THE POISONING OF A HYDROTREATING CATALYST
BY PYRIDINE AND ITS HYDROGENATION
DERIVATIVES

By

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THE POISONING OF A HYDROTREATING CATALYST BY PYRIDINE AND ITS HYDROGENATION DERIVATIVES

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PREFACE

During the hydrodenitrogenation of coal-derived liquids, some of the basic nitrogen compounds poison the hydrotreating catalysts. I have studied this problem by investigating the hydrodenitrogenation of pryidine. Also, I have studied the effect that poisons have on hydrogen adsorption.

I wish to express my sincere gratitude and appreciation to my major adviser, Dr. Mayis Seapan, for his valuable suggestions and guidance. I would also like to thank Dr. Gary Foutch and Dr. Billy Crynes as members of my examining committee.

I am also grateful to the Oklahoma State University School of Chemical Engineering and the University Center for Energy Research (UCER) for providing space, facilities, materials and financial assistance.

Finally, I would like to thank all my friends and family for their help in completing this project. I am especially grateful to my mother, Mrs. Sherry Entz, for her patience in typing this report.

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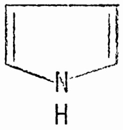
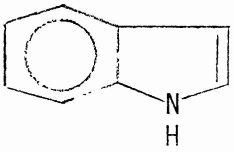
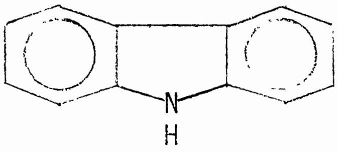
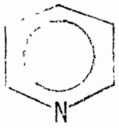
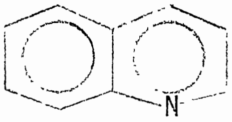
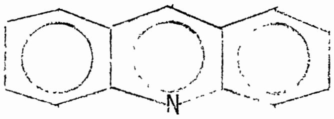
INTRODUCTION

Since resources of conventional crudes are declining, there is a growing need to produce liquid fuels from other fossil resources. One such material will be coal-derived liquids. Conversion of coal-derived liquids to a useful form, such as gasoline, requires, in general, an increase in hydrogen content of the coal liquid, and the removal of inorganic ash and heterocyclic compounds from the coal liquid. These heterocyclic compounds that need to be removed are organic nitrogen, sulfur, and oxygen compounds. Of these, removal of heterocyclic nitrogen compounds, hydrodenitrogenation (HDN), has proven to be the most difficult. Although difficult, hydrodenitrogenation is necessary because the fuel product may be unstable and emission restrictions may be exceeded if sufficient amounts of organic nitrogen compounds are present. Also, the carcinogenicity of coal liquids is attributed mainly to the presence of orgnaic nitrogen compounds. Most importantly, the poisoning of the catalysts by the organic nitrogen compounds can be detrimental to the activity of catalysts in subsequent processing steps.

Some of the more common heterocyclic nitrogen compounds found in coal-derived liquids are shown in Table I. Hydrodenitrogenation of these compounds is generally believed to occur by saturation of the heterocyclic ring, followed by ring fracture and subsequent removal of the nitrogen as ammonia. In usual operations, some amount of the basic

TABLE I

HETEROCYCLIC NITROGEN COMPOUNDS FOUND IN COAL-DERIVED LIQUIDS

Name	Formula	Structure
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Acridine	$C_{13}H_9N$	

heterocyclic nitrogen compounds irreversibly adsorb on the acidic catalyst sites causing the catalyst to deactivate. As a result, the organic nitrogen compounds act as poisons in their own hydrogenation.

The purpose of this study, in general, is to investigate the poisoning of hydrotreating catalysts by the heterocyclic nitrogen compounds typically found in coal-derived liquids. The specific objectives of this study are as follows:

1. to study the interactions between temperature, organic nitrogen compound poisoning and hydrogen adsorption on a hydrotreating catalyst;
2. to determine if the compounds that irreversibly adsorb on the catalyst during the reaction process are the original organic nitrogen compounds or are some intermediate compounds resulting from hydroprocessing of the nitrogen compounds.

CHAPTER II

LITERATURE REVIEW

Many studies concerning the relationships between catalyst acidity, activity, poisoning, and hydrodenitrogenation have been conducted. Many of the early studies dealt with the adsorption of basic organic nitrogen compounds on cracking catalysts in order to determine the acidic characteristics of the catalyst. More recent work has been concerned with determining the nature of acid sites on the catalyst. The acidic catalyst sites can theoretically be Lewis or Bronsted type sites. The Bronsted type involves proton transfer and the Lewis type depends on the acid site's ability to accept an electron pair.

Measurements of Bronsted and Lewis acid sites are commonly accomplished by use of infrared spectroscopy. Typically, ammonia or pyridine is adsorbed on the catalyst surface and the infrared spectrum is determined. For instance, with ammonia adsorbed on the surface, two kinds of adsorption, one of which indicates NH_3 adsorbed on Lewis acid sites, and the other NH_4^+ on Bronsted acid sites, are observed. Similarly for pyridine, the spectrum of the pyridinium ion is very different from that of pyridine, which permits differentiation between acid sites on the catalyst surface. (1)

In the early 1950's, Maxted (2) was one of the first to discover that the acidic characteristics of catalysts are essential to their hydrogenation and cracking activity. In his study, it was concluded that the reason that a molecule is toxic is because the molecule contains unshared external electron pairs which enable a strong chemisorptive bond to occur between the catalyst and the molecule. Maxted also proved that the toxic effect of poisoning is dependent on the size and average length of stay of the adsorbed molecule on the catalyst surface. As a result, toxicity increases with the molecular size of the poison and with the strength of the bond between the catalyst and the poisoning molecule.

Also, in the early 1950's, an excellent study on the poisoning of cracking catalysts was carried out by Mills, Boedeker, and Oblad (3). Partial poisoning studies of various organic nitrogen compounds were carried out with SiO_2-Al_2O_3 catalysts. It was determined that the basic organic nitrogen compounds were held by both physical and chemical forces on the catalyst surface. Also, in this study, the organic nitrogen compounds of interest were ranked as to their effectiveness as poisons as follows: quinoline $>$ pyrrole $>$ aniline. It was confirmed that these organic nitrogen compounds were irreversibly adsorbed on the catalyst instead of any reaction intermediates or products. In other words, the organic nitrogen molecules were solely responsible for the catalyst poisoning since these compounds are not decomposed to a significant extent at cracking conditions.

Adsorption of quinoline was used in the study by Mills et al. in order to gain insight into the acidic properties of the catalyst. The cracking activity of the catalysts studied proved to be proportional to the catalyst's capacity to chemisorb quinoline at cracking temperatures. The amount of chemisorbed base was determined to be a measure of the number of active catalyst sites. For a completely poisoned SiO_2-Al_2O_3

catalyst, it was found that only about four percent of the catalyst surface was covered by quinoline (assuming the quinoline molecule lies flat and covers about 36 $\mathring{A}^2$). As a result, the major part of the catalyst surface does not contribute to the cracking activity of the catalyst.

A few years later, Hirschler (4) did a similar study on the adsorption of quinoline. Contrary to Mills et al. (3), Hirschler discovered that a complete adsorption of quinoline does not deactivate all the acid sites. He found that chemisorbed quinoline only causes a modest reduction in the total number of acid sites, but strongly modifies the acid strength distribution. In other words, the largest number of acid sites on the surface have a very low acid strength, and as a result, only the strong acid sites are eliminated when quinoline is adsorbed.

Another study, concerning the activity of alumina as a catalyst support, was carried out by Pines and Haag (5). They discovered that acidity, isomerization activity, and surface hydration are all related. As a result, the degree of calcination (removal of water) affects the activity of the catalyst. Results showed that calcination temperatures ranging between 600 and 800°F provided the catalyst with the highest activity. At lower calcination temperatures, enough water remained as to inhibit the catalyst activity. At higher pretreatment temperatures, the acitivity was reduced due to changes in the catalyst structure. It was also determined that the catalyst surface was primarily made up of Lewis acid sites. Probably no Bronsted acids exist on the alumina, and if they do, they are of very low acid strength.

Recent work concerning activity and acidity of catalysts, has dealt mainly with the adsorption of pyridine on different catalysts and the determination of the nature of acid sites. Takahashi et al. (6) studied the adsorption of pyridine on silica-alumina catalysts and found that approximately 8 to 11 percent of the pyridine adsorbed was irreversibly chemisorbed to the catalyst. It was confirmed that, even above 300^{o}C, the strongly adsorbed compound was only pyridine, and not any reaction intermediates or products resulting from thermal decomposition.

The nature of acid sites on different types of catalysts has been studied extensively. Segawa and Hall (7), Fransen et al. (8), and Ratnasamy and Knozinger (9), have all presented studies that are representative of the majority of work done on this subject. In general, all three studies agree that for reduced catalysts, only Lewis acid sites play a role in catalytic reactions. All three studies agree that the oxidic form of the catalyst contains both Bronsted and Lewis sites, but when the catalyst is reduced or sulfided, the Bronsted acidity is either eliminated or does not play a role at reaction temperatures. As a result, catalyst activity is largely dependent on the Lewis acidity of the catalyst.

Most of the hydrodenitrogenation studies done in the past have dealt mainly with determining the effect that catalyst composition and pretreatment conditions have on the removal of organic nitrogen compounds. Shih et al. (10) and Thakkar, Baldwin, and Bain (11) conducted studies which compared the hydrodenitrogenation activity of hydrotreating catalysts of different compositions. Both studies agreed that Ni-Mo/Al_2O_3 catalysts are better for hydrodenitrogenation than Co-Mo/Al_2O_3 catalysts. One possible explanation is that Ni-Mo/Al_2O_3 catalysts have a higher hydrogenation activity than cobalt catalysts.

Also in Shih et al. (10), the effects that presulfiding the catalyst and the presence of hydrogen sulfide had on hydrodenitrogenation were investigated. Presulfiding the catalyst greatly improved the total nitrogen removal rate. Although presulfidation did not affect the hydrogenolysis step, it did increase the rate of hydrogenation. On the other hand, the presence of hydrogen sulfide increases the total nitrogen removal by enhancing the hydrogenolysis step.

Similar results were found by Goudrian, Gierman, and Vlugter (12) in their study on the effects of hydrogen sulfide on the hydrodenitrogenation of pyridine. It was found that the conversion of the pyridine ring by hydrogenation is 25 to 45 percent higher on the presulfided catalysts than on the oxidic catalyst. The presence of hydrogen sulfide had little effect on this conversion. The hydrogenolysis reaction is 5 to 15 percent higher at 250 to 350°C for the presulfided catalyst as compared to the oxidic catalyst. The presence of hydrogen sulfide increases this conversion by another 25 to 50 percent.

Satterfield and co-workers have also investigated the effects that presulfiding the catalyst and adding sulfur compounds to the process have on hydrodenitrogenation. For instance, in 1975, Satterfield, Modell, and Mayer (13) published work on the interactions between catalytic hydrodesulfurization of thiopene and hydrodenitrogenation of pyridine. Thiophene was found to have two different effects on the hydrodenitrogenation of pyridine. Below 325°C, thiophene inhibits the hydrodenitrogenation reaction. Above 325°C, the reaction is enhanced when thiophene is present. However, at 325°C, thiophene is more than 60 percent converted to hydrogen sulfide, and as a result, the hydrogen sulfide is responsible for the enhancement of the reaction. The inhibition of the hydrodenitrogenation reaction below 325^{o}C is explained by the theory that sulfur compounds (thiophene and hydrogen sulfide) compete for hydrogenation sites on the catalyst, and as a result, slow down the hydrogenation step of the hydrodenitrogenation reaction.

Above 325^{o}C, the overall rate of hydrodenitrogenation is probably limited by hydrogenolysis instead of hydrogenation. It is therefore postulated, that hydrogen sulfide improves catalyst activity for rupture of the C-N bond. Two possible explanations for this theory are (1) that the hydrogen sulfide maintains the catalyst in a fully sulfided state, or (2) that the beneficial effect of hydrogen sulfide may be due to its acidity. In other words, hydrogen sulfide molecules may aid in removing strongly adsorbed basic nitrogen compounds from the catalyst surface.

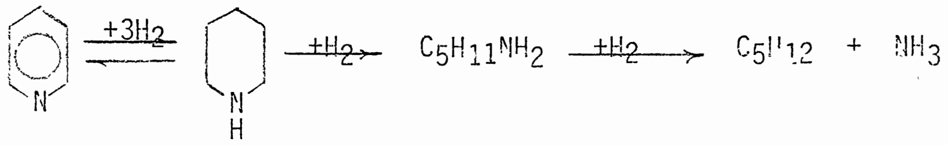
Yang and Satterfield (14) carried out similar studies with the effects of sulfiding on the hydrodenitrogenation of quinoline. As observed with pyridine, hydrodenitrogenation of quinoline was enhanced when hydrogen sulfide was present at high temperatures. Also in this work, the theory that hydrogen sulfide depresses the hydrogenation reactions but enhances the hydrogenolysis reactions was confirmed. Since the hydrogenolysis reactions in the quinoline hydrodenitrogenation reaction network are rate limiting, the net effect of hydrogen sulfide is an enhanced quinoline hydrodenitrogenation conversion.

Another study carried out by Satterfield and co-workers, dealt with the reaction network and kinetics of the hydrodenitrogenation of quinoline. Satterfield and Cocchetto (15) showed that the primary limiting factor on the overall hydrodenitrogenation rate is the very strong adsorption onto the catalyst of secondary amines formed as reaction intermediates. As a result, chemisorbed reaction intermediates and products can play a significant role in the poisoning of catalyst surfaces.

Massoth and co-workers have done a significant amount of work on catalyst poisoning. In 1978, Cowley and Massoth (16) showed that pyridine adsorbs on the active desulfurization sites of a sulfided Mo/Al_2O_3 catalyst. A value of 0.24 molecules of pyridine per molybdenum atom was the amount adsorbed on the fully poisoned (zero activity) Mo/Al_2O_3 catalyst. However, it was uncertain that each adsorbed molecule of pyridine was effective in poisoning an active site. As a result, the value of 0.24 is considered to be a maximum one. A few years later, Ramachandran and Massoth (17) showed that pyridine appeared to be site selective in its poisoning effect. In other words, after poisoning, some sites are not significantly altered, while other catalyst sites are completely deactivated.

Present work by Miciukiewicz and Massoth (18) consists of studying the effects of poisons on the activity of upgrading catalysts. Although this work is not complete, preliminary results include the following order of effectiveness as poisons in the hydrogenation of hexene on a Co-Mo/Al_2O_3 catalyst: quinoline $>$ pyridine $>$ indole $>$ analine.

Another area of interest in this literature review is the hydrodenitrogenation of pyridine. The hydrodenitrogenation of pyridine has been studied in the past because only a few intermediates are formed, and because many of the nitrogen compounds that occur naturally in petroleum, coal-derived liquids, and shale oils are pyridine derivatives. It is generally agreed that pyridine hydrodenitrogenation occurs by saturation of the heterocyclic ring to produce piperidine, followed by ring fracture to produce n-pentylamine and subsequent removal of the nitrogen as ammonia. This stepwise reaction process is shown below:



The basicity of the nitrogen compounds in the above reaction sequence increases through the reaction process. In other words, ammonia is the most basic and pyridine is the least basic of the intermediates and products shown above.

In 1967, Larson (19) conducted a study in which he qualitatively considered the poisoning of acid sites during the hydrogenation of pyridine. He determined that the normal acid-base concept is inadequate in explaining the relative poisoning ability of a group of bases over acidic catalysts. For instance, in pyridine hydrogenation, ammonia is the most basic reaction product but relatively ineffective as a poison at cracking temperatures in the vicinity of 500°C. He also concluded that the molecular weight and degree of aromaticity are also important in determining a compound's effectiveness as a poison.

As stated previously in this review, Satterfield, Modell and Mayer (13) published work on the hydrodenitrogenation of pyridine. They discovered that the pyridine conversion goes through a maximum at about 380°C. The maximum in pyridine conversion occurs due to the onset of a thermodynamic limitation on the reaction. This equilibrium limitation is in the first step of the reaction mechanism. At temperatures above 325°C, the equilibrium was found to shift increasingly in favor of pyridine at the expense of piperidine. As a result, the hydrogenolysis reaction (piperidine $\longrightarrow$ n-pentylamine) becomes starved of its reactant source which results in a decrease of pyridine conversion.

McIlvried (20) investigated the kinetics of the hydrodenitrogenation of pyridine on a Ni-Co-Mo/Al_2O_3 catalyst. The hydrodenitrogenation of pyridine was apparently a first order process with a reaction rate constant that was dependent on the initial partial pressure of the nitrogen compounds in the feed. The rate constant decreased with an increasing feed nitrogen content. This dependence on the initial nitrogen concentration was due to the strong adsorption of pyridine and its derivatives on the catalyst.

McIlvried also found that the degree of nitrogen removal was approximately the same for a given set of reaction conditions regardless of whether the compound in the feed was pyridine or piperidine. As a result, the rate of hydrogenation was found to be very fast compared to the rate of hydrodenitrogenation. It was also determined that the rate of n-pentylamine hydrodenitrogenation was considerably faster than the rate of piperidine hydrodenitrogenation.

In this study, McIlvried assumed that ammonia, piperidine and pyridine must be about equally strongly adsorbed. By using this assumption and fitting his model to experimental data, he was able to back out the value of the adsorption coefficient. The value for the adsorption coefficient on denitrification sites for ammonia, pryidine and piperidine was determined to be 1.57 $(psia)^{-1}$. Similarly, he assumed that ammonia was the only compound that strongly adsorbed on hydrogenation sites and its adsorption coefficient was calculated to be 10.5 $(psia)^{-1}$.

Sonnemans, Van Den Berg and Mars (21) also investigated the kinetics of the hydrodenitrification of pyridine. They measured the adsorption of the various nitrogen compounds directly. It was found that the amount adsorbed did not vary much with temperature. The relative strength of adsorption of the nitrogen compounds was found to be piperidine $>$ pyridine $>$ ammonia. On a 22% MoO_3 - Al_2O_3 catalyst at 300°C, the pyridine adsorption coefficient was found to be 4.3 times as high as the ammonia adsorption coefficient. Similarly, at 200°C, the piperdine coefficient was 6.1 times that of pyridine.

Sonnemans et al., like McIlvried, concluded that the kinetics indicated a first order reaction with all of the nitrogen compounds equally strongly adsorbed. This observation was not in accordance with the results of the adsorption measurements. A possible explanation was that the strong heterogeneity of the catalyst surface would invalidate the Langmuir adsorption assumed to calculate the adsorption coefficients. As a result, the adsorption coefficients calculated from direct adsorption measurements are only approximate.

In general, this literature review indicates that the acidic characteristics of catalysts are essential to their activity. The activity of catalysts was found to be proportional to their ability to chemisorb basic nitrogen compounds. The chemisorption of basic nitrogen compounds was concluded to only cause a modest reduction in the number of acid sites, but to strongly modify the acid strength distribution. Also, the major portion of the catalyst surface was determined to be inactive. The relative effectiveness as poisons for organic nitrogen compounds was found to be quinoline $>$ pyridine $>$ indole $>$ aniline.

The hydrodenitrogenation of basic organic nitrogen compounds was also investigated in this review. A $NiMo/Al_2O_3$ catalyst was generally agreed to be better for hydrodenitrogenation than a $CoMo/Al_2O_3$ catalyst. The presulfiding of catalysts increased the rate of the hydrodenitrogenation reaction but did not affect the hydrogenolysis step.

Likewise, the presence of H_2S was found to enhance the hydrogenolysis step but depress the hydrogenation step in a hydrodenitrogenation reaction. Also, in some hydrodenitrogenation reactions it was concluded that some of the reaction intermediates and products can play a significant role in the poisoning of catalyst sites.

In general, the hydrogenation of pyridine was regarded to be a first order process. Also, the conversion of pyridine went through a maximum as the temperature increased due to the onset of a thermodynamic limitation. The kinetics of the reaction indicated that pyridine and all of the nitrogen compounds resulting from pyridine hydrogenation were equally strongly adsorbed. However, the adsorption measurements indicated that the relative strength of adsorption of the compounds was piperidine $>$ pyridine $>$ ammonia.

In the pyridine hydrogenation literature there was very little information on the effect that the adsorbed nitrogen compounds had on the adsorption of hydrogen. Therefore, the purpose of this project is to study the adsorption of pyridine and its hydrogenation derivatives on a catalyst surface and to determine the effects that these adsorbed compounds have on hydrogen adsorption.

CHAPTER III

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The basic objective of this study was to investigate the adsorption/desorption cycle of a poisoned catalyst when hydrogen is used as the adsorbate. Heterocyclic nitrogen compounds, such as pyridine, were used as the poisons in this study. The adsorption and desorption processes were investigated by observing the weight changes of the catalyst during the adsorption/desorption cycle.

Equipment

The experimental apparatus of major importance in this study was a Cahn TGA (Thermal Gravimetric Analysis) System 113. Primarily, the system consists of a null beam type electrobalance that measures weight changes of the catalyst pellets suspended in a temperature controlled gas stream. The microbalance is designed for weight and forces up to 2.5 grams and is sensitive to weight changes as small as 0.1 micrograms. Basically, the balance converts weight changes to an electric current which in turn yields the weight change output on the strip chart recorder.

The Cahn System 113 also contains a Micricon controller. The Micricon consists of two basic devices. The first device is the programmer which enables a temperature profile to be programmed into the Micricon independently of the controller. The second device is the proportional-integral-derivative (PID) controller. This temperature controller is capable of raising the temperature at a rate between 0 and 50^oC/minute up to a maximum temperature of 1150^oC.

The Cahn System 113 also contains a time derivative computer (TDC) and an automatic range expander/percent sample weight accessory. The time derivative computer converts the weight change signal to a rate of weight change with respect to time signal. The automatic range expander keeps the output between two fixed limits and the percent sample weight attachment simply outputs the weight change in a percentage of the weight loss or gain. A schematic diagram of the Cahn System 113 including flowmeters, gas lines, and gas pretreaters is shown in Figure 1.

Supplemental equipment included a porosimeter, an elemental analyzer and an FTIR spectrometer. A Micromeritics 900/910 Series mercury penetration porosimeter was used to determine catalyst pore volume, pore distribution and surface area. Basically, the procedure consists of forcing mercury into an evacuated catalyst sample by generating pressure on the sample and then measuring the change in volume of the mercury by use of an electronic probe.

Elemental analysis of the catalysts was carried out in a Perkin-Elmer 240-B elemental analyzer. Combustion occurred in the analyzer between 950 and 1000^oC in an oxygen atmosphere. The analyzer yielded the weight percentages of hydrogen, carbon, and nitrogen that existed on the catalyst.

An IBM IR32 Fourier Transform Infrared spectrometer was used to determine the identities of the compounds adsorbed on the catalyst surface. This technique allows all of the frequencies of a broad region of infrared energy to be measured simultaneously by passing infrared

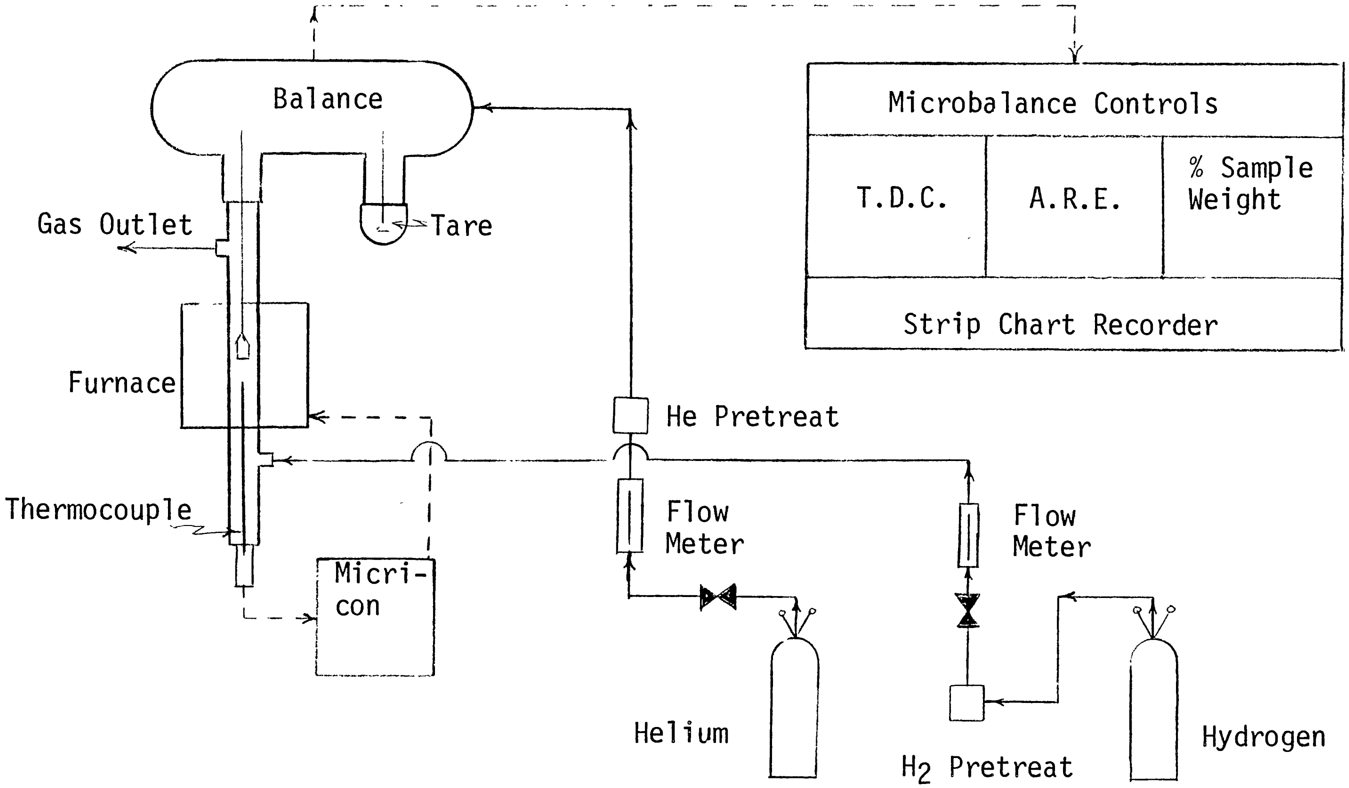


Figure 1. Cahn TGA System 113

energy through a sample and determining the interference pattern. A mathematical operation called a Fourier transform is then used to convert the interference pattern into a spectrum.

Experimental Procedure

The commercial Shell 324 NiMo/Al_2O_3 catalyst was used in this analysis due to its high activity for hydrodenitrogenation. Properties of the catalyst are given in Table II.

The catalyst sample (7-17 mg) is suspended from the microbalance on a nichrome wire. A wire mesh basket made of nichrome holds the sample and allows the gases to pass through and contact with the sample. The gases, helium and hydrogen, are pretreated to remove any impurities by passing them over a catalyst bed containing Shell 324 (Figure 1). Any impurity that would strongly adsorb on the catalyst sample would, theoretically, be adsorbed in the catalyst bed. Both gases are chromatographic grade with purities of 99.997%.

Certified grade pyridine, piperidine and n-pentylamine from Fisher Scientific and Kodak were used as poisons in this study. Ammonia was used to poison the catalyst by contacting an extracted catalyst sample with a 500 ppm ammonia in helium gas stream. Tetrahydrofuran was used as the solvent for extraction of poisoned catalyst samples. Tetrahydrofuran is a strong solvent and is often used in extraction of spent catalysts. In addition, it is nonbasic, and therefore it will not interfere with the experimental measurements.

Calcination of the sample was carried out first. This was done by heating the catalyst at 500°C for approximately 48 hours under a 10cc/ minute helium flow. A calcination time of 48 hours was necessary in

TABLE II

PROPERTIES OF SHELL 324 CATALYST*

Shape	Extrusion
Nominal Size, mm	1.6
Chemical Composition, % wt	
Nickel	3.4
MoO_3	19.3
Physical Properties	
Surface Area, m^2/kg (10^3)	159(150)
Pore Volume, m^3/kg (10^{-3})	0.46(0.48)
Most Frequent Pore Diameter, nm	14.8
Pore Size Distribution, % pore volume in pore diameter, nm	%
3.5 - 7.0	4.6
7.0 - 11.0	22.4
11.0 - 15.0	35.1
15.0 - 20.0	29.8
20.0 - 40.0	3.3
40.0	4.8
	100.0

*values in parenthesis are vendor's data order to obtain an accurate dry equilibrium weight.

A preliminary experiment consisted of adsorbing hydrogen on blank (nonpoisoned) calcined catalysts. The calcined catalyst sample was subjected to a 5cc/minute hydrogen flow for 6 hours at a certain temperature. After 6 hours, an equilibrium amount of hydrogen had adsorbed on the catalyst sample. This was indicated by no further weight gain by the catalyst. This adsorption procedure was repeated for different temperatures ranging between 200 and 400°C. All weight measurements for one sample were made at the same conditions (temperature, gas flows) and weight differences were then calculated.

Desorption of hydrogen from these blank catalyst samples was investigated by passing only helium (10cc/min) over the sample at the same temperature used in the adsorption process. Desorption was continued until constant weight was obtained, which usually required 10 to 16 hours. In this analysis, it was possible that some of the oxides that make up the catalyst might actually be reduced when the catalyst sample was subjected to hydrogen flow. If this occurred, the results obtained in the adsorption process would be inaccurate. However, from preliminary results, the weight after the desoprtion process was always equal to the initial calcined weight. It could be theorized that some reduction occurred and that there was some irreversible adsorption of hydrogen on the catalyst. However, if this occurred, it was improbable that the weight after desorption would always be equal to the intial calcined weight over a series of experimental runs. As a result, there was no weight loss due to reduction and there was no irreversibly held hydrogen on the catalyst after the desorption process.

Subsequent experimentation dealt with observing hydrogen adsorption on catalysts poisoned with nitrogen compounds. The catalysts were calcined as before and then poisoned by placing them in a pure nitrogen compound solution. The solution was held at a fixed temperature for 24 hours. The sample was then placed in a Soxhlet extraction unit and extracted with tetrahydrofuran for 24 hours. Extraction was carried out in order to remove excess nitrogen compounds from the catalyst pores and therefore yield a reproducible poisoning procedure.

The adsorption/desorption process was very similar to the adsorption/desorption process used for hydrogen on a blank calcined catalyst. After the poisoned catalyst had been extracted, the catalyst was placed in the TGA. The sample was kept at the temperature to be used in the adsorption/desorption cycle while under a 10cc/minute helium flow. This helium purge was necessary in order to remove tetrahydrofuran from the catalyst and to yield an equilibrium amount of adsorbed poison at the temperature of interest. This part of the procedure usually required approximately 3 days to reach a constant poisoned weight. Hydrogen flow was then introduced into the system at 5cc/minute. Hydrogen flow was continued for one to two days. During the hydrogen flow, there was a possibility of both hydrogen adsorption on the poisoned catalyst and hydrogen reacting with the adsorbed nitrogen compound. As a result, the constant weight obtained after the adsorption process represented adsorbed hydrogen, unreacted poison, and possibly some strongly adsorbed reaction intermediates or products from the hydrogenation reaction.

Desorption was then carried out by passing only helium over the catalyst sample at the same temperature used during adsorption. A constant weight was usually obtained within 24 hours. This constant weight represented irreversibly adsorbed poison and possibly some strongly adsorbed reaction products. It is probable that all the adsorbed hydrogen desorbed since this was the case for the blank calcined catalysts.

After desorption, one of two final steps in the procedure was taken. The first option was to take the sample out of the TGA and analyze the the adsorbed compounds. The second option was to leave the sample in the TGA and open the system to an air enviroment. The sample was then heated at 630°C until the strongly adsorbed compounds were burned off. After three days, a constant weight was achieved which would correspond to the initial nonpoisoned calcined weight.

A temperature of 630°C was chosen as the temperature to burn off the irreversibly held compounds because this was the maximum temperature that could be obtained without the catalyst undergoing physical changes. As can be seen in the calcination dynamics shown in Appendix A, above 630°C the catalyst weight drops suddenly and as a result, the catalyst probably changes in composition and physical structure. A high temperature was selected since a higher temperature enables the nitrogen compounds to be burned off quickly and completely.

CHAPTER IV

EXPERIMENTAL RESULTS

Preliminary experimentation consisted of investigating equilibrium hydrogen adsorption on a blank (nonpoisoned) catalyst. This adsorption was carried out at temperatures between 200 and 400°C and at atmospheric pressure. The hydrogen adsorption results can be seen in Table III and in Figure 2. All hydrogen adsorption was completely reversible. Also, the catalyst weight returned to its initial value after desorption. As a result, no reduction of the catalyst occurred.

Since the poisoning procedure required a tetrahydrofuran extraction step, an unpoisoned calcined catalyst was extracted with tetrahydrofuran in order to determine the amount of hydrogen adsorbed on a blank extracted sample. After extraction, the sample was dried and weighed. The calcined sample showed 3.8 percent weight loss due to extraction. In addition, the extracted sample adsorbed 3.4 μg/mg cat. (1.0×10^{18} molecules/mg cat.) of hydrogen at 400°C, which is almost 4 times the amount of hydrogen adsorbed on an unextracted catalyst sample (see Figure 2) at the same temperature.

The bulk of experimentation consisted of investigating the adsorption of hydrogen on poisoned catalyst samples. The poisons used were pyridine and its hydrogenation intermediates and products. The amount of the initially adsorbed compound, the weight change due to the introduction of hydrogen flow, the amount of hydrogen desorbed and the amount of

TABLE III

HYDROGEN ADSORPTION ON A CALCINED SHELL 324 CATALYST AT ATMOSPHERIC PRESSURE

Temperature (^{o}C)	Amount of H_2 Adsorbed (μg/mg cat.)	(molecules/ mg cat.) 10^{17}	Fractional Surface* Coverage
200	0.61	1.82	0.076
300	0.33	0.98	0.041
300	0.10	0.30	0.012
350	0.05	0.15	0.006
360	1.18	3.52	0.148
375	0.96	2.87	0.120
375	1.06	3.16	0.133
400	1.00	2.99	0.125
400	0.88	2.63	0.110

*assuming the surface area covered by hydrogen = $6.67 \times 10^{-20} \frac{m2}{molecule}$

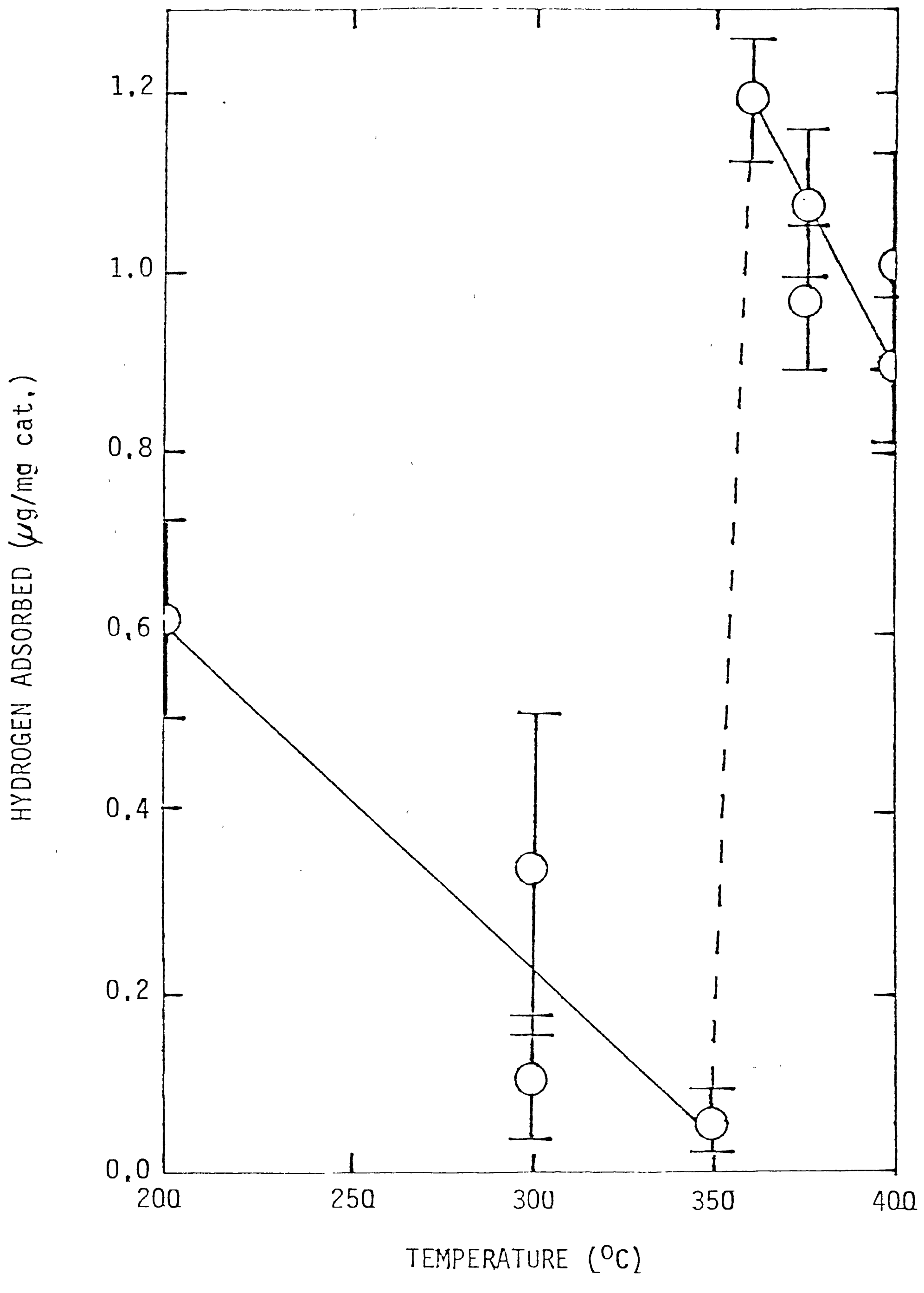


Figure 2. Hydrogen Adsorption on a Calcined Shell 324 Catalyst at Atmospheric Pressure

compounds irreversibly held were all determined for the various poisons of interest. These results are shown in Table IV. All of the adsorption data shown in Table IV are equilibrium values. The dynamic behavior (amount adsorbed/desorbed as a function of time) of various adsorption/desorption processes are shown in Appendix B.

The magnitude of the error bars given in Figure 2 results from the variance of the weight measurement signals produced on the strip chart recorder. The magnitude of the variance changed with each experimental run. Therefore, the amount of error associated with each point in Figure 2 also varied.

TABLE IV

EQUILIBRIUM ADSORPTION AMOUNTS OF PYRIDINE, ITS DERIVATIVES AND HYDROGEN ON SHELL 324 AT 400°C AND 1 ATM

Compound	Pyridine	Piperidine	n-Pentylamine	Ammonia
Amount of Initial Adsorbed Compound				
(μg/mg cat.)	7.5	9.2	11.3	0.4
(molecules/mg cat.)	5.7×10^{16}	6.5×10^{16}	7.8×10^{16}	1.4×10^{16}
*frac. surf. cover.	0.08	0.12	0.13	0.01
Weight Change due to Contact with H_2 (μg/mg cat.)	+2.7	+2.6	+1.5	+2.4
Amount of Hydrogen Desorbed (μg/mg cat.)	2.0	1.9	1.8	2.4
Amount Irreversibly Held (μg/mg cat.)	8.3	9.9	11.0	0.4

*assuming the surface area covered by pyridine = 2.18×10^{-19} m^2/molecule
piperidine = 2.91×10^{-19} m^2/molecule
pentylamine = 2.74×10^{-19} m^2/molecule
ammonia = 7.52×10^{-20} m^2/molecule

(these values were calculated by use of the Lennard-Jones collision diameter parameter for benzene, cyclohexane, hexane and ammonia)

CHAPTER V

DISCUSSION

The shape of the hydrogen adsorption curve shown in Figure 2 indicates that hydrogen adsorption on Shell 324 catalyst at atmospheric pressure is an activated type. Also, the adsorption is all chemisorption since the temperature range investigated is significantly higher than the boiling point of hydrogen (-252.8°C). The maximum amount of chemisorption that can occur is a monolayer, though physical adsorption can be multilayered. As expected for chemisorption, the amounts of hydrogen adsorbed (see Table III) correspond to a small fraction of a monolayer.

Activated chemisorption is characterized by both a maxima and a minima in the amount of gas adsorbed as the temperature increases. Apparently the surface chemisorbs the gas in different ways at different temperatures. One possible explanation, given by Satterfield (22) is that an equilibrium value is not actually reached at the lower temperatures (below 350°C in Figure 2) because the rate of chemisorption is low. At higher temperatures (above 350°C) the adsorption process is activated (the rate of adsorption is higher) and equilibrium is achieved.

Activated adsorption has been commonly found for adsorption of gases on powders. Benton and White (23) found that the quantity of hydrogen adsorbed went through a maxima and a minima on nickel powder at temperatures above the boiling point of hydrogen. Similar results were reported by Schwab (24), with hydrogen adsorbing on a variety of powder surfaces.

Relatively few studies have been conducted for adsorption of hydrogen onto catalysts at temperatues significantly higher than the boiling point of hydrogen. Emmett and Harkness (25) found that hydrogen adsorption on an iron catalyst was activated. More recently, Weatherbee and Bartholomew (26) discovered that hydrogen adsorption on a 14% Ni/Al_2O_3 catalyst is also activated. As a result, the activated behavior shown in Figure 2 is not unusual and agrees with the literature.

Fitting the adsorption data over the entire temperature range of interest with one model was impossible due to the activated behavior. The details of modeling this adsorption data are given in Appendix C. Both Langmuir and Freundlich models failed to fit the data adequately. An exponential (Arrhenius) model did adequately fit the data. The exponential models for hydrogen adsorption on Shell 324 catalyst at atmospheric pressure are given below:

$$\text{for} \quad 473K \leq T \leq 623K \qquad \theta = 2.04 \times 10^{-6} \exp\left[\frac{4980}{T}\right] \tag{1}$$

$$\text{for} \quad 633K \leq T \leq 673K \qquad \theta = 1.01 \times 10^{-3} \exp\left[\frac{3160}{T}\right] \tag{2}$$

where, θ = fractional surface coverage

T = temperature, K.

Two exponential models, for the two temperature ranges of interest, were necessary due to the activated nature of the adsorption. These two models are plotted in Figure 3, with the hydrogen adsorption data represented as fractional surface coverage.

The heats of adsorption calculated by the exponential model were 9900 cal/mol for temperatures betwee 473 and 623K, and 6300 cal/mol

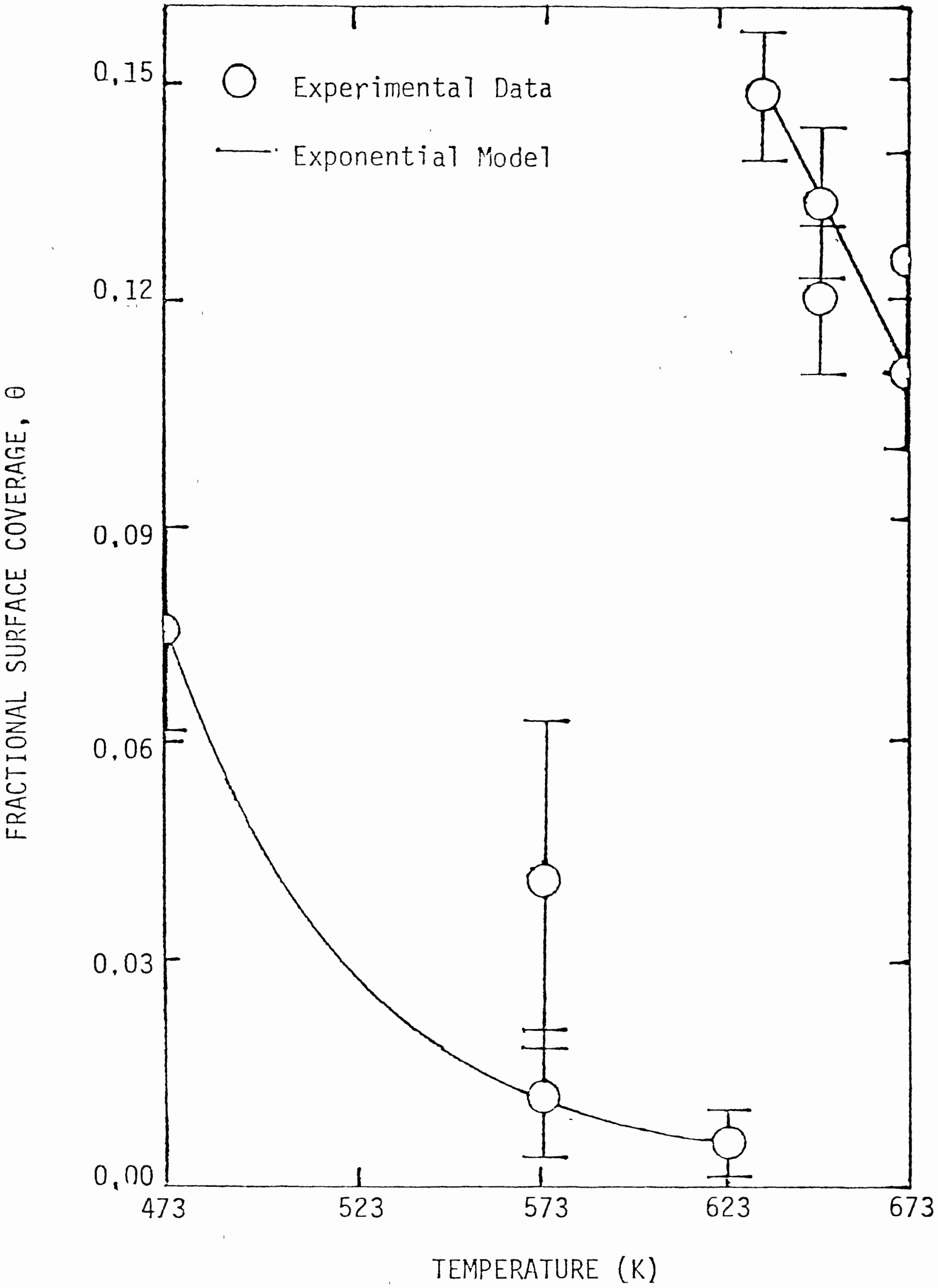
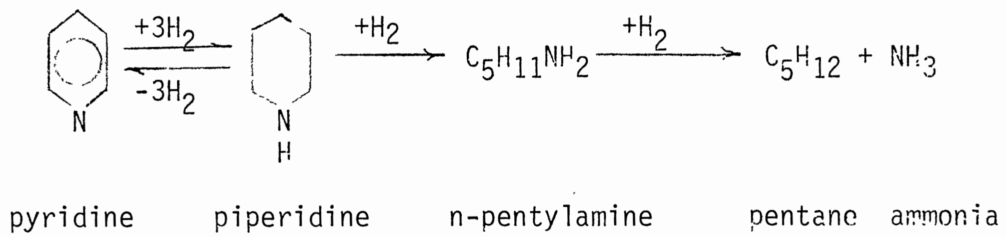


Figure 3. Exponential Model of Hydrogen Adsorption on a Calcined Shell 324 Catalyst at Atmospheric Pressure

for temperatures between 633 and 673K. Trapnell (27) reports that the heats of chemisorption for hydrogen on a variety of different surfaces range between 3,000 and 72,000 cal/mol. Weatherbee and Bartholomew (26) determined that the heat of adsorption for hydrogen adsorption on a 14% Ni/Al_2O_3 catalyst was 29,000 cal/mol. The values obtained in this analysis are lower than most values reported but not unreasonable.

In considering hydrogen adsorption on poisoned catalysts, the hydrodenitrogenation of pyridine was assumed to occur by the mechanism generally accepted by researchers and found in literature (12,18,19). This mechanism is shown below:



During the pyridine hydrogenation reaction, it was possible that any of the above intermediates or products could strongly adsorb on the catalyst.

The poisoning of the catalyst by pentane was not studied experimentally. Pentane was assumed not to adsorb on the catalyst sample at 400°C. This assumption that pentane does not adsorb is not unreasonable since pentane is not a basic compound.

As can be seen in Table IV, the amount of ammonia adsorbed initially and after contact with hydrogen was determined to be 0.4 μg/mg cat. (1.4×10^{16} molecules/mg cat.) at 400°C. The amount of hydrogen adsorbed on an ammonia poisoned catalyst was found to be 2.4 μg/mg cat. The amount of hydrogen adsorbed on a blank (unpoisoned) catalyst was determined previously to be 3.4 μg/mg cat. Therefore it is concluded that the small amount of adsorbed ammonia does inhibit hydrogen adsorption. The reduction of hydrogen adsorption by adsorbed ammonia was calculated to be 29 percent ((3.4 - 2.4)/3.4 x 100% = 29%).

The amount of n-pentylamine initally adsorbed was 11.3 μg/mg cat. (7.8 x 10^{16} molecules/mg cat.). After hydrogenation the amount of irreversibly adsorbed compounds was found to be 11.0 μg/mg cat., which is 0.3 μg/mg cat. lower than the amount initially held. Therefore, some of the reaction products do desorb. Since neither ammonia nor pentane adsorb strongly, it is concluded that a high percentage of the irreversibly adsorbed compounds is unreacted n-pentylamine. If it is assumed that the 0.3 μg/mg cat. desorbed during the process is pentane, then 2.5 x 10^{15} molecules/mg cat. of pentane are formed. Since one molecule of ammonia is produced for every molecule of pentane formed, 2.5 x 10^{15} molecules/mg cat. of ammonia are irreversibly adsorbed on the catalyst surface. Therefore, the irreversibly held compounds consist of 0.1 μg/mg cat. of ammonia and 10.9 μg/mg cat. of unreacted n-pentylamine.

Similar to ammonia, n-pentylamine did inhibit hydrogen adsorption. The amount of hydrogen adsorbed, and not reacted, on a n-pentylamine poisoned catalyst was found to be 1.8 μg/mg cat. The reduction of hydrogen adsorption due to the poisoning of the surface by n-pentylamine was calculated to be 47 percent ((3.4 - 1.8)/3.4 x 100% = 47%).

A piperidine poisoned catalyst was investigated next and the results are shown in Table IV. The piperidine initially adsorbed on the catalyst surface probably partially dehydrogenated into pyridine before hydrogen flow was introduced. This partial dehydrogenation to pyridine is believed to occur because 0.7 μg/mg cat. of hydrogen was consumed in the reaction process. If only piperidine were initially adsorbed on the surface, the amount of hydrogen consumed in converting the piperidine to ammonia and pentane would be 0.4 μg/mg cat. Therefore initially both piperidine and pyridine are adsorbed on the catalyst.

The amount of hydrogen reacted in the piperidine reaction, 0.7 μg/mg cat., is obtained from Table IV (2.6 - 1.9 μg/mg cat. = 0.7 μg/mg cat.). However, this value for the amount of hydrogen consumed is dependent on the assumption that no reaction products or intermediates desorb during the hydrogenation process. Since n-pentylamine was found to adsorb strongly and react only to a small degree (the amount of adsorbed n-pentylamine decreased only slightly after hydrogenation), the assumption that no hydrogenation intermediates or products desorb is concluded to be reasonable.

The amount of irreversibly adsorbed compounds is 0.7 μg/mg cat. higher than the initial adsorbed amount. This amount of a weight gain is expected since 0.7 μg/mg cat. of hydrogen was consumed and no desorption of reaction products probably occurred. If it is assumed that the irreversibly held compounds primarily consisted of n-pentylamine, then the initially adsorbed compounds were 3.1 μg/mg cat. piperidine and 6.1 μg/mg cat. pyridine.

The amount of hydrogen adsorbed on a catalyst poisoned with irreversibly adsorbed piperidine hydrogenation derivatives was found to be 1.9 μg/mg cat. This corresponds to a 44% reduction in the amount of hydrogen adsorbed ((3.4 - 1.9)/3.4 x 100% = 44%).

As can be seen in Table IV, 7.5 μg/mg cat. of pyridine were initially adsorbed on the catalyst at 400°C. The amount of irreversibly held compounds was 8.3 μg/mg cat., which is 0.8 μg/mg cat. higher than the initial amount of pyridine adsorbed. As a result, some of the reaction intermediates and products must have remained adsorbed on the catalyst to cause the increase in the sample weight.

For complete conversion of pyridine to pentane and ammonia, 0.95 μg/mg cat. of hydrogen, would be required. Since some reaction intermediates remain irreversibly adsorbed on the catalyst surface, pyridine conversion to pentane and ammonia was concluded to be incomplete (hydrogenation of pyridine was carried out for 48 hours). Therefore, the amount of hydrogen reacted was less than 0.95 μg/mg cat. If it is assumed that no reaction intermediates or products desorb from the catalyst during the entire reaction process, then 0.7 μg/mg cat. of hydrogen was consumed in the reaction (from Table IV: 2.7 - 2.0 = 0.7 μg/mg cat. H_2 consumed).

For conversion of pyridine to n-pentylamine, 0.8 μg/mg cat. of hydrogen would be required. This value is fairly close to the value for the amount of hydrogen consumed if no hydrogenation derivatives desorb during the process (0.7 μg/mg cat. of hydrogen). Furthermore, the weight of the irreversibly adsorbed compounds is exactly 0.8 μg/mg cat. higher than the amount of initially held pyridine. Therefore, a high percentage of the irreversibly adsorbed compounds is probably n-pentylamine.

The amount of hydrogen adsorbed, and not reacted, on a catalyst poisoned with pyridine hydrogenation derivatives was found to be 2.0 μg/mg cat. (the amount of hydrogen adsorbed is equal to the amount desorbed in Table IV). The reduction of hydrogen adsorption due to the poisoning of the surface by pyridine's hydrogenation derivatives (probably mostly n-pentylamine) was calculated to be 41 percent ((3.4 - 2.0)/3.4 x 100% = 41%).

The compounds remaining adsorbed on the catalyst surface were analyzed by both elemental analysis and FTIR spectroscopy. Elemental analysis indicated that carbon, nitrogen and hydrogen did exist on the catalyst surface. The carbon to nitrogen ratio was determined to be 4.0. For pyridine, piperidine and n-pentylamine, the carbon to nitrogen ratio should be equal to 5.0. Therefore, possibly some ammonia and pentane were formed and part of the ammonia remained adsorbed and the pentane desorbed.

The FTIR spectroscopy results are shown in Appendix D. The results are inconclusive because they indicate that no organic nitrogen compounds exist on the catalyst samples. A possible explanation is that since the compounds are adsorbed in such low concentrations (0.7 wt %) the spectrometer cannot detect them (the lower limit of detection is approximately 1.0 wt %).

All of the basic nitrogen compounds investigated do inhibit hydrogen adsorption. The reduction of hydrogen adsorption by these adsorbed compounds is summarized in Table V. This inhibition of hydrogen adsorption could be due to the possibility that some of the catalyst sites are open to both hydrogen and nitrogen compound adsorption. It is also possible that the large nitrogen compound molecules adsorb on denitrification sites and, due to their size, block some sites that can adsorb hydrogen.

A plot of the percent reduction of hydrogen adsorption versus the fraction of the catalyst surface covered by nitrogen compounds is shown in Figure 4. The irreversibly adsorbed compounds resulting from

TABLE V

INHIBITION OF HYDROGEN ADSORPTION BY ADSORBED NITROGEN COMPOUNDS

Adsorbed Nitrogen Compound(s)	Reduction of H_2 Adsorption
Ammonia	29%
n-Pentylamine	47%
Irreversibly Held Compounds Resulting From Piperidine Hydrogenation	44%
Irreversibly Held Compounds Resulting From Pyridine Hydrogenation	41%

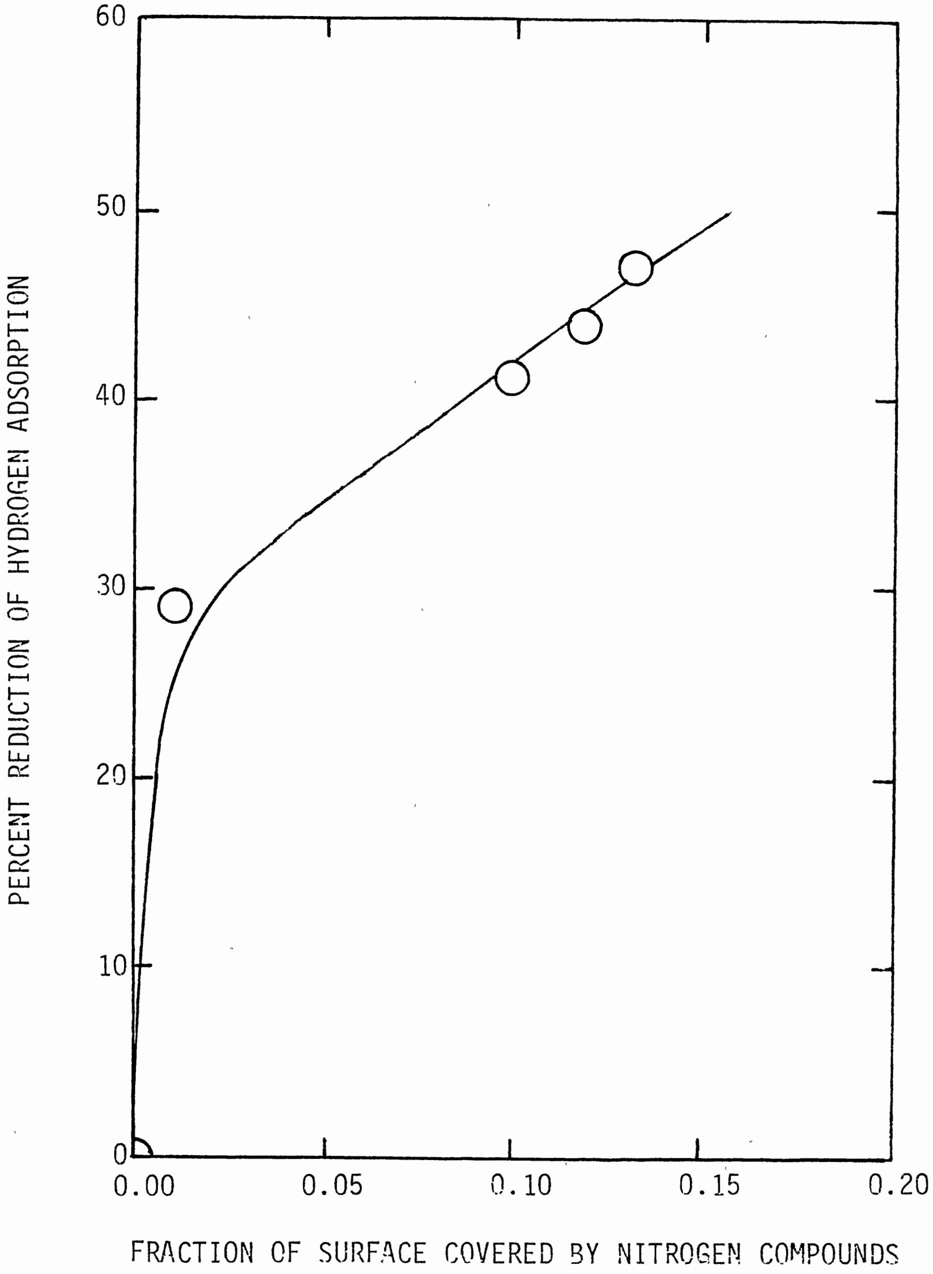


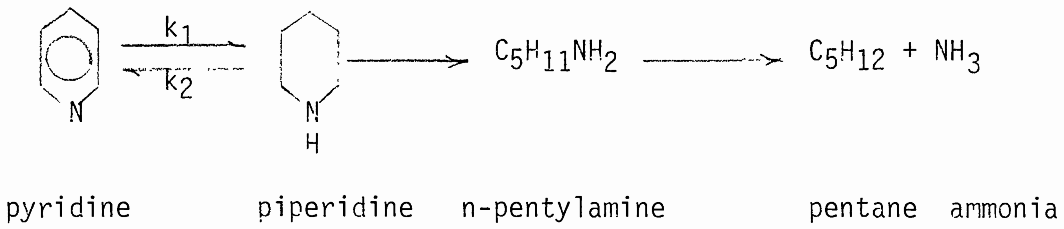
Figure 4. Effect of Adsorbed Nitrogen Compounds on Hydrogen Adsorption at 400^{o}C and 1 atm

pyridine and piperidine hydrogenation were assumed to be n-pentylamine for the purpose of calculating the fractional surface coverage. As can be seen in Figure 4, a small surface coverage yields a substantial reduction in the amount of hydrogen adsorbed. Therefore, an adsorbed nitrogen compound does significantly deactivate or at least block catalyst sites active toward hydrogen adsorption.

n-Pentylamine was found to be a more effective poison than ammonia since a large amount of n-pentylamine remained adsorbed on the surface after hydrogenation. The overall pyridine hydrogenation process at 400°C is characterized by incomplete conversion of pyridine to pentane and ammonia, resulting in strongly held intermediates (probably mostly n-pentylamine). However, ammonia (and probably pentane) are relatively weakly adsorbed. These generalizations correspond to the conclusions drawn by Larson (19) and by Sonnemans et al. (21). Larson found that ammonia was relatively ineffective as a poison, and Sonnemans et al. discovered from their adsorption measurements, that the effectiveness as poisons was piperidine > pyridine > ammonia.

A Langmuir-Hinshelwood model for pyridine hydrogenation was developed. The details of this modeling are given in Appendix E. The model is shown below:

for the mechanism



$$-r_A = \frac{k_1\phi_A\phi_{H2} - k_2\phi_B(1+\phi_A+\phi_B+\phi_{H2}+\phi_C+\phi_D+\phi_E)}{(1+\phi_A+\phi_B+\phi_{H2}+\phi_C+\phi_D+\phi_E)^2} \qquad (3)$$

where, k_1 = reaction rate constant of forward step (pyridine ⟶ piperidine)

k_2 = reaction rate constant of reverse step (piperidine ⟶ pyridine)

A = pyridine

B = piperidine

C = n-pentylamine

D = pentane

E = ammonia

ϕ = $\theta/(1-\theta)$, (θ = fractional surface coverage).

Values of θ and ϕ are given in Table VI. The value for pentane is only approximate. The value for pentane was assumed to be zero since pentane is not basic. Also, the value for hydrogen is based on the amount of hydrogen adsorbed on a pyridine poisoned catalyst. When these values are substituted into the above model, the following relation is obtained for pyridine hydrogenation at 1 atm and 400°C:

$$-r_A = 0.010k_1 - 0.081k_2. \qquad (4)$$

The surface reaction for pyridine hydrogenation is given by the following relation:

$$-r_A\big|_S = k_1\theta_A\theta_{H2} - k_2\theta_B \qquad (5)$$

When the values from Table VI are substituted into equation 5, the following relation is obtained:

TABLE VI

θ AND ϕ FOR PYRIDINE, ITS HYDROGENATION DERIVATIVES, AND HYDROGEN FOR SHELL 324 AT 400^{o}C AND 1 ATM

Compound	θ*	ϕ**
Pyridine	0.08	0.09
Hydrogen	0.25	0.33
Piperidine	0.12	0.14
n-Pentylamine	0.13	0.15
Pentane	0.00	0.00
Ammonia	0.01	0.01

* θ = fractional surface coverage
** $\phi = \theta/(1-\theta)$

$$-r_A\Big|_S = 0.02k_1 - 0.12k_2. \qquad (6)$$

If k_1 is significantly higher than k_2, then the overall reaction rate (equation 4) is approximately half of the surface reaction rate (equation 6).

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The objectives of this study were to investigate the adsorption of pyridine, its hydrogenation derivatives, and hydrogen on a $NiMo/Al_2O_3$ hydrotreating catalyst. Conclusions drawn from this research are:

1. Hydrogen adsorption on Shell 324 catalyst is activated at atmospheric pressure and temperatures between 200 and 400^oC.

2. At 400^oC and 1 atm, an extracted catalyst adsorbs 3.8 times more hydrogen than a calcined catalyst.

3. At 400^oC and 1 atm, pyridine is not completely converted to pentane and ammonia since some hydrogenation intermediates (probably mostly n-pentylamine) are irreversibly adsorbed on the catalyst.

4. The basic nitrogen compounds effectiveness as poisons is n-pentylamine $>$ ammonia.

5. Ammonia and n-pentylamine do inhibit the adsorption of hydrogen onto the catalyst surface. Ammonia reduces hydrogen adsorption by 29 percent and n-pentylmine reduces hydrogen adsorption by 47 percent. The irreversibly adsorbed compounds resulting from piperidine and pyridine hydrogenation reduce hydrogen adsorption by 44 and 41 percent respectively.

6. One recommendation for future experimental work is to investigate the phenomena of an extracted catalyst adsorbing significantly more hydrogen than an unextracted catalyst.

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APPENDIX A

CALCINATION DYNAMICS OF SHELL 324

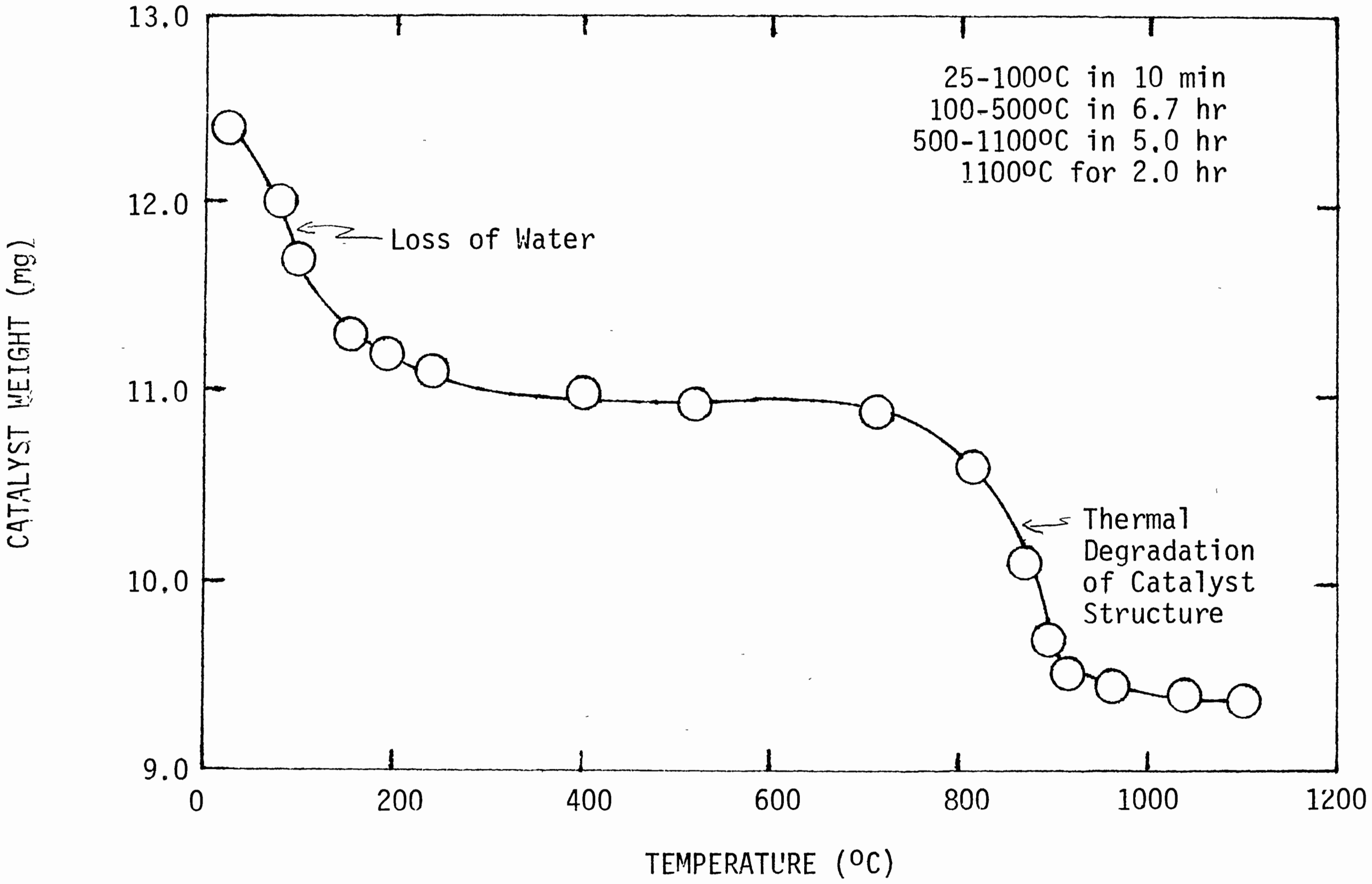


Figure 5. Calcination Dynamics of Shell 324 Under a 10 cc/min Helium Flow

APPENDIX B

ADSORPTION DYNAMICS

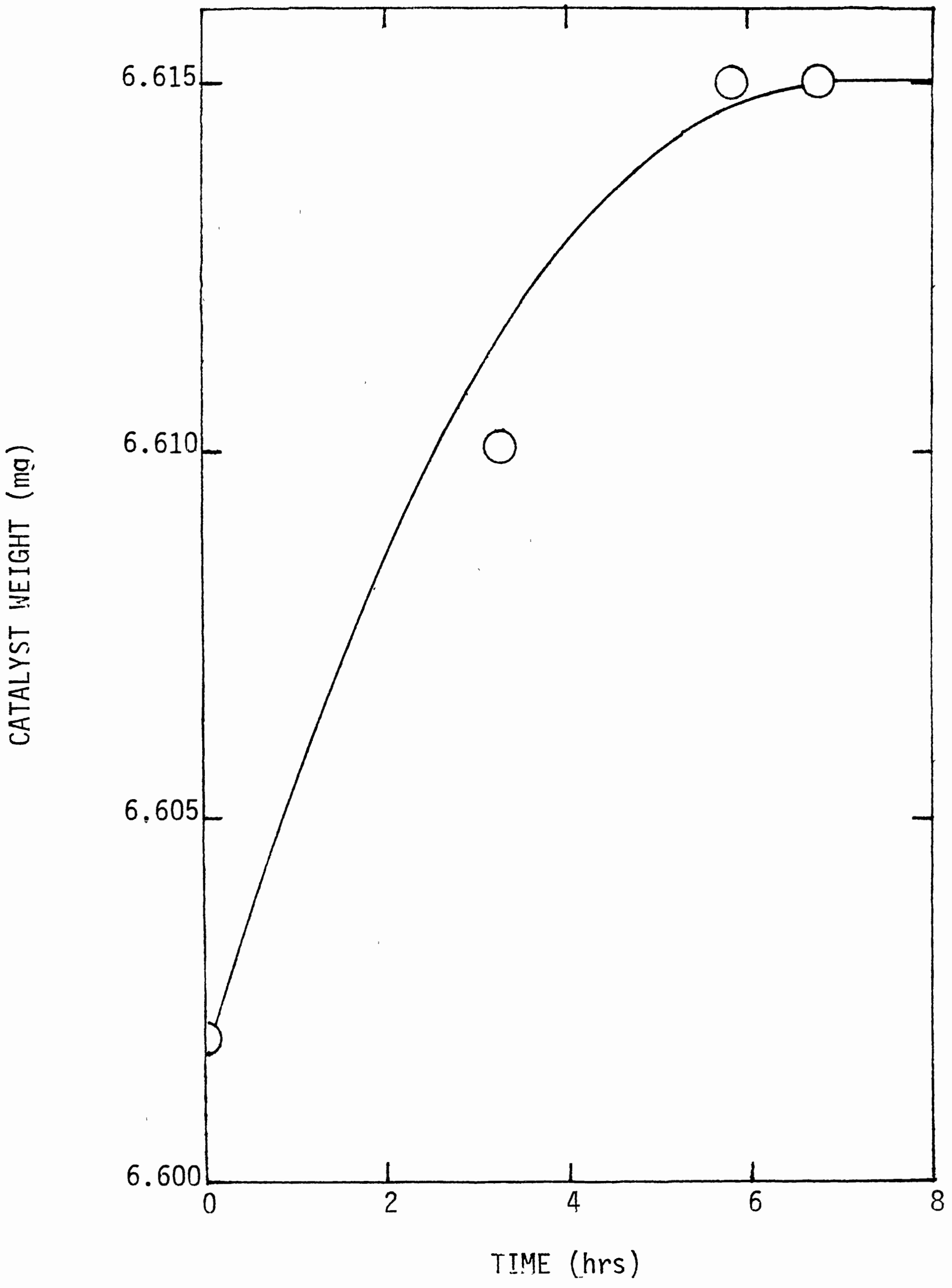


Figure 6. Hydrogen Adsorption on a Pyridine Poisoned Shell 324 Catalyst at 400°C and 1 atm

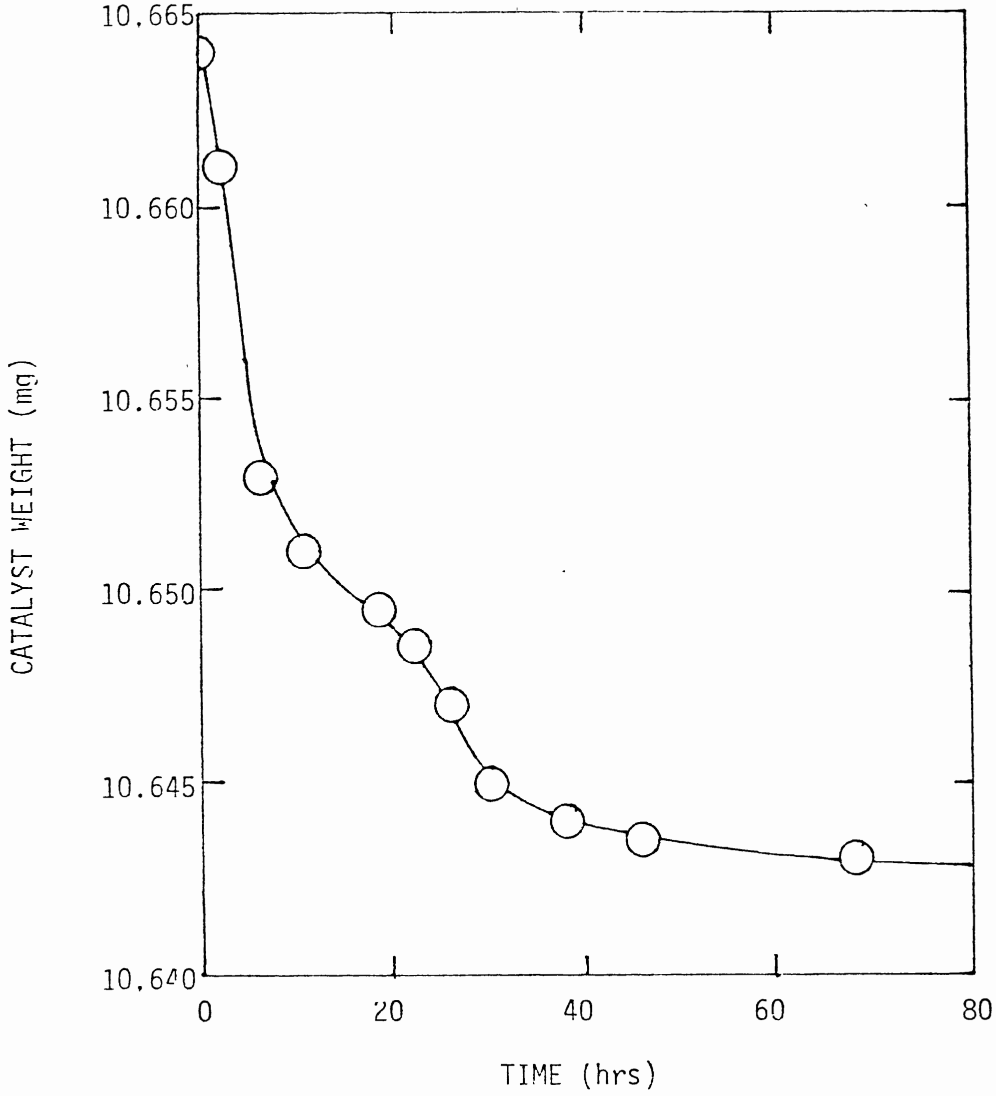


Figure 7. Hydrogen Desorption from a Pyridine Poisoned Shell 324 Catalyst at 400°C and 1 atm

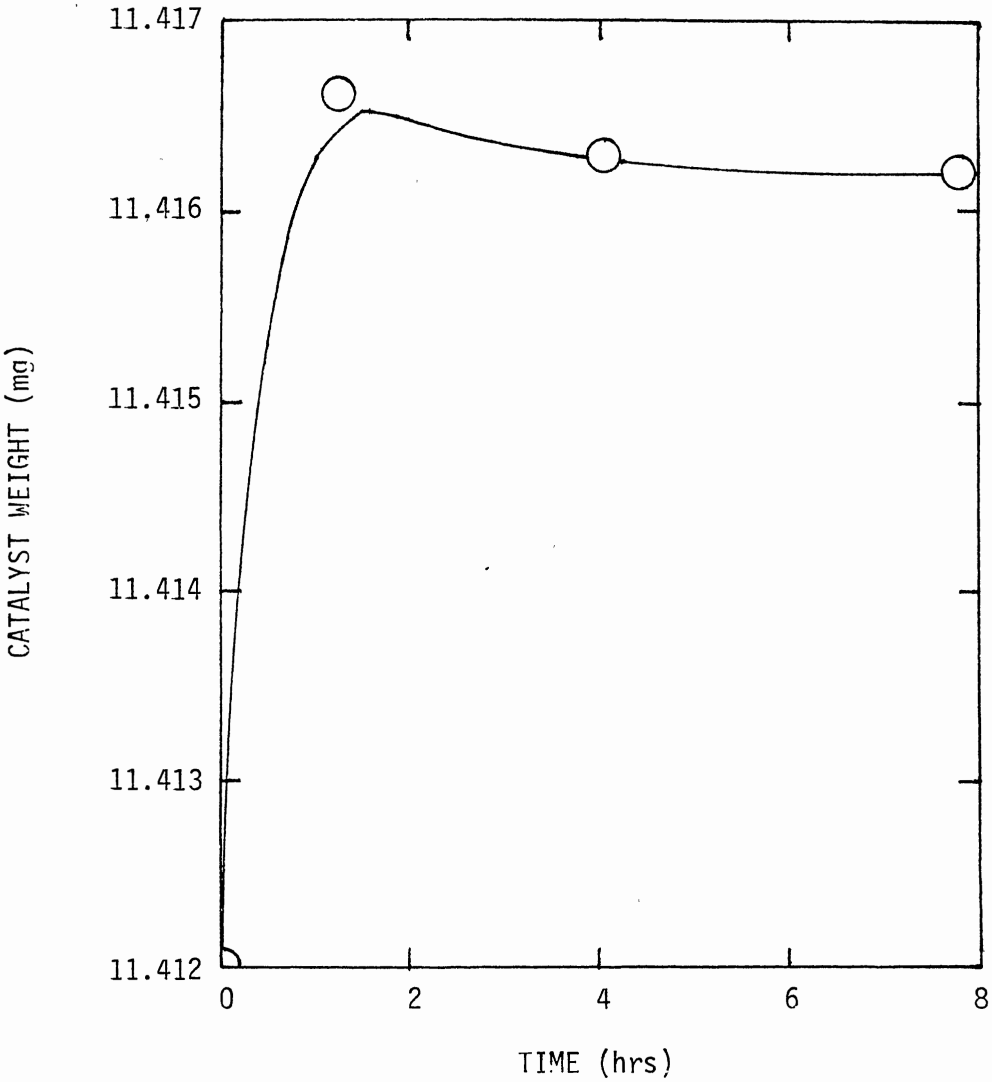


Figure 8. Adsorption of Ammonia on Extracted Calcined Shell 324 Catalyst at 400°C and 1atm

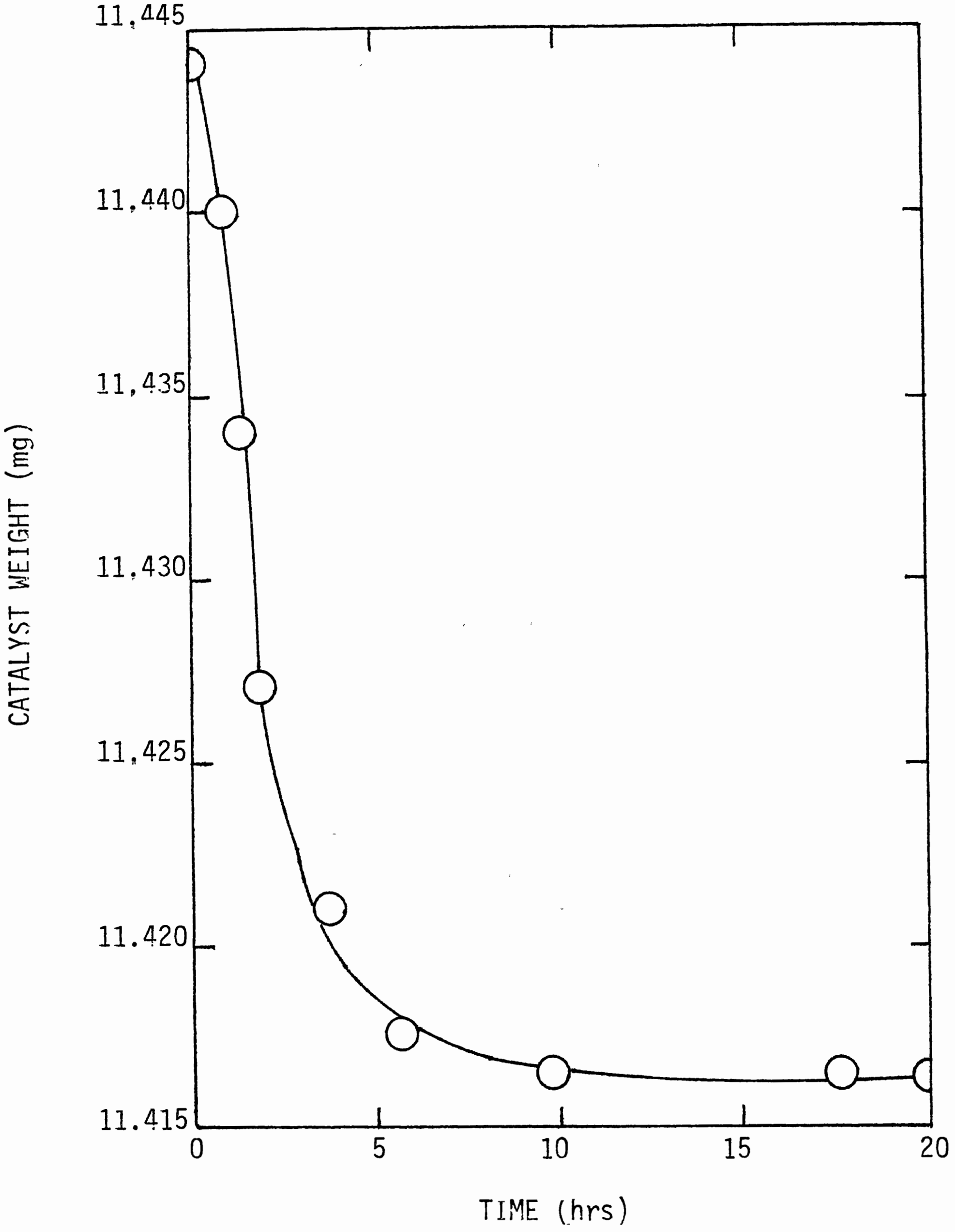


Figure 9. Desorption of Hydrogen from Extracted, Ammonia Poisoned Shell 324 Catalyst at 400°C and 1 atm

APPENDIX C

MODELING OF HYDROGEN ADSORPTION

MODELING OF HYDROGEN ADSORPTION

The hydrogen adsorption data for the unpoisoned catalysts (Table III) was investigated using both the Langmuir and Freundlich models. Also, an exponential (Arrhenius) type of model was investigated. The models were tested by plotting various functions of temperature and fractional surface coverage versus a temperature function. The graphical methods used were the same as those presented by Trapnell (27). These plots should result in a straight line if the model is adequate. Also, both models were investigated for the two types of adsorption possible. In the first type, the hydrogen molecule does not dissociate upon adsorption and therefore occupies only a single site. The second type of adsorption deals with the dissociation of the hydrogen molecule and subsequent adsorption on two sites. These plots are shown in Figures 10 through 14.

As can be seen in these figures, none of the models yield a continuous straight line over the entire temperature range of interest. In Figures 10 and 11, the linear portions of the plots (at temperatures above 633K) yield slopes of approximately 30 and 60 respectively. Since these slopes should be close to one, it is concluded that the Langmuir model is inadequate.

In Figure 12, the slope of the low temperature line is $9K^{-1}$ and the slope of the high temperature line is $4K^{-1}$. Similarly, in Figure 13, the slope of the low temperature line is $18K^{-1}$ and the slope of the high temperature line is $7K^{-1}$. The slope of these lines should be

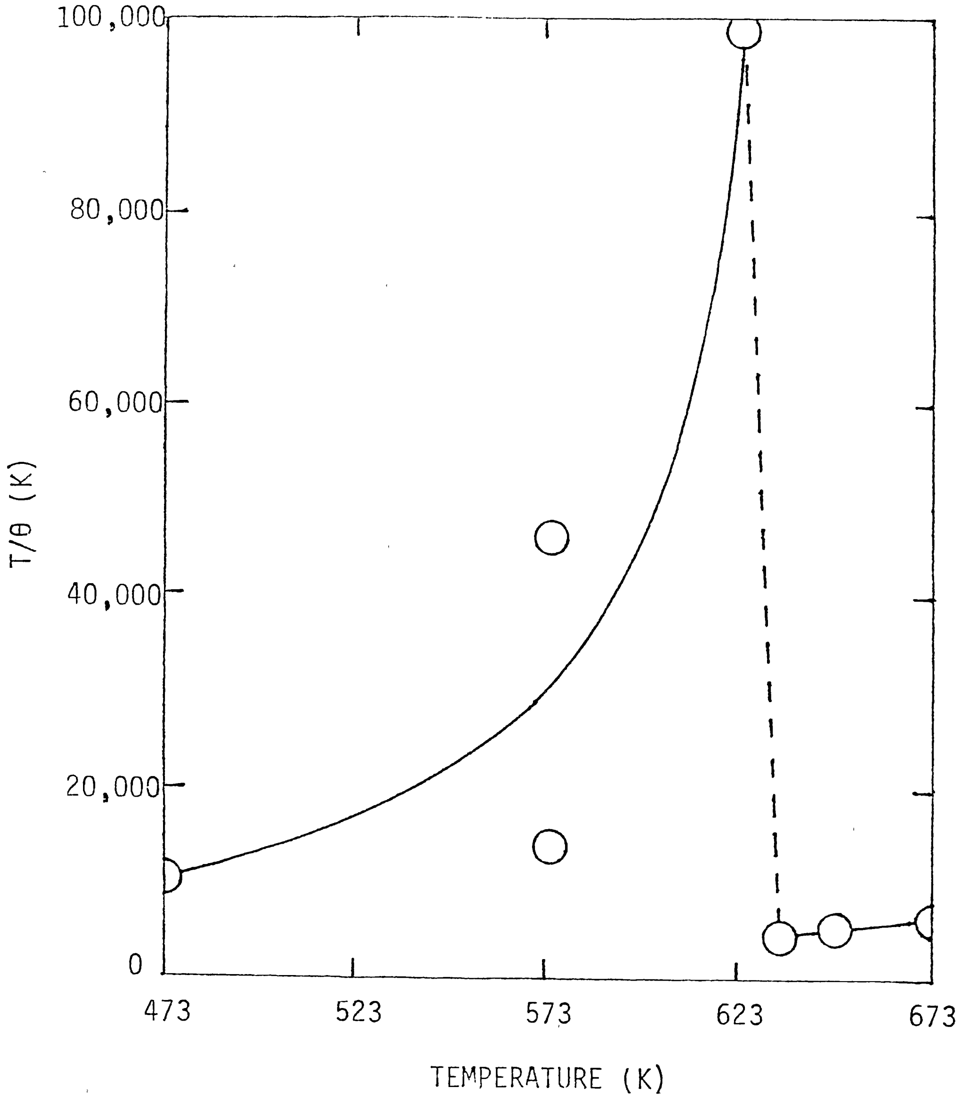


Figure 10. Test for Langmuir Adsorption Behavior for Hydrogen on a Calcined Shell 324 Catalyst at 1 atm (With No Hydrogen Dissociation)

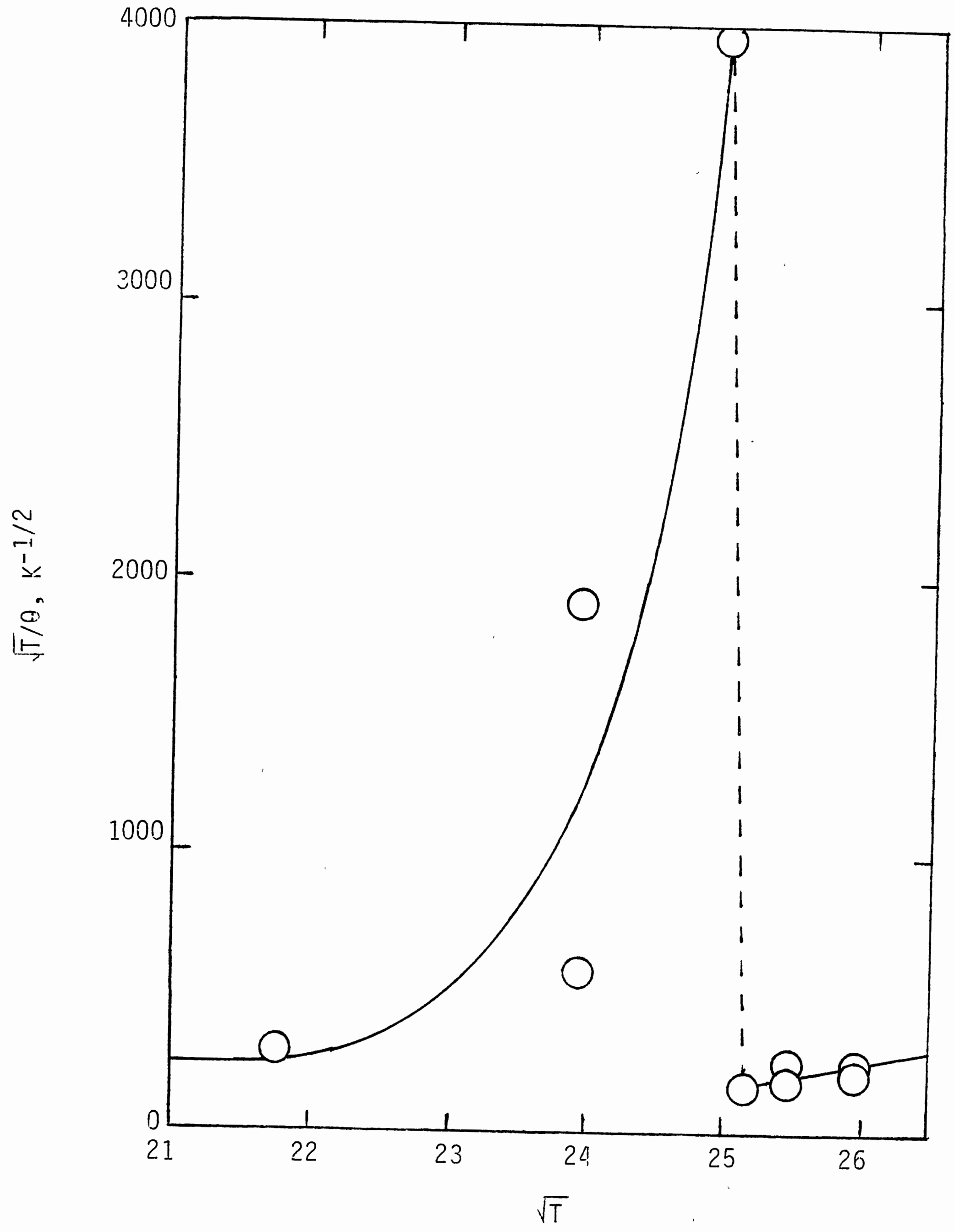


Figure 11. Test for Langmuir Adsorption Behavior for Hydrogen on a Calcined Shell 324 Catalyst at 1 atm (With Hydrogen Dissociation)

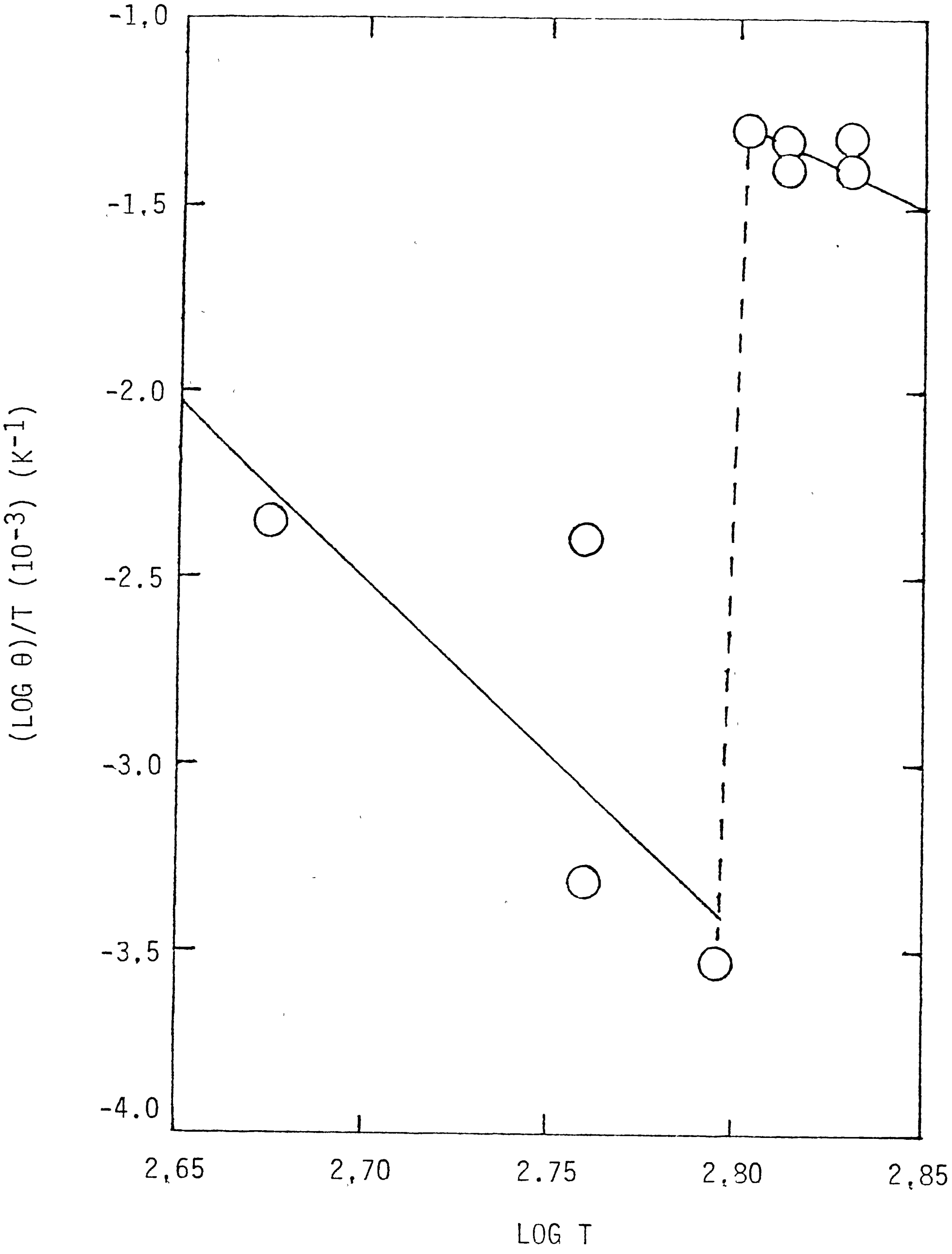


Figure 12. Test for Freundlich Adsorption Behavior for Hydrogen on a Calcined Shell 324 Catalyst at 1 atm (With No Hydrogen Dissociation)

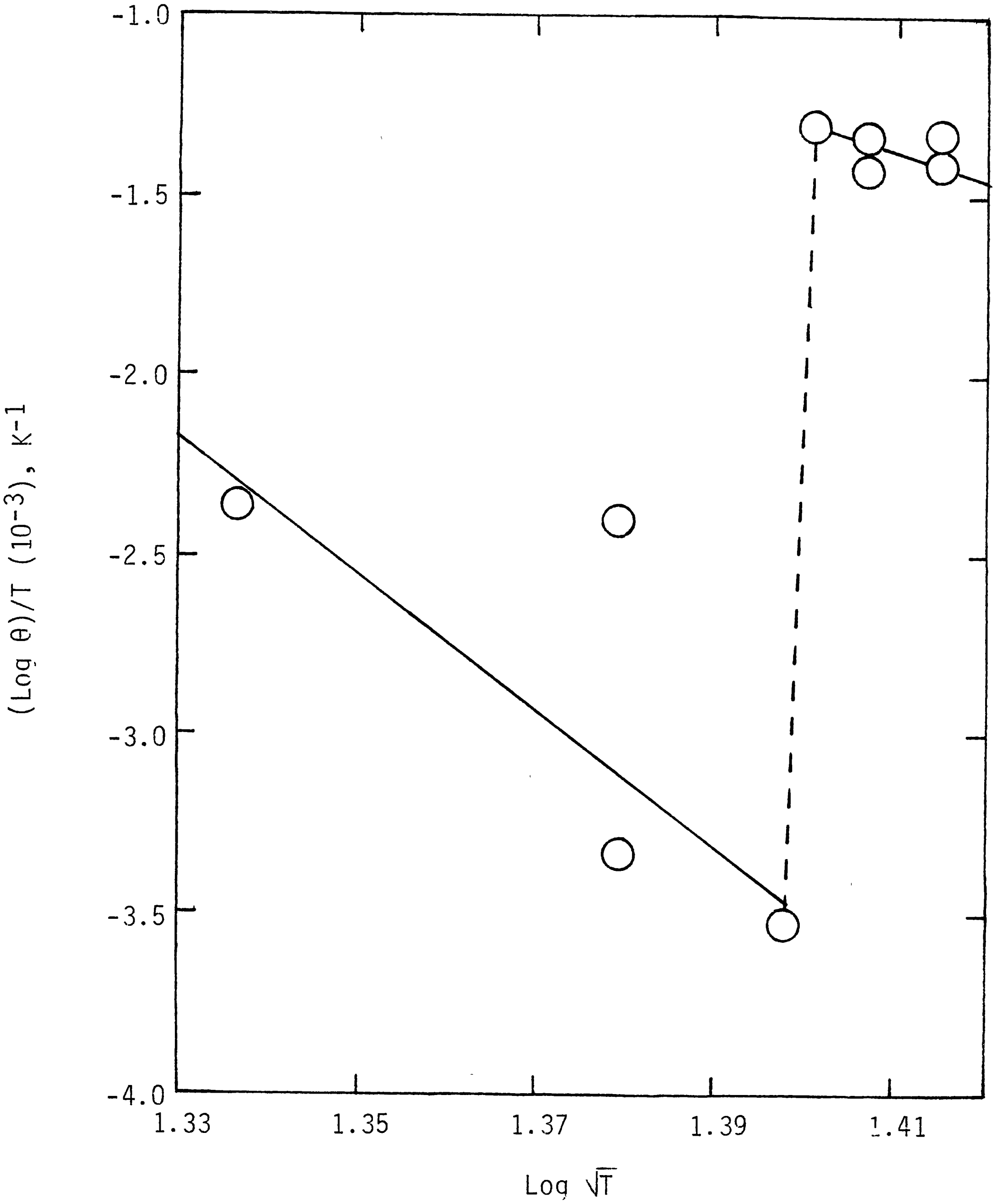


Figure 13. Test for Freundlich Adsorption Behavior for Hydrogen on a Calcined Shell 324 Catalyst at 1 atm (With Hydrogen Dissociation)

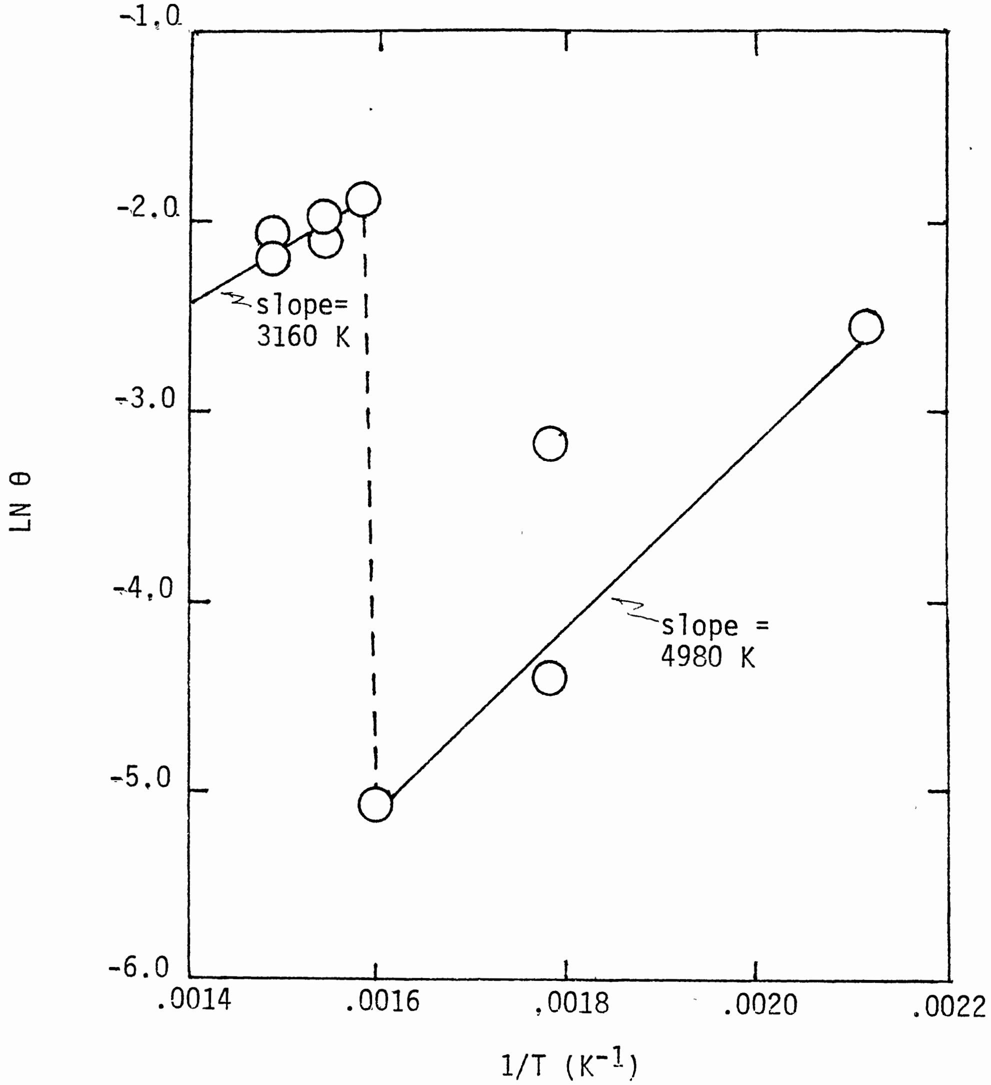


Figure 14. Test for Exponential Adsorption Behavior for Hydrogen on a Calcined Shell 324 Catalyst at 1 atm

equal to R/q_m (gas constant/heat of adsorption for a monolayer). A typical value for the heat of adsorption of hydrogen is 30,000 cal/mole. Using this value of q_m, the slope of the lines should be equal to $7\text{x}10^{-5}$ K^{-1}. This result is significantly different from the slopes in Figures 12 and 13. As a result, the Freundlich model is also deficient.

The plot for the exponential model is shown in Figure 14. The low temperature line (below 623K) yields a slope of 4980K which results in a heat of adsorption of 9900 cal/mole. Similarly, the high temperature line (above 633K) gives a heat of adsorption of 6300 cal/mole. Since these are reasonable values for the heat of adsorption, the exponential model is used to fit the data. From Figure 14, the resulting models for Shell 324 catalyst at atmospheric pressure are as shown below:

$$\text{for } 473 \leq T \leq 623\text{K} \qquad \theta = 2.04\text{x}10^{-6} \exp\left[\frac{4980}{T}\right]$$

$$\text{for } 633 \leq T \leq 673\text{K} \qquad \theta = 1.01\text{x}10^{-3} \exp\left[\frac{3160}{T}\right]$$

where, θ = fractional surface coverage

T = temperature, K.

APPENDIX D

FTIR SPECTROSCOPY RESULTS

FTIR SPECTROSCOPY RESULTS

FTIR spectroscopy was carried out on two catalyst samples in order to determine what compounds were adsorbed on the catalyst surface. The first sample consisted of irreversibly held organic nitrogen compounds that remain after the hydrogenation of pyridine. The results for this sample are shown in Figure 15. The second sample had been burned in air at 630°C in order to remove all adsorbed compounds. The results for the second sample are shown in Figure 16.

Both figures indicate that no organic nitrogen compounds exist on the samples. This is expected for the second sample where the compounds were burned at 630°C. However, the first sample (Figure 15) should have contained some organic compounds since there was a definite weight gain due to adsorption of the nitrogen compounds. Also, the catalyst sample was light brown in color which indicates that some compounds were adsorbed on the surface. A possible explanation for this inconsistency is that the compounds are adsorbed in such low concentrations (0.7 wt %) that the spectrometer cannot detect them (the lower limit of detection is approximately 1.0 wt %).

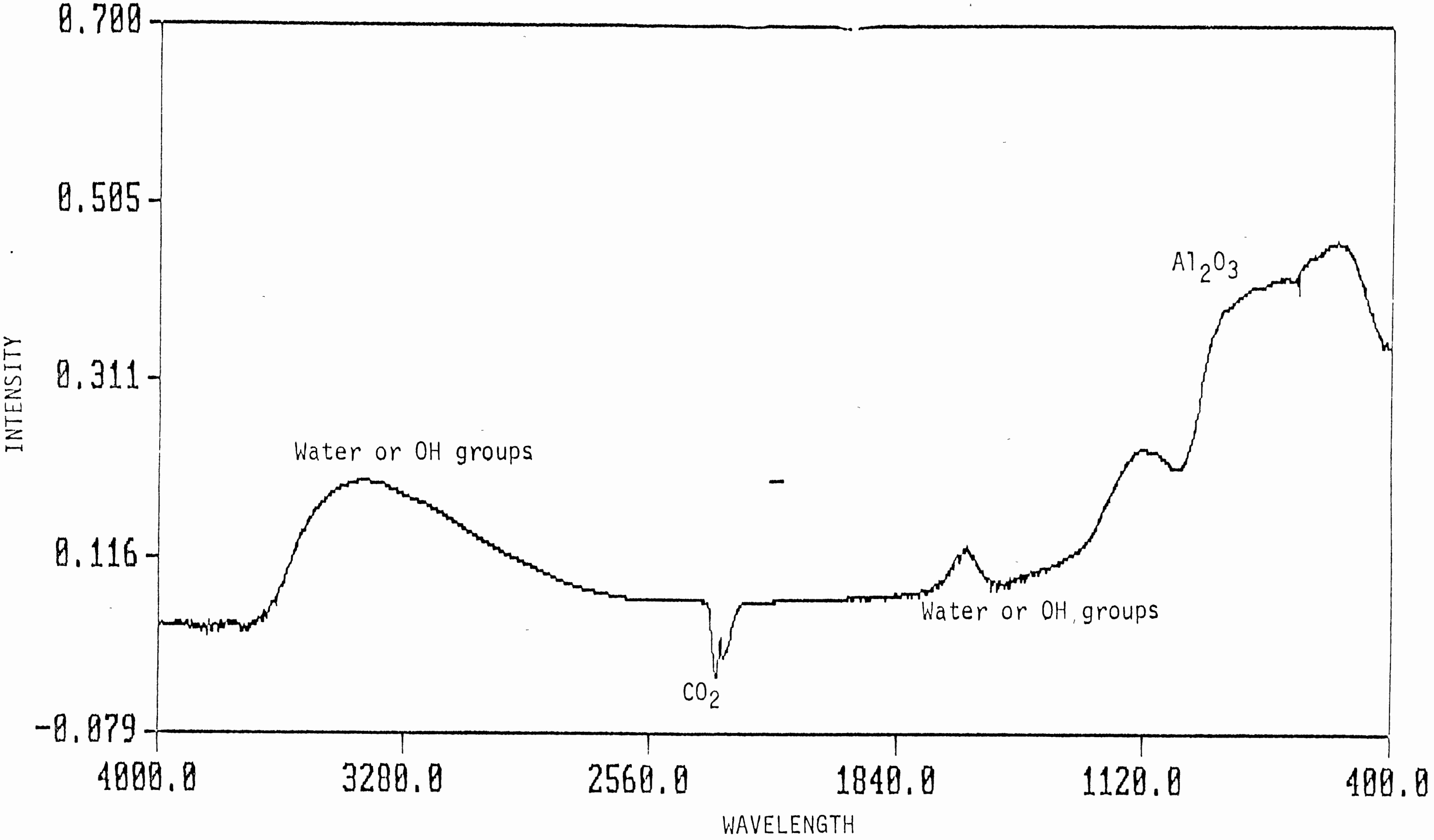


Figure 15. FTIR Results for a Shell 324 Catalyst Poisoned with Pyridine Hydrogenation Derivatives

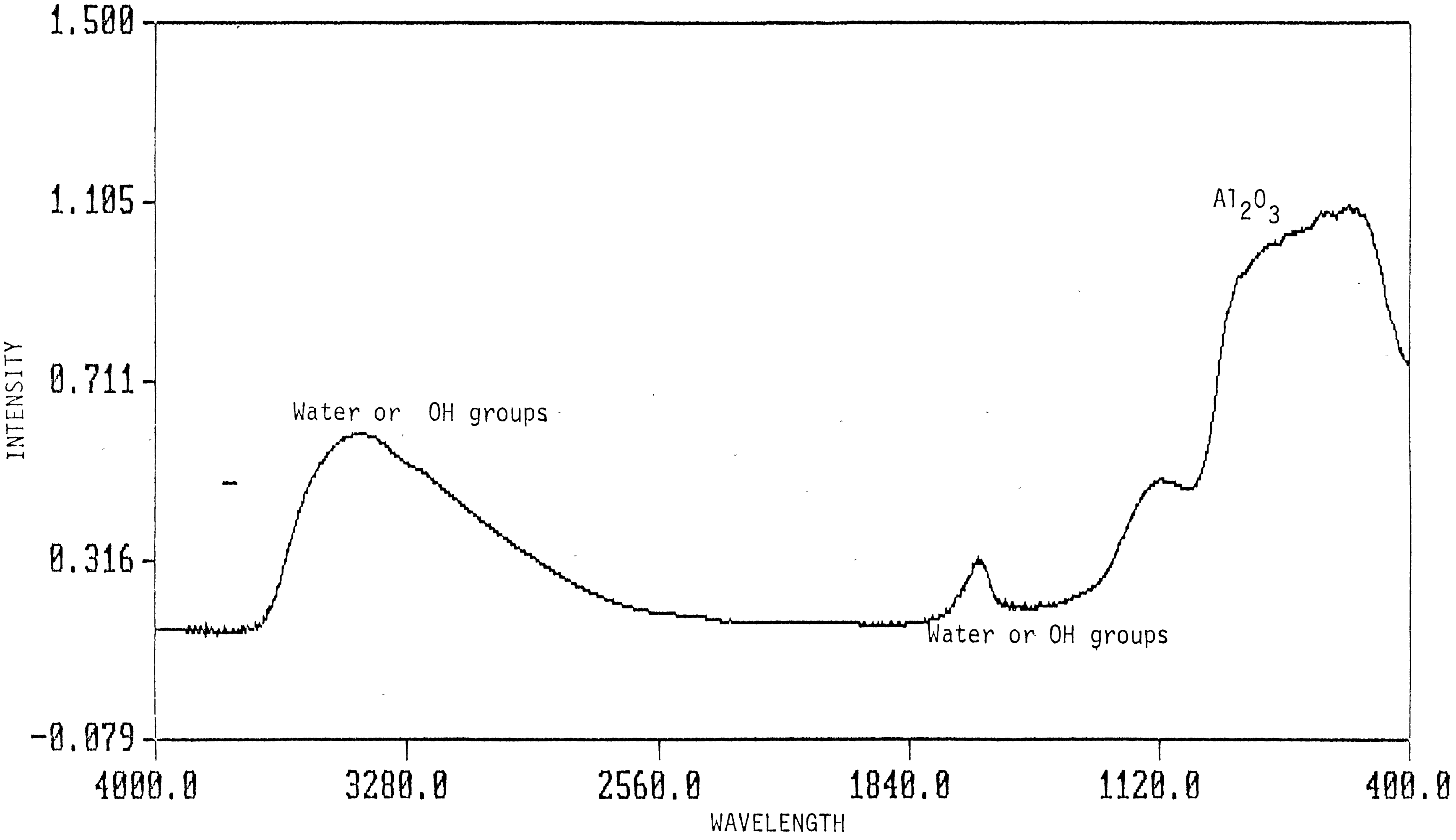


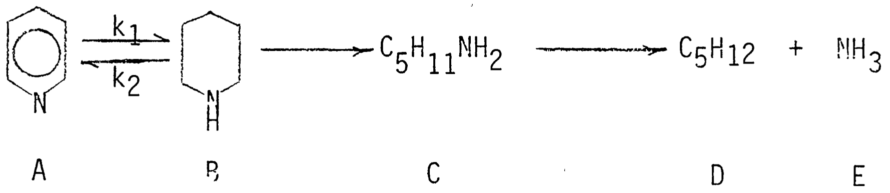
Figure 16. FTIR Results for Shell 324 Catalyst After Being Heated in Air at 630 °C

APPENDIX E

LANGMUIR-HINSHELWOOD MODEL FOR PYRIDINE HYDROGENATION

LANGMUIR-HINSHELWOOD MODEL FOR PYRIDINE HYDROGENATION

A model for pyridine hydrogenation has been developed using the assumption that all reactants, intermediates and products are adsorbed. Although a Langmuir model was inadequate in fitting hydrogen adsorption data on an unextracted calcined catalyst (Appendix C), it is used here because the adsorption behavior of hydrogen on an extracted catalyst is unknown. The derivation is shown below:



$$-r_A = k_1\theta_A\theta_{H_2} - k_2\theta_B$$

where,

θ = fractional surface coverage

k = reaction rate constant.

Using the Langmuir adsorption isotherm,

$$\theta_i = \frac{K_iP_i}{(1+K_AP_A+K_{H_2}P_{H_2}+K_BP_B+K_CP_C+K_DP_D+K_EP_E)}$$

where,

i = A,B,H_2

K = adsorption coefficient

P = partial pressure.

As a result,

$$-r_A = \frac{k_1K_AK_{H_2}P_AP_{H_2}}{(1+K_AP_A+K_{H_2}P_{H2}+K_BP_B+K_CP_C+K_DP_D+K_EP_E)^2} - \frac{k_2K_BP_B}{(1+K_AP_A+K_{H2}P_{H_2}+K_BP_B+K_CP_C+K_DP_D+K_EP_E)}$$

From Langmuir adsorption isotherm,

$$K_i = \frac{\theta_i}{(1-\theta_i)P_i} = \frac{\phi_i}{P_i} \quad \text{where } \phi_i = \theta_i/(1-\theta_i)$$

therefore, $K_iP_i = \phi_i$

and

$$-r_A = \frac{k_1\phi_A\phi_{H_2} - k_2\phi_B(1+\phi_A+\phi_B+\phi_{H_2}+\phi_C+\phi_D+\phi_E)}{(1+\phi_A+\phi_B+\phi_{H_2}+\phi_C+\phi_D+\phi_E)^2}$$

VITA 2

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Master of Science

Thesis: THE POISONING OF A HYDROTREATING CATALYST BY PYRIDINE AND ITS HYDROGENATION DERIVATIVES

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