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## **ABSTRACT**

### **CATALYTIC REDUCTION OF NITRIC OXIDE BY COPPER CATALYZED GRANULAR ACTIVATED CARBON IN THE PRESENCE OF OXYGEN**

**by  
Shan Xiao**

The catalytic reduction of nitric oxides by solid carbonaceous material consisting primarily of granular activated carbon or (GAC) was studied in a fixed bed catalytic reactor in order to develop the technology for removing NO<sub>x</sub> and soot simultaneously from diesel engine exhaust. The catalytic activity and conversion of NO as a function of reaction temperature was evaluated as a function of space velocity. The results show that at lean condition and high gaseous hourly space velocity, viz., 50,000 ~ 80,000, Cu-ZSM-5 does not perform as well with CO and GAC as it does with gaseous hydrocarbons(HC). Plain GAC has low activity for NO reduction at high temperature above 550°C under lean condition. However, copper-impregnated GAC has good activity for both NO reduction and carbon oxidation under lean conditions. Actually in presence of 1 to 10% oxygen, the activity and conversion of NO to N<sub>2</sub> due to reaction with carbon is enhanced at a lower light off temperature of 350°C. Over 60% conversion was obtained at gaseous hourly space velocity of 50,000 ~ 80,000. Almost 100% conversion was obtained when GHSV was lowered to 20,000. In order to get insight on the mechanism of this reaction, the reduction of NO with CO was studied over various catalysts at the same condition. It was determined that the results are consistent with CO being an intermediate for the reduction of NO with carbon. We also investigated the deactivation of these catalysts. The results

show that the presence of  $\text{SO}_2$  and water poison copper catalysts. For this reason, it is necessary to develop other catalysts for controlling both  $\text{NO}_x$  and soot. This research is part of a NSF project for developing a novel technique to remove  $\text{NO}_x$  and soot simultaneously from diesel engines.

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IN THE PRESENCE OF OXYGEN**

by  
**Shan Xiao**

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CATALYTIC REDUCTION OF NITRIC OXIDE BY  
COPPER CATALYZED GRANULAR ACTIVATED CARBON  
IN THE PRESENCE OF OXYGEN

Shan Xiao

Dr. Henry Shaw, Thesis Advisor  
Research Professor of Chemical Engineering, NJIT

5/6/99

Date

Dr. Robert Pfeffer, Committee Member  
Distinguished Professor of Chemical Engineering, NJIT

5/4/99

Date

Dr. James Grow, Committee Member  
Associate Professor of Chemistry, NJIT

5/6/99

Date

## BIOGRAPHICAL SKETCH

**Author:** Shan Xiao  
**Degree:** Master of Science  
**Date:** May 1999

### **Undergraduate and Graduate Education:**

- Master of Science in Applied Chemistry,  
New Jersey Institute of Technology, Newark, NJ, 1999
- Bachelor of Science in Chemistry,  
Sichuan University, Chengdu, Sichuan, P.R.China

**Major:** Applied Chemistry



This thesis is dedicated to my beloved parents

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## 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 hydrocarbon (HC), larger quantities of NO<sub>x</sub> 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<sub>x</sub> (primarily NO and NO<sub>2</sub>), unburned hydrocarbons (HC), CO, SO<sub>x</sub> (SO<sub>2</sub> + SO<sub>3</sub>), formaldehyde, polynuclear aromatics, etc. In urban areas, HC, CO and NO<sub>x</sub> 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<sub>x</sub> also contributes to health problems, like bronchitis, pneumonia, emphysema 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<sub>x</sub> ( Hightower, 1974). The Environmental Protection Agency (EPA) established a Federal Test Procedure (FTP) to allow measurement of CO, HC and NO<sub>x</sub> over a simulated average driving condition in the U.S. (EPA, 1971). Subsequent amendments to the Clean Air Act in 1976 and 1990 promulgate more stringent control requirements for automotive emissions. In recent years, significant progress was achieved in diesel emissions control through engine and fuel system design changes. This eventually made it possible to meet a particulate level of 0.25 G/BHP-HR for 1991 and next target level for particulate emissions is 0.05 G/BHP-HR for the 1998 diesel engine emissions (Hech and Farrauto, 1995). To meet the challenge, engine developers are not only considering engine and injection system design changes but also fuel improvements and exhaust after treatment.

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 from 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 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  $\text{NO}_x$  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.  $\text{NO}_x$  emissions increase due to the high flame temperature obtained from complete burning of fuel. At temperatures over  $1100^\circ\text{C}$  (McMann, et al., 1994), the atmospheric component nitrogen and oxygen react to form NO, which is the major component of  $\text{NO}_x$ . A small amount of additional results from the conversion of essentially all fuel-bound nitrogen compounds to  $\text{NO}_x$ .

In recent years, the emissions regulations and market acceptability have become strong motivates for controlling pollutants from the diesel engine. Advances in engine technology have made it possible for the diesel engine to meet very stringent emissions levels. Future standards have generated interest in other technologies such as exhaust aftertreatment, fuel composition and quality, as well as additional engine improvements. Faced with the  $\text{NO}_x$  - Particulate trade-off challenge, engine manufacturers made several design choices while being concerned with the increased production cost and competition. But exhaust aftertreatment techniques limiting particulate emissions from diesel engines remain the topic of intense interest and development activity. During the past several decades, a large R & D effort has been carried out to meet the provisions the Clear Air Act and its amendments. Two approach are being addressed for the emission regulations. One approach is particulate trap systems. The operating principle of the trap is simply based on the capture and periodic incineration (or regeneration) of the carbonaceous exhaust particulate. The regeneration is often achieved through the use of

heat provided by a variety of sources (fuel burners, electric heaters, engine intake throttling, etc). Regeneration is usually triggered after reaching a pre-established pressure drop measured across the trap, which is often made of a wall-flow honeycomb structure. Central to the development of the trap system is that the regeneration must function under all operating conditions with little or no negative impact on the engine performance. This premises adds to the complexity and cost of the trap. In addition to cost and complexity issues, some doubt remains about the reliability and durability of the trap systems.

Another method of diesel exhaust aftertreatment is that of the catalytic converter. Diesel catalysis is similar to the method used for gasoline engine emission control but differs in terms of the exhaust gas composition to be controlled and the lower exhaust temperature. Catalytic aftertreatment of diesel exhaust feasible with future use of low sulfur content diesel fuel. Using high sulfur fuel in conjunction with oxidation catalysts, leads to the formation of sulfate, thus increasing particulate mass emissions rather than decreasing them.

$\text{NO}_x$  is the other harmful pollutant.  $\text{NO}_x$  is a precursor to about 30% of acid rain and a major reactant in smog formation. Many methods to reduce  $\text{NO}_x$  have been developed. Some of the earliest  $\text{NO}_x$  control methods involved combustion modification approaches that included flue gas recirculation and staged combustion ( rich combustion followed by very lean burnout). 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 was reduced with the excess hydrocarbons over catalysts such as Pt and Pd. Another method involved staged

combustion in which little  $\text{NO}_x$  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  $\text{NO}_x$  was first discovered in 1957 in which  $\text{NH}_3$  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  $\text{NH}_3$ , a pollutant in its own right.

Direct decomposition of  $\text{NO}$  to  $\text{N}_2$  and  $\text{O}_2$ , though thermodynamically favorable, does not occur at low temperature in the absence of a catalyst. Iwamoto et al. found that Cu supported on ZSM-5 is a unique catalyst for this process; it is also quite active in  $\text{NO}_x$  reduction with hydrocarbons such as propane or propene in certain condition. Remarkably, this reduction is strongly enhanced by an excess of oxygen in the feed.

Transition metal exchanged zeolites were found to be very active for reducing  $\text{NO}_x$ . Among these, Cu-ZSM-5 though not necessarily the most promising, remains the most studied catalyst in this group. Zhang et al. (1994), with no reducing agent (soot) present, found a maximum  $\text{NO}$  conversion using Mg or Cu modified ZSM-5 of 80% in the absence of  $\text{O}_2$ , with a significant decrease in conversion in the presence of 5%  $\text{O}_2$ . Iwamoto et al (1989) and Held and co-workers (1990) discovered that Cu-exchanged ZSM-5 zeolites were the most active catalysts for this reaction.

Bartholomev, et al., (1992) reviewed selective catalytic reduction of  $\text{NO}$  with Hydrocarbons and presented data to show that propane reduces  $\text{NO}$  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<sub>2</sub> with nearly 100% selectivity and water poisons the catalyst at all temperatures. They also showed that the optimum reaction temperature was 350°C at 76000 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 55cm/s. They also found a significant decrease in conversion as the temperature of that gas is decrease 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<sub>x</sub>, the carbon in the soot and oxygen. An examination of the literature shows that NO<sub>x</sub> and

carbon do react in the presence of  $O_2$  and a catalyst at a temperature as low as  $400^\circ C$  (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  $500^\circ C$ , 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  $350^\circ C$  and  $700^\circ C$  by Lai, et al., (1998). Significant conversion of NO was observed above  $500^\circ C$ , with complete conversion at about  $700^\circ C$ .

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 remarkable promoted by the presence of oxygen at temperatures as low as  $300^\circ C$ . 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 remarkable enhanced by the presence of  $O_2$ . They investigated the formation of reactive surface intermediate (C(O)) and stable carbon-oxygen complexes (C-O) by the

combination of transient kinetics and temperatures programmed desorption techniques. They also found out that the concentration of reactive C(O) was increased by the presence of both O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>- containing reaction atmosphere.

M.J.Illan-Gomez et al., (1995) investigated the NO reduction activity of 10 different carbon and activated carbon, covering a wide range of surface areas and pore size distributions, they found that under the experimental conditions used in the current work, all the available surface area of the carbons seems to be effective for the reaction and accessibility problems due to diffusional limitations are not important. They also investigated some first series transition metals (Cr, Fe, Co, Ni, and Cu) as catalysts of the

NO reduction by carbon. They found that, at low temperatures, iron, cobalt, and nickel are the most effective, as they are metals able to chemisorb NO dissociatively; at high temperatures the activity is larger for cobalt and copper, metals whose oxides are reduced by carbon at a lower temperature.

D.Panayotov, et al., (1996) reported the interaction between NO, CO, and O<sub>2</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported copper-manganese oxides. They investigated the activity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> – supported Cu<sub>x</sub>Mn<sub>3-x</sub>O<sub>4</sub> catalysts towards the reduction of NO with CO at temperature in the range of 150-500°C. They found that the most active catalyst was Cu<sub>1.01</sub>Mn<sub>1.99</sub>O<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, i.e., the sample where CuMn<sub>2</sub>O<sub>4</sub> 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, et al., L.Dimitrov, M.Khristova, L.Petrov and D.Mehandjiev (1995) also reported that Cu-CoAPSO (where APSO refers to a structure containing Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>) 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<sub>2</sub>O and N<sub>2</sub>. He observed a competition between the CO+NO and CO+O (surface) interactions at a definite temperature, under the conditions of a NO+NO<sub>2</sub>+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<sub>2</sub>O+Ar gas mixture. They pointed out that the difference in catalytic behavior of the catalyst 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  $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$  spinel, where  $x=0.3, 0.54, 0.94$ . At temperature range up to the “light-off” temperature, where degrees of surface reduction below 50% of a monolayer of oxygen were realized, the formation of  $\text{N}_2\text{O}$  is an important intermediate step for the NO+CO reaction. At higher temperatures, the degree of surface reduction up to several monolayers was attained and a route for direct NO reduction to  $\text{N}_2$  became important. On oxidized surfaces, large amounts of NO were absorbed which, were inactive towards reduction. Under oxidizing conditions the NO+O<sub>2</sub>+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<sub>x</sub> reaction by requiring an intermediate, possibly CO, produced from the soot to react with NO on the catalyst. This hypothesis help 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 an intermediate on the reduction of NO reaction. This research is part of the overall project “Simultaneous Removal of Soot and NO<sub>x</sub> from Diesel Exhaust using a Rotating Fluidized Bed Reactor”.



## **CHAPTER 2**

### **EXPERIMENTAL**

#### **2.1 Experimental Apparatus**

The schematic flow diagram is shown in Figure 2.1. The major components of the system include a quartz tube reactor containing known volumes of catalyst, carbon black or mixtures of both. The flow rates of gases were measured by several calibrated rotameters. The reactor system was used for comparing the activities of commercial available catalysts synthesized on this project, these catalysts are used for determining product distributions and kinetics. The tubes containing the gas feed stream are mixed before being fed into the reactor and the effluent stream split into two parts. The first part goes to the gas chromatograph (GC) with a thermal conductive detector (TCD) to measure nitrogen produced using helium as the carrier gas. The second stream goes to a GC with a FID detector to measure CO and CO<sub>2</sub>. The GC with FID detector uses a nickel methanation catalyst to convert CO and CO<sub>2</sub> to methane which is then separated in a Poropak Q column, and measured as two distinct methane peaks by the FID detector.

#### **2.2 Equipment and Instrumentation**

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

##### **2.2.1 Reactor**

Experimental runs were performed by placing a measured quantity of powdered catalyst on a coarse quartz fritted disk in a quartz tubular reactor. The reactor consists of a 2.5 cm

diameter by 55 cm 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 is used to preheat the gases entering the central section that contains the powdered solids and the upper prevent condensation of the effluents. The middle zone has very uniform temperature profile that is good to  $\pm 1^\circ\text{C}$ . The granular bed materials such as catalyst and GAC are paced on a 90-150  $\mu\text{m}$  coarse porous quartz disk located at about two-thirds of the height of the reactor. The reactant gases enter the reactor from top and are discharged from the bottom in order to prevent fines carry over. The actual temperature of the bed is monitored with a chromel-alumel thermocouple which is inserted in the top of the reactor and placed in the center line touching 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 TCD and FID. The TCD is used to measure the concentration of  $\text{N}_2$  produced after separation over an 1/8 inch in diameter by 30 feet long stainless steel column packed with 100/120 mesh HayeSep DB. The column was put into a ice bath in order to effectively separate the relatively small  $\text{N}_2$  peak from the major  $\text{O}_2$  peak using helium as the carrier gas. A relatively large  $2.0\text{ cm}^3$  loop was used in the 6-port gas sampling valve in order to inject a large sample and improve the analysis of  $\text{N}_2$ .

$\text{CO}$  and  $\text{CO}_2$  were separated over 80/100 mesh Poropak Q column and hydrogenated over a nickel hydrogenation catalyst to convert  $\text{CO}$  and  $\text{CO}_2$  to methane and measuring the separate methane peaks with a FID.

The integration of the chromatographic peaks was performed with two HP 3396A integrators. Several standard gases containing known concentrations of CO, CO<sub>2</sub> and N<sub>2</sub> in helium were used to calibrate the GC.

The operation conditions of the dual column HP5860 GC are listed in Table 2.1

**Table 2.1** Operation Conditions of HP 5860A

Detector	TCD, HP 5860	FID, HP 5860
Detector Temperature, °C	140	300
Injection Temperature, °C	70	350
Column Temperature, °C	0	45
Carrier Gas	Helium	Helium
Loop Volume, cm <sup>3</sup>	2	0.02
Packing Materials Mesh	100/120HaySep DR	80/100 Porapak Q
Integrator	HP 3396A	HP3396A
TCD carrier Gas Flow rate, cm <sup>3</sup> /min	30	30
TCD Reference Gas Flow rate, cm <sup>3</sup> /min	50	-
Air Flow rate of FID, cm <sup>3</sup> /min	-	400
H <sub>2</sub> Flow rate of FID, cm <sup>3</sup> /min	-	20

### 2.2.3 Thermogravimetric Analysis (TGA)

TGA experiment was performed to determine the feasibility of direct denitration of Cu(NO<sub>3</sub>)<sub>2</sub> 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 computer control, 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 is used as a purge gas flowed to prevent any decomposition products or reactive gas product from entering into the balance chamber. The experimental parameter used to operate the TGA 7 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 Chemicals and Gases used

Gases: Supplied by Matheson Gas Products

NO: 1237 ppm in Helium

CO: 1010 ppm in Helium

C<sub>3</sub>H<sub>8</sub>: 1207 ppm in Helium

O<sub>2</sub>: 99.995%

He: 99.995%

Cu-ZSM-5: Appeared as solid light yellow powder, the catalyst consists of a mixture of 50% 70 to 80 micron Cu-ZSM-5 and 50% 70 to 80 micron SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and is used as a cracking catalyst. The ZSM-5 has been modified by ion exchanging the H<sup>+</sup> with Cu<sup>2+</sup>. The Cu<sup>2+</sup> exchange level is 100% in the ZSM-5, supplied by Mobil Technology Company.

Gamma Alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>): Was in the form of a solid white powder, supplied by the Alcoa Technical Center. Particle size 70 to 80 micron.

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

Cu-GAC: made in our lab.

Cu-Al<sub>2</sub>O<sub>3</sub>: made in our lab.

## 2.3 Experimental Procedure

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

### 2.3.1 Catalyst Testing

All experiments were performed in the quartz fixed bed reactor. The catalyst, or catalyst a mixed with 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<sup>3</sup>/min) in order to remove impurities such as oxygen and water which may have adsorbed on the solid materials. The experiment is started by switching the desired 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 desired mixture gaseous 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 GHSV, the less the residence time of the reaction. The two GHSV used in this research were 50,000 and 80,000.

### 2.3.2 Preparation of CuO on GAC and Gamma Alumina

Incipient wetness impregnation method described by 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 the desired 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,  $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , was used as the metal salt. The solubility of cupric nitrate is about 137 grams of salt per  $100\text{cm}^3$  cold water. The support particles were pretreated by heating to remove all pore moisture and other adsorbed gases. The required volume of metal ion solution is determined by measuring the volume of deionized water that is 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, i.e., no more water is adsorbed. The measure volume of deionized water per unit mass of support material is used as the value of the water pore volume for the synthesis of catalyst by the incipient wetness impregnation method due to 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  $100^\circ\text{C}$  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 TGA experiments. A weight-percentage loss versus temperature plot was obtained that showed the temperature at which  $\text{Cu}(\text{NO}_3)_2$  started to decompose to  $\text{CuO}$ . Since  $\text{Cu}(\text{NO}_3)_2$  started to decompose at about  $350^\circ\text{C}$ ,  $450^\circ\text{C}$  was chosen as the calcination temperature to make sure that all  $\text{Cu}(\text{NO}_3)_2$  would be decomposed to the oxide. Gamma alumina support 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  $\text{N}_2$  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 catalysts obtained commercially and synthesized on this project for NO reduction to N<sub>2</sub> 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 gaseous components of diesel exhaust. For a 1.8 dm<sup>3</sup> 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. Apart from noble metal (Pt, Rh, Pd, etc.), which are very active for the simultaneous NO reduction and CO oxidation, copper and iron based catalysts have been widely studied as less expensive alternatives to accomplish these tasks. Some reference have reported that the reduction of NO with CO occur under oxidative conditions over metal loaded catalysts at temperatures on the order of 400°C.

From Figure 3.1 (Ellingham Diagram), it can be seen that the reaction  $\text{NO}_2 + \text{C} \rightarrow \text{NO} + \text{CO}$  is thermodynamically favored. Free energy  $\Delta G$  becomes more and more negative, while the equilibrium constant  $K_p$  estimated by drawing straight lines between  $\Delta G = 0$  and increases with increasing reaction temperature.  $\Delta G$  is about  $-39$  kcal/mol at 400°C. The reaction  $\text{NO} + 1/2\text{C} \rightarrow 1/2\text{N}_2 + 1/2\text{CO}_2$  is the most thermodynamically favored compared to the other three reaction in Figure 3.1.  $\Delta G$  is about  $-66.5$  kcal/mol at 400°C. The value of  $\Delta G$  increases slightly with increasing temperatures. For The reaction



$\text{NO}_2 + \text{CO} \rightarrow \text{CO}_2 + \text{NO}$ , has a  $\Delta G$  of  $-50$  kcal/mol which is independent temperature. Thermodynamically, it is not as favored as the  $\text{NO} + \text{C}$  reaction. From this Ellingham diagram, it can be seen that the reaction  $2\text{NO} + 2\text{CO} \rightarrow \text{CO}_2 + \text{N}_2$  is not thermodynamically favored. The value of  $\Delta G$  is negative, but increases with increasing temperature and the slope is very large (slope is equal to the change in entropy). But, within the temperature range of interest,  $200\text{-}600^\circ\text{C}$ , the  $\Delta G$  value varies from  $-62$  to  $-42$  kcal/mol. This indicates that  $\text{NO}$  can react with  $\text{CO}$  spontaneously in this temperature range. Thus, this thermodynamic analysis clearly indicates that reactions being studied in this project are favored.

It was determined experimentally that, the presence of oxygen enhances the reaction  $\text{NO}$  with  $\text{CO}$ , producing higher yields of  $\text{N}_2$ . Figure 3.2 shows how the effluent  $\text{CO}_2$  concentration varies with temperature for the  $\text{NO} - \text{CO}$  reaction in the absence of oxygen over  $\text{Cu-ZSM5}$ . The gas outlet sample was monitored through the 6-port gas sampling valve on the GC using TCD for  $\text{N}_2$  and FID for methane produced by quantitatively hydrogenating  $\text{CO}$  and  $\text{CO}_2$ . Figure 3.2 shows that within the reaction temperature range of  $200$  to  $500^\circ\text{C}$ , the  $\text{CO}_2$  concentration increases monotonically with temperature. This result match the result in figure 3.3 which shows that the  $\text{NO}$  conversion to  $\text{N}_2$  increasing with increasing reaction temperature within the temperature range of  $200\text{-}500^\circ\text{C}$ . In this reaction,  $\text{NO}$  is the only oxidant that can oxidize  $\text{CO}$  to  $\text{CO}_2$ , and  $\text{CO}$  is the only reductant that can reduce  $\text{NO}$  to  $\text{N}_2$ . The reaction can be represented as  $2\text{NO} + 2\text{CO} \rightarrow \text{N}_2 + 2\text{CO}_2$

When  $10\%$  oxygen is present in the reaction mixture, Figure 3.3 shows that reduction  $\text{NO}$  with  $\text{CO}$  over  $\text{Cu-ZSM5}$  has a temperature window. The reaction has a

maximum conversion rate around 400°C , after that temperature , the conversion rate declines, at the same time we observe that there is condensed water drop at the bottom of the reactor. We assume that the reason why conversion rate decline is due to excessive oxidation of the carbon monoxide, which is thought to take place on the surface of the catalyst spheres while the formation of nitrogen occurs as a function of CO dispersion which occurs mostly inside the pores. Also, the structure of Cu-ZSM5 begins to change at that temperature.

The results presented in figure 3.4 help explain this phenomena. Figure 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-ZSM5. After 300°C, CO conversion increases slowly from 80% to 85% at 550°C. This indicates that at high temperature, there is a competition for CO between O<sub>2</sub> and NO. It appears that most of the CO is converted to be CO<sub>2</sub> that causes NO reduction to N<sub>2</sub> to decrease due to a lack of CO.

### **3.1.1 Effect of Space Velocity**

Space velocity was investigated by changing the total gas flow rate constant while keep the volume of catalyst power used constant.

Figure 3.5 compares the effect of gaseous hourly space velocity (GHSV) for the CO/NO/O<sub>2</sub> system over Cu-ZSM5. The three curves represents the conversion rate of NO to N<sub>2</sub> with temperature increasing at 2,000, 50,000, 80,000 /hr space velocity. Conversion rate of NO to N<sub>2</sub> decreases as a function of space velocity from 70% at 2,000/hr, to 15% at 50,000/hr and 10% at 80,000/hr. The results show that space velocity

inverse of resident time has an important effect on the reduction of NO. The conversion rates of NO to N<sub>2</sub> decrease with increasing space velocity, indicating that the higher the space velocity, the lower the reaction rate. The relationship between the inverse GHSV and conversion rate is not linear, that shows that the reaction is not kinetically limited. The Reynolds number (N<sub>Re</sub>) is a measure of fluid mixing inside the quartz reactor. If the flow is turbulent; N<sub>Re</sub> > 2100, then the gases mix much better than when N<sub>Re</sub> < 2100 and gas flow is laminar, the N<sub>Re</sub>, a dimension less quantity, is estimated as follows:

$$N_{Re} = Dv\rho/\mu$$

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.

$$D = 2.5 \text{ cm}$$

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

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

$$\text{Velocity (v)} = Q/A = 20.34 \text{ cm/min}$$

$$PV = nRT$$

= (m/M)RT, ρ = (PM)/(RT), where, P is the pressure in the reactor, M is the molecular weight 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).

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

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

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

When GHSV = 50,000,  $N_{Re} = 2.32 < 2100$

When GHSV = 80,000,  $N_{Re} = 3.72 < 2100$

Thus, the flow is laminar at all three space velocities in these considered experiments.

### 3.2 Reduction of NO by Granular Activated Carbon (GAC)

Reduction of NO by GAC with 10 % oxygen presence without catalyst, and over Cu-ZSM5 (5% GAC, 95% Cu-ZSM5), and reduction of NO by 20% , 10%, 1% Cu loaded GAC with 10% oxygen are discussed in this section.

#### 3.2.1 Reduction of NO with GAC with 10% oxygen

The GAC-nitric oxide (NO) reaction plays an important role in many process where the reduction of NO is attempted, especial for diesel emissions control because soot and  $NO_x$  are the two principal pollutants from diesel engines. The carbon porosity and surface area play an important role in this reaction, and the presence of oxygen can enhance this reaction. Suzuki (1994) reported that the formation of surface oxygen intermediates by the C- $O_2$  reaction is essential for C-NO reaction.

**3.2.1.1 Effect of Space Velocity:** Figure 3.6 summarizes the results of reducing NO with GAC to  $N_2$  as a function of temperature and GHSV. The 50,000/hr curve appears to 550°C and 25 to 30% NO conversion to  $N_2$  is observed. The other curve was obtained at a GHSV of 80,000/hr where conversion of NO to  $N_2$  begins just after 550°C and NO conversion to  $N_2$  of 25~30% is achieved at 600°C. If we compare those two curve, we

see that the curve which represent GHSV of 80,000/hr shifts to higher temperature, in order to obtain the same conversion as was obtained at 50,000/hr.

It has been generally agreed that the presence of oxygen enhances the rate of NO chemisorption on carbon (J.M. Calo, et al., 1993) and the rate of carbon-NO reaction (Yamashita, et al.,1993). It appears that a surface intermediates (CO), which is essential for the NO-carbon reaction, must be formed. However, some researchers consider the formation of NO<sub>2</sub> to be responsible for the rate enhancement, while others believe that surface oxygen intermediates produced by the coexistence oxygen and carbon is responsible. Suzuki (1994) found that the reactivity of NO<sub>2</sub> is large, but the main product is not N<sub>2</sub>, but NO. This means that the transformation of NO to NO<sub>2</sub> does not enhance the NO removal to N<sub>2</sub> reaction in the presence of O<sub>2</sub>. On the other hand, much evidence has been presented to support the hypothesis that O<sub>2</sub> enhances the carbon-NO reaction through formation of surface oxygen complexes.

**3.2.1.2 Effect of Water Vapor:** Figure3.7 summarizes the results for the reduction of NO with GAC in the presence of 10% water vapor as a function of temperature and GHSV. The two curves shows that at GHSV of 50,000/hr to 80,000/hr, light off begins at 550°C and conversion of 15 to 20% is achieved at 600°C. Comparing these results with those without water, we see that two curves shift to relatively high temperature and have a slightly lower conversion rate.

### 3.2.2 Reduction of NO with GAC with 10% Oxygen over Cu-ZSM5

Cu-ZSM5 as a selective catalyst is good in reduction NO with hydrocarbon ( $C_3H_8$ ) and CO at low space velocity, but at high space velocity, the performance of catalyst is poor. In this section, we will discuss the reduction of NO with GAC over Cu-ZSM5 in the presence of 10 % oxygen.

**3.2.2.1 Effect of Space Velocity:** Figure 3.8 summarizes the results of using GAC as the reducing agent for NO conversion to  $N_2$  as a function of temperature and GHSV. The two curves obtained at GHSV of 50,000 and 80,000 have maximum around  $500^\circ C$  and achieve 15 to 20% NO conversion. In these two experiments, we used 5% GAC (wt% catalyst). The low conversion rate at high GHSV is similar to the reaction of NO with CO. There are two possible causes for the low conversion rate: one is that we can not produce enough CO intermediates with 5% GAC to promote the NO conversion to  $N_2$ , or at the high temperature needed at high GHSV the reacts further CO with  $O_2$ . Not allowing the CO + NO reaction to occur. If we assume that CO is key intermediate, then as temperature increases, most of CO goes to  $CO_2$ . Also, the rate of the NO- $O_2$  reaction to  $N_2$  decreases as temperature increases (negative temperature coefficient) and consequently, the rate of dissociation of NO to  $N_2 + O_2$  increases. The NO concentration decreases 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 during the initial stages of reaction,  $N_2$  production is lower than the expected for NO reaction at  $600^\circ C$  and they did not find other nitrogen-containing gases like  $N_2O$ . Clearly they had a poor nitrogen balance. However, they found that after 120

minutes, the observed conversion to  $N_2$  increases to match the NO consumption and the nitrogen balance improved. It appears that the nitrogen initially trapped on the carbon is released, and thus, the observed  $N_2$  output increases.

### 3.2.3 Reduction of NO with CuO/GAC with 10% Oxygen

It is well known that the reaction of copper impregnated GAC and NO is remarkably enhanced by the presence of oxygen (Suzuki, et al., 1994). The results of this research show that the C/NO reaction is catalyzed by CuO loaded on GAC and is remarkably promoted in the presence of oxygen.

The CuO impregnated on GAC catalyzes the C/O<sub>2</sub> reaction and increases the concentration of active sites, C(O). The C/O<sub>2</sub> reaction produces a large amount of surface intermediate CO, which is present on the surface of GAC, and therefore contributes to the reaction  $2CO + 2NO \rightarrow 2CO_2 + N_2$ . Also, the formation of NO<sub>2</sub> 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<sub>2</sub> has much higher reactivity toward carbon than either NO or O<sub>2</sub>. Although a considerable fraction of NO<sub>2</sub> would regenerate NO, some NO<sub>2</sub> might be converted to N<sub>2</sub>. On the other hand, the surface state of the Cu catalyst is as a mixture of Cu<sup>I</sup> and Cu<sup>II</sup> in the region where Cu/carbon black exhibited a high NO<sub>x</sub> conversion (Yamashita, 1991). The oxidation of Cu by O<sub>2</sub> 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 compounds supplied by the catalyst. Yamashita, et al., (1993) proposed a mechanism for the reaction.



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<sub>2</sub> 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<sub>2</sub> 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).

The high conversion to N<sub>2</sub> of above 90% at low space velocity (less than 10,000/hr) is achieved with those copper loaded carbon black as the reactant and catalyst. At a higher space velocity, the conversion rate to N<sub>2</sub> still goes up to 60%. This reaction goes very fast, significant amount of solid disappear as the reaction process. 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 factors that affect the performance of the catalyst, will be discussed in the following sections.

### **3.2.3.1 Effect of Different CuO Loading on Reduction of NO with CuO/GAC:**

Experiments were conducted with three different CuO loadings 20%, 10%, 1% CuO/GAC. The results are compared in Figure 3.9. It can be seen that three curve have almost the same maximum conversion rate around 60%. We check this reaction at the temperature range from 200°C to 600°C. The curves which represent 20% CuO/GAC and 10% CuO/GAC have lower light off temperature 250°C, and the conversion rate is increased dramatically from 0 to 50% with increasing temperature between 250°C to 350°C. It indicates that the reaction is under chemical reaction control at this temperature range. After 350°C, the conversion rate increased slightly with temperature increasing and get to maximum conversion rate 60%. It appears that the reaction is mass transfer controlled at reaction temperatures above 350°C.

The other curve shows the result of reduction of NO with 1% CuO/GAC. It can be seen that the light-off temperature shifts to 350°C after we decrease CuO from 10% to 1%. At the temperature range 350° to 400°C, we still have a conversion region from 0 to 50%, and it remains constant around 55% after 400°C.

Comparing these three curves, it shows that the increasing CuO loaded on GAC can promotes the activity of GAC, and gets lower light off temperature but it does not increase conversion rate too much. All three reactions go very fast, once CuO/GAC light off, the reaction temperature will increase rapidly over 650°C in few seconds without

increasing the oven temperature. In that reaction region, the reaction process was controlled by chemical reaction:

The conversion rate  $\propto k \exp(-E/RT)$

Where T is reaction temperature.

As temperature is increased, the conversion rate does not increase substantially with temperature. It indicates that the reaction process may be mass transfer controlled.

The conversion rate  $\propto T^{3/2}$

Where T is reaction temperature.

In other words, chemical reaction is an exponential temperature, and mass transfer varies as viscosity (i.e.,  $T^{3/2}$ ). These results are consistent with our experiment results.

### **3.2.3.2 Effect of Space Velocity on Reduction of NO with GAC with 1% CuO:**

Experiments were conducted at two different space velocity 50,000/hr and 80,000/hr. The results are compare in Figure 3.10. It can be seen that the conversion to N<sub>2</sub> is relatively high at each space velocity. We conducted this experiment in the temperature range 200°C to 600°C. The conversion of NO to N<sub>2</sub> increases with temperature between 200°C to 450°C, and remains constant after 450°C. For the reaction at 50,000/hr space velocity, 10%, 58% and 61% conversion of NO to N<sub>2</sub> was obtained at 350°C, 400°C and 450°C. The conversion is much high than that obtained with Cu-ZSM5 in the same temperature range. For the reaction at 80,000/hr space velocity, only 5%, 20% nitrogen conversion was obtained at 350°C and 400°C. However at 450°C, the conversion rate of NO to N<sub>2</sub> increased to 55% which is close to 61% conversion rate at 50,000/hr reaction. Comparing these two curves, it is apparent that the curve at 80,000/hr space velocity shift to

relatively high temperature. At 50,000/hr space velocity, the light off temperature is 350°C, and the conversion rate increases to 55% at 400°C. In this temperature range (350~400°C), the rate of reaction is very sensitive to temperature. It indicates that chemical reaction rate is controlling. In case of 80,000/hr space velocity, the light off temperature shift to 400°C, and conversion rate increases with temperature, but the slope of the curve is decreases from the one at 50,000/hr space velocity. This may be an indication that pore diffusion is becoming the dominant mechanism. Pore diffusion is less sensitive to temperature than chemical reaction. After 450°C, the conversion rate remains constantly. The solid material contain 1% copper ion adsorbed onto GAC. The volume of the solid is 1.5 cm<sup>3</sup>. The calculation of moles of GAC, flow rate of NO, O<sub>2</sub> and residence time is listed below:

Bulk density of 1% CuO/GAC	0.4095 g/ml
Weight of 1.5 ml 1% CuO/GAC	0.6143 g
Weight of GAC content	0.6082g
Moles of GAC	0.05068
NO concentration	590 ppm 0.00059 ml NO/ml volume
When GHSV = 50,000/hr, total flow rate:	1250 ml/min
NO flow rate = 1250 ml/min * 0.00059 ml/ml	= 0.738 ml/min
Flow rate of 10% O <sub>2</sub>	125 ml/min
Residence time = 1 / [ (50,000/hr) * (1 hr/3600 sec) ]	= 0.072 sec

One can see that 3 cm<sup>3</sup> 1% copper loaded GAC contains much larger amount of carbon than 3 cm<sup>3</sup> of 5% GAC/ 95% Cu-ZSM-5. Copper loaded GAC is not only a reactant but also a catalyst in the reaction of Cu/GAC + NO + O<sub>2</sub>. Thus, copper loaded

GAC is an excellent source of carbon that can be oxidized to produce larger amount of CO even at low temperatures.

**3.2.3.3 Effect of Water on Reduction of NO with 1% CuO/GAC:** CuO/GAC exhibits fairly good performance for NO reduction in an oxidizing environment. 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) and containing about 8% ~ 10% water which could poison the catalyst in gas streams. The deactivation of CuO/GAC was studied in this section.

The effect of water was studied by bubbling the gaseous feed mixture through water. The water temperature was controlled by a constant temperature water bath in order to get desired water partial pressures. The experiment was carried out at water concentrations 10%. The gas mixture was bubbled through the water and to the catalytic reactor. The partial pressure of the water was determined by the percentage of water vapor needed in the reaction system. And then the water temperature can be found in chemistry handbook according to water partial pressure. The equation below is used to calculate the partial pressure of water:

$$(X\text{mmHg}/760\text{mmHg}) = 10\%$$

Where X refers to water partial pressure at 760mm Hg atmospheric pressure. In order to get 10% water in gas stream, the partial pressure of water should be 76mm Hg. From chemistry handbook, we get the desired temperature of water of 45°C.

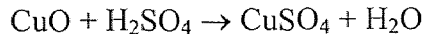
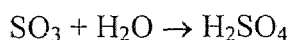
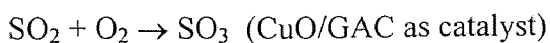
The influence of water vapor on  $N_2$  conversion is shown in Figure 3.11. The experiment was conducted in the temperature range 200°C to 600°C and space velocity of 50,000/hr, with 10% oxygen. The light off temperature remained unchanged, but maximum conversion to  $N_2$  dropped from 60% in the absence of water to 50% ~ 55% in the presence of 10% water. The slope of the curve also changed. The curve is very sensitive to temperature between 350°C to 400°C in the absence of water. After we introduced water, the slope of curve became lower. It seems that resistance to pore diffusion increased. Water could cause some change in pore structure or block pores by condensing in the pore entrance. Consequently, the catalyst loses some activity and gives lower conversion to  $N_2$ .

**3.2.3.4 Effect of Water and  $SO_2$ :**  $SO_2$  irreversibly poisons almost all catalysts. Sulfur is one of the impurities in diesel fuel that is difficult to remove completely. Consequently,  $SO_2$  becomes one of the components emitted in the diesel exhaust. The effect of the research on deactivation of Cu/GAC by  $SO_2$  and water is presented in this section.

Experiment of  $SO_2$  poisoning were conducted between 200°C to 600°C. A concentration of 20ppm  $SO_2$  was introduced into gas mixture prior to bubbling through the distilled water. The water temperature was controlled around 45°C, so there would be about 10% water vapor in gas stream. Finally, the gas mixture contained 590 ppm NO, 10%  $O_2$ , 10% water vapor and 20 ppm  $SO_2$  with helium as the balance.

Figure 3.12 summarizes the experiments on the effect of  $SO_2$  and water on NO reduction by CuO/GAC in the presence of 10% oxygen. If we compare this curve with the curve without water and the curve with water and no  $SO_2$ , we observe that the light

off temperature of shifts to higher temperature 400°C. The maximum conversion rate to N<sub>2</sub> dropped from 60% in absence SO<sub>2</sub> and water to around 45% in presence of water and SO<sub>2</sub>, the slope of the curve also decreased slightly. These results indicate that pore diffusion resistance increased and CuO/GAC lost some catalytic activity. When 10% oxygen is presented in the gas feed stream, it increased the oxidation activity of the feed, this would tend to increase the oxidation site of CuO supported on GAC. Then when SO<sub>2</sub> was absorbed on CuO/GAC, it can be oxidized to SO<sub>3</sub>, when water was absorbed on the surface of CuO/GAC, those chemical can react to produce sulfate, the following reaction equation show a possible this mechanism:



When CuSO<sub>4</sub> is formed, we lose active sites of the catalyst, that result lower conversion to N<sub>2</sub>.

### 3.3 Thermogravimetric Analysis

Figure 3.13 presents data from a TGA experiment to determines the temperature at which Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O will completely convert into CuO. Compressed air was used as reacting gas. It can be seen from Figure 3.13 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<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O = 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 loss. From the molecular weight, one can calculate the weight loss as the following:

$$\text{Weight loss (\%)} = (242-80)/242 = 67\%$$

Which is consistent with the experiment.

## CHAPTER 4

### CONCLUSIONS

1. Oxygen enhances the NO + CO reaction over Cu-ZSM-5. The catalyst can selectively catalyze this reaction. There is a temperature window when Cu-ZSM-5 is used as a catalyst, above 500°C, the conversion to N<sub>2</sub> decreases with temperature. With increasing space velocity, the conversion to N<sub>2</sub> decreases. At high space velocity 50,000/hr and 80,000/hr, the conversion to N<sub>2</sub> is very low. It is not a good catalyst for NO reduction in diesel exhaust.
2. For the reduction of NO with GAC over Cu-ZSM-5 with 10% oxygen present, the reaction rate and NO conversion to N<sub>2</sub> decrease with increasing space velocity. The highest NO conversion to N<sub>2</sub> occurs at the same temperature as the NO + CO + O<sub>2</sub> reaction. CO is an intermediate of the C/NO reaction. But at high space velocities, the maximum NO conversion to N<sub>2</sub> is lower than 20%, so it is not a good catalyst for this system.
3. GAC can reduce NO to N<sub>2</sub> without the presence of a metal catalyst, but conversion to N<sub>2</sub> is relatively low, about 20%. The conversion to N<sub>2</sub> was increased dramatically when copper supported on GAC is used.
4. For the reduction of NO with CuO supported GAC with 10% oxygen. A significant amount of CO is produced by the C-O<sub>2</sub> reaction with Cu ion presence even at relatively low temperature. When space velocity is lower than 20,000/hr, almost 100% NO conversion to N<sub>2</sub> is obtained at 600°C. At space velocity 50,000/hr, the 60% maximum conversion rate is obtained. The light off temperature is 300°C when we used 20%, 10% CuO/GAC.

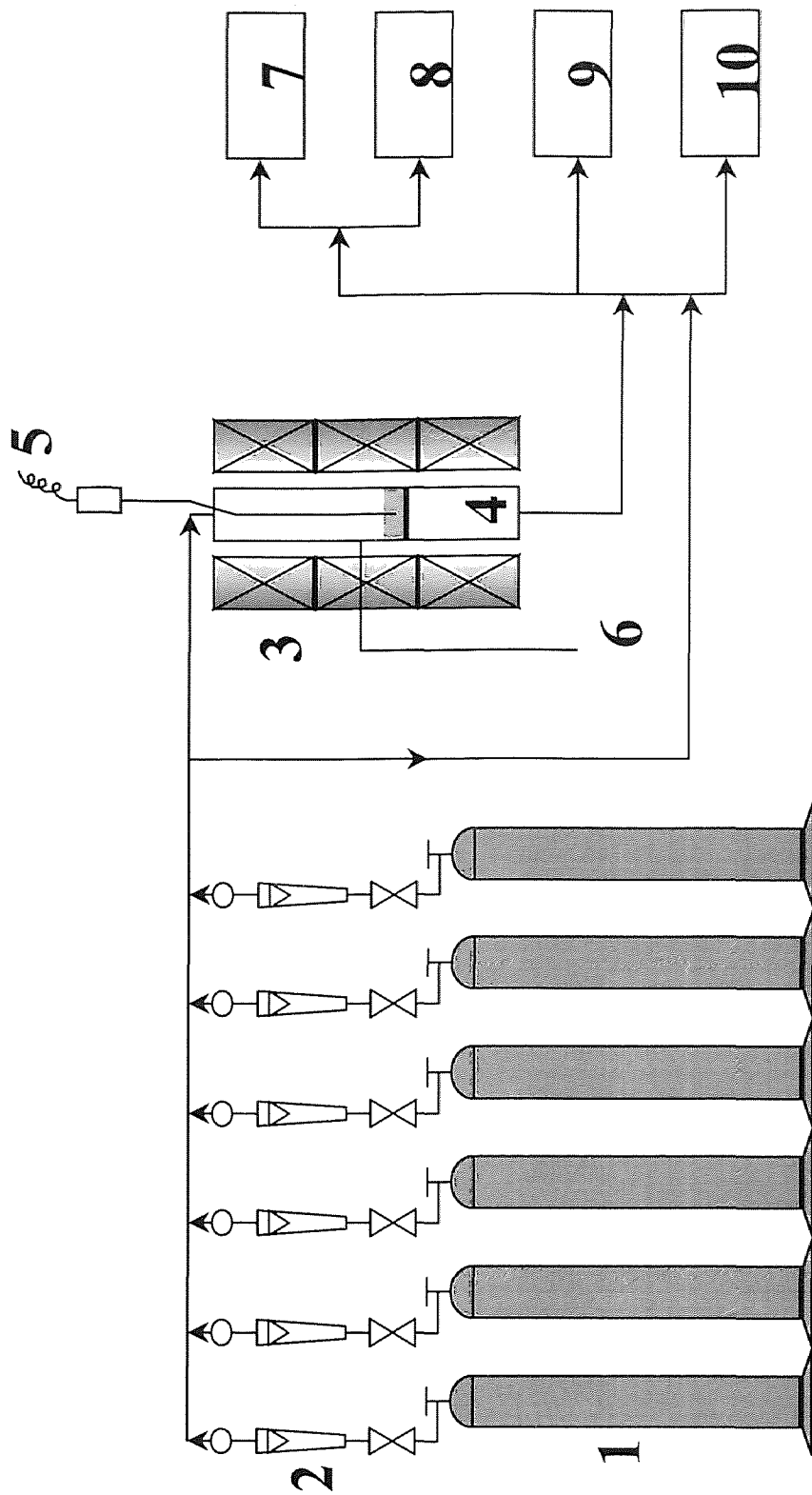


The light off temperature shift to 450°C when we used 1% CuO/GAC, but the maximum conversion to N<sub>2</sub> is the same as before.

5. Water can poison the reduction NO with GAC. When about 10% water vapor is present in this reaction system, the conversion rate declines from 60% to about 55%.

6. When SO<sub>2</sub> and water present at system, The conversion to N<sub>2</sub> will decrease from 60% to 40~45%. Sulfur is more detrimental to the system than water. The reason that SO<sub>2</sub> and water poison the catalyst is that they react with CuO to form copper sulfate. This causes the loss of catalytic activity by reducing active sites, and blocking access to metal through the pore structure of GAC.

**APPENDIX A**  
**FIGURES OF EXPERIMENT RESULTS**



**Figure 2.1 Schematic diagram of experimental apparatus**

1. Cylinders (He, NO, NO<sub>2</sub>, O<sub>2</sub>, CO, SO<sub>2</sub>) 2. Flow meters 3. 3-Zone Furnace 4. Quartz Reactor 5. Thermocouple 6. Temperature Controller 7. HP5890 GC-FID 8. HP5890 GC-TCD 9. GOW-MAC GC-TC 10. Thermoelectron NO/NO<sub>x</sub> Chemiluminescent Analyzer

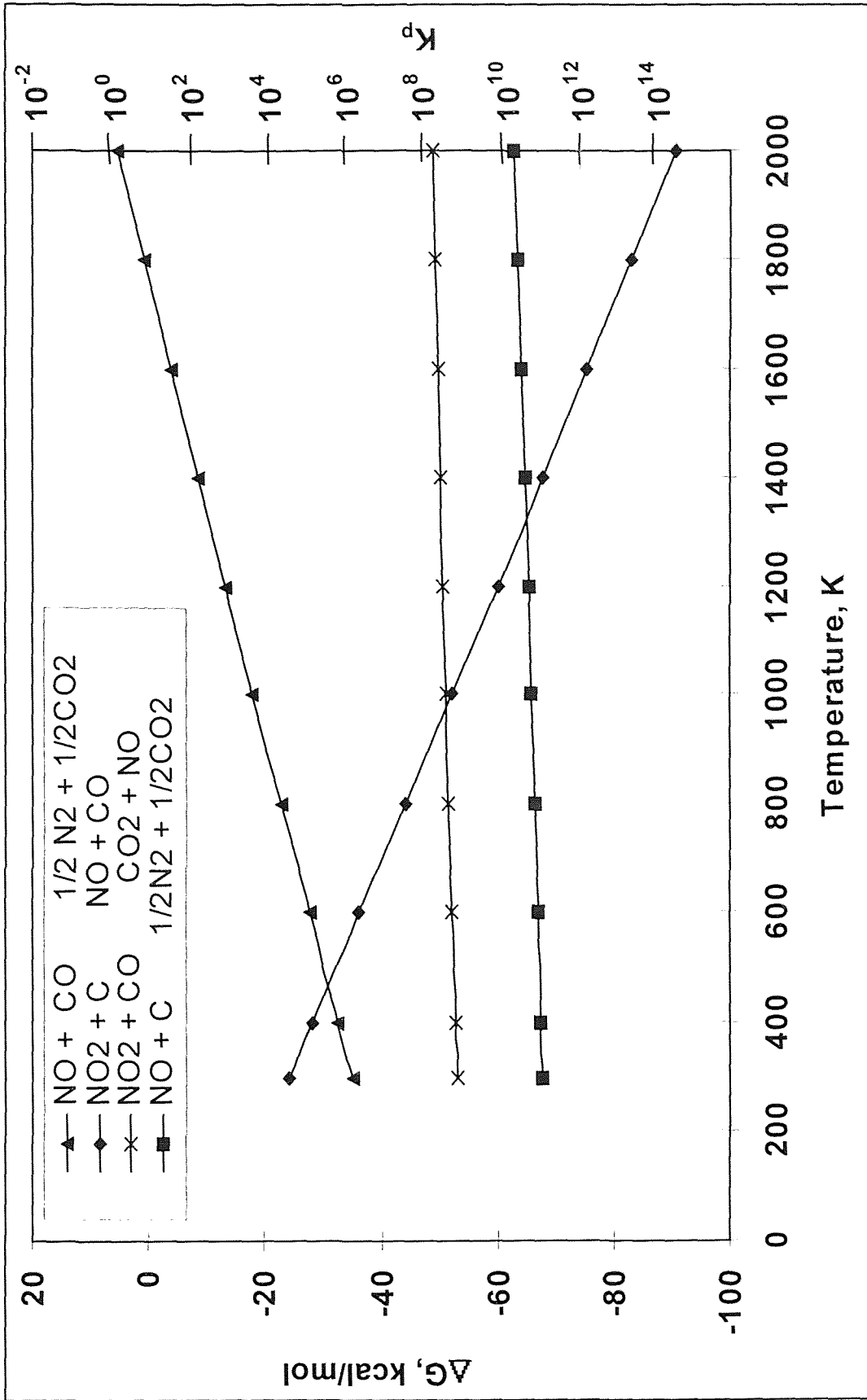
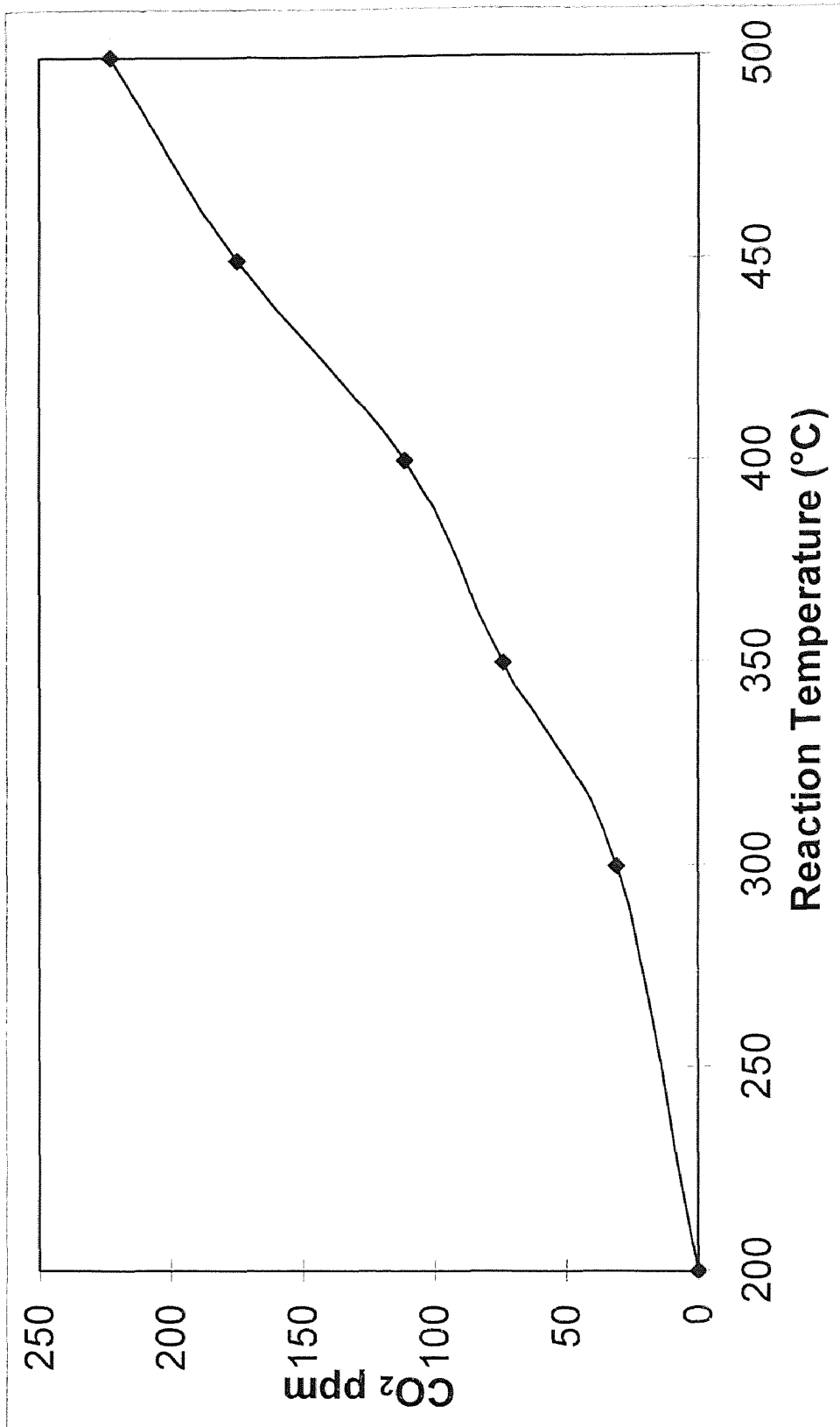
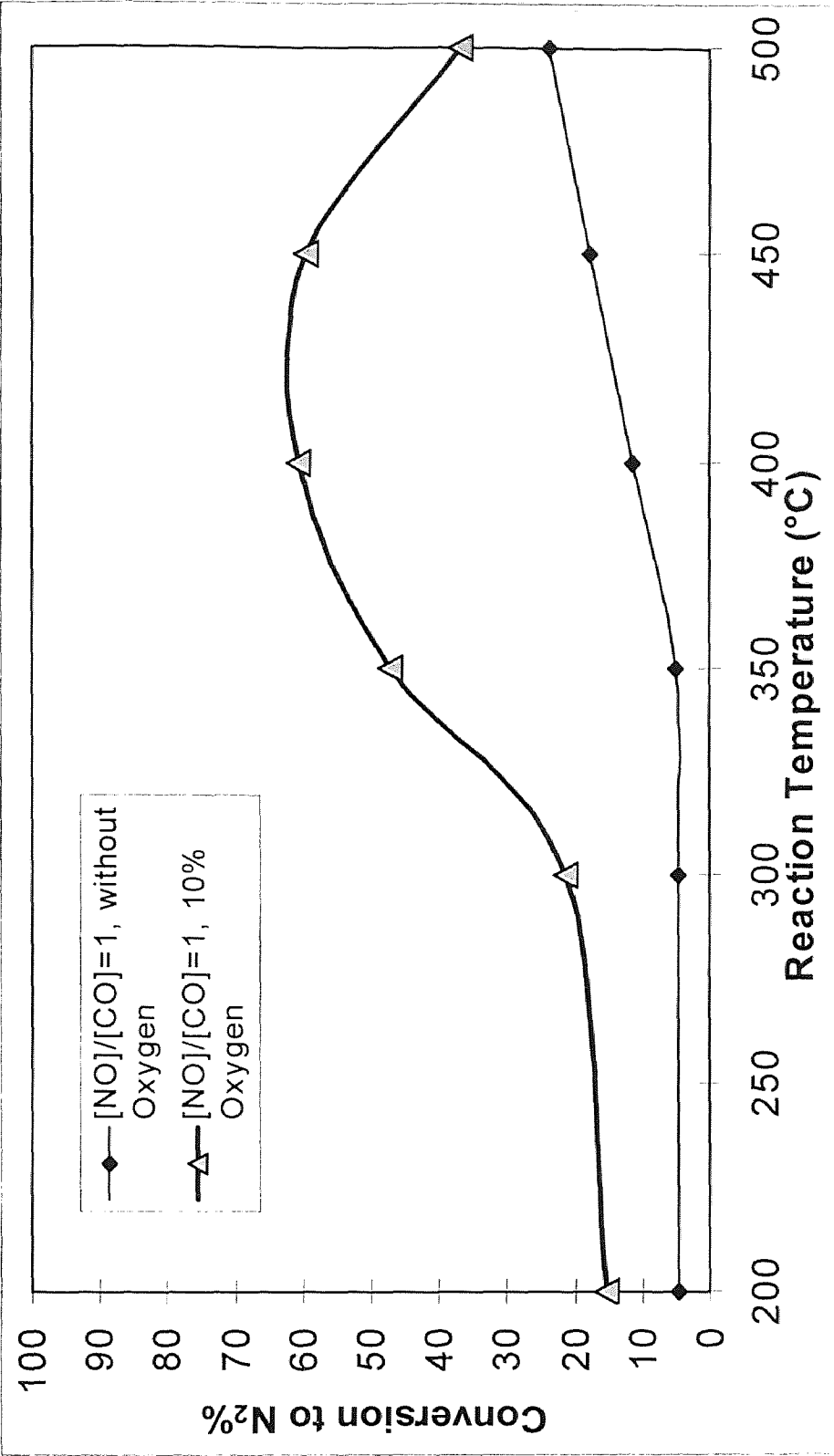


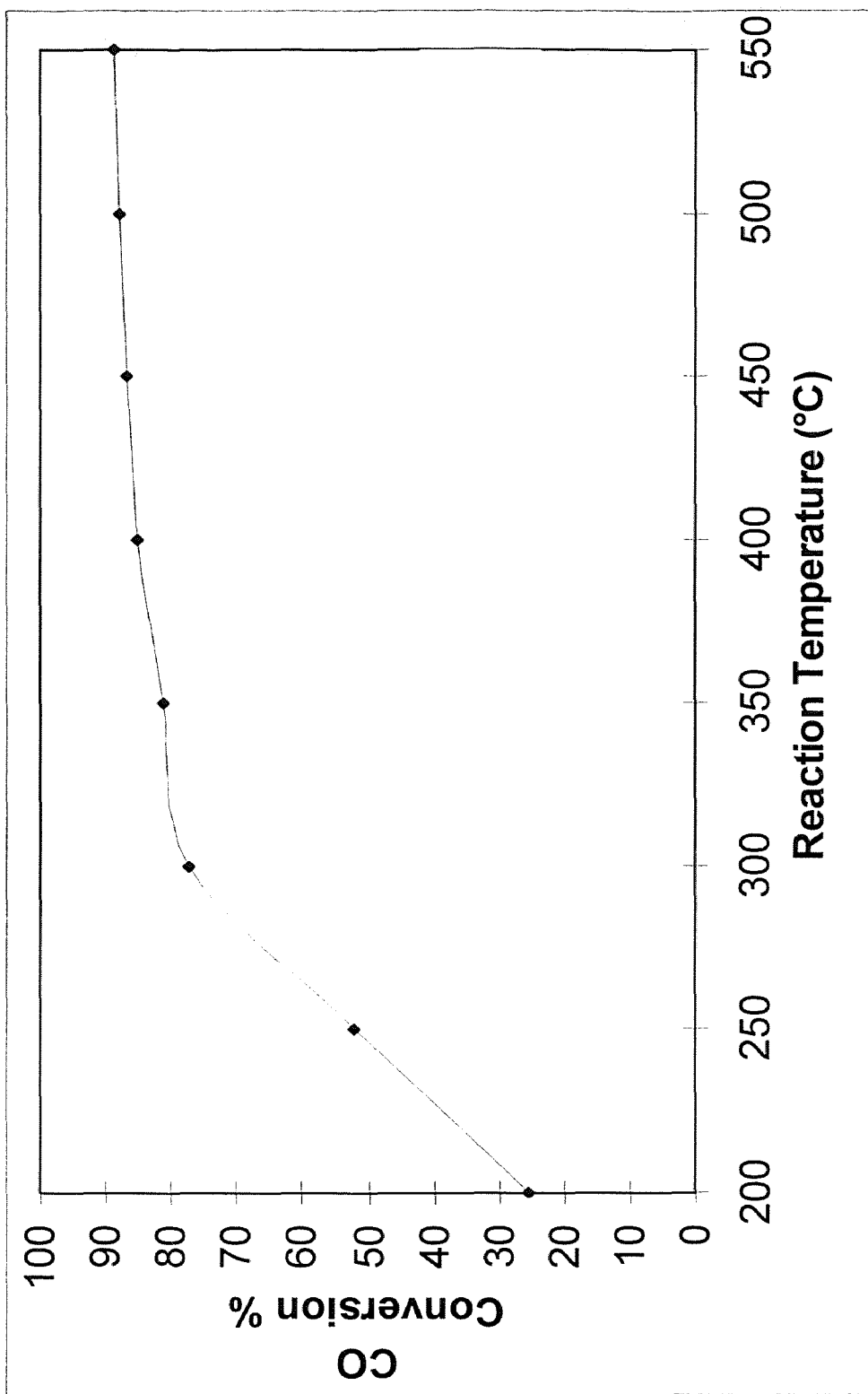
Figure 3.1 Ellingham diagram



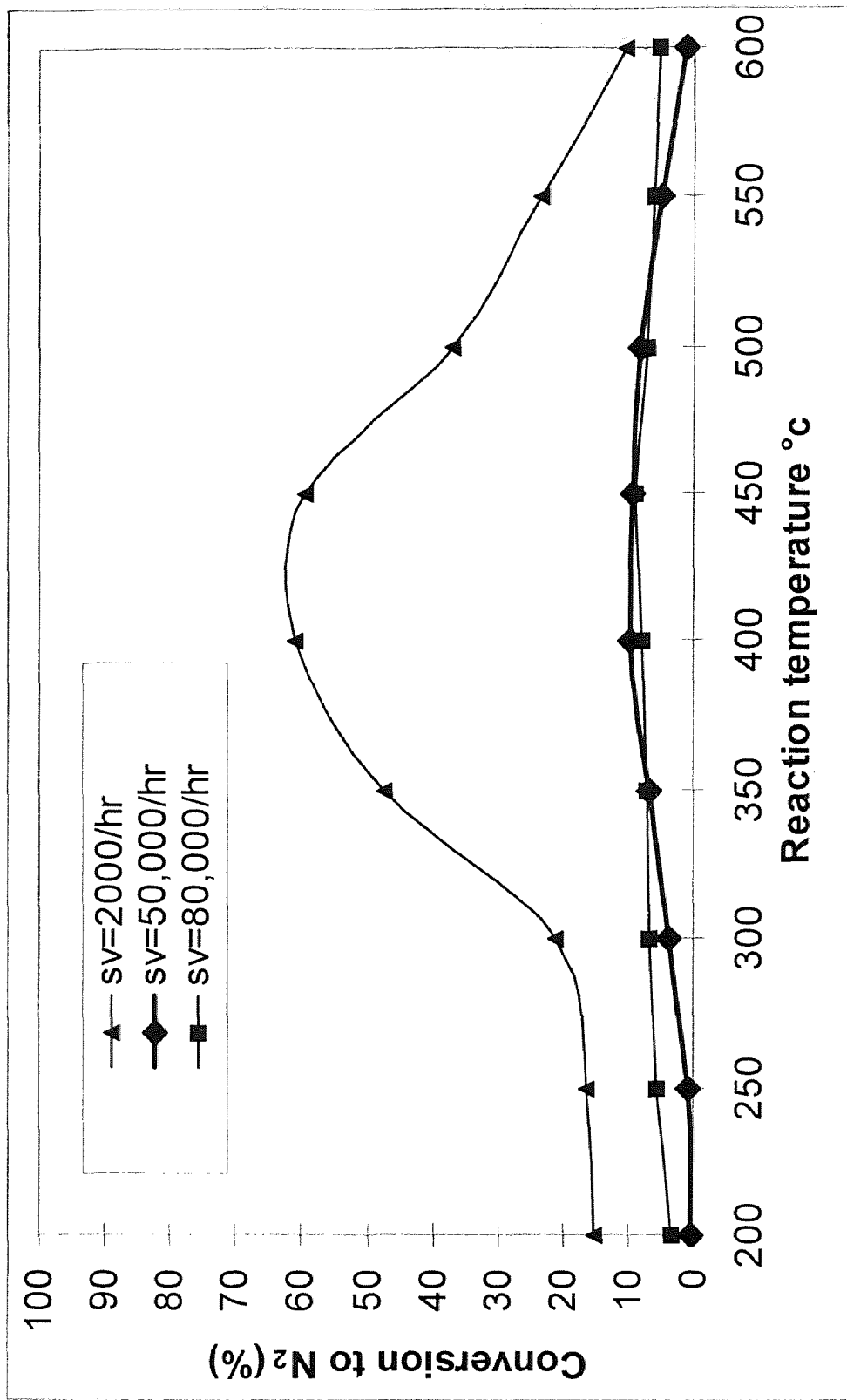
**Figure 3.2** CO<sub>2</sub> produced in the reduction of NO by CO in the absence of O<sub>2</sub>, sv=2,000 /hr, over Cu-ZSM-5



**Figure 3.3 Reduction of NO by CO in the presence and absence of O<sub>2</sub> over Cu-ZSM-5, sv=2000 /hr, [NO]=[CO]=500 ppm**

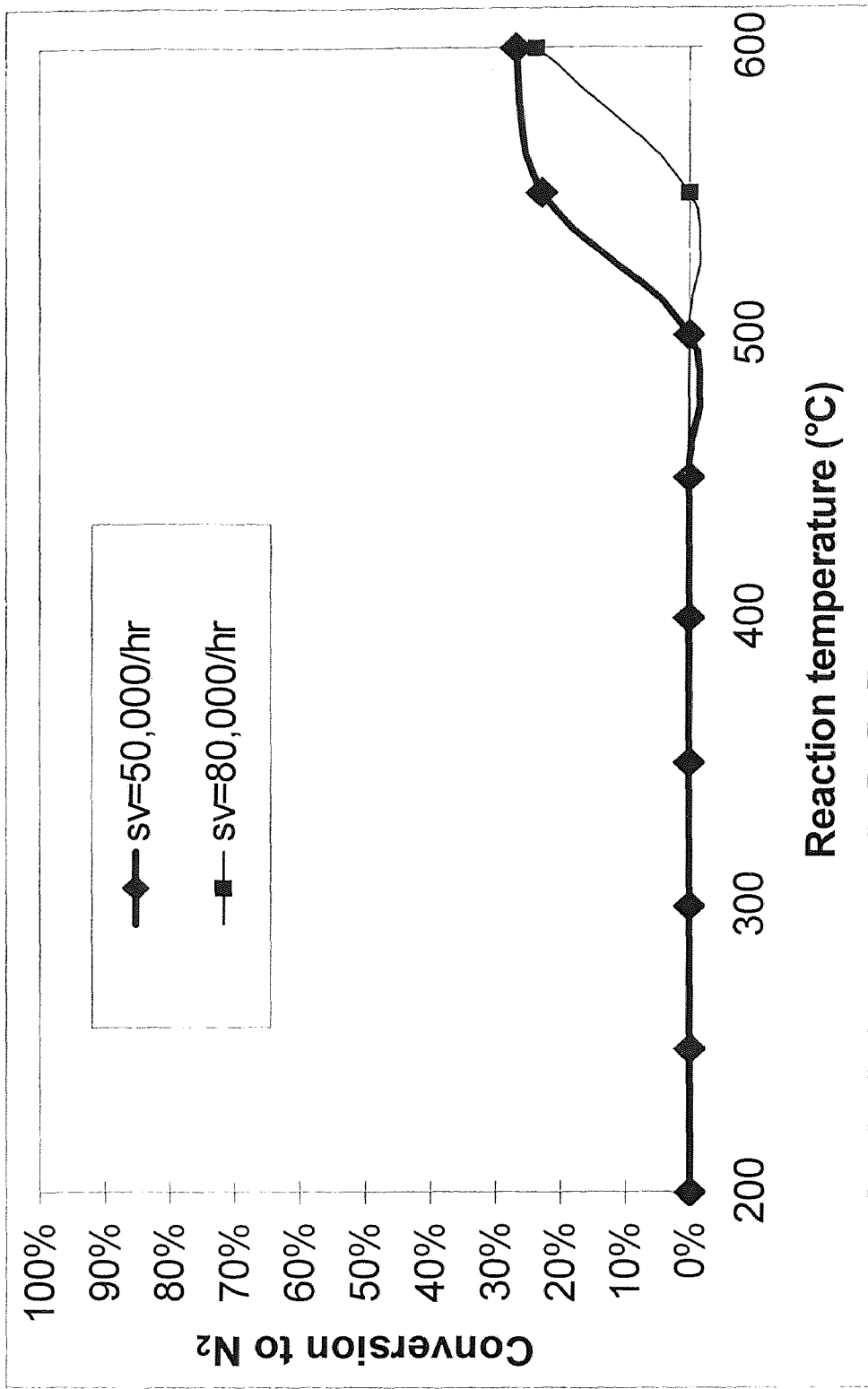


**Figure 3.4 Oxidation of CO by O<sub>2</sub> over Cu-ZSM-5, sv=2,000/hr**

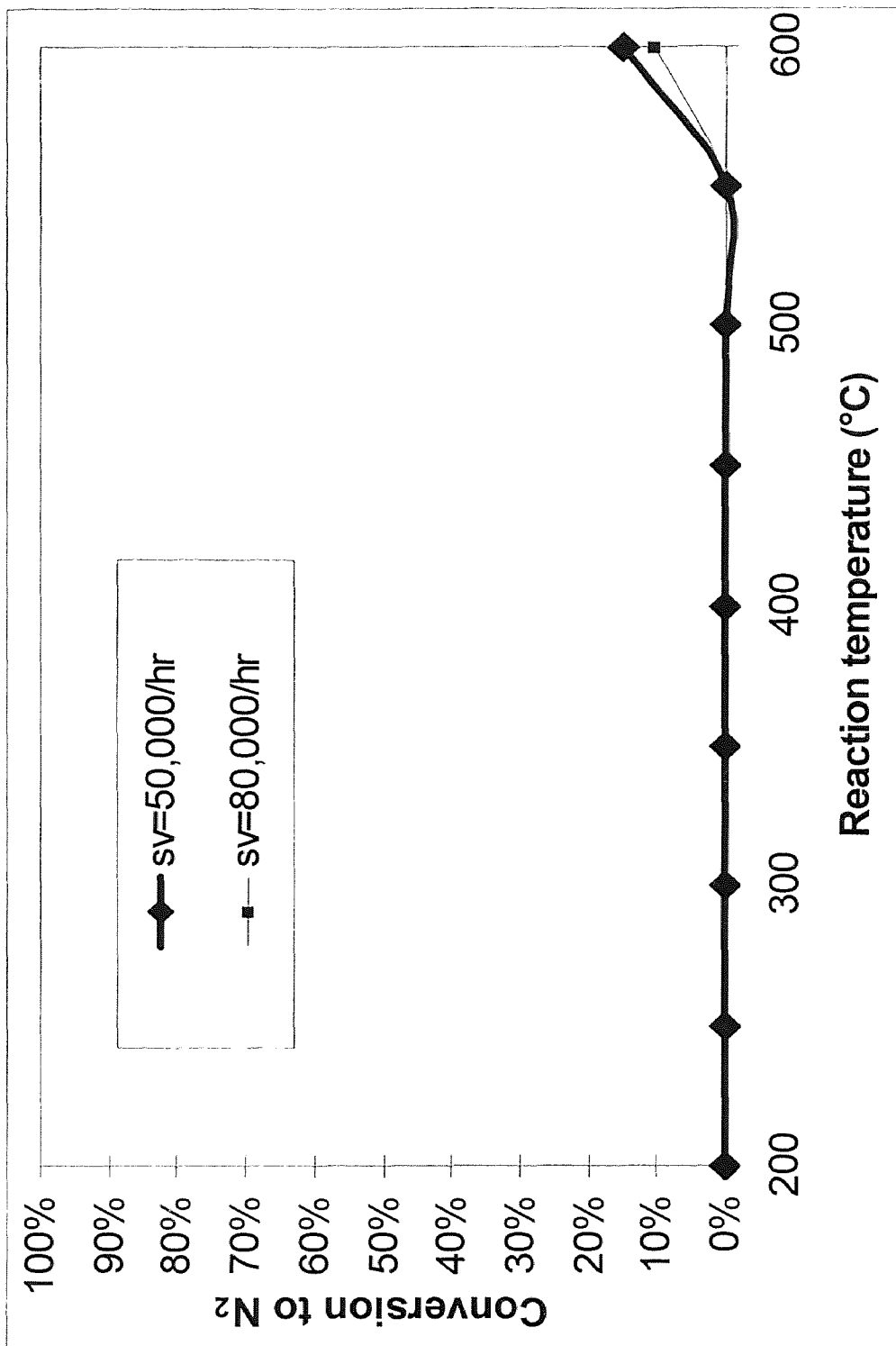


**Figure 3.5** Effect of space velocity on reduction of NO by CO over Cu-ZSM5, [O<sub>2</sub>]=10% [NO]=[CO]=430 ppm.

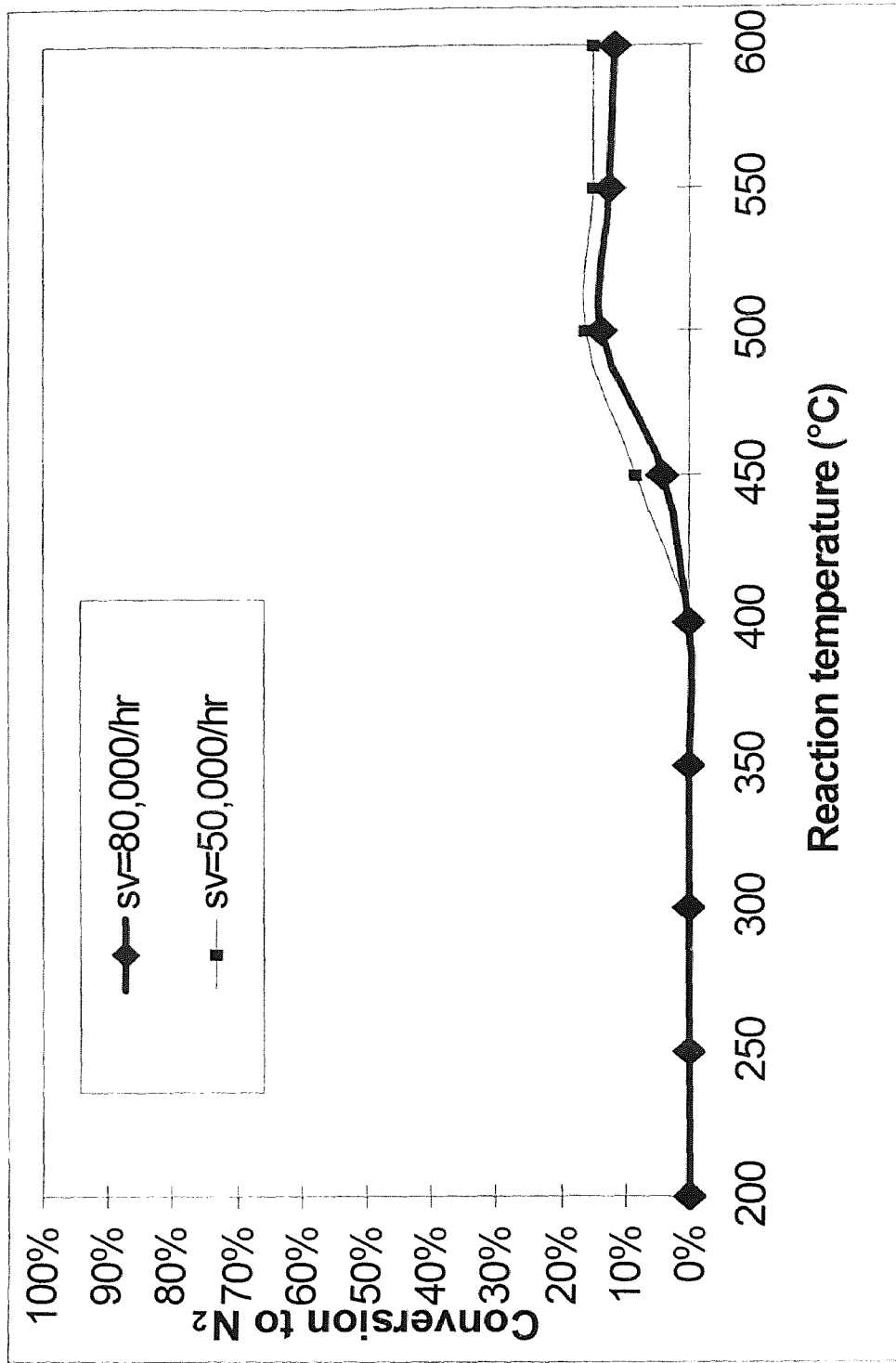




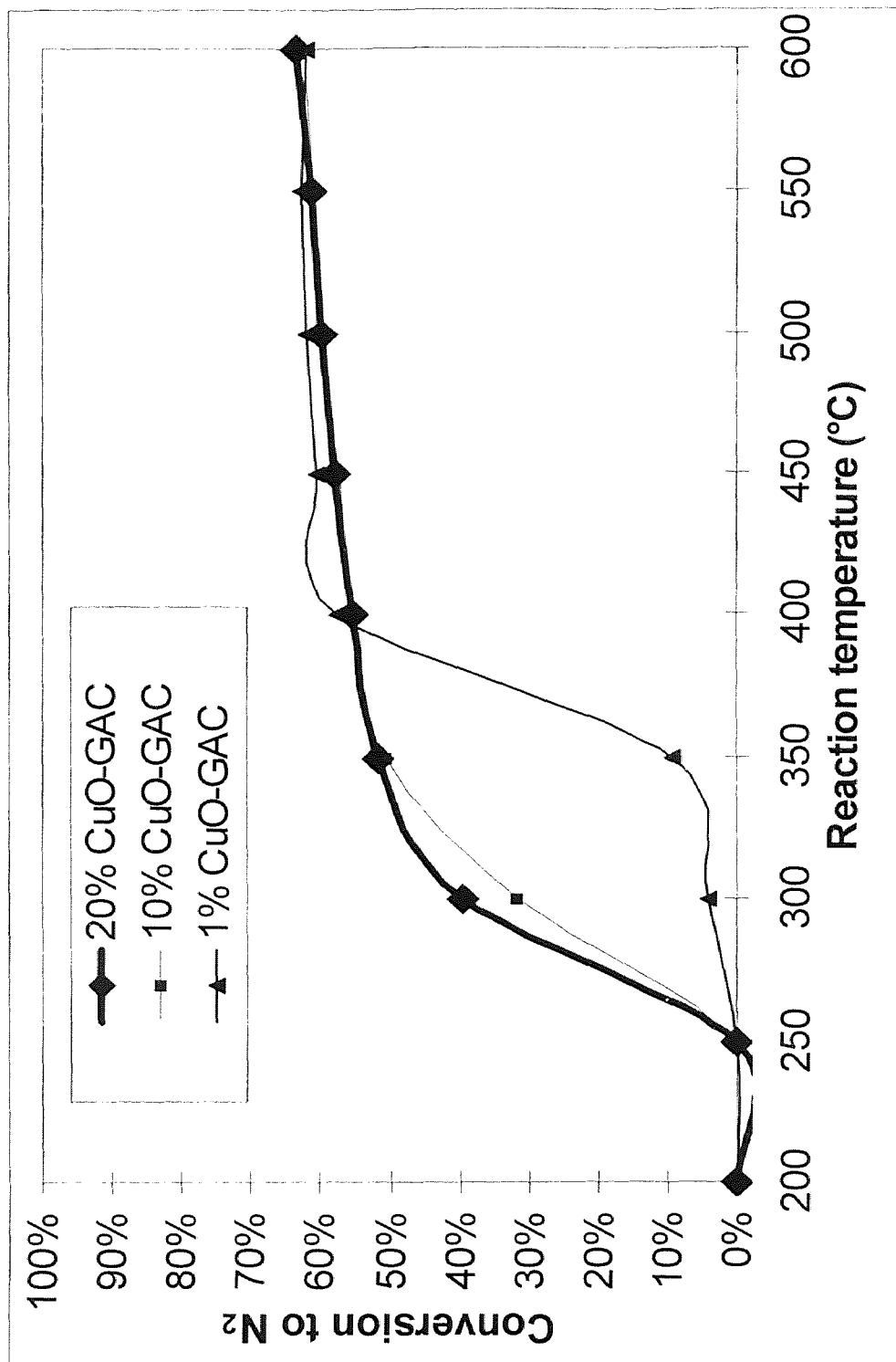
**Figure 3.6** Effect of space velocity on reduction of NO by GAC  
w/o catalyst, [NO]=590 ppm, [O<sub>2</sub>]=10%



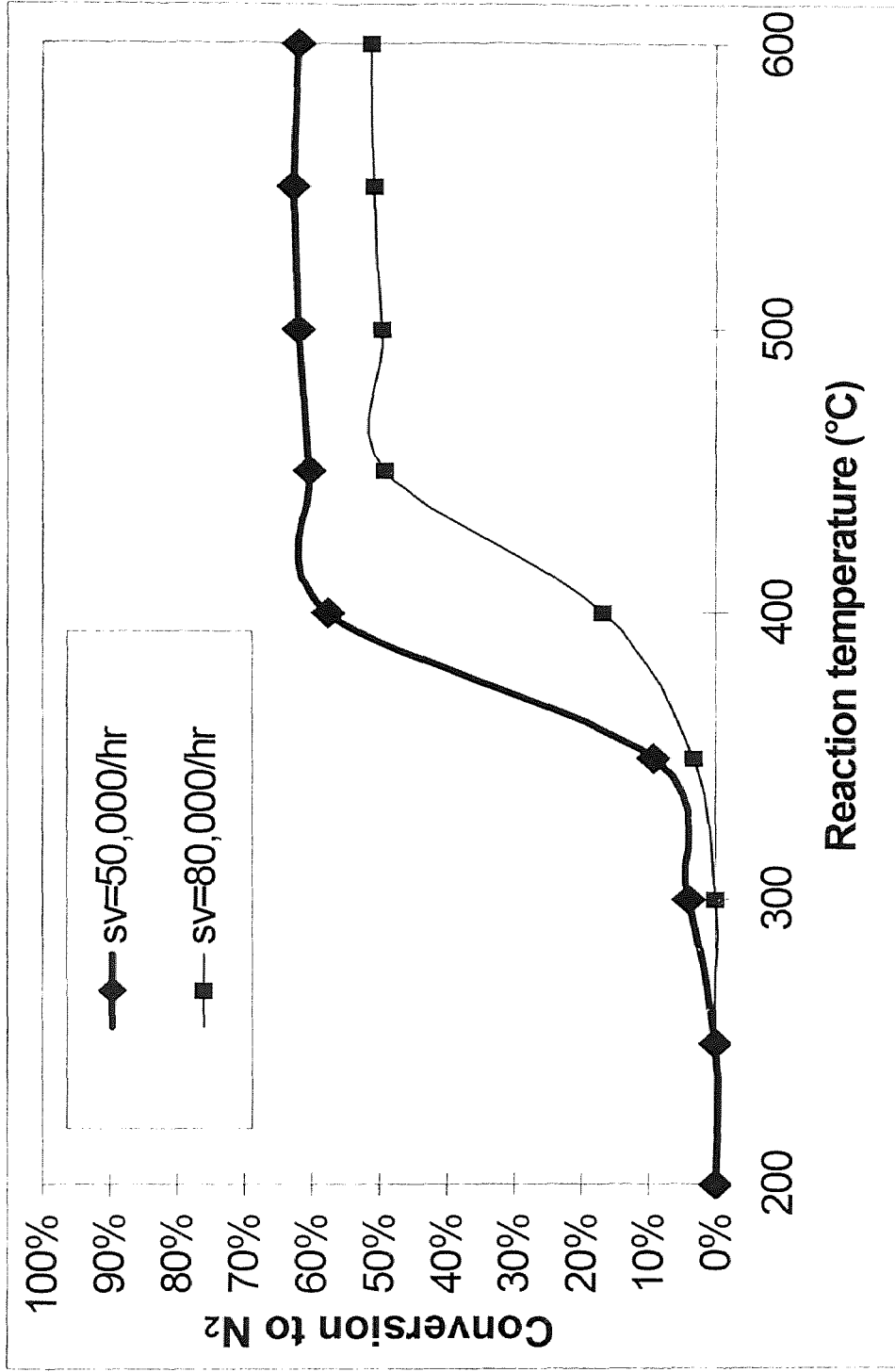
**Figure 3.7** Effect of water on reduction of NO by GAC w/o catalyst, [NO]=590 ppm, [O<sub>2</sub>]=10%, [H<sub>2</sub>O]=10%



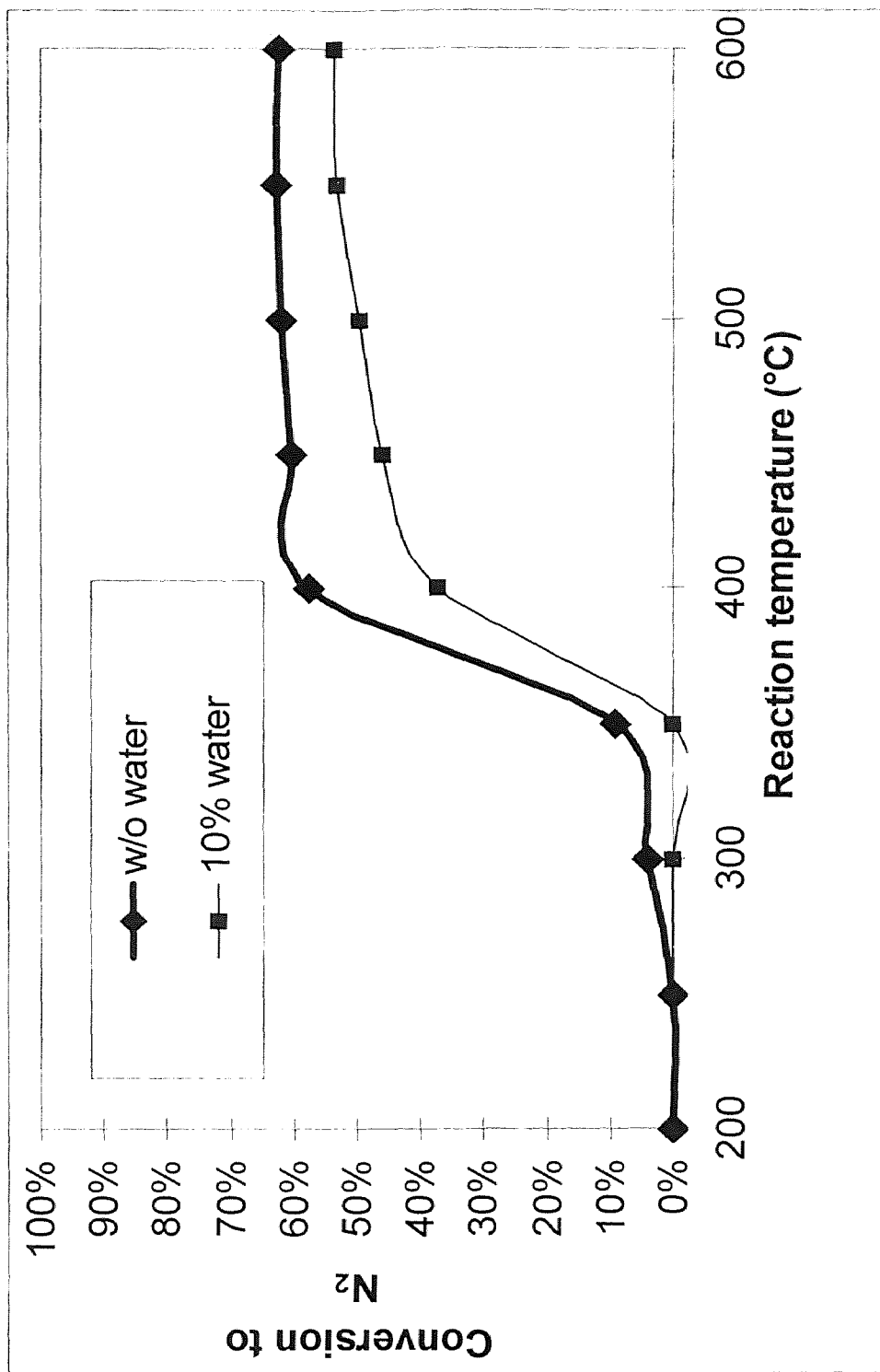
**Figure 3.8 Effect of space velocity on reduction of NO by 5% GAC over Cu-ZSM-5, [NO]=590 ppm, [O<sub>2</sub>]=10%**



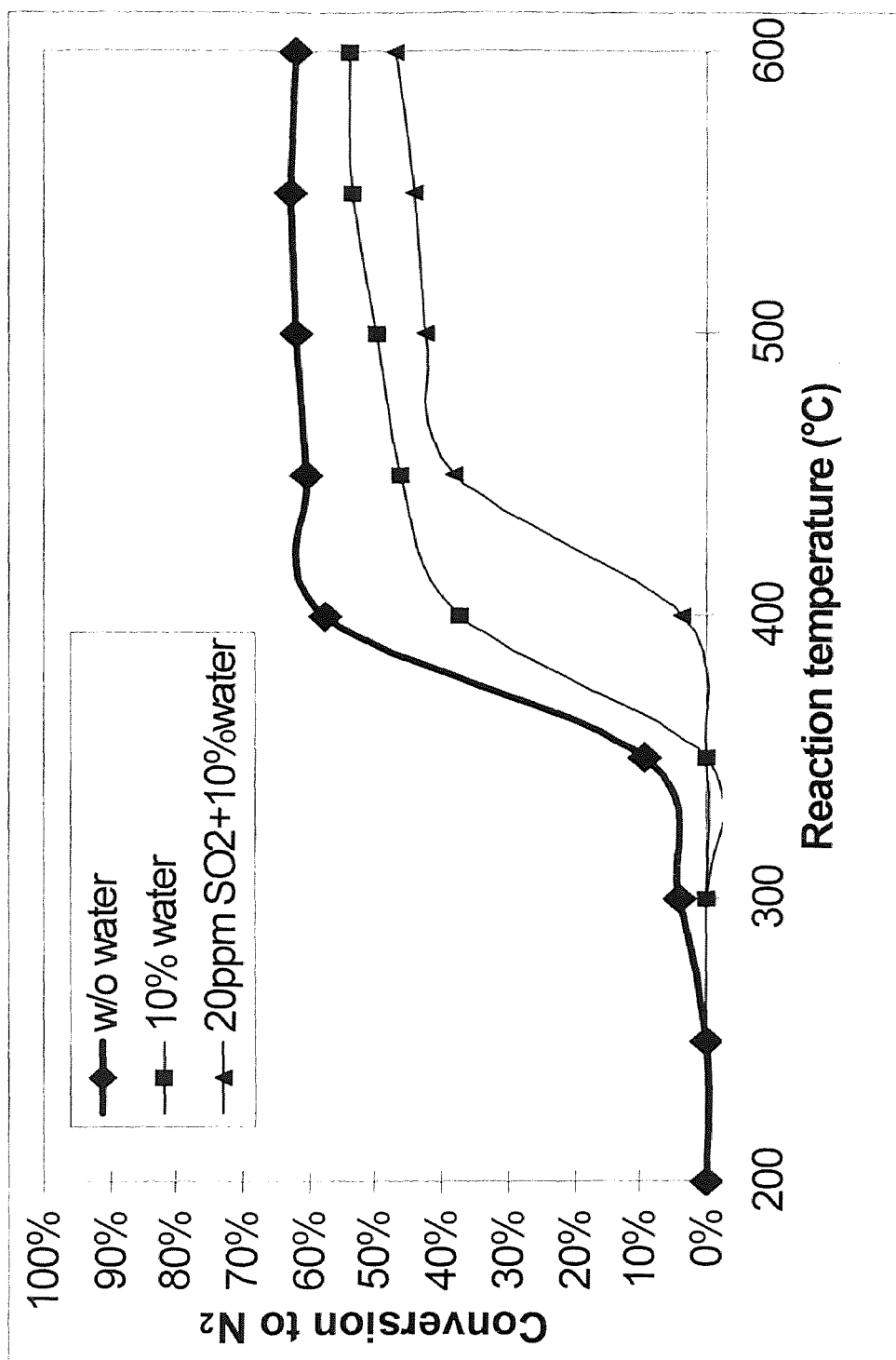
**Figure 3.9** Effect of CuO loading on reduction of NO by GAC,  
sv=50,000 /hr, [NO]=590 ppm, [O<sub>2</sub>]=10%



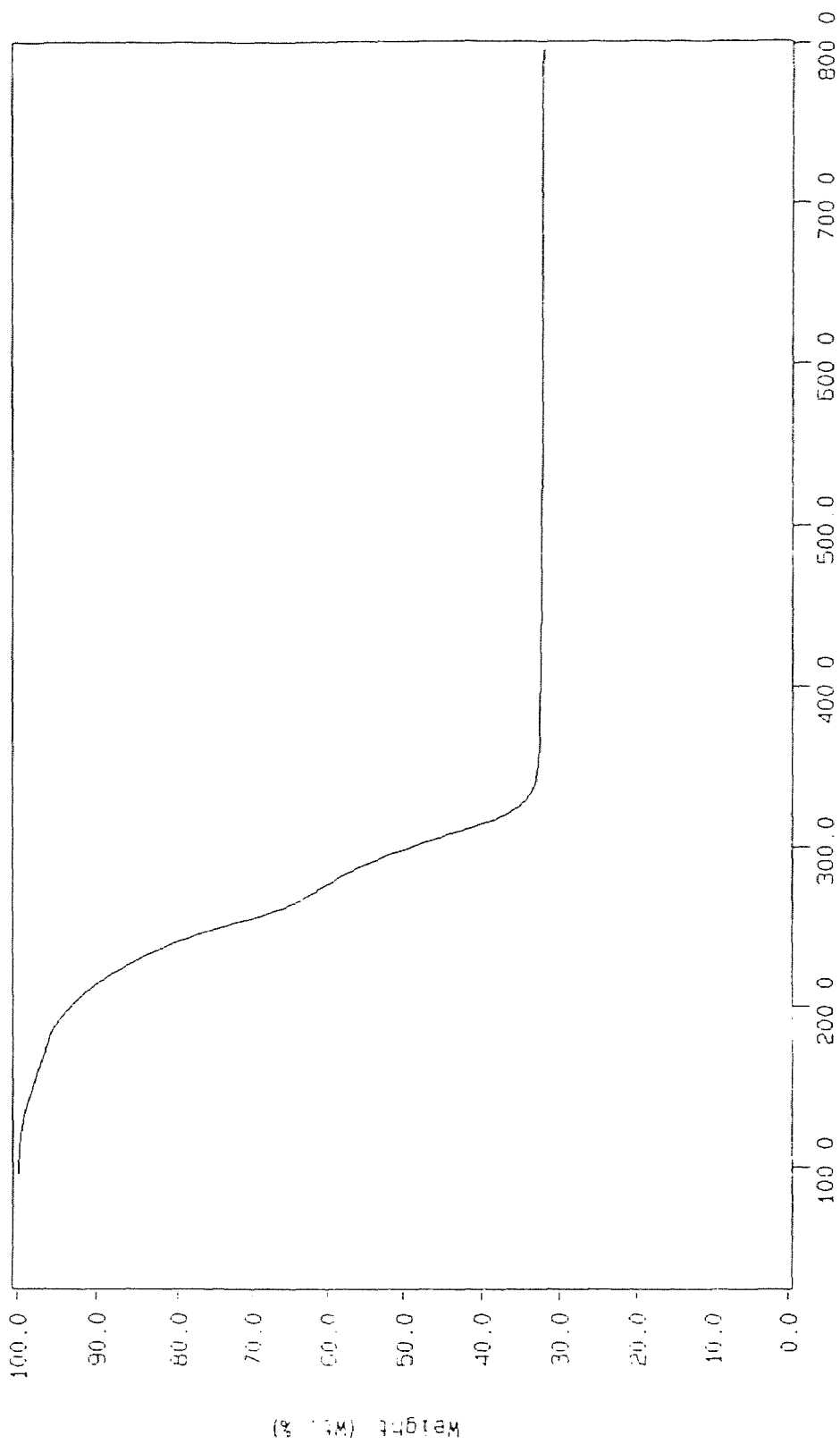
**Figure 3.10** Effect of space velocity on reduction of NO by 1% Cu-GAC, [NO]=590 ppm, [O<sub>2</sub>]=10%



**Figure 3.11** Effect of water vapor on reduction of NO by 1% CuO-GAC,  $sv=50,000/hr$ ,  $[NO]=590$  ppm,  $[O_2]=10\%$



**Figure 3.12** Effect of SO<sub>2</sub> on reduction of NO by 1% CuO-GAC, sv=50,000/hr, [NO]=590 ppm, [O<sub>2</sub>]=10%, [SO<sub>2</sub>]=20ppm



**Figure 3.13 TGA for decomposition of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  to  $\text{CuO}$**



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