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Quarterly Report: January 1, 1986-March 31, 1986

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QUARTERLY REPORT

January 1, 1986 - March 31, 1986

CHEMISTRY AND MORPHOLOGY OF COAL LIQUEFACTION

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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-tetrahydroquinoline, 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 qualitative predictions about the HDN activity of a yet untried materials.

II. HIGHLIGHTS

1. Studies with the 50% nickel oxide catalyst clearly show that 1,2,3,4-tetrahydroquinoline(THQ) provides approximately 20% more liquid product than does quinoline. Thus a first step selective hydrogenation to 1,2,3,4-THQ would enhance the overall HDN reaction to provide a more substantial conversion to substituted benzene and aniline derivatives.

2. The dramatic effect of the nitrogen atom is to inhibit aromatic ring hydrogenation and, to some extent, carbon-carbon bond hydrogenolysis reactivity. This is shown with proplybenzene as the substrate, where only methane gas is produced in the HDN reaction with the 50% nickel oxide catalyst.

3. The HDN reaction of cyclohexylamine only provides benzene and methane, with no apparent formation of cyclohexane. Thus dehydrogenation is an important side reaction.

III. PROGRESS OF STUDIES

1. HDN Chemistry of 1,2,3,4-Tetrahydroquinoline, 2-propylaniline, quinoline, cyclohexylamine and propylbenzene

We have continued our HDN chemistry experiments to verify the amount of methane being formed. We have rerun several of our substrates to substantiate the formation of the products and by using an internal standard (GC) we were able to ascertain, by difference, the amount of methane formed.

Table 1 compares the results of our HDN chemistry experiments with 1,2,3,4-THQ, 2-propylaniline and propylbenzene and shows that 22% of the 1,2,3,4-THQ is converted to methane, while only 8% methane was formed from 2-propylaniline. Dramatically, the non-nitrogen compound, propylbenzene, is entirely converted to methane. Thus, the nitrogen atom has a profound effect on the course of the HDN reaction.

Interestingly, we also ran quinoline (Table 2), the dehydrogenated product of 1,2,3,4-THQ, and found that it produced twice as much methane as 1,2,3,4-THQ. This suggests that prior selective hydrogenation could enhance the overall HDN reaction (with the 50% nickel oxide catalyst). Cyclohexylamine was also run under our HDN reaction condition to evaluate the fate of a possible cyclohexyl product. To our surprise, cyclohexylamine gives mostly benzene and methane, but no cyclohexane was detected by GC-EIMS analysis. Thus hydrogenolysis and dehydrogenation are important reactions for the substrates studied.

2. Surface Morphology Studies of the 50% Nickel Oxide Catalyst

We were able to obtain transmission electron micrographs, electron diffraction and x-ray diffraction patterns of the 50% nickel oxide catalyst and they showed three phases of nickel, with the surface a nickel oxide and possibly a nickel aluminate surrounding a Ni(0) inner phase.

From these preliminary surface analysis results, we can say definitively that nickel (2+) or higher valent nickel oxide species are responsible for the observed HDN chemistry, but that nickel (0) is not.

IV. PRESENTED AND SUBMITTED PAPERS

We recently (March 20, 1986) presented this study at the Spring California Catalysis Society meeting that was held at Chevron Research Corporation, Richmond, CA.

In addition, a paper of the same content was also submitted to the Journal of Catalysis: "Hydrodenitrogenation Chemistry, 1: Cleavage of Alkylcarbon-Nitrogen Bonds, Methane and Ammonia Formation in the HDN Reaction of 1,2,3,4-Tetrahydroquinoline with a Nickel Oxide Catalyst Supported on Silica", R.H. Fish, A.D. Thormodsen, R.S. Moore, D.L. Petty and H. Heinemann, J. Catal. 1986 (submitted).

TABLE 1

HDN chemistry of 1,2,3,4-tetrahydroquinoline, 2-propylaniline and propylbenzene with the 50% nickel oxide catalyst[a,b]

Products (mmol%)	1,2,3,4-Tetrahydroquinoline	2-propylaniline	propylbenzene
benzene	4.9	15.9	trace
toluene	0.9	2.1	-
ethylbenzene	0.4	0.4	-
propylbenzene	trace	14.4	-
aniline	4.6	2.6	-
2-methylaniline	8.5	5.3	-
2-ethylaniline	5.8	1.8	-
2-propylaniline	1.5	30.6	-
quinoline	21	-	-
5,6,7,8-tetrahydroquinoline	11	-	-
1,2,3,4-tetrahydroquinoline	7.3	0.4	-
indole	1.2	-	-
2-methylindole	3.6	0.4	-
unidentified products[c]	7.6	18.0	-
methane[d]	21.7	8.1	100

a) Quanitation and identification of the products was accomplished by capillary column gas chromatography with an internal standard and by GC-EIMS. These numbers are the average of three runs and are based on the mmoles of THQ reacted.

b) Reaction conditions are 250°C, 30 ml/min hydrogen gas flow at 1 atm. The 1,2,3,4-tetrahydroquinoline used was 3.3 mmol, 2-propylaniline 2.84 mmol and propylbenzene 2.84 mmol. The reaction time was 3hr.

c) While total identification of these products was not established (GC-EIMS), we did identify several substituted pyridine deriviatives such as 2,3-dimethylpyridine.

TABLE 2

HDN Chemistry of Quinoline and Cyclohexyl Amine[a]

Products (mmol%)	Quinoline	Cyclohexylamine
benzene	6.1	36
toluene	1.3	0.2
ethylbenzene	0.4	0.8
propylbenzene	0.1	-
		0.1 (cyclohexylamine)
aniline	4.5	3.0
2-methylaniline	6.1	-
2-ethylaniline	2.2	-
2-propylaniline	0.4	-
quinoline	24	-
5,6,7,8-tetrahydroquinoline	3.1	-
1,2,3,4-tetrahydroquinoline	2.7	-
indole	1.5	-
methylindole	1.5	-
unidentified	6.70	2.9
methane	39	57

a) 250 °C, 30 ml/min H_2

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