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Synthesis of $(MgO)_x(Fe_2O_3)_{1-x}$ nanoparticles via liquid feed flame spray pyrolysis. A non-stoichiometric spinel phase outside the normal phase diagram

Sameer Kumar, Jose A. Azurdia and Richard M. Laine*

Departments of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136, USA

Liquid-feed flame spray pyrolysis (LF-FSP) has been used to synthesize mixed-metal nanopowders in the (MgO)_x(Fe₂O_{3)_{1-x} system from metalloorganic precursors. Iron propionate [Fe(O₂CCH₂CH₃)₃] and magnesium acetylacetonate [Mg(C₅H₇O₂)₂·2H₂O] precursors were dissolved in ethanol, aerosolized with oxygen and combusted at temperatures > 1500 °C and thereafter quenched rapidly. The rate of nanopowder production was 30 g/h. The resulting nanopowders were collected in electrostatic precipitators, were un-aggregated with average particle sizes (APSs) < 45 nm and with specific surface areas (SSAs) of 40-65 m²/g as determined from both the SSAs and X-ray line broadening analyses. Powders with a range of compositions (x = 0.30, 0.45, 0.50, 0.65, 0.75 and 0.90 ± 0.02) were characterized by XRD, BET, SEM, EDS, FTIR, and TGA-DTA. Particle sizes generally increased as the fraction of MgO increased and a single-phase spinel was observed over the range x = 0.30 and 0.65 with the two extremes lying about 15 mol% outside of the published thermodynamic spinel phase boundaries.}

Key words: Liquid-Feed Flame spray pyrolysis, nano-magnesioferrite, off-stoichiometric spinel.

Introduction

Spinel group $(A^{2+}B^{3+}_{2}O_{4})$ materials are used currently for a wide range of applications, from commercial catalysts to pigments and refractory linings, and are still the subject of extensive investigation for newer applications such as contrast agents for medical imaging and nanocrystalline transparent structural materials, which are potentially tougher than traditional materials such as glass and micrometersized spinel [1-10]. We have previously reported the production of spinel materials including spinel (MgAl₂O₄) fibers from carboxylate precursors [11], and Mg, Co and Ni aluminate nanopowders by liquid-feed flame spray pyrolysis (LF-FSP) [12-14]. These studies showed that LF-FSP could be used to access spinel phases at previously unknown compositions, as discussed below. To extend this work to ferritic systems, a series of powders spanning the MgO-Fe₂O₃ tie line was produced and characterized. Ferritic nanopowders are especially interesting because of their superparamagnetic behavior.

Spinels and superparamagnetism

In the bulk form, the phase behavior and properties of magnesioferrite spinel (MgFe₂O₄) are well understood. The spinel phase is thermodynamically favored for x = 45-55 mol% MgO in the (MgO)_x(Fe₂O₃)_{1-x} system ($\approx 1000 \text{ °C}$), and normally offers paramagnetic properties [15-21]. Unpaired electron spins generate magnetic moments, which in

paramagnetic materials are randomly oriented resulting in a zero net magnetic field. In an externally applied magnetic field these moments align but revert to random order when the field is removed. Nano-sized MgFe₂O₄, unlike bulk MgFe₂O₄ offers the potential to be superparamagnetic [5, 22-24].

Biocompatability of superparamagnetic nanoparticles

Superparamagnetic nanoparticles are currently under investigation for a number of magnetically-driven applications including hard drive read/write heads [24, 26], recoverable and reusable catalysts [5, 23], and biomedical applications such as cell and protein separation, targeted drug delivery, and hyperthermic tumor treatment (strong heating due to absorption of IR radiation used to destroy cells bound to nanoparticles) [23, 27-29].

For biomedical applications, particularly in vivo, biocompatibility is obviously very important. Spinel nanopowders containing Fe, Ni and/or Co display superparamagnetism, often with induced magnetic moments much larger than MgFe₂O₄ [25, 26, 30-32]. For example, the coercivity of 5 nm CoFe₂O₄ particles (\approx 11 kOe) is approximately fifty times that of ferrite (\approx 0.2 kOe), and one hundred times that of MgFe₂O₄ (\approx 0.1 kOe) [25-26, 30]. Ferrite is mildly cytotoxic at high concentrations, and easily cleared by macrophages in vivo [33]; however, magnesioferrite is benign [27-28].

In contrast, Co, Ba and Ni, which are commonly used in superparamagnetic nanoparticles due to their magnetic moments, are all harmful [29, 34-37]. Ba is known to cause respiratory irritation, is cytotoxic and causes irreversible reproductive damage [29, 34]. Co ferrites are extremely cytotoxic and are regarded as mutagens [34-35]. For example,

^{*}Corresponding author:

Tel : +734- 764-6203 Fax: +734- 763-4788

E-mail: talsdad@umich.edu

Co and Ni initiate tumor growth in rats [35], and Co is known to cleave DNA, and oxidize proteins causing mutations [36-37].

To prevent these harmful effects, nano-sized Co, Ni and Ba ferrites have been encapsulated in biocompatible alginate gels; although this method is not very effective except at very high loadings of alginate (1 : 1 particles to alginate) [29, 34]. Clearly, avoiding any of these complications is desirable, potentially making magnesioferrite a superior choice from a biocompatibility perspective. The goal of the current work was to make magnesioferrite nanoparticles. In a separate effort we are in the process of exploring their magnetic properties.

Liquid-Feed flame spray pyrolysis (LF-FSP)

Liquid-feed flame spray pyrolysis (LF-FSP), as invented at the University of Michigan, is a simple method of producing oxide nanoparticles from liquid precursors. The LF-FSP process has been described extensively in previous publications [38-43], and will only be briefly described here. Alcohol solutions (usually EtOH) containing 5-20 wt% loading of ceramic precursors (e.g. metal carboxylates and/or alkoxides) are aerosolized with excess O₂, and ignited inside a quartz tube using methane pilot torches. Complete combustion of the precursor, with initial combustion temperatures of 1500-2000 °C, follows, generating nanopowder "soot".

The temperature in the system drops 300-500 °C within 1.5 m of the initial combustion; equivalent to a 1000 °C quench in \leq 100 ms. The resulting nanopowders (typically 15-100 nm APS with specific surface areas (SSAs) 30-100 m²/g) are usually unaggregated, although lightly agglomerated, and are typically kinetic products. Using wire-intube electrostatic precipitators (operating at 10 kV), powder can usually be recovered at up to 200 g/h.

The nanopowders generated are usually identical in composition to the precursors, including any contamination. The precursor compositions can be changed intentionally by varying the amount of each precursor, allowing the production of mixed-metal oxide materials of any composition desired, in one step. Since the properties of a material invariably depend upon its structure and composition, LF-FSP allows rapid property optimization.

In previous LF-FSP studies on $(MO)_x(Al_2O_3)_{(1-x)}$ systems (M = Mg, Ni, Co, Zn), the resulting nanopowders were observed to preferentially form the spinel phase, even at thermodynamically unfavorable compositions, e.g. as much as 30 mol% outside the phase field in CoO-Al_2O_3 at 1500 °C, effectively extending the currently accepted phase boundaries. $(MgO)_x(Fe_2O_3)_{1-x}$ was chosen to explore ferritic systems produced by LF-FSP, and determine if they behave similarly, since as mentioned above, nano-sized ferrites may hold promise for uses ranging from electronics [24, 26], to catalysts and biomedical applications, especially magnesioferrite [5, 23, 27, 28]. A series of powders spanning the MgO-Fe₂O₃ tie line was produced by LF-FSP, and characterized as described in the following section.

Experimental Section

Materials

Iron propionate [FeProp, Fe($O_2CCH_2CH_3$)₃]. Iron(III) nitrate nonahydrate, [Fe(NO_3)₃·9H₂O, 98%, 150 g, 0.37 mol] was reacted with excess propionic acid (CH₃CH₂COOH, 500 ml, 6.80 mol) for 6 h in a 1 l flask equipped with a reflux condenser and Ar sparge (11 kPa). The reflux condenser was removed and replaced by a distillation column, and approximately 150 ml of liquid was distilled to remove excess acid. The precursor was characterized by comparing TGA data with theoretically calculated mass losses, and was determined to have a 26.5 wt% ceramic yield (26.31 wt% theoretical, as discussed in results).

Magnesium AcetylAcetonate [MgAcAc₂ (Mg($C_5H_7O_2$)₂· 2H₂O), 99.9%]. MgAcAc₂ was purchased from MacKenzie Chemical (Bush, LA) and used without further purification.

XRD Studies As-shot, and heat treated powder samples were characterized using a Rigaku Rotating Anode Goniometer. Powder samples were prepared by placing ≈ 100 mg of powder on amorphous silica slides for data collection. Cu-K_a radiation ($\lambda = 1.54$ Å) with a Ni filter was used with a working voltage and current of 40 kV and 100 mA, respectively. Scans were continuous from 20-80° 20 with a continuous scan speed of 1.5° 20/minute, sampled at 0.02° 20. Jade software (Materials Data Incorporated, Version 7.0) was used to compare peak positions and relative intensities to PDF files of standard materials. Jade 7.0 was also used to determine the materials' phase compositions by simulation.

Specific surface area (SSA) was measured on a Micromeritics ASAP 2010 sorption analyzer. Samples (350 mg) were degassed at 300 °C until the outgas rate was <5 mmHg/ minute. Analyses was run at 77 K using liquid N₂. SSAs were determined by the BET multipoint method using at least five data points. APS was calculated using the equation $\langle D \rangle = 6/\rho \times SSA$ where $\langle D \rangle =$ diameter of the average particle, and r is the density of the material.

Scanning electron microscopy (SEM). A field emission SEM (FEI Nova Nanolab with EDAX attachment) was used to examine particle morphology (operating voltage 10.0-20.0 kV). EDS was used to confirm powder compositions, with an error of ± 0.02 mol%. Powder samples were dispersed in EtOH using an ultrasonic horn (Vibra-cell, Sonics and Materials, Inc., Newton, CT). A drop of the dispersed powder was placed on an aluminum SEM stub and allowed to dry in air for 1 h on a hot plate. Powders were sputter coated with 1-4 nm of Au-Pd to reduce charging effects.

FTIR. Diffuse reflectance Fourier transform (DRIFT) spectra were recorded on a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA). Optical grade, random cuttings of KBr (International Crystal Laboratories, Garfield, NJ) were ground using an alumina mortar and pestle, and 200 mg of KBr was mixed with 5 mg of each sample to be analyzed. For DRIFT analysis, samples were packed firmly in a stainless steel sample holder, and leveled off at the upper edge to provide a smooth surface. Fresh

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backgrounds of pure KBr were made every hour. The FTIR sample chamber was flushed continuously with N_2 for 15 minutes prior to data acquisition in the range 4000-400 cm⁻¹.

Thermal Gravimetric Analysis and Differential Thermal Analysis (TGA/DTA). TGA-DTA was performed using a SDT 2960 Simultaneous Differential Thermal Analyzer (TA Instruments, Inc., New Castle, DE). The instrument was calibrated with gold supplied by Perkin-Elmer. Samples (30 mg) of as-prepared powders were hand pressed in a 3 mm dual action die and placed inside Pt sample cups. Samples were heated at 10 K·minute⁻¹ from ambient temperature to 1300 °C. The reference material was a pellet of a-alumina, in a Pt sample cup. A flow of synthetic air (60 ml/minute) was maintained during all experiments.

Results and Discussion

In the following sections, we discuss the characterization of the Fe(O₂CCH₂CH₃)₃ precursor, followed by the phase behavior of (MgO)_x(Fe₂O₃)_{1-x} powders produced by LF-FSP (where x = 0.30, 0.45, 0.50, 0.65, 0.75 and 0.90). Thereafter we discuss the powder properties including their morphologies, surface chemistry, and thermal behavior in that order. Magnetic property studies are in process and will be reported elsewhere.

Iron Propionate Precursor

We previously reported the characterization of precursors including $[N(CH_2CH_2O)_3AI]$ [38-43], and $[Ni(O_2CCH_2CH_3)_2]$ [13]. Here we report the characterization of Fe(O_2CCH_2CH_3)_3. This precursor decomposes similarly to other carboxylate precursors reported previously [13, 38-43].

Fig. 1 shows the TGA of $Fe(O_2CCH_2CH_3)_3$ heated at 10 K·minute⁻¹ in synthetic air. The initial mass loss of 2 wt.% is attributed to evolution of waters of hydration. Subsequent mass loss events are due to decomposition of propionate ligands [13, 38-43], as suggested in equations (1)-(3):

Fe(O₂CCH₂CH₃)₃



Fig. 1. TGA of $Fe(O_2CCH_3CH_3)_3$ ramped at 10 k·minute⁻¹ in synthetic air showing initial 2 wt.% mass loss from adsorbed water, (1)-(2) decomposition of propionate ligands (18 wt.% each), and (3) decomposition of the last propionate ligand with water loss from hydroxyl groups (36 wt.%).

$$\rightarrow Fe(O_2CCH_2CH_3)_2(OH) + CH_3CH = C = O$$
(1)

Calc. (observed) Mass Loss = 17.92% (18%)

$$Fe(O_2CCH_2CH_3)_2 (OH)$$

$$\rightarrow Fe(O_2CCH_2CH_3)(OH)_2 + CH_3CH = C = O$$
(2)

Calc. (observed) Mass Loss = 17.92% (18%)

$$Fe(O_2CCH_2CH_3)(OH)_2$$

$$\rightarrow 0.5Fe_2O_3 + 1.5H_2O + CH_3CH = C = O$$
(3)

Calc. (observed) Mass Loss = 35.84% (36%)

The final ceramic yield (26.5%) for oxidation of the precursor $[Fe(O_2CCH_2CH_3)_3]$ to Fe_2O_3 is very close to the theoretical value of 26.31% [13, 38-43].

XRD Studies

The MgO-Fe₂O₃ binary phase diagram, depending on the composition [15], consists of mixtures of hematite, spinel, periclase and at higher temperatures, liquid phases. In the MgO rich compositions studied here, small amounts of KCl ($\approx 1 \text{ wt.\%}$) were observed by XRD (peak at 20° ~28.2) as a result of contamination from the Mg(CH₃COCHCOCH₃)₂ [Mg(AcAc)₂] precursor.

Of more importance is that $(MgO)_x(Fe_2O_3)_{1-x}$ powders, for MgO = 30 and 65 mol% (± 2 mol% error from EDS) seem to exhibit a single phase spinel structure, although the established thermodynamic phase field (at 1000 °C) indicates there should be two phases [15]. It is possible that MgO (periclase) peaks could underlay a more stoichiometrically correct spinel powder pattern. However, whole pattern fitting analysis shows that the lattice constants for MgO would be shifted by more than 2.5%. This extraordinarily large shift and our previous experience with spinel forming oxides leads us to believe that we indeed produced single phase spinel. XRD patterns of each asshot (MgO)_x(Fe_2O_3)_{1-x} nanopowders are shown in Fig. 2.

XRD spectra for all of the powders, except for MgO = 90 mol% which is mostly periclase (85 wt.%), appear very similar, they mainly exhibit the spinel crystal phase. Small intensity peaks corresponding to the (200) reflection of KCl (1 wt.%) are visible in the 65, 75 and 90 mol% MgO



Fig. 2. XRD powder patterns for all as-shot $(MgO)_x(Fe_2O_3)_{1-x}$ powders.

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powders. An SEM micrograph of a KCl particle in the $(MgO)_{0.65}(Fe_2O_3)_{0.35}$ powder is presented in Fig. S1 (see supporting information).

XRD phase analysis after heating shows that the offstoichiometry $(MgO)_x(Fe_2O_3)_{1-x}$ (x = 0.30, 0.45, 0.65) spinel materials transform to their thermodynamically-favored phases (see Fig. 3 and Table 1). Partial sintering occurs as a result of heating and leads to the expected peak narrowing, indicative of larger grain sizes (average grain size > 500 nm in all powders after heating) and higher crystallinity. KCl is not observed in any system after heating, presumably due to sublimation during heat treatment.

Table 1 summarizes the XRD phase analyses before and after heat treatment at 1400 °C, as discussed above. As-produced powder APS, calculated from X-ray linebroadening using the Debye-Scherer equation and BET derived APS values are presented in Fig. 4. Fig. 4 also shows a plot of SSAs with respect to composition. Both XRD and BET APSs show a general increase in particle size with increasing MgO content.

Particle Morphology

The values from XRD analyses tend to be slightly higher, possibly because of lower powder densities than those interpolated from the pure oxide values. A discussion and comparison of the APS values follows in the particle morphology section.



Fig. 3. XRD powder patterns for $(MgO)_x(Fe_2O_3)_{1-x}$ powders heat treated at 1400 °C in air, showing all of the expected thermo-dynamic phases at these compositions.

Table 1. Phase compositions of $(MgO)_x(Fe_2O_3)_{1-x}$ powders before and after heat treatment.

	As Shot (wt %)			Heat Treated 1400 °C (wt %)				
Mol % MgO	MgFe ₂ O ₄	MgO	Fe ₂ O ₃	KCl	MgFe ₂ O ₄	MgO	Fe ₂ O ₃	KCl
0.30	100	0	0	0	63	0	37	0
0.45	100	0	0	0	96	0	4	0
0.50	100	0	0	0	100	0	0	0
0.65	99	0	0	1	78	22	0	0
0.75	59	40	0	1	75	25	0	0
0.90	15	84	0	1	35	65	0	0

SEM micrographs indicate that the $(MgO)_x(Fe_2O_3)_{1-x}$ powders prepared by LF-FSP are uniformly sized (Figs. 5 and 6), lightly agglomerated spherical particles. BET analysis gives specific surface areas in the range 40 to 65 m²/g.

FTIR Studies

FTIR spectra of all powders are presented in Fig. 7, and show the evolution of the spectra from MgO-poor at the top to MgO-rich on the bottom, with the Fe-O peaks becoming less distinct as MgO becomes more prevalent.



Fig. 4. SSA and APS values (from XRD and BET) for all samples.



Fig. 5. SEM micrograph of $(MgO)_{0.90}(Fe_2O_3)_{0.10}$ powder from LF-FSP.



Fig. 6. SEM micrograph of (MgO)_{0.30}(Fe₂O₃)_{0.70} powder from LF-FSP.



Fig. 7. FTIR spectra for all of the samples in the $(MgO)_x(Fe_2O_3)_{1-x}$, tie-line.

Peaks observed at ≈ 570 and 480 cm^{-1} correspond to the known Fe-O vibrations for tetrahedral and octahedral coordination, respectively [46-47]. FTIR indicates the presence of chemisorbed (vOH at 3500-3700 cm⁻¹) and physisorbed H₂O (vOH 3500-3000 cm⁻¹) [13, 48], as well as carbonates (vCO at 1400-1700 cm⁻¹) [49-52] on the particle surfaces. These observations are consistent with the TGA mass losses of 3-4 wt.% observed on heating to 400 °C, and the later mass loss 800 °C which are in accord with other LF-FSP derived powders [13, 43-44].

Simultaneously with increases in Fe₂O₃ content, we observe increasing intensities for vC-H, stretching bands (2900-2700 cm⁻¹) [13, 47], most intensely for MgO = 30 and 45 mol% powders. Similar observations were previously observed in the $(CoO)_x(Al_2O_3)_{1-x}$ system and are believed to arise due to steam reforming of organics in the flame during LF-FSP [13].

TGA-DTA Studies

As mentioned above, TGA-DTA analysis (Fig. 8) reveals mass losses of 3-5 wt.% from adsorbed water and carbonate species on heating to 400 °C, as expected from other nano powder oxide systems [13, 43-44]. All powders continue to lose mass up to 1300 °C, except for the (MgO)_{0.50} (Fe₂O₃)_{0.50} sample, which seems to stabilize at ~1100 °C. This behavior is also seen in other nano spinel systems, as the stoichiometric spinel composition is stable to temperatures above 1300 °C [13].

In addition, the mass losses around 800 °C are attributed to CO_2 presumably adsorbed from the flame atmosphere during synthesis [53]. These losses of ~ 2 wt% are seen at temperatures > 800 °C for the samples with < 50 mol% MgO.

The (MgO)_{0.30}(Fe₂O₃)_{0.75} powder surprisingly showed small mass gains (0.03 wt% each) at \approx 750° and 1170 °C with corresponding small exotherms (DTA not shown). A mass gain and exotherm are consistent with further oxidation of a cationic species, and this is presumably



Fig. 8. TGA traces for all $(MgO)_x(Fe_2O_3)_{1-x}$ samples.

oxidation of a very small amount (≈ 0.1 wt% assuming addition of O^{2-} at each oxidation event) of Fe⁺/Fe²⁺ to the more stable Fe³⁺ phase at high temperature.

Conclusions

Rapid optimization of phases and stoichiometry in mixed-metal oxide nanopowders is desirable for a number of applications, and can be achieved by accurately controlling the precursor compositions used for LF-FSP. Here, we demonstrate the use of LF-FSP to produce, combinatorially, a series of powders with compositions spanning the MgO-Fe₂O₃ tie line. In particular, we demonstrate the synthesis and thereafter the characterization of spinel phase materials outside the known, published composition range. This is a consequence of producing nanopowders under conditions that strongly favor kinetic rather than thermodynamic products. We anticipate that these powders will show superparamagnetic properties as they do respond to a permanent magnet.

SSAs were observed to decrease with increasing MgO content across the MgO-Fe₂O₃ tie line. APSs derived from BET and XRD correspondingly increased (by as much as 100%) with increasing MgO content. All samples exhibited superparamagnetic properties; from their hysteresis loops showing zero coercivity at 300 K. XRD confirmed that, similar to MO-Al₂O₃ systems, single-phase MgO-Fe₂O₃ spinel nanopowders can be produced by LF-FSP. We conclude that single-phase spinel can be produced up to at least 15 mol% outside of the thermodynamic spinel phase boundary. Heating these powders resulted in the thermodynamically-favored phases, confirming that the spinel produced by LF-FSP is a kinetically-favored phase.

FTIR results were typical for nanopowders produced using LF-FSP, with the exception of nC-H peaks, which were previously only observed in the CoO-Al₂O₃ system. TGA-DTA results were also similar to other nanopowders produced using LF-FSP, with additional mass losses due to MgCO₃ (< 2 wt.% above 800 °C) formed by reaction of the Mg precursor with CO₂ during shooting. Small

mass gains and small exotherms at (750° and 1170 °C) were observed in the 35 mol% MgO powder, and are presumed to be due to oxidation of a small amount if Fe^{+}/Fe^{2+} to the Fe^{3+} phase.

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