

EVALUATION OF THE ACTIVITY OF NICKEL IN COPROCESSING USING MODEL SYSTEMS

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The coprocessing of coal with petroleum residuum offers an alternate technology to direct liquefaction by simultaneously upgrading coal, coal liquids and residuum into higher quality products (1-3). Residuum as the solvent contains indigenously the metals, nickel and vanadium, which may be present at a level of a few to several thousand ppm. The objective of this study is to evaluate the catalytic activity of the indigenous Ni in coprocessing by reacting model systems with Ni generated in situ from Ni complexes under coprocessing conditions.

Experimental

Model Reactants and Nickel Precursors. The model reactants used were naphthalene, indan, indene, benzothiophene, o-cresol, benzofuran, quinoline and indole. All of which were obtained from Aldrich. The nickel sources used were oil-soluble metal salts of organic acids, nickel naphthenate (NiNaph), and nickel octoate (NiOct), and solid complexes, nickel acetylacetonate (NiAcAc) and nickel citrate (NiCit), which were obtained from Air Products, Shepherd Chemical, Strem Chemical and Aldrich.

Reactions and Analyses. Hydrogenation reactions were conducted in 20 cm³ stainless steel microtubing bomb reactors. For each reaction, 4 grams of 2 weight percent naphthalene and/or 1 weight percent of each of the other reactants in hexadecane were charged. The nickel precursor was introduced at 2850 to 2950 ppm Ni; the Ni to reactant ratio was held constant. The reactions were conducted at 380°C for 30 minutes with 1250 psig H₂ (ambient) while being agitated at 550 cpm.

The liquid products were analyzed by gas chromatography using a 30m fused silica DB-5 column from J & W Scientific with FID detection and p-xylene as the internal standard. Some of the reaction products were identified by GC/MS using a VG 70EHF mass spectrometer and a Varian 3700 gas chromatograph.

Results and Discussion

The catalytic activity of Ni generated in situ from different nickel precursors were evaluated in the hydrogenation of hydrocarbons and heteroatomic species. The degree to which hydrogenation and heteroatom removal occurred in each reaction is reported in the defined terms of: (1) percent hydrogenation (% HYD) which is the number of moles of hydrogen required to achieve the final product distribution as a percentage of the moles of hydrogen required to achieve the most hydrogenated product; (2) percent hydrogenolysis (% HYG) which is the summation of the mole percents of products resulting from carbon-carbon or carbon-heteroatom bond cleavage; and (3) percent hydrodesulfurization (% HDS), percent hydrodeoxygenation (% HDO) and percent hydrodenitrogenation (% HDN) which are the summation of the mole percents of products not containing sulfur, oxygen, and nitrogen, respectively.

Catalytic Activities of Nickel from Different Precursors. The catalytic activity of in situ generated Ni catalysts produced from several different catalyst precursors were compared using a naphthalene-indan system at 380 and 400°C as shown in Table 1. Three of the Ni precursors, NiOct, NiCit, and NiAcAc, showed

activity for saturating the aromatic rings in both naphthalene and indan while NiNaph did not.

Effect of Sulfur. Since both residuum and coal contain substantial amounts of sulfur, the most likely form of Ni during coprocessing reaction is that of a sulfide. Sulfur was added to the naphthalene reactions to evaluate the catalytic activity of Ni sulfide during coprocessing. As shown in Table 2, elemental sulfur was added from zero to seven times the stoichiometric amount required to form Ni₃S₂, and organic sulfur as benzothiophene was added at a level of 0.1 to 1.0 weight percent. A small amount of sulfur completely inhibited the catalytic activity of Ni giving a % HYD of naphthalene similar to that observed with thermal reactions.

The inhibiting effect of sulfur on the catalytic activity of Ni from NiAcAc and NiCit was examined in naphthalene-indan combined reaction systems. When elemental sulfur was introduced at 0.01g level (2.3 times the amount of sulfur required to form Ni₃S₂) the naphthalene conversion was reduced from ~98% to 10% and 7%, respectively. No conversion of indan was observed.

Catalytic Activity of Ni for Saturating Aromatic Hydrocarbons. The activity of three different catalysts, NiOct, presulfided powdered NiMo/Al₂O₃ and in situ generated MoS₂ from molybdenum naphthenate, for saturating aromatic hydrocarbons are compared in Table 3. The model systems tested were reaction products observed from the model systems used in this study. Each reaction was reacted with the same amount of total metal, ~ 3000 ppm from each catalyst. Both NiOct and NiMo/Al₂O₃ showed high activity for saturating aromatic rings while MoS₂ did not. NiOct showed a higher activity for hydrogenating alkylaromatics to alkylalicyclics while presulfided NiMo/Al₂O₃ showed a higher activity for saturating aromatics to alicyclics and for slightly hydrogenolyzing aromatic and hydroaromatic species.

Catalytic Activity and Selectivity of Ni for Hydrogenation of Model Hydrocarbon and Heteroatomic Compounds. The catalytic activity and selectivity of Ni for hydrogenation, hydrogenolysis, and heteroatom removal were evaluated by performing reactions using partially saturated hydrocarbons, aromatics and heteroatom containing species.

Indan and Indene. The Ni catalysts produced from NiOct and NiAcAc showed high activity for saturating the aromatic ring of both indan and indene. The only products observed were saturated species of indan primarily hexahydroindan. No hydrogenolysis was observed.

Benzothiophene. Benzothiophene was not completely desulfurized with either NiOct or NiAcAc, producing ethylbenzene as the major product and dihydrobenzothiophene as the secondary product. Benzothiophene produced 25% HYD and 44% HDS with NiOct in the individual reaction and 26% HYD and 46% HDS in a combined system with naphthalene. The combined system with NiAcAc yielded 31% HYD and 54% HDS. Although NiAcAc yielded slightly higher desulfurization and conversion of benzothiophene, the presence of organic sulfur in benzothiophene appeared to severely poison both of these catalysts. The Ni catalysts did not show the activity previously observed for saturating aromatics in the presence of organic sulfur.

O-Cresol. O-cresol was highly reactive in the presence of NiOct where 98% was converted to methylcyclohexane and fully hydrogenated oxygen-containing hydrocarbons such as trans- and cis-methylcyclohexanol as the major product and methylcyclohexanone as the secondary product. In combined systems with either

naphthalene or indole, the products produced from o-cresol were very similar to those in the individual system. However, when elemental sulfur or benzothiophene was added to the system, the catalytic activity of Ni was completely eliminated. No o-cresol was converted.

Benzofuran. Nearly 100% of benzofuran was converted to alicyclic compounds but less than 17% of the oxygen was removed with NiOct. The major products were trans- and cis-ethylcyclohexanol and ethylcyclohexanone. All of the products produced were saturated yielding - 67% HYD. The hydrogenation of benzofuran remained the same when combined with naphthalene while HDO decreased to 7%. The addition of elemental sulfur or benzothiophene at 0.1 weight percent decreased the catalytic activity of Ni for benzofuran and yielded a product distribution similar to that of thermal reactions.

Indole. Indole was totally converted with NiOct or NiAcAc. Neither dihydroindole (indoline) nor o-ethylaniline was observed in the product distribution while small amounts of methylcyclohexane and ethylcyclohexane were observed. Several groupings of unknown chromatographic peaks with broad tailing that is usually characteristic of nitrogen containing compounds were observed. These peaks are postulated to be perhydroindole or o-ethylcyclohexylamine. The addition of sulfur to the reaction system completely eliminated any catalytic activity of NiOct and NiAcAc.

Quinoline. Hydrogenation of quinoline with NiOct or NiAcAc resulted in total conversion of quinoline; however, the reaction products typically seen from quinoline such as 1,2,3,4-tetrahydroquinoline, o-propylaniline, n-propylbenzene and n-propylcyclohexane were not present in the chromatograms (5). A small amount of 5,6,7,8-tetrahydroquinoline as well as a peak representing a substantial amount of decahydroquinoline was observed. Sulfur addition resulted in the elimination of the catalytic activity of the Ni catalyst and yielded a product slate similar to that of a thermal reaction.

Catalytic Reaction of Combined Systems. The effect of other hydrocarbon and heteroatomic compounds on the naphthalene hydrogenation in the presence of NiOct was evaluated. Table 4 shows the effects of these compounds on the hydrogenation of naphthalene. When reacted individually naphthalene yielded 36% tetralin and 64% decalin although the reproducibility was very poor. With the introduction of the other compounds, the reproducibility of naphthalene hydrogenation was improved substantially. None of the additional compounds except for benzothiophene had a significant effect on the naphthalene hydrogenation within the error bounds of the experiments.

Combining naphthalene or a mixture of naphthalene and other compounds with 0.1 weight percent and 1 weight percent benzothiophene severely inhibited the catalytic activity of NiOct. Under these conditions, naphthalene was hydrogenated only to the extent of that observed in thermal reactions.

Summary

The catalytic activity of the different Ni precursors for hydrogenating aromatics and partially hydrogenated aromatics ranked in the order of NiAcAc > NiCit > NiOct while NiNaph showed no activity. The reaction pathways observed with oxygen compounds such as o-cresol and benzofuran with NiOct produced methyl and ethyl cyclohexanols and methyl and ethyl cyclohexanones as the major products, respectively. The Ni catalyst from NiOct was highly active for hydrogenating both indole and quinoline but was not effective for removing nitrogen from the rings. Combinations of hydrocarbon and heteroatomic compounds

except for benzothiophene did not affect the hydrogenation of naphthalene in the presence of the Ni catalyst. However, even a small amount of elemental sulfur or benzothiophene completely inhibited the catalytic activity of Ni.

In actual coprocessing systems, a large portion of the nonporphyrinic complexes of Ni are contained in derivatives of naphthenic acid (6) which may be catalytically inactive based on the observed activity of NiNaph in this study. The sulfur content of both coal and residuum can be quite high (7,8). The release of this indigenous sulfur in the coprocessing system would readily poison any nickel released to the coprocessing system and render it inactive.

References

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Table 1. Catalytic Activity of Ni for Hydrogenation of Naphthalene and Indan Combined Using Different Precursors

	Ni Precursor			
	NiNaph	NiOct	NiCit	NiAcAc
<u>Reactions at 380°C</u>				
% HYD of Naphthalene*	2.4	71.3	97.0	98.8
% HYD of Indan*	0	84.0	100.0	100.0
<u>Reactions at 400°C</u>				
% HYD of Naphthalene	2.4	74.4	98.2	98.8
% HYD of Indan	0	85.0	100.0	99.0

Decalin and hexahydroindan were the most hydrogenated products from naphthalene and indan, respectively.

Table 2. Catalytic Activity of Ni for the Hydrogenation of Naphthalene in the Presence of Sulfur

<u>Amount of Elemental Sulfur^a</u>	<u>% HYD of Naphthalene</u>	<u>Amount of Benzothiophene^b</u>	<u>% HYD of Naphthalene</u>
0.0	78 ± 8	0.0	78 ± 8
0.2	0.1	0.1	1.6
0.6	0.2	0.2	0.8
3.5	1.0	0.5	0.8
7.0	0.8	1.0	0.8

^a Multiples of the stoichiometric amount of sulfur in Ni₃S₂ (0.0043g).

^b Weight percent of benzothiophene in hexadecane.

Table 3. Hydrogenation of Aromatic Compounds with Ni Octoate, Presulfided Powder NiMo/Al₂O₃ and Mo Naphthenate with Excess Sulfur

Reactants Products (mole %)	Catalyst		
	Ni Octoate	Presulfided NiMo/Al ₂ O ₃	Mo Naphthenate with Excess Sulfur
- Toluene			
Toluene	5	20	98
Methylcyclohexane	95	79	2
Ethylcyclopentane	0	1	Trace
- Ethylbenzene			
Ethylbenzene	8	18	97
Ethylcyclohexane	91	82	2
Toluene	0	0	1
Methylcyclohexane	1	Trace	Trace
- Propylbenzene			
Propylbenzene	16	20	100
Propylcyclohexane	83	78	0
Butylcyclopentane	0	2	0
Methylcyclohexane	1	Trace	0
- Butylbenzene			
Butylbenzene	11	23	98
Butylcyclohexane	89	75	2
Pentylcyclopentane	0	2	0
Ethylbenzene	0	0	Trace
- Tetralin			
Tetralin	27	13	95
Decalin	73	83	5
n-Butylbenzene	0	2	Trace
others ^a	0	2	0
t-D/c-D ^b	0.45	2.85	1.62
- Naphthalene			
Naphthalene	0	0	2
Tetralin	36	9	92
Decalin	64	87	6
n-Butylbenzene	0	2	Trace
others ^a	0	2	0
t-D/c-D ^b	0.43	2.93	1.39

(a) Unknown products of molecular weight = 138

(b) Approximate weight ratio of trans-decalin to cis-decalin

Table 4. Effect of Other Compounds on Catalytic Hydrogenation of Naphthalene Using Ni Octoate Without Additional Sulfur

(A)						
Additional Compound ^a	Indan	Indene	o-Cresol	Benzofuran	Quinoline	Indole
Products (mole %)						
Naphthalene	Trace	0	0	0	0	Trace
Tetralin	48	48	50	53	52	58
Decalin	52	52	50	47	48	42
t-D/C-p ^b	0.43	0.40	0.42	0.42	0.40	0.40
% Hydrogenation	71.3	71.0	70.1	68.0	69.1	64.5
(B)						
Additional Compound ^a	EZT (1 wt%)	EZT ^c (0.1 wt%)	Indene EZT ^c	o-Cresol EZT ^c	Benzofuran EZT ^c	Indole EZT ^c
Products (mole %)						
Naphthalene	95	88	95	93	90	96
Tetralin	5	12	5	7	10	4
Decalin	0	0	0	0	0	0
% Hydrogenation	1.8	5.0	2.1	3.0	3.8	1.5

(a) Amount of additional compound: 1 weight percent of each in the reactant solution.

(b) Approximate weight ratio of trans-decalin to cis-decalin.

(c) EZT (benzothioephene): 0.1 weight percent of EZT unless noted otherwise.