

CHAPTER IV

RESULTS AND DISCUSSION

Procedures

A fixed-bed reactor is used for investigation of hydrodesulfurization reaction on commercial catalysts. Thiophene and quinoline are used as model compounds of sulfur and nitrogen compounds, respectively. In this study, the experiments are divided into three parts.

Part A - The experiments are conducted to study repeatability and error of the experiments (Experiments 1-4).

Part B - The experiments are conducted to study effects of temperature on HDS of thiophene (Reference experiments, Experiments 5-8).

Part C - The experiments are conducted to study effects of temperature on HDS of thiophene in the presence of quinoline (Deactivation experiments, Experiments 9-14).

In each experiment, a solution containing 3 wt% sulfur as thiophene in liquid carrier is used as a feedstock. Total time of each experiment is 144 hours.

For deactivation experiments, feedstock is replaced by a solution containing 3 wt% sulfur as thiophene and 0.5 wt% nitrogen as quinoline at the times of 48 hours and 96 hours after start-up. The feedstock containing quinoline is used for 24 hours at each time. Two commercial catalysts used are CoMo/Al₂O₃ and NiMo/Al₂O₃. The experiments are conducted at a pressure of 400 psig and temperatures of 240, 250 and 260°C. The details of each experiment are given in Table 4.1.

Toluene and hexane are used as liquid carrier because they of their good solubility for sulfur and nitrogen model compounds and their negligible conversion at the operating conditions. Thiophene is chosen as sulfur model compound because its HDS reaction is known to be strongly poisoned by nitrogen compounds [LaVopa and Satterfield, 1988] and it is the least reactive organosulfur compound in petroleum. Quinoline is chosen as nitrogen model compound in order to study inhibiting effects on HDS of thiophene in each deactivation experiment. The details of feedstock and operating conditions of reference and deactivation experiments are given in Tables 4.2 and 4.3, respectively.

Before start-up of each experiment, the reactor is packed in the middle part with 3 grams of catalyst. The top part of the reactor is left empty and is used as vaporizing zone. The bottom part is packed with glass bead and is used as cooling zone. The reactor is then connected to a gas feed line and a liquid feed line at

Table 4.1 Operating Conditions in Each Experiment

Experiment No.	Catalyst	Temperature (°C)	Nitrogen Compound
1	CoMo	240	-
2	CoMo	240	-
3	NiMo	240	-
4	NiMo	240	-
5	CoMo	250	-
6	CoMo	260	-
7	NiMo	250	-
8	NiMo	260	-
9	CoMo	240	Quinoline
10	CoMo	250	Quinoline
11	CoMo	260	Quinoline
12	NiMo	240	Quinoline
13	NiMo	250	Quinoline
14	NiMo	260	Quinoline

Table 4.2 Procedure of Reference Experiments

<i>Feedstocks:</i>	
Feed I:	Toluene + 5 wt% Hexane + 3 wt% Sulfur (as Thiophene)
<i>Operating Conditions:</i>	
Temperature	: 240, 250, 260°C
Pressure	: 400 psig
WHSV	: 3.0 hr ⁻¹
Liquid Flow Rate	: 10 cc/hr
H ₂ : Oil Ratio	: 2400:1
Hydrogen Flow Rate	: 400 cc/min
Catalyst	: 3.0 grams of CoMo/Al ₂ O ₃ 3.0 grams of NiMo/Al ₂ O ₃
Sampling Time	: every 6 hours
Duration of Experiment:	144 hours

Table 4.3 Procedure of Deactivation Experiments

<i>Feedstocks:</i>	
Feed I	: Toluene + 5 wt% Hexane + 3 wt% Sulfur (as Thiophene)
Feed II	: Toluene + 5 wt% Hexane + 3 wt% Sulfur (as Thiophene)+ 0.5 wt% Nitrogen (as Quinoline)
<i>Operating Conditions:</i>	
Temperature	: 240, 250, 260°C
Pressure	: 400 psig
WHSV	: 3.0 hr ⁻¹
Liquid Flow Rate	: 10 cc/hr
H ₂ : Oil Ratio	: 2400:1
Hydrogen Flow Rate	: 400 cc/min
Catalyst	: 3.0 grams of CoMo/Al ₂ O ₃ 3.0 grams of NiMo/Al ₂ O ₃
Sampling Time	: every 6 hours
Duration of Experiment	: 144 hours
<i>Switching Feedstocks:</i>	
Feed I	: Duration of experiment 48 hours
Feed II	: Duration of experiment 24 hours
Feed I	: Duration of experiment 24 hours
Feed II	: Duration of experiment 24 hours
Feed I	: Duration of experiment 24 hours

the top of the reactor and is connected to a sample bomb at the bottom. The system is checked for leak by gradually pressurizing with nitrogen gas. The leak test is carried out at pressure of 500 psig which is 100 psig higher than operating pressure. A pressure drop of 5 psig in one hour is the maximum acceptable leak. Every experiment is started with fresh catalyst and the catalyst is sulfided in situ to increase catalyst activity for HDS reaction. Catalyst preparation in each experiment is conducted using identical sulfiding procedure.

During each experiment, liquid samples are collected every 12 hours interval during the first 24 hours and every 6 hours interval for the remaining time period. The liquid samples are analyzed for thiophene concentration by gas chromatographic analysis techniques. Conversion of thiophene is then calculated by

$$\text{Conversion of thiophene (\%)} = (1 - C_t / C_{t_0}) \times 100$$

where C_{t_0} = weight of thiophene in feedstock

C_t = weight of thiophene in product sample

Results and Discussion

Experimental Errors

This part is conducted to verify repeatability and to find error limits of the experiments. Conversions of thiophene are calculated for their average values from

two different experiments conducted using CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts at the same operating conditions. Maximum and minimum derivations from the average value are also calculated. Effects of nitrogen compound on conversion of thiophene are carried out by comparison of the average results of reference experiments with results of deactivation experiments at the same operating conditions.

Two set of experiments (experiments 1-4) are conducted at a temperature of 240°C and a pressure of 400 psig on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts, respectively. The reproducibility of the data is checked by performing duplicate experiments using CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts at identical conditions. Conversion of thiophene at any time of reference experiments, average conversion, and experimental deviation in the studies on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are shown in Tables 4.4 and 4.5, respectively. The reproducibility of the thiophene conversion of CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are presented in Figures 4.1 and 4.2, respectively. From these results, it is seen that the steady-state operation is reached after 24 hours from start-up. Total time to cover the whole range of experiment is 144 hours and the average conversions of thiophene throughout the experiments are 79.79%, for CoMo/Al₂O₃ catalyst and 68.74%, for NiMo/Al₂O₃ catalyst. The results are reproducible in a range of 0.02-5.62% with the average error of 1.85% for CoMo/Al₂O₃ catalyst (experiments 1 and

Table 4.4 Conversion of Thiophene with Time of Reference
Experiments on CoMo Catalyst at 240°C
(Experimental Error)

Time (hr.)	Conversion of Thiophene (%)			Deviation (%)
	Exp. 1	Exp. 2	Average Exp.	
12	76.22	77.93	77.07	1.11
24	78.71	77.81	78.26	0.58
30	77.24	76.56	76.90	0.44
36	77.54	80.02	78.78	1.58
42	80.41	82.42	81.42	1.24
48	80.36	82.15	81.26	1.10
54	83.39	83.11	83.25	0.16
60	84.60	75.59	80.10	5.62
66	82.48	76.44	79.46	3.80
72	81.35	81.32	81.33	0.02
78	80.53	78.83	79.68	1.07
84	77.66	74.67	76.16	1.96
90	76.65	76.54	76.60	0.07
96	81.03	81.91	81.47	0.54
102	78.64	81.94	80.29	2.06
108	73.02	80.91	76.97	5.13
114	77.28	81.24	79.26	2.50
120	83.26	82.22	82.74	0.63
126	85.42	79.21	82.32	3.78
132	81.24	77.14	79.19	2.59
138	82.94	76.31	79.62	4.16
144	83.72	82.93	83.32	0.48
Average			79.79	1.85

Table 4.5 Conversion of Thiophene with Time of Reference
Experiments on NiMo Catalyst at 240°C
(Experimental Error)

Time (hr.)	Conversion of Thiophene (%)			Deviation (%)
	Exp. 3	Exp. 4	Average Exp.	
12	71.47	78.50	74.99	4.69
24	65.24	72.36	68.80	5.17
30	67.07	63.86	65.47	2.45
36	68.66	66.97	67.82	1.25
42	61.05	70.46	65.76	7.16
48	63.33	71.79	67.56	6.26
54	63.54	71.59	67.57	5.96
60	65.30	68.10	66.70	2.10
66	64.85	68.18	66.51	2.51
72	72.44	73.52	72.98	0.74
78	67.74	71.71	69.72	2.85
84	61.48	70.48	65.98	6.82
90	62.36	68.44	65.40	4.65
96	66.37	74.49	70.43	5.76
102	65.45	72.29	68.87	4.96
108	68.53	70.38	69.45	1.33
114	64.48	72.09	68.28	5.57
120	72.01	71.12	71.56	0.63
126	68.18	67.48	67.83	0.52
132	70.79	73.80	72.29	2.08
138	67.75	73.27	70.51	3.92
144	65.42	70.24	67.83	3.55
Average			68.74	3.68

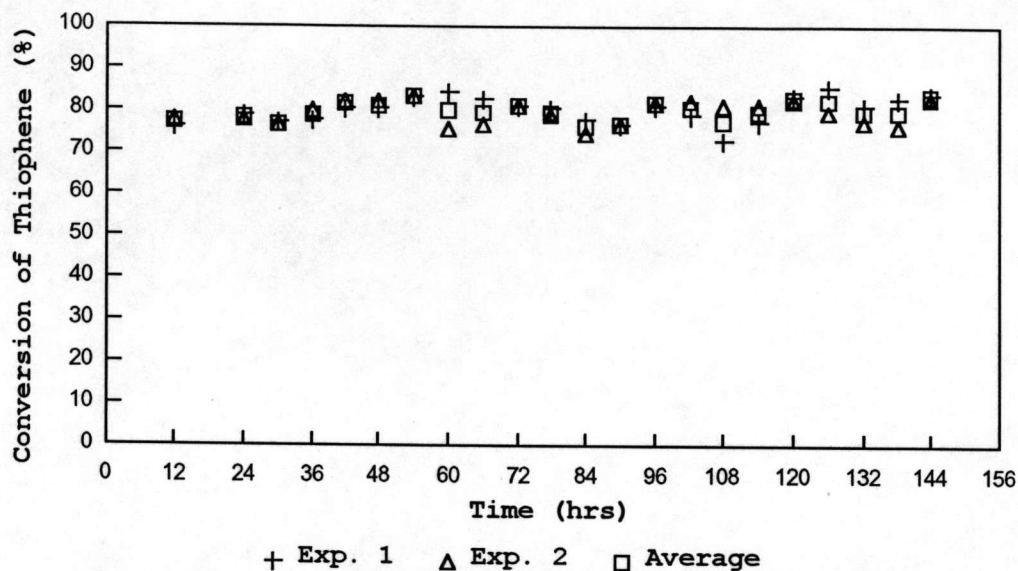


Figure 4.1 Conversion of Thiophene with Time in Study the Experimental Error of Reference Experiments on CoMo Catalyst.

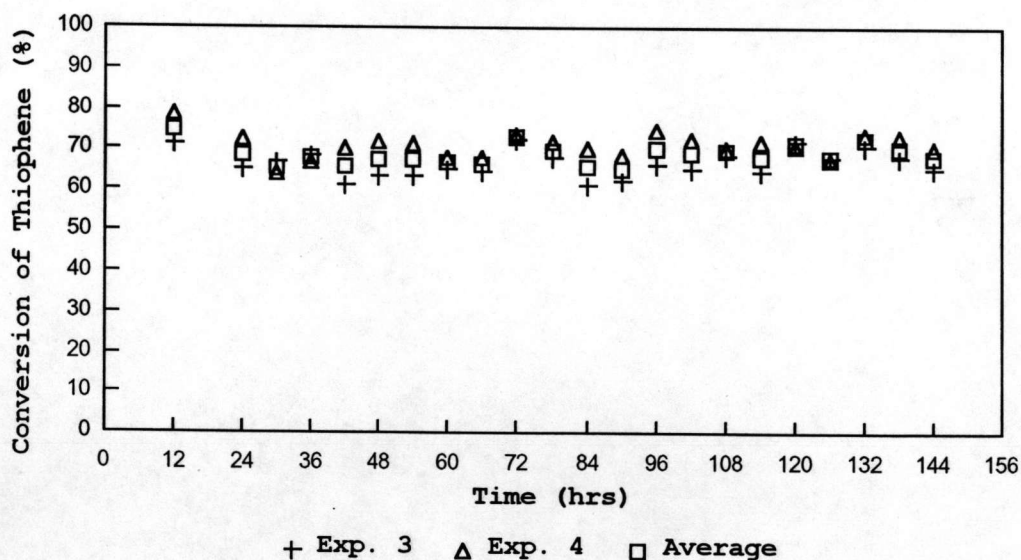


Figure 4.2 Conversion of Thiophene with Time in Study the Experimental Error of Reference Experiments on NiMo Catalyst.

2) and in a range of 0.52-7.16% with the average error of 3.68% for NiMo/Al₂O₃ catalyst (experiments 3 and 4). The experimental deviation of both sets of experiments on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are reproducible within an accuracy of 4%.

Effects of Temperature on HDS of Thiophene (Reference Experiments)

A set of experiments (experiments 5-8) is conducted to study the effects of operating temperature on thiophene HDS. This study is performed at various temperatures in order to compare conversion of thiophene on two commercial catalysts, CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts. The effects of temperature on the catalytic HDS of thiophene are studied at temperatures of 240, 250, and 260°C and at a pressure of 400 psig. Conversion of thiophene at any time of each experiment and the average conversion of each experiment at various temperatures are shown in Table 4.6. No significant catalyst deactivation is observed during the period of 144 hours.

Figures 4.3 and 4.4 show the comparison of thiophene conversion of each catalyst at different temperatures on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts, respectively. The results indicate that catalytic HDS activity is strongly dependent on operating temperature for both catalysts. Conversion of thiophene increases substantially with an increase in temperature.

Table 4.6 Conversion of Thiophene with Time of Reference
Experiments on CoMo and NiMo Catalysts at
Various Temperatures

Time (hr.)	Conversion of Thiophene (%)					
	CoMo			NiMo		
	240°C (Average)	250°C (Exp.5)	260°C (Exp.6)	240°C (Average)	250°C (Exp.7)	260°C (Exp.8)
12	77.07	88.48	97.07	74.99	86.87	96.39
24	78.26	89.10	98.81	68.80	85.39	96.82
30	76.90	88.73	99.87	65.47	86.83	95.06
36	78.78	88.22	96.06	67.82	81.31	95.54
42	81.42	92.15	96.98	65.76	80.15	95.61
48	81.26	92.45	97.76	67.56	87.16	97.03
54	83.25	87.22	97.17	67.57	86.75	96.82
60	80.10	87.65	94.29	66.70	80.17	93.69
66	79.46	92.49	99.83	66.51	84.30	94.19
72	81.33	92.14	94.92	72.98	83.92	96.95
78	79.68	89.53	94.73	69.72	80.10	96.27
84	76.16	90.61	97.15	65.98	84.74	96.44
90	76.60	93.22	97.90	65.40	85.20	96.63
96	81.47	90.38	99.94	70.43	83.26	97.95
102	80.29	87.74	98.85	68.87	81.82	92.75
108	76.97	88.55	99.85	69.45	82.60	96.12
114	79.26	86.27	99.71	68.28	85.59	96.73
120	82.74	93.74	98.45	71.56	87.12	96.13
126	82.32	91.71	97.22	67.83	85.68	94.05
132	79.19	89.74	97.70	72.29	84.51	93.04
138	76.62	92.23	99.96	70.51	87.61	93.45
144	83.32	92.19	99.82	67.83	85.15	95.88
Average	79.79	90.20	97.91	68.74	84.39	95.62

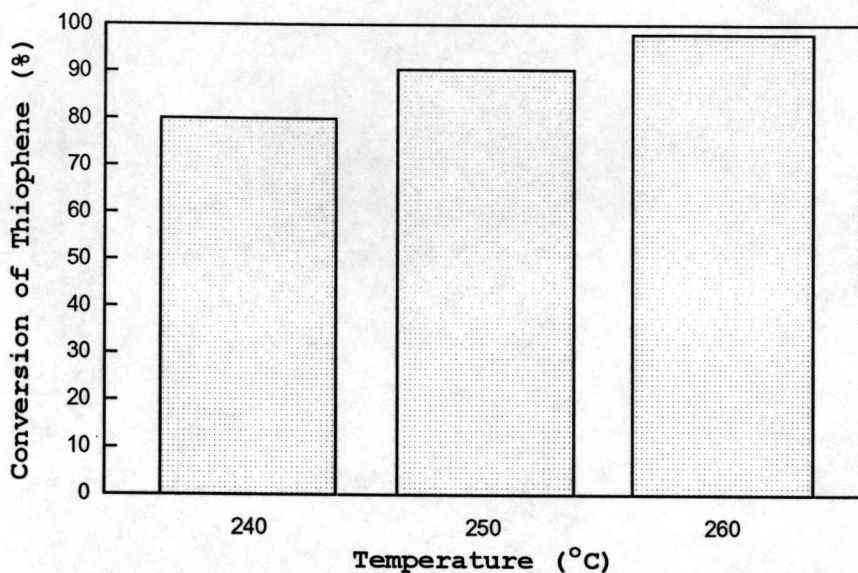


Figure 4.3 Conversion of Thiophene in Study the Effects of Temperature of Reference Experiments on CoMo Catalyst.

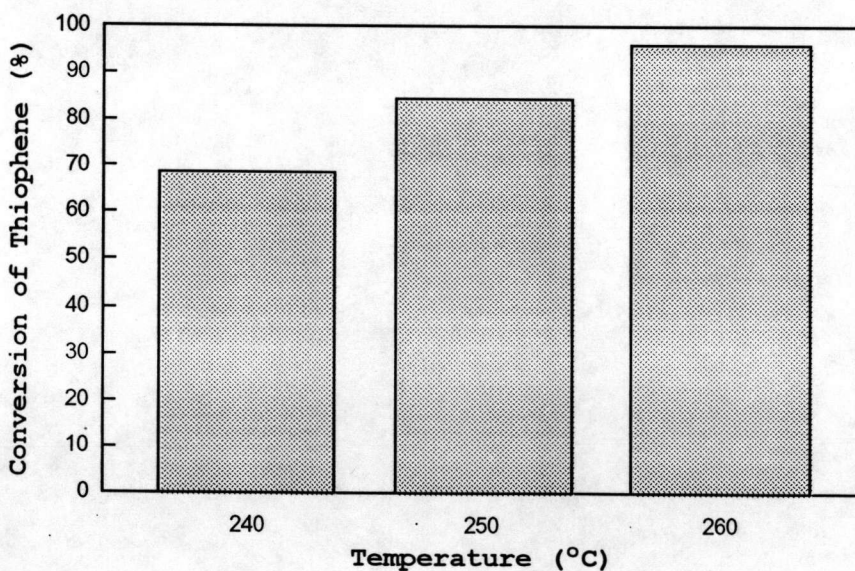


Figure 4.4 Conversion of Thiophene in Study the Effects of Temperature of Reference Experiments on NiMo Catalyst.

Similar results were observed by Satterfield and Roberts [1968] who studied HDS of thiophene on cobalt molybdate catalyst at atmospheric pressure. They reported that variation of temperature had some effect on the rate of reaction. The reaction rate of thiophene increased from 0.156×10^{-8} to 0.180×10^{-8} as the results of the increasing temperature from 235°C to 265°C . The similar study is conducted by Lipsch and Schuit [1969]. They concluded that the increase of thiophene conversion from 3% to 65% as the results of the increasing temperature from 250°C to 460°C . Above 400°C thiophene conversion increased suddenly but at $250\text{-}360^{\circ}\text{C}$ it increased slightly. These results are also in agreement with a document by Morooka and Hamrin [1977] who tried to obtain overall activation energy for HDS of thiophene over a cobalt molybdate catalyst at a pressure of 15 psig and temperature ranges from 250°C to 350°C . The conversions were in the range of 4-16% and the overall activation energy for thiophene HDS decreased gradually with an increase of temperature. Furthermore, similar results were also obtained by Van Parijs and Froment [1986] for the same reaction over a cobalt molybdate catalyst. They indicated that thiophene conversion increased in the range of 15-88% with increasing temperature from 260°C to 350°C at a pressure of 75 psig.

Our results for NiMo catalyst are similar to Mohammed et al. [1985] who studied sulfur removal of crude oil on nickel molybdate at a pressure of 885 psig and reaction temperatures varied from 320°C to 420°C . The

results revealed that desulfurization activity increased with increasing temperature. The sulfur removal varied from 23% to 67% at temperatures ranging from 320°C to 420°C at a LHSV of 2.0 h⁻¹.

The effects of different kinds of active metals on thiophene HDS are compared in Figure 4.5 at various temperatures. It shows that CoMo/Al₂O₃ catalyst is more effective than NiMo/Al₂O₃ catalyst for promoting the HDS reaction at all temperatures. The increase in HDS activity on NiMo/Al₂O₃ catalyst with increasing temperature is more significant in comparison with CoMo/Al₂O₃ catalyst. It is noted that thiophene conversion on NiMo/Al₂O₃ catalyst (95.62%) is close to thiophene conversion on CoMo/Al₂O₃ catalyst (97.91%) at higher temperature (260°C). While NiMo/Al₂O₃ catalyst is slightly less active than CoMo/Al₂O₃ catalyst at temperature of 260°C, CoMo/Al₂O₃ catalyst is significantly more active than NiMo/Al₂O₃ catalyst at temperature less than 250°C. Such results indicate that NiMo/Al₂O₃ catalyst is more sensitive to temperature than CoMo/Al₂O₃ catalyst. It can be concluded from the above results that both CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are effective for HDS activity at high temperature, whereas CoMo/Al₂O₃ catalyst is more effectively desulfurized than NiMo/Al₂O₃ catalyst at low temperature.

These results are similar to the result obtained by Cerreny [1986] who studied HDS of 2-methylthiophene over CoMoS/Al₂O₃, NiMoS/Al₂O₃, and NiWS/Al₂O₃ catalysts at

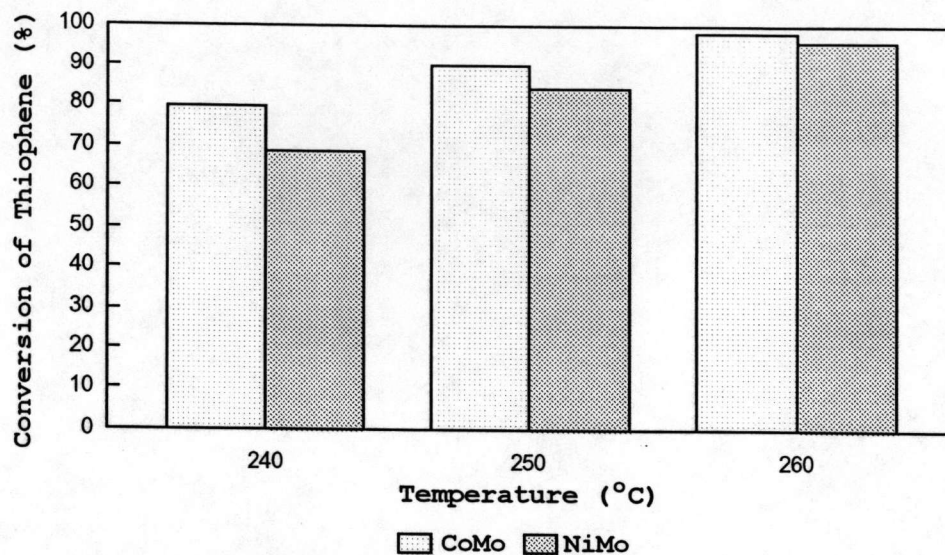


Figure 4.5 Comparison of Catalyst Activity on Thiophene Conversion of Reference Experiments at Various Temperatures.

a total pressure of 100 bar (1470 psig) and a temperature of 250°C. He presented that CoMoS/Al₂O₃ catalyst gave more than twice the conversion (51%) than the others (22% and 20% for NiMoS/Al₂O₃ catalyst and NiWS/Al₂O₃ catalyst, respectively). Obviously CoMoS/Al₂O₃ catalyst was the most active HDS catalyst. The result was also confirmed by Vit[1993] for thiophene HDS over Mo/Al₂O₃, CoMo/Al₂O₃, and NiMo/Al₂O₃ catalysts. He concluded that the presence of promoter (Co, Ni) on Mo catalysts accelerated the HDS of thiophene reaction at a temperature of 320°C and a hydrogen pressure of 290 psig. Thiophene activity of CoMo/Al₂O₃ catalyst [3.00 mol h⁻¹mol(Mo)⁻¹] possessed slightly higher than NiMo/Al₂O₃ catalyst [2.75 mol h⁻¹mol(Mo)⁻¹].

On the contrary, the results from many researchers are not in agreement with our results. Lindner et al. [1989] demonstrated that NiMo catalyst (60% thiophene conversion) was more active for HDS of thiophene than CoMo catalyst (50% thiophene conversion) at a temperature of 300°C and at atmospheric pressure. In addition, Ihm et al. [1990] reported the effects of three commercial catalytic systems, CoMo/Al₂O₃, NiMo/Al₂O₃, and NiW/Al₂O₃, that reaction rate of HDS of thiophene decreased in the order NiMo > CoMo > NiW at atmospheric pressure and temperatures between 275-325°C. It was also found that the reaction rate increased with increasing temperature. CoMo system and NiMo system showed similar rate constant at higher temperature (325°C). Furthermore, Mann et al. [1987] reported the results obtained in the hydrotreatment of heavy oil over alumina-supported Co-Mo, Ni-Mo, and Ni-W catalysts at temperatures between 300-450°C, a pressure of 1000 psig, and a LHSV of 2. HDS activities increased with increasing temperature for all three catalysts, the values of HDS activity were 20.1-82%, 35-82%, and 19-83% for Co-Mo, Ni-Mo, and Ni-W catalysts, respectively. Ni-Mo catalyst gave higher HDS activity than Co-Mo catalyst at temperatures less than 350°C, while Co-Mo catalyst gave slightly higher HDS activity than Ni-Mo catalyst at temperatures greater than 350°C.

Effects of Temperature on Deactivation Experiments

Deactivation experiments (experiments 9-14) are designed to verify the effects of operating temperature on thiophene conversion in the presence of quinoline on two different catalysts by comparison of the results with results of reference experiments conducted at the same operating conditions. The experiments are conducted at various temperatures in order to compare the conversion of thiophene on two commercial catalysts, CoMo/Al₂O₃ and NiMo/Al₂O₃. Temperatures are 240, 250, and 260°C and pressure is kept at 400 psig.

Total time of each experiment is 144 hours. During the first 48 hours of the experiments, feed solution is a mixture of liquid carrier (toluene and hexane) and 3 wt% of sulfur as thiophene. Steady state reaction is established within 48 hours. Quinoline is doctored into the feedstock twice in each experiment at the concentration of 0.5 wt% nitrogen as quinoline. The first quinoline doctoring period is between the hours of 48 to 72 and the second quinoline doctoring period is between the hours of 96 to 120.

Conversions of thiophene at any time on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts at different temperatures are shown in Table 4.7. Steady state thiophene conversion during the first 48 hours of the experiment is observed on both CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts. It is observed that operating temperature strongly influences

Table 4.7 Conversion of Thiophene with Time of Deactivation Experiments on CoMo and NiMo Catalysts at Various Temperatures

Time (hr.)	Conversion of Thiophene (%)					
	CoMo			NiMo		
	240°C (Exp.9)	250°C (Exp.10)	260°C (Exp.11)	240°C (Exp.12)	250°C (Exp.13)	260°C (Exp.14)
12	74.02	88.70	96.77	69.53	82.25	94.10
24	76.68	91.12	97.36	65.34	84.97	92.38
30	81.59	89.20	97.48	66.26	84.12	93.65
36	75.63	88.43	98.02	71.84	85.26	95.79
42	80.64	90.91	99.83	67.53	84.57	95.56
48	80.16	91.79	99.85	72.90	87.86	96.14
54	67.20	69.85	74.68	48.73	54.24	59.70
60	41.79	48.53	57.41	28.56	37.63	46.13
66	38.04	41.58	51.05	26.79	30.30	35.68
72	34.00	39.75	50.27	23.59	29.16	35.17
78	37.54	50.76	60.52	30.18	34.26	41.34
84	39.61	55.01	76.52	34.82	39.44	57.85
90	41.88	57.87	84.18	35.44	43.10	67.45
96	47.21	67.66	88.46	37.39	53.63	74.14
102	44.90	55.60	66.05	33.08	41.92	47.21
108	39.95	45.45	54.46	30.29	33.21	39.84
114	33.37	37.94	50.74	27.26	30.53	36.07
120	29.98	34.92	46.05	22.49	27.44	32.27
126	33.94	40.90	59.98	26.43	34.87	40.59
132	35.50	43.66	72.51	29.75	38.08	51.50
138	38.44	47.01	81.59	30.94	42.18	65.68
144	39.58	51.48	83.61	32.36	45.13	69.19

the HDS of thiophene on both catalysts. As the temperature is raised, the conversion of thiophene increases sharply. CoMo/Al₂O₃ catalyst appears to be more active than NiMo/Al₂O₃ catalyst at low temperature (240-250°C), while at high temperature (260°C) both catalysts achieve comparable thiophene conversion (98.22% for CoMo/Al₂O₃ catalyst and 94.60% for NiMo/Al₂O₃ catalyst). Therefore, it may be stated that NiMo/Al₂O₃ catalyst is sensitive to temperature than CoMo/Al₂O₃ catalyst. In other words, these results reveal that the activity of NiMo/Al₂O₃ catalyst is much more temperature dependent than CoMo/Al₂O₃ catalyst.

After 48 hours in each experiment, feedstock is doctored with quinoline. Our analysis of products on both CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts at all temperatures show that no hydrocarbon product from HDN of quinoline is detected at the reactor outlet, suggesting that quinoline does not react under the reaction conditions used in this study (240-260°C). It is known that denitrogenation reaction is more difficult and must be operated at more severe reaction conditions than those for desulfurization reaction. Rollmann [1977] determined the reactivities of sulfur and nitrogen compounds in terms of a pseudo-first-order rate constant for disappearance relative to that for naphthalene on CoMo/Al₂O₃ catalyst at a temperature of 344°C and a pressure of 48.6 atm (713 psig). The relative pseudo-first-order rate constants were 10 and 1.3 for thiophene

HDS and quinoline HDN. Therefore, under conditions unfavourable to denitrogenation, inhibition of desulfurization by quinoline is performed in this work.

Weight of quinoline in feed and product streams at any time on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts at different temperatures are shown in Table 4.8. Figures 4.6 to 4.8 show the profile of quinoline weight in feed and product streams at any time on CoMo/Al₂O₃ catalyst at temperatures of 240, 250, and 260°C, respectively. At 48 hours after the feedstock is doctored with quinoline, weight of quinoline in product stream increases dramatically in the initial period (48-60 hours) and it is then followed by an inflection at the latter period (60-72 hours), when the increasing in weight of quinoline in product stream is much less steep, approaching the same level as in feed stream. This means that quinoline entering the reactor is adsorbed on catalyst surface and the remaining of quinoline is passed through the reactor. In the meantime, quinoline is also desorbed from catalyst surface until weight of quinoline in product stream approaches to that in feed stream indicating that the quantity of quinoline which is adsorbed on catalyst surface is almost equal to that is desorbed from catalyst surface. In other words, adsorption of quinoline on catalyst surface decreases with time and it approaches constant value (nearly zero value) at the latter period. In the same time, it is also observed that total quantity of quinoline leaving the reactor is less than its

Table 4.8 Weight of Quinoline in Feed and Product Streams with Time of Deactivation
Experiments on CoMo and NiMo Catalysts at Various Temperatures

Time (hr.)	Weight of Quinoline (g)											
	CoMo						NiMo					
	240°C		250°C		260°C		240°C		250°C		260°C	
	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product	Feed	Product
12	-	-	-	-	-	-	-	-	-	-	-	-
24	-	-	-	-	-	-	-	-	-	-	-	-
30	-	-	-	-	-	-	-	-	-	-	-	-
36	-	-	-	-	-	-	-	-	-	-	-	-
42	-	-	-	-	-	-	-	-	-	-	-	-
48	-	-	-	-	-	-	-	-	-	-	-	-
54	2.12	0.99	2.21	1.10	2.20	1.13	2.37	1.15	2.30	1.12	2.26	1.14
60	2.12	1.70	2.18	1.72	2.13	1.67	2.45	2.03	2.50	1.93	2.23	1.63
66	2.08	1.75	2.16	1.90	2.05	1.80	2.18	1.83	2.17	1.90	2.09	1.84
72	2.32	2.05	2.13	1.89	1.92	1.69	1.92	1.59	2.16	1.89	2.14	1.89
78	-	0.51	-	0.52	-	0.53	-	0.51	-	0.53	-	0.54
84	-	0.06	-	0.06	-	0.06	-	0.07	-	0.06	-	0.06
90	-	0.01	-	0.02	-	0.01	-	0.01	-	0.02	-	0.01
96	-	0.01	-	0.01	-	0.00	-	0.01	-	0.01	-	0.00
102	2.04	1.15	2.18	1.27	2.03	1.13	2.22	1.37	2.38	1.53	2.29	1.45
108	2.16	1.73	2.17	1.74	2.17	1.72	2.73	2.19	2.38	1.92	2.08	1.62
114	2.09	1.80	1.89	1.65	1.80	1.55	2.20	1.86	2.15	1.84	1.98	1.69
120	2.04	1.82	2.15	1.92	2.29	2.10	2.13	1.85	2.09	1.82	1.93	1.69
126	-	0.51	-	0.52	-	0.55	-	0.48	-	0.53	-	0.53
132	-	0.06	-	0.06	-	0.05	-	0.07	-	0.05	-	0.06
138	-	0.01	-	0.02	-	0.01	-	0.01	-	0.02	-	0.01
144	-	0.00	-	0.01	-	0.00	-	0.00	-	0.01	-	0.01

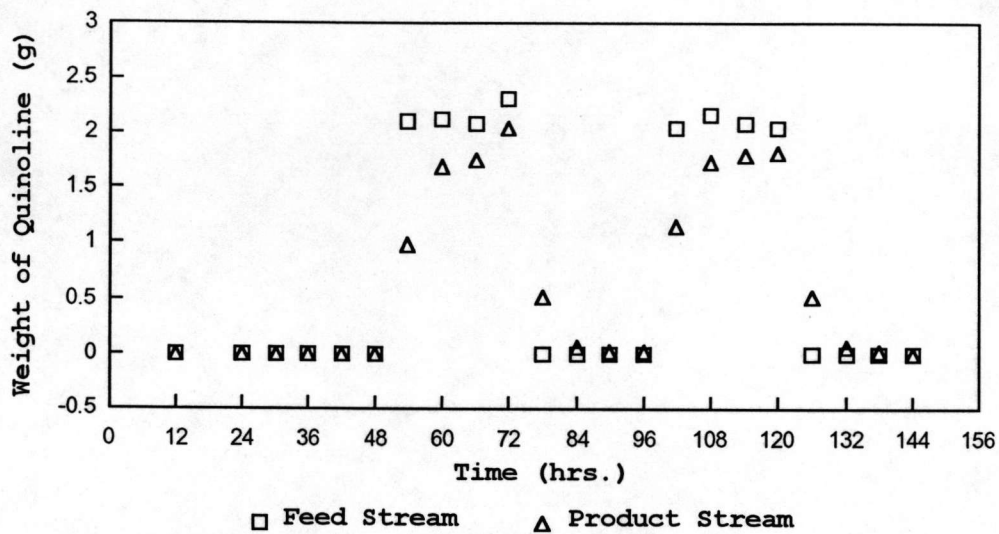


Figure 4.6 Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on CoMo Catalyst at 240°C

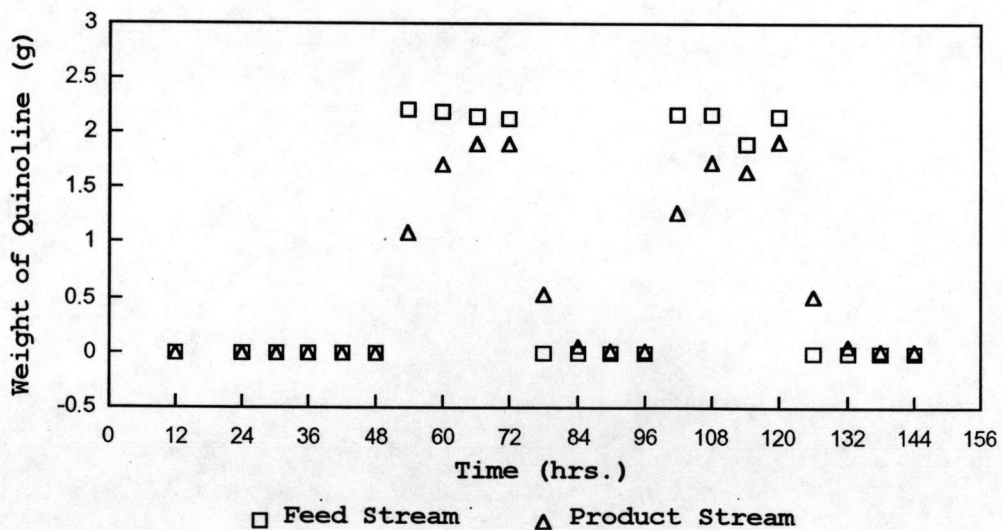


Figure 4.7 Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on CoMo Catalyst at 250°C

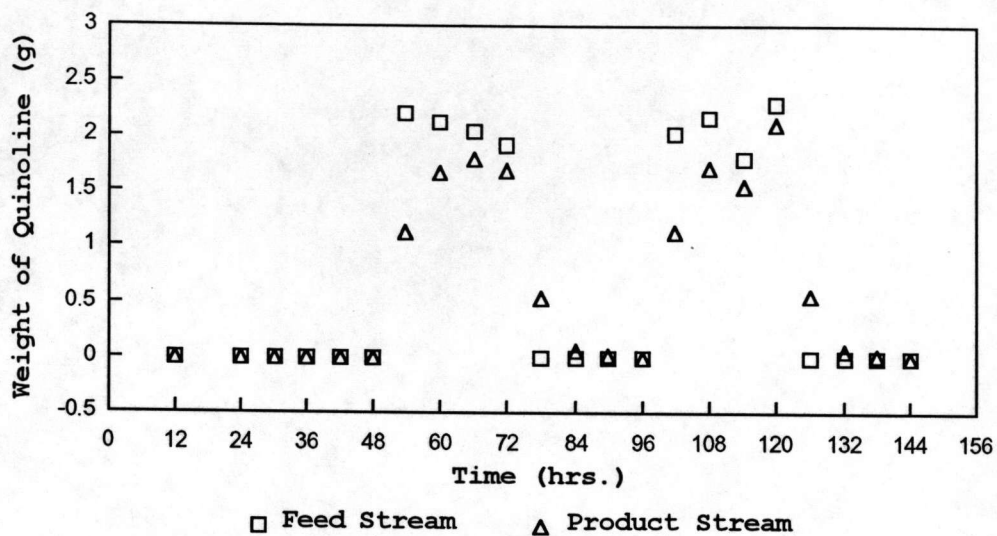


Figure 4.8 Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on CoMo Catalyst at 260°C

entering the reactor suggesting that some quantity of quinoline is adsorbed on catalyst surface. Since quinoline does not react during the experiment, the difference between the quantity of quinoline entering and leaving the reactor represents the quantity of quinoline which is adsorbed on the catalyst surface. It is observed that approximately 2.15 g of quinoline is adsorbed on CoMo/Al₂O₃ catalyst surface (equivalent to 25% of quinoline entering the reactor, as shown in Table 4.9). Quinoline is taken out of the feed stream at the hour of 72. It is observed that weight of quinoline in product stream decreases with time, eventually approaching zero value at 96 hours indicating that quinoline is desorbed from catalyst surface over this

Table 4.9 Quantity of Quinoline Adsorbed and Desorbed on CoMo and NiMo Catalysts of Deactivation Experiments at Various Temperatures

Time (hr.)	Weight of Quinoline Adsorbed and Desorbed on Catalyst Surface (g)					
	CoMo			NiMo		
	240°C	250°C	260°C	240°C	250°C	260°C
48-72 Adsorption	2.15 (24.94%)	2.08 (23.91%)	2.00 (24.16%)	2.34 (26.15%)	2.29 (25.14%)	2.23 (25.53%)
72-96 Desorption	0.60 (6.91%)	0.61 (7.07%)	0.60 (7.20%)	0.60 (6.69%)	0.62 (6.76%)	0.61 (7.02%)
48-96 Net Adsorption	1.56 (18.03%)	1.46 (16.83%)	1.41 (16.97%)	1.74 (19.46%)	1.68 (18.38%)	1.61 (18.51%)
96-120 Adsorption	1.84 (22.12%)	1.80 (21.48%)	1.79 (21.59%)	1.99 (21.51%)	1.88 (20.91%)	1.84 (22.20%)
120-144 Desorption	0.59 (7.11%)	0.61 (7.24%)	0.61 (7.42%)	0.57 (6.14%)	0.61 (6.80%)	0.61 (7.40%)
96-144 Net Adsorption	1.25 (15.00%)	1.19 (14.24%)	1.17 (14.18%)	1.43 (15.38%)	1.27 (14.11%)	1.23 (14.80%)

Numbers in parentheses are percentage of quinoline entering the reactor which is adsorbed or desorbed on catalyst surface.

period. It is found that approximately 0.60 g of quinoline is desorbed from CoMo/Al₂O₃ catalyst surface (equivalent to 7% of quinoline entering the reactor, as shown in Table 4.9). The net quantity of quinoline which is adsorbed on CoMo/Al₂O₃ catalyst surface during the first quinoline doctoring period is approximately 1.56 g (equivalent to 18% of quinoline entering the reactor, as shown in Table 4.9). Similar study with NiMo/Al₂O₃ catalyst at the same operating conditions shows virtually

identical quinoline weight profile in product stream at any time to those obtained with CoMo/Al₂O₃ catalyst (as shown in Figures 4.9 to 4.11). It is observed that the net quantity of quinoline which is adsorbed on NiMo/Al₂O₃ catalyst surface during the first quinoline doctoring period is approximately 1.74 g (equivalent to 19% of quinoline entering the reactor, as shown in Table 4.9) corresponding to 2.34 g of quinoline which is adsorbed on catalyst surface (equivalent to 26% of quinoline entering the reactor) and 0.60 g of quinoline which is desorbed from catalyst surface (equivalent to 7% of quinoline entering the reactor, as shown in Table 4.9). This is slightly larger quantity of quinoline which is adsorbed on NiMo/Al₂O₃ catalyst compared to CoMo/Al₂O₃ catalyst. The observation during the second quinoline doctoring period is also the same behavior as the first quinoline doctoring period. It is also observed that quantities of quinoline which are adsorbed (22% of quinoline entering the reactor) and desorbed (7% of quinoline entering the reactor) on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are comparable as those shown in Table 4.9. In addition, the net quantity of quinoline which is adsorbed on both CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts surface during the second quinoline doctoring period is approximately 15% of quinoline entering the reactor. The observation on Table 4.9 indicates that quantities of quinoline which are adsorbed and desorbed on both catalysts surface during the first and second quinoline doctoring periods are

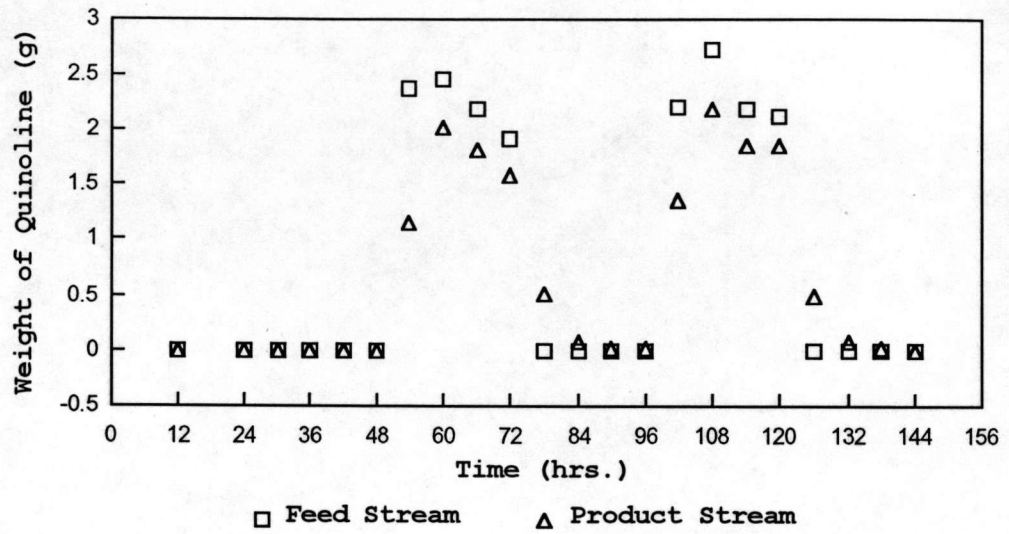


Figure 4.9 Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on NiMo Catalyst at 240°C

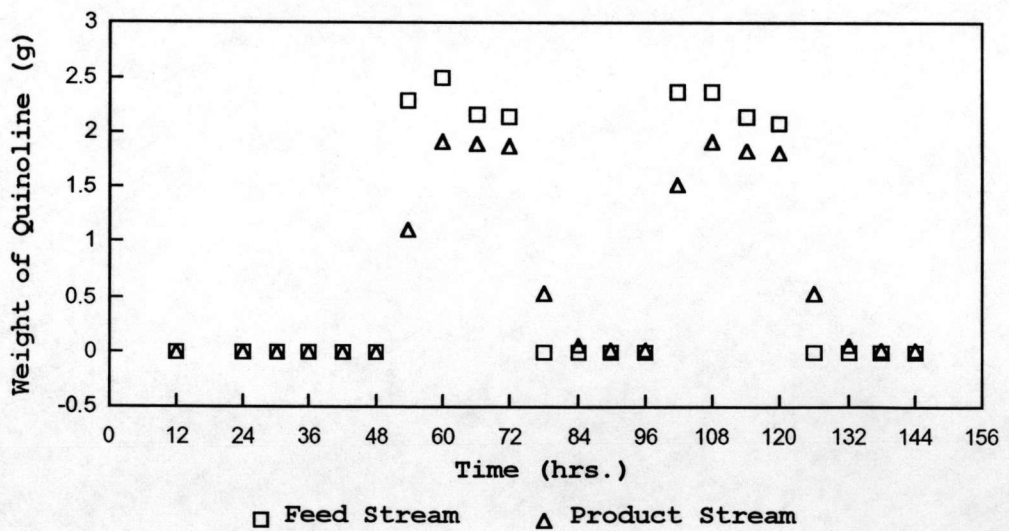


Figure 4.10 Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on NiMo Catalyst at 250°C

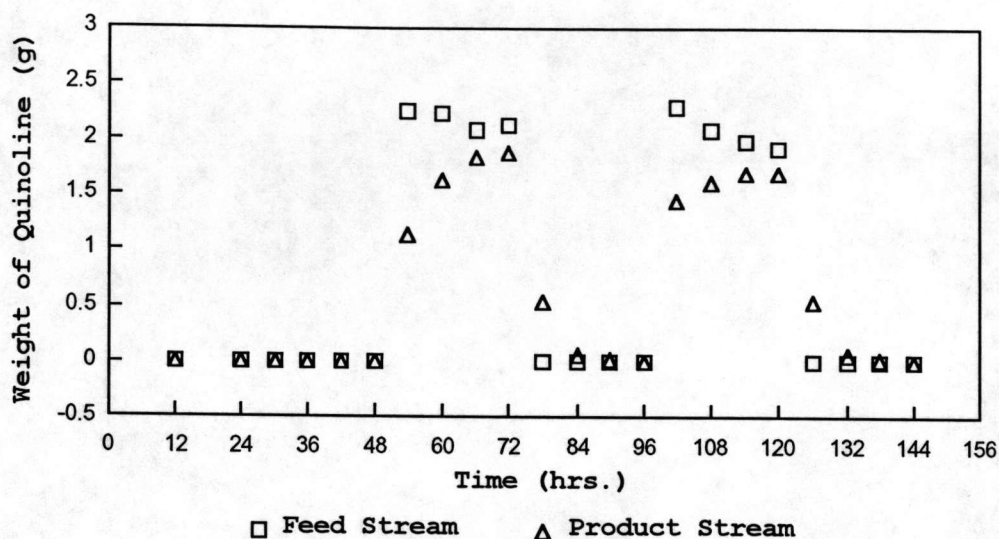


Figure 4.11. Weight of Quinoline in Feed and Product Streams of Deactivation Experiment on NiMo Catalyst at 260°C

independent of temperature. In addition, the net quantity of quinoline which is adsorbed on both catalysts surface during the first quinoline doctoring period is more than that of the second quinoline doctoring period at all temperatures. In the first quinoline doctoring period, catalyst surface has no quinoline, so quinoline entering the reactor is adsorbed on catalyst surface quickly. While during the second quinoline doctoring period, there is still some quantity of quinoline which is adsorbed on catalyst surface before the second doctoring of quinoline, so quinoline is less adsorbed on catalyst surface in comparison with the first period.

Figures 4.12 to 4.14 show thiophene conversion of reference and deactivation experiments and weight of

quinoline in product stream at any time on CoMo/Al₂O₃ catalyst at temperatures of 240, 250, and 260°C, respectively. It is clearly shown that, after the first quinoline doctoring starts, thiophene conversion decreases from 80% to 34% indicating that addition of quinoline even at low concentration remarkably affects HDS of thiophene. In other words, the presence of quinoline in feedstock causes major inhibition of thiophene HDS on CoMo/Al₂O₃ catalyst. Similar results were obtained by Kirsch et al. [1959] who studied the effect of nitrogen compounds on HDS of thiophene on CoMo catalyst at a temperature of 370°C and a pressure of 300 psig. Addition of nitrogen compounds in feedstock reduced sulfur removal from 79% to 59%. Similar study is conducted by Chantalakka [1993]. She concluded that the addition of quinoline in feedstock reduced thiophene conversion from 55% to 17% on CoMo/Al₂O₃ catalyst at a temperature of 210°C and a pressure of 400 psig. Satterfield et al. [1975] observed that the presence of pyridine in the feedstock severely inhibited HDS of thiophene on CoMo catalyst at temperatures between 280-320°C and a pressure of 50 psig. They postulated the pattern of this inhibition, suggesting there are two types of HDS sites involved (Type I and Type II). Type I sites are postulated to be very active and to be responsible for the majority of HDS activity but to be extremely sensitive to basic nitrogen compounds. Sufficient quantities of basic nitrogen compounds will

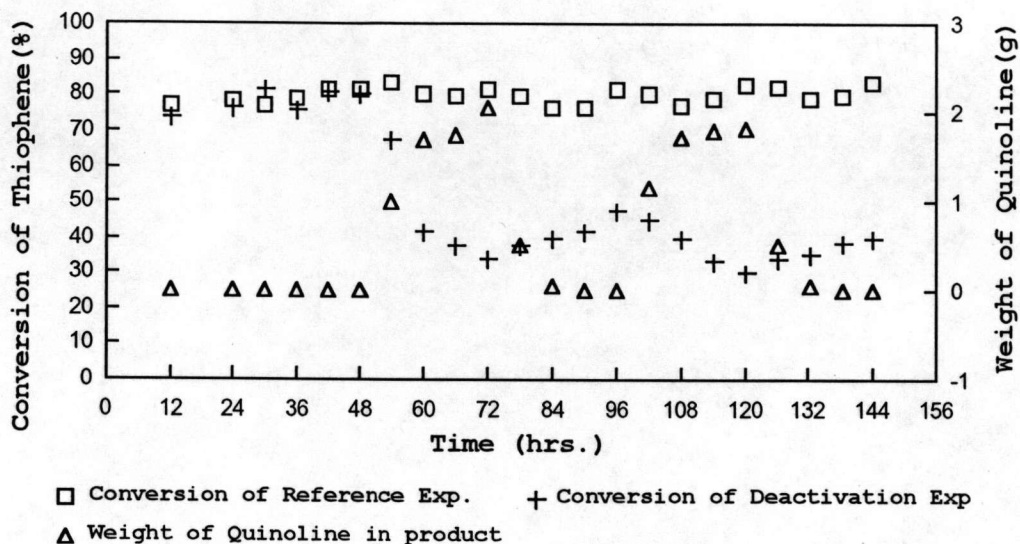


Figure 4.12 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on CoMo Catalyst at 240°C

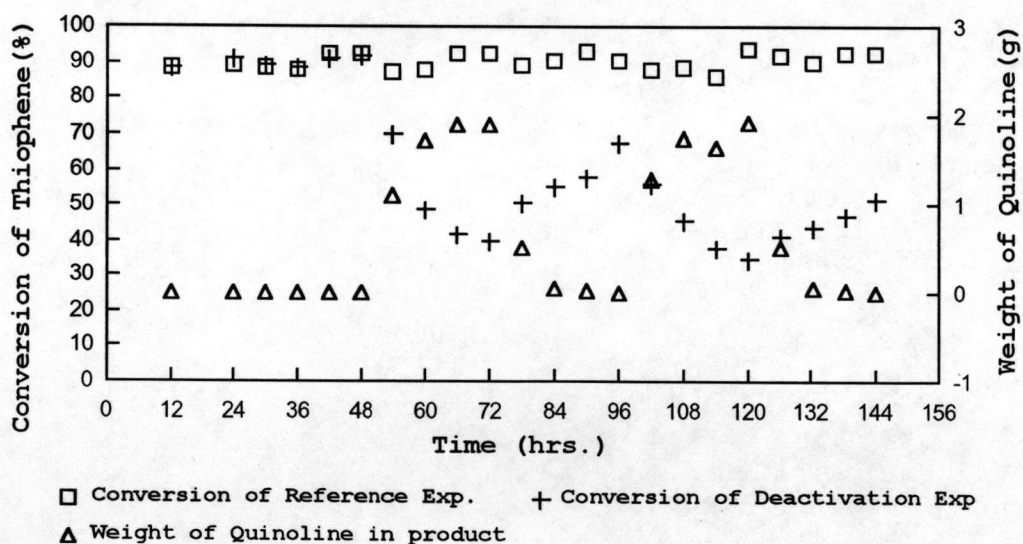


Figure 4.13 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on CoMo Catalyst at 250°C

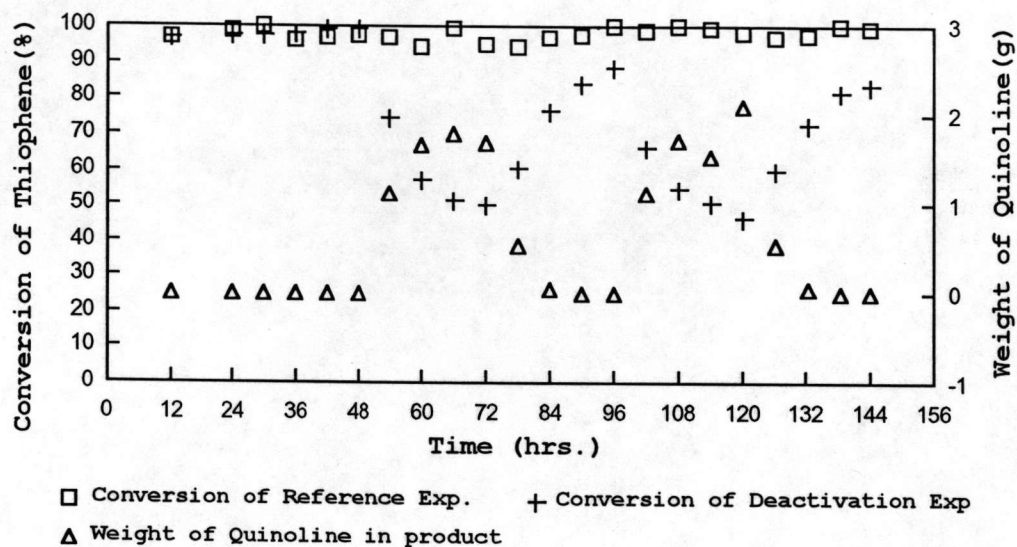


Figure 4.14 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on CoMo Catalyst at 260°C

completely block these sites and render them inactive for HDS. Type II sites are postulated to have less HDS activity but to be less susceptible to poisoning by basic nitrogen compounds, and therefore are responsible for HDS activity of the catalyst after all Type I sites are blocked. Thiophene and pyridine probably compete for Type II sites, but the competition is less than Type I sites.

During the first quinoline doctoring period, it is observed that in an initial period (48-60 hours), thiophene conversion decreases dramatically with increasing weight of quinoline in product stream and it is then followed by an inflection, when the decreasing of thiophene conversion is much less steep in the latter

period (60-72 hours), corresponding to a slight increase in weight of quinoline in product stream. A decrease in thiophene conversion probably due to competitive the adsorption of quinoline on active sites of catalyst since no reaction of quinoline at any of this experiment. In the same time, it is observed that thiophene conversion does not drop to zero value because quinoline does not adsorb on all active sites of catalyst. This inhibition may be explained by the postulation of two kinds of active sites [Satterfield et al., 1975]. Quinoline is preferable adsorbed on Type I sites which very active for HDS activity and sensitive to basic nitrogen compounds, so it is observed that thiophene conversion decreases dramatically with increasing quantity of quinoline which is adsorbed on catalyst surface until Type I sites are blocked by sufficient quantities of quinoline. Then, it is observed that thiophene conversion approaches constant value in the latter period which means that quinoline may be adsorbed on Type II sites which less susceptible to quinoline poisoning. These latter sites are responsible for HDS activity after the first sites have been blocked but less active for HDS, so it is observed that thiophene conversion does not drop to zero value.

At 72 hours after quinoline is taken out of feedstock, it is observed that thiophene conversion increases gently with time to 47% thiophene conversion at hour of 96, corresponding to a decrease in weight of quinoline in product stream. This increase of thiophene

conversion may be attributed to a decrease coverage of quinoline on active sites of catalyst. It is observed that only 7% of quinoline entering the reactor is desorbed from catalyst surface, although 25% of quinoline entering the reactor is adsorbed on catalyst surface, indicating there is still 18% of quinoline entering the reactor is permanent adsorbed on catalyst surface. Therefore, it is observed that thiophene conversion could not recover its initial conversion. These results agreed with the study of Massoth and Miciukiewicz [1986] who investigated the effect of pyridine poisoning on thiophene hydrogenolysis on $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst at temperature of 350°C and at atmospheric pressure. The effect of a poison on catalytic activity was generally site specific and might be either reversible or irreversible. He stated that the deactivation kinetics could be correlated with a quasiirreversible pyridine adsorption model, the rates of adsorption and desorption of pyridine were relatively slow compared to reaction rates. Thus, its effect on catalytic activity was reflected in a quasipermanent poisoning of active sites, lowering the reaction rate constant, rather than in a reversible competitive adsorption for active sites. Similar results were observed by Cowley and Massoth [1978] who found that pyridine inhibited benzothiophene HDS over a sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ catalyst at temperature of 345°C . Neither the weight nor catalyst activity returned to its original value when pyridine was removed from the

reaction stream, indicating a permanent poisoning of some sites.

As with the first quinoline doctoring period, the second quinoline doctoring at hour of 96 decreases thiophene conversion from 47% to 30%. This may be described by the competitive adsorption of quinoline on active sites of catalyst. Since in the first quinoline doctoring period, catalyst is not saturated with quinoline. Thus in the second quinoline doctoring period, it is observed that quinoline is additional adsorbed on catalyst surface, corresponding to an additional slightly decrease in thiophene conversion. It is suspected that in the second quinoline doctoring period, quinoline is probably adsorbed on Type II sites rather than on Type I sites.

Finally, quinoline is taken out of feedstock at hour of 120. As is observed over the time of 72-96 hours, thiophene conversion increases slightly to 40% thiophene conversion probably due to a decrease coverage of quinoline on active sites of catalyst. In addition, it is observed that thiophene conversion over this period is slightly less than thiophene conversion over the period of 72-96 hours probably due to a larger quantity of quinoline which is adsorbed on catalyst surface. It is also observed that only 7% of quinoline entering the reactor is desorbed from catalyst surface over this period, although 22% of quinoline entering the reactor is adsorbed on catalyst surface during the second quinoline

doctoring period, indicating there is still 15% of quinoline entering the reactor is permanent adsorbed on catalyst surface. Hence, thiophene conversion could not recover thiophene conversion as the same level at hour of 96.

From Figures 4.13 and 4.14, each curve has a similar characteristic shape to those curve in Figure 4.12 and these results are corresponded to that results obtained in Figure 4.12.

Figures 4.15 to 4.17 show thiophene conversion of reference and deactivation experiments and weight of quinoline in product stream at any time on NiMo/Al₂O₃ catalyst at temperatures of 240, 250, and 260°C, respectively. The similar activity behavior on CoMo/Al₂O₃ catalyst is also observed on NiMo/Al₂O₃ catalyst. Furthermore, the discussion previously for CoMo/Al₂O₃ catalyst applies equally well to NiMo/Al₂O₃ catalyst. After the first quinoline doctoring starts, thiophene conversion decreases from 72% to 24%, indicating quinoline also has a strong inhibiting effect on NiMo/Al₂O₃ catalyst. This inhibition is expected to be the result of competitive adsorption on active sites of catalyst. After quinoline is taken out of feed stream at hour of 72, thiophene conversion increases gently with time, corresponding to a decrease in weight of quinoline in product stream. It is observed that there is still 19% of quinoline entering the reactor is permanent adsorbed on catalyst surface, so it is obvious that

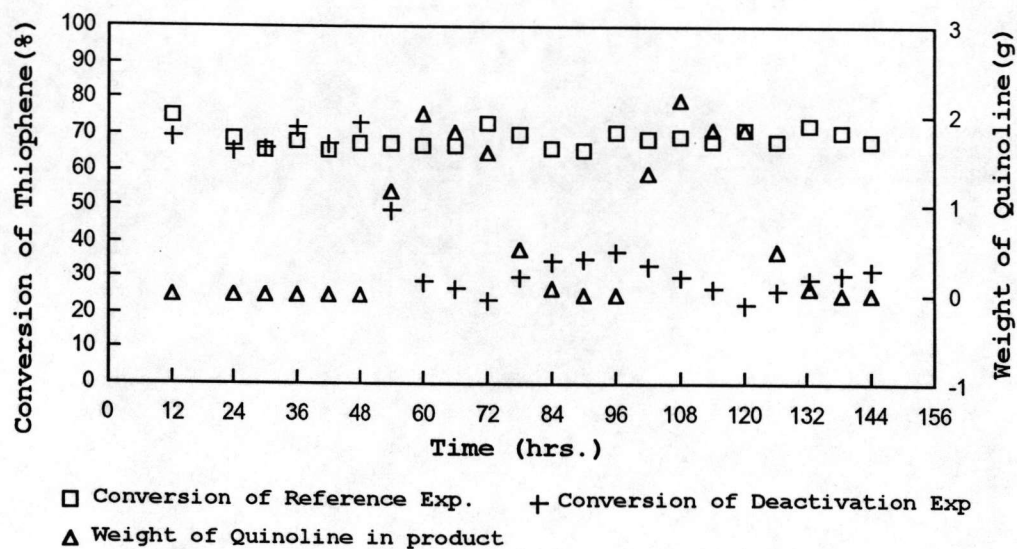


Figure 4.15 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on NiMo Catalyst at 240°C

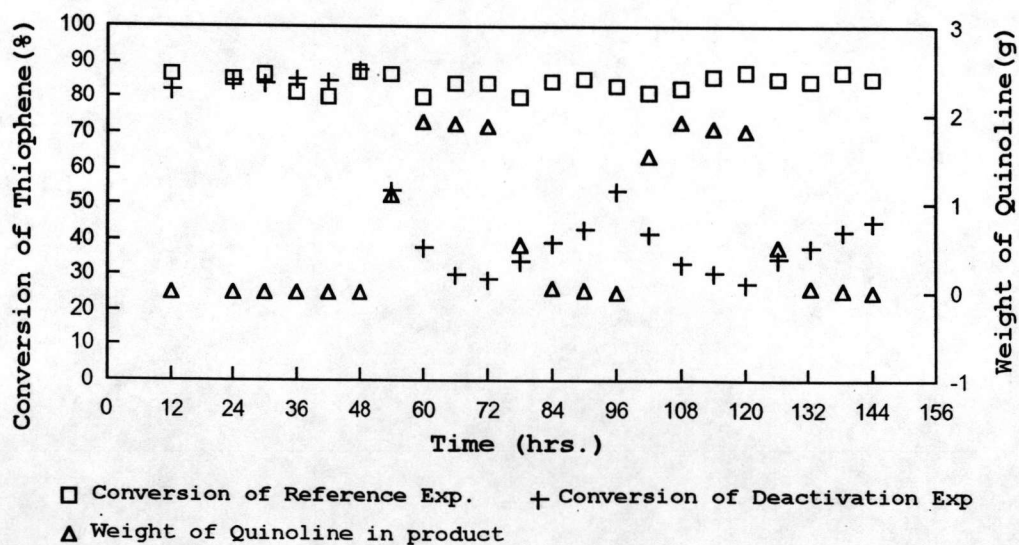


Figure 4.16 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on NiMo Catalyst at 250°C

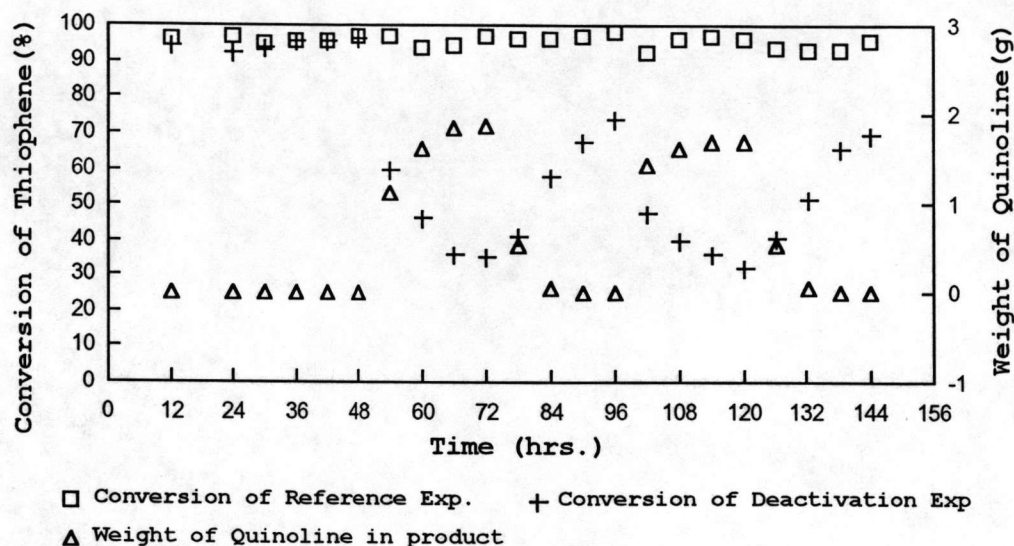


Figure 4.17 Thiophene Conversion of Reference and Deactivation Experiments and Weight of Quinoline in Product on NiMo Catalyst at 260°C

catalyst has not recover its initial activity. After the second quinoline doctoring at hour of 96, thiophene conversion decreases to a value which slightly lower than the first quinoline doctoring period, it may be described by the additional of quantity of quinoline which is adsorbed on catalyst surface. Finally, after quinoline is taken out of feedstock at hour of 120, thiophene conversion increases slightly to a value which slightly lower than the removal of quinoline over the time of 72-96 hours, it may be explained by a larger quantity of quinoline which is adsorbed on catalyst surface. Similar results were obtained by LaVopa and Satterfield [1988] who studied on a NiMo/Al₂O₃ catalyst at a pressure of 1000 psig and temperature ranges from 300 to 400°C. He

reported that quinoline strongly inhibited the HDS of thiophene through competitive adsorption.

From Figures 4.16 and 4.17, each curve has a similar characteristic shape to those curve in Figure 4.12 and these results are corresponded to that results obtained in Figure 4.15.

The effects of temperature on thiophene conversion in the presence of quinoline at any time are compared in Figure 4.18 on CoMo/Al₂O₃ catalyst. During the first quinoline doctoring period, thiophene conversion decreases dramatically at all temperatures probably due to the competitive adsorption of quinoline on active sites of catalyst. From Table 4.10 which presents the rate of catalyst deactivation and rate of catalytic activity recovery of deactivation experiments (calculation from the slope of curve with corresponding of the change conversion of thiophene with time), it can be observed that the rate of catalyst deactivation does not appreciably change by increasing reaction temperature from 240°C to 260°C, corresponding to approximately 24% of quinoline entering the reactor is adsorbed on catalyst surface. Therefore, a decrease in thiophene conversion may be considered as a surface coverage by quinoline. This means that rate of catalyst deactivation is independent of temperature corresponding to the quantity of quinoline on catalyst surface which constant as temperature is raised. It is suspected that quinoline is permanent adsorbed on Type I sites which may be represent

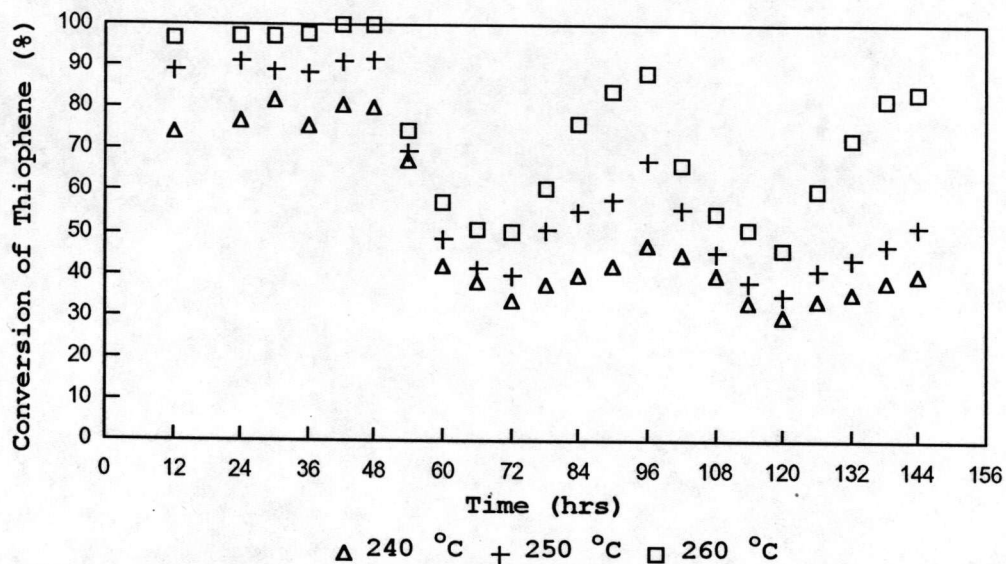


Figure 4.18 Conversion of Thiophene in Study the Effects of Temperature of Deactivation Experiments on CoMo Catalyst.

Table 4.10 Rate of Catalyst Deactivation and Rate of Catalytic Activity Recovery of Deactivation Experiments on CoMo and NiMo Catalysts at Various Temperatures

Time (hr.)	Rate of Catalyst Deactivation and Rate of Catalytic Activity Recovery (thiophene conversion \cdot h ⁻¹)					
	CoMo			NiMo		
	240°C	250°C	260°C	240°C	250°C	260°C
48-72 Deactivation	3.198	3.605	3.537	3.695	4.186	4.168
72-96 Recovery	0.513	1.049	1.667	0.548	0.963	1.734
96-120 Deactivation	0.605	1.85	2.818	0.592	1.702	2.858
120-144 Recovery	0.395	0.654	1.612	0.404	0.712	1.649

irreversible poisoning. In addition, the quantity of quinoline which is adsorbed on these sites is independent of temperature.

After quinoline is taken out of feed stream at hour of 72, thiophene conversion increases steadily with time at all temperatures. As the temperature is raised, the conversion of thiophene increases rapidly (however, the thiophene conversion of the fresh catalyst is not achieved). As can be observed in Table 4.10, the rates of catalytic activity recovery on CoMo/Al₂O₃ catalyst are strongly dependent on temperature. Despite the fact that quantity of quinoline which is desorbed from catalyst surface is comparable (7% of quinoline entering the reactor) at all temperatures, indicating an increase in thiophene conversion due to an increase of temperature. It is suspected that quinoline is desorbed from Type II sites which may be represent the reversible poisoning and these sites are suspected to be the temperature-sensitive sites. Thus thiophene conversion increases with increasing temperature.

During the second quinoline doctoring period, thiophene conversion decreases rapidly at all temperatures. It is found that temperature has a great effect on rate of catalyst deactivation on CoMo/Al₂O₃ catalyst, but the quantity of quinoline which is adsorbed on catalyst surface is comparable at all temperatures. In fact, it could not be concluded that rate of catalyst deactivation during the second quinoline doctoring period

is dependent on the operating temperature since thiophene conversion, before the second quinoline doctoring, does not reach its original value.

Finally, quinoline is taken out of feed stream at hour of 120, thiophene conversion increases at all temperatures. It appears that rate of catalytic activity recovery on CoMo/Al₂O₃ catalyst is strongly dependent on operating temperature. As temperature is raised, the rate of catalytic activity recovery increases significantly (as shown in Table 4.10), although the quantity of quinoline which is desorbed from catalyst surface is comparable (7% of quinoline entering the reactor) with increasing temperature. This may be explained by the desorption of quinoline from Type II sites of active sites which are suspected to be the temperature-sensitive sites.

Figure 4.19 shows the effects of temperature on thiophene conversion in the presence of quinoline at any time on NiMo/Al₂O₃ catalyst. The effects of temperature on thiophene conversion of NiMo/Al₂O₃ catalyst are similar behavior as is observed on CoMo/Al₂O₃ catalyst. It is observed that the rate of catalyst deactivation is independent of temperature, corresponding to 26% of quinoline entering the reactor which is adsorbed on catalyst surface, while the rate of catalytic activity recovery is strongly dependent on temperature. This observation shows that the coverage of catalyst surface by quinoline or the strength of quinoline is independent

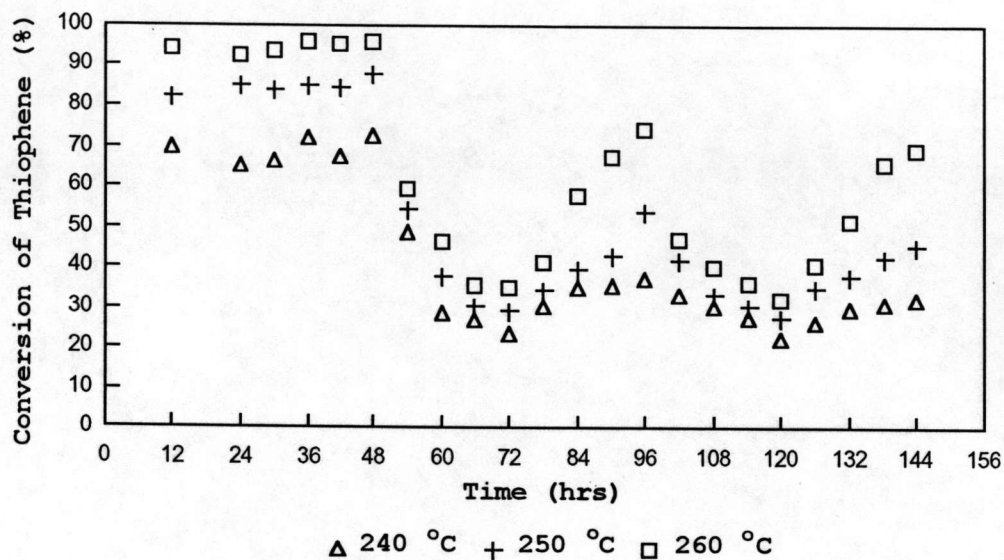


Figure 4.19 Conversion of Thiophene in Study the Effects of Temperature of Deactivation Experiments on NiMo Catalyst.

of temperature. These results are not in agreement with the results of LaVopa and Satterfield [1988]. He found that the fraction of surface of NiMo/Al₂O₃ catalyst blocked by nitrogen compounds decreases with increasing temperature since the strength of nitrogen compounds adsorption on the catalyst decreases with increasing temperature.

From Figures 4.18 and 4.19, each curve of both catalysts has a similar characteristic shape which is described in detail in previous section. In addition, the activity behavior on NiMo/Al₂O₃ catalyst is similar to CoMo/Al₂O₃ catalyst. The first and second quinoline doctoring cause a dramatic decrease in thiophene

conversion on both catalysts at all temperatures probably due to the competitive adsorption of quinoline on catalyst surface. From Table 4.10 it can be observed that the rate of catalyst deactivation on both catalysts are independent of temperature and are comparable to each other at three temperatures, corresponding to a comparable quantity of quinoline which is adsorbed on catalyst surface. These results indicate that nickel is close to cobalt in terms of efficiency when addition of quinoline, since the rate of deactivation of NiMo/Al₂O₃ catalyst is only slightly higher than CoMo/Al₂O₃ catalyst, corresponding to a slight larger quantity of quinoline which is adsorbed on catalyst surface. So the inhibition effects of quinoline HDS on CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts are almost identical.

After quinoline is taken out of feed stream at the hours of 72 and 120, thiophene conversion increases steadily with time for both catalysts at all temperatures. As can be observed in Table 4.10, the rates of catalytic activity recovery of both catalysts are strongly dependent on temperature and are comparable to each other at each temperature. Although the quantity of quinoline which is desorbed from catalyst surface is comparable with increasing temperature, it is suspected that these active sites (Type II sites) may be the temperature-sensitive sites. Therefore, it is observed that rate of catalytic activity recovery increases with increasing temperature.