

THE EFFECT OF REDUCTION TEMPERATURE
ON A SUPPORTED PLATINUM CATALYST

A Dissertation
Presented to
the Faculty of the Department of Chemistry
College of Natural Sciences and Mathematics
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
Wei-Chu Lu
December, 1978

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ABSTRACT

A series of cycloalkenes characterized by increasing steric hindrance were hydrogenated on four alumina-supported platinum catalysts reduced at different temperatures (250°C, 350°C, 450°C and 550°C) in order to ascertain the effect of reduction temperature on the properties of the catalyst. Kinetic data on the hydrogenation of cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and 1,2-dimethylcyclopentene were obtained and reaction mechanisms were scrutinized. The kinetic results for each catalyst were compared and analyzed, based on the information obtained from the catalyst characterizations, which included surface area measurements, platinum content determinations and microscopic structure examinations on the catalyst supports. Reduction temperatures were found to affect the catalyst activity and hydrogenation rates were obviously retarded by steric hindrance.

All four catalysts exhibited γ type hydrogen adsorption, and the catalyst with the most extensive heat treatment showed an additional δ type adsorption. The kinetic results revealed that only the γ type adsorbed hydrogen participated in the hydrogenation reactions. No structural change of the alumina support was found upon

reduction at different temperatures. The differences in hydrogenation rates were believed due to the differences in the structure of the surface platinum on the catalyst. The activation energies for 1,2-dimethylcyclopentene hydrogenation using different catalysts revealed that the rate differences were affected by the variations of activation energies.

Competitive hydrogenations gave relative adsorption coefficients for 1-methylcyclopentene and 3-methylcyclopentene which did not differ much over the series of the four catalysts. The hydrogenation rates were therefore believed not to be controlled by adsorption. It is proposed that as the reduction temperature increases, the surface rearranges to expose more active sites that either give the adsorbed hindered cycloalkenes a correct orientation to react with hydrogen atoms or promote the desorption of the hindered cycloalkane products. The relative adsorption coefficient decreased in the order of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene, which was the same decreasing order as in the hydrogenation rates.

The product analysis for 1,2-dimethylcyclopentene hydrogenation further confirmed the effect of the catalyst reduction temperature because changes in the product distributions were found using different catalysts.

Finally the atomic migration model was suggested for causing the surface rearrangement during the catalyst reducing process.

TABLE OF CONTENTS

	PAGE
ACKNOWLEDGEMENT.	iii
ABSTRACT	v
LIST OF FIGURES.	X
LIST OF TABLES	XI
CHAPTER	
I INTRODUCTION	1
II EXPERIMENTAL	
A. Introduction	6
B. Hydrogenation Apparatus.	8
C. Catalyst Preparation	11
1. Alumina Preparation.	11
2. Platinum Impregnation.	13
D. Catalyst Characterization.	14
1. Platinum Content Determination	14
2. Surface Area Measurement	14
3. Microscopic Structure Studies.	15
E. Purification of Solvents and Reactants	15
1. Solvent.	15
2. Reactants.	16
F. Procedure.	18
G. Chromatography	22
III RESULTS	
A. Catalyst Characterization.	24
B. Hydrogenation of Cyclic Olefins.	24
C. Hydrogenation of Cyclopentene.	33
D. Hydrogenation of 3-Methylcyclopentene.	34
E. Hydrogenation of 1-Methylcyclopentene.	35
F. Hydrogenation of 1,2-Dimethylcyclopentene.	36
G. Activation Energy on the Hydrogenation of 1,2-Dimethylcyclopentene.	37

CHAPTER	PAGE
H. Competitive Hydrogenations	41
I. Product Distribution of 1,2-Dimethylcyclopentene Hydrogenation.	44
IV DISCUSSION	
A. Introduction	47
B. Catalyst Characterization.	50
C. Hydrogenation of Cyclopentene, 3-Methylcyclopentene, 1-Methylcyclopentene and 1,2-Dimethylcyclopentene	54
D. Reaction Rate of 1,2-Dimethylcyclopentene Hydrogenation.	58
E. Reaction Mechanism and Stereochemistry of Cycloalkene Hydrogenations.	61
1. Mechanistic Studies on Olefin Hydrogenations	61
2. Modified Horiuti-Polanyi Mechanism	63
3. Hydrogenation of 1,2-Dimethylcyclopentene.	64
F. Competitive Hydrogenations	66
G. Mechanistic Models of the Catalyst Reducing Process.	72
1. Atomic Migration Model	72
2. Crystal Migration Model.	74
V CONCLUSION	76
BIBLIOGRAPHY.	91

LIST OF FIGURES

FIGURE		PAGE
1	Hydrogenation Apparatus.	9
2	Reaction Flask	12
3	Cyclohexane Receiver	17
4	Cyclic Olefin Receiver	19
5	Unpoisoned Cyclopentene Hydrogenation.	21
6	Electron Microscopic Structures for Pt/Al ₂ O ₃ Catalysts at 180 Magnification	25 & 26
7	Electron Microscopic Structures for Pt/Al ₂ O ₃ Catalysts at 480 Magnification	27 & 28
8	Electron Microscopic Structures for Pt/Al ₂ O ₃ Catalysts at 4800 Magnification.	29 & 30
9	Hydrogenation Rate of Cyclopentene on Catalyst V versus Catalyst Weight.	32
10	Specific Hydrogenation Rate of Cyclic Olefins versus Catalyst Reduction Temperature.	38
11	ln Specific Rate versus $\frac{1}{T} \times 10^3$ for 1,2-Dimethylcyclopentene Hydrogenations.	40
12	Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene on Catalyst IV.	42
13	Competitive Hydrogenation of Cyclopentene and 1,2-Dimethylcyclopentene on Catalyst IV.	43
14	Logarithmic Plot of Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene	45

LIST OF TABLES

TABLE		PAGE
1	Calculated Vapor Pressures at Different Temperatures.	80
2	Chromatographic Calibration Constants	81
3	Relative Surface Area Measurements of the Pt/Al ₂ O ₃ Catalysts.	81
4	Cyclopentene Hydrogenation.	82
5	3-Methylcyclopentene Hydrogenation.	83
6	1-Methylcyclopentene Hydrogenation.	84
7	1,2-Dimethylcyclopentene Hydrogenation.	85
8	Hydrogenation of 1,2-Dimethylcyclopentene at Various Temperatures.	86
9	Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene.	87
10	Competitive Hydrogenation of Cyclopentene and 3-Methylcyclopentene.	88
11	Relative Adsorption Coefficients of 1-Methylcyclopentene and Cyclopentene	89
12	Relative Adsorption Coefficients of 3-Methylcyclopentene and Cyclopentene	89
13	Product Distribution of 1,2-Dimethyl- Cyclopentene Hydrogenation.	90

CHAPTER I

INTRODUCTION

A catalyst is a substance which increases the rate at which a chemical system attains equilibrium without itself undergoing chemical change.¹ A heterogeneous catalyst is a solid which increases the rate of a chemical reaction by virtue of specific properties of its surface.¹ After years of investigations, the following catalytic properties are apparent: (i) a catalyst can increase the rate of only those processes that are thermodynamically favorable; (ii) any increase that a catalyst brings about in the velocity constant of the forward reaction is accompanied by a corresponding increase in the velocity constant of the reverse reaction; (iii) for a given reactant there may be several reaction paths, and by the appropriate choice of catalyst any one of these paths may be selected.²

The importance of catalysis today is obvious by virtue of the fact that nearly ninety percent of all chemical manufacturing processes are catalytic. Despite millions of dollars spent each year on catalytic studies, catalysis still remains more an art than a science. The problems involved in catalytic research are due to the multiplicity of variables

that affect the catalytic processes and the difficulty in reproducing catalytic surfaces. Since the theoretical underpinnings of catalysis have not been well established, the uses of catalysts are still widely guided by past experience.

Since most hydrogenation reactions can be effectively catalyzed by platinum under mild conditions, platinum has become one of the most frequently used catalysts in the laboratory. Because of its high catalytic activity as well as the large body of information available from previous investigations, platinum was chosen to be the catalyst for our hydrogenation studies. In order to increase the catalyst surface area, reduce the catalyst sintering and improve the mechanical strength of the catalyst, an alumina-supported platinum catalyst was employed instead of a pure metal catalyst.

There are three methods for preparing a supported metal catalyst; impregnation, co-precipitation, and deposition. The catalysts used by us were obtained by the impregnation method, which is frequently the simplest of the three. Our $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts were prepared by: (1) soaking the Al_2O_3 carrier in an impregnating solution of diammine platinum (II) nitrite; (2) drying the material; (3) oxidizing the impregnated diammine platinum (II) nitrite to platinum dioxide with oxygen, and (4) reducing the platinum dioxide to platinum metal by passing

hydrogen over the surface.

Geometric effects have long been known as one of the key factors for determining catalytic activity. The geometric effects include lattice spacing, and crystallographic symmetry as well as the arrangement of atoms in the catalyst surface. Balandin³⁻⁶ and Kobozev² have developed different theories to explain the geometric factor, but they both agreed that there are a number of active sites on the catalyst surface and these active sites determine catalytic activity.

The surface heterogeneity of a catalyst is believed to be affected by thermal treatment. Evidence of redispersion was found after sintering a supported Pt/Al₂O₃ catalyst in oxygen at 450 to 600°C.⁷ Compagnon and coworkers⁸ found that the first heat treatment at high temperature strongly influenced the platinum dispersion of their Pt-amorphous alumina catalysts. A number of researchers⁹⁻¹³ have studied the sintering of Pt/Al₂O₃ catalyst in an oxidizing atmosphere. Although various thermal treatments of a catalyst have been investigated, the effect of reduction temperature on the catalyst's surface heterogeneity has never been systematically studied. Only two references have been found that are related to the effect of reduction: one by Morikawa²¹ and another by Flynn and Wanke.⁷ Morikawa prepared his palladium on aluminosilicate catalysts by calcining the catalysts at

300°C for two hours and then reducing at temperatures of 300°C, 400°C and 500°C, respectively, for two hours. From kinetic studies made on hydrogenation of benzene, he declared that the number of active sites decreased with increasing reduction temperature. By supporting a 2.03% platinum on Alon catalyst on a holey carbon film mounted on a tungsten grid, Flynn and Wanke⁷ were able to take electron micrographs of the catalyst before and after reduction. In spite of problems with metal transport to carbon support film of the grid and carbon transport to the catalyst, they observed agglomeration of Pt after reduction in hydrogen at 300°C. Their findings may not apply to an alumina supported catalyst specimen. We therefore decided to study the effect of reduction temperature on an alumina-supported platinum catalyst.

The four Pt/Al₂O₃ catalysts used for our study were prepared from the same batch of catalyst, the only difference being that they were reduced at four different temperatures: 250°C, 350°C, 450°C and 550°C, respectively. This series of catalysts was examined to check if they were different in surface structure. Powerful catalyst characterizing tools such as an atomic absorption spectrophotometer, a hydrogen chemisorption apparatus and an electron microscope were employed to pinpoint those catalyst characteristics which provide a solid ground for rationalizing of individual catalytic performance.

The hydrogenation of a series of cycloolefins: cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and 1,2-dimethylcyclopentene, which increase in steric hindrance, was then studied. The hydrogenation of cyclopentene, known as a facile reaction²⁰ which is not affected by surface structure, was used as a basis to which all the other hydrogenation reactions could be compared. The role of steric hindrance in catalytic hydrogenation reactions and the effect of surface heterogeneity of the four catalysts was clarified after this scrutiny. Competitive hydrogenations between pairs of unsaturated compounds, e.g., cyclopentene and 1-methylcyclopentene, cyclopentene and 3-methylcyclopentene were also investigated. Information on surface structure as well as the relative adsorption coefficients for the cyclo-olefins was obtained. An activation energy study of the hydrogenation of 1,2-dimethylcyclopentene using two different catalysts was made and activation energies were calculated. Product analysis is very helpful for detecting the reaction mechanism and uncovering the catalyst's surface structure. Thus, the ratio between cis and trans products were examined for 1,2-dimethylcyclopentene hydrogenation. After reviewing the results from the aforementioned kinetic studies, the effect of reduction temperature on a $\text{Pt/Al}_2\text{O}_3$ catalyst is discussed and clarified.

CHAPTER II

EXPERIMENTAL

A. Introduction

Our experimental work involves the following four portions: (1) catalyst preparation, (2) catalyst characterization, (3) hydrogenation reaction and (4) chromatographic analysis. The rates of hydrogenation are reported in units of $\frac{\text{ml of H}_2}{\text{min}}$ which can easily be converted into $\frac{\text{ml of H}_2}{\text{min-atm}}$ by the equation:

$$\text{rate in } \frac{\text{ml of H}_2}{\text{min-atm}} = \frac{\text{rate in } \frac{\text{ml of H}_2}{\text{min}}}{P_{\text{H}_2} / 760}$$

where P_{H_2} is the partial pressure of hydrogen in units of mm Hg. The specific rates of hydrogenation in $\frac{\text{moles of H}_2}{\text{min-atm-g atom of platinum}}$ can be calculated by:

$$\text{specific rate in } \frac{\text{moles of H}_2}{\text{min-atm-g atom of platinum}} = \frac{\left(\frac{P_T}{760}\right) \left(\text{rate in } \frac{\text{liter of H}_2}{\text{min-atm}}\right)}{RT \left(\frac{\text{wt of catalyst}}{195.1}\right) \left(\frac{WP}{100}\right)}$$

where P_T = total pressure of system, mm Hg

$$R = 0.08205 \frac{\text{liter-atm}}{\text{mole-}^{\circ}\text{K}}$$

T = temperature in degree Kelvin

WP = weight percentage of platinum in the catalyst

195.1 = atomic weight of platinum, g

Wt of catalyst = weight of catalyst after being corrected
for splashing or sticking, g

Conversion of units is made under the assumption that all reactions were first order in hydrogen since Hussey and coworkers¹⁴ found that a number of cycloalkenes which included cyclopentene, 1-methylcyclopentene, 3-methylcyclopentene, exhibited a first-order dependence on hydrogen pressure.

The rates presented have been corrected for the partial pressures of the solvent and the reactants. The vapor pressure for each reactant, at different temperatures, are calculated from the Clausius-Clapeyron equation by adapting reported $\frac{dT}{dp}$ values.¹⁵ The Ideal Gas Law and Raoult's Law are then employed to calculate the partial pressure of the solvent and the reactants. Reported $\frac{dT}{dp}$ values for the solvent and the reactants, as well as their calculated vapor pressures, are given in Table 1. The difference in vapor pressures of the products and the reactants were not taken into account because of the difficulty in solving the time dependent equations.

The sticking of catalyst to the walls of the reaction flask, and the splattering of the catalyst into the neck

of the reaction flask caused problems in obtaining accurate hydrogenation rates. The weight of the catalyst, corrected for splashing or sticking is obtained by: (1) Plotting hydrogenation rate (in units of $\frac{\text{ml of H}_2}{\text{min-atm}}$) versus catalyst weight. The intercept on the catalyst weight axis is considered to be the weight loss due to splashing or sticking. (2) Subtracting the catalyst weight loss from the actual catalyst weight.

A method to detect the poisoning of the catalyst was developed by Hussey and coworkers.^{14,16} The technique is as follows: When the original reactant is completely hydrogenated, another sample of the same reactant is injected and hydrogenated. If the rates of the two reactants are the same, the reaction is said to be unpoisoned. We adopted this "bracketing" method to ensure that our reaction runs were not poisoned.

B. Hydrogenation Apparatus

A system similar to the one used by Barry¹⁷ was constructed for the hydrogenation reactions (Figure 1). Hydrogen (Linde, extra dry grade) passed through a palladium purifier (Protran Purifier, Bendix) and filled the pre-evacuated system up to 1 atmosphere. The hydrogen flowed through a molecular sieve (MS) (Linde 4A) before entering the reaction flask (RF). The manometer (M) was used to measure the precise hydrogen pressure. A

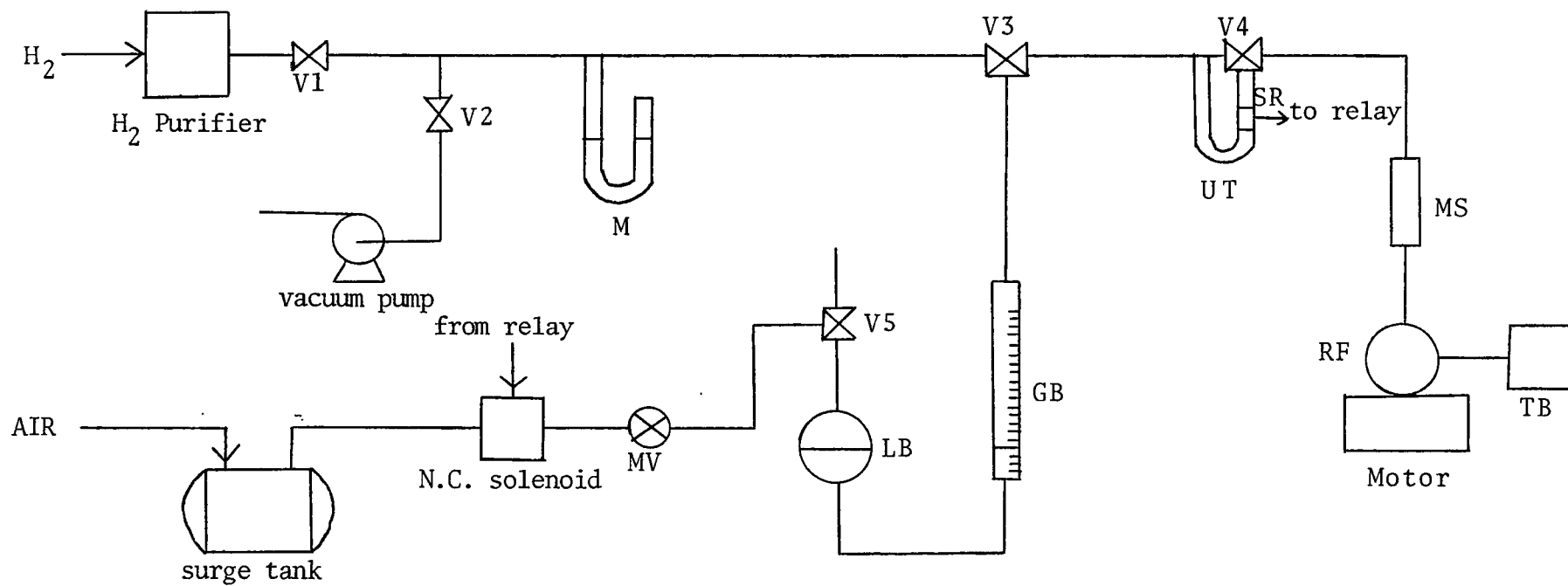


Figure 1: Hydrogenation Apparatus

three-way stopcock (V4) was installed above the reactor side of the U-tube (UT). With V4 opened to all three exits, the height of the dibutylphthalate in both sides of the U-tube remained level while hydrogen was introduced. Stopcock V4 was then adjusted to a position which would seal off the reactor side of the U-tube before the reaction started but allowed one side of the U-tube to remain open to the hydrogen reservoir contained in buret (GB). The hydrogen consumed during the reaction lowered the hydrogen pressure causing the dibutylphthalate level to fall below the slip rings (SR). A capacitance relay (thermocap relay, Niagare Electron Laboratories, Andover, New York) was then triggered, which activated and opened the solenoid. This allowed air, buffered by a five liter surge tank, to drive the mercury from the leveling bulb (LB) into the gas buret (GB). A micrometer valve (MV) (Whitney 22RS4316, Dearborn Valve and Fitting Company, Glenview, Illinois) was used to control the air flow. The rise of the mercury level in the gas buret forced the dibutylphthalate level in the reactor side U-tube up. When the dibutylphthalate rose to the initial level, the relay went off, and the solenoid returned to its normally closed position preventing any further air flow. By careful regulation of air flow, it was possible to keep the system pressure very constant.

The reaction flask (RF)(Figure 2) had a water jacket which kept the reaction under a constant temperature controlled by a low temperature bath (TB)(Benco/Grant Model LB low temperature thermostatic unit). The reactants and the solvent were injected into the reaction flask through a silicon rubber cap. The reaction flask fitted into a rubber conical cap which was attached 3 mm off center to a stainless steel cylinder. This cylinder was connected to the shaft of a 1/2 h.p., 1750 rpm motor to provide agitation. The reaction flask was pressed down on the rubber cup by a one-hole rubber stopper held by a three finger clamp.

C. Catalyst Preparation

1. Alumina Preparation

Selwood's⁵¹ method was used to prepare the alumina support. High purity aluminum metal (36g) was mixed with potassium hydroxide (224g) and distilled water (2 liters) in a polyethylene container. After the metal dissolved, the mixture was acidified with reagent grade nitric acid until aluminum hydroxide started to precipitate. The precipitation was completed by bubbling carbon dioxide through the solution until the solution reached a pH of 8. The precipitate was then washed with distilled water. When

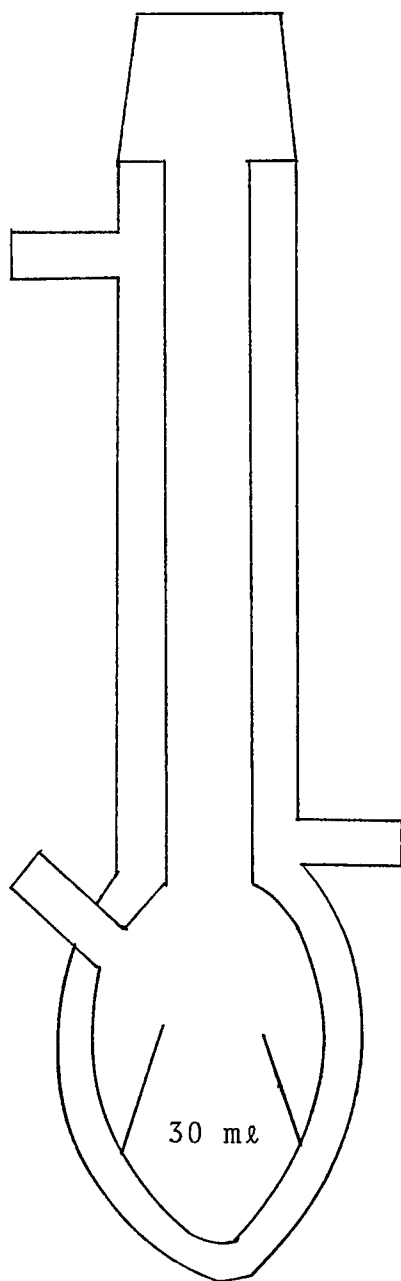


Figure 2: Reaction Flask

the washings were neutral, the alumina was washed six times with hot distilled water in a glass beaker. The alumina was then filtered, dried overnight at 140°C and calcined in a tube furnace under oxygen at 600°C for four hours. Keulks¹⁰ had identified the alumina made by this method as η -alumina. The alumina was then ground up until it was 200 mesh or smaller and stored in a desiccator.

2. Platinum Impregnation

Diammine platinum (II) nitrite (Alfa Inorganics, Beverly, Massachusetts) was twice recrystallized from hot water and dried. A quantity (50.220 grams) of alumina was put in an evaporating dish which was sitting on a steam bath. After the platinum complex (0.827 grams) dissolved in hot distilled water, it was added to the evaporating dish which was then moderately heated until all the water evaporated. The impregnated catalyst was ground and sieved with a 200 mesh sieve, then calcined in a tube furnace under oxygen at 600°C for four hours. The oxidized catalyst was divided into four equal samples, each of them was reduced with hydrogen at the respective temperatures: 250°C, 350°C, 450°C and 550°C for six hours. The system was cooled by purging with high purity Linde nitrogen. The catalysts were resieved with a 200 mesh sieve and, if necessary, crushed until all

particles were smaller than 200 mesh. The catalysts were stored in a desiccator between runs.

In this dissertation, the catalysts reduced at 250°C, 350°C, 450°C and 550°C will be specified as catalyst II, III, IV, and V, respectively.

D. Catalyst Characterization

1. Platinum Content Determination

An atomic absorption spectrophotometer (Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer) was used to determine the platinum content. Catalyst samples were dissolved in aqua regia and diluted before the analysis. A series of standard solutions of K_2PtCl_6 were made and used as calibrants. The platinum contents of the catalysts were then determined from atomic absorption measurements.

2. Surface Area Measurements

The relative hydrogen specific surface area measurements were made by the Baroid Company using the hydrogen chemisorption and desorption method. All samples were heated in argon at their corresponding reduction temperatures for thirty minutes and then were saturated in a stream of hydrogen at room temperature. Hydrogen desorption was carried out by heating the sample in a stream of argon at a controlled rate up to 600°C. The

effluents were analyzed by a gas chromatograph and the desorption peaks were measured by the triangulation method.

3. Microscopic Structure Studies

Microscopic structure studies of the catalysts were conducted with a scanning electron microscope (Model S4-10, Cambridge Scientific Instruments, England) at three different magnifications (x180, x480, x4800).

Aluminum specimen stubs were first coated with silver conductive paint and smoothed with a glass slide. Samples were then sprinkled on each stub. The electron microscope was operated at an accelerating voltage of 20 KV. Polaroid film type 52 was used on all photos taken from a CRT with a resolution of approximately 1000 lines.

E. Purification of Solvents and Reactants

Poisoning was the key problem for our catalytic hydrogenation study. The catalysts were extremely sensitive to any trace amounts of impurities either from the reactants or from the solvent. We developed the following purification procedures to conquer this problem.

1. Solvent

Cyclohexane was used as the solvent for all the hydrogenation reactions. 99+% cyclohexane (Aldrich Chemical Company, Milwaukee, Wisconsin) was refluxed over a sodium

and potassium alloy, under nitrogen, for three hours before it was distilled and collected in a 200 ml receiver (Figure 3). Nitrogen at a pressure greater than one atmosphere was kept inside the receiver at all times. Whenever a sample was desired, V2 was opened and the needed amount of cyclohexane was allowed to fill the sample cup. At this point V2 was closed and the sample was removed. The sample cup was always evacuated with an aspirator to remove excess cyclohexane when it was not in use. Before each hydrogenation run was started, a 2.5 ml sample of cyclohexane was taken from the receiver. It was next passed through a 4 cm³ activated alumina column (chromatographic, grade F-20, Alumina Company of America, St. Louis, Illinois) before being injected into the reaction vessel.

2. Reactants

Cyclopentene, 1-methylcyclopentene, 3-methylcyclopentene and 1,2-dimethylcyclopentene were used individually or in pairs as the reactants. All of the reactants (99%, Chemical Samples Company, Columbus, Ohio) were chromatographically purified. A one foot long, 3/4 inch I.D. glass column filled with Chromosorb P(non-acid washed, Johns-Manville Company) was used in the chromatographic purification step. The gas chromatograph (F-M Research Chromatograph 810) outlet was connected to a small volume

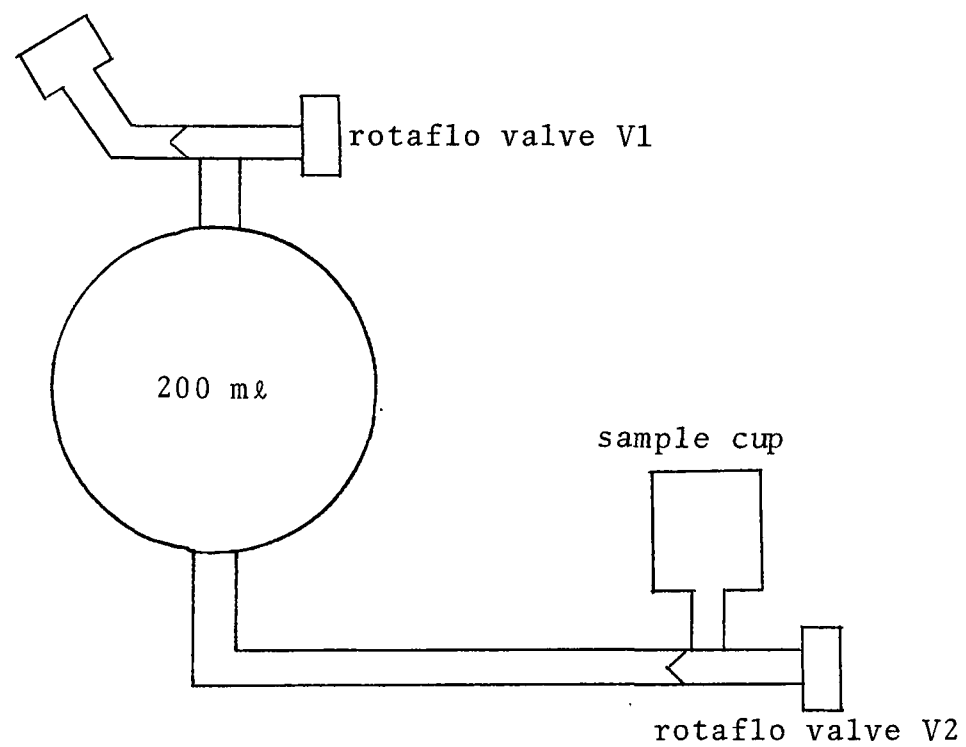


Figure 3: Cyclohexane Receiver

receiver (Figure 4). A hole was drilled in the Teflon valve of the receiver to allow the solution in the receiver to be protected from the atmosphere by the flow of nitrogen carrier from the chromatograph. The receiver was immersed in a beaker of ice water to trap the gaseous reactants. Before each hydrogenation run was started, 0.5 ml of reactant was injected into the gas chromatograph and collected in the receiver. The column temperature was maintained ten degrees below the boiling point of individual reactant. The sample was removed through a silicon gum rubber septum on the receiver neck by a syringe. It was necessary to clean all the glassware by initially rinsing with nanograde acetone (Mallinckrodt) and then heating the glassware in a glass oven at 600°C for three hours before using.

F. Procedure

In order to remove trace amounts of moisture absorbed by the catalyst, the preweighed catalyst was heated in a vacuum oven at 130°C for 40 minutes before use. The catalyst was weighed by difference using an aluminum foil dish. The reaction flask loaded with preheated catalyst was then quickly attached to the system. The system was evacuated to at least 0.1 torr for ten minutes, then filled with hydrogen (extra dry grade, Linde Company) which had passed through a palladium

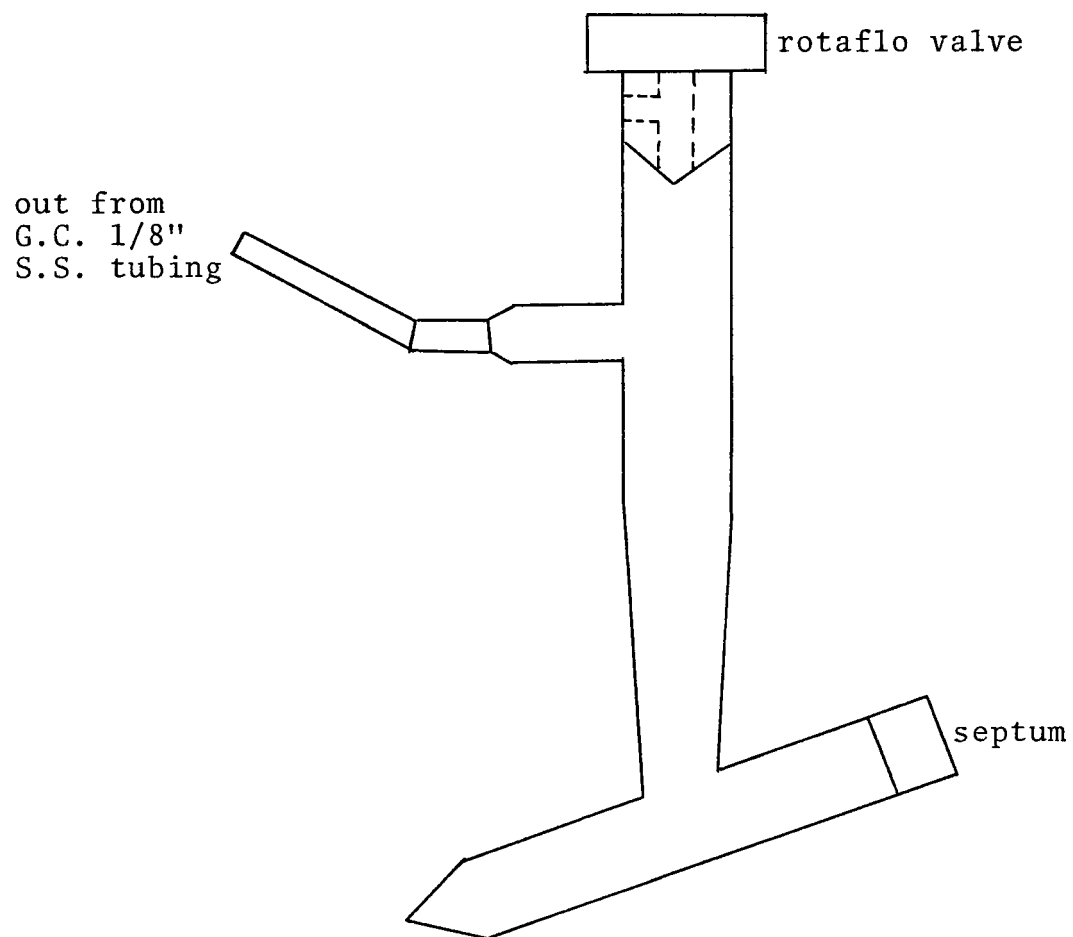


Figure 4: Cyclic Olefin Receiver

purifier to a pressure of 770 torr. After the catalyst was reduced for one hour, the system was evacuated for twenty minutes. 760-812 torr of hydrogen was then added to the entire system. The temperature of the reaction vessel was always maintained at 25°C except for the activation energy studies. A sample of 2 ml of purified cyclohexane (See section E) was injected into the reaction flask, then the cyclohexane and the catalyst were agitated for ten minutes. During the prereaction agitation, the reactant(s) was chromatographically purified. A sample of 0.1 ml of the reactant was then injected into the reaction vessel. The agitator and the timer were started simultaneously, and volume readings were taken every minute (refer to hydrogenation apparatus for the details of volumetric adjustments). When the reaction was completed, a second sample of reactant was injected. A typical plot of the unpoisoned cyclopentene hydrogenation is shown in Figure 5. For product distribution studies, samples were taken every five minutes for chromatographic analysis.

The procedures for the competitive hydrogenations were the same as that for the hydrogenation reactions, except 0.1 ml samples of each reactant was injected into the reactor consecutively. During competitive runs, samples were removed for chromatographic analysis.

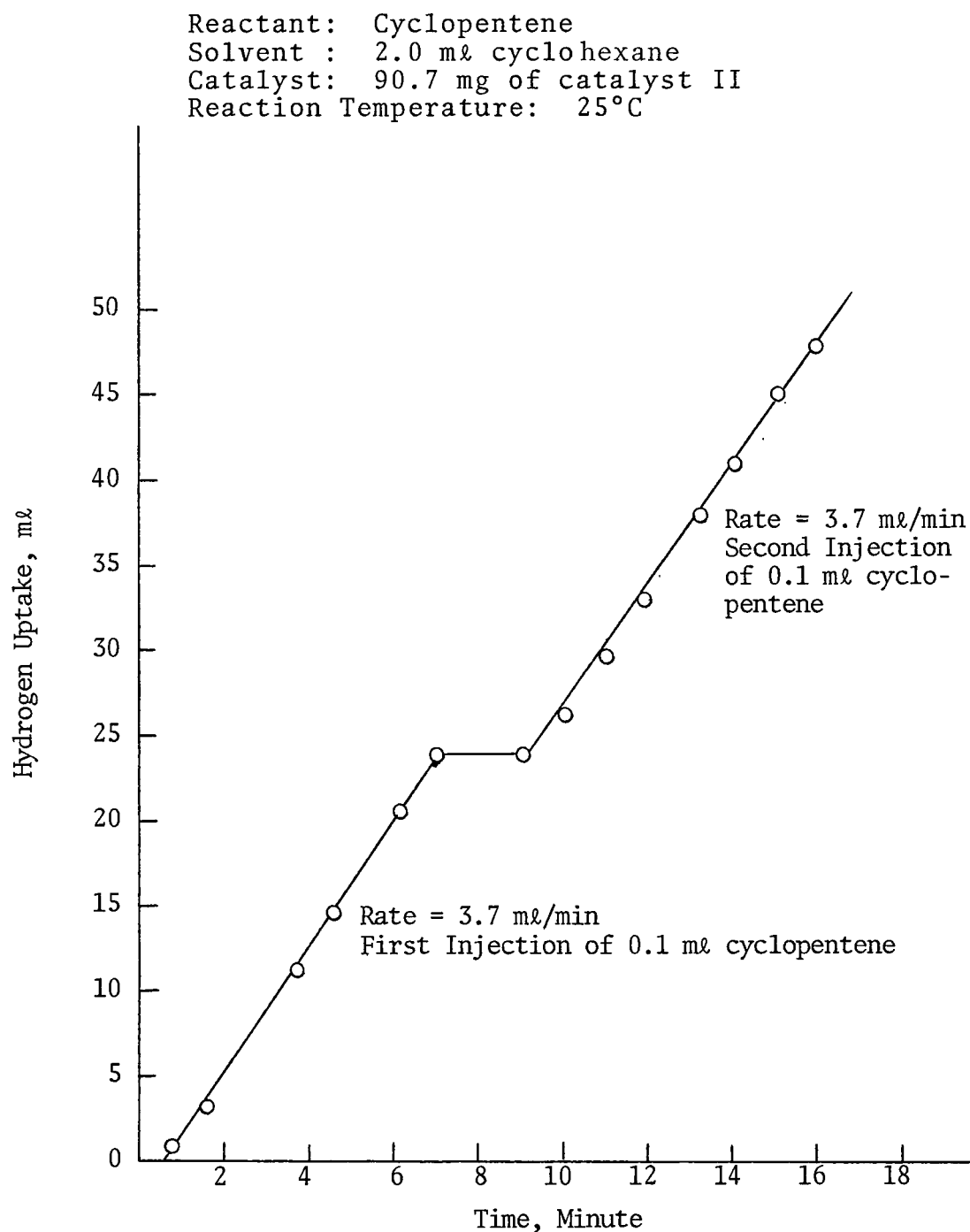


Figure 5: Unpoisoned Cyclopentene Hydrogenation

The same procedures were applied to the activation energy studies, but the hydrogenation reactions were run at a series of different temperatures.

G. Chromatography

The chromatographic measurements were carried out on a Varian Aerograph Series 1400 gas chromatograph with a flame ionization detector. A 1/8 inch, 20 foot stainless steel column of 20 percent dimethylsufolane on chromosorb P (80/100 mesh) was used in all analyses except the isomerization studies. The measurements were made at a column temperature of 25°C. The packed column used for isomerization studies was a 20 foot long, 1/8" stainless steel column filled with 20 percent squalane on chromosorb P (80/100 mesh). The column was kept at 70°C during the analysis. The injector and detector temperatures were set at 90°C and 170°C respectively for all the analyses. Nitrogen with a flow rate of 30 ml/min served as the carrier gas for all the G.C. measurements. During the reaction, 0.1 ml samples were removed from the reaction flask by a B-D Yale Tuberculin 1 cc syringe which had a six inch needle. The samples were either analyzed immediately by gas chromatography or kept in a short capillary tube closed with a silicon rubber cap and stored in a freezer.

Quantitative calibration factors relating moles to peak area for all the compounds were obtained by analyzing a known sample of each compound. Calibration factors are presented in Table 2. Peak areas were derived by triangulation of the peaks.

CHAPTER III

RESULTS

A. Catalyst Characterization

For the remainder of this dissertation, the catalysts reduced at 250°C, 350°C, 450°C and 550°C will be designated as catalyst II, III, IV and V respectively. In order to interpret the kinetic data, the characterization of these catalysts is necessary.

The four catalysts were analyzed by atomic absorption spectroscopy which disclosed the platinum content as 0.40 ± 0.05 percent platinum on Al_2O_3 for all the catalysts. The relative surface areas measured by hydrogen desorption for each catalyst are presented in Table 3. Two hydrogen desorption peaks were observed for catalyst V while only one peak was found for all of the other catalysts. The electron micrographs for catalysts II-V are shown in Figures 6-8 for the three different magnifications used (x180, x480 and x4800). No macroscopic or microscopic difference in particle size or distribution can be discerned.

B. Hydrogenation of Cyclic Olefins

The cyclic olefins that we studied include cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and

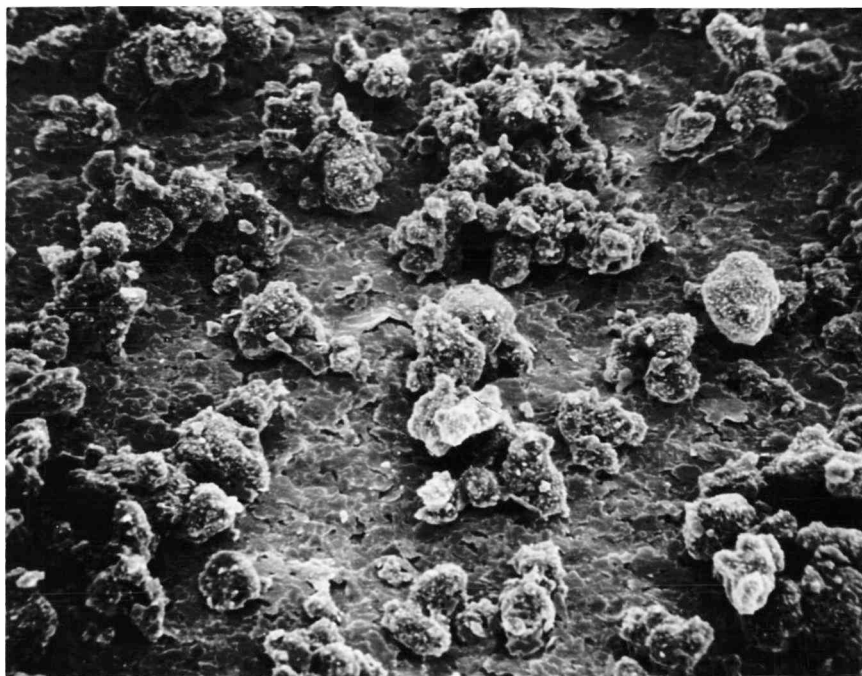


Figure 6a: Electron Microscopic Structure for Catalyst II-
at 180 Magnification

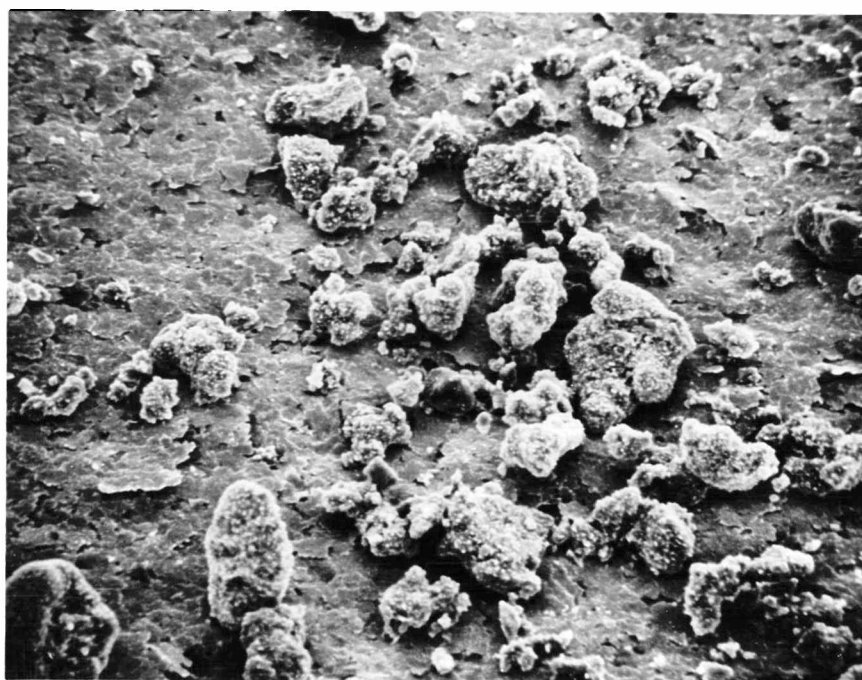


Figure 6b: Electron Microscopic Structure for Catalyst III
at 180 Magnification

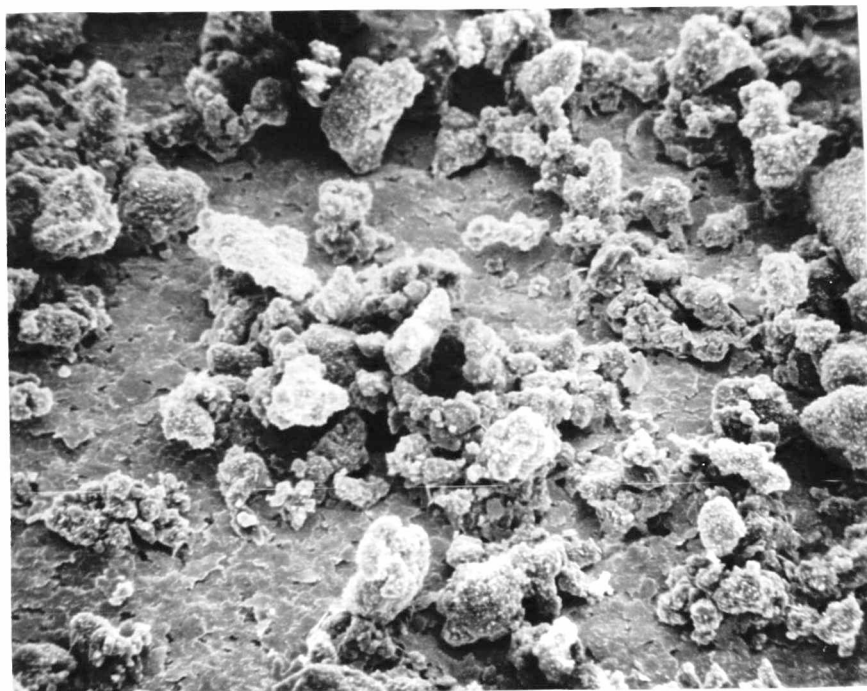


Figure 6c: Electron Microscopic Structure for Catalyst IV
at 180 Magnification

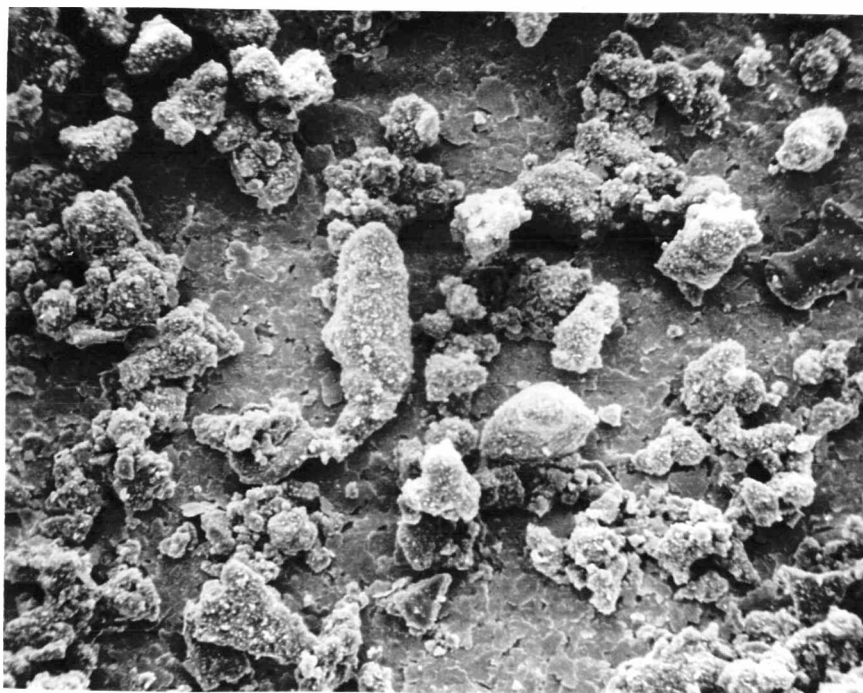


Figure 6d: Electron Microscopic Structure for Catalyst V
at 180 Magnification

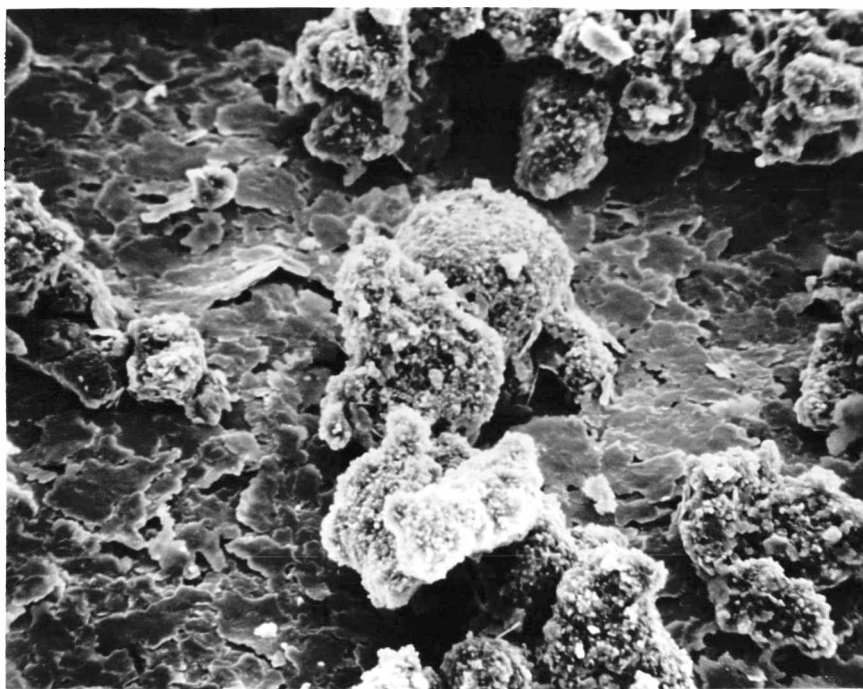


Figure 7a: Electron Microscopic Structure for Catalyst II
at 480 Magnification

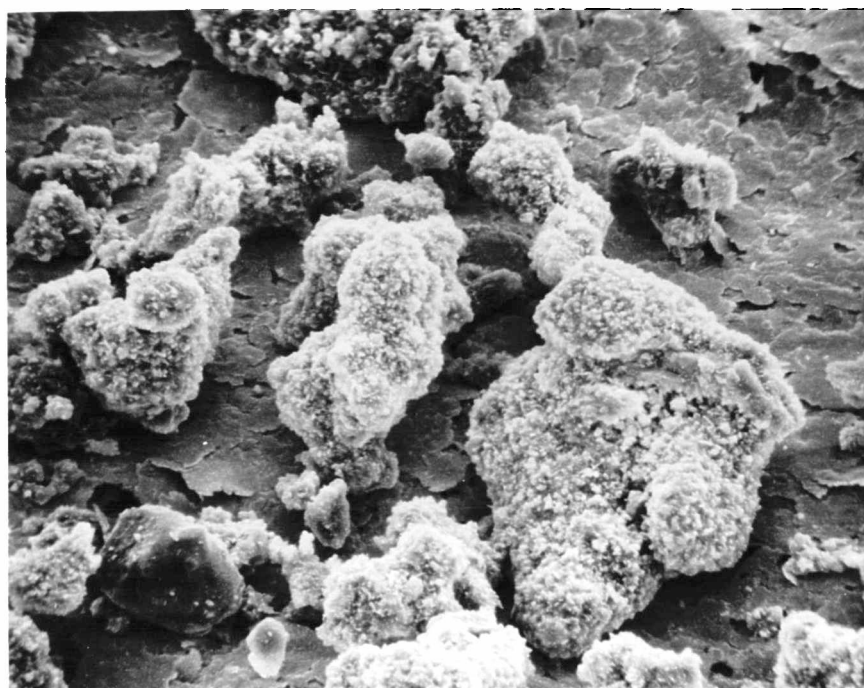


Figure 7b: Electron Microscopic Structure for Catalyst III
at 480 Magnification

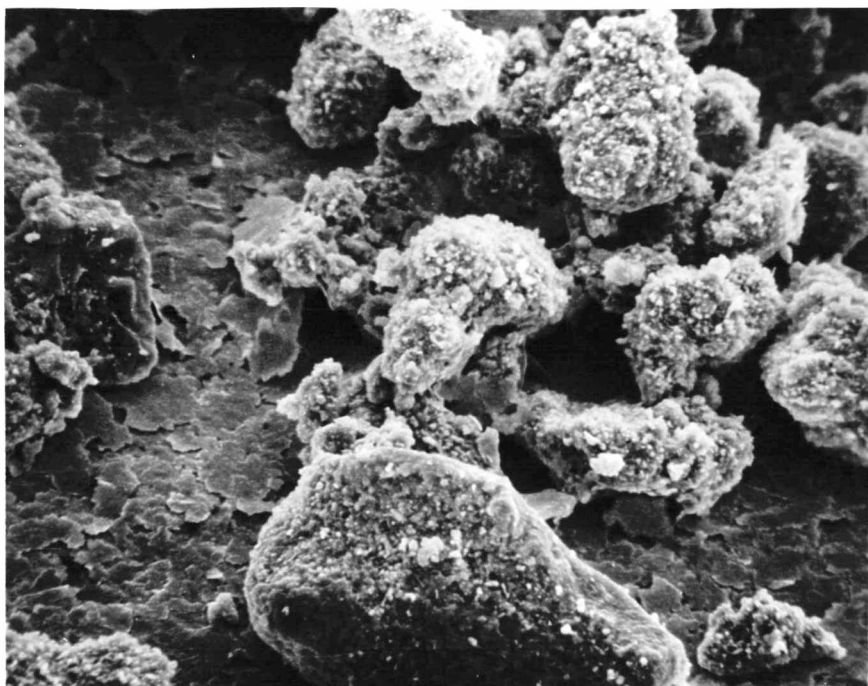


Figure 7c: Electron Microscopic Structure for Catalyst IV
at 480 Magnification

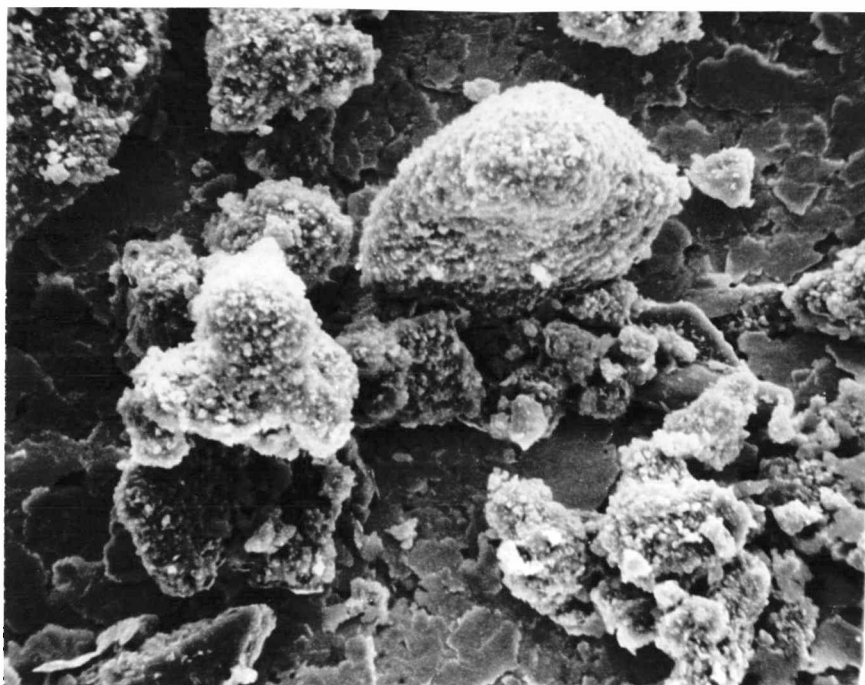


Figure 7d: Electron Microscopic Structure for Catalyst V
at 480 Magnification

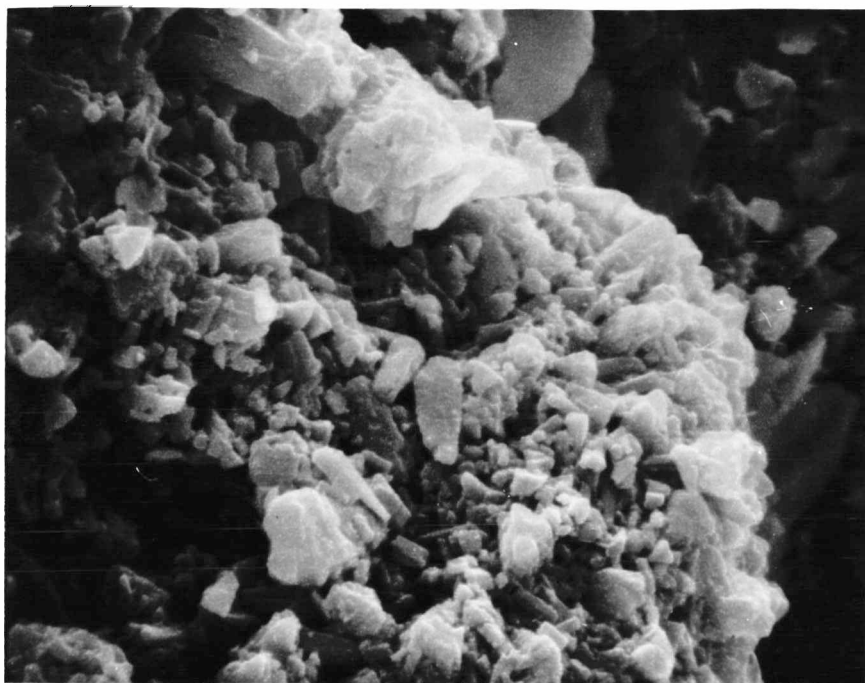


Figure 8a: Electron Microscopic Structure for Catalyst II
at 4800 Magnification

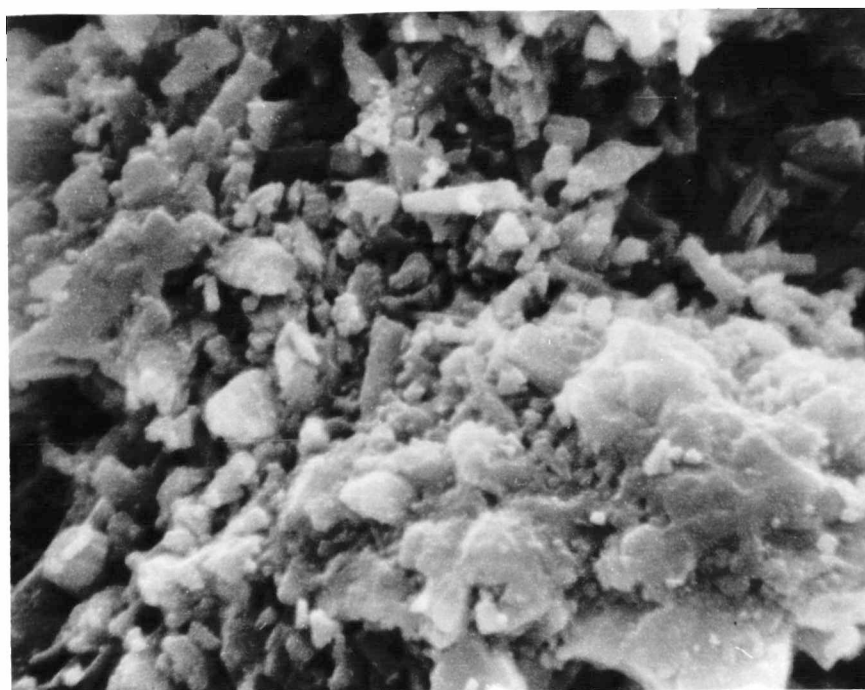


Figure 8b: Electron Microscopic Structure for Catalyst III
at 4800 Magnification

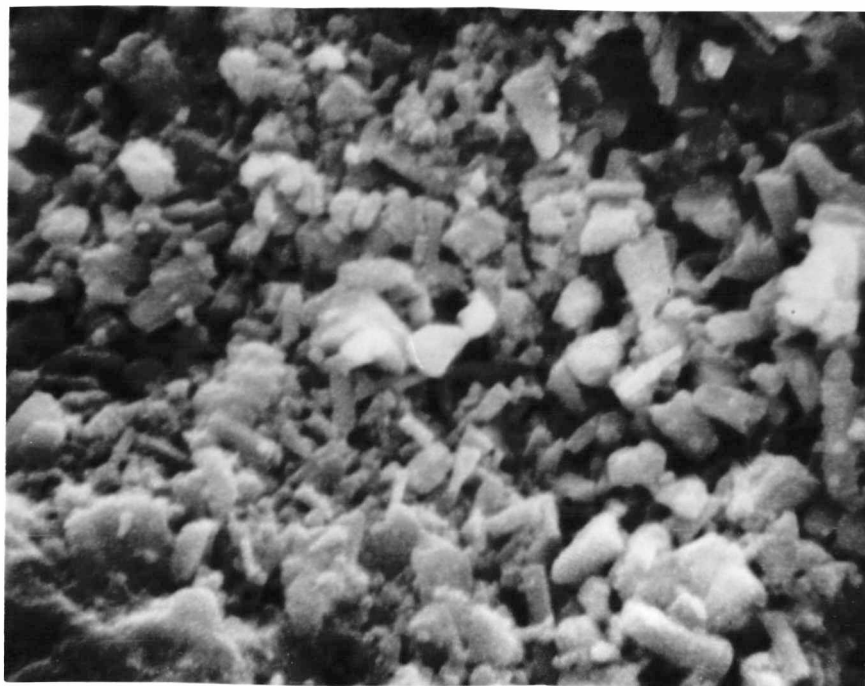


Figure 8c: Electron Microscopic Structure for Catalyst IV
at 4800 Magnification

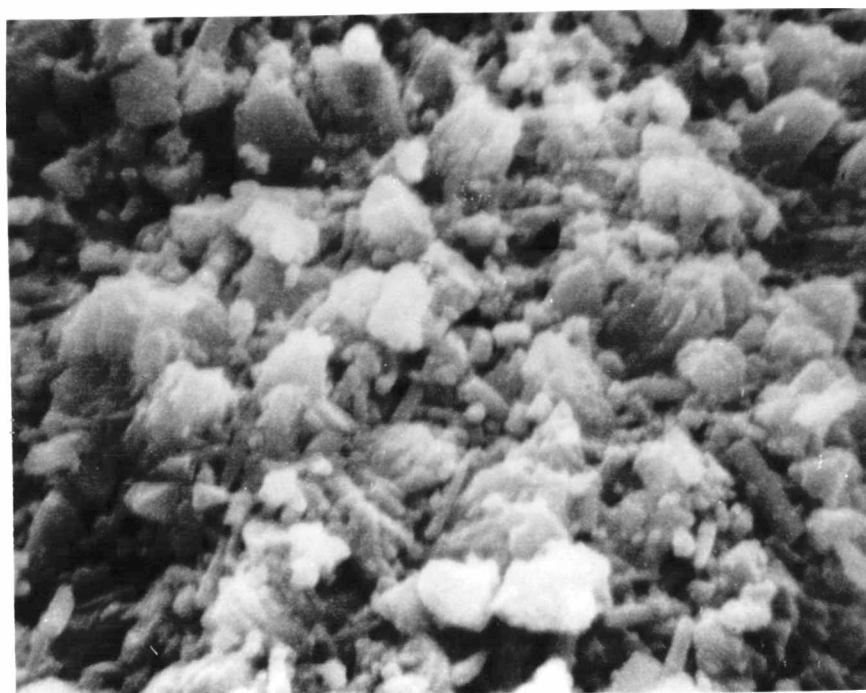


Figure 8d: Electron Microscopic Structure for Catalyst V
at 4800 Magnification

1,2-dimethylcyclopentene. The hydrogenations of these cyclic olefins were carried out at 25°C by employing catalysts II-V individually. For the hydrogenation of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene, five different runs were made with the specific catalyst weight varied from 30 mg to 90 mg for each. The catalyst weights used were approximately 30 mg, 45 mg, 60 mg, 75 mg and 90 mg. For the hydrogenation of 1,2-dimethylcyclopentene, three different runs were made for each catalyst with weights of catalyst of approximately 200 mg, 350 mg and 500 mg. The previously mentioned bracketing method was used during the hydrogenations to ensure that our runs were not poisoned.

All of the specific hydrogenation rates have been corrected for the partial pressure of the reactants and the solvent. A typical plot of the rates (ml/min/atm) versus amount of catalyst (mg) is given in Figure 9. The intersection on the weight axis is due to the constant loss of catalyst caused by sticking and splashing. The intersection from the rate versus amount of catalyst plot was found to be 20 mg for the 1,2-dimethylcyclopentene hydrogenations and 8 mg for the hydrogenations of the other three cyclic olefins (refer to the next four sections for the detailed kinetic data). The amount of catalyst lost to sticking is approximately 10% of the average

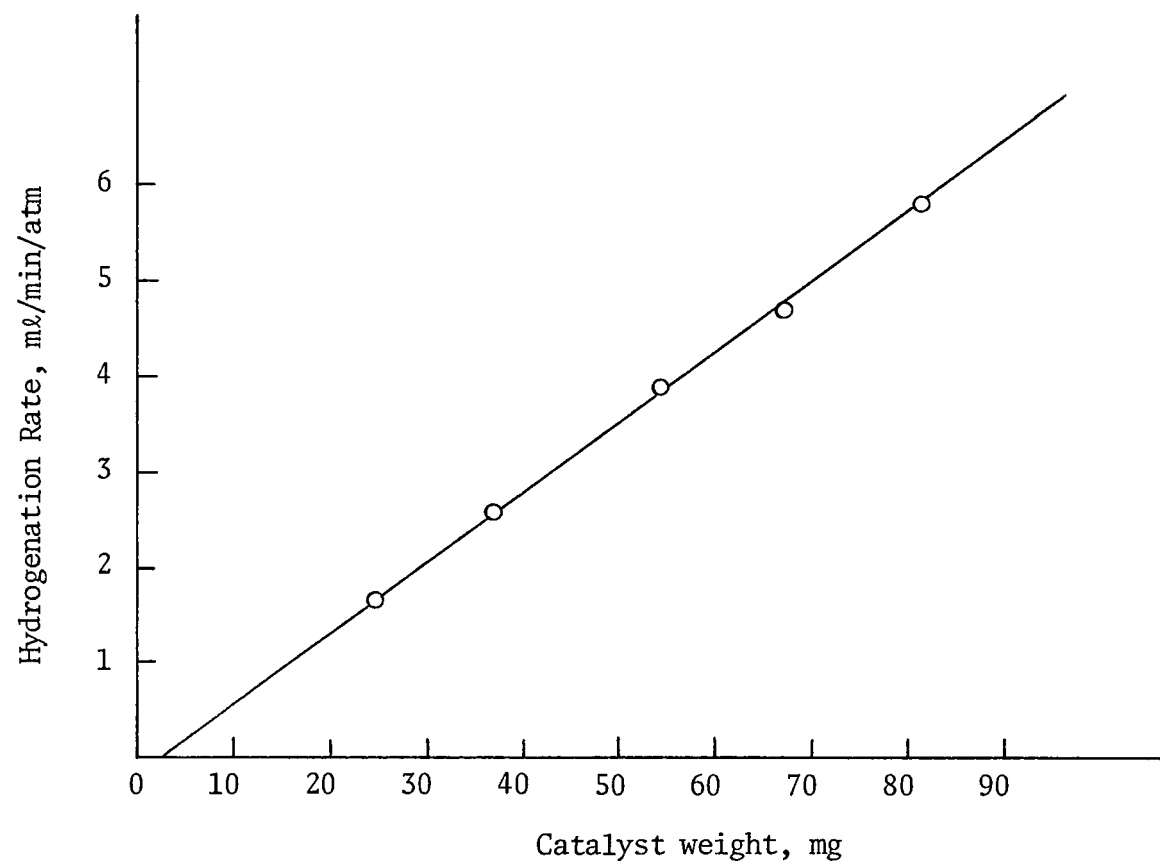


Figure 9: Hydrogenation Rate of Cyclopentene on Catalyst V versus Catalyst Weight

weight. All of the specific hydrogenation rates obtained have been corrected for the constant catalyst loss by following the calculations as specified in Section A of Chapter II. The variation of experimental error for all the specific hydrogenation rates is at most $\pm 10\%$.

C. Hydrogenation of Cyclopentene

The hydrogenation rates of cyclopentene along with the catalyst weights and reaction pressures are shown in Table 4. For convenience in comparing the relative activities of our four catalysts, the ratios of the average specific rate of each to the average specific rate of catalyst II are also presented in Table 4. The resultant specific rate for cyclopentene hydrogenation using catalyst III (131.2 moles/min/atm/g-atom of Pt) was somewhat higher than that reported by Hussey and coworkers¹⁴ using a 0.52 percent Pt catalyst (121 moles/min/atm/g-atom of Pt) and the same as that found by Barry¹⁷ using a 1.0 percent Pt catalyst (131.5 moles/min/atm/g-atom of Pt). Among the four, catalyst II gave a much lower specific hydrogenation rate while the specific rates with the other three catalysts were approximately the same.

The plot of rates (ml/min/atm) versus amount of catalyst (mg) gave a straight line (Figure 9), the reaction is therefore first order in the catalyst. The reaction is zero order in cyclopentene since the plot of hydrogen

uptake versus reaction time is linear throughout (Figure 5). The unchanged rate for various initial amounts of cyclopentene (0.1-0.3 ml) also verifies the zero order of cyclopentene. Hussey and coworkers¹⁴ have proven that the hydrogen dependence in the hydrogenation reactions of cyclo-olefins is first order. The rate equation for cyclopentene hydrogenation can then be summarized as follows:

$$\text{rate} = k(\text{Cyclopentene})^0 (\text{catalyst weight})^1 (P_{\text{H}_2})^1$$

This rate equation is in agreement with Barry's¹⁷ results as well as Hussey and coworkers'¹⁴ findings.

D. Hydrogenation of 3- Methylcyclopentene

The experimental results of the hydrogenation of 3-methylcyclopentene are presented in Table 5. The resultant specific hydrogenation rates were somewhat lower than those of cyclopentene. Similar to the hydrogenations of cyclopentene, the specific hydrogenation rate of 3-methylcyclopentene was much lower for catalyst II and remained constant for the other catalysts.

A straight line was obtained by plotting hydrogen uptake versus catalyst weight, which implies a first order dependence on the catalyst. The linear plot of hydrogen consumption versus reaction time along with the fact that reaction rate remains unchanged with various

volumes of 3-methylcyclopentene both indicate that the reaction is zero order in 3-methylcyclopentene. Hussey and coworkers¹⁴ have deduced a first order dependence for hydrogen, therefore the overall hydrogenation rate scheme for 3-methylcyclopentene can be expressed as:

$$\text{rate} = k(3\text{-methylcyclopentene})^0(\text{catalyst weight})^1(P_{\text{H}_2})^1$$

E. Hydrogenation of 1-Methylcyclopentene

The kinetic results for 1-methylcyclopentene hydrogenation are summarized in Table 6. The steric hindrance of 1-methylcyclopentene to the catalyst surface was immediately revealed by its much lower reaction rates compared to the hydrogenation rates of cyclopentene and 3-methylcyclopentene. The trend in specific reaction rates rise in going from catalyst II through catalyst V.

The plot of the rate versus amount of catalyst and the hydrogenation consumption versus reaction time both are linear throughout, which indicate that the reaction is first order in catalyst and zero order in 1-methylcyclopentene. Hussey and coworkers¹⁴ found the reaction exhibited a first-order dependence on hydrogen pressure, the rate equation for 1-methylcyclopentene hydrogenation is then:

$$\text{rate} = k(1\text{-methylcyclopentene})^0(\text{catalyst weight})^1(P_{\text{H}_2})^1$$

F. Hydrogenation of 1,2-Dimethylcyclopentene

The hydrogenation rates of 1,2-dimethylcyclopentene are given in Table 7. The extremely low reaction rates suggest that the methyl groups on 1,2-dimethylcyclopentene may have seriously hindered 1,2-dimethylcyclopentene from adsorbing on the catalyst surface or reacting with hydrogen or both. The specific hydrogenation rates remain the same for catalyst II and catalyst III, and show a marked rise in going to catalysts IV and V. The plot of the hydrogenation rate versus the catalyst weight is linear which reveals the reaction has a first-order dependence on catalyst concentration. The linear plot of hydrogen uptake versus reaction time shows the reaction is zero order in 1,2-dimethylcyclopentene. The effect of hydrogen pressure on this reaction is still undetermined. Due to the similarity of the reaction mechanism between the hydrogenation of 1,2-dimethylcyclopentene and the hydrogenation of 1-methylcyclopentene, we may assume the hydrogen dependence is also first-order for the hydrogenation of 1,2-dimethylcyclopentene. The overall rate scheme for 1,2-dimethylcyclopentene can then be summarized as:

$$\text{rate} = k(1,2\text{-Dimethylcyclopentene})^0(\text{catalyst weight})^1(P_{\text{H}_2})^1$$

For the convenience of comparing the catalytic performances of catalyst II-V, a specific hydrogenation

rate versus catalyst reducing temperature plot for the hydrogenation of cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and 1,2-dimethylcyclopentene is given in Figure 10. This plot clearly indicates that the catalyst reduction temperature affects the catalyst activity.

G. Activation Energy on the Hydrogenation of 1,2-Dimethylcyclopentene

1,2-Dimethylcyclopentene was hydrogenated at temperatures of 5°C, 25°C and 44°C using approximately 350 mg of catalyst II and catalyst V respectively. The kinetic results are presented in Table 8. The resultant specific hydrogenation rates have been corrected for the change in partial pressure of hydrogen as a result of the change in the vapor pressure of cyclohexane. They have also been corrected for the solubility of hydrogen in cyclohexane.¹⁸

Since the hydrogenation rate scheme for 1,2-dimethylcyclopentene has been shown to be:

$$\text{rate} = k(1,2\text{-Dimethylcyclopentene})^0(\text{catalyst weight})^1(P_{\text{H}_2})^1$$

the obtained specific hydrogenation rate can be expressed as:

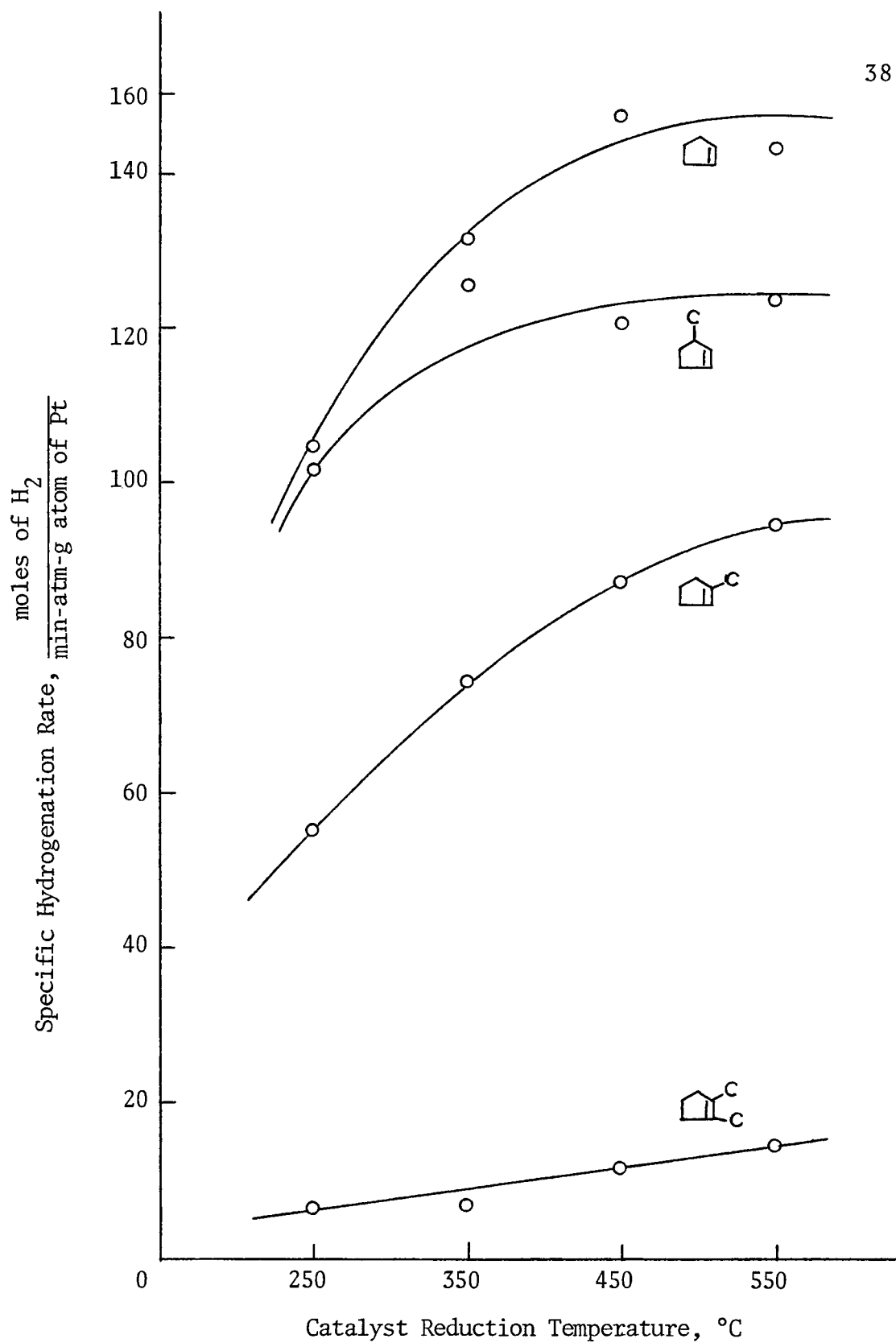


Figure 10: Specific Hydrogenation Rate of Cyclic Olefins versus Catalyst Reduction Temperature

$$\text{specific rate in } \frac{\text{moles of H}_2}{\text{min-atm-g atom of Pt}} = k(1,2\text{-Dimethylcyclopentene})^0$$

The activation energy can then be calculated from the Arrhenius equation⁵⁰:

$$k = Ae^{-E/RT} \text{ or } \ln k = \ln A - \frac{E}{RT}$$

where k = specific rate constant

A = frequency factor

E = activation energy, cal.

R = gas constant, $1.987 \frac{\text{cal}}{\text{mole} \cdot ^\circ\text{K}}$

T = temperature in Degree Kelvin

The Arrhenius type plots of $\ln$ (rate constant) versus $\frac{1}{T} \times 10^3$ for both of catalyst II and catalyst V are given in Figure 11. The activation energies for catalyst II and V calculated from the Arrhenius equation are 9.8 ± 0.3 Kcal/mole and 8.8 ± 0.3 Kcal/mole respectively. The calculated frequency factor for catalyst V is $3.8 \times 10^7 \pm 2.1 \times 10^7 \frac{\text{mole}}{\text{min-atm-g atom of Pt}}$ and that for catalyst II is $8.1 \times 10^7 \pm 4.4 \times 10^7 \frac{\text{mole}}{\text{min-atm-g atom of Pt}}$.

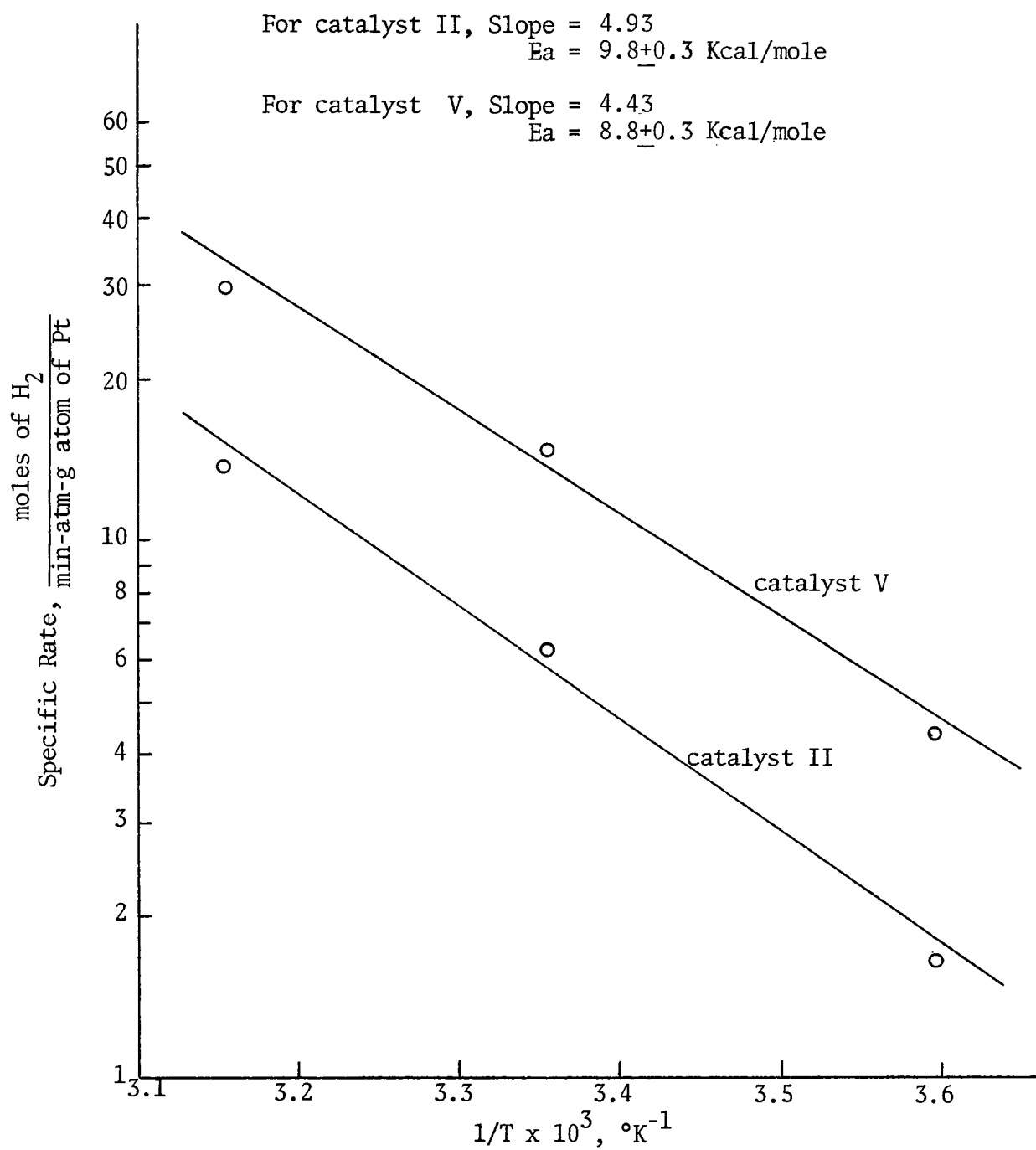


Figure 11: $\ln$ Specific Rate versus $1/T \times 10^3$ for
 1,2-Dimethylcyclopentene Hydrogenations

H. Competitive Hydrogenations

Competitive runs were conducted in pairs as cyclopentene+1-methylcyclopentene, cyclopentene+1,2-dimethylcyclopentene, and cyclopentene+3-methylcyclopentene on each of four catalysts. An unpoisoned competitive hydrogenation of cyclopentene and 1-methylcyclopentene and that of cyclopentene and 1,2-dimethylcyclopentene are illustrated in Figures 12 and 13. Samples were taken at intervals during the competitive hydrogenations and were analyzed by gas chromatography for their compositions. Samples on the pair of cyclopentene+1,2-dimethylcyclopentene could not be obtained because there was not enough product of the slow member to analyze.

In section IV-F, the expression for the competitive selectivity:

$$\frac{R_B}{R_A} = \frac{k_B K_B}{k_A K_A} = \log\left(\frac{C_{Bi}}{C_{Bi}-C_Q}\right) / \log\left(\frac{C_{Ai}}{C_{Ai}-C_P}\right) \quad (1)$$

will be derived for the hydrogenation of an A+B competitive pair, where R_A , R_B = reactivity for A, B

K_A , K_B = Adsorption coefficient for A, B

k_A = specific rate constant for hydrogenation of $A \longrightarrow P$

k_B = specific rate constant for hydrogenation of $B \longrightarrow Q$.

Reactants: 0.1 ml cyclopentene+0.1 ml 1-methylcyclopentene

Solvent : 2.0 ml cyclohexane

Catalyst : 61.4 mg of catalyst IV

Reaction Temperature: 25°C

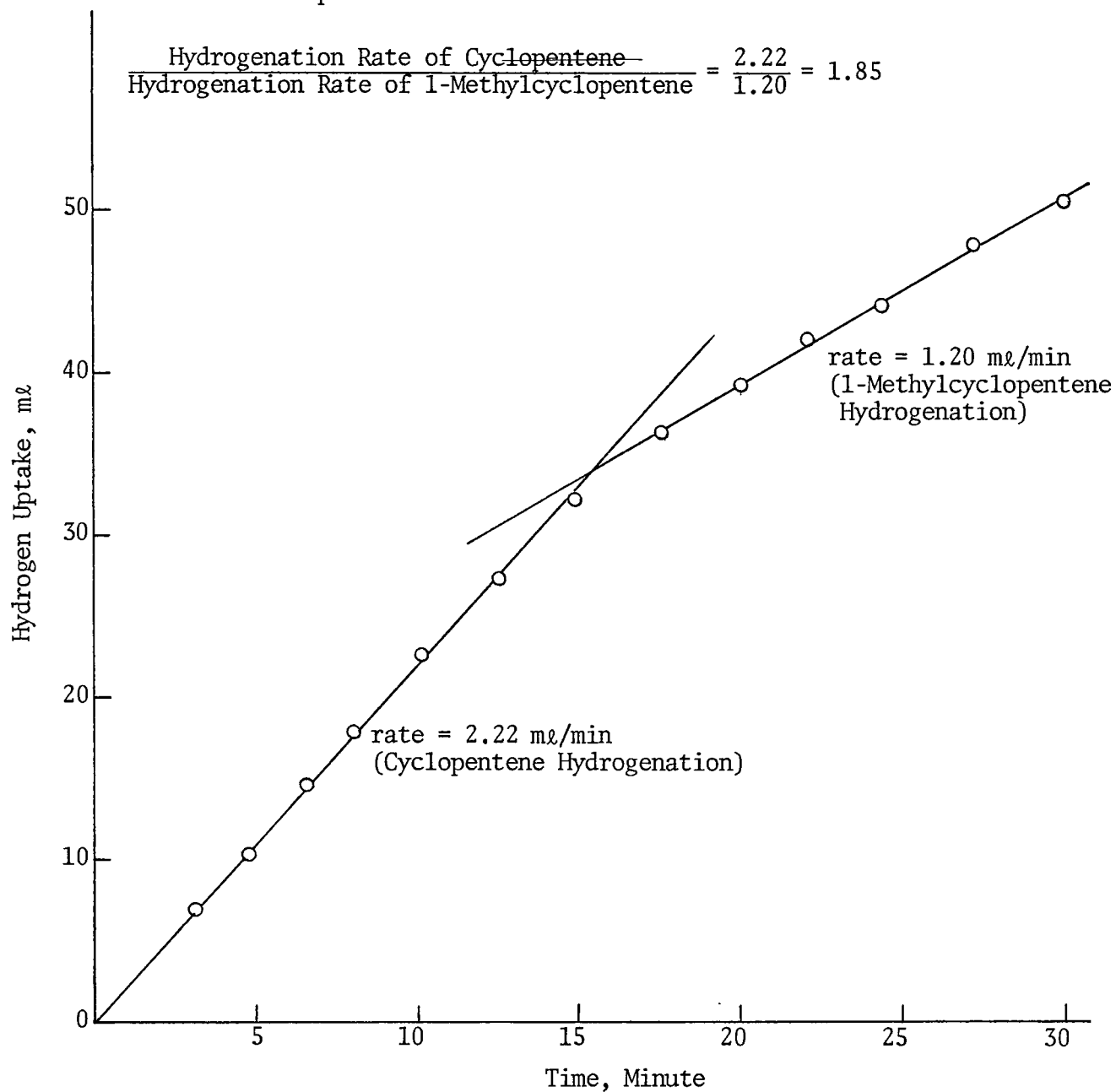


Figure 12: Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene on Catalyst IV

Reactants: 0.1 ml Cyclopentene+0.1 ml 1,2-Dimethylcyclopentene
 Solvent : 2.0 ml cyclohexane
 Catalyst : 58.3 mg of catalyst IV
 Reaction Temperature: 25°C

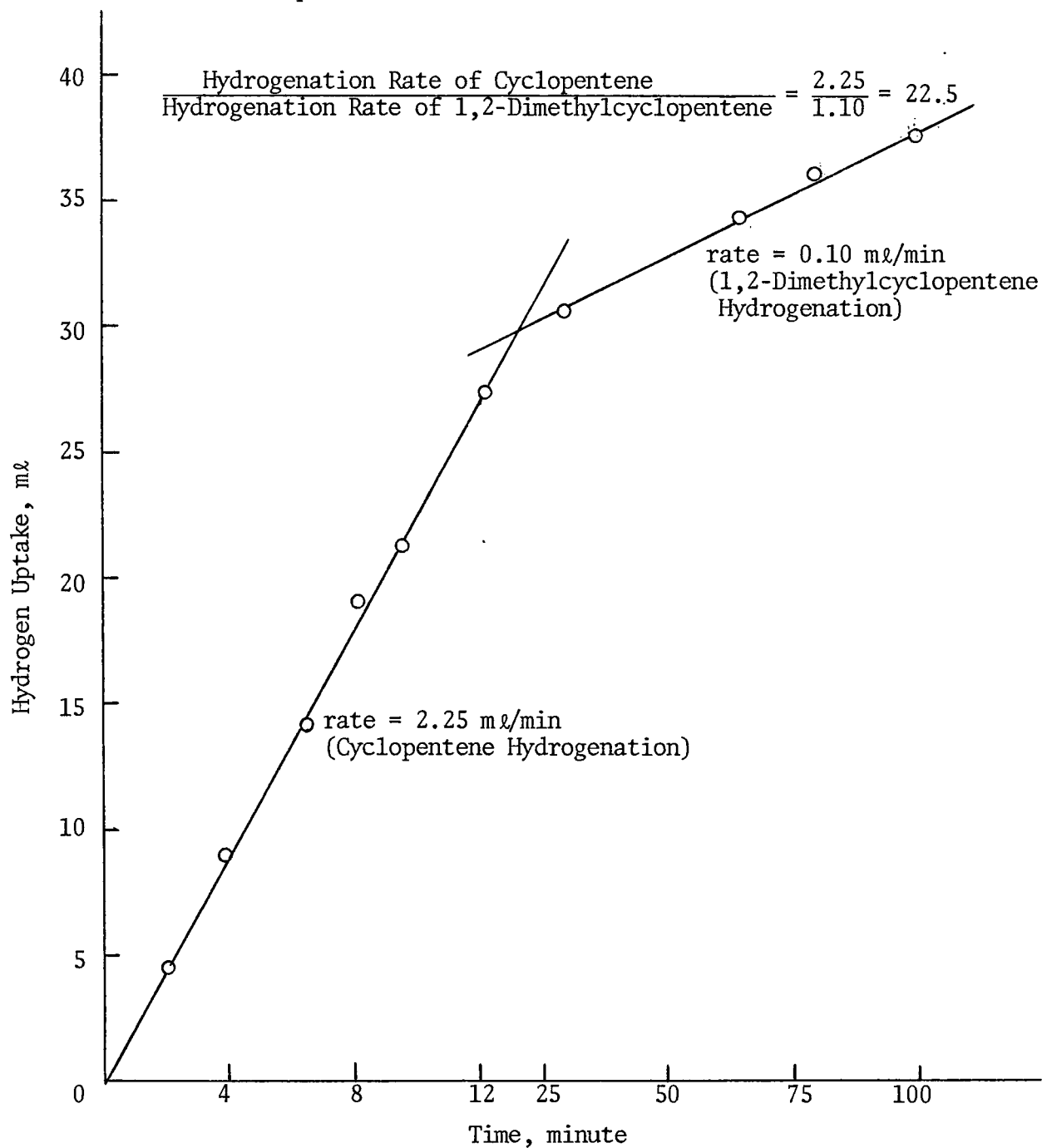


Figure 13: Competitive Hydrogenation of Cyclopentene and 1,2-Dimethylcyclopentene on Catalyst IV

P, Q = hydrogenated products of A, B

C = concentration

i = initial.

A sample plot of $\log\left(\frac{C_{Bi}}{C_{Bi}-C_Q}\right)$ versus $\log\left(\frac{C_{Ai}}{C_{Ai}-C_Q}\right)$ is given

in Figure 14. The results of competitive runs for the above mentioned reactions are summarized in Tables 9 and 10. The relative adsorption coefficients for the investigated compounds can then be calculated by using equation (1) and are shown in Tables 11 and 12. A small amount of 1-methylcyclopentene was found during the competitive hydrogenation of cyclopentene and 3-methylcyclopentene. The amount of 1-methylcyclopentene was gradually increased from 0.3% to 7% through the reaction period.

I. Product Distribution of 1,2-Dimethylcyclopentene Hydrogenation

1,2-Dimethylcyclopentene was hydrogenated at 25°C using each of our four catalysts. Both cis- and trans-1,2-dimethylcyclopentane were found as the only products. The major product was trans-1,2-dimethylcyclopentane. The $\frac{\text{cis}}{\text{trans}}$ product ratios at different stages during the hydrogenations are presented in Table 13. The $\frac{\text{cis}}{\text{trans}}$ product ratio stayed approximately the same for catalyst II and catalyst III and increased moderately from catalyst III to catalyst V. For all of the four catalysts, the

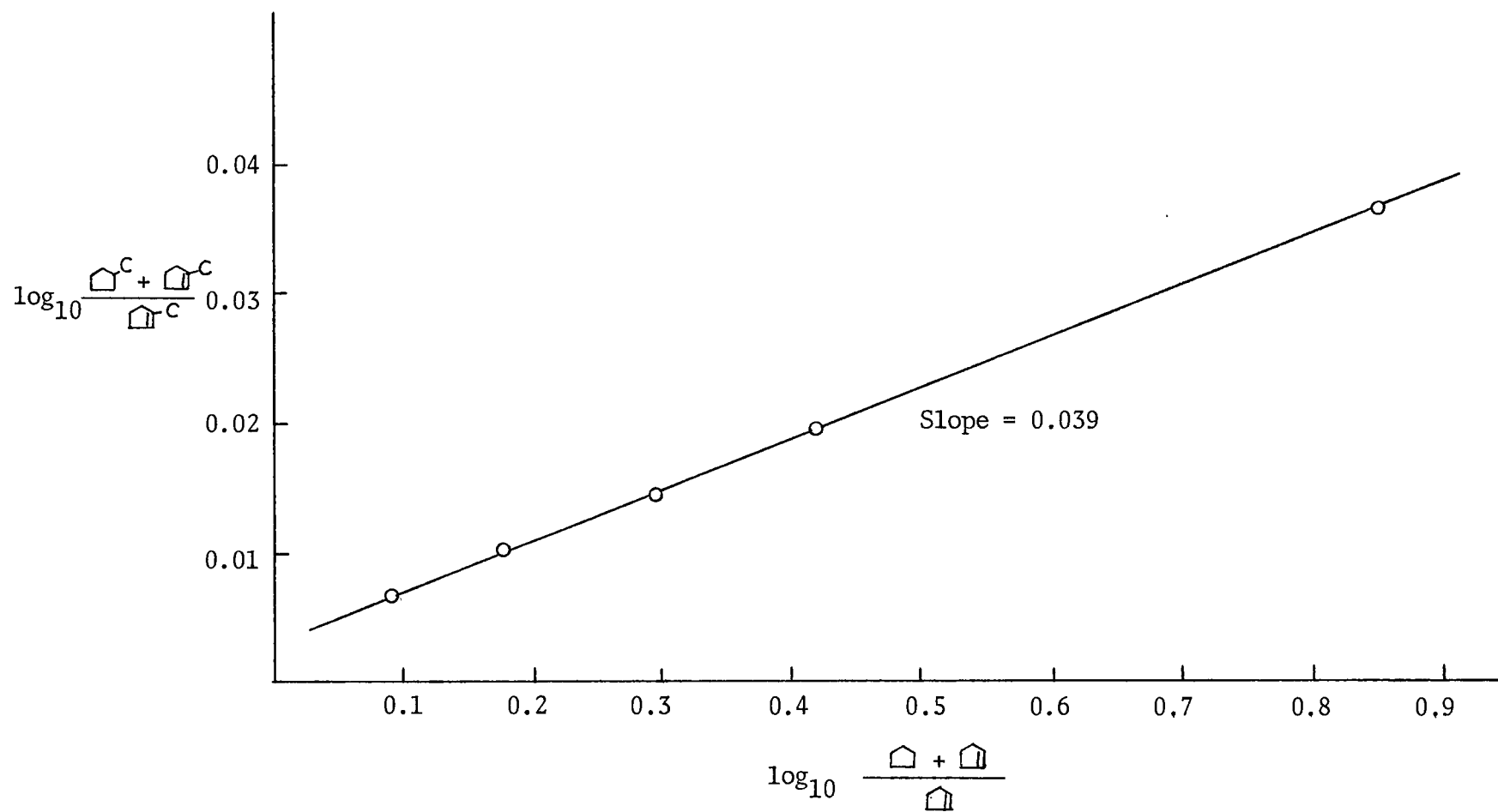


Figure 14: Logarithmic Plot of Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene

product distributions remained the same through the reaction periods. The results disclosed that the active sites for isomerization had been changed by the different heat treatments.

CHAPTER IV

DISCUSSION

A. Introduction

In heterogeneous catalysis, the reaction occurs on the catalyst's surface; the catalyst structure, therefore, plays a very important role. The catalyst surface structure may either be varied by the different constituents employed or by the different treatments received during the catalyst's preparation. The latter may cause catalysts to differ in activity, selectivity or stability. Extensive work has been done on the various modes of catalyst preparations but very little attention has been given to the effect of catalyst reduction temperature on selectivity, activity, etc. The two references that were found have been mentioned in Chapter I. The purpose of this dissertation is therefore to explore the effect of reduction temperature on the catalyst surface heterogeneity and its concomitant effect on catalyst activity.

The fact that there are active sites on the catalyst's surface and that the number of active sites determines the activity of a catalyst have been widely accepted. The concept of a surface active site was first mentioned

in Taylor's 1925 paper,¹⁹ where he wrote, "There will be all extremes between the case in which all the atoms in the surface are active and that in which relatively few are so active . . . the amount of surface which is catalytically active is determined by the reaction catalyzed." Boudart²⁰ later proposed the reaction with the Taylor ratio, i.e., the fraction of active sites, of unity to be called facile, and the others to be called demanding. The demanding reaction depends on the structure of the catalyst while the facile reaction ignores the details of surface structure. We therefore used a facile reaction as the reference to examine the active sites of the catalysts with different heat treatments.

In studying the kinetics of hydrogenation of cycloalkenes, Hussey¹⁴ found these reactions were first order in hydrogen pressure and in the amount of catalyst and zero order in cycloalkene. The platinum on alumina catalyst that he used was reduced at 350°C. We intended to investigate if the same kinetics would be obtained with catalysts reduced at different temperatures. Hydrogenation of a series of cyclo-olefins with an increasing degree of steric hindrance: cyclopentene, 3-methylcyclopentene, 1-methyl-cyclopentene and 1,2-dimethylcyclopentene were therefore carried out on Pt/Al₂O₃ catalysts reduced at 250°C, 350°C, 450°C and 550°C. Our study also aimed to verify the steric hindrance effect on the catalytic reactions.

A catalyst may increase the reaction rate by (1) lowering the activation energy of the transition state, or by (2) adsorbing the reactants in a proper position to increase the possibility for reaction to occur. We hydrogenated 1,2-dimethylcyclopentene over a Pt/Al₂O₃ catalyst reduced at 250°C and another identical catalyst reduced at 550°C. The activation energy of both hydrogenations were scrutinized to pinpoint the reason for the difference in reaction rates.

The method of competitive catalytic hydrogenation has frequently been used to compare the relative ease of adsorption of the hydrocarbons.²²⁻²⁵ Since the competitive hydrogenation is very sensitive to catalyst surface structure, it should be a powerful tool to detect the surface structure change of the catalysts caused by different heat treatments. Competitive hydrogenations on pairs of cyclopentene and 1-methylcyclopentene, and of cyclopentene and 3-methylcyclopentene were studied over our four catalysts. The relative adsorption coefficients of the studied compounds were calculated and the thermal effects on the catalyst surface structure were elucidated.

The product distribution is always helpful for understanding the reaction mechanisms and the catalysts' surface structures. We analyzed the products from the hydrogenation of 1,2-dimethylcyclopentene and correlated

the results with the heat treatments given the catalysts.

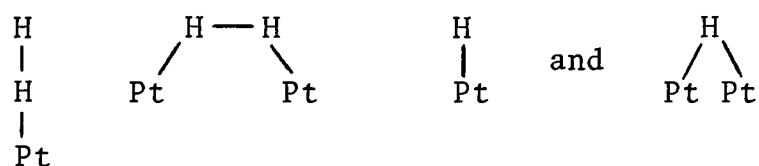
Gathering all of the above mentioned information, the effect of reduction temperature on an alumina supported platinum catalyst will be elucidated and the mechanistic model for the catalyst reducing process will be discussed in the last section of this chapter.

B. Catalyst Characterization

Atomic absorption measurements of our four catalysts indicated that the platinum content was the same for all the catalysts with 0.40 ± 0.05 percent platinum on alumina. Since the catalytic activities have to be compared on the same surface area basis, the relative surface areas for our catalysts were therefore determined by the hydrogen desorption method. The measurements showed that all four catalysts had approximately the same surface area for a specific type of active sites which desorbed hydrogen at 75-260°C, and the catalyst with the most extensive heat treatment at 550°C had an additional type of active sites which desorbed hydrogen at 295-365°C. The surface area of catalyst V was 30% higher than the other catalysts on the active sites that desorbed hydrogen at 75-260°C, which could be due to the experimental error since the surface area was derived by triangulation of the broad hydrogen desorption peaks. The kinetics also suggested that catalyst V had the same surface area as that of catalyst

IV for a specific type of active sites, since these two catalysts gave the same reaction rate for the facile hydrogenation reaction of cyclopentene. The additional hydrogen desorption peak appeared for catalyst V revealed that heat treatments on catalysts indeed generate surface heterogeneity, although the unique type of active sites possessed by catalyst V appeared not to influence the hydrogenation reaction.

Tsuchiya²⁶ investigated the chemisorption of hydrogen on a platinum black catalyst over a wide range of temperature (-196 to 400°C) by the temperature programmed desorption (TPD) technique. He found four different states of chemisorbed hydrogen on platinum indicated by the four TPD peaks, with peak maxima at about -100, -20, 90 and 300°C. He proposed four types of chemisorption of hydrogen, which were illustrated schematically as:



These peaks were referred as α , β , γ and δ respectively. Comparing our hydrogen chemisorption results with those obtained by Tsuchiya, all four of our catalysts showed a γ type adsorption, and catalyst V exhibited an additional δ type adsorption. Our kinetic results (refer to Figure 10) showed no change in the specific hydrogenation rate of

cyclopentene using catalyst IV or catalyst V. The specific hydrogenation rate of 3-methylcyclopentene also remained the same using these two catalysts. For the hydrogenation of 1-methylcyclopentene and that of 1,2-dimethylcyclopentene, the specific rate was gradually increased from catalyst II through catalyst V. If the δ type of active sites on catalyst V had participated in these hydrogenation reactions, the specific rates employing catalyst V would have been 30% higher than that using catalyst IV, and the increase in specific rates from catalyst II through catalyst V would not be evenly distributed. A sudden increase in specific rates from catalyst IV to catalyst V should have been noticed. Our kinetic results on cycloalkene hydrogenations therefore indicated that only the γ type adsorbed hydrogen participated in the hydrogenation reactions.

The different catalyst performances may be attributed to either the difference in the metal catalyst, catalyst support or both. The electron microscopic pictures of our four catalysts (Figures 6-8) indicated that there is no structural change of the alumina support upon different reduction temperatures. The differences in catalytic activities must be caused by the variations related to the metal catalysts. Since (1) from our atomic absorption spectroscopy study, all the catalysts were shown to contain 0.4 percent platinum, and (2) the relative surface area of the same type of active sites appeared to be

approximately the same for all the catalysts, any difference in hydrogenation rates must be due to the difference in the surface platinum structure.

The surface of a microcrystalline metal consists of many crystallographic planes, e.g., face (100), (110), (111), etc. Many authors have noticed that the different crystal faces have different chemical activities.^{47,48} Gwathmey and Cunningham⁴⁹ proposed that only certain faces might be stable on the surface of a working catalyst, and they were determined by the reacting species and the reaction conditions. During the reaction the surface would rearrange to expose these preferential faces. Gwathmey and Cunningham passed a mixture of 5% oxygen and 95% hydrogen over a copper single crystal at 400°C, the catalyst's surface was substantially rearranged. We reduced our catalysts at comparable temperatures except with no oxygen present. Since the metal-metal bond strength of copper is close to that of platinum, surface rearrangement during our catalyst reducing process is not impossible. As the reduction temperature increases, the surface rearranges to expose more facets that would give the hindered cycloalkenes a correct orientation. The hydrogenation of the hindered species is therefore accelerated.

C. Hydrogenation of Cyclopentene, 3-Methylcyclopentene,
1-Methylcyclopentene and 1,2-Dimethylcyclopentene

The specific hydrogenation rates for both cyclopentene and 3-methylcyclopentene were approximately the same using catalyst III, IV and V, but were much lower for catalyst II (Tables 4 and 5). This suggests that there is a minimum reduction temperature necessary to activate most of the active sites for cyclopentene and 3-methylcyclopentene hydrogenations. Although the relative surface area measured by the hydrogen desorption method indicated the same for all the catalysts, cyclopentene and 3-methylcyclopentene being a much larger molecule than hydrogen certainly require different sites on the catalyst for adsorption. A minimum temperature of 300°C seemed necessary to activate most of the active sites adequate for cyclopentene and 3-methylcyclopentene adsorption.

The specific rate for 1-methylcyclopentene hydrogenation showed a 27% increase in going from catalyst II through catalyst V, the increase was far beyond the utmost experimental error (10%). This is certainly a different rate pattern from that of cyclopentene and 3-methylcyclopentene hydrogenations. Since the only difference in 3-methylcyclopentene and 1-methylcyclopentene was the larger steric hindrance for the latter, the rate pattern of 1-methylcyclopentene hydrogenation was probably rendered different because the type of active sites in favor of the sterically hindered

reaction was gradually increased by a more extensive heat treatment. The active sites that favor a sterically hindered reaction may be the sites which can adsorb a more hindered cycloalkene, the sites which would give a higher reactivity of the adsorbed hindered species, or the sites which can better desorb the hindered product. The adsorption coefficients of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene on our four catalysts have been measured and will be discussed in Section F of this chapter.

The specific hydrogenation rate of 1,2-dimethylcyclopentene remained the same for catalyst II and III but increased sharply from catalyst III to catalyst IV, and rose slightly from catalyst IV to catalyst V. A 120% increase in the specific rate from catalyst III to catalyst V was definitely beyond the variation of experimental error. Comparing the specific hydrogenation rates of 1,2-dimethylcyclopentene with that of 1-methylcyclopentene, the active sites in favor of a more steric hindered reaction seem to emerge at a higher catalyst reduction temperature.

The hydrogenation of cyclopentene and 3-methylcyclopentene are considered to be facile reactions while the hydrogenation of 1-methylcyclopentene and 1,2-dimethylcyclopentene are categorized as demanding reactions. From the collected hydrogenation rates on our four catalysts, there is no doubt that the reduction temperature plays an important role on catalyst surface heterogeneity.

Using a 0.52% Pt/Al₂O₃ catalyst reduced at 350°C, Hussey¹⁴ determined the specific hydrogenation rate of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene to be 121, 153, and 85 moles/min/g-atom of Pt/atm respectively. He also found the specific hydrogenation rate of cyclohexene, 3-methylcyclohexene and 1-methylcyclohexene to be 113, 103 and 57 moles/min/g-atom of Pt/atm respectively. Barry¹⁷ obtained a specific rate of 131.5 moles/min/g-atom of Pt/atm for cyclopentene hydrogenation employing a 1.0% Pt/Al₂O₃ catalyst reduced at 350°C. Using a 0.40% Pt/Al₂O₃ catalyst reduced at 350°C, we found the specific hydrogenation rate of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene to be 131.2, 125.4 and 74.5 moles/min/g-atom of Pt/atm respectively. Our findings on cyclopentene and 1-methylcyclopentene hydrogenation were in good agreement with those obtained by the above mentioned authors. We experienced a relatively higher hydrogenation rate for cyclopentene and a lower hydrogenation rate for 3-methylcyclopentene. Our higher hydrogenation rate for cyclopentene is due to the lower platinum content of our catalyst. An increase in catalyst activity with decreasing platinum content has been observed before^{14,52,53} and is attributable to an increase in metal surface area per unit weight of catalyst. Since the studies that we made on the series of cyclopentenenes and that Hussey made on the series of cyclohexenes both indicated

the hydrogenation rate decreased with increased steric hindrance of the reactant, our result on 3-methylcyclopentene appeared to be more reliable than that obtained by Hussey. No reference was found for the specific hydrogenation rates of 1,2-dimethylcyclopentene, and a specific rate of 6.6 moles/min/g-atom of Pt/atm was determined using our 0.4% Pt/Al₂O₃ catalyst reduced at 350°C.

From the studies made on hydrogenation of cycloalkenes employing a platinum on alumina catalyst, Hussey¹⁴ proposed the overall kinetics for cycloalkene hydrogenations to be:

$$\text{rate} \propto [\text{P}_{\text{H}_2}]^1 [\text{catalyst}]^1 [\text{cycloalkene}]^0.$$

Barry¹⁷ found this rate equation valid on his cyclopentene hydrogenation study. We found this rate scheme held for all of our hydrogenation studies including the hydrogenation of cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and 1,2-dimethylcyclopentene (refer to Chapter III, Section C-F). The reaction rates were zero order in cycloalkenes and first order in hydrogen revealed that cycloalkenes were strongly adsorbed while hydrogen was not. Calculations of the rate of transfer of hydrogen using the established correlations revealed that the diffusion of hydrogen in the reaction solution could not be a controlling factor.

The data obtained clearly indicated that the hydrogenation rate of substituted cyclopentene decreases in the order

of its increased steric hindrance. The lower reaction rate of a more hindered reactant may be caused by (1) the catalyst surface being less densely populated by a more hindered species, (2) the repulsive interaction between the hindering methyl group and the catalyst during the adsorption, or by (3) the lower reactivity of the more hindered adsorbed species.

D. Reaction Rate of 1,2-Dimethylcyclopentene Hydrogenation

According to Arrhenius' equation, the difference in reaction rates can either be due to the different frequency factors or due to the different activation energies. The activation energy for 1,2-dimethylcyclopentene hydrogenation using catalyst II was found to be 9.8 ± 0.3 Kcal/mole, which was higher than that using catalyst V (8.8 ± 0.3 Kcal/mole). The frequency factor for catalyst II and V were $8.1 \times 10^7 \pm 4.4 \times 10^7 \frac{\text{mole}}{\text{min-atm-g atom of Pt}}$ and $3.8 \times 10^7 \pm 2.1 \times 10^7 \frac{\text{mole}}{\text{min-atm-g atom of Pt}}$ respectively.

There are two theories on reaction rates that have been developed; one is collision theory and the other is transition state theory. Collision theory assumes that the reaction occurs when the collision between reactant molecules involves a kinetic energy equal or exceeding

the activation energy. Transition state theory proposes that the reactants form an activated complex first, and then decomposes to the products. The rate constant derived from collision theory is: $k = PZe^{-E_a/RT}$ and that derived from transition state theory is:²⁷

$$k = \frac{\bar{k}T}{h} e^{\Delta S_0^*/R} \cdot e^2 \cdot e^{-E_a/RT}$$

where P = probability factor

Z = No. of collisions that occur between the reactant molecules which are at unit concentrations

E_a = activation energy

R = gas constant

T = absolute temperature

$\bar{k}$ = Boltzmann's constant

h = Plank's constant

ΔS_0^* = entropy of activation

Collision theory assumes that the reaction rate is controlled by the number of energetic collisions between reactants, while transition state theory suggests that rate is determined by the decomposition rate of the activated complex.²⁷ Comparing the rate constants derived from both theories with that derived from the Arrhenius equation, i.e, $k = Ae^{-E_a/RT}$, the A factor of the Arrhenius equation is equivalent to PZ of collision theory and is equivalent to $\frac{kT}{h} \cdot e^2 \cdot e^{\Delta S_0^*/R}$ of the transition state theory.

In view of the collision theory, the frequency factor of the Arrhenius equation is equivalent to the number of energetic collisions multiplied by a probability factor. This probability factor takes into account the lack or presence of the proper orientation of the reactant molecules. With respect to the transition state theory, the A factor of Arrhenius equation corresponds to $\frac{kT}{h} \cdot e^2 \cdot e^{\Delta S_0^*/R}$, which involves the entropy of activation. Bamford and Tipper²⁷ pointed out that the "steric" component of the probability factor in collision theory is equivalent to the operation of an entropy of activation in transition state theory. In any process involving specialized geometrical orientation for reaction, the formation of the activated complex will involve a decrease in entropy, and the term $e^{\Delta S_0^*/R}$ will become smaller than unity.

Reviewing the activation energies for 1,2-dimethylcyclopentene hydrogenations using catalyst II and catalyst V, we may conclude that the catalyst treated with the higher reduction temperature forms an activated complex which possesses a lower activation energy. Since the difference in frequency factors of these two catalysts can not be statistically estimated due to their large standard deviations, the difference in the numbers of active sites that give a proper orientation of the reactant molecules can not be determined.

E. Reaction Mechanism and Stereochemistry of Cycloalkene Hydrogenations

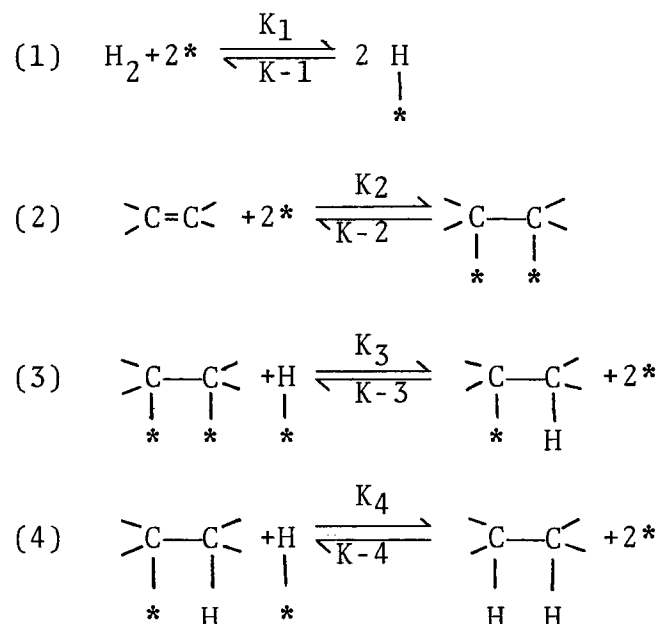
1. Mechanistic Studies on Olefin Hydrogenations

A substantial amount of work has been directed toward the mechanistic investigations of olefin hydrogenation. Through years of debate among catalytic researchers, agreement concerning reaction mechanisms has been limited to cases involving the simplest types of olefin hydrogenations.

In heterogeneous catalysis, the adsorption of reactants on the catalyst is one of the determining factors of the reaction rate and product selectivity. In the case of a bimolecular reaction, both the reactants may be adsorbed before reaction, the so-called Langmuir-Hinshelwood mechanism,²⁸ or only one reactant may be adsorbed, which is known as the Langmuir-Rideal mechanism.²⁹ The Langmuir-Hinshelwood mechanism has been overwhelmingly accepted because the majority of reactions were found to follow its predicted kinetics.^{30,31} To hydrogenate an olefin, hydrogen may be adsorbed as molecular hydrogen or as atomic hydrogen. Evidence on dissociative adsorption^{32,33} makes adsorbed atomic hydrogen much in favor. With dissociative adsorption, Farkas³⁴ proposed that both hydrogen atoms were simultaneously added to the olefins while Horiuti and Polanyi³⁵ suggested that there was a step-wise addition of hydrogen atoms. Farkas insisted that

the less stable "cis" isomer being the favored product necessarily implied the simultaneous addition of hydrogen atoms. Polanyi claimed that the step-wise addition of hydrogen atoms could also yield cis-products. The Horiuti and Polanyi mechanism has been more widely recognized because it was further supported by the facts that:

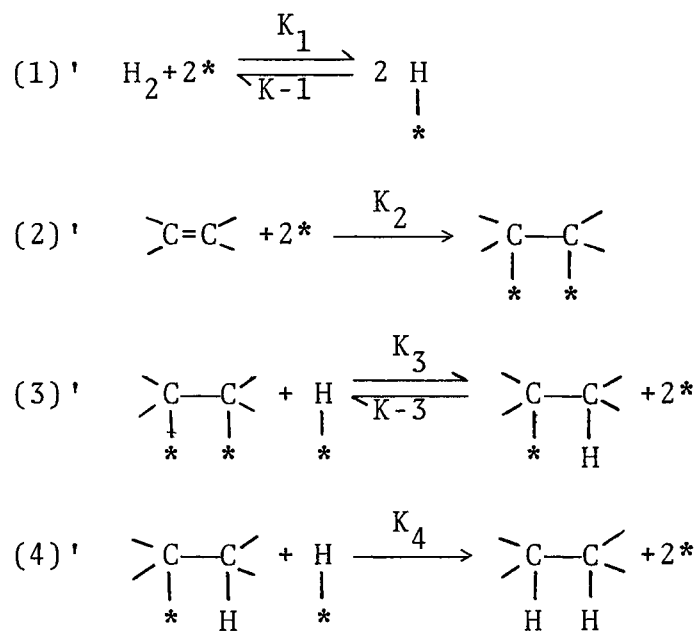
(a) intramolecular shifts of hydrogen atoms were found, (b) dideuterated products were not the only products in the deuteration of unsaturated compounds, (c) double bond migrations were found and (d) the intermediate species was identified by the infrared spectral studies of Eishens and Plisken.³⁶ The mechanism suggested by Horiuti and Polanyi, which is a specific application of the Langmuir-Hinshelwood mechanism, is represented as follows:



where * is the unoccupied site.

2. Modified Horiuti-Polanyi Mechanism

Hussey and coworkers¹⁴ studied the rates of hydrogenation of eighteen cycloalkenes from cyclohexane solution on alumina-supported platinum catalysts. To interpret their kinetic results, they proposed that platinum surfaces presented two types of catalytic sites. One of these type was for hydrogenation and the other type was for olefin exchange. They also found chemisorption of cycloalkenes on hydrogenation sites was irreversible. Germain³⁷ maintained that the readsorption of product alkane was negligible under a hydrogen atmosphere. The Horiuti-Polanyi mechanism applied to cycloalkene hydrogenations can therefore be summarized in what follows, as suggested by Barry:¹⁷



A rate scheme derived by Barry¹⁷ using this modified

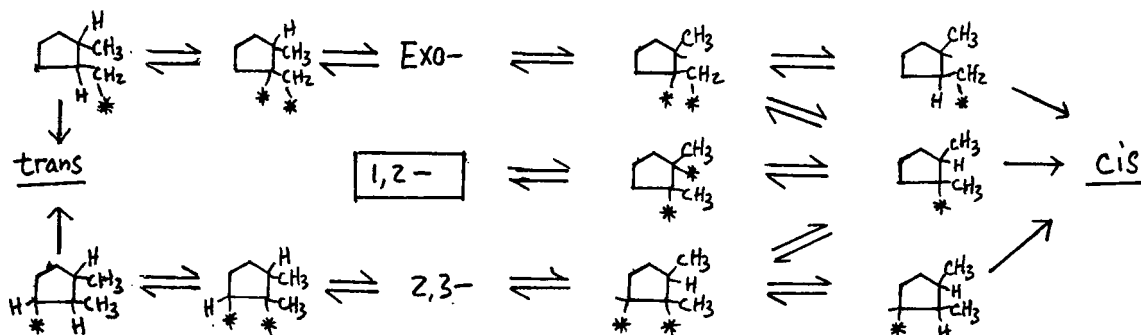
Horiuti-Polanyi mechanism gave a zero order dependence on cycloalkene and a first order dependence on hydrogen pressure. Our kinetic results on hydrogenations of cyclopentene, 3-methylcyclopentene, 1-methylcyclopentene and 1,2-dimethylcyclopentene agreed with the above mentioned mechanism.

3. Hydrogenation of 1,2-Dimethylcyclopentene

Hydrogenation of 1,2-dimethylcyclopentene is particularly interesting among the hydrogenations we studied because it forms isomeric products: cis- and trans-1,2-dimethylcyclopentane. Thus, by studying its product distribution, more details of the reaction mechanism may be described.

Many studies can be found on the stereochemistry of hydrogenation of cycloolefins.³⁸⁻⁴¹ Mitsui⁴⁰ and coworkers have studied the hydrogenation of 1,2-dimethylcyclopentene at room temperature and ordinary pressure using a PtO_2 catalyst. From a detailed product analysis, they found that the double bond migration occurred and 2,3-dimethylcyclopentene formed in advance of the hydrogenation. Siegel and coworkers^{38,42} investigated the hydrogenation of an equal molar mixture of 2,3-dimethylcyclopentene and 1,2-dimethylcyclopentene under the same conditions, the results showed the rates of the former was much greater than that of the latter. The mechanism for the reduction of 1,2-dimethylcyclopentene according to the Horiuti-Polanyi

mechanism is therefore believed to be:⁴³



After analyzing the products obtained from 1,2-dimethylcyclopentene hydrogenation using our four catalysts, we found some interesting results (refer to Table 13):

(a) For all of the four catalysts, the product distributions remained the same throughout the reaction period (excluding the initial product distributions, data on which was not available). No intermediate 2,3-dimethylcyclopentene was found.

(b) The $\frac{\text{cis}}{\text{trans}}$ product ratio stayed approximately the same for catalyst II and III, and increased moderately from catalyst III to IV and from catalyst IV to V.

Result (a) implied that the cis- and trans- products were either directly or indirectly in equilibrium throughout the reaction. According to the mentioned mechanism, all of the intermediate steps were reversible which would give equilibrium distributions. Our kinetic data therefore agreed with that mechanism in this aspect. We did not find any intermediate product of 2,3-dimethylcyclopentene because

the 2,3-isomer was selectively reduced.

Result (b) clearly indicates that the number of catalyst active sites for isomerization had been changed by the different catalyst reduction temperatures. More isomerization sites were generated by a more extensive heat treatment. The so-called isomerization site may simply be considered as an active site which is large enough and geometrically oriented to accomodate the double bond migration. The mechanistic models for the reducing of supported metal catalyst will be discussed in detail in Section G of this chapter.

F. Competitive Hydrogenations

When a mixture of two unsaturated compounds is hydrogenated, the initial and the final rate can be attributed to the rate of hydrogenation of the faster and slower component respectively. Hydrogenations of cycloalkene mixtures showing two kinetic regions are good examples (Figures 12 and 13). Hydrogenation of a mixture of cycloalkenes can therefore be considered as a competitive reaction because the reaction of one member does not interfere with the reaction of the others.

In competitive hydrogenations, the stronger the olefin adsorbs, the more competitive is its reaction rate. It was found that a compound with a higher degree

of unsaturation is more favorably adsorbed.^{37,44} Our experimental results showed that when a mixture of two cycloalkenes was hydrogenated, the initial rate was associated with the rate of hydrogenation of the less hindered member and the final rate was related to the rate of hydrogenation of the more hindered one (Figures 12 and 13). The specific rate ratio for individual hydrogenations of cyclopentene and 1-methylcyclopentene on catalyst IV was 1.69 ($= \frac{147.5}{87.3}$), (Table 4 and 6) and the specific rate ratio from competitive hydrogenation was 1.85 (Figure 12). The specific rate ratio for individual hydrogenations of cyclopentene and 1,2-dimethylcyclopentene on catalyst IV was 12.8 ($= \frac{147.5}{11.57}$), (Table 4 and 7) and the specific rate ratio of which, from competitive hydrogenation, was 22.5 (Figure 13). It is therefore clear that a more hindered cycloalkene is less competitive during a competitive reaction. Hussey and coworkers²⁴ studied competitive hydrogenations of cycloalkenes on alumina-supported platinum catalysts. They maintained that three main factors influence the chemisorption of cycloalkenes on platinum surfaces:

- (a) the degree of substitution at the double bond
- (b) internal strain, and (c) substituents at a distance from the double bond.

Jungers and Wauquier⁴⁵ investigated the hydrogenation of binary mixtures of benzene, toluene and the polymethylbenzenes on a Raney nickel catalyst from which they derived

equations for calculating the relative adsorption coefficients. Rader and Smith⁴⁶ and Hussey and coworkers²⁴ have applied this method to other competitive hydrogenations. The calculations can be described below:²³

For a mixture of A and B, assume that the chemisorption of olefins A and B obeys the Langmuir adsorption isotherm and the amount of the products adsorbed is negligible, the hydrogenation rates for A and B are:

$$\frac{dP}{dt} = \frac{k_A K_A C_A}{1 + K_A C_A + K_B C_B} \quad (1)$$

$$\frac{dQ}{dt} = \frac{k_B K_B C_B}{1 + K_A C_A + K_B C_B} \quad (2)$$

where P, Q = hydrogenated products of A, B

K_A, K_B = adsorption coefficients for A, B

k_A, k_B = specific rate constant for hydrogenation of A, B

C = concentration.

Dividing equation (2) by equation (1) gives:

$$\frac{dC_Q}{C_B} = \frac{k_B K_B}{k_A K_A} \frac{dC_P}{C_A} \quad (3)$$

let C_{Ai}, C_{Bi} = initial concentration of A, B;

$$\text{then } C_A = C_{Ai} - C_P \quad (4)$$

$$C_B = C_{Bi} - C_Q \quad (5)$$

Substituting equation (4), (5) into equation (3) and integrating dC_P from zero to C_P and dC_Q from zero to C_Q gives:

$$\frac{R_B}{R_A} = \frac{k_B K_B}{k_A K_A} = \log\left(\frac{C_{Bi}}{C_{Bi}-C_Q}\right) / \log\left(\frac{C_{Ai}}{C_{Ai}-C_P}\right) \quad (6)$$

R_B/R_A is the ratio of the reactivity of B to the reactivity of A which can be obtained from the slope of the plot of $\log\left(\frac{C_{Bi}}{C_{Bi}-C_Q}\right)$ versus $\log\left(\frac{C_{Ai}}{C_{Ai}-C_P}\right)$. If we assume that the specific rate constants, k_A and k_B , obtained from individual hydrogenation rate studies are the same as those in the competitive hydrogenations, then the adsorption coefficients K_A and K_B can then be calculated from equation (6).

Our competitive hydrogenation studies of cyclopentene+3-methylcyclopentene and cyclopentene+1-methylcyclopentene pairs on each of four catalysts (Tables 9-12) revealed the ratio for adsorption coefficients of cyclopentene : 3-methylcyclopentene : 1-methylcyclopentene was 1 : 0.794 : 0.067. This ratio is indicative of the steric hindrance effect caused by the methyl substituents. Thus, the fact that the adsorption coefficients decrease in the same decreasing order of the hydrogenation rates implies that the strength of the cycloalkene adsorption bond plays an important role in determining the cycloalkene hydrogenation rates. The relative adsorption coefficient obtained

for 1-methylcyclopentene (relative to that of cyclopentene) remained approximately the same for catalysts II, III and IV, and decreased slightly from catalyst IV to V. The relative adsorption coefficient of 3-methylcyclopentene (relative to that of cyclopentene) showed an opposite trend, moderately increasing from catalyst II to V. Since the data points of each set were within 18% of variance, and the calculations of relative adsorption coefficients involved the slopes of log-log plots as well as the values of specific rate constants which already contained some experimental errors, it is reasonable to consider that the 18% variance in the obtained relative adsorption coefficients was due to the experimental errors. The relative adsorption coefficients for both 3-methylcyclopentene and 1-methylcyclopentene probably were constant for all of the four catalysts.

The rate of a heterogeneous reaction is determined by (a) adsorption, (b) surface reaction and (c) desorption processes. Since 3-methylcyclopentene and 1-methylcyclopentene have the same adsorption coefficients for all of the four catalysts, the adsorption rate for either compound on different catalysts should be comparable. The rate difference in 1-methylcyclopentene hydrogenation using various catalysts was therefore due to the rate difference in either the reaction step or the product desorption step, i.e., the hydrogenation rate was controlled by

step (3)' and (4)' of the modified Horiuti-Polanyi mechanism (refer to Section E of Chapter IV). More active sites that could promote the rates of the hydrogen transfer step or the product desorption step during the 1-methylcyclopentene hydrogenation must have been generated with a more extensive thermal treatment. For the facile 3-methylcyclopentene hydrogenation, the surface reaction and the product desorption processes were not very sensitive to different catalyst surface structures, the hydrogenation rate was hence unchanged for catalyst III, IV and V.

A small amount of 1-methylcyclopentene was found during the competitive hydrogenation of cyclopentene and 3-methylcyclopentene. This evidence reinforces the idea that reaction (3) of Horiuti-Polanyi mechanism is reversible (refer to Section E of Chapter IV). During the competitive hydrogenation period, the amount of 1-methylcyclopentene was found to gradually increase from 0.3% to 7%. We propose that 3-methylcyclopentene was partially converted to 1-methylcyclopentene and was then converted to methylcyclopentane. The reaction rate for converting 3-methylcyclopentene to 1-methylcyclopentene should be slightly higher than the rate of hydrogenation of 1-methylcyclopentene, and the amount of unreacted 1-methylcyclopentene was therefore accumulated throughout the hydrogenation.

G. Mechanistic Models of the Catalyst Reducing Process

After reviewing the results of the studies we made on the effect of the reduction temperature on an alumina-supported catalyst, we believe that with reaction temperatures in the range of 350°C-550°C, a more extensive heat treatment generates more sites that either give the adsorbed hindered cycloalkene a higher reactivity or promote the desorption of the hindered product. Although the specific geometry of the active sites that would promote the hydrogenation of a more hindered species cannot be discerned until additional studies are carried out, it is clear that the catalyst's surface structure changes with reduction temperature and that the mobility of the catalyst surface during the heat treatment determines the degree of surface rearrangement. There are two possible mechanistic models of the catalyst reducing process that could cause such changes in the catalyst surface structure. They are as follows:

1. Atomic Migration Model

Flynn and Wanke^{54,55} developed a model to explain the sintering of supported metal catalysts. The model they proposed involves three steps: (1) individual metal atoms move from metal crystallite to the surface of the support, (2) the metal atoms migrate over the support surface and (3) the migrating atoms are either captured by collision

with a metal crystallite or are immobilized by a drop in temperature or by encountering an energy well on the support surface. Large metal-support interactions are essential for platinum atoms to escape from the crystallite to the support. Geus⁵⁰ pointed out that the presence of defects in the support structure, the impurities on the support surface, as well as the presence of oxygen would increase the interaction between the metal and support. We can also explain the catalyst reducing process by the above mentioned model. Because (1) the reducing process is carried out in a hydrogen atmosphere, the interaction of metal and support is much weaker than that in an oxygen atmosphere and (2) under the catalyst reduction temperatures (250°C-550°C) which are normally lower than catalyst sintering temperatures (greater than 550°C), metal atom migration over the support surface is much slower, and therefore the reducing process is probably terminated before the migrating atoms are recaptured by the crystallite upon collision. After this atomic migration process, the faces exposed on the catalyst surface are different from those of the original catalyst surface. The higher the reduction temperature is, the more faces which favor hydrogenation of the hindered cycloalkenes are exposed and the higher the reaction rate obtained.

2. Crystal Migration Model

The model proposed by Ruckenstein and Pulvermacher⁵⁶ to describe the sintering process suggested a migration of metal particles over the support surface, followed by the fusion of metal crystallite upon collision. Some crystallite rotation has been observed in the temperature range of 227°C-427°C^{57,58,59} which supports the postulate that the crystallites migrate on the support surface. However, crystallite migration occurs only when the metal crystallites are smaller than 5nm in diameter.⁶⁰ This model can also be applied to the catalyst reducing process. With reduction temperatures in the range of 350°C-550°C and in a hydrogen atmosphere, the mobility of metal particles is very small. During the catalyst reduction period, collisions between the metal crystallite may never occur, but the catalysts are likely to expose different metal faces before and after the crystallite migration.

Which of the above mentioned models actually participates in the catalyst reducing process can not be definitely pinpointed. Since the catalysts were reduced at low temperatures (250°C-550°C) and in a hydrogen atmosphere, the driving force to mobilize a catalyst surface was at a minimum. The atomic migration mechanism requires a lower mobility driving force and, therefore, better explains the surface rearrangement during the catalyst reducing process. If atomic migration indeed occurred during the

catalyst reduction, the migration of the atoms must have been very limited. Otherwise, we would have observed a higher surface dispersion, i.e., a higher metal surface area for the catalyst treated at a higher temperature.

CHAPTER V

CONCLUSION

This study was designed to make a systematic investigation on the effect of reduction temperature on four alumina-supported platinum catalysts reduced at different temperatures used in the hydrogenation of a series of cycloalkenes characterized by increasing steric hindrance. During our study, catalyst poisoning was found to be a tremendous barrier. Some specific techniques for purifying the reactants and catalysts were therefore developed to overcome this problem. Kinetic data on the hydrogenations of a series of cycloalkenes were obtained and the reaction mechanisms were scrutinized. The kinetic results for each catalyst were compared and were analyzed based on the information obtained from the catalyst characterizations. The reduction temperature was found to affect catalyst activity and hydrogenation rates were definitely retarded by steric hindrance.

All four of our catalysts indicated a γ type hydrogen adsorption, and catalyst V showed an additional δ type adsorption. The kinetic results revealed that only the

γ type adsorbed hydrogen participated in the hydrogenation reactions. No structural change of the alumina support was found upon reduction at different temperatures. The differences in hydrogenation rates were believed due to the differences in the structure of the surface platinum on the catalyst. The activation energies for 1,2-dimethylcyclopentene hydrogenation using different catalysts revealed that the rate differences were affected by the variations of activation energies.

Competitive hydrogenations gave relative adsorption coefficients for 1-methylcyclopentene and 3-methylcyclopentene which did not differ much over the series of the four catalysts. The hydrogenation rates were therefore believed not to be controlled by adsorption. It is proposed that as the reduction temperature increases, the surface rearranges to expose more active sites that either give the adsorbed hindered cycloalkenes a correct orientation to react with hydrogen atoms or promote the desorption of the hindered cycloalkane products. The relative adsorption coefficient decreased in the order of cyclopentene, 3-methylcyclopentene and 1-methylcyclopentene, which was the same decreasing order as in the hydrogenation rates.

The product analysis for 1,2-dimethylcyclopentene hydrogenation further confirmed the effect of the catalyst

reduction temperature because changes in the product distributions were found using different catalysts. The results were also helpful in analyzing the proposed Horiuti-Polanyi reaction mechanism. Finally, the atomic migration model was suggested as causing the surface rearrangement during the catalyst reducing process.

Our study has only partially elucidated the effects of catalyst reduction temperature. Further investigations are needed to understand this important effect. For this specific subject, the ideal case would be to directly observe the metal surface structure while the catalyst is being reduced. A technique to accomplish this is not presently available and presents a major technical challenge. The indirect methods for analyzing the thermal effect, e.g., kinetic studies, catalyst surface area measurements are very useful, but in order to pinpoint the mechanism of the reducing process, direct methods for examining the crystal structure, e.g., small-angle x-ray scattering (SAXS) and electron microscopy are necessary. Some specific techniques still need to be developed before these powerful tools can be applied to supported catalysts. Our hydrogen desorption study disclosed that the catalyst with the most extensive heat treatment had an additional type of active sites. The nature of the additional type of active sites may be a worthwhile subject of study. Although reaction mechanisms of cycloalkene hydrogenation were

given and had been accepted by the majority of catalytic researchers, the confirmation of the proposed mechanism is still needed since some alternative mechanisms⁴⁰ have been suggested but no evidence has been presented to document these mechanisms. Deuterium exchange of all the reactants over the series of catalysts is a very powerful tool to elucidate the reaction mechanism and it is also an important method to uncover the mechanism of the catalyst reducing process. The effect of reduction temperature on the catalyst may be different for the hydrogenation of cycloalkenes and for that of alkynes. It would be appropriate to make an identical study on the hydrogenation of a series of alkynes with increasing steric hindrance. Finally, the same investigations applied to other group VIII B metal catalysts would be very beneficial for understanding the effect of reduction temperature on catalyst activity as well as the elucidation of the overall picture of heterogeneous catalysis.

Table 1
Calculated Vapor Pressures at Different Temperatures

Component	$\frac{dT^a}{dP}$ ($\frac{^{\circ}C}{mm\ Hg}$)	V.P. at 5°C (mm Hg)	V.P. at 25°C (mm Hg)	V.P. at 44°C (mm Hg)
Cyclohexane	0.0437	41.9	103.9	221.5
Cyclopentene	0.0393		382.7	
1-Methylcyclopentene	0.0431		125.3	
3-Methylcyclopentene	0.0418		182.9	
1,2-Dimethylcyclopentene	0.0467	15.9	42.1	94.9

^a $\frac{dT}{dP}$ values were obtained from reference #15.

Table 2
Chromatographic Calibration Constants

Component	Factor x 10 ⁴ (Millimoles/Peak Area)
Cyclopentane	4.75
Cyclopentene	4.98
Methylcyclopentane	3.60
3-Methylcyclopentene	3.61
1-Methylcyclopentene	3.52
Cis-1,2-Dimethylcyclopentane	2.65
1,2-Dimethylcyclopentene	2.87
trans-1,2-Dimethylcyclopentane	2.60

Table 3
Relative Surface Area Measurements of the
Pt/Al₂O₃ Catalysts

Catalyst Sample	Relative Surface Area ^a	H ₂ Desorption Temperature, °C
Catalyst II	1.0	100-175
Catalyst III	1.0	75-260
Catalyst IV	1.0	140-210
Catalyst V	{ 1.3 0.3	{ 85-185 295-365

^aThe relative surface area based on Catalyst II sample.

Table 4

Cyclopentene Hydrogenation

Catalyst	P Total (mm Hg)	P _{H₂} (mm Hg)	Catalyst Weight (mg)	Corrected Catalyst Weight ^a (mg)	Reaction Rate ml of H ₂ ($\frac{\text{min-atm}}{\text{min-atm}}$)	Specific Rate moles of H ₂ ($\frac{\text{min-atm-g atom o}}{\text{min-atm-g atom o}}$)
II	788.1	658.5	31.5	23.5	1.15	101.6
II	772.4	642.8	45.4	37.4	1.70	92.3
II	786.7	657.1	62.7	54.7	2.95	111.3
II	788.8	659.2	75.1	67.1	3.57	110.3
II	785.7	656.1	90.7	82.7	4.38	109.2
II						
III	790.0	660.4	28.5	20.5	1.31	132.7
III	798.1	668.5	44.8	36.8	2.27	129.5
III	793.8	664.2	60.8	52.8	3.23	127.4
III	799.0	669.4	77.9	69.9	4.54	136.3
III	790.6	661.0	91.3	83.3	5.22	130.1
III						
IV	803.0	673.4	28.5	20.5	1.50	154.3
IV	788.5	658.9	44.9	36.9	2.71	152.1
IV	780.3	650.7	60.7	52.7	3.74	145.3
IV	781.3	651.7	78.0	70.0	4.96	145.2
IV	777.6	648.0	89.6	81.6	5.63	140.8
IV						
V	783.7	654.1	32.7	24.7	1.63	135.5
V	788.9	659.3	45.0	37.0	2.55	142.6
V	787.0	657.4	62.1	54.1	3.86	147.4
V	778.8	649.2	75.1	67.1	4.68	142.7
V	787.1	657.5	89.4	81.4	5.78	146.7
V						

^aRefer to Section A of Chapter II for calculations.

^bStandard deviation.

Table 5

3-Methylcyclopentene Hydrogena

Catalyst	P Total (mm Hg)	P _{H₂} (mm Hg)	Catalyst Weight (mg)	Corrected Catalyst Weight ^a (mg)	Reaction Rate ml of H ₂ ($\frac{\text{min-atm}}{\text{min-atm}}$)	Specific Rate ⁱ moles of H ₂ ($\frac{\text{min-atm-g atom o}}{\text{min-atm-g atom o}}$)
II	781.2	671.2	36.2	28.2	1.38	100.4
II	784.5	674.5	53.8	45.8	2.24	100.8
II	789.5	679.5	73.4	65.4	3.24	102.8
II	782.9	672.9	87.5	79.5	4.29	111.0
II	782.2	672.2	91.8	83.8	3.84	94.2
II						
III	790.8	680.8	34.5	26.5	1.43	111.9
III	789.3	688.3	48.8	40.8	2.51	128.7
III	803.2	693.2	70.0	62.0	3.73	126.8
III	802.3	692.3	89.3	81.3	5.17	134.0
III						
IV	789.7	679.7	31.2	23.2	1.31	116.9
IV	791.7	681.7	50.7	42.7	2.48	120.5
IV	799.3	689.3	73.0	65.0	3.82	123.1
IV	800.6	690.6	90.3	82.3	4.72	120.6
IV						
V	794.7	684.7	30.5	22.5	1.11	102.9
V	790.1	680.1	45.0	37.0	2.24	125.3
V	788.2	678.2	61.5	53.5	3.50	135.2
V	787.2	677.2	74.5	66.5	4.04	125.5
V	802.2	692.2	90.2	82.2	4.99	127.7
V						

^aRefer to Section A of Chapter II for calculations.

^bStandard deviation.

Table 6

1-Methylcyclopentene Hydrogena

Catalyst	P Total (mm Hg)	P _{H₂} (mm Hg)	Catalyst Weight (mg)	Corrected Catalyst Weight ^a (mg)	Reaction Rate ml of H ₂ ($\frac{\text{min-atm}}{\text{min-atm}}$)	Specific Rate ^b moles of H ₂ ($\frac{\text{min-atm-g atom o}}{\text{min-atm-g atom o}}$)
II	762.4	656.8	31.7	23.7	0.59	49.8
II	795.5	689.9	47.4	39.4	1.00	53.1
II	784.6	679.0	60.4	52.4	1.38	54.1
II	790.3	684.7	74.4	66.4	1.90	59.3
II	779.5	673.9	91.8	83.8	2.43	59.2
II						
III	791.5	685.9	32.0	24.0	0.82	71.0
III	770.0	664.4	50.2	42.2	1.59	76.2
III	770.0	664.4	57.0	49.0	1.87	76.9
III	775.6	670.0	74.7	66.7	2.43	74.1
III	774.0	668.4	91.9	83.9	3.07	74.3
III						
IV	795.7	690.1	31.2	23.2	0.93	83.3
IV	780.2	674.6	46.7	38.7	1.75	92.4
IV	776.4	670.8	59.7	51.7	2.27	89.3
IV	785.5	679.9	77.0	69.0	2.75	82.2
IV	796.6	691.0	90.2	82.2	3.52	89.5
IV						
V	799.5	693.9	31.7	23.7	1.01	89.3
V	794.9	689.3	45.1	37.1	1.76	99.2
V	791.7	686.1	63.0	55.0	2.55	96.3
V	774.3	668.7	75.6	67.6	3.04	91.3
V	780.6	675.0	88.7	80.7	3.86	98.1
V						

^aRefer to Section A of Chapter II for calculations.

^bStandard deviation.

Table 7

1,2-Dimethylcyclopentene Hydrogenation

Catalyst	P Total (mm Hg)	P _{H₂} (mm Hg)	Catalyst Weight (mg)	Corrected Catalyst Weight ^a (mg)	Reaction Rate ml of H ₂ ($\frac{\text{min-atm}}{\text{min-atm}}$)	Specific Rate ^b moles of H ₂ ($\frac{\text{min-atm-g atom o}}{\text{min-atm-g atom o}}$)
II	799.5	698.2	200.0	180.0	0.52	6.09
II	805.0	703.7	348.6	328.6	0.97	6.25
II	788.5	687.2	500.0	480.0	1.47	6.34
II						
III	785.0	683.7	202.1	182.1	0.52	5.91
III	795.6	694.3	335.7	315.7	1.08	7.17
III	784.3	683.0	464.9	444.9	1.46	6.75
III						
IV	776.8	675.5	252.1	232.1	1.19	10.48
IV	790.9	689.6	344.3	324.3	1.94	12.42
IV	789.3	688.0	484.5	464.5	2.65	11.82
IV						
V	790.5	689.2	252.1	232.1	1.65	14.79
V	760.8	659.5	350.7	330.7	2.43	14.69
V	812.1	710.8	499.2	479.2	3.21	14.27
V						

^aRefer to Section A of Chapter II for calculations.

^bStandard deviation.

Table 8

Hydrogenation of 1,2-Dimethylcyclopentene at 1

Catalyst	Temperature (T, °K)	1/T (°K ⁻¹)	P Total (mm Hg)	P _{H₂} (mm Hg)	Catalyst Weight (mg)	Corrected Catalyst ^a Weight (mg)	Reaction Rate ml of H ₂ ($\frac{\text{min}}{\text{min}}$)
II	278.0	3.597	785.7	744.9	367.0	347.0	0.234
II	298.0	3.356					
II	317.0	3.155	802.6	586.5	350.1	330.1	1.980
II							
V	278.0	3.597	785.4	744.6	348.2	328.2	0.588
V	298.0	3.356					
V	317.0	3.155	808.3	592.2	339.5	319.5	4.17
V							

^aRefer to Section A of Chapter II for calculations.^bSpecific rate have been corrected for the solubility of hydrogen in cyclohexane^cRefer to Section E of Chapter III for calculations.^dAverage specific rate from three hydrogenation runs. Refer to Table 7 for the s_i^eStandard deviation.

Table 9

Competitive Hydrogenation of Cyclopentene and 1-Methylcyclopentene

Catalyst	Sample No.	$\frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$ ^a	$\frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$ ^a	$\log \frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$	$\log \frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$	$\frac{R_{\text{Cyclopentene}}}{R_{\text{1-Methylcyclopentene}}}$ ^b
II	1	1.027	1.041	0.012	0.018	0.038
	2	1.210	1.051	0.083	0.022	
	3	1.386	1.057	0.142	0.024	
	4	1.767	1.062	0.247	0.026	
	5	2.361	1.075	0.373	0.032	
III	1	1.229	1.015	0.090	0.007	0.039
	2	1.492	1.023	0.174	0.010	
	3	1.962	1.033	0.293	0.014	
	4	2.592	1.046	0.414	0.020	
	5	7.102	1.088	0.851	0.036	
IV	1	1.209	1.085	0.083	0.036	0.040
	2	1.577	1.097	0.198	0.040	
	3	2.750	1.117	0.439	0.048	
	4	5.665	1.154	0.753	0.062	
V	1	1.043	1.011	0.019	0.005	0.040
	2	1.302	1.020	0.115	0.009	
	3	1.714	1.031	0.234	0.013	
	4	3.152	1.056	0.499	0.024	

^a molar ratio^b Slope from $\log \frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$ versus $\log \frac{\text{Cyclopentene} + \text{1-Methylcyclopentene}}{\text{Cyclopentene}}$ plot

Table 10

Competitive Hydrogenation of Cyclopentene and
3-Methylcyclopentene

Catalyst	Sample No.	^a		^a		^b
		$\frac{\text{Cyclopentene} + \text{Cyclopentene}}{\text{Cyclopentene}}$	$\frac{\text{Cyclopentene} + \text{3-Methylcyclopentene}}{\text{Cyclopentene} + \text{3-Methylcyclopentene}}$	$\log \frac{\text{Cyclopentene} + \text{Cyclopentene}}{\text{Cyclopentene}}$	$\log \frac{\text{Cyclopentene} + \text{3-Methylcyclopentene}}{\text{Cyclopentene} + \text{3-Methylcyclopentene}}$	
II	1	1.160	1.134	0.064	0.055	0.695
	2	1.322	1.251	0.121	0.097	
	3	1.562	1.394	0.194	0.144	
	4	2.131	1.728	0.329	0.237	
	5	3.032	2.250	0.482	0.352	
	6	5.068	3.039	0.705	0.483	
III	1	1.087	1.081	0.036	0.034	0.725
	2	1.187	1.149	0.074	0.060	
	3	1.385	1.284	0.141	0.109	
	4	1.583	1.421	0.199	0.153	
	5	1.760	1.527	0.246	0.184	
	6	2.941	2.206	0.468	0.344	
IV	1	1.134	1.066	0.055	0.028	0.692
	2	1.261	1.145	0.101	0.059	
	3	1.378	1.244	0.139	0.095	
	4	1.678	1.412	0.225	0.150	
	5	2.187	1.691	0.340	0.228	
	6	2.987	2.065	0.475	0.315	
	7	4.584	2.766	0.661	0.442	
V	1	1.111	1.112	0.046	0.046	0.737
	2	1.217	1.205	0.085	0.081	
	3	1.398	1.309	0.145	0.117	
	4	1.627	1.459	0.211	0.164	
	5	1.890	1.638	0.276	0.214	
	6	2.508	2.027	0.399	0.307	

^a molar ratio^b Slope from $\log \frac{\text{Cyclopentene} + \text{3-Methylcyclopentene}}{\text{Cyclopentene} + \text{3-Methylcyclopentene}}$ versus $\log \frac{\text{Cyclopentene} + \text{Cyclopentene}}{\text{Cyclopentene}}$ plot

Table 11

Relative Adsorption Coefficients of
1-Methylcyclopentene and Cyclopentene

Catalyst	$\frac{R_{\text{MC}}}{R_{\text{C}}}$	k_{MC}	k_{C}	$\frac{k_{\text{MC}}}{k_{\text{C}}}$	$\frac{K_{\text{MC}}}{K_{\text{C}}}$
II	0.038	55.1	104.9	0.525	0.072
III	0.039	74.5	131.2	0.568	0.069
IV	0.040	87.3	147.5	0.592	0.068
V	0.040	94.8	143.0	0.663	0.060
					0.067 average

^aRefer to Section H of Chapter III for calculations.

Table 12

Relative Adsorption Coefficients of
3-Methylcyclopentene and Cyclopentene

Catalyst	$\frac{R_{\text{3MC}}}{R_{\text{C}}}$	k_{3MC}	k_{C}	$\frac{k_{\text{3MC}}}{k_{\text{C}}}$	$\frac{K_{\text{3MC}}}{K_{\text{C}}}$
II	0.695	101.8	104.9	0.970	0.716
III	0.725	125.4	131.2	0.956	0.758
IV	0.692	120.3	147.5	0.816	0.848
V	0.737	123.3	143.0	0.862	0.855
					0.794 average

^aRefer to Section H of Chapter III for calculations.

Table 13

Product Distribution of
1,2-Dimethylcyclopentene Hydrogenation

<u>Catalyst</u>	<u>%  C reacted</u>	<u> [trans ]</u>	
		<u>[cis ]</u>	
II	25.0		2.37
	46.47		2.30
	87.10		2.20
	99.07		<u>2.37</u>
		AVG.	2.31
III	23.52		2.38
	40.24		2.44
	57.49		2.35
	70.75		<u>2.29</u>
		AVG.	2.37
IV	37.52		2.67
	63.57		2.50
	95.28		2.42
	98.78		<u>2.60</u>
		AVG.	2.55
V	31.96		3.05
	54.56		3.03
	96.49		<u>2.88</u>
		AVG.	2.99

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