Reduction of nitric oxide using metal sulfides
by Richard Henry White

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemical Engineering
Montana State University

Abstract:
Oxides of nitrogen, nitric oxide and nitrogen dioxide, are major pollutants in the atmosphere today, ranking second only in quantity to sulfur dioxide. The principle pollutant of these two is nitric oxide which may be oxidized to form nitrogen dioxide. To date no satisfactory, process has been developed to successfully rid the atmosphere from nitric oxide. This investigation is based on this problem. It is the major objective of this research to reduce nitric oxide by employing metal sulfides. The primary reaction for this approach appears to be: MeS + 4NO -----? MeSO4 + 2N 2 Fifteen metal sulfides were tested to determine the potential for reducing nitric oxide. Of these fifteen, several were found to warrant further study; barium sulfide, bismuth sulfide, cadmium sulfide, calcium sulfide, cuprous sulfide, ferric sulfide, molybdenum disulfde, strontium sulfide and zincs sulfide. Complete reduction of a pure nitric oxide gas stream was achieved at a temperature range of 400°C to 800°C.

After determining the feasibility of reducing nitric oxide with metal sulfides, work was then done to lower the temperature at which reduction of nitric oxide could be accomplished. This was done by mixing several chemical "catalysts" in a four to one, metal sulfide to "catalyst", weight ratio with the various metal sulfides. Reduction was accomplished at lower temperatures, 400° to 550°C, with K3FeF6, K3FeF6/NaCl and NaF being the most promising additives.

A gas mixture containing 2,5% NO and 97°5%. He was then used with the most promising "Catalyst"-metal sulfide combinations. Complete reduction of nitric oxide was again achieved from 500°C to 600°C depending upon the combination employed.

The presence of oxygen and/or water vapor has been found to be detrimental in many processes. To determine the effects of oxygen on this process, a gas mixture of 2.5% NO, 5.0% 02 and 92.5% He was used. The reduction was accomplished from 500°C tp 600°C, thus indicating no detrimental effect due to the presence of oxygen. In runs with water vapor present in the gas, reduction was attained by 500&deg,C, indicating no ill-effects due to the presence of water vapor.

Analysis of the solid product shows that at least 80% of the product is metal sulfate. With this amount of sulfate present, and possibly more, it may be possible to regenerate it back to the corresponding sulfide.

This is desirable to make this process more economical.

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Signature Richard H. White

Date June 4, 1993

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A thesis submitted to the Graduate Faculty in partial
fulfillment of the requirements for the degree

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Chemical Engineering

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August, 1973

ACKNOWLEDMENTS

The author wishes to thank the entire faculty of the Chemical Engineering Department at Montana State University for their encouragement and suggestions. In particular, the author is indebted to Dr. F.P. McCandless, whose direction and assistance aided him in the completion of this project. Also, special thanks must be given to Mr. James Tillery and Mr. Cyrus Huso for their help in constructing and repairing the apparatus used in this study.

Financial support for this study was provided by the Environmental Protection Agency, Grant No. R-800682.

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ABSTRACT

Oxides of nitrogen, nitric oxide and nitrogen dioxide, are major pollutants in the atmosphere today, ranking second only in quantity to sulfur dioxide. The principle pollutant of these two is nitric oxide which may be oxidized to form nitrogen dioxide. To date no satisfactory process has been developed to successfully rid the atmosphere from nitric oxide. This investigation is based on this problem. It is the major objective of this research to reduce nitric oxide by employing metal sulfides. The primary reaction for this approach appears to be:

$$\mathrm{MeS} + 4\mathrm{NO} \longrightarrow \mathrm{MeSO_4} + 2\mathrm{N_2}$$

Fifteen metal sulfides were tested to determine the potential for reducing nitric oxide. Of these fifteen, several were found to warrant further study; barium sulfide, bismuth sulfide, cadmium sulfide, calcium sulfide, cuprous sulfide, ferric sulfide, molybdenum disulfde, strontium sulfide and zinc sulfide. Complete reduction of a pure nitric oxide gas stream was achieved at a temperature range of 400°C to 800°C.

After determining the feasibility of reducing nitric oxide with metal sulfides, work was then done to lower the temperature at which reduction of nitric oxide could be accomplished. This was done by mixing several chemical "catalysts" in a four to one, metal sulfide to "catalyst", weight ratio with the various metal sulfides. Reduction was accomplished at lower temperatures, 400°C to 550°C, with K_3FeF_6, K_3FeF_6/NaCl and NaF being the most promising additives.

A gas mixture containing 2.5% NO and 97.5% He was then used with the most promising "catalyst"-metal sulfide combinations. Complete reduction of nitric oxide was again achieved from 500°C to 600°C depending upon the combination employed.

The presence of oxygen and/or water vapor has been found to be detrimental in many processes. To determine the effects of oxygen on this process, a gas mixture of 2.5% NO, 5.0% O_2 and 92.5% He was used. The reduction was accomplished from 500°C tp 600°C, thus indicating no detrimental effect due to the presence of oxygen. In runs with water vapor present in the gas, reduction was attained by 500°C, indicating no ill-effects due to the presence of water vapor.

Analysis of the solid product shows that at least 80% of the product is metal sulfate. With this amount of sulfate present, and possibly more, it may be possible to regenerate it back to the corresponding sulfide. This is desirable to make this process more economical.

INTRODUCTION

Oxides of nitrogen are currently one of the major air pollutants. The two oxides, NO (nitric oxide) and NO_2 (nitrogen dioxide), are commonly grouped together as NO_x and are emitted to the atmosphere in excess of eight million tons per year. This rate is about one third that of SO_2 (sulfur dioxide) which was the first target for the control of gaseous pollutants.[2]

The control of NO_x is necessary because they are the major reactants in photochemical smog. NO and NO_2 are easily interconverted in the atmosphere and their ratio changes with the time of day, depending upon the action of sunlight, oxygen and other reducing and oxidizing agents that may be present. The formation of smog under adverse conditions was found to be strongly influenced by these reactions. The participation of NO_x in smog reactions was established in 1952.[1]

Oxides of nitrogen are objectionable for two main reasons; 1) the brownish color that NO_2 gives the atmosphere and 2) they tend to promote the formation of various eye-irritating compounds such as formaldehyde, acrolein and a group of plant poisons (peroxyacyl nitrates).[2]

Nitrogen oxides are formed in all combustion processes involving air. Sources of NO_x fall into three major categories: mobile, stationary combustion and chemical sources. Included in mobile sources are gasoline, diesel and gas turbine engines. Power plants using coal, oil and gas, industrial boiling incinerators, home heating systems, and home appliances comprise the stationary combustion sources. Chemical sources are mainly plants where nitric acid is produced or used and where metallurgical or high temperature processes are employed.[2]

These groups emit NO_x in varying amounts and concentrations. Concentrations range from a few hundred to several thousand parts per million. The high concentrations are generally emitted in small amounts, whereas the lower concentrations are given off in larger quantities.[1]

Nearly all NO_x is formed initially as NO, not NO_2. NO is unreactive at ambient conditions, but can be easily oxidized to NO_2 with time and energy. Most processes for removal of NO_x are not effective for NO in the absence of NO_2.[1]

Several techniques for NO_x emission control fall into two main categories: 1)chemical decomposition or physical removal and 2) minimizing the formation of NO_x through modification of combustion processes.[2]

Processes for abatement of NO_x generally concern one of three techniques: 1) the thermal or catalytic decomposition of NO to O_2 (oxygen) and N_2 (nitrogen), 2) the chemical reduction of NO, thus producing N_2 and/or N_2O (nitrous oxide),[3] and 3) the complete removal of NO by physical or chemical absorption.[1]

PREVIOUS WORK

Work has been done regarding heterogeneous decomposition of NO. The decomposition of NO is thermodynamically favorable at temperatures below 1000°K, but it appears that the activation energy of NO is quite high ($\approx$90 Kcal/mole) thus kinetically limiting reactions with NO. Catalysts have been found that reduce this activation energy substantially, but the rates of reaction remain low, thus indicating that the pre-exponential factor in the rate constant is low. These decomposition rates are far too low to be of any practical application for the decomposition of NO formed in various combustion processes.[3]

The heterogeneous reduction of NO has also been studied employing a large number of catalysts with a variety of common reducing agents, such as carbon monoxide, hydrogen[3], and several hydrocarbons.[4] In reducing conditions a variety of catalysts and reducing agents were successfully employed to remove NO at the high space velocities and moderate temperatures occurring in practice. However, in the presence of excess O_2, the reaction was detered due to an undesirable influence on some catalysts.[3]

Favorable results have been obtained using NH_3 (ammonia) in the heterogeneous reduction of NO. NH_3 is selective toward the reduction of NO in an oxygen atmosphere and a narrow span of temperatures less than 350°C, with the optimum being about 250°C. At higher temperatures the NH_3 will oxidize to form NO_x. Reduction of NO with NH_3 has been practiced to a limited and unsuccessful extent however.[3]

Methods for absorbing the NO in stack gases from stationary sources are desirable, but there is no system commercially available. This is so because all absorbents currently available have a low capacity for NO, thus requiring vessels of enormous size to achieve separation. Aqueous absorption systems using alkaline solutions or sulfuric acid appear to be most promising for NO abatement. However, using such a process requires the feed gas to have equimolar concentrations of NO and NO_2 because the absorption of the combined oxide, N_2O_3, is most favorable.[1]

REDUCTION WITH METAL SULFIDES

Since there is a need for the reduction of NO and no processes have yet been perfected that accomplish this reduction, it is the purpose of this research to develop a suitable method for NO abatement. The approach taken in this investigation is to employ metal sulfides to chemically reduce NO to N_2.

Research has been done using CaS (calcium sulfide) to reduce SO_2. Based on the success of this work, the reduction of NO using metal sulfides is hypothesized.

A thermodynamic study was made to determine the feasibility of this approach to the problem. The results of this study are summarized in Table I.

Upon careful investigation of the free energy changes in Table I, it is evident that the reduction of NO with metal sulfides is thermodynamically feasible over a range of temperatures including practical operat-

Table I Free Energy Changes and Heats of Reaction for the Reduction of NO employing Metal Sulfides

General Reaction: $MeS + 4NO \longrightarrow MeSO_4 + 2N_2$

Metal Sulfide	Free Energy Change (Kcal/mole) 298°K	500°K	1000°K	1500°K	Heat of Reaction (Kcal/mole) 298°K
Calcium sulfide	-284.4	-264.6	-215.7	-166.8	-313.5
Cadmium sulfide	-245.3	-226.3	-179.3	-132.3	-273.3
Cobalt sulfide	-229.4	-209.5	-160.2	-110.9	-258.8
Cupric sulfide	-220.5	-199.6	-147.7	-95.8	-251.4
Cuprous sulfide	-254.7	-235.2	-187.0	-138.8	-283.4
Lead sulfide	-261.5	-241.0	-190.1	-139.2	-291.8
Molybdenum sulfide	-208.7	-190.2	-144.5	-98.8	-235.9
Mercuric sulfide	-209.9	-190.9	-143.9	-96.9	-237.9
Silver sulfide	-220.5	-200.9	-152.5	-104.1	-249.3
Tin sulfide	-220.7	-201.0	-152.0	-103.0	-249.9
Zinc sulfide	-243.8	-224.9	-178.0	-131.1	-271.8

ing temperatures. The reactions listed are all highly exothermic, thus indicating the possibility of difficulty in controlling the temperature of the reaction.

Another reason for this approach to the reduction of NO is the possibility of regenerating the metal sulfate produced during the reaction to its corresponding sulfide. Research has been done with success in regenerating calcium sulfate back to calcium sulfide.[6]

Therefore, based on the thermodynamic feasibility of NO reduction with metal sulfides, the success of SO_2 reduction with calcium sulfide and the possibility of sulfate regeneration, research is justified in investigating the reduction of NO employing metal sulfides.

OBJECTIVES

The primary objective of this research was to determine if NO could be reduced by employing metal sulfides. Provided this reduction was possible at moderate conditions, secondary objectives were established. These objectives included; 1) promoting the reaction at lower temperatures, 2) determination if the reaction occurred with dilute NO gas streams and 3) determination if a detrimental effect was caused by the presence of oxygen and/or water vapor. A final objective was to determine the approximate composition of the solid product at the completion of the reaction, thus indicating the possibility of regeneration.

APPARATUS

A schematic diagram of the apparatus used in this research is shown in Figure 1. The feed gas from a high pressure cylinder was passed through a rotameter where the flow rate of the gas was regulated. The feed stream then entered the bottom of the reactor and passed through the first section which was a gas preheat chamber. The gas then entered the reaction chamber where the powdered metal sulfide was located. After reacting, the product gas passed through the top of the reactor and through a cooling unit. At the exit of the cooling unit samples were periodically taken with a gas-tight syringe through a silicone rubber sampling septum. The remainder of the exit gas passed through a water scrubber and then was vented to a hood.

A detailed diagram of the reactor cross-section is presented in Figure 2. The reactor was constructed from an 18-inch piece of schedule 40 stainless steel pipe. The bottom 12 inches served as a gas preheating chamber and was packed with stainless steel wire rings to increase heat transfer. A stainless steel porous disc separated the preheating chamber from the 6-inch reaction chamber. A second stainless steel disc was mounted at the top of the reactor to eliminate the possibility of losing the metal sulfide with the gas stream. Mounted axially in the reactor was a thermowell which provided for the continual monitoring of the temperature at three locations in the reaction chamber.

When in operation, the reactor was mounted in a tubular bronze fur-

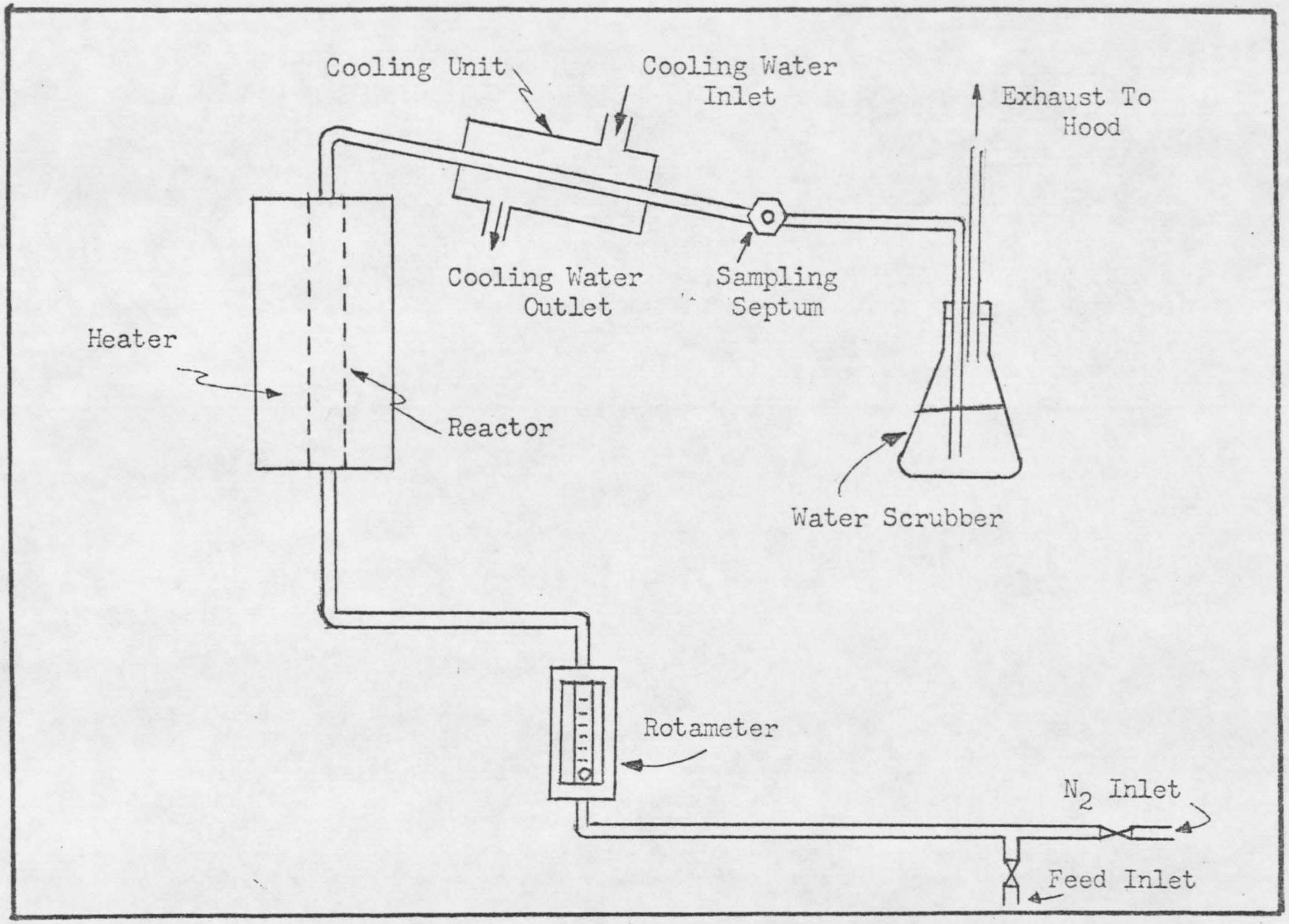

Figure 1. Schematic diagram of apparatus for NO reduction.

nace. The bronze cylinder was wrapped with three nichrome wire heating coils that were connected to variable transformer controllers.

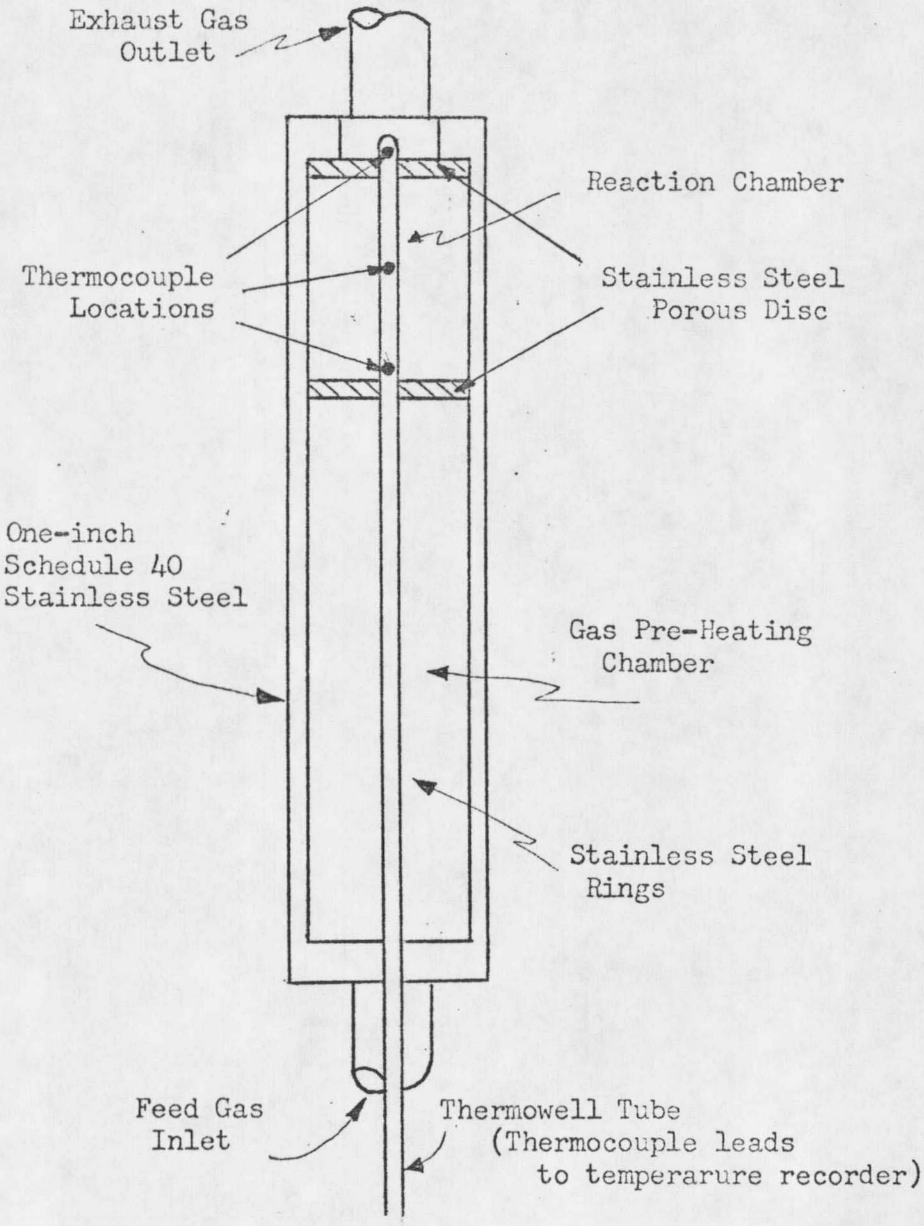

Figure 2. Reactor cross-section.

PROCEDURE

A two gram sample of metal sulfide was placed in the reaction chamber. The system was assembled and purged with nitrogen to check for possible leaks. When safety was assured, the feed stream was introduced to the system. After reaching steady state, the power to the heating elements was turned on. With the temperature of the reaction chamber continually monitored, samples of the exit gas were taken at 50 C° intervals and analyzed by gas chromatography. Two columns were used to analyze for NO, N_2, N_2O and SO_2. The conditions for these columns are presented in the appendix. The temperature at which the reaction initiated, where nitrogen was first formed, and the temperature where the reaction was complete, when nitric oxide was no longer detected, were noted and recorded. When the reaction was complete, the heaters were turned off and the system was again purged with nitrogen. When the reactor was cool it was opened and the solid product was weighed and tested for the presence of sulfate ion by barium sulfate precipitation.

In runs where chemicals were added to the metal sulfide in an attempt to lower the reaction temperature, the sulfide and the added chemical were mixed intimately using a mortar and pestle. The composition of the mixture was 20 weight per cent additive and 80 per cent metal sulfide. The same experimental procedure was followed as for runs with only the metal sulfide.

All runs were made using the above proceedure with the exception of those made with water vapor in the feed stream. In this case the feed from the cylinder was bubbled through a water reservoir before entering the rotameter. The remainder of the procedure was the same as stated above.

In the runs made to determine the amount of metal sulfate present in the solid product, modifications were made in the procedure. The sample of metal sulfide was only 0.5 grams and a lower gas flow rate was used. This was so in an attempt to react as much of the metal sulfide as possible. For these runs, the reactor was kept running continually at temperatures from 450°C to 700°C for periods up to ten days. The solid was analyzed using the barium sulfate precipitation procedure described in the appendix.

RESULTS AND DISCUSSION

PRELIMINARY TESTS

To further verify the feasibility of NO reduction employing metal sulfides, several runs were made with various metal sulfides. In these runs the temperature at which N_2 first formed and the temperature where NO was no longer present were determined. This procedure was used to find at what temperatures the reduction of NO appeared to initiate and conclude with each of the sulfides tested. At the conclusion of each run, the solid product in the reactor was weighed. The weight change gave an indication as to whether or not the desired reaction, oxidation of the sulfide to the corresponding sulfate, was occurring. A weight loss indicates that unknown competing side reactions may be proceeding at a greater rate than the desired oxidation. A gain in sample weight, however, indicates that the reaction to the sulfate may be proceeding.

Table II presents the results of these preliminary studies with fifteen metal sulfides. The temperature of initial conversion to N_2, the temperature where NO was no longer detected and the weight change in the solid product are shown.

From the data presented in Table II it is evident that the complete reduction of NO using metal sulfides is feasible over a temperature range of 400°C to 800°C.

Several of these sulfides were eliminated from further consideration for various reasons. Those sulfides such as aluminum sulfide, antimony trisulfide, cupric sulfide and tungsten disulfide were eliminated because

Table II

Reaction Temperatures and Weight Changes for Preliminary Tests

Metal Sulfide	Initial Conversion	100% Conversion	Weight Change
Aluminum sulfide	250°C	400°C	loss
Antimony trisulfide	200°C	550°C	loss
Barium sulfide	475°C	600°C	gain
Bismuth sulfide	350°C	600°C	loss
Cadmium sulfide	650°C	800°C	gain
Calcium sulfide	400°C	550°C	gain
Cupric sulfide	250°C	500°C	loss
Cuprous sulfide	450°C	700°C	gain
Ferric sulfide	300°C	525°C	loss
Lead sulfide	250°C	550°C	gain
Molybdenum disulfide	400°C	500°C	loss
Strontium sulfide	400°C	650°C	loss
Sulfurated potash	100°C	450°C	?
Tungsten disulfide	250°C	500°C	loss
Zinc sulfide	550°C	800°C	gain

of the loss in weight of the solid sample. These losses indicate that the desired reaction may not be occurring to a great extent. Lead sulfide was not considered further because as the temperature increased during the run, the flow of gas through the reactor was restricted. In the case of sulfurated potash, at the conclusion of the run the solid residue in the reactor could not be removed to be weighed. The solid caked severely and it was necessary to wash the solid out with hot water, thus making it impossible to determine the change in weight. It is because of this severe caking that sulfurated potash was no longer tested. The remaining metal sulfides were then tested with various chemicals added to attempt to lower the temperature at which the reduction of NO would proceed.

RUNS WITH "CATALYSTS"

The metal sulfides that exhibited promise while run by themselves were subsequently tested with a variety of "catalysts" in an attempt to lower the temperature for NO reduction. These "catalysts" were chemicals that were physically mixed with the metal sulfides. The term "catalyst" is used because it is not known whether these chemicals simply promote the reaction of NO with the sulfides or whether they take part in the reaction themselves. If they participate in the reaction and are consumed or chemically altered they can not be designated as catalysts.

In all runs with these "catalysts", they were intimately mixed with the powdered metal sulfide using a mortar and pestle. The "catalyst" was present in the mixture at twenty weight per cent.

The first "catalyst" tested was K_3FeF_6 (potassium ferric fluoride). Table III summarizes the results obtained with K_3FeF_6.

Table III

NO Reduction with K_3FeF_6 as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	350°C	700°C	200°C	gain
Bismuth sulfide	350°C	---	450°C	loss
Cadmium sulfide	350°C	---	350°C	loss
Calcium sulfide	---	400°C	---	gain
Cuprous sulfide	250°C	550°C	300°C	gain
Ferric sulfide	200°C	600°C	250°C	gain
Molybdenum disulfide	300°C	450°C	300°C	loss
Strontium sulfide	200°C	500°C	200°C	gain
Zinc sulfide	500°C	700°C	500°C	loss

It was discovered in this series of runs that a second gaseous product was formed, N_2O (nitrous oxide). The formation of N_2O has also been observed during chemisorption in the heterogeneous catalytic reduction of NO.[3] The temperature where N_2O was initially formed is shown in

Table III. The N_2O was never present in large amounts and was usually no longer detectable at temperatures near 600°C.

In all cases with K_3FeF_6 added, the temperature for initial reduction of NO was decreased and in all but the barium sulfide run, the temperature for 100% conversion was lowered. During the run made with cuprous sulfide, SO_2 was produced near the end of the run. This is undesirable, not only because SO_2 is also an air pollutant, but because the SO_2 was produced before complete reduction of NO was achieved. If complete reduction of NO had been accomplished before SO_2 formation, it may have been possible to control temperature well enough to curtail the undesirable formation of SO_2 and still reduce NO.

The next additive tested was CuCl (cupric chloride). Only a few of the metal sulfides ran with K_3FeF_6 were chosen to provide a comparison between the effects of CuCl and K_3FeF_6. These results are presented in Table IV.

Table IV

NO Reduction with CuCl as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Cadmium sulfide	300°C	—	300°C	loss
Calcium sulfide	—	450°C	—	gain
Cuprous sulfide	350°C	—	350°C	loss
Ferric sulfide	100°C	—	100°C	loss
Molybdenum disulfide	350°C	550°C	350°C	gain

Comparing the data from Tables III and IV, it appears that better results, lower temperatures for NO reduction, are obtained using K_3FeF_6 rather than CuCl as a "catalyst". The only exception to this is in the case of ferric sulfide. However, in the ferric sulfide run SO_2 was produced, thus negating the effect of the CuCl on the temperature for NO reduction.

CaCl (calcium chloride) was the next "catalyst" candidate. Again, only a few metal sulfides were tested to provide a comparison between CaCl and K_3FeF_6. Table V presents the results of these tests.

Table V

NO Reduction with CaCl as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	300°C	600°C	200°C	gain
Calcium sulfide	400°C	650°C	250°C	gain
Ferric sulfide	250°C	550°C	150°C	no change

Comparing these results with those in Table III, there appears to be no significant difference between the results obtained with K_3FeF_6 and CaCl. Again in the run with ferric sulfide, SO_2 was produced. This further indicates the possible undesirability of ferric sulfide.

Next to be tested as a "catalyst" was NiCl (nickel chloride). As before, several metal sulfides were run to provide a comparison with the results obtained using K_3FeF_6. These data are shown in Table VI.

Table VI

NO Reduction with NiCl as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	300°C	—	100°C	gain
Cadmium sulfide	250°C	—	100°C	no change
Calcium sulfide	—	450°C	—	gain
Cuprous sulfide	400°C	—	100°C	loss
Ferric sulfide	200°C	550°C	50°C	loss

With respect to N_2 formation, there is no significant difference between the results with NiCl and K_3FeF_6, however with NiCl as "catalyst", SO_2 was observed in the runs with cadmium sulfide and ferric sulfide. This was the third occurrance for the formation of SO_2 with ferric sulfide. For this reason ferric sulfide was no longer considered.

Upon examining the data presented in Tables III through VI, three metal sulfides were selected to be tested further with more possible "catalysts". These were barium sulfide, cadmium sulfide and calcium sulfide. These were selected because their temperatures for NO reduction were predominantly lower than those for the other metal sulfides and because the problem of SO_2 formation was not likely.

The next three "catalysts" tested were salts of sodium; NaCl (sodium chloride), NaF (sodium fluoride), and NaI (sodium iodide). The results of these runs are presented in Tables VII, VIII and IX. In all of these runs, the only reaction that appeared to have better results than those with K_3FeF_6 was the barium sulfide run with NaF. The temperature for initial conversion was only 50 C° (300°C) lower than that with K_3FeF_6, but the temperature for 100% conversion was only 450°C compared to 700°C with K_3FeF_6.

Table VII

NO Reduction with NaCl as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	450°C	650°C	400°C	gain
Cadmium sulfide	600°C	—	none formed	no change
Calcium sulfide	450°C	700°C	300°C	gain

Table VIII

NO Reduction with NaF as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	300°C	450°C	250°C	gain
Cadmium sulfide	450°C	—	350°C	gain
Calcium sulfide	400°C	—	250°C	gain

Table IX

NO Reduction with NaI as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	400°C	—	250°C	gain
Cadmium sulfide	500°C	—	500°C	gain
Calcium sulfide	400°C	650°C	250°C	gain

The final additive tested with these three sulfides was a combination of two previously tested "catalysts"; K_3FeF_6 and NaCl. The composition of this mixture was 50-50 weight per cent. The mixture was used to determine if a combination of "catalysts" would have a significant effect on NO reduction. Table X summarizes the results obtained from these tests.

Table X

NO Reduction with a 50-50 Mixture of
K_3FeF_6 and NaCl as "Catalyst"

Metal Sulfide	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Barium sulfide	350°C	450°C	250°C	gain
Cadmium sulfide	450°C	—	150°C	no change
Calcium sulfide	300°C	550°C	250°C	gain

It appears that the mixture does not have a significant effect, in fact the results are similar to those obtained with K_3FeF_6 alone, with respect to temperatures of initial N_2 formation.

Upon careful examination of Tables III through X, four promising combinations of metal sulfides with "catalysts" were decided upon to consider for further study. These combinations and their results are shown in Table XI. These combinations were then run with dilute NO gas feed to determine if they were still effective.

Table XI

Most Promising Metal Sulfide and "Catalyst" Combinations for NO Reduction

Metal Sulfide/"Catalyst"	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Calcium sulfide/K_3FeF_6	--	400°C	--	gain
Calcium sulfide/K_3FeF_6&NaCl	300°C	550°C	250°C	gain
Barium sulfide/NaF	300°C	450°C	250°C	gain
Barium sulfide/K_3FeF_6&NaCl	350°C	450°C	200°C	gain

RUNS WITH DILUTE NO

Since effluent gas streams are not pure NO, further studies were made with a dilute NO feed. A mixture of 2.5% NO and 97.5% He (helium) was used for this phase of the study. He was selected as the second component of the gas mixture because of its inertness and because it did not interfere with the chromatographic analysis. Dilute runs were made with the four combinations of metal sulfides and "catalysts" presented in Table XI and the data for these runs is shown in Table XII.

Table XII

Reduction of a 2.5% NO Feed Stream

Metal Sulfide/"Catalyst"	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Calcium sulfide/K_3FeF_6	150°C	600°C	50°C	gain
Calcium sulfide/K_3FeF_6&NaCl	200°C	600°C	100°C	gain
Barium sulfide/NaF	150°C	550°C	100°C	gain
Barium sulfide/K_3FeF_6&NaCl	200°C	600°C	100°C	gain

These data are significantly different from the results in Table XI. These discrepancies can be explained by a change in analytical procedure for the exit gas. For the runs made with the dilute NO, the attenuation on the gas chromatograph was lower than that for runs using pure NO. This was necessary to detect the lower concentration of NO in the feed gas. As a result, the gas chromatograph was more sensitive and therefore indicated a lower temperature for initial conversion; for N_2O as well as N_2. Also as result of the higher sensitivity of the gas chromatograph, the temperature of 100% conversion of NO appears higher than that observed with pure NO. This is expected because the gas chromatograph was capable of detecting lower concentrations of NO; therefore until all NO was reduced, NO was still detected.

Of the two conflicting sets of data, it appears that those for the dilute NO runs are the most accurate. This conclusion is based on the fact that with the increased sensitivity of the gas chromatograph, more precise measurement of the presence of N_2 or the absence of NO are possible.

After determining that the reduction of dilute streams of NO was possible, runs were made in an oxidizing atmosphere and with water vapor present in the gas mixture.

RUNS WITH OXYGEN AND WATER VAPOR

To further simulate actual conditions in an effluent gas stream, experimental runs were made with a gas composition of 2.5% NO, 5.0% O_2, and 92.5% He. Only two of the previously tested metal sulfide and "catalyst" mixtures were run with this gas composition; calcium sulfide/K_3FeF_6 and calcium sulfide/K_3FeF_6&NaCl. The results of these two runs are in Table XIII. These data do not indicate a significant difference from the runs made without oxygen present. However, toward the end of the runs with oxygen, the relative amounts of N_2 and NO in the exit gas decreased. This indicates the possible formation of another gaseous product, possibly NO_2. At these elevated temperatures it is possible that some NO and O_2 reacted to form NO_2, which is undesirable. It was not possible to positively determine the presence or absence of NO_2 due to the lack of suitable analytical techniques. At the time of this research a satisfactory method of analyzing for NO_2 was not available. From the runs made it appears that the reduction of NO was accomplished in an oxidizing atmosphere, but it was not determined if NO was also oxidized.

Table XIII

Reduction of NO in an Oxidizing Atmosphere

Metal Sulfide/"Catalyst"	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Calcium sulfide/K_3FeF_6	250°C	600°C	100°C	gain
Calcium sulfide/K_3FeF_6&NaCl	250°C	500°C	50°C	gain

A final set of runs was made with the two combinations used for the runs with oxygen. The gas composition for this set of runs was: 2.4% NO, 4.9% O_2, 90.0% He and 2.7% water vapor. The purpose of these runs was to determine the effects of the presence of water vapor on the reduction of NO. Table XIV presents the results of this work. These results are similar to those obtained in the oxygen runs, thus indicating no significant effects due to the presence of water vapor. In these runs also, the possibility exists for NO_2 formation.

Table XIV

Reduction of NO in an Oxidizing Atmosphere with Water Vapor Present

Metal Sulfide/"Catalyst"	N_2 Initial Conversion	NO 100% Conversion	N_2O Formation	Weight Change
Calcium sulfide/K_3FeF_6	200°C	500°C	50°C	gain
Calcium sulfide/K_3FeF_6&NaCl	200°C	500°C	100°C	gain

DETERMINATION OF SOLID PRODUCT COMPOSITION

The solid product of the reduction of NO with metal sulfides has been assumed to be the corresponding metal sulfates. To verify this assumption, two runs were made to determine the composition of the solid after extended run-times at elevated temperatures with pure NO.

The first run lasted nine days with the reactor operating continuously at temperatures between 400°C and 700°C yielding a solid product consisting of 87.24% calcium sulfate. A second run was made lasting eight days at temperatures from 450°C to 700°C giving a solid product that was 81.56% calcium sulfate. Both runs were terminated while N_2 was still being produced because the apparent rate of N_2 formation was slow. A possible reason for the slow reaction rate to N_2 may be poor diffusion of NO through the calcium sulfide bed resulting in limited contact between the solid and the gas. Also, as the reaction to calcium sulfate proceeds, a layer of calcium sulfate may form around the sulfide particle causing slow diffusion of the NO to the unreacted sulfide, thus reducing the reaction rate.

It is apparent from these runs that at least 80% of the solid product is sulfate. With this composition it may be feasible to regenerate the sulfate to the sulfide, thus reducing the requirement for the fresh sulfide substantially.

CONCLUSIONS

1. Reduction of nitric oxide was achieved with a variety of metal sulfides. The sulfides capable of reducing nitric oxide are: aluminum sulfide, antimony trisulfide, barium sulfide, bismuth sulfide, cadmium sulfide, calcium sulfide, cupric sulfide, cuprous sulfide, ferric sulfide, lead sulfide, molybdenum sulfide, strontium sulfide, sulfurated potash, tungsten disulfide and zinc sulfide. Complete reduction was attained over a temperature range of 400°C to 800°C.
2. The temperature for the reduction of nitric oxide was successfully lowered by the addition of various chemicals as "catalysts". The temperature range attained was from 400°C to 550°C. The degree to which the temperatures were lowered varied with "catalyst". The most promising additives are K_3FeF_6, K_3FeF_6 and NaCl, and NaF.
3. Using a gas mixture of 2.5% NO and 97.5% He, complete reduction of NO was again attained. The temperature for initial conversion being about 200°C and for 100% conversion, 500°C to 600°C depending upon the metal sulfide-"catalyst" combination employed.
4. With a gas composed of 2.5% NO, 5.0% O_2 and 92.5% He, reduction of NO was again achieved. This reduction occurred initially at 250°C and was complete between 500°C and 600°C. The presence of O_2 did not appear to have a detrimental effect upon the NO reduction reaction.
5. With a gas composition of 2.4% NO, 4.9% O_2, 90.0% He and 2.7% water

vapor, reduction of NO occurred initially at 200°C and was complete by 500°C. The presence of water vapor did not appear to deter the reduction of NO.

6. The solid product of the reduction of NO with calcium sulfide was determined to be at least 80 weight per cent calcium sulfate. The possibility therefore exists for the solid residue to be regenerated to calcium sulfide which may in turn be reused for the reduction of NO.

RECOMMENDATIONS

Several questions remain unanswered with respect to the reduction of nitric oxide by employing metal sulfides.

Although work has been done with a gas stream containing oxygen and water vapor, it is necessary to do more work with more components in the gas. Such compounds as carbon monoxide, carbon dioxide, and perhaps some hydrocarbons should be used to determine if any of these have a detrimental effect on the reduction of nitric oxide with metal sulfides.

To carry out the above properly, a more complete method for gas analysis must be devised. In particular, a procedure for the determination of the presence of nitrogen dioxide should be developed. This is necessary because nitrogen dioxide is one of the pollutants that this method must eliminate to be successful.

Further analysis of the solid product of this reaction should be made. Work should be done to determine exactly how much metal sulfate can be produced. Careful monitoring of the weight changes in the solid during the reaction should be made in an attempt to determine the mechanism for this reduction reaction. From this analysis it may be possible to determine whether the chemicals mixed with the metal sulfides actually take part in the reaction or whether they are actually catalytically promoting the reaction.

Upon completion of this work, an economic study of this process should be made to determine the cost of such an operation. Included in this study should be the cost for regeneration of the metal sulfate to the corresponding metal sulfide.

APPENDICES

COLUMN CONDITIONS

COLUMN 1 (Internal) : 12' x 1/8" stainless steel packed with Porapak Q-S
Gases Analyzed : N_2O and SO_2
Temperature : 130°C
Helium carrier gas flow rate : 10 cc./min.

COLUMN 2 (External) : 25' x 1/8" stainless steel packed with Porapak Q
Gases analyzed : NO and N_2
Column temperature : 0°C
Detector temperature : 130°C
Helium carrier gas flow rate : 10 cc./min.

ANALYSIS FOR SULFATE

The solid product was analyzed for calcium sulfate by using barium sulfate precipitation. This procedure was used to determine the composition of the solid product of the reduction of nitric oxide.

To begin the procedure, weigh a $\frac{1}{2}$-gram sample into a 250-ml beaker. All samples were weighed on a Metler Analytical Balance which could be easily read to 0.0001 gram with little difficulty. Next, add 150 ml of distilled water and 10 ml of concentrated hydrochloric acid to the beaker. Heat the solution to boiling, and boil the solution gently for one hour to eliminate all sulfide present as hydrogen sulfide. When this is complete, remove the beaker from the heat and let it cool. Filter the cooled solution through a retentive paper into a 400-ml beaker. Wash the insoluble residue with distilled water, then discard it.

Add few drops of methyl orange indicator to the filtrate. If the solution is not already neutralized to a yellow color, add enough 6 N ammonium hydroxide to do so. Titrate back with concentrated hydrochloric acid to a red color, then add 12 drops in excess. Precipitate barium sulfate by slowly adding about 15 ml of 10 per cent barium chloride solution.

The barium sulfate precipitate is a finely formed particle, almost invisible to the naked eye. To give these a chance to grow larger, one must digest the precipitate by heating the solution to near boiling temperatures for about one hour. At the end of digestion, the solution above the precipitate should be quite clear. Test for complete precipitation by adding a few drops of 10 per cent barium chloride. If the precipitate is stirred up, it should settle again in a minute or so if the solution is completely digested.

After the solution has cooled, filter it. Wash the precipitate carefully. Again check the filtrate for complete precipitation. Carefully lift each paper with its precipitate from the filtering apparatus and press it gently into a weighed crucuble. Set the crucible on a clay triangle and tilt it at about a 45-degree angle. Heat it with a very small flame so as to dry the paper smoothly without spurting. Char the paper without it having burning with a flame. Have a crucible cover and tongs handy so that if a flame starts in the crucible it can be extinguished by covering the crucible for a moment. When the paper is all carbonized, turn the burner on full and heat the crucible to redness. Keep the crucible tilted to give adequate circulation of air in it. Gradually the carbon will burn off, glowing red as it does. When all carbon is gone, heat the crucible for an additional 10 minutes. Cool the crucible in a desiccator. Weigh it after it has cooled. The weight per cent of the sulfate ion is given by:

$$\frac{\text{Weight } BaSO_4 \text{ x } 0.41158}{\text{Weight of sample}} \text{ X } 100 = \text{Weight \% Sulfate ion}$$

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