Quarterly Report

**LOW SEVERITY UPGRADING OF F-T WAXES WITH
SOLID SUPERACIDS****DISCLAIMER**

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SUMMARY

Work in the proceeding quarter focussed on the kinetic modeling of isomerization and hydrocracking reactions of long-chain paraffins over a $\text{Pt/ZrO}_2/\text{SO}_4$ catalyst. The model is based on a simplified reaction network. The effects of hydrogen pressure and platinum loading on catalytic activity of $\text{Pt/ZrO}_2/\text{SO}_4$ were included in the kinetic model. This model, which describes the lumping products as a function of time, was fitted with experimental data obtained from a batch reactor. The predicted product distribution agrees with the experimental data within $\pm 10\%$. In addition, following up previous work on the alkylation of aromatics in the presence of paraffinic compounds, the $\text{Pt/ZrO}_2/\text{SO}_4$ catalyzed reaction of neopentylbenzene was carried out. This compound cannot form an olefinic bond and was investigated to obtain evidence on the possibility of the alkylation of benzene proceeding via olefinic intermediates. It appears that the reaction proceeds by direct protonation of paraffinic structures.

EXPERIMENTAL

All experiments were conducted in a 41 ml microreactor at conditions of 160°C and 360-700 psig H_2 . n-Hexadecane was chosen as a substrate for kinetic modelling studies. Reaction time was varied from 10 minutes to 60 minutes and Pt loading was varied from 0.5 to 2.0 wt%. The conversion and selectivity of isomerized and cracked products were measured by GC (HP 5890 II). The experimental error in conversion was $\pm 2.0\text{ wt}\%$.

RESULTS AND CONCLUSIONS

Kinetic Modelling of Isomerization and Hydrocracking of n-Hexadecane

The objectives of this study were to describe the product distribution and to optimize the reaction parameters. A simplified reaction network was used:

The kinetic equations were derived based on the following assumptions:

- 1) The products of isomerization and hydrocracking of n-C₁₆ can be lumped as unreacted n-C₁₆, iso-C₁₆ and cracked products C₅-C₁₃. Gas products are neglected (2-3 wt%).
- 2) All reactions are irreversible and pseudo-first order.
- 3) At room temperature, the ideal gas law is assumed and vaporized light hydrocarbon products in the gas phase are negligible.
- 4) Rate constants are function only of temperature and are not affected by hydrogen pressure and Pt loading. Hydrogen pressure and Pt loading affect the cracking rate, but do not affect isomerization.
- 5) The reaction is first order in hydrogen consumption.

The rate of reaction equations are as follows:

$$dY_1/dt = -(k_1 + k_2 W_P^a P_{H_2}) Y_1$$

$$dY_2/dt = k_1 Y_1 - k_3 W_P^a P_{H_2} Y_2$$

$$dY_3/dt = 2(k_2 Y_1 + k_3 Y_2) W_P^a P_{H_2}$$

$$P_{H_2} = P_0 - n'RT/V = P_0 - Y_3 RT/2V$$

where,

Y_1 : n-hexadecane (mole)

Y_2 : iso-hexadecane (mole)

Y_3 : cracked products (mole)

k_1 (min^{-1}), k_2 ($\text{g}^{-1}\cdot\text{atm}^{-1}\cdot\text{min}^{-1}$) and k_3 ($\text{g}^{-1}\cdot\text{atm}^{-1}\cdot\text{min}^{-1}$): relative rate constants

n : reaction order of Pt

W_{Pt} : Pt concentration (g/g catalyst)

P_0 : initial hydrogen pressure at 160°C (atm)

V : reactor volume (ml)

n' : moles of hydrogen consumed

T : temperature, K

The objective function chosen to determine the reaction parameters was:

$$f = \sum_{i=1}^N [w_1(Y_{1,i} - \hat{Y}_{1,i})^2 + w_2(Y_{2,i} - \hat{Y}_{2,i})^2 + w_3(Y_{3,i} - \hat{Y}_{3,i})^2]$$

The w_i are weighting factors and are used to compensate for the fact that accuracy of measurement for the products may not be equal. In this analysis, they were all 1.0.

$Y_{n,i}$ ($n=1,2,3$) are the experimental values of Y_n , whereas $\hat{Y}_{n,i}$ are the predicted values of Y_n using the correlations.

The desired set of rate constants is that which gives the lowest value for f and can be found by a systematic search using one of the standard statistical routines which are available. We used a derivative free nonlinear regression program AR from the BMDP library (BMDP, 1990).

The results are summarized in Figures 1-5. Better fits were obtained at relatively lower hydrogen pressure. Hydrogen pressure and platinum loading have strong effects on the activity of the Pt/ZrO₂/SO₄ catalyst, probably because the generation of protonic acid sites is responsible for the cleavage of carbon-carbon bonds. It may be possible to control product distributions by choosing the proper pressure and platinum loading.

Possible Initiation Pathway in Isomerization and Hydrocracking of Paraffins

We have previously reported that olefins decrease the rate of isomerization and hydrocracking of n-paraffins (Quarterly report, September 1, 1992 through November 30, 1992), and we proposed that, over a Pt/ZrO₂/SO₄ catalyst, hydrocracking of paraffins may not occur through olefinic intermediates as is usually assumed. Recently, we carried out an experiment using a model compound, neopentylbenzene. It is not possible for the alkyl side chain of this compound to form an olefin, and therefore, the reactions of the alkyl chain cannot be initiated by forming olefinic intermediates. The aromatic ring captures any isomerized or cracked intermediates which are formed.

As shown in Table 1, at 160°C and 350 psig, isomerization and hydrocracking of neopentylbenzene did occur. Conversion of neopentylbenzene was 33 wt%. The products contained alkylaromatics with methyl, ethyl, propyl and isobutyl groups attached to a single aromatic ring, so that isomerization and hydrocracking of the alkyl chain did occur. It is likely that the reaction was initiated with the protonation of the alkyl chain to form carbonium intermediates which underwent isomerization and hydrocracking.

FUTURE WORK

The effect of olefins on isomerization and hydrocracking of paraffins will be further investigated by in-situ FT-IR.

The activities for isomerization and hydrocracking of n-hexadecane using Pt/ZrO₂/SO₄ catalysts prepared by different laboratories (Carnegie Mellon University, Magnesium Elektron, Inc. and this laboratory), will be compared. Characterization of these catalysts will be conducted using TPD or FT-IR to relate the acidities of these catalysts to their hydrocracking activities.

Table 1. Products from conversion of neopentylbenzene. Reaction conditions: 160°C, 350 psig H₂ (380-420 psig during reaction), 60 minutes, feed/catalyst=6/1, total conversion=32.7wt%

Product type	Selectivity
isopentane	15.8
benzene	5.8
isopentylbenzene	7.0
methylcyclohexane	11.2
trimethylbenzene	12.8
tetramethylbenzene	8.7
1,4-dimethyl-2-ethylbenzene	10.7
1,4-dimethyl-2-propylbenzene	12.0
1,1'-dimethylindin	4.4
2-methyltetralin	11.6

Figure 1. Plots of observed vs predicted products for Pt/ZrO₂/SO₄ (0.5 wt%) catalyst at 160°C. Initial pressure was 360 psig H₂ (cold); during reaction pressure varied between 250-420 psig).

Figure 2. Plots of observed vs predicted products for Pt/ZrO₂/SO₄ (0.5 wt%) catalyst at 160°C. Initial pressure was 460 psig H₂ (cold); during reaction pressure varied between 240-600 psig).

Figure 3. Plots of observed vs predicted products for Pt/ZrO₂/SO₄ (0.5 wt%) catalyst at 160°C. Initial pressure was 700 psig H₂ (cold); during reaction pressure varied between 380-920 psig).

Figure 4. Plots of observed vs predicted products for Pt/ZrO₂/SO₄ (1.0 wt%) catalyst at 160°C. Initial pressure was 360 psig H₂ (cold); during reaction pressure varied between 220-420 psig).

Figure 5. Plots of observed vs predicted products for Pt/ZrO₂/SO₄ (2.0 wt%) catalyst at 160°C. Initial pressure was 360 psig H₂ (cold); during reaction pressure varied between 190-420 psig).

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