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ABSTRACT

CATALYTIC CONTROL OF NITRIC OXIDE WITH GASEOUS OR SOLID REDUCING MATERIALS

by
Xiaoyong Tang

Air pollution from mobile sources is an increasingly serious problem throughout most of the industrialized world. Diesel powered vehicles, because of their higher thermal efficiency, tend to emit less carbon monoxide and unburned hydrocarbons than gasoline vehicles, but emit significant quantities of NO_x . Therefore, it is essential to develop improved emission control equipment in diesel engines. A fixed bed catalytic reactor was used to study the decomposition of NO and the reduction of NO to N_2 by different reductants that can be found in diesel exhaust, such as hydrocarbons, CO and elemental carbon over different catalysts. The effect of space velocity, feed concentrations, reaction temperature and catalyst deactivation were also investigated. A dual detector gas chromatograph equipped with a thermal conductivity and a flame ionization detection, a gas chromatograph with thermal conductivity detector and a chemiluminescent NO/NO_x analyzer were used for quantitative analysis of feed and product streams.

The results show that both Cu-ZSM-5 and high surface area alumina are effective in promoting the desired NO reduction reaction, especially the reduction of NO by hydrocarbon. It was also determined that copper loaded carbon and alumina containing copper reduce NO_x at lower temperature than these substrates do without copper. The results can be explained qualitatively using the hypothesis that the catalyst promotes the soot- NO_x reaction by requiring an intermediate, possibly CO, produced from the soot to react with NO on the catalyst. This hypothesis helps explain how the catalyst improves soot oxidation without invoking the requirement that soot adsorb on catalytic active

centers or diffuse into catalyst pores. The CO will rapidly reduce the NO to N₂ while being oxidized to CO₂. This research is part of an overall project directed at the development of a rotating fluidized bed reactor (RFBR) to catalytically promote the oxidation of diesel soot while reducing NO_x to nitrogen gas.

**CATALYTIC CONTROL OF NITRIC OXIDE
WITH GASEOUS OR SOLID REDUCING MATERIALS**

by
Xiaoyong Tang

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WITH GASEOUS OR SOLID REDUCING MATERIALS**

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This thesis is dedicated to
my parents, my husband and my son

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CHAPTER 1

INTRODUCTION

Improving the quality of our environment has become a growing concern in this country and around the world. Acid rain and air pollution are very important problems that must be solved in the near future because such pollution has major effects on the terrestrial and aquatic ecosystem. Limiting the amount of pollution released into the atmosphere is an important part of that effort. The sources of air pollution are mainly industrial or stationary sources, which includes a wide variety of manufacturing facilities, power plants and automobiles. All fossil fuel burning automotive engines emit harmful emission. In many urban areas, due to their sheer number, automobiles are major contributors to air pollution.

Air pollution is demonstrated dramatically by photochemical smog, although other pollution hazes hanging over urban areas are also observed quite often. Photochemical smog broadly refers to the interaction of nitrogen oxides, hydrocarbons, and sunlight to form oxidation products that cause eye irritation, respiratory irritation and disease, and plant damage. The effect of individual pollutants have been investigated, such as soot particulates, nitrogen oxides, carbon monoxide, sulfur dioxide and aromatic hydrocarbons. They have been found to contribute directly to photochemical smog and other forms of air pollution.

The greater use of diesel-engine vehicles is a major trend observed worldwide. Co-generation systems using stationary diesel engines have also been under development. While the energy advantages of the diesel engine are unquestionable, concern began to grow over the environmental consequences.

1.1 Composition of Diesel Exhaust and their Harmful Effects

Diesel exhaust is a complex mixture of organic and inorganic compounds and adsorbed gas, liquid, and solid phase materials. The organic or hydrocarbon compounds are made up of a continuous gradation of carbon-containing compounds that change from a hydrogen to carbon ratio of 2:1 down to eventually a ratio of 0:1. They include both oxygenated and non-oxygenated compounds such as aldehydes, alkanes and alkenes, (both straight and branched chain), and aromatic compounds (single rings, substituted, and polynuclear). Many of these compounds also contain functional groups such as carbonyl (C=O), hydroxyl (OH) and nitro (NO₂). These organic compounds originate primarily from the unburned fuel and the lubricating oil, although some may be formed during the combustion process and/or reaction with catalysts. The inorganic compounds include sulfur, oxygen, carbon, and nitrogen-containing compounds such as sulfate (SO₄²⁻), nitrate (NO₃⁻), elemental carbon, and water (H₂O). Some of these compounds may also have their origins from the fuel, especially those containing sulfur and carbon (see SAE paper 940233).

The gas phase emissions include components such as NO_x, CO and sulfur oxides (SO₂ and SO₃) as well as the usual combustion products (CO₂, H₂O, CO). As shown in Figure 1, the solid phase emissions are made up primarily of small (10-80 nm), spherical carbon containing particles; these are variously termed the solids (SOL), solid particulate or soot component. The liquid phase emissions are composed of the organic or hydrocarbon component and sulfate (SO₄²⁻-primarily H₂SO₄ and some metal ion sulfates). As also shown in Figure 1, some of hydrocarbons may be found adsorbed onto the SOL and some may be in the gas phase; in the latter case, this component is often referred to as belonging to the vapor phase or as vapor phase organics. Diesel particulate matter is, therefore, a complex mixture of organic and inorganic solid and liquid compounds (Figure 1). Total particulate matter (TPM) consists of an agglomerate of SOL; adsorbed on the SOL are hydrocarbons that can be removed by an organic solvent (termed the

soluble organic fraction or SOF) and SO_4^{2-} , that can be removed by water. Also associated with the TPM may be droplets of liquid, condensed hydrocarbons (Figure 1) and SO_4^{2-} particles, These hydrocarbons collected with the TPM are not volatile enough to exist in the vapor phase and may not be adsorbed on the SOL due to low SOL levels but will also be removed by an organic solvent as SOF.

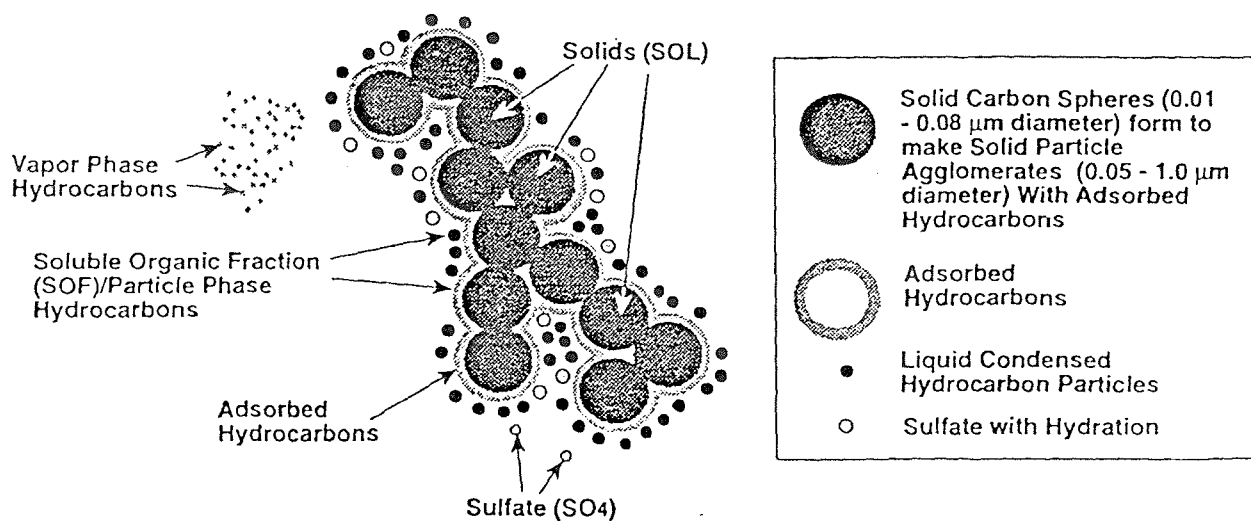


Figure 1.1 Schematic of Diesel Particles and Vapor Phase Compounds
(From SAE Paper 940233)

Considerable research has been done on the effect of specific components of diesel exhaust on human health. A wide variety of potential effects have been reported from laboratory animal and human studies; most of the attention has focused on the carcinogenic potential of inhaled exhaust components, particularly the highly respirable TPM. About 90% of diesel particulates encompass a size range from 0.0075 to 1.0 μm and are therefore important in terms of potential health impacts due to the ability of particles to be inhaled and eventually trapped in the bronchial passages and lungs. The carcinogenic effect related to exhaust particles is now considered to have at least two components, one related to the inorganic "carbon core" or SOL portion and one to the

adsorbed organics or SOF portion (Figure 1). Several recent laboratory studies with rats have indicated that the SOL portion is a contributor to tumor formation. The associated SOF, particularly the polynuclear aromatic hydrocarbons (PAH) and the nitro-PAH, seem to contribute to the overall carcinogenic effect.

At present, one of the most significant problems is removal of NO_x , which are produced during high-temperature combustion and are an important group of air contaminants. The nitrogen oxides found in nature are N_2O , NO , NO_2 , N_2O_3 , N_2O_4 and N_2O_5 . Among these nitrogen oxides, NO (nitric oxide) and NO_2 (nitrogen dioxide) predominate because they are emitted in large quantities from high temperature air oxidation processes. The term NO_x refers to all nitrogen oxides, but in air pollution jargon, NO_x refers only to NO (about 90% of the NO_x) and NO_2 . NO_x is emitted in the United States at a rate of about 20 million metric tons per year, about 40% of which is emitted from mobile sources. NO_x , once emitted to the atmosphere, becomes oxidized to nitrate through both gas and aqueous phase processes. In 1.5 days life time, it is transferred more than 1500 kilometers and removed by reaction with OH , dry deposition, or wet deposition. NO_x emission has four major environmental impacts: acid deposition, photochemical smog, ozone formation in the troposphere, and ozone depletion in the stratosphere. NO_x is a precursor to about 30% of acid rain and a major reactant in smog formation. NO_x has been the most difficult and expensive pollutant to control.

1.2 Control of Diesel Exhaust

As early as in 1909, the need to control undesirable air emissions from automobile engines was recognized. In recent years, concern over our environment has led to substantial action by the executive and legislative branches of government on both the state and federal levels. In the United States, both the federal government and many State governments are mandating large reductions in particulates, volatile organic compounds (VOC's) and nitrogen oxides (NO_x) in order to stem the continuous increase in the

formation of smog, ozone and other chemical irritants. Diesel-powered vehicles tend to emit significant quantities of particulate matter (soot) and NO_x . Therefore, it is essential to develop improved emission control in engines either by engine redesign or by treatment of the exhaust gases. During the 1980s and the early 1990s there have been significant advancements in the development of technology to control diesel particulate emissions. Efforts have focused on internal control of the engine by design, the use of aftertreatment devices, and improvements in fuel formulations to reduce all of the diesel emissions. The research and development activities have been driven by the need to meet the US EPA heavy-duty vehicle standards. Efforts to reduce NO_x in diesel exhaust by combustion modifications have not been successful because decreases in NO_x have resulted in increases in hydrocarbons, CO and other products of incomplete combustion since NO_x is essentially a product of an efficient combustion process. Furthermore, combustion processes which decrease NO_x also tend to reduce fuel economy which is a major attraction of diesel engines.

In the later 1960's, it was recognized that the national air quality standards would become more stringent and that substantial further reduction in auto exhaust emissions would be necessary. Thus, it became obvious that modifications to the internal combustion engine alone could not meet the anticipated standards. An auxiliary system was necessary and the catalytic converter was developed. Large cooperative efforts between petroleum companies and automobile manufacturers were organized. These cooperative programs were aimed at obtaining a low-emission vehicle in which catalytic converters are a part of the system. The catalyst's job is to mitigate the harmful emissions that automotive hardware cannot eliminate.

Some of the most promising controls for air pollution involve the use of catalysts. Catalysts are used to control emissions from both mobile sources and stationary sources. Developing catalysts for the former application is a tremendous challenge for the catalytic scientist. In general, the catalyst must be able to withstand considerable exposure to an

environment that is not friendly to catalytic systems. This is a far cry from the usual mode of operation for catalytic reactors in chemical plants or petroleum refineries where the keyword is stability. The catalyst must exhibit high efficiencies under transient conditions; it must further be effective at temperatures from ambient to about 1100°K, and it must withstand the poisoning action of additives in the fuel and combustion on products that are emitted with the exhaust. These specifications stress the chemical performance of the catalyst. Physically, it must be able to withstand thermal shock; be attrition-resistant to the highly turbulent exhaust gas through the converter; and last 100,000 miles.

Automotive exhaust emissions are controlled by catalytic converters located in the exhaust system so that all exhaust gases pass through them. The first large-scale effort to employ catalytic converters to control auto exhaust emissions began in the late 1950's. Most of the work was conducted by catalyst producers alone or jointly with muffler or converter manufacturers. This effort was directed at the California market and dealt with automobiles that had a high level of emissions. The catalytic converter was not adopted at this time because the auto manufacturers found it more economical and convenient to reduce the exhaust emissions by modifying ignition and to install devices to reduce venting emissions from the engine. Converters using oxidation catalysts were introduced in 1975 in response to the original Clean Air Act of 1970. They convert carbon monoxide and hydrocarbons produced by incomplete fuel combustion in IC engines into carbon dioxide and water.

1.3 Removal of Nitrogen Oxide

Basically, two different environments are required to purify the exhaust gases. For HC and CO control, an oxidation catalyst in a fuel-lean atmosphere must be used. For NO_x removal, a reduction catalyst operating in a fuel-rich atmosphere is employed to effect reduction by CO, H₂, and/or HC. With lean-burn spark-ignition engines, hydrocarbons in

the exhaust gas act as a reducing agent. Actually, the most straightforward way of removing NO_x is by simple decomposition into N_2 and O_2 , a reaction that is thermodynamically favored except at very high temperatures.

Nitrogen oxide pollutants are removed from auto exhaust emissions by “unfixing” nitrogen. In particular the decomposition or reduction of nitrogen monoxide (NO) is a major target to be achieved. In theory, nitrogen can be “unfixed” by

1. Direct decomposition into nitrogen or oxygen;
2. Reduction of the NO_x to N_2 with reducing agents such as CO, H_2 , and hydrocarbons.

Nitric oxide is thermodynamically unstable relative to nitrogen and oxygen. The thermal decomposition of NO into N_2 and O_2 is thermodynamically favored up to 1000°K , but the kinetics of the decomposition are extremely unfavorable. The catalytic decomposition of NO is the simplest and cheapest method for the removal of NO from exhaust streams. Most attempts to develop practical decomposition catalysts have dealt with a wide spectrum of transition metal oxide catalysts, noble metal catalysts, and alkali metal oxide catalysts. Some of the NO decomposition rates are too low to have practical significance in the treatment of auto exhaust. Some of these materials are active in the reduced state, but oxygen contained in the feed gas or released by the decomposition of NO competes with NO for the adsorption sites and poisons the activity. To remove surface oxygen and regenerate catalytic activity, high reaction temperatures and/or gaseous reductants are required.

The reduction of NO with a wide variety of reducing agents is similar to NO decomposition in that it is favored thermodynamically. Unlike NO decomposition, the rates of reduction are sufficient to warrant practical consideration as catalysts for treatment of auto exhaust.

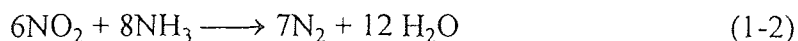
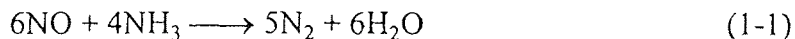
There are three possible processes of reducing nitrogen oxide in an oxidizing atmosphere:

1. Selective non-catalytic reduction (SNCR)

2. Non-selective catalytic reduction (NCR)

3. Selective catalytic reduction (SCR)

SNCR involves the reduction of NO_x with NH_3 or urea at temperatures of 900-1000°C without a catalyst.

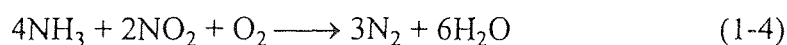
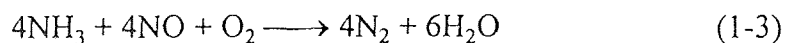


At $\text{NH}_3:\text{NO}_x$ molar ratios of 1:1 to 2:1, about 40% to 60% NO_x reduction can be achieved [EPA, 1983]. Two major SNCR systems are commercially available: The EXXON Thermal De NO_x ammonia injection system and the Fuel Tech NO_x OUT urea injection system. A third system, the Emcotek Two-Stage De NO_x urea/methanol injection system, has undergone extensive pilot testing and full scale demonstration. However, this approach is impractical for treating the oxygen-rich NO_x emissions, such as small-scale diesel engine exhausts, because it requires the on-board storage of NH_3 , a pollutant in its own right which is difficult to handle.

In 1979, the Three-Way-Catalyst (TWC) converter was first installed in gasoline burning IC vehicles, it belongs to the group of processes with non-selective reducing agents (NCR). The catalytic converter was designed to operate within a narrow air-to-fuel ratio in order to simultaneously reduce HC, CO and NO_x . It was adopted widely in 1981 to meet the federal 1.0 g/mile nitrogen oxides standard, catalyze these oxidation reactions and simultaneously reduce nitrogen oxides. The TWC converter is very successful in reducing pollutants from IC engines, but is not very effective for diesel engines. The reason is that under lean conditions, the removal efficiency for CO and HC is very high but NO_x is not affected. Moreover, particulate emissions tend to plug the channels of the catalytic converter and deactivate the catalyst. Therefore, TWC has not been applied to the exhaust from diesel engines..

Selective catalytic reduction (SCR) of NO_x was first discovered in 1957 in which NH_3 was used as the reducing agent. Selective catalytic reduction (SCR) process with

ammonia is now widely used to remove NO_x from stationary sources such as industrial boilers and power stations. The general SCR classes of catalyst, were platinum for low temperature (175-250°C), vanadium for medium temperature (300-450°C), and zeolite for high temperature (350-600°C). The major desired reactions are:



The principal advantage of this process is its ability to reduce NO_x in the presence of oxygen. But also because of the toxicity of NH_3 , it is not used for automotive exhaust cleaning.

In recent years, the application of zeolites has been one of the most exciting developments in catalysis. Zeolites are crystalline aluminosilicates of the general formula $\text{M}_v(\text{AlO}_2)_x(\text{SiO}_2)_y \cdot \text{ZH}_2\text{O}$ in which M is either a monovalent or divalent cation. In the former case v is equal to x, whereas if M is divalent v is equal to one-half x. The cation can be exchanged reversibly without destroying the aluminosilicate framework. The water can also be removed without destroying the framework and can be replaced by other molecules whose molecular dimensions are smaller than the pore size of the cavities that are regularly distributed in the framework. The frame work is based on the combination of AlO_4 and SiO_4 tetrahedrons. Various structures with different properties can occur. The zeolites both occur naturally and can be made synthetically on either laboratory or industrial scale. Synthetically produced zeolites are used for the majority of industrial applications, including catalysts.

Zeolites are available in a wide variety of types differing in structure from one another and each type of zeolite has a variety of coordination arrangements. Therefore, the performance of a catalyst for purifying exhaust gas depends on the type of zeolite which is employed and its coordination arrangement.

Transition metal exchanged zeolites were found to be very active for reducing NO_x . Among these, Cu-ZSM-5 is the most active one. Zhang et al.(1994), with no

reducing agent (soot) present, found a maximum NO conversion using Mg or Cu modified ZSM-5 of 80% in the absence of O₂, with a significant decrease in conversion in the presence of 5% O₂. Iwamoto and co-workers (1989) and Held and co-workers (1990) discovered that Cu-exchanged ZSM-5 Zeolites were the most active catalysts for this reaction.

Bartholomew et al.(1992) reviewed selective catalytic reduction of NO with hydrocarbons and presented data to show that propane reduces NO by up to 95% over Cu ion-exchanged ZSM-5 in the temperature range of 200°C to 600°C and at space velocities of over 100,000v/v/hr. They showed that NO is converted to N₂ with nearly 100% selectivity and water poisons the catalyst at all temperatures. In a kinetic study, they determined the overall reaction order to be between 1 and 2 and the activation energy to be approximately 20 kcal/mol. Bartholomew et al.(1992) also showed that the optimum reaction temperature was 350°C at 76,000v/v/hr and 1% oxygen in the reactant. Additional oxygen seemed to oxidize propane and reduce its availability for NO reduction. On the other hand, the reaction rate was essentially zero with no oxygen present.

Tsutsumi et al.(1993, 1994), using a rotating fluidized bed to treat diesel engine exhaust gases, reported a considerably higher NO conversion over Cu-ZSM-5 catalyst than reported elsewhere in the literature.(Iwamoto et al., 1989;1991; Sato et al., 1991; Zhang et al., 1994). Conversion of NO at 693°K as high as 95% was reported at low superficial velocity (15 cm/s) but conversion decreased rapidly to 5% at a superficial velocity of 55 cm/s. They also found a significant decrease in conversion as the temperature of the gas is decreased to 623°K. The soot removal efficiency was also very high (99%) at a superficial velocity of 18 cm/s, decreasing to about 77-83% at higher gas velocities.

Kintaichi et al.(1990) reported that the reduction of NO occurs highly selectively in the presence of about 10% oxygen by using H-form zeolite, alumina, silica-alumina

catalysts and small amount of hydrocarbons as reducing agents. This study suggests that catalysts other than Cu-ZSM-5 can also show good performance for the removal of NO.

The reduction of NO by coke deposited over CaO was studied at temperatures between 350°C and 700°C by Lai et al.(1988). Significant conversion of NO was observed above 500°C, with complete conversion at about 700°C.

The C-NO reaction catalyzed by metal loaded on coal-char both in the presence and in the absence of oxygen was studied by Yamashita et al. (1991). They found that the C-NO reaction was remarkably promoted by the presence of oxygen at temperatures as low as 300°C. The ratio of the activity for NO_x decomposition to that for carbon combustion in the coexistence of nitric oxide and oxygen depended on the kind of metal catalyst. The order of catalytic activity was Cu>Ca>Ni>none for the C-NO reaction. A high conversion for the C-NO reaction in the presence of oxygen was achieved by copper-loaded brown coal-char.

Water vapor, present in the diesel exhaust from fossil fuel combustion, acts as a poison to the zeolite catalyst, because it tends to dissolve the alumina matrix. Also, the relatively small amount of sulfur present in automotive fuel influences the functioning of automotive catalysts to a greater extent than may be anticipated. During combustion, organosulfur compounds in the fuel are converted to SO₂. Over automotive emission control catalysts, the SO₂ can be converted to other sulfur compounds such as SO₃, COS, and H₂SO₄. The chemistry of sulfur over catalysts is a function of temperature, redox potential of the exhaust, composition of the catalyst, and presence of other impurities in the exhaust gas system. The sulfur dioxide can undergo a complex variety of interactions. In turn, these interactions can, influence the catalyst activity (Gandhi et al.1991).

1.4 Objective of the Research

The objective of this research is to obtain fundamental understanding of the decomposition and reduction of NO over different catalysts and different reductants that

can be found in diesel exhaust, such as hydrocarbons, CO and elemental carbon. The effect of space velocity, feed concentrations, the reaction temperature and catalyst deactivation will also be studied. This will allow us to choose an appropriate catalyst and optimum operating parameters for the catalyst. Based on the literature, the suggested catalyst is copper ion-exchanged ZSM-5, a zeolite catalyst which has been shown to be the most active promoter of the reduction of NO with hydrocarbons. However, this catalyst may be poisoned by two products of diesel fuel combustion, water and SO₂ and may not be an optimal choice. Thus, the activity of other types of catalyst will also be tested.

We will also try to gain an understanding of how a solid substance like SOL in diesel soot that does not diffuse into catalyst pores can be influenced by catalytic sites that are present predominantly in pores. This research is part of the overall project “Simultaneous Removal of Soot and NO_x from Diesel Exhaust using Rotating Fluidized Bed Reactor”.

1.5 Basic Principles of Catalysis

The use of catalysts to control rate and direction of a chemical reactions has captured the imagination of scientists and technologists since Berzelius in 1835. Ideas of what constitutes a catalyst and the mechanism of catalytic activity have undergone continuous refinement, spurred by the enormous industrial importance of catalysts as illustrated by the variety of catalytic processes used in modern petroleum refineries and in the chemical process industries, in general. Most of these processes involve heterogeneous catalysts, and an understanding of catalysis from both the theoretical and practical point of view is essential to chemists and chemical engineers (Bond, G.C., 1974).

Catalyst: The definitions of catalysis and of what constitutes a catalyst have gradually evolved as our understanding of the causes of catalytic phenomena has grown. Even today, there is no universal agreement on definitions; the point of view varies somewhat

depending on the investigators, for example, between the fundamental investigator and the practitioner, and among researchers concerned with heterogeneous catalysis, homogeneous catalysis, and enzymes. For present purposes, however, the definition is: A catalyst is a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process (Bond, 1974). The phenomenon occurring when a catalyst acts is termed catalysis. The fundamental concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on the catalyst forms a complex with one or more reactants, from which products are desorbed, thereby restoring the original site and continuing the cycle.

Catalyst Activity: The activity of a catalyst refers to the rate at which it causes the reaction to proceed to chemical equilibrium. The rate may be expressed in any of several ways. The rate of reaction depends on pressure, temperature, concentration of reactants and products, and other variables (Rideal, 1968). For a comparison of the activity of different catalysts, any of several methods may be used. For example, catalyst activity may be expressed as the temperature required for a given conversion at a fixed feed composition and pressure.

Catalyst Selectivity: The selectivity of a catalyst is a measure of the extent to which the catalyst accelerated the reaction to form one or more of the desired products, which are usually intermediates, instead of those formed by reaction to the overall state of lowest free energy. The selectivity of a catalyst may be related to its ability to direct one reaction essentially to equilibrium while having little or no effect on alternate pathways, so that the most stable products are not necessarily formed. Selectivity effects are intimately related to the selective chemisorption characteristics of the catalyst.

Steps in Catalysis: In a catalytic process, reactants must interact with the “active site” on the catalyst. The term “active site” is thought to be that site (or sites) on the catalyst surface on which chemisorption and reaction occur. Basically, a catalytic process includes: (Augustine et al. 1988)

1. Bulk diffusion: reactants must pass through stagnant film from the gas or liquid phase.
2. Pore diffusion: reactants diffuse or are transported through pore structures to the active sites.
3. Chemisorption: a reactant chemically adsorbs on active sites i.e., by bonding.
4. Chemical reaction: a reactant converts to a product on the active sites.
5. Desorption: products desorb from the active sites.
6. Product diffusion: products diffuse through pore from the active sites.
7. Product diffusion: products diffuse through the film to the bulk gas or liquid phase.

Steps 1 and 7 are controlled by mass transfer limitations; steps 2 and 6 are controlled by pore diffusion limitations; and steps 3, 4 and 5 are controlled by chemical reaction limitations. The physical and chemical properties of catalysts and operating condition that control the rate of reaction should be carefully chosen. Figure 1.2 illustrates a conversion versus temperature profile.

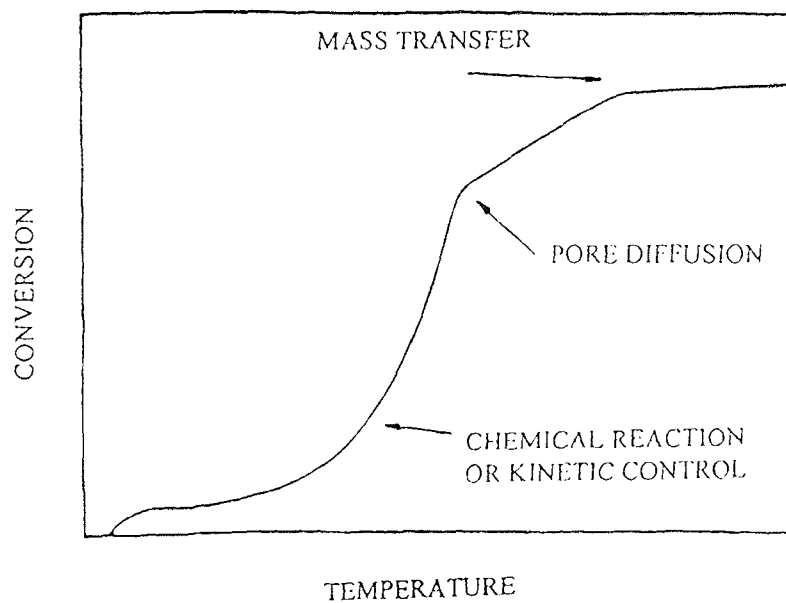


Figure 1.2 Conversion of Reactant as a Function of Temperature Showing Rate Controlling Regions

Catalyst Characterization: The characterization of a heterogeneous catalyst is the quantitative measure of the physical and chemical properties assumed to be responsible for its performance in a given reaction. These measurements have value in the preparation and optimization of a catalyst and, even more importantly, in elucidating mechanisms of deactivation and subsequent catalyst design to minimize such deactivation.

BET Surface Area The most common method of measuring surface area, and one used routinely in most catalyst studies, is that developed by Brunauer, Emmett, and Teller in 1938. This standardized procedure for determining the internal surface area of a porous material with surface areas greater than 1 or 2 m²/g is based on the adsorption of nitrogen at liquid nitrogen temperature onto the internal surface of the carrier.

Each adsorbed nitrogen molecule occupies an area of the surface comparable to its cross sectional area 0.162 nm. By measuring the number of N₂ molecules adsorbed at monolayer coverage, one can calculate the internal surface area. The BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage:

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

Where:

P = partial pressure of N

P₀ = Saturation pressure at the experimental temperature

V = volume adsorbed at P

V_m = Volume adsorbed at monolayer coverage

C = constant

If the above equation is obeyed, a graph of P/ V(P₀-P) should give a straight line, the slope and intercept of which can be used to evaluate V_m and C.

Thermal Gravimetric Analysis: Thermal gravimetric analysis (TGA) is a useful technique to measure microscopic weight changes. A few milligrams of catalyst are

loaded into a sample pan suspended from a microbalance inside a quartz tube. A controlled gas flow and temperature ramp is initiated, and a profile of weight change versus temperature is recorded. The weight versus temperature profile is helpful in establishing procedures for regenerating the catalyst in a process reactor.

Catalyst Deactivation: General reviews of catalyst deactivation have been given by Butt and Levenspiel and they have laid foundations of a better understanding of catalyst deactivation processes (John B. Butt et al.1988). A catalyst may lose its activity or its selectivity for a wide variety of reasons. The cause may be grouped loosely into:

1. Poisoning
2. Sintering
3. Fouling

Poison was once the generic name applied to all forms of catalyst deactivation. In this study, we defined a catalyst poison as an impurity present in the feed stream that reduces catalyst activity. It adsorbs on active sites of the catalyst and, if not adsorbed too strongly, is gradually desorbed when the poison is eliminated from the feed stream. The phenomenon is then temporary or reversible. If adsorption is strong, the effect is permanent or irreversible.

Two general classes of poisoning: selective and nonselective can result in catalyst deactivation. Selective poisoning occurs when a feed compound specifically and discriminately interacts with a specific catalytic component resulting in a poisoning of the active sites. Nonselective poisoning can be caused by a number of reasons, all of which are nondiscriminating in that accumulations of foreign substances occur on both the carrier and active catalytic opponents (Hughes, 1984).

Sintering is a physical process associated with loss of area of the catalyst which occurs when the catalyst is operated above its normal range of temperature. Two different kinds of sintering may be distinguished, depending on the type of catalyst employed. If the catalyst is a normal high-area support type material, operation at high temperatures

will cause a loss of specific surface with associated change in the pore structure, giving a corresponding loss in activity. The second type of catalyst deactivation occurs when the active ingredient, usually a metal, which is supported on a high-area oxide support becomes mobile at elevated temperature. Here, sintering can occur not only by reduction of the support area but by a “coalescence” or loss of dispersion of the metal crystallites (Peterson, 1987). This loss of area of the active constituent of the catalyst causes a sharp drop in activity.

Fouling is a process of catalyst deactivation that may be either physical or chemical in nature. In general, much larger amounts of material are responsible for deactivation in fouling processes than in poisoning. The most typical of fouling processes is that of the carbonaceous deposit or “coke”. The major fouling material in the automotive exhaust which deactivate the catalyst comes from unburned engine oil additive ZDP.

CHAPTER 2

EXPERIMENTAL

2.1 Experimental Apparatus

The experimental apparatus flow schematic is shown in Figure 2.1. This system consists of a laboratory-scale quartz tube reactor (Kontes Scientific Glassware, Inc.) residing in a vertical three zone controlled furnace (Applied Test System, Inc.) containing known volumes of powder catalyst. The flow rates of gases were measured by several calibrated rotameters. The inlet and outlet gases were analyzed by gas chromatography (GC) and a chemiluminescent NO/NO_x analyzer to determine the concentrations of each of them.

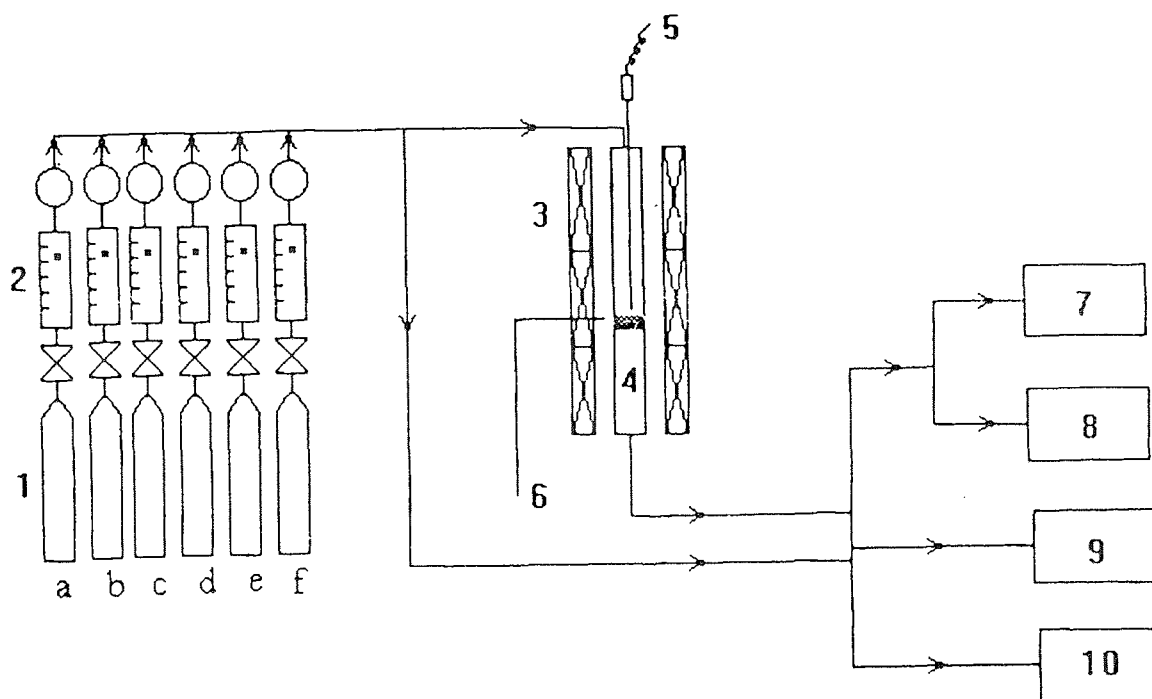


Figure 2.1 Schematic Diagram of Experimental Apparatus

1. Cylinders (He, NO, NO₂, C₃H₈, O₂, CO, SO₂), 2. Flowmeters, 3. 3-Zone Furnace, 4. Quartz Reactor, 5. Thermocouple, 6. Temperature Controller, 7. HP5890 GC-FID, 8. HP5890 GC-TCD, 9. GOW-MAC GC-TCD, 10. NO/NO_x Chemiluminescent Analyzer

A tubular flow reactor is shown in Figure 2.2. The quartz tube reactor is 2.5 cm inside diameter, and 55 cm long. The bed materials consisting of catalyst or carbon black or a mixture of catalyst and carbon black were placed on a 90-150 μm coarse porous quartz disk located at about two-thirds of the height of the reactor. The reactant gases enter into the reactor from the top and are discharged from the bottom (downflow).

The quartz reactor is placed in a three zone electric furnace with three independent temperature controllers. The catalyst samples were contained in the middle zone of the furnace at various residence times and temperatures. The reactor temperature was monitored by a calibrated 0.16 cm Chromel-Alumel (K-type) thermocouple (Omega Engineering, Inc.) which is inserted at the top of the reactor and placed on the center line of the tube immediately before the solid sample. The thermocouple was calibrated using boiling water.

2.2 Instrumental Analysis

Analytical techniques were a very important part of this research. The catalyst surface area, the catalyst particle size, the concentrations of feed and product compounds were all measured. All of the analytical techniques that were used in this study are discussed in this section.

2.2.1 Altamira (AMI-1) Catalysts Characterization Instrument

The Brunauer, Emmett, and Teller (BET) surface area measurement method was used to determine the surface area of the catalysts. All the samples used were weighed and inserted in a quartz U tube. The U-tube was installed on the Altamira (AMI-1) catalyst characterization instrument to measure BET surface area. The AMI-1 is a computer operated catalyst characterization instrument, and is used to conduct standard catalyst characterization tests including BET surface area.

The operating manual for BET measurement was followed exactly. Figure 2.3 shows the BET operating procedure. The parameters used for a three point BET run are shown in Table 2.1.

Table 2.1 Operating Parameters used for BET Surface Area Measurements

Treatment	Treatment Gas	Nitrogen		
		Flow Rate	30 ml/min	
	Hold Time	5 min		
		1st	2nd	3rd
Flow BET	Adsorbate Gas	10% N ₂ in He	20% N ₂ in He	30% N ₂ in He
	Flow Rate	20 ml/min	20 ml/min	20 ml/min
	Adsorption Time	4 min	4 min	4 min
	Desorption time	4 min	4 min	4 min
		1st	2nd	3rd
	Carrier Gas	10% N ₂ in He	20% N ₂ in He	30% N ₂ in He
	Flow Rate	20 ml/min	20 ml/min	20 ml/min
	Response Factor	1.00	1.333	1.280
BET Calibration	Adsorbing Gas	N ₂		
	Flow rate	30 cm ³ /min		
	Time Between Pulse	1.5 min		
	Initial Data Delay	12 sec		
	Data Collection Interval	60 sec		

2.2.2 MasterSizer X Laser Particle Sizer Instrument

The MasterSizer X Particle Sizer measures the size of particles by means of laser diffraction. Laser light scattering is an exceptionally flexible sizing technique able, in principle, to measure the size structure of any one material phase in another. The instrument comprises an optical measurement unit which forms the basic particle size sensor, and a computer which manages the measurement and performs result analysis and presentation.

The MasterSizer X can analyze continuous liquid sprays. The spray merely needs to be directed through the analyzer beam. The MasterSizer X optical laser particle sizer measurement unit comprises a transmitter, a receiver, sample area cover and an optical bench. The transmitter houses the laser, its power supplies and the beam expanding optics

that create the analyzer beam. The receiver houses the range lens, the detector and associated electronics and computer interfaces.

The most important dispersion decision is the choice of the liquid type. The dispersant can be any clear optically homogeneous liquid that does not interact with the sample and change its size. In this experiment, water was used as the dispersant liquid.

The essential steps in measuring a sample are:

1. Prepare the sample.
2. Check the optical alignment.
3. Enter sample documentation.
4. Measure the background.
5. Add the sample to the system at a suitable concentration.
6. Measure the sample.
7. Calculate the size distribution.

The results reported by the instrument have several meanings. The most common result from laser diffraction is that the fundamental size distribution derived by this techniques is reported based on volume. This means that when the result lists, for example, 10% of the distribution in the size category 5-6 μm , this means that the total volume of all particles with diameters in this range represents 10% of the total volume of all particles in the distribution.

It is useful to consider a numerical example. Suppose the sample consists of only two sizes of particle, 50% by number having diameter 1 μm and 50% by number 10 μm . Assuming spherical particles, the volume of each of the larger particles is 1000 times the volume of one of the smaller ones. Thus, as a volume distribution, the larger particles represent 99.9% of the total volume.

2.2.3 Gas Chromatography

Gas chromatography (GC) is the most common analytical technique for the quantitative determination of chemical compounds. Two types of gas chromatographs were used in the experiments, an HP5890A and a GOW-MAC. In both cases, the inlet reactant and outlet effluent products stream entered an on-line GC, flowed through a six-point gas sampling valve, from which it was picked up by the carrier gas to an on-line gas chromatograph.

2.2.3.1 Hewlett Packard 5890A Gas Chromatograph: The Hewlett Packard 5890A gas chromatograph has two detectors: a thermal conductivity detector (TCD) and a flame ionization detector (FID). TCD was used to measure the concentration of N_2 and O_2 . The GC column used with the TCD was a 1/8 inch in diameter by 3 feet long stainless steel tube. The oven temperature of the GC was controlled at $25^\circ C$ so that N_2 and O_2 peaks can be adequately separated.

The CO, CO_2 and propane concentrations were analyzed by flame ionization detector (FID). Generally, FID is not suitable for the measurement of CO and CO_2 . Due to the limitations of TCD sensitivity, the sample gas of CO, CO_2 or propane was introduced into a nickel hydrogenation catalytic reactor to produce methane allowing the use of the very sensitive FID system. The operating method for the nickel hydrogenation catalyst system is shown in Figure 2.4. When the ten-point sampling valve is at the off position, the product effluents pass through the sampling loop and discharge to the hood. Once the valve is switched over to the on position, the effluents are carried out by Helium from the sampling loop into the column. The individual peaks are then hydrogenated with hydrogen to CH_4 using the Ni-catalyst at $350^\circ C$. Thus, the CO and CO_2 peaks are detected as CH_4 and recognized based on retention time. The GC column used with FID is a 1/8 inch in diameter by 6 feet long stainless steel tube.

The detailed operation conditions are listed in Table 2.2.

Table 2.2 Operation Conditions of HP 5860A

Detector	TCD, HP5890	FID, HP5890
Detector Temperature	120°C	250°C
Injection Temperature	120°C	350°C
Column Temperature	25°C	25°C
Carrier Gas	Helium	Helium
Loop Volume	20 μ l	20 μ l
Packing Materials	Molecular Sieve 5A 60/80	Porapak Q 80/100
Integrator	HP3396A	HP3396A
TCD Carrier Gas Flowrate	20 ml/min	-
TCD Reference Gas Flowrate	20 ml/min	-
Ni Catalyst Reaction Temperature	-	350°C
Air Flowrate of FID	-	400 ml/min
H ₂ Flowrate of FID	-	35 ml/min

2.2.3.2 GOW-MAC Gas Chromatograph: The purpose of using this GOW-MAC Series 550P was to measure the NO concentration in the inlet and outlet gas stream at low space velocity. The GOW-MAC GC was equipped with a thermal conductivity detector (TCD). The column used was a 1/8 inch in diameter by 12 feet in length stainless steel tube. To obtain a good separation of NO and O₂ peaks, the column was extended from the oven and was immersed in an ice bath to keep the column temperature at 0°C.

The GC operating conditions are listed in Table 2.3.

Table 2.3 Operation Conditions of GOW-MAC Series 550P

Detector Temperature	200°C
Injection Temperature	150°C
Column Temperature	0°C
Detector Current	200 mA
Carrier Gas	Helium
Loop Volume	1 ml
Packing Material	Porapak Q 80/100
Carrier Gas Flowrate	26 ml/min
Reference Gas Flowrate	26 ml/min
Integrator	HP3396A

2.2.4 Chemiluminescent NO/NO_x Analyzer

A chemiluminescent Thermo Electron model 10A NO/NO_x analyzer manufactured by Thermo Electron Corp. was used to measure gaseous NO and NO_x. The chemiluminescent producing reaction of NO and O₃ provides the analysis signal for this technique. Specifically,



Light emission results when electronically excited NO₂ molecules revert to their ground state.

To measure NO concentration, the gas sample to be analyzed is blended with O₃ in the instrument's reaction chamber. The O₃ is generated in situ by a high voltage arc ozone generator. The resulting chemiluminescence is monitored through an optical filter by a high sensitivity photomultiplier positioned at one end of the chamber. The filter/photomultiplier combination responds to light in a narrow wavelength band unique to the above reaction. The output from the photomultiplier is linearly proportional to the NO concentration.

Basically, chemiluminescent analysis is only sensitive to NO. To measure NO_x concentrations, the sample gas flow is diverted through a high temperature NO₂ to NO converter. A temperature controller is used to maintain the proper temperature for NO₂ thermal conversion to NO which is 650°C. The chemiluminescent response in the reaction chamber to the converter effluent is linearly proportional to the NO_x concentration entering the converter. By taking the difference between NO_x and NO, one can obtain the quantity of NO₂ in the gas stream.

A minimum gaseous flowrate of 2 SCFH (about 1L/min) is required by the instrument to measure NO and NO_x.

2.2.5 Thermal Gravimetric Analysis

The TGA tests were conducted to study the catalyst and carbon black weight change with changing temperature. The TGA 7 is made up of two major components: a sensitive ultramicrobalance which permits the measurement of weight changes as small as 0.1 μg and a furnace element capable of achieving temperatures of 1000°C. With the PE 7500 Professional Computer and UNIX operating system, the modular TGA 7 permits the measurement of weight changes in a sample material as a function of temperature or time resulting from chemical reactions, decomposition, solvent and water evolution, curie point transitions and oxidation of sample materials.

2.3 Gases and Catalysts

All gases were supplied by Matheson Gas Products. The concentration of the active gas in different gases is listed below:

NO: 1180 ppm (in Helium)

NO₂: 1070 ppm (in Helium)

C₃H₈: 1207 ppm (in Helium)

CO: 1010 ppm (in Helium)

SO₂: 211 ppm (in Helium)

O₂: 99.995%

Helium: 99.995%

Mobil Research and Development Company provided us with a sample of 100% Cu-exchanged ZSM-5 catalyst combined with a silica-alumina binder designed to resist attrition in the fluidized bed. The mixture was 50% by weight catalyst and 50% by weight binder. It is a solid powder with light-yellow color. Mobil also provided separate samples of SiO₂/Al₂O₃, which is a solid powder with yellow color. The Al₂O₃ is a white solid powder provided by the Alcoa Technical Center.

2.4 Experimental Procedure

2.4.1 Fixed Bed

The experiments of NO decomposition and NO reduction by different reductants were carried out in the quartz fixed bed reactor described above. A volume of 3 ml of solid sample was first put on the porous quartz disk inside the reactor and heated to the desired temperature under helium flow for a short period of time in order to remove impurities such as water and oxygen which may be adsorbed on the solid materials. Then the experiment was started by switching different sample gases to flow through the reactor. Activity tests were carried out in a temperature range of 300°C to 600°C. The gaseous compositions were measured by the GC and NO_x analyzer.

In order to know the effect of space velocity on the reaction, two different space velocities were used. The space velocity can be calculated as follows:

$$\text{Space Velocity} = \text{Total flow rate} / \text{Solid sample volume} \quad (2-3)$$

The aging experiments were run to determine catalyst deactivation over time. A fresh catalyst was used to catalyze a reaction at a certain temperature. After this run, the catalyst bed was cooled down to room temperature. Then the furnace was heated and the activity of the catalyst was checked.

2.4.2 Thermogravimetric Analysis

In this experiment, the empty sample pan was first weighed to get a zero point reading. Then 4-6 mg of sample was loaded into the sample pan, and after the reading became stable, the initial weight was recorded. The next step was to set the desired temperature program, and start the experiment. During the experiment, flow of reactant gas was added at the required temperature. The procedure developed for conducting these tests was to heat the sample to the desired temperature, wait until the percentage weight reading stabilized, and then introduce the desired reactant gas into the furnace at the required temperature. Finally, a weight percentage versus temperature curve was obtained.

During the experiments a Helium purge gas flowed through the TGA to prevent any decomposition products or reactive gas sample from entering into the balance chamber.

The experimental parameters used to operate the TGA 7 are listed in Table 2.4.

Table 2.4 The Parameters Used in TGA Analysis.

Sample Parameter		Sample weight: Sample Zero:	
Atmosphere Parameter		Purge Gas: Helium	
Temperature Program	Initial	Temperature	Rate
	Final	120°C 800°C	40°C/min

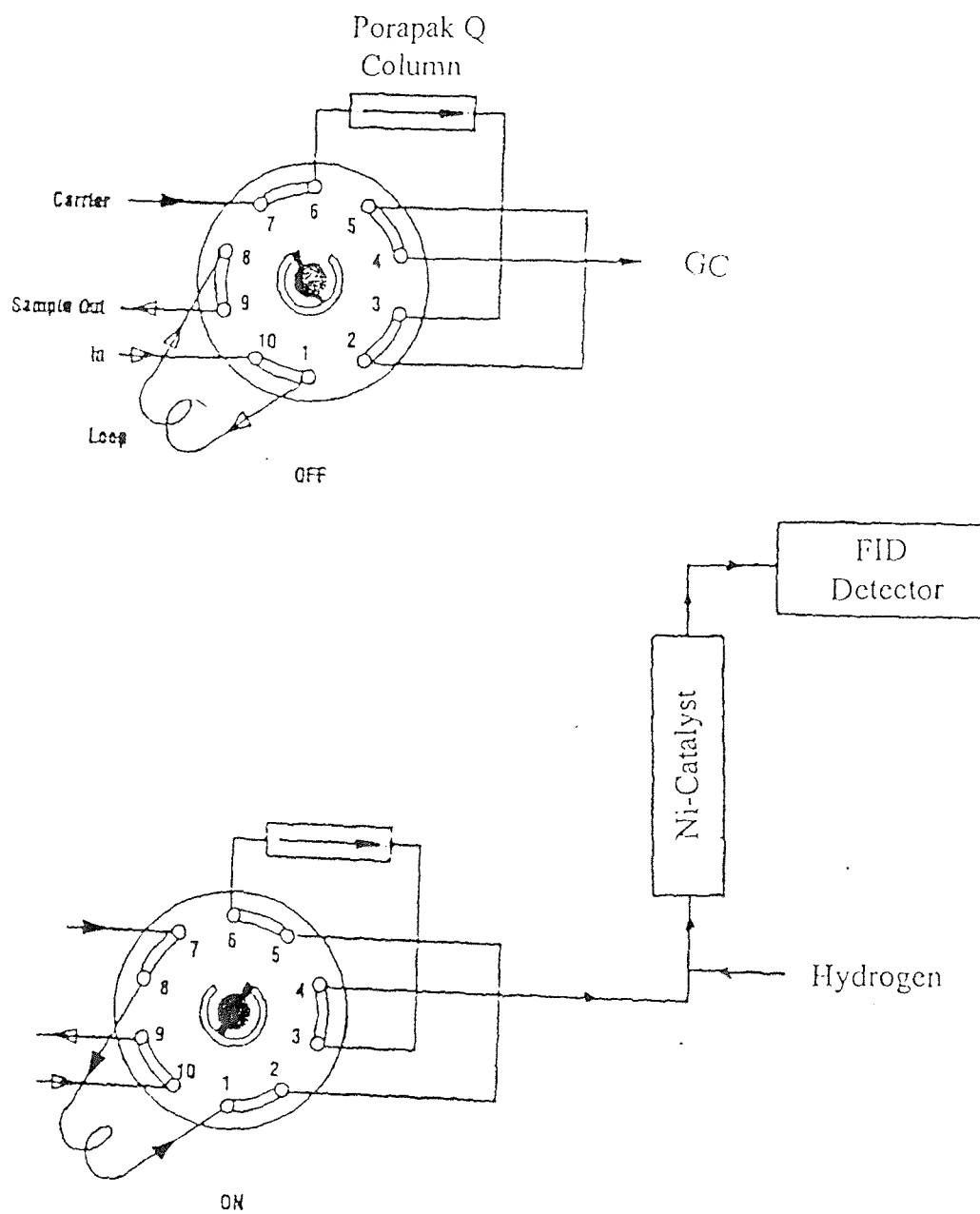


Figure 2.4 Nickel Hydrogenation Catalyst System

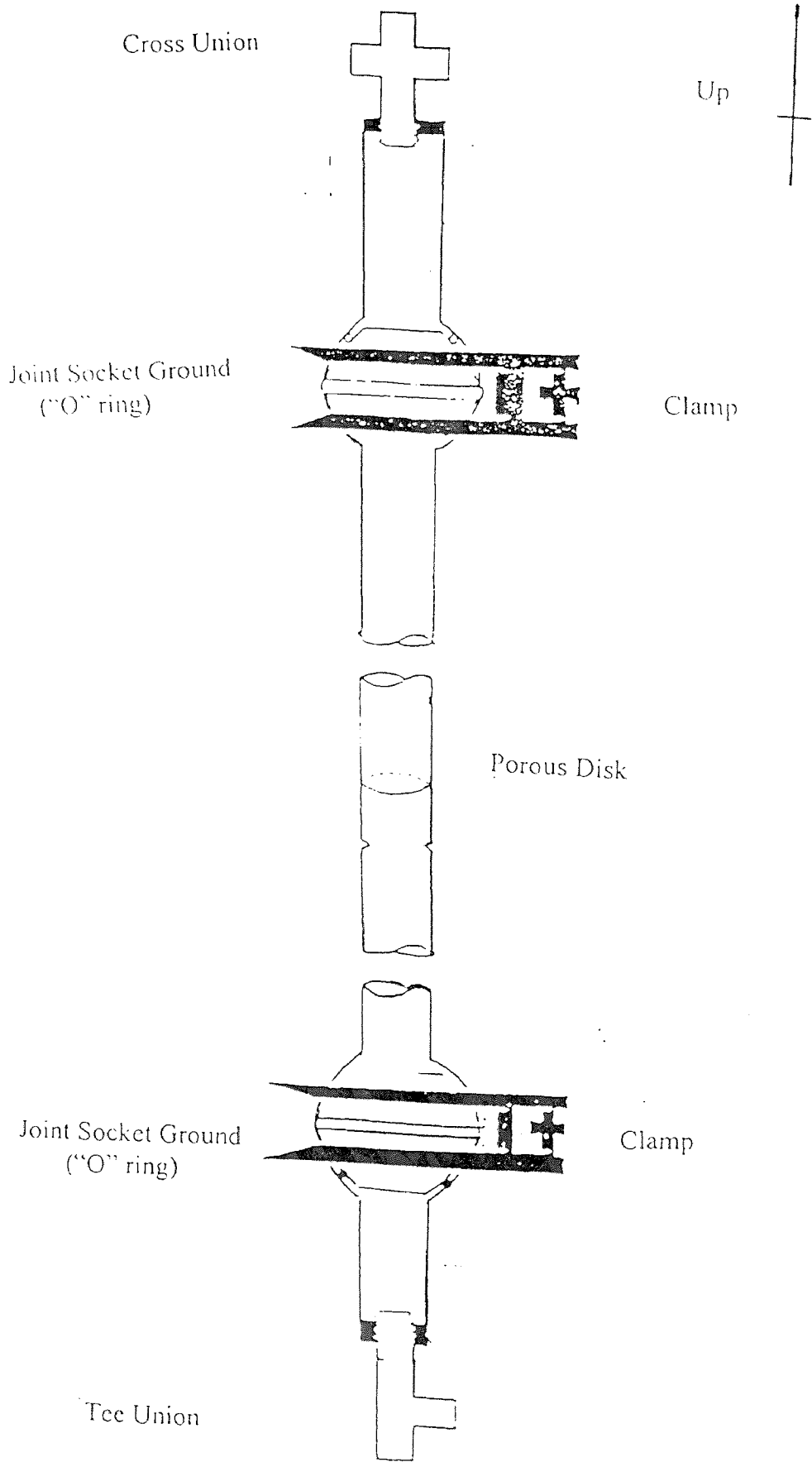


Figure 2.2 Design of Quartz Reactor

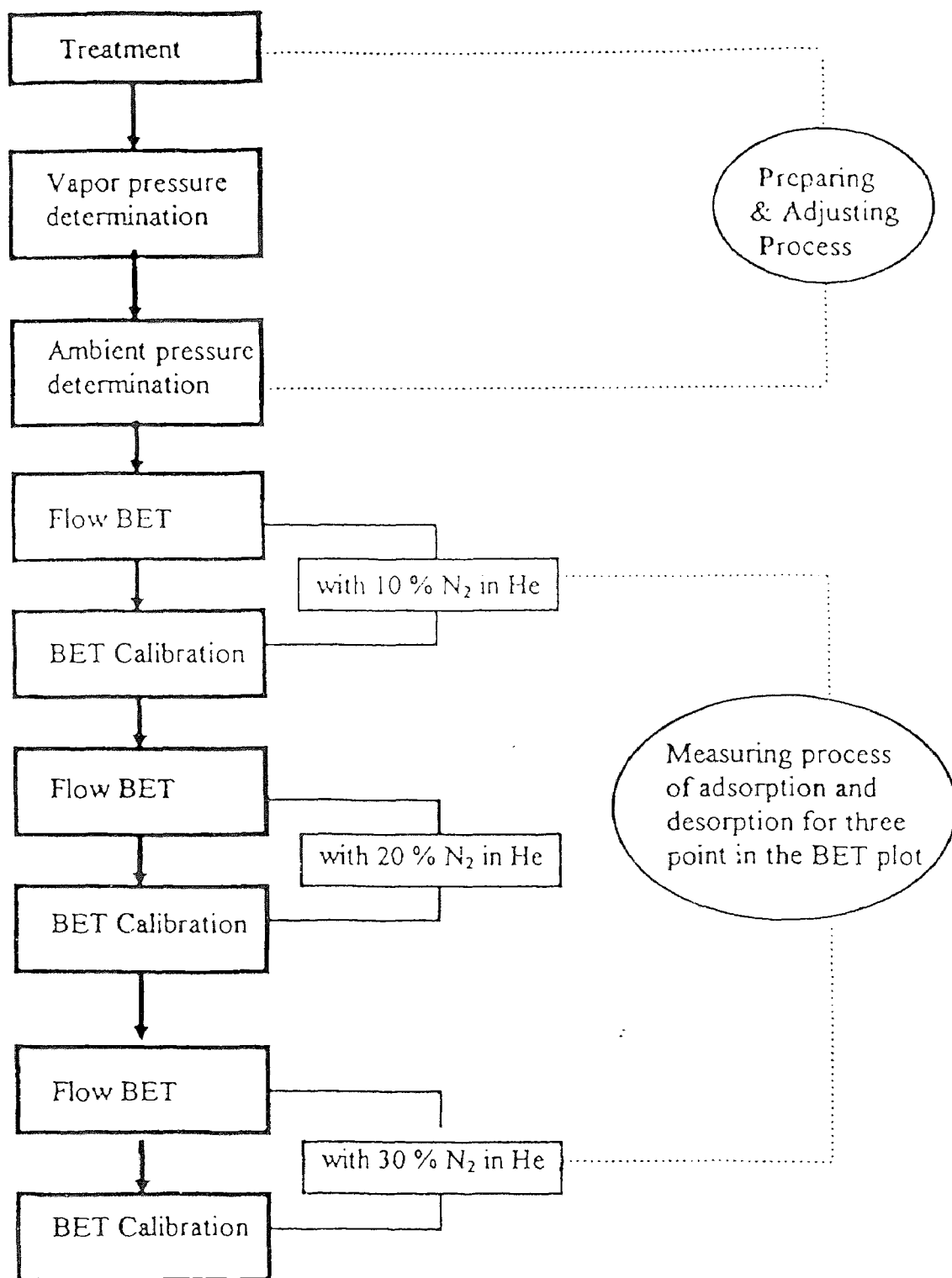


Figure 2.3 Procedure of BET Surface Measurement by AMI-1

CHAPTER 3

RESULTS AND DISCUSSION

3.1 BET Surface Measurement

The BET surface areas of the catalysts and powders used in the experiment were measured using the Altamira catalyst characterization instrument model AMI-1. A weight of 0.05 g of each catalyst was used to conduct the measurement. The procedure was described in Chapter 2. The results of the BET surface area measurements using the computer integrated system of the Altamira are given in Table 3.1. Figure 3.1 is a typical BET plot for the Cu-ZSM-5 used in this research (i.e., 50% Cu-ZSM-5 and 50% SiO₂/Al₂O₃).

Table 3.1 Surface Area of Catalysts and Powders used in This Research (m²/g)

	Cu-ZSM-5	ZSM-5	Al ₂ O ₃	SiO ₂ /Al ₂ O ₃	Calcined Al ₂ O ₃
ADS.	118	169	109	59	112
DES	123	132	110	45	104
AVERAGE	120.5	150.5	109.5	52	108

3.2 Measurement of Particle Size

The particle size distributions of the powders and catalysts were determined using a MasterSizer X Particles Sizer described in Chapter 2. Table 3.2 shows the experimental results. It lists mean particle size in volume percent as well as in number percent. The mean particle size is based on volume and number distribution. In the case of Cu-ZSM-5, 83.82 μm is the mean particle size for the Cu-ZSM-5 volume distribution. The volume particle size of alumina after calcining to 400°C is larger than before, this is because the agglomeration of the sample resulting from sintering.

Table 3.2 Particle Size of Different Particles (μm)

	Cu-ZSM-5	ZSM-5	Al_2O_3	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Cal. Al_2O_3
Volume	83.82	66.91	89.78	54.92	124.92
Number	4.08	1.33	1.47	1.26	1.37

3.3 Decomposition of NO

A NO_x decomposition catalyst, which would not require a reductant to destroy NO_x , would be ideal for diesel applications because of the low availability of engine exhaust hydrocarbon reductants. The NO_x decomposition reaction is shown below:



The catalytic activity of Cu-ZSM-5 for the NO decomposition was measured as a function of reaction temperature at a fairly low space velocity of 2,140v/v/hr. The temperature dependence of NO decomposition over Cu-ZSM-5 is shown in Figure 3.2. The maximum activity was observed around 400-450°C. Above this temperature, the percentage conversion decreased with increasing temperature. When the reaction temperature was again set at 400°C after the experiment at 500°C, the amount of conversion of NO into N_2 and O_2 was the same as those of the original samples, within experimental error. Hence the decrease in the catalytic activity at higher temperatures was not attributable to the deactivation of the catalyst. It is presumably due to changes in the reaction mechanism as a function of temperature.

In the absence of the catalyst, the formation of N_2 and O_2 was not observed under these conditions, indicating the catalytic nature of the decomposition. As shown in Figure 3.2, the percent (volume) conversion of NO was not equal to the percent (volume) formation of N_2 and O_2 based on stoichiometry. The difference between the amount of NO reacted and N_2 and O_2 produced can be attributed to:

1. The formation of NO_2 , which could not be detected by usual gas chromatographic techniques. The reaction, $2\text{NO} \longrightarrow \text{N}_2 + \text{O}_2$, proceeds first on the catalyst, then part of O_2 produced reacts further with unreacted NO to form NO_2 by reaction (3-2).



2. N_2O was detected by Iwamoto et al.(1991) at temperatures below 400°C . But in this experiment, N_2O was not detected.

3. Recent results by Y.Li et al.(1994) suggest that N_2O_3 -like species formed on Na exchanged zeolites by co-adsorbing NO and NO_2 . This compound could also be formed on Cu-ZSM-5 which we used in our experiment.

It is very important to conduct a material balance for this reaction. The nitrogen balance can be obtained from the inlet and outlet nitrogen concentration. Table 3.3 summarizes the nitrogen balance.

Table 3.3 Nitrogen Balance of NO Decomposition

Temp. ($^\circ\text{C}$)	Inlet NO C (ppm)	Outlet conc. (ppm)			NO conv.(%)	N balance
		NO	N_2	O_2		
300	590	388	85	61	34.21	94.58%
350	590	333	111	93	43.57	94.08%
400	590	246	154	136	58.30	93.90%
450	590	262	145	118	55.59	93.54%
500	590	346	110	98	41.36	95.93%

As mentioned before, the quantity of nitrogen and oxygen recovered are lower than expected. If one assumes that the difference in nitrogen is due to NO_2 formation, then NO_2 concentration can be calculated. From this calculation, one can check the O_2 balance, which is listed in Table 3.4.

Table 3.4 Oxygen Balance of NO Decomposition

NO_2 Concentration Required to Obtain 100% N Balance (ppm)	O_2 Balance
32	97.3%
35	99.8%
36	106.1%
38	97.3%
24	100.0%

The temperature dependence of the catalytic activities of Al_2O_3 and $\text{SiO}_2/\text{Al}_2\text{O}_3$ are also shown in Figure 3.3. Cu-ZSM-5 displayed the best activity among the three catalysts at temperature below 450°C . Al_2O_3 shows the highest catalytic activity at 500°C . It can be seen that NO conversion to N_2 increases with alumina content.

3.3.1 Effect of Space Velocity

Conversion of NO to N_2 and O_2 is expected to be a strong function of space velocity. Consequently, tests were run at high space velocity in an attempt to test the catalyst performance in the practical application range. The degree of NO removal over Cu-ZSM-5 was investigated at two space velocities: a low space velocity of 2,140/h and a high space velocity of 20,000/h. The desired space velocity was obtained by varying the flow rate of the reactant gas mixture through the catalyst in the quartz reactor.

As shown in Figure 3.4, conversion to N_2 was 52% at 2,140/h and 17% at 20,000/h at 400°C . For NO decomposition, conversion to N_2 is lower at high gas space velocities. This is because at high gas space velocities, residence time and contact time of NO with the catalyst is shorter, and thus rate of product formation is reduced. The results, nevertheless, demonstrate that the catalyst has activity for the catalytic decomposition of NO even at high gas velocity, which is important for practical use.

3.3.2 Effect of Oxygen

To get further information concerning the activity of the catalysts under practical conditions, the activity was reinvestigated in the presence of large excess of O_2 . When 1% O_2 was introduced into the reaction system, the degree of decomposition of NO was greatly decreased to about half of the values without O_2 . In the presence of 10% of O_2 , which corresponds to the exhaust gases from conventional diesel engines, the conversion did not exceed 10%

3.3.3 Effect of SO₂ and Water

SO_x poisoning of catalyst for NO decomposition is another problem that needs to be solved. The activity of the catalysts was measured after being treated with a mixture of SO₂ (22 ppm), O₂ (10%) and H₂O (10%) at 400°C for 10 hr. In that period of time, the activity of Cu-ZSM-5 for NO decomposition decreased drastically.

Then the deactivated catalyst was exposed to a helium stream at 500°C for an hour. After that, the catalytic activity of the catalyst was tested again. It was found that the catalytic activity of Cu-ZSM-5 was completely regenerated. That is, the SO₂ was desorbed at the higher temperatures resulting in regeneration of the decomposition activity. This suggests almost no change in the active sites due to the SO₂ treatment. SO₂ would compete with NO for the adsorption sites and prevent the catalytic reaction.

3.4 Reduction of NO by CO

As mentioned in the previous sections, Cu-ZSM-5 is very active for the decomposition of NO. But the catalytic activity is inhibited by O₂, SO₂ and H₂O, all of which are always present in diesel exhausts. In light of the enormous challenges involved in developing viable NO_x decomposition catalysts, an alternative approach of selective NO_x reduction is now under intensive investigation.

The reducing gases have been classified into two groups, selective reductants (for example, C₂H₄, C₃H₆, C₄H₈ and C₃H₈) and non-selective reductants (H₂, CO, CH₄ and C₂H₆). The results of the propane NO reaction will be depicted in section 3.5 as an example of the former group. From the non-selective reductants, CO was selected to be used in these experiments.

In diesel exhaust, CO concentration is relatively high. For a 1.8L diesel engine, the CO concentration in the exhaust is around 200 ppm. It is possible to use CO as a reductant for the NO removal in diesel exhaust.

3.4.1 Effect of CO Concentration

In order to know if NO and CO can react in the absence of a catalyst, a stream of 590 ppm NO and 505 ppm CO was passed through the quartz reactor at 500°C and a space velocity of 2,140/hr. The results showed no detectable NO or CO conversion.

When Cu-ZSM-5 was used, N₂ conversion can be detected. The experiment was conducted under different NO and CO concentrations. The result is shown in Figure 3.5.

From the figure, we can see that:

1. NO conversion increases in the presence of CO as compare to without CO.
2. NO conversion will increase when CO/NO ratio increases.
3. The highest NO conversion can be achieved around 400°C .

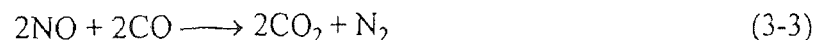
3.4.2 Effect of Oxygen

When 10% O₂ was added in this reaction system, the conversion of NO into N₂ was inhibited in the temperature range examined (Almost no N₂ was found). It follows that CO is not an effective reductant for NO in the presence of O₂.

3.4.3 Reaction Mechanism

CO and NO adsorption on CuO was studied by Davydov and Budneva (1984). The original heterogeneity of the CuO surface was suggested to account for the presence of two states of surface copper cations with different effective charges. Interaction between NO and CO resulted in the formation of isocyanate (-NCO) structures, while CO and NO molecules were competing for the same active sites of Cu⁺.

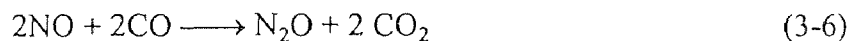
The rate of NO reduction into N₂ with catalyst Cu-ZSM-5 is enhanced in the presence of CO. The improvement may be due to either a direct reaction of CO with NO catalyzed by Cu-ZSM-5,



or a reaction of CO with O₂ which comes from the direct decomposition of NO,



which is equivalent to $2\text{NO} + 2\text{CO} \longrightarrow 2\text{CO}_2 + \text{N}_2$. N_2O may be a intermediate in this reaction. First, N_2O is produced by the reaction by NO and CO.



Then, $\text{CO} + \text{N}_2\text{O} \longrightarrow \text{N}_2 + \text{CO}_2$. However, no N_2O was detected in our experiments.

Copper atoms and ions (Cu^+ , Cu^{2+}) in Cu-ZSM-5 take part in the formation of isocyanate complexes and carbonyl compounds. There are surface oxygen molecules on the catalyst. At elevated temperatures, the catalyst can lose surface oxygen, plus the oxygen from NO. Thus Cu^{2+} ions can be rather easily reduced to Cu^+ .

The reason why oxygen inhibits the NO conversion in the (NO + CO) reaction system may be due to two factors. First, NO reduction is inhibited by active sites tied up by chemisorbed oxygen. Second, oxygen prevents the redox behavior of the copper ion in the catalyst.

3.5 Reduction of NO by Hydrocarbon over Cu-ZSM-5

Selective catalytic reduction (SCR) is presently one of the most technically advanced technologies for efficient removal of NO_x from large and small scale combustion processes. In general, hydrocarbons have a certain degree of selectivity for promoting NO reduction. The SCR process using hydrocarbons has potential applications in NO_x removal from small to large-scale power plants and diesel engines. Based on previous studies, there are several factors that govern the overall performance of zeolite SCR catalysts. The nature of the metal ion, extent of metal loading, catalyst acidity, nature of hydrocarbons, hydrocarbon to NO ratio, space velocity of the feed gas, oxygen concentration, and the presence of water vapor and SO_2 are some of the important factors that determine overall NO conversion and the temperature of maximum conversion. In

our experiments, propane (C_3H_8) is used as a reductant. NO reduction was carried out over Cu-ZSM-5 and Al_2O_3 respectively.

As shown in Figure 3.6, nitrogen conversion in the ($NO + C_3H_8$) system in the absence of O_2 is low in the temperature range of $200^\circ C$ to $500^\circ C$. The catalytic activity is small. The N_2 conversion that occurs is probably due to NO decomposition.

3.5.1 Effect of Oxygen

The effect of oxygen on the catalytic activity is also shown in Figure 3.6. The conversion level of NO rapidly increased with only 1% of oxygen. N_2 conversion is very significant both at O_2 concentrations of 1% and 2%, indicating that O_2 is necessary for the catalytic reaction. When the O_2 concentration is raised from 1% to 2%, there is a slight decrease in the maximum N_2 conversion level. After that, a decrease in N_2 conversion occurs in 2% O_2 compared to 1% O_2 . This is because at high O_2 concentrations, propane is consumed by direct oxidation by O_2 at high temperatures and its availability for NO reduction is reduced.

Another experiment was run at $350^\circ C$, the temperature at which maximum conversion to N_2 is attained. The system was consisted of ($NO + C_3H_8$) and different concentrations of O_2 . From Figure 3.7, it can be seen that when the O_2 concentration is around 1% to 2%, the highest NO reduction to N_2 is attained. At higher concentration of oxygen, the catalytic activity decreased slightly. However, the catalytic activity at 12% oxygen is still 7 times greater than that without any oxygen.

3.5.2 Effect of C_3H_8 Concentration

Figure 3.8 shows the effect of NO and C_3H_8 concentrations on N_2 conversion over Cu-ZSM-5 in 1% O_2 . Reactant concentrations and C_3H_8/NO ratio is listed in Table 3.5.

Table 3.5 Reactant Conc. and C₃H₈/NO Ratios of (NO + C₃H₈) Reaction System

C ₃ H ₈ (ppm)	NO (ppm)	C ₃ H ₈ /NO
295	590	0.5
590	590	1
708	354	2

From the data, we can see that low propane/NO ratios result in low N₂ conversion. On the other hand, high propane/NO ratios will increase N₂ conversion. The increase in conversion with increasing propane concentration (NO concentration held constant) indicates a positive propane concentration dependence on the rate of reaction. The decrease in NO conversion above 350°C is consistent with the previous suggestion of competing reactions decreasing the conversion of NO. It should be noted that the amount of oxygen introduced was much larger than the amount necessary to oxidize 590 ppm propane completely.

3.5.3 Effect of Space Velocity

A high space velocity of 20,000/h was chosen for the reaction system of (NO + C₃H₈ + O₂). As can be seen in Figure 3.9, a maximum N₂ conversion of 85.1% is reached at a space velocity of 2,140/h and a temperature of 350°C. At the space velocity of 20,000/h, the conversion reaches a maximum of 83.0% at 400°C.

For NO decomposition, an increase in space velocity will result in a decrease in N₂ conversion, but things are quite different for NO reduction by propane. In both low space velocity and high space velocity cases, below the maximum N₂ conversion temperature, the selectivity of hydrocarbons toward the reduction of NO increases with temperature, whereas the selectivity decreases with temperature above the maximum N₂ conversion temperature. From Figure 1.2, we can see that after the temperature reaches the light off point, the reaction rate increases dramatically. At certain temperature, the conversion curve begins to flat out. The higher curve slope, the faster the reaction rate.

So from Figure 3.9, we can say that the reaction rate is higher at low space velocity than high space velocity.

3.5.4 Effect of Water

Cu-ZSM-5 exhibits fairly good performance for NO reduction by hydrocarbons under oxidizing conditions. But catalytic deactivation is an area of vital importance in auto exhaust catalysis. Practical automotive emissions control catalysis involves very demanding conditions: highly exothermic catalytic redox reactions at high temperatures (over 800°C, sometimes over 1000°C) and in gas streams containing about 10% water which could poison the catalyst. The deactivation of Cu-ZSM-5 was studied in this section.

The effect of water was studied by bubbling propane through water. The water temperature was controlled by a furnace in order to get different water partial pressures. Propane was bubbled through the water first before mixing with NO and O₂ as feed to the catalytic reactor. The experiment was carried out at three different water concentrations, 5%, 10% and 15%. The partial pressure of the water was determined by the percentage of water vapor needed in the reaction system (See equation below, where X refers to water partial pressure at different water temperature, 760mmHg is the atmosphere pressure. Propane occupied 39.1% of the total gas volume). And then the water temperature can be found in chemistry handbooks according to water partial pressure. The result is shown in Table 3.6.

$$\frac{X\text{mmHg}}{760\text{mmHg}} * 100\% = 5\% \text{ (or 10\%, 15\%)} \quad (3-7)$$

Table 3.6 Concentration of Water Vapor in the Aging Experiment

Conc. of Water	Vapor Pressure (mmHg)	Temp. of Water (°C)	Conc. of Water (measured)
5%	77.71	47	4.61%
10%	155.42	61	9.73%
15%	233.13	70	14.31%

In order to know the precise concentration of water vapor concentration, GC-TCD was used to measure the concentration of water vapor in the propane and water mixture. Deionized water was used to get the calibration curve of water. The experiment condition are summarized below:

Column: Poropac Q

Injection Temperature: 160°C

Detector Temperature: 120°C

Oven Temperature: 110°C

The influence of water vapor concentration on the N₂ conversion is shown in Figure 3.10. The experiment was conducted at 400°C and the space velocity was 20,000/h. It can be seen that the conversion to N₂ dropped from 82.4% in the absence of water to 53.1% in the presence of 14.31% water.

Figure 3.11 shows the effect of water vapor on NO reduction by propane in the presence of 1% O₂. In Run 1, without water vapor, a maximum NO conversion of 83% was observed at 400°C. In the presence of 9.73% water vapor in Run 2, N₂ conversions are decreased and reach a maximum of 72% at 450°C, indicating a significant decrease in activity of Cu-ZSM-5 in the presence of water vapor. After Run 2, the water-exposed Cu-ZSM-5 was flushed with helium at 300°C for 30min in the absence of water and the catalytic activity was tested again. From the curve of Run 3, it is apparent that maximum N₂ conversion at around 400°C is only 73%. The original high activity can not be restored, which means a permanent loss of activity for the catalyst.

The aging was carried out by heating either in a flow of 10% water steam of helium or in gas containing 472 ppm NO, 472 ppm propane, 1% O₂ and 10% water vapor. The flow conditions were 1 liter/min over a sample of 3 ml of catalyst at 400°C. At given aging intervals, the NO_x and hydrocarbon conversions were measured. Dependence of conversion on temperature for different aging times were also investigated. As described above, after 5 hrs and 10 hrs of aging, experiments were conducted at the same operating conditions that were used with the fresh catalyst. At the end of aging, an activity run was carried out ramping the temperature up to 500°C. Different pretreatment conditions can be seen in the table below (at 400°C). The result is shown in Figure 3.12.

Table 3.7 Pretreatment Conditions for the Catalyst Aging in Figure 3.12

	Pretreat	NO	C ₃ H ₈	O ₂	H ₂ O	Time (hr)
Fresh	No	-	-	-	-	-
Steam	Yes	-	-	-	+	5
Wet Cat.	Yes	+	+	+	+	5
Wet Cat.	Yes	+	+	+	+	10
Dry Cat.	Yes	+	+	+	-	5

- : No reagent

+: Reagent at standard concentration

Comparison of the catalysis aged catalyst with the catalyst aged in steam confirms that hydrothermal aging is not the only deactivation factor for this type of material. This is a curious result, especially since both the catalytic gas stream and the hydrothermal gas stream contain 10% steam. Catalysis might cause plugging, as might decomposition of the zeolite (to yield amorphous silica-alumina), sintering of copper ions to oxides, and rapid loss of micropore volume. It is reported that Zn-ZSM-5 materials have no dealumination after hydrothermal treatments at 800°C for time periods considerably longer than required to cause substantial sintering of copper in Cu-ZSM-5.

Dealumination is synonymous with the loss of Bronsted acid sites and with the destruction of the geometric integrity of the exchanged Cu-ion sites. If either of these sites is important in NO reduction, dealumination will result in deactivation. Suzuki et al.(1987) investigated the effect of exchanging alkali or alkaline earth metals on the dealumination of HZSM-5. After exposure to flowing steam at ambient pressure and 600°C for 13.5hr, HZSM-5 was 90% dealuminated. The exchanged cations inhibited the dealumination, leaving one framework Al for each exchanged metal cation equivalent. Grinsted et al.(1993) reported that at the harsh conditions of the high-temperature steam treatment, both the protonated and Cu-ZSM-5 are dealuminated to a large degree as evidenced by the sharp decrease in the 54 ppm peak. The treatment of 43%-exchanged Cu-ZSM-5 in a static system at 700°C established that Cu inhibits the dealumination. For a different Cu-ZSM-5 with a high SiO₂/Al₂O₃ ratio of 80 and 'overexchanged' at 147%, it was observed that the activity decreases rapidly at 410°C if the catalyst is exposed to moist air, whereas it is not affected by dry air. The decrease in activity is accompanied by dealumination.

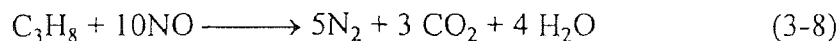
3.5.5 Effect of SO₂

The influence of sulfur dioxide on the catalytic activity of Cu-ZSM-5 was also studied. The dependence of the reaction temperature on the catalytic activity in the (NO + C₃H₈ + O₂ + SO₂) system over Cu-ZSM-5 was first measured. When 22 ppm sulfur dioxide was introduced into the reaction system of (NO + C₃H₈ + O₂), the extent of N₂ conversion decreased and turned into a steady state process after about 30 min. The results are shown in Figure 3.13. The catalytic activity increased with increasing reaction temperature, reached a maximum at 400°C, and then decreased at higher reaction temperatures. By comparing the two curves in Figure 3.13, we can conclude that the addition of sulfur dioxide in the (NO + C₃H₈ + O₂) system results in a decrease in catalytic activity. For

example, the conversion of NO into nitrogen was 57% at 400°C in the presence of sulfur dioxide while it was 81% in its absence.

3.5.6 Reaction Mechanism

Catalytic reduction of NO_x by hydrocarbons in an oxidizing atmosphere appears to be the most efficient process for removing NO from exhaust gases. Reduction of NO by propane can be explained by the reaction below:



Factor Analysis data reported by C.Marquez-Alvarez et al. (1996) identifies 4 copper species in the Cu-ZSM-5 sample through the experiment of (NO + C₃H₆ + O₂). The spectra can be assigned to Cu²⁺ and Cu⁺ ions inside the zeolite structure and to CuO- and Cu₂O- like aggregates. There must be a correlation between the activity of the catalyst and the concentration of Cu ions during NO reduction by propane in excess oxygen. Propane can reduce Cu²⁺ to Cu⁺, and O₂ tends to oxidize Cu⁺ to Cu²⁺. When O₂ is present in the NO gas mixture, a reaction tends to occur that produces NO₂, which can oxidize Cu⁺ to Cu²⁺ even at room temperature. The oxidation may be due to the dissociation of NO₂ molecule on the Cu⁺ ion. The complex Cu²⁺-NO₂ is an intermediate in NO_x reduction by propane.

3.6 Reduction of NO by Hydrocarbon over Al₂O₃

During investigations of NO_x reduction with hydrocarbons over various catalysts, alumina and silica-alumina were tested for the selective reduction of NO_x with hydrocarbons in oxidizing atmospheres.

When a catalyst was not used, reduction of NO to N₂ did not occur, although homogeneous gas phase oxidation of propane to CO₂ and CO was observed. When silica-alumina and alumina were used, the formation of nitrogen was clearly observed. The more active catalyst was pure alumina, with which a conversion of NO to 51% N₂ was

attained. It should be noted from Figure 3.14 that the temperature at which maximum NO conversion is obtained tends to become lower as alumina content increases. Kintaichi et al.(1990) used ammonia TPD measurements to get information on the active centers of the catalysts: $\text{SiO}_2/\text{Al}_2\text{O}_3$ and Al_2O_3 . The results shows that silica is not acidic and that total acid amount increases with alumina content. This tendency agrees quite well with the activity change for the selective reduction. Thus the acidity of the catalysts is a major factor that determines catalytic activity.

3.6.1 Effect of Oxygen Concentration

To obtain information on the selective reduction, the influence of the oxygen concentration was examined. Figure 3.15 indicates the variation in the percentage conversion of nitric oxide to nitrogen as a function of oxygen concentration at 500°C. In the absence of oxygen, only 7.1% nitric oxide was reduced to nitrogen. However, the conversion of nitric oxide to nitrogen increased with increasing oxygen concentration to 51% at 10% oxygen. These facts clearly show that the reduction is not inhibited but enhanced by the presence of oxygen. This effect of oxygen was also the same for the reduction of nitric oxide over Cu-ZSM-5.

3.6.2 Effect of Propane Concentration

Since propane concentration was expected to affect the nitric oxide reduction level, a reaction was conducted with 590 ppm propane over alumina catalyst, other reaction conditions remained the same. The result is shown in Figure 3.16. In this case, nitric oxide conversion to nitrogen of about 58% was attained at 500°C. Again, increase the propane concentration will increase the rate of the reaction.

3.6.3 Effect of Nitrogen Dioxide

The main environmental problem associated with NO_x emissions is actually due to NO_2 . NO is the major precursor to NO_2 formation. Nitrogen dioxide contributes to pollution by reacting with hydrocarbons, ozone and light to produce smog. In addition, NO_2 reacts with water to produce acid which causes corrosion problems, and it absorbs visible light which reduces visibility as well as the contrast and brightness of distant objects. Most important, NO_2 is extremely toxic to humans. Concentration greater than 100 ppm are lethal.

From the standpoint of minimizing total NO_x emissions, it is fortunate that the concentration of NO_2 in and near the combustion zone is very low. This results from the fact that NO_2 is not favored thermodynamically at combustion temperatures. In addition to this thermodynamic limitation, there is also a kinetic limitation at high temperature. The oxidation of NO by O_2 via the reaction $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ is one of the few known reactions where rate decreases with increasing temperature. The consequence of these thermodynamic and kinetic limitations is that the amount of NO_2 emitted by combustion sources is generally limited to a few percent of NO , and only as the combustion gases cool in the atmosphere does any significant amount of the reddish brown NO_2 begin to form. The other six oxides of nitrogen (N_2O , N_2O_2 , N_2O_3 , N_2O_4 , N_2O_5 , NO_3) play only insignificant roles in combustion processes.

Since the participation of nitrogen dioxide in this reaction was suggested from the effect of oxygen, the reduction of nitrogen dioxide was next investigated. Figure 3.17 shows the effect of oxygen concentration on the reduction of nitrogen dioxide over alumina at 500°C . It can be seen that the conversion of nitrogen dioxide to nitrogen is not affected much by the oxygen concentration. At a lower temperature (400°C), the conversion was almost constant in spite of a very large change in the oxygen concentration.

The high nitrogen dioxide conversion of 34.6% at 0% oxygen, compared with the corresponding value of 7.1% of nitric oxide in Figure 3.15, clearly indicates that the reduction of nitrogen dioxide to nitrogen occurs more effectively than that of nitric oxide in the absence of oxygen. The nitrogen and carbon balance at different temperatures in this reaction is listed in Table 3.8. The nitrogen balance can be obtained from the inlet NO_2 and outlet N_2 , NO and NO_2 concentration. The carbon balance can be obtained from the inlet C_3H_8 and outlet CO , CO_2 and C_3H_8 concentration.

As we all know, soot exists in diesel exhaust. It may react with NO_2 to form NO . To verify the hypothesis, carbon black was added into the quartz reactor together with propane to reduce NO_2 . From Table 3.9, it can be seen that the concentration of NO_2 in the outlet gas flow is very low compared with the outlet NO_2 concentration in Table 3.8. On the other hand, the outlet NO concentration in Table 3.9 is very high, which confirms that NO is the product of the reaction between carbon black and NO_2 . The nitrogen balance of NO_2 reduction by propane and carbon over alumina is also shown in Table 3.9.

From the results described above, it can be concluded that nitrogen dioxide plays an important role in the selective reduction of nitric oxide over alumina. In other words, nitrogen dioxide may be a reaction intermediate at least in the temperature range below 500°C . Therefore, the need to use oxygen for the selective reduction of nitric oxide can be explained mainly by the oxidation of nitric oxide to form the nitrogen dioxide intermediate. This is also hypothesized by Tsutsumi et al.(1995). To confirm this idea, the oxidation of nitric oxide to nitrogen dioxide was examined with an alumina catalyst. Figure 3.18 shows the experimental results along with empty tube (no catalyst) experiments under various reaction conditions. The empty tube experiments indicate that the oxidation of nitric oxide to nitrogen dioxide proceeds homogeneously to some extent, the percentage conversion of nitric oxide to nitrogen dioxide increasing with oxygen concentration. It can also be seen that nitric oxide conversion to nitrogen dioxide in the

presence of alumina is mostly homogeneous, suggesting that alumina has very little activity in the oxidation. It should be noted that the formation of nitrogen dioxide was not promoted by higher reaction temperature. This is due to the equilibrium limitation of the reaction: $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$, although the reaction rates are probably high (Shaw, 1976).

All the above mentioned data can be considered to support the idea that the oxidation of nitric oxide to nitrogen dioxide is an important step in the selective reduction of nitric oxide over alumina. The following reaction scheme is suggested:

1. $\text{NO} + \text{O}_2 \longrightarrow \text{NO}_2$ This is the oxidation of nitric oxide to nitrogen dioxide intermediate.
2. $\text{NO}_2 + \text{C}_3\text{H}_8 \longrightarrow \text{N}_2 + \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$ The nitrogen dioxide intermediate is reduced to nitrogen by reaction with propane.
3. $\text{C}_3\text{H}_8 + \text{O}_2 \longrightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$ The direct oxidation of propane with oxygen is a side reaction.

Probably the high selectivity of the reduction is caused by the higher reactivity of nitrogen dioxide with hydrocarbons than oxygen over alumina, which is a poor catalyst for the activation of molecular oxygen. The decrease in nitric oxide conversion to nitrogen at high temperatures can be explained by the high rates of the propane-oxygen reaction.

3.7 Reduction of NO by Carbon Black

Emissions of nitrogen oxides (NO_x) and soot particulates from diesel engines have been causing serious environmental and health problems. In recent years, efforts have been made to search for the most cost-effective process to remove or reduce NO_x and soot particulates from diesel exhausts. One promising process to meet this demand is the simultaneous removal of NO_x and soot, that is, the reduction of NO_x by soot in an oxidizing atmosphere. The development of an active catalyst for this reaction is

considered to be most important. The purpose of this study is to investigate the catalytic performance of Cu-ZSM-5 and Al_2O_3 for the simultaneous removal of NO_x and diesel soot particulates.

Soot itself is a high surface area material that is known to promote NO reduction under appropriate conditions. The use of carbon as both the reducing agent and SCR catalyst has been shown to be feasible.

The reactions between soot and NO_x are very complicated. As a result, the catalytic reactions are also complicated. The experiments were run in the fixed bed reactor. The gases flowed through the reactor which contained carbon black and catalyst.

3.7.1 Effect of Oxygen

As shown in Figure 3.19, the NO reaction with carbon black over Cu-ZSM-5 catalyst resulted in a high conversion of NO to N_2 . The maximum NO conversion is 36% in the absence of oxygen. The reduction of NO by carbon was found to be enhanced by the presence of oxygen. When 10% oxygen was present, the NO conversion at 400°C is raised to 45%. This is consistent with what was reported by Tsutsumi et al.(1995). They found that for the NO-soot- O_2 system the NO reaction with soot had a high conversion form NO to N_2 , whereas in the absence of oxygen, low NO reduction activity was observed.

Using Al_2O_3 as the catalyst, oxygen will also enhance the NO-carbon reaction. The NO conversion is somewhat lower than that with Cu-ZSM-5. The highest N_2 conversion occurred at 500°C rather than at 400°C with Cu-ZSM-5. (Figure 3.20)

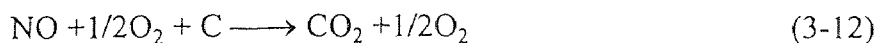
A major disadvantage in the use of carbon is the possible consumption by combustion with oxygen. Considerable amounts of CO_2 and CO were produced during these reactions. This indicated that carbon was consumed by the C-NO reaction and/or by the C- O_2 reaction. Most of the carbon consumption was due to the oxidation of carbon

with O₂, because the concentration of O₂ (10%) in the feed was much higher than that of NO (590ppm) and the concentration of O₂ greatly decreased in the outlet gas.

Thermodynamically, the NO_x-carbon reaction is favorable. Several investigators have reported that carbon has a certain degree of selectivity for reducing NO emissions in the presence of excess oxygen. The presence of oxygen significantly modifies the reaction rate. Chu and Schmidt (1993) found that during the NO-graphite reaction at low temperature the formation of stable (CN)_x polymers hinders the diffusion of the NO_x, reducing the reaction rate. Akhter et al.(1984) directly identified the surface species produced on soot after the reaction with NO₂/N₂O₄ by using FTIR technique. But in the presence of oxygen, the NO-carbon reaction rate increases because there is no formation of (CN)_x polymers. In addition, they reported that the rates of noncatalytic reaction with graphite follow the order of rNO₂>rN₂O>rNO>rO₂. Nitrogen dioxide is the more thermodynamically stable compound at low temperatures. Tsutsumi et al.(1995) suggested a reaction scheme of the NO soot reaction, which is



The overall reaction is expressed as



3.7.2 Effect of Cu Ion

Tsutsumi et al.(1995) reported that the typical NO concentration in diesel engine exhaust is 530 ppm. Johnson et al, 1994 estimate the average ratio of particulate matter to NO_x to be about 0.05 g particulate/g NO_x. Assuming a molecular weight of NO_x as 28, a molecular weight of particulate (carbon) of 12, and that 2 moles of NO react with 1 mole of C to produce 1 mole of CO₂ and 1 mole of N₂, it is obvious that, based on these numbers, the stoichiometric amount of NO_x is approximately 4 times as great as the

amount of soot. Thus if all the soot is consumed by reaction with NO_x , there still be some unreacted NO_x delivered into the atmosphere. Therefore, it may be necessary to add some diesel fuel or carbon in order to remove all of the NO_x . If carbon were to be added, it may be advantageous to add a metal-loaded carbon to utilize the catalytic properties of this material.

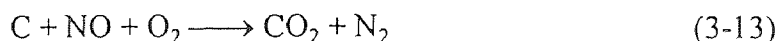
Copper was introduced onto carbon black by impregnation using saturated copper acetate (10 ml of solution/g of carbon) overnight. The impregnated samples were dried in an oven at 120°C for a period of 12h. The results of NO reduction by carbon black is shown in Figure 3.21. The efficiency of NO removal is higher by using carbon black with Cu ion as compared with that using only carbon black. This is consistent with the results of Yamashita et al.(1991) who observed that the reaction between NO and metal-loaded carbon was remarkably promoted by the presence of oxygen at a temperature as low as 572K . The oxidation of carbon black was studied using TGA. For pure carbon black, the oxidation of carbon black begins around 500°C . But for Cu-carbon, it begins to oxidize before 400°C as can be seen in Figure 3.23.

The same impregnation procedure was used for Al_2O_3 instead of carbon black. Figure 3.22 shows the effect of Cu ion on the reduction of NO by carbon black over alumina. It can be seen that the presence of Cu ion shifts the maximum nitrogen conversion temperature down about 50°C . But the maximum conversion is somewhat lower than the pure alumina. This is probably due to the loss of fine particles during the preparation of $\text{Cu}/\text{Al}_2\text{O}_3$.

Ismailov et al.(1993) investigated the oxidation of CO and the reactions of CO and NO on the surface of activated Al_2O_3 catalysts that contain Co, Ni and Cu ions. They studied the structure and reactivity of the surface complexes formed during the adsorption and reaction of the components. They found that carbonyl, carboxylate and nitrate complexes formed, and the oxidic catalysts containing 10-40wt.% of Cu were the most active. The conversion rate of the carboxylate complexes is three orders of magnitude less

than that of CO₂ formation. The intermediate in CO oxidation and the CO and NO reactions is a carbonyl complex.

It is difficult to understand how a catalyst can promote the reaction between a solid, which is too large to penetrate the catalyst pores, and a gas. It is possible that intermediates diffuse between the catalyst pores and carbon black particles which are much larger than the size of the pores of the catalyst (Weisz and Swegler, 1955). We speculate that the reaction of oxygen with carbon black could produce CO which would react very fast with NO in the catalyst pores to produce CO₂ and N₂. In this manner carbon black would participate in the reaction without being in direct contact with the active sites of the catalyst. Furthermore, this hypothetical mechanism explains the need for oxygen in the gas stream to promote the NO reduction by oxidizing the carbonaceous material to form a stronger reducing agent (CO). The overall reaction is expressed as



The metal ions Cu, in contact with carbon, does not change the fundamental thermodynamics which favors the reduction of NO, but only increases the rate at which this reduction is achieved.

For Cu-ZSM-5, it is possible that as a result of the copper ion exchange, there are accessible copper sites on the catalyst surface, which are not inside the zeolite framework and may be associated with Cu⁺ or Cu²⁺ sites on the alumina binder. Indeed, copper is an excellent catalyst for the reduction of NO by carbon.

Table 3.8 Material Balance of NO₂ Reduction by Propane over Alumina as a Function of Temperature
 Reaction Conditions: [NO₂] = [C₃H₈] = 590 ppm, [O₂] = 10%, GHSV = 20,000/hr

Temp. (°C)	Inlet Conc. (ppm)		Outlet Conc. (ppm)								Material Balance (%)	
	NO ₂	C ₃ H ₈	N ₂	NO	NO ₂	CO	CO ₂	C ₃ H ₈	Nitrogen	Carbon	Nitrogen	Carbon
300	590	590	0	58	520	54	59	555	97.8	100.5	97.8	100.5
400	590	590	28	49	478	57	821	299	98.8	100.3	98.8	100.3
500	590	590	82	30	382	130	1544	31	97.6	99.8	97.6	99.8
600	590	590	61	12	437	0	1683	26	96.8	99.5	96.8	99.5

Table 3.9 Nitrogen Balance of NO₂ Reduction by Propane and Carbon over Alumina as a Function of Temperature
 Reaction Conditions: [NO₂] = [C₃H₈] = 590 ppm, [O₂] = 10%, [Carbon] = 5%, GHSV = 20,000/hr

Temp. (°C)	Inlet Conc. (ppm)		Outlet Conc. (ppm)					Nitrogen Balance(%)
	NO ₂	N ₂	NO	CO	CO ₂	C ₃ H ₈	Nitrogen	
300	590	24	514	10	10	96.9		
400	590	44	480	12	12	98.3		
500	590	103	360	11	11	97.8		
600	590	81	402	12	12	97.6		

CHAPTER 4

CONCLUSIONS

As a consequence of the research, the following conclusions were reached:

- Cu-ZSM-5 can catalyze the direct decomposition of NO to N₂ and O₂, but oxygen can greatly inhibit the reaction. SO₂ and water can poison the reaction, but the catalytic activity of Cu-ZSM-5 can be regenerated by the desorption of SO₂ at higher temperatures.
- Cu-ZSM-5 shows activity for the reduction of NO by CO. Its highest activity appears at around 400°C for NO/CO = 1.28. The conversion to N₂ was inhibited by oxygen.
- High N₂ conversion can be attained by selective catalytic reduction of NO by C₃H₈ over Cu-ZSM-5. Oxygen is necessary for the reaction. The highest NO reduction can be attained when the oxygen concentration is around 1% to 2%. The rate of NO conversion to N₂ increased monotonically with propane addition. When there is water vapor presence in the feed gas, catalyst activity is permanently impaired.
- Al₂O₃ catalyze the reduction of NO to N₂ by C₃H₈. The conversion to N₂ increases with increasing oxygen concentration. The highest N₂ conversion appears at 500°C. High C₃H₈ concentration can enhance the activity of the catalyst. No detrimental effect of water vapor was observed.
- The reduction of NO₂ to N₂ occurs more rapidly than that of NO over Al₂O₃. Oxygen is necessary for the reaction, although the concentration of oxygen does not effect much. NO₂ may be a reaction intermediate of NO reduction to N₂ over Al₂O₃.
- Both Cu-ZSM-5 and Al₂O₃ catalyze the reduction of NO by carbon black. The conversion is enhanced by the presence of oxygen. The rate of NO conversion is relatively slower in the presence of Al₂O₃ than that with Cu-ZSM-5. The highest rate of reduction reaction over Al₂O₃ is at 500°C, and over Cu-ZSM-5 at 400°C.

- The presence of Cu enhances the NO reduction by carbon black. It can also reduce the oxidation temperature of the carbon black.
- The presence of Cu on Al_2O_3 can reduce the maximum temperature of the reaction of NO to N_2 by carbon black from 500°C to 450°C . It is possible that CO, a stable intermediate, reacts with NO over Cu.

APPENDIX
FIGURES OF EXPERIMENT RESULTS

C:\TANG\cu2sm.dfn

BET Plot

04-05-1995

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SAMPLE NAME: CU-ZSM-5
 ADS. SURFACE AREA 118 m2/g
 DES. SURFACE AREA 123 m2/g

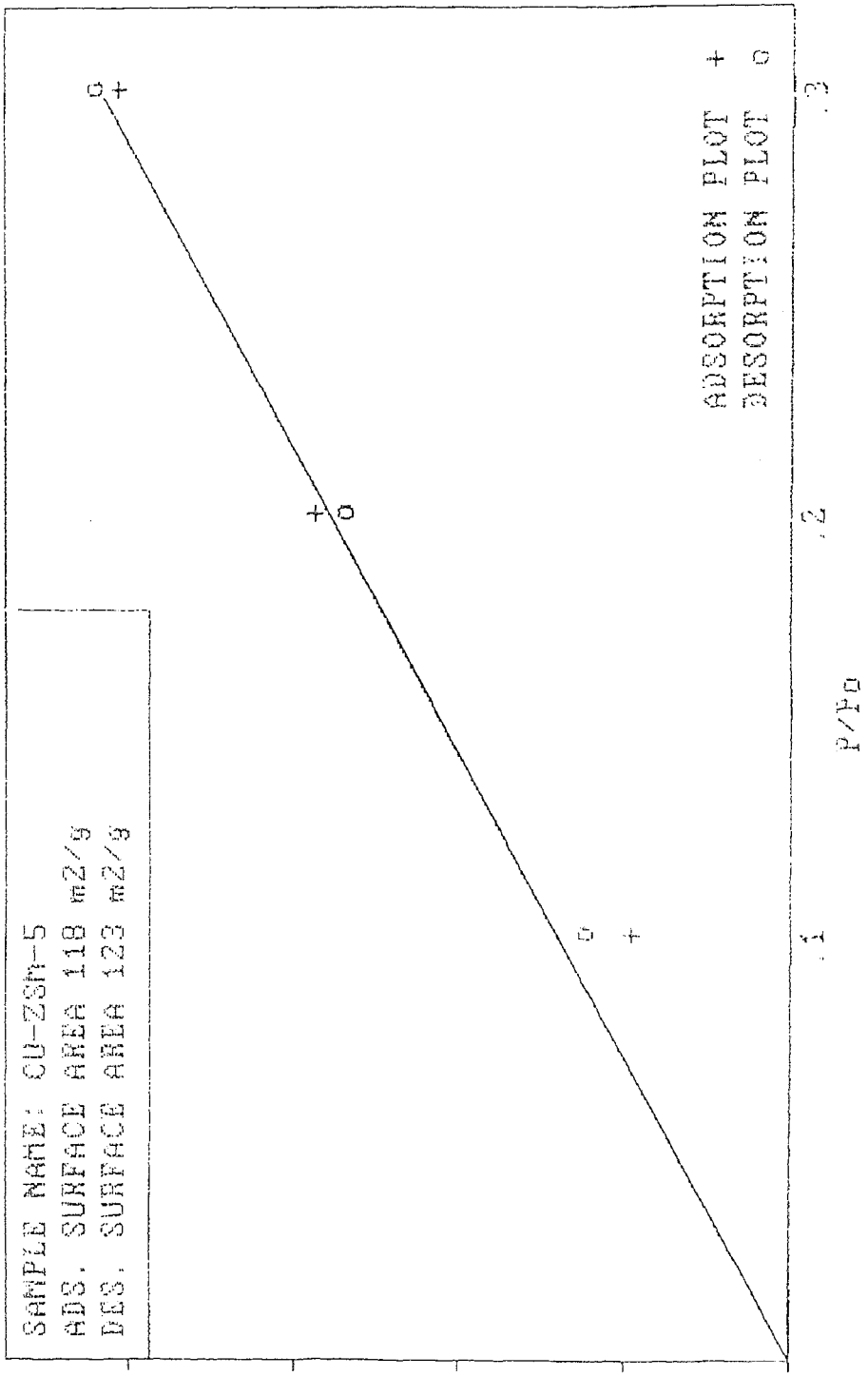


Figure 3.1 BET Plot of Cu-ZSM-5

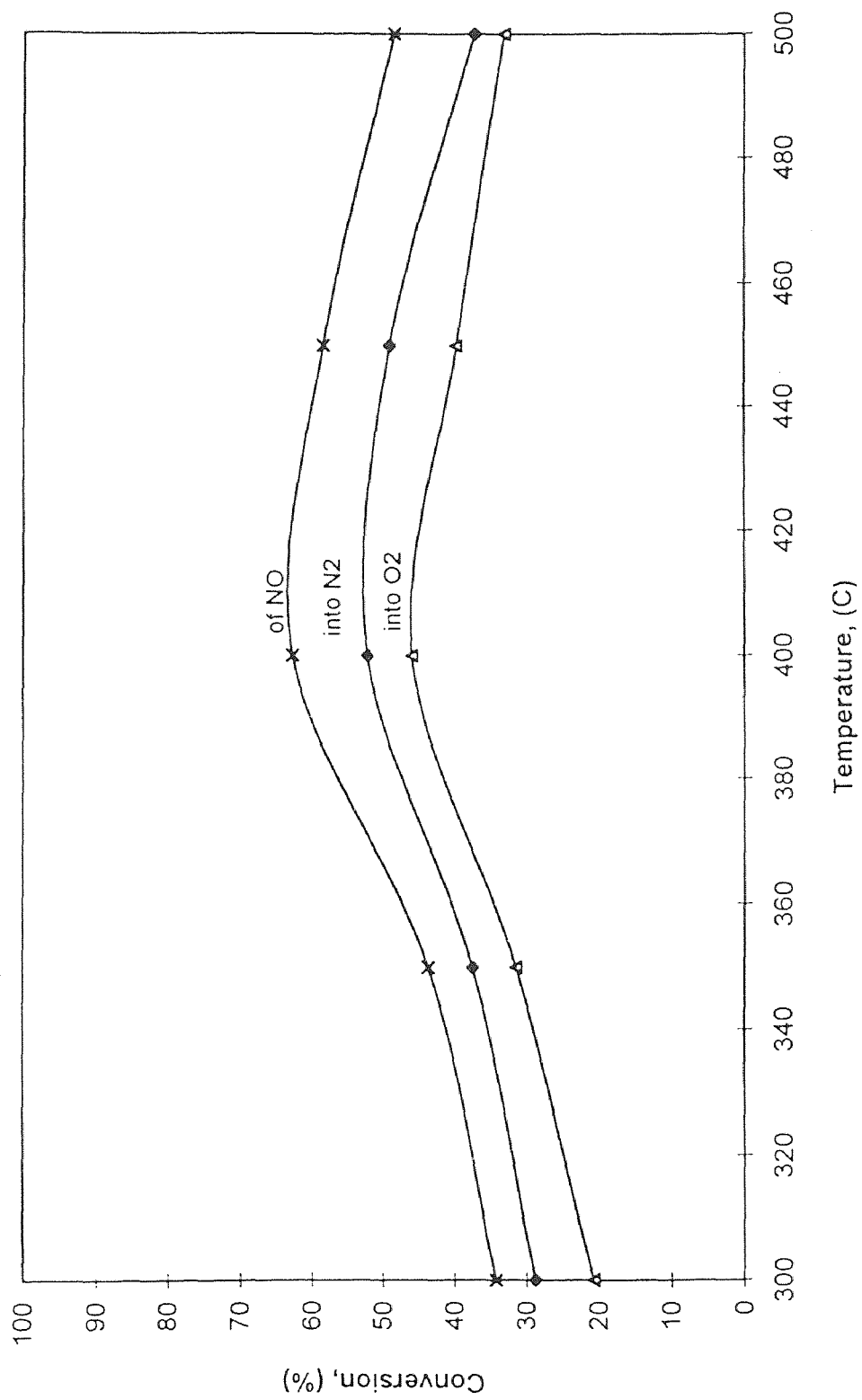


Figure 3.2 Temperature Dependence of Decomposition of NO over Cu-ZSM-5;
GHSV=2,140/h, [NO]=590ppm

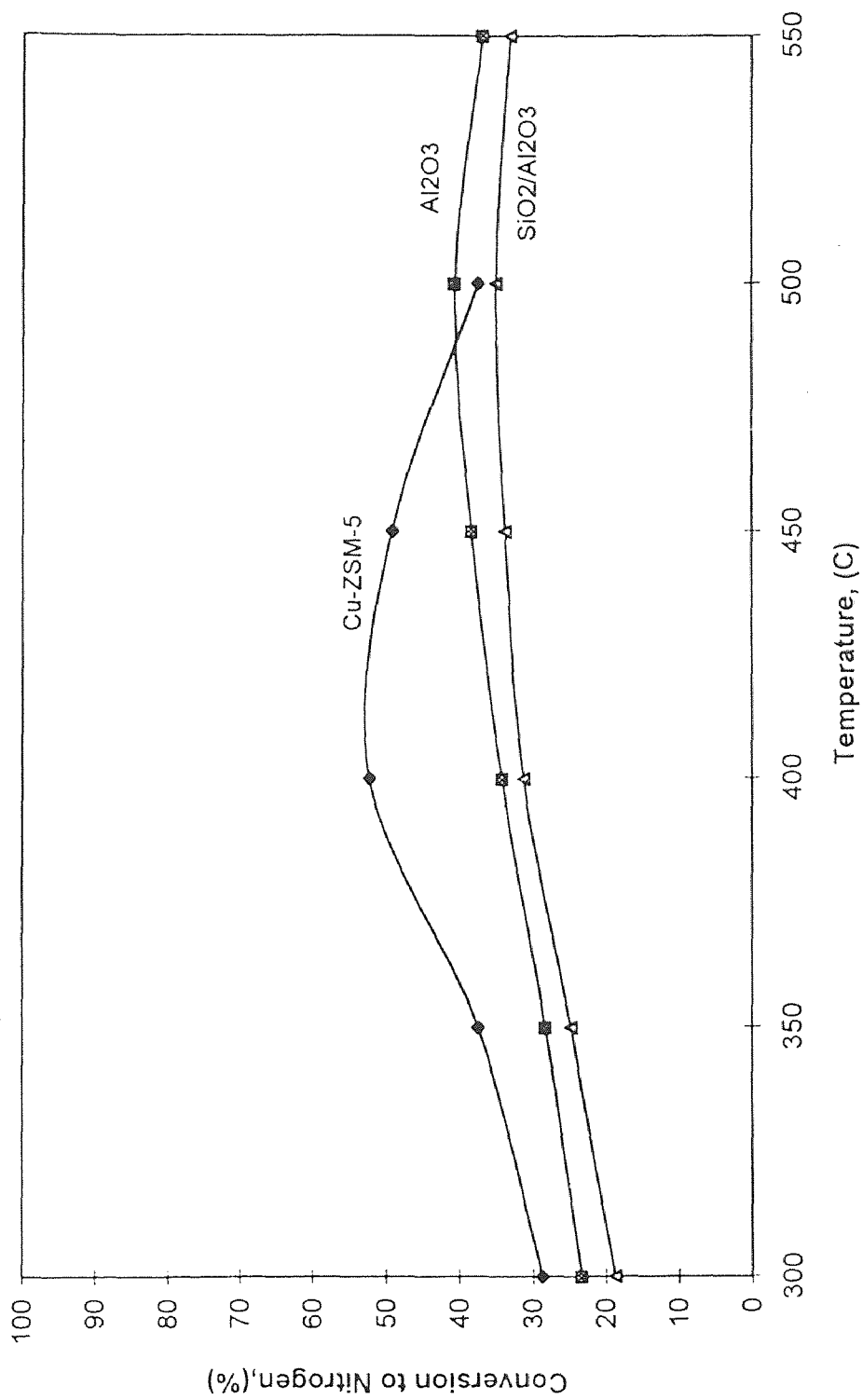


Figure 3.3 Temperature Dependence of Decomposition of NO over Different Kind of Catalysts; GHSV=2,140/h, [NO]=590ppm

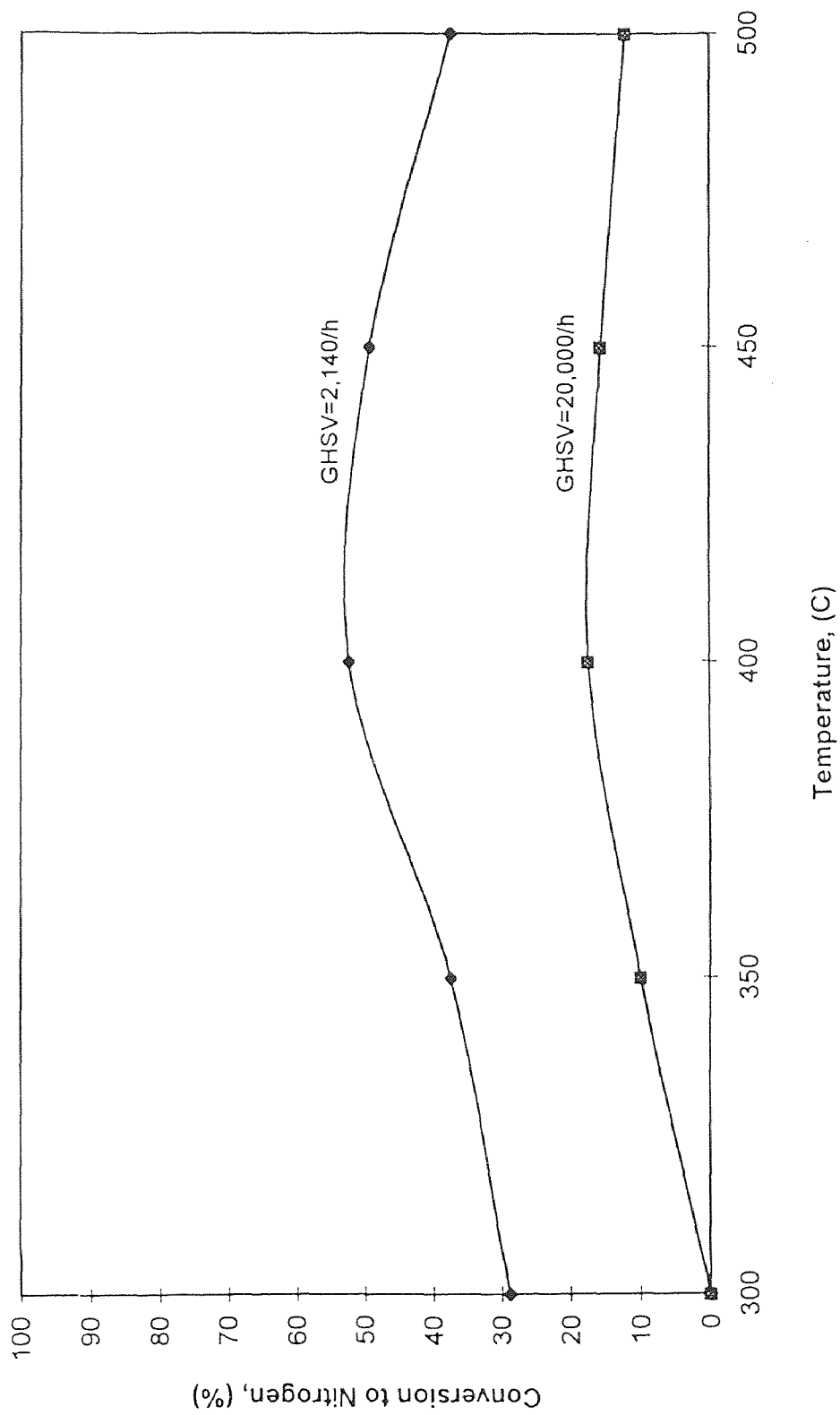


Figure 3.4 Effect of Space Velocity on NO Decomposition over Cu-ZSM-5; [NO]=590ppm

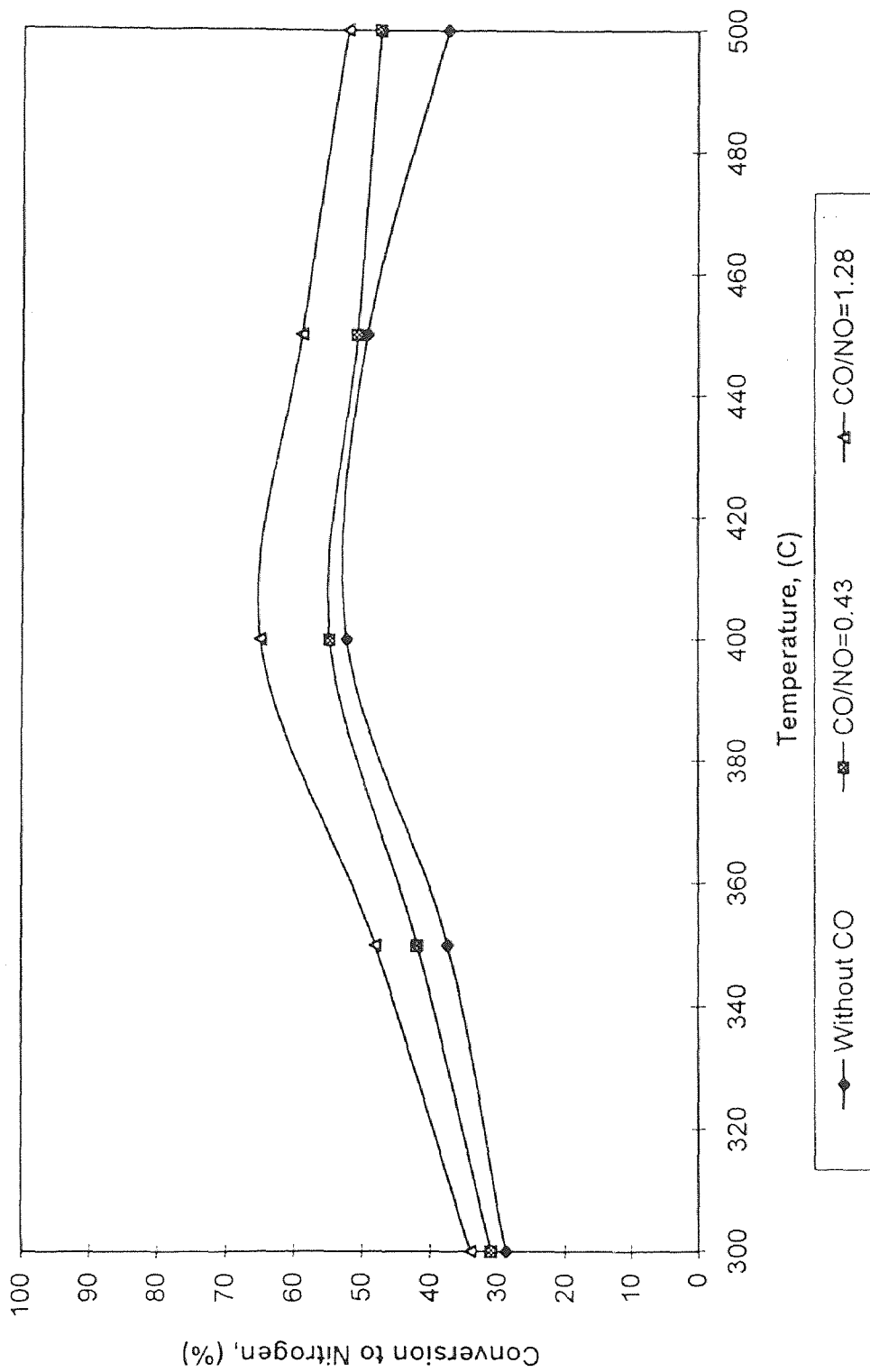


Figure 3.5 Effect of CO Concentration on the Reduction of NO by CO over Cu-ZSM-5, GHSV=2,140/h

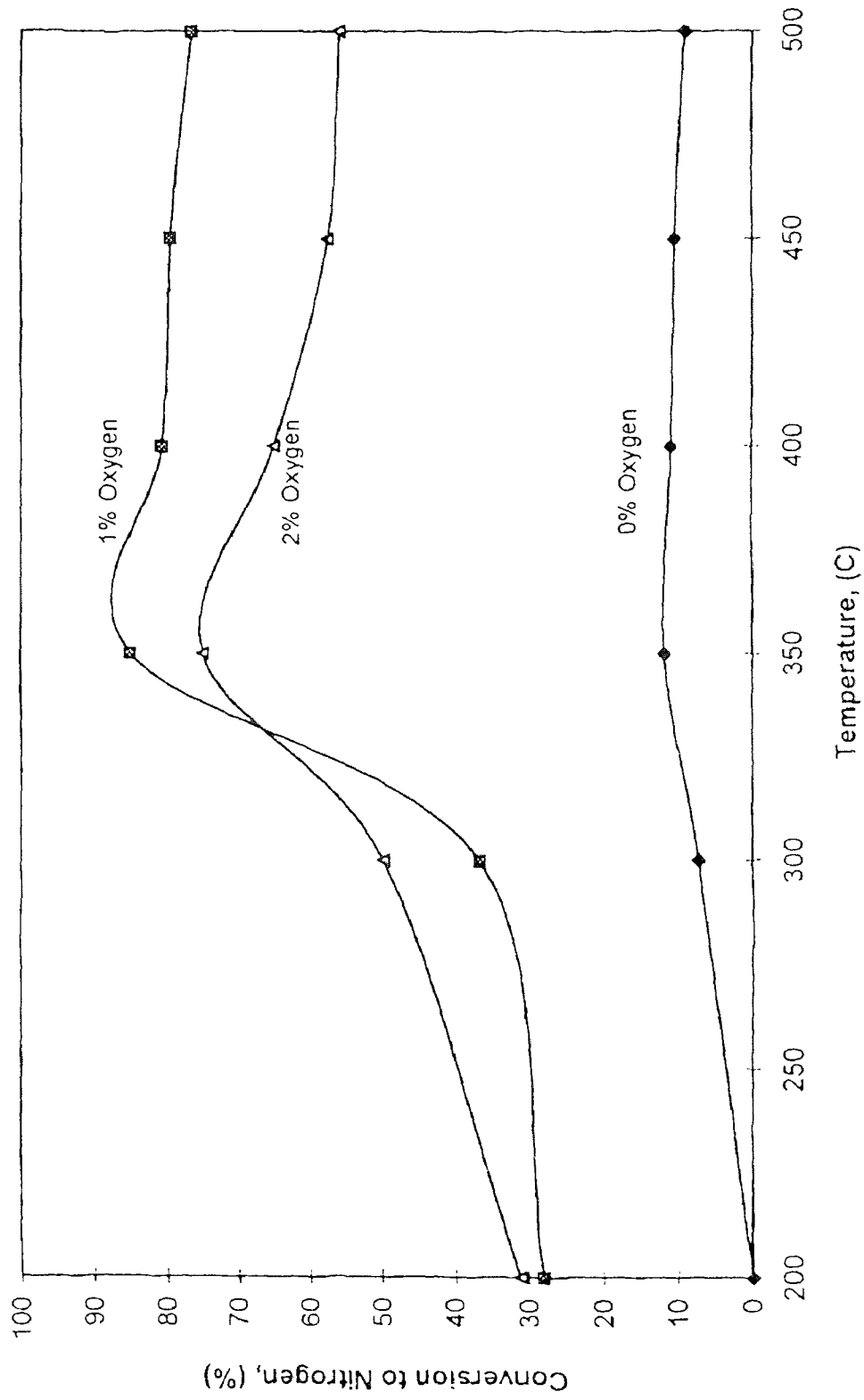


Figure 3.6 Effect of Oxygen Concentration on NO Reduction by Propane over Cu-ZSM-5; GHSV=2,140/h, [NO]=[Propane]=590ppm

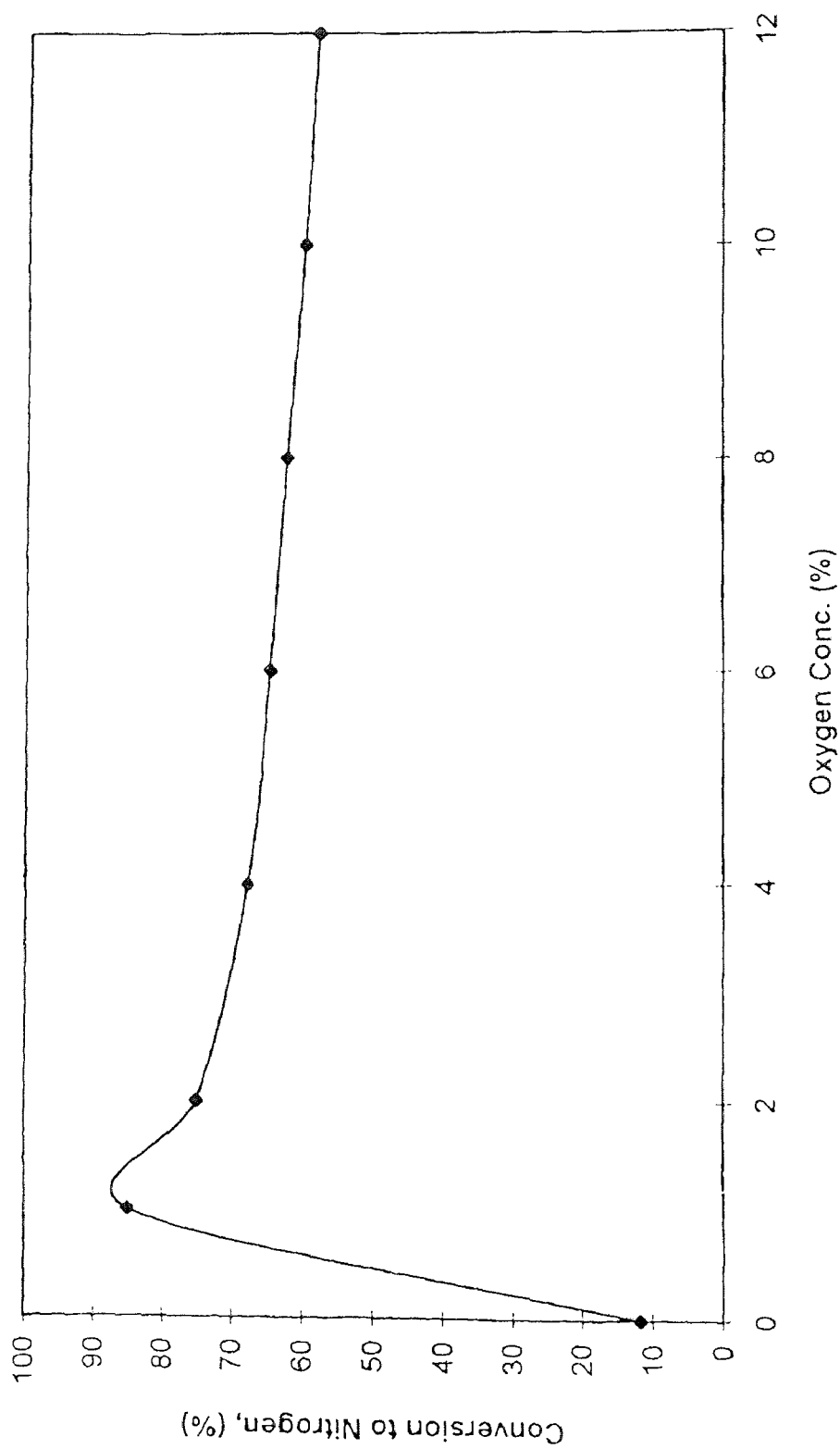


Figure 3.7 Effect of Oxygen Concentration on the Reduction of NO by Propane over Cu-ZSM-5 at 350C; GHSV=2,140/h, [NO]=[Propane]=590ppm

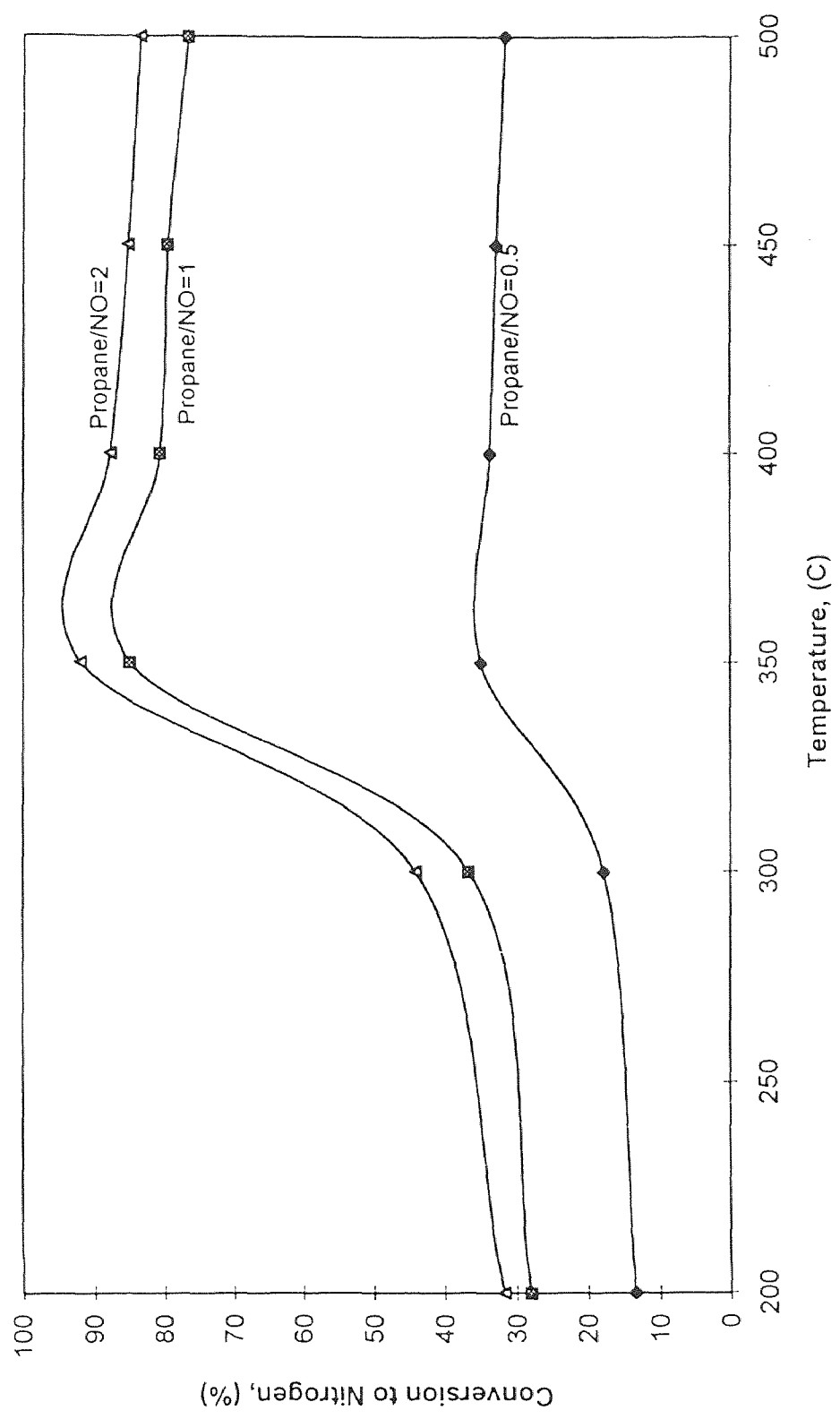


Figure 3.8 Effect of Propane/NO Ratio on NO Reduction by Propane over Cu-ZSM-5; GHSV=2,140/h, [O2]=1%

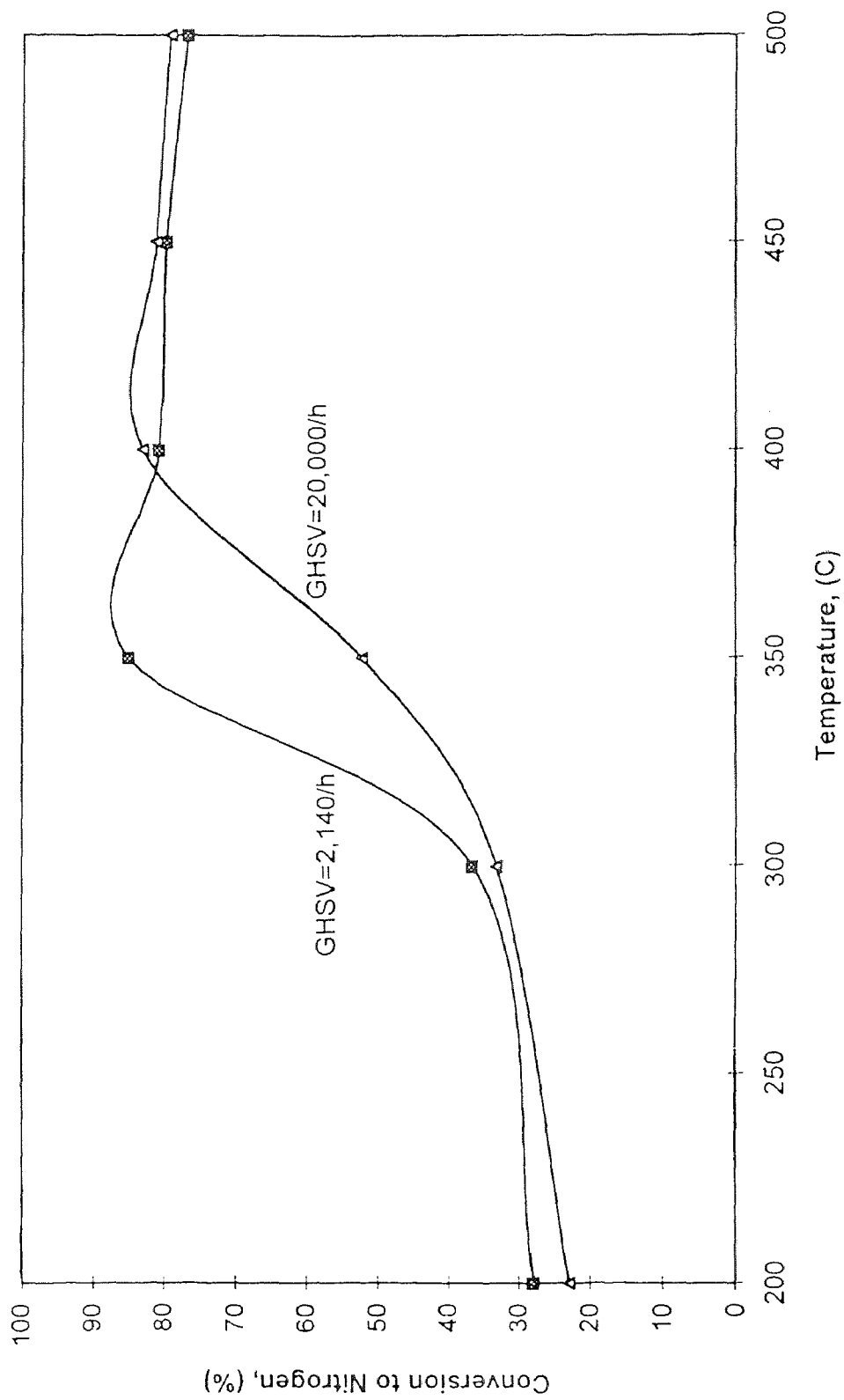


Figure 3.9 Effect of Space Velocity on NO Reduction by Propane over Cu-ZSM-5; [NO]=[Propane]=590ppm, [O₂]=1%

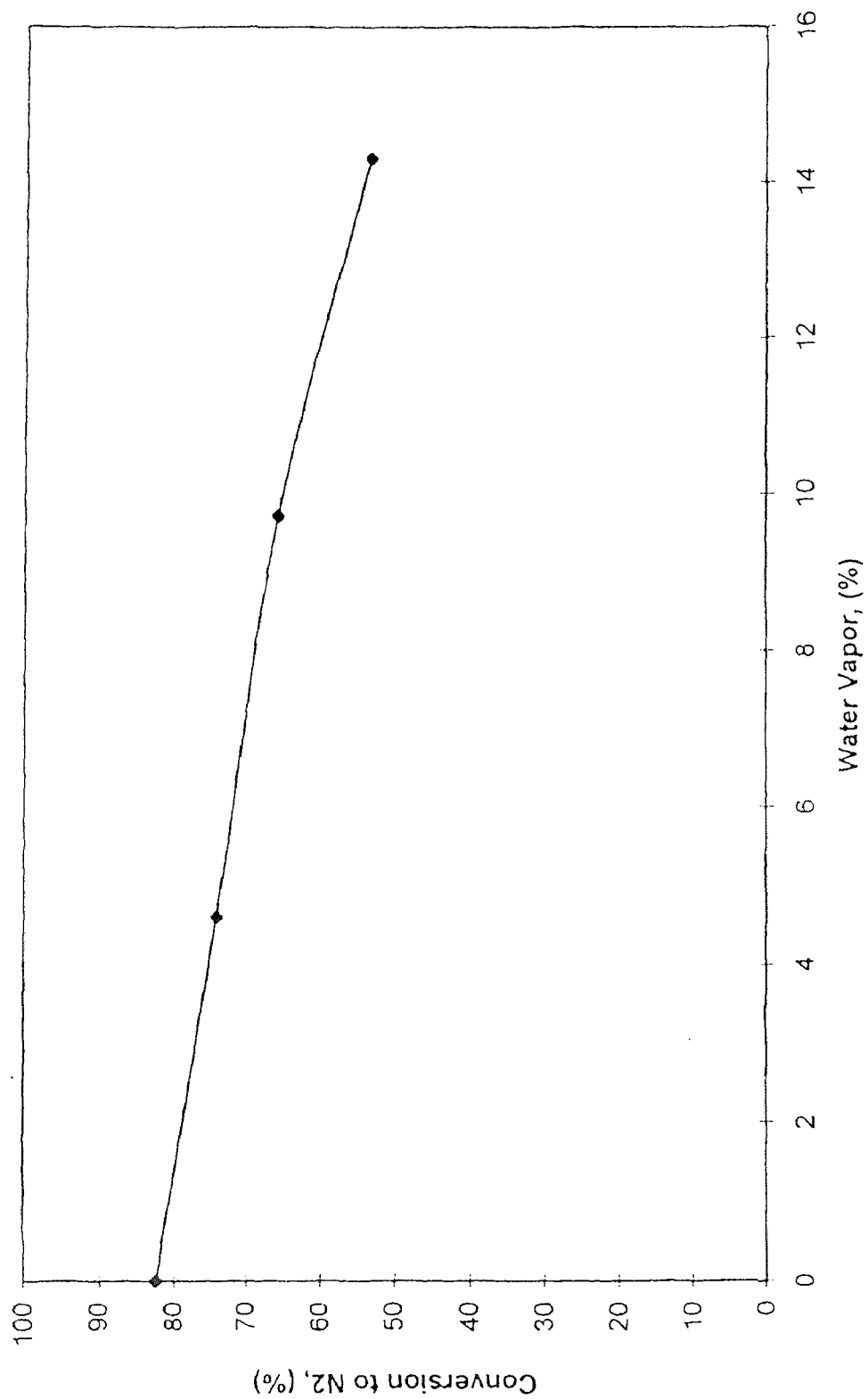


Figure 3.10 Effect of Water Vapor on NO Reduction by Propane over Cu-ZSM-5 at 400C; GHSV=20,000/h, [NO]=[propane]=472ppm, [O₂]=1%

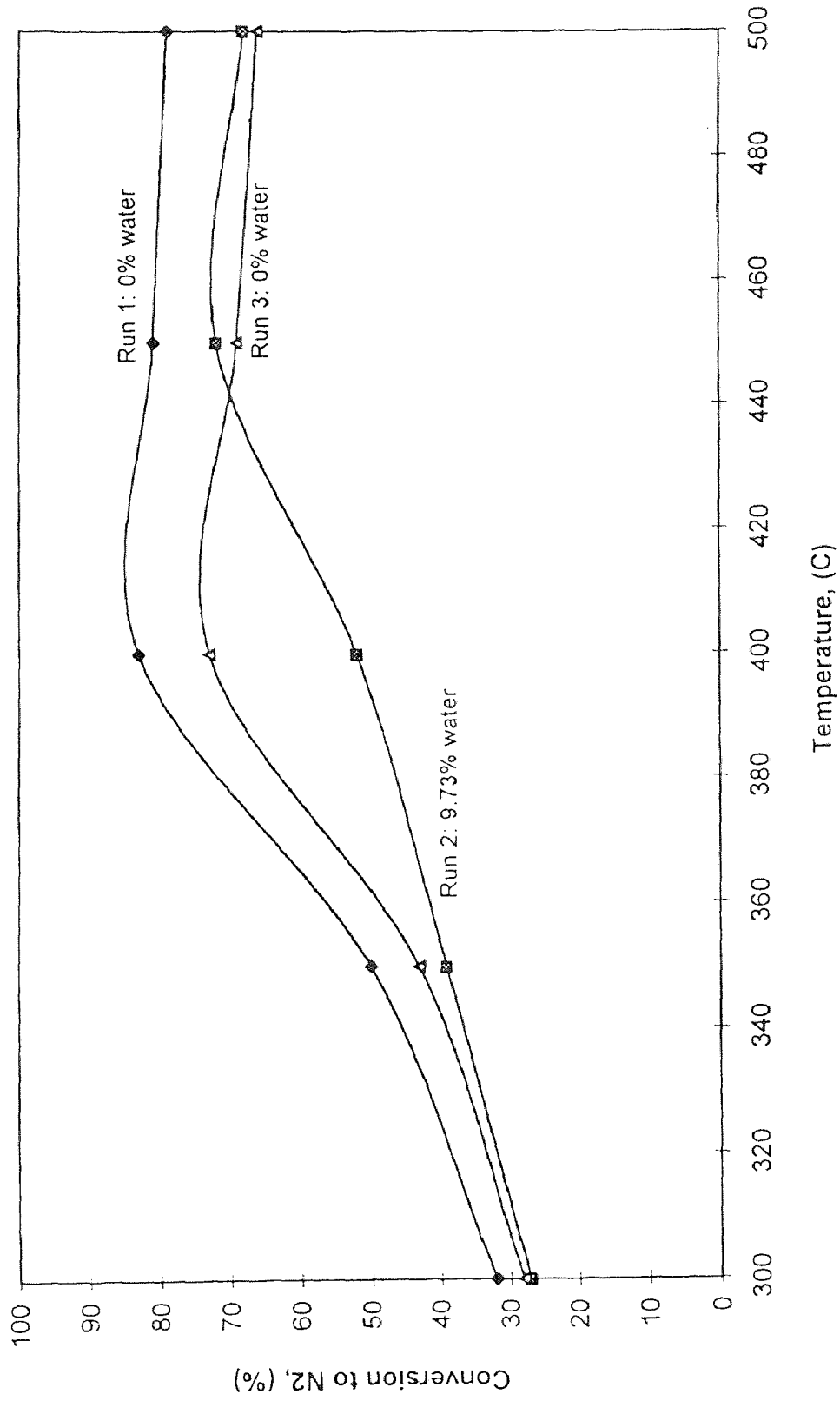


Figure 3.11 Effect of Water Vapor on NO Reduction by Propane over Cu-ZSM-5; GHSV=20,000/h, [NO]=[propane]=472ppm, [O₂]=1%

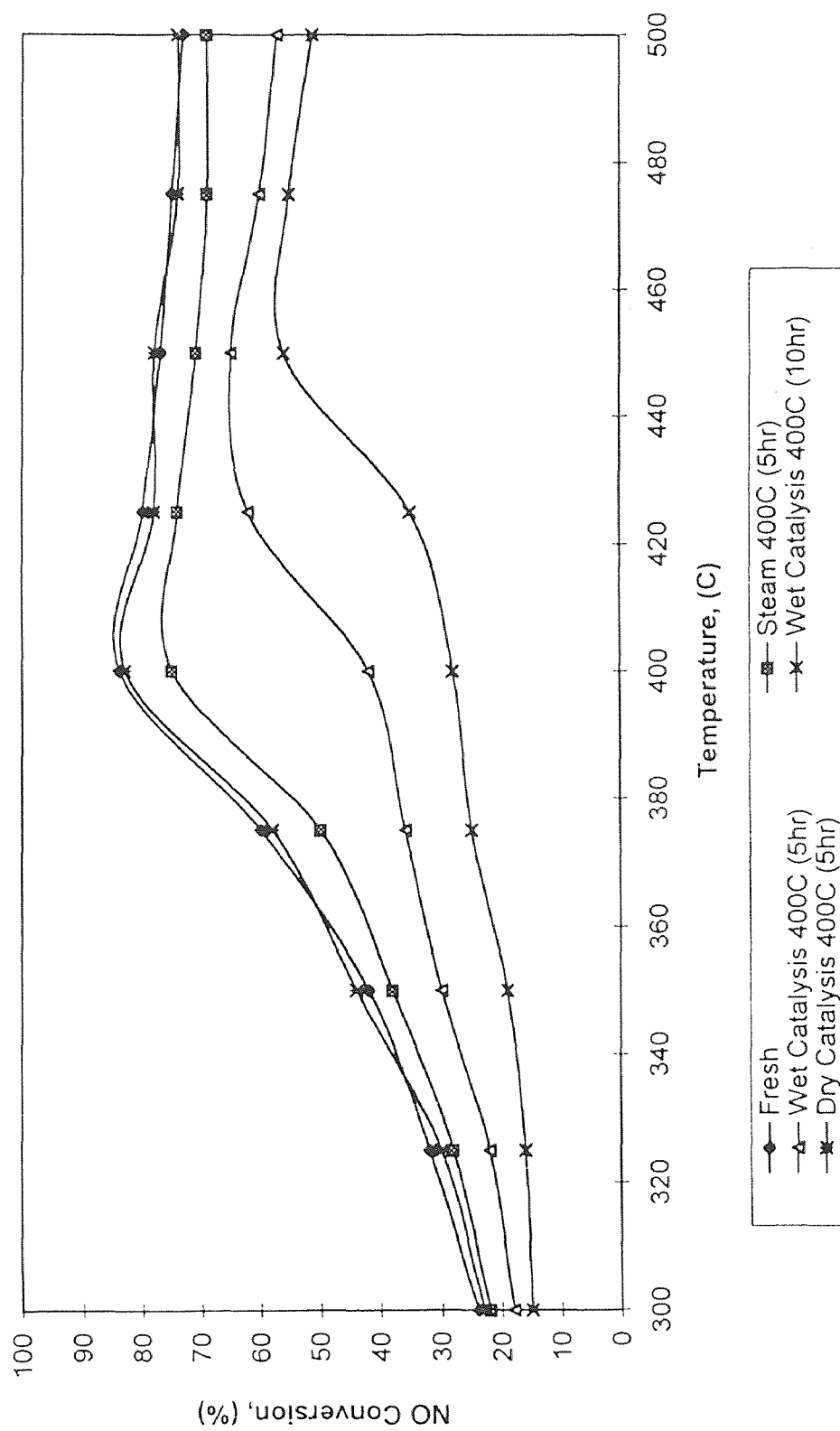


Figure 3.12 Deactivation of Cu-ZSM-5;
 GHSV=20,000/h,[NO]=[Propane]=472ppm,[O₂]=1%,[H₂O]=9.73%

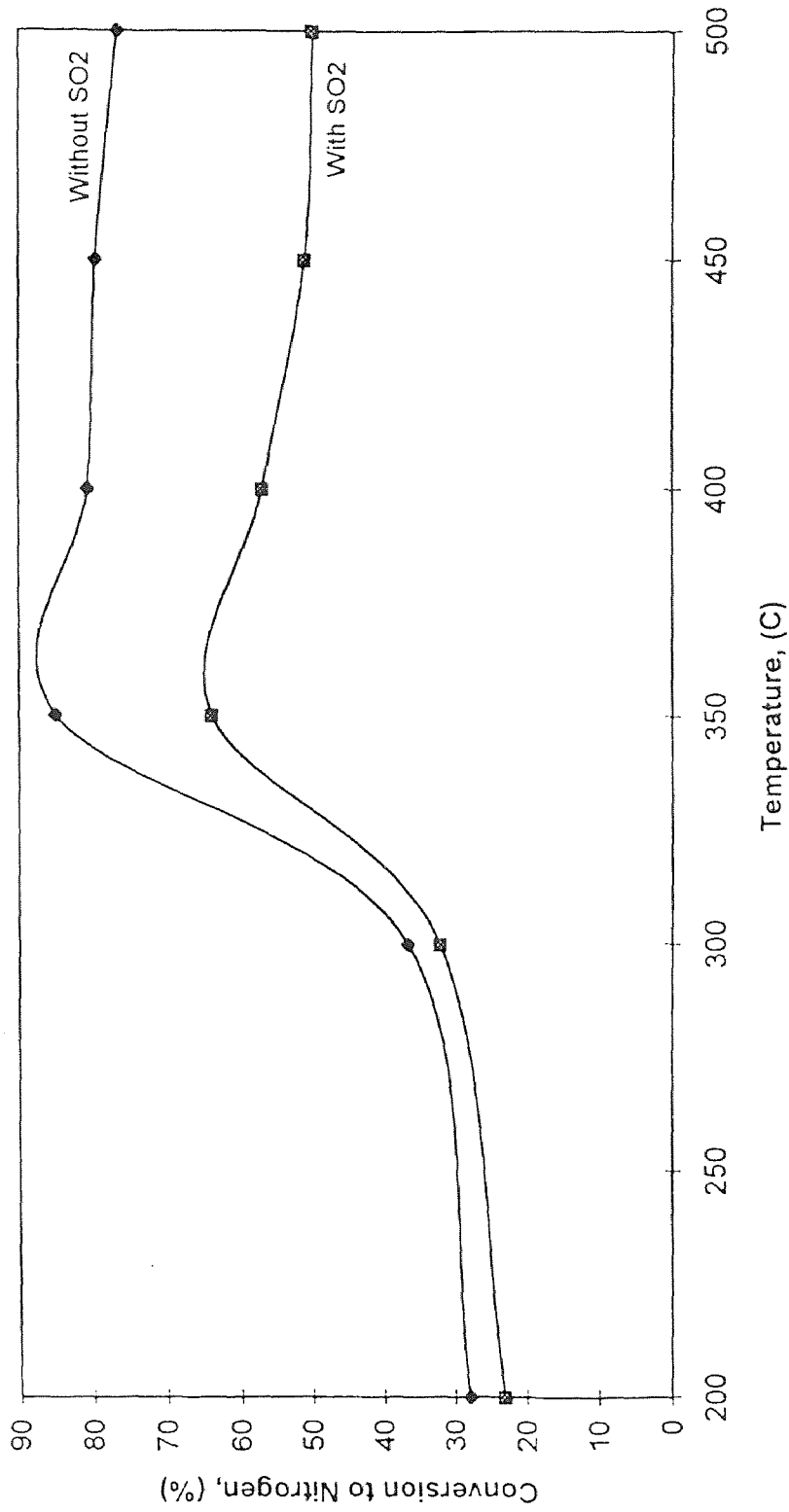


Figure 3.13 Effect of Sulfur Dioxide in NO Reduction by Propane over Cu-ZSM-5; GHSV=2,140/h, [NO]=[Propane]=590ppm, [Oxygen]=1%, [SO2]=22ppm

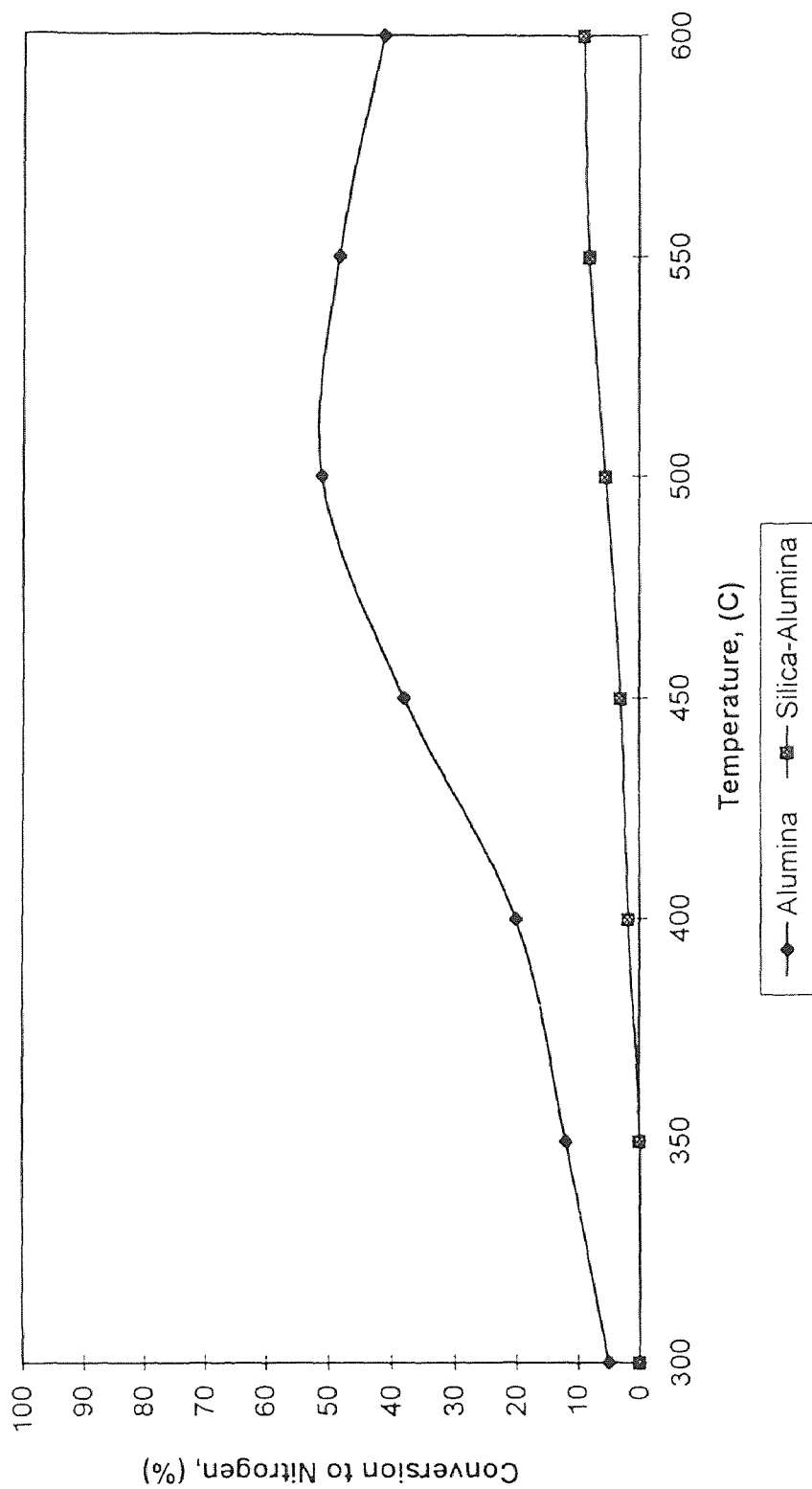


Figure 3.14 Effect of Reaction Temperature on the Selective Reduction of NO by Propane over Alumina and Silica-Alumina; [NO]=[Propane]=590ppm, [oxygen]=10%, GHSV=2,140/h

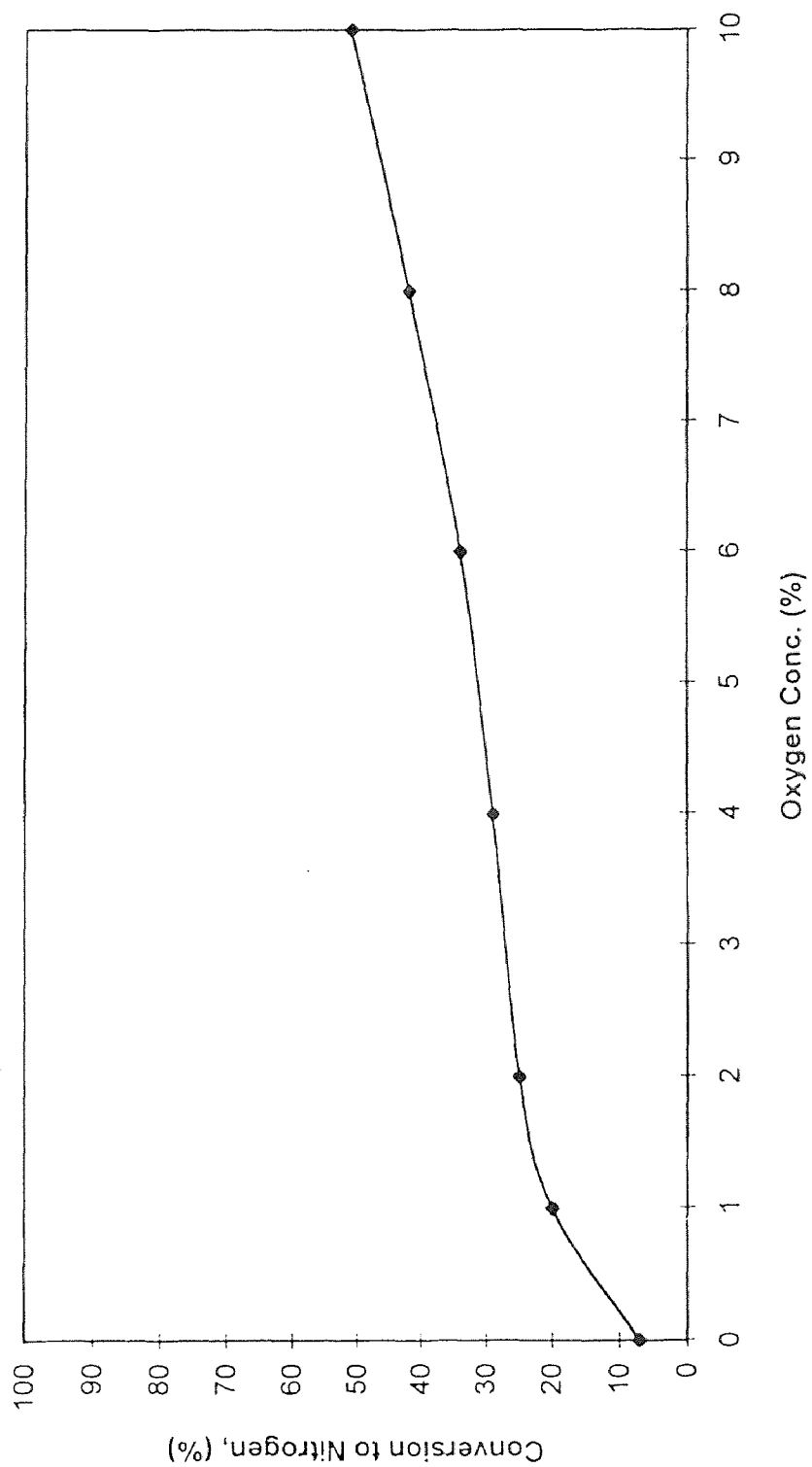


Figure 3.15 Effect of Oxygen Concentration on the Reduction of NO by Propane over Alumina at 500C; [NO]=[propane]=590ppm, GHSV=2,140/h

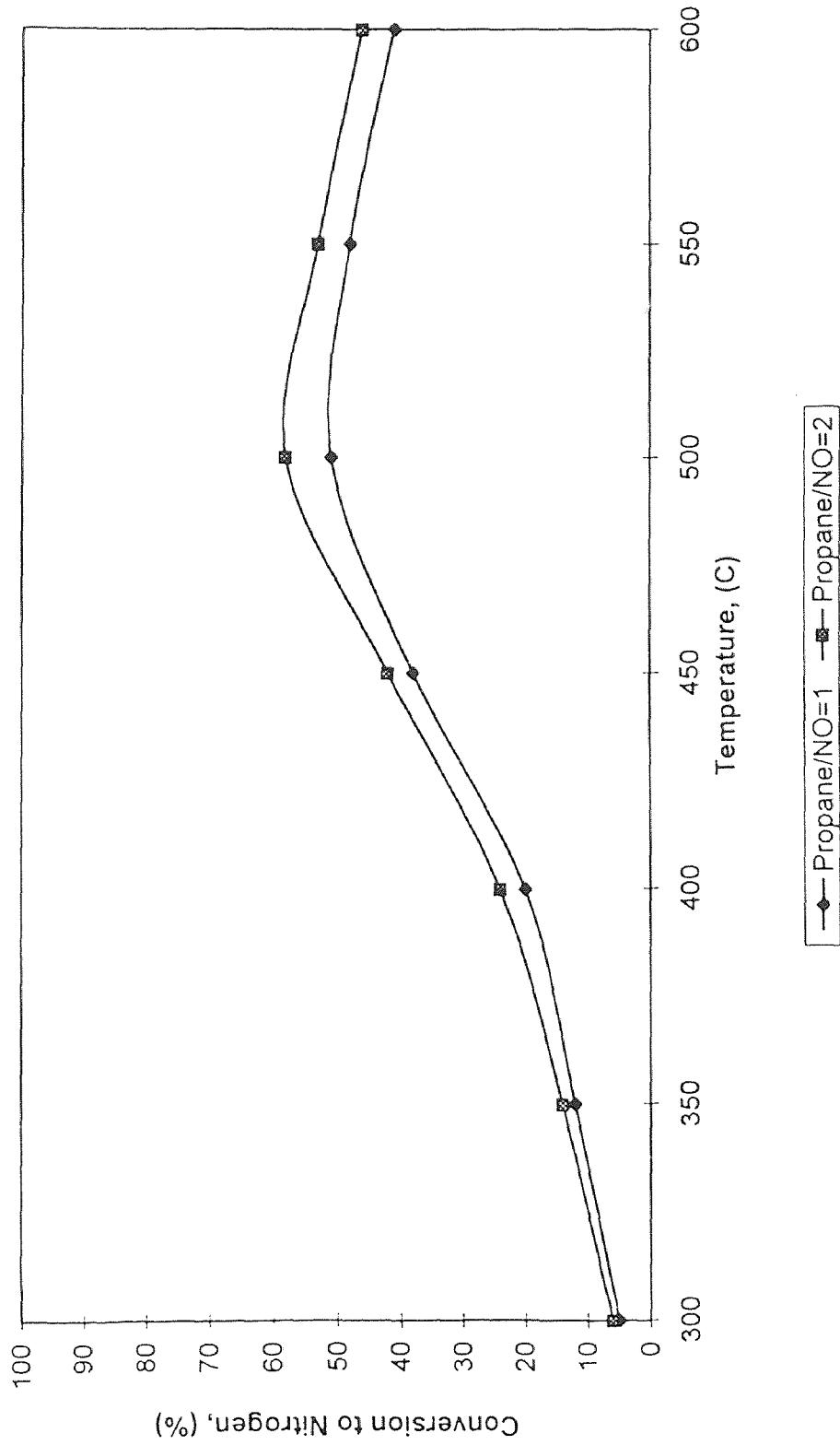


Figure 3.16 Effect of Propane/NO Ratio on NO Reduction over Alumina;
[Oxygen]=10%, GHSV=2,140/h

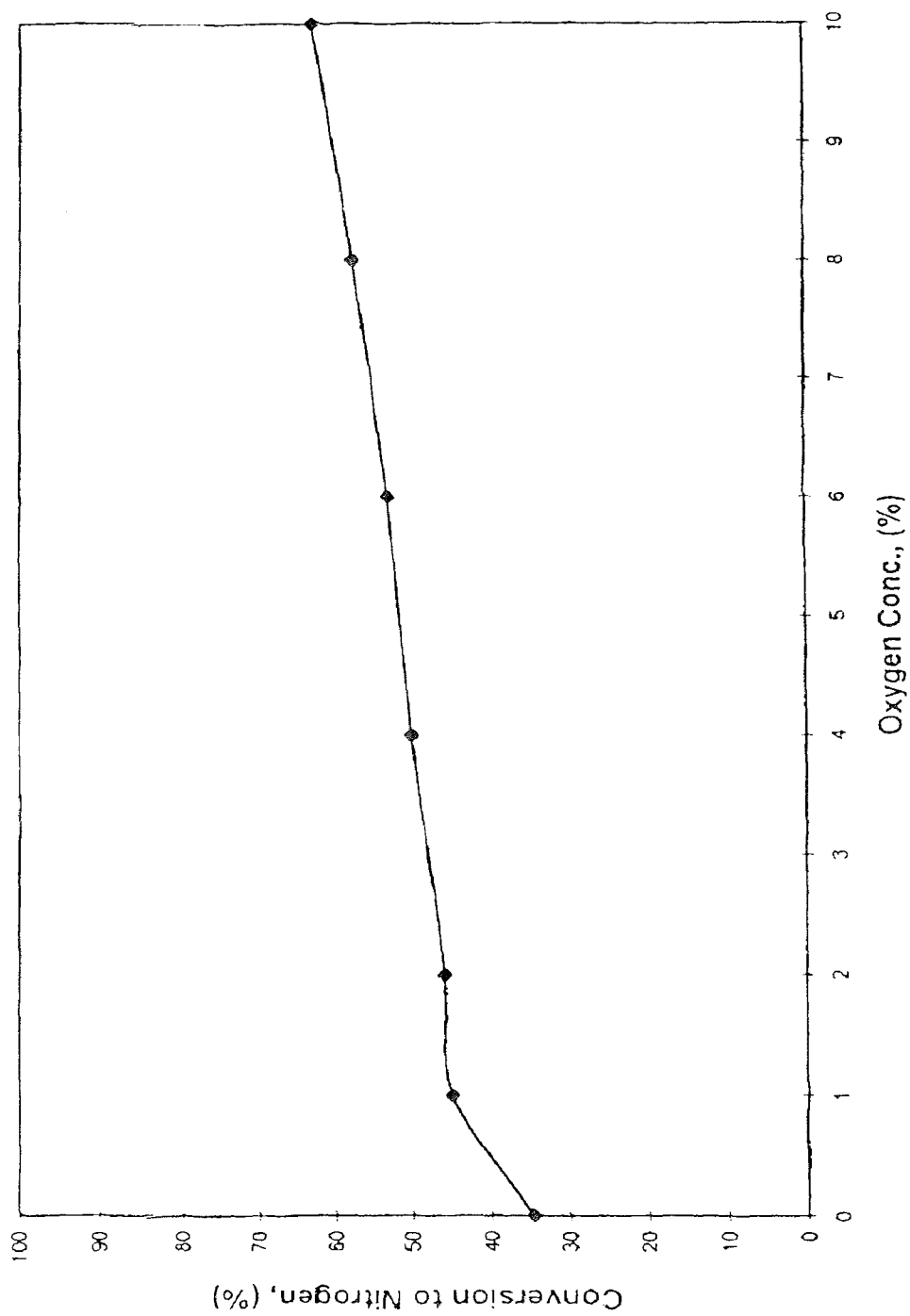


Figure 3.17 Effect of Oxygen Concentration on the Reduction of NO₂ by Propane over Alumina at 500C; GHSV=2,140/h, [NO₂]=[C₃H₈]=590ppm

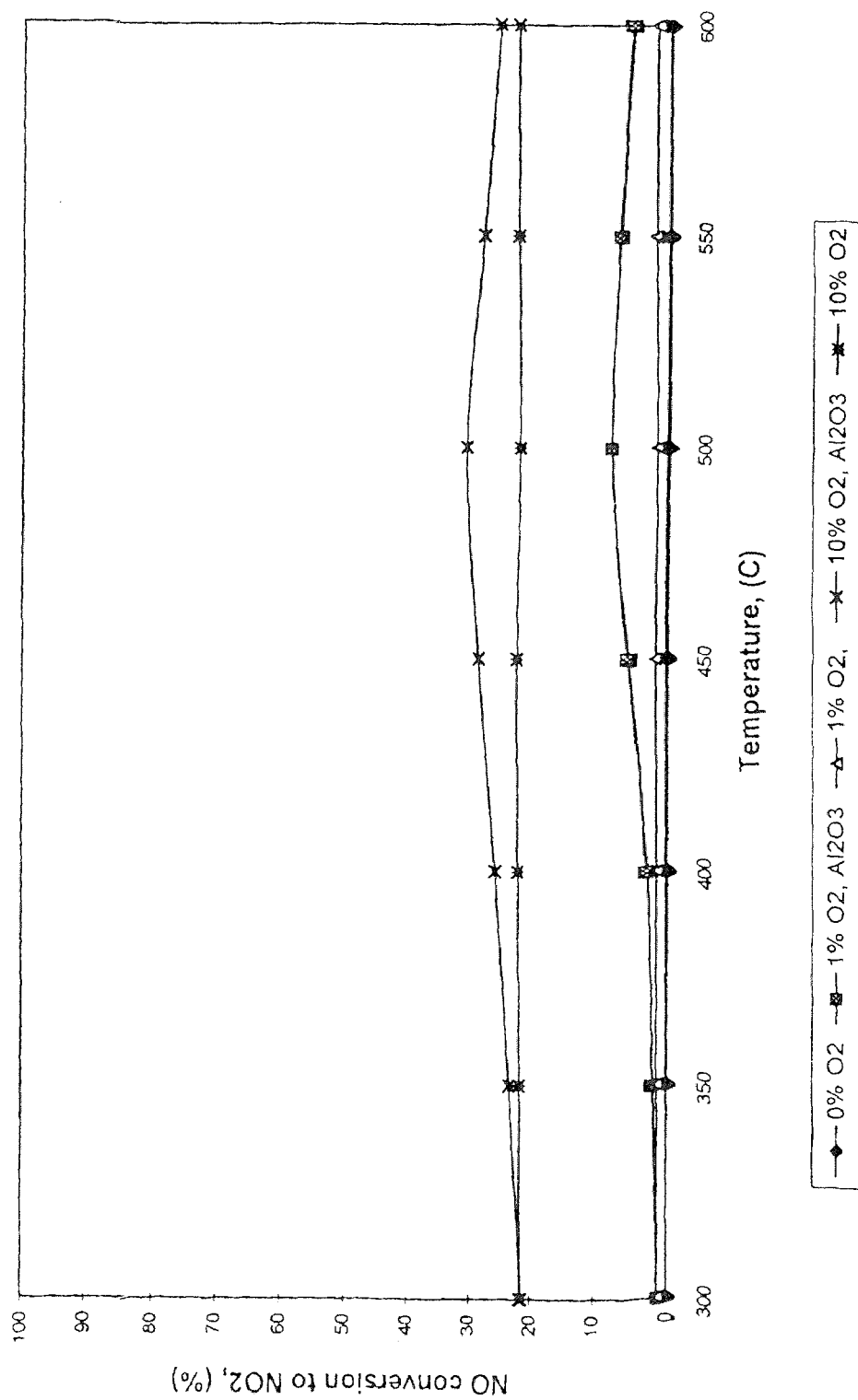


Figure 3.18 Effect of Temperature and Oxygen in NO Conversion to NO₂ over Alumina; GHSV=20,000/h, [NO]=590ppm

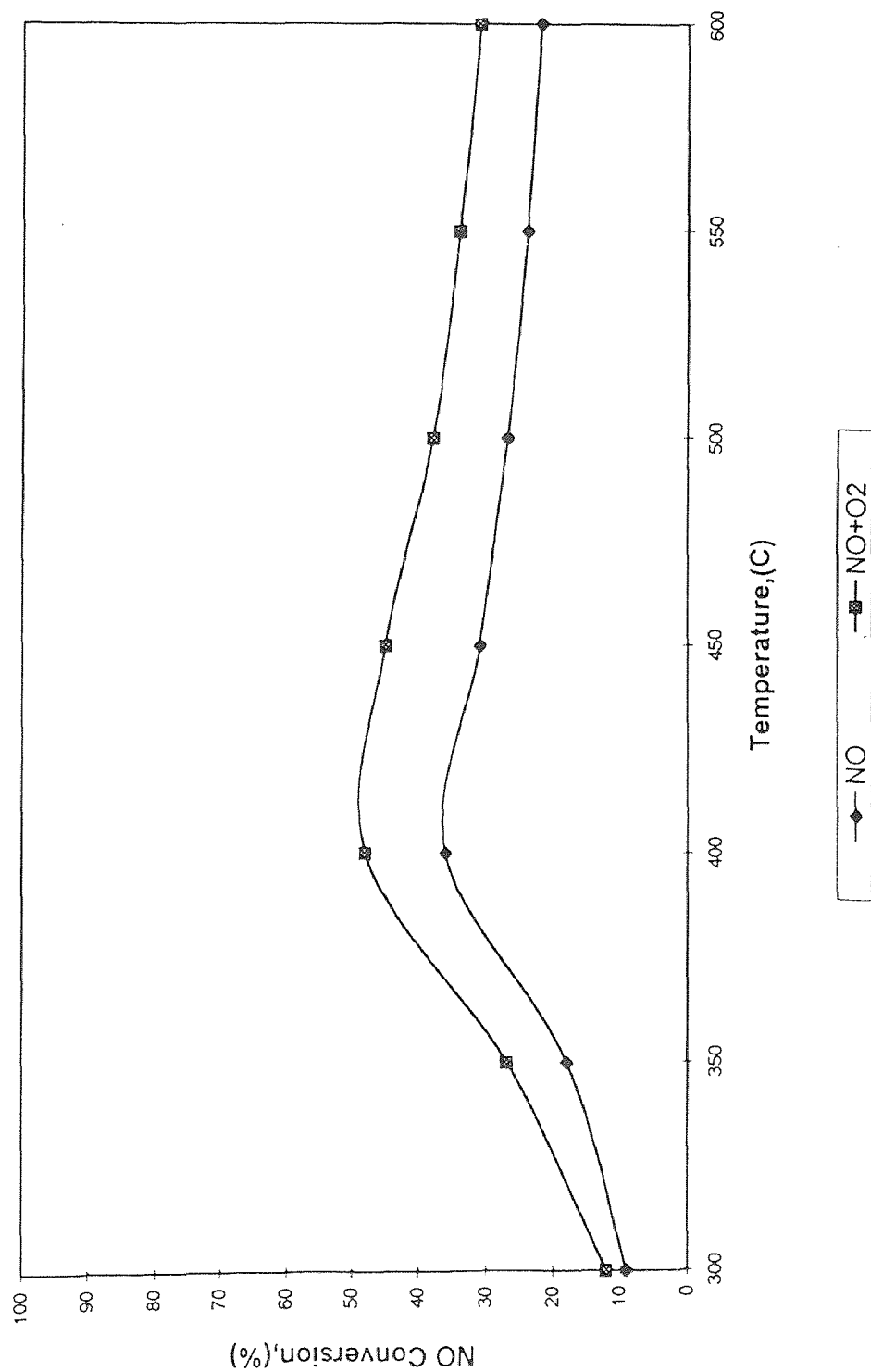
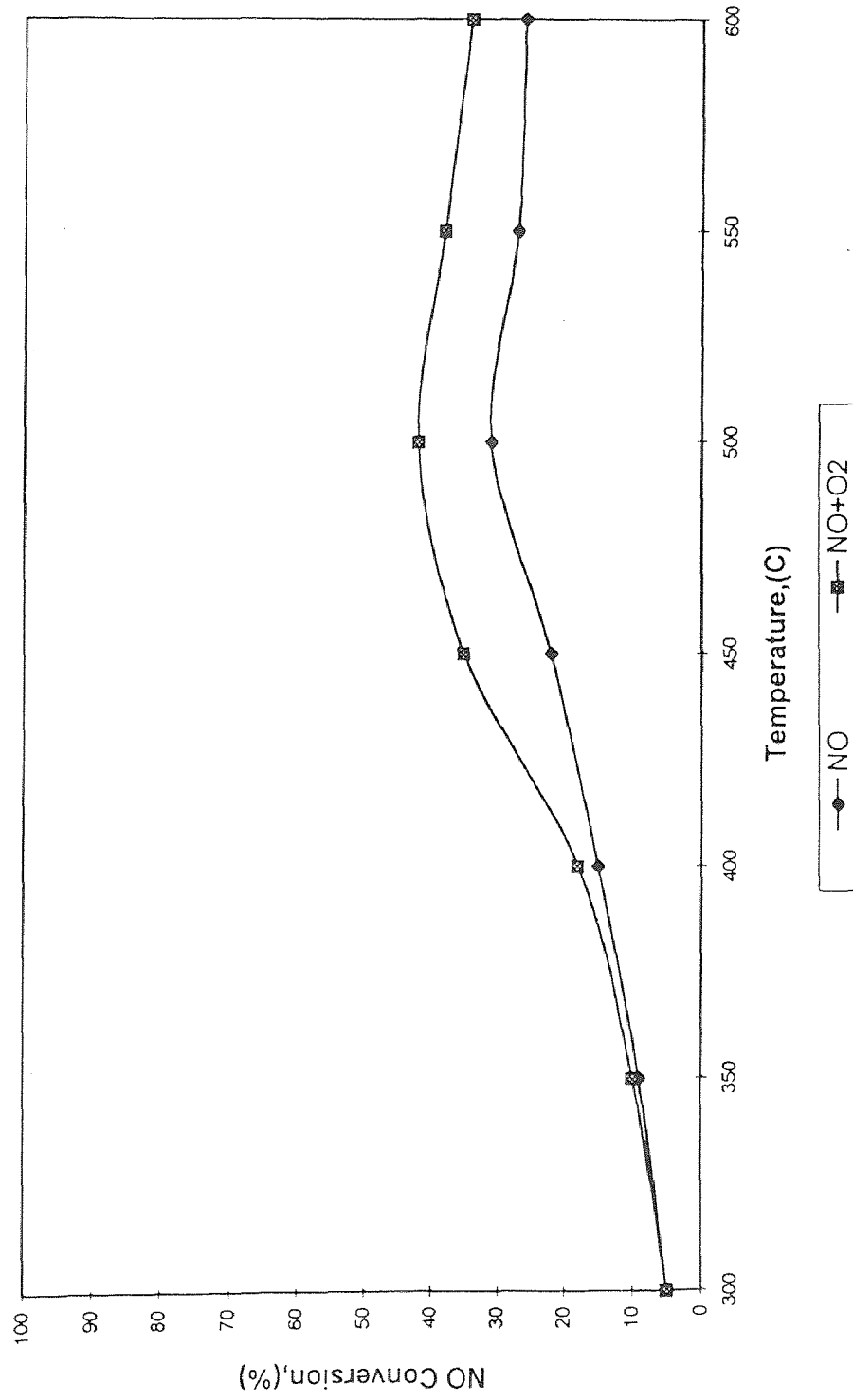


Figure 3.19 Effect of Oxygen on the Reduction of NO by Carbon Black over Cu-ZSM-5, [Carbon Black]=5%, GHSV=20,000/hr, [NO]=590ppm, [O2]=10%



3.20 Effect of Oxygen on the Reduction of NO by Carbon over Alumina;
GHSV=20,000/hr, [NO]=590ppm, [O₂]=10%

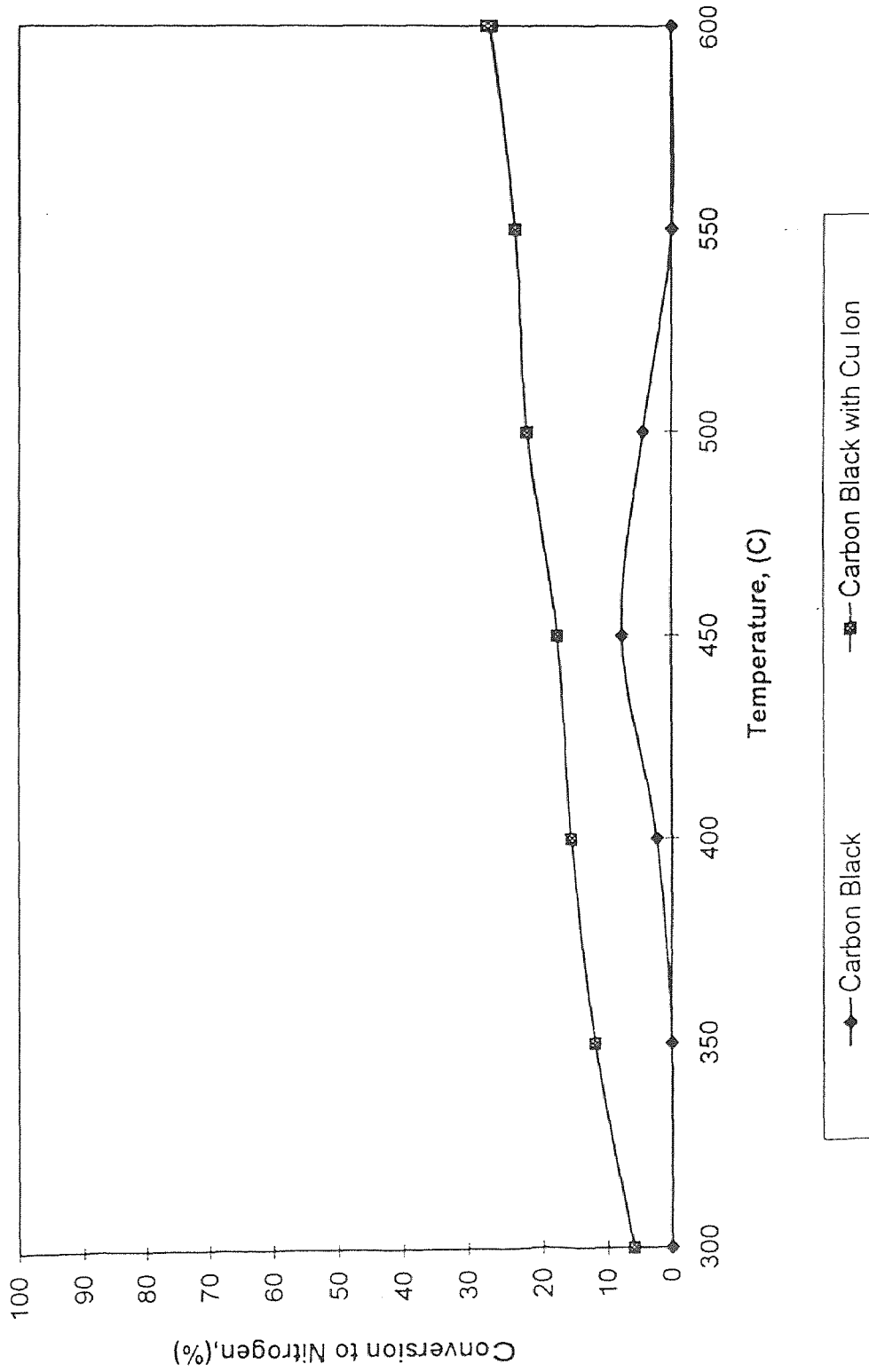


Figure 3.21 Effect of Cu Ion on the Reduction of NO over Carbon Black;
 GHSV=2,140/h, [NO]=590ppm, [O2]=10%

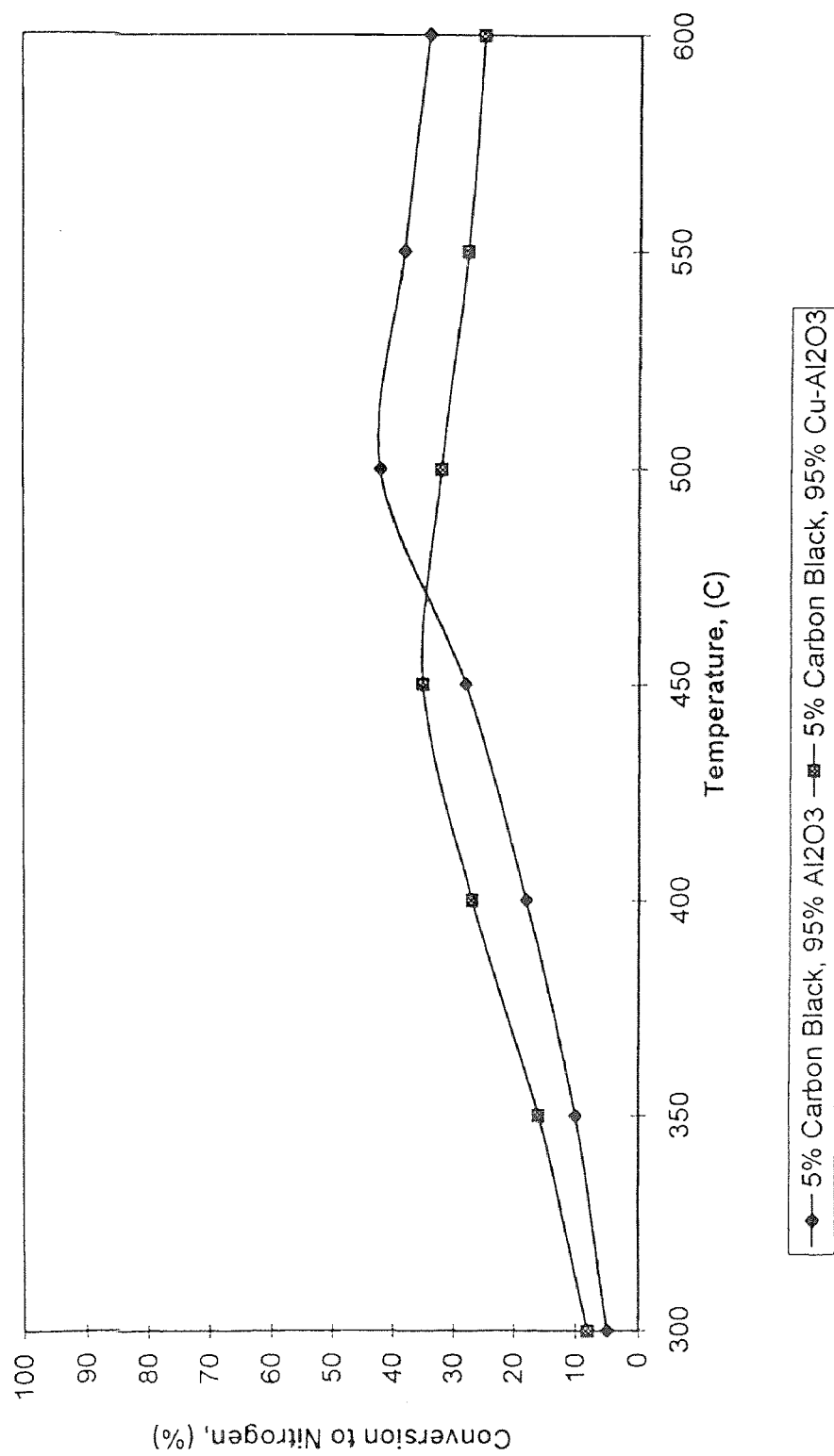


Figure 3.22 Effect of Cu Ion on the Reduction of NO by Carbon Black over Alumina; GHSV=2,140, [NO]=590ppm, [O₂]=10%

Curve 1: TGA
 File info: T-CuCarbon Thu Oct 17 12 53 16 1996
 Sample Weight: 4.240 mg
 Cu-Carbon

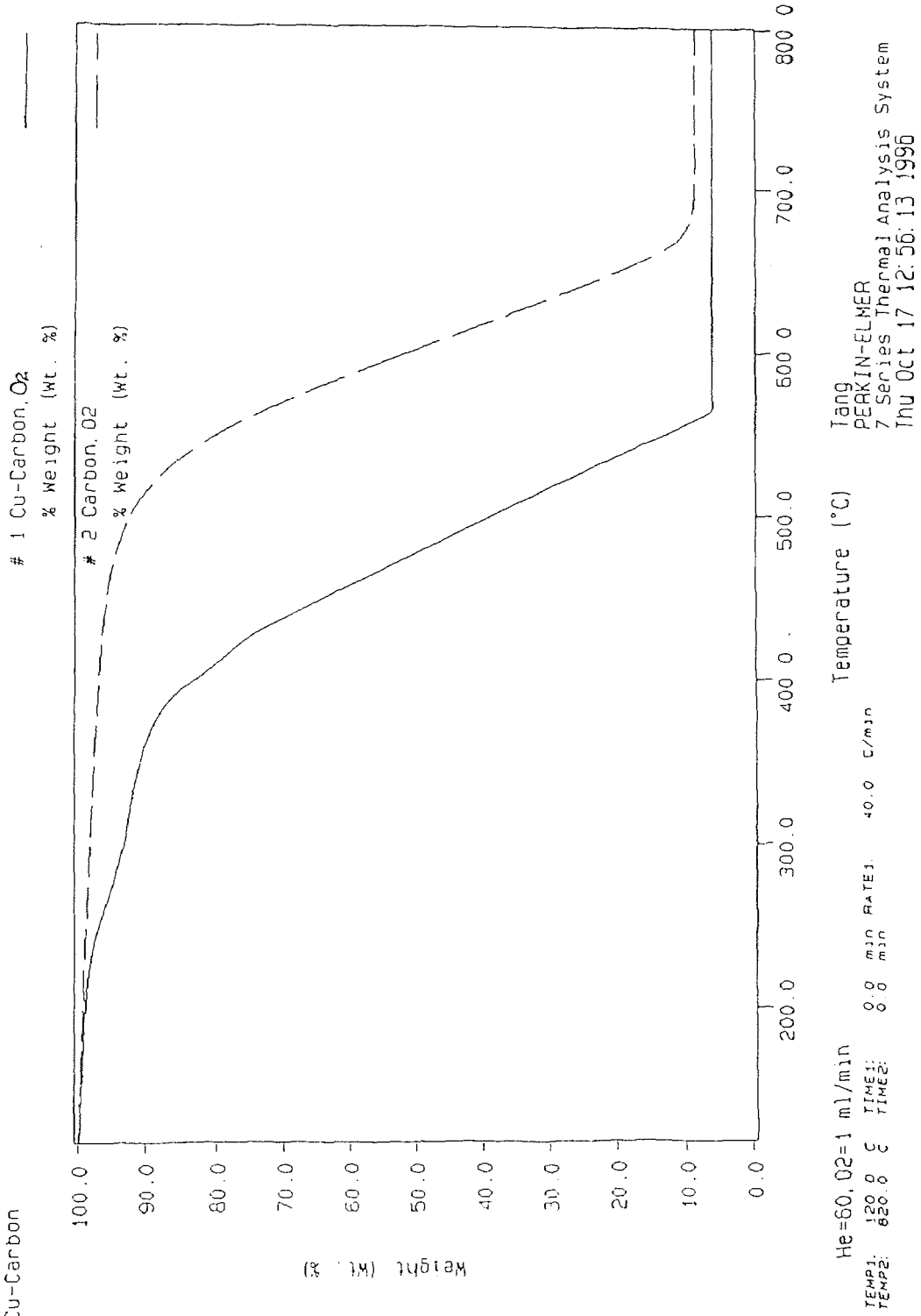


Figure 3.23 Effect of Cu Ion on the Combustion Temperature of Carbon Black

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