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Homogeneous Iron Phosphate Nanoparticles by Combustion of Sprays

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Abstract

Low-cost synthesis of iron phosphate nanostructured particles is attractive for large scale fortification of basic foods (rice, bread, etc.) as well as for Li-battery materials. This is achieved here by flame-assisted and flame spray pyrolysis (FASP and FSP) of inexpensive precursors (iron nitrate, phosphate), solvents (ethanol), and support gases (acetylene and methane). The iron phosphate powders produced here were mostly amorphous and exhibited excellent solubility in dilute acid, an indicator of relative iron bioavailability. The amorphous and crystalline fractions of such powders were determined by X-ray diffraction (XRD) and their cumulative size distribution by X-ray disk centrifuge. Fine and coarse size fractions were obtained also by sedimentation and characterized by microscopy and XRD. The coarse size fraction contained maghemite Fe_2O_3 while the fine was amorphous iron phosphate. Furthermore, the effect of increased production rate (up to 11 g/h) on product morphology and solubility was explored. Using increased methane flow rates through the ignition/pilot flame of the FSP-burner and inexpensive powder precursors resulted in also homogeneous iron phosphate nanoparticles essentially converting the FSP to a FASP process. The powders produced by FSP at increased methane flow had excellent solubility in dilute acid as well. Such use of methane or even natural gas might be economically attractive for large scale flame-synthesis of nanoparticles.

INTRODUCTION

A broad spectrum of sophisticated nanomaterials can be made by spray combustion of appropriate precursor solutions such as catalysts,¹ electroceramics (e.g., fuel cells² and battery materials³), biomaterials,⁴ and even microdevices (e.g., sensors⁵). This is a scalable technology broadly used in the manufacture of carbon black by the so-called “furnace” process.⁶ Furthermore flame spray processes lead to synthesis of nano ceramics like ZrO_2 and yttria-stabilized zirconia, SiO_2 , and others with production rates of 100–1000 g/h even at academic laboratories.⁷

A major hurdle, however, for commercial deployment of this technology for synthesis of sophisticated nanomaterials beyond carbon black is the cost of its liquid precursors and solvents. Precursor and solvent costs constitute the largest expense (43–80%) in large scale production (10–100 t/year) of nanoparticles by spray combustion.⁸ Reduction of the nanoparticle production cost can be achieved using inexpensive precursors (nitrates, carbonates, etc.) and solvents (ethanol and water). Such precursor solutions, however, tend

to combust into mixtures of fine nanoparticles made by gas-to-particle conversion and much larger (hollow or fragmented) particles made by droplet-to-particle conversion.⁹

To overcome this, costly metal organic precursors (i.e., alkoxides, acetylacetonates, or carboxylates) are typically used.¹⁰ Furthermore, by selecting appropriate solvents, more homogeneous nanoparticles are made.¹¹ For example, in Bi_2O_3 synthesis from bismuth nitrate, using acetic acid as solvent resulted in volatile bismuth acetates and eventually homogeneous nanoparticles, whereas the use of ethanol resulted in inhomogeneous products.¹² Another way to reduce product inhomogeneity is the conversion of cheap inorganic metal precursors to metal organic complexes by chemical methods.¹³ The presence of a carboxylic acid in the flame spray pyrolysis (FSP) precursor solution resulted in homogeneous Al_2O_3 , Fe_2O_3 , and Co_3O_4 nanoparticles by formation of a more volatile carboxylate from the metal nitrate.¹⁴ However, such solvents are quite costly compared to pure ethanol or water.

Nanoparticles with uniform characteristics have been made also by flame-assisted spray pyrolysis¹⁵ (FASP) of inexpensive inorganic precursors and solvents^{16,17} (e.g., ethanol). In FASP, cheap fuel gases (acetylene or methane) are used to promote solution droplet evaporation and gas-to-particle conversion preventing formation of inhomogeneous product by droplet-to-powder conversion.^{18,19} Acetylene was chosen as the main fuel gas for its high adiabatic flame temperature. Here FASP is explored for synthesis of iron phosphate nanoparticles with potential applications in food fortification²⁰ and as cathode materials in lithium batteries.³

Recently flame-made iron phosphate nanoparticles have become attractive for iron food fortification.²¹ Iron deficiency is still a major global public health issue. Food fortification is an effective way to improve iron intake.^{22,23} Fortification with iron phosphates is advantageous over other Fe-containing compounds (e.g., Fe-sulfates) as they cause fewer sensory changes to fortified food.²¹ Iron phosphate should be delivered in nanostructured form, as the relative iron bioavailability increases dramatically with decreasing particle size.^{20,24,25} Flame-made FePO_4 nanoparticles for food fortification have to be, however, cost-competitive to other iron-containing compounds.

Here, FASP and FSP are explored for synthesis of homogeneous FePO_4 nanoparticles from inexpensive precursors and fuels (C_2H_2 or CH_4) at increased production rates. The focus is on iron phosphate having high solubility in dilute hydrochloric acid (pH 1) after 30 min, a measure that is used to reliably predict the relative bioavailability of iron compounds.²⁶

MATERIALS AND METHODS

Particle Synthesis

Iron phosphate nanoparticles were produced by FASP¹⁹ and standard FSP⁹ depicted in parts a and b of Figure 1, respectively. Iron nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; purity >98%; Aldrich) was dissolved in denaturized absolute ethanol (A15, Alcosuisse) and tributyl phosphate ($(\text{CH}_3(\text{CH}_2)_3\text{O})_3\text{PO}$; purity 97%; Aldrich) was dosed to give final Fe and phosphate concentrations of 0.2 mol/L each. This standard precursor solution was fed at 2–6 mL/min through the FASP or FSP spray nozzles by a syringe pump (Lambda, VIT-FIT) and atomized by coflowing 6 L/min of oxygen (Pangas 99.5%) at 1.5 bar pressure drop. Additionally, 5 L/min (sheath) O_2 was supplied through 32 holes of 0.8 mm diameter each surrounding the capillary tube at a radius of 15 mm. All gas flow rates were controlled by mass flow controllers (Bronkhorst, EL-FLOW). Using a vacuum pump (Busch, Mink MM1202 AV), product particles were collected on water-cooled glass microfiber filters (Albet LabScience GF 6, 25.7 cm in diameter) placed at least 60 cm above the burner.

In FASP, the ignition/supporting flame was issued from a cylindrical torus ring (hereafter called ring) at 1 cm above the nozzle while 1–2.5 L/min C_2H_2 (Pangas, 99.5%) were fed through the ring. A stainless steel tube was placed between the burner face and the ring to shield the precursor solution spray from air entrainment.¹⁹ In FSP, the precursor-oxygen spray was ignited by a circular premixed flame⁹ of CH_4 (Pangas, 99.5%) and O_2 surrounding the nozzle at the burner face.

Particle Characterization

The specific surface area (SSA) of the nanopowders was determined by N_2 adsorption at 77 K (Tristar, Micromeritics Inc.), and their morphology was obtained by transmission electron microscopy (TEM, Philips CM30) and scanning electron microscopy (SEM, Zeiss Gemini 1530 FEG). X-ray diffraction (XRD; Bruker D8 Advance, equipped with Lynxeye detector, 40 kV, 40 mA, Cu $K\alpha$ radiation, Bragg–Brentano geometry) over a range of $15^\circ < 2\theta < 70^\circ$ with a step size of 0.01° was used to determine powder crystallinity using Topas 4.2 software (Bruker AXS). Crystal sizes were obtained by Rietveld refinement²⁷ based on the crystalline data of Fe_2O_3 . Quantitative determination of the amorphous or crystalline powder content was done using Rietveld refinement with an internal crystalline standard²⁸ (FSP-made crystalline cerium oxide, $SSA = 117 \text{ m}^2/\text{g}$) with an accuracy close to 1%. Weighed quantities of this standard were mixed with the powders in a dual asymmetric centrifuge (FlackTek SpeedMixer 150 FVZ, Hauschild, Germany) for 1 min at 1800 rpm before XRD measurement. The accuracy of this method was validated with a known mixture of commercial iron(III) oxide (Aldrich) with amorphous iron phosphate. Raman spectra were measured on a Renishaw inVia Raman microscope equipped with a 785 nm diode laser and a CCD detector. Iron phosphate density was determined with a homogeneous FSP-made powder ($SSA = 104 \text{ m}^2/\text{g}$) dried overnight in vacuum at 110°C . The volume was measured in a 10 cm^3 chamber in a gas pycnometer (Accupyc 1330, Micromeritics Inc.) using He at 10 psig.

Agglomerate (and aggregate) size distributions were measured with an X-ray disk centrifuge (XDC, Brookhaven Instruments, BI XDC) at 3000 rpm for 5 h. Aqueous particle suspensions (0.6 wt %) were stabilized by addition of 0.06 wt % sodium polyphosphate (puriss; Reidel de Haën) and 10 min of ultrasonic dispersion (Vibracell VCX 600, Sonics & Materials Inc. 600 W, 20 kHz, 13 mm tip, 0.5 s pulse, 0.3 s pause, 80% amplitude) before XDC analysis. Powder suspensions used for separation by settling were prepared similarly and allowed to settle for 1 day.

The powder solubility in dilute acid²⁶ was measured in triplicate.²¹ Powder samples (approximately 50 mg) were put in 250 mL of a prewarmed aqueous solution of 0.1 M hydrochloric acid (pH 1.00–1.05) and mixed at 130 rpm and 37°C (Polytest 30, Fisher Bioblock Scientific). After 15, 30, and 60 min mixing, 1.5 mL aliquots were taken from the samples and immediately centrifuged for 4 min (11 000g) to remove any remaining particles.²¹ The Fe content of the supernatant solution was measured by flame atomic absorption spectroscopy (AAS; SpectrAA-240FS; Varian) with external calibration. The total iron content was separately measured by dissolving 30–40 mg of the powders in 100 mL of ~5 M hydrochloric acid and measurement by AAS.²⁰

Flame Temperature Measurement

Flame temperatures were measured by non-intrusive Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy²⁹ using a Bomem MB155S FTIR spectrometer.³⁰ Here, the measurements were done at $8000\text{--}500 \text{ cm}^{-1}$ ($1.25\text{--}20 \mu\text{m}$) with a resolution of 32 cm^{-1} and a beam diameter of 4 mm. Path correction spectra for the emission measurements³¹ were taken using a calibrated blackbody cavity (PYROcal LAB;

TRANSMETRA GmbH, Switzerland) in place of the flame. Transmission measurements were averages of 512–1024 scans using an IR bandpass filter (Laser components; Germany; 3850–4910 nm) in front of the detector allowing one to selectively trace the radiation from the hot CO₂ band (≈ 2100 – 2400 cm^{-1}). Emission spectra were taken without such a filter averaging 256 to 512 scans for each measurement point. The average flame temperature was determined averaging the values obtained from the Normrad and E/T procedure.^{32,33} The blackbody Planck function was matched with the hot CO₂ bands³¹ from³⁰ 2300 to 2220 cm^{-1} . The average flame temperature is an integral along the IR-beam path through the flame centerline (line of sight measurement). Error bars represent the deviation from Normrad and E/T procedures.³²

RESULTS AND DISCUSSION

Product morphology and particle formation mechanisms of iron phosphate particles made from low-cost precursor solutions by FASP are discussed first. The influence of C₂H₂ flow rate on particle formation by gas- and droplet-to-particle conversions is explored. Second, the increased powder production rate by FASP and its effect on product performance is explored as well as the use of increased CH₄ flow rate in classic FSP converting it essentially to FASP.

Product Morphology and Crystallinity

The standard precursor (0.2 M iron nitrate with 0.2 M tributyl phosphate in denaturated ethanol) solution is similar to Hilty et al.²¹ without, however, addition of costly 2-ethylhexanoic acid (2-EHA). This formulation cuts the raw materials (precursor and solvent) cost by one-third for the iron and phosphate concentrations (0.2 M) used here. During standard FSP synthesis⁹ of iron phosphate using this precursor solution, inhomogeneous product is obtained as with Fe₂O₃.¹⁴ Addition of 2-EHA in this solution (1:1, ethanol/2-EHA) prevents product inhomogeneities, and Raman measurements²¹ confirmed the product was FePO₄.

Figure 2 shows XRD patterns of powders made by FASP of 2 mL/min standard precursor solution at different C₂H₂ flow rates with constant spray parameters. Common to all XRD patterns, a broad hump appears at 15–40°, indicating amorphous iron phosphate.²¹ At 1 and 1.5 L/min C₂H₂, the patterns show peaks corresponding to Fe₂O₃ with crystallite sizes of 26 and 30 nm, respectively. Maghemite is typically formed in flames,^{34–36} however, it is difficult to distinguish it from magnetite, as their major XRD peaks overlap. FSP using Fe(III)-naphthenate or even nitrate in reducing flame conditions (equivalence ratios, Φ , near or above 1) resulted in magnetite and wustite.³⁷ To make magnetite particles at such Φ , the flames were enclosed to control the combustion atmosphere.^{37,38} At the present highly oxidizing conditions ($\Phi = 0.8$), maghemite formation is expected and its structure well fitted the XRD patterns (goodness of fit <1.1) with a background function accounting for the amorphous hump of iron phosphate. The XRD patterns of powders made at 1 and 1.5 L/min C₂H₂ thus indicate inhomogeneous product powders that consist of amorphous iron phosphate and crystalline maghemite. At higher C₂H₂ flow rates, however, the peaks of iron oxide gradually disappear resulting in purely amorphous iron phosphate. This is consistent to FASP synthesis of homogeneous bismuth oxide at similar conditions.¹⁹

Figure 2 shows also photographs of the FASP-made powders. With increasing C₂H₂ flow rate, their color changed from dark to a light brown. Iron oxide is dark brown-blackish while amorphous iron-phosphate typically is light brown. The light color of the iron phosphate is desired as the resulting color (sensory) changes in food products are lighter.²¹

Figure 3 shows TEM, SEM, and electron diffraction images of the powders of Figure 2 made at 1 (a,c,e) and 2.5 L/min C_2H_2 (b,d,f). Large spherical particles of 40–200 nm in diameter are observed in TEM images of the powder made at a low C_2H_2 flow rate (a). The corresponding electron diffraction pattern (e) shows bright diffraction speckles (please see inset arrows) that indicate large crystallites along with the diffuse halo in the center indicating amorphous material, consistent with XRD (Figure 2). At 2.5 L/min C_2H_2 , however, mostly homogeneous, nanosized iron-phosphate particles are observed (b) even though very few large particles might be present also (not shown). The corresponding electron diffraction pattern (f) does not show speckles that would indicate the presence of large crystallites nor diffraction rings that would indicate nanosized crystals. The broad diffuse halo in the center points out the presence of a mostly amorphous material. SEM images (c,d) corroborate the observations from TEM showing many large spherical particles (bright) in-between the agglomerated nanosized ones (diffuse gray) for 1 L/min C_2H_2 flow (c) while for 2.5 L/min mostly nanosized particles are present in large agglomerates even though some large spherical ones are observed as well (d).

The maghemite observed by XRD and the speckles in the electron diffraction patterns are traced to the large spherical particles. These particles are formed by droplet-to-particle conversion at low C_2H_2 flow rates and flame temperatures resulting in partial droplet evaporation. As a result, such particles might be precipitating⁹ in the spray droplets or on their surface. The TEM size of these particles (50–400 nm) is larger than the average crystallite sizes (≈ 30 nm) by XRD. This indicates that particles from droplet-to-particle conversion might be polycrystalline and/or partially amorphous.

Figure 4 shows Raman spectra of FASP-made iron-phosphate with 1 and 2.5 L/min C_2H_2 together with commercial iron phosphate (top, black) and FASP-made, pure iron oxide (bottom, red). Both FASP-made iron phosphate powders exhibit the main peak of the desired Fe-orthophosphate³⁹ (≈ 1000 – 1100 cm^{-1}). FASP-made Fe_2O_3 showed Raman peaks typical for maghemite^{37,40} consistent with XRD. Quantitative analysis of powder homogeneity from Raman spectra is difficult as iron oxide contents are small and the primary peak positions of maghemite overlap with the secondary ones for Feposphate.

Figure 5 shows the average FTIR temperature profile (HAN = height above spray nozzle) through the centerline of the flame for increasing C_2H_2 flows from 1 to 2.5 L/min and a precursor solution spray of 2 mL/min. Higher flame temperatures are reached for increasing C_2H_2 flows. The maximum flame temperature measured is 2390 K for 2.5 L/min C_2H_2 at lowest HAN = 2.2 cm. The temperatures decrease downstream as entraining ambient air effectively cools the flame. Together with the higher temperatures, the increasing C_2H_2 flow rates resulted in prolonged visible flame lengths from 3 to 6 cm (at 1–2.5 L/min, respectively). The maximum temperature is comparable to those (2400–2600 K) measured by FTIR for spray combustion of ethanol with silica precursor.³⁰ One has to bear in mind, however, that FTIR measures an average temperature along the line of sight through the flame. The adiabatic flame temperature of C_2H_2 is considerably higher (up to 3430 K)⁴¹ than the measured temperatures and thus higher temperatures might be reached locally in the flame where mixing of the fuel with oxygen is optimal. The obtained temperatures by FTIR compare well to temperatures measured using a flow of water inside a steel pipe across the flame. For example, temperatures of 1900 °C¹⁸ or 2300 °C⁴² were reported for FASP using 7 L/min propane instead of C_2H_2 used here.

With increasing C_2H_2 flow, the zone with high temperatures (> 2000 K) is prolonged to about 4 cm. The longer high temperature zones prolong the high temperature residence time of the spray droplets and particles. The high temperature and longer high temperature residence time promote the evaporation of all precursor components.

Figure 6 shows the specific surface area (SSA, squares) and maghemite content (circles) in the powders of Figure 2. This content decreases from 5.7 to 0.9 wt % from 1 to 2.5 L/min C_2H_2 , respectively. The maghemite content of the powders is reduced most noticeably from 1.5 to 2 L/min C_2H_2 as seen in Figure 2 with the drastic reduction of its peak intensity. The powder SSA remains rather constant between 179 and 190 m^2/g with increased C_2H_2 flow that increases the flame length and temperature. This increases the high temperature particle residence time and the size of primary nanoparticles, mostly by sintering. Apparently, the additional SSA from new nanoparticles made by gas- instead of droplet-to-particle conversion at high C_2H_2 flows is balanced by the reduction in nanoparticle surface area by sintering at these higher temperatures. Further increase of the fuel gas flow eventually decreases the SSA and increases d_{BET} as will be shown below (Figure 14). This SSA corresponds to an equivalent primary particle diameter of about 12–13 nm ($d_{BET} = 6/(SSA \times \rho)$; $\rho = 2.63 \text{ g/cm}^3$). The present SSA is comparable to those obtained by standard FSP^{20,21} (195–220 m^2/g).

Powder Size Distributions and Crystallinity

Figure 7 shows the cumulative (a) and standard (b) mass-based agglomerate size distributions by XDC of powders made at 1.0 (blue diamonds), 1.5 (green triangles), 2.0 (orange squares), and 2.5 L/min C_2H_2 (red circles). The XDC particle sizes are larger than those obtained from XRD, BET, or TEM indicating some extent of aggregation and agglomeration.⁴³ This may result from aggregates with sinter necks between individual primary nanoparticles and/or strongly adhering agglomerates that have not been broken at the present ultrasonication conditions.⁴⁴ Breakage here depends on the time and power of ultrasonication.^{45,46}

All powders show bimodal particle size distributions. The mass fraction of small particles (< 45 nm) is increasing for increased C_2H_2 flow from about 50 wt % to about 75 wt % following the steep increase in cumulative mass fraction at about 45 nm (Figure 7a). For larger sizes, the mass fraction increases more gently, indicating a broad size distribution above 45 nm.

For powders made with 2 and 2.5 L/min C_2H_2 , the shape of the distribution is almost identical, while the fraction of small particles varies for powders made at lower C_2H_2 flow rates. The difference in weight fraction at 45 nm between powders made with 1 or 1.5 L/min C_2H_2 to the powder made with 2.5 L/min C_2H_2 is about 20 or 13 wt %, respectively. These weight fractions are larger than the crystalline fraction determined by XRD (Figure 6, circles). This indicates that during XDC, either nanoparticles have adhered to large particles as shown in Figure 3a enlarging these large XDC fractions or the large particles from droplet-to-particle conversion are not fully crystalline but contain amorphous material as well. XRD analysis would then underestimate the weight fraction of these particles. Clearly, XDC size distributions indicate that with increasing C_2H_2 flow rate, the fractions of large particles are reduced, consistent with TEM and XRD (Figures 2 and 3).

Powder constituents could be separated also by their size and density. Powder suspensions were allowed to settle resulting in a black residue and a lighter colored supernatant after 1 day only. Figure 8a shows the settling tube filled with a stabilized and ultrasonicated aqueous dispersion of powder made at 1.5 L/min C_2H_2 . The resulting supernatant powder (Figure 8b) is shown along with the blackish residue at the tube bottom (Figure 8c) after drying. The powder color indicates their differing composition. TEM images of the supernatant (Figure 8d) and residue (Figure 8e) powders show their different morphology also. The black residue consists of large particles with a few fine ones, while the light brownish supernatant powder contains no large particles. The large particles in the residue

are 45–800 nm in diameter with a mean of 137 nm consistent with the large XDC fraction (>45 nm, Figure 7).

Figure 9 shows the XRD patterns of the black residue (bottom blue pattern) and the supernatant (top green pattern). These patterns clearly reveal that iron oxide is present in the black residue as seen by its strong diffraction peaks. The XRD crystallite size is 29 nm quite close to that (30 nm) of the total powder (Figure 2). As this is smaller than the TEM diameter, it indicates polycrystalline or partially amorphous particles from droplet-to-particle conversion. Determination of the maghemite/magnetite³⁷ content of this powder reveals that most of the crystalline material is maghemite, while a small part (4 wt % of crystalline material) of magnetite is present as well. The residue is not free from amorphous material either, as seen by the broad hump between 15° and 40°. The maghemite content of the residue determined by XRD is 26 wt %. This is 5 to 6 times more maghemite than in the whole powder (4.8 wt %; Figure 6). The remaining amorphous part originates from nanoparticles adhering to the large particles (Figure 8e) or from the latter being partially amorphous. On the other hand, the supernatant is free from maghemite particles as indicated by the lack of any diffraction peaks. These results indicate that the amorphous phosphate^{21,47} nanosized particle fraction is formed by precursor evaporation, reaction, and particle nucleation in the gas phase and subsequent coagulation and/or surface growth (gas-to-particle conversion)⁴⁸ while the large fraction is formed by droplet-to-particle conversion.⁹

Solubility in Dilute Acid

Figure 10 shows the iron solubility (diamonds) of the powders in Figure 2 along with their BET equivalent diameters (d_{BET} , squares; from Figure 6). Error bars represent the standard deviation between triplicate measurements of solubility. With increasing C_2H_2 flow rate, the d_{BET} does not significantly change and is constant at 12–13 nm (Figure 6). The iron solubility in dilute acid, however, is increased from 81% to 100% with increasing C_2H_2 flow rate. The iron solubility of powders made at 2.5 L/min C_2H_2 is excellent. Previous studies reported Fe-solubility of flame-made iron-phosphate ($\text{Fe}/\text{PO}_4 = 1:1$) around 85%²⁰ and 90%.²¹ The FASP configuration at low C_2H_2 flows produces similar products to standard FSP¹⁹ and thus comparable solubility could be expected. Rohner et al.²⁰ reported an increase in powder solubility with increasing SSA finally reaching the best solubility (85%) with nanostructured FePO_4 of SSA 195 m²/g. Here, however, increased solubility was obtained at constant SSA.

The increased solubility is attributed to the reduced particle content from droplet-to-particle conversion in the powders made at high C_2H_2 flows. These particles are larger than nanoparticles and therefore will dissolve slower resulting in lower Fe solubility and relative bioavailability. The difference in solubility of about 19% between the FASP-made powders at the lowest and highest C_2H_2 flow rates is almost the same as the difference in weight fraction of particles larger than 45 nm measured by XDC for these powders (Figure 7). While the SSA is not sensitive to particle inhomogeneity,⁴⁹ the solubility is quite sensitive to the content of large particles from droplet-to-particle conversion in the powder. The content of crystalline Fe_2O_3 determined by XRD (Figure 6) is smaller than the undissolved fraction in the solubility tests. One has to note, however, that the iron content in Fe_2O_3 is almost double (69.9%) than the iron content in FePO_4 (37%). The resulting iron fraction that is bound in the Fe_2O_3 crystals ranges from 10.2% to 1.7% for the powders made with 1–2.5 L/min C_2H_2 . The value for the low C_2H_2 flow is still smaller than the undissolved fraction (19% with 1 L/min C_2H_2) indicating that the large particles are not fully crystalline and their Fe content is underestimated by XRD.

Production Rate

Figure 11 shows XRD patterns of FASP-made powders at 2.5 L/min C_2H_2 flow rate and increasing precursor feed rate from 3 to 6 mL/min (bottom-up). The patterns look the same as the purely amorphous, homogeneous iron phosphate made at 2 mL/min precursor solution flow rate (Figure 2 top), with a broad hump between 15° and 40° . For increased production rates at constant C_2H_2 flow rate, the use of FASP becomes economically more and more attractive as the cost share for the fuel gas per product mass decreases.

Figure 12 shows the iron solubility in dilute acid of FASP-made powders as a function of precursor solution flow rate at standard conditions and 2.5 L/min C_2H_2 . The iron solubility ($\diamond$) remains at approximately 100% for all precursor flows. This is an excellent value and predicts a high relative bioavailability for powders made at all precursor flow rates. The SSA is decreased from 160 to 120 m^2/g so the corresponding BET equivalent diameters ($\square$) increase from 13 to 18 nm with increased precursor flow rate (bottom axis) and subsequently the production rate (top axis). This is typical for flame synthesis of particles and is attributed to increased high temperature particle residence times and precursor/particle concentration that lead to enhanced coalescence and sintering reducing the specific surface area.⁴⁸ Again, the solubility of the powders did not depend on specific surface area but rather on the presence of iron oxide impurities. A slight reduction in solubility to 97% is seen at the highest precursor flow rate (6 mL/min) as particle size increases. The fabrication of highly soluble product can be achieved with FASP at increased production rates. This may allow one to reduce the product price for a cost-competitive compound for iron food fortification.²¹

FSP with Increased CH_4 Fuel Flow

Figure 13 shows XRD patterns of iron-phosphate made with standard FSP and 6 (red, bottom pattern) or 2 mL/min (black) precursor solution feed rate with increasing pilot flame CH_4 flow rates (bottom up): 1.25 L/min CH_4 was premixed with 2.5 L/min O_2 or 3–9 L/min CH_4 were premixed with 2 L/min O_2 . Complete combustion of the precursor and solvents is achieved by the oxygen fed to the burner and by air entrainment.⁵⁰ With increased CH_4 flows, the visible flame length increased similarly to that by increased precursor flow rates.¹² For a 2 mL/min precursor solution feed rate, the XRD patterns of 1.25 and 3 L/min CH_4 show iron oxide peaks indicating the presence of iron oxide crystals (23 and 26 nm) and the inhomogeneous nature of the product powder (Figure 13). The maghemite content is 8 and 2.3 wt % for 1.25 and 3 L/min CH_4 , respectively. At 3 L/min CH_4 , the maghemite peaks' intensity is reduced even though the crystallite size is slightly larger. The increased CH_4 flow facilitated droplet evaporation reducing the fraction of particles formed by droplet-to-particle conversion. However, some iron oxide might still precipitate within such droplets. The increased overall flame temperature and residence time at this high CH_4 flow might have facilitated crystal growth of any of these remaining iron oxide particles leading to reduced crystalline fraction from 8 to 2.3 wt % but slight crystal growth from 23 to 26 nm.

The additional combustion enthalpy of the CH_4 reduced the powder inhomogeneity and maghemite content similar to FASP with increased C_2H_2 flow rates (Figure 2). In FASP, the product powders become fully amorphous (Figure 2) between 2 and 2.5 L/min C_2H_2 while in FSP the iron oxide peaks disappear between 3 and 5 L/min CH_4 (Figure 13). The total combustion enthalpy densities of the FASP with 2 and 2.5 L/min C_2H_2 are 12.8 and 14.4 kJ/g_{gas}, respectively (assuming pure ethanol spray without sheath O_2). The enthalpy densities using the FSP-burner with 3 and 5 L/min CH_4 premixed with O_2 are 10.3 and 13.7 kJ/g_{gas}, respectively, which is close to the values using the FASP-burner to produce homogeneous nanopowders. Previously, the enthalpy density of the spray (precursor solution flow/

dispersion O₂) was used as a criterion for product homogeneity from such metal-nitrate ethanol precursor solutions.¹¹ The above results show that the gaseous fuel flow of the ignition/support flamelets needs to be accounted for in such a criterion.

Figure 13 (bottom) shows the XRD pattern from a FSP-made powder at 6 mL/min precursor solution flow rate and 1.25 L/min CH₄. The maghemite peaks ($d_{\text{XRD}} = 43$ nm) are clearly visible (especially the strongest peak at 35.6°), indicating an inhomogeneous product. Compared to the pattern with the same CH₄ flow rate but lower precursor flow rate (2 mL/min), the peaks intensities are decreased. The maghemite crystallite contents are reduced from 8 to 3 wt % with the increased precursor solution feed rate from 2 to 6 mL/min. This reduction is explained with the increased enthalpy density content in the spray flame from the increased flow rate of the combustible precursor solution as with FSP synthesis of bismuth oxide¹¹ and cerium oxide.⁹ The increased powder production rate promoted the formation of more homogeneous powders by FSP as hotter flames were created by their increased enthalpy content. This resulted in longer high temperature residence time of the spray droplets and thus facilitated precursor evaporation from the droplets and promotion of gas-to-particle conversion. This was seen with FASP also in Figures 11 and 12 where increased precursor solution feed rates led to larger iron phosphate particles but free from maghemite. Note that by increasing the solution flow rate (e.g., by doubling it to 12 mL/min) does not remove the crystalline residue or prevent the formation of large particles by droplet-to-particle conversion. At this precursor flow rate, the SSA was reduced to 90 m²/g. As the precursor droplet concentration increases with increased precursor solution feed rate, there is not enough energy in that solution to fully evaporate these droplets without providing additional energy, e.g., by increasing the flow of the supporting CH₄ gas.

Figure 14 shows the Fe-solubility in dilute acid (diamonds) and the BET-equivalent particle diameters (squares) for powders produced with 2 (open symbols) and 6 mL/min (filled symbols) precursor solution feed rate and 1.25–9 L/min CH₄ (powders of Figure 13). The Fe-solubility is increased from 79% (in agreement with Rohner et al.²⁰) to 100% from 1.25 to 5 L/min CH₄ and remains constant around 100% for larger CH₄ flows. This coincides with the disappearance of the maghemite peaks in Figure 13. This is analogous to the results obtained by FASP (Figure 10).

The Fe-solubility (79%) of the powder made at 1.25 L/min CH₄ is the same regardless of precursor flow rate (Figure 13: two bottom patterns) despite the difference in d_{BET} . The increase in combustion enthalpy density by the spray thus does not improve the Fe-solubility in dilute acid. Even though the XRD peak intensity and maghemite content are decreased, the crystalline size increased from 23 to 43 nm. This along with the increased BET diameter from 11 to 15 nm hindered solubility.²⁰

On the other hand, the BET-diameter increases from 11 to 15 nm from 1.25 to 9 L/min CH₄ at low precursor flow rate (open squares) but the solubility is perfect (100%). This is similar to FASP where d_{BET} up to 18 nm was reached at 100% Fe-solubility. This was possible as no crystalline phases were developed for both FASP and FSP. This again points out that the FSP-burner can be operated as a FASP-burner with increased fuel gas (CH₄) flow rates. One, however, has to keep in mind the interplay between droplet evaporation and product particle growth driven by combustion enthalpy.

The use of CH₄ instead of C₂H₂ could even further reduce the process costs as CH₄ is cheaper than C₂H₂. Methane has very similar enthalpy and characteristics to natural gas, which is an abundant and inexpensive fuel today and might be applied in particle synthesis. So it seems possible, however, to use the FSP or FASP burner design and make use of

natural gas together with inorganic precursors and inexpensive solvents to produce high-quality, homogeneous nanostructured powders.

CONCLUSIONS

Homogeneous iron-phosphate nanoparticles were made from inexpensive inorganic Fe-nitrate precursor and solvents by flame spray combustion using acetylene or methane as supporting fuel. Inhomogeneous powder morphology and composition was observed at low acetylene flow rates in flame assisted spray pyrolysis (FASP) and low methane flow rates in flame spray pyrolysis (FSP). The resulting powders consisted of a small fraction of large (mostly >50 nm) particles made by droplet-to-particle conversion that consisted of maghemite iron oxide and a large fraction of nanoparticles 10-20 nm in diameter made by gas-to-particle conversion, which consisted of the desired amorphous iron phosphate. Most of the large particles could be easily separated from the nanosized ones by sedimentation. At increased acetylene flow rates in FASP, homogeneous, nanostructured powders were made that showed excellent (100%) iron solubility in dilute acid (pH = 1) after 30 min, a common measure of relative bioavailability of iron. With increased precursor solution flow rates resulting in increased powder production rate, homogeneous nanoparticle powders were produced also.

High methane flow rates in FSP could also be used to promote the powder homogeneity and solubility in dilute acid. This might allow optimization of production costs, replacing complex and expensive precursors and solvents with inexpensive gaseous fuels like natural gas. For both FSP and FASP, one has to be aware of the effect of increased enthalpy and high-temperature droplet or particle residence time as the production rate is increased. This facilitates droplet evaporation and formation of nanoparticles by gas-to-particle conversion leading to high Fe-solubility. At the same time, this facilitates grain growth of such nanoparticles that may hinder their solubility and eventually bioavailability, a key feature to be accounted for in scaling-up such processes.

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Figure 1.

Sketch of nanoparticle synthesis by (a) flame assisted spray pyrolysis and (b) a flame spray pyrolysis burner. A liquid precursor solution is fed at the center capillary and atomized with O_2 . The resulting spray is ignited by (a) C_2H_2 injected to the spray or (b) by premixed pilot flames.

Figure 2.

XRD patterns of iron phosphate particles produced by FASP at 1–2.5 L/min acetylene and 2 mL/min precursor solution. The amorphous iron phosphate is visible as a broad hump between 15° and 40°. Maghemite Fe_2O_3 appears in powders made with C_2H_2 flow rates less than 2 L/min. Above that, the iron oxide peaks disappear. The color of powders becomes lighter as Fe_2O_3 content decreases (corresponding powders are shown to the right).

Figure 3.

TEM-, SEM-, and ED-images of FASP-made iron phosphate with (a, c, e) 1 and (b, d, f) 2.5 L/min C_2H_2 flow. In part a, large spherical particles of 40–200 nm in diameter coexist with nanoparticles. These large particles from droplet-to-particle conversion contain iron oxide crystallites as can be seen from diffraction spots in the electron diffraction pattern (part e). In part b, no such droplet-derived particles appear and mostly agglomerates of nanosized iron-phosphate are found. SEM images (c,d) corroborate the observations from TEM, showing many large spherical particles (bright) in-between the agglomerated nanosized ones (diffuse gray) for 1 L/min C_2H_2 flow (c) while nanosized particles are present in large agglomerates for 2.5 L/min C_2H_2 (d) even though some large spherical ones are present as well. The electron diffraction image of this powder (f) is free from any diffraction spots of crystallites.

Figure 4.

Raman spectra of FASP-made iron-phosphate at 1 (green) and 2.5 (blue) L/min C₂H₂ with commercial iron phosphate (top, black) and pure FASP made iron oxide (bottom, red). Both FASP-made iron phosphate powders show the main peak of the desired Fe-orthophosphate³⁹ ($\approx 1000\text{--}1100\text{ cm}^{-1}$). FASP-made Fe₂O₃ showed Raman peaks typical for maghemite.^{37,40}

Figure 5.

FTIR flame temperatures of FASP producing $FePO_4$ with a 2 mL/min precursor solution spray dispersed by 6 L/min O_2 as a function of height above nozzle (HAN) for 1–2.5 L/min C_2H_2 . Flame temperatures increase with increasing C_2H_2 flow. The maximum (≈ 2400 K) is observed at the lowest measurement height (HAN = 2.2 cm) near the C_2H_2 ring. The temperature decreases further downstream with the dilution of the flame by air entrainment. In addition to higher temperatures, the visible flame length increases from 3 to 6 cm with increasing C_2H_2 flow.

Figure 6.

Crystallinity and specific surface area (SSA) of FASP-made powders (Figure 2) as a function of FASP C₂H₂ flow rate. The crystalline content decreases with increasing C₂H₂ flow as the formation of large crystallites is minimized at the hotter FASP flames. The SSA, however, does not change as these few large particles hardly contribute to the SSA.

Figure 7.

Cumulative (a) and standard (b) agglomerate mass size distributions by X-ray disk centrifuge of FASP-made powders at 1–2.5 L/min acetylene flow rate. At lower C_2H_2 flows (e.g., 1 and 1.5 L/min), a larger fraction of particles bigger than 45 nm is obtained consistent with TEM analysis. This fraction contains large crystallites along with large aggregates or agglomerates of nanoparticles.

Figure 8. Segregation by sedimentation for 1 day of a powder produced by FASP at 1.5 L/min C_2H_2 in a tube (a) resulting in a light brown supernatant (b) and a dark residue (c). The TEM pictures show the corresponding powders: The supernatant (d) is free from large spherical droplet-derived particles that are present in the residue (e).

Figure 9. XRD pattern of the residue (bottom) and supernatant (top) powders of Figure 8. Maghemite crystallites ($d_{\text{XRD}} = 29$ nm) and traces of magnetite (4%) are present in the residue along with amorphous material (73 wt %) while the supernatant is amorphous.

Figure 10.

Iron solubility in dilute acid (diamonds) and BET equivalent diameters (squares) of FASP-made powders as a function of C₂H₂ fuel flow rate. Error-bars represent the standard deviation of triplicate measurements. The solubility increased with acetylene flow rate to 100% while the BET diameter is rather constant at 12–13 nm. The increased solubility is attributed to the improved powder homogeneity (lack of Fe₂O₃ crystals) with increased C₂H₂ flow (Figure 2).

Figure 11.

XRD patterns of powders made by FASP at increased production rate by increased precursor flow rate (bottom-up) at 2.5 L/min acetylene flow. The broad hump between 20° and 40° indicates amorphous iron phosphate. The iron oxide peaks (compare Figure 2 top, for 2 mL/min precursor flow rate) are not visible at all production rates. This indicates few, if any, droplet-derived Fe_2O_3 particles.

Figure 12.

Iron solubility in dilute acid (diamonds) and BET equivalent particle diameter (squares) of powders made by FASP as a function of precursor flow rate. Error-bars represent standard deviation in triplicate measurement of the solubility. The solubility remains constant at around 100% for all FASP-made powders indicating perfect relative bioavailability. The powders d_{BET} increases for increased precursor flow rate as particle concentration and flame temperature increase.

Figure 13.

XRD patterns of FSP-made iron-phosphate with iron oxide produced with 6 (bottom red) and 2 mL/min (top five black) precursor solution flow rate ignited with 1.25 (bottom) to 9 L/min (top) of methane in the pilot flamelets. For 1.25–3 L/min CH_4 , iron oxide peaks ($d_{\text{XRD}} = 23$ and 26 nm, respectively) are visible indicating the inhomogeneous product powder. With increased CH_4 flow rate, the peaks disappear indicating a homogeneous product.

Figure 14.

Iron solubility in dilute acid (diamonds) and BET equivalent particle diameter (d_{BET} , squares) of powders made by FSP for increasing pilot flame methane flow rates with 2 (open symbols) and 6 mL/min (filled symbols) precursor solution feed rate. Error-bars represent standard deviation in triplicate measurements. The solubility increases from 79% to 100% from 1.25 to 5 L/min CH₄ and then remains constant at around 100% for larger flow rates, indicating a good relative bioavailability. The d_{BET} increases from 11 to 15 nm for increased CH₄ flow rate indicating grain growth by sintering as the process enthalpy increases. With increased precursor feed rate, the Fe-solubility was equal (79%) to that of the same CH₄ flow rate. The increased precursor concentration in the flame results in fewer but larger crystallites (from 23 to 43 nm) and d_{BET} (from 11 to 15 nm).