous conditions. Shelef and Gandhi (1972) examined ammonia formation (NH_3) from the reaction of NO and hydrocarbons in the absence of oxygen on a number of catalysts. The absence of ammonia formed from hydrogen with paraffins was associated with the low hydrogen saturation of the surface. Olefins were noted to react more readily with NO and even under dry conditions some NH_3 formation was observed in catalytic interaction.

Roth and Doerr (1961) observed that hydrocarbon oxidation in the presence of NO and O_2 is appreciable at temperatures above 250°C with a chromite catalyst. The amount of oxygen added was 4% and space velocity was 10000 hr^{-1}.

Myerson (1975) and Myerson and Blair (1976) have observed homogeneous gas phase removal of NO in the presence of hydrocarbons at elevated temperatures (1100-1700°K) including gas phase removal of NO in automobile exhaust. Dimitriades (1967) associated observed losses of NO_2 to

hydrocarbon exhaust products of the automobile. The extent of NO_2 removal was dependent on the type of fuel being used as well as the engine conditions. However, the type of fuel affecting the extent of the NO_2-hydrocarbon reaction could not be indicated. Fuels included indolene, isoctane, olefin rich fuel, and aromatic rich fuel.

The gas phase reduction of NO_2 by methane has been studied by a number of investigators. Bromberg and Taylor (1955) studied the reaction in a static system (350-400^{o}C) in a cylindrically fused silica reactor and observed that the principal products were CO, CO_2, N_2, and unreacted CH_4 for residence times of approximately one minute. Studies conducted by Gagarina and Emanuel (1959) identified CO, CO_2, NO, and traces of nitromethane, formaldehyde and HCN as products of the methane-nitrogen dioxide reaction in a cylinder of molybdenum glass. The sampling times ranged from 0-30 minutes.

2.4 STAINLESS VS. SILICA PROBES

The levels of NO and NO_2 while sampling from a stainless steel and silica probe have been shown to depend on equivalence ratio. England et al. (1973) observed NC measurements from a flue gas with a 321 SS probe were considerably less than in near stoichiometric and fuel rich methane air flames. At equivalence ratios of .7 or less (fuel lean), no difference in NO measurements was detected

between a 321 stainless steel tube and a quartz tube. Halstead et al. (1972) also observed conflicting readings between stainless steel and silica probes under rich fire conditions. NO_x was removed in excess of 90% in the stainless probe while no NO_x removal was observed in the silica probe.

Under certain conditions, quartz probes have been observed to significantly transform oxides of nitrogen. Cernansky (1974) reported that measurements using hydrogen fuel in a laboratory diffusion flame resulted in the aging of probes. The surfaces of both quartz and stainless cooled probes were reduced by the hydrogen gas such that NO and NO_2 decreased with time. Water cooling has been shown to be a necessity in quartz probes to prevent significant reduction of NO (England et al., 1973) and formation of NO (Cernansky, 1976). However, Allen et al. (1974) found for temperatures less than 750°C no evidence of NO or NO_2 loss was observed while sampling with uncooled silica probes.

The probability of NO removal from sampling probes and lines used in practice has been reinforced by employing optical techniques. Few, Bryson, and McGregor (1977) have examined NO measurement at the exhaust plane of a gas turbine combustor using conventional methods and optical techniques. Conventional probing measured NO concentrations by a factor of three to six fold lower than optical

measurements.

2.5 SUMMARY

Although the evidence of NO_x transformations in the presence of oxidizing and reducing species is supported by several investigations, key questions pertinent to the present study still remain. A systematic, controlled experiment simulating the probe and sampling environment has been designed to assess the conditions and the extent to which oxides of nitrogen experience change while sampling. The following questions are addressed:

(1) What concentrations of oxidizing and reducing species promote the transformation of NO and NO_2?

(2) At what temperature is transformation promoted?

(3) How does the effect differ between probe and sample line materials of interest, namely 316 stainless steel and silica quartz?

To assess these questions, an experimental system was designed to explore the transformation of nitrogen oxides.

Chapter 3

EXPERIMENT

The experimental study was designed to assess NO and NO_2 transformations that may be encountered from combustion devices that operate fuel rich (e.g. automobile engines) and air rich (e.g. boilers, diesel engines, and gas turbine engines). A schematic of the experimental system is shown in Figure 3-1. Test parameters included carrier gas composition, concentration and composition of the dopant gases, temperature, pressure, and sample tube material. The combustion products were simulated to control maintenance of the inlet composition of the carrier gas and dopant gases.

High concentration cylinder sources of doping gases (NO, NO_2, CO, H_2, and HC's) were diluted by a carrier gas (0,1, or 5%O_2, 12%CO_2, bal N_2) to simulate primary combustion products. The rationale for selecting the carrier gas is specified quantitatively by the stoichiometric mixture of methane gas with air:

$$CH_4 + n_{O_2}O_2 + 3.76n_{O_2}N_2 \longrightarrow n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{N_2}N_2$$

Table 3-1 shows the percent composition of exhaust products by volume on both a dry and wet basis. Since the exhaust gas simulation was performed without introducing water (H_2O) to the system, a typical dry basis composition of 12%CO_2, 0,1, or 5%O_2, bal N_2 was selected. Porous sintered flow restrictors were utilized to control the doping gas

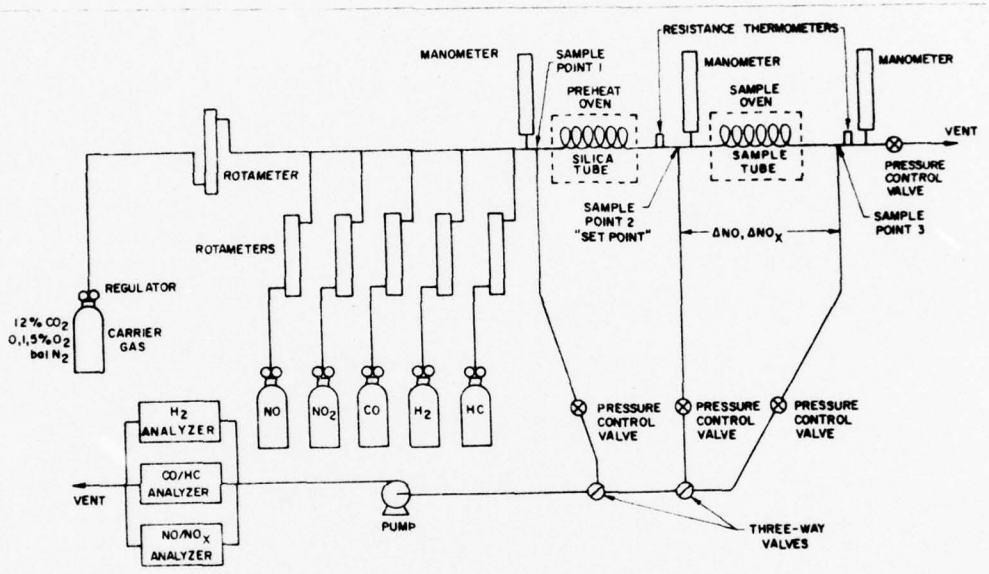


FIGURE 3-1 EXPERIMENTAL SYSTEM

Table 3-1

STOICHIOMETRIC COMBUSTION OF METHANE-AIR (VOLUME BASIS)

	CO_2	H_2O	N_2
Dry Basis	11.7%	---	88.3%
Wet Basis	9.4%	19.1%	71.5%

flowrates. The carrier gas flowrate was maintained at 4.0 liters/minute (STP). A pyrex glass manifold was designed to enable sufficient mixing of the carrier gas with the doping gases. After doping the carrier gas entered a silica preheat oven to raise the temperature of the gas to the test temperature. A test oven maintained the gas temperature constant thru the sample tube.

Sample tube materials evaluated in the present study included 2 meter lengths of 6.4 mm (0.250 inch) O.D., 4.0 mm (0.180 inch) I.D., 316 stainless steel and silica glass (Vycor, Corning Glass Works). The gas temperature was incrementally increased from 25°C to 400°C. Temperatures of the gas stream (T_2 and T_3) were measured with insulated platinum resistance thermometers centered in the probe bore at the inlet and outlet of the sample tube. The space velocity in the sample tube ranged from 7600 hr^{-1} (25°C) to 19500 hr^{-1} (400°C) for the 4.0 liter/minute inlet volumetric flowrate selected for the present study. Table 3-2 shows the variation of residence time and space velocity with temperature and probe material.

Table 3-3 presents the test matrix used in the experiment. The NO and NO_2 input levels to the sample tube (Sample Point 2) were chosen to be 500 ppm and 75 ppm respectively. Gas composition was measured at Points 2 & 3 to assess the extent of NO and NO_2 concentration change within the 2 meter sample tube. Gas composition was also

Table 3-2

RESIDENCE TIME AND SPACE VELOCITY VERSUS

TEMPERATURE AND SAMPLE TUBE

	Silica (2m)		316 SS (2m)	
Temperature $^{o}C/^{o}K$	t(sec)	$t^{-1}(hr^{-1})$	t(sec)	$t^{-1}(hr^{-1})$
25/298	.469	7676	.475	7579
100/373	.369	9756	.376	9575
200/473	.283	12721	.286	12587
300/573	.223	16143	.228	15789
400/673	.183	19672	.187	19251

t = residence time (seconds)

t^{-1} = space velocity ($hours^{-1}$)

Table 3-3

TEST MATRIX FOR EXPERIMENTAL STUDY

Carrier Gas	CO(ppm)	H_2 (%)	HC Species	HC(ppm)
0%	- - - -	- - - -	- - - - - - -	- - - -
1%	- - - -	- - - -	- - - - - - -	- - - -
5%	- - - -	- - - -	- - - - - - -	- - - -
0%	100	- - - -	- - - - - - -	- - - -
5%	100	- - - -	- - - - - - -	- - - -
0%	1000	- - - -	- - - - - - -	- - - -
5%	1000	- - - -	- - - - - - -	- - - -
0%	2500	- - - -	- - - - - - -	- - - -
5%	2500	- - - -	- - - - - - -	- - - -
0%	- - - -	.5	- - - - - - -	- - - -
0%	- - - -	3	- - - - - - -	- - - -
0%	- - - -	- - - -	CH_4	500,1000
5%	- - - -	- - - -	CH_4	500,1000
0%	- - - -	- - - -	C_2H_4	500,1000
5%	- - - -	- - - -	C_2H_4	500,1000
0%	- - - -	- - - -	C_3H_6	500,1000
5%	- - - -	- - - -	C_3H_6	500,1000

Temperature Range: 25-400°C

NO=500 ppm, NO_2=75 ppm

Sample Tube Materials: 316 Stainless Steel and Silica (2 meters long)

measured at Sample Point 1 to assess whether chemical concentration change occurred in the preheat oven. Sample lines leading from points 1, 2, and 3 were short, equidistant, and made of 6.4 mm (0.250 inch) O.D. TFE teflon. Screening tests using varying lengths of TFE teflon were conducted for the current study to assure that NO_2 absorption was not a significant factor in the present experiment.

Mercury manometers were used to measure and maintain the pressure at each of the three sampling points. The pressures at Sample Points 1, 2, and 3 increased with temperature and were ten percent higher for the silica. The pressures are presented in Table 3-4.

Analysis of NO and NO_x was conducted with a Beckman Model 951H chemiluminescent oxides of nitrogen analyzer. NO_2 was determined by the difference between the measured NO_x and NO concentrations. The (carbon) converter was tested following the procedure outlined in the Federal Register (1974). Hydrogen was measured with a Beckman Model 7C Thermal Conductivity Analyzer. Carbon monoxide and hydrocarbon concentrations were monitored with a Beckman Model 590 nondispersive infrared analyzer. Ammonia and cynanide were measured for a few, select conditions using wet chemical techniques. The doped carrier gas downstream of Sample Point 3 was bubbled through a series of two impingers. The contents of the two impingers were combined, a 100 ml sample was taken and either

Table 3-4

PRESSURE VS. TEMPERATURE AND SAMPLE TUBE

Sample Tube	Temp. (^{o}C)	P_1 (atm)	P_2 (atm)	P_3 (atm)
Silica	25	1.06	1.03	1.00
	100	1.09	1.04	1.00
	200	1.14	1.07	1.00
	300	1.22	1.11	1.00
	400	1.29	1.15	1.00
Stainless	25	1.04	1.01	1.00
	100	1.06	1.01	1.00
	200	1.10	1.02	1.00
	300	1.14	1.02	1.00
	400	1.19	1.02	1.00

ammonia or cynanide were measured using a specific ion electrode (Orion 95-10 and 94-06 respectively).

The instrumentation employed to measure carbon monoxide, hydrogen, and hydrocarbons was designed to establish and monitor the set point concentrations at Sample Point 2. The sensitivity of the instrumentation was not sufficient to quantitatively evaluate CO, H_2, and HC concentration changes between Sample Points 1 and 2 and Sample Points 2 and 3. The subsequent discussions in the results section relating to observed changes in CO, H_2, and HC are qualitative and conjective.

Chapter 4

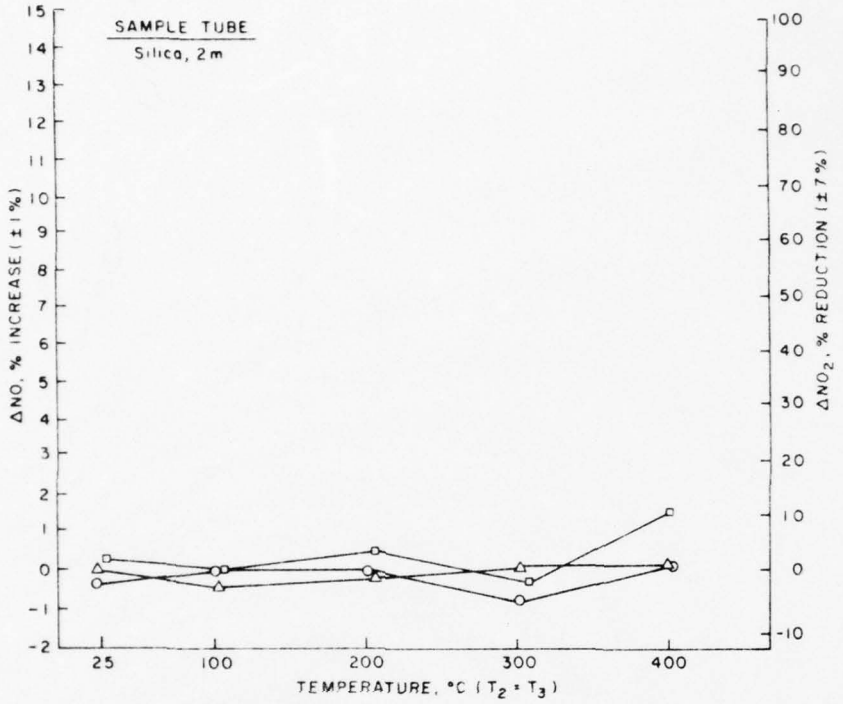
RESULTS

The results are presented in Figure 4-1 for oxidizing mixtures. Results for mixtures with carbon monoxide are presented in Figure 4-2. Results for mixtures with hydrogen are presented in Figure 4-3. Results for mixtures with hydrocarbons are presented in Figures 4-4, 4-5, and 4-6. The percent change of NO and NO_2 represents the percent change in concentration between Sample Points 2 and 3 unless otherwise noted. In the figures, points above the horizontal temperature scale identify those cases for which total NO_X is conserved. In such cases, changes in nitric oxide (NO) are proportional to changes in nitrogen dioxide (NO_2) concentration. In those cases for which NO_X was removed, data are presented in an inset below the horizontal temperature line. The temperature shown is the gas temperature (maintained uniform) at Sample Points 2 and 3.

4.1 OXYGEN MIXTURES

The results for silica are presented in Figure 4-1a. No significant transformation was observed.

The results for stainless steel are presented in Figure 4-1b. In contrast to the results with silica, NO_2 reduction to NO occurred at gas temperatures exceeding $200^{o}C$ in the absence of oxygen and at temperatures

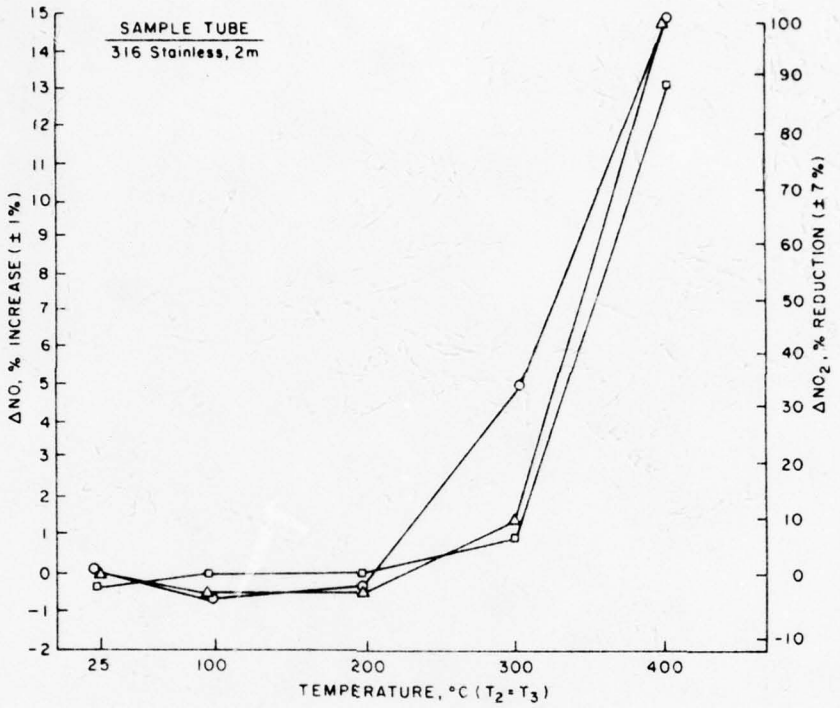


SET POINT CONCENTRATIONS

NO: 500 ppm
NO_2: 75ppm
CO_2: 12%
O_2: 0% (O), 1% (△), 5% (□)
CO: 0
H_2: 0
HC: 0
N_2: Balance

FIGURE 4-1 RESULTS WITH OXYGEN

a) Silica Sample Tube



SET POINT CONCENTRATIONS

NO: 500 ppm
NO_2: 75 ppm
CO_2: 12%
O_2: 0% (○), 1% (△), 5% (□)
CO: 0
H_2: 0
HC: 0
N_2: Balance

FIGURE 4-1 RESULTS WITH OXYGEN

b) 316 SS Sample Tube

exceeding 300°C in the presence of oxygen. The experimental results are consistent with observations by Halstead (1971), Hodgeson et al. (1971), Sigsby et al. (1973), Breitenbach and Shelef (1973), and White and Beddows (1973), and are attributed to the following heterogeneous wall reaction:

$$NO_2 + \text{metal} \longrightarrow \text{metal oxide} + NO \qquad (2)$$

The effectiveness of stainless steel in promoting this reaction likely depends on the condition of the surface layer. Stainless steel is characterizied by a thin oxide surface layer. A well prepared and maintained oxide surface will suppress the heterogeneous reaction. However, continued exposure of stainless steel to reducing atmospheres degrades the oxide surface layer and increases the vulnerability of NO_2 to reduction. The condition of the stainless wall is expected to influence the result and, in fact, such observations have been made in this experiment and others (Tuttle et al., 1973).

For the present experiment, the same off-the-shelf stainless steel sample tube was used under both oxidizing and reducing conditions. The oxide surface layer was not preconditioned or reconditioned for any test run. The presence of O_2 likely served to protect the integrity of the thin oxide surface layer.

The decreased conversion efficiency of NO_2 to NO observed with 5% O_2 at 400°C is attributed to a redox

reaction linked to the chromium content of the stainless steel:

$$Cr_2O_3 + O_2 + NO \longrightarrow NO_2 + 2\ CrO_2 \qquad (3)$$

This redox reaction is initiated at or about 400°C and has been identified by Hilliard and Wheeler (1977) as likely responsible for the oxidation of NO to NO_2 at temperatures exceeding 400°C in the presence of stainless steel.

4.2 CARBON MONOXIDE MIXTURES

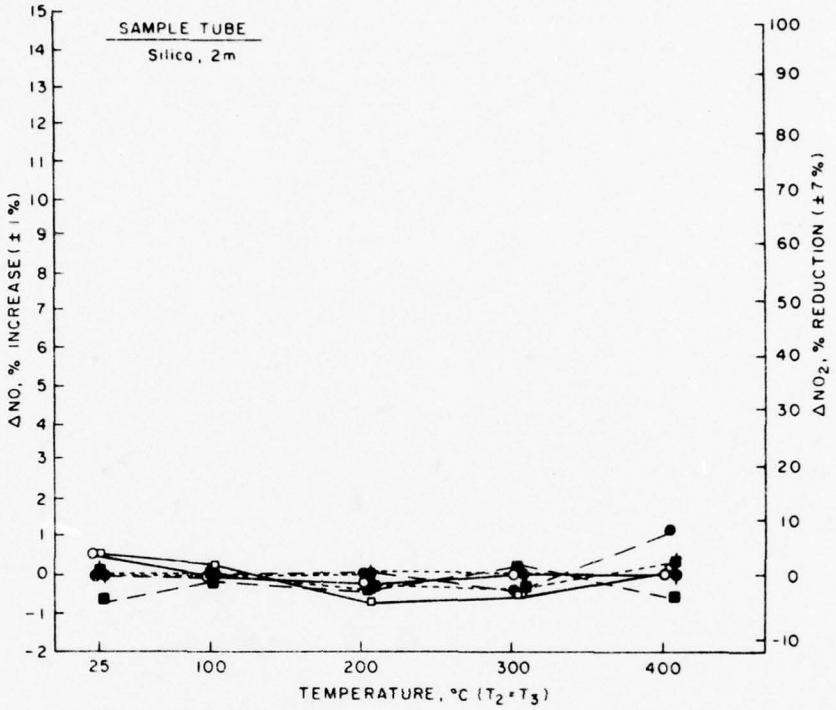
The results for silica are presented in Figure 4-2a. No significant transformation was observed.

The results for stainless steel are presented in Figure 4-2b. Reduction of NO_2 to NO was observed at temperatures of 100°C and higher. The reduction became more pronounced with increasing CO concentration and increasing temperature. The presence of oxygen suppressed the extent of reduction at a given condition but did not prevent the occurrence of reduction. Note that the results at 100 ppm CO are essentially similar to those obtained in the absence of CO (Figure 4-1b).

The behavior observed in the presence of CO is attributed to the following catalytic reaction:

$$CO + NO_2 \longrightarrow CO_2 + NO \qquad (4)$$

This observation follows work by others who have addressed the catalytic reduction of NO_2 by CO. For example, Ayen



SET POINT CONCENTRATIONS

NO : 500 ppm

NO_2 : 75 ppm

CO_2 : 12 %

O_2 : 0% , 0% , 0% , 5% , 5% , 5%

CO : 100 ppm (○), 1000 ppm (●), 2500 ppm (◆) ; 100 ppm (□), 1000 ppm (■), 2500 ppm (◆)

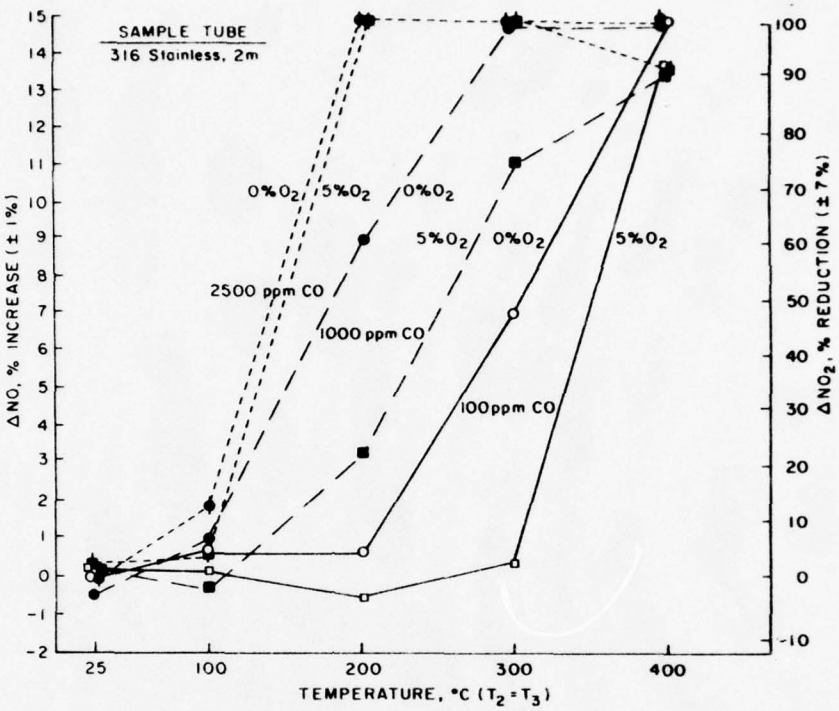
H_2 : 0

HC : 0

N_2 : Balance

FIGURE 4-2 RESULTS WITH CARBON MONOXIDE

a) Silica Sample Tube



SET POINT CONCENTRATIONS

NO : 500 ppm
NO_2 : 75 ppm
CO_2 : 12 %
O_2 : 0% , 0% , 0% , 5% , 5% , 5%
CO : 100 ppm (○), 1000 ppm (●), 2500 ppm (◆) ; 100 ppm (□), 1000 ppm (■), 2500 ppm (◆)
H_2 : 0
HC : 0
N_2 : Balance

FIGURE 4-2 RESULTS WITH CARBON MONOXIDE

b) 316 SS Sample Tube

and Yonebayashi (1967) used a barium promoted copper chromite catalyst and observed the reduction of NO_2 by CO at temperatures of 180-240°C. The reaction products observed were limited to CO_2 and NO. Similarly, White and Beddows (1973) observed NO_2 reduction by CO in a 321 stainless steel sampling line.

At 400°C, the effect of oxygen in suppressing the NO_2 to NO reduction is attributed to the competition between NO_2 and O_2 in oxidizing CO. The 5% O_2 data are independent of CO concentration and converge to the percent reduction observed in the absence of CO (Figure 4-1b). The chromium oxide wall redox reaction (3) is apparently dominant.

4.3 HYDROGEN MIXTURES

The results for silica are presented in Figure 4-3a. No significant transformation was observed up to 200°C in silica with slight reduction (15%) of NO_2 to NO observed at 300°C. At 400°C, the changes are dramatic and depend on hydrogen concentration. NO_2 is totally reduced in the silica preheat oven at the lower hydrogen concentration (.5%) with very slight removal of NO_x in the silica sample tube. NO_x is totally removed in the silica preheat oven at the elevated hydrogen concentration of 3%. The reduction of NO_2 in silica at 400°C is consistent with results obtained by Ashmore and Levitt (1956, 1957). Complete NO

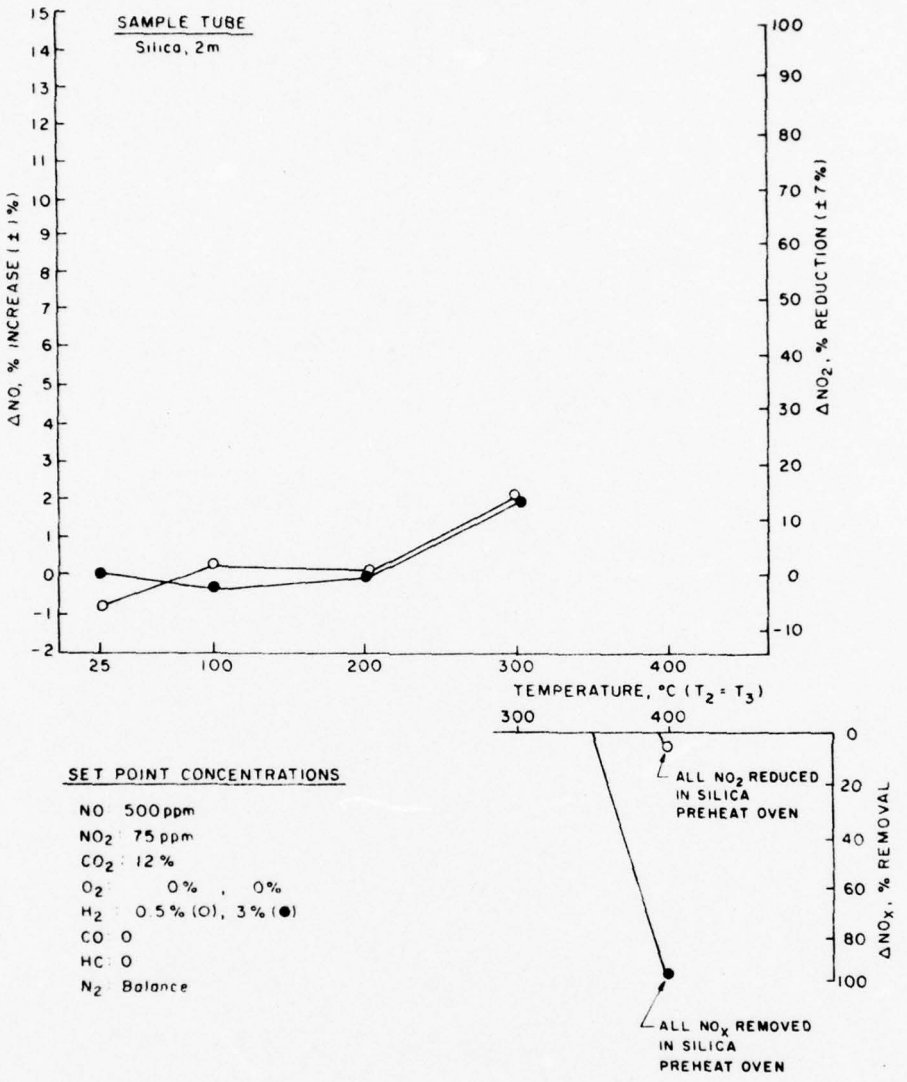


FIGURE 4-3 RESULTS WITH HYDROGEN

a) Silica Sample Tube

reduction by hydrogen may be attributed to (1) the catalytic activity of silica and (2) the elevated concentration of hydrogen.

The results for stainless steel are presented in Figure 4-3b. Complete reduction of NO_2 to NO was promoted at 200°C in the presence of hydrogen. At 300°C, the chemical transformation depended upon hydrogen concentration. Nearly total removal of NO_x by .5% H_2 was observed in the 316 stainless sample tube with no significant change observed in the silica preheat oven. However, all NO_2 was reduced in the silica preheat oven with 3% H_2, and total NO_x removal occurred in the sample tube. At 400°C, NO_x was removed for both hydrogen concentrations. All NO_2 was reduced in the silica preheat oven for .5% H_2, and all NO_x was removed in the silica preheat oven for 3% H_2. The catalytic reduction of NO in stainless steel is consistent with data collected by Klimisch and Barnes (1972), Shelef and Gandhi (1972) and others using various types of catalytic material.

Formation of carbon monoxide was observed in both the silica preheat oven and stainless steel sample tube. Evidence of CO formation (400 ppm) with 3% H_2 appeared at Sample Point 3 (300°C) in the stainless steel sample tube. The presence of CO was more significant at Sample Points 2 and 3 while sampling at 400°C. The concentrations of CO at Sample Point 2 (400°C, 3% H_2) for silica and stainless

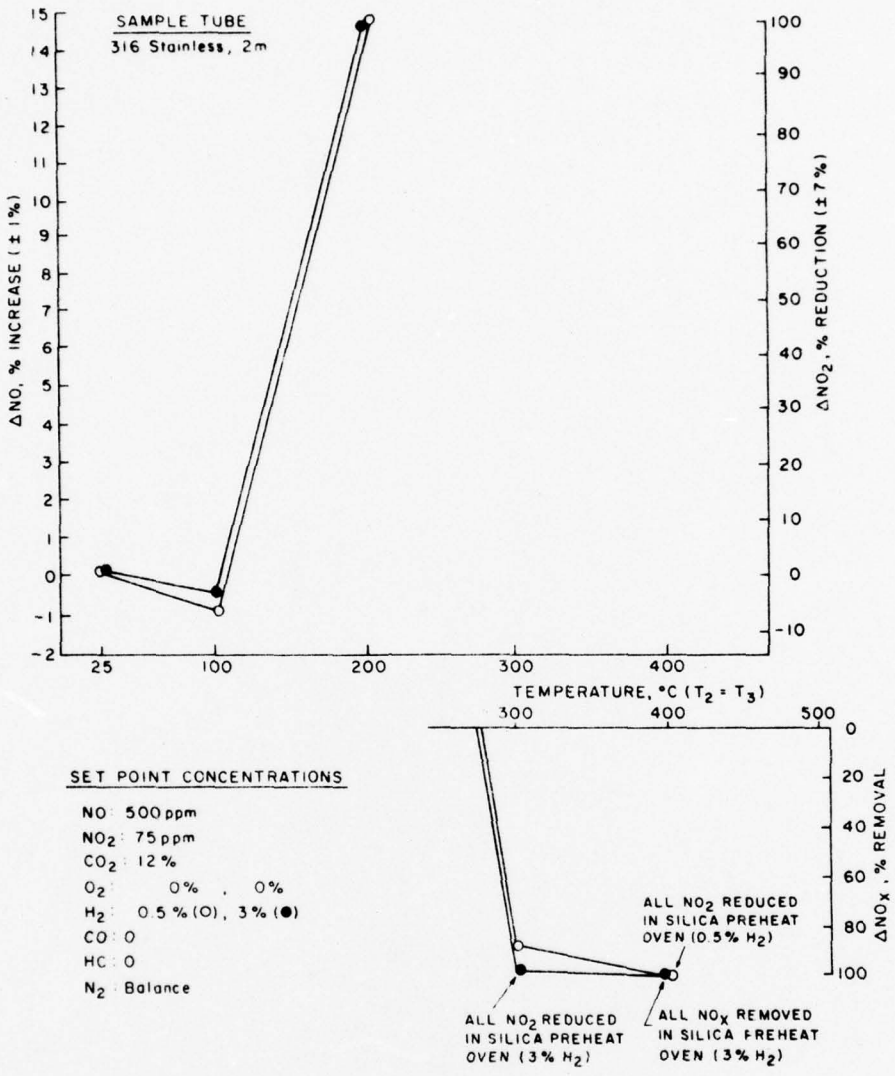


FIGURE 4-3 RESULTS WITH HYDROGEN

b) 316 SS Sample Tube

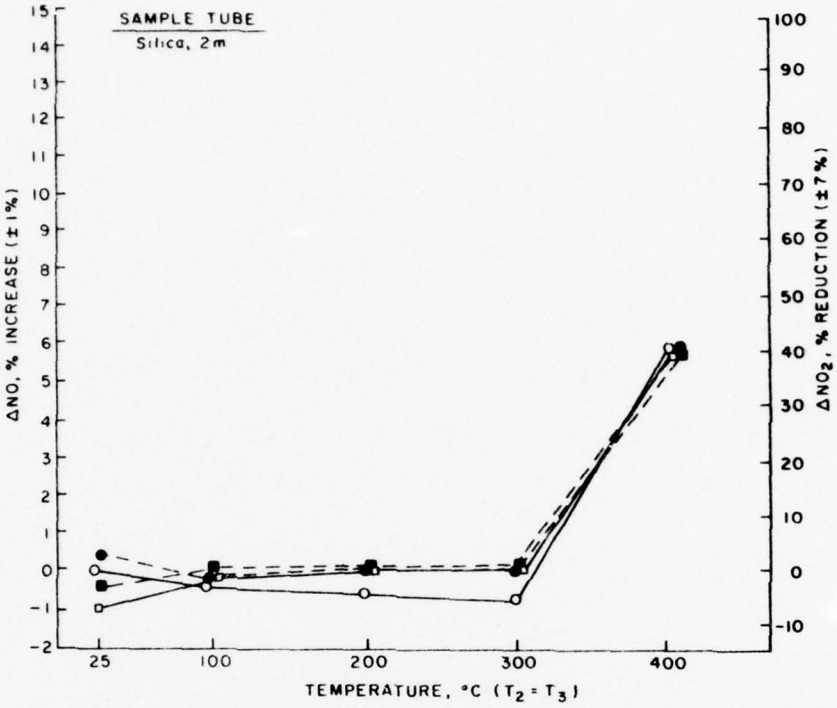
steel tests were 1200 and 900 ppm respectively. The Sample Point 1 concentration of H_2 had to be increased to maintain the desired set point concentration at Sample Point 2. At Sample Point 3, 2800 ppm CO and 3900 ppm CO were formed in the stainless steel tube at 400°C with .5% H_2 and 3% H_2 respectively.

The only source of carbon available from the carrier gas mixture for CO formation is CO_2. A reaction mechanism involving hydrogen and carbon dioxide is proposed for both the silica preheat oven and stainless steel sample tube. The formation of more CO in stainless than silica is attributed to the higher catalytic activity of stainless. Hydrogen will significantly degrade the oxide layer present in stainless and thus increase the catalytic activity to CO formation and NO_x transformations. Hydrogen also promotes the catalytic activity of silica. However, the presence of CO at Sample Point 2 does not appear to promote either NO_2 reduction or NO_x removal in silica (Figure 4-2a).

4.4 HYDROCARBON MIXTURES

Methane

The results for silica are presented in Figure 4-4a. No significant chemical transformation was observed up to and including 300°C. At 400°C, NO_2 to NO reduction occurred. The results were insensitive to the presence of oxygen and the methane concentration.



SET POINT CONCENTRATIONS

NO: 500ppm
NO_2: 75ppm
CO_2: 12%
O_2: 0% , 0% , 5% , 5%
CH_4: 500ppm(○), 1000ppm(●), 500ppm(□), 1000ppm(■)
CO: 0
H_2: 0
N_2: Balance

FIGURE 4-4 RESULTS WITH METHANE

a) Silica Sample Tube

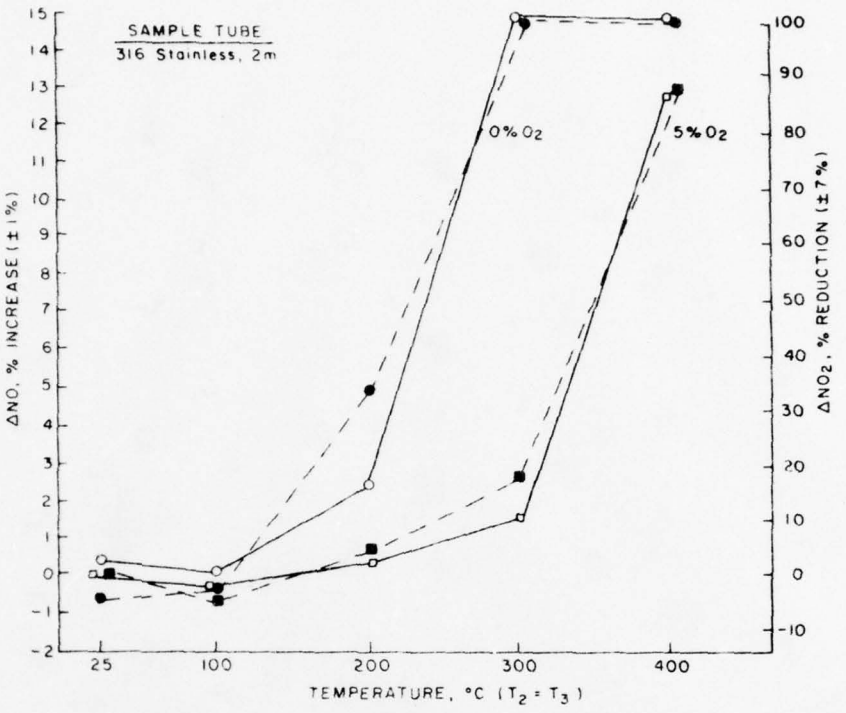
The reduction of NO_2 to NO in silica at 400°C is attributed to the following homogeneous gas-phase reaction:

$$CH_4 + NO_2 \longrightarrow NO + \text{products} \qquad (5)$$

This observation is reinforced by the results of studies directed to the gas phase reduction of NO_2 by methane (Bromberg and Taylor, 1955 and Gagarina and Emanuel, 1959).

The results for stainless steel are presented in Figure 4-4b. NO_2 reduction is promoted at temperatures exceeding 100°C in the absence of oxygen and 200°C in the presence of oxygen. Complete NO_2 reduction was observed at 300°C and 400°C with 0% O_2 while only 85% reduction was observed at 400°C and 5% O_2. The 5% O_2 data at 400°C converged to the percent reduction observed in the absence of reducing species (Figure 4-1b).

Changes in methane and carbon monoxide concentration at 400°C and at 5% O_2 within the silica preheat oven and silica and stainless sample tubes are noteworthy. CH_4 was oxidized by oxygen in addition to NO_2 in the silica sample tube. Oxidation approached 70%. Some methane oxidation also occurred in the silica preheat oven and the Sample Point 1 concentration had to be increased to attain the set point concentration at Sample Point 2. Although the dimensions of the preheat oven are identical to the silica sample tube, the methane oxidation in the preheat oven was small by comparison because of the thermal gradient



SET POINT CONCENTRATIONS

NO: 500ppm
NO_2: 75ppm
CO_2: 12%
O_2: 0% , 0% , 5% , 5%
CH_4: 500ppm (○), 1000ppm (●), 500ppm (□), 1000ppm (■)
CO: 0
H_2: 0
N_2: Balance

FIGURE 4-4 RESULTS WITH METHANE

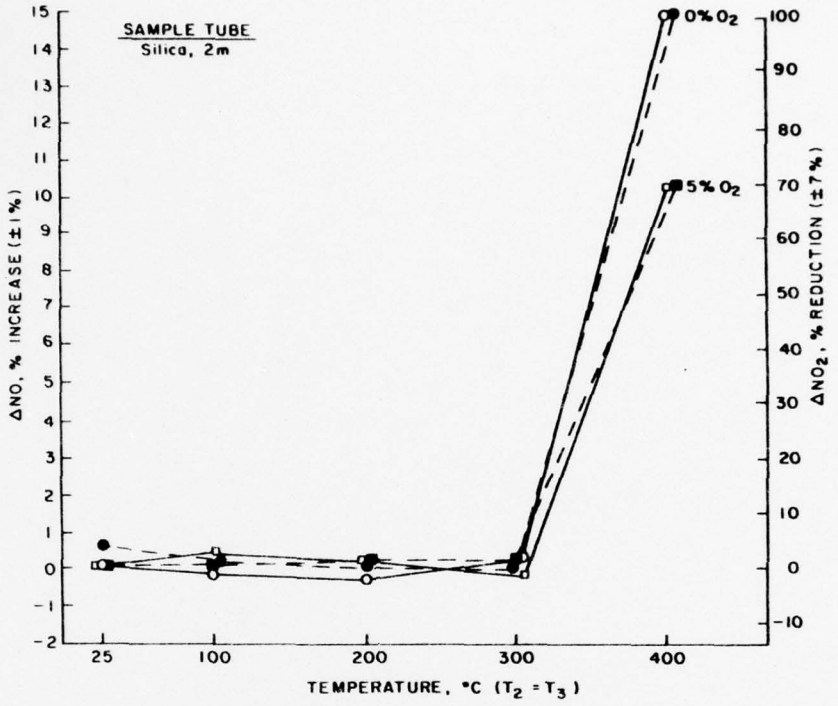
b) 316 SS Sample Tube

from ambient to 400°C. Nevertheless, the methane oxidation by O_2 and NO_2 produced CO. The CO concentration at Sample Point 2 was approximately 100 ppm. At Sample Point 3, the CO concentrations were 400 ppm and 800 ppm respectively for the 500 and 1000 ppm CH_4 set point conditions. CO was not observed within the sample tube for the stainless steel tests. The difference is attributed to (1) the lower overall pressure in the stainless (Table 3-4), (2) the competition for O_2 at the stainless wall between the CH_4 and the chromium oxide (reaction 3), and (3) the catalytic activity of the silica at 400°C (Stadnik and Gomonai, 1963) in promoting HC oxidation.

Ethylene

The results for silica are presented in Figure 4-5a. Total reduction to NO was observed at 400°C in the absence of oxygen and seventy percent reduction was observed in the presence of 5% oxygen. The ethylene was totally consumed within the sample tube compared to the 70% oxidation for methane in the presence of oxygen, and explains the less than complete reduction of NO_2 to NO in the presence of oxygen.

The results for 316 stainless steel (Figure 4-5b) indicate that NO_2 reduction is promoted at temperatures exceeding 100°C. Complete NO_2 reduction was observed



SET POINT CONCENTRATIONS

NO: 500ppm
NO_2: 75ppm
CO_2: 12%
O_2: 0% , 0% , 5% , 5%
C_2H_4: 500ppm (○), 1000ppm (●), 500ppm (□), 1000ppm (■)
CO: 0
H_2: 0
N_2: Balance

FIGURE 4-5 RESULTS WITH ETHYLENE

a) Silica Sample Tube

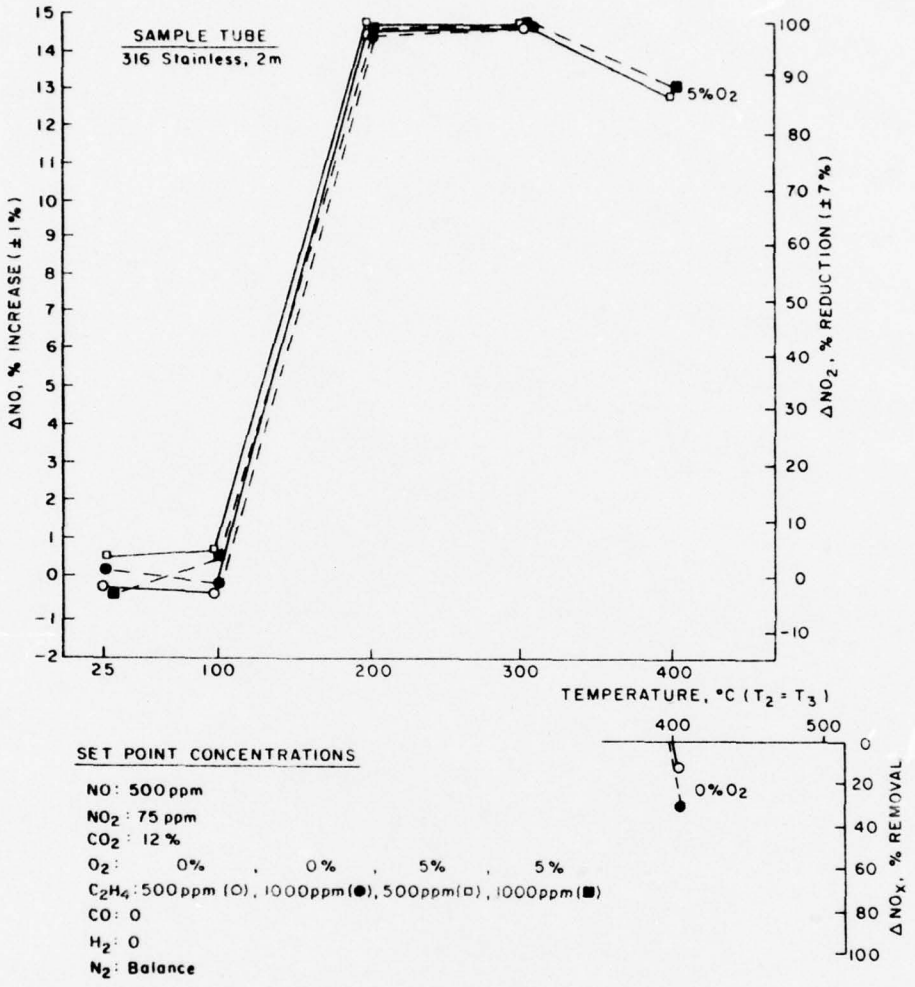


FIGURE 4-5 RESULTS WITH ETHYLENE

b) 316 SS Sample Tube

at 200°C and 300°C with both 0% and 5% O_2. At 400°C, two types of transformations were observed: NO_2 reduction to NO in the presence of oxygen, and NO removal in the absence of oxygen (the residual NO_x was composed of NO only). The 5% O_2 data at 400°C once more converged to the percent reduction observed in the absence of reducing species (Figure 4-1b).

The concentrations of CO at Sample Point 2 for both the silica and stainless tests were 1400 ppm and 3000 ppm CO for 500 ppm and 1000 ppm C_2H_4 respectively as a result of ethylene oxidation in the silica preheat oven. The ethylene flowrate was adjusted to maintain the set point sample tube inlet concentrations at Sample Point 2.

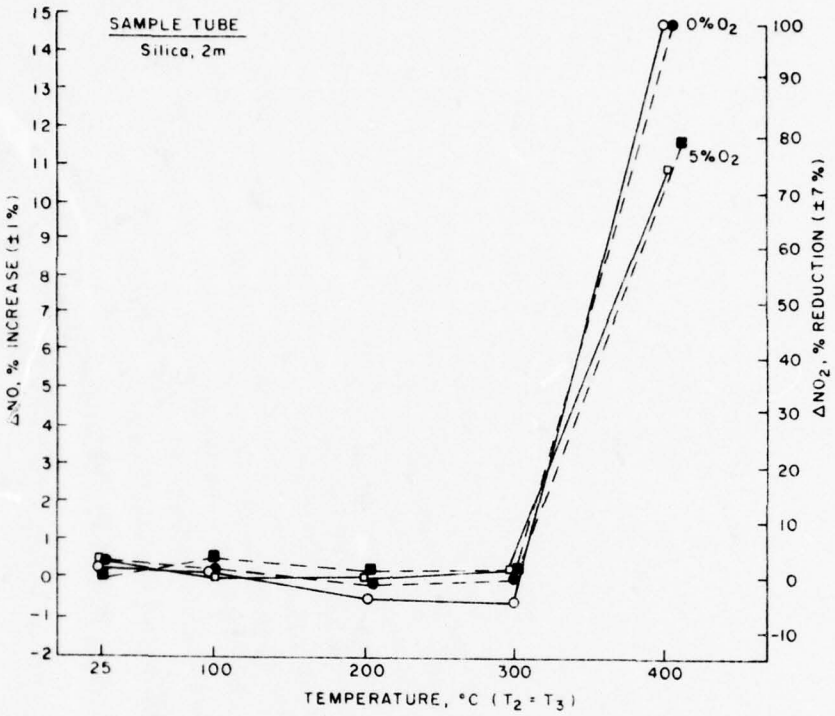
Also notable were the observed differences in ethylene and carbon monoxide concentration change in the silica and stainless steel sample tubes. The consumption of ethylene in the silica sample tube was complete whereas in the 316SS sample tube conversion was approximately 80% for both ethylene inlet concentrations. The difference is attributed to (1) the higher pressure in the silica tests (Table 3-4), (2) the competition for O_2 at the stainless wall between the ethylene and the chromium oxide (reaction 3), and (3) the catalytic activity of the silica. In addition to the difference in hydrocarbon consumption,

a net increase in carbon monoxide concentration was observed across the silica sample tube, whereas a net decrease in carbon monoxide concentration was observed across the stainless steel sample tube. This is attributed to the longer path to CO_2 in the presence of silica in contrast to CO_2 yield in the presence of metal or metal oxides (Stadnik and Gomonai, 1963).

Propylene

The results for propylene are presented in Figure 4-6. The data are basically identical to those with C_2H_4 with one significant exception: NO_x removal. Propylene is more reactive in the removal of NO_x. In the absence of oxygen, slight removal is observed at 300°C and total removal is observed at 400°C. Note the consistency of the data at 400°C, 5% O_2 with the results in the absence of reducing species (Figure 4-1b).

The higher reactivity displayed by ethylene and propylene with NO_x is supported by intuition and reports (Shelef and Gandhi, 1974 and Germain, 1969) that olefins (such as propylene) react more readily with NO than paraffins (such as propane) to form ammonia and/or HCN in the temperature range (420°C-500°C) for a variety of catalysts. Parenthetically, a brief test was conducted in the present study to determine whether ammonia or HCN were present for the most reactive condition (propylene at 400°C in stainless steel in the absence of oxygen). Specific ion electrode



SET POINT CONCENTRATIONS

NO: 500ppm
NO_2: 75ppm
CO_2: 12%
O_2: 0% , 0% , 5% , 5%
C_3H_6: 500ppm (○), 1000ppm (●), 500ppm (□), 1000ppm (■)
CO: 0
H_2: 0
N_2: Balance

FIGURE 4-6 RESULTS WITH PROPYLENE

a) Silica Sample Tube

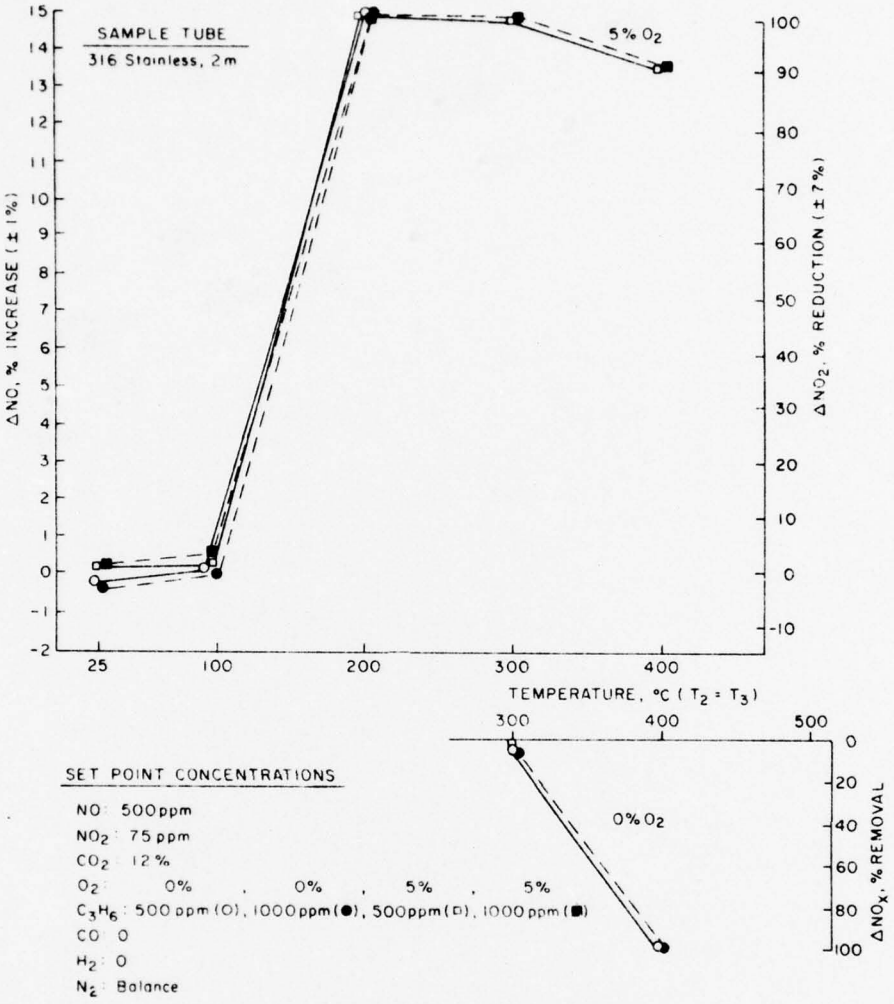


FIGURE 4-6 RESULTS WITH PROPYLENE

b) 316 SS Sample Tube

methods were. The cursory measurement gave no evidence of either species.

Chapter 5

SUMMARY AND CONCLUSIONS

5.1 SUMMARY

For the sampling conditions associated with the experiment, transformation of nitrogen oxides do occur in the presence of oxidizing and reducing species. Transformations of NO_x were more prevalent in reducing mixtures than oxidizing mixtures. The absence of oxygen in the gas stream favored NO_x removal by both hydrogen and reactive hydrocarbons. The presence of oxygen in the gas stream prevented NO_x removal in both stainless and silica sample tubes. The presence of 5% O_2 in silica suppressed but did not prevent the reduction of NO_2 to NO with hydrocarbons at 400°C. With hydrogen, NO_x was removed from both stainless and silica. Higher temperatures and pressures were required for the less reactive species such as carbon monoxide and methane to reduce NO_2 completely in stainless steel. The temperature at which effects were observed, the extent of transformation, and the transformation type depended upon the species present. In particular:

Oxygen and Carbon Monoxide

- NO_x is conserved in silica and 316 stainless for the temperature range 25-400°C in the presence of oxygen and carbon monoxide.

- Reduction of NO_2 in 316 stainless steel tubes is observed at temperatures exceeding 200°C. When carbon monoxide is present, reduction of NO_2 occurs at temperatures exceeding 100°C.
- In silica probes, no significant transformation of nitrogen oxides in the the absence or presence of carbon monoxide is observed.

Hydrogen

- NO_x is conserved in silica and 316 stainless sample tubes for the temperature range 25-200°C in the presence of hydrogen.
- NO_2 is reduced to NO in 316 stainless steel at temperatures exceeding 100°C in the presence of hydrogen.
- NO_x is removed in 316 stainless steel tubes at temperatures exceeding 200°C and silica tubes at temperatures exceeding 300°C in the presence of hydrogen.

Hydrocarbons

- NO_x is conserved in silica and 316 stainless sample tubes for the temperature range of 25-200°C in the presence of methane, ethylene, or propylene (500, 1000 ppm).

- o NO_2 is reduced to NO in silica at temperatures exceeding 300°C in the presence of methane, ethylene, or propylene.
- o NO_2 is completely reduced to NO in 316 stainless steel at temperatures exceeding 100°C in the presence of ethylene and propylene, and at temperatures exceeding 200°C in the presence of methane.
- o NO_X is removed in 316 stainless steel at temperatures exceeding 200°C in the presence of propylene and 300°C in the presence of ethylene.
- o The presence of excess oxygen (5%) inhibits total reduction of NO_2 to NO at 400°C at in gas streams containing methane, ethylene, and propylene with 316 stainless steel tubes.
- o The presence of excess oxygen (5%) inhibits total reduction of NO_2 to NO at 400°C with silica tubes in gas streams containing ethylene and propylene.

5.2 CONCLUSIONS

Although the combustion effluents were simulated and controlled under laboratory conditions, the results provide some important information concerning probe and

sampling materials. Silica, as expected, limits but does not prevent NO_x transformations. NO_2 reduction to NO occurs at 400°C in the presence of methane, ethylene, and propylene and NO_x removal occurs in the presence of hydrogen. For the species and species concentrations explored, silica would be acceptable for both oxidizing and reducing environments up to 300°C.

Based on the experimental conditions, conventional 316 stainless steel material effectively promotes transformations of nitrogen oxides and thus may not be an acceptable probe material in the moderate temperature range. NO_2 reduction is prevalent in both oxidizing and reducing atmospheres, and NO_x removal is prevalent in gas mixtures containing hydrogen and reactive hydrocarbons. NO_x transformations in 316 stainless steel can be expected in the moderate temperature range leading to errors involved in monitoring the NO/NO_2 ratio from the exhaust plane of a combustion source. For the species and species concentrations explored, 316 SS would be acceptable for oxidizing environments up to 200°C and for reducing environments up to 100°C

Stated below are a list of general conclusions drawn from the results for sampling combustion effluents:

- The NO/NO_2 ratio can be conserved in environments containing oxygen, carbon monoxide, hydrogen, and hydrocarbons with a silica tube at temperatures below 300°C.

- Sampling errors regarding the NO/NO_2 ratio can be expected with silica in the presence of methane, ethylene, and propylene and hydrogen at 400°C, and hydrogen at 300°C.
- NO_X can be conserved in silica for oxidizing and reducing environments with the exception of hydrogen from 25°C to 400°C.
- Sampling errors regarding the NO/NO_2 ratio can be expected with 316 stainless steel in the absence and presence of oxygen at temperatures exceeding 200°C, and in the presence of carbon monoxide, hydrogen, and hydrocarbons at temperatures exceeding 100°C.
- NO_X can be conserved in stainless steel for environments containing oxygen, carbon monoxide and methane from 25-400°C. NO_X removal can be expected at 300°C and 400°C in the presence of hydrogen and olefins.
- Additional information is needed to more completely assess the role of sample lines and probes in NO_X transformations. Residence time, probe history, surface to volume ratio, pressure (at conditions of sub-atmospheric and atmospheric), higher temperatures (400-900°C), additional hydrocarbon species, particulate matter, and alternative

probe materials must be assessed to more fully understand the complex nature of sampling lines and probes for sampling NO_x.

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