



Rate of reaction of nitric oxide by calcium sulfide on high surface area supports
by John Carl McIntyre

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
Montana State University
© Copyright by John Carl McIntyre (1974)

Abstract:

Oxides of nitrogen are one of the major air pollutants in the United States today. Because of the kinetics, most of the oxides of nitrogen are emitted in the form NO, which is converted into NO₂ at equilibrium.

NO and NO₂ are both harmful in themselves, and have been linked to other harmful constituents of smog.

Previous work has shown that calcium sulfide is a good reducing agent for NO. Therefore this research, was performed to study the rate of the following reaction; (Formula not captured by OCR) where CaS was adsorbed on some high surface area support.

In runs using 2.5% NO, 97.5% He at .15 to .20 standard cm³ per second reacting with 8.6% CaS impregnated on a high alumina, high surface area pellet, the average global rates of reaction increased with increasing temperature. At 390°C the rate was .25 x 10⁻⁴ moles CaSO₄ formed per hour per gram of pellet. At 493°C the average rate was .45 x 10⁻⁴ moles per hour per gram.

At each temperature and flow rate, a molecular sieve support gave greater average rates than the alumina pellets. At 392°C the rate was .32 x 10⁻⁴, at 410°C the rate was .64 x 10⁻⁴, and at 438°C the rate was .47 x 10⁻⁴ moles CaSO₄ formed per hour per gram. Some difficulty was encountered with oxidation of the pellets in air during storage.

The average global rate of reaction was lower using five pellets in a bed than using one pellet. The average rate at 442°C for five alumina pellets was .05 x 10⁻⁴ moles per hour per gram using a 2.5% NO, 97.5% He feed at .16 standard cm³ per second. This corresponds to .31 to .34 x 10⁻⁴ moles per hour per gram at about the same conditions using one pellet. The apparent cause of this lower rate is an added diffusional resistance.

It was found that, for the flow rates in this experiment, external film diffusion was probably not important. At 440°C and 3.48 standard cm³ per second the average global rate was .25 x 10⁻⁴ moles per hour per gram. At 444°C and .12 standard cm³ per second the average global rate was .22 x 10⁻⁴ moles per hour per gram. This difference in rate is within the experimental error for the test.

Oxygen was found to react with CaS faster than nitric oxide under the same conditions for an alumina pellet. In a 2.5% O₂, 97.5% He stream at .12 standard cm³ per second and at a temperature of 444°C, the average global rate of reaction was .41 x 10⁻⁴ moles CaSO₄ formed per hour per gram of pellet. In a 2.5% NO, 97.5% He stream at .12 standard cm³ per second reacting with a pellet from the same batch, the average rate was .22 x 10⁻⁴ moles per hour per gram. Thus it is probably desirable to remove oxygen from the feed gas since oxygen apparently reacts faster than NO at the same concentration and would therefore reduce pellet life.

STATEMENT OF PERMISSION TO COPY

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at Montana State University, I agree that the Library shall make it freely available for inspection. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by my major professor, or, in his absence, by the Director of Libraries. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature

John C McIntyre

Date

12/5/74

RATE OF REACTION OF NITRIC OXIDE BY CALCIUM
SULFIDE ON HIGH SURFACE AREA SUPPORTS

by

JOHN CARL MCINTYRE

A thesis submitted in partial fulfillment
of the requirements for the degree

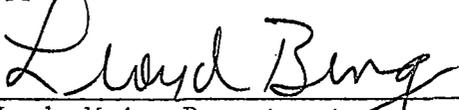
of

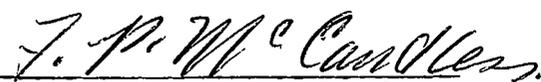
MASTER OF SCIENCE

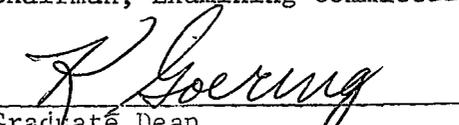
in

Chemical Engineering

Approved:


Head, Major Department


Chairman, Examining Committee


Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1974

ACKNOWLEDGMENTS

The author wishes to thank the faculty and staff of the Department of Chemical Engineering at Montana State University for the training and assistance they rendered to him. He also wishes to thank the Environmental Protection Agency who funded his research and schooling under EPA Grant No. R-800682-03-0. The author also thanks Dr. F. P. McCandless for his guidance and help, and Mr. James Tillery and Mr. Silas Huso for their help in constructing and repairing the equipment used in the experiment. Finally, the author wishes to thank his family and friends for their understanding and encouragement and without whose help this project would have been infinitely more difficult.

TABLE OF CONTENTS

	<u>Page</u>
VITA	ii
ACKNOWLEDGMENTS	iii
LIST OF TABLES	v
LIST OF FIGURES	vi
ABSTRACT	vii
INTRODUCTION	1
PREVIOUS WORK	2
REDUCTION WITH METAL SULFIDES	5
OBJECTIVES	7
APPARATUS	8
PROCEDURE	12
RESULTS AND DISCUSSION	14
CONCLUSIONS	43
RECOMMENDATIONS FOR FUTURE STUDY	45
LITERATURE CITED	46

LIST OF TABLES

Table	Page
I Support Material Properties	15
II Reaction Conditions	16
III Average Rates of Reaction vs. Temperature	38

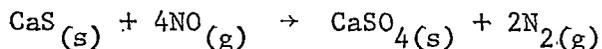
LIST OF FIGURES

Figure		Page
1	Flow Diagram of Apparatus for Measuring Rate of Reduction of NO	9
2	Reactor Cross-Section.	11
3	Reaction Data for a Harshaw Pellet at 390°C.	17
4	Reaction Data for a Harshaw Pellet at 410°C.	19
5	Reaction Data for a Harshaw Pellet at 437°C.	21
6	Reaction Data for a Harshaw Pellet at 438°C.	22
7	Reaction Data for a Harshaw Pellet at 468°C.	23
8	Reaction Data for a Harshaw Pellet at 493°C.	25
9	Reaction Data for Five Harshaw Pellets at 442°C.	26
10	Reaction Data for a Harshaw Pellet at High Flow Rates.	28
11	Reaction Data for a Harshaw Pellet at Low Flow Rates	30
12	Reaction Data for a Harshaw Pellet Using Oxygen.	32
13	Reaction Data for a Linde Sieve at 392°C	33
14	Reaction Data for a Linde Sieve at 410°C	34
15	Reaction Data for a Linde Sieve at 438°C	36

ABSTRACT

Oxides of nitrogen are one of the major air pollutants in the United States today. Because of the kinetics, most of the oxides of nitrogen are emitted in the form NO, which is converted into NO₂ at equilibrium. NO and NO₂ are both harmful in themselves, and have been linked to other harmful constituents of smog.

Previous work has shown that calcium sulfide is a good reducing agent for NO. Therefore this research was performed to study the rate of the following reaction:



where CaS was adsorbed on some high surface area support.

In runs using 2.5% NO, 97.5% He at .15 to .20 standard cm³ per second reacting with 8.6% CaS impregnated on a high alumina, high surface area pellet, the average global rates of reaction increased with increasing temperature. At 390°C the rate was .25 x 10⁻⁴ moles CaSO₄ formed per hour per gram of pellet. At 493°C the average rate was .45 x 10⁻⁴ moles per hour per gram.

At each temperature and flow rate, a molecular sieve support gave greater average rates than the alumina pellets. At 392°C the rate was .32 x 10⁻⁴, at 410°C the rate was .64 x 10⁻⁴, and at 438°C the rate was .47 x 10⁻⁴ moles CaSO₄ formed per hour per gram. Some difficulty was encountered with oxidation of the pellets in air during storage.

The average global rate of reaction was lower using five pellets in a bed than using one pellet. The average rate at 442°C for five alumina pellets was .05 x 10⁻⁴ moles per hour per gram using a 2.5% NO, 97.5% He feed at .16 standard cm³ per second. This corresponds to .31 to .34 x 10⁻⁴ moles per hour per gram at about the same conditions using one pellet. The apparent cause of this lower rate is an added diffusional resistance.

It was found that, for the flow rates in this experiment, external film diffusion was probably not important. At 440°C and 3.48 standard cm³ per second the average global rate was .25 x 10⁻⁴ moles per hour per gram. At 444°C and .12 standard cm³ per second the average global rate was .22 x 10⁻⁴ moles per hour per gram. This difference in rate is within the experimental error for the test.

Oxygen was found to react with CaS faster than nitric oxide under the same conditions for an alumina pellet. In a 2.5% O₂, 97.5% He stream at .12 standard cm³ per second and at a temperature of 444°C, the average global rate of reaction was .41 x 10⁻⁴ moles CaSO₄ formed per hour per gram of pellet. In a 2.5% NO, 97.5% He stream at .12 standard cm³ per second reacting with a pellet from the same batch, the average rate was .22 x 10⁻⁴ moles per hour per gram. Thus it is probably desirable to remove oxygen from the feed gas since oxygen apparently reacts faster than NO at the same concentration and would therefore reduce pellet life.

INTRODUCTION

Oxides of nitrogen (NO_x) are among the major pollutants in the United States today. In 1968 alone, 16 million tons of NO_x (calculated as NO_2) were released into the atmosphere (1). By comparison, in 1967 30.8 million tons of SO_2 were released (2). The principal sources of the oxides of nitrogen are stationary fossil fuel power generation plants. Stationary sources are accredited with 60% of the total NO_x released to the air (1).

Oxides of nitrogen are present in many forms, though by far the most common are nitrogen dioxide (NO_2), nitric oxide (NO), and nitrous oxide (N_2O). NO_2 and NO are poisonous irritants while N_2O , commonly called laughing gas, is a relatively harmless anesthetic. NO_2 is reddish-brown and this is what gives the air over Los Angeles its distinctive color. NO and N_2O are both colorless. Although N_2O is a narcotic and can be harmful at high concentrations, it is harmless at ordinary low concentrations and can be dismissed as a serious pollutant. However, NO_2 and NO must be removed from the air because of their toxicity at high concentrations and irritating qualities at low concentrations.

Oxides of nitrogen are formed in many ways. For instance, the action of bacteria in the soil causes the concentration of N_2O to reach about .3 ppm in the air. NO is produced by the oxidation of nitrogen (N_2) by oxygen (O_2) at high temperatures. For instance, the equilibrium concentration of NO with N_2 and O_2 is about 25,000 ppm at 4400°F (the approximate combustion temperature in a car engine). By comparison, the

equilibrium concentration is only .001 ppm at 70°F (3).

NO₂ is formed in a somewhat different manner. At 4400°F the kinetics of the N₂, O₂, NO₂, and NO reactions are such that only 5 to 10% of the NO_x formed is NO₂ with most of the rest being NO (1). However at 70°F the equilibrium between NO₂, O₂ and NO highly favors NO₂. Thus in car engine exhausts, for example, most of the excess oxygen in the exhaust gases leaves the engine as NO, while at equilibrium most of these gases are converted to NO₂.

Kinetics plays a very important role in NO_x formation. At 4400°F the formation of NO from N₂ and O₂ is very fast, while at 70°F the decomposition of NO to N₂ and O₂ is very slow. In fact, the decomposition is so slow that in one experiment several containers of NO were sealed with various catalysts at ordinary temperatures in 1917. Upon opening the containers in 1958 there was no detectable N₂ (1). Thus, though thermodynamically unstable at ordinary temperatures, oxides of nitrogen can be particularly long lived.

PREVIOUS WORK

NO₂ has been linked to various photochemical oxidation products of hydrocarbons which are irritating to the eyes and harmful to plant life (3). Because of this it is necessary to control NO_x emissions. Research into abatement of oxides of nitrogen generally falls into one of four categories; a) process modification; b) chemical or physical adsorption; c) thermal or catalytic reduction of NO to O₂ and N₂ or

N₂O; or d) chemical reduction of NO with N₂ or N₂O as a product.

Process modification is specific to each NO_x source. Generally it involves adjustment of flame temperatures, recycle of exhaust streams, and changes in fuel/air ratio (1).

Chemical adsorption was studied by Bartok, et. al (1) who concluded that common adsorbents such as silica gel, alumina, molecular sieves, char, and ion exchange resins all had insufficient capacities necessitating very large contactors and frequent regeneration. Aqueous absorption systems of alkaline solutions or sulfuric acid looked promising but these require equimolar NO and NO₂ in the gas, since the soluble product is probably N₂O₃. Most promising of the alkaline solutions were lime-water and magnesium hydroxide (1).

Thermal decomposition of NO is thermodynamically favored below about 1000°K as noted previously. However, the rate of decomposition is extremely low which agrees with the experimentally observed high activation energy. Catalysts have been developed which lower this activation energy by as much as a factor of 4 but the decomposition rate remained low. This has been linked to an exceptionally low pre-exponential factor in the rate constant. Rates for heterogeneous catalytic decompositions fell within the range 9×10^{-8} to $6 \times 10^{-6} \frac{\text{moles NO removed}}{\text{m}^2 \text{ hr}}$ which was considered too slow to be commercially practical (4).

None of the methods mentioned so far has proven entirely satisfactory so that considerable effort has been turned to the use of chemical reducing agents. Shelef and Kummer (4) studied carbon monoxide,

hydrogen, and methane which all proved successful in reducing NO at temperatures between 110 and 800°C depending on the catalyst and support used. Catalysts showing the most promise were supported precious metals and supported copper oxides or copper chromite. Ammonia was another excellent reducing agent over precious metal catalysts and transition metal oxides at temperatures around 250°C. Activated carbon was found to be a slow reducing agent (4).

In all these tests of reducing agents, it was found that oxygen was selectively reduced before NO. Thus the reduction of NO was slowed by the presence of O₂. Ammonia was the only exception and it was found that the presence of oxygen actually enhanced the rate. Water vapor was found to have no effect or, in the case of CO and H₂O, the rates were improved (4).

Urea has also been tried as a reducing agent. Optimum temperatures for this reaction were between 40 and 100°C. Oxygen was necessary for the reaction but at 16% O₂ the catalyst became poisoned after 16 hours. The main disadvantage stems from the fact that urea decomposes at 110°C so that temperatures, and therefore rates, were limited. The greatest observed rate was 3.4×10^{-4} mole NO removed/g-hr, which the author felt would be too slow for practical catalyst bed sizes (5).

Ault and Ayen studied the hydrocarbon series C₁ to C₈ as reducing agents over a barium-promoted copper chromite catalyst. They found appreciable reduction of NO at temperatures between 300 and 500°C. They found that an increase in number of carbon atoms per molecule decreased

the temperature required for a given conversion. Also, for a given number of carbon atoms per molecule a decrease in saturation led to a decrease in temperature required for a given conversion. They used a constant feed rate of 1×10^{-2} mole NO/g-hr, and obtained 20 to 80% conversions for various hydrocarbons at 500°C. They observed that CO₂ and H₂O had a deactivating influence on the catalyst (6).

REDUCTION WITH METAL SULFIDES

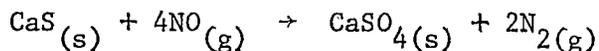
White (7) showed that metal sulfides could be used to reduce NO at temperatures between 400 and 800°C. He showed that addition of various chemicals lowered the needed temperature for conversion of NO to N₂. He also showed that the solid products of the reaction of calcium sulfide (CaS) with NO were at least 80% calcium sulfate (CaSO₄). CaS was found to be one of the best metal sulfides because of its low cost and stability of the sulfate.

Erickson (8) studied the effects of different support materials for CaS and different contaminants in the feed. He discovered that a high alumina high surface area support, the Harshaw 1602-T, was very favorable for reduction of NO with no H₂S or SO₂ released. Some H₂S was observed in the exhaust gases from a high silica support, the Nalco 2910-A. A molecular sieve, the 1/8 inch Linde TM-Q-1114, gave good reduction of NO but also released some SO₂. In the contaminants tests he found that neither oxygen nor carbon dioxide have a detrimental effect on the reduction. Water gave H₂S and decreased reduction. Natural gas,

acetylene, and hydrogen each gave some H_2S (8).

If calcium sulfide could be regenerated from the sulfate the process could become economically more attractive. Zadick found that calcium sulfide could be generated from the sulfate at temperatures between 600 and 760°C by using various catalysts and reducing agents. He was able to get up to 95% conversion on some runs so that it is possible to regenerate the sulfide from the sulfate (9).

This research is closely related to the work of Erickson and White. The main reaction to be studied is:



As can be seen, four nitric oxide molecules are removed per molecule of calcium sulfate formed. The solid will increase in weight from 72 g/mole to 136 g/mole so that by continuously weighing the solid the rate of reaction vs time can be easily determined.

For this reaction $\Delta H_{298^\circ K}^\circ = -313.5$ kcal/mole and $\Delta F_{1000^\circ K}^\circ = -215.7$ kcal/mole so that the reaction is thermodynamically very favorable and highly exothermic. Because of the favorable thermodynamics, the ease of measuring global rates, the possibility of regeneration of the sulfide, and the lowering of the temperature required for reduction of NO by the use of high surface area supports, the study of global rates using different high surface area supports seems justified for this reaction.

OBJECTIVES

The primary objective of this research was to find the global rate of reaction of NO with CaS adsorbed on various high surface area supports at different ambient temperatures. Another purpose of this research was to determine the relative rate of reaction of oxygen with calcium sulfide to find out if oxygen contamination of the feed could be a problem.

APPARATUS

Figure 1 is a schematic diagram of the apparatus used to study the reaction. The balance mechanism is a Cahn R-100 Electrobalance. This device is used to measure the weight of a sample continuously as it hangs suspended into the reactor. The R-100 Electrobalance has a 100 gram capacity for sample weight and container. Tare capacity is 100 g mechanically and 50 mg with the coarse zero. The electrobalance has three electrical weight suppression ranges capable of electronically taring as little as 10 μg or as much as 10 g.

The readability of the electrobalance is .5 μg and it has six weight ranges: 10 g, 1 g, 100 mg, 10 mg, 1 mg, and 100 μg full chart scale. An automatic range expander automatically brings the chart pen back to zero up to ten times when a weight change takes the weight outside of the recorder weight range. The precision of the instrument is $\pm 10^{-3}$ of meter and recorder range and $\pm 10^{-6}$ of load and the accuracy is $\pm 5 \times 10^{-4}$ of mass suppression range for absolute weighings. The maximum weight change is 10 g increase or decrease.

The system shown in Figure 1 normally operates with feed gas passing through a rotameter and entering the bottom of the reactor. Exhaust gases leave just above the reactor and are vented to a hood. A helium line is run into the glass bell housing the balance mechanism to keep the bell purged of exhaust gases. During startup the valve arrangement makes it possible to pass helium through the reactor as well as over the balance mechanism.

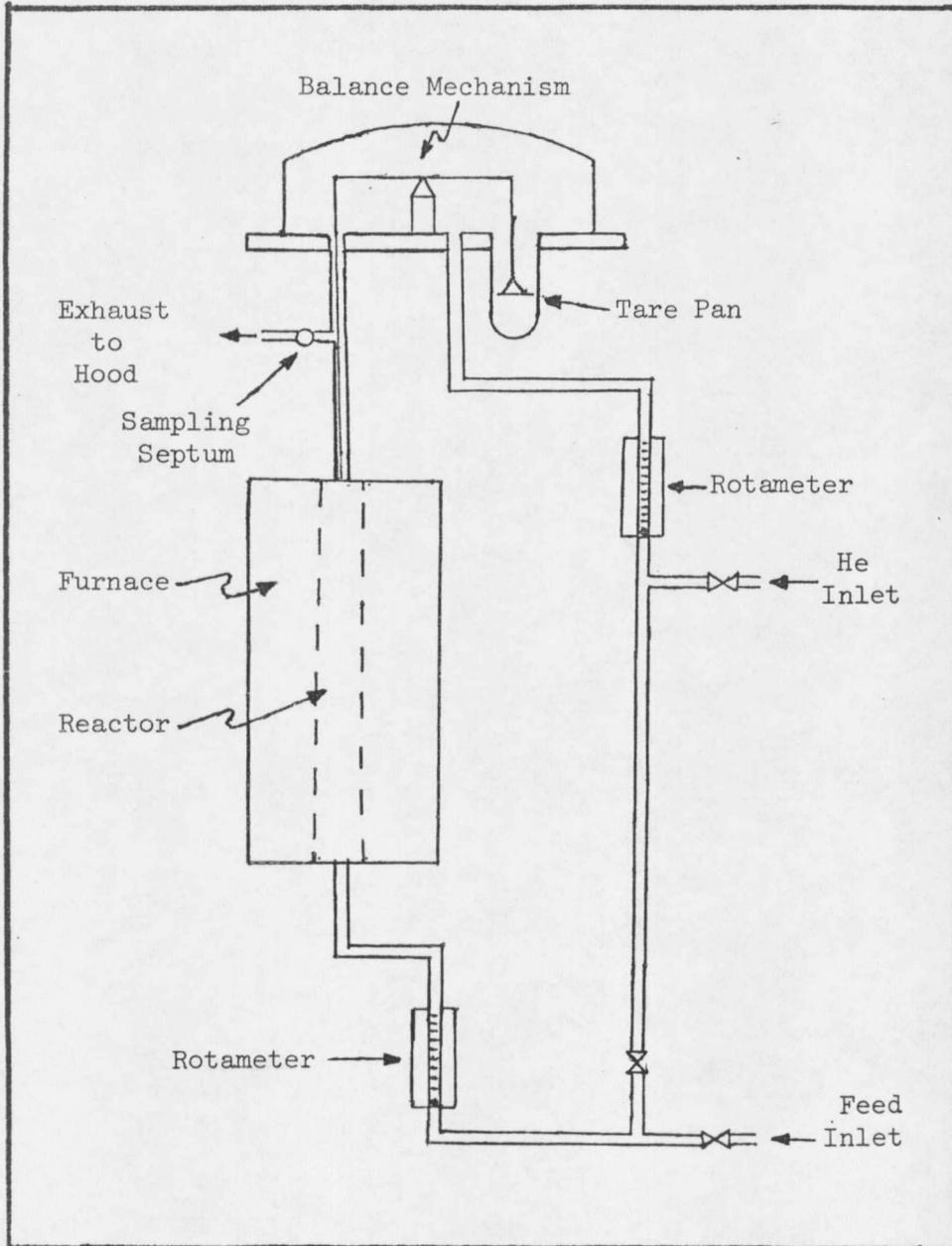


Figure 1. Flow diagram of apparatus for measuring rate of reduction of NO

The reactor is enclosed in a Lindberg 54031 hinged tube furnace during normal operation. It can be removed to allow access to the reactor tube before and after a run. It is controlled by a Teco TC-1000 proportional temperature controller (not shown).

The reactor cross-section is shown in Figure 2. The catalyst support pellet rests on a 9mm diameter, 200-mesh stainless steel screen suspended by a .1 mm nickel wire from the balance arm. The reactor is a 16 mm diameter, 78 cm long ATM Mullite tube with a ground glass joint at the bottom and a ground glass ball joint at the top.

Attached to the bottom joint of the reactor is a glass connector, and in this connector is mounted a porous glass plate. Two thermocouples are cemented with epoxy into a hole in the side of the glass connector and extend up the Mullite tube to a point just below the support pan. One thermocouple wire is attached to a proportional temperature controller and the other is attached to a temperature recorder. The Mullite tube is filled with 40-mesh Ottawa sand to preheat the feed gas. The gas is fed into the bottom of the reactor, passes over the pellet and is exhausted out the top.

