

IMPROVED OIL YIELDS FROM SUBBITUMINOUS COAL WITH NOVEL HYDROGEN-DONOR CONTAINING CATALYSTS

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INTRODUCTION

Previous work in this laboratory has shown improved liquefaction conversion as well as improved oil yield when using temperature staging and a molybdenum sulfide catalyst (1-3). Using a subbituminous coal (Wyodak), temperature-staging improved total conversion and oil/asphaltene ratio from 57 to 73% and 0.4 to 0.6, respectively (1). Use of a molybdenum sulfide catalyst showed increased total conversion and oil yield from 42 to 91% and 22 to 35%, respectively (2). In the prior work (1-3), an assumption was made that ammonium heptamolybdate [AHM] reacted with hydrogen sulfide to form ammonium tetrathiomolybdate [ATTM], when in fact an intermediate containing both oxygen and sulfur (tentatively identified as $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$) is formed, as described by Garcia and Schobert (4). The decomposition products of ATTMM are H_2S , NH_3 , and $\text{MoS}_3/\text{MoS}_2$ at the liquefaction reaction temperatures used (5), but the products from $(\text{NH}_4)_2\text{MoO}_2\text{S}_2$ have not been established, and therefore, the form of the catalyst with the highest activity was not known.

To gain a better understanding of the active catalyst, work was done by Garcia and Schobert showing comparative behavior between ATTMM, sulfided ammonium molybdate [SAM], and MoS_2 (crystalline). At 275°C, MoS_2 produced better results with respect to total conversion, liquid yield, and hydrodesulfurization (4). However, at 325 °C, the precursor salts ATTMM and SAM produced improved results, most probably because the precursor salts had decomposed at this temperature to an amorphous and better dispersed MoS_2 (4). At all reaction temperatures, SAM provided superior results to ATTMM. These results lent support to the idea that precursor salts other than the ATTMM- MoS_2 system could have improved potential as liquefaction catalysts.

A new approach was taken in the work reported here to synthesize a novel molybdate precursor. In order to balance the charged molybdate species, a cation had to be introduced. According to Naumann, various molybdenum sulfide salts could be produced having similar decomposition temperatures if the cation contained a protonated nitrogen system (5). It was thought that addition of a hydrogen donor at the catalyst surface could greatly enhance conversion. Since tetrahydroquinoline (THQ) contains nitrogen, and it is an excellent hydrogen donor liquefaction solvent, it was decided to replace the ammonium ion with THQH^+ (THQH^+ represents the empirical formula $\text{C}_9\text{H}_{11}\text{NH}^+$).

EXPERIMENTAL

In order to use THQ in the synthesis of the catalyst precursor, it was necessary to protonate it. A 6M solution of THQ in dimethyl sulfoxide (THQ was water insoluble) was mixed with a 6M aqueous solution of HCl. Crystals precipitated, the mixture was filtered and rinsed with THF, and the solid was dried under reduced pressure at room temperature. An elemental analysis was done to ensure that THQH^+Cl^- was produced.

To produce the catalyst precursor, aqueous solutions of ATTm and THQH^+Cl^- were mixed together for 48 hours; subsequently a water insoluble precipitate, reddish-brown in color, formed. The solution was suction filtered, was rinsed thoroughly with water, and the filtrate was tested for Cl and Mo until the effluent contained trace amounts of these elements. The resulting precipitate was dried at room temperature and ground to -60 mesh under nitrogen. An elemental analysis led to the preliminary empirical formula $\text{THQHMo}_2\text{S}_7$. Since the precursor SAM produced better liquefaction results to ATTm (4), it was decided to use SAM instead of ATTm as a precursor for the hydrogenation catalyst, and using the same procedure, $(\text{THQH})_6\text{Mo}_8\text{S}_{22}\text{O}_9$ [STM] (preliminary empirical formula) was produced. Both $\text{THQHMo}_2\text{S}_7$ and STM were compared in preliminary experiments to determine the better liquefaction catalyst, and STM was eventually chosen as the primary catalyst in this research.

The coal was impregnated in the same manner as done previously in this laboratory (1-4). Coal was slurried with precursor solutions for 2 hours and vacuum freeze dried to less than 1% moisture. The degree of dispersion of the catalyst precursors on coal could be different because SAM was soluble in water and STM was not soluble in water.

The reaction conditions for liquefaction were as follows. The coal used was PSOC 1488, a subbituminous coal from the Deitz seam in Montana. It was chosen because of the low sulfur and mineral matter contents and had been used in previous Penn State liquefaction work. The reactions were carried out in 25ml microautoclave (tubing bombs) reactors in a temperature controlled fluidized sandbath. The catalyst loading was 1% expressed as weight of Mo on a daf basis. The solvent used was naphthalene at a 2/1 solvent to coal ratio, and the mass of the coal reacted was 2.5g. The reactor was flushed three times with hydrogen, with the final addition pressurized to 6.9 MPa (cold). The reaction sequence included heating to 350 °C for 1 hour, quenching and replacing reacted gas with hydrogen, and then heating to 425 °C for 10 minutes followed by quenching. The reactor was vertically oscillated 2.5 cm at 200 cycles per minute. Further experiments were conducted at the first stage only, and THQ was incorporated into the solvent in later experiments to determine its effect on the reaction system.

The cooled reactor was vented into a glass expansion bulb, and the contents were analyzed by gas chromatography using a Varian model 3700. The contents of the reactor were then rinsed with THF into a dried Soxhlet thimble and extracted for about 12 hours under nitrogen. The THF was removed by rotary evaporation. The solid residue was dried at 100 °C for 12 hours before weighing. Conversion was calculated by subtracting the weight of the residue from the dmmf weight of the coal and dividing

by the dmmf weight of the coal. Liquids were further separated into asphaltenes and oils by adding hexane to the THF soluble portion. This mixture was refluxed for 12 hours under nitrogen, followed by filtration into hexane solubles and insolubles. The hexane was removed by rotary evaporation, and the samples were dried at 100°C for 1 hour before weighing. The oil (hexane solubles) yield was calculated by difference from the conversion percentages of the gas yield, THF solubles, and the THF insolubles.

RESULTS AND DISCUSSION

Table 1 contains the conversion data completed for temperature-staged liquefaction for thermal (in absence of catalyst) and catalytic systems with and without incorporated THQ in the solvent. Experiments B/1,3,5/89 show that addition of either molybdenum catalyst improves total conversion significantly, with the thermal system producing 30% conversion and both catalyst systems producing ~80% conversion. There was little difference between the two catalysts for total conversion. In this series of experiments, there was no significant variation in gas make ($5 \pm 0.5\%$). The interesting results in this group of reactions were in the comparison of liquid yields between the two catalysts. STM had reduced asphaltene yield but increased oil yield when compared to the conventional SAM catalyst, with O/A ratios at 0.55 for STM and 0.28 for SAM.

Comparable conversion results at equal conditions using SAM and STM suggest that THQH^+ plays no role in the dissolution of coal. The superior O/A ratio with STM suggests presence of the H-donor on the catalyst surface facilitates hydrogenation of asphaltenes. Attaching THQ to the catalyst allows it to function in conjunction with the catalyst, but could possibly be reducing the effective surface area of the Mo-O-S compound to react with the coal. The next step was to add a small amount of free THQ to the system to see if the reaction proceeded differently.

The solvent mixtures used in experiments B/1/89, C/1/89, and C/2/89 contain 0g, 0.591g, and 0.121g of THQ, respectively. Table 1 contains the conversion data for these experiments. The solvent to coal ratio still remains 2/1 because an equal amount of naphthalene was removed. Total conversion increases in proportion to the amount of THQ added. These results were expected based on the known behavior of THQ in liquefaction reactions. Gas make increased slightly with increasing THQ in the solvent. For liquid yields, asphaltene yield increased only at high THQ content, and the oil yield passed through an apparent maximum. At this point, it was decided to add ~0.1g of THQ for the rest of the reactions because the addition of 0.5g appeared to increase conversion so much that it would be difficult to elucidate differences with the addition of each catalyst.

The effect of THQ with the catalysts in the temperature-staged system is not as clear at this time. In Table 1, the experiments B/1,3,5/89 and C/2-4/89 show these results. There is increased conversion with the addition of THQ to the thermal and SAM systems, but this was not the case for the STM catalytic system. The increase in conversion for the first two systems appears to be mainly derived from an increase in the oil yield, while in the STM case the oil yield actually decreased slightly.

Finally, it is important to compare STM, SAM + "Free" THQ, and SAM as has been done in Table 2 because this information may indicate how THQ best participates in this reaction system. The addition of THQ with SAM increases conversion by increasing the oil yield when comparing to SAM alone (same as thermal experiments), and by increasing the asphaltene yield when comparing to STM ("locked" THQ) alone. This suggests that when the THQ is "free" from the catalyst surface, the catalyst and THQ can participate more freely in coal dissolution and asphaltene hydrogenation. Analytical work in progress on the reaction products will elucidate how this happens.

The next step was to see what the effect of the catalysts and THQ would be at the initial stage of 350°C. Table 3 shows the reaction information for experiments D/1-3/89 and E/1-3/89. For the effect of catalyst with no additional THQ (D experiments), the results are similar to the temperature staged results. The catalysts improve conversion compared to the thermal experiment, but there is little difference in conversion between catalysts. The liquid yields increase with the addition of catalyst, but there is little difference between catalysts, with the O/A ratios being 0.3 for SAM and 0.33 for STM.

With the addition of THQ (E experiments), there was little difference in total conversion, possibly because this hydrogen donor does not participate in coal dissolution at 350°C. However, liquid yields showed some slight changes, with a slight increase in asphaltene yield and a slight decrease in oil yield with added THQ. It was initially assumed that the THQ was part of the oil fraction along with the naphthalene, but a future experiment may indicate THQ is part of the asphaltene fraction, and if true, conversions will have to be corrected.

Table 4 does a similar comparison as in Table 2, but little effect can be seen with the addition of THQ at 350°C. Future experiments will include data for the single stage at 425°C. It can be noticed in Tables 1 and 3 that just adding the stage at 425°C for 10 minutes increases conversion in all cases.

CONCLUSIONS

There is still more data being collected at this time in order to elucidate further the role of the Mo-O-S catalyst with a hydrogen donor in temperature-staged liquefaction. At 350°C, the use of any Mo-O-S compound improves conversion relative to thermal experiments. The addition of catalyst with "free" or "locked" THQ gives no additional benefit. At 350°C, with temperature staging to 425°C, the addition of "free" THQ increases conversion and improves the dissolution of coal, while the addition of "locked" THQ cannot aid coal dissolution, but it does improve conversion of asphaltenes to oils.

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TABLE 1 Liquefaction Results for Two-Stage System* Comparison of SAM and STM Catalysts and the Addition of THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
B/1/89	None	0	30.8	13.9	11.7	5.2	0.84
B/3/89	SAM	0	78.5	57.7	16.2	5.5	0.28
B/5/89	STM	0	80.1	49.5	25.2	5.5	0.52
C/1/89	None	0.591	58.4	33.1	16	9.3	0.48
C/2/89	None	0.121	39.5	14.5	17.3	7.7	1.19
C/3/89	SAM	0.107	86.5	55.1	26.3	5.1	0.48
C/4/89	STM	0.104	79.4	51.9	21.5	6	0.41

TABLE 2 Liquefaction Results for Two-Stage System* Using SAM and STM Catalysts Comparison of STM, SAM, and SAM with THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
B/5/89	STM	0	80.1	49.5	25.2	5.5	0.52
C/3/89	SAM	0.107	86.5	55.1	26.3	5.1	0.48
B/3/89	SAM	0	78.5	57.7	16.2	5.5	0.28

TABLE 3 Liquefaction Results for Single Stage (350°C) Using SAM and STM Catalysts Addition of THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
D/1/89	None	0	18.3	7.1	6.8	4.4	0.96
D/3/89	SAM	0	47.8	33.9	10.2	3.8	0.3
D/2/89	STM	0	48.5	33.8	11.1	3.6	0.33
E/1/89	None	0.112	20	11.9	2.8	5.2	0.24
E/3/89	SAM	0.119	46.2	34	8	4.1	0.24
E/2/89	STM	0.103	52	39.8	8.4	3.8	0.21

TABLE 4 Liquefaction Results for Single Stage (350°C) Using SAM and STM Catalysts Comparison of STM, SAM, and SAM with THQ

Exp #	Catalyst	THQ g	Conversion %	Asphaltenes %	Oils %	Gas %	O/A
D/2/89	STM	0	48.5	33.8	11.1	3.6	0.33
E/3/89	SAM	0.119	46.2	34	8	4.1	0.24
D/3/89	SAM	0	47.8	33.9	10.2	3.8	0.3

*350°C, 1hr-425°C 10 min

Results of experiments in hydrogen atmosphere at 6.9MPa gas pressure (cold), naph solv. Results expressed on a dry mineral matter free basis.