

ULTRAFINE IRON CARBIDE AS LIQUEFACTION CATALYST PRECURSOR

G T Hager, X-X Bi*, F J Derbyshire, P C Eklund*, and J M Stencel
University of Kentucky
Center for Applied Energy Research
3572 Iron Works Pike, Lexington, KY 40511-8433
*Department of Physics and Astronomy

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ABSTRACT

Novel ultrafine particles (UFPs) of iron carbide have been synthesized and evaluated for their catalytic activity in coal liquefaction. The particles, with average diameters of 5 - 10 nm, were prepared by the laser driven pyrolysis reactions of ethylene and iron pentacarbonyl. Two different crystalline phases, Fe_7C_3 and Fe_3C , have been prepared and these unsupported catalysts have been characterized using a range of analytical techniques. Results of microautoclave studies indicate the high catalytic activity of these UFPs for coal liquefaction compared to iron added as iron pentacarbonyl, and to a thermal baseline. The transformation of the catalyst under liquefaction conditions in the presence of sulfur is reported. The presence and catalytic role of monolayer pyrolytic carbon coatings formed on the catalyst surface during laser synthesis will also be addressed.

INTRODUCTION

The primary use of highly dispersed slurry phase catalysts is in the first stage of a two stage liquefaction process. The preferred catalyst is one that will aid in the conversion of the coal to soluble products which may then be further upgraded in the second stage to more useful products using conventional supported catalysts. A successful slurry phase catalyst should improve product selectivity, allow increased throughput, and yield a first stage product which will reduce the rate of catalyst deactivation in the second stage. The effective use of a slurry phase catalyst may also offer an efficient means of liquefying low rank western U. S. coals which can produce more desirable products [1,2] and reduce second stage catalyst deactivation [3]. Subbituminous coals are generally found,

however, to convert at a lower rate and to a lesser extent than higher rank coals. This is purported to be caused by an imbalance in the rates of bond cleavage and hydrogenation. Dissolution promoted by an effective slurry phase catalyst may be able to correct this imbalance.

Historically, the oxides and sulfides of molybdenum, tungsten and the iron group metals were among the first catalysts used in coal liquefaction. Molybdenum compounds are generally considered to exhibit higher activity in dissolution and hydrogenation than iron compounds. However, due to the higher cost of the molybdenum and the fact that dissolution catalysts are not easily recovered, iron based catalysts are usually preferred for industrial operations.

Since the catalytic process takes place at the surface-liquid interphase, the amount of surface area available for reaction is critical. By increasing the surface area per unit volume the relative activity of a catalyst may be increased. In supported catalysts this is often done by depositing the catalyst over a high surface area porous substrate such as alumina or a zeolite. Unsupported catalysts, on the other hand, can present a high surface area by maintaining a high dispersion. The majority of the active catalyst surface is on the outside of the particles and therefore is not subject to pore diffusion limitations. Further, ultrafine particles, measuring only a few nanometers in diameter, may exhibit markedly different properties than bulk particles of the same composition and may therefore present a means to improve the activity.

The current research program is concerned with the production of ultrafine iron carbide particles by laser pyrolysis and their catalytic behavior as related to composition, structure, size, and other properties.

EXPERIMENTAL

PARTICLE SYNTHESIS

The use of laser pyrolysis for ultrafine particle synthesis was first performed by Haggerty and co-workers [4] for the production of silicon-containing ceramics. The technique was later adopted by researchers at Exxon who used it to produce transition metal carbide particles for use as catalysts in synthesis gas reactions [5,6]. One such carbide described in an Exxon patent was Fe_3C . To produce this carbide a stream of the

reactant gases, ethylene and iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), was intersected with a tunable cw CO_2 laser. The same method was used in the present research. Approximately 5% of the incident energy from the laser is adsorbed by the ethylene. The added heat causes the thermal decomposition of the iron pentacarbonyl which leads to the formation of ultrafine (2-20 nm) spherical iron carbide particles. The exact mechanism of the particle formation is still under investigation.

The apparatus used for the synthesis of these particles has been described previously [7]. The reaction cell is shown in Figure 1. Particles generated in the reaction volume were originally collected on a teflon membrane filter. In this system the production limiting factor was the pressure drop across the filter.

The collection mechanism has since been improved to allow for production of large (>1g) batches of particles. A large magnet, placed upstream of the previously used teflon membrane filter, effectively traps most of the particles in a sample chamber. This sample chamber may be sealed and removed from the system when full and the particles may then be passivated (see Results and Discussion). The use of the magnetic trap is possible due to the ferromagnetic properties of the particles. However, this ferromagnetism leads to particle agglomeration which may adversely affect dispersion in liquefaction experiments.

LIQUEFACTION

Since it has been reported that some transition metal carbide catalysts resist sulfiding under liquefaction conditions [8,9], coal-free experiments were conducted to determine the catalyst behavior under both sulfiding and nonsulfiding conditions. These experiments were carried out in 18 mL batch microautoclaves, in the absence of coal, with 4 wt% Fe_7C_3 in 5 g of tetralin, with and without sulfur added as dimethyldisulfide (DMDS) at twice the stoichiometric ratio required for formation of FeS_2 . The reaction conditions used in this study were 385 °C with 800 psig (cold) hydrogen pressure and the reaction time was 30 minutes.

The liquefaction experiments were conducted in the same batch microautoclaves using 3 g of a subbituminous Wyodak coal and 5 g of tetralin. The reaction conditions were the same as the coal-free runs and

the reaction time was 15 minutes. Two passivated iron carbide catalysts, Fe_7C_3 and Fe_3C , were used in the study. A thermal run and a catalytic run using $\text{Fe}(\text{CO})_5$ were also made for comparison. The catalyst loading was 1 wt % Fe, as determined from precursor stoichiometry, and dimethyldisulfide (DMDS) was added in 20 % excess for the formation of FeS_2 . The addition of DMDS was based on the results of the previous coal-free experiments with added sulfur. The conversions (daf) of the coal liquefaction runs were determined using solubility in pyridine (preasphaltenes), benzene (asphaltenes), and pentane (oils). Gas yields were determined by gas chromatography.

RESULTS AND DISCUSSION

Two distinct phases of iron carbide particles, orthorhombic Fe_3C and metastable hexagonal Fe_7C_3 , have been synthesized. These particles have been characterized by XRD, transmission electron microscopy, electron diffraction, and Mössbauer spectroscopy. The phase and size of the particles is controlled by the gas flow rate, pressure and laser intensity. Adjustment of these parameters allows the control and reproducible production of different size ranges and both phases.

The particles are formed with a thin layer of pyrolytic carbon coating the surfaces of the particles. The particles are also pyrophoric which necessitates their passivation prior to exposure to air. The passivation process involves the gradual introduction of 10% O_2 in helium with constant temperature monitoring to prevent runaway reaction. While the effect of the process on the carbon coating is unclear, X-ray photoelectron spectroscopy (XPS) has shown that the passivated particles possess a surface layer of Fe_3O_4 .

The results of the coal-free experiments showed that the iron carbide particles will sulfide under liquefaction conditions in the presence of added sulfur to form pyrrhotite. While it is believed that the addition of coal will not prevent this transformation from occurring, Mössbauer spectroscopy of the liquefaction residues are being done to provide evidence of the final state of the catalyst after reaction. Particle growth, as shown by SEM micrographs and the narrowing of X-ray diffraction lines (Figure 2), is seen in both the coal-free runs. TEM micrographs of the particles formed in the absence of sulfur confirm the increase in size due to the agglomeration of the smaller particles. The

larger particles have a relatively narrow size distribution and appear to be made up of the small particles which have agglomerated to form spheres around a hollow or carbon center. The XRD analysis indicates that in the absence of added sulfur the catalyst undergoes a phase change to an iron carbide, or mixture of carbides, and some Fe_3O_4 . It seems unlikely that this oxide phase could have been produced in the reducing atmosphere present in the reactor. Its presence may be due to the fact that the surface oxide layer on the passivated particles was not effectively reduced or it may be an artefact of sample handling. In the presence of added sulfur the Fe_7C_3 is converted to pyrrhotite and sintering is again observed by SEM and XRD. TEM micrographs show that the sulfided catalyst exists as both small particles and as larger agglomerated crystals. Energy dispersive X-ray analysis indicates an approximate stoichiometry of $\text{Fe}_{0.85}\text{S}$, or approximately Fe_7S_8 , for the pyrrhotite. The rate of the conversion to pyrrhotite is not known. The effect of coal on this transformation is under investigation.

Based on the results from the coal-free experiments with sulfur, excess sulfur was added in the liquefaction experiments to allow for the catalyst transformation to pyrrhotite, since pyrrhotite has widely been reported to be the active form of iron catalysts. Table 1 shows the results of the liquefaction experiments. When compared to the thermal run and a run using iron carbonyl as the catalyst precursor, both carbide forms showed enhanced total conversion. This increase in conversion may be more significant than these results indicate since the pyrolytic carbon coating has been suggested by the results of thermogravimetric analysis (TGA) to account for approximately 30 % of the particle weight. The exact quantity of carbon in the coating is being determined by current experiments. The corrected iron loading for the catalytic runs with iron carbide precursors was then approximately 0.75 wt. %. This shows higher conversion at lower iron loading for the heterogeneous iron carbide precursors compared to the homogeneous iron pentacarbonyl precursor. The result corresponds with other research [10-12] which has shown that aerosol iron oxide precursors produce higher activity than organometallic or salt precursors. This may be due to the unexpectedly large (70 -110 nm) crystallites which are reportedly formed by the soluble precursors and the relative stable size of the particle precursor. The reason for the larger crystallite formation by the soluble precursors is not understood at present. In addition to the higher overall conversion, there are also some differences in the product selectivity. The catalytic effect, if any,

of the carbon coating has not been determined.

Comparing the data from these experiments to the work of Keogh and Davis [13] plotted on a Wei-Prater diagram (Figure 3), a similar, but slightly different, pathway from the subbituminous pathway seems to be shown. The reason for this deviation is unclear at present. Since the deviation in the trend is present in the thermal baseline as well as the catalytic runs, it is expected that a difference in the coal and/or reactor, rather than the catalyst, is the cause. However, it is clearly seen in this plot that the addition of the iron carbide catalyst precursors increase the rate of progress along the proposed pathway with Fe_7C_3 progressing furthest in the 15 minute runs. The high conversion is particularly promising since no efforts have been made to maximize or stabilize the precursor dispersion in the slurry.

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Table 1 Conversion Analysis of Liquefaction Experiments

	YOM	Pre-asphaltenes	Asphaltenes	Oil & Gas	Total Conversion
Thermal	58.13	15.02	15.14	11.71	41.87
Fe(CO) ₅	53.15	9.34	23.43	14.08	46.85
Fe ₃ C	48.88	18.74	21.07	11.32	51.12
Fe ₇ C ₃	43.74	22.29	18.01	15.96	56.26

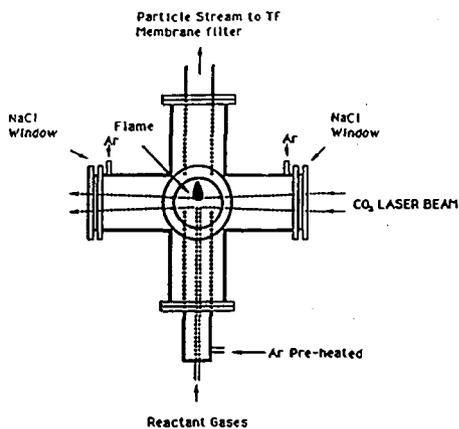


Fig. 1. Schematic Laser Pyrolysis Cell.

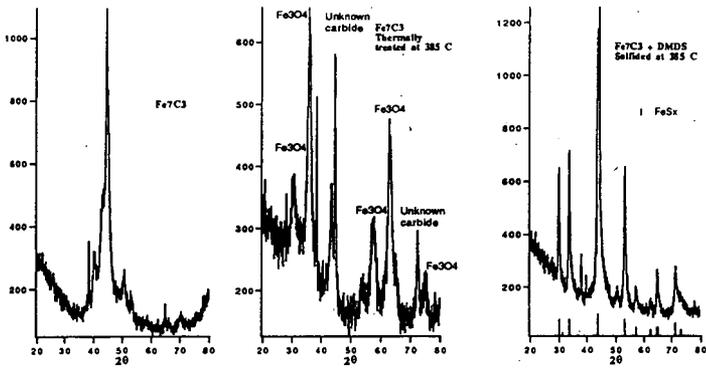


Figure 2. X-Ray Diffraction of Iron Carbide

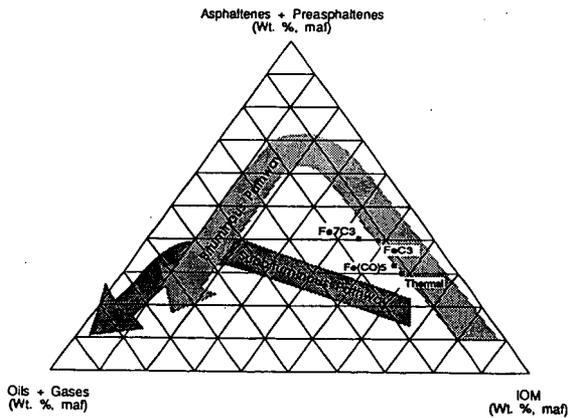


Figure 3. Liquefaction Data Compared to Reported Pathways