

IMPREGNATION ALTERNATIVES FOR Fe-BASED COAL LIQUEFACTION CATALYSTS

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Introduction

Because of the cost effective and environmentally compatible nature of Fe, attention has been directed towards improving the utilization of this metal in direct coal liquefaction. Among the several factors thought to affect catalyst activity, much of this work has focused on dispersion. Weller and Pelipetz¹ reported the importance of catalyst dispersion, based on experiments with a wide variety of catalysts in solvent-free liquefaction studies. And in the presence of solvent, other studies have demonstrated the advantages of adding the precursor by impregnation over its addition in the form of particulates. In general, a high surface/volume ratio, along with intimate contact between the active catalyst and coal, are thought to be the controlling factors.² Dispersion, as normally inferred from changes in catalyst activity, may be affected by the mode of addition, the presence of solvent, and the initial composition of the precursor (e.g., soluble organometallics); and for coal-impregnated catalyst precursors, the choice of impregnation solvent³ and impregnation conditions.

A variety of innovative strategies have been developed to introduce catalyst precursors to the liquefaction reaction while seeking to maintain particle size and distribution. These have included the use of emulsions and colloids,^{4,5,6} direct addition of ultra-fine particles to the slurry,^{7,8,9,10} addition of oil soluble organometallics and carbonyls,^{11,12,13} ion exchange¹⁴ and impregnating the coal.^{1,15,16}

One of the more effective ways of introducing an Fe catalyst precursor to the coal liquefaction process is to disperse the iron salt onto the coal surface using a liquid medium to impregnate the feedstock. In one technique, coal is impregnated with a metal salt solution up to the point where the unbound moisture begins to form drops.¹⁷ Additionally, the Fe salt may be precipitated with a base solution to fix the precursor onto the coal surface, called incipient wetness/ precipitation (IW/P). Cugini and his co-workers,¹⁵ using ferric nitrate and ammonium hydroxide, recorded the benefits of this last method of preparation, which included high Fe dispersion levels and exploiting the sub-micron particle size of the FeOOH precursor, and follow-on active pyrrhotite phase. Andres, et al.,¹⁸ earlier verified that iron particles, in various forms as oxides and oxyhydroxides, retained their small size upon conversion to pyrrhotite under coal hydroliquefaction conditions.

The IW/P preparation is a multistep process, consisting of coal preparation, metal impregnation, base precipitation, filtration, washing, and drying. The influence of these various steps on coal surface chemistry and liquefaction performance was reported previously.¹⁹ XPS studies showed the iron on IW/P coals to be highly dispersed, more concentrated on the coal surface, and present as both FeOOH and Fe₂O₃.

Because of the cost of the several processing steps and related material handling requirements, the promise of IW/P coal preparation may not be realized commercially without some simplification. In the case of Mo, studies have suggested that complete dispersion of the catalyst precursor at the outset of the reaction may not be essential for satisfactory results. Bockrath, et al.,²⁰ recognized that molybdenum sulfide concentrated in THF extracted liquefaction residues retained its catalytic activity when mixed with fresh coal slurry. In related work, molybdenum was impregnated onto coal which was then exposed to liquefaction conditions in a microautoclave. The products, which were subsequently mixed with 20 times as much fresh coal, were found to be active even in the initial stages of liquefaction.

The work presented here addresses impregnation alternatives which reduce the amount of prepared coal by loading the precursor Fe on only a fraction of the feedstock. Concentrating the Fe on only a portion of the feed, referred to here as the "vector", would reduce the cost of handling the coal, which could be a significant factor in the overall economics of the project. Additionally, if the metal added in this way remains quite active, other more robust and/or active substrates might be considered as the catalyst carrier. Since it had been determined that ferrous sulfate is currently the lowest cost form of soluble iron commercially available (as copperas), work was performed

exclusively with this salt.

Experimental

Materials- Reagents were purchased as follows: Practical grade dimethyl disulfide (DMDS) from Fluka AG; 99% purity UV grade tetralin, high purity tetrahydrofuran (THF), and high purity pentane were Burdick & Jackson Brand from Baxter S/P; 98% purity $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ from Aldrich; and concentrated ammonium hydroxide from Mallinkrodt. Ultra High Purity Grade hydrogen was supplied by Air Products and Chemicals, Inc. Burn Away™ petroleum coke was supplied by HRI, Inc. Coulometrics brand carbon black, commercially reduced in a 95% N_2 /5% H_2 gas stream at 400°C, was purchased from UIC Inc. The coke and carbon black are described further in Table I, which shows they are predominantly fixed carbon. Wyodak subbituminous coal from the Black Thunder mine, supplied by CONSOL, Inc., was ground to -200 mesh, riffled and stored under nitrogen at 4°C. The analysis of the coal (dry basis) was: C- 72.2%; H- 4.3%; N-1.2%; S- 0.5%; O (by difference)- 16.0%; ash- 5.8%. It had a moisture content of about 21 wt%.

Preparation of vectors- Four coal samples were impregnated with Fe using the IW/P technique. The first (termed 100% IW/P) had an Fe concentration of 0.8 wt% mf coal. The other three were impregnated with additional Fe sufficient to mix them with fresh coal in the proportions of 10:90, 50:50, and 90:10, to yield an overall Fe concentration the same as the 100% IW/P sample. The coke and carbon black were also prepared using the same IW/P technique as for the coal, at concentrations that would allow the Fe to be added on 10 wt% of the reactor feed. The 100% IW/P sample and the mixed feed coals were then liquefied to compare product yields among the various ways Fe had been introduced to the reaction.

For each vector prepared, the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ required was dissolved in 0.76 g H_2O /g vector coal (dry basis). The solubility of ferrous sulfate presented no problems in the preparations. This solution was added dropwise while stirring and then allowed to stand for ¼ hour. A 3% ammonium hydroxide solution was added at a ratio of 138 mol NH_3 /mol Fe and filtered. The filter cake was washed with 25 ml distilled water/g coal until the odor of ammonia was absent, and dried for 20 hours to about 20% water content with flowing N_2 at 25°C. Recovery of Fe on the samples was greater than 98%.

Liquefaction experiments- Typical liquefaction experiments were carried out using a total of 3.0 g coal and 5.4 g tetralin in 50 ml microautoclaves. A blend of Fe-impregnated substrate and as-received coal comprised the reactor feed. When Fe was added to the reaction mixture, sulfur, as DMDS, was added at a minimum ratio of 1.5 mol S/mol Fe, sufficient to produce pyrrhotite as the final form of the catalyst. The reactors were pressurized to 6.89 MPa with hydrogen and shaken at 400 cpm in an air-fluidized sand bath at 415°C for 30 minutes. Experiments were duplicated, at a minimum.

In the first step of product work-up, gases were collected and analyzed by gas chromatography. The other products were then scraped from the reactor with THF and extracted in a Soxhlet apparatus. The THF solubles were subsequently separated into pentane soluble (Oils) and pentane insoluble (PA+A) fractions. Total conversion was determined from the amount of THF insoluble material that remained. Added Fe was subtracted from this residue at the equivalent weight of pyrrhotite. Oils were calculated by difference, and as a result, water produced during liquefaction, as well as any experimental error, is included in that fraction. All product yields are stated on an maf coal basis.

In liquefaction experiments using the coke and carbon black substrates, the substrates (and later, vector) weights were subtracted from the final THF insoluble residues at their mf starting weight, even though both substrates showed a slight propensity (~2-3 wt%) to adsorb THF during Soxhlet extraction. As before, liquefaction product yields were calculated on an maf coal basis.

Results and Discussion

Limited Fe dispersion- To examine very limited dispersion of the starting Fe, the powdered $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added directly to the reactor without mixing with the coal feed. Additionally, to examine an alternate, simplified preparation similar to the IW/P method, an aqueous solution of the same salt was added directly to the reactor using only 12% the solution weight needed to impregnate the coal by the IW/P method, without base precipitation or drying. The results of these two experiments are shown in Table II in comparison with the thermal conversion of coal (uncatalyzed), and with liquefaction of the 100% IW/P coal. Both the powdered and aqueous Fe additions showed only slight catalyst activity, with any added conversion reporting to the PA+A fraction. In contrast,

impregnating the coal improved THF conversion by 8%. Again the increase in conversion reported primarily to the PA+A fraction; the slight increase in Oils yield is not significant.

Liquefaction with vector coals- To investigate the effects of limited dispersion using IW/P coals, liquefaction experiments were performed by impregnating Fe on the vector portion of the total feed coal. The greater the Fe concentration on the vector portion of the feed mixture, the less disperse Fe is at the outset of the liquefaction experiment. As the Fe and salt concentrations in the vector mixtures show in Table III, the extreme case is the 10% vector, where the Fe concentration was nearly 8% mf coal, equal to 10 wt% salt (as FeOOH). At the start of liquefaction, the iron salt is highly concentrated on this portion of the feed coal, while the other 90% of the coal is relatively iron-free.

Liquefaction results using the vectors mixed with as-received coal are also shown in Table III. THF conversions of the mixed feed coals are all very similar, taken as a group, to the 100% IW/P coal, and clearly higher than the uncatalyzed reaction. Oils yields also appear to be about the same, with a slight advantage for the 10% case, which carried a somewhat higher iron load. Overall, the results suggest that IW/P impregnation of the iron on a portion of the coal does not hinder its availability to participate in the liquefaction reaction in tetralin.

Liquefaction with coke and carbon black substrates- Two stable, non-reactive substrates, coke and carbon black, were selected for comparison with coal, which rapidly dissolves during liquefaction. First, to determine a liquefaction yield background, experiments were performed using the coke and carbon black at 10 wt% of the reaction feed mix, without any added Fe. The coke alone improved coal conversion about 2%, but the carbon black did not affect conversion (see Table IV). As a commercial filtration aid, the coke may have improved Soxhlet extraction of the liquefaction products, or perhaps introduced a trace amount of catalyst material that will be revealed through ongoing analytical work.

After Fe impregnation of the two carbon substrates, SEM studies showed that the larger petroleum coke (see Table I) retained its size and structure after impregnation, but the nanometer-fine structure of the carbon black was lost and resulted in nominal 300 micron agglomerates. These larger agglomerates appeared to be completely coated with the Fe salt, an effect not visible on the coke.

Coal liquefaction experiments were performed as before, with the Fe-laden vectors at 10 wt% of the reactor feed. Iron added on the coke increased THF conversion about 4% compared with its background, as did Fe added to the carbon black. The increases in product yield were 3-4% less than with Fe dispersed on the 10% coal vector, but the yields evidence that Fe distributed on the two stable non-coal vectors participates in the liquefaction reaction.

Conclusions

Very little activity was seen for ferrous sulfate added directly to the reactor either as a powder, or molecularly dispersed in an immiscible aqueous solution. High activity is observed when a coal vector is employed, and we can postulate the effect arises from dispersion throughout the reactor as the coal structure rapidly dissolves. Moreover, if catalyst dispersion may be inferred from its activity, then Fe added on a coal vector comprising only 10% of the feed coal is sufficiently dispersed through the course of a 30 minute reaction to give yields comparable to experiments where Fe is added to the entire feedstock. Some activity is observed when the Fe is dispersed on a carbon substrate that is stable under liquefaction conditions, but not as much as when dispersed on some fraction of the coal itself. However, this activity may be commensurate with the level of dispersion provided by the >100 μm coke and carbon black particles that were added to the reaction system.

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Table I. Non-coal Carbon Substrates Used for Fe Impregnation.

	petroleum coke	carbon black
BET surface area, m ² /g	< 1 (non-porous)	90
Particle size, μm (by TEM)	100	.01-.06, in clusters
THF insolubles, wt% mf sample	102.5	102.9
Proximate analysis, wt % as-determined		
Water	1.0	0.8
Ash	trace	3.3
Volatile matter	5.3	2.8
Fixed carbon	93.7	93.1
Total	100.0	100.0

Table II. Effect of Alternate Ferrous Sulfate Addition Methods on Coal Liquefaction.*

Addition Method	none	Powdered	Aqueous	IW/P
Added Fe, wt% mf Coal	0	0.79	0.78	0.78
Products, wt% maf Coal				
HC Gases	0.7	0.8	0.9	1.1
CO+CO ₂	4.7	5.3	4.8	5.7
Oils	33.2	32.2	31.5	34.3
PA+A	37.8	40.0	40.0	43.6
IOM	23.6	21.7	22.8	15.3
THF Conversion	76.4	78.3	77.2	84.7

a. Results of liquefaction studies at 415°C for 30 minutes, 2.3 tetralin:coal ratio.

Table III. Effect of Limited IW/P Fe Dispersion on Coal Liquefaction.

Impregnated Coal/total Coal, wt%	10	50	90	100
Added Fe, wt% mf total Coal	0.81	0.78	0.78	0.78
Vector properties				
Added Fe, wt% mf vector (salt-free basis)	7.59	1.55	0.87	0.78
Added FeOOH, wt% wet vector mixture	10.3	2.0	1.1	0.8
Products, wt% maf total Coal*				
HC Gases	1.0	1.0	0.8	1.1
CO+CO ₂	4.8	4.9	4.7	5.7
Oils	38.2	33.3	32.5	34.3
PA+A	41.1	44.0	44.6	43.6
IOM	14.9	16.8	17.4	15.3
THF Conversion	85.1	83.2	82.6	84.7

a. Results of liquefaction studies at 415°C for 30 minutes, 2.3 tetralin:coal ratio.

Table IV. Effect of Limited Fe Dispersion on Non-coal Vectors.

Substrate	coke blank	coke with Fe	Δ	carbon black blank	carbon black with Fe	Δ
Vector /total mixture, wt%	10	10		10	10	
Added Fe, wt% mf Coal	0.0	0.74		0.0	0.79	
Vector properties						
Added Fe, wt% mf vector (salt-free basis)	0.0	6.10		0.0	6.23	
Added FeOOH, wt% wet vector mixture	0.0	8.6		0.0	9.1	
Products, wt% maf Coal*						
HC Gases	0.7	0.5	-0.2	0.6	0.9	0.3
CO+CO ₂	5.1	4.7	-0.4	5.1	4.7	-0.4
Oils	37.3	38.2	0.9	32.6	38.3	5.7
PA+A	35.7	39.0	3.3	38.2	37.1	-1.1
IOM	21.2	17.6	-3.6	23.5	19.0	-4.5
THF Conversion	78.8	82.4	3.6	76.5	81.0	4.5

a. Results of liquefaction studies at 415°C for 30 minutes, 2.6 tetralin:coal ratio.