CATALYST DISPERSION AND ACTIVITY UNDER CONDITIONS OF TEMPERATURE-STAGED LIQUEFACTION

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INTRODUCTION

It has been known for some time that improvements in catalytic liquefaction can be obtained by having the catalyst or catalyst precursor (i.e., a compound that would decompose to an active catalyst at reaction temperature) impregnated into the coal rather than simply mixed with the coal as a powder.[1] Having catalyst particles present at the sites of bond cleavage in the coal structure facilitates hydrogenation; away from the vicinity of the catalyst both carbonization and cracking to gases will be favored.[2] Hence both the total liquid yield and product quality improve as the extent of catalyst dispersion improves. The use of red mud and supported cobalt-molybdenum catalysts in liquefaction of bituminous coals was effective only when there was a rapid plasticizing of the coal and generation of hydrogen donor species, because these catalysts could not be effectively dispersed through the coal.[3] Prior work at this university has demonstrated the effectiveness of impregnating a water-soluble sulfided ammonium molybdate into coal before liquefaction.[4,5] Impregnated ammonium thiomolybdates were more effective catalysts for liquefaction and hydrodesulfurization of Spanish lignite than admixed molybdenum disulfide, a fact attributed to the superior dispersion of the soluble molybdenum salts relative to that obtained from the insoluble disulfide.[6]

Hawk and Hiteshue have cited results in which ammonium molybdate was found effective for liquefaction of Wyoming subbituminous coal regardless of whether the salt had been dispersed in aqueous solution or not.[2] It seemed that in this case the organic liquefaction solvent could itself act as the vehicle for impregnating the catalyst, even though the salt would be essentially insoluble in the solvent. The dispersal of the catalyst by the vehicle has been invoked as a reason for the improved catalyst activity (though it must be recognized that solvent-catalyst interactions may also be an important factor). The dispersal of metal halide catalysts was achieved more effectively with organic solvents, methanol and acetone, than with aqueous solutions.[7] A further approach to improve effectiveness of catalyst dispersion involves the use of metal salts of organic compounds or

organometallic compounds. Thus metal naphthenates, which would be oil-soluble, were found to be very effective catalysts even at quite low (e.g., 0.01%) metal loadings.[2] Iron pentacarbonyl, which is soluble in organic media, is considered readily to penetrate the pore structure of coals and decompose to finely dispersed metallic iron or iron sulfide.[8-10]

Besides affecting catalyst behavior by dispersion, the activity of a catalyst may also vary, depending on structural modification of the coal. By modifying the structure of coal, the hydrogenation and dissolution activity of the catalyst can be promoted, because the weakened structure could be more susceptible to hydrogenation and depolymerization reactions. One method to modify coal structure is solvent swelling. The coal network can be swollen using appropriate solvents, leading to expansion of the pores. The swelling may facilitate impregnation of catalysts or catalyst precursors and diffusion of reagents to the reactive sites of coal. Therefore, it can be presumed that the swelling as a pretreatment operation may increase conversion and quality of yield obtained from liquefaction. Rincon and Cruz found that the conversion of a Colombian coal increased when it is swollen with tetrahydrofuran (THF).[11] Joseph determined a direct correlation between the extent of preswelling and the conversion of coal under liquefaction conditions.[12] Baldwin and co-workers also confirmed the beneficial effect of solvent swelling on coal liquefaction by obtaining better yield quality for the THF-swollen Illinois #6 coal.[13]

Temperature-staging of liquefaction involves reaction at two temperatures, an initial low-temperature (275-350°C) stage, followed by further reaction at higher temperature (375-450°C). The first, low-temperature stage is sometimes considered to be a pretreatment, since most of the desirable liquid products are still formed in the higher temperature stage. This strategy is known to improve net conversion to liquids, relative to operation at a single temperature, and selectively improves the yield of oils at the expense of asphaltenes without an attendant increase in gas production.[14] During the low-temperature stage a partial depolymerization of the coal structure could increase the amount of extractable liquids and the coal fluidity.[15] Weaker bonds might be broken and stabilized by hydrogen transfer at low temperature, reducing the potential for retrogressive condensation reactions at higher temperature. Thus effective hydrogenation at the mild reaction conditions of the first stage may minimize condensation reactions. In the case of low-rank coals, improvement in conversion to soluble products is also aided by the loss of carboxyl groups, but without formation of crosslinks.[16] The combination of a low-temperature catalytic liquefaction step followed by a higher temperature catalytic reaction significantly improved product selectivity concomitant with attaining the highest conversion.[17] Although the use of a catalytic low-severity first stage, using an impregnated molybdenum catalyst, provided processing advantages relative to single-stage reactions, few chemically significant changes were detected in the residual materials.[18]

In the present paper, we report results of a study using various types of iron and molybdenum catalyst precursors for coal liquefaction have been investigated. The study involved an

examination of the effects of impregnation of the catalyst onto the coal, the effects of swelling the coal prior to reaction, and the combined effects of swelling and catalyst impregnation. The focus of this work was on improvements to be obtained in the first, low-temperature (or pretreatment) stage; consequently all results reported in this paper are for reactions at a pretreatment temperature of 275°C.

EXPERIMENTAL

Coal sampling and characterization

Samples of Blind Canyon high volatile bituminous coal (PSOC-1503 and DECS-6) and Big Brown Texas lignite (PSOC-1444 and DECS-1) collected at different dates were used for this work. The origin and analyses of the coals are given in Table 1. The coals were ground without drying to minus 60 mesh and stored under a nitrogen atmosphere. One gram of air-dried coal (PSOC-1444 and PSOC-1503) was placed in a 15 ml conical graduated screw-top centrifuge tube and centrifuged at 2900 rpm for 10 minutes. The height of the coal in the tube was recorded in mL/g. Twelve mL of solvent (methanol, pyridine, tetrahydrofuran, or tetrabutylammonium hydroxide) was added to the coal in two increments. The first 6 ml was combined with the coal and the mixture was stirred carefully until all the coal particles were wetted, then the remaining solvent was added and the tube was sealed with a cap. After a period of time (6-30h), the tube was centrifuged again at 2900 rpm for 10 min and the height was recorded. The volumetric swelling ratio is defined as $Q=h2/h1$, where $h1$=height of unswollen coal and $h2$=height of swollen coal.

Swelling of coals prior to liquefaction

The coal samples (DECS-1 and DECS-6) were swollen using methanol, pyridine, THF and 10% tetrabutylammonium hydroxide (TBAH) solution (1:1 (w/w) ratio water:methanol mixture). The coal samples, which were predried at 110°C in vacuum, were mixed with the swelling reagent to give approximately a solvent-to-coal ratio of 3:1 and were stirred for 6 hours under nitrogen. The solvent was removed and dried at 50°C in vacuum. In the case of pyridine, the sample was dried at 100°C in vacuum in an attempt to remove pyridine completely. In the case of TBAH, a TBAH solution was added to undried coal and only methanol and water of the mixture were removed, so that TBAH was retained in the swollen coal matrix.

Catalyst preparation and testing

Examination of three separate lots of ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ (ATTM), obtained from a commercial source showed that all were distinctly different in behavior and appearance. The solubilities in water, behavior during thermogravimetric analysis, appearance

Table 1. Characteristics of coals.

Sample No.	PSOC-1444	PSOC-1503	DECS-1	DECS-6
Seam	Unnamed	Blind Canyon	Bottom	Blind Canyon
County	Freestone	Emery	Freestone	Emery
State	Texas	Utah	Texas	Utah
Province	Gulf	Rocky Mt.	Gulf	Rocky Mt.
Sampling Date	3/30/85	10/01/85	12/11/89	6/07/90
ASTM rank class	Lignite	hvC b	Sub	hvB b
Moisture Content % wt	31.91	10.35	30.00	4.73
Min. Matter % wt (dry)	19.02	4.36	17.97	6.67
Elem. Comp.(% dmmf)				
C	76.21	80.80	76.13	81.72
H	4.71	6.12	5.54	6.22
N	1.42	1.55	1.5	1.56
S (org)	1.36	0.54	1.05	0.40
O (diff)	16.29	10.58	15.78	10.10

under the microscope, and even odor were different among the three lots. It is obvious that the quality control on the commercial synthesis of this material is very poor. Consequently, ATTM was synthesized in our laboratory following the procedure of Naumann.[19] Briefly, 20 g ammonium heptamolybdate and 20 mL ammonium hydroxide are added to 100 mL deionized water and cooled to ~5°C in an ice bath. H_2S is bubbled through the solution until an initial yellow precipitate turns red; the flow is continued for an additional 30 minutes. The precipitate is filtered, washed with ethanol, and dried in vacuum at room temperature. Molybdenum trisulfide was prepared by acidifying an aqueous solution of ATTM with formic acid, followed by washing and drying the precipitate at 110°C in a vacuum oven. Ferrous sulfate, molybdenum hexacarbonyl, and iron pentacarbonyl were purchased as reagent-grade chemicals and used without further treatment.

Thermogravimetric analysis of ATTM was performed using a Perkin Elmer model TGA-7 thermal analyzer in nitrogen (limitations of the equipment, as well as safety considerations, did not permit thermogravimetric analyses in hydrogen). Approximately 15 mg of catalyst precursor was placed in a small platinum crucible and heated at selected rates (5, 20, and 125°C/min) to several

final temperatures (350, 425, and 500°C). Sulfur analyses were performed by the Penn State Materials Characterization Laboratory using a Leco iodimetric titration sulfur analyzer and in the Penn State Combustion Laboratory using a Leco Model SC-132 sulfur analyzer. Carbon, hydrogen, nitrogen analyses were performed using a Leco Model CHN-600 elemental analyzer. Molybdenum, iron and water (by the Karl Fisher method) analyses were performed by Galbraith Laboratories Inc. Elemental values and water content of synthesized molybdenum compounds are given in Table 2.

Catalyst precursors were reacted in a microautoclave at 7 MPa (cold) H_2 or 5:95 H_2S:H_2 at temperature of 275°C for one hour. X-Ray diffraction measurement of the products (XRD) were made using Cu-Kα radiation with Rigaku equipment and operated at 40 kV and 20 mA.

Impregnation of swollen and unswollen coals with catalyst precursors

The catalyst precursor was loaded onto the coal in an amount based on 1% molybdenum or 0.59% iron (as the metal, not the metal compound) on a dry ash free (daf) basis regardless of whether the coal had been swollen or not. Unswollen coals were impregnated with a water solution of ATTM, ferrous sulphate or suspension of molybdenum trisulfide and with a pentane solution of $Fe(CO)_5$ and $Mo(CO)_6$.

In the case of swollen coal, the swelling reagent (except TBAH) was removed in vacuum at room temperature. While the coal was still wet with swelling reagent, enough ATTM solution (which had been prepared by dissolving ATTM in 1:1 (v/v) ratio methanol:water mixture) to give solution-to-coal ratio of 1:1 was added to coal and stirred for 30 min. In the case of TBAH, ATTM was dissolved in a 10% TBAH solution of a 1:1 ratio (w/w) water:methanol mixture; then this solution was added to undried coal and stirred for 6 hours in order to give enough time for the swelling of coal under nitrogen. After stirring, excess solvent was removed at room temperature in vacuum while it was continuously being stirred, until a mud-like consistency was observed. Finally, vacuum drying was applied at 50°C for the coals swollen with methanol, THF or TBAH, or at 100°C for pyridine-swollen coal. TBAH was allowed to remain in the coal. When carbonyl compounds were used as catalyst precursor, THF and methanol were removed in vacuum at 50°C, and pyridine was removed in vacuum at 100°C prior to impregnation with pentane solution. Again in the case of TBAH, any residual TBAH was allowed to retain in coal.

The TBAH content of samples, whether catalyst-impregnated or not, was calculated from the increase of the nitrogen content of the TBAH-treated material relative to that of the untreated coals.

Table 2. Elemental analysis of ATTM, MoS_3 and the product obtained from microautoclave reaction of ATTM at 7MPa psi (cold) hydrogen gas at a temperature of 275 °C.

Catalyst	%N	%H	%Mo	%S	%H$_2$O	nS:nMo
ATTM	10.81	3.10	37.01	49.15	ND	3.98
MoS$_3$	ND	ND	44.45	50.50	1.39	3.41
HATTM*	3.26	1.40	49.74	39.40	6.36	2.38

ND: Not determined

* Reacted ATTM in 7 MPa (cold) H_2 at 275°C.

Examination of catalyst dispersion

To establish the physical relationship between catalysts and coal surfaces following impregnation, the interfaces were studied by scanning electron microscopy (SEM), to determine whether catalyst materials are deeply impregnated into the coal structure or whether they form only surface dispersions. Two types of samples were prepared from the Texas lignite (DECS-1 and PSOC 1444) and Blind Canyon bituminous coal (DECS-6): particulate (-60 mesh) samples, and single particles of about 5x20 mm embedded in plastic and polished to expose the bedding plane structures of the coal. The particulate samples were impregnated with catalyst or solvent swollen, or both, as described above, and were coated with gold for observation with an ISI model SX-40A SEM. Ferrous sulfate and ATTM catalysts were impregnated into methanol- and THF-swollen coals and moist coals. An energy dispersive spectrometer (EDS) was used for qualitative analysis of elements greater in atomic number than sodium. The single-particle samples were stored under high humidity or were soaked in methanol for 48 h. Without allowing the polished surface to dry, ferrous sulfate (~1 mg) or ATTM (~0.5 mg) in the appropriate solvent (i.e., water or methanol) was applied in drops to the surface. Samples were then dried in vacuum at 25°C for 48 h and coated with carbon for SEM examination.

Liquefaction reactions and product work-up

The liquefaction reactions were performed in horizontal microautoclave reactors (tubing bombs) of nominal 25 mL capacity. The procedure was the same for both preswollen and unswollen coals and also the same whether they had been impregnated with a catalyst or not.

Five grams of each prepared coal sample and five grams of phenanthrene were placed in the reactor. After mixing the contents with a spatula, the reactor was sealed, pressurized to 7 MPa with nitrogen and checked for leaks. The depressurized reactor was purged with hydrogen twice. Subsequently, the reactors were pressurized to 7 MPa (at room temperature) with hydrogen or

H2S:H2 (5:95) and were attached to a vertically oscillating fluidized sand bath which was heated to 283°C. Immediately after the reactors were placed in the sand bath, the thermostat was reset to 275°C, which was the desired pretreatment temperature. The reactors attained a temperature of 275°C in about 30 seconds. The reaction time was 30 minutes. During this period, the reactors were oscillated through an amplitude of 2 cm at 350 cycles/min. All the pretreatment experiments were done in duplicate.

At the end of the reaction, the reactors were rapidly quenched to room temperature by immersion in cold water. After venting the gas, the contents of each reactor were quantitatively washed into a tared ceramic thimble using toluene and Soxhlet-extracted with toluene under nitrogen until the solvent appeared colorless. The toluene extract was concentrated to 10-20 mL by rotary evaporation. The extract was diluted with 400 mL of hexane. The mixture was stirred for 1 h and asphaltenes were allowed to settle overnight and separated with a 0.45 micron filter. The filtrate, containing hexane-solubles, was treated by rotary evaporation to remove the hexane. Toluene-insolubles were Soxhlet-extracted with THF to separate preasphaltenes and the solid residue under a nitrogen atmosphere. THF was removed from the extract by rotary evaporation. Preasphaltenes, asphaltenes and residue were dried overnight in vacuum at 110°C. The conversion was calculated by subtracting the residue weight (corrected as appropriate for the weight of added catalyst) from the weight of coal and dividing by the daf weight of the coal. It was assumed that in the liquefaction system the catalyst precursors transformed to the same materials as they did in reactions in the absence of coal in hydrogen or H2S:H2 at 275°C (Tables 2 and 3).

RESULTS AND DISCUSSION

Swelling of coals

Solvent swelling ratios as a function of contact time for four different solvents are given in Tables 4 and 5 (next page) for the Texas lignite (PSOC-1444) and the Blind Canyon hvCb (PSOC-1503), respectively. The maximum level of swelling was attained within 6 h; additional solvent-coal contact in excess of 26 h did not produce a significant increase in swelling ratio. The extent of swelling experienced by each coal was slightly different with respect to the individual solvents. For the Texas lignite, swelling increased in order of methanol < THF < pyridine < 10% TBAH; for the Blind Canyon hvCb coal the order was 10% TBAH < methanol < THF < pyridine. The extent of the swelling in the different solvents is rank-dependent. Lignites are more crosslinked than bituminous coals. Therefore, lignites give less swelling and extractability in methanol, THF and pyridine than do bituminous coals. Lignites have higher concentrations of acidic functional groups (phenolic hydroxyl and carboxylic groups) than bituminous coals; therefore, swelling of lignite

Table 3. Elemental analysis of products obtained from microautoclave reaction of $Mo(CO)_6$ and $Fe(CO)_5$ at 7MPa of H_2 and $H_2S:H_2$ (5:95) at 275°C

Catalyst Precursor	Reaction Gas	%Mo	%Fe	%S	%C
$Mo(CO)_6$	H_2	40.77	—	—	24.50
$Mo(CO)_6$	$H_2S:H_2$	57.35	—	32.90	0.87
$Fe(CO)_5$	H_2	—	71.70	—	3.99
$Fe(CO)_5$	$H_2S:H_2$	—	60.63	37.6	0.22

increases with increasing basicity of solvents. TBAH is quite basic and has been shown to react strongly with the types of oxygen functionalities in most lower rank coals.[20] Our results with the Blind Canyon bituminous coal differ from those of Joseph,[12] who determined for Illinois #6 bituminous coal that the highest swelling was obtained with 15% TBAH (compared with those of THF and methanol). This difference can be explained, at least in part, by the higher oxygen functionality of the Illinois #6 coal than that of the Blind Canyon coal and by the tendency for TBAH to react with these functional groups.[11] In an attempt to remove TBAH from the coal before subsequent reaction, a ten-fold excess of water was added to the mixture to dilute the TBAH, and the coal was then recovered by vacuum filtration with subsequent Soxhlet extraction overnight in methanol to remove as much of the TBAH as possible. During filtration and methanol extraction of PSOC-1444 lignite treated with 10% aqueous TBAH, a black colloidal extract was observed. The weight loss after filtration was found to be 32% (dry basis) for PSOC-1444, compared with 1.4% for PSOC-1503 bituminous coal. Since aqueous TBAH is a highly basic medium, this reagent may be solubilizing some of the humic acids in the lignite.

Comparison of molybdenum and iron catalyst precursors for pretreatment

In this section, we discuss results obtained without swelling the coals. Table 6 (following page) shows the conversion data for thermal (non-catalytic) reactions and reactions with catalyst-impregnation. Higher total conversion was obtained from Blind Canyon bituminous coal than from Texas lignite when catalyst was not used (17.7% vs. 6.6%). A major contribution to the higher conversion of Blind Canyon is the greatly increased yield of preasphaltenes (10.7 vs. 2.8%). This may indicate a greater liberation of mobile phase from the bituminous coal. A greater oil+gas yield is also noted for Blind Canyon (4.9 vs. 1.6%). Experiments in $H_2S:H_2$ (5:95) show increased conversions relative to H_2. This is more noticeable for the lignite than for the bituminous coal. This

Table 4. Change in solvent swelling ratio (Q) with time for the Texas lignite (PSOC-1444).

Methanol		THF		Pyridine		TBAH	
Time (h)	Q	Time (h)	Q	Time (h)	Q	Time (h)	Q
5.0	1.1	6.0	1.2	6.5	1.6	6.0	2.6
11.5	1.1	16.5	1.2	21.5	1.6	14.5	2.6
23.0	1.1	22.0	1.3	42.0	1.6	24.5	2.7
27.5	1.1	28.0	1.3				

Table 5. Change in solvent swelling ratio (Q) with time for the Blind Canyon hvCb coal (PSOC-1503).

	Methanol	THF	Pyridine	TBAH (10%)
Time (h)	Q	Q	Q	Q
6.0	1.2	1.9	2.4	1.2
10.0	1.3	1.8	2.3	1.2
20.0	1.3	1.8	2.2	1.2
26.0	1.3	1.8	2.3	1.2

behavior is attributed to the well-known role of H_2S as a liquefaction catalyst. The greater improvement for the lignite, relative to the bituminous coal, may indicate H_2S interactions with oxygen functional groups.

The conversions of both coals impregnated with sulphided catalysts are greater than those obtained without catalyst. In the case of Texas lignite, ATTM improves total conversion slightly (9.0% vs. 6.6%). The increased conversion is due to increased asphaltenes and preasphaltenes. MoS_3 also improves conversion slightly. Improvement is via increased preasphaltenes (2.8 vs. 3.9). In the case of Blind Canyon bituminous coal, impregnation with ATTM increased the total conversion from 17.7% to 25%, mainly as a result of increased preasphaltenes. Oil yield also increased slightly (6.9% vs. 4.9%). MoS_3 does even better (26.9% conversion) by nearly doubling the yield of preasphaltenes (19.0% vs. 10.7%). However, the oil yield was not improved with MoS_3. Utz and co-workers have shown that the conversion of Illinois #6 coal with MoS_3 was comparable to that obtained with ATTM.[21] This entire body of results with ATTM and MoS_3 is in general agreement with previous findings from this laboratory, which have suggested that the Table

6. Comparison of Molybdenum and Iron catalysts on the liquefaction of Texas coal (DECS-1) and Blind Canyon coal (DECS-6).

Coal	Catalyst	React. Gas	Conversion% (daf)			
			Total	Preasph	Asphalt	Oil+Gas
DECS-1	None	H_2	6.6	2.8	2.2	1.6
DECS-1	None	$H_2S:H_2$	9.0	3.7	2.0	2.3
DECS-1	FeSO$_4$	H_2	6.4	2.4	2.2	1.8
DECS-1	Fe(CO)$_5$	H_2	6.2	2.1	2.3	1.8
DECS-1	Fe(CO)$_5$	$H_2S:H_2$	11.2	4.2	3.5	3.5
DECS-1	ATTM	H_2	9.0	3.9	3.6	1.5
DECS-1	MoS3	H_2	7.2	3.9	1.7	1.6
DECS-1	Mo(CO)$_6$	H_2	6.7	2.9	2.0	1.8
DECS-1	Mo(CO)$_6$	$H_2S:H_2$	9.1	4.2	2.8	2.2
DECS-6	None	H_2	17.7	10.7	2.1	4.9
DECS-6	None	$H_2S:H_2$	18.5	9.7	1.9	6.9
DECS-6	FeSO4	H_2	16.9	9.2	2.6	5.1
DECS-6	Fe(CO)$_5$	H_2	17.3	8.4	1.6	7.3
DECS-6	Fe(CO)$_5$	$H_2S:H_2$	22.9	14.1	2.7	6.1
DECS-6	ATTM	H_2	25.0	15.1	3.0	6.9
DECS-6	MoS3	H_2	26.9	19.0	3.3	4.6
DECS-6	Mo(CO)$_6$	H_2	16.5	8.1	1.5	6.9
DECS-6	Mo(CO)$_6$	$H_2S:H_2$	26.6	15.7	3.3	7.6

principal role of sulfided catalysts in liquefaction is to enhance conversion via breakdown of the macromolecular structure of the coal, and hence the predominant contribution to enhanced total conversion comes from increased yields of preasphaltenes and asphaltenes.[22]

The similarity of results obtained using ATTM and MoS3 can be explained by the decomposition behavior of ATTM in the reaction system. Thermal analysis of ATTM showed two regions of decomposition. The first decomposition of ATTM occurs around 160°C with loss of 24.5% weight (for the conversion of ATTM to MoS3, the calculated weight loss is 26.15%). The second decomposition occurs around 370°C and the total weight loss was 38.8% (from ATTM to MoS$_2$ the theoretical weight loss is 38.46%). ATTM was reacted at 275°C in hydrogen atmosphere (7 MPa cold) without coal in order to determine the fate of ATTM at the preliquefaction conditions used in this work. Elemental analysis of the product shows it transforms to MoS$_{2+x}$ containing

3.26% of nitrogen (Table 2). The slightly different activities of these two molybdenum-based catalysts with both coals may be due to a difference in catalyst dispersion for each coal and on the destructive effect of ammonia (released from decomposition of ATTM) on the activity of the molybdenum sulfide catalyst derived from ATTM.

For all reactions of ATTM in microautoclaves at 275, 350, and 425°C in N_2, H_2, or H_2:H_2S the product has a S/Mo atomic ratio between 2 and 3, with the single exception of reaction at 275° in N_2, for which S/Mo = 3.4. The excess of sulfur above the theoretical S/Mo of 2.00 seems to be able to be controlled, at least somewhat, by choice of gaseous atmosphere for reactions at 350° and 425°. The S/Mo ratio varies as a function of atmosphere, for a given temperature, in the order N_2 > H_2 > H_2:H_2S. For example, at 350° the S/Mo ratio after reaction in these atmospheres is, respectively, 2.57, 2.50, and 2.44. XRD patterns for reaction products obtained at 275°C indicate a predominance of amorphous material, regardless of atmosphere. As the reaction temperature increases, the characteristic (002), (101) and (110) lines of the hexagonal MoS_2 structure become more distinct. Even at the highest temperatures, however, there is little crystalline material (MoS_2 in particular) greater than 1 μm present in the reaction products.

Ferrous sulphate produces no change in conversion or product slate for liquefaction of the Texas lignite. Furthermore, ferrous sulphate is not an active catalyst for liquefaction of the bituminous coal at 275°C. TGA of $FeSO_4 \cdot 7H_2O$ showed three regions of decomposition. The first, at 136°, is the transition from the hepta- to the monohydrate. The second, in the region 230-264°, is the transition from the monohydrate to anhydrous ferrous sulfate. At a heating rate of 20°C/min a third transition is effected at temperatures above 575°; the product of this reaction is ferric oxide. XRD of the product of heating $FeSO_4 \cdot 7H_2O$ in a microautoclave in hydrogen but in the absence of coal showed mono- and tetrahydrated ferrous sulphate phases as the primary products at 275°C. Conversion of ferrous sulfate to an active sulfide phase was achieved only at temperatures in excess of 350°C. For example, at 425° in hydrogen the reaction products are troilite and pyrrhotite, and in a H_2:H_2S atmosphere the sole product is pyrrhotite. Therefore, ferrous sulfate may only be effective as a high-temperature single-stage catalyst.

The single-particle impregnation studies using a methanol-pretreated or moist surface of the Texas lignite indicate that a good surface dispersion of ferrous sulfate was achieved. Two crystal types were found; one occurred as large prismatic crystals ranging in size from 100 to 300 μm, and the other type occurred as acicular crystals that were distributed as 30 μm size clusters across the coal surface. EDS examination revealed that the larger crystals were ferrous sulfate, whereas the more highly disseminated acicular form was calcium sulfate. At higher magnification, the needle-like clusters of calcium sulfate were found to be associated with a core of ferrous sulfate. When ferrous sulfate in aqueous or methanol solution is applied to a moist lignite surface, ion exchange of iron with organically associated calcium may be promoted. (The calcium content of DECS-1 is

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1.2% on a dry basis.) Blind Canyon bituminous coal has much less calcium (0.2%, dry coal basis), but some acicular crystals were observed on the single-particle surfaces among crystals of ferrous sulfate.

Both calcium and iron sulfate particles were observed on surfaces in the particulate samples impregnated with ferrous sulfate in aqueous solution. Different concentrations of iron and calcium sulfates observed between the two coals closely follow those seen with the single-particle samples. However, a much better dispersion of sulfate crystals was observed in the Blind Canyon sample. EDS examination showed that one particle in five had an iron peak or had recognizable crystalline material. A similar analysis of the Texas lignite particulate sample demonstrated that sulfate materials were not as uniformly dispersed, most being found in large deposits not associated with the lignite.

Impregnated iron carbonyl provided no change in conversion of the Texas lignite in a H_2 atmosphere, but slight increases in asphaltene and oil+gas yields (and thus decreased preasphaltenes) were observed. However, in a $H_2S:H_2$ atmosphere, iron carbonyl provides an increase in conversion (11.2% vs. 6.6%), with a doubling of preasphaltenes and increased asphaltenes and oil+gas. For the bituminous coal reacted in H_2, iron carbonyl does not enhance total conversion, but shifts product slate toward lighter materials at expense of preasphaltenes and asphaltenes. In $H_2:H_2S$, iron carbonyl enhances total conversion (22.9% vs. 17.7%), mainly via increased preasphaltenes (14.1% vs. 10.7%). Elemental and XRD analyses revealed that $Fe(CO)_5$ transforms to iron oxides with accumulated carbon (FeO and Fe_3O_4 possibly with some Fe_3C) in H_2 and transforms to pyrrhotite in $H_2S:H_2$ (Table 2). Thus the behavior of the catalyst can be influenced by the choice of atmosphere. In the absence of H_2S, the catalyst is not sulfided, and appears to have no effect at facilitating the breakdown of the coal structure, because the total conversion is essentially unchanged. However, in this system the catalyst does facilitate hydrogenation of the heavier materials, as indicated by a change in the product distribution. On the other hand, reaction in a $H_2S:H_2$ atmosphere forms a sulfided catalyst, which, like other sulfided catalysts, increases total conversion of the coal by increasing the yields of the heavier preasphaltenes and asphaltenes.

Molybdenum carbonyl in H_2 provides no change in conversion or product slate for reaction of the Texas lignite. In $H_2S:H_2$, an increase in conversion (9.1% vs. 6.6%) results, primarily from increased asphaltenes and preasphaltenes. Similarly, molybdenum carbonyl in H_2 does not affect conversion of the bituminous coal, but shifts products to lighter materials. In $H_2S:H_2$, it enhances conversion, mainly via formation of more preasphaltenes. In absence of coal, molybdenum carbonyl is largely unreactive in H_2, but transforms to sulphided catalyst in $H_2S:H_2$ (Table 2). (However, it is interesting to note that an analysis of the headspace gases after reaction of $Mo(CO)_6$

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in H_2 but without coal showed some hydrocarbon products, suggesting possible Fischer-Tropsch reactions, or at least reactions similar to the F-T synthesis.)

Sulphided molybdenum catalysts are very active for hydrogenation. Hydrogen absorption from the gas phase is approximately 18 mg with sulphided molybdenum catalyst at 275°C, while it was almost zero without catalyst for the both coals. The gas product of the reaction at 275°C is only CO_2, and varies in the range 0.3-0.6% for the Blind Canyon coal and 1.3-2.5% for the Texas lignite.

The effect of preswelling on non-catalytic liquefaction

The conversion results of solvent swollen coals without catalyst impregnation are given in Table 7. Treatment with methanol enhanced oil formation, decreased preasphaltenes and asphaltenes for the Texas lignite (DECS-1); and enhanced oils and preasphaltenes and decreased asphaltenes for the Blind Canyon coal (DECS-6).

THF is the least effective swelling reagent for the liquefaction of the Texas lignite, but it provided great conversion, commensurate with its good swelling ability, for the Blind Canyon coal (Q = 1.9). THF pretreatment increased the total conversion of the Blind Canyon coal from 17.7% to 22.1% and oil formation from 4.9% to 9.2%. Its effect on formation of preasphaltenes and asphaltenes was not significant.

Pyridine pretreatment provided greater total conversion and oil formation for the Texas lignite than those obtained from methanol and THF treatment. However, this treatment diminished the formation of preasphaltenes from this coal. The pyridine treatment for Blind Canyon coal, surprisingly, decreased total conversion from 17.7% to 16.0%. Significant reductions in the yields of preasphaltenes, from 10.7% to 6.4%, and asphaltenes, from 2.1% to 1.3%, were observed. However, the yield of oils increased from 4.9% to 9.2%.

TBAH treatment provided the highest conversion for both coals relative to the other solvents, even though a 10% TBAH solution in a 1:1 water:methanol mixture swelled the Blind Canyon coal least . There might be two reasons for the high conversion with TBAH addition to coals. The first is an increased swelling effect that may result as solvent is evaporated. The evaporation of methanol and water from the coal-solvent-TBAH mixture increases the concentration of TBAH in the coal. The TBAH, thus concentrated by evaporation, can increase the level of swelling of the coal, even for Blind Canyon. Second, in a reaction of 40% TBAH in a microautoclave at the same reaction conditions as used for the pretreatment experiments (but without coal), butane and butene were observed in the gaseous products. It can be expected that TBAH likely transformed to amine compounds, such as tributylamine. Therefore, TBAH can be envisioned to act as a "solvent precursor," in that the TBAH remaining in the coal after the swelling

Table 7. Effect of preswelling treatment on liquefaction of Texas lignite (DECS-1) and Blind Canyon hvB (DECS-6) at 275°C.

Coal	Solvent	Conversion %(daf)			
		Total	Preasph	Asphalt	Oil+Gas
DECS-1	None	6.6	2.8	2.2	1.6
DECS-1	Methanol	8.4	2.2	1.8	4.4
DECS-1	THF	7.4	2.9	0.9	3.6
DECS-1	Pyridine	10.0	1.7	2.0	6.4
DECS-1	TBAH	17.5	5.2	3.9	8.4
DECS-6	None	17.7	10.7	2.1	4.9
DECS-6	Methanol	19.8	12.2	1.6	6.0
DECS-6	THF	22.1	11.1	2.2	9.2
DECS-6	Pyridine	16.0	6.4	1.3	8.2
DECS-6	TBAH	24.0	15.1	3.6	5.3

procedure can undergo thermal decomposition to compounds that are good solvents for coal. It has been found that amines are very good promoters for coal liquefaction.[23-25] The nitrogen contents of residue, preasphaltenes and asphaltenes were found to be higher for TBAH-swollen coal than those of unswollen coal. This increase is attributed to the incorporation of amines. Therefore, assuming that TBAH transformed to tributylamine, the amount of tributylamine incorporated in residue, asphaltenes and preasphaltenes can be determined from the difference between the nitrogen contents of these materials and those of the respective products from unswollen coal. The incorporation of amine compound in these products varied between 2-9%. Addition of TBAH provided the highest increase in yields of preasphaltenes, asphaltenes and oil for the Texas lignite compared to those of coals swollen with other solvents. For the Blind Canyon coal, TBAH addition provided the greatest conversion, yields of preasphaltenes and asphaltenes, but a lower yield of oil relative to those for coals swollen with the other solvents.

For the Texas lignite, conversion of solvent-pretreated samples without catalyst increased in the order of none ~ THF < methanol < pyridine << TBAH. TBAH and pyridine are the most effective swelling agents, and provide highest conversions of swollen samples. Furthermore, these two solvents also provided the highest oil + gas yields. For the Blind Canyon coal, conversion without catalyst increased in the order of pyridine < none < methanol < THF < TBAH. The behavior of the bituminous coal, with respect to total conversion, is quite different from that of the

lignite, since in this case pyridine was the most effective swelling solvent, yet pyridine pretreatment actually suppressed total conversion. However, the two best swelling solvents, pyridine and THF, produced the highest oil + gas yields. The extractive ability of a particular solvent is related to the swelling effect of that solvent for a particular coal. A good extractive solvent can disrupt weak bonds in the coal network or in material trapped in the coal structure. Therefore, the molecules released by this disruption and the weakened structure can be liquefied at less severe conditions.

In addition, thermal analyses of solvent-treated DECS-6 and DECS-1 were performed, and weight losses were determined at 275, 350, and 425°C. Methanol treatment of these coals did not promote weight loss, and in fact slightly decreased weight loss at 350 and 425°. THF and pyridine treatments both promoted increased weight loss. For example, the weight losses of un-treated DECS-1 and DECS-6 at 275° were 3.9% and 2.1%, respectively (daf basis). At the same temperature, the weight losses of the THF-treated coals were 6.4% and 5.9% respectively. Furthermore, it was remarkable that treatment of the coals with these two solvents also lowered the temperature at which the first weight loss could be observed in the TGA. Both THF and pyridine are strong organic solvents. Good extractive solvents like these may have two functions: a disruption of the weak non-covalent bonds in the coal network (i.e, swelling) and mobilization of the material trapped in the coal network, facilitating its transport to the coal particle surface and subsequent evaporation in the TGA. In the case of TBAH-treated coals, the weight loss values, after correction for the TBAH content of the coal, were less than those of the untreated coal. This observation can be explained to be a result of incorporation of compounds, derived from the thermal decomposition of TBAH, into the coal. Thermal analysis of a 40% solution of TBAH showed a water loss at 100°C followed by a second weight loss at 215°C. The handbook value of the boiling point of tributylamine, a likely decomposition product of TBAH, is 213°. All material had decomposed or evaporated by the time 265° was reached. Even though some TBAH-derived material may have been incorporated into the coals, there was nevertheless a shift of the initial weight loss temperatures of the TBAH-treated coals to lower values.

We have observed that removal of solvent from the coals after solvent treatment can actually cause shrinkage of the coal.Thus the reason for the beneficial effect of swelling as a pretreatment should be ascribed to some effect other than the facilitated diffusion of reagents toward the reactive sites in the structure, because of the shrinkage. The swelling and shrinking nevertheless likely alters the coal structure from its original configuration. In addition, a good extractive solvent can disrupt the weak non-covalent molecules in the coal network or between material trapped in the network and the network itself. Therefore, molecules released by this disruption and subsequently weakened structure can be liquefied, or at least report to the liquid products, at reaction conditions less severe than those needed for coals without solvent treatment. THF is not a good swelling solvent for the Texas lignite and in fact did not increase total conversion. The extractive effect of this solvent on

liquefaction can be seen in the increase of oil + gas yield and in the increase in weight loss observed in the TGA.

Combined effects of swelling and catalyst impregnation

Comparative conversion data for ATTM-impregnated swollen Texas lignite and Blind Canyon bituminous coal are given in Table 8. A comparison of the results presented in Tables 7 and 8 shows that, for the Texas lignite swollen with any given solvent, the addition of ATTM improved total conversion relative to that obtained for experiments without catalyst. The increase in total conversion obtained by adding ATTM is approximately the same for all samples, suggesting that the effects of swelling and catalyst impregnation are independent. However, the improvement in conversion obtained by combining ATTM impregnation and swelling is less than that obtained by adding ATTM to unswollen lignite. For example, impregnation with ATTM increased conversion from 6.6% to 9.0% (i.e., an increase of 2.4%) when the lignite was not pretreated with solvent, but for the solvent-treated samples the conversions increased only by 1.1 - 1.9%. The oil + gas yields are essentially unchanged (relative to the solvent pretreated samples without catalyst) on adding ATTM, with the increase in conversion being obtained via increased yields of preasphaltenes and asphaltenes. Since sulfided molybdenum catalysts appear to act mainly to increase the yields of these two products from unswollen coals, this observation further corroborates the suggestion that the effects of catalyst and swelling solvent are independent. If the effects of swelling and catalyst impregnation are compared with results for catalyst impregnation without swelling, it can be seen that solvent treatment increases conversion, and that generally the yields of preasphaltenes and asphaltenes are reduced relative to the case without solvent treatment. Hence the solvent swelling facilitates shifting the product slate toward lighter materials. The greatest conversions and formation of all types of products were obtained with TBAH addition. In this case, the TBAH was by far the most effective solvent pretreatment, because the total conversion doubled, relative to the unswollen lignite, and yields of all products were increased significantly. The order of conversion can be given as none ~ THF ~ methanol < pyridine << TBAH for the Texas lignite. This is essentially the same as the order obtained without impregnation of ATTM.

Microscopic examination of ATTM dispersed onto the Texas lignite from methanol shows intergrown crystals of ATTM that are associated with fractures in the coal. This observation suggests that the ATTM in methanol solution may once have impregnated into the fractures, but during evaporation of the solvent and remaining coal moisture in vacuum the ATTM may have been drawn out of the fracture system. It appears from microscopic evidence that a more uniform dispersion of ATTM can be obtained when it is applied to a moist coal surface, relative to a methanol-soaked and pre-swollen surface. A cross-sectional area of a methanol-soaked sample treated with ATTM was examined by scanning electron microscopy with x-ray energy dispersive

Table 8. Effect of preswelling on liquefaction of Texas Lignite (DECS-1) and Blind Canyon hvB (DECS-6) with ATTM catalyst at 275°C.

Coal	Solvent	Conversion %(daf)			
		Total	Preasph	Asphalt	Oil+Gas
DECS-1	None	9.0	3.9	3.6	1.5
DECS-1	Methanol	9.5	2.8	2.2	4.5
DECS-1	THF	9.3	3.1	2.8	3.4
DECS-1	Pyridine	11.8	2.9	2.4	6.5
DECS-1	TBAH	18.7	6.2	4.6	7.9
DECS-6	None	25.0	15.1	3.0	6.9
DECS-6	Methanol	24.7	15.4	2.4	6.9
DECS-6	THF	25.1	12.4	2.4	10.3
DECS-6	Pyridine	26.7	14.6	2.6	9.5
DECS-6	TBAH	23.7	13.5	3.9	6.3

spectrometry (SEM-EDS). No molybdenum or sulfur peaks were detected on either the interior or exterior surfaces of the coal. From this we conclude that the ATTM-methanol solution does not effectively penetrate a methanol-soaked, pre-swollen surface of the lignite.

For the Blind Canyon bituminous coal, the results are not as consistent as in the case of the lignite. The addition of ATTM increased conversions for solvent-treated samples, relative to comparable samples without ATTM, except in the case of TBAH-treated coal. In fact, TBAH addition seemed to decrease the activity of the molybdenum sulfide catalyst, because the conversion of TBAH-treated coal was slightly less than that of the unswollen coal. Again the increased conversion is mainly in the form of enhanced yields of preasphaltenes and asphaltenes. For this coal, the effects of solvent pretreatment on total conversion at 275°C are negligible, but THF, pyridine, and TBAH effect slight changes in the product distribution. THF and pyridine treatments increase oil and gas yields at the expense of preasphaltenes and asphaltenes. TBAH treatment increases asphaltene yield while decreasing preasphaltenes.

One reason for improved conversion and product yield for THF-treated Blind Canyon coal is suggested SEM examination, which showed the surface of several coal particles coated with hemispherical bodies following swelling in THF and impregnation with ATTM. These bodies were easily destroyed by a focused electron beam and are carbon-rich. We conclude that this material was part of the THF-soluble fraction that was extracted from the coal during swelling and that was

subsequently redeposited on the coal surface when the THF was evaporated before catalyst impregnation. The THF-soluble material has been separated from the coal during swelling, and in so doing has created more surface area for catalyst deposition. The significant increase in oil + gas yield (Table 7) suggests that by improving access of the THF-soluble fraction to the hydrogenation environment may be beneficial. The improved oil + gas yields and reduced preasphaltene and asphaltene yields shown in Table 8 imply that the increased surface area for catalyst/coal contact resulting from swelling in THF has little influence on conversion of the THF-insoluble fraction of this coal under pretreatment conditions. Improved access of catalyst to the THF-soluble coal fraction does not significantly increase yield relative to the non-catalytic reaction, but may improve overall product quality.

Addition of ATTM in water:methanol solutions was studied for both coals using single particles as well as particulate samples. The distribution of catalyst was the same regardless of the coal or whether the samples were pretreated in methanol. When the solvent was evaporated most of the ATTM aggregated in clusters on the coal surface. For the single coal particles, the clusters were generally large. Individual 10 μm platelets of ATTM occurred in some areas of the sample. Coal surfaces in close proximity to the clusters gave no molybdenum or sulfur peaks in EDS, suggesting that ATTM forms a deposit only on the exterior surface of the coal and does not penetrate deeply into the interior of the particles. In the particulate sample, clusters of ATTM were not found uniformly on all particles, and they were typically much smaller (<5 μm).

Using molybdenum carbonyl in $H_2S:H_2$ atmosphere, in general, little is gained by solvent treatment for the Blind Canyon coal (Table 9). Increased conversion with pyridine is mainly a result of increased asphaltenes. For the Texas lignite, similar trends are observed as were seen with ATTM and in the non-catalytic reactions. The principal effect of solvent pretreatment is an increase in oil + gas yield. The conversion of this coal increases in the order none ~ THF < methanol < pyridine < TBAH. With iron carbonyl in $H_2S:H_2$, TBAH addition provided the highest conversion for the Texas lignite, and increase the yields of all products. Other solvent treatments did not enhance total conversion. Pyridine treatment caused an increase of oil+gas yield, and a decrease of preasphaltenes. Solvent treatment provided little improvement conversion of Blind Canyon coal. TBAH and pyridine pretreatments slightly increased total conversion via an increase of oil + gas yields.

Ferrous sulfate is completely soluble in 10% aqueous TBAH. However, because the TGA and microautoclave results, discussed above, suggest that ferrous sulfate would not form an active catalyst at 275°, we have not examined the behavior of this system. It should be recognized that for temperature-staged liquefaction, in which the high-temperature stage would be adequate to convert ferrous sulfate to an active catalyst, some advantages may derive from combining this catalyst precursor with this good swelling agent.

Table 9. Effect of preswelling on liquefaction of Texas lignite (DECS-1) and Blind Canyon coal (DECS-6) with $Mo(CO)_6$ at 275°C.

Coal	React. Gas	Solvent	Conversion (%)			
			Total	Preasph	Asphalt	Oil+Gas
DECS-1	H_2	None	6.7	2.9	2.0	1.8
DECS-1	H_2S:H2	None	9.1	4.2	2.8	2.2
DECS-1	H_2S:H_2	Methanol	10.6	3.2	2.3	5.1
DECS-1	H_2S:H_2	THF	9.3	3.3	3.2	2.8
DECS-1	H_2S:H_2	Pyridine	13.9	3.1	3.6	7.2
DECS-1	H_2S:H_2	TBAH	15.3	4.5	3.5	7.3
DECS-6	H_2	None	16.5	8.1	1.5	6.9
DECS-6	H_2S:H_2	None	26.6	15.7	3.3	7.6
DECS-6	H_2S:H_2	Methanol	25.7	15.6	3.8	6.3
DECS-6	H_2	THF	15.2	6.8	1.3	7.1
DECS-6	H_2S:H_2	THF	27.5	17.4	4.4	5.7
DECS-6	H_2S:H_2	Pyridine	28.1	15.9	5.7	6.5
DECS-6	H_2S:H_2	TBAH	26.4	15.7	6.0	3.8

Table 10 provides conversion data for coals impregnated with iron pentacarbonyl. For the Texas lignite, iron pentacarbonyl impregnation provided the greatest total conversion and oil + gas formation in H_2:H_2S, relative to molybdenum sulfide catalysts. Iron pentacarbonyl did not affect conversion of the lignite in hydrogen. For the bituminous coal, iron pentacarbonyl impregnation increased total conversion mainly by effecting formation of preasphaltenes, as in the case of molybdenum sulfide catalysts. As also observed with molybdenum hexacarbonyl, there was a decreased formation of preasphaltenes and asphaltenes and increased formation of oil + gas in hydrogen. In general the data obtained in H2:H2S with solvent treatment shown in Table 10 are fairly consistent with results reported earlier. For the lignite, improved conversions are in the order of solvent swelling ratio, suggesting again that the catalyst and solvent may work independently. For the bituminous coal, conversions in all cases are, at least roughly, similar, suggesting that solvent treatment provides no benefit in total conversion not already obtained by catalyst addition.

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Table 10. Effect of preswelling on liquefaction of Texas lignite (DECS-1) and Bind Canyon hvB (DECS-6) with $Fe(CO)_5$ in $H_2S:H_2$ (5:95) at temperature of 275°C.

Coal	Solvent	Conversion% (daf)			
		Total	Preasph	Asphalt	oil+gas
DECS-1	None	11.2	4.2	3.5	3.5
DECS-1	Methanol	9.7	2.5	3.6	3.6
DECS-1	THF	10.7	3.5	2.3	4.9
DECS-1	Pyridine	11.0	1.8	3.0	6.2
DECS-1	TBAH	23.6	7.5	10.0	6.1
DECS-6	None	22.9	14.1	2.7	6.1
DECS-6	Methanol	19.8	9.8	2.3	7.7
DECS-6	THF	20.6	10.2	3.0	7.4
DECS-6	Pyridine	23.6	11.7	3.1	8.8
DECS-6	TBAH	25.6	11.7	3.7	10.2

CONCLUSIONS

Without swelling pretreatment, impregnation of both coals increased conversion at 275°C. The increased conversion was mainly a result of an increased yield of preasphaltenes. In the absence of catalyst, swelling the Texas lignite before liquefaction improves conversion, with the increase mainly a result of additional (oil+gas) yield. The relative effectiveness of various solvents for improving conversion is in the same general order as their effectiveness at swelling the coal. Preswelling with methanol or pyridine has little effect on liquefaction of the Blind Canyon coal, but both THF and TBAH provide increased conversion as a result of improved preasphaltene yields. With this coal, the effectiveness of solvents at improving liquefaction is not in the same order as their ability to swell the coal. The combined effect of catalyst addition and swelling is to enhance conversion of the lignite, with a doubling of conversion obtained by impregnation with catalyst and swelling by TBAH. The yields of all products are enhanced by this pretreatment. In contrast, little improvement in total conversion of the Blind Canyon coal is obtained by combining catalyst impregnation and solvent swelling, but changes in the relative proportions of the products can be obtained.

Investigation of catalyst impregnation of solvent-swollen or moist coals with SEM demonstrates that ferrous sulfate and ATTM form only surface dispersions. Pretreatment in

methanol or THF appears to have little influence on impregnation. Impregnation with ATTM before and after solvent swelling results in a surface dispersion. Aggregates of small crystals were observed on the surface of single particles and on particulate samples. Molybdenum and sulfur peaks were not detected in areas where these crystals were absent.

The results with $Fe(CO)_5$ in the different gas atmospheres are noteworthy because they suggest the possibility of tailoring the catalyst action to the characteristics of the coal and the kind of transformations desired. We have shown elsewhere that sulfided catalysts generally seem to intervene in the initial breakdown of the coal, producing preasphaltenes and asphaltenes.[22] For coals which do not have a high inherent reactivity, a catalyst facilitating breakdown of the structure may be very useful. On the other hand, some coals appear to undergo a facile thermal depolymerization even in the absence of catalyst, and in such cases a catalyst that acts mainly to help hydrogenate heavier products to oils might be preferable. We have demonstrated with impregnated $Fe(CO)_5$ that the choice of atmosphere, H_2 vs. $H_2S:H_2$, provides the opportunity of generating an active catalyst that acts either for coal breakdown or for shifting the product slate to lighter materials. It is interesting to speculate that one could, for example, use a $H_2S:H_2$ atmosphere to provide a sulfided, dissolution catalyst for the first stage, re-impregnate with $Fe(CO)_5$ between stages, and use a H_2 atmosphere in the second stage to enhance hydrogenation of the preasphaltenes and asphaltenes.

An added benefit of solvent swelling could be the formation of good solvent inside the coal, as in the case of the thermal decomposition of TBAH to tributylamine. Previous work in this laboratory has shown that the transport of the mobile phase to catalyst particles on the surface of the coal is an important factor in short-contact time liquefaction of bituminous coals.[26] The use of a good swelling agent as a "solvent precursor," with subsequent in situ generation of a good extractive solvent could increase the amount of mobile phase moving out of the coal and reduce its viscosity. In addition, we have also shown that combining an excellent hydrogen donor (tetrahydro-quinoline) into the same molecular species as a catalyst precursor facilitates hydrogenation by keeping the donor in, or near, the catalyst.[27] Hence the prospect exists for future developments of combined "solvent-and-catalyst precursors."

It is important to recognize that the first-stage liquefaction reactions of coals may produce changes in coal structure or behavior that significantly enhance conversion in the second, high-temperature stage, but which are not necessarily evident in the macroscopic characteristics (e.g., formation of soluble materials) of the products of the first stage. That is, a particular coal-catalyst-solvent combination may provide small conversions or yields of soluble products at the end of the first stage, yet may have experienced subtle changes of structure which then facilitate significant conversion in the second stage. Hence the ultimate assessment of the utility of catalyst impregnation, solvent swelling, or both in improving liquefaction behavior in temperature-staged

processes is to determine conversions and product yields at the end of the second stage. Furthermore, it is also important to understand the molecular changes caused in the coal or residues by solvent and catalyst treatment, as well as to observe differences in the compositions of the liquid products caused by these treatments. The former can be assessed by ^{13}C nuclear magnetic resonance and Fourier transform infrared spectroscopy; the latter, by gas chromatography alone or in combination with mass spectrometry. Such work is in progress in our laboratory and the results will be reported in due course.

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