ABSTRACT

THE EFFECT OF DEPOSITION OF H_2S ON THE CATALYST ACTIVITY OF 1.5% Pt ON γ-Al_2O_3

by
Ping Zhu

The impact of hydrogen sulfide (H_2S) pretreatment on the oxidation activity of powdered 1.5% Pt/γ-Al_2O_3 catalyst was investigated in this study. Fresh 1.5% Pt/γ-Al_2O_3 catalyst was aged with different concentrations of H_2S in air at 400 °C for 24 hours. Then, the aged and fresh catalysts were tested to determine the oxidation activity with diagnostic gases which contained either 1% propane or 1% carbon monoxide in dry air. The test results indicated that the catalysts were deactivated for carbon monoxide oxidation and promoted for propane oxidation as a function of the quantity of H_2S pretreatment. The results showed that peak catalyst activity for propane oxidation was achieved when the catalyst was pretreated with 750 ppm H_2S in air at 400 °C for 24 hours.

The properties of fresh and aged catalysts were compared by Fourier transform infrared spectroscopy (FT-IR), thermal gravimetrical analysis (TGA), dynamic BET surface area, and pulse chemisorption. With FT-IR, the formations of aluminum sulfate and aluminum sulfite were observed, and their quantity increased with increased concentrations of H_2S. TGA analysis indicated the mass of the catalyst increased monotonically with increasing interaction of H_2S dose. BET and chemisorption tests showed both the total surface area and active surface area decrease with increasing quantities of H_2S deposited.

Based on the analysis of the test results, it is inferred that the deactivation of 1.5% Pt/γ-Al_2O_3 catalyst treated with H_2S for CO oxidation is attributed to the presence of aluminum sulfate and sulfite as support for Pt. The enhancement of activity of the H_2S aged catalysts for propane oxidation appears to be due to the formation of alumina sulfate and sulfite near the Pt site.

One possible explanation for the H_2S poisoning of CO oxidation while enhancing the oxidation of propane can be attributed to Somorjai (1972). In accordance with Somorjai's theory, if the adsorbed sulfur changes the surface free energy of the various platinum crystal planes, it can induce the rearrangement of the surface structure to expose crystal planes that have lower surface free energy in the presence of the adsorbed sulfur than the crystal planes that bond to the clean support. This model of sulfur poisoning of platinum surfaces indicates that the chemical surface reactions which are inhibited (or enhanced) by sulfur are sensitive to changes of the surface structure of platinum. Electron microscopy studies also have shown that platinum wire catalysts used in the catalytic oxidation of ammonia which are composed of predominantly (111) crystal planes restructure in the presence of H_2S to (100) crystal planes (Schmidt, et al., 1971). Combining these references with the experimental results in this research, it suggests that the activity of the aged catalyst for CO oxidation decreases due to the formation of aluminum sulfate and sulfite which changes the platinum crystal structure so that platinum crystal planes inhibit CO oxidation. On the other hand, the same crystal structure favors propane oxidation so that the catalyst activity for propane oxidation is enhanced.

THE EFFECT OF DEPOSITION OF H_2S ON THE CATALYST ACTIVITY OF 1.5% Pt ON γ-Al_2O_3

by
Ping Zhu

A Thesis
Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Applied Chemistry

Department of Chemical Engineering,
Chemistry, and Environmental Science

October 1996

APPROVAL PAGE

THE EFFECT OF DEPOSITION OF H_2S ON THE CATALYST ACTIVITY OF 1.5% Pt ON γ-Al_2O_3

Ping Zhu

Dr. Henry Shaw, Thesis Advisor Date
Professor of Chemical Engineering, Chemistry,
and Environmental Science, NJIT

Dr. Barbara Kebbekus, Committee Member Date
Professor of Chemical Engineering, Chemistry, and Environmental Science,
and Associate Chairperson and Graduate Advisor
for Chemistry, NJIT

Dr. Reginald P. Tomkins, Committee Member Date
Professor of Chemical Engineering, Chemistry,
and Environmental Science, NJIT

BIOGRAPHICAL SKETCH

Author: Ping Zhu

Degree: Master of Science

Date: October, 1996

Undergraduate and Graduate Education:

- Master of Science in Applied Chemistry,
  New Jersey Institute of Technology, Newark, New Jersey, 1996

- Bachelor of Science in Chemical Engineering,
  East China University of Chemical Technology, Shanghai, People's Republic of China, 1983

Major: Applied Chemistry

This thesis is dedicated to
my dear parents and my dear husband

ACKNOWLEDGMENT

I wish to express my thanks to all those who helped me complete the research discussed in this thesis.

The author would like to express her sincere appreciation to her advisor, Professor Henry Shaw, for his guidance, encouragement and support in conducting this research.

Sincere thanks go to Dr. Barbara Kebbekus and Dr. Reginald P. Tomkins for their serving as Committee Members and reviewing my thesis.

I am indebted to Mr. Clint Brockway, Ms. G. San Agustin for their advise and help in instrumental and analytical application.

The many thanks extend to Drs. Yi Wang, Taichaing Yu and Chen Gu for their timely help and suggestions in the course of this research.

Finally, I would like to express my deep appreciation to my husband for his considerable help, patience and encouragement and to my parents for their interest and support during my studies at New Jersey Institute of Technology.

TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

Chapter **Page**

LIST OF FIGURES

LIST OF FIGURES
(Continued)

LIST OF TABLES

Table Page

CHAPTER 1

INTRODUCTION

Catalytic processes are involved in most chemical production technologies today. Catalysts are used in over 90% of the processes carried out in chemical plants and petroleum refineries. Highly active and selective catalysts are essential for the economic viability of these processes. Also, catalysts and catalytic technologies may transform harmful products to less polluting materials in order to control air pollution. Several new catalytic approaches for reducing emissions from mobile and stationary sources are under development.

The Clean Air Act (CAA) of 1970 was instrumental in the development and deployment of auto exhaust catalysts. Most new gasoline-powered cars sold in the U.S. were equipped with an oxidation catalyst beginning in the fall of 1974 to reduce the emissions of carbon monoxide (CO) and hydrocarbons (HC) by oxidizing them to CO_2. This of course required the replacement of leaded gasoline with blends that did not contain lead in order to avoid Pb — induced poisoning of the catalysts. The results have been dramatic. As a consequence of the 1989 CAA Amendments (CAAA), emission levels of the three regulated pollutants — CO, HC and NOx — decreased by 96, 98 and 90%, respectively (Calvert, et al., 1993).

In stationary sources, complete catalytic oxidation of various compounds in air has been applied to the control of industrial gas emissions (Palazzolo, et al., 1984), volatile organic (Spivey, 1987), and military life support systems (Lester, et al., 1988).

Control of NOx emissions can also be achieved by using catalytic reduction on transition noble metal catalysts (Bosch, et al., 1987) and zeolitic catalysts (Byrne, et al., 1992).

Despite the gains which have been made, the greatest challenges lie ahead. U.S. EPA has estimated that approximately 130 million people live in 96 areas that do not meet air quality standards, either for ozone, carbon monoxide, or both (EPA, 1993). In response to this, the 1990 CAAA address nonattainment, including standards for ozone (due to nitrogen oxides and volatile organic compounds) and carbon monoxide. CAAA also addresses mobile source emissions, air toxics, and acid rain. To meet these regulations, which will become more stringent with time, it will be necessary to improve the catalysts continually.

Many metallic catalysts, such as platinum supported on various oxides , were widely used for air pollution controls and demonstrated satisfactory results. Unfortunately, catalysts may be poisoned by certain impurities which are present in the feed stream or formed during reactions. The poison can be adsorbed on the active metal sites to form a chemisorbed complex. A low concentration of poison may cause a very marked deactivation effect. Therefore, the test on impact of catalyst poisoning become critical in catalyst application research.

Platinum catalyst can be deactivated by many kinds of poisons such as chlorinated compounds (Lindberg, et al., 1977), sulfur compounds (Butt, et al., 1988) and phosphorus compounds (Williamson, et al., 1985). The effects of some poisons on platinum catalyst has been investigated by Yi Wang (Wang, 1991 and 1995) in our laboratory. His study showed that (1) when an inlet concentration of 50 ppm of a chlorinated hydrocarbon (trichloroethylene) was passed over Pt/γ-Al_2O_3 / monolith / 400 cpsi at 30,000 v/v/hr, no substantial deactivation effect was observed for a period of 100 hours at 450 °C at a conversion of about 80%, (2) a phosphorus compound (tributyl phosphate) poisoned Pt/γ-Al_2O_3 catalyst at both 400 °C and 500 °C. The catalyst was deactivated for carbon monoxide, methane, and propane oxidation, and (3) platinum supported on γ-Al_2O_3 catalyst, after treatment with a sulfur compound (H_2S) in air at 400 °C, was deactivated for carbon monoxide and methane oxidation, and promoted propane oxidation.

To fully understand activation and deactivation mechanism of platinum catalysts due to poisoning, a research program has been set up in our laboratory. The objective of this thesis was to study the impact of the total quantity of hydrogen sulfide (H_2S) dosed over the catalyst on catalytic activity for propane and carbon monoxide oxidation. In this research, 1.5% Pt/γ-Al_2O_3 catalyst was first pretreated by various concentrations of H_2S in air at 400 °C for 24 hours, then propane and carbon monoxide oxidation reactions were performed over these poisoned catalysts respectively, evaluating catalyst activity. The catalyst characterization studies also were conducted to figure out catalyst deactivation and promotion mechanism by using dynamic Brunauer-Emmett-Teller (BET) surface area measurement, pulse chemisorption, Fourier transform infrared (FT-IR) spectroscopy, and thermal gravimetric analysis (TGA). Refer to Chapter 3 for a detailed description of research procedures.

CHAPTER 2

LITERATURE REVIEW

2.1 Fundamental Principles of Heterogeneous Catalysis

2.1.1 Heterogeneous Catalysis and Catalysts

Since Berzelius used catalysis in 1836 to describe some enhanced chemical reactions, the term catalysis has been used to describe a wide variety of phenomena, but in all instances the catalyst exerts a more-than-proportional influence over some change (Happel, 1986). A catalyst is frequently defined as a substance that increases the rate of reaction without being appreciably consumed in the process (Bond, 1974). However, increasing the rate of a reaction with the catalyst is complicated, because the simplicity of the overall chemistry of the catalyzed reaction usually hides a bewildering complexity of separate reaction steps on the catalyst surface. A catalyst does not alter the equilibrium of a system (thermodynamics). Thus, if the rate of the forward reaction is increased, then the reverse reaction must also increase to maintain the equilibrium constant invariant. The separate stages of a heterogeneously catalyzed gas-phase reaction can be summarized as follows (Spencer, 1989):

1. Transport of reactants through the gas phase to the surface or exterior of a catalyst pellet
2. Transport of reactants through the surface or pore system of the catalyst pellet to a catalytically-active site
3. Adsorption of reactants at the catalytically-active site

4. Chemical reactions between reactants at the catalytically-active site (frequently several steps)
5. Desorption of products from the catalytically-active site
6. Transport of products through the catalyst surface or pore system from the catalytically-active site to the exterior of the catalyst pellet
7. Transport of products into the gas phase from the surface or exterior of the catalyst pellet

Any of these stages, if slow, may limit the overall rate of a catalytic reaction. Distinctions are often drawn between catalysts which are "film-diffusion controlled" (i.e. limited by stages 1 and/or 7), "pore-diffusion controlled" and "reaction controlled" (i.e. limited by stages 3, 4 and/or 5). Film diffusion controlled reactions are also called mass transfer limited reactions and tend to occur at elevated temperatures where the rate of reaction is much faster then diffusion. But, in practice, the situation will be more complicated than these simple distinctions. There is a complex interaction between the relative importance of these different stages and the resulting selectivity when several products are formed. Also the rates of the different stages can be changed by experimental conditions such as temperature, bulk-fluid velocity, and properties of the catalyst, etc (Rideal, 1968). Therefore the study of reaction mechanisms is important both for the development of effective catalysts and for finding conditions required for their optimal application.

2.1.2 Catalyst Characterization

Obtaining catalyst characterization data is necessary at every stage of catalyst development. Critical parameters, classified as bulk chemical properties, surface chemical properties and physical properties, are measured not only to check the effectiveness of each operation but also to provide specifications for products.

2.1.2.1 Bulk Properties Bulk properties include bulk elemental composition, crystalline phases present, particle shapes and sizes, particle compositions and particle crystal structures, etc. X-ray diffraction and electron microscopy (Baird, 1982) can be used for determination of these properties. In the x-ray diffraction method, monochromatic x-rays are reflected from the sample with diffraction lines produced from the repetitive dimension of crystal planes. Each crystal type gives a characteristic pattern, so that the position of lines is a clue to the presence of a particular compound. Electron microscopy is also often used to determine bulk catalyst properties. The electrons in a microscope are emitted from an electron gun, which is a heated pointed cathode (filament), accelerated through two electrodes, the second of which is an anode. The electrons then pass through a condenser system, the specimen, and a magnetic lens system, so that size or microstructure can be determined for catalysts.

Some other experimental techniques can be used in special cases for determining the properties of catalysts. One of these techniques is Thermal Gravimetric Analysis (TGA) in which small weight changes of catalysts are measured by changing experimental conditions. TGA has been applied in adsorption-desorption studies and has been particularly useful for studying the rate of coking, dehydration, sorption of poisons, and catalyst regeneration as a function of reaction conditions (Satterfield, 1980).

2.1.2.2 Surface Area Total surface area of a catalyst is possibly the most important particle parameter specified without regard to the type of surface. The most common method for measuring catalyst surface area was developed by Brunauer, Emmett, and Teller in 1938. The principle of the method is by adsorption of a monolayer of nitrogen at liquid nitrogen temperatures onto the surface. The cross-sectional area of a nitrogen molecule when packed on the catalyst surface is 0.162 nm^2, hence the quantity of nitrogen molecules adsorbed at monolayer coverage gives directly the total surface area of the catalyst.

2.1.2.3 Metal Area and Dispersion With a supported metal catalyst, it is frequently desirable to determine the ratio of exposed metal area to the total surface area, since metal surface area is directly proportional to catalyst activity. These measurements are obtained by measuring the uptake of a gas that is chemisorbed on the metal, but negligibly on the support, under conditions that allow the coverage corresponding to a monolayer to be determined. One chemisorption technique is pulse chemisorption. Pulse chemisorption is performed by sequentially pulsing a known volume of adsorbent gas, typically hydrogen or carbon monoxide, on the catalyst sample. The initial pulse volumes increase until a steady state is reached indicating saturation. The amount of adsorbed gas is determined by the difference with the sum of the non-adsorbed pulse areas.

Metal dispersion is most commonly used as a measure of active sites on a catalyst. Dispersion is defined as the ratio of the number of surface metal atoms available as catalyst sites to the total number present. The value of metal dispersion can be determined by the above mentioned pulse chemisorption method.

2.1.3 Catalyst Activity and Selectivity

The activity of a catalyst reflects the degree to which the rate of a chemical reaction proceeds to steady state relatively to the same reaction without the catalyst. Because activity responds in a different way to experimental variables such as pressure, temperature, residence time, and chemical and physical structure of the catalyst, the study of catalyst activity has become an approach to enhance the understanding of catalytic reaction mechanisms.

Catalyst selectivity is a measure of the extent to which it accelerates the reaction to form one or more of the desired products. The selectivity of a catalyst will usually vary with pressure, temperature, reactant composition, and extent of conversion as well as with the nature of the catalyst. It can be enhanced by the addition of small amounts of poisons (Karanth and Luss, 1975). Therefore, effective control of various parameters will result in optimum selectivity.

2.1.4 Catalyst Deactivation

Any process, chemical or physical, which decreases the intrinsic activity of a catalyst can be classified as deactivation. General reviews of catalyst deactivation have been given by Butt and by Levenspiel. Basically, three kinds of deactivation may occur (Levenspiel, 1972): (1) sintering or thermal deactivation of the catalyst; (2) poisoning; (3) fouling.

Sintering refers to the loss of area of the catalyst which occurs when the catalyst is operated above the normal range of temperature. From the sintering aspect alone, catalysts may be divided into two groups. The first of these are composed of normal high-area support type materials (usually an oxide or mixed oxide). When such a material is operated at high temperatures over a long period of time, loss of area will occur due to a coalescing of the individual particles or grains making up the compact structure. The second group of catalysts affected by sintering comprises the supported metal type. In this type of catalyst, a metal is present in a highly dispersed form on a high surface area ceramic oxide support. For catalysts of this type, sintering can occur by reduction of the support area, loss of dispersion of the metal crystallites or reduction of the area of both components (Wynblatt, et al, 1975). All of these sintering methods can cause a catalyst deactivation.

The most usual type of catalyst poisoning is caused by impurities that are either present in the gas stream or are formed by some process during the reaction. In both cases, this poison becomes adsorbed on the active sites of the catalyst, causing a fall-off in the activity of the catalyst (Hughes, 1984). Poisoning may be either temporary or permanent. The former implies that the poisoning process is reversible and catalyst activity may be restored by removing the source of the poison or the poison itself, if the adsorption of poison is not too strong. The latter is irreversible and catalyst can not be reactivated due to strong or irreversible adsorption of the poison. Besides the adsorption of poison, the compound formation between the poison and the catalyst represents another class of poisoning problems, it may poison the activity of catalysts even more seriously. However, poisons are not always undesirable. In some cases selective poisons may enhance the activity or selectivity of the catalyst for a reaction while inhibiting for another one (Hegedus, et al., 1984).

Catalyst deactivation by fouling may be either physical or chemical in nature and usually involves significant amounts of deposited material. Basically, two types of fouling may occur due to (1) the reaction system itself and (2) deposition by an impurity in the feed stream. The first is the most typical fouling process in which a carbonaceous deposit or "coke" forms on most catalysts used in processing of petroleum fractions or other organic chemical feedstocks. The second type is fouling of metal sulphide deposition arises from the organometallic constituents of petroleum which react with sulfur-containing molecules and deposit within the pores of the catalyst during hydrotreating operations. It should be mentioned that fouling may not occur solely as the means of catalyst deactivation. In many processes, fouling, especially coking, will occur simultaneously with poisoning and also possibly with some sintering of the catalyst (Hughes, 1984).

2.2 The Effect of Sulfur Compounds on Metal Catalysts

Impurities (in the feed to a catalyst) can affect catalyst performance when their interaction with the catalyst is stronger than that of the feed. Sulfur is a commonly encountered impurity. Less concentrated sulfur dioxide (SO_2) such as 10 ~ 60 ppm presented in the exhaust gas is known to poison noble metal catalysts even though the poisoning is considerably less severe than base metal catalyst poisoning (Shelef, et al., 1978). The causes have not been well studied, though they include sulfate formation and poisoning. This poisoning for supported platinum oxidation catalysts may be due to the weakening of the Pt-adsorbate bond (whether the adsorbate is oxygen or the oxidizable contaminant) by the very strong Pt-S bond (Butt, et al., 1988).

Sulfur poisoning of noble metal catalysts has been widely studied. Gandhi and Shelef (Gandhi, et al., 1991) studied the effects of sulfur on $Pt/\gamma\text{-}Al_2O_3$ catalyst. Their results showed that SO_2 in the feed gas enhances propane oxidation but suppresses both propylene and carbon monoxide oxidation over a $Pt/\gamma\text{-}Al_2O_3$ catalyst. In accordance with infrared data, the sulfates were formed on γ-Al_2O_3 after the SO_2 adsorption and oxidation, which could be interpreted to be the major reason for enhancing propane oxidation and inhibiting both carbon monoxide and propylene adsorption on Pt/γ-Al_2O_3 catalyst. The sulfur compound effect on methane over supported palladium, rhodium and iridium catalysts has been studied by Deng, et al. (Deng, et al., 1993). They reported that the activity of all these catalysts decreased for methane oxidation. This deactivation was due to the sulfur compound adsorbed and oxidized to sulfate at the reaction condition. Menon and Prasad (Menon, et al., 1977) compared the sulfur poisoning of Pt-alumina with that of Pt-Re-alumina during reforming reactions. The Pt in both catalysts is converted to a sulfided state. The sulfided catalysts are still active for dehydrogenation, dehydroisomerization, dehydrocyclization, and hydrocracking, but the relative contributions of these pathways are altered. Thus, sulfidation decreases excessive dehydrogenation and so reduces coke formation. It also results in lowering the hydrocracking activity, leading to better selectivity toward aromatization and increased liquid yields.

Several studies have shown that SO_2 is a temporary poison for Pt/Rh catalysts in automotive exhaust (Gandhi, et al., 1978). The introduction of SO_2 into the exhaust instantaneously resulted in a reduction of emission control performance, which is rapidly restored upon removal of SO_2 from the exhaust feed stream (Wiliamson, et al., 1979). Pt and Rh appear to recover their activity rapidly upon the removal of SO_2 from the exhaust (Monroe, et al., 1991).

Sulfur is also an issue with diesel catalysts. Diesel fuel contains relatively high levels of sulfur which are combusted to SO_2, adsorbed on the catalyst support and further oxidized to sulfate compounds. The sulfate species mostly end up as hydrated sulfuric acid which is counted as particulate matter. However, it can be controlled by an adequate method. Surface modifiers, such as vanadia, are effective in mitigating the formation of sulfate on alumina-supported diesel catalysts (McCabe, et al., 1995).

CHAPTER 3

EXPERIMENTAL

3.1 Catalyst and Materials

Catalysts play a critical role in controlling the emissions of gaseous pollutants into the atmosphere, mostly from automobiles, manufacturing and electric power plants. One of the most effective catalysts for air pollution controls is platinum supported on various oxides such as γ-alumina. This is a consequence of its high activity for oxidation of organics at relatively low temperatures.

The catalysts, 1.5% platinum (Pt) supported on gamma (γ) alumina powder, employed to evaluate the impact of sulfur compounds on the oxidation of CO and C_3H_8. These catalysts were provided by Engelhard Corporation. The physical properties were measured with BET surface area of 80 m^2/g, particle size between 30μm and 95μm, and a bulk density of 0.92 g/cm^3.

The different kinds of analytical gases from Matheson Gas Co. were used either individually or mixed with each other for different experiments. The certified gas mixtures and pure gases were included in Table 3.1. All these gases were used directly from the cylinder without additional pretreatment.

The major equipment units of the experimental systems with their characteristic and vendor names are listed in the Table 3.2.

Table 3.1 Analytical Gases

Certified Gas Mixtures	Pure Gases
500 ppm H_2S in N_2	Air, Dry
6,100 ppm H_2S in N_2	99.998% Argon, Prepurified
1% CO in air	99.995% Helium, High Purity
1% C_3H_8 in air	99.99% Hydrogen, Prepurified
10% N_2 in He	99.998% Nitrogen, Extra Dry
20% N_2 in He	-
30% N_2 in He	-

Table 3.2 Experimental Equipment

Equipment Name	Function	Characteristic	Vendor
Reactor	Providing reaction bed for catalysts	1 inch I.D. quartz tube	Q. Glass Co.
Furnace	Providing heating source for reaction	Three zone controlled type	Applied Test Systems Inc.
Rotameter	Measuring gas flow rates	0 ~ 150 cm^3/min 0 ~ 700 cm^3/min	Cole Parmer Instrument Co.
Thermocouple	Monitoring temperatures in reactor and furnace	K-type Temperature range 0 ~ 990 °C Accuracy: ± 10 °C	OMEGA Engineering Inc.

3.2 Experimental Procedures and Equipment

3.2.1 Catalyst Aging Test

Catalyst poisoning tests lead to deactivation of a catalyst. Our goal, however, was to study the catalyst enhancing parameters of sulfur for propane oxidation and poisoning for CO oxidation. In order to distinguish the sulfur treatment phase from the diagnostic testing phase of the research, we referred to sulfur deposition as aging test.

3.2.1.1 Catalysts and Space Velocity The fresh catalyst used in this study was 1.5% platinum supported on γ-alumina powder. Since the measured bulk density of the fresh catalyst is 0.92 g/cm^3, the catalyst net volume is 1.09 cm^3 per gram weight. The total gas flow rate for aging tests was set at about 300 cm^3/min. The space velocity (SV), a critical factor in the design of catalytic system, was defined as the total gas flow rate per unit volume of catalyst. The SV value used in this study was obtained using the following correlation:

$$\begin{aligned} SV &= \frac{\text{total gas flow rate}}{\text{catalyst volume}} \\ &= \frac{300\ (\text{cm}^3/\text{min}) * 60\ (\text{min/hr})}{1.09\ (\text{cm}^3)} \\ &\approx 16{,}500\ (\text{v/v/hr}) \end{aligned}$$

3.2.1.2 Aging Test System Figure 3.1 is a schematic of the catalyst aging system showing the major components as well as auxiliary equipment. Fresh catalyst powder was loaded into a 2.54 cm inside diameter quartz tubular reactor, and held on a course fritted quartz disk mounted in the reactor center. The reactor was placed in a three (3) zone controlled furnace for heating up. The catalyst bed temperature was maintained by a thermal controller and monitored by three Chromel-Alumel (K-type) thermocouples. One of the thermocouples was located in the furnace to control the heater. The other two thermocouples, which were respectively located about 0.5 inch away from the top

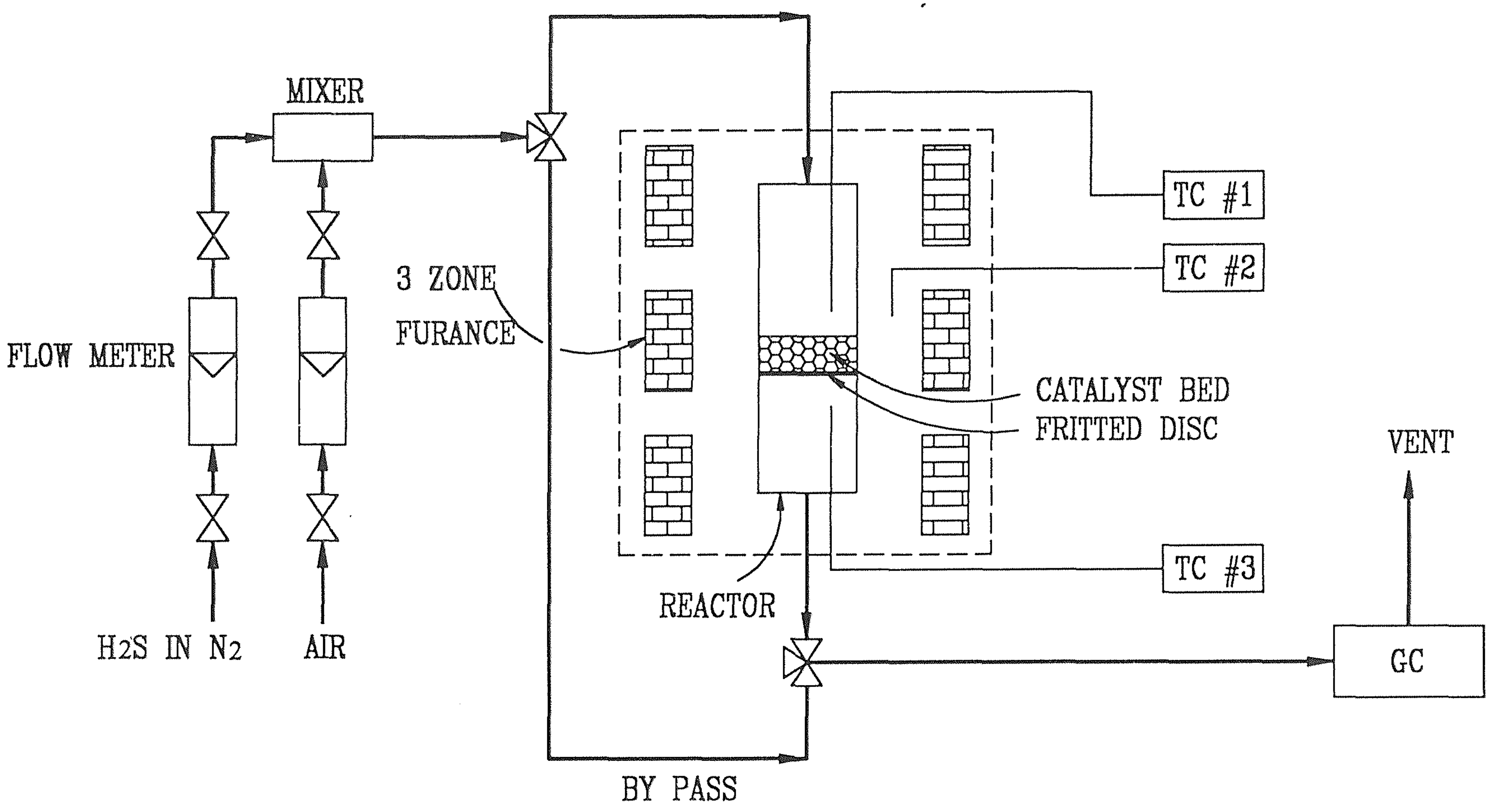


Figure 3.1 Catalyst Aging System

and bottom of the catalyst bed, were used to measure inlet and outlet temperature for the catalyst bed. The test gases were prepared by mixing 6,100 ppm hydrogen sulphide (H_2S) with the balance dry air from a certified gas cylinder with various flows of dry air from a cylinder using two (2) rotameters. The resulting mixture was not checked using a GC with FPD because the instrument was not working. The concentration of H_2S used to treat the catalyst is based on the flow measurements which are accurate to 10%. After obtaining a desired mixture, it was used to age the catalyst at 400 °C for 24 hours of continuous operation. At the inlet and outlet of the reactor, these gas streams were analyzed with an on-line gas chromatograph with flame photometric detector (GC-FPD).

3.2.2 Catalyst Activity Test

Catalyst activity refers to the degree to which a chemical reaction rate is increased compared with the same reaction without the catalyst. Catalysts can also be selective (more active for the production of some compounds, less active for others). Therefore, catalyst activity is a key parameter in design, selection, and optimization of catalysts. The method used in this research was based on varying the concentration of active sites in the catalyst. The catalyst activity can be evaluated in accordance with the relationship between the observed results of the diagnostic test and the concentration of active sites.

3.2.2.1 Catalysts and Space Velocity In order to evaluate the effect of H_2S on catalyst activity, catalysts were aged with 80 ppm, 100 ppm, 270 ppm, 500 ppm, 750 ppm, 1,000 ppm, 1,200 ppm and 1,750 ppm H_2S in air and nitrogen. The effect from the cylinder containing 6,100 ppm H_2S, balance N_2, was mixed with air in order to obtain the desired concentration. The activity of the aged catalysts were compared with the activity of fresh catalysts for CO and propane oxidation.

The diagnostic gas mixture was introduced into the catalyst bed which consisted of 0.05 g catalyst diluted with 0.25 g γ-Al_2O_3, and the flow rate of feedstream was set at 50 cm^3/min, equivalent to a space velocity of 55,000 v/v/hr. The diagnostic gases were propane and carbon monoxide and each gas was tested on an otherwise untreated fraction of the aged catalysts.

3.2.2.2 Catalyst Activity Test System Figure 3.2 presents a schematic of the equipment used for activity testing. The Altamira Instrument, a specially designed analytical device, was employed in this system to serve as a controller for catalyst bed temperature and gas flow rate. A 0.05 g catalyst sample diluted with 0.25 g gamma alumina which increases the mass of sample and does not affect the catalyst activity was packed in a quartz U-tube reactor for diagnostic gas oxidation activity testing. The U-tube was placed in a temperature controlled furnace. For monitoring the temperature, one thermocouple was inserted inside the catalyst bed, and the other was located in the furnace. The diagnostic gas flow rate into the reactor was 55 ± 1 cm^3/min. At the outlet of the reactor, the diagnostic gas stream was analyzed by an on-line gas chromatograph with a flame ionization detector (GC-FID) and a Ni-catalyst system to quantitatively oxidize CO and CO_2 , and measure them as methane.

In this research, we chose carbon monoxide and propane as diagnostic gases, since they are representative of the major pollutants in automobile emissions and the

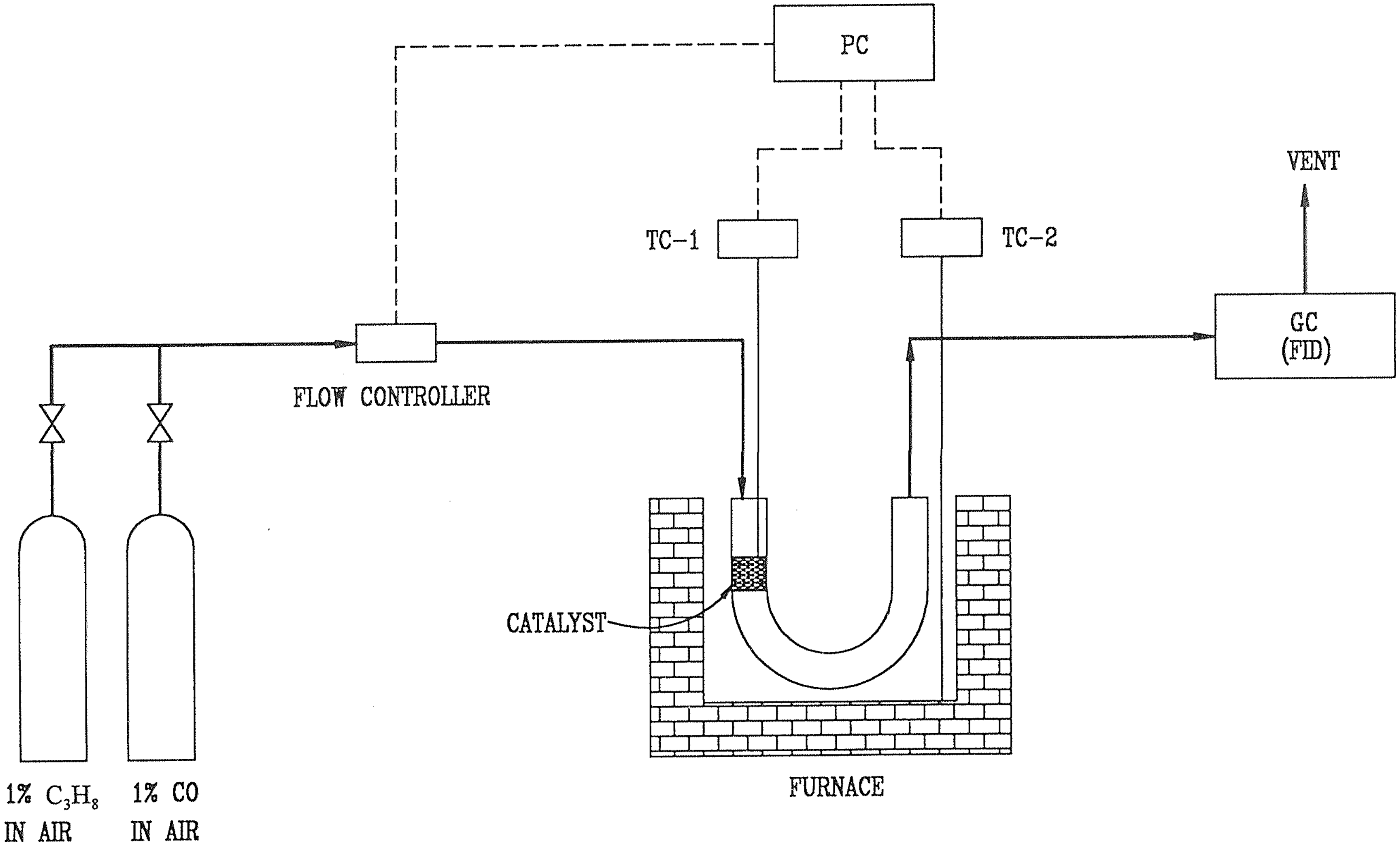


Figure 3.2 Catalyst Activity Test System

experimental results could be used to improve the design of the automobile catalytic pollution control systems.

3.3 Instrumental Analysis

3.3.1 Gas Chromatography (GC)

Gas chromatography (GC) is the most commonly used analytical technique for the quantitative determination of many chemicals. In this research, GC was utilized to analyze various gas compositions at the inlet and outlet of the reactor.

GC-FID was used for detecting the concentration of carbon monoxide (CO), carbon dioxide (CO_2) and propane (C_3H_8). The carbon monoxide, carbon dioxide and propane were separated on a Porapak Q packed column Porapak Q. Carbon monoxide and carbon dioxide were hydrogenated into methane in a Ni-catalyst system before analysis with a flame ionization detector. The schematic diagram for the nickel hydrogenation catalyst (Ni-catalyst) system is shown in Figure 3.3. The effluent gas streams normally passed through the sampling loop of the gas injection valve and discharged to a hood. On the other hand, if this valve was switched to the "on" position, the sample gas stream was carried out by the helium carrier gas from the sampling loop into the packed column. The gas stream, therefore, after separation into individual gas components and hydrogenation using the Ni-catalyst system at 350 ^{0}C was analyzed using FID, based on retention time. Typical peak resolution and retention times for the reactants and products of gas samples are illustrated in Figures 3.4 and 3.5. The operating conditions for GC-FID are listed in Table 3.3.

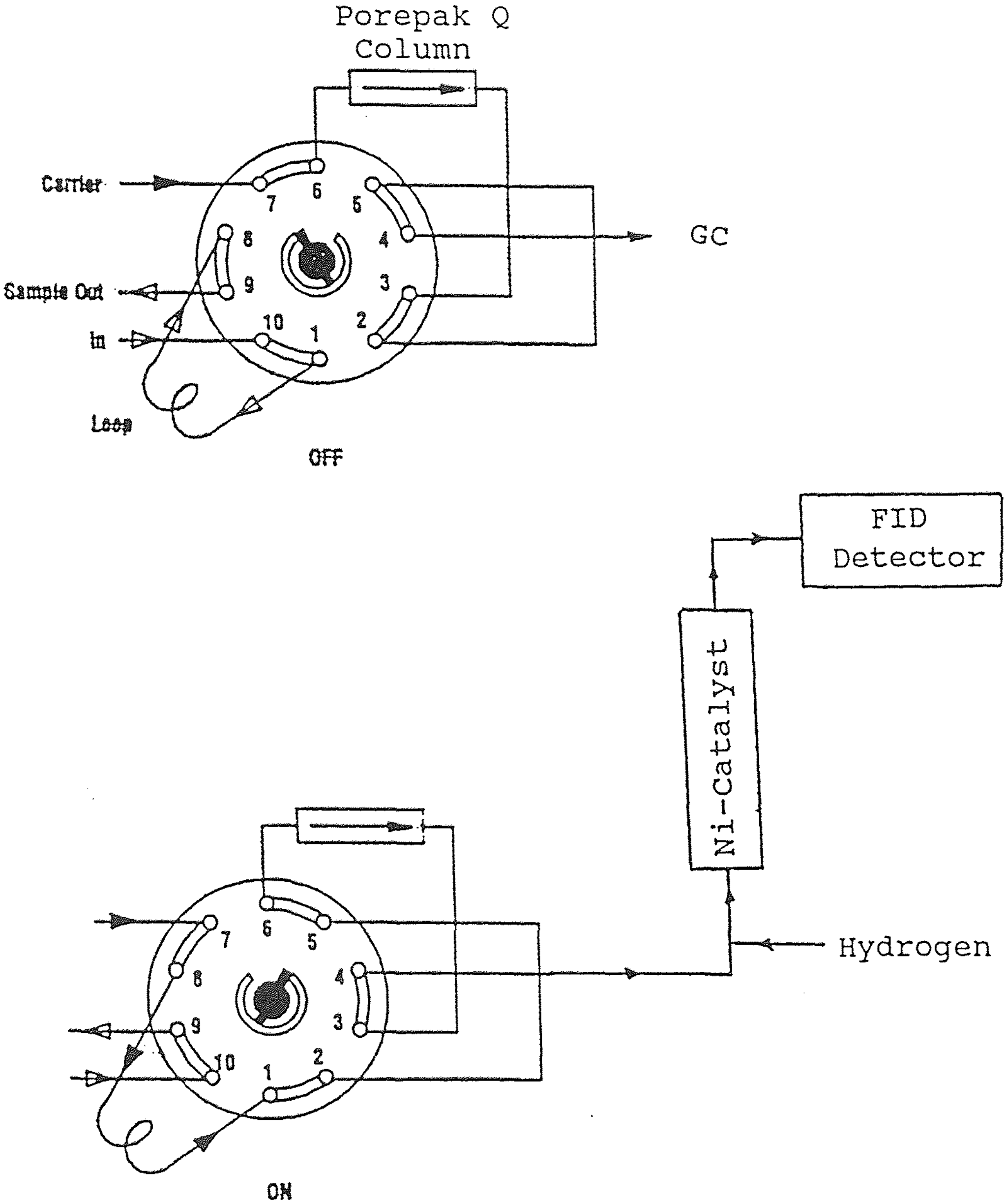
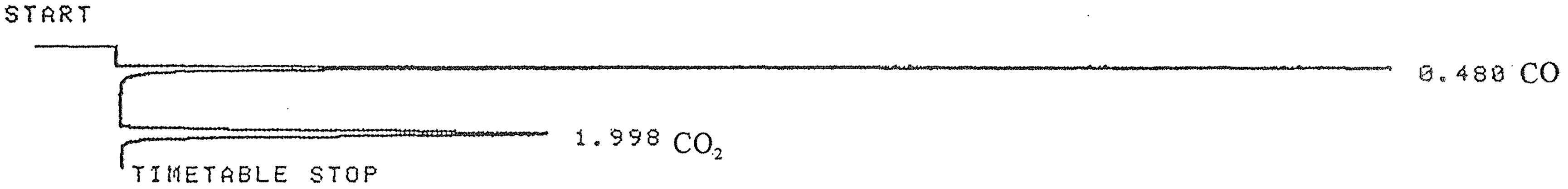


Figure 3.3 Nickel Catalyst System

```
*  RUN # 2282      JUN 28, 1995  20:42:38
```



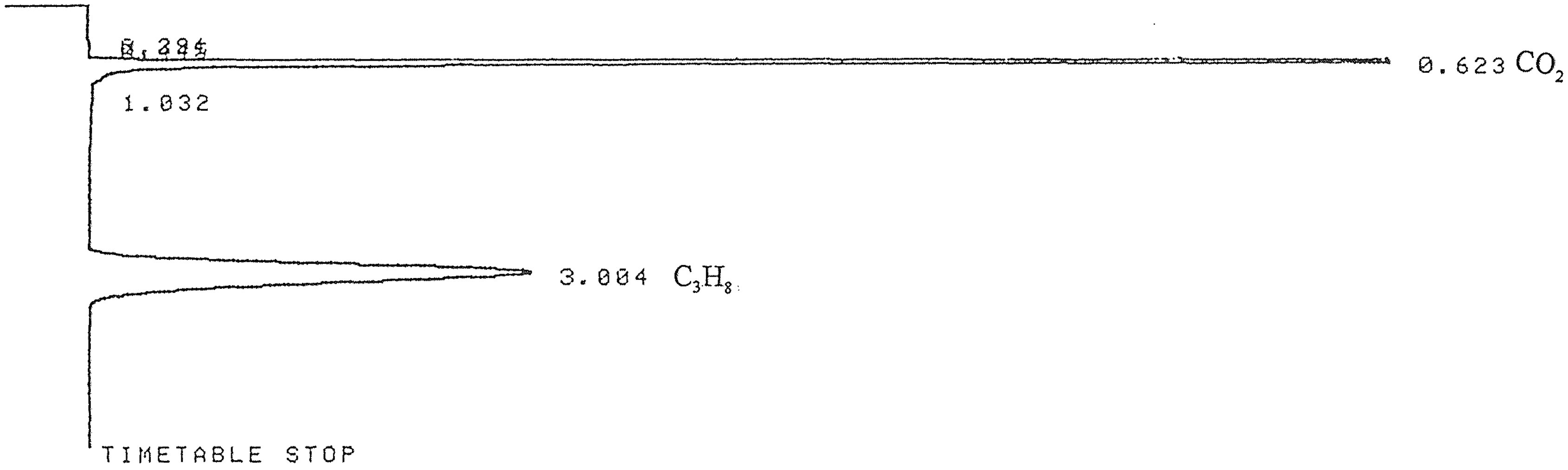
```
RUN#  2282          JUN 28, 1995  20:42:38

AREA%
      RT       AREA TYPE  WIDTH       AREA%
    .480     498994   PB    .037   56.77994
   1.998     379827   BB    .148   43.22006

TOTAL AREA= 878821
MUL FACTOR=1.0000E+00
```

Figure 3.4 Peak Resolution and Retention Time for CO and CO_2 with FID

```
*  RUN # 2024      JUN 19, 1995  16:29:55
START
```



```
RUN#  2024             JUN 19, 1995  16:29:55

AREA%
      RT       AREA TYPE  WIDTH       AREA%
    .391       4695   PV   .042      .04836
    .445       2910   VP   .034      .02997
    .623    4482720   PB   .044    46.17128
   1.032       9844   BB   .058      .10139
   3.004    5208723   PB   .250    53.64902

TOTAL AREA=9.7089E+06
MUL FACTOR=1.0000E+00
```

Figure 3.5 Peak Resolution and Retention Time for C_3H_8 and CO_2 with FID

Table 3.3 Gas Chromatography Operating Conditions

Item	Descriptions & Conditions
Flame Ionization Detector	Analyzing CO, CO_2 and C_3H_8
Detected Temperature	250 °C
Injection Temperature	350 °C
Oven Temperature	Room temperature for CO oxidation reaction analysis 100 °C for C_3H_8 oxidation reaction analysis
Carrier Gas	Helium (He) at 30 ml / min
Air	400 ml / min
Hydrogen (H_2)	40 ml / min
Packed Column	Porapak Q, 80 / 100 mesh
Integrator	HP 3396A

Carbon monoxide and propane concentrations were separately calibrated with purchased standard gases (using single a point calibration method). The areas of sample peaks were integrated and recorded by integrator (HP 3396A).

3.3.2 Fourier Transform Infrared (FT-IR) Spectroscopy

The principle of infrared (IR) is that a molecule may absorb infrared radiation of the appropriate frequency to excite it from one vibrational or rotational state to another. When a beam of infrared energy with a broad frequency range passes through a sample, the energy at certain frequencies is absorbed by the sample. A graph of energy absorbed versus frequency is the absorption spectrum for this sample. The spectrum is the characteristic of the particular molecule and its molecular motions.

Infrared Spectrometer model FTS-40 by Bio-Red Laboratories, Inc. was used to identify the sulfur compounds produced on catalysts. The experimental procedure consisted of the following steps:

(1) Taking a background interferogram.

(2) The background interferogram was Fourier transformed into a single-beam spectrum.

(3) The sample was inserted between an interferometer and a detector. The sample interferogram was taken.

(4) The sample interferogram was also Fourier transformed into a single-beam spectrum.

(5) The absorbance spectrum was obtained by computing the logarithm to the base 10 of the reciprocal of the transmittance spectrum.

$$A = \log_{10} (1/T)$$

$$T = \frac{\text{Sample spectrum}}{\text{Background spectrum}}$$

Where:

A= the absorbance of a sample

T= the transmittance of a sample

(6) The final spectrum was displayed on a monitor or plotted with an X-Y plotter.

The integral part of the instrument is a model 3200 computer which stores all experimental spectra. These spectra can be retrieved at a later time to be re-examined, manipulated and plotted. The FTS-40 operating parameters are provided in Table 3.4.

Table 3.4 Operating Conditions for Infrared Spectrometer (Model FTS-40)

Item	Conditions
Detector	Internal
Scan Speed	5 KHz
Delay	1.0 sec.
Aperture	For 2 cm^{-1}
Sample Beam	Internal
Controller Signal Path	Auto
Set-Up X-Axis Maximum	Auto
Set-Up Y-Axis Minimum	Auto
Low Pass Filter	1.12 KHz
Collect Sensitivity	3
Spectral Region Start	4,000 cm^{-1}
Spectral Region End	450 cm^{-1}
Resolution	8
Number of Scans	64

The spectrometer was used primarily to obtain a qualitative understanding of the production of $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$. The IR peaks for these aluminum compounds was compared with standard spectra found in (Nyquist, 1971).

3.3.3 Catalyst Property Analysis (Altamira Instrument)

The Altamira Instrument combines a variety of catalyst characterization techniques into one integrated computer-controlled system. Experimental operation and data collection are handled by a MS-DOS compatible computer. This convenient system was used for measuring BET surface area and metal dispersion.

3.3.3.1 Dynamic BET Surface Area Measurement Measurement of surface area involves the principles of physical adsorption which is equilibrium coverage similar to surface liquefaction. The coverage proceeds with adsorption on surface atoms and is quickly followed by the generation of additional layers even before a complete monolayer forms. Since the process is exothermic, at equilibrium the amount decreases as temperature increases. Easily measurable quantities are found close to the normal boiling point of the adsorbate. A theoretical model was derived by Brunauer, Emmett, and Teller (Brunauer, et al., 1938):

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

Where:

P = partial pressure of nitrogen

P_o = saturation pressure at measured temperature

C = constant

V = volume adsorbed

V_m = monolayer volume adsorbed

The technique that the Altamira Instrument used for BET adsorption measurement is based on the flow system shown in Figure 3.6. It is rapid and accurate (although it consistently gives results about 10% lower then the more conventional static technique) with the advantage of requiring no high vacuum or pressure measuring devices. In this test, a small amount of catalyst was loaded into a quartz U-tube. Gas cylinders containing 10% , 20%, and 30% concentration of nitrogen with the balance He supply the flow that passes over the catalyst sample at liquid-nitrogen temperature. The adsorption is measured from the disappearance of nitrogen, and detected by a thermal

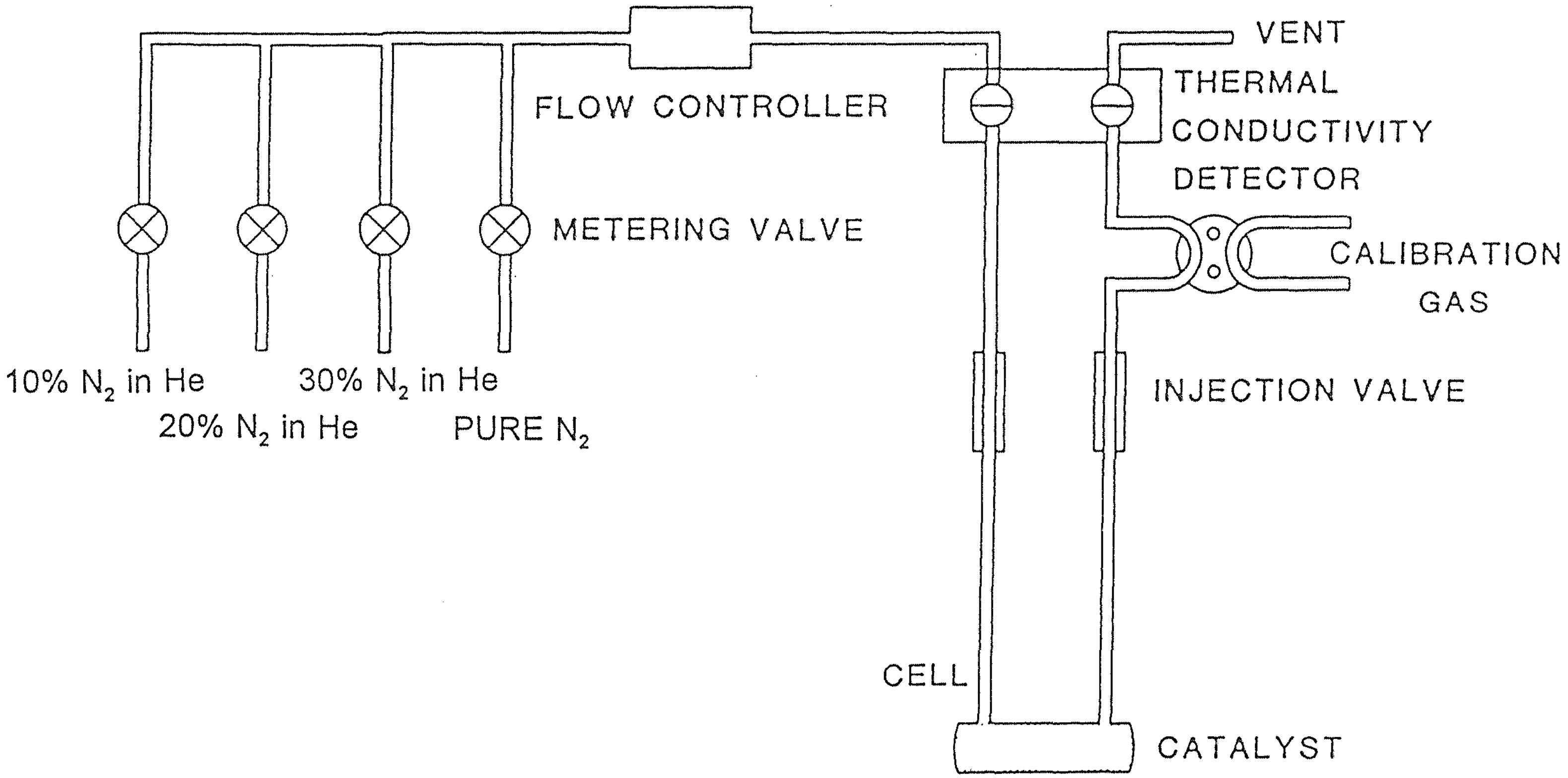


Figure 3.6 Dynamic BET Surface Area Measurement System

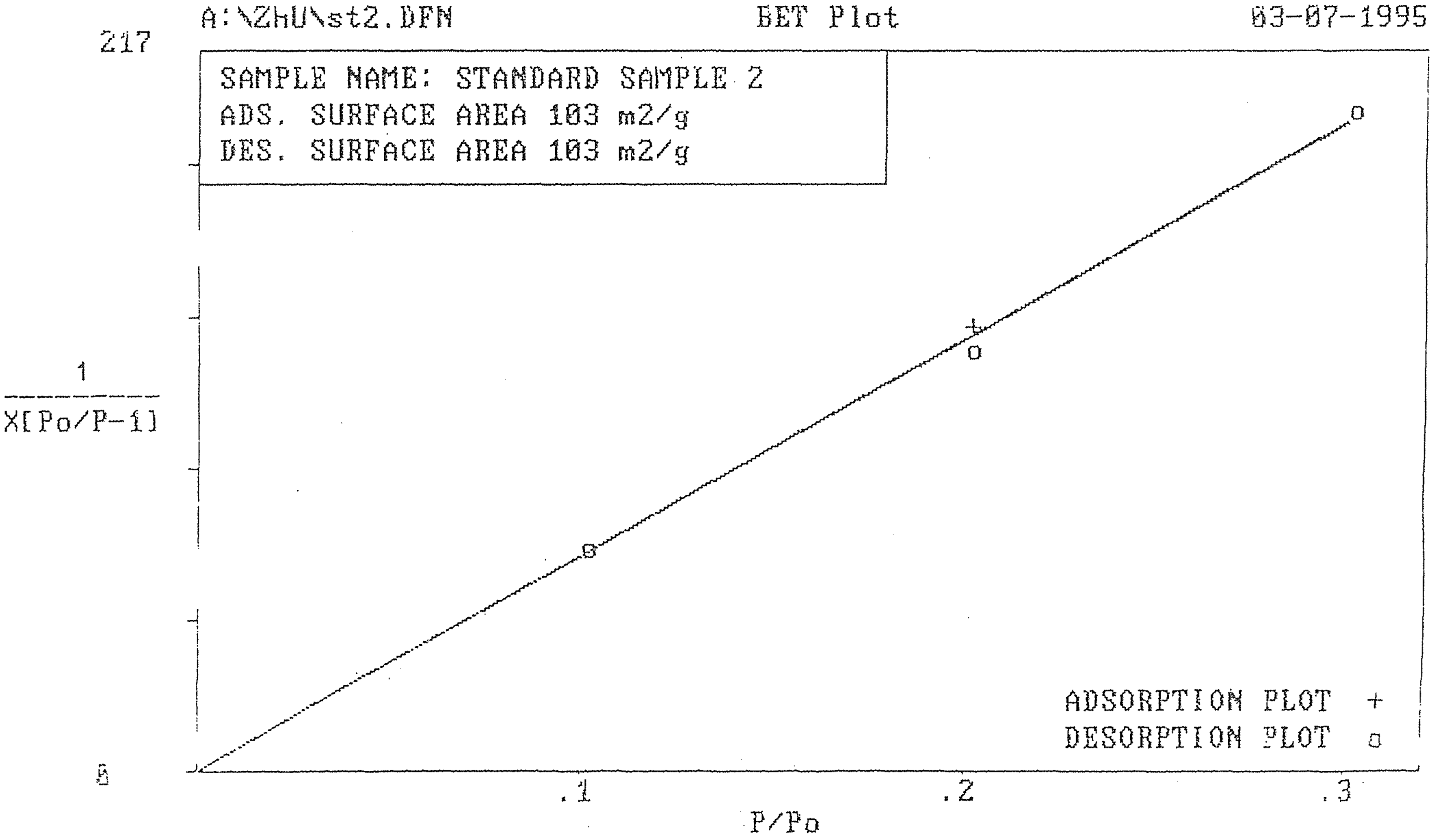


Figure 3.7 Typical Plot of BET Surface Area

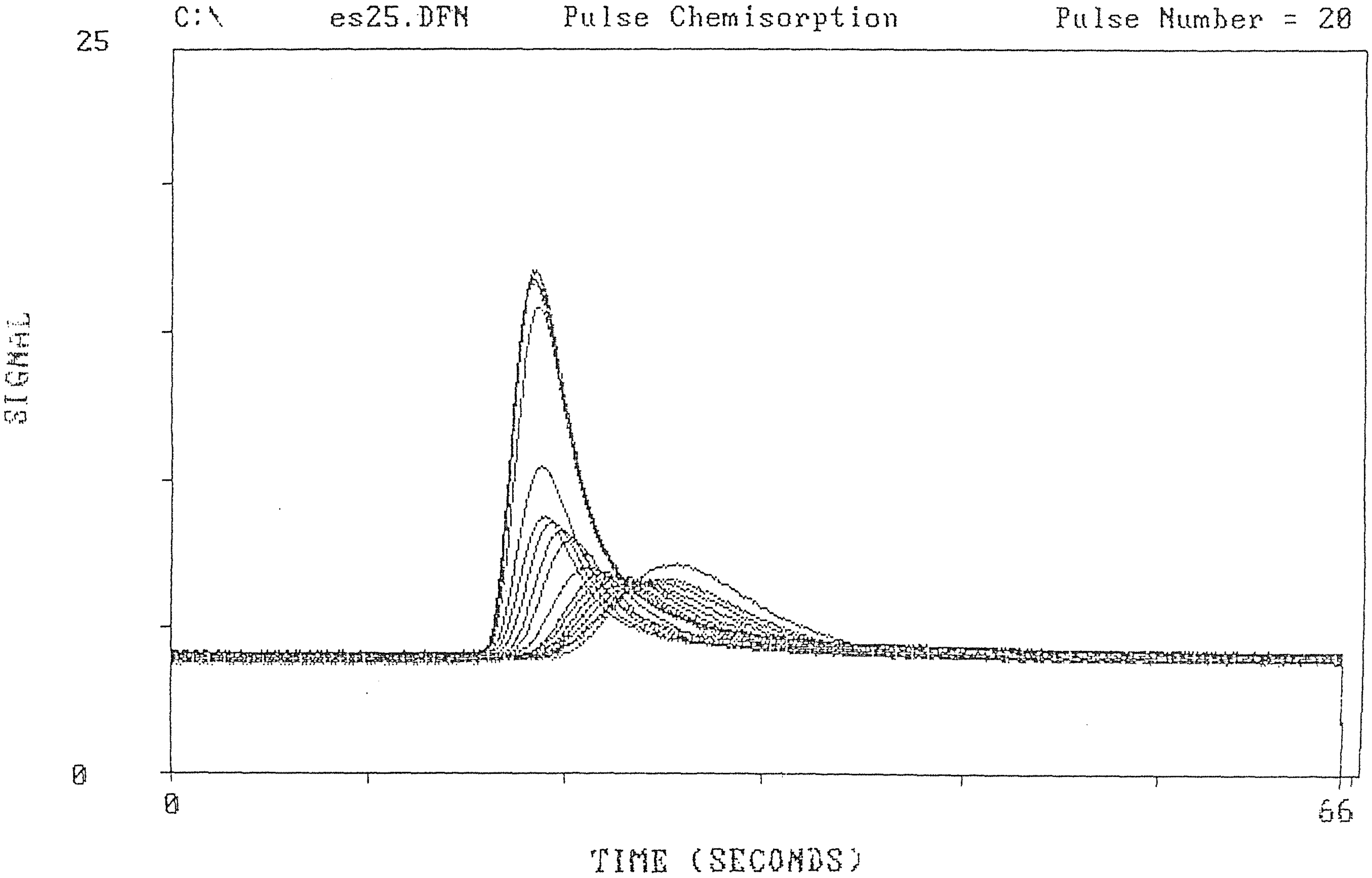


Figure 3.8 Typical Plot of Pulse Chemisorption.

conductivity detector (TCD). The operating procedures is available in the Altamira Instrument manual, and a typical BET plot is given in Figure 3.7.

3.3.3.2 Chemisorption Test In order to measure the active surface area and determine metal percent dispersion and crystallite size, chemisorption tests were conducted which involved chemical bonding of the adsorbate with the adsorbing solid. For the platinum catalyst, pulse chemisorption measurements were conducted with the Altamira Instrument. This experiment was carried out at atmospheric pressure and 80 ^{0}C. On the order of 0.05 g of catalyst was placed in the U-tube. After appropriate pretreatment to provide a clean, reduced metal surface, the sample was subjected to flow of argon gas. A certain amount of chemisorbing H_2 gas was injected and mixed with this argon stream before it contacted the catalyst. The composition of the stream exiting the U-tube was monitored quantitatively by the thermal conductivity detector, and the detected signal was compared to the one produced by the injected pulse of chemisorbing gas bypassing the U-tube. The initial several pulses were more completely adsorbed. As the surface site became saturated, detected pulse volumes increase until a steady state was reached which indicated saturation. Figure 3.8 shows a typical plot of pulses over catalyst sample. Pulse chemisorption and calibration can be automatically performed by the Altamira Instrument. Metal dispersion is computed by the following equation:

$$\text{Dispersion} = \frac{\text{Micromoles of Adsorbing Gas / grams of Sample}}{\text{Micromoles of Active Metal / grams of Sample}}$$

Where:

$$\frac{\text{Micromoles of Adsorbing Gas}}{\text{grams of Sample}} = \frac{\text{Micromoles of Gas Molecules / grams of Sample}}{\text{Stoichiometric Factor}}$$

$$\frac{\text{Micromoles of Metal}}{\text{grams of Sample}} = \frac{(\text{Percent Metal}/100)\,(10^6\ \text{micromole}/\text{mole})}{\text{Atomic Weight}}$$

Crystallite sizes can be calculated by following the formula from the Altamira instrument manual:

$$\text{Diameter of Spherical Crystallite (Å)} = \frac{60{,}000}{(\text{Density})\ (\text{Maximum Area})\ (\text{Dispersion})}$$

Where:

Density = density of the metal in grams per cubic centimeter

Maximum area = maximum area (meters squared per gram) the metal would have if it was 100% dispersed.

For a five-side cubic crystallite, the length of one side is given by the above formula with the constant of 50,000 substituted in the numerator.

3.3.3.3 Thermogravimetric Analysis (TGA) Thermogravimetric analysis is a technique for measuring the weight change of a solid sample induced by gaseous reactions.

In this case, a Perkin-Elmer thermogravimetric analyzer (TGA), illustrated in Figure 3.9, was used to analyze the weight change of a catalyst samples as a function of concentration of H_2S in air. The TGA provides weight change data as a function of

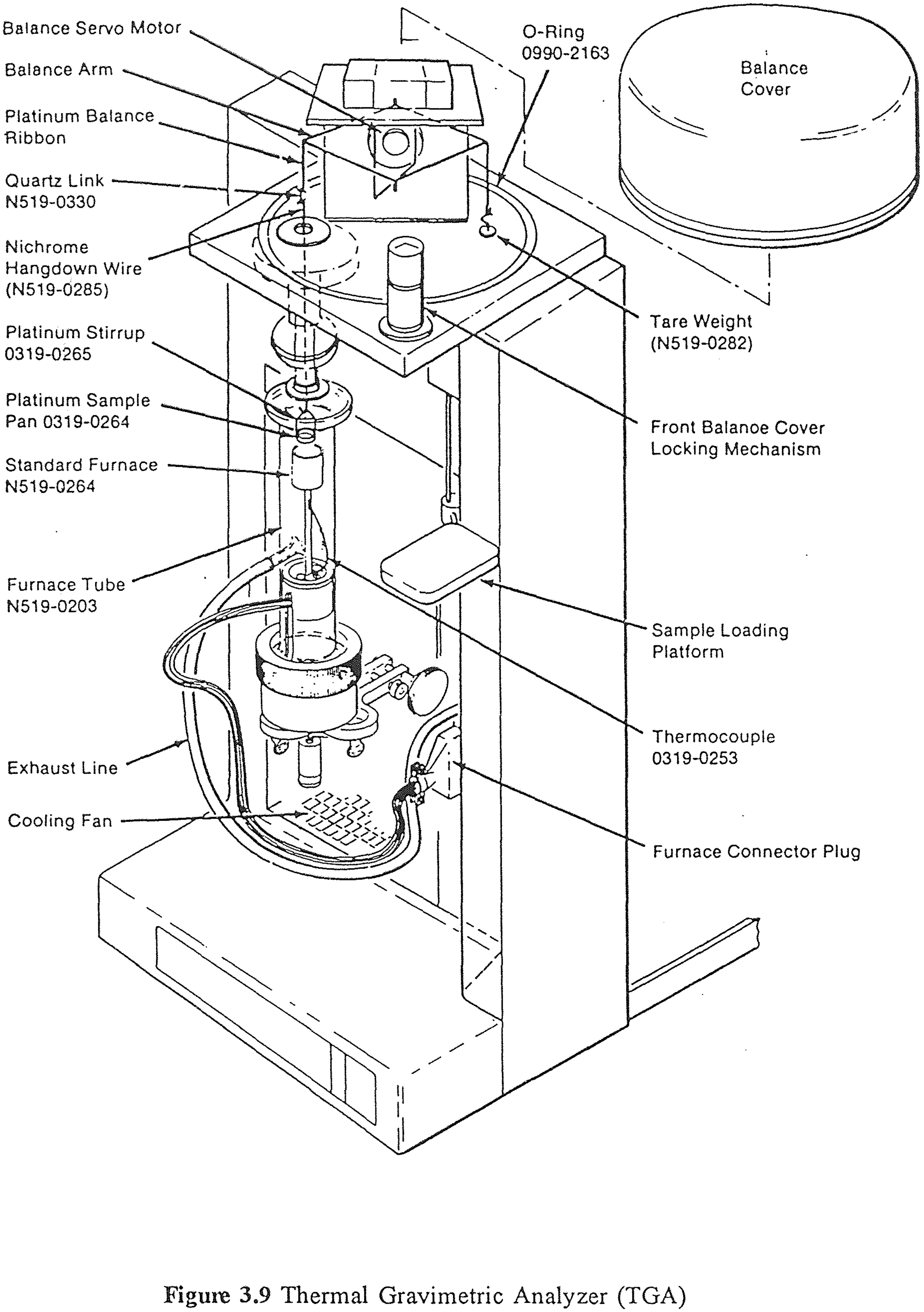


Figure 3.9 Thermal Gravimetric Analyzer (TGA)

exposure time at constant temperature or as a function of temperature for a constant exposure time.

An empty sample pan suspended in the microbalance was weighed to get sample zero reading, then about 10 mg of catalyst was placed to the sample pan located in the furnace of the TGA with temperature being set at 400 °C. When the weight of catalyst sample became stable at the desired reaction temperature, the H_2S analyzed mixture in nitrogen was mixed with air and introduced into the sample pan. The sample weight changed as the gas mixture reacted with the catalyst sample. The results of weight changes were recorded as a function of time and plotted for study.

CHAPTER 4

EXPERIMENTAL RESULTS AND DISCUSSION

4.1 Aging Experiments

Exposing catalysts to different concentration of poison streams at a fixed reaction temperature and stream flow rate may be an effective way to determine catalyst deactivation parameters. For this reason, aging tests were run, in which various concentrations of H_2S passed through the fresh catalyst at 400 °C for 24 hours.

4.1.1 Hydrogen Sulphide Feed Concentration

H_2S gas streams were used to pretreat the catalyst in order to measure the impact of the presence of S on catalyst activation. In order to evaluate the poison-tolerance for a specific catalyst, a variety of concentrations of hydrogen sulphide gases was prepared and fed into the catalyst bed for aging tests.

The various H_2S gas feed concentrations were prepared by mixing dry air from a gas cylinder with a certified cylinder containing 6,100 ppm H_2S in nitrogen. Two rotameters were used to measure the flow each cylinder and thus the concentration of H_2S in the nitrogen and air mixture. The mixture reproducibility was 10% based on the errors in reading the rotameters. No independent check of the concentration of H_2S in the mixture was used because the GC-FPD was broken. The total flow rate of the mixed gas stream was maintained at 300 cm^3/min in order to obtain a space velocity (SV) of 16,500 v/v/hr. The equation for calculation of feed concentration of H_2S is:

$$C_{H2S} = \frac{C_o\ V_{H2S}}{V_T}$$

$$= \frac{6100\ V_{H2S}}{300}$$

Where:

C_{H2S} = feed concentration of H_2S, ppm

C_o = original concentration of H_2S, ppm

V_{H2S} = flow rate of original H_2S gas, cm^3/min

V_T = total flow rate, cm^3/min

4.1.2 Results

The aging experiments were conducted in the test system shown in Figure 3.1. One gram of the fresh catalyst (1.5% Pt/Al_2O_3) powder was exposed to a H_2S feed stream at 400 °C temperature and 16,500 v/v/hr space velocity. The 400 °C aging temperature was used to be consistent with the previous research of Yi Wang (Wang, 1995). In his tests, aged 1.5% $Pt/\gamma\text{-}Al_2O_3$ catalyst showed deactivation for carbon monoxide but promotion for propane oxidation. In order to further investigate the levels of catalyst deactivation or promotion, the effect of much larger concentrations of sulfur compounds on aging were studied. The intent was to see if deactivation of the catalyst for propane oxidation could be achieved at sufficiently high concentration. The concentrations of H_2S were set at 80 ppm, 100 ppm, 270 ppm, 500 ppm, 750 ppm, 1,000 ppm, 1,200 ppm and 1,750 ppm, respectively. Each of these aging tests was conducted for 24 hours at 400 °C and 16,500 v/v/hr.

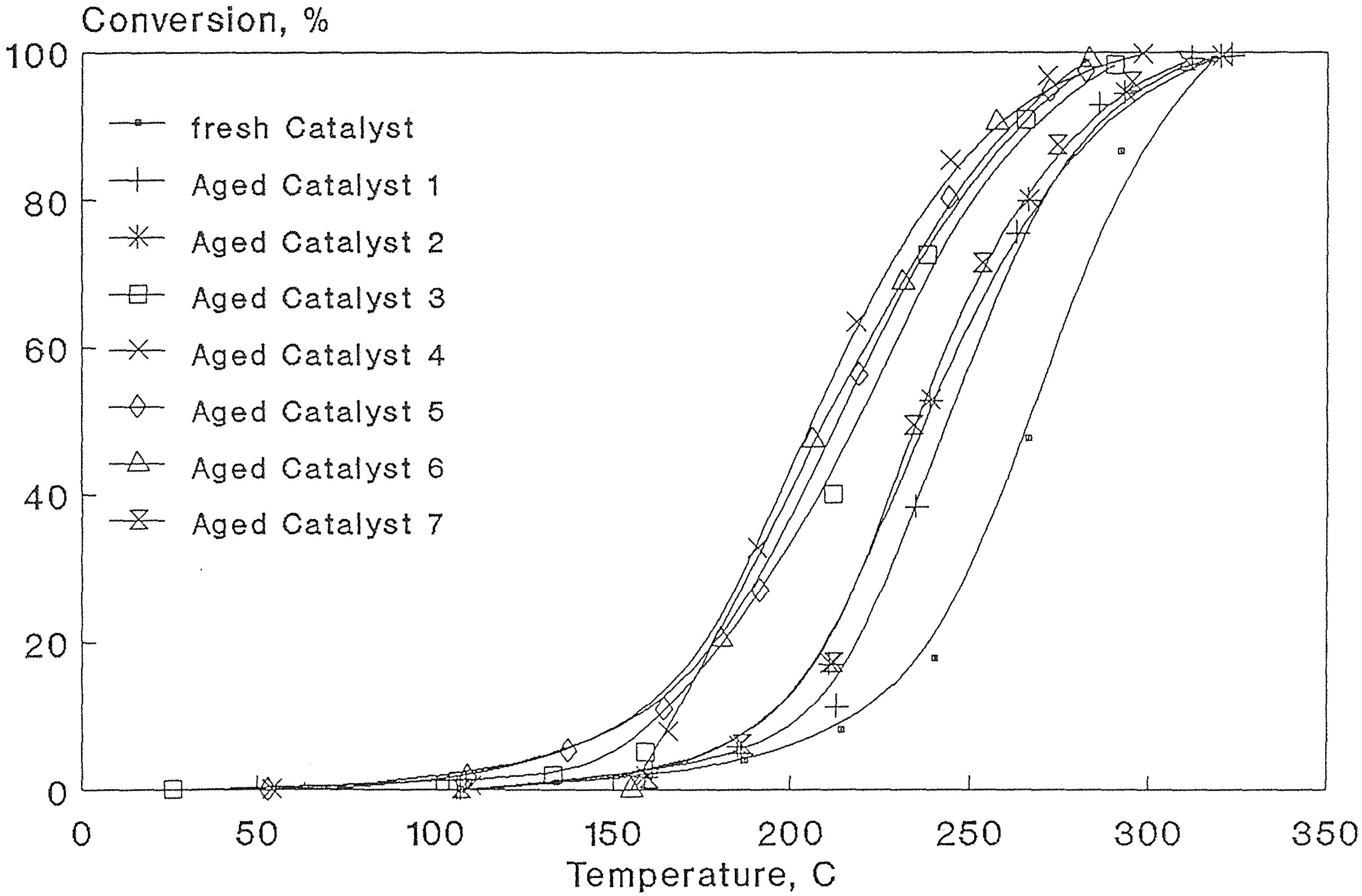
After the aging tests, the catalysts turned darker gray color from the light gray of fresh catalyst, and the color became much darker with increasing H_2S exposure. This suggested that H_2S was adsorbed on Pt catalytic centers to form sulfur-containing compounds and the concentration of these compounds increased with increasing hydrogen sulfide concentration in the feed. Aged catalysts were stored in a desiccator before removing small samples for measuring BET area, dispersion, and activity to CO and propane oxidation. Each sample was retained in the desiccator after testing, but was not used again.

4.2 Activity Experiments

4.2.1 Oxidation of Propane

A mixture containing 1% propane, balance dry air, was used to determine catalyst activity. The fresh catalyst as well as aged catalysts were separately tested in the 2.5 cm quartz reactor. In each test, the propane gas stream passed through the reactor at a rate of 50 cm^3/min over the temperature range of 50 °C to 300 °C. The feed and exhaust gases were analyzed by GC-FID.

Figure 4.1 summaries the results from runs of propane conversion as the function of temperature. It was found that the interaction between the sulfur treated 1.5% Pt/Al_2O_3 catalyst and the propane stream resulted in enhanced catalytic oxidation. This suggests that new active sites were created for propane oxidation due to sulfate and sulfite compounds produced on the Pt/Al_2O_3 catalyst by hydrogen sulfide treatment. This was verified by FT-IR analysis that showed higher concentrations of $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$ with higher concentrations of H_2S in the treatment stream. Figure 4.2 and Figure 4.3 compare propane conversions as a function of exposure to H_2S. Figure 4.2



Aged Catalyst1,2,3,4,5 and 6 aged by 80, 270,500,750,1000,1200 and 1750ppm H2S in at 400°C for 24hrs, respectively.

Figure 4.1 1% Propane Oxidation over 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts as Functions of Temperature

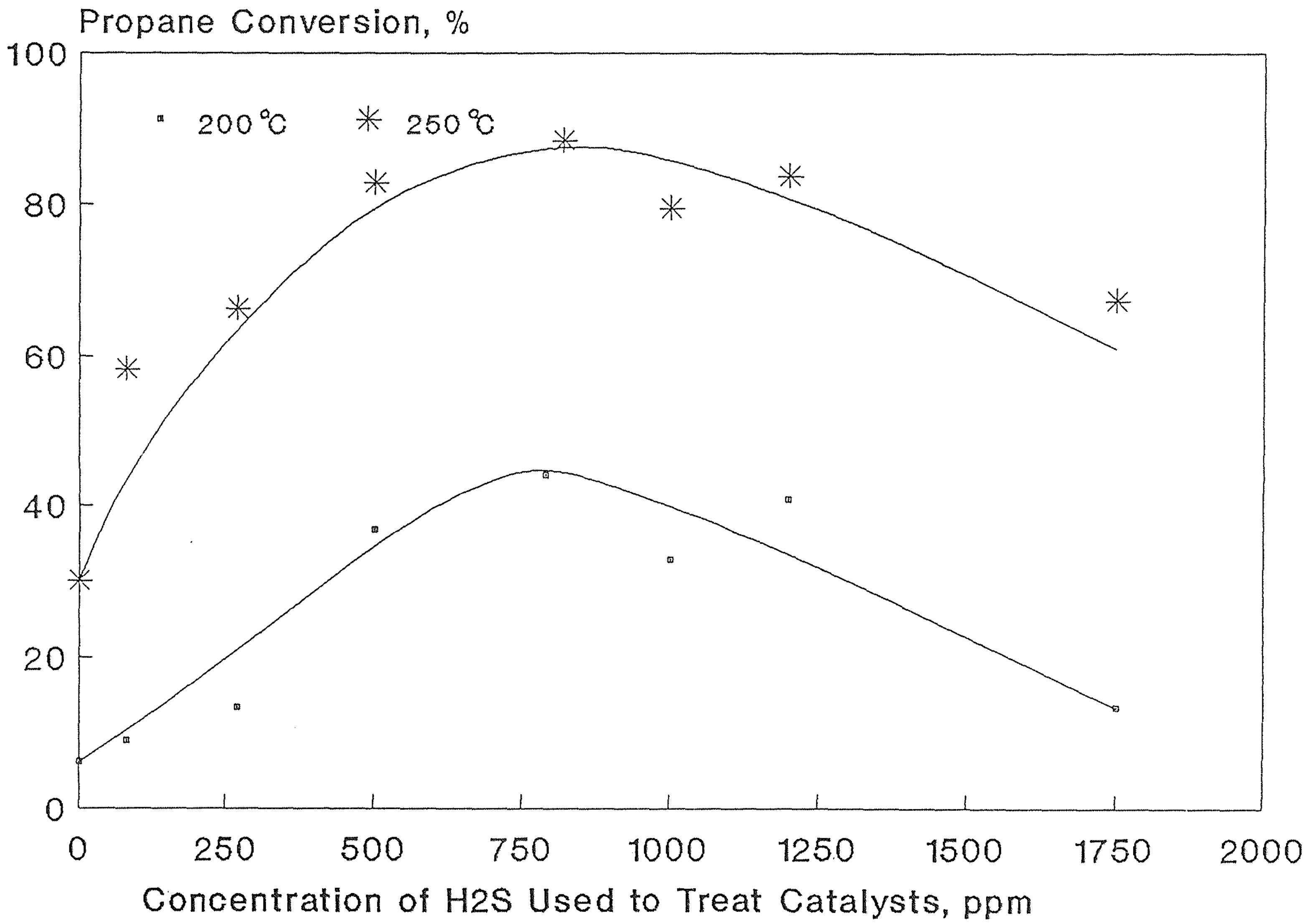
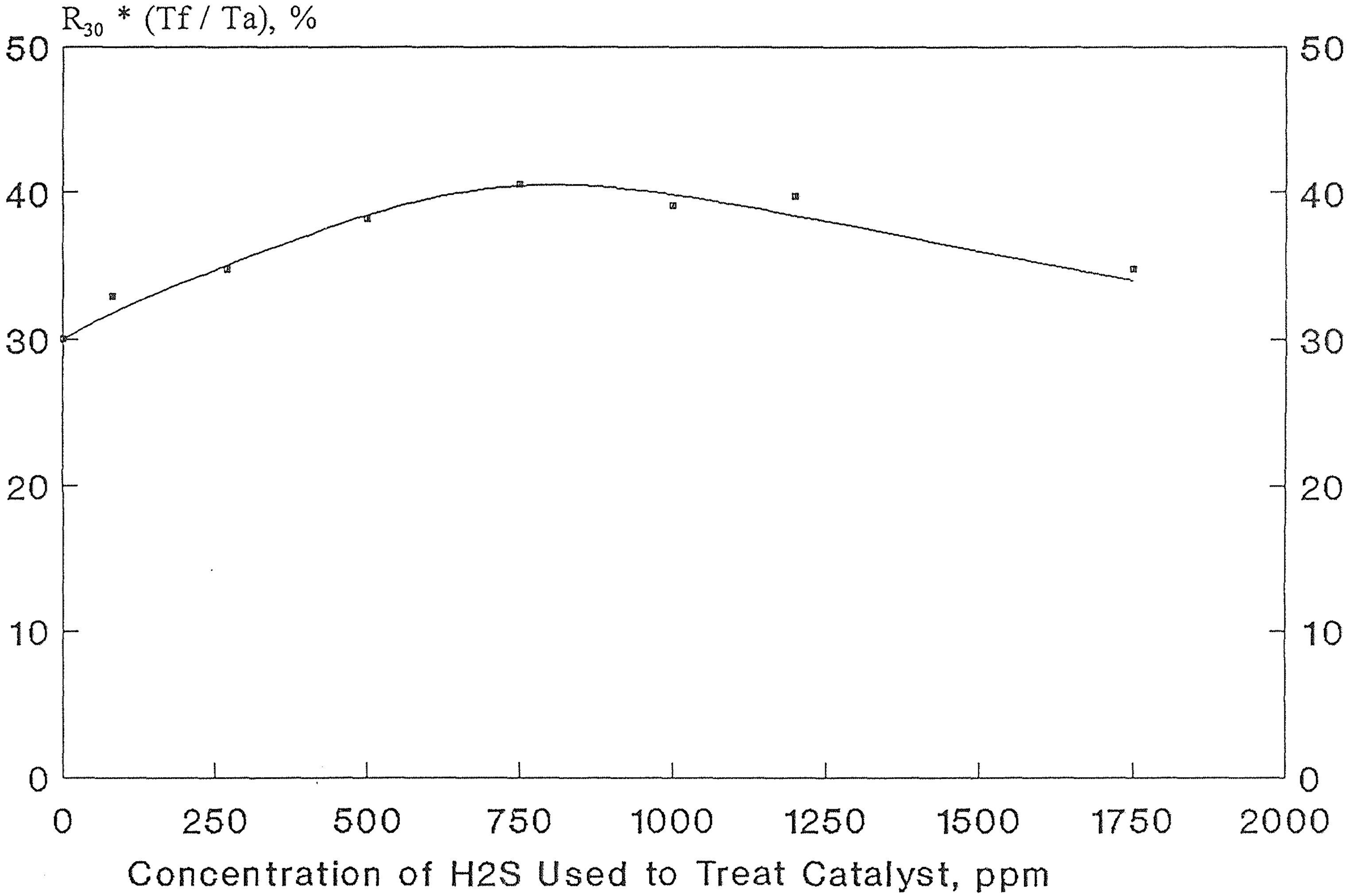


Figure 4.2 Comparison of Catalyst Activity: Propane Oxidation over 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts as a Function of Concentrations of H_2S at 200 ^0C and 250 ^0C, respectively



Ta --- Temperature of aged catalyst at 30% propane conversion.
Tf --- Temperature of fresh catalyst at 30% propane conversion.
R_{30} --- 30% conversion of propane.

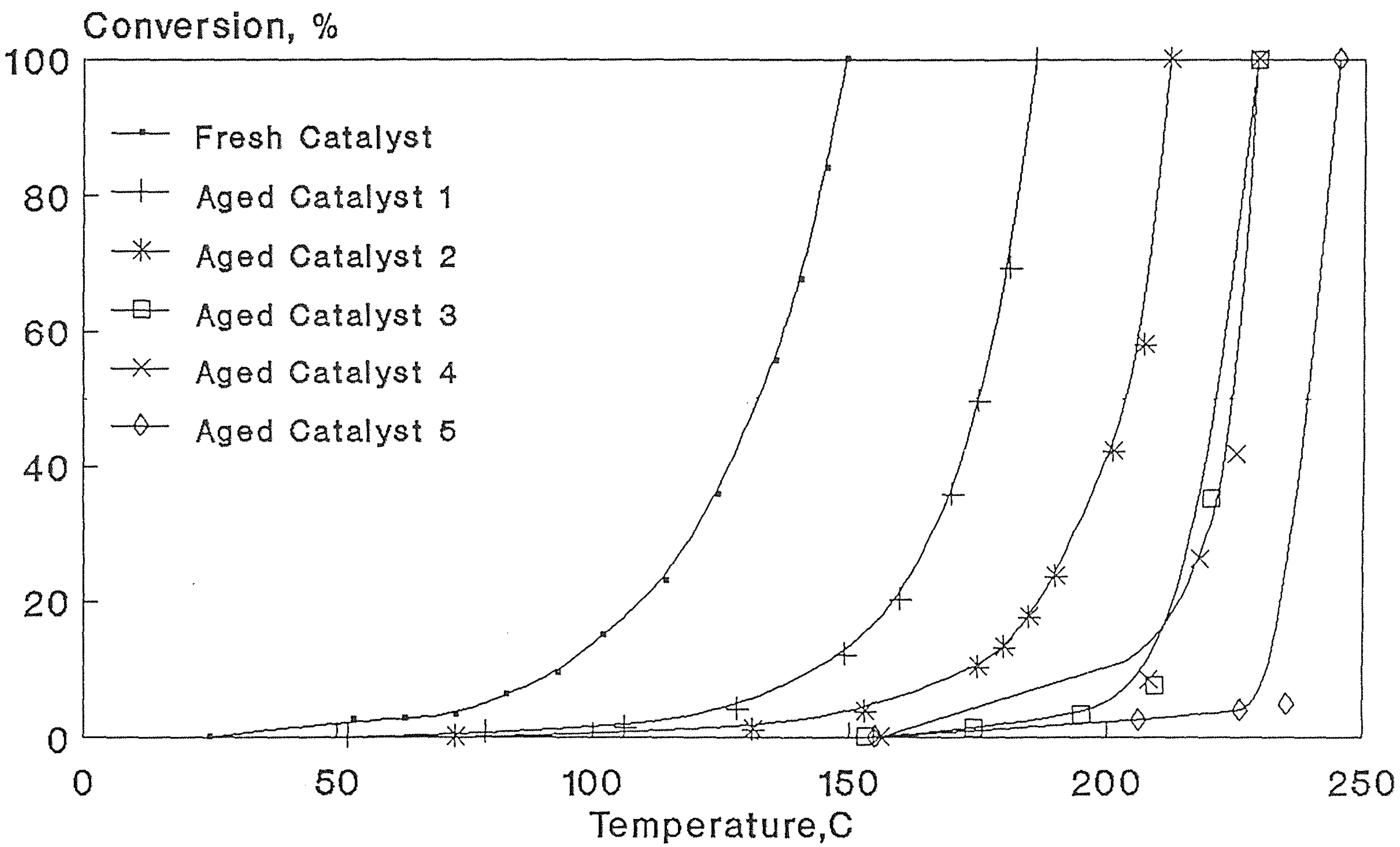
Figure 4.3 Comparison of 1% Propane Oxidation over Fresh and Aged Catalysts: R_{30}*(Tf/Ta) as a Function of Concentration of H_2S

shows how the activity increased sharply with increasing concentrations of hydrogen sulfide at the beginning, and then the rate of increase in activity reached a steady state with increasing H_2S concentrations. In Maxted (1951) theory, catalyst poisoning based on the electronic structural properties of the poison in the gas phase and the effect of H_2S on the solid metal catalyst. This theory can be used to explain how at the lower concentration of H_2S, the electronic overlap between the Pt and the sulfided alumina is strong, but there is insufficient sulfate and sulfite to maximize the interaction. When the concentration of H_2S increased, the interaction between the Pt and sulfate and sulfite achieved their optimum value (possibly stoichiometric). Additional increases of sulfate and sulfite tend to dilute this interaction and thus, we see a decrease in activity. Both Figure 4.2 and Figure 4.3 show that the highest conversion of the propane oxidation was appeared under the condition of using the aged catalyst which was aged by 750 ppm H_2S in air at 400 °C for 24 hours. This result may be helpful in catalyst preparation for enhancing the activity and selectivity of catalysts.

4.2.2 Oxidation of Carbon Monoxide

The diagnostic testing with the CO oxidation reaction was similar to that of propane oxidation. Six sets of different sulfided catalysts were tested with flowing 1% carbon monoxide in dry air (total rate of 50 cm^3/min) by heating from 25 °C to 230 °C. After passing through the catalyst bed the gas streams were analyzed by the on-line GC-FID instrument.

The percentage conversion versus temperature curves were plotted in Figure 4.4. The figure shows that all aged catalysts were severely deactivated for carbon monoxide oxidation. It appears that the sulfur compounds interacted with Pt/γ-Al_2O_3 catalyst and



Catalyst1,2,3,4 and5 aged by 100,500,750
1000 and 1200ppm H2S in air at 400c for
24hrs, respectively.

Figure 4.4 Carbon Monoxide Oxidation over 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts as Functions of Temperature adsorbed on the washcoal adjacent active metal sites, apparently reducing the number of active catalyst sites and inhibiting carbon monoxide oxidation. Table 4.1 and Figure 4.5 show the detrimental impact of sulfur compound on catalyst activity for carbon monoxide oxidation. The T_{50} value (temperature at which 50% of CO is converted) increased with increasing concentration of sulfur compound exposed to the catalyst. This means that the catalysts were deactivated as a function of the concentration of H_2S used in pretreating the catalysts.

Table 4.1 Comparison of the Activity Changes for Carbon Monoxide Oxidation Reaction

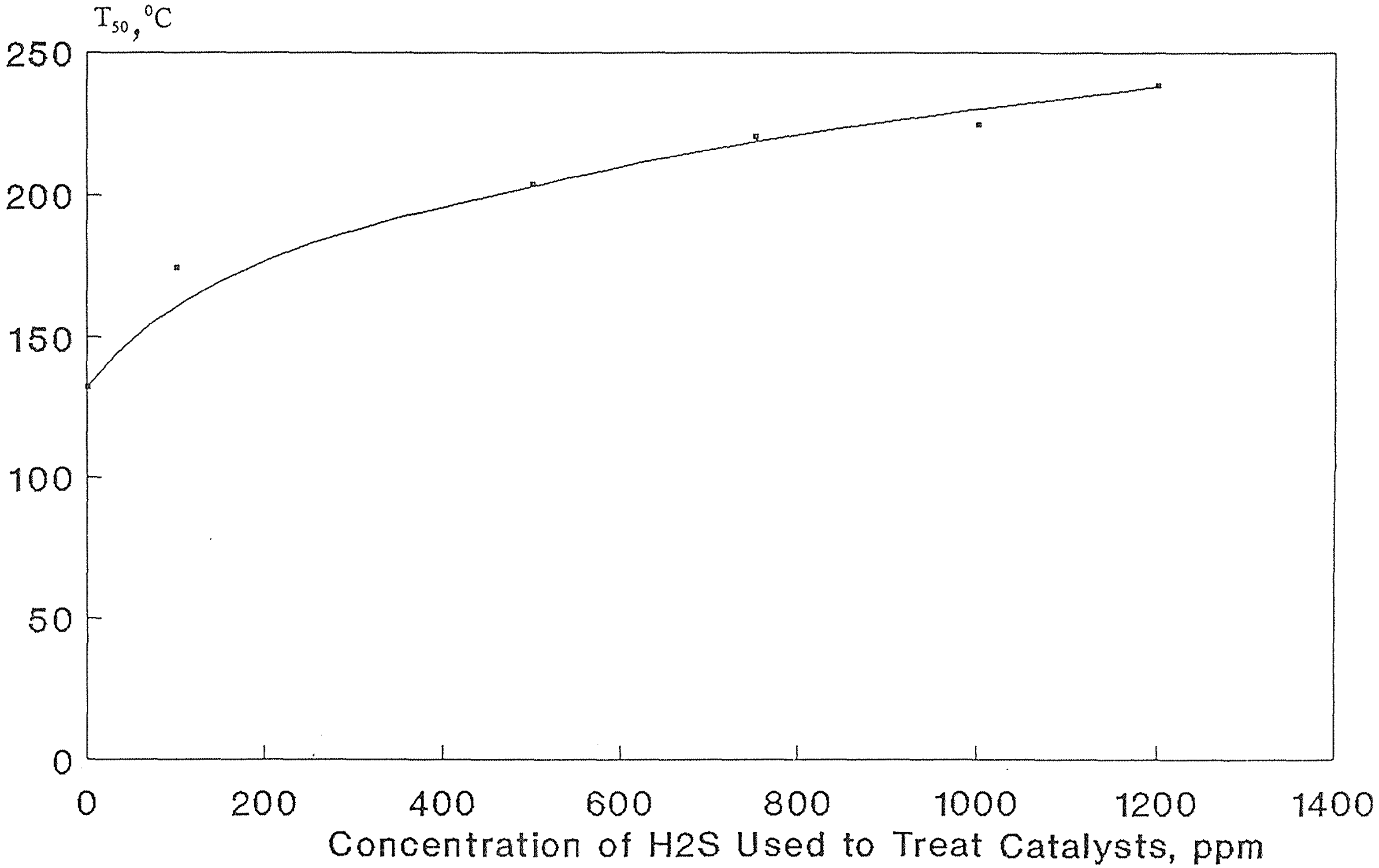
Catalysts	Fresh Catalyst	Catalyst #1	Catalyst #2	Catalyst #3	Catalyst #4	Catalyst #5
T_{50} for CO (°C)	132	174	203	220	224	238

Note: 1. T_{50}= the temperature at which the catalytic oxidation of CO achieves 50% conversion.

2. Catalyst #1, #2, #3, #4, and #5 were aged by 100 ppm, 500 ppm, 750 ppm, 1,000 ppm, and 1,200 ppm H_2S at 400 °C for 24 hours, respectively.

4.3 Catalyst Characteristics Analysis

The chemical and physical properties of a catalyst directly influence the performance of a catalyst in a catalytic reaction. Some properties, classified as surface chemical properties and physical properties, were determined in this research. The methods for measuring these properties were reviewed in Chapter 3, and the results obtained from the measurements are discussed later in this Chapter.



T_{50} = the temperature at which the catalytic oxidation reaction achieves 50% conversation

Figure 4.5 Comparison of 1% Carbon Monoxide Oxidation over 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts: T_{50} as a Function of Concentration of H_2S

4.3.1 Dynamic BET Surface Area Measurement

The fresh catalyst (1.5% Pt/γ-Al_2O_3) and the six catalyst samples that were aged at the indicated H_2S concentrations were tested for BET surface area as a function of H_2S concentration. The BET measurements were conducted with 0.05 g catalyst in a U-tube reactor placed in the Altamira Instrument system. BET surface area was measured by following the Altamira Instrument operating manual. The experimental results were handled by Altamira computer operated measurement system.

As shown in Figure 4.6 and Table 4.2, the surface areas of aged catalysts were all lower than the fresh catalyst and the values of the surface areas decreased monotonically with increasing concentration of H_2S. It also was found that the rate of decreasing surface area was larger at the lower concentration of H_2S than that of higher concentration of H_2S. The test results suggest that the surface area of the catalyst was affected by the sulfur compounds until a steady state was achieved in which the products reacted with the catalyst and caused poisoning.

4.3.2 Chemisorption Experiments

Pulse chemisorption experiments provide a facile way of determining metal surface area. It was used here for measuring catalyst metal dispersion, since the magnitude of metal dispersion is proportional to catalytic active sites. Test procedures were described in Chapter 3. The tests were automatically performed on the Altamira Instrument, and the results are shown in Table 4.3 and Figure 4.7. The test outcome indicated that the metal dispersion declined sharply at first and then reached a point where the catalyst dispersion decreased much more slowly with increasing the concentration of hydrogen sulfide. It is believed that the poison, H_2S, was adsorbed on the active metal sites to form the chemisorbed compounds so that the catalyst active sites decreased.

In addition, the pulse chemisorption tests also provided the data for crystallite size of fresh and aged $Pt/\gamma\text{-}Al_2O_3$ catalysts. As shown in Table 4.4, the crystallite growth with increasing of H_2S concentration indicated that the sulfur compound interacted with the catalyst to form the products which changed the catalyst crystal structure. The crystallite growth gave a corresponding loss in the metal dispersion, so that the activity of catalyst was lost especially for structure-sensitive CO oxidation reaction. This was consistent with the results obtained from CO oxidation reaction experiments.

Table 4.2 Comparison of BET Surface Areas

Catalyst	**BET Surface Area (m^2/g)**
Fresh Catalyst (1.5% $Pt/\gamma\text{-}Al_2O_3$)	80
Aged Catalyst #1	70
Aged Catalyst #2	61
Aged Catalyst #3	57
Aged Catalyst #4	53
Aged Catalyst #5	45
Aged Catalyst #6	45

Note: Aged Catalyst #1, #2, #3, #4, #5 and #6 were correspondingly aged by H_2S in air with concentration of 80, 270, 500, 750, 1,000 and 1,200 ppm at 400 °C temperature for 24 hours.

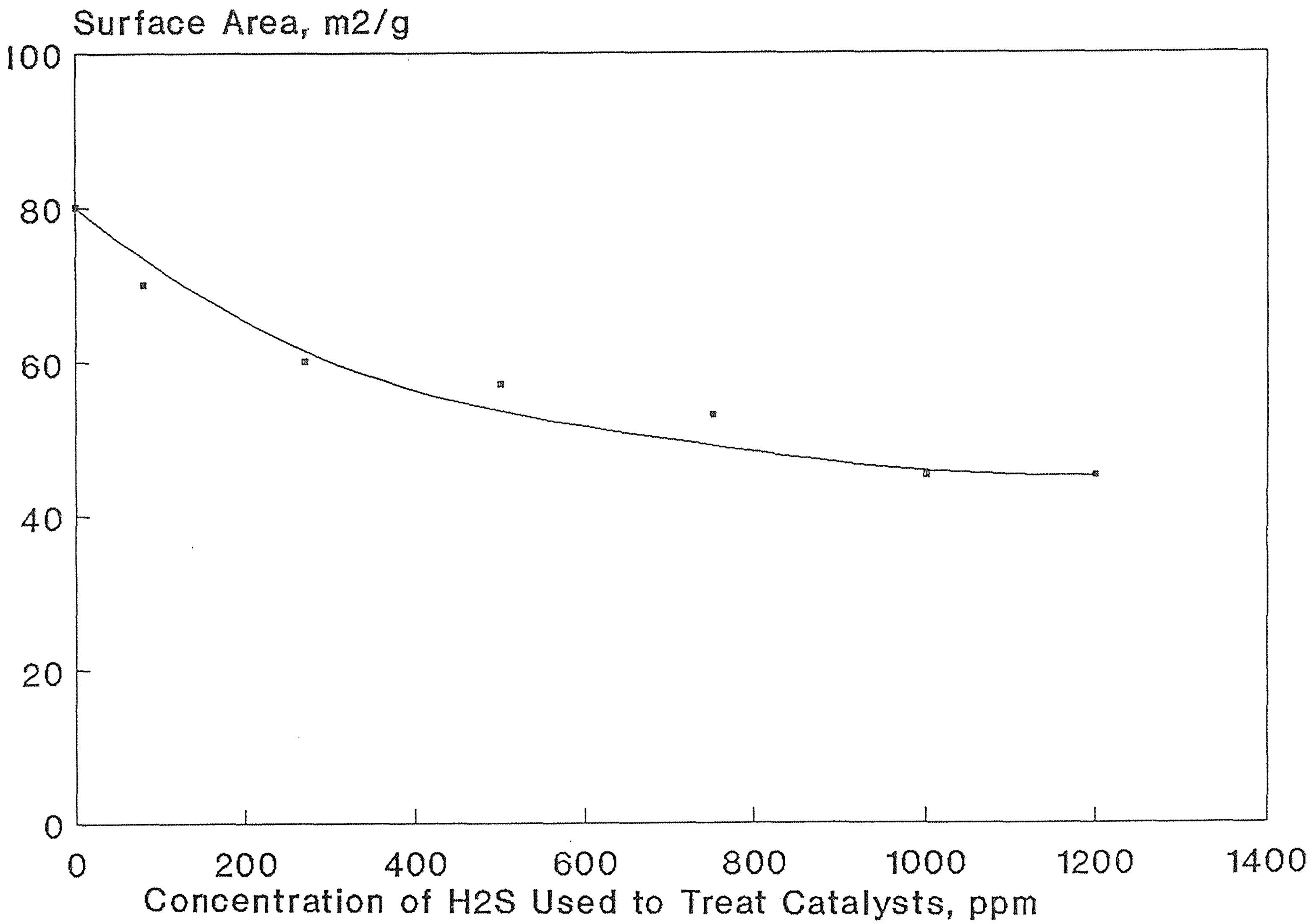


Figure 4.6 Comparison of BET Surface Area: BET Surface Areas of Fresh and Aged Catalysts vs.Concentrations of H_2S over Catalysts

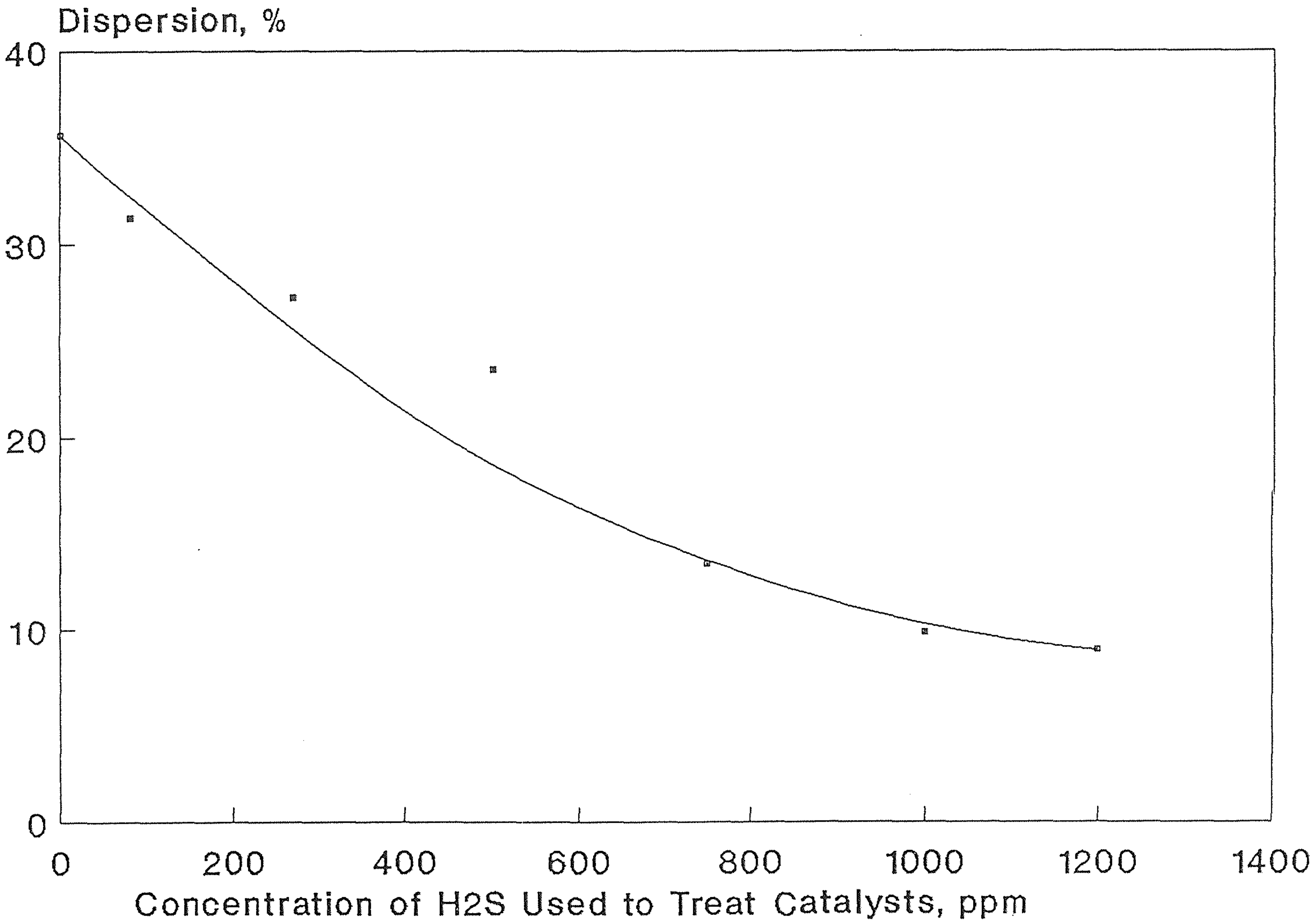


Figure 4.7 Comparison of Catalyst Metal Dispersion: Dispersion Values of Fresh and Aged Catalysts vs. Concentrations of H_2S over Catalysts

Table 4.3 Comparison of Metal Dispersion

Catalyst	**Metal Dispersion (%)**
Fresh Catalyst (Pt/γ-Al_2O_3)	35.6
Aged Catalyst #1	31.3
Aged Catalyst #2	27.2
Aged Catalyst #3	23.5
Aged Catalyst #4	13.4
Aged Catalyst #5	9.8
Aged Catalyst #6	8.9

Note: 1. Aged Catalyst #1, #2, #3, #4, #5 and #6 were aged by 80, 270, 500, 750, 1,000 and 1,200 ppm H_2S in air at 400 °C for 24 hours, respectively.
2. The experiments were performed at 80 °C.

Table 4.4 Comparison of Crystallite Size

Catalyst	**Length of Side of Cubic Crystallite (Å)**	**Diameter of Spherical Crystallite (Å)**
Fresh Catalyst (Pt/γ-Al_2O_3)	28	33
Aged Catalyst #1	32	38
Aged Catalyst #2	36	44
Aged Catalyst #3	42	51
Aged Catalyst #4	74	89
Aged Catalyst #5	101	121
Aged Catalyst #6	112	134

Note: 1. Aged catalysts are the same as those used in metal dispersion measurements.
2. The results are calculated using the formula shown in Section 3.3.3.2.

4.3.3 TGA Tests

Thermogravimetric analysis was performed on about 10 mg of 1.5% Pt/γ-Al_2O_3 catalyst using the TGA system at 400 °C for up to 50 minutes. The operating procedure was described in Chapter 3. The test was repeated with 500 ppm, 750 ppm and 1,000 ppm H_2S in air, respectively. The results compared with background (catalyst treated by air alone), are plotted in Figures 4.8, 4.9, 4.10 and 4.11. From Figure 4.8, the sample weight gain due to the introduction of H_2S indicated that sulfur compound interacted with catalyst in all cases except the test without H_2S. Weight gain increased with increasing concentration of H_2S. This was consistent with the observed color becoming darker gray with increasing H_2S concentration because the quantity of $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$ products increased. Figures 4.9, 4.10, and 4.11 give the sample weight gain due to treatment with 500, 750 and 1,000 ppm H_2S at 400 °C for 50 minutes, respectively.

Another set of tests were conducted on pure γ-Al_2O_3 to analyze the products resulted from the interaction between catalyst and sulfur compound. The treatment gases were the same as those in TGA tests of 1.5% Pt/γ-Al_2O_3 catalyst. Comparing Figures 4.12, 4.13, 4.14 and 4.15 the same conclusion could be reached that the sulfur compound also interacted with pure γ-Al_2O_3.

The TGA test results on 1.5% Pt/γ-Al_2O_3 catalyst and on pure γ-Al_2O_3 were compared in Table 4.5. It points out that sulfur compound not only reacted with platinum but also reacted with γ-Al_2O_3, and the sulfur compound bonded with γ-Al_2O_3 even more strongly than with platinum based upon the amount of sample weight gain.

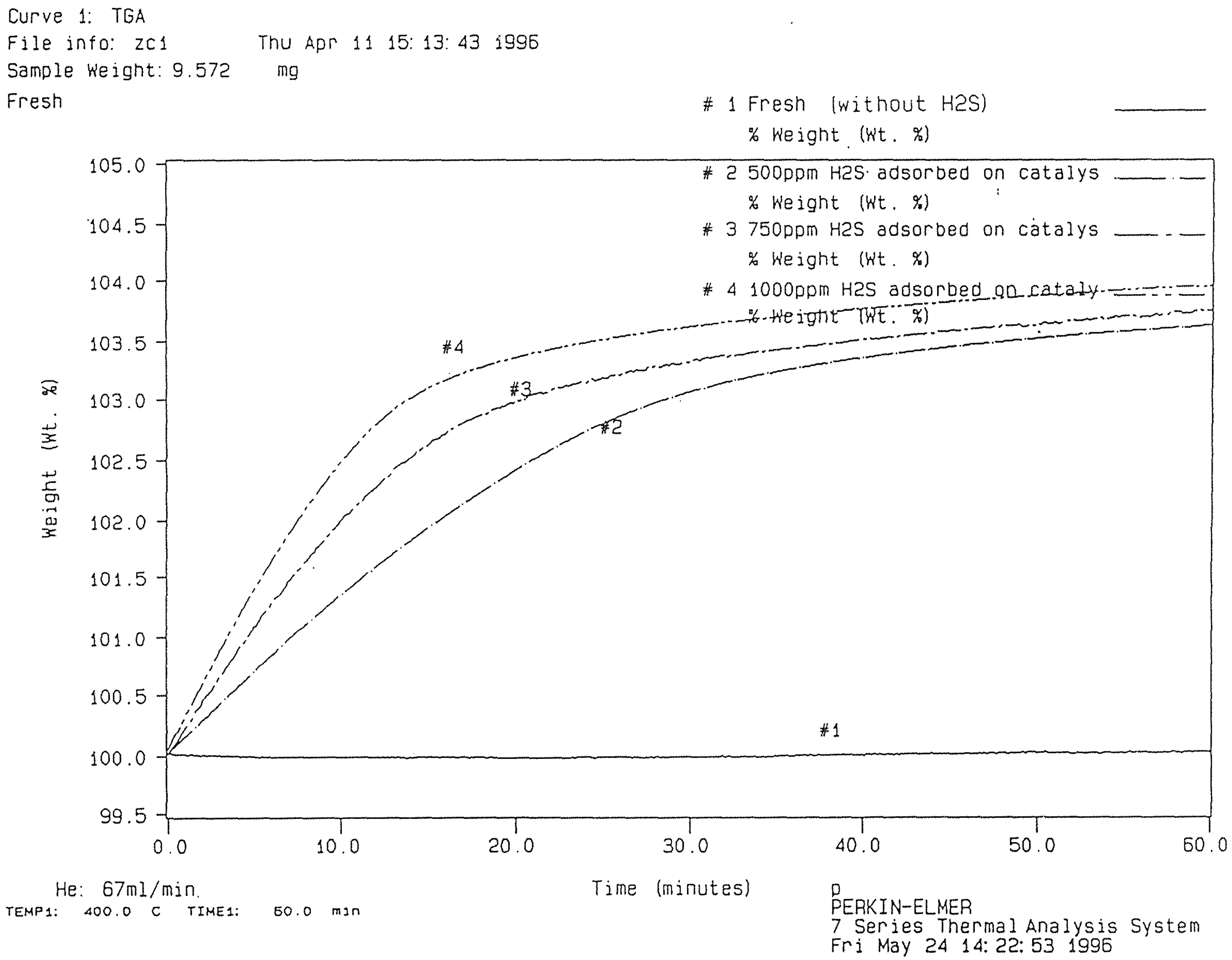


Figure 4.8 TGA Test: 1.5% Pt/γ-Al_2O_3 Catalyst Weight Changes with Different Concentrations of H_2S in Air, vs., Time

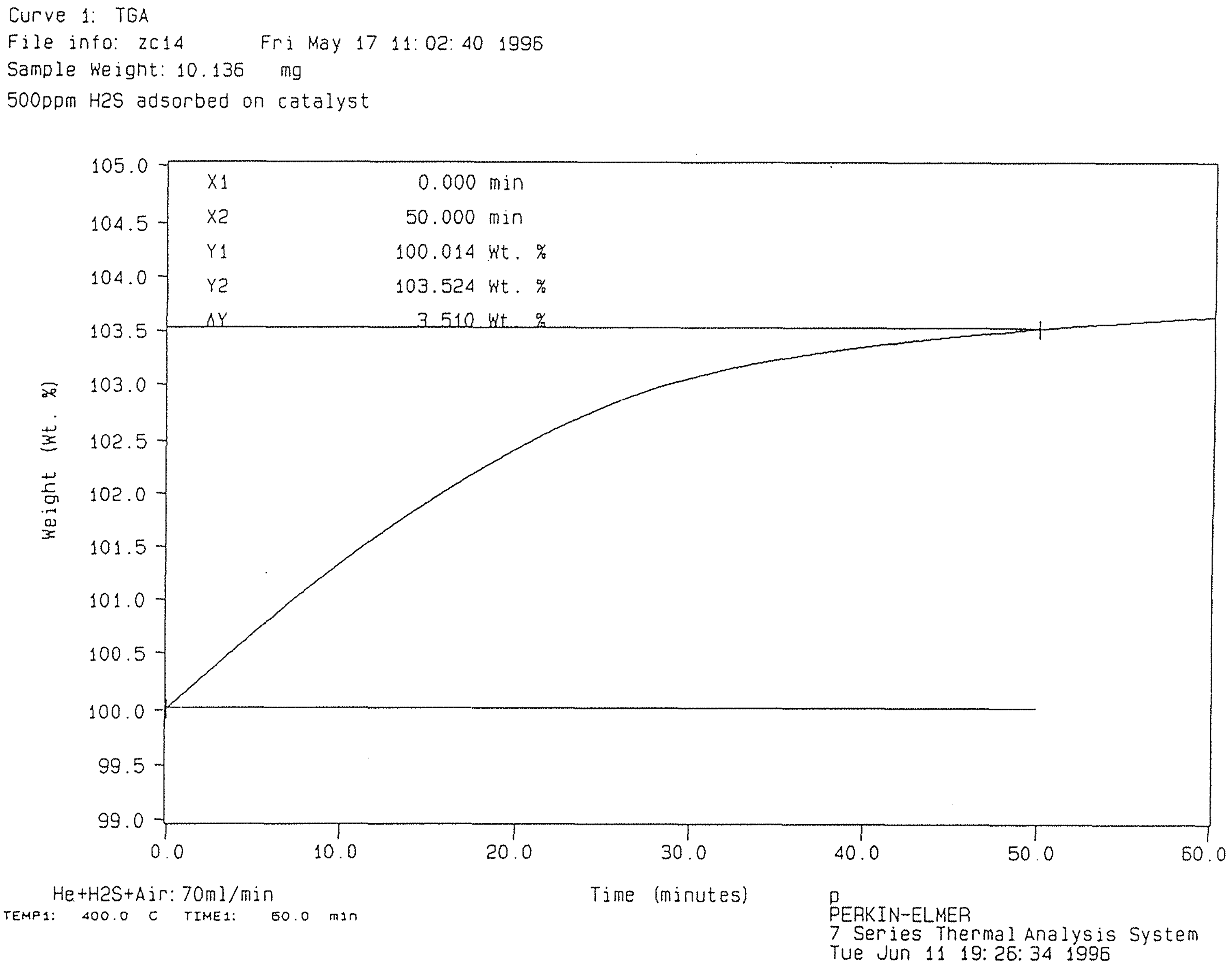


Figure 4.9 TGA Test: 1.5% Pt/γ-Al_2O_3 Catalyst Weight Gain from Exposure to 500 ppm H_2S in Air

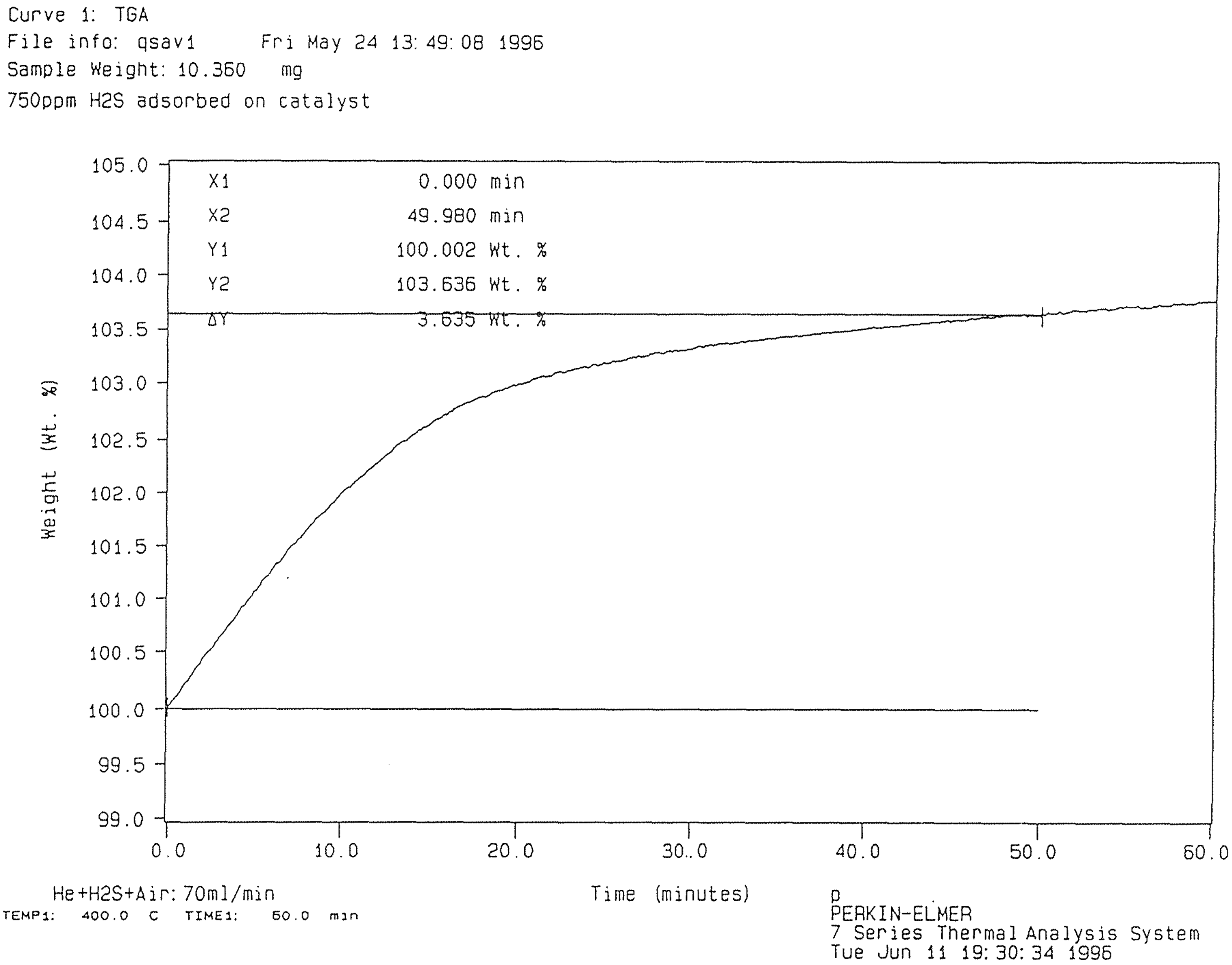


Figure 4.10 TGA Test: 1.5% Pt/γ-Al_2O_3 Catalyst Weight Gain from Exposure to 750 ppm H_2S in Air

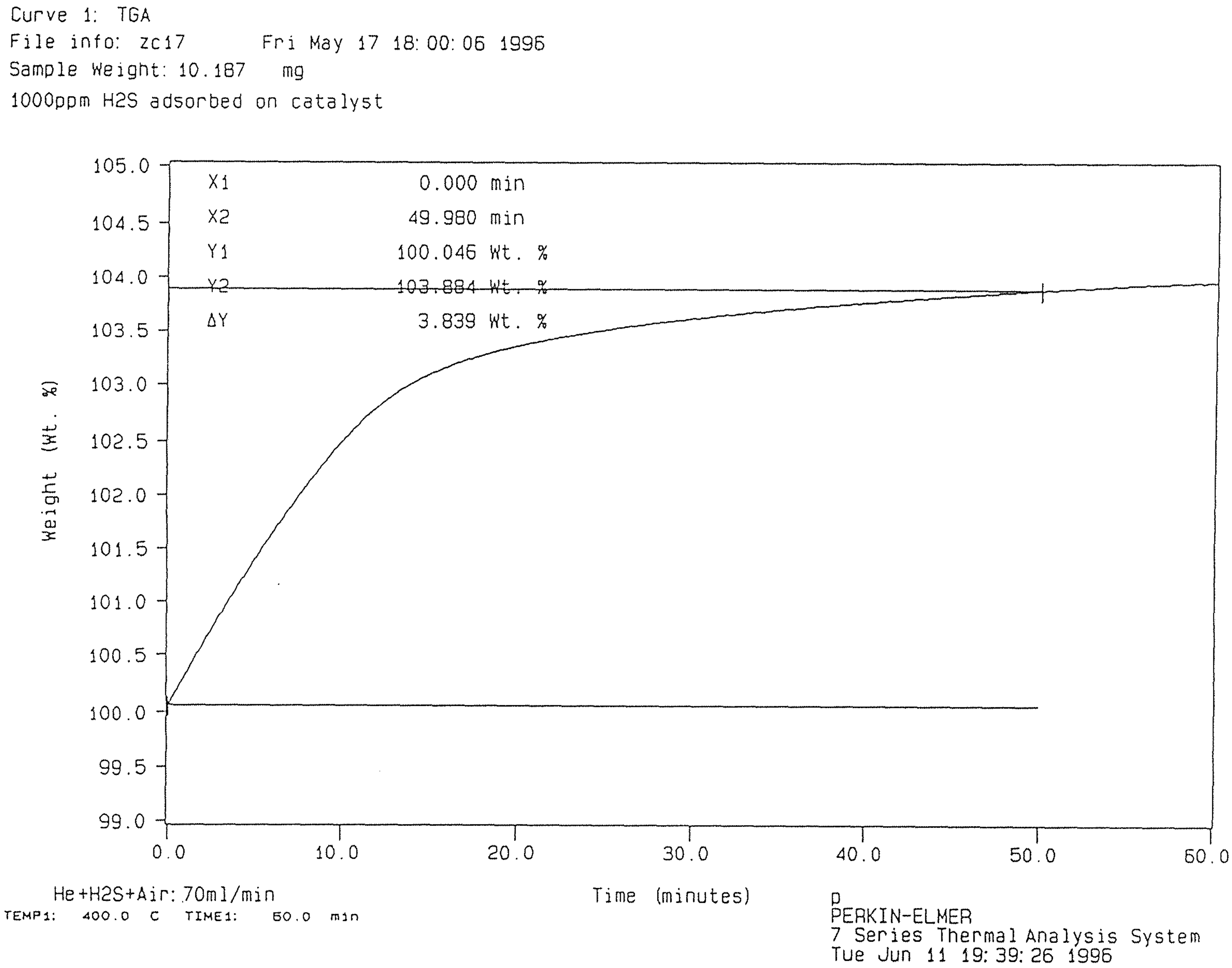


Figure 4.11 TGA Test: 1.5% Pt/γ-Al_2O_3 Catalyst Weight Gain from Exposure to 1,000 ppm H_2S in Air

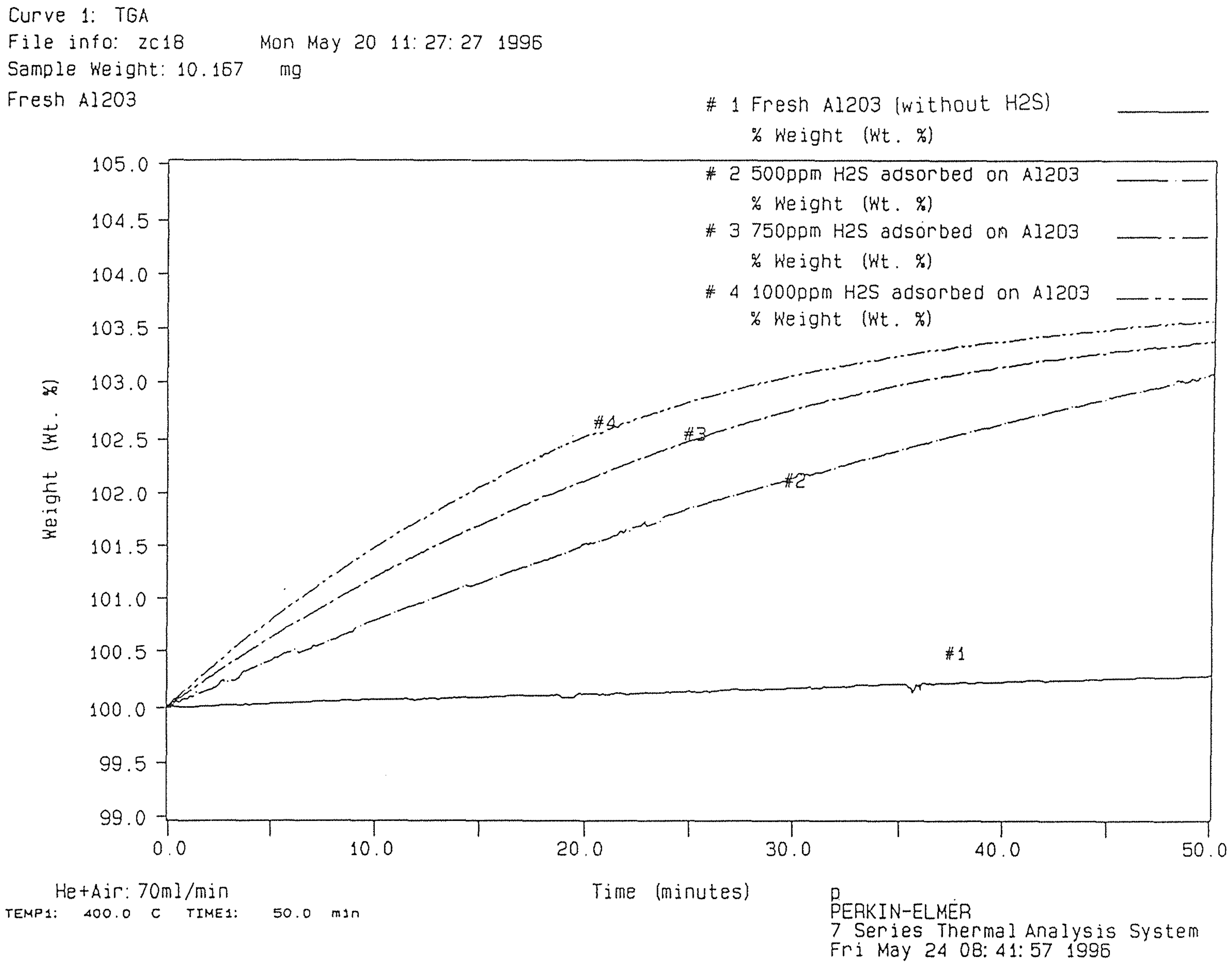
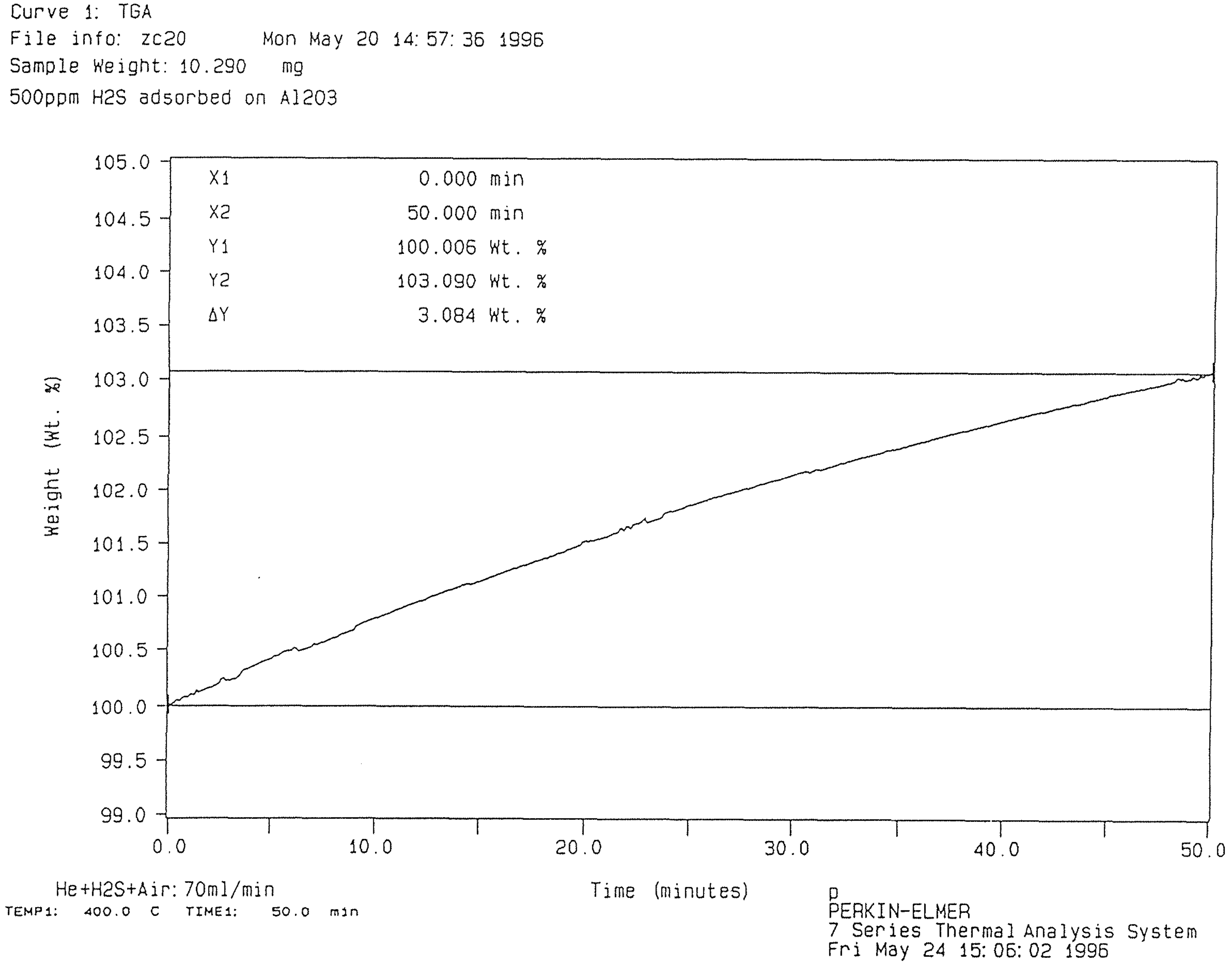


Figure 4.12 TGA Test: Pure γ-Al_2O_3 Catalyst Weight due to Exposure to Different Concentrations of H_2S in Air, vs., Time



Curve 1: TGA
File info: zc20 Mon May 20 14:57:36 1996
Sample Weight: 10.290 mg
500ppm H2S adsorbed on Al2O3

X1	0.000	min
X2	50.000	min
Y1	100.006	Wt. %
Y2	103.090	Wt. %
ΔY	3.084	Wt. %

He+H2S+Air: 70ml/min
TEMP1: 400.0 C TIME1: 50.0 min

p
PERKIN-ELMER
7 Series Thermal Analysis System
Fri May 24 15:06:02 1996

Figure 4.13 TGA Test: Pure γ-Al_2O_3 Catalyst Weight Gain due to Exposure to 500 ppm H_2S in Air

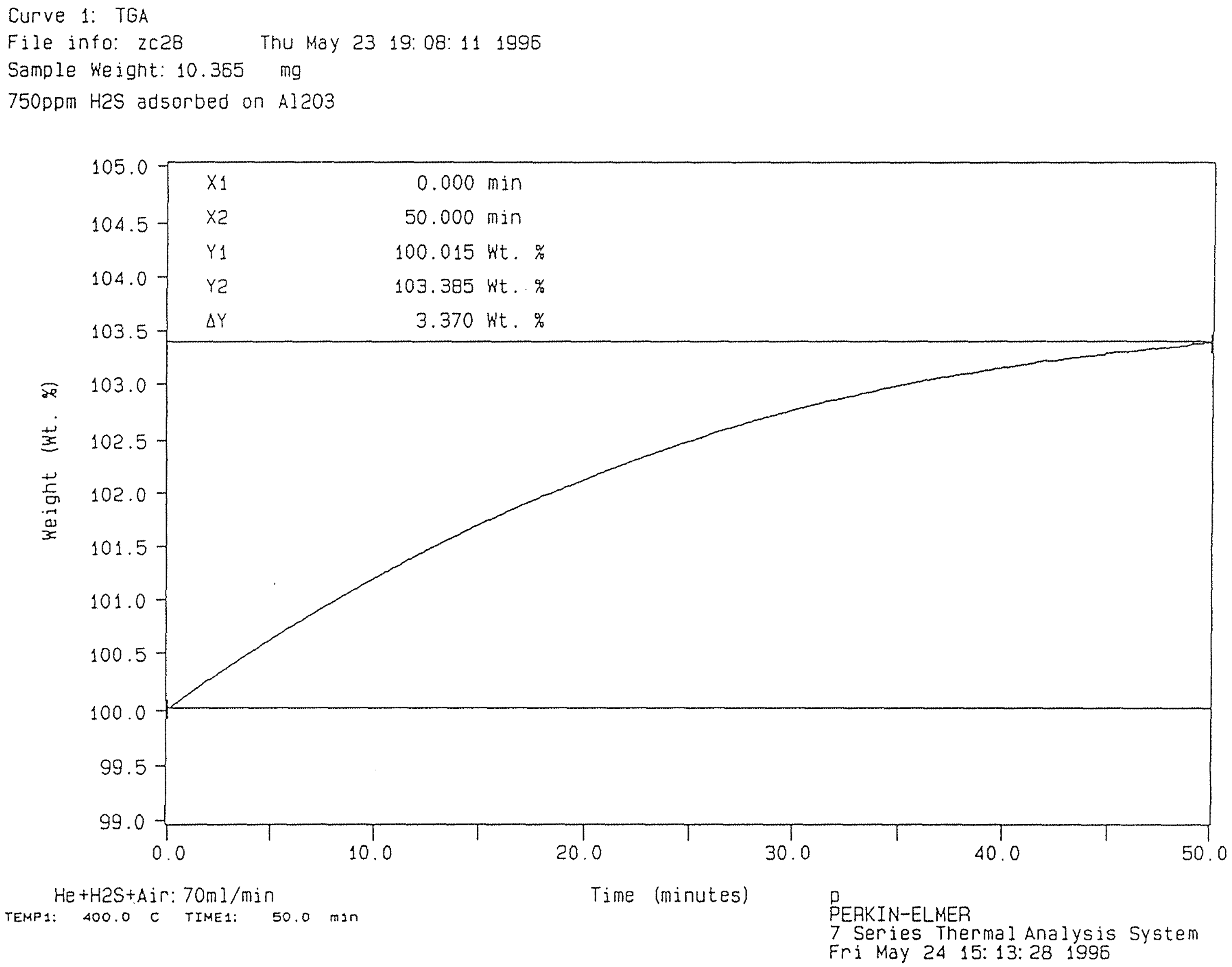


Figure 4.14 TGA Test: Pure γ-Al_2O_3 Catalyst Weight Gain due to Exposure to 750 ppm H_2S in Air

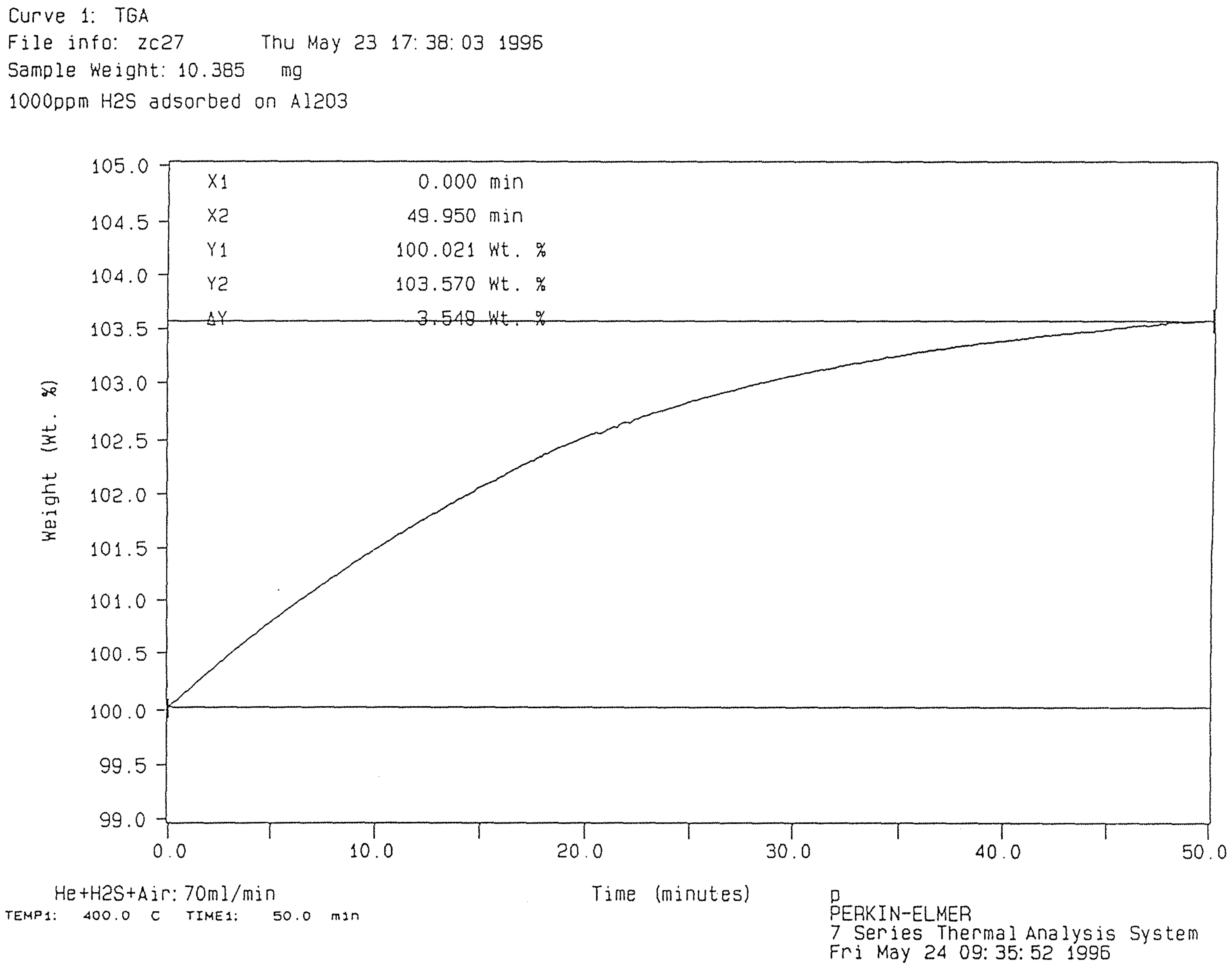


Figure 4.15 TGA Test: Pure γ-Al_2O_3 Catalyst Weight Gain due to Exposure to 1,000 ppm H_2S in Air

Table 4.5 Comparison of Weight Changes in TGA Test

Sample	**ΔWc (%)**	**ΔWa (%)**	**ΔWc - ΔWa (%)**
500 ppm H_2S adsorbed on Pt/γ-Al_2O_3	3.510	-	0.426
500 ppm H_2S adsorbed on γ-Al_2O_3	-	3.084	
750 ppm H_2S adsorbed on Pt/γ-Al_2O_3	3.635	-	0.265
750 ppm H_2S adsorbed on γ-Al_2O_3	-	3.370	
1,000 ppm H_2S adsorbed on Pt/γ-Al_2O_3	3.839	-	0.290
1,000 ppm H_2S adsorbed on γ-Al_2O_3	-	3.549	

Note: ΔWc = Sample weight change percentage for 1.5% Pt/γ-Al_2O_3 catalyst.
ΔWa = Sample weight change percentage for pure γ-Al_2O_3 catalyst.

4.3.4 FT-IR Experiments

Infrared spectroscopy is a conventional technique for the study of catalytic surfaces. In this case, FT-IR tests were conducted to identify the products formed on catalyst due to H_2S poisoning. The fresh catalyst and several aged catalysts were individually tested and compared. A catalyst sample consisted of about 0.005 g Pt/γ-Al_2O_3 catalyst diluted with 0.195 g KBr and pressed into a self-supporting disk. The disk was put in an FT-IR instrument to be analyzed (refer to Chapter 3 for operating procedures). Figure 4.16 shows the FT-IR spectra for the fresh Pt/γ-Al_2O_3 and aged Pt/γ-Al_2O_3 catalysts, whereas the spectra obtained by subtracting aged catalysts and the fresh catalyst are given in Figure 4.17. It can be seen that the all aged Pt/γ-Al_2O_3 catalysts had an absorption peak in region of 1,000~1,300 cm^{-1} and the strongest absorption peak occurs at about

1,150 cm^{-1}. According to "Infrared Spectra of Inorganic Compounds" (Nyquist, 1971), the characteristic absorption of SO_4^{2-} group is located between 1,040 ~ 1,210 cm^{-1} and the absorption of SO_3^{2-} group is located in 990 ~ 1,090 cm^{-1}. From this information, it was inferred that the sulfite and sulfate compounds were produced on aged Pt/γ-Al_2O_3 catalysts because of the interaction between sulfur compound and Pt/γ-Al_2O_3 catalyst and sulfate compounds were the predominant product. In addition, the intensity of the absorption peaks in Figure 4.16 and 4.17 increased with increasing concentration of sulfur compound. This phenomenon was consistent with the TGA experiments in which sample weight increased with increasing H_2S concentration.

To determine the constituent of sulfate and sulfite salts formed on catalysts, the FT-IR tests also were performed on pure γ-Al_2O_3 and poisoned γ-Al_2O_3 samples that were treated with H_2S in TGA tests. The results are presented on Figure 4.18 and Figure 4.19. It is obvious that the absorption peaks of poisoned γ-Al_2O_3 samples fell in the range of 1,010 ~ 1,300 cm^{-1}, which was within the region of SO_3^{2-} group (990 ~ 1,090 cm^{-1}) and the region of SO_4^{2-} group (1,040 ~ 1,210 cm^{-1}). The results proved that hydrogen sulfide reacts with γ-Al_2O_3 samples to produce $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$.

A comparison for the absorption peaks of the pure γ-Al_2O_3 sample and the Pt/γ-Al_2O_3 catalyst that had been exposed to H_2S shows that the shapes of both peaks were very similar and both absorption bands were located in an almost same region of the spectrum. This means that the H_2S can react with pure γ-Al_2O_3 in air at 400 °C to form $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$. As catalyst, Pt would enhance the reaction of H_2S with γ-Al_2O_3. Therefore, the absorption peaks of the Pt/γ-Al_2O_3 exposed to H_2S were larger than that of pure γ-Al_2O_3 exposed to H_2S. The reaction of H_2S with Pt/γ-Al_2O_3 appears to occur in the following steps. First, H_2S is adsorbed on Pt/γ-Al_2O_3 this is followed by the air oxidation of H_2S to form SO_2 and SO_3. Finally, the SO_2 and SO_3 react with the support (γ-Al_2O_3) to form $Al_2(SO_3)_3$ and $Al_2(SO_4)_3$ which help created new active sites for propane oxidation and inhibition carbon monoxide oxidation.

H_2S oxidation reaction steps over platinum catalyst can be interpreted to occur as follows:

$$\begin{aligned}
H_2S + 3/2O_2 &\overset{\text{Catalyst}}{\rightleftarrows} SO_2 + H_2O \\
SO_2 + 1/2O_2 &\overset{\text{Catalyst}}{\rightleftarrows} SO_3 \\
3SO_2 + Al_2O_3 &\overset{\text{Catalyst}}{\rightleftarrows} Al_2(SO_3)_3 \\
3SO_3 + Al_2O_3 &\overset{\text{Catalyst}}{\rightleftarrows} Al_2(SO_4)_3
\end{aligned}$$

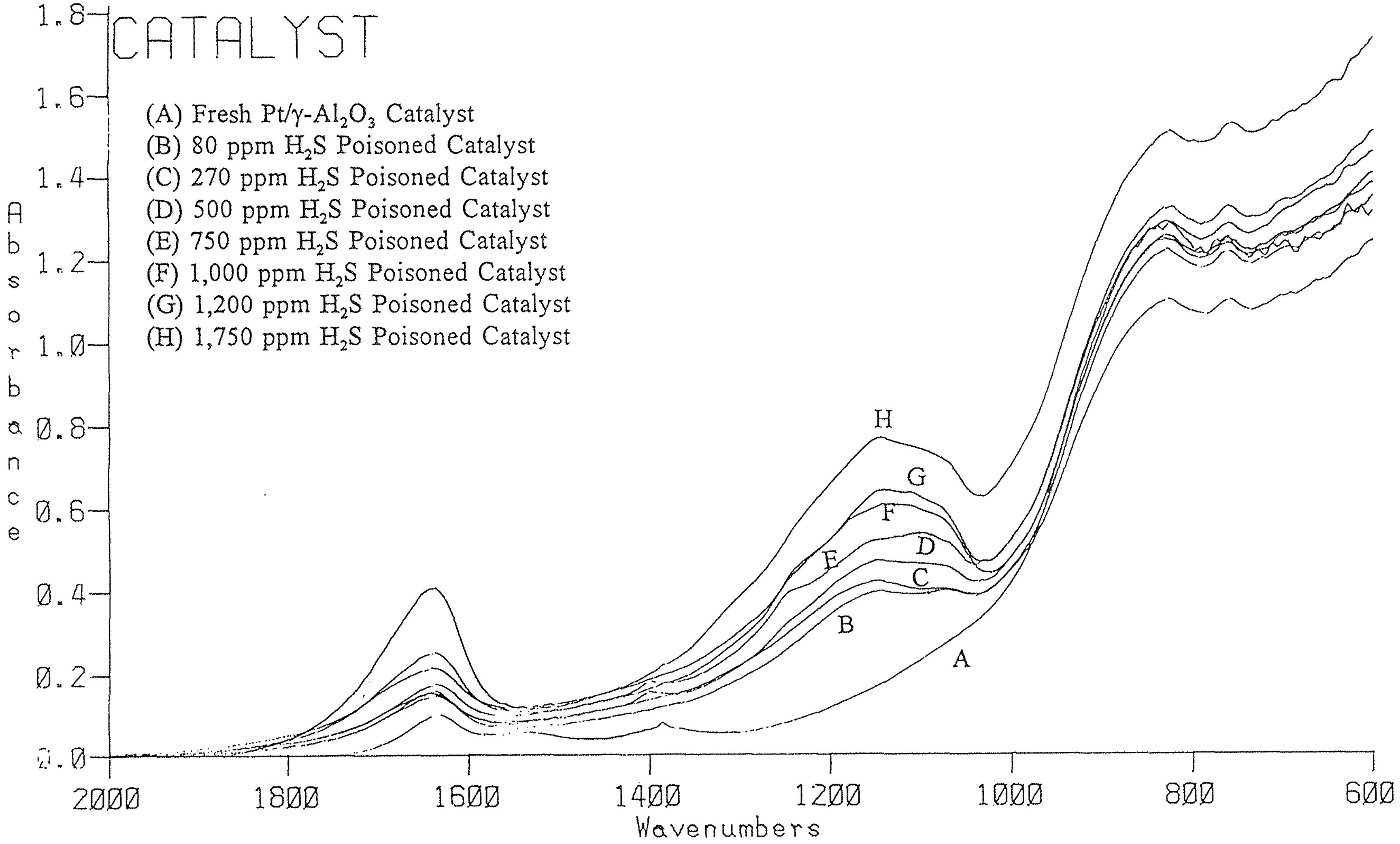


Figure 4.16 FT-IR Spectra of 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts

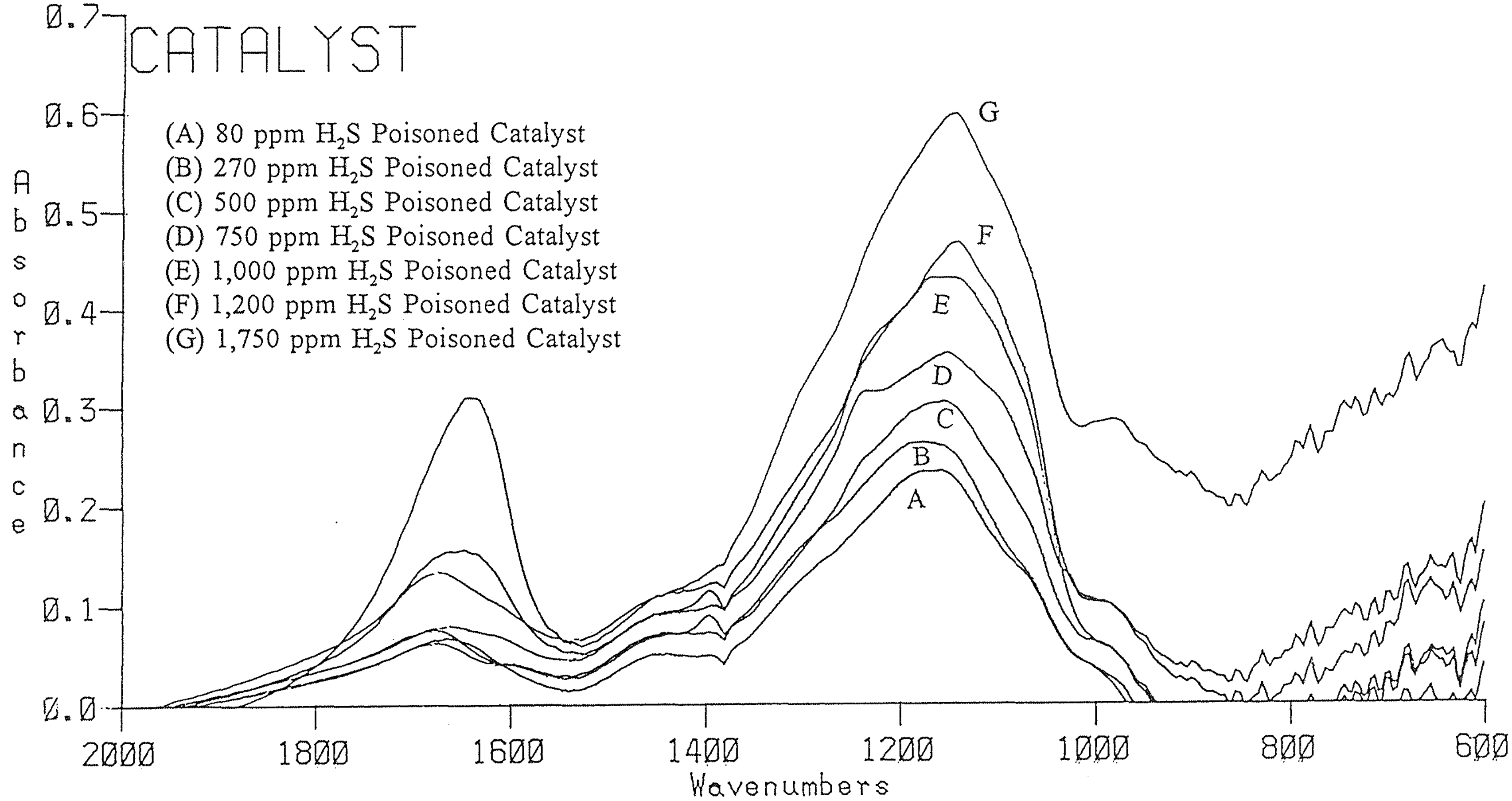


Figure 4.17 FT-IR Subtract Spectra of 1.5% Pt/γ-Al_2O_3 Fresh and Aged Catalysts

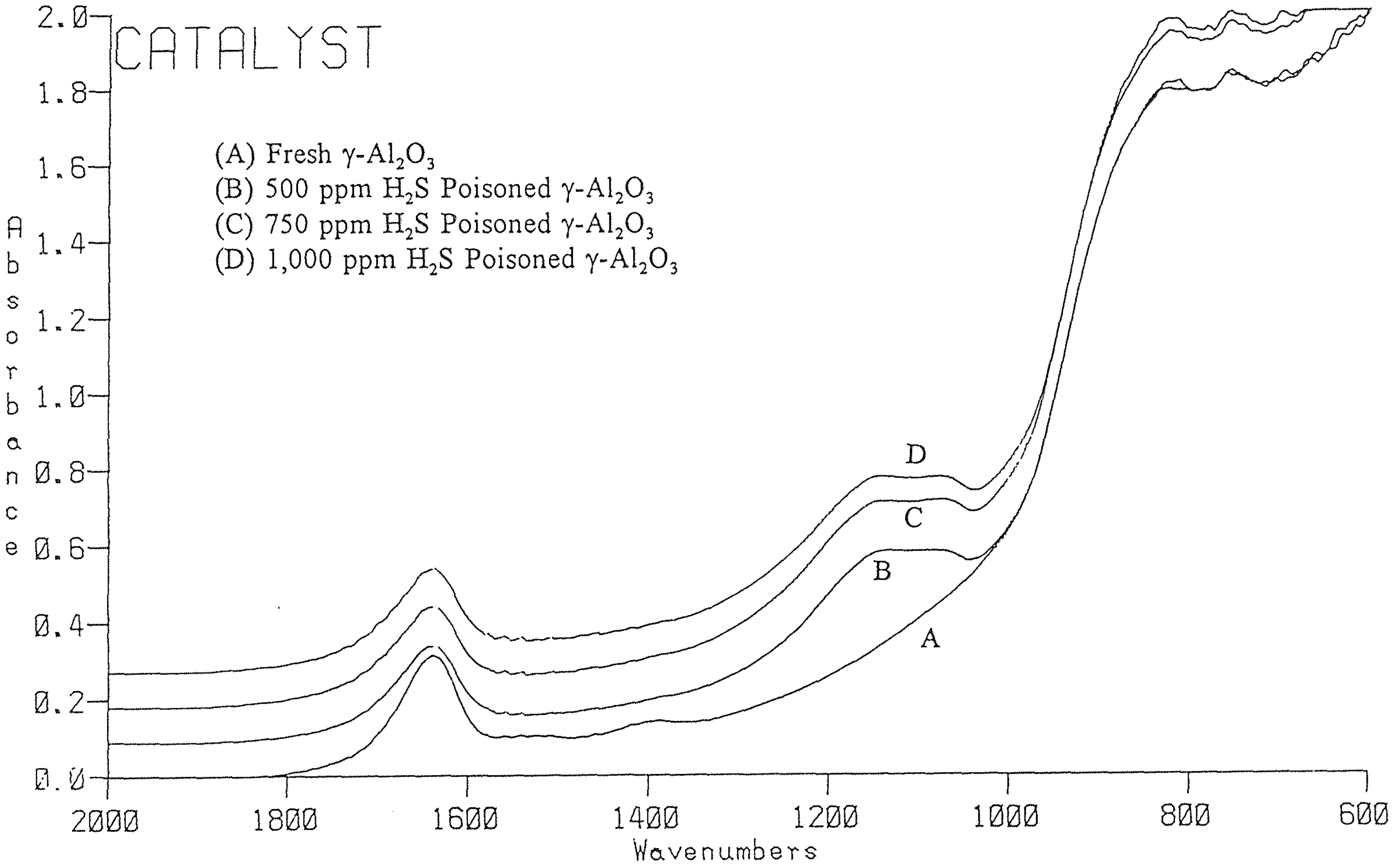


Figure 4.18 FT-IR Spectra of Fresh and poisoned γ-Al_2O_3

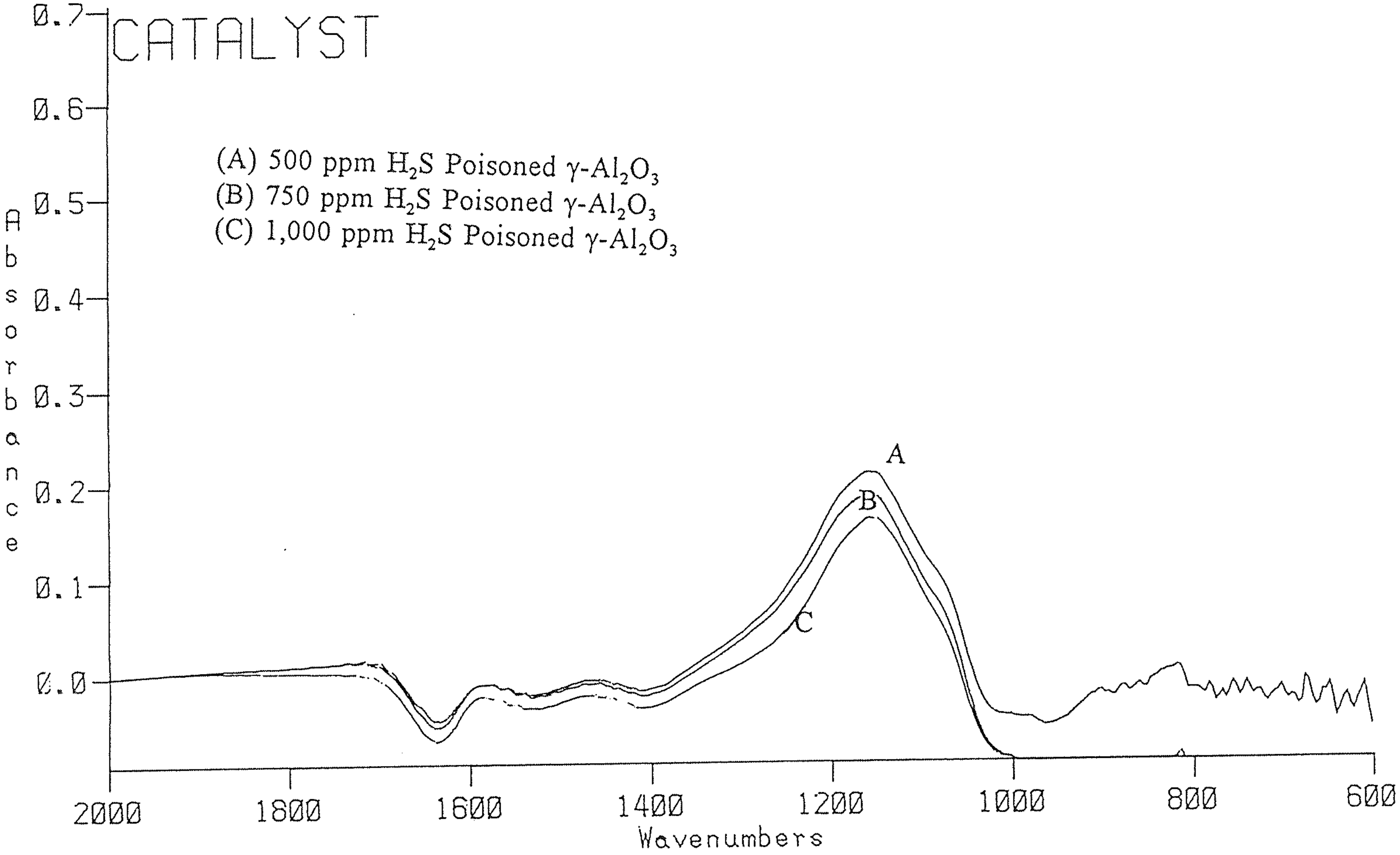


Figure 4.19 FT-IR Subtract Spectra of Fresh and poisoned γ-Al_2O_3

CHAPTER 5

CONCLUSIONS

The impacts of different concentrations of sulfur compounds on 1.5% platinum/γ-alumina catalyst were investigated by measuring the changes of catalyst activity with propane and carbon monoxide oxidation reactions. Catalyst characteristics tests also were conducted to further understand the deactivation mechanism. From the research results, the conclusions are summarized as follows:

1. 1.5% Pt/γ-Al_2O_3 catalyst treated with various concentrations of H_2S in air at 400 °C for 24 hours can promote the catalysts ability to oxidize propane and inhibit carbon monoxide oxidation.
2. The optimum catalyst activity for propane oxidation occurs for aged Pt/γ-Al_2O_3 catalyst that was aged with 750 ppm H_2S in air at 400 °C for 24 hours.
3. BET surface area measurements show that the surface areas of Pt/γ-Al_2O_3 catalysts decreased monotonically with H_2S concentration.
4. Pulse chemisorption experiments show catalyst metal dispersion decreases with increasing the concentration of H_2S. And the catalyst crystallites become larger because of the impact of sulfur compounds.
5. TGA test results indicate that sulfur compounds not only interact with Pt/γ-Al_2O_3 catalysts but also interact with pure γ-Al_2O_3 in air at 400 °C temperature.

6. FT-IR experiment results indicate that both alumina sulfite and alumina sulfate are formed on aged Pt/γ -Al_2O_3 catalysts which were aged with hydrogen sulfide in air at 400 °C for 24 hours.
7. The mechanism of Pt/γ -Al_2O_3 catalyst activity promotion for propane oxidation and deactivation for carbon monoxide oxidation involve aluminum sulfate and sulfite formation which makes the platinum crystal planes changing. The new platinum crystal planes favor propane oxidation, but the same planes do not favor CO oxidation so that the catalyst activity for propane oxidation is enhanced and reversed for CO.
8. The concentration of H_2S in the gas feed was set by rotameters. The H_2S concentration was not checked with GC-FPD because of the FPD broken. However, it will be necessary to check the results from this thesis with an independent analytical method such as GC with FPD in order to make sure the correlation with H_2S concentration and activity are accurate.

APPENDIXES

DATA OBTAINED FOR CHAPTER 4

Table A.1 Effect of Different Catalysts on Propane Conversion

Catalyst	Ta, (°C)	Tf, (°C)	R_{30}*Tf / Ta, (%)
Fresh Catalyst	-	250	30.0
Catalyst #1	228	-	32.9
Catalyst #2	220	-	34.7
Catalyst #3	194	-	38.2
Catalyst #4	187	-	40.5
Catalyst #5	192	-	39.1
Catalyst #6	189	-	39.7
Catalyst #7	220	-	34.7

Note:
1. Ta = Temperature of aged catalyst at 30% propane conversion.
2. Tf = Temperature of fresh catalyst at 30% propane conversion.
3. R_{30} = 30% conversion of propane.
4. Catalyst #1 to #7 refer to catalysts aged by 80, 270, 500, 750, 1,000, 1,200, and 1,750 ppm H_2S in air at 400 °C for 24 hours, respectively.

Table A.2 1% Propane Oxidation Conversion Changing with Different Catalysts at 200 °C

Catalyst	Cat. Fresh	Cat. #1	Cat. #2	Cat. #3	Cat. #4	Cat. #5	Cat. #6	Cat. #7
Conversion (%)	6.1	8.9	13.4	36.8	44	32.8	40.8	13.4

Note:
1. Cat. #1 to #7 refer to catalysts aged by 80, 270, 500, 750, 1,000, 1,200, and 1,750 ppm H_2S in air at 400 °C for 24 hours, respectively.
2. All the catalysts were aged at space velocity 16,500 v/v/hr and 400 °C for 24 hour.
3. The propane oxidation conversion was tested at space velocity 55,000 v/v/hr.

Table A.3 1% Propane Oxidation Conversion Changing with Different Catalysts at 250 °C

Catalyst	Cat. Fresh	Cat. #1	Cat. #2	Cat. #3	Cat. #4	Cat. #5	Cat. #6	Cat. #7
Conversion (%)	30	57.3	66.3	82.8	88.4	79.4	83.7	67.3

Note:
1. Cat. #1 to #7 refer to catalysts aged by 80, 270, 500, 750, 1,000, 1,200, and 1,750 ppm H_2S in air at 400 °C for 24 hours, respectively.
2. All the catalysts were aged at space velocity 16,500 v/v/hr and 400 °C for 24 hour.
3. The propane oxidation conversion was tested at space velocity 55,000 v/v/hr.

REFERENCES

Baird, T., 1982. in: *Catalyst*, Volume 5, edited by G. C. Bond and G. Webb, Royal Society of Chemistry, London.

Bond, G. C., 1974. *Heterogeneous Catalysis: Principles and Applications*, Clarendon Press, Oxford, England.

Bosch, H, and F. Janssen, 1987. "Catalytic Reduction of Nitrogen Oxides — A Review on the Fundamentals and Technology," Catalysis Today, **2**(4), 369.

Brunauer, S., P. H. Emmett, and E. Teller, 1938, "Adsorption of Gases in Multimolecular Layers," J. Am. Chem. Soc., **60**, 309.

Byrne, J. W., et al., 1992. "Selective Catalytic Reduction of NOx Using Zeolitic Catalysts for High Temperature Applications," Catalysis Today, **13**, 33.

Deng, Youquan and Thomas G. Nevell, 1993. "Studies of the Partial Oxidation of Methane over Heterogeneous Catalysts," J. of Catalysis, **19**, 378-385.

Gandhi, H. S., H. C. Yao, H. K. Stepien and M. Shelef, 1978. "Evaluation of Three Way Catalysts - Part III: Formation of Ammonia, Its Suppression by SO_2 and Re-Oxidation," SAE Paper No. 780606.

Gandhi, H. S. and M. Shelef, 1991. "Effects of Sulphur on Noble Metal Automotive Catalysts," Applied Catalysis, **77**, 175-186.

Happel, John, 1986. *Isotopic Assessment of Heterogeneous Catalysis*, Academic Press Inc., London.

Hegedus, L. Louis and Robert W. McCabe, 1984. *Catalyst Poisoning*, Marcel Dekker, Inc., New York and Besel.

Hughes, R., 1984. *Deactivation of Catalysts,* Academic Press Inc., London.

Karanth, N. G. and D. Luss, 1975. Chemical Engineering Science, **30**, 695.

Levenspiel, Octave, 1972. *Chemical Reaction Engineering*, John Wiley and Sons, Inc., New York.

Lester, G. R., G. C. Joy and C. C. Hsu, 1988. Report CRDEC-CR-003, U.S. Army CRDEC (Aberdeen, MD).

Lindberg, R. C., J. D. Reedy and K. Yang, 1977. "Catalytic Destruction of Chlorinated Hydrocarbon," U.S. Patent No. 4, 059, 683, November 22.

Maxted, D., 1951. *The Poisoning of Metallic Catalysts*, Advances in Catalysis, Academic Press, New York.

McCabe, Robert W. and Jonathan M. Kisenyi, 1995. "Advances in Automotive Catalyst Technology," Chemistry & Industry, Aug. 7, P. 605.

Menon, P. G. and J. Prasad, 1977. "Proceedings of the Sixth International Congress on Catalysis," The Chemical Society, London.

Monroe, D. R., M. H. Krueger, D. D. Beck and M. J. D'Aniello, 1991. "Catalysis and Automotive Pollution Control II; A. Crucq, Ed.; Studies in Surface Science and Catalysis," Elsevier: Amsterdam, **71**, 593.

Nyquist, Richard A. and Ronald O. Kegel, 1971. *Infrared Spectra of Inorganic Compounds (3800 ~ 45 cm^{-1})*, Academic Press, London.

Palazzolo, M. A., R. M. Parks and K. K. Fidler, 1984. "Control of Industrial Emissions by Catalytic Incineration," EPA-600/2-84-1186.

Rideal, Eric K., 1968. *Concepts in Catalysis*, Academic Press Inc., London.

Satterfield, Charles N., 1980. *Heterogeneous Catalysis in Practice*, McGraw Hill Book Co., New York.

Schmidt, L. D., and D. Luss, 1971. "Physical and Chemical Characterization of Platinum-Rhodium Gauze Catalysts," J. Catalysis, **22**, 269.

Shelef, M., K. Otto and N. C. Otto, 1978. *Advances in Catalysis and Related Subjects*, Academic Press, New York / London, **27**, 311.

Somorjai, G. A., 1972. "On the Mechanism of Sulfur Poisoning of Platinum catalysts," Catalysis Notes, 453

Spencer, M. S., 1989. in: *Catalyst Handbook*, edited by Martyn V. Twigg, Wolfe Publishing Ltd., England.

Spivey, J. J., 1987. "Complete Catalytic Oxidation of Volatile Organics," Ind. Eng. Chem. Res., **26**, 2165.

U.S. Environmental Protection Agency, 1993. *National air Quality and Emissions Trends Report 1992*, U.S. EPA, Research Triangle Park, NC.

Wang, Y., 1991. "Catalytic Oxidation of Trace Concentrations of Chlorinated Hydrocarbons over 1.5% Platinum on Alumina / Monolith, " MS Thesis, Department of Chemical Engineering, Chemistry, and Environmental Science, NJIT, Newark, New Jersey.

Wang, Y., 1995. " The Effect of Sulfur and Phosphorus Compounds on Supported Platinum Catalyst Activity," Ph.D Dissertation, Department of Chemical Engineering, Chemistry, and Environmental Science. NJIT, Newark, New Jersey.

Wiliamson, W. B., H. S. Gandhi, M. E. Heyde and C. A. Zawacki, 1979. "Deactivation of Three Way Catalysts by Fuel Contaminants: Lead. Phosphorus and Sulfur," SAE Paper No. 790842.

Williamson, W. B., J. Perry, H. S. Gandhi and J. L. Bomback, 1985. "Effect of Oil Phosphorus on Deactivation of Monlithic Three Way Automotive Catalysts," Applied Catalysis, **15**, 277.

Wynblatt, P., R. A. Della Betta, and N. A. Gjostein, 1975. in: *The Physical Basis for Heterogeneous Catalysis*, edited by E. Drouglis and R. I. Jaffe, Plenum Press, (9th Batyl Institute Materials Science Colloquia, Gstaad).