ABSTRACT

CATALYTIC REDUCTION OF NITRIC OXIDE BY CARBON MONOXIDE AND COPPER LOADED GRANULAR ACTIVATED CARBON IN THE PRESENCE OF OXYGEN

by
Kaiwen Ma

The reduction reaction of nitric oxide (NO) by carbon monoxide (CO), and granular activated carbon (GAC) in the presence and absence of oxygen was studied in a fixed bed catalytic reactor. The conversion of NO as a function of reaction temperature was evaluated for various reductant to NO ratios and space velocities. The results show that oxygen enhanced the NO+CO reaction over copper (Cu) ion exchanged ZSM-5. About 60% NO conversion to nitrogen (N_2) was obtained at 400°C and 2,000 v/v/hr. This result is consistent with the hypothesis that CO is an intermediate in the soot-NO reaction. The apparent mechanism seems to be the soot-O_2 reaction produces CO on the surface, the CO diffuses into the catalyst pores where it preferentially reacts with NO to produce carbon dioxide (CO_2) and N_2. The overall observation is that soot or GAC in the presence of oxygen reduces NO to N_2 and CO_2 if a Cu containing catalyst is present. One observes that Cu ion dispersed in GAC in the presence of 10% oxygen promotes the formation of CO at a relatively low temperature. This is followed by essentially complete NO conversion to N_2 at 600°C and 2,000 v/v/hr and 20,000 v/v/hr. At 450°C, 95% NO is converted to N_2 at 2,000 v/v/hr. The reaction rate of NO conversion to N_2 decreases with increasing space velocity with either CO or carbon black as the reducing materials. Based on the results presented here, additional research on the catalytic reduction of NO by CO

on the results presented here, additional research on the catalytic reduction of NO by CO and copper loaded GAC in the presence of O_2 at higher space velocities between 50,000 and 100,000 v/v/hr is warranted. Effect of water on the two reactions is also needed to be studied.

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This thesis is dedicated to my beloved parents and my fiancee

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TABLE OF CONTENTS

Chapters **Page**

TABLE OF CONTENTS
(Continued)

Chapters **Page**

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES
(Continued)

CHAPTER 1

INTRODUCTION

Air pollution from mobile sources is an increasingly serious problem throughout most of the industrialized world. Diesel powered vehicles, because of their high thermal efficiency, tend to emit less carbon monoxide (CO) and unburned hydrocarbons (HC), larger quantities of NO_x and a much higher concentration of particulate than gasoline fueled internal combustion (IC) engines. The exhaust from Diesel engines can be divided into visible smoke and invisible gas pollutants. The visible pollutants include primarily soot and in older engines unburned lubricating oil. The invisible pollutants include NO_x (primarily NO and NO_2), unburned hydrocarbons (HC), CO, SO_x (SO_2+SO_3), formaldehyde, polynuclear aromatics, etc. In urban areas, HC, CO and NO_x are the major invisible pollutants. Although both types of pollutants are extremely harmful to human health and the environment, there is greater concern for eliminating the visible pollutants because of their odor and obvious presence. Nitrogen oxides are gaseous pollutants that contribute to the acid rain formation, photochemical smog, and tropospheric ozone. NO_x also contributes to health problems, like bronchitis, pneumonia, emphysemra and susceptibility to viral infection. Therefore, it is essential to develop improved emission control equipment in diesel engines to minimize these pollutants.

Diesel engines have been used for over sixty years since they were first introduced to road transport in the early 1930's. As early as in 1909, the need to control undesirable air emissions from automobile engines was recognized (Frankel, 1909). In the early

1970's, the U.S. Congress passed the Clean Air Act. One of its most important provisions was to restrict emissions from automobile engines. The 1975 and 1976 federal (49 states) requirements were to limit the tail pipe emissions to 1.5 g/mile HC, 15.0 g/mile CO and 3.1 g/mile NO_x (Hightower, 1974). The Environmental Protection Agency (EPA) established a Federal Test Procedure (FTP) to allow measurement of CO, HC and NO_x over a simulated average driving condition in the U.S. (EPA, 1971). Subsequent amendments to the Clean Air in 1976 and 1990 promulgates more stringent control requirements for automotive emissions (Calvert, J., et al., 1993). Furthermore, California, a leader in air pollution control regulation, promulgated new standards for emissions from automobile engines. At the same time, other countries also established control standards for emissions of pollutants from automobile engines.

The "particulate" as defined in the FTP is collected on a filter at 52°C to condense the soluble organic fraction (SOF) (Heck and Farrauto, 1995), which results in the formation of smoke. In this thesis, we call the particulate matter emitted form the Diesel engine "soot". On average, it consists of 43 percent solid carbonaceous matter, 2 percent inorganic oxides (primarily sulfates) and 55 percent liquids (Hech and Farrauto, 1995). Current Diesel engines tend to emit a dryer soot. (Johnson, et al., 1994). Inorganic oxides are caused by the oxidation of sulfur and other heteroatoms in the fuel. The SOF is a combination of 20 percent unburned fuel and 35 percent lubricating oils. The composition of soot is very complicated. X-ray spectroscopy shows it has a graphitic structure with hexagonal basic carbon units linked into platelets (Millington, et al., 1967). Its surface area is very large. About 90 percent of NO_x formed in combustion process consists of NO, because Diesel engines operate under lean conditions (air in excess of its stoichiometric requirement for combustion) and high temperature and pressure. The amounts of HC and CO generated are relatively very small. Thus, their concentrations usually satisfy the emission standards. NO_x emissions increase due to the high flame temperature obtained form complete burning of fuel. At temperatures over 1100°C (McMann, et al., 1994), the atmospheric components nitrogen and oxygen react to form NO, which is the major component of NO_x. A small amount of additional NO_x results from the conversion of essentially all fuel-bound nitrogen compounds to NO_x.

During the past several decades, a large R & D effort has been carried out to meet the provisions the Clean Air Act and its amendments. The emissions of particulate matter have been significantly reduced with new Diesel engine designs. Diesel oxidation catalysts, on the other hand, indirectly caused an increase in SOF. This is a consequence of the need to allow fuel to leak into the exhaust in order to provide sufficient fuel to operate the catalyst above the light-off temperature. Particulate filters or traps were also introduced into Diesel exhaust system. However, their use is limited by difficulties in obtaining temperature above 400°C, which are required for oxidizing dry carbon particulate.

NO_x is a precursor to about 30% of acid rain and a major reactant in smog formation. Many methods to reduce NO_x have been developed. Some of the earliest NO_x control methods involved combustion modification approaches that included flue gas recirculation and staged combustion (rich combustion followed by very lean burn-out). One of the earliest technologies that used catalysts was called nonselective catalytic reduction (NSCR). It first depleted the oxygen by operating the engine near stoichiometric conditions or slightly rich. Then NO_x was reduced with the excess hydrocarbons over catalysts such as Pt and Pd. Another method involved staged combustion in which little NO_x was formed under rich conditions. The excess fuel was then burned out (with heat recovery) over noble metal containing catalysts.

Selective catalytic reduction (SCR) of NO_x was first discovered in 1957 in which NH_3 was used as the reducing agent. The general SCR classes of catalyst were platinum for low temperature (175 - 250°C), vanadia/titania for medium temperature (300 - 450°C), and zeolite for high temperature (350 - 600°C). However, this approach is impractical for treating the exhaust from automotive Diesel engines because it requires the on-board storage of NH_3, a pollutant in its own right.

Recently, catalytic reduction of nitric oxide with hydrocarbons has received great attention both from an academic and an industrial point of view because this may offer an effective way of removing nitric oxides even in the presence of a large excess of oxygen, whereas present automotive catalyst do not work effectively under these conditions. This process is called lean catalytic NO_x control. During the past several years interest in oxide catalysts for neutralization of nitrogen oxides has increased. This concerns, above all, Cu-containing catalysts based on zeolites, perovskites, etc. Since 1986, when Iwamoto, et al.,(1989) reported the high activity in direct nitrogen oxide decomposition of copper ion exchanged ZSM-5 zeolites, the interest in ion exchanged zeolites and other analogous catalytic systems has considerably increased. The removal of nitric oxide from the exhaust stream of various combustion sources has become increasingly important. The catalytic decomposition of NO into N_2 and O_2 is preferred. However, sufficient catalytic activity for decomposition of NO in oxygen rich atmosphere has not been realized because of the inhibition effect of oxygen in the NO decomposition reaction. For this reason, the reduction of NO has been attempted using reducing gases like NH_3, CO, H_2, and hydrocarbon gases. Carbon in the form of soot would be another candidate as a reducing agent.

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 O_2, with a significant decrease in conversion in the presence of 5% O_2. 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 100,000 v/v/hr. They showed that NO is converted to N_2 with nearly 100% selectivity and water poisons the catalyst at all temperatures. They also showed that the optimum reaction temperature was 350°C at 76,000 v/v/hr and 1% oxygen in the reactant gaseous mixture. 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 420°C 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 350°C. 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.

Tsutsumi's results are very encouraging, especially at the much higher conversion of NO observed using the Cu-ZSM-5 catalyst in the presence of soot and oxygen. He pointed out that the mass of soot deposited on the catalyst particles increased to about 50% of the soot throughout at 90 minutes of operation, the mass of soot then started to decrease with time until it dropped to zero at 200 minutes. This result suggests that the elimination of soot from the catalyst particles must be due to an interaction between NO_x, the carbon in the soot and oxygen. An examination of the literature shows that NO_x and carbon do react in the presence of O_2 and a catalyst at a temperature as low as 400°C (Teng, et al., 1992; Yamashita, et al., 1991).

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. He found that alumina showed considerable catalytic activity for the reduction of NO by propane in the presence of oxygen, obtaining 97% conversion to N_2 at 500°C, with no conversion in the absence of the catalyst. 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.

Yamashita, et al., (1993) reported that the copper catalyzed char-NO reaction was remarkably enhanced by the presence of O_2. They investigated the formation of reactive surface intermediates (C(O)) and stable carbon-oxygen complexes (C-O) by the combination of transient kinetics and temperature programmed desorption techniques. They also found out that the concentration of reactive C(O) was increased by the presence of both O_2 and Cu catalyst. The enhancing effect of oxygen in the reduction of nitric oxide with chars can be understood in terms of the presence of carbon-oxygen complexes on the char surface. The key feature of the proposed mechanism in this paper of both Cu-catalyzed and uncatalyzed C/NO-O_2 reaction is the enhanced formation of reactive C(O) intermediates, and thus free carbon sites, analogous to that proposed for other carbon gasification reactions. These active sites function either by directly reacting with NO or as acceptors of oxygen species generated on the catalyst surface.

Suzuki, et al., (1994) also found out that the formation of surface oxygen complexes by C/O_2 reaction is essential for the C/NO reaction. In addition to oxygen complexes, a considerable amount of nitrogen was also trapped in the carbon matrix during reaction. They pointed out that in the initial stage of the reaction, the concentration of nitrogen-containing product gas was much lower than expected from the NO consumption. The surface nitrogen complexes were identified by X-ray photoelectron spectroscopy. These are rather stable in an inert atmosphere even at 950°C, but they can easily be removed at 600°C in the NO- or O_2- containing reaction atmosphere.

D. Panayotov, et al., (1996) reported the interaction between NO, CO, and O_2 on γ-Al_2O_3 supported copper-manganese oxides. They investigated the activity of γ-Al_2O_3-supported $Cu_xMn_{3-x}O_4$ catalysts towards the reduction of NO with CO at temperatures in the range of 150-500°C. They found that the most active catalyst was $Cu_{1.01}Mn_{1.99}O_4/\gamma$-$Al_2O_3$, i.e., the sample where $CuMn_2O_4$ spinel is formed. In the presence of oxygen and the reducing agents CO, oxygen had no blocking effect on the NO+CO reaction.

D. Panayotov, L. Dimitrov, M. Khristova, L. Petrov and D. Mehandjiev (1995) also reported that Cu-CoAPSO (where APSO refers to a structure containing Al_2O_3, SiO_2, P_2O_5) and Cu-ZSM-5 exhibited activity towards conversion of nitric oxide to nitrogen (above 100°C). The heat-treated in an inert (argon) atmosphere Cu-ZSM-5 catalyst exhibits activity towards the reduction of NO by CO to N_2O and N_2. He observed a competition between the CO+NO and CO+O (surface) interactions at a definite temperature under the conditions of a $NO+N_2O+Ar$ gas mixture. He also found that competitive carbon monoxide adsorption occurred, depending on the temperature and degree of surface reduction, which poisoned the catalyst surface with respect to the reduction of nitric oxide to nitrogen. The surface of heat-treated Cu-ZSM-5 catalyst possesses active centers for the decomposition of nitrous oxide and nitric oxide to nitrogen from a $NO+N_2O+Ar$ gas mixture. They pointed out that the difference in catalytic behavior of the catalysts studied in their paper was explained by the hypothesis about the dependence of the catalyst activity on the ability of the catalyst surface to stabilize various intermediates during adsorption of nitric oxide and its interaction with carbon monoxide.

D. Panayotov, M. Khristova, and D. Mehandjiev (1995) studied the NO+CO interaction in the temperature range 60 to 240°C on the $Cu_xCo_{3-x}O_4$ spinel, where x=0.3, 0.54, and 0.94. At temperatures up to the "light-off" temperature, where degrees of surface reduction below 50% of a monolayer of oxygen were realized, the formation of N_2O is an important intermediate step for the NO+CO reaction. At higher temperatures, the degree of surface reduction up to several monlayers was attained and a route for direct NO reduction to N_2 became important. On oxidized surfaces, large amounts of NO were adsorbed which, were inactive towards reduction. Under oxidizing conditions the $NO+O_2+CO$ interaction proceeded with slow reoxidation of the catalyst surface. They found that the activity towards NO reduction even in oxidizing conditions was increase with increasing copper content (x). This was attributed to the enhanced capability of catalysts with x>0.5 to accumulate reduced sites in the surface layer.

A hypothesis was formulated 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 to explain how the catalyst improves soot oxidation without invoking the requirement that soot adsorb on catalytic active centers or diffuse into catalyst pores. The objective of this research is to obtain some understanding of CO as a reductant or a intermediate on the reduction of NO reaction. This research is part of the overall project "Simultaneous Removal of Soot and NO_x from Diesel Exhaust using a Rotating Fluidized Bed Reactor".

CHAPTER 2

EXPERIMENTAL

2.1 Experimental Apparatus

The flow experimental schematic diagram is shown in Figure 2.1. The major components of the system include a laboratory-scale quartz tube reactor containing known volumes of catalyst, carbon black or a mixture of both. The flow rates of gases were measured by several calibrated rotameters. The reactor system was used for comparing activities of commercial and synthesized catalysts and for determining product distributions and kinetics. The tube containing the gas stream passed through reactor and the effluent split into two parts. The first one went to the gas chromatography (GC) with thermal conductive detector (TCD) to measure nitrogen produced using helium as the carrier gas. The second one went to gas chromatography (GC) with a nickel hydrogenation catalyst to convert carbon monoxide and carbon dioxide to methane after separation over a Poropak Q column and measure the two methane peaks so produced with a flame ionization detector (FID) using helium as the carrier gas.

2.2 Instruments and Chemicals

The equipment and analytical instruments used in this research are described in this section.

2.2.1 Reactor

Experimental runs were performed by placing a fixed powdered catalyst bed on a coarse quartz fritted disk in a tubular reactor. The reactor consists of a 2.5 cm diameter by 55 cm

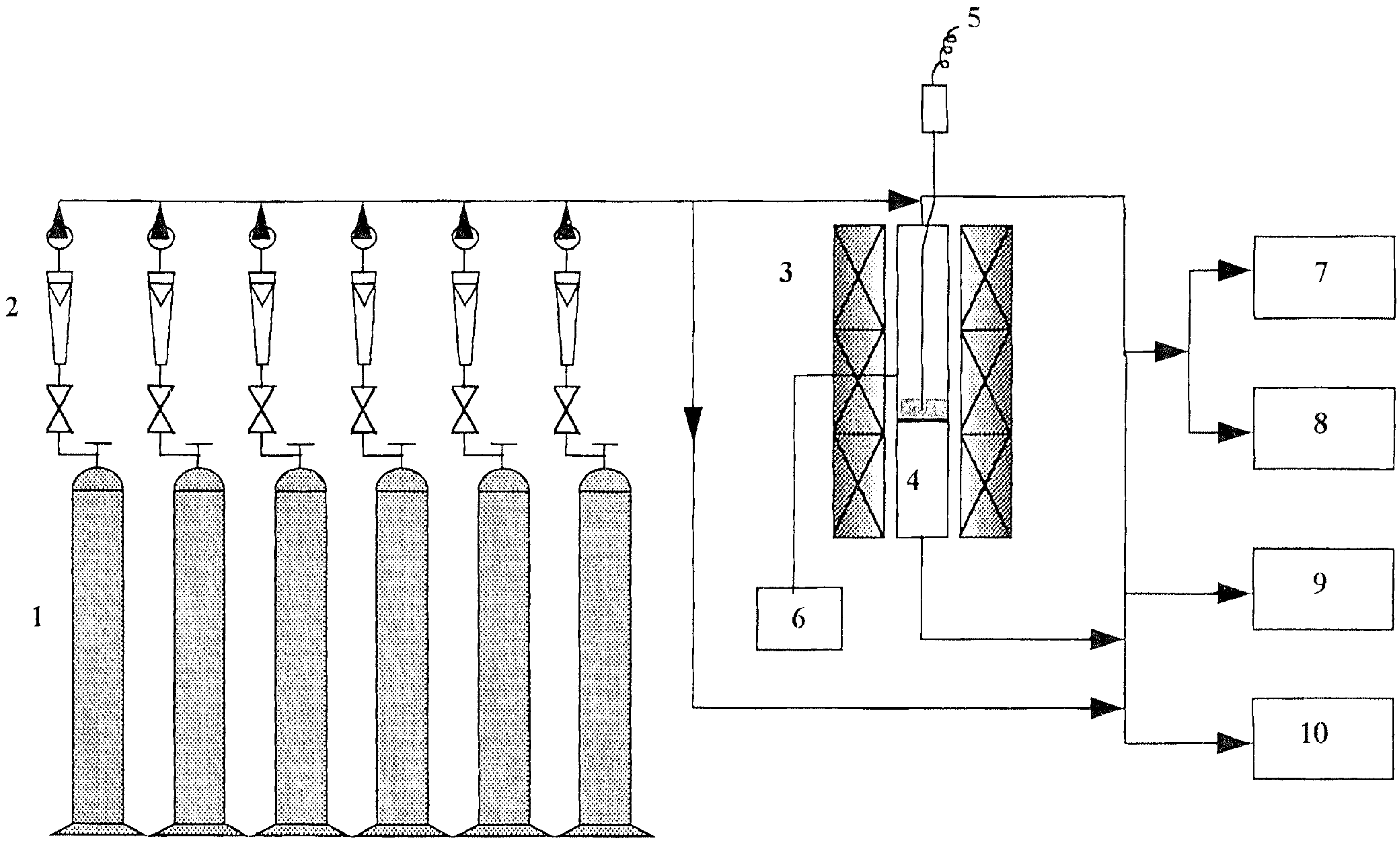

Figure 2.1 Schematic Diagram of Experimental Apparatus

1. Cylinders (He, NO, NO_2, C_3H_8, O_2, CO, SO_2) **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 Thermo Electron Chemiluminescent Analyzer long quartz tube which is residing in a vertical three zone tubular furnace. The temperature is controlled by three independent temperature controllers. The multizone furnace was used to preheat the gases entering the central section that contains the powdered solids and prevent condensation of the effluents. The middle zone has an very uniform temperature profile that is good to ± 1°C.. The bed materials such as catalyst, granular activated carbon (GAC) were paced 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 top and are discharged from the bottom in order to prevent fines carry over. The actual temperature of the bed was monitored with a chromel-alumel thermocouples which was inserted at the top of the reactor and placed in the center line immediately before the solids on the packed bed.

2.2.2 Gas Chromatography

The GC used in this research is a model HP 5860A with dual detectors consisting of a Thermal Conductivity Detector (TCD) and Flame Ionization Detector (FID). TCD was used to measure the concentration of N_2 produced after separation over an 1/8 inch in diameter by 3 feet long stainless steel column containing 60/80 mesh molecular sieve 5A. The column was put into a ice bath in order to effectively separate the relatively small N_2 peak from the major O_2 peak using helium as the carrier gas. A relatively large 1.0 cm^3 loop was used in the 6-port gas sampling valve in order to improve the analysis of N_2.

CO and CO_2 were detected by Gas Chromatography (GC) using a nickel hydrogenation catalyst to convert CO and CO_2 to methane after separating these components over a 80/100 mesh Poropak Q column and measuring the separate methane peaks with a Flame Ionization Detector (FID).

The integration of the chromatographic peaks was performed with HP 3396A integrators. Several standard gases containing known concentrations of CO, CO_2 and N_2 (Helium balanced) were used to calibrate the GC.

The detailed operation conditions of TCD and FID are listed in Table 2.1.

Table 2.1 Operation Conditions of HP 5860A

Detector	TCD, HP 5860	FID, HP 5860
Detector Temperature	120°C	250°C
Injection Temperature	120°C	350°C
Column Temperature	0°C	25°C
Carrier Gas	Helium	Helium
Loop Volume	1 cm^3	0.02 cm^3
Packing Materials	Molecular Sieve 5A	Porapak Q 80/100
Integrator	HP 3396A	HP 3396A
TCD Carrier Gas Flowrate	20 cm^3/min	30 cm^3/min
TCD Reference Gas Flowrate	30 cm^3/min	-
Ni Catalyst Reaction Temperature	-	350°C
Air Flowrate of FID	-	400 cm^3/min
H2 Flowrate of FID	-	35 cm^3 /min

2.2.3 Thermogravimetric Analysis (TGA)

TGA experiment was performed to determine the feasibility of direct denitration of $Cu(NO_3)_2$ to CuO within the temperature region between drying and calcination. Perkin Elmer TGA 7 permits the measurement of weight changes in a sample material as a function of temperature or time. Under the control of the computer, the TGA 7 is programmed from initial to final temperature and measures weight changes resulting from physical and chemical changes. The TGA is made up of two major components: a sensitive ultramicrobalance and furnace element capable of achieving temperatures of up to 1000°C. The microbalance operates as a high gain electromechanical servo system which permits the measurement of weight changes as small as 0.1 μg. During the experiments, Nitrogen gas was used as a purge gas flowed through the TGA to prevent any decomposition products or reactive gas product from entering into the balance chamber. The experimental parameter used to operate the TGA 7 as described above are listed in the Table 2.2

Table 2.2 The Parameters Used in TGA Analysis

Sample Parameter	Sample weight: Sample Zero:	
Atmosphere Parameter	Purge Gas: Nitrogen	
Temperature Program: Initial Final	25°C 800°C	Rate 40°C/min

2.2.4 X-ray Diffraction

The crystalline nature of the prepared catalysts was checked with x-ray diffraction crystallography. Crystal structures possess planes made by repetitive arrangements of atoms which are capable of diffracting x-rays. The angles of diffraction differ for the various planes within the crystal. Thus, every crystalline compound or element has unique diffraction patterns. The differences in these patterns allow the differentiation of various structures. In general, the crystallites of CuO on γ-Al_2O_3 were so small that no typical CuO spectrum was observed which means that the CuO diffused into the support particle pores and distributed very well so that the sites were microcrystalline, and no crystal structure could be detected.

2.2.5 Chemicals

Gases: Supplied by Matheson Gas Products

NO: 1180 ppm (in Helium)

CO: 1010 ppm (in Helium)

C_3H_8: 1207 ppm (in Helium)

O_2: 99.995%

He: 99.995%

Catalysts: Supplied by Mobil Technology Company

Cu-ZSM-5: Appeared as solid light yellow powder, the catalyst consists of a mixture of 50% Cu-ZSM-5 and 50% SiO_2/Al_2O_3 and is used as a cracking catalyst. The ZSM-5 has been modified by ion exchanging the H^+ with Cu^{2+}. The Cu^{2+} exchange level is 100% in the ZSM-5.

Gamma Alumina (γ-Al_2O_3): Was in the form of a solid white powder, supplied by the Alcoa Technical Center.

Granular Activated Carbon (GAC): Supplied by J.T. Chemical Company.

Cu ion /Carbon black: made in our lab

Cu ion /γ-Al_2O_3: made in our lab

2.3 Experimental Procedure

This part of Chapter 2 contains details of the experimental procedure.

2.3.1 Fixed Bed Gas Experimental Procedure

All experiments were performed in the quartz fixed bed reactor. The catalyst, or catalyst and carbon black were placed on a porous quartz disk inside the reactor and heated to 150°C for about an hour under He flow (about 200 cm^3/min) in order to remove impurities such as oxygen and water which may have adsorbed on the solid materials. The experiment was then started by switching different gases from cylinders to flow through the reactor. Each gas flow rate was controlled by a needle valve based on flow rate measurements from a calibrated set of rotameters. The mixture gases flowed through the whole experimental system for about half an hour in order to minimize any residual air in the system and then the effluent gaseous composition was measured by the GC. The outlet gas was analyzed on-line each 50°C by GC in the temperature range of 200°C to 500°C or 600°C. The desired operating temperature of the reactor was maintained by a temperature controller. Three different space velocity experiments were conducted for each parametric catalytic study. The space velocity was calculated as follows:

Space Velocity = Total flow rate / Solid sample volume

The higher the space velocity, the less the residence time of the reaction. The three space velocities used in this research were 2,000, 20,000, and 40,000 v/v/hr.

2.3.2 Preparation of CuO on GAC and Gamma Alumina

Impregnation method (Richardson, 1989) was used to synthesize metal loaded catalysts on the support materials mentioned before. This method fills the pores of the support particles with a solution of metal salt of sufficient concentration to give the desired metal loading. In this research, GAC and gamma alumina were used as the support particles and Cupric Nitrate, $Cu(NO_3)_2 \cdot 3H_2O$, was used as the metal salt. The solubility of cupric nitrate is about 137 grams of salt per 100 cm^3 cold water. The support particles were pretreated by heating to remove all pore moisture and other adsorbed gases. The volume of metal ion solution that was needed was determined by measuring the volume of deionized water that was adsorbed and confirmed by calculation of the volume from the measured pore volume. The maximum water which a certain mass of alumina can absorb is referred to as the water pore volume. To determine the water pore volume, deionized water was slowly added to a known mass of dried support materials until it was saturated as indicated by beading of excess water. The measure volume of deionized water per unit mass of support material was used as the value of the water pore volume for the synthesis of catalyst by the incipient wetness impregnation method (Richardson, 1989). The mass of cupric nitrate could be calculated by the known mass of support material and the percentage of Cu ion wanted. The support material was soaked in the exact volume of cupric nitrate solution which was determined by the water pore volume and the mass of the support material over night. The slurry was then dried at 100°C for four hours to evaporate the water. The salt crystallized in the pores as the water was removed. Finally, the catalyst was calcined to convert the salt crystals in the pores to oxides. Crystallized salt redissolves when the dehydrated catalyst is exposed to moist environments. The purpose of the calcination is to convert the salt to an oxide and "freezes" the distribution. The required calcination temperature was determined by Thermal Gravimeric Analyzer (TGA) experiments. A weight-percentage loss versus temperature plot was obtained that showed the temperature at which $Cu(NO_3)_2$ started to decompose to CuO. Since $Cu(NO_3)_2$ started to decompose at about 350°C, 550°C was chosen as the calcination temperature to make sure that all $Cu(NO_3)_2$ would decomposed to the oxide. Gamma alumina supported catalysts were calcined in the furnace with air flow for six hours. Calcination of GAC supported catalyst was conducted in the fixed bed quartz reactor by flowing N_2 through the powdered solid because GAC could react with oxygen from the air at the relatively elevated calcination temperatures.

CHAPTER 3

RESULTS AND DISCUSSION

The results of testing the commercial and synthesized catalysts for NO reduction to N_2 are presented and discussed in this section.

3.1 Reduction of NO by CO over Cu-ZSM-5

Carbon Monoxide (CO) is one of the trace gaseous components of Diesel exhaust. For a 1.8 dm^3 Diesel engine, CO concentration in the exhaust is around 200 ppm. It is possible to use CO as a reductant for NO reduction in diesel exhaust. CO and NO are among the polluting components in the exhaust emitted from vehicular engines and industrial boilers. Apart from noble metal (Rh, Pt, Pd, etc.), which are very active for the simultaneous NO reduction and CO oxidation, copper based catalysts have been widely studied as less expensive alternatives for these reactions. Some researchers have reported that the reduction of NO with CO occur under oxidative conditions over metal loaded catalysts at tempertures on the order of 400°C.

From Figure 3.1 (Ellingham Diagram), it can be seen that the reaction $NO_2 + C \rightarrow NO + CO$ is thermodynamically favored. Free energy ΔG becomes more and more negative, while the equilibrium constant K_p increases with increasing reaction temperature. ΔG is about -39 kcal/mol at 400°C. The reaction $2NO + C \rightarrow N_2 + CO_2$ is the most thermodynamically favored compared to the other three reaction in the diagram. ΔG is about -133 kcal/mol at 400°C. The value of ΔG increases slightly with increasing temperature. For the reaction $NO_2 + CO \rightarrow CO_2 + NO$, ΔG is about -50 kcal/mol at all temperature. Thermodynamically, it is not as favored as the NO+C reaction. From this diagram, it can be seen that the reaction $2NO + 2CO \rightarrow N_2 + CO_2$ is not thermodynamically favored. The value of ΔG increases with increasing temperature and the slope is very large (slope is related to entropy). But, within the temperature range of 200-600°C, the ΔG value varies from -62 to -42 kcal/mol. This indicates that NO can react with CO spontaneously in this temperature range. Thus, this thermodynamic analysis clearly indicates that the reactions being studied in this project are favored.

Experimentally, NO and CO react in the absence of O_2, but give much lower NO conversion to N_2 than they do in the presence of O_2. Figure 3.2 shows the difference between the NO, CO reaction over Cu-ZSM-5 with 10% oxygen and in the absence of oxygen. The highest NO conversion to N_2 with 10% oxygen is about 60% at 400°C. In the absence of oxygen, NO conversion to N_2 appears to increase monotonically with temperature reaching 28% conversion at 500°C. It appears that the presence of O_2 is necessary for the reduction of NO by CO below 500°C.

Figure 3.3 shows how the CO_2 product concentration varies with temperature for the NO-CO reaction without oxygen over Cu-ZSM-5. The gas outlet sample was continuously passed through the 6-port gas sampling volve of GC and analyzed by using TCD for N_2 and FID for CO and CO_2. Figure 3.3 shows that within the reaction temperature range of 200 to 500°C, the CO_2 concentration increases monotonically with temperature. This result matches the result in Figure 3.2 which shows that the NO conversion to N_2 increases with increasing reaction temperature within the temperature range of 200-500°C. In this reaction, NO is the only oxidant that can oxidize CO to CO_2, and CO is the only reductant that can reduce NO to N_2. The reaction can be represented as: $2NO + 2CO \longrightarrow N_2 + 2CO_2$

When 10% oxygen is present in the reaction mixture, a maximum NO conversion to N_2 is obtained at 400°C and N_2 production decreases after 400°C. The results presented in Figure 3.4 help explain this phenomena. Figure 3.4 shows that CO conversion reaches a slowly increasing plateau as a function of reaction temperature when 500 ppm CO are oxidized by 10 % oxygen over Cu-ZSM-5. After 300°C, CO conversion increases slowly from 80% to 85% at 550°C. This indicates that at high temperature, most of the CO is converted to be CO_2 which causes NO reduction to N_2 to decrease due to a lack of CO.

3.1.1 Effect of Oxygen Concentration

The NO-CO reaction was studied over Cu-ZSM-5 at the optimum temperature of 400°C by changing oxygen concentration from 0 to 10%. The results are depicted in Figure 3.5 which show that as long as there is at least 0.1% oxygen present in the gas stream, the NO conversion to N_2 is reasonably high. However, when no oxygen is present, the quantity of NO converted to N_2 drops to 11% at 400°C, instead of 60% above 0.1% O_2. Because the concentration of oxygen is very high compared to ppm level concentration of the other gaseous component, the effect of 0.1% to 10% oxygen causes no large difference in rate.

D. Panayotov (1996) did experiments with $NO+CO+O_2$ gas mixture over $Cu_{1.01}Mn_{1.99}O_4/\gamma\text{-}Al_2O_3$ catalyst. The results shows that the effect of oxygen on the NO+CO reaction proceeding on the $Cu_{1.01}Mn_{1.99}O_4/\gamma\text{-}Al_2O_3$ catalyst cannot be attributed to blocking of the active sites for NO reduction. Panayotov observed such a blocking effect of oxygen on NO reduction to N_2O and N_2 in the case of CuO without support. However, in this research, such a blocking was not observed.

3.1.2 Effect of CO Concentration

Figure 3.6 compares the effect of CO to NO mole ratio on NO to N_2 conversion as a function of temperature in the presence of 10% O_2. The results show that the higher the CO/NO concentration ratio, the higher the NO conversion to N_2 over Cu-ZSM-5. About 88% NO conversion to N_2 is obtained when the CO/NO ratio is 2, about 60% conversion is obtained at equal quantities of CO and NO, and 50% conversion is obtained when CO/NO ratio is 0.5.

The results of runing at an initial mole ratio of 2.0 in CO/NO experiments with $NO+CO+O_2$ over Cu-ZSM-5 with 10% and 1% oxygen are presented in Figure 3.7. The maximum NO conversion to N_2 is 88% for 10% oxygen reaction and 86% conversion for 1% oxygen reaction showing that there is a small oxygen concentration effect. Furthermore, CO is very good reducing gas for NO conversion to N_2.

3.1.3 Effect of Space Velocity

Figure 3.8 compares the effect of gaseous hourly space velocity (GHSV) for the CO/NO/O2 system over Cu-ZSM-5. The three curves which represents 2,000, 20,000 and 40,000 /hr space velocity produce maximum conversion of NO to N_2 at 400°C. The effect of space velocity on conversion decreases from 60 % at 2,000 /hr, to 32% at 20,000 /hr and the lowest conversion is 18% at 40,000 /hr. The results show clearly that space velocity has an important effect on the reduction of NO. The conversion at the maximum temperature of 400°C decreases with increasing space velocity, indicating that the higher the space velocity, the lower the reaction rate. The relationship between the inverse GHSV (e.g., residence time) and conversion is not linear, indicating that the reaction is not kinetically limited. The Reynolds number (N_{Re}) is calculated as a check if the flow is laminar or turbulent:

$$N_{Re} = Dv\rho/\mu \qquad (3.1)$$

where, D is the diameter of the reactor, v is the average velocity of the gas mixture, ρ is the gas density, μ is the gas viscosity .

$D = 2.5$ cm

cross-sectional area of the reactor $(A) = \pi(D^2 / 4) = 4.91\ \text{cm}^2$

When GHSV = 2,000, flow rate $(Q) = 100\ \text{cm}^3/\text{min}$

Velocity $(v) = Q/A = 20.38$ cm/min

$$PV = nRT \qquad (3.2)$$

$= (m/M)RT$, $\rho = (PM)/(RT)$, where, P is the pressure in the reactor, M is the molecular weight of gas mixture (in this case, helium is the major component, other gas components can be neglected.), R is the gas constant, T is the reaction temperature (use 400°C).

$\rho = (1\ \text{atm}*2\ \text{g/mol}) / (82.057\ \text{cm}^3\cdot\text{atm/g}\cdot\text{mol}\cdot\text{K}*673\ \text{K}) = 3.62\text{E-}5\ \text{g/cm}^3$

$\mu = 0.033\text{E-}3\ \text{kg/m}\cdot\text{s} = 0.0198\ \text{g/cm}\cdot\text{min}$ (Christie J. Geankoplis, "Transport Processes and Unit Operations", Appendix A3 for helium at 673 K)

$N_{Re} = (2.5\ \text{cm}*20.38\ \text{cm/min}*3.62\text{E-}5\ \text{g/cm}^3) / (0.0198\ \text{g/cm}\cdot\text{min}) = 0.093 < 2100$

When GHSV = 20,000, $N_{Re} = 0.93 < 2100$

When GHSV = 40,000, $N_{Re} = 1.86 < 2100$

Thus, the flow is always laminar at three space velocities in this research experiments.

Figure 3.9 indicates that when the space velocity is 20,000 /hr, the maximum NO conversion to N_2 is 62% at 400°C when [CO]/[NO]=2 and 32% when [CO]/[NO]=1.

3.2 Reduction of NO by Granular Activated Carbon (GAC)

Reduction of NO by GAC with 10% oxygen over Cu-ZSM-5 (5% GAC, 95% Cu-ZSM-5) and reduction of NO by 20% Cu ion loaded GAC with 10% oxygen are discussed in this section.

3.2.1 Reduction of NO by GAC with 10% oxygen over Cu-ZSM-5

The GAC-nitric oxide (NO) reaction plays an important role in many processes where the reduction of NO is attempted. It is well known that there is a certain amount of oxygen which significantly increases the rate of C-NO reaction. Suzuki (1994) reported that the formation of surface oxygen complexes by the C-O_2 reaction is essential for the C-NO reaction.

3.2.1.1 Effect of Space Velocity: Figure 3.10 summarizes the results of using GAC as the reducing agent for NO conversion to N_2 as a function of temperature and GHSV. The three curves which represent GHSV of 2,000, 20,000 and 40,000 have maxima at 400°C and a NO conversions to N_2 of 66%, 38% and 18%, respectively. These results match the result from NO+CO+O_2 reaction at the same space velocities. In both cases, the rate determining step does not appear to be the reduction kinetics.

It has been generally agreed that the presence of oxygen enhances the rate of NO chemisorption on carbon (Mochida, et al., 1991) and the rate of carbon-NO reaction (Yamashita, et al., 1993). Some researchers consider the formation of NO_2 to be responsible for the rate enhancement, while others point out that the surface oxygen complex produced by the coexistence oxygen is responsible. Suzuki (1994) found that the reactivity of NO_2 is large but the main product is not N_2, but NO. This means that the transformation of NO to NO_2 is not beneficial for the NO removal to N_2 reaction in the presence of O_2. On the other hand, they found much evidence to support the hypothesis that O_2 enhances the carbon-NO reaction through formation of surface oxygen complexes.

It can be seen in Figure 3.10 that as the temperature increases above 400°C, the conversion to N_2 decreases. If we assume that CO is the intermediate and as temperture increases, most of the CO goes to CO_2. Also, the rate of the NO-O_2 reaction to NO_2 decreases as temperture increases (negative temperature coefficient) and consequently, the rate of recombination of NO to N_2+O_2 increases. The NO concentration decrease and conversion to N_2 decreases as well. Another explanation due to Suzuki, et al., (1994) is that the missing nitrogen is trapped as surface complexes on the carbon. They observed that in the initial stage, N_2 production is much less than the expected NO consumption at 600°C and they did not observe other nitrogen-containing gases like N_2O during the initial stage. They also found that after 120 min from the initial stage, the observed coversion to

N_2 increases to match the NO consumption. It shows that the nitrogen initially trapped on the carbon is released, and thus, the observed N_2 output increases.

The solid material contains 5% GAC and 95% Cu-ZSM-5. The volume of GAC / Cu-ZSM-5 is 3 cm^3. Calculations of moles of GAC, flow rate of NO, O_2 and residence time are listed below:

Density of GAC: 0.3553 g/cm^3

Density of Cu-ZSM-5: 0.9533 g/cm^3

Avg. Density = 0.3553*0.05 + 0.9533*0.95 = 0.9234 g/cm^3

Mass of 3 cm^3 GAC/Cu-ZSM-5 = 0.9234*3 = 2.7702 g

Weight of 5% GAC = 2.7702*0.05 = 0.1385 g

Moles of 5% GAC = 0.1385/12 = 0.011542 mol

NO Concentration: 590 ppm
0.00059 cm^3 NO/cm^3 volume

When GHSV = 2,000, total flow rate: 100 cm^3/min

NO flow rate = 100 cm^3/min * 0.00059 cm^3/cm^3 = 0.059 cm^3/min

Flow rate of 10% O_2 10 cm^3/min

Residence time = 1 / [(2000 /hr) * (1 hr/60 min)] = 0.03 min

3.2.2 Reduction of NO by Cu ion/GAC with 10% Oxygen

It is well known that copper catalyzed GAC and NO reaction is remarkably enhanced by the presence of oxygen (Suzuki, et al., 1994). The results in this research shows that the C/NO reaction is catalyzed by Cu ion loaded on GAC and is remarkably promoted in the presence of oxygen at temperature of 450°C. Figure 3.11 indicates that a high conversion to N_2 of about 95% at 2,000 v/v/hr space velocity is achieved with a copper loaded carbon black as the reductant. This reaction goes very fast, significant amount of solid disappear at temperature of 450°C and above. So it is necessary to run the experiment separately at each temperature point in order to obtain the same condition for each temperature point.

The Cu ion catalyzes the C/O_2 reaction and increases the concentration of active sites, C(O). The C/O_2 reaction produces a considerable amount of CO, and therefore the contribution of $2CO + 2NO \rightarrow 2CO_2 + N_2$ is important. Also, the formation of NO_2 via gas phase reaction from $2NO + O_2 \rightarrow 2NO_2$ can play an important role as an intermediate in NO reduction, even though this reaction is very slow (Shaw, 1976). It has been reported that NO_2 has much higher reactivity toward carbon than either NO or O_2. Although a considerable fraction of NO_2 would regenerate NO, some NO_2 might be converted to N_2. On the other hand, the surface state of the Cu catalyst is as a mixture of Cu_I and Cu_{II} in the region where Cu/carbon black exhibited a high NO_x conversion (Yamashita, 1991). The oxidation of Cu by O_2 may be an important factor leading to high activity. Even in this case, however, the C sites are likely to play an important role, as acceptors of oxygen species supplied by the catalyst. Yamashita, et al., (1993) proposed a mechanism for the reaction.

$$2C + 2NO \rightarrow 2C(O) + N_2 \tag{3.3}$$

$$2C + O_2 \rightarrow 2C(O) \tag{3.4}$$

$$2C(O) \rightarrow CO_2 + nC \tag{3.5}$$

$$C(O) \rightarrow CO + nC \tag{3.6}$$

$$C(O) \rightarrow C\text{-}O \tag{3.7}$$

$$2C(O) + 2NO \rightarrow 2CO_2 + N_2 + nC \quad (3.8)$$

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \quad (3.9)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (3.10)$$

$$C + NO_2 \rightarrow C(O) + NO \quad (3.11)$$

The initial step is the chemisorption of NO on very active C site, followed by the regeneration of C sites according to reaction (3.5) and (3.6). The role of oxygen is to enhance the concentration of both reactive C(O) intermediates and stable C-O complexes, according to reaction (3.4) and (3.7). Also, these two reactions reinforce each other. The increase in the concentration of C(O) sites drives reaction (3.5) and (3.6) forward, thus creating additional active sites of C for the reaction. The C/O_2 reaction produces a considerable amount of CO, and therefore the contribution of reaction (3.9) cannot be neglected. Another role of oxygen is the formation of NO_2 via reaction before entering reaction zone. It can play an important role as an intermediate in NO reduction, as shown in reaction (3.10) and (3.11).

3.2.2.1 Effect of Space Velocity on GAC Reduction with 20% Cu ion: Experiments were conducted at three different space velocity 2,000, 20,000 and 40,000 /hr. The results are compared in Figure 3.11. It can be seen that the conversion to N_2 is very high at each space velocity. The reaction temperature range is 200°C to 600°C. The conversion to N_2 increases with increasing temperature between 200° to 450°C and remains constant after 450°C. For the reaction at 2,000 /hr space velocity, 56%, 77% and 91% conversion to N_2 was obtained at 300°C, 350°C and 400°C. The conversion is much higher than that obtained with any other type of NO reduction reaction in the same temperature range. For the reaction at 20,000 /hr space velocity, only 20%, 32% and 51% nitrogen conversion was obtained at the same three temperatures. However at 450°C, nitrogen conversion dramatically increased to 91% which is very close to the 95% conversion at 2,000 /hr reaction. For the reaction at 40,000 /hr space velocity, the conversion to N_2 at each temperature point was lower than the equivalent ones at 20,000 /hr reaction. At 450°C, the conversion increased to 82%. As opposed to results at 2,000 and 20,000 GHSV, no 100% conversion to N_2 was obtained in the reaction temperature range for 40,000 /hr reaction. The solid material contains 20% copper ion adsorbed onto GAC. The volume of the solid is 3 cm^3. The calculation of moles of GAC, flow rate of NO, O_2 and the residence time is listed below:

Density of 20% Cu ion/GAC	0.4347	g/cm^3
Weight of 3 cm^3 20% Cu ion/GAC	1.3041	g
Weight of GAC Content	1.04328	g
Moles of GAC	0.08694	mole
NO Concentration	590 0.00059	ppm cm^3 NO/cm^3 volume

When GHSV = 2,000, total flow rate: 100 cm^3/min

NO flow rate = 100 cm^3/min * 0.00059 cm^3/cm^3 = 0.059 cm^3/min

Flow rate of 10% O_2 10 cm^3/min

Residence time = 1 / [(2000 /hr) * (1 hr/60 min)] = 0.03 min

One can see that 3 cm^3 20% Copper loaded GAC contains much larger amount of carbon than 3 cm^3 of 5% GAC / 95% Cu-ZSM-5. Copper loaded GAC is not only a reactant but also a catalyst in the reaction. Thus, copper loaded GAC is an excellent source of carbon that can be oxidized to produce larger amount of CO even at low temperatures.

In order to support the idea that CO is the intermediate of $C+NO+O_2$ reaction, a set of GAC and 10% oxygen over different catalysts experiments was run to obtain CO amount for each reaction and to compare whether higher CO concentrations present in the system result in higher NO conversion to N_2. Figure 3.12 shows the results of this set of experiments. GAC does not react with oxygen until 550°C at which point there are about 100 ppm CO produced, and at 600°C, there are about 200 ppm CO produced. When the reaction is conducted over SiO_2/Al_2O_3 catalyst, CO can be detected at lower temperature compare to the reaction without any catalyst and higher CO ppm are obtained as well. The Cu-ZSM-5 has a significant effect on the reaction between GAC and oxygen. At low temperature, starting from 300°C, large quantities CO are produced. At 400°C, about 210 ppm CO was detected; at 450°C, about 270 ppm CO was detected. The CO which was produced by this reaction at these temperature could be higher than detected concentration because there is always a significant quantity of CO on the surface of GAC or catalyst. When 20% Cu ion loaded GAC reacted with oxygen, very high concentration of CO was obtained. About 2500 ppm CO was detected at 350°C and 5600 ppm was detected at 450°C which was much higher than 590 ppm NO concentration when it was used as the reductant to convert NO to N_2. High CO concentration produced from the reaction of Cu ion loaded carbon black with 10% oxygen could be the reason that high conversion to N_2 was achieved from the $NO+C+O_2$ reaction.

3.2.3 Reduction of NO by GAC with 10% Oxygen

Figure 3.13 shows that the reduction of NO by GAC with 10% oxygen in the absence of a catalyst produces no conversion to N_2 until 550°C. Compare to the results discussed above, it can be seen that the reaction with catalysts present increases the conversion to N_2. In this case, at temperature as high as above 550°C, the reaction $CO + NO \longrightarrow N_2 + CO_2$ might occur, even if the possibility is very low because the CO concentration is much lower than the NO concentration. But, on the other hand, the NO decomposition reaction might be preferred at high temperature which could contribute about 20% conversion to N_2 at 2,000 /hr space velocity.

3.2.3.1 Effect of Space Velocity: For the three space velocities considered, no conversion to N_2 was observed until 550°C. The rate of conversion decreases with increasing reaction space velocity.

3.3 Effect of Cu ion on $NO+C_3H_8+O_2$ Reaction over γ-Al_2O_3

Copper was introduced on Al_2O_3 by impregnation method described in Chapter 2. Figure 3.14 shows the effect of Cu ion on the reduction of NO by propane over Al_2O_3. It can be seen that the presence of Cu ion shifts the maximum nitrogen conversion temperature down about 100°C and while keeping almost the same nitrogen conversion that was obtained with pore γ-Al_2O_3 which is 40%.

3.4 Thermogravimetric Analysis

Figure 3.15 represents a TGA experiment which determines the temperature at which $Cu(NO_3)_2 \bullet 3H_2O$ will completely convert into CuO. Compressed air was used as sample gas. It can be seen from Figure 3.15 that at above 300°C, the weight percentage becomes constant which means all the copper salt is converted to copper oxide. The molecular weight calculation is consistent with the observed TGA data

Molecular Weight of $Cu(NO_3)_2 \cdot 3H_2O$ = 242 g/mole

Molecular Weight of CuO = 80 g/mole

Weight percentage is 100% when the experiment starts, and it keeps decreasing until the weight percentage becomes 31%. This corresponds to a 69% weight loses. From the molecular weight, one can calculate the weight loss as the following:

Weight loss (%) = (242-80)/242 = 67%

which is consistent with the experiment.

3.5 X-ray Diffraction Crystallography

To determine crystalline structure of synthesized 20% $CuO/\gamma\text{-}Al_2O_3$, the x-ray diffraction pattern of the synthesized 20% $CuO/\gamma\text{-}Al_2O_3$ is shown in Figure 3.16. From X-ray diffraction crystallography hand book, crystallized CuO has a peak at $2\theta = 34^\circ$. Figure 3.16 shows that at $2\theta = 34^\circ$, no peak is found. However, CuO on a synthesized catalyst is believed to exist as extremely small crystallites. In fact, most catalytic reactions are favored by either amorphous materials or extremely small crystallites. The purpose of the preparation technique is to disperse the catalytic components in such a way as to maximize their availability to reactants. When this is done effectively, only small crystals are present, and the diffraction of x-rays is minimized, because little long-range structure exists. As the crystals get smaller and smaller, the x-ray peaks get broader and broader and eventually are undetectable above the background.

CHAPTER 4

CONCLUSIONS

1. Oxygen enhances the NO+CO reaction over Cu-ZSM-5. The highest NO conversion to N_2 appears at 400°C. High CO concentration enhance this catalytic reaction. The higher [CO]/[NO] ratio, the higher NO conversion to N_2 is obtained. The reaction rate and NO conversion to N_2 decrease with increasing reaction space velocity. At 400°C, when [CO]/[NO] = 1, the maximum NO conversion to N_2 with 10% O_2 is 60%, 32%, and 18% at GHSV of 2,000, 20,000 and 40,000, respectively. In a similar manner, 88% and 50% NO conversion to N_2 are obtained when [CO]/[NO] is decreased from 2 to 0.5 at 400°C and GHSV of 2,000.
2. For the reduction of NO by GAC over Cu-ZSM-5 with 10% oxygen, the reaction rate and NO conversion to N_2 decrease with increasing space velocity. The highest NO conversion to N_2 occurs at 400°C which is the same as NO+CO+O_2 reaction. CO is the intermediate of C/NO reaction. At 400°C, the maximum NO conversion to N_2 is 66%, 38% and 18% at GHSV of 2,000, 20,000 and 40,000, respectively.
3. For the reduction of NO by Cu ion loaded carbon black with 10% oxygen. A significant amount of CO is produced by C/O_2 reaction with Cu ion presence even at relatively low temperature. At 600°C, 100% NO conversion to N_2 is obtained at GHSV of 2,000 and 20,000. At 450°C, 95% NO conversion to N_2 is

obtained at GHSV of 2,000. The reaction rate and NO conversion to N_2 decrease with increasing space velocity.

4. The presence of Cu ion on Al_2O_3 reduces the temperature of maximum NO conversion to N_2 for the reduction of NO by C_3H_8 about 100°C.

APPENDIX A

FIGURES OF EXPERIMENT RESULTS

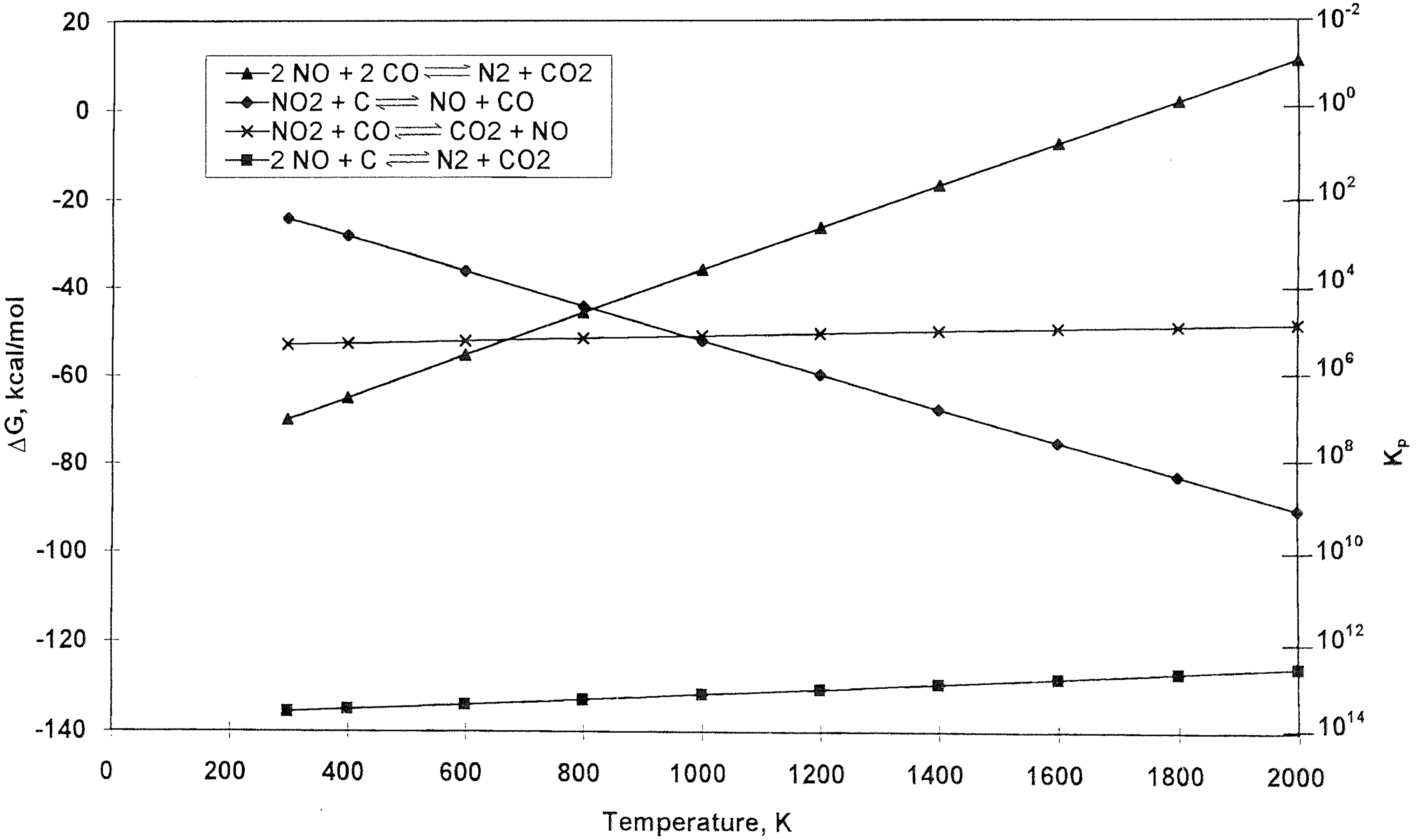

Figure 3.1 Ellingham Diagram

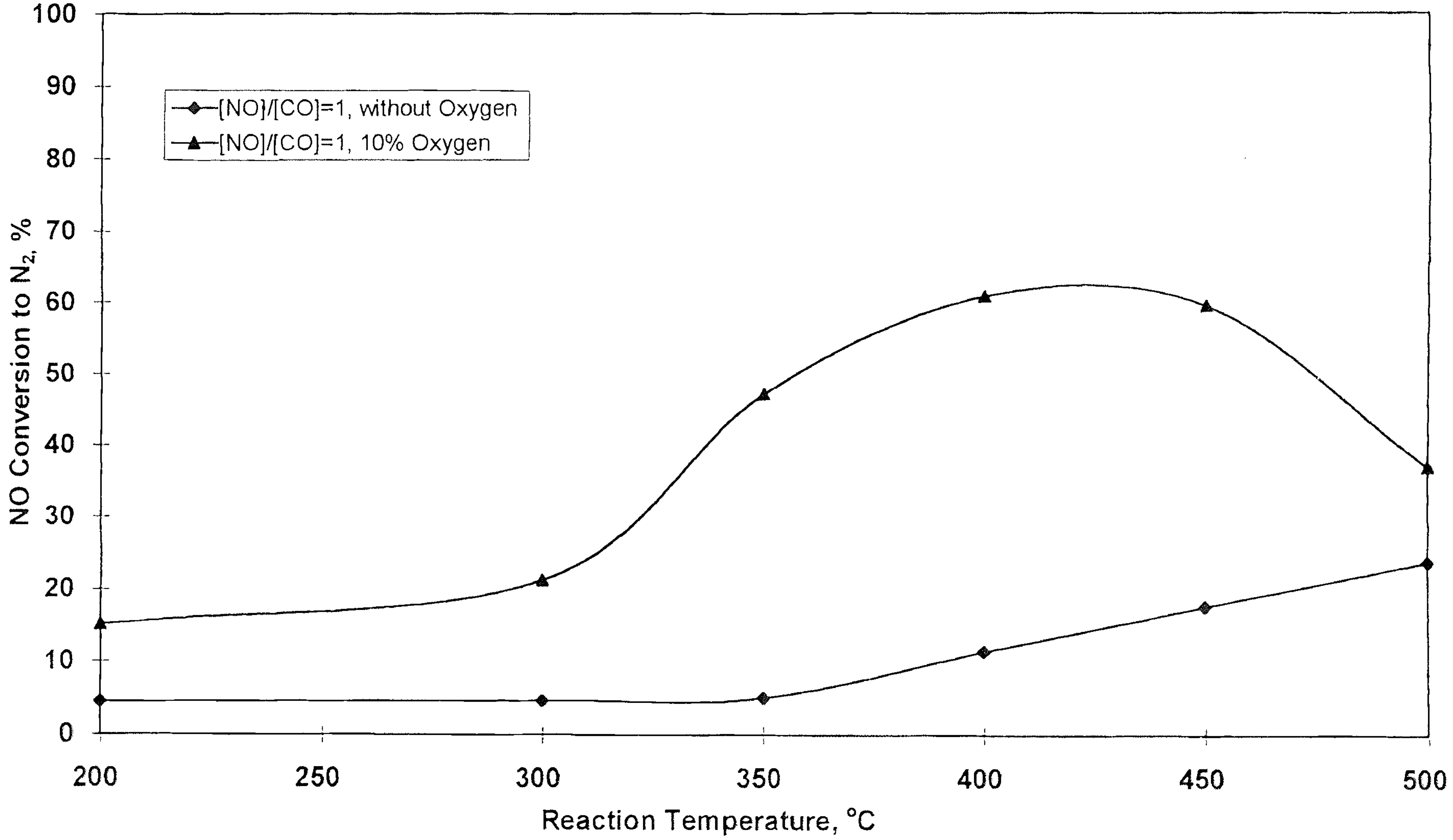

Figure 3.2 Reduction of NO by CO in the Presence and absence of O_2 over Cu-ZSM-5, GHSV=2,000, $[NO]_i$=$[CO]_i$=500 ppm

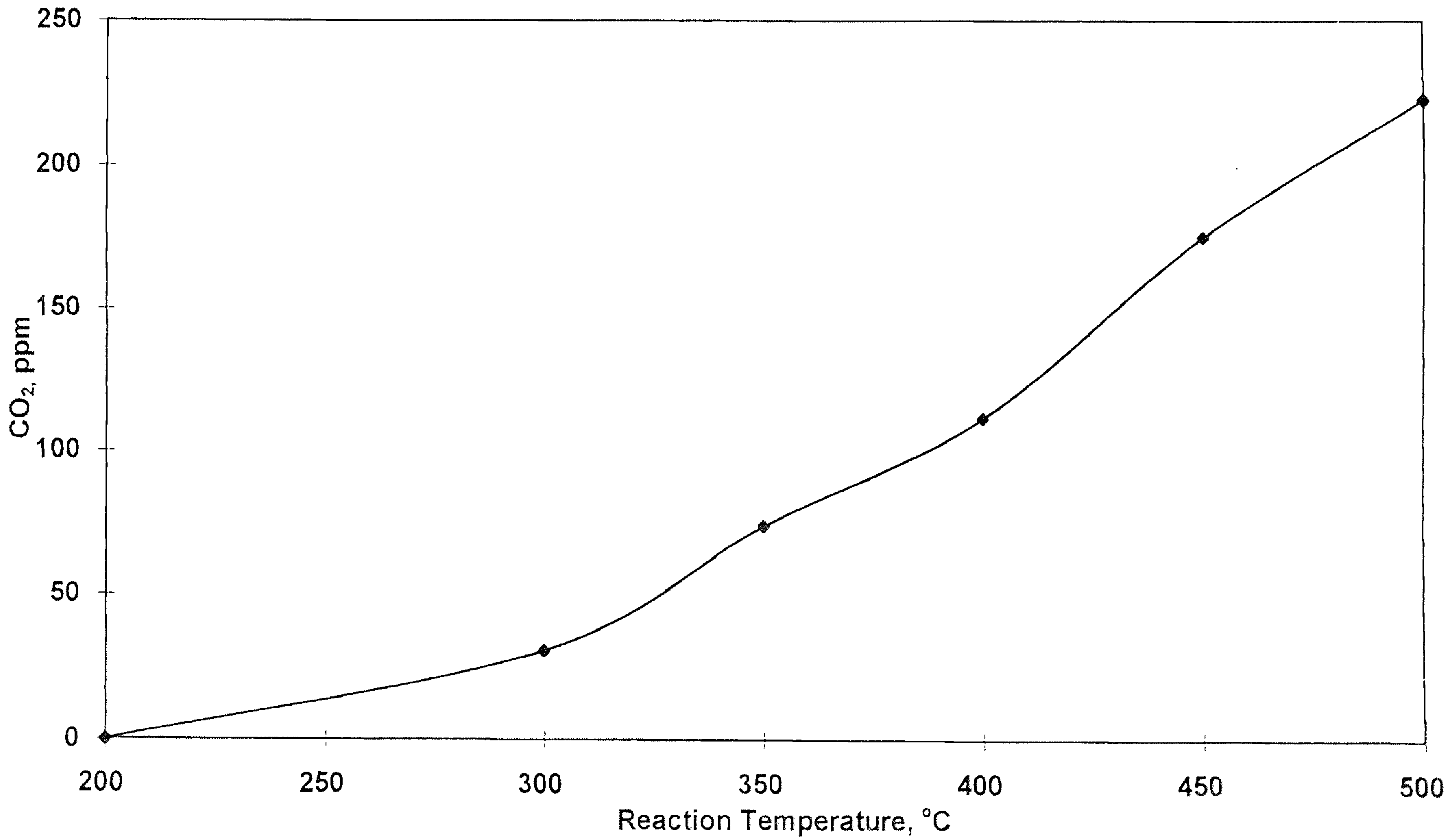

Figure 3.3 CO_2 Produced in the Reduction of NO by CO in the Absence of O_2, GHSV=2,000, over Cu-ZSM-5

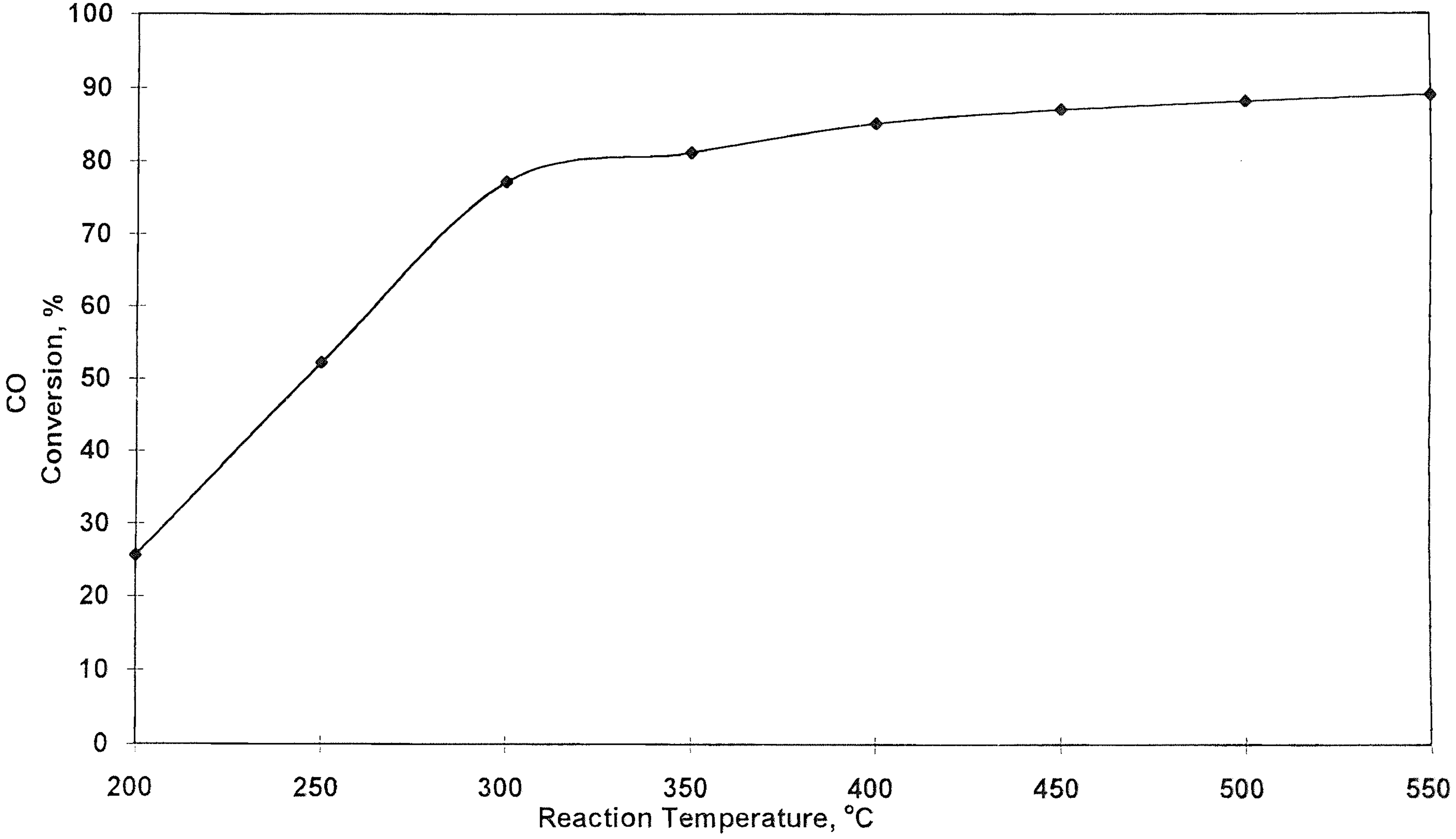

Figure 3.4 Oxidation of CO by O_2 over Cu-ZSM-5, GHSV=2,000

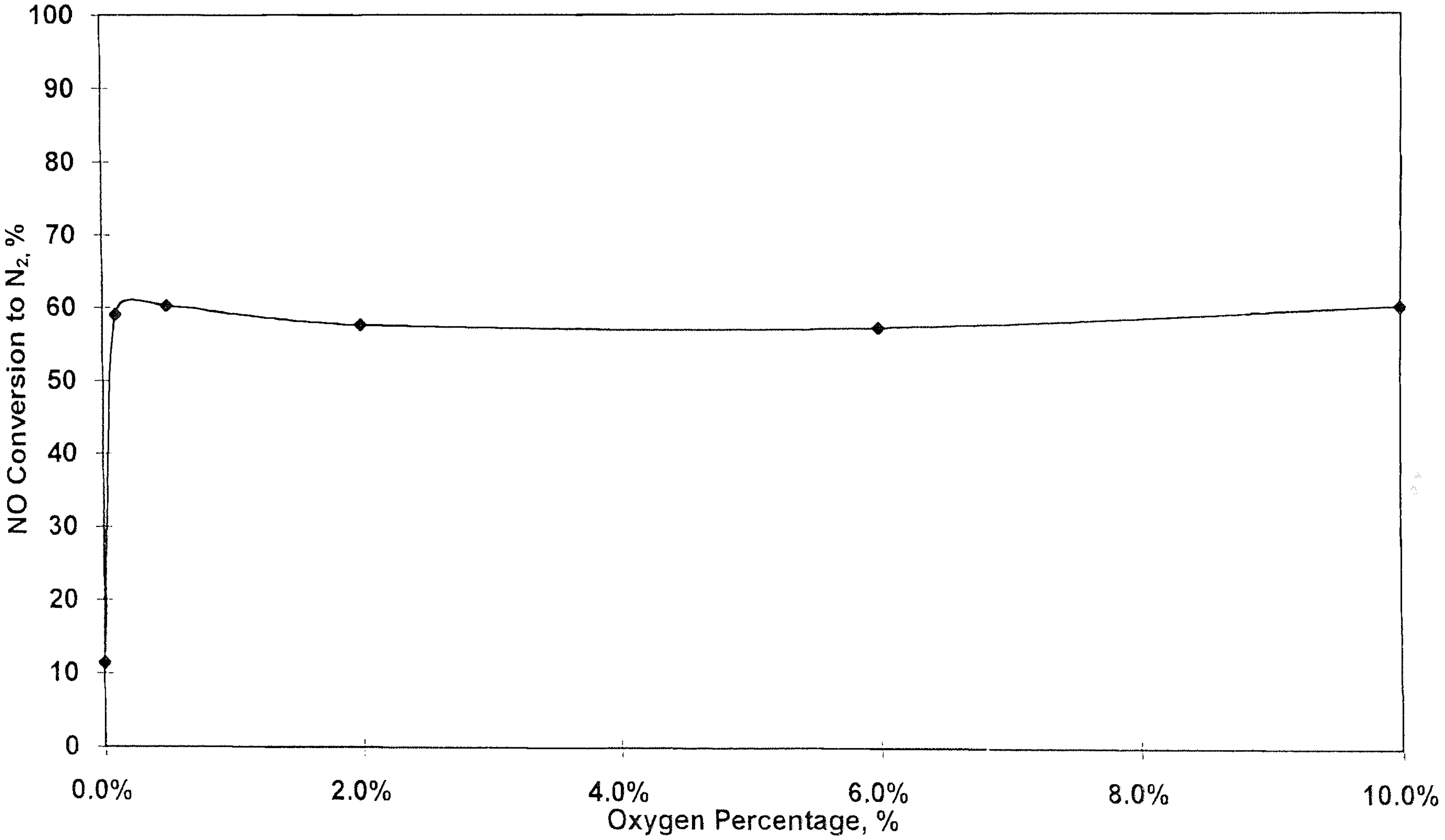

Figure 3.5 Effect of Oxygen Concentration on NO Reduction by CO over Cu-ZSM-5 at 400°C, $[NO]_i=[CO]_i=490$ ppm, GHSV=2,000

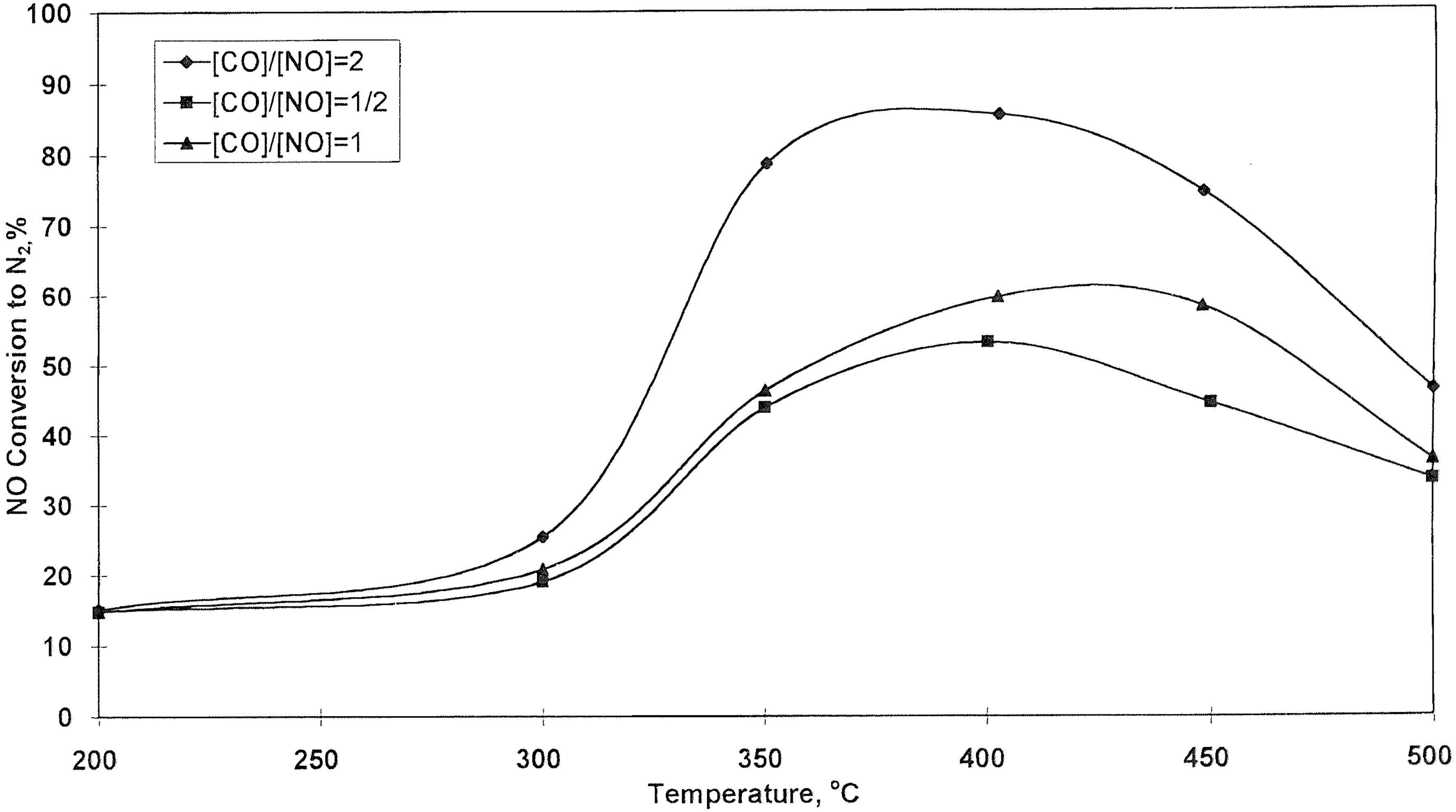

Figure 3.6 Effect of CO to NO Mole Ratio on NO Reduction over Cu-ZSM-5; GHSV=2,000, 10% O_2

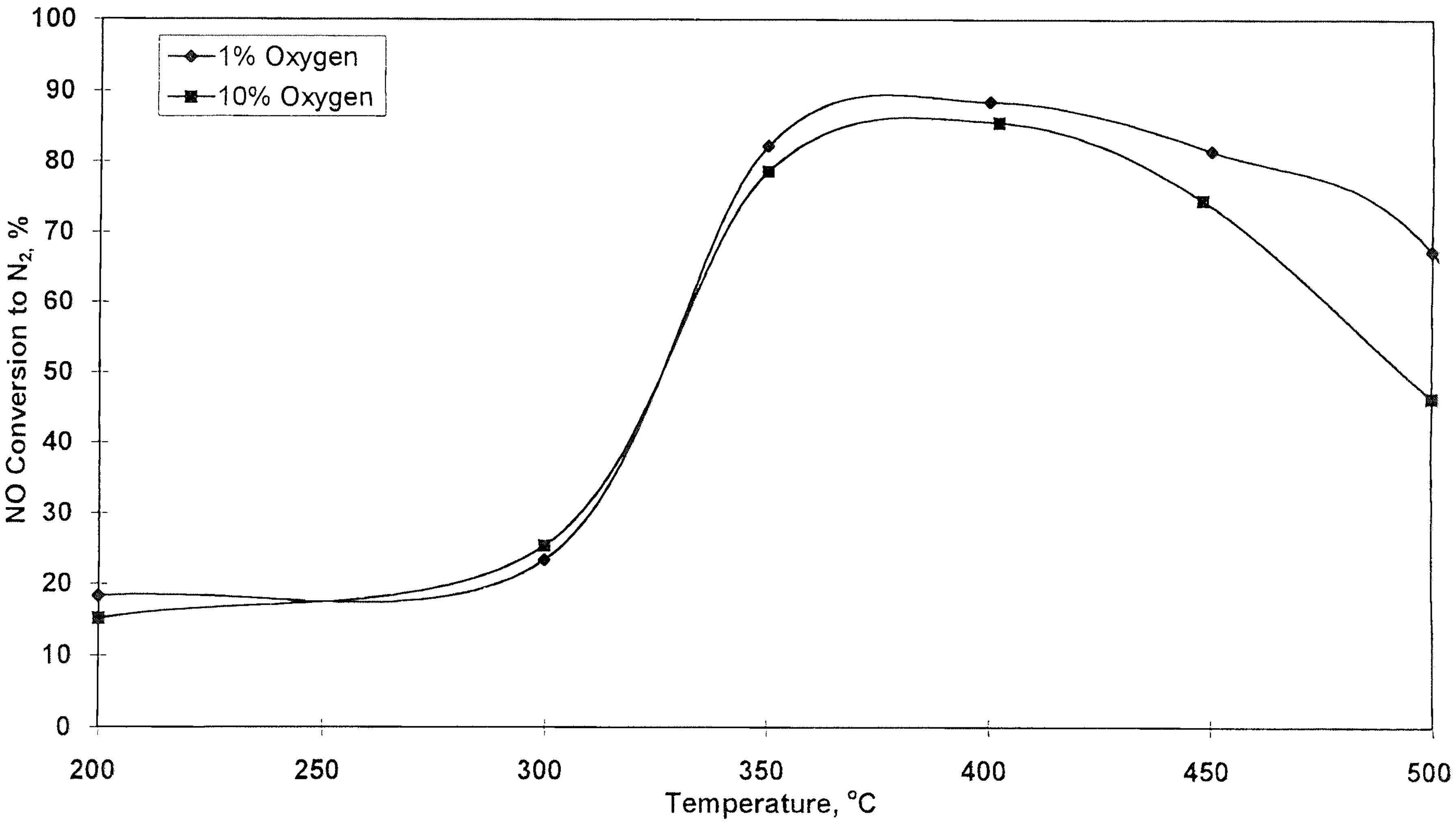

Figure 3.7 Effect of Oxygen Concentration on NO Reduction by CO over Cu-ZSM-5; GHSV=2,000, $[CO]_i=2[NO]_i$

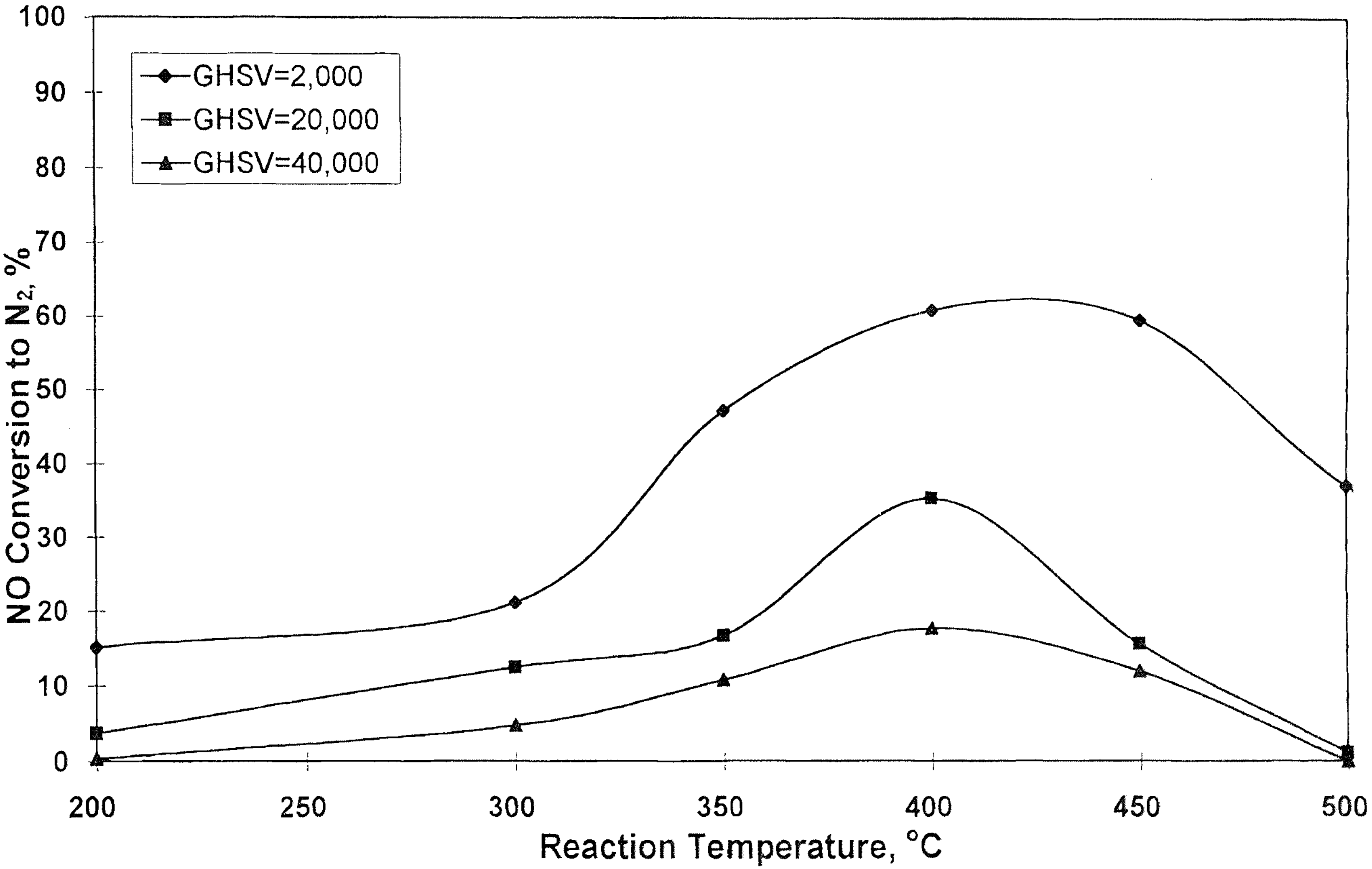

Figure 3.8 Effect of Space velocity on NO Reduction by CO over Cu-ZSM-5, $[NO]_i=[CO]_i=490$ ppm, 10% Oxygen

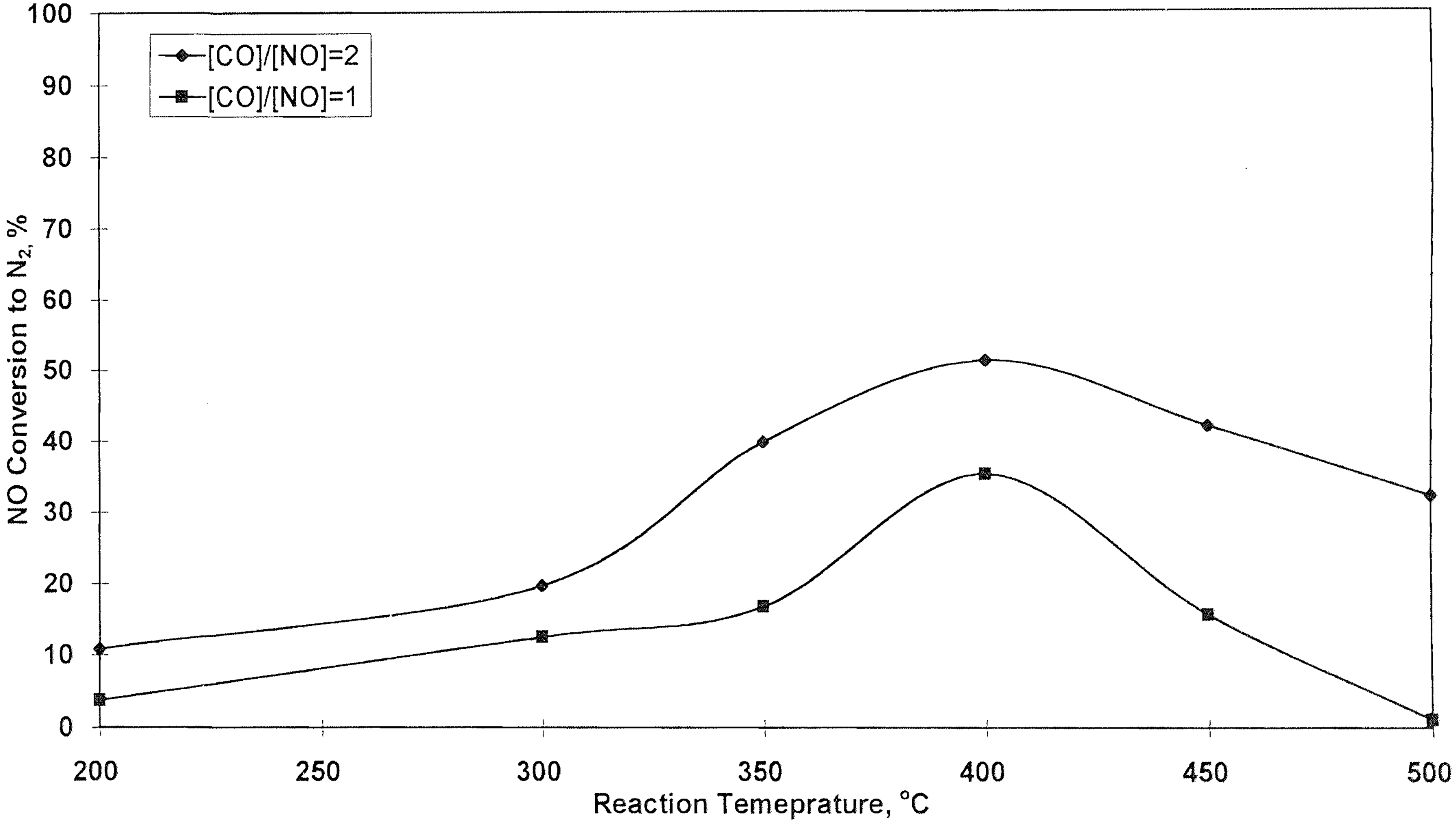

Figure 3.9 Effect of [CO]/[NO] Mole Ratio on NO Reduction by CO over Cu-ZSM-5, GHSV=20,000, 10% Oxygen

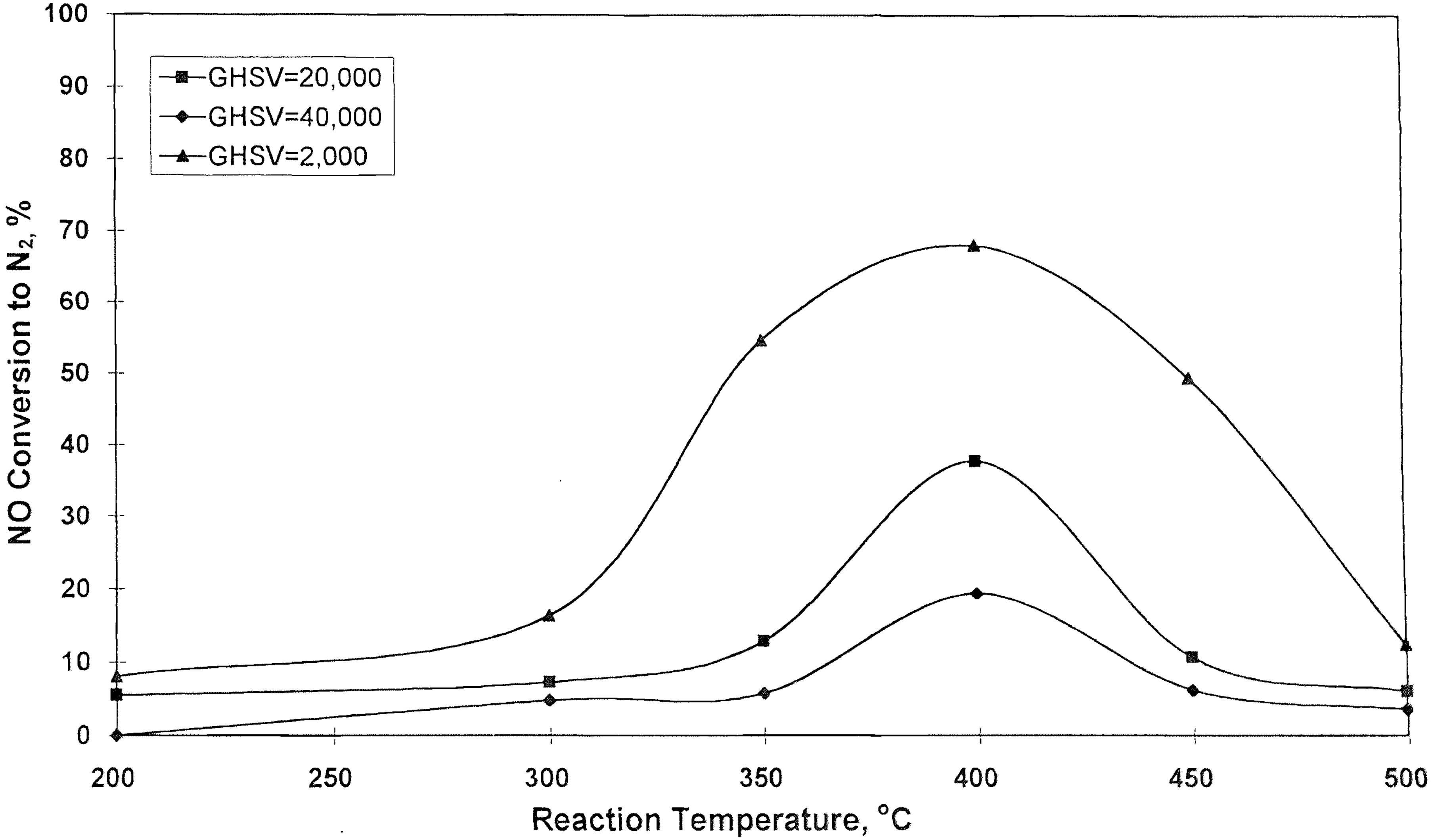

Figure 3.10 Effect of Space Velocity on Reduction of NO by Activated Carbon Present as 5% GAC over 95% Cu-ZSM-5, $[NO]_i$=590 ppm, 10% O_2

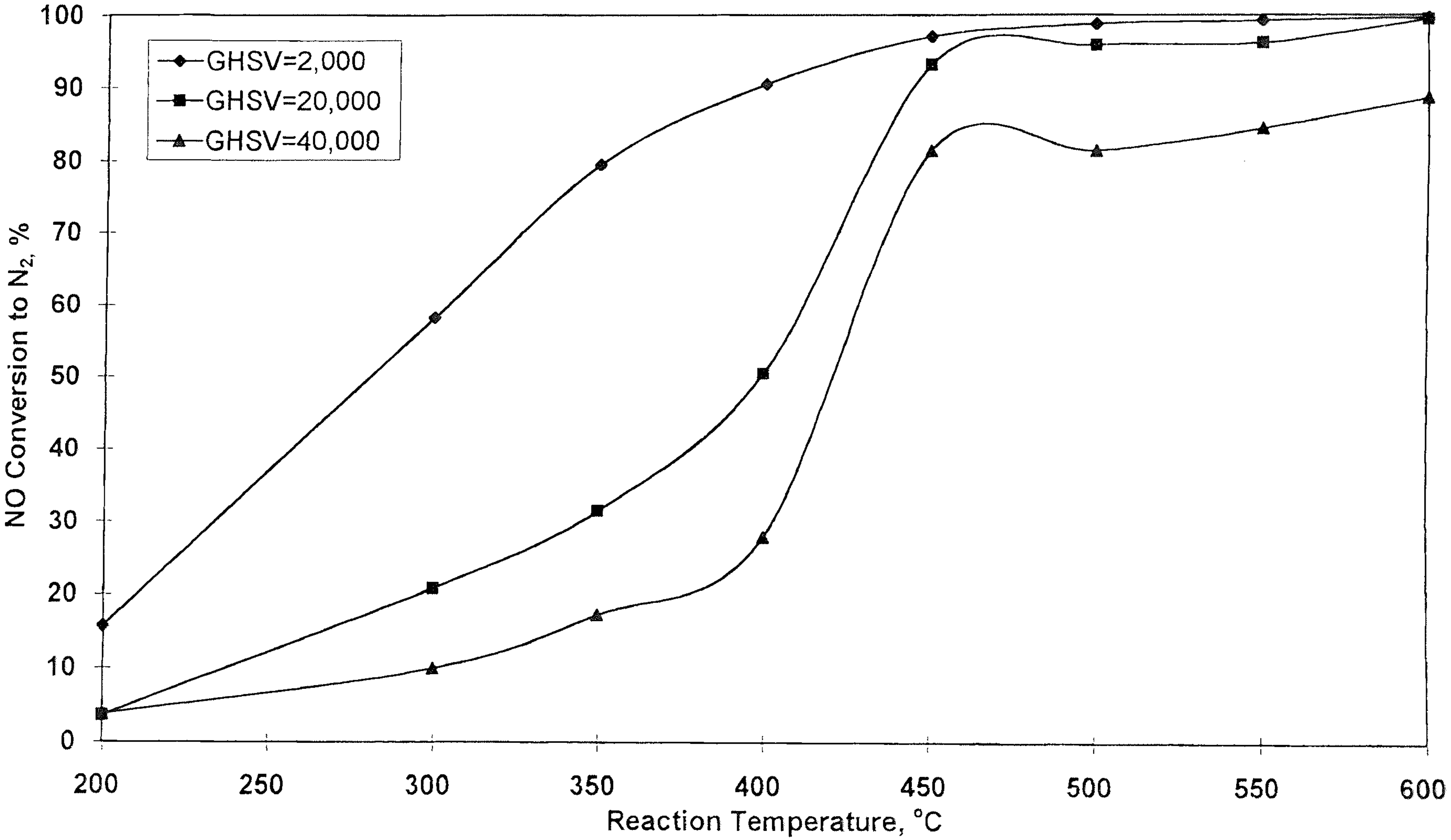

Figure 3.11 Effect of Space Velocity on the Reduction of NO by 20% Copper Loaded GAC, $[NO]_i$=590 ppm, 10% Oxygen

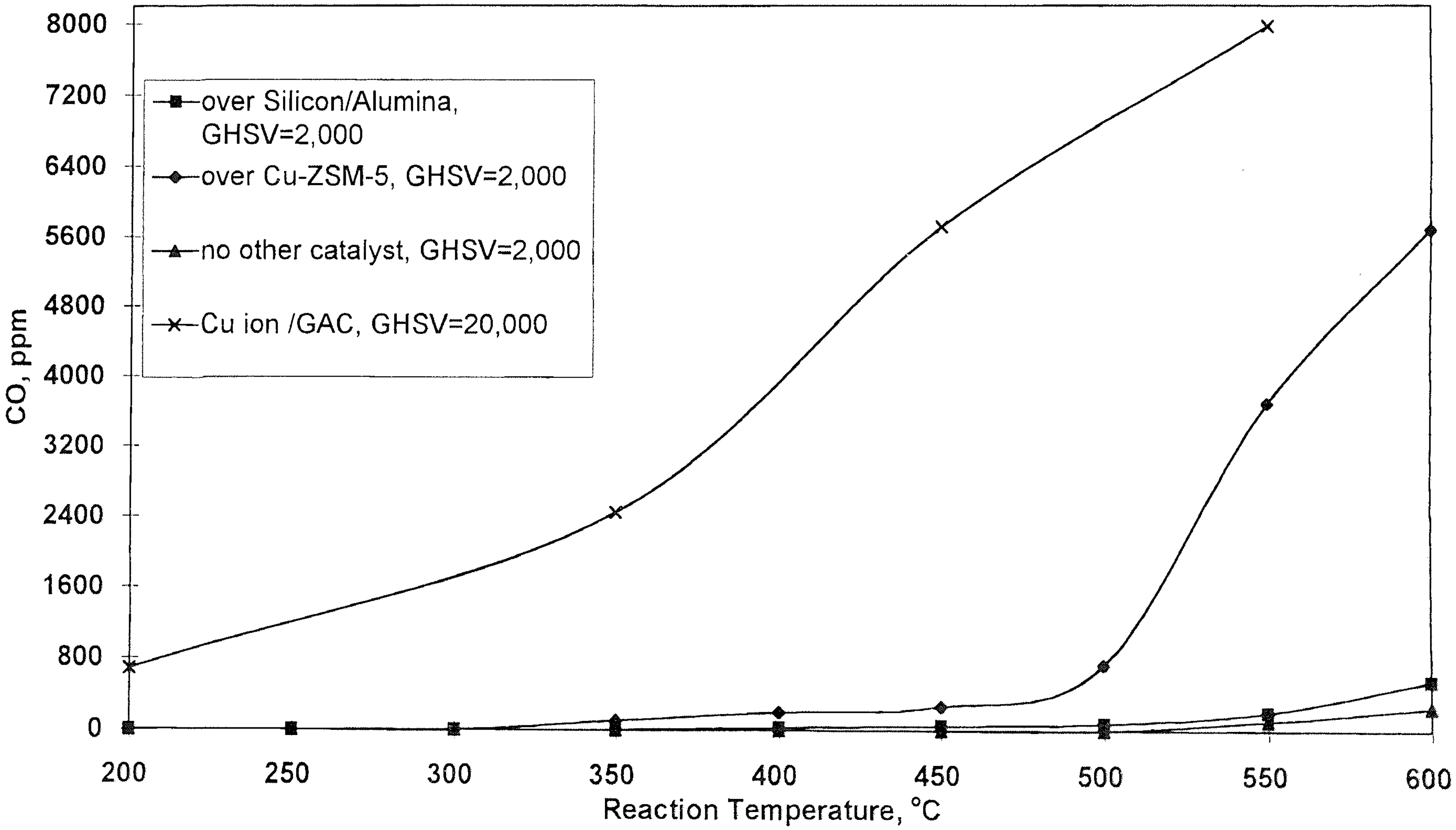

Figure 3.12 Reaction of GAC with 10% Oxygen over Different Catalysts

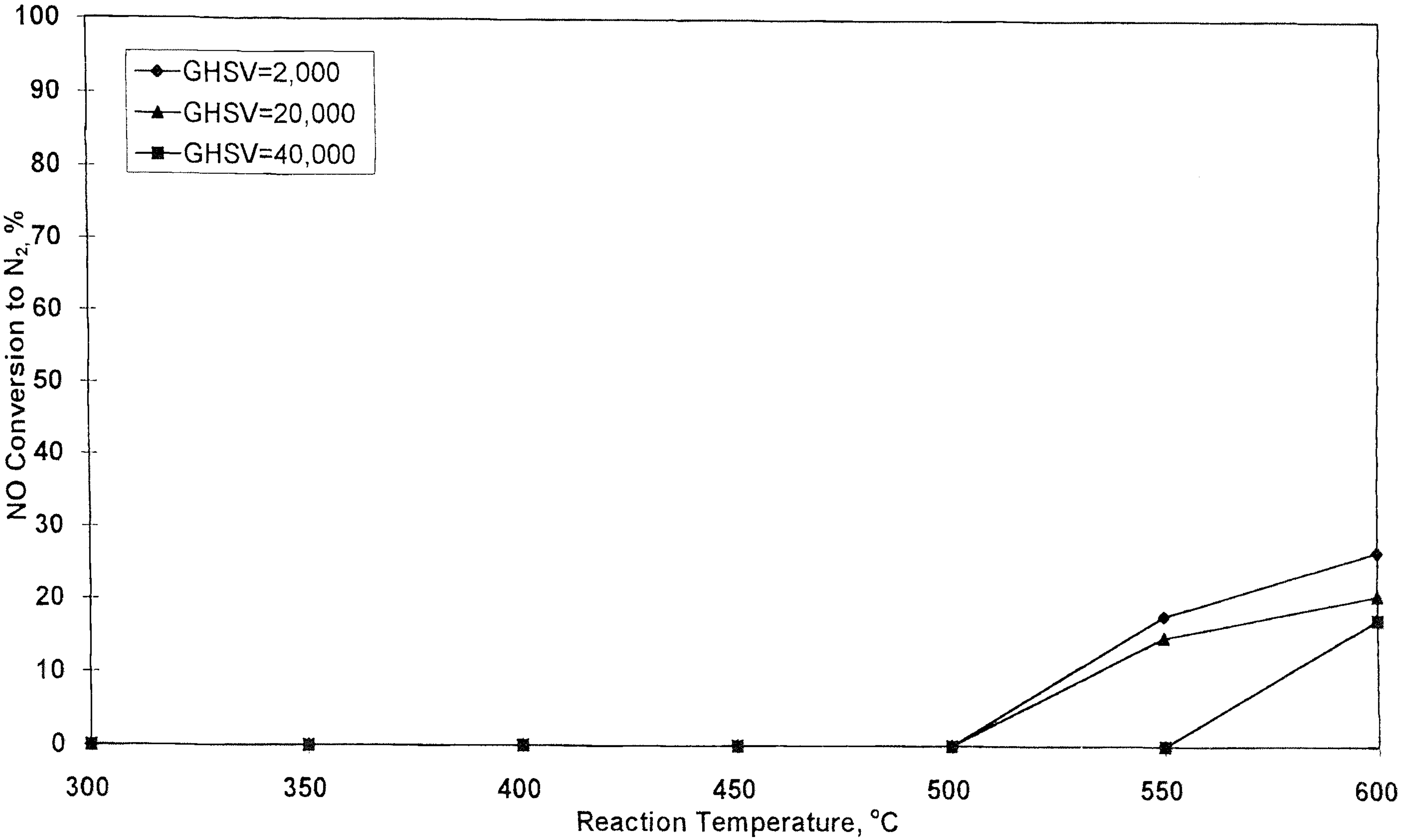

Figure 3.13 Effect of Space Velocity on Reduction of NO by GAC; $[NO]_i$=590 ppm, 10% Oxygen

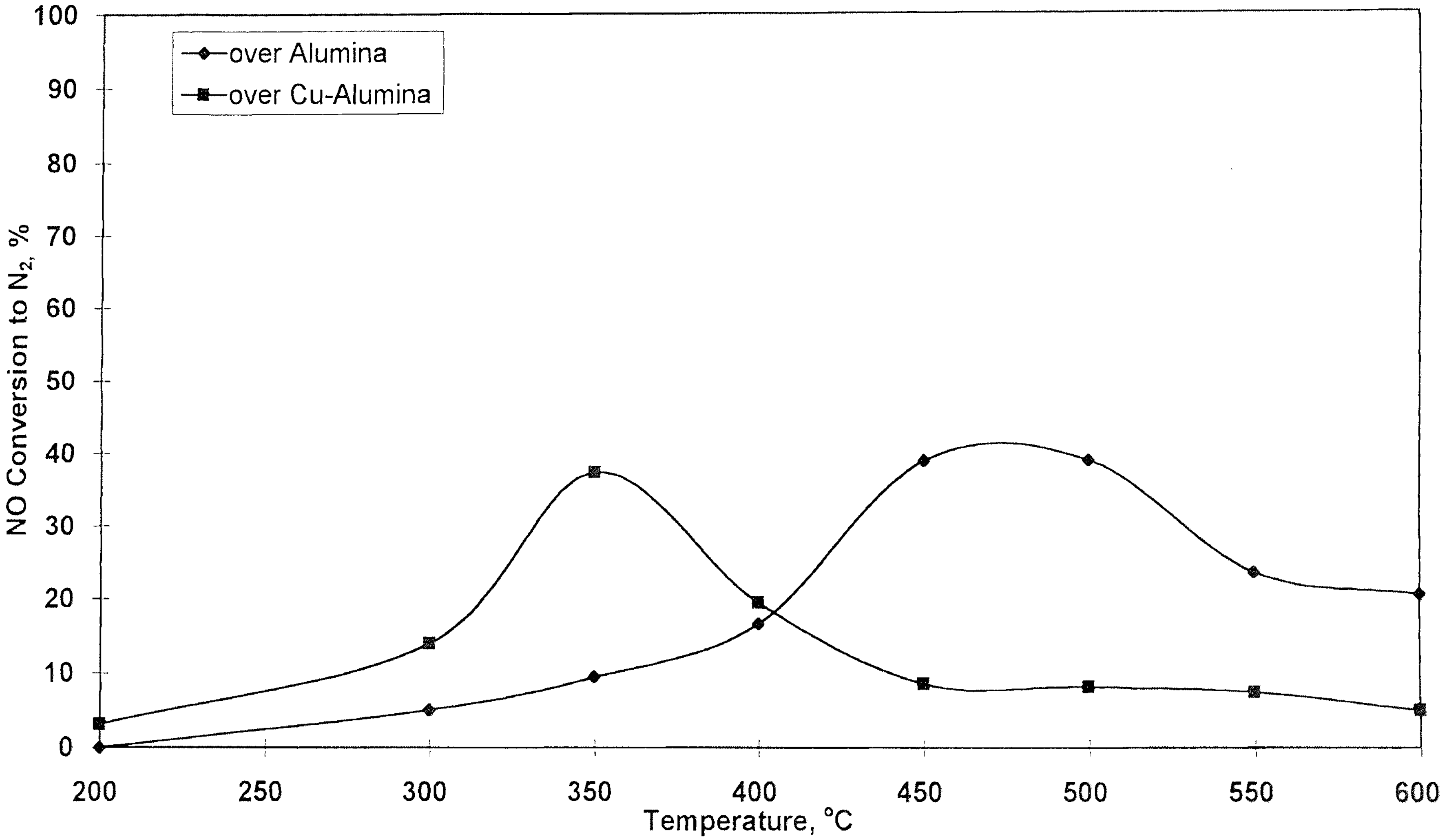

Figure 3.14 Effect of Cu ion on the Reduction of NO by C_3H_8 over Gamma-Alumina, $[NO]_i$=400ppm, $[C_3H_8]_i$=500ppm, O_2=10%, GHSV=2,000

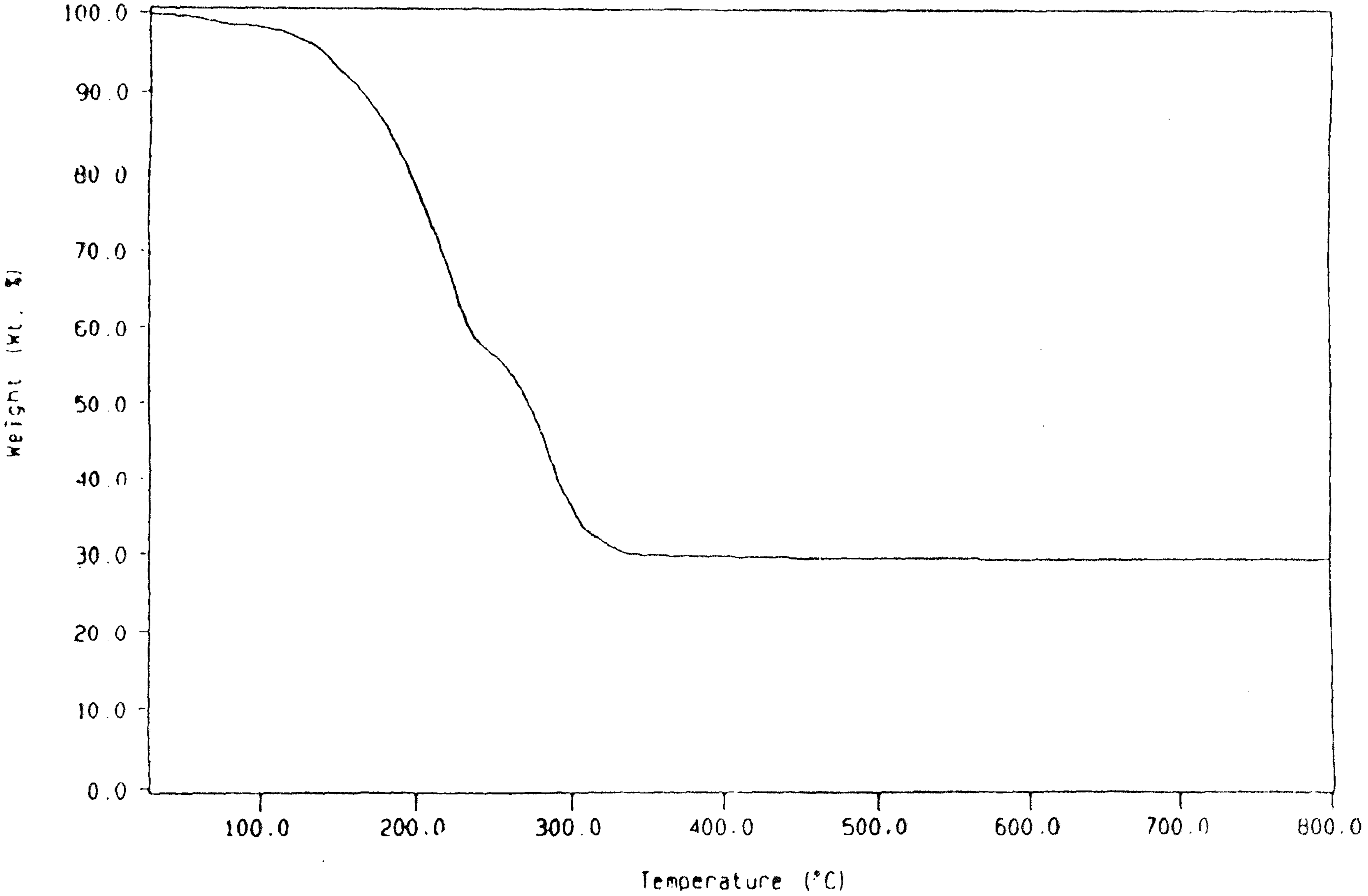

Figure 3.15 TGA for Decomposition of $Cu(NO_3)_2.3H_2O$ to CuO

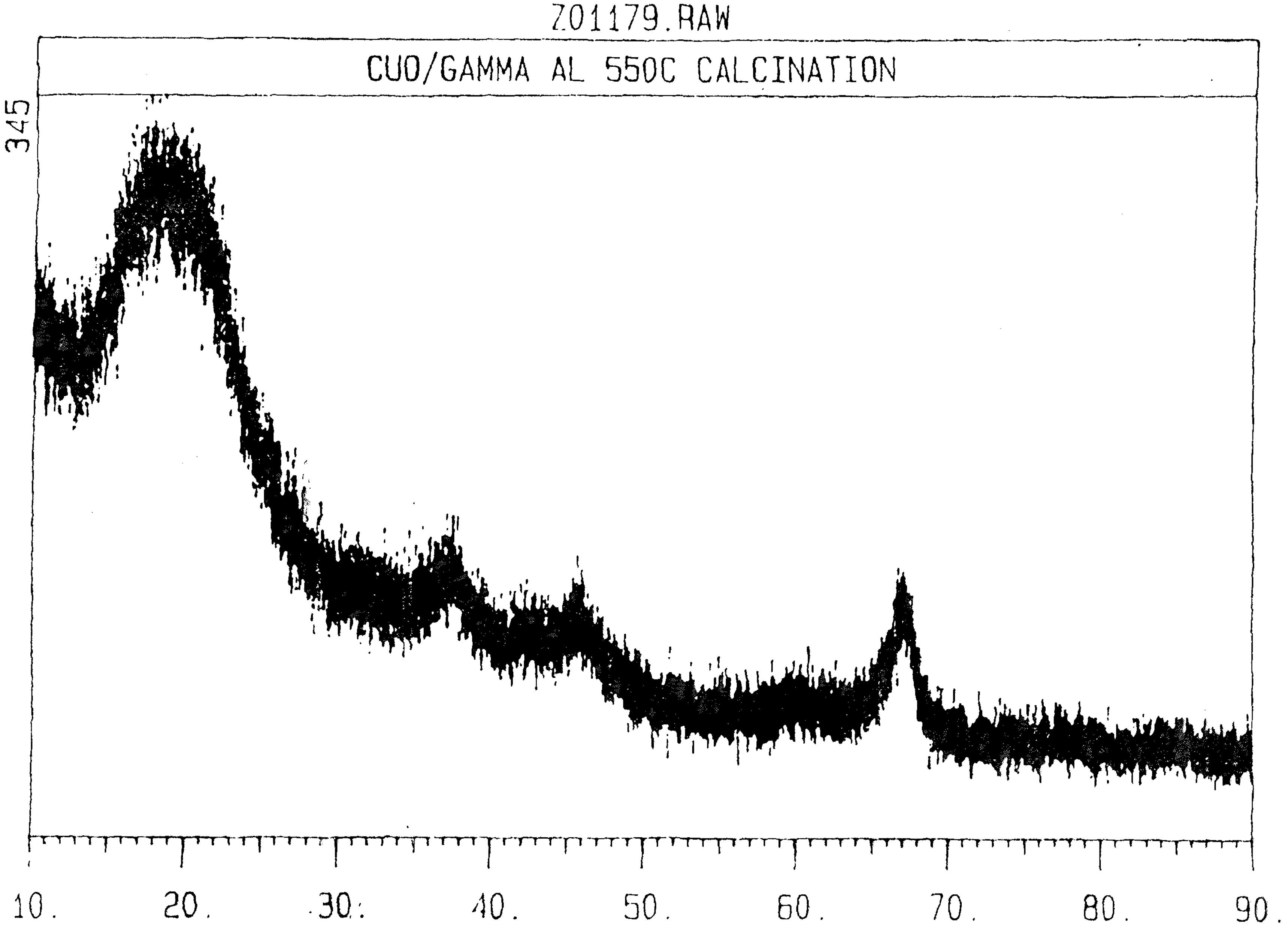

Figure 3.16 X-ray Diffraction Pattern of 20% Copper Loaded Alumina

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