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FOSSIL ENERGY

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

Annual Report for Period September 15, 1978—September 14, 1979

By
James R. Katzer
Alvin B. Stiles
Harold Kwart

October 1, 1980
Date Published

Work Performed Under Contract No. AS22-78ET03297

University of Delaware
Chemical Engineering Department
Newark, Delaware

U. S. DEPARTMENT OF ENERGY

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DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

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James R. Katzer, Alvin B. Stiles and Harold Kwart
Center for Catalytic Science and Technology
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Prepared for:

Fossil Energy
Department of Energy
Washington, D. C.

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

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I. ABSTRACT

Preliminary results from decahydroquinoline hydrodenitrogenation runs show that Brønsted acidity by itself will not catalyze carbon-nitrogen bond scission. The C-N bond cleavage must therefore be catalyzed by an active site, which consists of a transition metal ion in close proximity to an acid site. It appears that hydrodenitrogenation requires both an acidic and a basic site for the Hoffman E_2 elimination reaction to occur.

Several catalysts have been prepared and tested, including Brønsted and Lewis acid catalysts without metal, and silica-alumina and γ-alumina impregnated with molybdenum, vanadium, nickel or iron. Our results show that the nitrogen removal rate was highest for molybdenum on γ-alumina catalyst and the rate decreased with lower Mo concentrations.

Aluminum borate and aluminum borate phosphate catalysts (with or without nickel) were prepared to develop novel catalysts that would selectively coordinate the nitrogen atom and remove it without excessive hydrogenation. Results show that the support plays an important role in the nitrogen-removal process.

Hydrodenitrogenation of aniline has been studied over a presulfided Ni-Mo/γ-Al_2O_3 catalyst, and a reaction network has been proposed. Aniline hydrodenitrogenation appears to involve partial hydrogenation of the benzene ring to reduce aromatic resonance with the nitrogen atom, thus reducing the C-N bond strength and facilitating NH_3 elimination.

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

A. Determine the nature of C-N bond scission

The main thrust of this research is an improved understanding of the catalyst function required by C-N bond scission, since this is a critical but poorly understood process. During the first year, substantial progress has been made in defining the chemistry of C-N bond cleavage, using decahydroquinoline as a model compound.

Decahydroquinoline hydrodenitrogenation results indicate that C-N bond scission is not thermal but catalytic. Our results indicate that Brønsted acidity by itself does catalyze the C-N cleavage, and, therefore, such bond splitting must occur on other catalytic sites. One possibility is that C-N bond scission is catalyzed by active sites, which consist of a transition metal ion in close proximity to an acidic feature. This suggests that hydrodenitrogenation requires both an acidic and a basic site for the elimination reaction to occur.

B. Development of hydrodenitrogenation catalysts

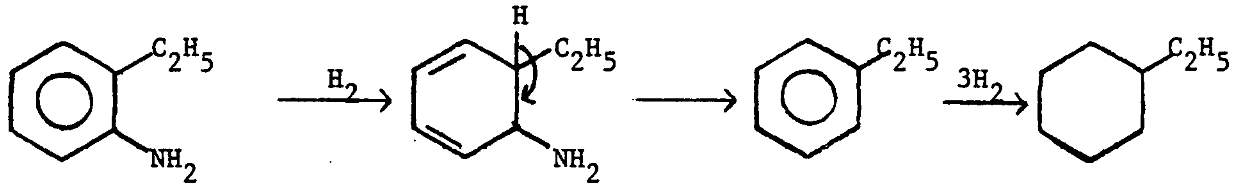
Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. Several catalysts have been synthesized and examined, including Brønsted and Lewis acid catalysts without metal and silica-alumina and γ-alumina impregnated with molybdenum, vanadium, nickel or iron. The nature of the catalytic functions responsible for C-N bond scission was studied employing decahydroquinoline as a model compound with set of above catalysts. Our results indicate that the nitrogen removal rate is highest for molybdenum on γ-alumina catalyst. Experiments also show that this rate decreased with lower molybdenum concentrations.

Experimental runs have been made using quinoline, to develop catalysts that will selectively coordinate and remove the nitrogen atom with minimum hydrogenation, thereby reducing hydrogen consumption. Catalysts used for this study were aluminum borate and aluminum borate phosphate, with or without nickel. Even though the total nitrogen removal rates were the same for the co-precipitated and standard HDS-9A catalyst, results show that there is a reduction in the relative rate constants for total hydrogenation prior to deamination.

C. Catalytic Hydrodenitrogenation

Hydrodenitrogenation of aniline was studied in a 300 c.c. autoclave fitted with a magnetic drive stirrer. The reaction was run at a temperature of 350°C and a pressure of 500 psig. The catalyst used was a typical commercial Ni-Mo/γ-Al_2O_3 (HDS-9A, American Cyanamid; 3.5%NiO-18%MoO_3/Al_2O_3). The catalyst was presulfided and CS_2 added to the reaction mixture to keep the catalyst in sulfided form during the process. Liquid samples were analyzed using a Perkin-Elmer 3920 gas chromatograph.

The results from o-ethylaniline (OEA) hydrodenitrogenation runs show that OEA was rapidly converted to ethylbenzene and ethylcyclohexane. Based on these results, the following reaction netowrk is proposed for hydrodenitrogenation.



o-ethylaniline **ethylbenzene** **ethylcyclohexane**

In the above network, the ring must be partially hydrogenated to weaken the C-N bond (since the C-N bond in o-ethylaniline is strong due to resonance with the ring) before denitrogenation can occur.

TIME PLAN AND MILESTONE CHART

YEAR
One

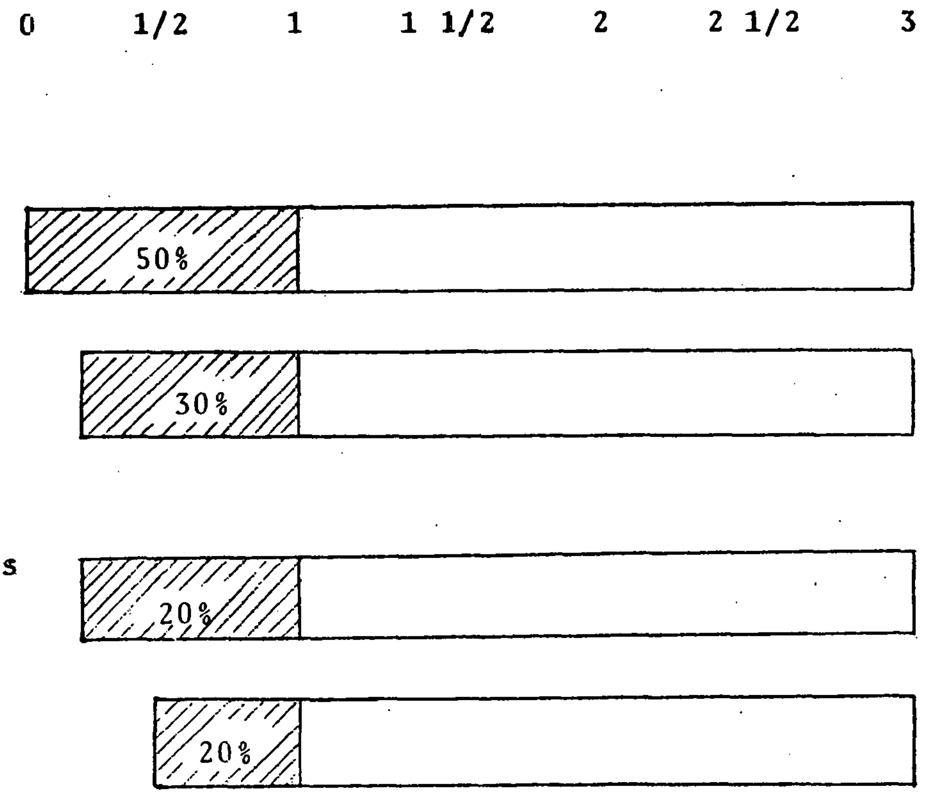
TASK STATEMENT

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

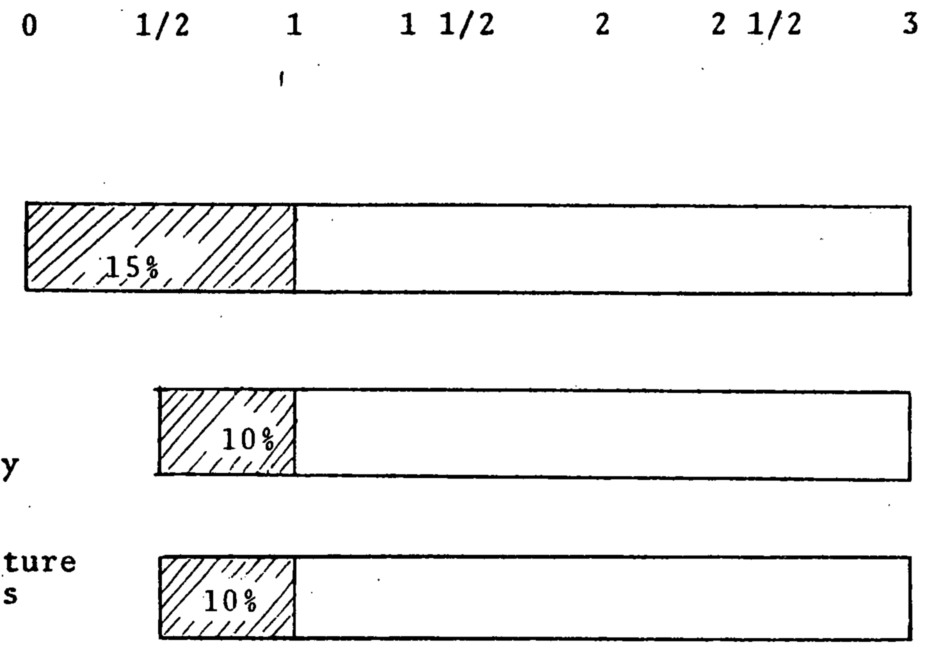
One

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

	First Quarter	Second Quarter	Third Quarter	Fourth Quarter
PERSONNEL	5,334	21,252	38,755	59,966
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)	2,868	10,653	20,056	30,532
	$9,139	$48,274	$81,940	$119,195

IV. PUBLICATIONS

Katzer, J. R., Sivasubramanian, R., "Process and Catalyst Needs for Hydrodenitrogenation" Catalysis Review--Science and Engineering, Vol. 20, No. 2, pp. 155-208.

V. APPENDICES

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

APPENDIX A

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

First Quarterly Report for Period

September 15, 1978 to December 15, 1978

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

March 1, 1979

Prepared for:

Fossil Energy
Department of Energy
Washington, D. C.

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

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I. ABSTRACT

Four experimental runs were made in this quarter. Two of them used decahydroquinoline as reactant and the other two runs were made using orthoethylaniline and quinoline-N-oxide respectively. The decahydroquinoline runs indicate that the carbon-nitrogen bond scission is not thermal but clearly catalytic. Important findings resulted from the run using o-ethylaniline and future runs will help define reaction pathways. Quinoline-N-oxide was rapidly deoxygenated to form quinoline under the conditions tested. Future runs will be conducted in the absence of hydrogen to avoid deoxidation of quinoline-N-oxide and to find out whether carbon-nitrogen bond scission can be promoted by the addition of oxygen to the quinoline molecule.

A review paper has been prepared that reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful direction to be followed in both catalyst and process development.

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, thereby developing improved catalysts for hydrodenitrogenation.

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

- 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 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 C-N bond scission using mainly decahydroquinoline over a set of catalysts prepared specifically to evaluate the catalyst requirements for the C-N bond scission. The catalysts to be tested include acid catalysts without metal, alumina impregnated with Co and Ni with various levels of sulfiding and *in situ* H_2S partial pressure 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, 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 uniquely-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 with only limited or no 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 benzenoid ring and nitrogen-containing aromatic rings 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 give quantitative measures of the rates of C-N bond scission and the extents and rates of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties and recommendations will be made as to what further work needs to be done and the potentially most fruitful directions to be followed.

III. SUMMARY OF PROGRESS TO DATE

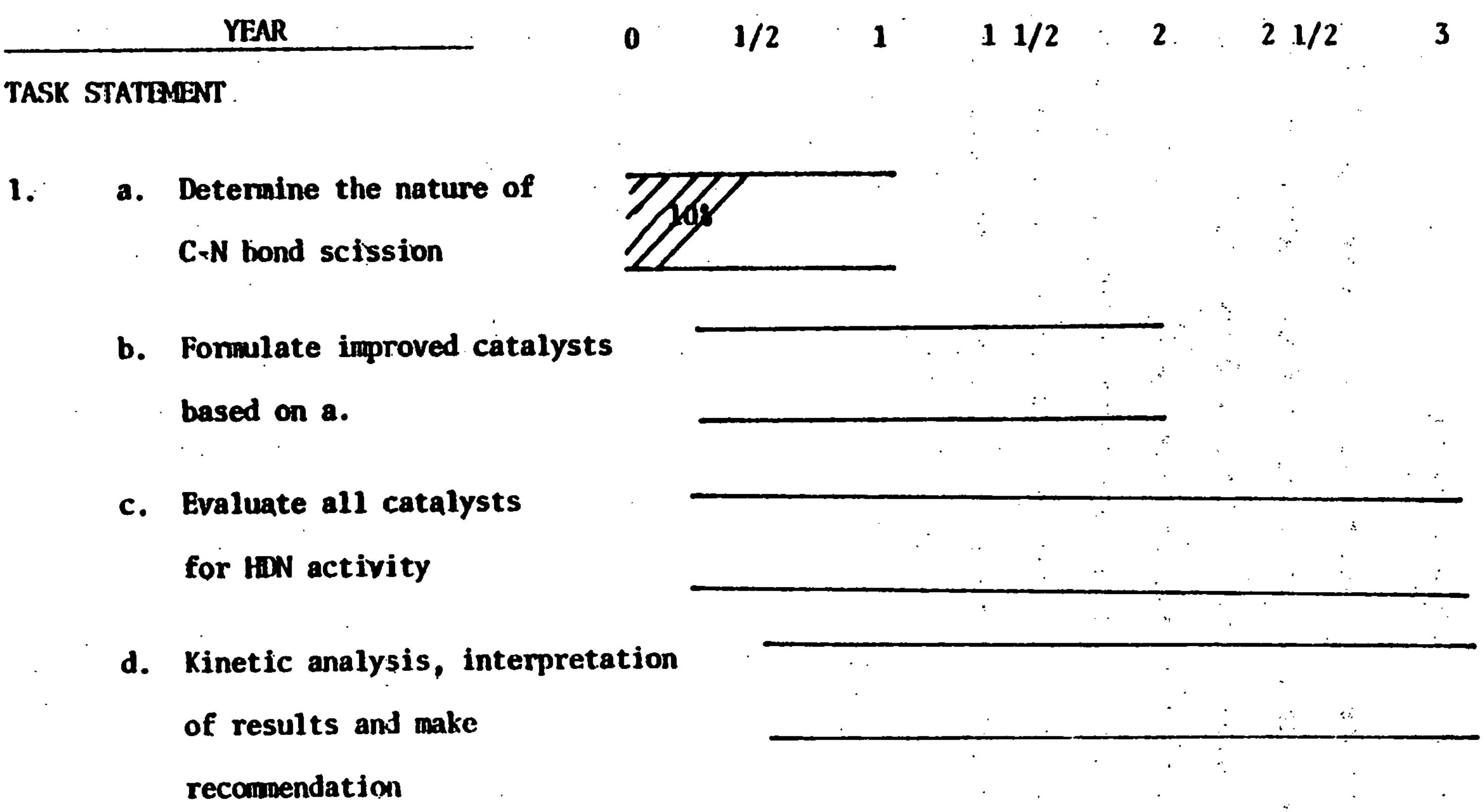
During the first quarter a Gas Chromotograph with a flame ionization detector and a nitrogen specific detector was purchased and analytical techniques were established. An integrator and a recorder were purchased and installed. Chemicals and catalytic materials, including catalyst supports, to be used in this research of this project were obtained.

A high-temperature controlled-atmosphere furnace was purchased and set up. Samples of several catalysts have been prepared; these will be tested in the upcoming quarter.

Four experimental runs were made in this quarter. Two of them used decahydroquinoline as reactant and the other two runs were made using orthoethylaniline and quinoline-N-oxide, respectively. The decahydroquinoline runs were made to determine whether the carbon-nitrogen bond scission is non-ctalytic and also to determine whether the metal surface present in the autoclave reactor (wall and miscellaneous tubes) increase the hydrodenitrogenation activity. Preliminary results indicate that the autoclave walls do not increase the activity, and that carbon nitrogen bond scission is not thermal but is clearly catalytic. In order to better understand the mechanism of hydrodenitrogenation of anilines and substituted anilines, a run was made using orthoethylaniline. Important findings resulted, and future runs will help define reaction pathways. A run was made using quinoline-N-oxide to determine whether the addition of oxygen to the quinoline molecule would reduce the aromaticity of the nitrogen-containing ring thereby making it easier to remove nitrogen directly. Results indicated that quinoline-N-oxide undergoes rapid deoxidation to form quinoline. Future runs will be conducted in the absence of hydrogen to determine the usefulness of this technique.

A paper has been prepared that reviews the existing chemistry and technology for hydrodenitrogenation and projects catalyst and process needs for hydrodenitrogenation of synthetic feedstocks and heavy petroleum liquids. It projects what should be a more effective means and a more rational basis for the design and development of more active and more selective catalysts for hydrodenitrogenation and attempts some speculations on potentially fruitful directions to be followed in both catalyst and process development. A draft of the paper submitted to "Catalysis Reviews" is given in Appendix B.

*TIME PLAN AND MILESTONE CHART



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

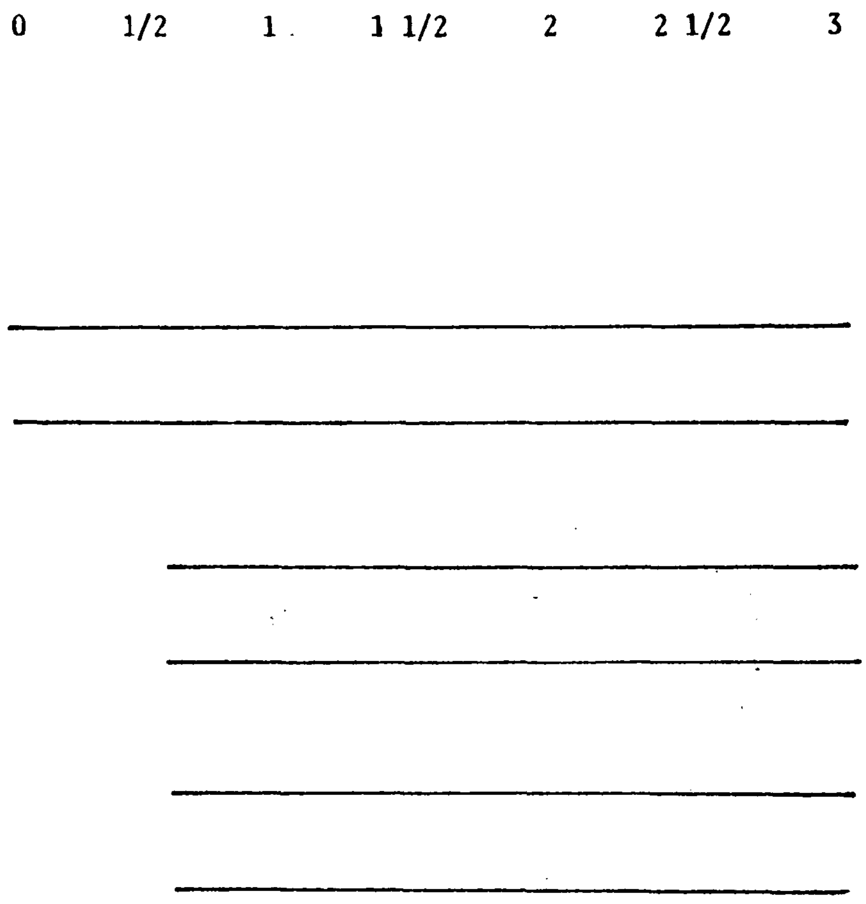
b. Formulate improved catalysts based on a.

c. Evaluate all catalysts for HDN activity

d. Kinetic analysis, interpretation of results and make recommendation

YEAR

TASK STATEMENT



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

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

g. Kinetic analysis interpretation of results and make recommendations.

☐ Scheduled

▨ Underway

■ Completed

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	FIRST QUARTER
PERSONNEL	5334
TRAVEL	0
SUPPLIES AND EXPENSES	212
OCCUPANCY AND MAINTENANCE	0
EQUIPMENT	585
OTHER EXPENSES	140
TRANSFERS (OVERHEAD)	2868
	9,139

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Task 1 - Development of Improved Hydrodenitrogenation Catalysts

Three experiments were conducted in a batch reactor during this quarter. The reactor used was a 300 cm^3 autoclave fitted with a magnetic drive stirrer. Two of the experiments used decahydroquinoline as reactant; orthoethylaniline was used as reactant in the third experiment. Liquid samples were analyzed using a Perkin-Elmer gas chromotograph equipped with a flame ionization detector. A glass capillary column (75 m OV-101) was used for all reactant and product analysis.

a) Decahydroquinoline

The major objective of the runs using decahydroquinoline is to characterize the nature of the carbon-nitrogen bond scission. Since decahydroquinoline is a completely hydrogenated derivative of quinoline, it is an ideal reactant for studying the rates of carbon-nitrogen bond scission. Two experimental runs were conducted in this quarter to determine whether the carbon-nitrogen bond scission reaction is non-catalytic. These runs were conducted in the absence of a catalyst. In order to study the effects of metal surface (walls of the autoclave) present in the reactor, the first run was conducted using a glass liner and the second run was conducted without the glass liner. Reaction conditions were identical for both runs. They were:

- Temperature: 350 ± 2°C
- Total Pressure: 136 ± 2 atm
- Reactant Concentration: 0.5 weight percent decahydroquinoline in hexadecane
- CS_2 loading: 0.05 wt %
- Catalyst Concentration: 0.00

The results from the two runs are presented in Figures 1 and 2. These results indicate some minor differences between the two runs. The products from the run using the glass liner showed traces of quinoline, 1,2,3,4-tetrahydroquinoline, benzene, propylbenzene and normal propylcyclohexane with 5,6,7,8-tetrahydroquinoline and decahydroquinoline as major products. However, the products from the run without glass liner showed only decahydroquinoline, propylbenzene and propylcyclohexane. The dehydrogenation reaction between decahydroquinoline and 5,6,7,8-tetrahydroquinoline was absent in the second run. Also, material balance analysis indicated that all the decahydroquinoline that was placed in the catalyst loader was not injected into the autoclave. Due to experimental difficulties in the second run, the decahydroquinoline was left in the catalyst loader during the operation of the run without glass liner, under a pressure of 500 psig at a temperature of about 80°C for a period of 48 hours. This could have caused some of the differences between the two runs. The run without glass liner will be repeated.

However, preliminary conclusions can still be drawn from these two runs as to whether the carbon-nitrogen bond scission reaction is non-catalytic (thermal). The pseudo first-order rate constant for the carbon-nitrogen bond breaking step for decahydroquinoline can be obtained from earlier quinoline hydrodenitrogenation network studies. Using this value, and assuming that the rate constant will be the same if one starts with decahydroquinoline, the concentration of decahydroquinoline as a function of time can be predicted. Figure 3 presents the predicted curve. Comparison of Figures 1 and 3 indicate that the non-catalytic removal of nitrogen from decahydroquinoline is extremely small; this clearly shows that the C-N bond scission reaction requires a catalyst.

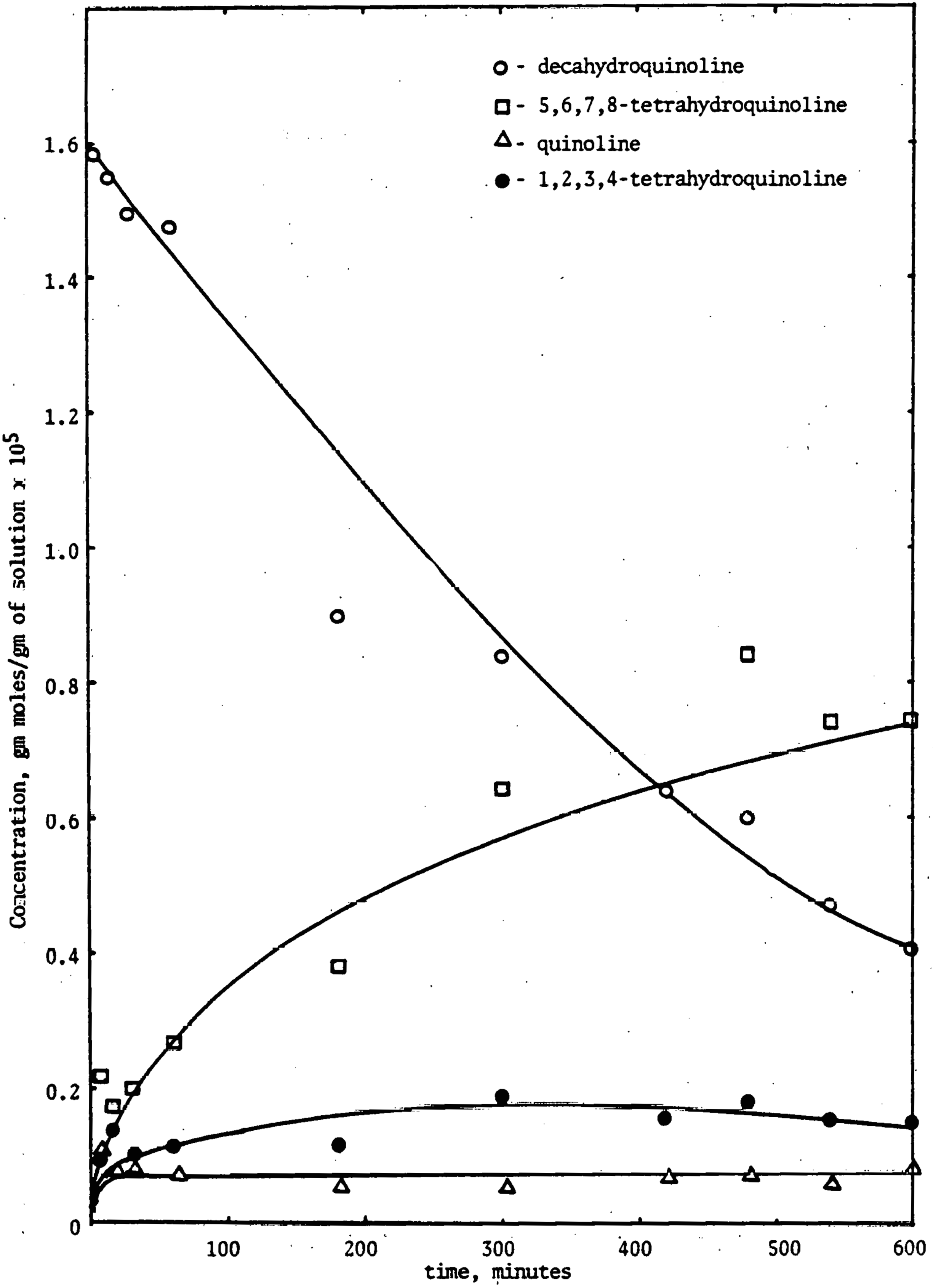


Figure 1. Concentration profiles for hydrodenitrogenation of decahydroquinoline using a glass liner in the reactor.

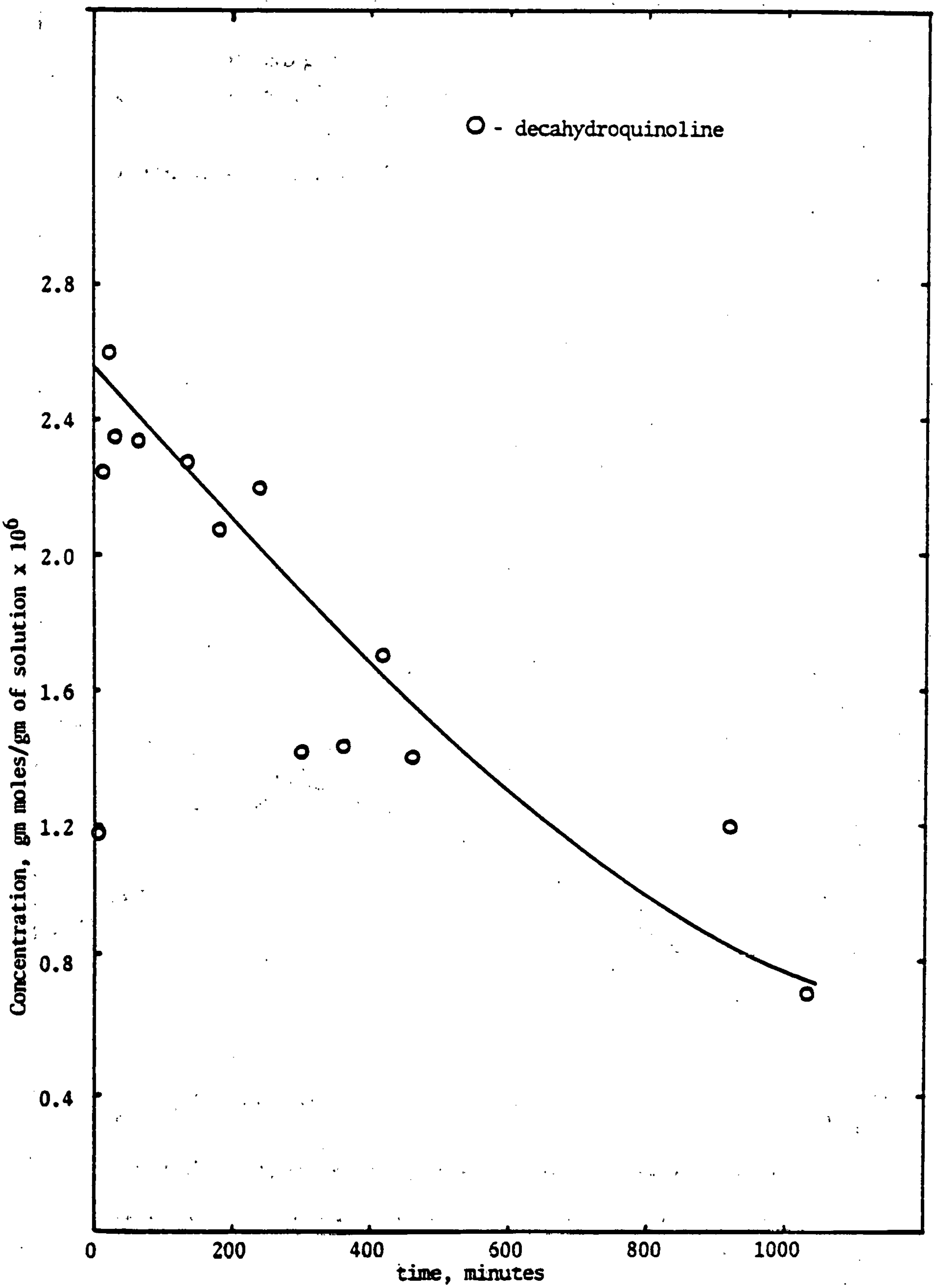


Figure 2. Concentration profile for hydrodenitrogenation of decahydroquinoline without a glass liner.

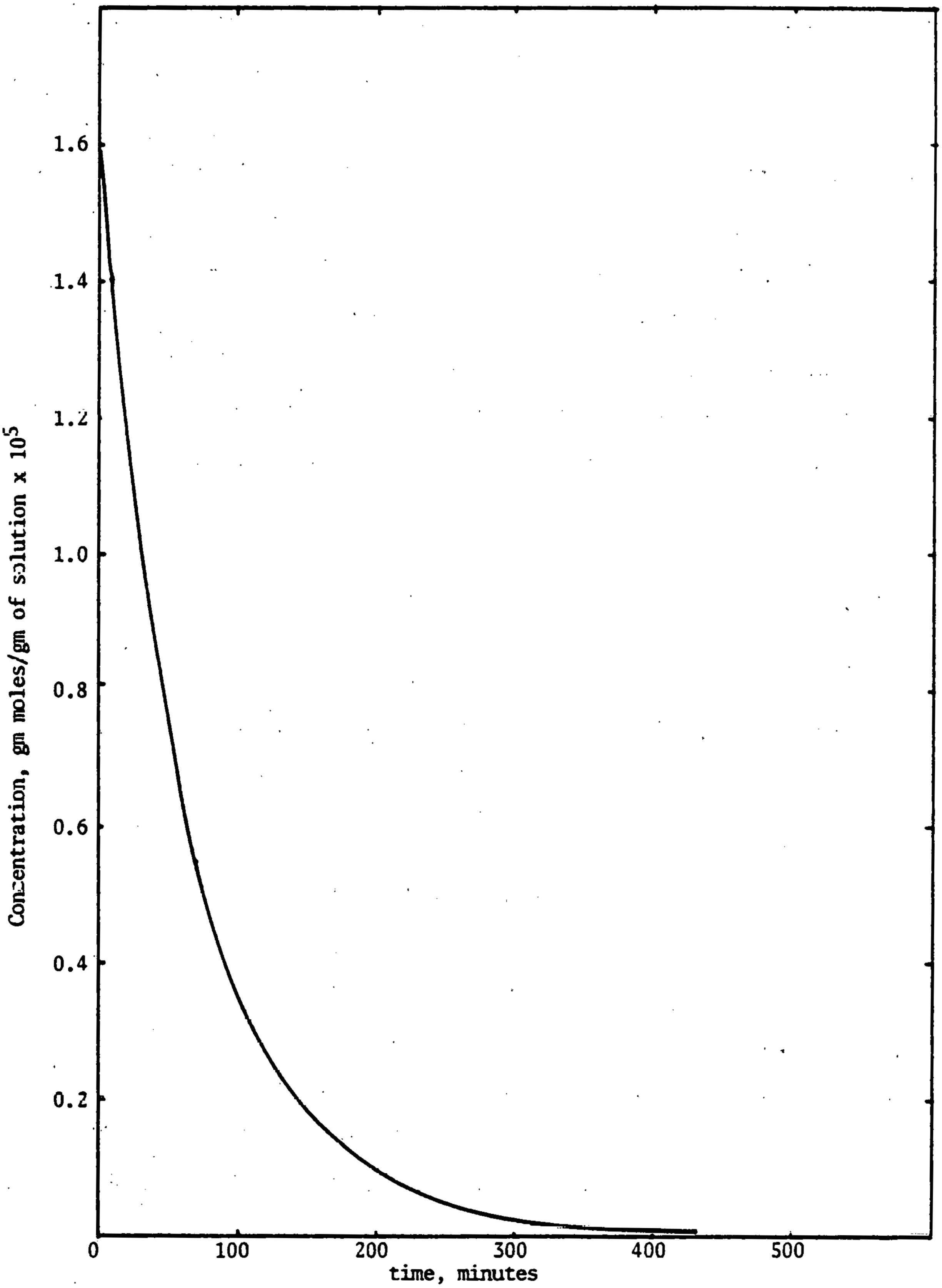


Figure 3. Predicted concentration of decahydroquinoline using pseudo first-order rate constants determined earlier using quinoline network.

The pseudo first-order rate constants for the disappearance of decahydroquinoline were 0.0022 min^{-1} and 0.0012 min^{-1} for the runs with glass liner and without glass liner respectively. If these pseudo first-order rate constants are normalized to a weight of inert solid (non-catalytic) which is the same as the weight of catalyst, then the rate constants are 0.44 and 0.24 (g oil)/(gmol-min) respectively for the two runs. The rate constant for the disappearance of decahydroquinoline using a Ni-Mo/ Al_2O_3 at the same operating conditions calculated from quinoline hydrodenitrogenation is 3.2 (g oil)/g cat-min). Hence, the above results indicate that the increase in metal surface due to removal of glass liner did not appreciably increase the rate of reaction and that the carbon-nitrogen bond scission function is catalytic, i.e., its rate in the absence of catalyst is less than 1/10 that from the catalyst.

In the next quarter, runs will be made using supports with no active metals present and also using several catalysts. These runs should give us an insight into the catalyst requirements for the C-N bond scission.

b) Orthoethylaniline

Hydrodenitrogenation of anilines and substituted anilines have not been studied extensively. Our earlier work on quinoline hydrodenitrogenation indicated that orthopropylaniline may require hydrogenation of the benzene ring before nitrogen can be removed. Since anilines and substituted anilines are the end products from most nitrogen-containing compounds (quinoline, indole), the chemistry of nitrogen removal from these compounds is extremely important. Hence, an experimental run was conducted using orthoethylaniline as a reactant.

Experimental:

The catalyst used was a typical commercial Ni-Mo/γ-Al_2O_3 (HDS 9A, American Cyanamid; NiO 3.5%, MoO_3 18%, Na_2O 0.04%, Fe 0.05%, Al_2O_3 balance).

O-Ethylaniline was used as received (Aldrich Chemical Co., over 99% purity). Solvent n-hexadecane was supplied by Humphrey Chemical Company.

The detailed operating conditions are shown in Table 1. A 300 c.c. autoclave was used in batch mode. The reactor temperature was controlled to ±2°C. The catalyst was presulfided for two hours with a mixture of 10 vol % H_2S in H_2 at atmospheric pressure and 400°C. In order to maintain the catalyst in the sulfided form during the reaction, 0.05 wt % CS_2 solution in hexadecane was added to injection tubing together with catalyst and reactant. Under the operating conditions carbon disulfide rapidly converts to methane and hydrogen sulfide.

Reaction products were analyzed with a Perkin-Elmer Model 3920 gas chromotograph equipped with a flame ionization detector and an electronic integrator.

TABLE 1

EXPERIMENTAL CONDITIONS

Temperature:	350°C
Total Pressure:	500 psig
Catalyst:	Ni-Mo/Al_2O_3, 150-200 mesh sulfided for 2 hours at 400°C i the presence of 10% H_2S/H_2
Catalyst loading:	0.5 wt %
CS_2 conc. in feed:	0.05 wt %
Carrier oil (solvent):	n-hexadecane
Reactant Conc.: (OEA or QNO)	1 wt %
Autoclave Volume:	300 c.c.

Results and Discussion:

The results from o-ethylaniline hydrodenitrogenation runs are discussed below.

The results of a standard run are shown in Figure 4. O-ethylaniline was rapidly converted to ethylbenzene and ethylcyclohexane. Preliminary studies show that indoline was also present in the reaction products. There were no other nitrogen-containing compounds detected.

It can be seen from Figure 4 that formation of ethylbenzene and ethylcyclohexane was relatively rapid while the conversion of o-ethylaniline to indoline was relatively slow. Figure 4 shows that both ethylcyclohexane and ethylbenzene are the primary products of the reaction. As shown in Figure 5, the initial concentration of ethylbenzene is higher than the concentration of ethylcyclohexane (network I). While after initial 40 minutes the concentration of ethylcyclohexane increases very rapidly while the concentration of ethylbenzene remains approximately constant.

Based on the results presented in Figures 4 and 5, two different reaction networks can be defined as shown in Figure 6. In reaction network I, o-ethylaniline forms ethylbenzene by β-elimination process, which on hydrogenation gives ethylcyclohexane. In network II, o-ethylaniline forms intermediate 1-ethylcyclohexane,which on hydrogenation forms ethylcyclohexane. However, ethylbenzene can also be formed from this intermediate as shown in network II. In network II, the benzene ring of o-ethylaniline first must be hydrogenated to weaken the C-N bond (since aromatic C-N bond and o-ethylaniline is strong due to resonance with the benzene ring) sufficiently for hydrogenolysis to occur. Thus from networks I and II two

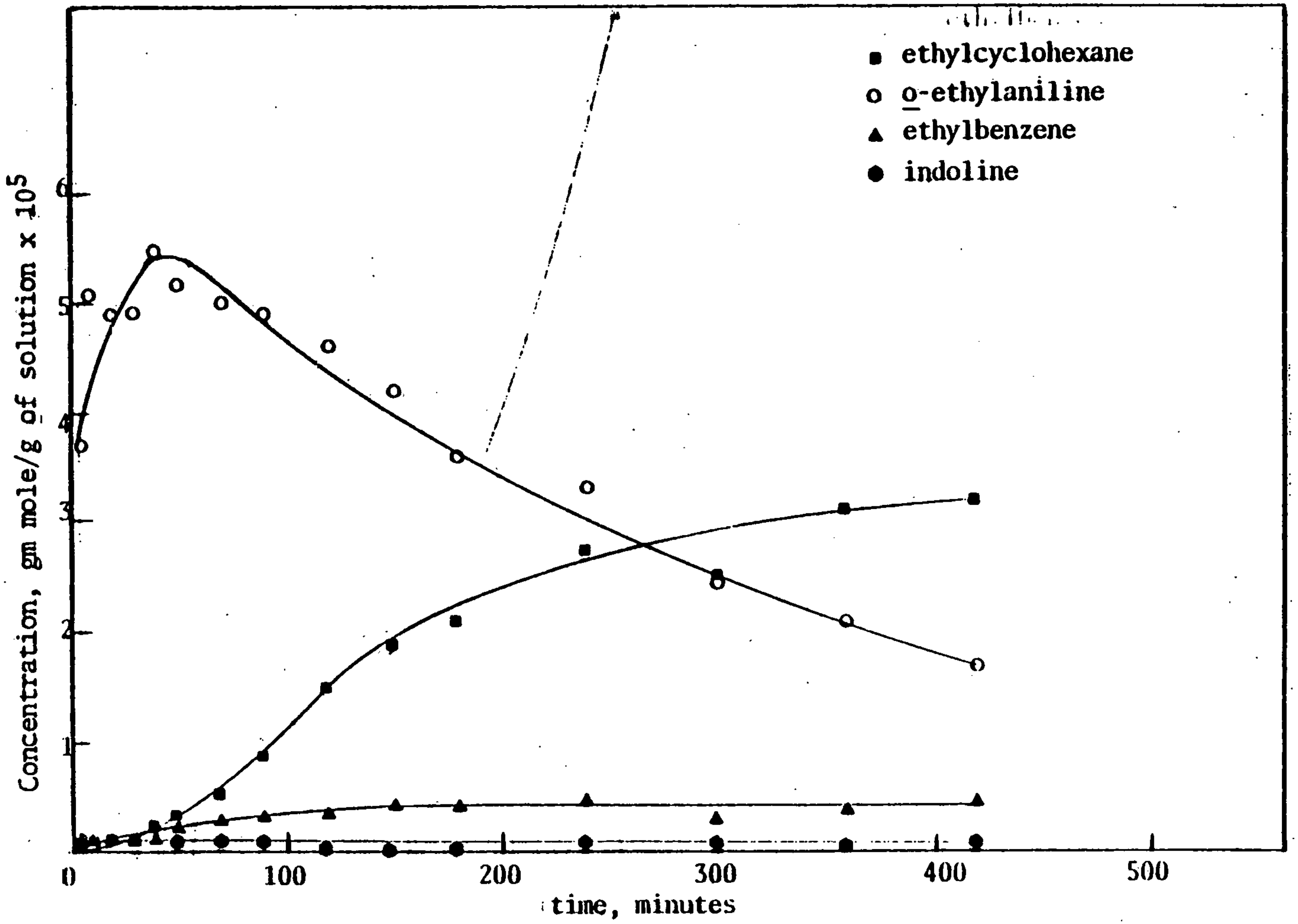


Figure 4. Concentration profiles of various hydrodenitrogenation products of orthoethylaniline.

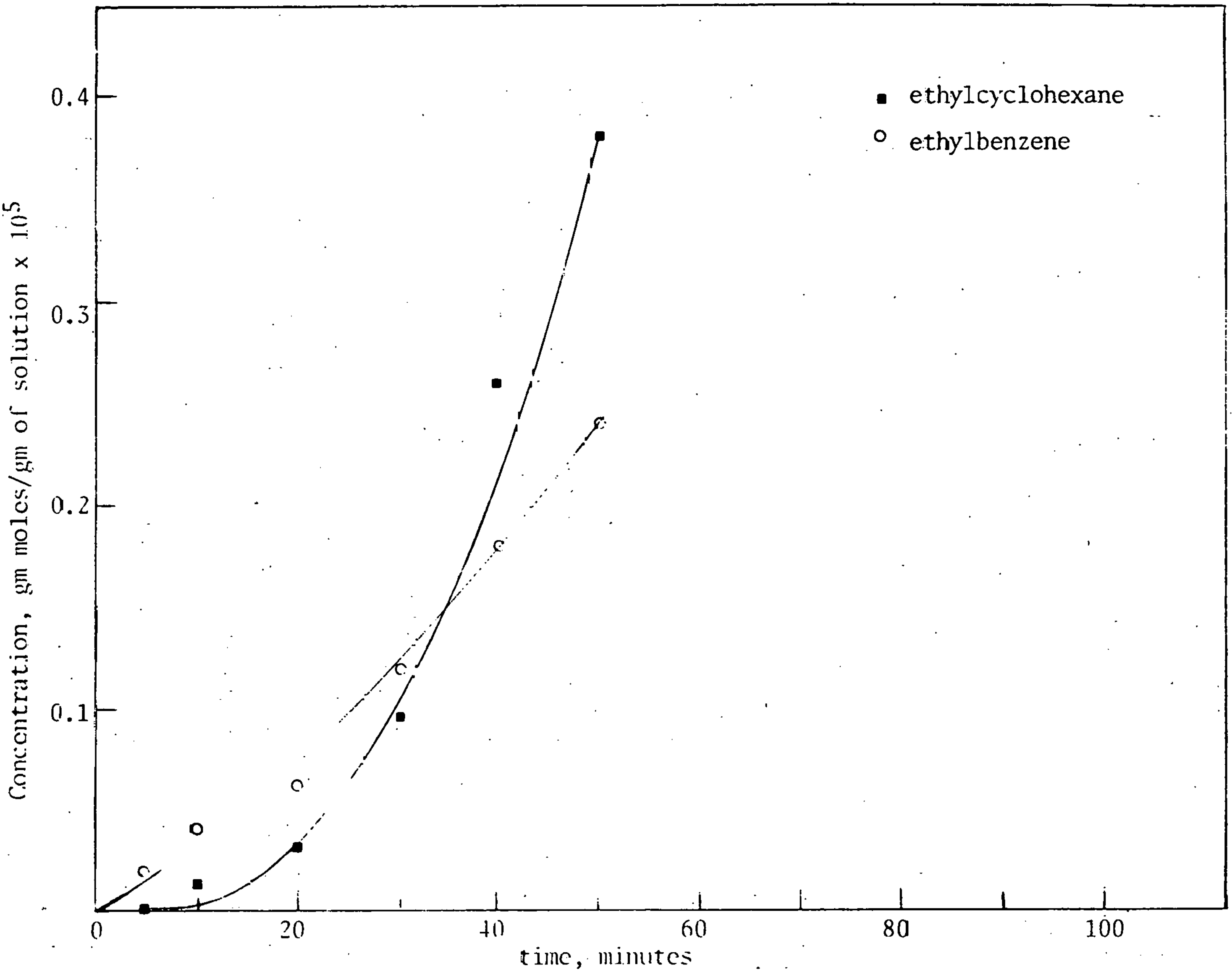
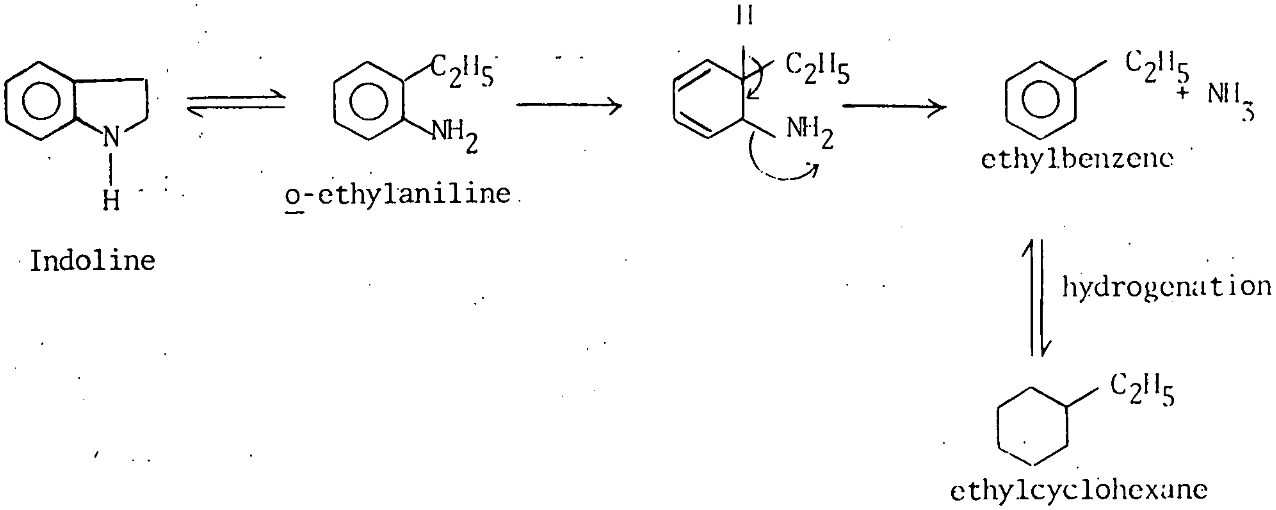


Figure 5. Concentration profiles of ethylcyclohexane and ethylbenzene during the initial period for hydrodenitrogenation of o-ethylaniline.

REACTION NETWORK I



REACTION NETWORK II

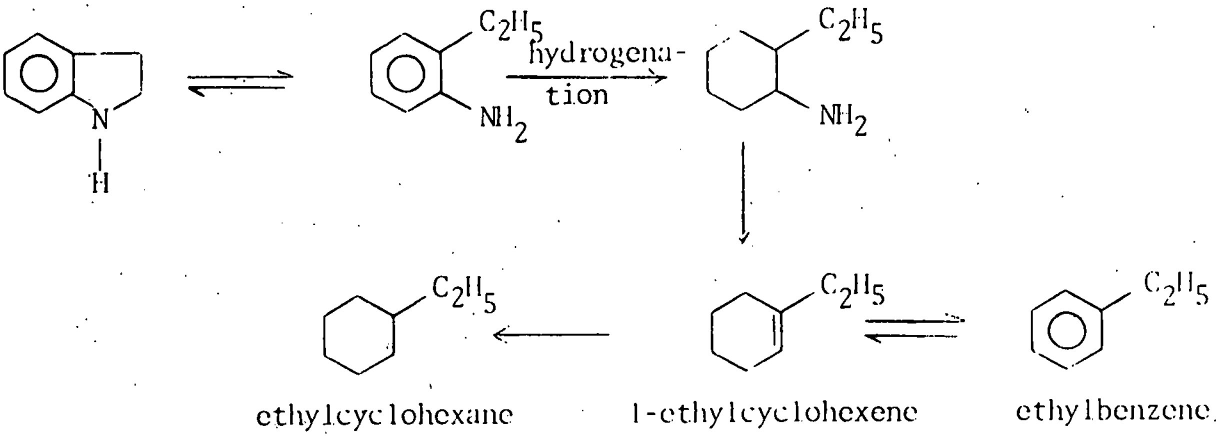


Figure 6. Preliminary networks for hydrodenitrogenation of o-ethylaniline.

different reaction paths are possible and from the present data it is not clear which one is the actual reaction path. There is no dealkylation of the o-ethylaniline as indicated by the fact that benzene and cyclohexane were not present in the reaction mixture.

Two runs will be made to further clarify and define the reaction network more fully for hydrodenitrogenation of o-ethylaniline and other anilines. The first run will be made with o-ethylaniline at a lower temperature (320°C) so that the initial concentration profiles for ethylbenzene and ethylcyclohexane can be studied more closely. In the second run the hydrodenitrogenation of aniline will be studied. This should also be helpful in identifying the intermediates and the reaction network.

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 uniquely new hydrodenitrogenation catalysts that will selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring thereby reducing hydrogen consumption. Hence, a run was made using a synthesized compound, quinoline-N-oxide to determine whether the addition of oxygen to the quinoline molecule would reduce the aromaticity of the nitrogen-containing ring thereby making it easier to remove nitrogen directly. The results are presented below.

Hydrodenitrogenation of Quinoline-N-Oxide

The work reported here was performed to study the reaction network of catalytic hydrodenitrogenation of quinoline-N-oxide. The main objective of the study was to remove nitrogen*

Experimental conditions were the same as shown in Table 1. The quinoline-N-oxide was synthesized. The solvent n-hexadecane was supplied by Humphrey Chemical.

Results and Discussion

The quinoline-N-oxide conversion data show (Figures 7 and 8) the presence of propylcyclohexane and propylbenzene products and the intermediates quinoline, 1,2,3,4-tetrahydroquinoline, o-propylaniline, 5,6,7,8-tetrahydroquinoline and decahydroquinoline. The components mentioned above

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*from the quinoline-N-oxide as NO.

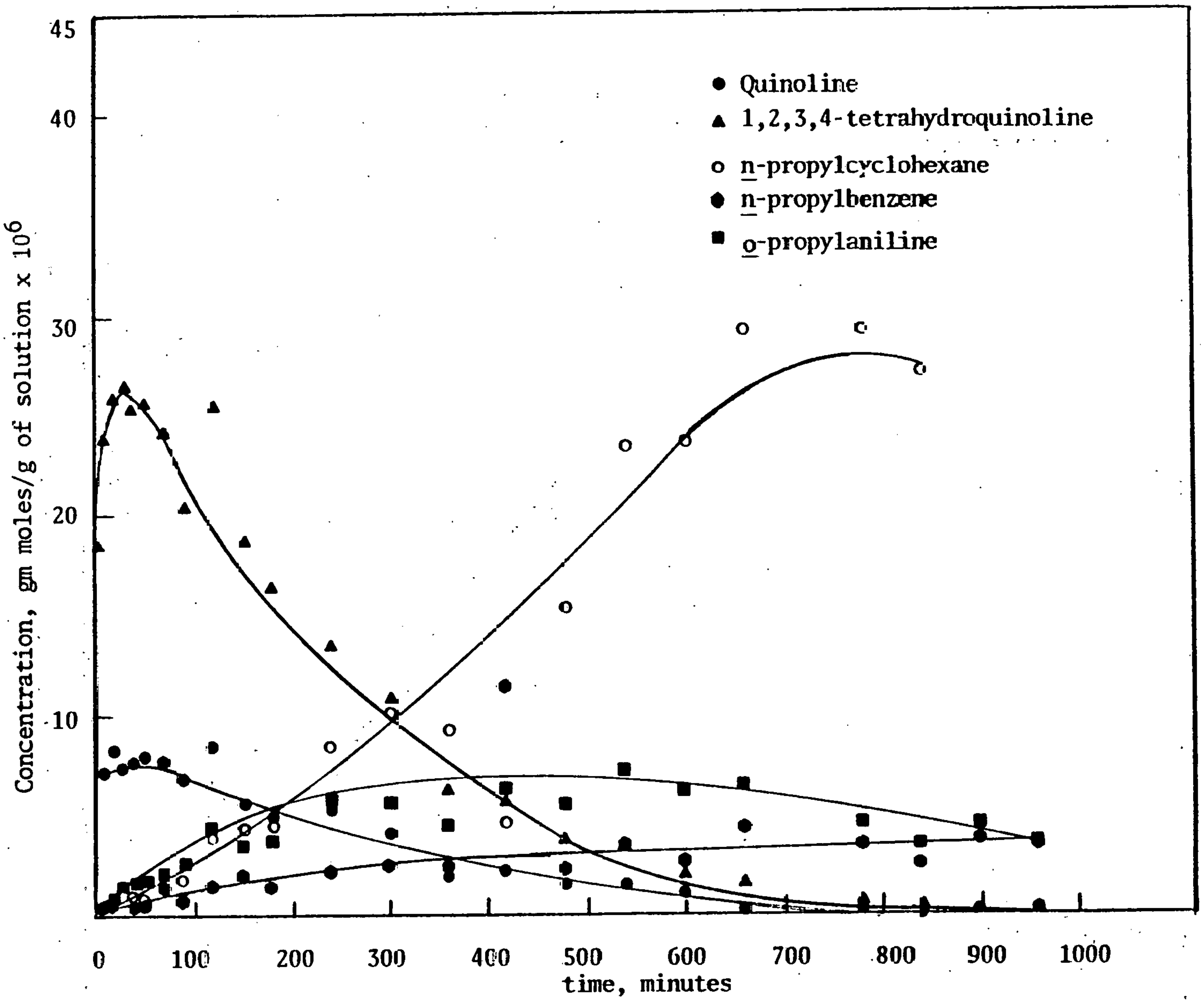


Figure 7. Concentration profiles of various hydrodenitrogenation products of quinoline-N-oxide.

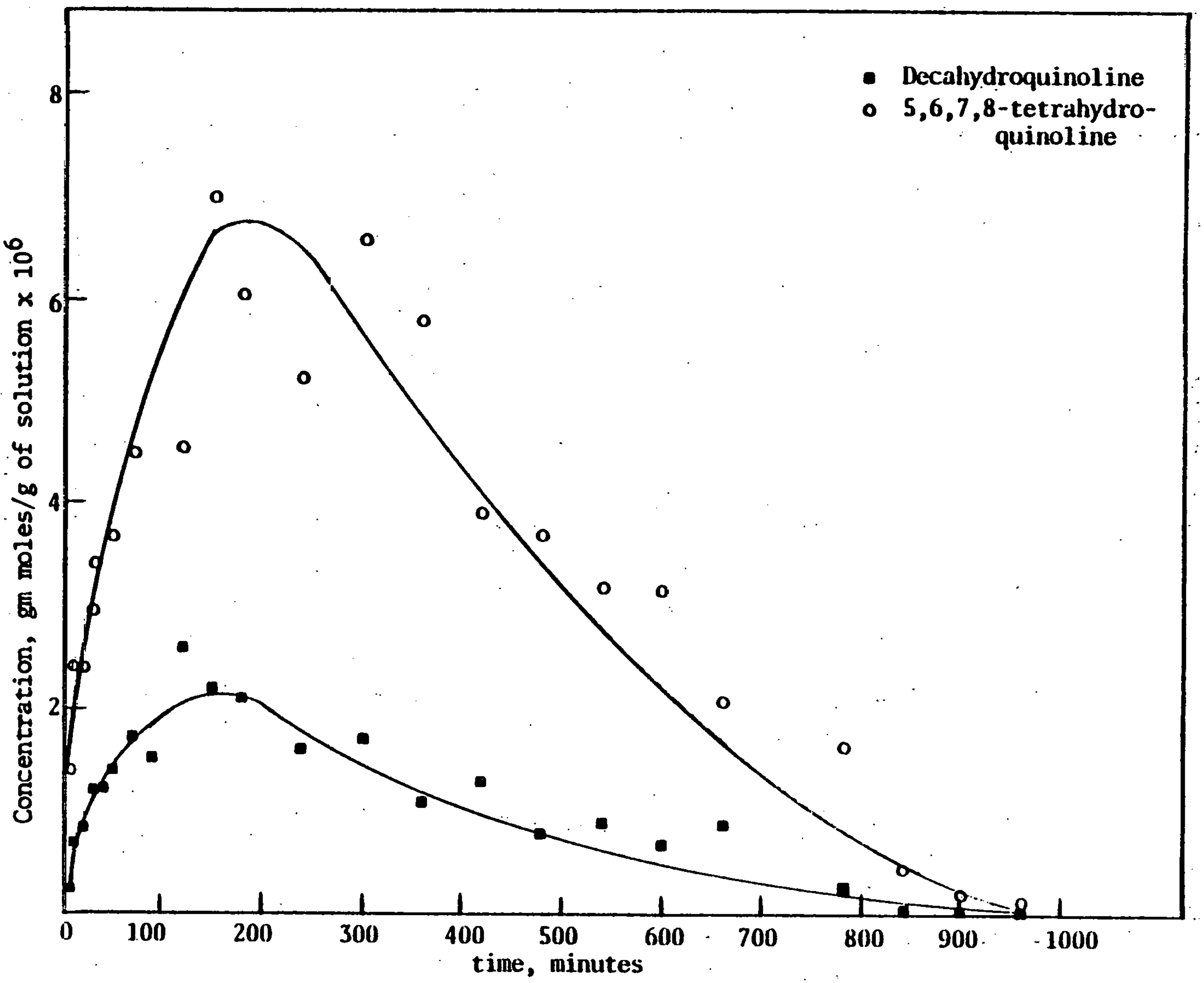


Figure 8. Concentration profiles of various hydrodenitrogenation products of quinoline-N-oxide.

are also present in hydrogenation of quinoline indicating that quinoline-N-oxide changes to quinoline very rapidly by deoxidation of the molecule. The C-N bond is very strong compared to NO bond, and in the presence of hydrogen the NO bond is broken easily resulting in the production of quinoline. The quinoline thus produced is subsequently converted into 1,2,3,4-tetrahydroquinoline, o-propylaniline, propylbenzene, 5,6,7,8-tetrahydroquinoline, decahydroquinoline and propylcyclohexane. A possible reaction network for quinoline-N-oxide hydrodenitrogenation is shown in Figure 9. The reaction network in Figure 9 shows that both benzene and pyridine rings are saturated before the C-N bond is broken.

An infrared analysis of the quinoline-N-oxide in hexadecane shows a -NO band in the stretching region (Figure 10). However, an IR analysis of the reaction product sample does not show -NO band. Disappearance of the NO band indicates that quinoline-N-oxide is rapidly converted to quinoline (Figure 11). To check this rapid conversion of quinoline-N-oxide to quinoline, an experiment has been made by replacing hydrogen with helium and the samples are being analyzed. It is expected that by substituting helium for hydrogen, quinoline-N-oxide may not deoxidize and therefore C-N bond scission may be promoted.

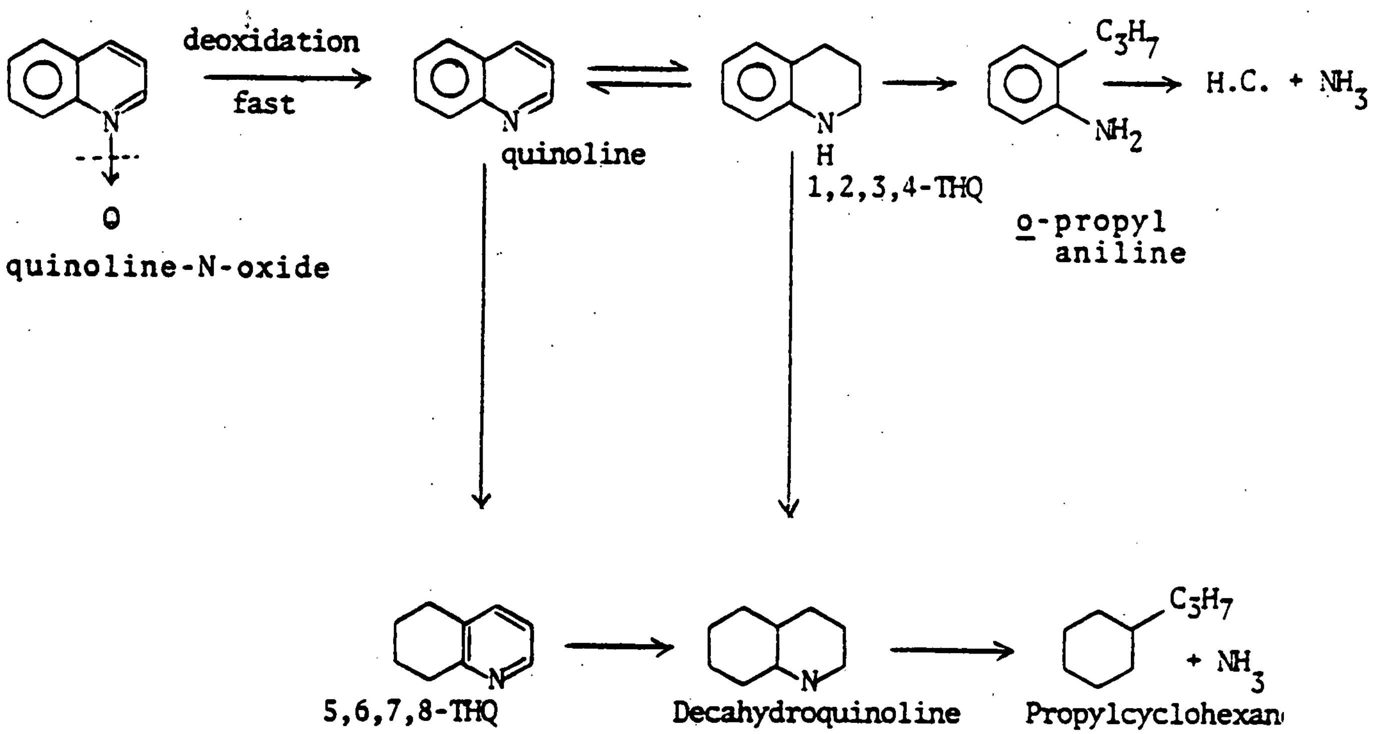
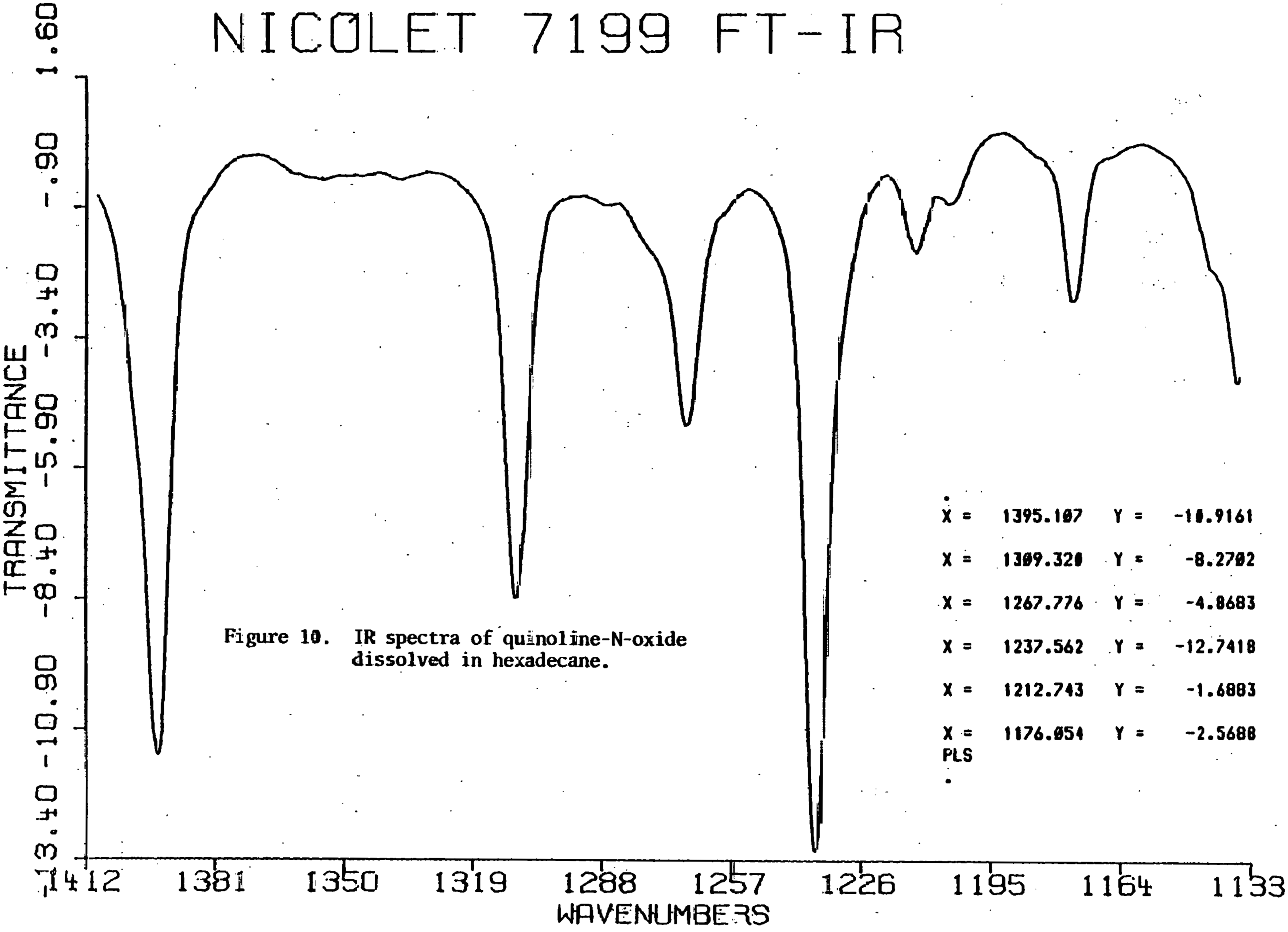


Figure 9. Reaction network for quinoline-N-oxide hydrodenitrogenation.

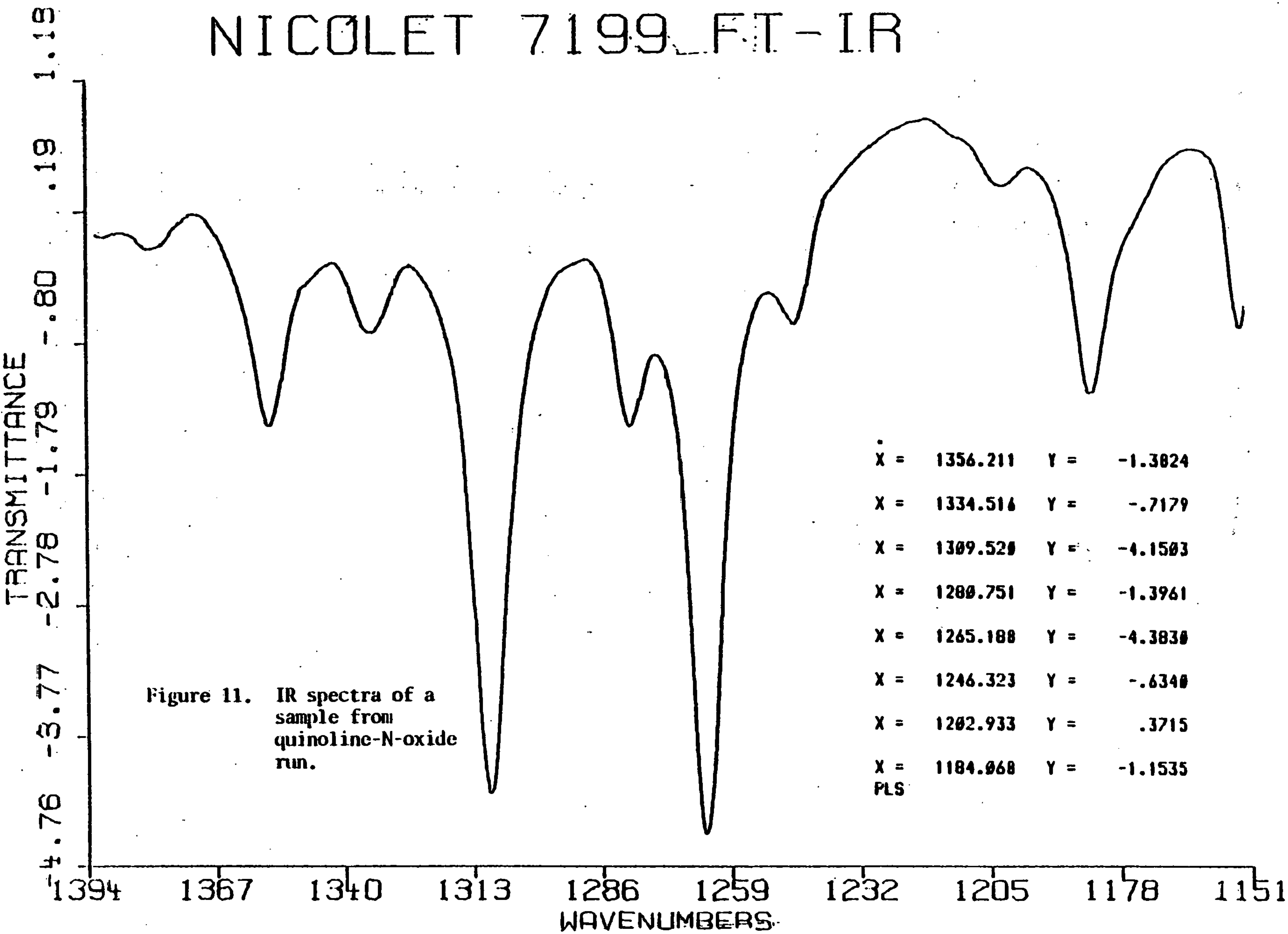
S



```
X =   1395.107   Y =   -10.9161
X =   1309.320   Y =    -8.2702
X =   1267.776   Y =    -4.8683
X =   1237.562   Y =   -12.7418
X =   1212.743   Y =    -1.6883
X =   1176.054   Y =    -2.5688
PLS
```

Figure 10. IR spectra of quinoline-N-oxide dissolved in hexadecane.

K-QNO-410-2



```
X =   1356.211   Y =   -1.3824
X =   1334.516   Y =    -.7179
X =   1309.520   Y =   -4.1503
X =   1280.751   Y =   -1.3961
X =   1265.188   Y =   -4.3830
X =   1246.323   Y =    -.6340
X =   1202.933   Y =     .3715
X =   1184.068   Y =   -1.1535
PLS
```

Figure 11. IR spectra of a sample from quinoline-N-oxide run.

V. PERSONNEL

The project started on September 15, 1978. Dr. R. Sivasubramanian, a post doctoral fellow joined this project on October 16, 1978.

APPENDIX A

Tabulated Data for Hydrodenitrogenation Runs

TABLE II

Data From Decahydroquinoline Run Using Glass Liner

Concentration gm moles/gm x 10^5

Sample No.	Time Min.	Benzene	n-propyl cyclohexane	propyl benzene	decahydroquinoline	5,6,7,8-tetrahydroquinoline	quinoline	1,2,3,4-tetrahydro quinoline
1	5				1.585	0.217	0.106	0.096
2	15				1.547	0.173	0.076	0.140
3	30				1.493	0.205	0.080	0.098
4	60				1.474	0.261	0.076	0.111
5	180	0.063	0.037	0.028	0.897	0.380	0.041	0.115
6	300	0.071	0.056	0.009	0.843	0.645	0.060	0.188
7	420	0.085	0.055	0.047	0.643	0.632	0.062	0.156
8	480	0.108	0.060	0.045	0.601	0.844	0.068	0.180
9	540	0.103	0.056	0.048	0.468	0.774	0.059	0.159
10	600	0.087	0.048	0.043	0.405	0.774	0.081	0.154

Operating conditions are given on page 6.

TABLE III

Data From Decahydroquinoline Run Without Glass Liner

Concentration, gm moles/gm x 10^7

Sample Number	Time, Minutes	n-propyl cyclohexane	propyl benzene	decahydro-quinoline
1	5			11.775
2	10			22.486
3	20			25.966
4	30			23.564
5	60			23.397
6	132	1.446		22.773
7	183	2.602	1.609	20.800
8	240	1.798	--	22.072
9	303	4.827	1.699	15.273
10	360	4.815	2.099	15.393
11	420	5.105	1.895	17.237
12	462	3.177	--	15.091
13	923	3.708	1.568	12.05
14	1032	5.204	2.209	7.102

Operating conditions are given on page 6.

TABLE IV

Data From Orthoethylaniline Run

Concentration, gm moles/gm x 10^5

Sample Number	Time, minutes	Ethylcyclo hexane	Ethyl benzene	Orthoethyl aniline	Indoline	Indole
1	5	0.00	0.02	3.70	0.07	0.49
2	10	0.02	0.04	5.10	0.06	
3	20	0.03	0.06	4.90	0.06	
4	30	0.10	0.12	4.90	0.07	
5	40	0.26	0.18	5.50	0.11	
6	50	0.38	0.24	5.20	0.10	
7	70	0.55	0.30	5.00	0.12	
8	90	0.85	0.36	4.90	0.13	
9	120	1.48	0.39	4.60	--	
10	150	1.90	0.41	4.20	--	
11	180	2.10	0.40	3.60	--	
12	240	2.74	0.44	3.30	0.15	
13	300	2.54	0.36	2.50	0.12	
14	360	3.10	0.40	2.10	0.13	
15	420	3.20	0.48	1.70	0.15	

Operating conditions are given in Table I.

TABLE V

Data from Quinoline-N-Oxide Run

Concentration, gm moles/gm x 10^6

Sample Number	Time, Minutes	n-propyl cyclohexane	propyl benzene	deca-hydro quinoline	5,6,7,8-tetra-hydro quinoline	ortho-propyl-aniline	quinoline	1,2,3,4-tetra-hydro-quinoline
1	5	0.30	0.00	0.28	1.55	0.40	13.40	18.80
2	10	0.34	0.28	0.69	2.35	0.35	7.10	24.00
3	20	0.61	0.27	0.83	2.30	0.95	8.20	26.00
4	30	0.75	0.40	1.19	2.95	1.30	7.40	26.80
5	40	1.10	0.55	1.20	3.40	1.60	7.70	25.60
6	50	0.88	0.86	1.40	3.70	1.80	8.00	25.90
7	70	1.76	1.80	1.70	4.50	2.10	7.90	24.10
8	90	1.97	0.93	1.50	4.70	2.70	6.90	20.50
9	120	4.00	1.64	2.60	7.00	4.20	8.60	25.80
10	150	4.20	2.00	2.20	6.10	3.60	5.90	18.90
11	180	4.60	1.40	2.10	5.30	3.80	5.00	16.40
12	240	8.50	2.15	1.60	6.60	5.50	5.30	13.40
13	300	10.10	2.40	1.70	5.80	5.70	4.10	10.90
14	360	9.30	2.30	1.50	3.90	4.50	2.30	6.20
15	420	4.50	11.50	1.30	3.70	6.20	2.20	5.80
16	480	15.60	2.30	0.80	3.20	5.60	1.70	3.80
17	540	24.80	3.40	0.90	3.20	7.10	1.80	3.50
18	600	24.90	2.90	0.66	2.10	6.20	1.40	2.00
19	660	24.10	4.40	0.96	1.70	6.60	0.59	1.80
20	780	29.50	3.50	0.25	0.47	4.90	0.19	0.44
21	840	27.10	2.60	0.00	0.22	3.80	0.00	0.17
22	900	40.70	3.90	0.00	0.14	4.70	0.00	0.00
23	960	38.20	3.80	0.00	0.00	3.80	0.00	0.00

Operating conditions are given in Table I.

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APPENDIX B

Review Paper Submitted to "Catalysis Reviews"

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

Second Quarterly Report for Period
December 15, 1978 to March 15, 1979

Prepared by:

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Date Published

May 15, 1979

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

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

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I. ABSTRACT

Experimental runs using decahydroquinoline, o-ethylaniline, and aniline as reactants have been made. Results from decahydroquinoline runs show that carbon-nitrogen bond scission occurs by a catalytic route; it is not thermal. Strong Brønsted acid sites do not crack carbon-nitrogen bonds; carbon-nitrogen bond scission must therefore occur on other sites on the catalyst. Anilines are an important species in hydrodenitrogenation of multi-ring aromatic systems. Hydrodenitrogenation of anilines clearly shows kinetic behavior characteristic of hydrogenation including positive order dependence on hydrogen pressure and an activation energy between that for hydrogenation and that for cracking; yet the primary product appears to be the fully aromatic ring. To better understand the mechanism of hydrodenitrogenation of anilines and of substituted anilines, hydrodenitrogenation of aniline and o-ethylaniline was studied over a presulfided Ni-Mo/Al_2O_3 catalyst, and a reaction network has been determined for aniline hydrodenitrogenation. Aniline hydrodenitrogenation appears to involve partial hydrogenation of the benzene ring to reduce aromatic resonance with the nitrogen atom reducing the C-N bond strength and facilitating elimination of NH_3.

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, thereby developing improved catalysts for hydrodenitrogenation.
- To develop an improved understanding of the catalyst function required for carbon-nitrogen bond scission since this function is critical to hydrodenitrogenation but is not understood.
- 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 developing for processing coal-derived liquids.

Scope:

Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. The carbon-nitrogen bond scission reaction needs to be better understood to facilitate development of new and improved catalysts. The nature of the catalytic function responsible for carbon-nitrogen bond scission is being determined by measuring the rates of carbon-nitrogen bond scission using mainly decahydroquinoline over a set of catalysts prepared specifically to evaluate the catalyst requirements for the carbon-nitrogen bond scission reaction. The catalysts being tested include Lewis and Brønsted acid catalysts without metal, alumina impregnated with Mo, Co, and Ni, promoted with halogens and various levels of sulfiding and <u>in situ</u> H_2S partial pressure and 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 carbon-nitrogen 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, involves the development of uniquely-new, highly-selective hydrodenitrogenation catalysts. This work is focusing on developing catalysts that can selectively coördinate nitrogen and remove it from multi-ring nitrogen-containing aromatic compounds with only limited or no hydrogenation of the aromatic rings, thus achieving major savings in hydrogen consumption. The catalysts formulated are being tested under high-pressure liquid-phase conditions using quinoline and possibly acridine in a carrier oil as a reactant. Since quinoline contains the requisite benzenoid ring and nitrogen-containing aromatic rings characteristic of nitrogen-containing compounds present in coal-derived liquids, it is considered to be a good compound for characterizing catalyst behavior.

The results of all of the above work are being evaluated utilizing our kinetic analysis schemes to give quantitative measures of the rates of carbon-nitrogen bond scission and the extents and rates of hydrogenation. These results are being interpreted in terms of the catalysts and their properties and recommendations will be made as to what further work needs to be done and the potentially most fruitful directions to be followed.

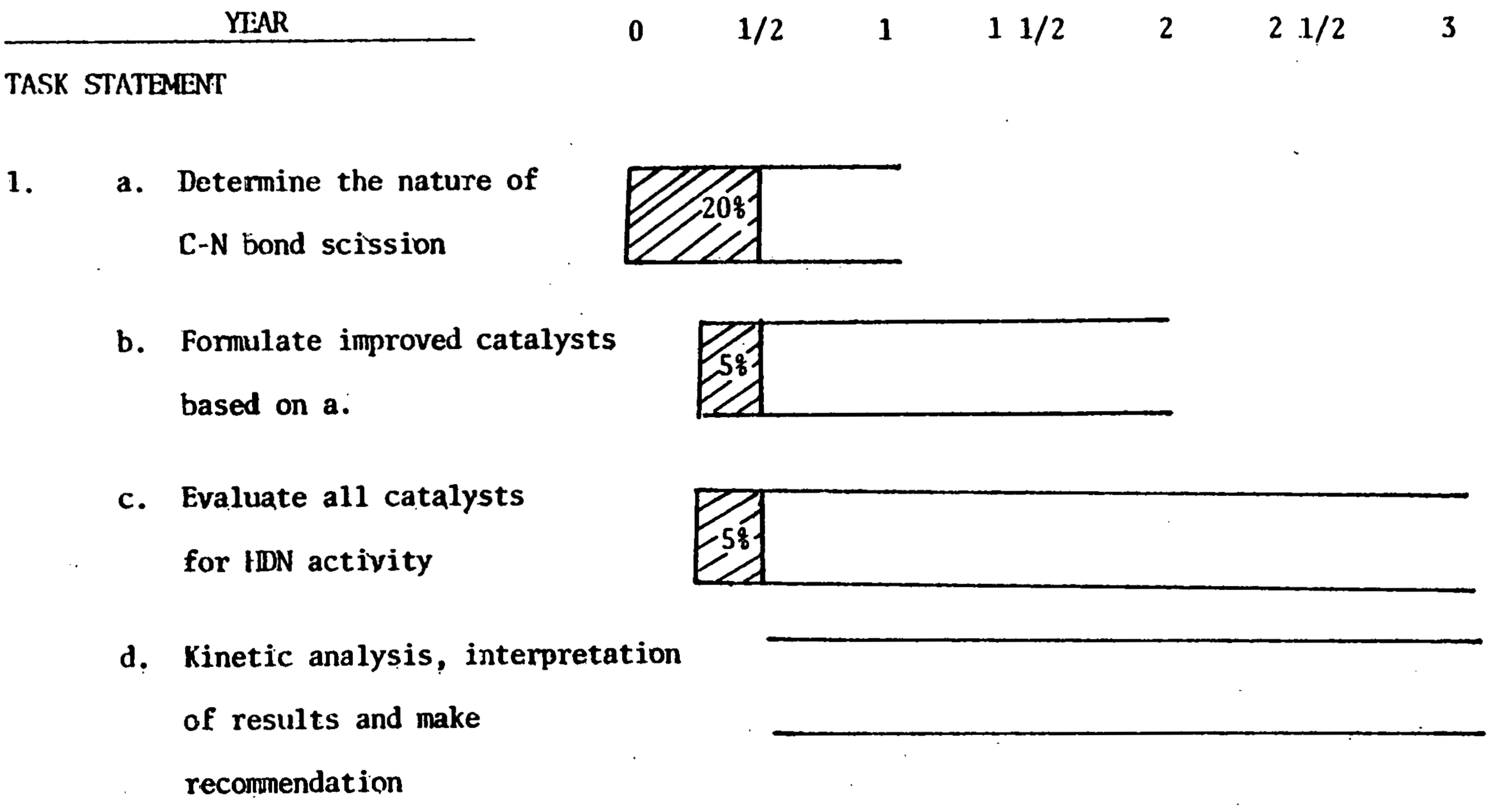
III. SUMMARY OF PROGRESS TO DATE

Substantial progress has been made in understanding the chemistry of catalytic carbon-nitrogen bond scission. Our results clearly indicate that the carbon-nitrogen bond scission reaction is catalytic and that strong Brønsted acid sites do not catalyze carbon-nitrogen bond scission. We now speculate that the surface site for carbon-nitrogen bond scission is a transition metal ion (atom) in close proximity of a Brønsted acid site on the surface of the alumina, and our research is progressing toward synthesizing such materials to illucidate the required surface properties. Our results also show that aniline hydrodenitrogenation occurs via a partial hydrogenation of the aromatic ring.

In continuing our effort to develop the understanding required to guide the development of improved catalysts that will selectively remove nitrogen without first requiring hydrogenation of the rings, runs were conducted using quinoline-N-oxide. Quinoline-N-oxide was chosen because the electron pair on nitrogen is removed from resonance with the aromatic ring by being bound to oxygen. The results from the first run, which were reported in the previous quarterly report, indicated that in the presence of H_2 the quinoline-N-oxide undergoes rapid deoxidation to form quinoline. During this quarter, runs were conducted using quinoline-N-oxide in the absence of hydrogen and using tetralin as a hydrogen donor. Results will be presented in the next report.

Several catalysts have been prepared, and these are being tested. A commercial firm (Cyanamid) has agreed to prepare for us catalyst samples with varying acidity and metals content. These catalysts will be tested for quinoline hydrodenitrogenation in upcoming quarters; emphasis is on the understanding of the role of acidity and transition metals on the carbon-nitrogen bond scission reaction and on direct removal of nitrogen without ring hydrogenation.

*TIME PLAN AND MILESTONE CHART



TASK STATEMENT

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

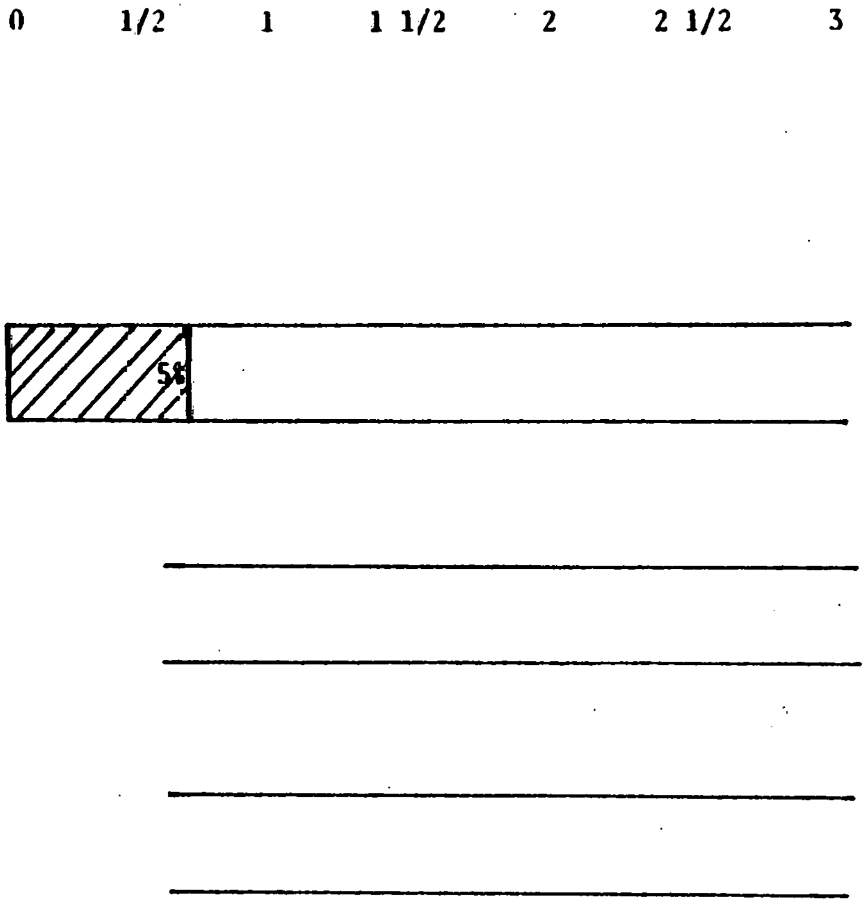
b. Formulate improved catalysts based on a.

c. Evaluate all catalysts for HDN activity

d. Kinetic analysis, interpretation of results and make recommendation

YEAR

TASK STATEMENT



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

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

g. Kinetic analysis interpretation o results and make recommendations.

☐ Scheduled

▨ Underway

■ Completed

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	FIRST QUARTER	SECOND QUARTER
PERSONNEL	5334	21252
TRAVEL	0	0
SUPPLIES AND EXPENSES	212	2635
OCCUPANCY AND MAINTENANCE	0	0
EQUIPMENT	585	11893
OTHER EXPENSES	140	1841
TRANSFERS (OVERHEAD)	2868	10653
	9,139	48,274

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 route for removal of nitrogen from quinoline, a major 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.

Anilines and substituted anilines are often formed as intermediate compounds during hydrodenitrogenation of multi-ring aromatic nitrogen-containing compounds such as quinoline, carbazole, and acridine. These aniline compounds are very unreactive. Our past studies of quinoline hydrodenitrogenation and reaction network analysis indicate that the hydrogenation reactions in the network show a positive order of dependence on hydrogen pressure with an activation energy of 18-20 kcal/mole, whereas the hydrogenolysis reactions show zero or negative order dependence on hydrogen pressure with an activation energy greater than 30 kcal/mole. However, nitrogen removal from o-propylaniline shows a positive order dependence on hydrogen pressure with an activation energy of about 24 kcal/mole. These findings suggest that ring hydrogenation is necessary for nitrogen removal from anilines. The literature does not provide sufficient evidence as to whether hydrogenation of the aromatic ring is necessary or not. Since anilines are important intermediates in hydrodenitrogenation of multi-ring aromatic nitrogen-containing compounds, nitrogen removal from anilines can become a rate-limiting step in total nitrogen removal. Hence hydrodenitrogenation of anilines needs to be better understood to facilitate development of improved catalysts for hydrodenitrogenation.

a) <u>Carbon-Nitrogen Bond Scission</u>:

Hydrodenitrogenation of decahydroquinoline was studied over HY zeolite and a Ni-Mo/Al_2O_3 catalyst. The reactor used was a 300 cm^3 autoclave fitted with a magnetic drive stirrer. Standard operating conditions (Table I) were used for all the experimental runs. Liquid samples were analyzed using a Perkin-Elmer gas chromotograph equipped with a flame-ionization detector. A glass capillary column (75m-OV101) was used for all reactant and product analysis.

Figures 1 and 2 present results from runs using HY zeolite and Ni-Mo/Al_2O_3. The disappearance of decahydroquinoline using the Ni-Mo/Al_2O_3 compares very well with the predicted curve presented in the previous quarterly report (Fig. 3, p. 10). The major products from the run using Ni-Mo/Al_2O_3 were decahydroquinoline (both trans and cis forms), 5,6,7,8-tetrahydroquinoline and n-propylcyclohexane; minor products included benzene, o-propylaniline, n-propylbenzene and 1,2,3,4-tetrahydroquinoline. However, products formed with HY-zeolite did not contain n-propylcyclohexane or o-propylaniline. Normal-propylcyclohexane is formed when the carbon-nitrogen bond in decahydroquinoline breaks. Hence the results indicate that the HY-zeolite did not catalyze the cracking or carbon-nitrogen bonds. Significant amounts of benzene were formed when the HY-zeolite was used. Results

TABLE I

Standard Operating Conditions

Temperature:	350 ± 2°C
Total Pressure:	34 ± 1 atm*
Reactant Concentration:	0.5 weight percent in *n*-hexadecane
CS_2 Loading:	0.05 wt % (1.4 vol % H_2S in gas phase)
Catalyst Loading:	0.5 wt % of reaction mixture

---

*Partial pressure of *n*-hexadecane @ 350°C ≅ 3.24 atm.

indicated that the benzene did not come from the nitrogen-containing compounds but that it came from the n-hexadecane, its formation being catalyzed by the HY zeolite.

Figure 3 compares total nitrogen removal from decahydroquinoline for several runs. Figure 3 shows that when no catalyst was present, nitrogen removal was extremely slow. However, when a Ni-Mo/Al_2O_3 catalyst was used, the nitrogen removal rate increased tenfold. These results conclusively show that the carbon-nitrogen bond scission occurs by a catalytic route; it is not thermal. A strongly Brønsted acid catalyst such as HY-zeolite does not catalyze nitrogen removal. In fact, there is no significant difference in nitrogen removal rate between the run with no catalyst and the run using HY-zeolite. These results indicate that carbon-nitrogen bond scission is not catalyzed by Brønsted acid sites.

b) Anilines

Anilines are one of the important species in the hydrodenitrogenation of multi-ring aromatic compounds. They form during reaction and appear to be very refractory; thus to achieve high degrees of nitrogen removal, anilines must be effectively hydrodenitrogenated. To better understand the mechanism of hydrodenitrogenation of anilines and substituted anilines, hydrodenitrogenation of aniline and o-ethylaniline was studied over Ni-Mo/Al_2O_3 catalyst.

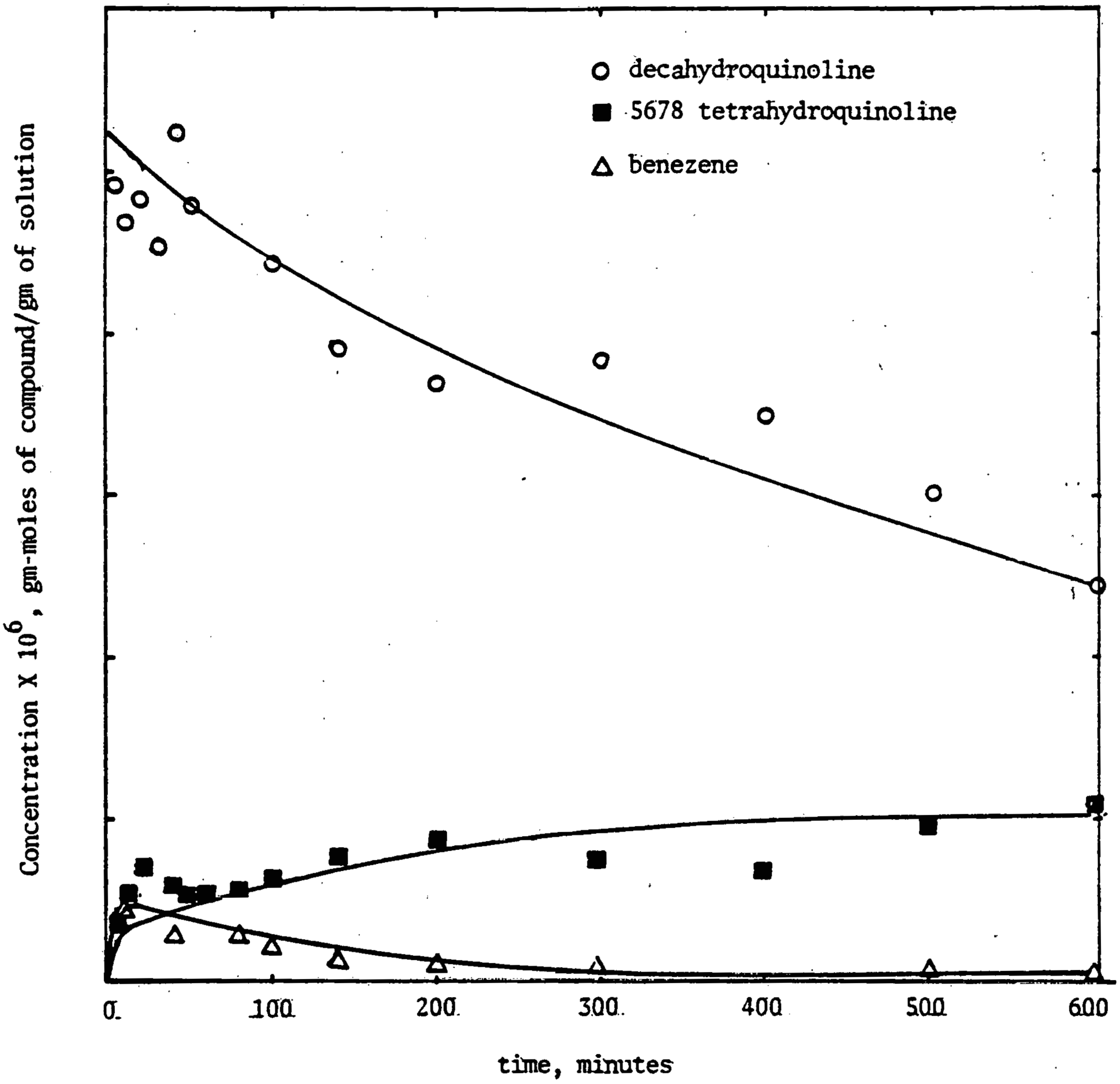


Fig 1. Concentration profiles for hydrodenitrogenation of decahydroquinoline using HY zeolite.

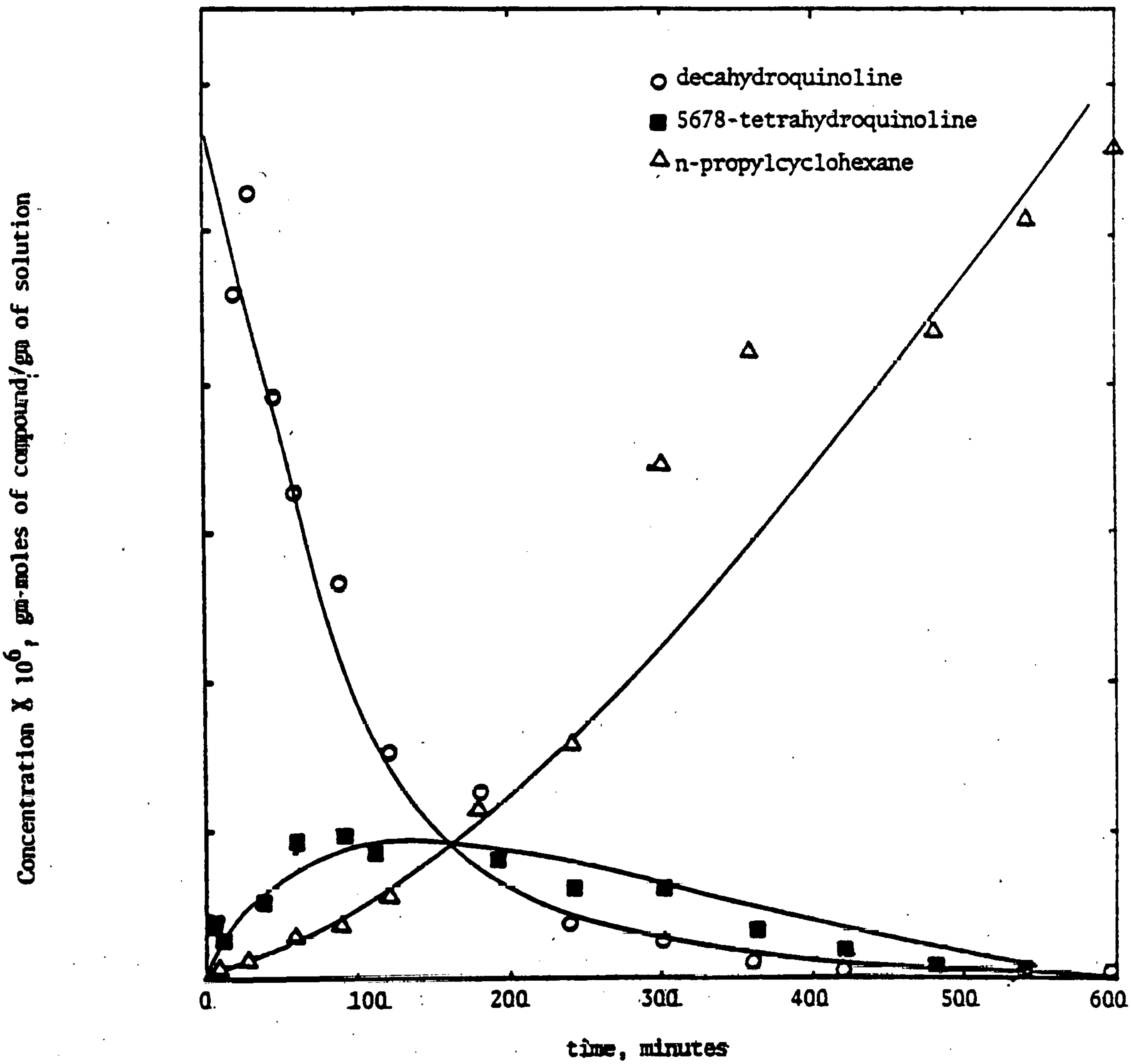


Fig. 2 Concentration profiles for hydrodenitrogenation of decahydroquinoline using a Ni-1%/Al_2O_3 catalyst.

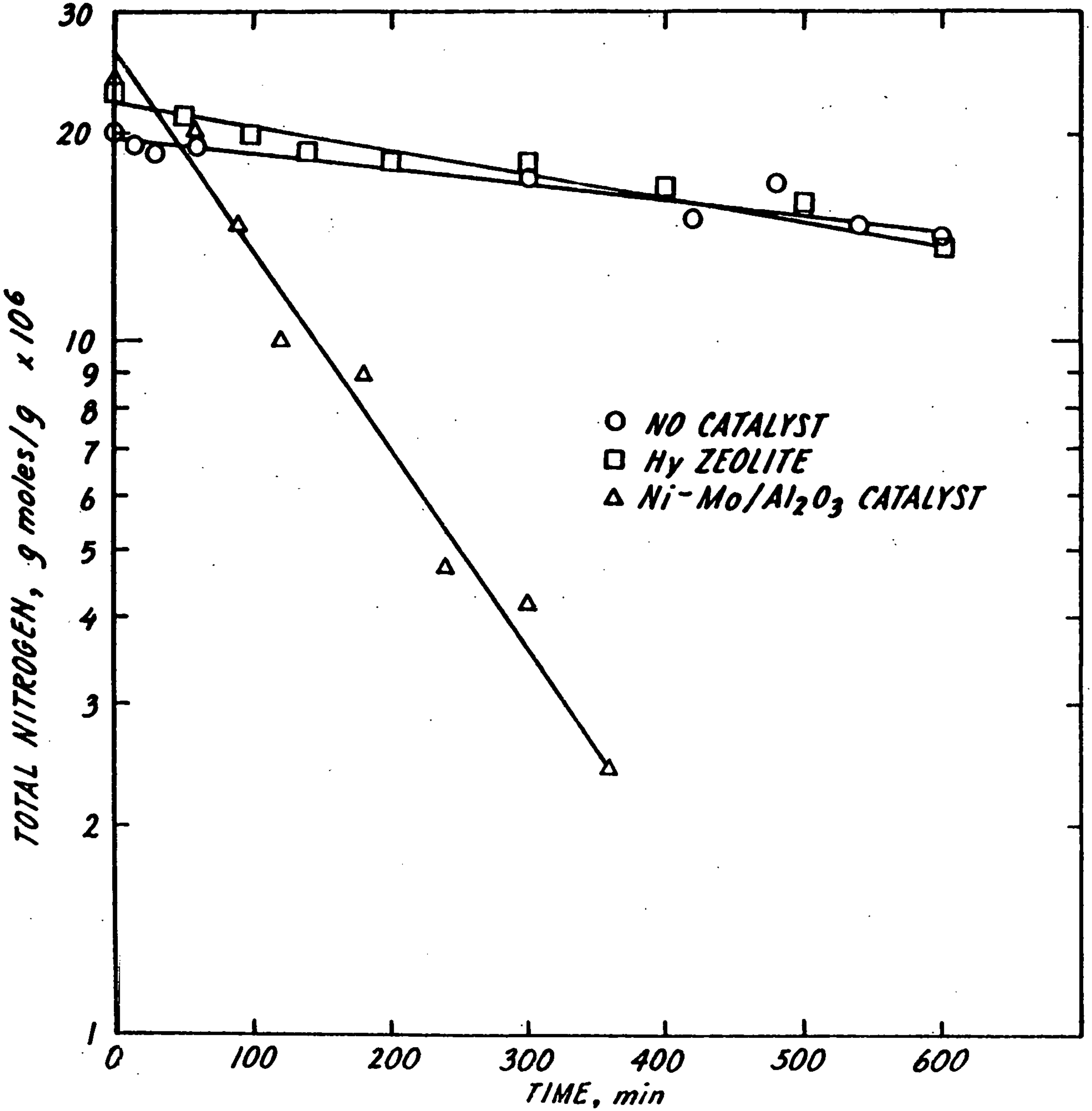


Fig. 3 Total nitrogen removal from decahydroquinoline using various catalysts

o-Ethylaniline

The standard operating conditions are given in Table I. The preliminary work on hydrodenitrogenation of o-ethylaniline at 350°C indicated that o-ethylaniline rapidly converts to ethylbenzene and ethylcyclohexane, but it was not clear which compound was the primary reaction product. Therefore runs were made at a lower reaction temperature (320°C) so that the initial concentration profiles for ethylbenzene and ethylcyclohexane could be determined more precisely.

The results of a standard run are shown in Figure 4. Ethylbenzene and ethylcyclohexane are formed very rapidly. However, ethylbenzene is the primary product of the hydrodenitrogenation of o-ethylaniline; no ethylcyclohexane formed during the first 15 minutes of reaction. The ethylbenzene concentration increased linearly with time during this time period. Hence it is clear that ethylbenzene is the primary product and that hydrogenation of ethylbenzene results in the formation of ethylcyclohexane. After 90 minutes the concentration of ethylcyclohexane increased very rapidly while the concentration of ethylbenzene remained approximately constant. There is no dealkylation of o-ethylaniline since benzene and cyclohexane were not present in detectable concentrations in the reaction mixture.

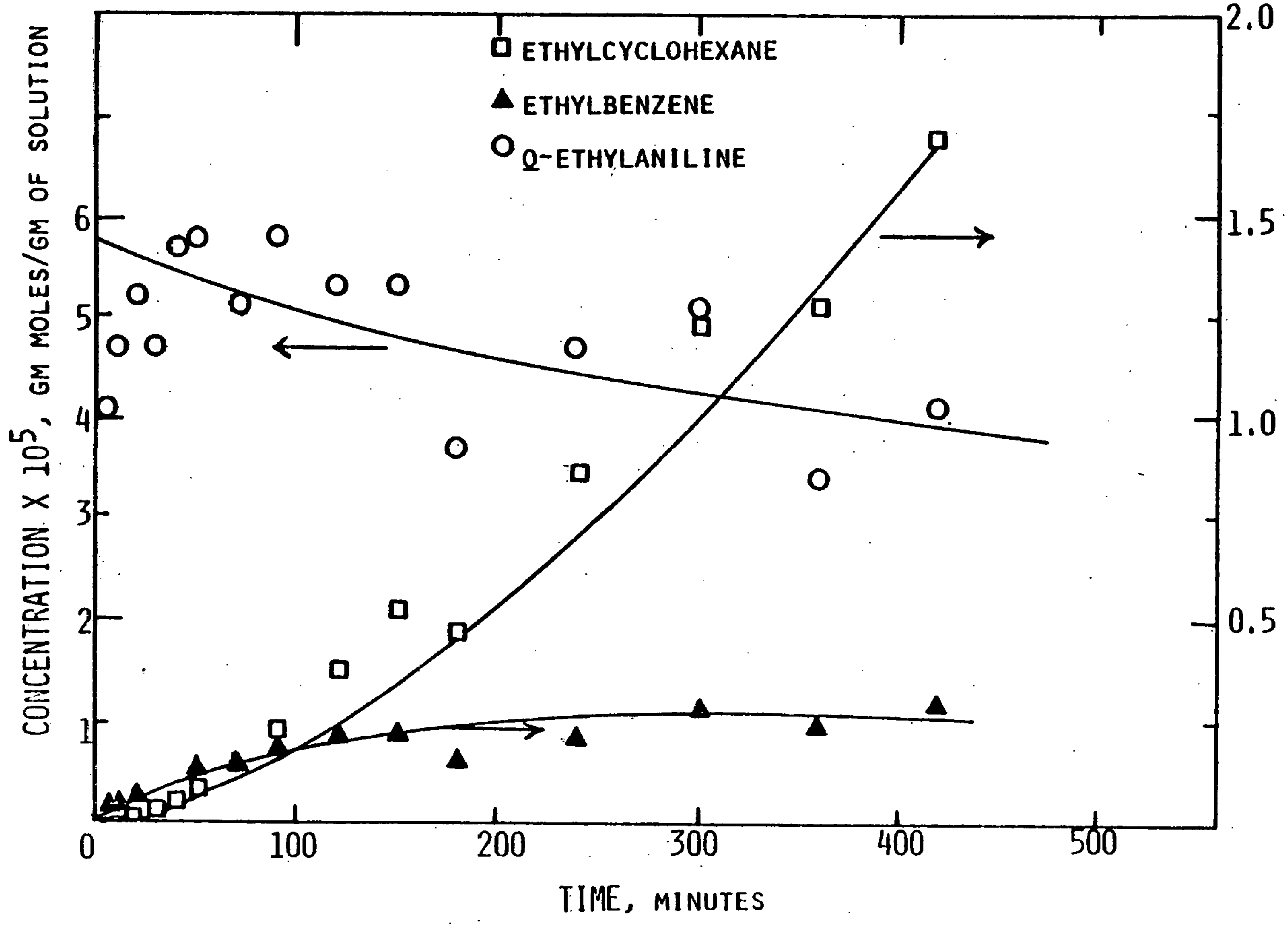


Fig. 4 Concentration profiles for hydrodenitrogenation of o - ethylaniline

Aniline

Runs were also made with aniline to further identify the reaction intermediates and the products and to clearly identify the reaction network. These runs were made at 320°C; Figure 5 shows the results of aniline hydrodenitrogenation.

These results indicate that the formation of benzene is relatively rapid, while the formation of cyclohexane was slow. During the first 15 minutes of the run no cyclohexane was found in the products; on the other hand, the benzene concentration was increasing linearly with time during this period. However, after 70 minutes the concentration of cyclohexane increased very rapidly. Thus it is clear from these results that benzene is the primary reaction product in the hydrodenitrogenation of aniline. Cyclohexane must be forming by hydrogenation of benzene.

Based on the results presented in Figures 4 and 5, the following reaction network can be proposed for the hydrodenitrogenation of anilines:

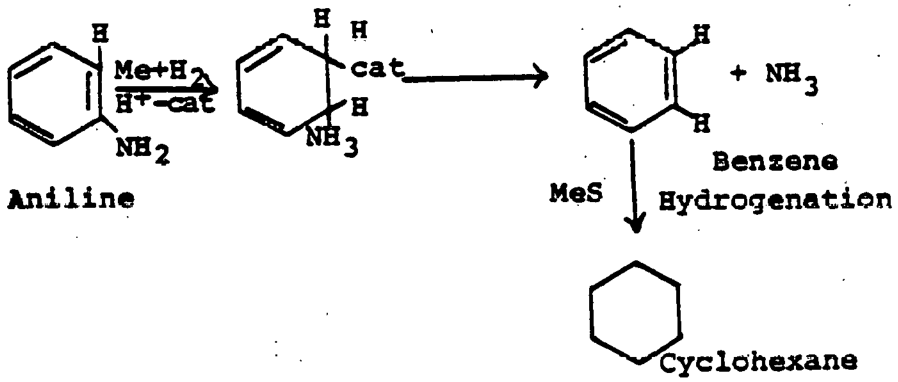


Figure 5. Reaction network for hydrodenitrogenation of anilines.

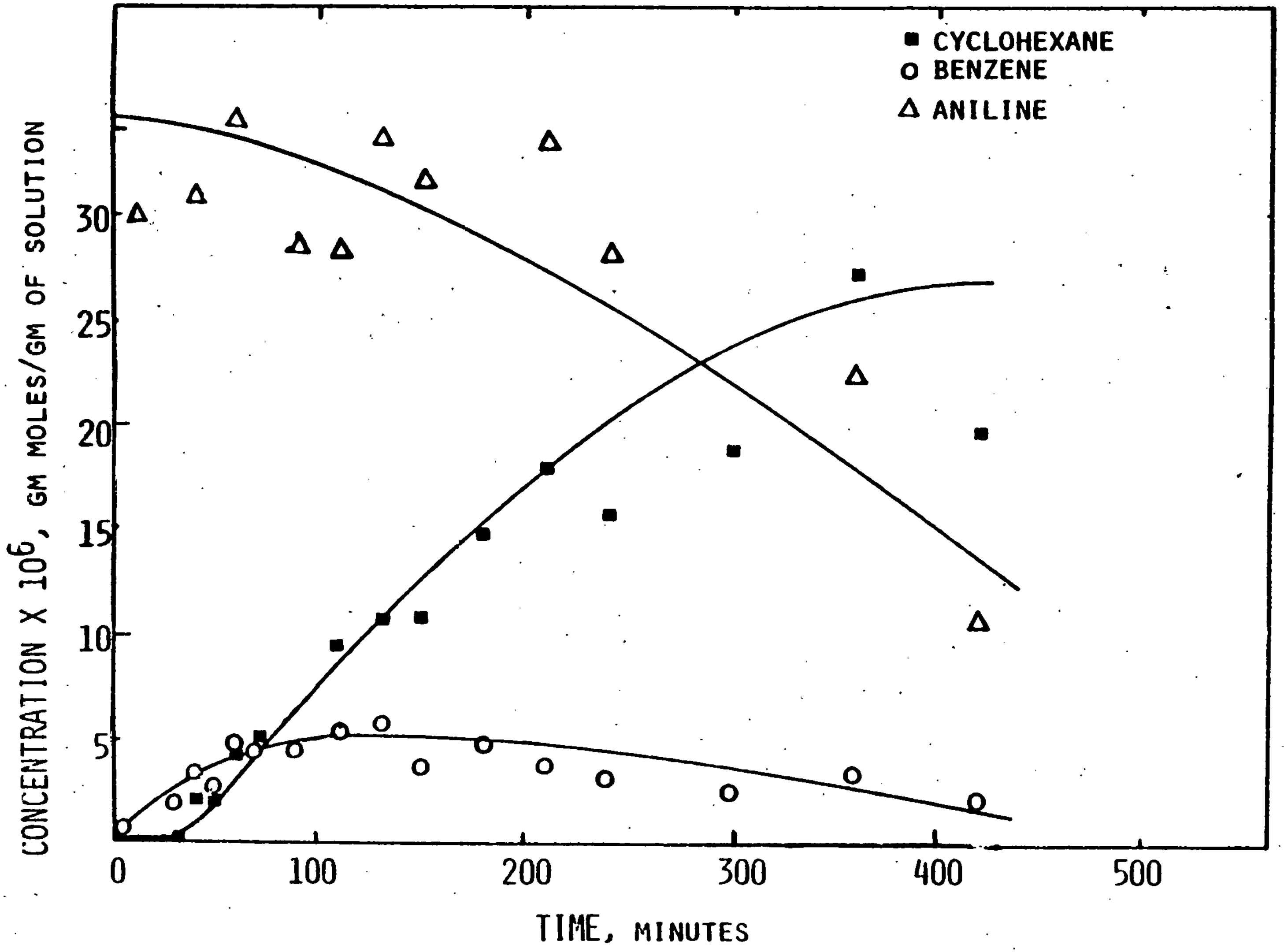


Fig. 5 Concentration profiles for hydrodenitrogenation of aniline

In the above reaction network, aniline undergoes deamination forming benzene by a β-elimination process; the benzene is hydrogenated to give cyclohexane. Since the hydrodenitrogenation of anilines shows positive order dependence on H_2 partial pressure and exhibits an activation energy which is considerably less than that observed for carbon-nitrogen bond scission, it would appear to not be a straightforward hydrogenolysis reaction but would appear to involve hydrogenation. The relatively high strength of the carbon-nitrogen bond in anilines is also indicated by the 6 kcal/mole higher resonance energy for aniline over benzene (Table II). This increased energy is due to resonance between lone pair of the nitrogen atom and the aromatic ring making the carbon-nitrogen bond significantly stronger than for a single carbon-nitrogen bond. Thus, all information with the exception of the products of reaction indicate that ring hydrogenation is a requirement for hydrodenitrogenation. Thus partial hydrogenation of the ring to reduce the resonance energy of the ring and of the carbon-nitrogen bond as shown in Figure 5 is the most probable mechanism for hydrodenitrogenation of aniline. Further the conversion of the partially hydrogenated ring to the aromatic (benzene) ring upon β-elimination provides a very favorable energetics for this reaction.

TABLE II

Resonance Energies

Compound	Resonance Energy kcal/mole
Benzene	37
Naphthalene	75
Anthracene	105
Aniline	43
Pyridine	43
Quinoline	69
Thiophene	31

Hence, the above results indicate that in hydrodenitrogenation of anilines a partial (or complete) hydrogenation is required to lower the resonance energy of the benzene ring and thereby facilitating the carbon-nitrogen bond scission.

TASK 2 - Development of catalysts which will effect hydrodenitrogenation with only limited or hydrogenation of the heterocyclic rings present in the molecule.

The objective of this task is to develop uniquely new hydrodenitrogenation catalysts that will selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring thereby reducing hydrogen consumption. Hence runs were conducted using quinoline-N-oxide to determine whether the addition of oxygen to the quinoline molecule would reduce the resonance energy of the nitrogen-containing ring by binding the nitrogen lone pair to 0 thereby making it easier to remove nitrogen directly.

Results presented in the previous report indicate that quinoline-N-oxide rapidly undergoes deoxidation in the presence of H_2 to form quinoline. Experiments have been conducted in which hydrogen was replaced with helium and in which tetralin was used as a hydrogen donor. Product analysis is being done and results will be presented in the next report.

As part of this task, several catalysts, which have as an objective strongly complexing the nitrogen atom, have been prepared, and these are being used in quinoline hydrodenitrogenation. A commercial catalyst supplier (Cyanamid) is preparing catalyst samples for us with various levels of acidity and metals, and these catalysts will be used in hydrodenitrogenation studies.

V . PERSONNEL:

There has been only one change in personnel during this quarter. Dr. K. Mathur joined the project as a post doctoral fellow on February 1, 1979.

APPENDIX C

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

Third Quarterly Report for Period
March 15, 1979 to June 15, 1979

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Date Published
August 1, 1979

Prepared for:

Fossil Energy
Department of Energy
Washington, D. C.

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

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I. ABSTRACT

Experimental runs using decahydroquinoline and quinoline as reactants have been made. Results from decahydroquinoline runs show 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. The carbon-nitrogen bond scission must therefore occur on other sites on the catalyst. In all likelihood, the olefinic products formed with these nonhydrogenating catalysts are polymerized on the surfaces of these acidic catalysts thereby making them inactive. There was no significant difference in nitrogen removal rate between the sulfided and unsulfided HY-zeolite catalyst, which indicated that sulfiding does not deactivate the HY-zeolite catalyst.

The nature of catalytic function responsible for carbon-nitrogen bond scission has been studied using decahydroquinoline over a set of catalysts. The catalysts tested include catalysts with Co, Ni, Mo impregnated on silica-alumina or γ-alumina. The results showed that the rate of nitrogen removal was highest for Mo on γ-alumina catalyst.

Several catalysts with the objective to develop uniquely new hydrogenation catalysts that will selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring thereby reducing hydrogen consumption, were prepared. The catalysts chosen for this study

were aluminum borate and aluminum borate phosphate, impregnated with 4 wt % Nickel. Preliminary results showed that 4 wt % Ni on aluminum borate catalyst gives a marked increase in nitrogen removal in quinoline.

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, thereby developing improved catalysts for hydrodenitrogenation.

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

- 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 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 C-N bond scission using mainly decahydroquinoline over a set of catalysts prepared specifically to evaluate the catalyst requirements for the C-N bond scission. The catalysts to be tested include acid catalysts without metal, alumina impregnated with Co and Ni with various levels of sulfiding and *in situ* H_2S partial pressure 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, 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 uniquely-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 with only limited or no 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 benzenoid ring and nitrogen-containing aromatic rings 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 give quantitative measures of the rates of C-N bond scission and the extents and rates of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties and recommendations will be made as to what further work needs to be done and the potentially most fruitful directions to be followed.

III. SUMMARY OF PROGRESS TO DATE

During the first three quarters, substantial progress has been made in understanding the chemistry of carbon-nitrogen bond scission. Preliminary results from hydrodenitrogenation of decahydroquinoline indicate that the carbon-nitrogen bond scission is not thermal but clearly catalytic. Our results clearly indicate that strong Brønsted acid sites alone or in combination with Lewis acid sites do not catalyze carbon-nitrogen bond scission and carbon-nitrogen bond scission must therefore occur on other sites on the catalyst.

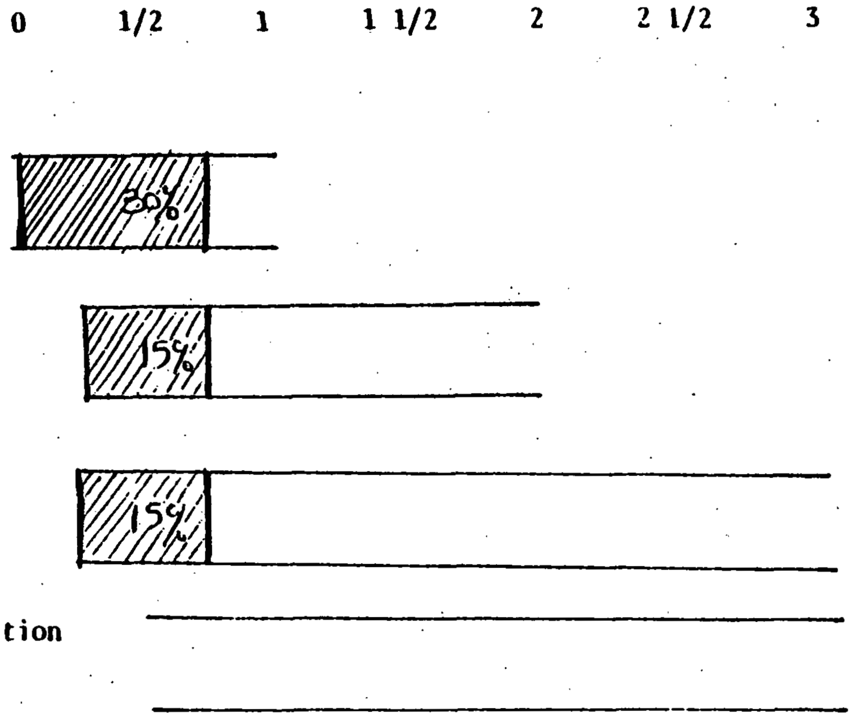
Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. Several catalysts have been prepared and tested recently which include Brønsted and Lewis acid catalysts without metal, alumina-impregnated with Mo, Co and Ni, promoted with in situ H_2S partial pressure and with and without Ni promotion to separate out the role of support. 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 Mo on γ-alumina catalyst.

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. The catalysts chosen for this study were aluminum borate and aluminum borate phosphate loaded with 4 wt % nickel.

Preliminary results indicate that 4 wt % Ni/aluminum borate catalyst gives a marked increase in nitrogen removal in quinoline. However, there was no increase in rate of nitrogen removal with increase in temperature.

Several other catalysts have been prepared recently and these are being tested. A commercial firm (American Cyanamid) has agreed to prepare for us catalyst samples with varying acidity and metals content. These catalysts will be tested in the near future.

*TIME PLAN AND MILESTONE CHART



TASK STATEMENT

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

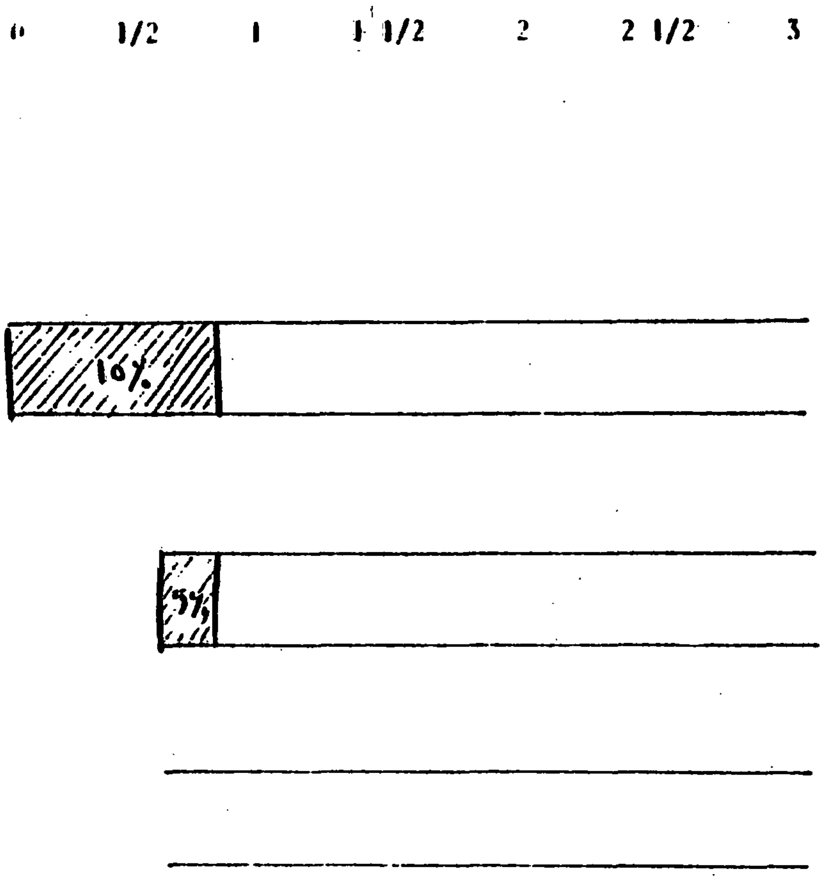
b. Formulate improved catalysts based on a.

c. Evaluate all catalysts for HDN activity

d. Kinetic analysis, interpretation of results and make recommendation

YEAR

TASK STATEMENT



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

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

g. Kinetic analysis interpretation of results and make recommendations.

☐ Scheduled

▨ Underway

■ Completed

* Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	FIRST QUARTER	SECOND QUARTER	THIRD QUARTER
PERSONNEL	5,334	21,252	39,431
TRAVEL	0	0	0
SUPPLIES AND EXPENSES	212	2,635	8,318
OCCUPANCY AND MAINTENANCE	0	0	0
EQUIPMENT	585	11,893	12,333
OTHER EXPENSES	140	1,841	5,023
TRANSFERS (OVERHEAD)	2,868	10,653	24,589
	9,139	48,274	90,141

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 route for removal of nitrogen from quinoline, a major 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.

Preparation of HDN Catalysts

Several catalysts with various levels of acidity and metals were prepared and used in hydrodenitrogenation of decahydroquinoline. The preparation of HDN catalysts typically involved the introduction of a metal into either a γ-alumina or silica alumina support. The supports were used in their hydrated forms (e.g., $\gamma\text{-}Al_2O_3 \cdot \chi H_2O$), as small particles with a diameter not smaller than 0.0029 inches and not larger than 0.0041 inches.

The metals were introduced into the support by mixing the particulate solid support with a small volume of either a mildly alkaline or acidic aqueous solution of a metal containing salt to form a thick paste. The metal containing aqueous solutions were always prepared from salts which contained only the metal to be studied and ligands which could be volatilized--typical salts used were metal nitrates or ammonium salts which contained metal. The pH of the aqueous solutions was adjusted by adding only nitric acid (HNO_3) or hydrated ammonia (NH_4OH) as needed.

All pastes formed by the addition of the particulate support to the aqueous salt solutions were placed in ceramic drying dishes and dried at 200°C and atmospheric pressure for a minimum of ten (10) hours. All resulting solids were then calcined at 350°C and atmospheric pressure for exactly four (4) hours. The calcined solids were then screened so that the particles had a diameter within the range of 0.0029 to 0.0041 inches. Particles within this size range were then bottled and were ready to use as HDN catalysts.

A summary of all the catalysts made appears in Table I.

TABLE I

Composition of HDN-Catalysts

Metal	Support	Mole % Metal	Metal Containing Salt	pH of Metal Containing Soln.
Ni	γ-alumina	8.4	$Ni(NO_3)_2 \cdot 6H_2O$	7.50
Ni	silica-alumina	8.4	$Ni(NO_3)_2 \cdot 6H_2O$	7.60
Mo	γ-alumina	23	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	5.31
Co	γ-alumina	8.4	$Co(NO_3)_2 \cdot 6H_2O$	7.52
V	γ-alumina	4.0	NH_4VO_3	7.58

a) 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 II) were used for all the experimental runs. The catalyst was presulfided (or heated in helium) for two hours with a mixture of 10 vol % H_2S in H_2 at atmospheric pressure and 400°C. In order to maintain 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 a Perkin-Elmer Model 3920 gas chromatograph equipped with a flame-ionization detector. A glass capillary column (75m-OV101) was used for all reactant and product analysis.

Figures 1 and 2 show the results from runs using silica-alumina and γ-alumina. The major products from both the runs were decahydroquinoline (both trans and Cis forms) and 5,6,7,8-tetrahydroquinoline; no other products were detected. However, products formed with HY-zeolite (Fig. 3) show that significant amounts of benzene is also formed. 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. Figures 4-6 show the total nitrogen removal from decahydroquinoline

TABLE II

Standard Operating Conditions

Temperature:	350 ± 2°C
Total Pressure:	34 ± 1 atm*
Reactant Concentration:	0.5 wt % in n-hexadecane
CS_2 Loading:	0.05 wt % ($\approx$1.4 vol % H_2S in gas phase)
Catalyst Loading:	0.5 wt % of reaction mixture (150-200 mesh size)

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*Partial pressure of n-hexadecane @ 350°C $\approx$ 3.24 atm.

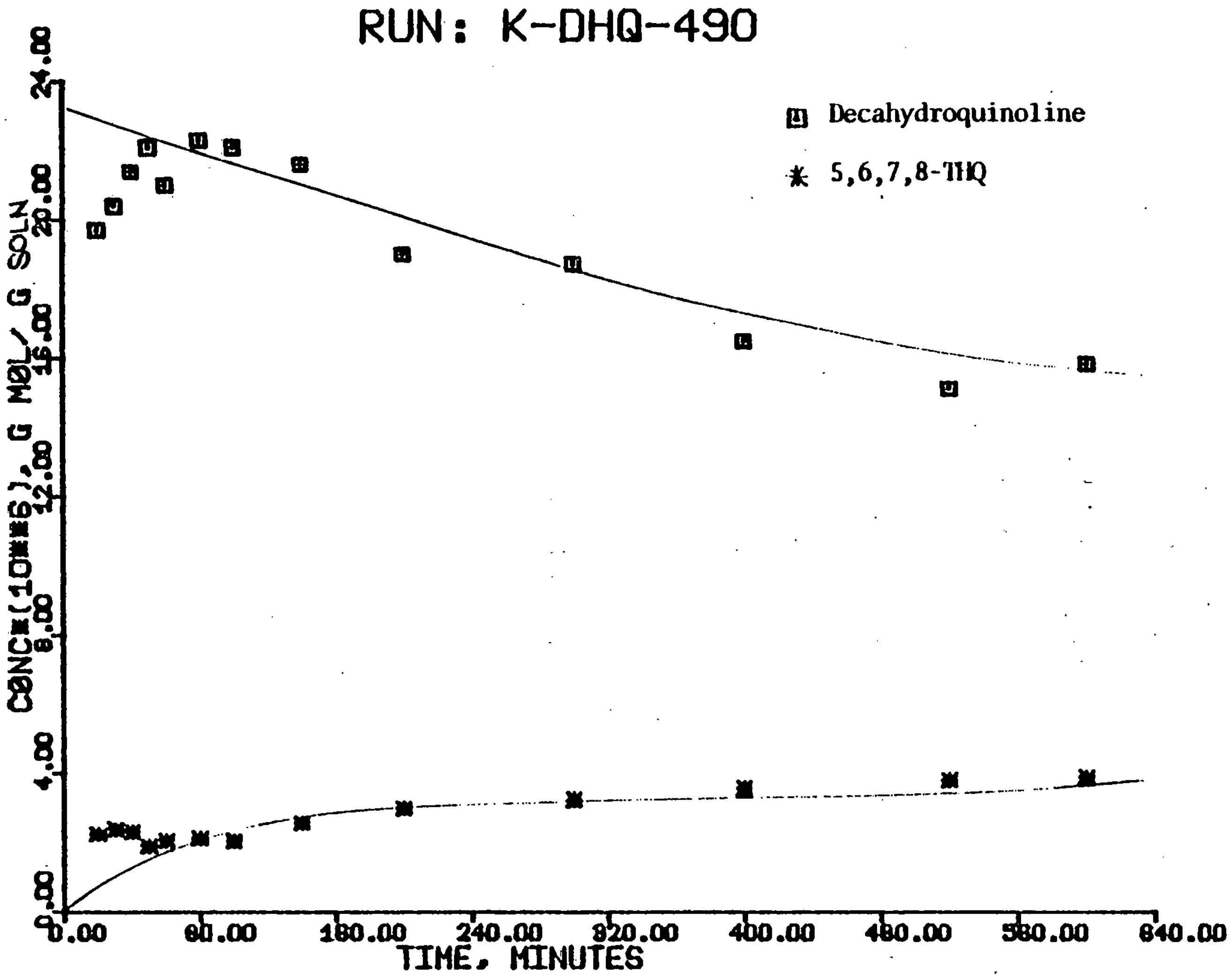

Figure 1: Concentration profiles for hydrodenitrogenation of decahydroquinoline using silica-alumina.

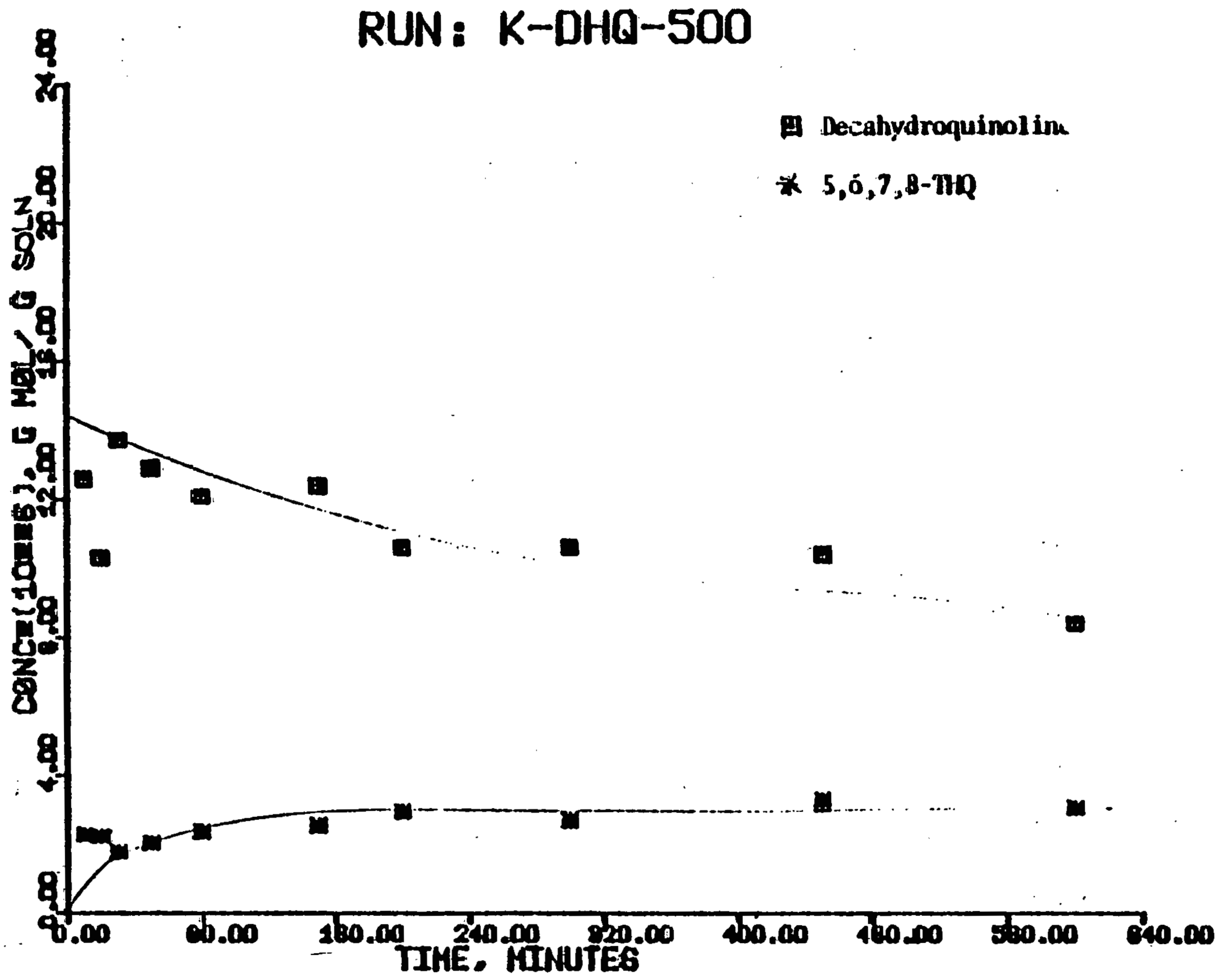

Figure 2: Concentration profiles for hydrodenitrogenation of decahydroquinoline using γ-alumina.

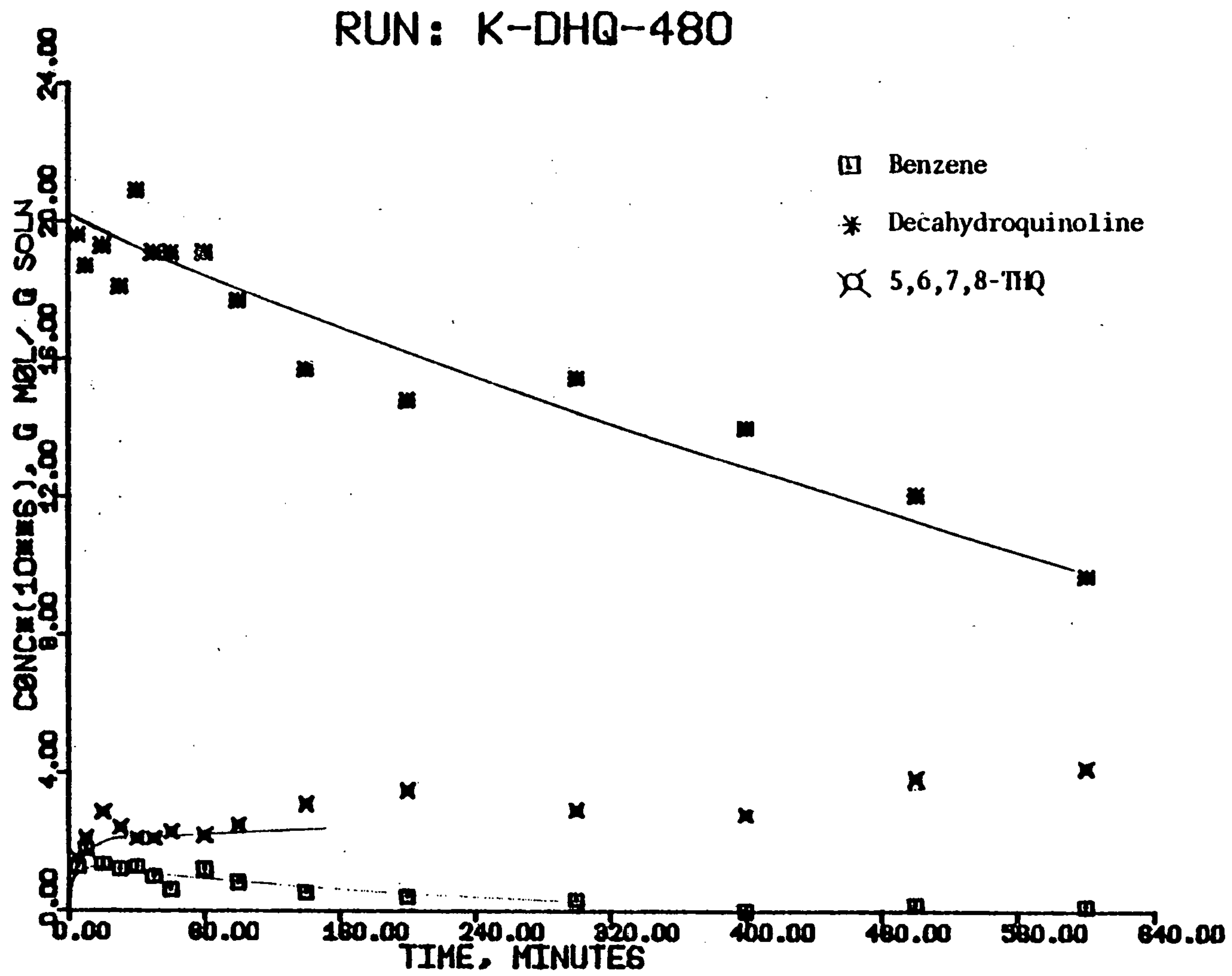

Figure 3: Concentration profiles for hydrodenitrogenation of decahydroquinoline using HY-zeolite.

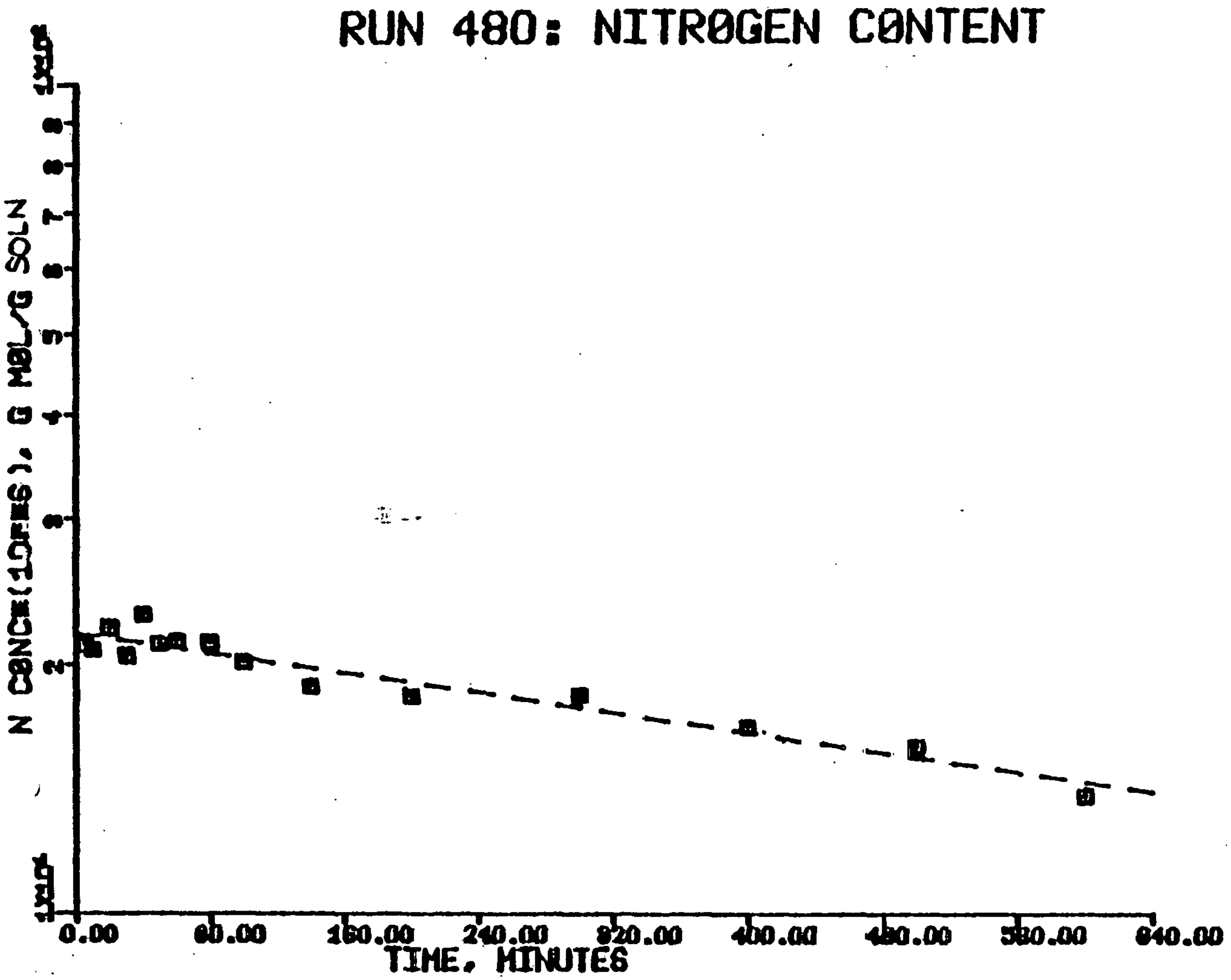

Figure 4: Total nitrogen removal from decahydroquinoline using HY-zeolite.

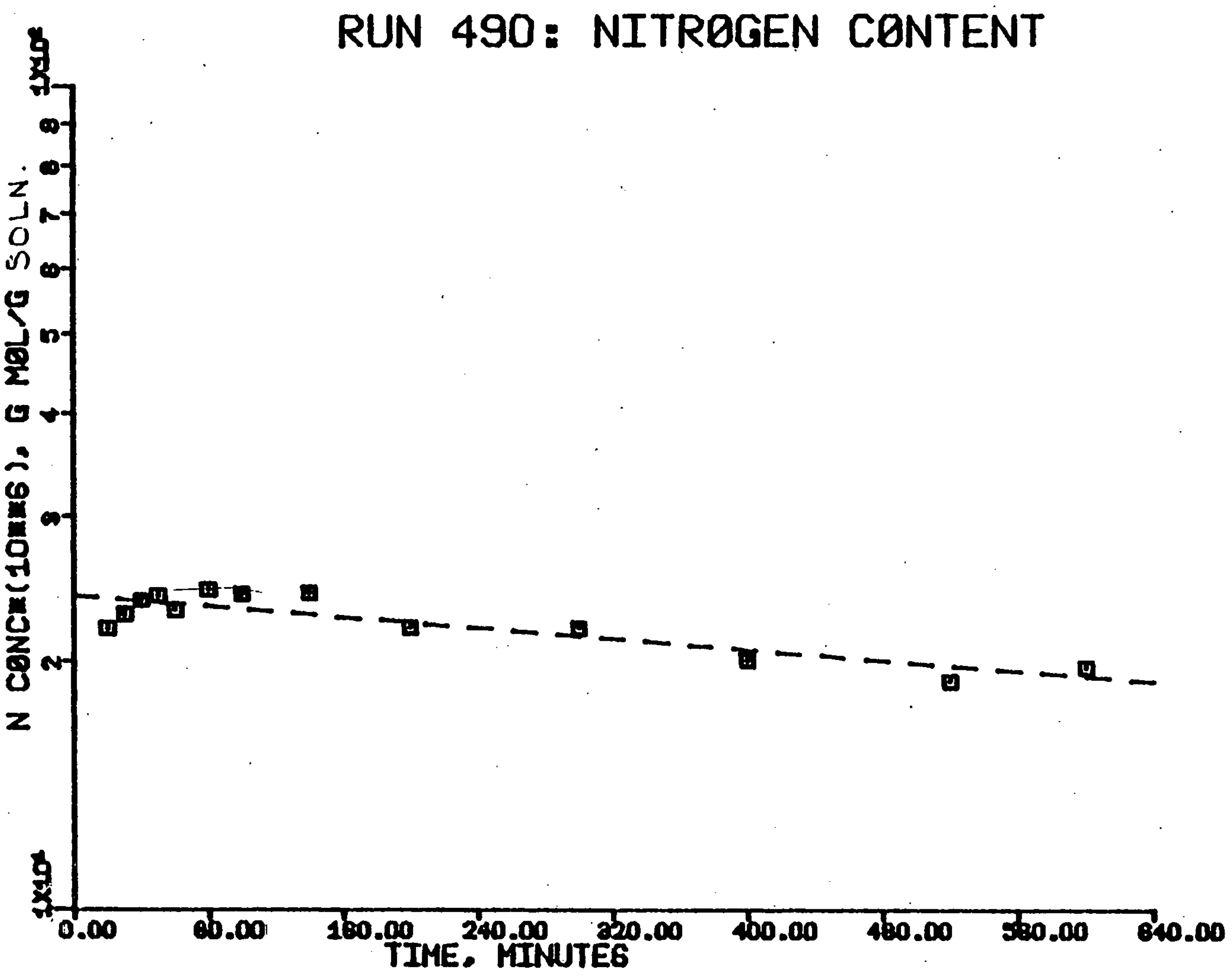

Figure 5: Total nitrogen removal from decahydroquinoline using silica-alumina.

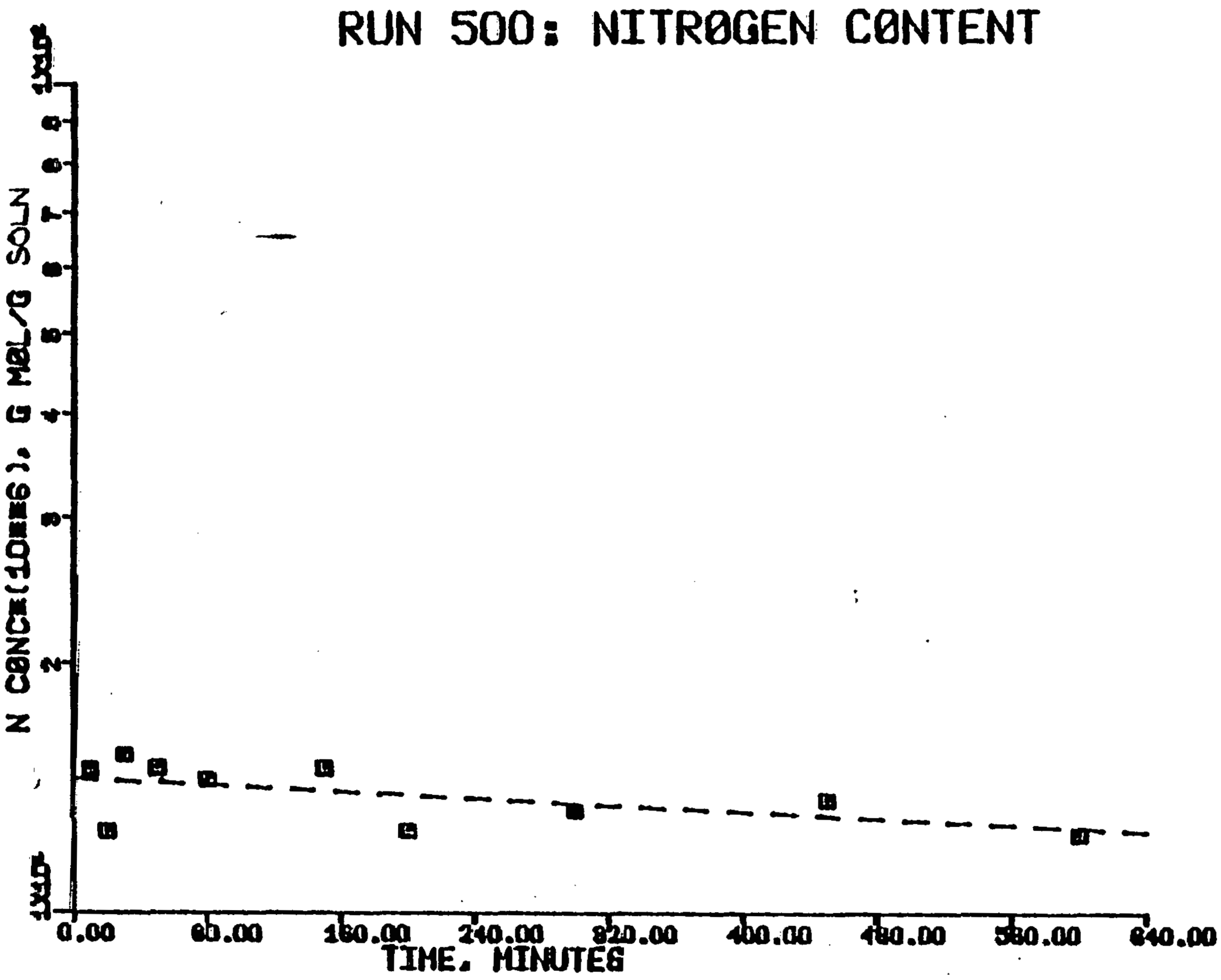

Figure 6: Total nitrogen removal from decahydroquinoline using γ-alumina.

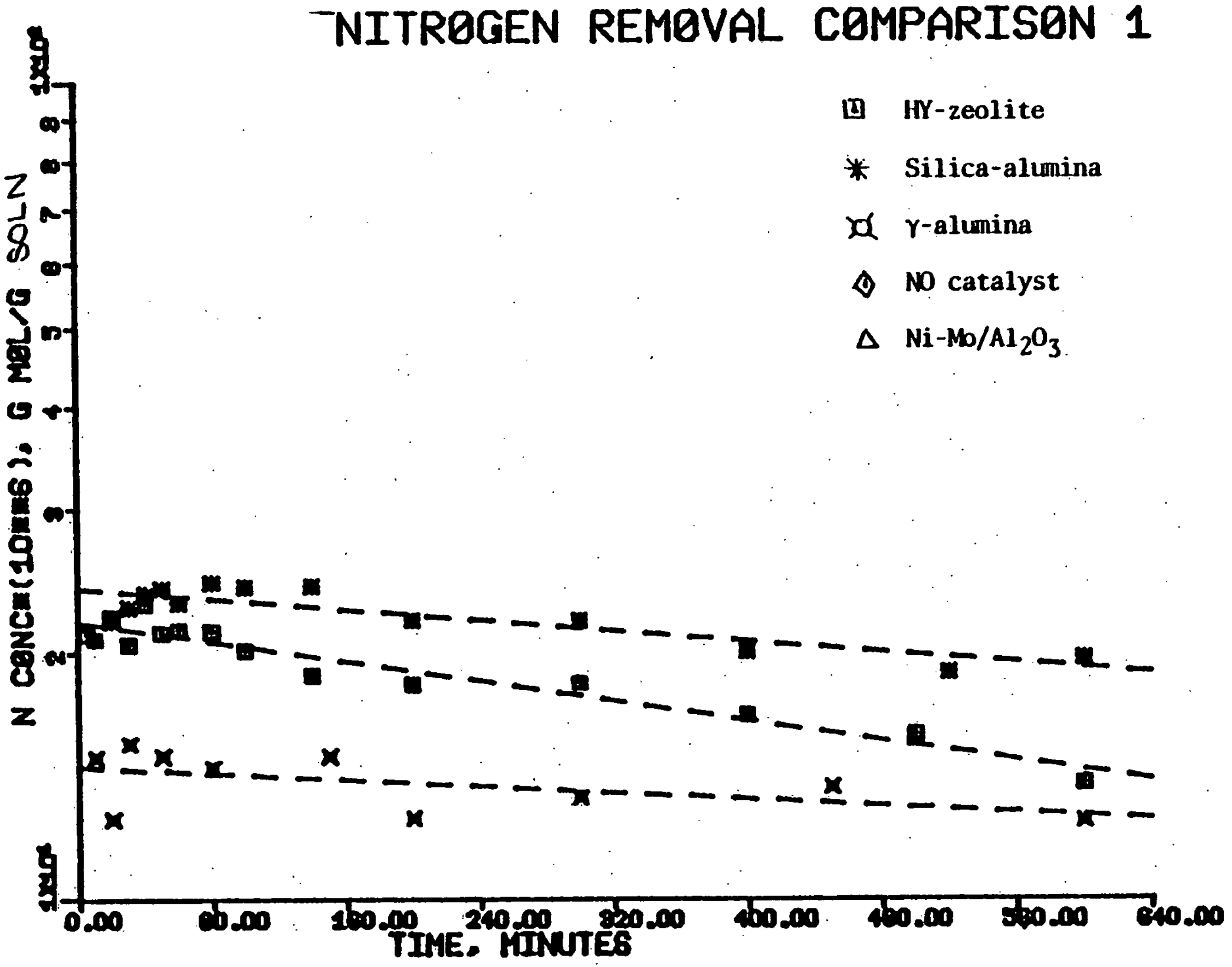

Figure 7: Total nitrogen removal from decahydroquinoline using various catalysts.

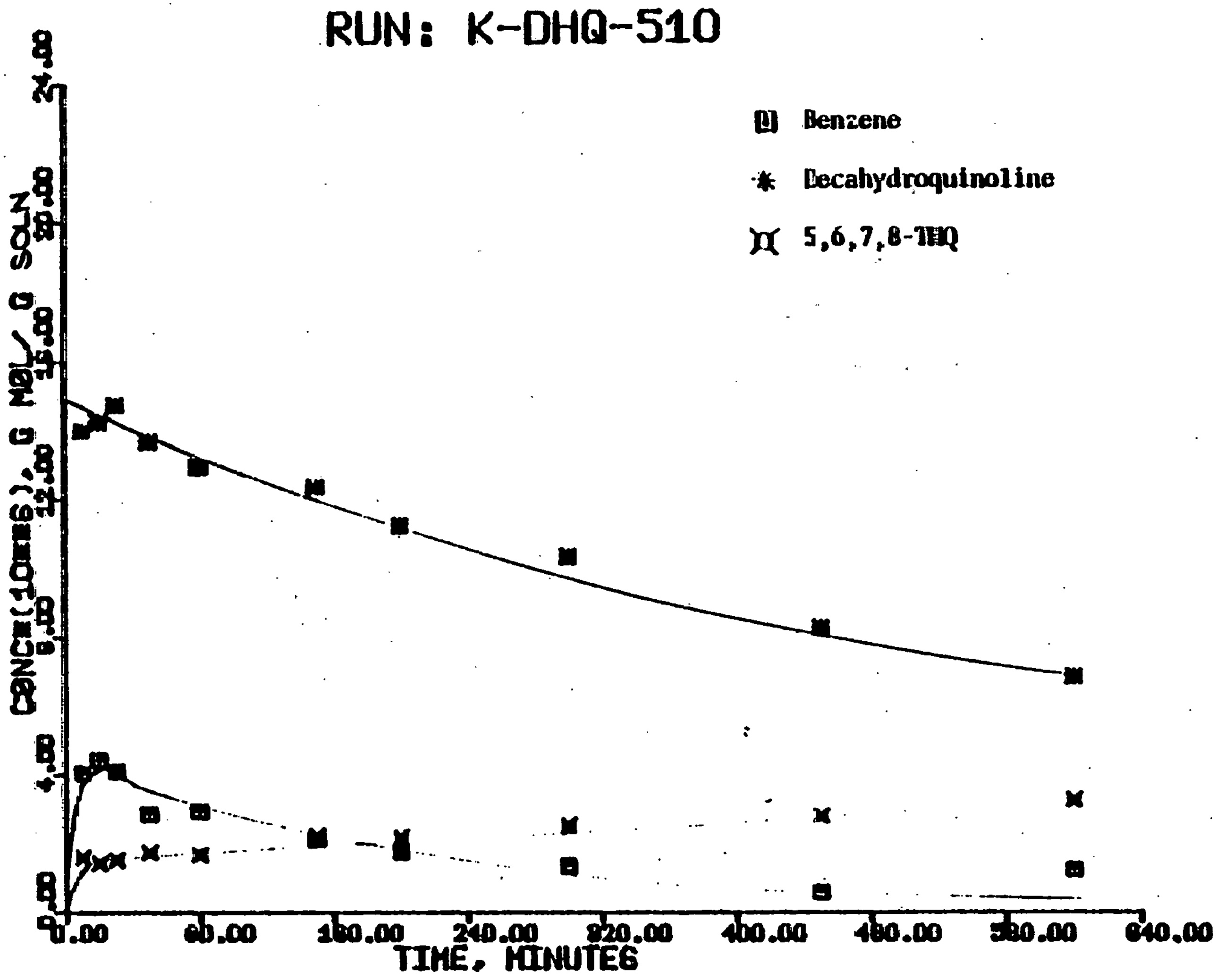

Figure 8: Concentration profiles for hydrodenitrogenation of decahydroquinoline using unsulfided HY-zeolite.

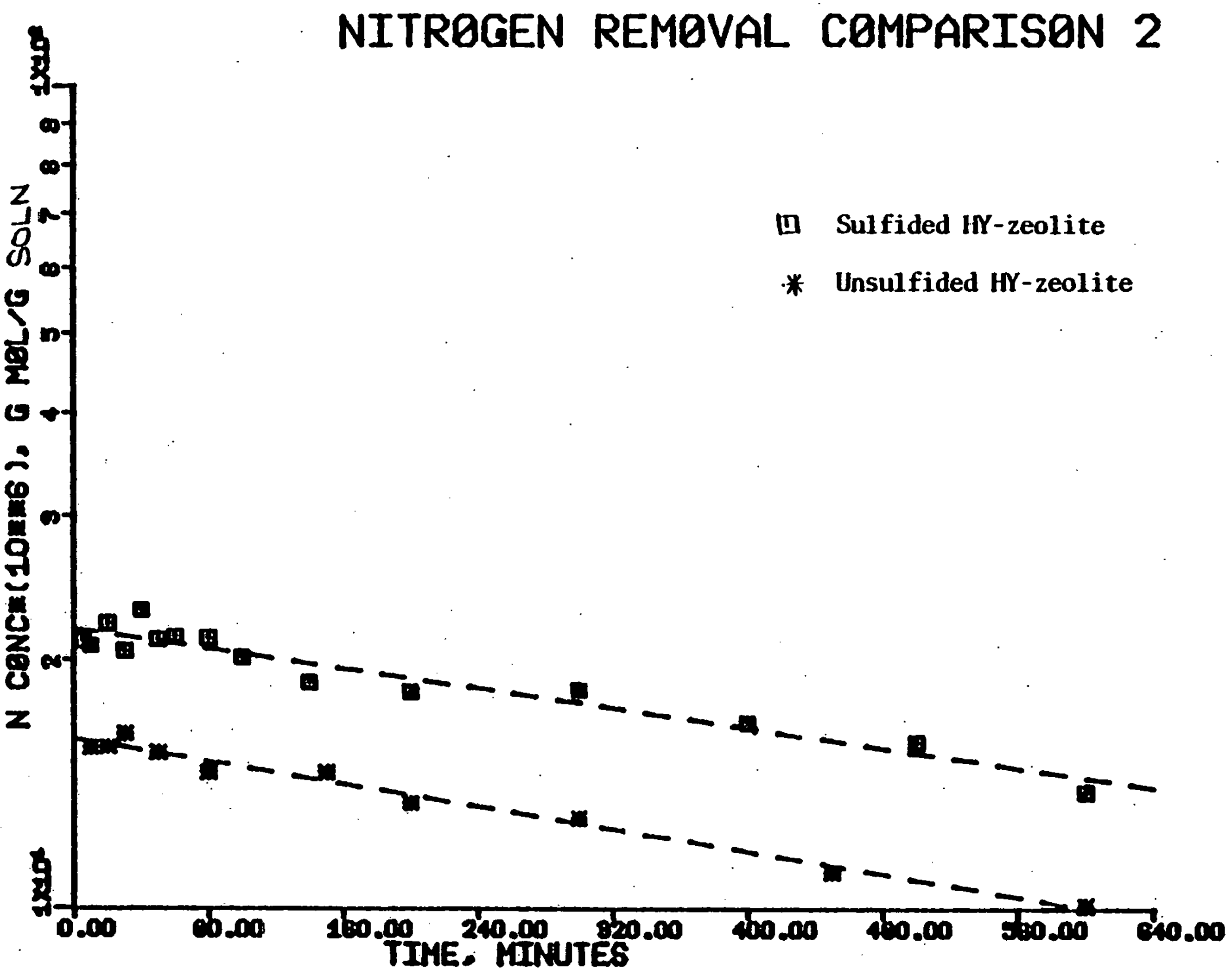

Figure 9: Total nitrogen removal from decahydroquinoline using sulfided and unsulfided HY-zeolite.

using HY-zeolite, silica-alumina and γ-alumina catalysts. In fact, there is no significant difference in nitrogen removal rate between the run with no catalyst and the run using Brønsted acid catalysts as shown in Figure 7. These results conclusively show that carbon-nitrogen bond scission is not catalyzed by Brønsted acid sites. Results from HY-zeolite runs indicate that the benzene did not come from the nitrogen containing compounds but that it came from the n-hexadecane, its formation being catalyzed by the HY-zeolite. In all likelihood, the olefinic products formed with these non-hydrogenating catalysts are polymerized on the surfaces of these acidic catalysts, thereby inhibiting further catalytic activity.

Figure 8 shows the concentration profiles for hydrodenitrogenation of decahydroquinoline using unsulfided HY-zeolite. It was thought that during sulfiding of the zeolite. Sulfur is formed, which may block the active sites of the HY-zeolite, making it inactive. However, some products namely benzene and 5,6,7,8-tetrahydroquinoline are formed with unsulfided HY-zeolite. In fact, there is no significant difference in nitrogen removal rate between (Figure 9) the run with sulfided HY-zeolite (34.1% N-removal) and the run using unsulfided HY-zeolite (37.6% N-removal). These results indicate that sulfiding of HY-zeolite does not deactivate the catalyst.

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 over a set of catalysts. The

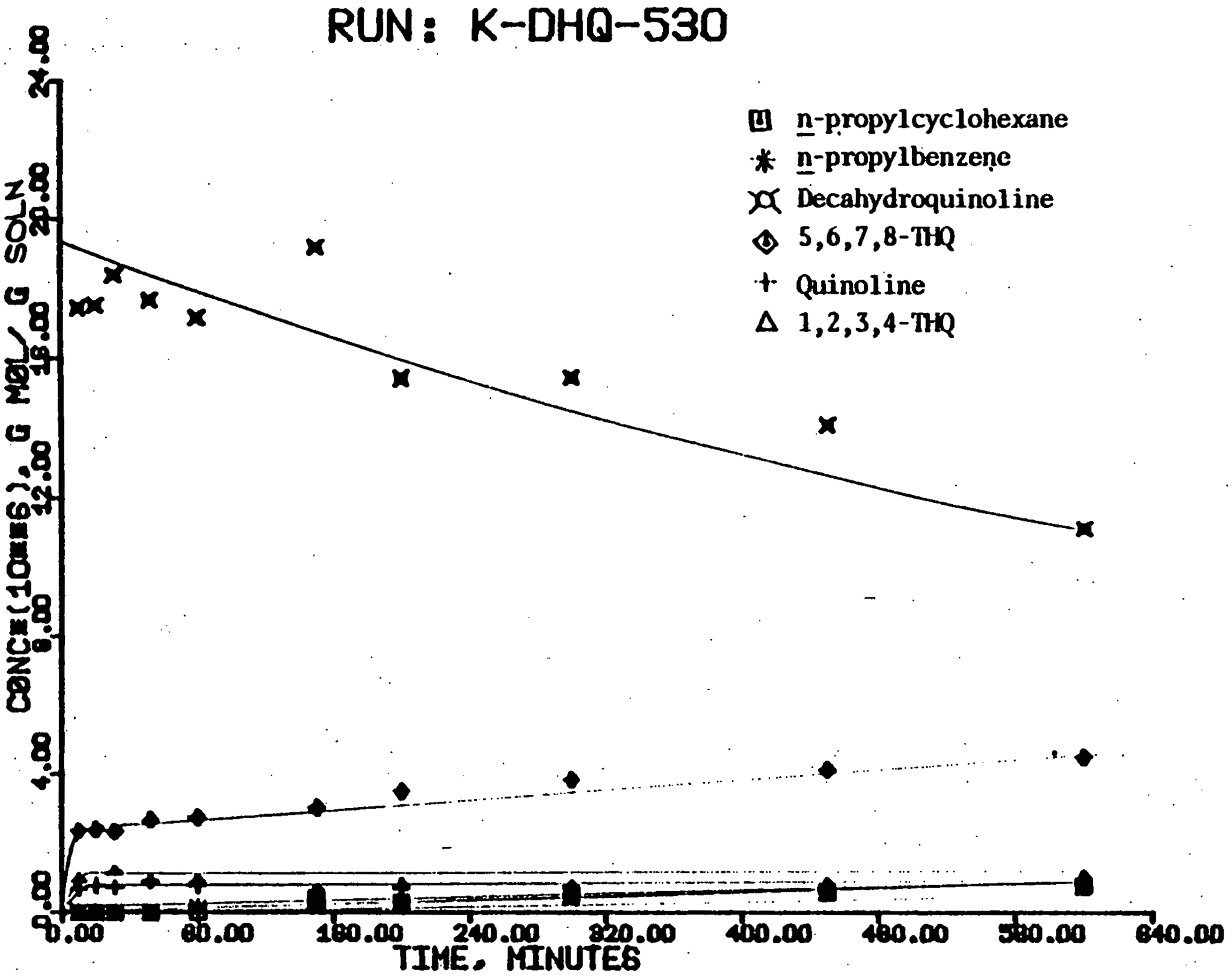

Figure 10: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Ni on γ-alumina.

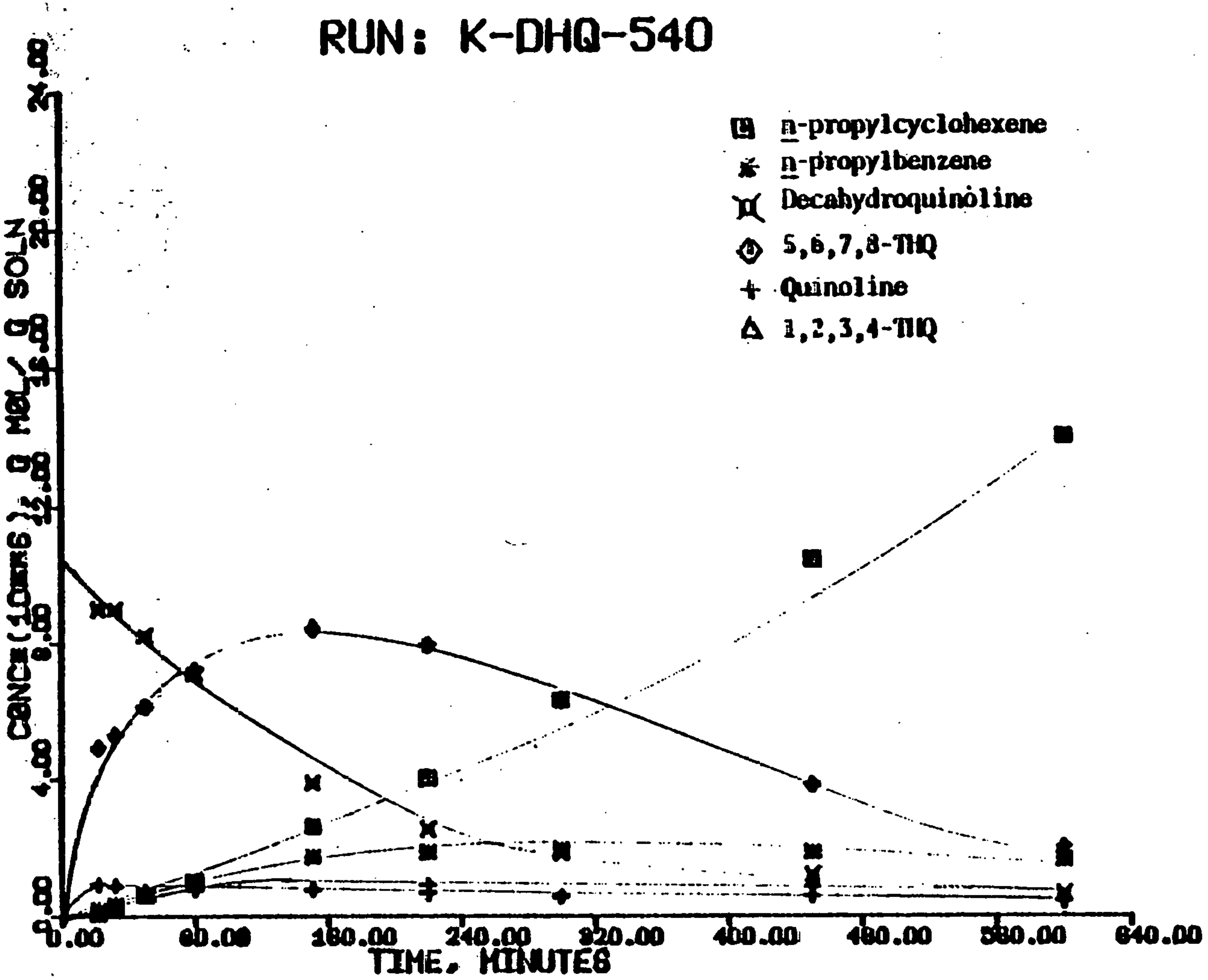

Figure 11: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 23% Mo on γ-alumina.

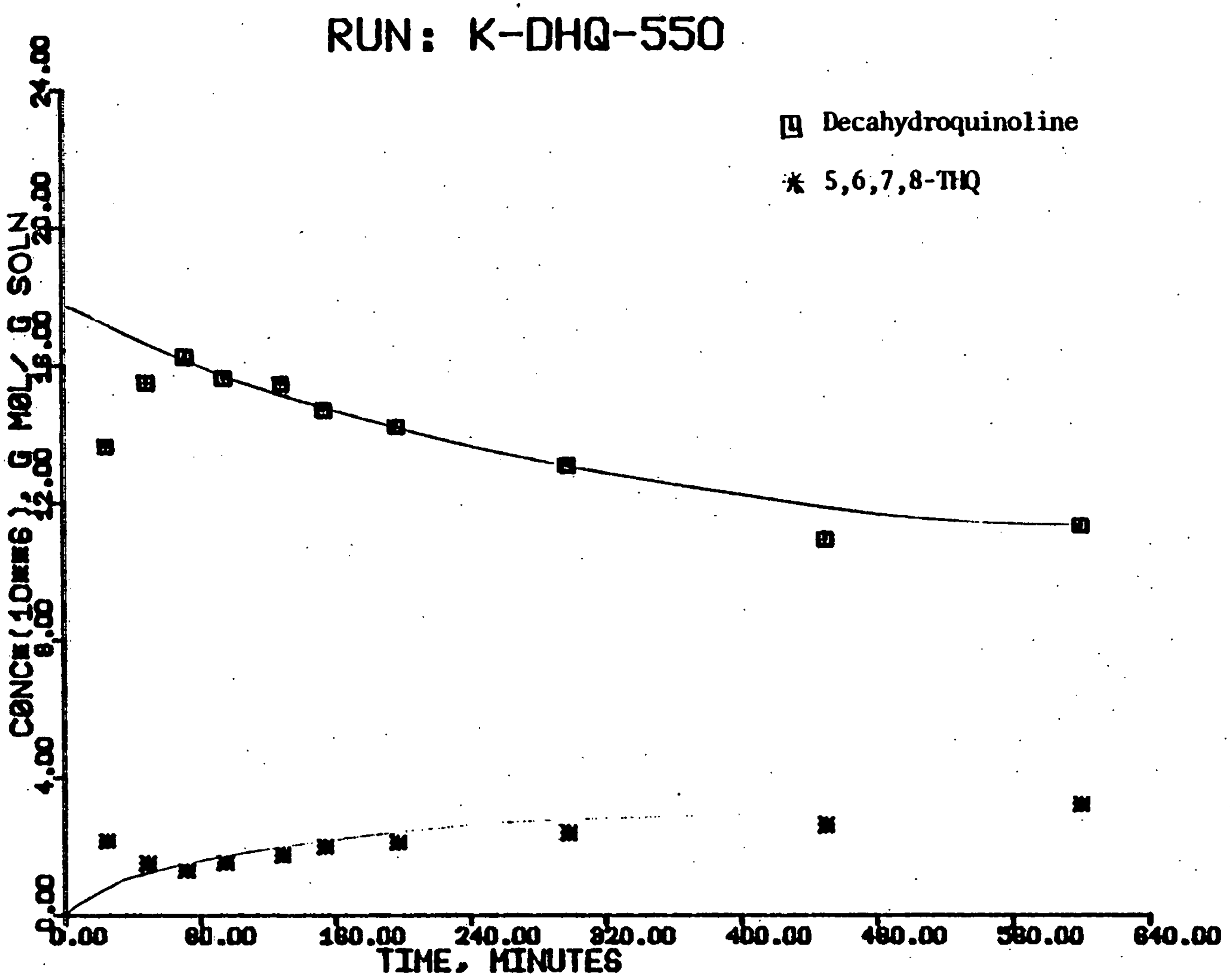

Figure 12: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Ni on silica-alumina.

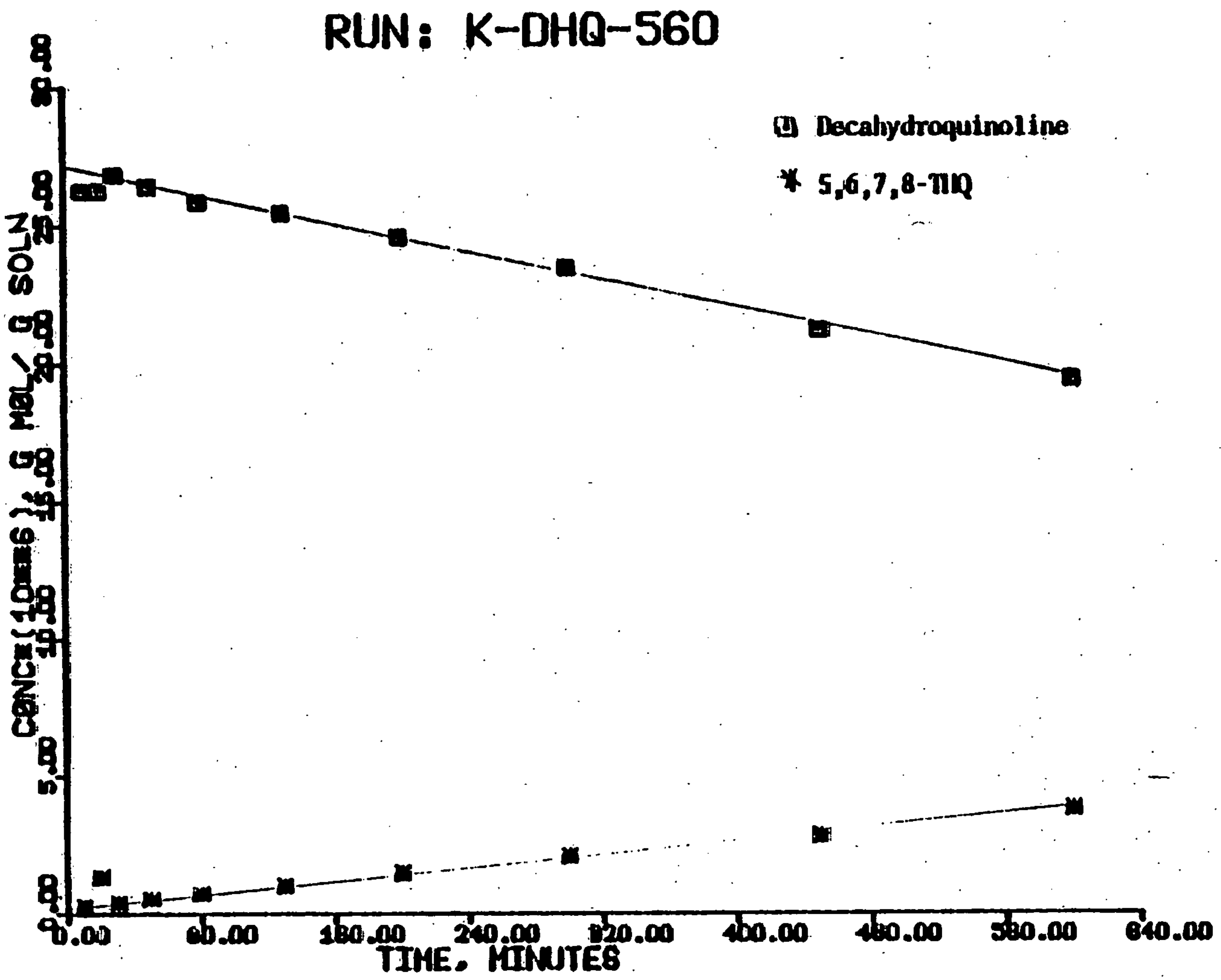

Figure 13: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Co on γ-alumina.

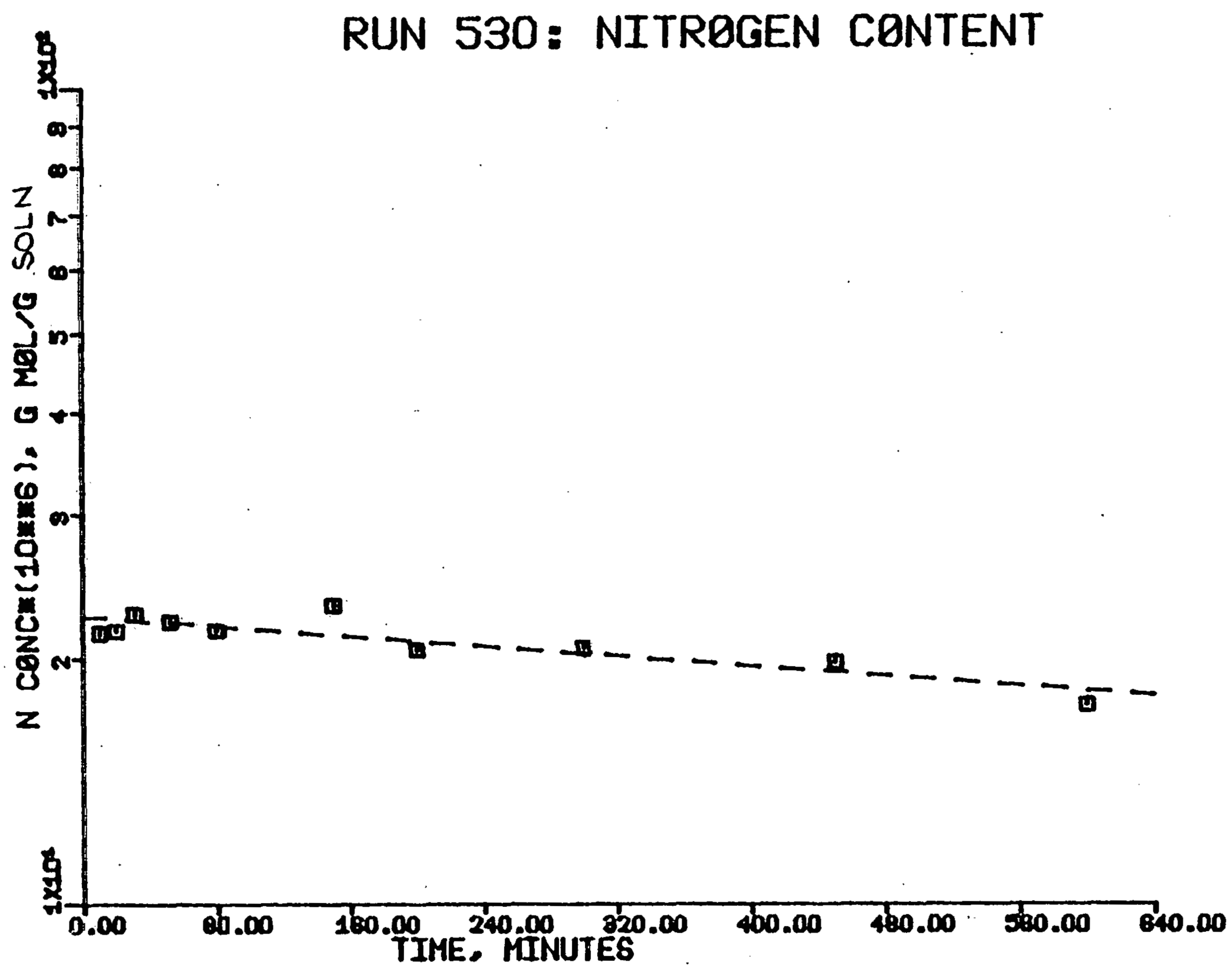

Figure 14: Total nitrogen removal from decahydroquinoline using 8.4% Ni on γ-alumina.

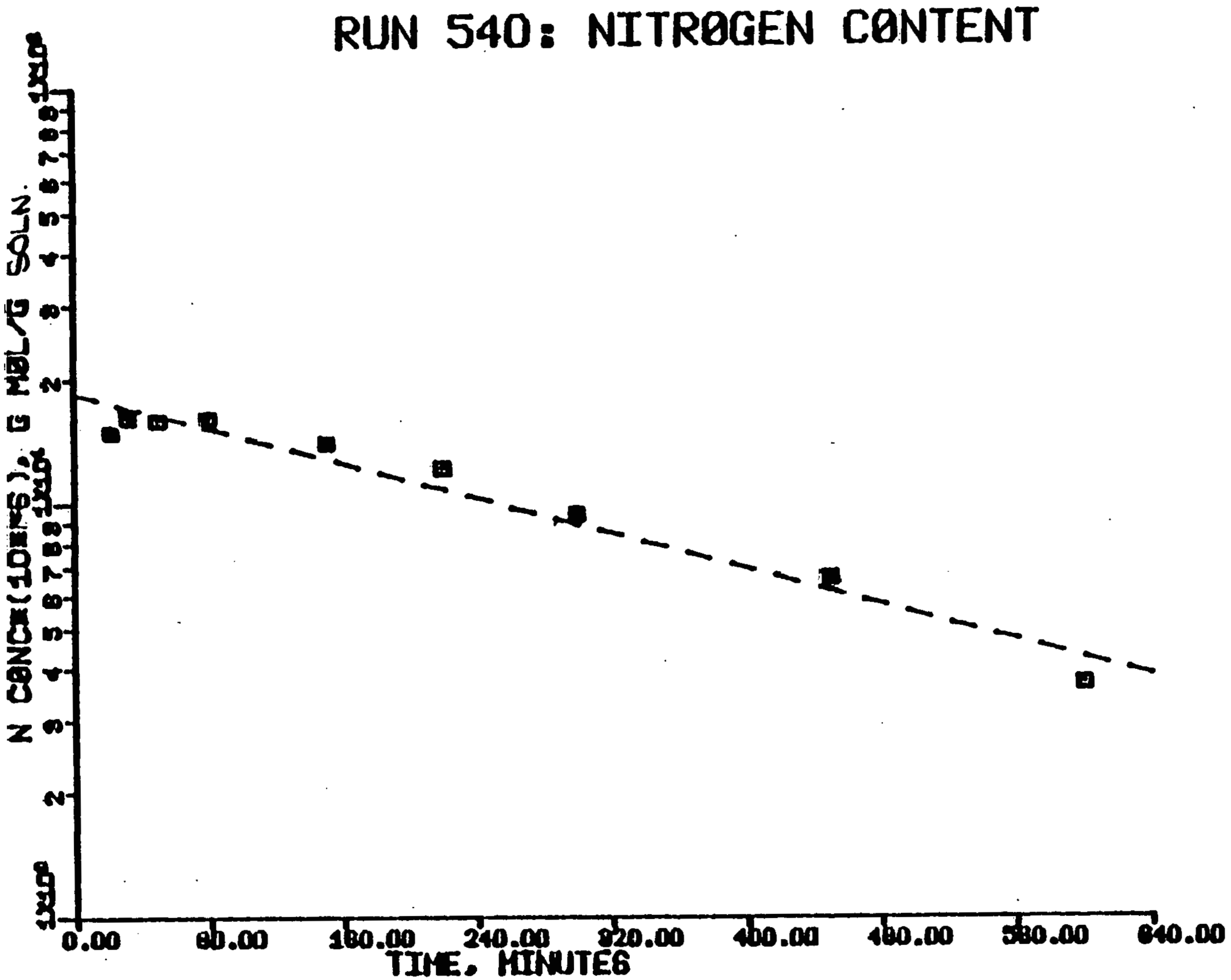

Figure 15: Total nitrogen removal from decahydroquinoline using 23% Mo on γ-alumina.

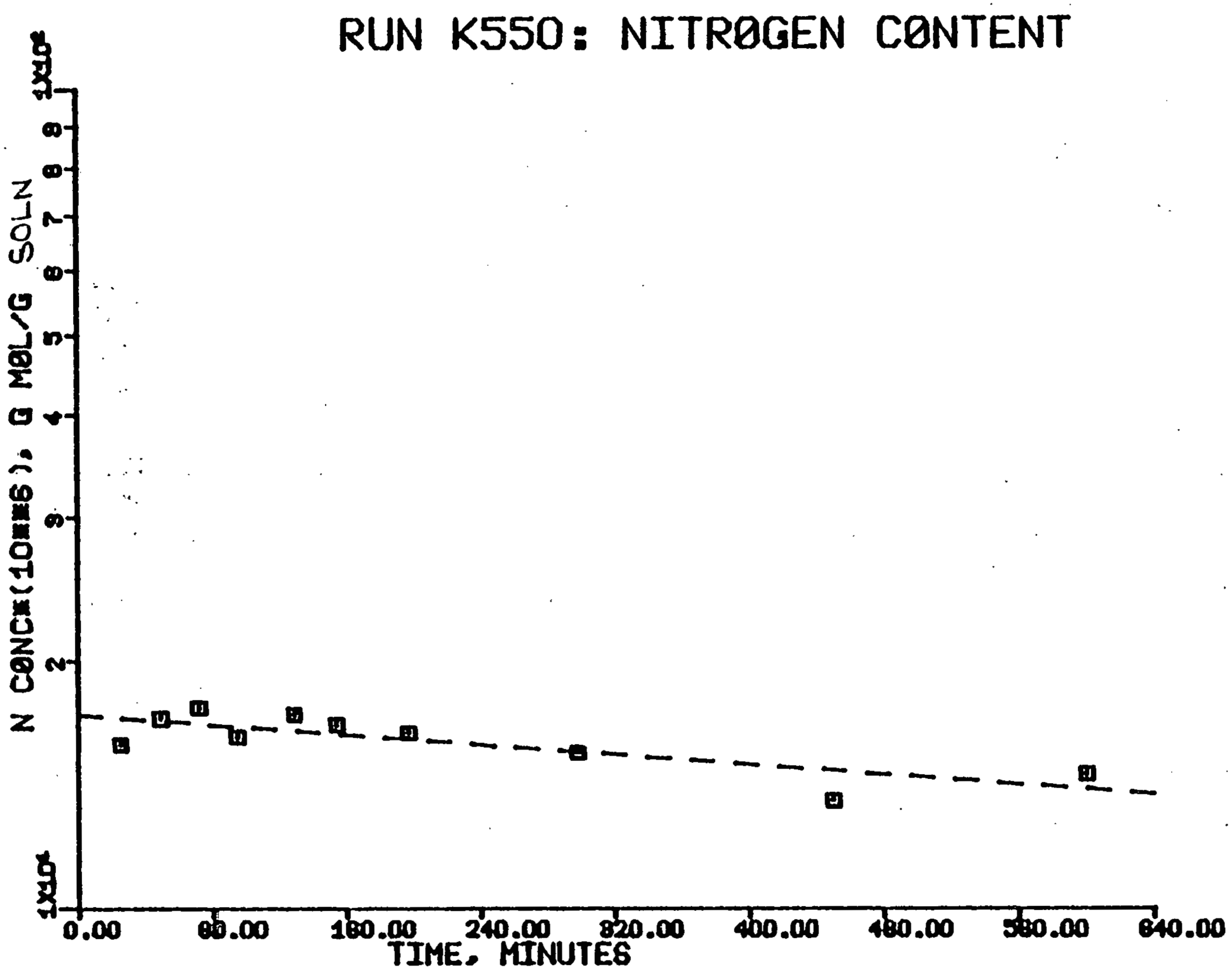

Figure 16: Total nitrogen removal from decahydroquinoline using 8.4% Ni on silica-alumina.

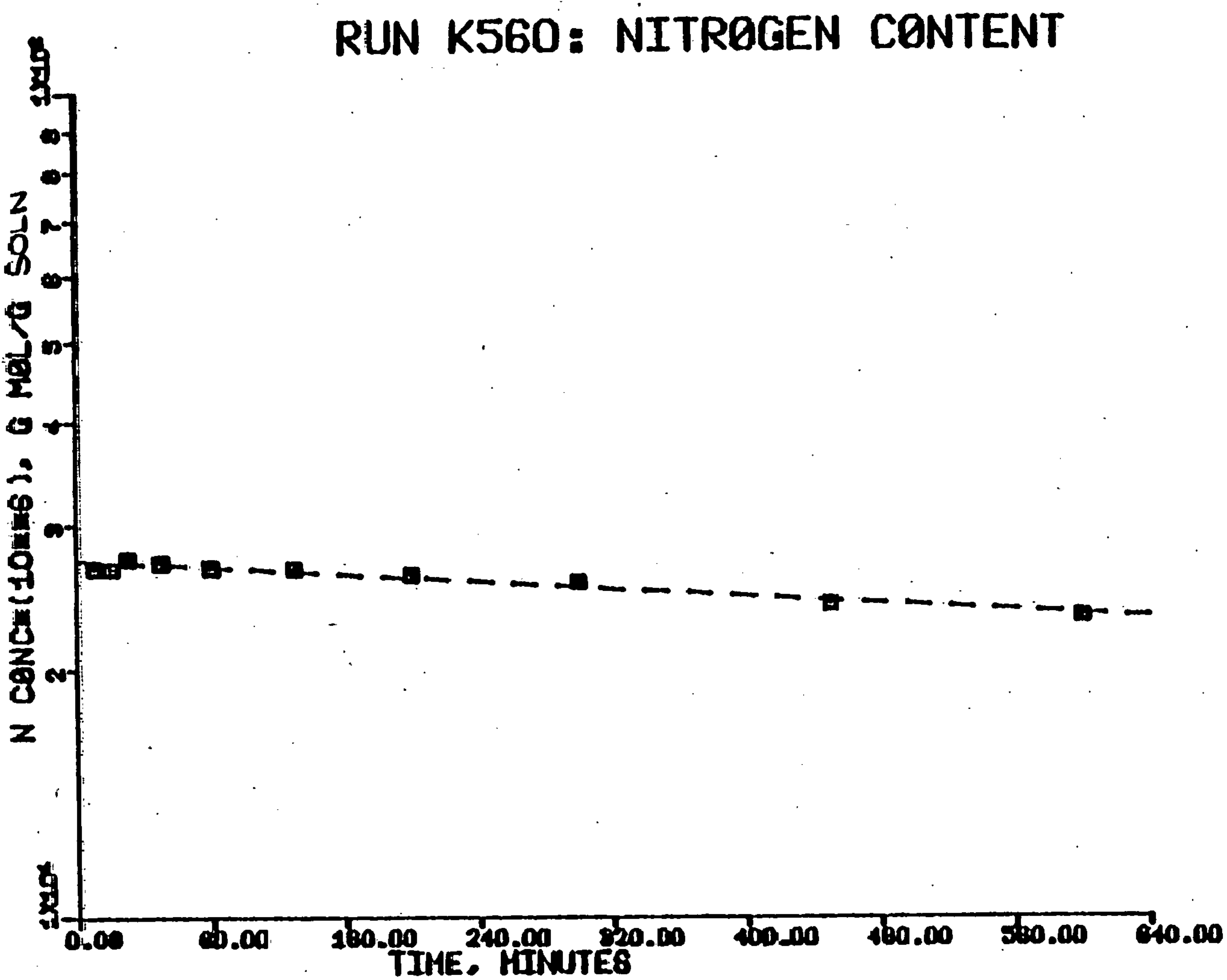

Figure 17: Total nitrogen removal from decahydroquinoline using 8.4% Co on γ-alumina.

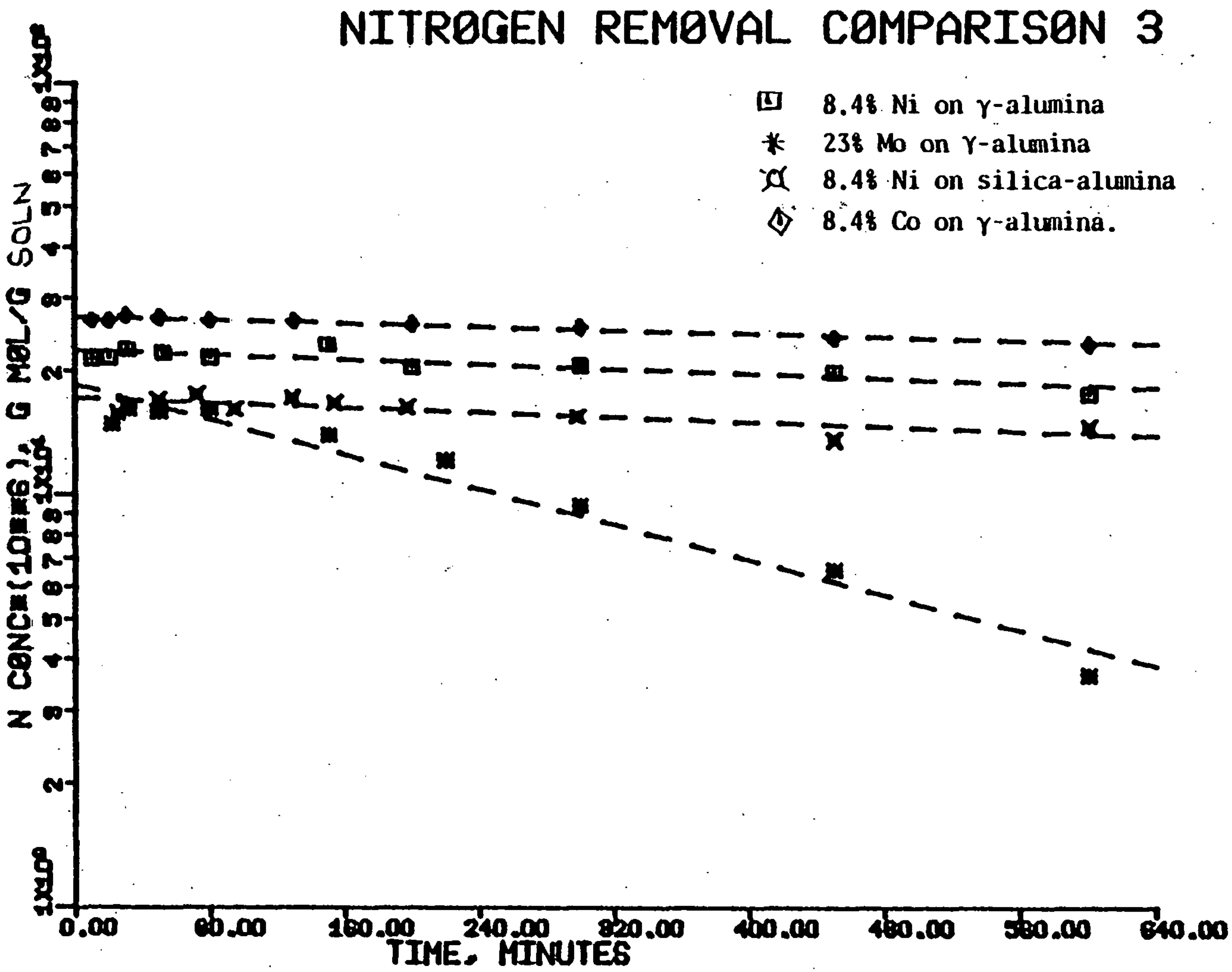

Figure 18: Total nitrogen removal from decahydroquinoline using various metal supported catalysts.

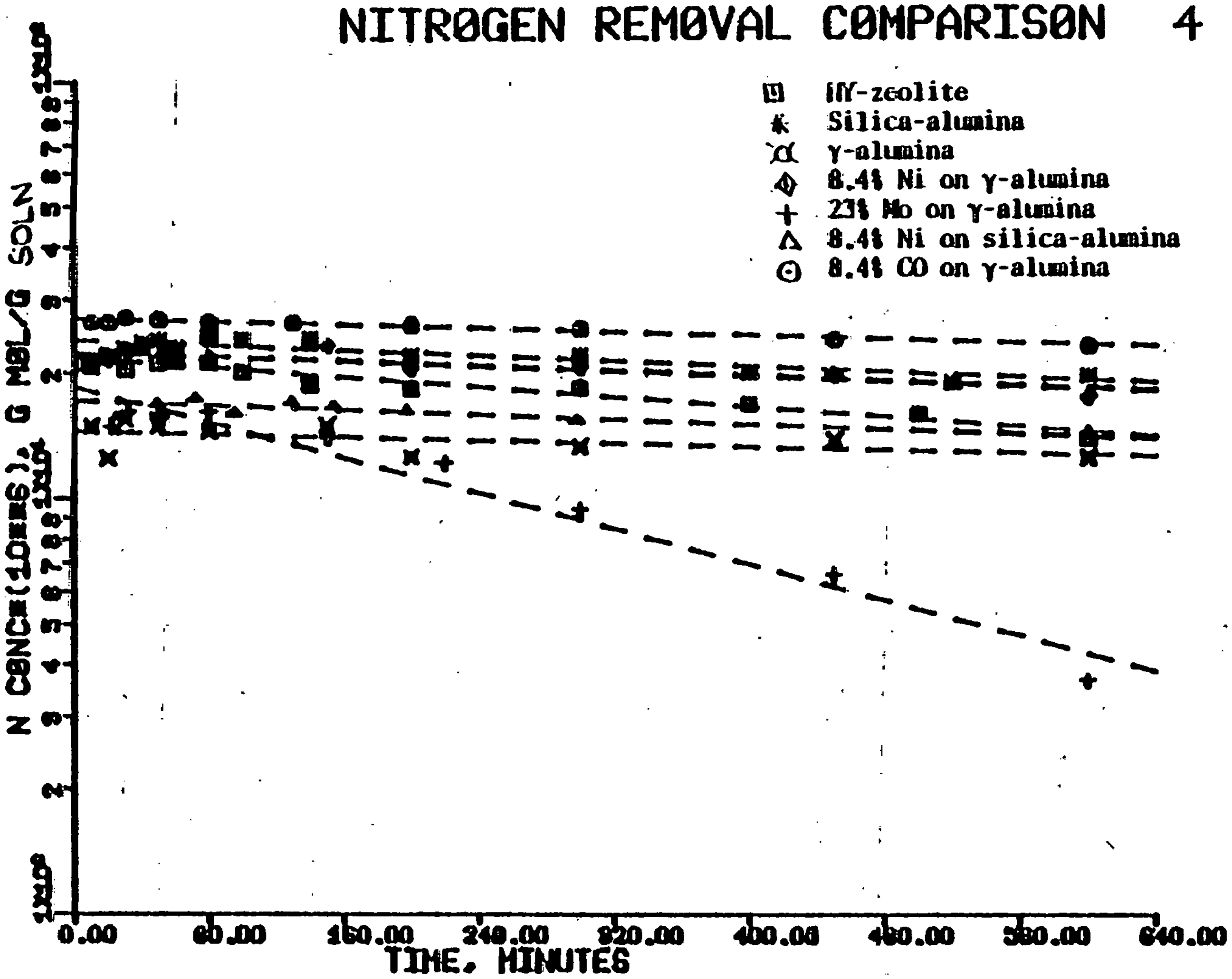

Figure 19: Total nitrogen removal from decahydroquinoline using various catalysts.

catalysts tested include catalysts with Co, Ni, Mo impregnated on silica-alumina or γ-alumina.

Runs were made using decahydroquinoline to determine the rates of C-N bond scission over the set of catalysts prepared above. The results indicate (Figures 10-13) that the products from the run using Ni and Mo on γ-alumina showed traces of quinoline, 1,2,3,4-tetrahydroquinoline, n-propylbenzene, and n-propylcyclohexane with 5,6,7,8-tetrahydroquinoline and decahydroquinoline as major products. However the products from the runs with Ni on silica-alumina and Co on γ-alumina catalysts showed only decahydroquinoline and 5,6,7,8-tetrahydroquinoline. The dehydrogenation reaction between decahydroquinoline and 5,6,7,8-tetrahydroquinoline was absent in the second set of runs.

Figures 14-17 show the total nitrogen removal from decahydroquinoline for the above runs. The percentage of nitrogen removed was: Ni on alumina: 18.9%; Mo on alumina: 77.2%; Ni on silica-alumina: 18.8%; and Co on alumina: 14.3%. These results show that the nitrogen removal rate was highest for Mo on γ-alumina catalyst. Figure 18 compares total nitrogen removal from decahydroquinoline for above set of catalysts.

Figure 19 compares the total nitrogen removal from decahydroquinoline for acid catalysts and metal impregnated on acid support catalysts. Figure 19 shows that there is no significant difference in nitrogen removal rate between the two sets of catalysts except when a Mo/γ-alumina catalyst was used. With Mo on γ-alumina the nitrogen removal rate increased fourfold. 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 Brønsted acidity does not play any role in the carbon-nitrogen bond scission. Even with some Lewis acidity present (such as in silica-alumina and alumina) we do not see any carbon-nitrogen bond scission. Out of all the catalysts tested Mo on γ-alumina catalyst gives the highest rate of nitrogen removal.

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 a uniquely new, highly selective hydrodenitrogenation catalyst that can selectively coordinate nitrogen and remove it from multi-ring nitrogen containing aromatic compounds with only limited or no hydrogenation of the aromatic ring; thereby achieving major savings in hydrogen consumption.

Quinoline has been chosen as the reactant since it has a benzenoid ring and nitrogen-containing aromatic rings characteristic of nitrogen-containing compounds in coal-derived liquids.

A catalyst was desired that could act as a Lewis acid and selectively coordinate with the basic lone electron pair on nitrogen in Quinoline. The coordination with nitrogen would reduce the aromaticity of the nitrogen-containing ring thus facilitating nitrogen removal without hydrogenation of the neighboring aromatic rings. On this basis the initial catalyst chosen for study was aluminum borate with 4% nickel, $AlBO_3/4\%$ Ni, a Lewis acid catalyst. A second Lewis acid catalyst chosen was aluminum borate phosphate with 4% nickel, $AlBO_3 \cdot PO_4/4\%$ Ni.

Preparation of $AlBO_3/4\%$ wt Ni:

The aluminum borate, $AlBO_3$, support was prepared from equal weights of aluminum hydrate (Hydral 710 from ALCOA) and boric acid. This was mixed with mortar and pestal while adding small amounts of heated (≈50°C) distilled water. The mixture was mixed until a homogeneous white paste was obtained. The aluminum borate mixture was then dried 18 hours at 211.6°C then calcinated for 3 hours at 350.6°C. This was ground to 150-200 mesh size. The 150-200 mesh aluminum borate was then mixed in a similar manner with 4 wt % nickel in nickel nitrate solution adjusted to a pH of 7.5 with ammonium hydroxide. This was again dried at 211.6°C for 18 hours; calcinated at 350.6°C for 3 hours, and ground to 150-200 mesh size.

Preparation of $AlBO_3 \cdot PO_4/4$ wt % Ni:

150-200 mesh $AlBO_3$ was mixed with 20 wt % (to $AlBO_3$) of 85% H_3PO_4 and a small amount of distilled water until a homogeneous glassy white paste was obtained. This was dried at 112°C for 18 hours, calcinated at 350.6°C for 3 hours, then ground to 150-200 mesh size.

The 150-200 mesh $AlBO_3 \cdot PO_4$ was then impregnated with 4 wt % nickel in an identical manner as discussed previously with $AlBO_3/4$ wt % Ni.

Runs were made using the $AlBO_3$/4% Ni catalyst (MS-Q-1 through MS-Q-5) and quinoline reactant under a variety of conditions to determine the carbon-nitrogen bond scission ability, the effects of the metal surface present in the autoclave, and the effect of temperature. One run was made with $AlBO_3 \cdot PO_4$/4% Ni to compare the results with $AlBO_3$/4% Ni.

Preliminary results indicate that $AlBO_3$/4% Ni catalyst gives a marked increase of nitrogen removal in quinoline over other catalysts studied, a decrease in activity of the catalyst was observed when the reaction was run in contact with the metal autoclave walls, temperature change has not yet been determined to have a definite effect on the nitrogen removal rate. The initial results of the $AlBO_3 \cdot PO_4$/4% Ni catalyst indicate that the nitrogen removal process is strongly inhibited by the phosphate group.

Experimental:

The detailed operating conditions of each run are shown in Table II. The autoclave for each run was used in the batch mode. A glass liner was used for Runs 4 and 5. All of the other runs were without glass liner. The reaction temperature was controlled to ±2°C. The catalyst for each was presulfided for 2 hours with a mixture of 10 vol % H_2S in H_2 at atmospheric pressure and 400°C. In order to maintain the catalyst in the sulfided form during the reaction, 0.05 wt % CS_2 solution in hexadecane was added to injection tubing together with catalyst and reactant.

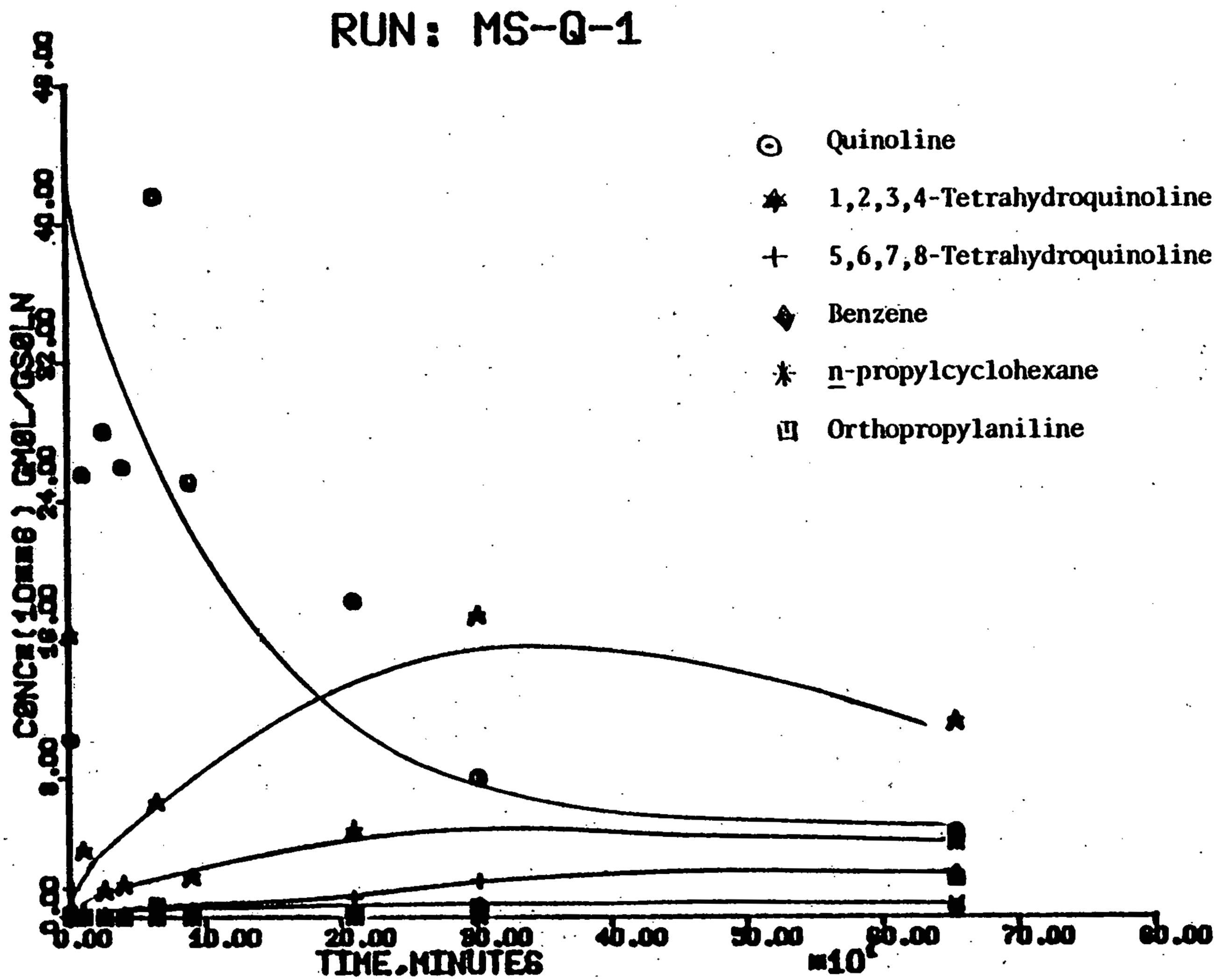

Figure 20: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % $Ni/AlBO_3$ at 350°C.

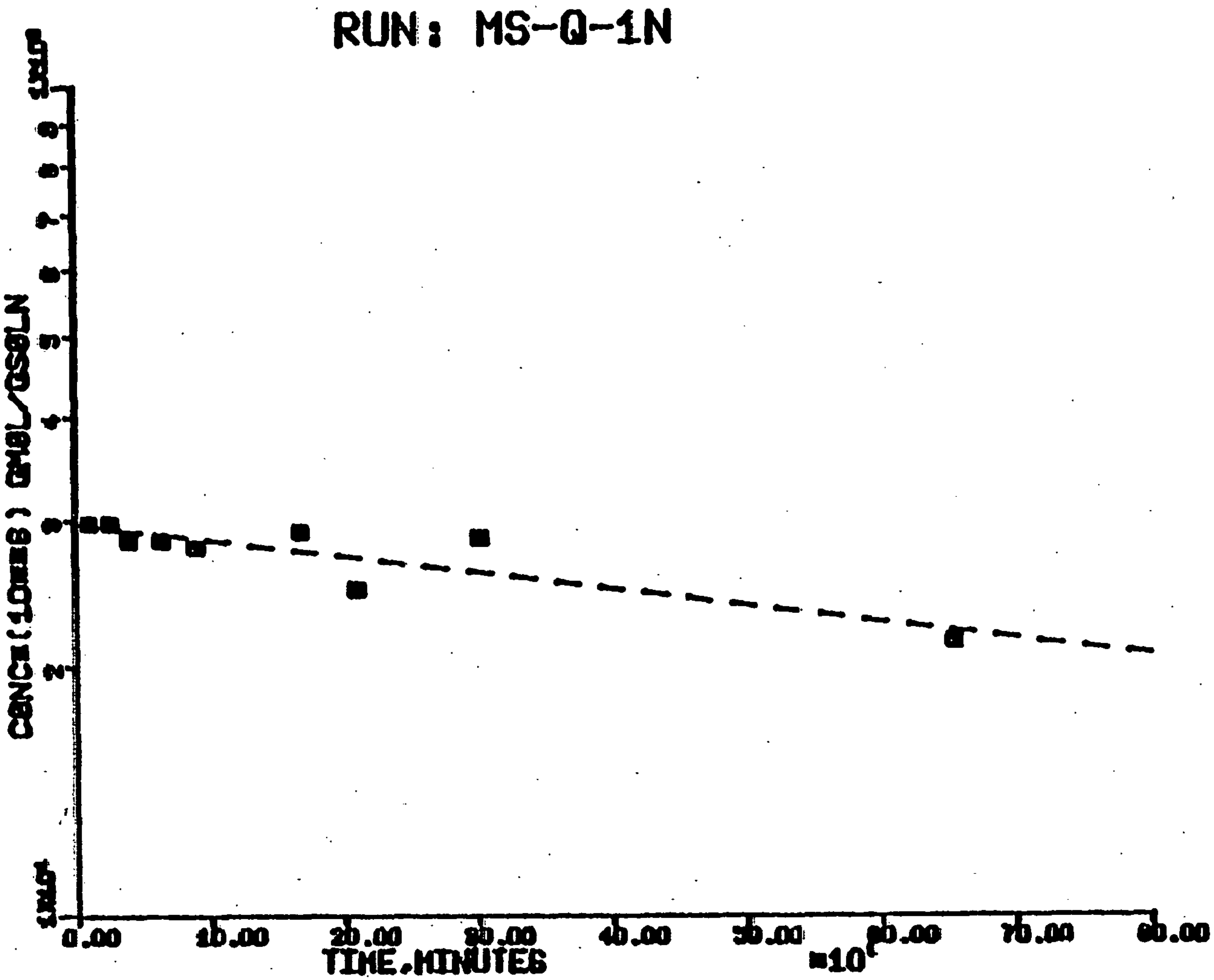

Figure 21: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 350°C.

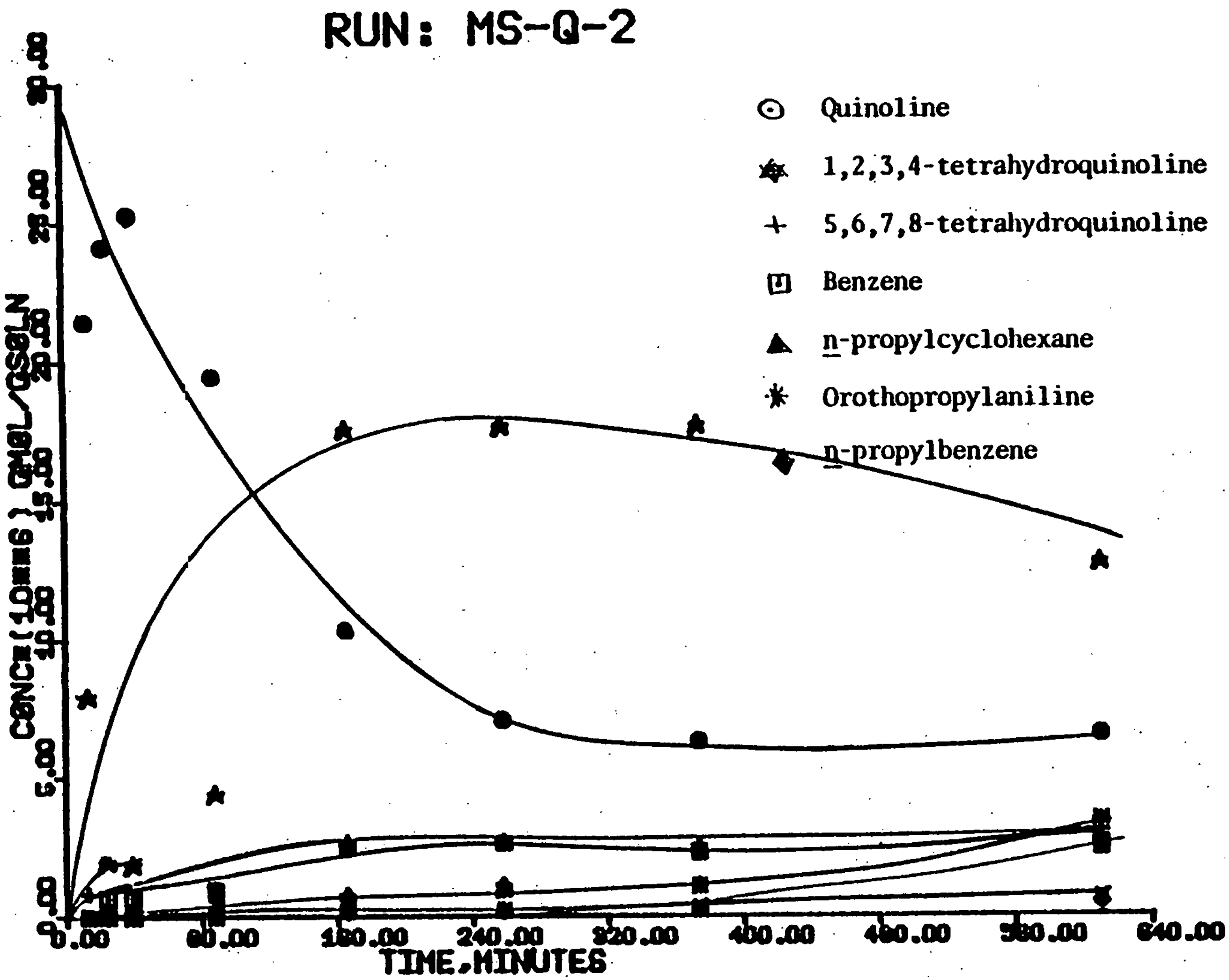

Figure 22: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt %/AlBO$_3$ at 357°C.

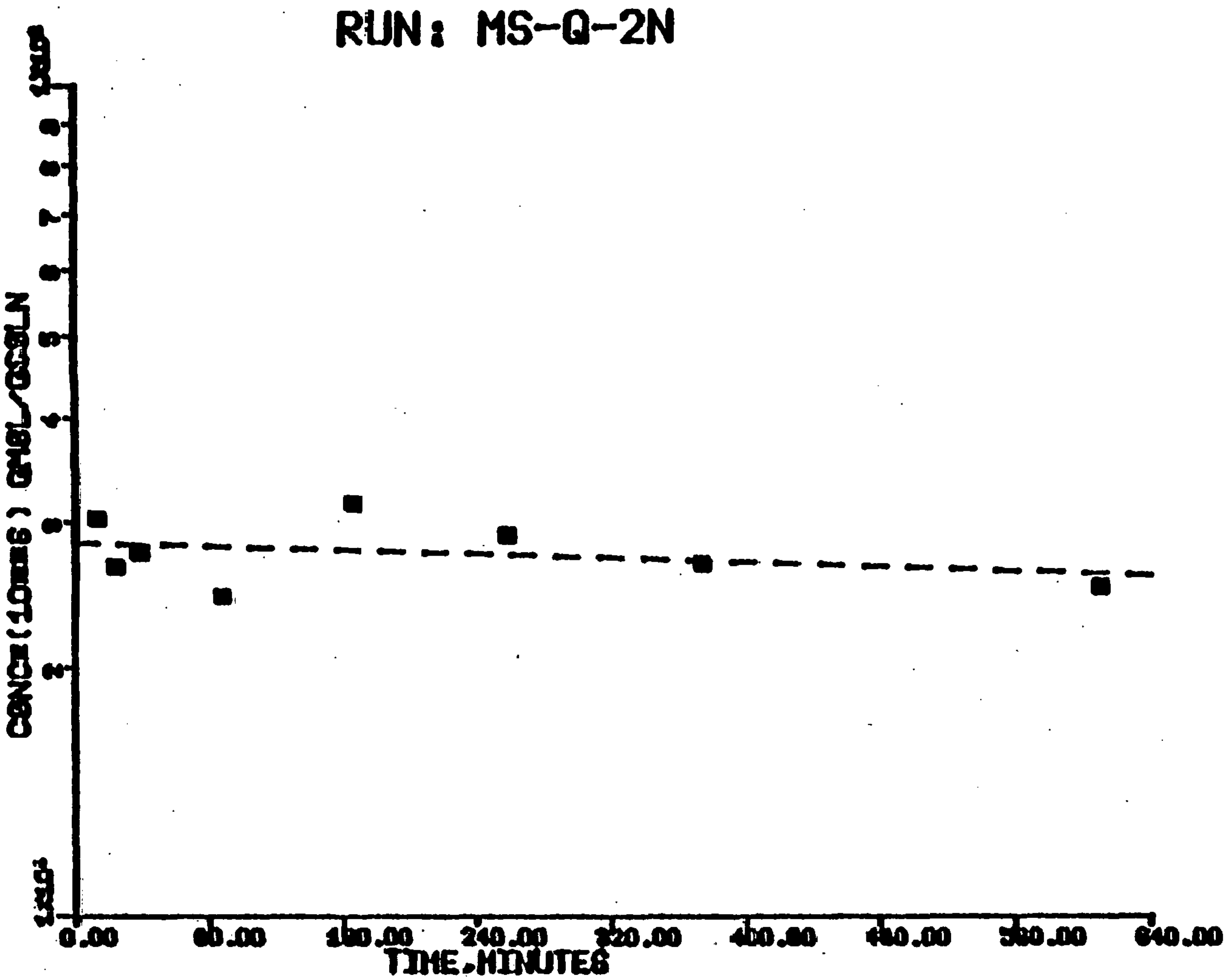

Figure 23: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 357°C.

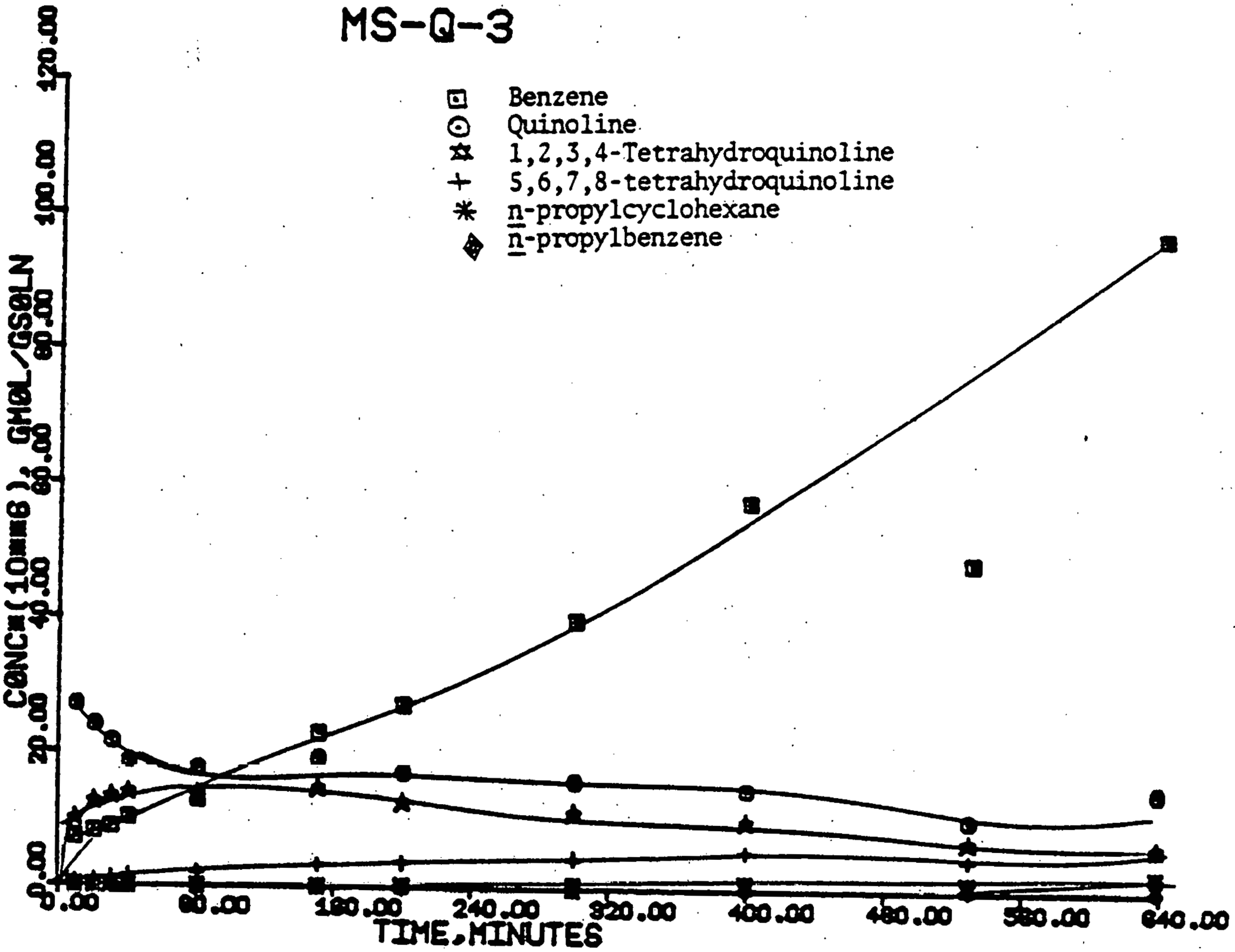

Figure 24: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/AlBO3 at 380°C.

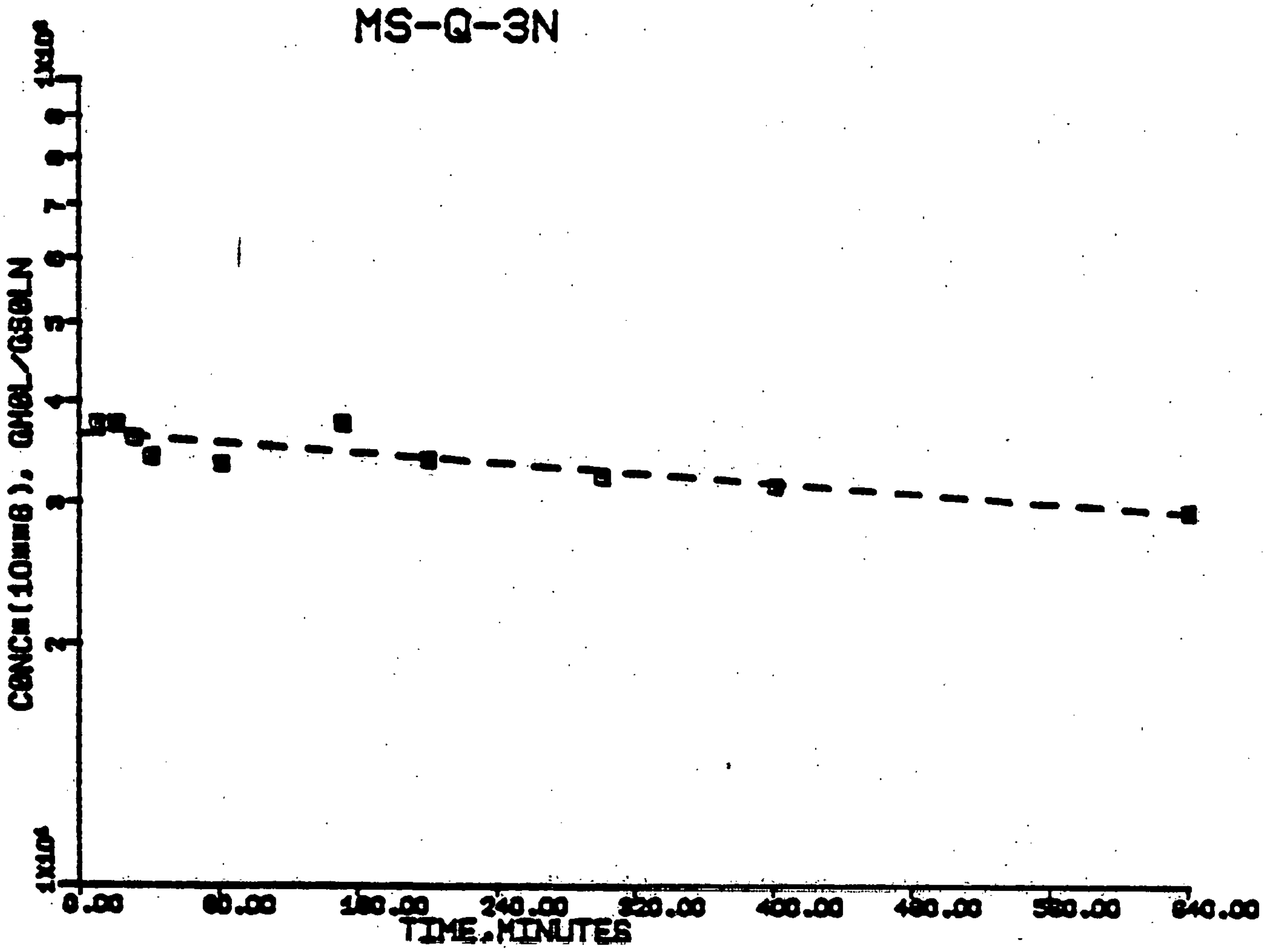

Figure 25: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 380°C.

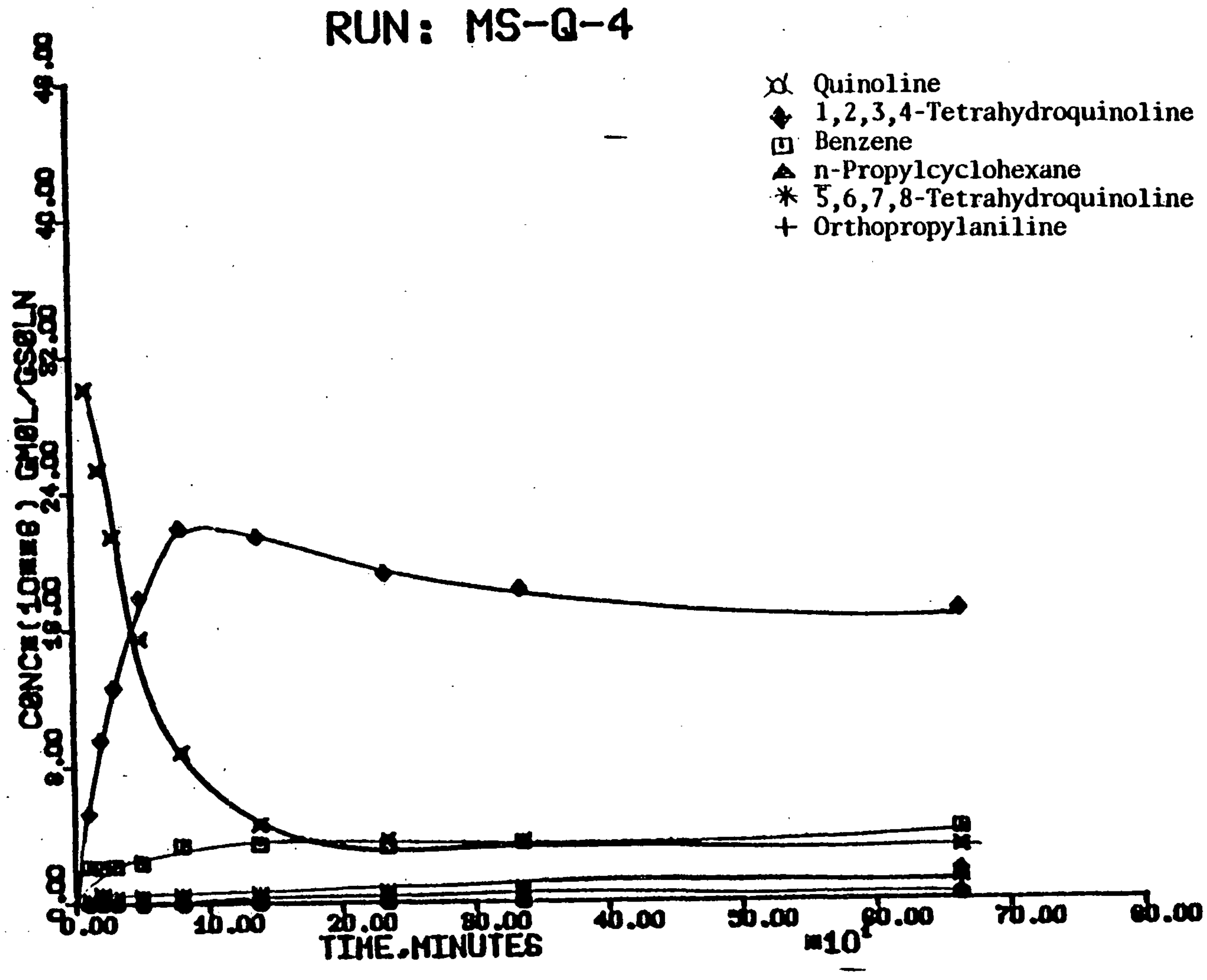

Figure 26: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/AlBO$_3$ at 350°C (glass liner used).

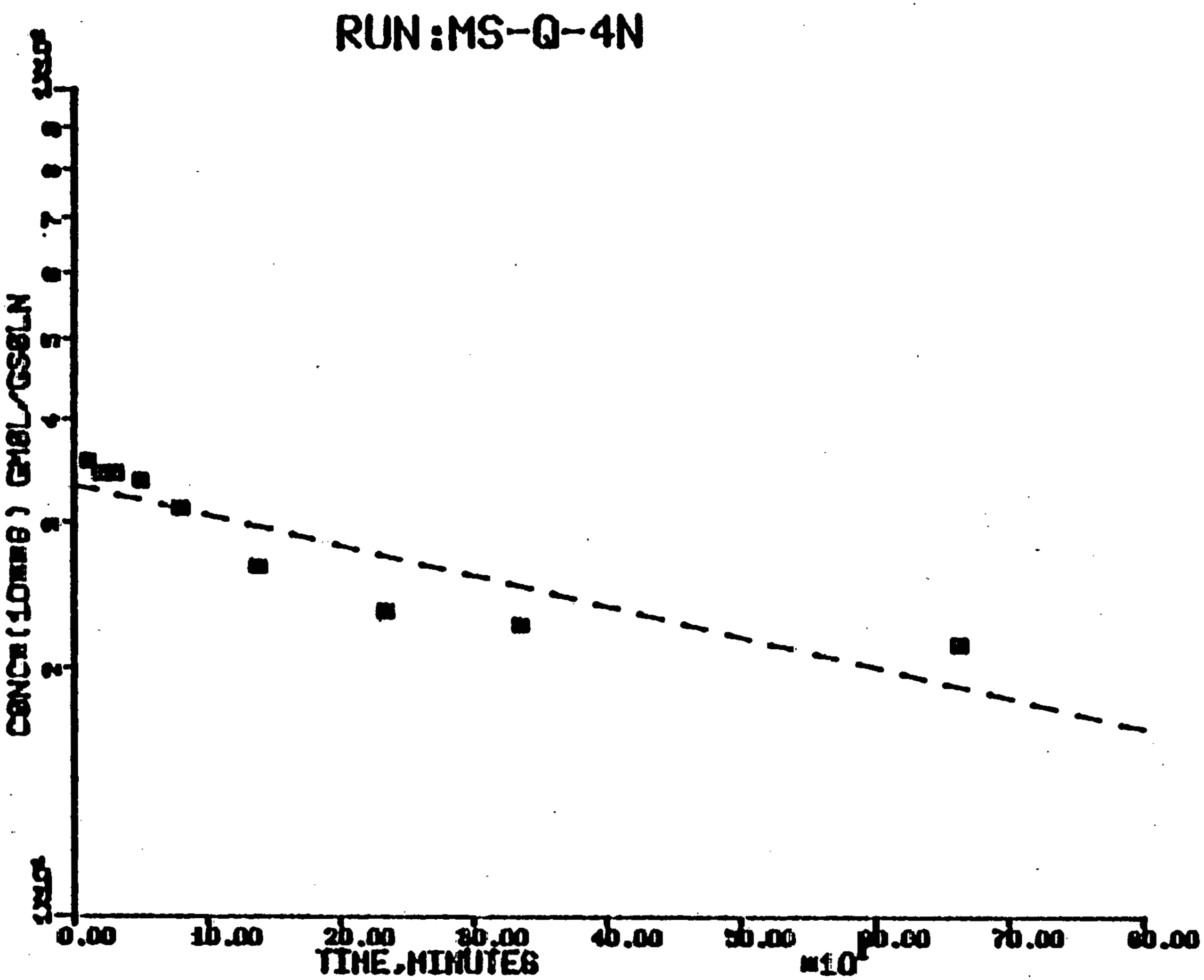

Figure 27: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 350°C (glass liner used).

Reaction products were analyzed with a Perkin-Elmer Model 3920 gas chromatograph equipped with flame ionization detector and an electronic integrator.

Results and Discussion:

Results for each run are shown in conc. vs time graphs of products and total nitrogen conc. vs. time graph illustrated in Figures 20-29. In each run quinoline was rapidly converted to 1,2,3,4-tetrahydroquinoline. Other side products observed in each run were 5,6,7,8-tetrahydroquinoline, benzene, n-propylcyclohexane, n-propylbenzene, decahydroquinoline, and orthopropylaniline.

Runs 1 and 2 (Figures 20 and 22) run at 350°C and 357°C without a glass liner showed 28% and 20% nitrogen removal, a relatively high amount of nitrogen removal compared to previously tested catalysts with quinoline. Run 3 at 380°C showed 22% of the nitrogen removed indicating no significant change in nitrogen removal at the higher temperature. The extremely high benzene concentrations in Run 3 which can not be account for by a material balance probably is due to cracking of the solvent, n-hexadecane, at the higher temperatures. Run 4 was made under identical conditions using a glass liner to determine the effect of the metal walls of the autoclave. As shown in Figures 26 and 27 there was a significant increase in nitrogen removal with 40% of the nitrogen removed after 5 hours. These results indicate that the metal in the autoclave decreases the activity of the catalyst. The large percent of nitrogen removal can

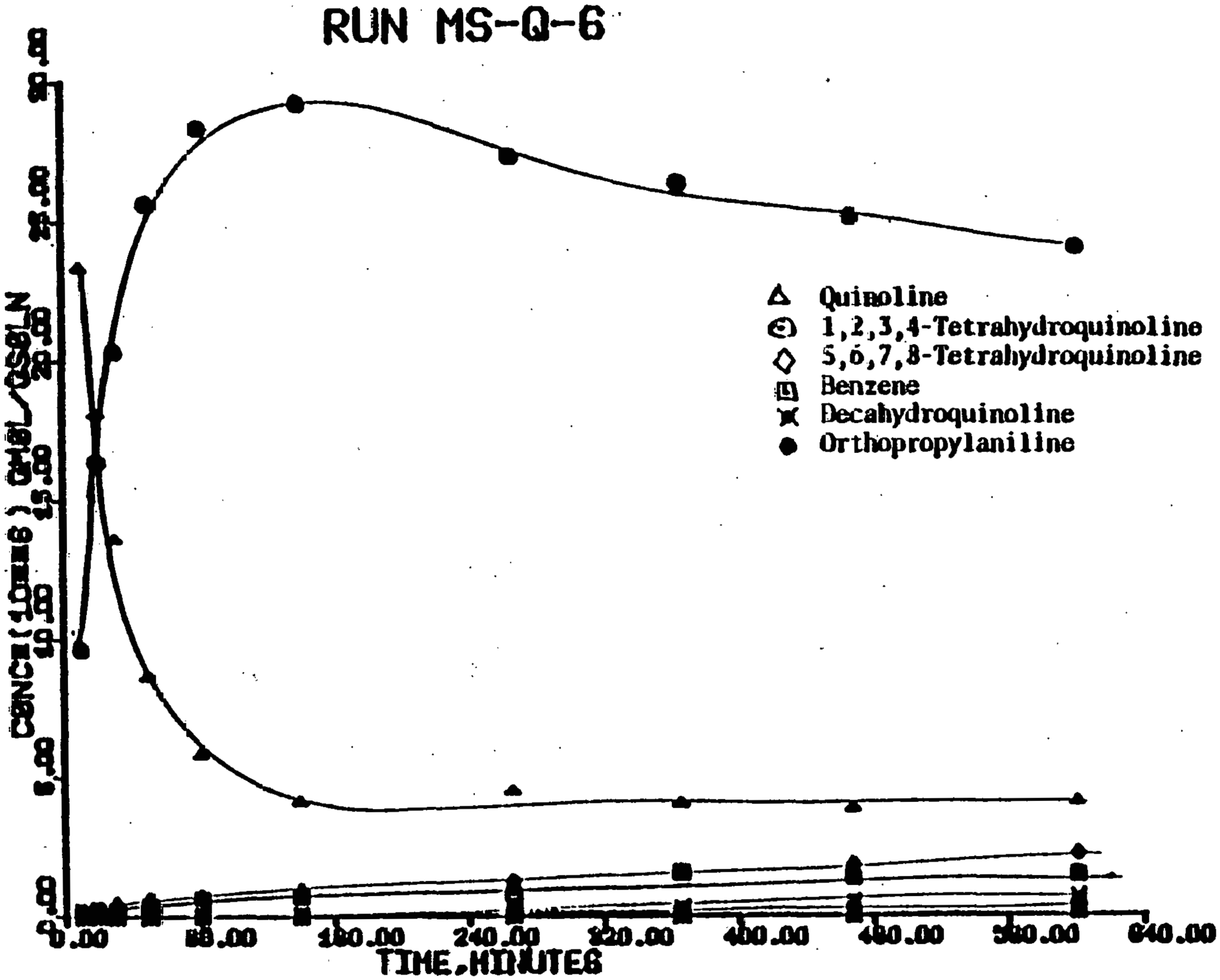

Figure 28: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/AlBO$_3$·PO$_4$.

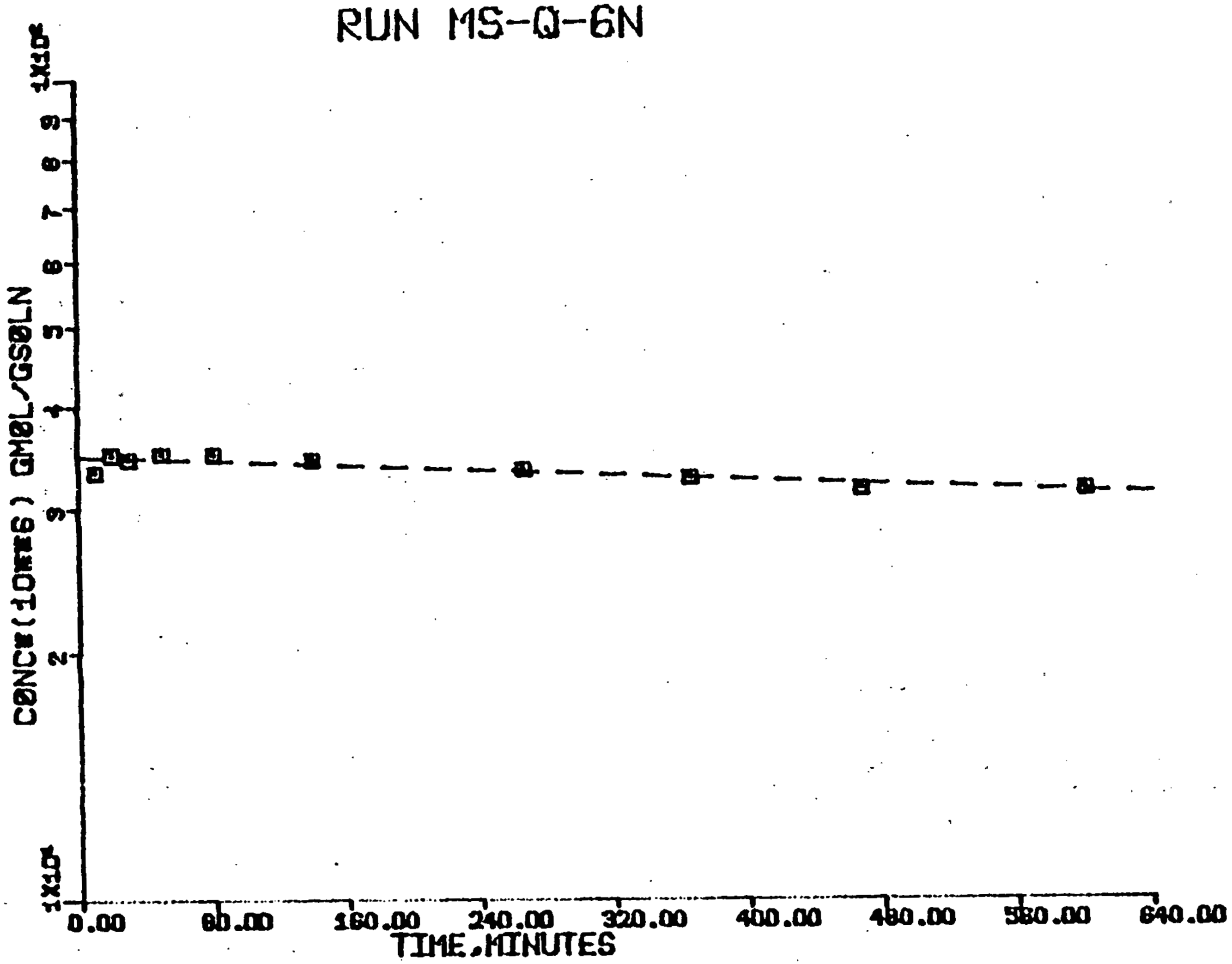

Figure 29: Total nitrogen removal from quinoline using 4 wt % Ni/$AlBO_3 \cdot PO_4$.

not be explained by a material balance of the products observed, i.e., n-propylcyclohexane, n-propylbenzene, or benzene. This would indicate that other products are forming not observed under the conditions of analysis. To try to account for the nitrogen removed, the catalysts are being analyzed for carbon-hydrogen-nitrogen content and an analysis of the samples from these two runs are being made using a nitrogen specific detector.

Run 6 was made using $AlBO_3 \cdot PO_4$/4% Ni as the catalyst. Though the products observed were the same as in previous runs, there was only 4% nitrogen removed after 10 hours as shown in Figure 28. This would appear to indicate that the phosphate acts as a strong inhibitor to nitrogen removal. A possible explanation for this result may lie in the fact that boron can not expand its octet as easily as phosphorous. Runs to determine the effect of the metal walls of the autoclave on the $AlBO_3 \cdot PO_4$/4% Ni catalyst reaction are currently in progress.

Runs will also be made to determine the effect of the support, $AlBO_3$, without nickel and the effects of different metals on the support.

A commercial catalyst supplier (American Cyanamid) is also preparing catalyst samples for us with various levels of acidity and metals, and these catalysts will be used in future hydrodenitrogenation studies.

V. PERSONNEL

There has been no change in personnel during this quarter.

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APPENDIX D

DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

Fourth Quarterly Report for Period

June 15, 1979 to September 15, 1979

Prepared by:

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Date Published

November 15, 1979

Prepared for:

Fossil Energy
Department of Energy
Washington, D.C.

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

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I. ABSTRACT

Experimental runs using decahydroquinoline and quinoline as reactants have been made. Preliminary results from decahydroquinoline runs show that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission. The olefinic products formed with these catalysts make them inactive during the course of reaction. The carbon-nitrogen bond scission must therefore occur on 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. Therefore it would appear that hydrodenitrogenation requires an acidic site and a basic site for the Hoffman E_2 elimination reaction to occur.

The nature of catalyst function responsible for C-N bond scission has been studied using decahydroquinoline over a set of catalysts. The catalysts tested include catalysts with vanadium, molybdenum, iron impregnated on silica-alumina or γ-alumina supports. As shown in previous reports, the rate of nitrogen removal was highest for the molybdenum on γ-alumina catalyst. However with the decrease in the concentration of Mo on the γ-alumina support the nitrogen removal rates also decreased accordingly.

Experimental runs were also made using quinoline and several catalysts with the objective to develop uniquely new

catalysts that will selectively coordinate the nitrogen atom and remove it without hydrogenating the entire ring thereby reducing hydrogen consumption were prepared. Catalysts used for this study were aluminum borate and aluminum borate phosphate, with or without nickel. Preliminary results indicate that metal ligand (nickel) plays an important role in the nitrogen removal process.

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, thereby developing improved catalysts for hydrodenitrogenation.
- To develop an improved understanding of the catalyst function required for C-N bond scission since this function is critical to hydrodenitrogenation but is not understood.
- 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 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 C-N bond scission using mainly decahydroquinoline over a set of catalysts prepared specifically to evaluate the catalyst requirements for the C-N bond scission. The catalysts to be tested include acid catalysts without metal, alumina impregnated with Co and Ni with various levels of sulfiding and <u>in situ</u> H_2S partial pressure 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, 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 uniquely-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 with only limited or no 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 benzenoid ring and nitrogen-containing aromatic rings 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 give quantitative measures of the rates of C-N bond scission and the extents and rates of hydrogenation. These results will then be interpreted in terms of the catalysts and their properties and recommendations will be made as to what further work needs to be done and the potentially most fruitful directions to be followed.

III. SUMMARY OF PROGRESS TO DATE

During the first year of the project, substantial progress has been made in understanding the chemistry and mechanism of carbon-nitrogen bond breakage. Our results clearly indicate that the carbon-nitrogen bond scission in hydrodenitrogenation of decahydroquinoline is not thermal but catalytic. Preliminary results also show that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission. The carbon-nitrogen bond scission therefore must occur on 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 and vanadium. The nature of catalytic function responsible for carbon-nitrogen bond scission was studied using decahydroquinoline over the set of above catalysts. The preliminary 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 a decrease in the concentration of the molybdenum on the γ-alumina support.

Runs have also been made using quinoline. Several catalysts were 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. The catalysts chosen for this study were aluminum borate and aluminum borate phosphate loaded with or without 4 wt% nickel. Preliminary results indicate that 4 wt% nickel on aluminum borate catalyst gives a marked increase in nitrogen removal rate of quinoline. These results indicate that metal ligand plays an important role in the nitrogen removal process.

Several other catalysts with different metal ligand and supports have been prepared recently and are being tested. American cyanamid is also preparing some catalysts for us with varying acidity and metal content. These catalysts will be studied in the near future.

*TIME PLAN AND MILESTONE CHART

YEAR

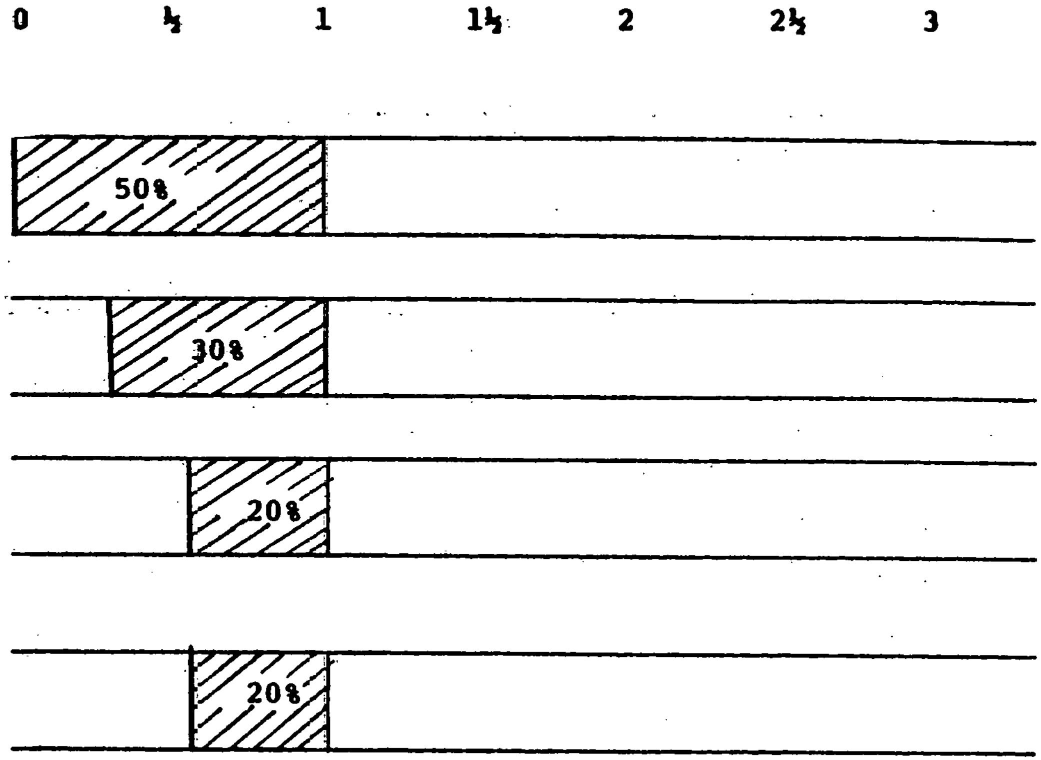
TASK STATEMENT

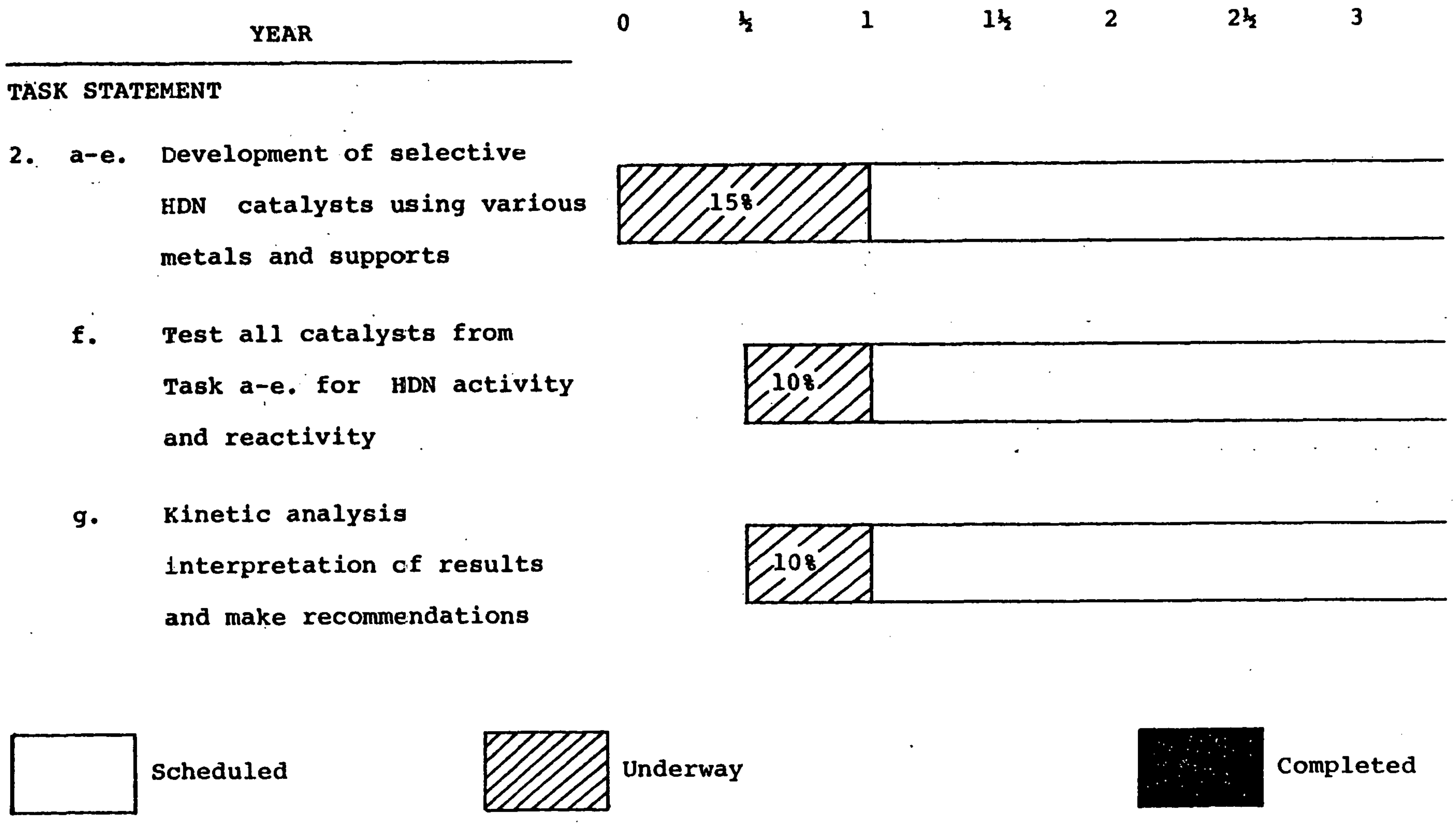
1. a. Determine the nature of C-N bond scission

   b. Formulate improved catalysts based on a.

   c. Evaluate all catalysts for HDN activity

   d. Kinetic analysis, interpretation of results and make recommendation





*Number in hatched region indicates the percentage completed.

CUMULATIVE EXPENDITURES

	First Quarter	Second Quarter	Third Quarter	Fourth Quarter
PERSONNEL	5,334	21,252	38,755	59,966
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)	2,868	10,653	20,056	30,532
	9,139	48,274	81,940	119,195

TABLE I

Standard Operating Conditions

Temperature:	350 ± 2°C
Total Pressure:	34 ± 1 atm*
Reactant Concentration:	0.5 weight percent in n-hexadecane
CS_2 Loading:	0.05 wt% (1.4 vol% H_2S in gas phase)
Catalyst Loading:	0.5 wt% of reaction mixture

---

*Partial pressure of n-hexadecane @ 350°C ≅ 3.24 atm.

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 route for removal of nitrogen from quinoline, a major 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.

Hydrodenitrogenation of decahydroquinoline was studied by using several catalysts with various metals impregnated on γ-alumina support. The preparation of the hydrodenitrogenation catalysts involved the introduction of a metal into the support. The support was used in the hydrated form as small particles. A detailed description of the catalyst preparation procedure was given in third quarterly report.

Carbon-Nitrogen Bond Scission:

Hydrodenitrogenation of decahydroquinoline was studied over several different catalysts. The reactor used was a 300 cc autoclave fitted with a magnetic drive stirrer. Standard operating conditions (Table I) 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°C. In order to maintain the catalyst in the sulfided form during the reaction, 0.05 wt% CS_2 solution 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 a Perkin-Elmer Model 3920 gas chromatograph equipped with a flame-ionization detector. A glass capillary column (75m-OV101) was used for all reactant and product analysis.

Figure 1 shows the results for the hydrodenitrogenation of decahydroquinoline using 4% vanadium on γ-alumina. The products from this run were n-propylcyclohexane, n-propylbenzene, 5,6,7,8-tetrahydroquinoline, quinoline, and 1,2,3,4-tetrahydroquinoline. However, 5,6,7,8-tetrahydroquinoline was the only major product. Figure 2 shows the nitrogen removal from decahydroquinoline using vanadium on alumina catalyst. As shown in the figure, the nitrogen removal rate is very low (∿17%).

Runs were also made with two Mo-on-γ-alumina catalysts with varying concentrations of molybdenum. The results are shown in Figures 3-7. Figure 7 shows a comparison of the nitrogen removal rate from decahydroquinoline. As the concentration of the molybdenum on the γ-alumina support decreases, the nitrogen removal rate also decreases. These results show that molybdenum does take part in the C-N bond scission. A run was made without sulfiding the Mo-on-γ-alumina catalyst to study the effect of sulfiding on the C-N bond scission. However, as shown in Figures 8 and 9 there is no significant difference between the nitrogen removal rate of sulfided and unsulfided Mo-on-γ-alumina catalyst.

Figures 10 and 11 show the concentration profiles and nitrogen removal rate from decahydroquinoline when 4% Fe on γ-alumina catalyst was used. The major product in this run was 5,6,7,8-tetrahydroquinoline. With Fe on γ-alumina the nitrogen removal rate was very low (∿22%).

From the above results it can be concluded that Brønsted acidity by itself will not catalyze the carbon-nitrogen bond scission and therefore it would appear that hydrodenitrogenation may require an acidic site and a basic site to facilitate the Hoffman E_2 elimination reaction. From our results it is also clear that Mo-on-γ-alumina gives the highest rate of nitrogen removal. Presently we are looking at some basic supports such as magnesium oxide to further clarify the role of basic sites in the C-N bond scission.

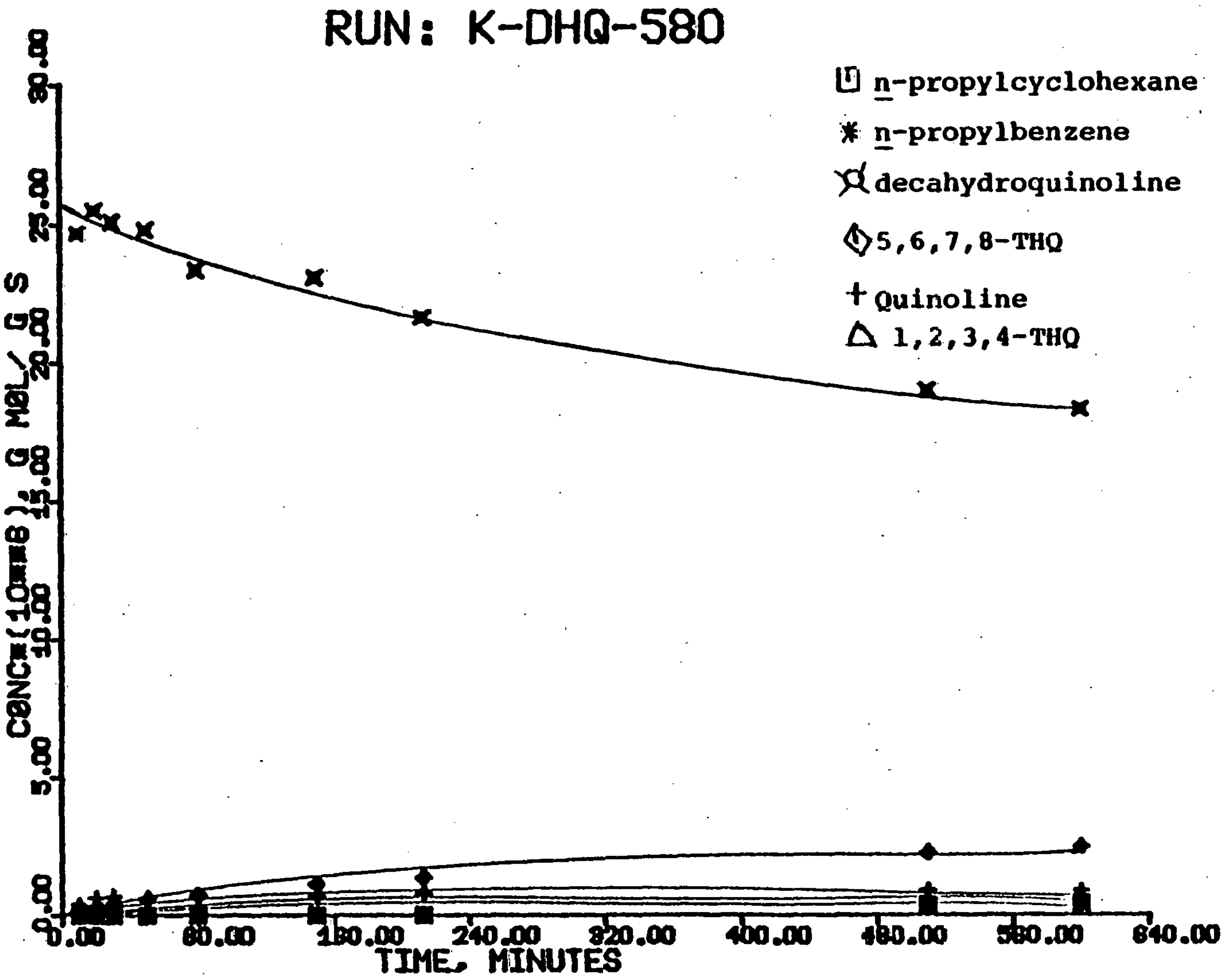


Figure 1. Concentration Profiles for hydrodenitrogenation of decahydroquinoline using 4% vanadium on γ-alumina catalyst.

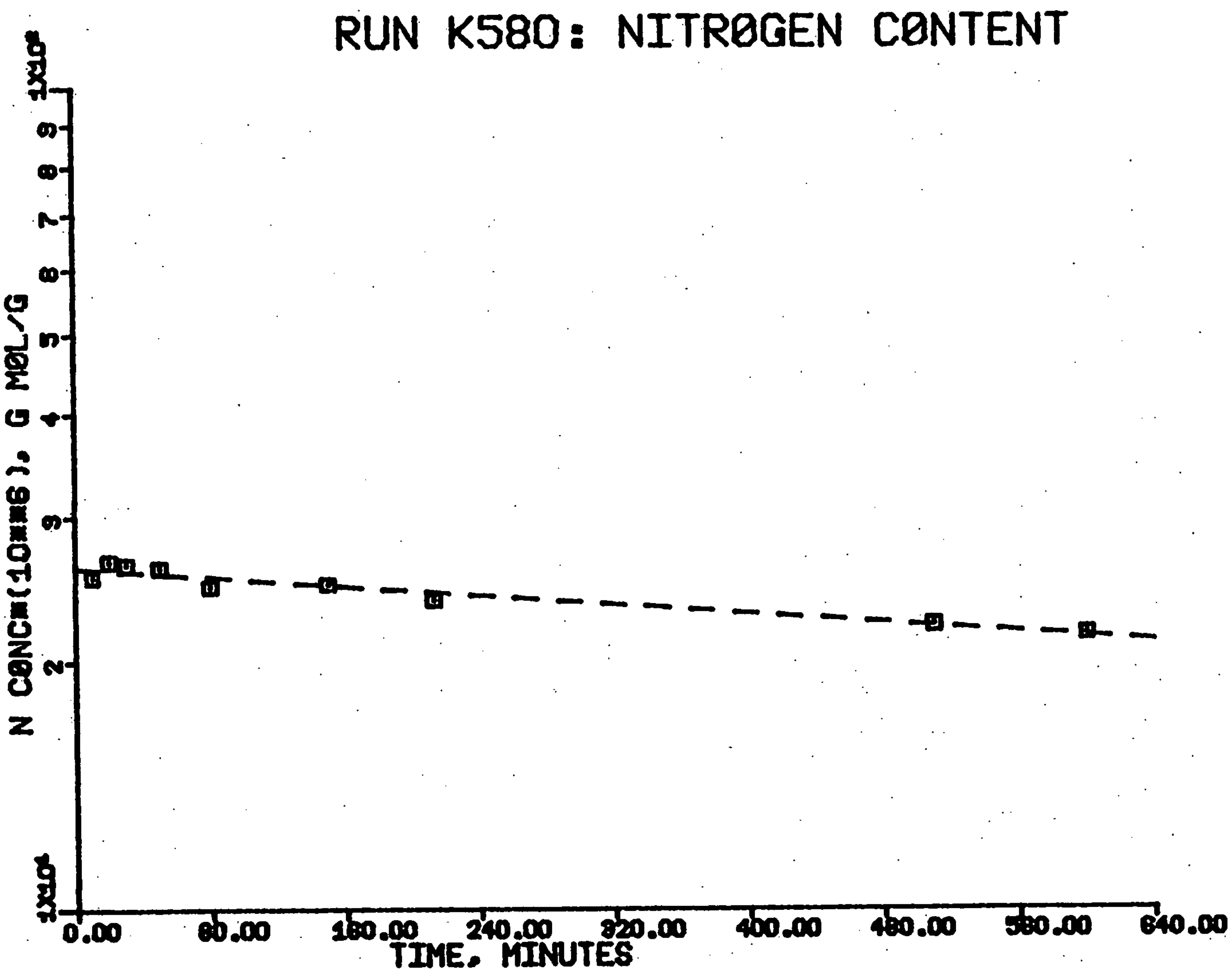


Figure 2. Total nitrogen removal from decahydroquinoline using 4% vanadium on γ-alumina.

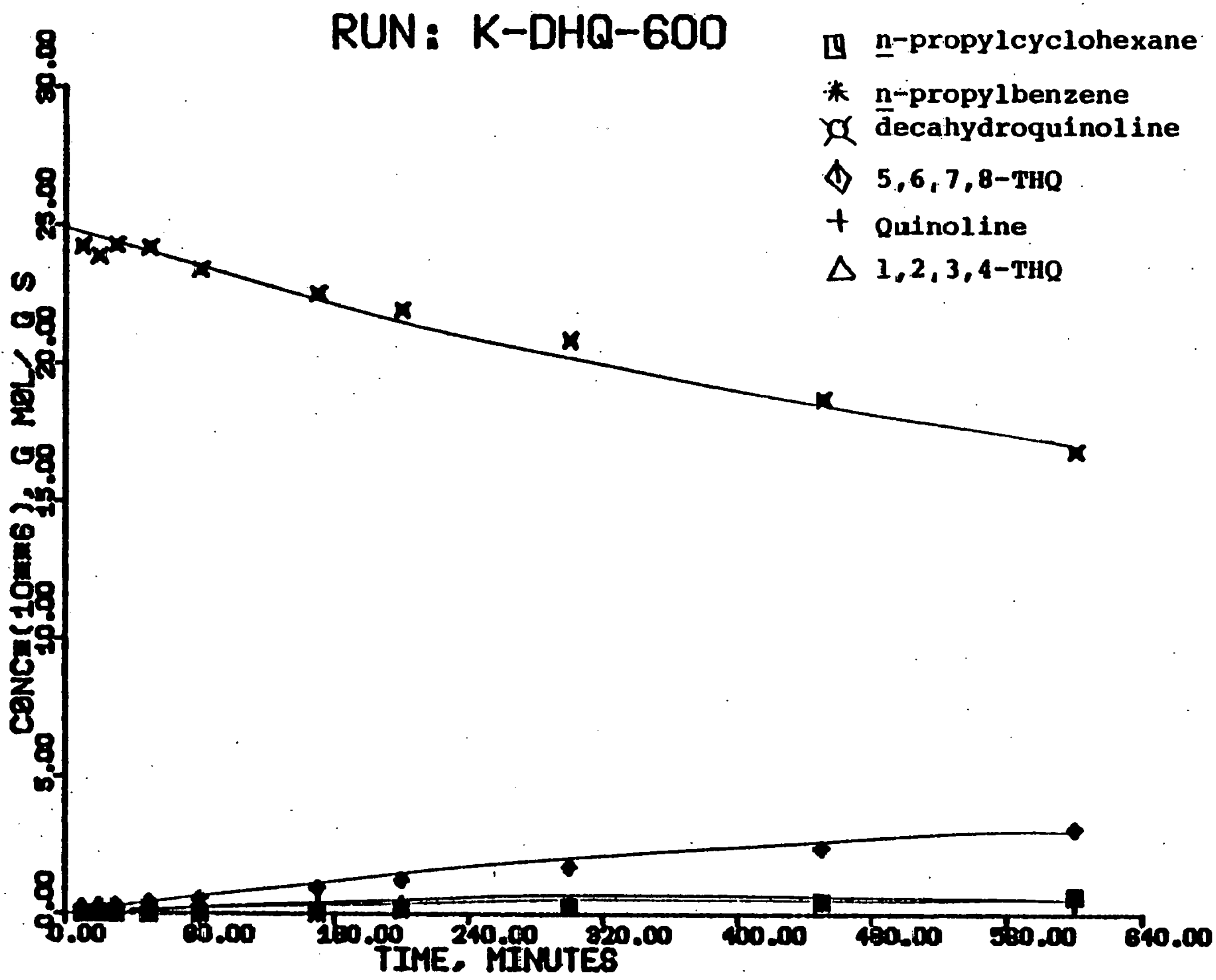


Figure 3. Concentration profiles for hydrodenitrogenation of decahydroquinoline using 2% Mo on γ-alumina.

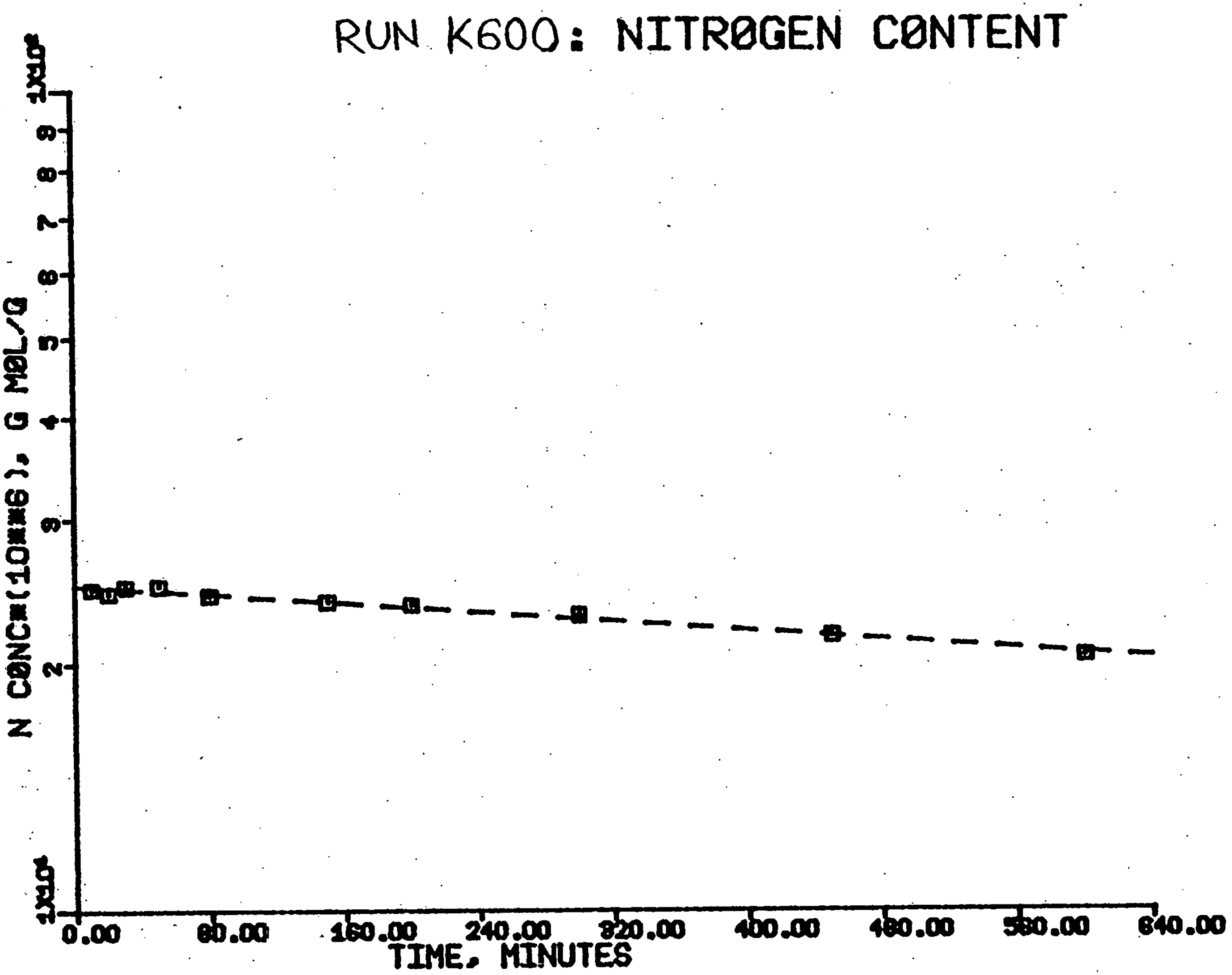


Figure 4. Total nitrogen removal from decahydroquinoline using 2% Mo on γ-alumina.

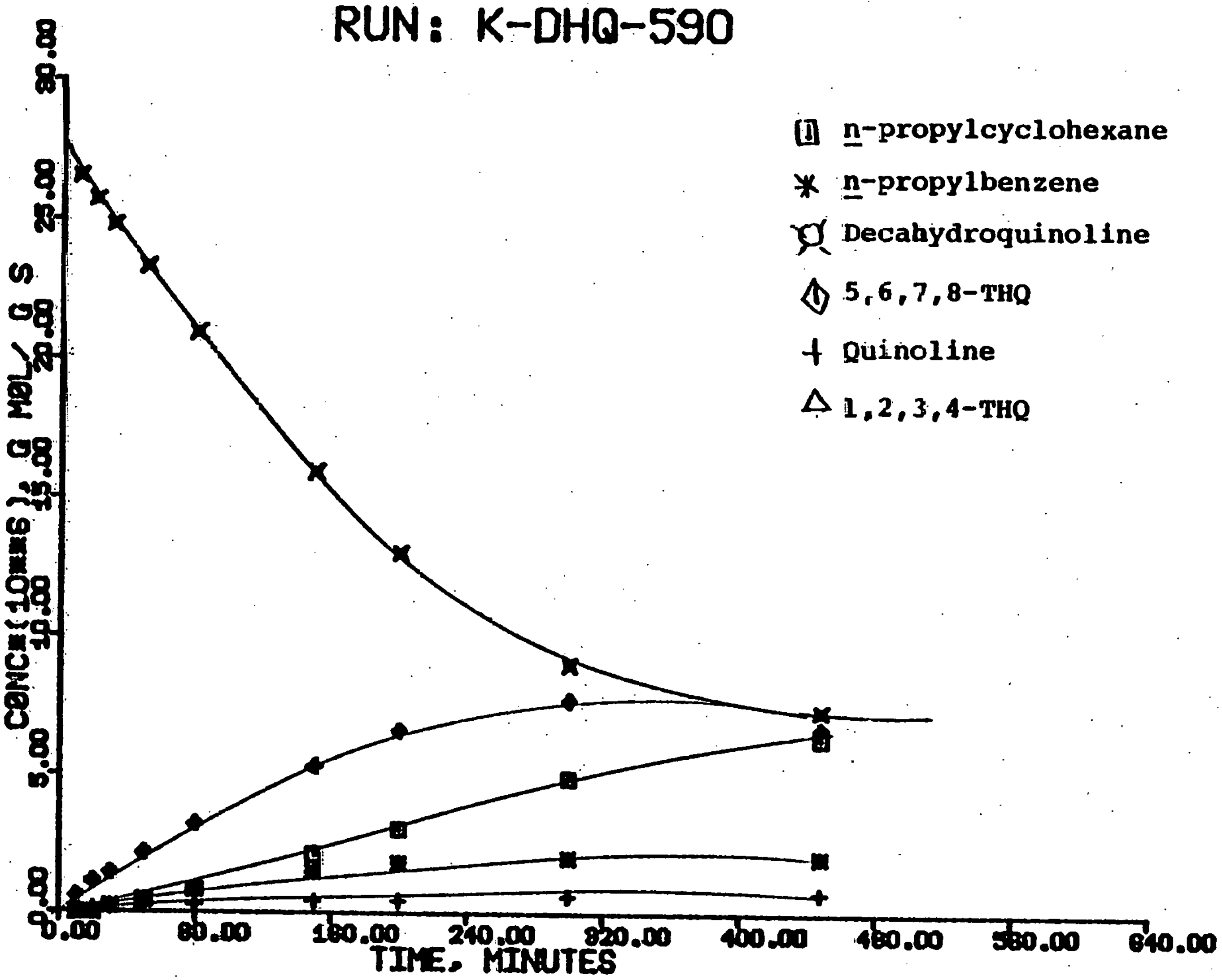


Figure 5. Concentration profiles for hydrodenitrogenation of decahydroquinoline using 10% Mo on γ-alumina.

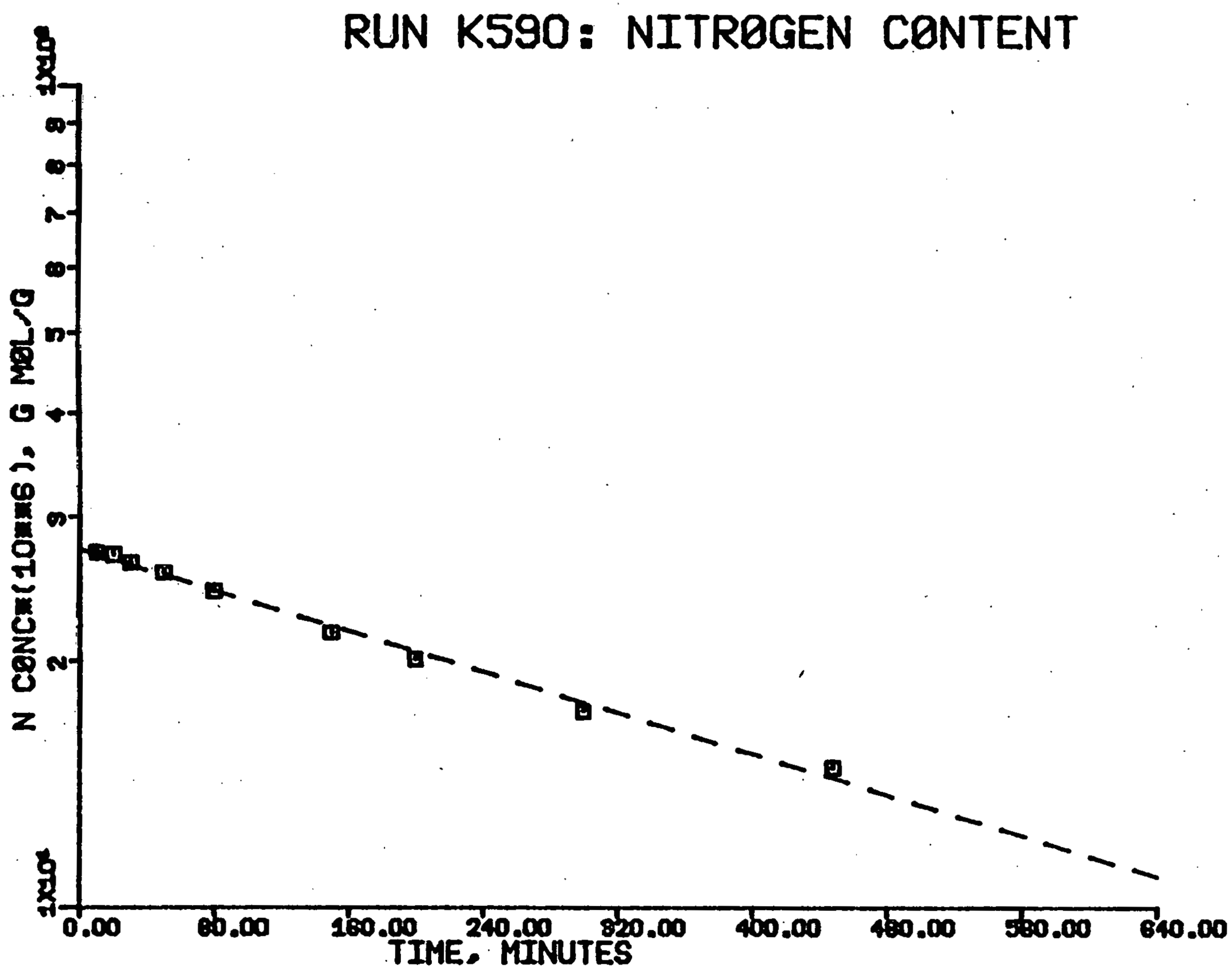


Figure 6. Total nitrogen removal from decahydroquinoline using 10% Mo on γ-alumina.

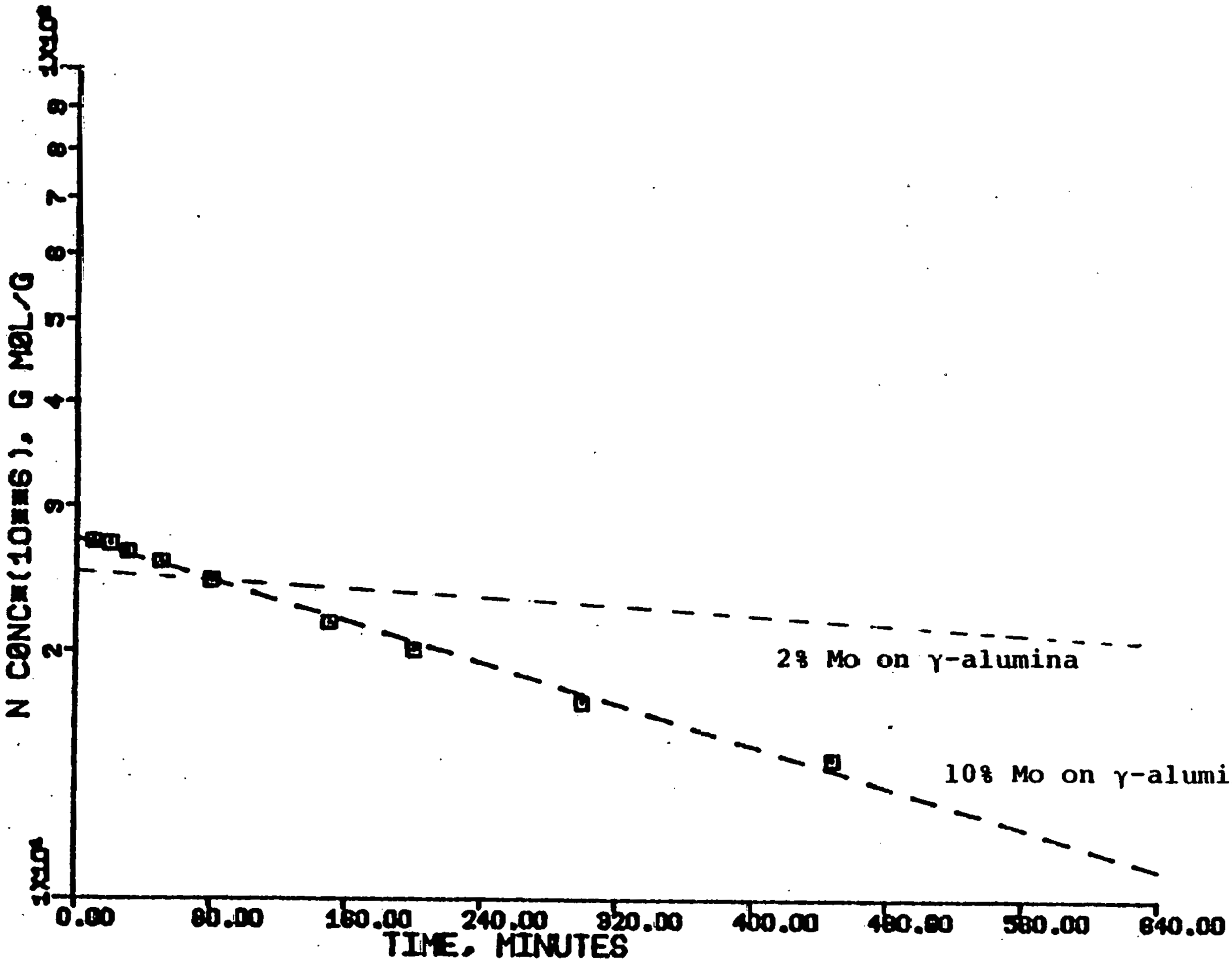


Figure 7. Total nitrogen removal from decahydroquinoline using different molybdenum on γ-alumina catalysts.

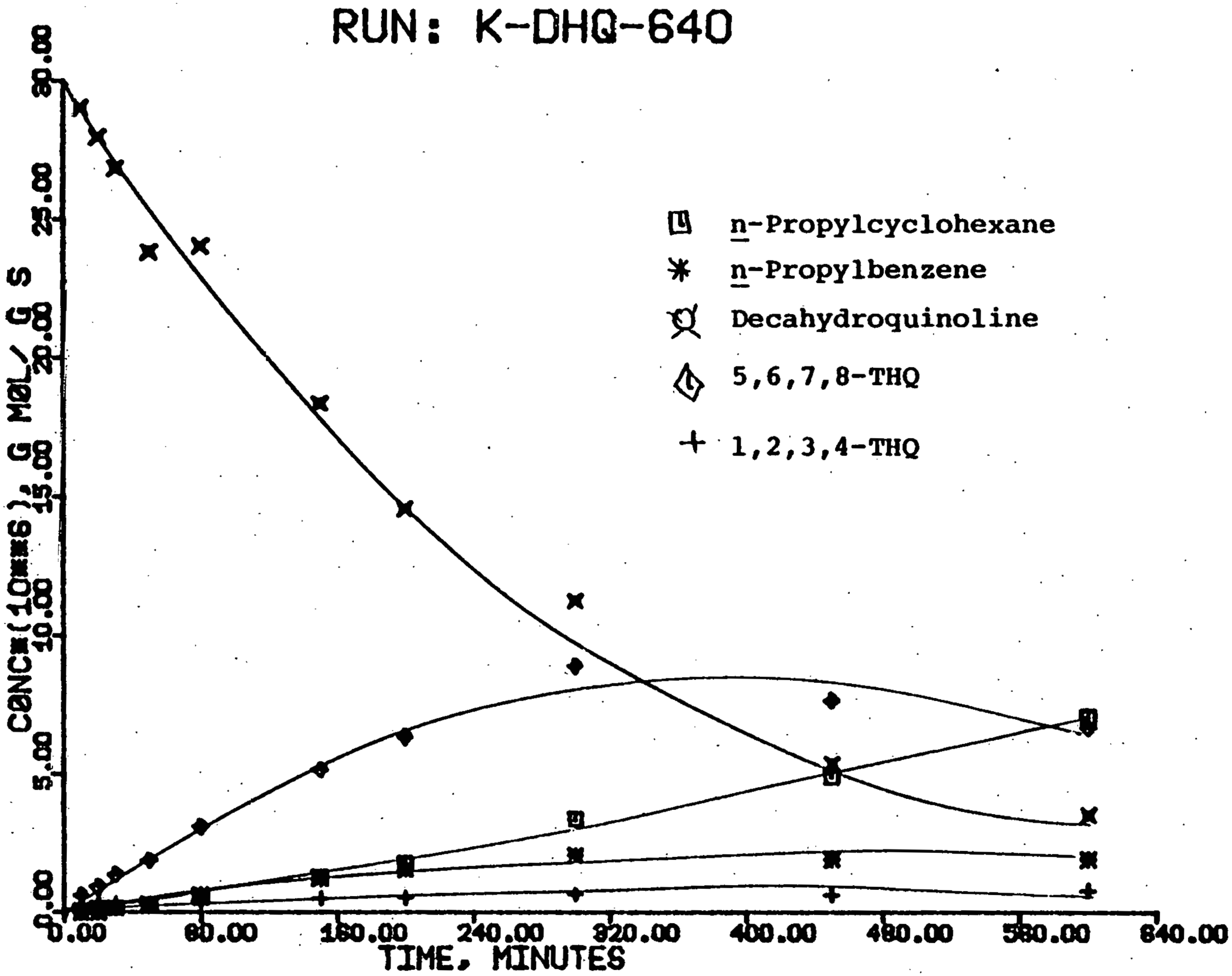


Figure 8. Concentration profile for hydrodenitrogenation of decahydroquinoline using unsulfided 10% Mo on γ-alumina.

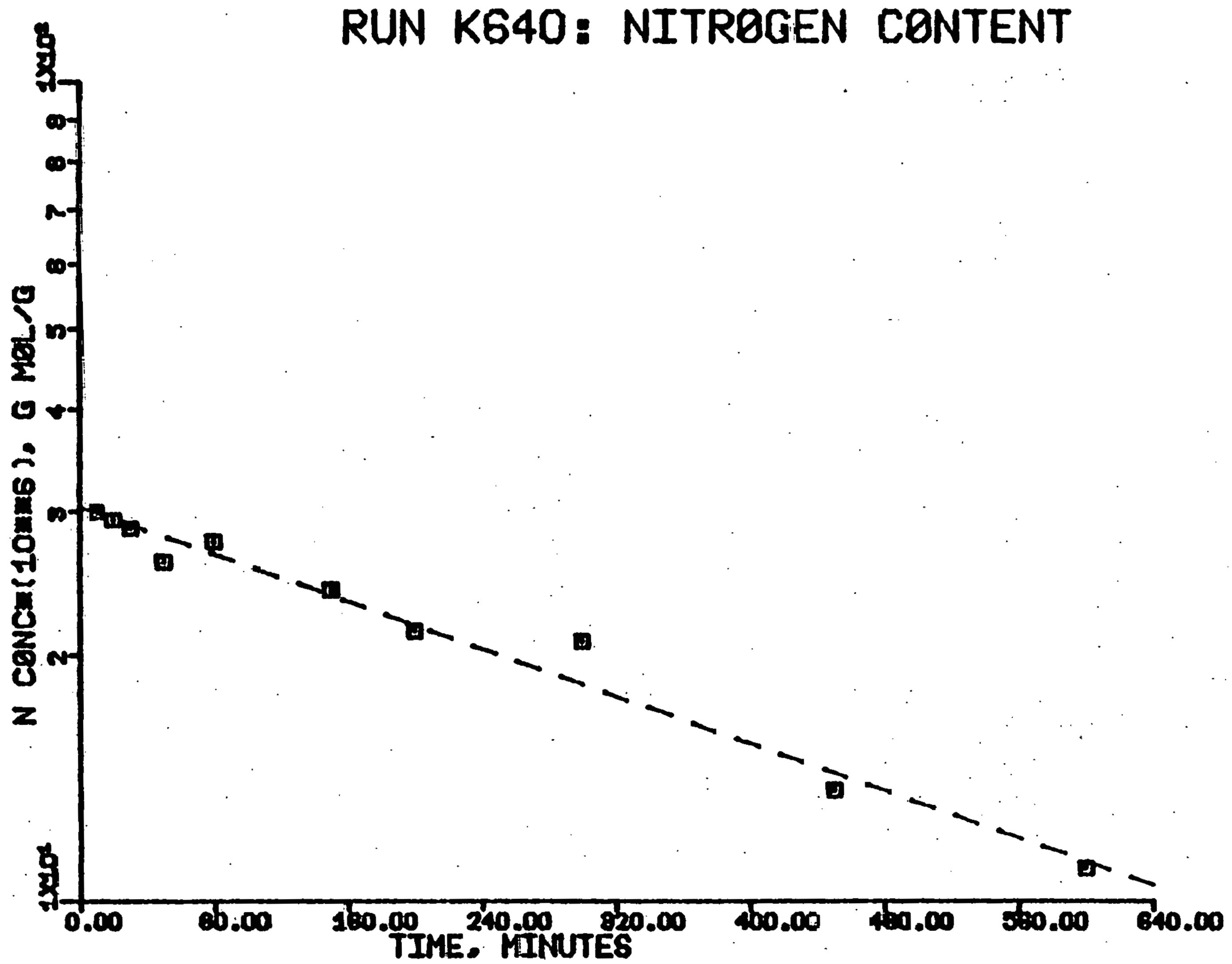


Figure 9. Total nitrogen removal from decahydroquinoline using unsulfided 10% Mo on γ-alumina.

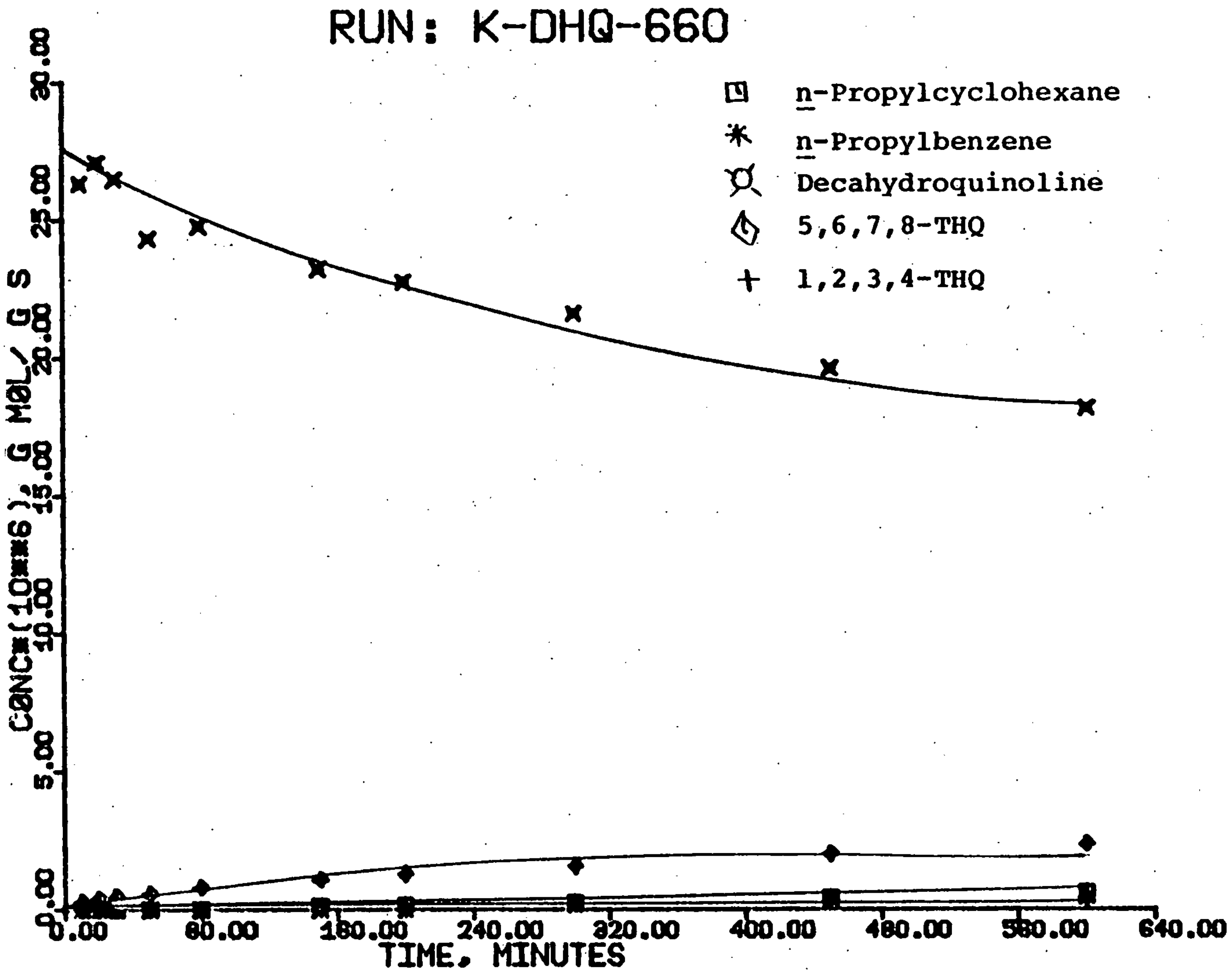


Figure 10. Concentration profile for hydrodenitrogenation of decahydroquinoline using 4% Fe on γ-alumina.

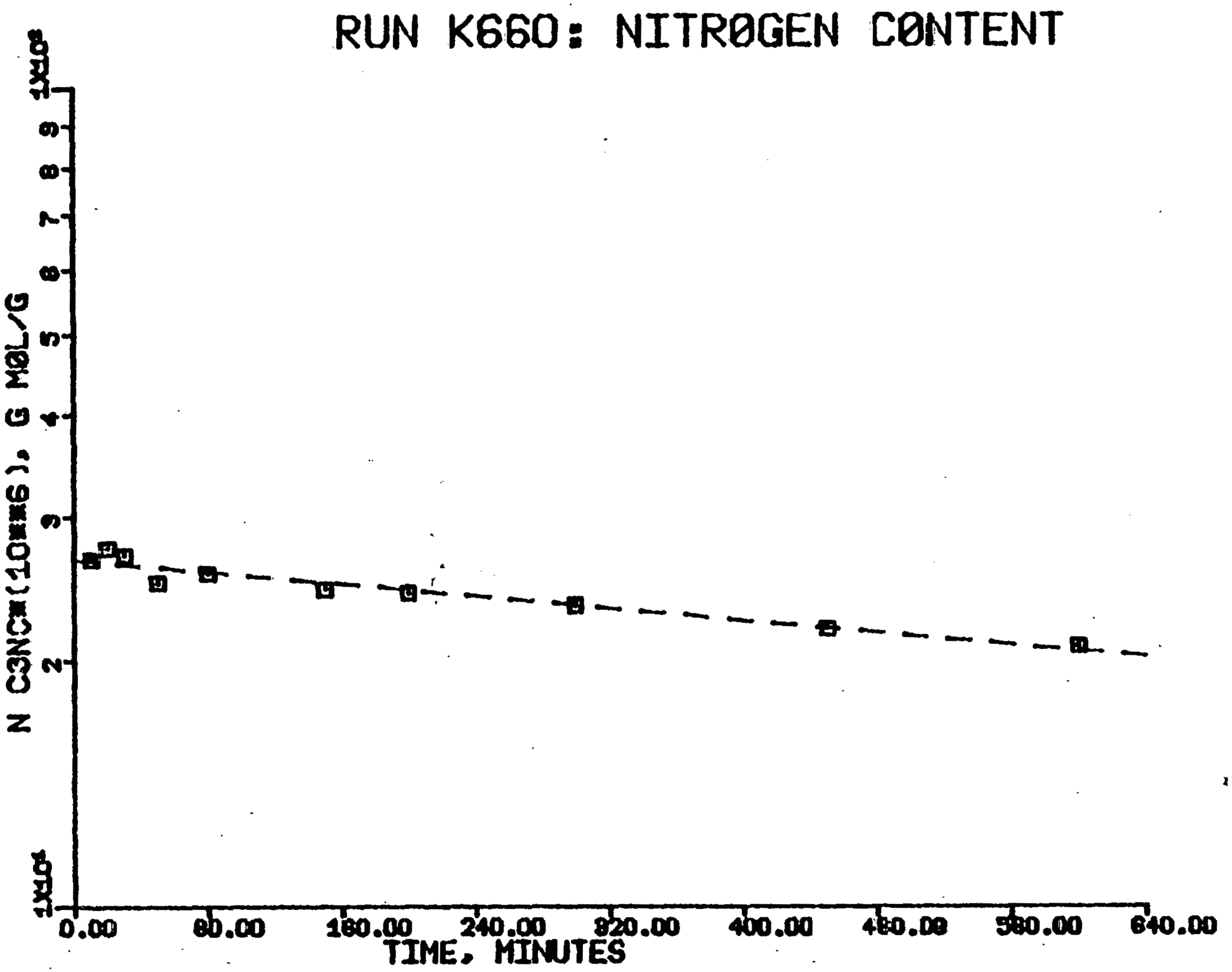


Figure 11. Total nitrogen removal from decahydroquinoline using 4% Fe on γ-alumina.

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 a uniquely new, highly selective hydrodenitrogenation catalyst that can selectively coordinate nitrogen and remove it from multi-ring nitrogen-containing aromatic compounds with only limited or no hydrogenation of the aromatic ring; thereby achieving major savings in hydrogen consumption.

Quinoline has been chosen as the reactant since it has a benzenoid ring and nitrogen-containing aromatic rings characteristic of nitrogen-containing compounds in coal-derived liquids.

A catalyst was desired that could act as a Lewis Acid and selectively coordinate with the basic lone electron pair on nitrogen in quinoline. The coordination with nitrogen would reduce the aromaticity of the nitrogen-containing ring, thus facilitating nitrogen removal without hydrogenation of the neighboring aromatic rings. On this basis the initial catalyst chosen for study was aluminum borate with 4% by weight nickel, $AlBO_3$/4% Ni , a Lewis acid catalyst. A second Lewis acid chosen was aluminum borate phosphate with 4% by weight nickel, $AlBO_3 \cdot PO_4$/4% Ni . As described in the previous progress report, the $AlBO_3$/4% Ni showed a marked increase in nitrogen removal rate in quinoline over other catalysts previously studied. A decrease in activity of the catalyst was observed when the reaction was run in contact with the metal autoclave walls. $AlBO_3 \cdot PO_4$/4% Ni, when run in contact with the metal walls of the autoclave, showed little (5%) nitrogen removal after 10 hours.

In current work runs were made on $AlBO_3 \cdot PO_4$/4% Ni with glass liner to determine the effect of the metal walls on this catalyst; $AlBO_3$/4% Ni unsulfided to observe the effect of sulfiding on nitrogen removal; $AlBO_3$ without any metal ligand and Al/4% Ni to help determine the role of the support and metal ligand; a run was also made using a different metal, molybdenum, $AlBO_3$/4% Mo , to compare with the nitrogen removal rate of nickel.

Preliminary results indicate that $AlBO_3 \cdot PO_4$/4% Ni, though strongly inhibited when run in contact with the metal walls of the autoclave, produces very similar nitrogen removal rates to that of the $AlBO_3$/4% Ni when run with a glass liner; $AlBO_3$/4% Ni unsulfided reduced the amount of nitrogen removed by 25%; $AlBO_3$ without any metal ligand reduced the amount of nitrogen removed by 20%. The Al/4% Ni showed 37% nitrogen removed, indicating that it has similar nitrogen removal qualities to that of $AlBO_3$/4% Ni and $AlBO_3 \cdot PO_4$/4% Ni . The $AlBO_3$/4% Mo run reduced the rate of nitrogen removal when compared to the $AlBO_3$/4% Ni study.

Experimental:

A glass liner was used for every run and the autoclave was operated in the batch mode. The reaction temperature was maintained at 350°C ± 2°C. The catalyst for each run

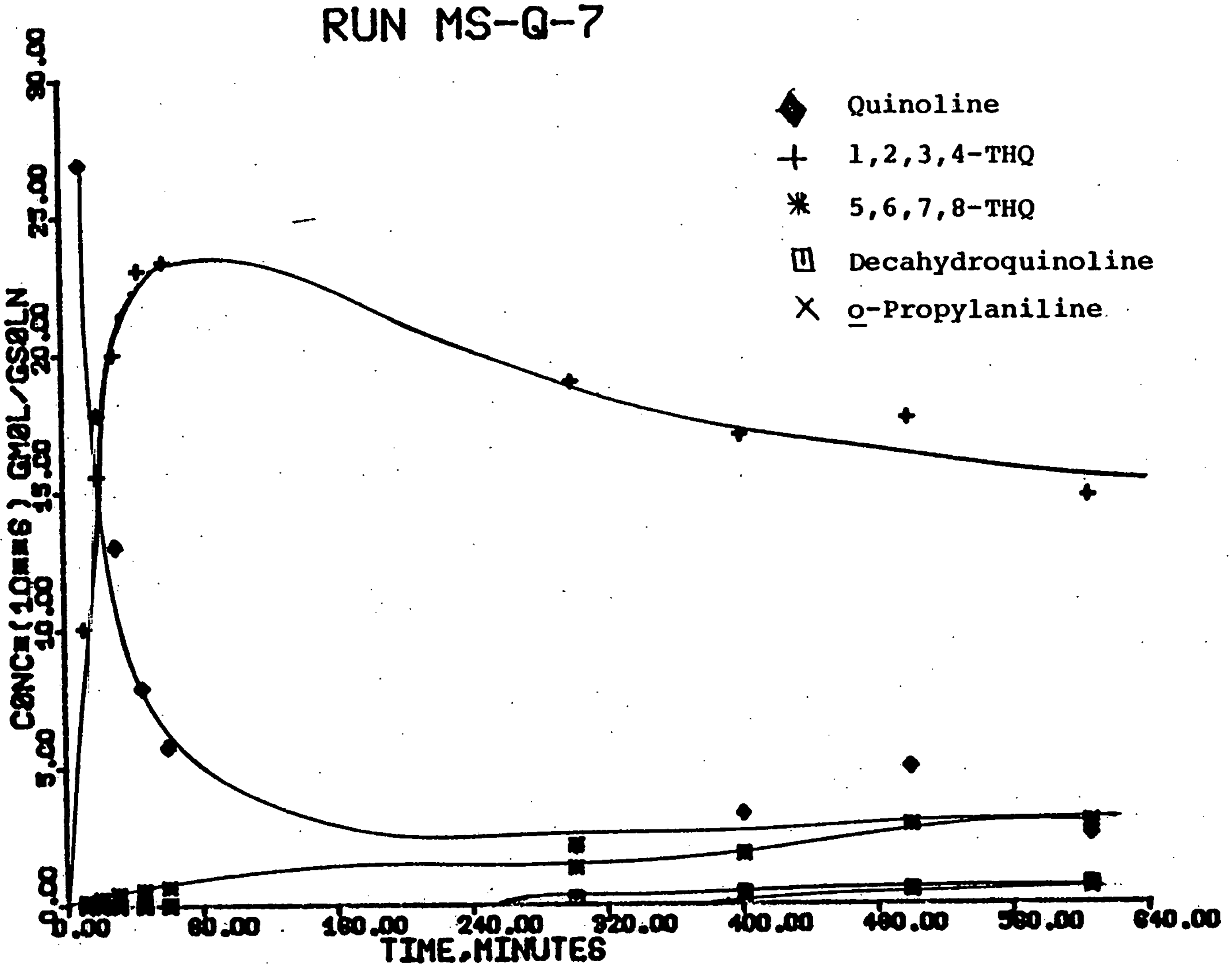


Figure 12. Concentration profile for the hydrodenitrogenation of quinoline using 4% Ni on $AlBO_3 \cdot PO_4$ (glass liner used).

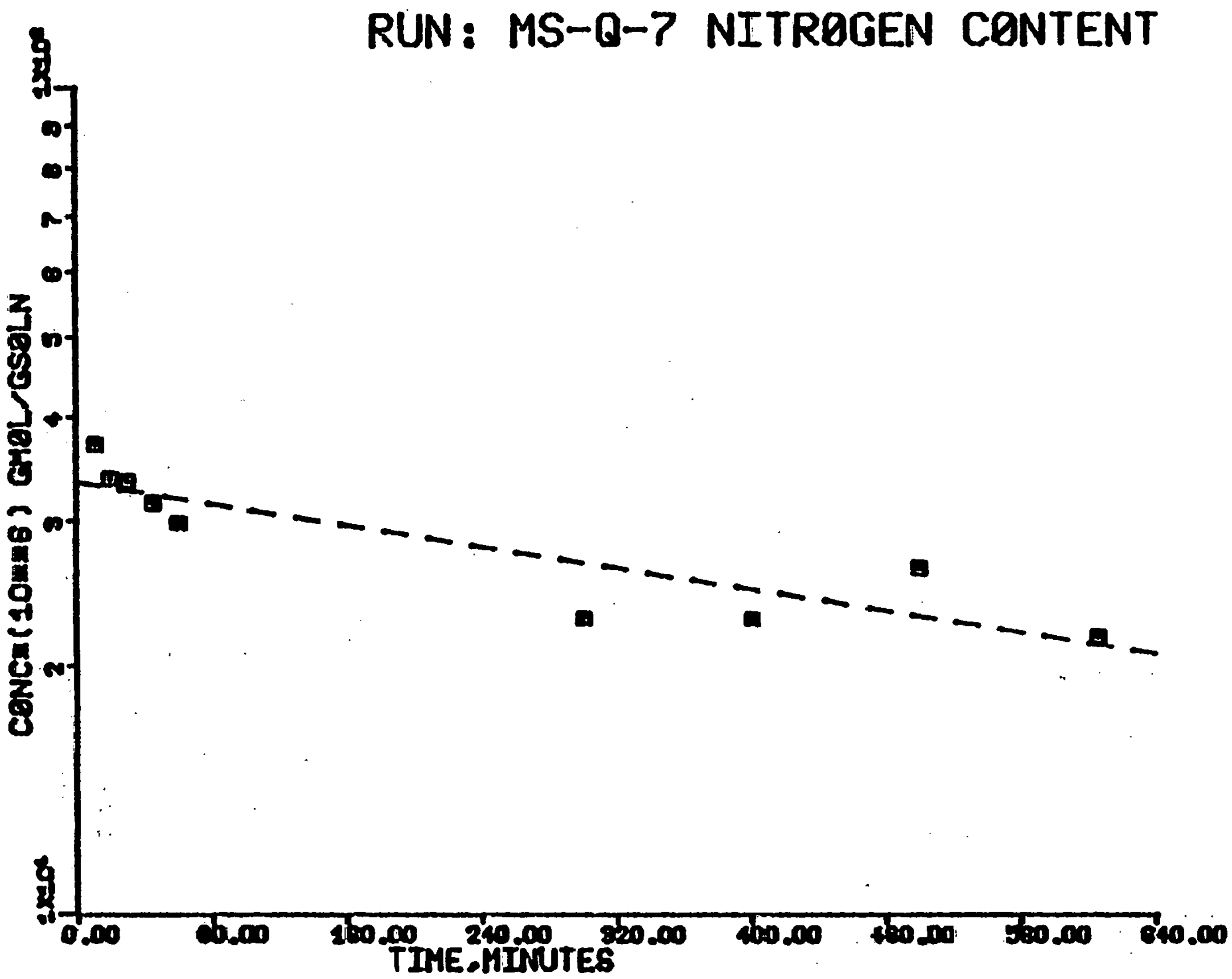


Figure 13. Total nitrogen removal from quinoline using 4% Ni on $AlBO_3 \cdot PO_4$.

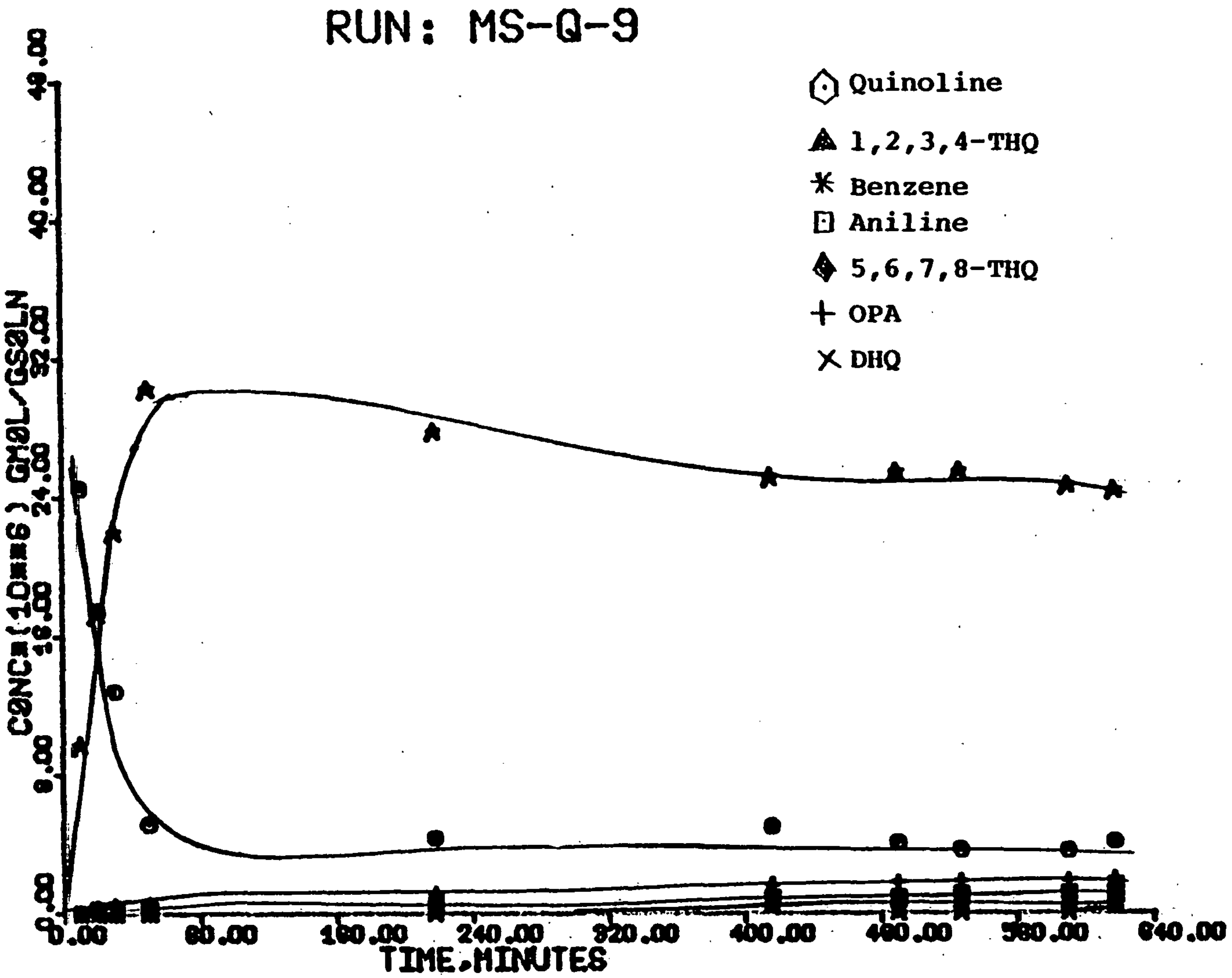


Figure 14. Concentration profiles for the hydrodenitrogenation of quinoline using unsulfided 4% Ni on AlBO$_3$ (glass liner used).

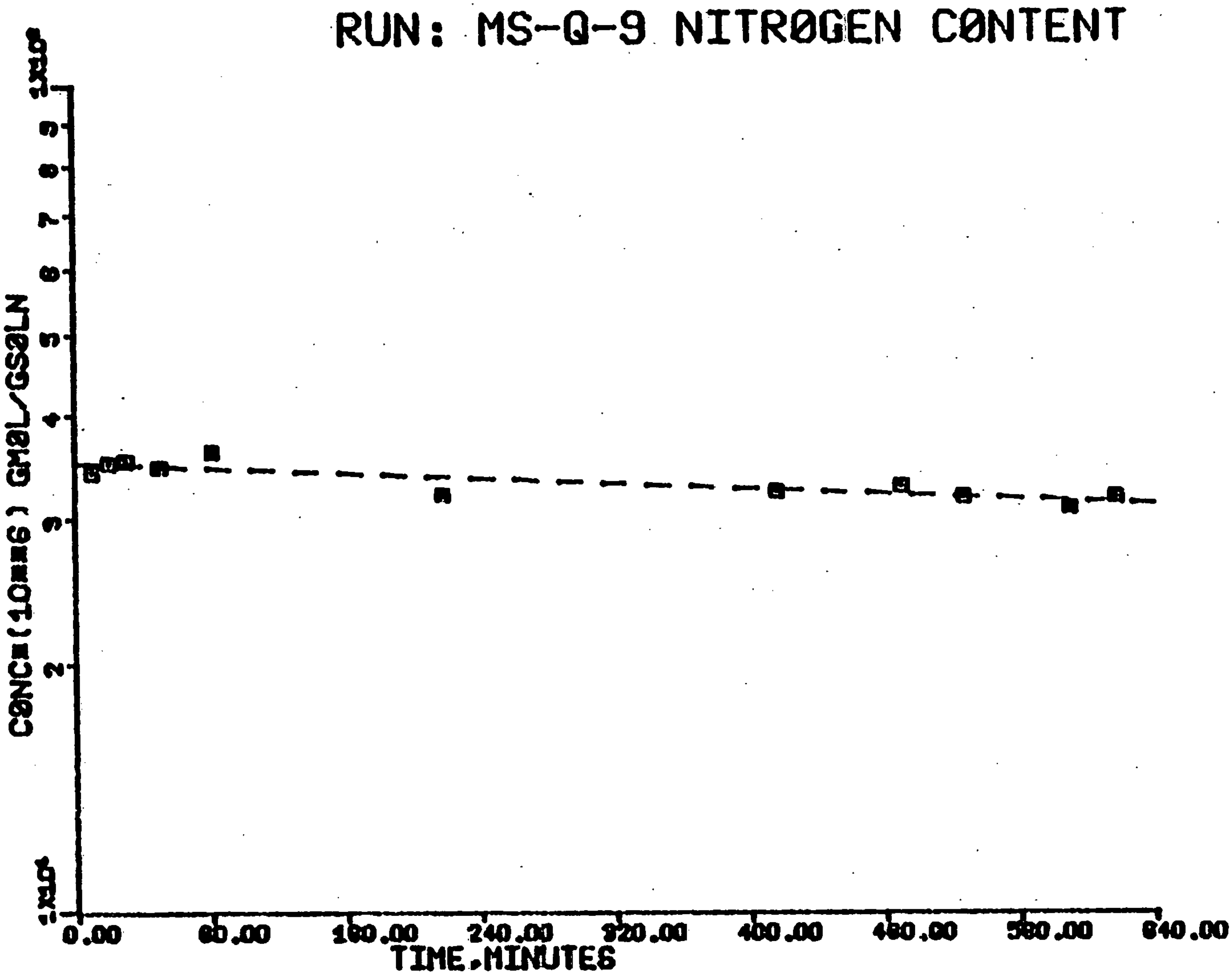


Figure 15. Total nitrogen removal from quinoline using unsulfided 4% Ni on AlBO$_3$.

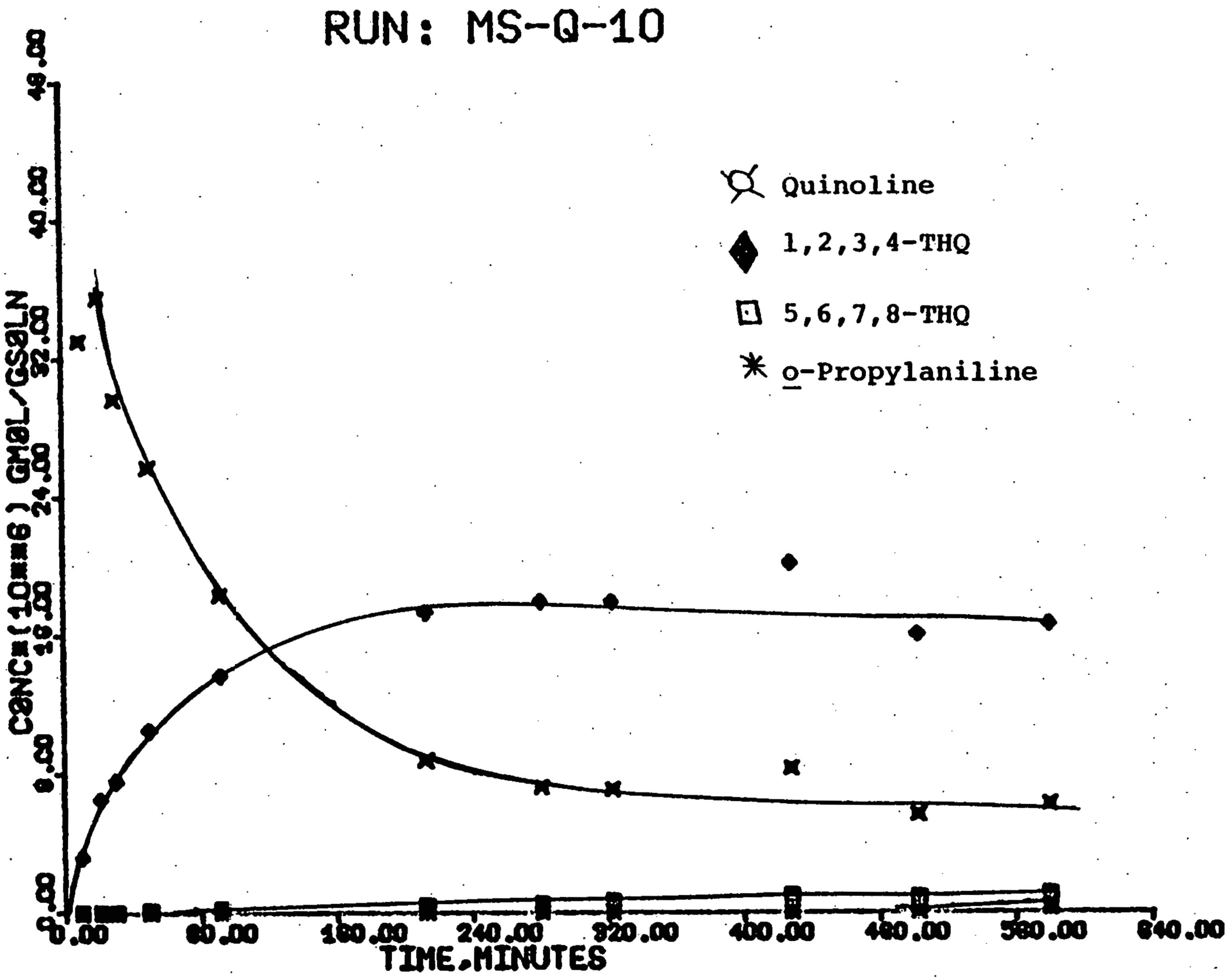


Figure 16. Concentration profile for the hydrodenitrogenation of quinoline using $AlBO_3$ (glass liner used).

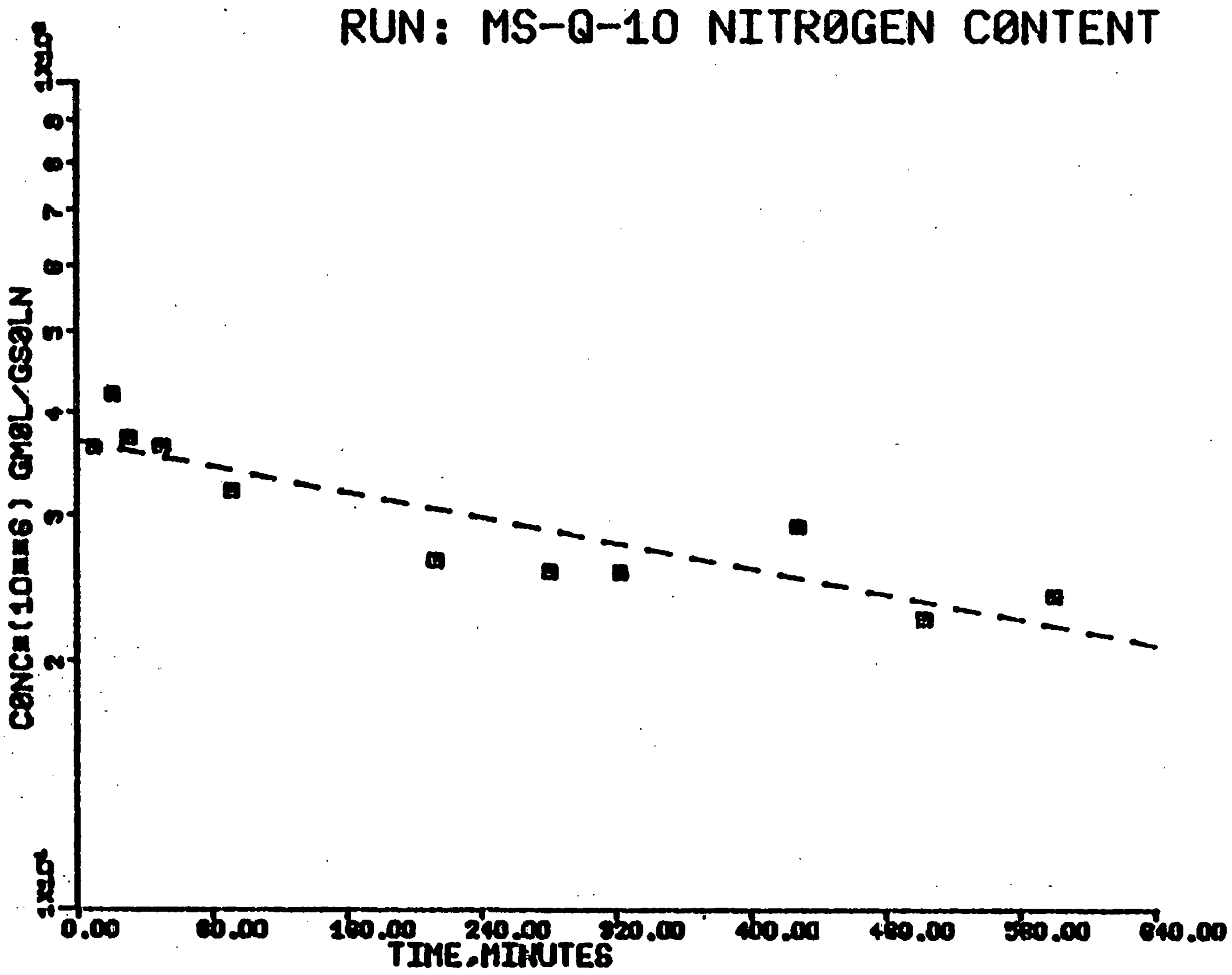


Figure 17. Total nitrogen removal from quinoline using $AlBO_3$.

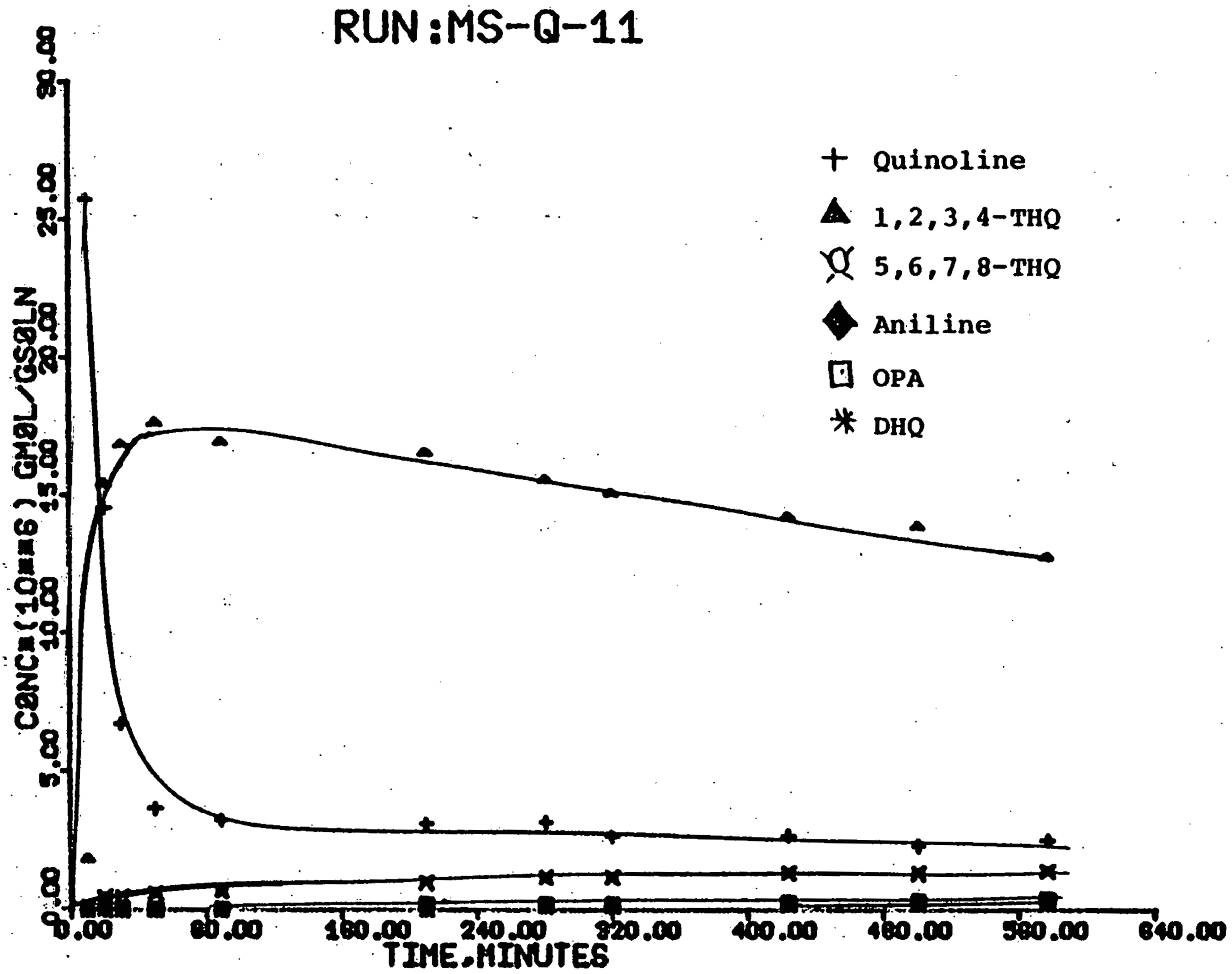


Figure 18. Concentration profile for the hydrodenitrogenation of quinoline using 4% Ni on γ-alumina (glass liner used).

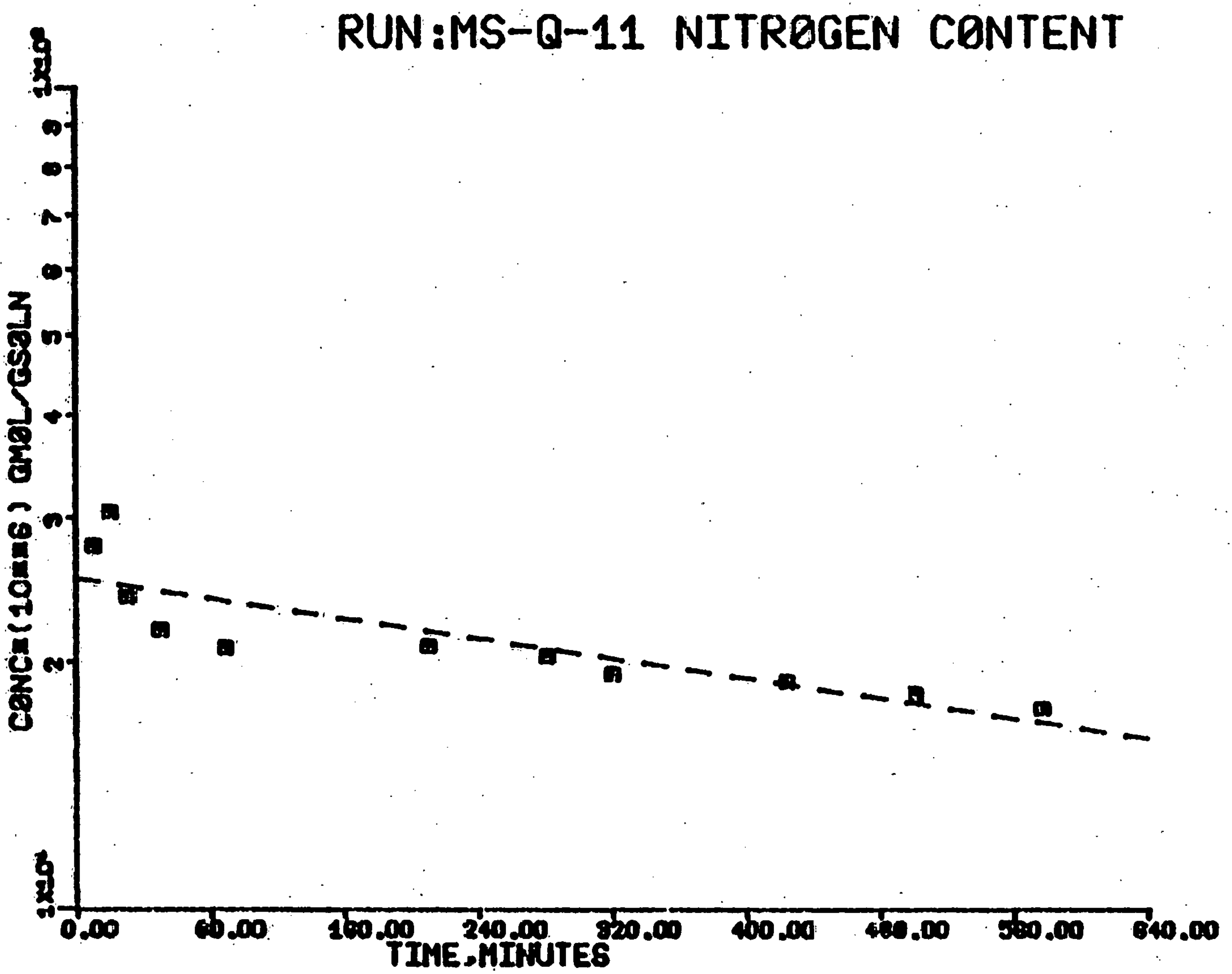


Figure 19. Total nitrogen removal from quinoline using 4% Ni on γ-alumina.

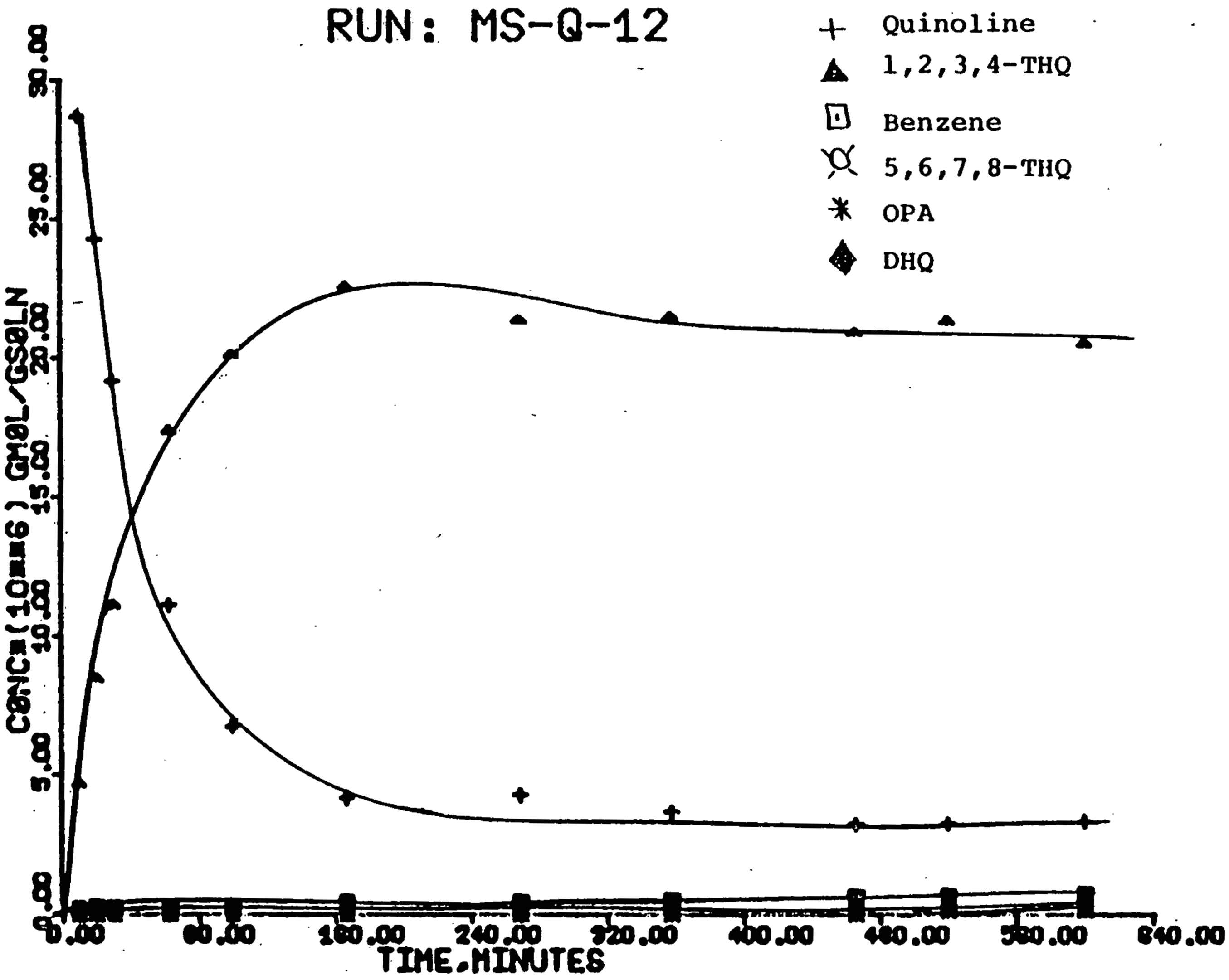


Figure 20. Concentration profile for the hydrodenitrogenation of quinoline using 4% Mo on $AlBO_3$ (glass liner used).

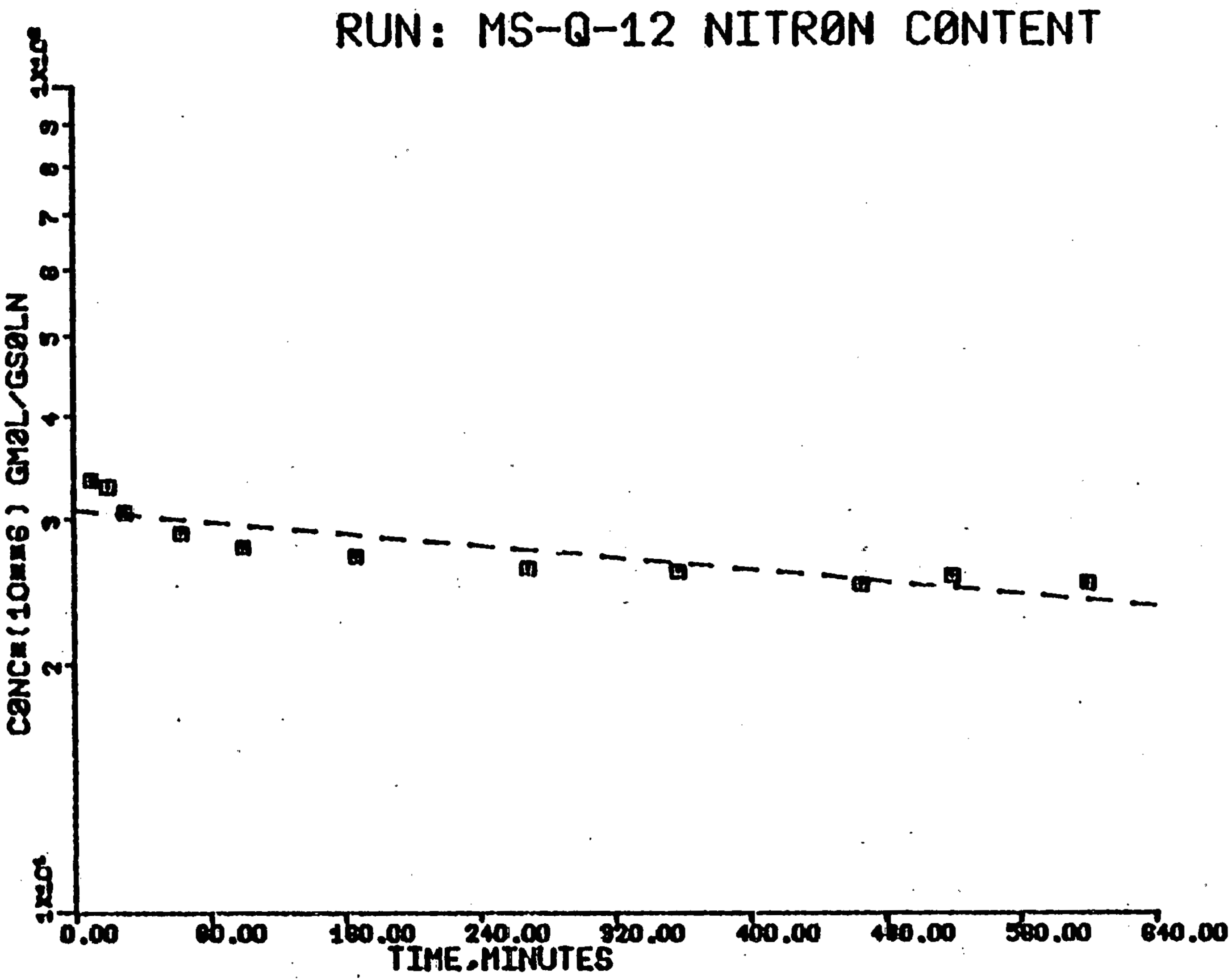


Figure 21. Total nitrogen removal from quinoline using 4% Mo on $AlBO_3$.

except MS-Q-8 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:

Concentration vs. time graphs of products and total nitrogen conc. vs. time graphs are shown in Figures 12-21. In each run quinoline was rapidly converted to 1,2,3,4 tetrahydroquinoline. Other side products observed in each run were 5,6,7,8 tetrahydroquinoline, benzene, decahydroquinoline orthopropylaniline, aniline, and n-propylcyclohexane. Run MS-Q-7 showed 40% nitrogen removed at 10 hours, indicating that the metal walls of the autoclave significantly inhibit the $AlBO_3 \cdot PO_4$/4% Ni catalyst, yet when run with glass liner shows high nitrogen removal rates similar to the $AlBO_3$/4% Ni (41%) runs. The unsulfided $AlBO_3$/4% Ni run, MS-Q-8 , indicates that sulfiding enhances nitrogen removal for the $AlBO_3$/4% Ni catalyst by 25% over the unsulfided catalyst. When the $AlBO_3$ support was run without a metal ligand, MS-Q-10 , the amount of nitrogen removed, compared to that of $AlBO_3$/4% Ni , was reduced by 25%, indicating that the metal ligand plays an important role in the nitrogen removal process. The Al/4% Ni , MS-Q-11 , run showed comparable nitrogen removal capabilities to the $AlBO_3$/4% Ni and $AlBO_3 \cdot PO_4$/4% Ni (37% compared to 41%) indicating that the borate and borate · phosphate groups play a minor role in nitrogen removal process, contrary to what was previously hypothesized. The aluminum support is a major contributor to the nitrogen removal process, along with the metal ligand in the $AlBO_3/Ni$ and $AlBO_3 \cdot PO_4/Ni$ catalysts. The $AlBO_3/4\%$ Mo run showed only 25% nitrogen removed after 10 hours, initially indicating that the molybdenum contributed, contrary to nickel, little if any to the nitrogen-removing properties of the support. In the Al/4% Ni run, as in the $AlBO_3/4\%$ Ni and $AlBO \cdot PO_4/4\%$ Ni runs, the large percent of nitrogen removed could not be explained by a material balance of the products observed, i.e. n-propylcyclohexane, benzene, or n-propylbenzene, indicating other products are being formed not observed under the conditions of analysis. The catalysts are currently being analyzed for carbon-hydrogen-nitrogen content and analysis of the samples from these runs are being made using a nitrogen-specific detector. Runs are now also being made on different supports with varying metal ligands.

V. PERSONNEL

There has been no change in personnel during this quarter.

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