

## PREPARATION OF ULTRAFINE CATALYST POWDERS USING A FLOW-THROUGH HYDROTHERMAL PROCESS

Dean W. Matson, John C. Linehan, and John G. Darab  
Pacific Northwest Laboratory,  
P.O. Box 999, Richland, WA 99352.

Keywords: Catalyst synthesis, Iron catalysts, Catalyst characterization

### ABSTRACT

The rapid thermal decomposition of solutes (RTDS) process was used to produce ultrafine iron-bearing oxide and hydroxide powders for use as coal liquefaction catalysts. The RTDS process subjects aqueous solutions containing dissolved metal salts to elevated temperatures and pressures in a flow-through apparatus. Particle formation is initiated during brief exposure of the solution to a heated region, then is quenched by abruptly cooling and depressurizing the suspension. Powders having individual crystallites on the nanometer to tens-of-nanometer size scale are readily produced by the RTDS method. Variations in RTDS processing parameters (e.g., solute concentration, flow rate, processing temperature) affect the crystallinity, morphology, and size of particles produced. Powders generated using the RTDS process were characterized using XRD, EXAFS, electron microscopy, Mossbauer spectroscopy, and BET surface area analysis.

### INTRODUCTION

The development of inexpensive and environmentally benign materials exhibiting catalytic activity toward coal liquefaction processes will enhance the economic viability of coal liquefaction as a source of liquid transportation fuels. If active materials can be developed which meet these criteria, the application of single-use "throw away" catalysts will eliminate the need for costly catalyst reclamation steps in the liquefaction process. Inexpensive iron-based materials have been shown to be catalytically active in coal liquefaction processes, although their activities are typically low compared to other, much more expensive and/or toxic molybdenum-based materials.<sup>1</sup> One approach which can be taken to counteract the inherently lower catalytic activity of iron-based materials is to increase the surface site availability per unit weight of catalyst. The production of finely divided catalyst precursor powders having particle sizes on the nanometer to tens of nanometer size scale offers specific surface areas of up to several hundred m<sup>2</sup>/g. In addition to the increase in availability of active sites, ultrafine particles have a much higher mobility within the reaction medium, increasing the potential for coal/catalyst contact.<sup>2</sup>

We have shown that ultrafine iron-bearing particles can be generated quickly in a flow-through hydrothermal process referred to as the rapid thermal decomposition of solutes (RTDS) process.<sup>3</sup> The RTDS process offers a method of generating both ultrafine iron (hydroxy) oxides and mixed metal (hydroxy) oxides using inexpensive water soluble precursors. The RTDS process is amenable to variations in a number of processing parameters. Among those readily adjusted are the precursor salt and its concentration in solution, the processing temperature and pressure, and the length of exposure to the heated region. In this report we present the results of efforts to characterize iron-bearing powders generated using the RTDS method and to relate the effects of varying processing parameters on the powder characteristics. Results of catalytic activity runs using RTDS products are presented in a companion paper.<sup>4</sup>

### EXPERIMENTAL

Details of the RTDS powder formation method have been presented elsewhere<sup>3</sup> but are summarized here for convenience. As it is used for the preparation of iron-bearing powders from aqueous solutions, the RTDS technique involves rapid transport of the precursor solution through a high temperature, high pressure region followed by an abrupt transition to low temperature and

ambient pressure. Solutions were pressurized using a high pressure reciprocating piston pump and subsequently passed through a length of stainless steel tubing which was resistively heated using the temperature regulated output from a DC power supply. Temperatures of the solutions at the downstream end of the heated tube were monitored by a thermocouple mounted in the fluid flow. Typical fluid residence times in the heated region of the apparatus were less than 2 seconds. After passing through the heated tube, the solution was depressurized by passing it through a small orifice. The resulting spray was directed into a flask immersed in an ice bath, where the resulting suspension was collected. For the purposes of investigating the RTDS process as a method of ultrafine powder production, a standard metals concentration of 0.1 M was chosen for the feed solutions.

Iron-bearing RTDS suspensions were separated by allowing the particulate fraction to settle, either gravitationally or by centrifugation. If required, additional salts were added to the suspensions to flocculate the particles and assist the settling process. Liquid above the particulate layer was decanted off, the particles were washed with deionized water, and the process was repeated. The resulting solid product was dried under flowing nitrogen or air.

A variety of techniques were used to characterize the RTDS-generated powder products. Powder X-ray diffraction (XRD) was routinely used to determine crystalline phases present in the RTDS powder product, and XRD line broadening analysis provided crystallite size data. Selected samples were also analyzed using Mossbauer spectroscopy, BET nitrogen adsorption analysis, extended X-ray absorption fine structure (EXAFS) spectroscopy, and electron microscopy.

## RESULTS and DISCUSSION

In the absence of other components, ferric nitrate solutions processed using the RTDS method yielded deep red to red-brown suspensions characteristic of polymeric ferric oxides and hydroxides.<sup>5</sup> The 0.1 M  $\text{Fe}(\text{NO}_3)_3$  solutions processed at RTDS temperatures above 250°C formed solids which settled readily, while those produced at lower temperatures (200-250°C) settled much more slowly or remained suspended until salted out.

The pH of the 0.1 M  $\text{Fe}(\text{NO}_3)_3$  solutions was roughly 2.0 as prepared, and dropped approximately 0.3 pH units during the RTDS processing. This decrease in pH resulted from hydrolysis reactions occurring under the hydrothermal conditions present in the RTDS apparatus:

$\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+$  and  $2\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+$ . Efforts to modify the pH of RTDS solutions by adding an acetate buffer (0.36 M sodium acetate and 0.04 M acetic acid) raised both the before- and after-processing pH values above 4.0. Processing of the buffered solution at low temperature (225°C) generated a dark reddish brown suspension that did not settle, although a solid product was salted out by addition of sodium sulfate.

The analytical results from iron (hydroxy) oxide powders produced by RTDS processing of aqueous 0.1 M  $\text{Fe}(\text{NO}_3)_3$  solutions at various temperatures are summarized in Table 1. These results suggest that at low processing temperatures (< 250°C), the phase obtained was 2-line ferrihydrite or mixtures of ferrihydrite and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ). Both XRD and transmission electron microscopy (TEM) analyses indicated that these low-temperature RTDS products consisted of powders containing crystallites smaller than 10 nm in diameter. Higher RTDS processing temperatures (300-400°C) yielded the hematite form of iron oxide exclusively, and crystallite sizes were observed to increase as a result of higher processing temperatures (Fig. 1, Table 1). The increase in crystallite size with increasing RTDS processing temperature was also reflected in the room temperature Mossbauer spectra of the powder products as a shift from the 2-line quadrupole doublet spectrum characteristic of particles less than 8.5 nm in diameter to the 6-line hyperfine spectrum which is characteristic of bulk hematite (Fig. 2).<sup>5,6</sup>

Figure 3 shows plots of the iron nearest neighbor shell radii (uncorrected for phase shift) determined from the iron K-edge EXAFS spectra of the powders produced from 0.1 M ferric nitrate solutions as a function of increasing RTDS processing temperature. At the lowest RTDS temperature (200°C), the nearest neighbor shell radii are indicative of low molecular weight oligomers. As the RTDS temperature is increased, the radii approach those which are representative of bulk hematite (2.730 Å for iron and 1.473 Å for oxygen).

The effect of adding urea (1.0 M) to ferric nitrate solutions being processed by the RTDS method was also investigated (Table 1). Decomposition of the urea to carbon dioxide and ammonia at RTDS processing temperatures resulted in a rapid rise in solution pH simultaneously with the development of hydrothermal conditions, producing a competing cation precipitation mechanism. Little effect was noted below 250°C because, at the short residence times of the solutions in the elevated temperature region of the RTDS apparatus, the decomposition of the urea was insufficient to significantly change the solution pH. At 250°C and 300°C RTDS temperatures the pH of the processed solutions was above 8.5, and the product was a reddish brown opaque gel. XRD analysis of the solid product indicated the presence of a poorly crystallized material, consisting primarily of 6-line ferrihydrite.

Catalytic activity and/or selectivity of ultrafine iron oxides may be significantly affected by the doping of other metals into the solid matrix.<sup>1</sup> Consequently, the production of iron oxide powders doped with other cations by co-precipitation during RTDS processing was investigated. Results of representative RTDS runs using additional cationic species as dopants are presented in Table 2. Empirically, the results obtained from the runs containing dopants were consistent with the results of ferric iron-only runs, although some differences were detected in secondary iron oxide phases which were produced. The principle phases identified in the resulting products were those of hematite and 6-line ferrihydrite (a hematite precursor). 2-line ferrihydrite may also have been present in some samples, but was not identified due to the weakness of its XRD pattern relative to that of the other phases. Some additional phases were identified in samples in which urea had been added to the feed solutions.

Efforts at obtaining magnetite ( $\text{Fe}_3\text{O}_4$ ) by processing a solution containing both  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  salts yielded only hematite and ferrihydrite phases under the conditions investigated, with the relative concentration of those phases dependent on the processing temperature. At 225°C the mixed iron system yielded both hematite and 6-line ferrihydrite, although only 2-line ferrihydrite was observed in the product of ferric nitrate only runs at similar processing conditions. At higher processing temperatures the relative concentration of hematite to 6-line ferrihydrite increased until at 400°C the product obtained was almost identical to that produced from a solution containing ferric nitrate only (Table 1). Clearly, under the RTDS processing conditions used for these experiments, the  $\text{Fe}^{2+}$  was rapidly oxidized to  $\text{Fe}^{3+}$ .

Doping of the iron feed solution with  $\text{Cr}^{3+}$  salt at a 10:1 iron to chromium ratio yielded a solid powder consisting of hematite and 6-line ferrihydrite after processing at 300°C. No distinct chromium-only phase was detected in the powder collected. Because of significant broadening of the lines in the XRD pattern due to the fine crystallite size in this material, it was not clear whether significant amounts of chromium had been incorporated into the hematite structure.

RTDS processing at 350°C of a feed solution consisting of  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Ni}(\text{NO}_3)_2$  in a 2:1 mole ratio (0.067 M: 0.033 M, respectively) yielded a reddish-brown solid powder product. XRD analysis of the powder indicated the presence of only the hematite phase. No nickel-bearing phase was detected. Addition of 0.5 M urea to the  $\text{Fe}^{3+}/\text{Ni}^{2+}$  solution and processing at 350°C yielded a powder consisting primarily of the nickel ferrite, trevorite ( $\text{NiFe}_2\text{O}_4$ ), with a smaller concentration of its hydroxide precursor.

Powder generated from a  $\text{Fe}^{3+}/\text{Cu}^{2+}$  salt solution at a 350°C processing temperature consisted of a mixture of hematite and 6-line ferrihydrite. No copper-only phase was detected in the XRD analysis of the precipitated solid. Addition of 0.5 M urea to the  $\text{Fe}^{3+}/\text{Cu}^{2+}$  feed solution and processing at 350°C resulted in precipitation of the copper oxide phase, tenorite ( $\text{CuO}$ ) and a separate hematite phase. XRD results on the settled powder gave no indication of the formation of a ferrite phase similar to that observed in the  $\text{Fe}^{3+}/\text{Ni}^{2+}$  system with the use of urea as a precipitating agent.

## SUMMARY

The RTDS process is a viable method for hydrothermally generating ultrafine iron-bearing catalyst powders having crystallite sizes into the nanometer size range. Specific crystalline phases and crystallite sizes of the iron-based powders generated by this method are influenced by the

processing conditions to which the feed solutions are subjected and to the species present in those solutions.

## ACKNOWLEDGEMENTS

Pacific Northwest Laboratory (PNL) is operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. The work reported here was sponsored by the DOE Office of Fossil Energy and by DOE under the Advanced Processing Technology Initiative at PNL.

## REFERENCES

- (1) Pradhan, V.R.; Herrick, D.E.; Tierney, J.W.; Wender, I. *Energy Fuels* **1991**, *5*, 712-720.
- (2) Suzuki, T.; Yamada, H.; Sears, P.; Watanabe, Y. *Energy Fuels* **1989**, *3*, 707-713.
- (3) Matson, D.W.; Linehan, J.C.; Bean, R.M. *Mater. Lett.* **1992**, *14*, 222-226.
- (4) Linehan, J.C.; Darab, J.G.; Matson, D.W. "Results of Catalyst Testing Using Iron-Based Catalysts," This proceedings.
- (5) Schwertmann, U.; Cornell, R.M. *Iron Oxides in the Laboratory*, Weinheim: New York, 1991.
- (6) Huffman, G.P.; Ganguly, B.; Taghiei, M.; Huggins, F.E.; Shah, N. *Preprints, Div. of Fuel Chem., American Chemical Society* **1991**, *36*, 561-569.

TABLE I  
RTDS Powders Produced from 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub> Solutions

Added Component	RTDS Temp. (°C)	Identified Phase <sup>a</sup>	Crystallite Diameter (nm) by:			BET Surface Area (m <sup>2</sup> /g)
			XRD <sup>b</sup>	TEM <sup>c</sup>	Mossbauer <sup>d</sup>	
---	225	2-line Ferrihydrate <sup>e</sup>	<<10	2-10	---	212
---	300	Hematite	11	4-10	56% > 8.5	167
---	400	Hematite	23	20-40	100% > 8.5	---
acetate buffer	225	---	<<10	2-10	100% < 8.5	184
urea	200	---	---	---	---	---
urea	250	6-line Ferrihydrate	<<10	---	---	---
urea	300	6-line Ferrihydrate	<<10	---	---	---

<sup>a</sup>Determined by XRD

<sup>b</sup>Estimates of uncertainties in XRD size results are  $\pm 10\%$  for crystallites in the 10 to 120 nm range.

<sup>c</sup>TEM size estimates are qualitative and based on both bright-field and dark-field observations.

<sup>d</sup>Size distribution about 8.5 nm was based on relative areas of the quadrupole doublet vs. the 6-line hyperfine feature in room temperature spectra.<sup>6</sup>

<sup>e</sup>Two-line ferrihydrate and 6-line ferrihydrate are poorly defined hydrated iron (hydroxy) oxide phases which are distinguished from each other by the number of broad lines present in their XRD patterns.

TABLE 2  
Results of Co-Processing Aqueous Ferric  
Nitrate Solutions with Other Metal Ions<sup>a</sup> using RTDS

Other Salt	[Fe <sup>3+</sup> ]:[M]	Reaction Temperature	Identified Products <sup>b</sup>	Crystallite Diameter <sup>c</sup>
FeSO <sub>4</sub>	1:1	225°C	50% Hematite, 50% 6-Line Ferrihydrite	37 nm <<10 nm
FeSO <sub>4</sub>	1:1	300°C	90% Hematite, 10% 6-Line Ferrihydrite	36 nm <<10 nm
FeSO <sub>4</sub>	1:1	400°C	100% Hematite	32 nm
Cr(NO <sub>3</sub> ) <sub>3</sub>	10:1	300°C	40% Hematite, 60% 6-Line Ferrihydrite	12 nm << 10 nm
Cu(NO <sub>3</sub> ) <sub>2</sub>	2:1	350°C	70% Hematite, 30% 6-Line Ferrihydrite	11 nm <<10 nm
Cu(NO <sub>3</sub> ) <sub>2</sub> + Urea	2:1	350°C	30% Hematite, 70% Tenorite (CuO)	11 nm 22 nm
Ni(NO <sub>3</sub> ) <sub>2</sub>	2:1	350°C	100% Hematite	15 nm
Ni(NO <sub>3</sub> ) <sub>2</sub> + Urea	2:1	350°C	80% Trevorite (NiFe <sub>2</sub> O <sub>4</sub> ), 20% δ-(Fe <sub>0.67</sub> Ni <sub>0.33</sub> )OOH	8.5 nm <<10 nm
Ni(NO <sub>3</sub> ) <sub>2</sub> + Urea	2:1	400°C	90% Trevorite (NiFe <sub>2</sub> O <sub>4</sub> ), 10% δ-(Fe <sub>0.67</sub> Ni <sub>0.33</sub> )OOH	7.4 nm <<10 nm

<sup>a</sup>Total cation concentration 0.1 M for all starting solutions  
<sup>c</sup>By XRD line broadening

<sup>b</sup>Determined by XRD analysis

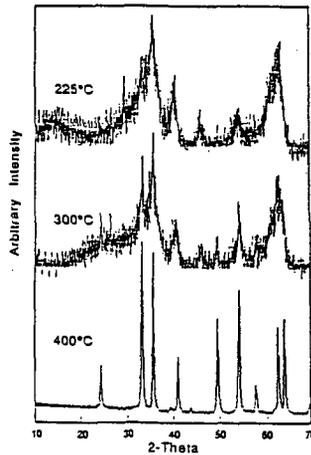


Figure 1. Variations in XRD patterns of RTDS-generated iron oxide powders as a function of increasing RTDS processing temperature.

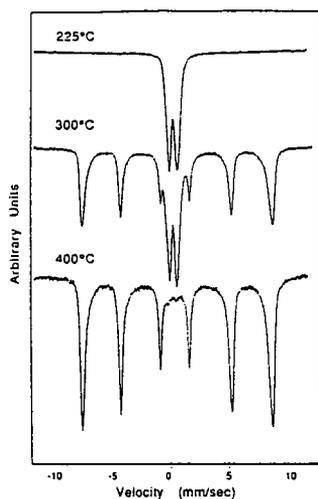


Figure 2. Variations in Mossbauer spectra of RTDS-generated iron oxide powders as a function of increasing RTDS processing temperature.

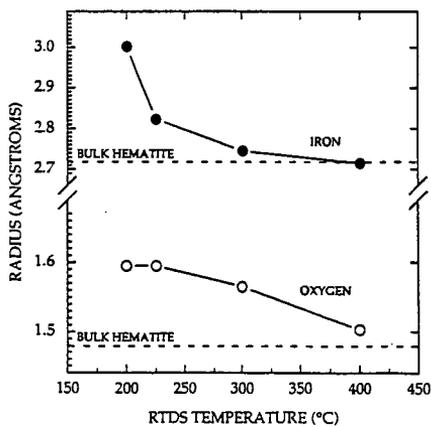


Figure 3. Plot of iron nearest neighbor radii determined from the iron K-edge EXAFS spectra of RTDS powders produced from 0.1 M ferric nitrate solutions