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ADDITIVES FOR NO$_x$ EMISSIONS CONTROL FROM FIXED SOURCES

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This project tested several additives and catalysts as potential additive/catalyst combinations for a new NO$_x$ abatement process. The goal was to identify an effective, economical NO$_x$ emissions control process for application to post combustion, exhaust gas streams from jet engine test cells (JETC) and incinerators.

The most useful results from this project are that: (1) an additive was identified that achieved gas-phase removal, with no catalyst, of NO$_x$ at temperatures as low as 350°C, and (2) good NO$_x$ removals can be achieved with additive:NO$_x$ ratios less than one. These results offer good possibilities for new low-temperature (350 to 500°C) gas phase NO$_x$ reduction processes of the selective noncatalytic reduction (SNR) type for both JETCs and incinerators.

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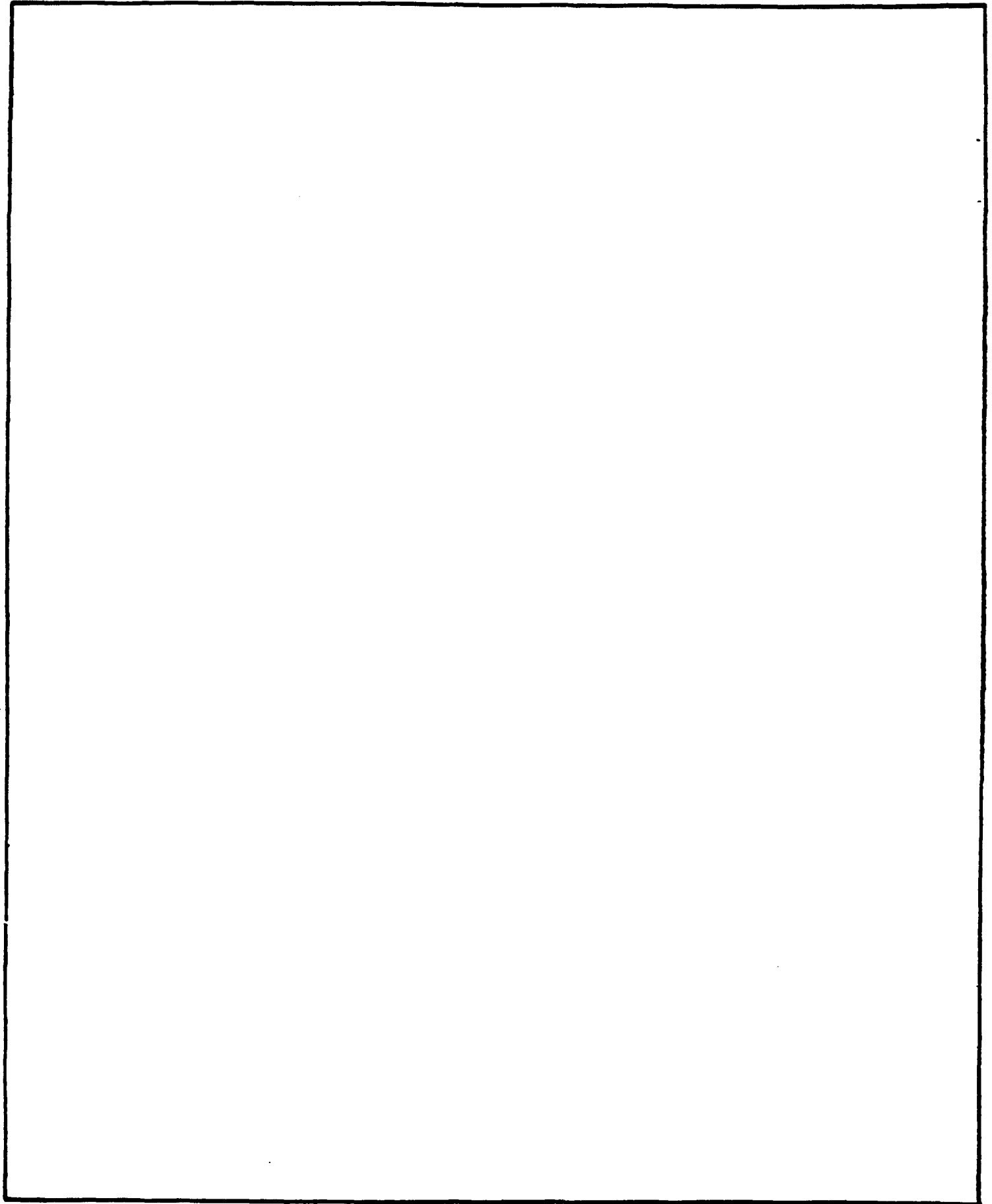
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EXECUTIVE SUMMARY

This project tested several additives and catalysts as potential additive/catalyst combinations for a new NO_x abatement process. The goal was to identify an effective, economical NO_x emissions control process for application to post combustion, exhaust gas streams from jet engine test cells (JETC) and incinerators.

Five additives were tested under conditions that simulated JETC exhaust gases, methylamine (MMA), dimethyl amine (DMA), hydrazine (HZ), methyl-hydrazine (MMH) and ammonia (NH_3). We also tested a variety of inexpensive catalyst materials were also tested, mostly with MMA. Good results were achieved on several catalysts.

The surprising results from this project are that: (1) gas-phase removal, with no catalyst, of NO_x occurs with MMA, DMA and MMH at temperatures as low as 350°C, and (2) good NO_x removals can be achieved with MMA for ratios of MMA:NO less than one.

These results offer good possibilities for new low-temperature (350 to 500°C) gas phase NO_x reduction processes of the selective noncatalytic reduction (SNR) type for both JETCs and incinerators.

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PREFACE

This report was prepared by PSI Technology Company, Andover, Massachuetts, under Contract FO8635-88-C-0261. The Small Business Innovative Research (SBIR) was funded by the Air Force Engineering and Services Center, Air Force Engineering and Services Laboratory (AFESC/RDVS), Tyndall Air Force Base, Florida 32403-6001, to conduct this study for the Air Force.

This report summarizes the work done by PSI Technology Company between August 1988 and February 1989. It was performed under the direction of D. O. Ham, G. Moniz, and M. Gouveia. Capt Wayne Chepren, AFESC/RDVS, was the Air Force project officer for this contract.

These SBIR data are furnished with SBIR rights under Contract No. FO8635-88-C-0261. For a period of two years after acceptance of all items to be delivered under this contract, the Government agrees to use these data for Government purposes only, and they shall not be disclosed outside the Government (including disclosure for procurement purposes) during such period without permission of the Contractor, except that, subject to the foregoing use and disclosure prohibitions, such data may be disclosed for use by support contractors. After the aforesaid two-year period, the Government has a royalty-free license to use, and to authorize others to use on its behalf, these data for Government purposes, but is relieved of all disclosure prohibitions and assumes not liability for unauthorized use of these dat by third parties. This Notice shall be affixed to any reproductions of these dat, in whole or in part.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This report has been reviewed and is approved for public release.

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INTRODUCTION

A. OBJECTIVE

The objective of this project is to develop a process for reducing NO_x emissions combining features of commercial Selective Catalytic Reduction (SCR) technology and employing more reactive additives that will be better than any existing technology for many applications. In particular, such a process could be preferred for Jet Engine Test Cells (JETC) and incinerators. The Phase I approach to developing this opportunity for an improved process involved two features: (1) test new additives for NO_x reduction that are more reactive than NH_3, and (2) explicitly investigate the catalysis of reactions of these additives with NO_x to identify effective, inexpensive catalyst materials.

B. BACKGROUND

The least expensive and generally preferred approaches for controlling NO_x emissions from combustion processes are combustion modification; however, modification would compromise the design purpose of JETCs. For other Air Force applications, especially incinerators, combustion modification such as changes in operating conditions, typically lead to NO_x reductions of less than 60 percent. These approaches may not provide sufficient NO_x reduction to meet evolving NO_x emissions regulations.

Exhaust gas treatment processes will be necessary for JETCs and may be necessary and preferred to combustion modifications for other applications. Several flue gas treatment processes that can achieve up to 90 percent NO_x removal have been developed and are commercially available. Commercially available processed includes SCR, the copper oxide system or Shell flue gas treatment (SFGT) process, and selective noncatalytic reduction (SNR). SFGT requires high levels of SO_2 in the flue gas to generate the copper catalyst, and SNR operates only in a narrow range of high temperatures (900 to $100^{\circ}C$,

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Lyon and Hardy, 1986), so that neither of these is appropriate for treating low-sulfur, exhaust gases from incinerators or JETC. In the SCR process, NO_x emissions are reduced to N_2 and H_2O by reaction with NH_3 or urea $((NH_2)_2CO)$ over an appropriate catalyst. In these processes, reaction temperatures are reduced to 200 to 425°C by the catalyst (Kiovsky et al., 1980), so SCR is more appropriate for exhaust gas treatment. However, the reaction rates with NH_3 are slow so that large systems with expensive catalysts are required. SCR catalyst lifetimes are limited, leading to catalyst cost of about half of the total revenue requirements for sCR processes. Even though catalyst costs have dropped dramatically within the last year, they still represent a significant fraction of SCR costs.

Recently, much excitement has been generated in the popular press by a new NO_x removal process named RAPRENOX for Rapid Removal of NO_x. Dr R. A. Perry initiated work on RAPRENOX while at Sandia Livermore Laboratories and has submitted patent applications covering his concepts. In this approach cyanuric acid $((HOCN)_3)$ is heated in the gas stream to temperatures above 330°C, where it decomposes to form isocyanic acid (HNCO) in gas phase. Initial tests at Sandia Livermore Laboratories showed that cyanuric acid leads to rapid removal of NO_x from a predominantly argon gas stream. However, evidence has accumulated that the RAPRENOX process actually occurs heterogeneously, as opposed to homogeneously in the gas phase as has been believed. Also, recent test have shown that cyanuric acid does not reduce NO_x at all at higher temperatures with significant amounts of O_2 present. The minimum temperature for reaction of cyanuric acid, about 700 K with a catalyst (Siebers and Caton, 1988), is much too high for convenient use in the augmenter section of a JETC.

C. SCOPE AND APPROACH

The program involved screening several potential additive materials for NO_x reduction over catalysts in a gas flow that simulated typical JETC exhaust conditions. Under these conditions, conventional sCR processes and the existing RAPRENOX process are not effective or cost-effective to achieve

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submitted patent applications covering his concepts. In this approach cyanuric acid ($(HOCN)_3$) is heated in the gas stream to temperatures above 330°C, where it decomposes to form isocyanic acid (HNCO) in the gas phase. Initial tests at Sandia Livermore Laboratories showed that cyanuric acid leads to rapid removal of NO_x from a predominantly argon gas stream. However, evidence has accumulated that the RAPRENOX process actually occurs heterogeneously, as opposed to homogeneously in the gas phase as has been believed. Also, recent tests have shown that cyanuric acid does not reduce NO_x at all at higher temperatures and with significant amounts of O_2 present. The minimum temperature for reaction of cyanuric acid, about 700 K with a catalyst (Siebers and Caton, 1988), is much too high for convenient use in the augmenter section of a JETC.

Based on this background, it seemed feasible to develop a process combining features of commercial SCR technology and employing more reactive additives that will be better than any existing technology for many applications. In particular, such a process could be preferred for JETC and incinerators. The Phase I approach to developing this opportunity for an improved process involved two features: (1) test new additives for NO_x reduction that are more reactive than NH_3, and (2) explicitly investigate the catalysis of reactions of these additives with NO_x to identify effective, inexpensive catalyst materials.

The Our Phase I program involved screening several potential additive materials for NO_x reduction over catalysts in a gas flow that simulated typical JETC exhaust conditions. Under these conditions, conventional SCR processes and the existing RAPRENOX process are not effective or cost-effective to achieve proposed NO_x removals. We have shown that a new additive/catalyst combination can lead to a relatively simple and inexpensive NO_x reduction process that is preferred for a variety of applications including JETCs and incinerator exhausts.

The Phase I Program tested promising combinations of new NO_x reduction additives with potentially economical catalysts in fixed-bed screening tests. All tests were performed in a gas flow that simulated JETC exhaust gas. This

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laboratory measured NO and NO_x remaining from an initial NO level for realistic space velocities through the catalyst bed and tested NH_3 under the same conditions. This allowed comparison of various combinations and established an economic baseline with standard SCR processes.
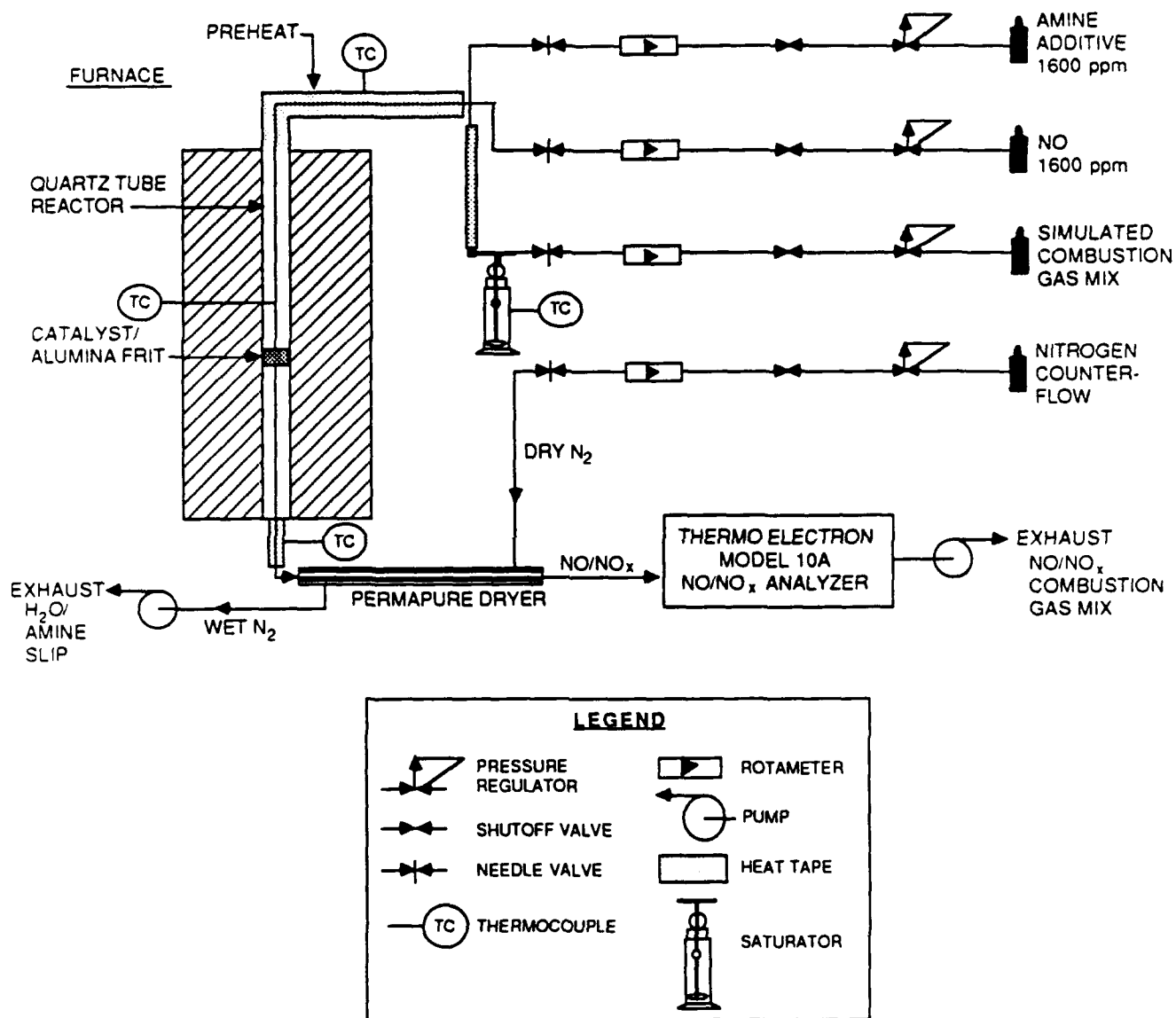
A. EXPERIMENTAL APPARATUS

This Phase I project entailed initial screening tests of additives and catalysts in a fixed-bed flow reactor. These tests provided a means to quickly measure relative reactivities at simulated process conditions. They also allowed simple determinations of the qualitative effects of varying such parameters as temperature, gas composition and space velocity.

Figure 1 presents a schematic diagram of our test facility, where simulated exhaust gas was prepared by combining three compressed gas mixtures, NO in N_2, a $N_2/O_2/CO_2/CO$ mix, and an additive in N_2, each at a delivery pressure of 15 psig. The flow rates of these three gas streams were monitored by Matheson 601 rotameters with operating ranges between 10 and 350 sccm with ± 5 percent absolute accuracy. Flow was controlled with high-precision Matheson regulating needle valves. The $N_2/O_2/CO_2/CO$ gas stream passed through a heated water saturator to form a humidified gas mix. The three gas streams were combined in a stainless steel preheat chamber, where the temperature was elevated to the range 100 to 350°C. From here, the gas mixture flowed into the furnace and quartz tube reactor. Note that all lines (stainless steel or Teflon [R]) conducting wet gas mixtures were heated to prevent condensation.

A single-zone Hoskins vertical furnace was used, with the temperature regulated by a Silicon-Controlled Rectifier temperature controller up to a maximum of 800°C. The simulated exhaust gas stream flowed through a quartz tube reactor, encased in a 1-in. inner diameter (i.d.) stainless steel tube, as shown in Figure 2. The quartz-lined reaction tube inhibited heterogeneous reactions on the wall. A Viton [R] O-ring was used at the base of the reaction tube to prevent gas flow between the quartz insert and the stainless steel tube, with an alumina frit as a support platform for catalyst material in the quartz tube. A shielded chromel-alumel thermocouple external to the stainless steel tube was used to monitor and control the furnace and reactor temperature.

Figure 1
Diagram of Fixed Bed Test Facility

QUARTZ TUBE INSIDE
STAINLESS STEEL TUBE

FURNACE

STAINLESS STEEL

VITON® GASKET

VITON® O-RING
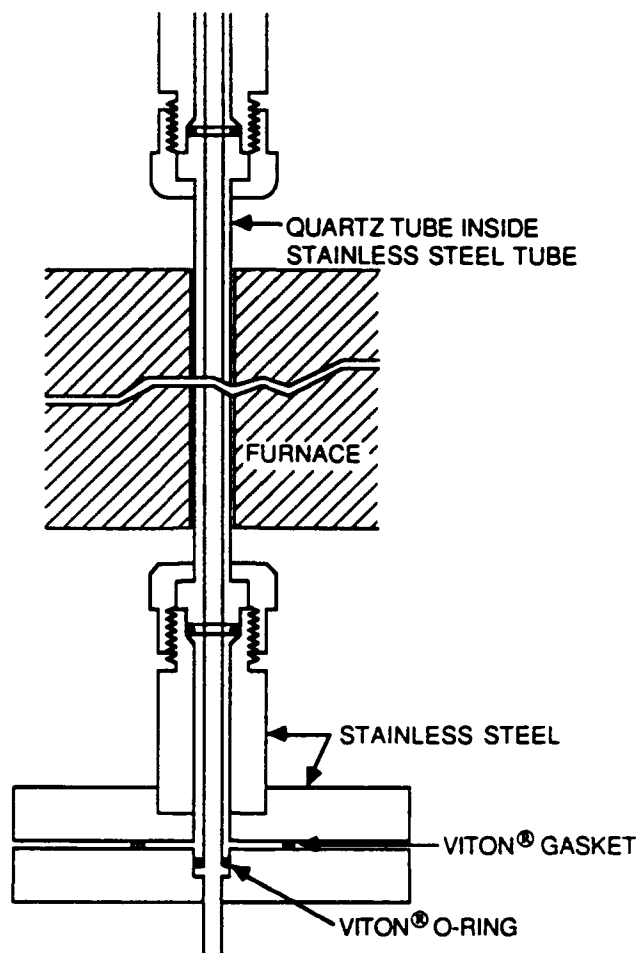
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Figure 2
Diagram of Quartz Reactor Tube in Furnace

As the gas mix exited the quartz tube reactor, water was removed by a Perma Pure [R] Model 750 permeation tube dryer before gas analysis. This dryer consisted of many sulfonic acid membrane tubes through which the gas mix passed. Water was removed by passing a counter flow of dry nitrogen around the outside surface of these tubes. The wet nitrogen was exhausted, and the dried gas mix was sent to a Thermo Environmental Instruments Inc. Model 10 NO/NO_x Chemiluminescent Analyzer to monitor total NO and NO_x out. The manufacturer of the dryer reported no loss of N_2, O_2, CO_2, CO, or NO_x through the membranes. In fact, many air pollution control monitoring devices incorporate these dryers into their gas conditioning systems.

B. EXPERIMENTAL PROCEDURE

A typical experiment involved addition of an additive mixture and the NO gas mixture to a $N_2/O_2/CO_2/CO$ gas mix to provide a total gas flow through the quartz reactor of 300 sccm. The composition of the gas mix used is listed in Table 1. The quartz tube reactor was used either alone or with an alumina frit and catalyst in place. The procedure involved stepping the reactor temperature at 50°C intervals every 30 min from 100 to 600°C while we monitored the NO and NO_x emissions with the NO/NO_x analyzer. The temperature of the preheater was stepped with that of the furnace from 100°C to a maximum of 350°C.

The quartz tube used had an inside diameter of 1.6 cm, and we used a catalyst bed height of about 3 cm in most experiments. This 6 cm^3 bed volume, coupled with the 300 sccm total flow, provided a space velocity of 3000 hr^{-1} for most experiments.

Table 1. Simulated JETC Exhaust Gas Mix

N_2	71%
CO_2	3%
O_2	14%
H_2O	12%
CO	45 ppm
amine additive	150 ppm
NO	150 ppm

C. EXPERIMENTAL VALIDITY

Once the experimental test facility was assembled and the experimental procedure was finalized the following verification tests were performed to establish the validity of the results:

1. Recorded the instrumental drift of the NO/NO_x monitor

2. Investigated the effect of the preheater temperature on NO_x reduction

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3. Determined a NO_x baseline in the absence of an additive and catalyst

4. Investigated reported interference effects by amines with the chemiluminescent detection of NO_x

5. Determined the catalytic nature of the alumina frit

6. Determined the ability of our most active catalyst (Cr_2O_3) to reduce NO_x in the absence of an additive.

Each verification test is described below.

1. Calibration of the chemiluminescent NO/NO_x detector at the beginning of each day by passing an analyzed NO/N_2 mixture through our experimental test apparatus at room temperature (18 to 24°C) and into the detector. In addition, on several days we calibrated after running experiments to monitor instrumental drift. In this check we found a positive drift of less than 6 percent, which we attributed to the cumulative drift of our rotameters and not to the NO/NO_x analyzer.

2. Conducted a series of experiments to determine what effect our stainless steel preheater had on the NO and NO_x levels in our combustion gas mix. Others (Siebers and Caton, 1988) have reported that NO reduction can occur over certain stainless steel surfaces, though at temperatures greater than 600°C. In these validation experiments, the temperature of the preheater was varied between 100 and 350°C; the exit gas analyzed by our NO/NO_x analyzer showed no change in either NO or NO_x concentration over this temperature range.

3. Next we determined the baseline NO/NO_x concentrations without an additive or catalyst over the temperature range of interest (100 to 600°C). This involved monitoring the NO/NO_x emissions from a NO and $N_2/O_2/CO_2$ mix using our standard experimental procedure with a quartz tube reactor in place.

We found no change from the initial NO/NO_x concentration of the simulated exhaust gas mix.

4. Investigated reports from other investigators (Matthews, Sawyer, and Schefer, 1977) that amines can interfere with the chemiluminescent detection of NO_x. We found that whenever our amine additives were passed directly into the NO_x analyzer, they could be detected as "NO_x." When these same amines were passed through the complete experimental apparatus the Perma Pure dryer's sulfonic acid membrane removed the amines. Our observations were consistent with those of the manufacturer (Perma Pure Products Bulletin 104). Apparently ppm concentrations of ammonia and amines are completely soluble in water and are exhausted with the wet nitrogen. Our data, therefore, do not include any effects of the unreacted amine additive (amine slip).

5. Determined that the alumina frit has no effect in reducing NO and NO_x by conducting a typical experiment over the full temperature range with and without an alumina frit in place. In both instances NO and NO_x reductions were identical. Therefore, any NO_x reduction shown by a catalyst was due wholly to the presence of the catalyst and not the alumina frit.

6. Verified that a catalyst alone would not reduce NO_x. We found that our chromia catalyst, in the absence of an additive, did not reduce NO_x at all for temperatures up to 600°C. We did, however, observe about 30 percent conversion of NO to NO_x between 300 and 400°C. This result did not affect our conclusion that additives are required for NO_x removal, so in all other experiments we included additives.

RESULTS

In our experiments under this program we tested four NO_x reduction additives that have not been previously reported for this application. We also tested NH_3 for comparison. Since recent reports on cyanuric acid (Wicke et al., 1988; Caton and Siebers, 1988, and Siebers and Caton, 1988) have indicated significant problems with this additive, we decided not to spend time in this limited program to test cyanuric acid. We tested two different types of catalysts. We also determined the effect of additive:NO ratio for one of our amine additives and performed a preliminary study of the effect of water content on NO_x reduction.

A. SELECTION OF ADDITIVES AND CATALYSTS

For effective NO_x emissions control, we need to produce a reactive reducing species, such as NH_2, NH, or N, from a stable additive. This additive should react faster than NH_3 in order to rely on a less expensive catalyst than those used in the SCR process. We chose four additives that we expected to react quickly to produce the reducing species: monomethylamine (CH_3NH_2), dimethylamine ((CH_3)$_2$NH), hydrazine (NH_2NH_2), and methylhydrazine (CH_3NHNH_2). We also included comparison tests with ammonia (NH_3).

Two types of catalysts were chosen for these screening tests. Iron and chromium oxides are known to be active as SCR catalysts. In a recently completed, EPA-sponsored program to study a NO_x emissions control process for application to flue gases from coal-fired power plants, we discovered that ruthenium, the most active metal catalyst for NH_3 decomposition, is not a good catalyst for NO_x reduction (Ham et al., 1989). This catalyst was therefore eliminated for our Air Force tests. Previous investigators (Siebers and Caton, 1988) have found that NO reduction can occur over a stainless steel surface. Since some types of stainless steel have an outer layer of chromia, we decided to use a 19 percent chromium (III) oxide supported on alumina as our first catalyst. Siebers and Caton (1988) also reported that an iron oxide powder

lowered the temperature at which cyanuric acid reduced NO from 877 to 423°C.
Iron oxide is also a very inexpensive catalyst. Because beds of fine powders
produce large pressure drops, we elected to use supported iron oxide. Five
iron oxide, or hematite, catalysts for these experiments were prepared or
purchased for these experiments.

We purchased a high-purity, very low surface area, unsupported iron oxide,
consisting of 1/8 to 1/2 in. pieces was purchased. An attempt was made to
purchase inexpensive iron oxide supported on alumina spheres, but found that it
had been discontinued by the commercial supplier. We then prepared this
catalyst in-house. We also prepared a hematite catalyst on honeycomb alumina
(the same alumina used as a catalyst platform frit in our quartz tube reactor).
Very late into this program a colleague prepared an iron oxide catalyst on two
support materials that differed in pore structure. These materials will be
referred to as EC-007 and EC-010.

B. COMPARISON OF VARIOUS ADDITIVES

The first test series examined a number of additives for NO_x reduction
with a simulated JETC exhaust gas mix. A previous program had revealed that
the supported chromia catalyst gave very good NO_x reduction (Ham et al., 1989),
so this catalyst was used for our tests with various additives. We compared
reduction with and without the chromia catalyst for methylamine (MMA),
dimethylamine (DMA), ammonia (NH_3), hydrazine (HZ), and methylhydrazine (MMH).
For these tests, analyzed dilute gas mixtures of the additives MMA, DMA, and
NH_3 were added to the gas stream to give a 1:1 ratio with NO. Dilute gas
mixtures were unavailable for HZ and MMH, so the liquid amines were mixed with
water to form an aqueous solution and added to the gas stream with nitrogen and
water at the heated saturator. Based on the phase diagrams of these amines and
water, 1:1 additive:NO ratios were attempted. In the Phase II program we will
need to make direct concentration measurements. For the catalyst tests with
these five additives, a bed height of 3 cm was used to give an approximate
space velocity of 3000/hr. Total NO_x reduction is shown in Figure 3 for the
gas phase process and Figure 4 for the catalytic process on chromia.
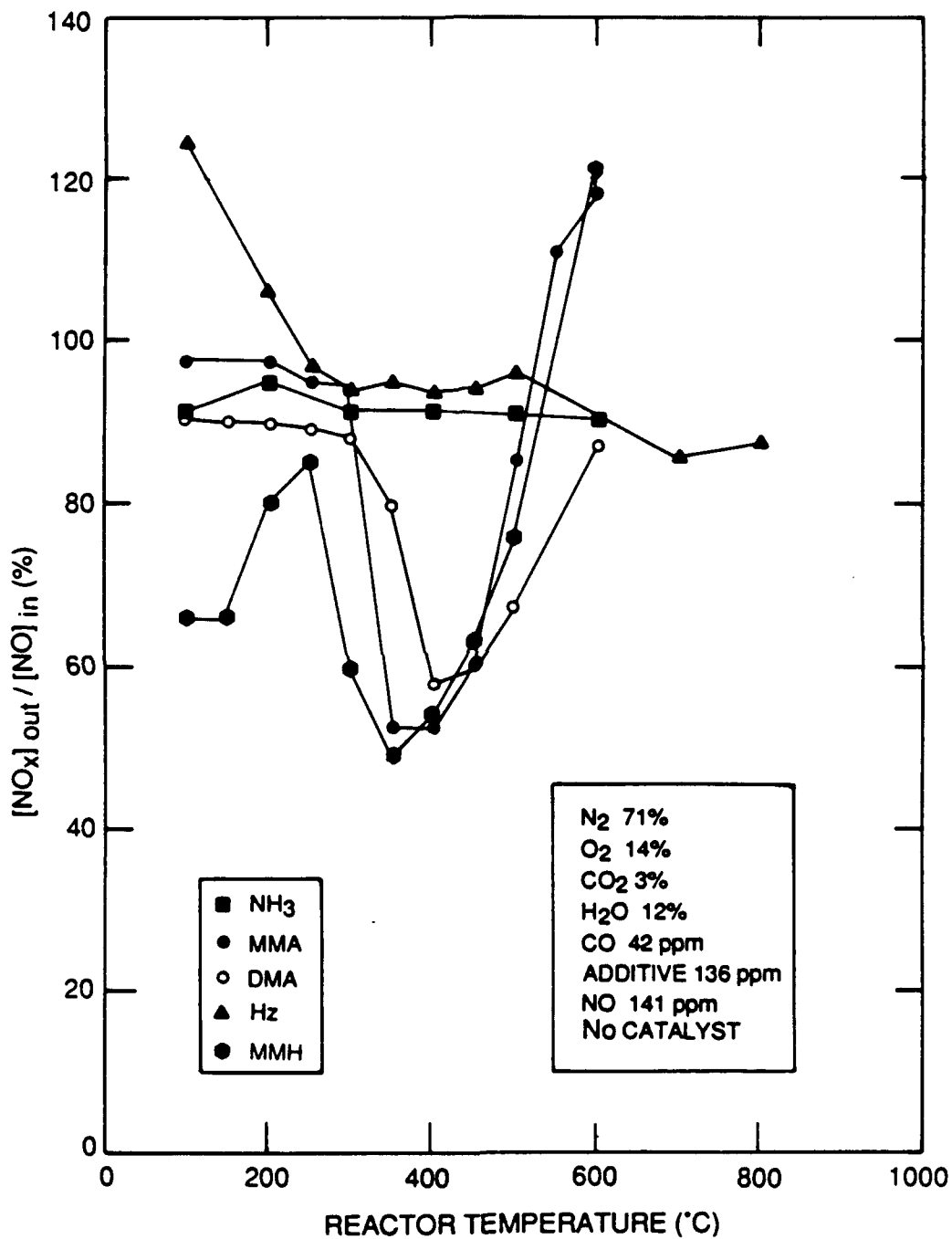
Figure 3
NO_x Reduction for Various Additives with No Catalyst
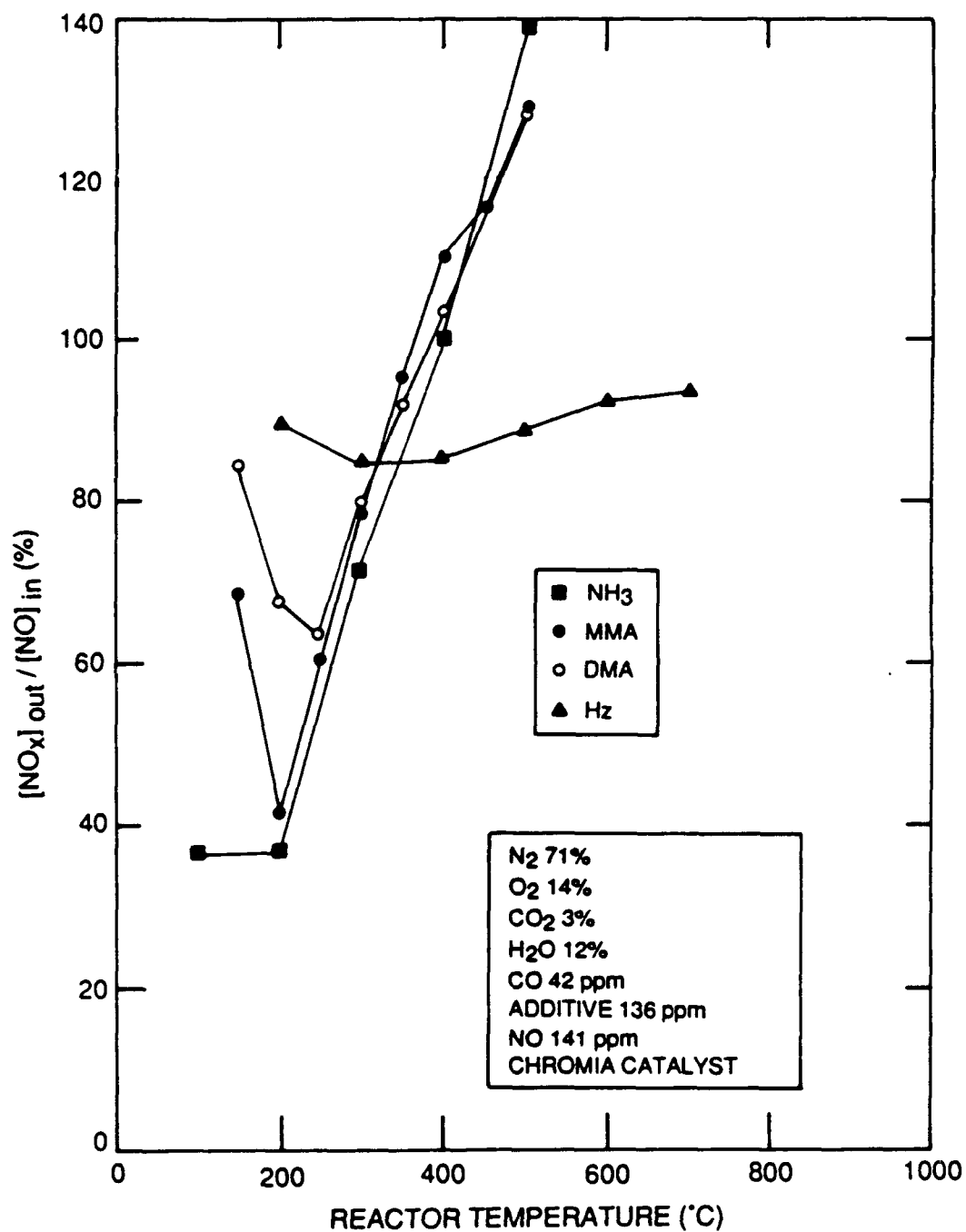
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Figure 4
NO$_x$ Reduction for Various Additives with a Chromia Catalyst

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These tests showed that without a catalyst NH_3 and HZ gave no reduction. MMA, DMA, and MMH reduced NO_x by 40 to 50 percent from 350 to 450°C. This NO_x reduction occurred at temperatures 400 to 500°C lower than those reported for the RAPRENOX process by Caton and Siebers (1988) for NO removal by ammonia and cyanuric acid. With a supported chromia catalyst MMA, MMH, and NH_3 gave 60 percent NO_x reduction, DMA gave 36 percent, and HZ again gave no reduction. MMH/chromia results have not been included in Figure 4. MMA and MMH are the additives that work best under both gas phase and catalytic conditions. Since we could easily determine MMA:NO ratios, we used this additive for further studies.

C. EFFECT OF MMA:NO RATIO ON NO_x REDUCTION

The effect of additive MMA:NO ratio on NO_x reduction was measured with and without the chromia catalyst. We tested ratios of 1.5 and less. For the catalyst tests, the bed height was kept constant at 3 cm. Total NO_x reduction for various MMA:NO ratios is shown in Figure 5 for the gas-phase process and Figure 6 for the catalytic process.

Without a catalyst MMA:NO ratios of 0.1 to 1.5 gave 45 to 55 percent NO_x reduction. A ratio of 0.02 gave no reduction. With a catalyst ratios of 1.0 and 1.5 gave 58 percent reduction, while ratios of 0.3 and 0.6 gave 35 to 40 percent NO_x reduction. For the gas-phase NO_x reduction process, a MMA:NO ratio as small as 0.1 can be used. The Thermal De-NO_x process, on the other hand, requires an NH_3:NO ratio of 1.65 to 2.0 (Caton and Siebers, 1988; Wasser and Perry, 1987). Testing to date indicates that the catalytic NO_x reduction process requires a MMA:NO ratio of 1.0 for good reduction, but can go at least as low as 0.3 for fair reduction. In Phase II will need to test ratios down to 0.1 for catalytic reduction. Current SCR processes require NH_3:NO ratios of 0.95 to 1.1 (Engler et al., 1988; Damon et al., 1987; Wasser and Perry, 1987). Although we have not optimized our process, we believe that both gas phase and catalytic reduction can occur with less additive than SCR or Thermal De-NO_x. Less additive will mean lower cost and less additive slip.
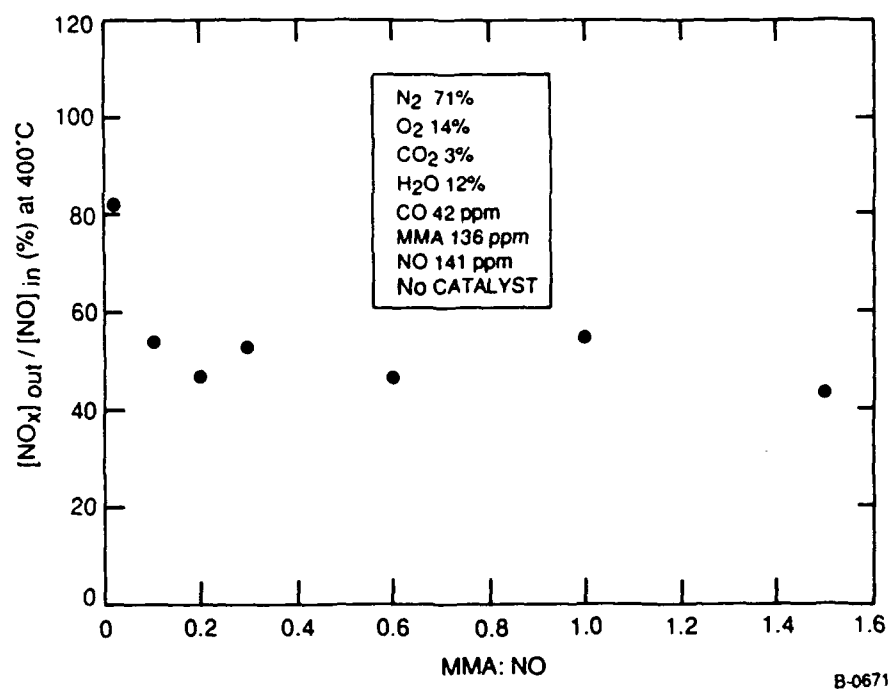
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Figure 5
NO_x Reduction for Various MMA:NO Ratios with No Catalyst
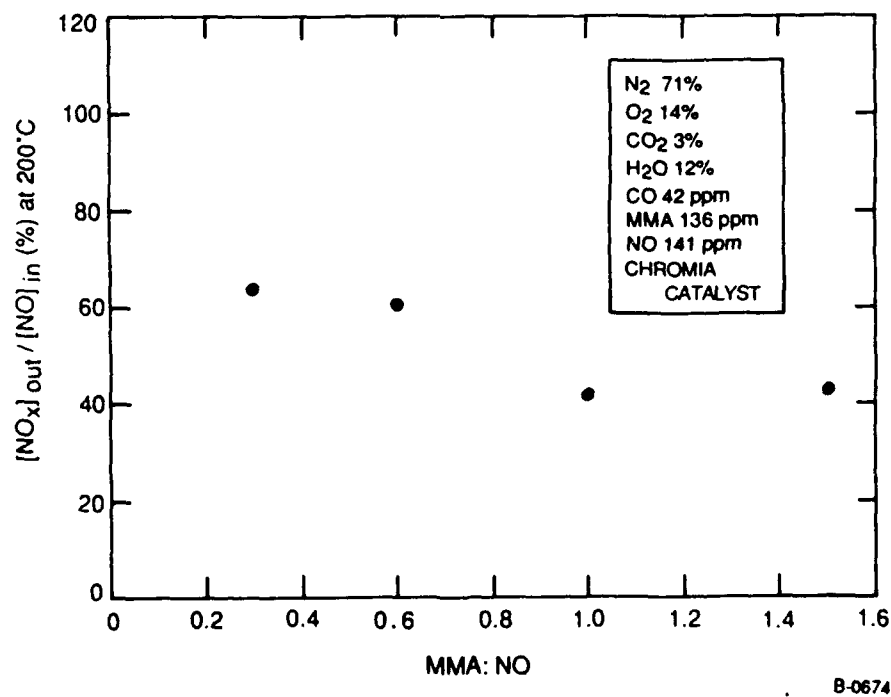

Figure 6
NO_x Reduction for Various MMA:NO Ratios with a Chromia Catalyst

D. EFFECT OF WATER ON NO_x REDUCTION

The augmenter tube of a JETC typically operates with water sprays generating from 6 to 25 percent water. The effect of water concentration on NO_x reduction with a MMA additive and no catalyst was examined. Table 2 summarizes the results for 6, 12, and 25 percent H_2O. Total NO_x reduction remained constant over this range, with an average of 45 percent. Since water concentration seems to have no effect on NO_x reduction, a dilute aqueous solution of MMA sprayed into the augmenter tube might be a viable means of introducing the MMA additive into the JETC exhaust gas stream.

Table 2. Effect of Water on NO_x Reduction with Monomethylamine and no Catalyst

|	$\%H_2O$		
	6%	12%	25%
Temp. maximum NO_x reduction	400°C	400°C	400°C
$[NO]_{out}/[NO]_{in}$	26%	10%	34%
$[NO_x]_{out}/[NO]_{in}$	56%	55%	52%

E. COMPARISON OF VARIOUS CATALYSTS

The last test series examined a number of catalysts for NO_x reduction with our simulated JETC exhaust gas mix. Since MMA was consistently the best additive and NH_3 is the most widely used additive in commercial NO_x reduction technology, we compared NO_x reduction with these two additives for no catalyst, a supported chromia catalyst, and several iron oxide catalysts. An additive:NO ratio of 1:1 was used for all of these tests. For most of the catalyst tests, a bed height of 3 cm was used to give an approximate space velocity of 3000/hr.

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A bed height of 6 cm was used in some of the tests to give a space velocity of about 1500/hr.

Figure 7 shows total NO_x reduction for MMA with no catalyst and with the chromia catalyst at two different space velocities. With no catalyst we obtained over 45 percent NO_x reduction at 400°C with MMA. As we have already shown, NH_3 gave no reduction. Our most thoroughly tested catalyst to date, chromia reduced NO_x by 60 percent at 200°C with both MMA and NH_3 at our standard space velocity of 3000/hr. At a space velocity of 1500/hr. our MMA/chromia combination gave nearly 80 percent NO_x reduction. As expected, halving the space velocity nearly doubled the amount of reduction.

Total NO_x reduction with MMA is shown in Figure 8 for various iron oxide catalysts at a space velocity of 3000/hr. Unsupported, low surface area, iron oxide pieces gave no NO_x reduction with MMA. Supported iron oxide catalysts with varying loadings and porosities reduced NO_x by 50 to 90 percent at 350 to 500°C. These results demonstrate that varying the hematite loading and pore structure can achieve excellent NO_x removal levels and can shift the temperature of maximum reduction. The iron oxide supported on alumina spheres was not tested with simulated JETC exhaust gas. This catalyst was tested with a simulated flue gas containing less O_2 and CO and more CO_2 and NO. We conducted tests to compare the two gas mixtures and found a 6 to 8 percent difference in NO_x reduction. This difference is probably insignificant and we have included the results with this iron oxide catalyst in Figure 8 for completeness.

The temperatures of maximum NO_x reduction for these supported iron oxide catalysts lie in the range of 350 to 500°C. This is no lower than the temperature of maximum reduction for MMA in the gas phase. As stated earlier, Siebers and Caton (1988) reported that iron oxide lowered the temperature of NO reduction for cyanuric acid from 877 to 423°C. No temperature lowering was noticed perhaps because gas-phase reduction with MMA already occurs at the low temperature of 400°C. Although the temperature stayed about the same, the supported hematites reduced more NO_x than did gas phase MMA alone.
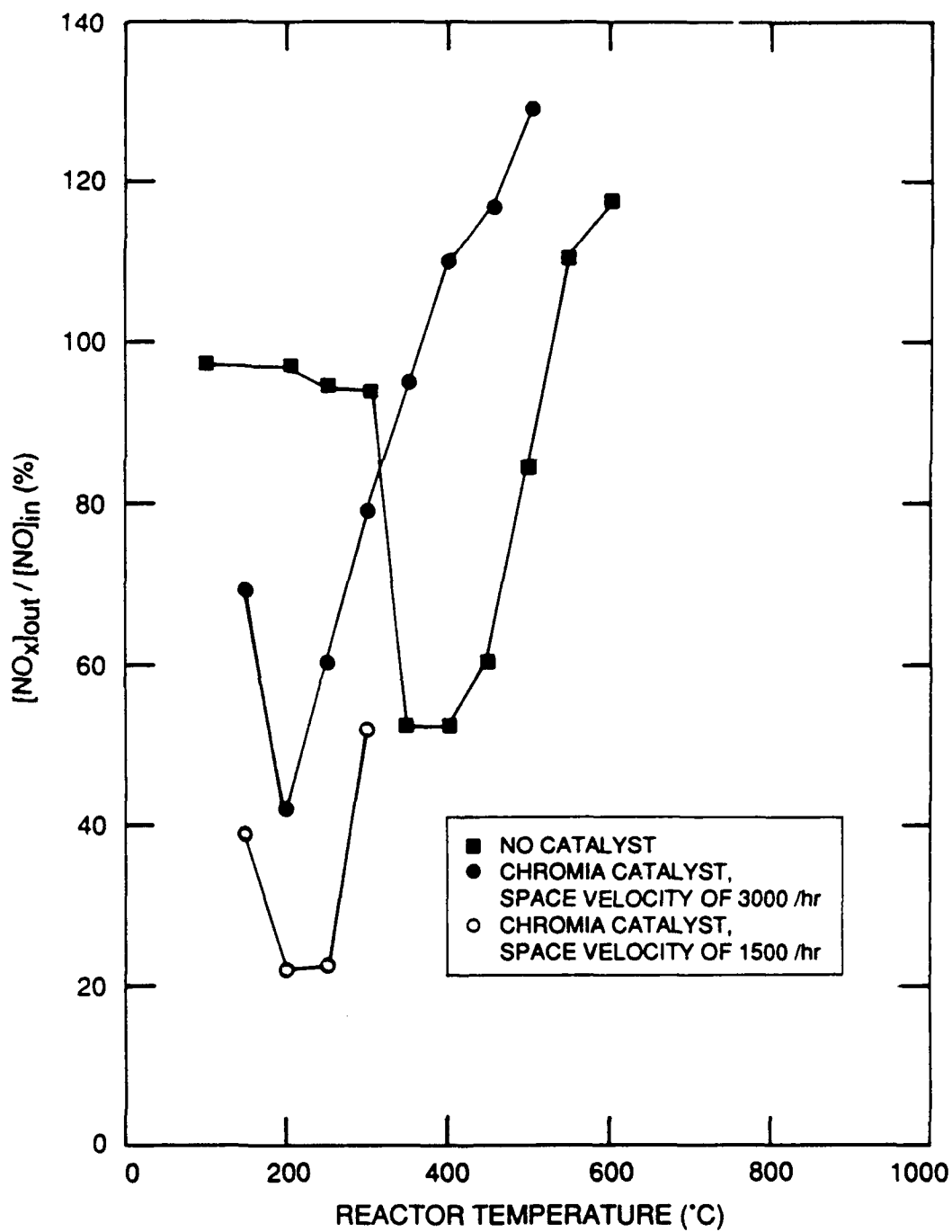
Figure 7
NO_x Reduction for an MMA Additive with No Catalyst and a Chromia
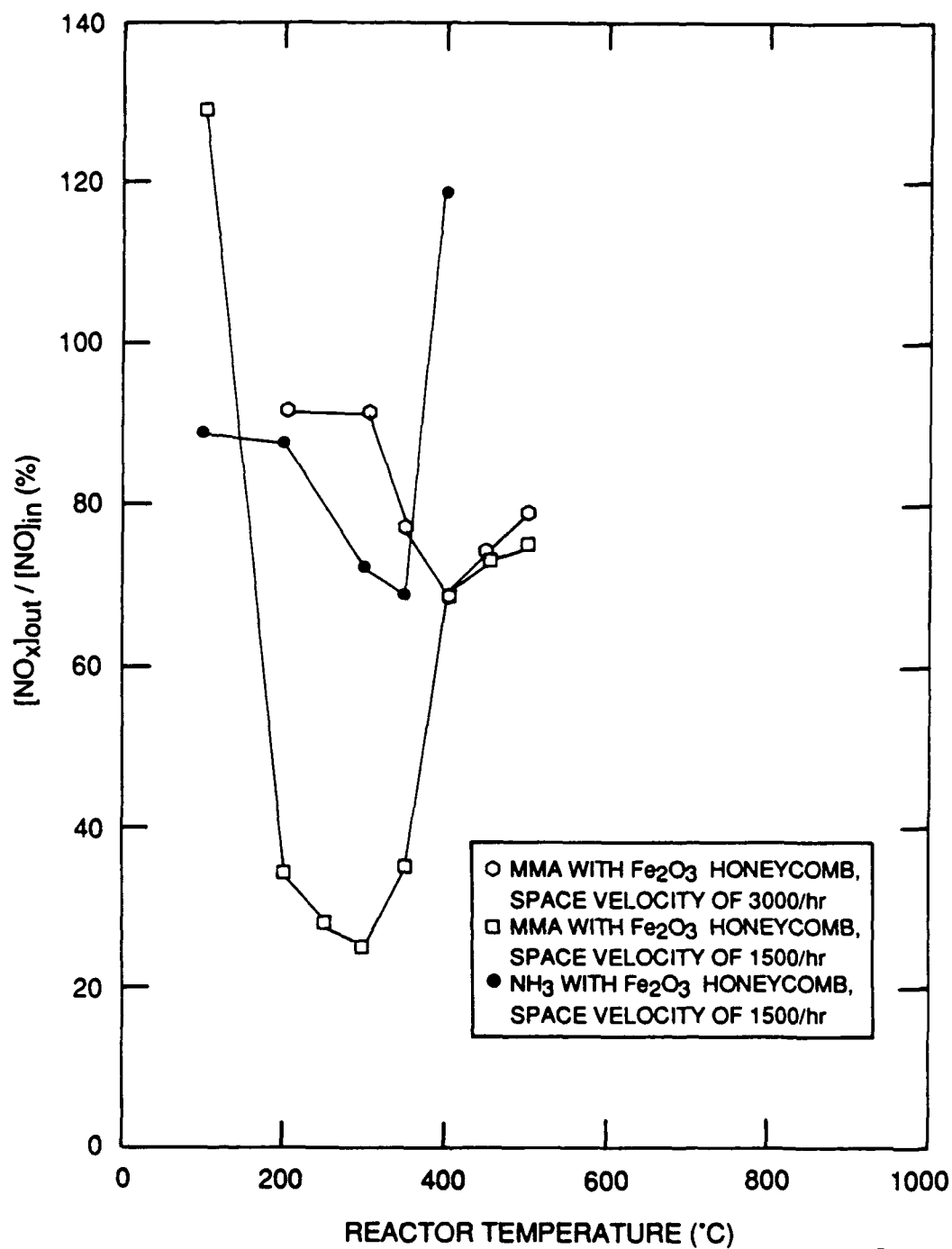Catalyst with Varying Space Velocities

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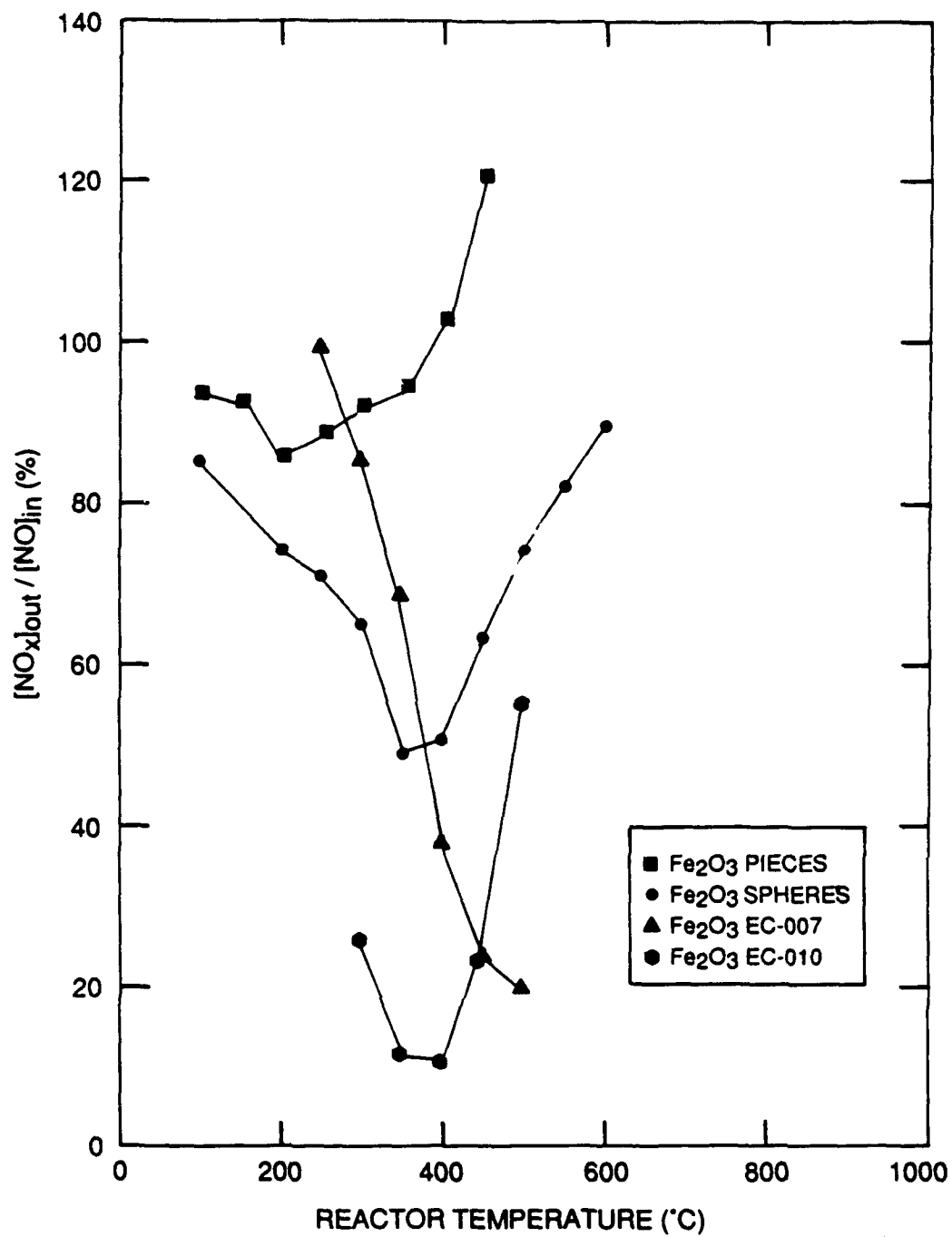
Figure 8
NO$_x$ Reduction for an MMA Additive with Various Iron Oxide Catalysts
with a Constant Space Velocity

An iron oxide was prepared, supported on an alumina honeycomb monolith. Total NO_x reduction for this catalyst with MMA and NH_3 is shown in Figure 9. This catalyst is particularly exciting because honeycomb supports are used in a number of gas stack applications; unlike spheres and large pieces, they cause very little pressure drop in high velocity gas streams. With the MMA additive, this catalyst reduced NO_x by 30 percent at 400°C and a space velocity of 3000/hr. and by 75 percent at 300°C and a space velocity of 1500/hr. It is surprising that halving the space velocity more than quadrupled the amount of NO_x reduction and shifted the temperature of maximum reduction. Also, the hematite on alumina honeycomb catalyst reduced NO_x by only 30 percent with NH_3 at a space velocity of 1500/hr. Figure 4 shows that NH_3 and MMA gave the same amount of NO_x reduction on a chromia catalyst. Figure 9 shows that MMA is much more effective than NH_3 on an iron oxide honeycomb catalyst. The Phase II program will need to study this type of catalyst in-depth. MMA, combined with an iron oxide or iron oxide/chromia catalyst, supported on alumina honeycomb could provide an effective, low cost NO_x reduction process for JETC with a temperature window of 200 to 500°C.

F. CONVERSION OF NO TO NO_2

Since the primary concern is the removal of NO_x, all results so far have been reported as percent NO_x reduction. The NO/NO_x analyzer allows measurement of both NO and total NO_x concentrations, where NO_x is composed mainly of $NO + NO_2$. As shown in Figure 10, in the gas-phase MMA process 90 percent of the NO is removed at 400°C, but only 45 percent of the total NO_x is eliminated. This large difference in the measured values of [NO] and [NO_x] indicates that 45 percent of the NO was apparently reduced to N_2, 45 percent oxidized to NO_2, and 10 percent remained unconverted. For our MMA/chromia catalytic process 60 percent of the NO and total NO_x is removed at 200°C. The measured values of [NO] and [NO_x] are nearly identical. This indicates that 60 percent of the NO was reduced to N_2 and 40 percent remained unconverted.

Figure 9
NO$_x$ Reduction for MMA and NH$_3$ Additives with an Iron Oxide Honeycomb
Catalyst with Varying Space Velocities
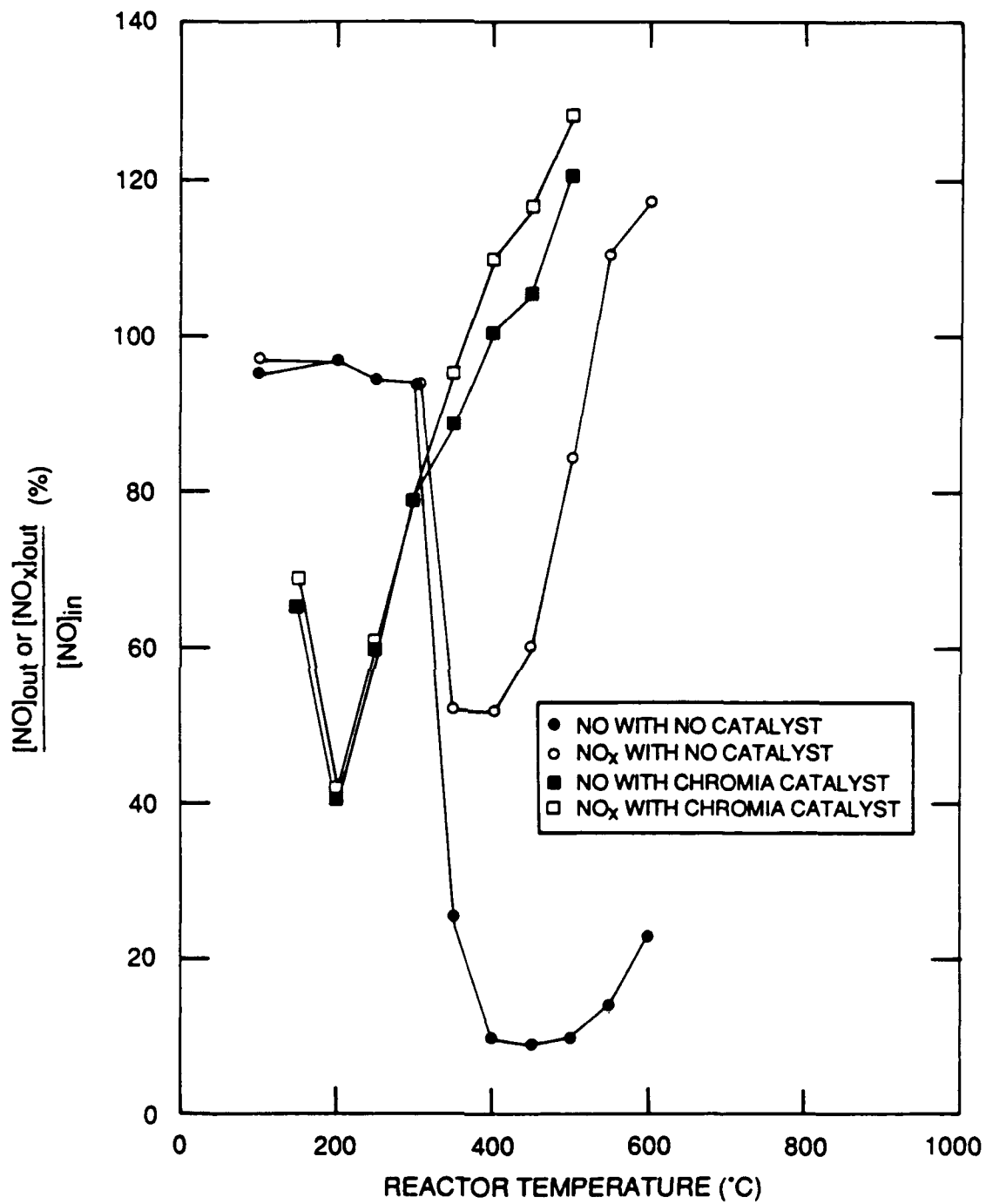
Figure 10
Comparison of NO and Total NO_x Reduction for an MMA Additive with No
Catalyst and with a Chromia Catalyst

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SECTION IV

CONCLUSIONS

The Phase I project tested reactions of four possible NO_x reduction addi-
tives that had not been previously investigated: monomethylamine, dimethyl-
amine, hydrazine, and methylhydrazine. One of the most exciting results of
this project is that the methylamines and methylhydrazine react rapidly to
reduce NO_x in gas phase reactions, with no catalyst, at temperatures as low as
350°C, as shown in Figure 3. This is about 500°C lower in temperature than gas
phase NO_x reduction by ammonia, cyanuric acid, or any other additive reported
so far MMA, in particular, seems most promising. At 400°C 90 percent of the NO
reacted with MMA, with 45 percent apparently reduced to N_2 and 45 percent oxi-
dized to NO_2. This gas-phase chemistry opens up opportunities for improved NO_x
removal processes, since for many applications zones with temperatures above
350°C are accessible for MMA additions. Table 2 shows that water concentration
does not affect gas phase NO_x reduction with MMA, so the augmenter tube of a
JETC may be a viable place for MMA addition. Processes initiated by this gas
phase chemistry can have several advantages over any existing processes, specif-
ically NH_3 based processes. Again, in our experiments, as in all other reported
results, NH_3 does not react with NO at such low temperatures without a catalyst.

In addition to our gas phase process, our catalytic process also looks
promising. MMA and MMH reacted to reduce NO_x by the same amount as ammonia at
temperatures in the 200°C range on a supported chromia catalyst. These results,
shown in Figure 4, indicate that the reaction of MMA with NO is similar to the
reaction of NH_3 with NO and that the rates of these reactions are limited by the
rate of conversion of NO to NO_2 on the catalyst surface (Kiovsky et al., 1980).
MMA gave much better NO_x reduction than NH_3 on our iron oxide supported on
alumina honeycomb catalyst, as we show in Figure 9. This type of catalyst would
be inexpensive and nontoxic and would cause very little pressure drop in high
velocity gas streams.

The low-temperature chemistry initiated by MMA leads to three distinct
advantages for MMA compared to NH_3 in post combustion NO_x reduction processes.

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1. Partial reduction and partial oxidation of NO prior to encountering a
    catalyst can enhance the performance of a SCR process using MMA. This
    behavior can be expected because MMA reacts similarly to NH_3 on a catalyst
    and the NH_3 SCR reaction is limited by NO conversion to NO_2 (Kiovsky
    et al., 1980). NO_2 is the species that reacts with NH_3 on the catalyst.
    Thus, if roughly half of the NO is reduced to N_2 and half oxidized to NO_2
    prior to the catalyst, the requirements for volume and activity of the
    catalyst will be reduced, leading to less expensive, smaller SCR
    processes.

2. NO_2 can be removed along with SO_2 in a wet scrubber, whereas NO cannot be
    washed out. Partial reduction and oxidation of NO by MMA in a duct prior
    to a wet scrubber can therefore enable a simple NO_x removal with no
    catalyst at all. Based on results shown in Figure 10, expect such an
    approach should readily achieve greater than 90 percent NO_x removal.

3. A major problem for NH_3 based SCR processes is formation of $(NH_4)_2SO_4$
    downstream of the process. $(NH_4)_2SO_4$ is formed from unreacted NH_3 and
    SO_3, which forms H_2SO_4 with water. MMA is expected to cause fewer
    problems than NH_3 with $(NH_4)_2SO_4$ deposition for two reasons: (1) since
    NH_3 is not added, NH_3 slip should be less and (2) the gas phase oxidation
    of NO to NO_2 must occur primarily by the reaction $NO + HO_2 = NO_2 + OH$; the
    HO_2 radical that causes this oxidation has been shown to reduce SO_3 to SO_2
    and inhibit H_2SO_4 formation (Lyon, 1989). Although this benefit of less
    NH_4SO_4 deposition has not been demonstrated for MMA, it is predicted,
    based on our results. If $(NH_4)_4SO_4$ deposition can be reduced, then SCR
    processes could be run at lower temperatures with MMA than with NH_3 since
    it is the deposition that presently limits the minimum temperature.

    Another extremely promising aspect of the NO_x removal chemistry initiated
    by MMA is shown in Figures 5 and 6. NO_x can be reduced with a MMA:NO ratio of
    less than 1.0. For the gas-phase process, MMA:NO ratios as low as 0.1 give
    good NO_x reduction. For the catalytic process on chromia, ratios at least as
    low as 0.3 give fair reduction. This result implies that the NO_x removal

chemistry initiated by MMA involves a chain reaction mechanism capable of removing up to 4.5 NO molecules per MMA molecule added. The benefits of using less additive include lower cost, less additive or product carry-over, and less NH_4SO_4 deposition with resulting lower temperatures.

One other aspect of our results will lead to less expensive processes. Since MMA and DMA gave similar reductions, we do not expect any problems operating with commercial grade MMA, which contains some DMA, rather than pure MMA. Commercial grade MMA costs only 30 to 40 percent more per pound than NH_3. Given our results that (1) MMA reacts in the gas phase, (2) MMA reacts at least as well on a catalyst as does NH_3, and (3) the MMA:NO ratio can be lower than 0.3, we expect additive costs for MMA to be about half those for NH_3 to achieve similar removals. Since we have shown that inexpensive catalysts can be used, we expect significant cost reductions for SCR processes using MMA instead of NH_3.

SECTION V

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