in the reactor was varied between 300 and 1600 psig (cold) and reaction temperature between 433 and 453 K. Reactions were carried out at lengths from 10 to 60 minutes.

**Table 13** Chemicals Used in This Study

| | Chemical | Formula | Purity (%) |
|---|---|---|---|
| Hydrocarbons | n-heptane, n-C7 | $CH_3(CH_2)_5CH_3$ | 99 |
| | n-hexadecane (n-C16) | $CH_3(CH_2)_{14}CH_3$ | 99 |
| | n-dotriacontane (n-C32) | $CH_3(CH_2)_{30}CH_3$ | 97 |
| | FT waxes | C58 - C64 | unknown |
| Hydride transfer agents | methylcyclopentane (MCP) | $CH_3(C_5H_9)$ | 98 |
| | adamantane | $C_{10}H_{16}$ | 99+ |
| Olefins | 1-heptene | $CH_2=CH(CH_2)_4CH_3$ | 97 |
| | 5-decene | $CH_3(CH_2)_3CH=CH(CH_2)_3CH_3$ | 99+ |
| | 1-hexadecene | $CH_2=CH(CH_2)_{13}CH_3$ | 92 |

The hydrocracking and hydroisomerization of n-hexadecane was also carried out in a fixed-bed continuous reactor for 96 hours. The reaction temperature was measured with a thermocouple which was placed in the catalyst bed. Before reaction, the $Pt/ZrO_2/SO_4$ catalyst was pressed into pellets in a hydraulic press at about 20,000 psig. The pellets were crushed and then screened to obtain catalyst beads of 20-30 mesh. They were then loaded to the reactor preheated at 383 K. The catalyst was preheated in a 723 K furnace under a continuous air flow for one hour and a half, and then cooled down to room temperature. The reactor was purged with hydrogen (99.99%) for five minutes, then pressurized to 360 psig. The hydrogen flow rate was controlled by a mass flow controller to obtain a suitable molar ratio of reactant feed to hydrogen. The flow rate of n-hexadecane was controlled by an instrument mini pump (flow rate range: 39 - 390 $cm^3$

per hour; maximum pressure: 5000 psig). After desired flow rates of hydrogen and n-hexadecane were reached, the reactor was heated by the furnace up to the reaction temperature. The system reached a steady state in about 40 minutes with 60 ml per minute of hydrogen and 100 $cm^3$ per hour of n-hexadecane. The liquid products were taken from the product receiver and then analyzed using an HP-5890 II GC.

## 7.4 Results and Discussion

### 7.4.1 Catalytic Activity of $Pt/ZrO_2/SO_4$ Toward Different Long Chain Hydrocarbons

Three long chain hydrocarbons, n-hexadecane, n-dotriacontane and Sasol wax (C58-C64) were chosen for testing the catalytic activity of the $Pt/ZrO_2/SO_4$ catalyst (**SZD1**). Under relatively mild reaction conditions (433 - 443 K and 360 psig), this catalyst exhibited a high catalytic activity for long chain hydrocarbons such as n-C16 and n-C32) Sasol wax (**Figure 13**). After 60 minutes, about 90 wt.% of these paraffins had reacted. Selectivities to cracked products were high, but those to isomerized products (i-C16, i-C32 and isomerized C58-C64) were low (about 10 wt.%). The cracked product distributions of these three feeds are shown in **Figure 14**. Methane and ethane were not found in the cracked products from these three feeds. In the case of the Sasol wax, the cracked products consisted mainly of C5-C22, encompassing the range of gasoline, diesel and jet fuel; cracked products higher than C22 were not found. It appears that the $Pt/ZrO_2/SO_4$ catalyst is promising for upgrading FT waxes into valuable liquid fuels.

### 7.4.2 Effect of Reaction Conditions

The effects of temperature, time and reactant loading on the hydrocracking and hydroisomerization of waxes were investigated. n-Dotriacontane (n-C32) was chosen as a model compound of waxes. Methylcyclopentane (MCP) was chosen as a solvent. In the presence of MCP, the conversion as well as cracked products (C5-C9 and C10-C13), increased with increasing temperature or reaction time. For n-C32, a higher temperature or a longer reaction time favored the production of cracked products rather than i-C32.

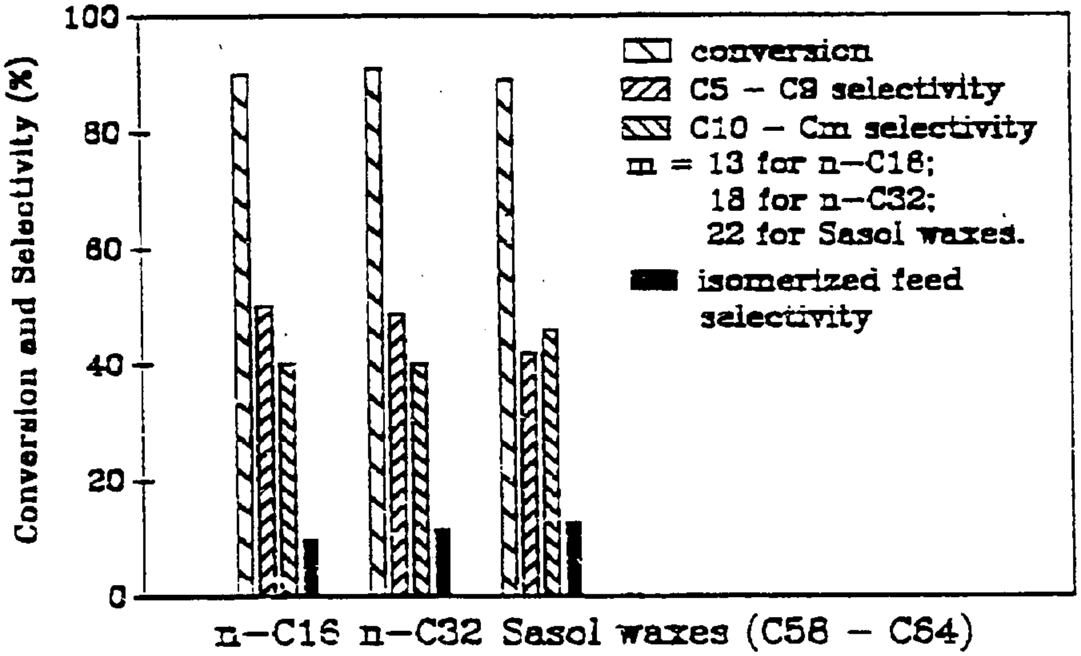

Figure 14. Conversion and Product Selectivity from the Hydrocracking and Hydroisomerization of n-C16, n-C32 and Sasol Wax over the Pt/$ZrO_2$/$SO_4$ Catalyst (cat./n-C16 = 1/6, cat./n-C32 = 1/3,cat./Sasol wax =1/3,433K for n-C16, 443 K for n-C32, 360 psig $H_2$ (cold) and 60 min)(m: the highest carbon number of cracked products from the reaction of alkanes).

### 7.4.2.1 Reaction of n-Dotriacontane.

The effect of reactant loading on catalytic activity of Pt/$ZrO_2$/$SO_4$ for the hydrocracking and hydroisomerization of n-C32 was studied in the absence of MCP. The conversion of n-C32 decreased dramatically with an increase in the n-C32 to catalyst ratio. It appears that, at high n-C32 loadings (n-C32/cat. ratios greater than 4), the Pt/$ZrO_2$/$SO_4$ catalyst was essentially deactivated during reaction as observed by its color change from grey before reaction to yellow after reaction. The color of this catalyst did not change after the reaction of n-C16 when the ratio of n-C16 / catalyst was 6/1, suggesting that it was not deactivated. It appears that the higher viscosity of n-C32 compared to that of n-C16 was responsible for the catalyst deactivation; a high viscosity reacting medium likely hinders hydrogen transfer from the reactant bulk to the catalyst surface and subsequent hydrogenation of carbocation and possibly olefinic intermediates. These intermediates cannot desorb quickly and so block the active catalytic sites.

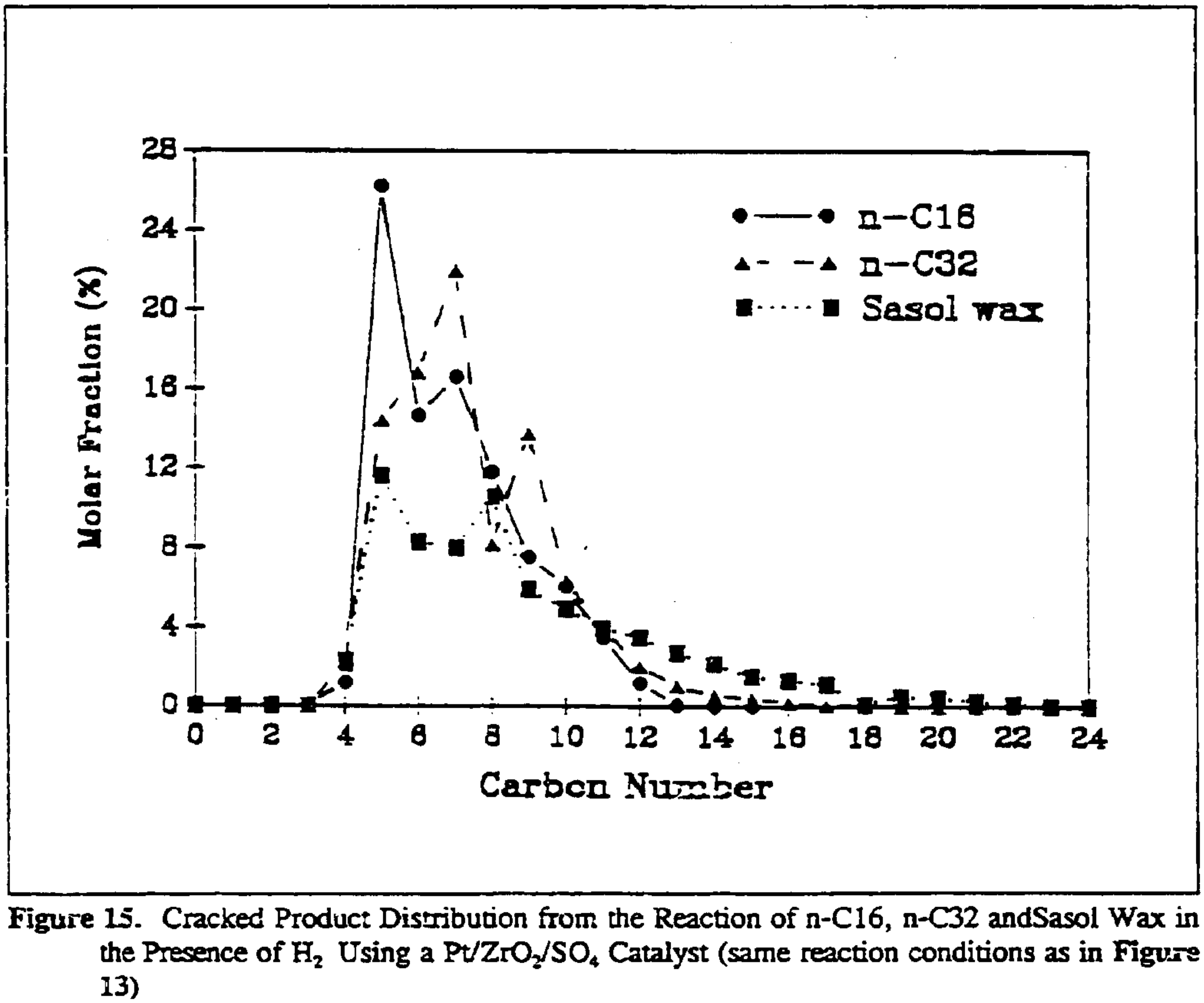

Figure 15. Cracked Product Distribution from the Reaction of n-C16, n-C32 andSasol Wax in the Presence of $H_2$ Using a $Pt/ZrO_2/SO_4$ Catalyst (same reaction conditions as in Figure 13)

**7.4.2.2 Effect of Initial Hydrogen Pressure.** Hydrogen pressure is an important operating parameter, which strongly affects catalytic activity and product selectivity in hydrocracking and hydroisomerization of n-hexadecane catalyzed by $Pt/ZrO_2/SO_4$. The conversion of n-hexadecane as a function of reaction time at various initial $H_2$ pressures (cold) at 433 K is shown in **Figure 16.** The initial reaction rate increased with an increase in the initial hydrogen pressure. For example, the conversions obtained at 460 psig and 700 psig $H_2$ were 78.0% and 94.3%, respectively, after 40 minutes of reaction; it was reduced to 62% under 360 psig $H_2$ for the same

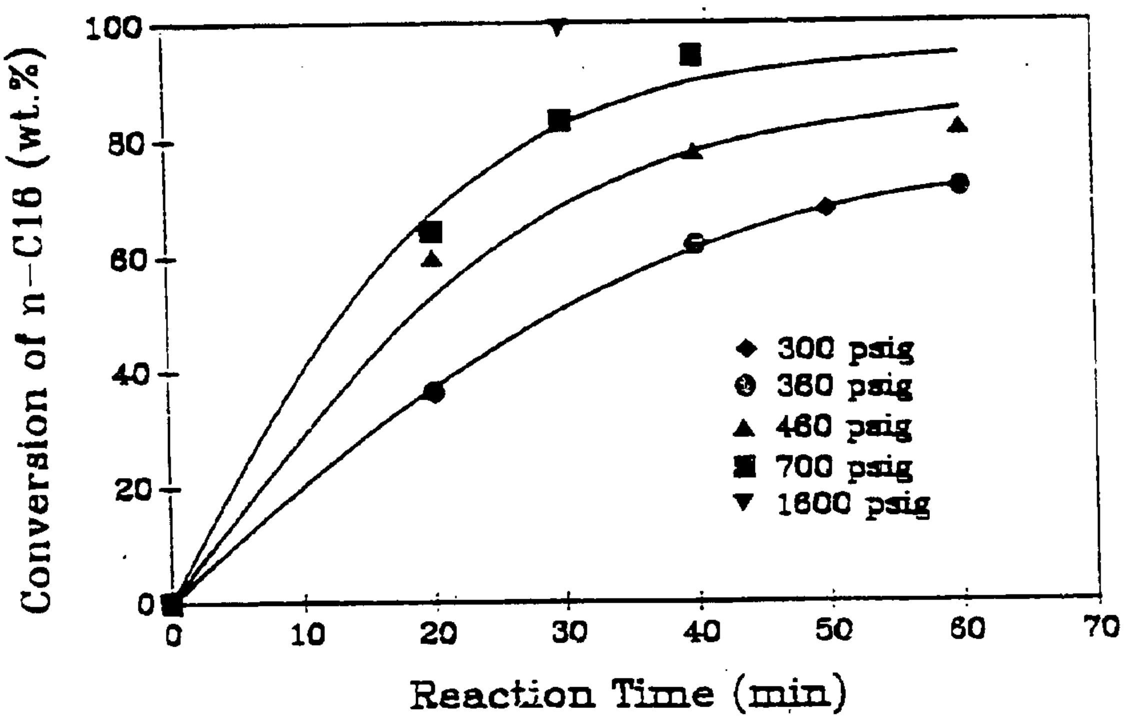

**Figure 16.** Effect of the Initial Hydrogen Pressure (cold) on the Conversion of n-C16 Using the $Pt/ZrO_2/SO_4$ (0.5 wt.% of Pt) Catalyst at 433 K.

reaction time. A similar experimental finding was also reported when the reactions of n-C16 were carried out in a continuous trickle bed reactor(128). The significant increase in the catalytic activity of the $Pt/ZrO_2/SO_4$ catalyst with increasing hydrogen pressure was due to the fact that a high hydrogen pressure favored formation of highly active protonic acid sites(111,113). The product distributions at similar conversion levels obtained at different initial hydrogen pressures (cold) are depicted in Figure 17. Unlike the effect of the initial hydrogen pressure on the reaction rate, the initial hydrogen pressure did not greatly affected the product distribution.

**7.4.2.3** **Long-Term Performance of $Pt/ZrO_2/SO_4$.** The long-term performance of the $Pt/ZrO_2/SO_4$ catalyst was evaluated using the hydrocracking and hydroisomerization of n-hexadecane in a continuous fixed-bed reactor. Hosoi et al.(106) reported that the $Pt/ZrO_2/SO_4$ catalyst was not deactivated in hydroisomerization of n-butane for as long as 1000 hours at 473 K and 150 psig. However, its catalytic behavior with long chain hydrocarbon reactions has not been studied in a similar manner.

The long-term catalytic performance of $Pt/ZrO_2/SO_4$ (0.5 wt% of Pt) for the reaction using n-hexadecane as a feedstock was evaluated. After 96 hours on-stream, the activity of the $Pt/ZrO_2/SO_4$ catalyst remained as high as its initial activity without deactivation. The product distribution obtained from the continuous fixed-bed reactor was similar to that obtained with the batch reactor. A similar finding was also reported in the literature(128).

It was reported that the catalytic performance of $ZrO_2/SO_4$ without hydrogenation metal deteriorated as a result of reduction of the sulfate group in a hydrogen environment(108). A hydrocracking and hydroisomerization reaction of n-hexadecane in the presence of SZD1 was carried out in the tubing bomb microreactor at 1600 psig to determine the effect of high hydrogen pressure on its catalytic activity and product selectivity. At 433 K, the overall conversion reached 99.6 wt.% in 30 minutes; the selectivity to cracked products reached 99.9 % with 99.0 % of the cracked products being in the gasoline range (C5-C9). This confirms our earlier experimental finding that cracking activity increased significantly by increasing hydrogen pressure. The sulfur contents of the $Pt/ZrO_2/SO_2$ catalyst before and after reaction were 1.58 and 1.55 wt.%,

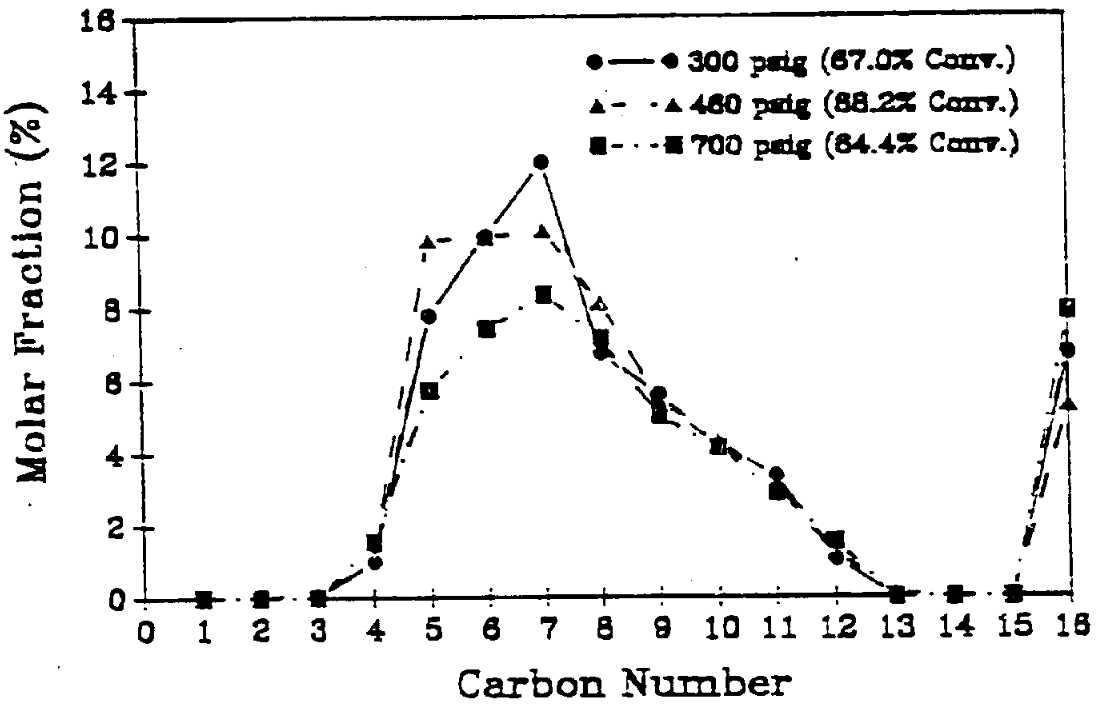

Figure 17. Effect of the Initial Hydrogen Pressure (cold) on the Product Distribution from the Reaction of n-C16 and $H_2$ Using the Pt/$ZrO_2$/$SO_4$ (0.5 wt.% of Pt) Catalyst at 433 K.

respectively, showing that the surface sulfur complex responsible for the generation of highly acidic sites was not reduced under high hydrogen pressures.

### 7.4.2.4 Effect of Reaction Temperature.

This was examined by carrying out the hydrocracking and hydroisomerization of n-hexadecane in the tubing bomb microreactor at two different temperatures (393 and 433 K) under 1600 psig hydrogen pressure. After 30 minutes of reaction, the conversion of n-hexadecane reached 99.6 wt.% at 433 K, but only 33.4 wt.% at 393 K.

### 7.4.2.5 Effect of Addition of Hydride Transfer Agents (Methylcyclopentane and Adamantane).

A hydride transfer agent, adamantane or methylcyclopentane (MCP), was added to the hydrocracking and hydroisomerization of n-C16 and n-C32 systems in order to study their influence on the catalytic activity and product selectivity of the $Pt/ZrO_2/SO_4$. The experimental results are summarized in **Table 14**.

The conversion and selectivity to i-C16 or i-C32 was increased upon addition of a hydride transfer agent (adamantane or MCP), and the selectivity to cracked products was decreased. Similar experimental findings were also reported when adamantane was added to n-heptane and n-octane feeds(130,131). The added adamantane was recovered quantitatively, but about 5% of the MCP was lost under the above reaction conditions. The results show that adamantane or MCP is a good hydride transfer agent.

MCP not only played the role of a hydride transfer agent, as did adamantane, but it also served as a solvent to decrease the viscosity of the n-C32 reacting system. The beneficial effect of adding a hydride transfer agent lies in that it acts as a co-catalyst, enhancing the catalytic activity and modifying product selectivities.

A mechanism of hydride transfer of adamantane in the hydrocracking and hydroisomerization of n-hexadecane is proposed and shown in **Figure 18.**

Adamantane (**structure I**) possesses a very reactive tertiary hydrogen atom with a low binding energy attached to a tertiary carbon. In the presence of a strong acid catalyst, the more stable bridgehead 1-adamantyl cation (**structure II**) is readily formed by release of a hydride(132). This hydride transfer leads to rapid termination of the surface carbocation intermediates of isomerized products from hexadecane, decreasing therefore their average surface lifetime. As a result, it suppresses cracking reaction and favors formation of isomerized hexadecanes.

### 7.4.2.6 Effect of Addition of Olefins.

Commercial raw waxes without being hydrogenated may contain small amounts of olefins(133). In this work, the effect of the presence of olefins on the catalytic activity of the

$Pt/ZrO_2/SO_4$ catalyst for hydrocracking and hydroisomerization of n-heptane and n-hexadecane was studied using three different olefins (1-heptene, 1-hexadecene and 5-decene). The experimental results are given in **Table 15.**

**Table 14.** Effect of Addition of a Hydride Transfer Agent on the Catalytic Activity and Product Selectivity of the $Pt/ZrO_2/SO_4$ Catalyst

| Run No. | Feed | Hydride transfer agent | Conversion (wt.%) | Selectivity (wt.%) | | |
|---|---|---|---|---|---|---|
| | | | | C5-C9 | C10-Cm$^a$ | i-C16 or i-C32 |
| R014 | n-C16 | none | 70.5 | 54.5 | 22.3 | 23.2 |
| R015 | n-C16 | adamantane (0.5 wt.%) | 70.8 | 61.8 | 18.0 | 20.2 |
| R016 | n-C16 | adamantane (7.7 wt.%) | 83.6 | 42.2 | 19.7 | 38.1 |
| R017 | n-C32 | none | 80.5 | 67.0 | 30.0 | 2.3 |
| R018 | n-C32 | MCP (50 wt.%) | 86.7 | 37.7 | 57.7 | 3.9 |

a: m = 13 in the case of n-C16 and 15 in the case of n-C32

Reaction conditions: (i) n-C16: cat./feed: 1/6, 433 K, 360 psig $H_2$ (cold) and 60 min;
(ii) n-C32: cat./feed: 1/3, 443 K, 460 psig $H_2$ (cold) and 60 min.

The conversions of n-heptane and n-hexadecane decreased when an olefin was added. The decrease was much more significant in the case of n-heptane in the presence of 1-heptene: addition of 0.6 wt.% of 1-heptene reduced the conversion of n-heptane from 75.0 to 3.0 wt.%; when 50.0 wt.% of 1-heptene was added, the conversion was undetectable. Also, when an olefin was present

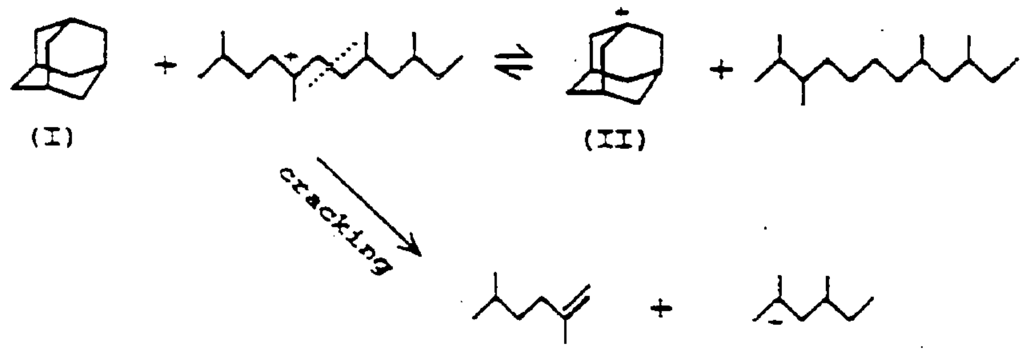

Figure 18. Hydride Transfer Mechanism of Adamantane in the Acid-Catalyzed Hydrocracking of n-Hexadecane

in n-hexadecane, the selectivity to C5-C9 decreased with a concomitant increase in selectivity to C10-C13 and i-C16. In all cases, olefins were hydrogenated rapidly and completely to their corresponding paraffins. In the case of n-heptane with added 1-heptene, the catalyst appeared to be deactivated after reaction (its color was changed from grey to yellow). The presence of an olefin reduces the catalytic activity of the Pt/ZrO$_2$/SO$_4$ catalyst.

The negative effect of the presence of olefins can be understood as follows: olefins are comparatively rich in electrons so that they compete with n-alkanes for active acid sites, adsorbing strongly on the sites of high acid strength, slowing down the reaction rate. In the hydrocracking and hydroisomerization of n-hexadecane, the negative effect of 1-hexadecene on the activity of the Pt/ZrO$_2$/SO$_4$ catalyst was greater than that of 5-decene, indicating that the location of the double bond in an olefin affects its interaction with the acid sites on the catalyst surface. Olefins with a terminal double bond are more reactive towards acid sites than those with an internal double bond mainly because the former have a higher electron density and lower steric hindrance

**Table 15** Effect of Addition of Olefins on the Hydrocracking and Hydroisomerization of n-Heptane and n-Hexadecane Catalyzed by $Pt/ZrO_2/SO_4$

| Run No. | Feed | Olefin | Conversion (wt.%) | Selectivity (wt.%) | | |
|---|---|---|---|---|---|---|
| | | | | C5 -C9 | C10 - C13 | i-C16 |
| R019 | n-C7 | none | 75 | NA | | |
| R020 | n-C7 | 1-heptene (0.6 wt.%) | 3.0 | | | |
| R021 | n-C7 | 1-heptene (50.0 wt.%) | 0.0 | | | |
| R022 | n-C16 | none | 69 | 58.2 | 19.2 | 22.6 |
| R023 | n-C16 | 1-hexadecene (1.5 wt.%) | 59.9 | 52.3 | 21.4 | 26.3 |
| R024 | n-C16 | 5-decene (1.5 wt.%) | 52.7 | 53.9 | 22.4 | 23.7 |
| R025 | n-C16 | 5-decene (10.0 wt.%) | 43.0 | 43.2 | 26.7 | 30.1 |

Reaction conditions: i) n-heptane: cat./feed: 1/10, 423 K, 350 psig $H_2$ (cold) and 60 min
ii) n-hexadecane: cat./feed: 1/6, 433 K, 360 psig $H_2$ (cold) and 60min

### 7.4.3 Further Comments on the Mechanism of Hydrocracking and Hydroisomerization

The mechanism of hydrocracking and hydroisomerization of n-alkanes catalyzed by a bifunctional catalyst remains controversial. According to the classic bifunctional mechanism proposed by Coonradt and Garwood,(30) the initial carbocation intermediates are generated from direct protonation of olefins, which result from the dehydrogenation of their corresponding paraffins on metal sites. It was then expected that a minor amount of olefins, introduced as impurities or formed in-situ by cracking or dehydrogenation of paraffins, could act as initiators to form carbocation intermediates. Hydrogen pressure was perhaps expected to have an inhibitive effect on reaction rate because it was unfavorable for formation of olefins in the dehydrogenation step. However, our experimental findings showed that addition of olefins (on the order of several percent) had a strong inhibitive effect on the acid-catalyzed reactions of n-alkanes, and that an increase in hydrogen pressure significantly enhanced the catalytic activity of the $Pt/ZrO_2/SO_4$ in the hydrocracking and hydroisomerization of n-alkanes. It implies that dehydrogenation of paraffins might not occur in our reacting systems and the $Pt/ZrO_4/SO_4$ catalyst in the hydrocracking and hydroisomerization of n-alkanes did not act as conventional bifunctional catalysts. Carbocation intermediates, however, could be generated in the following ways: hydride abstraction by Lewis sites, carbon-hydrogen bond attack by the protons of Brõnsted acid sites, and/or intermolecular hydride transfer.

## 7.5 Summary

It has been found in this work that the $Pt/ZrO_2/SO_4$ catalyst is active for the conversion of heavy waxes to liquid fuels by hydrocracking and hydroisomerization under relatively mild reaction conditions. Reaction conditions such as hydrogen pressure, reaction temperature and catalyst loading have strong effects on catalytic activity and product selectivity. With increasing hydrogen pressure, the conversion of n-hexadecane increases greatly. We have demonstrated that the $Pt/ZrO_2/SO_4$ catalyst is also active at 1600 psig of hydrogen pressure without deactivation. The long-term performance of the $Pt/ZrO_2/SO_4$ catalyst evidently showed that the activity of this catalyst did not change after 96 hours of reaction. Addition of a hydride transfer agent such as adamantane or methylcyclopentane enhances the catalytic activity for conversion of alkanes and increases the selectivity to long chain products. The activity of the $Pt/ZrO_2/SO_4$ catalyst for conversion of n-hexadecane and n-heptane was reduced greatly upon addition of olefins due to their ability to compete with paraffins for active acid sites.

# 8.0 KINETIC MODELING OF HYDROCRACKING AND HYDROISOMERIZATION OF n-HEXADECANE

## 8.1 Objectives

(1) To develop a simplified reaction network using lumped components for describing hydrocracking and hydroisomerization of n-hexadecane as a function of reaction time in a batch reactor.

(2) To estimate the model parameters and predict the effect of Pt loading as well as hydrogen pressure on the yield of product fractions with respect to reaction time.

## 8.2 Background

Hydrocracking and hydroisomerization of paraffins catalyzed by bifunctional catalysts have been widely used in the petroleum refining industry. Kinetic modeling of this process has been undertaken to investigate the reaction mechanism and predict product distributions. Froment et al.(134) developed a kinetic model for describing hydrocracking and hydroisomerization of n-decane and n-dodecane over zeolite catalysts in a continuously stirred reactor (CSTR). The products were lumped into monobranched and multibranched isomers of the initial reactants, and cracked products. They found that models incorporating physical adsorption of the initial reactants and their isomers in the zeolite pores could adequately fit the experimental data. The same reaction network and lumping structure used for n-decane and n-dodecane were also found to be applicable to n-octane.(135) However, in the case of a low boiling point hydrocarbon such as n-octane, besides considering physical adsorption of the initial reactants and their isomers, adsorption of cracked products must be taken into account. Kennedy et al.(136) developed a kinetic model to describe the hydroisomerization of n-heptane over Pt/zeolite catalyst. This model was used to reveal the effect of the balance between acid and metal activities on product selectivities. The kinetic models mentioned above were based on the classic bifunctional reaction mechanism proposed by Weisz and Coonradt(30), in which the first step involves dehydrogenation of n-alkanes to form olefins. This model is inconsistent with our experimental findings for the hydrocracking and hydroisomerization of n-hexadecane over the $Pt/ZrO_2/SO_4$ catalyst as described in the preceding chapters. The initial attempt in the kinetic modeling of the hydrocracking and hydroisomerization of n-hexadecane catalyzed by $Pt/ZrO_2/SO_4$ was to propose a simplified reaction network with regard to lumped components (n-C16, i-C16 and cracked products). A kinetic model based on this reaction network was developed and then used for predicting the overall conversion of n-hexadecane and selectivity of isohexadecanes and cracked products.

## 8.3 Experimental

In order to validate the kinetic model, reactions of n-hexadecane were carried out in the tubing bomb microreactor shown in **Figure 2** following the procedure described in **Section 6.3.1**. For all reactions, six grams of n-hexadecane and one gram of $Pt/ZrO_2/SO_4$ catalyst (SZD1) were charged to the reactor. A summary of these reactions is given in **Table 16**.

## 8.4 Results and Discussion

### 8.4.1 Kinetic Model

Conversion of a normal hydrocarbon into isomerized and cracked products by hydrocracking and hydroisomerization in the presence of $Pt/ZrO_2/SO_4$ involves both series and parallel reaction pathways. In the case of n-hexadecane, the reaction network is simplified as shown in **Figure 19**.

This reaction network involves the following experimental facts or assumptions:

(1) The lumped liquid products obtained from the hydrocracking and hydroisomerization are unreacted hexadecane, isohexadecanes and cracking products (C5-C13). The gas products lighter than C4 are not considered. Typically, the gas products were less than 2 wt%, mainly in C4. This observation was also confirmed by others(9,128)

(2) All reactions are irreversible and pseudo-first order.

(3) Secondary cracking is considered unimportant to simplify the kinetic model.

(4) The ideal gas law can be used. The gas phase was about 99% $H_2$, and the compressibility factor (Z) of hydrogen is about 1.02 under our reaction conditions (440 psig and 433K).[137]

Table 16 Reaction Conditions and Product Yields for the Kinetic Modeling Studies (n-C16: 0.0256 mole; Catalyst: $Pt/ZrO_2/SO_4$; Temperature: 433 K)

| Run No. | Pt loading (wt.%) | Pressure (psig) | Time (min) | Product yield (mole) | | |
|---|---|---|---|---|---|---|
| | | | | n-C16 | i-C16 | C5-C13 |
| R029 | 0.5 | 360 | 20 | 0.0169 | 0.0031 | 0.0130 |
| R030 | 0.5 | 360 | 40 | 0.0101 | 0.0041 | 0.0258 |
| R031 | 0.5 | 360 | 60 | 0.0075 | 0.0034 | 0.0331 |
| R042 | 0.5 | 460 | 20 | 0.0110 | 0.0300 | 0.0258 |
| R043 | 0.5 | 460 | 40 | 0.0058 | 0.0037 | 0.0320 |
| R044 | 0.5 | 460 | 60 | 0.0040 | 0.0027 | 0.0395 |
| R045 | 0.5 | 700 | 20 | 0.0095 | 0.0047 | 0.0254 |
| R046 | 0.5 | 700 | 30 | 0.0045 | 0.0028 | 0.0455 |
| R047 | 0.5 | 700 | 40 | 0.0015 | 0.0012 | 0.0543 |
| R036 | 1.0 | 360 | 30 | 0.0079 | 0.0044 | 0.0288 |
| R037 | 1.0 | 360 | 60 | 0.0057 | 0.0043 | 0.0320 |
| R038 | 2.0 | 360 | 10 | 0.0134 | 0.0041 | 0.0187 |
| R039 | 2.0 | 360 | 20 | 0.0059 | 0.0030 | 0.0389 |

(5) The apparent rate constants ($k_1$, $k_2$ and $k_3$) depend only on reaction temperature, and not on hydrogen pressure and Pt loading.

(6) Hydrogen pressure and Pt loading affect the rate of cracking, but not the rate of isomerization because isomerization does not consume hydrogen and Pt plays a role to saturate

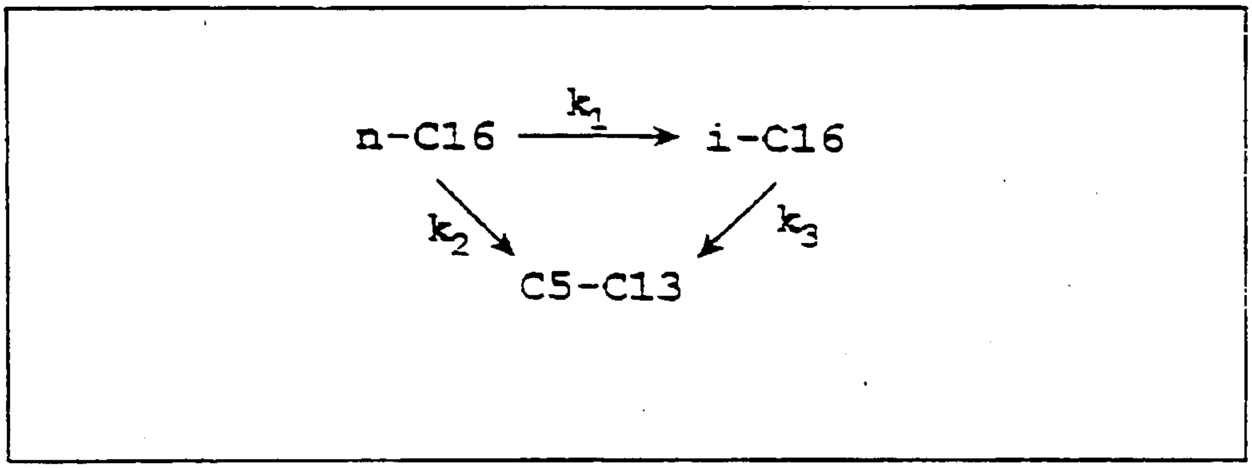

**Figure 19.** Simplified Reaction Network Used for Hydrocracking and Isomerization of n-Hexadecane.

cracked products by hydrogenation. Preliminary analysis of the data indicated that the power for hydrogen pressure was not significantly different from 1.0 but that the power for platinum loading was significantly different from one. Formation of two moles of cracked products consumes one mole of hydrogen.

(7) No thermal reactions occurred at these reaction conditions

Using the experimental facts or assumptions mentioned above, the molar changes in n-hexadecanes, isohexadecanes and cracked products can be written as:

$$\frac{dY_1}{w_{cat}dt} = -(k_1 + k_2 w_{Pt}^{n} P_{H_2})Y_1 \tag{8-1}$$

$$\frac{dY_2}{w_{cat}dt} = k_1 Y_1 - k_3 w_{Pt}{}^{n} P_{H_2} Y_2 \tag{8-2}$$

$$\frac{dY_3}{w_{cat}dt} = 2(k_2Y_1 + k_3Y_2)w_{Pt}^{n}P_{H_2} \tag{8-3}$$

The initial conditions are:

for t=0: $Y_1$=0.0256, $Y_2$ = $Y_3$ = 0.0 where

$Y_1$ = unreacted n-C16 [mole]
$Y_2$ = i-C16 [mole]
$Y_3$ = cracked products, C5-C13 [mole]
$k_1$ = apparent rate constant for isomerization of n-C16 $[(\text{gcat}\cdot\text{min})^{-1}]$
$k_2$ = apparent rate constant for hydrocracking of n-C16 $[(\text{gcat})^{n-1}\cdot(\text{gPt}^{n}\cdot\text{atm}\cdot\text{min})^{-1}]$
$k_3$ = apparent rate constant for hydrocracking of i-C16 $[(\text{gcat})^{n-1}\cdot(\text{gPt}^{n}\cdot\text{atm}\cdot\text{min})^{-1}]$
$w_{cat}$ = amount of catalyst [g]
$w_{Pt}$ = weight percentage of Pt [gPt/gcat]
n = reaction order with respect to Pt
$P_{H2}$ = hydrogen pressure during reaction [atm]

The hydrogen pressure during the batch runs was not constant, and it is given by:

$$P_{H_2} = P_0 - \frac{n'RT}{V} = P_0 - \frac{Y_3RT}{2V}$$

where $P_o$ = initial hydrogen pressure [atm]
T = reaction temperature [K]
V = gas volume (39) $[\text{cm}^3]$
n' = molar number of hydrogen consumed [mole]

### 8.4.2 Kinetic Parameter Estimation

A total of 13 experimental runs were made at 433 K (**Table 19**). For each run, the amounts of unreacted n-hexadecanes, isohexadecanes and cracked products were determined. The kinetic parameters ($k_1$, $k_2$, $k_3$ and n) were obtained by minimizing the following objective function:

$$f = \sum_{i=1}^{N} \left[ w_n(Y_{1,i} - \hat{Y}_{1,i})^2 + w_i(Y_{2,i}-\hat{Y}_{2,i})^2 + w_c(Y_{3,i} - \hat{Y}_{3,i})^2 \right] \qquad (8\text{-}5)$$

where: f = objective function,

$w_n$, $w_i$, $w_c$ = weighting factors for n-C16, i-C16 and cracked products,

N = number of experiments,

$\hat{Y}_{1,i}$, $\hat{Y}_{2,i}$, $\hat{Y}_{3,i}$ = moles of unreacted n-C16, i-C16 and cracked products C5-C13 for run i given by the model, respectively.

$Y_{1,i}$, $Y_{2,i}$, $Y_{3,i}$ = moles of unreacted n-C16, i-C16 and cracked products C5-C13 measured experimentally for run i, respectively.

The $w_n$, $w_i$ and $w_c$ in **equation 8-5** were set to unity for all three products because the accuracy of measurements for these three products were equal. For a given set of kinetic parameters, **equations 8-1 through 8-3** can be used to predict the yield of cracked products and i-C16. The calculated and experimental data are then used to determine f. The desired set of parameters is that which gives the lowest value of f. This was done using a standard statistical routine: a derivative free nonlinear regression program AR from the BMDP library.(138)

**Equations 8-1 to 8-4** contain the four parameters which are to be determined, three rate constants and one reaction order with respect to Pt loading. The equations are nonlinear because of **equation 8-4**, and must be solved numerically. This can be done using an integration routine in AR. For each run, $\hat{Y}_{1,i}$, $\hat{Y}_{2,i}$, and $\hat{Y}_{3,i}$ were calculated using a set of assumed parameters and substituted into **equation 8-5**. The assumed parameters were then corrected in AR using a pseudo-Gauss-Newton iterative algorithm to reduce f. The minimum f obtained was 1.319897E-3. The corresponding kinetic parameters are given in **Table 17** together with the standard deviations. The pseudo $R^2$, a scale-free measure of approximately how much of the variation of the dependent variable is accounted for b the model was 0.87.

Four starting estimates of these four parameters were used. Since these parameters are highly correlated, the computed values were not identical, but a similar value of f was obtained for each initial set of estimates.

**Table 17** Kinetic Parameters and Asymptotic Standard Deviations in the Kinetic Model

| Parameter | Computed Value | Asymptotic standard deviation |
|---|---|---|
| $k_1$ | 0.022 | 0.017 |
| $k_2$ | 0.044 (0.015)$^a$ | 0.024 |
| $k_3$ | 0.058 (0.020)$^a$ | 0.0092 |
| n | 0.84 | 0.078 |

a: the data in the brackets are calculated values of $k_2w_{pt}^{0.84}P_{H2}$ and $k_3w_{pt}^{0.84}P_{H2}$ using initial value of $P_{H2}$ (30 atm at 433 K) and 0.5 wt.% of Pt loading.

The solution given above was selected because all calculated parameters had small estimated standard deviations. The apparent rate constant for isomerization of n-C16 ($k_1$) has different units than the apparent rate constant for hydrocracking of n-C16 ($k_2$) or i-C16 ($k_3$). In **equations 8-1 and 8-2**, $k_2$ or $k_3$ must be multiplied by Pt loading ($w_{Pt}^n$) and hydrogen pressure ($P_{H2}$) to be comparable to $k_1$. Values are shown in **Table 17** in brackets. The calculated value of $k_2w_{pt}^{0.84}P_{H2}$ was 68% of $k_1$. This indicates that, under these conditions, isomerization of n-C16 does not necessarily precede hydrocracking; cracked products from n-C16 can be obtained by either isomerization of n-C16 to form i-C16 followed by hydrocracking or direct hydrocracking of n-C16. With increasing conversion of n-C16, $P_{H2}$ decreases with a concomitant decrease in $k_2w_{pt}^{0.84}P_{H2}$ and $k_3w_{pt}^{0.84}P_{H2}$. The rate of isomerization may further increase. The apparent rate constant for hydrocracking of isohexadecanes ($k_3$) was 33% greater than that for cracking of n-hexadecanes ($k_2$), in agreement with the experimental finding(139) that isoparaffins were more easily cracked than n-paraffins because they form stable tertiary carbonium ion intermediates more easily.

### 8.4.3 Application of the Kinetic Model

The kinetic model was used to predict the effects of hydrogen pressure and Pt loading on the reactivity and product selectivities in hydrocracking and hydroisomerization of n-hexadecane.

Using the four kinetic parameters obtained above in **equations 8-1 to 8-4**, the yields of unreacted n-C16 ($Y_1$), i-C16 ($Y_2$) and cracked products ($Y_3$) were calculated using the IVPAG program from the IMSL library(140) for solving a system of differential equations. The average relative error between between experimental and calculated data points for four sets of hydrogen pressures (cold) and Pt loadings was about 25%, which was acceptable considering the simplified reaction network employed. Nevertheless, at high conversions of n-hexadecane, the calculated cracked fractions are visibly lower than the experimental ones likely due to secondary cracking.

Using the kinetic model, the yields of cracked fractions and isohexadecanes with respect to reaction time can be calculated for different hydrogen pressures (cold) and Pt loadings. The yield of isohexadecanes increases with increasing reaction time at the initial stage of reaction. It reaches a maximum and then decreases with a further increase in time. The yield of cracked fractions increases with increasing reaction time. An increase in hydrogen pressure or Pt loading increases the yield of cracked products significantly, with however a concomitant decrease in the yield of isohexadecanes. These results indicate that product yields can be controlled by reaction variables such as reaction time, hydrogen pressure or the composition of $Pt/ZrO_2/SO_4$. Low hydrogen pressures, low Pt loadings or short reaction times favor the formation of isohexadecanes. Conversely, high hydrogen pressures, high Pt loadings or long reaction times are favorable for the formation of cracked products.

To check the predictability of the kinetic model, reactions were carried out under different conditions from those used for generating the kinetic parameters. The predicted and experimental yields are compared in **Table 18.** The results show that the model predicts the yield of cracked products better than that of isohexadecanes under all conditions. The yield of isomerized products should not be extrapolated using this model. The predicted yields at high Pt loading (5 wt.%, R040) or hydrogen pressure (300 psig, R041) were close to the experimental ones. However, at