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CONTROL OF CATALYTIC HYDROTREATING SELECTIVITY
WITH AMMONIA

Final Technical Report

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November 1993

Prepared for the
U.S. Department of Energy
under
Grant No. DE-FG22-89PC89775

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Executive Summary

The purpose of this study was to explore the possibility of control of product selectivity in the hydroprocessing of coal liquids and related substances by adding small amounts of ammonia. Several sets of selected model compounds were used under representative industrial reaction conditions (6.9 MPa of hydrogen pressure, 300-360°C) utilizing a sulfided commercial NiMo/Al₂O₃ catalyst in a vapor-phase plug flow reactor. Emphasis was directed to control of hydrogenation and hydrocracking reactions that may occur during or subsequent to hydrodenitrogenation reactions. The study consisted of five parts as outlined below and in the Table of Contents.

Quinoline was used in this study and in many others as representative of heterocyclic N compounds found in coal liquids. Coal liquids also contain hydroxy pyridines, but by studies with 8-OH quinoline, a representative compound (Part I), we demonstrated that the OH group was rapidly removed at the beginning of reaction to form quinoline, which reacted in the same manner as quinoline fed as such. This finding extends the usefulness of using quinoline as a model N-compound.

In Part II we showed that in a mixture of naphthalene and quinoline, with the addition of ammonia there is an operating region in which complete HDN of quinoline can be achieved, but with greater conversion of naphthalene to tetralin instead of to decalin than was the case in the absence of added ammonia. This is of some significance to coal liquefaction since tetralin is a good hydrogen donor, but decalin is not.

In Part III we showed that NH₃ addition to a mixture of quinoline and phenanthrene provides an operating region where complete HDN of quinoline can be achieved with reduced formation of hydrogenated phenanthrenes and cracking to biphenyl.

Part IV, a study of the hydrodeoxygenation (DHO) of dibenzofuran in the presence of naphthalene showed that NH_3 strongly inhibits HDO reactions and its effects on naphthalene here were much the same as in Part II.

In Part V it was demonstrated that in the hydrotreating of propylbenzene, the addition of ammonia increased the selectivity towards ring hydrogenation (generally desired for reformulated motor fuels) and away from dealkylation (generally undesired), but the overall reaction rate at a fixed temperature drops substantially.

The results of the various portions of the study are interpreted in terms of competitive adsorption effects and the role of ammonia, a gaseous base, in counteracting acid catalyst sites.

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Introduction

In our research work several years ago we discovered that the presence of a low concentration of ammonia greatly reduced the rate of hydrogenation of an aromatic compound (propylbenzene) on an industrial NiMo/Al₂O₃ catalyst while under similar conditions it had only a mild inhibiting effect on hydrodenitrogenation (of quinoline). This suggested a method under industrial reaction conditions of significantly reducing hydrogen consumption. With the more recent emphasis on reformulated fuels the emphasis shifted to focussing on effects of NH₃ on hydrotreatment reactions more generally and for some purposes it may be desirable to emphasize aromatic hydrogenation. Several model compound studies were made.

We proposed to use initially a mixture of naphthalene and quinoline as model compounds since we have an extensive background on the HDN kinetics of quinoline, and it is a good selection for this purpose. However, coal liquids contain substantial amounts of a base fraction that consists of hydroxy pyridines, hydroxy indoles and/or hydroxy anilines. No information has been published on the HDN-HDO hydrotreating reactions of a compound in which a hydroxyl (phenolic) group is attached to a heterocyclic N compound. Thus an early question was raised as to the extent to which quinoline HDN may or may not reflect the behaviour of such compounds. We therefore first performed a limited study with 8-hydroxy quinoline dissolved in tetralin utilizing a NiMo/Al₂O₃ catalyst in a packed bed reactor operating at 360°C and 385°C and 6.9 MPa.

We found that the N-heterocyclic ring is hydrogenated first to form an equilibrium mixture with a reaction intermediate that has been identified as 8-OH-1,2,3,4 tetrahydroquinoline. Oxygen is then removed to form the same reaction intermediates we have observed from quinoline alone, but in somewhat different ratios.

The important conclusion, by extension, is that with hydroxy-N-heterocyclic compounds in general the OH group will likely be removed rapidly at the beginning of reaction and that the subsequent reaction network will be similar to that previously established for the parent N-heterocyclic compound as such. This study is discussed in summary below as Part I. This also outlines the experimental methods, analytical methods, catalyst and other procedures used generally in all parts of the study. We then studied the effect of ammonia on the hydrogenation of naphthalene or butylbenzene during the HDN of quinoline (Part II). This was followed by the effect of ammonia on hydrogenation of phenanthrene during HDN of quinoline (Part III), and on hydrogenation of naphthalene during the HDO of dibenzofuran (Part IV). Finally we studied the effect of ammonia on ring hydro-genation of propylbenzene versus hydrocracking to propane and benzene (Part V).

Part I.

Hydrotreatment of 8-Hydroxyquinoline on a NiMo/Al₂O₃ Catalyst

I.A. Introduction

Petrakis et al. (1) found a substantial fraction of compounds with two heteroatoms, both oxygen and nitrogen in SRC-II heavy distillate fractions. These compounds were classified as hydroxypyridines, hydroxyindoles, and hydroxyanilines. We are not aware of any study of hydrotreatment in which both oxygen and nitrogen are in the same molecule.

The objective of Part I was to determine how the hydrotreatment of a representative compound with both oxygen and nitrogen in its structure might differ from that of related compounds with one heteroatom only. We chose 8-hydroxy-

quinoline (8HQ) as the model compound because it is readily available and its parent molecule, quinoline, has been studied extensively in the past by our group and by others. It is a hydroxypyridine. We were specifically interested in determining the reaction network by which 8-hydroxyquinoline is converted to clean products.

I.B. Experimental

The reactor used in this and subsequent parts of the study consisted of a vertical 0.52 cm-i.d. tube immersed in a fluidized sand bath to maintain isothermal conditions. Liquid was fed through a preheater coil to the top of the catalyst bed by a high-pressure liquid chromatography pump (Milton Roy Constametric III). Similarly, hydrogen was fed through a preheater coil by a mass flow controller (Brooks). The liquid and hydrogen feeds were mixed at the reactor inlet, passed downward through the catalyst bed, and flashed through a back-pressure regulator (Grove). This equipment has been used in our laboratory in previous studies of hydrodenitrogenation, -deoxygenation, and -desulfurization (HDN, HDO, and HDS) and is described in more detail elsewhere (2).

I.C. Reactants

The feed consisted of a solution of 0.245 mol/L of 8-hydroxyquinoline (99+% pure, Aldrich) in tetralin (99% pure, Aldrich). This corresponds to ~ 3.7 wt % of 8-hydroxyquinoline in solution or 0.35 wt % N and 0.4 wt % O. H₂S was produced in situ by the hydrotreatment of 0.12 mol/L of 1-dodecanethiol (98% pure, Aldrich) which was added to the feed. Under reaction conditions, this reacts rapidly and generates 12 kPa of H₂S. The operating conditions were 360 and 385 °C and 6.9 MPa total pressure. Hydrogen (Airco grade 4.5 and Med-Tech prepurified, >99.99% purity, were used interchangeably) was fed at a rate of 1520 mL(STP)/mL of liquid, equivalent to 9000 scf H₂/barrel (scf = standard cubic feet at 60 °F), to produce an initial 8-hydroxyquinoline

pressure of 24 kPa. Note that our definition of space time is based on the moles of 8HQ fed, not total moles of liquid. Hence, a space time of 320 (h g of catalyst)/mol of 8HQ corresponds to a liquid hourly space velocity (LHSV) of 9.4 h^{-1} for the 8HQ concentration used here. A few studies at 360 °C were also done with quinoline for comparison purposes.

Catalyst. The catalyst was a commercial NiMo/Al₂O₃ (American Cyanamid HDS-3A). It was crushed and sieved to a size range of 150-212 μm . After drying in air at 110 °C overnight, a full charge of catalyst (1.6 g) was diluted 4:1 with a similar sized inert SiC and packed into the reactor tube. After the reactor was purged under helium flow for 12 h at 100 °C, the catalyst was presulfided with a 10 mol % H₂S in H₂ gas mixture. The gas flow rate was 40 mL/min at a total pressure of 0.24 MPa. Sulfiding temperature was maintained at 175 °C for 6 hr, and the temperature was then raised to 315 °C at a rate of 1 °C/min. The gas flow was switched to helium after sulfiding had continued for 1 h at 315 °C.

For the first 200 h after sulfiding, the HDN of 4 wt % quinoline in a C₁₆ paraffin mixture was conducted at 360 °C and 6.9 MPa total pressure for routine deactivation of the catalyst until there was a steady level of activity. Standard catalyst activity was measured at a space time of 320 (h g of catalyst)/mol of quinoline under the same conditions.

I.D. Analysis

Liquid samples of the reactor effluent were collected downstream from a low-pressure phase separator and analyzed on a Perkin-Elmer Sigma 1B gas chromatograph equipped with dual flame ionization detectors. Concentrations of the products were related to the starting liquid feed. Carbon mass balances on total products compared to 8-hydroxyquinoline disappearance ranged from 90 to 105%. Separation of reaction

species was accomplished by using either Supelco SPB-35 (30 m, 0.25 mm i.d., 0.25 μ m) or Supelcowax 10 (30 m, 0.25 mm i.d., 0.25 μ m) columns. Compounds were identified by comparing their retention times with those of pure standards. An unknown intermediate was identified by electron-impact ionization (EI) and ND₃/chemical ionization (CI) mass spectrometry.

I.E. Results

Figure I-1 shows a simplified version of the reaction pathways of the HDN of quinoline as adapted from Satterfield and Smith (3). Quinoline (Q) undergoes rapid hydrogenation equilibrium to form 1,2,3,4-tetrahydroquinoline (PyTHQ) which reacts to form either 2-propylaniline (OPA) or decahydroquinoline (DHQ). Both OPA and DHQ undergo C-N hydrogenolysis to form the clean denitrogenated products. In addition, quinoline is hydrogenated to 5,6,7,8-tetrahydroquinoline (BzTHQ) which can be further hydrogenated to DHQ.

The hydrotreatment of 8HQ produced the same reaction intermediates found during the HDN of Q, but the amount of BzTHQ formed was much greater. Further, a new intermediate was observed, that is in equilibrium with 8HQ. The equilibrium is established rapidly and decreases with increased temperature. Analysis using electron-impact ionization (EI) and ND₃/chemical ionization (CI) mass spectrometric techniques, showed it to be 8-hydroxy-1,2,3,4 tetrahydroquinoline (8HTHQ).

A detailed kinetic analysis is described elsewhere (3). We find that in the hydrotreatment of 8-hydroxyquinoline three new routes are introduced beyond those encountered in the HDN of quinoline. The core of the new kinetic model is adapted from Satterfield and Smith as applied to quinoline and uses the same nomenclature. The detailed network is shown on Fig. I-2 and a comparison of the kinetic model to data at 360 °C is shown on Fig. I-3.

I.F. Discussion

The course of the reaction as shown in Figure I-3 establishes that HDO goes to completion before HDN for 8HQ. The species observed are the same as those found during the HDN of Q, plus 8HTHQ. The clean products include propylcyclohexane (PCH), propylcyclohexene (PCH_e), and propylbenzene (PB) with PCH predominating. The ratio of PB to PCH was the same in hydrotreatment of 8HQ as in that of quinoline. The overall rate of conversion of 8-hydroxyquinoline to non-nitrogen compounds was essentially the same as that of quinoline. For example, at a space time of 320 (h g of catalyst)/mol of feed, the HDN of Q was 58% and the HDN of 8HQ was 57%.

I.G. Summary

During the hydrotreatment of 8-hydroxyquinoline (8HQ) an intermediate is formed in equilibrium with 8HQ, identified as 8-hydroxy-1,2,3,4-tetrahydroquinoline. The hydrotreatment of 8-hydroxyquinoline enters the HDN of quinoline network via three routes. Route 1 is hydrogenation of the heterocyclic ring to 8HTHQ followed by abstraction of oxygen through hydrogenation of the other aromatic ring to 8HDDHQ followed by C-O hydrogenolysis to form DHQ. Route 2 is direct C-O hydrogenolysis to form PyTHQ. Route 3 is hydrogenation of the benzene ring in 8HQ to 8HTHQa followed by the removal of the oxygen to enter the HDN of quinoline network through BzTHQ. The activity and selectivity to clean hydrocarbons both remain unchanged by the presence of the hydroxyl group on 8HQ. The HDO reactions of 8-hydroxyquinoline to form N compounds are much faster than the HDN reactions of the N compounds to form hydrocarbons.

This work has been published in *Energy & Fuels*, 1991, 5, p. 163.

Figure I-1 Simplified version of the reaction pathways of HDN of quinoline, adapted from Satterfield and Smith, 1986.

Figure I-2 Proposed reaction pathways of 8-hydroxyquinoline.

Figure I-3 Comparison of kinetic model to data at 360 °C.

I.H. References

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Part II.

Effect of Ammonia on the Hydrogenation of Naphthalene or Butylbenzene during the Hydrodenitrogenation of Quinoline

II.A. Introduction

In coal liquefaction by solvent hydrogen transfer, it is desirable to maximize partially hydrogenated aromatics such as tetralin which are good hydrogen donors rather than completely saturated hydrocarbons such as decalins, which are poor hydrogen donors. Our focus here was on the extent to which ammonia might improve the selectivity to the partially hydrogenated product of naphthalene (tetralin) instead of decalin.

The reactions of quinoline are well-known and nitrogen removal is particularly of concern in hydrotreatment. Naphthalene is readily available and its hydrogenation products are only tetralin and *cis/trans*- decalin, simplifying analysis.

From a practical point of view, NH_3 can be readily added and removed from a reacting system if it is found that it produces a desired effect. The hydrogenation of butylbenzene during the HDN of quinoline was also studied in brief to compare the effect of ammonia on hydrogenation of a single-ring aromatic hydrocarbon.

II.B. Experimental

The equipment, the catalyst and analytical methods are described in Part I. For Part II, seven different feed compositions were studied. For the first five, naphthalene (99+ % pure, Aldrich) was dissolved at a concentration of 0.245 mol/L together with 0.0245 mol/L of quinoline (99% pure, American Tokyo Kasei) in a C_{16} paraffin solvent consisting of about 93% $\text{C}_{16}\text{H}_{34}$ and 7% other paraffins, mostly $\text{C}_{14}\text{H}_{30}$ and $\text{C}_{18}\text{H}_{38}$. Ammonia concentrations were produced in situ by the hydrotreating of various amounts of *n*-propylamine (98% pure, Aldrich) added to the feed. H_2S was also produced similarly from 1-dodecanethiol (98% pure, Aldrich) which was added to the feed to comprise 0.12 mol/L. Under reaction conditions, *n*-propylamine and 1-dodecanethiol react rapidly to generate NH_3 and H_2S . The partial pressure of the H_2S thus formed was about 12 kPa for all experiments and this kept the catalyst in the fully sulfided form. For feeds 6 and 7, naphthalene was replaced with butylbenzene at the same molar concentration.

All runs were made at 360 °C and 6.9 MPa total pressure. Hydrogen (Airco grade 4.5 and Med-Tech high purity, >99.95% purity, were used interchangeably) was fed at a rate of 1520 mL (STP)/mL of liquid, equivalent to 9000 scf H_2 /barrel (scf = standard cubic feet at 60 °F). Note that our definition here of space-time is based on the moles of aromatic hydrocarbon fed, not total moles of liquid. A liquid hourly space velocity (LHSV) of 10.0 h^{-1} corresponds to a space time of 296 (h/g of catalyst)/(mol of

naphthalene) for feeds 1-5 and 263 (h/g of catalyst)/(mol of butylbenzene) for feeds 6 and 7.

II.C. Results

The principal products from the HDN of quinoline are the two tetrahydroquinolines, decahydroquinoline, *o*-propylaniline, and various hydrocarbons, plus NH₃. (See Part I.) Tetralin and *cis/trans*-decalin are the main products from the hydrogenation of naphthalene.

Each of feeds 1 through 5 was studied at six different space-times, resulting in data on the relative concentration of naphthalene, tetralin, and decalins in the product as a function of space-time for reaction in the absence of added ammonia and for four increasing concentrations of NH₃ from the added propylamine. Figures II-1 and II-2 show illustrative results for no added NH₃ and for 48 kPa of NH₃ present. Complete HDN of the quantity of quinoline present produces a NH₃ partial pressure of only 3 kPa, so the effects of NH₃ may be attributed to that deliberately added via propylamine. The solid lines in Figures II-1 and II-2 represent kinetic model predictions for naphthalene hydrogenation as discussed in more detail elsewhere. (HDN is defined here as the degree of complete removal of nitrogen from the sum of quinoline and N-containing intermediates, to form hydrocarbons.) These figures show that ammonia inhibits both naphthalene hydrogenation and quinoline HDN.

Figure II-3 shows a plot of the ratio of decalins to tetralin as a function of NH₃ concentration for two space-times at which HDN was complete. This shows the considerable effect of added NH₃ on increasing the selectivity to tetralin.

Butylbenzene. The principal product from the hydrogenation of butylbenzene (BB) is butylcyclohexane (BCH). There was no significant reaction to butylcyclohexane

under our conditions. Runs 6 and 7 were designed to in effect replace naphthalene with butylbenzene holding all other variables as constant as possible, maintaining the same solvent. Propylamine was added in run 7 to generate 24 kPa of NH_3 but none was added in run 6. As with naphthalene, the presence of 24 kPa of NH_3 slightly reduced the percent HDN of quinoline. However, even after the HDN of quinoline was completed, the 24 kPa of NH_3 moderately suppressed the hydrogenation of butylbenzene.

II.D. Discussion

Ammonia inhibits the hydrogenation of tetralin to decalins more than the hydrogenation of naphthalene to tetralin. The effects can be interpreted in terms of competitive adsorption. Ammonia is weakly adsorbed, but as its concentration is increased, its coverage of hydrogenation sites increases. Tetralin is much more weakly adsorbed than naphthalene or ammonia; thus, as ammonia concentration is increased, the added coverage of ammonia prevents the tetralin from adsorbing onto the surface preventing hydrogenation. Naphthalene, which is more strongly adsorbed than tetralin, better competes with ammonia for the hydrogenation site. The net effect is improved product selectivity to tetralin.

II.E. Summary

In a mixture of naphthalene and quinoline with a low concentration of added ammonia, there is an operating region in which essentially complete hydrodenitrogenation of quinoline can be achieved, but the naphthalene is converted to a greater extent to tetralin instead of decalin than is the case in the absence of added

Figure II-1 Space-time plot for the hydrogenation of naphthalene during the HDN of quinoline. Feed 1, no added ammonia.

Figure II-2 Space-time plot for the hydrogenation of naphthalene during the HDN of quinoline. Feed 4, 48 kPa of added ammonia.

Figure II-3 Selectivity to tetralin improved by the addition of ammonia at space times with essentially complete HDN of quinoline.

ammonia. This observation may be of importance in coal liquefaction in which tetralin is a good hydrogen donor but decalin is not.

This work has been published in *Energy & Fuels*, 1992, 6, p. 315.

Part III.

Effect of Ammonia on the Hydrogenation of Phenanthrene During the Hydrodenitrogenation of Quinoline

III.A. Introduction

Part II showed the effect of ammonia on the selective hydrogenation of naphthalene. Here we studied the hydrogenation of phenanthrene as a representative three-ring aromatic hydrocarbon, in contrast to naphthalene as a two-ring aromatic.

Limited literature is available on the hydrogenation of phenanthrene. Shabtai et al. (1) reported on the hydrogenation of phenanthrene and pyrene in a semi-batch autoclave reactor. Under their conditions, they found 1,2,3,4-tetrahydrophenanthrene (P4H), rather than 9,10-dihydrophenanthrene (P2H), to be the principal first product formed. Lemberon and Guisnet (2) recommended phenanthrene hydroconversion as a test reaction for studying hydrogenation and cracking properties of coal hydroliquefaction catalysts. In a brief study, LaVopa (3) found that the addition of piperidine restricted the amount of hydrogenation of phenanthrene during its purification by hydrotreatment.

III.B. Experimental

To achieve the desired solubility of phenanthrene it was necessary to use tetralin (99% pure, Aldrich) as the solvent rather than hexadecane, used in the study of

naphthalene. All runs were made with feeds consisting of 0.24 mol/L of phenanthrene (99+% pure, Aldrich) and 0.024 mol/L of quinoline (99% pure, American Tokyo Kasei). Propylamine (98% pure, Aldrich) when desired was added at a concentration of 0.24 mol/L to generate *in situ* an ammonia partial pressure of 24 kPa in the reactor. Complete HDN of the quantity of quinoline in the feed produces a NH_3 partial pressure of only 3 kPa, so the effects of NH_3 may be attributed to that deliberately formed via propylamine. Hydrogen sulfide partial pressure of 12 kPa, for maintaining the sulfided state of the catalyst, was generated *in situ* in the reactor by the addition of 0.12 mol/L of 1-dodecanethiol (98% pure, Aldrich) to the feed.

Analyses were performed as described in Part I. Carbon mass balances on total products compared to phenanthrene disappearance exceeded 93%. Phenanthrene and 9,10-dihydrophenanthrene (P2H) were identified by comparing their retention times with those of pure standards. The presence of other products was identified by GC/MS.

III.C. Results

All data were obtained at 360°C, 6.9 MPa total pressure, in the presence of 12 kPa of H_2S and 24 kPa of NH_3 or its absence, both generated *in situ*. Space-times, expressed relative to phenanthrene, were varied from 100 to 600 h.g.cat/mol phenanthrene.

Figure III-1 shows a plot of the hydrodenitrogenation of quinoline in the presence of 24 kPa of ammonia and its absence versus space-time. As in the previous studies with naphthalene and butylbenzene, ammonia had only a slight inhibiting effect on the overall removal of nitrogen from quinoline and its intermediate reaction products. Essentially complete HDN was achieved at the highest space times. (Percent HDN is defined here as degree of conversion of quinoline and N-containing intermediates into hydrocarbons.)

Figure III-2 shows a plot of concentrations of phenanthrene and its products for the same runs shown in Figure III-1. Five species of hydrogenated phenanthrenes were detected, 9,10-dihydrophenanthrene (P2H), 1,2,3,4-tetrahydrophenanthrene (P4H), perhydrophenanthrene (PHP), and two species of octahydrophenanthrene (P8H), 1,2,3,4,5,6,7,8-P8H and 1,2,3,4,9,10,11,12-P8H. The two species of P8H were lumped together as one because of poor resolution of their peaks on the GC. Some hydrocracking also occurred, as shown by the formation of biphenyl. From 1 to 4% of the solvent, tetralin, was hydrogenated to decalin or dehydrogenated to naphthalene, but there was no significant effect of the presence or absence of 24 kPa of ammonia here on the degree of tetralin hydrogenation.

NH₃ has no significant effect on the phenanthrene hydrogenation network until the HDN reactions are nearly complete as shown in Figures III-3 and III-4. Figure III-3 shows that NH₃ suppresses complete hydrogenation to PHP and Figure III-4 shows that it reduces cracking to biphenyl. These data are from Figure III-2, shown on a larger scale for clarity. Recall that these results were obtained with an integral reactor. With a differential reactor the effects of NH₃ would presumably be much more marked.

III.D. Kinetic Model.

The most detailed information on the reaction network (Figure III-5) appears to be that of Shabtai et al. (1). They studied the hydrogenation of pure phenanthrene over several catalysts, particularly a sulfided NiW/Al₂O₃, at temperatures of 200-380°C and 2900 psig. They concluded that the main primary product is P4H, which is converted to P8H and then PHP. P2H was formed in considerably lower yield. Moreau and Geneste (4) took phenanthrene as being hydrogenated to either P2H or P4H by parallel pathways. Subsequent steps were not specified, but they assumed that P2H could be hydrogenated to P8H, whereas our model assumes that P8H is formed from P4H. Lemberston and Guisnet reported limited studies at 430°C and 10 MPa of hydrogen

pressure using neat phenanthrene on a NiMo/Al₂O₃ catalyst. A variety of cracked products were formed as well as various partially hydrogenated products, but no PHP.

Assuming that each successive hydrogenating and hydrocracking step in Figure III-5 proceeds via first order reaction, then first order rate constants can be calculated for the sets of data with and without added ammonia as shown in Table 1.

Table 1 First order rate constants for the hydrogenation of phenanthrene to products.

Added ammonia concentration, kPa	First order reaction rate constants				
	k ₁	k ₂	k ₃	k ₄	k ₅
0	0.00405	0.00240	0.00304	0.000290	0.000244
24	0.00403	0.00210	0.00270	0.000103	0.000114

unit of k = (mol of phenanthrene)/(hr. g of catalyst)

III.E. Discussion

The results can be well interpreted in terms of competitive adsorption effects between phenanthrene and its hydrogenated products on the one hand and quinoline and its nitrogen-containing HDN products and NH₃ on the other. It is seen that phenanthrene is readily converted to partially hydrogenated products even in the presence of quinoline and its nitrogen-products. In Part II it was shown that NH₃ can inhibit the hydrogenation of tetralin to decalins but here the effect of ammonia on tetralin hydrogenation was negligible largely because of the much higher concentration of tetralin.

The effect of added ammonia is insignificant or minor on the hydrogenation of phenanthrene and intermediates until quinoline and its nitrogen-containing HDN products are largely removed (Figures III-3 and III-4), because of the greater

Hydrodenitrogenation of quinoline without added NH₃ in the presence or absence of 24 kPa of NH₃, generated *in situ*.

Figure III-1

Effect of ammonia on the hydrogenation of phenanthrene during the HDN of quinoline at 360°C, 6.9 MPa. Open symbols represent no added ammonia; filled symbols represent 24 kPa of ammonia generated *in situ*.

Figure III-2

Ammonia inhibits the formation of perhydrophenanthrene when HDN is nearly complete.

Figure III-3

Ammonia reduces the amount of hydrocracking to form biphenyl when HDN is nearly complete.

Figure III-4

Kinetic model of the hydrogenation of phenanthrene.

Figure III-5

adsorptivity of the latter relative to NH_3 . Therefore, k_1 , k_2 , and k_3 , which represent upstream behavior, show no significant effect of ammonia. On the other hand k_4 and k_5 , which represent downstream behavior when nitrogen-containing hydrocarbons have been effectively eliminated, show the substantial inhibiting effect of NH_3 on hydrocracking and further hydrogenation.

The addition of ammonia has little effect on the overall HDN of quinoline. Thus, NH_3 addition provides an operating region where complete HDN of quinoline can be achieved with reduced formation of hydrogenated phenanthrenes and biphenyl. The undesirable hydrocracking is presumably suppressed by the effects of ammonia neutralizing the acidic sites on the catalyst.

A paper summarizing this work is in press at *Energy & Fuels*.

III.F. References

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Part IV.

Hydrogenation of Naphthalene during Hydrodeoxygenation of Dibenzofuran (DBF).

IV.A. Experimental

All runs were made with feeds consisting of 0.25 mol/L of naphthalene (99+% pure, Aldrich) and 0.035 mol/L of dibenzofuran (99% pure, Aldrich), except when base-

line runs were made in the absence of both naphthalene and ammonia. Propylamine (98% pure, Aldrich) when desired was added at concentrations of 0.24 mol/L or 0.48 mol/L to generate *in situ* ammonia partial pressures of 24 kPa or 48 kPa in the reactor. Hydrogen sulfide partial pressure of 12 kPa, for maintaining the sulfided state of the catalyst, was generated *in situ* in the reactor by the addition of 0.12 mol/L of 1-dodecanethiol (98% pure, Aldrich) to the feed. The solvent was essentially a C₁₆ n-paraffin consisting of about 93% C₁₆H₃₄ and 7% other paraffins, mostly C₁₄H₃₀ and C₁₈H₃₈. Carbon mass balances on total products compared to naphthalene disappearance exceeded 96%. Analytical methods were as previously described.

IV.B. Results

Data are presented in two alternate forms. In order to make comparisons against the base-line operation in the absence of naphthalene, % conversion and selectivities from the HDO of DBF are plotted versus LHSV. For other comparisons data are plotted versus space time relative to naphthalene.

Figure IV-1 shows the extent of HDO versus LHSV. HDO of dibenzofuran is not affected by the presence of naphthalene, but ammonia does inhibit HDO. Interestingly, the additional ammonia from 24 kPa to 48 kPa had marginally less inhibition. Although the addition of ammonia inhibited the hydrogenation of naphthalene, its presence caused more dicyclohexyl to form relative to the amount of cyclohexylbenzene formed, see Figure IV-2.

Figure IV-3 shows the effect of ammonia on the HDO of dibenzofuran during the hydrogenation of naphthalene, as plotted versus space time. The products from the HDO of dibenzofuran have been identified by LaVopa and Satterfield (1987). In agreement with the earlier work, under present reaction conditions dibenzofuran was the only observed oxygenated species, i.e., no intermediates containing oxygen were observed. Double-ring deoxygenated products consisted of biphenyl,

cyclohexylbenzene, and dicyclohexyl. Single-ring deoxygenated products consisted of methylcyclohexane, benzene, cyclohexane, methylcyclopentane, and pentane. (See Fig. IV-4.) Since the HDO of DBF exhibits first-order behavior, the lines in Figure IV-3 represent linear regression lines. The presence of naphthalene mildly affects product selectivity in the HDO of DBF. Its presence slightly increased the selectivity to double-ring products while hampering the formation of single-ring products. Thus the net effect of naphthalene on the overall HDO of DBF is negligible.

Figure IV-5 shows the inhibition of the hydrogenation of naphthalene by the addition of ammonia, which occurred simultaneously with the HDO reactions. Figure IV-6 shows the increase in selectivity to tetralin over decalins by the addition of ammonia. This is similar to the selectivity effect we observed in mixtures of naphthalene and quinoline.

Reference: LaVopa, V.; Satterfield, C.N. *Energy Fuels* 1987, 1, 323.

IV.C. Discussion

The addition of ammonia inhibits the HDO of dibenzofuran more strongly than the HDN of quinoline. The addition of 24 kPa of ammonia resulted in a fractional loss of HDO activity of 65%. The further addition of ammonia to 48 kPa had only a little more inhibition; the fractional loss of activity was 68%. Quinoline is a basic compound and dibenzofuran is nearly neutral so it is not as strongly adsorbed as quinoline. Thus ammonia more readily competes with DBF for adsorption sites. The addition of ammonia prevents complete HDO of DBF even at the highest space times studied.

We conclude that the addition of ammonia may not be suitable when emphasis is on HDO reactions. As long as there are intermediate nitrogen-containing products from the HDN of quinoline, HDO of dibenzofuran is suppressed. Therefore, all nitrogen-containing species, including ammonia, may have to be removed from the system

Effect of NH₃ on HDO of dibenzofuran

Figure IV-1

Ammonia increases the ratio of dicyclohexyl to cyclohexylbenzene

Figure IV-2

Hydrodeoxygenation of dibenzofuran during the hydrogenation of naphthalene without ammonia and with 24 and 48 kPa of ammonia (360°C, 6.9 MPa).

Figure IV-3

Reaction Scheme for Hydrodeoxygenation of Dibenzofuran

Figure IV-4

The effect of ammonia on the hydrogenation of naphthalene during the HDO of dibenzofuran (360°C, 6.9 MPa).

Figure IV-5

Ammonia increases the selectivity of tetralin (360° C , 6.9 MPa).

Figure IV-6

The effect of dibenzofuran on the hydrogenation of naphthalene (360° C, 6.9 MPa).

Figure IV-7

before HDO can effectively progress. Thus during hydrotreating, while the addition of ammonia may help in reducing the hydrogenation of aromatics during the HDN reactions, it may be necessary to remove the ammonia before HDO to achieve the level of HDO desired.

Figure IV-7 shows that the HDO of dibenzofuran has little effect on the hydrogenation of naphthalene. Thus the inhibition that occurs with the addition of ammonia is caused by the ammonia and not by dibenzofuran or its HDO products. Detailed analysis shows that there is more inhibition of the hydrogenation of naphthalene caused by ammonia in the naphthalene/dibenzofuran system than in the naphthalene/quinoline system. Without the presence of strongly adsorbed nitrogen compounds such as quinoline and its partially denitrogenated products, ammonia readily inhibits the hydrogenation of naphthalene.

Part V.

Effect of Ammonia on Ring Hydrogenation versus Hydrocracking of an Alkyl Aromatic

V.A. Introduction

Our most recent studies take notice of the recent emphasis on reformulated gasolines which has focused attention on methods of limiting aromatics concentrations in motor fuels. Hence there is new emphasis on hydrogenation of high aromatic feedstocks of suitable volatility range yet to do so with minimum hydrocracking to form gaseous products, which are less valuable. In this study we tested the effect of ammonia on the rate of hydrogenation of an aromatic ring (desired) relative to the rate of hydrocracking to remove an alkyl group (undesired) by studies with n-propyl

benzene (PBz) which may cleave to C₃H₈ plus benzene (Bz) versus ring hydrogenation to form propyl cyclohexane (PCH).

V.B. Experimental

Methods were essentially the same as previously. We chose as our standard reaction conditions: $T = 360^\circ$, total pressure about 6.9 MPa, partial pressure of PBz = 24.4 kPa, partial pressure of H₂S = 13.3 kPa, partial pressure of NH₃ = 13.3 kPa, space-time = 200 h. g. cat/mol Pbz. The carrier liquid was hexadecane (C₁₆H₃₄). As before, the H₂S and NH₃ were generated in situ by hydrogenation of 1-dodecane thiol and n-propyl amine, respectively, added to the C₁₆ feed.

Fresh catalyst was used, whose activity dropped to a steady state level after about 120 hours on stream following which Runs 1-4 were carried out at p.p. NH₃ values of 0, 13.3 24.4 and 48.8 kPa, respectively. For each NH₃ p.p. , space-times were varied at the following levels: 50, 100, 200, 400 and 600. Analyses were made for propylcyclohexene (CA), propylcyclohexane (CB) and benzene (CD). No other products were found in any significant amounts. The ratio CB/CD is a measure of the activity of ring hydrogenation relative to hydrocracking.

Four more runs (5-8) were then made at 330°C with four levels of NH₃ and one more at 300°C and 13.3 kPa.

V.C. Results

The results of all 9 runs were analyzed kinetically. The two reactions were treated as being each first order, i.e.,

where A = PBz, B = PCH and D = Bz. If the overall reaction is first order, then

$$-\frac{dC_A}{dt} = (k_1 + k_2) C_A \text{ and } -\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t$$

A plot of $-\ln C_A/C_{A0}$ versus space time should then give a straight line, as indeed it does for all runs. An example is shown on the attached Figure V-1 for run #5.

To determine individual rate constants (k_1 and k_2), the following relationships hold for first order reactions:

$$C_B/C_{A0} = \frac{k_1(1 - C_A/C_{A0})}{k_1 + k_2}$$

and
$$C_D/C_{A0} = \frac{k_2(1 - C_A/C_{A0})}{k_1 + k_2}$$

Plotting C_B/C_{A0} or C_D/C_{A0} versus $1 - (C_A/C_{A0})$ yields a straight line with slope of $k_1/(k_1 + k_2)$ or $k_2/(k_1 + k_2)$ respectively. An example, again for run #5, is shown on Fig. V-2. With the value of $(k_1 + k_2)$ from Fig. 1, k_1 and k_2 can each be determined.

The selectivity, $S = k_1/k_2$. Values at 360°C as a function of NH_3 partial pressure are shown on Figure V-3 based on the data from Runs #1-4. The addition of NH_3 substantially decreases the overall rate (see values of $k_1 + k_2$ in the tables for runs #1-4) while increasing the selectivity towards hydrogenation and away from hydrocracking as shown on Fig. V-3. The NH_3 effect is less than first order in NH_3 , i.e. increasing quantities of NH_3 have progressively lesser effects. These observations are consistent with the generalization that catalyst acidity accelerates hydrocracking and that NH_3 acts to neutralize acid sites.

Similar analyses of data at 330°C and 300°C yield information on the effect of temperature on selectivity. Fig. V-4, utilizing run #9 at 13.3 kPa and 300°C, shows that selectivity is markedly increased at lower temperatures. This is consistent with a broad

generalization that activation energies for hydrogenation reactions are typically substantially less than for hydrocracking reactions. The activation energy for the overall reaction at 13.3 kPa is about 60 kJ, as shown on Figure V-5.

V.D. Summary

For the model reaction studied, the addition of NH_3 increases the selectivity towards ring hydrogenation (generally desired) and away from dealkylation (generally undesired). However the overall reaction rate for a fixed temperature drops substantially. Selectivity is the greatest at the lowest temperatures. The effect of NH_3 is less than proportional to its partial pressure. The results obtained here suggest how operating conditions might be adjusted to obtain an optimum amongst desired reaction rates, conversion and selectivity, in the presence of small concentrations of NH_3 or other bases.

Figure V-1 Run #5

Figure V-2 Determination of k_1 and k_2

Figure V-3 Selectivity versus P_{NH_3}

Figure V-4 Selectivity versus Temperature

Figure V-5 Activation Energy

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