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DEVELOPMENT OF UNIQUE CATALYSTS FOR HYDRODENITROGENATION OF COAL-DERIVED LIQUIDS

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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.

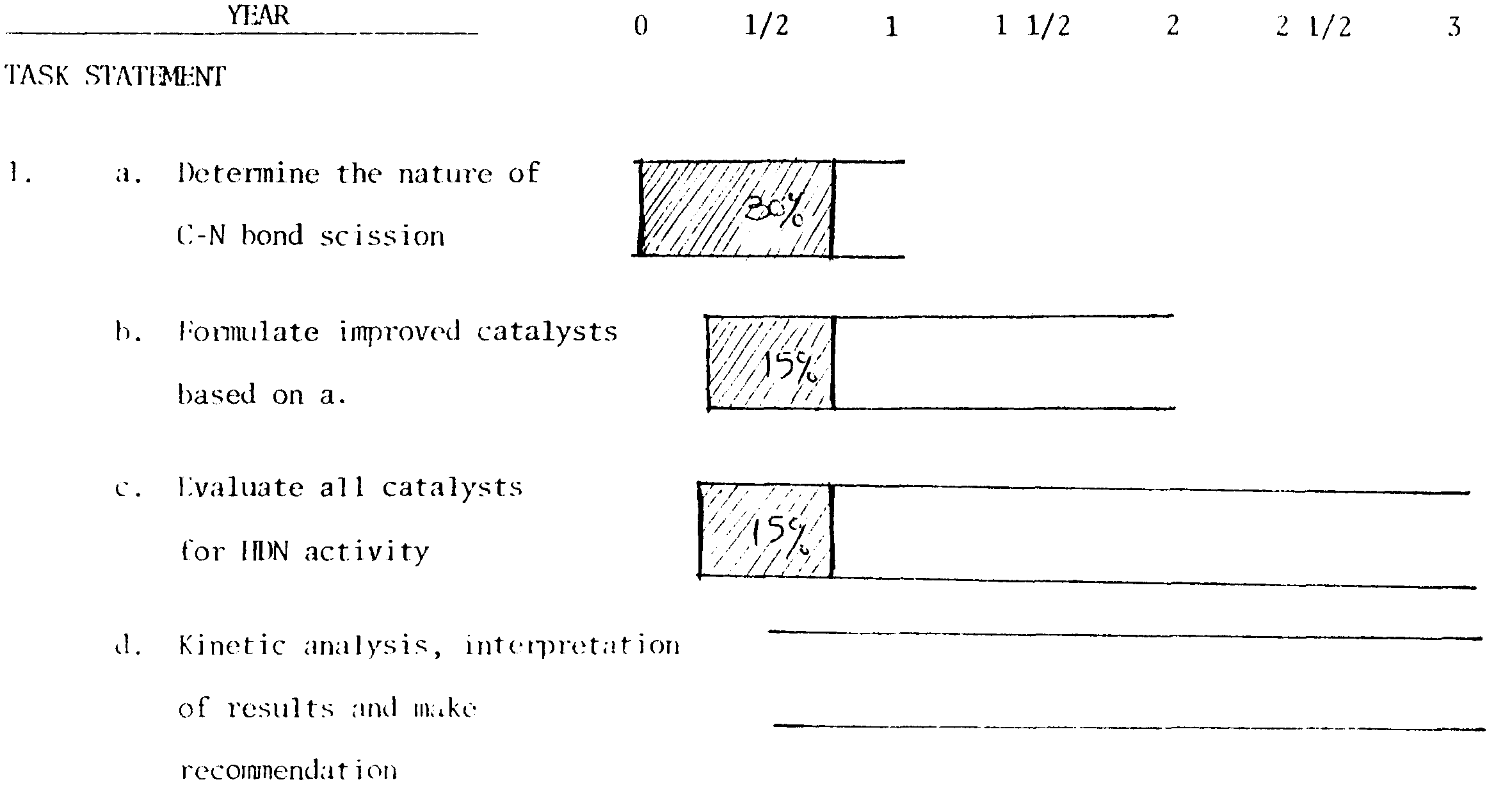
Improved hydrodenitrogenation catalysts require a balance between hydrogenation and carbon-nitrogen bond scission. Several catalysts have been prepared and tested recently which include Brønsted and Lewis acid catalysts without metal, alumina-impregnated with Mo, Co and Ni, promoted with in situ H_2S 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

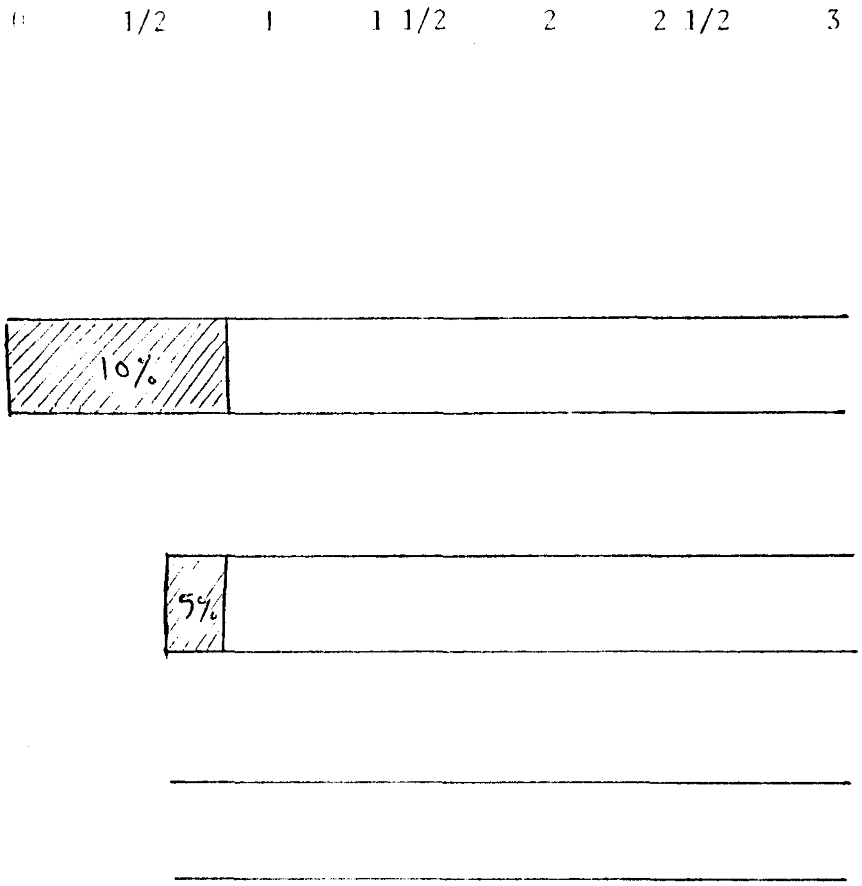
b. Formulate improved catalysts based on a.

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 Soltn.
Ni	γ-alumina	8.4	$Ni(NO_3)_2 \cdot 6H_2O$	7.50
Ni	silica-alumina	8.4	$Ni(NO_3)_2 \cdot 6H_2O$	7.50
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 % (≈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 ≈ 3.24 atm.

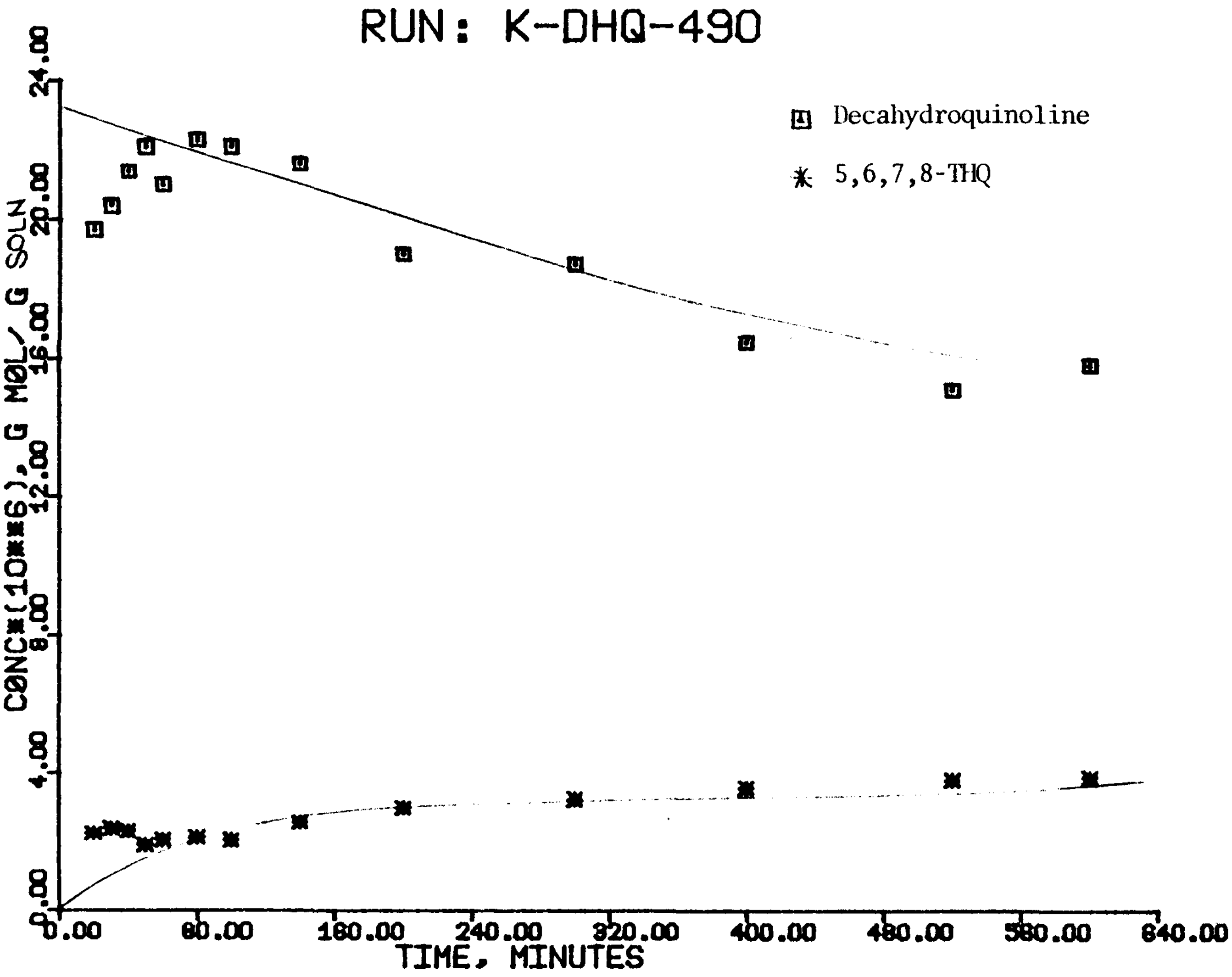

Figure 1: Concentration profiles for hydrodenitrogenation of decahydroquinoline using silica-alumina.

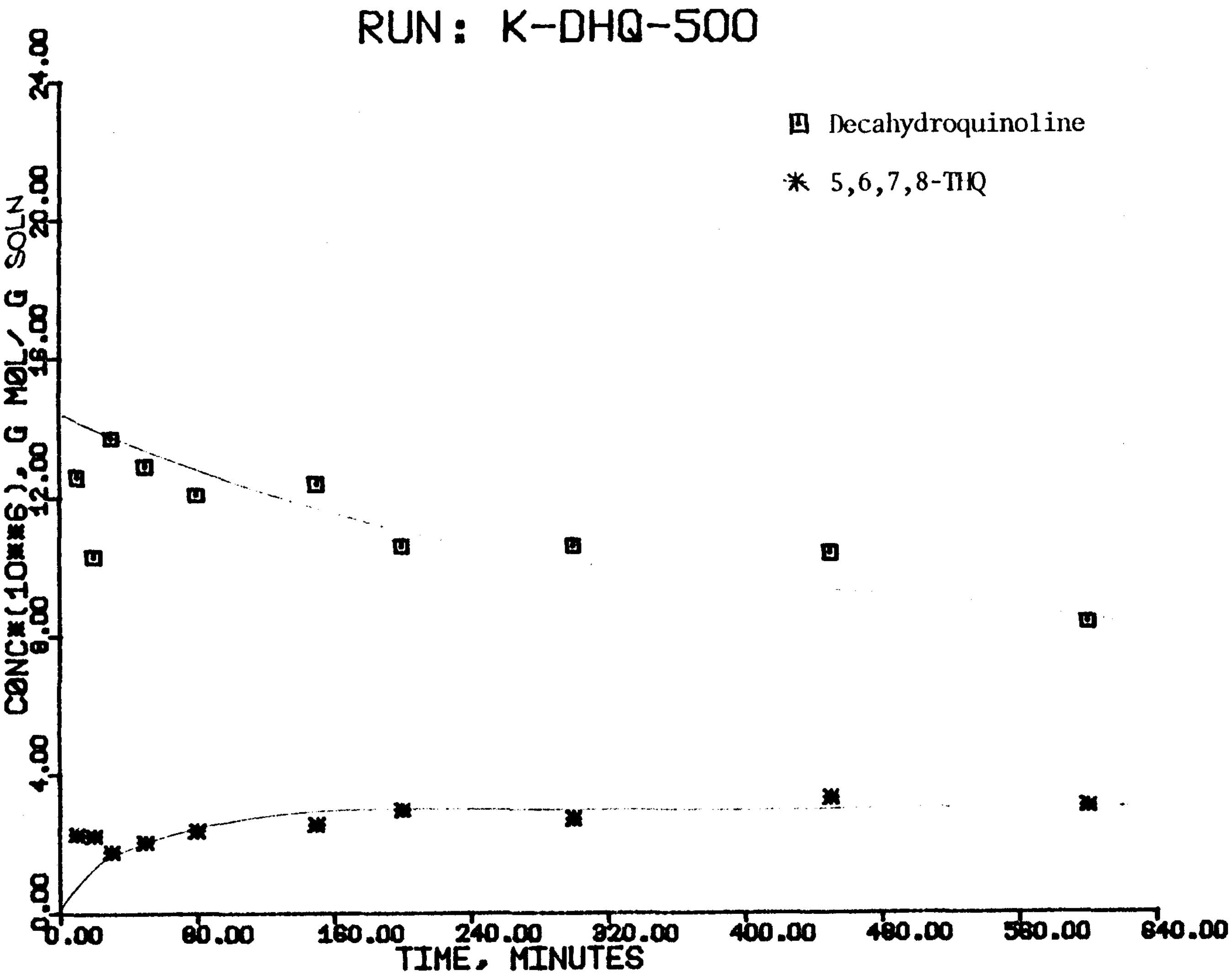

Figure 2: Concentration profiles for hydrodenitrogenation of decahydroquinoline using γ-alumina.

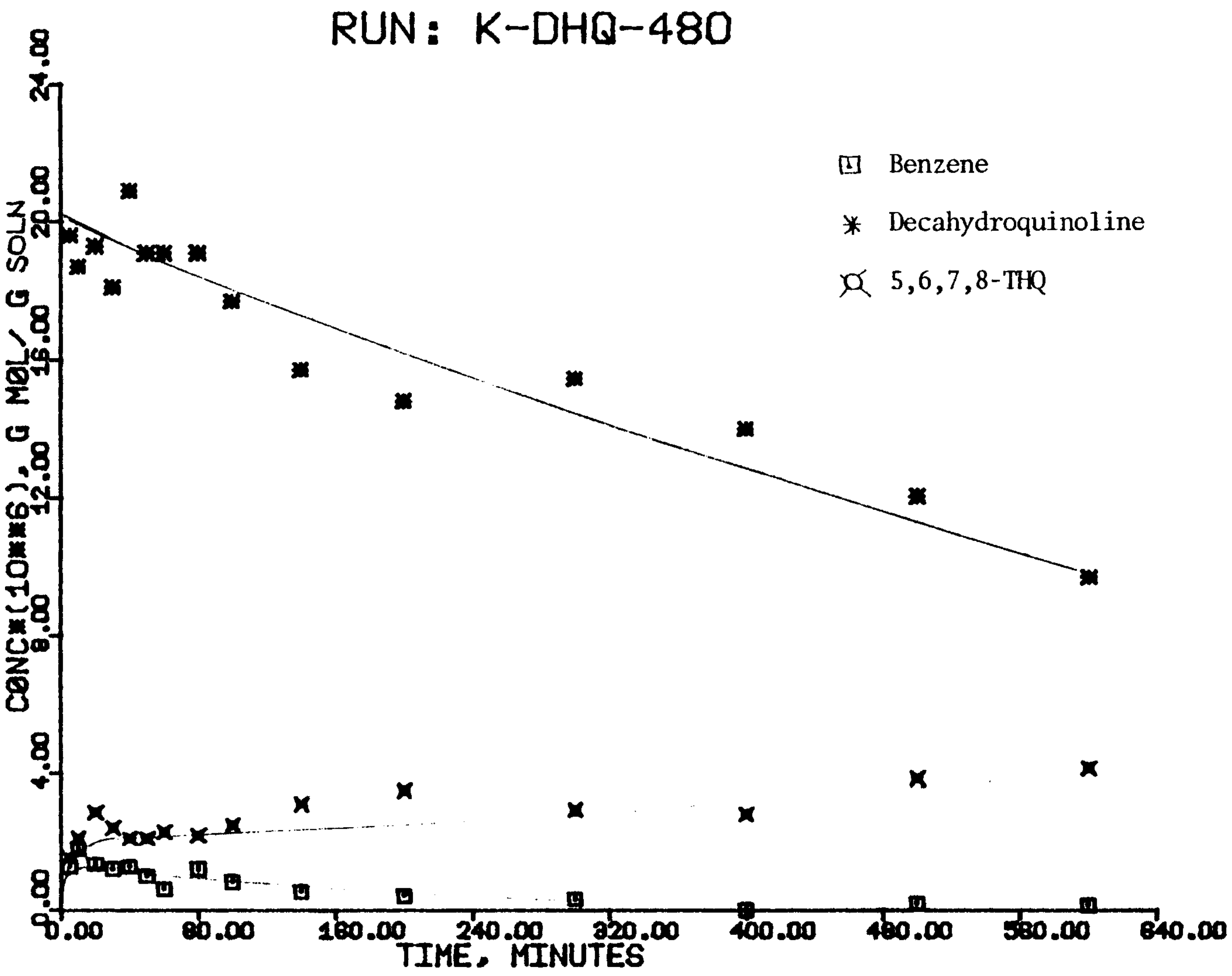

Figure 3: Concentration profiles for hydrodenitrogenation of decahydroquinoline using HY-zeolite.

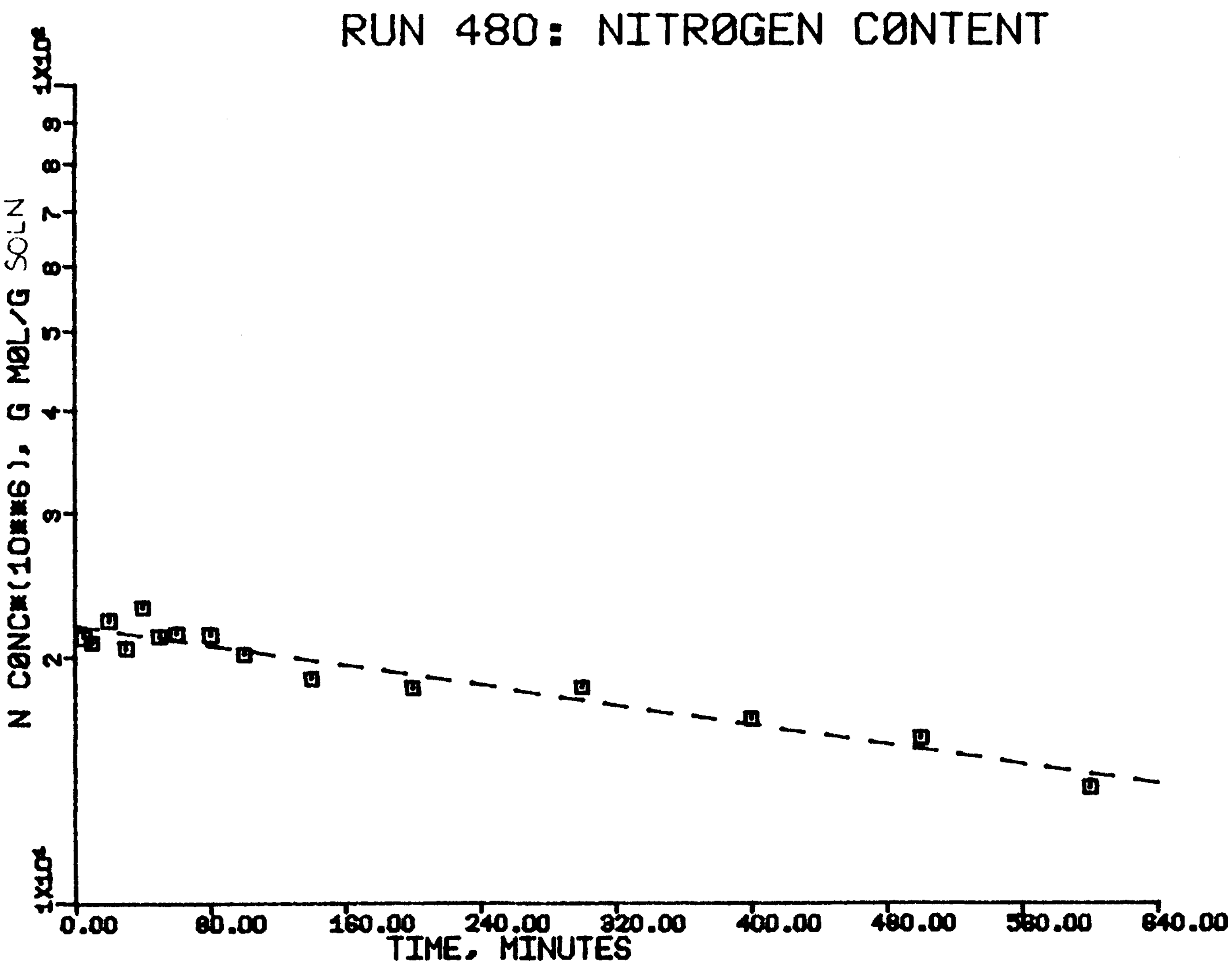

Figure 4: Total nitrogen removal from decahydroquinoline using HY-zeolite.

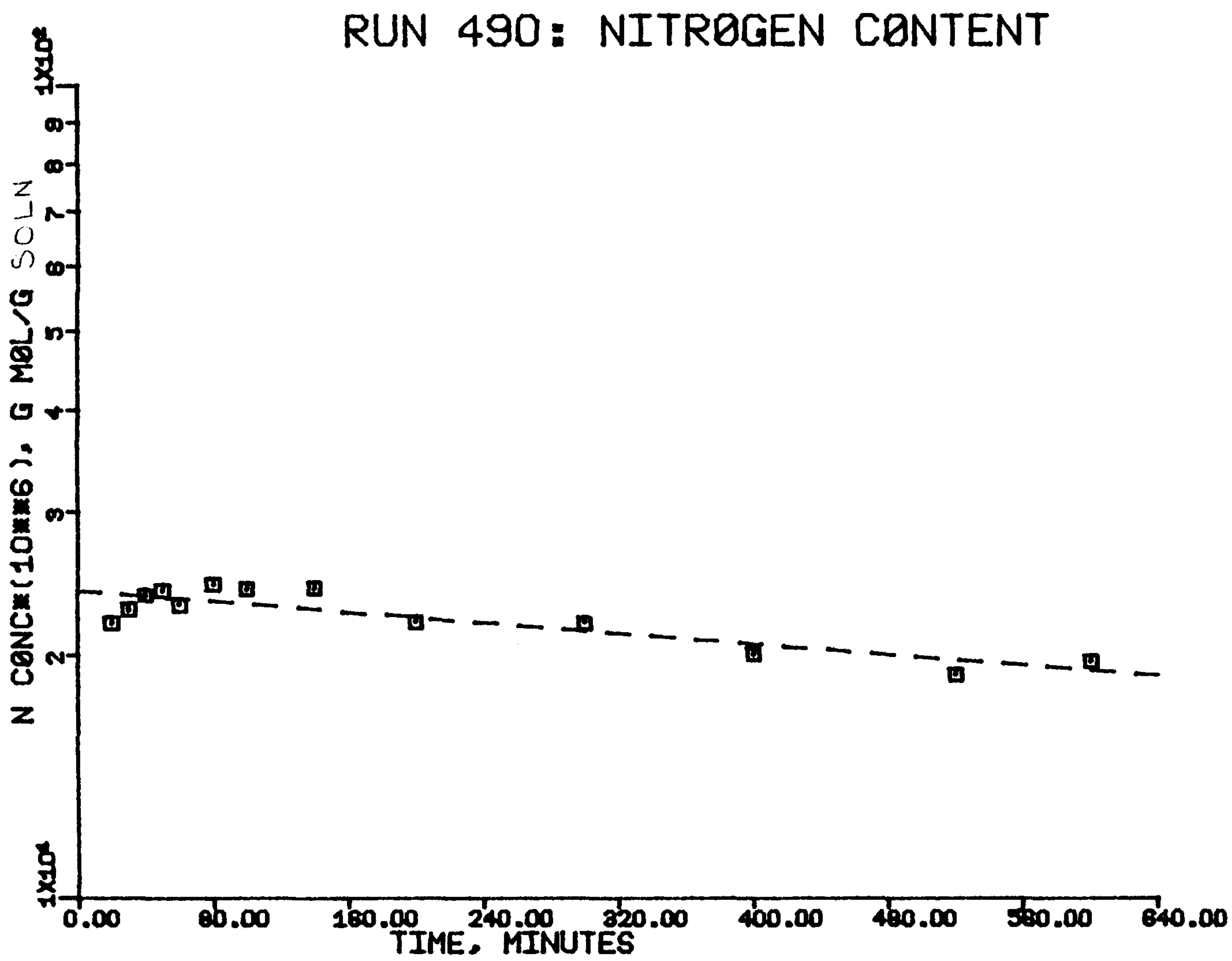

Figure 5: Total nitrogen removal from decahydroquinoline using silica-alumina.

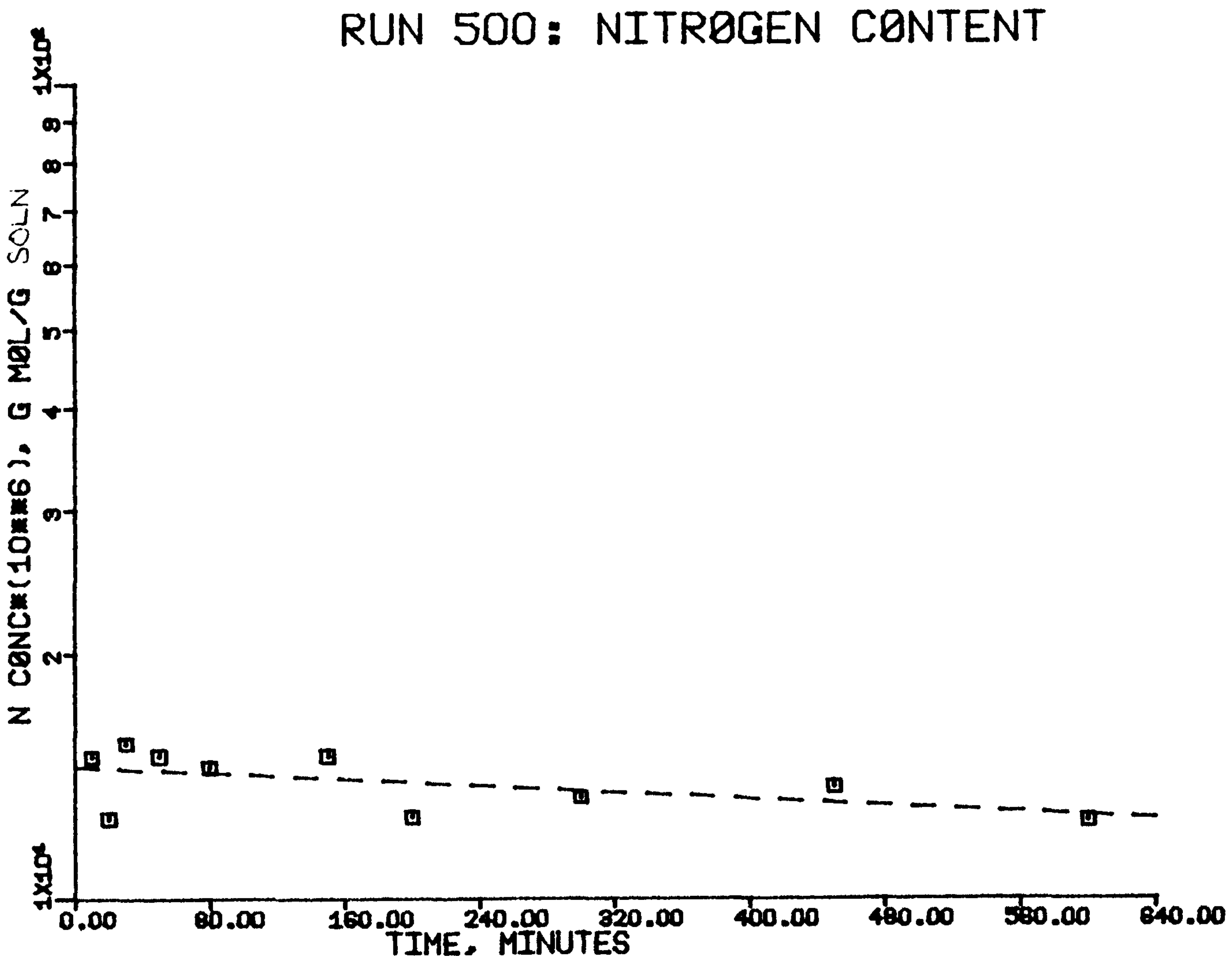

Figure 6: Total nitrogen removal from decahydroquinoline using γ-alumina.

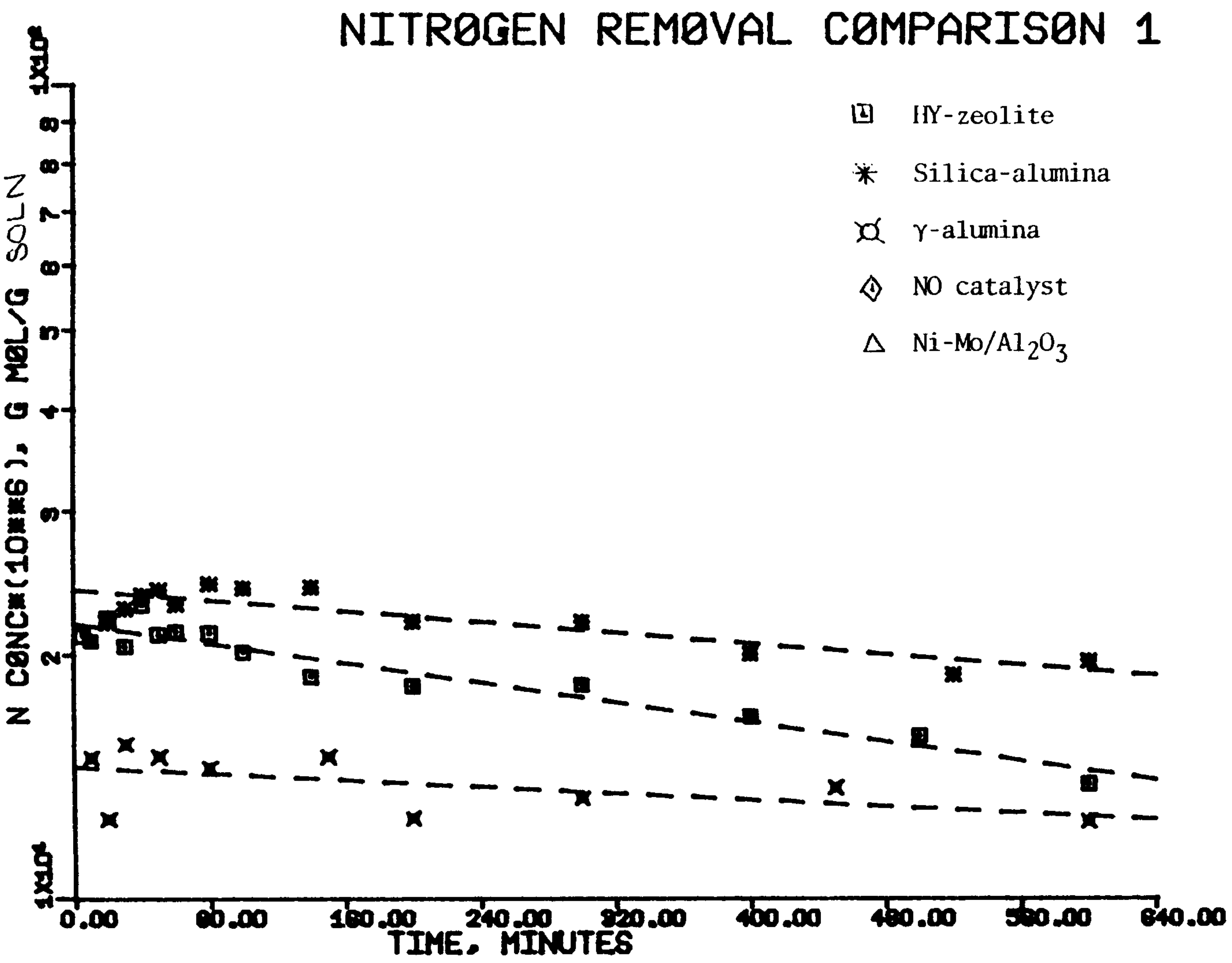

Figure 7: Total nitrogen removal from decahydroquinoline using various catalysts.

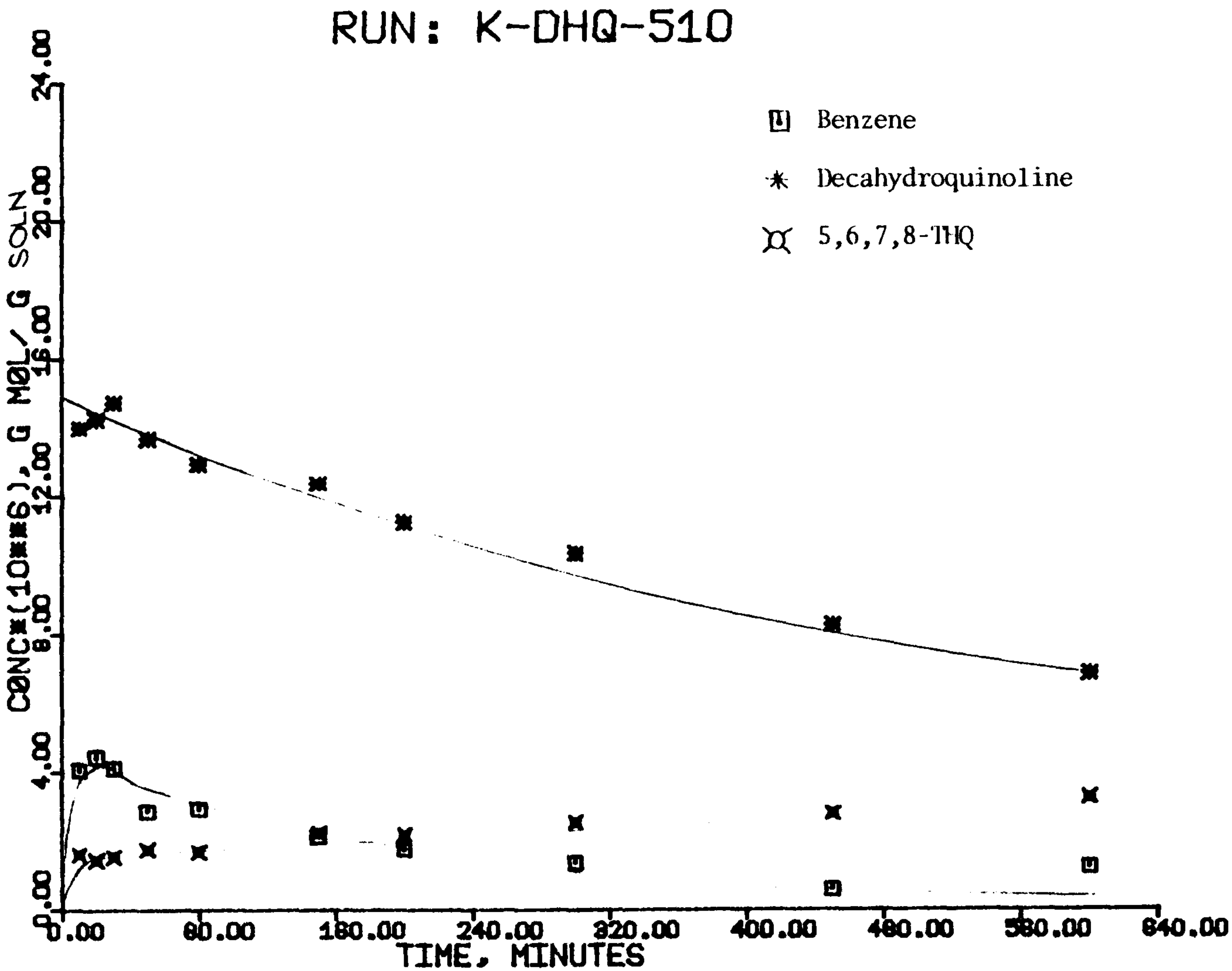

Figure 8: Concentration profiles for hydrodenitrogenation of decahydroquinoline using unsulfided HY-zeolite.

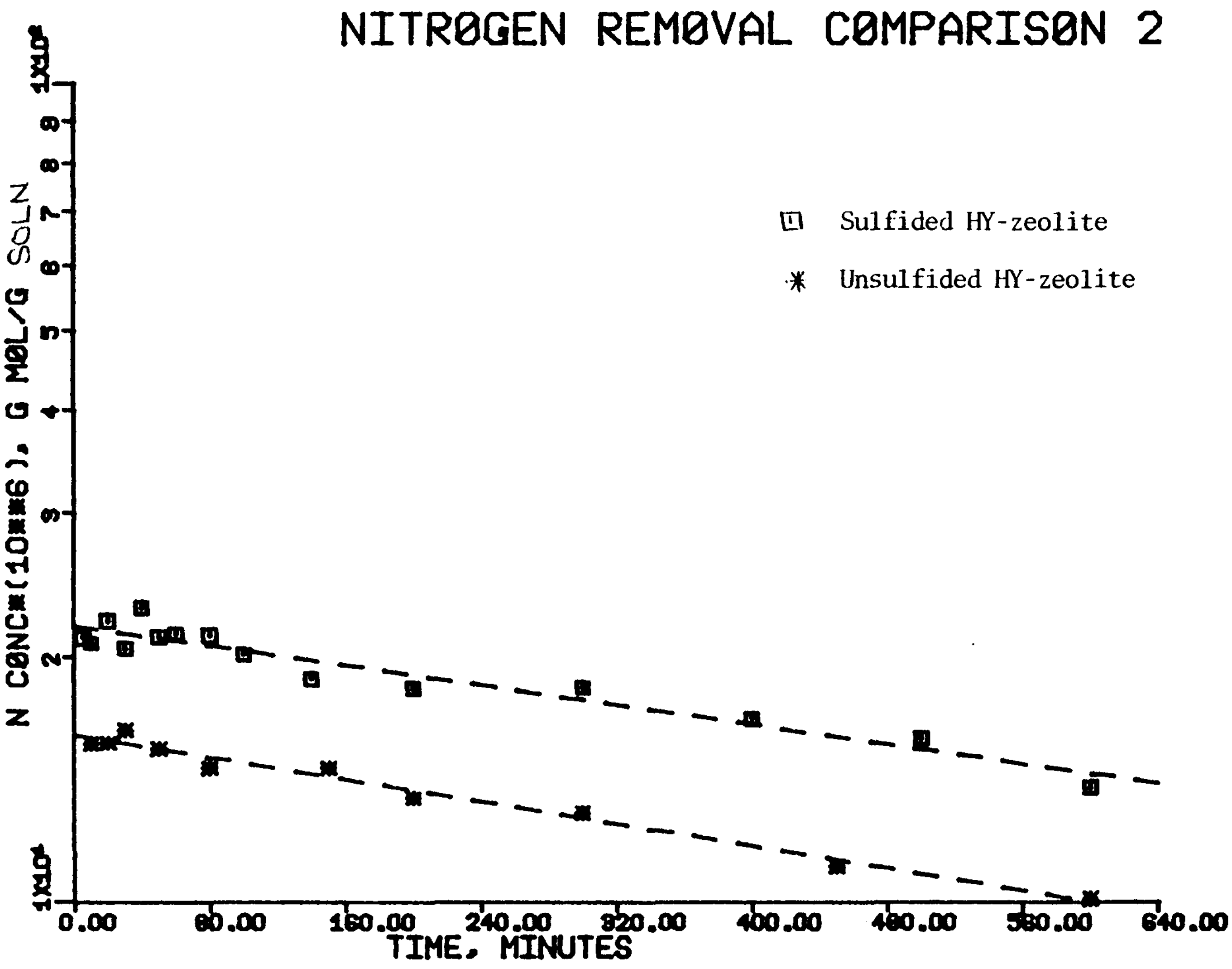

Figure 9: Total nitrogen removal from decahydroquinoline using sulfided and unsulfided HY-zeolite.

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

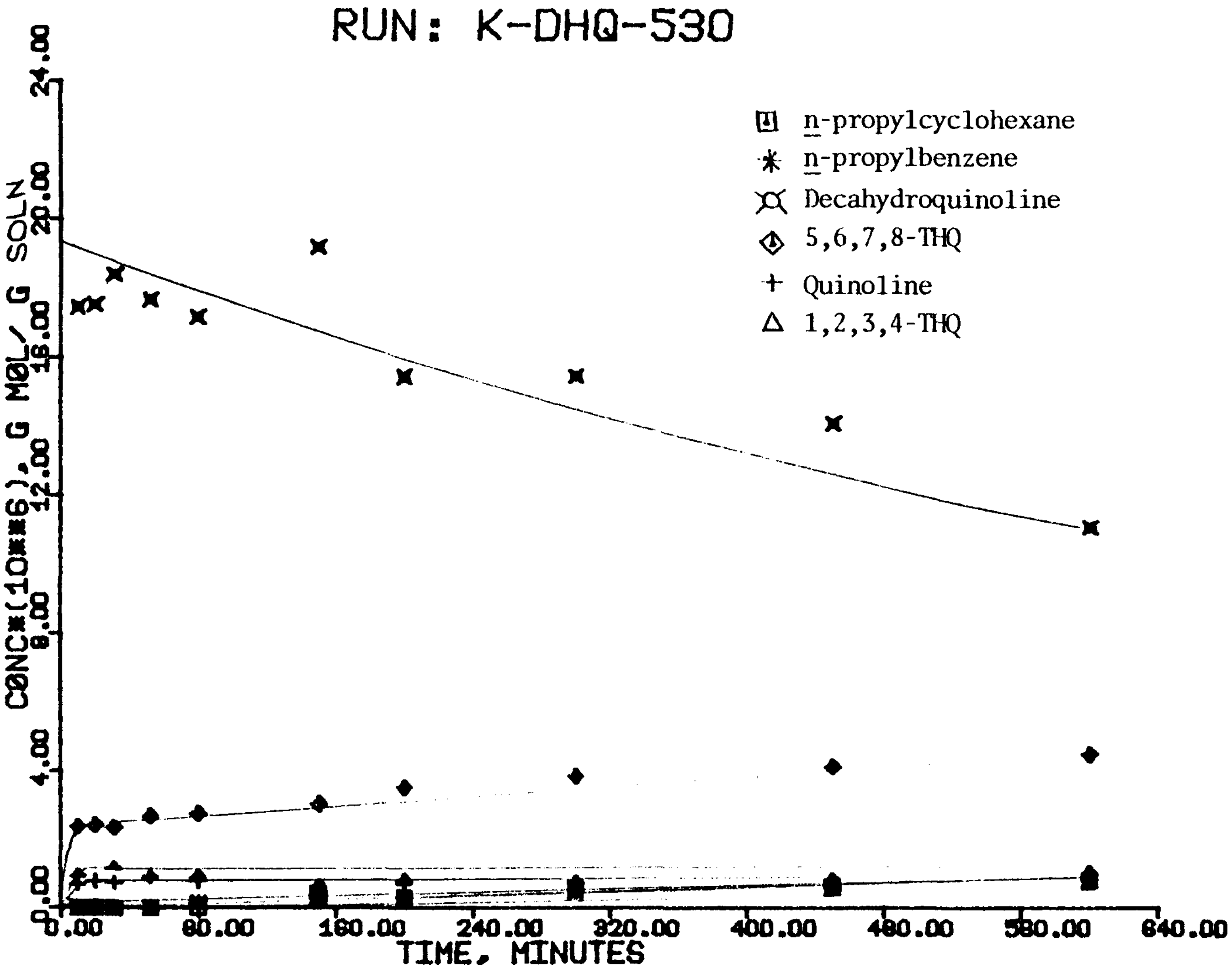

Figure 10: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Ni on γ-alumina.

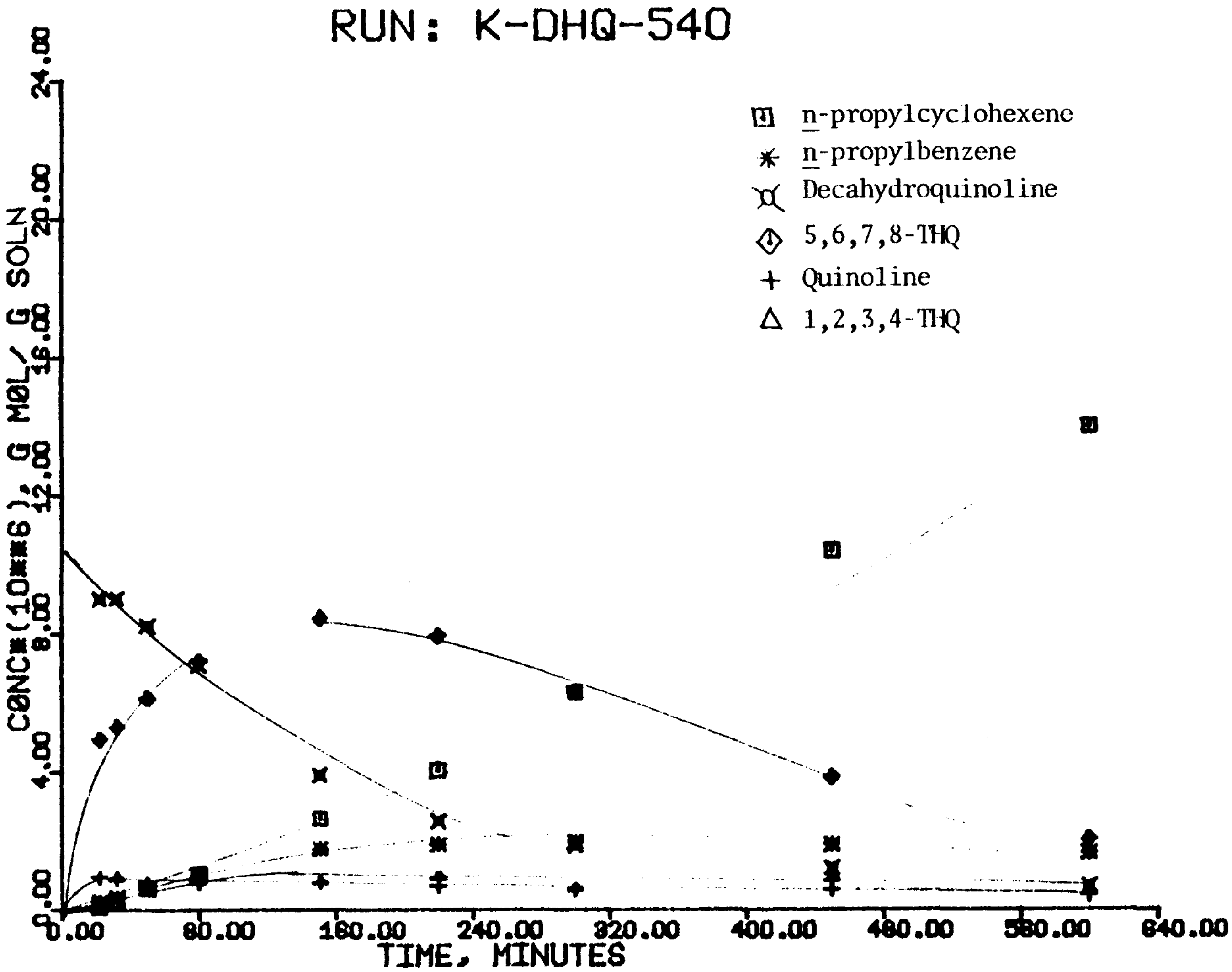

Figure 11: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 23% Mo on γ-alumina.

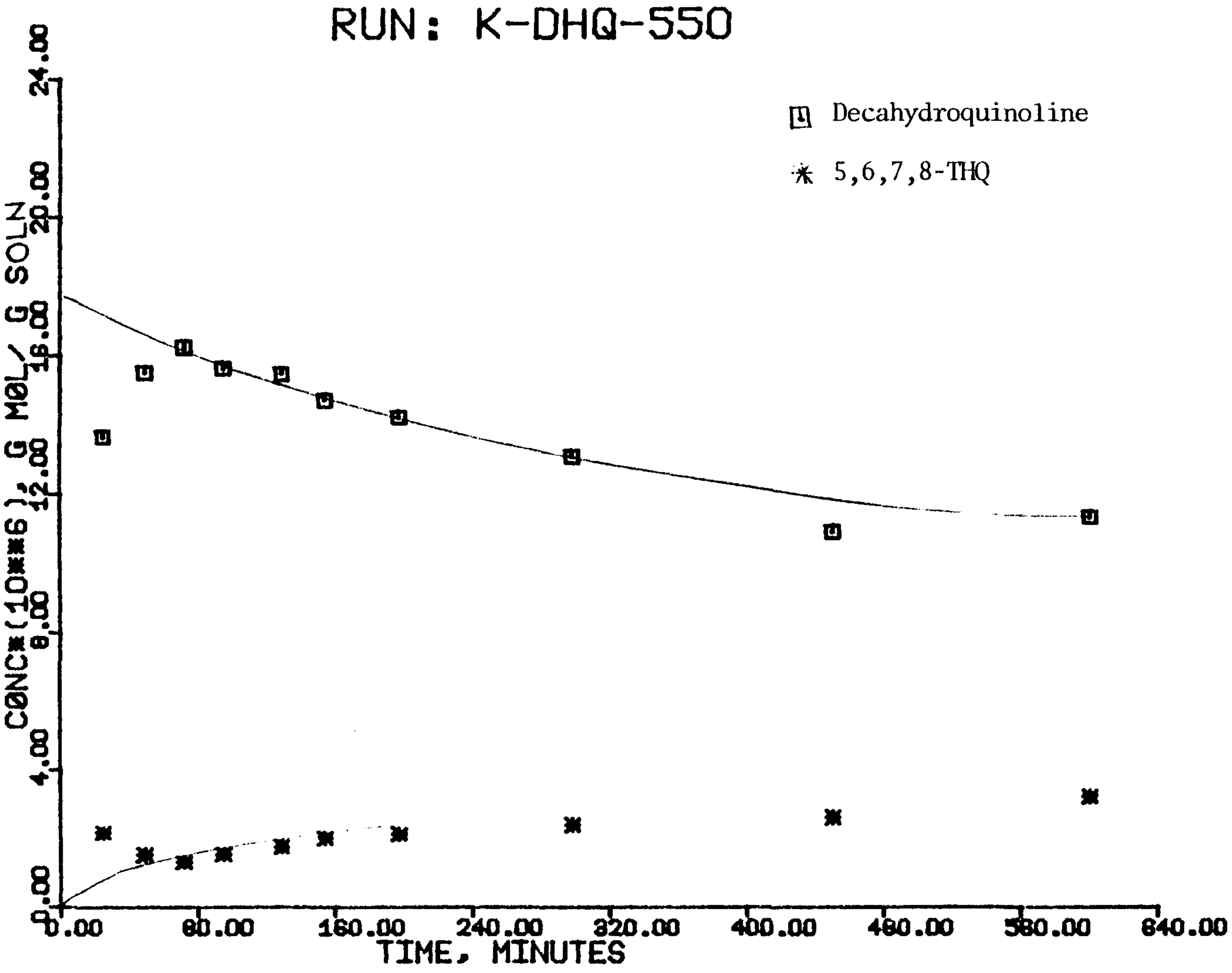

Figure 12: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Ni on silica-alumina.

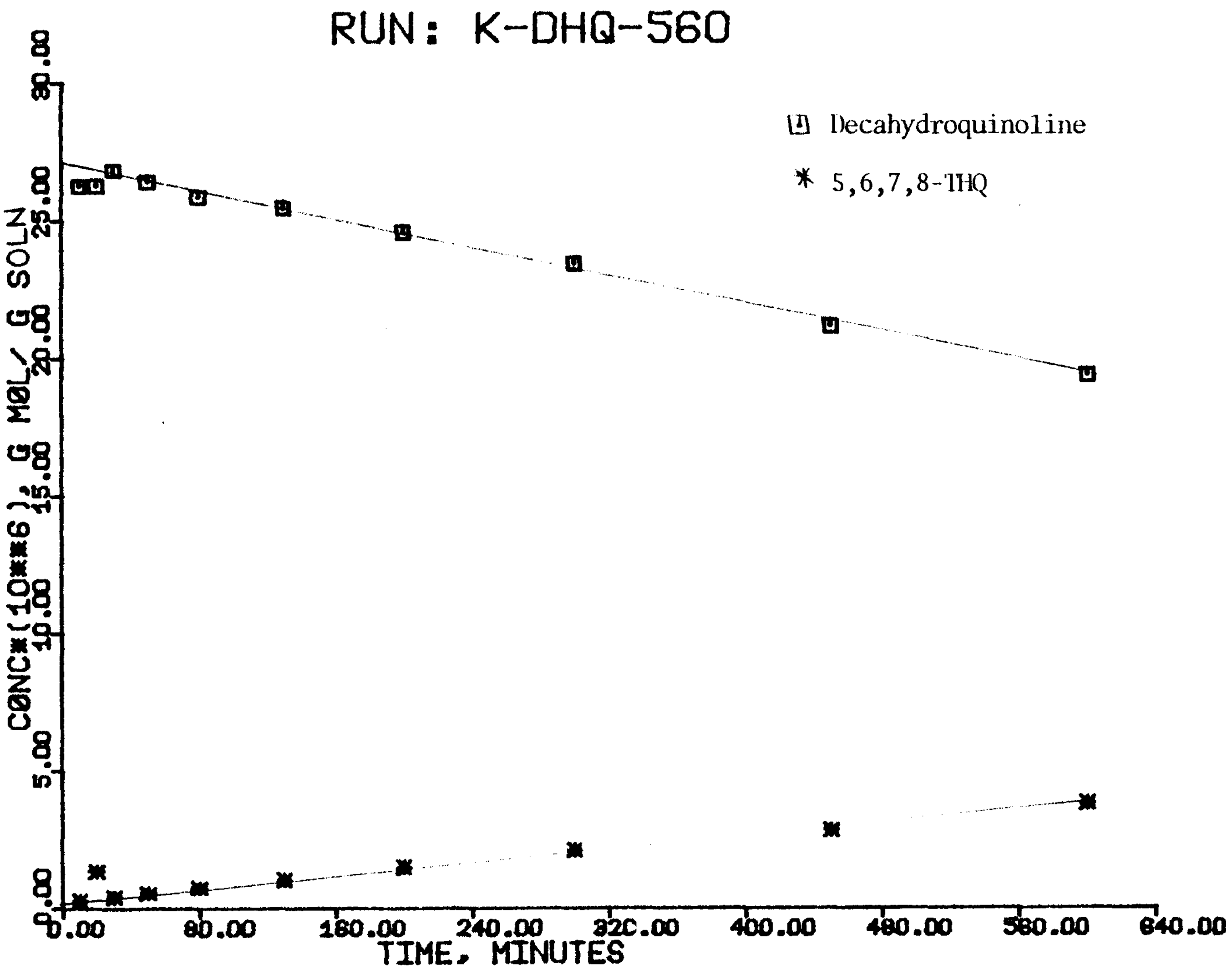

Figure 13: Concentration profiles for hydrodenitrogenation of decahydroquinoline using 8.4% Co on γ-alumina.

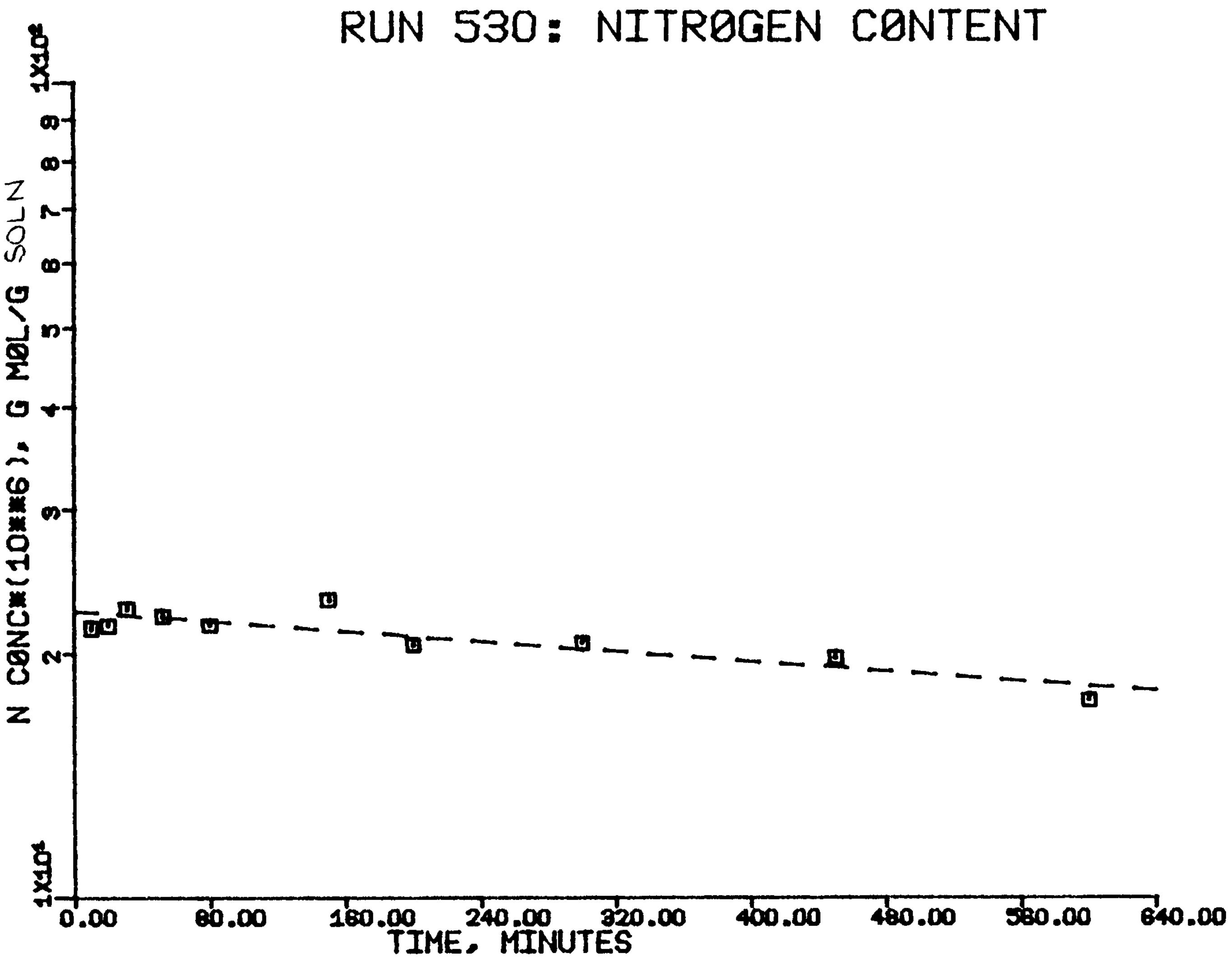

Figure 14: Total nitrogen removal from decahydroquinoline using 8.4% Ni on γ-alumina.

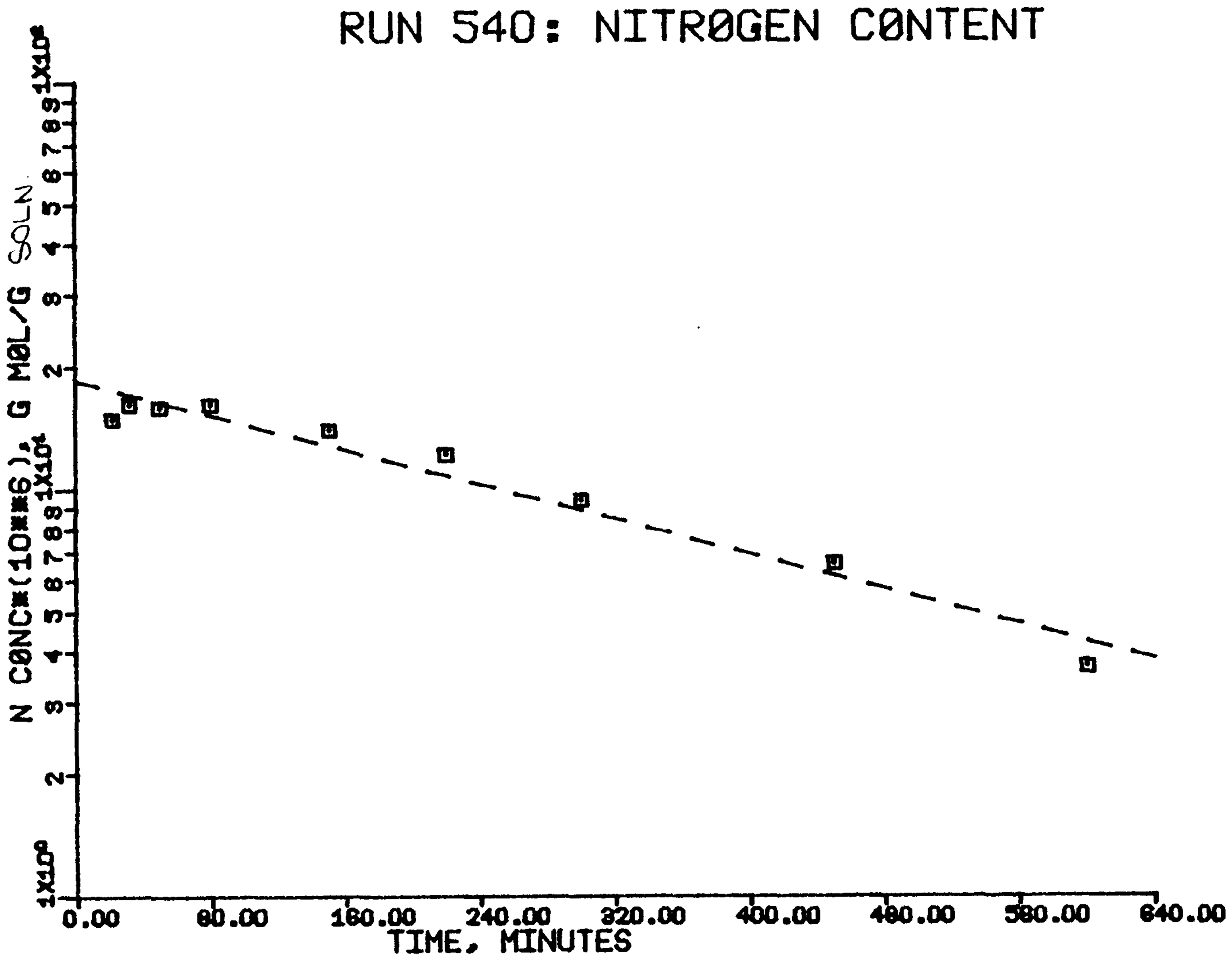

Figure 15: Total nitrogen removal from decahydroquinoline using 23% Mo on γ-alumina.

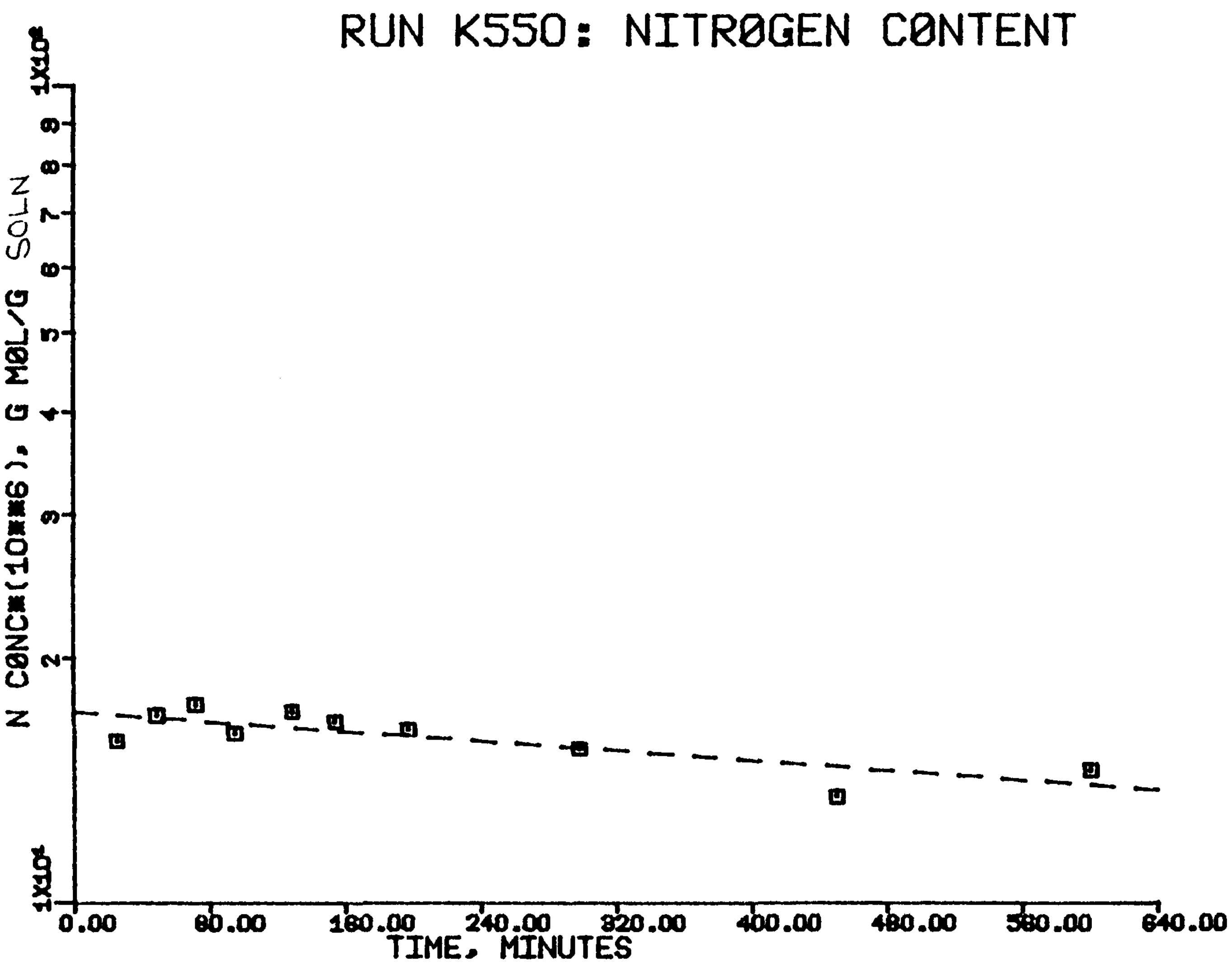

Figure 16: Total nitrogen removal from decahydroquinoline using 8.4% Ni on silica-alumina.

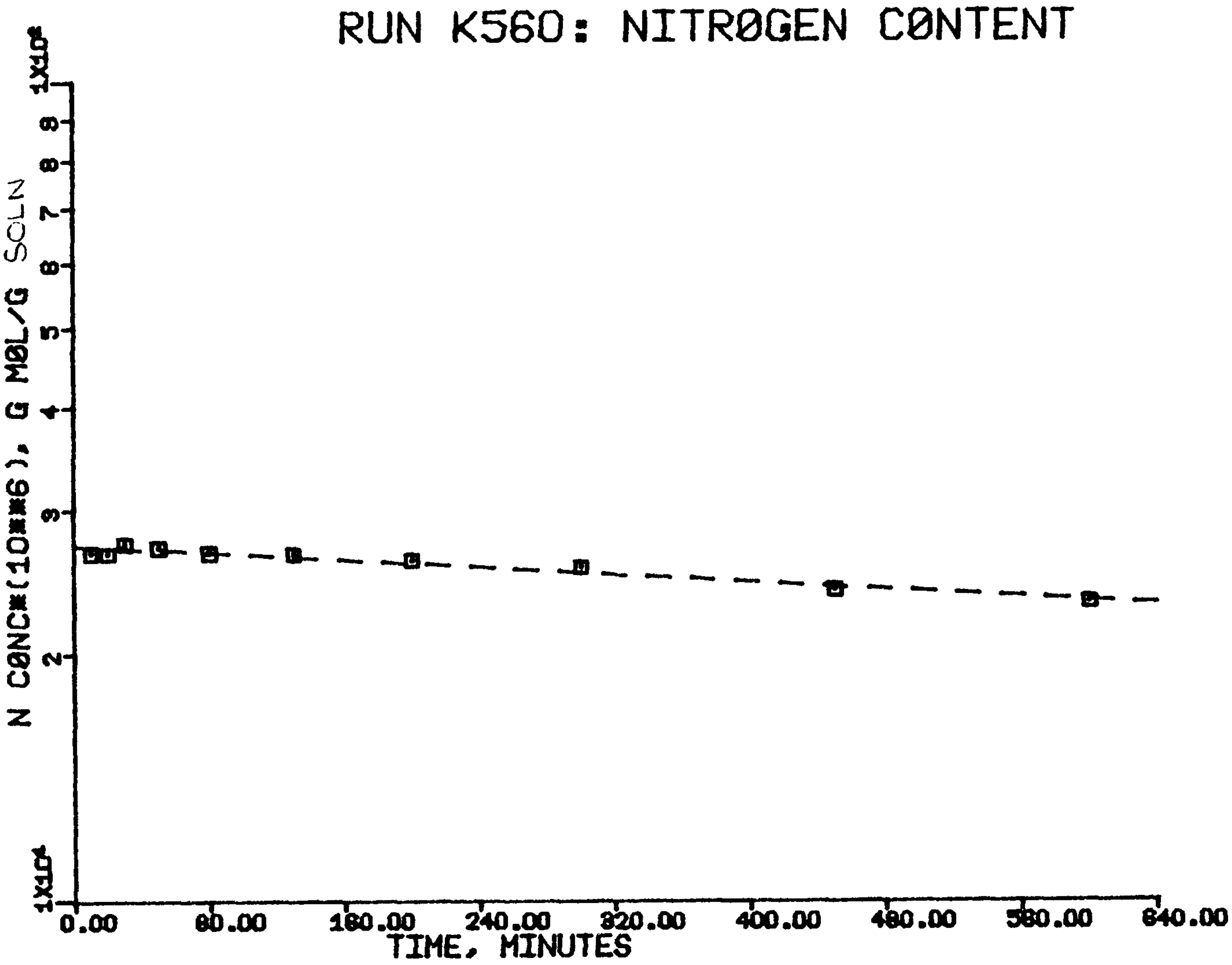

Figure 17: Total nitrogen removal from decahydroquinoline using 8.4% Co on γ-alumina.

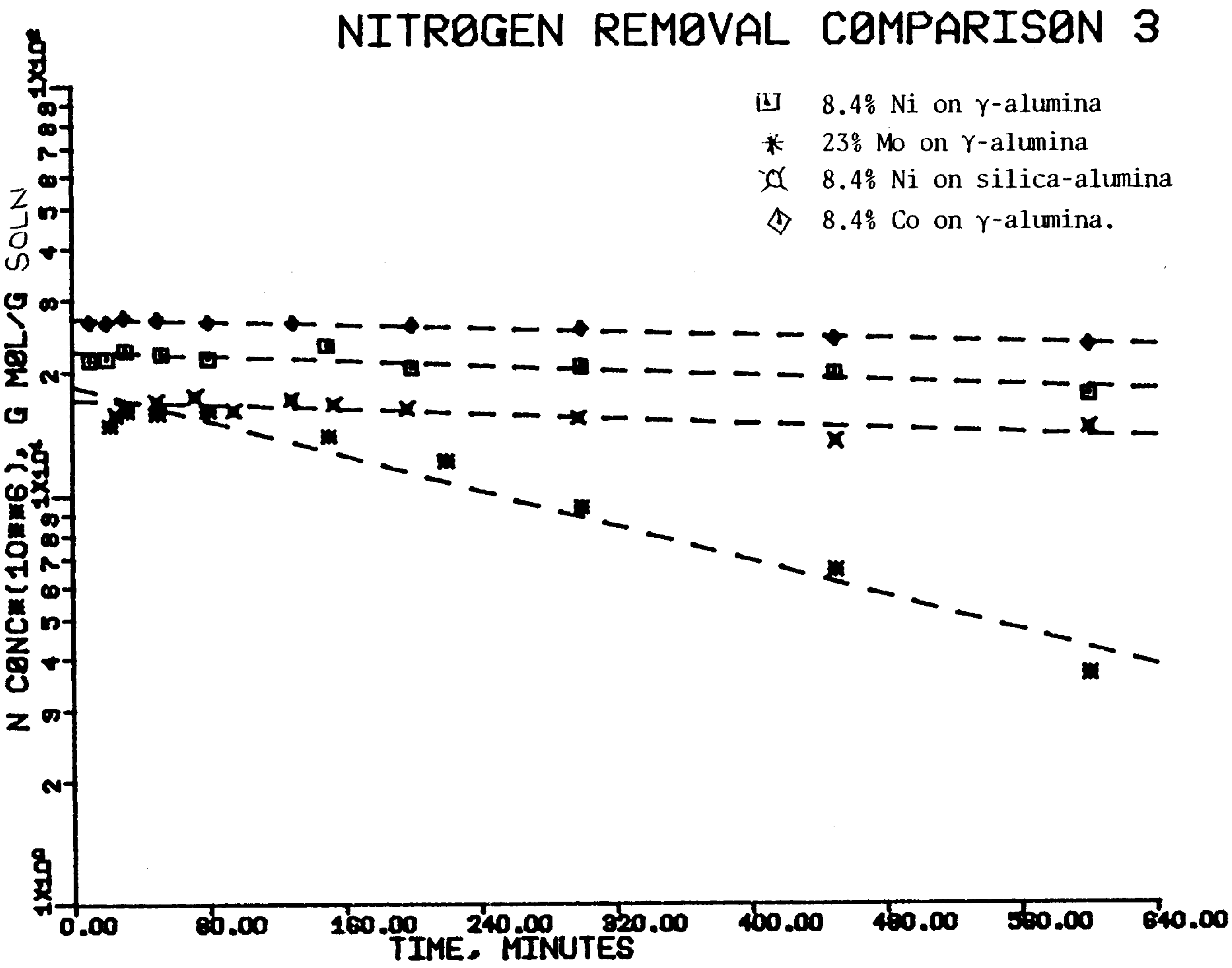

Figure 18: Total nitrogen removal from decahydroquinoline using various metal supported catalysts.

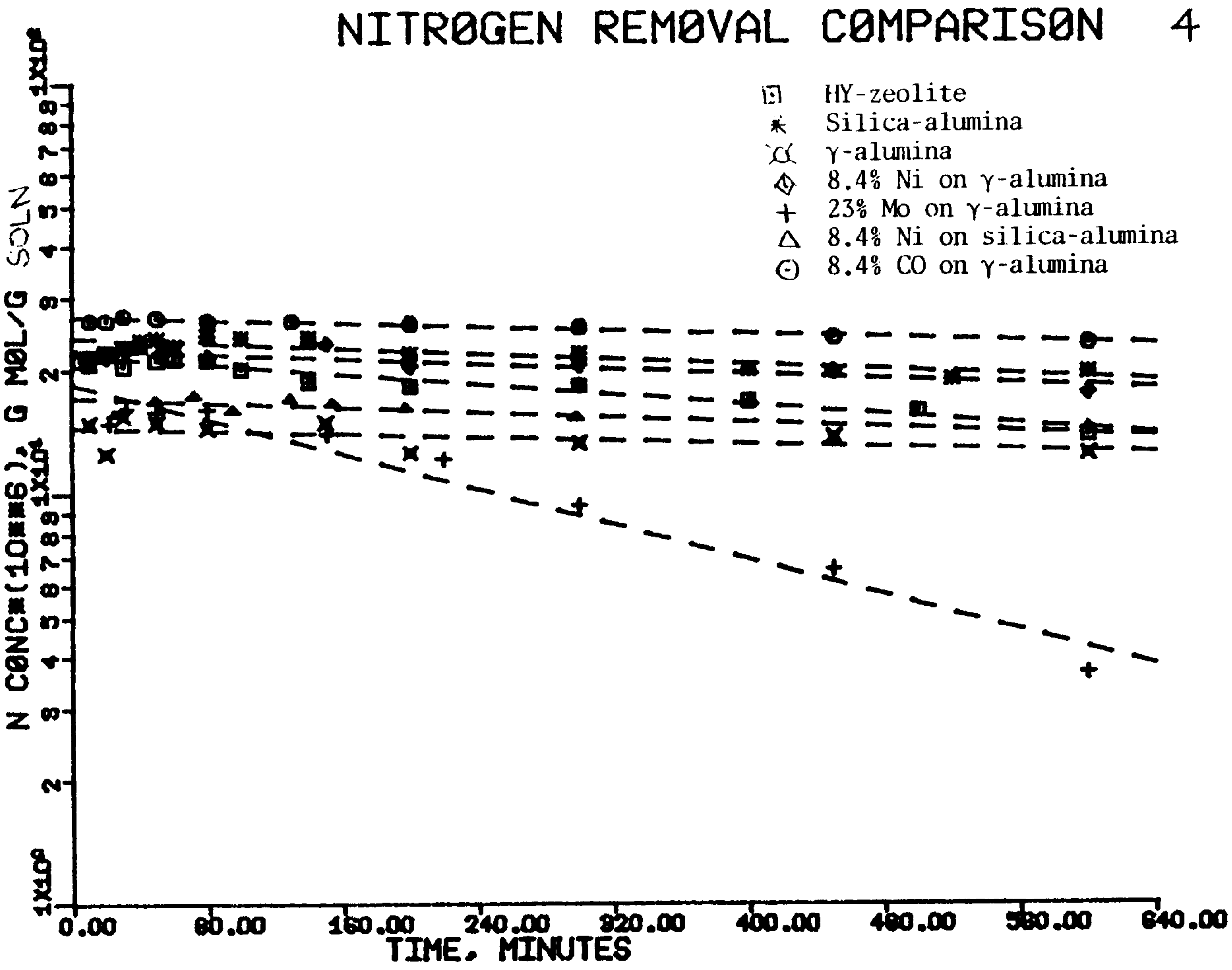

Figure 19: Total nitrogen removal from decahydroquinoline using various catalysts.

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.

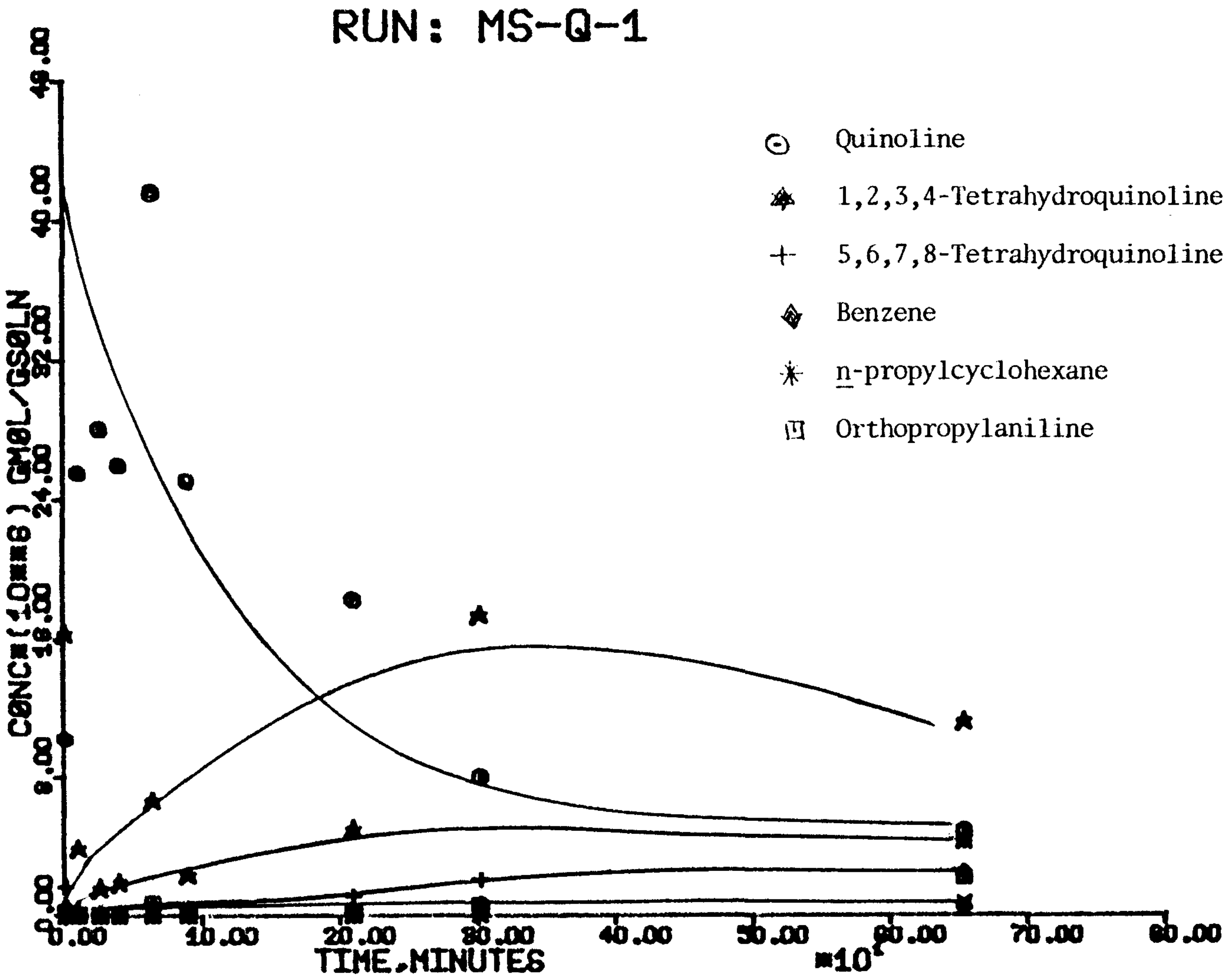

Figure 20: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/$AlBO_3$ at 350°C.

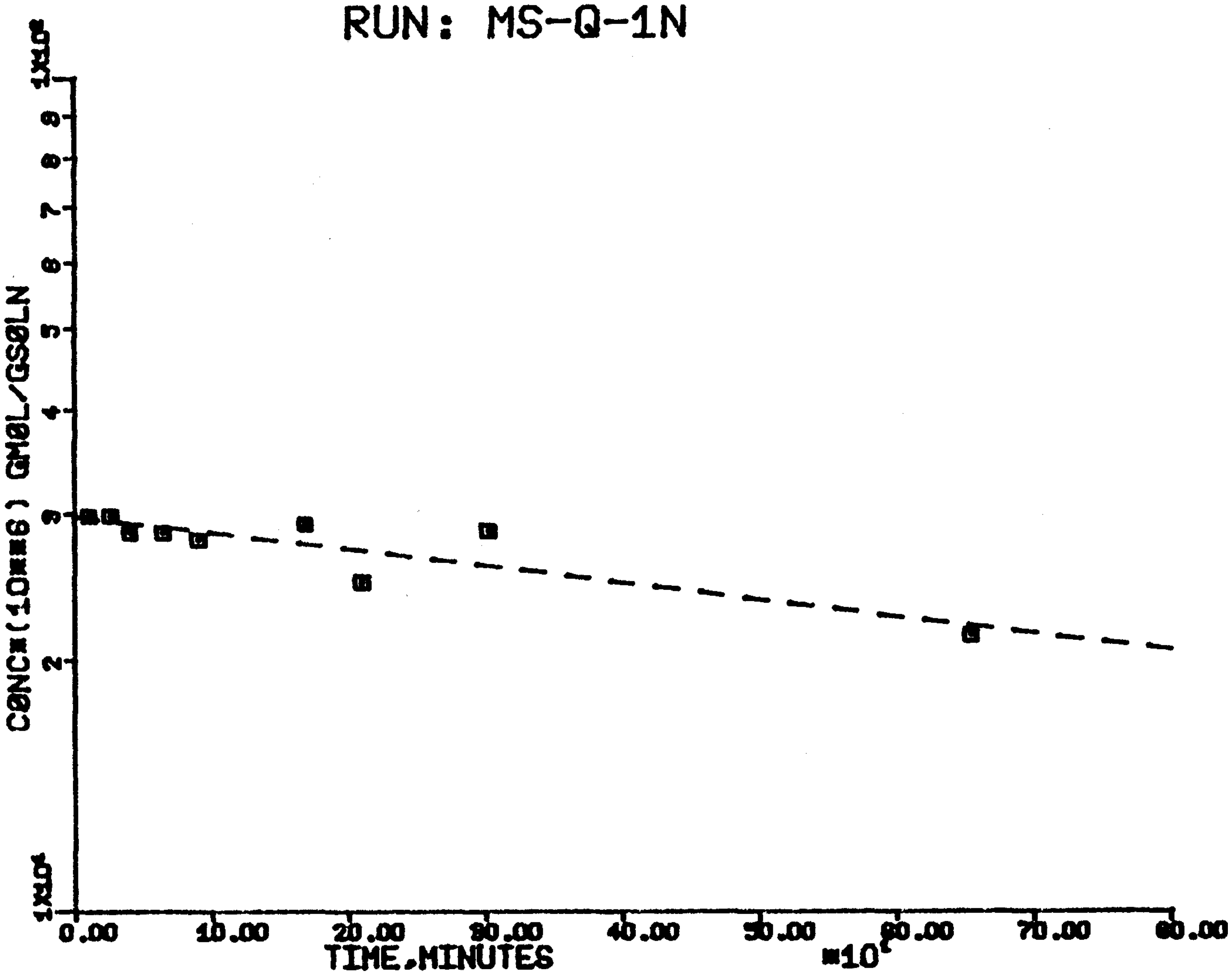

Figure 21: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 350°C.

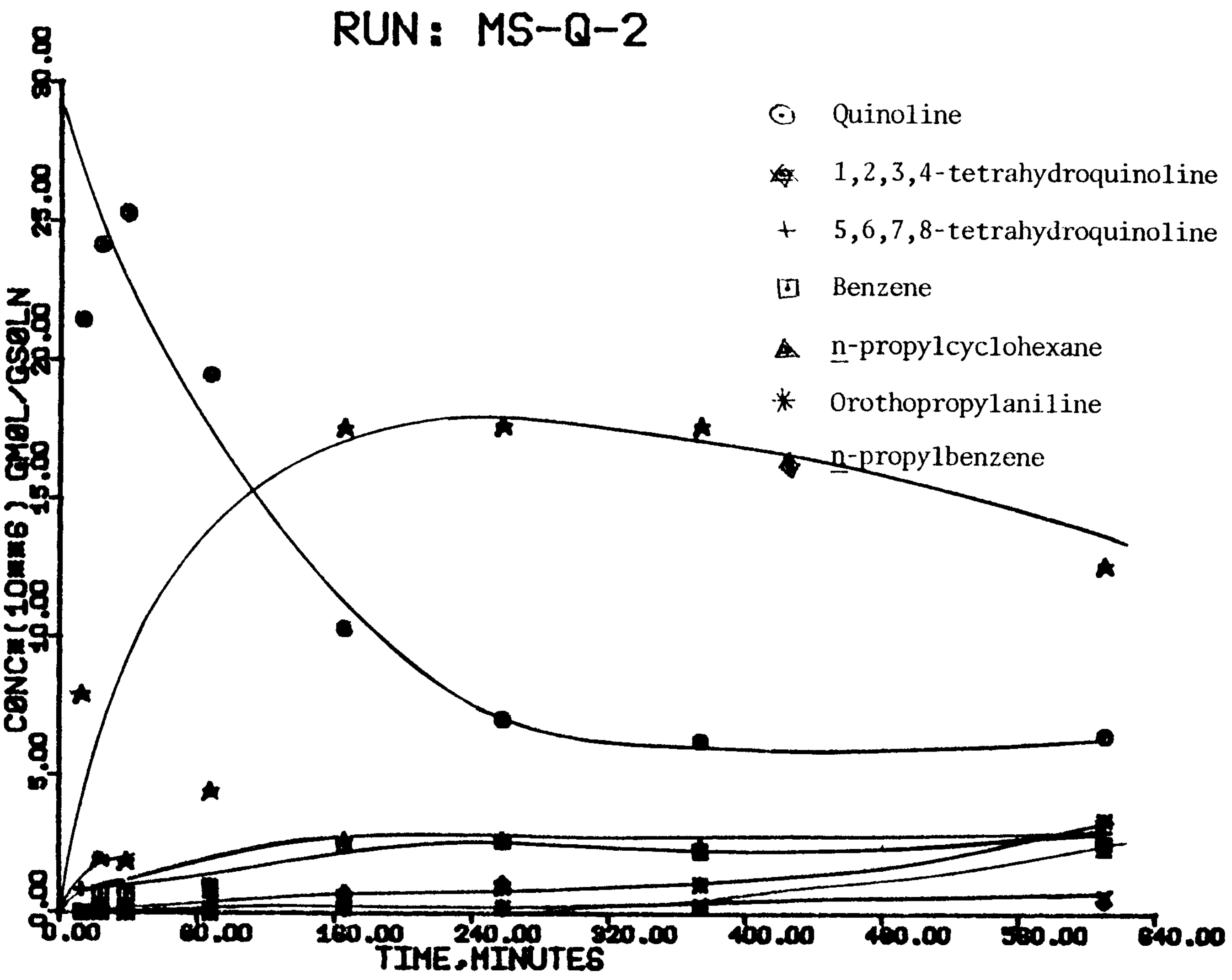

Figure 22: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt %/AlBO$_3$ at 357°C.

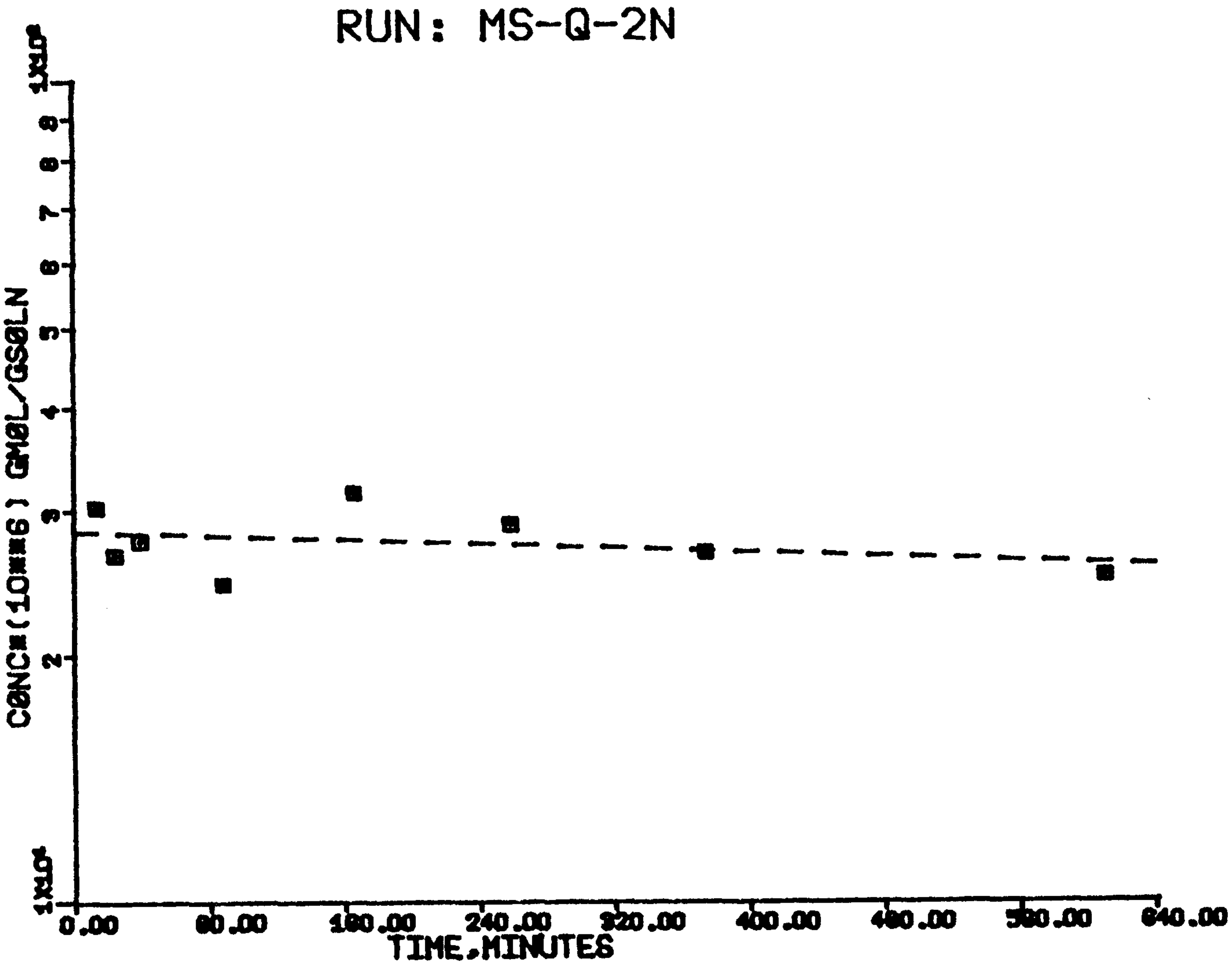

Figure 23: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 357°C.

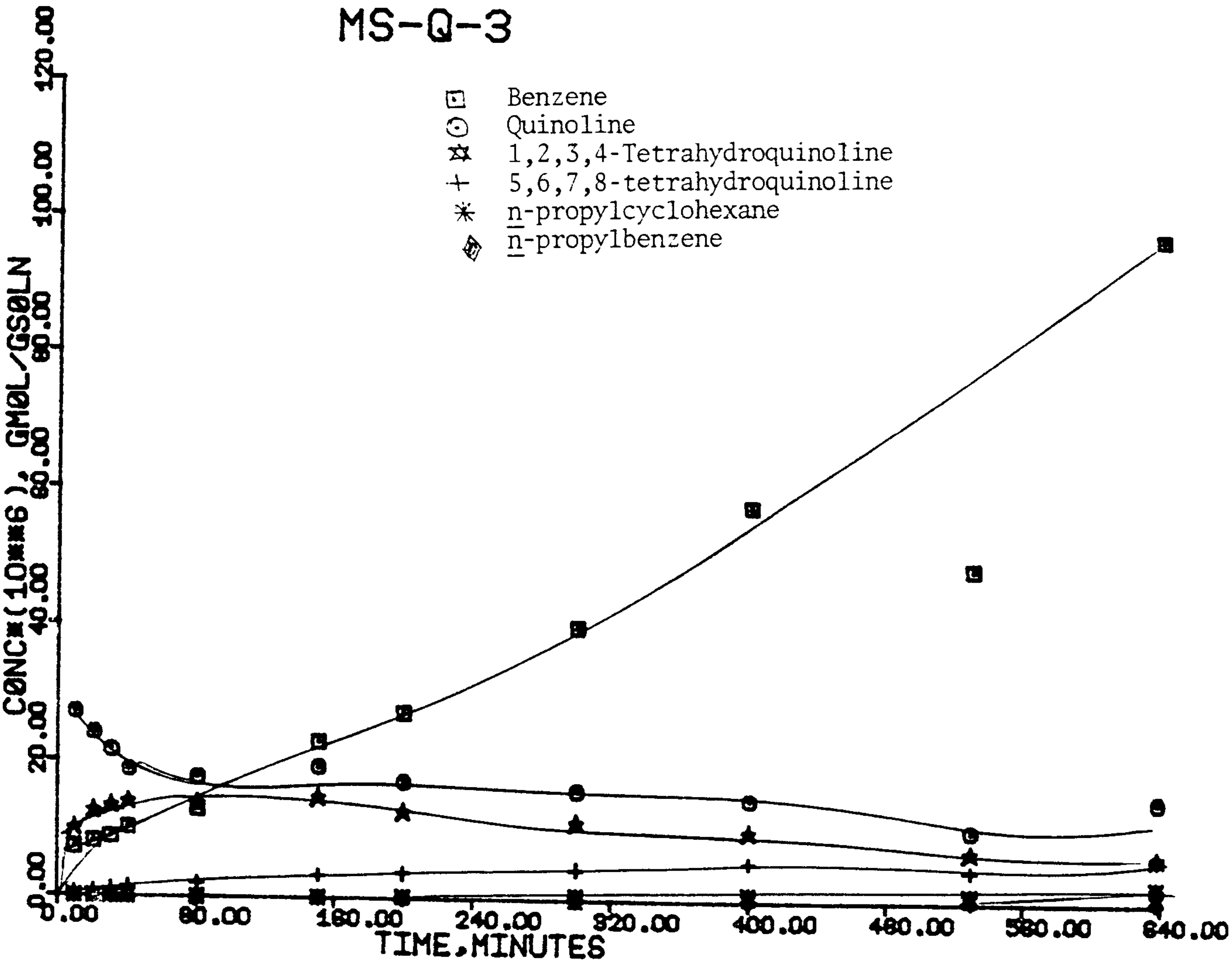

Figure 24: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/AlBO$_3$ at 380°C.

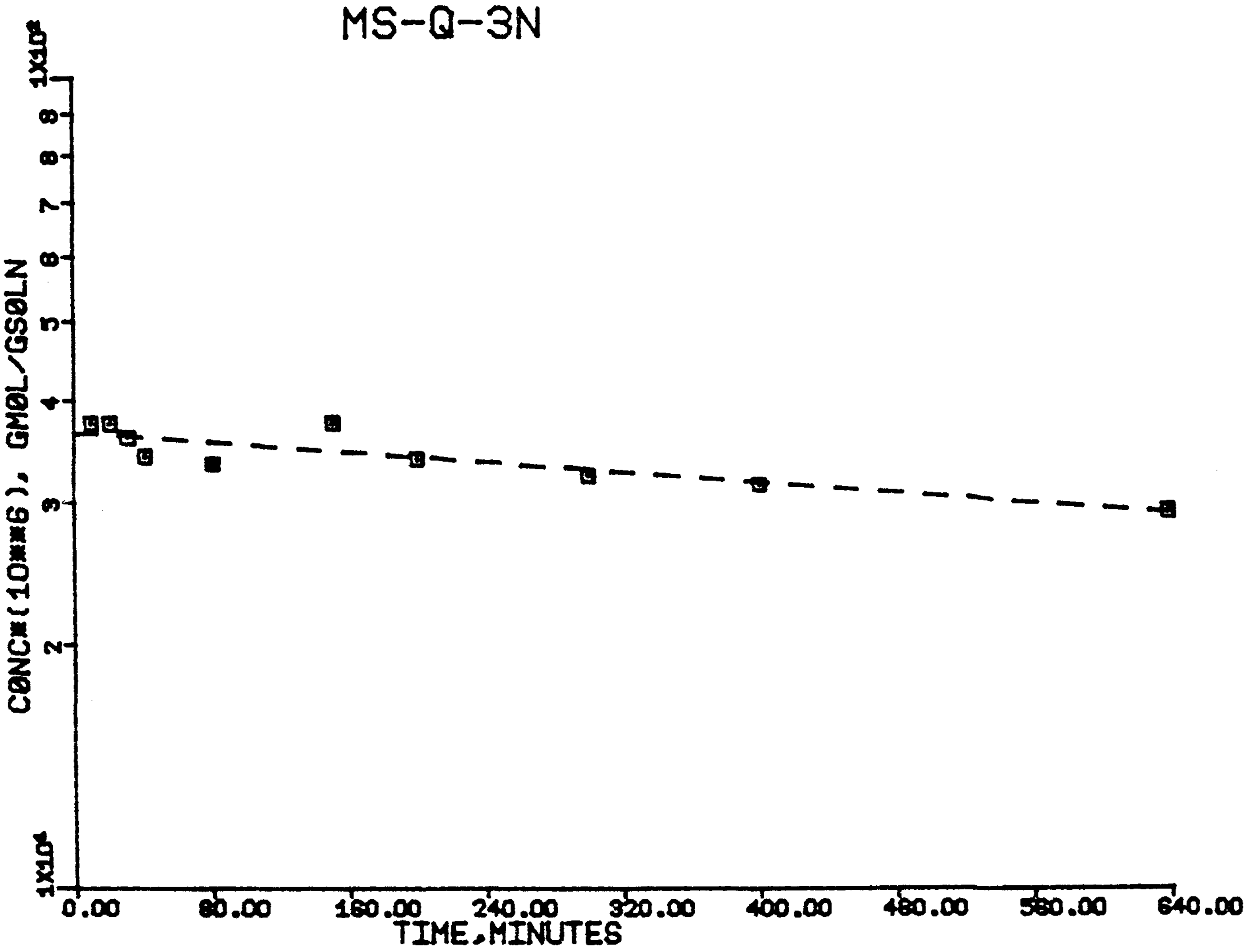

Figure 25: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 380°C.

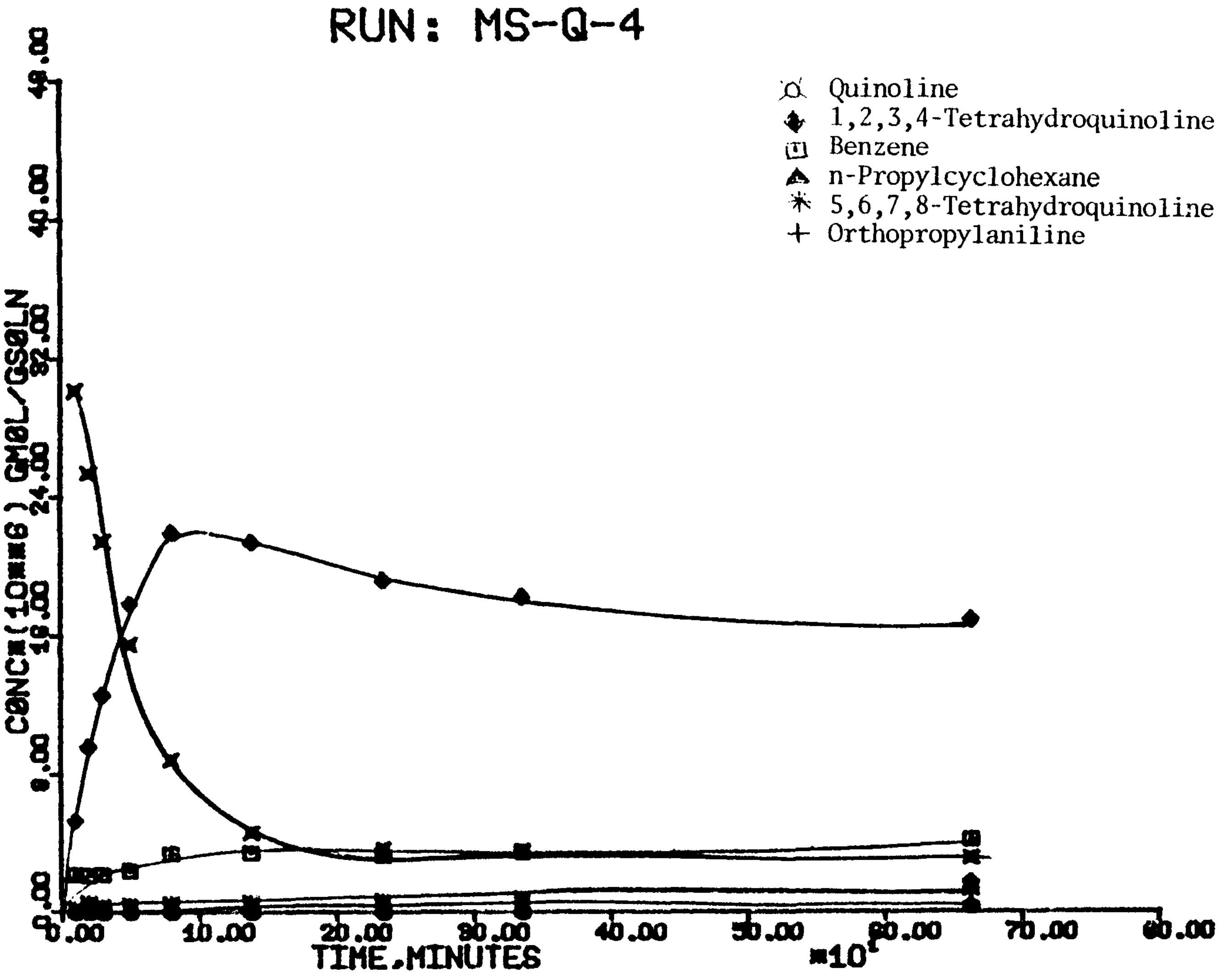

Figure 26: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % Ni/AlBO$_3$ at 350°C (glass liner used).

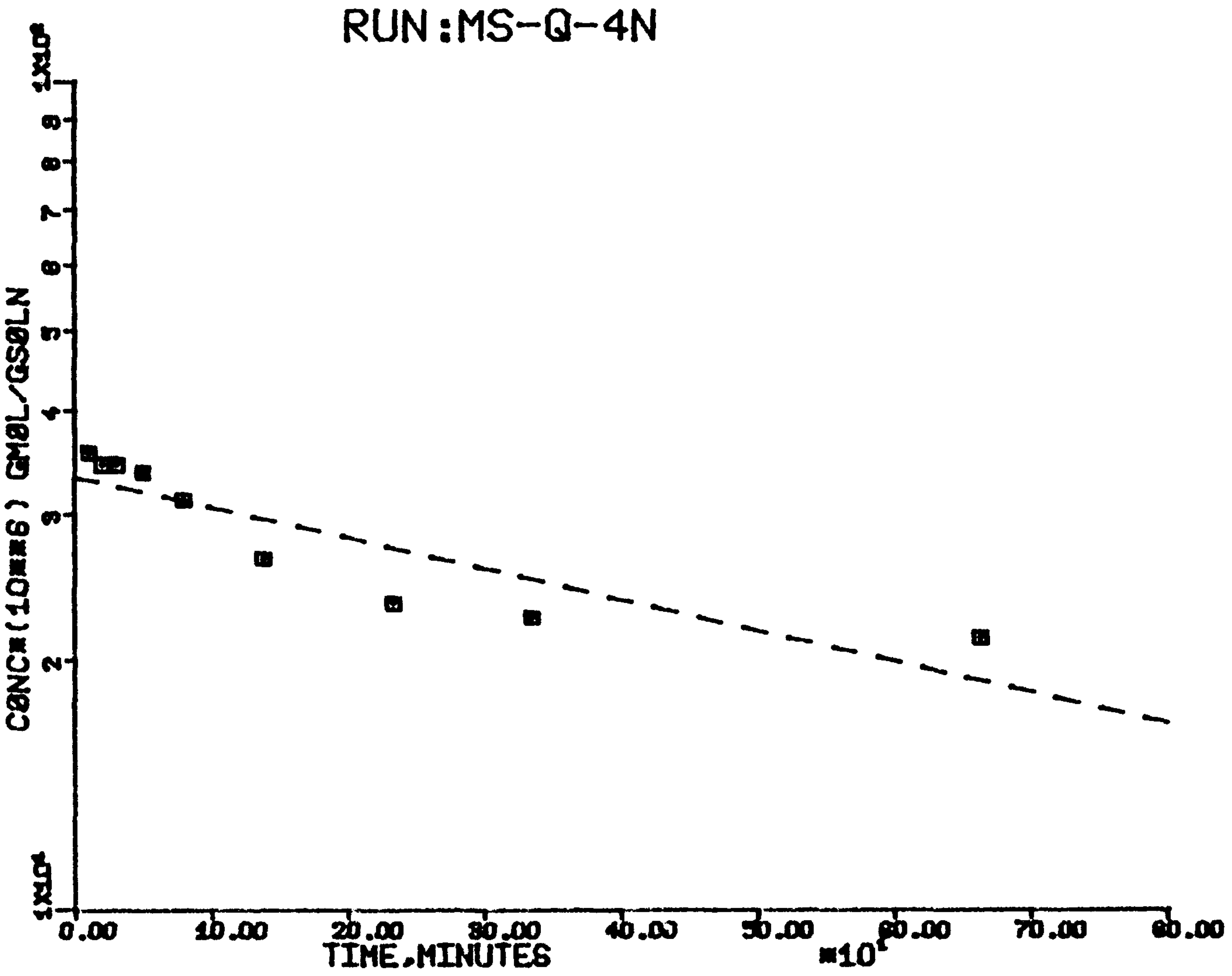

Figure 27: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$ at 350°C (glass liner used).

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

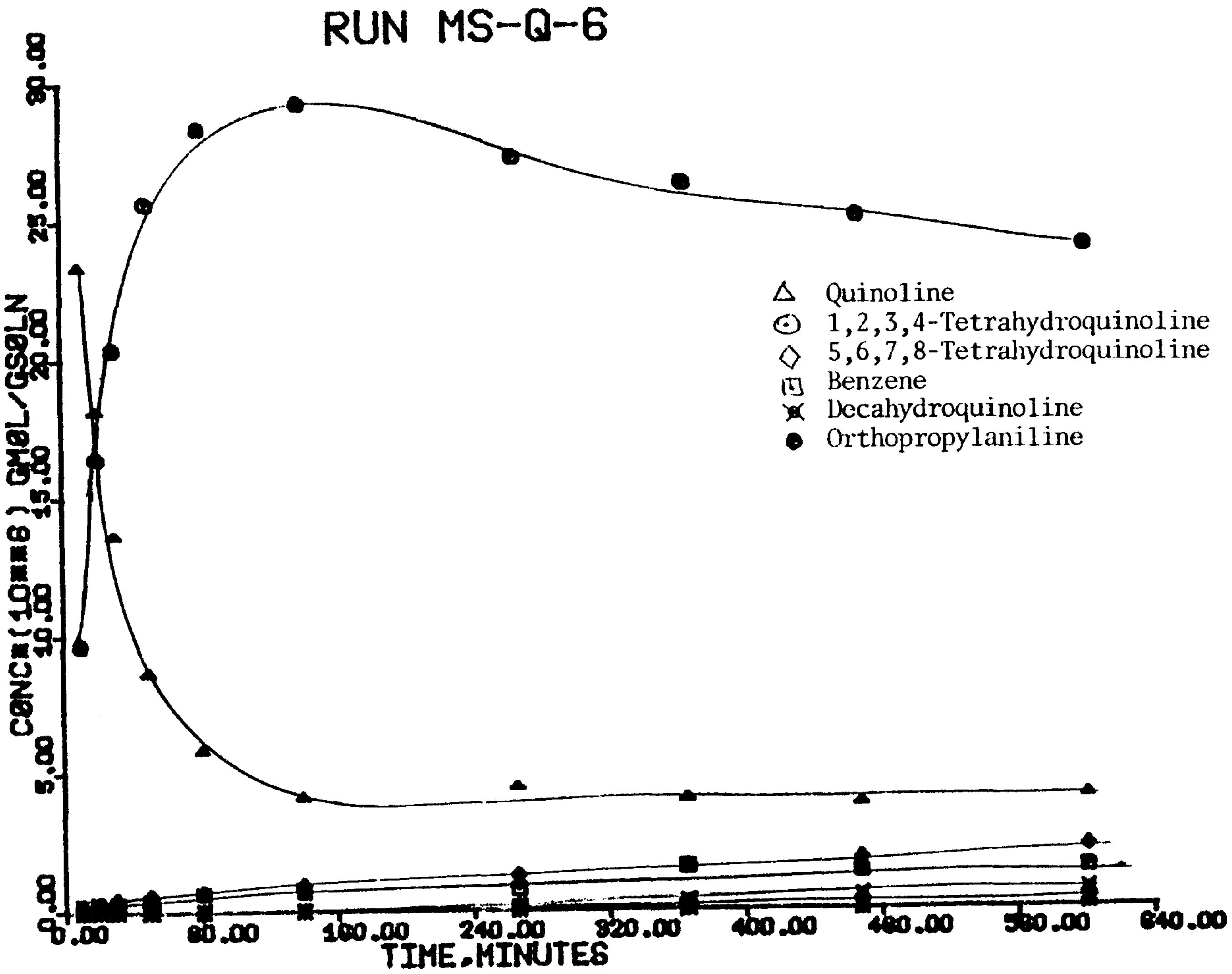

Figure 28: Concentration profiles for hydrodenitrogenation of quinoline using 4 wt % $Ni/AlBO_3 \cdot PO_4$.

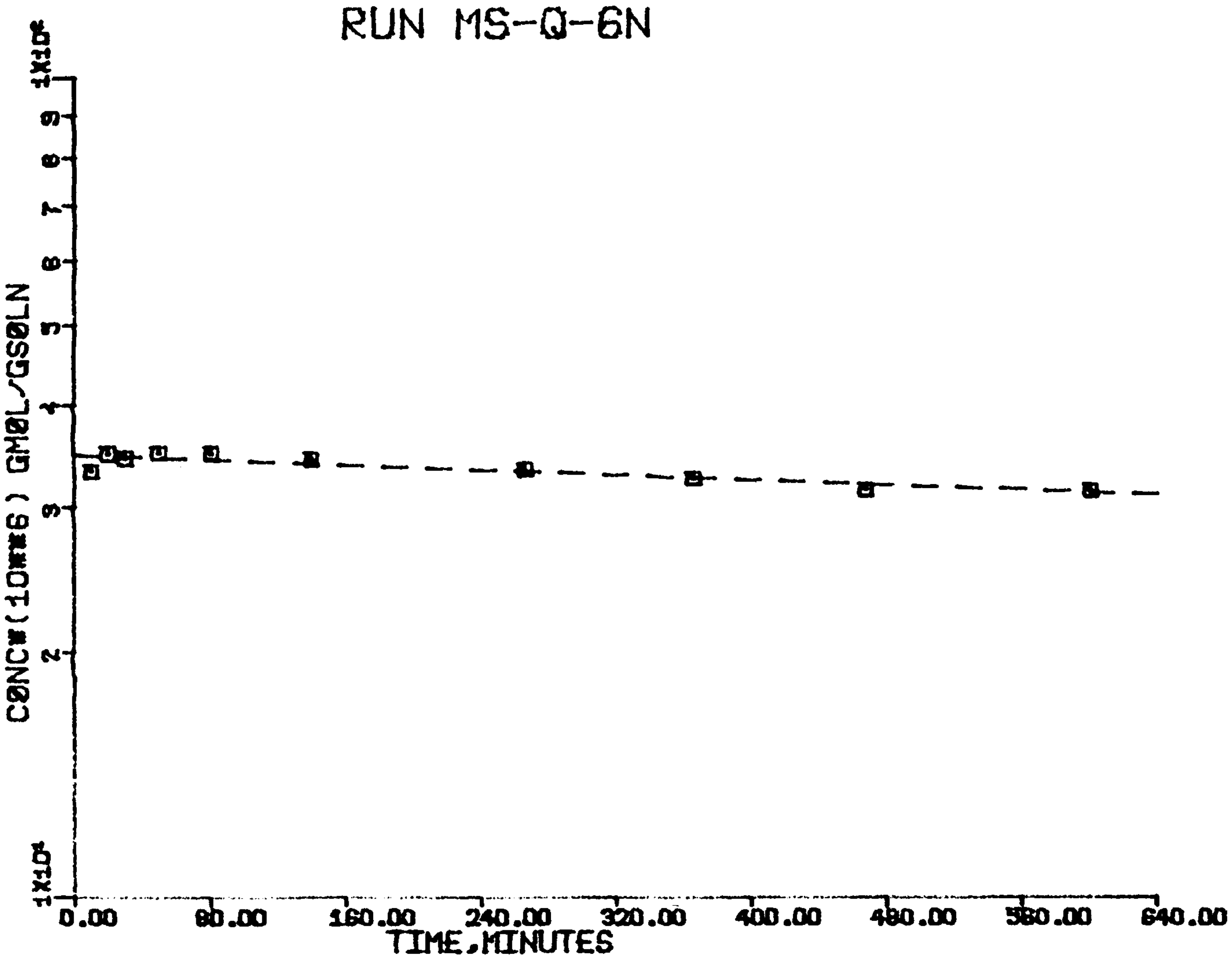

Figure 29: Total nitrogen removal from quinoline using 4 wt % Ni/AlBO$_3$·PO$_4$.

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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