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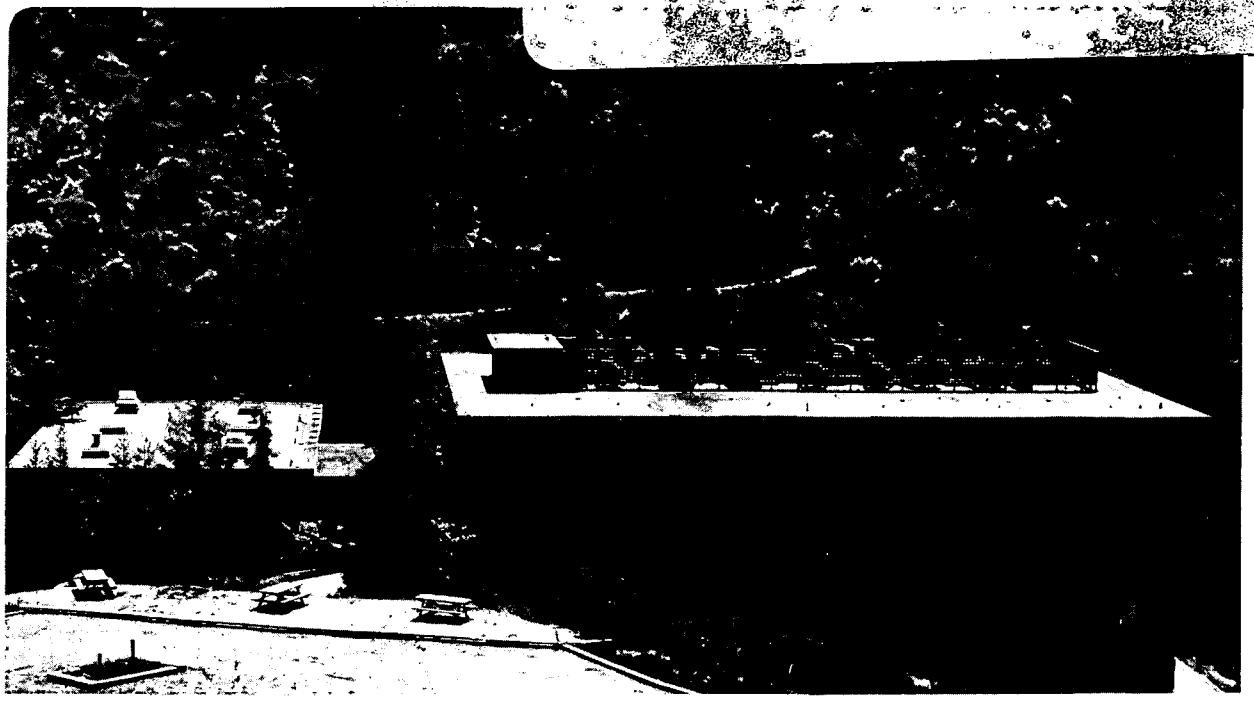
Materials & Molecular Research Division

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION
Quarterly Report, October 5 - December 31, 1985

H. Heinemann and R.H. Fish

December 1985

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Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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QUARTERLY REPORT

October 5, 1985 - December 31, 1985

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

Project 4048

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

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I. TECHNICAL PROGRAM FOR FY 1986

Hydrodenitrogenation - Novel Methods for Nitrogen Removal from Polynuclear, Nitrogen Containing, Heteroaromatic Model Coal Compounds

Having recently discovered that polynuclear heteroaromatic nitrogen compounds can be selectively reduced only at the nitrogen containing ring, we have now turned our attention towards the cleavage of the carbon nitrogen bonds in this reduced ring.

We are currently focusing on the use of highly loaded supported nickel catalysts for the hydrodenitrogenation of the selectively reduced aromatic, 1,2,3,4-tetrahydro-quinoline, as well as for the HDN of quinoline. The conditions we are investigating are mild, 1 atm hydrogen at 200°C to 300°C.

We need to characterize better all of the products being formed in these reactions, both liquids and gasses. We also need to determine the kinetics of the various reactions involved in HDN. We are currently planning to construct a new reactor system that will allow for on-line product sampling (both gas and liquid) and so facilitate the above studies.

Additionally, more information is needed about the morphology and structure/activity relations for the catalysts we are studying. We plan to obtain XPS, TEM, SEM and BET surface area data for various catalysts in used and unused states. Hopefully this data will allow us to explain more effectively the different HDN activities we have observed in various catalysts, and will enable us to make qualitatitive predictions about the HDN activity of as yet untried materials.

II. HIGHLIGHTS

1. Hydrodenitrogenation Using Nickel Catalysts:

Both 30wt% and 50wt% nickel on silica catalysts have been found to promote alkyl carbon-nitrogen bond cleavage in 1,2,3,4-tetrahydroquinoline to form various anilines and benzenes, under 1 atm of hydrogen. Side reactions include the formation of quinoline, 5,6,7,8-tetrahydroquinoline and indoles. Additionally the HDN of quinoline has been found to occur over the 50% Ni catalyst. In all cases the major gaseous product is methane, part of which is apparently being formed by the complete hydrogenolysis of the substrate. In experiments using the 50% Ni catalyst approximately 20% of the 1,2,3,4-tetrahydroquinoline and up to 70% of the quinoline fed into the reactor seems to undergo complete hydrogenolysis in this manner.

A scheme has been proposed incorporating the various products found in the HDN experiments into a reaction network. Cleavage of 1,2,3,4-tetrahydroquinoline to form 2-propylaniline is hypothesized to be the first step of hydrodenitrogenation. Competing with this are various hydrogenation, dehydrogenation and cyclization reactions.

2. XPS Study of the 50% Nickel Catalyst:

X-ray photoelectron spectra have been obtained for various used, unused and reduced (with H_2 gas) samples of the 50% nickel on silica catalyst. In all cases the predominant nickel species is nickel (II) oxide, not nickel metal.

Aluminum was also found to be present, indicating that the catalyst support is not pure silica but rather a silica-aluminate.

III. PROGRESS OF STUDIES

1. HDN Chemistry with Nickel on Silica Catalysts

The results of two series of hydrodenitrogenation investigations utilizing highly loaded nickel on silica catalysts (30wt% and 50wt% Ni) with 1,2,3,4-tetrahydroquinoline, 2-propylaniline and propylbenzene are shown in tables 1 and 2. Results for the reaction of quinoline over the 50% nickel catalyst appear in table 3. In all cases the reactions were carried out under one atmosphere of hydrogen, but the two catalysts were used at different temperatures and in differing amounts to compensate for the much higher activity of the 50% Ni on silica catalyst (United Catalyst C46-7-03, Tables 2,3).

30% Ni Catalyst Results:

Table 1 presents the results obtained with a 30% Ni on silica catalyst prepared in our laboratory. At 320°C 1,2,3,4-tetrahydroquinoline was converted into a variety of products, the principal ones being (in order of amount): quinoline (34.0%), aniline (27.5%), benzene (8.4%), 2-methylaniline (7.2%) and indole (6.5%). The aniline and benzene derivatives are formed via the cleavage of C-N bonds in 1,2,3,4-tetrahydroquinoline and are thus the desired products. Quinoline, formed through dehydrogenation of tetrahydroquinoline, and the side-product indole, are unwanted. At a higher temperature, 360°C, the relative amounts of quinoline and benzene increased while the relative amount of aniline derivatives in the product mixture decreased. Importantly, little reduction of the 5,6,7,8 ring of 1,2,3,4-tetrahydroquinoline was observed, indicating the higher selectivity of this system towards bond cleavage as compared to hydrogenation.

TABLE 1

Results Using 30% Ni/SiO_2 Catalyst[1]				
Substrate: Temperature: Products (mol%)[2]	1,2,3,4-THQ 320 °C	1,2,3,4-THQ 360 °C	2-Pr-aniline 320 °C	Pr-benzene 320 °C
Benzene	8.4%	12.2%	19.3%	trace
Toluene	1.4%	1.8%	2.9%	trace
Et-benzene	trace	trace	trace	0.0%
Pr-benzene	trace	trace	5.3%	0.0%
Aniline	27.5%	18.9%	9.3%	0.0%
2-Me-aniline	7.2%	2.7%	5.7%	0.0%
2-Et-aniline	trace	trace	trace	0.0%
2-Pr-aniline	trace	trace	37.0%	0.0%
Quinoline	34.0%	44.5%	0.0%	0.0%
5,6,7,8-THQ	trace	trace	0.0%	0.0%
1,2,3,4-THQ	5.3%	3.5%	5.8%	0.0%
Indole	6.5%	9.1%	trace	0.0%
2-Me-indole	2.1%	0.9%	2.3%	0.0%
Unidentified	7.6%	6.4%	12.4%	0.0%

1) CONDITIONS: 0.86 g catalyst, 0.14 cc/hr substrate, 30 cc/min H_2 at 1 atm. Products identified by GCMS and verified by comparison with standards (except 2-methylaniline and 2-ethylaniline).

2) Not included in the product normalization is the amount of gaseous products obtained. For a 340 °C 1,2,3,4-tetrahydroquinoline run the hydrocarbon gasses produced were analyzed by gas chromatography to give 99.5% CH_4, e.g., 0.1% C_2H_6, 0.4% C_3H_8, e.g., 0.02% C_4H_{10}. Ammonia was also produced.

2-Propylaniline, and propylbenzene, both plausible intermediates in the HDN of 1,2,3,4-tetrahydroquinoline, were also investigated as substrates. With propylaniline, in addition to the expected products of C-N bond cleavage (benzenes) and propyl chain cleavage (anilines) both 1,2,3,4-tetrahydroquinoline and 2-methylindole were formed. Apparently, a catalyzed or free radical mechanism may lead to ring closure of propylaniline to form these two latter products. Since ring opening of tetrahydroquinoline to form propylaniline may be the first step in the HDN of tetrahydroquinoline, the potential reversibility of this ring opening is of great interest.

When propylbenzene was used as a substrate virtually no condensible products were formed, with only a trace of benzene and toluene observed. The very high activity of the catalyst towards this material is probably a result of the lack of any basic nitrogen compounds (quinoline or aniline derivatives) in this reaction. These materials are known to be strong catalyst poisons, and in this particular case when they are present they apparently moderate the activity of the catalyst, preventing it from completely reducing and/or cleaving substrates. In the absence of these nitrogen bases complete hydrogenolysis of the substrate (to methane, see below) or conversion to coke must occur, resulting in no condensible products being observed.

Some of the gas generated during the HDN of 1,2,3,4-tetrahydroquinoline at 320°C was trapped in a water trough (eliminating ammonia) and analyzed by gas chromatography. It was found to be almost entirely methane (99.5%), with traces of ethane, propane and butane. Much of this methane is presumably formed by the partial or complete hydrogenolysis of only the saturated 1,2,3,4 ring in tetrahydroquinoline. Some may as well result from the entire hydrogenolysis of tetrahydroquinoline, the results of a mass balance with the 50% Ni catalyst (see below)

indicate that this total hydrogenolysis may be an important reaction.

50% Ni Catalyst Results:

The results for the 50% nickel catalyst, in table 2, are quite similar to the those discussed above. The primary difference between the two catalysts is the degree of activity. At temperatures 100°C lower, and with one third as much catalyst, the 50% Ni material exhibited the same overall conversion of 1,2,3,4-tetrahydroquinoline as the 30% catalyst. Additionally, the 50% Ni catalyst was more efficient in catalysing C-N bond cleavage relative to dehydrogenation to form quinoline.

The major products formed from the HDN of tetrahydroquinoline using this 50% Ni catalyst at 250°C were (in order of amount) : 2-methylaniline (14.3%), quinoline (14.3%), 5,6,7,8-THQ (14.1%), aniline (9.4%), benzene (9.2%), 2-ethylaniline (8.6%). Relative to the 30% nickel catalyst more aniline and benzene derivatives and less quinoline are produced by this catalyst. Combined with the higher overall activity of this catalyst, this result indicates that the 50% Ni material is more suitable than the 30% Ni material for the HDN of 1,2,3,4-tetrahydroquinoline. This situation is improved further at the slightly higher reaction temperature of 260°C, with the relative amounts of benzenes and anilines increasing, and the amount of quinoline and 5,6,7,8-tetrahydroquinoline decreasing.

Less cyclization was seen when 2-propylaniline was reacted over the 50% Ni catalyst than in the 30% Ni case. Only traces of 1,2,3,4-tetrahydroquinoline and indoles were produced. The primary products were benzene and propylbenzene, with surprisingly small amounts of toluene and ethylbenzene being formed. Aniline derivatives were also formed in this reaction. As with the 30% Ni catalyst, reaction of propylbenzene over the 50% Ni

TABLE 2

Results Using 50% Ni/SiO_2 Catalyst[1] (United Catalyst C46-7-03)				
Substrate: Temperature: Products (mol%)[2]	1,2,3,4-THQ 250 °C	1,2,3,4-THQ 260 °C	2-Pr-aniline 250 °C	Pr-benzene 250 °C
Benzene	9.2%	15.8%	29.9%	trace
Toluene	1.8%	2.8%	4.3%	trace
Et-benzene	trace	trace	trace	0.0%
Pr-benzene	trace	trace	20.8%	0.0%
Aniline	9.4%	16.7%	6.0%	0.0%
2-Me-aniline	14.3%	20.0%	5.4%	0.0%
2-Et-aniline	8.6%	8.6%	1.4%	0.0%
2-Pr-aniline	2.0%	1.6%	21.5%	0.0%
Quinoline	14.3%	9.8%	0.0%	0.0%
5,6,7,8-THQ	14.1%	5.9%	0.0%	0.0%
1,2,3,4-THQ	4.7%	1.6%	trace	0.0%
Indole	2.7%	3.1%	trace	0.0%
2-Me-indole	5.0%	4.5%	trace	0.0%
Unidentified	13.9%	9.6%	10.7%	0.0%

1) CONDITIONS: 0.26 g catalyst, 0.14 cc/hr substrate, 30 cc/min H_2 at 1 atm. Products identified by GCMS and verified by comparison with standards (except 2-methylaniline and 2-ethylaniline).

2) Not included in the product normalization is the amount of gaseous products obtained. For the 1,2,3,4-tetrahydroquinoline runs the hydrocarbon gasses produced were analyzed by gas chromatography to give at least 99.8% CH_4, other hydrocarbons (if present) were below the detection threshold of the instrument. Ammonia was also produced.

catalyst provided only trace amounts of benzene and toluene as products. In the absence of the moderating effects of nitrogen bases, the catalyst seems to be extremely active towards total hydrogenolysis.

An analysis of the gas formed during the HDN of tetrahydroquinoline with the 50% Ni catalyst showed that it was almost entirely methane, at least 99.8%. Other gasses, if present, were below the detection limit of the GC. A mass balance on the liquid products revealed that about 70% of the tetrahydroquinoline is converted to the identified products in the table, and about 10% of the reactant is converted to unidentified liquids. The 20% that remains cannot be accounted for in the condensible products and presumably is converted to methane (although some may be converted to coke as well). Our apparatus does not trap all of the gasses formed, so a mass balance on the non-condensible products could not be performed.

Additional experiments were done with the 50% nickel on silica catalyst in which quinoline was used as the substrate. The results of these runs, at three different temperatures, are in table 3. In this case the nitrogen-containing 1,2,3,4 ring in the quinoline must presumably be reduced prior to any cleavage of C-N bonds. At the highest temperature, 280°C, the overall HDN of quinoline was more efficient than that of 1,2,3,4-tetrahydroquinoline, while at 250°C less HDN of quinoline took place. However, for all three of these runs mass balances reveal that a considerable amount of the quinoline is converted to non-condensible products, ranging from approximately 50% at 250°C to 70% at 280°C. This is clearly not a desired reaction, and in this regard the results with tetrahydroquinoline, in which only 20% was "lost" in this way, are superior to those with quinoline.

General Hydrodenitrogenation Scheme:

Figure 4 is a schematic representation of the kinds

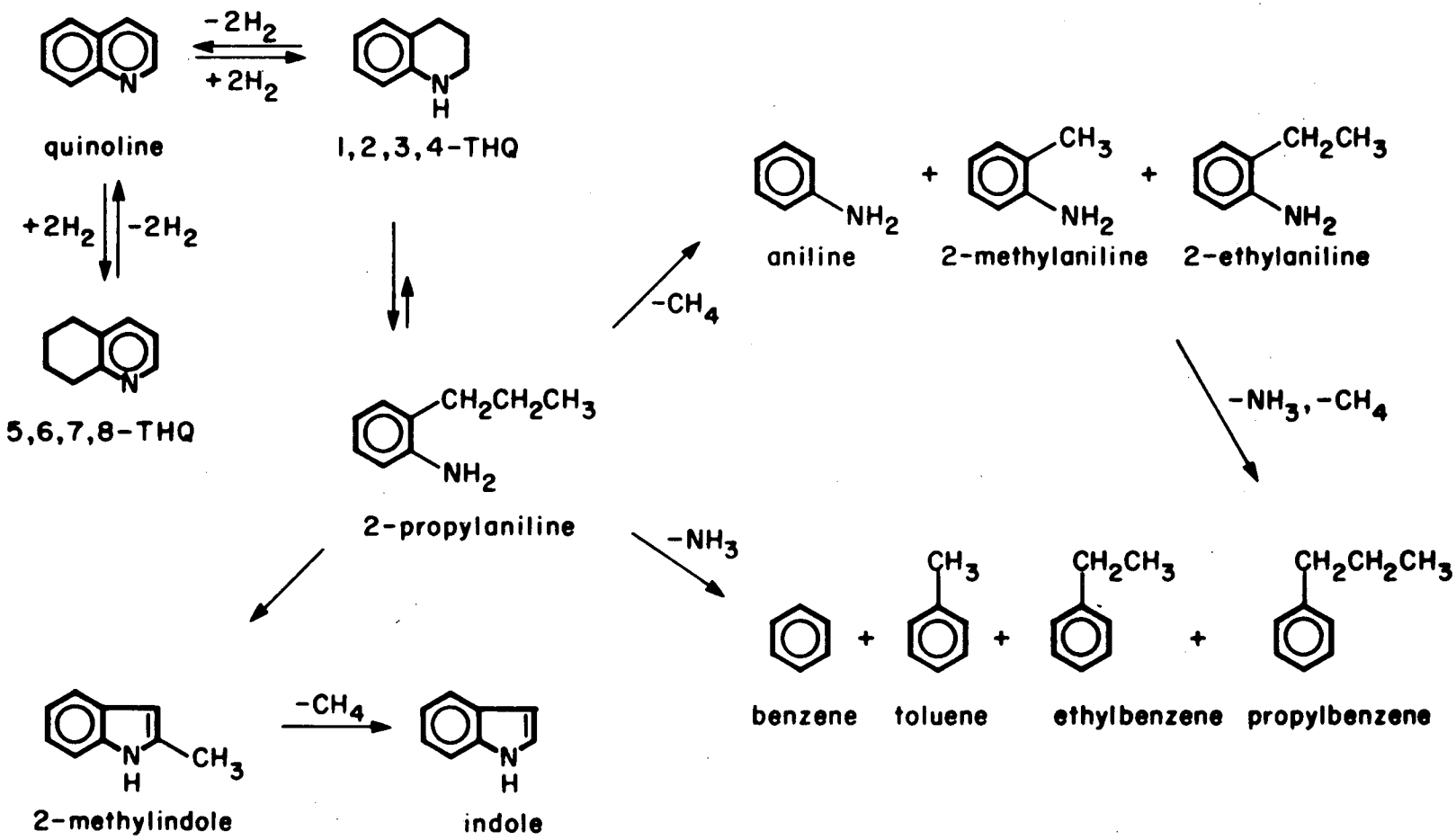
TABLE 3

Results Using 50% Ni/SiO_2 Catalyst[1]			
Substrate Temperature Products (mol%)	Quinoline 250°C	Quinoline 260°C	Quinoline 280°C
Benzene	0.6	3.2	21
Toluene	0.7	1.6	5
Et-benzene	trace	trace	trace
Pr-benzene	0.1	0.24	trace
Aniline	6	12	20
2-Me-aniline	12	16	15
2-Et-aniline	8	6.5	2.7
2-Pr-aniline	2	1.2	trace
Quinoline	26	26	19
5,6,7,8-THQ	15	7	1.2
1,2,3,4-THQ	9	5	1
Indole	1.5	2	1.6
2-Me-indole	5	5	3
Unidentified	15	14	10.5

1) CONDITIONS: 0.26 g catalyst, 0.14 cc/hr substrate, 30 cc/min H_2 at 1 atm. Products identified by GCMS and verified by comparision with standards (except 2-methylaniline and 2-ethylaniline).

FIGURE 4

Proposed Reaction Network for HDN Using Supported Nickel Catalysts



of reactions we propose to account for the products observed in the various reactions described above. 1,2,3,4-Tetrahydroquinoline may either be ring opened to form 2-propylaniline or dehydrogenated/hydrogenated to form quinoline and 5,6,7,8-tetrahydroquinoline.

2-propylaniline may undergo cyclizations to form indoles, or reform tetrahydroquinoline. Instead, propylaniline can have the nitrogen atom cleaved off to form various derivatives of benzene, or have carbon atoms cleaved off of the propyl group to form other anilines. These anilines may in turn be converted to benzene derivatives.

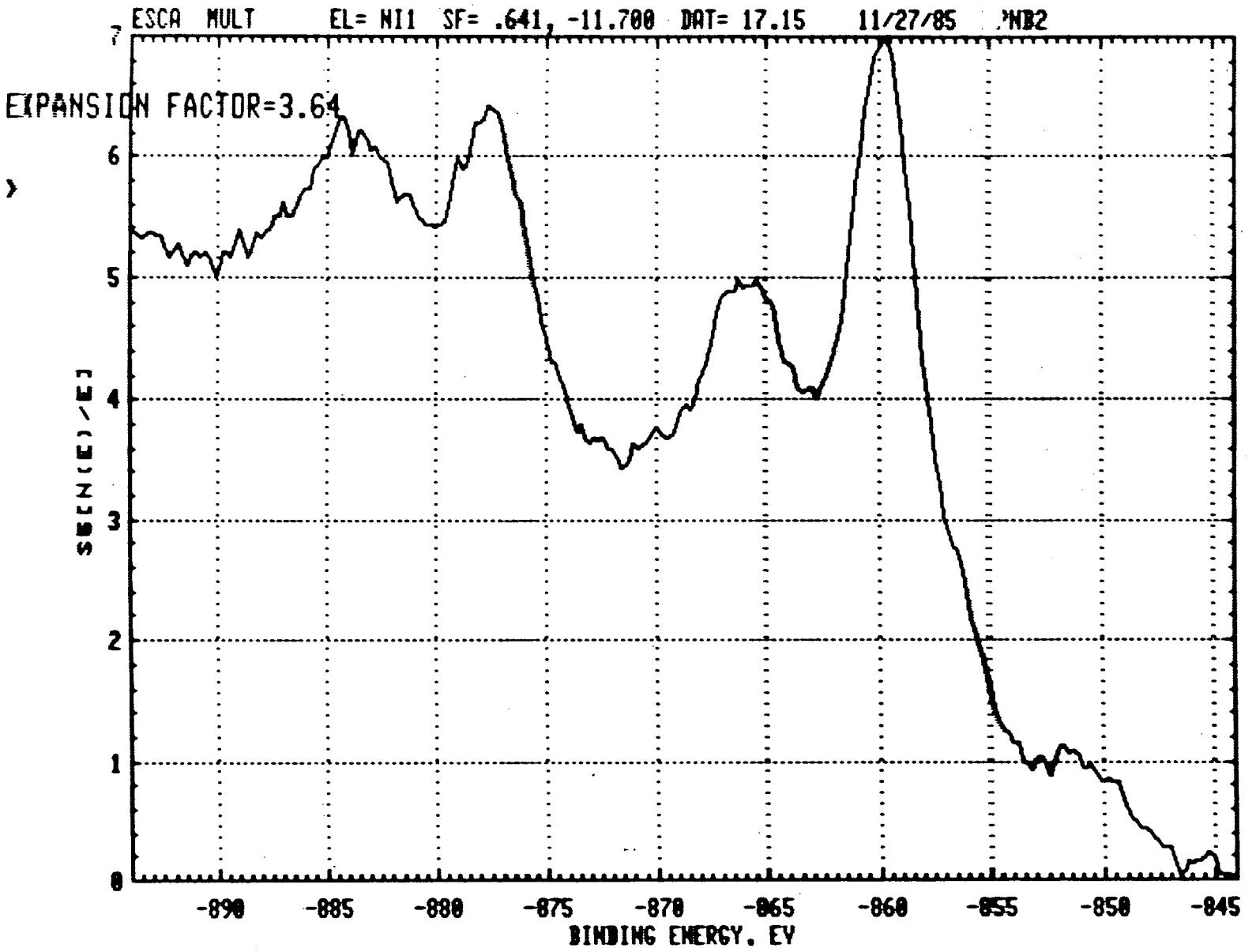
The path that leads from quinoline to 1,2,3,4-tetrahydroquinoline to propylaniline and finally to the benzenes and anilines is the desired course of hydrodenitrogenation. The other paths shown, and the partial reversibility of the above path, are reactions that we wish to avoid. Understanding further the nature of these catalysts will hopefully allow us to control better these different types of reactions.

2. XPS Study of 50% Nickel on Silica Catalyst

Three samples of the 50% Ni catalyst, used, unused and reduced under hydrogen but unused otherwise, were all examined by X-ray photoelectron spectroscopy. A typical XPS spectrum is shown in figure 5. This spectra is for a used sample of catalyst, showing the nickel $2P_{3/2,1/2}$ lines. The spectra obtained for all of the other samples were essentially identical to this spectrum.

In all cases, the predominant nickel species present appears to be nickel (II) oxide, not nickel metal. This is a significant finding, especially since our 30% nickel catalyst had in previous examinations appeared to be predominantly nickel (0). In fact, virtually no nickel (0)

FIGURE 5



XPS Spectrum of Ni $2P_{3/2,1/2}$ Lines in Used 50% Ni/SiO_2 Catalyst

was found in the 50% catalyst. The presence of aluminum in the support was also indicated, indicating that the support is in fact a mixture of silica and alumina, not pure silica.

The differences we see between the two catalysts may thus in part be explained by this difference in the state of the nickel on the surface of the catalyst. We are planning further morphological examination of both nickel catalysts in an effort to resolve this issue.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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