1 of 1

THE ROLE OF THE RESID SOLVENT IN CO-PROCESSING WITH FINELY DIVIDED CATALYSTS

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Table of Contents

INTRODUCTION

The overall objective of this project is to evaluate the role of the resid in coprocessing. The primary purpose of the work performed this quarter was to establish under thermal and catalytic reaction conditions whether hydrogen transfer occurred between cycloalkane type structures that are present in resids and heteroatomic species that are present in coal and liquefied coal.

The research this quarter focused upon evaluating benzophenone (BENZ) as a model acceptor for hydrogen that might be transferred from a cycloalkane, perhydropyrene (PHP), under coprocessing conditions. Hence, a number of reactions was performed in which BENZ was reacted alone in hydrogen and nitrogen atmospheres in the presence and absence of a catalytic agent, molybdenum naphthenate. Reactions were also performed using a combination of PHP and BENZ at a 1 to 1 weight ratio. These reactions were performed under thermal and catalytic conditions using two temperatures, two types of atmospheres, N_2 and H_2, and two pressures, 500 and 1250 psig. The catalyst used was Mo naphthenate with excess sulfur being added as elemental sulfur.

Also performed this quarter were initial separations with petroleum resids. Two different resids were used, Maya and LHC-362. The literature was also surveyed to determine important characteristics that should be evaluated for selecting resids. On the basis of the literature, resids with high metal and sulfur contents will most likely cause catalytic deactivation during the coprocessing of coal and resid. Hence, those characteristics should be minimized. The resids that are desired for this project are resids with high-, medium-, and low-naphthenic content. Different levels of asphaltenes are also desirable. Resids with these characteristics are currently being sought.

The model compound PHP that had been commercially available as naphthene representative of resids is now no longer available. Hence, several scoping experiments were performed in order to determine conditions for synthesizing PHP. The synthesis procedure reported in US Patent 3,303,227 was used as a basis for this work. Although more than 85% PHP was synthesized, partially hydrogenated pyrenes were also produced which will require separation in order to obtain pure PHP.

EXPERIMENTAL

Benzophenone and Perhydropyrene Reactions. The reactants, BENZ and PHP, were purchased from Aldrich Chemical Company and were used as received. Other chemical species used in the analysis, diphenylmethane (DPM) and biphenyl (BP), were also obtained from Aldrich Chemical Company and were used as received. Molybdenum naphthenate was obtained from Shepherd Chemical Company.

Reactions were performed with BENZ alone and with BENZ combined with PHP. All of the reactions were performed in $\sim 20\ cm^3$ stainless steel microtubular reactors. The reactor was charged first with catalyst and then the reactants, which were usually about 0.1 g each and were added in an amount so that the active metal content of the charge was approximately 1000 ppm. The loaded reactor was then charged with either hydrogen or nitrogen gas of either 500 or 1250 psig at ambient temperature. The reactions were then performed at two different temperatures, 400 and 440 °C, at an agitation rate of 450 rpm with the reactors being shaken horizontally.

The liquid and solid reaction products were recovered by THF and analyzed using a Varian 3300 gas chromatograph (GC) equipped with a 30 m HT-5 capillary column and flame ionization detection. Quantitation was performed using the internal standard method with

biphenyl as the internal standard. The GC retention times and response factors for the reactants and predicted products were determined by analyzing authentic compounds. Peaks of unknown products in the GC chromatogram were analyzed by GC-mass spectrometer using a VG 70 EHF mass spectrometer.

Resid Fractionation. Preliminary experiments were performed fractionating resid in which 2 g of resid were first dissolved in 450 ml hexane which was introduced as three 150-ml aliquots. The resid-hexane solution was sonicated and then the hexane soluble material was decanted from the insoluble materials. The hexane insoluble materials were then extracted with 450 ml toluene in 150 ml aliquots. The last extraction used 450 ml THF, also in 150 ml aliquots. Both the resid-toluene and the resid-THF solutions were sonicated. The solvents were removed from the soluble resid fractions by rotary evaporation. The recovered resid fractions were dried in a vacuum desiccator for 36 hr. The resid fraction were then stored in a vacuum desiccator.

Synthesis of Perhydropyrene. Perhydropyrene was synthesized in ~50 cm^3 stainless steel tubular reactors. The initial reactor charge was 2.0 g pyrene, 0.3 g Pt/Al_2O_3, and 1250 psig H_2 pressure at ambient temperature. The reaction was performed at 375 °C for 5 hr, at which time, the gaseous products were released and the liquid products were analyzed by gas chromatography. Subsequently, 0.3 g of fresh Pt/Al_2O_3 and 1250 psig H_2 at ambient were charged to the reactors. The reaction was repeated at 375 °C for 3 hr and then 4 hr yielding a total reaction time of 12 hr.

Definitions. The amount of hydrogen donated by PHP in the reactions is calculated on the basis of the products achieved and the moles of H_2 released in forming the dehydrogenation products. The equation used in the calculation was

$$H_2 \text{ Donated} = (3 \times \text{DCP mol\%} + 5 \times \text{HHP mol\%} + 6 \times \text{THP mol\%} + 7 \times \text{DHP mol\%} + 8 \times \text{PYR mol\%}) \times 100$$

where DCP is decahydropyrene, HHP is hexahydropyrene, THP is tetrahydropyrene and PYR is pyrene. The amount of hydrogen accepted by benzophenone is calculated in terms of the formation of the reaction product, diphenylmethane (DPM). The equation used in calculating hydrogen accepted for BENZ is

$$H_2 \text{ Accepted} = (1 \times \text{DPM mol\%}) \times 100.$$

RESULTS AND DISCUSSIONS

Perhydropyrene and Phenanthrene Reactions. Last quarter reactions were performed using PHP as a naphthene hydrogen donor and phenanthrene (PHEN) as an aromatic acceptor. Thermal and catalytic reactions were performed both in hydrogen and nitrogen atmospheres and at two weight ratios of PHP to PHEN. Two reaction temperatures were used, 400 and 440 °C; the results from the reactions at these two temperatures are given in Tables 1 and 2, respectively. This quarter the amount of H_2 accepted and the amount of H_2 donated for each reaction system was calculated. The amount of hydrogen accepted by PHEN is defined as

$$H_2 \text{ accepted} = (1 \times \text{DHPN mol\%} + 2 \times \text{THPN mol\%}) \times 100$$

where DHPN is dihydrophenanthrene and THPN is tetrahydrophenanthrene. The amount of H_2 donated by PHP is defined as

$$H_2 \text{ donated} = (3 \times \text{DCP mol\%} + 5 \times \text{HHP mol\%} + 6 \times \text{THP mol\%} + 7 \times \text{DHP mol\%} + 8 \times \text{PYR mol\%}) \times 100$$

where DCP is decahydropyrene, HHP is hexahydropyrene, THP is tetrahydropyrene, DHP is dihydropyrene, and PYR is pyrene. The values given in the tables for H_2 accepted and H_2 donated are based on 100 mol of product.

The moles of H_2 donated in a H_2 atmosphere was based totally on the dehydrogenated products formed from PHP. The reactions in H_2 which contained MoNaph and sulfur resulted in the most dehydrogenation of PHP at 400 °C at both PHP to PHEN weight ratios of 1:1 and 5:1 (Table 1). The amount of H_2 donated in the thermal reactions and the reactions with NiOct was very similar at both weight ratios.

The moles of H_2 accepted were based on the hydrogenated products of PHEN; however, the source of H_2 for hydrogenated came from both PHP and the H_2 atmosphere. Hence, when a H_2 atmosphere was used at 400 °C, more H_2 was accepted by PHEN than was donated by PHP (Table 1). At both weight ratios, the reaction with MoNaph and sulfur gave the most amount of H_2 accepted. The amount of H_2 accepted for both the thermal reactions and the reactions with NiOct were similar and less than that observed with MoNaph and sulfur.

The amount of H_2 donated and accepted at 440°C was similar to those observed at 400 °C as shown in Table 2. In a H_2 atmosphere, substantially more H_2 was accepted than was donated. The reactions with MoNaph and sulfur showed the largest amount of H_2 transferred at both weight ratios.

The reactions of PHEN alone at 400 and 440 °C in H_2 gave hydrogenated products of DHPN and THPN (Table 3). This hydrogenation resulted from hydrogenation by molecular H_2. As with the PHP and PHEN combined reactions, the reactions with PHEN alone in the presence of MoNaph and sulfur resulted in the most hydrogenation of PHEN. When the H_2 accepted with PHEN alone was compared to the H_2 accepted with PHP and PHEN combined in a 5:1 weight ratio, the reactions of PHEN with PHP resulted in more H_2 being accepted for every reaction. This comparison is given in Table 4.

Perhydropyrene and Benzophenone Reactions. Reactions were performed with PHP and BENZ under both thermal and catalytic conditions in H_2 and N_2 atmospheres as shown in Table 5. Two hydrogen pressures were used in the reactions, 500 and 1250 psig. Most of the reactions were conducted at 440 °C although a few were performed at 400 °C. The reaction products achieved from the dehydrogenation of PHP were decahydropyrene (DCP), hexahydropyrene (HHP), tetrahydropyrene (THP), dihydropyrene (DHP), and pyrene (PYR). The reaction product achieved from the hydrogenation of BENZ was diphenylmethane (DPM).

Catalytic reactions using Mo naphthenate at 1000 ppm of active metal resulted in more dehydrogenation of PHP than did thermal reactions under the same conditions. BENZ also hydrogenated substantially more under catalytic conditions than under thermal conditions regardless of the H_2 pressure.

Comparison of reactions of BENZ and PHP under N_2 atmosphere to those in H_2 showed that BENZ was much more reactive in H_2 than in N_2. The presence of the MoNaph catalyst with N_2 had little effect on the conversion of BENZ as would be expected. The moles of hydrogen accepted by BENZ in the reactions with N_2 had to come from the H_2 donated from PHP. The moles of H_2 accepted by BENZ in N_2 were less than that donated by PHP. The hydrogen efficiency in N_2 is defined as the moles of H_2 accepted by BENZ divided by the moles of H_2 donated by PHP. The hydrogen efficiency ranged from 32 to 72%. The hydrogen efficiency of the reactions were all substantially greater than one, indicating that H_2 for hydrogenation of BENZ came from molecular H_2 as well as from PHP.

Reactions were also performed under similar reaction conditions with BENZ alone as presented in Table 6. For the thermal reactions without PHP, the amount of BENZ conversion to DPM was greater than in the reactions with PHP. Hence, the presence of PHP inhibited the

hydrogenation of BENZ (Table 7). The moles of H_2 accepted by BENZ based on 100 moles of product was 17.4 with PHP and 30.6 without PHP for reaction conditions of 500 psig H_2 at 400 °C. At 440 °C and 500 psig H_2, the moles of H_2 accepted were 48.6 with PHP compared to 65 without PHP. Likewise, at 1250 psig H_2 and 440 °C, the moles H_2 accepted were 54.8 with PHP and 77.1 without PHP. The reactions with MoNaph+S at 440 °C and 500 or 1250 psig H_2 reacted with PHP resulted in slightly less H_2 accepted than the reactions with BENZ alone.

In N_2, a background level of DPM was observed for both thermal and catalytic reactors. This hydrogen could have been transferred from H_2 released if any dimerization of BENZ occurred. However, the moles of H_2 accepted by BENZ in N_2 was less when BENZ was reacted alone than that accepted in N_2 with PHP present.

Resid Analysis. The solvent fractionation of two resids that were available in our laboratory was performed. The resids were fractionated to determine if they contained different amounts of oils and asphaltenes. The resid LHC-362 contained considerably more hexane solubles at 83.4% that did Maya at 62.8% (Table 9). These resids will be used in the initial work that is done. However, resids of different naphthene contents, high, medium, and low, are being sought for the project.

Synthesis of Perhydropyrene. The supplier of PHP has ceased to carry the chemical. Hence, some preliminary work was performed in order to synthesize PHP from PYR. The synthesis of PHP was based on the information given in U.S. Patent 3,303,227. The reaction was begun with PYR since no partially hydrogenated pyrenes were available. Initially, reactions were performed with presulfided $NiMo/Al_2O_3$; however, insufficient hydrogenation of PYR occurred. The catalyst was then changed to Pt/Al_2O_3. The hydrogenation of PYR was then

performed in microtubular reactors. A reaction temperature of 375 °C was used after several other reaction temperatures were tested. The reaction was performed in three stages. After the first 5 hr, the reaction was stopped and a sample taken. The primary product was DCP; a small amount of PHP was formed (Table 10). Additional catalyst and hydrogen was added to the reactor and the reaction was performed for another 3 hr. After a cumulative reaction time of 8 hr, 86.6% PHP was formed. An additional 4 hr of reaction had no effect on the product distribution. Hence, at 375°C the reaction seemed to reach equilibrium. Other reaction conditions will be evaluated in order to determine if more PHP can be formed.

Summary and Future Work

The research performed this quarter involved both experimental and calculational work. Calculation of the amount of H_2 accepted based on 100 moles of product for the phenanthrene and perhydropyrene system showed that more H_2 was accepted at all the reaction conditions when PHP was present than when it was not present. At the lower temperature of 400 °C, the presence of PHP made a greater difference than at 440 °C.

Reactions were also performed using benzophenone as an acceptor. Benzophenone was quite reactive under high temperature and catalytic conditions. For BENZ, the presence of PHP was detrimental to the amount of H_2 accepted in the reactions performed in a H_2 atmosphere. More H_2 was accepted by BENZ in the reaction where it was reacted alone. In N_2 the opposite was true; BENZ accepted more H_2 when PHP was present than when BENZ was reacted alone.

Next quarter, experimentation will begin using resids. Initially, the resids will be separated into saturate and aromatic fractions in order to evaluate the amount of naphthenes present and also to determine the effect of naphthenes on the coprocessing of coal with resids.

Table 1. Reactions of Perhydropyrene and Phenanthrene at 400°C[a]

Reaction Condition	Atmosphere	PHP:PHEN Ratio	Product Distribution (mol%)			PHEN Conversion %	H_2 Accepted[e] Based on 100 moles of Product (mol)	H_2 Donated[f] Based on 100 moles of Product (mol)
			PHEN[c]	DHPN	THPN			
Thermal	H_2	5:1	95.4(1.2)	1.8(0.4)	2.8(0.8)	4.6	7.4(2.1)	1.8(0)
MoNaph+S[b]	H_2	5:1	82.8(0.1)	10.7(0.6)	6.5(0.1)	17.2	23.7(0.1)	6.3(0)
NiOct	H_2	5:1	94.2(0.1)	2.0(0.1)	3.8(0.0)	5.8	9.6(0.1)	1.7(0.1)
Thermal	H_2	1:1	97.1(0.2)	1.5(0.0)	1.4(0.2)	2.9	4.4(0.3)	1.2(0.1)
MoNaph+S	H_2	1:1	86.9(2.0)	9.0(1.5)	4.1(0.5)	13.1	17.2(2.5)	6.2(0)
NiOct	H_2	1:1	97.9(0.1)	1.1(0.3)	1.0(0.3)	2.1	3.1(0.7)	1.7(0.1)
Benzothiophene[d]	H_2	1:1	98.1(0.5)	0.9(0.3)	1.0(0.3)	1.9	2.9(0.7)	0.0(0)
Thermal	N_2	5:1	98.4(0.2)	0.0	1.6(0.2)	1.6	3.2(0.4)	3.8(0)
MoNaph+S	N_2	5:1	99.0(0.0)	0.0	1.0(0.0)	1.0	2.0(0.0)	3.9(0)

[a] Reaction Conditions: 30 min; 1250 psig H_2 or N_2 charged at ambient temperature.
[b] Mo = Mo naphthenate
Ni = Ni octoate
S = sulfur
[c] PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene
[d] Benzothiophene: 1000 ppm S used as a catalyst to promote hydrogen transfer between cycloalkanes and aromatics.
[e] H_2 Accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100
[f] H_2 Donated = (3 x DCP mol% + 5 x HHP mol% + 6 x THP mol% + 7 x DHP mol% + 8 x PYR mol%) x 100

Table 2. Reactions of Perhydropyrene and Phenanthrene at 440°C[a]

Reaction Condition	Atmosphere	PHP:PHEN Ratio	Product Distribution (mol%)			PHEN Conversion (%)	H_2 Accepted Based on 100 moles of Product[d] (mol)	H_2 Donated Based on 100 moles of Product (mol)
			PHEN[c]	DHPN	THPN			
Thermal	H_2	5:1	87.1(1.1)	9.0(0.0)	3.9(1.2)	12.9	16.8(2.3)	8.6(0.1)
MoNaph+S[b]	H_2	5:1	79.5(3.6)	14.9(2.1)	5.6(1.5)	20.5	26.2(5.1)	10.7(0.6)
NiOct	H_2	5:1	87.0(3.4)	9.0(1.3)	4.0(2.1)	13.0	17.1(5.4)	8.7(0)
Thermal	H_2	1:1	93.2(1.4)	4.4(0.8)	2.4(0.6)	6.8	9.3(2.1)	0.9(0.1)
MoNaph+S	H_2	1:1	87.2(1.3)	9.9(0.7)	2.9(0.6)	12.8	15.8(1.9)	7.5(0.1)
S	H_2	1:1	93.3(0.0)	5.1(0.0)	1.5(0.0)	6.7	8.2(0.0)	7.5(0)
MoNaph+S	N_2	5:1	97.8(0.2)	0.5(0.1)	1.7(0.7)	2.2	3.9(1.0)	8.9(0.1)

[a] Reaction Conditions: 30 min; 1250 psig H_2 or N_2 at ambient temperature.
[b] MoNaph = Mo naphthenate
NiOct = Ni octoate
S = sulfur
[c] PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene
[d e] H_2 Accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100
[e] H_2 Donated = (3 x DCP mol% + 5 x HHP mol% + 6 x THP mol% + 7 x DHP mol% + 8 x PYR mol%) x 100

Table 2. Reactions of Perhydropyrene and Phenanthrene at 440°C[a]

Reaction Condition	Atmosphere	PHP:PHEN Ratio	Product Distribution (mol%)			PHEN Conversion (%)	H_2 Accepted Based on 100 moles of Product[d] (mol)	H_2 Donated Based on 100 moles of Product (mol)
			PHEN[c]	DHPN	THPN			
Thermal	H_2	5:1	87.1(1.1)	9.0(0.0)	3.9(1.2)	12.9	16.8(2.3)	8.6(0.1)
MoNaph+S[b]	H_2	5:1	79.5(3.6)	14.9(2.1)	5.6(1.5)	20.5	26.2(5.1)	10.7(0.6)
NiOct	H_2	5:1	87.0(3.4)	9.0(1.3)	4.0(2.1)	13.0	17.1(5.4)	8.7(0)
Thermal	H_2	1:1	93.2(1.4)	4.4(0.8)	2.4(0.6)	6.8	9.3(2.1)	0.9(0.1)
MoNaph+S	H_2	1:1	87.2(1.3)	9.9(0.7)	2.9(0.6)	12.8	15.8(1.9)	7.5(0.1)
S	H_2	1:1	93.3(0.0)	5.1(0.0)	1.5(0.0)	6.7	8.2(0.0)	7.5(0)
MoNaph+S	N_2	5:1	97.8(0.2)	0.5(0.1)	1.7(0.7)	2.2	3.9(1.0)	8.9(0.1)

[a] Reaction Conditions: 30 min; 1250 psig H_2 or N_2 at ambient temperature.
[b] MoNaph = Mo naphthenate
NiOct = Ni octoate
S = sulfur
[c] PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene
[d e] H_2 Accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100
[e] H_2 Donated = (3 x DCP mol% + 5 x HHP mol% + 6 x THP mol% + 7 x DHP mol% + 8 x PYR mol%) x 100

Table 3. Reactions of Phenanthrene at 400 and 440°C[a]

Reaction Condition	Atmosphere	Temperature (°C)	Product Distribution (mol %)			PHEN Conversion (%)	H_2 accepted (mol) Based on 100 mol Product[d]
			PHEN[c]	DHPN	THPN		
Thermal	H_2	400	95.3(0.7)	2.6(0.5)	2.1(0.2)	4.7	6.8(0.9)
MoNaph+S[b]	H_2	400	91.0(0.0)	6.0(0.0)	3.0(0.1)	9.0	12.0(0.1)
NiOct	H_2	400	98.4(0.4)	0.7(0.4)	0.9(0.0)	1.6	2.5(0.4)
Thermal	H_2	440	90.9(1.2)	5.9(0.7)	3.2(0.5)	9.1	12.3(1.7)
MoNaph+S	H_2	440	81.3(3.8)	12.8(2.4)	5.9(1.4)	18.7	24.6(5.2)

[a] Reaction Conditions: 30 min; 1250 psig H_2 at ambient temperature.
[b] MoNaph = Mo naphthenate
NiOct = Ni octoate
S = sulfur
[c] PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene
[e] H_2 Accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100

Table 4. Comparison of H_2 Accepted in Reactions of Perhydropyrene with Phenanthrene and Phenanthrene Alone

Reaction Condition	Atmosphere	Temperature (°C)	H_2 Accepted Based on 100 moles of Product (mol)	
			PHEN	PHP:PHEN 5:1
Thermal	H_2	400	6.8(0.9)	7.4(2.1)
MoNaph+S	H_2	400	12.0(0.1)	23.7(0.1)
NiOct	H_2	400	2.5(0.4)	9.6(0.1)
Thermal	H_2	440	12.3(1.7)	16.8(2.3)
MoNaph+S	H_2	440	24.6(5.2)	26.2(5.1)

Table 5. Product Distributions from Reactions of Benzophenone and Perhydropyrene[a]

Reaction[a] Condition	Catalyst Loading (ppm)	Atmos-phere	Pressure (psig)	Reaction Tempera-ture (°C)	Product Distribution (mole %)								H_2 Accepted Based on 100 moles of product	H_2 Donated Based on 100 moles of product
					BENZ[d]	DPM	PHP	DCP	HHP	THP	DHP	PYR		
Thermal	0	H_2	500	400	82.6 (5.4)	17.4 (5.4)	99.6 (0)	0.40 (0)	0	0	0	0	17.4	1.2
Thermal	0	H_2	500	440	51.4 (0.4)	48.6 (0.3)	97.0 (0.3)	0.9 (0.05)	0.7 (0.0)	0.7 (0.1)	0	0.7 (0.1)	48.6	16.0
Thermal	0	H_2	1250	440	45.2 (1.3)	54.8 (1.3)	99.1 (0.5)	0.6 (0)	0.2 (0.02)	0.0 (0)	0	0.1 (0)	54.8	3.6
Mo Naph +S[b]	500	H_2	500	440	0.2 (0.1)	99.8 (0.1)	96.4 (0.3)	1.1 (0.0)	1.3 (0.1)	0 (0)	0	1.2 (0.3)	99.8	19.4
Mo Naph+S	500	H_2	1250	440	9.0 (1.3)	91.0 (1.3)	97.8 (0.5)	0.7 (0)	0.4 (0)	0.3 (0)	0	0.8 (0)	91.0	12.2
Thermal[c]*	0	N_2	500	440	94.5	5.5	98.3	0.6	0.3	0	0.3	0.5	5.5	9.4
Mo Naph+S	1000	N_2	500	400	92.4	7.6	98.1	0.3	0.4	0.2	0	0.9 (0.3)	7.6	10.5
Mo Naph+S	1000	N_2	1250	400	96.2 (0.1)	3.8 (0.1)	97.2 (1.5)	0.5 (0.1)	1.5 (0.1)	0	0	0.8 (0.4)	3.8	15.4
MoNaph+S[c]*	1000	N_2	500	440	94.0 (0.4)	6.0 (0.4)	98.0 (0.3)	0.3 (0.1)	0.8 (0.1)	0	0	0.9 (0.3)	6.0	12.1

[a]Reaction Conditions: 30 min, 1:1 BENZ to PHP weight ratio
[b]Mo Naph + S = Mo Naphthenate + Sulfur
[c]Numbers in parenthesis are standard deviations
[d]BENZ = benzophenone; DPM = diphenylmethane; PHP = perhydropyrene; DCP = decahydropyrene; HHP = hexahydropyrene; THP = tetrahydropyrene; DHP = dihydropyrene; PYR = pyrene
[e]Only one reaction performed.
*Asterik indicates reactions performed in July.

Table 6. Product Distribution from Reactions of Benzophenone[a]

Reaction Condition	Catalyst Loading (ppm)	Atmosphere	Pressure	Reaction Temperature (°C)	Product Distribution (mol%)		BENZ Conversion (%)
					BENZ	DPM	
Thermal	0	H_2	500	400	69.4(4.0)[c]	30.6(4.0)	30.6
Thermal	0	H_2	500	440	35.0(6.2)	65.0(6.2)	65.0
Thermal	0	H_2	1250	440	22.9(2.5)	77.1(2.5)	77.1
MoNaph+S*	1000	H_2	500	400	4.2(0.8)	95.8(0.8)	95.8
MoNaph+S*	500	H_2	500	440	0.(0)	100.0(0)	100
MoNaph+S*	500	H_2	1250	440	0.2(0)	99.8(0)	99.8
MoNaph+S*[d]	1000	H_2	500	440	0.4(0.2)	99.6(0.2)	99.6
MoNaph+S*	1000	H_2	1250	440	1.8(0.1)	98.2(0.1)	98.2
Thermal*	0	N_2	500	400	97.5(0.8)	2.5(0.8)	2.5
MoNaph+S*	1000	N_2	500	400	97.8(0.5)	2.2(0.5)	2.2
Thermal*	0	N_2	500	440	98.9(0.0)	1.1(0.0)	1.1
MoNaph+S*	1000	N_2	500	440	94.2(0.7)	5.8(0.7)	5.8

[a]Reaction Conditions: 30 min, 0.1 g of BENZ
[b]BENZ = benzophenone, DPM = diphenylmethane
[c]Numbers in parenthesis indicate standard deviation
[d]*indicate reactions performed during July

Table 7. Comparison of H_2 Accepted in Reactions of Perhydropyrene with Benzophenone and Benzophenone Alone

Reaction Condition	Catalyst Loading (ppm)	Atmosphere	Pressure (psig)	Temperature (°C)	H_2 Accepted Based on 100 moles of Product (mol)	
					BENZ	BENZ+PHP
Thermal	0	H_2	500	400	30.6	17.4
Thermal	0	H_2	500	440	65.0	48.6
Thermal	0	H_2	1250	440	77.1	54.8
MoNaph+S	500	H_2	500	440	100.0	99.8
MoNaph+S	500	H_2	1250	440	99.8	91.0
Thermal	0	N_2	500	440	1.1	5.5
MoNaph+S	1000	N_2	500	400	2.2	7.6
MoNaph+S	1000	N_2	500	440	5.8	12.1

Table 8. Reaction Products from Catalytic Anthracene Reaction in Hydrogen at 440°C[a]

Reaction Condition	Product Distribution (mol%)			H_2 Accepted Based on 100 moles of Product
	ANT[b]	DHA	THA	
ANT alone	9.33 (0.52)	81.34 (0.74)	9.33 (1.27)	100
ANT + PHP	9.59	72.61	17.80	108.21

[a] Reaction Condition: Mo naphthenate, 500 ppm, 440°C, 1250 psig N_2, 30 min.
[b] ANT = anthracene, THA = tetrahydroanthracene, DHA = dihydroanthracene.

Table 9. Analysis of Resid

Resid[a]	Hexane Soluble	Toluene Solubles	THF Solubles
LHC-362	83.4(1.1)	14.8(0.3)	1.8(0.8)
Maya	62.8(1.1)	37.2(1.1)	0(0)

[a]Resids Obtained from Amoco

Table 10. Catalytic Hydrogenation of Pyrene[a]

Composition	After 5 Hours	After 8 Hours	After 12 Hours
PHP	6.7	86.6	87.0
DCP	40.6	5.5	5.4
HHP	16.7	2.5	2.4
THP	27.6	4.0	3.9
DHP	5.1	0.7	0.7
PYR	3.3	0.7	0.5

Reaction Conditions: 375°C, 1250 psig H_2 at ambient, 0.3 g Pt/Al_2O_3 for the first stage. Each subsequent stage contained an additional 0.3 g Pt/Al_2O_3 and 1250 psig H_2 charged at ambient temperature.

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