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LOW SEVERITY COAL LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

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Table of Contents

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Introduction

Low severity coal liquefaction allows for solubilization of coal with reduced gas make. These lower severity conditions may result in some selective bond rupture. However, usually at low severity conditions, the amount of coal solubilization is much lower than what is normally obtained at higher severity conditions. Promotion of coal solubilization through hydrogen transfer using highly active and effective hydrogen donors is the objective of this study.

The highly effective donors being tested are cyclic olefins. Representative cyclic olefins are isotetralin, which is 1,4,5,8-tetrahydronaphthalene, and 1,4,5,8,9,10-hexahydroanthracene. These compounds are hydroaromatics without aromatic rings and have been shown to be highly effective donors (Bedell and Curtis, 1991). Some recent studies have compared the ability of isotetralin to release hydrogen at 380°C in both nitrogen and hydrogen atmospheres to that of tetralin. Likewise, at 380°C the ability of hexahydroanthracene to release hydrogen in nitrogen and hydrogen atmospheres was compared to that of dihydroanthracene. At equivalent reaction conditions and in the presence of anthracene as a hydrogen acceptor, isotetralin released more than 200 times as much hydrogen as tetralin and hexahydroanthracene released 18 to 25 times as much as dihydroanthracene (Wang, 1992).

The objective of the work performed in this study during this quarter was to evaluate reaction parameters for low severity liquefaction reactions using the cyclic olefin, hexahydroanthracene, and the aromatic, anthracene. These model compounds were reacted under a variety of conditions to evaluate their reactivity without coal. The reactions were performed under both thermal and catalytic conditions. Finely divided catalysts from different molybdenum precursors were used to determine their activity in promoting hydrogenation and hydrogen transfer at low severity conditions. The catalysts used were Molyvan L, sulfurized oxymolybdenum dithiocarbamate, molybdenum naphthenate, and Molyvan 822, organo molybdenum dithiocarbamate.

Experimental

A parametric evaluation of the reactivity of two model systems, anthracene (ANT) and hexahydroanthracene (HHA) was performed under both thermal and catalytic reaction conditions. Both ANT (99% purity) and HHA (97% purity) were obtained from Aldrich Chemical Co. The solvent used in the reaction was hexadecane (99% purity) also from Adlrich Chemical Company. Molyvan L and Molyvan 822 were obtained from Vanderbilt Company and molybdenum naphthenate was obtained from Shepherd Chemical Company.

Low severity reaction conditions were employed. A parametric evaluation of ANT hydrogenation was undertaken with Molyvan L and Molyvan 822 as catalyst precursors. The reaction conditions were reaction temperatures of 300, 350, and 400°C at hydrogen pressures of 500 and 1000 psig introduced at ambient temperature. The catalyst precursors were introduced at 1500 ppm of Mo and tested with and without sulfur. The sulfur level was a 3:1 S to Mo stoichiometric ratio. ANT was introduced at 2 wt % in a hexadecane solution to the stainless steel tubular reactor of ~20 cm^3. The reactions were conducted for 30 minutes and were well-agitated.

The reaction conditions for the ANT hydrogenation reactions were reaction temperatures of 300, 350, and 400°C and a hydrogen pressure of 500 psig introduced at ambient temperature. The reactions were performed for 30 minutes in a ~20 cm^3 stainless steel tubular reactor. ANT was introduced at 2 wt % in hexadecane; a 4 g total charge of liquid was introduced into the reactor. The catalysts precursors used were Molyvan L, Molyvan 822, and Mo naphthenate. All of the catalyst precursors were introduced at a level of 500 ppm of Mo. Molyvan 822 and Mo naphthenate were reacted in the presence of sulfur where sulfur was added at a 3:1 S to Mo stoichiometric ratio. Molyvan L was reacted in the absence of sulfur. The reaction was conducted for 30 minutes and the reactor was well-agitated. HHA was reacted under similar conditions as ANT except that the temperature range was shifted lower. The reaction temperatures used were 250, 300, and 350°C.

The product analysis was conducted using a Varian 3700 gas chromatograph equipped with a Supelco DB5 column, spetumless injector and flame ionization detector. The products were qualitatively identified by spiking with authentic compounds and by analyzing with GC mass spectrometry using a VG70 EHF GC mass spectrometer. Quantitative analysis of the products were achieved using the internal standard method with p-xylene as the internal standard.

The following term, percent hydrogenation (% HYD), is defined to assist in comparing the results from a number of different reactions. Percent hydrogenation is the number of moles of hydrogen required to produce the liquid reaction products as a percentage of the moles of hydrogen required to achieve the most hydrogenated product. For anthracene, the most hydrogenated product was considered to be perhydroanthracene.

Results and Discussion

The objective of the experiments performed this quarter was to evaluate the reactivity of the model systems at low severity conditions and to determine the activity of the catalyst precursors at those conditions. The experiments performed involved a parametric evaluation of the activity of two catalyst precursors with ANT and an examination of the thermal and catalytic hydrogenation of ANT and HHA under low severity conditions. Next quarter, these reactions will be performed with coal to evaluate the effect of hydrogen transfer from the cyclic olefin HHA on coal conversion in comparison to an aromatic ANT under thermal and catalytic low severity conditions.

Parametric Evaluations. The parametric evaluations of ANT hydrogenation using catalyst precursors, Molyvan L and Molyvan 822, are presented in Tables 1 and 2. The purpose of this evaluation was to determine if the presence of sulfur in the reactor helped or hindered the activity of the catalyst precursor for ANT hydrogenation. Previous experiments involving naphthalene indicated that sulfur present in the reaction with Molyvan L was detrimental to naphthalene hydrogenation (January-March 1992 Quarterly Report).

The data in Table 1 present the activity of Molyvan L for ANT hydrogenation with and without sulfur. The loading of the catalyst was 1500 ppm of Mo. In the reactions without sulfur, two partially hydrogenated anthracene products were observed, dihydroanthracene (DHA) and tetrahydroanthracene (THA). At the higher temperature of 400°C, more THA was produced than at the lower temperatures of 350 and 300°C. For each temperature, the amount of ANT hydrogenation was slightly higher for the higher hydrogen pressure of 1000 psi than for the lower pressure of 500 psi. The % HYD did not vary much from the most severe condition at

400°C and 1000 psi where 15.2% HYD was obtained compared to the least severe condition of 300°C and 500 psi which yielded 13.6% HYD.

The Molyvan L reactions with sulfur yielded less % HYD of ANT than did the reactions without sulfur. Only the 400°C reaction produced any THA; the lower temperature reactions only produced DHA as a product. The influence of the sulfur seemed particularly evident at the lowest severity conditions where the conversion of ANT was only 40 to 50%, depending on the amount of hydrogen present. The range for the % HYD from the highest to the lowest severity condition was much greater than in the reactions without sulfur.

The hydrogenation of ANT with Molyvan 822 is presented in Table 2. In these reactions, the effect of sulfur, temperature and hydrogen pressure on ANT hydrogenation was evaluated. The amount of hydrogenation observed with Molyvan 822 was considerably more than that observed with Molyvan L. At 400°C, the hydrogenated products obtained were THA, HHA, and octahydroanthracene (OHA); at 350°C, the products were DHA, THA, and OHA; and at 300°C only DHA was produced. The % HYD of ANT with Molyvan 822 was similar with and without sulfur, although the activity in terms of % HYD of ANT with Molyvan 822 without sulfur at 350°C was considerably less than the corresponding reaction with sulfur. Temperature seemed to have the most effect on ANT hydrogenation with Molyvan 822: the highest temperature of 400°C resulted in substantially more hydrogenation of ANT than did the lowest temperature of 300°C. Hydrogen pressure had only a slight effect on % HYD with the effect being more apparent at higher temperature.

Anthracene Hydrogenation Under Thermal and Catalytic Conditions. ANT hydrogenation under four conditions was examined and is shown in Table 3. The conditions were thermal reaction with no catalyst, catalytic reaction with Molyvan L without sulfur, catalytic reactions with Molyvan 822 with sulfur, and Mo naphthenate with sulfur. The conditions were selected from the parametric evaluation. The temperature range was 300 to 400°C, the hydrogen pressure was 500 psi introduced at ambient temperature and the reaction time was 30 minutes.

The thermal reactions only hydrogenated ANT at 400°C; at lower temperatures ANT did not react. The product at 400°C was DHA. The catalytic reactions produced substantial differences in their reactivity. At 400°C Molyvan 822 and Mo naphthenate with sulfur both hydrogenated ANT to DHA, THA, and OHA, yielding % HYD of 28 to 30%. The primary product was THA. By contrast, Molyvan L without sulfur gave ~ 14% HYD with DHA as the primary product and THA as the secondary one. At 350°C, all three catalyst precursors had similar activity for promoting ANT hydrogenation yielding DHA as the only hydrogenated product with the % HYD ranging from nearly 13 to 14.3%. At 300°C, differences were again observed in the activities of the catalyst precursors with Molyvan 822 being the most active at 12.5% HYD, Mo naphthenate being intermediate at 8.1% HYD and Molyvan L least active at 6% HYD.

Hexahydroanthracene Reactions Under Thermal and Catalytic Conditions. HHA was reacted thermally and catalytically with the same catalyst precursors and conditions as the ANT reactions except that the temperature range was between 250 and 350°C. The results from these reactions are given in Table 4. Under thermal conditions, the amount of hydrogen released from HHA was dependent upon the reaction temperature. Only 8% conversion of HHA occurred at 250°C while slightly more than 75% was converted at 350°C. The products obtained were

DHA and OHA at 300 and 350°C while only OHA was produced at 250°C.

The three catalysts had different activities for hydrogenating HHA. Molyvan L converted 55 to 61% of HHA to OHA, but no dehydrogenation products were observed. Although the amount of conversion varied somewhat for the three reaction temperatures, temperature did not have a substantial effect on the activity of Molyvan L. More OHA was produced at each temperature compared to the corresponding thermal reaction. Both Molyvan 822 and Mo naphthenate yielded some dehydrogenation products: DHA at 350 and 300°C and DHA and ANT at 250°C. Conversion of HHA was between 55 and 62% at the three temperatures with Molyvan 822 and between 55 and 71% with Mo naphthenate. The highest conversion for Molyvan 822 was observed at 300°C while that for Mo naphthenate was at 250°C.

Summary

The activity of the catalyst precursors was dependent upon their structure and their sensitivity to sulfur. Molyvan L was more active in the absence of sulfur while Molyvan 822 and Mo naphthenate were more active with sulfur.

At higher reaction temperature, anthracene converted more to hydrogenated products than at lower temperatures. Under equivalent temperature conditions, Molyvan 822 and Mo naphthenate both converted more anthracene than did Molyvan L. Likewise higher hydrogen pressures resulted in higher conversion of anthracene. The activity of both Molyvan L and Molyvan 822 were similarly affected by hydrogen pressure. The loading level of the catalyst precursor affected the rate of reaction, with the higher loading resulting in higher conversion for the given reaction time of 30 min. The increased catalyst loading affected the reaction system with Molyvan 822 more at higher reaction temperature than at lower, while Molyvan L was affected oppositely.

Hexahydroanthracene showed more reactivity thermally than did anthracene. Hexahydroanthracene readily gave up its hydrogen particularly at higher reaction temperatures. The reactivity of hexahydroanthracene varied with catalyst precursor and temperature.

Future Work

Reactions will be performed with anthracene and coal and with hexahydroanthracene and coal during the next quarter at these same low severity conditions. The ability of hexahydroanthracene to transfer hydrogen to coal at these lower temperatures and pressures will be evaluated in terms of coal conversion and product fractionation. The coal conversion and amount of solvent fractionated products will be compared between the thermal and catalytic systems using anthracene and hexahydroanthracene as nondonor and donor solvents, respectively.

Nomenclature

ANT = anthracene
DHA = dihydroanthracene
THA = tetrahydroanthracene
HHA = hexahydroanthracene
OHA = octahydroanthracene
Mo naphthenate = molybdenum naphthenate

References

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Bedell, M.W. and Curtis, C.W. *Energy and Fuels*, 5, 469, 1991.

Table 1. Anthracene Hydrogenation Using Molyvan L

Reaction Conditions			Product Distribution (wt %)				
Catalyst	Temperature (°C)	Pressure (psi)	ANT	DHA	THA	HHA	% HYD
Molyvan L (1500 ppm) Without Sulfur	400	1000	8.01±0.76	77.38±0.89	14.61±0.49	0±0	15.2
	400	500	13.80±0.15	75.43±1.36	10.77±1.36	0±0	13.8
	350	1000	0±0	95.57±0.17	4.43±0.17	0±0	14.9
	350	500	9.12±1.26	87.22±0.78	3.66±0.53	0±0	13.5
	300	1000	0±0	100.0±0.0	0±0	0±0	14.3
	300	500	6.99±0.31	90.39±0.47	2.62±0.32	0±0	13.6
Molyvan L (1500 ppm) With Sulfur	400	1000	8.54±0.63	82.77±0.30	8.68±0.48	0±0	14.3
	400	500	17.30±1.57	75.62±1.64	7.08±0.24	0±0	12.8
	350	1000	21.41±2.48	78.59±2.26	0±0	0±0	11.2
	350	500	41.58±1.16	58.42±1.16	0±0	0±0	8.3
	300	1000	47.41±1.89	52.59±1.89	0±0	0±0	7.5
	300	500	58.61±1.78	41.39±1.78	0±0	0±0	5.9

Table 2. Anthracene Hydrogenation Using Molyvan 822

Reaction Conditions			Product Distribution (wt %)				
Catalyst	Temperature (°C)	Pressure (psi)	DHA	THA	HHA	OHA	% HYD
Molyvan L (1500 ppm) Without Sulfur	400	1000	0±0	9.26±0.66	32.23±4.55	58.51±4.41	49.9
	400	500	0±0	43.63±1.38	13.83±0.42	42.54±1.24	42.6
	350	1000	54.67±1.74	31.67±1.37	0±0	13.66±0.57	24.5
	350	500	48.11±2.49	42.39±1.68	0±0	9.50±0.85	24.3
	300	1000	100.0±0	0±0	0±0	0±0	14.3
	300	500	100.0±0	0±0	0±0	0±0	14.3
Molyvan L (1500 ppm) With Sulfur	400	1000	0±0	10.46±2.26	28.83±5.49	60.71±3.47	50.0
	400	500	0±0	33.14±1.05	14.32±0.79	52.62±0.38	45.5
	350	1000	28.43±0.49	31.85±0.67	0±0	39.72±1.08	35.6
	350	500	23.58±0.79	50.45±1.26	0±0	25.97±2.03	32.4
	300	1000	100.0±0	0±0	0±0	0±0	14.3
	300	500	100.0±0	0±0	0±0	0±0	14.3

ANT = Anthracene
DHA = Dihydroanthracene
THA = Tetrahydroanthracene
HHD = Hexahydroanthracene
OHA = Octahydroanthracene

Reaction Conditions: 2 wt % anthracene in hexadecane, 4.0 g total charge, 30 min, hydrogen pressure given at ambient temperature.

Table 3. Anthracene Hydrogenation Under Thermal and Catalytic Conditions

Reaction Conditions			Product Distribution (wt %)				
Catalyst	**Temperature (°C)**	**Pressure (psi)**	**ANT**	**DHA**	**THA**	**OHA**	**HYD %**
None	400	500	78.44±2.21	21.56±2.21	0±0	0±0	3.1
	350	500	100.0±0	0±0	0±0	0±0	0
	300	500	100.0±0	0±0	0±0	0±0	0
Molyvan L (500 ppm) Sulfur	400	500	17.83±1.36	67.09±0.53	15.08±1.12	0±0	13.8
	350	500	9.41±2.84	90.59±2.84	0±0	0±0	12.9
	350	500	57.76±2.49	42.24±2.49	0±0	0±0	6.0
Molyvan 822 (500 ppm) Sulfur	400	500	0±0	27.66±1.33	59.42±1.10	12.92±1.09	28.2
	350	500	0±0	100.0±0	0±0	0±0	14.3
	300	500	12.58±4.12	87.42±4.12	0±0	0±0	12.5
Mo Naph (500 ppm) Sulfur	400	500	0±0	23.18±2.01	60.42±1.76	16.40±0.48	29.8
	350	500	3.41±1.41	96.59±1.41	0±0	0±0	13.8
	300	500	42.74±3.34	57.26±3.34	0±0	0±0	8.1

Reaction Conditions: 2 wt % anthracene in hexadecane, 30 min, 4 g total charge, 500 psi at ambient temperature.

Table 4. Hexahydroanthracene Hydrogenation Under Thermal and Catalytic Conditions

Reaction Conditions			Product Distribution (wt %)			
Catalyst	**Temperature (°C)**	**Pressure (psi)**	**ANT**	**DHA**	**HHA**	**OHA**
None	350	500	0±0	41.55±2.07	23.28±0.66	35.17±1.53
	300	500	0±0	6.65±0.84	70.83±3.19	22.52±2.83
	250	500	0±0	0±0	92.05±2.14	7.95±2.14
Molyvan L (500 ppm) Mo without Sulfur	350	500	0±0	0±0	42.55±1.64	57.45±1.64
	300	500	0±0	0±0	39.02±1.07	60.98±1.07
	250	500	0±0	0±0	46.73±0.99	53.27±0.99
Molyvan 822 (500 ppm) Mo with Sulfur	350	500	0±0	11.15±0.51	40.50±1.03	48.35±1.30
	300	500	0±0	17.78±0.65	38.19±0.62	44.03±0.51
	250	500	4.92±0.93	9.56±0.84	45.42±1.66	40.10±1.49
Mo Naph (500 ppm) Mo with Sulfur	350	500	0±0	13.86±0.84	44.76±1.76	41.38±0.96
	300	500	0±0	12.62±1.57	40.26±0.83	47.12±1.82
	250	500	6.70±1.02	9.81±0.88	29.16±2.43	54.33±0.65

ANT = Anthracene
DHA = Dihydroanthracene
THA = Tetrahydroanthracene
OHA = Octahydroanthracene
HYD = Hydrogenation
Naph = Naphthenate

Reaction Conditions: 2 wt % hexahydroanthracene in hexadecane, 30 min, 4 g total charge, 500 psi at ambient temperature.

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