

**THE EFFECT OF CATALYST DISPERSION ON
COAL LIQUEFACTION WITH IRON CATALYSTS**

Cugini, A.V., Krastman, D., Martello, D.V. and Holder G.D.*
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236
University of Pittsburgh

INTRODUCTION

Dispersed catalysts have been used for first stage direct coal liquefaction studies. Compared to supported catalysts, dispersed catalysts offer many advantages for first-stage coal liquefaction, such as the lack of aging and, for inexpensive catalysts, such as iron, the ability to simply dispose of the catalysts. The effectiveness of dispersed catalysts depends on the dispersion of the catalyst in the coal-vehicle system. Catalyst dispersion can potentially be improved by two methods in coal/catalyst systems: improving contact between coal and catalyst during the initial stages of coal liquefaction and optimizing the physical properties of the catalyst, i.e. increased surface area, smaller particle size, or smaller crystallite size.

Dispersion is usually treated qualitatively. Studies have shown that methods of catalyst preparation that should result in enhanced levels of catalyst dispersion also result in the highest levels of catalyst activities as measured by coal conversion to soluble or distillable products.¹⁻⁷ Methods of enhancing catalyst dispersion which have been investigated include developing techniques to increase the surface areas and/or reduce the particle sizes of catalysts, using aqueous catalyst impregnation of coal, and coupling aqueous impregnation with coal swelling.

Enhancing catalyst dispersion has been found to be effective with iron systems. It has been reported that the effectiveness of iron catalysts can be improved by decreasing their initial particle size.⁸⁻¹⁰ However, sintering or agglomeration has been observed under liquefaction conditions.¹¹⁻¹⁴ Coal as well as sulfate pretreatments can act to mitigate this effect.¹³⁻¹⁵

Another means of enhancing the activity obtained with iron catalysts is to improve the contacting between the coal and catalyst. Workers have attempted to use forms of iron catalyst precursors that are soluble in oil or aqueous media. The solubilized precursor could then either be precipitated onto the coal's surface prior to charging the reactor or directly mixed with the coal/solvent mixture in the reaction. Studies have shown that

Reference in this manuscript to any specific commercial product, or service is to facilitate understanding and does not necessarily imply it endorsement or favoring by the United States Department of Energy.

catalyst pretreatments that result in enhanced levels of contacting between coal and catalyst also result in higher levels of coal conversion.^{3,16 and 17}

Recent work at PETC has centered on the development of an iron catalyst precursor that is intimately contacted with the coal and maintains a fine particle size upon conversion to the active, sulfided phase. The procedure, reported previously,³ results in the precipitation of FeOOH directly on the coal surface. Failure to intimately contact the FeOOH with the coal surface resulted in the loss of iron activity. The present study investigates the surface area and particle size changes resulting from the transformation of the precursor, FeOOH, to the active phase, presumably pyrrhotite. The effect of improved contacting between the FeOOH and coal was also investigated.

EXPERIMENTAL

Experiments were conducted with Blind Canyon bituminous (DECS-6, from the DOE/Penn State Coal Sample Bank) and Black Thunder subbituminous coals. Properties of the feed coals are presented in Table 1.

The catalyst precursor was added to the reactor as a dry powder, aqueous solution or by precipitation onto the coal. Hydrated iron oxide (FeOOH) was dispersed onto the feed coals by an incipient wetness impregnation/precipitation approach.³ Forms of iron tested include powdered Fe₂O₃, aqueous ferric nitrate, aqueous ferrous sulfate, and powdered FeOOH. A sample of Fe₂O₃, with a nominal particle size of 1 μ (from Spang and Company) was added as a dry powder. High surface area, powdered FeOOH was prepared by precipitating FeOOH from an aqueous solution of ferric nitrate by the addition of ammonium hydroxide. The precipitate was recovered by filtration through a 0.45 μ filter, was vacuum dried at 40°C, and ground to a powder. The N₂ BET surface area of the FeOOH prepared in this manner was 138 m²/g. Catalyst prepared in this way was added to the reactor in a physical mixture with the coal.

The effectiveness of each catalyst precursor was determined by using each precursor in a 40-mL tubular microautoclave reactor. Experiments were conducted by adding 3.3 g coal to the reactor with 6.6 g of Panasol (a mixture of alkylated naphthalenes obtained from Crowley Chemical). Elemental sulfur (0.1 g) was added to the reactor to sulfide the catalyst precursors. The reactor was charged with 1000 psig (6.9 MPa) of hydrogen and sealed. The pressurized reactor was then heated to the liquefaction temperature in a fluidized sandbath. The heating period lasted 30-40 minutes. Following the liquefaction period (0.5 h), the reactor was cooled and depressurized. Coal conversion was calculated from the solubility of the coal-derived products in THF and in heptane as determined by a pressure filtration technique.¹⁸

Microautoclaves were also employed to investigate the transition of impregnated FeOOH to pyrrhotite. In these

experiments, FeOOH was impregnated onto carbon black rather than coal to eliminate interferences on subsequent analyses from the indigenous pyrite in the coal. The carbon black was Raven 22 Powder obtained from Columbian Chemicals Co. The iron-loaded carbon black and tetralin were heated (under H_2 in the presence of CS_2) to $400^\circ C$ and held at temperature for 5 minutes. The products were mixed with THF and filtered through a 0.45μ filter. The filter cake, containing the iron loaded carbon, was recovered and analyzed by X-ray diffraction (XRD).

A series of iron sulfide catalysts (pyrrhotite, as analyzed by XRD) were prepared from the iron oxide precursors as well as from aqueous ferric nitrate solution and aqueous ferrous sulfate solution. The iron sulfide was prepared by adding the precursor to a 1-L autoclave containing tetralin. The mixture contained 400 g of tetralin and sufficient precursor to produce 4 g of iron sulfide. To convert the precursor to catalyst, the mixture was heated to $400^\circ C$ and held for 0.5 h under 2500 psig (17.3 MPa) of $H_2/3\%H_2S$ which was passed through the reactor at 4 SCFH. The recovered iron sulfide catalysts were extracted with THF.

RESULTS AND DISCUSSION

Catalyst Surface Area

The effect of iron oxide surface area was investigated using powdered FeOOH with a surface area of $138\ m^2/g$ and micronized Fe_2O_3 with a surface area of $5\ m^2/g$. Table 2 gives the effect of precursor surface area (iron oxide) on coal conversion. The precursor surface area does not appear to be important. This was expected to some extent since the precursor undergoes a chemical reaction to form the catalyst. The surface area of the catalyst itself is the important variable. Consequently, a series of tests were conducted to determine the relationship between the surface area of the catalyst (pyrrhotite) and the surface area of the original iron oxide. The catalyst was formed from the precursor in tetralin with an H_2/H_2S atmosphere as described in the experimental section. XRD and BET surface area were conducted on the resulting pyrrhotite. Table 3 presents the surface areas and crystallite sizes of the resulting iron sulfides (pyrrhotites). Also shown in Table 3 are the characteristics of pyrrhotites resulting from soluble iron precursors (ferric nitrate and ferrous sulfate). The analyses showed that the pyrrhotite was crystalline with estimated crystallite sizes ranging from 42 to 82 nm by XRD. The BET surface area analysis indicated that the surface area of the resulting pyrrhotite was significantly different than that of the original iron oxide. For the high surface area precursor, the surface area dropped from $138\ m^2/g$ to $17\ m^2/g$, while the low surface area precursor increased its surface area from $6\ m^2/g$ to $9\ m^2/g$. The similarity of the surface areas of the pyrrhotites resulting from the solid iron oxide precursors helps to explain the similar coal conversions observed with each. The surface areas of the pyrrhotites prepared by aqueous precipitation were both about $30\ m^2/g$, which is greater than those from either of the iron oxide

precursors.

The next series of tests conducted was aimed at investigating the effect of pyrrhotite surface area on coal conversion. Table 4 presents coal conversion as a function of iron sulfide surface area and crystallite size. It appears that there is a relationship between surface area and coal conversion. Clearly the precipitated precursors produced a higher surface area pyrrhotite and subsequently higher coal conversions.

Impregnation

The effectiveness of catalysts formed from FeOOH depends on the method by which FeOOH is added to the system. Table 5 compares coal conversion using physically mixed FeOOH with impregnated FeOOH. The impregnated FeOOH is more active and results in higher coal conversion than the physically mixed FeOOH. As shown in Table 3, the surface area of the iron sulfide formed from powdered FeOOH (not impregnated) in tetralin dropped to 17 m²/g compared to 138 m²/g for its precursor. This large reduction in surface area produced a catalyst which resulted in lower coal conversions compared to the conversions obtained when the precursor was precipitated onto the coal.

The surface area and crystallite size for the catalyst precipitated onto the coal may not be the same as those measured for the catalysts formed in pure tetralin. The pyrrhotite formed from coal-impregnated FeOOH is not easily characterized because of the presence of pyrite and other crystalline material in the coal. Therefore, a separate preparation of impregnated carbon black was prepared in order to see what effect impregnation has on crystallite size. The impregnated carbon black was subjected to liquefaction conditions and recovered by THF extraction. XRD analysis of the iron sulfide on the carbon black revealed that the average crystallite size of the catalyst was 27 nm. This is significantly lower than the pyrrhotite crystallite size formed from powdered FeOOH (56 nm). One of the effects of impregnation of the FeOOH appeared to be the generation of smaller iron sulfide particles in the system.

CONCLUSIONS

In the absence of a carbonaceous support, the transformation of FeOOH to iron sulfide results in a loss of surface area, possibly due to sintering. This effect has been previously documented.¹¹⁻¹⁴ The loss in surface area prevents a correlation between precursor surface area and coal conversion from being established. However, an increase in the surface area of the actual (iron sulfide) catalyst does appear to improve liquefaction yields. Iron sulfide preparations with a broader range of surface area need to be investigated.

The presence of a carbonaceous support for FeOOH tends to mitigate the sintering and favors the formation of smaller particle

size iron sulfide catalysts which are likely to have higher specific surface areas. It is likely that the same effect occurs in coal impregnated with FeOOH since addition of the precursor through impregnation results in higher coal conversions. However, the better contacting between coal and catalyst achieved by impregnation may also contribute to the higher conversions.

ACKNOWLEDGEMENTS

The authors thank Sidney S. Pollack and Elizabeth A. Frommell for their assistance in the X-ray diffraction study.

REFERENCES

1. Derbyshire, F.J., "Catalysis in Coal Liquefaction: New Directions for Research," IEA CR/08, IEA Coal Research, June 1988.
2. Cugini, A.V., Ruether, J., Krastman, D., Cillo, D.L., Balsone, V., and Smith, D.N., Fuel Div. Preprints, 33(1), 6 (1988).
3. Utz, B.R. and Cugini, A.V., U. S. Patent 5,096,570, 1992.
4. Derbyshire, F.J., Davis, A., Lin, R., Stansberry, P.G., and Terrer, M.T. Fuel Proc. Tech. 12, 127 (1986).
5. Joseph, J., Fuel, 70, 459 (1991).
6. Artok, L., Davis, A., Mitchell, G.D., and Schobert, H.H., Fuel, 71, 981 (1992).
7. Weller, S.W., Proceedings: 4th International Conference on the Chemistry and Uses of Molybdenum, 1982.
8. Pregermain, S. Fuel Processing Technology, 12, 155 (1986).
9. Andres, M., Charcosset, H., Chiche, P., Dvignon, L., Djega-Maradassou, G., Joly, J.P., and Simone, P., Fuel, 62, 69 (1983).
10. Fukuyama, T., Okada, T., Takekawa, T., Matsubara, K., and Moriguchi, S., Proceedings: International Conference on Coal Science, 181 (1985).
11. Srinivasan, R., Keough, R.A., and Davis, B.H., ACS Div. of Fuel Chemistry Preprints, 37(3) 1265 (1992).
12. Bacad, R., Fuel Processing Technology, 28, 203 (1991).
13. Djega-Maradassou, G., Besson, M., Brodzik, D., Charcosset, H., Huu, T.V., and Varloud, J., Fuel Processing Technology, 12, 143 (1986).
14. Stephens, H.P., Stohl, F., and Padrick, T.D., Proceedings: International Conference on Coal Science, 368 (1981).
15. Pradhan, V. R., Tierney, J., and Wender, I., Sixth Annual Technical Meeting of the Consortium for Fossil Fuel Liquefaction Science, 1992.
16. Garg, D. and Givens, E.N., Fuel Processing Technology, 7, 59 (1983).
17. Mitra, J.R., Chowdhury, P.B., and Mukherjee, D.K., Fuel Processing Technology, 8, 283 (1984).
18. Utz, B.R., Narain, N.K., Appell, H.R., and Blaustein, B.D., "Coal and Coal Products: Analytical Characterization Techniques" (Ed. E.L. Fuller, Jr.), Am. Chem. Soc. Symp. Ser. 205, 225 (1982).

Table 1. Analyses of Coal Feeds

	Black Thunder	Blind Canyon DECS-6
Proximate Analysis (wt%, as received)		
Moisture	19.2	4.7
Volatile Matter	34.8	42.4
Fixed Carbon	40.6	47.3
Ash	5.4	5.6
Ultimate Analysis (wt%, Moisture Free)		
Carbon	68.2	76.5
Hydrogen	4.8	5.9
Nitrogen	1.0	1.5
Sulfur	0.4	0.4
Oxygen (Difference)	18.8	9.9
Ash	6.8	5.8
Sulfur Forms (wt%)		
Sulfate	0.02	0.01
Pyritic	0.04	0.02
Organic	0.30	0.41

Table 2. Effect of Iron Precursor Surface Area on Coal Conversion of DECS-6 Blind Canyon Coal at 425°C, 0.5 h, 1000 psig (cold) H₂, 5000 ppm Fe, 0.1 g S added to 9.9 g of a 2:1 mixture of Panasol to DECS-6 Coal.

Precursor	Precursor Surface Area, m²/g	Coal Conversion(%) To:	
		THF Sols.	Heptane Sols.
None	None	58	30
FeOOH	138	66	34
Fe ₂ O ₃	6	73	35

Table 3. Effect of Precursor Type and Surface Area on the Resulting Iron Sulfide Crystallite Size and Surface Area Produced in a 1-L Autoclave at 400°C, 0.5 h, 2500 psig $H_2/3\%H_2S$.

Catalyst Precursor	Surface Area m^2/g	Iron Sulfide Crystallite Size, nm @ 20=53.2	Iron Sulfide Surface Area m^2/g
Micronized Fe_2O_3	6	82.0	9
FeOOH	138	56.0	17
Aqueous Ferric Nitrate	n/a	43.0	30
Aqueous Ferrous Sulfate	n/a	42.1 ¹	32

¹ Calculated based on surface area.

Table 4. Effect of Iron Sulfide Precursor Surface Area and Crystallite Size on Coal Conversion of DECS-6 Blind Canyon Coal at 425°C, 0.5 h, 1000 psig (cold) H_2 , 5000 ppm Fe, 0.1 g S added to 9.9 g of a 2:1 mixture of Panasol to DECS-6 Coal.

Precursor Surface Area, m^2/g	Crystallite Size, nm @ 20=53.2	Coal Conversion(%) To:	
		THF Sols.	Heptane Sols.
None	na	58	30
9	82.0	73	31
17	56.0	70	31
30	43.0	84	38
32	42.1 ¹	76	35

¹ Calculated based on surface area.

Table 5. Effect of FeOOH Mode of Addition on Coal Conversion of DECS-6 Blind Canyon Coal and Black Thunder Coal at 425°C, 0.5 h, 1000 psig (cold) H₂, 5000 ppm Fe, 0.1 g S added to 9.9 g of a 2:1 mixture of Panasol to Coal.

Precursor	Coal Conversion(%) To:	
	THF Sols.	Heptane Sols.
Blind Canyon		
None	58	30
Physically Mixed FeOOH	66	34
Impregnated FeOOH	85	41
Black Thunder		
None	54	30
Physically Mixed FeOOH	64	35
Impregnated FeOOH	73	33