

COAL-LIQUEFACTION CATALYSTS FROM FERRIC SULFIDE DISPROPORTIONATION

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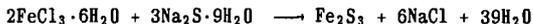
INTRODUCTION

The use of iron-based catalysts of small particle sizes in the liquefaction of coal is widespread in laboratories and in practice due to the cost-efficiency of the catalyst and the ability of the small particles to penetrate the pore structure of the coal, at least to some extent. Of the iron-based catalysts, pyrite (PY, FeS_2) is found indigenously in coal and has a well-documented ability [1] to enhance liquefaction rates. PY is known [2] to be converted to nonstoichiometric pyrrhotite (PH, FeS_x , $x \approx 1$) under hydrogen atmospheres at high temperatures and pressures, conditions expected in liquefaction. Whether PY or PH or a combination of the two is the catalytically active agent is a matter of current debate.

We have developed mixtures of PY and PH of small crystallite size. The mixtures contain different PH stoichiometries, and different amounts of PH and PY in intimate contact. The expectation is that the different valencies of Fe in atomic-range proximity give rise to a very efficient catalyst. These mixtures are made by disproportionating ferric sulfide (Fe_2S_3) at various temperatures and for various times. The PH/PY ratio and the value of x defined above change with these disproportionation parameters.

EXPERIMENTAL PROCEDURE

Ferric sulfide is prepared by mixing stoichiometric amounts of ferric chloride and sodium sulfide in a cold room below 5°C. The formation of ferric sulfide is instantaneous, following the reaction:



PH, PY and elemental S are the products of disproportionation, through a general reaction of the type:



The solid is washed to remove NaCl and dried. A portion of the resulting solid is separated into PH (soluble in 6M HCl) and PY (soluble in 8M HNO_3), and the amount of Fe in each of these sulfide forms is analyzed by atomic absorption (AA). The rest of the solid is mixed with coal, solvent tetralin and CS_2 presulfider for the liquefaction runs. Occasionally the solid is analyzed by X-ray diffraction (XRD) and Auger Electron Spectroscopy (AES).

Liquefaction runs were carried out in a batch tubing-bomb reactor with vertical agitation. Most experiments were performed on DECS-17 coal, a low-PY, high-exinite material. After liquefaction, the solid is analyzed for

conversion (THF-soluble material) and asphaltenes/preasphaltenes (THF-soluble, hexane-insoluble material). The amount of oil (+ gas) is obtained by difference. The THF-insoluble solid is analyzed for PH and PY.

RESULTS

Ratios of pyrrhotite to pyrite (PH/PY) in the products of Fe_2S_3 disproportionation are shown as a function of disproportionation temperature, T_d , in Table I. Note that elemental S is not shown. Table I indicates that the room-temperature disproportionation yields only PH, for all practical purposes. Increasing T_d increases the relative amount of PY in the solid. Only a few S peaks are visible in the X-ray diffraction XRD pattern for the room-temperature case; presumably the PH crystallites are too small to exhibit peaks. Disproportionation at a temperature $T_d = 100^\circ\text{C}$ shows significant PY peaks but smaller S peaks; again the PH crystallites are X-ray-invisible. When $T_d = 200^\circ\text{C}$, the PH crystallites are large enough to exhibit peaks, PY peaks are larger than at $T_d = 100^\circ\text{C}$, and S peaks are vanishingly small.

Auger electron spectra for the PH/PY mixture after $T_d = 200^\circ\text{C}$ are shown in Figure 1. The shape of the Fe line at around 40 eV indicates that PH of composition Fe_7S_8 ($x = 1.143$) is present. Further, the line shape for S indicates that the elemental form is present. The intensity ratios of the S (LVV) peak to the Fe (LMM) are plotted in Figure 2 as a function of the ratio S/Fe for standard samples of FeS_2 and Fe_7S_8 . Also shown in Figure 2 is the intensity ratio for the product corresponding to $T_d = 200^\circ\text{C}$. This allows one to estimate the amount of surface S (elemental and ionic) to surface Fe for the disproportionated product.

The PH/PY ratio of the catalyst changes after liquefaction. As can be seen in Table I, the changes depend upon both T_d and T_ℓ . Table II shows the changes in the S/Fe ratio in the iron-based catalyst after liquefaction at $T_\ell = 350^\circ\text{C}$ as a function of T_d .

In Figure 3 are plotted the overall conversion, asphaltene/preasphaltene yield and oil (+ gas) yield for DECS-17 coal as a function of the S/Fe ratio of the iron-based catalyst after liquefaction at $T_\ell = 350^\circ\text{C}$. Other choices of the independent variable obviously exist, yet this one appears to give linear relationships for conversion and yields. Results for the unsulfided catalysts, and for liquefaction at $T_\ell = 400^\circ\text{C}$ with sulfided and unsulfided catalysts, have been tabulated elsewhere [3]. We did not test catalyst prepared at disproportionation temperatures higher than 200°C for conversion of DECS-17 coal. However, previous work [4] using Humphrey mine coal (Pittsburgh No. 8 seam) indicates that catalysts corresponding to a PH/PY ratio of unity ($T_d = 200^\circ\text{C}$) have higher conversions and oil (+ gas) yields than those corresponding to larger and smaller ratios ($T_d = 100^\circ\text{C}$, 250°C). These results are shown in Figure 4. Because of the superior performance of the catalyst formed by disproportionation at 200°C for 1 h, we concentrated on this catalyst for further evaluation.

To investigate the efficacy of catalyst-coal mixing, a catalyst impregnation procedure was attempted and conversions and yields were compared to those from the "standard" catalyst preparation procedure described above. In the impregnation procedure, an aqueous solution of FeCl_3 was sonicated with coal, then Na_2S was added, followed by additional sonication. After

disproportionation at 200°C for 1 h, the solid was washed with distilled water to remove NaCl, dried and then placed in the liquefaction reactor with tetralin and CS₂. The conversion and oil (+ gas) yield after liquefaction at T_l = 350°C for 1 h are shown in Figure 5 as catalyst preparation IDW. Also shown in Figure 5 are liquefaction results for preparation procedure IWD, wherein the washing step was carried out between impregnation and disproportionation. Comparing the results of these procedures with the "standard" procedure, labelled DWM, shows that impregnation of the catalyst yields no particular advantage.

Also shown in Figure 5 are the effects of various NaCl-washing techniques on liquefaction. In procedure DNM, the catalyst was mixed directly after disproportionation, without any washing step. Conversions and yield are noticeably lower than DWM, where the washing step is not omitted. Finally, in procedure DWAM, the catalyst was disproportionated and washed (as in DWM), but then a calculated amount of NaCl was added to the solid before mixing with coal. The liquefaction results here are very similar to those where washing was eliminated, thus indicating that the washing step eliminates only the NaCl. In Figure 5, NC represents the results for thermal liquefaction, with no catalyst addition.

Figure 6 shows the effect of catalyst loading on the overall conversion and the yield of oil (+ gas). The loading of the PH/PY mixture catalyst affects the conversion and oil (+ gas) yield of DECS-17 coal in a nonlinear manner. The conversion increases for upto 1 percent loading; at higher loadings, the conversion continues to increase but to a lesser extent. At low catalyst loadings, the yield of oil (+ gas) is less than under non-catalytic conditions. The yield is a minimum around 1 percent loading, after which the yield increases.

Finally, it is worth comparing the disproportionated catalyst with other iron-based catalysts. Figure 7 shows the overall conversion and the oil (+ gas) yield for the case of no catalyst (NC), the catalyst mixture after T_d = 200°C (DFS), and an iron oxide catalyst, FeOOH, developed by Mobay Corporation and provided by Dr. Farcasiu, USDOE/PETC. Results of this catalyst are labelled IO in Figure 7. Liquefaction in each case was at T_l = 350°C for 1 h.

For DFS and IO, catalyst was added corresponding to 0.5 percent Fe. The DFS catalyst was prepared according to the "standard" procedure described above. Figure 7 shows that conversions for the two sulfided catalysts are comparable and greater than the (sulfided) NC case. Unsulfided IO is comparable to the unsulfided NC. Sulfiding improves IO considerably. The yields of oil (+ gas) with both catalysts are smaller than for the NC case, with the DFS yield being somewhat less than the IO yield. This is consistent with Figure 6 which shows the oil (+ gas) yield decreasing for small additions of catalyst (less than 1 percent).

CONCLUSIONS

Hydrothermal disproportionation of ferric sulfide yields a mixture of iron sulfides and elemental sulfur. The sulfides, FeS₂ and various pyrrhotites FeS_x, are present as intimately mixed crystallites in small particles. The relative amount and composition of the FeS_x can be controlled by varying the time and temperature of disproportionation. Thus these iron sulfides are suitable catalysts for coal liquefaction. The activity and selectivity of

these catalysts are comparable to those of other iron-based catalysts.

ACKNOWLEDGMENTS

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TABLE I

Pyrrhotite/Pyrite (PH/PY) Ratio Before and After Liquefaction as Functions of Disproportionation Temperature (T_d) and Liquefaction Temperature (T_l).

T_d [°C]	PH/PY Ratios		
	Before Liquefaction	After Liquefaction	
		$T_l = 350^\circ\text{C}$	$T_l = 400^\circ\text{C}$
25	286	2.5	8.4
100	1.8	5.7	3.2
200	0.87	0.38	0.13

TABLE II

Final S/Fe Ratio in PH/PY Mixtures After Liquefaction at $T_l = 350^\circ\text{C}$

T_d [°C]	S/Fe
25	1.3
100	1.4
200	1.7

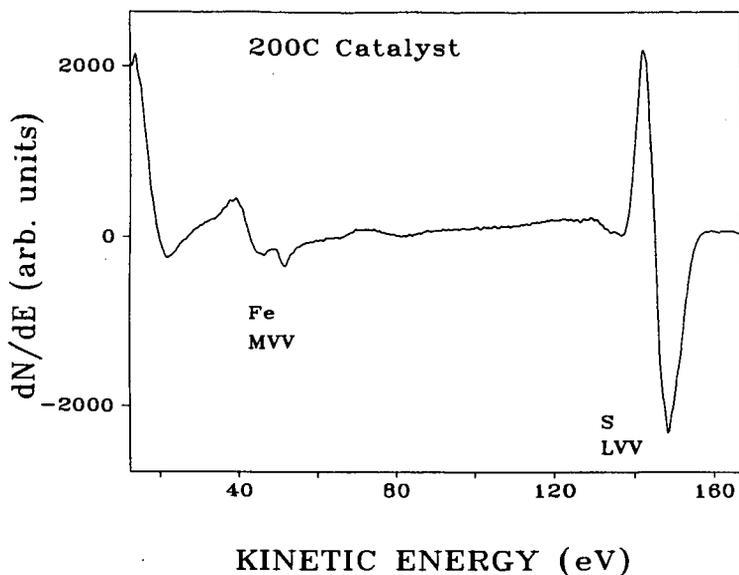


Figure 1. Auger electron spectrum for disproportionated catalyst, $T_d = 200^\circ\text{C}$.

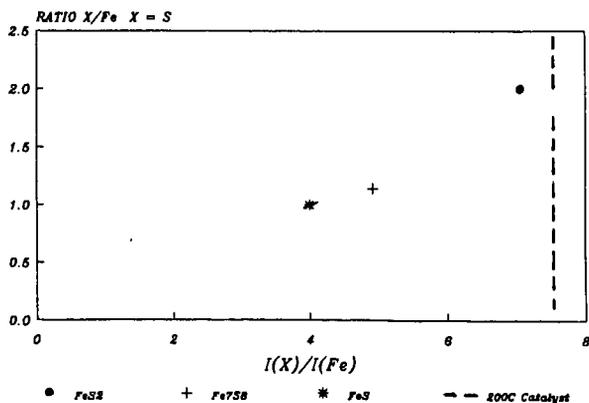


Figure 2. Sensitivity factors of Fe and S for FeS_2 , Fe_7S_8 , and disproportionated catalyst, $T_d=200^\circ\text{C}$.

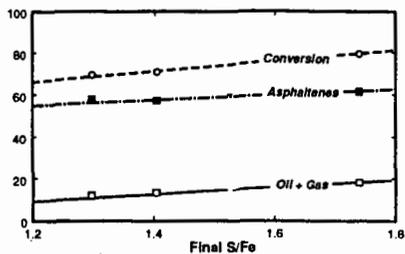


Figure 3. Conversion and yields of preasphaltenes/asphaltenes and oil(+gas) from DECS-17 coal as functions of the final S/Fe ratio of catalyst.

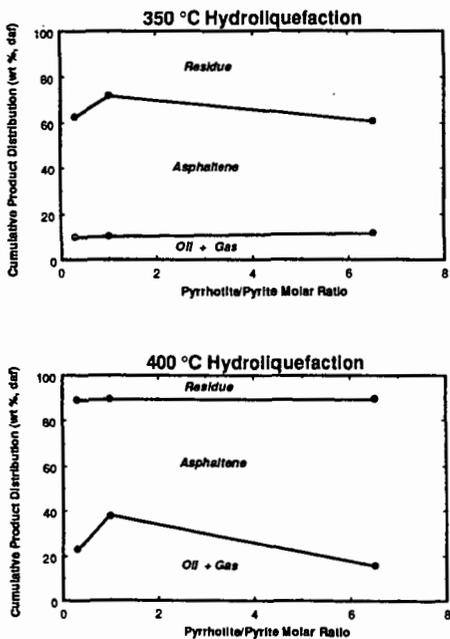


Figure 4. Conversion and yield of oil (+gas) as functions of PH/PY for liquefaction of Humphrey Mine coal [4].

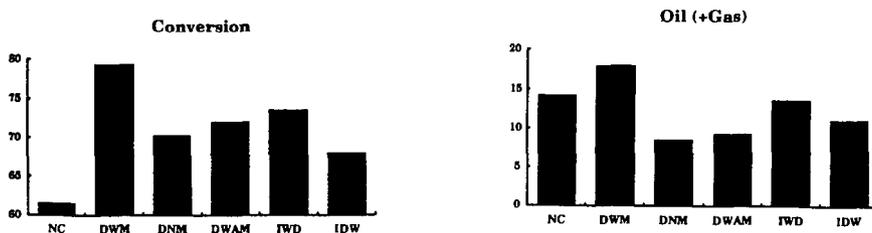


Figure 5. Conversion and yield of oil(+gas) for various procedures of catalyst manufacture. See text for nomenclature.

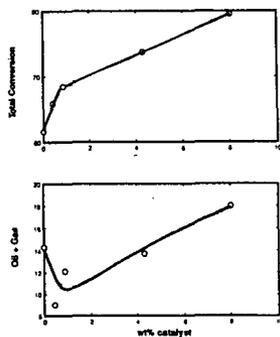


Figure 6. Conversion and yield of oil(+gas) as functions of catalyst loading.

Figure 7. Comparison of conversion (left) and yield of oil(+gas) (right) over disproportionated catalyst (DFS) and over iron oxide catalyst (IO).

