



Rate of reaction of nitric oxide and oxygen by metal sulfides
by Kent Moroni Hodgson

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
Montana State University
© Copyright by Kent Moroni Hodgson (1975)

Abstract:

Nitric oxide has received a great deal of attention as- one of the major air pollutants- with which environmentalists are concerned. Nitric, oxide is emitted into the atmosphere -where it can then be oxidized to NO₂ in the presence of sunlight and oxidizing agents. No. commercially acceptable method for removing NO from exhaust and flue gas has been developed yet.

This research is concerned with the rate of two reactions.

$\text{MeS} + 4\text{NO} \rightarrow \text{MeSO}_4 + 2\text{N}_2$ $\text{MeS} + 2\text{O}_2 \rightarrow \text{MeSO}_4$ The rates of reaction at 300°C, 400°C, 500°C for these two reactions were determined for ten metal sulfides, The rates of reaction were studied using a Cahn R-100 continuous recording electrobalance. This device was used to measure the weight of a sample continuously as it hung suspended from one arm of the balance into the reactor. The rate of reaction was calculated, from the continuously recorded weight increase. The rate of reaction of NO with metal sulfides was determined using a gas mixture with a composition of 2.5% NO and 97.5% He. The rate of reaction of O₂ with metal sulfides was determined using a gas mixture with a composition of 2.5% O₂ and 97.5% He, In general, the reaction of the metal sulfide with oxygen proceeds faster for all temperatures tested. The reaction rates with NO ranged from 3.38×10^{-6} grams of FeSO₄ formed per minute per gram of FeS to 2.076×10^{-4} grams of FeSO₄ formed per minute per gram of FeS. The reaction rates with O₂ ranged from 5.9×10^{-6} grams of ZnSO₄ formed per minute per gram of ZnS to 6.48×10^{-4} grams of PbSO₄ formed per minute per gram of > PbS. The sulfides of Ba, Fe, Sr, Cd, Pb, Ca, Zn and sulfurated potash -reacted with both the O₂ and the NO to form the sulfate.

The relative reaction rates of NO with a given amount of ZnS or SrS at 300°C and a given amount of BaS, SrS or CdS at 400°C for a given time are greater than the relative rates of reaction of O₂ with the same amount of BaS, SrS or CdS at 400 and the same amount of ZnS or SrS at 300°C for the same time.

Cupric sulfide, thallium sulfide, manganese sulfide, and molybdenum disulfide could not be used because they decompose below- 300°C.

Tungsten disulfide when reacting with NO and O₂ produced a net weight lost indicating that undesirable side reactions were controlling, Sulfurated potash produced the fastest reaction rates with NO and O₂. However, since the composition was unknown, rates of reaction of the solid could not be calculated.

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 Kent M. Hodgson

Date November 18, 1975

111

RATE OF REACTION OF NITRIC OXIDE AND OXYGEN
BY METAL SULFIDES

by

KENT MORONI HODGSON

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

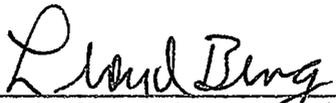
of

MASTER OF SCIENCE

in

Chemical Engineering

Approved:



Head, Major Department



Chairman, Examining Committee



Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1975

ACKNOWLEDGMENTS

The author wishes to thank the faculty and staff of the Department of Chemical Engineering for their suggestions and assistance. The author wishes to thank Dr. F.P. McCandless, his advisor, for his help and suggestions. The author wishes to thank his wife for her support and help in preparing this thesis.

Financial support for this study was provided by the Environmental Protection Agency, Grant No. R-800682-03-0.

TABLE OF CONTENTS

	<u>Page</u>
VITA.	ii
ACKNOWLEDGMENTS.	iii
LIST OF TABLES.	v
LIST OF FIGURES	vi
ABSTRACT.	vii
INTRODUCTION.	1
PREVIOUS WORK.	1
REDUCTION WITH METAL SULFIDES.	4
OBJECTIVES.	8
APPARATUS	9
PROCEDURE	13
RESULTS AND DISCUSSION.	14
CONCLUSIONS	22
RECOMMENDATIONS	24
LITERATURE CITED.	25

LIST OF TABLES

Table		Page
I	Free Energy Changes and Heats of Reaction for the Reduction of NO Employing Metal Sulfides	7
II	Reaction Rates of NO and O ₂ with Various Metal Sulfides.	16
III	A Summary of the Weight Gained or Lost for the Various Sulfides Reacting with NO and O ₂	19
IV	The Relative Rates at which NO and O ₂ React with the Various Sulfides.	21

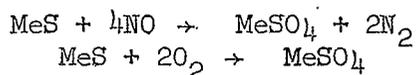
LIST OF FIGURES

Figure		Page
1	Flow Diagram of Apparatus for Measuring Rate of Reduction of NO	10
2	Reactor Cross-Section.	12
3	A Sample Recording from the Cahn R-100 Continuously Recording Electrobalance	15

ABSTRACT

Nitric oxide has received a great deal of attention as one of the major air pollutants with which environmentalists are concerned. Nitric oxide is emitted into the atmosphere where it can then be oxidized to NO_2 in the presence of sunlight and oxidizing agents. No commercially acceptable method for removing NO from exhaust and flue gas has been developed yet.

This research is concerned with the rate of two reactions.



The rates of reaction at 300°C , 400°C , 500°C for these two reactions were determined for ten metal sulfides.

The rates of reaction were studied using a Cahn R-100 continuous-recording electrobalance. This device was used to measure the weight of a sample continuously as it hung suspended from one arm of the balance into the reactor. The rate of reaction was calculated from the continuously recorded weight increase. The rate of reaction of NO with metal sulfides was determined using a gas mixture with a composition of 2.5% NO and 97.5% He. The rate of reaction of O_2 with metal sulfides was determined using a gas mixture with a composition of 2.5% O_2 and 97.5% He.

In general, the reaction of the metal sulfide with oxygen proceeds faster for all temperatures tested. The reaction rates with NO ranged from 3.38×10^{-6} grams of FeSO_4 formed per minute per gram of FeS to 2.076×10^{-4} grams of FeSO_4 formed per minute per gram of FeS. The reaction rates with O_2 ranged from 5.9×10^{-6} grams of ZnSO_4 formed per minute per gram of ZnS to 6.48×10^{-4} grams of PbSO_4 formed per minute per gram of PbS.

The sulfides of Ba, Fe, Sr, Cd, Pb, Ca, Zn and sulfurated potash reacted with both the O_2 and the NO to form the sulfate.

The relative reaction rates of NO with a given amount of ZnS or SrS at 300°C and a given amount of BaS, SrS or CdS at 400°C for a given time are greater than the relative rates of reaction of O_2 with the same amount of BaS, SrS or CdS at 400° and the same amount of ZnS or SrS at 300°C for the same time.

Cupric sulfide, thallium sulfide, manganese sulfide, and molybdenum disulfide could not be used because they decompose below 300°C .

Tungsten disulfide when reacting with NO and O_2 produced a net weight lost indicating that undesirable side reactions were controlling.

Sulfurated potash produced the fastest reaction rates with NO and O_2 . However, since the composition was unknown, rates of reaction of the solid could not be calculated.

INTRODUCTION

The elimination of NO_x as an air pollutant has been a major concern of environmentalists since it was established in 1952 that NO_x participates in smog reactions (Bartok et al., 1971). NO_x represents the two oxides of nitrogen, NO (nitric oxide) and NO_2 (nitrogen dioxide). The average U.S. urban concentration of nitrogen oxides in air is 20-25 times the natural atmospheric condition (Hopper and Yaws, 1974). On a nationwide basis about half the NO_x comes from stationary sources and about half from mobile sources (Science News, 1972).

Most of these oxides are released in the form of NO . The conditions for the formation of these two oxides are quite different. In high temperature combustion processes NO is almost exclusively formed (Bartok et al., 1971). However, at the ambient temperature of the atmosphere, the equilibrium between NO_2 , O_2 and NO highly favors NO_2 .

PREVIOUS WORK

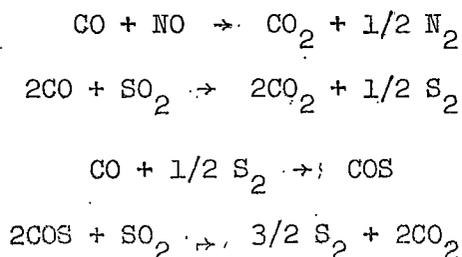
There has been a great deal of work done concerning oxides of nitrogen. The author does not intend to give a comprehensive summary of all the work done. This is only a summary of some of the work that seems to offer promise of being significant in the control of NO_x .

Shaw (1973) in studying the reduction of nitrogen oxide emissions from a gas turbine combustor by fuel modification found that soluble organo metallic additives which became heterogeneous reduction or decomposition catalysts would reduce the NO_x emission by 30%. A number of other additives were experimented with; however, the organo metallic

additives produced the best results. The major drawback of these additives is that it seems to be a case of trading one pollutant for another.

The Bell Laboratory has developed a manganese, rare earths, lead on a ceramic support catalyst. This is mainly for use in automobiles. Good results have been obtained, however, a small amount of NH_3 is produced. In experimenting with this catalyst their experience showed that when CO and hydrocarbon emissions were controlled effectively the NO yield increased. And when the NO was controlled effectively the CO and hydrocarbon yield increased. (Scientific American, 1973).

A dual bed catalyst system for the simultaneous reduction of SO_2 and NO has been developed by Sood and Kittrell (1974). The reactions:



are considered to take place in this system. To get 90% removal stoichiometric quantities are necessary and the catalyst bed temperature must be controlled very carefully.

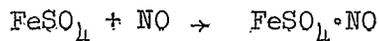
The reduction of nitric oxide with various hydrocarbons as studied by Ault and Ayen (1971) has shown that in general, an increase in carbon number in the hydrocarbon studied resulted in a decrease in the required temperature for a given nitric oxide conversion. For a given carbon number the required temperature for a given nitric oxide conversion

decreased with degree of saturation. The catalyst used was a barium promoted copper chromite catalyst.

Good results were obtained by reducing nitric oxide using a copper nickel catalyst. The results indicated that the catalyst activity was dependent on the copper-nickel ratio. In general, activity increases with increasing copper content. Activation of the catalyst in CO at 500°C led to the opposite trend in activity; that is activity increased with an increase in nickel content. (Bauerle et al., March, 1974).

Ammonia has been the only reductant purported to show true selectivity for the heterogeneous reduction of nitric oxide to nitrogen in the presence of excess oxygen. A study by Bauerle et al. (December, 1974) indicates that the catalytic reduction of NO with NH₃ on Pt in a simulated plant exhaust is not strictly selective in the sense that the NH₃-O₂ reaction has little appreciable effect on NO reduction. Nitrous oxide (N₂O) is a major reaction product and is produced by the reduction of both NO and O₂ with NH₃.

Regenerative sorption of nitric oxide has been found to work good for small concentrations of NO (Gidaspow and Onischak, 1973). The NO is sorbed with FeSO₄.



This reaction can be reversed with heat. The main drawback is that the flue gas and exhaust gases must be cooled below 100°C.

A fluidized bed of catalyst to catalytically reduce nitric oxide

has been studied. Using a platinum silica alumina catalyst a conversion efficiency of over 99% was obtained. This was using a stream of pure NO (Dieteven et al., 1973).

REDUCTION WITH METAL SULFIDES

It was shown by White (1973) initially that metal sulfides will reduce nitric oxide. Complete reduction was attained over a temperature range of 400°C to 800°C. White also successfully lowered the temperature for the reduction of nitric oxide by the addition of various chemicals, the temperature range was from 400°C to 550°C. It was also shown that NO would be reduced in the presence of O₂ and that the presence of water vapor did not appear to deter the reduction of NO. White also determined that in the reduction of NO with calcium sulfide the solid product was 80 weight per cent calcium sulfate.

Erickson (1974) determined that the best support material for CaS was Harshaw 1602 . 1/8 inch pellets. He also tested Nalco 2910-B 1/8 inch, Alcoa T-71 1/4 inch and Linde TM-0-1114 pellets. The Harshaw 1602 gave good reduction of NO without forming any H₂S or SO₂.

In testing NiS as a reducing agent Erickson found that SO₂ was produced along with the reduction of NO. In working with contaminants in the NO gas stream it was found by Erickson that H₂O produced small amounts of H₂S and decreased the reduction of NO. The presence of H₂ seemed to increase the reductions of NO by CaS but caused the formation of H₂S. Natural gas also produced H₂S but did not seem to effect the

reduction of CaS. He also found that O_2 and CO_2 did not effect the reduction of CaS.

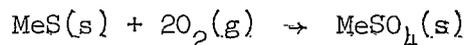
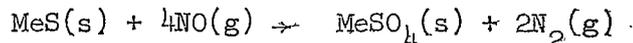
McIntyre (1974) in studying the reaction



found that the global rates for the reduction of CaS on high alumina Harshaw pellets increased from $.25 \times 10^{-4}$ at $390^\circ C$ to $.45 \times 10^{-4}$ moles of $CaSO_4$ formed per hour per gram of pellet at $493^\circ C$. Linde molecular sieves gave greater average rates. Rates varied between $.32 \times 10^{-4}$ and $.64 \times 10^{-4}$ moles $CaSO_4$ formed per hour per gram of pellet for three temperatures between 392° and $438^\circ C$. McIntyre also determined that at $440^\circ C$ and with a flow rate ranging from $.12 \text{ std. cm}^3$ per second to 3.8 std. cm^3 per second, external film diffusion was not important for the reaction using Harshaw pellets. It was also shown by McIntyre that the rate of reaction of CaS with O_2 is greater than the rate of reaction of CaS with NO.

This work is closely related to the work of White and McIntyre.

The general reactions to be studied are:

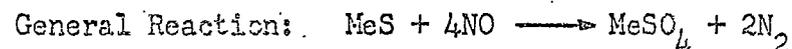


As can be seen for every mole of $MeSO_4$ formed the solid will increase in weight by 64 grams. Therefore, by continually weighing the solid, the rate of reaction with time can be determined.

White has summarized in Table I the enthalpy and free energy of

reactions for these various sulfides with NO. McIntyre has also shown that at least one sulfide (CaS) reacts very rapidly with oxygen. Since O_2 and NO are commonly found together it is desirable to know the rates of reactions of these two compounds with the various sulfides. This will help determine if a metal sulfide can be profitably used to remove NO from flue and exhaust gases.

Table I Free Energy Changes and Heats of Reaction for
the Reduction of NO employing Metal Sulfides (White, 1973)



Metal Sulfide	Free Energy Change (Kcal/mole)				Heat of Reaction (Kcal/mole) 298°K
	298°K	500°K	1000°K	1500°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

OBJECTIVES

The objective of this research is to determine and compare the reaction rates of the formation of metal sulfates from NO and O₂ with various metal sulfides.

APPARATUS

Figure 1 is a schematic diagram of the apparatus used to study the reactions. The balance mechanism is a Cahn R-100 continuous recording electrobalance. This device is used to measure the weight of a sample continuously as it hangs suspended from one arm of the balance in the reactor. The R-100 electrobalance has a 100 gram capacity for sample weight and container. Tare capacity is 100 grams mechanically and 50 milligram with the coarse zero. The electrobalance has three electrical weight suppression ranges capable of electronically taring as little as 10 micrograms or as much as 10 grams.

The readability of the electrobalance is .5 micrograms and it has six weight ranges: 10 grams, 1 gram, 100 milligrams, 1 milligram and 100 micrograms 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 the 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 grams increase or decrease.

The system shown in Figure 1 normally operates with feed gas passing through a rotometer and entering the bottom of the reactor. Exhaust gases leave just above the reactor and are vented to 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

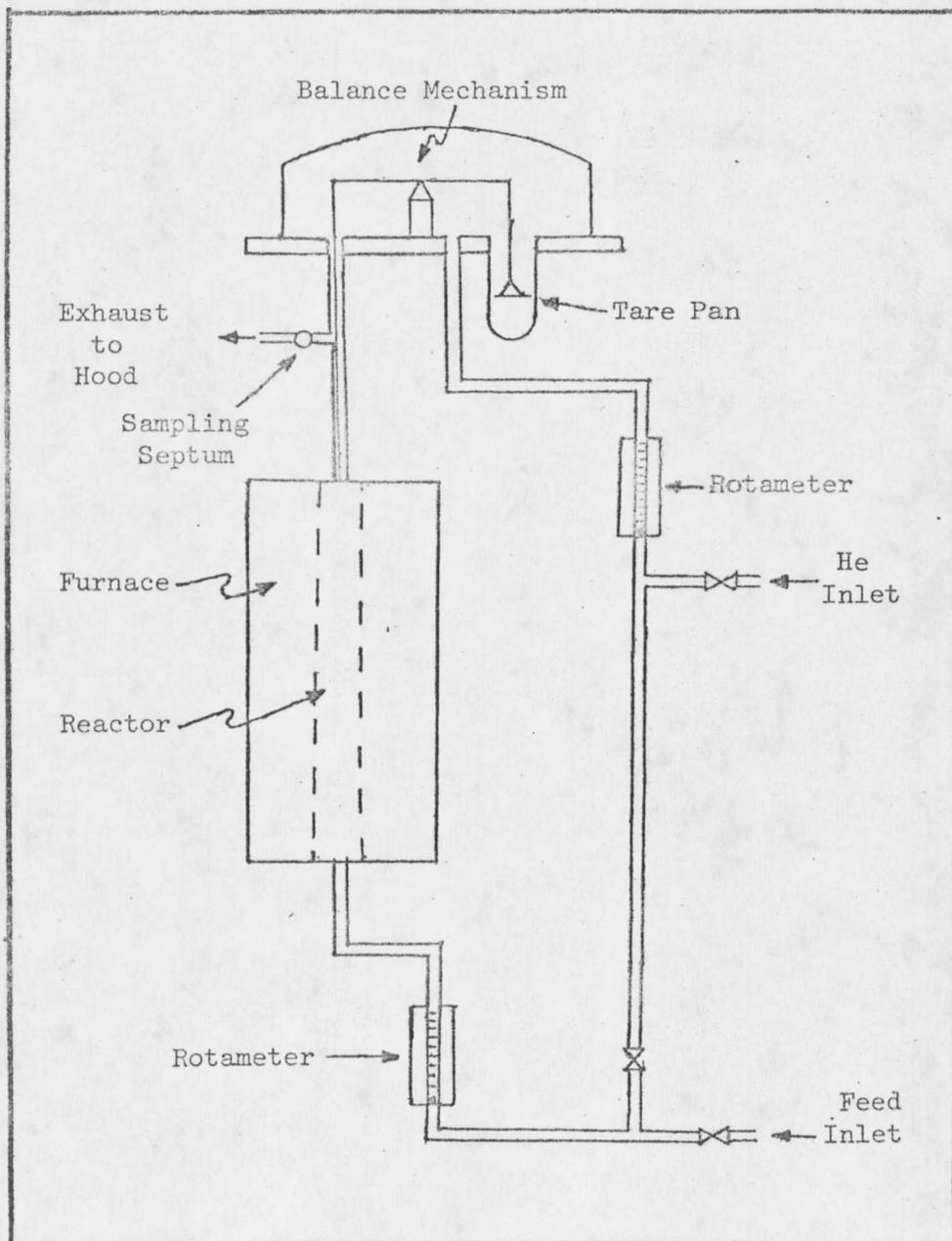


Figure 1. Flow diagram of apparatus for measuring rate of reduction of NO

the balance mechanism.

The reactor is enclosed in a Lindberg 54331 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 powdered sulfide rests on a 39mm diameter circular stainless steel pan suspended by a .1mm nickel wire from the balance arm. The reactor is a 57mm diameter, 840mm long Flothru Vycor, S_j75/50, 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 Vycor tube to a point just below the support pan. One thermocouple wire is attached to a proportional controller and the other is attached to a temperature recorder. The 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 powdered sulfide and is exhausted out the top.

