

# SYNTHESIS OF CARBON-SUPPORTED IRON NANOPARTICLES USING ULTRASONIC SPRAY PYROLYSIS

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## Introduction

Iron and/or iron oxide nanoparticles are employed in numerous environmental and industrial applications including adsorption (e.g., CO and arsenic), catalysis (e.g., Fischer-Tropsch process), environmental remediation (e.g., PCDD/F destruction), electronic sensing, and those requiring magnetic materials (e.g., removable magnetic storage media, MRI) [1].

Carbon provides several advantages as a metal nanoparticle support including inertness in acidic and basic conditions, thermal and mechanical stability of the porous structure, and high surface area and defined/modifiable porous structure [2]. Metal impregnated carbon materials are traditionally prepared in a multi-step process that includes: (1) selection, preparation, and modification of the carbon support, (2) loading of the metal precursor onto carbon using incipient wetness, excess solution, ion exchange impregnation techniques, or chemical vapor deposition (CVD), and (3) conversion of the metal precursor to the desired metal oxide or zero-valent form by physical (e.g., heating) or chemical (e.g., reduction) treatments [3].

Here, a continuous, single-step process is developed for preparing  $\mu\text{m}$ -scale, nanostructured porous carbon spheres impregnated with magnetite ( $\text{Fe}_3\text{O}_4$ ) or zero-valent iron (ZVI) nanoparticles (Fe-C). The objectives of this paper are to describe the synthesis and select properties of the Fe-C products and propose mechanisms for their formation.

## Experimental

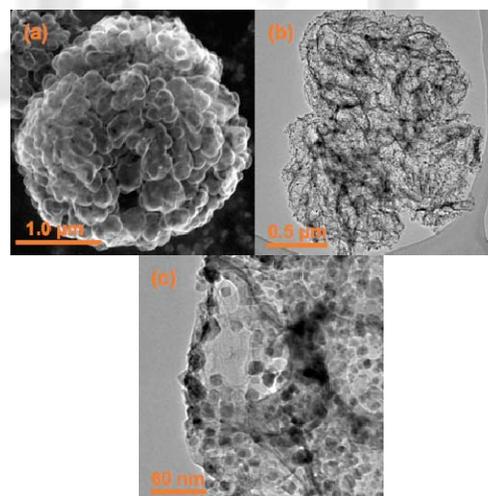
Aqueous precursor solutions containing 4:1 molar ratio of NaCl and sucrose were mixed with  $\text{FeCl}_3$  solutions. The concentration of  $\text{FeCl}_3$ , calculated as the percent mass ratio of iron to carbon, varied from 0 to 25%. An Ultrasonic Spray Pyrolysis (USP) system was employed for this work [4]. The precursor solution was injected into a nebulization cell and ultrasonically nebulized. The resulting aerosol was entrained in nitrogen (0.5-2.0 SLPM) and carried into a quartz reactor (ID = 3 cm) in a preheated tube furnace. The pyrolysis products were collected in deionized water bubblers at the reactor's exit. Particles were isolated from water by vacuum filtration. An experimental test matrix included pyrolysis temperature (500-900 °C), aerosol residence time (3-20 sec), and iron concentration (0-25% Fe/C).

Surface morphology of the Fe-C products was determined using Scanning Electron Microscopy (SEM, Hitachi S4700) at 10 kV. Iron dispersion was qualitatively analyzed using Transmission Electron Microscopy (TEM, JEOL-2100) at 200 kV. The size and crystallinity of impregnated iron species was determined with X-Ray Diffraction (XRD, Siemens-Bruker D5000), and bulk iron content was characterized with Inductively-Coupled Plasma Mass Spectroscopy (ICP-MS). Fe-C surface areas were provided by a single-point ( $P/P_0 = 0.30$ ) BET surface analyzer (Quantachrome Monosorb).

## Results and Discussion

Initial results revealed that under the experimental conditions employed, solid carbon particles are not visible when  $\text{FeCl}_3$  is not in the precursor solution. Furthermore, only  $\text{Fe}_2\text{O}_3$  forms when sucrose is not in the precursor solution. Possible explanations for these results are provided later.

SEM and TEM images of prepared Fe-C products indicate that carbon supports have diameters between 1 and 3  $\mu\text{m}$  and have a raisin-like surface morphology (Fig. 1). Impregnated iron species, which were identified as magnetite or ZVI by XRD, are dispersed within the carbon particles and have diameters ranging between 4 and 50 nm, depending on their chemical composition. Magnetite's crystallinity depends on the pyrolysis temperature. Generally,  $\text{Fe}_3\text{O}_4$  nanoparticles prepared at < 600 °C are amorphous while those prepared at > 600 °C are crystalline. Diameters of the crystalline magnetite particles generally are between 4 and 10 nm.  $\text{Fe}_3\text{O}_4$  sintering is not observed (Table 1).



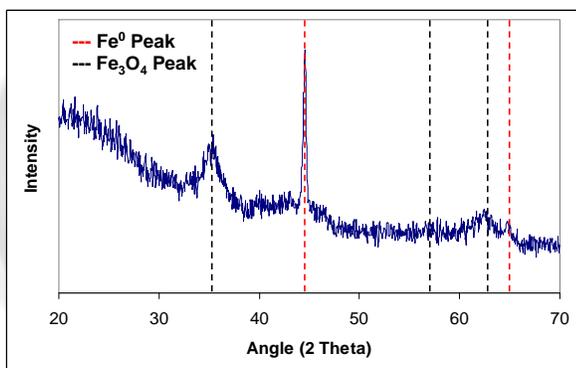
**Fig 1.** Representative SEM (a) and TEM (b and c) images of USP-prepared Fe-C materials.

Based on experimental results obtained to date, two possible mechanisms for the formation of magnetite are proposed. The first possibility is that in the presence of  $\text{FeCl}_3$  (an acidic dehydrating agent), sucrose is partially hydrolyzed to glucose and fructose [5]. As aerosol droplets enter the reactor, water and HCl evaporate and solid particles

containing glucose, fructose, NaCl, and ferric hydroxide form. As the particle's temperature increases, ferric hydroxide reacts with glucose via redox reactions to form magnetite, gluconic acid, and hydrogen [5]. The second possibility is that  $\text{Fe}_2\text{O}_3$  is initially formed when the droplets' water evaporates and is reduced by CO and  $\text{H}_2$  (products from glucose and fructose pyrolysis and gasification) to form  $\text{Fe}_3\text{O}_4$ . On-going research is in progress to examine these proposed mechanisms in detail and provide further insight into the following questions: 1) is the decomposition/dehydration of sugar catalytically enhanced by ferric chloride?, 2) is the formation of carbon nano-spheres around iron species comparable to the formation of other carbon nanomaterials (e.g, CNT) on catalyst seeds?

**Table 1. Characteristics of Iron Species in Fe-C Products at Different Temperatures (Q = 0.5 SLPM, 8% Fe/C).**

Reactor Temperature (°C)	Iron Form	Metal Diameter (nm)
500	Amorphous	Unknown
700	$\text{Fe}_3\text{O}_4$	$\text{Fe}_3\text{O}_4 = 6$
900	65% $\text{Fe}_3\text{O}_4$ 35% $\text{Fe}^0$	$\text{Fe}_3\text{O}_4 = 4 - 5$ $\text{Fe}^0 = 30$



**Fig 2.** XRD spectra for USP Fe-C material prepared at 900 °C.

Generation of the carbon's porosity occurs via two pathways, depending on pyrolysis temperature. At low temperatures ( $< 700$  °C), an *in situ* templating mechanism generates carbon porosity. Because the melting point of NaCl is 800 °C, isolated carbon atoms aromatize around the solid salt template. When the carbon products are collected in water bubblers, the template dissolves, leaving a porous structure in the carbon particle [4]. At  $< 700$  °C, high surface areas carbon products are only observed when the salt template is present (Table 2). At higher temperatures (e.g., 900 °C), a different mechanism is postulated for porosity formation. Fresh, edge-site carbon atoms isolated from decomposition of glucose, fructose, and gluconic acid are highly reactive with oxidizing gases and are partially gasified *in situ* with steam, generating additional carbon porosity. At 900 °C, carbon products with higher surface areas are generated when NaCl is absent because some of the salt particles may block reactive carbon sites and hinder gasification (Table 2).

**Table 2. Surface Area of Fe-C Products Prepared with and without NaCl in Precursor (Q = 0.5 SLPM, 8% Fe/C).**

Reactor Temperature (°C)	BET Surface Area ( $\text{m}^2/\text{g}$ )	
	With NaCl	Without NaCl
600	390	10
700	520	200
900	520	710

Carbon spheres prepared at 900 °C also contained dispersed nano-ZVI (Table 1, Fig. 2). This is attributed to the oxidation of carbon by magnetite to produce CO/CO<sub>2</sub> and subsequent reduction of magnetite by CO/CO<sub>2</sub> at  $> 700$  °C [6]. The diameter of ZVI nanoparticles (30 nm) is larger than that of magnetite. It is hypothesized that ZVI sintering occurs at the highest pyrolysis temperature tested.

## Conclusions

Porous carbons with  $\mu\text{m}$  diameters can be prepared with impregnated  $\text{Fe}_3\text{O}_4$  and/or ZVI nanoparticles in a single step using ultrasonic spray pyrolysis. The production mechanism is complex: sucrose dehydration is catalyzed by iron, pore development occurs via *in situ* salt templating and/or *in situ* carbon gasification, and reaction temperatures control the structure of iron species and carbon porosity. The as-produced Fe-C materials have specific surface areas as high as  $710 \text{ m}^2/\text{g}$ , and contain as high as 35 wt% nano-diameter (4-50 nm) iron particles dispersed uniformly in the carbon skeleton. This new production technique is a simple alternative to the traditional multi-step impregnation procedures for preparing carbon supported catalysts. Future work will explore possible environmental applications for these new Fe-C materials.

**Acknowledgment.** Support is provided by EPRI and the University of Illinois. SEM, TEM, and XRD were carried out in part in the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under grants DE-FG02-07ER46453 and DE-FG02-07ER46471.

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