

TOWARDS IMPROVED IRON-BASED CATALYSTS
FOR DIRECT COAL LIQUEFACTION

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INTRODUCTION

Iron-based catalysts for direct coal liquefaction (DCL) have several advantages: they are cheap and environmentally benign, and have a reasonable activity in the sulfide form. Work in this area has recently been collected and published [1].

Work in our laboratory has focussed on catalysts made with ferric sulfide as a precursor. This material is unstable even at room temperature, and disproportionates to form pyrite (FeS_2 ; PY), non-stoichiometric pyrrhotite (FeS_x , $x \approx 1$; PH), and elemental S [2]. The value of x and the relative amounts of PY and PH depend upon the time and temperature of disproportionation [3,4]. Materials from hydrothermal disproportionation at 200°C for 1 h have roughly equal amounts of PH and PY (on an iron basis), and these materials appear to make the most active and selective catalysts for DCL [3,5]. These catalyst precursors and catalyst materials have been characterized by atomic adsorption spectroscopy (AA), Auger electron spectroscopy (AES) and x-ray diffraction (XRD). The characterizations have been correlated to the reactions of Fe during disproportionation and to the performance of the catalysts [4,6].

Improvements in these catalysts can be made in two ways: by altering the active sites, and by decreasing the particle sizes. In the present work, we present examples of both types. The active sites are altered by using small amounts of a second metal. The particle sizes are reduced by using an aerosol technique for preparation.

AEROSOL-BASED PREPARATION OF IRON CATALYSTS

Advantages of the aerosol process have been described earlier [7]. Besides generating particles of small size, the process is inherently scalable (so that large quantities of catalyst are possible). Further, the solvent need not be aqueous, and the potential exists for making materials not stable under other conditions.

A sketch of the apparatus is shown in Figure 1. A solution of a ferric salt, typically acetate, is pumped at high pressure through a nozzle to a reactor. The micron-sized droplets react with H_2S in the vapor phase (as 10% of an $\text{H}_2\text{S}/\text{N}_2$ mixture) to form ferric sulfide at the interface. At the high temperatures involved, water evaporates from the liquid droplet. Hence the particle may be an annulus or a solid sphere. The ferric sulfide quickly reacts to PY, PH and elemental sulfur. The final size achieved depends upon the pump pressure, the diameter of the nozzle orifice, the viscosity and surface tension of the liquid, the concentration of reactants in liquid and vapor phases, and the effect of pH and anion basicity on the reaction rate. The particles stay in the reactor, where they are collected in tetralin; the vapor bubbles through an NaOH scrubber before being safely vented. The particles, collected after the process is complete, have been characterized and used for DCL.

XRD data, taken in the laboratory of Professor M.S. Seehra at West Virginia University, indicate interesting effects when conditions are changed. At low precursor conditions, 0.01M, when aerosol reactor conditions are maintained at 200°C and 200 psi, peaks are observed corresponding to FeS_2 , monoclinic pyrrhotite (Fe_7S_8 , i.e., $x = 1.143$) and elemental S. This is consistent with XRD patterns obtained using earlier preparation techniques such as hydrothermal disproportionation [3,4]. However, when the

precursor concentration is higher, 0.1M, and the temperature is 165°C, peaks observed include not only FeS₂ and S but now greigite (Fe₃S₄, x = 1.333). But greigite is stable typically only below 100°C [8]. Perhaps the thermodynamically unstable form is trapped in the particle due to the rapid quenching that takes place in the aerosol reactor. The role of the higher precursor concentration in facilitating the unstable form is not clear.

Other characterization data can be found in Table I. The samples are characterized in terms of the precursor concentration as well as the pressure and temperature in the reactor. Density was measured using He pycnometry. For sample 9, grinding the solid increased the density measurement by 0.1 g/cc, probably within the accuracy of the measurement. Hence the values measured are those of the density of the actual material, whether present as a solid or an annular shell, and not the bulk density of an annular shell. Accordingly, the changes in density between samples 8 and 9 and between samples 9 and 10 are related to the different solids produced under those two conditions, not changes in the inner and/or outer diameters of the particles. Note that increasing the temperature of the aerosol reactor causes less change than increasing the precursor concentration.

The mean diameter in Table I is measured using multiple-angle laser light scattering with photon correlation spectroscopy. For these measurements, the particles were suspended in tetralin, the same solvent used for the DCL experiments. In addition, a transmission electron microscope (TEM) in Professor G.P. Huffman's laboratory at the University of Kentucky was used. In the latter measurements, the particles were suspended in ethyl alcohol, which was then evaporated on the TEM slide. Sizes measured by TEM range from 3 - 580 nm, with a majority of particles in the lower portion of the range. The 1-2 orders of magnitude by which the two techniques differ is probably due to clumping of the particles in the tetralin. Since the physical situation with tetralin is closer to the conditions during liquefaction, the values in Table I are probably more realistic than TEM values. The larger particle size observed in sample 9 relative to sample 8 is probably due to the increased concentration of precursor used.

Bulk ratios of S to Fe and the corresponding surface ratios, obtained from energy-dispersive x-ray spectroscopy (EDX) and AES respectively, are also shown in Table I. Bulk ratios for samples 7 and 8 are similar, and greater than 1.5, the value expected for Fe₂S₃. A smaller value is obtained for sample 12, and the value decreases further for sample 9. The decreasing values may be due to loss of elemental S (found after disproportionation of the Fe₂S₃) in sample handling. Hence the decreasing values may indicate increasing amounts of elemental S formed, and increasing amounts of PH relative to PY. The decreasing bulk values are consistent with decreasing surface S/Fe values as well. The ratios are higher on the surface than in the bulk, again consistent with the formation of elemental S and its migration to the surface. The AES peak shape corresponding to S is, in fact, characteristic of that ascribed to elemental sulfur.

The performance of these catalysts in DCL is shown in Table II. The experiments were carried out at 350°C and 1000 psi H₂ (cold) for 1 h using DECS-6 coal in tetralin with 0.1 ml CS₂ added. The catalyst loading was 5% and the reactor was agitated vertically at 500 rpm. Full experimental details have been provided earlier [3,4]. All catalyst samples used show noticeable improvements in conversion and asphaltene yield relative to the thermal runs, although oil yields are not improved. The improvement in conversion is most striking for catalysts prepared using the lower precursor concentration, and the oil yield is best for the catalyst prepared at the highest temperature.

MULTI-METAL IRON-BASED CATALYSTS

The Hume-Rothery rules (of thumb) govern which metals can be substituted into an existing lattice. The major requirement is that the substituent and the original metal should have ionic radii no more than 15% apart. For the Fe ion, this requirement provides a large number of potential substituents. For any of these to be useful, conversion and/or oil yield should increase at least marginally when the material is used as a DCL catalyst,

and the material should be only marginally less attractive, economically and environmentally, than the iron-alone catalyst. Because of space constraints, we report here only on Fe-Ni-S catalysts. However, preliminary data have been gathered when other metals have been used, including Co, Mg, Mo and Cu.

Because of the long set-up times required for the aerosol reactor, the Fe-Ni-S catalysts were not prepared in this manner. Instead, variants of the old hydrothermal disproportionation technique [3,4] were used. When relatively low disproportionation temperatures, T_d , were required, appropriate ratios of FeCl_3 and NiCl_3 solutions were combined with Na_2S in a glass ampule in a cold room. This formed the precursors instantaneously as a gelatinous precipitate. For disproportionation of the ferric sulfide, the ampule was then sealed and placed in an autoclave containing water. The autoclave was maintained at T_d , equal to 200°C or 250°C, for 1h. The presence of high-temperature steam at equal pressure on both sides of the ampule prevented it from being destroyed. The ampule seal was broken and the material washed (to remove NaCl formed as a byproduct) and vacuum-dried. When a high-temperature disproportionation (HTD) was required, the precursors formed as above were washed and dried first, then heated (at 350°C or 375°C) for 15 min. in 1500 psig H_2 (hot). In both cases, the material was formulated to have nickel fractions ($\text{Ni}/\{\text{Ni} + \text{Fe}\}$) of 0.0, 0.01, 0.1, 0.5, 0.9 and 1.0.

DCL results for a series of the Fe-Ni-S catalysts are shown in Figure 2. Reaction conditions are the same as those in Table II. Conversions using these catalysts go through a shallow maximum between nickel fractions of 0.1 and 0.5, regardless of the T_d value. For $T_d = 200^\circ\text{C}$, the oil + gas yield passes through a minimum with increasing nickel fraction. Hence this is clearly not a viable catalyst, even though the corresponding catalyst in the absence of Ni was shown [3-5] to be the preferred catalyst. For $T_d = 375^\circ\text{C}$, the yield passes through a maximum corresponding to a nickel fraction of 0.5. Since the yield and the conversion of this HTD catalyst are superior to any other in Figure 2, this is the preferred catalyst in the Fe-Ni-S family.

Figure 3 represents XRD peaks for this HTD catalyst and for the two extreme values of the nickel fraction. The XRD pattern for the catalyst containing Fe alone shows stronger pyrrhotite peaks than those corresponding to the catalyst hydrothermally disproportionated at 200°C. This is consistent with the higher value of T_d and the presence of H_2 during disproportionation. When Ni alone is present, the XRD peaks correspond to those of Ni_3S_2 . However, when both Ni and Fe are present, a completely different pattern is seen. The major peaks correspond to those of $(\text{Fe,Ni})_9\text{S}_8$. Hence, XRD indicates that the present method of forming multi-metal catalysts results in alloy formation, not just a combination of two sulfides. The alloy appears to result in higher conversion and yield when used as a catalyst in DCL.

AES data for the HTD catalyst are shown in Figure 4 as a function of nickel fraction. The nickel fraction on the surface is never higher than the fraction in the bulk. This implies that, at all levels of nickel formulation, the nickel is preferentially found in the bulk, not the surface. S is enriched on the surface relative to the bulk, since almost all values can be seen to be greater than 1.5. However, comparing the values with that for zero nickel fraction indicates that there is less S on the surface when Ni is present than when it is absent. Further, comparing the latter value with those from Table II indicates that an aerosol catalyst typically contains more S on the surface than does the HTD catalyst. Finally, it is worth noting the complementary nature of the curves for S and for O. If the S and O fractions are added, the numbers correspond to the surface S/O ratios for the aerosol catalyst. Since oxygen is not present in the formulation, oxidation must be occurring during handling. The role, if any, of the surface oxygen on the catalytic properties of the materials deserves further investigation.

SUMMARY AND CONCLUSIONS

Iron-based sulfide catalysts can be modified to improve their performance in DCL. Preparation using an aerosol formulation results in small particle sizes and the possibility of forming thermodynamically unstable structures. Preparation using Ni as a

second metal results in multi-metal sulfides being formed. With both techniques, surface characterization correlates well with DCL results. Surface oxidation may be affecting the catalytic behavior of these materials.

REFERENCES

1. Energy and Fuels, **8**, 3-140 (1994).
2. Stiller, A.H., McCormick, B.J., Russel, P. and Montano, P.A., J. Amer. Chem. Soc. **100**, 2553 (1978).
3. Stansberry, P.G., Wann, J.-P., Stewart, W.R., Yang, J., Zondlo, J.W., Stiller, A.H. and Dadyburjor, D.B., Fuel **72**, 793 (1993).
4. Dadyburjor, D.B., Stewart, W.E., Stiller, A.H., Stinespring, C.D., Wann, J.-P. and J.W. Zondlo, Energy and Fuels **8**, 19 (1994).
5. Stansberry, P.G., Yang, J. and Wann, J.-P., Paper presented at AIChE Annual Meeting, Los Angeles, CA (1991).
6. Dadyburjor, D.B., Stewart, W.E., Stiller, A.H., Stinespring, C.D., Wann, J.-P. and J.W. Zondlo, Prepr. ACS Div. Fuel Chem. **1**, 39 (1993).
7. Stiller, A.H., Agarwal, S., Zondlo, J.W. and Dadyburjor, D.B., Proc. 10th Ann. Intern. Pittsburgh Coal Conf., Chiang, S.-H., Editor (1993).
8. Power, L.F. and Fine, H.A., Miner. Sci. Eng. **8**, 106 (1976).

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TABLE I
Characterization of Aerosol-Generated Catalysts

SAMPLE #	PRECURSOR CONC, [M]	PREP PRES [psi]	PREP TEMP [°C]	DENSITY [g/cc]	DIA [nm]	BULK S/Fe EDX	SFCE S/Fe AES
7	0.01	200	200	---	---	2.5	3.6
8	0.01	100	200	4.60	507	2.5	3.3
9	0.10	100	200	4.27	1200	0.9	2.0
12	0.01	100	250	4.66	---	1.9	---

TABLE II
DCL with Aerosol-Generated Catalysts

SAMPLE #	CONVERSION [%]	ASPHALTENE YIELD [%]	OIL + GAS YIELD [%]
thermal	54.9	41.2	13.6
8	64.9	55.6	9.3
9	63.0	52.1	10.8
12	64.4	54.8	10.9

FIGURE 1. Apparatus for generation of aerosol particles of catalyst.

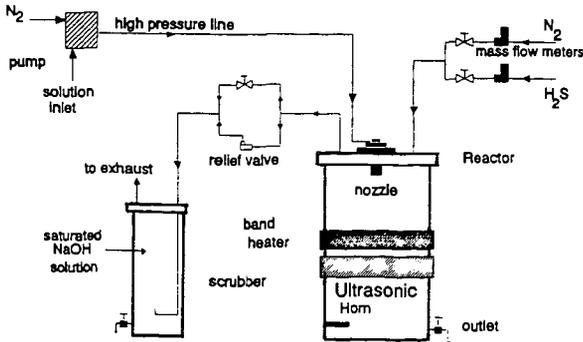


FIGURE 2. DCL using Fe-Ni-S catalysts, as a function of T_d , disproportionation temperature, and nickel fraction, $Ni/(Ni+Fe)$.

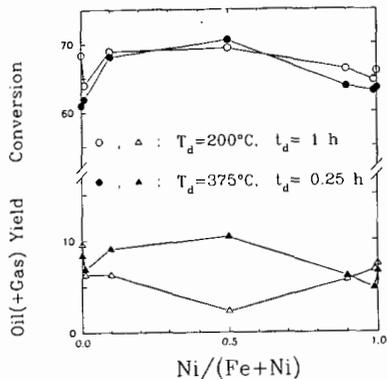


FIGURE 3. XRD for HTD catalyst with $Ni/(Ni+Fe) = 0$ (bottom), 0.5 (middle), and 1.0 (top).

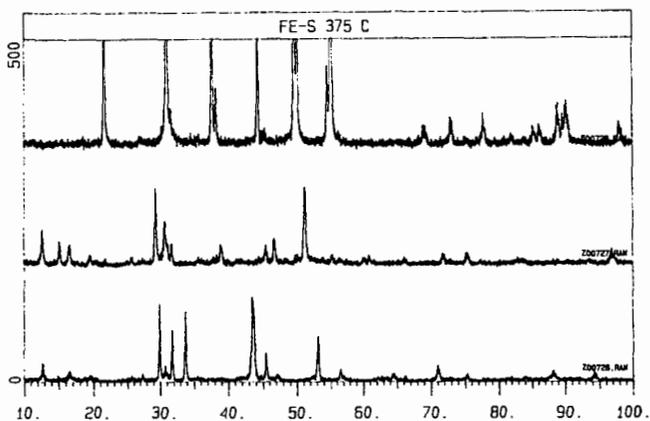


FIGURE 4. AES for HTD catalyst as a function of Ni fraction.

