In-Situ Study Under Direct Coal Liquefaction Conditions of the Surface Interaction Between Iron Sulfides and Selected Number of Model Compounds

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Abstract:

The importance of iron sulfides in direct coal liquefaction has been noted by several investigators; an increase in coal conversion and quality of the products has been observed in their studies. In order to gain a better understanding of the role of iron sulfides in coal liquefaction we have investigated "in-situ" the interaction of FeS_2 and Fe_7S_8 with a series of model compounds. In our experiments 10% catalysts by weight were added to the model compounds. The model compounds studied were dibenzothiophene, pyrene, phenanthrene, 1,4-naphthoquinone, phenothiazine, and quinoline. The experiments were performed in nitrogen and hydrogen atmospheres. We find evidence of interaction between the pyrrhotites and some of the model compounds. The formation of intermediate iron oxides in 1,4-naphthoquinone indicates a strong interaction between the iron on the pyrrhotite surface and oxygen. The surface composition of pyrrhotite at 450°C was also studied in a UHV reaction chamber and the interaction with H_2, O_2 and CO was investigated using electron energy loss spectroscopy.

I. INTRODUCTION

Direct coal liquefaction is a process that has been known for a number of years. The liquefaction of coal is a complex process involving a close interaction between coal, hydrogen-donor solvent, and catalysts. The role of mineral matter and particularly iron sulfides in coal liquefaction has been the subject of several investigations (1-3). Mukherjee and Chowdbury observed an increase in coal conversion in the presence of mineral matter (2). Recycling the mineral matter tends to increase the reaction rate and enhance the conversion of pyridine-solubles to benzene solubles (4). The addition or presence of pyrite enhances the production of liquid products from coal (5). The specific effect of each mineral has not been well established (6) because some of the minerals occur in very small amounts. Some of the clay minerals may have only a simple physical effect (6). All the experimental results suggest the iron sulfides as the most actively involved minerals in coal liquefaction.

It has been observed that the conversion to liquid products for four different coals correlates with the stoichiometry of the pyrrhotites present in the residues (7). Stephens et.al. (8) carried out a series of experiments with various additives on an ILL#6 coal and observed an enhancement in conversion to benzene solubles with the addition of pyrrhotite and H_2S. Mössbauer studies (9,10) of the iron sulfides in coal indicate the existence of an interaction between coal components and the pyrrhotites at high temperatures. These experiments suggest an active role of the pyrrhotites in coal liquefaction. However, still many questions remain unanswered concerning the catalytic roles of H_2S and $Fe_{1-x}S$. Lambert points out that the catalytic activity observed for pyrite is solely due to H_2S acting as a hydrogen transfer catalyst (11).

More research is needed in order to clearly distinguish between the role of H_2S and the behavior of the pyrrhotites during coal liquefaction. In a complex material such as coal, it is difficult to identify the roles of vastly differing organic functional groups and their interaction with $Fe_{1-x}S$ and/or H_2S. A simpler approach

is the study of model compounds. Several studies have appeared in the literature on the effect of pyrite and pyrrhotite on model compounds. Guin et.al.(12) studied the hydrogenolysis of benzothiophene in the presence of pyrite. The main product was 2,3-dihydrobenzothiophene. When pyrite was used, the selectivity was shifted toward ethylbenzene. Pyrite seems to catalyze the hydrogenation of pyrene to dihydropyrene (13). Bockrath and Schroeder (14) observed that when pyrrhotite is heated in tetralin, only dehydrogenation is catalyzed. We report in the present work "in-situ" Mossbauer measurements of FeS_2 and Fe_7S_8 in six different model compounds. The behavior of the sulfide surfaces is also studied using electron energy loss spectroscopy. In addition, the changes taking place on the surfaces during reactions with simple gases are investigated using this technique.

Experimental

The "in-situ" Mössbauer measurements were carried out using the reactor shown in Figure 1. A more detailed description of this reactor can be found in Reference (9). The FeS_2 and Fe_7S_8 additives used were from natural mineral samples and were characterized by x-ray diffraction and Mössbauer spectroscopy. In the experiments with model compounds, 10% catalyst (200 mesh) by weight was added and mixed with 1 gm of the model compounds. The model compounds studied using Mössbauer spectroscopy were pyrene, phenanthrene, dibenzothiophene, 1,4-naphthoquinone, phenothiazine and quinoline. The experiments were carried out at 440°C in a nitrogen or hydrogen atmosphere. The reaction time was one hour. The residues were measured at room temperature. The stoichiometry of the pyrrhotites present in the residues was determined using the method described in references (7,15). Data acquisition and analysis were conducted on a microprocessor-based computer. The source was a 200 mCi ^{57}Co:Rh. All the isomer shift values are given in reference to α-Fe at room temperature. The surface properties of FeS_2 and Fe_7S_8 we studied using Auger and electron energy loss spectroscopy. The samples were mounted in an UHV chamber with a specially-designed high pressure reactor. In this reactor the samples were exposed to various gases (CO, H_2, O_2) and high temperatures.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Mössbauer Measurements

The most important Mössbauer parameters in the study of the transformations and interactions of iron sulfides in coal are the isomer shift, the magnetic hyperfine and quadrupole splittings. The isomer shift (IS) results from the electrostatic interaction of the nuclear and electron charge distributions inside the nuclear region. The observed IS in the Mössbauer spectrum is the difference between the shifts in the source and absorber. The IS is given by the following relation:

$$IS = \frac{2\pi}{5} Ze^2R^2 \frac{\delta R}{R} \left(|\Psi_{abs}(0)|^2 - |\Psi_s(0)|^2 \right) \quad (1$$

The quantity $\delta R/R$ is a nuclear property and can be estimated using well characterized standards. The IS gives unique information on the valence state of the Mössbauer atom or ion. The range of IS values for iron compounds in reference to α-Fe covers values between -0.78 mm/sec for Fe^0 isolated in nitrogen to +1.9 mm/sec for Fe^+. (1 mm/sec = 0.48 x 10^{-7}eV for the 14.4 keV transition of ^{57}Fe.) The IS values reported include the second order Doppler shift (SODS). The SODS can

be easily distinguished by its temperature dependence. Its contribution to the present work is not large enough to justify the correction of the measured centroid.

The magnetic hyperfine splitting arises from the interaction of the nuclear dipole moment with a magnetic field due to the atom's own electrons. The Hamiltonian describing this interaction can be written as:

$$H_m = -\left(\frac{\mu}{I} M_I B\right) \qquad (2$$

where I is the spin of the nucleus, μ is the magnetic moment, M_I the magnetic quantum number, and B the magnetic field at the nucleus. For a pure magnetic interaction six transitions are possible between the 14.4 keV level (I=3/2) and the ground state (I=1/2). The presence of vacancies in the pyrrhotites results in a lower magnetic field at the iron ion; this feature is used to calculate the stoichiometry of the pyrrhotites in coal liquefaction residues. The atomic percentage of iron is calculated according to (15)

$$\text{at.\%Fe} = 100 \times \left[0.6836 \times 10^{-3} \times \bar{H}_{mhf} + 0.2881\right]$$

$$\bar{H}_{mhf} = \frac{1}{A_{Total}} \sum_i A_i H_i \qquad (3$$

$\bar{H}_{mhf}$ = average magnetic hyperfine field

A_{Total} = total Mössbauer spectral area

A_i = spectral area under i-th site

H_i = mhf on i-th site

The quadrupole splitting (QS) occurs when the Mössbauer ion electrons and/or the neighboring atoms produce an inhomogeneous electric field at the nucleus and when the nucleus possesses a quadrupole moment. The quadrupole splitting for the excited state 14.4 keV of ^{57}Fe is given by

$$QS = \frac{1}{2} e^2 qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

where

$eq = V_{ZZ}$ = principal axis of the field gradient tensor

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} = \text{asymmetry parameter}$$

Q = quadrupole moment of the nucleus

The combination of IS and QS is very useful in the identification of minerals in coal. The procedure followed is to measure these parameters for standard well characterized compounds and to compare with the values obtained for the coal minerals.

The above Mössbauer parameters will be used to study the transformations and inversions of several model compounds with FeS_2 and Fe_7S_8.

A. Interaction and Decomposition of FeS_2 in the Presence of Model Compounds

Pyrene: Pyrite partially decomposes in the presence of pyrene even in the absence of hydrogen. The observed IS at 440°C for the sample in a nitrogen atmosphere is close to zero. The spectrum shows a well-defined doublet with a quadrupole splitting (QS) close to the value observed for pure pyrite. The spectrum of the residue shows the presence of a pyrrhotite with a stoichiometry close to that observed for Fe_7S_8, about 46% of the original pyrite remains unreacted. The conversion of pyrite to pyrrhotite is larger than the one obtained in the absence of pyrene. In the presence of H_2 the transformation of pyrite to pyrrhotite is complete. At 440°C the Mössbauer spectrum shows only a broad singlet with an IS = 0.35 mm/sec, this value is smaller than the one obtained for the pure pyrrhotites in the absence of pyrene (Table I). This is given as evidence of an interaction between the pyrrhotite and the gases present in the reactor. It is possible that what we observed in this experiment is an intermediate state of the iron on the pyrrhotite, probably interacting with molecular hydrogen and pyrene. The hexagonal pyrrhotite obtained after the reaction is very similar to the one observed in residues from coal liquefaction. H_2S apparently does not play any other role but that of controlling the H_2/H_2S ratio in the reactor.

Phenanthrene: The results of the Mössbauer measurements in a nitrogen atmosphere are very similar to those obtained for pyrene. There is partial conversion to $Fe_{1-x}S$ and the presence of a doublet with parameters close to those of pyrite at 440°C (no real evidence of an interaction). By contrast in the presence of hydrogen, the IS at 440°C is the same of pure $Fe_{1-x}S$. The conversion of pyrite to pyrrhotite is complete (Table II). We must again emphasize that the conversion of pyrite in the presence of the model compound is faster than in the absence of phenanthrene. If there is hydrogenation (1) of the phenanthrene, it is possible that the pyrrhotite does not play any direct role, or that the intermediates decompose faster than 10^{-7} sec (the lifetime of the Mössbauer level).

Dibenzothiophene: In the presence of this compound and in a nitrogen atmosphere, pyrite fully decomposes to $Fe_{1-x}S$. The pyrrhotite formed from this reaction has a stoichiometry close to that of Fe_7S_8 (Table II). There is evidence of interaction with DBZ at 440°C, a doublet is observed with IS close to zero and QS = 0.63 mm/sec (Figure 2). These values are similar to those of pyrite, however there is no pyrite left in the residues (Figure 3). In a hydrogen atmosphere the Mössbauer spectrum at 440°C is very different from that observed in nitrogen. A single Mössbauer line with an IS = 0.36 mm/sec is observed. The residue of this run is an hexagonal pyrrhotite. The present results indicate a reaction with the pyrrhotite. It is very probable that hydrogenation is the major catalytic role of the pyrrhotites in this system.

Phenothiazine: There is partial decomposition of pyrite in a nitrogen atmosphere, however in this case there is less decomposition than for pyrene or phenanthrene. Decomposition takes place in the presence of hydrogen but it is incomplete. The IS and QS at 440°C are clearly due to the unreacted pyrite (Table II). These measurements do not indicate any kind of strong reaction for FeS_2 or $Fe_{1-x}S$ with the model compounds. If any reaction occurs, it is very weak compared to pyrene, phenanthrene or DBZ.

Quinoline: There is only partial decomposition of pyrite to pyrrhotite in nitrogen or hydrogen atmospheres. The stoichiometry of the pyrrhotite present in the residues is very close to Fe_7S_8. In order to obtain such a stoichiometry, a high partial pressure of H_2S must be present in the reactor. The Mössbauer spectrum at 440°C can be attributed to FeS_2 alone; there is a very small contribution from the pyrrhotite and no evidence of reaction. These results suggest no active role for the pyrrhotite in catalyzing the hydrogenation of quinoline to tetrahydroquinoline

(THQ), only H_2S remains as a possible catalyst. We will come back to this problem when discussing the interaction with Fe_7S_8.

1,4-Naphthoquinone: A very interesting result is obtained when the reaction takes place in a nitrogen atmosphere. It is observed that Fe_3O_4 is present in the residue. In order for this to happen the pyrrhotite formed from the partial decomposition of pyrite must react with the oxygen present in the model compound. In a hydrogen atmosphere the magnetite is absent from the final products and full conversion of pyrite to pyrrhotite occurs. The present results indicate a strong affinity of the pyrrhotite surface towards oxygen, and indicates that breaking of oxygen bonds in coal is a possible mechanism by which coal conversion is enhanced.

B. Interactions and Transformations of $Fe_{7-8}S$ in the Presence of Model Compounds. (All the experiments in a hydrogen atmosphere.)

Pyrene: A single Mössbauer line is observed at 440°C with an IS ≈ 0.35 mm/sec. The residue shows the presence of FeS (troilite) and $F_{1-x}S$ with 48.2 at% Fe (Table III). Figures 4 and 5 show the Mössbauer spectra for this run at 440°C and room temperature respectively. The presence of troilite requires a very low partial pressure of H_2S in the reactor. This is not totally unexpected since the amount of free sulfur available from Fe_7S_8 is very limited. There is evidence of a reaction with the pyrene, but the sulfides obtained in this case differ markedly from those obtained for FeS_2. This difference may be attributed to the excess of H_2S when pyrite is the precursor of pyrrhotite.

Phenanthrene: The Mössbauer measurements in this case give very similar results to the ones obtained for pyrene. There is a reaction at 440°C; there troilite is present in the residues. These results contrast with the ones obtained when pyrite is added to phenanthrene. There is a marked difference between the behavior of the nascent pyrrhotite and Fe_7S_8. The excess of sulfur atoms on the pyrite surface is probably responsible for such a difference.

DBZ: There is evidence of a reaction at high temperatures (IS = 0.30 ± 0.06 mm/sec). The residue contains troilite. Since DBZ has sulfur, there must be a reaction between H_2S and the compound in order to effectively reduce the partial pressure of H_2S and allow the formation of FeS. There is evidence of active involvement of H_2S in the reactions.

Quinoline: There is some evidence of a reaction at high temperature (440°C), the IS = 0.40 ± 0.07 mm/sec close to that of pure pyrrhotite, but still slightly more negative. The residue of this run does not show any FeS, the pyrrhotite obtained has 48.2 at.% iron. We attribute this behavior to the presence of unreacted H_2S, otherwise FeS can be formed. This behavior is different from that observed for pyrite, again pointing out the difference between the nascent pyrrhotite (from pyrite) and Fe_7S_8.

Phenothiazine: Similar results to those obtained for quinoline, but in this case the at.% iron in the residues is lower (Table III). This last result is clear evidence of a higher partial pressure of H_2S in the reactor. This behavior contrasts with the one observed for DBZ. In both molecules sulfur is present, however in phenothiazine there is also nitrogen. It is tempting to attribute some reactivity to the pyrrhotite and nitrogen, although the present experimental evidence is insufficient to characterize pyrrhotite as an HDN catalyst.

1,4-Naphthoquinone: No troilite is observed in the residues; hexagonal pyrrhotite is obtained with 48.1 at.% iron. Results are very similar to the ones obtained for FeS_2.

In the present experiments we have studied the reactions of FeS_2 and Fe_7S_8 with

a selected number of model compounds. From the results of such experiments we suggest that one of the mechanisms by which pyrrhotite enhances coal liquefaction is through interactions with oxygen bonds in coal. There is also evidence from the present experiments as well as those reported in the literature that the pyrrhotites act as hydrogenation catalyst. However, the role of H_2S cannot be completely ignored. There is clear evidence of direct involvement of H_2S in the reactions. The reactions with nitrogen compounds are not very clear and more work remains to be done in this area of research. We are of the opinion that hydrodesulfurization has to be excluded as one of the roles of the pyrrhotites. In the following paragraph we will discuss the behavior of the pyrrhotite surfaces interacting with simple gases.

Electron Energy Loss Measurements

Normal incidence was used for the EEL measurements. The EEL spectra were measured in the second derivative mode for various primary electron energies (50 eV, 150 eV, 250 eV). A small modulation was applied to the CMA (v_{pp}=1 volt) and used as a reference signal. The major impurities were carbon and oxygen. The samples were subjected to Ar^+ ion bombardment for several cycles until a clean surface was obtained.

Electron energy loss spectroscopy is strongly surface sensitive. By varying the electron primary energy one is able to distinguish between volume and surface properties (16). Interband and intraband transitions can be identified with this technique. Ionization losses can be easily studied using electron energy loss spectroscopy. In the present work the major ionization losses studied are the $M_{2,3}$ and M_1 of sulfur and iron.

A. EEL Study of Fe_7S_8 At High Temperatures and in the Presence of CO, O_2 and H_2

Effect of Temperature: The effect of temperature on the EEL spectrum of a single crystal of Fe_7S_8 is shown in Figure 6 (Ep=150eV). One observes the transformation of the EEL spectrum as the temperature is increased, at 320°C there is iron enrichment of the surface. This is detected by the observed enhancement of peak C (surface plasmon of Fe). The peaks J,K are due to a 3p →3d transition ($M_{2,3}$ levels of iron). At 450°C the spectrum of the iron sulfide is different from that observed at RT with B peak shifted in energy from 5.1 to 6.2 eV. The new iron sulfide on the surface has a different electronic structure although some iron character is retained.

Interaction with Co, O_2 and H_2: The Auger spectrum of Fe_7S_8 after reaction with CO (4×10^{-4} torr) at 450°C is shown in Figure 7. One observes the presence of oxygen on the surface. This oxygen is bonded to the iron in the pyrrhotite. This is clearly seen in Figure 8 where the low energy iron Auger peak shows the characteristic shape of the oxide (a strong doublet around 50 eV). No carbon is detected on the surface; the absence of carbon can be explained only by the formation of some volatile species of carbon and sulfur (like CS_2). The electron energy loss spectrum at Ep=150eV is shown in Figure 9. The two strong peaks at low energies are characteristic of the Fe-O system. The Auger spectrum for Fe_7S_8 exposed to O_2 (4×10^{-4} torr, 450°C for five minutes) is shown in Figure 7. One can observe the strong similarities with the spectrum obtained for CO exposure. In Figure 9 the EEL spectrum for oxygen exposure is also shown. There is a great similarity to that of Fe_7S_8 exposed to CO. The lower J,K peak positions and sharpness are characteristic of iron oxides. If hydrogen is used instead of O_2 or CO one obtains the spectrum shown in Figure 9. This spectrum is that of an iron sulfide where some of the sulfur has been removed from the surface. The iron character of the surface is still retained as shown by the presence of the 3p →3d

transitions. If a combination of CO/H_2 (1:1) is used at 450°C the oxygen is totally removed from the surface (formation of H_2O). The iron sulfide surface is restored but with a stoichiometry different from that of Fe_7S_8. In all the experiments described here, a clean Fe_7S_8 sample was used as a starting material. An iron foil doped on the surface with sulfur was also studied using EEL spectroscopy. A very similar spectrum to that obtained at 450°C for Fe_7S_8 was measured. Such a result indicates a strong iron character of the pyrrhotite surface.

B. EEL Study of FeS_2 at High Temperatures and in the Presence of CO, O_2 and H_2

A typical energy loss spectrum of a pyrite single crystal surface is shown in Figure 10 (top). After heating the sample to 220°C one observes a dramatic change in the spectrum. We attribute this change to the presence of elemental sulfur, and probably some $Fe_{1-x}S$. At 320°C the spectrum of the surface is more similar to that of $Fe_{1-x}S$. It is noted that the 3p→3d transitions show the presence of more than two lines. This spectrum for the J,K transitions can be produced by the presence of two iron species ($Fe_{1-x}S$ and FeS_2). At 450°C the surface is that of pyrrhotite with no pyrite character retained. The spectrum is almost identical to that obtained at 450°C from Fe_7S_8 (Figure 7). We want to point out that the high temperature pyrrhotite is not Fe_7S_8.

The behavior of pyrite at 450°C in the presence of CO and O_2 contrasts markedly with that of Fe_7S_8 (see Figures 10 and 11). We believe that this difference in the EEL spectra between the two samples is related to the excess of elemental sulfur present on the pyrite surface at 450°C. This excess of sulfur does not permit the iron in the pyrrhotite to react with CO or oxygen. If H_2 is used as a gas instead of CO or O_2 a small change is observed in the EEL spectrum, probably due to the removal of the sulfur from the surface. If a combination of CO/H_2 (1:1) is used in the reactor, an EEL spectrum very similar to that observed for Fe_7S_8 is obtained. In this case elemental sulfur is removed from the surface and the surface behaves as that of a pure pyrrhotite.

In conclusion we find that the major difference in the behavior of the pyrrhotite and pyrite surfaces at high temperature is due to the presence of an excess of sulfur on the latter. We also observe that the pyrrhotite surface has a strong iron character and great affinity to oxygen. Although the present study is only on very simple gases, these gases are present in the reactor during direct coal liquefaction.

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Table I

ISOMER SHIFT AT 420 °C

Sample	I.S. ($mmsec^{-1}$) (at 420 °C)
IL6	0.38 ± 0.05
KY 9/14	0.34 ± 0.05
Powhatan 5	0.35 ± 0.05
Blacksville #2	0.21 ± 0.05
Fe_7S_8	0.50 ± 0.03
FeS	0.51 ± 0.05

TABLE III

Compositions of the residues obtained from Fe_7S_8 + H_2 + model compounds

Dibenzothiophene	$Fe_{1-x}S$	(25%) : at.% Fe	48.2 ± 0.1
	FeS	(75%)	
Pyrene	$Fe_{1-x}S$	(11%): at.% Fe	48.2 ± 0.1
	FeS	(89%)	
Phenanthrene	$Fe_{1-x}S$	(23%): at.% Fe	47.7 ± 0.1
	FeS	(77%)	
1,4 Naphthoquinone	$Fe_{1-x}S$	(100%): at.% Fe	48.1
Phenothiazine	$Fe_{1-x}S$	(100%): at.% Fe	47.6
Quinoline	$Fe_{1-x}S$	(100%): at.% Fe	48.2

TABLE II

Mössbauer Parameters

COMPOUND	IS mm/s T=440°C	FeS_2 + N_2 QS mm/s T=440°C	RESIDUES at RT	IS mm/s T=440°C	FeS_2 + H_2 QS mm/s T=440°C	RESIDUES at RT
Dibenzothiophene	~ 0.0	0.63 ± 0.1	$Fe_{1-x}S$ at.%Fe 46.8	0.36 ± 0.05	-	$Fe_{1-x}S$ at.%Fe 48.2
Pyrene	~ 0.0	0.57 ± 0.1	FeS_2 (47%) $Fe_{1-x}S$(53%) at.% Fe 46.8	0.35 ± 0.05	-	at.%Fe 47.8
Phenanthrene	~ 0.0	0.45 ± 0.1	FeS_2 (24%) $Fe_{1-x}S$(76%) at.%Fe 46.8	0.50 ± 0.05		at.%Fe 48.1
1,4 Naphthoquinone	~ 0.04	0.57 ± 0.05	FeS_2 (70%) Fe_3O_4 $Fe_{1-x}S$ 46.7 at.%Fe	0.02 ± 0.05	0.53 ± 0.05	$Fe_{1-x}S$ at.% Fe 48.0
Phenothiazine	~ 0.04 ± 0.05	0.58 ± 0.05	FeS_2 (82%) $Fe_{1-x}S$ (18%) 46.8 at.%Fe	0.0	0.61 ± 0.05	FeS_2 (17%) $Fe_{1-x}S$ (83%)
Quinoline	~ 0.03 ± 0.05	0.56 ± 0.05	FeS_2 (73%) $Fe_{1-x}S$(27%) 46.7 at.%Fe	0.0	0.55 ± 0.05	FeS_2(64%) $Fe_{1-x}S$(26%) at.% Fe 47.8

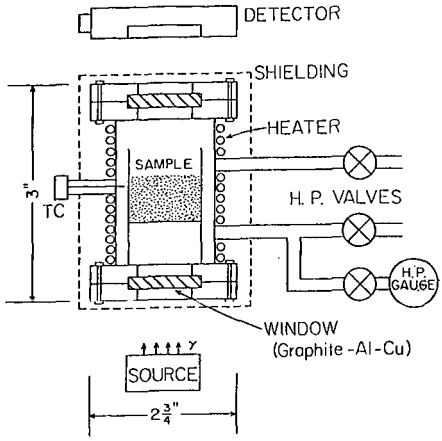

FIGURE 1 Reactor for Mössbauer "in-situ" measurements.

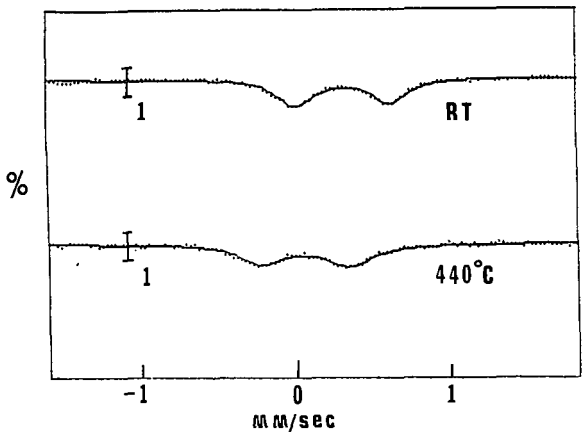

FIGURE 2 Mössbauer spectra at RT for a mixture of FeS_2 and DBZ.

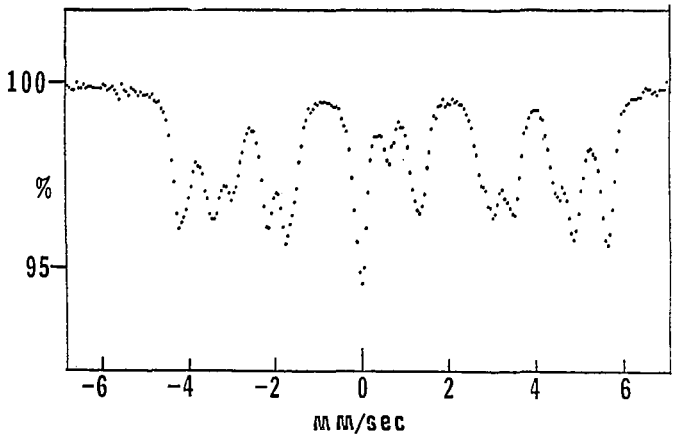

FIGURE 3 Mössbauer spectra at RT of the residue of the reaction of FeS_2 and DBZ.

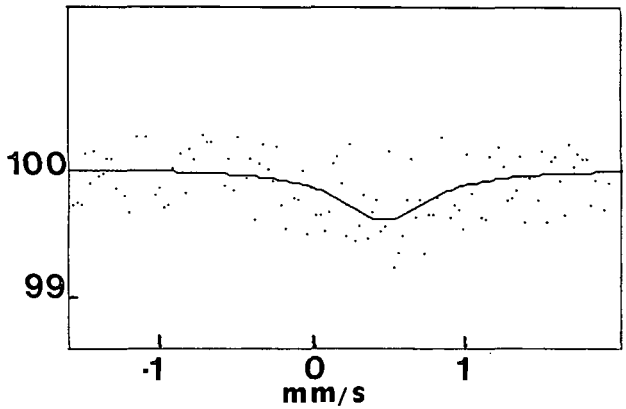

FIGURE 4 Mössbauer spectra at 450°C of Fe_7S_8 and pyrene in a hydrogen atmosphere.

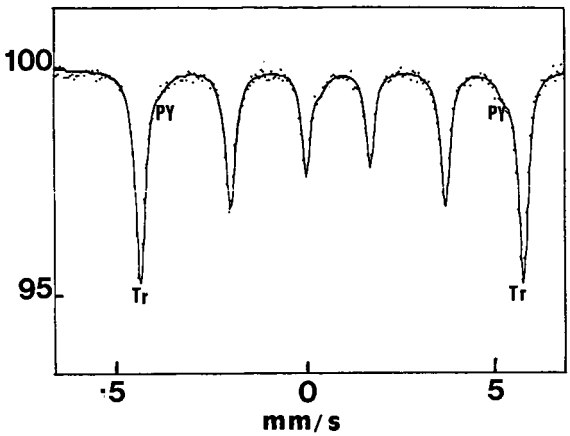

FIGURE 5 Mössbauer spectra of the residue of the reaction of Fe_7S_8 with pyrene. Tr: troilite
Pr: pyrrhotite

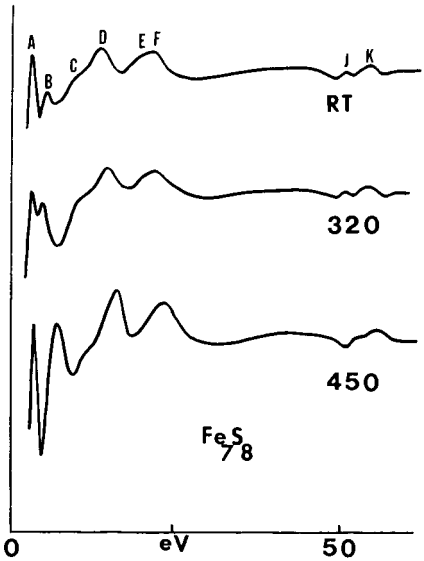

FIGURE 6 EEL spectra of Fe_7S_8 at various temperatures.

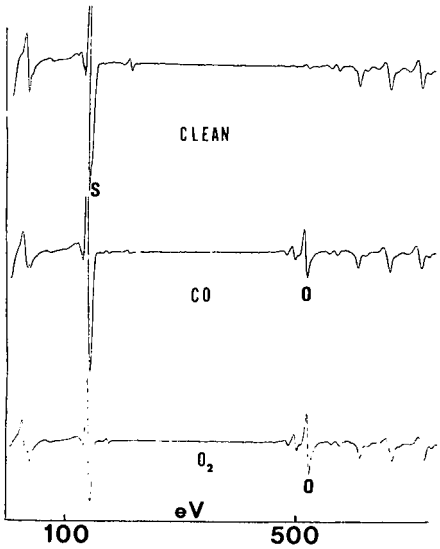

FIGURE 7 Auger spectra of Fe_7S_8 after a reaction with CO and O_2.

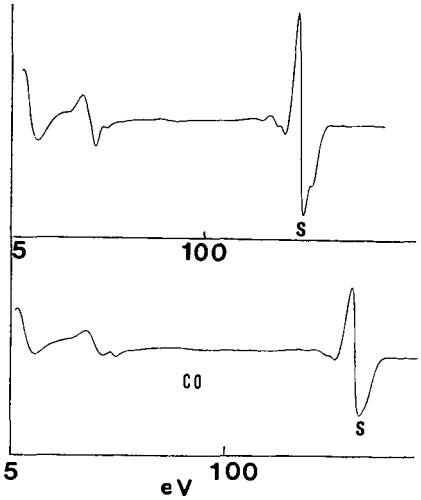

FIGURE 8 Auger spectra of Fe_7S_8 at low energies, clean and in the presence of CO (450° C).

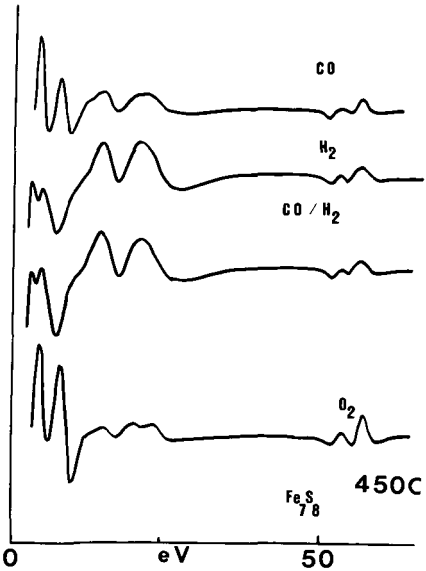

FIGURE 9 EEL spectra of Fe_7S_8 after reactions at 450° C with CO, H_2 and O_2.

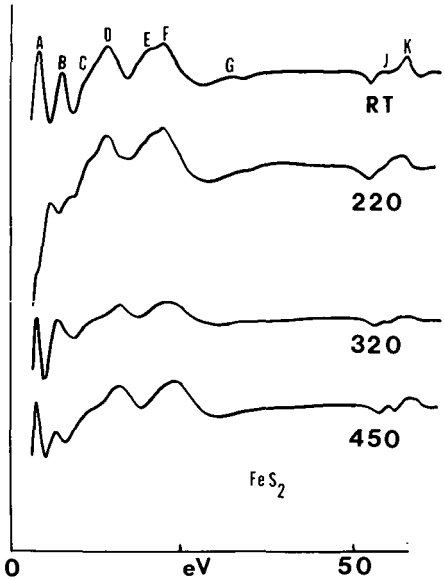

FIGURE 10 EEL spectra of FeS_2 after heating to various temperatures (RT to 450° C).

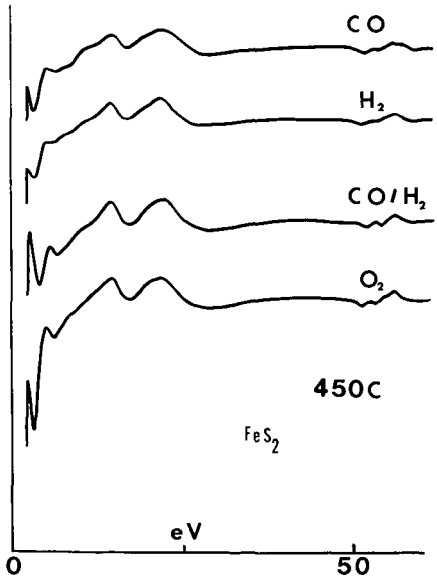

FIGURE 11 EEL spectra of FeS_2 after reaction with CO, H_2 and O_2 at 450° C.

IRON-BASED CATALYSTS, H_2S AND LIQUEFACTION

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INTRODUCTION

One of the most promising advances of the past 50 years of coal liquefaction catalysis is learning of the iron and sulfur synergism. Now with the promotional effects of hydrogen sulfide demonstrated (1) and its mechanism of action being unveiled (2,3), the interaction of hydrogen sulfide with iron needs to be understood for explaining the basis of presulfiding catalysts and for new catalyst design. Presulfiding metal oxide hydrogenation catalysts has long been known to enhance liquefaction yields. However, the chemistry-based reason(s) for the enhancement is unclear. The metal oxides are probably converted to a mixed oxide-sulfide under sulfur-rich conditions. Using differential thermal analysis under high pressure for coal hydrogenation, Takeya (4) rates red mud + S at 297°C as having better catalytic activity than red red mud at 429°C. A combination of iron oxides and sulfur have been used for coal liquefaction effectively (5,6).

In related studies, Beardon and Aldridge have patented the pretreatment of coal with hydrogen sulfide to enhance conversions (7). Gatsis (8) utilized 4 to 8 volume percent hydrogen sulfide (based on hydrogen gas) to enhance the conversion of bituminous coal (Pittsburgh Seam Coal) into a more filterable, higher hydrogen content product using a solvent. The operating conditions in the extraction zone were 250°-500°C and 500 to 5,000 psig with a solvent to coal weight ratio of 0.2 to 10 and a residence time from 30 seconds to 5 hours. If hydrogen is not present in the extraction zone, then it is recommended that the H_2S amount be increased to 40% based upon the amount of coal fed into the extraction zone. Hettinger has shown that hydrogen sulfide causes a significant increase in hydrocracking (9). Goudrian et al. (10) and Satterfield and Model (11) conclude that hydrogen sulfide improved hydroliquefaction of bituminous coals using hydrogen gas and lignites using synthesis gas. Sondreal, Willson and Stenberg (1) have demonstrated the positive effect of H_2S on lignite liquefaction using synthesis gas. The product stream on the continuous flow unit has lower viscosity, lower gas yield and higher distillable oil yield. This enhancement could be due to the interaction of H_2S with the minerals present in coal.

EXPERIMENTAL

Diphenylmethane was purchased (Aldrich) and recrystallized from its ethyl alcohol solution, cooled and the purity of diphenylmethane determined by GC was over 99.9%. Sulfur (Aldrich) and H_2S (Matheson, Coleman and Bell) were used directly without purification. All the reactions were carried out in a 12-ml 316 stainless steel batch microautoclave (12). The heat-up time was at 2 minutes and cool-down time at 0.5 minutes, respectively. The reaction conditions were as follows: temperature, 300-425°C, mainly 425°C; time, 0-120 minutes, not including heat-up and cool-down times; the molar ratio of sulfur reactants are designated in each table. After the autoclave was cooled, the volume or pressure of gas was measured. The liquid products were washed out from the autoclave with ether, and then analyzed by GC. Instruments for identifying the products were GC-MS and ^{1}H-nmr. A gas chromatograph (Varian 2100) used for the separation of liquid products. Separation was effected by a column (0.64 cm x 183 cm) with 3% OV-17 supported on Suplecoport A.

RESULTS AND DISCUSSION

Diphenylmethane was selected as the model compound for these studies to exemplify the chemical reactions of an aromatic ring-aliphatic side chain in coal. Its chemical structure denies aliphatic elimination reactions. The aromatic-methylene-aromatic bonds apparent absence in SRL, SRC and the lower boiling liquids from coal liquefaction does not detract from diphenylmethane's theoretical value nor

prove its absence of its strucural relatives in coals. Its ability to reflect improved conditions for the liquefaction of coals in the ultimate criterion of value as a model compound. Its behavior under liquefaction conditions has already accurately reflected the H_2S enhancement of coal liquefaction.

The thermal stability of diphenylmethane is higher than bibenzyl and diphenylpropane. Diphenylmethane is thought to be one of the most thermally stable coal-related model compounds. This is bourne out by the data on the pyrolysis of diphenylmethane under various reaction conditions as illustrated in Table 1. Diphenylmethane does not decompose in the argon at the temperature of 425°C and reaction time of 60 minutes. Similar results were obtained in the presence of hydrogen sulfide. However, the decomposition of diphenylmethane was enhanced in the presence of either sulfur alone or a mixture of hydrogen sulfide and sulfur. In the pyrolysis reactions of diphenylmethane, sulfur functions as a reactant and 13 products are formed together with a polymer, cf. Table 1. With either elemental sulfur under argon or under H_2S atmospheres for 30 min, the conversions are 49.9 and 35.8%, respectively.

The presence of H_2S during the reaction of diphenylmethane with sulfur influences the product distribution. With H_2S, the yields of the low molecular weight products, toluene and thiophenol, are higher than those of the comparable reaction with S_8 despite the reduction in diphenylmethane conversion, cf. Table 1. The yield of high molecular weight products, classified as "polymer" in Table 1, was reduced which accounts for the difference.

The yields of gaseous and polymeric products increased with temperature and relative concentration of sulfur with little dependence on time, cf. Table 2. The amounts of gas evolved correlated with the yield of polymeric products under these conditions except when the S_8:diphenylmethane ratio was low. The reactions to form both gaseous and polymeric products are rapid and the yields appear to stabilize after 30 minutes.

Table 3 illustrates that diphenylmethane-S_8 product distribution does indeed change before 30 minutes even though the conversion did within experimental error. Tetraphenylethylene was the principal product in the initial stages of the reaction, and it vanished after 60 minutes reaction time. Benzene, toluene and thiophenol yields appear to be the main benefactors of these secondary reactions. Since the formation of tetraphenylethylene occurs largely within the 2-minute heat-up time, its formation is one of the principal primary reactions occurring in the diphenylmethane mixture. Its incomplete conversion into products is possibly due to either the diphenylmethane-S_8 reaction occurring only in the liquid phase at lower temperatures where sulfur-induced radical reactions are known to occur or a change in the chemical nature and reactivity of sulfur occurred with the reaction time.

In addition to tetraphenylethylene, tetraphenylethane and thiobenzophenone were detected at 300° and 350°C and their concentration decreases with increasing temperature. The low boiling products, benzene, toluene and thiophenol are not formed at 300° and 350°C. Therefore these must be categorized as secondary products.

In the hydrogen gas and/or the H_2S gas, the diphenylmethane conversion was about 4%. Benzene and toluene were formed in about equal amounts. On the other hand, the diphenylmethane conversion was enhanced in a H_2-H_2S mixture gas. The diphenylmethane conversion was H_2S concentration dependent, especially at lower H_2S concentrations, and independent of H_2 concentration under the conditions employed in this study. The main products with the H_2-H_2S mixture gas were again benzene and toluene. Several minor products were formed in less than 1% of the weight of diphenylmethane charged.

The results obtained in a presulfided reactor tube showed that the diphenylmethane hydrocracking was promoted in part by the metal sulfide layer formed on the stainless steel reactor wall. The reactor wall was sulfided with H_2S before the introduction of diphenylmethane which results in a black coating being formed on the reactor wall. Since the metal sulfide is being formed as the reaction proceeds in the nonsulfided metal reactor tube, it is difficult to be certain of the percentage, if any, of the hydrocracking which occurs in the gas phase.

With pyrrhotite, H_2 gas causes considerable hydrocracking of diphenylmethane which contrasts with its behavior in the absence of the iron sulfide. Benzene and toluene are the main products with benzene in excess.

The H_2-H_2S gas mixture over pyrrhotite enhanced the diphenylmethane hydrocracking reaction considerably more than H_2 alone did. Moreover, the diphenylmethane conversion in the presence of pyrrhotite was much higher than that in its absence. The effect of pyrrhotite particle size was not important.

Using pyrrhotite, the diphenylmethane conversion increases rectilinearly with increasing hydrogen pressure. A similar effect on conversion occurs when the hydrogen pressure is kept constant and the reaction time increased. As the rigor of the diphenylmethane reaction solution is enhanced by either increasing the hydrogen concentration or the reaction time, the benzene:toluene ratio increases from the value of 1.

The conversion of diphenylmethane is dependent on the H_2S concentration only until slightly more than a 1:1 mole stoichiometry is achieved whether or not pyrrhotite is present. The yields of benzene and toluene are similarly effected. The increasing concentration of H_2S inhibited the formation of products other than benzene and toluene. The amount of pyrrhotite present influences the conversion but not the product distribution. The pyrrhotite loading attained its optimum effect at a weight ratio to diphenylmethane of 0.5.

The thermal hydrocracking of diphenylmethane in the presence of initiating radicals has been suggested to proceed by reactions 1 and 2. In the absence of initiating molecules such as bibenzyl, the slow thermal decomposition reaction of

$$R^{\cdot} + H_2 \rightarrow RH + H^{\cdot} \qquad 1)$$

$$H^{\cdot} + Ph_2CH_2 \rightarrow PhH + PhCH_2^{\cdot} \qquad 2)$$

$$Ph_2CH_2 \rightarrow 2\,Ph^{\cdot} + PhCH_2^{\cdot} \qquad 3)$$

diphenylmethane, reaction 3 and the thermal decomposition data obtained under argon, provides the only source of $R^{\cdot}$ for reaction 1 with the consequence of slow kinetics of the thermal decomposition of diphenylmethane under hydrogen. Another reason for the slow kinetics of the diphenylmethane decomposition under hydrogen is the endothermic character of reaction 1. From bond dissociation data, one can expect this reaction to be endothermic by 0 to +25 kcal/mole depending on the nature of $R^{\cdot}$. The lack of hydrogen pressure dependence with no additives present is probably an artifact attributed to the low level of conversion and obscurred by experimental error.

With hydrogen sulfide and hydrogen present, the conversion and product yields are significantly higher. These results are consistent with reactions 4 and 5 becoming operational in the reaction mixture. The hydrogen sulfide pressure

$$R^{\cdot} + H_2S \rightarrow RH + {}^{\cdot}SH \qquad 4)$$

$${}^{\cdot}SH + H_2 \rightarrow H_2S + H^{\cdot} \qquad 5)$$

dependence is rationalized by reaction 4 and its maximum concentration optimum is controlled by reaction 5 which regenerates H_2S. The reaction sequence 4 and 5 is a thermodynamic stepwise alternative to the highly endothermic reaction 1. Thus, the hydrogen sulfide effect is suggested to take place by replacing reaction 1 with two potentially faster reactions which accomplished the same end result. Reaction 4 is estimated to be endothermic or exothermic by the range of -9 to +16 kcal/mole and 5 endothermic by +9 kcal/mole. Therefore, hydrogen sulfide functions as a H-transfer catalyst in a hydrogen-hydrogen sulfide gas mixture, and this results in an enhanced diphenylmethane hydrocracking reaction.

The significant changes on using pyrrhotite together with hydrogen and hydrogen sulfide is rate enhancement, hydrogen and hydrogen sulfide dependence and increased benzene formation. The rate enhancement can be attributed to a weakening of the SH bonds or outright dissociation of H_2S on the pyrrhotite surface which serves to enhance the rate of reaction 4. The hydrogen pressure dependence with pyrrhotite is attributed to the increased concentration of an active ${}^{\cdot}SH$ and reaction 5 becoming a significant factor in the reaction mixture. Since benzene is formed in higher yields than toluene and toluene is converted in low yield into benzene under these conditions in the absence of pyrrhotite, adsorption of diphenylmethane on the

pyrrhotite surface is indicated and the benzene in excess of a stoichiometric ratio with toluene formed from some adsorbed species.

Two factors were considered in the design of new iron oxide supported catalysts: (a) iron is the principal transition metal to be used based on the cost factor, and (b) the acidity of the support oxide should be varied to determine the optimum acidity. These metal oxides have been screened and the promising results published (3). Since then, we have continued work with these catalysts using sulfur additives and have obtained much more exciting results than those published, cf. Tables 5 and 6.

Diphenylmethane is converted into mainly benzene and toluene when exposed to reducing conditions at liquefaction temperatures such as 425°C (Table 5). When hydrogen is used in the stainless steel reactor with no added catalyst there is no conversion of the starting material. When metal oxide heterogeneous catalysts are added, the starting material is converted into the observed products to varying degrees (Table 6). All three newly designed and synthesized catalysts are active and compare favorably with the commercially available $CoO-MoO_3$. Table 6 gives data which demonstrate the positive effect of sulfiding the catalysts before or during use. The SiO_2- supported catalyst was selected for the present study on the basis of cost effectiveness.

ACKNOWLEDGEMENT

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Table 1 The Pyrolysis of Diphenylmethane with S_8 and H_2S/S_8[a]

Products[b]	S	H_2S/S
Benzene	1.1	1.0
Toluene	3.9	8.0
Thiophenol	6.9	9.0
Diphenyl sulfide	Trace	0.4
Unknown	0.0	0.7
Dibenzothiophene	0.0	0.8
Thioxanthene	0.7	2.0
Triphenylmethane	1.3	0.4
9-Phenylthioxanthene	Trace	Trace
9,10-Dihydro-9,10-diphenylanthracene	0.2	Trace
Tetraphenylethylene	0.2	0.0
12,13-Dihydrodinaphthothiophene	1.6	0.4
1,1,1-Triphenyl-2-phenylethane	0.3	Trace
Polymer	35.2	25.2
Conversion	49.9	35.8

[a]The reactions were done at 425°C for 30 min. at temperature with $H_2S:Ph_2CH_2:S$ ratio of 2.5:1:1. The sulfur reaction was done under an argon atmosphere.
[b]The results are given in mole percent based on the amount of starting material except for the amount of polymer. The latter is given in weight percent of Ph_2CH_2 plus S charged.

Table 2 The Reaction of S_8 with Diphenylmethane

Temp, °C	Time, min	Mole ratio $S:Ph_2CH_2$	Gaseous products, wt%[a]	Polymeric products, wt%[a]
300	30	1	1.0	14.8
350	30	1	2.7	29.8
425	30	1	6.6	35.2
425	60	1	7.0	33.6
425	120	1	6.8	34.0
425	30	0.5	4.6	9.9
425	30	2	18.1	44.2
425	0[b]	1	5.6	24.2

[a]Weight percent of total sulfur plus diphenylmethane charged.
[b]The heat-up time was 2 minutes with an immediate temperature quench.

Table 3 Time Dependence of S_8-Ph_2CH_2 Product Distribution[a]

Products[b]	Time at temperature, min			
	0[c]	30	60	120
Benzene	0.4	1.1	1.3	1.8
Toluene	0.6	3.9	4.2	3.3
Thiophenol	2.0	6.9	7.3	5.5
Unknown	1.2	0	0	0
Thiobenzophenone	0.9	0	0	0
Thioxanthene	1.3	0.7	0.9	0.7
Triphenylmethane	0.5	1.3	1.6	1.1
9-Phenylfluorene	0.9	0	0	0
9,10-Dihydro-9,10-diphenylanthracene	0.2	0.2	0.3	0.3
Tetraphenylethylene	7.6	0.4	0	0
12,13-Dihydrodinaphthothiophene	1.6	1.6	1.5	1.7
1,1,1-Triphenyl-2-phenylethane	0.2	0.3	0	0.3
Conversion	46.9	49.9	48.8	47.5

[a]The reaction temperature was 425°C; the S:Ph_2CH_2 mole ratio was 1; and the reactions were done under an atmosphere of argon.
[b]The results are given in mole percent based on the diphenylmethane charged.
[c]The heat-up time was 2 min with an immediate temperature quench.

Table 4 Diphenylmethane Conversion with S_8-H_2S[a]

Products[b]	Time at temperature, min				
	0[c]	15	30	60	120
Benzene	0	0.4	1.0	1.1	1.3
Toluene	0	6.7	8.0	6.9	6.7
Thiophenol	0	7.5	9.0	8.6	8.2
Diphenyl sulfide	0	Trace	0.4	0.2	0.4
Unknown	0	0.7	0.7	0.6	0.6
Dibenzothiophene	0	0.5	0.8	0.7	0.7
Thioxanthene	0.8	1.5	2.0	1.4	1.2
Triphenylmethane	0	0.2	0.4	0.3	0.2
Tetraphenylethylene	0.3	0	0	0	0
12,13-Dihydrodinaphthothiophene	0	Trace	0.4	Trace	Trace
Polymer	24.4	27.9	25.2	27.6	29.0
Ph_2CH_2 conversion	7.8	34.3	35.8	32.9	31.5

[a]The reaction temperature was 425°C and the H_2S:S:Ph_2CH_2 molar ratios were 2.5:1:1.
[b]The results are given in mole percent based upon the amount of starting material except for the amount of polymer. The latter is given in weight percent of Ph_2CH_2 plus S_8 charged.
[c]The heat-up time was 2 min with an immediate quench.

Table 5. Diphenylmethane Product Distribution Using the Fe_2O_3 - SiO_2 Catalyst[a]

Gases Added / Products	CO H_2O H_2S (P)	H_2 H_2S (P)	H_2 S	H_2[b] (U)	H_2 H_2S (U)
Benzene	1	83	71	43	105
Toluene	1	75	67	21	88
Cyclohexanes	0	3	7	0	5
Others	0	1	2	8	1
Conversion	1	88	81	41	100

P=presulfided
U=unsulfided

[a]The reactions were done in the 12ml rocking autoclaves at 425°C for 1 hr. H_2 (4.9 x 10^{-1} moles), H_2S (3.9 x 10^{-3} moles), and diphenylmethane (3 x 10^{-3} moles) were used. A 10 weight percent load of catalyst was used. The cited data is duplicate results. The presulfiding was done by exposing the catalyst to 250 psi H_2S, 1400 psi H_2 and raising the temperature to 425°C and keeping it there for 1 hr.

[b]The reaction temperatrue was 450°C.

Table 6. The Reaction of Diphenylmethane Using the Tanabe Newly Synthesized Catalysts[a]

	None	Fe_2O_3	Fe_2O_3 on ZrO_2	Fe_2O_3 on TiO_2	Fe_2O_3 on SiO_2	$CoO \cdot MoO_3$
$CO/H_2O/H_2S$	NA	Trace	4	2	Trace	34
H_2/H_2S	NA	30	82	98	100	99
H_2/S	9	30	92	95	81	99
H_2[b]	NA	5	45	16	23	96
$H_2/H_2S/H_2O$	NA	2	3	4	4	26

[a]The reactions were done in the 12ml rocking autoclaves at 425°C for 1 hr. H_2 (4.9 x 10^{-1} moles), H_2S (3.9 x 10^{-3} moles), and diphenylmethane (3 x 10^{-3} moles) were used. A 10 weight percent load of catalyst was used. The cited data is duplicate results. The presulfiding was done by exposing the catalyst to 250 psi H_2S, 1400 psi H_2 and raising the temperature to 425°C and keeping it there for 1 hr.

[b]The catalyst is presulfided for this run.

INCREASING THE ACTIVITY OF COAL MINERAL MATTER FOR HYDRODESULFURIZATION AND HYDRODENITROGENATION

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Catalysis by coal minerals has been the subject of much work in recent years by Guin et al. (1,2), Granoff, et al. (3,4,5), Given and coworkers (6,7), and Mukhejee and Chowdhury (8) since its discovery by Wright and Severson (9) in 1972. Several studies using model compounds such as thiophene, benzothiophene, pyrrole, pyrrolidene, and n-butyl amine have also been published based on work performed at the University of Kentucky (10-16). It is the purpose of this paper to compare the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activities of mineral matter modified by iron or nickel additions to the activities of untreated mineral matter.

EXPERIMENTAL - A pulse micro-reactor packed with mineral matter using hydrogen as the carrier gas was used to evaluate catalytic activity over the temperature range of 573 to 723 K at 101 kPa. Conversions were calculated from the total of C_4 gases detected in the product stream by gas chromatography. Details of the system are presented elsewhere (16). Modification of mineral matter was carried out by preparing physical mixtures of Ky #9 and Ky #11 with Harshaw Ni-4301 (6% Ni and 19% W as oxides on silica-alumina) and by evaporating various iron and nickel solutions containing Ky #9 and Ky #11. Physical mixtures were prepared in two different ways. In one method H_2-pretreated, -24+42 mesh particles of LTA and the Harshaw catalyst were combined to give 10 w/o nickel and loaded into the reactor for activity testing. The activity was between that of the LTA and the catalyst. A second physical method was used which gave more interesting results. The catalyst was ground in a mortar and pestle and combined with either of the LTAs, pressed, crushed to -24+42 mesh, and H_2 pretreated as for other test samples. The catalyst charged was 5×10^{-4} kg containing 10 w/o nickel (calculated).

Two grams of LTA were mixed with the corresponding amount of $Ni(NO_3)_2 \cdot 6H_2O$ to give 10, 25, and 50 w/o Ni mixtures. A small quantity of double distilled water (0.021) was added to dissolve the salt. If necessary, heat was added for about 30 seconds to carry out the dissolution. The slurry was then placed in a 383 K oven overnight to evaporate the liquid. The remaining solid was pressed, sieved, and pretreated as described earlier. Similar treatments were carried out with $FeCl_3 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $NiCl_2 \cdot 6H_2O$.

RESULTS AND DISCUSSION - The HDN conversion for the combination of the Ky #11 LTA with the ground Harshaw catalyst is shown in Figure 1, along with the pure components. On the left is the Ky #11 LTA showing total conversion along with the amount of butane and unsaturates. This contrasts sharply with the catalyst which produces only butane, gives lower conversion, and loses activity as pulsing continues. The mixture (3rd graph from left) pro-

duces a mean conversion of 72.5 which is much higher than either of the components indicating a synergistic effect. The first pulse produced only butane but thereafter the butane accounted for about 12.5%, 1-butene for about 9%, and 2-butenes for about 51% of the total 72.5% conversion. Apparently, the hydrogenation sites are quite sensitive to nitrogen poisoning, but they do not affect the denitrogenation activity.

The effect is even more impressive when Ky #9 which was third lowest in activity was combined with the powdered catalyst. As shown in Figure 2, the mixture (right graph) gave a mean conversion of 77.2% which was the highest of any material tested. Again the first pulse gave pure butane; thereafter about 32% (of the 77.2%). After five pulses cis-2 butene appears and is about the same value as butane with the remainder trans-2-butene. No 1-butene was observed.

The catalyst produced from $Ni(NO_3)_2$ $6H_2O$ and Ky #11 evidenced quite stable performance with a mean conversion of 53.6% which is very close to the LTA value (Figure 1). Unsaturates make up almost all of the products.

Results for all of the Fe and Ni solution-type catalyst are presented in Table I which gives both HDN and HDS conversion. None of the mixtures improve the HDN conversion appreciably and the ferric nitrate decreases it by 26%. Very large changes in HDS conversion are apparent since the LTA gives $<1\%$ and the 50% Ni yields a value of 38.8%. The values of the surface area for the Ni treated mixtures give a mean value of 28.9 $m^2/g \pm 2.2$ which is slightly less than the untreated LTA value of 32.0. This indicates the added Ni is responsible for the increase in activity and the surface area is unaffected by the treatment. The iron treatment shows some improvement as does the nickel chloride, but the nitrate is by far the most effective treatment rivaling the Harshaw mixtures as shown in Figure 3. Here it is seen that 10% Harshaw with Ky #11 gives 23% conversion compared to 21% for the above treatment. The highest HDS conversion was 24.2% for the Ky#9-Harshaw mixture. It is also interesting to note that the Harshaw catalyst does not give a high concentration of n-butane as it did for HDN. Probably H_2S poisoning is responsible for the lack of hydrogenation.

The effect of temperature on HDS conversion for Ky #11 mineral matter, 25% Ni, and 50% Ni is shown on Figure 4. The 25% Ni mixture increases linearly by almost 3-fold from 600 to 700 K. The 50 w/o mixture increases 7-fold from 500 to 700 K. It is also obvious that the activity has increased significantly for the Ni-mixtures over the untreated mineral matter. One measure of this is the temperature required for the more active materials to give the same conversion as the mineral matter; i.e. 1% at 683 K. This requires considerable extrapolation, but it is estimated that the 25% Ni mixture would require a temperature of 523 K and the 50 w/o about 453 K.

Another comparison is shown in Figure 5 where log conversion is plotted against the reciprocal temperature. A previously reported curve is shown for presulfided Ky #11 LTA (Morooka and Hamrin, 10) which gave an activation energy of 58.6 kJ/mole. In this study a value of 57.5 kJ/mole was found for H_2-treated Ky #11 which is in good agreement with the earlier value indicating that pretreatment by H_2 or H_2S does not affect the activation energy. Shown on the figure are the data for the 25% Ni mixture which gave a value of 30.4 kJ/mole with a correlation coefficient ($r = 0.97$). For the 50%

Ni-LTA, a value of 30.3 kJ/mole (r = 0.97) was found. The Ni treatment cut the activation energy almost in half, but increasing the amount of Ni from 25 to 50 w/o had no effect on it.

Additional H_2-treatment on the Ni-modified LTA catalyst increases its HDS activity but decreased its HDN activity. Typical results are given in Table II for the 25% Ni mixture where the HDN activity decreased from 54.7 to 47.5 when additional H_2 treatment of 95 hours was carried out. This may be explained by the increase of cracking activity of the catalyst as the reduction of Ni sites proceeded.

The fact that Ni-added catalyst increased the HDS activity up to 56 times seems due to the high hydrogenation activity of Ni metal which plays an important role on the hydrocracking of thiophene as the first step to give 1,3-butadiene followed by hydrogenation to give n-butenes and butane. On the other hand, since the Ni added catalyst only keeps the HDN activity unchanged implies that the hydrogenation activity of Ni metal does not contribute to the n-butylamine conversion; therefore the n-butylamine HDN conversion is not a hydrocracking reaction but a cracking reaction in which dehydrogenation occurs.

Pyrrole and pyrrolidine pulsing on Ni modified Ky #11 LTA catalyst showed some poisoning effect on the n-butylamine HDN activity while thiophene pulsing increased the HDN activity from 41% to 51% but decreased the selectivity to n-butane.

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TABLE I

Effect of Fe and Ni Modification of Ky #11 LTA
on HDN and HDS Conversions

Addition Compound	w/o Added Element	Surface Area m^2/g	Conversion* HDN	HDS
None	0	32.0	52.0	0.78
$Fe(NO_3)_3 \cdot 9H_2O$	10		38.6	1.98
$FeCl_3 \cdot 6H_2O$	10		48.0	0.96
$NiCl_2 \cdot 6H_2O$	10		48.8	4.73
$Ni(NO_3)_2 \cdot 6H_2O$	10	27.0	53.6	14.0**
$Ni(NO_3)_2 \cdot 6H_2O$	25	31.3	54.7	16.0
$Ni(NO_3)_2 \cdot 6H_2O$	50	28.3	60.7	38.8

* At 673 K, W/F = 2.91 g cat-hr/mole, 4 hr hydrogen pretreatment at 673 K.

** Extrapolated to 0 additional H_2 treatment.

TABLE II

Effect of Additional H_2 Treatment on
HDN Activity of 25% Ni-Ky #11 Mixture

	Additional H_2 Treatment at 673 K, hr			
	0	14	39	95
HDN Conversion From C_4's Produced, %	54.7 ± 0.9	51.0 ± 0.7	50.1 ± 1.3	47.5 ± 1.7
C_1 - C_3 By Cracking, %	6.0 ± 0.7	7.4 ± 4.1	11.0 ± 1.1	18.2 ± 1.9
Total Conversion, %	60.7	58.4	61.1	65.7
n-Butane in Total, %	7.9 ± 1.4	9.1 ± 1.1	16.5 ± 3.3	49.6 ± 12.0

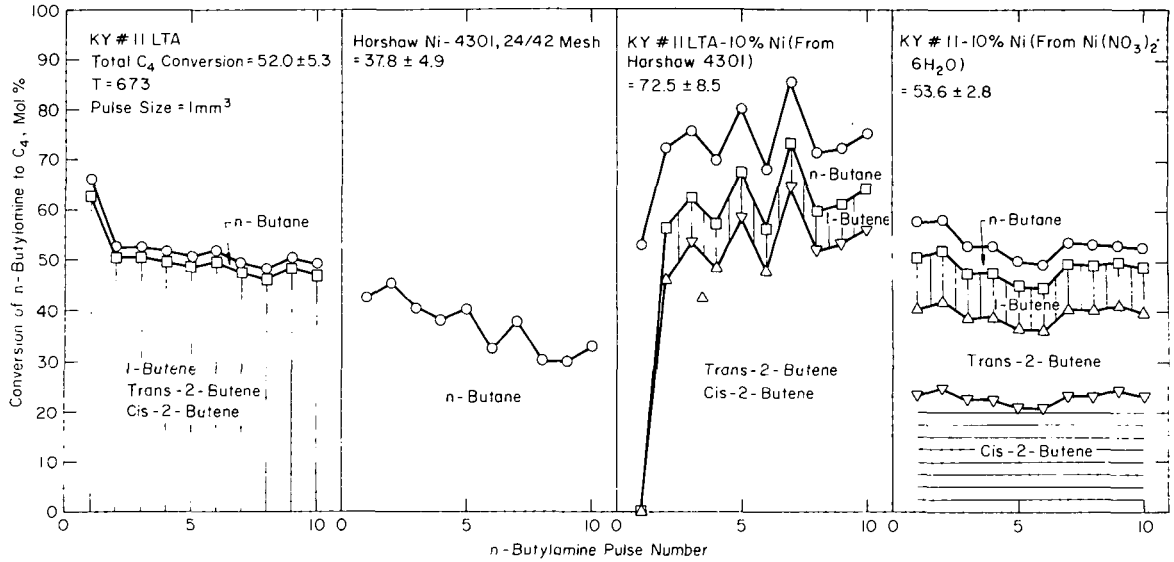

Figure 1. HDN Conversion and Selectivity for KY # 11 and Different Nickel Catalysts.

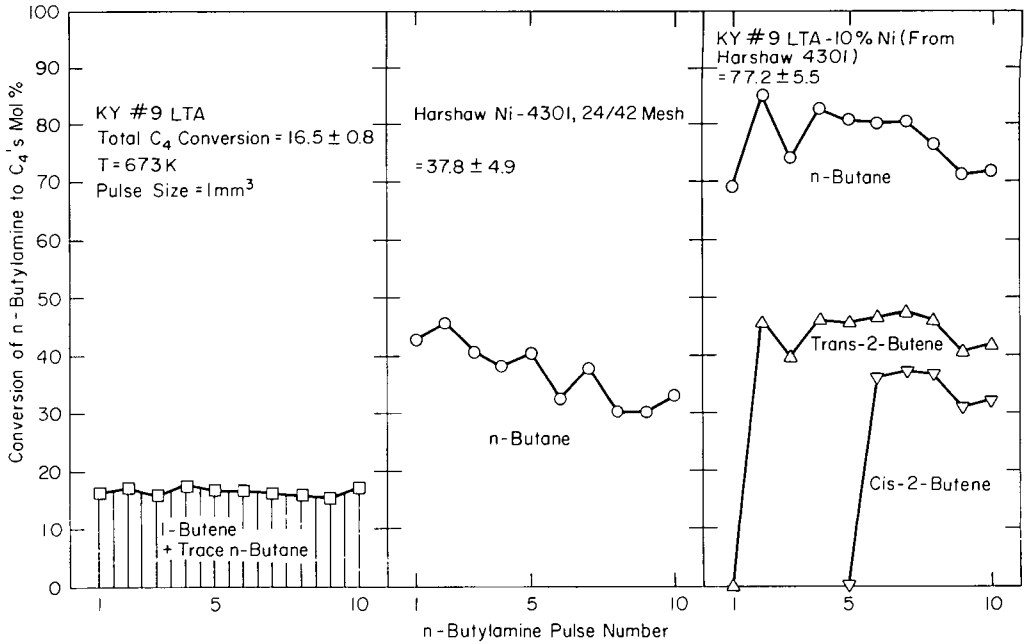

Figure 2. HDN Conversion and Selectivity for KY # 9 and Ni Catalysts.

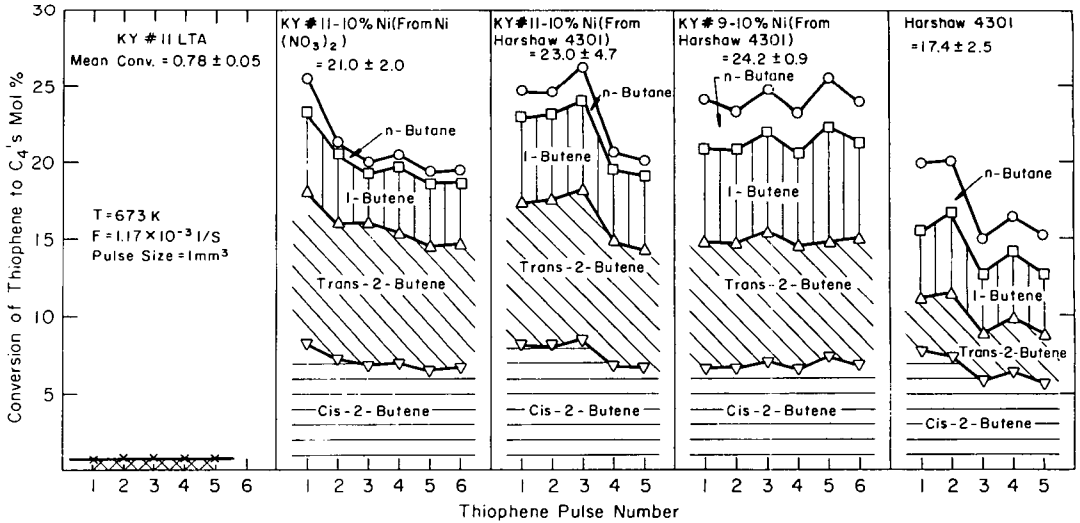

Figure 3. HDS Activity and Selectivity for KY LTA-Ni Mixtures with KY # 11 and Harshaw 4301.

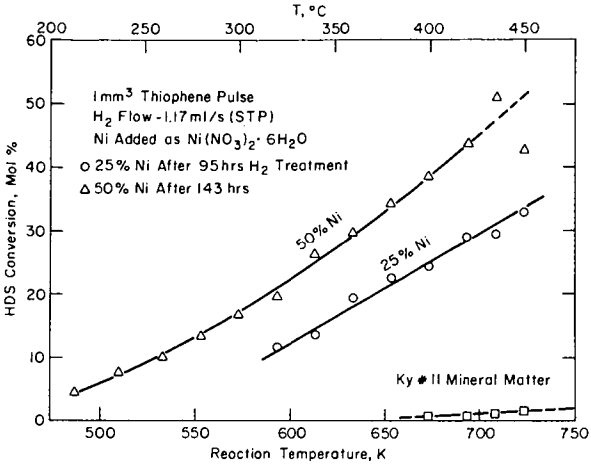

Figure 4. HDS Conversion versus Reaction Temperatures for KY # 11 with and without Nickel.

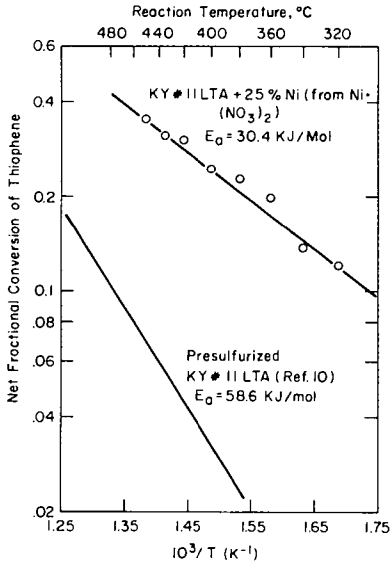

Figure 5. Comparison of Thiophene Conversion - Temperature Relationships for KY # 11 and KY # 11 - Ni Mixture.

Relative Activity of Transition Metal Catalysts in Coal Liquefaction

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Abstract

The catalytic activity of transition metals for coal liquefaction was studied and compared. Impregnation of coal with transition metals significantly increased the production of oils and the conversion of asphaltenes and preasphaltenes in coal liquefaction. Overall conversion of coal increased marginally with transition metals. The production of hydrocarbon gases decreased slightly with metals. Iron impregnation was more active in preasphaltenes conversion than cobalt, nickel, and molybdenum; whereas the other metals were more active in asphaltenes conversion than iron. Hydrogen consumption decreased with the use of metals. The quality of generated solvent decreased with iron, whereas it increased with other metals. Significant synergism was observed between iron and molybdenum. Simultaneous impregnation of coal with iron and molybdenum significantly increased the conversion of coal, asphaltenes, and preasphaltenes, and the production of oils compared to individual metals. The mixture of iron and molybdenum also decreased the hydrocarbon gas production over iron and molybdenum alone. In addition, the quality of generated solvent was higher with iron and molybdenum mixture compared to iron alone.

Introduction

Extensive research has been performed in the areas of catalytic and non-catalytic coal liquefaction. It is well known that in coal liquefaction, high-molecular weight compounds rupture thermally, producing unstable free radicals. These free radicals react with hydrogen donated by hydrogen donor species present in the process solvent to form stable species. Therefore, the presence of sufficient hydrogen donor compounds in the coal liquefaction reaction mixture is necessary to prevent the repolymerization of free radicals thereby aiding the production of lower-molecular-weight oils and asphaltenes. It has been speculated that mineral matter catalyzes the coal liquefaction reaction by enhancing the transfer of hydrogen from the gas to liquid phase thus maintaining the hydrogen donor capability of the process solvent.

The catalytic effect of mineral matter on hydrogenation of model compounds and coal has been investigated by a number of investigators.(1-12) Iron compounds which are abundant both in nature and as an article of commerce were studied extensively. The Germans found that adding iron sulfate and Bayermasse (iorn oxide containing material obtained from aluminum manufacture) to feed slurry improved coal liquefaction.(13) Numerous researchers who have studied the catalytic activity of iron as either iron pyrite or pyrrhotite in liquefaction have reported improved results.(14-22)

Like iron, molybdenum and several other transition metal have been shown to catalyze coal liquefaction.(13,23,24,25,26) Since transition metals are both expensive and scarce, their application in liquefaction will depend greatly on their activity at low concentrations. Interestingly, several metals have been shown to be very active in coal liquefaction at very low concentrations.(13,25,26)

In the present paper, the activity of iron, molybdenum, cobalt, and nickel in catalyzing the liquefaction of coal is discussed. The catalytic activity will be related to the product distribution which will include hydrocarbon gas make, oil yield, asphaltene and preasphaltene yields, and degree of coal conversion. The effect of iron and molybdenum mixtures was also studied. All the data reported in this paper refer to results in a continuous 100 pounds per day coal process unit.

Experimental Section

Materials. A low-ash, low-pyrite Eastern Kentucky Elkhorn #2 coal obtained from a mine in Letcher County was used in the study. The sample was treated in a coal preparation plant to reduce the ash and pyrite contents. This sample was purposely selected to minimize the influence of the coal ash and pyrite on the liquefaction. The coal sample was ground to 95% minus 200 mesh particles, dried in air and screened through a 150 mesh sieve prior to use. The detailed analysis of the screened coal is reported in Table 1.

SRC-II heavy distillate supplied by the Pittsburg and Midway Coal Mining Company was used as a process solvent. The chemical analysis of the process solvent is shown in Table 2. The solvent contained 93.8% pentane-soluble oils, 5.0% asphaltenes, 0.4% preasphaltenes, and 0.8% insoluble organic material (pyridine insolubles). The process solvent contained organic compounds boiling in the range of 550 to 850°F temperature.

Iron sulfate ($FeSO_4.7H_2O$) was received from Textile Chemical Company, Reading, Pennsylvania. The sample contained approximately 97% iron sulfate cyrstals and minor quantities of iron oxide, titanium dioxide and magneisum sulfate as impurities. Ammonium molybdate, nickel nitrate, and cobalt nitrate were reagent grade materials obtained from Fischer Scientific Company, Fair Lawn, New Jersey.

Metals Impregnation. A sample of coal was impregnated with 1% iron by adding a 10.0% ferrous sulfate solution in distilled water to ground coal. Three different samples of coal were impregnated with 0.02% molybdenum, nickel, and cobalt by mixing the samples with 0.5% ammonium molybdate, nickel nitrate and cobalt nitrate solutions, respectively. Since molybdenum, nickel, and cobalt are very expensive compared to iron, very low concentrations (200 ppm) of these metals based on coal were used. Another sample of coal was impregnated simultaneously with a mixture of 1 wt.% iron and 0.02 wt.% molybdenum based on coal. The impregnated coal samples were dried at 60°C for 72 hours and ground under nitrogen before use in liquefaction experiments.

Equipment. Process studies were done in a continuous 100 pound/day coal liquefaction unit equipped with a continuous stirred autoclave. The use of a stirred tank reactor ensured that solvent vaporization matched that of an actual coal liquefaction dissolver and that coal minerals did not accumulate.

Since there was no slurry preheater, all of the sensible heat was provided by resistance heaters on the reactor. Because of this high heat flux, the reactor wall was about 27°F hotter than the bulk slurry. Multiple thermocouples revealed that the slurry temperature inside the reactor varied by only 9°F from top to bottom. A detailed description of the reactor is presented elsewhere.(27)

The products were quenched to 320°F before flowing to a gas/liquid separator that was operated at system pressure. The slurry was throttled into the product receiver while the product gases were cooled to recover the product water and organic condensate. The product gases were then analyzed by an on-line gas chromatograph.

Procedure. Coal liquefaction runs were performed at 825°F, 2,000 psig hydrogen pressure, 1,000 rpm stirrer speed, hydrogen feed rate equivalent to 5.5 wt. % of coal, and a superficial slurry space velocity of 1.5 inverse hours. The coal concentration in the feed was 30 wt.%.

At least 10 reactor volumes of the product were discarded prior to collecting a product sample. A complete sample consisted of one 8-oz product slurry, one 1-L product slurry as back-up sample, a light condensate sample, and a product gas sample.

The product slurry from the continuous reactor was solvent separated into four fractions: (1) pentane-soluble material (oil), (2) pentane-insoluble and benzene-soluble material (asphaltene), (3) benzene-insoluble and pyrdine-soluble material (preasphaltene), and (4) pyridine-insoluble material. The latter contains insoluble organic material (IOM) and mineral residue. The overall coal conversion is calculated as the fraction of organic material (moisture-ash-free coal) soluble in pyridine.

Results and Discussion

Effect of Transition Metals - The impregnation of Elkhorn #2 coal with 1 wt.% iron had no effect on overall coal conversion but increased the production of oils from 12 to 25% (Table 3). The production of hydrocarbon gases decreased with iron; the decrease in the production of hydrocarbon gases is statistically significant at this level. The production of heteroatom gases changed marginally with iron impregnation. The preasphaltene concentration decreased from 44 to 36% with iron impregnation. Hydrogen consumption based on elemental hydrogen balance decreased from 0.6 to 0.4 percent with iron impregnation.

The hydrogen contents of the oil, asphaltene and preasphaltene fractions were lower with iron impregnation compared to the baseline run (Table 4). Apparently the dispersed iron system was not effective in hydrogenating the liquefaction products. This would be advantageous in that expensive hydrogen would not wasted in hydrogenating SRC (asphaltenes and preasphaltenes), which would be used ultimately as a boiler fuel. The SRC sulfur content was unchanged with iron impregnation. Likewise, the sulfur contents in the various fractions were unaffected with iron (Table 4). Nitrogen content in the oil and asphaltene fractions decreased slightly, whereas it increased in the preasphaltene fraction. The oxygen content of oils decreased slightly, but it increased

significantly in the asphaltene and preasphaltene fractions with iron impregnation. No definite conclusion could be drawn concerning deoxygenation because oxygen content was determined by difference.

The hydrogen distribution in the solvent generated by coal liquefaction was determined by proton NMR to determine the changes in solvent quality by iron impregnation. The hydrogen donor capability of a solvent was measured in terms of the combined concentration of H_a and H_o. The higher the combined concentration of H_a and H_o, the better would be the quality of the process solvent. Data in Table 5 revealed that the hydrogen donor capability of the solvent generated with no catalyst and with iron was lower than that of the original process solvent. The aromatic hydrogen content of solvent increased with both no catalyst and with iron. However, the increase in aromatic hydrogen content was more dramatic with iron. The decrease in the quality of the solvent generated with iron was contrary to the speculation made by several researchers that mineral matter improved coal liquefaction by enhancing hydrogen transfer from gas to liquid. In terms of actual plant operation, a decrease in solvent quality means a decrease in the liquefaction performance. Therefore, the generated solvent has to be hydrogenated externally to increase its hydrogen donor capability and to maintain the liquefaction performance of the iron catalyst.

The impregnation of coal with 0.02 wt.% (200 ppm) cobalt and molybdenum increased the coal conversion slightly. The magnitude of the increase in coal conversion was very similar to that obtained with 1 wt.% iron (Table 3). The coal conversion, however, decreased with nickel impregnation. The production of oils increased significantly from 12 to 20-21% with cobalt, nickel, and molybdenum. The increase was slightly lower than that obtained with iron. The production of hydrocarbon gases was higher with cobalt, nickel and molybdenum than iron but still lower than the base-line run. Preasphaltenes conversion increased with cobalt, nickel, and molybdenum, but it was much lower than that noted with iron. Asphaltenes yield was slightly lower with cobalt, nickel, and molybdenum than iron; asphaltene concentration decreased from 21 to 18 with cobalt, nickel, and molybdenum, whereas it decreased to 19 percent with iron.

Hydrogen consumption based on elemental hydrogen balance was lower with cobalt, nickel and molybdenum compared to baseline run (Table 3). Lower hydrogen consumption was due to lower production of hydrocarbon gases and lower hydrogen contents in the asphaltene and preasphaltene fractions (Table 4). Like iron, other metals were also found to be ineffective in hydrogenating asphaltenes and preasphaltenes. Nitrogen and sulfur contents in various fractions were very similar with and without metals. The hydrogen contents of the oil fractions obtained with metals were similar to the base-line run except for nickel (Table 4).

The quality of solvent generated with cobalt, nickel and molybdenum was higher than that generated either with iron or without metals (Table 5). The concentration of H_{AR} decreased and that of H_a and H_o either increased or maintained with cobalt, nickel and molybdenum. The increase in the quality of generated solvent is an indicative of enhancement of hydrogen transfer from gas to liquid phase with cobalt, nickel and molybdenum catalysts.

The above discussion showed that the impregnation of Elkhorn #2 coal with metals significantly increased oils production, increased preasphaltene conversion and decreased hydrocarbon gas make. The metals, however, did not change SRC sulfur content.

Comparing the activity of iron to that of other metals, it was found that iron impregnation yielded higher oils production and preasphaltenes conversion than other metals. However, other metals were more active in asphaltenes conversion than iron. The hydrogen content of generated solvent decreased with iron and nickel, whereas it was maintained with cobalt and molybdenum. The quality of generated solvent decreased with iron, but it increased with other metals.

Interaction of Metals in Coal Liquefaction - To utilize the selective activity of iron for the conversion of preasphaltenes and of other metals for the conversion of asphaltenes, a sample of coal impregnated simultaneously with iron and molybdenum was liquefied. The conversion of both asphaltenes and preasphaltenes increased with iron/molybdenum mixture compared to iron and molybdenum alone (Table 6). In addition, oils production increased significantly with the mixture compared to iron and molybdenum alone. Iron and molybdenum together not only increased oils production and asphaltenes and preasphaltenes conversion but also significantly increased the overall coal conversion from 87 to 91%. The production of hydrocarbon gas was lower with mixture than either alone. The SRC sulfur content changed slightly, but the change was within the limits of experimental error. These increase in coal conversion, oils production and asphaltenes and preasphaltenes conversion indicated a significant synergistic effect of the two metals.

Hydrogen consumption with the iron/molybdenum mixture was higher than molybdenum and iron alone (Table 6). The hydrogen content of the various fractions generated with iron/molybdenum mixture was very similar to that obtained with iron and molybdenum alone (Table 7). No significant differences were noted in the nitrogen and oxygen contents in the various fractions generated with iron and molybdenum alone or used together except for slightly lower nitrogen content noted in preasphaltene fraction obtained with iron/molybdenum mixture. The quality of solvent generated with iron/molybdenum mixture was higher than iron alone, but was lower than that obtained with molybdenum alone (Table 8).

The above discussion shows that a synergism exists between iron and molybdenum in the catalysis of coal liquefaction reaction. This synergism can be effectively utilized to increase the oils production and the conversion of asphaltenes and preasphaltenes. Furthermore, the increase in oil production can be obtained without significantly increasing hydrogen consumption by taking advantage of synergistic effect. The combination of iron and molybdenum, however, is ineffective in reducing SRC sulfur content.

Conclusion

The impregnation of coal with transition metals like iron, cobalt, nickel, and molybdenum increases the oils production by increasing the asphaltenes and preasphaltenes conversion. Metals impregnation also help in improving overall coal conversion except for nickel. The production of hydrocarbon gases decreases with metals. Likewise, hydrogen consumption decreases with metals. Iron is more active for the conversion of preasphaltenes and the production of oils than other metals, whereas it is less active for the conversion of asphaltenes.

These differences may partly be due to the use of higher concentration of iron than other metals. Since iron is rather inexpensive compared to other metals, it is economically feasbible to use higher concentration. On the other hand, it is not economically feasible to use higher concentration (greater than 200 ppm) of other metals. Simultaneous impregnation of coal with iron and molybdenum shows significant synergism in coal liquefaction. The conversion of coal, asphaltenes, and preasphaltenes and the production of oils are much greater with iron/molybdenum mixture than either of them alone. The mixture also results in lower hydrocarbon gas make than iron and molybdenum alone. The mixture, however, is ineffective in reducing the SRC sulfur content.

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Table 1

Chemical Analysis of Elkhorn #2 Coal Sample

	Weight %
Carbon	77.84
Hydrogen	5.24
Oxygen	7.20
Sulfur	1.08
Nitrogen	1.75
Moisture	1.55
Dry Ash	6.29
Distribution of Sulfur	
Total	1.08
Sulfate	0.04
Pyrite	0.25
Organic	0.79

Table 2

Analysis of SRC-II Heavy Distillate

Element	Weight %
Carbon	89.4
Hydrogen	7.2
Oxygen	1.7
Nitrogen	1.1
Sulfur	0.6

Table 3

Effect of Transition Metals on Coal Liquefaction

Catalyst	None	Iron	Cobalt	Nickel	Molybdenum
Metal Concentration, wt.% Coal	-	1.0	0.02	0.02	0.02
Feed Composition		70% Solvent + 30% Coal			
Temperature, °F	825	825	825	825	825
Pressure, psig	2,000	2,000	2,000	2,000	2,000
Hydrogen Flow Rate, MSCF/T	18.9	20.6	23.8	23.8	23.7
Reaction Time, Min.	35	32.8	36.7	37	36.5
Product Distribution, wt.% MAF Coal					
HC	5.2	3.5	3.8	4.8	4.1
CO, CO_2	0.7	0.6	0.7	0.7	0.7
H_2S	0.3	0.2	0.4	0.6	0.6
Oils	12.2	25.0	21.5	20.0	21.7
Asphaltenes	21.2	19.1	17.7	17.0	17.6
Preasphaltenes	44.2	35.8	40.2	38.5	40.3
I.O.M.	14.7	13.5	14.3	16.5	13.7
Water	1.5	2.3	1.4	1.9	1.8
Conversion	85.3	86.5	85.7	83.7	86.8
Hydrogen Consumption, Wt.% MAF Coal	0.64	0.40	0.39	0.33	0.40
SRC Sulfur, %	0.6	0.6	0.6	0.5	0.6

Table 4

Distribution of Elements in Various Liquefaction Reaction Fractions

Catalyst	None	Iron	Cobalt	Nickel	Molybdenum
Oil Fraction, wt.%					
C	89.5	89.9	89.6	89.8	89.5
H	7.2	7.1	7.2	7.1	7.2
O[a]	1.7	1.5	1.7	1.7	1.7
N	0.9	0.8	0.8	0.8	0.9
S	0.7	0.7	0.7	0.6	0.7
Asphaltene Fraction, wt.%					
C	85.9	85.6	85.6	85.0	85.3
H	6.3	6.0	5.8	5.9	5.9
O[a]	4.8	5.5	5.7	6.2	6.0
N	2.4	2.4	2.3	2.4	2.2
S	0.6	0.5	0.6	0.5	0.6
Preasphaltene Fraction, wt.%					
C	85.3	82.9	83.5	83.6	83.4
H	5.2	4.9	4.7	4.6	5.1
O[a]	6.2	8.9	8.9	9.0	8.3
N	2.2	2.6	2.3	2.3	2.6
S	0.6	0.7	0.6	0.5	0.6

[a] Oxygen is determined by difference.

Table 5

Distribution of Protons in the Oil Fraction

Catalyst	Process Solvent	Generated Solvent				
		None	Iron	Cobalt	Nickel	Molybdenum
Total Hydrogen, wt.%	7.2	7.2	7.1	7.2	7.1	7.1
H_{AR}	3.20	3.26	3.64	2.90	2.88	2.75
H_a	2.02	1.95	1.80	2.12	2.24	2.32
H_o	1.98	1.99	1.66	2.18	1.97	2.13

H_{AR} = concentration of aromatic protons

H_a = concentration of alpha protons defined as protons on carbon atoms immediately adjacent to an aromatic ring.

H_o = concentration of beta and higher protons defined as those protons residing on two or more carbon atoms removed from an aromatic ring.

Table 6

Synergistic Effect in Coal Liquefaction

Catalyst	Iron	Molybdenum	Iron + Molybdenum
Metal Concentration, wt.% coal	1.0	0.02	1.0 iron + 0.02 molybdenum
Feed Composition	70% Solvent + 30% Coal		
Temperature, °F	825	825	825
Pressure, psig	2,000	2,000	2,000
Hydrogen Flow Rate, MSCF/T	20.6	23.7	23.4
Reaction Time, Min	32.8	36.5	37.2
Product Distribution, wt.% MAF Coal			
HC	3.5	4.1	3.1
CO, CO_2	0.6	0.7	0.7
H_2S	0.2	0.6	0.6
Oils	25.0	21.7	36.3
Asphaltenes	19.1	17.6	15.2
Preasphaltenes	35.8	40.3	33.0
I.O.M.	13.5	13.7	9.3
Water	2.3	1.8	1.8
Conversion	85.6	86.8	90.7
Hydrogen Consumption, wt.% MAF Coal	0.4	0.40	0.59
SRC Sulfur, %	0.6	0.6	0.7

Table 7

Distribution of Elements in Various Liquefaction Fractions

Catalyst	Iron	Molybdenum	Iron • Molybdenum
Oil Fraction, %			
C	89.9	89.5	89.8
H	7.1	7.2	7.2
O[a]	1.5	1.7	1.6
N	0.8	0.9	0.8
S	0.7	0.7	0.6
Asphaltene Fraction, %			
C	85.6	85.3	85.1
H	6.0	5.9	5.9
O[a]	5.5	6.0	6.0
N	2.4	2.2	2.4
S	0.5	0.6	0.6
Preasphaltene Fraction, %			
C	82.9	83.4	83.7
H	4.9	5.1	4.9
O[a]	8.9	8.3	8.4
N	2.6	2.6	2.3
S	0.7	0.6	0.7

[a] Oxygen is determined by difference.

Table 8

Distribution of Protons in the Oil Fraction

Catalyst	Iron	Molybdenum	Iron + Molybdenum
Total Hydrogen, wt.%	7.1	7.2	7.2
H_{AR}	3.64	2.75	2.92
H_a	1.80	2.32	2.15
H_o	1.66	2.13	2.13

DISPOSABLE CATALYSTS IN TWO-STAGE COAL LIQUEFACTION

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Introduction

In Two Stage Liquefaction, coal is dissolved and partially hydrogenated in the short contact time first stage using process derived solvent as vehicle oil. The unreacted coal and ash are removed by antisolvent deashing and the product oil is upgraded in a separate catalytic reactor (Stage II). This scheme is proposed as a means of converting coal to distillate with higher yield, reduction in hydrogen consumption, and minimal catalyst poisoning since no catalyst is used in the first stage. A number of papers have been published discussing various aspects of this technique (1,2,3,4,5).

In this investigation a disposable ore catalyst consisting of a mixture of bauxite, limonite, and molybdenum ore concentrate is added to the first stage and its effect on the yield and quality of the product oil from the second stage is studied.

Rationale for the Use of Ores as Catalysts

Our research work (6,7) as well as a literature review reveals that cobalt and molybdenum are eminently suited catalysts for hydrogenation and hydrodesulfurization of coal, whereas nickel and molybdenum are good for hydrodenitrogenation. Other metals like iron, copper, tin, zinc, platinum, and tungston have also been found to be effective in coal liquefaction (8). The most inexpensive sources of these metals are their ores where they are present mostly as sufides or oxides.

A number of researchers (9,10) have shown iron pyrites to be an effective catalyst in coal liquefaction. Our earlier studies (11,12,13) have shown that mixtures of iron pyrites and minerals containing other catalytic active transition metals were better liquefaction catalysts than iron pyrites alone. The best ore catalysts tested, in terms of high liquid yield and low product oil viscosities, were mixtures of pyrites, molybdenum ore concentrate, and cobalt-containing ores.

In this study an acid treated (14) mixture of bauxite, limonite and molybdenum ore concentrate was used as a disposable catalyst in the first stage. In the second stage a commercial supported nickel-molybdenum catalyst was used for hydroprocessing.

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Materials, Experimental Equipment, and Experimental Procedure

The major materials used in this study consisted of bituminous coal, a coal-derived heavy distillate, and a disposable ore catalyst. Bitminous coal from the Blacksville No. 2 mine, West Virginia (Pittsburgh seam) whose proximate and ultimate analyses are presented in Table I was used. The vehicle oil was distillate with a boiling range 232-455°C produced at the Ft. Lewis pilot plant running in the SRC-II mode.

A mixture of acid treated bauxite, limonite, and molybdenum ore concentrate (analyses of ores given in Table II) was used as a disposable catalyst in Stage I. A commercially available supported Ni-Mo-alumina catalyst from American Cynamid Co. (HDS-3) was used as a hydroprocessing catalyst for the Stage II. The catalyst and coal used were ground to minus 200 mesh. Hydrogen gas of > 99.95% purity was used.

Experimental Equipment

The hydrogenation reaction was carried out in a stainless steel liner placed in a high pressure internally stirred autoclave of one liter capacity. The experiments were carried out at a stirrer speed of 1000 rpm. The autoclave was provided with a cooling coil through which water could be passed to reduce the reaction temperature if so desired. The autoclave had an electric furnace controlled with a proportional temperature controller. The temperature of the reaction mass was continuously monitored by a temperature recorder. In addition, the autoclave was provided with a thermowell, a pressure gauge, a vent, a sampling valve, and a safety rupture disc. A compressor was used to pressurize the autoclave with hydrogen.

Experimental Procedure

Each of the experimental runs consisted of two stages. In the first, SRC-II distillate was used as the vehicle while in the second, the liquid product from the first stage was used instead. This procedure was followed to approximate the use of product oil from the Stage I for hydroprocessing in Stage II.

Stage I Liquefaction: Forty grams of crushed coal were placed in the liner. About 83.6 gms of SRC-II distillate (in approximately 1:2.1 ratio) were then added to the liner. A pre-determined amount of the disposable ore catalyst was next added to the contents of the liner. The stirrer assembly was fitted onto the autoclave and securely bolted. After testing for leakage, the autoclave was purged with hydrogen. It was then pressurized to a predetermined value so that a pressure of about 2000 psig (13.79 MPa) was reached at the reaction temperature. The heating was initiated thereafter. It usually took 65-70 minutes to heat the autoclave and its contents from room temperature to reaction temperature. The reaction was then allowed to proceed for a given period of time. The temperature was maintained at the reaction temperature during this period. After the elapse of reaction time, the reaction was arrested by turning off the power to the furnace and cooling the contents down rapidly by passing cold water through the cooling coil. The autoclave was allowed to cool down to room temperature by leaving it overnight. The lique-

Table I

Proximate and Ultimate Analyses of Coal Sample

Proximate Analysis	As Recd. %	Moist. Free %	Moist., Ash Free %
Moisture	1.2	N/A	N/A
Volatile	35.8	36.2	41.0
Fixed Carbon	51.5	52.1	59.0
Ash	11.5	11.7	N/A

Ultimate Analysis	As Recd. %	Moist. Free %	Moist., Ash Free %
Hydrogen	5.0	4.9	5.5
Carbon	72.0	72.9	82.5
Nitrogen	1.0	1.2	1.4
Sulfur	2.7	2.7	3.1
Oxygen	7.7	6.7	7.6
Ash	11.5	11.7	N/A
Btu/lbm	12,892	13,052	14,776

Table II

Mineral Ores and Their Percent Composition

1.	Limonite	Ni	1.1	Si	16.4
		Mg	9.8	Fe	20.2
		Al	1.4	Cr	0.5
2.	Molybdenum Oxide Concentrate (Moly. Corp.)	Mo	47.0	Ca	0.4
		Fe	2.8	Cu	0.5
		Si	3.5	Sn	0.4
		Mg	0.6	Zn	0.2
		Al	0.6	K	0.2
		S	0.4		
3.	Bauxite (Canada)	Mn	0.1	Si	1.9
		Ni	0.5	Ca	0.3
		S	0.1	Co	0.1
		Sn	0.7	Al	28.8
		Ti	10.1	Cr	0.3
		Mo	0.2	Cu	0.1
		Ag	0.1	Fe	5.6
		Na	0.6	K	0.3
				Mg	0.1

fied products were then taken out of the autoclave and hot filtered to remove unconverted coal, ash, and catalyst. The filtered liquid and residue were weighed and percent conversion and liquefaction calculated. Viscosity of the product liquid at 60°C was determined using a Brookfield viscometer.

Stage II Liquefaction: The same procedure was repeated using filtered product liquid from the Stage I. A commercial supported Ni-Mo catalyst was used for this stage.

Results and Discussion

The main objective of this investigation was to study the effect of addition of a disposable catalyst in the Stage I on the yield and quality of product oil from the Stage II. The percent conversion, percent oil yield and viscosity of the product oils are presented in Table III.

Percent conversion and liquefaction of coal are defined as follows:

Percent Conversion = {Original Coal (macf) - Residue (macf)} x 100/Original Coal (macf)

Percent Liquefaction = Liquid Products x 100/Original Coal (macf)

where macf = moisture, ash, catalyst free

Experiments S.N. 1 through 12 show the effect of addition of a disposable catalyst to Stage I. Experiments were conducted at reaction time of 30, 10, and 6.5 minutes for Stage I, whereas reaction time for Stage II was kept constant at 30 mintues. The other operating conditions were maintained the same as mentioned earlier under experimental procedure. It was found that percent coal liquefaction for all Stage I reaction time was about 10 percent higher when the disposable catalyst was used. Similarly, viscosity of product oil, from both Stage I and II, was lower for all Stage I reaction time when the disposable catalyst was used. Product oil from Stage II showed about 35 percent reduction in viscosity with the use of our disposable catalyst in Stage I.

In another set of experiments S.N. 13 through 16, effect of reaction temperature on product oil viscosity from Stage II was studied. Experiments were conducted at reaction time and temperature of 30 minutes and 400°C in Stage II, respectively, with and without the use of the disposable catalyst in Stage I. The first stage liquefaction was conducted at reaction time and temperature of 6.5 minutes and 425°C, respectively. The viscosity of product oil from Stage II was found to be lower by only about 20 percent as compared to 35 percent in earlier experiments S.N. 9 through 12. This is considered due to lower reaction temperature in Stage II.

Solvent analysis (15) was performed on product oil from Stage II for experiments S.N. 14 and 16. It was found that asphaltene content (cyclohexane insolubles) of product oil with no catalyst used in Stage I was 12.3 against 8.3 percent when liquefaction was conducted in Stage I in presence of the disposable catalyst. Preasphaltene (THF insolubles) content was found to be 0.3 percent in both the cases.

Table III

Liquefaction of Coal Using Two Stage Process

Serial Number	Name of Catalyst/Ore	Stage Number	%Catalyst (Based on maf coal/oil)	Reaction Time (mins.)	Reaction Temperature (C)	%Conversion	%Liquefaction	Viscosity, cp @60 C	Difference (% conv.-% Liq.)
1	--	I	--	30	425	85	70	28.5	15
2	Co-Mo Harshaw 0402T	II	1.0*	30	425	--	--	9.8	--
3	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	30	425	88	82	21.0	6
4	Co-Mo Harshaw 0402T	II	1.0*	30	425	--	--	6.1	--
5	--	I	--	10	425	83	69	42.4	14
6	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	18.0	--
7	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	10	425	85	81	31.2	4
8	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	11.0	--

Table III (cont.)

Serial Number	Name of Catalyst/Ore	Stage Number	%Catalyst (Based on maf coal/oil)	Reaction Time (mins.)	Reaction Temperature (C)	%Conversion	%Liquefaction	Viscosity, cp @60 C	Difference (% conv.-% Liq.)
9	--	I	--	6.5	425	83	69	68.0	14
10	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30.0	425	--	--	22.0	--
11	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	6.5	425	85	80	38.4	5
12	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	425	--	--	14.25	--
13	--	I	--	6.5	425	84	70	66.0	14
14	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30.0	400	--	--	29.0	--
15	Limonite Moly. Oxide Conc. Bauxite	I	1.19 0.572 3.58	6.5	425	87	81	36.0	6
16	Ni-Mo HDS-3 MTG-S-0658	II	1.0*	30	400	--	--	23.0	--

* Percentage Catalyst Based on Product Oil from Stage I.

Conclusions

The disposable catalyst containing acid treated bauxite, limonite, and molybdenum ore concentrate when used in the first stage of the Two-Stage Liquefaction process improved the yield and quality of product oil. Coal liquefaction yield in Stage I increased by about 10 percent with the use of this catalyst. Similarly, the viscosity of product oil from Stage II showed a decrease of 20-35 percent when the disposable ore catalyst was used in Stage I.

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