

CHATER IV

EXPERIMENTAL RESULTS AND DISCUSSIONS

4.1 Experimental Results

The results of analyses of liquid products and catalyst samples from each experiment are showed in this chapter. There was a total of seven experiments in this study. Experiments 1 was conducted to find the suitable operating conditions. The reference experiments were studied in experiments 2 and 3. The effects of iron (as ferrocene) on reaction were studied in experiments 4 and 5, while the effects of titanium (as titanocene dichloride) and of mercury (as diphenylmercury) were studied in experiments 6 and 7, respectively.

The main reaction products of the HDN of quino- line on NiMo/alumina in liquid product sample detected by gas chromatographic technique were quinoline (Q), 1,2,3,4-tetrahydroquinoline (PyTHQ), 5,6,7,8-tetrahydro- quinoline (BzTHQ), decahydroquinoline (DHQ), propylcyclo- hexane (PCH), and propylbenzene (PB). These reaction products were observed at 300 °C, 450 psig.

Preliminary experiment, experiment 1, was con- ducted to find the suitable operating temperature for other experiments in this study. The temperature of reaction was varied from 200 to 300 °C at a step increment of 50 °C and at constant pressure of 450 psig. The

suitable operating conditions found in this experiment was subsequently used in experiments 2 to 7. Table 4.1 shows the results of liquid sample from experiment 1. At 200 and 250 °C, the results show that the reaction products are quinoline (Q) and 1,2,3,4-tetrahydroquinoline (PyTHQ). Other reaction products, BzTHQ, DHQ, PCH, and PB, were found at a temperature of 300 °C. These results indicate that the suitable operating conditions are a temperature of 300 °C and a pressure of 450 psig.

Experiments 2 and 3 are reference experiments. Tables 4.2 and 4.3 show the reaction products found in experiments 2 and 3, respectively. Experiment 3 was the reproduction of experiments in order to test the deviation of the experimental data. The results are reproducible within an accuracy of 4 %. The coking results, surface area, and pore volume are reproducible within an accuracy of 5.6%, 7%, and 5.88%, respectively.

The reaction products in these experiments detected by a gas chromatograph and then compared with standard compounds were Q, PyTHQ, BzTHQ, DHQ, PCH, and PB. The main hydrocarbon product was propylcyclohexane (PCH). The result showed that the steady-state of the system was reached after 48 hours from start-up which was observed by the constant amount of each reaction product. The reaction products of the samples during this period were used for comparison. In other experiments, organometallic compounds were added to the feedstock after the system reached its steady-state. Deviation of results of other runs when compared with the reference run will indicate that it occurred from the effects of

Table 4.1 Experiment 1 Results

Temperature (°C)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
200	16.72	83.28	-	-	-	-
250	11.94	88.06	-	-	-	-
300	12.05	58.24	8.75	12.59	5.33	3.04

Table 4.2 Reaction Products in Experiment 2 (Reference Experiment)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	17.04	47.04	10.06	11.89	11.01	2.96
24	13.32	53.29	9.29	12.39	8.95	2.75
36	16.46	53.76	9.45	10.71	7.12	2.51
48	12.82	55.80	8.84	11.65	8.20	2.69
60	13.49	57.22	8.48	11.64	6.90	2.27
72	13.29	56.47	8.13	11.43	7.12	2.37
84	13.39	56.26	9.17	11.31	7.21	2.65
96	13.89	57.63	8.96	12.15	5.30	2.06
108	11.65	58.76	8.01	11.86	7.32	2.40
120	11.97	59.22	7.87	11.82	6.81	2.30

Table 4.3 Reaction Products in Experiment 3 (Reference Experiment)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	13.07	52.65	9.88	12.68	9.21	2.51
24	11.86	52.75	9.14	12.40	10.99	2.87
36	12.95	55.08	9.61	12.45	7.57	2.34
48	13.86	54.31	10.00	11.79	7.59	2.45
60	12.02	54.27	9.97	12.16	8.65	2.93
72	11.89	53.55	8.96	12.33	10.23	3.03
84	13.14	55.17	9.46	11.24	7.31	2.66
96	11.82	57.81	7.76	11.87	8.07	2.67
108	13.45	55.02	9.98	11.25	7.41	2.87
120	13.09	54.89	8.53	13.45	7.58	2.46

organometallic compound.

The effects of iron as ferrocene on reaction were studied in experiments 4 and 5. The operating conditions used were the same as in the reference experiment. Tables 4.4 and 4.5 show reaction products in experiments 4 and 5, respectively. Experiment 5 was the reproduction of experiments in order to test the consistency of the experimental data. The results of reaction products are reproducible within an accuracy of 4 %, while the coking results, surface area, and pore volume are 2.04%, 3.42%, and 5.88%, respectively. The results indicated that the presence of ferrocene in the feedstock reduces the reaction of quinoline HDN. The amounts of BzTHQ, DHQ, PCH, and PB found in liquid sample also decreased, while PyTHQ increased.

The reaction products of experiments 6 and 7 are shown in Table 4.6 and 4.7, respectively. These results indicate that titanocene dichloride has slight effects, but diphenylmercury has no effects on the reaction.

Table 4.8 shows the amount of coke in experiments 2 to 7. The coking results of experiment 2 are the same as the results of experiment 3, but at slightly higher amounts. The amounts of coke on the catalyst in the reference run were approximately 12.46 wt%. When organometallic compounds were added in the feedstock, the amounts of coke reduced.

Table 4.9 shows the results of catalyst surface area and pore volume in experiments 2 to 7. Surface area and pore volume of the catalyst in the reference run were approximately 66.31 m²/g and 0.1216 ml/g, respectively.

Table 4.4 Reaction Products in Experiment 4 (Fe)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	14.37	45.54	10.96	12.75	12.78	3.59
24	13.25	47.39	11.23	12.06	12.85	3.24
36	13.91	45.42	10.46	12.93	13.82	3.42
48	14.33	47.29	10.95	12.18	12.03	3.22
60	13.62	48.07	12.27	12.43	10.68	2.94
72	12.04	59.20	9.33	11.90	5.73	1.80
84	12.37	62.27	8.20	10.81	4.80	1.55
96	12.50	68.40	7.34	7.25	3.27	1.23
108	14.59	68.40	6.69	5.75	3.32	1.26
120	12.65	71.59	6.86	6.02	1.85	1.02

Table 4.5 Reaction Products in Experiment 5 (Fe)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	10.79	53.18	10.15	13.70	9.45	2.73
24	11.61	53.22	12.73	11.92	8.00	2.82
36	10.04	55.21	10.45	12.56	8.86	2.88
48	11.13	54.81	11.51	11.75	7.97	2.88
60	11.08	59.08	9.68	10.90	7.14	2.12
72	12.99	65.52	9.13	7.59	2.25	1.41
84	11.89	69.97	7.69	6.95	2.25	1.25
96	12.25	71.30	8.79	5.01	1.32	1.33
108	11.08	72.76	7.58	6.20	1.37	1.01
120	13.23	71.71	6.89	6.69	0.87	0.61

Table 4.6 Reaction Products in Experiment 6 (Ti)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	14.09	47.03	10.44	13.23	12.16	3.04
24	12.64	49.70	9.99	13.94	10.84	2.90
36	12.74	51.11	10.97	13.83	9.09	2.67
48	11.44	51.77	9.50	14.29	9.41	2.59
60	11.51	53.33	9.91	13.30	8.80	2.95
72	12.40	57.77	8.20	12.57	6.79	3.27
84	13.59	56.91	8.75	11.52	6.78	3.47
96	12.01	58.86	7.94	10.66	6.30	3.23
108	12.58	59.41	8.38	10.02	6.35	3.27
120	12.87	56.93	7.86	12.14	6.88	3.23

Table 4.7 Reaction Products in Experiment 7 (Hg)

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	11.62	48.14	9.54	11.99	12.53	3.18
24	12.64	51.78	9.89	11.90	10.69	3.10
36	12.79	50.84	9.86	13.57	9.97	2.97
48	11.68	53.28	9.59	12.82	9.59	3.03
60	11.91	53.70	9.56	13.01	8.86	2.95
72	13.28	53.32	9.12	13.00	8.47	2.81
84	14.01	52.09	8.96	14.34	7.88	2.72
96	13.78	54.55	8.98	11.97	8.07	2.65
108	13.02	56.11	9.76	11.44	7.05	2.61
120	12.85	53.87	9.64	12.50	8.43	2.71

Table 4.8 Coke Content on the Catalyst in Experiments 2 to 7

Experiment	wt % of coke
2 (ref.)	13.16
3 (ref.)	11.76
4 (Fe)	8.61
5 (Fe)	8.97
6 (Ti)	9.72
7 (Hg)	7.49

Table 4.9 Surface Area and Pore Volume Results

Exp.	Before cat. burning		After cat. burning	
	Surface area (sq.m/g)	Pore vol. (ml/g)	Surface area (sq.m/g)	Pore vol. (ml/g)
Fresh	142.45	0.2578	143.32	0.3547
2 (ref.)	71.38	0.1297	141.80	0.3361
3 (ref.)	61.24	0.1136	122.97	0.3204
4 (Fe)	56.70	0.1214	113.97	0.2812
5 (Fe)	60.17	0.1208	117.92	0.2811
6 (Ti)	52.39	0.1312	128.97	0.3311
7 (Hg)	72.35	0.1256	122.23	0.3632



The presence of organometallic compounds in the feedstock reduced the surface area of the catalyst. After burning the catalyst, surface area and pore volume of the catalyst recovered to their original physical properties .

Table 4.10 shows the distribution of iron and titanium in catalyst in experiments 4 and 6 as analyzed by EDX analyzer. Unfortunately, the EDX analyzer can not analyze mercury because it will evaporate in the sample chamber of this equipment.

4.2 Discussion

4.2.1 Experiment 1

This experiment was conducted to find the suitable operating conditions. The temperature of reaction was varied from 200 to 300 °C at a constant hydrogen-pressure of 450 psig. At temperatures of 200 and 250 °C, quinoline converted to PyTHQ only while at a temperature of 300 °C, quinoline converted to PyTHQ, BzTHQ, DHQ, PCH, and PB. These results indicate that at lower temperature, the HDN of quinoline favored PyTHQ while at higher temperature, the HDN of quinoline to BzTHQ and subsequently to DHQ became significant. Furthermore, it indicate that hydrogenation of quinoline to PyTHQ is much more rapid than to BzTHQ. Quinoline and PyTHQ were thermodynamically in equilibrium under all reaction conditions (84). Thus at high temperature the equilibrium shifts back toward quinoline and the second pathway which produces BzTHQ, DHQ, and PCH becomes more important. So, the operating conditions chosen for other

Table 4.10 Metal Distribution in Catalyst

Metal	% element in each position			
	Edge	1	2	Center
Fe	9.45	1.21	0.76	0.25
Ti	0.16	0.12		0.13
Hg	-	-	-	-

experiments were a temperature of 300 °C and a pressure of 450 psig. The amounts of reaction intermediates products at 300 °C are 12.05% Q, 58.24% PyTHQ, 8.75% BzTHQ, 12.59% DHQ, 5.33% PCH, and 3.04% PB.

Earlier study (84) also reported that at lower temperature, quinoline was converted rapidly and completely to PyTHQ, but at higher temperature quinoline converted to BzTHQ and subsequently to DHQ became significant.

4.2.2 Reference Experiment

The reference experiments are experiments 2 and 3. These experiment were used as a basis of comparison with other experiments. The distribution of nitrogen compounds, coke content, surface area, and pore volume of the catalyst were compared with those of other experiments.

The experiment was conducted on NiMo/alumina at 300 °C and 450 psig. The experimental conditions are shown in Table 4.11. The results of reaction products of two experimental runs (experiments 2 and 3) are reproducible within an accuracy of 4 %. The average experimental results of reaction products between experiments 2 and 3 are shown in Table 4.12. Figure 4.1 shows the distribution of nitrogen compounds of the reference runs. It shows that the steady-state operation is reached after 48 hours from start-up and the distribution of nitrogen compounds during this period are used for comparison. The conversion of quinoline is approximately 87.09 %. The percentages of reaction products are

Table 4.11 Experiment Conditions in the Reference
Experiment

Operating Condition :

Temperature	:	300 °C
H ₂ -Pressure	:	450 psig
Feedstock flowrate	:	10 cm ³ /hour
H ₂ -Flowrate	:	400 cm ³ /minute
Time	:	120 hours
Sampling	:	every 12 hours
Catalyst	:	1/8 " extrudate of NiMO/ alumina
Catalyst weight	:	3 grams

Table 4.12 Results between Experiments 2 and 3

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	15.05	49.85	9.97	12.29	10.11	2.74
24	12.59	53.02	9.22	12.40	9.97	2.81
36	14.70	54.42	9.53	11.58	7.35	2.43
48	13.36	55.06	9.42	11.72	7.90	2.57
60	12.75	55.75	9.23	11.90	7.78	2.60
72	12.59	55.01	8.55	11.80	8.86	2.70
84	13.76	55.72	9.33	11.28	7.26	2.66
96	12.85	57.72	8.36	12.06	6.69	2.37
108	12.55	56.89	9.00	11.56	7.37	2.64
120	12.53	57.06	8.20	12.64	7.20	2.38

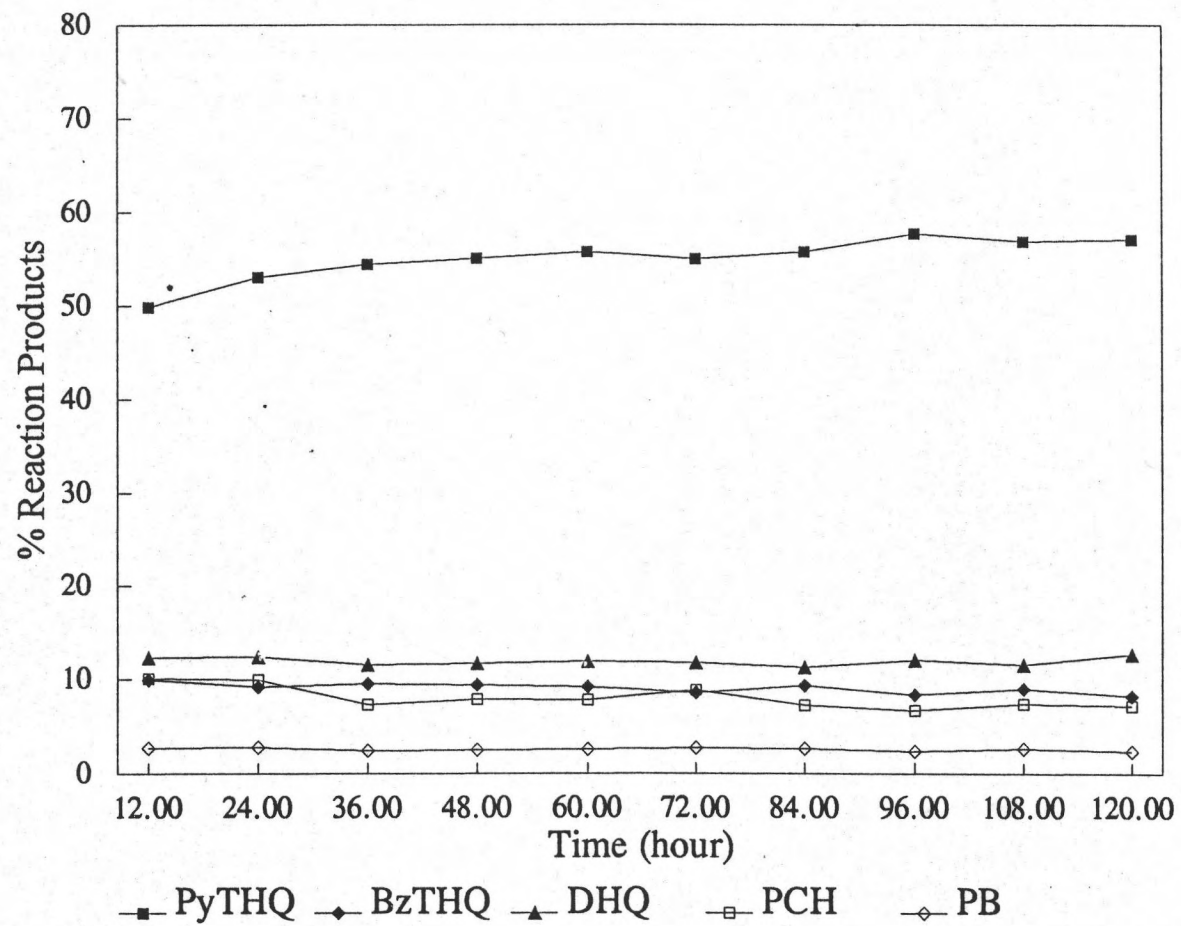


Figure 4.1 Distribution of Reaction Products of the Reference Experiment

approximately 56.17 % of PyTHQ, 8.87 % of BzTHQ, 11.84 % of DHQ, 7.55 % of PCH, and 2.56 % of PB. Table 4.13 shows the experimental deviation of the reaction products between experiments 2 and 3.

Coke content on the catalyst is approximately 12.46 wt%. The coking results of experiment 2 is the same amount as the result of experiment 3, but at slightly higher amounts. The coking results, surface area, and pore volume of two experimental runs are reproducible within an accuracy of 2%, 7%, and 5.88%. Table 4.8 shows the coking results in experiments 2 to 7. The results of catalyst surface area and pore volume are shown in Table 4.9. In experiment 2, surface area and pore volume of the coking catalyst are 71.39 m²/g and 0.1297 ml/g, respectively. Similar results are obtained from experiment 3, even though these results are slightly different from experiment 2.

These results indicate that coke reduces surface area and pore volume of the catalyst, approximately 53.45% and 49.69%, respectively. Tables 4.14 and 4.15 show the comparison of results of surface area and pore volume, respectively. Figures 4.2 and 4.3 show the comparison of surface area and pore volume of the catalyst in each experiment. After catalyst regeneration surface area and pore volume of the catalyst recovered to their original physical properties. These results show that coke on the catalyst blocks catalyst pores and causes the reduction of catalyst surface area and pore volume. Figures 4.4 and 4.5 show the comparison of surface area and pore volume of the catalyst after regeneration, respectively.

Table 4.13 Deviation of Reaction Products between Experiments 2 and 3

Time (hr)	% deviation of reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	-4.00	-5.61	-0.18	0.79	-1.80	-0.45
24	-1.46	0.54	-0.15	0.01	2.04	0.12
36	-3.51	-1.32	0.16	1.74	0.45	-0.17
48	1.04	1.49	1.16	0.14	-0.61	-0.24
60	-1.47	2.95	1.49	0.52	1.66	0.66
72	-1.40	-2.92	0.83	0.90	3.11	0.66
84	0.75	-1.09	0.32	-0.07	0.10	0.01
96	-2.07	0.18	-1.20	-0.28	2.77	0.61
108	1.81	-3.47	1.97	-0.61	0.09	0.47
120	1.12	-4.33	0.66	1.63	0.77	0.16

Table 4.14 Comparison of Surface Area Results

Exp.	Before catalyst burning		After catalyst burning	
	Surface area (sq.m/g)	% reduction	Surface area (sq.m/g)	% recovery
fresh	142.45	0.00	143.32	0.00
2 (ref.)	66.31	53.45	134.22	93.65
4 (Fe)	58.43	58.98	115.94	80.90
6 (Ti)	52.39	63.22	128.97	89.99
7 (Hg)	72.35	49.21	122.23	85.28

Table 4.15 Comparison of Pore Volume Results

Exp.	Before cat. burning		After cat. burning
	Pore Volume (ml/g)	% reduct.	Pore volume (ml/g)
Fresh	0.2578	0	0.3547
Ref.	0.1297	49.69	0.3361
4 (Fe)	0.1214	52.91	0.2812
6 (Ti)	0.1312	49.11	0.3311
7 (Hg)	0.1256	51.28	0.3632

Surface Area of Catalyst Before Catalyst Regeneration

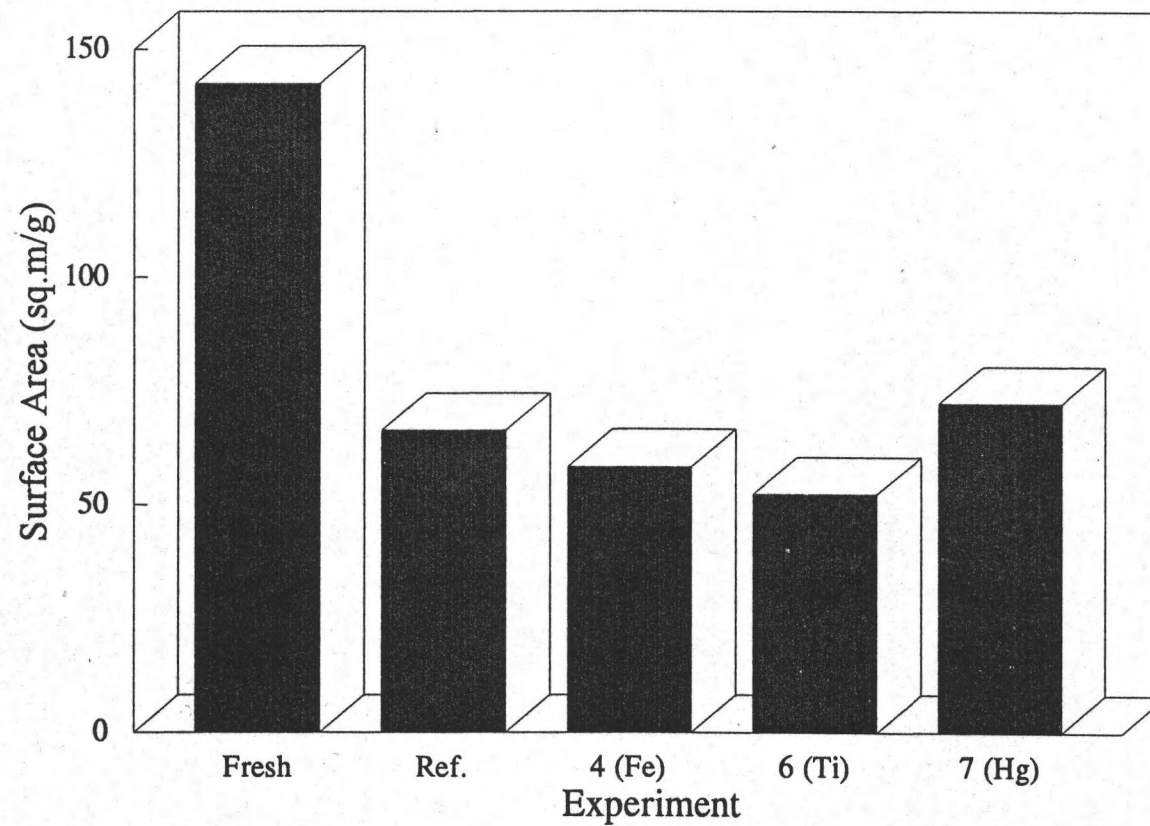


Figure 4.2 The Comparison of Surface Area of Catalyst in Each Experiment

Pore Volume of Catalyst Before Catalyst Regeneration

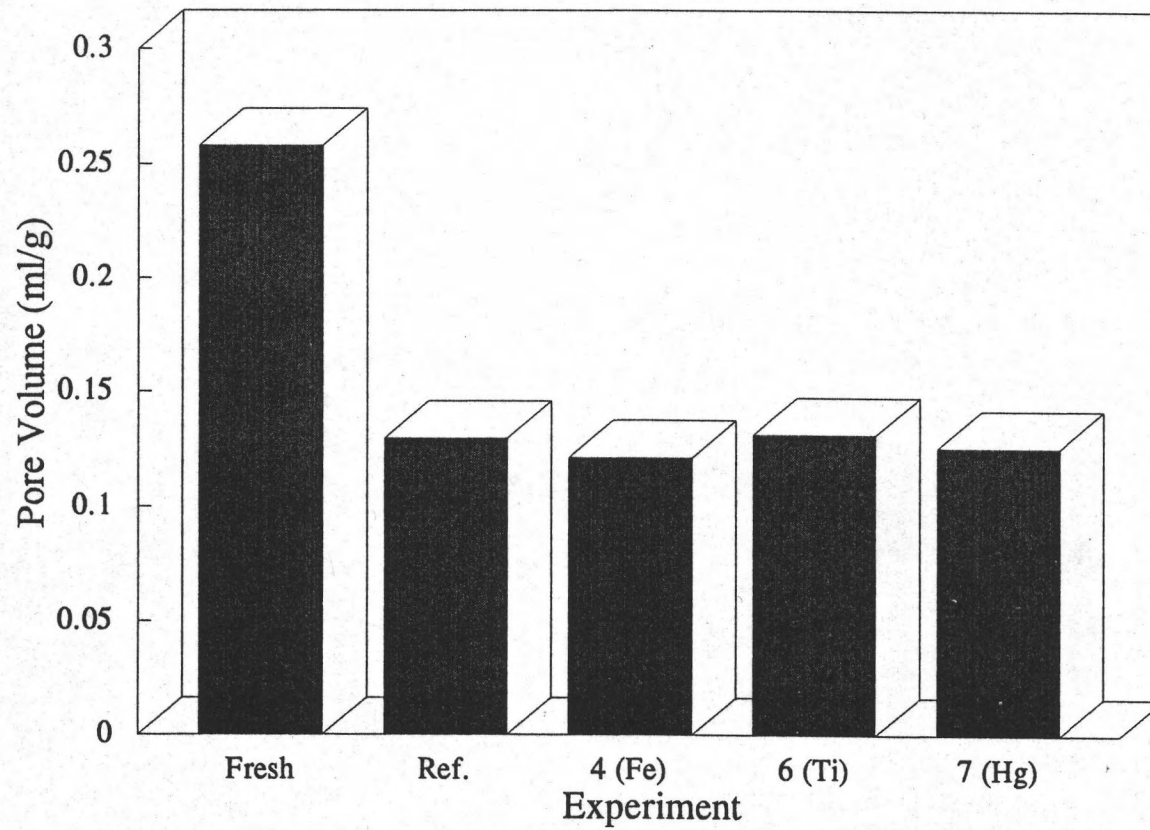


Figure 4.3 Pore Volume of Catalyst in Each Experiment

Surface Area of Catalyst After Catalyst Regeneration

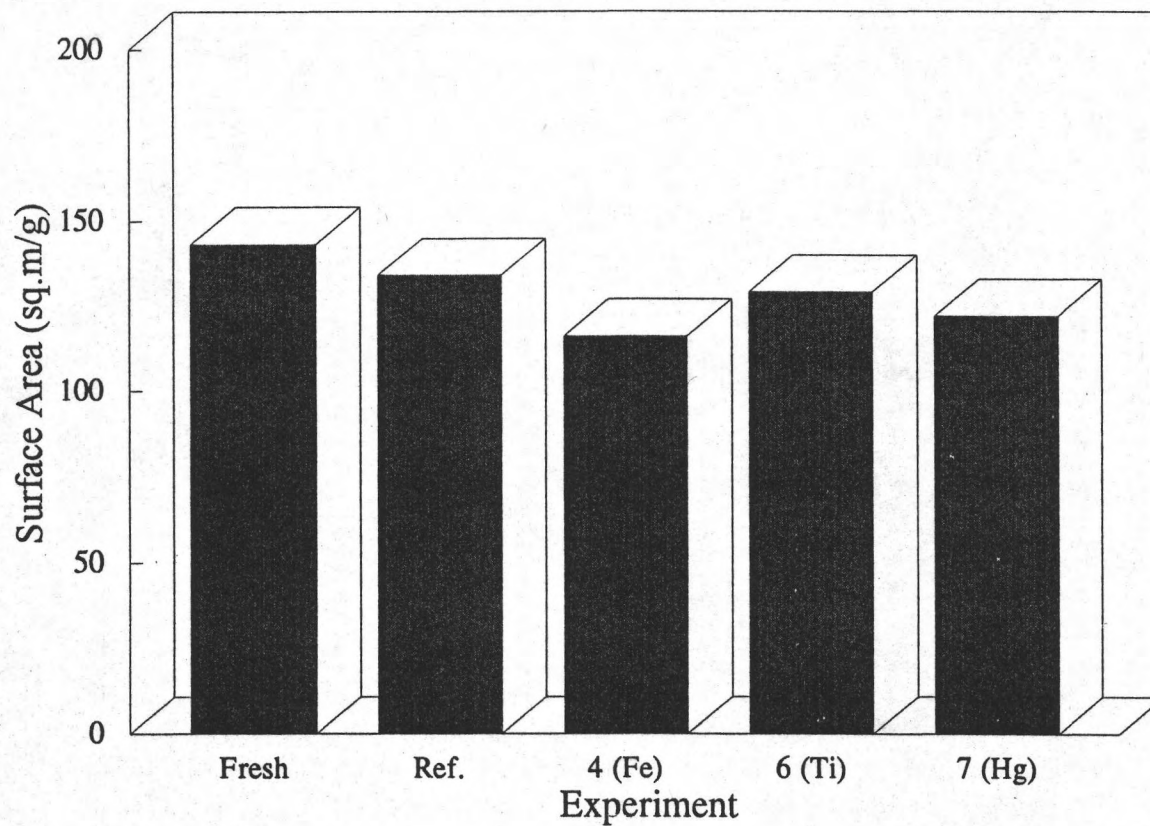


Figure 4.4 The Comparison of Surface Area of Catalyst in Each Experiment

Pore Volume of Catalyst After Catalyst Regeneration

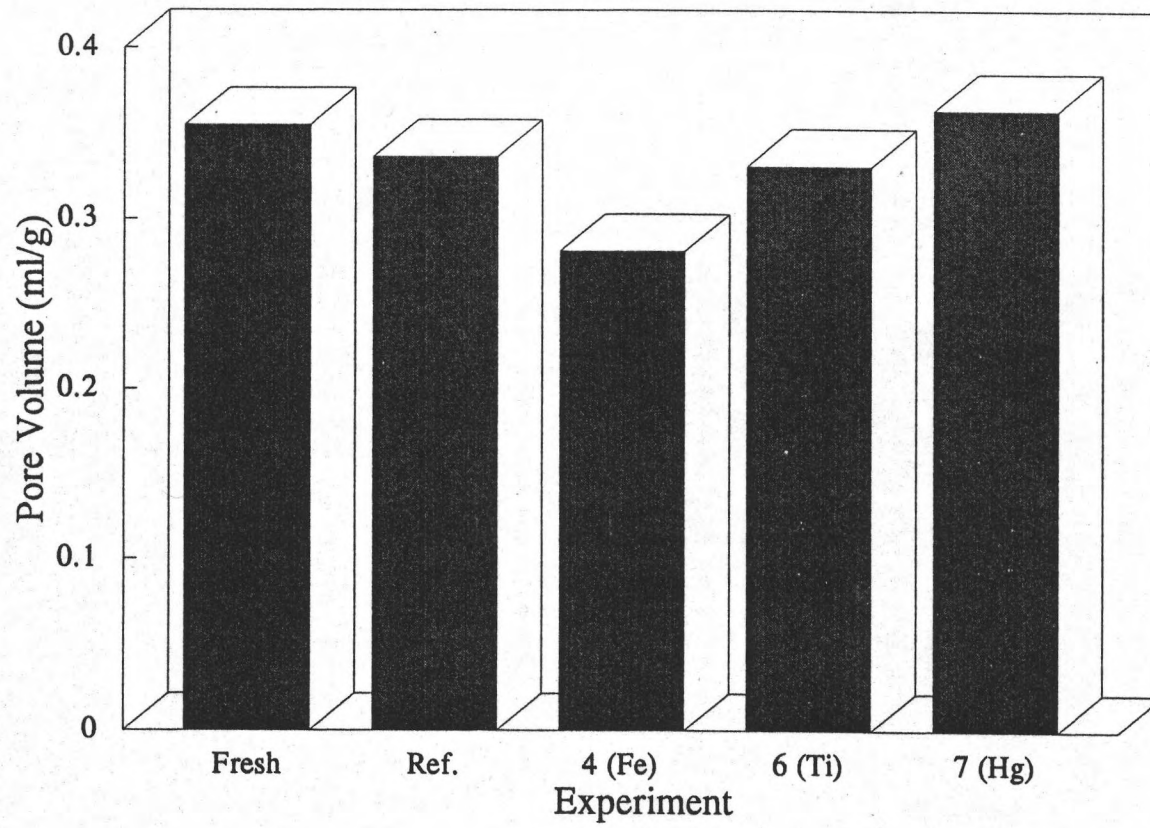


Figure 4.5 Pore Volume of Catalyst in Each Experiment

Similar results were obtained by Thomas and Sample (48). They found that all physical properties decreased with increasing coke content and coke was found in internal pore mouth. The major change of the catalyst during the test was 17-22 % coke.

4.2.3 Effects of Ferrocene

In experiments 4 and 5, 200 ppm of iron as ferrocene was added to the feedstock. The operating condition used was the same as in the reference experiment. Figure 4.6 shows the distribution of nitrogen compounds in these experiments. Two experimental runs (experiments 4 and 5) were reproduced in order to test the consistency of the experimental data. The results of reaction products are reproducible within an accuracy of 4 %. Table 4.16 shows the results of reaction products between experiments 4 and 5. Table 4.17 shows the deviation of the results which occurs in these experiments.

The presence of ferrocene reduces the amounts of BzTHQ, DHQ, PCH, and PB, while PyTHQ is increased with time. The distribution curves of these experiments are shown that PyTHQ is increased from 51.05 % to 71.65 % while other reaction products are decreased approximately 2 % to 10 %. These results indicate that ferrocene disturbs the reaction of quinoline HDN. Conversion of quinoline to PyTHQ is almost constant, while other reactions are disturbed by the presence of ferrocene in the feedstock.

The amounts of coke in these experiments are

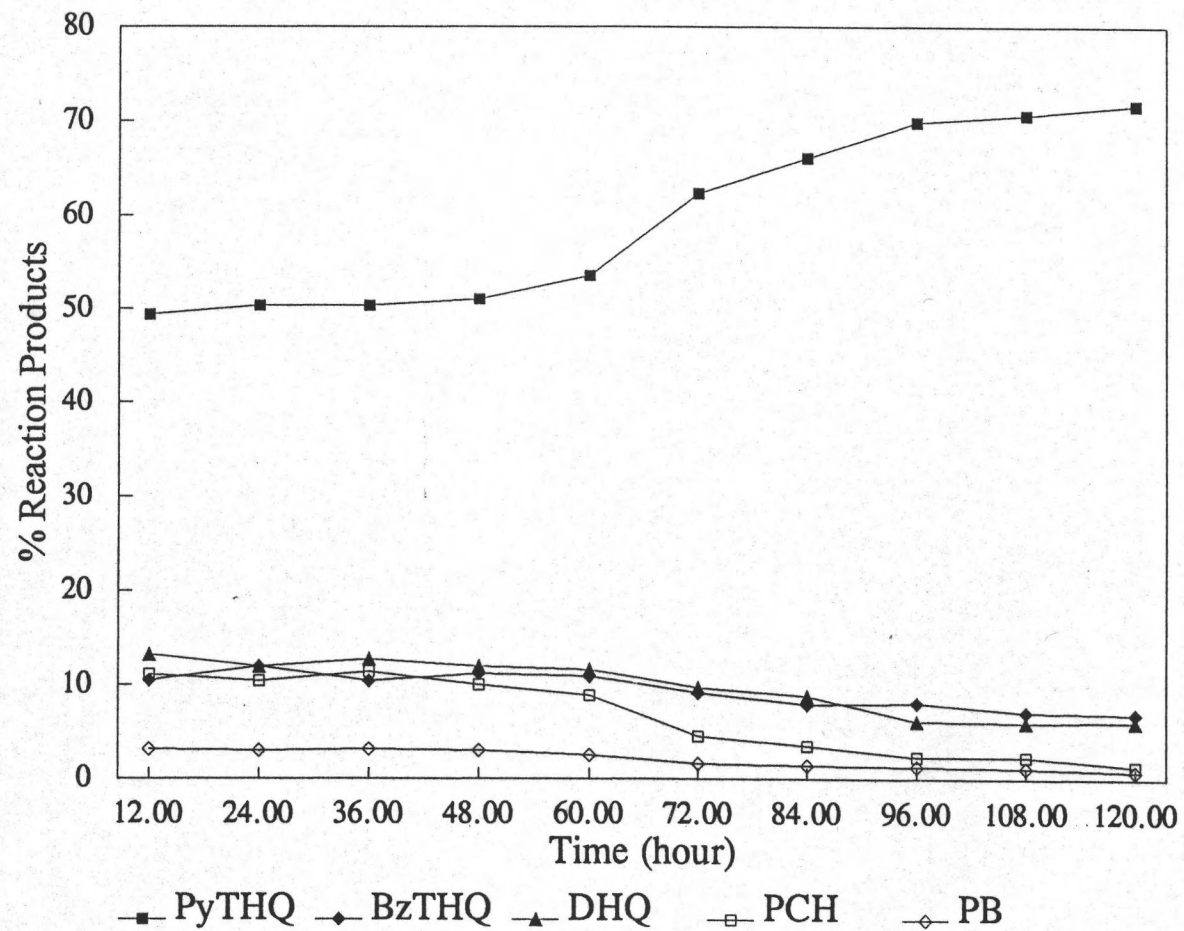


Figure 4.6 Distribution of Reaction Products in Experiments 4 and 5

Table 4.16 Results between Experiments 4 and 5

Time (hr)	% reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	12.58	49.36	10.56	13.23	11.12	3.16
24	12.28	50.31	11.96	11.99	10.43	3.03
36	11.98	50.32	10.47	12.75	11.43	3.15
48	12.73	51.05	11.23	11.97	10.00	3.03
60	12.35	53.58	10.98	11.67	8.91	2.53
72	12.51	62.36	9.23	9.75	4.55	1.61
84	12.31	66.12	7.95	8.88	3.53	1.40
96	12.38	69.85	8.07	6.13	2.30	1.28
108	12.83	70.58	7.14	5.98	2.35	1.14
120	12.94	71.65	6.88	6.06	1.36	0.82

Table 4.17 Deviation of Reaction Products between Experiments 4 and 5

Time (hr)	% deviation of reaction products					
	Q	PyTHQ	BzTHQ	DHQ	PCH	PB
12	-3.58	-7.64	0.81	-0.95	3.33	0.86
24	-1.94	-5.83	-1.50	0.14	4.85	0.42
36	-3.87	-9.69	0.04	0.37	4.96	0.54
48	-3.20	-7.52	-0.56	0.43	4.06	0.39
60	-2.54	-11.01	2.29	1.53	3.54	0.82
72	0.95	-6.32	0.20	4.31	2.37	0.39
84	-0.48	-7.70	0.51	3.86	2.55	0.30
96	-0.26	-2.90	-1.45	2.24	1.95	-0.10
108	-3.51	-4.36	-0.89	-0.45	1.95	0.25
120	0.58	-0.12	-0.03	-0.07	0.98	0.41



shown in Table 4.8. The coking results of experiment 4 is the same as the results of experiment 5. It is reproducible within an accuracy of 2.04 %. The coke content on NiMo/alumina is approximately 8.79 wt%. It is shown that the addition of ferrocene to the feedstock reduces coke formation on NiMo/alumina catalyst. Figure 4.7 shows the comparison of coke content on catalyst in each experiment.

The comparison of catalyst surface area and pore volume in each experiments are shown in Figures 4.2 and 4.3, respectively. The comparison of catalyst surface area before and after burning the catalyst are shown in Table 4.14. It is shown that in the presence of ferrocene, surface area is reduced approximately 58.98 % (Figure 4.2), while catalyst pore volume is reduced approximately 52.19%, as shown in Table 4.15. These results indicate that iron from ferrocene may covers the outer surface of the catalyst, resulting in a reduction of surface area and pore volume of the catalyst.

Figure 4.8 shows the results of the distribution of iron in the catalyst pellet. The results show the deposition of iron at 4 different locations from the edge to the center of the catalyst pellet. It shows that iron deposits mostly on the edge of the pellet and decrease at other locations till the center of the pellet.

These results of catalyst sample indicate that iron from ferrocene mostly deposits on the outer surface of the catalyst. This iron coverage decreases the catalyst surface and increases the mass transfer resistance into the pores of the catalyst. The decreasing of

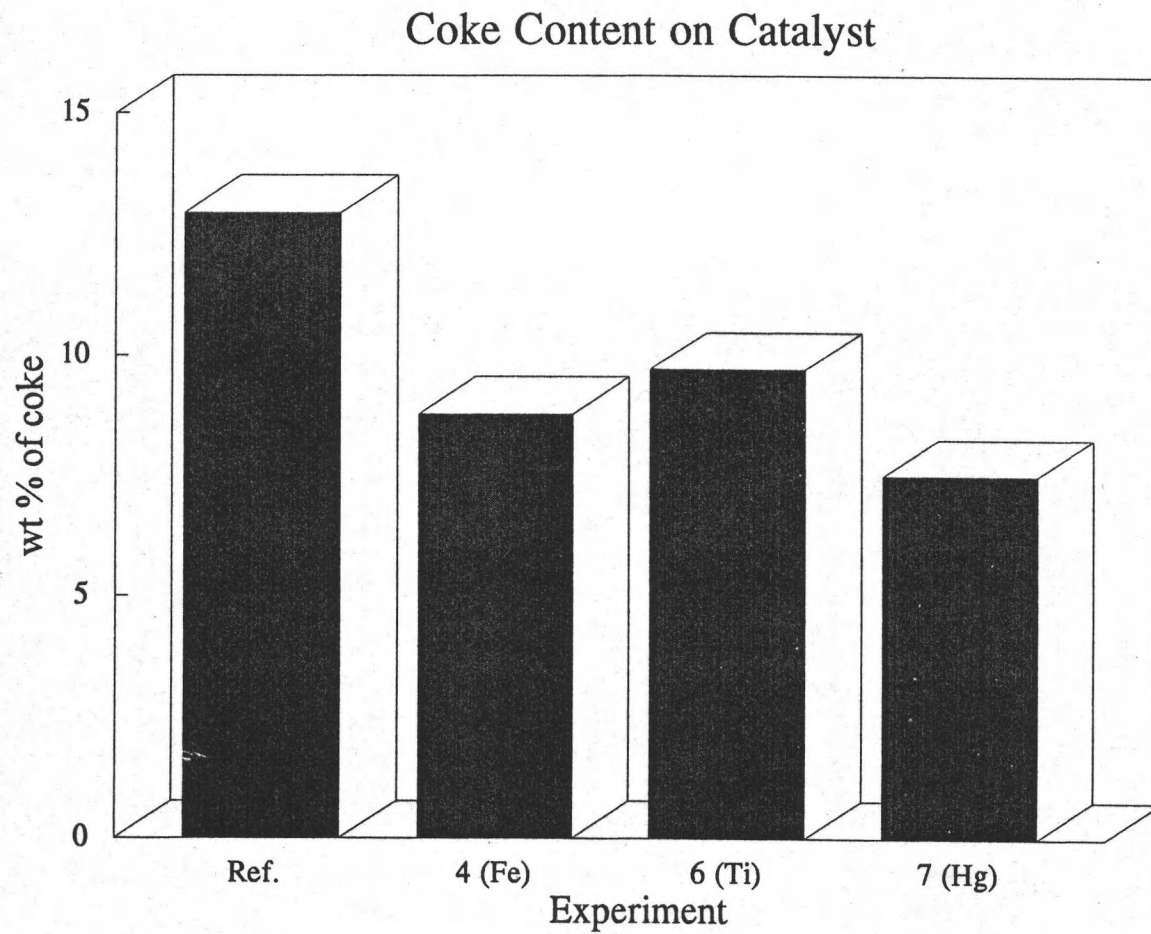


Figure 4.7 The Comparison of Coke Content on the Catalyst

Distribution of Fe

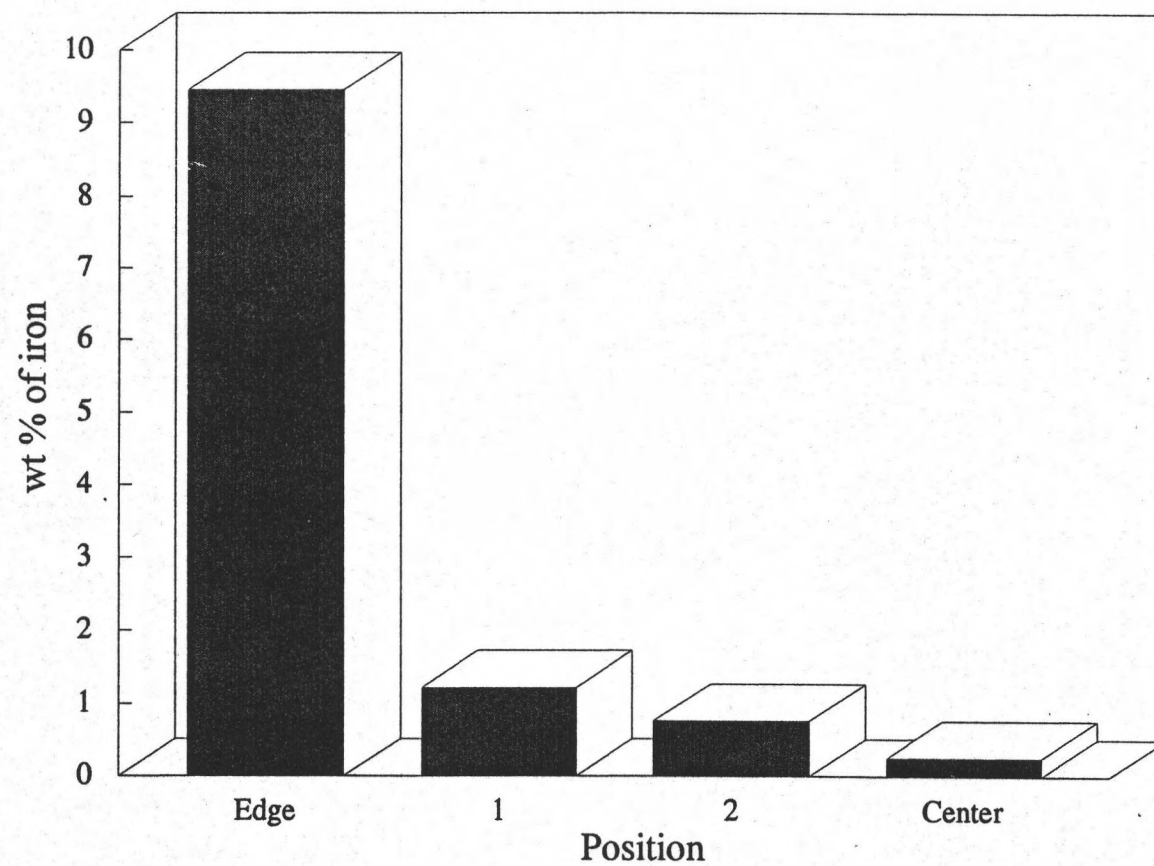


Figure 4.8 Distribution of Iron in the Catalyst Pellet

of the catalyst. This iron coverage decreases the catalyst surface and increases the mass transfer resistance into the pores of the catalyst. The decreasing of surface area results in the reduction of active sites, while the increasing of mass transfer resistance results in the reduction of reactant to transfer to the active site which reduces the reaction on the catalyst surface. The reaction on catalyst surface is reduced, so coke formation on the catalyst also reduced. After regeneration, catalyst surface area and pore volume can not recover to its original property, as shown in Figures 4.4 and 4.5, respectively. This indicates that iron blocks catalyst pores and causes reduction of surface area.

Earlier studies (45, 50, 98) showed that coke and metal (Fe) were major contaminants. Samples of deactivated catalyst was 50 - 70 % covered with a crush of FeS which was responsible for activity reduction. The decline in activity was proportional to the coke and metal contents of the catalysts. The iron deposition was limited to the outer surface of the catalyst.

4.2.4 Effects of Titanocene dichloride

Experiment 6 was conducted to study the effects of titanium on the reaction of quinoline HDN. It was studied at the same operating conditions as in the reference experiment. Titanium dichloride was added to the feedstock to make a mixture of 200 ppm of titanium. Figure 4.9 shows the distribution of nitrogen compound in this experiment. It shows that the addition of titanocene dichloride slightly decreases the reaction

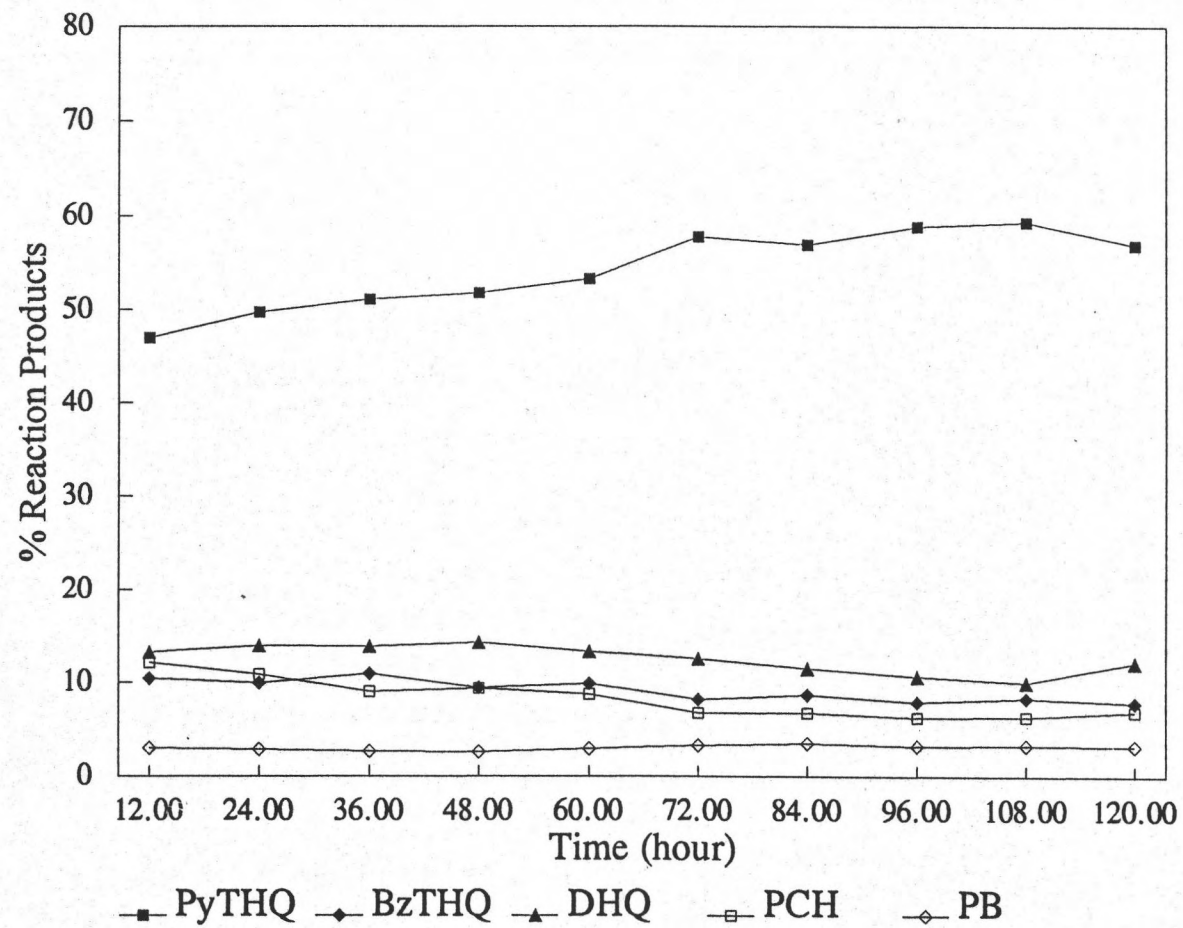


Figure 4.9 Distribution of Reaction Products in Experiment 6

reactions of quinoline HDN are decreased, except the reaction of quinoline to PyTHQ, resulting in an increasing of PyTHQ.

Figure 4.7 shows the coking results in this experiment. The coke content on the catalyst sample is lower than that of reference run. It is shown that titanocene dichloride in the feedstock reduces coke formation on catalyst.

Table 4.9 shows the analysis of catalyst surface area and pore volume. It shows that titanocene dichloride reduces surface area from 142.45 to 58.43 m²/g, approximately 58.98 %, while pore volume is decreased from 0.2578 to 0.1312 ml/g, approximately 49.11%. When comparison of the results of surface area and pore volume of the reference run is made, the results show that the presence of titanocene dichloride reduces the surface area, while pore volume of the catalyst does not change. After catalyst regeneration, surface area and pore volume of the catalyst recovered nearly the same as in the reference run. These results indicate that surface area and pore volume of the catalyst is reduced by coke deposition, while titanium deposition does not affect to these physical properties (Figures 4.4 and 4.5).

Figure 4.10 shows the distribution of titanium in the catalyst pellet. It shows that small amounts of titanium are found in the catalyst. Titanocene dichloride is known to react with many compounds at room temperature (67). Titanocene dichloride forms an insoluble titanium compound suspended in the feedstock when it was added to the feedstock. This effect results

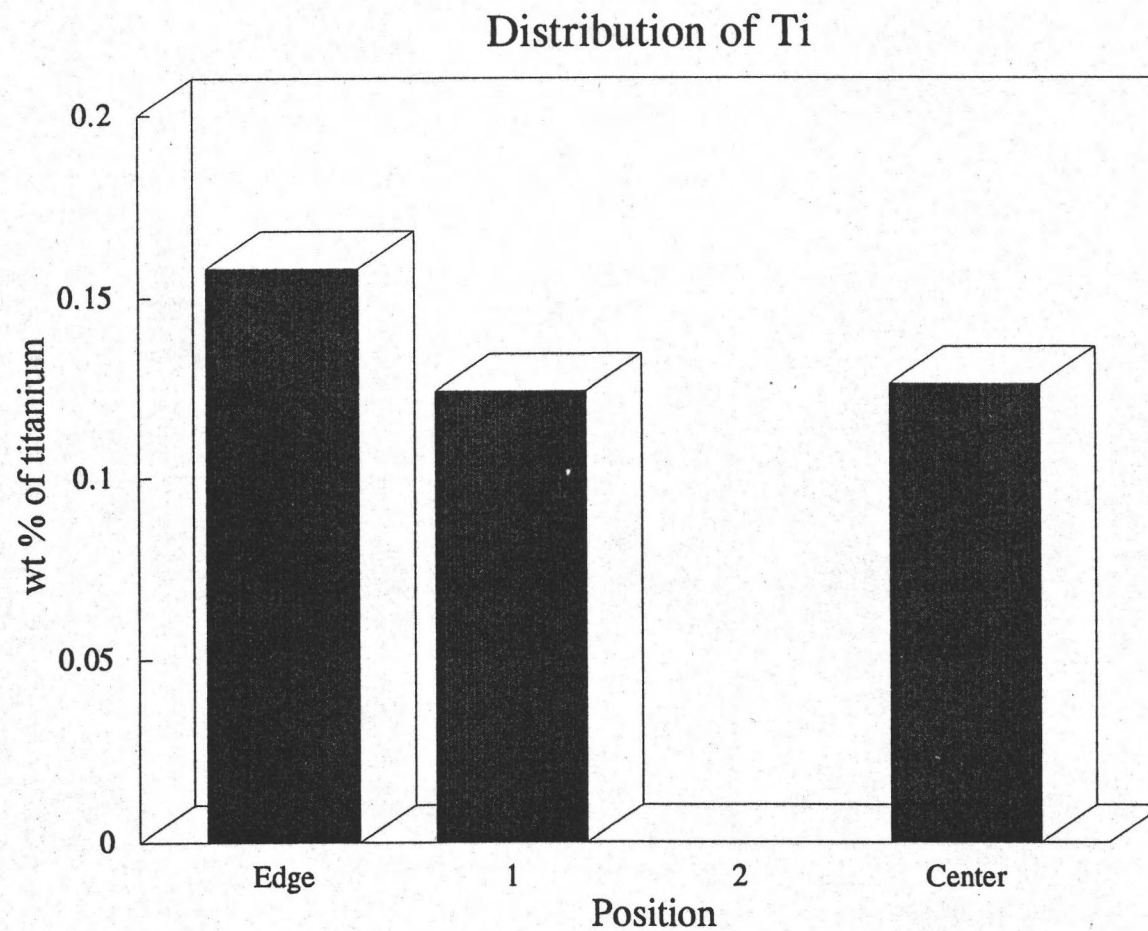


Figure 4.10 Distribution of Titanium in the Catalyst Pellet

in the reduction of titanium from the feedstock and causes the lower concentration of titanium on the catalyst.

These results of the catalyst pellet indicate that titanium covers the catalyst surface, although it has a few amount on the catalyst surface. This effect results in the reduction of reaction on catalyst surface, so coke formation is also reduced.

Earlier studies (50, 66, 67, 98) reported that titanium had little effect on the hydrodenitrogenation activity of the catalyst and also decreased the formation of coke on catalyst. Titanocene dichloride formed an insoluble particles suspended in the feedstock, resulting in a reduction of titanium from the feedstock. This effect would demonstrate the lower concentration of titanium on the catalyst.

4.2.5 Effects of Diphenylmercury

In experiment 7, Diphenylmercury was added to the feedstock to make a mixture of 200 ppm of mercury and was studied at the same operating conditions as in the reference experiment. Figure 4.11 shows the distribution of nitrogen compounds in experiment 7. When the distribution curves of the reference experiment and experiment 7 are compared, it showed that the intermediate products are nearly the same as in the reference run. The gas chromatograph analyses show that the amounts of intermediate products are 53.85% of PyTHQ, 9.37% of BzTHQ, 12.73% of DHQ, 8.34% of PCH, and 2.78% of PB which are nearly the same as in the reference run.

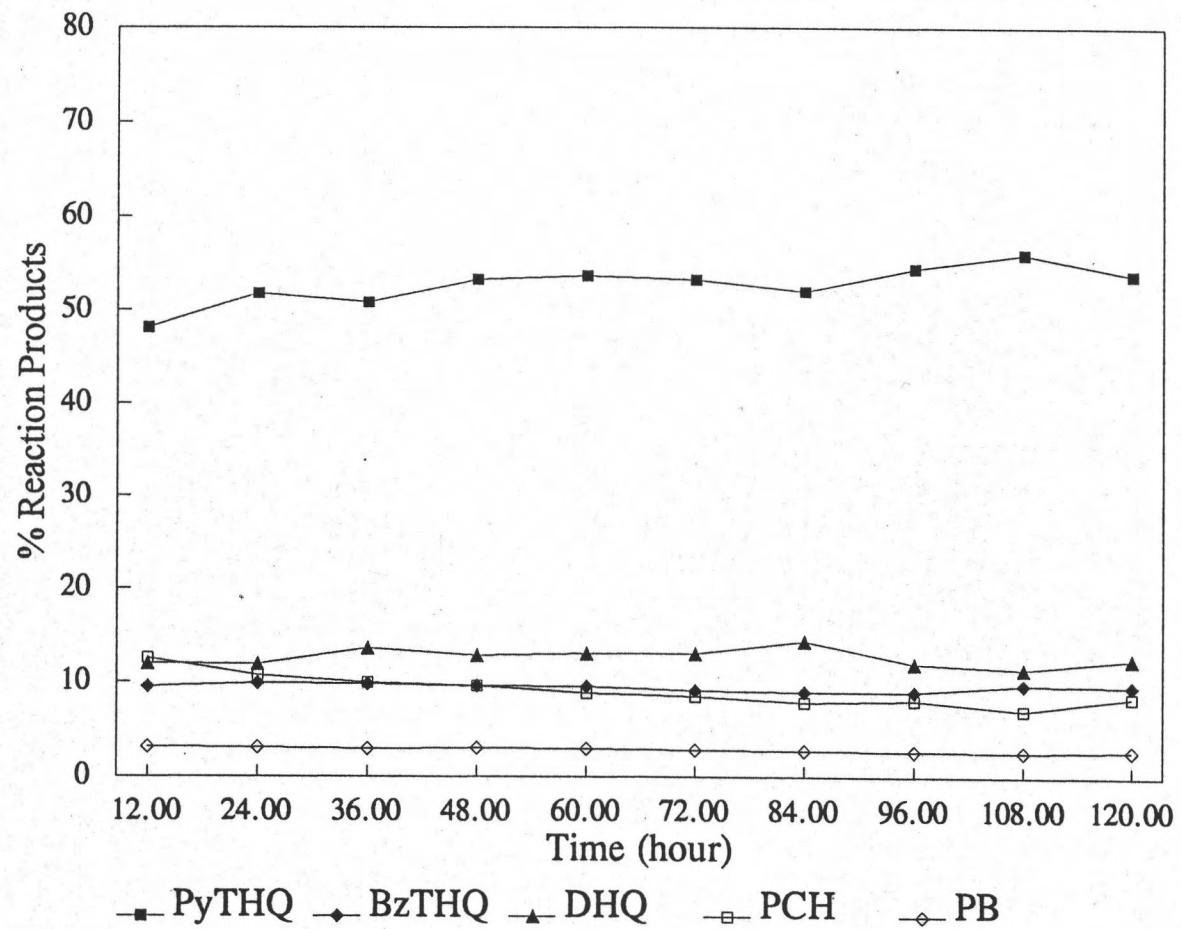


Figure 4.11 Distribution of Reaction Products in Experiment 7

The result of coke analysis in Table 4.8 shows that the amount of coke formed on the catalyst is lower than the coking result in the reference run when diphenylmercury is in the feedstock, as shown in Figure 4.7. Figures 4.2 and 4.3 show the comparison of catalyst surface area and pore volume, respectively. The results indicated that diphenylmercury does not change surface area and pore volume of the catalyst.

Diphenylmercury in the feedstock probably evaporate to the vapor phase at this operating temperature, so it does not cover or deposit on the surface area of the catalyst. Eventhough the coke content on the catalyst reduces from the promotion of diphenylmercury, but the catalyst activity is still the same as in the reference experiment.