EFFECTS OF TITANOCENE DICHLORIDE ON CATALYTIC HYDROGENATION OF SOME MODEL COMPOUNDS

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ABSTRACT

Catalyst deactivation by metal deposition and coke formation on the catalyst surface is one of the major problems in hydrotreatment processes. When titanocene dichloride was added to a coal derived liquid and hydrotreated, an increase in the catalyst activity and a decrease in the coke was observed.

In order to study this phenomena in pure compounds, Tetralin, a mixture of methyl isobutyl ketone (MIBK) in Tetralin and a mixture of MIBK and quinoline in Tetralin are selected as model feedstocks. The study on the effects of titanocene dichloride is devided into two modes. In the first mode, the feedstock is doctored with 100 ppm of titanium as titanocene dichloride and hydrotreated. In the second mode, the catalyst is impregnated with titanocene dichloride and is used to hydrotreat the model feedstocks. The results of these experiments are compared with the results of experiments using pure model feedstocks and fresh catalysts.

The experiments are conducted in a gradientless reactor with Berty type internals. The reactor was originally designed for gas-solid reactions. The available information on the use of this reactor for gas-liquid-solid system was very limited and to our knowledge nothing was published. A set of experiments is conducted to study the performance of this reactor for the gas-liquid-solid system.

The results shows that the Berty type gradientless reactor can be used in the study of gas-liquid-solid reaction kinetics if the operating conditions are selected carefully to assure a steady state for phase equilibria, reactor flow dynamics, and chemical conversions. The presence of titanocene dichloride in the system causes a deposition of titanium on the external surface of the catalysts resulting in an increase in mass transfer resistance which decreases the conversion of the reactant. The conversion of Tetralin and the catalyst coking depend on the level of catalyst sulfidation. The catalyst with high levels of sulfidation gives higher conversion and lower coke. Since MIBK and quinoline are completely converted at the operating conditions, the effect of titanocene dichloride on these compounds can not be observed.

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CHAPTER II

F_{AO} = Mole flow rate of reactant A into the reactor

$-r_A$ = Rate of reaction of reactant A

R = Recirculation ratio

T = Temperature difference between inlet and outlet of the catalyst basket.

W = Weight of the catalyst

X_A = Conversion of reactant A

CHAPTER III

C_i = Concentration of compound i in mole percent

k, k', k'' = First order rate constant

K = Equilibrium constant

$-r_i$ = Rate of reaction of compound i

Subscript

BB = Butylbenzene

BC = Butylcyclohexane

CD = Cis-decalin

D = Decalin

H2 = Hydrogen

M1 = 1-Methylindan

M2 = 2-Methylindan

M4 = 4-Methylindan

T = Tetralin

TD = Trans-decalin

CHAPTER V

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CHAPTER I

INTRODUCTION

Introduction

Catalyst deactivation is one of the major problems in the petroleum and petrochemical industries, especially in hydrotreatment processes. The main factors for catalyst deactivition are coking and pore plugging by carbonaceous material, adsorption of basic nitrogen containing compounds on acidic sites, deposition of trace metal impurities of the feedstock on active sites of the catalyst, and sintering of the catalyst.

Both metal and coke deposition result in the covering of catalyst surface and plugging of catalyst pores by a layer of metal compounds or carbonaceous material. This obstruction of pores increases the mass transfer resistance to the catalyst surface and reduces the rate of transfer of reactants to the active sites. Trace metals in the feedstock can permanently deposit on the catalyst surface and cause a loss of catalyst activity whereas coke deposition can be burned off the catalyst surface by controlled combustion. There are different types of metal impurities in petroleum and coal-derived liquid feedstocks. Nickel and vanadium are commonly found in petroleum feedstocks while titanium and iron are found in coal-derived liquids. The form of titanium in coal derived liquids is not positively identified, but an organometallic compound like titanocene was proposed by Filby et al. (Reference 7, Chapter IV).

Chan et al. (Reference 8, Chapter IV) doctored titanocene dichloride in an SRC-II coal liquid and hydrotreated it with a Shell 324, a NiMo/alumina catalyst, in a trickle bed reactor system. They concluded that the addition of titanocene dichloride to the feedstock improves hydrotreatment activity of the catalyst and suppresses coke formation on the catalyst. The extent of improvement depends on the concentration of titanocene dichloride. Titanium concentration of 100-200 ppm is the optimum amount to promote the catalyst.

Tscheikuna and Seapan (Reference 9, Chapter IV) studied the effects of titanocene dichloride on catalytic hydrogenation of Tetralin and phenanthrene in a trickle bed reactor. They found that addition of titanocene dichloride to the feedstocks affects the coke formation on the catalyst and the hydrogenation activities of the catalyst. The effects depend on the type of hydrocarbon. Titanocene dichloride appears to increase coke formation on the catalyst when the feedstock is Tetralin. In contrast, the addition of titanocene dichloride to a mixture of phenanthrene and Tetralin reduces the catalyst coking.

Williams (Reference 26, Chapter III) doctored titanocene dichloride in Tetralin and a mixture of phenanthrene and Tetralin and hydrogenated the oils over a NiMo/alumina catalyst in a gradientless reactor. He found that the addition of titanocene dichloride to Tetralin increases the hydrogenation of Tetralin. Titanocene dichloride does not enhance the hydrogenation of Tetralin when phenanthrene is in the feedstock.

In this work, the roles of titanocene dichloride on catalytic hydrotreatment of pure compounds are studied. The catalysts used in the study are NiMo/alumina, CoMo/alumina and alumina catalysts. Tetrahydronaphthalene (Tetralin), methyl isobutyl ketone (MIBK) and quinoline are selected to represent the pure compounds for hydrogenation, hydrodeoxygenation and hydrodenitrogenation studies, respectively. The experiments are conducted in a gradientless reactor with Berty type internals.

The effect of titanocene dichloride is studied on two modes. In the first mode, the feedstock is doctored with 100 ppm of titanium as titanocene dichloride and hydrotreated. In the second mode, the catalyst is impregnated with titanocene dichloride and is used to hydrotreat the model feedstock. The results of these experiments are compared with the results of experiments using pure model feedstocks and fresh catalysts.

The gradientless reactor with Berty type internals was originally designed for gas-solid reaction studies. The available information on the use of this reactor for gas-liquid-solid system was very limited and to our knowledge nothing was published. A set of experiments was conducted to study the performance of the reactor for the gas-liquid-solid system. The results of these experiments are presented in Chapter II.

Chapter III presents the reaction mechanism of Tetralin hydrogenation and the effect of titanocene dichloride on the reaction. The effects of titanocene dichloride and catalyst presulfidation on catalyst coking are discussed in Chapter IV.

The interference of MIBK and quinoline combined with the effect of titanocene dichloride on Tetralin hydrogenation and catalyst coking is presented in Chapter V. The results of the hydrodeoxygenation and hydrodenitrogenation studies are summarized in Chapter VI.

Additional information on G. C. analysis, reactor performance model, Tetralin reaction rate, homogeneous reaction between titanocene dichloride and Tetralin, and isomerization of decalin are presented in Appendices

There was a total of 75 experiments conducted during this project. The data for all the experiments are stored in a computer diskette. The diskette and the user guide are available at the School of Chemical Engineering, Oklahoma State University, Stillwater, OK 74078.

CHAPTER II

BEHAVIOR OF A GRADIENTLESS REACTOR FOR THE KINETIC STUDY OF A GAS-LIQUID-SOLID SYSTEM

BEHAVIOR OF A GRADIENTLESS REACTOR FOR THE KINETIC STUDY OF A GAS-LIQUID-SOLID SYSTEM

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ABSTRACT

The behavior of a gradientless autoclave reactor with Berty-type internals was evaluated for a gas-liquid-solid system. The operation of this reactor for gas phase reactions have been documented in the literature but limited information exists for its operation with gas-liquid mixtures. Catalytic hydrogenation of Tetralin with hydrotreatment catalysts was used as a typical gas-liquid system. The role of phase equilibria, liquid holdup, circulation ratio, heat and mass transfer limitations, flow pattern and non-uniformities of catalyst-reactant contact were studied at different operating conditions. While in gas phase systems the circulation rate affects the heat and mass transfer coefficients only, in gas-liquid systems it also affects the liquid holdup and catalyst-oil contact patterns. The phase equilibria has a major role during the start-up of the reactor. A mathematical model was developed and used to discuss the role of phase equilibria in behavior of the reactor.

BEHAVIOR OF A GRADIENTLESS REACTOR FOR THE KINETIC STUDY OF A GAS-LIQUID SYSTEM

Introduction

Gradientless reactors have been successfully used in kinetic studies and catalyst testing (1-8). There are currently three types of gradientless reactors avaliable for kinetic studies : the Robinson-Amoco, Carberry, and Berty. Each type of gradientless reactor has different design and arrangement of the internals of the reactor. The catalyst inside the reactor either stays in a catalyst basket and the reactants flow through the catalyst or the catalyst basket moves through the reactants. The reported studies dealing with the use of the gradientless reactor have been mainly on gas phase reactions. Myers and Robinson (9) reported the use of the gradientless reactor on gas-liquid system in their study of dibenzothiophene hydrodesulfurization reaction. They concluded that the spinning basket reactor system was better than the trickle bed reactor for the study of fundamental kinetics of liquid-vapor-solid catalyzed reaction.

The Berty-type gradientless reactor is a fixed catalyst bed reactor with a catalyst basket placed in the middle of the reactor. The reactants are mixed and forced to flow into the catalyst basket by means of a propeller. The reactor was originally designed for vapor-phase catalytic studies (5). Even though the reactor was widely used by many researchers, most of the available works were conducted in gas phase systems. Published information on the use of the reactor for gas-liquid-solid systems was very limited and to our knowledge nothing has been published about its flow dynamics and performance in gas-liquid-solid systems (17).

It was our intention to study the performance of the Berty-type gradientless reactor for gas-liquid-solid systems. The reactor performance is expected to be affected by the following independent variables : magnedrive speed, gas and liquid flow rates, temperature, pressure, and size and amount of catalyst. The magnedrive speed has a major role in determining the fluid dynamics and the heat and mass transfer resistances in the reactor. Operating temperature and pressure affect the vapor-liquid equilibria and the reaction kinetics. These factors along with the catalyst affect the conversion of reactants. Therefore any use of the conversion data to measure rate constants requires a good knowledge of the role of these parameters.

Experimental Procedures

Materials

Tetralin (tetrahydronaphthalene), obtained from Aldrich Chemicals, was 98.8 % pure on our gas chromatograph and was used as received. The impurities were mainly naphthalene, cis-decalin and trans-decalin. The catalyst was a commercial Ni-Mo/alumina catalyst (Shell 324) obtained from Shell Chemical Co. The catalyst was sulfided before each experiment by passing a mixture of 5 % hydrogen sulfide in hydrogen through the catalyst at a flow rate of 24 l/h (400 ml/min) and a pressure of 551 kPa (80 psig). During presulfidation, the temperature was maintained at 250 C (482 F) for 1 h.

Description of the process and the reactor

The schematic diagram of the gradientless reactor system used in this study is shown in Figure 1. The reactor is made of stainless steel with an internal diameter of 76.4 mm (3 in.) and a volume of 300 cm^3. Figure 2 shows the details of the reactor internals and fluid flow direction.

Both hydrogen gas and liquid reactant are fed into the bottom of the reactor where they are mixed inside the reactor by a propeller which is rotated by the magnedrive. The mixture flows upward outside the catalyst basket to the top of the reactor and is forced to flow into the catalyst basket. The mixture flows downward through the catalyst basket before it mixes with the new gas and liquid feedstock.

A small portion of the mixture flows out of the reactor at the top of the reactor through an opening in the reactor cap. The gas and liquid mixture flow into sample bombs where they are separated. The liquid samples are taken every 2 h. After completion of each experiment, the catalyst basket is taken out and the catalyst is sampled at 10 different locations inside the catalyst bed, as shown in Figure 3. The remaining catalyst is mixed and used to represent the overall catalyst sample.

The hydrogenation experiments were conducted at 10.4 MPa (1500 psig) and 350 C (662 F). The hydrogen gas flow rate was maintained at 24 l/h (400 ml/min). Liquid feed flow rate and magnedrive speed were varied in different experiments. The liquid holdup measurement and flow pattern observations were conducted at room temperature and atmospheric pressure.

Sample analyses

The liquid samples were analyzed by a Varian Model 3740 Gas Chromatograph equipped with an Analabs 25 m capillary GB-5 column and a flame ionization detector. The output of the detector is processed and recorded by a Hewlett Packard Integrator Model 3390A.

The catalyst samples were extracted with tetrahydrofuran in a Soxhlet extraction unit for 24 h to remove the oil from the catalyst surface. The extracted samples were air dried for 48 h before they were analyzed for coke content. The coke content was defined as the weight percent of loss of carbonaceous material by burning the catalyst at 550 C (1022 F) in air for 60 h.

Results and Discussion

Fluid Dynamics of the Reactor

Liquid Holdup: During the continuous flow operation of the reactor, the liquid and gas feed enter the reactor through the feed lines at the bottom of the reactor while the gas-liquid mixture leaves the reactor through a small hole located in the reactor cap. The "Liquid Holdup" is defined as the amount of liquid mixture, reactants and products, which circulates inside the reactor at steady state and at any time. The liquid holdup of a reactor is expected to depend on the magnedrive speed.

The true liquid holdup volumes under the reaction conditions are extremely difficult to determine due to the volatility of liquid at high temperatures. However, the measurements at room conditions should provide valuable information regarding the effect of magnedrive speed on the liquid holdup.

The liquid holdup volume at room temperature and pressure was determined using the following procedure. The gas-liquid line connecting the reactor and the sample bomb was disconnected. The sample bomb was replaced by a measuring cylinder to measure the volume of liquid flowing out of the reactor. Approximately 100 ml of Tetralin was pumped into the reactor. Then nitrogen gas flow and magnedrive were started while Tetralin was continuously pumped into the reactor. For a set value of magnedrive speed and gas flow rate the system was operated until the flow rate of Tetralin into the reactor was equal to its flow out of the reactor. The system was shut down and Tetralin inside the reactor was drained from the bottom of the reactor and measured.

Table I lists the liquid holdup volume measured for a nitrogen flowrate of 24 l/h (400 ml/min). The duplicate measurements indicate that reproducibility is better than +/- 1 %. Figure 4 shows the plot of these data which indicates that the liquid holdup volume decreases with magnedrive speed at low speeds, however, it becomes independent of magnedrive speed at the magnedrive speeds higher than approximately 1000 rpm.

Flow Pattern Inside the Reactor: The flow pattern of the gas-liquid mixture inside the reactor could not be observed under hydrogenation conditions since the reactor operated at high temperature and pressure. Our observation of the flow pattern was conducted at atmospheric pressure and room temperature. The reactor cap was taken out and replaced with a 6.4 mm (1/4 inch) clear plastic cut to the size of the reactor cap. The liquid reactant was pumped into the reactor along with sufficient amount of gas. The motion of the gas-liquid mixture in the reactor was observed through the clear plastic at different magnedrive speeds, ranging from 100 to 2000 rpm. Nitrogen was used instead of hydrogen for safety reasons. Both nitrogen gas and Tetralin were fed into the reactor with magnedrive operating at the desired speed. The flow of Tetralin feed was stopped when the gas-liquid mixture started to flow into the catalyst basket.

From our visual observations, the gas-liquid system forms a foamy mixture which flows upward through the annular space between the catalyst basket and reactor wall to the top of the reactor without contacting the catalyst. A portion of this mixture flows down into the catalyst basket along the wall of the basket under the gravity force. The remaining portion flows up to the reactor cap and is forced by the donut shaped surface of the reactor cap to flow down towards the center of the catalyst basket.

At high magnedrive speeds, the gas-liquid mixture mixes with new liquid reactant and feed gas and is forced by high speed propeller to flow upward outside the catalyst basket. At low magnedrive speeds, the propeller does not have enough power to push the mixture out of the area under the catalyst basket. This results in the accumulation of the gas-liquid mixture under the catalyst basket which rises to gradually wet the catalyst at the bottom part of the catalyst basket.

Catalyst basket flooding occurs at magnedrive speeds less than 500 rpm. At higher speeds, the flow through the catalyst bed is consistently downwards. At speeds higher than 1000 rpm, no significant changes can be observed in the flow pattern, except that the circulation becomes more rapid and the size of the gas bubbles decrease.

The uniformity of flow patterns and the constancy of liquid holdup at speeds above 1000 rpm indicate that kinetic studies should be conducted at magnedrive speeds higher than 1000 rpm. At high speeds, any change in the conversion with magnedrive speed will be essentially due to variations in heat and mass transfer resistances and will not be affected by circulation pattern and holdup volume.

Gas-Liquid-Solid Reactions In Gradientless Reactor

One of the advantages of a recycle reactor is that an integral catalytic reactor can be operated as a CSTR reactor. Furthermore, in the gradientless reactors, by generating high relative velocities between the fluid and the catalyst, the external heat and mass transfer resistances can be essentially eliminated or at least minimized (7,16). In Berty type reactors, the temperature gradient between the catalyst and the liquid can be measured directly. This temperature gradient can be used to calculate the recirculation ratio of the fluid in the reactor (5). A test to check the lack of external mass transfer resistance can be conducted by varying the stirring rate and observing the conversion of the reactant (4,7). In this project, the catalytic hydrogenation of Tetralin was used as a typical three phase reaction system to study the behavior of this reactor in reaction kinetic studies.

Effect of Phase Equilibria: In order to evaluate the role of phase behavior during the start-up of the reactor, the phase equilibria of Tetralin-hydrogen system was considered. The vapor-liquid equilibria of hydrogen-Tetralin system was studied by Simnick et al. (10), Nasir et al. (11), Harrison (12) and Kara et al. (13). The phase equilibrium constants at 350 C (662 F) and 10.4 MPa (1500 psig) were approximately 7.2 and 0.19 for hydrogen and Tetralin, respectively (14). Vapor liquid equilibrium calculations show that under these conditions, the vapor phase at equilibrium contains 16.5 percent Tetralin.

Phase behavior of the feed is very important during the start-up of the experiment. In our experiments, after catalyst calcination and sulfidation are completed, the reactor is heated to the reaction temperature of 350 C under hydrogen atmosphere. When the flow of hydrogen and Tetralin are started into the reactor, the initial drops of Tetralin flash and evaporate into the gas phase. Tetralin is expected to evaporate into the gas phase until the gas phase is saturated with Tetralin vapor. Then the liquid phase of Tetralin starts to accumulate until the liquid holdup volume is reached. The amount of liquid inside the reactor remains constant and the system approaches its steady state.

The unsteady-state start up period can be minimized by quickly charging liquid reactant into the reactor until the liquid holdup volume was reached. During liquid charging period, gas flow rate should be maintained as low as possible.

Reactor Performance Model: In most recycle reactors, the feed to process is mixed with the recycle stream which then passes through the reactor. A fraction of the reactor outlet stream is separated as the product of process while the rest is recycled. However, the recycle pattern in the Berty type reactor is different from that of the normal recycle reactor. In Berty type reactor, the feed to the process is mixed with the recycle stream. A fraction of this mixture leaves the system as the product of the process while the remaining mixture enters the catalyst bed. A schematic of flow in this reactor is shown in Figure 5.

The reactor performance model for the Berty type reactor is derived by using a differential material balance in the reactor (18) and is given as:

$$\frac{W}{F_{AO}} = (R-1) \int_{X_{A,in}}^{\frac{R}{R-1} X_{A,in}} \frac{dX_A}{-r_A}$$

However, at high recycle ratios it can be reduced to the equation for CSTR reactor.

$$\frac{W}{F_{AO}} = \frac{X_{A,in}}{-r_A}$$

Carberry (1) states that a recycle ratio higher than 25 is adequate to assume CSTR behavior whereas Berty (3) considers a value higher than 20 to be adequate. In this project the recycle ratio is determined to be always higher than 25, varying between 60-200 depending on the flow rate.

Heat Transfer Limitations: One major advantage of the Berty type gradientless reactor is that the catalyst and fluid bulk temperatures can be directly measured. The difference between these two temperatures will indicate the heat transfer resistance in the catalyst bed. The temperature difference is expected to decrease with an increase in the velocity of fluid through the bed since the heat transfer coefficient increases with the velocity of fluid.

An evaluation of the heat transfer resistance in the catalyst bed was conducted with variable magnedrive speeds. The temperature differences between the catalyst and the bulk of the fluid were measured at each magnedrive speed.

Table II shows the temperature differences and magnedrive speeds. It indicates that there is a significant amount of heat transfer resistance at magnedrive speeds less than 750 rpm, but the heat transfer resistance is essentially negligible at the magnedrive speeds higher than 1000 rpm for Tetralin hydrogenation reaction.

Mass Transfer Limitations: The absence of mass transfer limitations in the reactor can be determined by measuring the conversion of reactant as a function of mixing rate. Brown (15), Bennett et al. (7) and Myers and Robinson (9) used this technique to determine the stirrer speed that minimized the mass transfer resistances.

Six experiments were conducted with magnedrive speeds ranging from 500 to 2000 rpm. Each experiment lasted 12 h.

The conversion data indicate that the steady state for each experiment was reached after 6 h, the conversion of 8, 10 and 12 hour samples were averaged and used to represent the overall conversion of the reactant at the steady state.

The conversions at different magnedrive speeds are tabulated in Table III and plotted in Figure 6. It indicates that mass transfer limitation is minimized at magnedrive speeds higher than 1500 rpm. A similar result is obtained when the conversions from the first unsteady state samples are plotted versus magnedrive speed, as shown in Figure 6.

Recirculation Ratio: An estimation technique of recirculation ratio in the reactor is originally developed by Berty et al. (3,5) for a gas-solid system and is applied to gas-liquid-solid system in this work. The recirculation ratio is calculated by

$$R = \frac{\text{Flow rate through the catalyst bed}}{\text{Flow rate out of the reactor}} = \frac{\Delta T_{\text{adiabatic}}}{\Delta T_{\text{measured}}}$$

The numerator, $\Delta T_{\text{adiabatic}}$, is obtained from calculation of the adiabatic temperature change for the measured conversion. The denominator, $\Delta T_{\text{measured}}$, is the temperature difference measured between the catalyst bed inlet and outlet.

The recirculation ratio, determined from 7 different runs at 1500 rpm, varied from 42 to 210 with an average of 107. The ratio was much higher than 25 which was recommended by Carberry (1) for approach to CSTR.

The accuracy in measuring the temperature difference is very important since the recirculation ratio is very sensitive to the measured temperature difference. A one degree difference in $\Delta T_{measured}$ could cause a 20 to 100 percent error in the value of R. In our experiments, the temperature measurement was accurate only within 1 C which explains the wide variation in the magnitude of R. We did not attempt to measure the temperature more accurately since the values of R in our experiment were higher than 25 in all cases.

Catalyst Wetting: The observation at room conditions shows that the flow of the gas-liquid mixture into the catalyst bed is not as uniform as one would expect. A portion of the mixture tends to flow into the catalyst basket along the wall of the basket. The other portion flows up to the reactor cap and is forced to flow down to the center of the catalyst basket. This non-uniformity of the flow is also expected to exist under the reaction conditions.

Non-uniformity of the flow into the catalyst bed causes a non-uniformity in the contact between catalyst and gas-liquid mixture. This results in non-uniformity in coking on the catalyst. The coking results of four different runs, labeled D-1 through D-4, in which the catalyst was sampled at different locations to study the profile of coke in the catalyst bed, are tabulated in Table IV through VII. Figure 3 shows the locations of catalyst samples in the catalyst bed. Table VIII summarizes the coke analysis results showing the average coke contents and the standard deviations.

Figures 7 through 9 show the plot of the coke content on the catalyst at different locations. A large scatter of the catalyst coke contents with the position in the catalyst bed is observed in these figures. Furthermore, when the averages of the standard deviations for each location are compared with the standard deviation of the average coke content in the bed, we conclude that the catalyst bed is not coked uniformly. The catalyst pellets at the center of the bed coke more than the pellets near the edges. This is primarily due to the circulation pattern of the oil inside the reactor.

This large scatter in coking results directed us to modify the coke analysis procedure. It should be pointed out that in the coke analysis procedure mentioned above, the coke content at each location was measured using a catalyst sample containing a single pellet which was not a true representative of the whole catalyst sample. Therefore in later experiments, the catalyst was mapped at the top of the bed from locations A, B, C, and D. The remaining catalyst was well mixed and approximately 0.5 g sample, containing about 30-40 pellets was used for coke analysis. This coking analysis, shown in Figure 10, shows that the modified catalyst sampling technique gives us a more reproducible result.

Conclusion

Our studies on the behavior of the gradientless reactor showed that at magnedrive speeds higher than 1000 rpm, the reactor is gradientless and behaves similarly to a continuously stirred tank reactor (CSTR). The reactor can be used for kinetic measurements of catalytic gas-liquid-solid system. However, one has to consider the phase equilibria and reactor dynamics to assure that a flow and reaction steady state are attained before the data are used for kinetic calculations. Catalyst coking is not uniform throughout the catalyst bed. Careful catalyst sampling techniques must be used to obtain representative average coke values.

Acknowledgment

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NOTATION

F_{AO} = Mole flow rate of reactant A into the reactor

$-r_A$ = Rate of reaction of reactant A

R = Recirculation ratio

ΔT = Temperature difference between inlet and outlet of the catalyst basket.

W = Weight of the catalyst

X_A = Conversion of reactant A

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LIST OF TABLES

TABLE I

EFFECT OF MAGNEDRIVE SPEED ON THE LIQUID HOLDUP VOLUME (AMBIENT CONDITIONS, 500 ML/MIN N_2 FLOW RATE)

Magnedrive Speed rpm	Liquid Holdup Volume ml
500	157
750	140
1000	117,116
1250	114
1500	115,115
1750	113
2000	119

TABLE II

EFFECT OF MAGNEDRIVE SPEED ON CATALYST-FLUID TEMPERATURE DIFFERENCE

Magnedrive Speed rpm	Temp. Difference C
500	25.68
750	2.13
1000	-0.52
1250	1.33
1500	0.45

TABLE III

EFFECT OF MAGNEDRIVE SPEED ON TETRALIN CONVERSION (STEADY STATE CONVERSION)

Magnedrive Speed rpm	% Conversion
500	31.8
1000	41.6
1250	38.9
1500	43.7
1750	43.7
2000	39.9

TABLE IV

DISTRIBUTION OF COKE ON CATALYST FOR RUN D-1 (wt%)

Location	Sample # 1	2	3	Average	Standard Deviation
A	6.45	7.18	5.76	6.47	0.71
B	5.08	4.25	3.44	4.26	0.82
C	5.01	4.63	4.80	4.85	0.20
D	4.10	3.53	4.64	4.09	0.56
E	4.79	4.56	4.39	4.61	0.20
F	5.85	5.85	5.92	5.88	0.04
G	5.23	5.55	5.75	5.51	0.26
H	3.90	4.23	4.45	4.20	0.28
K	5.90	5.98	6.02	5.97	0.06
L	4.95	4.90	4.88	4.91	0.04
		Average of standard deviations			0.32

TABLE V

DISTRIBUTION OF COKE ON CATALYST FOR RUN D-2 (wt%)

Location	Sample # 1	2	3	Average	Standard Deviation
A	3.68	2.65	3.18	3.16	0.52
B	4.40	3.06	1.75	3.07	1.33
C	6.35	7.61	6.98	6.98	0.63
D	3.31	6.72	4.99	4.96	1.71
E	2.81	2.55	2.50	2.61	0.17
F	4.65	7.52	6.18	6.13	1.44
G	6.62	4.22	5.51	5.45	1.20
H	2.95	3.16	3.42	3.18	0.24
K	2.21	5.28	4.45	3.98	1.59
L	2.14	1.82	2.70	2.16	0.45
		Average of standard deviations			0.93

TABLE VI

DISTRIBUTION OF COKE ON CATALYST FOR RUN D-3 (wt%)

Location	Sample # 1	2	3	Average	Standard Deviation
A	4.30	4.22	4.20	4.24	0.05
B	5.30	5.50	5.43	5.41	0.10
C	6.83	8.99	7.90	7.91	1.08
D	6.95	7.69	8.55	7.73	0.80
E	4.50	4.36	4.31	4.39	0.10
F	5.87	5.75	5.81	5.81	0.06
G	6.49	6.55	6.59	6.54	0.05
H	2.94	3.49	4.19	3.54	0.63
K	6.07	6.82	6.44	6.45	0.38
L	4.38	4.19	3.96	4.17	0.21
		Average of standard deviations			0.35

TABLE VII

DISTRIBUTION OF COKE ON CATALYST FOR RUN D-4 (wt%)

Location	Sample # 1	2	Average	Standard Deviation
A	6.43	5.94	6.19	0.33
B	7.08	5.93	6.51	0.81
C	6.51	6.38	6.45	0.09
D	7.04	3.56	5.30	2.46
E	2.53	4.42	3.47	1.34
F	6.77	7.65	7.21	0.62
G	6.26	6.81	6.53	0.93
H	4.36	5.75	5.06	0.98
K	6.72	7.66	7.19	0.66
L	6.02	7.13	6.58	0.78
		Average of standard deviations		0.85

TABLE VIII

SUMMARY OF DISTRIBUTION OF COKE ON CATALYSTS (wt%)

Locations	D-1	D-2	D-3	D-4
A	6.47	3.16	4.24	6.19
B	4.26	3.07	5.41	6.51
C	4.85	6.98	7.91	6.45
D	4.09	4.96	7.73	5.30
E	4.61	2.61	4.39	3.47
F	5.88	6.13	5.81	7.21
G	5.51	5.45	6.54	6.53
H	4.20	3.18	3.54	5.06
K	5.97	3.98	6.45	7.19
L	4.91	2.16	4.17	6.58
average	5.07	4.18	5.62	6.05
stand.devia.	0.88	1.80	1.53	1.35

LIST OF FIGURES

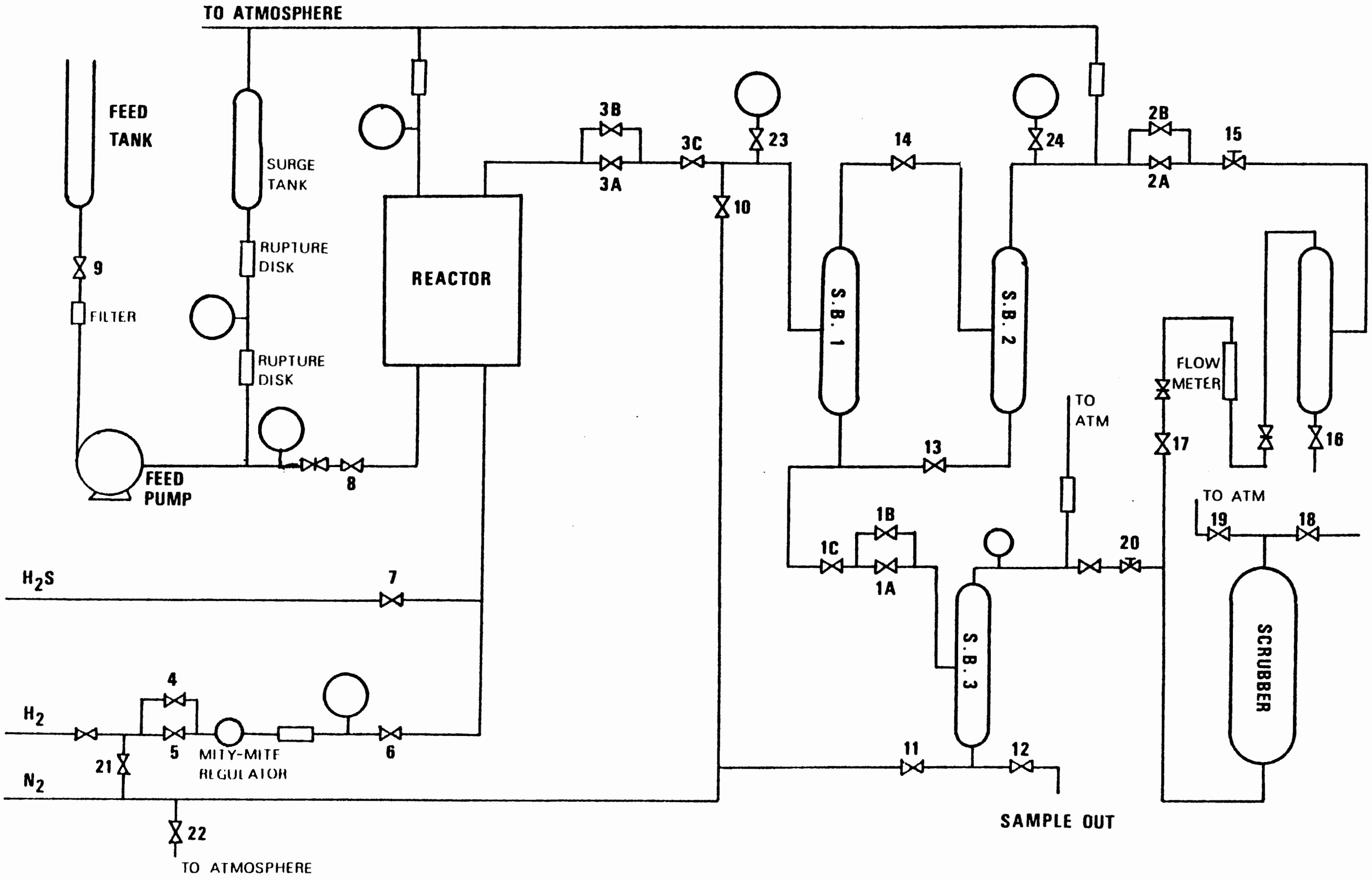

Figure 1. Schematic Diagram of Reactor System

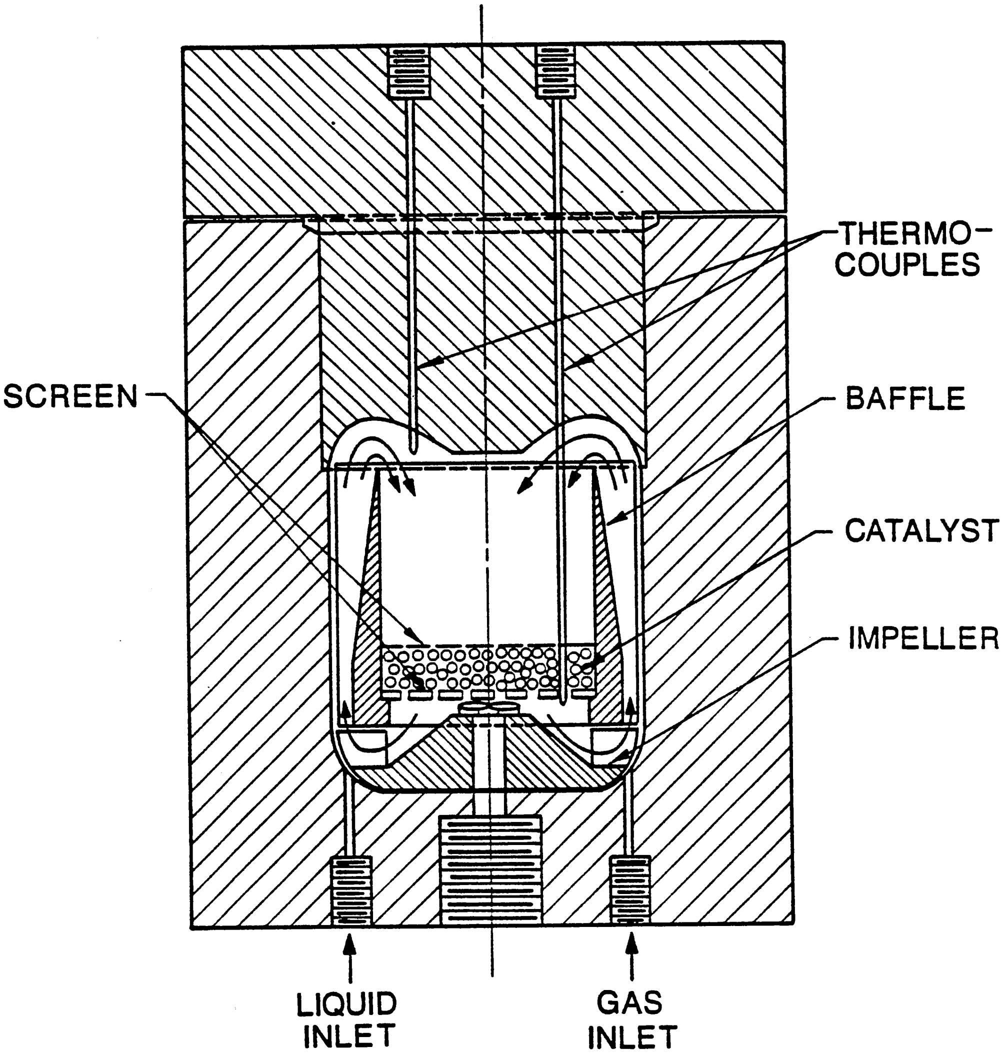

Figure 2. Internals of Berty Reactor

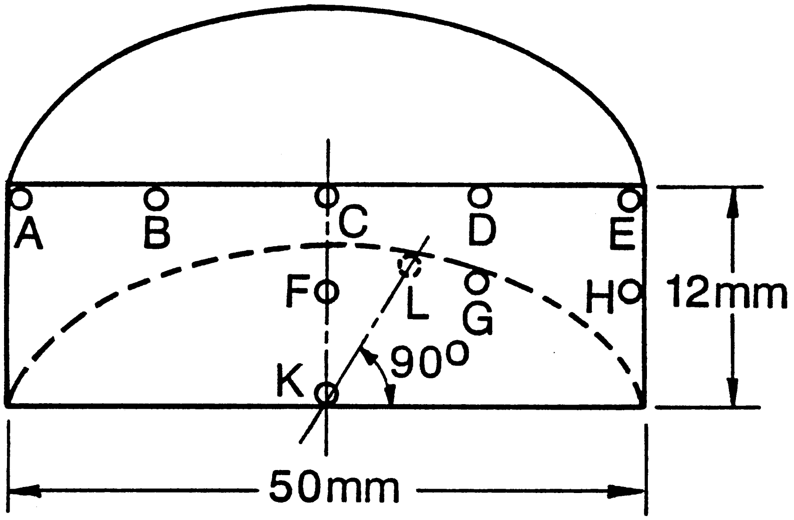

Figure 3. Locations of Catalyst Samples in the Catalyst Basket

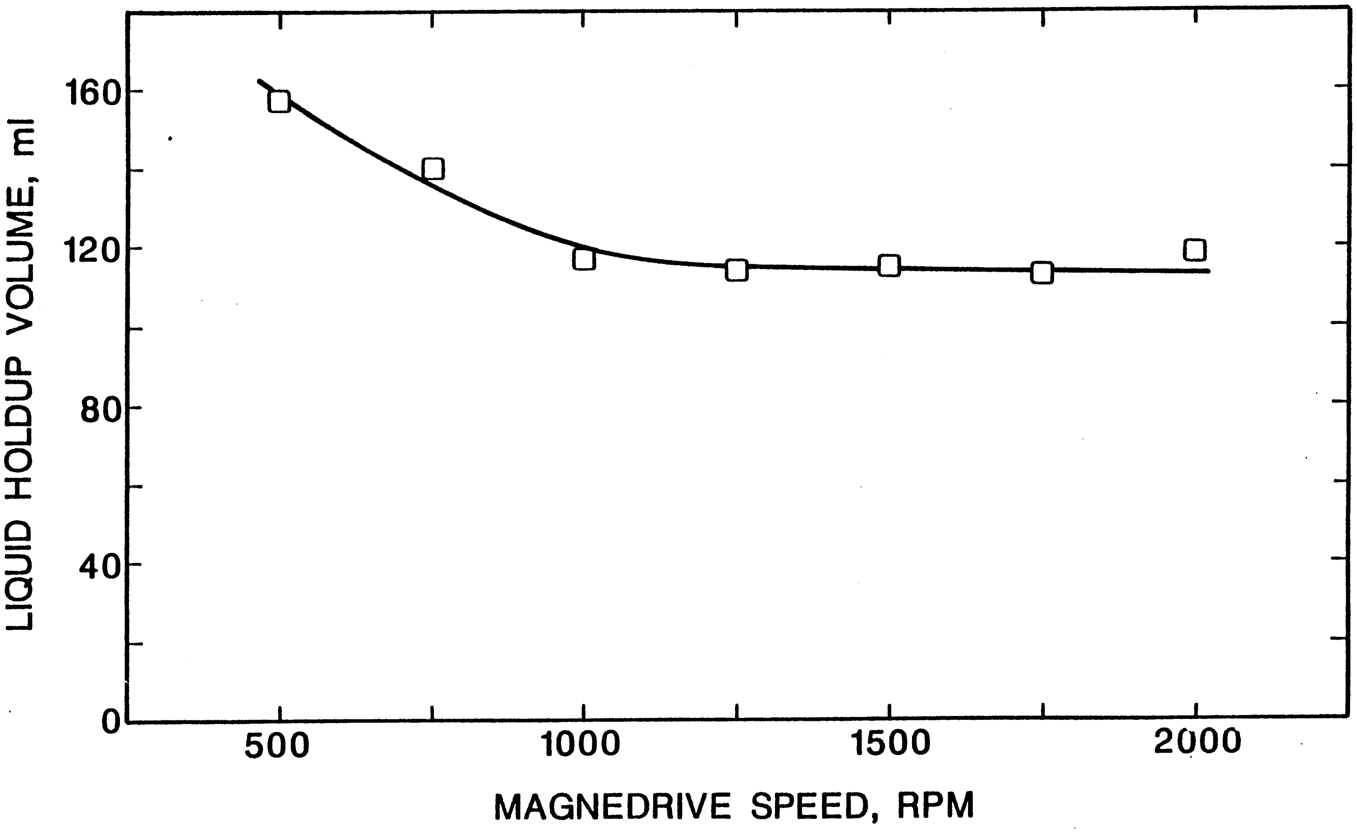

Figure 4. Effect of Magnedrive Speed on Holdup Volume

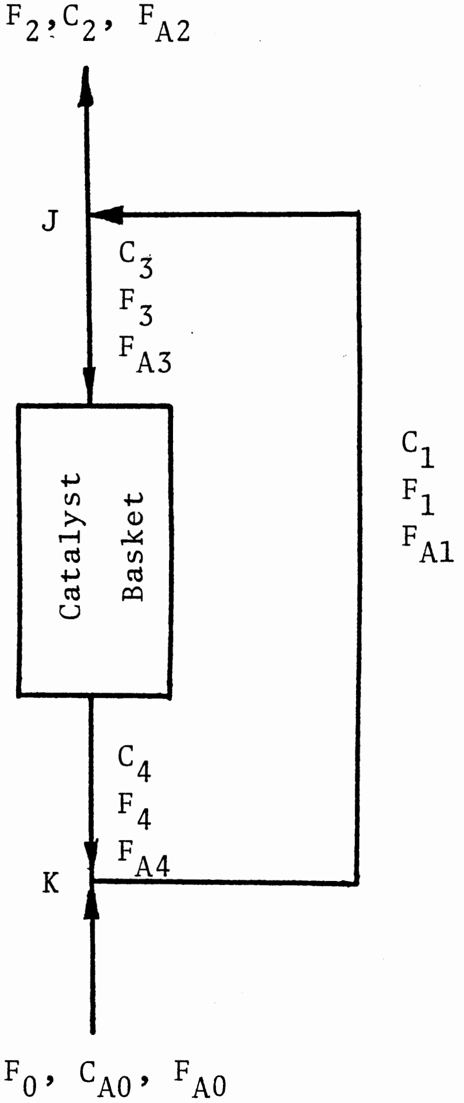

Figure 5. Schematic Diagram of Flow inside the Reactor

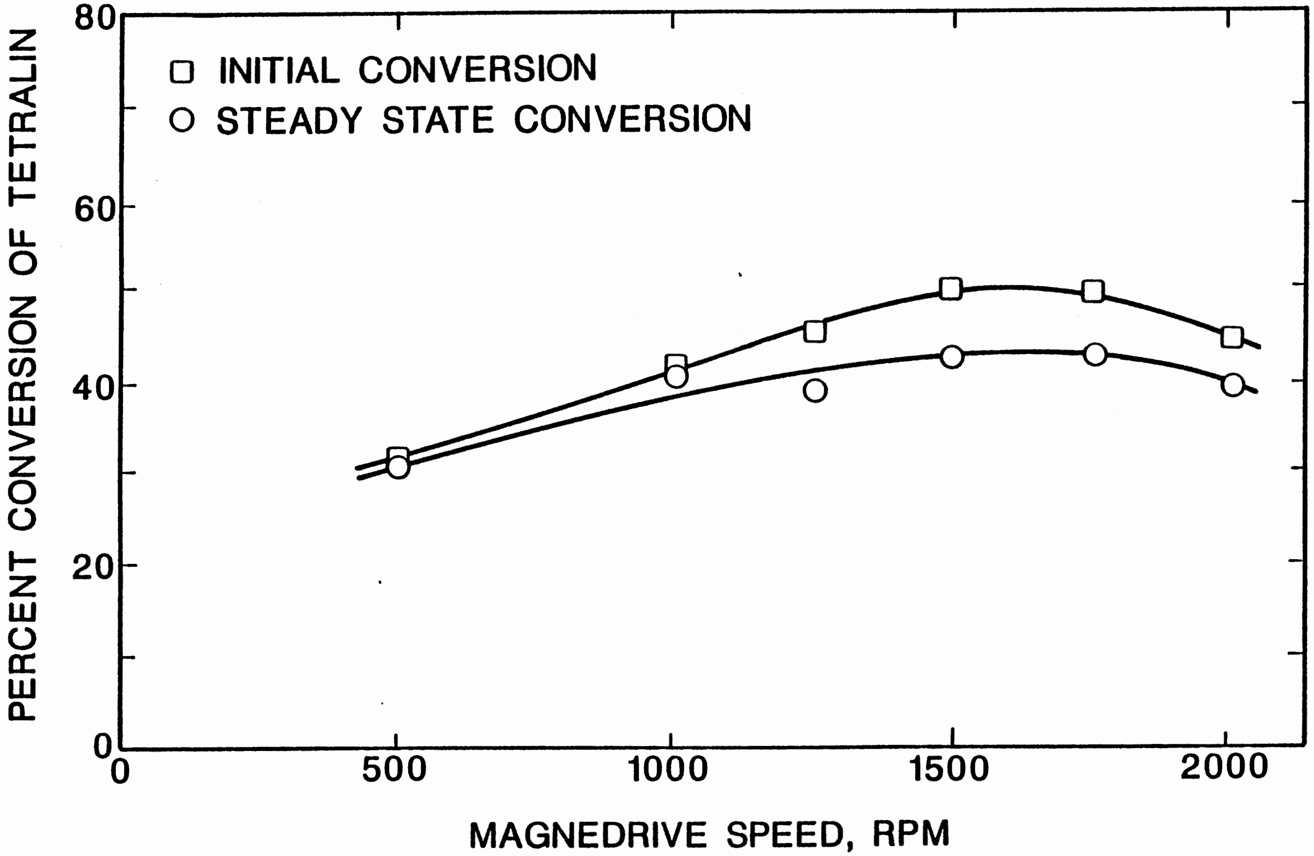

Figure 6. Effect of Magnedrive Speed on Conversion

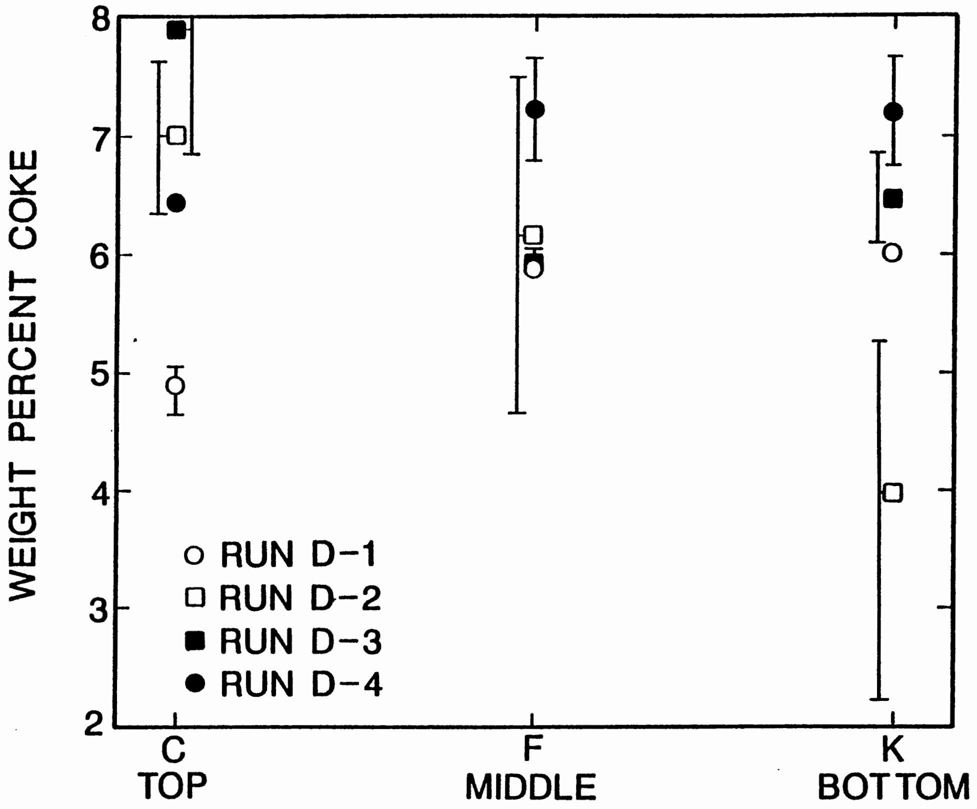

Figure 7. Vertical Distribution of Coke along the Centerline of the Catalyst Bed

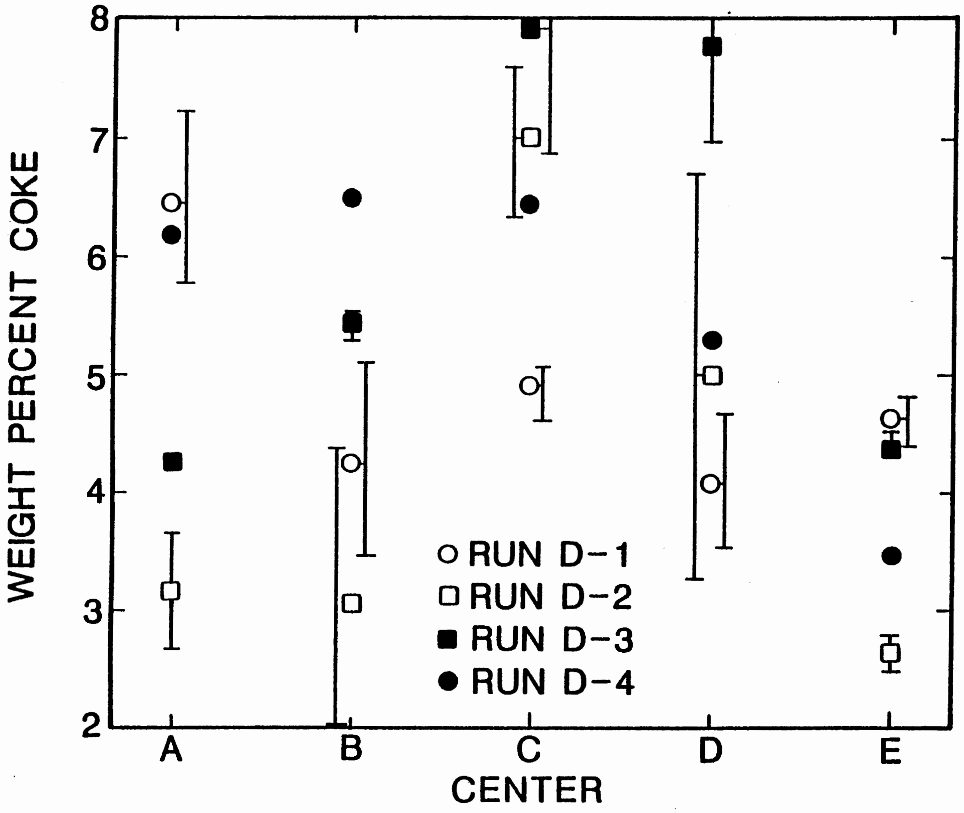

Figure 8. Horizontal Distribution of Coke at the Top Layer of Catalyst Bed

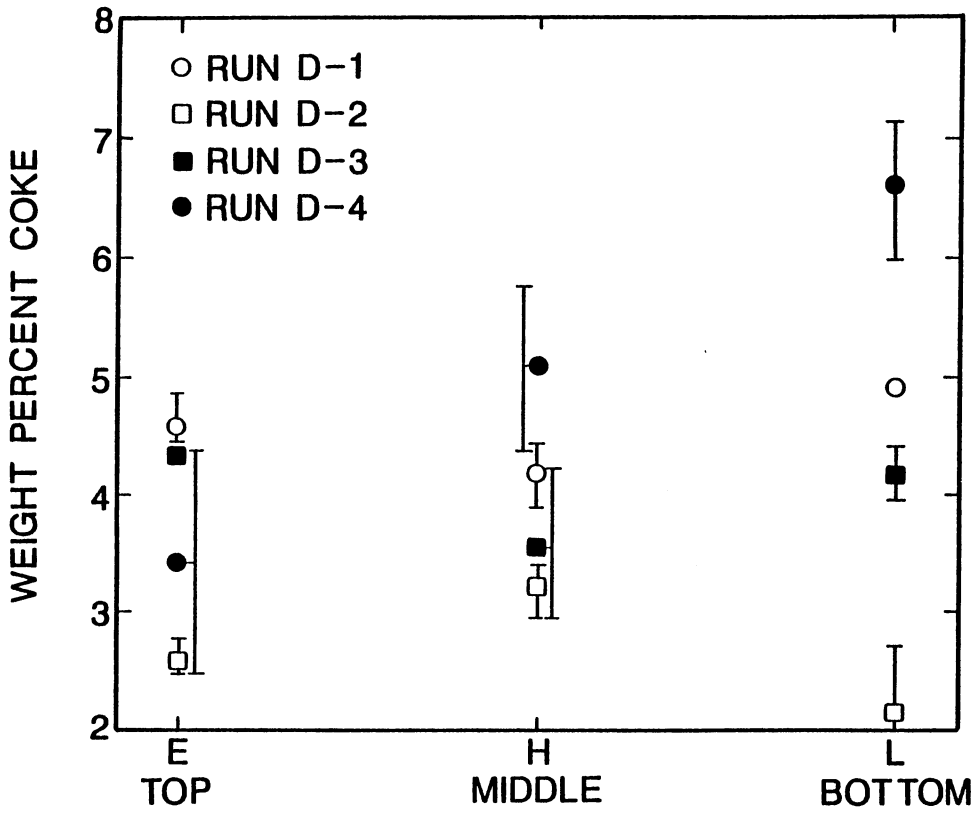

Figure 9. Vertical Distribution of Coke near the edge of Catalyst Bed

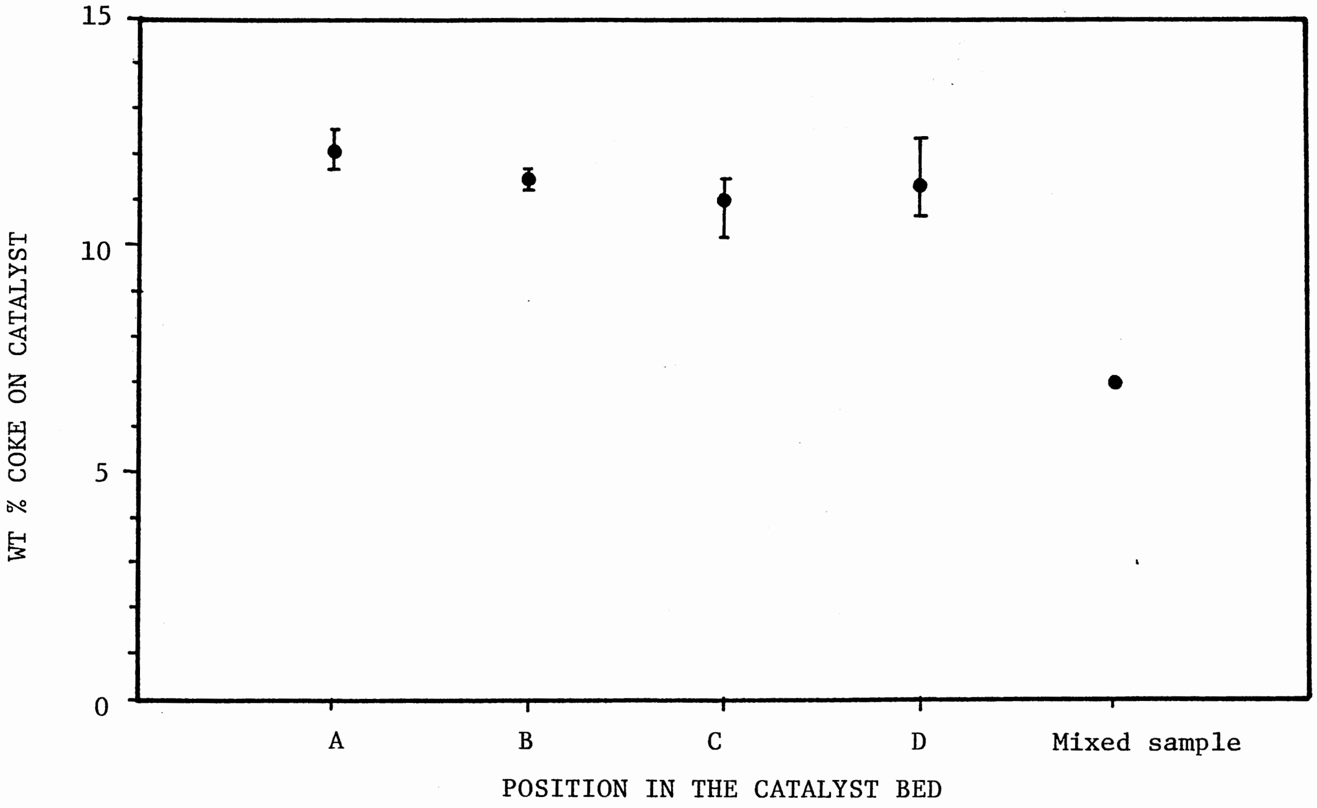

Figure 10. Comparisons of Coking Results between the Top Layer of Catalyst Bed and the Mixed Sample

CHAPTER III

EFFECT OF TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

EFFECT OF TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

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ABSTRACT

Effects of titanocene dichloride on hydrogenation of Tetralin and catalyst coking were investigated over NiMo/alumina and CoMo/alumina catalysts and alumina support. A comprehensive reaction network including hydrogenation and hydrocracking reactions is developed. The role of titanocene dichloride was evaluated in two modes:
a) titanocene dichloride was added to the feedstock and hydrotreated, b) the catalysts were impregnated with titanocene dichloride then used to hydrotreat the feedstock. The results were compared with the results from experiments using pure feedstock and fresh catalysts. Titanocene dichloride forms a layer of titanium covering the external surface of the catalyst which reduces the catalyst activity and the catalyst coking.

EFFECT OF TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

Introduction

Tetralin, tetrahydronaphthalene, is a common compound which is used as a hydrogen donor in coal liquefaction processes. It has also been used as a model compound in the study of chemical reactions such as thermal and catalytic cracking, pyrolysis, isomerization, hydrogenation, and dehydrogenation. Eventhough a large number of general articles are available on Tetralin, the study of hydrogenation of Tetralin is very limited. Most investigators selected naphthalene instead of Tetralin in their hydrogenation studies.

Sapre and Gates (1) studied hydrogenation of naphthalene catalyzed by sulfided CoMo/alumina in a batch reactor at 7.6 MPa (1100 psig) and 325 C (617 F). They found that naphthalene hydrogenated, giving Tetralin as a primary product. Tetralin was further hydrogenated to cis- and trans-decalin. The predominant isomer of decalin was trans-decalin. The rate constants found in their studies for conversion from Tetralin to trans-decalin and cis-decalin were 1.4 and 0.4, respectively. There was no report on isomerization of decalin in their study. They also concluded that the Tetralin-naphthalene reaction was a reversible reaction. There was no other hydrocarbon product detected in their experiments.

Tishchenko and Perin (2) investigated isomerization of

Tetralin catalyzed by gumbrin at temperatures of 225-250 C (437-482 F). They concluded that the conversion of Tetralin proceeds in two directions. First, a conjugated hydrogenation reaction resulted in formation of decalin, dihydronaphthalene, and naphthalene. Second, the hydrogenated part of naphthalene underwent scission to form diethyl- and butylbenzene. The radicals of diethyl- and butylbenzene could be split in the presence of hydrogen with the formation of benzene, butane, and ethane.

Vrinat and Germain (3) studied kinetics of Tetralin hydrogenation over a nickel-kieselguhr catalyst. Tetralin was hydrogenated in a continuous flow stainless steel reactor at temperatures of 195-235 C (383-455 F) and under pressures of 2-8 MPa (290-1150 psig). They concluded that the overall reaction of Tetralin hydrogenation was zero order.

Kalechits et al. (4) studied hydrogenation of naphthalene, Tetralin and decalin in an autoclave over WS_2, WS_2-NiS-Al_2O_3 and WS_2-clay. Their experiments were conducted at a hydrogen pressure of 14.2 MPa (140 atm) and a temperature of 420 C (788 F). They found that the hydrogenation products of naphthalene were Tetralin and decalin. Small amounts of monoalkylated benzene isomers were also detected, supporting the view that the bond of the hydrogenated ring of Tetralin was split.

Cracking of Tetralin, either with or without hydrogen and a catalyst, has also been a topic for many researchers.

Their studies covered the temperature and pressure ranges as high as 850 C (1562 F) and 60.8 MPa (8820 psig). In most cases the cracking products of Tetralin are naphthalene, toluene, methylindans, alkyl benzenes, indan, and styrene. The discussions of reaction mechanisms, reaction schemes and kinetics are available in the literature (5-22).

Titanium is a trace metal commonly found in coal and is believed to survive the conditions of coal liquefaction processes. Titanium in coal-derived liquid is in the form of organometallic compounds such as titanocene dichloride (23). An earlier study (24) showed that addition of titanocene dichloride to an SRC II coal-derived liquid and hydrotreated over a NiMo/alumina catalyst improved the hydrotreatment activities of the catalyst and suppressed the coke formation on the catalyst. Our study (25) on the hydrogenation of Tetralin over Ni-Mo/alumina catalyst in a trickle bed reactor also showed that the addition of titanocene dichloride to Tetralin resulted in an increase in hydrogen-to-carbon atom ratio.

In this project hydrogenation of Tetralin was investigated over commercial NiMo/alumina and CoMo/alumina catalysts at 350 C (662 F) and 10.4 MPa (1500 psig). The effects of titanocene dichloride on hydrogenation activity were studied in two modes. In the first mode, 100 ppm of titanium as titanocene dichloride was doctored into Tetralin feedstock and hydrogenated. In the second mode, the catalysts were impregnated with titanocene dichloride and used to hydrogenate Tetralin. The results of these experiments were compared with the results of those using undoctored Tetralin and the regular catalysts. Blank experiments were conducted over alumina support to investigate the noncatalytic effects of titanocene dichloride on Tetralin and the stability of Tetralin at our operating conditions. Decalin, decahydronaphthalene, was also hydrogenated at the same conditions in order to determine the by-products of its reactions and to obtain kinetic data.

Experimental Procedures

Equipment and Procedures

The experiments were conducted in a gradientless recycle reactor with Berty-type internals. The reactor has an internal volume of 300 cm^3. Hydrogen gas and liquid feed flow into the bottom of the reactor where they are mixed by means of a high speed magnedrive. Product oils and gases flow through the opening at the reactor cap to the sample bombs where gases and liquid oils are separated. The details of the gradientless reactor are described elsewhere (26).

Tetralin, obtained from Aldrich Chemicals, was 98.8% pure by our analysis and was used as received. The impurities in Tetralin were mainly naphthalene, cis-decalin and trans-decalin. Decalin, obtained from Alfa Products, was a mixture of approximately 53.4 % trans-decalin and 46.6 % cis-decalin. It was used without further purification. The catalysts were commercial NiMo/alumina (Shell 324) and CoMo/alumina (Shell 344), obtained from Shell Chemical Co. and the alumina support was SN6313 alumina substrate obtained from American Cyanamid Company. Twenty grams of catalyst was used in each experiment. This amount of catalyst filled the catalyst basket to a height of 10 mm. The properties of the catalysts are shown in Table I. Hydrogen gas was obtained in bottles and was used as received.

Before each experiment, the catalyst was calcined inside the reactor by heating to 300 C (572 F) under nitrogen gas. The temperature was maintained at 300 C (572 F) for one hour at a nitrogen flow rate of 24 l/h (400 ml/min) and a pressure of 2.07 MPa (300 psig). The catalyst was allowed to cool down to 250 C (482 F) under nitrogen gas before it was sulfided with a mixture of 5% hydrogen sulfide in hydrogen at a pressure of 551 kPa (80 psig) and a flow rate of 24 l/h (400 ml/min). During sulfidation, the catalyst was heated from 250 to 360 C (482 to 680 F) at a rate of 60 C/h (1 C/min) and was maintained at 360 C (680 F) for 2 h.

The experiments were conducted at 10.4 MPa (1500 psig) and 350 C (662 F). The hydrogen flow rate was maintained at 24 l/h (400 ml/min) and the liquid feed flow rate was set at 30 ml/h. The magnedrive was operated at 1500 rpm. The duration of each experiment was 12 h, and the liquid samples were taken every 2 h. Table II summarizes the type of the feed oils and the type of the catalysts used in each experiment.

Sample Analysis

The liquid samples were analyzed qualitatively and quantitatively by using a Hewlett Packard Model 5890 Gas Chromatograph equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was recorded and integrated by a Hewlett Packard Integrator Model 3392A. The compounds were identified by comparing the retention times of liquid samples with the retention times of known compounds. Cis-decalin, trans-decalin, Tetralin, and naphthalene were further confirmed by a combined gas chromatograph/mass spectrometer. The titanium contents of the liquid samples were analyzed by a Perkin Elmer 503 Atomic Absorption Spectrometer.

The catalyst samples were extracted with tetrahydrofuran in a Soxhlet extraction unit for 24 h. The washed catalysts were air-dried at room temperature for 48 h before they were analyzed for titanium content. A JOEL model JFM-35 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX) was used to determine the titanium distribution inside the catalyst pellets. The catalyst pellets were cut and analyzed at 5 different locations from the edge to the center of the pellet.

Experimental Results

Reaction Products

In the Tetralin experiments the main products of Tetralin hydrogenation on both catalysts were identified as cis-decalin and trans-decalin. Small amounts of naphthalene were detected in every experiment. We also found trace amounts of other compounds, a total of less than 1.0 %, in the sample oils. These compounds were identified as n-butylbenzene, n-butylcyclohexane, 1-methylindan, and 5-methylindan.

Two unidentified peaks having retention times between 1-methylindan and cis-decalin were observed in small quantities, a total of less than 2.0 %. Two compounds, 2-methylindan and 4-methylindan, were documented to be prepared from decalin by using a NiMo catalyst in the presence of hydrogen (27). We also found that the boiling points of these two compounds were between those of 1-methylindan and 5-methylindan. Based on these observations, we presume that these two unidentified peaks were 2-methylindan and 4-methylindan.

The results from decalin experiments showed that cis-decalin transformed to its isomer, trans-decalin. Trace amounts of methylindans, a total of less than 0.5 %, were also detected. A small amount of Tetralin was found in every sample, indicating that the reaction between Tetralin and decalin was reversible.

Blank experiments, conducted using alumina support instead of catalysts, showed that there was no observable conversion of the reactants, Tetralin and decalin, at our operating conditions. This indicated that the observed reactions were catalytic. Tetralin and decalin were stable at the operating conditions and were not subjected to thermal dissociation.

The presence of titanocene dichloride, either in the feedstock or on the impregnated catalysts, did not affect the formation of compounds at all. Every compound detected in non-titanocene dichloride experiments was also detected in titanocene dichloride experiments.

Reaction Mechanism

Figure 1 shows the reaction products and the reaction paths of Tetralin hydrogenation. Since naphthalene was found in every sample, it indicated that primary hydrogenation reaction of naphthalene was reversible and that naphthalene and Tetralin were believed to approach their equilibrium.

The main products of Tetralin hydrogenation in our experiments were cis- and trans-decalin. The predominant isomer of decalins was trans-decalin. There was no evidence to believe that Tetralin was hydrogenated to only one of the products. Even though cis-decalin was found to transform to trans-decalin in our experiments, the isomerization reaction of decalins was reported as a reversible reaction (28,29).

Boelhouwer et al. (29) also reported that an equilibrium mixture of decalins at 250-300 C (482-572 F) and 20.3 MPa (200 atm) of hydrogen atmosphere contained 90 % trans- and 10 % cis-isomer, regardless of the starting isomer.

Formation of n-butylbenzene occurred through a ring-opening mechanism and proceeded by hydrogenation of an unsaturated benzene ring which yielded n-butylcyclohexane as a final product. The amounts of n-butylbenzene and n-butylcyclohexane were very small and depended on the catalyst type.

Methylindans were expected to form directly from Tetralin rather than decalin. Even though methylindans could be prepared from decalin (27), we observed only trace amounts of methylindans in our decalin experiments. On the contrary, the amounts of methylindans found in Tetralin experiments were much more than those in the decalin experiments. 1-methylindan was reported to be found in the cracking products of Tetralin (5-22). It was also possible that other methylindan isomers were formed from Tetralin.

Kinetic Modeling

Tetralin hydrogenation reaction was reported earlier in the literature as a zero order reaction (3). Our derivation, based on the Langmuir-Hinshelwood expression, shows that the rate expression for Tetralin hydrogenation is

$$-r_T = \frac{k\left(C_T C_{H_2}^{1/2} - k' \frac{C_D}{(K_2 C_{H_2})^{5/2}} \right)}{\left(1 + K_1 C_T + K_2 C_{H_2} + K_3 C_D \right)^2}$$

This model was developed based upon the assumptions that the surface reaction is the rate controlling step and Tetralin and hydrogen are adsorped on the same type of site on the catalyst surface.

At our operating conditions, this rate expression can be reduced to a pseudo-first order rate expression with the assumption that hydrogen concentration does not change during the reaction (30). The rate expression is written as

$$-r_T = k'' C_T$$

Rates of reaction of products are also assumed pseudo-first order and are written as

$$-r_T = (k_2+k_3+k_6+k_8+k_9+k_{10})\ C_T$$

$$-r_{CD} = -\ k_2 C_T + k_4 C_{CD} - k_5 C_{TD}$$

$$-r_{TD} = -\ k_3 C_T - k_4 C_{CD} + k_5 C_{TD}$$

$$-r_{BB} = -\ k_6 C_T + k_7 C_{BB}$$

$$-r_{BC} = -\ k_7 C_{BB}$$

$$-r_{M1} = -\ k_8 C_T$$

$$-r_{M2} = -\ k_9 C_T$$

$$-r_{M4} = -\ k_{10} C_T$$

The rate constants were calculated directly from the rate expressions by using data obtained from Tetralin experiments with the exception of k_4 and k_5. The rates of isomerizaton of decalin, k_4 and k_5, were calculated from decalin experiments for both catalysts. It was assumed that cis- and trans-decalin were at chemical equilibrium with each other and that titanocene dichloride did not affect the rate of decalin isomerization. Table III summarizes the rate constants of decalin isomerization for NiMo/alumina and CoMo/alumina catalysts. Tables IV and V summarize the rate constants for both catalysts.

Discussion

In our experiments the overall conversion of Tetralin is defined as

$$\% \text{ conversion} = \left(1 - \frac{C_{T,out}}{C_{T,in}} \right) \times 100$$

where $C_{T,in}$ and $C_{T,out}$ are mole fractions of Tetralin in the inlet and outlet streams of the reactor.

Since it took the system approximately 6 hours to reach its steady state conditions, the mole fraction of the product samples taken at 8, 10 and 12 hours were averaged and used to represent the sample composition. These analyses were used to calculate the conversions.

Figure 2 shows the overall Tetralin conversion for NiMo/alumina and CoMo/alumina catalysts. It is clearly shown that the conversion of Tetralin on NiMo/alumina catalyst is higher than the conversion on CoMo/alumina catalyst. The conversion of Tetralin on NiMo/alumina catalyst is approximately 90 % while the conversion on CoMo/alumina catalyst is 63 %. The addition of titanocene dichloride to the reactant reduces the overall conversion on both catalysts. The reduction of conversion appears to be higher on the impregnated catalysts.

Our earlier study (25) showed that approximately 40 % of Tetralin was converted when it was hydrotreated in the trickle bed reactor over a NiMo/alumina catalyst. Unfortunately, those results could not be compared with the results in this work due to the differences in the presulfidation conditions of the catalyst. The catalysts used in this study were sulfided following a more severe condition than the ones used in earlier studies.

Figures 3 and 4 show comparisons of rate constants for NiMo/alumina and CoMo/alumina catalysts. In every case, the rate constants for NiMo/alumina catalyst are 3 to 10 times higher than the rate constants for CoMo/alumina catalyst. These results, combined with the overall conversion results, indicated that NiMo/alumina is a better catalyst for Tetralin hydrogenation than CoMo/alumina.

For NiMo/alumina catalyst, the addition of titanocene dichloride to the reactant reduces the rate constants for the formation of every compound except 1-methylindan, which appears to increase by a factor of 6, as shown in Figure 3. The reduction of rate constants is also observed on

CoMo/alumina catalyst with the exception of two rate constants. The rate constants of n-butylbenzene and n-butylcyclohexane are slightly higher when the reactant is doctored with titanocene dichloride, as shown in Figure 4. Figures 3 and 4 also indicate that both impregnated catalysts show a higher reduction of rate constants of every compound.

The analyses of the liquid products show no titanium in the product samples. However, the analyses of the catalyst samples show that titanium is deposited on the outer surface of the catalyst pellets for both impregnated catalysts and the catalysts taken from experiments with titanocene dichloride in the feedstock. Furthermore, the titanium concentration detected on the impregnated catalyst samples is relatively higher than those on the catalyst samples taken from the doctored runs.

A homogeneous reaction between Tetralin and titanocene dichloride was observed during the experiment. The reaction occurred in the feed tank and resulted in the formation of small particles suspended in the feedstock. Tscheikuna and Seapan (25) reported earlier that the suspended matter was an insoluble titanium compound which was the product of the Tetralin and titanocene dichloride reaction. This reaction resulted in the removal of titanium from the feedstock before it reached the catalyst. This observation would explain the lower titanium concentration on the catalyst samples taken from the experiments using the feedstock containing titanocene dichloride.

These results show that the presence of titanocene dichloride in the system, either on the impregnated catalysts or in the feedstock, results in the deposition of titanium on the outer surface of the catalysts. This deposited titanium covers the external surface of the catalyst resulting in an increase in mass transfer resistance to diffusion of reactants into catalyst pores, thus reducing the catalyst activity. The reduction of the catalyst activity depends on the amount of titanium deposited on the surface of the catalysts.

Since titanium is found to poison the catalyst, the increase in formation of n-butylbenzene and n-butylcyclohexane must have been caused by another factor. A homogeneous reaction between Tetralin and titanocene dichloride combined with cobalt on CoMo/alumina catalyst possibly generates an intermediate compound which helps accerelate the formation of n-butylbenzene. This conclusion is only a speculation, and the existence of this intermediate compound has not been proven. However, since formation of n-butylbenzene from Tetralin is a ring sission which can be accelerated by acidic groups, a chlorine compound resulting from titanocene dichloride decomposition may have been responsible for this reaction.

Conclusions

From our observations, we conclude that

1. Addition of titanocene dichloride to the feedstock or impregnation of catalysts with titanocene dichloride causes deposition of titanium on the external surface of the catalyst, resulting in a reduction of catalyst activity.
2. Addition of titanocene dichloride to the feedstock promotes the formation of 1-methylindan on NiMo/alumina catalyst and with the formation of n-butylbenzene and n-butylcyclohexane on CoMo/alumina catalyst.
3. Impregnation of alumina with titanocene dichloride or addition of titanocene dichloride to the feedstock in alumina run did not improve the hydrogenation activity of the alumina. Thus titanocene dichloride, by itself, does not have any catalytic activity in hydrogenation of Tetralin.

Acknowledgment

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NOTATION

C_i = Concentration of compound i in mole percent

k,k',k" = First order rate constant

K = Equilibrium constant

$-r_i$ = Rate of reaction of compound i

Subscript

BB = Butylbenzene

BC = Butylcyclohexane

CD = Cis-decalin

D = Decalin

H2 = Hydrogen

M1 = 1-Methylindan

M2 = 2-Methylindan

M4 = 4-Methylindan

T = Tetralin

TD = Trans-decalin

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TABLE I

PROPERTIES OF CATALYSTS

	Shell 324	Shell 344
Chemical Composition wt%		
Co	-	2.4
Ni	2.7	-
Mo	13.2	9.8
Physical Properties :		
Geometry	1.6 mm (1/16") extrudate	1.6 mm (1/16") extrudate
Surface area, m^2/kg	195E03	236E03
Pore Volume, m^3/kg	4.9E-04	6.0E-04
	ALUMINA	
Physical Properties :		
Geometry	1.6 mm (1/16") trilobe	
Surface area, m^2/kg	320E03	
Pore Volume, m^3/kg	8.1E-04	

TABLE II

TYPE OF CATALYSTS AND FEED STOCKS

RUN	CATALYST*	FEED**
1	324	T
2	324	T,TDC
3	324I	T
4	344	T
5	344	T,TDC
6	344I	T
7	Al	T
8	Al	T,TDC
9	Al I	T
10	324	D
11	344	D
12	Al	D

* 324 - SHELL 324 (NiMo/alumina)
344 - SHELL 344 (CoMo/alumina)
324I - Impregnated SHELL 324
344I - Impregnated SHELL 344
Al - Alumina Support
Al I - Impregnated Alumina Support

** T - Tetralin
D - Decalin
TDC - Titanocene Dichloride

TABLE III

RATE CONSTANTS FOR ISOMERIZATION OF DECALIN

Rate Constant (mole/gm. of cat. sec)	Shell 324	Shell 344
k_4 x 1E06	2.66	3.41
k_5 x 1E07	3.12	3.99

TABLE IV

RATE CONSTANTS FOR SHELL 324
FEEDSTOCK : TETRALIN

* Rate Constant (mole/gm. of cat. sec)	W/O TDC	W/ TDC	IMP.CAT
k_2 x 1E06	6.13	4.90	3.43
k_3 x 1E05	2.23	1.53	0.93
k_6 x 1E07	2.00	1.10	0.83
k_7 x 1E06	1.42	1.26	1.22
k_8 x 1E07	0.46	3.16	0.23
k_9 x 1E07	3.86	2.58	1.77
k_{10} x 1E07	1.02	0.75	0.53

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

TABLE V

RATE CONSTANTS FOR SHELL 344
FEEDSTOCK : TETRALIN

Rate Constant* (mole/gm. of cat. sec)	W/O TDC	W/ TDC	IMP.CAT
$k_2 \times 1E06$	2.06	1.43	1.15
$k_3 \times 1E06$	2.96	1.83	1.47
$k_6 \times 1E08$	3.16	4.02	2.27
$k_7 \times 1E07$	6.39	8.00	4.49
$k_8 \times 1E09$	9.90	9.10	6.59
$k_9 \times 1E08$	6.98	6.21	4.47
$k_{10} \times 1E08$	2.02	1.65	1.25

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

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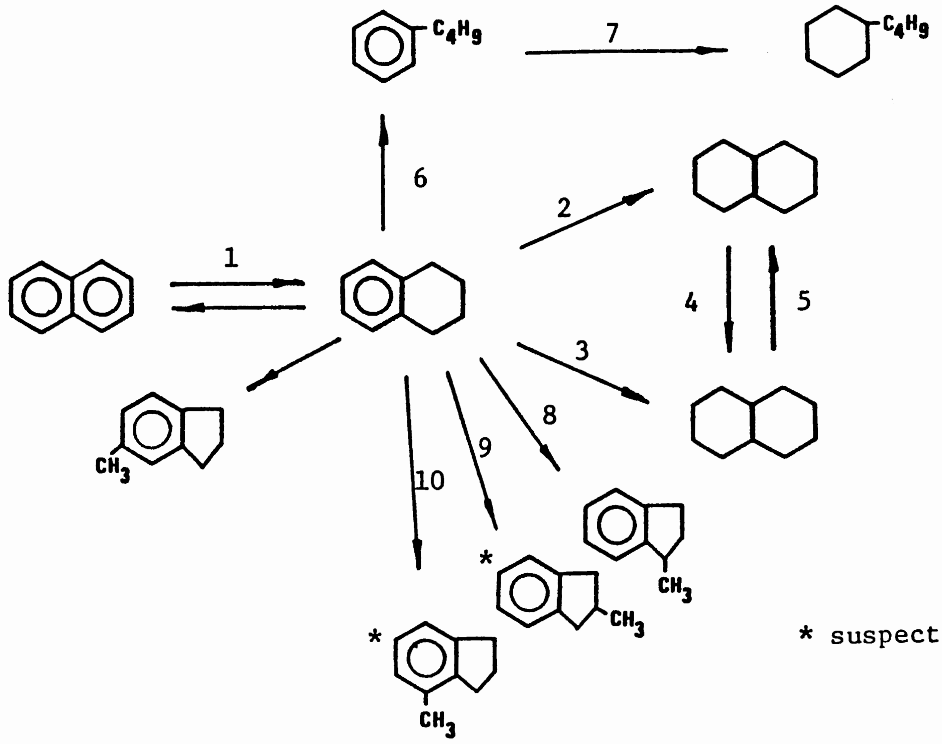

* suspected to be present

Figure 1. Schematic Diagram of Reaction Mechanism

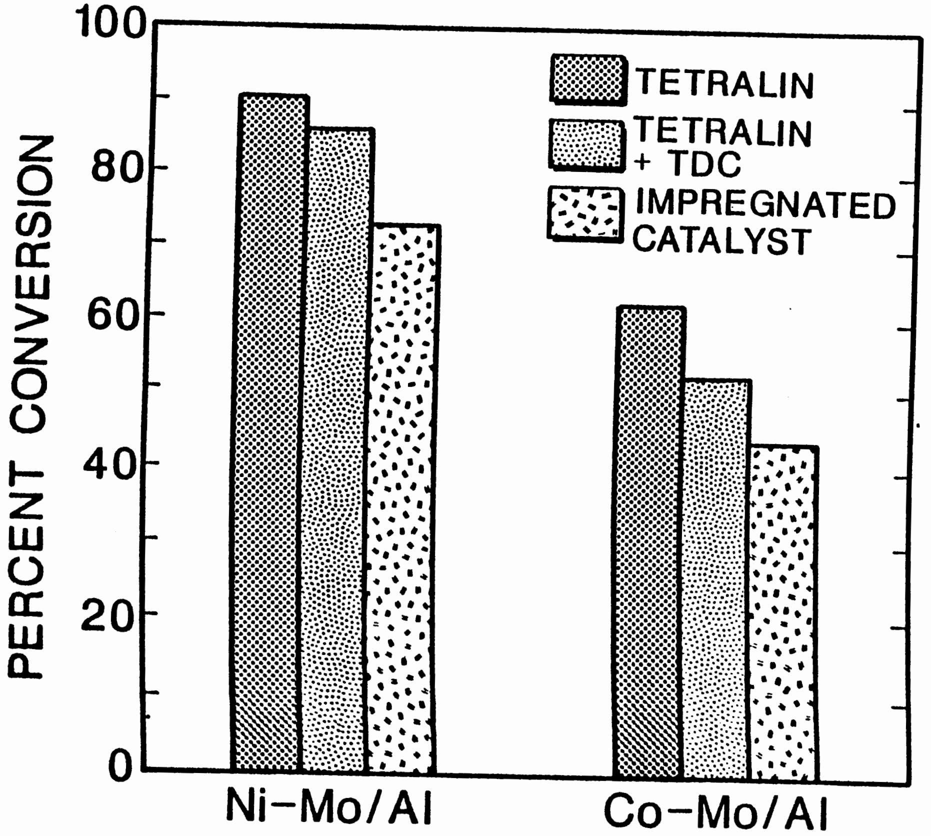

Figure 2. Effect of Titanocene Dichloride on Tetralin Conversion

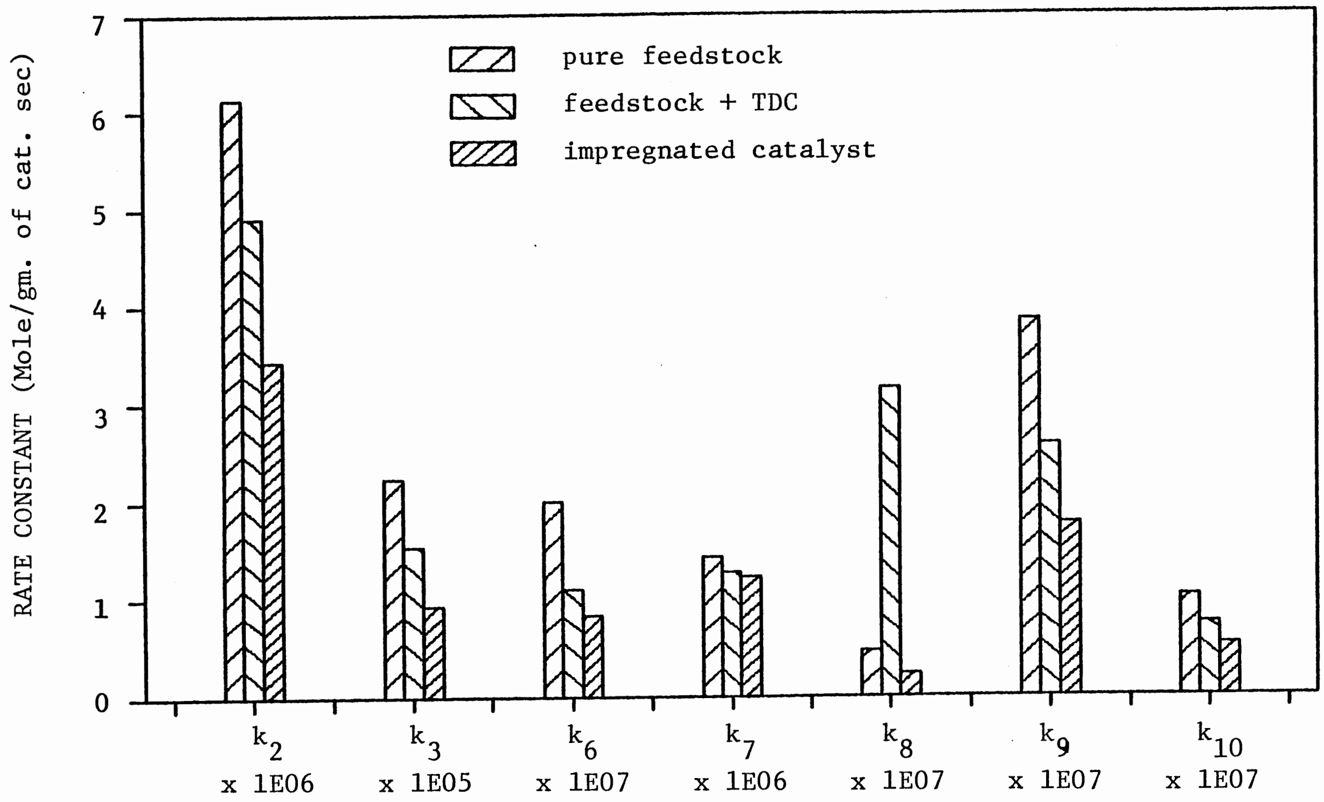

Figure 3. Effect of Titanocene Dichloride on Rate Constants for NiMo/alumina Catalyst

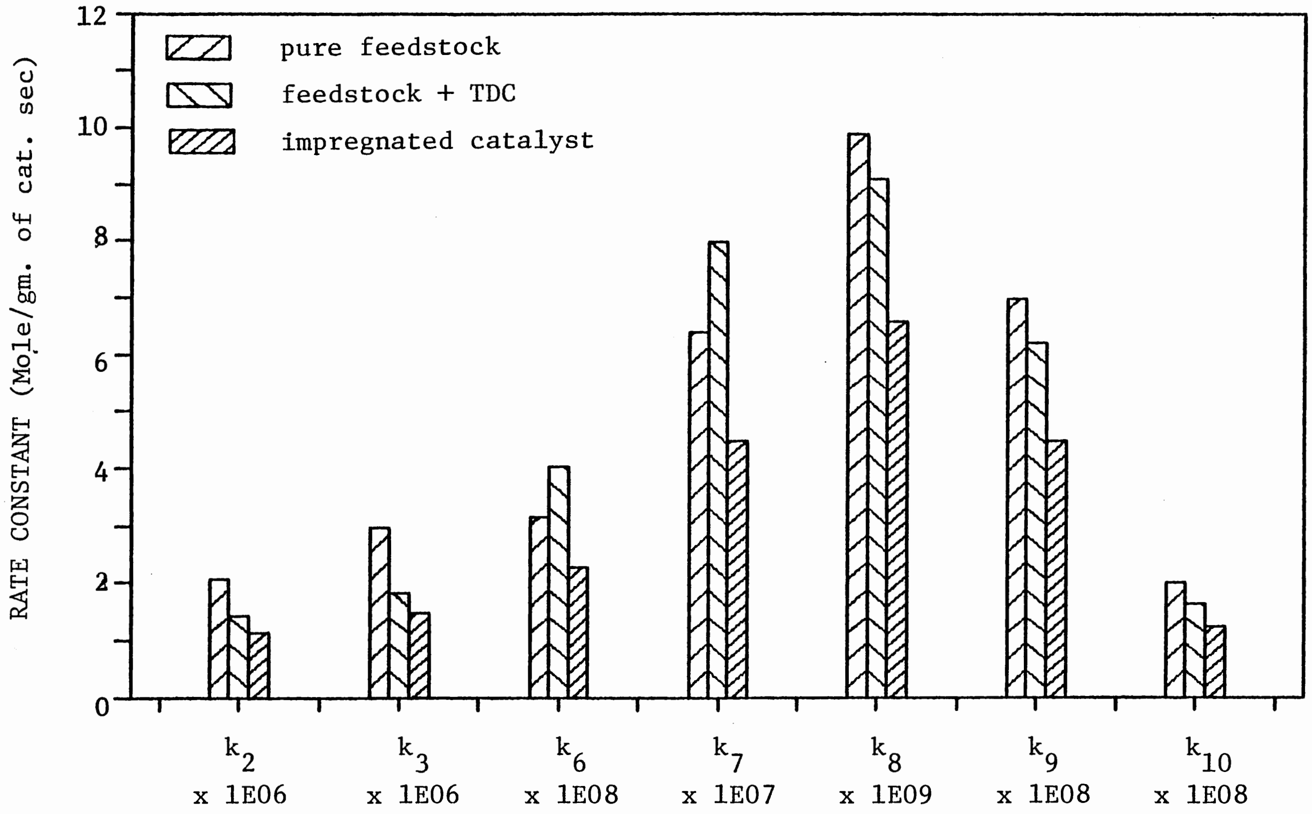

Figure 4. Effect of Titanocene Dichloride on Rate Constants for CoMo/alumina Catalyst

CHAPTER IV

EFFECT OF TITANOCENE DICHLORIDE ON COKING OF HYDROTREATING CATALYSTS

EFFECT OF TITANOCENE DICHLORIDE ON COKING
OF HYDROTREATING CATALYSTS

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ABSTRACT

In hydrotreatment of an SRC coal liquid, addition of titanocene dichloride to the feedstock increased catalyst activity and reduced catalyst coking. In order to understand the role of titanocene dichloride, hydrogenation of Tetralin over alumina, NiMo/alumina and CoMo/alumina catalysts was studied. The experiments were conducted under 10.4 MPa (1500psig) and 350 C (662 F) in a gradientless. recycle reactor with Berty-type internals. The role of titanocene dichloride was studied in two modes. The catalyst was impregnated with titanocene dichloride and its activity and coking tendency were compared with those of unimpregnated catalyst. In the second series of experiments, the catalyst activity and its coking characteristics were studied when the oil was doctored with titanocene dichloride and compared with the undoctored runs. On both catalysts, titanium from titanocene dichloride was found to be deposited on the outer surface of the catalyst pellets, resulting in reductions in catalyst activity and catalyst coking. Titanocene dichloride increases the catalyst activity and reduces the catalyst coking on catalysts with low level of sulfidation.

EFFECT OF TITANOCENE DICHLORIDE ON COKING OF HYDROTREATING CATALYSTS

Introduction

Catalyst deactivation is one of the major problems in catalytic hydrotreatment processes. There are two major mechanisms involved in catalyst deactivation. Coke formation on the catalyst surface results in the plugging of the catalyst pores by carbonaceous material. This obstruction of the pores increases the mass transfer resistance and reduces the rate of transfer of the reactants to the active sites of the catalyst. Trace metal impurities in the feedstock can permanently deposit on the active sites of the catalyst and block them. Studies on deactivation of hydrotreatment catalysts under coal liquefaction conditions show that the deposition of carbonaceous material is the major factor in deactivation of the catalysts, while the deposition of metal impurities is considered to have a long term deactivation effect (1,2).

Titanium is a trace metal commonly found in coals and is shown to also exist in coal-derived liquids. Many investigators (3-6) have suggested that different forms of titanium compounds are present in coal-derived liquids. McGinnis (3) suggested that titanium in coal liquids was in the form of organic complexes composed of aromatic rings connected with low molecular weight aliphatic bridges. Filby et al. (7) proposed that stable organometallic compounds like titanocene dichloride are formed during coal liquefaction processes.

Organometallic compounds are known to affect catalyst coking. Chan et al. (8) doctored bis-cyclopentadienyl titanium dichloride (titanocene dichloride) to an SRC-II coal liquid and hydrotreated it over a NiMo/alumina catalyst in a trickle bed reactor. They found that the amount of coke formed on the catalyst was reduced and the catalyst activity was increased. The catalyst activity enhancement depended on the concentration of titanocene dichloride. Titanium concentrations of 100 to 200 ppm showed the best promotion of the catalyst activity.

Our earlier studies (9), which were conducted on hydrogenation of Tetralin (tetrahydronaphthalene) and a mixture of Tetralin and phenanthrene in a trickle bed reactor over a NiMo/alumina catalyst, also showed that the addition of titanocene dichloride to the feedstock affected both the coke formation on catalyst and hydrogenation activity of the catalyst. The effects depended on the type of hydrocarbon feedstock. We also found a homogeneous reaction between Tetralin and titanocene dichloride which resulted in the decomposition of titanocene dichloride and the formation of an insoluble titanium compound. The decomposition of titanocene dichloride was suspected to generate some free radicals or other intermediate compounds which would interfere with coke formation and change the hydrogenation mechanisms.

In this project the role of titanocene dichloride on catalyst coking and Tetralin hydrogenation was studied over commercial alumina, NiMo/alumina, and CoMo/alumina catalysts. The experiments were conducted in a gradientless recycle reactor with Berty-type internals. The studies were divided into two series. In the first series, the catalyst activity and its coking characteristics were studied when Tetralin was doctored with titanocene dichloride (100 ppm of titanium). In the second series, the catalyst was impregnated with titanocene dichloride and was used to hydrotreat the pure feedstock. These results were compared with the results from the experiments using the pure feedstock and fresh catalysts. Additional studies on coke suppression phenomenon due to catalyst sulfidation was also conducted.

Experimental Procedures

Equipment and Procedures

The experiments were conducted in a gradientless recycle reactor with Berty-type internals. The reactor has an internal volume of 300 cm^3. Hydrogen gas and liquid feed flow into the bottom of the reactor where they are mixed by means of a high speed magnedrive. Product oils and gases flow through the opening at the reactor cap to the sample bomb where gases and liquid oils are separated. Details of the reactor system are described elsewhere (10).

Tetralin, obtained from Aldrich Chemicals, was 98.8 % pure and was used as received. The impurities were eventially cis- and trans- decalin and naphthalene. The catalysts were commercial NiMo/alumina, CoMo/alumina, and alumina. The properties of these catalysts are shown in Table I. The NiMo/alumina and the CoMo/alumina catalysts were obtained from the Shell Chemical Co. and the alumina was the SN6313 alumina substrate obtained from the American Cyanamid Company.

Table II summarizes the type of feed oil, type of catalyst, and sulfidation state of the catalyst for each experiment. The catalyst was sulfided by passing a mixture of 5 % hydrogen sulfide in hydrogen through the catalyst bed at a pressure of 6.5 kPa (80 psig) and a gas flow rate of 24 l/h (400 ml/min). Two different sulfidation procedures were used in these experiments. Under low presulfidation condition, the catalyst temperature was maintained at 250 C (482 F) for 1 h. In high presulfidation condition, the catalyst was heated under hydrogen sulfide from 250 C (482 F) to 360 C (680 F) at a rate of 60 C/h (1 C/min) and maintained at 360 C (680 F) for 2 h. The total presulfidation time for high presulfidation condition was approximately 4 h.

The liquid samples were taken every 2 h during the 12 hour-experiment. The catalyst sample was taken after the reactor was shut down and was allowed to cool to room temperature. The catalyst sample was a mixed sample of the catalyst from the basket and was used to represent the average catalyst in the basket.

The experiments were conducted at 10.4 MPa (1500 psig) and 350 C (662F). The hydrogen flow rate was maintained at 24 l/h (400 ml/min) and the liquid feedstock flow rate was set at 30 ml/h. The megnedrive was operated at 1500 rpm.

Sample Analyses

The liquid samples were analyzed by a Hewlett Packard Model 5890A Gas Chromatograph equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was integrated and recorded by a Hewlett Packard Integrator Model 3392A.

The catalyst samples were extracted with tetrahydrofuran in a Soxhlet extraction unit for 24 h to remove any remaining oil from the catalyst pores. The extracted samples were dried at room temperature for at least 24 h. The catalyst samples were analyzed for coke content and titanium distribution in the pellet. The coke content was defined as the weight percent of loss of carbonaceous material by burning the catalyst at 550 C (1022 F) in air for 60 h. The catalyst pellet was analyzed for titanium distribution by using a JEOL Model JFM-35 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX). The samples were analyzed at several locations from the edge to the center of the pellets.

Catalyst Impregnation

The fresh catalyst was impregnated with titanocene dichloride before each experiment. 20 grams of catalyst was placed in 50 grams of 0.75 wt% titanocene dichloride in methyl isobutyl ketone (MIBK) solution for 24 h. The catalyst was allowed to dry at room temperature for at least 24 h before it was packed in the reactor.

At the end of the impregnation period, there was no titanocene dichloride left in the solution. However a homogeneous reaction between titanocene dichloride and MIBK was observed during this impregnation period. This homogeneous reaction resulted in the formation of an insoluble compound similar to the one observed in the reaction between titanocene dichloride and Tetralin which was reported by Tscheikuna and Seapan (9) and a decrease in the amount of titanocene dichloride in the solution. If all titanocene dichloride is assumed to deposit on the catalyst, it would represent an average of 0.36 % titanium deposited on the catalyst. In comparison, in the runs doctored with 100 ppm of titanium as titanocene dichloride, the average titanium deposited on the catalyst would correspond to 0.18 %.

Results and Discussion

Catalyst samples from selected experiments were analyzed for titanium distribution inside the catalyst pellets. The sample pellets were selected randomly from the top layer of the catalyst bed. Each sample was analyzed for overall titanium content on the outer surface of the pellet and also at 5 different locations from the edge to the center of the catalyst pellet.

For impregnated catalysts the analyses show that titanium deposits only on the outer surface of NiMo/alumina and CoMo/alumina catalysts. On the other hand, the alumina catalyst showed a uniform distribution of titanium throughout the catalyst pellet. Titanocene dichloride is known to react with many compounds even at room temperatures. In the presence of NiMo/alumina and CoMo/alumina catalysts, titanocene dichloride reacts quickly with the catalyst. The reaction is so fast that it does not allow the titanocene dichloride to penetrate into the catalyst pores, which resulted in deposition of titanium only on the outer surface of the catalyst. Figure 1 shows the profile of titanium deposited in the catalyst pellets.

The analyses of the catalyst samples taken from the doctored runs also showed that titanium deposited only on the surface of the catalyst. The concentration of titanium detected in this case was relatively lower than those on the impregnated catalysts.

Figure 2 shows a comparison of the coking results of the catalysts taken from experiments using the pure feedstock, the feedstock doctored with titanocene dichloride and the impregnated catalysts. These coking results do not take into account the change in the catalyst weight due to the change from sulfided state to oxided state during combustion of coke. This weight change reduces the catalyst weight by approximately 3 %. If this change of state is considered, all the coke contents should be increased by 3. However, since the true extent of sulfidation and oxidation is not clear, the corresponding weight change is not included in our results.

In these experiments the catalysts were sulfided using high presulfidation conditions. The results show that the addition of titanocene dichloride to the feedstock or the impregnation of the catalysts with titanocene dichloride reduces coke formation on NiMo/alumina and alumina catalysts. The coke reduction observed on the impregnated catalysts was higher than those on the catalysts taken from the experiments using the doctored feedstock. For CoMo/alumina catalyst, the presence of titanocene dichloride in the system, either in the feedstock or on the impregnated catalyst, increases coke formation on the catalyst. The amount of coke on the impregnated catalyst was less than the one taken from the experiment using doctored feedstock. These results indicate that coke reduction due to the presence of titanocene dichloride depends on the type of catalyst.

Figure 3 shows the overall conversion of Tetralin for NiMo/alumina, CoMo/alumina, and alumina catalysts. The presence of titanocene dichloride reduces the conversion of Tetralin in all cases. The reduction of Tetralin conversion is higher when the catalysts are impregnated with titanocene dichloride. It also shows that NiMo/alumina catalyst gives higher Tetralin conversion than CoMo/alumina catalyst. The conversion of Tetralin on alumina catalyst is very small when it is compared with the conversions on NiMo/alumina and CoMo/alumina catalysts. One can assume that there is no conversion on the alumina catalyst.

These results indicate that titanium from titanocene dichloride covers the outer surface of the catalyst pellets. This titanium coverage increases the mass transfer resistance into the pores of the catalyst, resulting in a reduction of the rate of transfer of the reactants. This reduction of the mass transfer rate reduces the amount of the reactant being transferred to the catalytic sites which in turn reduces the total conversion of the reactant. For NiMo/alumina and alumina catalysts, because the reaction on the surface of the catalyst is reduced, coke formation is also reduced.

This observation indicates that coke formation on NiMo/alumina and alumina catalysts is parallel with the reaction of Tetralin. On the contrary, coke on CoMo/alumina catalyst must be generated by a different mechanism since the presence of titanocene dichloride reduces the conversion but increases coke formation.

The analysis of catalyst surface area, shown in Figures 4 and 5, indicated that titanocene dichloride reduces surface area of impregnated NiMo/alumina catalyst but does not show any effect on impregnated CoMo/alumina catalyst. The coked catalyst samples showed increase in surface areas when titanocene dichloride was in the system. The catalysts regained their original surface area after regeneation.

A set of experiments, listed in Table II as runs 10-13, was conducted to study the effect of catalyst presulfidation conditions on coke formation. The catalyst was NiMo/alumina and was sulfided following the procedure for the low presulfidation condition. The feedstocks used in this set of experiments were Tetralin and 0.5 wt% carbon disulfide in Tetralin. Carbon disulfide was added to maintain the catalyst sulfidation condition. The experiments were also conducted when both feedstocks were doctored with titanocene dichloride. The results of these experiments are compared with the ones in which the catalyst was sulfided following the high presulfidation condition.

Figure 6 shows a comparison of the coking results of this set of experiments along with the ones with high presulfidation condition. The results show that the addition of carbon disulfide to the feedstock does not affect the amount of coke formed on the catalyst.

Comparison between the two presulfidation conditions shows that coke formation on the catalyst is reduced when the catalyst presulfidation is extended.

When titanocene dichloride is added to the feedstocks, runs 11 and 13, coke formation on the catalyst is reduced drastically. The coke reduction of the run using Tetralin as a feedstock is more significant than the one using a mixture of carbon disulfide and Tetralin as a feedstock. The results of the runs using high presulfidation condition catalyst also show that titanocene dichloride slightly reduces coke formation on the catalyst. The catalysts were extensively presulfided in these cases. These results indicate that coke reduction due to titanocene dichloride depends on the extent of catalyst presulfidation.

The conversion results, shown in Figure 7, indicate that the overall conversion of Tetralin depends on the presulfidation condition of the catalyst. The catalysts with extensive presulfidation give higher conversion of Tetralin than the ones having the low presulfidation condition. This result indicates that hydrogenation of Tetralin over NiMo/alumina catalyst requires sulfided active sites on the catalyst surface. The low presulfidation condition converted only a fraction of oxided catalyst when it was compared with the high presulfidation condition.

Comparison of the results of runs 10 through 13 shows that the conversions of the runs in which carbon disulfide was added to the feedstock are slightly higher than those without carbon disulfide. Carbon disulfide caused in situ sulfidation of the catalyst during the experiment.

The addition of titanocene dichloride reduces the conversion of pure Tetralin but increases the conversion of a mixture of carbon disulfide and Tetralin. This result indicates that, in the absence of carbon disulfide, titanocene dichloride deposits and poisons the active sites of the catalyst. When carbon disulfide is added to the feedstock, titanocene dichloride can react with carbon disulfide forming titanium sulfide. Titanium sulfide then probably acts as a catalyst and improves the catalyst activity. Further investigation of this observation has to be conducted to confirm the role of titanium sulfide in Tetralin hydrogenation.

Conclusions

1. Titanocene dichloride, when used to impregnate the catalyst or when added to the oil, forms a layer of titanium covering the external surface of the CoMo/alumina and NiMo/alumina catalysts but forms a uniform deposit in the pores of alumina support.
2. This shell of titanium reduces the diffusion of reactants into catalyst pores, reducing both the catalyst activity and catalyst coking.
3. On catalysts with low levels of sulfidation, titanocene dichloride may simultaneously increase the activity and decrease the catalyst coking, probably due to titanium

sulfide formation.

Acknowledgment

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Surface area, m^2/kg	195E03	236E03
Pore Volume, m^3/kg	4.9E-04	6.0E-04

	ALUMINA
Physical Properties :	
Geometry	1.6 mm (1/16") trilobe
Surface area, m^2/kg	320E03
Pore Volume, m^3/kg	8.1E-04

TABLE II

TYPE OF CATALYSTS AND FEED STOCKS

RUN	CATALYST*	SULFIDATION**	FEED***
1	324	B	T
2	324	B	T,TDC
3	324I	B	T
4	344	B	T
5	344	B	T,TDC
6	344I	B	T
7	Al	-	T
8	Al	-	T,TDC
9	Al I	-	T
10	324	A	T
11	324	A	T,TDC
12	324	A	T,CS
13	324	A	T,CS,TDC

* 324 - SHELL 324 (NiMo/alumina)
344 - SHELL 344 (CoMo/alumina)
324I - Impregnated SHELL 324
344I - Impregnated SHELL 344
Al - Alumina Support
Al I - Impregnated Alumina Support

** A - Low Presulfidation
B - High Presulfidation

*** T - Tetralin
TDC - Titanocene Dichloride
CS - Carbon Disulfide

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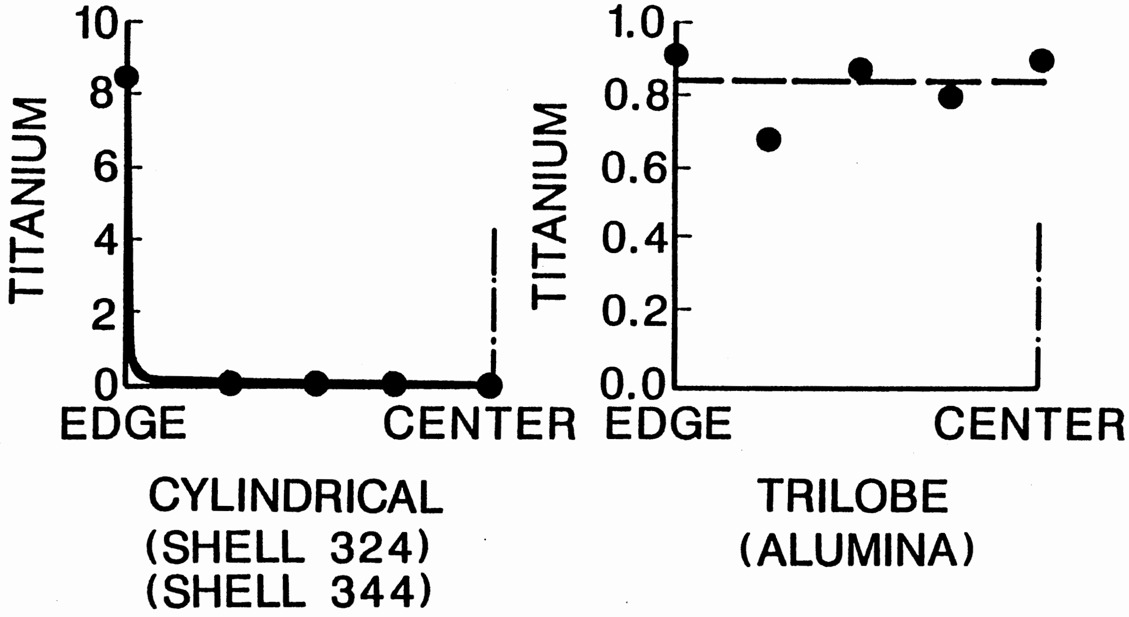

Figure 1. Profile of Titanium Deposited in Catalyst Pellets (Titanium Concentration in Arbitrary Units)

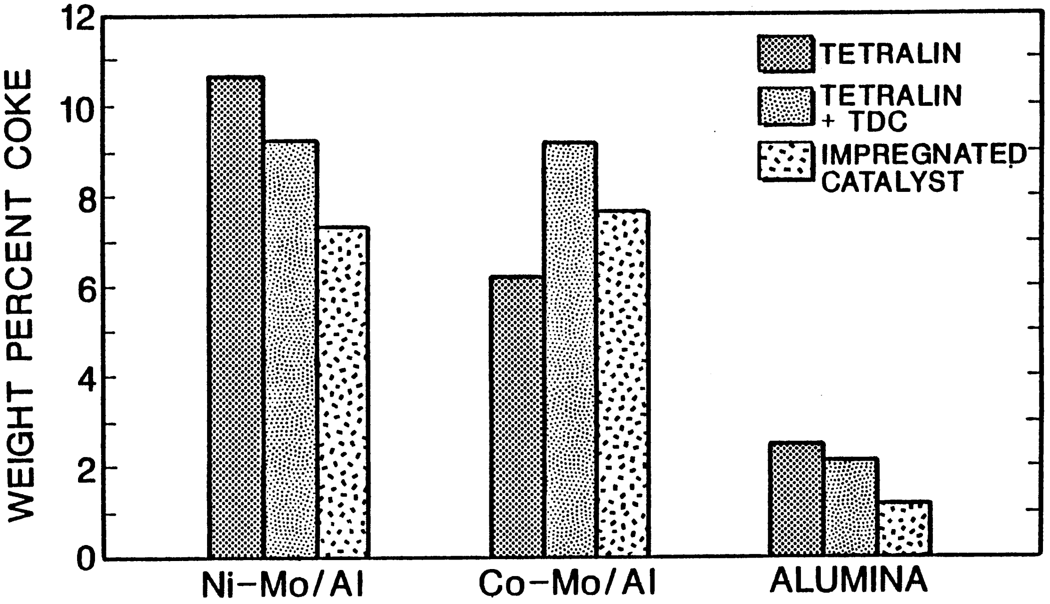

Figure 2. Effect of Titanocene Dichloride on Catalyst Coking

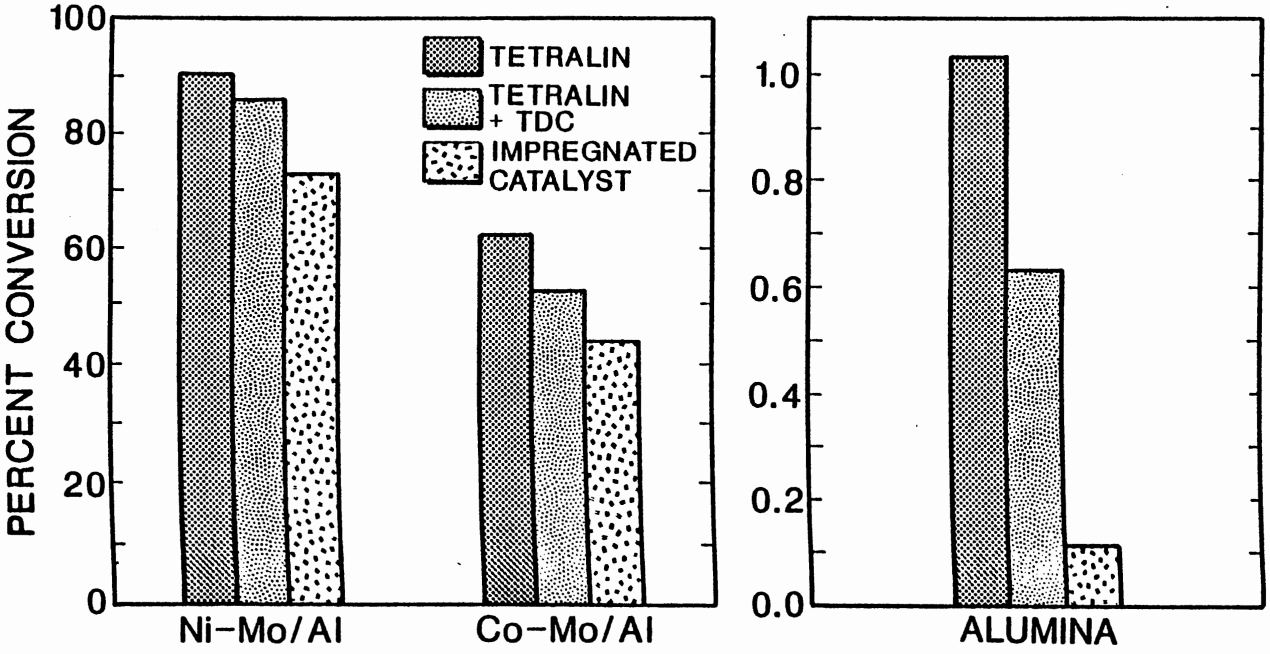

Figure 3. Effect of Titanocene Dichloride on Tetralin Conversion

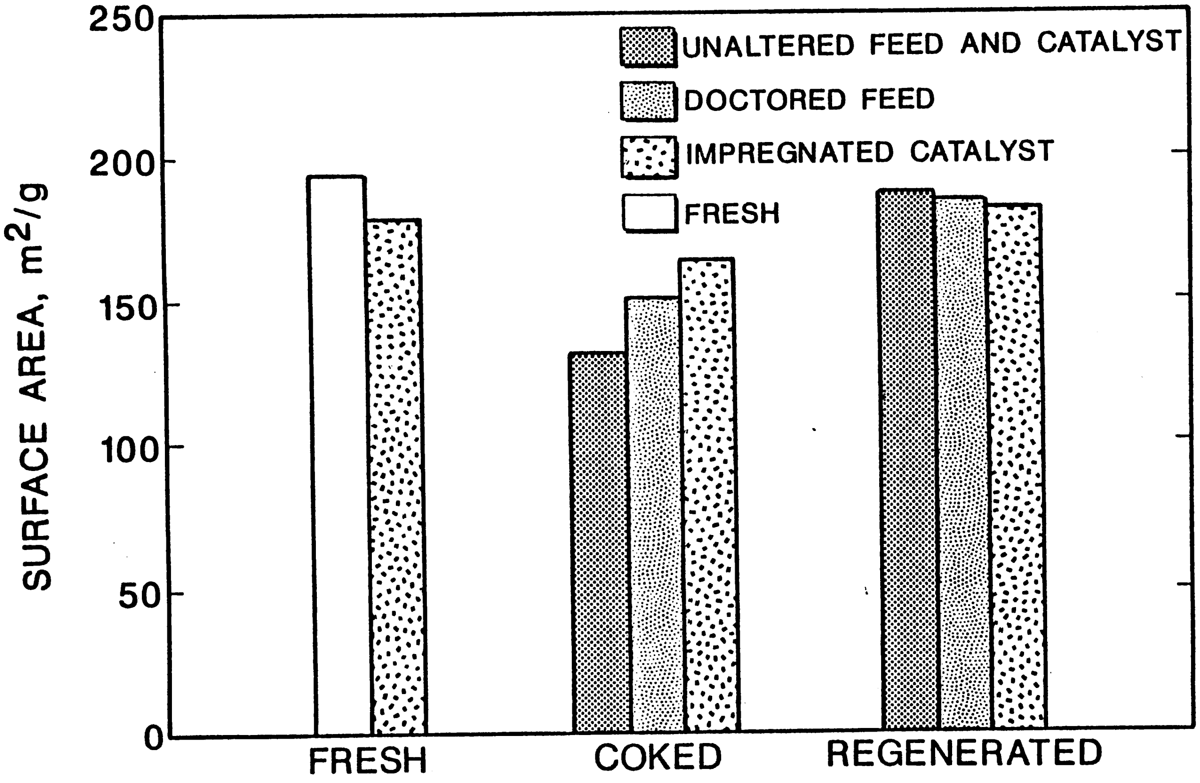

Figure 4. Effect of Titanocene Dichloride on Catalyst Surface Area (NiMo/alumina)

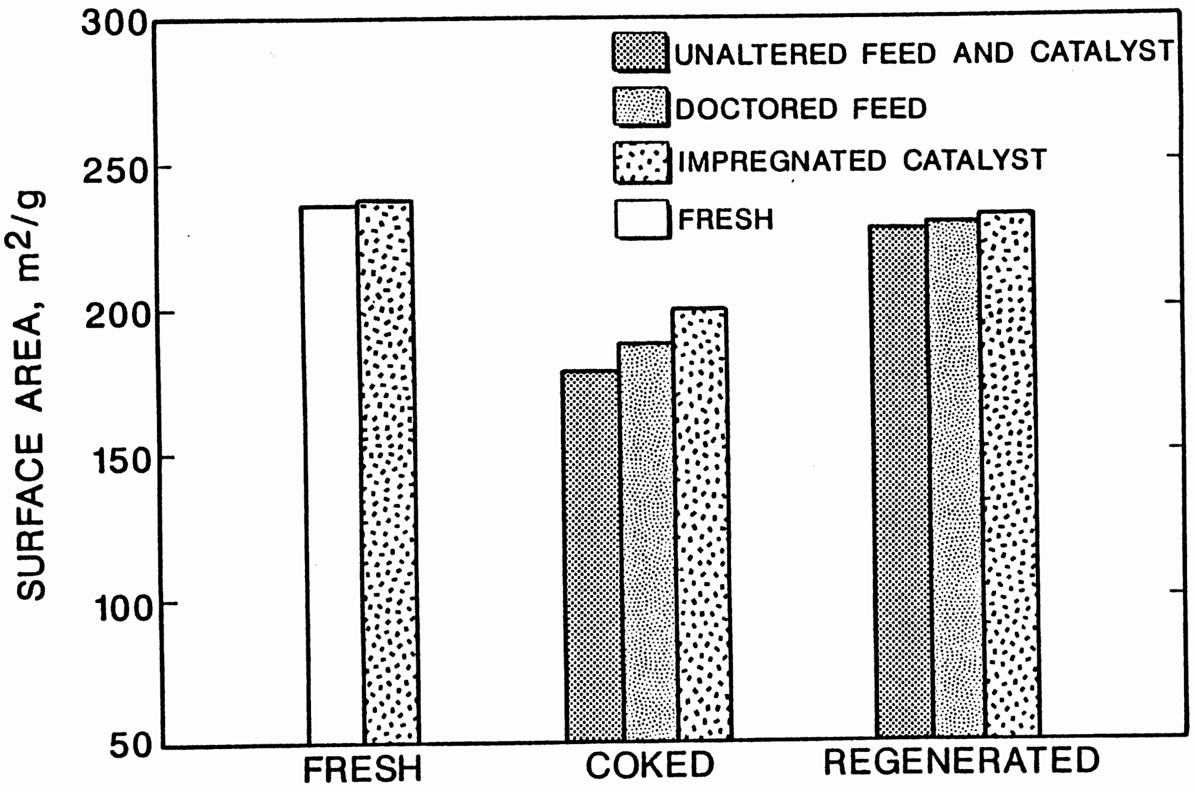

Figure 5. Effect of Titanocene Dichloride on Catalyst Surface Area (CoMo/alumina)

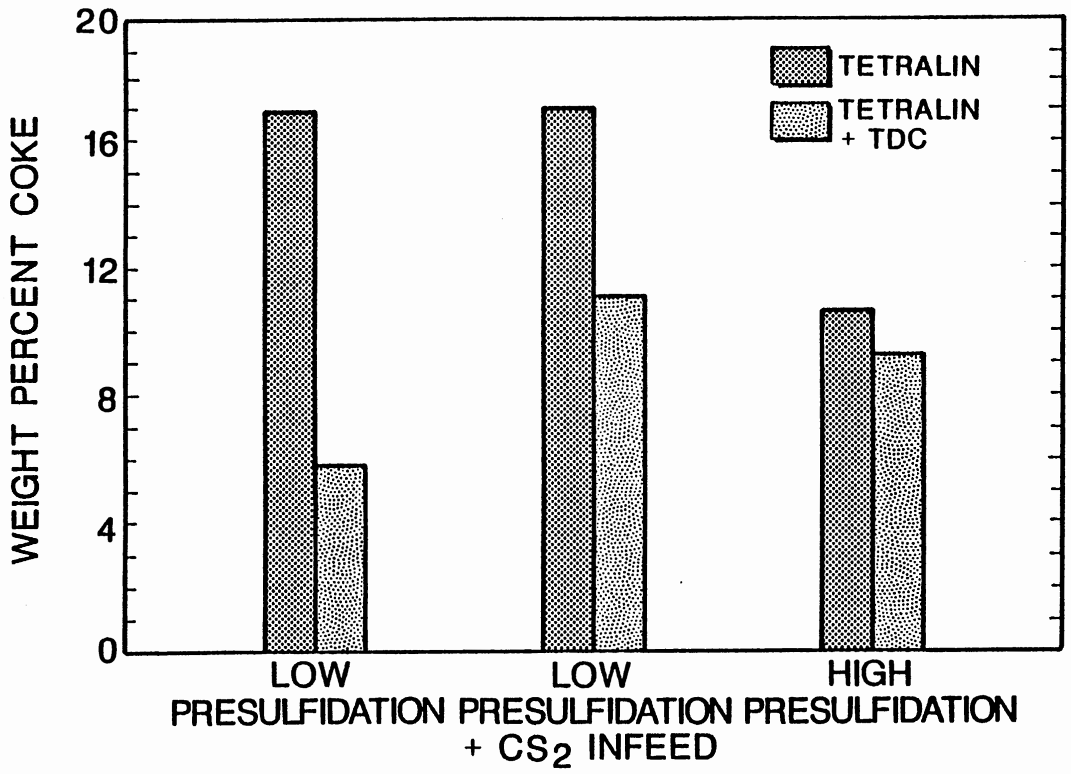

Figure 6. Effect of Titanocene Dichloride and Sulfidation on Catalyst Coking

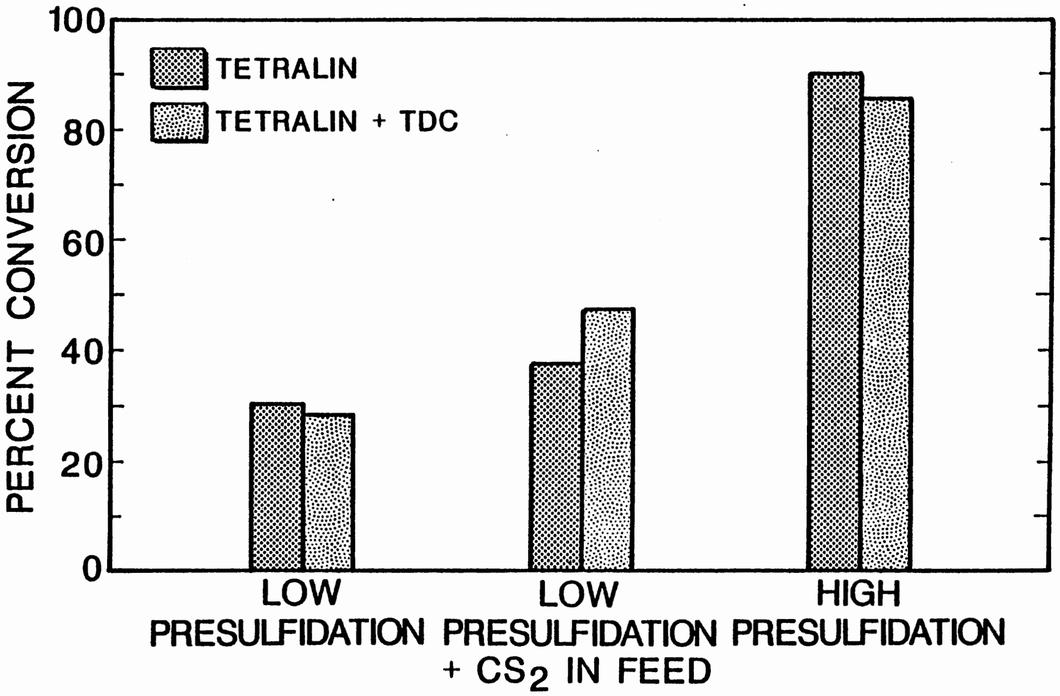

Figure 7. Effect of Titanocene Dichloride and Sulfidation on Tetralin Conversion

CHAPTER V

EFFECTS OF METHYL ISOBUTYL KETONE, QUINOLINE, AND TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

EFFECTS OF METHYL ISOBUTYL KETONE, QUINOLINE, AND TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

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ABSTRACT

The effects of methyl isobutyl ketone (MIBK), quinoline, and titanocene dichloride on hydrogenation of Tetralin and catalyst coking were studied over NiMo/alumina and CoMo/alumina catalysts. The addition of MIBK into Tetralin slightly reduces the conversion of Tetralin but the addition of quinoline into the feedstock drastically reduces the conversion of Tetralin. Titanocene dichloride appears to form a layer of titanium on the catalyst surface. The combined effects of titanocene dichloride and MIBK result in a reduction of catalyst coking on NiMo/alumina catalyst.

EFFECTS OF METHYL ISOBUTYL KETONE, QUINOLINE, AND TITANOCENE DICHLORIDE ON HYDROGENATION OF TETRALIN

Introduction

This work is a continuation of the study on hydrogenation of Tetralin and the effect of titanocene dichloride on the catalyst activity and catalyst coking. In this study, the effects of methyl isobutyl ketone (MIBK), quinoline and titanocene dichloride on hydrogenation of Tetralin and on catalyst coking were studied over alumina, NiMo/alumina, and CoMo/alumina catalysts in a gradientless reactor with Berty type internals. The feedstocks were 7.5 wt % methyl isobutyl ketone (MIBK) in Tetralin (tetrahydronaphthalene) and in decalin (decahydronaphthalene) and 10 wt % quinoline in Tetralin-MIBK and decalin-MIBK solutions. The studies of the effect of titanocene dichloride were divided into two series. In the first series, the feedstocks were doctored with 100 ppm of titanium as titanocene dichloride and hydrotreated. In the second series, the catalysts were impregnated with titanocene dichloride and used to hydrotreat the model feedstocks. The results of these experiments were compared with the results of the experiments using pure model compounds and unimpregnated catalysts. The experiments using the mixtures of decalin as the feedstocks were conducted to obtain the necessary kinetic information.

The effect of MIBK, quinoline and titanocene dichloride on the Tetralin conversion and the catalyst coke contents catalysts are presented. These results are compared with the results of the pure Tetralin experiments taken from a separate work (1). The effect of titanocene dichloride on rate constants is also discussed.

Experimental Procedures

Equipment and Procedure

The experiments were conducted in a gradientless recycle reactor with Berty-type internals. The reactor has an internal volume of 300 cm3. Hydrogen gas and liquid feed flow into the bottom of the reactor where they are mixed by a magnedrive. Product oils and gases flow through the opening in the reactor cap to the sampling bombs where the gases and the liquid oils are separated. The details of the gradientless reactor are described elsewhere (2).

Tetralin, obtained from Aldrich Chemicals, was 98.8 % pure by our analysis and was used as received. The impurities in Tetralin were mainly naphthalene, cis-decalin and trans-decalin. Decalin, obtained from Alfa Products, was a mixture of approximately 53.4 % trans-decalin and 46.6 % cis-decalin. It was used without further purification. Quinoline, obtained from Fisher Products, was 95 % pure and MIBK was 98 % pure. The impurity in quinoline was isoquinoline. Both compounds were used as received. The catalysts were commercial alumina, NiMo/alumina and

CoMo/alumina catalysts. NiMo/alumina (Shell 324) and CoMo/alumina (Shell 344) catalysts were obtained from Shell Chemical Co. and alumina catalyst was SN6313 alumina substrate obtained from American Cyanamid Company. In each experiment twenty grams of catalyst was used. The properties of the catalysts are shown in Table I.

Before each experiment, the catalyst was calcined inside the reactor by heating the catalyst to 300 C (572 F) under nitrogen atmosphere. The temperature was maintained at 300 C (572 F) for 2 h under nitrogen flow rate of 24 l/h (400 ml/min) and at 2.07 MPa (300 psig). The catalyst was allowed to cool down to 250 C (482 F) under nitrogen gas before it was sulfided with a mixture of 5% hydrogen sulfide in hydrogen at a pressure of 551 kPa (80 psig) and flow rate of 24 l/h (400 ml/min). During sulfidation, the catalyst was heated from 250 to 360 C (482 to 680 F) at a rate of 60 C/h (1 C/min) and was then maintained at 360 C (680 F) for 2 h. The total presulfidation time was approximately 4 h.

The experiments were conducted at 10.4 MPa (1500 psig) and 350 C (662 F). The hydrogen flow rate was maintained at 24 l/h (400 ml/min). Liquid feed flow rate was set at 30 ml/h. The magnedrive was operated at 1500 rpm. The duration of each experiment was 12 h, and the liquid samples were taken every 2 h. Table II summarizes the type of the feed oils and the type of the catalysts used in each experiment.

Sample Analyses

The liquid samples were analyzed qualitatively and quantitatively by a Hewlett Packard Model 5890A Gas Chromatograph equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was integrated and recorded by a Hewlett Packard Integrator Model 3392A. The compounds were identified by comparing the retention times of the liquid samples with the retention times of known compounds. Some compounds were also further confirmed by a combined gas chromatograph / mass spectrometer. Table III shows the identified compounds in the samples and the techniques which was used to identify the compounds. The titanium contents of the liquid samples were analyzed by a Perkin Elmer 503 Atomic Absorption Spectrophotometer.

After completion of each experiment, the catalyst was sampled and extracted with tetrahydrofuran in a Soxhlet extraction unit for 24 h. The extracted samples were air-dried for 48 h before analyzing for coke content and titanium distribution in the catalyst pellet. The coke content was defined as the weight percent of loss of carbonaceous material by burning the catalyst at 550 C (1022 F) in air for 60 h. The catalyst pellet was analyzed for titanium distribution by a JEOL Model JFM-35 Scanning Electron Microscope equipped with an Energy Dispersive X-ray Analyzer (EDAX). The samples were analyzed at several locations from the edge to the center of the pellets.

Results and Discussion

Reaction Products

The main products of hydrogenation of Tetralin for both catalysts were cis-decalin and trans-decalin. Trace amounts of cracking products such as n-butylbenzene, n-butylcyclohexane and methylindans were also detected. Most of the products formed in these experiments were identical to the products found in the hydrogenation of pure Tetralin. The discussion of the formation of each compound was presented in a separate work (1). The results of the experiments using alumina catalyst showed that there was no observable conversion of Tetralin.

The major product of MIBK hydrogenation was 2-methylpentane. MIBK was expected to undergo a hydrogenation reaction forming 2-methyl 4-pentanol followed by a subsequent reaction to form 2-methylpentane. Only trace amounts of 2-methyl 4-pentanol was detected in the samples indicating a rapid conversion of 2-methyl 4-pentanol to 2-methylpentane. This reaction was also observed when alumina was used as catalyst.

At our operating conditions, the major product of quinoline hydrodenitrogenation was propylcyclohexane. Small amounts of proplybenzene, o-ethylaniline, decahydroquinoline, and 1,2,3,4-tetrahydroquinoline were detected. Trace amounts of 5,6,7,8-tetrahydroquinoline and propylaniline were also found. The hydrodenitrogenation reaction of quinoline has already been discussed by many investigator (3-8). No further discussion will be given in this work. The main product of quinoline hydrogenation over alumina catalyst was 1,2,3,4-tetrahydroquinoline. The conversion of quinoline was almost completed and there was no other product found in the samples.

Mathematical Model

The schematic diagram of Tetralin hydrogenation reaction is shown in Figure 1. The reaction rate of Tetralin hydrogenation under our operating conditions was found to be first order (9). The rate expression for each reaction can be written as :

$$-r_T = (k_2+k_3+k_6+k_8+k_9+k_{10})\ C_T$$

$$-r_{CD} = -\ k_2C_T + k_4C_{CD} - k_5C_{TD}$$

$$-r_{TD} = -\ k_3C_T - k_4C_{CD} + k_5C_{TD}$$

$$-r_{BB} = -\ k_6C_T + k_7C_{BB}$$

$$-r_{BC} = -\ k_7C_{BB}$$

$$-r_{M1} = -\ k_8C_T$$

$$-r_{M2} = -\ k_9C_T$$

$$-r_{M4} = -\ k_{10}C_T$$

These rate expressions can be solved directly for the rate constants. The rate constants for isomerization of decalins, k4 and k5, were calculated using the data obtained from decalin experiments and assuming that cis- and trans-decalins were at the equilibrium. Table IV summarizes the rate constants for isomerization of decalins and Tables V through VIII summarize the rate constants calculated for NiMo/alumina and CoMo/alumina catalysts, respectively. These results are also shown in Figures 2 through 5.

Discussion

In our experiments the conversion of Tetralin is defined as

$$\% \text{ conversion} = \left(1 - \frac{C_{T,out}}{C_{T,in}} \right) \times 100$$

where $C_{T,in}$ and $C_{T,out}$ are mole fractions of Tetralin in the inlet and outlet streams of the reactor.

Since it took the system approximately 6 hours to reach its steady state conditions, the mole fraction of the product samples taken at 8, 10 and 12 hours were averaged and used to represent the sample composition. These average results were used to calculate the conversions.

Figures 6 and 7 show the overall Tetralin conversion for NiMo/alumina and CoMo/alumina catalysts, respectively. The results of the conversion of pure Tetralin are taken from a separate work (1). These figures indicate that the addition of MIBK to Tetralin slightly reduces the overall conversion of Tetralin while the addition of quinoline drastically reduces the conversion by a factor of 2 for NiMo/alumina catalyst and by a factor of 6 for CoMo/alumina catalyst.

The interference of Tetralin and quinoline on their hydrotreatment reactions was studied by Yang and Satterfield (3). They found that the presence of Tetralin in the feedstock inhibits the overall hydrodenitrogenation reaction of quinoline. The inhibition is caused by adsorption competition between Tetralin and quinoline. This is in agreement with our observation that both Tetralin and quinoline compete with each other to adsorb on the same type of active sites on the catalyst. This adsorption competition results in a reduction in Tetralin conversion. Since quinoline is a basic compound and strongly adsorbs on the acidic sites of the catalyst, hydrogenation of Tetralin is concluded to occur on the acidic sites of the catalyst.

The presence of titanocene dichloride, either in the feedstocks or on the impregnated catalysts, results in a reduction of Tetralin conversion in all cases, except when the feedstock is a mixture of MIBK and Tetralin and the catalyst is NiMo/alumina catalyst. The conversion of Tetralin in this case does not change or slightly increases when titanocene dichloride is in the system.

A homogeneous reaction between titanocene dichloride and the feedstock was observed during the experiments. The reaction occurred in the feed tank resulting in the formation of small particles suspended in the feedstock. The reaction was observed earlier by Tacheikuna and Seapan (10) when they doctored titanocene dichloride into Tetralin. They reported that the suspended particle was an insoluble titanium compound which was the product of the homogeneous reaction between Tetralin and titanocene dichloride. This homogeneous reaction possibly generated some intermediate compounds and, when combined with MIBK, modified the surface of NiMo/alumina catalyst resulting in an improvement in catalyst activity.

The analyses of the liquid samples show no titanium in the product samples. However, the analyses of the catalyst samples show that titanium is deposited on the outer surface of the catalyst pellets for both impregnated catalysts and catalysts taken from the experiments using doctored feedstocks. The titanium concentration detected on the impregnated catalyst samples is relatively higher than on the catalyst samples taken from the doctored runs.

These results indicated that titanocene dichloride decomposed when it adsorbed on the catalyst surface. The titanium metal deposited and formed a layer on the external surface of the catalyst causing an increase in mass transfer resistance which resulted in a decrease in Tetralin conversion.

Figure 8 shows the catalyst coking results of NiMo/alumina catalyst. These results indicated that the addition of MIBK to the feedstock increased the catalyst coking while the addition of MIBK and quinoline to the feedstock reduced the catalyst coking. The presence of titanocene dichloride in the system reduces the catalyst coking when the feedstocks were Tetralin and a mixture of MIBK and Tetralin. A reverse effect was observed when the feedstock was a mixture of MIBK, quinoline, and Tetralin.

The coking results of CoMo/alumina catalyst, presented in Figure 9, showed that the presence of titanocene dichloride reduced the coking when the feedstock was a mixture of MIBK, quinoline, and Tetralin. When the feedstock was a mixture of MIBK and Tetralin, the addition of titanocene dichloride to the feedstock increased the catalyst coking while titanocene dichloride on the impregnated catalyst caused a coke reduction.

Figures 2 and 3 show the effect of titanocene dichloride on the rate constants for NiMo/alumina and CoMo/alumina catalysts, when the feedstock was the mixture of MIBK and Tetralin. For the NiMo/alumina catalyst the presence of titanocene dichloride in the system increases the rate constants of every compound, except n-butylcyclohexane which appears to increase slightly. On the contrary, for CoMo/alumina catalyst the addition of titanocene dichloride to the feedstock decreases the rate constants of cis- and trans-decalin but increases the rate constants of every by-product. The impregnated CoMo/alumina catalyst shows a reduction in every rate constant.

Figures 4 and 5 show the effect of titanocene dichloride on the rate constants when the feedstock is a mixture of quinoline, MIBK, and Tetralin. The presence of titanocene dichloride in the system appears to reduce the rate constant of every compound, except 1-methylindan. The rate constant of 1-methylindan on NiMo/alumina catalyst drastically increases when titanocene dichloride is added into the feedstock. A slight increase of this rate constant is observed on CoMo/alumina catalyst.

Conclusions

1. Titanocene dichloride, when added to the feedstock or used to impregnate the catalyst, forms a layer of titanium covering the external surface of the catalyst.
2. This shell of titanium reduces the diffusion of reactants into catalyst pores, resulting in reductions in both catalyst activity and catalyst coking, except the case of NiMo/alumina and MIBK-Tetralin solution.
3. The homogeneous between titanocene dichloride and MIBK-Tetralin solution possibly generated some intermediate compounds which can combined with NiMo/alumina catalyst resulting in an activity improvement.

Acknowledgement

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NOTATION

C_i = Concentration of compound i in mole percent

k = First order rate constant

$-r_i$ = Rate of reaction of compound i

Subscript

BB = Butylbenzene

BC = Butylcyclohexane

CD = Cis-decalin

D = Decalin

H2 = Hydrogen

M1 = 1-Methylindan

M2 = 2-Methylindan

M4 = 4-Methylindan

T = Tetralin

TD = Trans-decalin

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LIST OF TABLES

TABLE I

PROPERTIES OF CATALYSTS

	Shell 324	Shell 344
Chemical Composition wt%		
Co	-	2.4
Ni	2.7	-
Mo	13.2	9.8
Physical Properties :		
Geometry	1.6 mm (1/16") extrudate	1.6 mm (1/16") extrudate
Surface area, m^2/kg	195E03	236E03
Pore Volume, m^3/kg	4.9E-04	6.0E-04

	ALUMINA
Physical Properties :	
Geometry	1.6 mm (1/16") trilobe
Surface area, m^2/kg	320E03
Pore Volume, m^3/kg	8.1E-04

TABLE II

TYPE OF CATALYSTS AND FEED STOCKS

RUN	CATALYST*	FEED**
1	324	T,MIBK
2	324	T,MIBK,TDC
3	324I	T,MIBK
4	344	T,MIBK
5	344	T,MIBK,TDC
6	344I	T,MIBK
7	Al	T,MIBK
8	Al	T,MIBK,TDC
9	Al I	T,MIBK
10	324	T,MIBK,Q
11	324	T,MIBK,Q,TDC
12	324I	T,MIBK,Q
13	344	T,MIBK,Q
14	344	T,MIBK,Q,TDC
15	344I	T,MIBK,Q
16	Al	T,MIBK,Q
17	Al	T,MIBK,Q,TDC
18	Al I	T,MIBK,Q
19	324	D,MIBK
20	324	D,MIBK,TDC
21	344	D,MIBK
22	344	D,MIBK,TDC
23	324	D,MIBK,Q
24	324	D,MIBK,Q,TDC
25	344	D,MIBK,Q
26	344	D,MIBK,Q,TDC

* 324 - SHELL 324 (NiMo/alumina)
344 - SHELL 344 (CoMo/alumina)
324I - Impregnated SHELL 324
344I - Impregnated SHELL 344
Al - Alumina Support
Al I - Impregnated Alumina Support

** T - Tetralin
D - Decalin
MIBK - Methyl Isobutyl Ketone
Q - Quinoline
TDC - Titanocene Dichloride

TABLE III

COMPOUND FOUND IN OUR SAMPLES AND THE TECHNIQUES THAT USED TO IDENTIFY

Compounds	G.C.	G.C./M.S.
Trans-decalin	X	X
Cis-decalin	X	X
Tetralin	X	X
Naphthalene	X	X
Butylbenzene	X	
Butylcyclohexane	X	
1-Methylindan	X	
5-Methylindan	X	
MIBK	X	X
2-Methylpentane	X	
2-Methyl 4-pentanol	X	
Quinoline	X	X
1,2,3,4-Tetrahydroquinoline	X	X
5,6,7,8-Tetrahydroquinoline	X	
Decahydroquinoline	X	
Propylaniline	X	
Propylbenzene	X	X
Propylcyclohexane	X	X
Isoquinoline	X	

TABLE IV

RATE CONSTANTS FOR ISOMERIZATION OF DECALIN

Rate Constant* (mole/gm. of cat. sec)	Shell 324		Shell 344	
	W/O TDC	W/ TDC	W/O TDC	W/ TDC
Decalin + MIBK				
k_4 x 1E06	2.16	2.83	1.22	0.62
k_5 x 1E07	2.53	3.31	1.43	0.73
Decalin + MIBK + Quinoline				
k_4 x 1E07	2.12	1.86	2.34	1.38
k_5 x 1E08	2.48	2.18	2.74	1.61

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock

TABLE V

RATE CONSTANTS FOR SHELL 324
FEEDSTOCK : TETRALIN + MIBK

Rate* Constant (mole/gm. of cat. sec)	W/O TDC	W/ TDC	IMP.CAT
k_2 x 1E06	4.08	4.52	4.88
k_3 x 1E05	1.19	1.20	1.31
k_6 x 1E07	1.74	2.07	2.57
k_7 x 1E06	1.52	1.35	1.45
k_8 x 1E08	3.39	3.73	4.11
k_9 x 1E07	3.08	3.50	3.87
k_{10} x 1E08	7.84	8.70	9.64

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

TABLE VI

RATE CONSTANTS FOR SHELL 344 FEEDSTOCK : TETRALIN + MIBK

Rate Constant* (mole/gm. of cat. sec)	W/O TDC	W/ TDC	IMP.CAT
k_2 x 1E06	1.29	1.10	0.68
k_3 x 1E06	2.81	2.67	1.56
k_6 x 1E08	5.61	8.66	4.84
k_7 x 1E07	6.93	8.55	4.30
k_8 x 1E08	1.21	1.40	0.98
k_9 x 1E08	8.99	9.40	5.62
k_{10} x 1E08	2.24	2.33	1.39

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

TABLE VII

RATE CONSTANTS FOR SHELL 324
FEEDSTOCK : TETRALIN + MIBK + QUINOLINE

Rate* Constant (mole/gm. of cat. sec)	W/O TDC	W/ TDC	IMP.CAT
k_2 x 1E07	3.99	1.95	2.54
k_3 x 1E06	1.28	0.55	0.77
k_6 x 1E09	2.61	5.20	3.91
k_7 x 1E06	4.52	0.45	3.32
k_8 x 1E10	4.63	8.56	4.20
k_9 x 1E10	8.56	5.25	6.69
k_{10} x 1E10	5.00	1.92	3.68

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

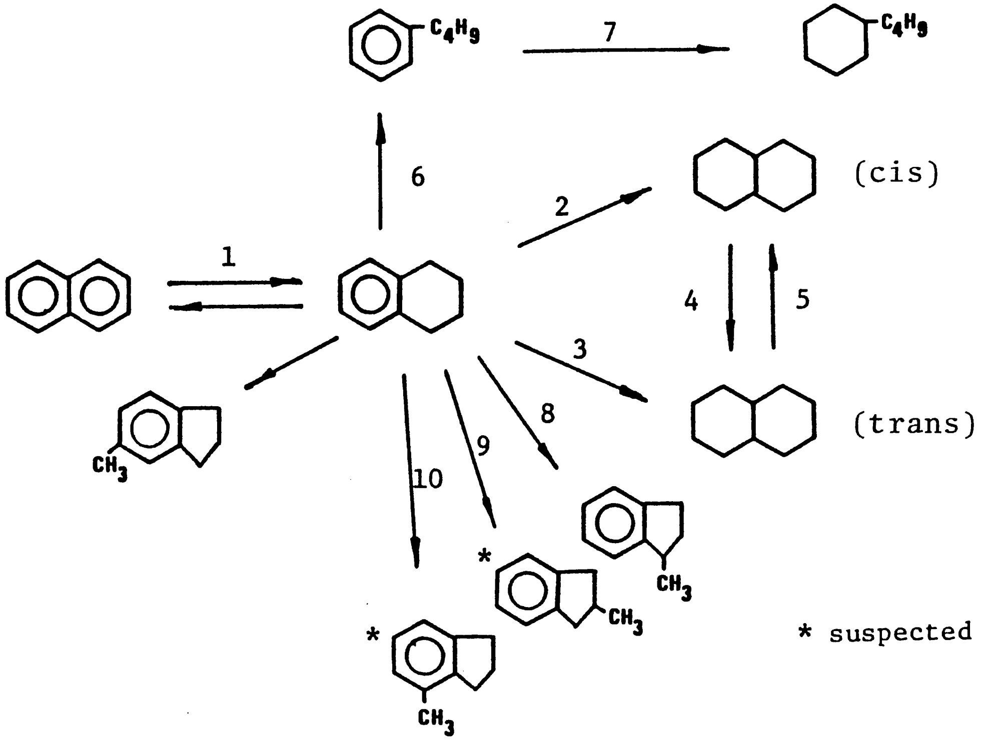
TABLE VIII

RATE CONSTANTS FOR SHELL 344
FEEDSTOCK : TETRALIN + MIBK + QUINOLINE

Rate Constant (mole/gm. of cat. sec)	W/O TDC*	W/ TDC*	IMP.CAT*
k_2 x 1E07	1.23	0.80	0.48
k_3 x 1E07	1.86	1.21	0.73
k_6 x 1E09	3.77	1.99	2.70
k_7 x 1E06	1.85	0.47	2.17
k_8 x 1E10	3.15	3.18	3.06
k_9 x 1E10	2.45	0.64	0.63
k_{10} x 1E10	2.38	0.58	0.00

* W/O TDC - without titanocene dichloride
W/ TDC - with titanocene dichloride in feedstock
IMP.CAT - impregnated catalyst

LIST OF FIGURES



* suspected to be present

Figure 1. Schematic Diagram of Reaction Mechanism

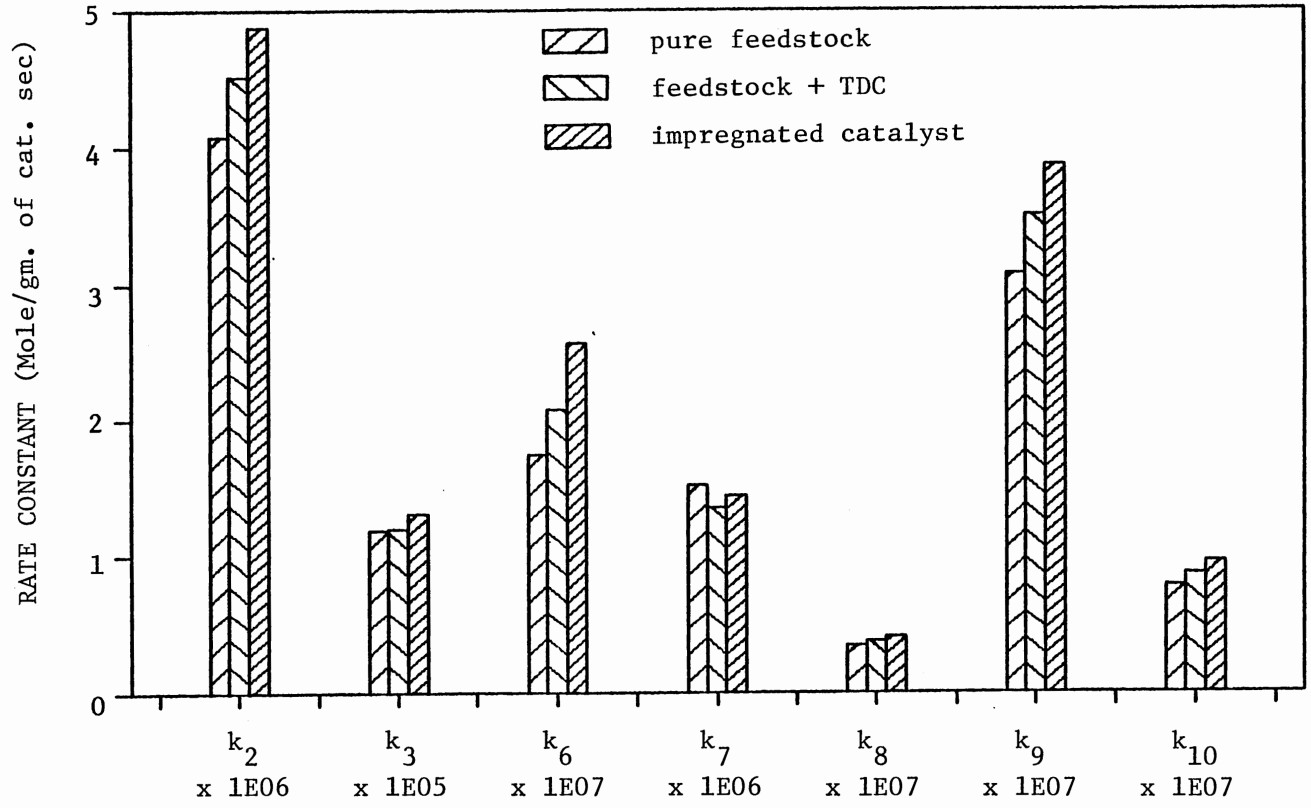


Figure 2. Effect of Titanocene Dichloride on Rate Constants for Shell 324 and a Mixture of MIBK and Tetralin

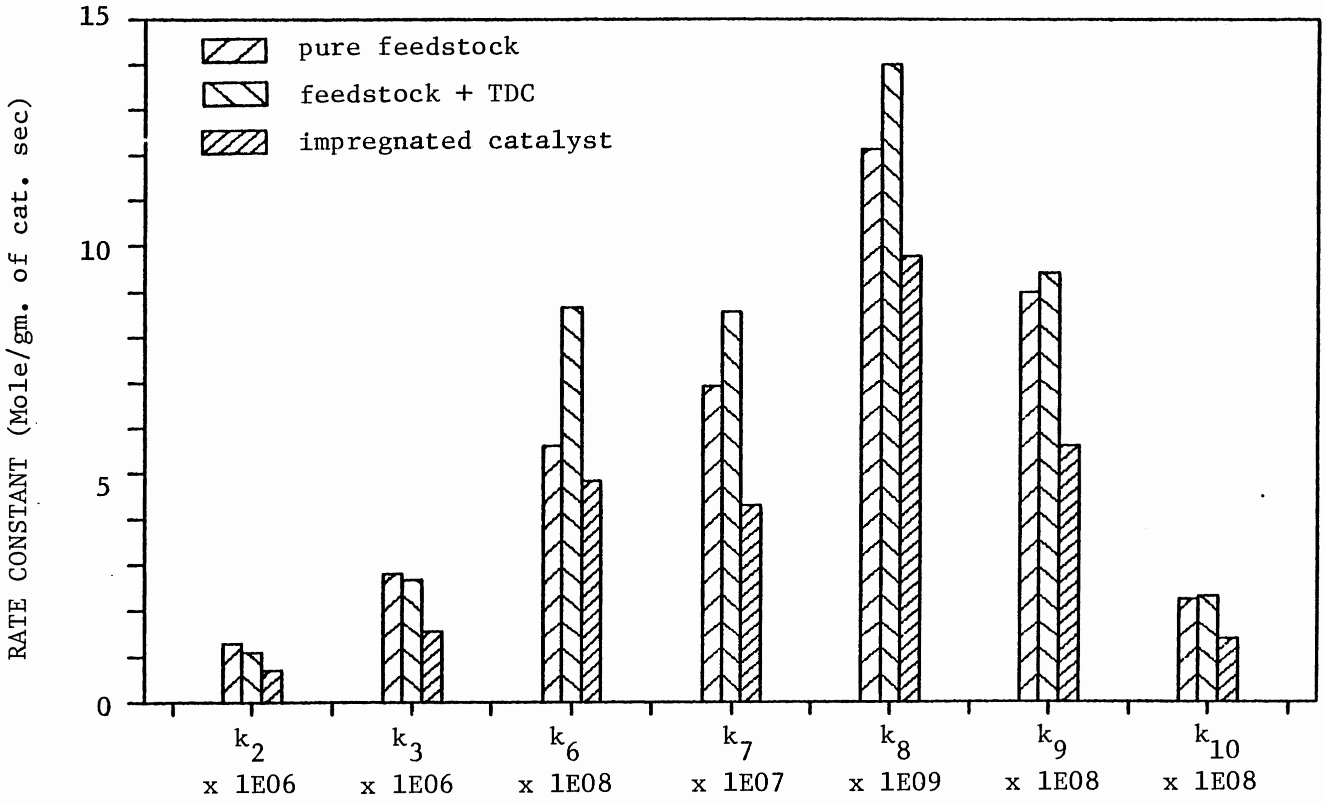


Figure 3. Effect of Titanocene Dichloride on Rate Constants for Shell 344 and a Mixture of MIBK and Tetralin

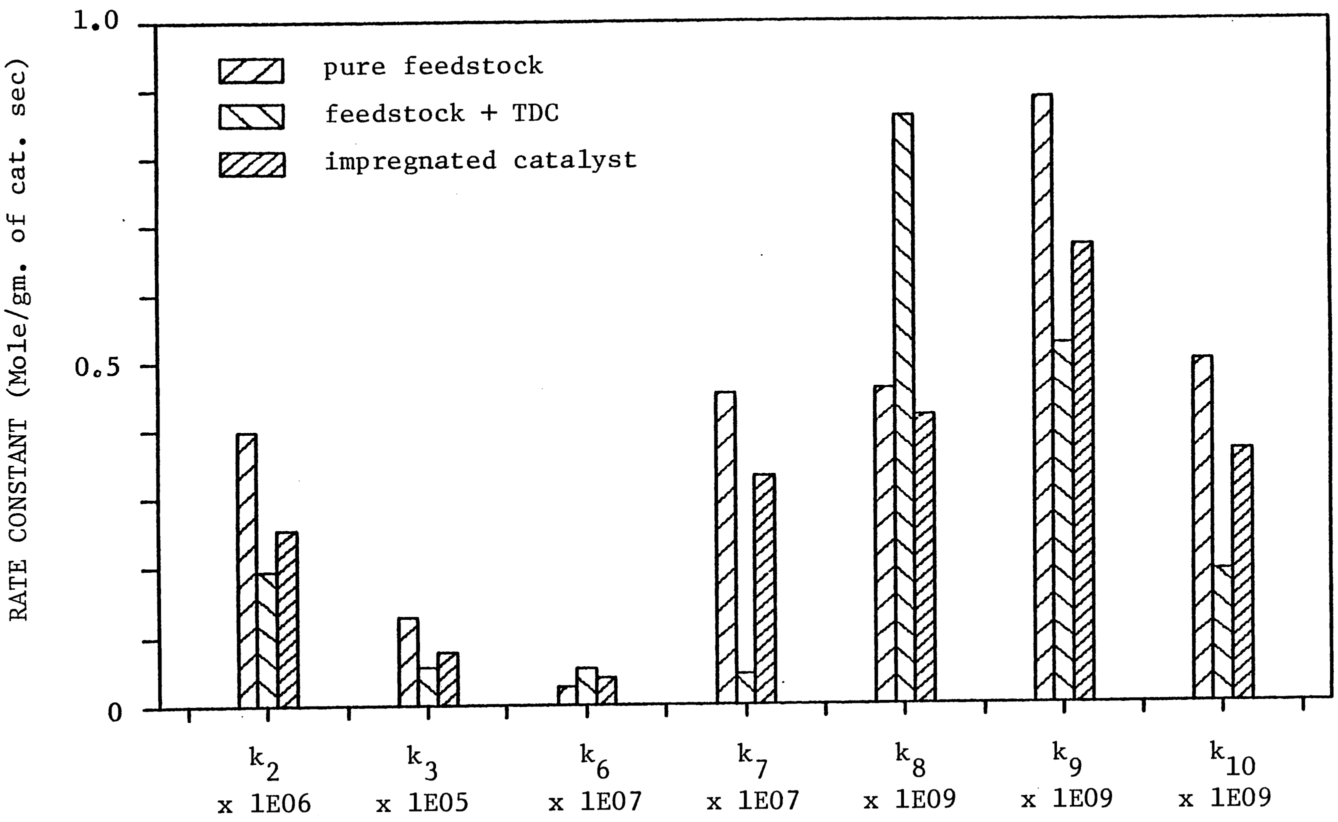


Figure 4. Effect of Titanocene Dichloride on Rate Constants for Shell 324 and a Mixture of Quinoline, MIBK, and Tetralin

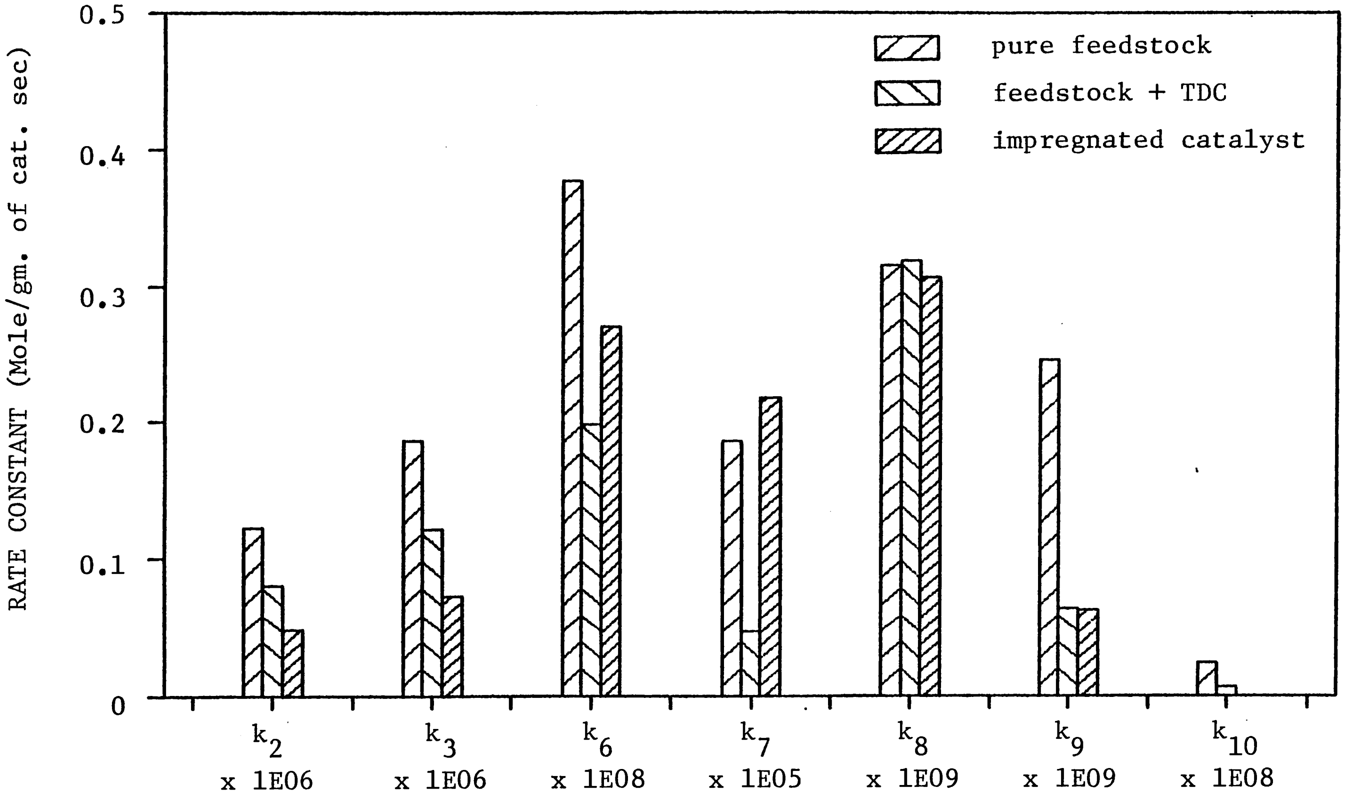


Figure 5. Effect of Titanocene Dichloride on Rate Constants for Shell 344 and a Mixture of Quinoline, MIBK, and Tetralin

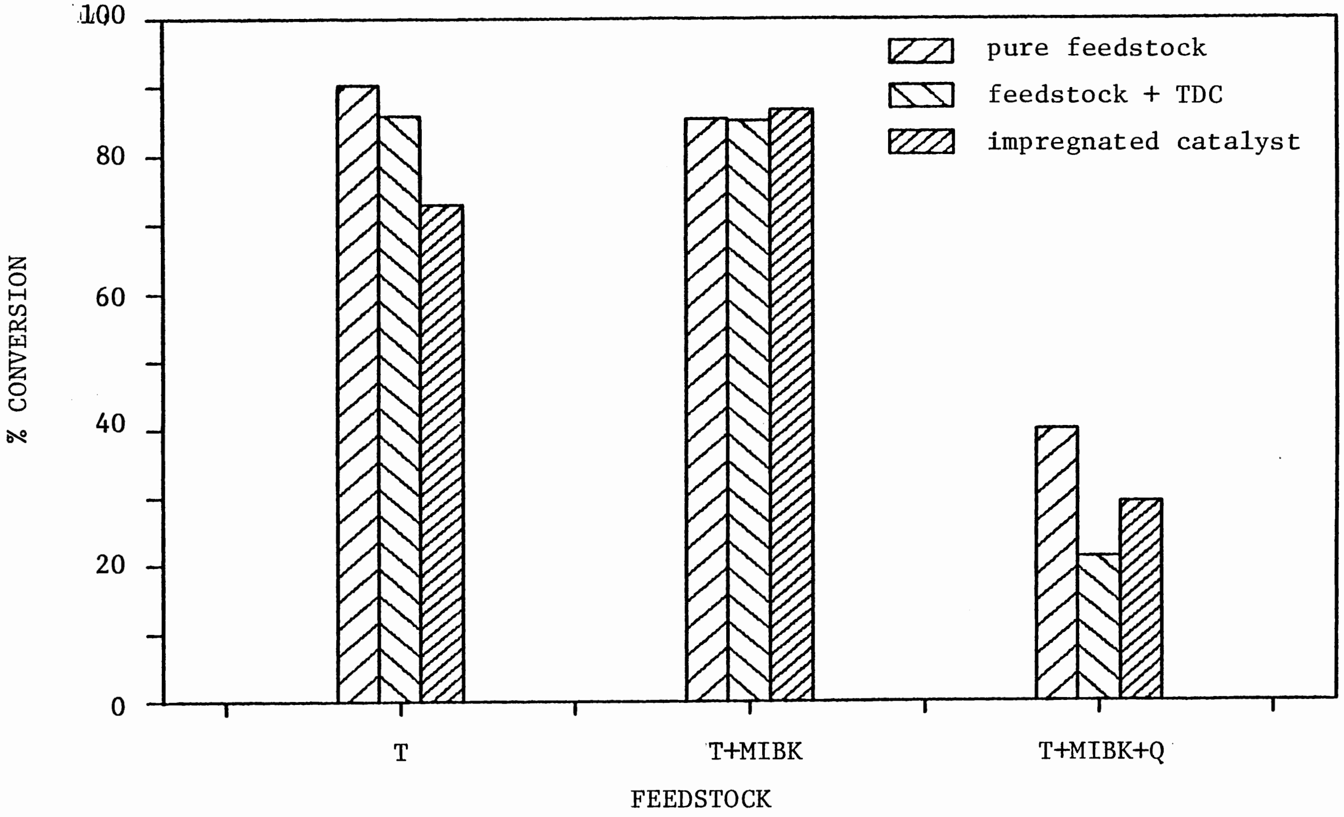


Figure 6. Effect of Titanocene Dichloride on Tetralin Conversion (Shell 324)

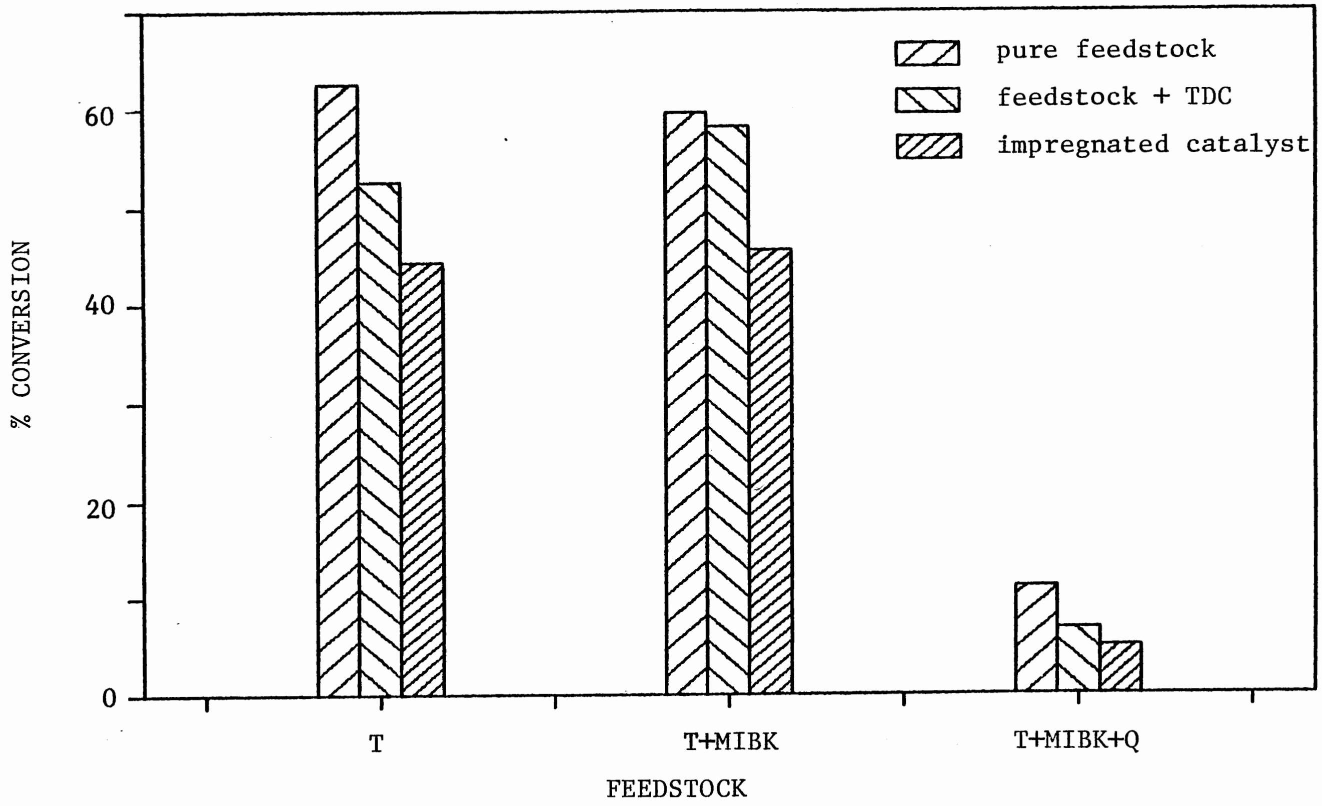


Figure 7. Effect of Titanocene Dichloride on Tetralin Conversion (Shell 344)

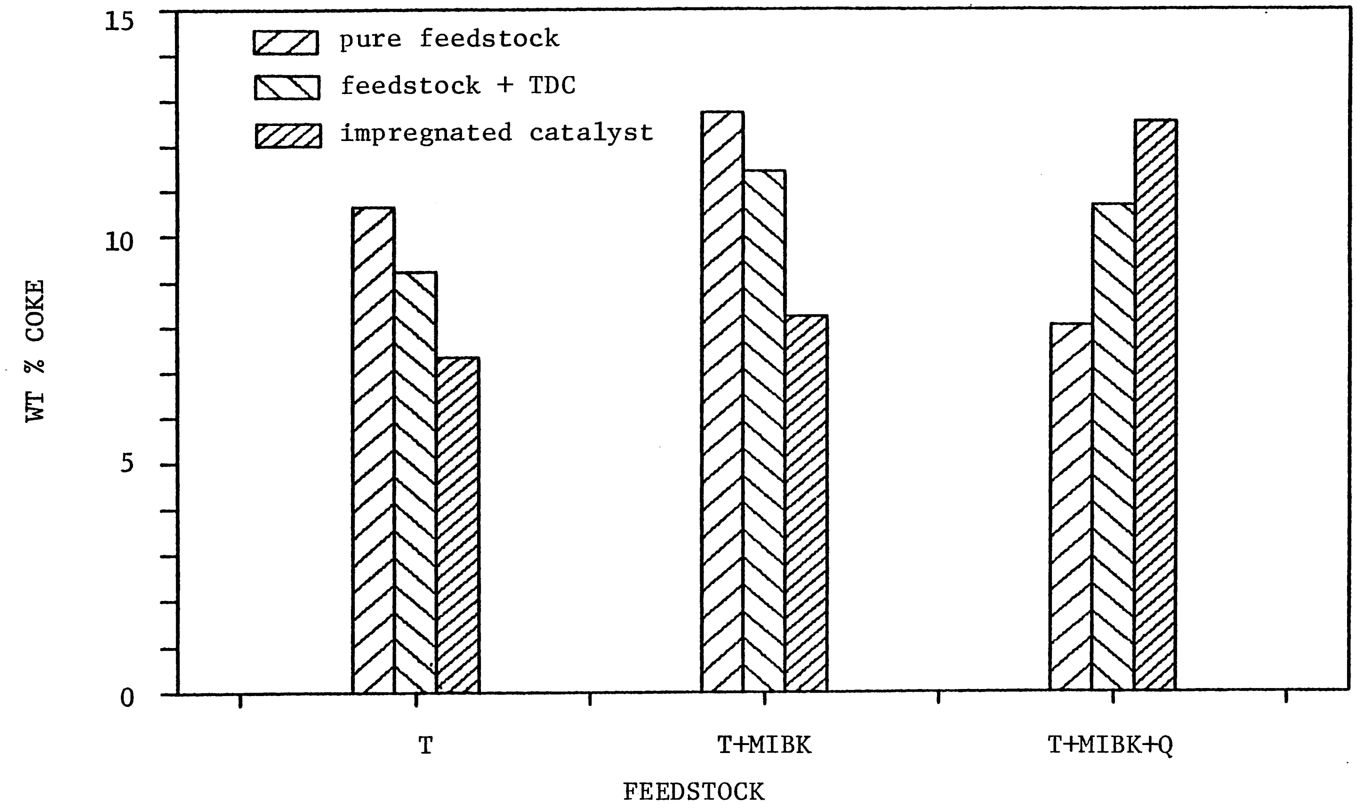


Figure 8. Effect of Titanocene Dichloride on Catalyst Coking (Shell 324)

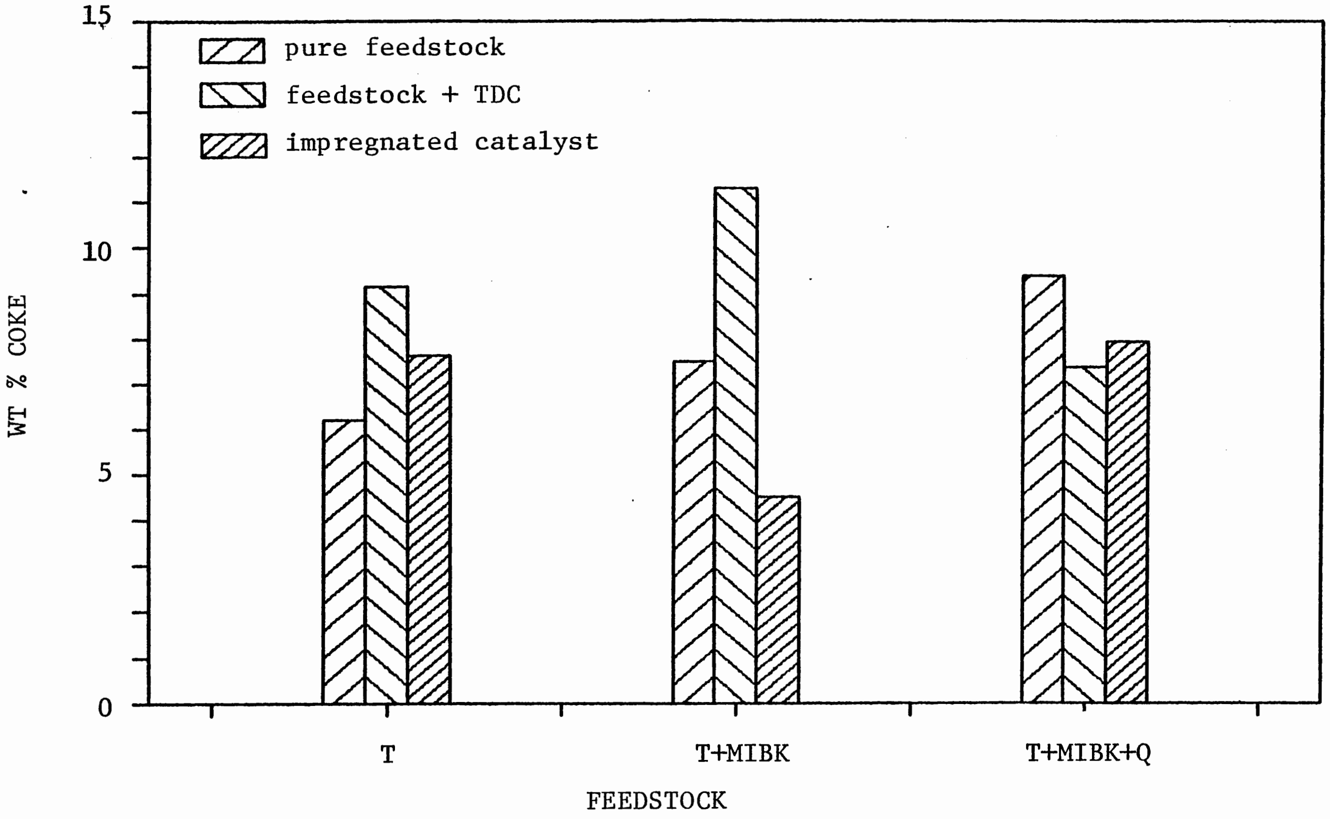


Figure 9. Effect of Titanocene Dichloride on Catalyst Coking (Shell 344)

CHAPTER VI

SUPPLEMENTARY WORKS

Supplementary Study

Effect ot Titanocene Dichloride on Reaction of Methyl Isobutyl Ketone

The catalytic hydrogenation of methyl isobutyl ketone (MIBK) over Raney Ni catalyst was studied by Gaudemaris (1). The reaction was reported as a zero-order reaction with respect to hydrogen at temperatures above 110 C (230 F) and hydrogen pressures greater than 68-106 atm (1000-1570 psig). The formation of 4-methyl 2-pentanol (methyl isobutyl alcohol) does not appear to inhibit the reaction.

At our operating conditions, the major product of MIBK hydrogenation was 2-methylpentane. MIBK was expected to undergo a hydrogenation reaction forming 4-methyl 2-pentanol followed by a subsequent reaction to form 2-methylpentane. Only trace amounts of 4-methyl 2-pentanol was detected in the samples indicating rapid conversion of 4-methyl 2-pentanol to 2-methylpentane. In our catalytic experiments, since MIBK always converts completely, we were not able to observe any effect of titanocene dichloride on hydrodeoxygenation of MIBK. When quinoline was added to the mixture of MIBK and Tetralin, a trace amount of 4-methyl 2-pentanol was detected. This result indicated that hydrodeoxygenation of MIBK required acidic sites on the catalyst. The acidic sites were poisoned by quinoline, a basic compound, causing a decrease in the formation of 4-methyl 2-pentanol.

The results of the non-catalytic experiments, using alumina support instead of the catalysts, showed that approximately 31 % of MIBK in the feedstock converted to 2-methylpentane. When titanocene dichloride was in the system, either in the feedstock or on the impregnated catalysts, the conversion increased to 33 % . This improvement is too small to conclude that titanocene dichloride has any catalytic effect on the reaction. Further study has to be conducted to varify this observation.

In every experiment, only 50-65 % of MIBK in the feedstock was recovered in the liquid samples. Because of the severe operating conditions, part of MIBK and its hydrogenated or cracked products evaporate into the gas phase, leaving the system via the gas outlet, which causes an error in the material balance of MIBK. Even though the analysis of the gas samples with a gas chromatograph did not show any MIBK or its products, be present, we believe that it is because of very low concentrations of these compounds in the outlet gas, and the lack of material balance was due to evaporative losses of the light compounds.

Effect of Titanocene Dichloride on Reaction of Quinoline

At our operating conditions, the major product of quinoline hydrodenitrogenation reaction was propylcyclohexane. Small amounts of propylbenzene, ethylaniline, decahydroquinoline, and 1,2,3,4-tetrahydroquinoline were detected. Trace amounts of 5,6,7,8-tetrahydroquinoline and propylaniline were also found. The hydrodenitrogenation (HDN) reaction of quinoline was studied and published by many investigators (2-7). No further discussion would be given in this work.

The presence of titanocene dichloride in the system does not appear to affect quinoline reaction. Quinoline completely reacted in every experiment. There is no observable interference of titanocene dichloride on the reaction mechanisms.

When the alumina support was used instead of the catalysts, the main product of quinoline hydrogenation was 1, 2, 3, 4-tetrahydroquinoline. Small amounts of propylaniline and ethylaniline were also detected. Trace amounts of 5, 6, 7, 8-tetrahydroquinoline and decahydroquinoline were also found. These results showed that the hydrogenation reaction of quinoline can occur in alumina substrate whereas the hydrodenitrogenation reaction required an active site of the catalyst.

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CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The following conclusions can be drawn from the results of this work :

1. The presence of titanocene dichloride in the system, either in the feedstock or on the impregnated catalyst, causes a deposition of titanium on the external surface of the catalyst pellet.

2. This shell of deposited titanium causes an increase of mass transfer resistance to the catalyst surface, resulting in a decrease of conversion and catalyst coking.

3. The presence of methyl isobutyl ketone and titanocene dichloride in the system does not affect the conversion of Tetralin but reduces the coking on NiMo/alumina catalyst.

4. The addition of quinoline to the feedstock results in a reduction of Tetralin conversion due to the adsorption competition and the poisoning of the acidic sites by quinoline.

5. The conversion of Tetralin is found to depend on the extent of the catalyst sulfidation state. The catalyst with high levels of sulfidation gives higher Tetralin conversion than the one with low levels of sulfidation.

6. The Berty type gradientless reactor can be used in the study of gas-liquid-solid reaction kinetics if the operating conditions are selected carefully to assure a

steady state for phase equilibria, reactor flow dynamics, and chemical conversions.

RECOMMENDATIONS

1. The studies on methyl isobutyl ketone and quinoline should be conducted at lower temperatures so that these compounds will not be completely converted.

2. Different organometallic compounds such as ferrocene and nickelocene can be used to study the effect of other metalocene compounds without the presence of chlorine.

3. A complete study of the performance of the Berty type gradientless reactor should be conducted.

4. After each experiment, a blank experiment, using the feedstock of the next experiment, should be conducted at the operating conditions to assure that there is no feedstock of the previuos experiment left in the system.

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APPENDIXES

APPENDIX A

GAS CHROMATOGRAPHIC ANALYSIS

GAS CHROMATOGRAPHIC ANALYSIS

Liquid feedstocks and their reaction products were analyzed qualitatively and quantitatively by using a Hewlett Packard Model 5890A Gas Chromatograph equipped with a 60 m DB-1 capillary column and a thermal conductivity detector. The output of the detector was integrated and recorded on a Hewlett Packard Integrator Model 3392A. The column was operated with a temperature program to achieve high peak resulation. The column conditions are summarized in Table I.

Approximately 0.1 microliter of liquid sample was injected into the Gas Chromatograph. The sample is vaporized at the high temperature of the injection port and mixed with a carrier gas. Part of the gas mixture is split and vented to the atmosphere, only a small portion of the gas mixture flows into the capillary column. Compounds in the gas mixture adsorb and desorb in the capillary column at different rates. The desorbed gas mixture flows through a thermal conductivity detector. The signal outputs from the detector are integrated and plotted by the integrator.

Qualitative Analysis

The compounds are identified by comparing the retention times of the unknown peaks with the retention times of the standard compounds. Some compounds are also identified by using a combined Gas Chromatograph/Mass Spectormeter.

TABLE I

COLUMN CONDITIONS

Initial Temperature : 60 C
Initial Time : 2 minutes
Heating Rate : 8 C/min
Final Temperature : 200 C
Final Time : 10 minutes
Injector Temperature : 225 C
Detector Temperature : 225 C

Table II shows the retention times of all standard compounds suspected to be present in the samples. The standard retention times were measured in our laboratory using the same Gas Chromatograph and operating conditions. Table III summarized the compounds found in our samples and the techniques used to identify the compounds.

Quantitative Analysis

The results obtained from the gas chromatograph were used to determine composition of the samples. The integrated areas shown on the chromatogram were used to calculate weight percents of compounds in the solution. In order to minimize the error associated with detector performance, detector response factor or weight factor for each compound was determined in our laboratory. Table IV summarized the response factor used in our calculation. The calculation of weight percent of the compounds is shown in the following example.

Example : A sample was analyzed showing that it consisted of trans-decalin, cis-decalin, Tetralin, and naphthalene. The areas of these compounds shown on the chromatogram were 51624000, 9497100, 6029600, and 1037500, respectively. What is the percentage of each compound in the mixture ?

TABLE II

RETENTION TIME

Compounds	Retention Time (min)
Pentane	3.14
2-Methylpentane	3.75
Benzene	4.92
2-Pentanone	5.06
Cyclohexane	5.09
2-Pentanol	5.33
MIBK	6.13
Methylcyclohexane	6.26
4-Methyl 2-pentanol	6.58
Methylbenzene (toluene)	6.98
Trans 1,2 dimethylcyclohexane	7.97
Cis 1,2 dimethylcyclohexane	8.71
Ethylcyclohexane	8.80
Cyclohexylamine	9.02
Ethylbenzene	9.19
Styrene	9.80
o-Xylene	9.97
Nonane	10.31
2-Methylcyclohexylamine	10.60 & 11.08
Propylcyclohexane	11.17
Propylbenzene	11.48
Aniline	11.60
2-Ethyltoluene	12.08
n-Ethylcyclohexylamine	12.44
sec-Butylbenzene	12.86
Indan	13.42
n-Butylcyclohexane	13.59
Indene	13.67
n-Butylbenzene	13.88
Methylaniline	13.93
1,2 Diethylbenzene	14.02
Trans-decalin	14.58
1-Methylindan	14.69
Cis-decalin	15.59
Ethylaniline	15.81
5-Methylindan	15.90
Decahydroquinoline	16.11
1-Methylindene	16.21
1,2 Dihydronaphthalene	16.33
Tetralin	16.36
Naphthalene	16.81
5,6,7,8 Tetrahydroquinoline	17.43

TABLE II (Continued)

Compounds	Retention Time (min)
Isotetralin	17.50
Propylaniline	17.60
Quinoline	17.70
Isoquinoline	18.19
1,2,3,4 Tetrahydroisoquinoline	18.47
1-Methylnaphthalene	19.08 & 19.43
1,2,3,4 Tetrahydroquinoline	19.52

TABLE III

COMPOUND FOUND IN OUR SAMPLES AND THE TECHNIQUES THAT USED TO IDENTIFY

Compounds	G.C.	G.C./M.S.
Trans-decalin	X	X
Cis-decalin	X	X
Tetralin	X	X
Naphthalene	X	X
Butylbenzene	X	
Butylcyclohexane	X	
1-Methylindan	X	
5-Methylindan	X	
1-Methylindene	X	
MIBK	X	X
2-Methylpentane	X	
2-Methyl 4-pentanol	X	
Quinoline	X	X
1,2,3,4-Tetrahydroquinoline	X	X
5,6,7,8-Tetrahydroquinoline	X	
Decahydroquinoline	X	
Propylaniline	X	
Ethylaniline	X	
Propylbenzene	X	X
Propylcyclohexane	X	X
Methylcyclohexane	X	
Isoquinoline	X	

TABLE IV

RESPONSE FACTORS

Compounds	Response Factor
2-Methylpentane	0.820
2-Methyl-4-pentanol	0.946
2-Methyl-4-pentanone (MIBK)	0.899
Methylcyclohexane	0.880
Ethylcyclohexane	1.002
Propylcyclohexane	0.824
Butylcyclohexane	0.912
Propylbenzene	0.894
Butylbenzene	0.923
Trans-decalin	1.012
Cis-decalin	1.030
Tetralin	0.998
Naphthalene	1.041
Quinoline	1.484
Isoquinoline	2.303
1,2,3,4 Tetrahydroquinoline	1.628
5,6,7,8 Tetrahydroquinoline	1.395
Decahydroquinoline	2.796
Aniline	1.930
Methylaniline	0.941
Ethylaniline	1.286
Propylaniline	1.293
1-Methylindan	1.013

Solution :

step #1

COMPOUND	AREA	RESPONSE FACTOR
Trans-decalin	51624000	1.012
Cis-decalin	9497100	1.030
Tetralin	6029600	0.998
Naphthalene	1037500	1.040

Step #2 : Multiply the peak area by the response factor.

Trans-decalin = (51624000)(1.012) = 52243488

Cis-decalin = (9497100)(1.030) = 9782013

Tetralin = (6029600)(0.998) = 6017541

Naphthalene = (1037500)(1.040) = 1079000

Total = 69122042

Step #3 : Normalize to obtain the answer in weight percent.

percent.

Trans-decalin = (52243488/69122042)x100 = 75.58 %

Cis-decalin = (9782013/69122042)x100 = 14.15 %

Tetralin = (6017541/69122042)x100 = 8.71 %

Naphthalene = (1079000/69122942)x100 = 1.56 %

Total = 100 %

APPENDIX B

REACTOR PERFORMANCE MODEL

REACTOR PERFORMANCE MODEL

The gradientless reactor with Berty type internal used in this study has a catalyst basket in the middle of the reactor and an internal circulation. Feed gas and liquid reactants flow into the bottom of the reactor and are mixed by means of the high speed propeller. The mixture flows upward through the annular space between the catalyst basket and the reactor wall before it is forced to flow down into the catalyst basket. The mixture leaves the bottom of the catalyst basket and is mixed with the new feedstocks. This internal arrangement can be viewed as a recycle reactor. Figure 1 shows the schematics of the internal of the reactor and Figure 2 shows the flow diagram of the mixture inside the reactor. Berty (1) and other investigators have developed a recycle reactor model for this type of gradientless reactor.

Levenspiel (2) suggested that the reactor performance equation for a differential reactor is

$$\frac{W}{F_{AO}} = \int_{X_{A,in}}^{X_{A,out}} \frac{dX_A}{-r_A} \qquad (1)$$

where F_{A0} is the feed rate of A into the catalyst basket.

The recycle ratio of the system is defined as

$$R = \frac{\text{molar flowrate of fluid returned to the reactor}}{\text{molar flowrate of fluid leaving the system}}$$

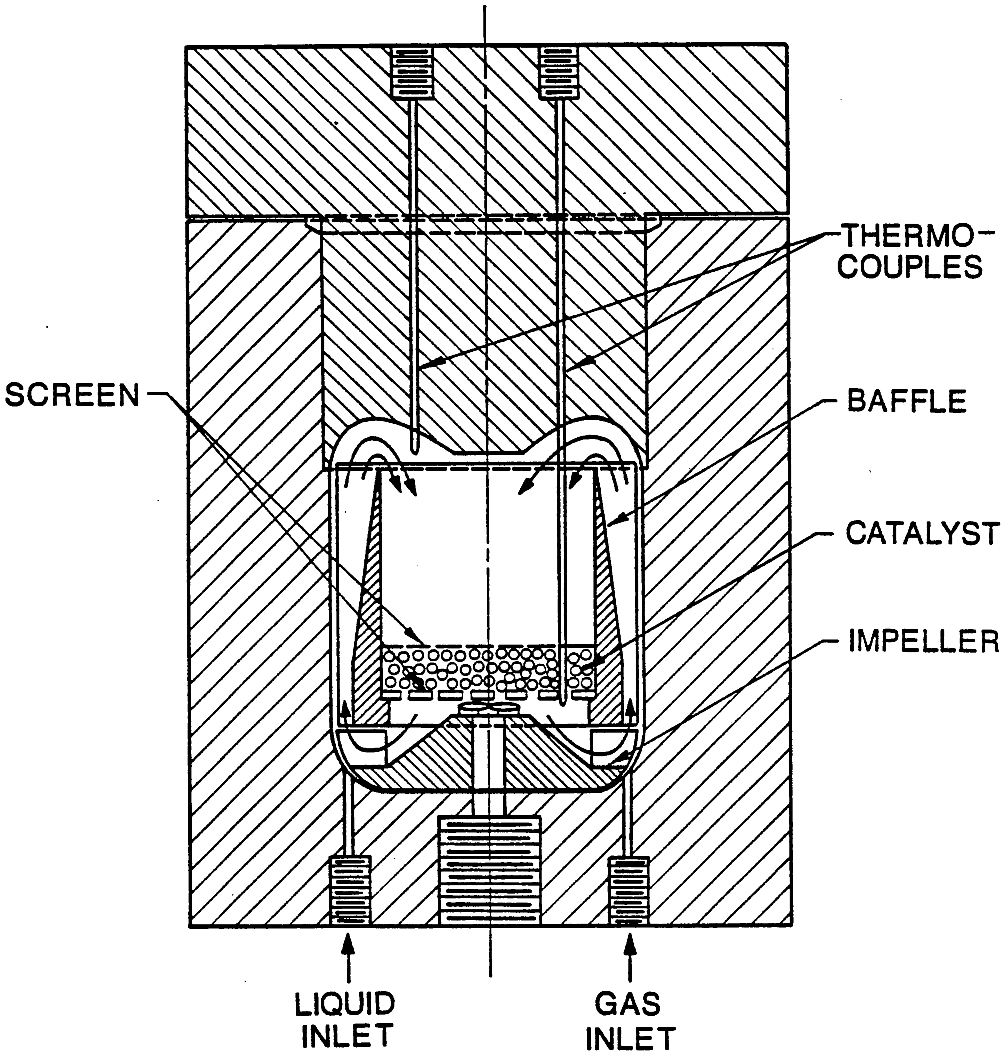


Figure 1. Internals of Berty Reactor

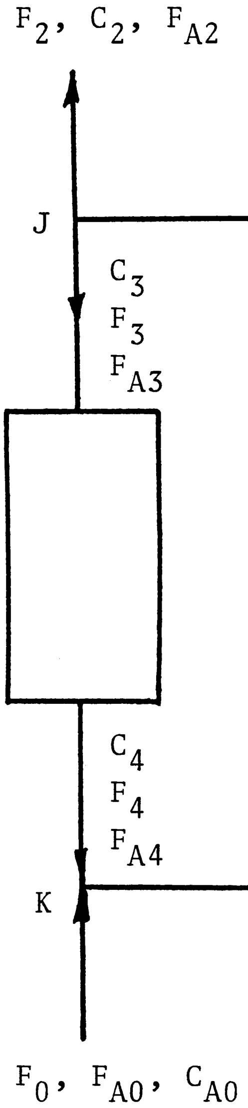


Figure 2. Schematic Diagram of Flow Inside the Reactor

$$R = \frac{F_1}{F_2}$$

But at steady state, the molar flowrate of fluid entering the system is equal to the molar flowrate of fluid leaving the system (in our system only) or

$$F_0 = F_2$$

Then the recycle ratio is written as

$$R = \frac{F_1}{F_0}$$

$$F_1 = RF_0$$

The flow of fluid entering the catalyst basket consists of both the fresh feed and the recycle products. The material balance at point J gives

$$F_1 = F_2 + F_3$$

Substitution of F_1 and F_2 gives

$$RF_0 = F_0 + F_3$$

$$F_3 = (R-1)F_0$$

The same material balance can be written for reactant A as

$$F_{A3} = (R-1)F_{A0}$$

The conversions of the reactant can be written for input and output of the catalyst basket as

$$X_{A,in} = 1 - \frac{C_{A3}}{C_{A0}} \qquad (2)$$

$$X_{A,out} = 1 - \frac{C_{A4}}{C_{A0}} \qquad (3)$$

Material balance of A at point K gives

$$F_0 C_{A0} + F_4 C_{A4} = F_1 C_{A1}$$

$$F_0 C_{A0} + (R-1) F_0 C_{A4} = R F_0 C_{A1}$$

$$C_{A4} = \frac{R F_0 C_{A1} - F_0 C_{A0}}{(R-1) F_0}$$

$$C_{A4} = \frac{R C_{A1} - C_{A0}}{(R-1)}$$

Substitution of C_{A4} in equation (3) gives

$$X_{A,out} = 1 - \frac{R C_{A1} - C_{A0}}{(R-1) C_{A0}}$$

$$= \frac{(R-1) C_{A0} - R C_{A1} + C_{A0}}{(R-1) C_{A0}}$$

$$= \frac{(R-1) C_{A0} - R C_{A0} (1-X_{A,in}) + C_{A0}}{(R-1) C_{A0}}$$

$$= \frac{C_{A0}((R-1) - R(1-X_{A,in}) + 1)}{(R-1) C_{A0}}$$

$$= \frac{R - R(1-X_{A,in})}{(R-1)}$$

$$= \frac{R X_{A,in}}{R-1}$$

Substitution of F_{A3} and $X_{A,out}$ into equation (1) gives

$$\frac{W}{(R-1)F_{A0}} = \int_{X_{A,in}}^{\frac{R}{R-1}X_{A,in}} \frac{dX_A}{-r_A}$$

$$\frac{W}{F_{A0}} = (R-1)\int_{X_{A,in}}^{\frac{R}{R-1}X_{A,in}} \frac{dX_A}{-r_A}$$

Berty (1) suggested that the reactor would approximate a continuous stirred tank reactor (CSTR) when the recycle ratio was higher than 20. Base on our observation, the recycle ratio at our operating conditions varied between 42 to 210 with an average of 107 which is higher than 20. Then the reactor performance equation becomes

$$\frac{W}{F_{A0}} = \frac{X_{A,in}}{-r_A}$$

$$-r_A = \frac{F_{A0}X_{A,in}}{W}$$

$$= \frac{F_{A0}(1 - C_{A3}/C_{A0})}{W}$$

$$= \frac{F_{A0}(C_{A0} - C_{A,out})}{WC_{A0}}$$

$$= \frac{F_{in}}{W}(C_{A,in} - C_{A,out})$$

APPENDIX C

RATE EXPRESSION FOR TETRALIN HYDROGENATION

RATE EXPRESSION FOR TETRALIN HYDROGENATION

Reaction of Tetralin hydrogenation, assumed irreversible reaction, could be written as :

$$C_{10}H_{12} + 3H_2 \longrightarrow C_{10}H_{18}$$

The reaction was catalytic and it was assumed that hydrogen and Tetralin were adsorbed on same type of sites on the catalyst. Hydrogen was adsorbed in atomic form and reacted with adsorbed Tetralin. The intermediate products of the reaction were assumed to remain on the sites until the final product, decalin, was formed. The general reaction scheme was

$$T + S \longrightarrow T.S \qquad (1)$$

$$H_2 + 2S \longrightarrow 2H.S \qquad (2)$$

$$T.S + H.S \longrightarrow P.S + S \qquad (3)$$

$$P.S + H.S \longrightarrow Hx.S + S \qquad (4)$$

$$H_2 + 2S \longrightarrow 2H.S \qquad (5)$$

$$Hx.S + H.S \longrightarrow Hp.S + S \qquad (6)$$

$$Hp.S + H.S \longrightarrow Oc.S + S \qquad (7)$$

$$H_2 + 2S \longrightarrow 2H.S \qquad (8)$$

$$Oc.S + H.S \longrightarrow N.S + S \qquad (9)$$

$$N.S + H.S \longrightarrow D.S + S \qquad (10)$$

$$D.S \longrightarrow D + S \qquad (11)$$

where S is adsorption site on the catalyst

T is tetrahydronaphthalene (tetralin)

H is hydrogen atom

P is pentahydronaphthalene

Hx is hexahydronaphthalene
Hp is heptahydronaphthalene
Oc is octahydronaphthalene
N is nonahydronaphthalene
D is decahydronaphthalene (decalin)

The rates of the reactions (1-11) can be written as :

$$r_1 = k_1 C_T C_S - k_{-1} C_{TS} \tag{12}$$

$$r_2 = k_2 C_{H_2} C_S^2 - k_{-2} C_{HS}^2 \tag{13}$$

$$r_3 = k_3 C_{TS} C_{HS} - k_{-3} C_{PS} C_S \tag{14}$$

$$r_4 = k_4 C_{PS} C_{HS} - k_{-4} C_{HxS} C_S \tag{15}$$

$$r_5 = r_8 = r_2$$

$$r_6 = k_6 C_{HxS} C_{HS} - k_{-6} C_{HpS} C_S \tag{16}$$

$$r_7 = k_7 C_{HpS} C_{HS} - k_{-7} C_{OcS} C_S \tag{17}$$

$$r_9 = k_9 C_{OcS} C_{HS} - k_{-9} C_{NS} C_S \tag{18}$$

$$r_{10} = k_{10} C_{NS} C_{HS} - k_{-10} C_{DS} C_S \tag{19}$$

$$r_{11} = k_{11} C_{DS} - k_{-11} C_D C_S \tag{20}$$

where r_i is the rate of reaction i,
k_i is the rate constant of reaction i in forward direction,
k_{-i} is the rate constant of reaction i in reverse direction,
C_j is the concentration of component j,
and C_S is the concentration of sites.

Let

$$K_1 = k_1/k_{-1} \tag{21}$$

$$K_2 = k_2/k_{-2} \tag{22}$$

$$K_3 = k_3/k_{-3} \tag{23}$$

$$K_4 = k_4/k_{-4} \tag{24}$$

$$K_6 = k_6/k_{-6} \tag{25}$$

$$K_7 = k_7/k_{-7} \tag{26}$$

$$K_9 = k_9/k_{-9} \tag{27}$$

$$K_{10} = k_{10}/k_{-10} \tag{28}$$

$$K_{11} = k_{-11}/k_{11} \tag{29}$$

where K_1 is the adsorption equilibrium constant of compound 1,

and K_3 is the equilibrium constant of the surface reaction.

Substitution of equations 21-29 into equations 12-20 yields the following equations :

$$r_1 = k_1(C_T C_S - C_{TS}/K_1) \tag{30}$$

$$r_2 = k_2(C_{H_2} C_S^2 - C_{HS}^2/K_2) \tag{31}$$

$$r_3 = k_3(C_{TS} C_{HS} - C_{PS} C_S/K_3) \tag{32}$$

$$r_4 = k_4(C_{PS} C_{HS} - C_{HxS} C_S/K_4) \tag{33}$$

$$r_6 = k_6(C_{HxS} C_{HS} - C_{HpS} C_S/K_6) \tag{34}$$

$$r_7 = k_7(C_{HpS} C_{HS} - C_{OcS} C_S/K_7) \tag{35}$$

$$r_9 = k_9(C_{OcS}C_{HS} - C_{NS}C_S/K_9) \tag{36}$$

$$r_{10} = k_{10}(C_{NS}C_{HS} - C_{DS}C_S/K_{10}) \tag{37}$$

$$r_{11} = k_{-11}(C_{DS}/K_{11} - C_D C_S) \tag{38}$$

Assuming surface reaction, r_3, to be the rate controlling step, then :

$$k_1 \longrightarrow \infty$$

$$k_2 \longrightarrow \infty$$

$$k_4 \longrightarrow \infty$$

$$k_6 \longrightarrow \infty$$

$$k_7 \longrightarrow \infty$$

$$k_9 \longrightarrow \infty$$

$$k_{10} \longrightarrow \infty$$

$$k_{-11} \longrightarrow \infty$$

Since the rates must be finite, then the value in parenthesis in each of the equations 30, 31, 33, 34, 35, 36, 37, and 38 must be equal to zero. The following relations are obtained:

$$C_{TS} = K_1 C_T C_S \tag{39}$$

$$C_{HS} = K_2 C_{H_2} C_S \tag{40}$$

$$C_{PS} = C_{HxS} \frac{C_S}{C_{HS}} \frac{1}{K_4} \tag{41}$$

$$C_{HxS} = C_{HpS} \frac{C_S}{C_{HS}} \frac{1}{K_6} \tag{42}$$

$$C_{HpS} = C_{OcS} \frac{C_S}{C_{HS}} \frac{1}{K_7} \tag{43}$$

$$C_{OcS} = C_{NS} \frac{C_S}{C_{HS}} \frac{1}{K_9} \tag{44}$$

$$C_{NS} = C_{DS} \frac{C_S}{C_{HS}} \frac{1}{K_{10}} \tag{45}$$

$$C_{DS} = K_{11} C_D C_S \tag{46}$$

Equations 41-45 can be rewritten as :

$$C_{PS} = \frac{K_{11}}{K_4 K_6 K_7 K_9 K_{10}} \quad \frac{C_D C_S}{(\sqrt{K_2 C_{H_2}})^5} \tag{47}$$

$$C_{HxS} = \frac{K_{11}}{K_6 K_7 K_9 K_{10}} \quad \frac{C_D C_S}{(\sqrt{K_2 C_{H_2}})^4} \tag{48}$$

$$C_{HpS} = \frac{K_{11}}{K_7 K_9 K_{10}} \quad \frac{C_D C_S}{(\sqrt{K_2 C_{H_2}})^3} \tag{49}$$

$$C_{OcS} = \frac{K_{11}}{K_9 K_{10}} \quad \frac{C_D C_S}{(\sqrt{K_2 C_{H_2}})^2} \tag{50}$$

$$C_{NS} = \frac{K_{11}}{K_{10}} \quad \frac{C_D C_S}{(\sqrt{K_2 C_{H_2}})} \tag{51}$$

By assuming the surface reaction (step 3) a rate controlling step, we can write

$$-r_T = r_3 = k_3(C_{TS}C_{HS} - C_{PS}C_S/K_3) \qquad (52)$$

Substitution of C_{TS}, C_{HS}, C_{PS}, we obtain :

$$-r_T = k_3\left(K_1 C_T C_S \; K_2 C_{H_2} \; C_S - \frac{K_{12} C_D C_S \left(\frac{C_S}{C_{HS}}\right)^5 C_S}{K_3}\right) \qquad (53)$$

$$-r_T = k_3\left(K_1 \; K_2 C_{H_2} \; C_T C_S^2 - \frac{K_{12} C_D C_S^7}{C_{HS}^5 \; K_3}\right) \qquad (54)$$

$$-r_T = k_3\left(K_1 \; K_2 C_{H_2} \; C_T C_S^2 - \frac{K_{12} C_D C_S^7}{K_3(\; K_2 C_{H_2})^5 C_S^5}\right) \qquad (55)$$

$$-r_T = k_3\left(K_1 \; K_2 C_{H_2} \; C_T C_S^2 - \frac{K_{12} C_D}{K_3 (K_2 C_{H_2})^{5/2}} \; C_S^2\right) \qquad (56)$$

$$-r_T = k_3 K_1 K_2^{\frac{1}{2}} \; C_S^2 \; \left(C_{H_2}^{\frac{1}{2}} \; C_T - \frac{K_{12}}{K_3 K_1 K_2^{\frac{1}{2}}} \; \frac{C_D}{(K_2 C_{H_2})^{5/2}}\right) \qquad (57)$$

where

$$K_{12} = \frac{K_{11}}{K_4 K_6 K_7 K_9 K_{10}}$$

Let

$$C_t = C_S + C_{TS} + C_{HS} + C_{PS} + C_{HxS} + C_{HpS} + C_{OcS} + C_{NS} + C_{DS} \tag{58}$$

Substitution of equations 39-46 into equation 58, we obtain:

$$C_t = C_S \left(1 + K_1C_T + K_2C_{H_2} + \frac{K_{11}}{K_4K_6K_7K_9K_{10}} \frac{C_D}{(\sqrt{K_2C_{H_2}})^5} + \frac{K_{11}}{K_6K_7K_9K_{10}} \frac{C_D}{(\sqrt{K_2C_{H_2}})^4} + \frac{K_{11}}{K_7K_9K_{10}} \frac{C_D}{(\sqrt{K_2C_{H_2}})^3} + \frac{K_{11}}{K_9K_{10}} \frac{C_D}{(\sqrt{K_2C_{H_2}})^2} + \frac{K_{11}}{K_{10}} \frac{C_D}{(\sqrt{K_2C_{H_2}})} + K_{11}C_D \right) \tag{59}$$

Let

$$K_{13} = \frac{K_{11}}{K_4K_6K_7K_9K_{10}(\sqrt{K_2C_{H_2}})^5} + \frac{K_{11}}{K_6K_7K_9K_{10}(\sqrt{K_2C_{H_2}})^4} + \frac{K_{11}}{K_7K_9K_{10}(\sqrt{K_2C_{H_2}})^3} + \frac{K_{11}}{K_9K_{10}(\sqrt{K_2C_{H_2}})^2} + \frac{K_{11}}{K_{10}(\sqrt{K_2C_{H_2}})} + K_{11} \tag{60}$$

Then equation 59 can be written as

$$C_S = \frac{C_t}{(1 + K_1 C_T + \sqrt{K_2 C_{H_2}} + K_{13} C_D)} \qquad (61)$$

Substitution of equation 61 into equation 52 gives

$$-r_T = \frac{k_3 K_1 K_2^{\frac{1}{2}} C_t^2 \left(C_{H_2}^{\frac{1}{2}} C_T - \frac{K_{12}}{K_3 K_1 K_2^{\frac{1}{2}}} \frac{C_D}{(K_2 C_{H_2})^{5/2}} \right)}{(1 + K_1 C_T + \sqrt{K_2 C_{H_2}} + K_{13} C_D)^2} \qquad (62)$$

Concentration of hydrogen is assumed to be constant at our operating conditions and $K_{13}C_D << 1$, we can rewrite equation 62 as

$$-r_T = \frac{K\ C_T}{(1 + K_1 C_T)^2} \qquad (63)$$

Figure 3 shows the plot of CT versus $-r_T$ taken from the experiment with variable liquid feed flow rate. It is shown that the reaction can be assumed a pseudo first order reaction at low C_T. Equation 63 can be written as

$$-r_T = K\ C_T \qquad (64)$$

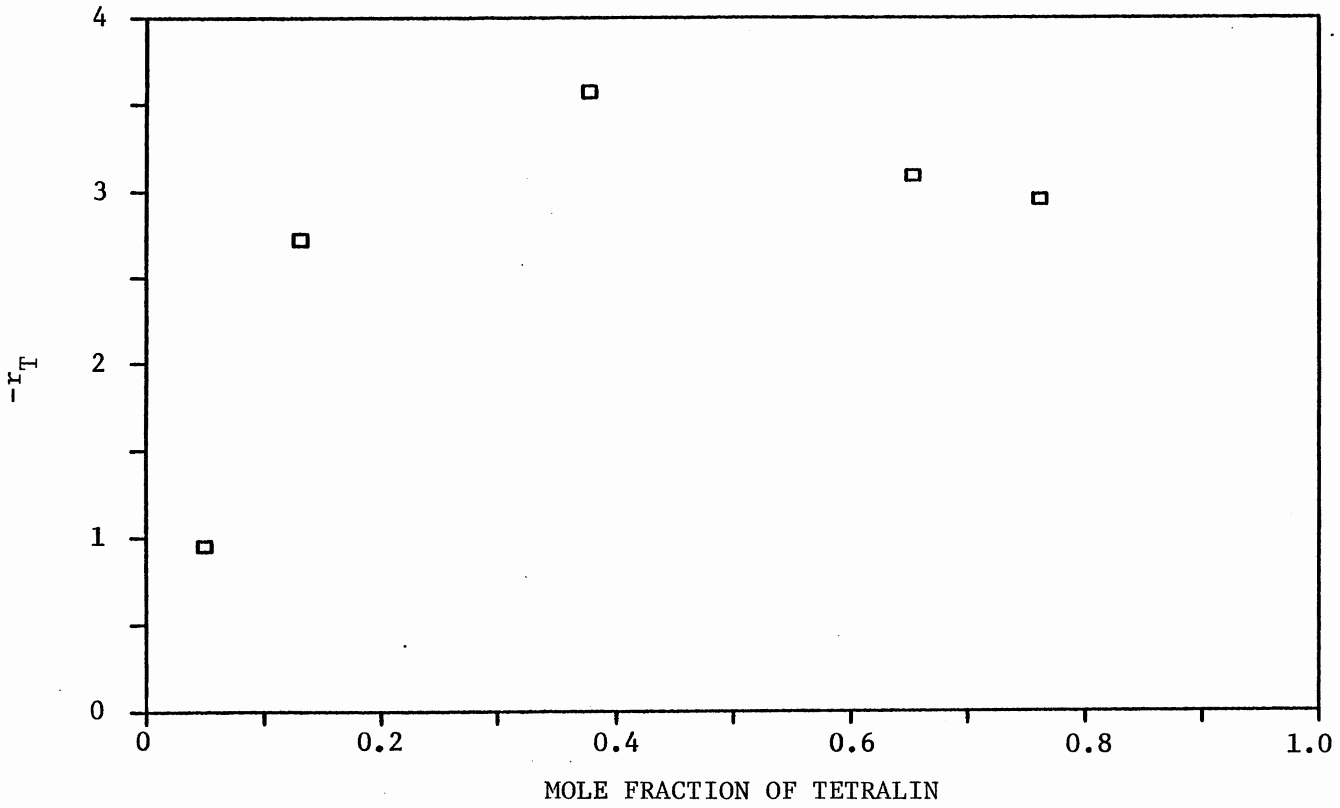


Figure 3. Plot of Tetralin Concentration Versus Rate

APPENDIX D

HOMOGENEOUS REACTION

HOMOGENEOUS REACTION

During our experiments, a homogeneous reaction between titanocene dichloride and Tetralin was observed when the mixture of these two compounds was stored in the feed tank. This homogeneous reaction was also observed by Tscheikuna (3) and was reported to cause a reduction of titanocene dichloride concentration in the mixture.

In order to understand the change in the titanocene dichloride concentration causing by this homogeneous reaction, two experiments were conducted at room temperature and atmospheric pressure. In the first experiment, the specific spectra for titanocene dichloride was identified and used to measure the kinetics of its reaction with Tetralin. In the second experiment, the concentration of soluble titanium in the mixture was measured by atomic absorption spectroscopy.

A Perkin Elmer Lambda 3 UV/VIS Spectrophotometer was used to monitor the concentration of titanocene dichloride. The adsorption at 323.3 nm was used as the wavelength representing titanocene dichloride. A calibration curve for titanocene dichloride in Tetralin was prepared for the range of 0 to 40 ppm titanium as shown in Figure 4. Higher concentrations of titanocene dichloride were not used due to the limits of the UV/VIS spectrophotometer. However, higher concentrations can be analyzed by dilution with the solvent.

One sample of 100 ppm titanium as titanocene dichloride

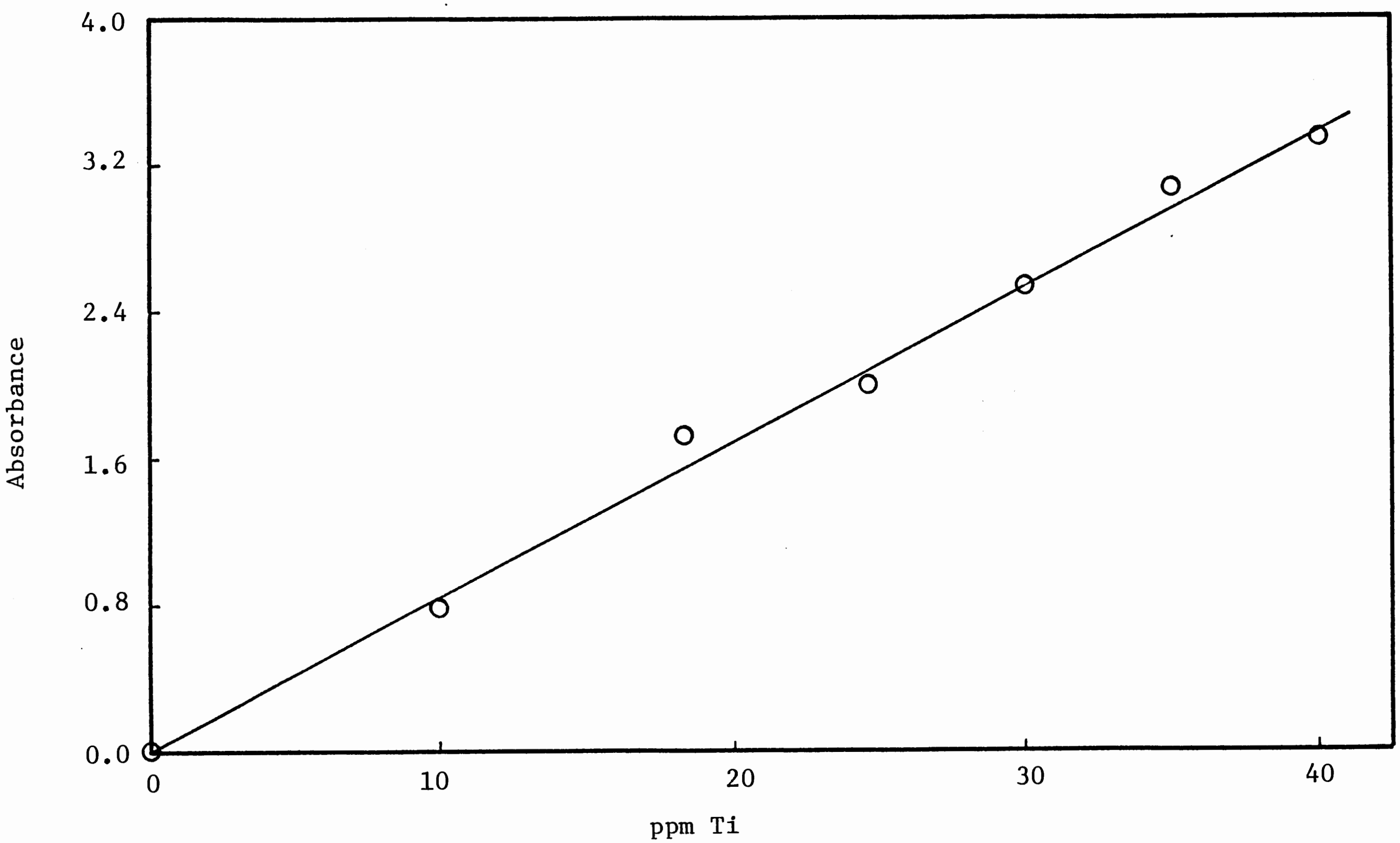


Figure 4. Calibration Curve for Concentration of Titanocene Dichloride in Tetralin at 323.3 nm wavelength

in Tetralin was analyzed using the UV/VIS spectrophotometer at different times. The results are shown in Table V.

From these results, the order of reaction was determined by plotting the data as a zero, first and second order reaction. The data can be fitted to the first order equation as shown in Figure 5. This first order reaction showed a rate constant of 6.17×10^{-6} 1/sec (0.0222 1/hr).

The results of the atomic absorption study are shown in Table VI. Tetralin was doctored with 100 ppm of titanium as titanocene dichloride. The samples were analyzed for titanium using a Perkin Elmer 403 Atomic Absorption Spectrometer. Figure 6 shows the variation of titanium concentration as a function of time. In this case, a differential technique was used for data analysis. Figure 7 shows the reaction rate versus concentration on a log-log plot. The reaction order is graphically determined to be 1.93, approximating a second order reaction, with a rate constant of 3.5×10^{-4} 1/(ppm)(hr).

The differences in the reaction kinetics observed in this study may be described by the differences in the experimental techniques. When titanocene dichloride reacts with Tetralin, it forms a fine insoluble compound suspended in the solution. This compound requires time to precipitate. The particles, that are not precipitated, can be detected by the atomic absorption spectrometer and are registered as titanium along with the unreacted titanocene dichloride. However, the UV/VIS spectrophotometer is

TABLE V

RESULTS OF THE HOMOGENEOUS REACTION OF TETRALIN AND TITANOCENE DICHLORIDE AT 23 C, AS MEASURED BY UV SPECTROSCOPY

Time (hours)	Ti Concentration (ppm)
0	104.0
22	73.6
49	39.8
77.5	18.8

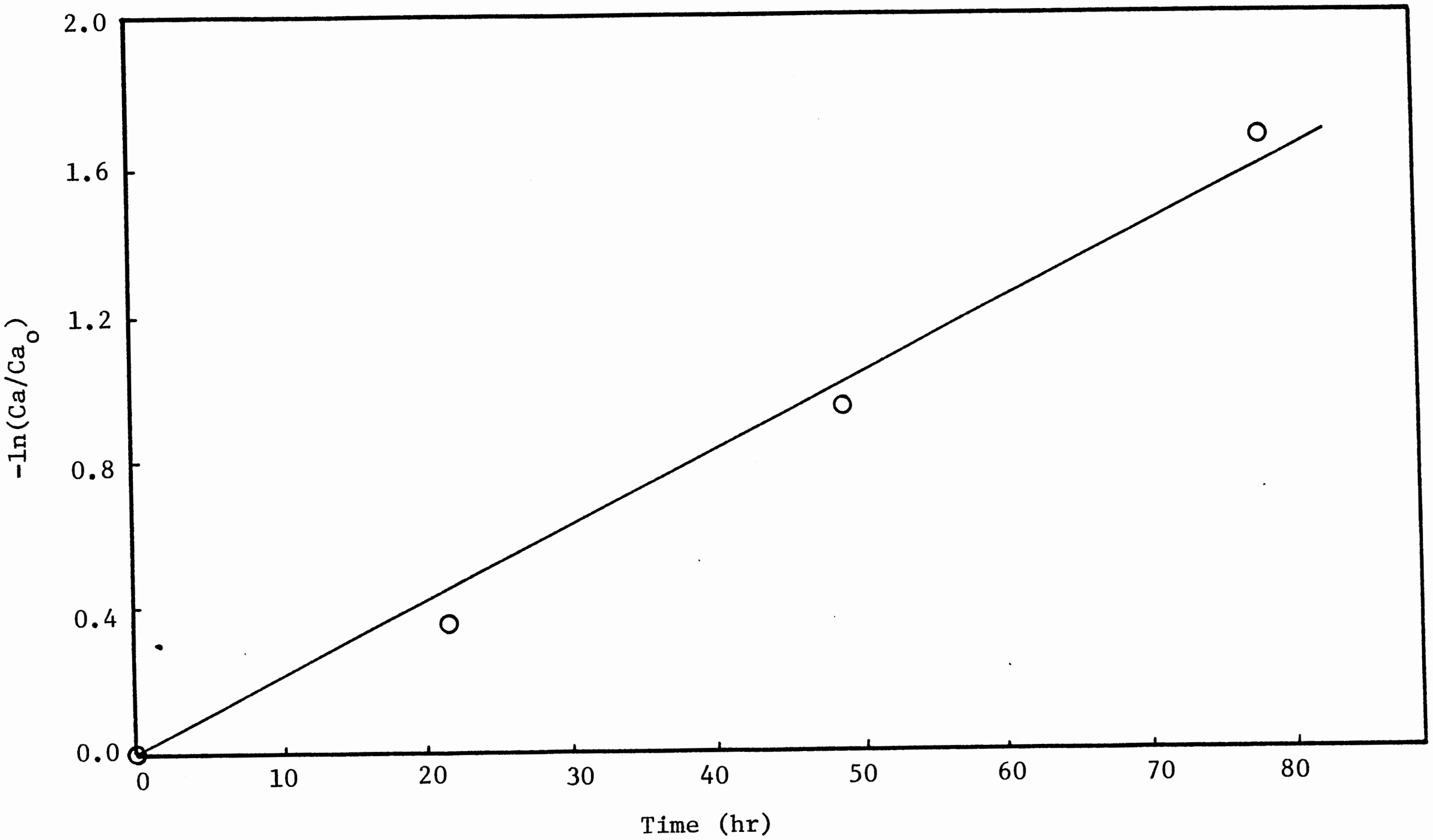


Figure 5. First Order Rate Equation of the Homogeneous Reaction of Titanocene Dichloride in Tetralin

TABLE VI

RESULTS OF THE HOMOGENEOUS REACTION OF TETRALIN AND TITANOCENE DICHLORIDE AT 23 C, AS MEASURED BY ATOMIC ABSORPTION

Time (hours)	Ti Concentration (ppm)
0	100
18	60
45	40
69	30
114	20
2600	5

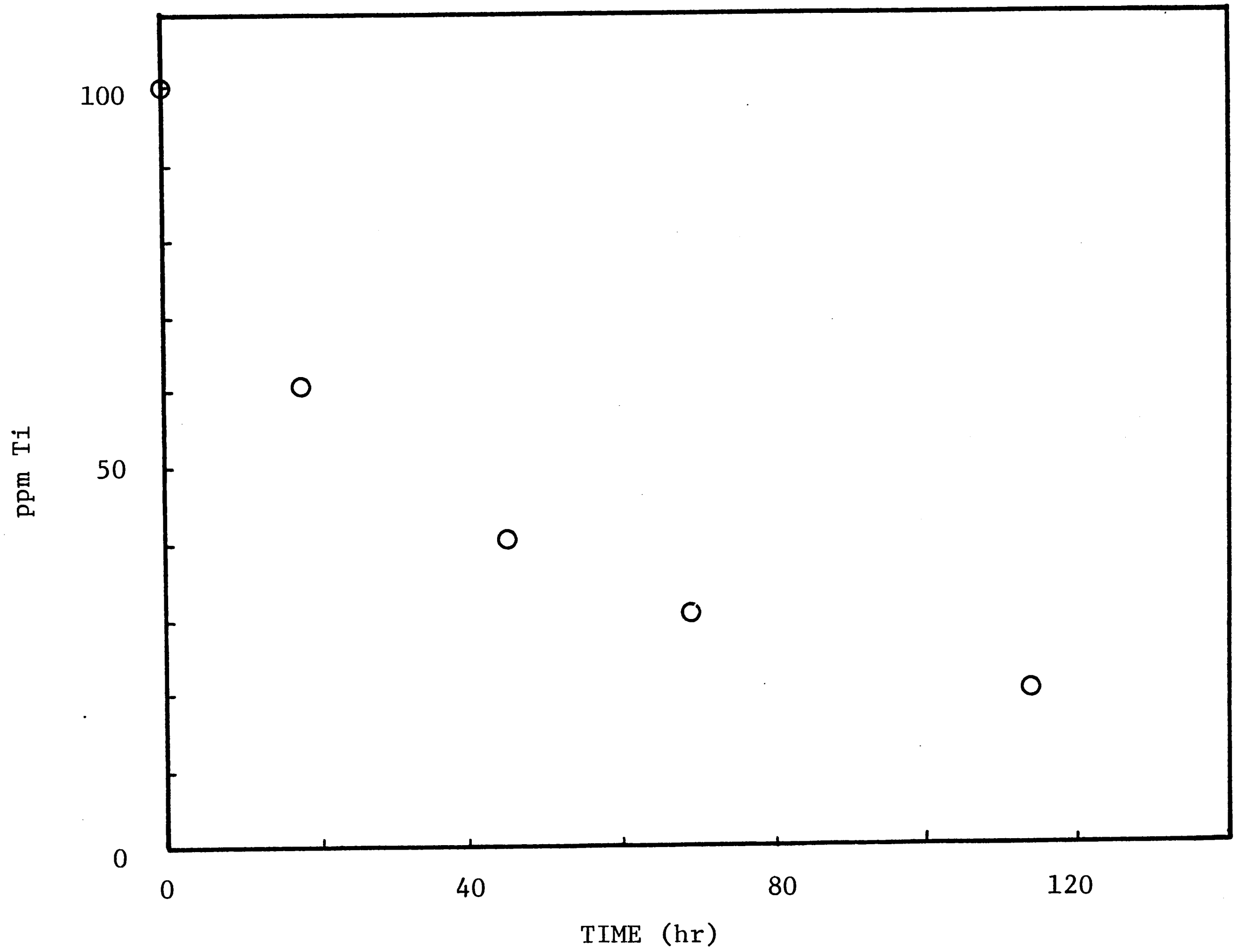


Figure 6. Variation of Concentration of Titanium with Time as Measured by Atomic Absorption

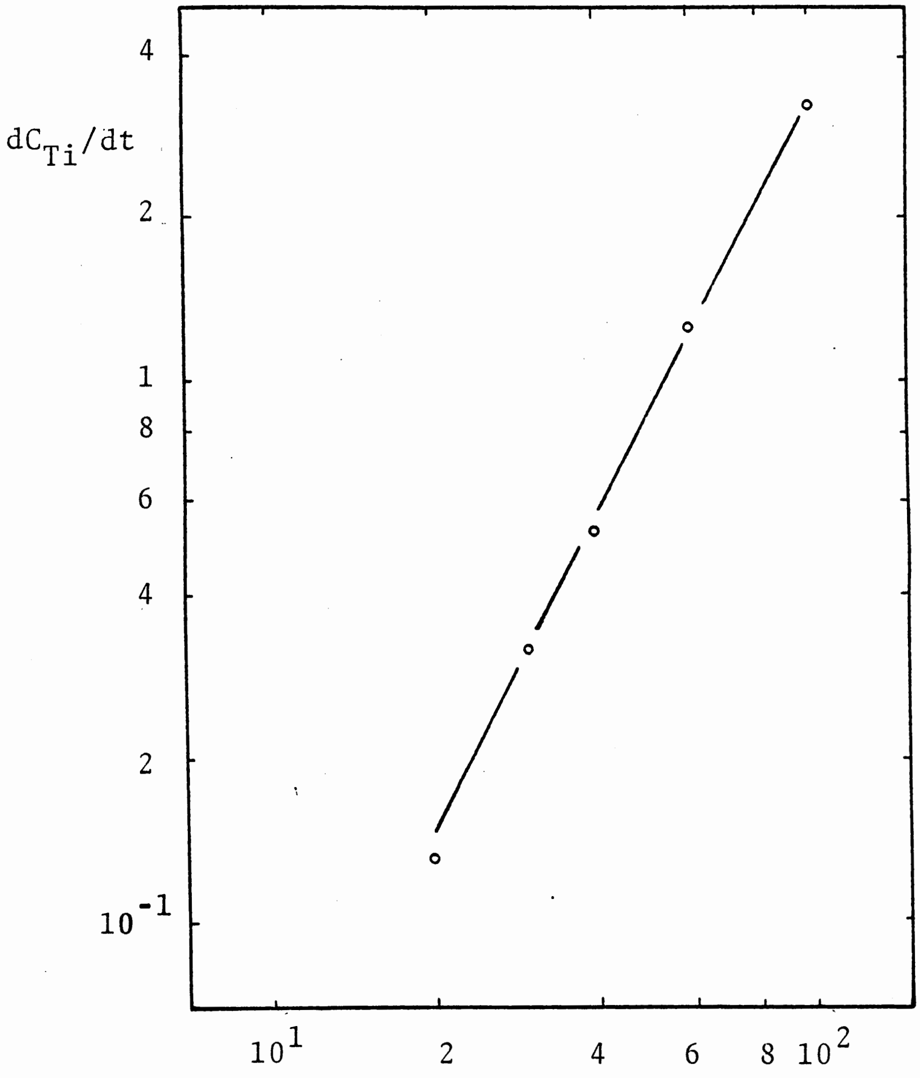


Figure 7. Titanocene Dichloride Decomposition Rate Versus Titanium Concentration

sensitive only to the titanocene dichloride. Therefore the UV spectrophotometric technique is considered to be more accurate. The homogeneous reaction between titanocene dichloride and Tetralin is concluded to be first order with respect to titanocene dichloride concentration. Additional information dealing with this homogeneous reaction are reported elsewhere (4,5,6).

APPENDIX E

SAMPLE CALCULATION FOR RATE CONSTANTS

SAMPLE CALCULATION FOR RATE CONSTANTS

Rate equations for hydrogenation of Tetralin, shown in Figure 8, are written as

$$-r_T = (k_2+k_3+k_6+k_8+k_9+k_{10})\ C_T$$

$$-r_{CD} = -\ k_2C_T + k_4C_{CD} - k_5C_{TD}$$

$$-r_{TD} = -\ k_3C_T - k_4C_{CD} + k_5C_{TD}$$

$$-r_{BB} = -\ k_6C_T + k_7C_{BB}$$

$$-r_{BC} = -\ k_7C_{BB}$$

$$-r_{M1} = -\ k_8C_T$$

$$-r_{M2} = -\ k_9C_T$$

$$-r_{M4} = -\ k_{10}C_T$$

where r_i is the rate of reaction of compound i

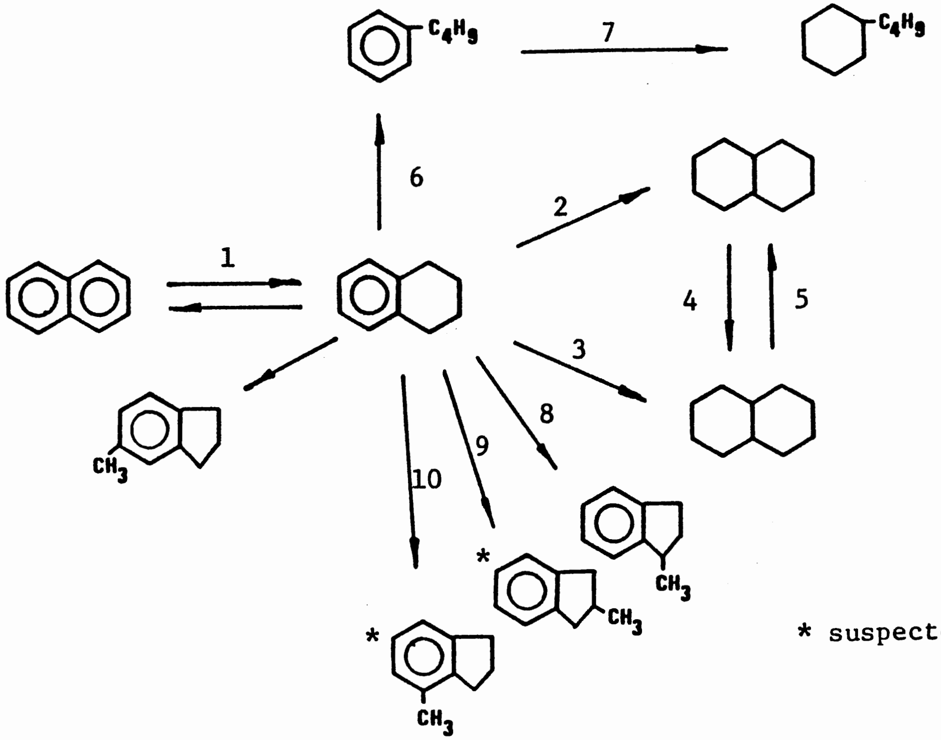
k_j is the first order rate constant of reaction j

C_i is the mole fraction of compound i

The rate constants in these equations can be calculated using the experimental results obtained from the gas chromatographic analysis. Table VII shows a sample of the results which is used in the calculation. The compositions of the products are the average compositions of the samples taken during the last six hours.

The reaction rates are calculated using the reactor performance model which is written as

$$-r_i = \frac{F}{W}\ (C_{i,in} - C_{i,out})$$



* suspected to be present

Figure 8. Schematic Diagram of Reaction Mechanism

TABLE VII

FEED AND PRODUCT COMPOSITIONS

Compounds	Feed mole percent	Product mole percent
Tetralin	98.90	9.43
Cis-decalin	0.33	14.53
Trans-decalin	0.19	73.58
Naphthalene	0.58	0.08
n-Butylbenzene	0.00	0.31
n-butylcyclohexane	0.00	0.13
1-Methylindan	0.00	0.13
2-Methylindan	0.00	1.01
4-Methylindan	0.00	0.29
Unknown	0.00	0.51

where F is the mole flow rate of the reactant (mole/sec).

W is the weight of the catalyst (gm).

$C_{i,in}$ is the mole fraction of compound i flowing into the reactor.

$C_{i,out}$ is the mole fraction of compound i flowing out of the reactor.

For the case when the feed flow rate is 33.3 ml/hr (6.70 E-05 mole/sec) and the weight of the catalayst is 20 grams, the calculation results of the rate constants are shown in Table VIII.

TABLE VIII

RATE CONSTANTS FOR NiMo/ALUMINA CATALYST

Rate Constant	(mole/gm of cat. sec)
k_2 x 1E06	6.13
k_3 x 1E05	2.23
k_4 x 1E06*	2.66
k_5 x 1E05*	3.12
k_6 x 1E07	2.00
k_7 x 1E06	1.42
k_8 x 1E07	0.46
k_9 x 1E07	3.86
k_{10} x 1E07	1.02

* Note: k_4 and k_5 are obtained from the calculation of Decalin Isomerization

APPENDIX F

ERRORS IN SAMPLE ANALYSES

ERRORS IN SAMPLE ANALYSES

Gas Chromatographic Error

Four samples selected from Tetralin experiments are used to determine the error in gas chromatographic analysis. Each sample is analyzed three times. The results, shown in Tables IX through XII, are reported as the weight percent of each compound in the sample. The error in our G. C. analysis depends on the concentration of each compound. The error in the analysis varies from 0.1 to 2.5 % depending on the concentration of the compound.

Coke Analysis Error

Table XIII shows the coke analysis of six different samples. Each sample is analyzed three times. The possible error in coke analysis is found to be less than 5 %.

TABLE IX

RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS FOR SAMPLE I

	Weight Percent			
	Trans Decalin	Cis Decalin	Tetralin	Naphthalene
Injection 1	67.04	15.96	15.65	0.132
Injection 2	67.30	15.91	15.45	0.129
Injection 3	66.99	15.97	15.69	0.133
Injection 4	67.04	15.96	15.65	0.131
Average	67.09	15.95	15.61	0.131
Max. Error	0.21	0.04	0.16	0.002
Max. Error (%)	0.31	0.25	1.02	1.53

TABLE X

RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS FOR SAMPLE II

	Weight Percent			
	Trans Decalin	Cis Decalin	Tetralin	Naphthalene
Injection 1	58.03	14.84	25.99	0.175
Injection 2	57.76	14.86	26.23	0.182
Injection 3	58.19	14.85	25.81	0.176
Average	57.99	14.85	26.01	0.178
Max. Error	0.23	0.01	0.22	0.004
Max. Error (%)	0.40	0.10	0.85	2.25

TABLE XI

RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS FOR SAMPLE III

	Weight Percent			
	Trans Decalin	Cis Decalin	Tetralin	Naphthalene
Injection 1	52.83	14.39	30.91	0.236
Injection 2	53.09	14.37	30.67	0.232
Injection 3	52.69	14.41	31.03	0.228
Average	52.87	14.39	30.87	0.232
Max. Error	0.22	0.02	0.20	0.004
Max. Error (%)	0.42	0.14	0.65	1.72

TABLE XII

RESULTS OF GAS CHROMATOGRAPHIC ANALYSIS FOR SAMPLE IV

	Weight Percent			
	Trans Decalin	Cis Decalin	Tetralin	Naphthalene
Injection 1	53.62	14.62	29.94	0.202
Injection 2	53.54	14.60	30.03	0.212
Injection 3	53.95	14.57	29.64	0.207
Average	53.71	14.60	29.87	0.207
Max. Error	0.24	0.03	0.23	0.005
Max. Error (%)	0.47	0.21	0.77	2.41

TABLE XIII

ERROR IN COKE ANALYSIS

Sample	1	2	3	average	Max. Error	Maximum Error (%)
1	13.79	13.78	14.29	13.95	0.36	2.44
2	9.38	9.52	8.83	9.24	0.41	4.44
3	5.94	6.35	6.47	6.25	0.31	4.96
4	11.63	11.53	10.79	11.32	0.53	4.68
5	8.07	8.61	8.47	8.38	0.31	3.70
6	12.65	12.51	12.43	12.53	0.12	0.96

APPENDIX G

CALCULATIONS OF CHEMICAL EQUILIBRIA AND RATE CONSTANTS FOR DECALIN

CALCULATIONS OF CHEMICAL EQUILIBRIA AND RATE CONSTANTS FOR DECALIN

In our decalin experiments, we observed a conversion from cis-decalin to trans-decalin in the presence of catalyst. However, the isomerization of decalin is reported as a reversible reaction (7,8) which can be written as

Cis-decalin Trans-decalin (1)

The equilibrium constant, K, for this reaction can be calculated from

$$\ln K = \frac{\Delta G}{-RT} \qquad (2)$$

where K is the equilibrium constant

ΔG is the change in Gibb Energy (J/mole)

R is gas constant (J/K. k mole)

T is the temperature (K)

By using equation 2 and the data from API Monograph Series (9), the equilibrium constant at 298.15 K is found to be 92.8 .

The equilibrium constant at our operating temperature, 350 C (662 F), can be calculated from

$$\frac{d\ \ln K}{d\ T} = \frac{\Delta H}{RT^2} \qquad (3)$$

where ΔH is the standard enthalpy change and is given in the form of

$$\Delta H = \Delta H_o + \int \Delta C_p \, dT \qquad (4)$$

where ΔH_o is the change of enthalpy at standard conditions

Cp is the heat capacity

The equilibrium constant can be determined if the relation of the heat capacity is known. Table XIV summarizes the equilibrium constant calculated using the heat capacity data from different sources. The results of our calculation are widely scattered because of the differences in heat capacity data. We also calculated the equilibrium constant using our experimental data obtained from the experiment with variable flow rate and found that the equilibrium constant is 8.54 . This equilibrium constant will be used in further calculation.

Rate of disappearance of cis-decalin in equation 1 can be written as

$$-r_{CD} = k_4 C_{CD} - k_5 C_{TD} \tag{5}$$

where k_i is the rate constant of compound i

C_j is the mole fraction of compound j

The reaction is assumed to be at equilibrium and the equilibrium constant is given as

$$K = \frac{k_4}{k_5} = 8.54 \tag{6}$$

$$k_4 = 8.54 k_5 \tag{7}$$

Substitute k_4 into equation 5 gives

$$-r_{CD} = 8.54 k_5 C_{CD} - k_5 C_{TD} \tag{8}$$

TABLE XIV

CALCULATED CHEMICAL EQUILIBRIUM CONSTANT FOR DECALIN ISOMERIZATION REACTION

Data Source	K
Reference 10 @ 20 bars	5.86
Reference 10 @ 100 bars	2.13
Reference 7	9.04
Reference 11	5.83

Equation 8 can be rearrange to

$$k_5 = \frac{-r_{CD}}{8.54C_{CD} - C_{TD}} \tag{9}$$

Substitution of the rate equation by the reactor performance model, we obtain

$$k_5 = \frac{F\ (C_{CD,in} - C_{CD,out})}{W\ (8.54C_{CD,out} - C_{TD,out})} \tag{10}$$

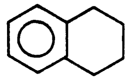
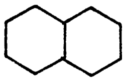
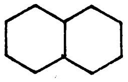
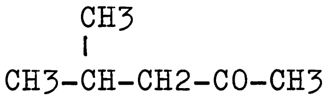
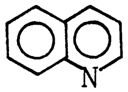
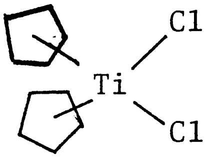
and k_4 is calculated from

$$k_4 = 8.54\ k_5 \tag{11}$$

APPENDIX H

PROPERTIES OF FEEDSTOCKS

PROPERTIES OF FEED STOCKS

Compound	Structure	B.P.(C)	M.P.(C)	M.W.
Tetralin		206	-31	132
Cis-Decalin		193	-51	138
Trans-Decalin		185	-32	138
MIBK	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-CO-CH_3$	117	-85	100
Quinoline		237	-15	129
Titanocene Dichloride		-	287-9	249

B.P. - Boiling Point
M.P. - Melting Point
M.W. - Molecular Weight

Source - Perry, R. H. and Chilton, C. H., Chemical Engineers' Handbook, fifth edition, McGraw-Hill, 1973.

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VITA

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