

Ultrafine Iron Catalysts for Coal Dissolution

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Introduction

Over the last several years, developments in coal liquefaction technology have significantly lowered the estimated cost of producing coal liquids (1-3). Among the notable improvements and innovations have been the introduction of the ebullated bed reactor, the adoption of two-stage processing with the additional use of catalyst in the first as well as second stage, and the recycling of residual products to extinction with the production of higher yields of distillate liquids. Progress can be measured in terms of increased selectivity to distillates, improved hydrogen utilization and reduced operating severity.

At this time it is considered that further cost reductions could be realized through a combination of incremental measures rather than any single radical one (although there is always hope that this type of statement will prove to be hopelessly incorrect). One example of a physical process step which can benefit liquefaction economics is to use a cleaned coal feed (4). This would reduce the inventory of inert material in the reactor system, allowing a reduction in reactor size, decreased wear on engineering components and reducing the loss of valuable product with the rejection of these solids. Relatedly, more efficient methods for solid separation would be advantageous.

With regard to the chemistry of coal liquefaction, positive gains could be made by the development of supported catalysts with improved activity, selectivity and life. However, it is considered that a more fruitful approach lies in trying to achieve a greater degree of control over the initial

dissolution reactions through the use of highly dispersed catalysts (5). The specific objectives of research into the development and application of slurry phase catalysts are to increase the rate of conversion and to produce a solubilized product which can be upgraded with greater facility in the second stage. The anticipated outcome of successful research would be to alleviate the problems encountered by the supported catalysts in the second stage, increase throughput, and further improve selectivity to distillates. Moreover, the effective use of slurry phase catalysts can provide the means to liquefy efficiently low-rank coals. Subbituminous coals from the western US are much cheaper feedstocks than eastern bituminous coals. It has been shown that they can produce lower boiling and higher quality liquids (6-8), and that they cause less rapid deactivation of the second stage catalyst (2). The main problem is their lower rate and extent of conversion which causes inefficient use of reactor space and the loss of additional product on solids separation. If, as supposed, this is related to an imbalance between the rates of bond cleavage and hydrogenation, then it is possible that the situation can be redressed by the use of appropriate catalysts.

Molybdenum and iron are the most commonly investigated catalyst metals and both form an active sulfide under liquefaction conditions, or can be introduced after presulfiding. Although iron catalysts are less active, they are preferred for reasons of economy. A great deal of research has been spent in attempting to understand the chemistry of liquefaction in the presence of iron catalysts and the composition of the active phase. It has also been demonstrated that the use of powdered iron catalysts has allowed the liquefaction of subbituminous coals which could not otherwise be processed (see 8). Nevertheless, the activity of these catalysts is still much less than desired and means to enhance their activity are under investigation.

The catalyst activity is determined principally by its composition and the extent of its dispersion and intimate contact with the coal-solvent slurry. While it is generally considered that the active phase of Fe and Mo is a sulfide form, recent studies by Oyama and co-workers have shown that supported and unsupported Mo carbides and nitrides exhibit high activity for hydrodenitrogenation and hydrodesulfurization reactions (9-12), raising the possibility that the carbides and nitrides of Mo and other metals may be active liquefaction catalysts.

The catalyst dispersion is dependent upon the form and mode of addition of

the catalyst precursor. High activities are reportedly favored by catalysts introduced as oil-soluble organometallic precursors such as naphthenates and carbonyls (13-15). The results of some studies, however, indicate that even with these precursors, quite large crystallites or agglomerates can be formed during liquefaction and hence the potentially high dispersion is not maintained. There is some evidence to indicate that, if introduced as particulates, there is less tendency for agglomeration. Fine iron particles (50 nm mean diameter) synthesized by a flame pyrolysis technique appeared to have retained their particle size and shape during presulfiding and coal liquefaction (16,17). Other work has shown that FeS is more active as a colloid than in powder form (18).

The increase in catalytic activity that is expected with decreasing particle size may be due to a combination of effects: an increase in exterior surface and an associated enhancement of sulfiding kinetics; a radical departure from bulk properties, especially with regard to surface energetics as the particle size is reduced below about 10 nm. The synthesis of ultrafine catalyst particles could therefore provide a means to enhance the activity of dispersed iron (or other metal) catalysts.

To examine this proposition, a program of research has been initiated to synthesize ultrafine iron-based particles by a laser pyrolysis technique and to relate their composition, structure and other properties to their behavior as liquefaction catalysts. Later it is intended to investigate effect of the modifying their composition by the addition of promoters during synthesis. This paper describes some of the early findings of this research.

Experimental

Particle Synthesis

The technique for synthesizing ultrafine particles by laser pyrolysis appears to have first been performed by Haggerty and co-workers (19) whose interest was the preparation of silicon-containing ceramics. The method was utilized by researchers at Exxon to produce transition metal carbide particles for use as catalysts for synthesis gas reactions (20,21). One of the examples in the patents involved the synthesis of Fe₃C particles by the laser pyrolysis of vapor mixtures of Fe(CO)₅ and ethylene. This has been the starting point for the present program and the primary aim in the initial studies has been to produce reproducibly iron carbide particles of nanometer

size.

The apparatus used for synthesis has been described previously (22). The reaction cell is shown schematically in Figure 1.

The cell was fabricated from a six-way cross made from 3.8 mm diameter stainless steel tubing. The reactant gases ($\text{Fe}(\text{CO})_5$ and C_2H_4) flow vertically out of the tip of a ~ 1 mm dia. stainless tube and intersect the horizontal beam from a tunable cw CO_2 laser. The reactant gas mixture is heated in a small volume above the reactant gas nozzle by tuning the laser frequency to a strong rotational-vibrational band of C_2H_4 at $\sim 940 \text{ cm}^{-1}$. Thermal decomposition of $\text{Fe}(\text{CO})_5$ to Fe and CO occurs and the Fe reacts with the ethylene to produce ultrafine spherical particles which drift in a well-collimated stream vertically out of the cell. The particles are collected in a teflon membrane filter with average pore size 200 nm.

The reactant gases are confined near the vertical axis of the cross via a coaxial flow of argon which passes through a larger tube (~ 15 mm diameter) concentric with the much smaller reactant gas tube. Pre-heating the Ar flowing into the coaxial sheath to temperatures $T \sim 150^\circ\text{C}$, raised the pyrolysis temperature. Argon is also passed over the inside of NaCl windows to prevent the deposition of stray particles on the windows. Mass flow controllers were used to establish steady flows of Ar to the windows (~ 70 sccm) and coaxial sheath (~ 70 sccm). Another mass flow controller was used to regulate the flow of C_2H_4 (~ 4 -8 sccm) through a pyrex bubbler containing liquid $\text{Fe}(\text{CO})_5$. The relative concentrations of $\text{Fe}(\text{CO})_5$ and C_2H_4 in the reactant gas stream were determined from the cell pressure (measured by a capacitance manometer) and the equilibrium vapor pressure of the $\text{Fe}(\text{CO})_5$. Cell pressure was controlled by adjustment of a needle valve located between a rotary vacuum pump and the cross. To control the laser power density and the size of the "pyrolysis zone", a ZnSe lens was used to position the laser beam waist either directly above the reactant gas nozzle for maximum power density, or to one side of the nozzle or the other to reduce the power density. Approximately $\sim 5\%$ of the power was absorbed in the reactant gas mixture.

Liquefaction

The liquefaction experiments were conducted in 50 mL batch autoclaves using a reaction temperature of 658 K, a 15 minute residence time, tetralin

as the solvent and a hydrogen atmosphere (5.5 MPa, ambient). The reactor was charged with 5g of dry coal and 7.5 g of tetralin. Catalyst precursors, including $\text{Fe}(\text{CO})_5$, $\text{Fe}(\text{C}_5\text{O}_2\text{H}_7)_3$ and molybdenum naphthenate, were added to the reactor in concentrations required to produce equal amounts of metal sulfide during the liquefaction experiment. Two ultrafine, iron-containing catalyst preparations (referred as Fe1 and Fe2) produced by laser pyrolysis were added in 0.1g quantities. Dimethyldisulfide was added for all tests as the sulfiding agent. Coal conversion was obtained by determining the amount of pyridine insolubles (daf) after soxhlet extraction of the reactor products.

The coals used were a Western Kentucky #6 (bituminous) and a Wyodak coal (subbituminous). The analytical data for the two coals are given in Table 1.

Results and Discussion

Two preparations of spherical iron carbide particles were produced with diameters in the range 3 to 13 nm, both exhibiting the cementite (Fe_3C) structure as indicated by X-ray and electron diffraction. The two preparations are referred to as Fe1 and Fe2. They were prepared at laser power densities of about 1200 and 500 $\text{W}\cdot\text{cm}^{-2}$, respectively. The particles differed in that Fe1 was stable in air whereas Fe2 was not and spontaneously ignited. To allow their removal from the system for further study, the Fe2 particles were first slowly passivated in the reaction cell with an Ar/O_2 mixture (99%/1%). It is presently believed that Fe2 has a cementite core and a monolayer coating of Fe.

Examination by high resolution transmission electron microscopy showed that the particles were almost spherical in shape and confirmed their small particle size. Analyses of Fe1 particles by XPS, after exposure to air, were consistent with a surface stoichiometry of $\text{Fe}:\text{C}:\text{O}$ of 1:1:2. Hence a significant amount of oxygen is attached to the surface of these particles. The XPS spectra indicated that the surface iron was predominantly as Fe^{3+} in oxide form with about 10% as the carbide.

The conversions obtained in coal liquefaction experiments in the presence of the different additives are summarized in Table 2.

All of the catalysts enhanced the coal conversion over that obtained in the thermal case. For the bituminous coal, the highest conversions were obtained with Fe2 and molybdenum naphthenate. The other iron catalyst precursors

were significantly less effective.

For the subbituminous coal, the conversions tended to be lower. The highest was produced in the presence of molybdenum naphthenate and the iron catalysts all behaved similarly. In view of the high activity displayed by Fe₂ with the bituminous coal, the low conversion obtained with the lower rank coal is unexpected. The findings are preliminary and will be confirmed in future work.

At this point at least it may be concluded that the synthesis technique can satisfactorily produce nanometer size particles and that there are some indications that these iron carbides may possess moderate to high activity for coal conversion. Whether they also influence the product distribution and composition is yet to be determined.

Current work continues to focus on catalyst synthesis and on investigations of the catalyst phase after sulfiding and after liquefaction, and studies are being initiated of the catalyst functions through the use of model compounds.

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Table 1
Coal Properties

	<u>C(daf)</u>	<u>H(daf)</u>	<u>N(daf)</u>	<u>IS(daf)</u>	<u>O(daf)</u> ¹	<u>VM(daf)</u>
W.Ky.#6	82.87	5.42	1.72	5.15	4.8	43.10
Wyodak	71.02	5.42	1.37	1.00	21.2	59.92

¹ By difference

Table 2
Coal Conversion Data

Wt. Conversion (daf)

<u>Coal</u>	<u>None</u>	<u>Molybdenum</u>		<u>Fe (CO)₅</u>	<u>Fe1</u>	<u>Fe2</u>
		<u>Naphthenate</u>	<u>Fe(C₅H₇O₂)₃</u>			
Bituminous (W.Ky.#6)	47.1	80.3	62.7	70.4	n.d. ¹	80.9
Subbituminous (Wyodak)	45.0	73.7	64.6	66.5	61.5	65.0

¹ Not determined

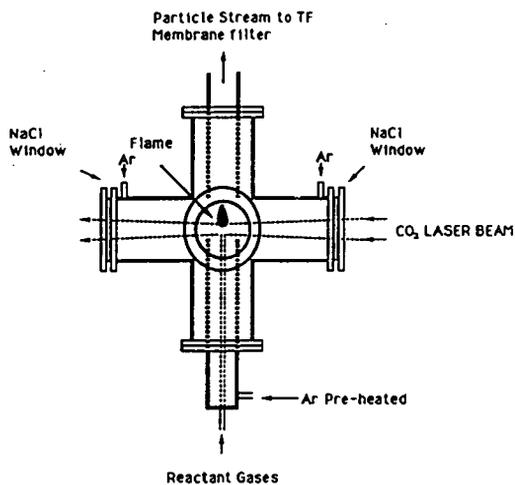


Fig. 1. Schematic Laser Pyrolysis Cell.