2

DOE/PC/89775--2
NOV 14 1990

CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY WITH AMMONIA

DOE/PC/89775--2

DE91 005511

Report for July 1, 1990 to September 30, 1990

Report No.: DOE/PC89775-2

Grant No.: DE-FG22-89PC89775

Submitted by:

Charles N. Satterfield

Chung M. Lee

RECEIVED BY JUNE
11 1990

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Kinetic Model

In the last quarterly we presented results of the HDN of 8-OH quinoline (8HQ) and showed that three routes are involved beyond those encountered in the HDN of quinoline. We have now developed a new kinetic model for this reaction, which is adapted from Satterfield and Smith (1986) as applied to quinoline. Some basic assumptions of the model include: 1) the Langmuir-Hinshelwood kinetic model with all sites occupied is applicable, 2) the dehydrogenation rates of BzTHQ and DHQ to Q and PyTHQ are small enough to be neglected, and 3) the clean hydrocarbon products are not appreciably adsorbed. With the additional reaction pathways outlined above, we obtain the following equations:

$$\frac{dY_1}{dt} = \frac{k_1 K_5 Y_5 - k_2 K_1 Y_1}{\Phi} \quad (1)$$

$$\frac{dY_2}{dt} = \frac{k_3 K_4 Y_4 - k_5 K_2 Y_2 + k_6 K_3 Y_3 + k_{17} K_7 Y_7}{\Phi} \quad (2)$$

$$\frac{dY_3}{dt} = \frac{k_4 K_5 Y_5 + k_5 K_2 Y_2 - k_6 K_3 Y_3 - k_7 K_3 Y_3 + k_{15} K_8 Y_8}{\Phi} \quad (3)$$

$$\frac{dY_4}{dt} = \frac{k_9 K_5 Y_5 - k_8 K_4 Y_4 - k_3 K_4 Y_4}{\Phi} \quad (4)$$

$$\frac{dY_5}{dt} = \frac{k_8 K_4 Y_4 - k_9 K_5 Y_5 - k_1 K_5 Y_5 - k_4 K_5 Y_5 + k_{14} K_8 Y_8}{\Phi} \quad (5)$$

$$\frac{dY_6}{dt} = \frac{k_2 K_1 Y_1 + k_7 K_3 Y_3}{\Phi} \quad (6)$$

$$\frac{dY_7}{dt} = \frac{k_{13} K_8 Y_8 - k_{12} K_7 Y_7 - k_{17} K_7 Y_7}{\Phi} \quad (7)$$

$$\frac{dY_8}{dt} = \frac{k_{12} K_7 Y_7 - k_{13} K_8 Y_8 - k_{14} K_8 Y_8 - k_{15} K_8 Y_8}{\Phi} \quad (8)$$

where $\Phi = K_1 Y_1 + K_2 Y_2 + K_3 Y_3 + K_4 Y_4 + K_5 Y_5 + K_6 Y_6 + K_7 Y_7 + K_8 Y_8$, k_i is the rate constant of reaction i identified in Figure 1 in units of mol of 8HQ/(h g of catalyst), K_j is the adsorption equilibrium constant of component j , Y_j is the mole

fraction of component j (based on total moles of 8HQ fed), and t is space time in units of (h g of catalyst)/mol of 8HQ.

Several additional approximations used by Satterfield and Smith (1986) are employed to reduce the number of parameters. First, rate Equations (4) and (5) are combined to eliminate terms containing k_8 and k_9 ; rate Equations (7) and (8) are also combined to eliminate terms containing k_{12} and k_{13} :

$$\frac{d(Y_4+Y_5)}{dt} = \frac{-k_3K_4Y_4 - k_1K_5Y_5 - k_4K_5Y_5 + k_{14}K_8Y_8}{\Phi} \quad (9)$$

$$\frac{d(Y_7+Y_8)}{dt} = \frac{-k_{14}K_8Y_8 - k_{15}K_8Y_8 - k_{17}K_7Y_7}{\Phi} \quad (10)$$

Since thermodynamic equilibrium exists between Y_4 and Y_5 , they should be present in a constant ratio, that is $K_{Eq1} = k_8/k_9 = Y_5/Y_4$. Thermodynamic equilibrium also exists between Y_7 and Y_8 , so $K_{Eq2} = k_{12}/k_{13} = Y_8/Y_7$. Using these two equilibrium constants, Equations (9) and (10) become:

$$\frac{d(Y_4+Y_5)}{dt} = \frac{-k'_3K_4(Y_4+Y_5) - (k'_1+k'_4)K_5(Y_4+Y_5) + k'_{14}K_8(Y_7+Y_8)}{\Phi} \quad (11)$$

$$\frac{d(Y_7+Y_8)}{dt} = \frac{-(k'_{14}+k'_{15})K_8(Y_7+Y_8) - k'_{17}K_7(Y_7+Y_8)}{\Phi} \quad (12)$$

where

$$\begin{aligned} k'_1 &= k_1K_{Eq1}/(1+K_{Eq1}) & k'_{14} &= k_{14}K_{Eq2}/(1+K_{Eq2}) \\ k'_3 &= k_3/(1+K_{Eq1}) & k'_{15} &= k_{15}K_{Eq2}/(1+K_{Eq2}) \\ k'_4 &= k_4K_{Eq1}/(1+K_{Eq1}) & k'_{17} &= k_{17}/(1+K_{Eq2}) \end{aligned}$$

The adsorption constants are grouped into three categories according to their basicities or the basicities of like compounds (1984). First, the compounds Q, PyTHQ, BzTHQ, OPA, 8HQ, and 8HTHQ are treated as aromatic amines, all with the same adsorption constant K_{aa} . Because the nitrogen molecule is adsorbed on the surface via the nitrogen atom, the above assumption is plausible also for 8HQ and 8HTHQ. Second, DHQ, a secondary amine, has a higher basicity than the aromatic amine and is expected to be more strongly adsorbed; its adsorption constant is termed K_{sa} . Third, ammonia is treated separately because of its much lower basicity; its adsorption constant is termed K_{am} .

Two adsorption constant ratios are developed using the above adsorption constants, $A_1 = K_{sa}/K_{aa}$ and $A_2 = K_{am}/K_{aa}$. Previously established values (1984) of $A_1 = 2$ and $A_2 = 0.7$ are used here. Now $\Phi = Y_1 + Y_2 + A_1 Y_3 + Y_4 + Y_5 + A_2 Y_6 + Y_7 + Y_8$. The simplified mathematical model is:

$$\frac{dY_1}{dt} = \frac{k'_1(Y_4 + Y_5) - k_2 Y_1}{\Phi} \quad (13)$$

$$\frac{dY_2}{dt} = \frac{k'_3(Y_4 + Y_5) - k_5 Y_2 + k_6 A_1 Y_3 + k'_{17} Y_7}{\Phi} \quad (14)$$

$$\frac{dY_3}{dt} = \frac{k'_4(Y_4 + Y_5) + k_5 Y_2 - (k_6 + k_7) A_1 Y_3 + k'_{15}(Y_7 + Y_8)}{\Phi} \quad (15)$$

$$\frac{d(Y_4+Y_5)}{dt} = \frac{-(k'_3+k'_1+k'_4)(Y_4+Y_5)+k'_{14}(Y_7+Y_8)}{\Phi} \quad (16)$$

$$\frac{dY_6}{dt} = \frac{k_2Y_1+k_7A_1Y_3}{\Phi} \quad (17)$$

$$\frac{d(Y_7+Y_8)}{dt} = \frac{-(k'_{14}+k'_{15}+k'_{17})(Y_7+Y_8)}{\Phi} \quad (18)$$

Rate constants, k'_1 , k_2 , k'_3 , k'_4 , k_5 , k_6 , and k_7 , for the quinoline network were first regressed using data from the HDN of quinoline. The regressed values were comparable to the results of Satterfield and Smith (1986) at 375°C. Using these values of k'_1 , k_2 , k'_3 , k'_4 , k_5 , k_6 and a lower value of k_7 , k'_{14} , k'_{15} , and k'_{17} were regressed using the new model. A lower value of k_7 had to be used in order to fit the model more closely to the concentration profile of the hydrocarbon products. The parameters were fitted using a Nelder-Meade simplex algorithm. Table I lists the values of the rate constants. The values of k'_{14} , k'_{15} , and k'_{17} indicate that direct abstraction of 8HTHQ to PyTHQ (Route 2) is slower than the other two routes that require hydrogenation of the benzene ring followed by C-O hydrogenolysis to form BzTHQ or DHQ. Figure 2 shows the results of the model compared with data. The model fits observed data well. Eliminating any one of the three routes from the kinetic network gave much poorer fitting.

Figure 3 shows a space time plot of reaction species at 385°C. Calculation of the reaction rate constants was not attempted, but Figure 3 shows that 8HQ and

8HTHQ concentration fall off more quickly than at 360°C, as would be expected.

There is a higher build up of BzTHQ than at 360°C.

Discussion

The course of the reaction as shown in Figure 2 establishes that HDO goes to completion before HDN for 8HQ. The species observed are the same as those found during the HDN of Q, plus 8HTHQ. The clean products include propylcyclohexane (PCH), propylcyclohexene (PCH_e), and propylbenzene (PB) with PCH predominating. The ratio of PB to PCH was the same in hydrotreatment of 8HQ as in that of quinoline. The overall rate of conversion of 8-hydroxyquinoline to non-nitrogen compounds was essentially the same as that of quinoline. For example, at the a space time of 320 (h g of catalyst)/mol of feed, the HDN of Q was 58% and the HDN of 8HQ was 57%.

Summary

During the hydrotreatment of 8-hydroxyquinoline (8HQ) an intermediate is formed in equilibrium with 8HQ, identified as 8-hydroxy-1,2,3,4-tetrahydroquinoline. The hydrotreatment of 8-hydroxyquinoline enters the HDN of quinoline network via three routes. Route 1: hydrogenation of the heterocyclic ring to 8HTHQ followed by abstraction of oxygen through hydrogenation of the other aromatic ring to 8HDHQ followed by C-O hydrogenolysis to form DHQ. Route 2: direct C-O hydrogenolysis to form PyTHQ. Route 3: hydrogenation of the benzene ring in 8HQ to 8HTHQa

followed by the removal of the oxygen to enter the HDN of quinoline network through BzTHQ. The selectivity to clean hydrocarbons remain unchanged by the presence of the hydroxyl group on 8HQ.

Future Plans

We are starting experimental studies with a mixture of quinoline and naphthalene in the presence of various partial pressures of ammonia.

List of Acronyms

BzTHQ	5,6,7,8-tetrahydroquinoline
CI	chemical ionization
DHQ	decahydroquinoline
EI	electron ionization
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
OPA	2-propylaniline
PB	propylbenzene
PCH	propylcyclohexane
PCH _e	propylcyclohexene
PyTHQ	1,2,3,4-tetrahydroquinoline
Q	quinoline
8HQ	8-hydroxyquinoline
8HDHQ	8-hydroxydecahydroquinoline
8HTHQ	8-hydroxy-1,2,3,4-tetrahydroquinoline
8HTHQ _a	8-hydroxy-5,6,7,8-tetrahydroquinoline

List of Variables

A_1, A_2	Ratio of adsorption constants.
k_i	Rate constant of reaction i, mol of 8HQ/(h g of catalyst).
k_i'	Rate constant of reaction i adjusted by K_{Eq} 's.
K_{Eq1}, K_{Eq2}	Reaction equilibrium constants.
K_j	Adsorption equilibrium constants.
t	Space time, (h g of catalyst)/mol of 8HQ.
Y_j	Mole fraction of component j, based on moles of 8HQ fed.
Φ	Denominator of Langmuir-Hinshelwood expression.

References

1. Satterfield, C.N. and Yang, S.H., Ind. Eng. Chem., Proc. Des. Dev., **23**, 11-13 (1984).
2. Satterfield, C.N. and Smith, C.M., Ind. Eng. Chem., Proc. Des. Dev., **25**, 942-949 (1986).

Figure 1: Simplified scheme for mathematical model.

Figure 2: Comparison of kinetic model to data at 360°C.

Figure 3: Hydrotreatment of 8HQ at 385°C.

Table I. Rate constants of the HDN of quinoline and additional rate constants of the hydrotreatment of 8HQ, [mol of 8HQ/(h g of catalyst)].

Rate constants for HDN of Q ^a	Additional rate constants in the hydrotreatment of 8HQ
$k'_1 = 0.0014$	
$k_2 = 0.0028$	
$k'_3 = 0.0029$	$k'_{14} = 0.0047$
$k_4 = 0.0051$	$k'_{15} = 0.0070$
$k_5 = 0.0150$	$k'_{17} = 0.0128$
$k_6 = 0.0000$	
$k_7 = 0.0030$	

^aUnits are moles/g.cat.hrs.

END

DATE FILMED

02 / 22 / 91