# ABSTRACT

# THE REACTIONS OF $NO_x$ WITH DIESEL SOOT OVER CU-ZSM-5 CATALYST

by

**Shu Sun**

Air pollution from the exhaust of Diesel engines consisting of relatively high concentrations of $NO_x$ and particulates is a difficult problem to overcome because no fully effective technology to control these emission is available. The existing methods to reduce $NO_x$ and soot can not satisfy the provisions of the 1990 CAAA (Clean Air Act Amendment). Cu-ZSM-5, a catalyst in which Cu has been ion-exchanged with $H^+$, can catalyze the decomposition of NO to $N_2$ and $O_2$ and reduction to $N_2$ and $O_2$ with light hydrocarbons such as propene or Diesel soot in the presence of oxygen. The latter catalytic approach, refered to as lean $NO_x$ control, is attracting much attention in the automotive industry. Moreover, a new approach for using the catalyst to treat the exhaust from Diesel engines with a Rotating Fluidized Bed Reactor (RFBR) is being developed in Japan and at NJIT. This reactor captures soot at low power operation and reacts it with $NO_x$ at high power allowing "self-cleaning" of these emissions from Diesel engines.

In order to better understand the chemistry taking place between $NO_x$ and soot, a fixed bed was used to study the decomposition of $NO_x$ and the reaction of $NO_x$ with soot. The goal of the research is to find the optimal conditions that will allow maximum soot and $NO_x$ destruction. Differences in decomposition activity were compared between NO and $NO_2$ over Cu-ZSM-5, ZSM-5 and $SiO_2/Al_2O_3$. This was followed with experiments designed to study the ability of soot to reduce NO and $NO_2$ over the same catalyst. The effect of oxygen on the decomposition of $NO_x$ and reduction of $NO_x$ with soot was also evaluated.

# THE REACTIONS OF $NO_x$ WITH DIESEL SOOT OVER CU-ZSM-5 CATALYST

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To my beloved parents

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# CHAPTER 1

# INTRODUCTION

Diesel engines have been used for over sixty years since they were first introduced to road transport in the early 1930's. Because of their very favorable economic advantages and high combustion efficiency, Diesel engines are used widely all over the world primarily for trucks, but also in passenger automobiles and buses.

All fossil fuel burning automotive engines emit harmful emission. The exhaust from these 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. 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.

Air pollution is increasingly becoming a serious problem through the world. In urban areas, HC, CO and $NO_X$ are the major invisible pollutants. Compared with the exhaust from gasoline fueled internal combustion (IC) engines, Diesel engines emit higher concentrations of $NO_X$ and lower concentrations of CO and HC as a consequence of their higher combustion efficiency. In addition, unlike IC engines, Diesel engines emit a much higher concentration of particulates.

As early as in 1909, the need to control undesirable air emissions from automobile engines was recognized (Frankel, 1909). In 1970, the US 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 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 Act 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 current and proposed worldwide emission standards are summarized in Table 1.

**Table 1** Worldwide Diesel Emission Standards (unit: g/bhp-h) (Heck and Farrauto, 1995)

| Country/Year(Vehicle) | HC | CO | $NO_X$ | Particulate | HC + $NO_X$ |
|---|---|---|---|---|---|
| U.S./1991(truck) | 1.3 | 15.5 | 5.0 | 0.1 | |
| U.S./1994(truck) | 1.3 | 15.5 | 5.0 | 0.1, 0.07 Bus | |
| U.S./1998(truck) | 1.3 | 15.5 | 4.0 | 0.1 | |
| Calif./1998(truck) | 0.025 HCHO | | | 0.05(ULEV) | 2.5(ULEV) |
| Europe/1995(truck) | 1.1 | 4.0 | 7.0 | 0.15 | |
| Europe/1996(car) | | 1.0 | | 0.10(DI) | 0.9(DI) |
| Europe/1999(car) | | 0.5 | | 0.04 | 0.5 |
| Japan/1998(car) | | | 0.4 | 0.08 | |

U.S. truck: Heavy Duty FTP Transient Cycle, g/bhp-h(i.e.grams per brake horsepower generated in an hour), Europe truck: R-49 13 Mode. Europe car: Cycle A, g/km, DI=Dir. Inj. Japan car: 10 Mode, g/km, ULEV=Ultra Low Emi. Veh.

The present emissions of HC and CO from Diesel engines meet the California air quality standards, except for the concentration of $NO_X$ (Heck and Farrauto, 1995) which is often higher than the standard. Clearly, new vehicles meet all standards. It is just older vehicles that may not meet all standards. On the other hand, the public is objecting to smoke emitted from the Diesel engines because it is visible and has a characteristic smell. Therefore, the reduction of $NO_X$ and particulates has become a major research challenge.

The "particulate" defined by 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 per cent inorganic oxides (primarily sulfates) and 55 per cent liquids.(Heck 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 per cent unburned fuel and 35 per cent 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 per cent of $NO_X$ formed in combustion process consists of NO. Because Diesel engines operate under lean conditions (air is in excess of its stoichiometric requirement for combustion), the amounts of HC and CO generated are very small. Thus their concentrations usually satisfy the emission standards. However, other engine emissions increase as the air/fuel ratio increases slightly above stoichiometric. Thus $NO_X$ emissions increase due to the high flame temperature obtained from complete burning of fuel. At a temperature 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.(Shaw, 1974).

During the past several decades, a large R & D effort has been carried out to meet the provisions of 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 systems. 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 conbusion (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. (Siminski and Shaw, 1978).

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), vanadium for medium temperature (300 -- 450 °C), and zeolite for high temperature (350--600 °C). The major desired reactions are:

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (1\text{-}1)$$

$$4\,NH_3 + 2\,NO_2 + O_2 \rightarrow 3\,N_2 + 6\,H_2O \qquad (1\text{-}2)$$

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.

In 1979, the Three-Way-Catalyst (TWC) converter was first installed in gasoline burning IC vehicles. The catalytic converter was designed to operate within a narrow air-to-fuel ratio in order to simultaneously reduce HC, CO and $NO_x$. The narrow window of air-to-fuel is maintained between 14.5 to 14.6 kg air/kg fuel. The TWC converter is very successful in reducing pollutants from IC engines, but is not very effective for Diesel engines. The reason is that under lean conditions, the removal efficiency for CO and HC is very high but $NO_x$ is not affected. Moreover, particulate emissions tend to plug the channels of the catalytic converter and deactivate the catalyst. Therefore, TWC has not been applied to the exhaust from Diesel engines.

Cooper and Thoss (1990) designed a two-step process to reduce particulates from Diesel engine exhaust based on the higher oxidative reactivity of $NO_2$ over NO and $O_2$. The first step is to use a precious metal catalyst to convert NO to $NO_2$ and then use $NO_2$ to react with the particulates. This design increased the removal efficiency of particulates, but didn't reduce $NO_x$. This is a consequence of $NO_2$ being reduced by the soot to NO and not $N_2$.

The present approach to reduce the emissions from the exhaust of Diesel engines is a flow-through monolithic honeycomb catalyst that is structurally similar to that used in gasoline engines (Heck and Farrauto, 1994). It is designed to function only as a soot oxidation system which bootstraps SOF oxidation to also oxidize the solid carbon compound of soot, as follows. The reactions can be represented as follows:

$$\text{SOF} + \text{Air} \rightarrow CO_2 + H_2O + O_2 + N_2 \text{ (hot exhaust gas)} \qquad (1\text{-}3)$$

$$\text{Soot (carbon)} + \text{hot exhaust gas} + \text{Air} \rightarrow CO_2 + H_2O + O_2 + N_2 \qquad (1\text{-}4)$$

The SOF can be completely oxidized and eliminated from the solid matrix. However, sulfate particulate emissions are formed by oxidizing sulfur containing compounds in the fuel.

The objective is to have the catalyst oxidize the SOF without oxidizing the sulfur containing compounds to sulfate, a particulate which poses health hazards. The catalysts used in this application are precious metals such as Pt and Pd. In addition, for such a system to function, the dry soot also has to be oxidized to eliminate plugging of the monolith channels.

In recent years, the application of zeolites has been one of the most exciting developments in catalysis. Transition metal exchanged zeolites were found to be very active for reducing $NO_X$. Of these, Cu-ZSM-5 is one of the most active. In fact, as early as 1989, Cu-ZSM-5 was disclosed in the technical literature by Iwamoto et al., (1989 ). It was shown that catalytic decomposition of NO occurs over various Cu ion-exchanged zeolites. The catalytic activity of excessively copper ion-exchanged ZSM-5 zeolite was found to be very high at 573 to 823 K even for NO reduction in the presence of oxygen. In the 1990's, Sato, et al. (1991); Cho (1993); and Liu and Robota (1994), reported that different hydrocarbons can be used to reduce NO over Cu-ZSM-5. These results show Cu-ZSM-5 has very high activity for the reaction of NO with hydrocarbons and this activity is enhanced in the presence of oxygen. Therefore, it can be concluded that Cu-ZSM-5 not only catalyzes the decomposition of NO, but also promotes the NO-hydrocarbon reaction.

The reactions between NO and carbon were examined by many researchers (Iuni, et al., 1982; ; Teng, et al., 1992; Chu and Schmidt, 1993; and Illan-Gomez, et al., 1993). Their results show that the reaction of NO with carbon is first order with respect to NO partial pressure and proportional to the total surface area of carbon.

These results are very encouraging, because particulate matter emitted from Diesel engines consisting mainly of SOF and dry carbon can be oxidized to $CO_2$. Furthermore, discussed above, Tsutsumi, et al., (1993, 1994) succeeded in using copper ion-exchanged ZSM-5 as the fluidized solids in a rotating fluidized bed reactor to simultaneously remove soot and catalytically react it with $NO_X$ from the exhaust of a Diesel engine. They found that at a temperature of 693 K, the filter became "self-cleaning," i.e., the captured soot particles on the catalyst granules reacted with the NO in the exhaust gas removing NO and soot simultaneously. These results are very exciting and suggest that a properly designed RFBR can be used to effectively simultaneously remove soot and $NO_X$. Such a device has enormous potential for reducing air pollution from mobile Diesel sources in a relatively simple and inexpensive manner. Therefore, our current research project entitled "Simultaneous Removal of Soot and $NO_X$ from the Exhaust of Diesel Powered Vehicles Using a Rotating Fluidized Bed Reactor." is under way. As a part of the project, this thesis, is directed at finding the optimal parameters for promoting the decomposition of $NO_X$ , and determining the products from the reduction of $NO_x$ with soot. This research is conducted with laboratory equipment consisting of a 2.5 cm packed-bed flow reactor and a thermal gavimetric analyzer (TGA).

# CHAPTER 2

# EXPERIMENTAL

## 2.1 Instruments and Chemicals

The apparatus, equipment and analytical instruments used in this research is described in this chapter.

### 2.1.1 Reactor

Most experiments were performed using a fixed bed in a quartz tubular reactor. The reactor consists of a 2.5 cm diameter by 55 cm longer quartz tube. The bed materials consisting of catalyst, soot or a mixture of both were placed on a 90 - 150 µm coarse porous quartz disk located at about two-thirds of the height of the reactor. The reactant gases enter into the reactor from top and are discharged from the bottom. The quartz reactor is placed in a three zone electric furnace with three independent temperature controllers. The multizone furnace was used to preheat the gases entering the central section that contains the solids and prevent condensation of the efflents. Thus, the middle zone has a very uniform temperature profile. The actual temperature profile of the bed was measured by a calibrated thermocouple inserted into the top of the catalyst bed. The flowrate of the feed gases is measured with calibrated rotometers.

### 2.1.2 TGA

The Thermal Gravimetric Analyzer (TGA) used is a Perkin-Elmer TGA 7. It is a computer-controlled laboratory instrument used in a broad range of applications dealing with measuring the change in mass of a solid due to a reaction with a gas as a function of time or temperature. Under computer control, TGA experiments can be performed over a wide range in temperature up to 1000 °C and measures changes in mass resulting from chemical reactions to 0.1 μg.

The TGA consists of two major components: a sensitive ultra-microbalance and furnace element. The microbalance operates as a high gain electromechanical servo system which permits the measurement of weight changes as small as 0.1 μg. Therefore, the TGA can be used to examine the effects of different catalysts and gases on soot removal.

### 2.1.3 Gas Chromatography

Gas chromatography (GC) is the most common analytical technique for the quantitative determination of organic compounds. 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). Two different columns, molecular sieve 5A with mesh of 60/80 for TCD and Porapak Q with mesh of 80/100 for FID, were used. A catalytic converter is mounted on the FID side to convert CO and $CO_2$ into $CH_4$ to increase the sensitivity to these fixed gases. TCD was used to measure nitrogen and oxygen. A six point gas sampling valve was used to inject the gas sample with a loop of 20 $mm^3$. The oven temperature of the GC was controlled at 28 °C so that $N_2$ and $O_2$ peaks can be adequately separated. The integration of the chromatographic peaks is performed with two HP 3396A integrators. Several standard gases containing known concentrations of CO, $CO_2$, $N_2$ and $O_2$ were used to calibrate the GC.

### 2.1.4 $NO_x$ Analyzer

A chemiluminescent NO/$NO_x$ analyzer manufactured by Thermo Electron Corp. was used to measure gaseous NO and $NO_x$. By taking the difference between $NO_x$ and NO, one obtains the quantity of $NO_2$ in the gas stream.

The instrument functions based on the following chemiluminescent reaction of NO and $O_3$:

$$NO + O_3 \rightarrow NO_2 + O_2 + h\nu \qquad (2\text{-}1)$$

Light emission results when the electronically excited $NO_2$ molecules revert to their ground state.

To measure NO concentration, the gas sample to be analyzed is blended with $O_3$ in the instrument's reaction chamber. The resulting chemiluminescence is monitored through an optical filter by a high-sensitivity photomultplier positioned at one end of the chamber. The filter/photomultiplier combination responds to light in a narrow-wavelength band unique to the above reaction (hence, no interference). The output from the photomultiplier tube is linearly proportional to the NO concentration.

To measure $NO_x$ concentration (i.e., NO plus $NO_2$), the sample gas flow is diverted through an $NO_2$-to-NO thermal converter that is operated at 650 °C. The original NO plus the NO from the thermal decomposition of $NO_2$ are analyzed as NO. Thus, by difference, one can determine the concentration of $NO_2$ in the feed stream.

A minimum gaseous flowrate of 2 SCFH (about 1 $dm^3$/min.) is required by the instrument to measure NO and $NO_x$.

### 2.1.5 Chemicals

Gases: Supplied by Matheson Gas Products.

NO: 1200 ppm (in He)

$NO_2$: 490 ppm (in He)

$O_2$: 99.6 %

He: 99.995 %

Soot: Collected from a filter located in the exhaust pipe from the Diesel engine in our laboratory. It is a black powder with a bulk density of 0.20 $g/cm^3$.

Catalysts: Supplied by Mobil Research and Development Company.

Cu-ZSM-5: Solid powder with light-yellow color. The catalyst consists of 50 % Cu-ZSM-5 and 50 % $SiO_2/Al_2O_3$ which is a cracking catalyst. The ZSM-5 has been treated to ion exchange the $H^+$ with $Cu^{2+}$. The $Cu^{2+}$ exchange level is 100 % in the ZSM-5.

ZSM-5: Solid powder with yellow color. The same material as above but without exchanging the $H^+$ with $Cu^{2+}$.

$SiO_2/Al_2O_3$: Solid powder with yellow color.

## 2.2 Experimental Procedure

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

All experiments were performed in a 2.5 cm quartz fixed bed reactor or with the TGA.

### 2.2.1 Fixed Bed

The studies of the decomposition of NO and $NO_2$, and the reaction between soot and NO and $NO_2$ were carried out in the quartz fixed bed reactor mentioned above. The catalyst, soot, or a combination of both solids was placed on a porous disk inside the reactor and heated to 150 $^{o}C$ for 1 hour under He flow (about 100 $cm^3$/min.) in order to remove impurities such as oxygen and water which may have adsorbed on the solid materials. An experiment is started by switching the gas flow through the bed from He to NO, $O_2$ or $NO_2$ . After about 2 to 3 minutes, the effluent gaseous composition is measured with the GC and $NO_x$ analyzer.

For the decomposition of $NO_x$, 1 $cm^3$ (0.8 g) Cu-ZSM-5 is used. The flowrate of the NO mixture is varied to obtain different space velocities. For the NO-soot reaction, 1 $cm^3$ (0.2 g) soot is used. For the NO/catalyst/soot reactions, a mixture of 1 $cm^3$ Cu-ZSM-5 and 1 $cm^3$ soot( soot is 20 % wt. of the mixture) is used. The mixture of soot and Cu-ZSM-5 is blended with a glass rod on the quartz fritted disc.

In order to maintain the same concentration of NO when different concentrations of $O_2$ are introduced, the 1200 ppm NO mixture is diluted with He to 1080 ppm.

The experiments conducted in the fixed bed reactor are marked in Table 2:

**Table 2** Experiments in the Fixed Bed Reactor

| Experiments | Soot | Cu-ZSM-5 | NO | $O_2$ | $NO_2$ |
|---|---|---|---|---|---|
| 1 A | + | | + | | |
| 1 B | + | | + | | |
| 1 C(2)$^{(1)}$ | + | | + | | |
| 1 D | + | | + | | |
| 2 A | + | | | + | |
| 2 B | + | | | + | |
| 2 C(2) | + | | | + | |
| 2 D | + | | | + | |
| 3 A | + | | + | + | |
| 3 B(2) | + | | + | + | |
| 3 C(2) | + | | + | + | |
| 3 D | + | | + | + | |
| 4 A | + | | | | + |
| 4 B | + | | | | + |
| 4 C | + | | | | + |
| 4 D | + | | | | + |
| 5 A | | + | + | | |
| 5 B(2) | | + | + | | |
| 5 C(2) | | + | + | | |
| 5 D | | + | + | | |

| | | | | |
|---|---|---|---|---|
| 6 A | + | | + | |
| 6 B | + | | + | |
| 6 C | + | | + | |
| 6 D | + | | + | |
| 7 A | + | + | + | |
| 7 B(2) | + | + | + | |
| 7 C(3) | + | + | + | |
| 7 D | + | + | + | |
| 8 A | + | | | + |
| 8 B | + | | | + |
| 8 C(2) | + | | | + |
| 8 D | + | | | + |

+ indicates component present

(1) the number in the parentheses indicates the number of runs made, no number indicates that the experiment was run only once.

All the experiments were run at the following temperatures 200 (A), 300 (B), 400 (C) and 500 (D) °C.

### 2.2.2 TGA

Experiments were performed to examine soot removal as a function of either time or temperature.

After the empty TGA pan is weighed to adjust sample zero, the solid sample is loaded. Then the furnace temperature is raised to 140 °C and maintained for 20 minutes with He flow to remove water and other volatile impurities adsorbed on the sample.

Then, for the experiments measuring rate of soot reaction as a function of temperature, a temperature program from 140 to 1000 °C at 40 °C/min. is initiated. At the same time, the reactant gas is passed into the furnace containing the microbalance and solid reactant. For the experiments examining soot removal as a function of time, the temperature is raised to 400 °C at a temperature ramp of 20 °C/min., then the reacting gas is introduced into system to start the experiment. During the experiment, the temperature is maintained at a constant at 400 °C for 20 minutes.

Seven kinds of solid samples and five reactant gases were evaluated. They are:

Solid samples:

Soot, Cu-ZSM-5, ZSM-5, $SiO_2/Al_2O_3$, Cu-ZSM-5+soot, ZSM-5+soot, $SiO_2/Al_2O_3$+soot

Gas reactants (the following concentrations of gases were used by diluting the analyzed mixtures from the gas cylinders):

He, $O_2$( 10 % ), NO( 200 ppm), NO+$O_2$ (NO: 200 ppm, $O_2$: 10%), $NO_2$(200 ppm)

The mixtures of catalyst and soot are blended on a watch glass with a glass stirring rod before they were loaded onto the TGA pan. NO was diluted with He from 1200 to 200 ppm and $NO_2$ from 490 to 200 ppm using rotometers. Consequently, the dilution accuracy is no better than ±10 %.

Almost the same weight of solid sample, 5.5 to 6.0 mg soot, 10.0 to 10.5 mg catalyst or a mixture of soot and catalysts, is used. The mixture of soot-catalyst contains 10.0 to 10.1 %(wt.) soot.

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

The experiments conducted on TGA are marked in Table 3.

**Table 3** TGA Experiments were run at either constant temperature of 400 °C and 20 minutes, or as a function of temperature to 1000 °C at 40 °C/min.

| | He | NO | $NO/O_2$ (1) | $O_2$ | $NO_2$ |
|---|---|---|---|---|---|
| Soot | + | + | + | + | + |
| Cu-ZSM-5 | + | + | + | + | + |
| ZSM-5 | + | + | + | + | + |
| $SiO_2/Al_2O_3$ | + | + | + | + | + |
| Cu-ZSM-5 + Soot | + | + | + | + | + |
| ZSM-5 + Soot | + | + | + | + | + |
| $SiO_2/Al_2O_3$ + Soot | + | + | + | + | + |

+ indicate component present

(1) This group experiments were run twice.

# CHAPTER 3

# RESULTS AND DISCUSSION

## 3.1 Decomposition of $NO_x$

### 3.1.1 Decomposition of NO

The desired reaction for NO decomposition is:

$$2NO \rightarrow N_2 + O_2 \qquad \Delta H° = -43.2\ \text{kcal/mol} \qquad [3\text{-}1]$$

This homogenous reaction is exothermic. The free energy increases with temperature, so the equilibrium constant decreases as temperature increases. The equilibrium constant $Kp=10^{10}$ at 800 K and $Kp=10^{7}$ at 1150 K. Consequently, one would expect the catalytic reaction to accelerate the approach to equilibrium.

In order to measure the catalytic activity of Cu-ZSM-5, the fixed bed reactor described in Chapter 2 was used to study the decomposition of NO both in the presence and absence of oxygen. Because space velocity and temperature are the major parameters that affect the decomposition of NO, the experiments were performed as a function of space velocity (SV) and temperature. Figures 1, 2 and 3 show the relationships between conversion and temperature both in the absence and presence of oxygen. It can be shown from these figures that the higher the SV, the lower the conversion of NO to $N_2$ and $O_2$. The reason is that at higher SV, the residence time of the reaction gases such as NO and $O_2$ is not long enough for the complete reaction of the gases on the surface of Cu-ZSM-5.

Figures 1 and 2 show that the rate of conversion starts to increase at 300 °C to a peak in the 400 to 500 °C range for $N_2$ production and 450 °C for $O_2$ production. The highest conversions are 26.8 % for $N_2$ and 22.0 % for $O_2$. At temperature above 450 °C activity decreases. The decreasing activity at higher temperature is attributed to sintering of Cu-ZSM-5. Alternatively, the reaction rate increases with temperature from 300 to 450 °C and then become themodynamically limited. These results are consistent with those reported in the literature (Iwamoto et al., 1991). The difference of conversion to $N_2$ and $O_2$ results from the formation of $NO_2$ at 450 °C (Iwamoto, et al., 1989). It should be noted, however, that the equilibrium constant for the formation of $NO_2$ becomes less than one at approximately 500 °C and the Gibbs free energy goes to zero.

According to reaction equation [3-1], the same volume and number of moles of $N_2$ and $O_2$ should be released. However, Figures 1 and 2 show that more $N_2$ than $O_2$ is formed. This phenomenon suggests that some other byproducts are produced. $NO_2$ and $N_2O$, are probably the important byproducts.

$NO_2$ is formed according to the following reaction:

$$2NO + O_2 \rightarrow NO_2 \qquad \Delta H^{\circ}=-27.3 \text{ kcal/mol} \qquad [3\text{-}2]$$

This reaction consumes $O_2$ released from the decomposition of NO and therefore reduces the amount of $O_2$ present.

The rate constant k in the reaction [3-2] is $1.2 \times 10^{9} \exp^{[4390/RT]} \text{cm}^{6} \text{ mol}^{-2} \text{ s}^{-1}$ (R in J $\text{mol}^{-1}$ K) (Baulch, D. L., 1973), which shows that the decomposition of NO has a negative temperature coefficent, i.e., it becomes less important at high temperature. The rate of decomposition of NO can be expressed as:

$$-d(NO)/dt = 2\ k\ [O_2][NO]^2 \qquad [3\text{-}3]$$

When the oxygen concentration is much larger than the NO concentration, the NO concentration after decomposition can be calculated according to the following equation (Shaw, 1976):

$$X_{NOF} = 1/[1/X_{NO(I)} + 2kX_{O2}(P/RT)^2t] \qquad [3\text{-}4]$$

$X_{NOF}$ : final NO in mole fraction

$X_{NOI}= 1.08 \times 10^{-3}$ , initial NO in mole fraction

$X_{O2} = 0.1$, the mole fraction of $O_2$

$R= 8.31$ J $mol^{-1}$ $s^{-1}$, gas constant

$P= 1.013 \times 10^5$ Pa, pressure

T: K, temperature

t = 1/SV=3600/2202=1.63 s, residence time

Moreover, the conversion of NO to $NO_2$ at SV of 2202 (1/h) can be calculated from the following equation:

$$\text{Conversion to } NO_2\ (\%) = 2kX_{O2}X_{NOF}t\ (P/RT)^2 \qquad [3\text{-}5]$$

Using equation [3-4] and [3-5], we can obtain the conversion of NO to $NO_2$ at SV of 2202 (1/h) in the presence of 10 % $O_2$. The results and the practical conversions to $N_2$ are listed in Table 4. Table 4 shows that the conversion to $NO_2$ decreases with increasing temperature while the conversion to $N_2$ increases with increasing temperature.Table 4 confirms that the formation of $NO_2$ becomes less important at high temperature. Furthermore, the very low conversion to $NO_2$ indicates $NO_2$ is not a major product of NO decomposition.

**Table 4** Conversion of NO into $NO_2$ and $N_2$ in the presence of 10 % $O_2$

| Temp.(°C) | Conv. to $NO_2$ (%) (calculated) | Conv. to $N_2$ (%) (measured) |
|---|---|---|
| 200 | 0.085 | 3.88 |
| 300 | 0.048 | 5.14 |
| 350 | 0.038 | 13.29 |
| 400 | 0.030 | 15.99 |
| 450 | 0.025 | 16.21 |
| 500 | 0.021 | 16.04 |

Another byproduct, $N_2O$, is an intermediate in the decomposition of NO (Iwamoto, et al., 1989). Actually, NO decomposes to $N_2O$, and $N_2O$ decomposes further to $N_2$ and $O_2$. according to the following reaction equations,

$$4NO \rightarrow 2N_2O + O_2 \qquad \Delta H° = -47.1 \text{ kcal/mol} \qquad [3\text{-}6]$$

$$2\,N_2O \rightarrow 2\,N_2 + O_2 \qquad \Delta H° = -39.2 \text{ kcal/mol} \qquad [3\text{-}7]$$

Accordingly, the formation of $N_2O$ produces $O_2$, which would shift the balance towards equimolar production of $N_2$ and $O_2$.

Therefore, the formation of $NO_2$ and $N_2O$ are contradictory with regard to oxygen production and consumption. Since $N_2O$ and $NO_2$ are formed during the decomposition of NO, the difference in the amount of $N_2$ and $O_2$ results from the competition of the two reactions above. If reaction [3-2] dominates reactions [3-6] and [3-7], the amount of $O_2$ will be lower than $N_2$. At temperatures above 350 °C, the decomposition of $N_2O$ is faster than that that of NO, and $N_2O$ is converted into $N_2$ and $O_2$ as soon as NO is converted into $N_2O$. Thus reaction [3-2] dominates, therefore the amount of $N_2$ is larger than that of $O_2$.

### 3.1.2 Effects of $O_2$

Figure 3 shows the conversion of NO in the presence of 10 % $O_2$ to $N_2$ as a function of temperature for the three space velocities considered above. Comparing these results with those in Figure 1, it can be inferred that at the same space velocity, the conversion to $N_2$ when $O_2$ is present is lower than that in the absence of $O_2$. This indicates that the presence of 10 % $O_2$ affects the decomposition of NO. This is in agreement with the results of Zhang et al.(1994).

Figure 4 shows the effects of $O_2$ mole per cent concentration on the conversion of NO at different temperatures and at a space velocity of 2202 (1/h). As shown in this figure, the conversion to $N_2$ at a constant space velocity decreases with increasing $O_2$ mole per cent. The Law of Mass Action indicates that as product concentrations increase, they drive the reverse reaction. Therefore, excess $O_2$, a product of the reaction, will tend to decrease the decomposition of NO and reduce the conversion of NO to $N_2$ and $O_2$. Thus, the higher the $O_2$ concentration, the lower the conversion.

In order to understand the change of NO concentration during the decomposition, another experiment as a function of temperature was run at a much higher space velocity (60000 1/h). The results of NO conversion to $N_2$ were similar to those at low SV but lower conversions were observed. Figure 5 shows the amount of NO converted decreases as a function of temperature and $O_2$ concentration. It reaffirms that the presence of $O_2$ reduces conversion of NO as discussed above. Figure 6 confirms that $NO_2$ is produced when $O_2$ is present and shows that there is no obvious difference of $NO_2$ mole per cent when $O_2$ concentration is increased from 4.2 to 8.3 %. The reason is that the concentration of $O_2$ is not the rate determining step in the decomposition of NO. Figure 6 also indicates that $NO_2$ concentration increases with increasing temperature when $O_2$ is present. However $NO_2$ is the more thermodynamically stable compound at low temperature. The results in Figure 6 imply that Cu-ZSM-5 plays a key role in the decomposition of NO. When $O_2$ is absent, no $NO_2$ was found. This seems to be contradictory to the results presented above and those of Iwamoto et al., 1989. In fact, the rate of reaction of NO with $O_2$ to $NO_2$ is low. When the space velocity is very high, there is not enough time for NO to react with $O_2$. That is why no $NO_2$ is found at very high space velocity unless $O_2$ is already present in the reactant gases..

### 3.1.3. Decomposition of $NO_2$

$NO_2$ is more reactive than NO and is a stronger oxidant. The decomposition of $NO_2$ was examined using the same method as that for NO. All the experiments were run at two different space velocities of 19300 (1/h) and 3800 (1/h).

Figure 7 shows the overall conversion of $NO_2$ into all products and specifically into NO at a space velocity of 19300(1/h) as a function of temperature. As seen from this figure, at temperatures between 350° and 600 °C, $NO_2$ is converted only to NO. However, at temperatures lower than 350 °C, there is a slight difference between the moles of $NO_2$ converted and moles of NO formed. A possible reason for the low temperature difference could be that $N_2O$ is produced and this reaction consumes some of the $NO_2$ converted, as discussed above. As reported in the literature (Iwamoto et al., 1991). $N_2O$ is the intermediate of the decomposition of NO. The reaction described by equation [3-1] is a global reaction, which could include at least two global steps described by reactions [3-6] and [3-7].

At temperatures above 350 °C, the decomposition of $N_2O$ is faster than that of NO. $N_2O$ is converted into $N_2$ and $O_2$ as soon as NO is converted into $N_2O$. In other words, the step reaction [3-6] is the rate determining step of the decomposition of NO at high temperatures.

As shown in Figure 7, NO is the major product of decomposition of $NO_2$, especially at high temperature and it is possible that NO produced from $NO_2$ to decompose further to $N_2$ and $O_2$. Therefore, an experiment of the decomposition of $NO_2$ was run at lower SV to allow enough time for NO to decompose into $N_2$ and $O_2$. The results are shown in Figure 8.

From this figure, one can see that compared with the decomposition of NO shown in Figures 1 and 2, much less volume per cent of $N_2$ and $O_2$ are released in the decomposition of $NO_2$. The step reactions are:

$$4NO_2 \rightarrow 4NO + 2O_2 \qquad [3\text{-}8]$$

$$4NO \rightarrow 2N_2O + O_2 \qquad [3\text{-}9]$$

$$2N_2O \rightarrow 2N_2 + O_2 \qquad [3\text{-}10]$$

The global reaction is :

$$2NO_2 \rightarrow N_2 + 2O_2 \qquad [3\text{-}11]$$

The reason for the low volume per cent of $N_2$ and $O_2$ is that the step reaction [3-9] is the rate controlling step of the decomposition of NO at high temperatures and it takes most of the retention time on the surface of catalyst. There is not enough time left for the production of $N_2$ and $O_2$, which were released to some extent by the reaction at temperatures of over 400 °C.

Like the decomposition of NO, Figure 8 shows that the amount of $N_2$ produced is different from that of $O_2$. The $O_2$ concentration is much higher than the $N_2$ concentration. At high temperature, $N_2O$ decomposes very fast and is not the rate controling step of the reaction. Because the life time of $N_2O$ is very short at temperatures above 350 °C, no $N_2O$ can be measured. On the other hand, the NO produced from $NO_2$ can continue to decompose to produce $N_2$ and $O_2$. Therefore, every step of the decomposition of $NO_2$ produces $O_2$. As a result, the $O_2$ concentration is much higher than that of $N_2$. Figure 8 shows the ratio of $O_2$ to $N_2$ decreases with temperature and reaches 2 at 600 °C; that is consistent with equation [3-11].

## 3.2 Reactions between Soot and $NO_x$

The reactions between soot and $NO_x$ are very complicated because of the complex composition and structure of soot. As a result, the catalytic reactions are also complicated. The major products in the $NO_x$/soot reactions include: $N_2$, $O_2$, NO, $NO_2$, CO, $CO_2$. The minor products including $N_2O$ and HCN have also been observed.

The experiments were run in the fixed bed reactor under both catalytic and non-catalytic conditions. Four gas mixtures were used which include, NO, NO/$O_2$, $NO_2$ and $O_2$. The gases flowed through the reactor which contained soot and Cu-ZSM-5 catalyst, The inlet gas flowrate is 270 $cm^3$/min.

### 3.2.1 Conversion to $N_2$

Figures 9 and 10 show the conversion to $N_2$ of the different gases as a function of temperature at a space velocity of 16200 (1/h) in the presence and absence of Cu-ZSM-5. From these figures, we can show that no $N_2$ is produced from $NO_2$ and $O_2$ regardless of the presence of Cu-ZSM-5. But this is not true for the NO/soot and the NO/$O_2$/soot systems.

When Cu-ZSM-5 is not present, $N_2$ begins to be produced at around 300 °C and the amount reaches a maximum at 400 °C for NO only. However, the amount of $N_2$ produced increased monotonically with increasing temperature to 500 °C in the NO/10%$O_2$ system. This result indicates the reaction between soot and NO proceeds although the rate is low (Chu et al., 1993). It is interesting that the conversion to $N_2$ is lower when 10% $O_2$ is present below 470 °C. The reason is that some soot reacts with $O_2$ instead of NO because of the much higher concentration of $O_2$, thereby lowering the conversion to $N_2$. When the temperature is higher than 400 °C, the rate of soot/$O_2$ reaction is very fast. Most of the soot reacts with $O_2$ to form CO and $CO_2$. Much less soot reacts with NO to produce $N_2$. That is why less $N_2$ is formed at 500 °C. The following section will show that the concentration of CO and $CO_2$ were increased at high temperature. $NO_2$ is a stronger oxidizing agent than NO but the major product of decomposition reaction is NO. Therefore no $N_2$ is measured. The $O_2$/soot reaction is an oxidation reaction, so no $N_2$ is produced.

Comparing Figure 10 with Figure 9, it can be seen that the presence of Cu-ZSM-5 promotes the conversion to $N_2$ for both the NO and the NO/10%$O_2$ systems to a much higher degree than just the soot system. Cu-ZSM-5 accelerates the reaction rates between soot and NO. This result is in agreement with the results of reactions between NO and hydrocarbons as reported in the literature (Tsutsumi, et al., 1994). Almost half of the mass of soot is composed of SOF which includes unburned Diesel fuel. Because Diesel fuel consists mainly of hydrocarbons, a similar result was expected. Figure 10 also shows that the highest catalytic activity of Cu-ZSM-5 appears at around 400 to 450 °C. This experiment confirms the fact that the reaction between soot and NO over Cu-ZSM-5 is enhanced by $O_2$.

Many researchers (Inui, et al., ; Teng, et al., 1992; and Chu and Schmidt, 1993; 1982; Illan-Gomez, et al., 1993) examined the reactions between carbon and $NO_x$ and found carbon can effectively reduce $NO_x$ in spite of the low reaction rate. Chu and Schmidt (1993) found that there is a high melting point $(CN)_x$ polymer formed during NO/graphite reactions. This polymer can be formed at about 450 °C and can deposit on the surface of graphite. Thereby it hinders further reactions between graphite and $NO_x$. A similar situation can occur for the soot/$NO_x$ reactions at 450 °C or lower temperature because of the similarities in the structure of graphite and soot. $(CN)_x$ or some other unknown compounds may form and deposit on the surface of the soot. That is why the rate of NO/soot reaction is not very fast. When $O_2$ is present, it is possible that $O_2$ can destroy the polymer $(CN)_x$ or the unknown compounds by oxidation at around 400 °C.

TGA experiments in the following section will show that when NO and $O_2$ were introduced into soot/catalyst systems simultaneously, the rate of weight loss is low in the beginning but increases several minutes later. This result supports the possibility of the formation of $(CN)_x$ or some other compounds. In the initial phases of the reaction, because NO reacts with soot faster than $O_2$, the deposit will be formed first. At the same time, $O_2$ begins to oxidize the deposit at a lower rate. When the compounds which are able to form a deposit are consumed by NO, no new deposit is formed and $O_2$ continues to oxidize the deposit until it is completely removed. Thus, soot can react with NO faster. This is a possible hypothesis of why the $NO_x$/soot reactions can be enhanced by oxygen.

### 3.2.2 CO and $CO_2$/CO

The composition of soot is very complicated. C and H are its major elements. At high temperature, especially when $O_2$ is present, the $NO_x/O_2$/soot system will form CO and $CO_2$. The reactions can be expressed by the following chemical reaction equation (not balanced):

$$NO_x + \text{Soot} + O_2 \rightarrow CO + CO_2 + N_2 + NO + \text{others} \qquad [3\text{-}12]$$

As we know, CO is an air pollutant and should be reduced as much as possible.

Figures 11 and 12 show the relationship between CO concentration and temperature both in the absence and presence of Cu-ZSM-5 catalyst. For both catalytic and non-catalytic systems, the mole % of CO is increased with increasing temperature. When 10 % $O_2$ is present, the concentration of CO is much greater than that observed without 10 % $O_2$, especially at temperatures above 400 °C. This result implies that the soot/$O_2$ reaction dominates all of the reactions above 400 °C. According to the results reported in literature (Chu and Schmidt, 1993), the reaction rates with carbon decrease in the order of: $NO_2 > N_2O > NO > O_2$. But in the experiments reported here, the mole % of $O_2$ used is 10%

which is much higher than that of NO or $NO_2$. Therefore, $O_2$ contribute more than NO in the formation of CO. From Figures 11 and 12, it is also found that the mole % CO, formed from reaction with soot, in an $NO/O_2$ system, is higher than that with $O_2$ alone both in the presence and absence of the catalyst. A possible explanation for this observation is that NO can promote the soot/$O_2$ reaction, thereby more CO is formed. Since $NO_2$ is a stronger oxidant than NO, and although its concentration is 490 ppm, lower than that of NO, more CO is emitted than that from NO.

The ratios of $CO_2$ to CO for different reaction systems, under the conditions mentioned above, are very interesting. Figures 13 and 14 show the relationship between the ratio of $CO_2$ to CO and temperature. For $NO_2$, the ratio of $CO_2$/CO decreases as temperature increases both in the catalytic and non-catalytic systems. The reason is that $NO_2$ reacts with soot or decomposes directly over Cu-ZSM-5 to form CO, NO and $O_2$. The higher the temperature, the larger the mole % CO in the effluent. On the other hand, the $O_2$ emitted from the $NO_2$/soot reaction is not enough for the complete conversion of CO to $CO_2$. Therefore, the ratio of $CO_2$ to CO decreases.

For NO, the ratio of $CO_2$ to CO is almost a constant at different temperatures both in the catalytic and non-catalytic system. The reaction rate of the NO/soot reaction is slow for low concentrations of NO. The quantity of CO released by the NO/soot reaction is lower than that from the $NO_2$/soot reaction. The $O_2$ released matches the mole per cent CO. Thus, the ratio of $CO_2$/CO is almost the same at different temperatures. However, when 10 % $O_2$ is introduced into NO/soot system, much more $CO_2$ is produced due to the high concentration of $O_2$, especially at high temperatures. Therefore the ratio of $CO_2$ to CO increases as temperature increases.

For $O_2$, when compared to the NO/$O_2$/soot system, the ratio of $CO_2$ to CO follows the same trend, but the ratio is slightly lower. The reason is that the $O_2$/soot reaction dominates all of the reactions due to its much higher concentration and NO may promote the $O_2$/soot reaction.

### 3.2.3 Conversion of NO and $NO_2$

In order to examine the mole per cent change of NO in the NO/soot reaction, an experiment at high space velocity of 60000 (1/h) was run both in the absence and presence of Cu-ZSM-5. The results were shown in the Figures 15 and 16. It can be seen that both for the catalytic and non-catalytic reactions, the higher the temperature, the more NO is converted. When the temperature is below 300 °C, a relatively small difference in conversion occurs between the non-catalytic and catalytic systems. This result indicates that Cu-ZSM-5 has lower activity for the NO/soot reaction at low temperatures.

However, when the temperature is increased above 300 °C, much higher NO conversion over Cu-ZSM-5 is obtained. In the non-catalytic system, NO conversion without $O_2$ is slightly higher than that with $O_2$. The reason is that the soot/$O_2$ reaction predominates at high temperatures. In other words, the presence of $O_2$ limits the NO/soot reaction. By contrast, in the catalytic system, Cu-ZSM-5 accelerates the reaction between NO and soot. The effect of $O_2$ actually enhances the reaction.

Figure 17 show the results of the $NO_2$/soot reaction both in the absence and presence of Cu-ZSM-5. When Cu-ZSM-5 is absent, most of the $NO_2$ is converted into NO. When Cu-ZSM-5 is present, all the $NO_2$ is converted into NO even at low temperatures. In the catalytic reaction, Cu-ZSM-5 has very high activity to decompose $NO_2$ into NO especially at high temperatures as shown in Figure 7 and promote the soot/$NO_2$ reaction, the conversion of $NO_2$ is the result of these two reactions. However, in the non-catalytic reaction, the conversion of $NO_2$ results mainly from the $NO_2$/soot reaction. Only a small amount of $NO_2$ can decompose to NO and $O_2$.

Comparing Figure 17 with Figures 15 and 16, it can be seen that both in the non-catalytic and catalytic reactions, $NO_2$ is a stronger oxidant than NO, in spite of the lower concentration (490 ppm) of $NO_2$ than NO (1200 ppm). In the reactions above, no $N_2$ was produced. These results are in agreement with the results described in 3.2.1.

### 3.2.4 $NO/O_2$/Soot Reaction as a Function of Time

Soot is composed of many organic and inorganic compounds, including mainly unburned hydrocarbons (HC), the soluble organic fraction (SOF), and dry carbon. Different components show different reaction rates with $NO_x$ , $O_2$, and other gases.

In order to examine the relationship between the $NO/O_2$/soot reaction and time, an experiment was performed with the TGA. Temperature was controlled at 400 °C. NO feed concentration was 754 ppm and $O_2$ concentration is 9.0 %. The total flowrate ($NO+O_2+He$) was 80 $cm^3$/min. The solid samples contained 10% (wt.) soot and 90% (wt.) Cu-ZSM-5. $N_2$, CO and $CO_2$ were measured. The change of their concentrations with time is shown in Figures 18 and 19. The change of weight with time is shown in Figure 20.

From these figures it can be shown that not only $N_2$ but also CO and $CO_2$ decrease as time increases. At the beginning of the reaction, as shown in Figure 18, the conversion of NO to $N_2$ is as high as 32 %, but forty minutes later, no $N_2$ is produced. The decrease of the concentration of CO and $CO_2$ occurs mainly in the first ten minutes of the reaction, as shown in Figure 19. After ten minutes, the concentration of CO and $CO_2$ remains constant. The weight of the solid sample also decreases as time increases. However, the change of the solid sample weight (see Figure 20) and the $CO_2$ and CO concentrations indicate that it still contains soot after 40 minutes. The reason is that soot is composed mainly of dry carbon and SOF. Cu-ZSM-5 has a high activity for the NO/SOF reaction but much lower activity for the NO/carbon reaction. On the other hand, SOF reacts at a higher rate with $O_2$, especially at the temperatures above 400 °C. Therefore, the SOF/NO and SOF/$O_2$ reactions dominate in the initial period of reaction. In other words, most of the soot removed is SOF rather than carbon in the beginning of the reaction. As time increases, the relative content of the dry carbon increase to become the dominant fraction. The rate of NO/soot reaction becomes slower and slower. Therefore the reaction rate to remove soot decreases with increasing time.

## 3.3 TGA

TGA experiments were used to examine the removal effect of soot by $NO_x$ and $O_2$. In order to simulate the practical composition of exhaust from a Diesel engine, the concentration of $O_2$ is controlled at 10 %. Furthermore, the same concentration of NO and $NO_2$ (200 ppm) were used to compare their oxidizing power.

### 3.3.1 Reaction as a Function of Temperature

Figures 21 to 23 shows the weight loss of a Cu-ZSM-5, ZSM-5 and $SiO_2/Al_2O_3$ solid sample without soot as a function of temperature for different gases. From these figures, we can see that Cu-ZSM-5 and ZSM-5 are stable and their weight loss is less than 1.5 % as shown in Figures 21 and 22. This loss result mainly from the evaporation of water or oxidation of impurities contained in the solid sample. However, the weight loss of the $SiO_2/Al_2O_3$ sample is as much as 13 % at 1000 °C as shown in Figure 23. Most of the weight loss (9 % of total weight ) took place between 400 and 600 °C. The difference in the weight loss is due to the different manufacturing processes of these catalysts. Cu-ZSM-5 and ZSM-5 are zeolitic and were calcined at 700 °C which drives off any chemically attached water while $SiO_2/Al_2O_3$ is nonzeolitic and was not calcined at high temperature.

Figures 24 to 27 show the weight loss of pure soot and the different catalysts mixed with 10 % wt. soot with the different gases. As shown in these figures, the weight of all the solid samples decreases with increasing temperature. The removal of soot both in the absence and in the presence of catalysts at 500 °C were quantitatively summarized in Table 5:

From Table 5, it can be seen that every solid sample lost weight including those samples treated with Helium. An important reason for the weight loss is the distillation of the light components of SOF in soot. However, because the contents of soot in all of the solid samples are the same, their weight loss by distillation should be the same. Therefore the difference results from different reactions with other gases can be compared by subtracting the SOF weight loss obtained with Helium, where no chemical reaction was possible.

**Table 5** Removal (%) of soot in catalyst/soot system with different gases at 500 °C

| | Soot | Cu-ZSM-5/Soot | ZSM-5/Soot | $SiO_2/Al_2O_3$/Soot |
|---|---|---|---|---|
| He | 12.0 | 12.5 | 12.4 | 12.5 |
| $O_2$ | 16.4 | 21.0 | 18.0 | 16.2 |
| NO | 11.8 | 11.0 | 11.2 | 11.4 |
| NO+$O_2$ | 16.3 | 18.2 | 17.4 | 17.6 |
| $NO_2$ | 12.0 | 16.0 | 15.6 | 14.0 |

From Table 5, it can be concluded that weight loss with $O_2$ present is larger than that without $O_2$. The obvious difference appears beginning at 400 °C, as shown in Figures 24 to 27, which indicates at a temperature higher than 400 °C the soot/$O_2$ reaction dominates. This agrees with the results in 3.2. Table 5 also shows that the rate of $NO_x$/soot reaction is low. This result confirms that the reaction between 10% $O_2$ and soot dominates among all the reactions when the $O_2$ concentration is much higher than that of $NO_x$. In fact, the results for NO show a smaller loss in weight than with the inert Helium.

Interestingly, from Figures 24 to 27, we can see that the weight loss of solid sample with the mixture of NO and $O_2$ is smaller than those with $O_2$ alone especially at the temperature over 400 °C. However, the NO/$O_2$/soot reactions are very complicated due to the composition of soot. NO can react with soot to form some other compounds depositing on the surface of solid sample which can limit the further NO/soot reaction and the soot/$O_2$ reaction. The higher the temperature, the larger the residual carbon weight.

This deposit will be probably removed by oxygen at high temperature. When Cu-ZSM-5, ZSM-5 and $SiO_2/Al_2O_3$ are present, the NO/soot reaction is accelerated and the deposit maybe formed earlier than in the absence of the catalysts.

### 3.3.2 Reaction as a Function of Time

As described in 3.2.4, the reaction between soot and $NO_x$ varies as a function of time. Since the highest activity of Cu-ZSM-5 to catalyze the $NO_x$/soot reactions appears at around 400 °C, all the experiments were run at a constant temperature of 400 °C.

Figures 28 to 31 show the weight loss of soot, Cu-ZSM-5/soot, ZSM-5/soot and $SiO_2/Al_2O_3$/soot as a function of time. From the curves of the $O_2$/soot reaction and the $O_2$/catalyst/soot system in Figures 28 to 29 and 30, it can be concluded that the $O_2$/soot reaction is promoted by NO. This result is in agreement with that of Cooper and Thoss (1989). From these figures, one can also find two other interesting phenomena. The first is that the weight of the sample decreases slowly in the beginning of reaction but becomes fast several minutes later when NO and $O_2$ were passed through simultaneously. The second is that the weight of the sample with NO decreases less than that with He. This result was related to the complicated reactions between soot and the gases. The rate of NO/soot reaction is faster than that of $O_2$/soot reaction. Therefore, it is possible that NO firstly reacts with some components in soot to form $(CN)_x$ or some other unknown compounds. These compounds deposit on the surface of soot to form a "protection layer" which hinders the further reactions between soot and other gases. Furthermore, the formation of the deposit increases the weight of solid sample. Thus the rate of change of weight loss is reduced. At a temperature of about 400 °C, when $O_2$ is passed through, the "protection layer" may be damaged by oxidation. When all the components in soot which can form the "protection layer" are consumed, the weight of the solid sample decreases faster. It was attempted to use FTIR to identify the C-N bond of the compounds which “protection layer” may be damaged by oxidation. When all the components in soot which can form the “protection layer” are consumed, the weight of the solid sample decreases faster. It was attempted to use FTIR to identify the C-N bond of the compounds which deposit on the surface of soot. However, too many peaks appeared making this not feasible.

Table 6 summarizes the removal of soot both in the absence and in the presence of catalysts after 20 minutes without and with Cu-ZSM-5 and ZSM-5 catalysts.

**Table 6** Removal of soot (%) in soot/catalyst system with different gases at 20 minutes at 400 °C

| | Soot | Cu-ZSM-5/soot | ZSM-5/soot |
|---|---|---|---|
| He | 2.95 | 2.97 | 2.92 |
| $O_2$ | 5.00 | 6.05 | 5.82 |
| NO | 2.35 | 2.37 | 2.53 |
| NO+$O_2$ | 5.50 | 6.40 | 0.37 |
| $NO_2$ | 0.35 | 3.85 | 3.65 |

The data in Table 6 indicate that when 10 % $O_2$ was passed through the system the weight loss is more than that without $O_2$. Although the rate of $O_2$/soot reaction is slower than that of the NO/soot reaction, the concentration of $O_2$, (10 per cent), is much higher than that of NO, (200 ppm). $NO_2$ is more active to react with soot than NO, as discussed before.

### 3.3.3 Comparison of Cu-ZSM-5, ZSM-5 and $SiO_2/Al_2O_3$

The ZSM-5 used in the present experiments is a zeolite catalyst, which is calcined with a $SiO_2/Al_2O_3$ mixture, 50 % by weight. The Cu-ZSM-5 catalyst is prepared from ZSM-5 by ion exchange.The $SiO_2/Al_2O_3$ is a mixture of $SiO_2$ and $Al_2O_3$. The Cu-ZSM-5-$SiO_2/Al_2O_3$ mix and ZSM-5/$SiO_2/Al_2O_3$ were calcined at 700 °C while $SiO_2/Al_2O_3$ alone is nonzeolitic and was not calcined.

Figures 32 to 34 compare the results of Cu-ZSM-5 and ZSM-5 in the removal of soot using NO, NO+$O_2$ and $NO_2$ at the temperature of 400 °C respectively as a function of time. It can be seen from the slope of curve and the weight loss of the soot (Tables 5 and 6) that catalysts can increase the removal of soot and no matter which gas is passed through and that Cu-ZSM-5 is better than ZSM-5. This result confirms the fact that $Cu^{2+}$ makes ZSM-5 more active.

Because $SiO_2/Al_2O_3$ is not stable at 400 °C, its weight loss in the $SiO_2/Al_2O_3$/soot system dominates the weight loss of the solid samples. Therefore it cannot be compared with the other two catalysts.

# CHAPTER 4

# CONCLUSIONS

1. Cu-ZSM-5 can catalyze the direct decomposition of NO to $N_2$ and $O_2$ even in the presence of oxygen. Its highest activity appears at around 400 to 450 °C. The presence of oxygen, however, lowers its activity.

2. Cu-ZSM-5 shows very high activity for the decomposition of $NO_2$. The major products are NO and $O_2$.

3. Diesel soot can be oxidized by NO, $NO_2$ or $O_2$. The final products include CO, $CO_2$, $N_2$ and $O_2$. The reaction rates with different gases are listed in the order of: 10 % $O_2$>200 ppm $NO_2$>200 ppm NO.

4. Cu-ZSM-5 has very high activity for the $NO_x$/soot reactions to form $N_2$, $O_2$, CO, and $CO_2$.

5. The presence of $O_2$, while inhibiting the decomposition of NO, enhances the $NO_x$/soot reactions.

6. $NO_2$ is a stronger oxidant than NO in reacting with soot. The major products of the $NO_2$/soot reaction are NO and $CO_2$.

7. The reaction of $NO_x$/$O_2$/soot is a function of time because of the complicated composition of soot.

8. The catalytic activity of Cu-ZSM-5 for the $NO_x$/soot reactions is higher than that of ZSM-5, which has not been ion exchanged.

# APPENDIX A

# FIGURES OF EXPERIMENT RESULTS

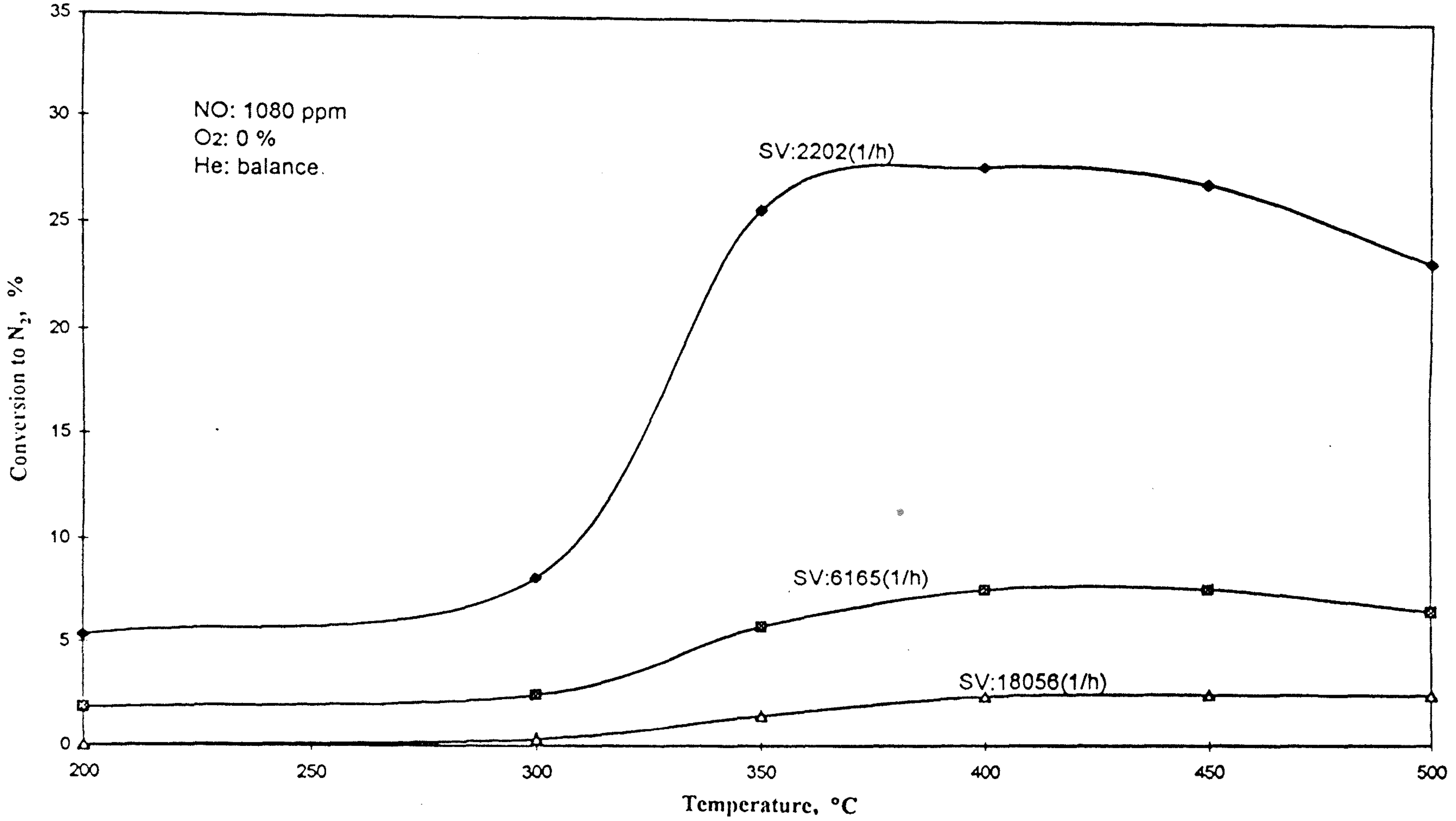


Figure 1 Decomposition of NO to $N_2$ as a function of temperature and space velocity in the absence of $O_2$

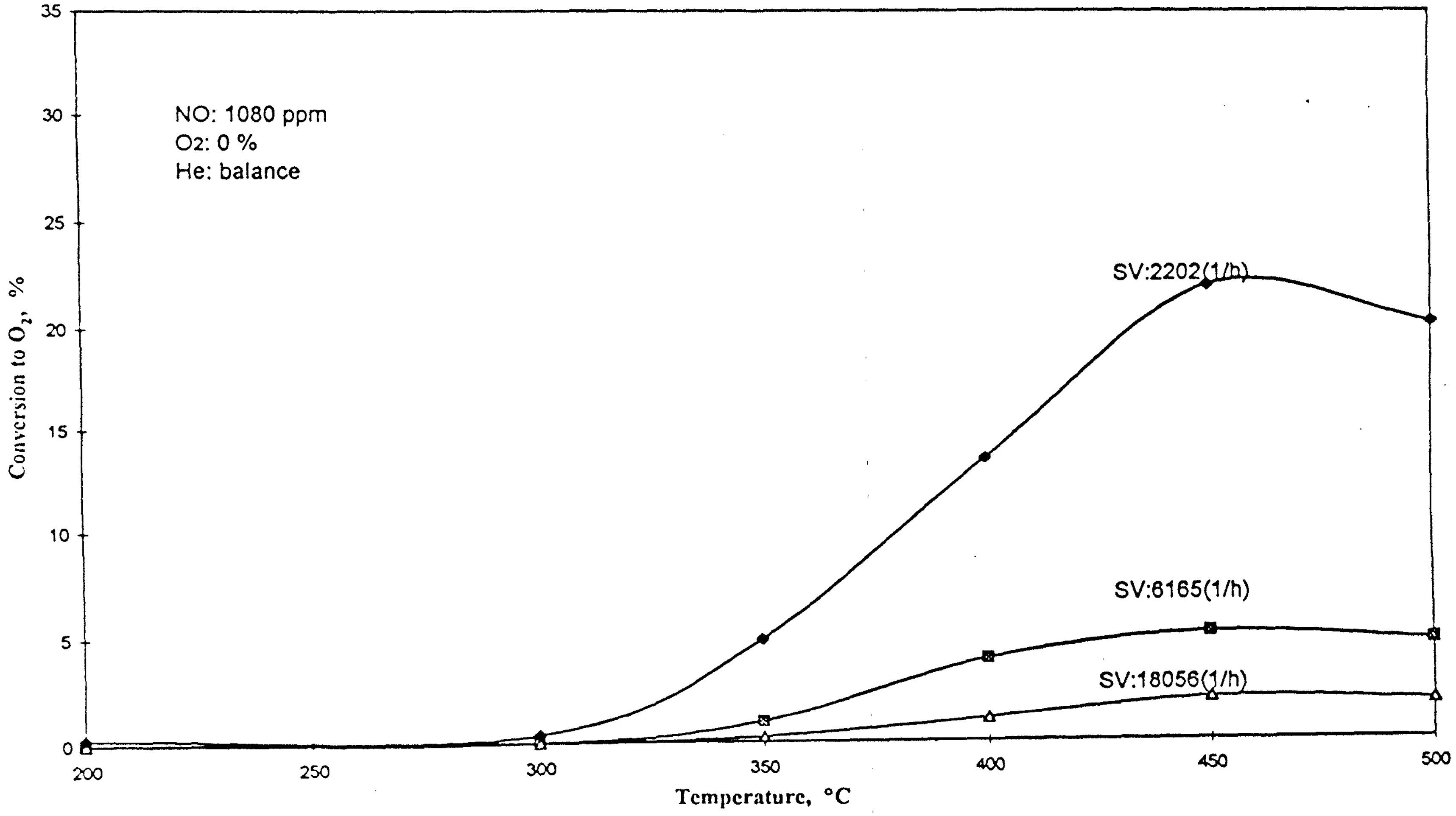


**Figure 2** Decomposition of NO into $O_2$ as a function of temperature and space velocity in the absence of $O_2$

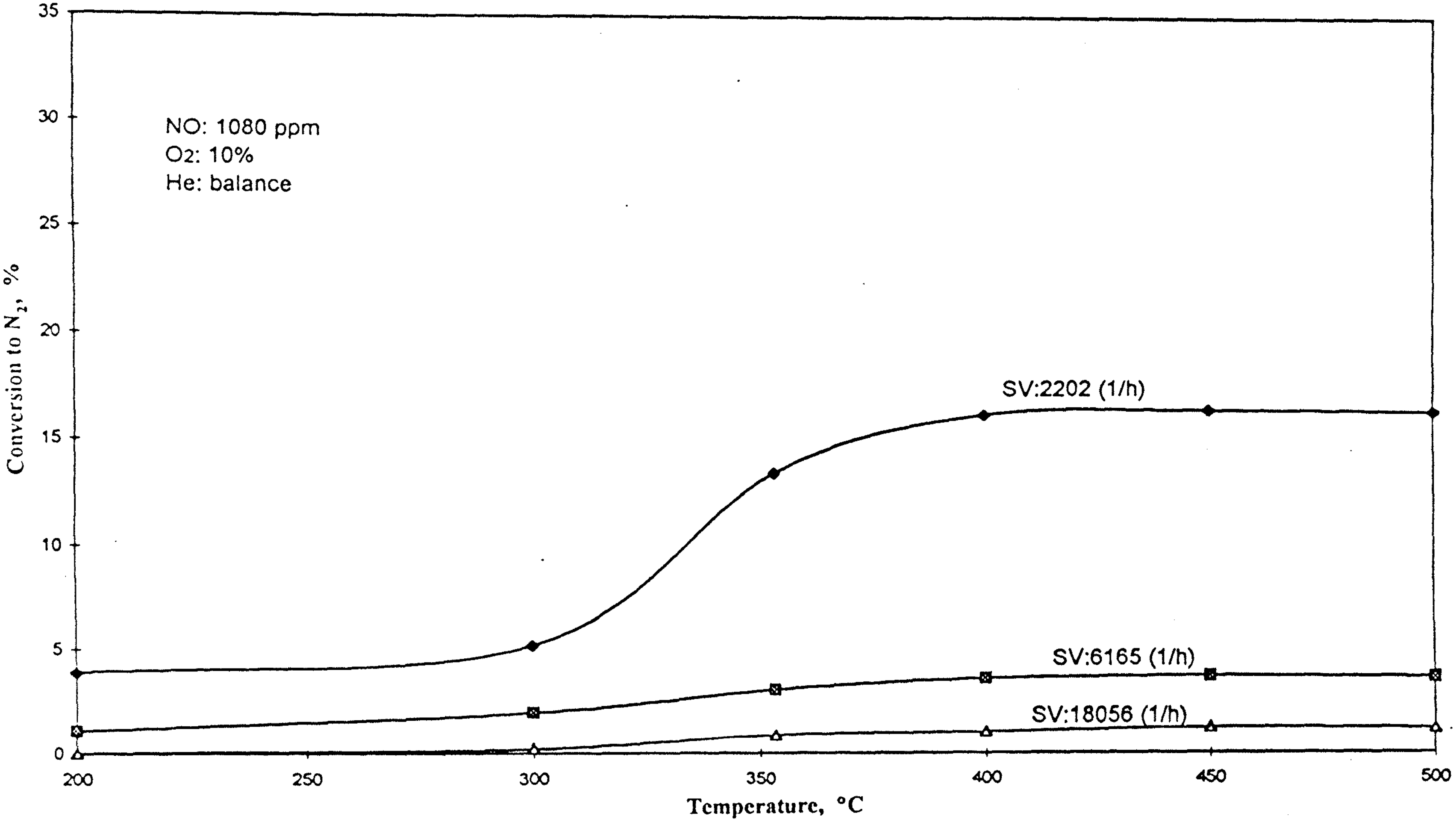


**Figure 3** Decomposition of NO into $N_2$ as a function of temperature and space velocity in the presence of $O_2$

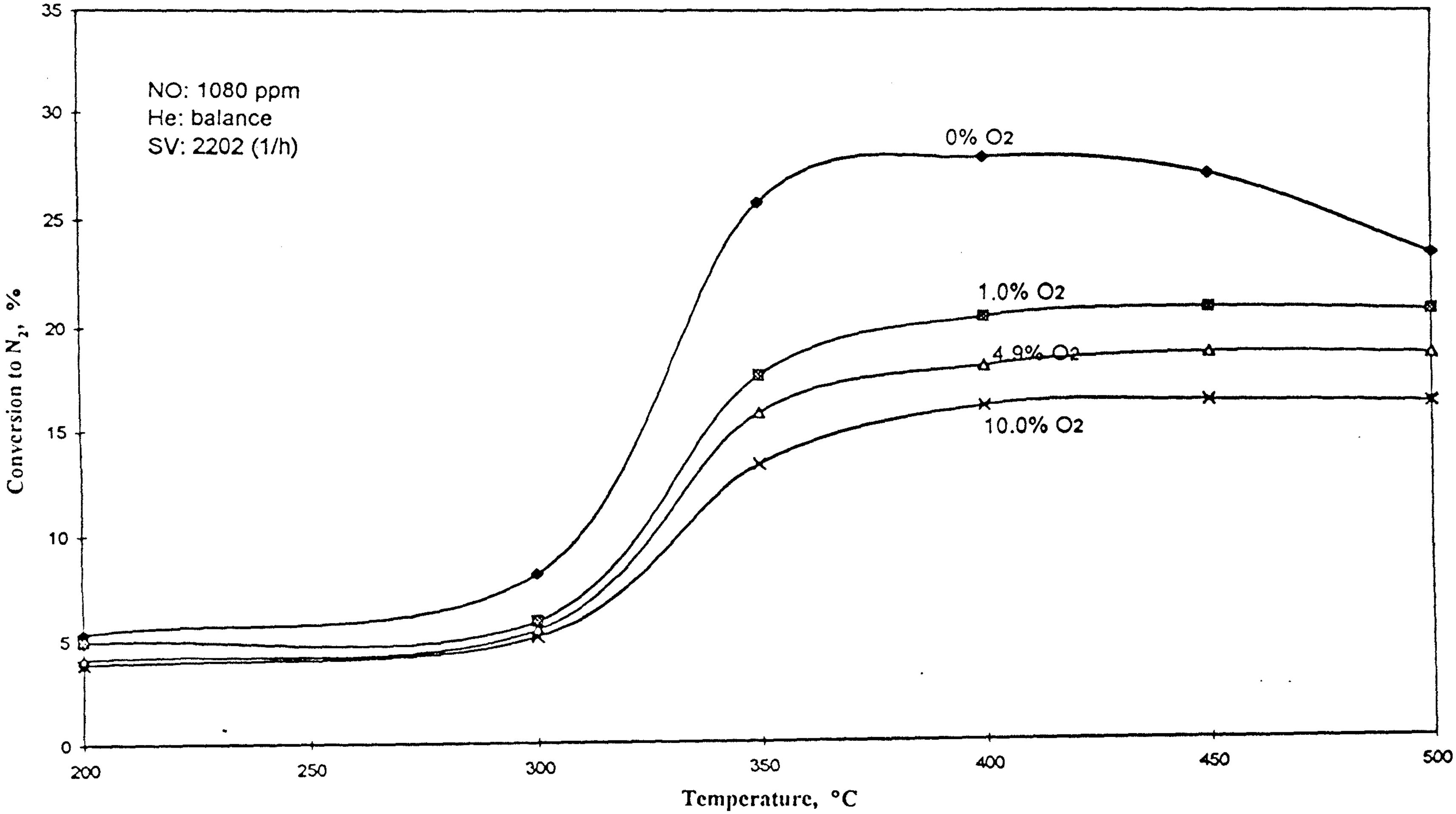


**Figure 4** Effects of $O_2$ on the decomposition of NO into $N_2$ at different temperatures

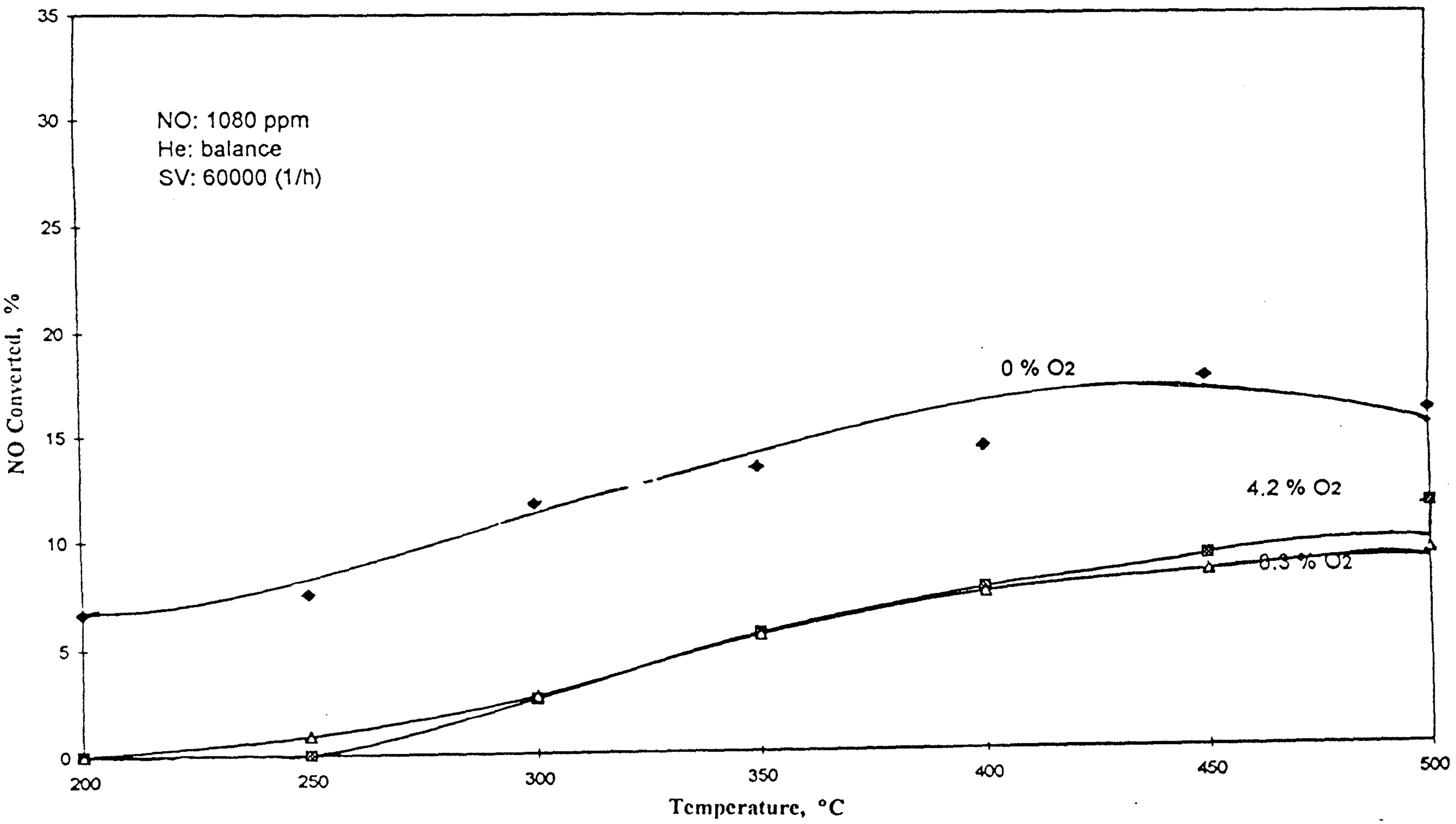


**Figure 5** Conversion of NO as a function of temperature and $O_2$ concentration

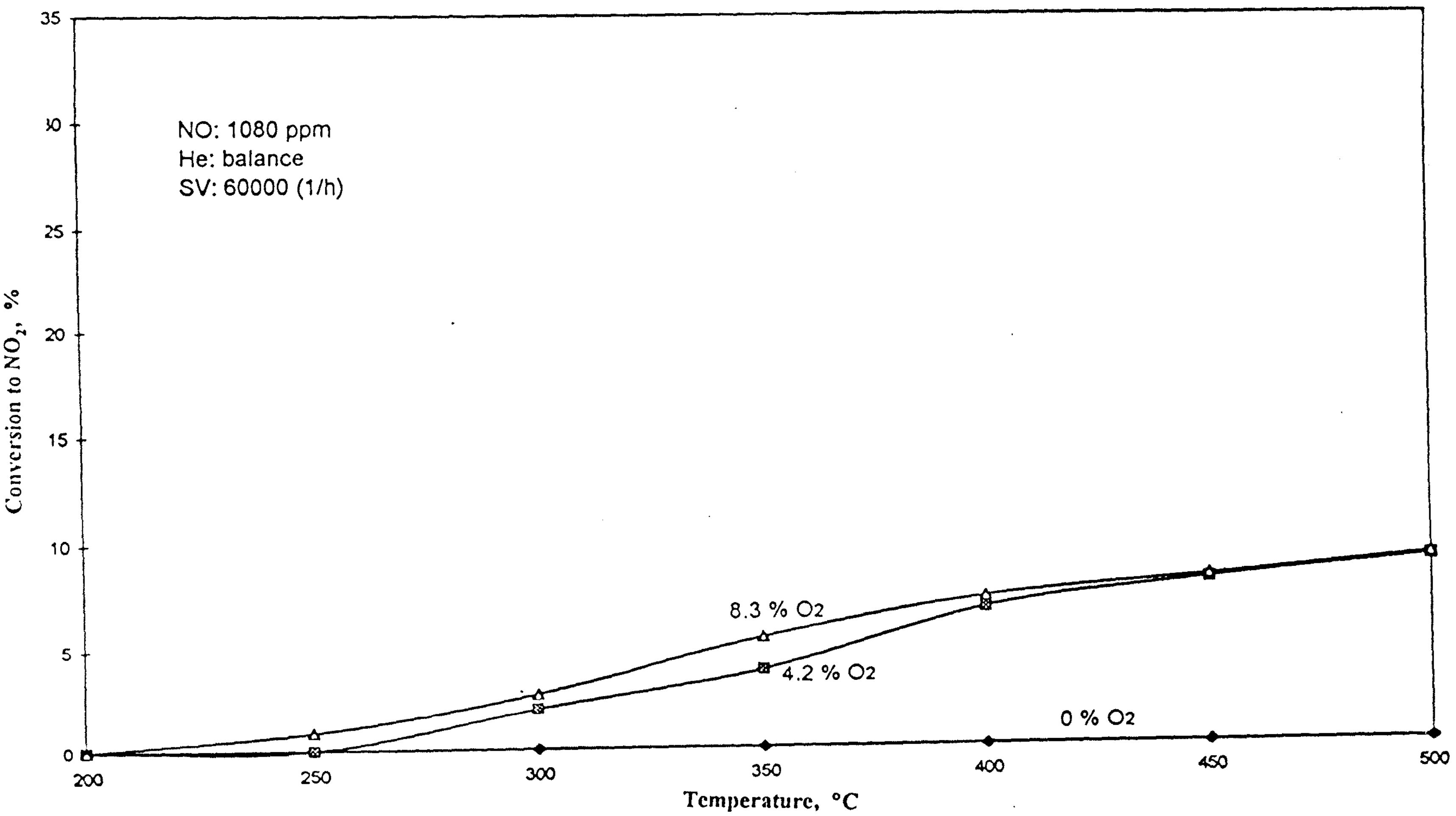


**Figure 6** Effects of $O_2$ on the conversion of NO into $NO_2$

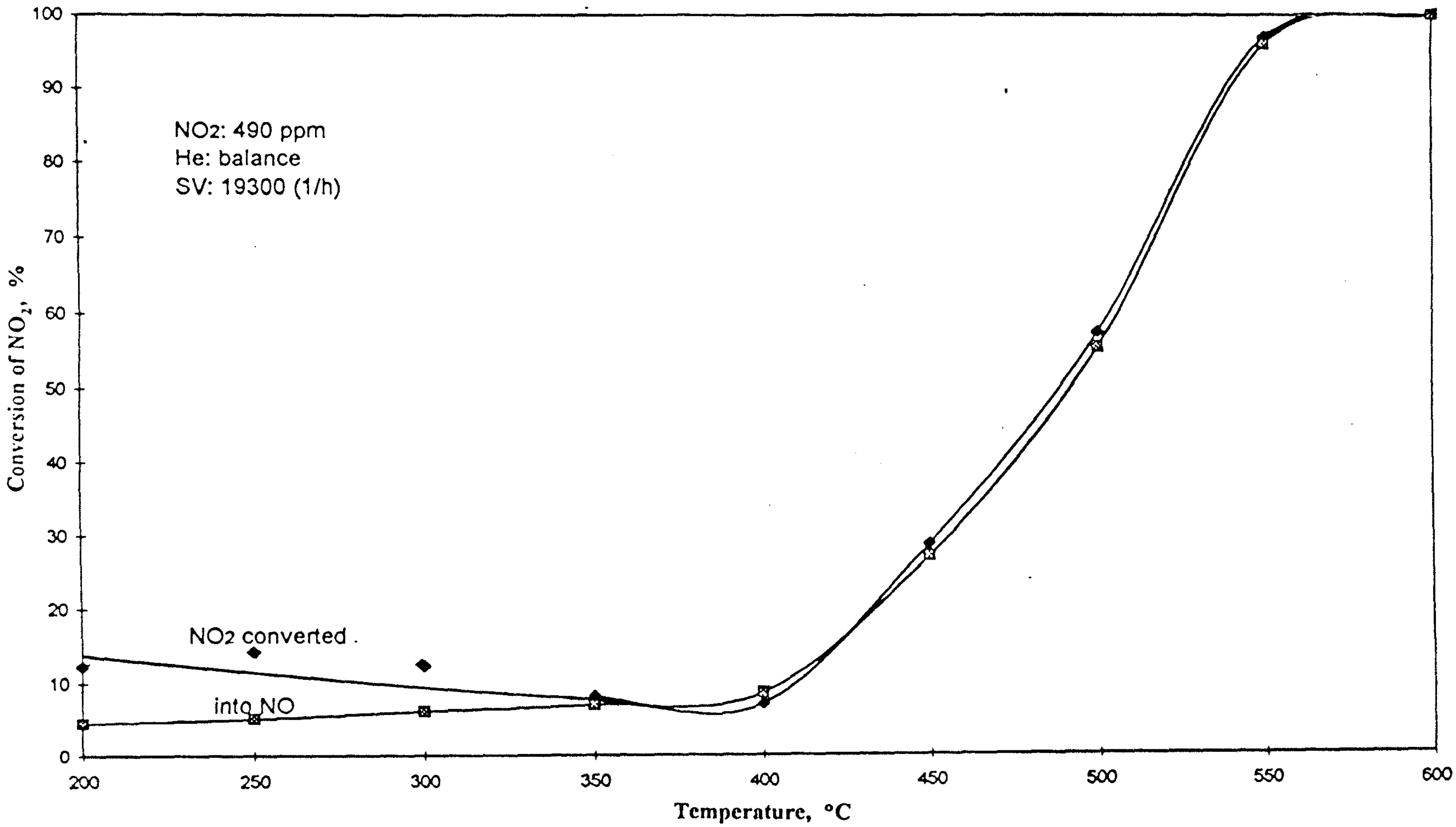


**Figure 7** Conversion of $NO_2$ into NO and overall conversion of $NO_2$ and conversion to NO as a function of temperature

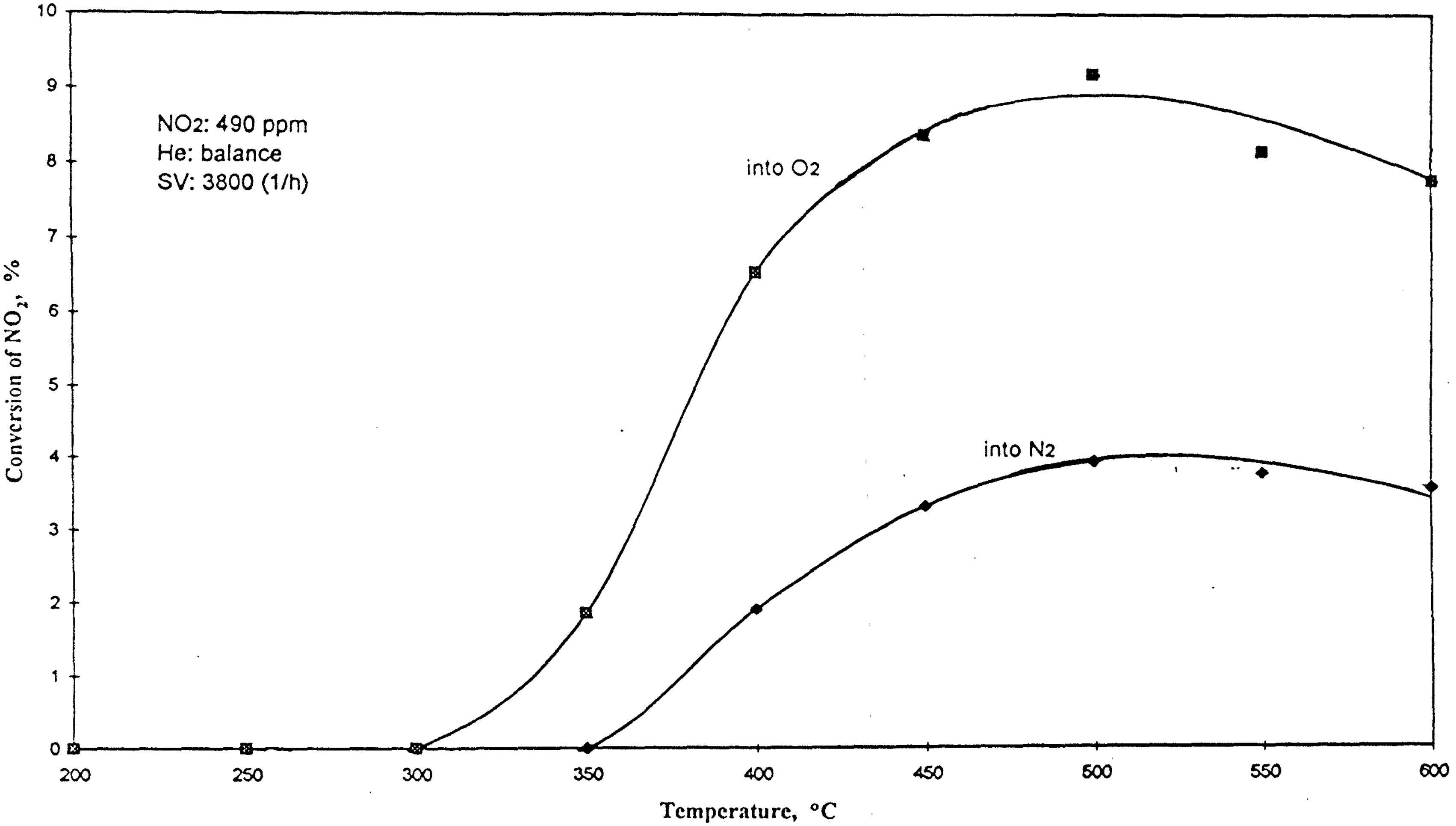


**Figure 8** Decomposition of $NO_2$ into $N_2$ and $O_2$ as a function of temperature in the absence of $O_2$

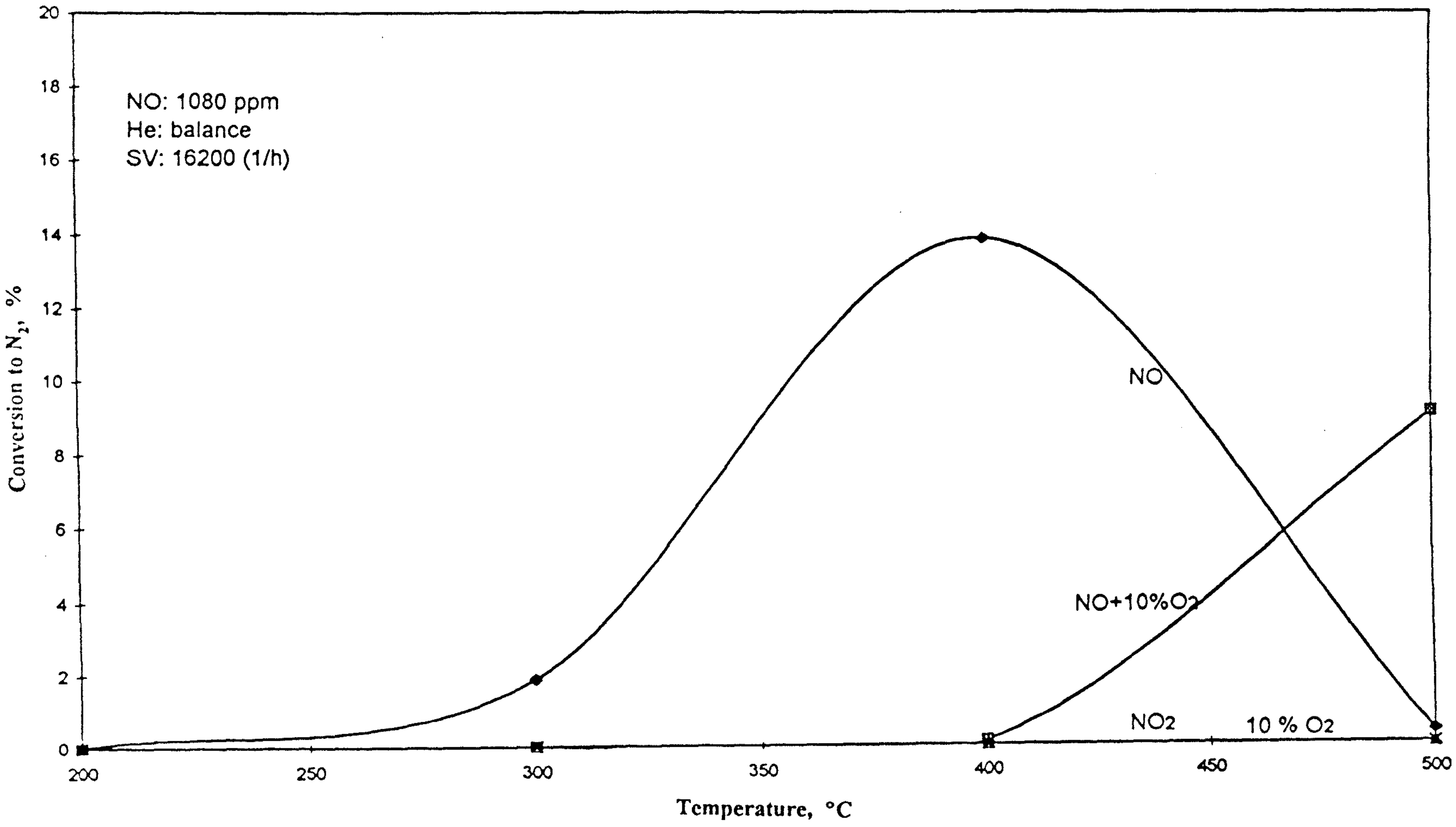


Figure 9 Temperature dependence of the conversion of different gases into $N_2$ for the gas/soot reaction

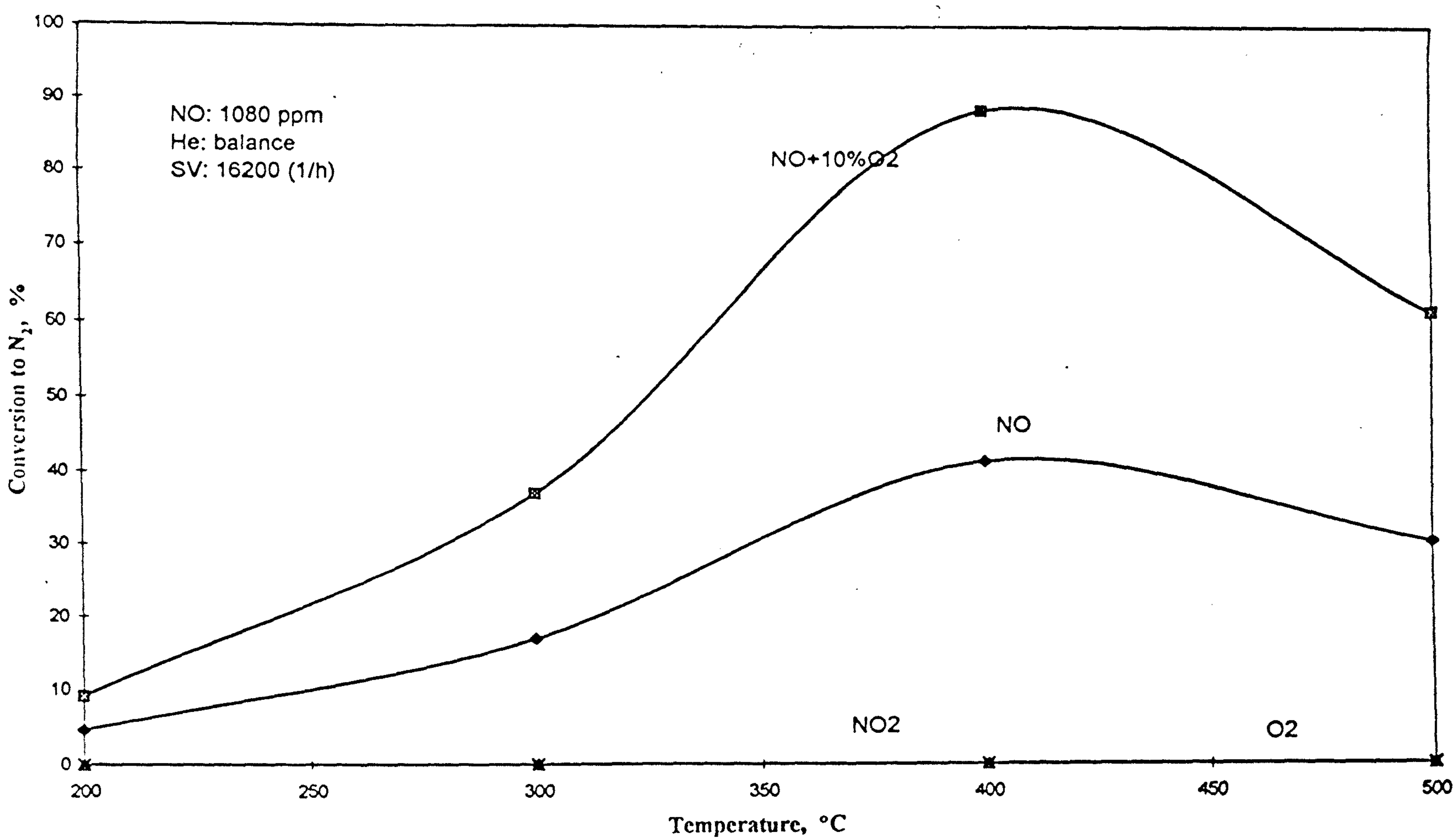


**Figure 10** Temperature dependence of the conversion of different gases into $N_2$ for the gas/soot reaction over Cu-ZSM-5

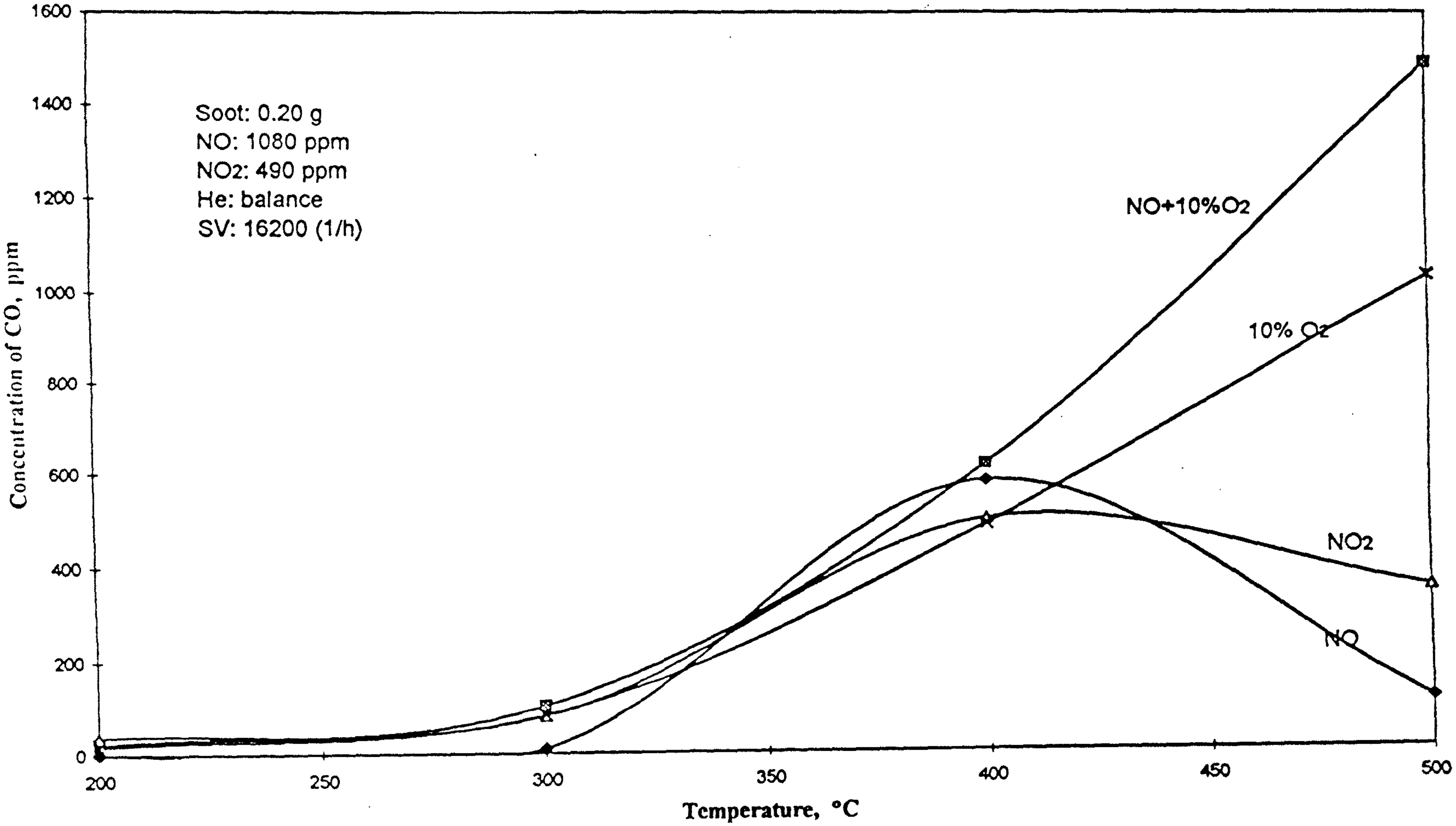
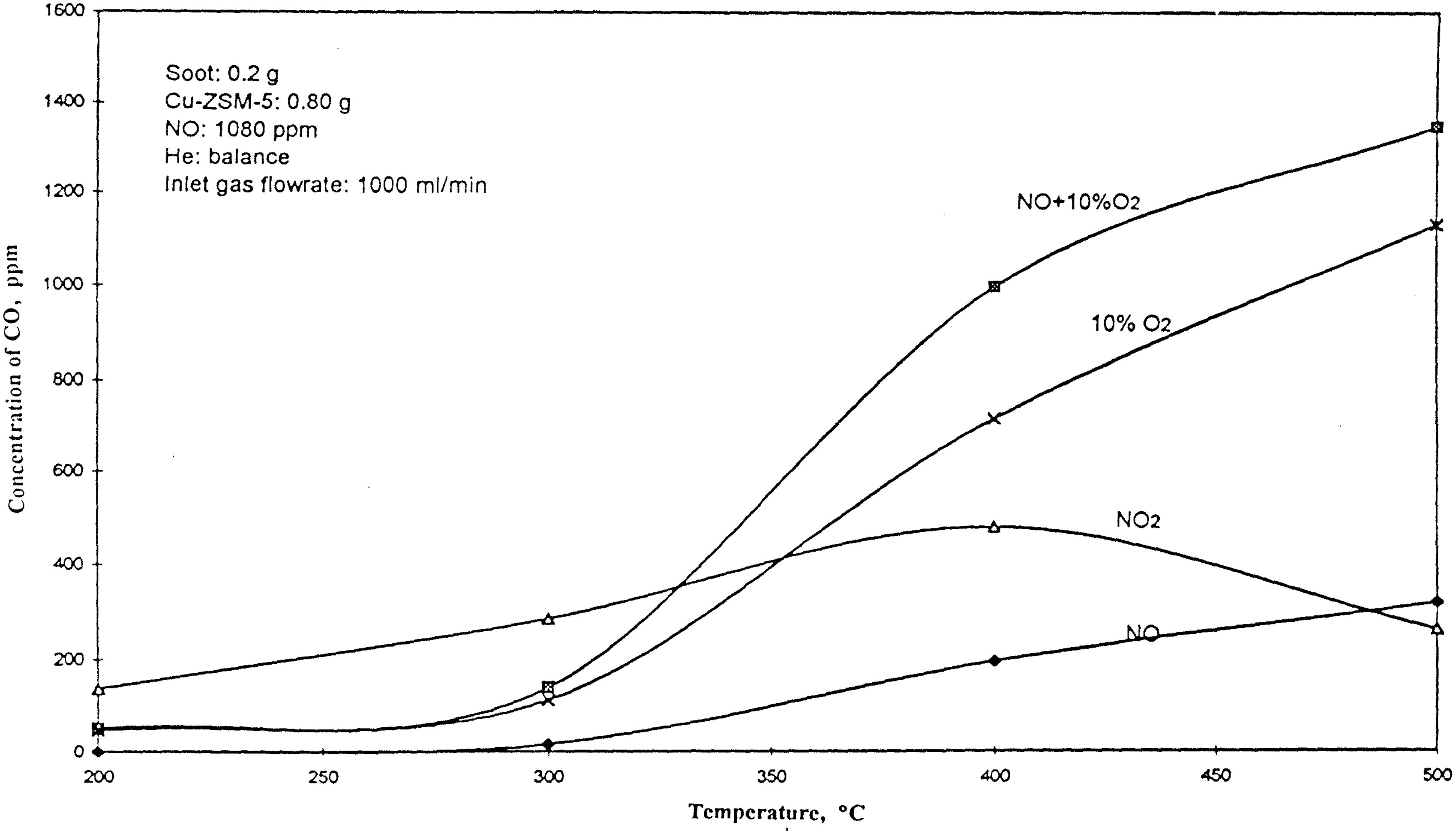


**Figure 11** Temperature dependence of the concentration of CO for the gas/soot reactions



Soot: 0.2 g
Cu-ZSM-5: 0.80 g
NO: 1080 ppm
He: balance
Inlet gas flowrate: 1000 ml/min

**Figure 12** Temperature dependence of the concentration of CO for the gas/soot reactions over Cu-ZSM-5

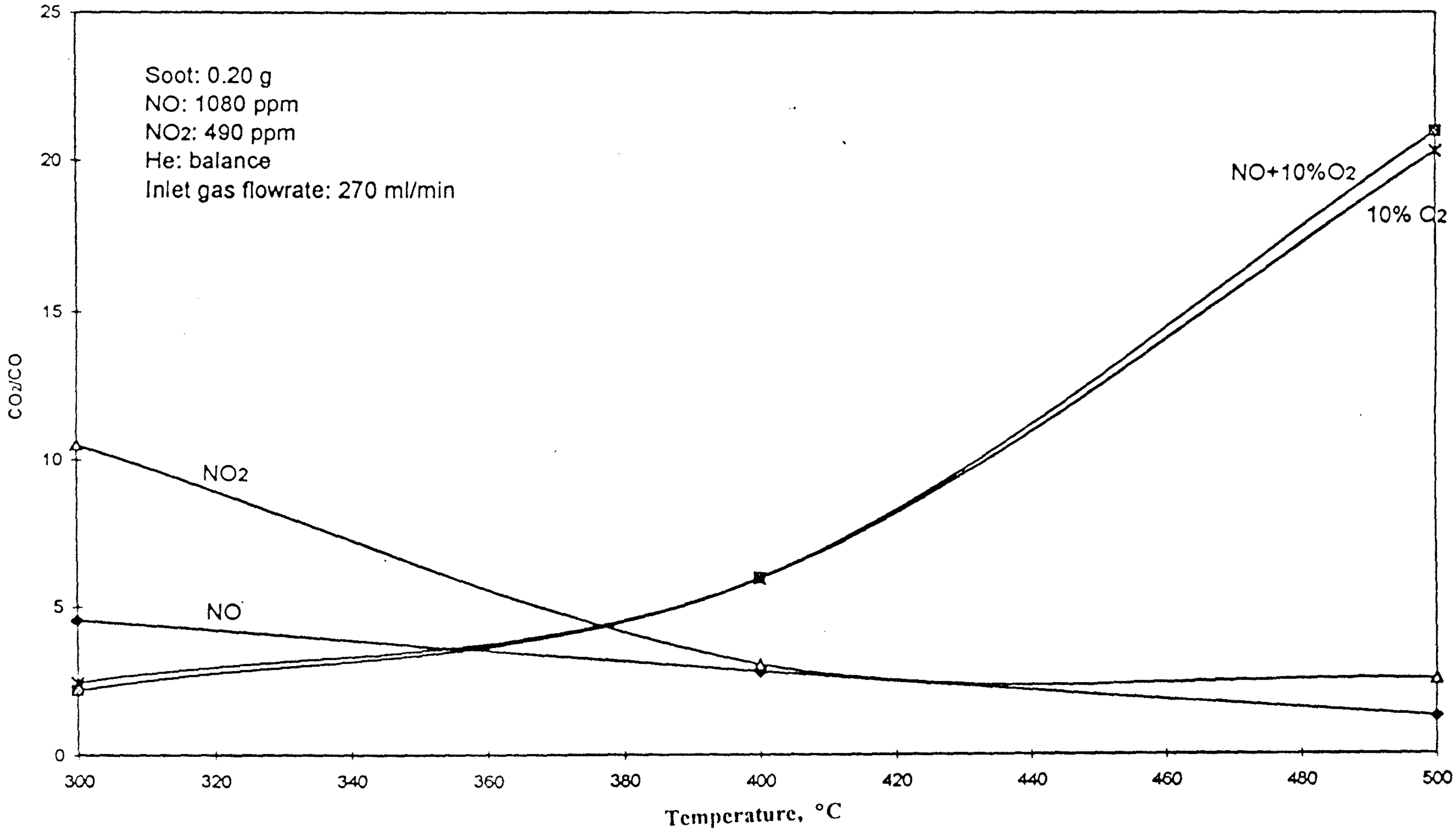


**Figure 13** Temperature dependence of the ratio of $CO_2$ to CO for the gas/soot reactions

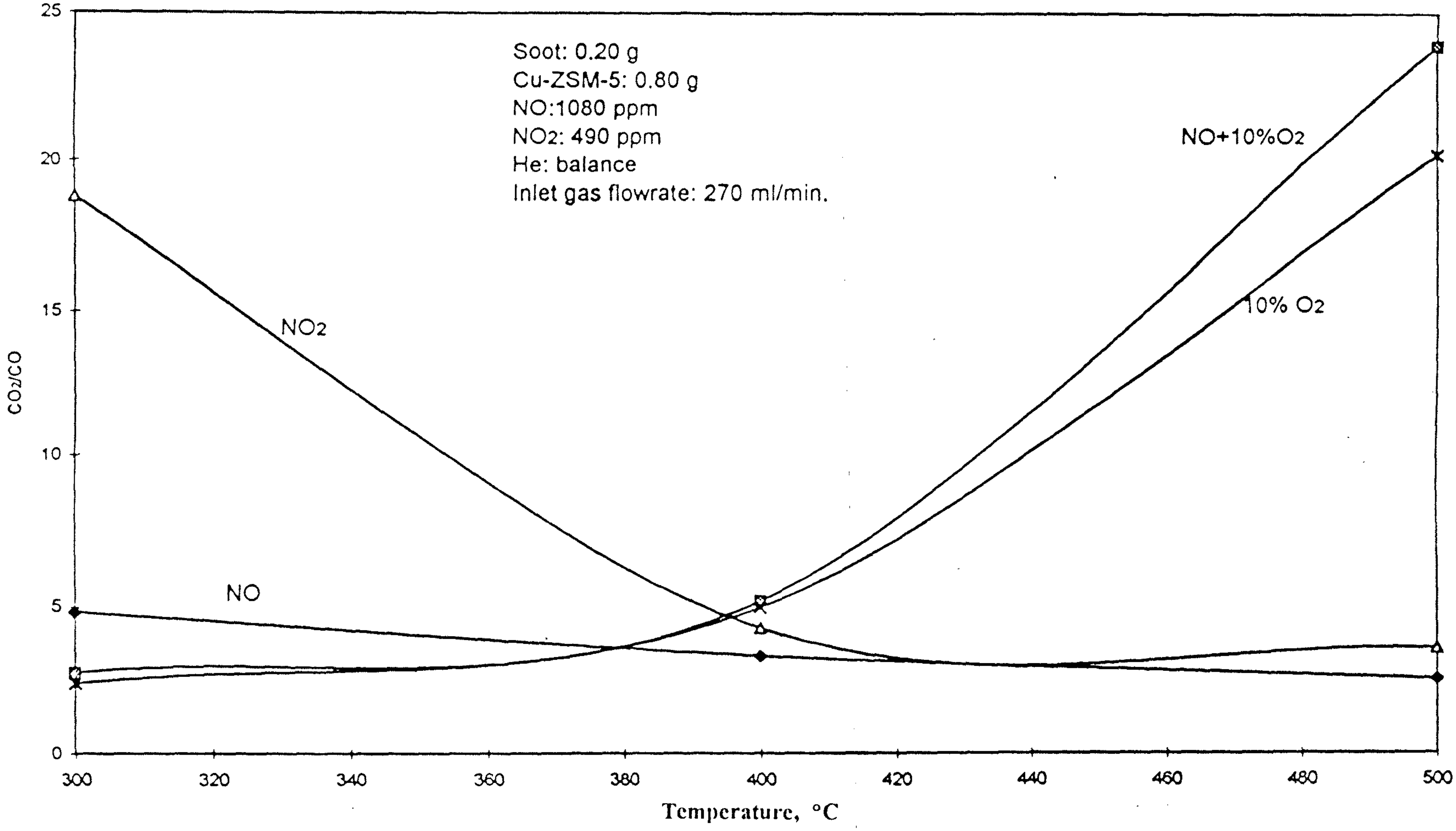


**Figure 14** Temperature dependence of the ratio of $CO_2$ to CO for the gas/soot reactions over Cu-ZSM-5

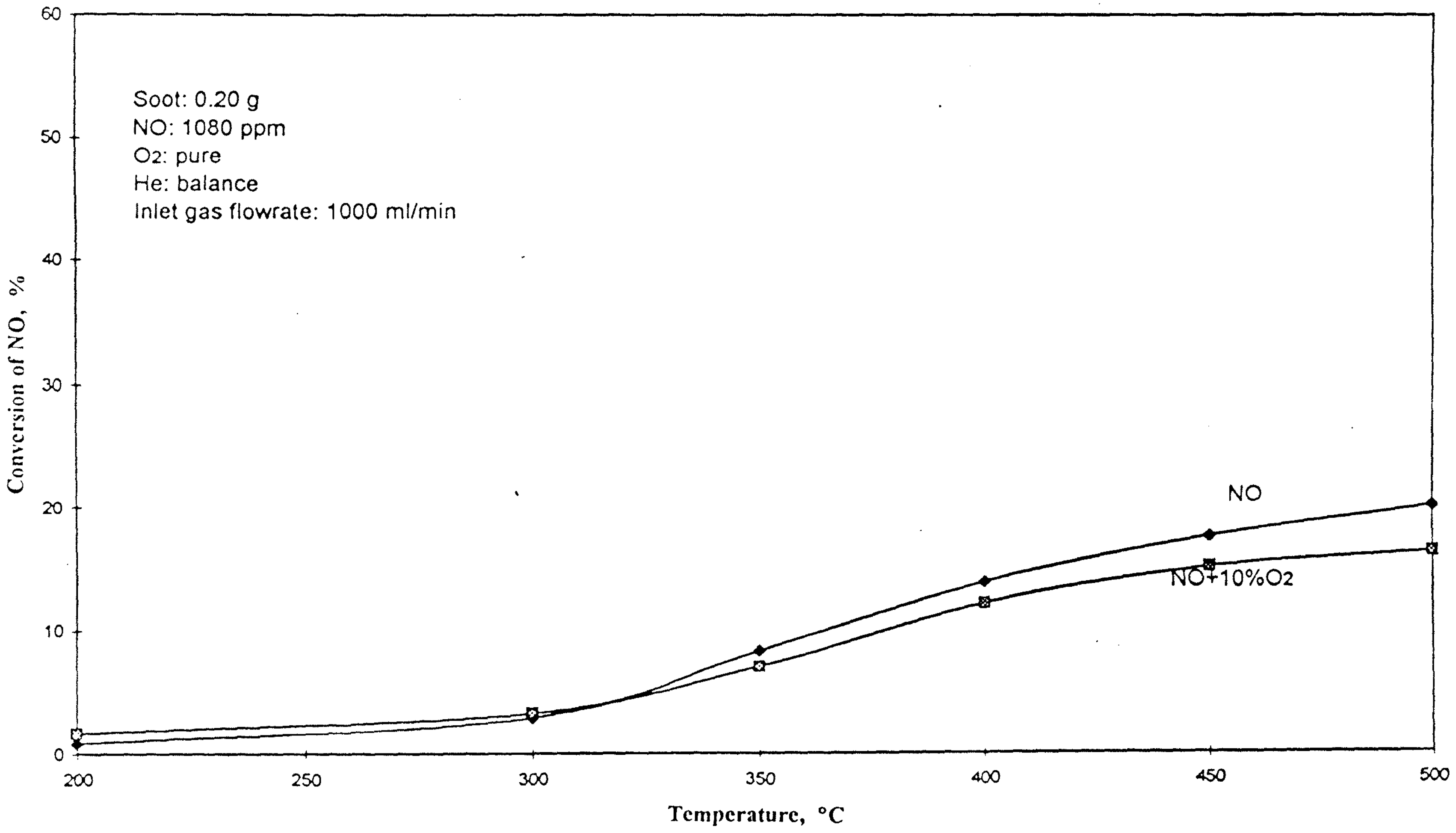


**Figure 15** Correlation between the conversion of NO and temperature in the NO/soot reaction

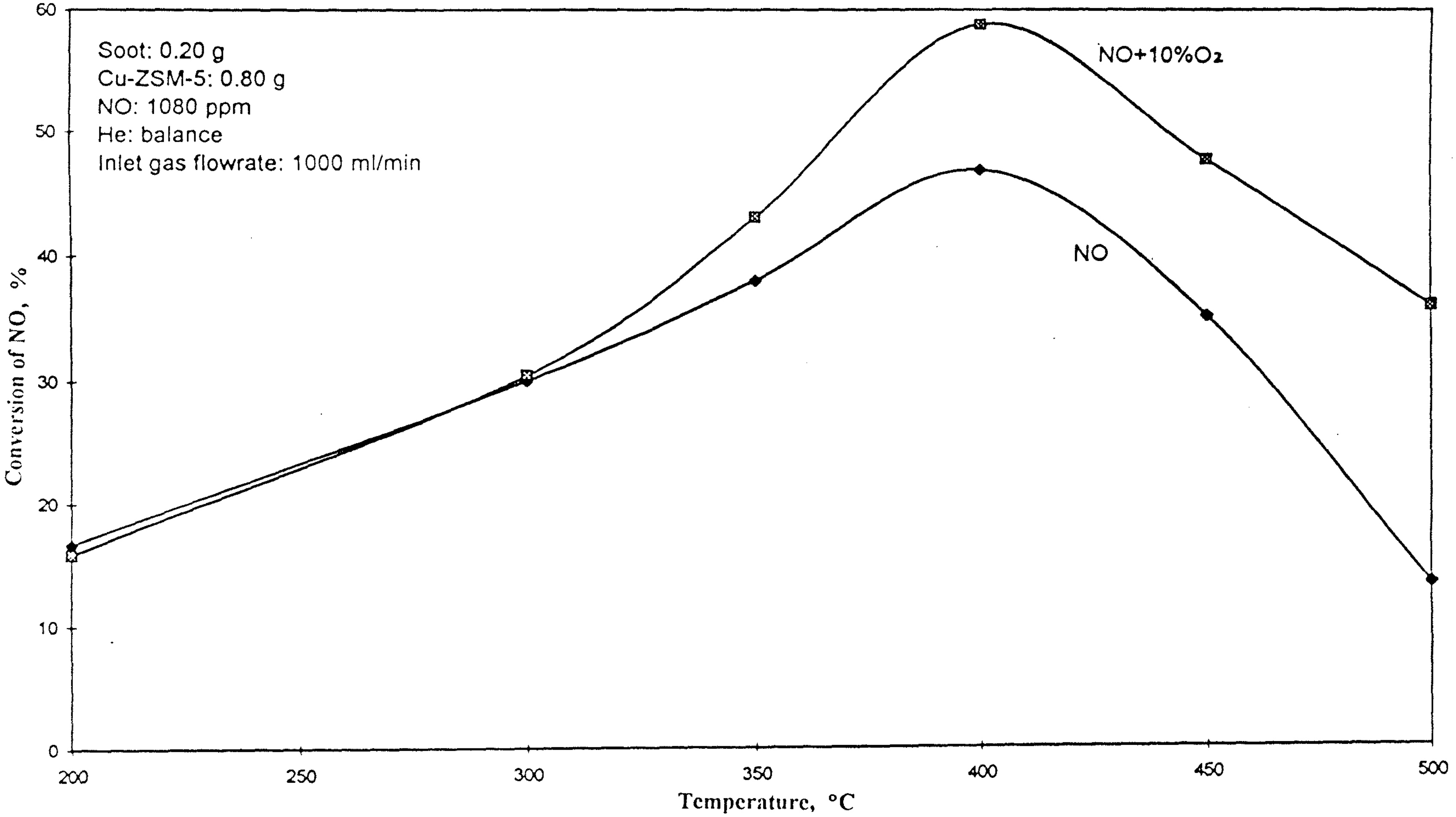


**Figure 16** Correlation between the conversion of NO and temperature in the NO/soot reaction over Cu-ZSM-5

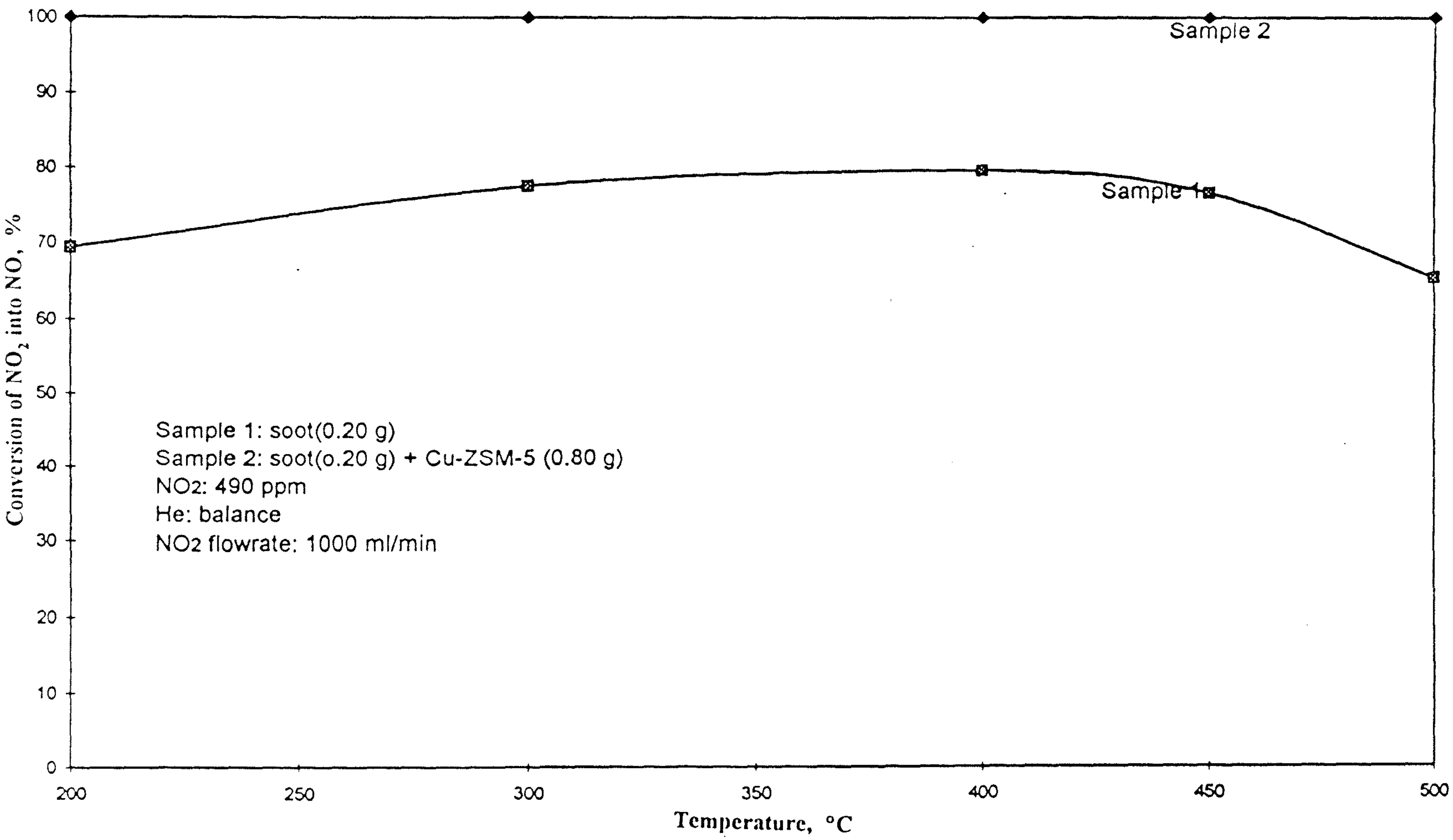


**Figure 17** Correlation between the conversion of $NO_2$ into NO and temperature in the NO/soot reaction

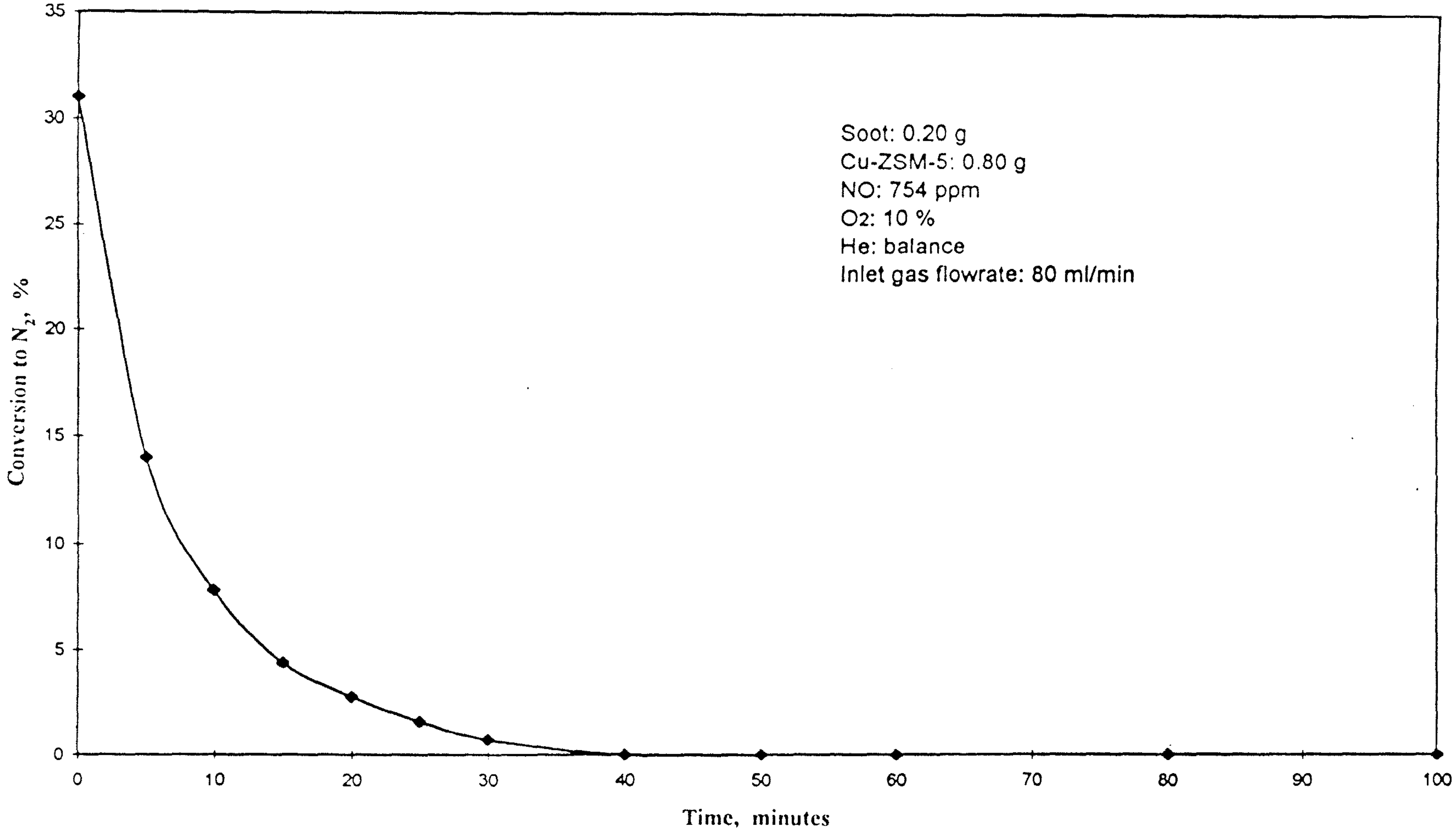


**Figure 18** Time dependence of the conversion of NO into $N_2$ for the $NO/O_2$/soot reaction over Cu-ZSM-5 with the TGA

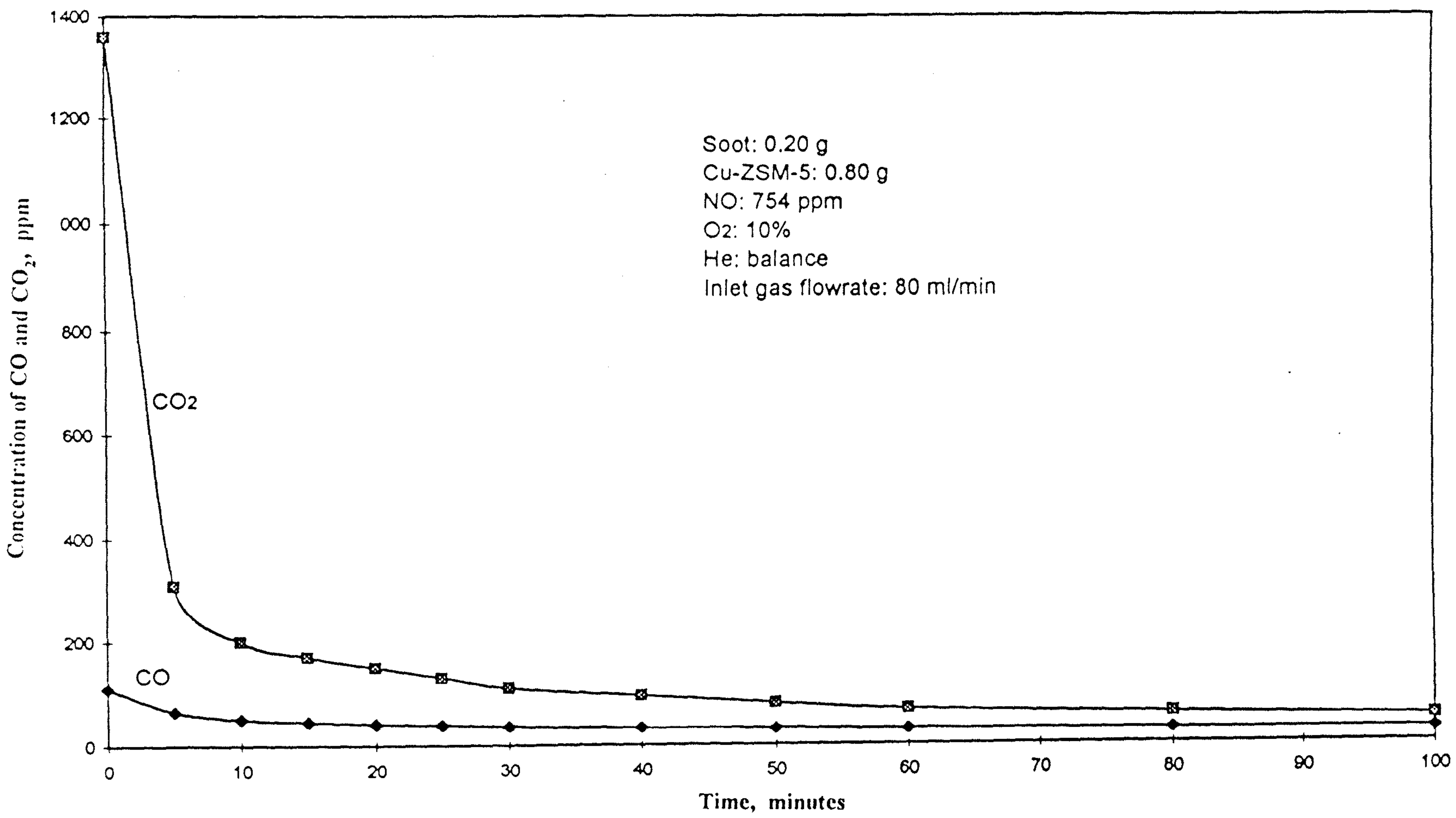


**Figure 19** Time dependence of the conversion of soot into CO and $CO_2$ for the NO/$O_2$/soot reaction over Cu-ZSM-5 with the TGA

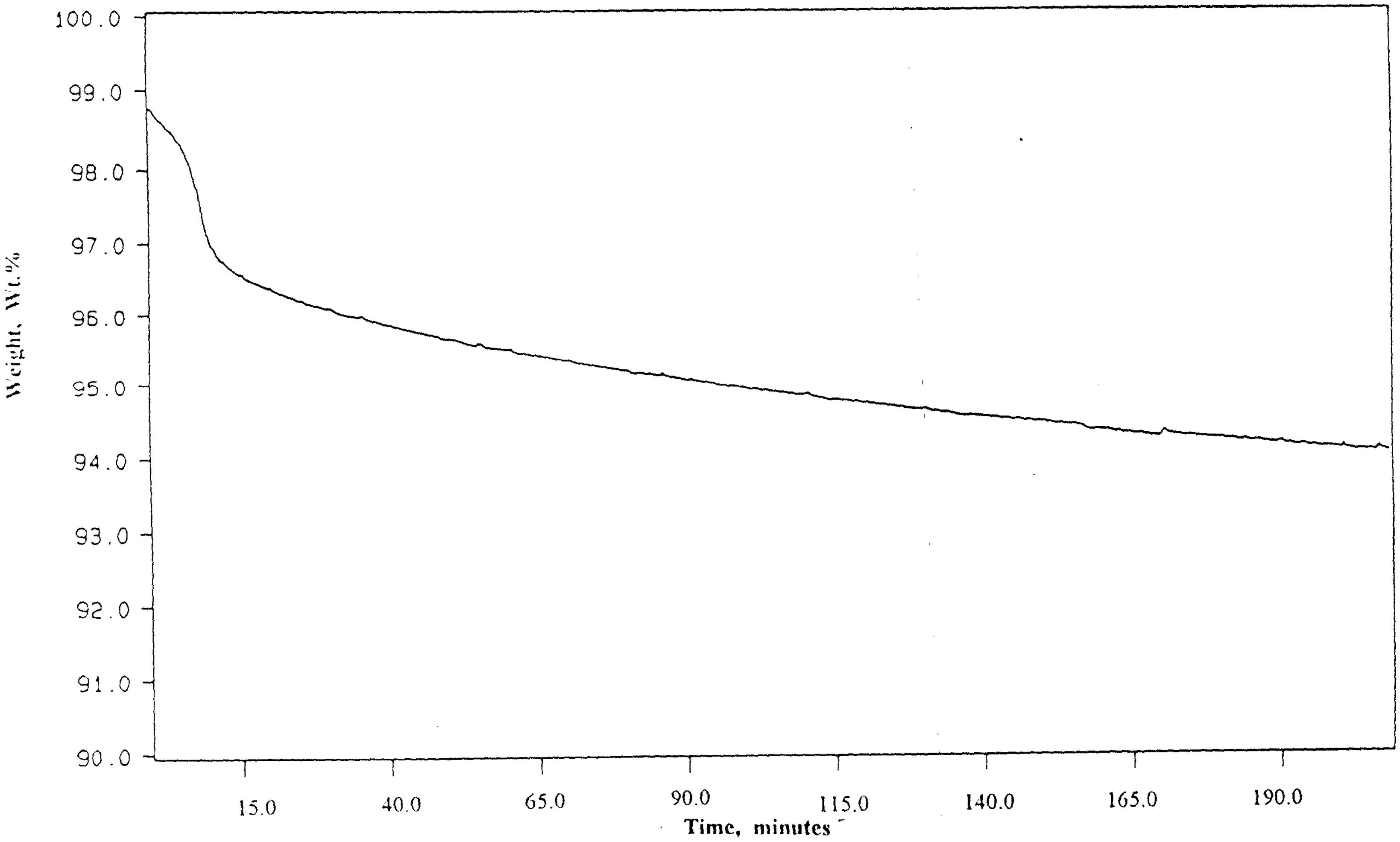


**Figure 20** Time dependence of the weight loss of soot for the NO/$O_2$/soot reaction over Cu-ZSM-5 with the TGA

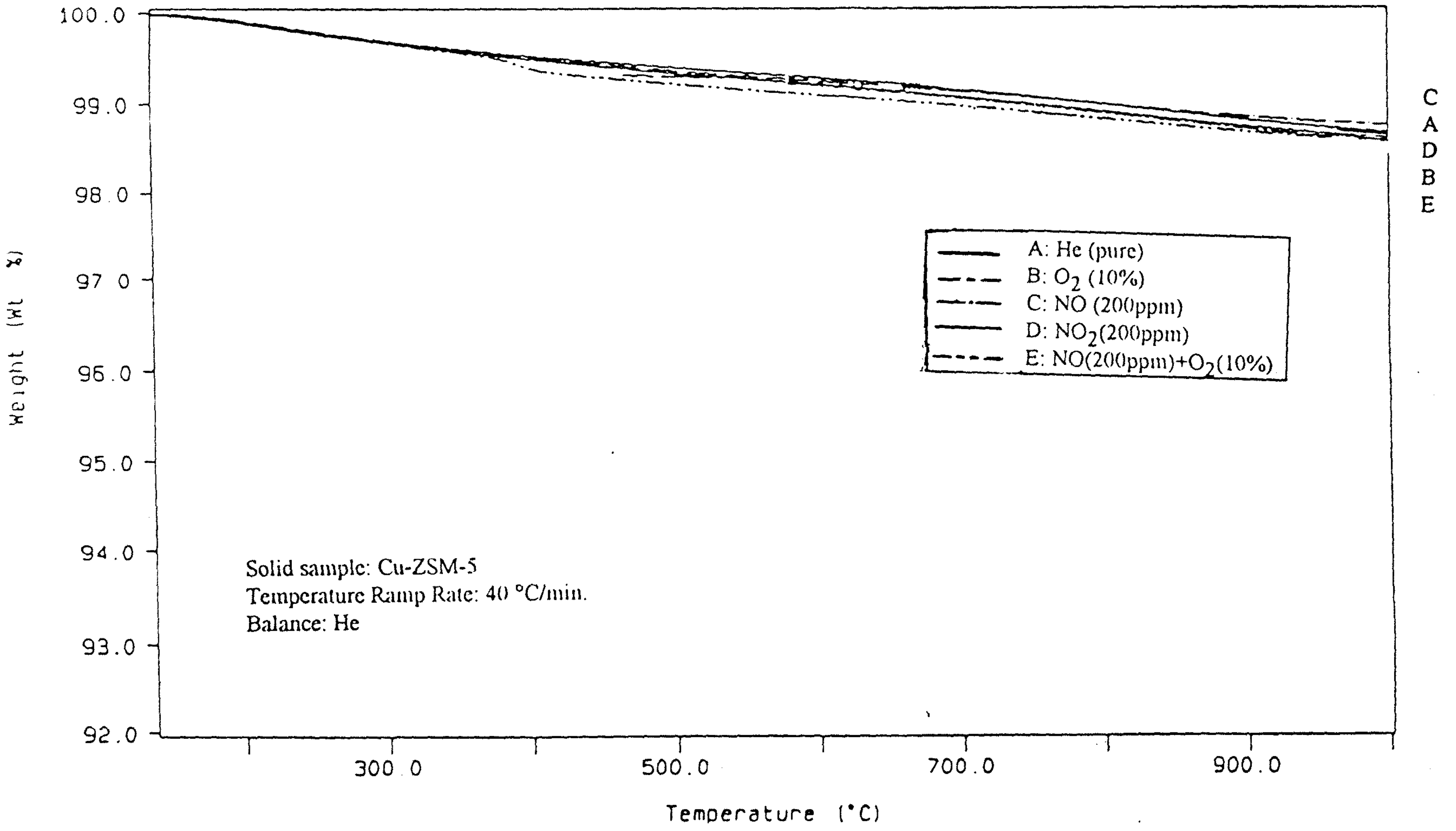


**Figure 21** Weight loss of Cu-ZSM-5 by different gases as a function of temperature

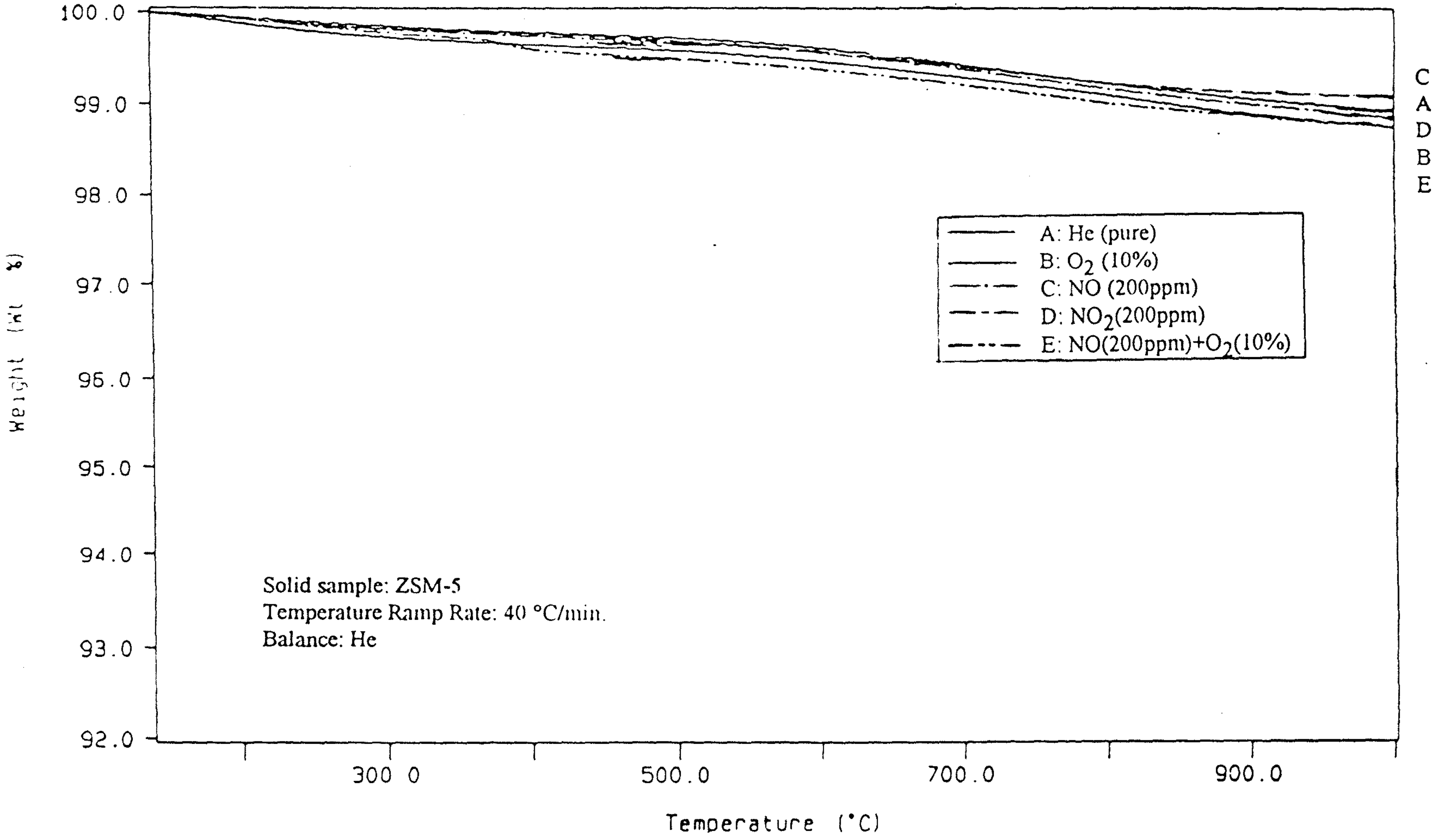


**Figure 22** Weight loss of ZSM-5 by different gases as a function of temperature

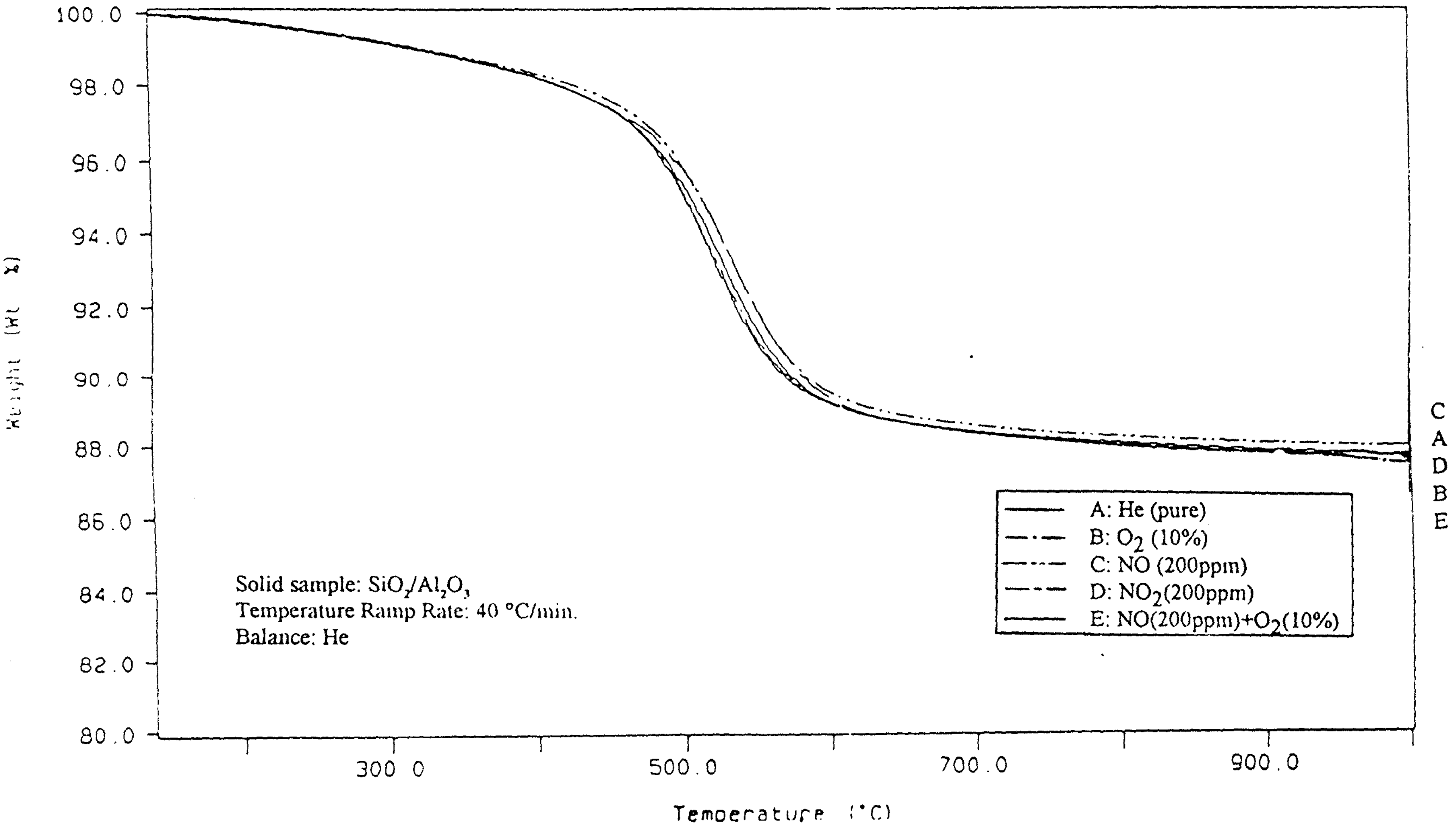


**Figure 23** Weight loss of $SiO_2/Al_2O_3$ by different gases as a function of temperature

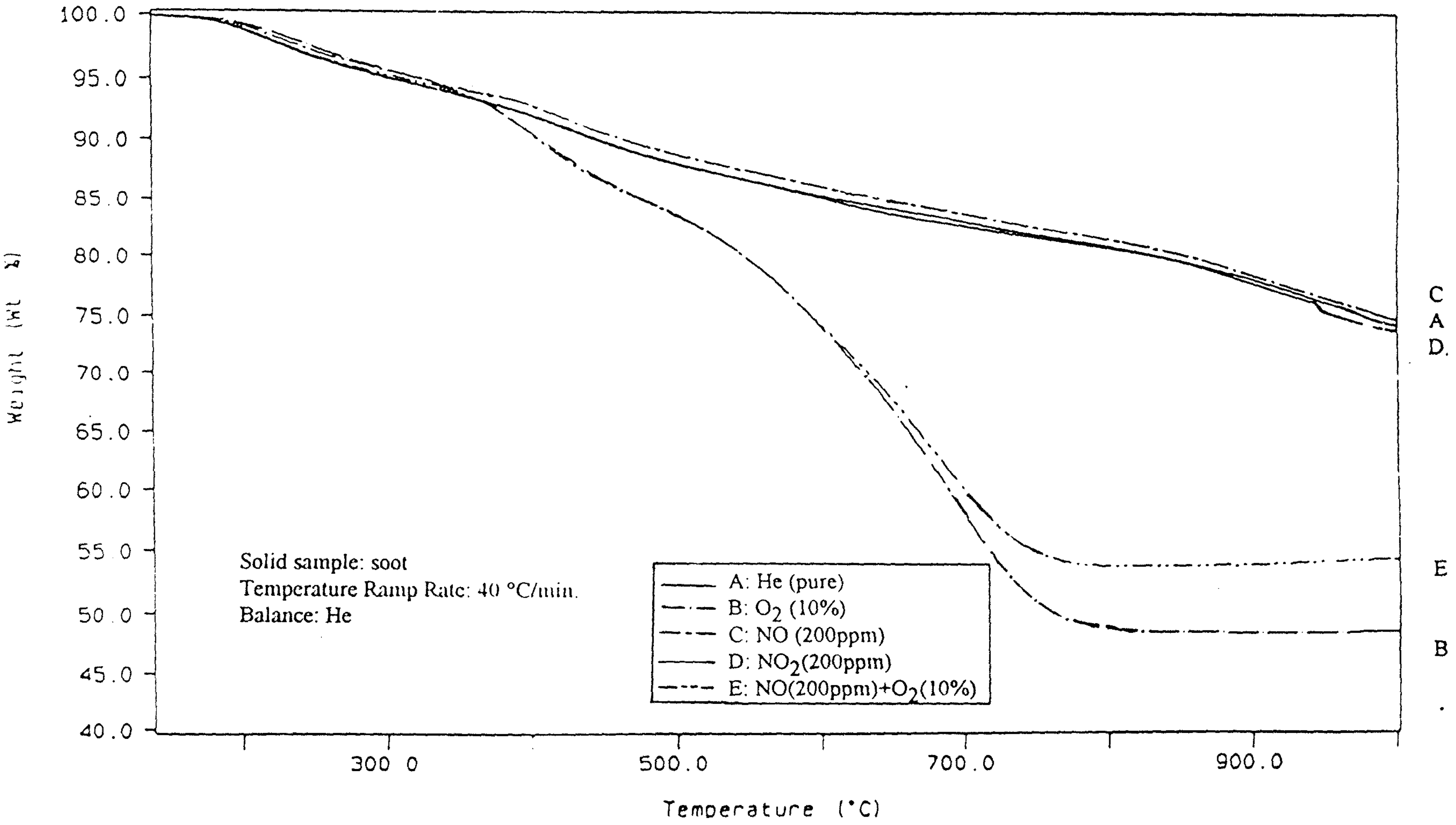
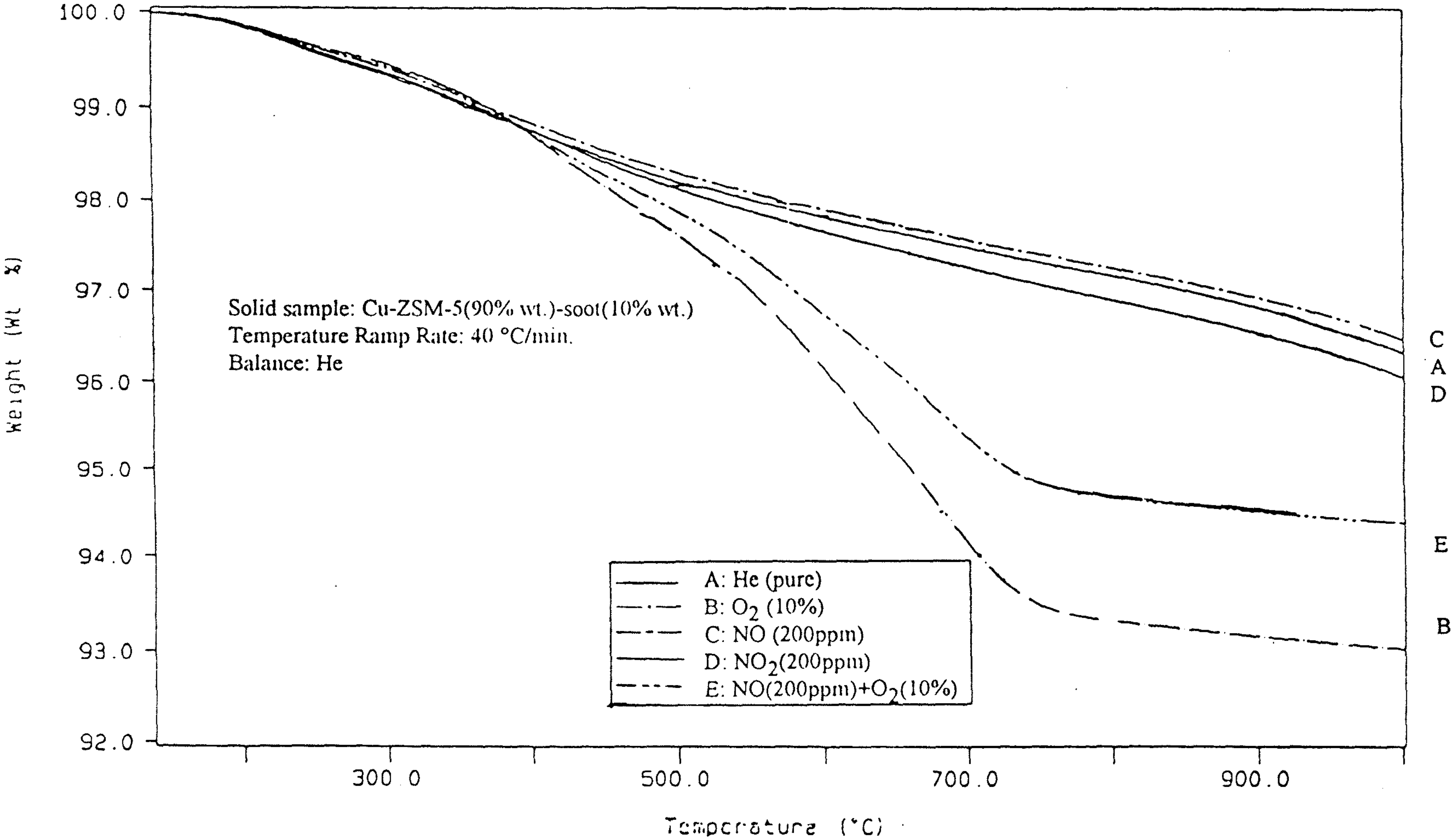


**Figure 24** Weight loss of soot by different gases as a function of temperature



Solid sample: Cu-ZSM-5(90% wt.)-soot(10% wt.)
Temperature Ramp Rate: 40 °C/min.
Balance: He

**Figure 25** Weight loss of the soot/gas reactions over Cu-ZSM-5 as a function of temperature

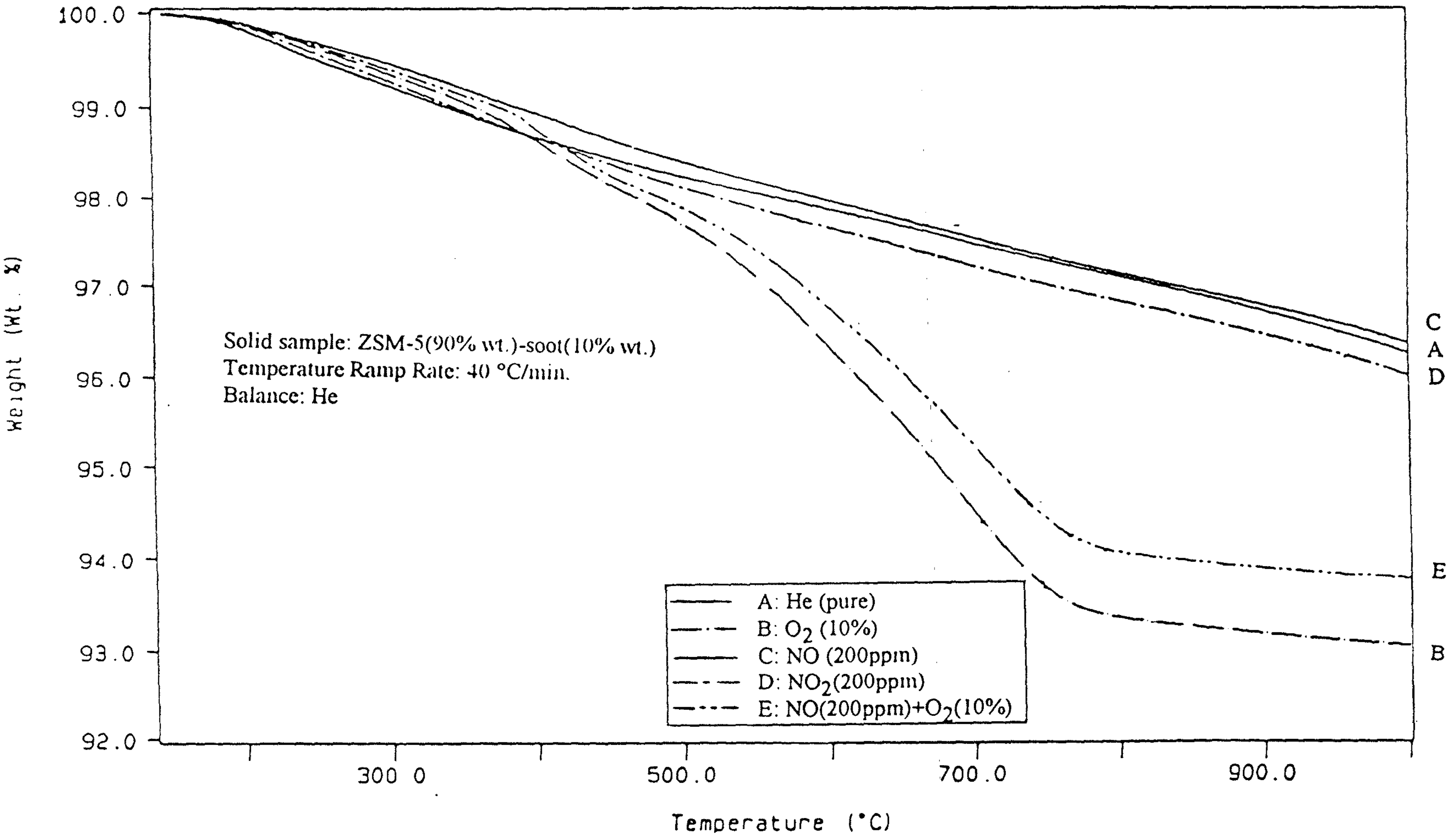


**Figure 26** Weight loss of the soot/gas reactions over ZSM-5 as a function of temperature

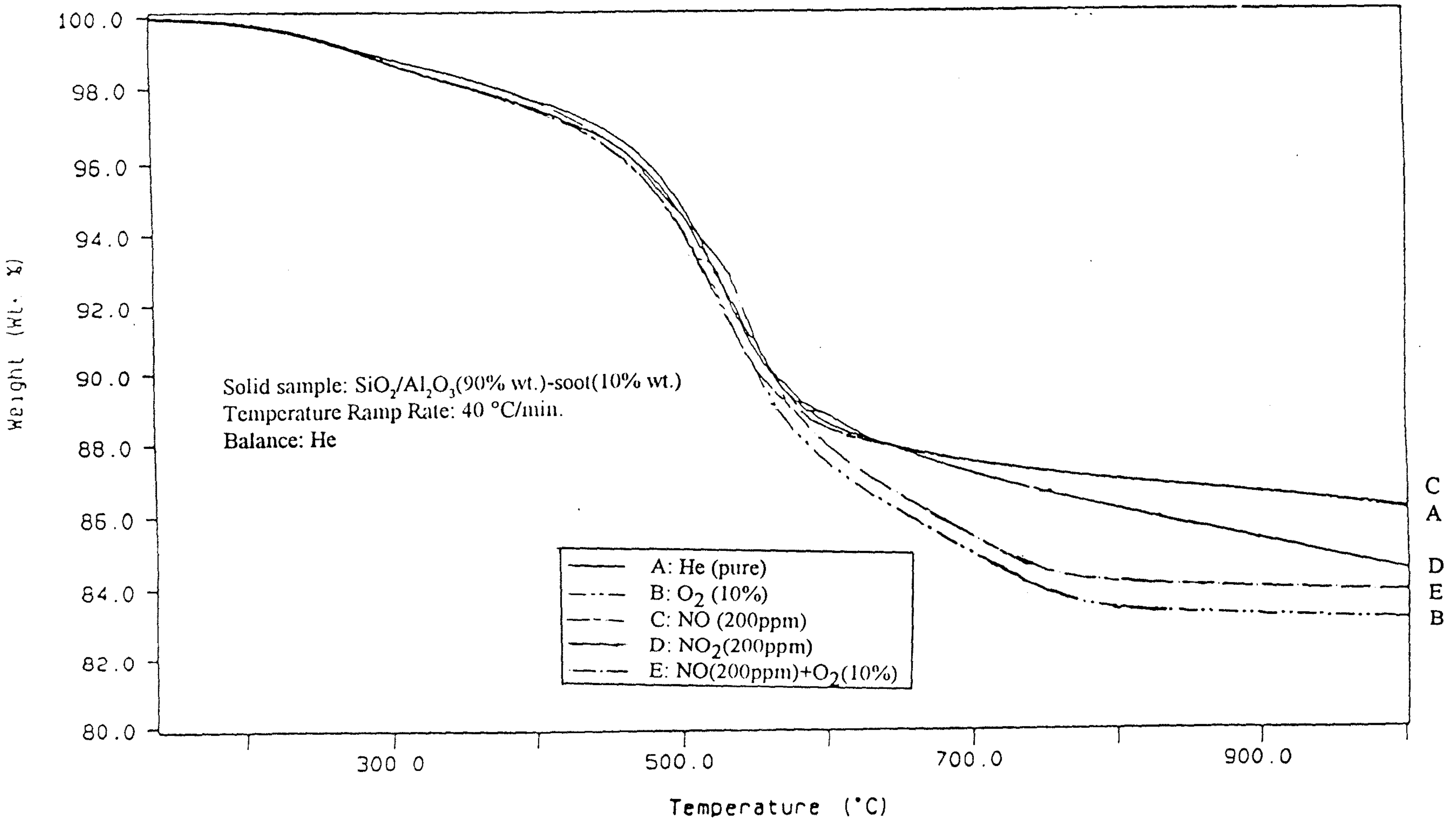


**Figure 27** Weight loss of the soot/gas reactions over $SiO_2/Al_2O_3$ as a function of temperature

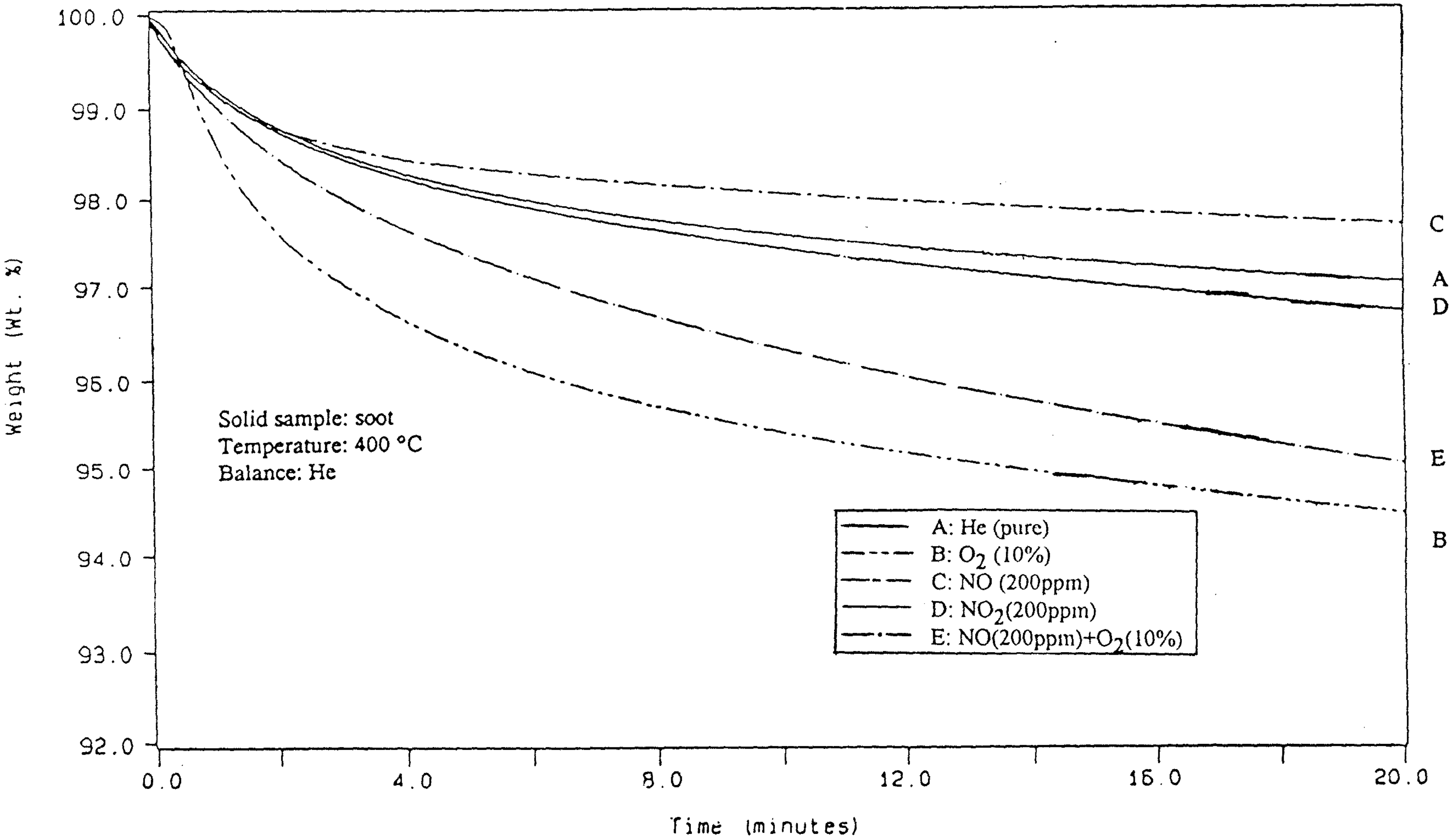


**Figure 28** Weight loss of the soot/gas reactions as a function of time

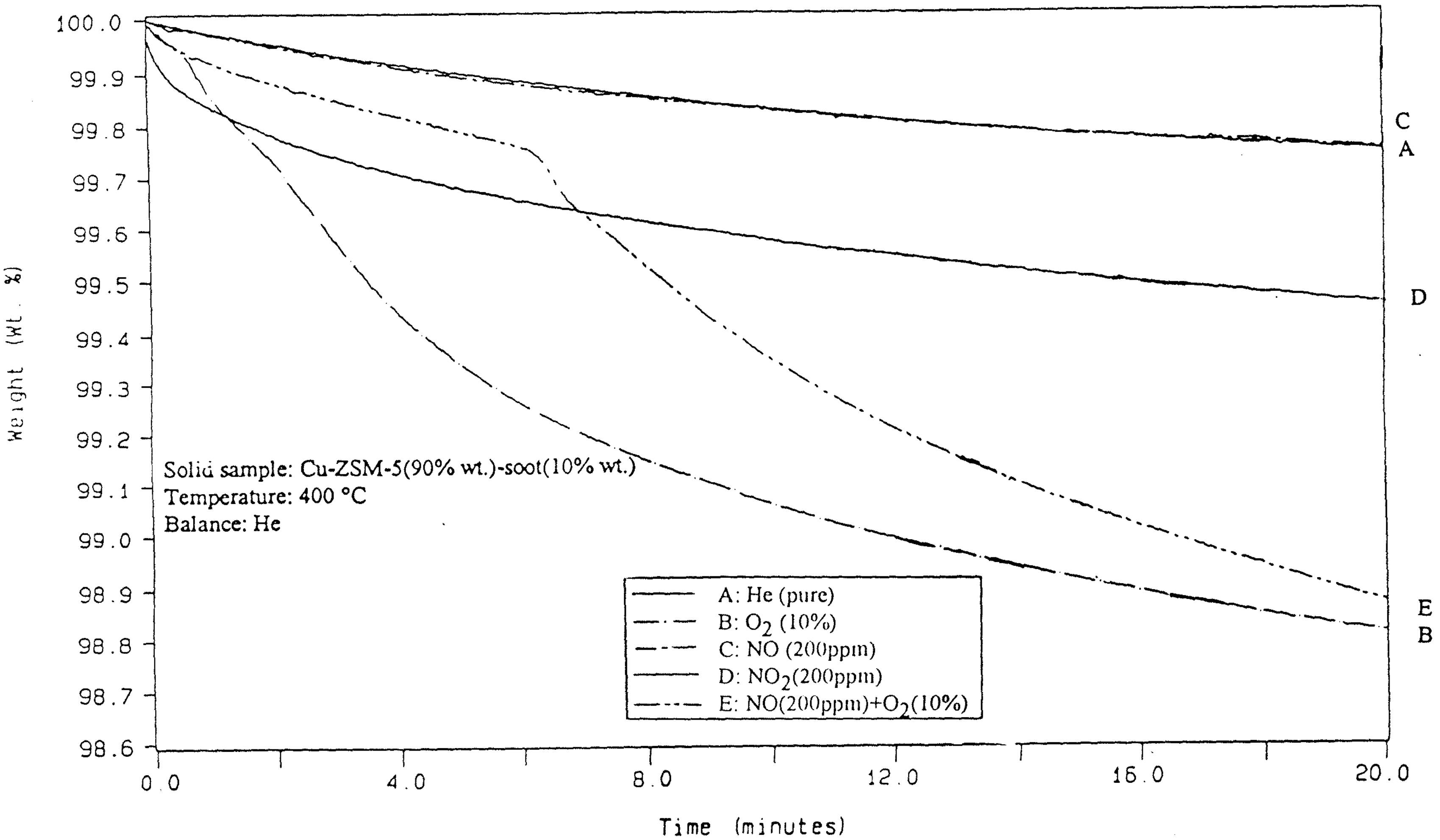


**Figure 29** Weight loss of the soot/gas reactions over Cu-ZSM-5 as a function of time

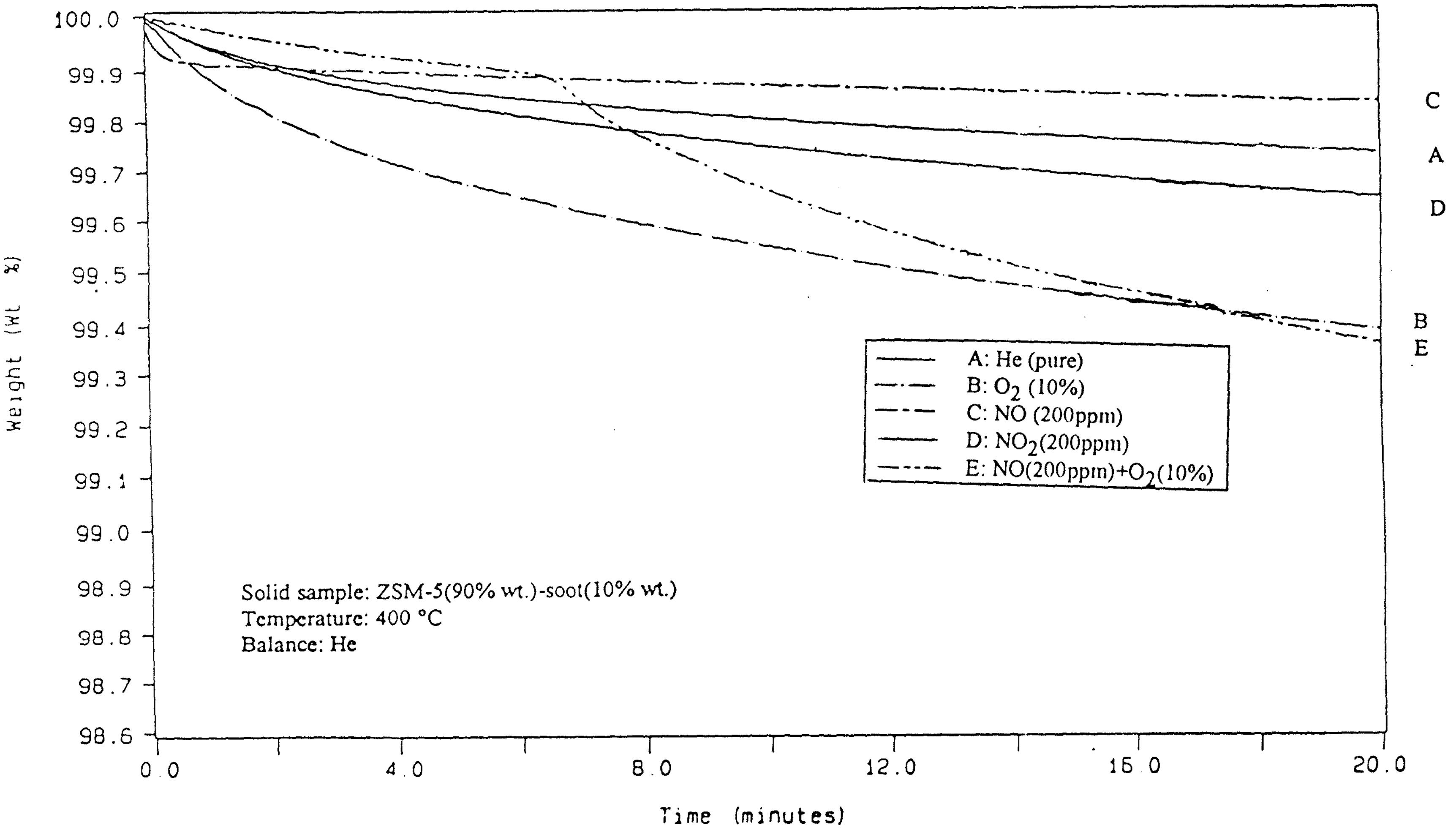
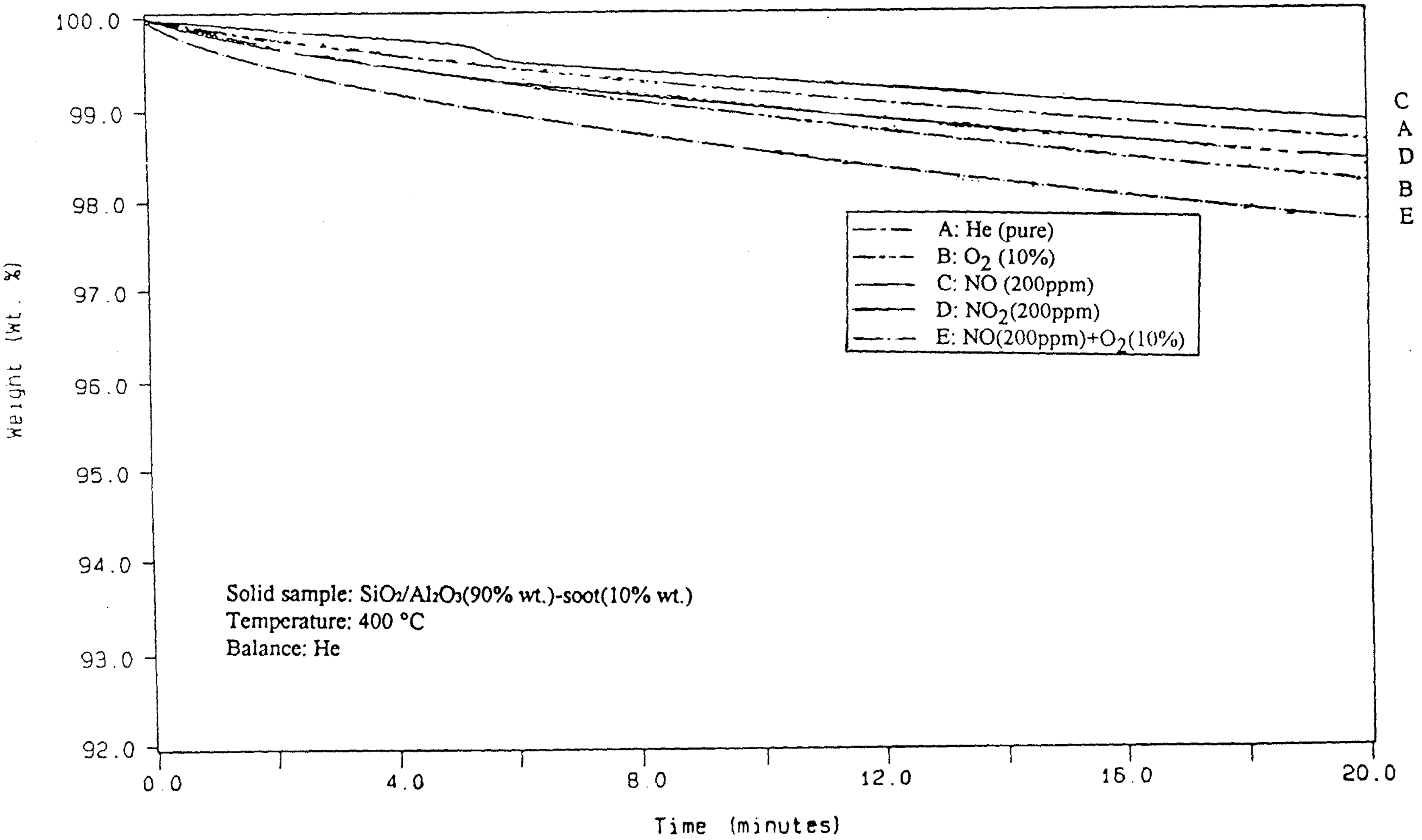


**Figure 30** Weight loss of the soot/gas reactions over ZSM-5 as a function of time



Solid sample: $SiO_2/Al_2O_3$(90% wt.)-soot(10% wt.)
Temperature: 400 °C
Balance: He

**Figure 31** Weight loss of the soot/gas reactions over $SiO_2/Al_2O_3$ as a function of time

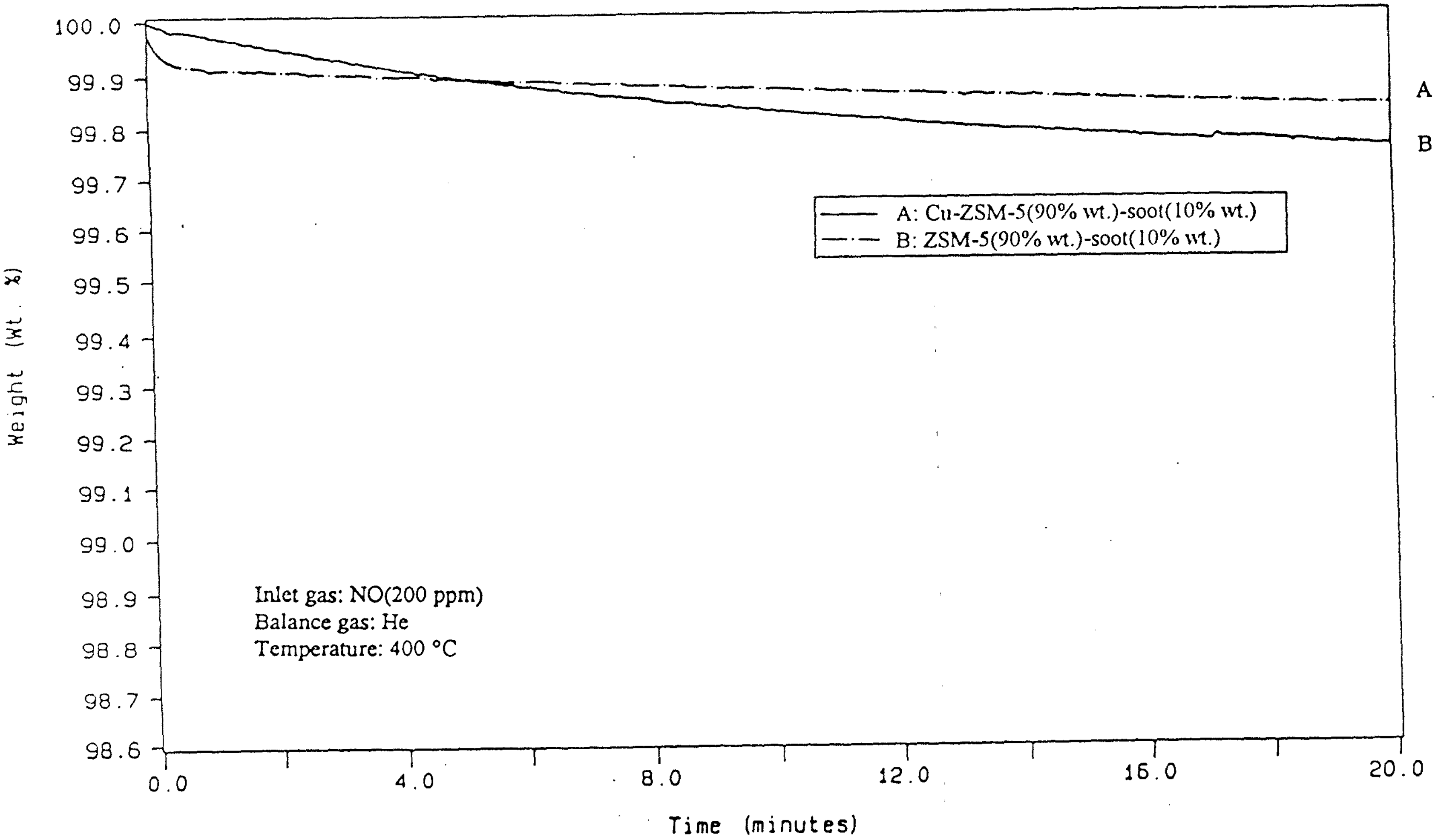
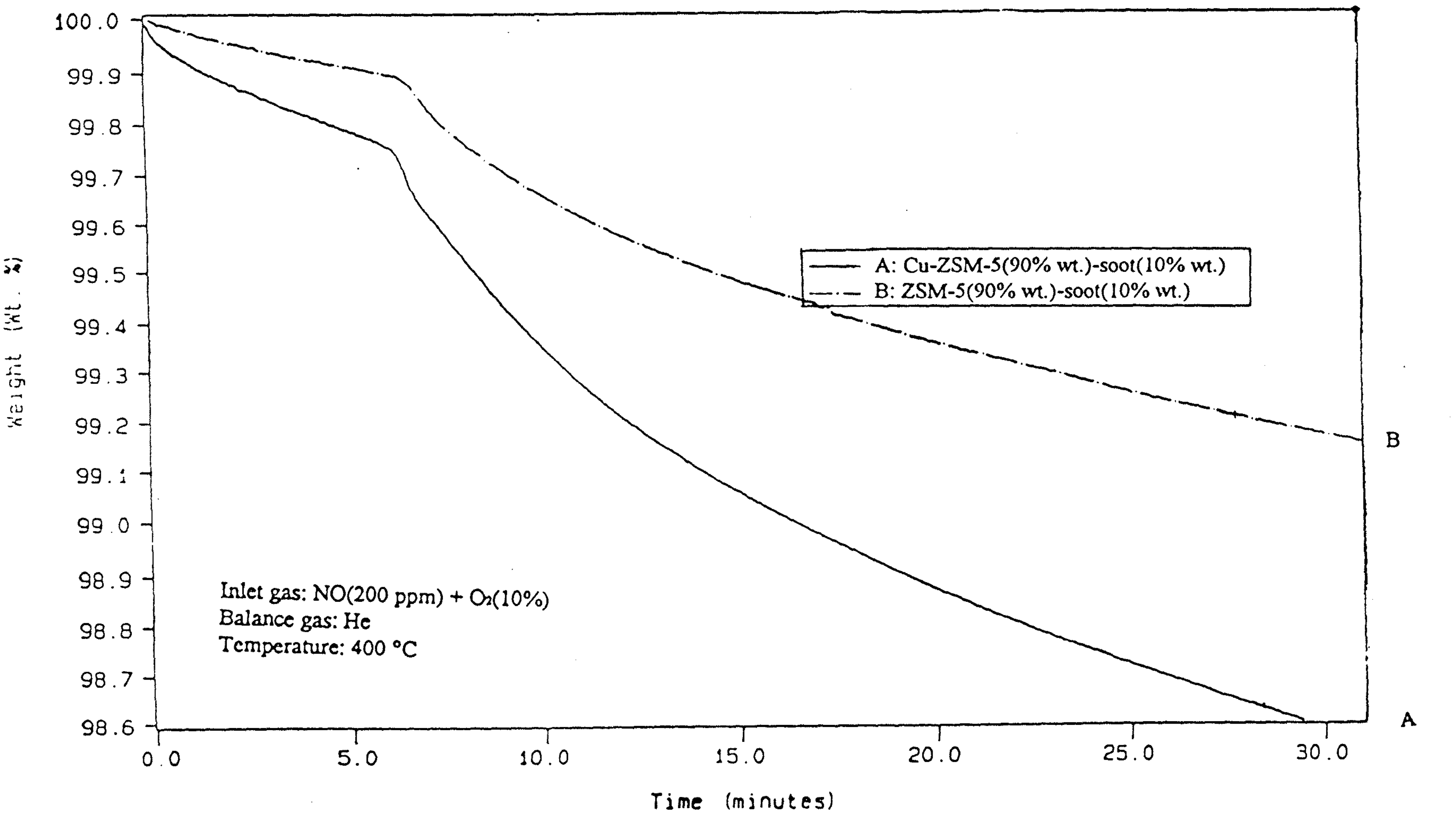


**Figure 32** Comparison of the activitity of Cu-ZSM-5 and ZSM-5 in the soot/NO reaction as a function of time



Inlet gas: NO(200 ppm) + $O_2$(10%)
Balance gas: He
Temperature: 400 °C

**Figure 33** Comparison of the activitity of Cu-ZSM-5 and ZSM-5 in the soot/NO/$O_2$ reaction as a function of time

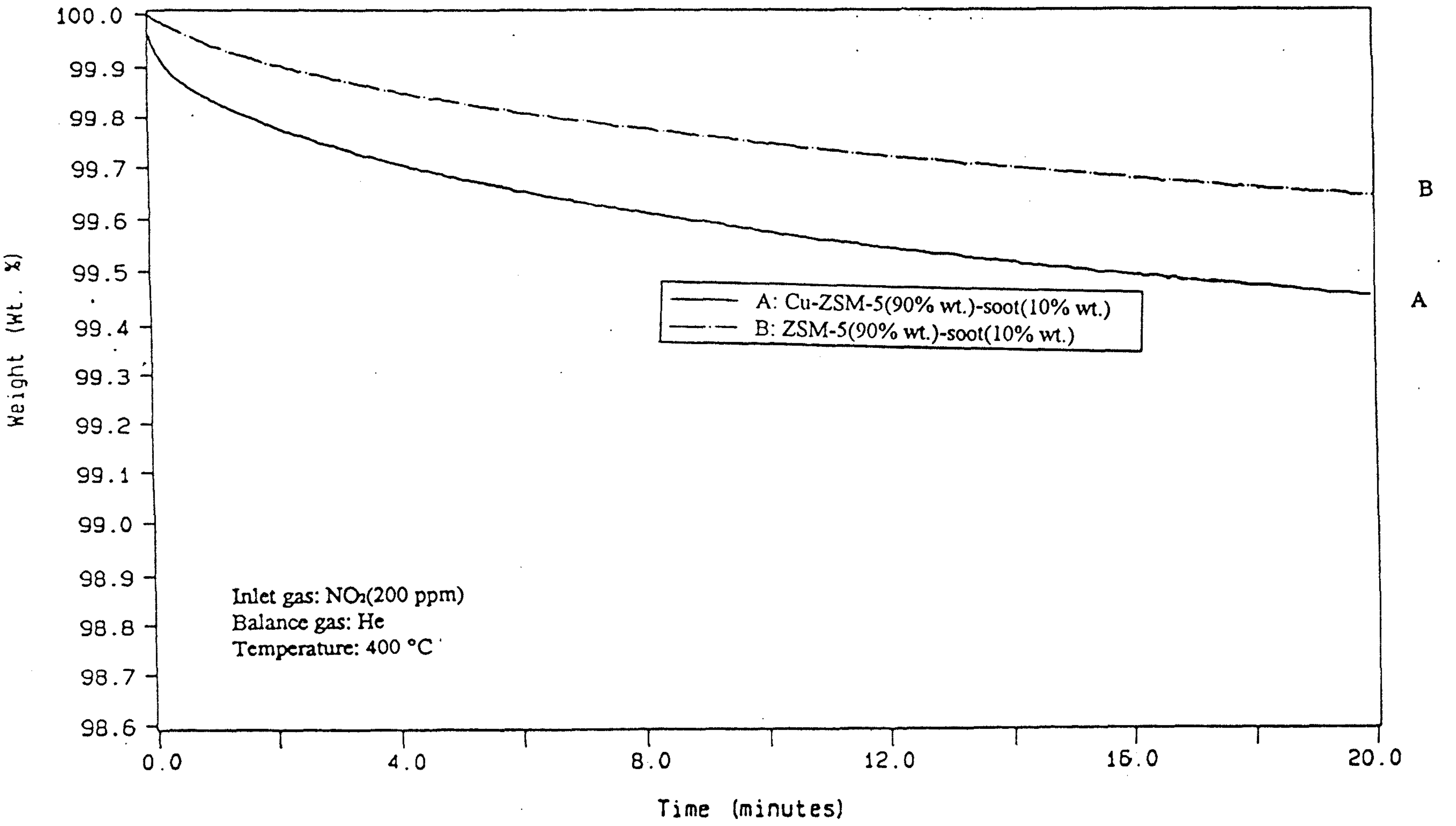


**Figure 34** Comparison of the activitity of Cu-ZSM-5 and ZSM-5 in soot/$NO_2$ reaction as a function of time

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