INTERACTIVE CHEMISTRY
OF

DOE/PC/80502--T16

DE90 006317

COAL-PETROLEUM PROCESSING

Quarterly Report

for

September 16, 1989 to December 15, 1989

under

Grant No. DEFG-2285PC80502

Christine W. Curtis
James A. Guin
A. Ray Tarrer

Chemical Engineering Department
Auburn University
Auburn, Alabama 36849-5127

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 *do*

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Acknowledgement

The contributions of the following individuals to this research project are gratefully acknowledged.

Choowong Sirivejakul
Honggon Kim
Yan Zhou
Franklin Bowers
Joseph Aderholdt

TABLE OF CONTENTS

	Page
List of Tables	iii
List of Figures	iv
Objective	1
Major Tasks	1
Research Performed This Quarter	1
Experimental	2
Results and Discussion	4
Catalytic Hydrodeoxygenation of Dibenzofuran	4
Effect of Vanadium Sulfide in Combined Catalyst Systems on Dibenzofuran Hydrodeoxygenation	4
Catalytic Hydrodesulfurization of Dibenzothiophene	9
Effect of Vanadium Sulfide in Combined Catalyst Systems on Dibenzothiophene Hydrodesulfurization	9
Catalytic Hydrogenation of Fluorene	14
Effect of Vanadium Sulfide in Combined Catalyst Systems on Fluorene Hydrogenation	14
Catalytic Hydrodenitrogenation of Carbazole	18
Effect of Vanadium Sulfide in Combined Catalyst Systems on Carbazole Hydrodenitrogenation	18
Summary	22

LIST OF TABLES

Table 1	Catalytic Reactions of Dibenzofuran at Different Metal Contents	5
Table 2	Catalytic Reactions of Dibenzothiophene at Different Metal Contents	7
Table 3	Catalytic Reactions of Fluorene at Different Metal Contents	15
Table 4	Catalytic Reactions of Carbazole at Different Metal Contents	19

LIST OF FIGURES

Figure 1	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodeoxygenation of Dibenzofuran	8
Figure 2	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenolysis of Dibenzofuran	9
Figure 3	Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Dibenzofuran	10
Figure 4	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodesulfurization of Dibenzothiophene	11
Figure 5	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenolysis of Dibenzothiophene	12
Figure 6	Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Dibenzothiophene	13
Figure 7	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenation of Fluorene	17
Figure 8	Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Fluorene	18
Figure 9	Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodenitrogenation of Carbazole	21
Figure 10	Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Carbazole	22

INTERACTIVE CHEMISTRY OF COAL-PETROLEUM PROCESSING

OBJECTIVE

To investigate the interactive thermal and catalytic chemistry of coal and petroleum processing using model compounds and actual petroleum-coal materials.

MAJOR TASKS

1. Evaluate the thermal chemistry in three different model coal-petroleum systems composed of (a) hydrocarbons, (b) hydrocarbons and compounds containing heteroatoms and (c) hydrocarbons, heteroatomic species and metalloporphyrins.
2. Evaluate the catalytic chemistry of coal-petroleum processing using three different model systems - hydrocarbons, heteroatomic species and metalloporphyrins with selected transition metal sulfide catalysts.
3. Evaluate the thermal and catalytic chemistry of actual coal-petroleum systems.

RESEARCH PERFORMED THIS QUARTER

During this quarter the interactive catalytic chemistry of model coal and petroleum systems was investigated using combined catalysts of molybdenum naphthenate and vanadyl acetylacetonate. This combination was performed in order to evaluate the effect of the presence of an indigenous residuum metal, vanadium, on model reactions that occur in coprocessing. In addition, the effect of the vanadium sulfide on the catalysis of in situ sulfided molybdenum naphthenate was investigated. In the reactions performed, the vanadium was present in the form of vanadium sulfide.

Each model compound was catalytically reacted with a combination of molybdenum naphthenate and vanadyl acetylacetonate in the presence of excess sulfur with a total metal loading of ~3000 ppm. Combinations of each metal catalyst precursor were fixed at the relative compositions $V/(V+Mo) = 0.33$ and 0.67 to observe the effect of vanadium on the catalysis and the

activity of the system. The reactions were also performed at 3000 ppm molybdenum and ~3000 ppm vanadium levels.

This report shows the results of the reactions of selected model compounds in the presence of unsupported combined metal catalysts using molybdenum naphthenate and vanadyl acetylacetonate with excess sulfur as hydrogenation catalyst precursors. The catalytic effect on the different model compound slates of the vanadium sulfide generated by vanadyl acetylacetonate is also presented.

EXPERIMENTAL

For the reactions discussed in this report, the following terminology has been defined:

% Hydrogenation: The moles of H₂ consumed for the achieved liquid product distribution as a percentage of that required to produce the most hydrogenated product.

% Hydrogenolysis: Summation of the product mole percents which have undergone cleavage of a C-C bridge.

% Hydrodeoxygenation: Summation of the product mole percents not containing oxygen.

% Hydrodesulfurization: Summation of the product mole percents not containing sulfur.

% Hydrodenitrogenation: Summation of the product mole percents not containing nitrogen.

% Conversion: Summation of the product mole percents containing fully saturated two ring structure connecting with C-C bridge.

Feed Materials. The catalyst used for the hydrogenation of model compounds was vanadyl acetylacetonate from Aldrich Chemicals (V, 18.25 weight percent) which was used as received.

The model compounds supplied by Aldrich were dibenzofuran, 99%; dibenzothiophene, 98%; fluorene, 98%; and carbazole, 99%. Dibenzofuran and Nb27/inter

carbazole were used without further purification. Dibenzothiophene and fluorene were purified by recrystallization before they were used.

Reaction Procedure. The hydrogenation reactions were performed in 20 cm³ horizontal tubing bomb reactors. The charge to the reactor for each model compound reaction was 4 grams of 1 weight percent solution of each model compound in hexadecane. For the catalytic reaction, the metal catalyst precursors were premixed in the reactant solution at 2850 to 3000 ppm unless stated otherwise. The combinations of the metal precursors were fixed at the V/V⁺M₀ ratios of 0.33 and 0.67. Elemental sulfur was added at a level which was three times the stoichiometric amount required to convert elemental V to V₂S₃. In the case of the thermal reaction with sulfur, two-thirds of the amount of elemental sulfur introduced to the catalytic reaction was added. In all the reactions, the initial hydrogen pressure was 1250 psig at ambient temperature. The agitation rate in a horizontal orientation was 550 cpm. Reactions were performed at 380°C for 30 minutes.

Analyses. The product was withdrawn from the reactor and then the black powder produced from in situ catalyst generation was separated by centrifuging the reaction product solution for about 3 hours. For carbazole, THF and p-xylene were both added to help dissolve the carbazole. Sonication was used to promote dissolution.

The reaction products were analyzed by gas chromatography and gas chromatography-mass spectroscopy. The gas chromatograph used was a Varian Model 3700 with FID detection and a 30 m DB-5 column. The column was heated from 50°C to 280°C at the rate of 2°C/min and held at 280°C for 15 minutes. Peak identification was carried out by using standard compounds or by mass spectroscopy.

RESULTS AND DISCUSSION

Catalytic Hydrodeoxygenation of Dibenzofuran

The catalytic activity of combined molybdenum naphthenate and vanadyl acetylacetonate for oxygen removal from dibenzofuran was investigated. The reaction products detected from the hydrodeoxygenation of dibenzofuran in the presence of combined catalysts and excess sulfur were dibenzofuran, 1,2,3,4-tetrahydrodibenzofuran, cyclohexylbenzene, dicyclohexyl, cyclopentylmethylcyclohexane, phenol, cyclohexene, benzene, cyclohexane, and methylcyclopentane. The quantitative results for each reaction product given in Table 1 showed that unconverted dibenzofuran present at about 50 mole percent constituted the major product, and a mixture of benzene and cyclohexane at about 23 mole percent was the secondary product. Under the selected operating conditions and in the presence of mixed-metal catalysts at both V/(V+Mo) ratios, the hydrodeoxygenation of dibenzofuran was incomplete yielding less than 30 mole percent of oxygen removal from dibenzofuran.

Effect of Vanadium Sulfide in Combined Catalyst Systems on Dibenzofuran Hydrodeoxygenation

The effect on the catalysis of replacing molybdenum with vanadium, present as vanadium sulfide, was explored by reacting dibenzofuran in different combinations of molybdenum naphthenate and vanadyl acetylacetonate at V/(V+Mo) = 0.33 and 0.67. On the basis of the quantitative evaluation of the product distribution presented in Table 1, the addition of vanadyl acetylacetonate to the dibenzofuran reaction, with an ultimate metal loading of 2900 to 3100 ppm of vanadium and no molybdenum present, decreased the hydrodeoxygenation relative to molybdenum naphthenate. This inhibiting effect also resulted in both a decrease in the hydrogenolysis and in the conversion of dibenzofuran. In other words, the hydrodeoxygenation, hydrogenolysis and

Table 1
Catalytic Reactions of Dibenzofuran at Different Metal Contents

Metal Content (ppm)	3000 ppm Mo 0 ppm V	2000 ppm Mo* 1000 ppm V	1000 ppm Mo** 2000 ppm V	0 ppm Mo*** 3000 ppm V
(1) Product Distribution, mole%				
Methylcyclopentane	11.9±0.3	10.3±1.7	9.6±0.8	3.7±0.5
Mixture of Benzene & Cyclohexane	38.0±0.7	23.0±1.6	25.0±2.1	16.3±1.2
Cyclohexene	0	3.3±0.2	3.0±0.3	3.9±0.2
Phenol	12.6±0.9	Trace	5.6±1.7	10.3±0.6
Cyclopentylmethylcyclohexane				
isomer 1	Trace	0	Trace	0
isomer 2	Trace	0	Trace	Trace
isomer 3	4.3±0.3	Trace	1.3±0.3	1.3±0.1
isomer 4	1.3±0.2	0	Trace	Trace
Dicyclohexyl	8.2±0.5	2.5±0.3	1.8±0.5	1.2±0.1
Cyclohexylbenzene	4.7±0.3	2.3±0.1	1.7±0.2	0.9±0.1
1,2,3,4-Tetrahydrodibenzofuran	0	0	0.8±0.1	1.2±0.2
Dibenzofuran	19.0±2.2	58.6±3.5	51.2±4.6	61.2±2.3
(2) Hydrodeoxygenation, %	54.1±1.5	28.3±2.9	26.7±2.6	12.5±1.1
(3) Hydrogenolysis, %	45.5±1.9	22.4±2.4	27.5±3.3	20.6±1.7
(4) Conversion, %	72.3±2.8	28.3±2.9	34.9±4.2	26.2±1.8
(5) Recovery, %	75.1±2.7	90.0±5.0	87.1±0.7	94.2±2.0

Reaction Conditions: 380°C, 30 min, 1250 psig H₂, 550 cpm (horizontal shaking), 4 grams solution

Reactants: 1 wt% of Dibenzofuran in Hexadecane, 3000 ppm Mo & 0 ppm V, 0.0240 gram Sulfur
 * 1 wt% of Dibenzofuran in Hexadecane, 2000 ppm Mo & 1000 ppm V, 0.0273 gram Sulfur
 ** 1 wt% of Dibenzofuran in Hexadecane, 1000 ppm Mo & 2000 ppm V, 0.0306 gram Sulfur
 *** 1 wt% of Dibenzofuran in Hexadecane, 0 ppm Mo & 3000 ppm V, 0.0339 gram Sulfur

conversion of dibenzofuran decreased as the amount of vanadium gradually increased, as shown in Figures 1, 2, and 3, respectively.

Catalytic Hydrodesulfurization of Dibenzothiophene

Catalytic reactions of dibenzothiophene performed with combined catalysts of molybdenum naphthenate and vanadyl acetylacetonate yielded the same product as those with the individual catalysts. Dibenzothiophene, 1,2,3,4-tetrahydrodibenzothiophene, biphenyl, cyclohexylbenzene, dicyclohexyl, cyclopentylmethylcyclohexane, benzene, cyclohexane, and methylcyclopentane were detected as the reaction products. When the quantitative results of each reaction product given in Table 2 were examined, cyclohexylbenzene was found to be the primary product yielding about 30 mole percent of the total reaction products. Dibenzothiophene was not completely desulfurized under the reaction conditions; more than 20 mole percent of dibenzothiophene remained unconverted in the liquid product. However, the order of sulfur and oxygen removal with combined catalysts was the same as with individual catalysts, indicating that the rate of hydrodesulfurization was greater than that of hydrodeoxygenation.

Effect of Vanadium Sulfide in Combined Catalyst Systems on Dibenzothiophene Hydrodesulfurization

A graphical representation of the results present in Table 2 on the catalytic effects of added vanadium concentration as vanadyl acetylacetonate in the combined catalyst system with molybdenum naphthenate on dibenzothiophene is given in Figures 4 through 6. As can be seen in Figures 4 through 6, similar results are indicated for hydrodesulfurization, hydrogenolysis, and conversion as vanadyl acetylacetonate is progressively added; when the amount of vanadium is increased, hydrodesulfurization of dibenzothiophene is substantially removed, from 100 percent down to 60

Table 2

Catalytic Reactions of Dibenzothiophene at Different Metal Contents

Metal Content (ppm)	3000 ppm Mo 0 ppm V	2000 ppm Mo* 1000 ppm V	1000 ppm Mo** 2000 ppm V	0 ppm Mo*** 3000 ppm V
(1) Product Distribution, mole%				
Methylcyclopentane	4.2±0.4	3.0±0.1	1.9±0.1	1.0±0.1
Cyclohexane	4.2±0.7	1.9±0.4	1.6±0.2	1.4±0.1
Benzene	8.4±1.0	4.9±0.5	3.5±0.2	2.4±0.2
Cyclopentylmethylcyclohexane				
isomer 1	Trace	Trace	Trace	Trace
isomer 2	2.2±0.7	Trace	2.0±0.3	2.1±0.2
isomer 3	7.3±0.7	2.1±0.6	5.9±0.8	8.0±0.6
isomer 4	1.3±0.5	Trace	1.8±0.4	1.9±0.2
Dicyclohexyl	14.4±1.7	7.2±1.0	8.8±1.3	11.3±0.9
Cyclohexylbenzene	52.1±2.3	31.6±1.4	29.2±1.2	21.4±1.1
Biphenyl	5.9±0.8	20.8±1.4	13.5±0.4	9.0±1.0
1,2,3,4-Tetrahydrodibenzofuran	0	3.0±0.9	7.7±1.0	10.5±0.6
Dibenzothiophene	0	25.5±3.4	24.1±2.5	31.0±2.9
(2) Hydrodesulfurization, %	100.0±0.0	70.1±4.0	67.0±3.2	57.5±3.1
(3) Hydrogenolysis, %	9.2±1.2	5.2±0.5	3.6±0.3	2.4±0.2
(4) Conversion, %	100.0±0.0	73.2±3.5	75.1±2.5	68.2±2.9
(5) Recovery, %	74.3±2.4	87.1±5.4	85.6±6.7	86.7±5.5

Reaction Conditions: 380°C, 30 min, 1250 psig H₂, 550 cpm (horizontal shaking), 4 grams solution

Reactants: 1 wt% of Dibenzofuran in Hexadecane, 3000 ppm Mo & 0 ppm V, 0.0240 gram Sulfur
 * 1 wt% of Dibenzofuran in Hexadecane, 2000 ppm Mo & 1000 ppm V, 0.0273 gram Sulfur
 ** 1 wt% of Dibenzofuran in Hexadecane, 1000 ppm Mo & 2000 ppm V, 0.0306 gram Sulfur
 *** 1 wt% of Dibenzofuran in Hexadecane, 0 ppm Mo & 3000 ppm V, 0.0339 gram Sulfur

Figure 1. Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodeoxygenation of Dibenzofuran

Figure 2. Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenolysis of Dibenzofuran

Figure 3. Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Dibenzofuran

Figure 4. Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodesulfurization of Dibenzothiophene

Figure 5 . Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenolysis of Dibenzothiophene

Figure 6. Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Dibenzothiophene

percent. Hydrogenolysis and conversion of dibenzothiophene were also influenced by the vanadium added and decreased with increased concentration of vanadium, in relation to molybdenum naphthenate.

From these results, it can be concluded that vanadium added as vanadyl acetylacetonate in the presence of sulfur to the dibenzothiophene reaction, when compared to molybdenum naphthenate alone reduced in the amount of reactivity occurring in all three reactions: hydrodesulfurization, hydrogenolysis, and conversion.

Catalytic Hydrogenation of Fluorene

Hydrogenation of fluorene was investigated using the active catalytic species generated in situ from combined molybdenum naphthenate and vanadyl acetylacetonate in the presence of excess sulfur. As observed with the individual catalysts, fluorene, hexahydrofluorene, and dodecahydrofluorene were obtained as the reaction products. The results of catalytic hydrogenation of fluorene summarized in Table 3 indicate that in the presence of the combined catalysts or vanadyl acetylacetonate itself, fluorene was hydrogenated at only 25 percent compared to 30 percent for molybdenum sulfide reactions, yielding hexahydrofluorene at about 50 mole percent and unconverted fluorene at about 50 mole percent of the recovered products.

Effect of Vanadium Sulfide in Combined Catalyst Systems on Fluorene Hydrogenation

The effect of vanadium sulfide, in combination with MoS_2 , on the catalytic hydrogenation of fluorene was examined. As in the other systems, when fluorene was used as the reactant, the replacement of molybdenum by vanadium decreased the hydrogenation of fluorene. However, the hydrogenation of fluorene was not as severely inhibited by the presence of vanadium sulfide

Table 3

Catalytic Reactions of Fluorene at Different Metal Contents

Metal Content (ppm)	3000 ppm Mo 0 ppm V	2000 ppm Mo* 1000 ppm V	1000 ppm Mo** 2000 ppm V	0 ppm Mo*** 3000 ppm V
(1) Product Distribution, mole%				
Dodecahydrofluorene				
isomer 1	Trace	Trace	0	0
isomer 2	Trace	Trace	0	0
isomer 3	1.5±0.3	0.8±0.2	Trace	Trace
Hexahydrofluorene				
isomer 1	2.7±0.5	Trace	Trace	Trace
isomer 2	46.3±2.3	40.7±1.6	46.8±1.3	41.5±1.5
isomer 3	9.7±0.9	8.0±0.5	7.3±1.4	7.9±0.8
Fluorene	39.8±2.7	50.5±2.1	45.9±1.0	50.7±2.3
(2) Hydrogenation, %	30.9±1.5	25.1±1.0	27.1±0.5	24.7±1.1
(3) Hydrogenolysis, %	0	0	0	0
(4) Conversion, %	60.2±2.7	49.5±2.1	54.1±1.0	49.3±2.2
(5) Recovery, %	94.0±2.1	97.6±2.5	92.4±0.1	99.8±2.9

Reaction Conditions: 380°C, 30 min, 1250 psig H₂, 550 cpm (horizontal shaking), 4 grams solution

Reactants: 1 wt% of Dibenzofuran in Hexadecane, 3000 ppm Mo & 0 ppm V, 0.0240 gram Sulfur
 * 1 wt% of Dibenzofuran in Hexadecane, 2000 ppm Mo & 1000 ppm V, 0.0273 gram Sulfur
 ** 1 wt% of Dibenzofuran in Hexadecane, 1000 ppm Mo & 2000 ppm V, 0.0306 gram Sulfur
 *** 1 wt% of Dibenzofuran in Hexadecane, 0 ppm Mo & 3000 ppm V, 0.0339 gram Sulfur

with molybdenum naphthenate as the heteroatom removal of heteroatomic species. Fluorene hydrogenation showed a reduction from 31 percent to 24 percent, as presented in Figure 7. A similar result was also observed on the conversion of fluorene, as shown in Figure 8. These results agree with the previous work performed by Furimsky (3), who stated that indigenous residuum metals, particularly vanadium and nickel, inhibited the hydrodeoxygenation, hydrodesulfurization, and hydrodenitrogenation but did not substantially affect the hydrogenation.

Catalytic Hydrodenitrogenation of Carbazole

The catalytic activity of combined catalyst precursors for the removal of nitrogen from carbazole was investigated. In the catalytic reactions of carbazole, and the same product distributions were obtained with the combined catalyst systems at $V/(V+Mo) = 0.33$ and 0.67 as given in Table 4 as were observed with the individual catalytic systems. The reaction products detected from the hydrodenitrogenation of carbazole were carbazole, 1,2,3,4-tetrahydrocarbazole, cyclohexylcyclohexene, dicyclohexyl, cyclopentylmethylcyclohexane, heptylcyclopentane, and hexylcyclohexane. As can be seen from Table 4, complete hydrodenitrogenation was not achieved in the presence of mixed-metal sulfur catalysts; more than 30 mole percent of carbazole remained unconverted.

Effect of Vanadium Sulfide in Combined Catalyst Systems on Carbazole Hydrodenitrogenation

The effect of indigenous vanadium, in the form of vanadium sulfide, on the catalytic hydrodenitrogenation of carbazole was examined. Like the other model systems, various vanadium sulfide amounts were added to the carbazole system in the presence of MoS_2 to examine the catalytic effects. The effects

Figure 7. Effect of Vanadium Sulfide in Combined Catalysts on the Hydrogenation of Fluorene

Figure 8. Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Fluorene

Table 4

Catalytic Reactions of Carbazole at Different Metal Contents

Metal Content (ppm)	3000 ppm Mo 0 ppm V	2000 ppm Mo* 1000 ppm V	1000 ppm Mo** 2000 ppm V	0 ppm Mo*** 3000 ppm V
(1) Product Distribution, mole%				
Hexylcyclohexane	32.3±1.7	19.3±2.4	17.4±0.7	7.0±0.6
Heptylcyclopentane	7.2±0.4	4.7±0.5	2.4±0.3	0
Cyclopentylmethylcyclohexane				
isomer 1	Trace	0	0	0
isomer 2	0	0	0	0
isomer 3	14.1±0.7	7.8±0.7	5.9±0.3	3.0±0.3
isomer 4	1.4±0.4	0	0	0
Dicyclohexyl	17.2±1.7	18.1±1.8	16.1±0.8	11.9±1.4
Cyclohexylcyclohexene	0	4.6±0.5	5.6±0.6	6.1±0.5
1,2,3,4-Tetrahydrocarbazole	0	12.9±1.8	15.9±1.2	22.2±2.9
Carbazole	27.8±4.0	32.6±3.8	36.7±3.0	49.8±4.7
(2) Hydrodenitrogenation, %	72.2±4.0	54.6±2.4	47.4±3.4	27.9±1.9
(3) Hydrogenolysis, %	0	0	0	0
(4) Conversion, %	72.2±4.0	67.4±3.8	63.3±3.0	50.2±4.7
(5) Recovery, %	81.6±4.6	66.9±8.7	66.7±6.3	76.0±4.5

Reaction Conditions: 380°C, 30 min, 1250 psig H₂, 550 cpm (horizontal shaking), 4 grams solution

Reactants: 1 wt% of Dibenzofuran in Hexadecane, 3000 ppm Mo & 0 ppm V, 0.0240 gram Sulfur
 * 1 wt% of Dibenzofuran in Hexadecane, 2000 ppm Mo & 1000 ppm V, 0.0273 gram Sulfur
 ** 1 wt% of Dibenzofuran in Hexadecane, 1000 ppm Mo & 2000 ppm V, 0.0306 gram Sulfur
 *** 1 wt% of Dibenzofuran in Hexadecane, 0 ppm Mo & 3000 ppm V, 0.0339 gram Sulfur

of adding vanadium on the hydrodenitrogenation and conversion of carbazole as shown in Figures 9 and 10, respectively. From these figures, the hydrodenitrogenation of carbazole was decreased in relation to molybdenum naphthenate with the introduction of vanadium. Also, a similar result of the inhibiting effect of vanadium was observed on conversion of carbazole.

Summary

The effect of combined catalysts on the interactive chemistry of coal and petroleum model systems was examined. All of the selected model compounds were reacted at different combinations of molybdenum naphthenate and vanadyl acetylacetonate to observe the catalytic interactive effect of vanadium, present as vanadium sulfide, among the various reactants. Under selected operating conditions and in the presence of combined catalysts, the product distributions for each model system were similar to those obtained with individual catalysts. However, the quantitative results of all model systems showed that the increase of vanadium concentration in the combined catalysts resulted in substantial reductions in the amount of reactants converted. These results suggest that the increase in vanadium content was detrimental to the hydrogenation of model hydrocarbon as well as the hydrodeoxygenation, hydrodesulfurization, and hydrodenitrogenation of heteroatomic species. In particular, vanadium sulfide showed much less effective in removing heteroatoms than in promoting hydrogenations.

Figure 9. Effect of Vanadium Sulfide in Combined Catalysts on the Hydrodenitrogenation of Carbazole

Figure 10. Effect of Vanadium Sulfide in Combined Catalysts on the Conversion of Carbazole