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ENHANCED NANOSCALE CATALYST PRECURSOR POWDERS
GENERATED USING A FLOW-THROUGH HYDROTHERMAL PROCESS

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ENHANCED NANOSCALE CATALYST PRECURSOR POWDERS GENERATED USING A FLOW-THROUGH HYDROTHERMAL PROCESS

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Abstract

A novel flow-through hydrothermal process, termed the Rapid Thermal Decomposition of precursors in Solution (RTDS), has been used to generate large quantities of ultra-fine, nano-crystalline hematite ($\alpha\text{-Fe}_2\text{O}_3$), 6-line ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) and ferric oxyhydroxysulfate powders. The heterogeneous catalytic activity of these powders towards C-C bond scission in the model compound naphthyl bibenzylmethane and in the first-stage liquefaction of Blind Canyon seam coal was investigated. The effects of the crystalline phase and the agglomerate size of these powders on their catalytic activity are reported.

I. Introduction

Metal oxide and oxyhydroxide powders and suspensions of such powders are useful in a variety of traditional and advanced industrial applications, including their use as catalysts, pigments, abrasives and as precursors for advanced structural, filtration and magnetic materials. For some of the more advanced applications, the phase and morphology of the particles which the powder or suspension consists of need to be controlled to particle diameters below ten micrometers (microns), and preferably below one micron. Until recently, however, few synthetic approaches to such "ultra-fine" particles have been scalable to an industrially attractive level. Researchers at the Pacific Northwest Laboratory (PNL) have undertaken the development of a continuous particle production technology that is capable of generating ultra-fine particulate feedstocks at rates attractive to industrial applications. Termed the Rapid Thermal Decomposition of precursors in Solution (RTDS), the technology is capable of producing a variety of single and multi-component oxyhydroxide and oxide ultra-

fine, nano-crystalline powders and suspensions.

In the RTDS process, an aqueous solution containing dissolved metal precursor salt(s) is passed through a short section of heated tubing at high pressures and flow rates before exiting through a nozzle. Ultra-fine (generally, around 0.1 microns), nano-crystalline (less than 10 nm) metal oxyhydroxide or oxide particle formation is initiated as the solution is heated and abruptly stops at the exit point.

The rudiments of the RTDS technology stem from another process developed at PNL: Rapid Expansion of Supercritical Solutions (RESS).¹ A bench-scale RTDS system was initially developed under a Department of Energy, Fossil Energy program aimed at advancing techniques to synthesize nano-crystalline iron oxides and oxyhydroxides for use as first stage direct coal liquefaction catalyst precursors.^{2,3} Subsequently, internal funding sources at PNL enabled us to explore the processing of other nano-crystalline powders⁴ and to build a scaled-up version of the RTDS technology.³ Here we discuss the production and catalytic activity of pure and doped iron oxides and oxyhydroxides toward C-C bond scission in a coal model compound and in an actual coal sample.

II. Background

The conversion of coal to distillate fuels and other chemicals has been a technological concern since World War II.⁵ Currently, coal liquefaction is performed in a two-stage process involving coal dissolution through C-C bond scission (first stage) followed by product upgrading (second stage). Ultra-fine, nano-crystalline iron oxides and oxyhydroxides have been shown to be highly active heterogeneous catalyst precursors for the first-stage direct liquefaction of coal to predominantly asphaltenes and pre-asphaltenes.⁶⁻⁸ The second stage uses conventional petroleum refining catalysts such as cobalt, nickel, molybdenum, or tungsten-based metals and alloys supported on porous alumina or silica-alumina to upgrade the first-stage products to higher hydrogen contents.

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The first-stage direct liquefaction of coal is normally performed in the presence of an appropriate solvent (model solvents include phenanthrene, 9,10-dihydro-phenanthrene, 1,2,3,4-tetrahydronaphthalene, etc.), a source of sulfur (e.g., elemental sulfur, H_2S , CS_2 , etc.), hydrogen gas (>800 psig), and catalyst with reaction temperatures ranging from 350 to 480°C. The active first-stage heterogeneous catalyst, which is believed to be some form of metal sulfide, needs to be highly dispersible throughout the coal-solvent slurry. This necessitates the use of ultra-fine catalyst or catalyst precursor powders. Unless costly catalyst recovery steps are to be employed, the active catalyst needs to be "disposable" with the rest of the unreacted coal, ash, and mineral waste that results from the liquefaction of coal. In contrast to nickel or molybdenum-based first stage coal liquefaction catalysts, which are more expensive and would pose enormously greater environmental hazards around disposal sites, the iron-based catalysts are preferred.

Many iron-based materials exhibit inherently poorer catalytic activity toward heterogeneous coal liquefaction than do the nickel or molybdenum-based analogs. Even among the eleven or so commonly encountered phases of iron oxide/oxyhydroxide, there is a wide range of inherent catalytic activity. However, it is generally believed that the catalytic activities of iron-based catalysts may be improved considerably by preparing them as nanoscale powders. The rationale behind this belief is that such nanoscale powders possess extremely high specific surface areas and have the potential of being highly dispersible under coal liquefaction conditions.

Current research efforts throughout the fuel science community are thus being directed at developing technologies to produce nanoscale iron oxide and oxyhydroxide powders of a catalytically active phase for use as precursors for the first-stage direct coal liquefaction. Perusing the literature, one finds terms such as "ultra-fine", "nano-crystalline", "nanoscale", "nanophase", "nano-particle", etc. used (or misused), often interchangeably, to describe powders or particles produced by these technologies. In this article we define particulate materials as being "nano-crystalline" if they contain crystallites of diameter less than 20 nanometers. Individual nano-crystals, i.e., "nano-particles" are not typically encountered; nano-crystals generally form the building blocks of larger structured assemblies such as porous

aggregates or fully dense polycrystalline particles. Thus, in general, the particle size of a powder and the crystallite size of the corresponding particle are different. Often, this difference is not distinguished in the literature. Particles which are approximately ten microns or less in diameter we define as being "ultra-fine".

The nano-crystalline nature of certain powders may endow them with enhanced catalytic properties, however, the particle (i.e., agglomerate or aggregate) size of the powders may inevitably limit their usefulness. Although particles containing nano-crystals may still exhibit relatively high specific surface areas, as determined through N_2 BET analysis, it does not necessarily follow that the surfaces that result from heating these particles under liquefaction conditions are similarly accessible by the larger *organic* molecules present in typical reaction schemes of interest here. Furthermore, large, non-dispersible particles consisting of aggregated or agglomerated nano-crystals may exhibit greater sedimentation rates and will therefore be less active in a heterogeneous reaction scheme than smaller particles or individual nano-particles.

The development of processes that generate nano-crystals is certainly of relevance in the area of heterogeneous catalysis. However, of even more relevance are those processes which can produce industrially useful quantities of controlled phase nano-crystals contained within particles of controlled size and morphology. The RTDS process is one such technology.

III. The RTDS Process

The RTDS apparatus is schematically illustrated in Figure 1. Aqueous suspensions of nano-crystalline oxyhydroxide/oxide particles are generally prepared by passing a 0.01-0.5M aqueous solution containing one or several labile metal salts through the RTDS apparatus operating at pressures of 40-55 MPa (6000-8000 psi), flow rates as high as 100 ml/min and temperatures of up to 400°C.²⁻⁴ The metal salt solution can also be co-processed with pH regulating additives such as urea. If control over stoichiometry is not a critical issue, appropriately treated industrial waste solutions can be used as feed stocks for the RTDS process.

Rapid metal oxide or oxyhydroxide particle nucleation occurs during the relatively short residence time of the precursor containing solution in the heated region (5-20 seconds) and is

Figure 1. Schematic diagram of the Rapid Thermal Decomposition of precursors in Solution technology.

then quenched as the particle-fluid mixture exits through the nozzle. The particle phase and morphology can be manipulated by varying the RTDS processing temperature, residence time, or precursor concentration. The resulting suspensions can be used in slurry-based processing schemes or the particles can be separated by typical industrial unit operations such as spray drying or centrifuging. Using existing equipment operating at 30% of the maximum throughput, the RTDS process can generate as much as 100 grams of ultra-fine, nano-crystalline particulates per hour. Increased throughput using existing or upgraded equipment may provide even greater production rates. The large production rate, control over particle phase and morphology, and use of relatively inexpensive precursors or industrial waste solutions makes the RTDS process attractive to industry.

IV. RTDS Nanoscale Powders

A complete description of all the materials that PNL researchers have produced using the

RTDS process is beyond the scope of this article. Table 1 is a selected list of some of the ultra-fine, nano-crystalline, particulates currently being produced using the RTDS technology.

Table 1. Selected nano-crystalline powders and suspensions produced using RTDS.

Powder	Composition
six-line ferrihydrite/ hematite	$5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}/$ Fe_2O_3
hematite	Fe_2O_3
magnetite	Fe_3O_4
trevorite	NiFe_2O_4
cubic zirconia/ monoclinic zirconia	$c\text{-ZrO}_2/$ $m\text{-ZrO}_2$
anatase	TiO_2
bunsenite/ cubic zirconia	$\text{NiO}/$ $c\text{-ZrO}_2$
bunsenite/ brindleyite isomorph	$\text{NiO}/$ $\text{Ni}_2\text{Cr}_3\text{O}_5(\text{OH})_4$

Although the RTDS process involves passing a suspension through a nozzle at elevated temperatures, it is *not* a spray drying operation. The nozzle simply acts as a method by which hydrothermal conditions can be maintained in the heated region. It is in this hydrothermal region—not in the spray downstream of the nozzle—that all the chemistry, crystal nucleation, and crystal growth occurs. Spray-drying the RTDS-generated suspension collected after exiting the nozzle, however, is a convenient and efficient method of reducing the product to an ultra-fine, nano-crystalline powder.

Detailed descriptions of the most catalytically active RTDS nano-crystalline powders follows.

Ferrihydrite/Hematite Powders

By varying the reaction temperature for a 0.1M $\text{Fe}(\text{NO}_3)_3$ solution we have produced nano-crystalline particles of pure nano-crystalline 6-line ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$)⁹, hematite ($\alpha\text{-Fe}_2\text{O}_3$) or a mixture of the two phases.³ The structure of hematite is analogous to that of corundum ($\alpha\text{-Al}_2\text{O}_3$) in that the oxygen atoms form a nearly close-packed hexagonal array with the iron atoms occupying two-thirds of the resulting octahedral interstices. The structure of 6-line ferrihydrite is not fully understood, but is believed to be a hydrated substructure of hematite. In terms of the catalytic activity toward C-C bond scission, the active phase formed from 6-line ferrihydrite exhibits much greater activity than obtained from hematite for powders of similar morphology.¹⁰ Here, one can see the importance of a powder production process that allows for control over product phase and chemistry.

Using X-ray diffraction³ and Mossbauer spectroscopy, the phases present in these powders have been determined. At 200°C, nano-crystalline 6-line ferrihydrite is the predominate phase generated through RTDS, whereas at 350°C, nano-crystalline phase-pure hematite is produced. At intermediate temperatures a mixture of the two phases is produced. In this example, lower RTDS processing temperatures are preferred in order to generate a powder with a higher content of the more catalytically active 6-line ferrihydrite.

Although there are other aqueous-based techniques available for synthesizing nano-crystalline 6-line ferrihydrite¹¹, they generally

require at least three days of dialysis in order to separate the particulates from solution. Iron salt solutions treated with traditional hydrothermal processes with much longer residence times than that obtainable using RTDS, generally yield hematite rather than 6-line ferrihydrite. The RTDS process allows for the rapid and immediate preparation of the catalytically active phase, 6-line ferrihydrite.

Ferric Oxyhydroxysulfate

RTDS co-processing of an aqueous solution of 0.01M $\text{Fe}(\text{NO}_3)_3$ and 0.05M NH_4SO_4 at 150-200°C yields a suspension, which upon dialyzing for one day produces a yellow precipitate. X-ray diffraction analysis on this powder enabled it to be identified as ferric oxyhydroxysulfate. The structure of ferric oxyhydroxysulfate is similar to that of akaganeite ($\beta\text{-FeOOH}$) in that double-straight chains of $\text{FeO}(\text{OH})$ octahedra are connected together to form a tetragonal crystal system with a tunnel structure. In akaganeite, the tunnels are supported by Cl^- anions, whereas in ferric oxyhydroxysulfate they are supported by SO_4^- groups.¹¹

As was the case for 6-line ferrihydrite, the RTDS process allows for the more efficient preparation of ferric oxyhydroxysulfate powder than that which could be prepared from literature methods¹¹—reducing the dialysis time from 30 days to one.

V. Catalytic Activity of RTDS Powders

The ultra-fine, nano-crystalline nature of the powders produced by RTDS make them ideally suited as heterogeneous catalysts. Many of the RTDS powders are being tested by PNL researchers and clients for their usefulness in industrial catalytic processes, including coal liquefaction.

Unlike many of the iron-based catalyst precursors generated using other techniques, the RTDS catalyst powders typically have excellent run-to-run reproducibility and an indefinite shelf-life, are easily transported and handled, and require no special pre-treatments in order to make them catalytically active.

We have extensively tested RTDS iron oxide and oxyhydroxide powders, as heterogeneous first-stage coal liquefaction catalyst precursors using a variety of coal model compounds and well characterized coal samples.

Model Compound Studies

Direct testing of first-stage coal liquefaction catalyst precursors using coal samples is time-consuming and the broad spectrum of products formed during liquefaction makes mechanistic studies difficult. To screen potential catalyst precursors, the compound naphthyl bibenzylmethane (NBBM) is used as a model substrate. The products that form after bond scission in the presence of a hydrogen donating solvent are well known and are easily identified using gas chromatography (GC). Scission of bonds "a" or "b" to yield naphthalene plus methyl bibenzyl or methyl naphthalene plus bibenzyl is the result of catalyzed reactions.

Model liquefaction testing on catalyst precursors was performed using 25-mg NBBM, 10-mg catalyst precursor, 10-mg elemental sulfur and 100-mg 9,10-dihydrophenanthrene (a hydrogen donating solvent). The reaction mixture was placed in a glass tube and sealed under vacuum. The tube was then closed in a stainless steel reaction bomb containing 1,2,3,4-tetrahydronaphthalene (which acts as a heat transfer medium and helps to counterbalance the pressure build-up inside the glass tube) then heated at 400°C for one hour in a fluidized sand bath. After the reaction, the products inside the glass tube were extracted with methylene chloride containing an internal GC standard. The product distribution was determined using GC.^{3,4}

Table 2 summarizes the results of C-C bond scission yields from NBBM using RTDS-derived powders as catalyst precursors. For comparison, the thermal background yield and sulfur-only yields are also reported. The catalyst precursor powders were prepared from RTDS-generated suspensions by centrifugation and drying. No special precautions were taken to optimize agglomerate size—mean particle sizes were in the 100 μm range. The effect of precursor phase on catalytic activity is clearly discernible.

As discussed previously, particle (i.e. agglomerate or aggregate size) is also an important factor that may influence the activity of a given catalyst precursor powder. Table 3 summarizes the effects of RTDS powder particle size on C-C bond scission yields from NBBM.

Table 2. Bond scission yields from NBBM using RTDS-derived catalyst precursors.

Catalyst precursor	Yield ($\pm 3\%$)
no catalyst, no S	5
S only	20
RTDS hematite + S	23
RTDS 6-line ferrihydrite + S	77
RTDS ferric oxyhydroxysulfate + S	83

Table 3. Bond scission yields from NBBM using RTDS-derived catalyst precursors of controlled mean particle diameter (D_m).

RTDS catalyst precursor plus S	Screen fraction	D_m (μm)	Yield ($\pm 3\%$)
6-line ferrihydrite	+230	135	34
	+325/-230	53	49
	-325	13	90
Ferric oxyhydroxysulfate	+230	nm	81
	+325/-230	nm	83
	-325	nm	78
Hematite-SD	-	4	63

The catalytic activity of as-prepared RTDS 6-line ferrihydrite powder (Table 2) shows a significant dependence on particle diameter after sieving through 230 mesh (63 μm openings) and 325 mesh (45 μm openings) standardized wire screens (Table 3). The catalytic activity of RTDS ferric oxyhydroxysulfate, however, shows little dependence on particle diameter.

Although for some materials, concentrating the smaller particles into one fraction by sieving enhances the effective catalytic activity of the powder, the additional powder attritioning and separation steps makes this method less efficient. An alternative approach to the production of individual particles having small diameters (and large exposed surface areas) is spray drying. Spray-drying an RTDS-generated nano-crystalline hematite suspension efficiently produces a powder which exhibits much greater catalytic activity (hematite-SD in Table 3) than that which was prepared by centrifuging, drying and sieving the same suspension.

First-Stage Coal Liquefaction Studies

Although RTDS ferric oxyhydroxysulfate exhibits slightly better catalytic activity than RTDS 6-line ferrihydrite (Table 2) and shows

little dependence on particle size (Table 3), it still requires a dialysis step. Thus, we have concentrated on RTDS 6-line ferrihydrite as the ideal catalyst precursor for the first-stage liquefaction of Blind Canyon seam sub-bituminous coal. Catalyst precursor testing was performed by heating 1.2 g Blind Canyon seam coal (Argonne Premium Coal Sample Program), 2.0 ml 1,2,3,4-tetrahydronaphthalene, 0.01 g elemental sulfur and 0.01 g 6-line ferrihydrite (-325 mesh) at 350°C for one hour under 800 psig of hydrogen gas in a stainless steel reactor. The liquefied light oils, asphaltenes and pre-asphaltenes were then Soxhlet extracted from the unreacted coal and ash residue using tetrahydrofuran (THF) as the extraction solvent. Table 1 shows the results of this testing, indicating that there was a 22% absolute increase in liquefied THF-soluble products over thermal background using the RTDS six-line ferrihydrite catalyst precursor.

Summary

The Rapid Thermal Decomposition of precursors in Solution (RTDS) process has been used to generate large quantities of ultra-fine, nano-crystalline hematite ($\alpha\text{-Fe}_2\text{O}_3$), 6-line ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) and ferric oxyhydroxysulfate particles in aqueous suspensions. Relatively short residence times in the hydrothermal region limit crystallite diameters to typically below 10 nm and aggregate diameter to less than 100 nm. Subsequent centrifuging or spray drying of the RTDS-generated suspensions yields highly active catalytic powders. For RTDS hematite and 6-line ferrihydrite, control over agglomerate diameter, through spray drying or sieving, is important in optimizing the catalytic activity of these powders towards C-C bond scission in the model compound naphthyl bibenzyl-methane. In general, powders having smaller

Table 4. Results of RTDS catalyst precursor testing toward first-stage Blind Canyon Seam coal liquefaction.

Catalyst precursor	Yield ($\pm 3\%$)
no catalyst, no S	58
S only	63
RTDS hematite + S	62
RTDS 6-line ferrihydrite, no S	61
RTDS 6-line ferrihydrite + S	80

mean agglomerate diameters were more active than those which contained larger agglomerates. The catalytic activity of RTDS ferric oxyhydroxysulfate, however, showed little dependence on agglomerate size. Finally, ultra-fine, nano-crystalline RTDS 6-line ferrihydrite powder increases the first-stage liquefaction yield from Blind Canyon seam coal by 22% absolute over thermal background at 350°C.

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