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ABSTRACT

THE EFFECT OF SULFUR AND PHOSPHORUS COMPOUNDS ON SUPPORTED PLATINUM CATALYST ACTIVITY

by
Yi Wang

The effect of sulfur poisoning on the activity of catalysts containing 1.5% platinum supported on γ -Al₂O₃, TiO₂, ZrO₂, or SiO₂ was investigated in this study. These four catalysts were aged with 100 ppmv H₂S in air at 400°C for 24 hours to determine the effect of sulfur poisoning under oxidizing conditions. In separate experiments, 1.5% Pt/ γ -Al₂O₃ catalyst was aged in nitrogen containing 100 ppmv H₂S to obtain a frame of reference for non-oxidizing conditions.

The oxidation of 1% CO, 1% methane, and 1% propane was used with both fresh and aged catalysts as diagnostic reactions to evaluate catalyst activity changes. Catalyst characteristics of both fresh and aged catalysts were determined to obtain possible deactivation pathways.

It was found that all aged catalysts were deactivated for both CO and methane oxidation, and promoted for propane oxidation except for 1.5% Pt/SiO₂ catalyst. Catalyst characterization studies suggest that the enhancement of activity for propane oxidation is due to the formation of sulfate on the γ -Al₂O₃, TiO₂, and ZrO₂ supports. The decrease in activity for CO oxidation is due to strong adsorption of sulfur compounds (SO_x) on the Pt active sites which inhibited CO adsorption. Both sulfur effects, i.e., sulfate formation and strong adsorption of sulfur compound on Pt active sites, deactivate catalyst for methane oxidation. The activity loss for CO oxidation was greater than that for methane oxidation.

It was found that 1.5% Pt/ γ -Al₂O₃ catalysts aged with H₂S in air and nitrogen could be regenerated by hydrogen treatment at 350°C. After regeneration, CO and

propane diagnostic oxidation tests showed that activity of catalyst aged in nitrogen for both CO and propane oxidation can partially recover fresh catalyst activity. However, catalyst aged in air can partially recover its activity only for CO oxidation. This suggests that catalyst once poisoned by sulfur to form sulfate on the support, will permanently maintain the enhanced activity for propane oxidation, even after sulfur has been partially removed. The effect of increased dose of sulfur on the enhancement of activity for propane oxidation was not investigated, nor were lifetime effects.

Phosphorus poisoning effects on supported platinum catalyst due to tributyl phosphate (TBP) was also studied. Catalyst containing 0.05 gram 1.5% Pt/ γ -Al₂O₃ were poisoned by 1 cm³ TBP in air at both 400 and 550°C, respectively. Diagnostic oxidation of CO, methane, and propane with fresh and poisoned catalysts showed that catalyst poisoned at 400°C were slightly deactivated due to the formation of P₂O₅ which deposited on catalyst surface and blocked the pore entrance. Catalyst poisoned by TBP at 550°C were irreversibly deactivated. At the higher temperature, not only did the activity for methane oxidation decreased, but selectivity to CO₂ decreased producing predominately CO. It is believed that this effect is due to the modification of Pt sites with the phosphorus compounds and the formation of Al PO₄ on the catalyst surface.

**THE EFFECT OF SULFUR AND PHOSPHORUS COMPOUNDS ON
SUPPORTED PLATINUM CATALYST ACTIVITY**

by
Yi Wang

**A Dissertation
Submitted to the Faculty of
New Jersey Institute of Technology
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**Department of Chemical Engineering,
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**This dissertation is dedicated to
my parents, my sisters and my wife**

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CHAPTER 1

INTRODUCTION

1.1 General Description

Improving the quality of our environment has become a growing concern in this country and around the world. Limiting the amount of pollution released into the atmosphere is an important part of that effort. Some of the most promising controls for air pollution involve the use of catalysts. Catalysts are used to control emissions from both mobile sources, such as automobiles, and stationary sources, such as industrial and power plants. In order to improve and expand the capabilities of these pollution controls, it is important to understand the catalytic chemistry of these systems.

Research efforts in this field have recently been accelerated by the passage of the 1990 Clean Air Act. This legislation tightens the limits on currently controlled emissions and expands the list of regulated emissions. The new law also introduces the concept of alternative fuels for lower emissions from vehicles. It will also impose new standards and will require improved technologies to meet them. Among other things, these laws define limits for harmful emissions from industry, transportation, power generation, and other sources.

The new requirements, which become increasingly restrictive through the 1990s and beyond, are expected to prompt strong growth for environmental catalysts. Most of the growth will come from new or improved products that reduce such air pollutants as carbon monoxide, volatile organic compounds (VOCs), nitrogen oxides (which react photochemically with VOCs to form ground-level ozone and also contribute to acid rain), and particulates. In all, the 1990 amendments to the Clean Air Act set limits for 189 toxic air pollutants (Farrauto, et al., 1992).

Catalysts have been used in the U.S. to control automotive emissions since 1975 and gaseous emissions from industrial facilities since 1940s. Now, the new regulations are pressing for wider applications and better catalytic performance. For example, the new rules require:

- Automobile catalytic converters to last 100,000 miles and to reduce pollutant emissions even further.
- Many diesel trucks and buses to be equipped with "aftertreatment" devices, such as flow-through catalysts and soot filters, to control particulate and nitrogen oxides.
- Catalytic oxidation of VOCs from industrial exhausts containing certain constituents such as halogen-containing compounds that need special treatment.
- Use of oxygenated and reformulated gasoline in heavily polluted urban areas, which will alter the refinery flow scheme, especially in catalytic units (Farrauto, et al., 1992).

1.2 Importance of Catalyst Deactivation Study

It is well known that the catalytic activity of platinum and of most transition metals is drastically reduced when the reagents contain even trace quantities of poison compounds. This poisoning of the catalyst is an important industrial processes problem because it prevents the catalytic conversion of many feeds. On the other hand, the controlled partial poisoning of catalysts has been found useful in industrial processes and in scientific investigations to enhance selectivity for desired products. Thus, a knowledge of the diverse mechanisms by which poison compounds prevent or inhibit chemical reactions on a catalyst surface is desirable.

1.2.1 In Automotive Industry

Automotive exhaust emissions are controlled by catalytic converters located in the exhaust system so that all exhaust gases pass through them. Converters using oxidation catalysts were introduced in 1975 in response to the original Clean Air Act of 1970. They convert

carbon monoxide and hydrocarbons produced by incomplete fuel combustion into carbon dioxide and water. Three-way automobile converters (TWC), adopted widely in 1981 to meet the federal 1.0 g/mile nitrogen oxides standard, catalyze these oxidation reactions and simultaneously reduce nitrogen oxides .

Catalyst longevity is a very important issue since converters are required to operate for 100,000 miles. The switch to unleaded gasoline in the U.S. has eliminated catalyst deactivation caused by lead. Other contaminants in fuel and engine oil still present problems however, especially phosphorus, zinc, and sulfur.

The relatively small amount of sulfur present in automotive fuel influences the functioning of automotive catalysts to a greater extent than may be anticipated. Unleaded gasoline used in vehicles equipped with catalytic converters contains residual amounts of organic sulfur of about 300 ppm on the average. During combustion, organosulfur compounds are converted to SO_2 . Over automotive emission control catalysts, the SO_2 can be converted to other sulfur compounds such as H_2S , COS , and H_2SO_4 . The chemistry of sulfur over catalysts is a function of temperature, redox potential of the exhaust, composition of the catalyst, and presence of the other impurities in the exhaust gas system. The sulfur dioxide can undergo a complex variety of interactions. In turn, these interactions can, influence the catalyst activity in both undesirable and beneficial ways (Gandhi, et al., 1991). A brief summary of previous research on the effect of sulfur on automotive catalysts will be given in the literature review section

Catalyst deactivation and reaction inhibition due to P and Zn are still the concern of modern TWC catalyst. Phosphorus and zinc compounds such as zinc dialkyldithiophosphate (ZDP) in lubrication oil (a wear-retardant additive) reduce catalyst performance because they are deposited on the washcoat surface and form an amorphous glaze, which keeps exhaust molecules from reaching catalytic sites within the washcoat (Chen, et al., 1992). One explanation as to why the phosphorus in engine oil poisons catalysts has been reported by Williamson et al. (Williamson, et al., 1985), who described that glass-like zinc

pyrophosphates were formed from noncombusted ZDP at temperature below 450°C. In contrast, Bell et al. (Bell, et al., 1988) reported that the phosphorus in engine oil had no negative effect on the catalyst, and that there was no change in the catalyst's performance or life when the phosphorus content was between 0.05% and 0.13%. However, no clear conclusions have been reached about any detrimental effect of engine oil composition on catalyst life.

1.2.2 In Industrial Plants

The complete catalytic oxidation of various volatile organic compounds with air is finding wide application in air purification. Changes in activity and selectivity associated with deactivation of these catalysts have important consequence for the performance of commercial and developmental air pollution control system.

In the manufacture of many consumer products, at least one processing step involves the use of organic compounds. Subsequent processing results in removal of varying amounts of these compounds which subsequently end up in the plant emissions. These VOCs may be solvents, unreacted feedstocks, or decomposition products. Since the concentration of VOC in the air is usually low, thermal incineration is costly because substantial amount of fuel must be added. Similarly, recovery and recycling system are expensive because of the equipment needed to recover relatively small quantities of organic compounds. For these reasons, a catalytic system is often selected for pollution control. One of the most widely used catalysts for control of many types of gaseous emissions is platinum supported on various oxides such as $\gamma\text{-Al}_2\text{O}_3$. Platinum is one component of automotive exhaust catalysts and is widely applied to gases containing hydrocarbon compounds. Because platinum, containing catalysts are poisoned by chlorinated hydrocarbons (Lindberg, et al., 1977), understanding how to prevent deactivation of these catalysts, when used to oxidize chlorinated hydrocarbon in air is of particular interest.

Based on the importance of this poisoning effect on catalyst deactivation mentioned above, three major poisons, i.e., chlorine, sulfur, and phosphorus were chosen for detailed study in order to enhance our understanding of catalyst deactivation mechanisms

1.3 Objective

The objective of this research is to obtain fundamental understanding of the deactivation mechanism of platinum catalyst due to the effect of chlorine, sulfur and phosphorus compounds. This will allow us to modify catalyst formulations, redesign catalytic reactors, develop methods for regeneration and determine the optimum operating parameters for the catalyst being evaluated.

This study emphasized the effect of sulfur compounds on catalytic activity because of an interesting activity enhancement that promises to give insight on deactivation mechanism. the catalyst activity. A series of platinum catalysts supported on various metal oxides, i.e., γ -Al₂O₃, SiO₂, TiO₂ and ZrO₂ were studied. The catalysts were first poisoned by 100 ppm H₂S in air at 400°C for 24 h, then a series of tests i.e. diagnostic oxidations of methane, propane and carbon monoxide and other catalyst characterization studies were conducted to evaluate catalyst deactivation pathway.

A study on the effect of chlorinated compounds on catalysts deactivation was conducted previously (Wang, 1991). The oxidation of two chlorinated hydrocarbon, dichloromethane (DCM) and trichloroethylene (TCE) was studied over 1.5% Pt/ γ -Al₂O₃/monolith/400cpsi at 30,000v/v/hr and 200 to 550°C. At an inlet concentration of 50 ppm TCE , no substantial effect was observed over the test catalyst during a period of 100 hours at 450°C which yielded about 80% conversion. This lack of deactivation, which would almost certainly be observed at much longer reaction times, may be due to the high platinum loading.

Some initial work with phosphorus compound, i.e., the effect of tributylphosphate (TBP) on catalyst activity was conducted during this research. The results will be described and analyzed in a later chapter. Detailed studies of the poisoning of Pt catalysts due to phosphorus compound need to be continued.

CHAPTER 2

LITERATURE REVIEW

2.1 Basic Principles of Catalysis

2.1.1 Introduction

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

In practice, catalysis is primarily a science that draws on many fields such as organic chemistry, surface chemistry, chemical kinetics, thermodynamics, ceramics, and solid-state physics. No unified theory of catalysis exist, and there are frequently several alternative, and not necessarily mutually exclusive, theoretical explanations for any given set of facts (Rideal, 1968). The commonly accepted basic concept is that a catalyzed reaction involves the transitory adsorption (almost always chemisorption) of one or more of the reactants onto the surface of the catalyst, rearrangement of the bonding, and desorption of the products.

Both physical and chemical viewpoints may provide insight. To be able to relate catalytic activity to certain specific properties of the catalyst surface is desirable (Bond, 1974). Yet an understanding of the mechanism of action and a successful search for new and more effective catalysts may proceed predominantly through the chemical approach, which relates catalytic behavior to the vast body of knowledge concerning chemical

reactions. The approaches are, of course, interrelated. The fundamental question, about which little is yet known, is how the surface structure of a solid catalyst causes the reactants to be adsorbed, the chemical bonds to be rearranged, and the products to be desorbed.

Technologists must understand the method of thinking and theoretical framework within which investigators view their fundamental studies, so as to be able to utilize theories and advances in fundamental understanding and yet not be sidetracked by trying to apply them under the wrong conditions (Satterfield, 1991). Practicing technologists are primarily concerned with the effect of the catalyst: how the rate and direction of the reaction are altered by changes in catalyst composition and by changes in feed composition, impurities, pressure, temperature, degree of recycle, and reaction time. They are concerned with the incorporation of the catalyst into a process, how poisons may inadvertently be introduced into the catalyst system by the other parts of a process, and how this can be mitigated. The catalysts are usually highly active and of complex composition, they must show good stability over long periods of time, and have the requisite activity and selectivity (Hegedus, 1987).

Scientific investigators, on the other hand, are concerned primarily with mechanism. In trying to simplify their system for more fundamental interpretation, they frequently use catalysts of as simple a composition as possible, such as pure metal film or single pure metals or compounds, even if they are relatively inactive and would not be used in practice. The problem of mechanical strength and stability over long periods of time is of less importance. Many of the fundamental studies that are valuable in providing insight into the causes of catalyst behavior have not been made with reaction at all, but rather have been studied either of the structure of catalyst surface or of the nature and properties of adsorbed chemical intermediates.

2.1.2 Definitions

2.1.2.1 Catalyst The definitions of catalysis and of what constitutes a catalyst have gradually evolved as understanding of the causes of catalytic phenomena has grown. Even today there is no universal agreement on definitions; the point of view varies somewhat depending on the investigators, for example, between the fundamental investigator and the practitioner, and among researchers concerned with heterogeneous catalysis, homogeneous catalysis, and enzymes. For present purposes, however, the definition should be: *A catalyst is a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process* (Bond, 1974). The phenomenon occurring when a catalyst acts is termed catalysis. The fundamental concept, stemming from the chemical approach to catalysis, is that a reaction involves a cyclic process in which a site on a catalyst forms a complex with reactants, from which products are desorbed, thereby restoring the original site and continuing the cycle.

A catalyst cannot change the ultimate equilibrium determined by thermodynamics; its role is restricted to accelerating the rate of approach to equilibrium. It must be emphasized that the lowering of the activation energy is a fundamental principle of catalysis, and applies to all forms of catalysis homogeneous, heterogeneous, and enzymatic.

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

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

2.1.2.3 Steps in Catalysis Because catalytic gas-solid reactions involve the flow of gases past the solid materials there is always the possibility of a mass transfer limitation between the gas and the solid. Usually, in commercial practice, flow rates are sufficiently high to minimize any mass transfer resistance from this source but the effect can be important in some instances such as when relatively low gas velocities are used with large catalyst pellets (Bond, 1974).

Both internal diffusion and external mass transfer may act singly or combined to reduce the magnitude of the intrinsic chemical rate on the catalyst surface. A diagram showing the presence of a gas film resistance that reduces the rate of reactant flow to the surface and the rate of product evolution from the surface is shown in Figure 2-1. If the catalyst is very active the reactant concentration may drop to zero at some point within the pellet (Satterfield, 1991). The overall reaction may be assumed to consist of a number of steps:

- (1) Mass transfer of reactants from the bulk gas to the external surface of the catalyst pellet.
- (2) Diffusion of reactants through the pores of the pellet.
- (3) Adsorption of reactants onto the active sites of the catalyst.
- (4) Surface reaction on the active sites.
- (5) Desorption of the products from the active sites.

(6) Diffusion of the products back through the pores to the outside surface of the pellet.

(7) Mass transfer of the products from the external surface of the catalyst pellet to the bulk gas phase.

Each of these steps will proceed at a certain rate, and if a steady state is attained the slowest will be the rate-determining step. As shown in Figure 2-2, at low temperatures, the chemical reaction rate steps are slow relative to diffusion. As the temperature is increased, those steps with higher activation energies and exponential dependence increase the fastest, and control of the overall rate will shift from chemical to pore diffusion. Finally, at higher temperatures, both the chemical and pore diffusion rates become sufficiently fast that bulk mass transfer, having a small relative temperature dependence, becomes rate limiting (Heck, 1995).

The slope of the conversion versus temperature curve can give a qualitative picture of the rate-controlling steps. The steeply rising lower part of the curve is indicative of chemical control. The relative flat temperature-insensitive portion reflects bulk mass transfer control, while the intermediate portion is characteristic of pore diffusion control.

Because chemical rates have a much larger temperature coefficient and higher activation energy than rates of mass or heat transfer, the overall rate of a process tends to be controlled by the physical steps at high temperatures. The processes of mass and heat transfer outside and within the catalyst pellets will be considered next since they constitute an important factor in a detailed study of catalyst deactivation.

2.1.3 Catalyst Characterization

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

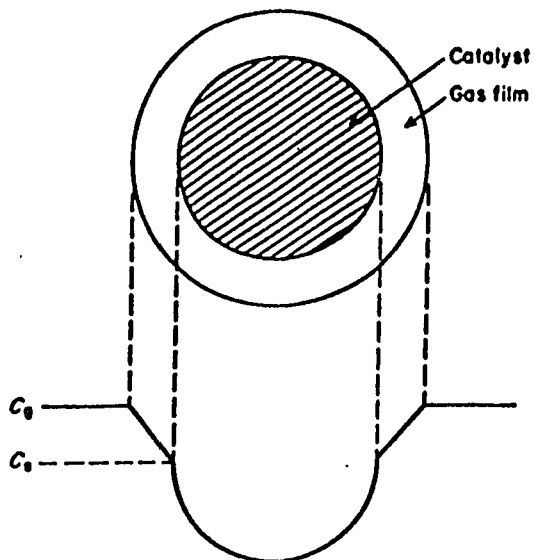


Figure 2-1 External and internal concentration gradients in a reacting catalyst pellet

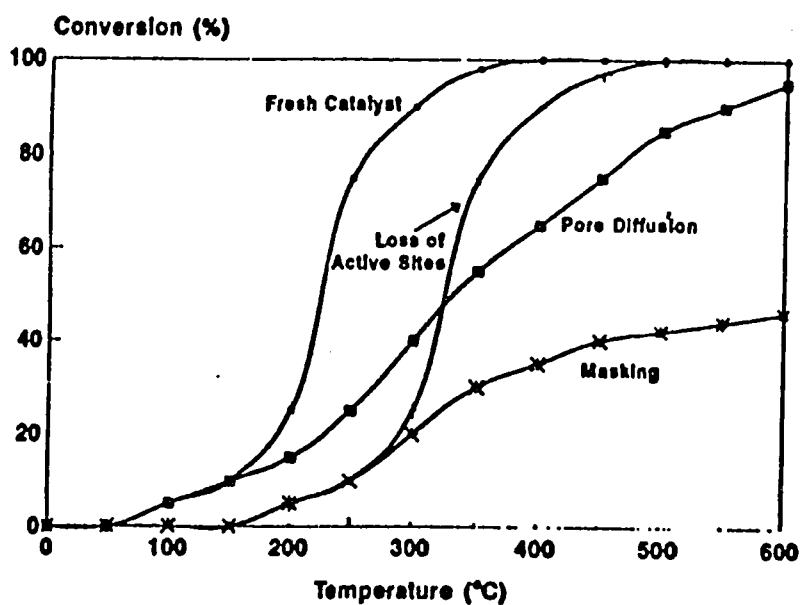


Figure 2-2 Relative changes in the conversion versus temperature profile for various deactivation mechanisms

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

Each adsorbed nitrogen molecule occupies an area of the surface comparable to its cross sectional area 0.162 nm². By measuring the number of N₂ molecules adsorbed at monolayer coverage, one can calculate the internal surface area. The BET equation describes the relationship between volume adsorbed at a given partial pressure and the volume adsorbed at monolayer coverage:

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

Where:

P = partial pressure of N

P₀ = saturation pressure at the experimental temperature

V = volume adsorbed at P

V_m = volume adsorbed at monolayer coverage

C = constant

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

2.1.3.2 Metal Dispersion The extent of dispersion is defined as the ratio of the number of surface metal atoms in a catalyst to the total number present. A value of unity means that all metal atoms are exposed to reactants. The IUPAC recommendation is that the term percentage exposed be used instead of dispersion. Standardized techniques exist,

however, for obtaining information regarding the distribution and number of catalytic components dispersed within or on the carrier.

$$\% \text{ Dispersion} = \frac{\text{Number of catalytic sites on the surface}}{\text{Theoretical number of sites present}} \times 100\%$$

The average fraction exposed is measured most directly by determining the selective chemisorption, the number of surface atoms present and combining that information with a knowledge of the total amount of metal present (Satterfield, 1991). Selective chemisorption can be used to measure the accessible catalytic components on the surface by noting the amount of gas adsorbed per unit weight of catalyst. The stoichiometry of the chemisorption process must be known to estimate the available catalytic surface area. One assumes that the catalytic surface area is proportional to the number of active sites. A gas that will selectively chemisorb only onto the metal and not onto the support is used under predetermined conditions. Hydrogen and carbon monoxide are most commonly used as selective adsorbates for many supported metals.

2.1.3.3 Thermal Gravimetric Analysis Thermal gravimetric analysis or TGA is a useful technique to measure microscopic weight changes. A few milligrams of catalyst are loaded into a sample pan suspended in the microbalance inside a quartz tube. A controlled gas flow and temperature ramp is initiated, and a profile of weight change versus temperature is recorded. The weight versus temperature profile is helpful in establishing procedures for regenerating the catalyst in a process reactor.

2.1.4 Catalyst Deactivation

2.1.4.1 Classification of Catalyst Deactivation Processes General reviews of catalyst deactivation have been given by Butt and Levenspiel and they have laid foundations of a

better understanding of catalyst deactivation processes (Butt, 1988). A catalyst may lose its activity or its selectivity for a wide variety of reasons. The cause may be grouped loosely into:

- (1) Poisoning
- (2) Sintering
- (3) Fouling

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

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

It should be emphasized that poisoning is not always undesirable; in some cases selective poisoning may be employed to enhance one reaction on a multifunctional catalyst while inhibiting a less desirable one.

Sintering is a physical process associated with loss of area of the catalyst which occurs when the catalyst is operated above its normal range of temperature. Two different kinds of sintering may be distinguished, depending on the type of catalyst employed. If the catalyst is a normal high-area support type material, operation at high temperatures will cause a loss of specific surface with associated changes in the pore structure, giving a corresponding loss in activity. The second type of catalyst deactivation occurs when the

active ingredient, usually a metal, which is supported on a high-area oxide support becomes mobile at elevated temperature. Here, sintering can occur not only by reduction of the support area but by a "coalescence" or loss of dispersion of the metal crystallites (Peterson, 1987). This loss of area of the active constituent of the catalyst causes a sharp drop in activity.

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

2.1.4.2 Poisoning of Catalysts Early work on the poisoning of metallic catalysts was assembled by Maxted (Maxted, 1951) in an excellent review. In this review, he proposed a theory of catalyst poisoning based on the electron structural properties of the poison in the gas phase and on the solid metal catalyst. The concept employed is that essentially the poison is adsorbed on the active metal sites to form a chemisorbed complex. Limitation to chemically bonded systems implies a specificity and also that a low concentration of poison may have a very marked deactivating effect.

Metallic catalysts susceptible to poisoning are confined mainly to metals of Group VIII of the periodic table and the closely related metals of Group IB (Cu, Ag, Au). These are listed in Table 1; most of them are employed for hydrogenation and reforming reactions, and much of the earlier work on poisoning was performed on this type of catalysts.

Table 1 Catalytic metals most susceptible to poisoning

Fe	Co	Ni	Cu
Ru	Rh	Pd	Ag
Os	Ir	Pt	Au

The principal poisons that are effective in deactivating these metal catalysts belong to the following groups:

- Molecules containing elements of the periodic table Group VB and VIB, i.e. N, P, As, Sb, and O, S, Se, Te.
- Compounds of a large number of catalytically toxic metals.
- Molecules containing multiple bonds, such as CO, cyanogen compounds, and strongly adsorbed organic molecules.

The toxicity of the compounds of Group VB and VIB was attributed by Maxted to the presence of unshared electron pairs which facilitated the chemisorption process. Catalyst poisons containing toxic metals were extensively investigated. It was found that the toxicity of the heavy metals was associated with all 5d electron orbitals being occupied by electron pairs or containing at least one electron in the d orbital. The most well known example of an unsaturated (multiple bonds) compound that causes poisoning is carbon monoxide. It should be emphasized that the toxicity of carbon monoxide is lost if the degree of unsaturation is reduced. Thus carbon monoxide when oxidized to carbon dioxide loses its poisoning effect.

An interesting aspect of Maxted's work that is often overlooked is his study of detoxification of catalysts. In Maxted's work this essentially consisted of washing the catalyst with a detoxifying agent. Although the use of liquid reagents would not be desirable in commercial practice, application of some of these treatments in the vapor phase might prove effective and would present an alternative to discarding the catalyst and reprocessing it to manufacture a new catalyst.

2.2 Technical Paper

2.2.1 Effect of Sulfur on Noble Metal Automotive Catalysts

Noble metals have been used since 1975 in the automotive exhaust catalysts to control hydrocarbon and carbon monoxide emissions. Small amounts of SO₂ (10 to 60 ppm) present in the exhaust gas are known to poison noble metal catalysts even though the poisoning is considerably less severe than base metal catalyst poisoning (Shelef, et al., 1978). Although the mechanism for the poisoning of noble metal catalysts is not clear (Summers, et al., 1979), it has been suggested that the severe poisoning of the base metal catalysts is due to the formation of surface sulfate on the base metal oxide, which decomposes in the temperature range of 500-700°C (Yao, et al., 1975). This is one of the important reasons why noble metals, notwithstanding their cost and scarcity, are the materials of choice for practical use.

The effect of gasoline sulfur level on emission performance is one variable under study in the Auto/Oil Air Improvement Research Program (AOAIRP, 1990). The maximum sulfur content in U.S. unleaded gasoline is limited to 1000 ppm by ASTM standards (SSAG, 1980). The Auto/Oil results examining the effect of fuel sulfur content show that lowering the fuel sulfur level from 466 ppm to 49 ppm results in an improvement of 16% HC, 13% CO, and 9% NO_x emission (Benson, et al., 1991).

The presence of organosulfur compounds in gasoline has led to numerous emission-related problems since automotive catalysts were first introduced in 1974. First, it was noted that cars equipped with catalytic converters exhibit increased emissions of "particulate" (Pierson, et al., 1974). This was quickly traced to the presence of sulfuric acid mist in the exhaust of vehicle equipped with platinum-containing oxidation catalysts which operate with a large excess of air. In retrospect, this should hardly have been surprising since at temperature of 300 to 600°C, with a large excess of oxygen, platinum was known to be an active catalyst for the oxidation of SO₂ to SO₃. In turn, the SO₃ is hydrated by the abundant water vapor in the exhaust to sulfuric acid mist. Most sulfur

emissions, whatever their origin, are gradually oxidized in the atmosphere, to the hexavalent state and contribute to what is known as "acid rain". The contribution of sulfur derived from automotive traffic is minor compared to that from power-generating facilities (Pierson, et al., 1974). Upon the introduction of catalyst-equipped vehicles, some cars exhibited emissions of offensive H₂S (Barnes, et al., 1975). The problem of H₂S formation that arose during the last half of the 1980s with the introduction of the first generation of high-tech three-way catalysts could not be solved so easily. This H₂S emission problem was associated with the storage and release properties of sulfur by the high level of cerium oxide (Henk, et al., 1987) that these catalysts contained. In the U.S., H₂S scavengers (e.g., nickel oxide) were incorporated into catalyst formulations in an attempt to control H₂S emissions during certain modes of vehicle operation (Rieck, et al., 1989).

Sulfur poisoning of noble metal-containing three-way catalysts is primarily associated with the deactivation of Pt or Pd. Little effect has been found over Rh, especially for NO conversions (Summers, et al., 1979). Several studies have shown even then that SO₂ is a temporary poison for Pt/Rh catalysts in automotive exhaust (Gandhi, et al., 1978). The introduction of SO₂ into the exhaust instantaneously resulted in a reduction of emission performance, which is rapidly restored upon removal of SO₂ from the exhaust feed stream (Williamson, et al., 1979). While Pt and Rh appear to recover their activity rapidly upon the removal of SO₂ from the exhaust, there is some concern that the activity of Pd-containing catalysts may not be fully recovered (Monroe, et al., 1991).

Sulfur has been found stored on noble metals as elemental sulfur and on the Al₂O₃ washcoat as sulfates and sulfites. After lean operation, sulfur is removed from the surface of the noble metal. After rich operation, the sulfur can be removed from the Al₂O₃ support (Beck, et al., 1991). Three-way catalyst washcoats containing significant quantities of CeO₂ increase the sulfur storage capacity markedly during vehicle operation due to the larger uptake on CeO₂ as compared to Al₂O₃. (Diwell, et al., 1987)

The results obtained from a flow reactor indicated that SO_2 in the feed gas enhances propane oxidation but suppresses both propylene and carbon monoxide oxidation over a $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst. These results are interpreted on the basis of the infrared data, which showed the formation of the surface sulfates on $\gamma\text{-Al}_2\text{O}_3$ after the SO_2 adsorption and oxidation, and the effects of the surface sulfates on the chemisorption properties of a $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst. It is suggested that the surface sulfates on $\gamma\text{-Al}_2\text{O}_3$ enhance C_3H_8 oxidation by increasing the dissociative C_3H_8 adsorption on Pt and suppress both CO and C_3H_6 adsorption on Pt (Gandhi, et al., 1991).

The support effect on the low temperature-catalytic combustion of propane over Pt catalyst was examined by using a series of support materials. It was revealed that the activity of Pt catalyst strongly depends on the acid-base property of the support: the activity is higher on the support having stronger acid, especially, on solid superacids. Basic supports facilitate the oxidation of Pt, resulting in lower catalytic activity. On the other hand, strongly acidic supports seem to prevent the oxidation of Pt and to enhance intrinsically the activity of Pt catalyst (Toshihiro, et al., 1991).

A study by Ansell's (Ansell, et. al 1991) indicated that during fuel-lean engine cycles, the conversion of alkanes occurs by direct oxidation on the metal sites of a three-way catalyst. The presence of SO_2 in the exhaust-gas induces the following related changes:

- The formation of sulfate species on the catalyst support;
- Enhanced conversion of higher alkanes. They interpret the response in oxidation activity as showing that the electronic properties of the precious metal are modified by the species adsorbed on the support .

There are two major theories regarding mechanism of sulfur poisoning noble metal supported catalyst: Gandhi's aluminum sulfation theory, and Somojai's sulfur induced structure-sensitive theory.

2.2.1.1 Aluminum Sulfate Formation Hypothesis The effect of sulfur dioxide on the oxidation of reactive hydrocarbons, such as alkanes has been studied by Gandhi et al (Gandhi, et al., 1991). A completely different and unexpected beneficial effect of sulfur dioxide is noted in the oxidation of a saturated hydrocarbon propane. The addition of 20 ppm SO₂ to a stream of reacting gas under overall oxidizing conditions raises the temperature of 50% conversion of carbon monoxide and propane by 40°C and 45°C, respectively, and lowers that of propane by 260°C.

According to Gandhi's study, the surface of sulfated γ -Al₂O₃ was examined by IR spectroscopy. While non-sulfated γ -Al₂O₃ does not chemisorb CO or C₃H₈, sulfated γ -Al₂O₃ strongly chemisorbs C₃H₈. Non-sulfated Pt/ γ -Al₂O₃ chemisorb CO only. Sulfated Pt/ γ -Al₂O₃ chemisorb both CO and C₃H₈.

A plausible explanation of the sharp enhanced activity for propane oxidation lies in the formation of new reaction sites for propane which did not exist in the absence of sulfur dioxide. As noted before, when exposed to a reacting gas, under oxidizing conditions, which contains 20 ppm SO₂, the alumina surface of a Pt/ γ -Al₂O₃ catalyst is sulfated. The infrared spectroscopy data suggest the formation of adsorption sites for propane oxidation associated with the sulfated alumina surface. It is plausible that the active sites for propane oxidation are located at the junction between platinum particles and the sulfated alumina. The sulfation of the support surface creates new catalytic sites responsible for this enhancement. The interaction of sulfur species with the support is in turn dependent on the composition of the noble metal catalyst. A good activity for the oxidation of SO₂ and SO₃ is a pre-requisite for the sulfation of the support.

2.2.1.2 Structure Sensitive Hypothesis According to Somorjai's theory (Somorjai, 1972), 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 form crystal planes that have lower surface free energy in the presence of the adsorbed sulfur than the

crystal planes that bond the clean solid. If this model of sulfur poisoning of platinum surfaces is correct, it indicates that the chemical surface reactions that are inhibited (or enhanced) by sulfur are sensitive to changes of the surface structure of platinum, i.e., are structure-sensitive.

Schmidt (Schmidt, et al., 1971) have reported that platinum wires used in the catalytic oxidation of ammonia have recrystallized in the presence of H_2S gas in the feed. Electron microscopy studies have shown that the wire surface that was composed of predominantly (111) crystal planes has restructured in the presence of H_2S to (100) crystal planes. It appears that adsorption of sulfur lowers the surface free energy of the (100) crystal face of platinum more than that of the (111) face and the surface free energy difference provides the driving force for surface diffusion-controlled recrystallization.

It is proposed that the addition of other impurities that lower the surface free energy of the (111) planes of face-centered cubic solid more than that of the (100) planes and that have binding energies similar to that of sulfur, could either prevent or reverse recrystallization of the platinum surface. If sulfur acts as an electron acceptor at the platinum surface in a manner similar to oxygen, it is likely that electron donors are good candidates for stabilizing the (111) crystal faces of platinum. However, if sulfur is an electron donor, electron acceptors may be used to stabilize the platinum (111) crystal face.

2.2.2 Effect of Sulfur on Environmental Catalyst Utilized by Stationary Facilities

The poisoning of metal catalysts by sulfur is an important industrial problem especially with the need to treat heavy feeds rich in sulfur compound. Sulfur poisoning of platinum-group metals has been widely studied and ever since the work of Maxted (Maxted, 1951), it is usually attributed to the occurrence of either sulfide or sulfite species.

The presence of sulfur oxides has been a major concern in many flue-gas applications. Sulfur oxides are known to deactivate a number of SCR NO_x catalysts (Wong, et. al 1986), particularly when Al_2O_3 is used as a carrier which will form alumina

sulfates. In addition, conversion of SO_2 to SO_3 by the SCR catalyst can result in equipment corrosion problem, both from the SO_3 acid gas and from the formation of ammonia sulfates.

The durability of catalyst in the presence of SO_2 is of great significance in gas turbines using fuel oils containing sulfur (Summers, 1979). The sulfur compounds in the fuel oil are converted to SO_2 at level of 40 to 150 ppm in the exhaust. The SO_2 inhibition effect on CO oxidation activity is due to strong adsorption of sulfur compounds on the Pt sites, blocking the adsorption of CO. The adsorbed sulfur compounds are removed by prolonged exposure at elevated temperatures without SO_2 present in the exhaust. That means the SO_2 inhibition effect is a reversible process. In addition to the short-term inhibition effect on CO removal activity, SO_2 may be catalytically converted to SO_3 and reacted with the carrier to form a sulfate ion. The activity loss caused by this sulfation reaction is not reversible. Catalysts are formulated to minimize SO_3 production by adding a species to suppress the activity of the metal toward this reaction without dramatically decreasing activity toward CO and HC. New washcoats have been developed that adequately disperse the active catalytic metal but are unreactive toward SO_3 such as SiO_2 and TiO_2 .

CHAPTER 3

EXPERIMENTAL DESCRIPTION

3.1 Materials

3.1.1 Catalysts

The original catalyst used to evaluate the sulfur effect was 1.5% Pt/ γ -Al₂O₃ powder. The reason why this catalyst was chosen is because platinum supported on γ -Al₂O₃ catalyst is most widely used in control of automotive exhaust and other industrial flue gases.

Based on the evaluation of sulfur effect on 1.5% Pt/ γ -Al₂O₃ which suggested that the catalyst was deactivated due to the formation of aluminum sulfate, three other catalysts, i.e., platinum supported on SiO₂, TiO₂, and ZrO₂ were tested to determine the effect of different supports on catalyst activity after sulfur poisoning.

The four catalysts mentioned above were supplied by Engelhard Corporation. Some of their physical and chemical properties are listed in Table 2.

Table 2 Physical and chemical properties of four catalysts

Catalyst	Metal Content %	BET Area m ² /g	Bulk Density g/cm ³	Metal Dispersion %
Pt/ γ -Al ₂ O ₃	1.5	48	3.7	13
Pt/SiO ₂	1.5	304	2.2	1
Pt/TiO ₂	1.5	38	4.2	166.4
Pt/ZrO ₂	1.5	93	5.6	40

The platinum metal loading of the catalysts was fixed at 1.5%, to provide a similar number of metal atoms in all cases. BET and metal dispersion data were obtained in this laboratory.

3.1.2 Experimental Accessories

The manufacturers of experimental accessories used in this study are listed as follow:

- Three heating zone ATS series 3210 furnace and 3-zone controller were purchased from Applied Test Systems Inc. $0-999^{\circ}\text{C} \pm 10^{\circ}\text{C}$, 30 AMP, 115 Volts, 60 Hz
- 1 inch I.D. quartz tubular reactor was also purchased from Kontes Glass. Refer to reactor design diagram.
- K-type thermocouples were purchased from OMEGA Engineering Inc.
- All rotameters were purchased from Cole Parmer Instrument Co. Calibrated with soap bubble meter.

3.1.3 Analytical Gases

All the analytical gases were purchased from Matheson Gas Products.

3.2 Description of Laboratory System

3.2.1 Aging System

Figure 3-1 shows the catalyst aging unit used in this study. Fresh catalyst powders were loaded into a 1 inch I.D. quartz tubular reactor in which a quartz disk was fixed with wrapped glass wool, and a cordierite monolith located upstream of the catalyst bed served as an inert heat transfer medium. The quartz tubular reactor was placed in a controlled three zone furnace. Three K-type thermocouples were used to monitor the temperature at different positions. One of them was inserted into the furnace to control the heating unit, the other two thermocouples, located about 0.5 inch away from the upstream and end of the catalyst bed respectively, were used to measure inlet and outlet catalyst temperatures. The treatment gases were 500 ppm H_2S in nitrogen and dry air. Flow of these two streams were regulated by two rotameters. Final concentration of 100 ppm of H_2S was achieved by mixing these two streams at certain ratio. Gas samples before and after the catalyst bed were delivered through sample lines to onstream GC-FPD.

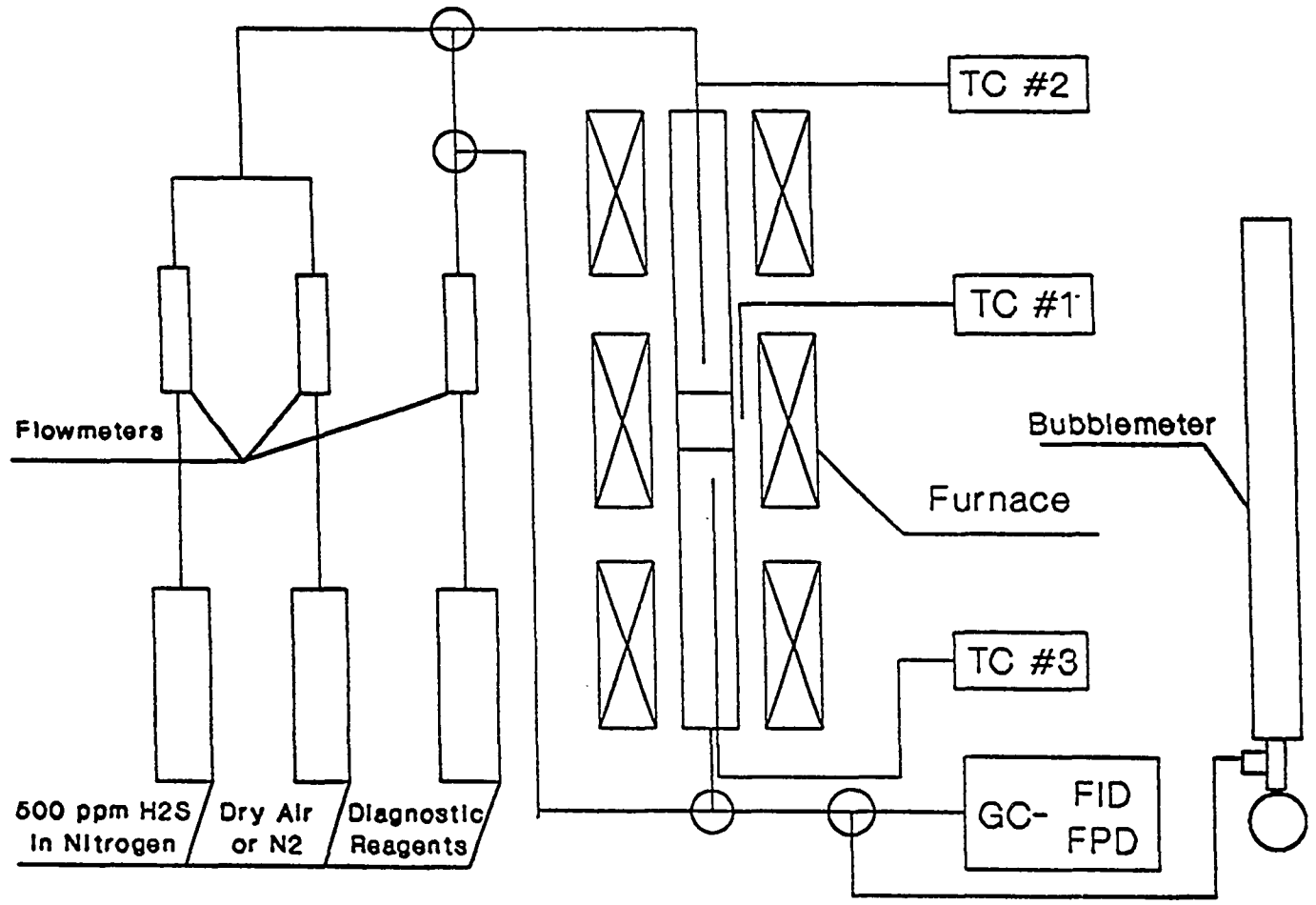


Figure 3-1 Catalyst aging and activity test system

3.2.2 Oxidation Reaction Diagnostic Test System

The oxidation reaction diagnostic test system was established to evaluate catalyst activity. As shown in Figure 3-1, small amount of test catalyst sample was diluted with $\gamma\text{-Al}_2\text{O}_3$, and loaded into a 1 inch ID quartz tubular reactor. Quartz wool was inserted into both side tubes to avoid catalyst loss. The tube was placed in a controlled furnace. Three K-type thermocouples were used. One of them was inserted into the furnace to control the heating unit, the other two thermocouples, located about 0.5 inch away from the upstream and end of the catalyst bed respectively, were used to measure inlet and outlet catalyst temperatures. The 1% diagnostic chemical in air as test gas was introduced into the reactor tube. The flow rate was varied to obtain different space velocity. Gas sample after the catalyst bed was delivered through sample line and analyzed by an online GC-FID with installed Ni-catalyst to convert CO and CO₂ into methane.

3.3 Analytical Techniques

3.3.1 Gas Chromatograph

3.3.1.1 GC-FID GC-FID with installed Ni-catalyst system was used to analyze CO, CO₂, CH₄, and C₃H₈ in this study. The function of nickel catalyst system was to hydrogenate CO and CO₂ into methane with supplied hydrogen sources.

GC type: HP 5890A Gas Chromatograph

Column: 8ft x 1/8" SS

Packing: Porapak Q, 80/100 Alltech

Detector: Flame Ionization Detector HP

Ni-catalyst system: HP Application Note 228-92

Operation Conditions:

Carrier gas: 30 ml/min Helium

Air flow rate: 400 ml/min

Hydrogen flow rate : 30 ml/min

Oven temperature:

- a. 40°C for CO and CH₄ oxidation reaction analysis
- b. 100°C for C₃H₈ oxidation reaction analysis

Detector temperature: 200°C

3.3.1.2 GC-FPD GC-FPD was used in this study to determine gas phase sulfur compounds. The FPD uses the principle that sulfur or phosphorus compounds produce chemiluminescent species when burned in an FID-type flame. The sensitivity of FPD for sulfur compounds can reach 20 picogram.

GC type: HP 5890A Gas Chromatograph

Column: 8ft x 1/8" SS

Packing: Porapak Q, 80/100 Alltech

Detector: Flame Photometric Detector

Operation Conditions

Carrier gas: 30 ml/min Helium

Air flow rate: 400 ml/min

Hydrogen flow rate: 30 ml/min

Oven temperature: 40°C

Detector temperature: 220°C

3.3.2 Altamira Instrument

Altamira instrument is a specially designed analytical device which can be used to study catalyst characteristics such as chemisorption, BET surface area, TPR, TPO, TPD, and isothermal reactions. The instrument is composed of an U type quartz tubular reactor, an electrical furnace, and a thermal conductivity detector, connected by a series of internal tubes, valves, and ports, and controlled by a computer system. The manufacturer of this instrument is Altamira Instruments, Inc. The principles of chemisorption and BET surface

area study have been given in the literature review section. A series of flow diagrams which can be used to describe each function of this instrument were shown in Figure 3-2, 3-3, 3-4, 3-5, and 3-6.

3.3.3 Thermal Gravimetric Analysis

The PERKIN ELMER TGA 7 Thermogravimetric Analyzer is a computer controlled laboratory instrument. With the DEC station Personal Workstation, the modular TGA 7 permits the measurement of weight changes in a sample material as a function of temperature or time. Under computer control, the TGA 7 is programmed from an initial to a final temperature and measures weight changes resulting from chemical reaction, adsorption, decomposition, solvent and water evolution, and oxidation in sample materials. Usually, the TGA 7 is programmed to scan a temperature range by changing at a linear rate over one to seven temperature ramps for the study of these transitions.

The TGA 7 is made up of two major components: a sensitive ultra-microbalance and a furnace element.

3.3.4 Infrared Spectroscopy

The PERKIN ELMER Infrared Spectrophotometer model 1310 was used to identify sulfation of metal oxide support materials. 1310 IR spectrophotometer is automatic-recording, double-beam, optical null instruments which features microprocessor-controlled abscissa functions.

The monochromator/photometer and electronics compartment houses the grating monochromator, the detector, and the associated electronics. The source compartment contains the source, the power supply and the fuses. Infrared energy, from a source selected for its emission characteristics in the infrared frequency region, is split into two beams, a sample beam and a reference beam. Both pass through the sample area. The intensities of the two beams at any frequency are compared by the Photometric system.

When the intensity of the sample beam changes, an electrical signal is generated which is proportional to the difference in optical energy between the sample and reference beams. The abscissa range of this IR instrument is 4000-600 cm^{-1} .

3.4 Experimental Procedures

3.4.1 Aging Experiments

3.4.1.1 Platinum Supported on $\gamma\text{-Al}_2\text{O}_3$ Catalyst

I. Aged in Dry Air

As described previously, 2 grams fresh Pt/ $\gamma\text{-Al}_2\text{O}_3$ powder catalyst was loaded into a quartz tubular reactor. The reactor was then placed in a three heating zone furnace. Two gas streams, 500 ppm H_2S in nitrogen and dry air, controlled by two separate flowmeters, were then introduced into the reactor, and the concentration of H_2S was controlled within 100 ± 5 ppm range. The total flow rate was controlled at 300 ml/min. The concentration of H_2S was calculated as follow:

60 ml/min (500 ppm H_2S in nitrogen) + 240 ml/min (dry air) = 300 ml/min (100 ppm H_2S)

The treatment temperature was set at 400°C. The effluent gas after the catalyst bed was analyzed by an online GC-FPD.

II. Aged in Nitrogen

The aging procedures of Pt/ $\gamma\text{-Al}_2\text{O}_3$ in nitrogen are the same as above. The only difference is that the aging atmosphere is nitrogen instead of dry air.

3.4.1.2 Platinum Supported on TiO_2 , ZrO_2 , and SiO_2 Catalysts All of these three catalysts were aged in air with 100 ppm H_2S . The aging procedures are the same as the Pt/ $\gamma\text{-Al}_2\text{O}_3$ aged in dry air.

3.4.2 Diagnostic Tests Procedures

Three diagnostic chemicals, methane, propane, and carbon monoxide, were used to conduct catalytic oxidation reaction in order to evaluate catalyst activity after being poisoned by sulfur compound. There are two reasons why the above three chemicals are chosen as model system representative. First of all, both methane and propane are hydrocarbons which can be used to represent automotive exhaust. Based on the same reason, we also chose carbon monoxide. Secondly, methane compared to other alkanes is the most refractory molecule, i.e., it is the most difficult molecule to combust, and propane and carbon monoxide are relatively easy to oxidize catalytically. By comparison, the catalyst activity can be evaluated more precisely. The concentrations of these three diagnostic chemicals are all 1% balanced in dry air.

As shown in Figure 3-1, certain quantities of catalysts and $\gamma\text{-Al}_2\text{O}_3$ which was used as a dilute were loaded into a tubular quartz reactor. The tube was placed in a temperature controlled furnace. The diagnostic gas was then introduced into the reactor at certain flow rate. The gas stream leaving the reactor was first analyzed at room temperature by GC-FID. As temperature increased, the effluent gases were analyzed at different temperature set points to get conversion versus temperature curves. Each diagnostic gas was tested separately.

All the experiments reported here were done using 0.05 gram catalyst plus 0.25 gram $\gamma\text{-Al}_2\text{O}_3$ and a total feedstream flow rate of 50 ml/min, for each test, yielding a space velocity of 30,000v/v/hr.

3.4.3 Catalyst Characteristics Test

Fresh and aged catalyst samples after diagnostic oxidation tests were tested for catalyst characteristics in order to understand the deactivation mechanism.

3.4.3.1 Catalyst Characterization Tests Conducted Using the Altamira Instrument

I. Chemisorption Tests

The catalyst to be tested was weighed and loaded into a quartz U-tube. The catalyst was first treated with hydrogen at 200°C to reduce catalyst into its metal state. Then pure nitrogen gas was introduced into the system to remove remaining hydrogen. The chemisorption test was conducted at room temperature through pulse injection of adsorbate gas. Hydrogen (99.8% purity) was used as adsorbate gas. The data was collected and stored on the computer used to operate the Altamira Instrument.

II. BET Surface Area Tests

BET surface area tests were conducted to evaluate catalyst support before and after aging. The catalyst was first weighed then loaded into a quartz U-tube. The operational procedures are referred to Altamira instrument manual.

III. TPR and Ammonia Titration

TPR and ammonia titration were conducted to evaluate changes in support acid strength, oxygen content and feasibility of sulfur removal. The operational procedures are referred to Altamira instrument manual.

3.4.3.2 Thermal Gravimetric Analysis The TGA tests were conducted to study the catalyst weight change with changing temperature. As shown in Figure 3-7, empty sample pan was first weighed to get zero point reading, then 6-10 mg of catalyst was loaded into the sample pan, and after the reading become stable, the initial weight was recorded. The next step was to set the desirable temperature program, and then start the experiment. During the experiment, flow of adsorbate or reactant gas was added at required temperature in order to study the adsorption effect with changing temperature. The procedure developed for conducting these tests was to heat the catalyst sample to a desirable temperature, wait until percentage weight reading stabilized, then introduce desired adsorbate or reactant gas into the furnace at the required temperature. Finally, a

weight percentage versus temperature curve was obtained. The whole system was controlled by a computer with installed UNIX operational system. The description of how to operate the computer system is referred to 7 Series/UNIX TGA 7 users manual (PE TGA).

3.4.3.3 Infrared Spectroscopy The IR technique was used to identify the formation of sulfate which was formed during the reaction between sulfur compound (H_2S) and platinum supported on various metal oxide catalysts. The fresh catalyst or aged catalyst was weighed and mixed with a weighed amount of KBr. The well mixed sample was put into a pellet press and pressed using Carver Laboratory press at 8 metric ton into a very thin and firm round shape pellet. Both fresh and aged catalyst pellets were fixed on the sample holders. The sample holder with fresh catalyst pellet on it was put in front of reference light beams. The aged catalyst one was put in front of sample light beams. The scan range is $4000-600\text{ cm}^{-1}$. All the tests reported here were done using 5 mg of catalyst and 95 mg of pure KBr.

3.4.4 Catalyst Regeneration

3.4.4.1 Regeneration of 1.5% Pt/ γ - Al_2O_3 Catalyst Aged by H_2S in Air at 400°C As shown in Figure 3-1, 0.05 gram of aged catalyst was mixed with 0.25 gram γ - Al_2O_3 and loaded into a tubular quartz reactor. Glass wool was inserted into both sides of tubes. The reactor tube was placed in an electrical furnace. The steps of catalyst regeneration are as follows:

- Raise furnace temperature to 300°C
- Introduce pure hydrogen at 300°C for 2 hours
- Cool furnace down to room temperature with hydrogen flow

3.4.4.2 Regeneration of 1.5% Pt/ γ -Al₂O₃ Aged by H₂S in Nitrogen at 400°C

The initial steps are the same as described above. The steps of catalyst regeneration are as follows:

- Raise furnace temperature to 300°C
- Introduce pure hydrogen at 300°C for 2 hours
- Cool furnace down to room temperature with hydrogen flow

3.5 Experimental Procedures: Phosphorus Effect

3.5.1 Materials

Only platinum supported on γ -Al₂O₃ catalyst was used to evaluate phosphorus effect on the catalyst. Tributyl phosphate was used as the poisoning reagent as representative of phosphorus compounds. Catalyst activity before and after poisoning were evaluated using diagnostic oxidation of methane, carbon monoxide, and propane.

Altamira instrument and GC-FID were used in this part of study. The description of these devices has been given previously.

3.5.2 Aging Procedures

The aging system is shown in Figure 3-8. 0.05 gram 1.5% Pt/ γ -Al₂O₃ catalyst was mixed with 0.25 gram γ -Al₂O₃ and loaded into a tubular quartz reactor. The reactor was placed in an electrical furnace. The aging steps are listed as follow:

- Introduce dry air into reactor
- Raise furnace temperature to 400°C
- Inject liquid tributyl phosphate into reactor with air at 400°C
- Total volume of TPB injected was 1 ml, this was accomplished in 20 injections of 50 μ l each..

Similar aging experiment was conducted at 550°C.

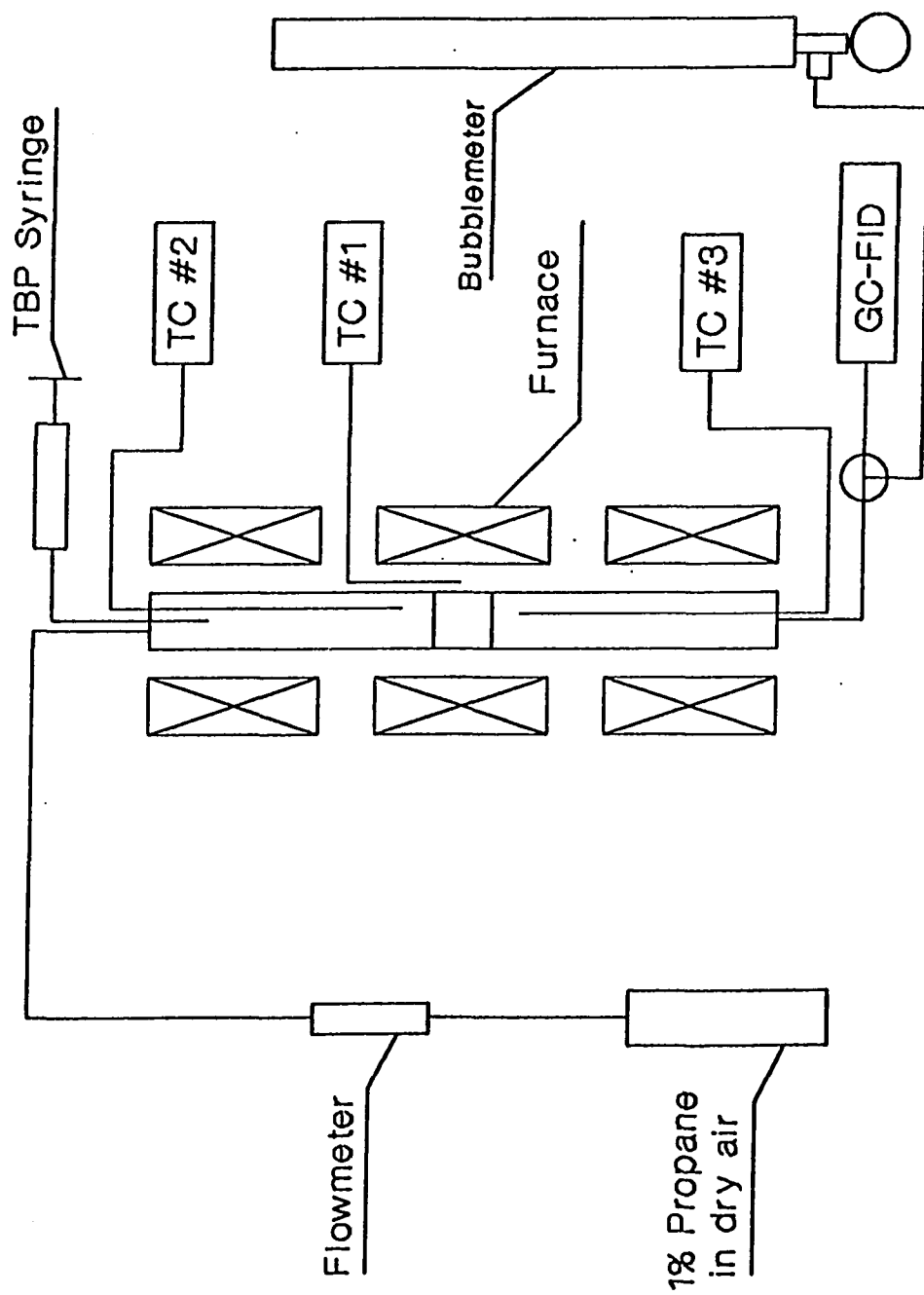


Figure 3-8 Catalyst aging system: TBP pulse injection

3.5.3 Diagnostic Oxidation Test Procedures

The diagnostic oxidation test system is shown in Figure 3-1. Three diagnostic gases methane, propane, and carbon monoxide were used to evaluate activity. The steps of conducting these tests are described in section 3.4.2. Fresh catalysts as well as aged at 400 °C and 550°C were tested.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Background Tests

4.1.1 Activity Tests of Fresh Catalysts

Activity tests were conducted to monitor catalysts activity changes. Four fresh catalysts, consisting of 1.5% platinum supported on γ -Al₂O₃, SiO₂, TiO₂, and ZrO₂ catalysts, were tested to determine the oxidation activity with the following these diagnostic gases, 1% methane, propane, and carbon monoxide in dry air. The tests results were used for comparison of activity before and after sulfur poisoning. The reasons why these four catalysts were selected, and methane, propane, and carbon monoxide were chosen as diagnostic chemicals to conduct oxidation test have been given in Chapter 3.

4.1.1.1 Methane Oxidation Percentage conversion as a function of temperature for methane oxidation over four 1.5% platinum catalysts supported on different substrate oxides is shown in Figure 4-1 (Append. B). The results indicate that catalyst activities vary sharply among the four catalysts. Platinum supported on TiO₂ catalyst is far more active than platinum supported on SiO₂ catalysts. The activities of four catalysts for methane oxidation follow the trend:

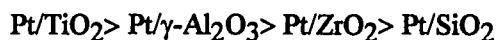


Table 4-1 summarized the trend for conversion of methane due to oxidation.

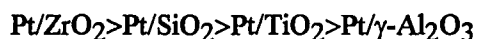
Table 4-1 1% methane oxidation over four catalysts at 400°C

Catalyst	Pt/TiO ₂	Pt/ γ -Al ₂ O ₃	Pt/ZrO ₂	Pt/SiO ₂
Conversion %	92.5	78	24.5	12

Note: Conversion (%) of CH₄ to CO₂ and H₂O at 400°C over four catalysts
0.05g catalyst was used, flow rate = 50 ml/min, SV = 30,000v/v/h

The reasons that the same platinum loading on different supports show different activities can be explained as, (1) platinum dispersion on those supports are different, (2) support may effect the adsorption of methane on the catalyst, and (3) catalyst preparation effect.

4.1.1.2 Propane Oxidation In separate experiments, 1% propane was oxidized in dry air using the four different catalysts. Similarly, percentage conversion as a function of temperature for propane oxidation over four catalysts is plotted in Figure 4-2 (Append. B). In this case, the oxidation activity of four catalysts follow order:



The differences in activity between them are not as much as in methane oxidation. The quantitative results are presented in Table 4-2.

Table 4-2 1% propane oxidation over four catalysts at 250°C

Catalyst	Pt/ZrO ₂	Pt/SiO ₂	Pt/TiO ₂	Pt/γ-Al ₂ O ₃
Conversion %	58.4	51.9	25.6	14.1

Note: Conversion (%) of C₃H₈ to CO₂ and H₂O at 250°C over four catalysts
0.05g catalyst, flow rate = 50 ml/min, SV = 30,000v/v/h

The results indicate that all four catalysts have a higher activity for propane oxidation than for methane. These results are not surprising since methane is known to be the most difficult hydrocarbon to oxidize. The differences in propane oxidation activity among the four catalysts can also be explained by the same reasons as these used for methane oxidation.

4.1.1.3 Carbon Monoxide Oxidation Carbon monoxide conversion for the four catalysts can reach 100% at a temperature as low as 190°C and at 30,000 v/v/hr space

velocity. The conversion curves are shown in Figure 4-3 (Append. B). It can be seen that platinum, supported on TiO₂ catalyst, is the most active of the four tested. It can completely convert carbon monoxide into carbon dioxide at only 120°C. The order of oxidation activity among the four catalysts in this case is follows the following order:

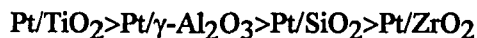


Table 4-3 shows carbon monoxide conversion for the four catalysts at 120°C.

Table 4-3 1% carbon monoxide oxidation over four catalyst at 120°C

Catalyst	Pt/TiO ₂	Pt/ γ -Al ₂ O ₃	Pt/SiO ₂	Pt/ZrO ₂
Conversion %	100	14.1	4.9	2.7

Note: Conversion (%) of CO to CO₂ at 120°C over four catalysts
0.05g catalyst, flow rate = 50 ml/min, SV = 30,000v/v/hr

4.1.1.4 Summary The results shown above indicate that the temperature required for four catalysts to completely oxidize three selected diagnostic gases i.e., methane, propane, and carbon monoxide are in the order: methane>propane>carbon monoxide. Another finding from the results is that the order of activity for the four catalysts are totally different for methane, propane, and carbon monoxide oxidation. There are three possible reasons for these, (1) catalyst preparation effects, (2) support material effects, both effects may change the adsorption efficiency of the diagnostic gases on the catalyst, and (3) platinum dispersion on these supports are different. Since one of our purposes is to study the sulfur effect on different supported catalysts, we are interested in activity changes before and after sulfur poisoning. The difference in activity between four catalysts is not the subject of this study.

4.1.2 Catalyst Characteristic Studies

4.1.2.1 BET Surface Area 0.05g of each catalysts were used to conduct BET surface area measurement. The procedures have been described in chapter 3. The experimental results are calculated using the computer integrated system of the Altamira are given in Table 4-4.

Table 4-4 BET surface area of four catalysts

Catalyst	Pt/ γ -Al ₂ O ₃	Pt/TiO ₂	Pt/ZrO ₂	Pt/SiO ₂
BET Surface Area m ² /g	48	38	93	304

Note: 0.05 gram catalyst was used to conduct each test

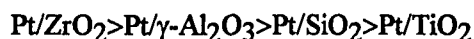
4.1.2.2 Chemisorption Studies Pulse chemisorption was used to measure catalyst metal dispersion. The procedures have been given in Chapter 3. The tests results are shown in Table 4-5.

Table 4-5 Metal dispersion of four catalysts

Catalyst	Pt/ γ -Al ₂ O ₃	Pt/TiO ₂	Pt/ZrO ₂	Pt/SiO ₂
Metal Dispersion %	13	166.4	40	1

According to the definition, metal dispersion or "percentage exposure" should be equal to the ratio of the number of surface metal atoms in a catalyst to the total number present. However, the chemisorption test results show that the metal dispersion of Pt/TiO₂ catalyst is higher than 100%. Does that mean anything? To answer this, one more test was conducted using pure TiO₂ to measure the hydrogen uptake. By subtracting Pt/TiO₂ catalyst hydrogen uptake during pulse chemisorption with hydrogen uptake by pure TiO₂, Pt/TiO₂ catalyst metal dispersion was recalculated. The real dispersion should be 56.4. Chemisorption of other three supports have not been tested.

4.1.2.3 Ammonia Titration Ammonia titration tests were conducted to determine catalyst acidity. Platinum supported on γ -Al₂O₃, TiO₂, ZrO₂, and SiO₂ catalysts were titrated. The results are shown in Figure 4-4, 4-5, 4-6, and 4-7 (Append. B). It was found that acid strength of platinum supported on different substrates catalysts is in the order:



According to Toshihiro's work (Toshihiro, 1994), support effect on the low temperature-catalytic combustion of propane over Pt catalyst was examined using a series of support materials. It was found that the activity of the Pt catalyst strongly depends on the acid-base property of the support. The activity is highest for the support having highest acidity. In contrast, the results of our study shown that catalyst activity for propane oxidation is not proportional to its acidity.

4.2 Aging Experiments

4.2.1 H₂S Tests

Two series of H₂S tests were conducted, one in the air, another in nitrogen, in order to determine what sulfur compounds are formed at different oxidizing conditions. The results are used to determine aging temperature.

4.2.1.1 H₂S Oxidation over 1.5% Pt/ γ -Al₂O₃ Catalyst H₂S oxidation was conducted to determine aging temperature. A mixture of 100 ppm H₂S in air was oxidized over 1.5% Pt/ γ -Al₂O₃ catalyst at 14,000 v/v/hr space velocity. Both Table 4-6 and Figure 4-8 shows oxidation reaction product distribution. It is found that H₂S was first converted to SO₂ at temperature between 25 - 220°C, then SO₂ was further oxidized to SO₃ at temperature between 220 - 340°C, and finally converted to Al₂(SO₄)₃ at 420°C.

Table 4-6 Products distribution of H₂S oxidation over 1.5% Pt/ γ -Al₂O₃

Temperature °C	H ₂ S %	SO ₂ %	SO ₃ %	Al ₂ (SO ₄) ₃ %
25	100	0	0	0
100	84	16	0	0
150	63	37	0	0
220	0	92	8	0
280	0	61	39	0
340	0	0	100	0
380	0	0	44	56
420	0	0	0	100

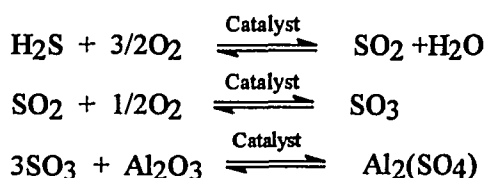
Notes: 100 ppm H₂S oxidation over 1.5% Pt/ γ -Al₂O₃ catalyst

Space velocity = 14,000v/v/hr

H₂S, SO₂ and SO₃ were analyzed by GC-FPD

Al₂(SO₄)₃ was not detected.

H₂S oxidation reaction steps over platinum catalyst can be interpreted as following:



4.2.1.2 H₂S Test in Nitrogen Same experiment was conducted with a mixture of H₂S in nitrogen instead of dry air. Table 4-7 shows the remaining H₂S at different temperature. It is assumed that H₂S has been converted to platinum sulfide. Only color change has been observed. No further test has been done to confirm this.

Table 4-7 H₂S remained at different temperature

H ₂ S Remained %	92.3	77.4	70	58.4	33.2
Temperature °C	100	200	250	300	400

Notes: 100 ppm H₂S in nitrogen

Space velocity = 14,000v/v/hr

H₂S was detected by GC-FPD

H₂S is the only gas phase sulfur compound being detected.

4.2.2 Aging Experiments

Catalysts were aged with H_2S at different temperatures and in different atmospheres. The purposes of doing this is to study temperature and atmosphere effect on catalyst deactivation due to the present of sulfur compounds.

4.2.2.1 Platinum Supported on $\gamma-Al_2O_3$ Catalyst Aging experiments were conducted under two different atmospheres, i.e., dry air and nitrogen, in order to simulate oxidizing and inert conditions. All the treatments were conducted at a space velocity of 14,000 v/v/hr.

I. Catalysts Aged in Dry Air with 100 ppm H_2S at 200 and 400 °C

Two Pt/ $\gamma-Al_2O_3$ catalyst samples were aged with H_2S in dry air for 24 hours at different temperatures. The purpose was to study the catalyst deactivation mechanism due to the effect of the different sulfur compounds which are produced at different temperatures. Each sample contained 2 gram fresh Pt/ $\gamma-Al_2O_3$ catalyst. Aging temperature were 200 and 400°C, which were determined based on previous H_2S oxidation test results. The morphology of aged catalysts were the same as fresh catalysts. Aged catalysts were collected and used for diagnostic oxidation tests and catalyst characteristics studies.

II. Catalyst Aged in Nitrogen with 100 ppm H_2S

Pt/ $\gamma-Al_2O_3$ catalysts were also aged by H_2S in nitrogen atmosphere at 200°C and 400°C, and 14,000 v/v/hr space velocity for 24 hours. The aged catalysts show a darker color than fresh catalyst, probably due to the formation of platinum sulfide.

4.2.2.2 Pt/TiO₂, Pt/ZrO₂, and Pt/SiO₂ Catalysts Based on the results of H_2S oxidation over Pt/ $\gamma-Al_2O_3$, all three catalysts were aged with H_2S in dry air at 400°C and 14,000 v/v/hr space velocity. The morphology of aged catalysts were not changed.

4.2.3 Tributyl Phosphate Aged Pt/ γ -Al₂O₃ Catalysts

TBP aging tests were conducted at 400 and 550°C over 0.05 gram Pt/ γ -Al₂O₃ catalysts to study phosphorus effects on platinum catalyst. The aging experiment procedures have been described in section 3.5.2. Total amount of 1 ml of TBP were injected. After aging, diagnostic oxidation of methane, propane, and carbon monoxide were conducted to evaluate catalyst activity changes.

4.3 H₂S Aged 1.5% Pt/ γ -Al₂O₃ Catalysts

4.3.1 Diagnostic Oxidation Tests

4.3.1.1 Catalysts Aged in Dry Air

I. 1.5% Pt/ γ -Al₂O₃ Catalyst Aged by H₂S at 200 °C

According to the results of H₂S oxidation, at this temperature, nearly 100% of H₂S has been converted to SO₂ (92%) and SO₃ (8%), although no Al₂(SO₄)₃ has been formed. Two diagnostic oxidation tests have been conducted.

(1) Carbon Monoxide Oxidation

As showed in Figure 4-9 (Append. B), the catalyst was severely deactivated for carbon monoxide oxidation. Temperature required to reach 50% conversion of CO are 150°C for fresh catalyst, and 175°C for aged catalyst. The results also indicate that conversion versus temperature curve shifted to a higher temperature with almost the same slope. This suggested that deactivation mechanism is due to the loss of active sites for CO oxidation caused by strong adsorption of sulfur compounds (SO_x) on the Pt sites, decreasing the adsorption of CO.

(2) Propane Oxidation

Percentage conversion as a function of temperature for propane oxidation over fresh and aged catalysts is shown in Figure 4-10 (Append. B). It can be seen that activity of aged catalyst for propane oxidation is strongly promoted. Temperature at 50% conversion T₅₀ decreased from 280°C to 235°C after aging. The conversion curves shifted to lower

temperature with the same slope (same activation energy) which suggested that new active sites are formed for propane oxidation due to the introduction of sulfur. It is believed that SO_2 are catalytically oxidized during propane oxidation to SO_3 and reacted with the carrier to form a sulfate species which somehow provided new active sites for propane oxidation. We will discuss this later.

II. 1.5% Pt/ γ - Al_2O_3 Catalyst Aged by H_2S at 400 °C

According to the results of H_2S oxidation over 1.5% Pt/ γ - Al_2O_3 , most of the H_2S was converted to $\text{Al}_2(\text{SO}_4)_3$ at 400°C. Three diagnostic oxidation tests have been conducted to monitor catalyst activity changes.

(1) Methane Oxidation

Both fresh and aged catalysts were used to conduct methane oxidation. The conversion curves are plotted in Figure 4-11 (Append. B). The results indicate that the catalyst activity is moderately inhibited. The conversion versus temperature curve shifted to higher temperature with a lower slope which suggest that pores are partially blocked due to the formation of $\text{Al}_2(\text{SO}_4)_3$, resulting in increased diffusion resistance.

(2) Carbon Monoxide Oxidation

The comparison of activity for carbon monoxide oxidation before and after sulfur treatment is shown in Figure 4-12 (Append. B). The catalyst aged at 400°C shows the same extent of deactivation for CO oxidation as catalyst aged at 200°C, with different deactivation mechanism. It is believed that deactivation mechanism in this case is the formation of aluminum sulfate. Figure 4-13 (Append. B) shows the activity difference between fresh catalyst, catalyst aged at 400°C, and catalyst aged at 200°C.

(3) Propane Oxidation

Percentage conversion as a function of temperature for propane oxidation over fresh and aged catalyst is shown in Figure 4-14 (Append. B). Again, propane oxidation is strongly promoted over catalyst aged at 400°C but not as much as catalyst aged at 200°C. It is believed that enhancement of activity of catalyst aged at 400°C for propane oxidation is

also due to the formation of $\text{Al}_2(\text{SO}_4)_3$. The reason why catalyst aged at 200°C is more active than catalyst aged at 400°C is not clear. The activity for propane oxidation between fresh catalyst, catalyst aged at 400°C, and catalyst aged at 200°C is compared in Figure 4-15 (Append. B).

4.3.1.2 Catalysts Aged in Nitrogen

I. 1.5% Pt/ γ - Al_2O_3 Catalyst Aged by H_2S at 200°C

As shown in Table 4-7, at 200°C in nitrogen, 77.4% H_2S still remained. Two diagnostic oxidation tests were conducted to evaluate catalyst activities before and after aging.

(1) Carbon Monoxide Oxidation

As show in Figure 4-16 (Append. B), CO oxidation activity of aged catalyst decreased severely compared to fresh catalyst. T_{50} that is temperature required to obtain 50% conversion, is 150°C for fresh catalyst, and 178°C for aged catalyst. The results also show that conversion versus temperature curve shift to higher temperature with similar slope which suggest that deactivation mechanism is due to the loss of active sites responsible for CO oxidation. It is believed that during CO oxidation, sulfur compound interacted with catalyst was catalytically oxidized to SO_2 which strongly adsorbed on Pt sites and inhibited CO oxidation.

(2) Propane Oxidation

Percentage conversion as a function of temperature curves for propane oxidation over fresh and aged catalysts is shown in Figure 4-17 (Append. B). Catalyst activity has been enhanced after aging. According to the comparison of activity in Figure 4-17, the activity of aged catalyst for propane oxidation was strongly promoted before light-off T_{30} then slightly enhanced with increasing temperature, which suggest that new active sites for propane oxidation are formed due to the sulfur effect, in the way, sulfur compound interacted with catalyst was first catalytically oxidized to SO_2 then further oxidized to

SO₃ and finally reacted with support material to form aluminum sulfate which provide new active sites for propane oxidation.

II. 1.5% Pt/γ-Al₂O₃ Catalyst Aged by H₂S at 400 °C

According to the results of H₂S treatment in nitrogen at different temperatures which are shown in Table 4-7, more than 65% H₂S disappeared. Based on the color changes of catalyst aged by H₂S in nitrogen at 400°C for 24 hours, it is suspect that H₂S was converted to sulfide.

(1) Carbon Monoxide Oxidation

Both fresh and aged catalysts were used to conduct carbon monoxide oxidation, the comparison of activity is shown in Figure 4-18 (Append. B). The results indicate that activity of aged catalyst decreased severely. The conversion versus temperature curve of aged catalyst shift to higher temperature compare to fresh catalyst, with same slope. It is believed that deactivation mechanism in this case is the same as catalyst aged in nitrogen at 200°C.

(2) Propane Oxidation

The conversion versus temperature curves of both fresh and aged catalysts are compared in Figure 4-19 (Append. B). According to the results, activity of aged catalyst for propane oxidation were enhanced slightly before light-off, then strongly enhanced with increasing temperature. It is believed that sulfur compound interacted with catalyst was first oxidized to SO₂ then further oxidized to SO₃ and finally reacted with alumina to form aluminum sulfate which provide new active sites for propane oxidation..

4.3.2 Catalyst Characteristic Tests

4.3.2.1 BET Surface Area Measurements The BET surface area of fresh catalyst and catalysts aged under different conditions were measured. The test results are listed in Table 4-8.

Table 4-8 BET surface area of fresh and aged catalysts

Catalyst	Fresh	Aged in Air at 400°C	Aged in Nitrogen at 400°C
BET Surface Area m ³ /g	48	40	42

The results indicate that surface area of catalyst aged by H₂S in both air and nitrogen decreased slightly compare to fresh catalyst. That means the support material, i.e. γ -Al₂O₃, which provides a large surface area, was slightly affected by sulfur compounds. This is because the amount of sulfur compound which was introduced during aging process, as calculated below, is relatively small compare to 2 gram catalyst used.

$$[100 \text{ ppm H}_2\text{S} * 10^{-6}] * 300 \text{ ml/min} * 60 \text{ min/hour} * 24 \text{ hour} = 4.32 \text{ ml H}_2\text{S}$$

4.3.2.2 Pulse Chemisorption Tests Pulse chemisorption testes were conducted to study catalyst dispersion. Both fresh catalyst and catalysts aged under different aging conditions were tested. The results are listed in Table 4-9.

Table 4-9 Metal dispersion of fresh and aged catalysts

Catalyst	Fresh	Aged in Air at 400°C	Aged in Nitrogen at 400°C
Percentage Dispersion %	13	11	10

It can be seen that only small decrease in catalyst dispersion has been caused due to the sulfur compound effect. In other words, the capability of hydrogen chemisorption of platinum catalyst has only slightly been affected by sulfur compound.

4.3.2.3 IR Tests The IR tests were conducted by comparing the spectra of fresh and aged catalysts, by putting fresh catalyst sample pellet in front of reference light beam and aged catalyst sample pellet in front sample light beam (see chapter 3). The results are shown in Figure 4-20 and 4-21 (Append. B). It can be noticed that the spectra of catalyst aged by

H₂S in air at 400°C shows a broad adsorption band at 1100 cm⁻¹. According to "*Infrared Spectra of Inorganic Compounds*"(Nyquist, 1971), aluminum sulfate also give a broad adsorption band at 1100 cm⁻¹, as shown in Figure 4-22 (Append. B). On the other hand, spectra of catalyst aged in nitrogen at 400°C shows no adsorption band at all. According to the same reference, sulfide group should give an adsorption band at below 400 cm⁻¹, since the abscissa range of this IR instrument is 4000-600 cm⁻¹, the formation of sulfide could not be detected.

4.3.2.4 TGA Tests TGA tests were conducted to study the interaction between H₂S and catalyst at different temperatures, and also in different atmospheres. The procedures have been described previously in Chapter 3. Tests were conducted at three temperatures, 100, 200, and 400°C, and in both air and nitrogen atmospheres. The results are shown in Figure 4-23, 4-24, 4-25, 4-26 and 4-27 (Append. B). It was found that (1) the weight gain due to the introduction of H₂S indicate sulfur compound indeed interact with catalysts in all cases, (2) the amount of weight gain caused by sulfur compound increased with increasing temperature in both air and nitrogen atmosphere, (3) According to Figure 4-25 and 4-26, amount of weight gain caused by sulfur compound in both air and nitrogen are almost the same at same temperature, and (4) According to Figure 4-25 and 4-27, the percentage weight gain of fresh catalyst caused by sulfur compound in air at 400°C is 3.031 wt%. Under the same conditions, weight gain of pure γ -Al₂O₃ is only 0.993 wt%.

Sulfur compound effects on catalyst at same temperature in both air and nitrogen were compared in Figure 4-28, 4-29 and 4-30 (Append. B). It can be seen that catalyst tested in nitrogen lost more weight than catalyst tested in air during heating step, but the weight gain caused by sulfur compound are almost the same.

Another two experiments were conducted to determine the possibility of removing sulfur compound interacted with catalyst through increasing temperature. As shown in

Figure 4-31 (Append. B), the first type experiment was conducted according to the following steps:

- Load 9.021 mg of fresh 1.5% Pt/ γ -Al₂O₃ catalyst in sample pan
- Heat sample from room temperature to 400°C
- wait until percentage weight reading stable
- Introduce H₂S in air into system for 30 minutes
- Stop H₂S input and wait for 15 minutes
- Heat sample from 400°C to 500°C.

The second type experiment was conducted according to the following steps:

- Load 8.427 mg of fresh 1.5% Pt/ γ -Al₂O₃ catalyst in sample pan
- Heat sample from room temperature to 400°C
- Wait until percentage weight reading stabilized
- Increase temperature from 400°C to 500°C.

The results in Figure 4-32 and 4-33 (Append. B) indicate that the weight loss (Δy) of catalyst tested with H₂S due to temperature increase from 400 to 500°C is little compare to catalyst tested without H₂S, which means that sulfur compound interacted with catalyst can not be removed by increasing temperature. In other words, the results suggested that the interaction between sulfur compound and catalyst is very strong.

4.3.2.5 Ammonia Titration Ammonia titration is a very popular technique used to evaluate catalyst acidity. As shown in Figure 4-34 (Append. B), two important messages were obtained using this method:

- Acid strength correspond to the temperature at which maximum ammonia desorption
- Number of acidic sites correspond to the amount of ammonia desorbed

According to catalysis chemistry, alumina formed at temperatures of about 300°C or more are not hydrated but contain small amounts of water of occlusion, which is

gradually evolved on heating to higher temperatures. The conversion of OH groups to water on heating leaves behind a structure with exposed aluminum atoms that behaves like a Lewis acid. In addition, a Bronsted-type acidity exists, stemming from the OH groups.

In this study, ammonia titration were conducted to evaluate catalyst acidity change before and after aging. The test results are shown in Figure 4-4, 4-35 and 4-36 (Append. B). The fresh catalyst titration results which is shown in Figure 4-4 indicate that both Lewis acid and Bronsted acid are existed. According to the results in Figure 4-35, catalyst aged by H₂S in air at 400°C containing only Lewis acid due to the removal of water, and the number of acidic sites has increased, which means acidity of catalyst aged by H₂S in air at 400°C has increased compare to fresh catalyst, probably due to the formation of surface sulfates on γ -Al₂O₃. On the other hand, acidity of catalyst aged by H₂S in nitrogen at 400°C shown in Figure 4-36 has decreased, only Lewis acid has been observed due to the removal of water during the aging process.

4.3.3 Catalyst Regeneration

4.3.3.1 TPR Tests of Aged Pt/ γ -Al₂O₃ Catalysts Temperature program reduction of 1.5% Pt/ γ -Al₂O₃ catalysts aged by H₂S at 400°C in both air and nitrogen were conducted, using 5% hydrogen in helium as reducing agent, to determine catalyst regeneration temperature. In order to obtain the contribution from the substrate and catalyst. TPR of fresh catalyst and pure γ -Al₂O₃ were also conducted to serve as background data. The results are shown in Figure 4-37, 4-38, 4-39 and 4-40 (Append. B).

As show in Figure 4-37, pure γ -Al₂O₃ was not reduced until temperature reached 400°C. In other words, no hydrogen uptake was observed. The TPR result of fresh catalyst in Figure 4-38 shows two hydrogen uptake peaks overlapped at 167°C and 250°C respectively which represent reduction of PtO₂ and PtO respectively.

Figure 4-39 shows the TPR of catalyst aged in air at 400°C. The results indicate that beside two hydrogen uptake peaks at 165°C and 234°C which also represent

reduction of PtO_2 and PtO , there is another hydrogen uptake peak at 342°C probably due to the removal of sulfur compound interacted with either support material or the catalyst itself.

The TPR results of catalyst aged in nitrogen at 400°C are shown in Figure 4-40. It is found that two hydrogen uptake peaks at about 165° and 240°C which represent reduction of PtO_2 and PtO disappeared probably due to the decomposition of PtO_2 and PtO during the aging process, but instead there are two new hydrogen uptake peaks which appeared at 131°C and 331°C . It is assumed that these two peaks are related to the removal of sulfur compounds interacted with the catalyst, possibly sulfide.

4.3.3.2 Diagnostic Oxidation Tests of Regenerated Catalysts According to TPR test results, 1.5% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst aged by H_2S at 400°C in both air and nitrogen were regenerated at 300°C with 100% hydrogen. The regeneration procedures have been described in Chapter 3. After the regeneration, two diagnostic oxidation, i.e. carbon monoxide and propane oxidation tests were conducted.

1 Regenerated 1.5% $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ Catalyst Aged by H_2S at 400°C in Dry Air

(1) Carbon Monoxide Oxidation

Percentage conversion as a function of temperature curves for CO oxidation over fresh, aged, and regenerated catalysts are shown in Figure 4-41 (Append. B). It is found that the regenerated catalyst partially recovered its activity. In other words, the curve of regenerated catalyst shifted back toward the curve of fresh catalyst, probably due to the removal of interacted sulfur compound.

(2) Propane Oxidation

The comparison of activity for propane oxidation over fresh, aged, and regenerated catalysts was plotted in Figure 4-42 (Append. B). The results show overlapped curves of conversion as a function of temperature of aged and regenerated catalysts. This is interpreted as the activity of aged catalyst did not change as a function of hydrogen

treatment for propane oxidation. According to TPR results, a hydrogen uptake peak, related to sulfur removal, has been observed, and also as described above, activity of aged catalyst for CO oxidation has been partially recovered. All of these suggested that, although part of sulfur compound has been removed, this had no effect on the activity of regenerated catalyst for propane oxidation. It appears that the crystal structure of platinum catalyst has been rearranged due to the introduction of sulfur, even though the sulfur compound has been removed. The platinum crystal structure remain in its rearranged form. This will be discussed later.

II Regenerated 1.5% Pt/ γ -Al₂O₃ Catalyst Aged by H₂S at 400°C in Nitrogen

(1) Carbon Monoxide Oxidation

The conversion versus temperature curves for CO oxidation over fresh, aged, and regenerated catalysts were plotted in Figure 4-43 (Append. B). The results indicate that the activity of the regenerated catalyst shifts back from aged catalyst to fresh catalyst, which means that catalyst was indeed regenerated by hydrogen, and this agrees with the results obtained from TPR tests.

(2) Propane Oxidation

Propane oxidation over fresh, aged and regenerated catalysts were conducted and plotted as conversion versus temperature curves in Figure 4-44 (Append. B). In this case, the activity of regenerated catalyst also shifts from aged catalyst back to fresh catalyst, which means 1.5% Pt/ γ -Al₂O₃ catalyst aged by H₂S in nitrogen loses its promotion effect by hydrogen treatment. In other words, sulfur compound has been removed before it forms sulfate, which can induce the rearrangement of platinum crystal structure. It can also be explained as sulfur compound existing only as sulfate can induce the rearrangement of platinum crystal structure and enhance the activity for propane oxidation.

4.3.5 Discussion

According to the activity test results described in sections 4.3.1 and 4.3.3.2, catalysts aged with H₂S at 200°C in both air and nitrogen atmospheres and catalyst aged with H₂S at 400°C in nitrogen were deactivated for CO oxidation, and promoted for propane oxidation, catalyst aged with H₂S at 400°C in air was slightly deactivated for methane oxidation, severely deactivated for CO oxidation, and enhanced for propane oxidation. All of these results suggest that catalytic activity for oxidation changed due to the pretreatment with H₂S. The activity tests of regenerated catalysts show that catalyst aged with H₂S in nitrogen at 400°C, after regeneration, recovered most of the activity for both CO oxidation and propane oxidation. The regenerated catalyst which was aged with H₂S in air at 400°C only recovered its activity for CO oxidation, since methane oxidation activity was slightly impaired and propane oxidation activity was improved and did not recover back to the original activity.

To determine the reasons that cause these changes in activity, several catalyst characteristic were studied. First, TGA tests were conducted which indicate strong interaction between catalyst and sulfur compound in both air and nitrogen. The IR tests indicate that the interaction between the catalyst and sulfur compound in air is the formation of aluminum sulfate. However, the product of the interaction between catalyst and sulfur compound in nitrogen was not determined, this was a result of not being able to obtain the spectra of sulfide groups at below 400 cm⁻¹ with our instrumentation. Furthermore, the test results of ammonia titration indicate strong increase in acidity of the catalyst aged in air, which is due to the formation of solid superacid SO₄⁻²-Al₂O₃. These results indicate that sulfate formation is a necessary step to cause activity changes in catalyst aged in air. About catalyst aged in nitrogen, it is apparent that whatever the sulfur compound that was deposited would be oxidized during the diagnostic oxidation tests, thus forming aluminum sulfate. That is the reason why this catalyst also shows enhanced activity for propane oxidation.

Another finding obtained from TPR tests and diagnostic oxidation over regenerated catalysts shows that although sulfur compounds deposited on both catalysts whether carried in air or nitrogen can be removed by hydrogen, only the activity of catalyst aged with H₂S in nitrogen do not experience the propane promotional effect because the sulfur deposited is removed before it has a chance to be oxidized. On the other hand, the activity for propane oxidation of catalyst aged with H₂S in air can not be recovered because sulfate had been formed. These results suggest that once the deposited sulfur compound reacts with alumina to form aluminum sulfate, it will permanently affect catalyst activity for propane oxidation, even after the sulfur compound has been removed. The results also suggest that activity of catalyst aged with H₂S for propane oxidation is enhanced only when aluminum sulfate is formed. These results are consistent with the observed phenomena.

The results obtained by Tai-Chiang Yu (Yu, 1995) show that PdO/ γ -Al₂O₃ catalyst after being aged with H₂S in air at 400°C was deactivated for propane oxidation. His IR test results also show the formation of aluminum sulfate and sulfite. Thus, the formation of sulfate does not enhance the activity of PdO/ γ -Al₂O₃ catalyst for propane oxidation.

Based on all the information described above, it is proposed that any deactivation mechanism of sulfur compounds on 1.5% Pt/ γ -Al₂O₃ catalyst must include the formation of aluminum sulfate. Based on Samorjai's theory (Samorjai, 1970), it appears that the activity of the aged catalyst for CO oxidation decreases, compared to fresh catalyst, due to the formation of aluminum sulfate which changes the platinum crystal structure, so that platinum crystal planes favoring CO oxidation decrease. In other words, CO oxidation over Pt/ γ -Al₂O₃ is a structure-sensitive reaction. The same crystal structure, on the other hand, enhances catalyst activity for propane oxidation over that for the fresh catalyst. Furthermore, according to Yu's results, which show that although PdO/ γ -Al₂O₃ catalyst was modified by sulfur compound due to the formation of aluminum sulfate, the aged

catalyst had lower activity for propane oxidation than fresh catalyst. This shows that aluminum sulfate formation is not the only requirement for propane oxidation enhanced activity. The other requirement is the presence of platinum. Consequently, both platinum and aluminum sulfate formation are necessary for propane oxidation activity enhancement. One can therefore postulate that activity enhancement for propane oxidation is due to the formation of new active sites for propane oxidation which are formed through sulfur induced platinum crystal structure rearrangement and located at the junction between platinum particles and sulfated alumina, so that, the platinum crystal planes favored for propane oxidation are increased. A check for this hypothesis is provided in Figure 4-45 (Append. B). In this experiment, pure aluminum sulfate was used to replace pure $\gamma\text{-Al}_2\text{O}_3$ as dilution material. Propane oxidation tests were conducted over both fresh catalyst diluted with $\gamma\text{-Al}_2\text{O}_3$ and fresh catalyst diluted with aluminum sulfate. The results show that their activity for propane oxidation were the same. This means that aluminum sulfate without Pt metal dispersed on it, can not provide new active sites for propane oxidation, in other words, the formation of new active sites for propane oxidation must located at the junction between platinum particles and aluminum sulfate. The results also show that activity for methane oxidation of Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst aged by H_2S in air at 400°C is moderately inhibited. The conversion versus temperature curve shifted to higher temperature. It is believed that this effect is also due to the formation of sulfate.

The deactivation mechanism of Pt/ $\gamma\text{-Al}_2\text{O}_3$ catalyst aged in air at 200°C is different. than that are at 400°C discussed above. The products of H_2S oxidation at 200°C are unreacted H_2S and SO_2 . It is proposed that catalyst deactivation due to the sulfur effect in this case is caused by strong adsorption of SO_2 on Pt sites. The reason this aged catalyst was deactivated for CO oxidation is because SO_2 adsorbed on Pt sites inhibit CO adsorption. The results also show that this aged catalyst has higher activity for propane oxidation than fresh catalyst. This is attributed to the higher temperature needed to oxidize propane which causes adsorbed SO_2 to further oxidize to SO_3 and then react with

alumina to form aluminum sulfate. As discussed above, the formation of aluminum sulfate can induce platinum crystal structure change, and promote platinum crystal rearrangement favored for propane oxidation.

Both activity tests of Pt/ γ -Al₂O₃ catalyst aged in nitrogen at 200 and 400°C show increased activity for propane oxidation and decreased activity for CO oxidation. It is apparent that in both cases, catalysts were deactivated due to the formation of sulfide either on Pt or on support material, according to the observed color changes of the catalyst. It is also suggested that the decreased activity of both aged catalysts for CO oxidation is due to strong adsorption of SO₂ on Pt sites which was produced during the lower temperature needed for CO oxidation through sulfide oxidation. The enhanced activity of both aged catalysts for propane oxidation is due to the formation of aluminum sulfate which was formed through sulfide oxidation to SO₂ and further oxidized to SO₃, at the higher temperatures needed for propane oxidation and finally reacted with support to give the higher propane oxidation activity.

4.4 H₂S Aged 1.5% Platinum Supported on TiO₂, ZrO₂ and SiO₂

Based on tests results of H₂S aged Pt/ γ -Al₂O₃ catalyst, which suggested that aluminum sulfate formation is the main deactivation mechanism. Three other catalysts, viz., platinum supported on SiO₂, TiO₂, and ZrO₂ were used to conduct similar tests. The purposes of conducting these experiments are (1) to determine if these three catalyst will also interact with sulfur to form sulfate when treated with H₂S in air at 400°C, (2) to determine other possible deactivation mechanism due to sulfur effect, and (3) to study the effect of support acidity on catalyst activity.

4.4.1 Diagnostic Oxidation Tests

Diagnostic oxidation tests were conducted over aged catalysts. The test results were used to compare with activity of fresh catalyst.

4.4.1.1 H₂S Aged 1.5% Pt/TiO₂ Catalyst As described previously, 1.5% Pt/TiO₂ catalyst was aged by H₂S in air at 400°C. The same three diagnostic oxidation were conducted to evaluate catalyst activity changes before and after aging.

(1) Carbon Monoxide Oxidation

As shown in Figure 4-46 (Append. B), activity of aged Pt/TiO₂ catalyst decreased sharply compare to fresh catalyst for CO oxidation. The temperatures required to oxidize 50% CO, T₅₀ were 100°C and 185°C for fresh and aged catalyst, respectively. This suggest that most active sites of aged catalyst for CO oxidation are removed due to sulfur poisoning. The reason will be discussed later.

(2) Methane Oxidation

A comparison of fresh and aged Pt/TiO₂ catalyst activity for methane oxidation is shown in Figure 4-47 (Append. B). It was found that the sulfur poisoned catalyst was deactivated for methane oxidation. The conversion versus temperature profiles for both catalysts suggest that deactivation pathway, in this case, is due to loss of active sites.

(3) Propane Oxidation

Percentage conversion as a function of temperature curves of fresh and aged catalysts are compared in Figure 4-48 (Append. B). It was found that catalyst activity for propane oxidation was dramatically enhanced after sulfur poisoning. T₅₀ of both fresh and aged catalysts are 270°C and 208°C. The results also indicate that propane oxidation over aged catalyst increased rapidly from 25% conversion to about 90% over a temperature increase of only 25°C.

4.4.1.2 H₂S Aged 1.5% Pt/ZrO₂ Catalyst 1.5% Pt/ZrO₂ catalyst was also poisoned by H₂S in air at 400°C. Diagnostic oxidation of CO, methane, and propane were conducted over fresh and aged catalysts to evaluation catalyst activity changes.

(1) Carbon Monoxide Oxidation

As show in Figure 4-49 (Append. B), catalyst activity for CO oxidation decreased after sulfur poisoning, but not as much as sulfur aged Pt/TiO₂ catalyst. T₅₀ are 180°C and 205°C for fresh and aged catalyst, respectively. The results suggest that the catalyst lost its active sites for CO oxidation due to introduction of sulfur compound.

(2) Methane Oxidation

Catalyst activity of fresh and aged catalyst were compared, for methane oxidation in Figure 4-50 (Append. B). It was found that catalyst activity decreased slightly after sulfur poisoning. The results also show that conversion curves shift to higher temperatures.

(3) Propane Oxidation

Propane oxidation over fresh and aged catalyst were conducted and compared in Figure 4-51 (Append. B). Catalyst activity for propane oxidation increased slightly after sulfur poisoning. The results suggest a small number of new active sites for propane oxidation were formed due to the sulfur effect.

4.4.1.3 H₂S Aged 1.5% Pt/SiO₂ Catalyst As described in section 4.2.2.2, 1.5% Pt/SiO₂ catalyst was poisoned by H₂S in air at 400°C for 24 hours. Diagnostic oxidation of CO, methane, and propane were also conducted over this aged catalyst. The results were used to compare with fresh catalyst, so that sulfur effects on catalyst activity could be evaluated.

(1) Carbon Monoxide Oxidation

The results show in Figure 4-52 (Append. B) indicate that catalyst was severely deactivated for CO oxidation after sulfur poisoning. Conversion versus temperature curve shifted to higher temperature with almost the same slope, which suggested that deactivation mechanism is due to the loss of active sites for CO oxidation caused by strong adsorption of sulfur compounds on the Pt sites, preventing the adsorption of CO.

(2) Methane Oxidation

Conversion as a function of temperature curves of both fresh and aged catalyst are plotted in Figure 4-53 (Append. B). It was found that both catalysts are not very active for methane oxidation. Catalyst activity slightly decreased after sulfur poisoning. Conversion versus temperature curve shifted to higher temperature with the same slope. This suggest that deactivation pathway is also due to loss of active sites for methane oxidation.

(3) Propane Oxidation

Interesting results were obtain when propane oxidation was conducted over sulfur poisoned Pt/SiO₂ catalyst. As show in Figure 4-54 (Append. B), it was found that catalyst activity for propane oxidation was not changed after sulfur poisoning.

4.4.1.4 Summary The results described in section 4.4.1 are summarized below. Activity changes of different catalysts due to sulfur effects are compared in Table 4-10. It can be seen that all catalysts were deactivated for CO and methane oxidation, and were promoted for propane oxidation except Pt/SiO₂. The extent of catalyst deactivation for CO and methane oxidation follow the trend:

For CO oxidation: Pt/TiO₂ > Pt/SiO₂ > Pt/γ-Al₂O₃ = Pt/ZrO₂

For methane oxidation: Pt/TiO₂ > Pt/ZrO₂ > Pt/γ-Al₂O₃ > Pt/SiO₂

The extent of catalyst activity enhancement for propane oxidation is in the order as follow:

$$\text{Pt/TiO}_2 > \text{Pt}/\gamma\text{-Al}_2\text{O}_3 > \text{Pt/ZrO}_2 > \text{Pt/SiO}_2$$

Table 4-10 Comparison of activity changes due to sulfur effects

Catalyst	CO T ₅₀ °C	ΔT ₅₀ °C	CH ₄ T ₅₀ °C	ΔT ₅₀ °C	C ₃ H ₈ T ₅₀ °C	ΔT ₅₀ °C
Fresh Pt/γAl ₂ O ₃	150		372		284	
Aged Pt/γAl ₂ O ₃	175	-25	382	-10	248	36
Fresh Pt/TiO ₂	100		335		273	
Aged Pt/TiO ₂	185	-85	388	-53	205	68
Fresh Pt/ZrO ₂	180		440		243	
Aged Pt/ZrO ₂	205	-25	468	-28	228	15
Fresh Pt/SiO ₂	164		38% at 500°C		248	
Aged Pt/SiO ₂	192	-28	32% at 500°C	N/A	247	1

4.4.2 Catalyst Characteristic Studies

4.4.2.1 BET Surface Area Measurements BET surface area measurements were conducted over H₂S aged platinum supported on TiO₂, ZrO₂, and SiO₂ catalysts. The results are compared with fresh catalysts and listed in Table 4-11.

Table 4-11 BET Surface area of fresh and aged catalysts

BET m ³ /g	Pt/γ-Al ₂ O ₃	Pt/TiO ₂	Pt/ZrO ₂	Pt/SiO ₂
Fresh	48	38	103	304
H ₂ S Aged	42	36	52	302

Note: H₂S Aged means catalyst aged by H₂S in air at 400°C for 24 hours.

It was found that surface area of platinum supported on γ-Al₂O₃, TiO₂, and SiO₂ catalysts have been slightly decreased after sulfur poisoning. This is because amount of sulfur introduced, during aging process, is relatively small compare to 2 grams of catalyst being treated. However the surface area of Pt/ZrO₂ catalyst has been decreased from 103 m³/g to 52 m³/g after sulfur poisoning. The reason for this is not clear. It is believed that ZrO₂ substrate has been sintered, induced by sulfur compound formed, during H₂S treatment at 400°C.

4.4.2.2 Pulse Chemisorption Tests Pulse chemisorption tests were conducted to determine catalyst metal dispersion. The test results of both fresh and aged catalyst are listed in Table 4-12.

Table 4-12 Metal dispersion of fresh and aged catalysts

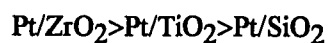
Dispersion (%)	Pt/ γ -Al ₂ O ₃	Pt/TiO ₂	Pt/ZrO ₂	Pt/SiO ₂
Fresh	13	166.4	40	1
H ₂ S Aged	11	160.8	35.4	1

Note: H₂S Aged means catalyst aged by H₂S in air at 400°C for 24 hours.

It is found that metal dispersion of all four catalysts have only been slightly decreased after sulfur poisoning. This means that sulfur can only slightly affect amount of hydrogen adsorbed on these catalysts. According to BET surface area measurement results, surface area of Pt/ZrO₂ catalyst has been decreased to only half of its original surface area due to sulfur effects. That means some of pores in ZrO₂ structure must be closed due to sulfur induced sintering, since most of Pt sites are located inside those pores. If this had been the case, then metal dispersion should also drop significantly. It is not clear why the BET and dispersion results for Pt/ZrO₂ catalyst disagree.

4.4.2.3 TGA Tests TGA tests were conducted to study interaction between catalyst and sulfur compounds at 400°C in both helium and dry air. The test procedures have been described in Chapter 3. Test results are shown in Figure 4-55, 4-56, 4-57, 4-58, and 4-59 (Append. B).

As shown in Figure 4-55 and 4-56, the interaction between sulfur compound and platinum supported on TiO₂, ZrO₂, and SiO₂ catalyst, at 400°C are compared for air and helium carriers. It was found that the strength of interaction (amount of weigh gain) between sulfur compound and catalyst is in the order:



the weight gain due to sulfur addition on the catalysts in air and helium are the same. This happened to all three catalysts tested.

The results shown in Figure 4-57, 4-58, and 4-59 indicate the percentage of weight gain due to sulfur, at 400°C in air, for Pt/ZrO₂, TiO₂, and SiO₂ catalysts, during same exposure of time, are 2.263%, 1.592%, and 0.618%.

4.4.2.4 IR Tests IR tests were conducted to detect both sulfite and sulfate formation. As described in Chapter 3, the tests were conducted through comparing the spectra of fresh and aged catalysts, by putting fresh catalyst sample pellet in front of reference light beam and aged catalyst sample pellet in front sample light beam. H₂S aged Pt/TiO₂, Pt/ZrO₂, and Pt/SiO₂ catalysts were tested. The results are shown in Figures 4-60, 4-61, and 4-62 (Append. B). It was found that spectra of H₂S aged Pt/TiO₂ catalyst shows three adsorption bands at 1210, 1140, and 1040 cm⁻¹. According to "*Infrared Spectra of Inorganic Compounds*", as shown in Table 4-13, the characteristic adsorption of SO₄²⁻ group is located between 1040 - 1210 cm⁻¹. It was also found that spectra of H₂S aged Pt/ZrO₂ catalyst shows three adsorption bands at 1210, 1080, and 1000 cm⁻¹ which also fall in the category of sulfate group shown in Table 4-13. Instead, the spectra of H₂S aged Pt/SiO₂ catalyst shows no adsorption band at all, which means that no sulfate or at least very small amount of sulfate was formed. Also according the same reference, the characteristic adsorption of sulfite group is located mostly below 1000 cm⁻¹, which means none of H₂S aged platinum catalyst forms sulfite.

4.4.2.5 Ammonia Titration Catalyst acidity change due to sulfur effects were evaluated through ammonia titration. Test results of fresh catalysts are given in section 4.1.2.3 and shown in Figure 4-5, 4-6, and 4-7. Test results of H₂S aged catalysts are shown in Figure 4-63, 4-64, and 4-65 (Append. B). It was found that acid strength of Pt/TiO₂ catalyst has

Element	Formula	Ion	Spectra	Characteristic absorption†
Antimony	SbO_3^-	antimonate(V)	304	~700, ~635, ~560, ~490
Vanadium	VO_4^{3-}	orthovanadate oxides	307-313 316-368	700-900 stg (O SMAX) Strong bands usually in region below 1300 cm^{-1} ; as a rule of thumb, frequencies decrease progressing down thru each group in the periodic table of the elements.
Oxygen	OH^-	hydroxide	372-378	3750-2000 stg (sp, M; or bd)
	$Sn(OH)_6^{2-}$	hexahydroxostannate (IV)	379-382	3000-3400 stg bd, 2200-2300 wk bd, 1500-1150 stg, 850-800 m bd, 500-550 stg, 250-300 stg
	$Sb(OH)_6^-$	hexahydroantimonate (V)	383-384	~3200 stg bd, ~1340 wk, 1075-1150 wk bd, ~720 and ~580, stg, ~450, 300-350 bd
	$BiOX$	bismuth oxyhalide (Cl, Br, and I)	388-390	480-530 wk, 240-375 stg bd, 70-150 m bd (bands decrease in frequency in the series Cl to I)
	UO_2X_2	uranyl halide (F and Cl)	393-394	850-1020 stg (M, SMAX), 380-470 bd, 250
Sulfur		sulfide	395-411	Bands below 400
	HSO_4^-	hydrogen sulfate (bisulfate)	414-417	3400-2000 bd (MAX near 2900; SMAX 2200-2600), 850-900, 605-620, 565-585, 450-480
	$S_2O_3^{2-}$	thiosulfate	418-421	1080-1150 stg (M or SMAX), 990-1010 stg, 640-690 m-s, 540-570 wk (o m)
	$S_2O_5^{2-}$	pyrosulfite	422-423	~1175 stg, 1040-1090 m, 970-990 stg, 650-660 s, 560-570 m, 510-540 m, 440-450 m
	SO_3^{2-}	sulfite	424-428	990-1090 stg (OH or SMAX), 615-660 m (o SMAX), 470-525 m (OD)
	$S_2O_8^{2-}$	dithionate	429	~1240 stg, ~995 m-stg, ~570 m-stg, ~520 m
	$S_2O_7^{2-}$	pyrosulfate	430	~1325 wk, ~1100 stg, ~920 m, ~700 wk, ~550 m
	SO_4^{2-}	sulfate	431-499	1040-1210 stg (OH or SMAX), (960-1030, often 1 or 2 wk sp bands), 570-680 m (OD or M)
	$S_2O_8^{2-}$	peroxydisulfate	501-503	1260-1310 stg, 1050-1070 m sp, 690-740 m, 580-600 wk m sp, ~560 m
	SO_3F^-	fluorosulfonate	504-505	1260-1300 stg, 1070-1080 m sp, ~740 m, ~580 m, ~480 wk
Selenium		selenide	506-516	Bands below 400
	SeO_3^{2-}	selenite	517-520	700-770 stg (SMAX 700-850), 430-540 m stg (OD), 360-410 (OD)
	SeO_4^{2-}	selenate	522-530	840-910 stg (o wk sh 810-850), 390-450 wk m
		telluride	531-538	No correlations

Table 4-13 Characteristic adsorption of sulfur compounds in IR test

been increased after sulfur poisoning, acid strength of Pt/ZrO₂ catalyst increased very slightly, and acid strength of Pt/SiO₂ catalyst was not affected by sulfur compounds.

4.4.2.6 TPR Tests TPR tests were conducted to determine the possibility of sulfur removal through hydrogen reduction. Test procedures are described in Chapter 3. Fresh catalysts, pure substrate oxides, and H₂S aged catalysts were compared. The results are shown in Figures 4-66 to 4-74 (Append. B). It was found that TiO₂, ZrO₂, and SiO₂ can not be reduced by hydrogen, in other words, no hydrogen consumption peak was observed. Comparison between fresh and H₂S aged Pt/TiO₂ catalysts, as shown in Figures 4-69 and 4-70, indicate that a large hydrogen uptake peak appear at 331°C in aged catalyst and is absent in fresh catalyst. This suggest that some of sulfur compounds interacted with catalyst can be removed by hydrogen. Tests conducted over fresh and H₂S aged Pt/ZrO₂ catalysts indicate that amount of hydrogen consumed in both cases are almost the same, which means hydrogen can not remove sulfur compounds interacted with this catalyst. TPR tests of fresh and H₂S aged Pt/SiO₂ catalysts are shown in Figures 4-73 and 4-74. It was found aged catalyst use more hydrogen than fresh catalyst. This suggest that hydrogen remove some of sulfur compounds present on the catalyst.

Catalyst regeneration studies for these three catalysts were not conducted.

4.4.3 Discussion

Platinum supported on TiO₂, ZrO₂, and SiO₂ catalysts deactivation due to sulfur effects was studied through diagnostic oxidation and catalyst characterization tests. Based on activity changes due to the presence of sulfur,, all three catalysts were deactivated for CO and methane oxidation, and promoted for propane oxidation except Pt/SiO₂. The extent of activity changes was different for all three catalysts.

To determine the reasons for these changes in activity, catalyst characterization studies were conducted.

Several catalyst characterization studies were conducted with Pt/SiO₂ catalyst. First, pulse chemisorption and BET surface area tests indicate very small changes between fresh and H₂S aged catalysts. In TGA test, it was found that the interaction between this catalyst and sulfur compounds is small compare to the other three catalysts. The percentage of weight gain due to the introduction of H₂S at 400°C in air is only 0.618% which is much lower than that observed for Pt/γ-Al₂O₃, Pt/TiO₂, and Pt/ZrO₂ catalysts, but still indicate some interaction. IR test show no adsorption band at all within 800 - 4000 cm⁻¹ range, which means little if any sulfate and sulfite were formed. Furthermore, the results of ammonia titration indicate that acidity of Pt/SiO₂ catalyst did not change after sulfur poisoning. All of these results suggest that deactivation mechanism of Pt/SiO₂ catalyst due to sulfur effects is different from that of Pt/γ-Al₂O₃ catalyst.

It is proposed that Pt/SiO₂ catalyst was deactivated by two mechanisms after sulfur poisoning. One of them is strong adsorption of sulfur compounds on Pt active sites. The other one is small amount of sulfate formation on the surface of the support. The reason Pt/SiO₂ catalyst activity for propane oxidation did not change after sulfur poisoning, is because sulfur compounds adsorbed on Pt sites inhibit propane adsorption. At the same time, small amount of sulfate formed on the surface provide new active sites for propane oxidation through sulfur induced platinum crystal changes as described before, so that, overall activity of Pt/SiO₂ catalyst for propane oxidation due to sulfur poisoning shows no change. Decreased activity of Pt/SiO₂ catalyst for CO and methane oxidation, after sulfur poisoning, is due to both deactivation mechanisms. In other words, strong adsorption of sulfur compounds on Pt sites inhibits both CO and methane adsorption. That is why conversion curves of H₂S aged catalyst for both CO and methane oxidation shifted to higher temperature compare to fresh catalyst.

As described in section 4.4.2, characterization studies of Pt/ZrO₂ catalyst were also conducted. Pulse chemisorption test indicate decreased metal dispersion from 40 to 35% due to sulfur effects. BET tests show a large decrease in surface area from 103 to 52

m^3/g , which suggests that catalyst was sintered after H_2S treatment. TGA test were conducted which indicate strong interaction between catalyst and sulfur compounds. As a matter of fact, percentage weight gain of Pt/ZrO_2 catalyst due to sulfur compounds is the highest among these three catalyst. IR test identified the interaction between catalyst and sulfur compounds is the formation of sulfate. Ammonia titration results show a slight increase of acidity of Pt/ZrO_2 catalyst due to sulfur effects.

Based on the results described above, it is proposed that Pt/ZrO_2 catalyst was deactivated, due to sulfur effects, by at least three possible catalyst deactivation mechanisms, which are (1) sintering, which means some of pores in ZrO_2 structure were closed. Since most of Pt sites are located inside those pores, this can dramatically reduce Pt active sites, (2) sulfate formation, which can induce Pt crystal change, and (3) strong adsorption of sulfur compounds on Pt sites, which can inhibit adsorption of desirable reactants. Both sintering and strong adsorption of sulfur compounds on Pt sites inhibit propane adsorption. That is why the enhancement of activity for propane oxidation over H_2S aged Pt/ZrO_2 catalyst is rather small compare to aged $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ and Pt/TiO_2 catalysts, although both TGA and IR tests show strong interaction between catalyst and sulfur compounds, i.e., the formation of sulfate on Pt/ZrO_2 surface. The results also show that Pt/ZrO_2 catalyst was deactivated for both CO and methane oxidation after sulfur poisoning. It is believed that all three deactivation mechanisms are responsible for its activity decrease. The reason that acidity of Pt/ZrO_2 catalyst only slightly increased after sulfur poisoning, although large amount of surface sulfate has been formed, is because some of zirconic sulfate formed is located inside the ZrO_2 structure due to sintering, yet, ammonia titration can only detect acid sites located on the surface. As described previously, surface area of Pt/ZrO_2 catalyst decreased to half of its original surface area due to sulfur effects. That means some of pores in ZrO_2 structure must be closed due to the sintering. Since most of Pt sites are located inside those pores, its metal dispersion should also drop dramatically. But the results show its dispersion only decreased from 40

to 35%. It is not clear why the results of BET test and dispersion tests for Pt/ZrO₂ catalyst disagree.

Catalyst characterization studies were conducted over Pt/TiO₂ catalyst to explain the cause of deactivation. Pulse chemisorption and BET surface area tests were conducted, which indicate slight decrease in these properties due to sulfur effects. TGA test indicate strong interaction between this catalyst and sulfur compounds. Further, IR test shows that the interaction between them is the formation of sulfate. The results of ammonia titration indicate that acidity of Pt/TiO₂ catalyst increased after sulfur poisoning. This is due to the formation of a solid superacid SO₄⁻²-TiO₂. All of these results suggest that sulfate formation is at least one of the mechanisms which cause the changes in catalyst activity after sulfur poisoning.

Based on all information obtained, it is proposed that deactivation pathway for Pt/TiO₂ catalyst due to sulfur effects is the formation of sulfate. Another possible deactivation mechanism is the strong adsorption of sulfur compounds on Pt sites, which was proposed in study of sulfur poisoned Pt/SiO₂ catalyst. Although, sulfur compounds adsorbed on Pt sites can inhibit propane adsorption, sulfate formation can provide new active sites for propane oxidation. These new sites are formed through sulfur induced platinum crystal structure rearrangement and are located at the junction between platinum and surface titanic sulfate, so that, platinum crystal structure that favor for propane oxidation is increased. In other words, both effects were competing, and sulfate formation predominates. Both sulfate formation effect and strong sulfur compounds adsorption on Pt sites effect are responsible for Pt/ZrO₂ catalyst deactivation for CO and methane oxidation.

4.5 Tributyl Phosphate aged 1.5% Pt/ γ -Al₂O₃ Catalyst

4.5.1 Diagnostic Oxidation Tests

1.5% Pt/ γ -Al₂O₃ catalysts were poisoned by TBP at 400 and 550°C in air. Diagnostic oxidation tests were conducted over both fresh and aged catalysts to evaluate catalyst activity changes.

4.5.1.1 Catalyst Aged at 400°C (1) Carbon Monoxide Oxidation

As shown in Figure 4-75 (Append. B), catalyst was slightly deactivated after phosphorus poisoning. The conversion curve shifted to higher temperature compared to fresh catalyst, which suggests loss of active sites for CO oxidation.

(2) Propane Oxidation

Comparison of activity before and after phosphorus poisoning are shown in Figure 4-76 (Append. B). It was found that aged catalyst activity for propane oxidation was enhanced before light-off temperature (T_{50}) then decreased with increasing temperature. In other words, the slope of aged catalyst conversion curve is lower than the one for fresh catalyst, which suggests that pore diffusion resistance has been increased probably due to oxidation of TBP to form P₂O₅ and deposit on the catalyst surface.

(3) Methane Oxidation

The results of diagnostic oxidation of methane, as shown in Figure 4-77 (Append. B), indicates the same deactivation mechanism as was found in propane oxidation. Conversion curve of aged catalyst shifted to higher temperature with lower slope, also indicating an increase in pore diffusion resistance.

4.5.1.2 Catalyst Aged at 550°C (1) Carbon Monoxide Oxidation

Percentage conversion as a function of temperature curves of fresh and aged catalysts are shown in Figure 4-78 (Append. B). The results indicate that catalyst was severely

deactivated for CO oxidation after phosphorus poisoning. The temperature required to reach 50% conversion T_{50} are 137 and 218°C for fresh and aged catalysts, respectively.

(2) Propane Oxidation

The activity of fresh and aged catalysts for propane oxidation are compared in Figure 4-79 (Append. B). It was found that aged catalyst conversion curve shifted to higher temperature, and maximum conversion can only reach 81.5%. This suggest that catalyst was not only deactivated by pore blocking, but also deactivated by masking. It appears that TBP is oxidized to P_2O_5 and covers the catalyst surface, so that both pore diffusion and mass transfer resistance increased.

(3) Methane Oxidation

The results of methane oxidation test show severe deactivation. As show in Figure 4-80 (Append. B), conversion of methane over aged catalyst reaches a maximum of 45% at 500 °C, then decreased with increasing temperature until 550°C, and then increase again with increasing temperature. At the same time, CO_2 produced also reached maximum at 500°C then is converted to CO. That means that at temperature higher than 550°C, selectivity of methane oxidation changes from CO_2 to CO.

4.5.2 Discussion

According to the diagnostic oxidation test results, $Pt/\gamma-Al_2O_3$ catalyst was deactivated for all three oxidation reaction at both 400° and 550°C after phosphorus poisoning. It is proposed that the deactivation mechanism of catalyst poisoned by TBP at 400°C is the formation of P_2O_5 which blocks pore entrance and increases pore diffusion resistance. A proposed deactivation mechanism of catalyst poisoned by TBP at 550°C is that P_2O_5 covers the catalyst surface and increases pore diffusion and mass transfer resistance, as is found in propane oxidation, and irreversible reaction between phosphorus compounds and

either alumina or platinum, which is suggested by methane oxidation results. Further investigation is needed to clarify the effect of phosphorus on platinum catalysts.

CHAPTER 5

CONCLUSION

The effect of sulfur deposition on platinum supported on γ -Al₂O₃, TiO₂, ZrO₂, and SiO₂ catalysts were investigated by measuring the resulting activity for CO, CH₄, and C₃H₈ oxidation. Similarly, the effect of phosphorus compounds on Pt/ γ -Al₂O₃ catalyst were investigated with the same diagnostic reactions. In addition to diagnostic reactions, catalyst characterization tests were conducted to compare the effect of sulfur and phosphorus compounds on treated catalyst activity with fresh catalysts. Based on the test results, the following conclusions have been reached:

- Platinum supported on γ -Al₂O₃, TiO₂, ZrO₂, and SiO₂ catalysts after treatment with H₂S in air at 400°C, were deactivated for carbon monoxide and methane oxidation, and experienced activity enhancement (promotion) for propane oxidation, except for Pt/SiO₂ catalyst. The extent of activity changes were not uniform for these catalysts.
- Pt/ γ -Al₂O₃ catalyst poisoned by H₂S in nitrogen at 400°C (in order to understanding sulfur effects in a non-oxidizing atmosphere) was also deactivated for carbon monoxide oxidation, and was promoted for propane oxidation. The extent of activity changes between catalyst poisoned in air and in nitrogen are almost the same.
- The results of pulse chemisorption with hydrogen indicate a slight decrease in metal dispersion in all cases after sulfur poisoning.
- The results of BET surface area measurement indicate a slight decrease after sulfur poisoning, in all cases except for the Pt/ZrO₂ catalyst.
- BET surface area of Pt/ZrO₂ catalyst decreased from 103 to 52 m³/g after sulfur poisoning.

- TGA test results indicate strong interaction between sulfur compounds and platinum supported on γ -Al₂O₃, TiO₂, and ZrO₂ catalysts in both air and nitrogen atmosphere. The interaction between sulfur compounds and Pt/SiO₂ catalyst was relatively weak.
- TGA test results indicate that Pt/ γ -Al₂O₃ catalyst weigh gain, due to the introduction of H₂S in both air and nitrogen, were the same.
- TGA test results also indicate that sulfur compounds interacted with Pt/ γ -Al₂O₃ catalyst can not be removed by increasing temperature.
- IR test results indicate sulfate formation on platinum supported on γ -Al₂O₃, TiO₂, and ZrO₂ catalysts poisoned by H₂S in air at 400°C. Small amount of sulfate may also formed on H₂S aged Pt/SiO₂ catalyst which were not detected by IR.
- The results of ammonia titration indicate acidity of Pt/ γ -Al₂O₃, Pt/TiO₂, and Pt/ZrO₂ catalysts were increased to different degree due to sulfur poisoning. Acidity did not change for aged Pt/SiO₂ catalyst and Pt/ γ -Al₂O₃ catalyst aged in nitrogen by H₂S.
- TPR tests show that sulfur compounds interacted with Pt/ γ -Al₂O₃ (both poisoned in air and nitrogen), Pt/TiO₂, and Pt/SiO₂ catalysts can be partially removed by hydrogen treatment at 350°C, sulfur compounds deposited on Pt/ZrO₂ catalyst can not be removed.
- The mechanisms affecting Pt/ γ -Al₂O₃ and Pt/TiO₂ catalysts aged by H₂S in air involves sulfate formation and strong adsorption of sulfur compounds on Pt sites.
- The deactivation mechanism of Pt/ γ -Al₂O₃ catalyst aged by H₂S in nitrogen is sulfide formation.
- The mechanisms for H₂S aging of Pt/ZrO₂ catalyst involves sulfur induced sintering, sulfate formation and strong adsorption of sulfur compounds on Pt sites.
- The mechanisms H₂S aging of Pt/SiO₂ catalyst involves sulfate formation and strong adsorption of sulfur compounds on Pt sites.
- Tributyl phosphate poisoned Pt/ γ -Al₂O₃ catalysts at both 400 and 550°C were deactivated for carbon monoxide, methane, and propane oxidation.

- The deactivation mechanism of TBP aged Pt/ γ -Al₂O₃ catalyst at 400°C is the formation of P₂O₅ which is deposited on the catalyst surface and blocks the pore entrance.
- The deactivation mechanisms of TBP aged Pt/ γ -Al₂O₃ catalyst at 550°C are formation of P₂O₅ and irreversible reaction between phosphorus compounds and catalyst.

APPENDIX A

FIGURES IN CHAPTER 3

This appendix includes the figures showing the schematic of Altamira instrument, and Thermal Gravimetric Analyzer, as listed in list of figures, form Figure 3-2 to 3-7.

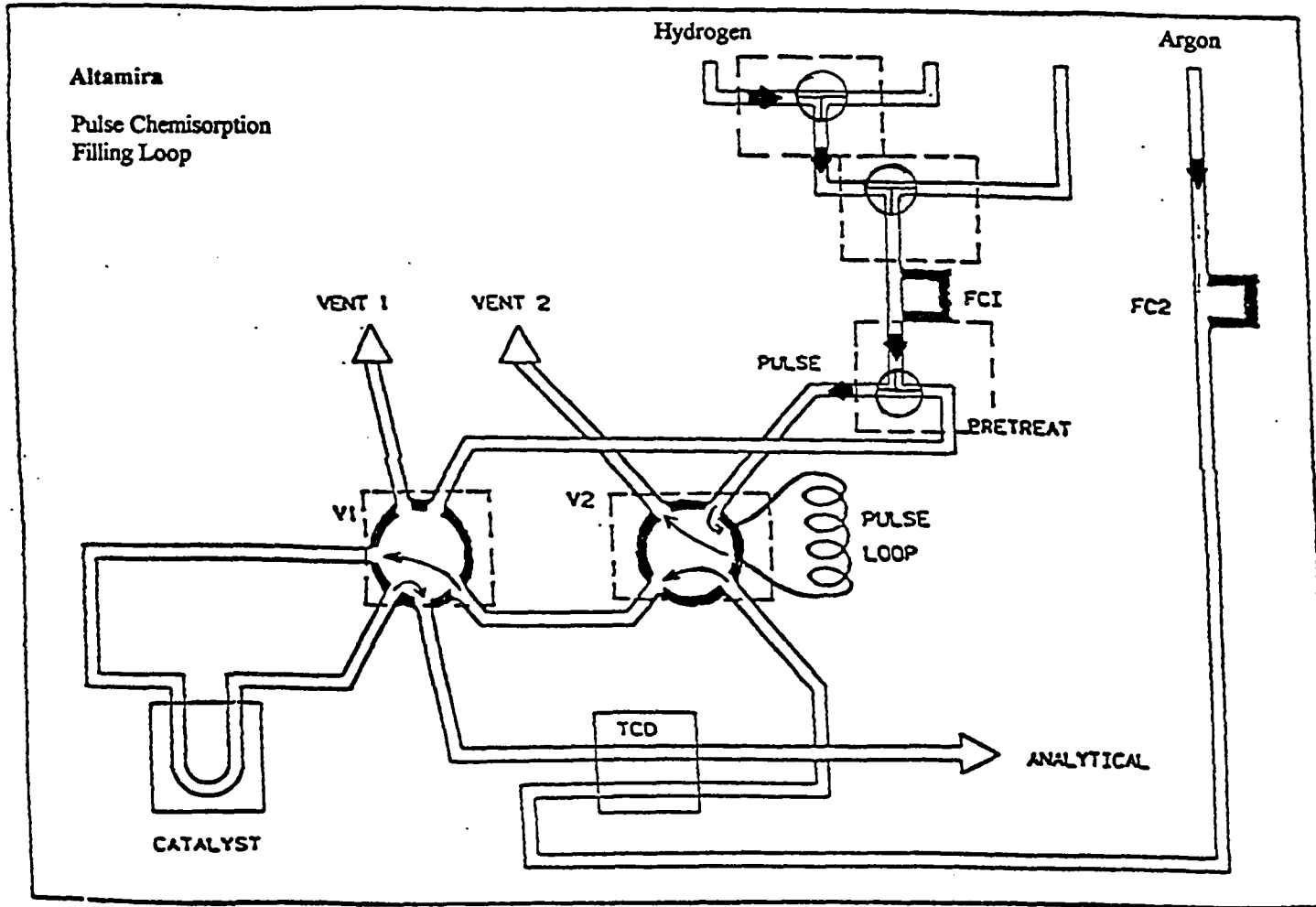


Figure 3-2 Schematic of pulse chemisorption: Filling loop

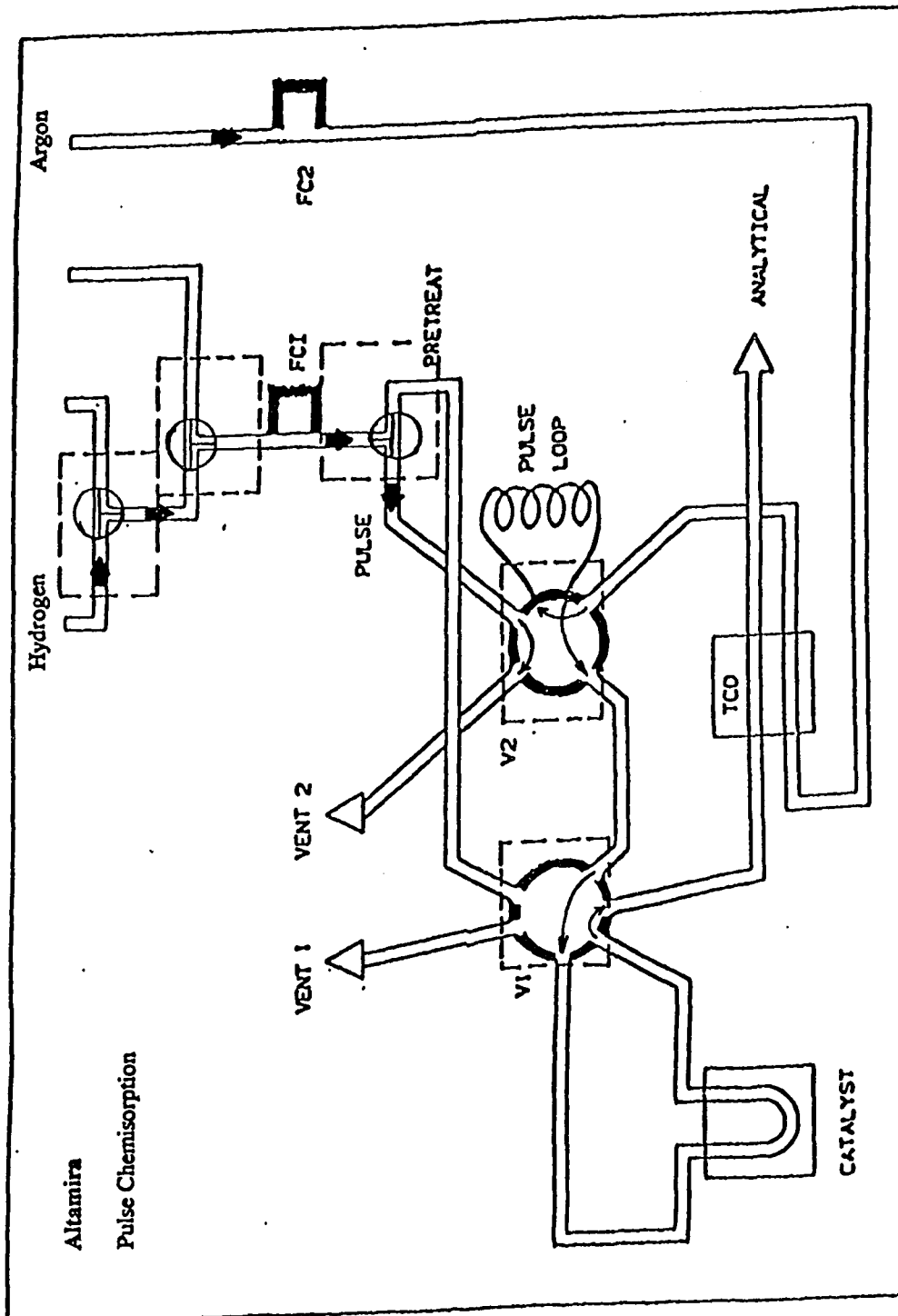


Figure 3-3 Schematic of pulse chemisorption: Chemisorption

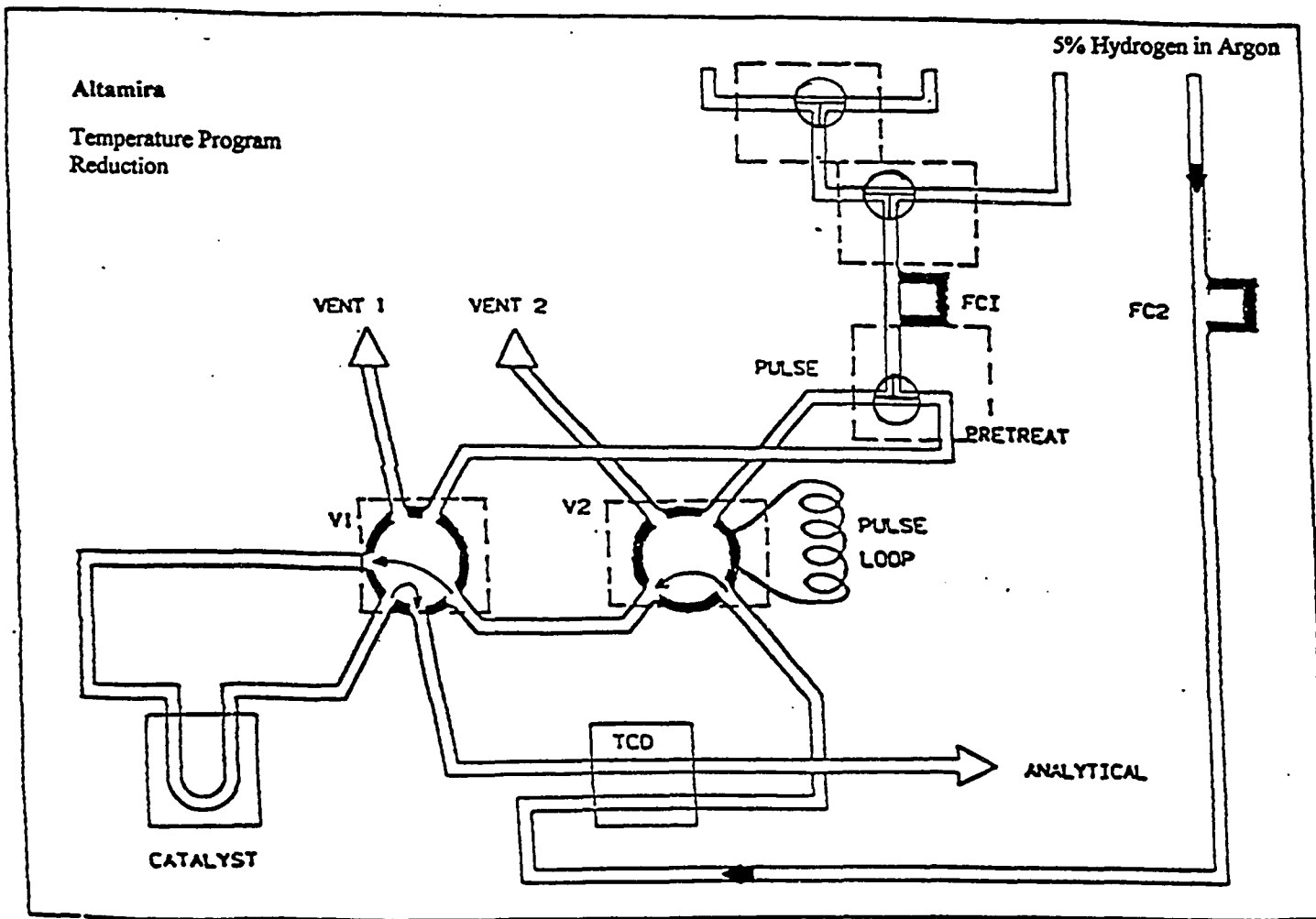


Figure 3-4 Schematic of temperature program reduction (TPR)

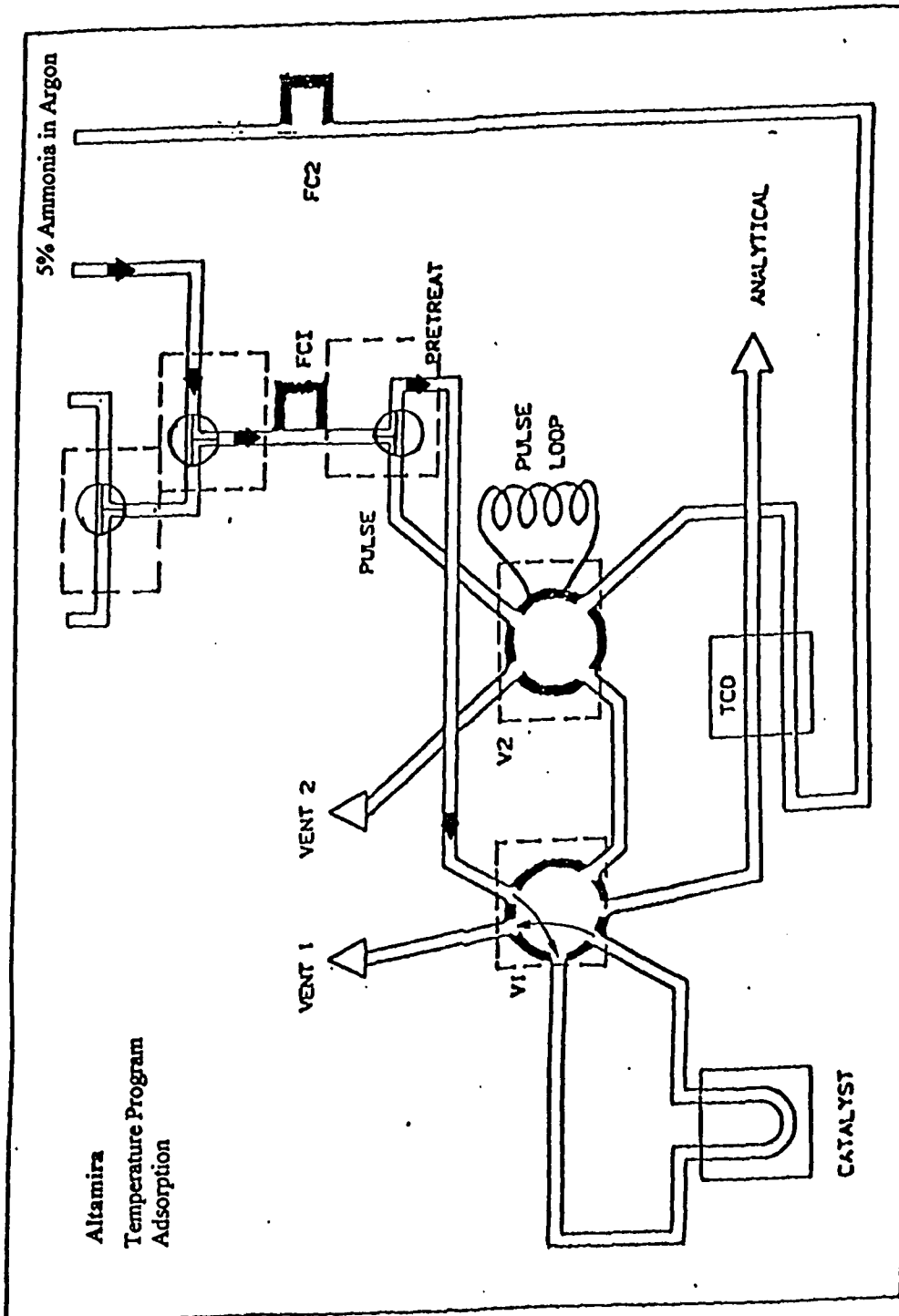


Figure 3-5 Schematic of temperature program adsorption (IPA)

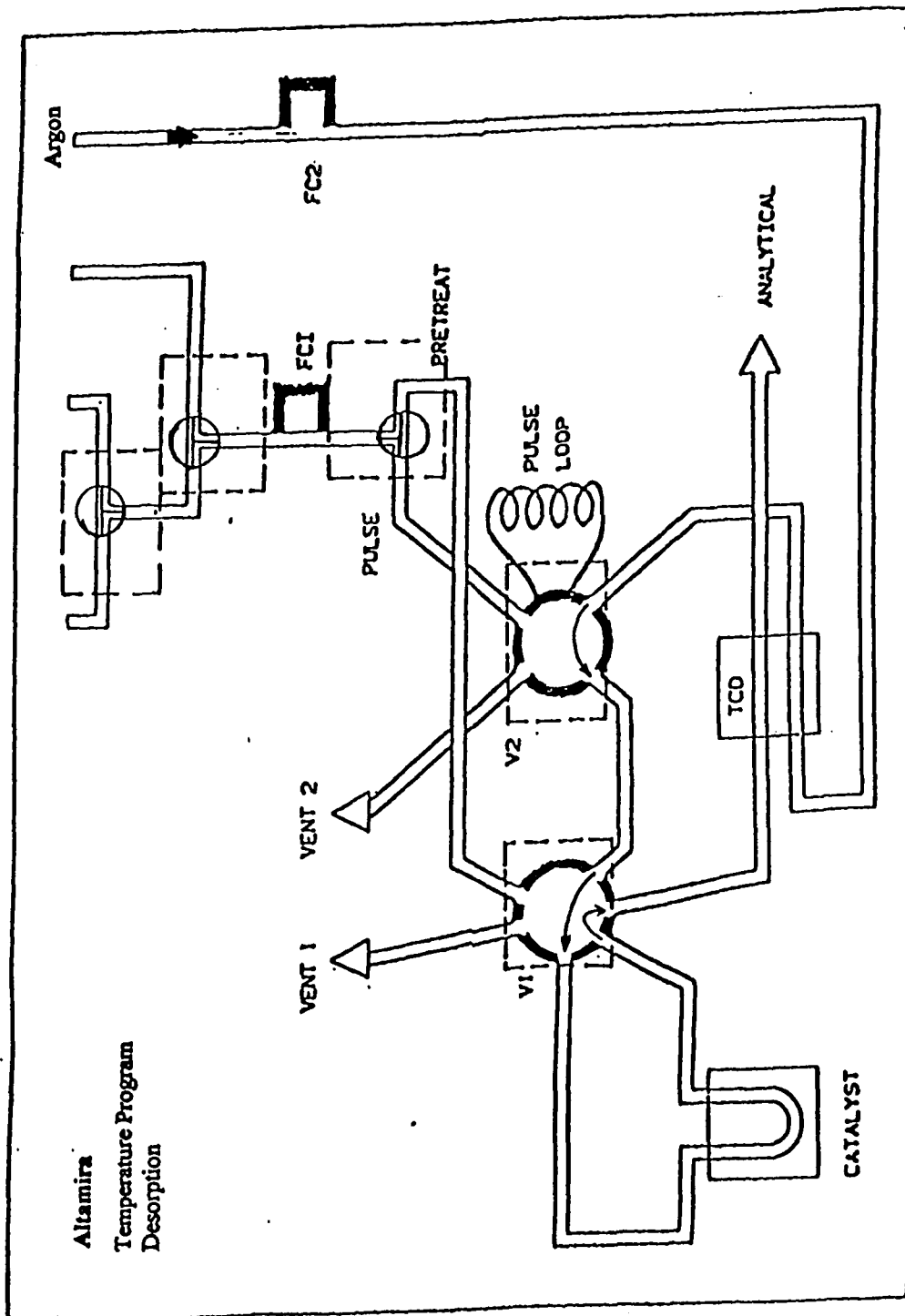


Figure 3-6 Schematic of temperature program desorption (TPD)

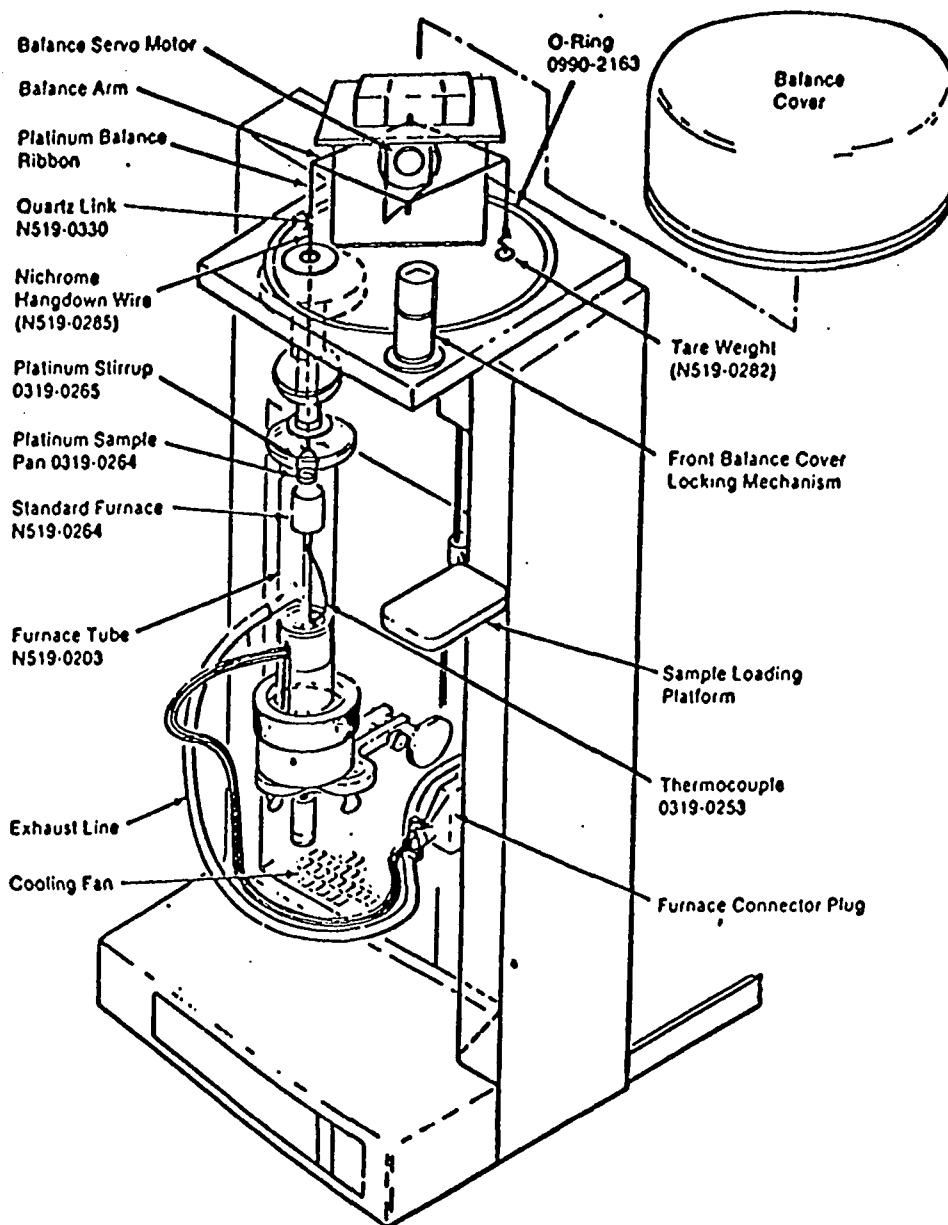
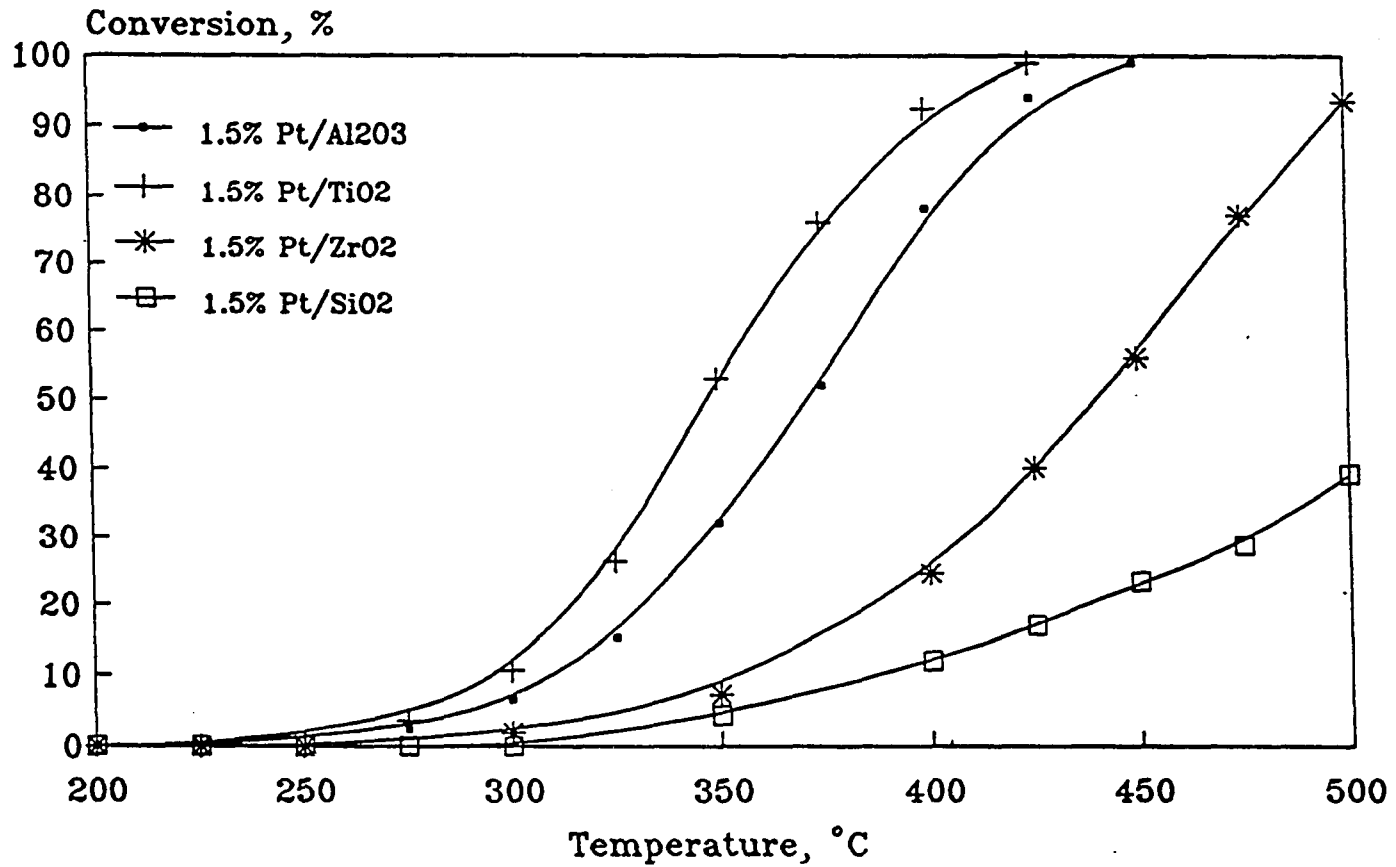


Figure 3-7 Schematic of thermal gravimetric analysis (TGA)

APPENDIX B

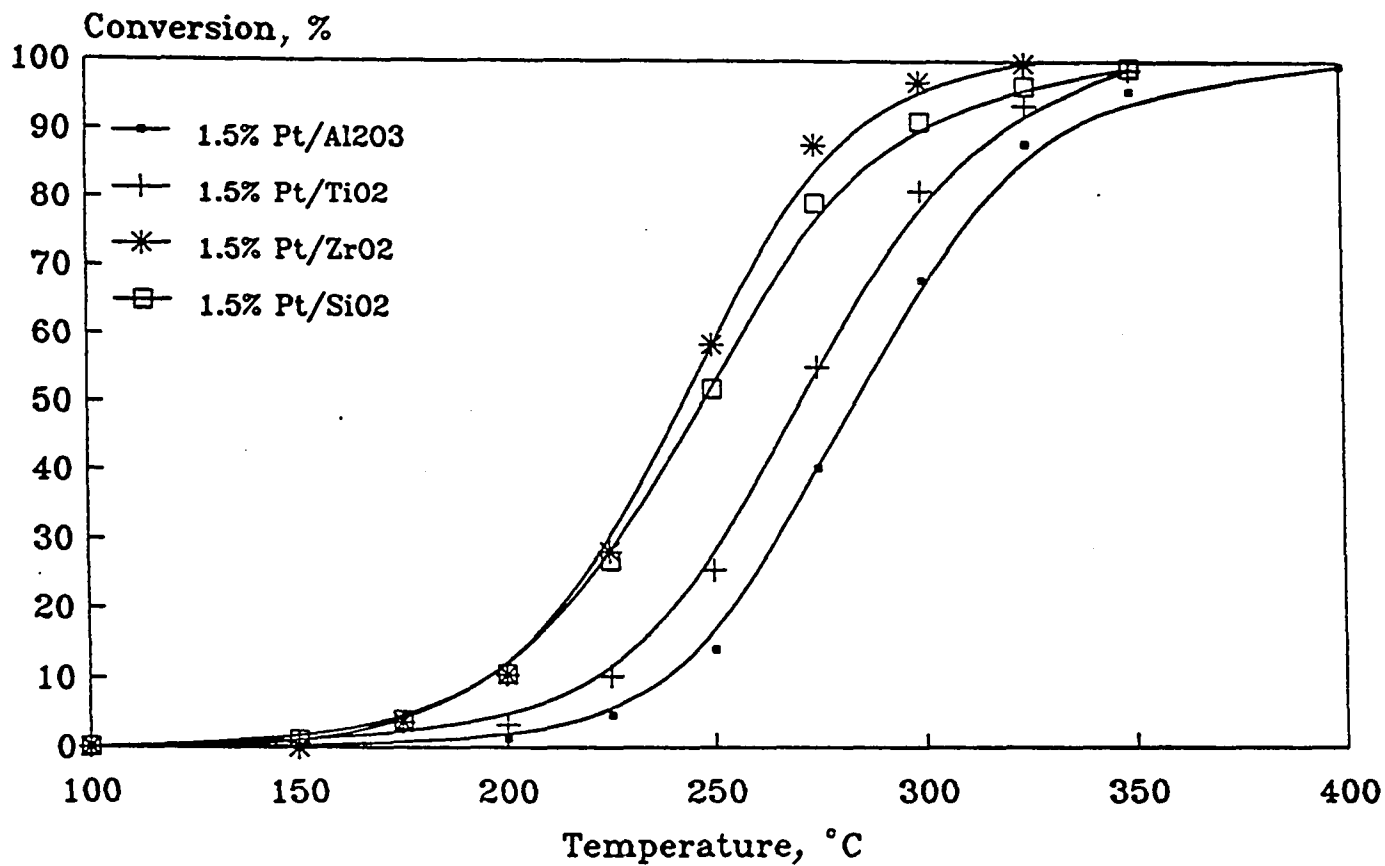
FIGURES IN CHAPTER 4

This appendix includes all the figures shown in chapter 4, from Figure 4-1 to 4-80, as listed in list of figures.



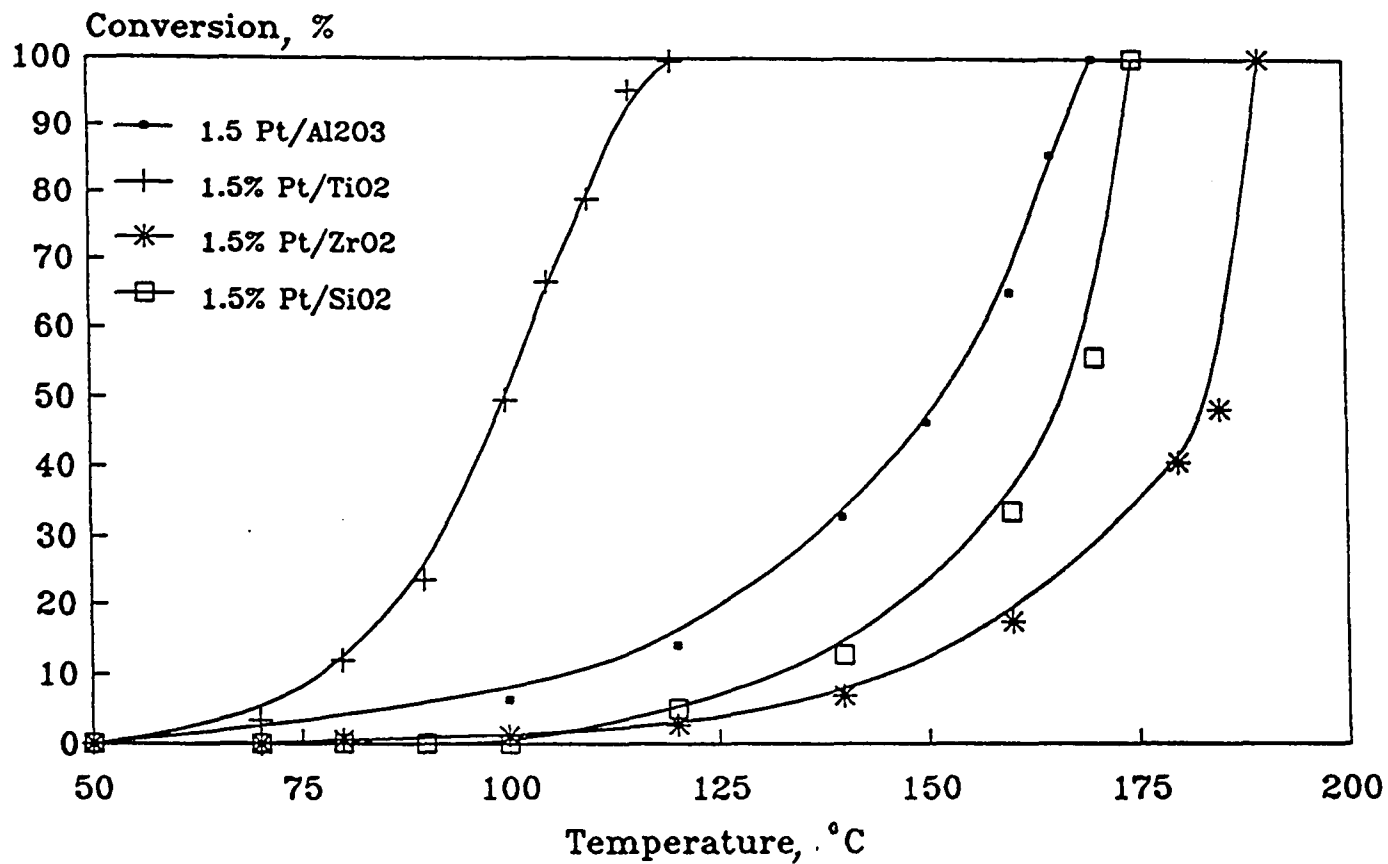
Fresh Catalyst
0.05 gram Catalyst
50 ml/min 1% CH₄ in Air SV=30,000/hr

Figure 4-1 Comparison of activity: 1% methane oxidation: Platinum supported on different substrate catalysts



Fresh Catalyst
0.05 gram Catalyst
50 ml/min 1% Propane in Air SV=30,000/hr

Figure 4-2 Comparison of activity: 1% propane oxidation: Platinum supported on different substrate catalysts



Fresh Catalyst
 0.05 gram Catalyst
 50 ml/min 1% CO in Air SV=30,000/hr

Figure 4-3 Comparison of activity: 1% CO oxidation: Platinum supported on different substrate catalysts

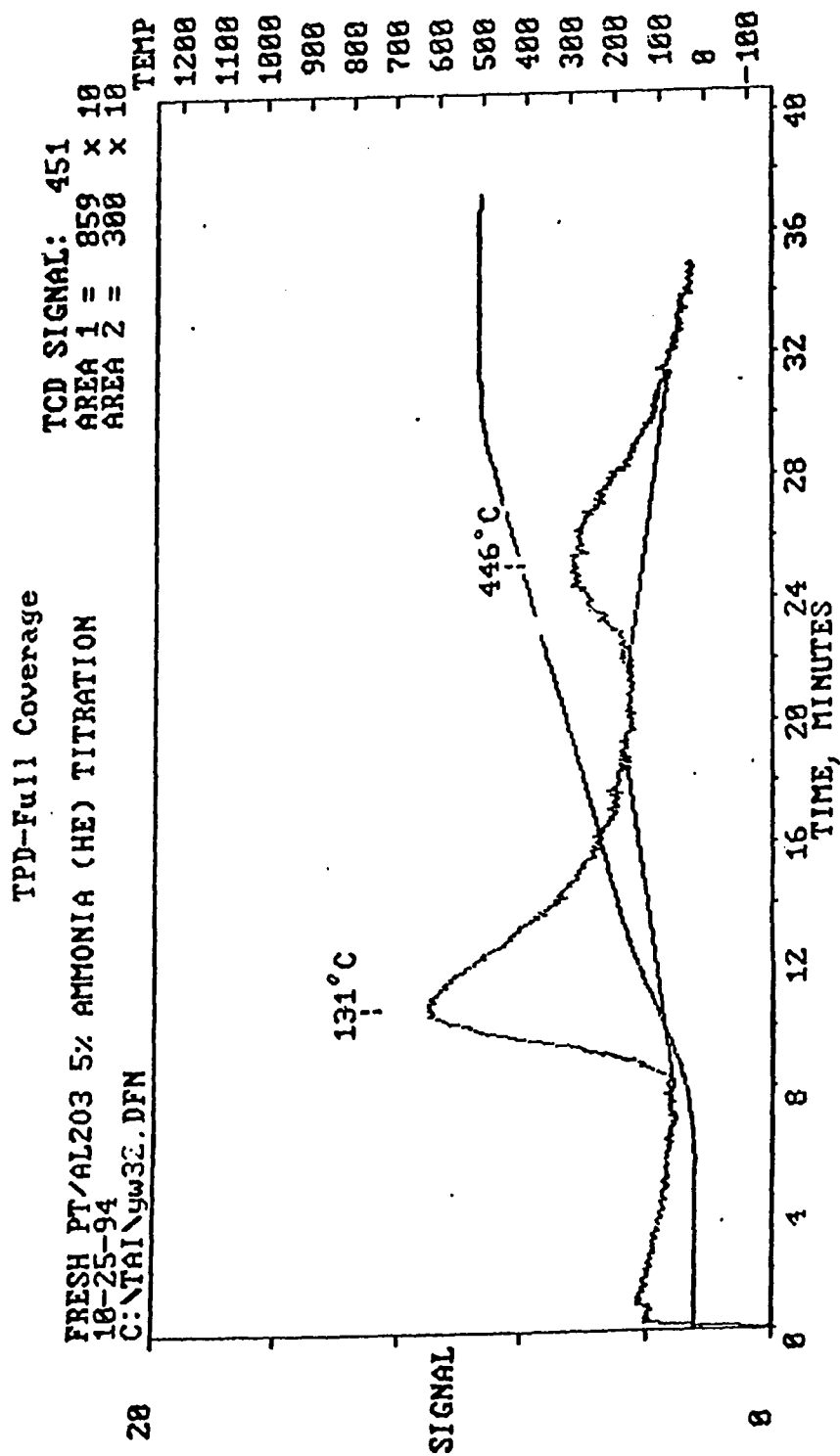


Figure 4-4 Ammonia titration: fresh 1.5% Pt/ γ -Al₂O₃ catalyst

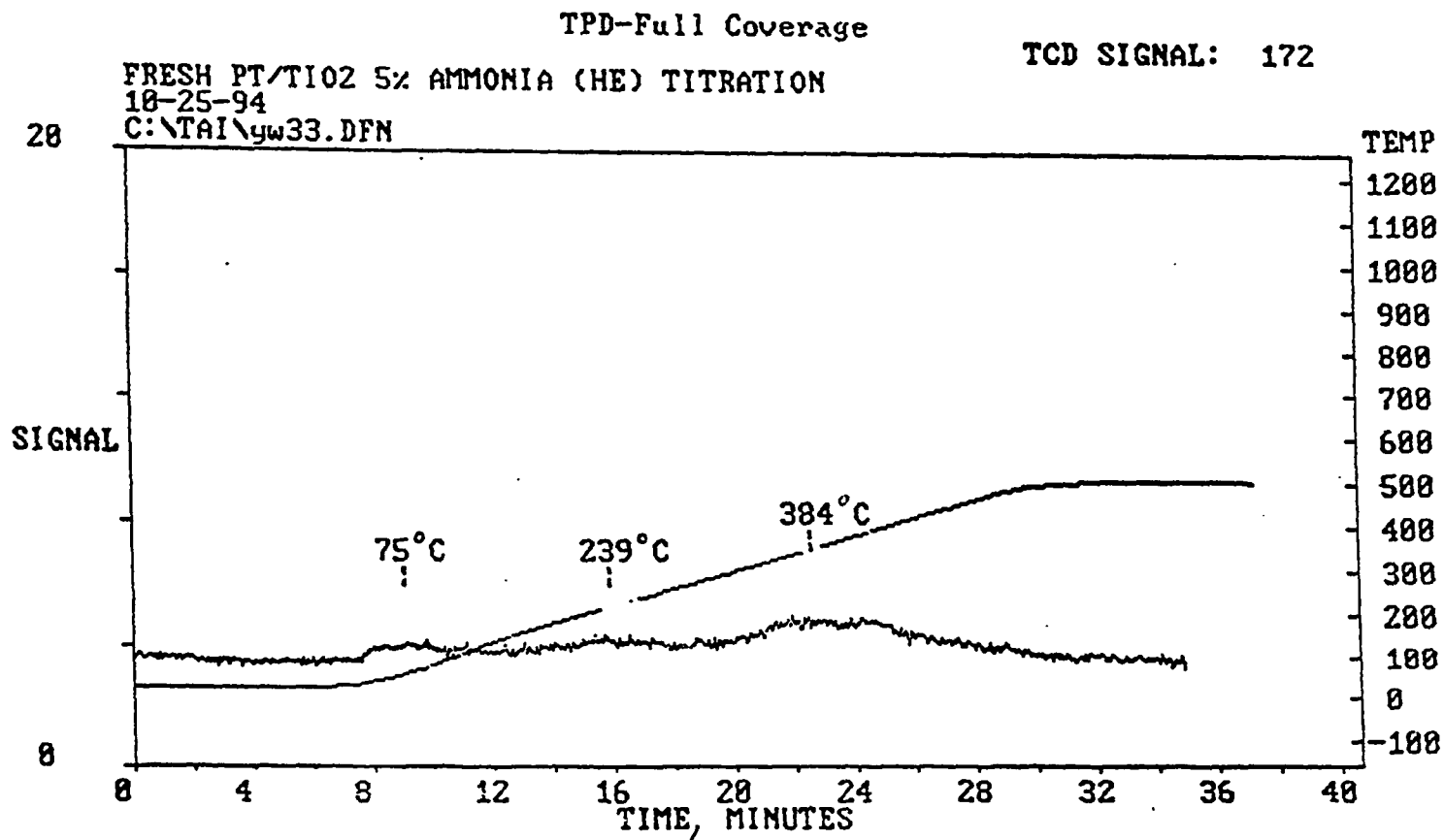


Figure 4-5 Ammonia titration: fresh 1.5% Pt/TiO₂ catalyst

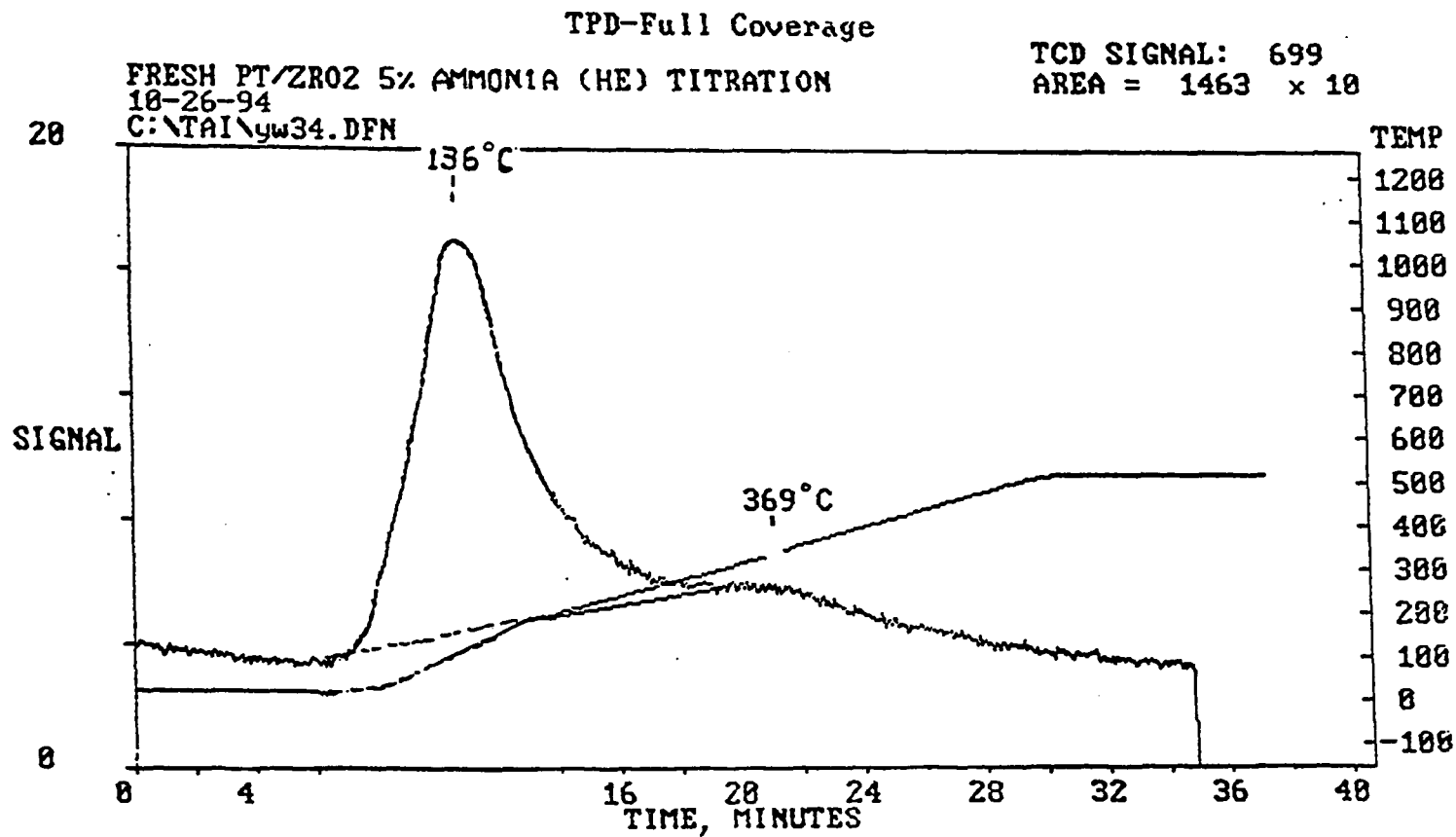


Figure 4-6 Ammonia titration: fresh 1.5% Pt/ZrO₂ catalyst

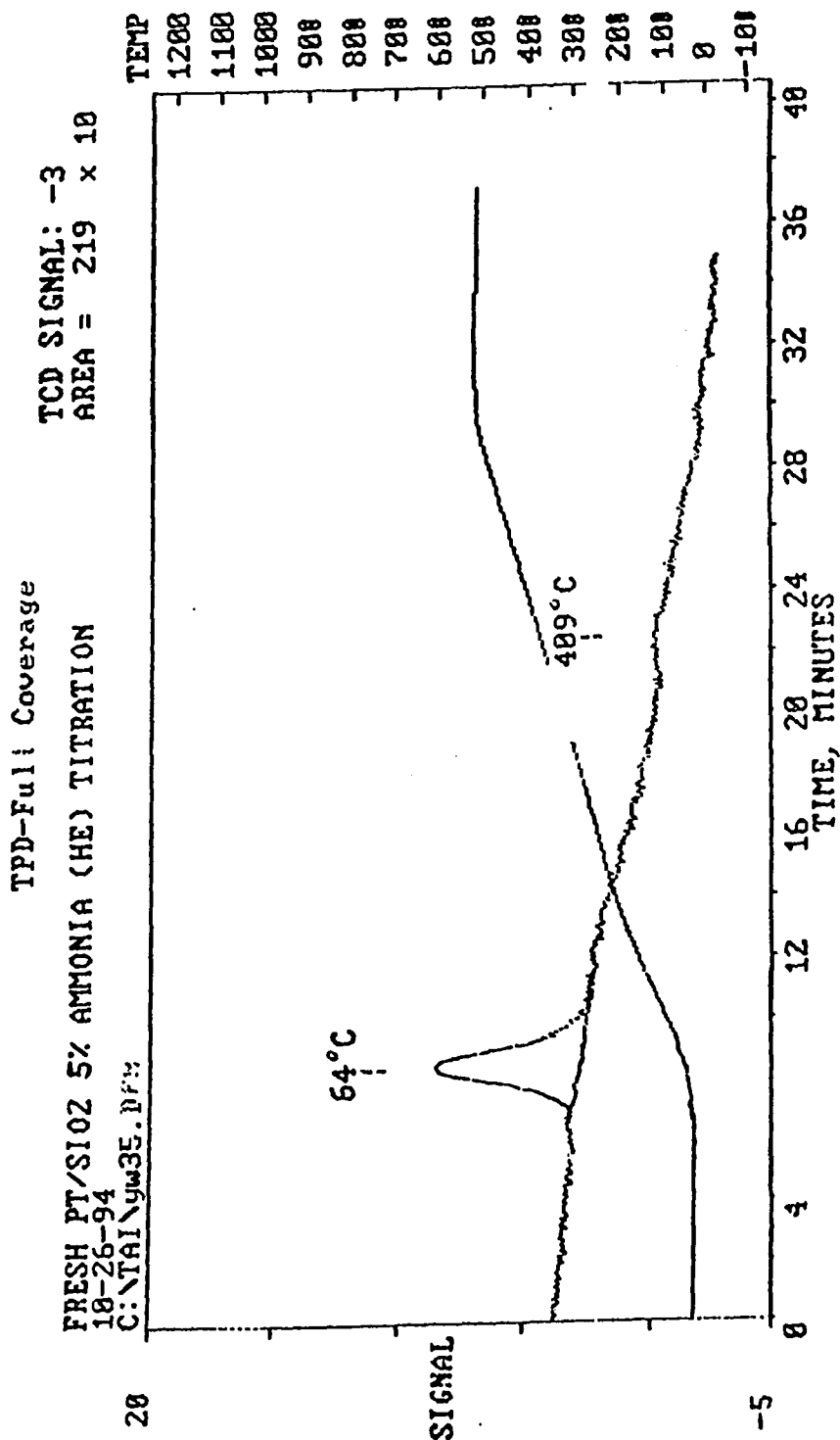
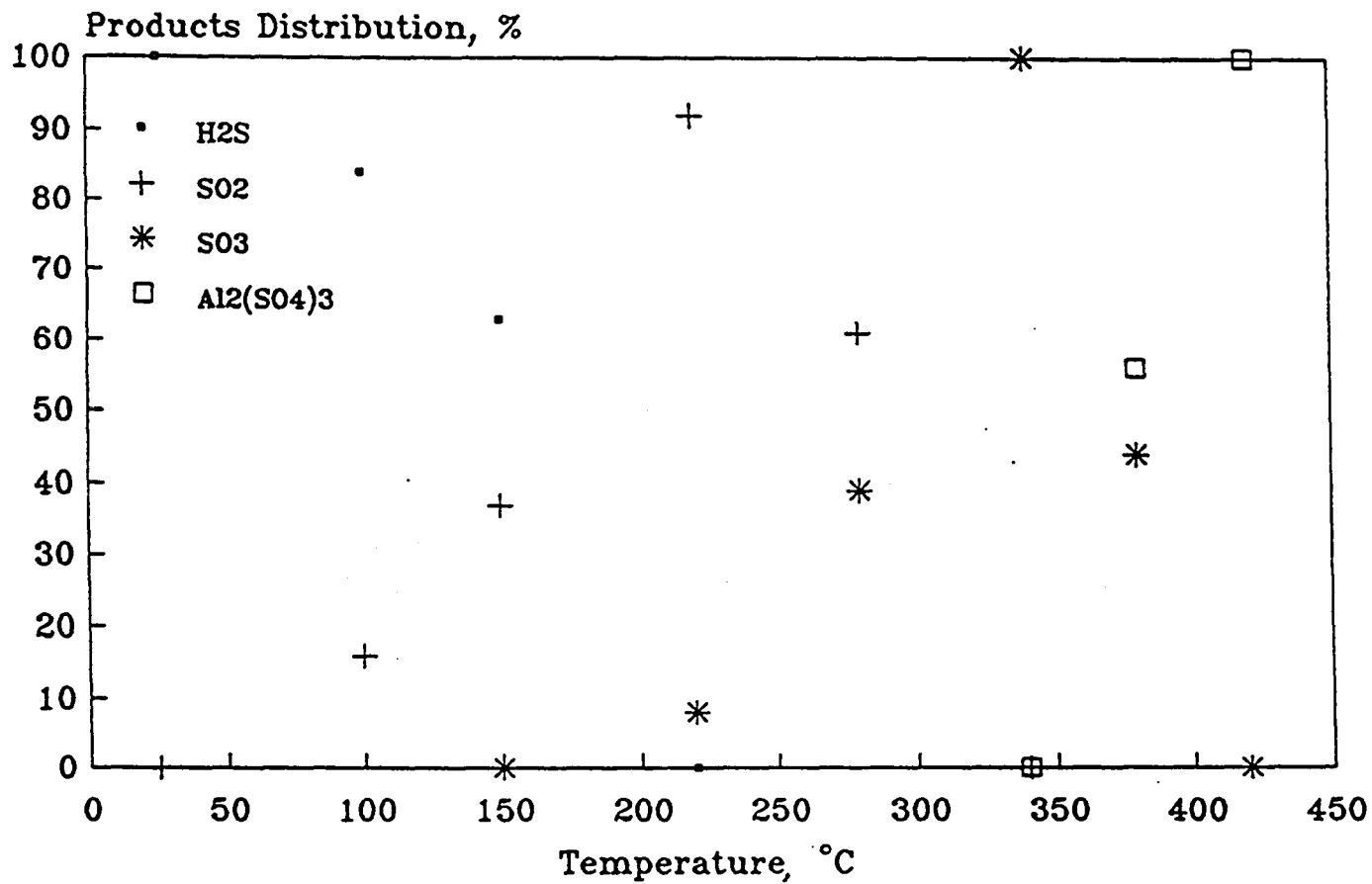
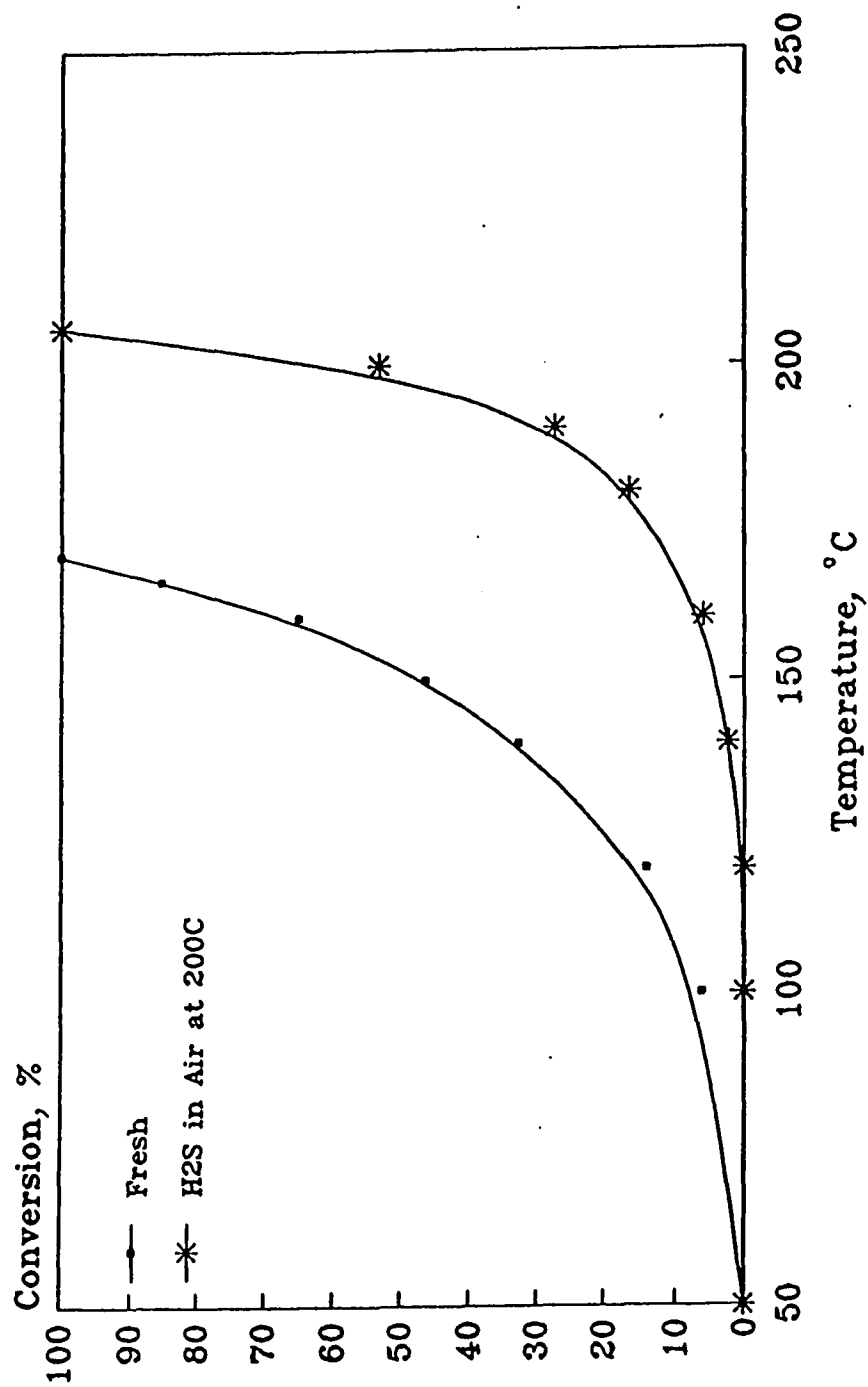


Figure 4-7 Ammonia titration: fresh 1.5% Pt/SiO₂ catalyst



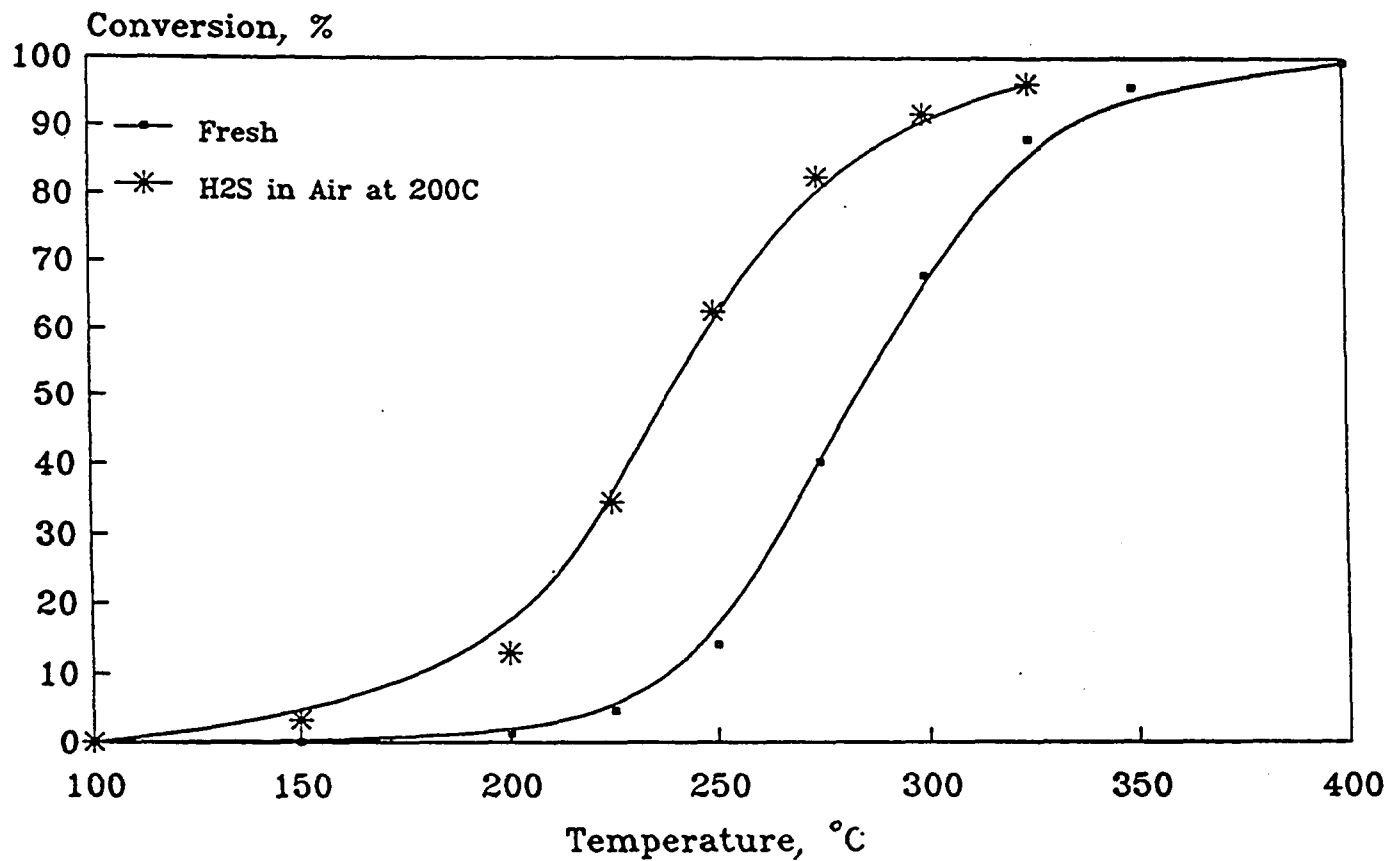
100 ppmv H₂S in Air
Pt/ γ -Al₂O₃ Catalyst

Figure 4-8 Products distribution: H₂S oxidation over Pt/ γ -Al₂O₃ catalyst



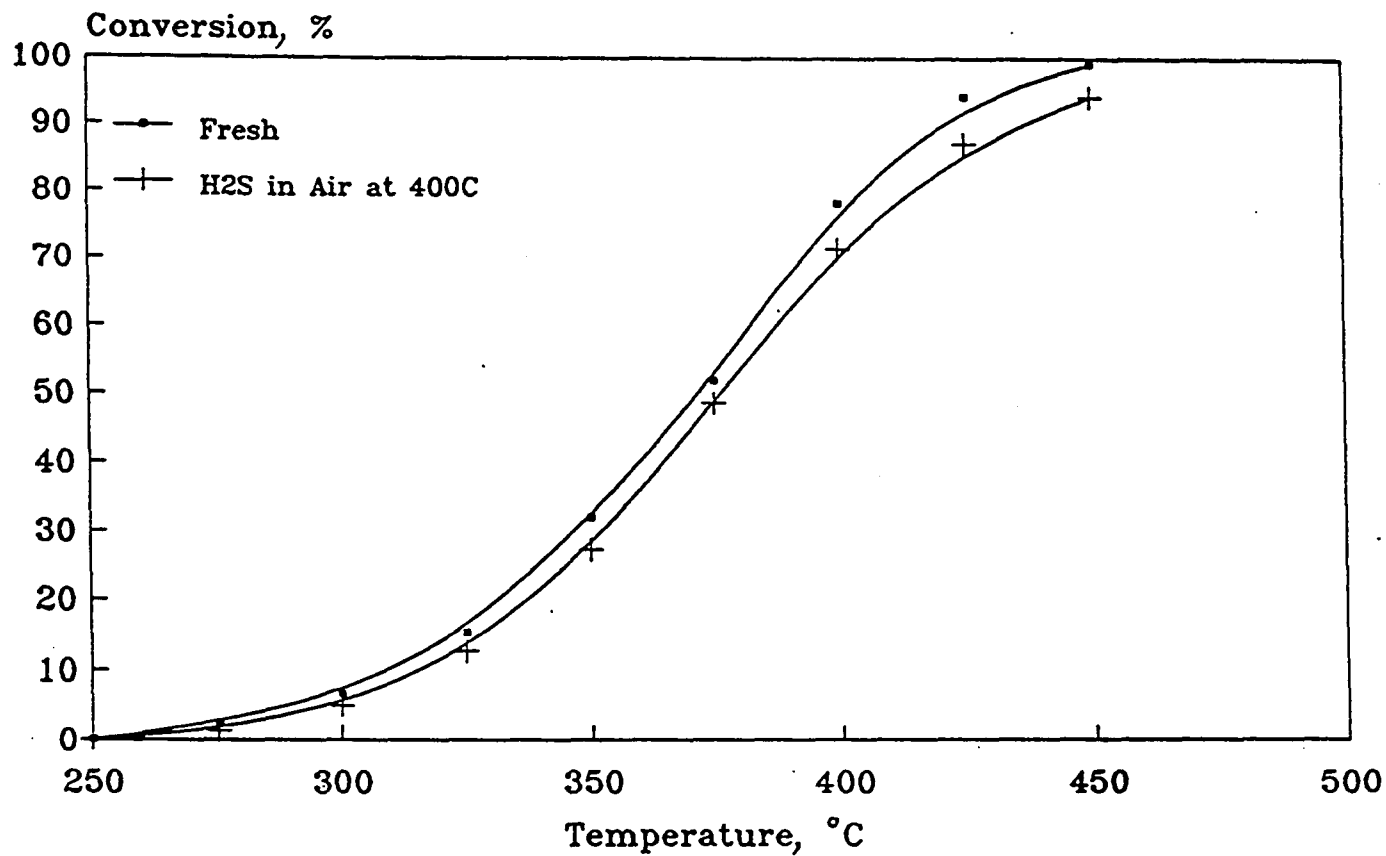
0.05 gram Catalyst
 50 ml/min 1% CO in Air SV=30,000/hr
 100ppm H2S Aged in Air at 200C for 24hrs

Figure 4-9 Comparison of activity: 1% CO oxidation; Fresh Pt/γ-Al₂O₃ vs Pt/γ-Al₂O₃ aged by H₂S in air at 200°C



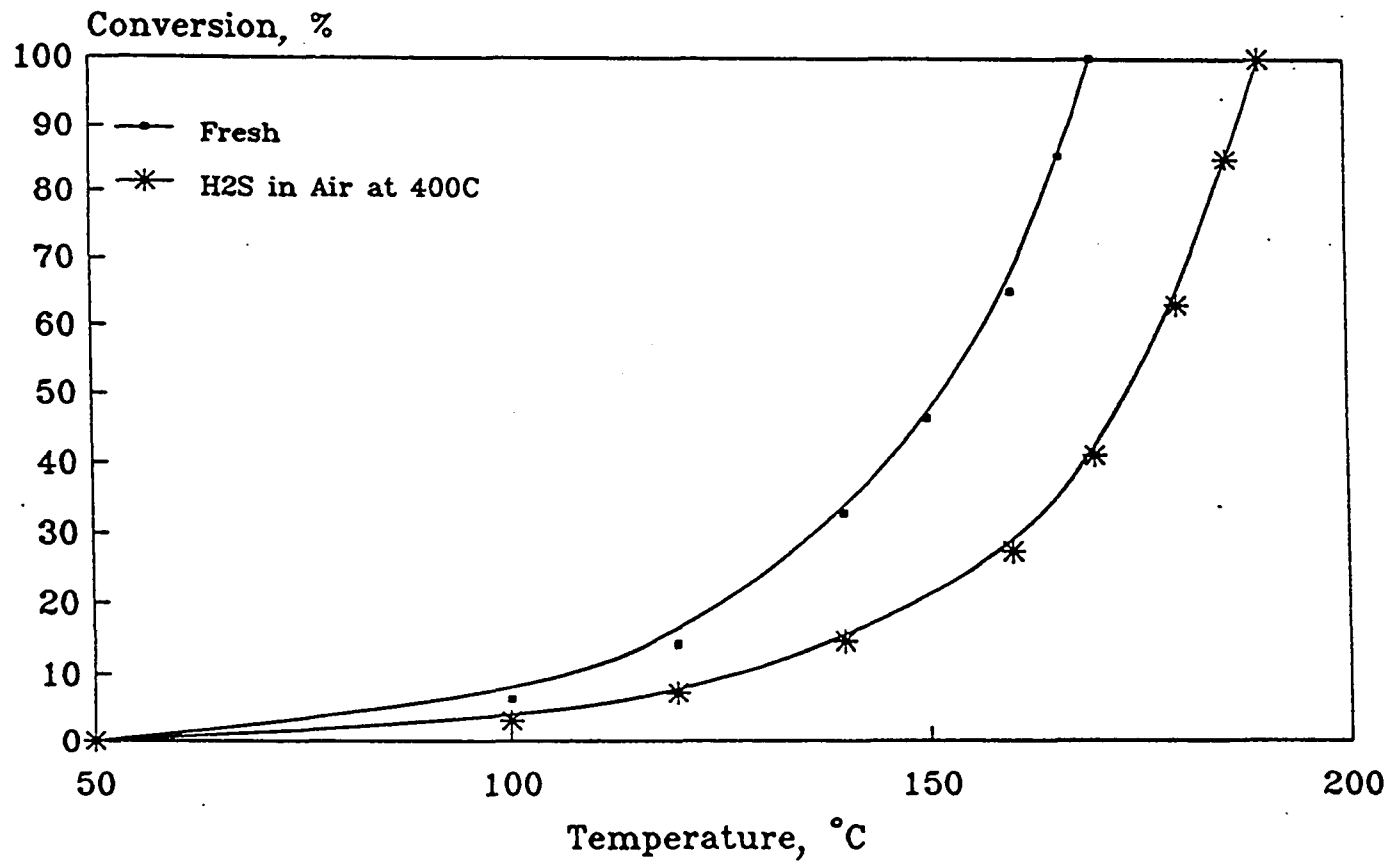
0.05 gram Catalyst
50 ml/min 1% Propane in Air SV=30,000/hr
100ppm H₂S Aged in Air at 200C for 24hrs

Figure 4-10 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in air at 200°C



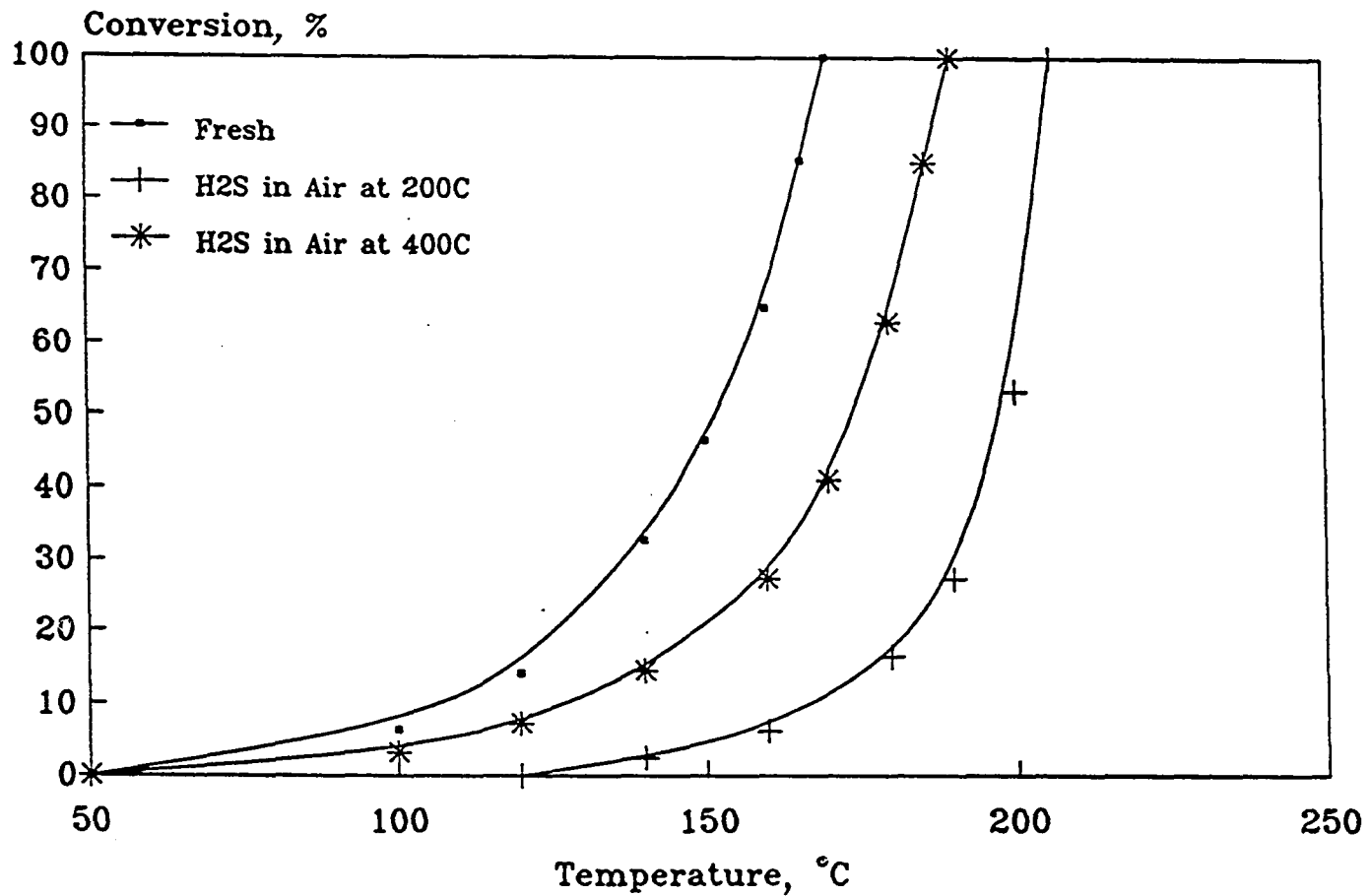
0.05 gram Catalyst
50ml/min 1% CH₄ in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs

Figure 4-11 Comparison of activity: 1% methane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in air at 400°C

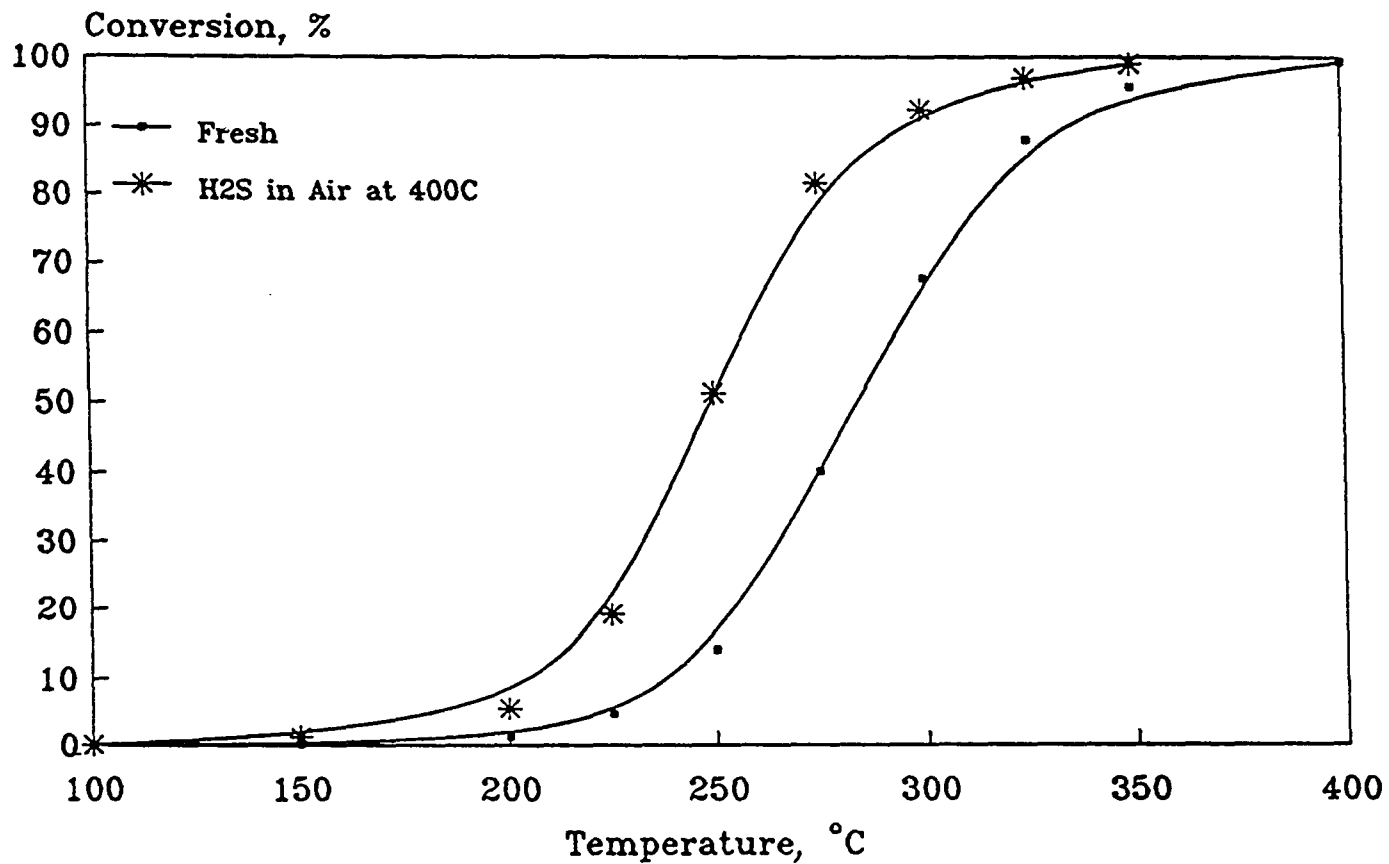


0.05 gram Catalyst
50ml/min 1% CO in Air SV=30,000/hr
100ppm H2S Aged in Air at 400C for 24hrs

Figure 4-12 Comparison of activity: 1% CO oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in air at 400°C



0.05 gram Catalyst
50ml/min 1% CO in Air SV=30,000/hr
Figure 4-13 Comparison of activity: 1% CO oxidation

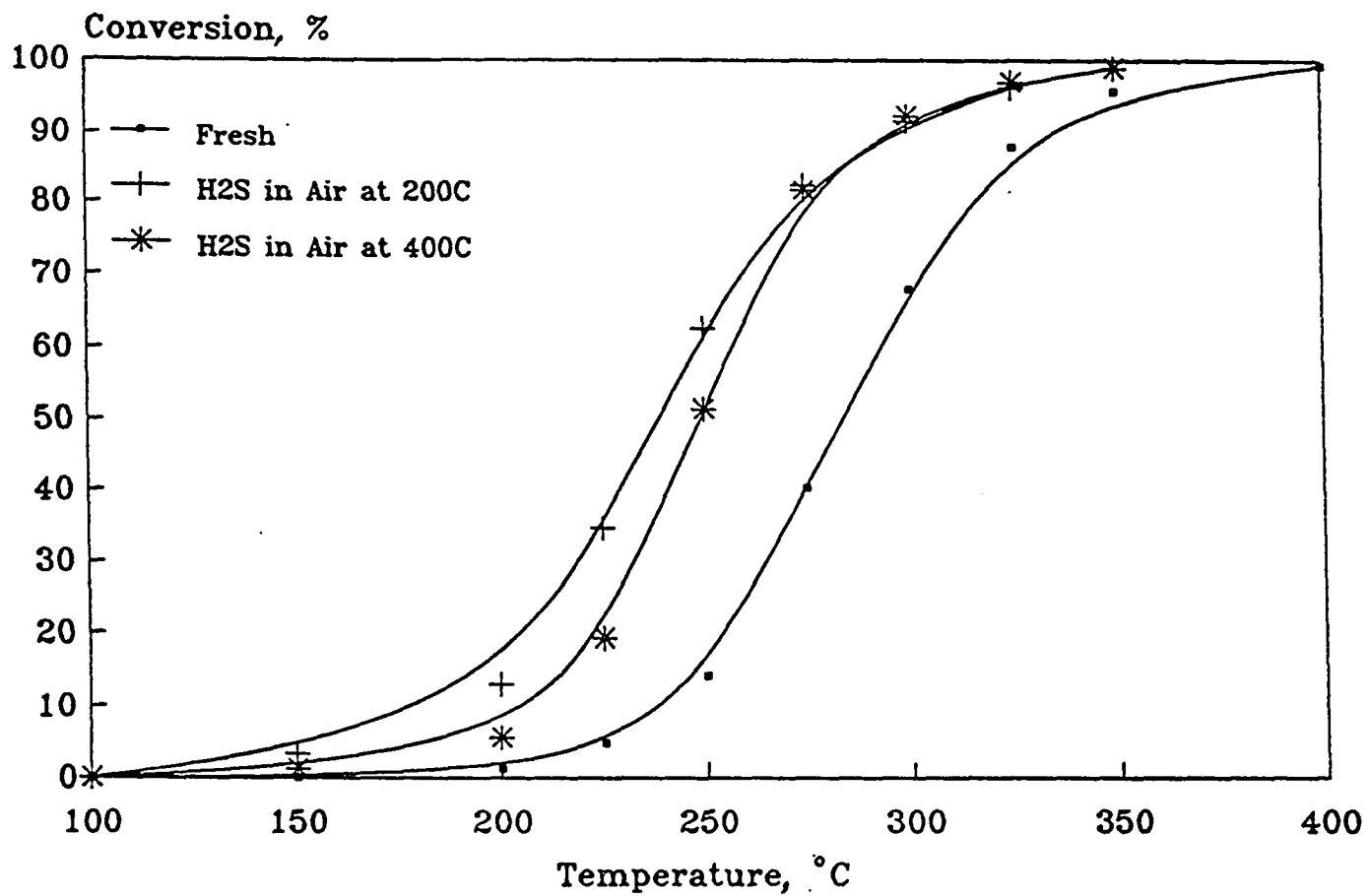


0.05 gram Catalyst

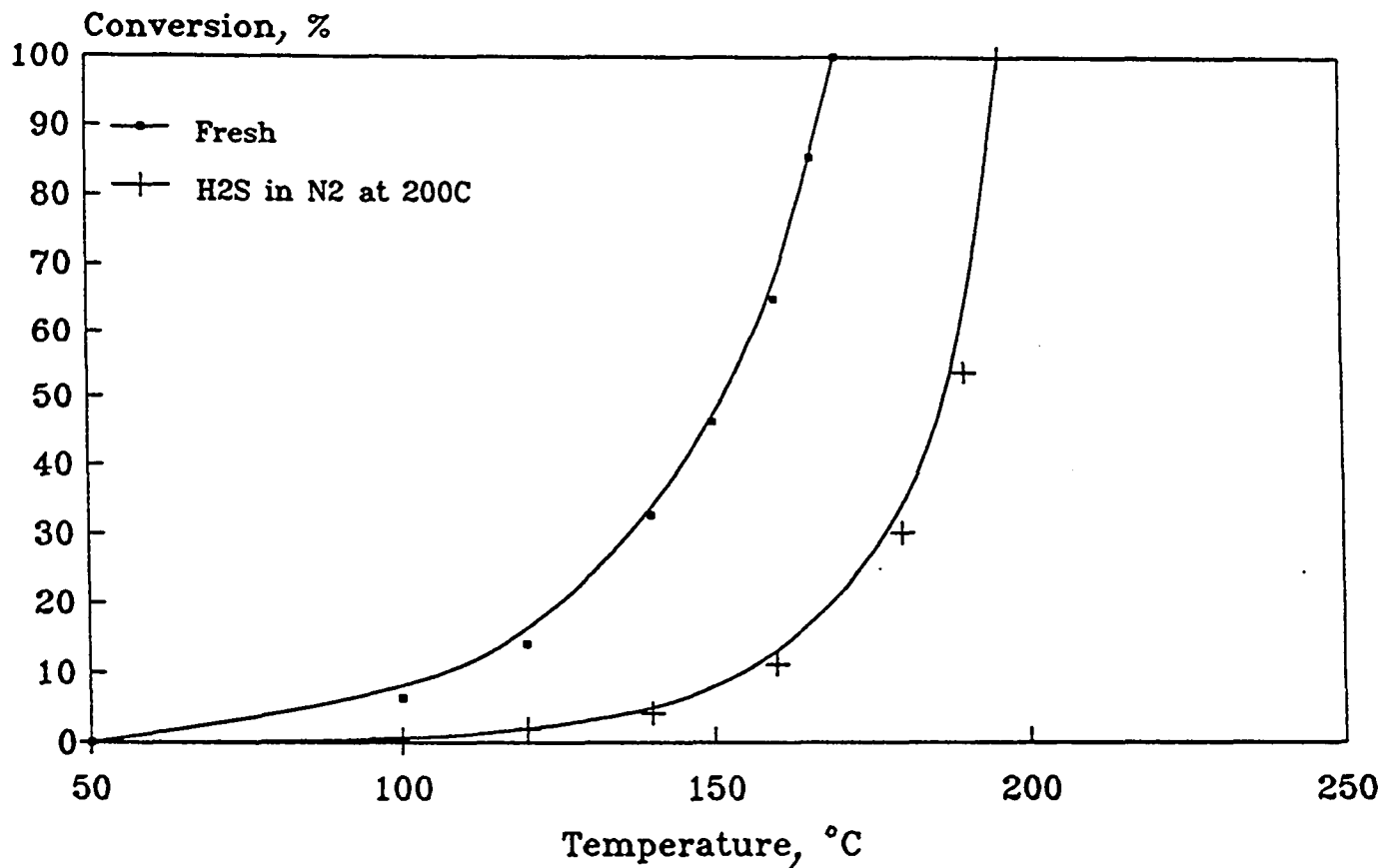
50ml/min 1% Propane in Air SV=30,000/hr

100ppm H2S Aged in Air at 400C for 24hrs

Figure 4-14 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in air at 400°C

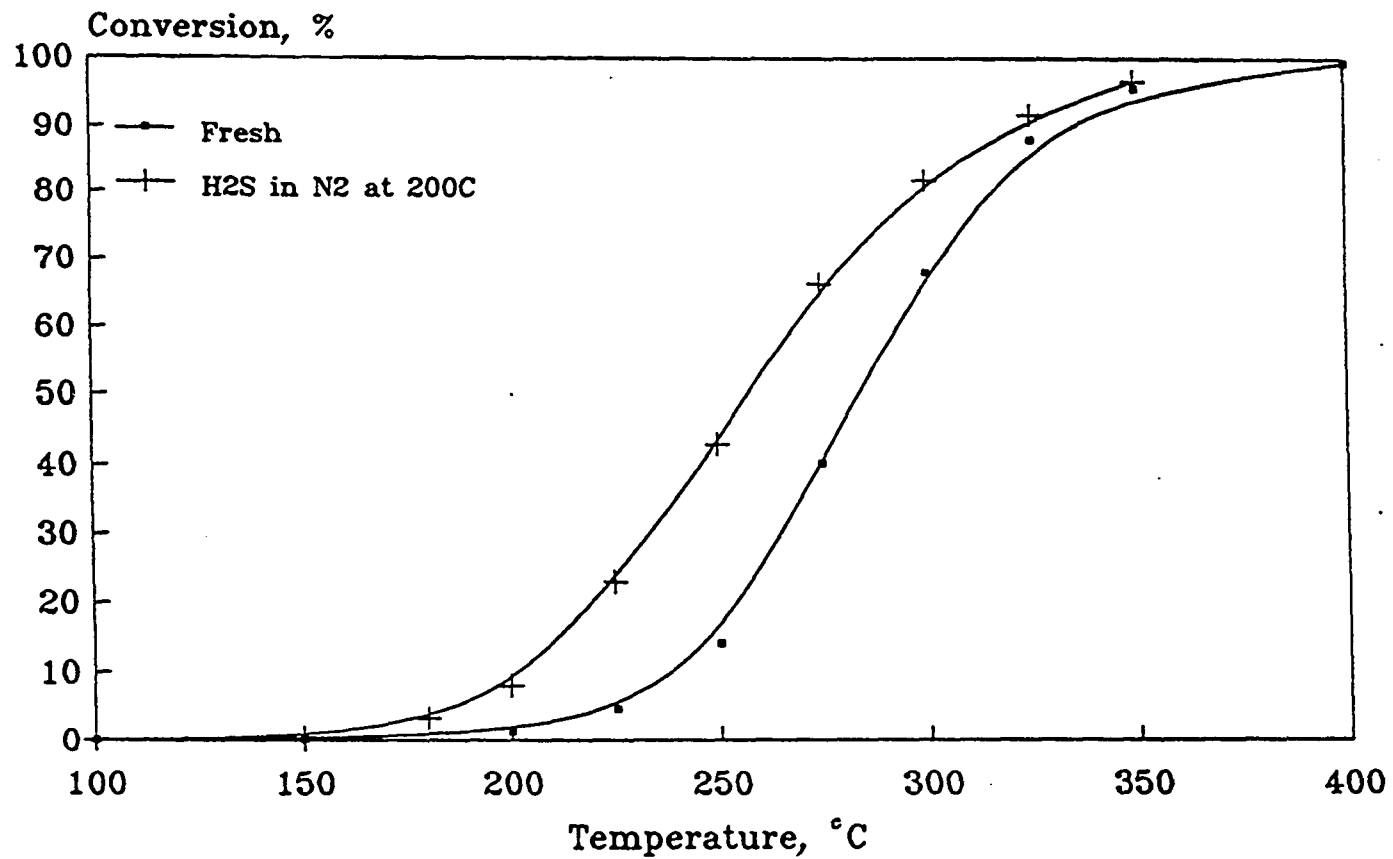


0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
Figure 4-15 Comparison of activity: 1% propane oxidation



0.05 gram Catalyst
50 ml/min 1% CO in Air SV=30,000/hr
100ppm H2S Aged in N2 at 200C for 24hrs

Figure 4-16 Comparison of activity: 1% CO oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in nitrogen at 200°C

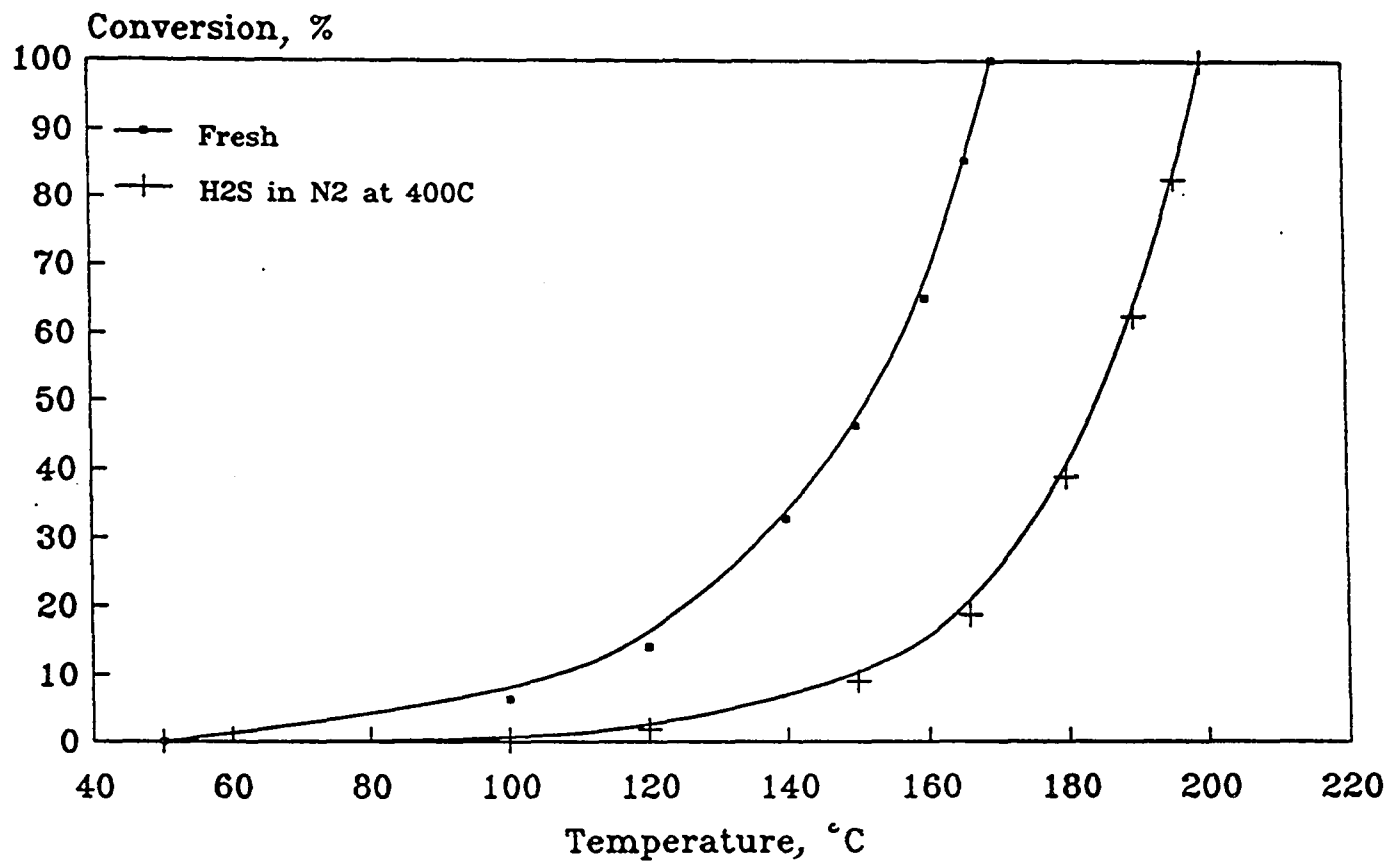


0.05 gram Catalyst

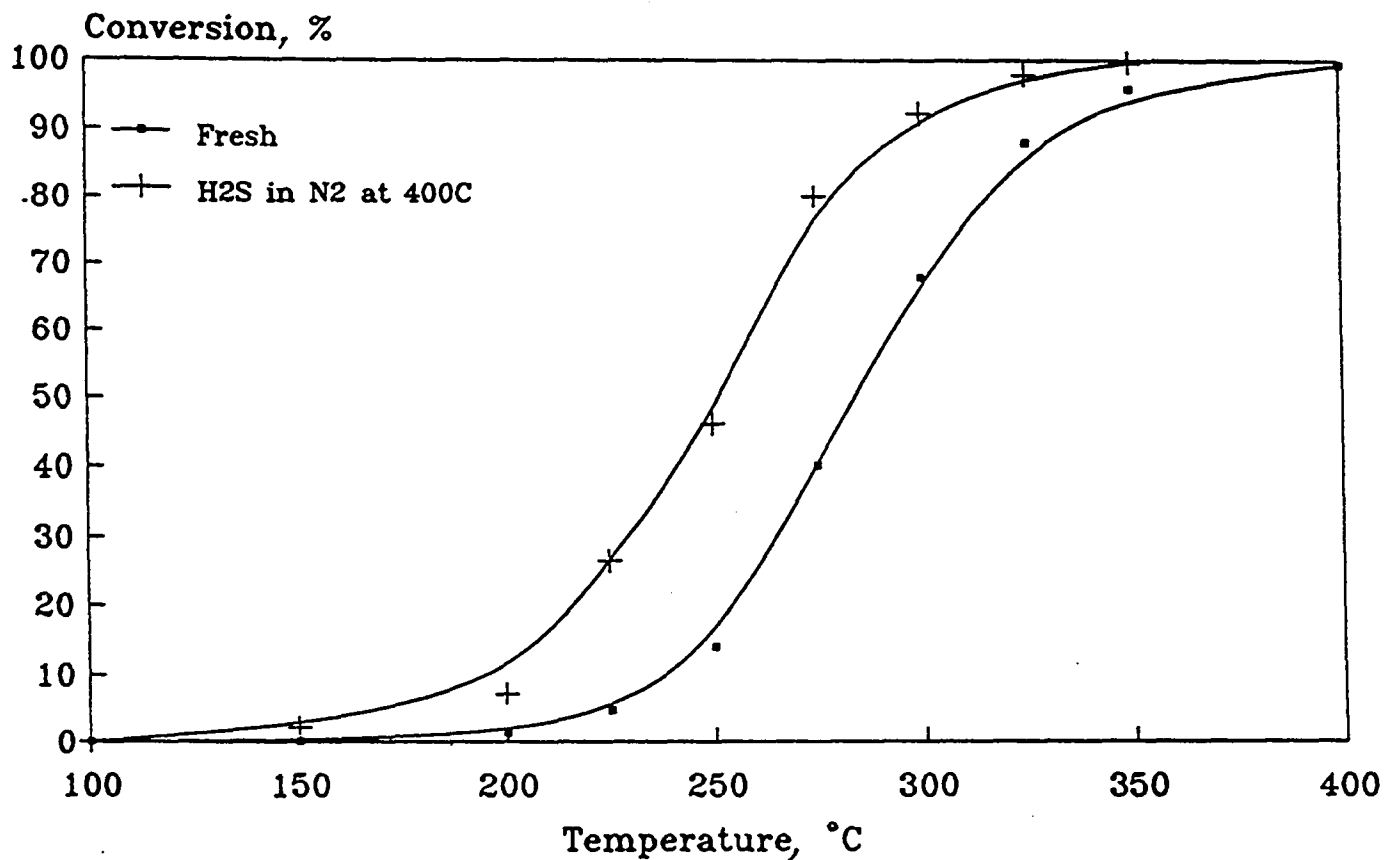
50 ml/min 1% Propane in Air SV=30,000/hr

100ppm H2S Aged in N2 at 200C for 24hrs

Figure 4-17 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in nitrogen at 200°C



0.05 gram Catalyst
50 ml/min 1% CO in Air SV=30,000/hr
100ppm H₂S Aged in N₂ at 400C for 24hrs
Figure 4-18 Comparison of activity: 1% CO oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in nitrogen at 400°C



0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
100ppm H2S Aged in N2 at 400C for 24hrs
Figure 4-19 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by H₂S in nitrogen at 400°C

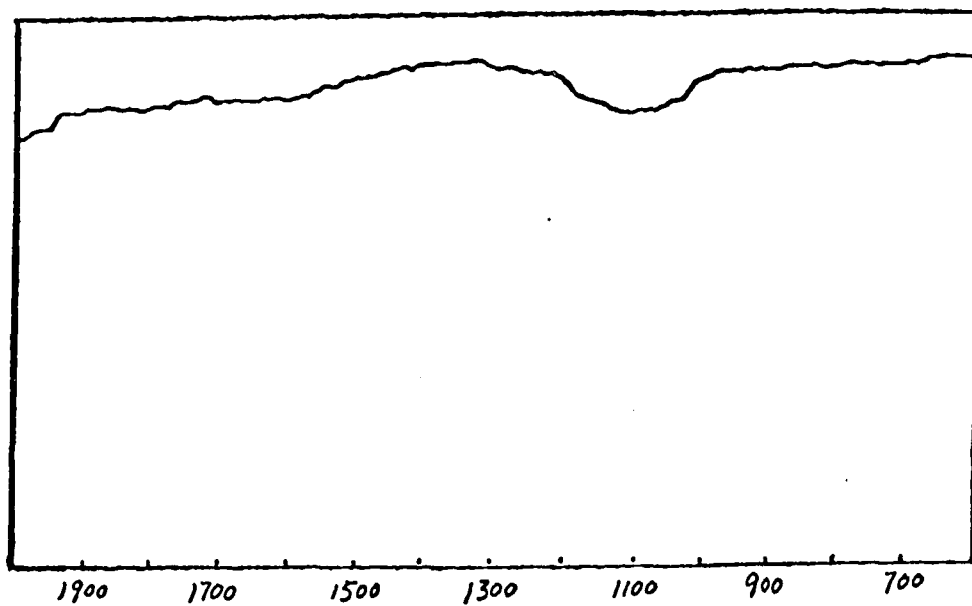


Figure 4-20 IR spectra of Pt/ γ -Al₂O₃ catalyst aged by H₂S in air at 400°C

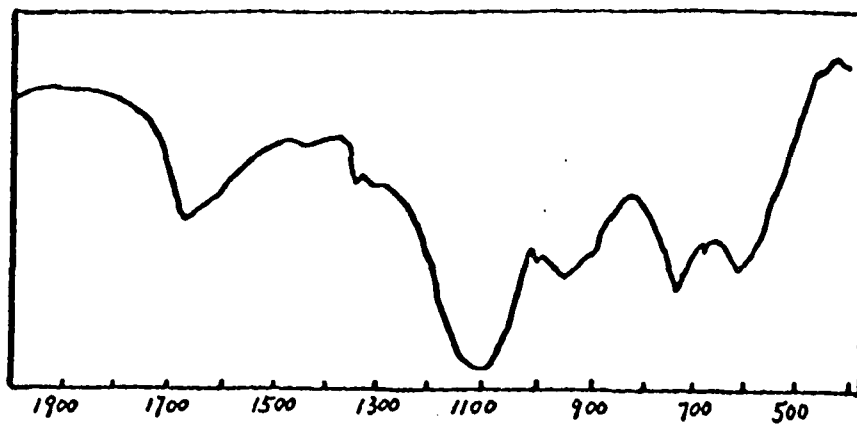


Figure 4-21 IR spectra of standard Al₂(SO₄)₃

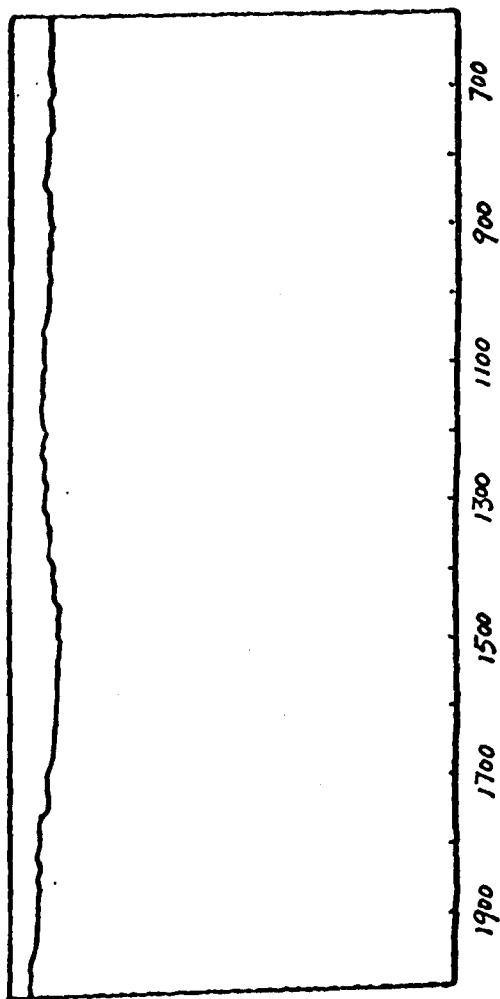


Figure 4-22 IR spectra of Pt γ -Al $_2$ O $_3$ catalyst aged by H $_2$ S in nitrogen at 400°C

Curve 1: TGA
 File info: yw-020 Fri May 14 12:37:29 1993
 Sample Weight: 7.718 mg
 1.5% Pt H₂S adsorption 100C

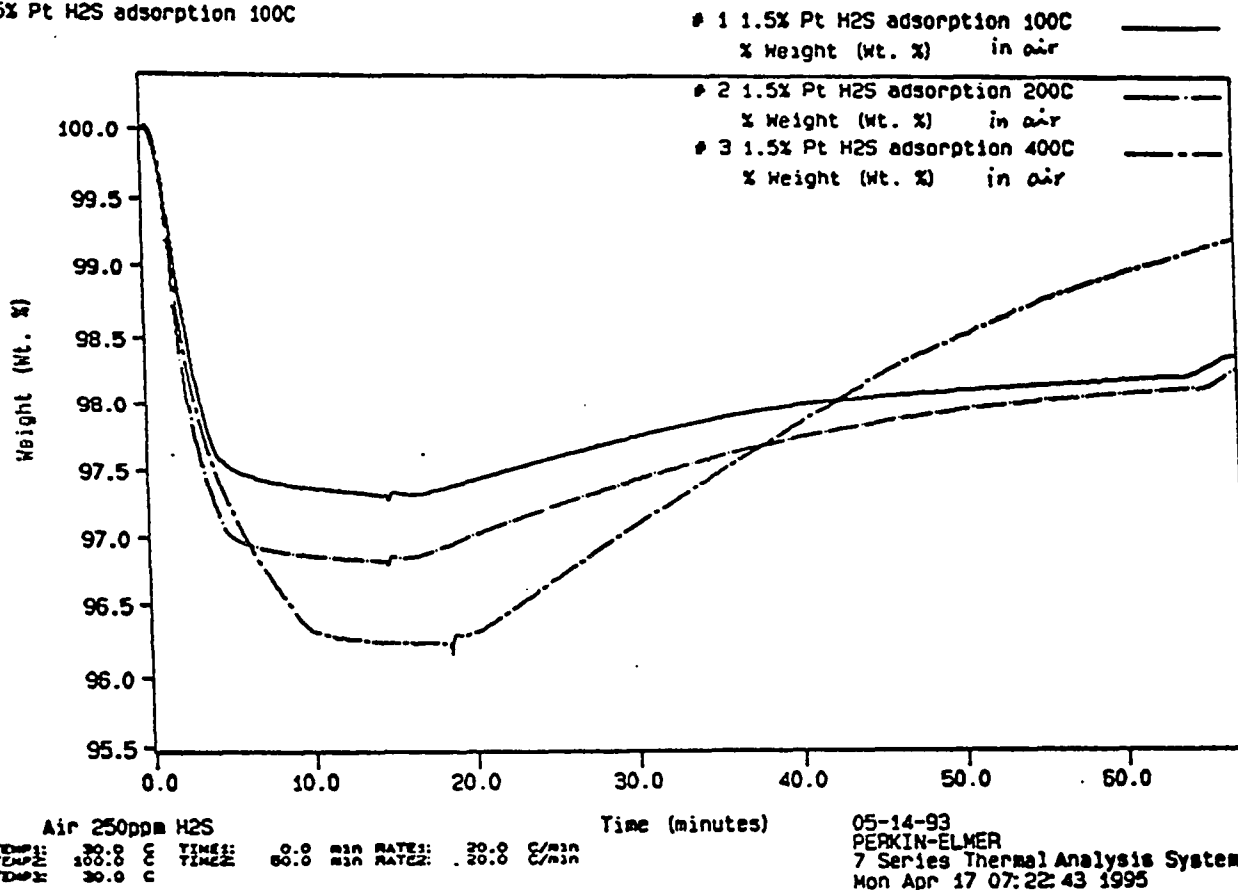


Figure 4-23 TGA test: H₂S adsorption: Pt/γ-Al₂O₃ catalyst in air at different temperature

Curve 1: TGA
 File info: yw-024 Tue May 18 11: 39: 46 1993
 Sample Weight: 8.207 mg
 1.5% Pt H₂S adsorption N₂ 100C

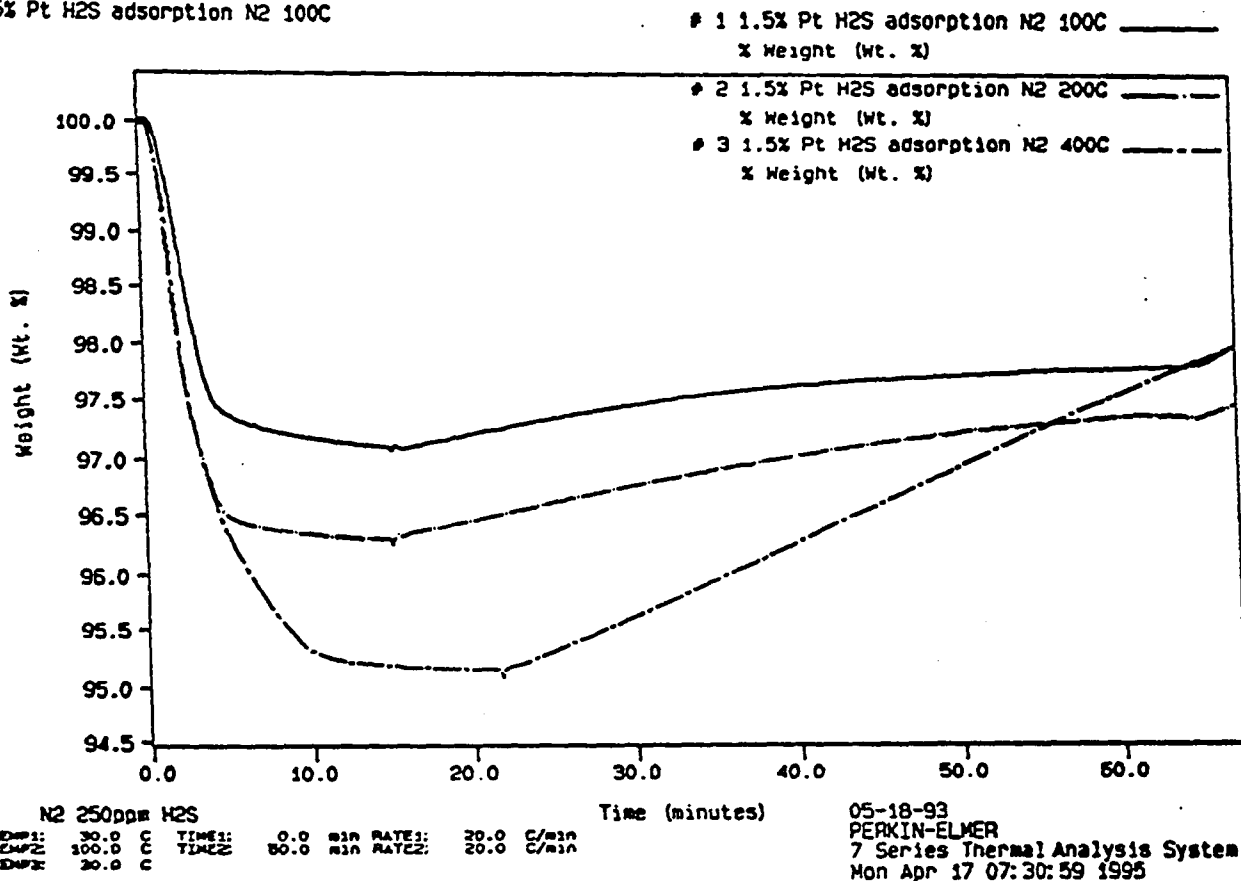


Figure 4-24 TGA test: H₂S adsorption: Pt/ γ -Al₂O₃ catalyst in nitrogen at different temperature

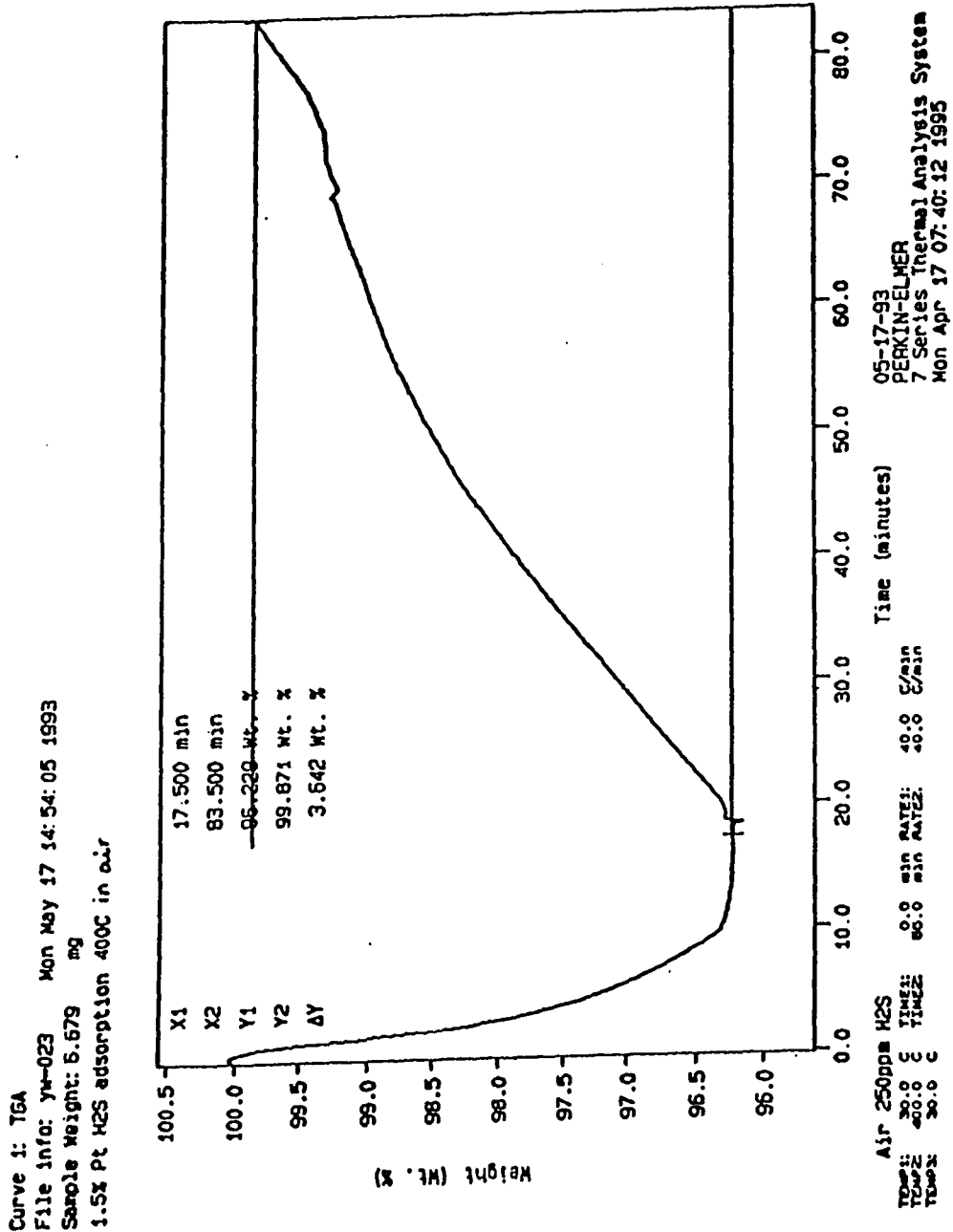


Figure 4-25 TGA test: H₂S induced weigh gain: Pt/γ-Al₂O₃ catalyst in air at 400°C

Curve 1: TGA
 File info: yw-027 Wed May 19 14: 34: 58 1993
 Sample Weight: 8.888 mg
 1.5% Pt H₂S adsorption N₂ 400C

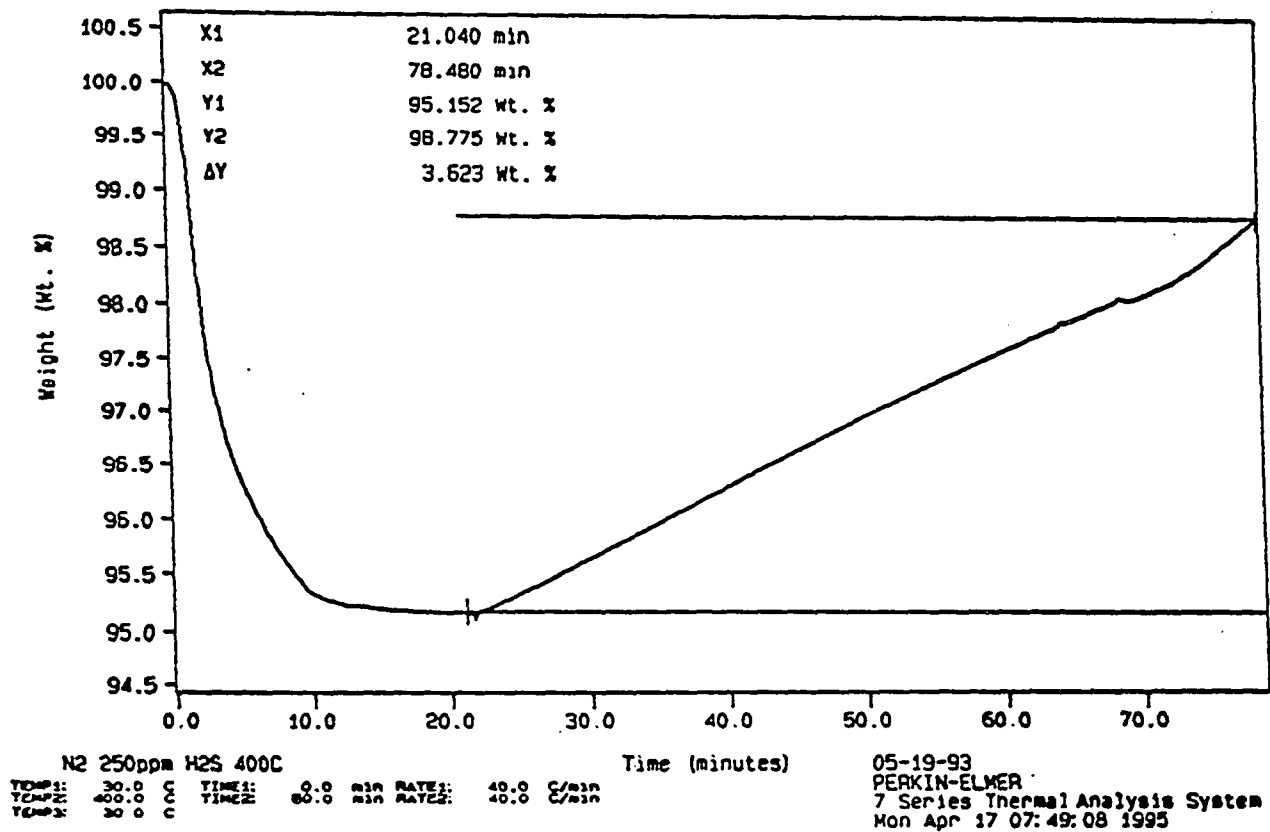


Figure 4-26 TGA test: H₂S induced weigh gain: Pt/γ-Al₂O₃ catalyst in nitrogen at 400°C

Curve 1: TGA
 File info: yw014 Mon May 3 16:38:27 1993
 Sample Weight: 5.389 mg
 Al2O3 H2S treatment in air

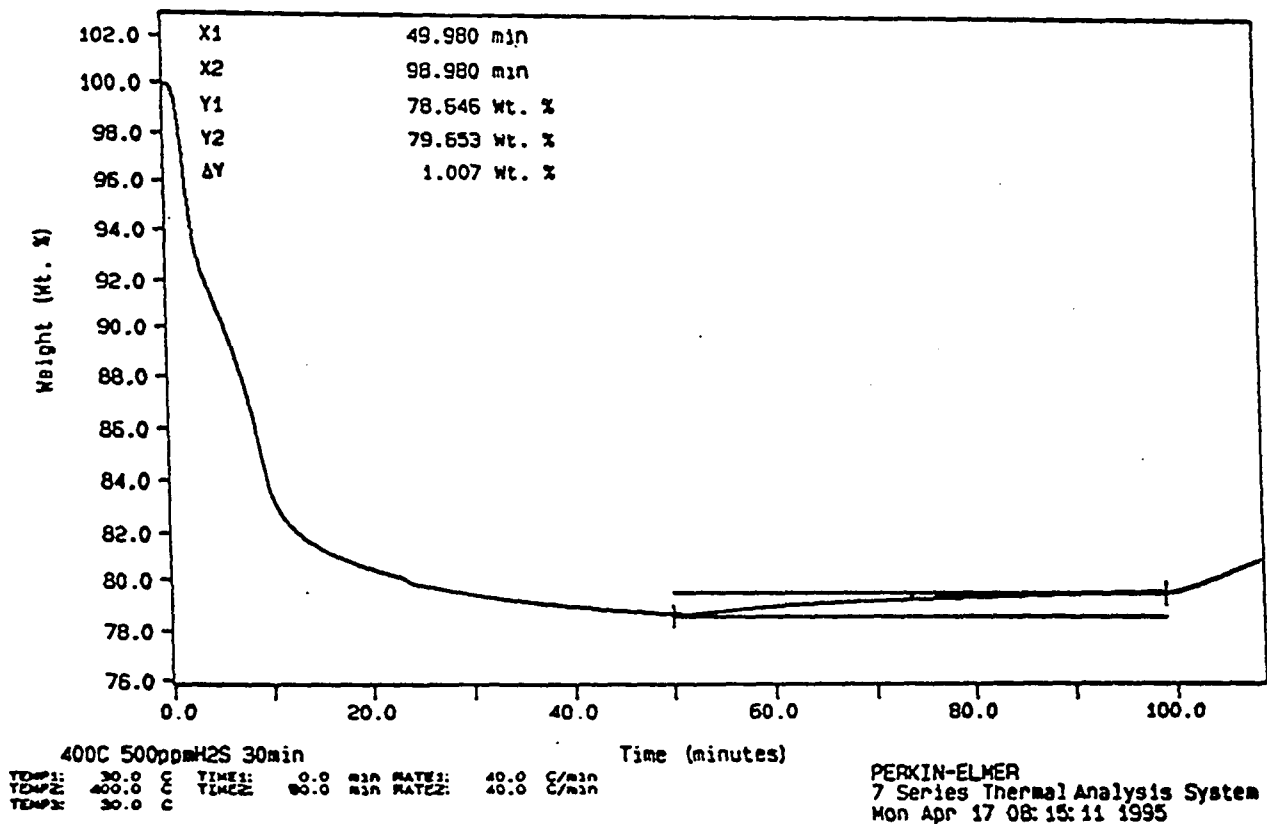


Figure 4-27 TGA test: H₂S induced weigh gain: Pure γ -Al₂O₃ in air at 400°C

Curve 1: TGA
File info: yw-024 Tue May 18 11:39:46 1993
Sample Weight: 8.207 mg
1.5% Pt H₂S adsorption N₂ 100C

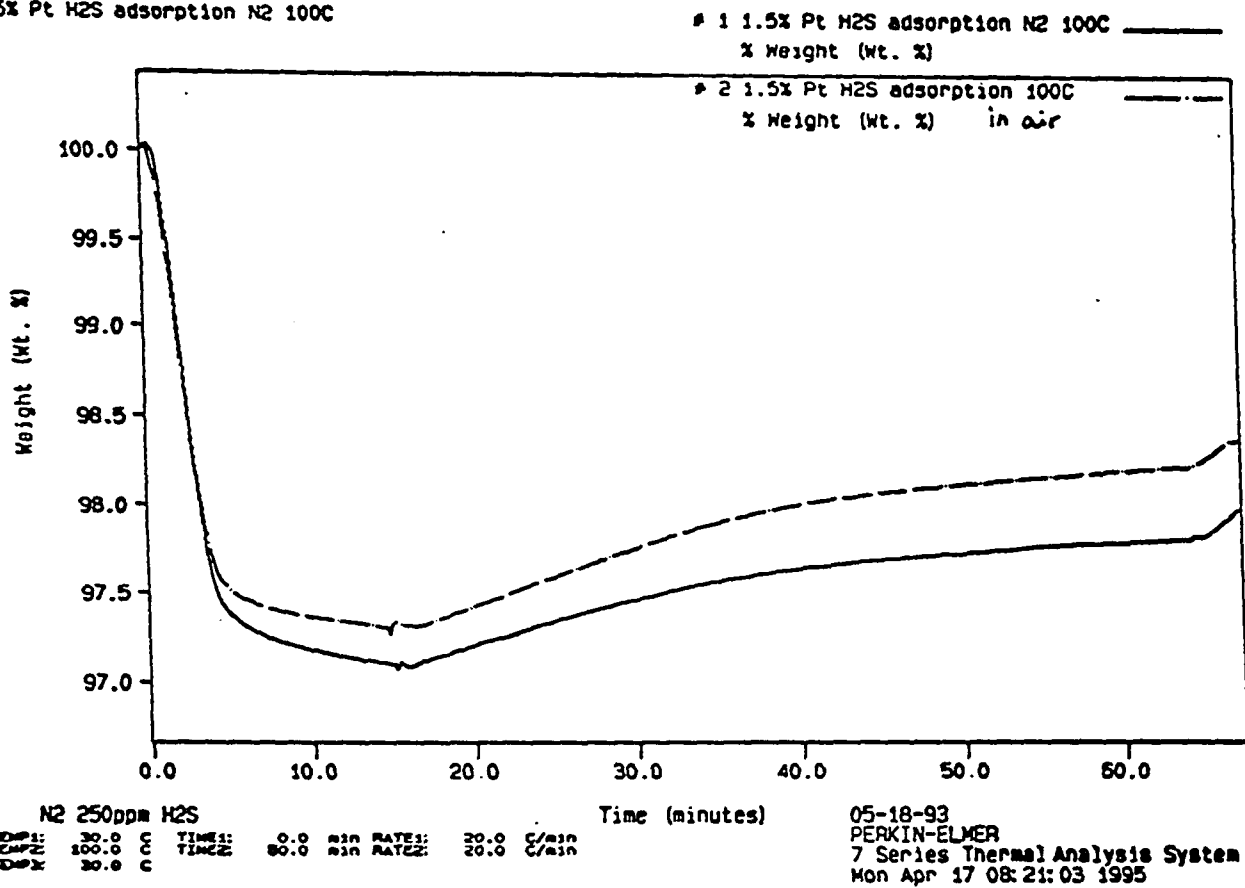


Figure 4-28 TGA test: H₂S adsorption: Comparison of different atmosphere at 100°C

Curve 1: TGA
 File info: yw-025 Tue May 18 14:39:23 1993
 Sample Weight: 6.991 mg
 1.5% Pt H₂S adsorption N₂ 200C

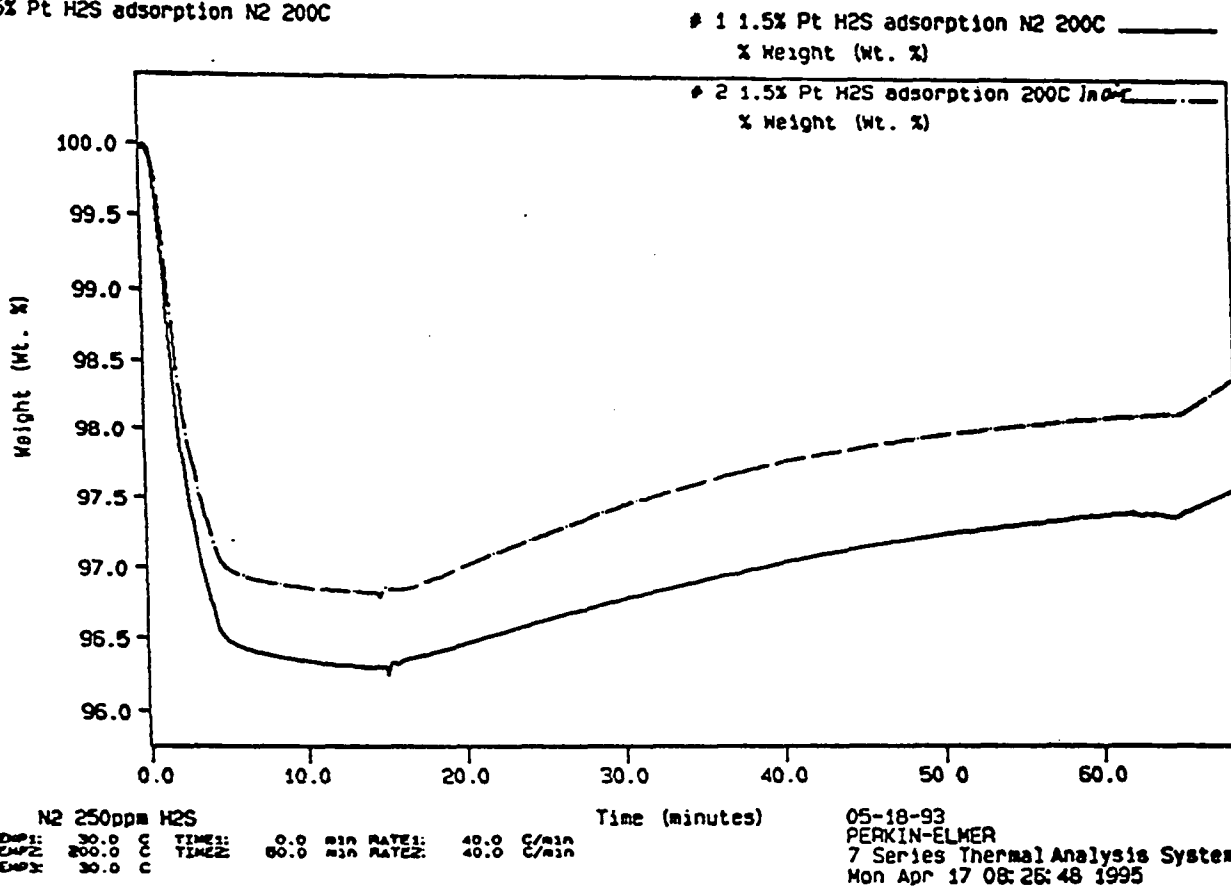


Figure 4-29 TGA test: H₂S adsorption: Comparison of different atmosphere at 200°C

Curve 1: TGA

File info: yw-027 Wed May 19 14: 34: 58 1993

Sample Weight: 8.888 mg

1.5% Pt H₂S adsorption N₂ 400C

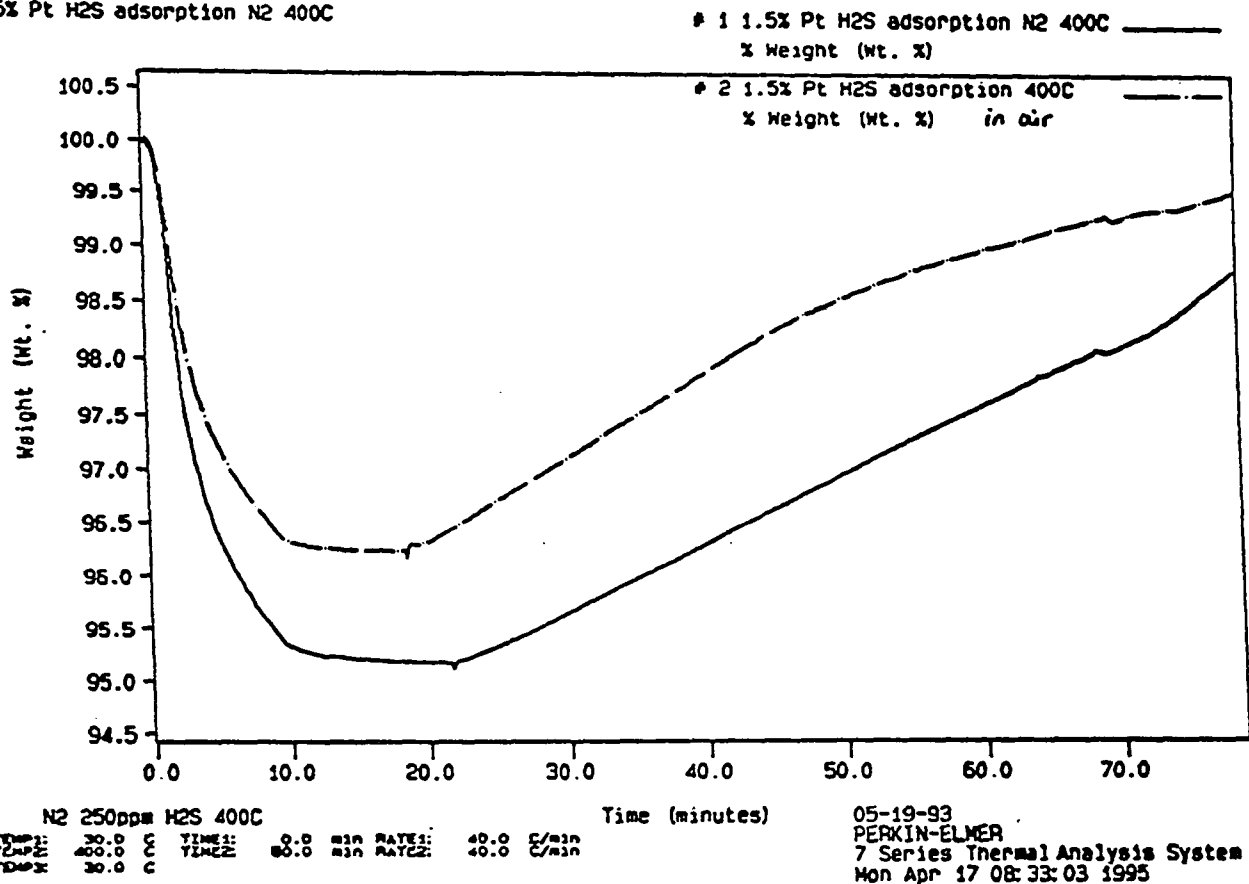


Figure 4-30 TGA test: H₂S adsorption: Comparison of different atmosphere at 400°C

Curve 1: TGA
 File info: yw-028 Fri May 21 15:31:18 1993
 Sample Weight: 8.427 mg
 1.5% Pt comparison with adsorption

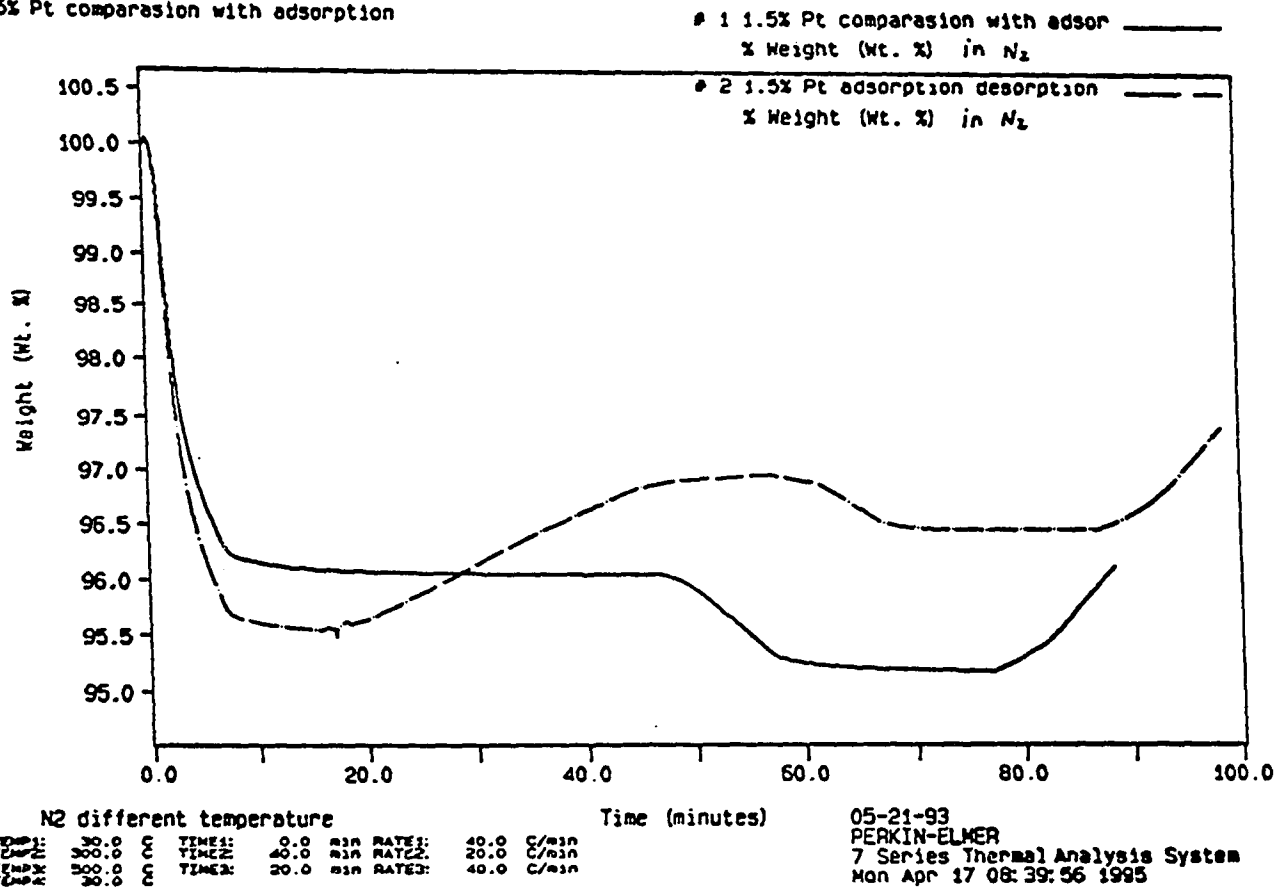


Figure 4-31 TGA test: comparison of weigh loss due to temperature increase: With H₂S vs without H₂S

Curve 1: TGA
 File info: yw-026 Fri May 21 12:46:46 1993
 Sample Weight: 9.021 mg
 1.5% Pt adsorption desorption in N₂

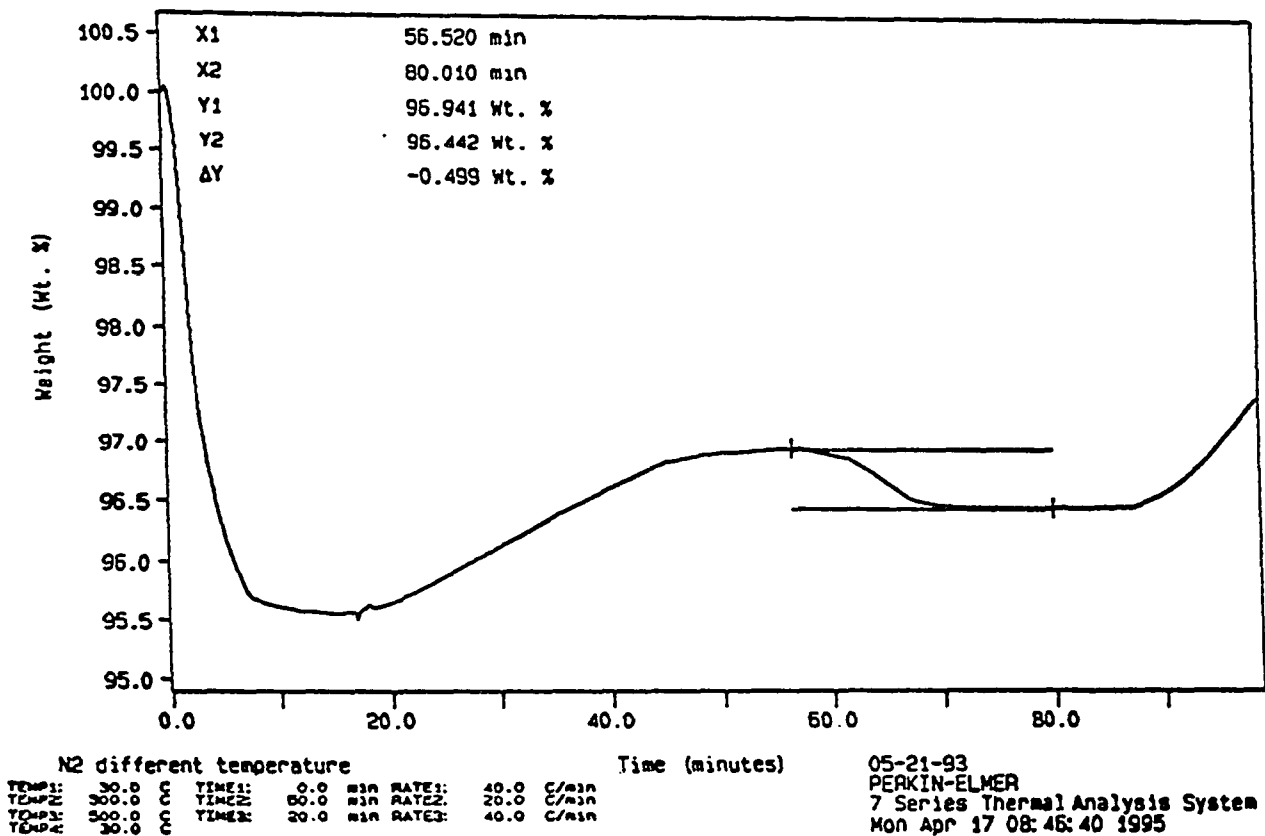


Figure 4-32 TGA test: weigh loss due to temperature increase (with H₂S)

Curve 1: TGA
 File info: yw-028 Fri May 21 15:31:18 1993
 Sample Weight: 8.427 mg
 1.5% Pt comparasion with adsorption

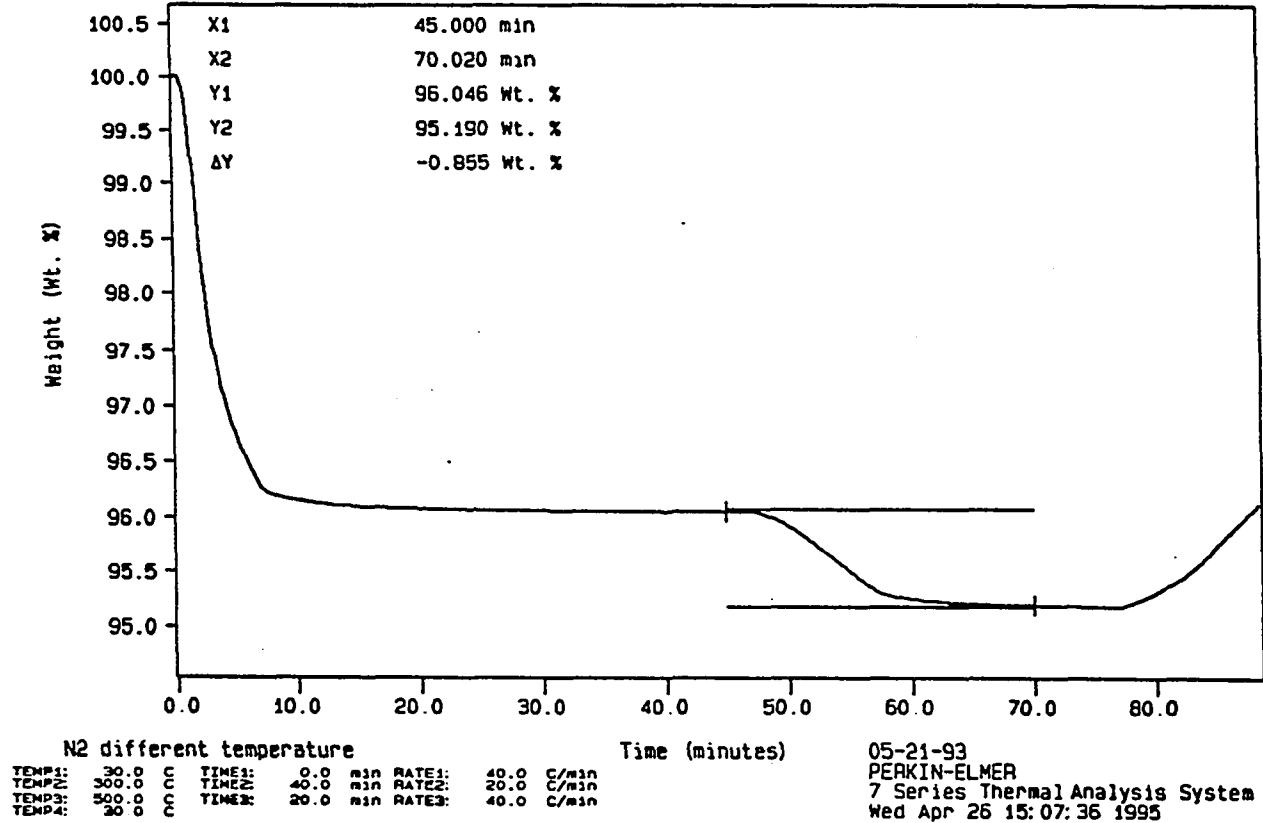
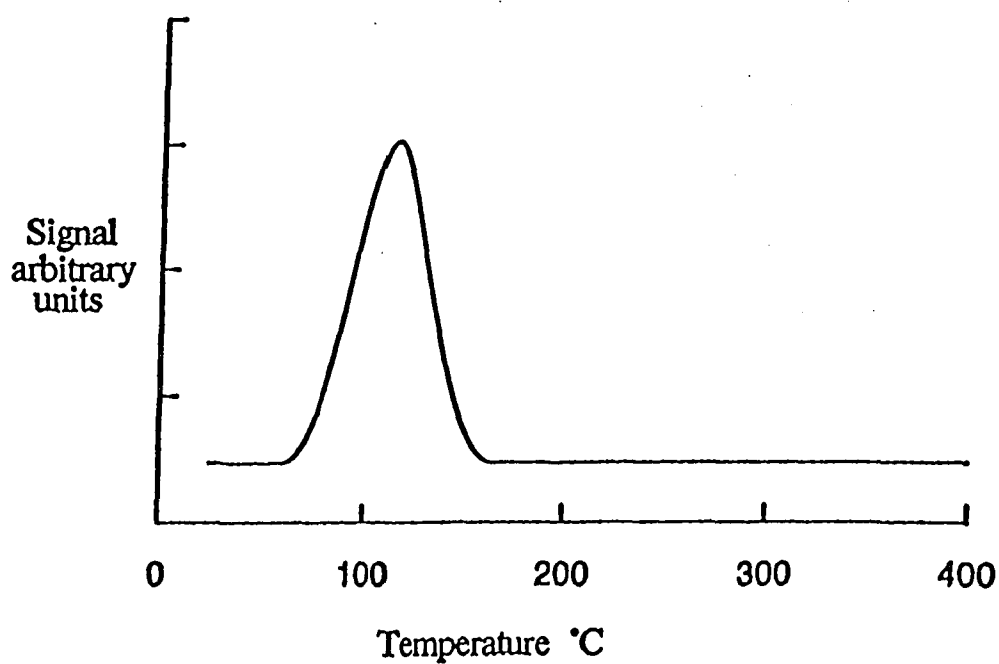


Figure 4-33 TGA test: weigh loss due to temperature increase (without H₂S)



Idealized TPD pattern for characterizing acid sites by desorption of a simple base like ammonia. Temperature at maximum gives information on the intensive factor; area under the curve gives quantitative information on the extensive factor.

Figure 4-34 Profile of typical ammonia titration test

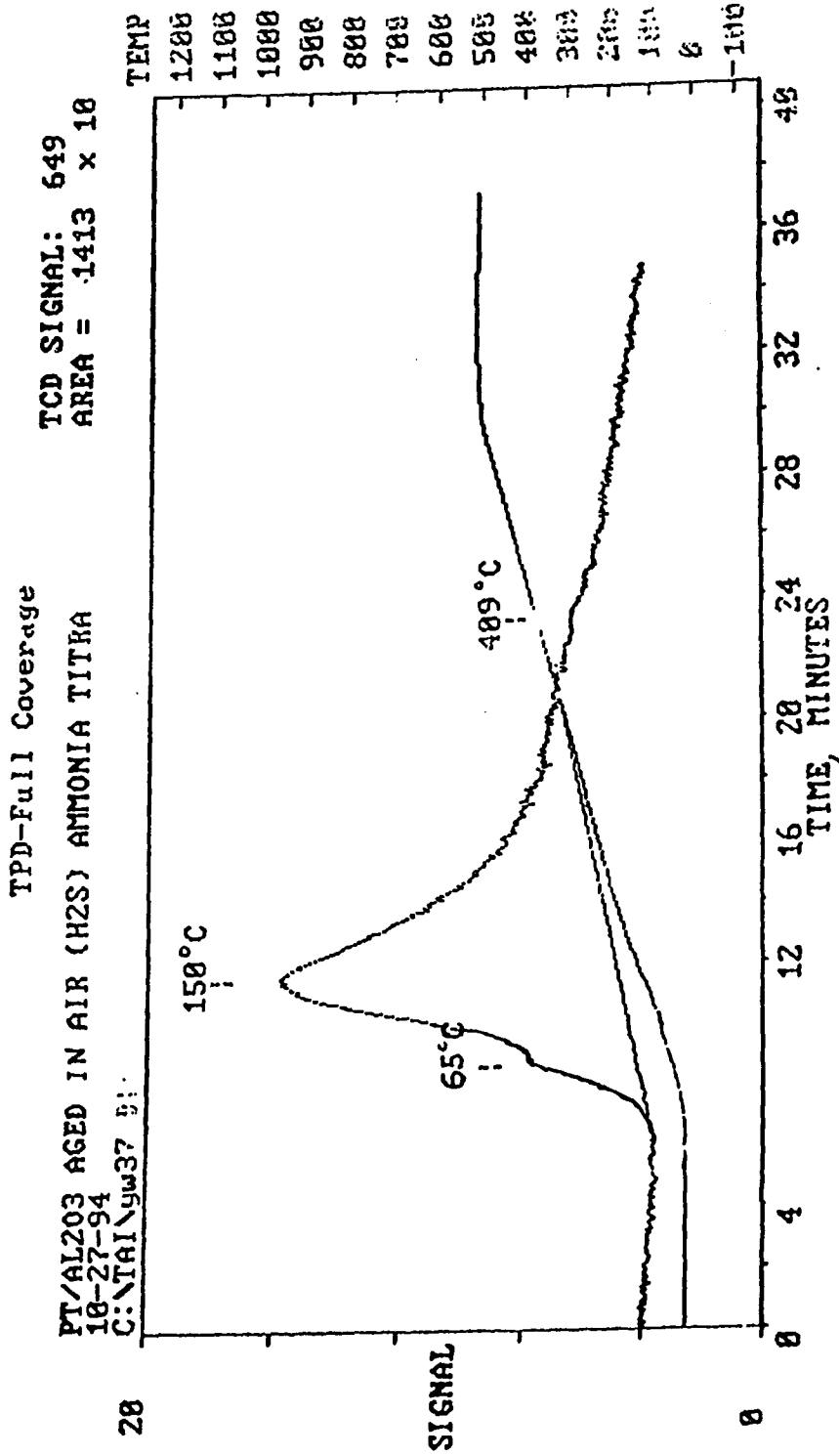


Figure 4-35 Ammonia titration: Pt/ γ -Al₂O₃ catalyst aged by H₂S in air at 400°C

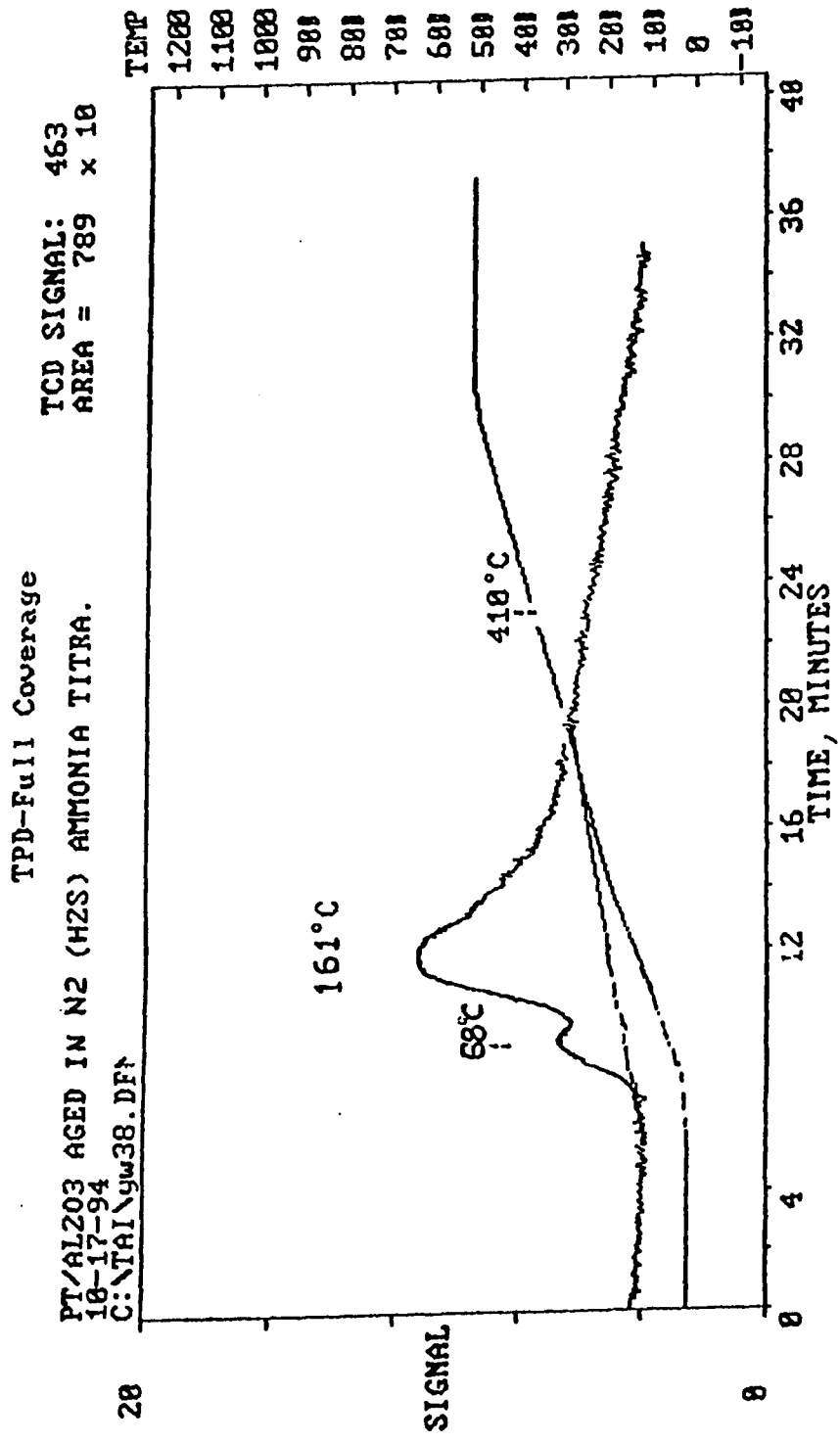


Figure 4-36 Ammonia titration: Pt/ γ -Al₂O₃ catalyst aged by H₂S in nitrogen at 400°C

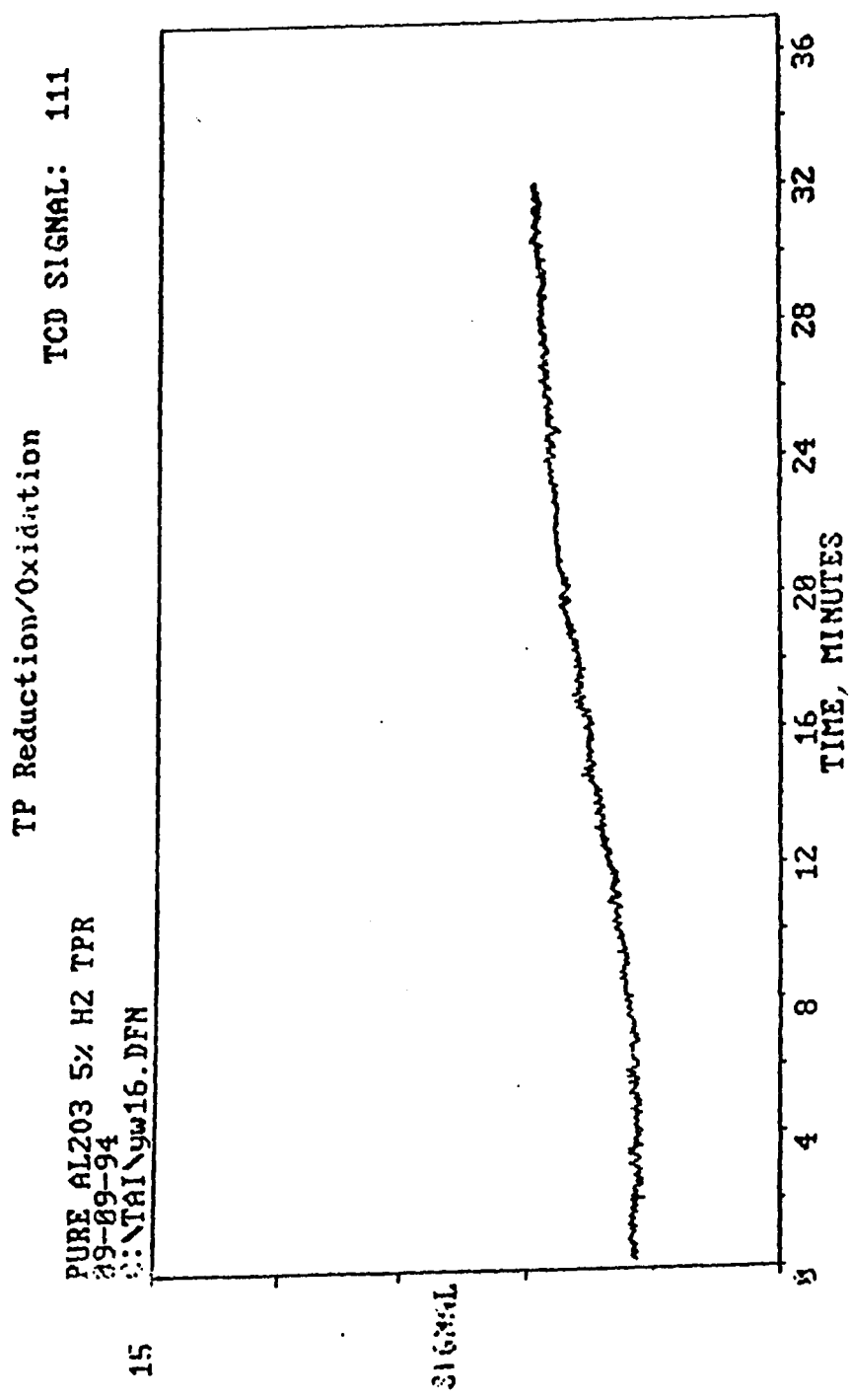


Figure 4-37 5% hydrogen temperature program reduction: Pure γ -Al₂O₃

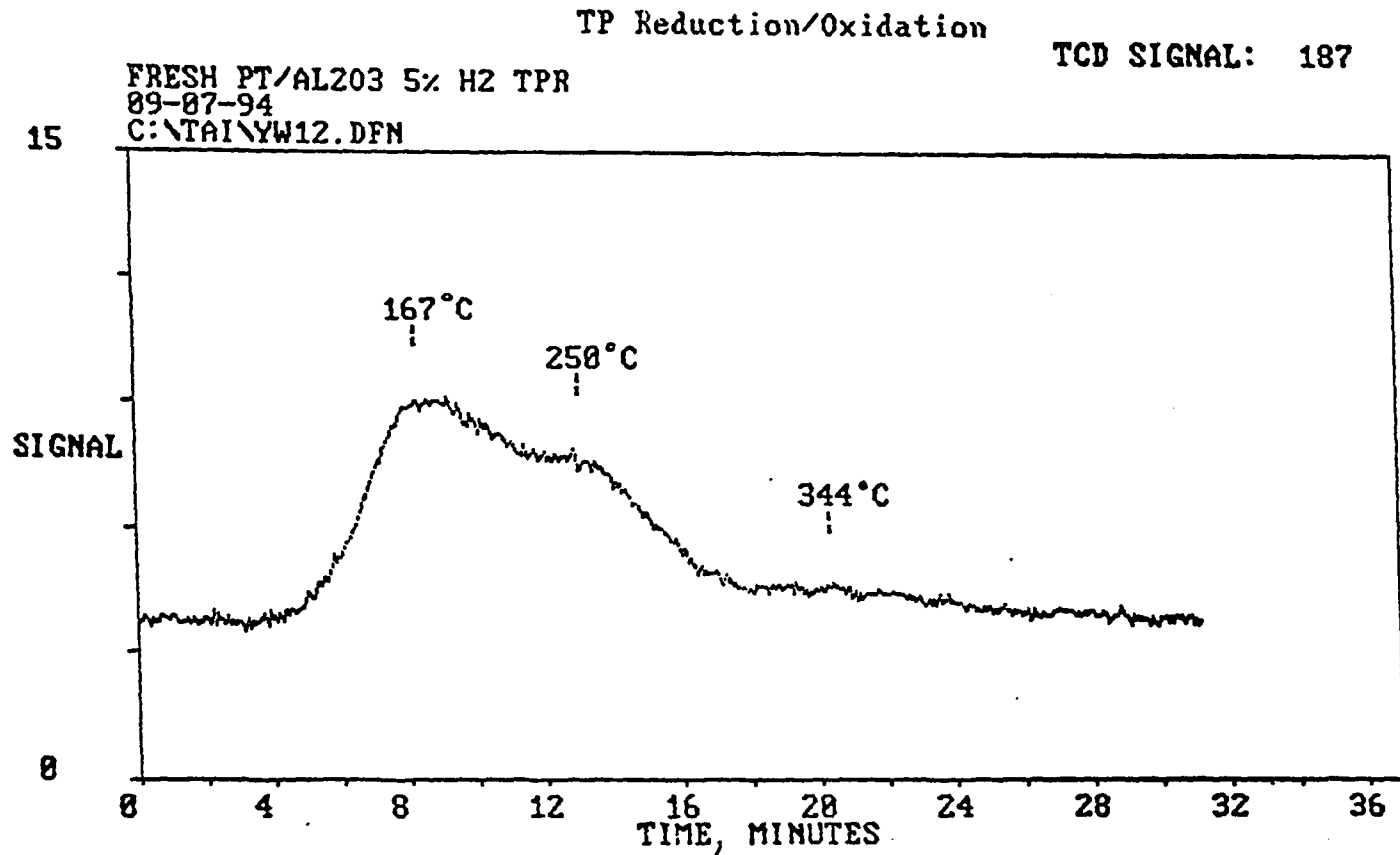


Figure 4-38 5% hydrogen temperature program reduction: Fresh Pt/ γ -Al₂O₃ catalyst

TP Reduction/Oxidation
TCD SIGNAL: 373
H2S AGED PT/AL2O3 IN AIR TPR
89-86-94
C:\TAI\yw86.DFN

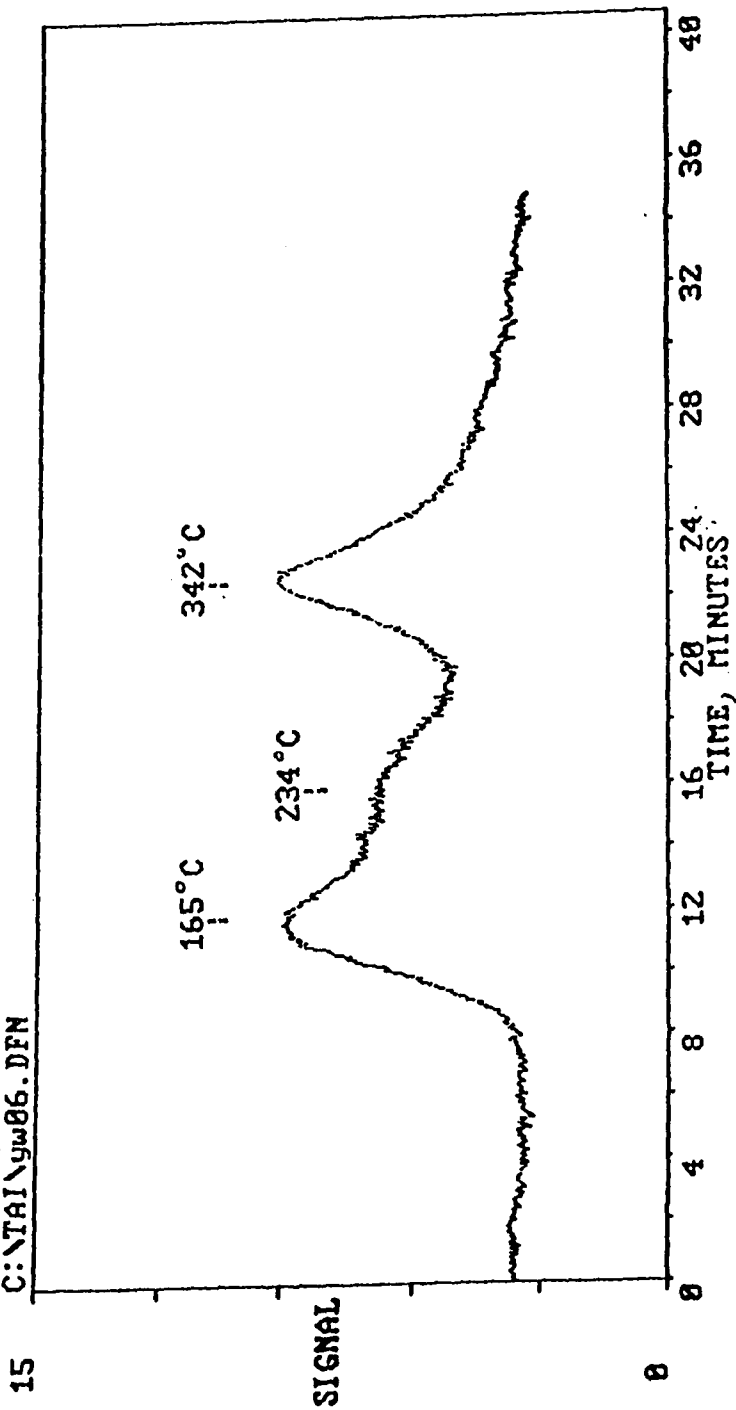


Figure 4-39 5% hydrogen temperature program reduction: Pt/ γ - Al_2O_3 catalyst aged by H_2S in air at 400°C

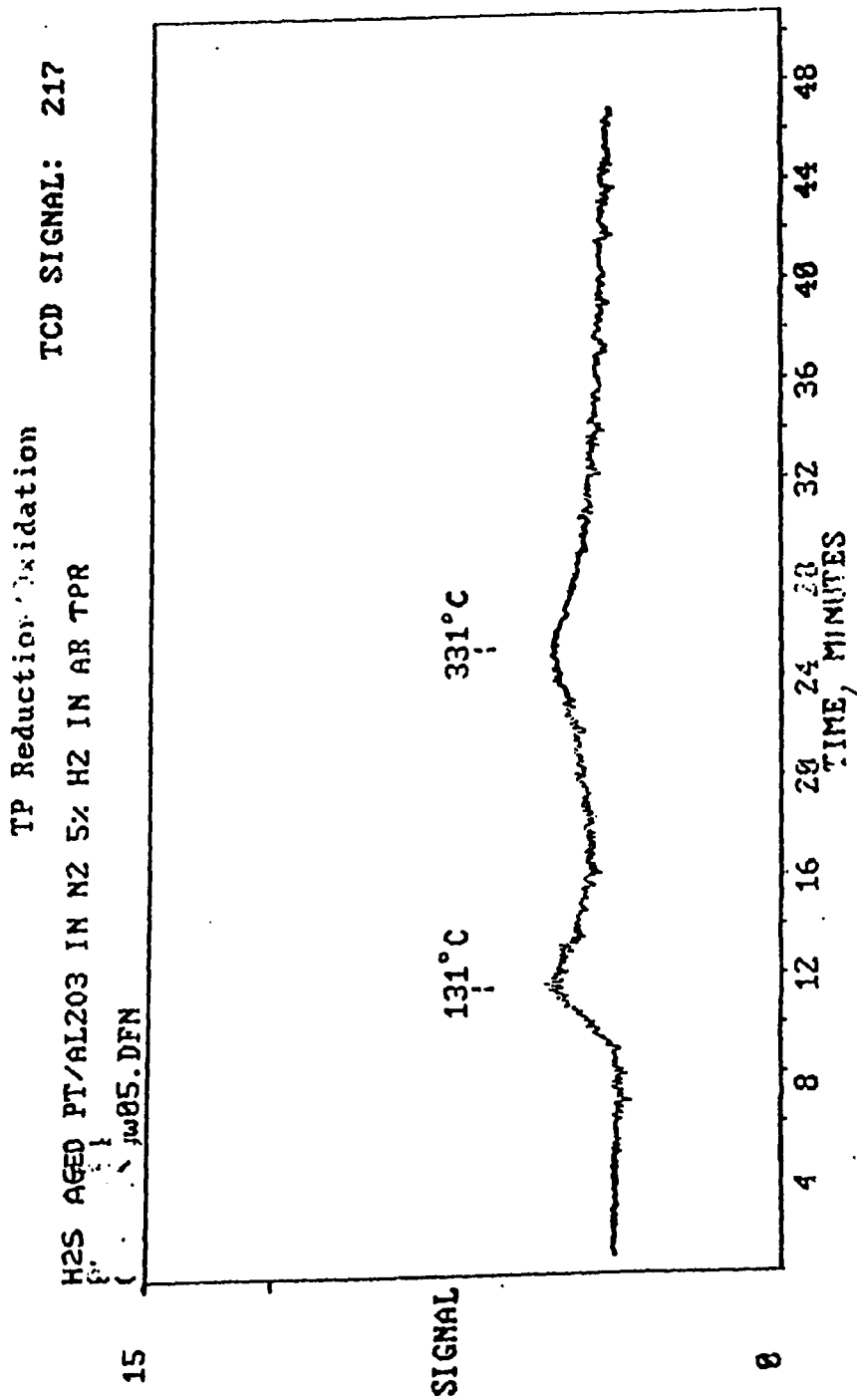
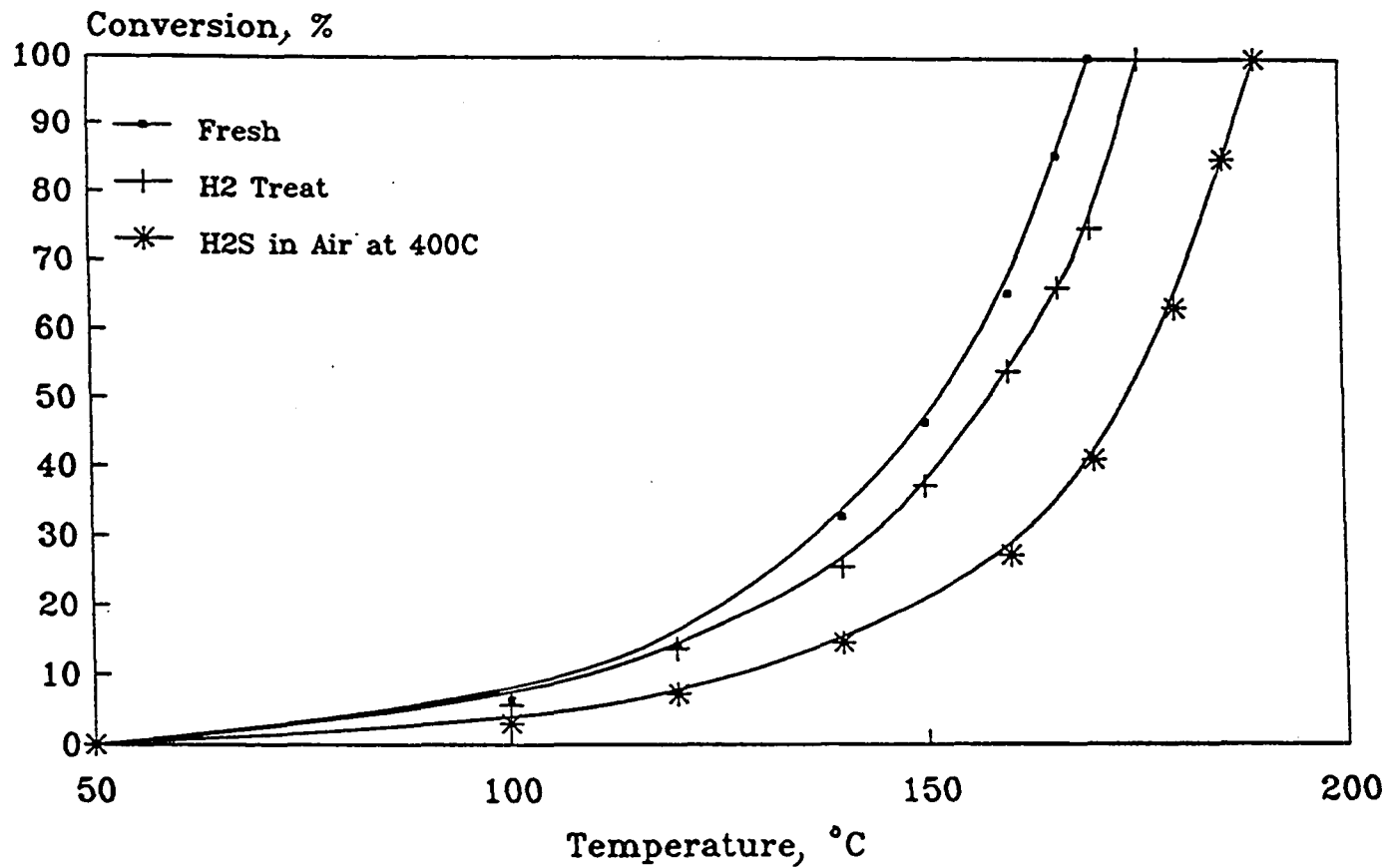
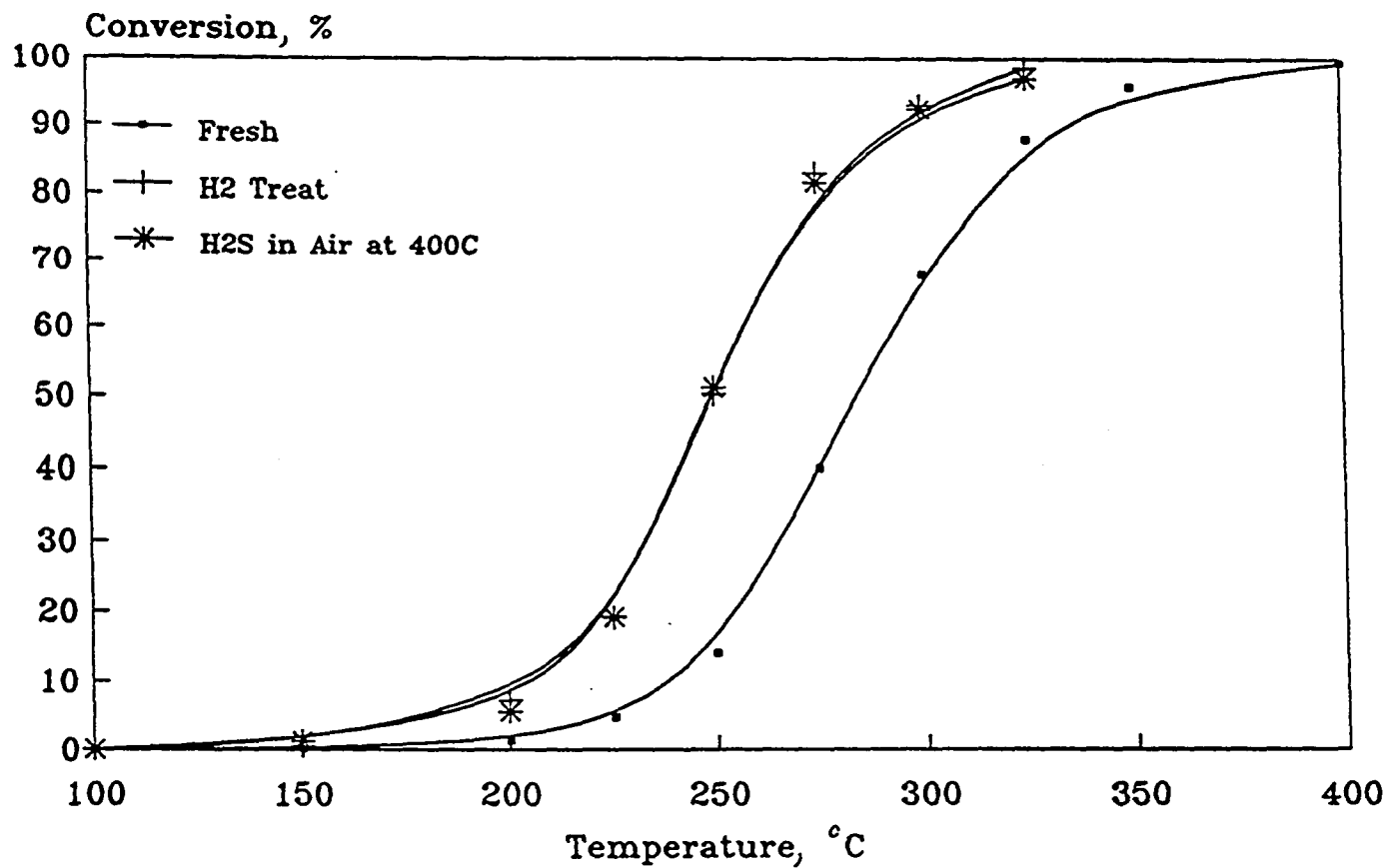


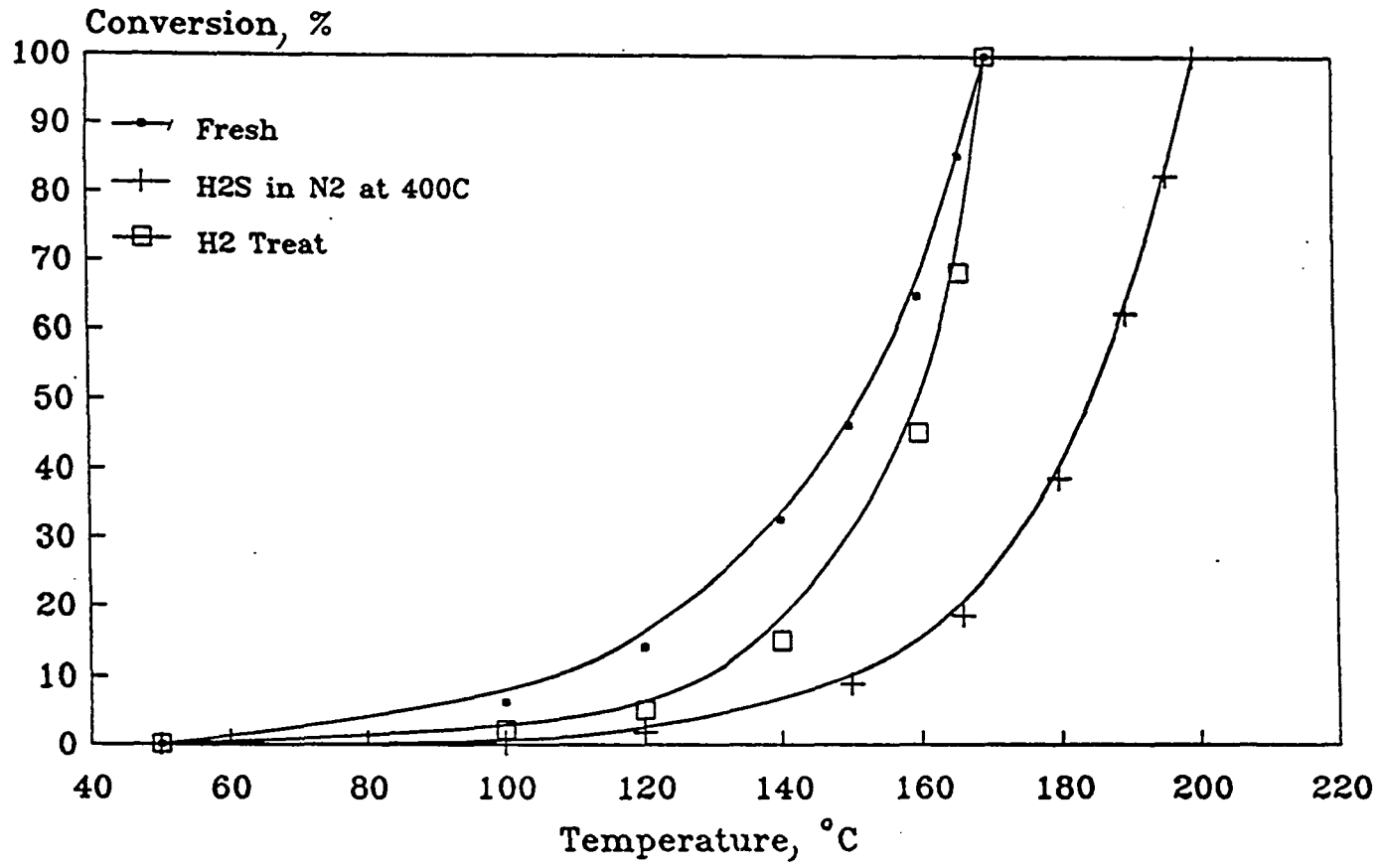
Figure 4-40 5% hydrogen temperature program reduction: Pt/γ-Al₂O₃ catalyst aged by H₂S in nitrogen at 400°C



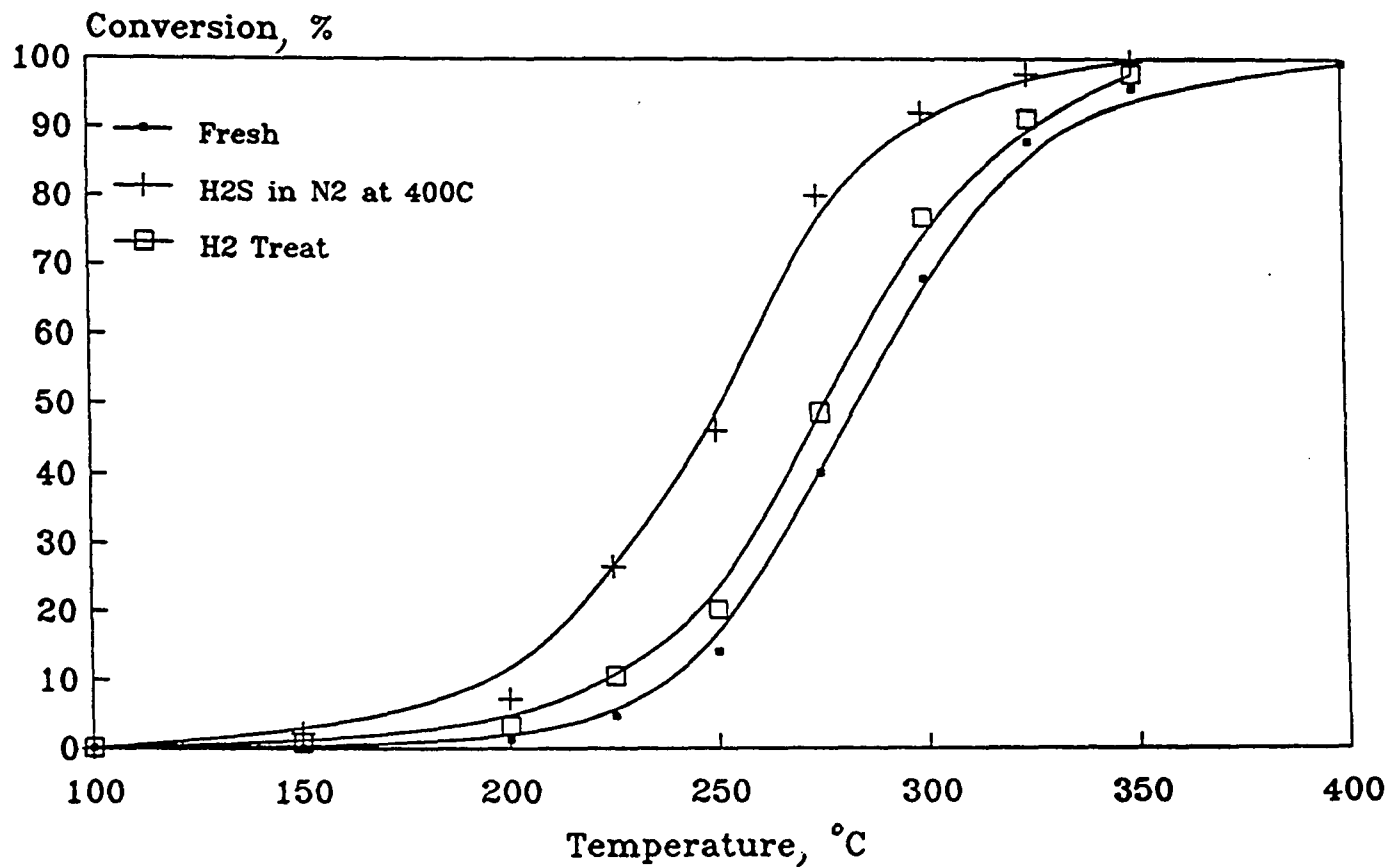
H2 Treat at 350 C for 3 hours
 0.05 gram Catalyst
 50 ml/min 1% CO in Air SV=30,000/hr
Figure 4-41 Comparison of activity: 1% CO oxidation: Fresh, H₂S aged in air, and regenerated catalysts



H2 Treat at 350 C for 3 hours
0.05 gram Catalyst
50 ml/min 1% Propane in Air SV=30,000/hr
Figure 4-42 Comparison of activity: 1% propane oxidation: Fresh, H₂S aged in air, and regenerated catalysts



H2 Treat at 350 C for 3 hours
0.05 gram Catalyst
50 ml/min 1% CO in Air SV=30,000/hr
Figure 4-43 Comparison of activity: 1% CO oxidation: Fresh, H₂S aged in nitrogen, and regenerated catalysts

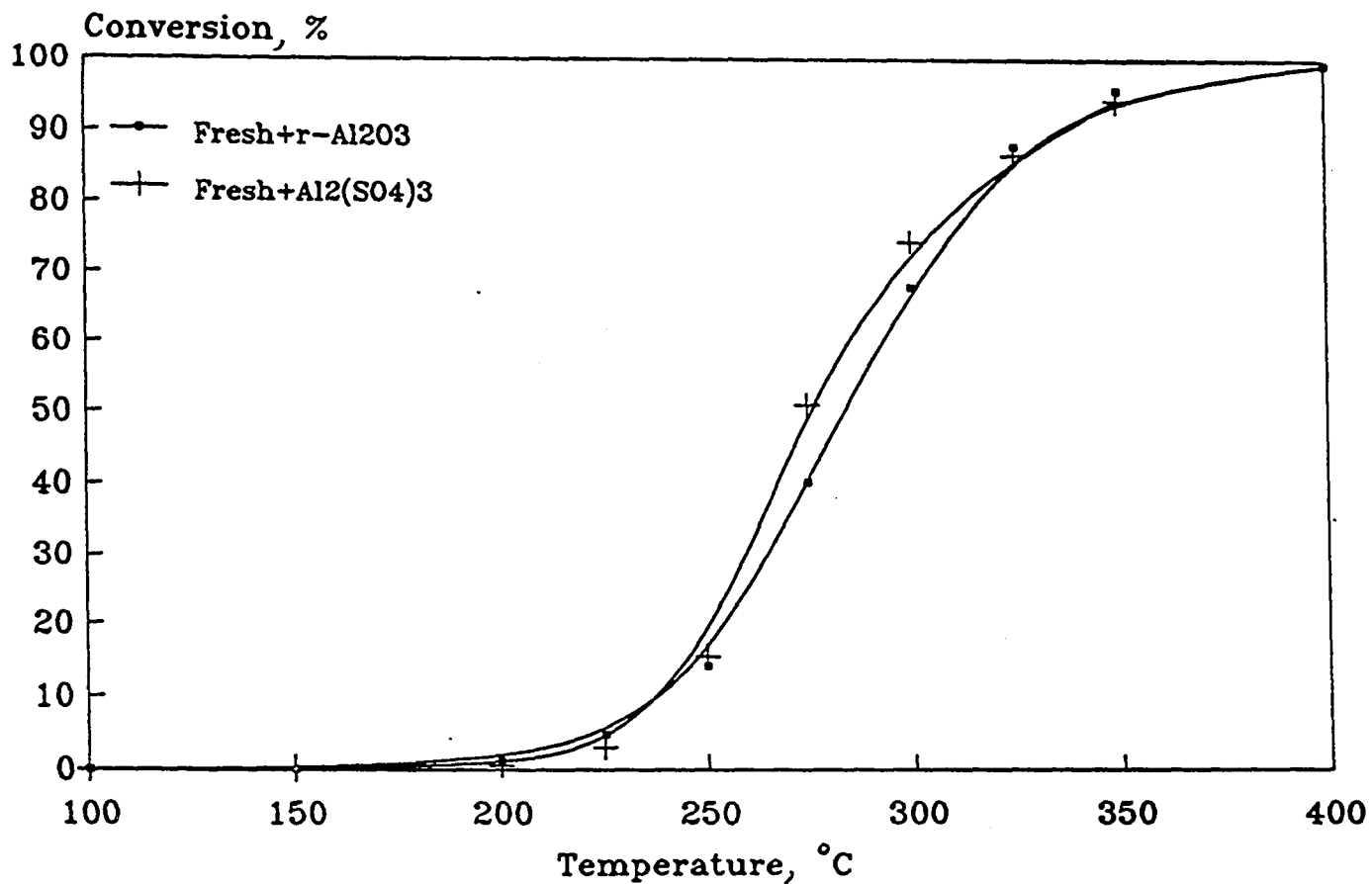


H2 Treat at 350 C for 3 hours

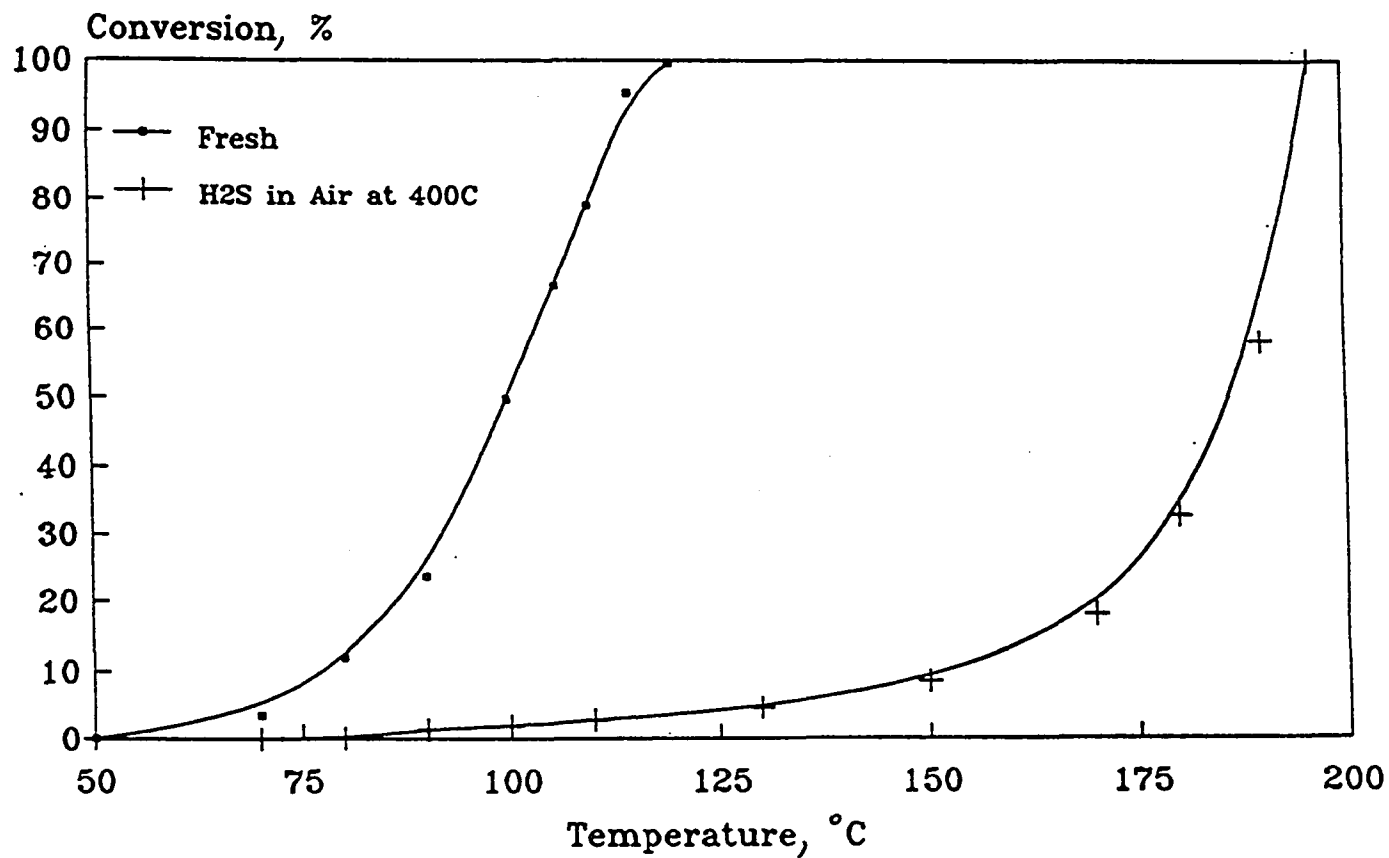
0.05 gram Catalyst

50 ml/min 1% Propane in Air SV=30,000/hr

Figure 4-44 Comparison of activity: 1% propane oxidation: Fresh, H₂S aged in nitrogen, and regenerated catalysts



0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
Figure 4-45 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ dilute with γ -Al₂O₃ vs dilute with Al₂(SO₄)₃

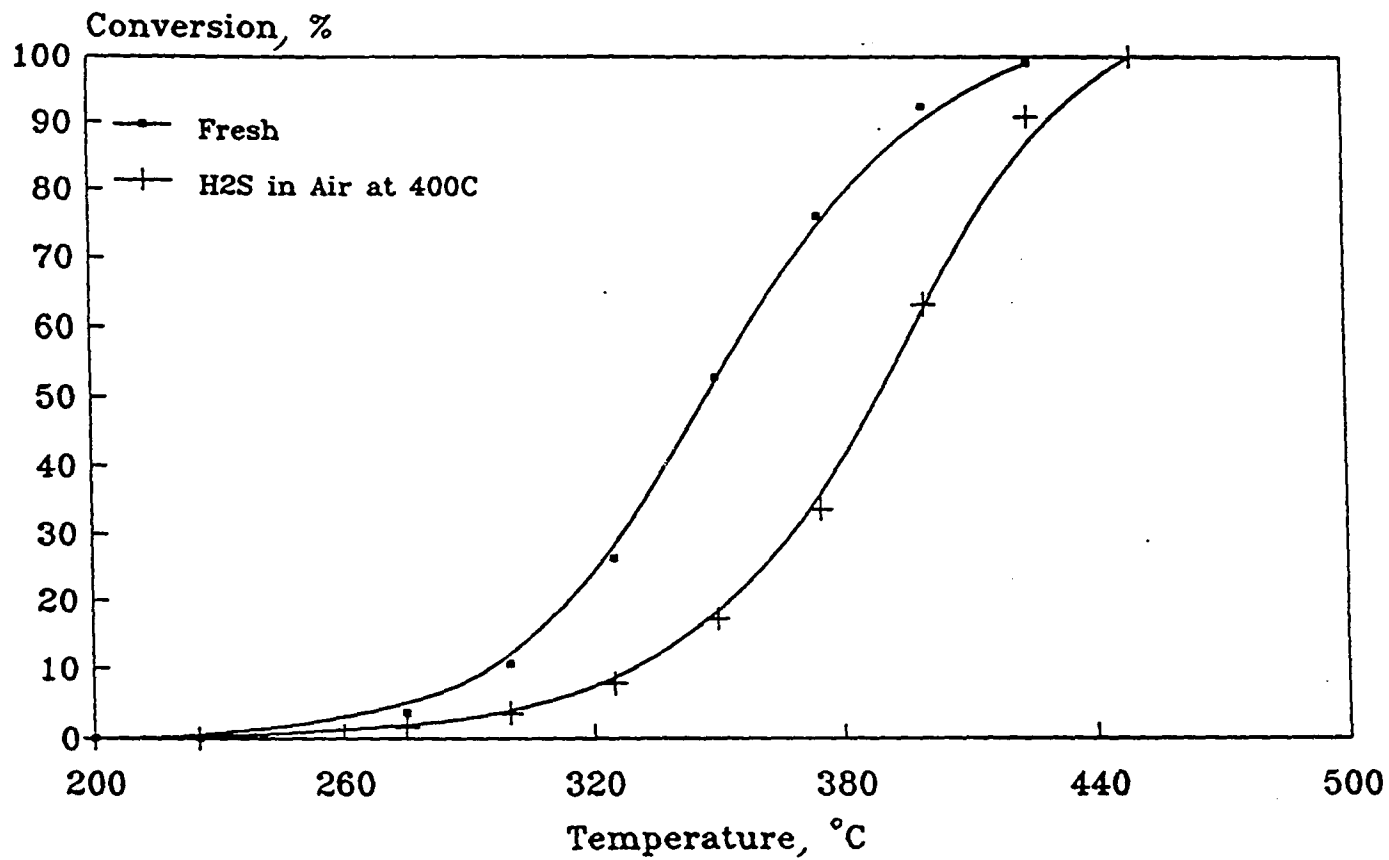


0.05 gram Catalyst

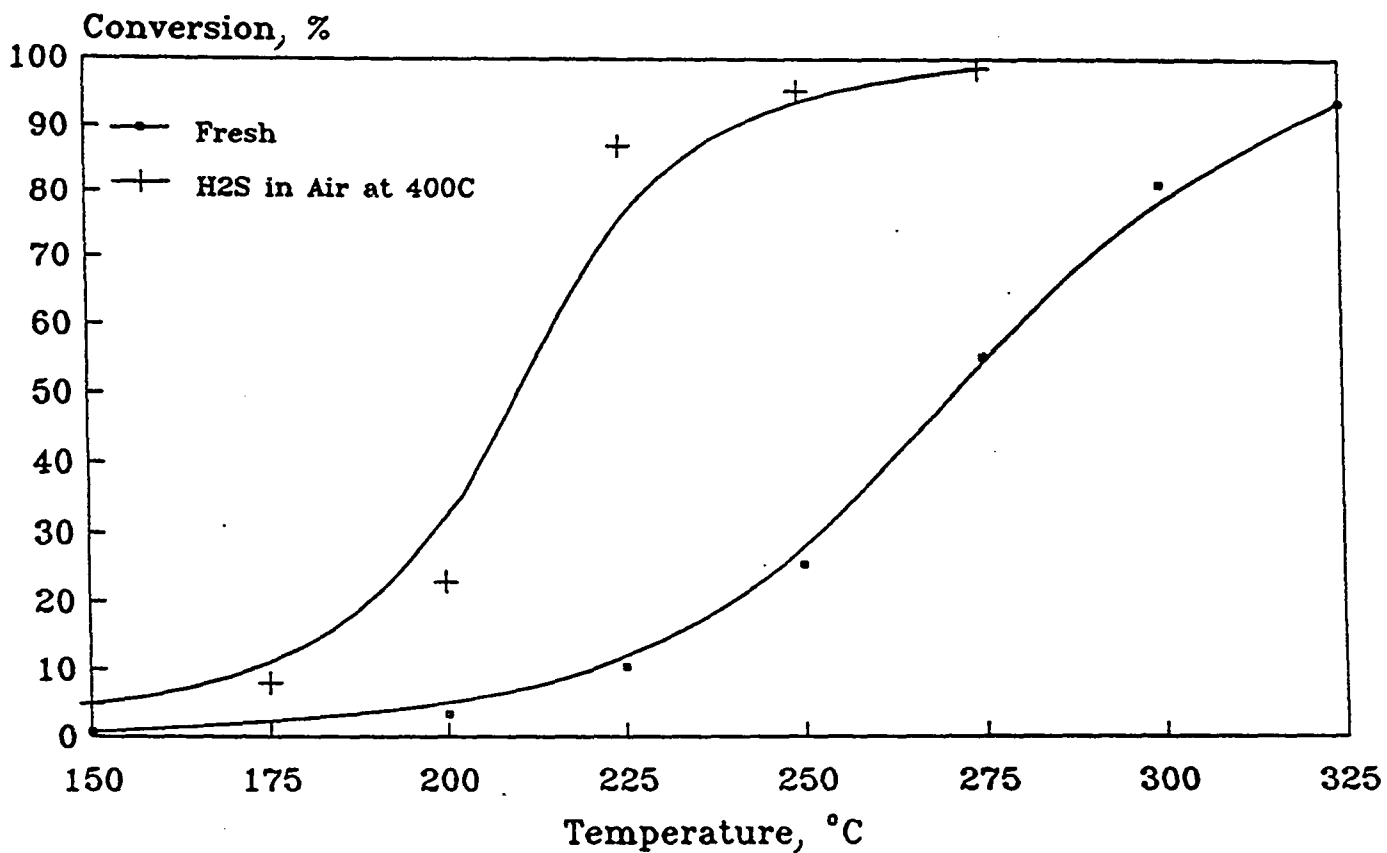
50ml/min 1% CO in Air SV=30,000/hr

100ppm H₂S Aged in Air at 400°C for 24hrs

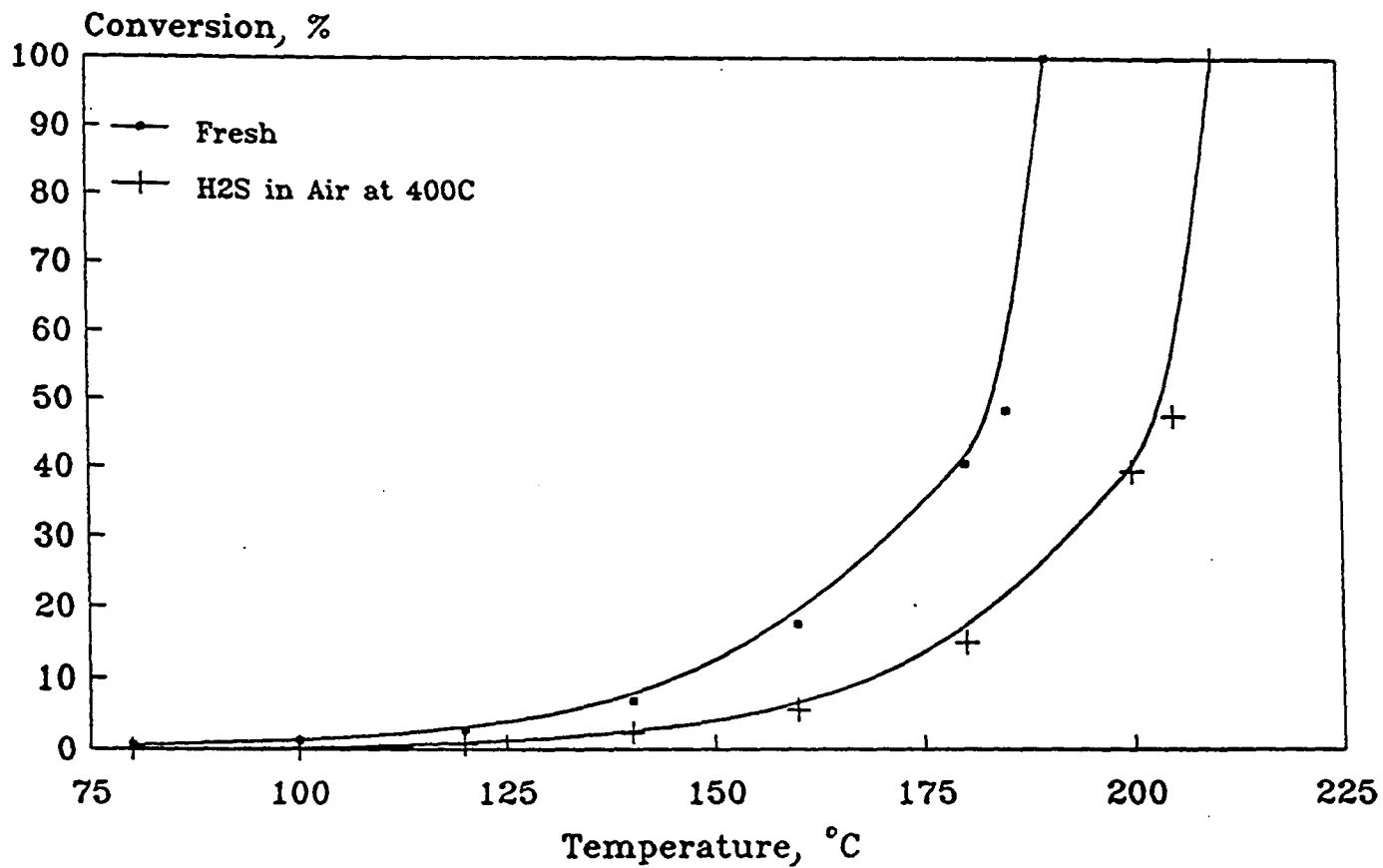
Figure 4-46 Comparison of activity: 1% CO oxidation: Fresh Pt/TiO₂ vs Pt/TiO₂ aged by H₂S in air at 400°C



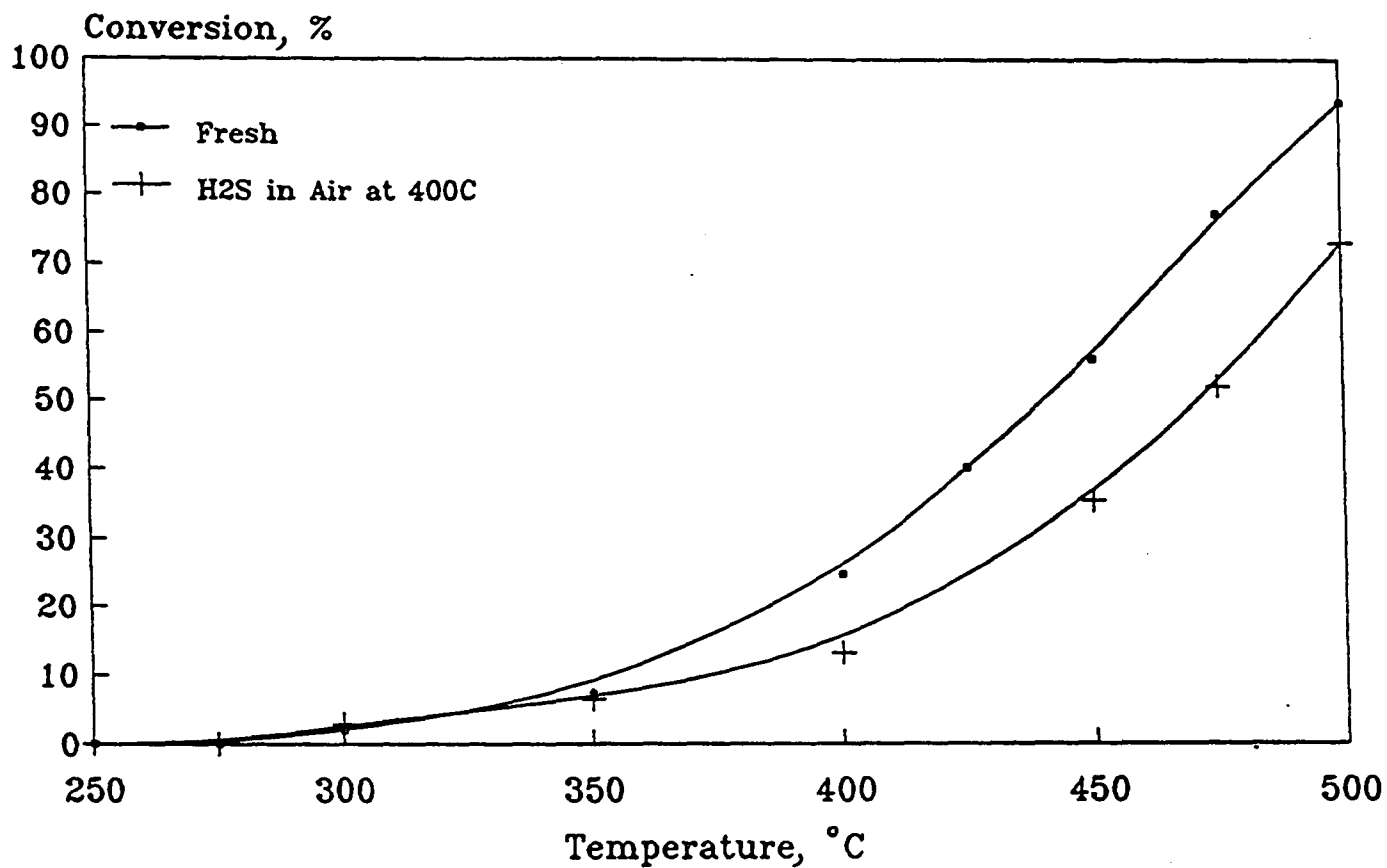
0.05 gram Catalyst
50ml/min 1% Methane in Air SV=30,000/hr
100ppm H2S Aged in Air at 400C for 24hrs
Figure 4-47 Comparison of activity: 1% methane oxidation: Fresh Pt/TiO₂ vs Pt/TiO₂ aged by H₂S in air at 400°C



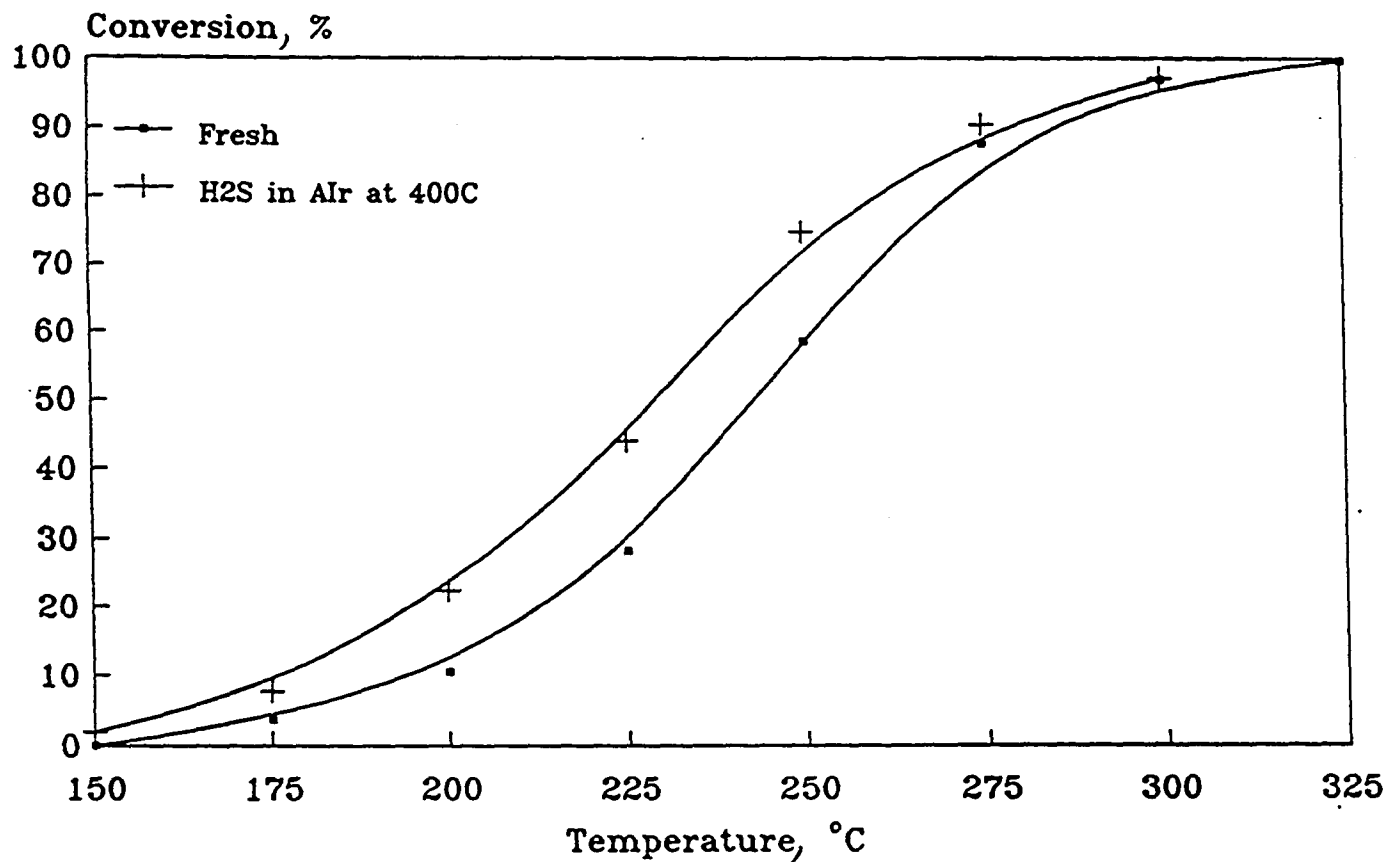
0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-48 Comparison of activity: 1% propane oxidation: Fresh Pt/TiO₂ vs Pt/TiO₂ aged by H₂S in air at 400°C



0.05 gram Catalyst
50ml/min 1% CO in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-49 Comparison of activity: 1% CO oxidation: Fresh Pt/ZrO₂ vs Pt/ZrO₂ aged by H₂S in air at 400°C

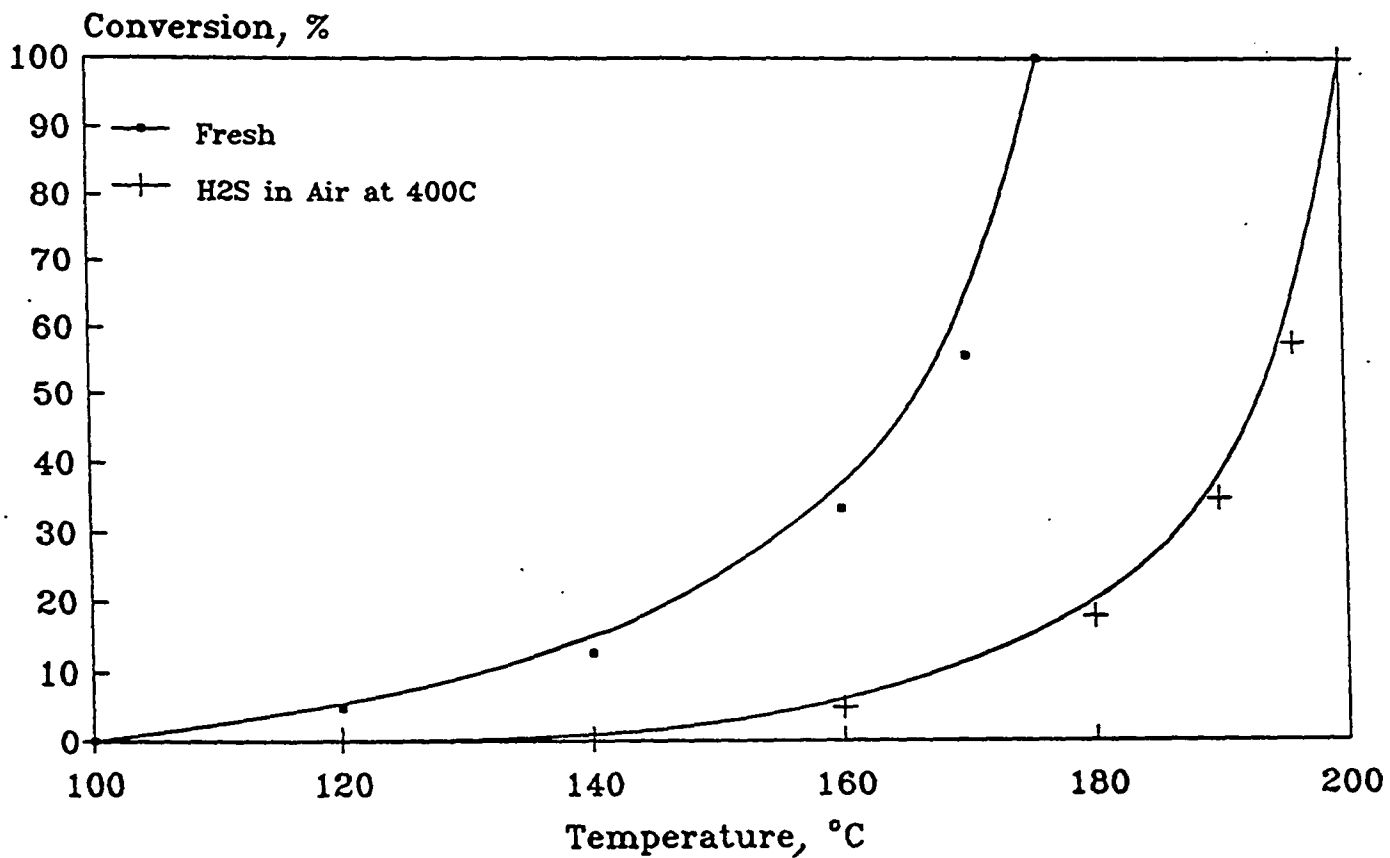


0.05 gram Catalyst
50ml/min 1% CH₄ in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-50 Comparison of activity: 1% methane oxidation: Fresh Pt/ZrO₂ vs Pt/ZrO₂ aged by H₂S in air at 400°C

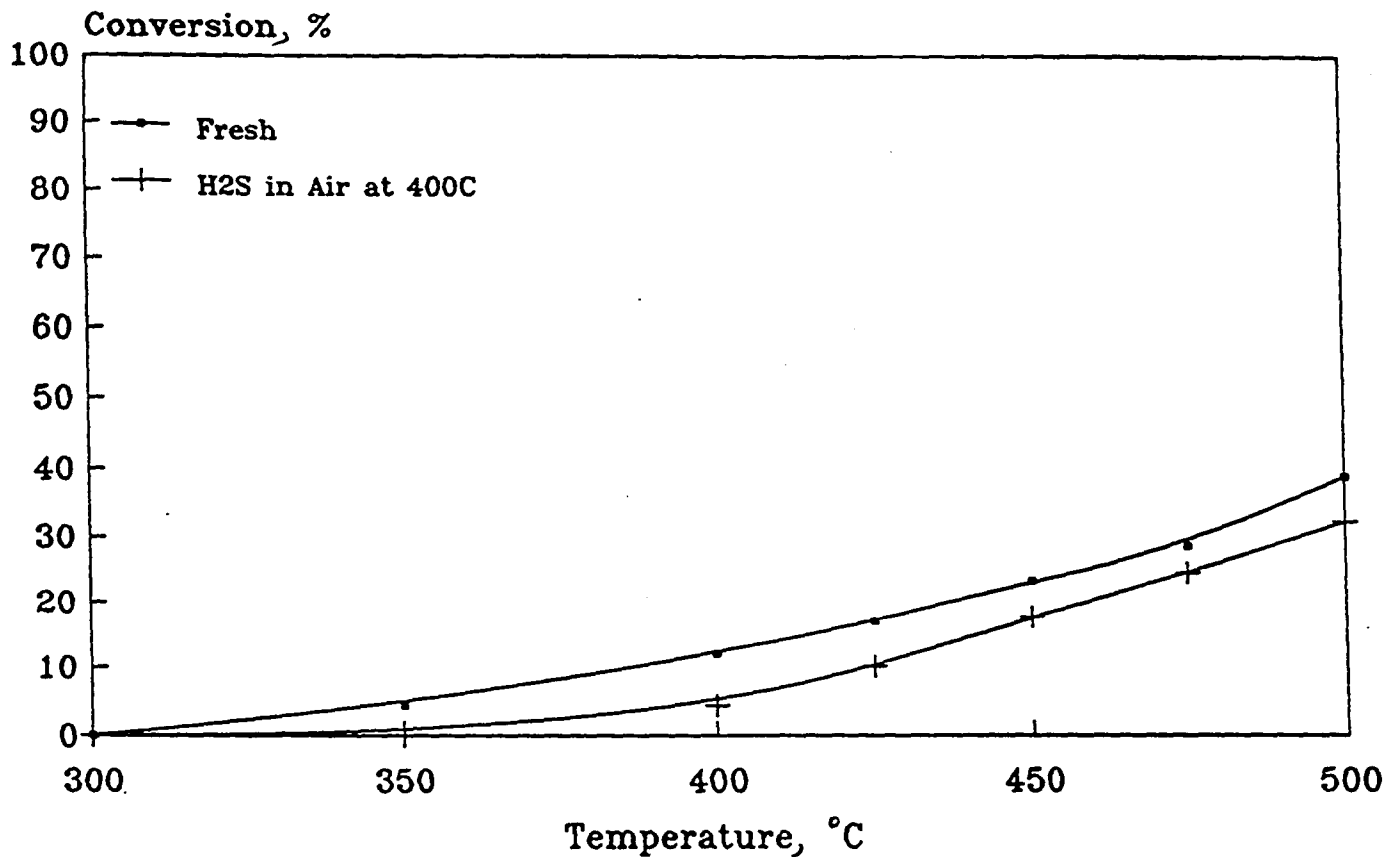


0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs

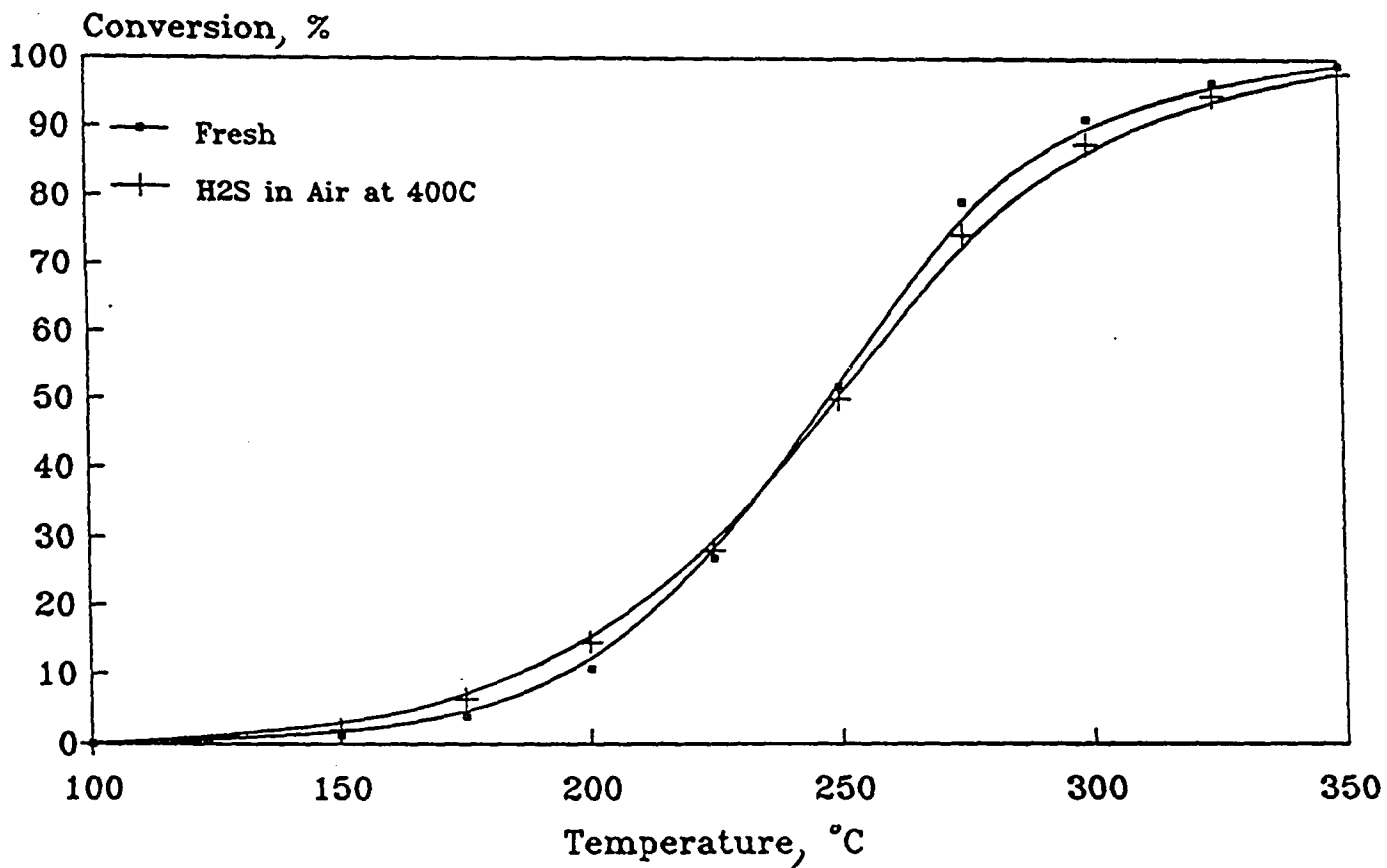
Figure 4-51 Comparison of activity: 1% propane oxidation: Fresh Pt/ZrO₂ vs Pt/ZrO₂ aged by H₂S in air at 400°C



0.05 gram Catalyst
50ml/min 1% CO in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-52 Comparison of activity: 1% CO oxidation: Fresh Pt/SiO₂ vs Pt/SiO₂ aged by H₂S in air at 400°C



0.05 gram Catalyst
50ml/min 1% CH₄ in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-53 Comparison of activity: 1% methane oxidation: Fresh Pt/SiO₂ vs Pt/SiO₂ aged by H₂S in air at 400°C



0.05 gram Catalyst
50ml/min 1% Propane in Air SV=30,000/hr
100ppm H₂S Aged in Air at 400C for 24hrs
Figure 4-54 Comparison of activity: 1% propane oxidation: Fresh Pt/SiO₂ vs Pt/SiO₂ aged by H₂S in air at 400°C

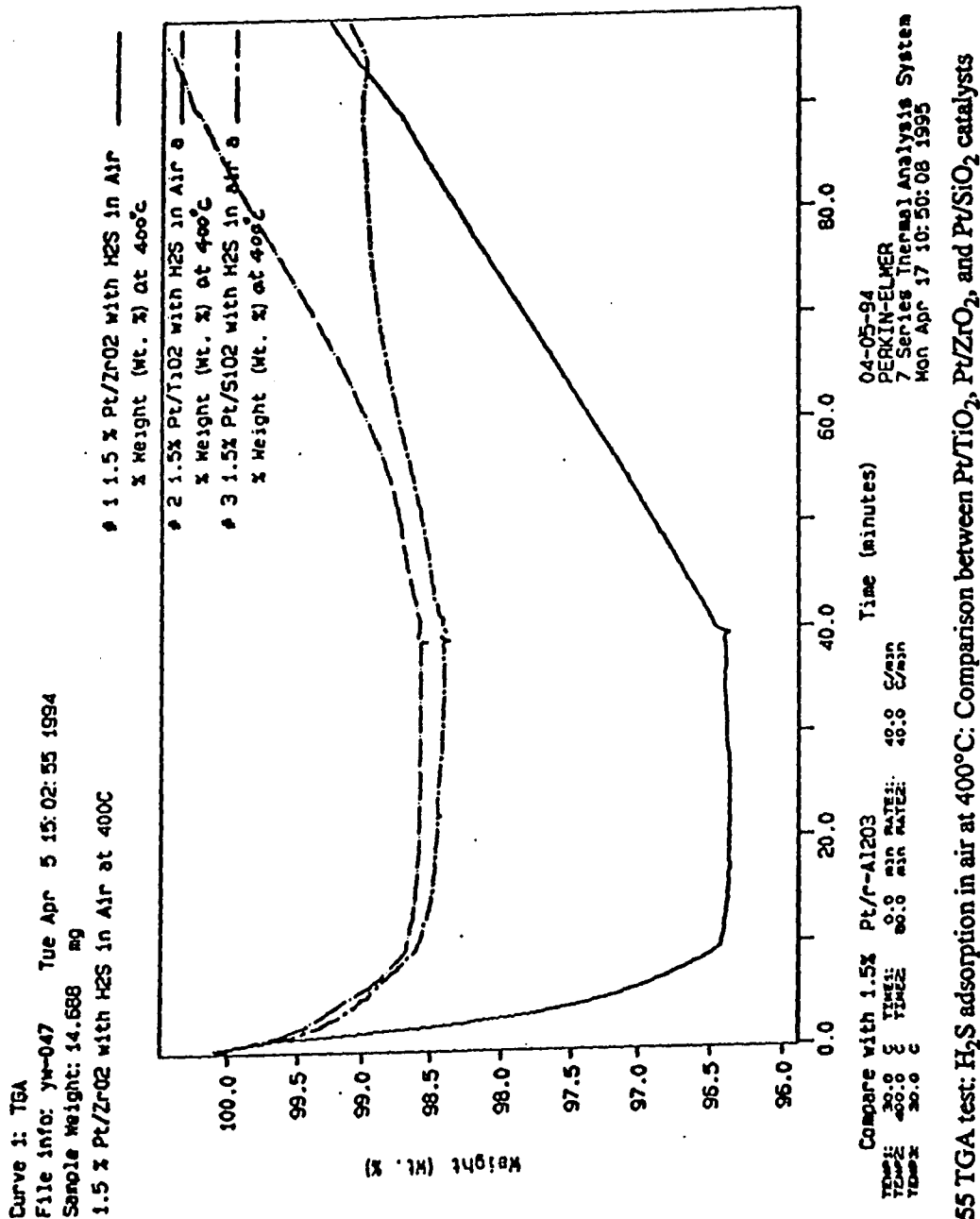


Figure 4-55 TGA test: H₂S adsorption in air at 400°C: Comparison between Pt/TiO₂, Pt/ZrO₂, and Pt/SiO₂ catalysts

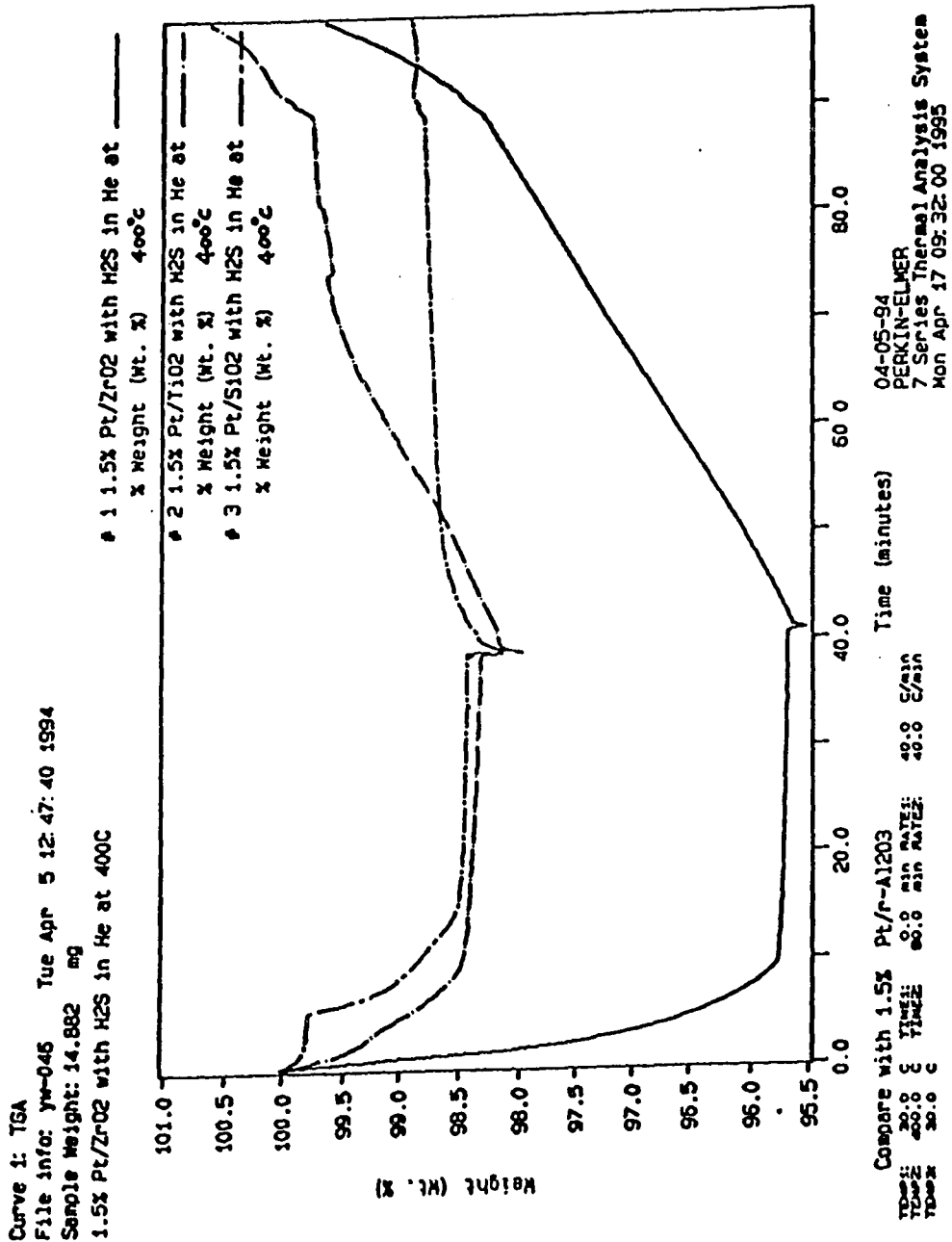


Figure 4-56 TGA test: H₂S adsorption in helium at 400°C: Comparison between Pt/TiO₂, Pt/ZrO₂, and Pt/SiO₂ catalysts

Curve 1: TGA
 File info: yn-044 Mon Apr 4 14: 54: 08 1994
 Sample Weight: 8.555 mg
 1.5% Pt/TiO2 with H2S in Air at 400C

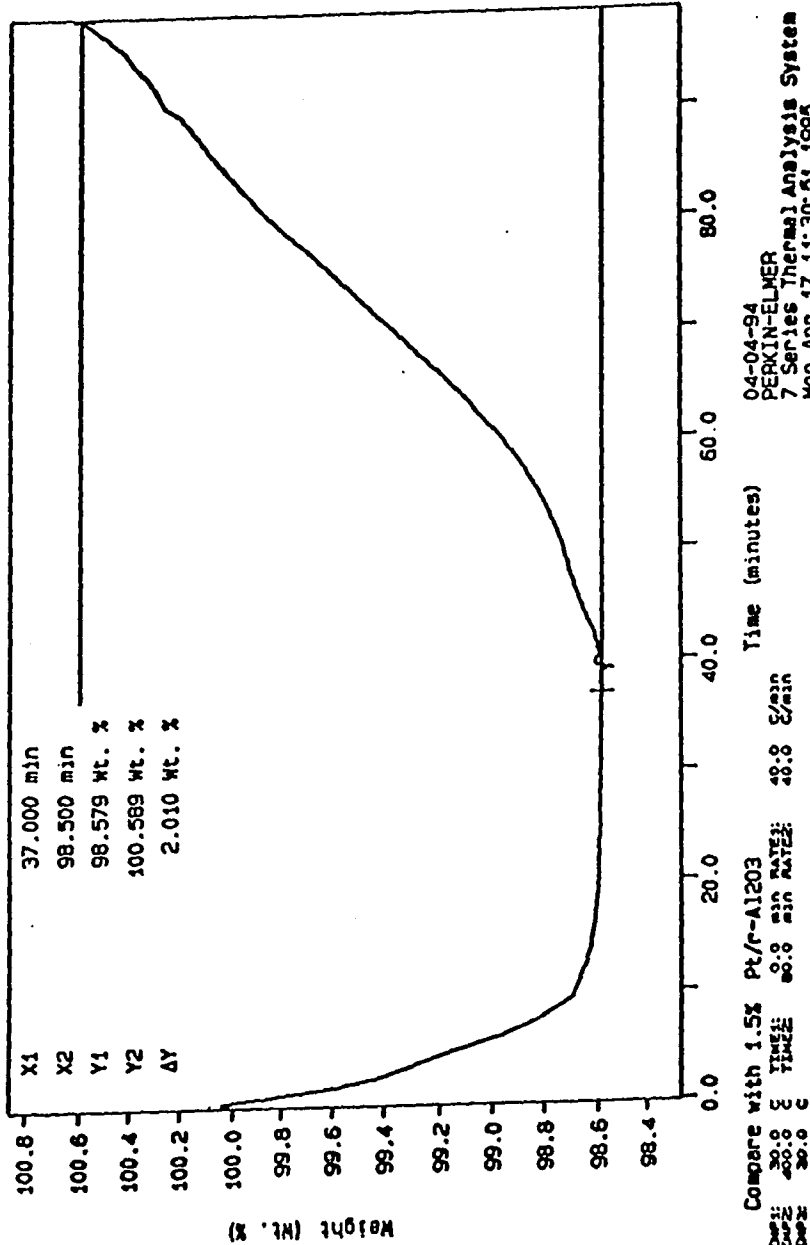


Figure 4-57 TGA test: H₂S induced weigh gain: Pt/TiO₂ catalyst in air at 400°C

Curve 1: TGA
 File info: yw-047 Tue Apr 5 15:02:55 1994
 Sample Weight: 14.688 mg
 1.5 % Pt/ZrO₂ with H₂S in Air at 400C

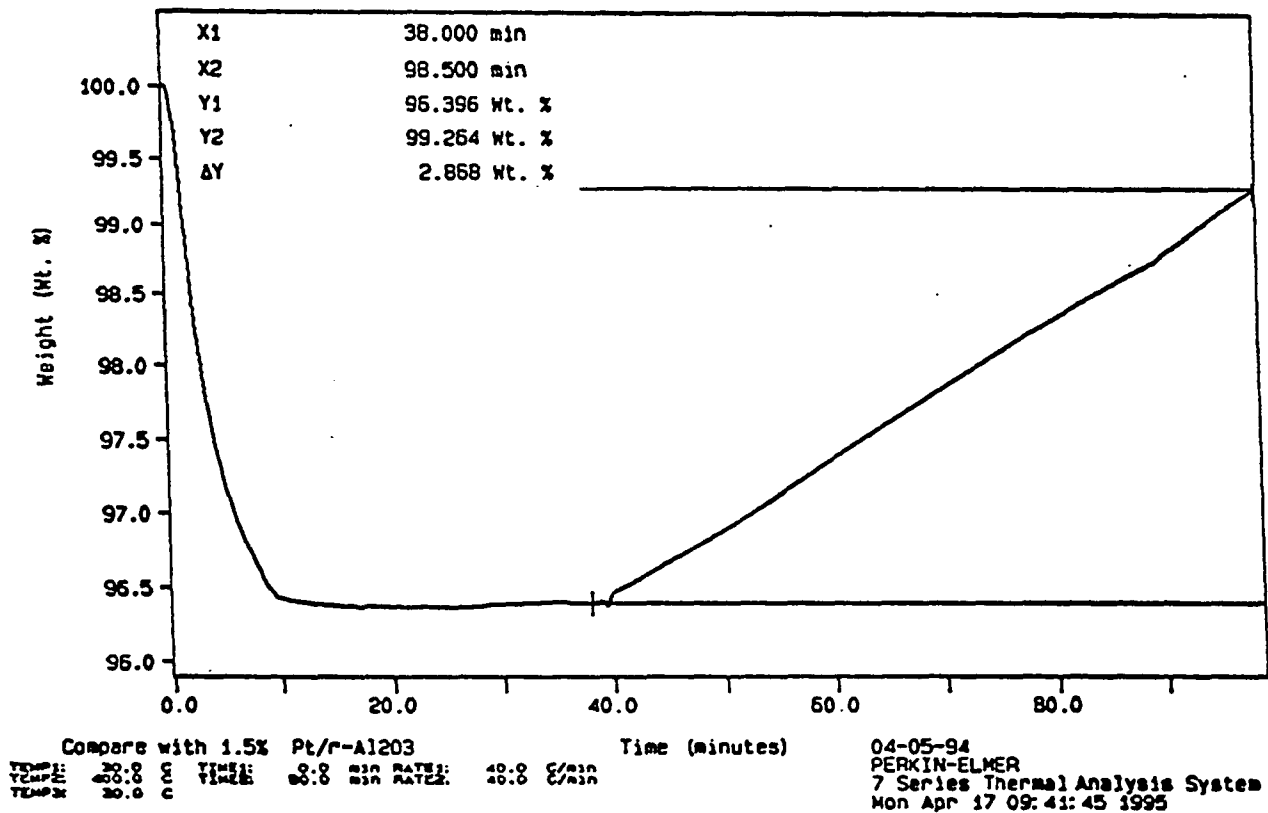
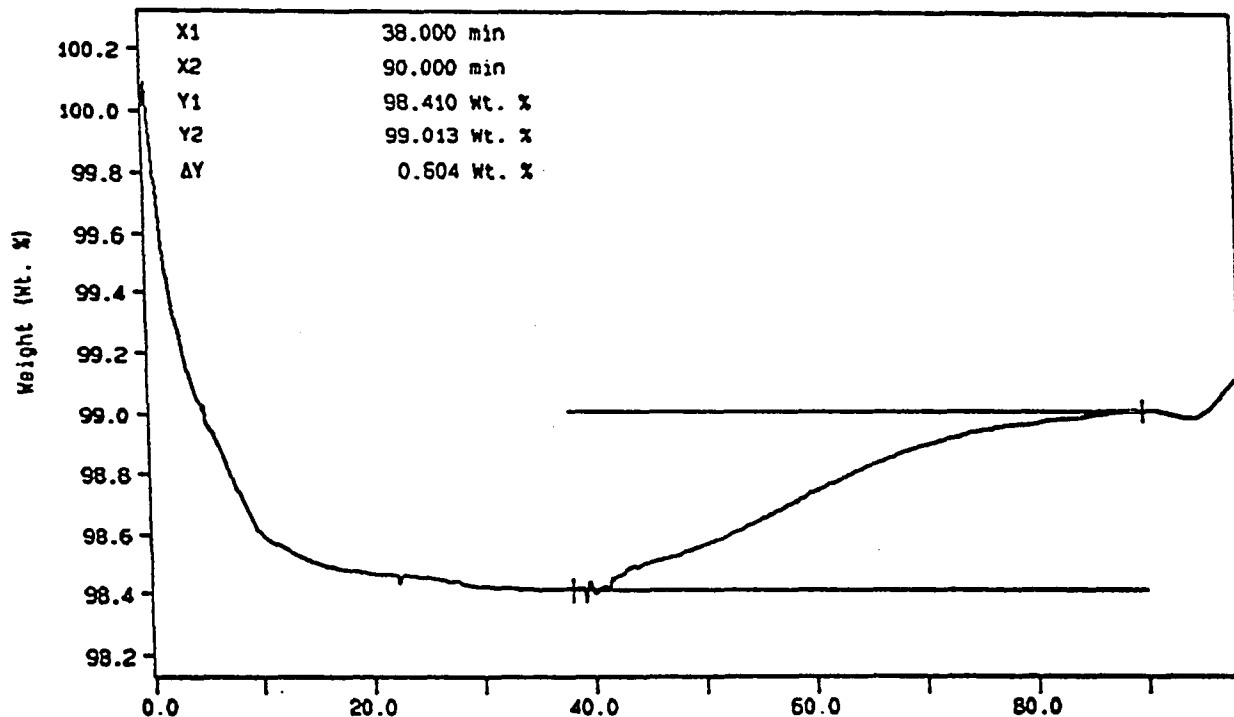


Figure 4-58 TGA test: H₂S induced weigh gain: Pt/ZrO₂ catalyst in air at 400°C

Curve 1: TGA
 File info: yw-042 Thu Mar 31 12:26:44 1994
 Sample Weight: 5.527 mg
 1.5% Pt/SiO₂ with H₂S in air at 400C



Comparison with 1.5% Pt/r-Al ₂ O ₃				Time (minutes)		03-31-94	
TEMP1:	30.0 C	TIME1:	0.0 min	RATE1:	40.0 C/min	PERKIN-ELMER	
TEMP2:	400.0 C	TIME2:	0.0 min	RATE2:	40.0 C/min	7 Series Thermal Analysis System	
TEMP3:	30.0 C	TIME3:	0.0 min	RATE3:	80.0 C/min	Mon Apr 17 10:25:46 1995	
TEMP4:	30.0 C	TIME4:	0.0 min	RATE4:	20.0 C/min		

Figure 4-59 TGA test: H₂S induced weigh gain: Pt/SiO₂ catalyst in air at 400°C

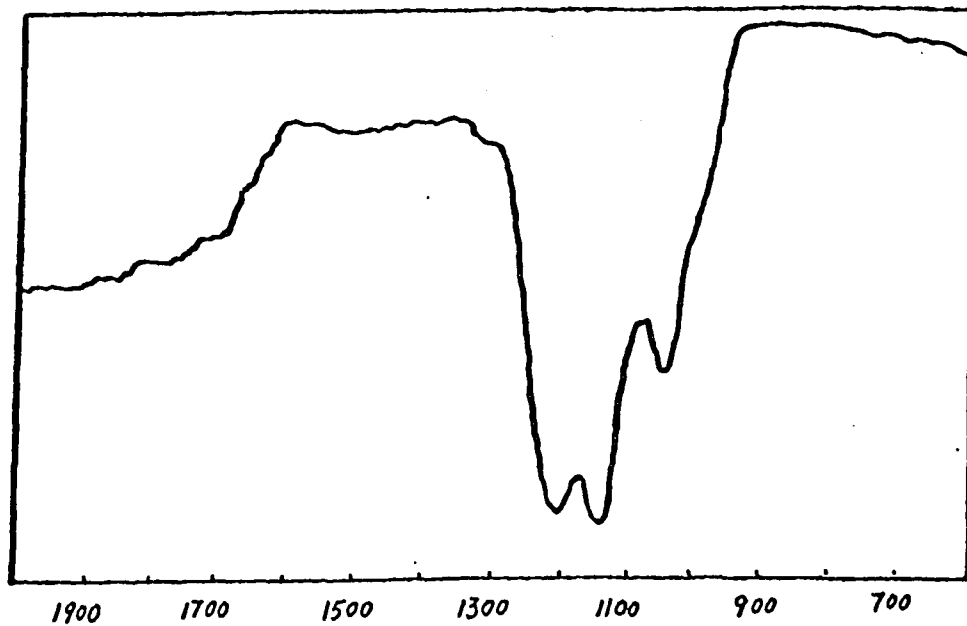


Figure 4-60 IR spectra of Pt/TiO₂ catalyst aged by H₂S in air at 400°C

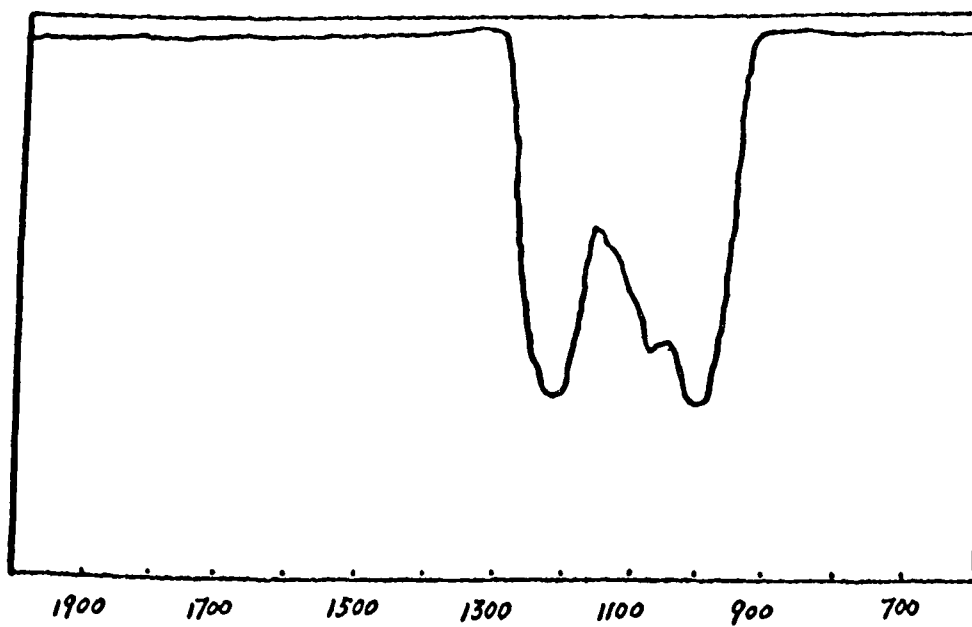


Figure 4-61 IR spectra of Pt/ZrO₂ catalyst aged by H₂S in air at 400°C

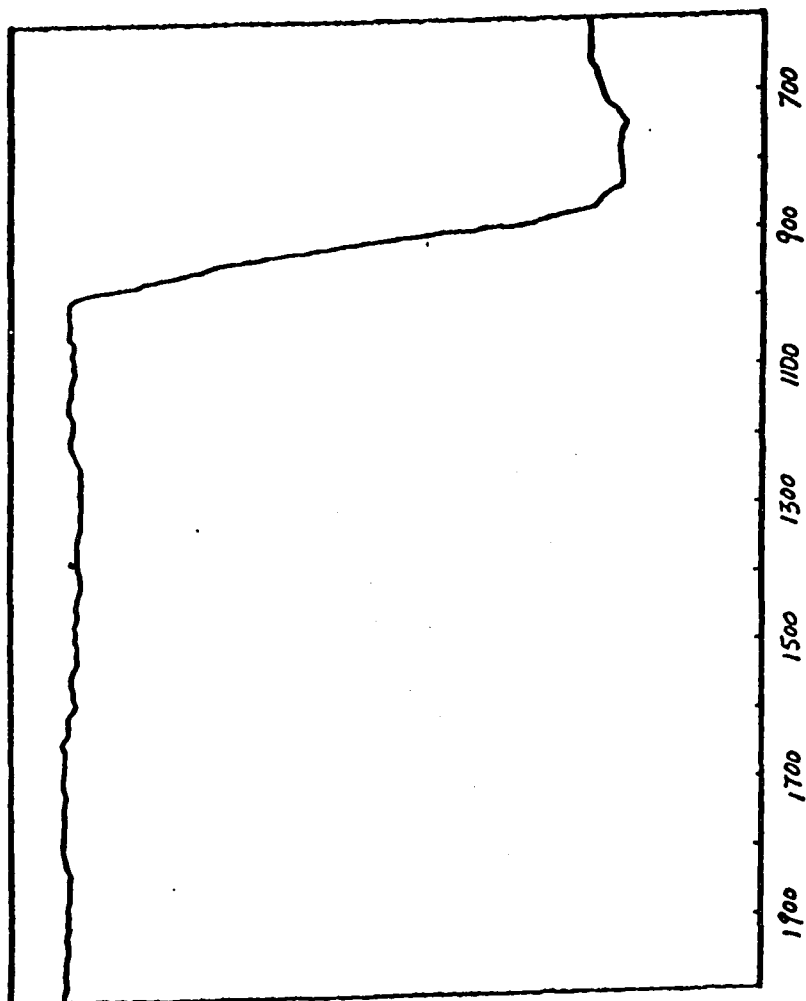


Figure 4-62 IR spectra of Pt/SiO₂ catalyst aged by H₂S in air at 400°C

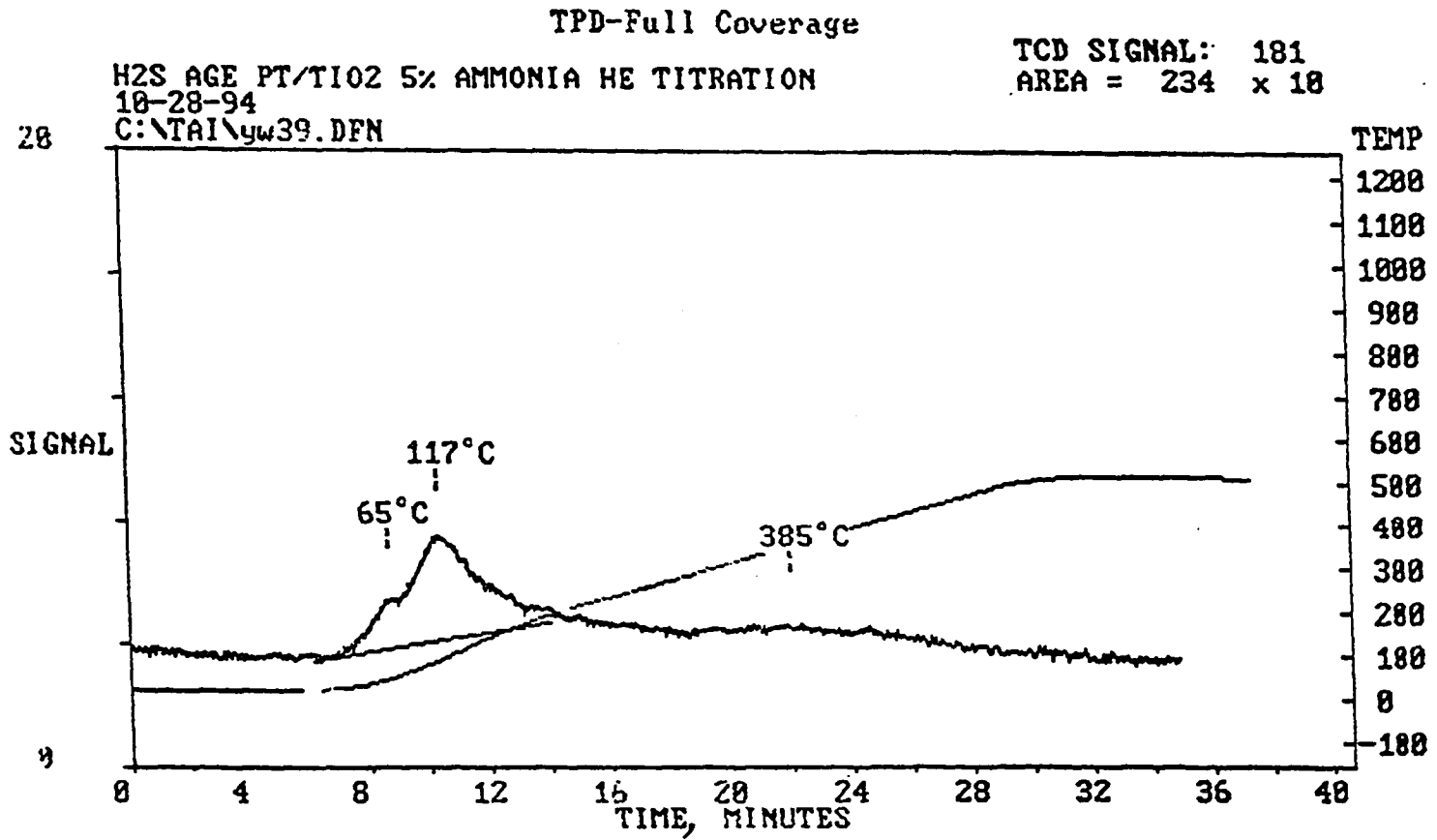


Figure 4-63 Ammonia titration: Pt/TiO₂ catalyst aged by H₂S in air at 400°C

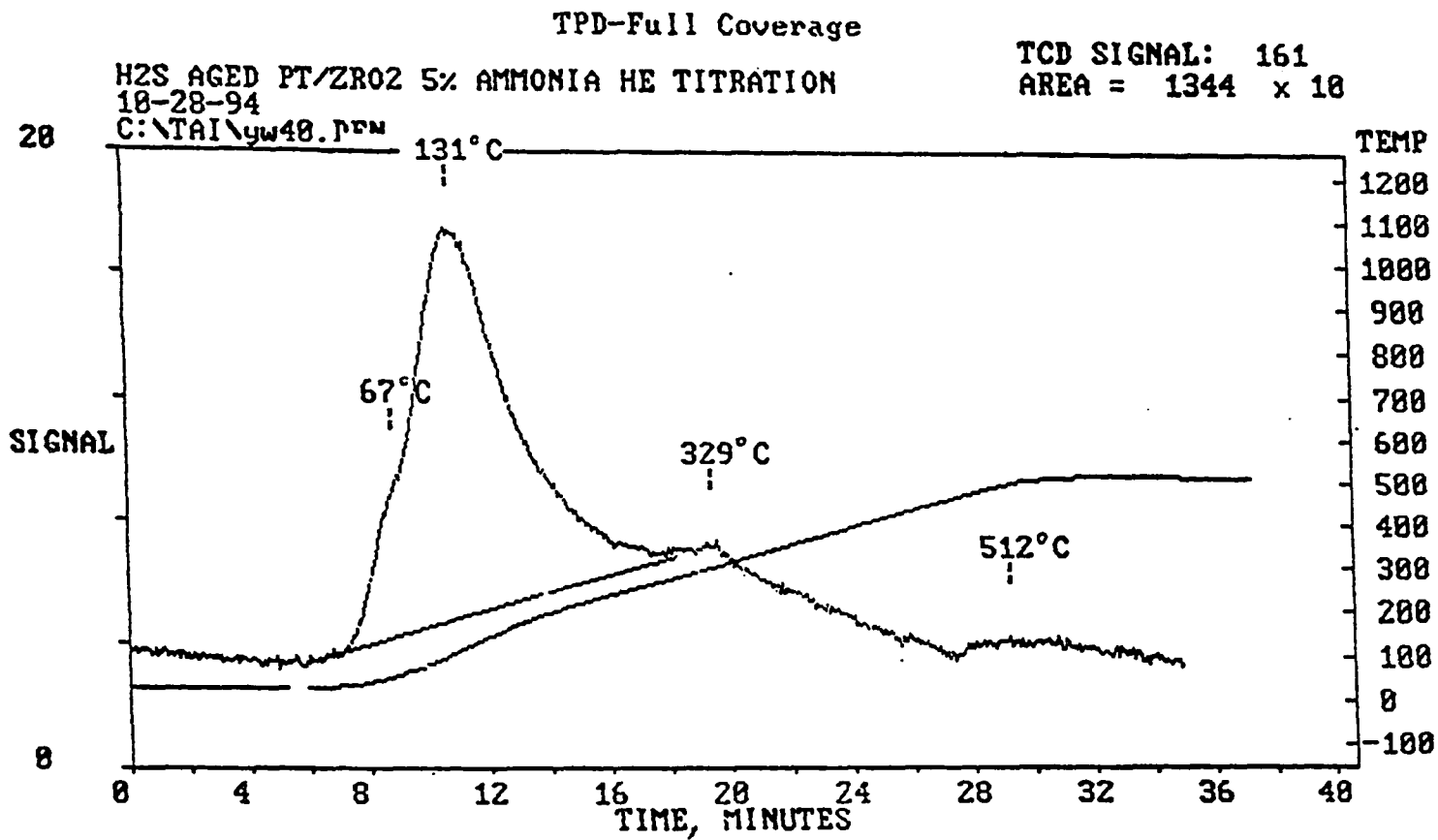


Figure 4-64 Ammonia titration: Pt/ZrO₂ catalyst aged by H₂S in air at 400°C

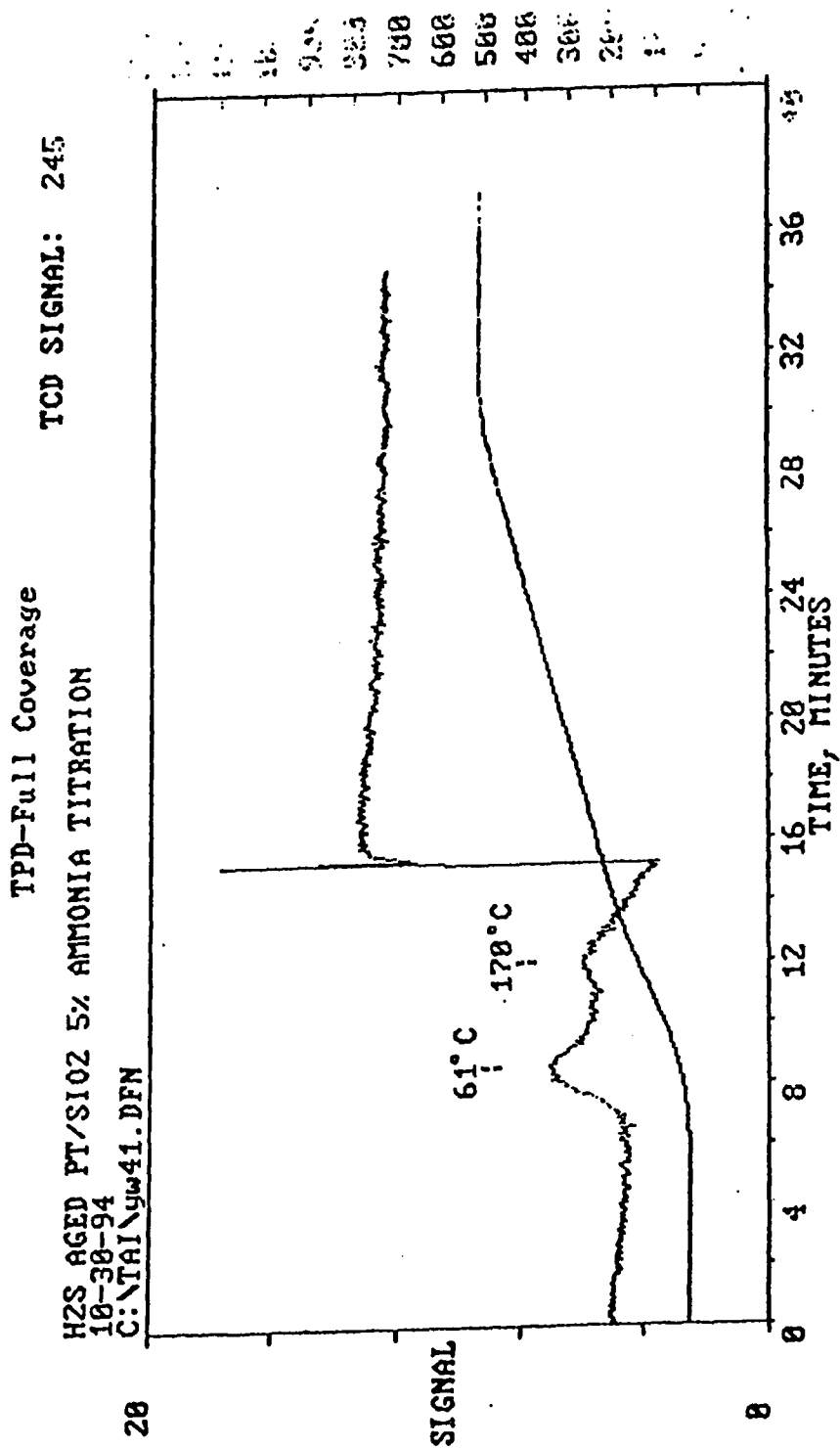
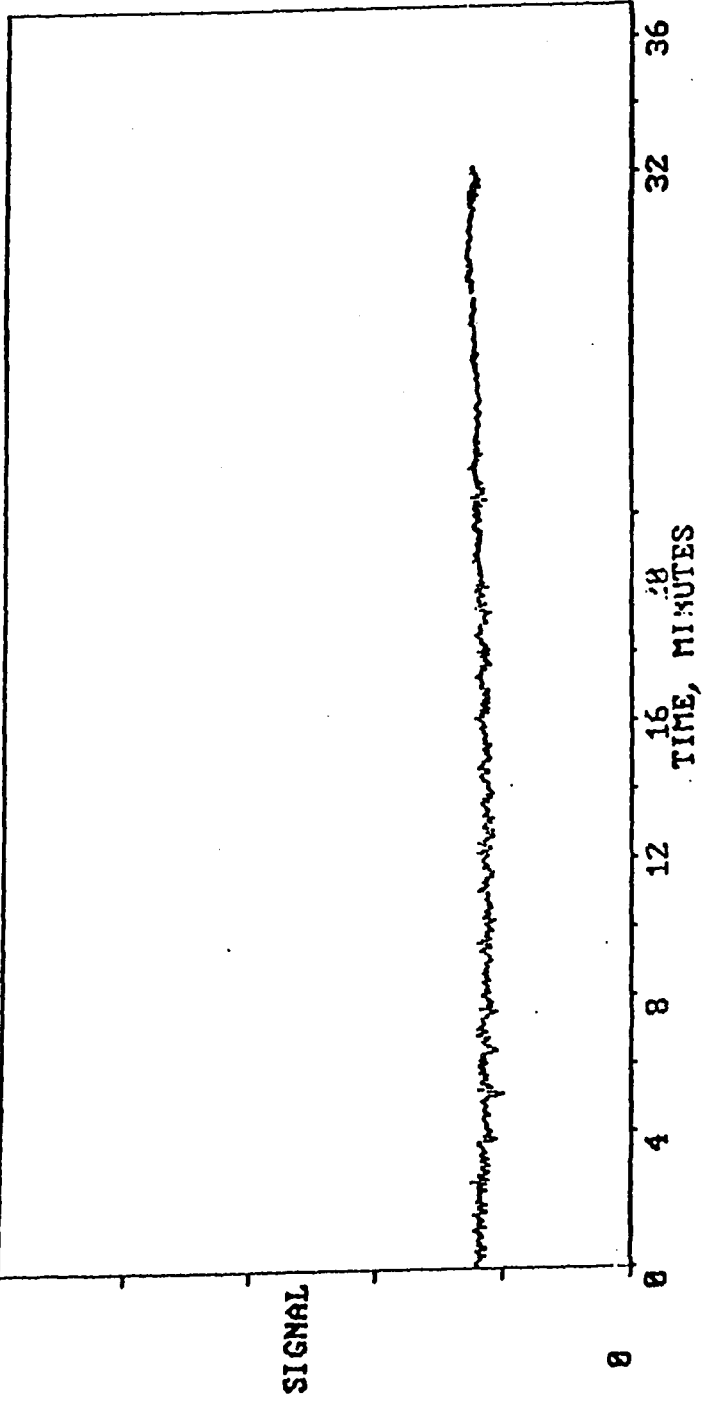


Figure 4-65 Ammonia titration: Pt/SiO₂ catalyst aged by H₂S in air at 400°C

TP Reduction/Oxidation

PURE TiO2 5% H2 TPR
89-12-94
C:\TAI\9418.DFN

15



SIGNAL

0

36

16
20
24
28
32

Figure 4-66 5% hydrogen temperature program reduction: Pure TiO₂

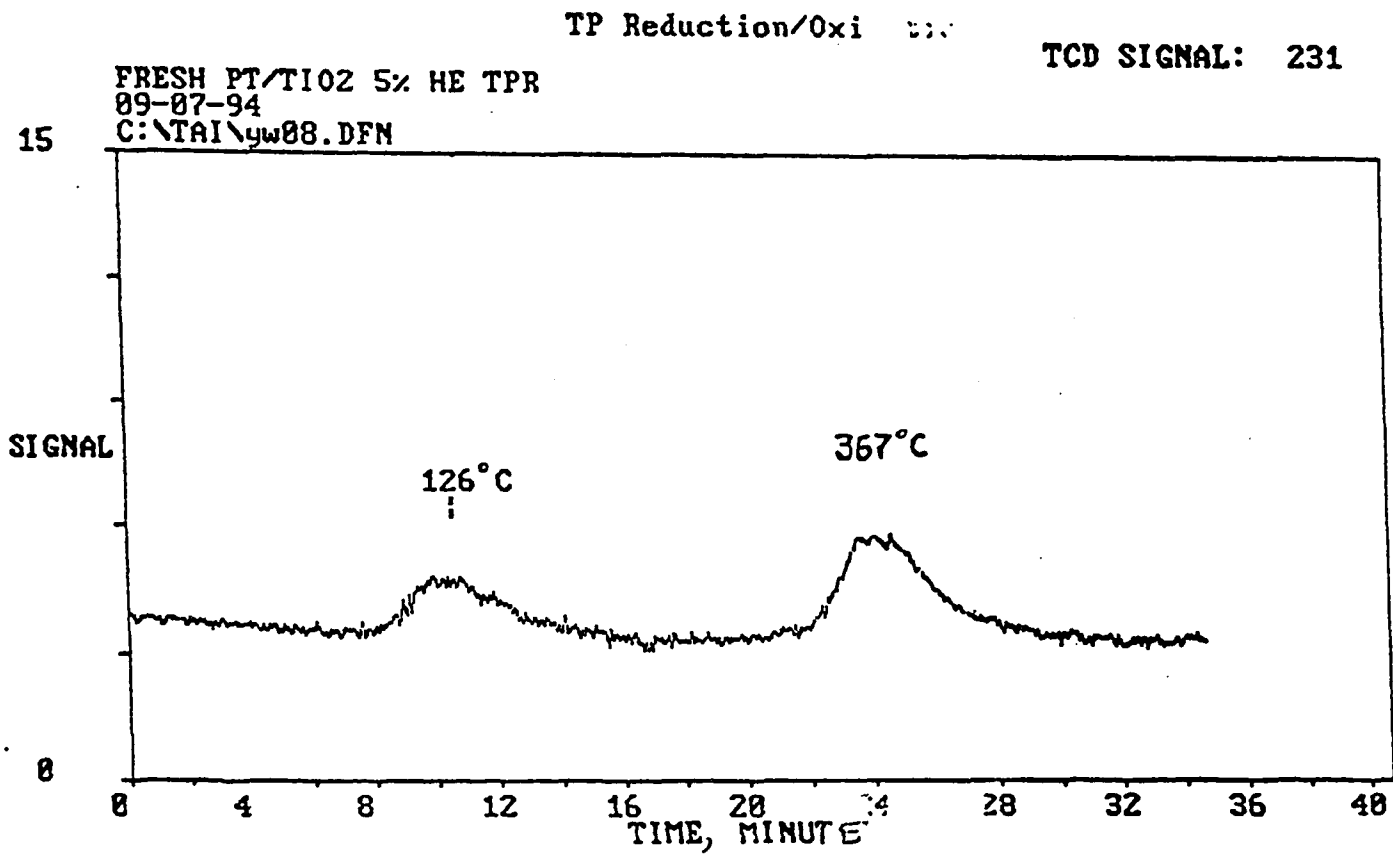


Figure 4-67 5% hydrogen temperature program reduction: Fresh Pt/TiO₂ catalyst

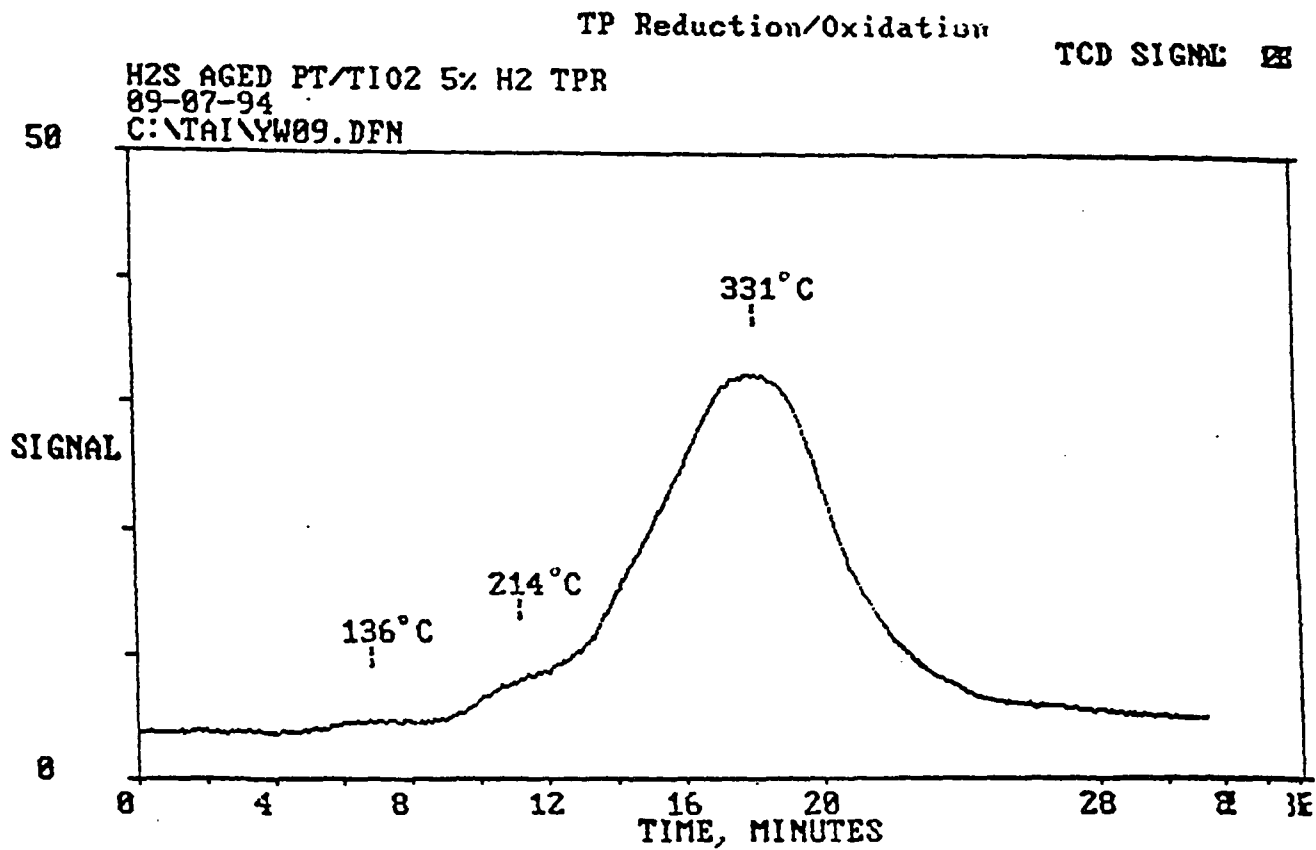


Figure 4-68 5% hydrogen temperature program reduction: Pt/TiO₂ catalyst aged by H₂S in air at 400°C

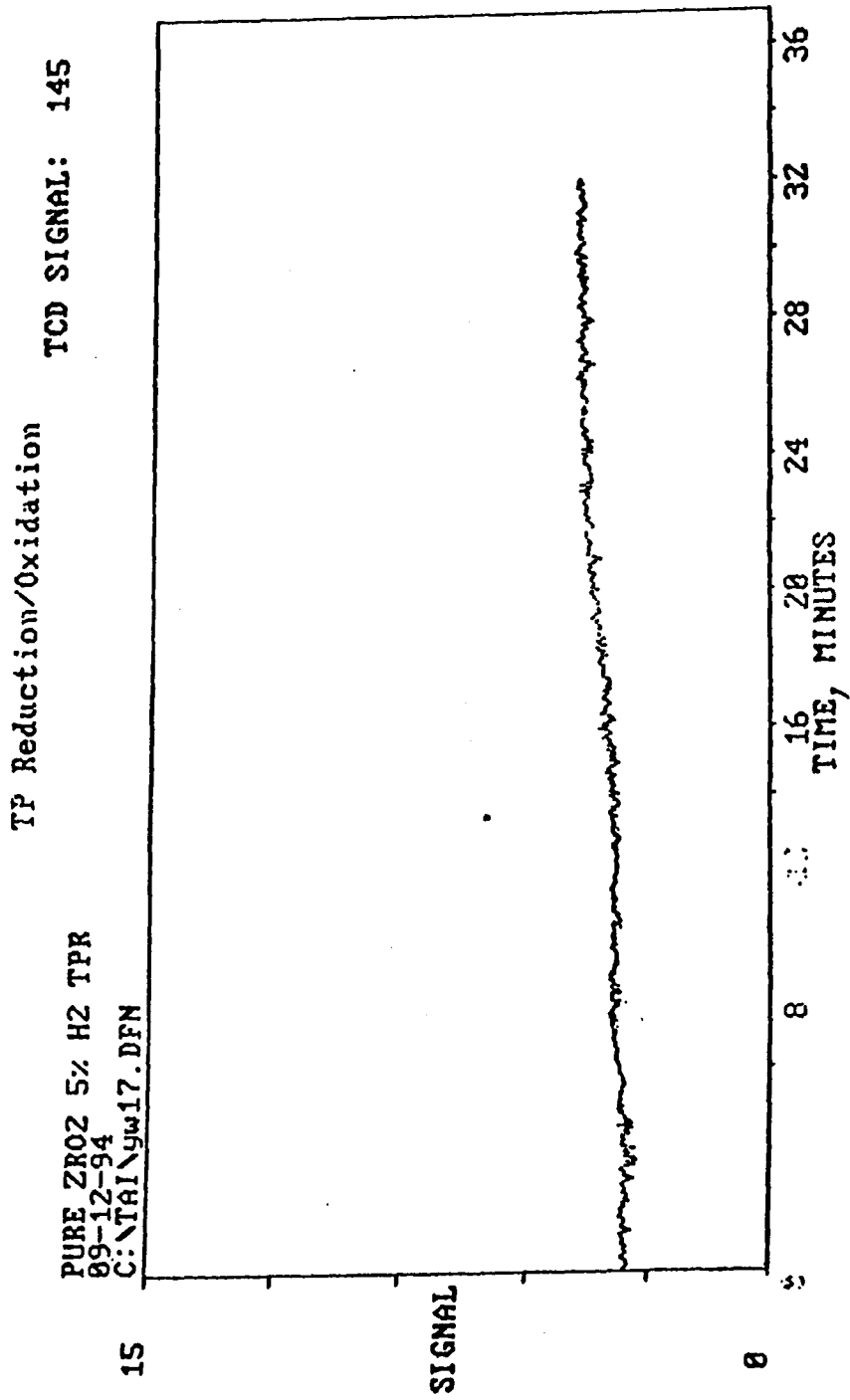


Figure 4-69 5% hydrogen temperature program reduction: Pure ZrO₂

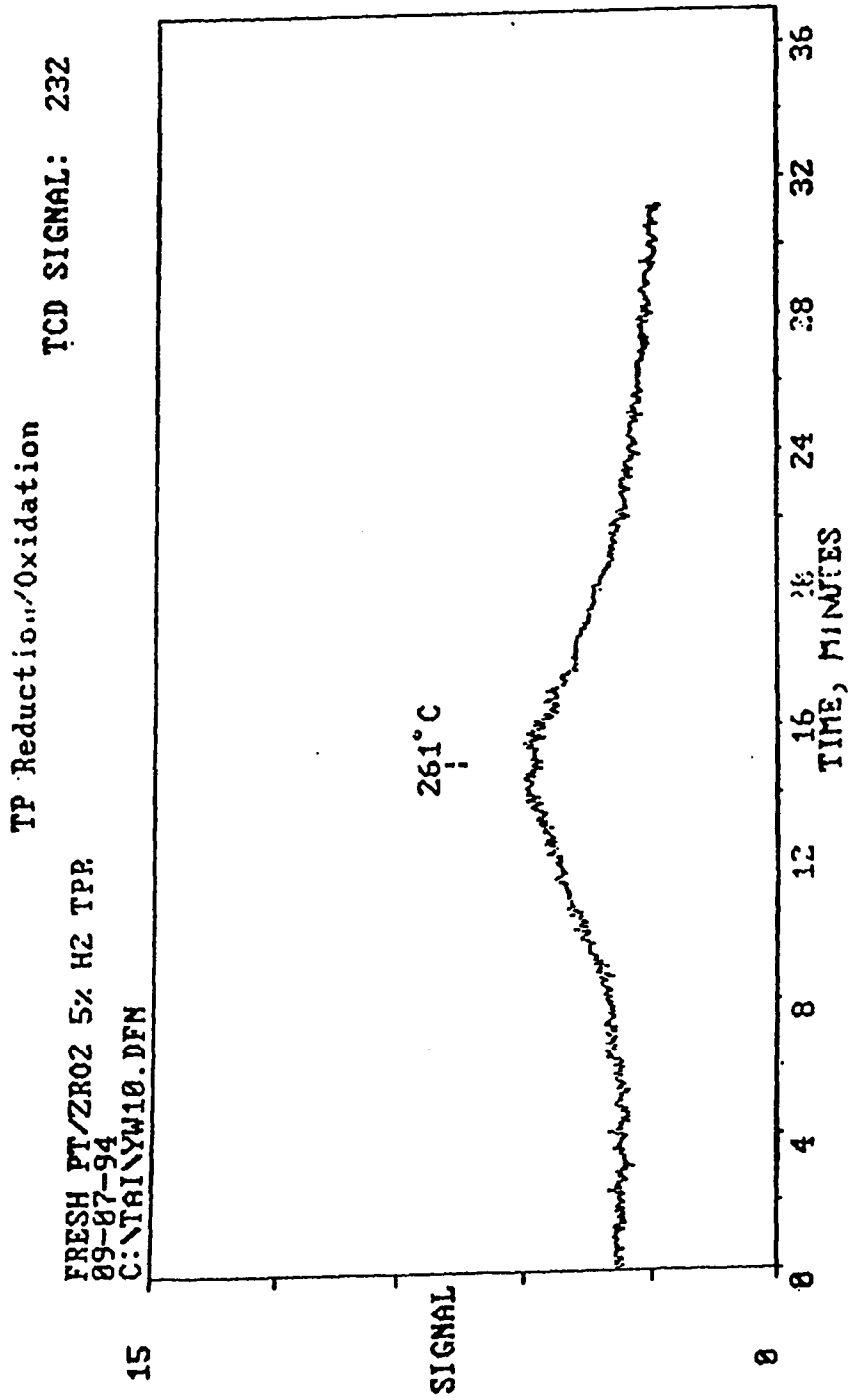


Figure 4-70 5% hydrogen temperature program reduction: Fresh Pt/ZrO₂ catalyst

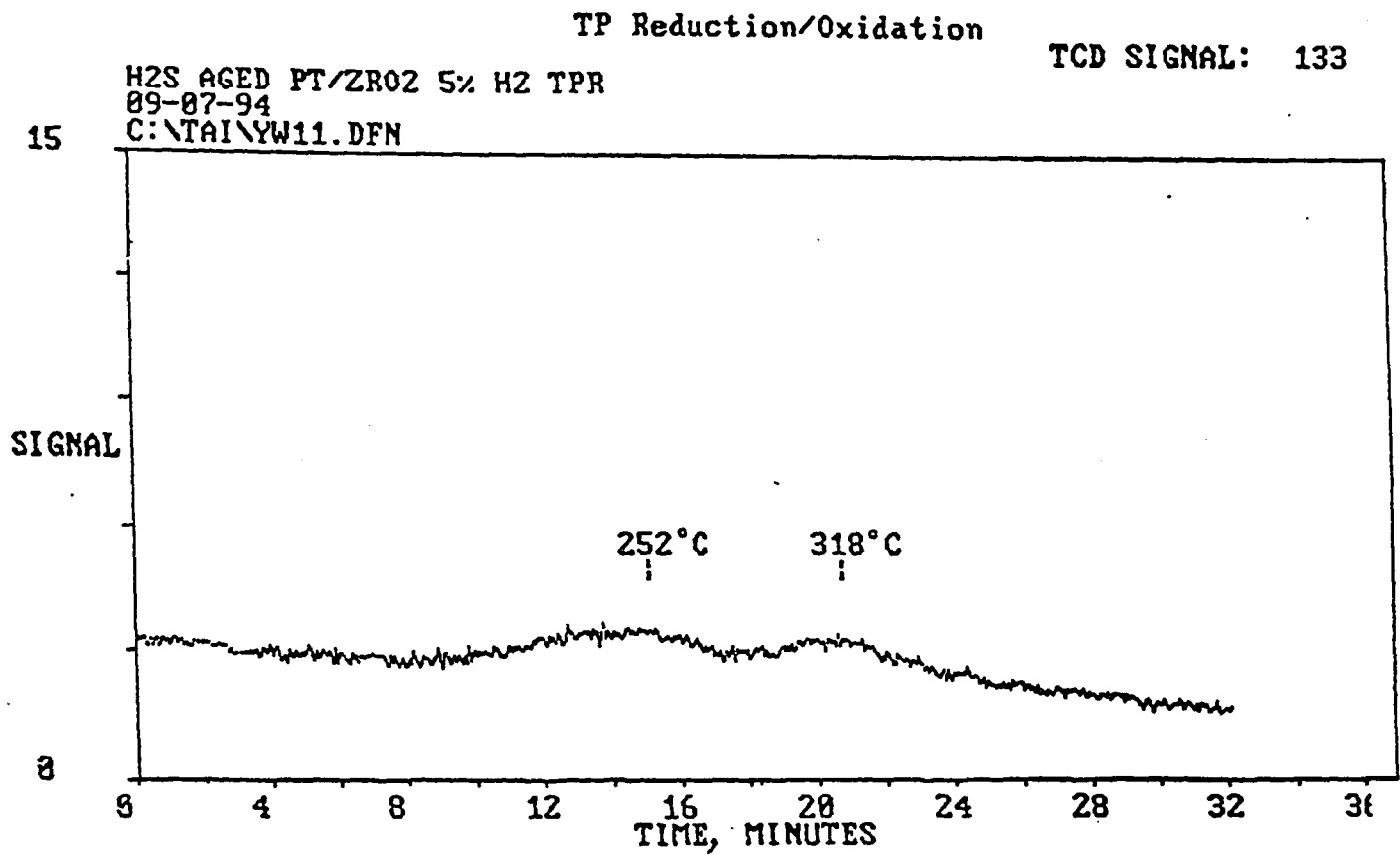


Figure 4-71 5% hydrogen temperature program reduction: Pt/ZrO₂ catalyst aged by H₂S in air at 400°C

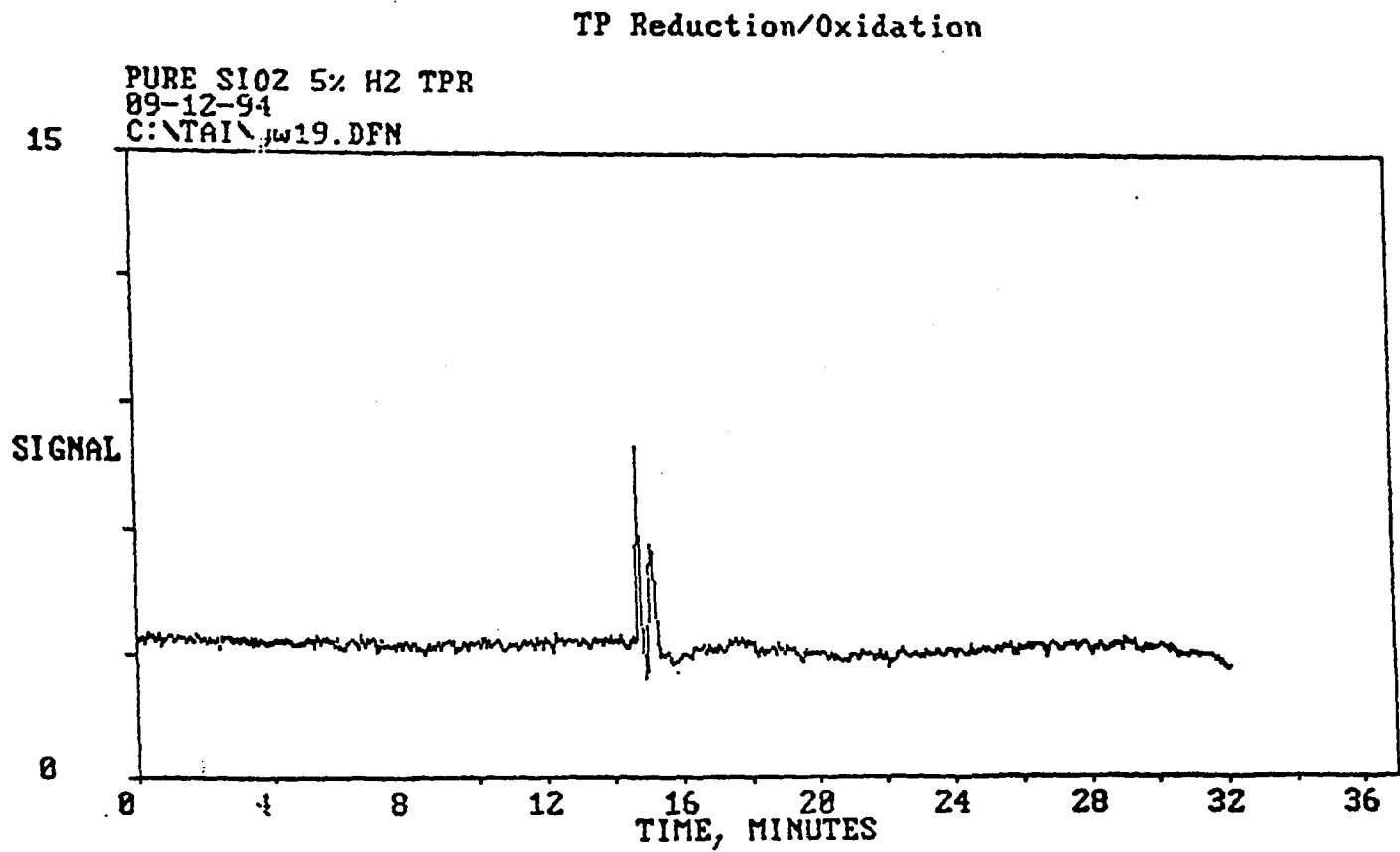


Figure 4-72 5% hydrogen temperature program reduction: Pure SiO₂

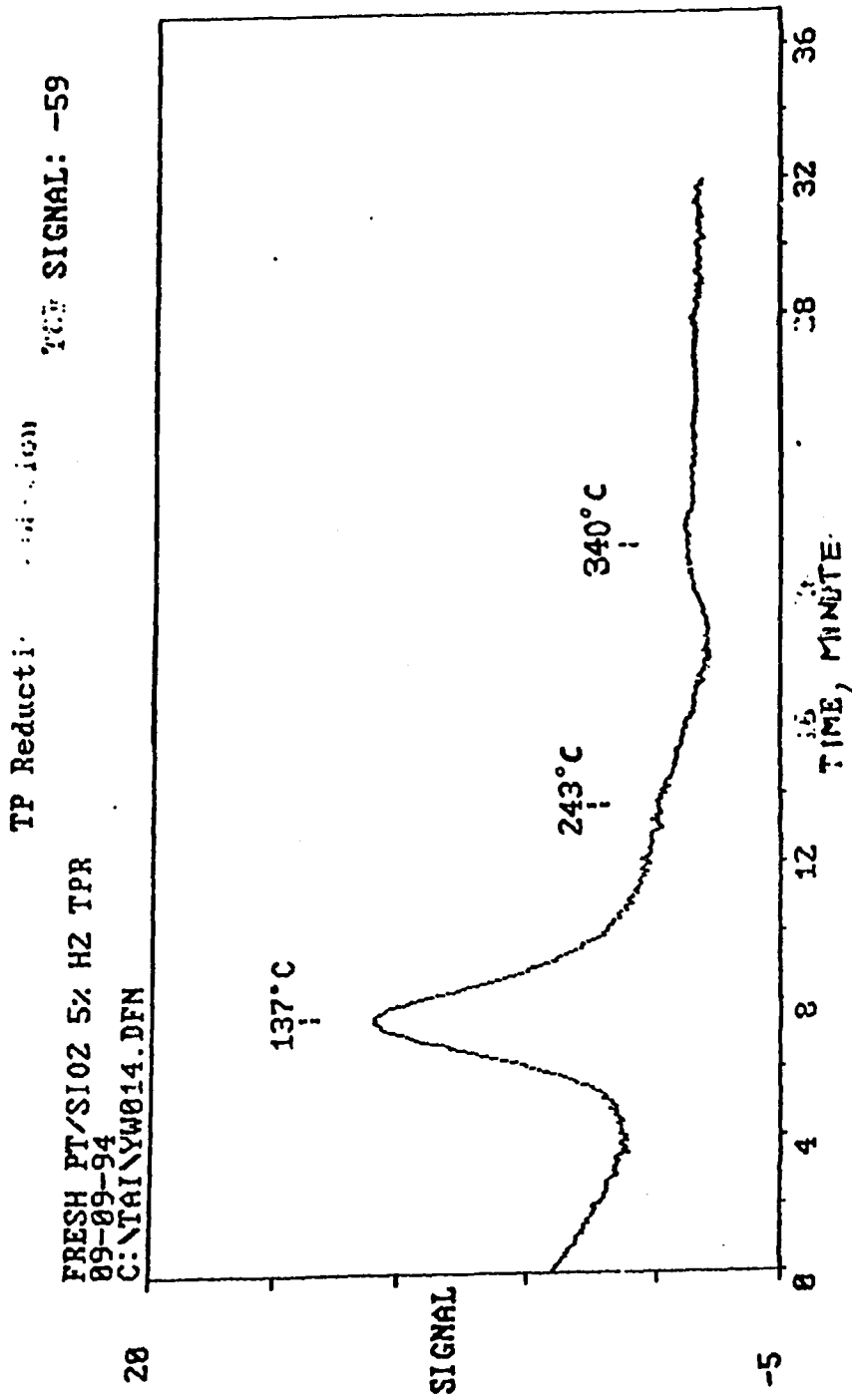


Figure 4-73 5% hydrogen temperature program reduction: Fresh Pt/SiO₂ catalyst

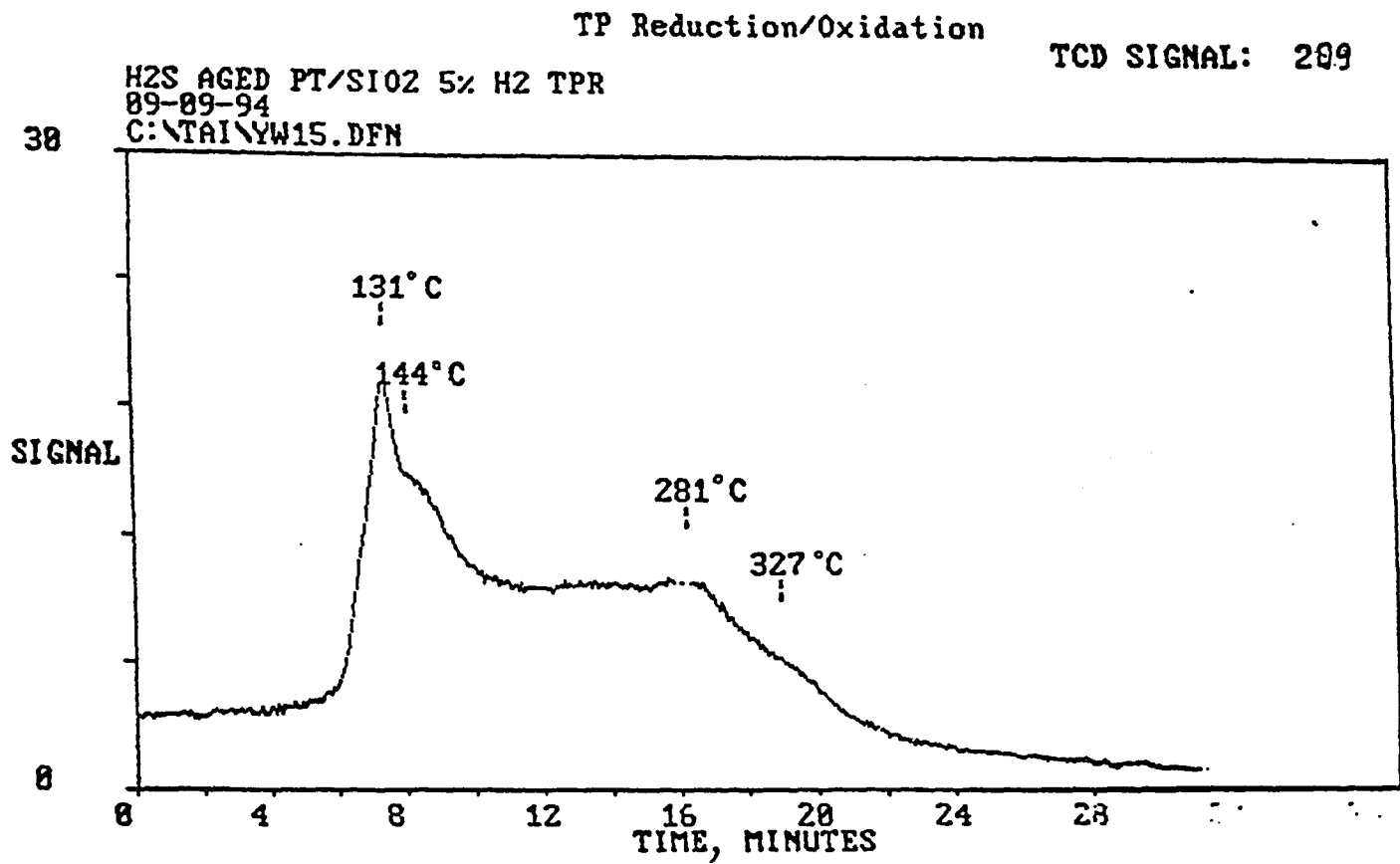
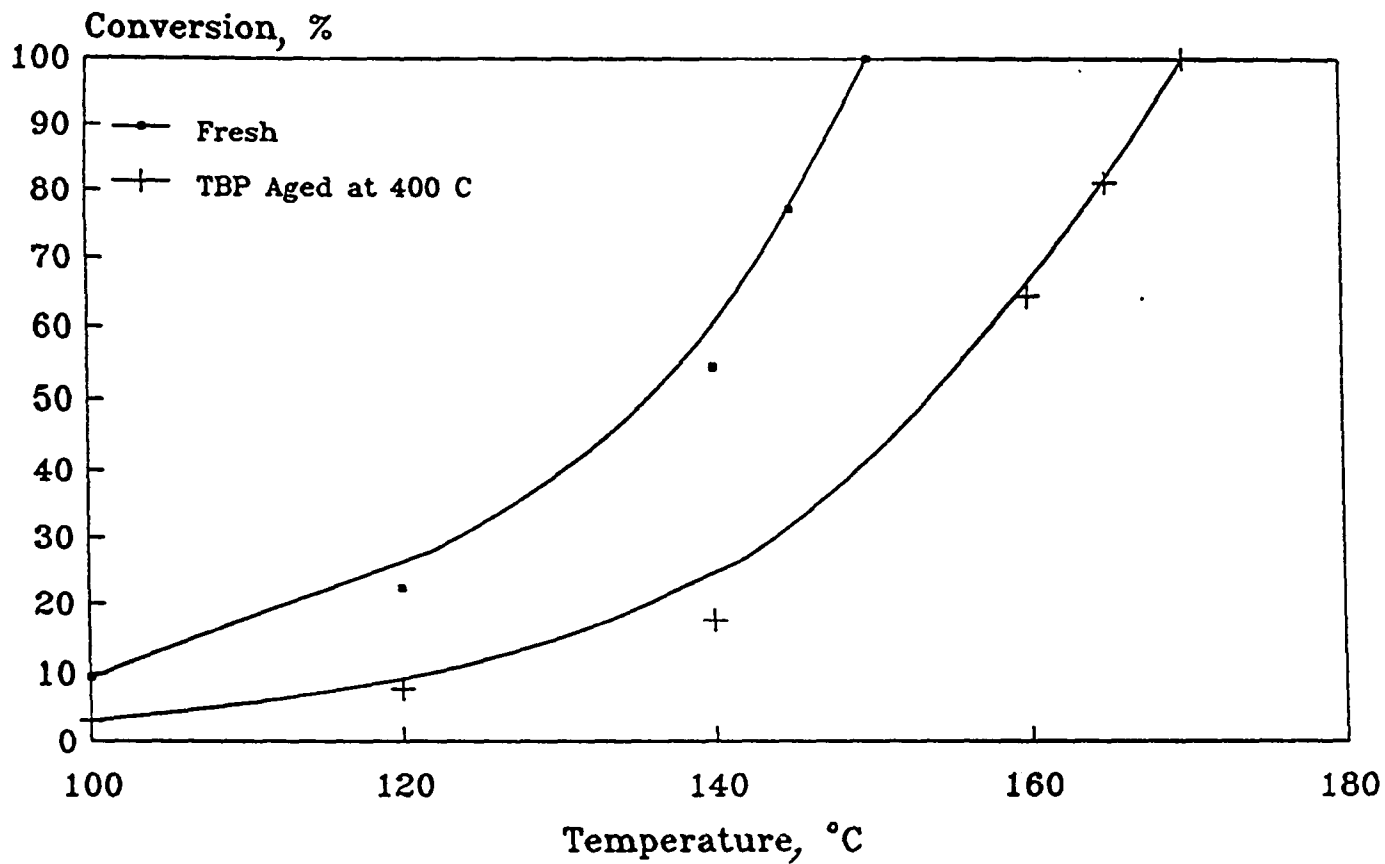
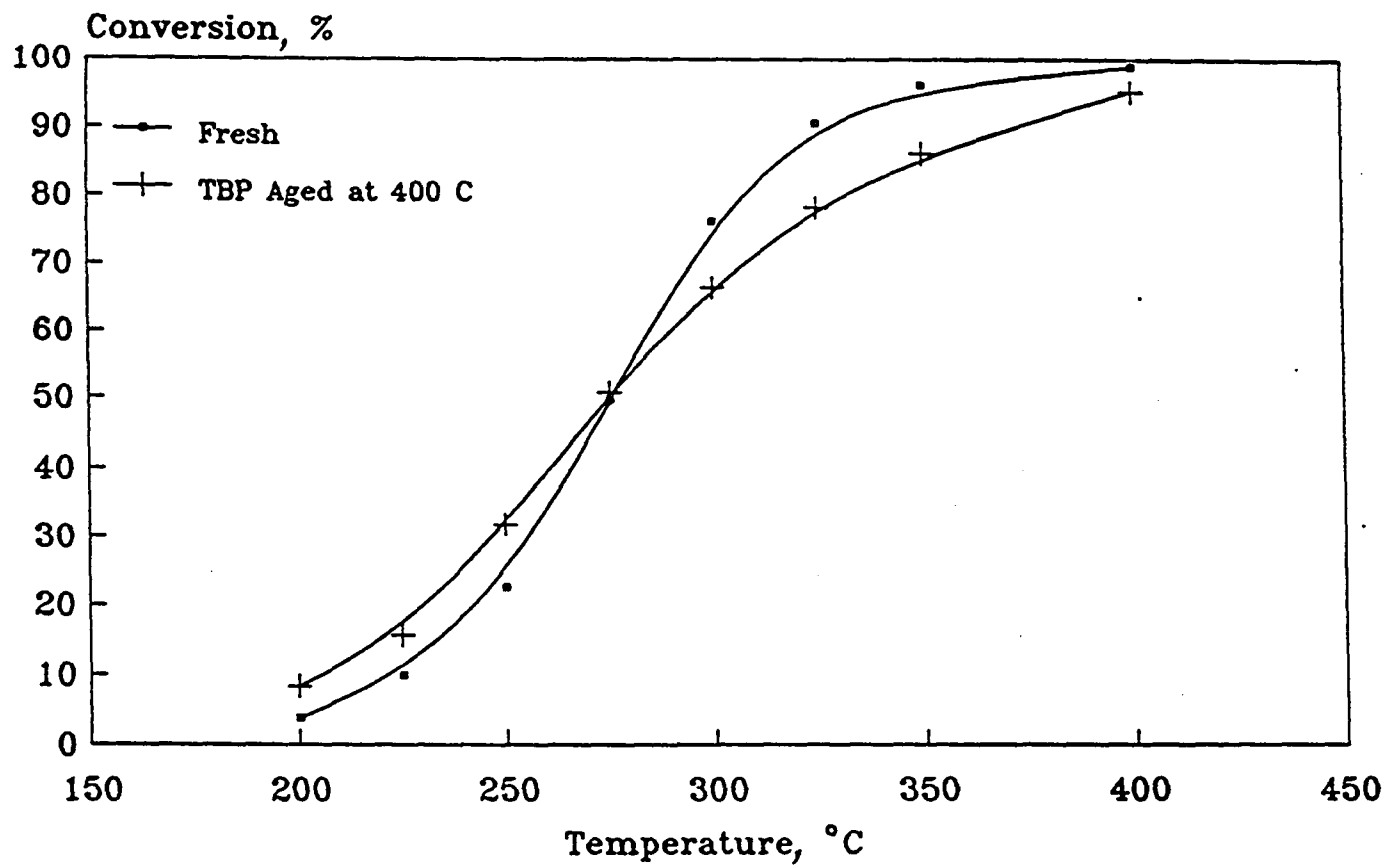


Figure 4-74 5% hydrogen temperature program reduction: Pt/SiO₂ catalyst aged by H₂S in air at 400°C

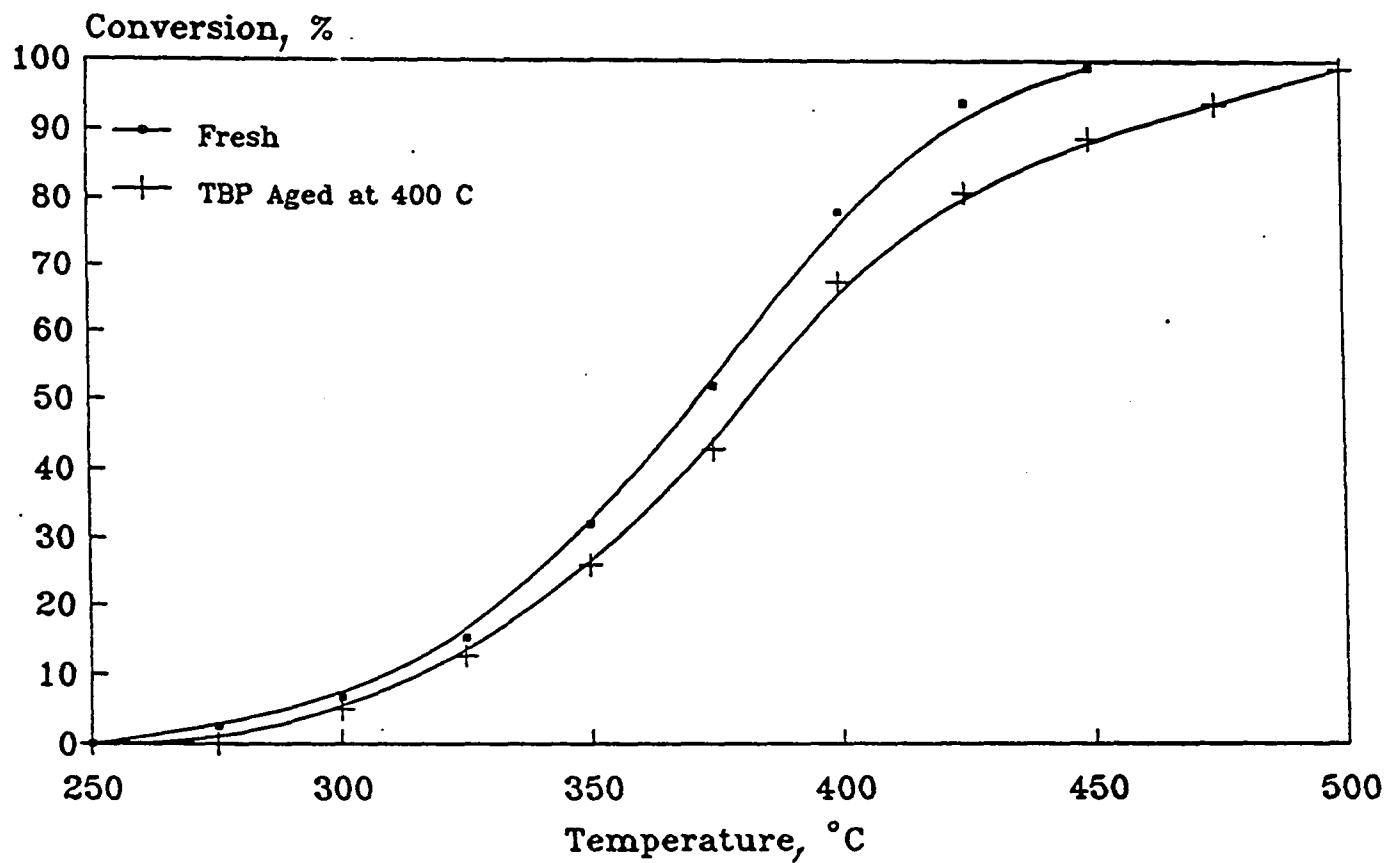


0.05 gram Catalyst
50 ml/min 1% CO in Air SV=30,000/hr
1 ml TBP Aged in Air at 400°C

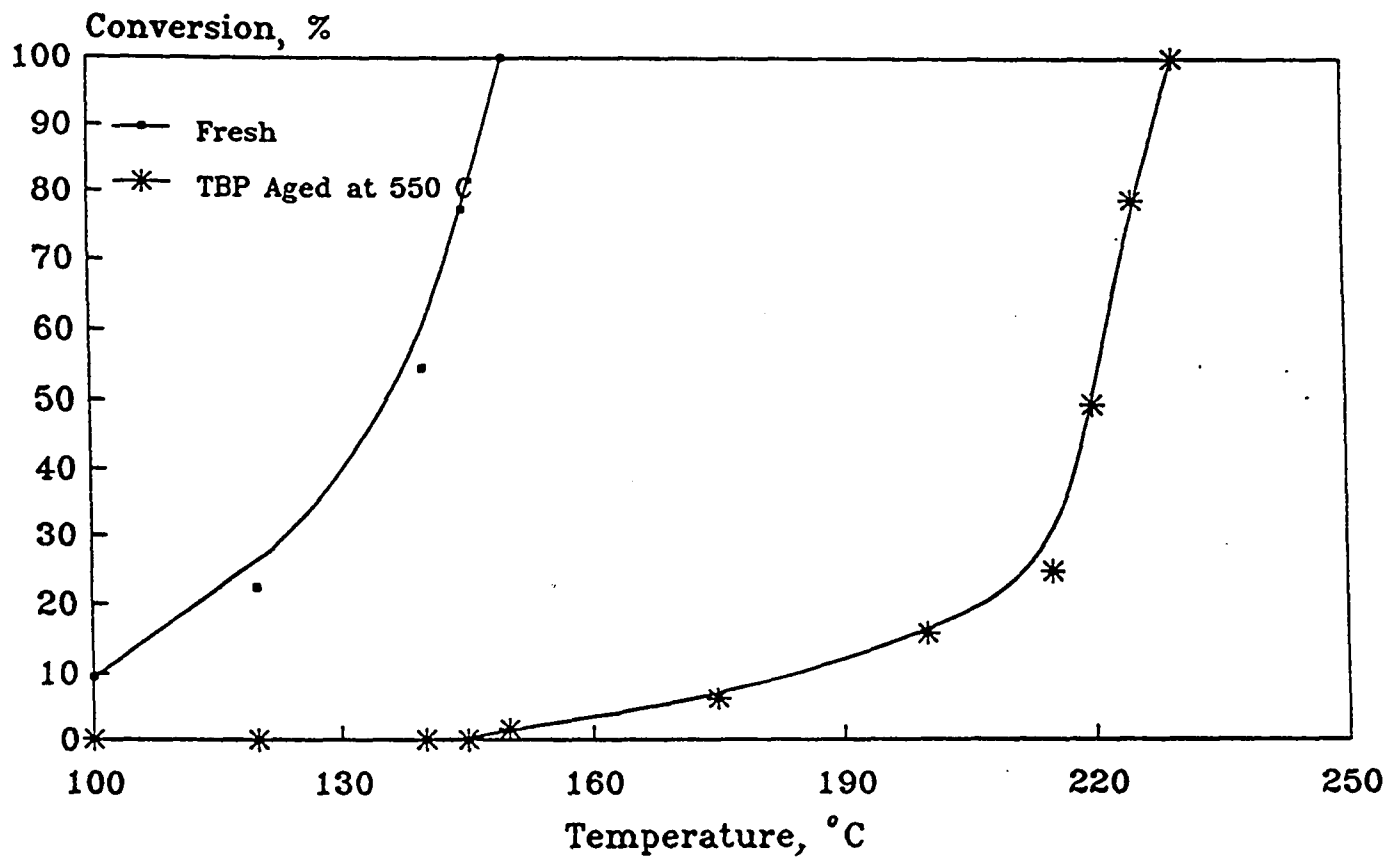
Figure 4-75 Comparison of activity: 1% CO oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by TBP in air at 400°C



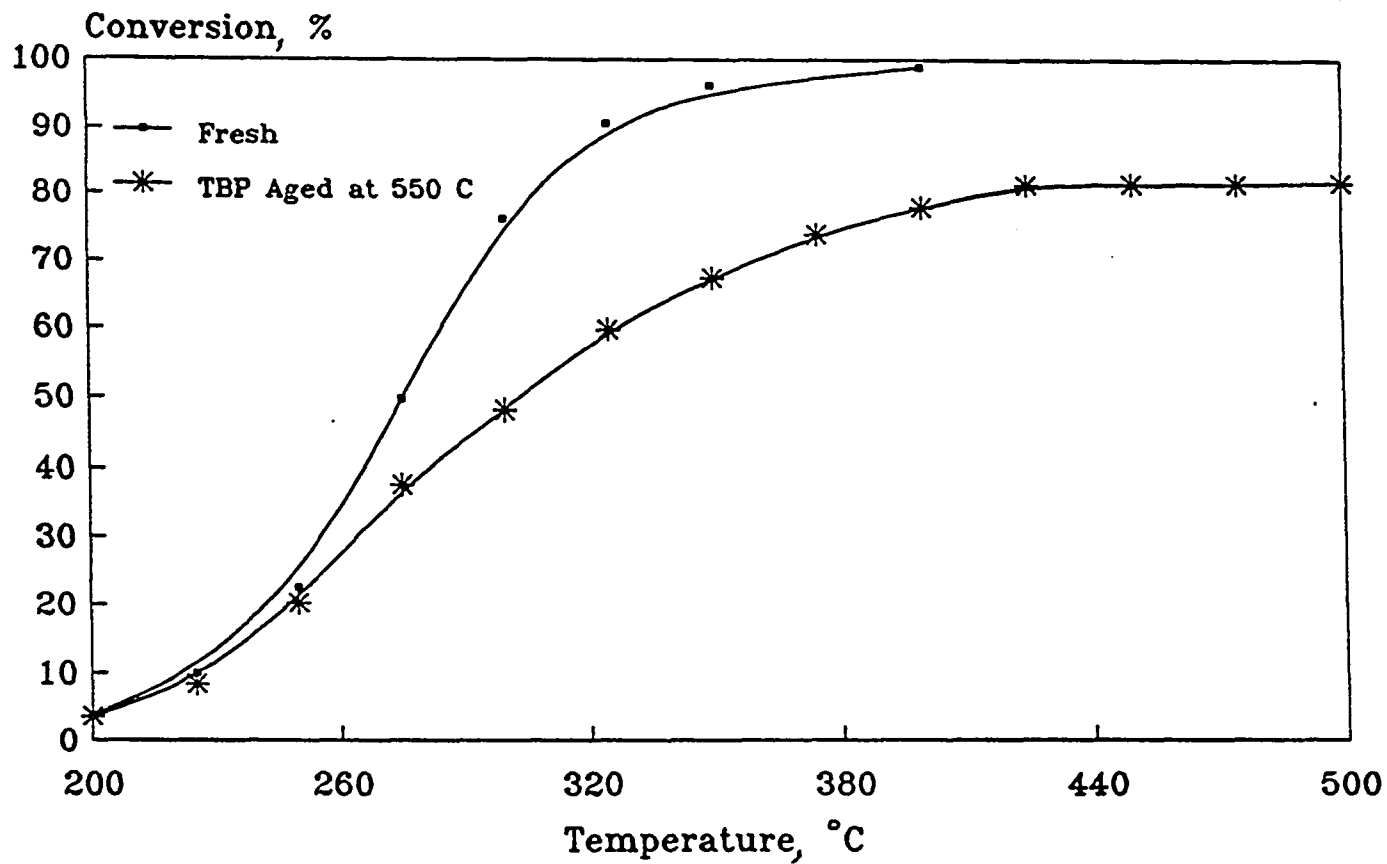
0.05 gram Catalyst 00v/v/hr
50 ml/min 1% Propane in Air SV=30,000/hr
1 ml TBP Aged in Air at 400°C
Figure 4-76 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by TBP in air at 400°C



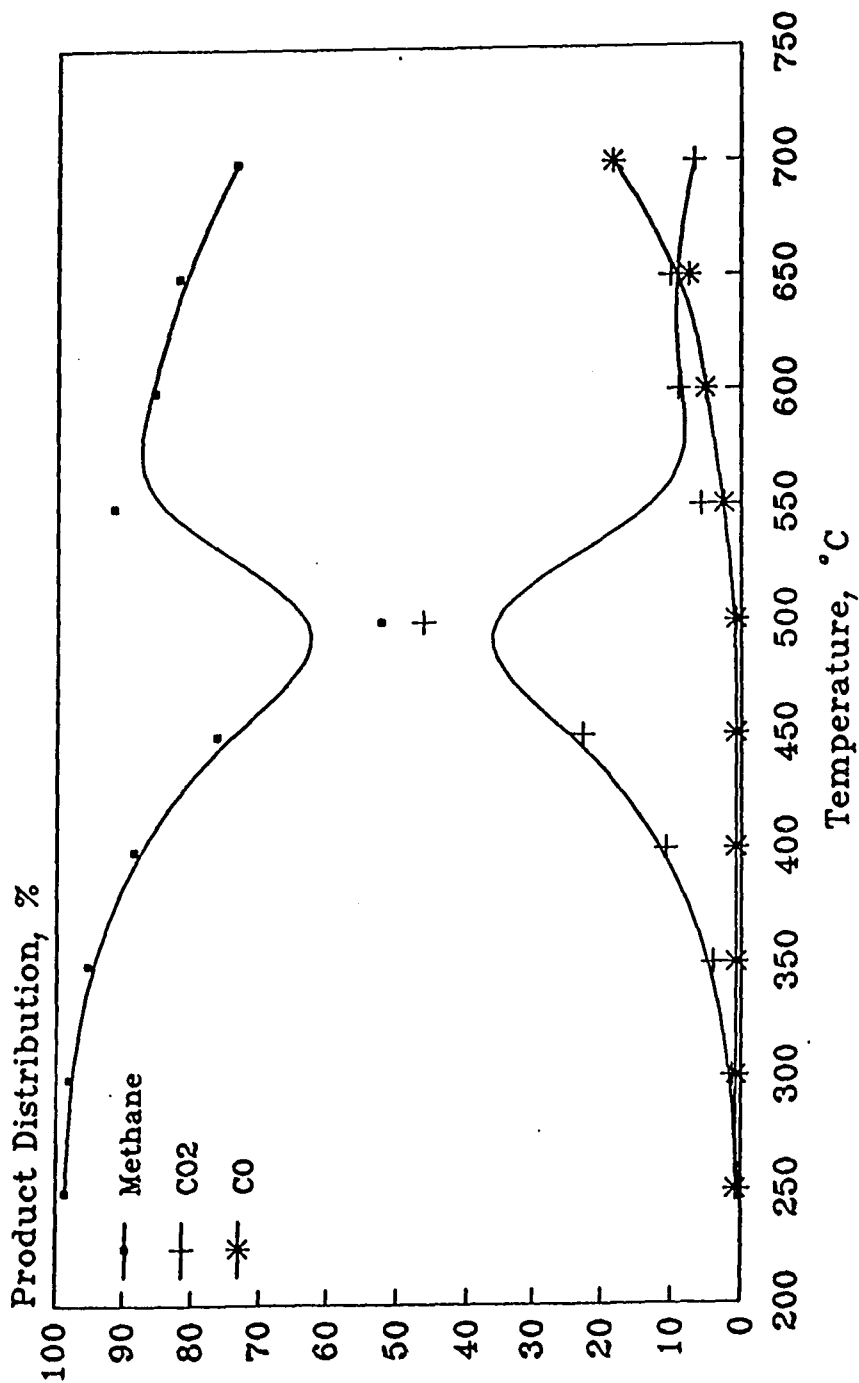
0.05 gram Catalyst
50ml/min 1% CH₄ in Air SV=30,000/hr
1 ml TBP Aged in Air at 400°C
Figure 4-77 Comparison of activity: 1% methane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by TBP in air at 400°C



0.05 gram Catalyst
50 ml/min 1% CO in Air SV=30,000/hr
1 ml TBP Aged in Air at 550°C
Figure 4-78 Comparison of activity: 1% CO oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by TBP in air at 550°C



0.05 gram Catalyst
50 ml/min 1% Propane in Air SV=30,000/hr
1 ml TBP Aged in Air at 550°C
Figure 4-79 Comparison of activity: 1% propane oxidation: Fresh Pt/ γ -Al₂O₃ vs Pt/ γ -Al₂O₃ aged by TBP in air at 550°C



0.05 gram Catalyst
 50 ml/min 1% CH₄ in Air SV=30,000/hr
 1 ml TBP Aged in Air at 550°C

Figure 4-80 Comparison of activity: 1% methane oxidation: Fresh Pt/γ-Al₂O₃ vs Pt/γ-Al₂O₃ aged by TBP in air at 550°C

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