ET-11429-Y2
Dist. Category UC-90d

NOTICE**PORTIONS OF THIS REPORT ARE ILLEGIBLE.**

It has been reproduced from the best available copy to permit the broadest possible availability.

MASTER

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION
OF COAL-DERIVED LIQUIDS

ANNUAL REPORT FOR PERIOD

September 15, 1979 to September 15, 1980

DOE/ET/11429--T1

DE81 018124

Prepared by:

James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
Chemical Engineering Department
University of Delaware
Newark, Delaware 19711

Date Published

December 15, 1980

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

DISCLAIMER

This book 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.

Under Contract No. DE-AC22-78ET11429

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.

NOTICE

PROPERTY OF THE UNITED STATES

DO NOT WRITE, COPY, REPRODUCE, OR DISSEMINATE

WITHOUT THE WRITTEN PERMISSION OF THE UNITED STATES

DEPARTMENT OF ENERGY

WASHINGTON, D.C. 20545

MASTER

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or 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.

I. ABSTRACT

Hydrodenitrogenation of quinoline and decahydroquinoline has been studied employing several catalysts: Brønsted and Lewis acid catalysts without metal, and silica-alumina, γ -alumina and magnesia impregnated with molybdenum, tungsten, nickel or cobalt. Our results show that nitrogen removal rate was highest for molybdenum on alumina and tungsten on silica-alumina or alumina catalysts. Nitrogen abstraction using γ -alumina support is considerably faster than with magnesia support.

Several catalysts have been prepared and tested, with the emphasis on understanding the role of acidity in the carbon-nitrogen bond scission reaction. Hydrodenitrogenation of quinoline has been studied by using Ni,Mo/chlorided or fluorided alumina catalysts, with various halide concentrations. Preliminary results from this study indicate that halogenation of γ -alumina catalysts slightly enhanced the hydrogenolysis activity but showed little effect on the hydrogenation activity.

Initial results from phenothiazine hydroprocessing show that carbon-sulfur bonds in the reactant are broken much faster than the carbon-nitrogen bonds. Data relevant to this reaction are being evaluated, utilizing kinetic analysis to give quantitative rates of C-N and C-S bond scission and the extents and rates of hydrogenation.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

1. To apply the reaction study and kinetic analysis techniques which we have developed in our past studies to the optimization of catalysts for hydrodenitrogenation of multi-ring heterocycles by balancing the hydrogenation and carbon-nitrogen bond scission functions.

2. To develop an improved understanding of the catalyst function required by C-N bond scission, since this function is critical to hydrodenitrogenation, but is not well understood.

3. To develop unique catalysts that do not require hydrogenation of the surrounding aromatic rings before hydrodenitrogenation of heterocycles.

4. To determine the stability of the catalysts developed for processing coal-derived liquids.

Scope

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and C-N bond scission, but the cleavage mechanism needs to be defined. The nature of the catalytic function responsible for C-N bond scission will be determined by comparing the scission rates (using mainly

decahydroquinoline) over a set of catalysts prepared specifically to evaluate the catalytic requirements for this reaction. The catalysts to be tested include acid catalysts without metal, Co/Ni-impregnated alumina with various levels of sulfiding from in situ H_2S at low partial pressures, and unsupported molybdenum sulfide with and without Ni promotion to separate out the role of the support. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the C-N bond scission function) will be demonstrated. Promising catalysts will be tested for selectivity and activity maintenance over long-term runs using highly aromatic synthetic feeds and, ultimately, coal-derived liquids.

Another section of this research, and potentially the most beneficial part, requires the development of new, highly-selective hydrodenitrogenation catalysts. This work will focus on developing catalysts that can selectively coordinate and remove nitrogen from multi-ring nitrogen-containing aromatic compounds while minimizing hydrogenation of the rings, thus achieving major savings in hydrogen consumption. The catalysts formulated will be tested under high-pressure liquid-phase conditions using quinoline in a carrier oil as a reactant, since quinoline has the unsaturated heterocyclic structure characteristic of nitrogen-containing compounds present in coal-derived liquids.

The results of all of the above work will be evaluated

utilizing our kinetic analysis schemes to quantify the rates of C-N bond scission and define the rates and extents of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties, and recommendations will be made regarding further studies, following the potentially most fruitful directions.

III. SUMMARY OF PROGRESS

This summary is organized to follow the task statements of the contract. The sections are very brief, containing only the most significant results and conclusions; detailed information can be obtained from the more complete progress reports provided as appendices.

A. Determine the nature of C-N bond scission

Hydrodenitrogenation of aromatic nitrogen-containing compounds occurs via a complex reaction network, involving hydrogenation of the aromatic rings, followed by carbon-nitrogen bond scission. Our primary research objective is to develop an improved understanding of the catalyst function for C-N cleavage, since this function is poorly defined and critical to hydrodenitrogenation.

In current work, runs have been made using phenothiazine as a reactant to quantify and compare the hydrodenitrogenation and hydrodesulfurization rates. Results show that carbon-sulfur bonds in the reactant are broken very fast, yielding either diphenylamine or N-cyclohexylaniline as an intermediate. A carbon-nitrogen bond is then broken in either instance, giving aniline and cyclohexane or benzene. The results from this reaction are being evaluated utilizing our computerized kinetic analysis, to yield quantitative rates of C-N and C-S bond scission and the

extents and rates of hydrogenation.

B. Development of hydrodenitrogenation catalysts

Hydrodenitrogenation of aromatic heterocycles occurs via a complex reaction network, involving hydrogenation of the aromatic rings followed by C-N bond breakage. Hence it is critical to determine the nature of the catalyst sites which promote the denitrogenation reactions, in order to rationally develop upgraded catalysts.

Several catalysts have been synthesized and examined, including Brønsted and Lewis acid catalysts without metal and silica-alumina, γ -alumina and magnesia impregnated with molybdenum, tungsten, cobalt or nickel. The nature of the catalytic functions responsible for C-N bond scission was studied employing quinoline or decahydroquinoline as a model compound, employing the range of catalysts above. Our results indicate that the nitrogen removal rate is highest for tungsten on alumina or silica-alumina and molybdenum on γ -alumina catalyst. The nitrogen removal rates using Mo or W on γ -alumina support are considerably higher than Mo on magnesia support.

Several catalysts have been prepared and tested to define the role of acidity in the carbon-nitrogen bond scission reaction. Several Ni, Mo/fluorided or chlorided alumina catalysts with various halide levels (to increase the alumina support acidity)

were prepared by a commercial catalyst supplier (American Cyanamid Company). Hydrodenitrogenation of quinoline has been studied by using these catalysts, and first results indicate that the presence of halide on γ -alumina catalysts slightly enhanced the hydrogenolysis activity, but showed little effect on the hydrogenation activity. Several other catalysts with different acidity functions have been prepared and are now being evaluated.

TIME PLAN AND MILESTONE CHART

YEAR

TASK STATEMENT

0 1/2 1 1 1/2 2 2 1/2 3

- a. Determine the nature of C-N bond scission

- b. Formulate improved catalysts based on a.

- c. Evaluate all catalysts for scission activity

- d. Kinetic analysis and interpretation of results; future plans

YEAR

0 1/2 1 1 1/2 2 2 1/2 3

TASK STATEMENT

- e. Development of selective HDN catalysts using various metals and supports

- f. Test catalysts from task e. for HDN activity and reactivity

- g. Kinetics analysis; future plans for HDN catalysis

Scheduled

Underway

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

<u>QUARTER</u>	<u>PERSONNEL</u>	<u>TRAVEL</u>	<u>SUPP. & EXP.</u>	<u>OCC. & MAINT.</u>	<u>EQUIPMENT</u>	<u>OTHER</u>	<u>OVERHEAD</u>	<u>TOTAL</u>
First	5,334	0	212	0	585	140	2,868	9,139
Second	21,252	0	2,635	0	11,893	1,841	10,653	48,274
Third	38,755	897	5,475	0	12,333	4,424	20,056	81,940
Fourth	59,966	1,011	9,916	25	12,333	5,412	30,532	119,195
Fifth	71,515	1,245	18,599	25	21,508	5,412	37,624	155,928
Sixth	87,255	1,245	20,641	1,657	26,493	7,158	48,459	192,908
Seventh	102,166	1,245	27,159	1,657	26,493	8,771	59,491	226,982
Eighth	125,475	1,631	28,988	1,657	26,493	9,759	70,876	264,879

IV. APPENDICES

The following appendices are the four progress reports prepared during this second year of this grant.

TABLE OF CONTENTS

	Page
I. ABSTRACT.....	1
II. OBJECTIVES.....	2
III. SUMMARY OF PROGRESS.....	5
Time Plan and Milestone Chart.....	8
Cumulative Expenditures.....	10
IV. APPENDICES.....	11
A. Fifth Progress Report.....	
B. Sixth Progress Report.....	
C. Seventh Progress Report.....	
D. Eighth Progress Report.....	

Appendix "A"

FE-3297-5
Dist. Category UC-90d

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION
OF COAL-DERIVED LIQUIDS

Fifth Quarterly Report for Period
September 15, 1979 to December 15, 1979

Prepared by:

James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
Chemical Engineering Department
University of Delaware
Newark, Delaware 19711

Date Published

February 1, 1980

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

Under Contract No. ET-78-5-01-3297

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or 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.

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Concentration profile for the hydrodenitrogenation of decahydroquinoline using unsulfided HY-Zeolites.	1
2.	Concentration profile for hydrodenitrogenation of decahydroquinoline using unsulfided silica-alumina.	1
3.	Concentration profiles for the hydrodenitrogenation of decahydroquinoline using 10% Fe on γ -alumina (no sulfiding).	1
4.	Total nitrogen removal from decahydroquinoline using 10% Fe on γ -alumina (no sulfiding).	1
5.	Concentration profiles for hydrodenitrogenation of decahydroquinoline using Co on silica-alumina.	1
6.	Total nitrogen removal from decahydroquinoline using Co on silica-alumina.	18
7.	Decahydroquinoline network.	24
8.	Calculated (-) and experimental ($\odot$) concentration profile of DHQ for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2%Mo catalyst.	25
9.	Calculated (-) and experimental (Δ) concentration profile of 1,2,3,4- and 5,6,7,8-tetrahydroquinoline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2% Mo catalyst.	26
10.	Calculated (-) and experimental (+) concentration profile of n-propylcyclohexane for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2%Mo catalyst.	27
11.	Calculated (-) and experimental (χ) concentration of n-propylbenzene for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2%Mo catalyst.	28
12.	Calculated (-) and experimental ($\diamond$) concentration profile of aniline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2%Mo catalyst.	29

13. Calculated (-) and experimental (†) concentration profile of o-propylaniline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, $2\% \text{Mo}$ catalyst. 30
14. Hydrogen elimination process. 34
15. Cut away view of autoclave with glass liner. 36

LIST OF TABLES

		<u>Page</u>
Table I	Standard Operating Conditions	12
Table II	Nitrogen removal rates for HDN catalysts	33

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT	1
II. OBJECTIVES AND SCOPE	3
III. SUMMARY OF PROGRESS TO DATE.	6
Time Plan and Milestone Chart	8
Cumulative Expenditures	10
IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS . . .	11
V. PERSONNEL.	39

I. ABSTRACT

Experimental runs using decahydroquinoline as a reactant have been made. Results show that the strong Brønsted acid catalyst (HY-Zeolite), intermediate Brønsted acid catalyst (silica-alumina) and weak Brønsted acid catalyst (γ -alumina) do not catalyze carbon-nitrogen bond scission alone. Therefore, the carbon-nitrogen bond scission must occur on other active sites on the catalyst. It would appear that hydrodenitrogenation requires an acidic site and a basic site for the β -elimination reaction to occur.

Runs have also been made using sulfided and unsulfided catalysts. Previously, it was thought that during sulfiding of the catalyst, sulfur is formed, which could block the active sites of the catalyst and inactivate it. However, there was no significant difference in nitrogen removal rate between the sulfided and unsulfided catalyst, indicating that sulfiding of these catalyst does not deactivate them.

Several catalysts have been prepared and tested with the emphasis on understanding the nature of catalyst function responsible for carbon-nitrogen bond scission. The catalysts tested include catalysts with Co and Ni impregnated on silica-alumina or γ -alumina supports. However, neither one displayed adequate nitrogen removal rates. As shown in previous reports, the rate of nitrogen removal was highest for the molybdenum on γ -alumina catalyst.

Several catalysts were prepared with the objective of developing new hydrodenitrogenation catalysts which would selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring. Catalysts prepared by two different techniques (coprecipitation and impregnation) were compared for their nitrogen removal rates, using decahydroquinoline as the reactant. Preliminary results indicate that the catalyst prepared by coprecipitation removed nitrogen much more quickly than the impregnation-type catalyst. From these results and using the criteria of chemical and mathematical feasibilities, a network for the hydrodenitrogenation of decahydroquinoline has been hypothesized.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- To apply reaction and kinetic analysis techniques (developed in prior hydrodenitrogenation studies) to the optimization of catalysts for hydrodenitrogenation of multi-ring nitrogen-containing compounds by balancing the hydrogenation and carbon-nitrogen bond scission functions, thereby developing improved hydrodenitrogenation catalysts.
- To develop an improved understanding of the catalyst function required by C-N bond scission since this function is critical to hydrodenitrogenation, but as yet is poorly defined.
- To develop unique catalysts for hydrodenitrogenation of multi-ring nitrogen-containing compounds without first requiring hydrogenation of the surrounding aromatic rings.
- To determine the stability of the catalysts developed for processing coal-derived liquids.

Scope

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. The carbon-nitrogen bond scission process needs to be better understood. The nature of the catalytic function responsible

for C-N bond scission will be determined by measuring the rates of scission (using primarily decahydroquinoline as a standard) over a set of catalysts prepared specifically to evaluate the catalyst requirements for this reaction. The catalysts to be tested include acid catalysts without metal, alumina impregnated with Co and Ni with various levels of sulfiding, and unsupported molybdenum sulfide with and without Ni promotion to separate out the role of the support. All these systems will be subjected to H_2S at a low partial pressure to test the effect of sulfur poisoning. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the C-N bond scission function) will be demonstrated, and promising catalysts will be tested for selectivity and activity maintenance for longer-term runs, using highly aromatic synthetic feeds and coal-derived liquids if possible.

Another part of this research, and potentially the most beneficial part, requires the development of new, highly-selective hydrodenitrogenation catalysts. This work will focus on developing catalysts that can selectively coordinate nitrogen and remove it from multi-ring nitrogen-containing aromatic compounds while minimizing hydrogenation of the aromatic rings, thus achieving major savings in hydrogen consumption. The catalysts formulated will be tested under high-pressure liquid-phase conditions using quinoline in a carrier oil as a reactant, since quinoline contains the requisite nitrogen-containing and aromatic rings

characteristic of heterocyclic compounds present in coal-derived liquids.

The results of all of the above work will be evaluated utilizing our kinetic analysis schemes to give quantitative measures of the rates of C-N bond scission and the extent and rates of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties, and further work will follow the potentially most fruitful directions.

III. SUMMARY OF PROGRESS TO DATE:

During the first five quarters, substantial progress has been made in understanding the chemistry of carbon-nitrogen bond scission. Decahydroquinoline hydrodenitrogenation results indicate that carbon-nitrogen bond scission is not thermal but catalytic. Our results clearly indicate that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission, and therefore such bond scission must occur on other sites in the catalyst. One such possibility is that carbon-nitrogen bond scission is catalyzed by an active site consisting of a transition metal ion in close proximity to an acid site. Hence, it would appear that hydrodenitrogenation requires an acid site and a basic site for the elimination reaction to occur.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. Several catalysts have been prepared and tested recently which include Brønsted and Lewis acid catalysts without metal such as Hy-Zeolite, silica-alumina, and γ -alumina, which are then impregnated with cobalt, molybdenum, nickel, iron and vanadium. The nature of the catalytic function responsible for carbon-nitrogen bond scission was studied using decahydroquinoline over the set of above catalysts. The results indicated that the nitrogen removal rate was highest for molybdenum on γ -alumina catalyst. These results also show that the nitrogen removal rate decreased in the

concentration of the molybdenum on the γ -alumina support.

Runs have also been made by using sulfided and unsulfided catalysts. Previously, it was thought that during sulfiding of the catalyst, sulfur is formed which may block the active sites of the catalyst. Our results indicate that sulfiding of these catalysts does not deactivate them.

Several catalysts have been prepared and tested with the emphasis on understanding the role of acidity on the carbon-nitrogen bond scission reaction and on direct removal of nitrogen without ring hydrogenation. Catalysts prepared by two different techniques, coprecipitation and impregnation, were compared using decahydroquinoline as the reactant. The catalyst prepared by the above techniques was 2%Ni, 2%Mo/ AlBO_3 . Preliminary results indicate that the catalyst prepared by coprecipitation removed nitrogen much more quickly than the catalyst prepared by impregnation techniques. From these results and using the criteria of chemical/mathematical feasibility, a network for the hydrodenitrogenation of decahydroquinoline has been hypothesized.

Many other catalysts with different metal ligand and supports have been prepared and are being tested. The results from all the catalysts tested so far are being evaluated utilizing our kinetic analysis scheme to give quantitative measures of rates of C-N bond scission and the extents and rates of hydrogenation. Catalysts with varying acidity, prepared by American Cyanamid, are also being tested.

*TIME PLAN AND MILESTONE CHART

Scheduled

Underway

Completed

*Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES.

	<u>First Quarter</u>	<u>Second Quarter</u>	<u>Third Quarter</u>	<u>Fourth Quarter</u>	<u>Fifth Quarter</u>
PERSONNEL	5,334	21,252	38,755	59,966	71,515
TRAVEL	0	0	897	1,011	1,245
SUPPLIES AND EXPENSES	212	2,635	5,475	9,916	18,599
OCCUPANCY AND MAINTENANCE	0	0	0	25	25
EQUIPMENT	585	11,893	12,333	12,333	21,508
OTHER EXPENSES	140	1,841	4,424	5,412	5,412
TRANSFERS (OVERHEAD)	<u>2,868</u>	<u>10,653</u>	<u>20,056</u>	<u>30,532</u>	<u>37,624</u>
	9,139	48,274	81,940	119,195	155,928

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Development of Improved Hydrodenitrogenation Catalysts

Hydrodenitrogenation of aromatic nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings followed by carbon-nitrogen bond scission, in contrast to hydrodesulfurization which involves mainly direct scission of carbon-sulfur bonds. Hence, it is critical to determine the nature of the catalyst sites which catalyze these two reaction types (hydrogenation and carbon-nitrogen bond scission) to rationally develop new and improved catalysts. The metal sulfide provides the hydrogenation function in typical commercial hydrotreating catalysts, although a detailed understanding of the nature of the active site and the reaction mechanism is still lacking. The origin of the carbon-nitrogen bond scission reaction is not clear. To better understand the chemistry of carbon-nitrogen bond scission one must choose a compound that is already hydrogenated so that further hydrogenation is not necessary. Decahydroquinoline is fully saturated and is a major product resulting from removal of nitrogen from quinoline, an abundant nitrogen-containing compound found in coal-derived liquids. Prior work has shown that quinoline shows the characteristic behavior of most nitrogen-containing compounds found in coal-derived liquids. Hence decahydroquinoline was chosen as a model compound for studying the chemistry of carbon-nitrogen bond scission.

TABLE I

Standard Operating Conditions

Temperature:	$350 \pm 2^{\circ}\text{C}$
Total Pressure:	$34 \pm 1 \text{ atm}^*$
Reactant Concentration:	0.5 weight percent in <u>n</u> -hexadecane
CS ₂ Loading:	0.05 wt% (1.4 vol % H ₂ S in gas phase)
Catalyst Loading:	0.5 wt% of reaction mixture

*Partial pressure of n-hexadecane @ $350^{\circ}\text{C} \approx 3.24 \text{ atm}$.

Figure 1: Concentration profile for hydrodenitrogenation of decahydroquinoline using unsulfided silica-alumina.

RUN: K-DHQ-620

Figure 2; Concentration profile for the hydrodenitrogenation of decahydroquinoline using unsulfided HY-zeolite (5:1).

Figure 3: Concentration profiles for the hydrodenitrogenation of decahydroquinoline using 10% Fe on γ -alumina (no sulfiding).

RUN K750: NITROGEN CONTENT

Figure 4: Total nitrogen removal from decahydroquinoline using 10% Fe on γ -alumina (no sulfiding).

RUN: K-DHQ-680

Figure 5: Concentration profiles for hydrodenitrogenation of decahydroquinoline using Co on silica-alumina.

RUN K680: NITROGEN CONTENT

Figure 6: Total nitrogen removal from decahydroquinoline using Co on silica-alumina.

Hydrodenitrogenation of decahydroquinoline was studied by using several catalysts with varying acidity and with various metals impregnated on γ -alumina support. The γ -alumina support was used in hydrated form as small particles. A detailed description of the catalyst preparation procedure was given in previous reports.

CARBON - NITROGEN BOND SCISSION

Hydrodenitrogenation of decahydroquinoline was studied over several different catalysts. The reactor used was a 300 c.c. autoclave fitted with a magnetic drive stirrer. Standard operating conditions (Table I) were used for all the experimental runs. The catalyst was presulfided (unless otherwise indicated) for two hours with a mixture of 10 vol% H_2S in hydrogen at atmospheric pressure and $400^\circ C$. To keep the catalyst in the sulfided form during the reaction, 0.05 wt% CS_2 solution in hexadecane was added to the catalyst and reactant. Under the operating conditions carbon disulfide rapidly converts to methane and hydrogen sulfide.

Liquid samples were analyzed using Perkin-Elmer Model 3920 gas chromatographs equipped with a flame - ionization detector and a nitrogen specific detector. A glass capillary column (75M-0V101) was used for all reactant and product analysis.

Figures 1 and 2 show results from runs with unsulfided HY-Zeolite and silica-alumina. The major products from these runs were decahydroquinoline (both Cis and Trans forms), 5,6,7,8-tetrahydroquinoline and n-propylcyclohexane; minor products included n-propylbenzene and 1,2,3,4-tetrahydroquinoline. However, products formed with silica-alumina also contains traces of benzene and cyclohexane. A comparison of these results with the results reported earlier (2nd quarterly report) with the sulfided catalysts does not show any significant difference between the nitrogen removal rates of the sulfided and unsulfided catalyst. Hence, these results indicate that the strong Brønsted acid catalyst such as HY-Zeolite; intermediate Brønsted acid catalyst such as silica-alumina; and weak Brønsted acid catalyst such as γ -alumina, does not catalyze carbon-nitrogen bond scission in either form (sulfided or unsulfided).

Figures 3 and 4 show the concentration profiles and nitrogen removal rate from decahydroquinoline when 10% Fe on γ -alumina catalyst was used without sulfiding. The major product in this run was 5,6,7,8-tetrahydroquinoline with traces of 1,2,3,4-tetrahydroquinoline, n-propylbenzene, and n-propylcyclohexane. There is no significant difference between the nitrogen removal rates of sulfided and unsulfided Fe catalysts. Previously it was thought that sulfur forms during sulfiding of the catalysts, which may block the active sites of the catalysts and render it inactive.

Above results indicate that sulfiding of these catalysts does not deactivate them.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. The nature of the catalytic function responsible for C-N bond scission has been studied using decahydroquinoline.

Runs were made using decahydroquinoline to determine the rates of C-N bond scission over Co on silica-alumina catalyst. The results indicate (Figure 5) that the products from the run using Co on silica-alumina showed traces of 1,2,3,4-tetrahydroquinoline, n-propylbenzene and n-propylcyclohexane, with 5,6,7,8-tetrahydroquinoline and decahydroquinoline (Cis and Trans) as major products. However, the products from the runs with Co on γ -alumina catalysts showed (3rd Quarterly Report) only decahydroquinoline and 5,6,7,8-tetrahydroquinoline. The dehydrogenation reaction between decahydroquinoline and 5,6,7,8-tetrahydroquinoline was absent in Co on γ -alumina runs. Figure 6 shows the total nitrogen removal (42%) from decahydroquinoline using Co on silica-alumina catalyst. With Co on silica-alumina the nitrogen removal rate increased when compared to Co on γ -alumina catalyst. However, the rate of nitrogen removal was still low when compared with the standard Ni-Mo/alumina catalyst.

From the above results it can be concluded that there is no significant difference in nitrogen removal rate between the sulfided and unsulfided catalysts, which indicate that sulfiding does not play any role in deactivation of the catalyst. From our results it is clear that Co on silica-alumina has lower activity compared to standard Ni-Mo/alumina catalysts (HDS-9A).

Presently, the results of all the above work are being evaluated, utilizing our kinetic analysis schemes to give quantitative measures of the rates of C-N bond scission and the extents and rates of hydrogenation.

TASK 2 - Development of Catalysts Effecting Hydrodenitrogenation with minimized Hydrogenation of Heterocyclic Rings.

The objective of this task is to develop novel, highly selective hydrodenitrogenation catalysts that can selectively coordinate nitrogen and remove it from multi-ring nitrogen-containing aromatic compounds with minimal hydrogenation of the aromatic ring. This would achieve major savings in industrial hydrogen consumption.

A catalyst is desired that can act as Lewis acid and selectively coordinate with the basic lone pair on nitrogen. The coordination with nitrogen would reduce the aromaticity of the nitrogen containing ring, thus facilitating nitrogen removal without hydrogenation of the neighboring aromatic rings.

In current work runs were made using decahydroquinoline as a reactant to compare the Lewis acid catalyst prepared by coprecipitation method to a similar catalyst prepared by impregnation techniques on a completely saturated nitrogen-containing ring system.

Preliminary results indicate that the catalyst prepared by coprecipitation removed nitrogen much more quickly than the catalyst prepared by impregnation techniques. These

FIGURE 7

DECAHYDROQUINOLINE NETWORK

Relative rates are indicated in brackets

Dashed lines are reaction paths for which rate constants could not be determined.

Figure 8: Calculated (—) and experimental (⊗) concentration profile of DHQ for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\%\text{Ni}$, 2% Mo catalyst.

Figure 9: Calculated (—) and Experimental (Δ) concentration profile of 1,2,3,4- and 5,6,7,8-Tetrahydroquinoline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\%\text{Ni}$, 2% Mo catalyst.

Figure 10; Calculated (—) and Experimental (+) concentration profile of n - propylcyclohexane for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlB}_3/\text{2\% Ni}$, 2% Mo catalyst.

Figure 11: Calculated (-) and Experimental (X) concentration of n - propylbenzene for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlB}_3/\text{2\%Ni}/\text{2\%Mo}$ catalyst.

Figure 12: Calculated (—) and Experimental ($\diamond$) concentration profile of Aniline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\%\text{Ni}$, 2%Mo catalyst.

Figure 13: Calculated (—) and Experimental (♦) concentration profile of O - propylaniline for hydrodenitrogenation of decahydroquinoline using coprecipitated $\text{AlBO}_3/2\% \text{Ni}$, 2% Mo catalyst.

results show that there is a strong geometric factor influencing the efficiency of the AlBO_3 -supported catalyst.

From the results shown in Figures 8-12, and using the criteria of chemical and mathematical feasibilities, and reproducibility of experimental results, a network for the decahydroquinoline deamination using the $\text{AlBO}_3/2\% \text{ Ni}$, $2\% \text{ Mo}$ prepared by coprecipitation was hypothesized (Figure 7). Figures 8-13 show the calculated and experimental concentration profiles for the hypothesized networks. Fitting the same network to the run made with the AlBO_3 -supported catalyst prepared by impregnation was not mathematically feasible, which could be a result of limitations in the HJB program and/or changes in the mechanistic pathway.

A comparison of the AlBO_3 -supported catalyst prepared by coprecipitation and impregnation to other catalyst runs with decahydroquinoline as the reactant (Table II) indicate the $\text{AlBO}_3/2\% \text{ Ni}$, $2\% \text{ Mo}$ coprecipitated catalyst gives the best nitrogen removal shown thus far, even with small percentages of metal compared to others listed.

EXPERIMENTAL:

The AlBO_3 support was prepared by adding equal amounts of AlCl_3 and BCl_3 in CH_2Cl_2 to a solution of rapidly stirring methanol at room temperature, with the evolution of HCl gas. To this reaction solution was added H_2O , followed by NH_4OH , causing the precipitation of AlBO_3 . The support was then

washed with H_2O and filtered by centrifugation. The washed AlBO_3 was then dried at 211.6°C for 24 hours and calcined at 454.6°C for 3 hours. The metal was added by methods described in previous reports at a pH of 7.5.

A glass liner was used for each catalytic run and the autoclave was operated in the batch mode. The reaction temperature was maintained at $350^\circ\text{C} \pm 2^\circ\text{C}$. The catalyst in each run was presulfided for 2 hours with a mixture of 10%/vol H_2S in H_2 at atmospheric pressure and 400°C .

RESULTS AND DISCUSSION:

Results for each run are shown in figures 8-13. As indicated in the results, both AlBO_3 -supported catalyst prepared by coprecipitation and impregnation dehydrogenate decahydroquinoline initially to 5,6,7,8-tetrahydroquinoline. This would suggest that both catalysts effectively act to increase the rate of dehydrogenation. However, besides greater nitrogen removal in the run using the coprecipitated catalysts, 1,2,3,4-tetrahydroquinoline appears in the first few minutes of the reaction, while it does not appear until late in the run (5 hours) with the impregnated catalyst. This indicates a dramatic difference in reaction rates, and possibly different reaction pathways, between the two geometrically different catalyst.

Using the product concentration profiles for the coprecipitated catalyst, chemically feasible networks, based

TABLE II

Nitrogen Removal Rates for HDN Catalysts
(Decahydroquinoline 350°C, 500 psig)

Catalyst	%N removed
AlBO ₃ /2% Ni, 2% Mo (Coprecipitated)	78%
γ-Alumina/23% Mo	77.2%
γ-Alumina/10% Mo	72.3%
γ-Alumina/3.5% Ni, 18% Mo	71.0%
AlBO ₃ /4% Ni (Impregnated)	55%
HY-Zeolite	34%
γ-Alumina/2% Mo	30.2%
γ-Alumina/10% Fe	26.5%
γ-Alumina/4% Fe	22.1%
Silica-Alumina	20.2%
γ-Alumina/8.4% Ni	18.9%
Silica-Alumina/8.4% Ni	18.8%
γ-Alumina/4% Vanadium	17%
γ-Alumina/8.4% Co	14.3%
γ-Alumina	13.0%

on the quinoline network already determined, were hypothesized. The networks were placed in the HJB program to determine their mathematical feasibility in generating positive rate constants for the entire reaction scheme. Then, using these calculated rate constants and the initial concentration determined on the gas chromatograph, the concentration profiles for each product was calculated and plotted using the GEAR program with a plotting subroutine. The concentration profiles from networks giving good comparison to experimental results were determined to be from a chemically and mathematically feasible route. Using the criteria of:

1. chemical feasibility
2. mathematical feasibility
3. reproducibility of experimental results

the most highly probable network can be determined, and less likely networks eliminated. The only network which met the three criteria is shown in Figure 1, along with the calculated and relative rate constants. An interesting observation of the network is the lumping of 5,6,7,8-tetrahydroquinoline with 1,2,3,4-tetrahydroquinoline, without which the network is mathematically impossible. This lumping indicates a rapid equilibrium of 1,2,3,4-THQ and 5,6,7,8-THQ in which the reactant is rapidly adsorbed, desorbed, and readsorbed on the catalyst surface with successive dehydrogenations and hydrogenations. The loss of decahydroquinoline through the

Figure 15. Cut away view of autoclave with glass liner

labeled volatiles, and consequent loss of mass from the material balance, can be explained through a hydrogen elimination process in which the decahydroquinoline ring system is cleaved into an amine and highly volatile cyclohexadiene (Figure 14). Another problem with conjunction with the hydrogen elimination ring cleavage volatilization is illustrated in figure 15. The initially concentrated decahydroquinoline is at 350°C above its boiling range and can be volatilized. Some of this vapor condenses on the outside walls of the glass liner. While this explanation would mask the true total nitrogen removed it would not effect the rate constants reported. Limitations in the HJB program explain why the very slow reverse reaction of the lumped 1,2,3,4-THQ and 5,6,7,8-THQ to DHQ, and the slow conversion of propyl aniline to n-propylbenzene, were not calculated from the concentration profiles determined experimentally. The reactions are known to occur and are depicted by dashed arrows in figure 7.

Fitting the network of figure 7 to the data provided by the AlBO_3 -supported catalyst prepared by impregnation was not mathematically feasible. This can again be explained by limitations in the HJB program and/or variations in the mechanistic pathway. Further work is continuing to determine the rate constants of the impregnated catalyst.

A comparison of the two AlBO_3 -supported catalysts to other catalysts run with decahydroquinoline as the reactant (Table II) indicates that the $\text{AlBO}_3/2\% \text{ Ni}, 2\% \text{ Mo}$ coprecipitated catalysts resulted in nearly optimal total nitrogen removal, even with small percentages of metal. (It was previously shown that with γ -alumina increased concentration of molybdenum increased total nitrogen removed.)

Analysis performed on the catalysts indicated that coking does not occur and no nitrogen forms on the catalyst, indicating the AlBO_3 support is acting as a true catalyst.

New catalysts are being prepared by the coprecipitation method with varying amounts of boron, and molybdenum, in order to evaluate their catalytic effects.

V. PERSONNEL

There has been only one change in personnel during this quarter. Dr. R. Sivasubramanian, a post doctoral fellow, left the project on October 31, 1979.

Appendix "B"

FE-3297-6

Dist. Category UC-90d

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION
OF COAL-DERIVED LIQUIDS

Sixth Quarterly Report for Period

December 15, 1979 to March 15, 1980.

Prepared by

James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
Chemical Engineering Department
University of Delaware
Newark, Delaware 19711

Date Published

June 1, 1980

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

Under Contract No. ET-78-5-01-3297

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, or 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.

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT	1
II. OBJECTIVES AND SCOPE.....	2
III. SUMMARY OF PROGRESS TO DATE.....	5
Time Plan and Milestone Chart.....	8
Cumulative Expenditures.....	10
IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS.....	12
V. PERSONNEL.....	44

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Standard Operating Conditions.....	16
2. Kinetic rate constants for hydrodenitrogenation of Quinoline using fluorided catalysts..	18
3. Experimental conditions for HDN of Diphenyl- amine.....	42

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1:	Nitrogen removal rates for Ni/MgO and Mo/MgO Catalysts-----	14
2:	Calculated (-) and Experimental (□) Concentration profile of N-propylcyclohexane for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	19
3:	Calculated (-) and Experimental (□) Concentration profile of Propylbenzene for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	20
4:	Calculated (-) and Experimental (□) Concentration profile of Aniline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	21
5:	Calculated (-) and Experimental (□) Concentration profile of O-propylaniline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	22
6:	Calculated (-) and Experimental (□) Concentration profile of Decahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	23
7:	Calculated (-) and Experimental (□) Concentration profile of 5,6,7,8-Tetrahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%F, on HDS-9A Catalyst-----	24
8:	Calculated (-) and Experimental (□) Concentration profile of 1,2,3,4-Tetrahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	25
9:	Calculated (-) and Experimental (□) Concentration profile of N-propylcyclohexane for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst-----	26
10:	Comparison of Nitrogen removal rates for hydrodenitrogenation of Quinoline using Ni-Mo/ γ -Al ₂ O ₃ Catalyst-----	27
11:	Reaction network for Quinoline hydrodenitrogenation----	28
12:	Mechanisms for Hydrodenitrogenation of Diphenylamine----	29
13:	Calculated (-) and Experimental (○) profile of DPA for Hydrodenitrogenation of diphenylamine-----	31

14:	Calculated (-) and Experimental (Δ) concentration profile of Aniline for hydrodenitrogenation of diphenylamine-----	32
15:	Calculated (-) and Experimental (+) concentration profile of Benzene for hydrodenitrogenation of diphenylamine-----	33
16:	Calculated (-) and Experimental (X) concentration of Cyclohexane for hydrodenitrogenation of diphenylamine-----	34
17:	Calculated (-) and Experimental (O) concentration of DPA for hydrodenitrogenation of diphenylamine-----	35
18:	Calculated (-) and Experimental (Δ) concentration profile of Aniline for hydrodenitrogenation of diphenylamine-----	36
19:	Calculated (-) and Experimental (+) concentration profile of Benzene for hydrodenitrogenation of Diphenylaniline-----	37
20:	Calculated (-) and Experimental (X) concentration profile of Cyclohexane for hydrodenitrogenation of diphenylaniline-----	38
21:	Different Mechanisms for hydrodenitrogenation of Diphenylamine-----	42
22:	Deamination of Aniline and Diphenylamine-----	43

I. ABSTRACT

Hydrodenitrogenation of decahydroquinoline has been studied using catalysts prepared by coprecipitation or impregnation of Ni, Mo on magnesium oxide support. Preliminary results show that molybdenum plays an important role in carbon-nitrogen bond scission. The nitrogen removal rates using Mo on γ -alumina support are considerably higher than Mo on magnesia support.

More runs have been made using sulfided and unsulfided catalysts. Recent results show that sulfiding of the catalysts does not deactivate them.

Catalysts have been prepared and tested with the emphasis on understanding the role of acidity on the carbon-nitrogen bond scission reaction and on direct removal of nitrogen without ring hydrogenation. A comparison of 2%Ni, 2%Mo/ AlBO_3 catalysts prepared by two different techniques (impregnation and coprecipitation) showed that the catalyst prepared by coprecipitation removed nitrogen more quickly than the catalyst prepared by impregnation.

Several Ni, Mo/fluorided alumina catalysts with various levels of fluorine content (to increase the acidity of alumina support) were prepared by a commercial catalyst supplier. Preliminary results from this study indicate that the fluorided γ -alumina catalysts slightly enhanced the hydrogenolysis activity but showed little effect on the hydrogenation activity. Several other catalysts with different acidity function have been prepared and are now being evaluated.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- To apply the reaction study and kinetic analysis techniques which we have developed in our past hydrodenitrogenation studies to the optimization of catalysts for hydrodenitrogenation of multi-ring nitrogen-containing compounds by balancing the hydrogenation and carbon-nitrogen bond scission functions.
- To develop an improved understanding of the catalyst function required by C-N bond scission, since this function is critical to hydrodenitrogenation, but is not well understood.
- To develop unique catalysts that do not require hydrogenation of the surrounding aromatic rings before hydrodenitrogenation of multi-ring nitrogen-containing compounds.
- To determine the stability of the catalysts developed for processing coal-derived liquids.

Scope

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission, but the carbon-nitrogen bond scission mechanism needs to be defined. The nature of the catalytic function responsible for C-N bond

scission will be determined by measuring the scission rates, using mainly decahydroquinoline, over a set of catalysts prepared specifically to evaluate the catalytic requirements for the C-N bond scission. The catalysts to be tested include acid catalysts without metal, Co/Ni- impregnated alumina with various levels of sulfiding from in situ H_2S at low partial pressures, and unsupported molybdenum sulfide with and without Ni promotion to separate out the role of the support. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the C-N bond scission function) will be demonstrated. Promising catalysts will be tested for selectivity and activity maintenance over long-term runs using highly aromatic synthetic feeds and, ultimately, coal-derived liquids.

Another part of this research, and potentially the most beneficial part, requires the development of new, highly-selective hydrodenitrogenation catalysts. This work will focus on developing catalysts that can selectively coordinate and remove nitrogen from multi-ring nitrogen-containing aromatic compounds while minimizing hydrogenation of the aromatic rings, thus achieving major savings in hydrogen consumption. The catalysts formulated will be tested under high-pressure liquid-phase conditions using quinoline in a carrier oil as a reactant since quinoline has the unsaturated heterocyclic ring structure characteristic of nitrogen-containing compounds present in coal-derived liquids.

The results of all of the above work will be evaluated utilizing our kinetic analysis schemes to quantify the rates of C-N bond scission and define the rates and extents of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties, and recommendations will be made regarding further studies, following the potentially most fruitful directions.

III. SUMMARY OF PROGRESS TO DATE

During the first six quarters, substantial progress has been made in understanding the chemistry and mechanism of carbon-nitrogen bond scission. Decahydroquinoline hydrodenitrogenation results indicate that carbon-nitrogen bond scission is not thermal but catalytic. Preliminary results clearly indicate that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission. The carbon-nitrogen bond scission therefore must occur at other sites on the catalyst. One such possibility is that carbon-nitrogen bond scission is catalyzed by an active site consisting of a transition metal ion in close proximity to an acid site. Hence, it would appear that hydrodenitrogenation requires an acid site and a basic site for the elimination reaction to occur.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. Several catalysts have been prepared and tested which include Brønsted and Lewis acid catalysts without metal, silica-alumina, or γ -alumina, impregnated with cobalt, molybdenum, nickel, iron, or vanadium. The nature of catalytic functions responsible for carbon-nitrogen bond scission was studied using decahydroquinoline over the set of above catalysts. Our results indicated that the nitrogen removal rate was highest for molybdenum on γ -alumina catalyst. These results also show

that the nitrogen removal decreased with lower concentrations of molybdenum on the γ -alumina support.

Hydrodenitrogenation of decahydroquinoline has also been studied over two magnesium oxide catalysts, prepared by coprecipitation and impregnation techniques. Under standard reaction conditions nickel/magnesia (10% NiO) and molybdenum/magnesia (10% Mo) gave total nitrogen removal of 20% and 50%, respectively. The above preliminary results indicate that molybdenum plays an important role in carbon-nitrogen bond scission. However, a comparison of the nitrogen removal rates for Mo/magnesia and Mo/ γ -alumina show that γ -alumina is superior to magnesita as a support.

Runs have also been made using sulfided and unsulfided catalysts. It was thought that sulfur formed during sulfiding of the catalyst, blocking the active sites and rendering the catalyst inactive. However, our results indicate that sulfiding of these catalysts does not deactivate them.

Catalysts have been prepared and tested with the emphasis on understanding the role of acidity on the carbon-nitrogen bond scission reaction and on direct removal of nitrogen without ring hydrogenation. A comparison of 2% Ni, 2% Mo/ AlBO_3 catalysts prepared by two different techniques (impregnation and coprecipitation) showed that the catalyst prepared by coprecipitation removed nitrogen more quickly than the

catalyst prepared by impregnation.

The acidity of alumina supports can be increased by the addition of fluorine, chlorine, or boria, as well as combining alumina with other metal oxides. Several Ni, Mo/fluorided alumina catalysts with various level of fluorine content were purchased from a commercial catalyst supplier (American Cyanamid Co.). Preliminary results indicate that the fluorided γ -alumina catalysts slightly enhance hydrogenoylsis but have little affect on the hydrodenitrogenation activities, relative to unfluorided analogs.

Many other catalysts with different metal ligands and supports have been prepared and are being examined. The results from all the catalysts tested are being evaluated, utilizing our kinetic analysis scheme to measure quantitatively the rates of C-N bond scission and the extents and rates of hydrogenation.

*TIME PLAN AND MILESTONE CHART

YEAR	0	1/2	1	1 1/2	2	2 1/2	3
TASK STATEMENT							

2. e. Development of selective HDN catalysts using various metals and supports

- f. Test all catalysts from task e for HDN activity and reactivity

- g. Kinetic analysis, interpretation of results, and recommendations

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	First Quarter <u>\$5,334</u>	Second Quarter <u>\$21,252</u>	Third Quarter <u>\$38,755</u>	Fourth Quarter <u>\$59,566</u>
PERSONNEL				
TRAVEL	0	0	897	1,011
SUPPLIES AND EXPENSES	212	2,635	5,475	9,916
OCCUPANCY AND MAINTENANCE	0	0	0	25
EQUIPMENT	585	11,893	12,333	12,333
OTHER EXPENSES	140	1,841	4,424	5,412
TRANSFERS (OVERHEAD)	<u>2,868</u>	<u>10,653</u>	<u>20,056</u>	<u>30,532</u>
	\$9,139	\$48,274	\$81,940	\$119,195

CUMULATIVE EXPENDITURES

	<u>Fifth Quarter</u>	<u>Sixth Quarter</u>
PERSONNEL	\$ 71,515	\$ 87,255
TRAVEL	1,245	1,245
SUPPLIES AND EXPENSES	18,599	20,641
OCCUPANCY AND MAINTENANCE	25	1,657
EQUIPMENT	21,508	26,493
OTHER EXPENSES	5,412	7,158
TRANSFERS (OVERHEAD)	<u>37,624</u>	<u>48,459</u>
	\$155,928	\$192,908

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Development of Improved Hydrodenitrogenation Catalysts

Hydrodenitrogenation of aromatic nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings, followed by carbon-nitrogen bond scission (in contrast to hydrodesulfurization, which involves mainly direct scission of carbon-sulfur bonds). Hence, it is critical to determine the nature of the catalyst sites which catalyze these two reaction types (hydrogenation and carbon-nitrogen bond scission) to rationally develop new and improved catalysts. Metal sulfides provide the hydrogenation function in typical commercial hydrotreating catalysts, although a detailed understanding of the nature of the active site and the reaction mechanism is still lacking.

The mechanism of the carbon-nitrogen bond scission reaction is not clear. To better understand the chemistry of this process, one must choose a compound that is already hydrogenated, to insure that further hydrogenation is not involved. Decahydroquinoline is fully saturated and a major reactant during nitrogen removal from quinoline (a compound characteristic of heterocyclic species found in coal-derived liquids). Therefore, decahydroquinoline was chosen as a model compound for studying the chemistry of carbon-nitrogen bond scission.

Hydrodenitrogenation of Decahydroquinoline

Hydrodenitrogenation (HDN) of decahydroquinoline was studied over two magnesium oxide catalysts, Ni/MgO and Mo/MgO. Nickel/magnesium oxide (10% NiO) was prepared by coprecipitation, as follows. Ammonium bicarbonate was added to a solution containing stoichiometric amounts of nickel nitrate and magnesium nitrate, precipitating the desired catalyst. The catalyst was washed, dried (120°C), and calcined at 400°C in an air furnace for 4 hours.

Molybdenum/magnesia (1% Mo/MgO) catalyst was prepared by impregnation. A mixture of 3g of MoO₃, 12g of MgO, and 135 ml of H₂O was stirred at 95°C for 10 hours, and H₂O was added periodically to maintain the original volume. The resulting product was washed with H₂O, dried (120°C), and calcined at 400°C in an air furnace for 4 hours. Both catalysts were pretreated by 10 vol % H₂S in hydrogen at atmospheric pressure and 400°C for 2 hours. Reactions were carried out under standard conditions (Table 1).

The products of hydrodenitrogenation of decahydroquinoline were n-propylcyclohexane, n-propylbenzene, 5,6,7,8-tetrahydroquinoline, 1,2,3,4-tetrahydroquinoline, and an unidentified hydrocarbon. It can be seen from Fig. 1 that

Figure 1: Comparison of Nitrogen removal rates for hydrodenitrogenation of decahydro Quinoline using Ni/MgO, Mo/MgO and Ni-Mo/ γ -Al₂O₃ (HDS-9A) Catalysts

the nitrogen removal rate for nickel/magnesia catalyst is very slow, and that molybdenum/magnesia exhibits a greater HDN activity. Under identical conditions, nickel/magnesia and molybdenum/magnesia gave a total nitrogen removal of 20% and 50%, respectively. Furthermore, the nitrogen removal rate for 10% Mo/ γ -Al₂O₃ was reported to be 72% in our earlier studies. The above results indicate that molybdenum plays an important role in HDN reactions. Thus, by comparing the activity of molybdenum/ γ -alumina and molybdenum/magnesia, we conclude that γ -alumina is superior to magnesia as a support.

TABLE I

Standard Operating Conditions

Temperature:	$350 \pm 2^{\circ}\text{C}$
Total Pressure:	$34 \pm 1 \text{ atm}^*$
Reactant Concentration:	0.5 weight percent in <u>n</u> -hexadecane
CS ₂ Loading:	0.05 wt% (1.4 vol% H ₂ S in gas phase)
Catalyst Loading:	0.5 wt% of reaction mixture

*Partial pressure of n-hexadecane @ $350^{\circ}\text{C} \approx 3.24 \text{ atm}$.

Role of Acidity in Hydrodenitrogenation of Quinoline

It has been suggested that breaking of the C-N bond of heterocycles takes place as a result of interaction with the support. Therefore, it is worthwhile to study the influence of the support on the HDN of the model compounds. We are currently examining the relationship between HDN activity and surface acidity of the catalyst. Alumina acidity can be promoted by addition of fluorine, chlorine, and boria, as well as combining alumina with other metal oxides. Several Ni,Mo/fluorided alumina catalysts with various levels of fluorine content have been obtained from American Cyanamid Company. The HDN activity of two fluorided alumina catalysts (1% and 0.25% F) have been examined and the results compared to those of the commercial HDS catalyst, HDS-9A.

The concentration profile of a typical run and the comparison of nitrogen removal rates for different catalysts are shown in Figs. 2-9 and Fig. 10, respectively. In addition, the reaction network (Fig. 11) and reaction kinetics for quinoline HDN were quantitatively determined. The rate parameters are listed in Table II. The fluorided γ -alumina catalysts slightly enhanced hydrogenolysis, but showed little effect on the dehydrodenitrogenation activities. It is difficult to draw wide-spread conclusions based on the results of our preliminary studies. In order to establish the relation between acidity and HDN activity of these catalysts, further experiments using catalysts with high levels of fluorine content and catalysts

TABLE II

Kinetic rate constants for HDN of quinoline

	1.0%F	CATALYST	0.25%F	HDS-9A
	Ni,Mo/Fluorided Al ₂ O ₃	Ni,Mo/Fluorided Al ₂ O ₃	Ni,Mo/Al ₂ O ₃	
Rate Constant (g oil/g cat.-min)				
K ₁	278.21		508.05	436.05
K ₂	45.23		55.36	65.51
K ₃	18.21		24.62	20.01
K ₄	6.37		6.36	4.78
K ₅	1.37		2.13	1.11
K ₆	1.68		1.60	1.19
K ₇	2.02		1.78	1.14
K ₈	0.65		0.65	0.54
K ₉	32.36		31.74	23.08
K ₁₀	2.15		2.41	1.36
K ₁₁	0.56		0.77	0.74
K ₁₂	3.36		4.52	1.95
K ₁₃	0.24		0.36	0.17
K ₁₄				1.86

Figure 2: Calculated (—) and Experimental (□) Concentration profile of *n*-propylcyclohexane for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 3: Calculated (-) and Experimental ($\square$) concentration profile of Propylbenzene for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 4: Calculated (-) and Experimental (□) concentration profile of Aniline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 5: Calculated (-) and Experimental ($\square$) concentration profile of O-propylaniline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 6: Calculated (-) and Experimental (E) concentration profile of Decahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 7: Calculated (-) and Experimental ($\square$) concentration profile of 5,6,7,8-Tetrahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 8: Calculated (-) and Experimental (□) concentration profile of 1,2,3,4-Tetrahydroquinoline for hydrodenitrogenation of Quinoline using 0.25%P on HDS-9A Catalyst.

Figure 9: Calculated (-) and Experimental ($\square$) concentration profile of N-propylcyclohexane for hydrodenitrogenation of Quinoline using 0.25%F on HDS-9A Catalyst.

Figure 10: Comparison of Nitrogen removal rates for hydrodenitrogenation of Quinoline using Ni-Mo/ γ -Al₂O₃ (HDS-9A) and fluoridated Ni-Mo/ γ -Al₂O₃ Catalysts.

(1) Ni-Mo/ γ -Al₂O₃ (HDS-9A)

(2) 0.25%F and 1.0%F on Ni-Mo/ γ -Al₂O₃

Figure 11: Reaction network for Quinoline hydrodenitrogenation.

Mechanism 1 Mechanism 2

Figure 12: Mechanisms for Hydrodenitrogenation of Diphenylamine (DPA).

Relative rates are shown in parenthesis.

containing other promoters will be studied in the near future.

TASK 2 - Development of Catalysts which will Effect
Hydrodenitrogenation with only Limited or No
Hydrogenation of the Heterocyclic Rings Present
in the Molecule.

The objective of this task is to develop new, highly specific hydrodenitrogenation catalysts that can selectively coordinate nitrogen and remove it from multi-ring, heterocyclic aromatic compounds while minimizing ring of hydrogenation, thereby achieving major savings in hydrogen consumption. The purpose of this study is to determine if deamination of diphenylamine and aniline occurs without complete ring hydrogenation, using Ni-Mo on γ -alumina (HDS-9A), a standard catalyst.

Experiments were undertaken with the autoclave in the batch mode; reaction conditions are shown in Table III. The results, using the criteria of chemical and mechanical feasibility, and reproducibility of experimental results, strongly indicate both diphenylamine and aniline undergo deamination through Hoffman elimination without first having to fully hydrogenate the aromatic ring. The networks, rate constants, and relative rate constants are shown in Fig. 12. The concentration profiles of the experimental and calculated results using these schemes are shown in Fig. 13-20.

Figure 13 ; Calculated (-) and Experimental ($\odot$) concentration profile of DPA for hydrodenitrogenation of diphenylamine

Figure 14: Calculated (-) and Experimental (Δ) concentration profile of Aniline for hydrodenitrogenation of diphenylamine.

Figure 15; Calculated (-) and Experimental (+) concentration profile of Benzene for hydrodenitrogenation of diphenylamine.

Figure 16; Calculated (-) and Experimental (X) concentration of Cyclohexane for hydrodenitrogenation of diphenylamine.

Figure 17: Calculated (-) and Experimental (⊙) concentration profile of DPA for hydrodenitrogenation of diphenylamine.

Figure 18: Calculated (—) and Experimental (Δ) concentration profile of Aniline for hydrodenitrogenation of diphenylamine.

Figure 19: Calculated (—) and Experimental (+) concentration profile of Benzene for hydrodenitrogenation of Diphenylaniline.

Figure 20: Calculated (—) and Experimental (X) concentration profile of Cyclohexane for hydrodenitrogenation of diphenylaniline.

a 9% increase in the mass balance. This is attributed to the accumulation of concentration data from two different gas chromatographs. One chromatograph employed a nitrogen detector to prevent masking of the diphenylamine signal by the n-hexadecane solvent peaks; the other used a FID detector to separate benzene and cyclohexane signals.

Runs were also made at 325° C and 500 psig. The temperature of 325° C, which is 25° C lower than standard runs, was chosen so that the decomposition of diphenylamine and further deamination of aniline could more easily be studied. Using the product concentration profiles, feasible networks were hypothesized. The networks were placed in the HJB program to determine their mathematical feasibility in generating positive rate constants for the entire network. Then, using these calculated rate constants and the initial concentrations determined on the gas chromatograph, the concentration profiles for each product was calculated and plotted with the GEAR program and plotting routine. The concentration profiles from networks giving good comparison of experimental results were adjudged to be chemically and mathematically feasible.

Using the established criteria above, the most highly probable network can be determined and less likely networks eliminated.

The only two networks which met the three criteria are shown in Fig. 12, with accompanying experimental and calculated

concentration profiles in Fig. 13-20. The calculated results and constants of the proposed networks are very similar, and further statistical and experimental analysis will have to be done to determine whether one or both networks are occurring in the deamination process. As would be expected, the rate constant of simultaneous deamination of diphenylamine is very small (0.2) relative to the other rate constants, since the compound would have to orient itself on the catalyst such that both phenyl groups could be partially hydrogenated and undergo Hoffman elimination simultaneously. For these reasons, mechanism 1 is preferred over mechanism 2.

Other mechanisms considered are shown in Fig. 21; model-experiment agreement was unsatisfactory, especially in calculations of benzene and cyclohexane concentrations. These mechanisms were based on the assumption that the appearance of aniline and its coproduct (from deamination of the diphenylamine into two species) do not necessarily occur at the same rate, since the two species could be nonsimultaneously adsorbed and desorbed from the catalyst surface. Also, these routes gave very poor mathematical agreement with experimental results, indicating that the pictured reactions were not occurring.

The excellent results from mechanisms 1 and 2 strongly indicate that the deamination of diphenylamine and aniline occurs by Hoffman elimination and the driving force is the maintenance of aromaticity after nitrogen elimination (Fig. 22).

TABLE III
EXPERIMENTAL CONDITIONS FOR HDN OF DIPHENYAMINE

Temperature	325° C ± 2° C
Total Pressure	500 Psig ± 5Psig
Catalyst	2% Ni-Mo on γ -Alumina (HDS-9A) 100-150 Mesh, Sulfided for 2 hours at 400° C using 10% H ₂ S/H ₂
Catalyst Loading	0.5 wt %
CS ₂ Conc. in feed	0.05 wt %
Carrier Oil	n-hexadecane
Reactant Conc. of DPA	0.8 wt %

Figure 21: Different Mechanisms for
hydrodenitrogenation of
Diphenylamine.

Mechanism 3.

Mechanism 4.

Mechanism 5.

Aniline

Diphenylamine

Figure 22: Deamination of Aniline and Diphenylamine

V. PERSONNEL

There has been only one change in personnel during this quarter. Dr. W-S. Liu joined the project as a post doctoral fellow on January 1, 1980.

Appendix "C"

FE-3297-7
Dist. Category UC-90d

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION
OF COAL-DERIVED LIQUIDS

Seventh Quarterly Report for Period
March 15, 1980 to June 15, 1980

Prepared by:

James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
Chemical Engineering Department
University of Delaware
Newark, Delaware 19711

Date Published

August 1, 1980

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

Under Contract No. ET-78-5-01-3297

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their contractors, subcontractors, or 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.

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT	1
II. OBJECTIVES AND SCOPE	2
III. SUMMARY OF PROGRESS TO DATE	4
Time Plan and Milestone Chart	8
Cumulative Expenditures	6-7
IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS	10
V. PERSONNEL	21

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Standard Operating Conditions.....	12

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Concentration profiles for hydrodenitrogenation of quinoline using nickel-tungsten/alumina catalyst....	13
2.	Concentration profiles for hydrodenitrogenation of quinoline using nickel-tungsten/silica-alumina catalyst.....	14
3.	Nitrogen removal rate for hydrodenitrogenation of quinoline using nickel-tungsten/alumina catalyst....	15
4.	Nitrogen removal rate for hydrodenitrogenation of quinoline using nickel-tungsten/silica-alumina catalyst.....	16
5.	Reaction mechanism for hydrodenitrogenation and hydro-desulfurization of phenothiazine.....	19

I. ABSTRACT

Hydrodenitrogenation of quinoline has been studied by using nickel-tungsten on alumina or silica-alumina catalysts. Preliminary results show that these catalysts have very high nitrogen removal rates.

Experimental runs were also made by using phenothiazine as a reactant, to quantify and compare the hydrodenitrogenation and hydrodesulfurization rates. From preliminary data, it appears that carbon-sulfur bonds in phenothiazine are broken very fast when compared to carbon-nitrogen bonds. Results from these runs are being evaluated to give quantitative measures of rates of C-N and C-S bond scissions.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- To apply the reaction study and kinetic analysis techniques which we have developed to the optimization of catalysts for hydrodenitrogenation of multi-ring organic compounds by balancing the hydrogenation and carbon-nitrogen bond scission functions, thereby developing improved hydrodenitrogenation catalysts.
- To define more completely the catalyst function required by C-N bond scission, since this function is critical to hydrodenitrogenation.
- To develop unique catalysts for hydrodenitrogenation of multi-ring heterocycles without first requiring hydrogenation of the attendant aromatic moieties.
- To determine the stability of catalysts developed for processing coal-derived liquids.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission, but the C-N bond scission mechanism needs to be defined. The nature of the catalytic function responsible for C-N bond scission will be determined by measuring the scission rates, using mainly decahydroquinoline, over a set of catalysts prepared specifically to evaluate the catalyst requirements for N extraction. The catalysts to be tested include acid catalysts without metal, Co/Ni-impregnated alumina

with various levels of sulfiding from in situ H_2S at low partial pressures, and unsupported molybdenum sulfide with and without Ni promotion to separate out the role of the support. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the C-N bond scission function) will be demonstrated. Promising catalysts will be tested for selectivity and activity maintenance over long-term runs using highly aromatic synthetic feeds and, ultimately, coal-derived liquids.

Another part of this research, and potentially the most beneficial part, requires the development of new, highly-selective hydrodenitrogenation catalysts. This work will focus on developing catalysts that can selectively coordinate and remove nitrogen from multi-ring aromatic heterocycles while minimizing hydrogenation of the aromatic rings, thus achieving major savings in hydrogen consumption. The catalysts formulated will be tested under high-pressure liquid-phase conditions using quinoline in a carrier oil as a reactant, since quinoline has the unsaturated heterocyclic ring structure characteristic of nitrogen-containing compounds present in coal-derived liquids.

The results of all of the above work will be evaluated utilizing our kinetic analysis schemes to quantify the rates of C-N bond scission and define the rates and extents of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties, and recommendations will be made regarding further studies, following the potentially most fruitful directions.

III. SUMMARY OF PROGRESS TO DATE

During the first seven quarters, substantial progress has been made in understanding the chemistry of carbon-nitrogen bond scission. Decahydroquinoline hydrodenitrogenation results indicate that C-N bond scission is not thermal but catalytic. Our preliminary results indicate that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission, and therefore such bond scission must occur at other sites in the catalyst. One such possibility is that C-N bond scission is catalyzed by an active site consisting of a transition metal ion in close proximity to an acid site. Hence, it would appear that hydrodenitrogenation requires an acid site and a basic site for the elimination reaction to occur.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and C-N bond scission. Several catalysts have been prepared and evaluated, including Brønsted and Lewis acid catalysts without metal (such as HY-zeolite, silica-alumina, and γ -alumina), which are then impregnated with cobalt, molybdenum, nickel, iron, or vanadium. The nature of the catalytic function responsible for C-N bond scission was studied using decahydroquinoline over the set of above catalysts. The results indicated that the nitrogen removal rate was highest for molybdenum on γ -alumina catalyst. These results also show that the nitrogen removal rate decreased with lower concentrations of molybdenum on the γ -alumina support.

Runs have also been made by using sulfided and unsulfided catalysts. It was thought that sulfur formed during sulfiding of the catalyst, blocking the active sites and rendering the catalyst inactive. However, our results indicate that sulfiding of these catalysts does not deactivate them.

Several catalysts have been prepared and tested with the emphasis on understanding the role of acidity on the C-N bond scission reaction and on direct removal of nitrogen without ring hydrogenation. Catalysts prepared by two different techniques, coprecipitation and impregnation, were compared using decahydroquinoline as the reactant. One catalyst synthesized by the above methods was 2%Ni, 2%Mo/AlBO₃. Results indicate that the catalyst prepared by coprecipitation removed nitrogen much faster than the catalyst prepared by impregnation techniques.

Hydrodenitrogenation of quinoline has been studied by using nickel-tungsten catalyst mixtures on alumina and silica-alumina supports. Initial results indicate that these catalysts have very high nitrogen removal rates.

Runs have been made using phenothiazine as a model compound to quantify and compare the hydrodenitrogenation and hydrodesulfurization rates. It appears that carbon-sulfur bonds in phenothiazine are broken very fast when compared to C-N bond cleavage. Data from these runs are being evaluated utilizing our kinetic analysis schemes to yield quantitative rates of C-N and C-S bond scission.

CUMULATIVE EXPENDITURES

	<u>First Quarter</u>	<u>Second Quarter</u>	<u>Third Quarter</u>	<u>Fourth Quarter</u>
PERSONNEL	5,334	21,252	38,755	59,956
TRAVEL	0	0	897	1,011
SUPPLIES AND EXPENSES	212	2,635	5,475	9,916
OCCUPANCY AND MAINTENANCE	0	0	0	25
EQUIPMENT	585	11,893	12,333	12,333
OTHER EXPENSES	140	1,841	4,424	5,412
TRANSFERS (OVERHEAD)	<u>2,868</u>	<u>10,653</u>	<u>20,056</u>	<u>30,532</u>
	9,139	48,274	81,940	119,195

CUMULATIVE EXPENDITURES

	Fifth Quarter	Sixth Quarter	Seventh Quarter
PERSONNEL	\$ 71,515	\$ 87,255	\$ 102,166
TRAVEL	1,245	1,245	1,245
SUPPLIES AND EXPENSES	18,599	20,641	27,159
OCCUPANCY AND MAINTENANCE	25	1,657	1,657
EQUIPMENT	21,508	26,493	26,493
OTHER EXPENSES	5,412	7,158	8,771
TRANSFERS (OVERHEAD)	37,624	48,459	59,491
	\$155,928	\$192,908	\$226,982

*TIME PLAN AND MILESTONE CHART

YEAR
TASK STATEMENT

0 1/2 1 1 1/2 2 2 1/2 3

e. Development of selective HDN catalysts using various metals and supports

f. Test all catalysts from task e for HDN activity and reactivity.

g. Kinetic analysis, interpretation of results, and recommendations.

Scheduled

Underway

* Number in hatched region indicates the percentage completed.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

TASK 1 - Development of Improved Hydrodenitrogenation Catalysts

Hydrodenitrogenation of aromatic heterocycles occurs via a complex reaction network, involving hydrogenation of the aromatic rings followed by C-N bond breakage, (in contrast, hydrodesulfurization occurs by direct scission of C-S bonds). Hence, it is critical to determine the nature of the catalyst sites which promote the denitrogenation reactions to rationally develop upgraded catalysts.

Metal sulfides provide the hydrogenation function in typical commercial hydrotreating catalysts, although a detailed understanding of the nature of the active site and reaction mechanism is still lacking. The function providing for C-N bond scission reactions is less clear. An understanding of the chemistry of C-N bond cleavage is approached by choosing a model compound; quinoline is representative of an abundant molecular group in coal-derived liquids. Prior work has shown that quinoline exhibits the behavior characteristic of most nitrogen-containing heterocycles derived from coal. Hydrodenitrogenation of quinoline was studied, employing nickel-tungsten oxides on alumina and zeolites as catalysts.

Preparation of Ni-W/Al₂O₃ and Ni-W/SiO₂-Al₂O₃ Catalysts

These catalysts were prepared by the impregnation technique. Ni(NO₃)₂·6H₂O and (NH₄)₆H₂W₁₂O₄·XH₂O were dissolved in

water, and the resulting pH was approximately 2.0. Since the supports are subject to attack at low pH, ammonium hydroxide was added to a pH of 5.0. The solution was allowed to stabilize for 30 minutes, and the acidity readjusted to pH 5.0 (higher pH created an insoluble light green precipitate). The support was added and stirred for 5 minutes, then filtered, dried at 120°C, and calcined for 4 hours at 400°C. The impregnation process was repeated three times for each catalyst, to a final composition of 6% NiO and 19% WO₃.

TABLE 1

Standard Operating Conditions

Temperature:	$350 \pm 2^{\circ}\text{C}$
Total Pressure:	$34 \pm 1 \text{ atm}^*$
Reactant Concentration:	0.5 wt % in <u>n</u> -hexadecane
CS ₂ Loading	0.05 wt % (≈ 1.4 vol % H ₂ S in gas phase)
Catalyst Loading:	0.5 wt % of reaction mixture (150-200 mesh size)

*Partial pressure of n-hexadecane @ $350^{\circ}\text{C} \approx 3.24 \text{ atm}$.

Figure 1: Concentration profiles for hydrogenation of quinoline, using nickel-tungsten/alumina catalyst.

Figure 2: Concentration profiles for hydrodenitrogenation of quinoline, using nickel-tungsten/silica-alumina catalyst.

Figure 3: Nitrogen removal rate for hydrodenitrogenation of quinoline, using nickel-tungsten/alumina catalyst

Figure 4; Nitrogen removal rate for hydrodenitrogenation of quinoline, using nickel-tungsten/silica-alumina catalyst

Hydrodenitrogenation of quinoline was studied using a 300 c.c. autoclave fitted with a magnetic drive stirrer. Standard operating conditions (Table 1) were used for all the experimental runs. The catalyst was presulfided for two hours with a mixture of 10 vol% H_2S in hydrogen at atmospheric pressure and $400^{\circ}C$. To keep the catalyst in the sulfided form during the reaction, 0.05 wt% CS_2 was introduced with the hexadecane carrier oil. Under the operating conditions, carbon disulfide rapidly converts to methane and hydrogen sulfide.

Liquid samples were analyzed using Perkin-Elmer model 3920 gas chromatographs equipped with both flame ionization and nitrogen-specific detectors. A glass capillary column (OV-101) was used for all reactant and product analysis.

Figure 1 and 2 show results from denitrogenation with nickel-tungsten on γ -alumina and on silica-alumina (Harshaw Ni-4301) catalysts. The major products from these runs were 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline, n-propylcyclohexane, and n-propylbenzene; minor products included o-propylaniline, decahydroquinoline, and aniline.

Figures 3 and 4 show the nitrogen removal rates for the above two catalysts. The total nitrogen removal for nickel-tungsten on γ -alumina and on silica-alumina were 74% and 91%, respectively. These results show that nickel-tungsten on γ -alumina or silica-alumina support has very high activity, and is comparable to standard Ni-Mo/ γ -alumina (HDS-9A) catalyst.

TASK 2- Development of Catalysts Effecting Hydrodenitrogenation with Minimized Hydrogenation of Heterocyclic Rings.

The objective of this task is to develop novel, highly selective hydrodenitrogenation catalysts that can selectively coordinate nitrogen and remove it from multi-ring heterocyclic aromatics with minimal hydrogenation of the rings. This could lead to major savings in industrial hydrogen consumption.

In current work, runs were made using phenothiazine as a reactant to quantify and compare the hydrodenitrogenation and hydrodesulfurization rates. Initial results indicate that all of the phenothiazine had fragmented within 5 minutes, and that no sulfur-or nitrogen-containing organics were present in the reaction solution after 450 minutes of reaction. It appears that carbon-sulfur bonds in the reactant are broken very fast, yielding either diphenylamine or N-cyclohexylaniline as an intermediate. A carbon-nitrogen bond is then broken in either instance, giving aniline and cyclohexane or benzene. The carbon-nitrogen bond in aniline is then cleaved to give benzene. Benzene formed is almost quantitatively hydrogenated, and the starting material is essentially transformed to cyclohexane after 450 minutes of reaction. Figure 5 shows the proposed route of reaction.

Presently, the results of this catalyzed reaction are being evaluated utilizing our computerized kinetic analyses, to give quantitative rates of C-N and C-S bond scission and the extents and rates of hydrogenation. Planned experimentation includes a

Figure 5: Reaction mechanism for hydrodenitrogenation and hydrodesulfurization of phenothiazine

comparison of different catalysts, temperatures, and pressures on the reaction rates.

Appendix "D"

FE-3297-8
Dist. Category UC-90d

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION
OF COAL-DERIVED LIQUIDS

Eighth Quarterly Report for Period
June 15, 1980 to September 15, 1980

Prepared by:

James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
Chemical Engineering Department
University of Delaware
Newark, Delaware 19711

Date Published:

October 1, 1980

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

Under Contract No. ET-78-5-01-3297

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their contractors, subcontractors, or 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.

TABLE OF CONTENTS

	<u>Page</u>
I. ABSTRACT.....	1
II. OBJECTIVES AND SCOPE.....	2
III. SUMMARY OF PROGRESS TO DATE.....	5
Time Plan and Milestone Chart.....	7
Cumulative Expenditures.....	9
IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS...	10
V. PERSONNEL.....	31

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Concentration profiles for HDN of quinoline using 3% NiO/18% MoO ₃ on 0.26% chlorided alumina catalyst	14
2. Total nitrogen removal from quinoline using HDS-9A catalyst	15
3. Total nitrogen removal from quinoline using 3% NiO/18%MoO ₃ on 0.26% chlorided alumina	16
4. Total nitrogen removal from quinoline using 3% NiO/18%MoO ₃ on 0.06% chlorided alumina	17
5. Reaction network for quinoline HDN	18
6. Concentration profile for quinoline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	22
7. Concentration profile for 1,2,3,4-tetrahydroquinoline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	23
8. Concentration profile for 5,6,7,8-tetrahydroquinoline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	24
9. Concentration profile for decahydroquinoline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	25
10. Concentration profile for propylaniline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	26
11. Concentration profile for aniline in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	27
12. Concentration profile for n-propylbenzene in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	28
13. Concentration profile for n-propylcyclohexane in HDN of quinoline using Ni-Mo/AlBO ₃ catalyst	29

LIST OF TABLES

<u>Table</u>	<u>Page</u>
1. Standard operating conditions	13
2. First-order rate constants for quinoline HDN using fluorided catalysts	19
3. Comparison of rate constants for hydrodenitrogenation of quinoline using Ni-Mo/AlBO ₃ and HDS-9A catalysts	30

I. ABSTRACT

Several catalysts have been prepared and tested with the emphasis on understanding the role of acidity in the carbon-nitrogen bond scission reaction. Hydrodenitrogenation of quinoline has been studied by using chlorided alumina catalysts. Preliminary results show a slight increase in nitrogen removal rate when chlorided versus unchlorided alumina supports are used.

Experimental runs have also been made using 3.5% NiO/18% MoO₃ on AlBO₃ catalyst (prepared by co-precipitation). Even though the total nitrogen removal rates were same for the co-precipitated and standard HDS-9A catalyst, there is a reduction in the relative rate constants which require total hydrogenation prior to deamination.

II. OBJECTIVES AND SCOPE

The major objectives of the proposed research are:

- To apply the reaction study and kinetic analysis techniques which we have developed to the optimization of catalysts for hydrodenitrogenation of unsaturated multi-ring organic compounds. Also, to balance the hydrogenation and carbon-nitrogen bond scission functions, thereby developing improved hydrodenitrogenation catalysts.
- To define more completely the catalyst function required by C-N bond scission, since this function is critical to hydrodenitrogenation.
- To develop unique catalysts for hydrodenitrogenation of multi-ring heterocycles without first requiring hydrogenation of the attendant aromatic moieties.
- To determine the stability of catalysts developed for processing coal-derived liquids.

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission, and the C-N cleavage mechanism needs to be defined. The nature of the catalytic function responsible for C-N bond scission will be determined, (using mainly decahydroquinoline) over a set of catalysts prepared specifically to evaluate the catalytic requirements

for nitrogen extraction. The catalysts to be tested include acid catalysts without metal, Co/Ni-impregnated alumina, and unsupported molybdenum sulfide with and without Ni promotion to separate out the role of the support. All these systems will be subjected to H_2S at a low partial pressure to test the effect of sulfur poisoning. Based on the above studies, methods of optimizing catalysts (by balancing the hydrogenation and the C-N bond scission functions) will be demonstrated. Promising catalysts will be tested for selectivity and activity maintenance over longer term runs, using highly aromatic synthetic feeds and, ultimately, coal-derived liquids.

Another part of this research, and potentially the most beneficial part, requires the development of new, highly-selective hydrodenitrogenation catalysts. This work will focus on developing catalysts that can selectively coordinate nitrogen and remove it from multi-ring aromatic heterocycles while minimizing hydrogenation of the rings, thus achieving major savings in hydrogen consumption. The catalysts formulated will be tested under high-pressure liquid-phase conditions using quinoline in a carrier oil as a reactant, since quinoline has the unsaturated heterocyclic ring structure characteristic of heterocyclic compounds present in coal-derived liquids.

The results of all of the above work will be evaluated utilizing our kinetic analysis schemes, to measure quantitatively the rates of C-N bond scission and the extent and rates

of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties, and further work will follow the potentially most fruitful directions.

III. SUMMARY OF PROGRESS TO DATE

During the first two years, substantial progress has been made in understanding the chemistry of carbon-nitrogen bond scission. Decahydroquinoline hydrodenitrogenation results indicate that C-N cleavage is not thermal but catalytic. Our preliminary results indicate that catalyst Brønsted acidity by itself will not promote C-N bond scission, and, therefore, such bond scission must occur on other catalyst sites. One possibility is that C-N bond scission is catalyzed by an active site consisting of a transition metal ion in close proximity to an acid site. Hence, it would appear that hydrodenitrogenation requires both an acidic and a basic site for the elimination reaction to occur.

Improved hydrodenitrogenation catalysts require a better balance between hydrogenation and C-N bond scission. Several catalysts have been prepared and evaluated, including Brønsted and Lewis acid catalysts without metal (such as HY-zeolite, silica-alumina, and γ -alumina), which are then impregnated with cobalt, molybdenum, nickel, iron, tungsten, or vanadium. The nature of the catalytic function responsible for C-N bond cleavage was studied using decahydroquinoline over the set of above catalysts. The results indicated that the nitrogen removal rate was highest for molybdenum and tungsten on γ -alumina catalysts. These results also show that the nitrogen removal rate decreased with lower concentrations of molybdenum on the γ -alumina support.

Runs have also been made by using sulfided and unsulfided catalysts. It was thought that sulfur formed during sulfiding of the catalyst, blocking the active catalytic sites. However, our results indicate that sulfiding of these catalysts does not deactivate them.

Several catalysts have been prepared and tested with the emphasis on understanding the role of acidity on the C-N bond scission reaction and on direct nitrogen removal without ring hydrogenation. Catalysts prepared by two different techniques (co-precipitation and impregnation) were compared using decahydroquinoline as the reactant. One catalyst prepared by the above techniques was 2%Ni,2%Mo/AlBO₃. Results indicate that the catalyst prepared by co-precipitation removed nitrogen more readily than the same catalyst prepared by impregnation techniques.

Runs have been made using phenothiazine as a reactant to quantify and compare the hydrodenitrogenation and hydrodesulfurization rates. It appears that carbon-sulfur bonds in phenothiazine are broken very fast, compared to carbon-nitrogen bonds in similar heterocycles.

To increase the acidity function, several catalysts have been prepared by addition of fluoride and chloride to the alumina support. Preliminary results show a slight increase in nitrogen removal with treated versus untreated supports.

TIME PLAN AND MILESTONE CHART

YEAR

TWO

TASK STATEMENT

0 1/2 1 1 1/2 2 2 1/2 3

- a. Determine the nature of C-N bond scission

- b. Formulate improved catalysts based on a.

- c. Evaluate all catalysts for scission activity

- d. Kinetic analysis and interpretation of results; future plans

YEAR

TWO

0 1/2 1 1 1/2 2 2 1/2 3

TASK STATEMENT

- e. Development of selective HDN catalysts using various metals and supports

- f. Test catalysts from task e for HDN activity and reactivity

- g. Kinetics analysis; future plans for HDN catalysis

Scheduled

Underway

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

<u>QUARTER</u>	<u>PERSONNEL</u>	<u>TRAVEL</u>	<u>SUPP. & EXP.</u>	<u>OCC. & MAINT.</u>	<u>EQUIPMENT</u>	<u>OTHER</u>	<u>OVERHEAD</u>	<u>TOTAL</u>
First	5,334	0	212	0	585	140	2,868	9,139
Second	21,252	0	2,635	0	11,893	1,841	10,653	48,274
Third	38,755	897	5,475	0	12,333	4,424	20,056	81,940
Fourth	59,966	1,011	9,916	25	12,333	5,412	30,532	119,195
Fifth	71,515	1,245	18,599	25	21,508	5,412	37,624	155,928
Sixth	87,255	1,245	20,641	1,657	26,493	7,158	48,459	192,908
Seventh	102,166	1,245	27,159	1,657	26,493	8,771	59,491	226,982
Eighth	125,475	1,631	28,988	1,657	26,493	9,759	70,876	264,879

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

~~TABLE I~~ - Development of Improved Hydrodenitrogenation Catalysts

Hydrodenitrogenation of aromatic heterocycles occurs via a complex reaction network involving hydrogenation of the aromatic rings, followed by carbon-nitrogen bond scission (in contrast to hydrodesulfurization, which involves mainly direct cleavage of carbon-sulfur bonds). Hence, it is critical to determine the nature of the catalytic sites which promote these two reaction types (hydrogenation and C-N bond scission) to rationally develop new and improved catalysts.

Metal sulfides provide the hydrogenation function in typical commercial hydrotreating catalysts, although a detailed understanding of the active sites and the reaction mechanism is still lacking. The origin of the C-N bond scission reaction also is not clear.

To better understand the chemistry of C-N bond cleavage a model compound must be chosen that is similar to coal-derived liquids. Quinoline was judged to exhibit behavior characteristic of coal-derived liquids, and was chosen to investigate the chemistry of C-N bond scission.

- Hydrodenitrogenation of Quinoline

The performances of several fluorided alumina catalysts have been examined, and the results given in an earlier

quarterly report. As in the case of fluoride promotion, addition of chloride to alumina enhances the surface acidity. In order to completely establish the relationship between catalyst acidity and its HDN activity, we initiated study of quinoline hydrodenitrogenation over chlorided alumina catalysts in this quarter. As a starting point, we used catalysts with low (0.06% and 0.26%) chloride levels.

The above chlorided alumina catalysts used in this study were prepared by American Cyanamid Co. (3%NiO, 18%MoO₃ on chlorided alumina). An experimental run using commercial HDS-9A catalyst (3%NiO, 18%MoO₃ on γ -alumina) was also made, to evaluate the effects of chloride. The catalysts were presulfided with 10% H₂S in H₂ at 400°C for 2 hours. All the experimental runs were carried out under standard conditions (Table 1). Figure 1 shows the concentration profiles for quinoline hydrodenitrogenation using 0.26% chlorided alumina catalyst. The same intermediates and products were observed in all experimental runs and the concentration profiles were similar. The total nitrogen removal from quinoline for different catalysts is shown in Figures 2-4.

Furthermore, the reaction network and reaction kinetics for quinoline hydrodenitrogenation were determined, to prove the chemistry of the catalytic action. The proposed reaction network is given in Figure 5. It was found that the system behaved as a first-order reaction with respect to nitrogen-containing

compounds for each step in the network. First-order rate constants were estimated according to the technique developed by Himmelblau et al. The results summarized in Table 2 demonstrate that the addition of chloride to alumina at low levels makes no significant difference in HDN activity.

Because of the inconclusiveness of these results, further experiments using more highly chlorided alumina have been planned. Strongly acidic alumina catalysts with elevated chlorine concentrations can be prepared by the reaction of alumina with chlorinating agents (such as aluminum chloride, carbon tetrachloride, thionyl chloride, and other chlorinated organic compounds). We have synthesized a catalyst by alumina-methylene chloride reaction, and the associated HDN activity examination is underway.

TABLE 1

Standard Operating Conditions

Temperature:	$350 \pm 2^\circ\text{C}$
Total Pressure:	$34 \pm 1 \text{ atm}^*$
Reactant Concentration:	0.5 wt % in <u>n</u> -hexadecane
CS ₂ Loading:	0.05 wt % (≈ 1.4 vol % H ₂ S in gas phase)
Catalyst Loading:	0.5 wt % of reaction mixture (150-200 mesh size)

*Partial pressure of n-hexadecane @ $350^\circ\text{C} \approx 3.24 \text{ atm}$.

Figure 1: Concentration profiles for HDN of quinoline using 3%NiO, 18% MoO₃ on 0.26% chlorided alumina catalyst.

Figure 2: Total nitrogen removal from quinoline using HDS-9A catalyst.

Figure 3: Total nitrogen removal from quinoline using 3%NiO, 18%MoO₃ on 0.26% chlorided alumina.

Figure 4: Total nitrogen removal from quinoline using 3%NiO, 18%MoO₃ on 0.06% chlorided alumina.

Figure 5: Reaction network for quinoline HDN.

TABLE 2. First-order rate constants for quinoline HDN.

Rate constant Run No.	K ₃	K ₄	K ₅	K ₆	K ₇	K ₈	K ₉	K ₁₀	K ₁₁	K ₁₂	K ₁₃	K ₁₄
(HDS-9A) (γ -Alumina)	20.23	4.83	1.12	1.20	1.15	0.54	23.30	1.38	0.75	1.97	0.17	1.88
(0.26% Cl) (γ -Alumina)	14.14	4.48	1.06	1.53	1.93	0.83	22.90	2.19	0.70	5.77	0.47	0.59
(0.06% Cl) (γ -Alumina)	18.57	3.64	2.00	1.54	1.93	0.75	28.46	2.23	0.73	5.2	0.48	1.74

TASK 2 - Development of catalysts effecting hydrodenitrogenation with minimized hydrogenation of heterocyclic rings.

The objective of this task is to develop novel, highly selective hydrodenitrogenation catalysts that can selectively coordinate nitrogen and remove it from multi-ring aromatic heterocycles with minimal ring hydrogenation. This could lead to major savings in industrial hydrogen consumption.

A catalyst is desired that can act as a Lewis acid, consequently coordinating selectively with the nitrogen lone pair. The nitrogen coordination would reduce the aromaticity of the nitrogen-containing ring, thus facilitating nitrogen removal and lessening the possibility of hydrogenating the neighboring aromatic rings.

In an attempt to compare the deamination rates of a Lewis acid catalyst against a standard catalyst, runs were made using aluminum borate with 3.5%NiO, 18%MoO₃ (Ni-Mo/AlBO₃, prepared by co-precipitation) as the Lewis acid catalyst and HDS-9A (γ-alumina with 3.5%NiO, 18%MoO₃) as the standard catalyst. The results indicate a reduction in those relative rate constants which require total hydrogenation prior to deamination (quinoline + 5,6,7,8-tetrahydroquinoline or 5-8 THQ).

The runs were made under standard conditions (500 psig, 350°C, sulfided catalyst) and the numerical results are shown in Table 3; concentration profiles, calculated and experimental,

are depicted in Figures 6-13. The amount of total nitrogen removed was similar with either catalyst. The relative rate constant for 5-8 THQ generation is doubled in the Ni-Mo/AlBO₃ runs when compared to the HDS-9A experiments. This indicates that the nitrogen removal process prefers the 1-4 THQ pathway in the Ni-Mo/AlBO₃ system, thus reducing the total hydrogen consumption observed in the standard (HDS-9A) deamination process.

Additional experiments are underway with the Ni-Mo/AlBO₃ catalyst using varying reactant concentrations.

Figure 6: Concentration profile for quinoline in HDN of quinoline using Ni-Mo/ Al_2O_3 catalyst.

Figure 7: Concentration profile for 1,2,3,4-tetrahydroquinoline in HDN of quinoline using Ni-Mo/ AlBO_3 catalyst.

Figure 8: Concentration profile for 5,6,7,8-tetrahydroquinoline in HDN of quinoline using Ni-Mo/ AlBO_3 catalyst.

Figure 9: Concentration profile for decahydroquinoline in HDN of quinoline using Ni-Mo/ AlBO_3 catalyst.

Figure 10: Concentration profile for o-propylaniline in HDN of quinoline using Ni-Mo/ Al_2O_3 catalyst.

Figure 11: Concentration profile for aniline in HDN of quinoline using Ni-Mo/ AlBO_3 catalyst.

Figure 12: Concentration profile for n-propylbenzene in PDN of quinoline using Ni-Mo/ AlBO_3 catalyst.

Figure 13: Concentration profile for n-propylcyclohexane in HDN of quinoline using Ni-Mo/Al₂O₃ catalyst.

Averaged rate constants, gm oil/gm catalyst

	AlBO ₃ /NiMo		HDS-9A	
	actual rates	relative	actual rates	relative
k ₁	218.17	32.5	185.57	15.7
k ₂	31.32	4.7	26.78	2.3
k ₃	6.7	1.0	11.31	1.0
k ₄	1.8	0.27	1.99	0.17
k ₅	0.82	0.12	1.02	0.086
k ₆	0.71	0.11	1.15	0.097
k ₇	0.58	0.087	1.20	0.10
k ₈	0.16	0.024	0.50	0.042
k ₉	4.8	0.72	14.44	1.2
k ₁₀	0.87	0.13	1.62	0.14
k ₁₁	0.36	0.054	0.73	0.062
k ₁₂	0.46	0.069	4.21	0.36

TABLE 3. Comparison of rate constants for HDN of quinoline using Ni-Mo/AlBO₃ and HDS-9A catalysts.

V. PERSONNEL

There has been no change in personnel during this quarter.

RECEIVED BY TIC MAY 14 1981