

Hydrodenitrogenation of Quinoline and Coal Using Transition Metal Sulfides

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This study investigates the effectiveness of unsupported, precipitated transition metal sulfides as HYD and HDN catalysts in both a quinoline system and a coal liquefaction system. The transition metal sulfides of moderate surface areas were produced by a method developed by Chianelli and Dines (1) in the late 1970's. These materials crystallize in weakly interacting layers which allow for ready intercalation of appropriate species. A number of different transition metal sulfides have been tested for HDS activity using dibenzothiophene (2) and are good candidates for hydrodenitrogenation (HDN) studies. The degree of HYD and HDN of quinoline and the reaction products from coal liquefaction were determined using precipitated transition metal sulfides and compared to commercial transition metal sulfides, commercial hydrotreating catalysts such as CoMo/Al₂O₃ and NiMo/Al₂O₃, and platinum containing catalysts such as Pt/SiO₂ and PtS₂.

Experimental

Preparation of Catalysts. Each precipitated transition metal sulfide was prepared by dissolving the metal chloride in ethyl acetate (EA) which was then added to a slurry of lithium sulfide (Li₂S), precipitating the metal sulfide. The product was annealed with pure H₂S at 400°C, washed with 12% acetic acid and then sulfided with 10% H₂S/H₂ at 400°C for 1 hour. The metal chlorides used were CrCl₃, MoCl₄, WCl₆, FeCl₃ and RuCl₃·3H₂O, producing Cr₂S₃, MoS₂, WS₂, FeS_x and RuS₂. All of the chemicals required for synthesis were obtained from Alfa Chemicals.

The composition of the metal sulfides was confirmed by X-ray diffraction by matching the d spacings of the sample with the reference. The experimental data matched the standards sufficiently to confirm the identity of the metal sulfides listed above. Sulfur analyses of both the precipitated and commercial transition metal sulfides are compared to the theoretical in Table 1. Surface area measurements by dynamic B.E.T. using N₂ in He are also given in Table 1. Differences in the surface areas of different batches of a given transition metal sulfide reflect the sensitivity of the surface area to preparation methods.

A platinum on silica (Pt/SiO₂) catalyst was prepared by adding 0.44 g SiO₂ to 12.46 g of a 5% solution of hydroplatanic acid. Water was removed by vacuum rotary evaporation and the catalyst was dried for 16 hr at 50°C under 25 mm Hg. After grinding, the Pt/SiO₂ was reduced in a 40 ml/min H₂ flow producing a slivery black material. PtS₂ was obtained from Alfa Chemicals. The NiMo/Al₂O₃ and CoMo/Al₂O₃ catalysts were presulfided in a stream of 10 volume percent H₂S in H₂; sulfiding was begun at 250°C and the temperature was raised by 50°C every fifteen minutes until 400°C was reached and maintained for one hour. Both catalysts were ground before use.

Quinoline Model System. Reactions were performed with the precipitated and commercial transition metal sulfides, Pt/SiO₂, PtS₂, CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts in 15 cm³ stainless steel tubing bomb reactors. Two weight percent quinoline in hexadecane was used as the reactant solution (5 g) with 0.025 g catalyst and 1250 psi hydrogen (cold). The reactor was maintained at 380°C while being agitated at 850 rpm. Most of the reactions were at least duplicated. Several lower temperatures were used with the Pt/SiO₂ catalyst. The liquid products were analyzed by gas chromatography using a fused silica 30 m capillary DB-5 column with a 0.2 micron film with FID detection and p-xylene as the internal standard. NH₃ was analyzed using a Chromosorb 103 column and TCD detection. Hydrogen consumption was determined using a molecular sieve column with TCD detection in conjunction with standard PVT methods.

Table 1. Analysis of Catalysts

Catalyst	Sulfur, %		Surface Area, m ² /g
	Sample	Theoretical	
Cr ₂ S ₃ -4	44.0	48.1	19.5
Cr ₂ S ₃ -C	49.6	48.1	12.5
MoS ₂ -3	37.7	40.1	30.8
MoS ₂ -7		40.1	24.1*
MoS ₂ -C	41.1	40.1	10.7
WS ₂ -2	25.1	25.9	13.5
WS ₂ -4		25.9	
WS ₂ -C	24.9	25.9	8.5
FeS-2	39.1	36.5	6.7
FeS ₂ -C	57.2	53.5	4.9
RuS ₂ -3	30.2	38.8	26.4*
			19.4
RuS ₂ -5			81.5*
NiMo/Al ₂ O ₃			174
CoMo/Al ₂ O ₃			180

*Analyses performed by Quantachrome Corporation

The concentration of the liquid phase products is given for each compound as a mole percentage of quinoline initially charged to the reactor. The data is summarized in terms of percent of maximum hydrogenation (PMH), percent hydrodenitrogenation (PHDN), and percent hydrogenolysis (PHYG). PMH is the number of moles of hydrogen required to produce the observed product distribution from quinoline as a percentage of the hydrogen required to produce the final end product, propylcyclohexane (PCH). PHDN is calculated by summing the mole percentage for the components which do not contain nitrogen. PHYG is obtained by summing the mole percentages for the compounds which have resulted from hydrogenolysis of the C-N bond.

Coal Liquefaction Reactions. Ground Kentucky #11 coal with a nitrogen content of 1.10% was used in the liquefaction reactions. Two batches of coal were used: Batch A, kept in a desiccator, dried during the course of the experiments, while the moisture content of Batch B remained fairly constant. Thermal and several catalytic reactions were performed using Batch A; the product distributions were corrected for the changing moisture composition of the coal.

Coal liquefaction reactions were performed with MoS₂, RuS₂, NiMo/Al₂O₃, and Pt/SiO₂ as well as thermally in 46 cc stainless steel tubing bomb reactors. The charge to the reactor was 0.5 g of coal with 0.5 g anthracene as solvent. Reactions were performed at 425°C for 60 minutes at an agitation rate of 850 rpm. Recovery of the product from the reactor was based upon the weights of the solid and liquid fractions. In calculating the product distributions, all losses were equally distributed among the solid and liquid fractions. The product distribution is reported on a maf coal basis.

The liquid and solid products were separated by sequential washing with methylene chloride - methanol (9:1 v/v) solution (MCM) and tetrahydrofuran (THF). This separation produced three fractions: MCM solubles (MCMS), MCM insolubles-THF solubles (THFS) and THF insolubles or ash-free insoluble organic matter (IOM). The MCMS fraction was further fractionated by the chromatographic method of Boduszynski et al.(3) into compound-class fractions: hydrocarbons (HC), nitrogen heterocycles (NH), hydroxylaromatics (HA) and polyfunctional compounds (PC). Model compounds such as anthracene, acridine, carbazole and 2-naphthol, were chromatographed and verified the procedure. The hydrocarbon fraction separated from the MCMS fraction was further analyzed for anthracene hydrogenation products using the same capillary column as for quinoline. The sample, dissolved in toluene with phenanthrene as the internal standard, was analyzed isothermally at

180°C. Anthracene and three major hydrogenation products were observed: 9,10-dihydroanthracene (DHA), 1,4,5,8,9,10-hexahydroanthracene (HHA), and 1,2,3,4,5,6,7,8-octahydroanthracene. In some reactions, a corrected sum (CRS) is used which includes the light cracked products produced during the reaction assuming a response factor of unity and disregarding molecular weight changes. This CRS was required to obtain reasonable recovery values due to cracking of anthracene during the reaction. The anthracene products are reported as a percentage of the anthracene charged, the sum of which represents the recovered anthracene.

Results and Discussion

The activity and selectivity of precipitated transition metal sulfides for HDN of quinoline were compared to that of NiMo/Al₂O₃, CoMo/Al₂O₃, commercial transition metal sulfides and Pt/SiO₂. Several transition metals from groups 6B and 8A were chosen. The catalysts which showed the highest level of HYD and HDN activity in the quinoline system were used for the coal liquefaction reactions. Quinoline Reaction System. The reaction pathway (Figure 1) for quinoline under catalytic conditions has been extensively investigated by Satterfield and coworkers (4-6). In the current study, the gaseous and liquid products from both thermal and catalytic reactions were analyzed and reasonable recoveries of the liquid products were attained. Methane (CH₄) was the only hydrocarbon gas observed. The ammonia (NH₃) observed was usually much less than it should have been based upon the denitrogenation of the liquid products. Solubility experiments in hexadecane showed that ~70% of the hexadecane was absorbed by the solvent, yielding low recoveries.

The product distribution achieved from the thermal and catalytic quinoline reactions are given in Table 2. The PMH and PHDN terms are good indicators of HYD activity and HDN selectivity. Precipitated RuS₂ and supported NiMo/Al₂O₃ showed the highest and nearly equivalent PMH of ~49%. Precipitated MoS₂ produced a PMH of ~42% and CoMo/Al₂O₃, 39%, while the other catalysts yielded lesser amounts of hydrogenation, ranging from 24 to 30% PMH. The catalysts can be ranked according to their ability to hydrogenate quinoline in terms of PMH: RuS₂-3 = NiMo/Al₂O₃ > MoS₂-3 = CoMo/Al₂O₃ > WS₂-2 = Cr₂S₃ -4 > FeS_x-2 > thermal. The number to the right of the sulfide indicates the batch number. Precipitated RuS₂ achieved the highest PHDN of 10.8%; NiMo/Al₂O₃ and precipitated MoS₂ achieved 8.9% and 8.0%, respectively. Likewise, RuS₂-3 and NiMo/Al₂O₃ also gave the highest PHYG, but, in this case, RuS₂ with a PHYG of 17.3% was substantially more effective than NiMo/Al₂O₃ at 10.2%. The remaining catalysts and the thermal reaction showed no denitrogenation and little hydrogenolysis.

A comparison of the precipitated transition metal sulfides to their commercial or mineralogical analogues is given in Table 3. Commercial RuS₂ was not available. Only in the case of WS₂ did the commercial metal sulfide give the same degree of HYD activity as the precipitated metal sulfide. For both MoS₂ and Cr₂S₃, the precipitated sulfide gave higher HYD activity and for MoS₂ higher PHDN and PHYG.

Table 3. Activity and Selectivity Comparison of Precipitated to Commercial Transition Metal Sulfides

Catalyst	PMH, %	PHDN, %	PHYG, %
None	5.0	0.0	0.0
Cr ₂ S ₃ -4	28.8	0.0	0.0
Cr ₂ S ₃ -C	25.9	0.0	3.1
MoS ₂ -3	41.7	8.0	10.4
MoS ₂ -C	29.4	0.0	1.7
WS ₂ -2	30.9	0.4	2.4
WS ₂ -C	32.9	0.0	2.5

Since NiMo/Al₂O₃ and precipitated RuS₂ gave comparable PMH of quinoline, the

Table 2

Product Distribution from Thermal and Catalytic Quinoline Reactions

Type Catalyst	None	Cr ₂ S ₃ -4	MoS ₂ -3	WS ₂ -2	FeSx-2	RuS ₂ -3	CoMo/Al ₂ O ₃	NiMo/Al ₂ O ₃
Mole NH ₃ x 100%								
Mole QI	2.8	0.2+0.1	2.8+1.5	0.34+0.48	0+0	0.42+(-)		1.06+1.4
Mole% CH ₄	0	0+0	0	0+0	0+0	0+(-)		0.004+0.006
H ₂ consumption, %	7.7	1.5+4.9	11.8+6.9	-7.1+7.1	3.3+15.6	18.1+(-)		13.1+18.6
M Q C	0+0	0+0	1.6+0.2	0.2+0	0+0	7.7+1.0	0.5+0.0	4.1+0.4
o u h	0+0	0+0	6.4+0.0	0.2+0.1	0+0	3.1+0.2	1.9+0.1	4.9+0.2
l i a	0+0	0.6+0.5	19.7+1.1	4.8+0.1	0.5+0.1	26.8+0.4	19.9+0.8	32.1+2.6
e n r	0+0	0.3+0.4	4.6+0.4	1.0+0.1	0.6+0.1	4.8+1.6	4.2+0.1	7.0+1.0
o g	0.2+0.3	1.2+1.1	2.4+0.7	0.5+0.1	1.4+0	1.8+0.2	1.2+0.1	3.3+0.8
% l e	0+0	3.1+0.1	2.4+0.1	0.9+0	0+0	6.5+0.4	1.3+0.2	1.3+0.1
i d	82.7+3.3	2.2+0.3	2.0+0.6	1.7+0	16.4+5.6	1.0+0	1.6+0.0	1.2+0.4
e	17.1+3.0	92.7+1.6	61.6+0.3	90.8+5.6	81.7+5.6	48.6+3.0	69.6+0.9	46.4+2.6
PMH, %	5.0+0.9	28.8+0.5	41.7+1.0	30.9+0.1	24.5+1.6	49.1+1.4	39.0+0.3	49.5+1.8
PHDN, %	0+0	0+0	8.0+0.2	0.4+0.1	0+0	10.8+1.2	2.4+0.1	8.9+0.1
PRB, %	0+0	3.1+0.1	10.4+0.1	1.3+0.1	0+0	17.3+1.6	3.7+0.4	10.2+0.0
Recovery, %	90.4+1.6	83.6+5.7	75.5+18.9	88.2+1.6	86.2+6.8	89.5+1.6	89.1+5.1	79.1+15.3

Reaction Conditions:

Time	30 min	PCH	propylcyclohexane
Temperature	380°C	PB	propylbenzene
Agitation Rate	850 cpm	DHQ	decahydroquinoline
H ₂ Charged Cold	1250 psig	CHP	2,3-cyclohexenopyridine
Reactant	2 wt% quinoline in hexadecane	PA	o-propylaniline
Reactor	15 cc microreactor	Q	quinoline
Catalyst Charge	~5.10 x 10 ⁻³ g catalyst g reaction mixture	THQ	1,2,3,4-tetrahydroquinoline

Compounds:

PCH	propylcyclohexane
PB	propylbenzene
DHQ	decahydroquinoline
CHP	2,3-cyclohexenopyridine
PA	o-propylaniline
Q	quinoline
THQ	1,2,3,4-tetrahydroquinoline

catalytic activity and selectivity of these two catalysts were tested with two individual products from quinoline hydrogenation: 1,2,3,4- tetrahydroquinoline (THQ) and 2-propylaniline (PA). The two catalysts achieved similar PMH and PHDN of THQ. NiMo/Al₂O₃ yielded more cis and trans decahydroquinoline (DHQ) than RuS₂ which produced more PA and nearly twice as much PHYG. When PA was used as the reactant, more hydrogenation and denitrogenation of PA was achieved with NiMo/Al₂O₃ than RuS₂. The lesser ability of RuS₂ to convert PA may explain the larger amount of PA observed in the THQ reaction with RuS₂.

Table 4. Catalytic Activity of NiMo/Al₂O₃ and RuS₂ in Several Reactant Systems

Catalytic Activity with THQ as a Reactant			
	Thermal	NiMo/Al ₂ O ₃	RuS ₂
PMH of THQ, %	0.7	27.8	25.4
PHDN, %	0.0	7.4	8.9
PHYG, %	0.0	8.5	14.6
Catalytic Activity with Propylaniline as Reactant			
PMH of PA, %	0.0	68.5	30.1
PHDN, %	0.0	81.4	36.5
Catalytic Activity with Propylaniline and Quinoline as Reactants			
PMH of PA, %		27.1	22.6
PHDN, %		35.6	27.1

To simulate the quinoline reaction system, 0.2 wt % quinoline was added to the PA solution (2 wt %). Quinoline served as a leveler of catalytic activity. The NiMo/Al₂O₃ was severely poisoned resulting in substantial reductions in both the HYD and HDN ability of NiMo/Al₂O₃ while RuS₂ was affected to a lesser extent showing a one-third reduction in PMH and PHDN. Thus, the presence of basic nitrogen in quinoline and THQ reduced the inherent activity of NiMo/Al₂O₃ to make NiMo/Al₂O₃ effectively equivalent to RuS₂ in both activity and selectivity in the quinoline system.

Recently, a catalyst containing 40% reduced Pt on silica has been shown to be an active HDN catalyst (7). The HDN ability of Pt/SiO₂ in the quinoline model system was investigated at temperatures ranging from 200 to 380°C as shown in Table 5. At 200°C, Pt/SiO₂ achieved the same activity as Cr₂S₃ and WS₂ at 380°C, with a PMH of ~35%. The activity of Pt/SiO₂ increased with temperature up to 340°C yielding 71% PMH and 9.8% PHDN; the PHDN was similar to that of RuS₂ with Pt/SiO₂ at 380°C. None of the products from the quinoline reaction pathway was observed; only higher boiling compounds were present. Even the solvent hexadecane was no longer present.

Table 5. Effect of Temperature on Activity of Pt/SiO₂ for Quinoline Hydrodenitrogenation

Temperature, °C	200	250	300	320	340	380
M Q C PCH	0	0	1.9	3.4	9.7	0
o u h PB	0	0	0	0	0.1	0
l i a DHQc	9.7	47.4	64.6	61.6	70.7	0
e n r DGQc	5.1	9.1	10.4	10.4	12.6	0
o g CHP	3.5	0.8	1.2	1.2	0.9	0
% l e PA	0	0	0	0	0.4	0
i d Q	0.9	1.0	0	0	0	0
n THQ	80.8	39.8	22.1	23.4	5.5	0
e						
PMH, %	34.0	53.4	62.1	61.8	71.3	-
PHDN, %	0	0	1.9	3.4	9.8	-
PHYG, %	0	0	1.9	3.4	10.2	-
Recovery, %	91.1	93.6	80.9	93.1	93.1	75.5

A comparison of the activity and selectivity of Pt/SiO₂, PtS₂ obtained from Alfa Chemicals and precipitated RuS₂ is given in Table 6. At 250°C, a temperature where Pt/SiO₂ showed considerable activity, PMH values of RuS₂ and PtS₂ showed equivalent HYD activity, ~29 to 30%, while Pt/SiO₂ showed considerably more, ~53%. None of the catalysts was able to denitrogenate quinoline and almost no hydrogenolysis occurred at this temperature.

Table 6. Comparison of the Activity and Selectivity of PtS₂, Pt/SiO₂ and RuS₂ in the Quinoline Model System at 250°C

Catalyst	PtS ₂ -C	Pt/SiO ₂ -1	RuS ₂
PMH, %	29.1	53.4	29.8
PHDN, %	0.0	0.0	0.0
PHYG, %	0.0	0.0	0.1

Coal Liquefaction Reactions. Two precipitated transition metal sulfides, RuS₂ and MoS₂, rivaled the commercial hydrotreating catalysts, NiMo/Al₂O₃ and CoMo/Al₂O₃, respectively, in their ability to hydrogenate and denitrogenate quinoline. Thus, RuS₂, MoS₂, NiMo/Al₂O₃ and Pt/SiO₂ were chosen as catalysts in coal liquefaction reactions to evaluate their efficiency in hydrogenating and removing nitrogen from coal.

Anthracene was used as the solvent for the coal liquefaction reactions. Since anthracene readily cracks under catalytic hydrogenation conditions (8), some hydrocracked products were expected; however, the presence of nitrogen heterocycles in the coal system moderated catalyst activity and reduced the amount of anthracene hydrocracking. For some of the reactions, the total anthracene products, including both hydrogenated and hydrocracked species, were measured, accounting for a 97 to 101% recovery of anthracene in thermal reactions and in reactions using NiMo/Al₂O₃ and RuS₂. However, when Pt/SiO₂ was used, only 74% recovery of the anthracene was achieved. With quinoline Pt/SiO₂ showed the production of high molecular weight materials at 380°C; this same phenomenon may have occurred in the coal reactions at the lower reaction temperature of 340°C.

The product distributions obtained from thermal and catalytic liquefaction reactions are given in Table 7. The reactions performed at 425°C yielded nearly equivalent coal conversions ranging from 94.5% for the thermal reaction to 99.0% for the reaction with RuS₂. The amount of light hydrocarbon gases produced was almost constant for all of the reactions yielding 15% for MoS₂ and RuS₂ and 14% for NiMo/Al₂O₃ while the thermal reaction produced nearly 19%. Therefore, the liquid products produced were quite similar in all reactions, ranging from 75.8% for the thermal reaction to 83.3% for RuS₂-5, thereby, providing a nearly equivalent basis for directly comparing the products from different reactions.

Comparing the product distributions, the sum of the polyfunctional compounds and THFS decreased from 20.5% for the thermal case to 9.0% for MoS₂-5&7, 6.4% for RuS₂-5 and 6.7% with NiMo/Al₂O₃. The total amount of product soluble in MCM increased by more than 10% in the catalytic compared to the thermal reactions. Considerably more of the heavier fractions was upgraded in the catalytic reactions producing a higher percentage of the products in the hydrocarbon (HC), nitrogen heterocycle (NH), and hydroxylaromatic (HA) fractions. In Figure 2, the product fractions produced from the different reactions are plotted against the catalyst specific surface area. The HC fraction produced followed the catalyst specific area: 17% for no catalyst, 34% for MoS₂-5&7, 49% for RuS₂-5 and 59% for NiMo/Al₂O₃. A maximum in Figure 2 is observed in the amount of NH produced, starting at 14% in the thermal reaction reaching ~19.5 and 18.2% with MoS₂-5&7 and RuS₂, respectively, and decreasing to ~11.0% with NiMo/Al₂O₃. Compared to the thermal reaction, the HA fraction decreased in the presence of the catalysts according to their specific surface area. Thus, the increased solubility of the coal-derived material in the MoS₂-5&7 and RuS₂ reactions was directly reflected in an increase in the NH and HC fractions since both the PC and HA fractions decreased. NiMo/Al₂O₃, attaining lower NH and higher HC fractions than the transition metal sulfides, performed better as a HDN catalyst than did RuS₂ in the coal

system.

Table 7. Product Distribution of Coal Liquefaction Reactions at 425°C

Type Catalyst	None	MoS ₂ -5&7	RuS ₂ -5	NiMo/Al ₂ O ₃
Surface Area, m ² /g	-	24.1	81.5	174
g cat/g reactant	0.20	0.20	0.20	0.20
Temperature, °C	425	425	425	425
H ₂ Consumption, %	6.2	8.5	14.2	15.3
Recovery, %	95.3	91.8	92.2	89.3
Coal Batch	A	A & B	B	B
M GAS	18.61	15.16	15.61	13.76
A M HC	17.02	34.08	48.83	58.80
F C NH	13.99	19.47	18.20	11.02
W M HA	24.36	20.11	10.33	6.74
t C S PC	9.70	2.98	0.61	1.82
O Total MCMS	65.07	76.64	77.97	78.37
% A THFS	10.78	6.01	5.83	4.85
L PC+THFS	20.48	8.99	6.44	6.67
IOM	5.54	2.19	1.05	3.04
Conversion, %	94.46	97.81	98.95	96.95
M A c DHA	16.11	13.36	4.00	2.17
o N h OHA	9.83	26.88	60.23	53.04
l T a HHA	58.43	38.26	17.97	16.30
e H r ANTH	2.61	0.20	0.0	0.0
g Total	86.97	79.05	80.49	71.51
% e CRS	96.96	-	101.91	100.55
d				

The anthracene hydrogenation products from the liquefaction reactions are plotted versus catalyst specific surface area in Figure 3. Anthracene is sequentially hydrogenated from anthracene to DHA to HHA to OHA, which then hydrocracks to lighter products. In the thermal reaction, 2.6% anthracene remained unconverted; this amount decreased rapidly below GC detectability limits under catalytic conditions. DHA and HHA were at a maximum in the thermal reaction and decreased as catalysts with increasing surface areas were used, while OHA showed a maximum at an intermediate catalyst surface area. Both the OHA maximum and decrease in the sum of the anthracene hydrogenation products were due to hydrocracking of OHA. The CRS of the anthracene products in Table 7 indicates that all the anthracene could be accounted for in hydrogenated and hydrocracked products.

Coal liquefaction reactions using Pt/SiO₂ employed two stage processing in which a thermal reaction at 425°C was performed to convert most of the coal, followed by an hour reaction at 340°C with Pt/SiO₂. The two stage reaction scheme was used to dissolve the coal in the first stage and possibly upgrade and eliminate some of the potential catalyst poisons before introduction of the catalyst. The Pt/SiO₂ did not produce either a satisfactory or a reproducible suite of products. High gas makes of ~34% were observed along with substantial losses in the HC fraction. The THFS amount was quite large ~38% compared to ~5 for the transition metal sulfides. Analysis of the anthracene solvent accounted for only ~74% of the original anthracene charged to the reactor, indicating production of higher molecular weight compounds as in the quinoline reaction.

Summary

Two precipitated transition metal sulfides MoS₂ and RuS₂ possessed both HYD activity and HDN selectivity in the quinoline model system. These transition metal sulfides rivaled the commercial hydrotreating catalysts in activity; RuS₂ was comparable to NiMo/Al₂O₃ and MoS₂ to CoMo/Al₂O₃. NiMo/Al₂O₃ possessed higher activity for PA hydrogenation than did RuS₂; however, RuS₂ was not as severely

poisoned by quinoline as NiMo/Al₂O₃. Pt/SiO₂ at 340°C was as active a catalyst for quinoline HDN as NiMo/Al₂O₃ at 380°C. Both precipitated MoS₂ and RuS₂ achieved upgrading in coal liquefaction reactions showing HYD activity; however, the higher surface area NiMo/Al₂O₃ showed greater HYD activity and considerably more nitrogen removal. Pt/SiO₂ was readily poisoned in the coal system and was not effective for coal HDN.

Table 8. Products from Two Stage Liquefaction Using Pt/SiO₂

Catalyst Loading		H ₂ Consumption, %	1.65 ± 2.33
g cat/g reactant	0.20	Recovery, %	111.74 ± 12.95
Temperature, °C	425/340	Coal Batch	B
(first stage/second stage)			
M GAS	33.81 ± 7.15	M A c DHA	4.48 ± 0.78
A M H	-9.57 ± 11.96	o N h OHA	40.92 ± 1.82
F C NH	19.13 ± 3.85	l T a HHA	14.79 ± 1.90
W M HA	24.09 ± 1.08	e H r ANTH	0.0 ± 0.0
t C S PC	4.95 ± 0.81	g Total	60.18 ± 4.50
O Total MCMS	38.95 ± 16.09	% e CRS	73.97 ± 10.85
% A THFS	33.29 ± 17.92	d	
L PC+THFS	38.24 ± 18.72		
IOM	-5.69 ± 8.97		
Conversion	105.69 ± 8.97		

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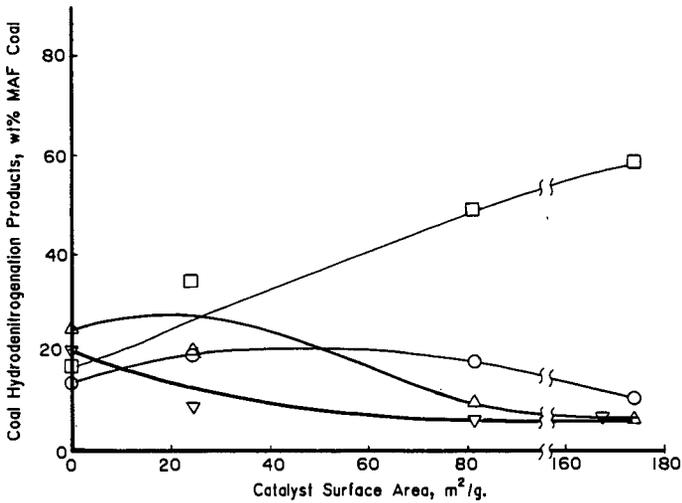


Figure 2. Effect of Catalyst Surface Area on Coal Hydrodenitrogenation Products: \square -Hydrocarbons, \circ -Nitrogen Heterocycles, \triangle -Hydroxyl Aromatics, ∇ -Polyfunctional Compound plus THF solubles.

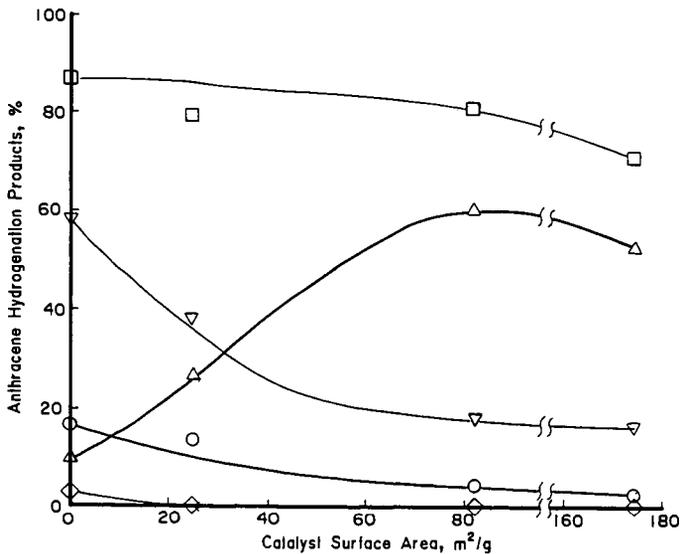


Figure 3. Effect of Catalyst Surface Area on Hydrogenation of Anthracene: \circ -DHA, \triangle -OHA, ∇ -HHA, \diamond -ANTH, \square -Sum.