

NEW SYNTHETIC METHODS FOR THE PRODUCTION OF ULTRA-FINE COAL LIQUEFACTION CATALYSTS.

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ABSTRACT

Nanometer-sized catalysts have several advantages over conventional micrometer-sized catalysts including higher surface area, better diffusion properties and longer catalytic lifetimes. We have developed methods to produce large quantities of very small iron-oxides using reverse micelle and rapid thermal decomposition of solutes (RTDS) technologies. The synthesis and characterization of these iron-based nanometer-sized catalysts will be presented. The catalytic activity of the iron particles toward model compounds and coals will also be discussed.

INTRODUCTION

There is currently extensive interest in new technologies for coal liquefaction that are economical and environmentally sound. One such new method of interest is the use of highly dispersed, ultra-fine, coal liquefaction catalysts. Of particular interest are catalysts containing iron as the major foundation and catalytic agent because of the low costs involved. A variety of iron containing catalysts and catalyst precursors have been used to liquefy coal and researchers have also shown the utility of highly dispersed iron compounds for the liquefaction of coal.²⁻¹⁰

We describe results from two different catalyst preparation technologies; rapid thermal decomposition of solutes (RTDS) and a modified reverse micelle synthesis. Both of these methods allow selective, gram-scale production of nanometer-sized iron-containing materials. These nanoscale particles have been tested for catalyst selectivity using a model compound.

EXPERIMENTAL

Particle Synthesis

In a typical small scale preparation of iron-oxide from reverse micelles, 12 ml of a 1 M aqueous solution of $\text{FeNH}_4(\text{SO}_4)_2$, 2 g sodium dodecyl sulfate, 150 ml of a 0.12 M isooctane solution of bis(2-ethylhexyl)sulfosuccinate sodium salt (AOT) were mixed together with vigorous stirring. Ammonia or another base was then added to the gold colored homogeneous reverse micellar solution to precipitate the iron-oxide. The iron-oxide product was washed with isooctane, water and acetone. Approximately 1.5 g of clean, dry, iron-bearing product was collected in a typical bench-scale run using this procedure. The RTDS process involves the rapid thermal decomposition of soluble precursors under controlled conditions at elevated pressures. Grams of the desired materials can be produced in minutes with this technique.

Catalyst Testing

The model coal compound naphthyl bibenzylmethane was synthesized using the method developed by Dr. Paul Dowd.¹¹ The synthetic procedure involved the Friedel-Crafts acylation of bibenzyl with 1-naphthoyl chloride in carbon disulfide followed by purification of the naphthyl bibenzyl ketone by column chromatography. The ketone was reduced using the Huang-Minlon modification of the Wolf-Kishner reduction. The purity of the model compound, after column chromatography, was greater than 98% as determined by gas chromatography (GC).

In our typical catalyst testing procedure, adapted from the method of Farcasiu and Smith,¹¹ 25 mg of naphthyl bibenzylmethane, 100 mg of 9,10-dihydrophenanthrene, 3 mg of sulfur, and 3 mg of catalyst were sealed in a pyrex tube under vacuum. The pyrex tube was heated inside a stainless steel bomb in a fluidized sand bath at 400°C for one hour and

then cooled quickly. The contents of the tube were dissolved in a known volume of methylene chloride containing a known amount of tert-butylbenzene as a GC calibration standard. The methylene chloride solution was filtered through silica gel to remove the suspended iron catalyst and analyzed by GC/FID or GC/MS on a 15 m DB-17 column. The GC analysis was conducted with on-column injection at 40°C with a 10°C/minute ramp to 100°C followed by a 5°C/minute ramp to 280°C. The temperature was held at 280°C for 38 minutes.

RESULTS and DISCUSSION

Table I shows sizes and morphologies determined by transmission electron microscopy (TEM) and X-ray diffraction (XRD) of selected iron containing catalysts produced by the RTDS and reverse micelle techniques. The RTDS and reverse micellar synthetic methods have the capability to produce different sizes and morphologies of iron containing catalysts depending upon the reaction conditions.

Iron bearing particle sizes determined by TEM and XRD generally agree for the highly crystalline materials produced. However, large differences are noted between the results of these analytical techniques for catalyst III which has a relatively small crystalline content as determined by dark field TEM and the weakness of the XRD pattern. The few crystallites present in catalyst III are large, >20 nm, which skews the XRD-based size results to larger sizes. Most of the materials produced by both particle formation methods have significant fractions which are not crystalline according to XRD or dark field TEM.

The iron-containing particles produced in the reverse micelle system are observed to be amorphous by both dark field TEM and XRD. Preliminary Mossbauer spectroscopy performed on the iron-oxides generated by the reverse micelle process reveals that α -FeOOH, β -FeOOH or α -Fe₂O₃ can be produced depending upon precipitation method and processing. The bulk aqueous chemistry of iron-oxide production¹² appears to be directly transferable to the reverse micellar system. Upon calcination of the reverse micelle produced iron-oxides at 450°C the primary phase becomes magnetite. The particle size of the materials produced can be as small as 1 nm. Surface area analysis of catalysts I, $S_g=164.77$ m²/g, and catalyst VIII, $S_g=150.68$ m²/g, as measured by the BET method are consistent with the small particle sizes determined by XRD and TEM.

The 298°K and 77°K Mossbauer spectra of catalyst I are shown in Figure 1. Using the methods developed by others, size distributions of the superparamagnetic hematite particles can be obtained with variable temperature Mossbauer.^{2,13-15} The size distribution for catalyst I is 52% > 8.5 nm, 31% between 8.5 and 5 nm and 17% < 5 nm if spherical geometry is assumed. These values agree well with the sizes of the particles determined by TEM and XRD (Table I). Mossbauer spectra of micelle produced α -FeOOH catalysts show no magnetic hyperfine structure even at 77°K. Care must be taken in using the Mossbauer results as a measure of particle size as the critical volume determined from Mossbauer spectroscopy can be due to "superparamagnetic clusters" and do not necessarily correspond to discrete particles.

The results of the catalyst testing are shown in Table II. These show that the materials produced by both RTDS and reverse micellar methods are good, selective, catalysts for carbon-carbon bond scission. While others have discussed the importance of hydration for iron catalysts² we have not attempted to optimize the degree of hydration in our materials. Our materials were tested as produced except for calcination of catalysts VII and VIII. We have found that iron containing materials contaminated with the surfactants from the reverse micelle synthetic method are not good catalysts. Commercial ferric-oxides, such as magnetite, were found not to catalyze the model reaction as well as our magnetite. Conversions of the model compound were typically 20-30%, with selectivity below 80% for commercial magnetite. Some of the best catalyst results are from micellar produced ferric-sulfides without the addition of sulfur, catalysts X and XIII. The structural phase of these ferric sulfides has not yet been determined. They are amorphous by XRD, and their catalytic activity varies with the precipitation technique used.

SUMMARY

Both the RTDS and the reverse micellar techniques can be used to produce catalytic iron containing compounds. The sizes and morphologies of the particles produced by both techniques can be controlled through experimental parameters. In addition, both techniques can produce large quantities of materials. We can produce grams of material in minutes with the RTDS technique, and with the reverse micelle technique we are currently producing greater than 11 grams of material per liter of organic solvent. The amount of material produced per liter is substantially more than the amounts which have been produced in other reverse micelle systems.¹⁶⁻¹⁹

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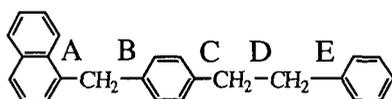
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Table I
Sizes and Morphologies of Representative Iron Catalysts
Produced by RTDS and Reverse Micelle Methods

Catalyst Number	Iron Compound	Phase	Average Particle Size (nm)	
			TEM	XRD
<u>RTDS Derived</u>				
I	Fe ₂ O ₃	Hematite	10-30	11 ± 2
II	Fe ₂ O ₃	Hematite	15-40	23 ± 2
III	Fe ₂ O ₃	Hematite	5-15	44 ± 4
IV	Fe ₂ O ₃	Hematite	30-50	42 ± 4
V	Fe ₃ O ₄	Magnetite	nd	29 ± 3
VI	Fe	α-Iron	nd	6 ± 4
<u>Reverse Micelle Derived</u>				
VII	Fe ₃ O ₄	Magnetite	5-10	10 ± 2
VIII	Fe ₃ O ₄ FeOOH/Fe ₂ O ₃	nd	4-10	nd
IX	FeOOH/Fe ₂ O ₃	nd	4-8	Amorphous
X	Fe ₂ S ₃	nd	8-15	Amorphous
XI	FeOOH/Fe ₂ O ₃	nd	10-20	Amorphous
XII	FeOOH/Fe ₂ O ₃	nd	10-20	Amorphous
XIII	Fe ₂ S ₃	nd	nd	Amorphous

nd- Not determined

Table II
Selected Results of Catalyst Testing Using
the Model Compound :



Naphthyl Bibenzylmethane

Catalyst	% Conversion ^a (±3%)	Selectivity ^b (±3)
None	2-5%	20-60
II	61%	98
III	49%	95
IV	23%	83
VII	67%	92
VIII	77%	89
X	68%	96 ^c
XI	51%	91
XII	70%	94
XIII	70%	98 ^c

a) Conversion is based on the model compound consumed. b) Selectivity is defined as the amount of products arising from cleavage of bonds A or B vs. the total amount of products. $([A]+[B])/([A]+[B]+[C]+[D]+[E])$ c) No sulfur added.

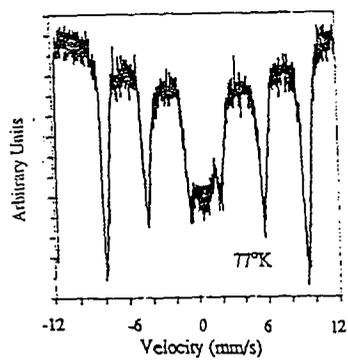
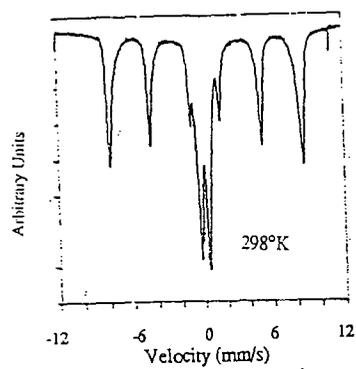


Figure 1. The Mossbauer spectra of catalyst I at room temperature and 77°K.