

Direct Synthesis of Iron Oxide Nanopowders by the Combustion Approach: Reaction Mechanism and Properties

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Solution combustion synthesis of different oxides involves a self-sustained reaction between an oxidizer (e.g., metal nitrate) and a fuel (e.g., glycine, hydrazine). The *mechanism* of synthesis for three major iron oxide phases, i.e., α - and γ -Fe₂O₃ and Fe₃O₄, using the combustion approach and a combination of simple precursors such as iron nitrate and oxalate, as well as different fuels, is investigated. Based on the obtained fundamental knowledge, for the first time in the literature, the above powders with well-crystalline structures and surface areas in the range 50–175 m²/g are produced using a *single* approach while simultaneously avoiding additional calcination procedures. It is also shown that utilizing *complex* fuels and *complex* oxidizers is an attractive methodology to control the product composition and properties.

Introduction

Iron oxide is one of the most used metal oxides in many scientific and industrial applications.^{1–3} For example, α -Fe₂O₃ (hematite) is widely utilized as a pigment, as well as a catalyst for oxidation of alcohols to aldehydes and ketones, while magnetite (Fe₃O₄) is a catalyst for various reactions such as ammonia synthesis. Also, γ -Fe₂O₃ (maghemite) has attracted much attention for numerous uses, including as magnetic material for recording and in biomedical applications.

For all the above needs, powders of desired phase compositions and high specific surface areas are required. Currently, there are several methods for synthesis of iron oxide nanoparticles, including pyrolysis, glycothermal, thermolysis, sol–gel, and hydrothermal processes (cf. refs 4–10). However, no prior work has been reported for the *direct* synthesis of these oxides, in a pure, crystalline state by a *single route*.

Aqueous (solution) combustion synthesis (CS) is an attractive technique for the production of different

oxides, including ferrites, perovskites, and zirconia (cf. refs 11–15). It involves a self-sustained reaction between an oxidizer (e.g., metal nitrate) and a fuel (e.g., glycine, hydrazine). First, reactants are dissolved in water and the obtained solution thoroughly mixed, to reach essentially molecular level homogenization of the reaction medium. After being preheated to the boiling point of water and its evaporation, the solution can be ignited or it self-ignites and the temperature rises rapidly (up to 10⁴ °C/s) to values as high as 1500 °C. Simultaneously, this self-sustained reaction converts the initial mixture typically to fine well-crystalline powders of desired compositions. Iron oxides have been previously synthesized by the combustion method using relatively rare and sophisticated iron-containing precursors such as Fe(N₂H₃COO)₂(N₂H₄)₂ and N₂H₅Fe(N₂H₃COO)₃·H₂O.^{16,17} Thermal decomposition of the above metal hydrazine carboxylates yielded primarily γ -Fe₂O₃ with an average particle size of ~25 nm and specific surface areas in the range 40–75 m²/g.

In the present work, the *mechanism* of synthesis for three major iron oxide phases, i.e., α - and γ -Fe₂O₃ and Fe₃O₄, by the combustion approach is investigated using a combination of simple precursors such as iron nitrate and oxalate as well as different fuels. Based on the obtained knowledge and optimizing synthesis param-

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Table 1. Some Characteristics of Precursor Chemicals

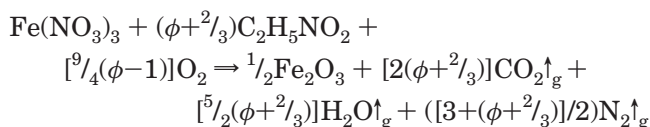
chemical	formula	purity and state	melting point (°C)	boiling point (°C)
hydrazine	H ₂ N-NH ₂	35% solution (aq)	1.4	113.55
glycine	CH ₂ NH ₂ COOH	98% (s)	262d	
citric acid	C ₆ H ₈ O ₇ ·H ₂ O	100% (s)	153d	
ferric nitrate	Fe(NO ₃) ₃ ·9H ₂ O	98% (s)	47.2	125d
ferrous oxalate	FeC ₂ O ₄ ·2H ₂ O	99% (s)	150d	
ammonium nitrate	NH ₄ (NO ₃)	98% (s)	210d	

eters (ambient atmosphere, fuel-to-oxidizer ratio, ϕ , system dilution, etc.), a novel one-step synthesis of the above monophasic oxide powders, with well-crystalline structure and surface area in the range 50–175 m²/g, is developed.

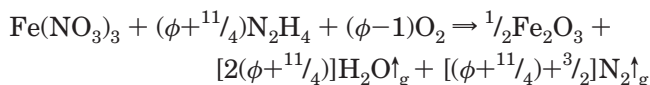
Systems under Investigation

Three basic systems were investigated where, under equilibrium conditions, the reactions can be represented as follows:

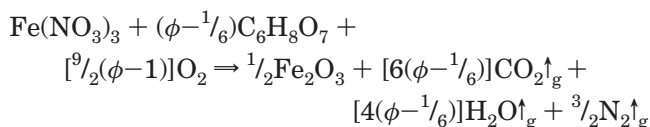
(i) Glycine (C₂H₅NO₂)–Ferric Nitrate [Fe(NO₃)₃]:



(ii) Hydrazine (N₂H₄)–Ferric Nitrate:



(iii) Citric Acid (C₆H₈O₇)–Ferric Nitrate:



In the above equations, $\phi = 1$ means that the initial mixture does not require atmospheric oxygen for complete oxidation of fuel, while $\phi > 1$ (< 1) implies fuel-rich (lean) conditions. In the present study, primarily compositions with $\phi \geq 1$ (i.e., stoichiometric and fuel-rich) were investigated because, as shown in our previous works,^{13,18} these fuel/oxidizer ratios lead to the synthesis of powders with high specific surface area.

In addition, *complex fuels*, i.e., mixtures of glycine and hydrazine, were also used to reach desired product composition and properties. In some cases, ferrous oxalate (C₂H₂O₄·Fe) was utilized as the iron-containing agent. Further, in some experiments, *complex oxidizers*, such as mixtures of iron nitrate and oxalate, as well as ammonium nitrate [NH₄(NO₃)] and oxalate, were examined. Finally, to establish interaction mechanisms in the above systems, additional experiments were conducted in an inert (argon) atmosphere. Some characteristics of all used precursor chemicals are presented in Table 1.

Experimental Procedure

A chemical reactor made of quartz was used (see Figure 1), which allows one to conduct experiments in different ambient

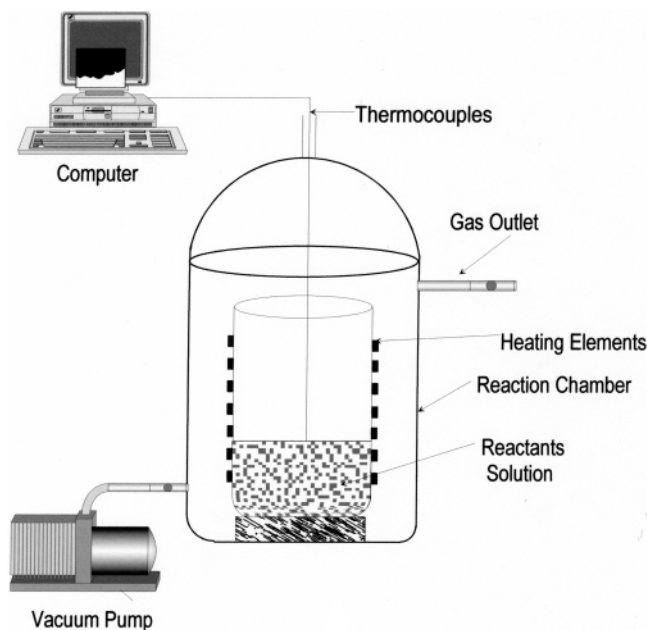


Figure 1. Schematic diagram of the experimental setup.

atmospheres (i.e., air, oxygen, argon), measurements of temperature–time history of the reaction, and process monitoring by using a digital camera (Panasonic Digital Camcorder, Model PV-DV103). Note that the temperature was measured by type K thermocouples (127 μm ; Omega Engineering Inc.) attached to a multichannel acquisition system (INET-200 controller card, Omega Engineering Inc.) with rates from 5 to 60 samplings per second.

After reactants dissolution in a sufficient amount of water and thorough mixing of the obtained solution, the reactor was placed on a hot plate (Cole Parmer model 4803-00) and the mixture was preheated uniformly up to the water boiling point at a rate of ~ 5 °C/min (see Stage I, Figure 2a). This was followed by a relatively long (~ 5 min) constant temperature Stage II during which all free and partially bound water evaporated. The next preheating stage (Stage III) was characterized by a higher rate (~ 12 °C/min) than that for Stage I and ended with either sudden (at some ignition temperature, T_{ig}) uniform temperature rise to a maximum value, T_{m} , or reaction initiated in a specific hot spot followed by steady wave propagation along the mixture (see Figure 3). In both cases, i.e., in the so-called volume combustion synthesis (VCS) and self-propagating high-temperature synthesis (SHS) modes, the rate of medium temperature change, dT/dt is high and in the range $10\text{--}10^4$ °C/s (Stage IV, Figure 2a). The duration of this high-temperature region varies from ~ 10 s (for SHS mode) to 100 s (VCS mode), and after cooling (Stage V), the synthesized products are typically fine solid powders.

The obtained products were analyzed for phase composition and crystallinity using an X₁ Advanced diffraction system (Scintag Inc., USA) and FTIR spectroscopy (Thermo Mattson, Satellite series, model 960M0027). The powder microstructure was studied by field emission scanning electron microscopy (Hitachi, model S-4500) and the specific surface area was measured using BET analysis (Autosorb1C, Quantachrome Instruments). Finally, differential thermal/thermogravimetric data on precursors decomposition were obtained using a DTA/TGA analyzer (model SDT 2960, TA Instruments).

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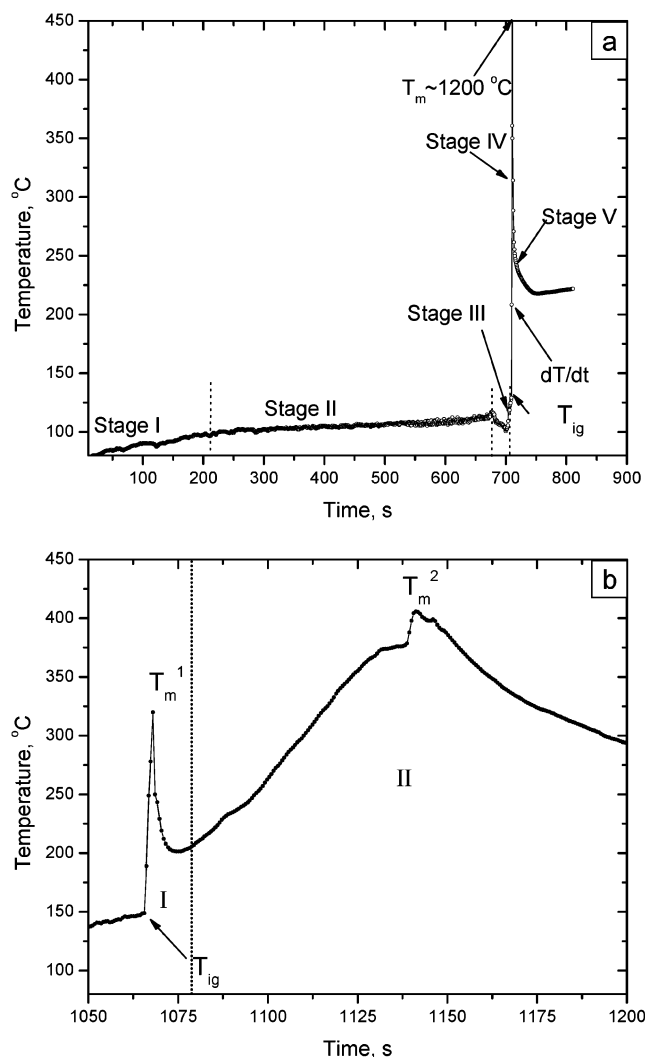


Figure 2. Temperature–time profile for the glycine–iron nitrate system in air for different ϕ : (a) $\phi = 1$; (b) $\phi = 3$.

Results

As noted above, a variety of oxidizer–fuel systems were investigated to determine the conditions for *one-step* synthesis of well-crystalline, nanoscale iron oxide powders of different phase compositions (α - Fe_2O_3 , γ - Fe_2O_3 , and Fe_3O_4) and high (50–175 m^2/g) specific surface areas. All experiments discussed below were conducted in air, unless noted otherwise.

Glycine–Iron Nitrate System. Glycine is the simplest amino acid, which is widely used for solution combustion reactions.^{19–21} The main parameter varied during the experiments was the ratio between fuel and oxidizer (i.e., glycine and iron nitrate), ϕ , in the range from 1 to 3. As shown in our previous work, properties (e.g., phase composition, purity, and specific surface area) of the synthesized powder are sensitive to changes of this parameter.¹⁸ The typical temperature–time profiles for the reactions in air at $\phi = 1$ (stoichiometric) and $\phi = 3$ (fuel-rich) are shown in Figure 2. The first

represents the case of SHS ($\phi = 1$; Figure 2a), while the second that of VCS ($\phi = 3$; Figure 2b) mode, which were described qualitatively above. At $\phi = 1$, interaction occurs in the form of a narrow (Figure 3) high-temperature (> 1000 °C) reaction front propagating with velocity ~ 1 cm/s, with rapid temperature change ($dT/dt > 10^3$ °C/s) in the front, while total reaction time is relatively short (~ 1 – 10 s). For $\phi = 3$, while reaction initiates at approximately the same temperature (~ 125 – 150 °C) as for $\phi = 1$ (see Figure 4), it proceeds slower ($dT/dt < 10^2$ °C/s) with longer duration (~ 100 s).

It is worth noting that while at $\phi = 1$ the temperature profile has only one sharp maximum, the reaction at $\phi = 3$ is characterized by two maxima, i.e., a relatively rapid temperature increase at the beginning of the reaction, followed by a decrease and a slower temperature rise to even higher values (Figure 2b). For this system, the transition from the SHS to VCS mode occurs at $\phi \sim 1.6$. It was observed that the maximum temperature, T_m decreases from ~ 1000 °C for $\phi = 1$ to ~ 450 °C for $\phi = 3$. Simultaneously, the amount of gas-phase products released during interaction increases significantly for mixtures with $\phi > 1.6$.

XRD and further confirmation by FTIR analysis indicated that all powders synthesized from mixtures with $\phi > 1$ had a well-crystalline structure of α - Fe_2O_3 phase, while product obtained with $\phi = 1$ was a mixture of α - and γ - Fe_2O_3 . A significant change in the specific surface area, S , of the oxide powder occurred at the transition between SHS and VCS reaction modes ($\phi = 1.6$; see Figure 5, hatched region), with a maximum achieved value for monophase α - Fe_2O_3 powder ~ 32 m^2/g ($\phi = 2.5$). Typical microstructures of pure hematite phases are shown in Figure 6. It may be seen that, on the micro level (Figure 6a), as-synthesized powder has a morphology of thin flakes, with width ~ 0.5 μm diameter and only several nanometers thickness. A closer examination of the product indicates that a flake surface (Figure 6b) has a well-developed nanostructure with characteristic scale ~ 5 – 10 nm (Figure 6c). The small flake thickness, as well as its nanoscale surface structure, explains the observed high specific surface area for the as-synthesized α - Fe_2O_3 powder.

Hydrazine–Iron Nitrate System. Hydrazine is among a series of compounds called hydronitrogens and is a powerful reducing agent. As compared to other fuels (see Table 1), it has relatively low melting and boiling points. These properties define the specifics of interaction in the N_2H_4 –iron nitrate system. Typical temperature–time profiles for synthesis of iron oxides using hydrazine as a fuel are shown in Figure 7. Following the first two preheating stages (see Figure 1) similar to those for the glycine-based system, one can observe a slight temperature decrease (down to 105–120 °C) with immediate rapid reaction. If the measured range of T_{ig} (130–150 °C) for the glycine–nitrate case (see Figure 4) may be explained by decomposition of nitrate, ignition in the N_2H_4 -based system is undoubtedly related to boiling of the fuel itself and its subsequent reaction with ambient oxygen (see Discussion for details). This conclusion is supported by another feature which makes combustion different in these two cases: for glycine–iron nitrate mixtures, as noted above, reaction rate decreases with increasing ϕ , while with hydrazine, the

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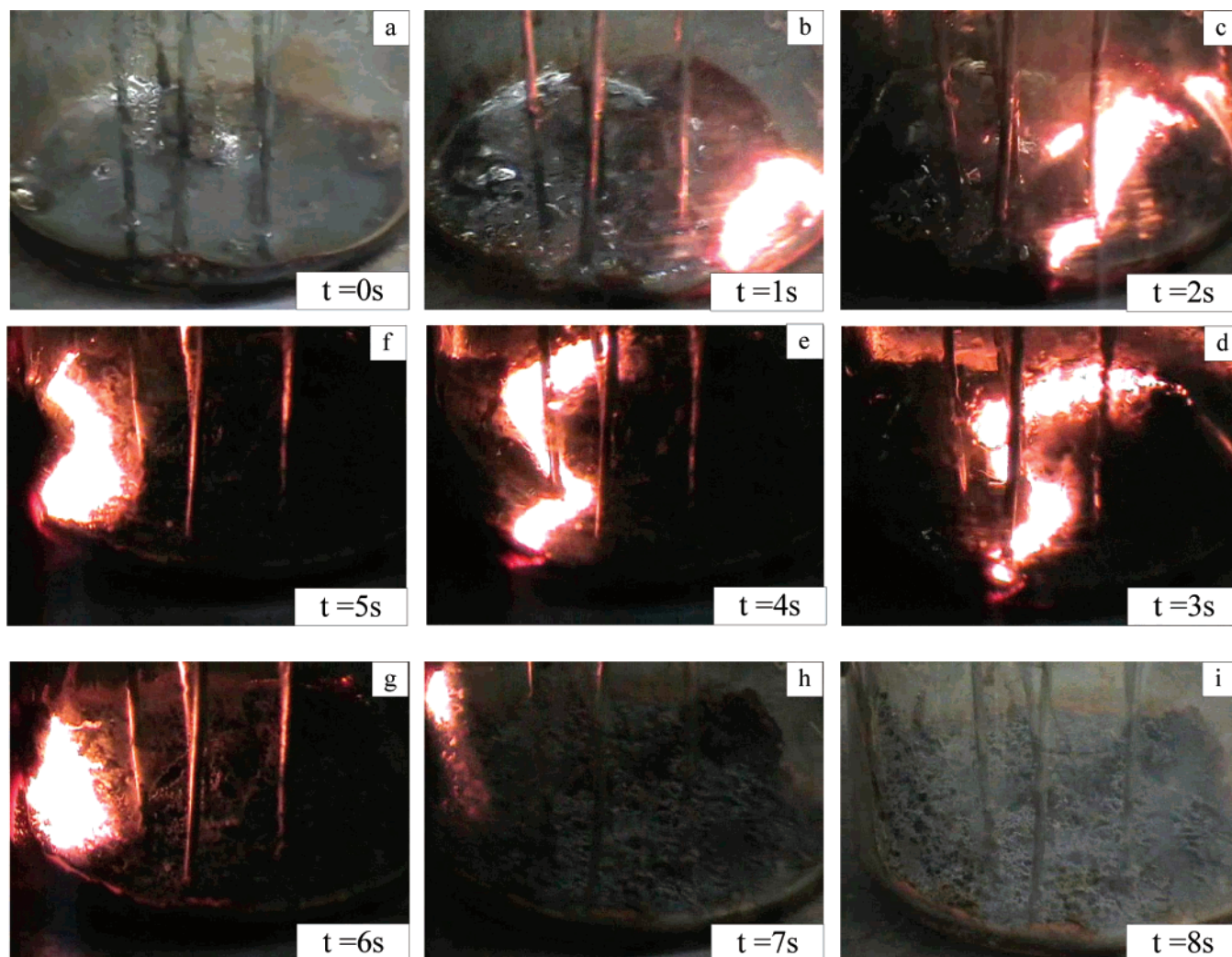


Figure 3. Reaction front propagation during solution combustion synthesis; glycine–iron nitrate system.

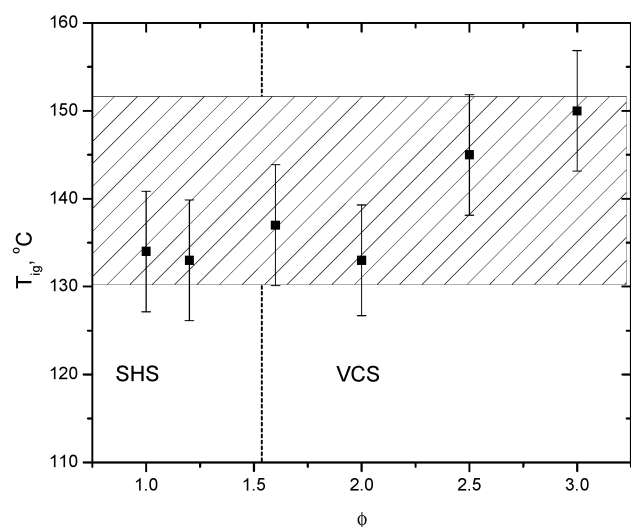


Figure 4. Reaction ignition temperatures for the glycine–iron nitrate system as a function of ϕ .

reaction is more vigorous for $\phi = 3$ than for the stoichiometric ($\phi = 1$) composition (see Figure 7).

In this system, the product phase composition and surface area also depend on parameter ϕ (Table 2). It may be seen that while for $\phi < 2.5$ the product consists of two iron oxide phases, i.e., α - and γ - Fe_2O_3 , for more fuel-rich initial mixtures well-crystalline monophase

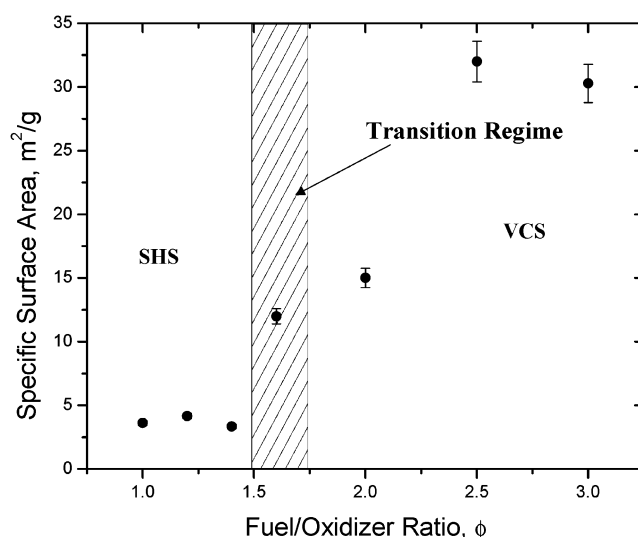


Figure 5. Surface area dependence for the glycine–iron nitrate system as a function of ϕ .

γ - Fe_2O_3 powder formed. For the ($\alpha + \gamma$) phases, powder specific surface area was high (up to $125 \text{ m}^2/\text{g}$), while pure γ - Fe_2O_3 product had $S \sim 30 \text{ m}^2/\text{g}$. The typical maghemite microstructure is shown in Figure 8. It may be seen that micro agglomerates of this powder are more uniform in shape and smaller (~ 25 – 50 nm) than those

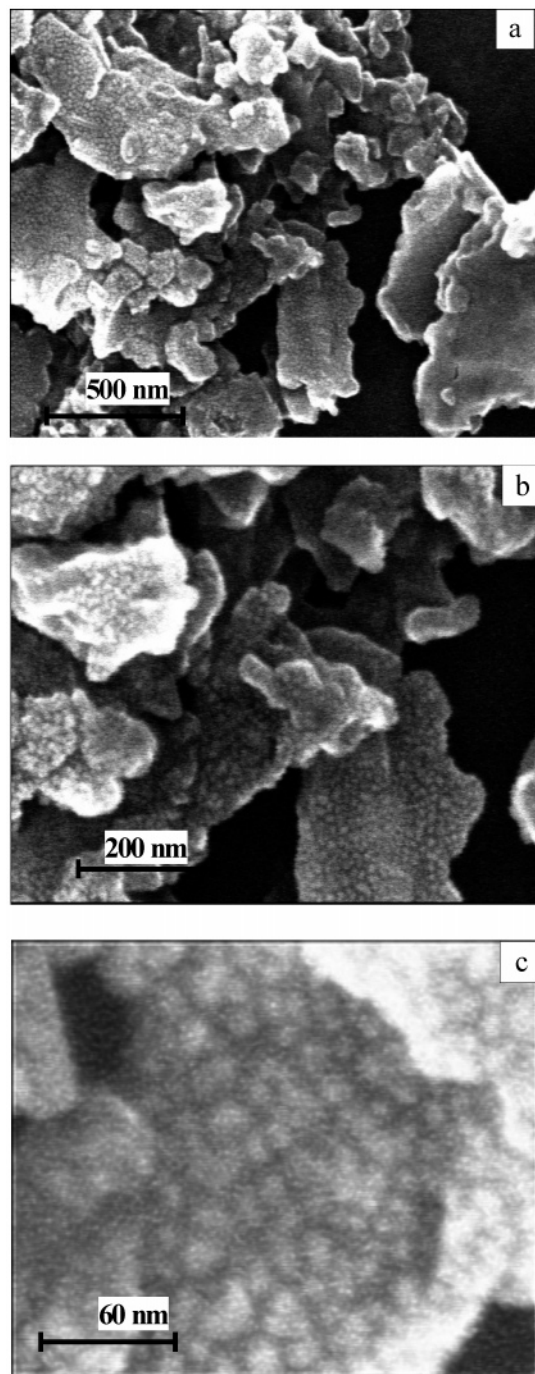


Figure 6. Characteristic microstructures (SEI) of synthesized α - Fe_2O_3 : (a) $\times 60\text{K}$; (b) $\times 130\text{K}$; (c) $\times 500\text{K}$.

for α - Fe_2O_3 powder (compare Figures 6a and 8a). Further, while nanostructures of particle surfaces are on the same scale ($\sim 10\text{ nm}$; see Figures 6c and 8c), their morphologies are different: compare separate islands for hematite (Figure 6b) and continuous skeleton for maghemite (Figure 8b).

Hydrazine/Glycine–Iron Nitrate System. In an attempt to use the advantages of hydrazine fuel to synthesize oxides with high surface area and of glycine forming pure hematite, we utilized a *mixture* of these fuels to produce α - Fe_2O_3 with high surface area. Table 3 presents data for product phase composition and specific surface area as a function of fuel composition. It can be seen that using pure N_2H_4 leads to the formation of amorphous product with surface area up to 85

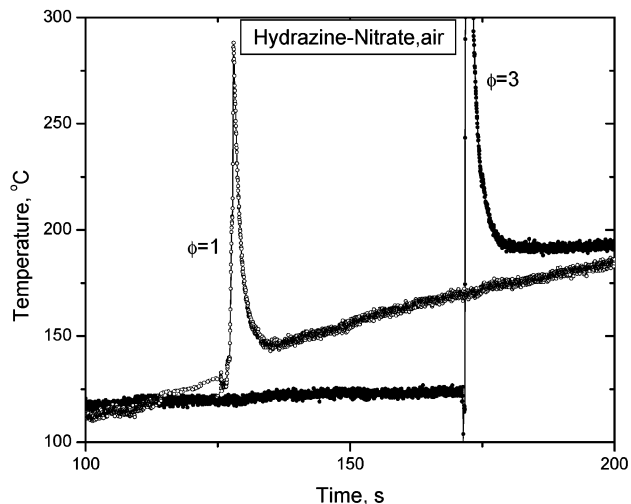


Figure 7. Temperature–time profile for the hydrazine–iron nitrate system in air for different ϕ : (a) $\phi = 1$; (b) $\phi = 3$.

Table 2. Phase Composition and Surface Area for the Hydrazine–Iron Nitrate System

ϕ	phase composition	surface area, m^2/g
0.34	amorphous	125
1	$(\gamma+\alpha)\text{-Fe}_2\text{O}_3$	52
2.0	$(\gamma+\alpha)\text{-Fe}_2\text{O}_3$	65
2.2	$(\gamma+\alpha)\text{-Fe}_2\text{O}_3$	50
3	$\gamma\text{-Fe}_2\text{O}_3$	28

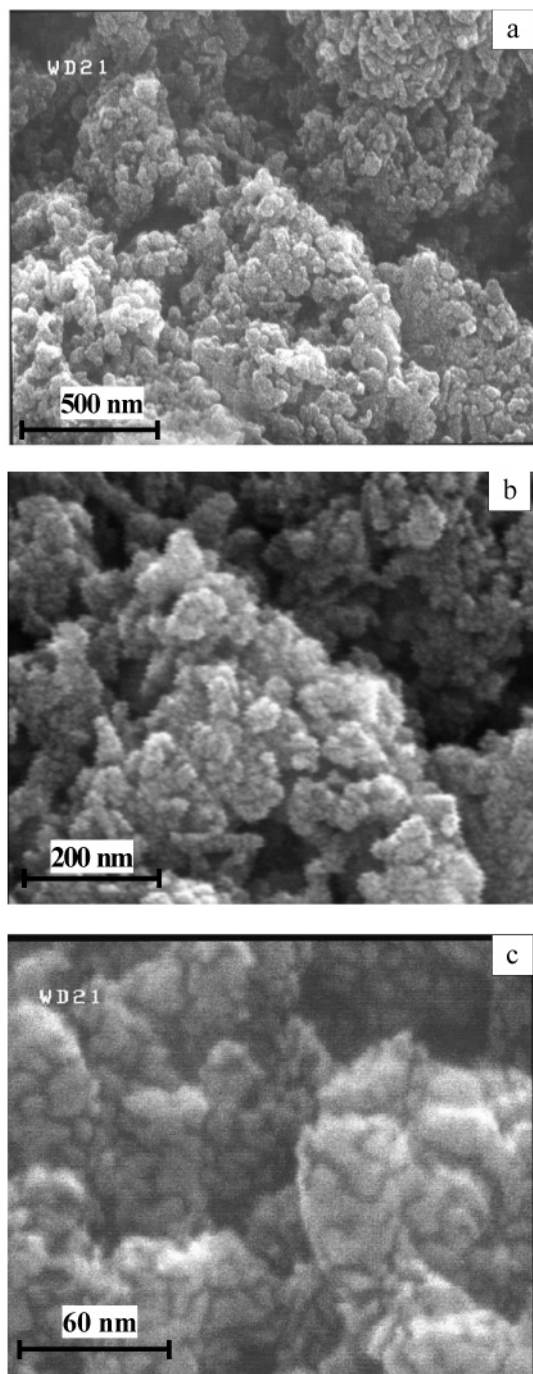
m^2/g , while pure glycine gives Fe_3O_4 powder with relatively low $S \sim 5\text{ m}^2/\text{g}$. However, adding a small amount of glycine to hydrazine immediately results in the formation of well-crystalline pure α - Fe_2O_3 with a surface area twice as large ($\sim 65\text{ m}^2/\text{g}$) as that obtained for the mono fuel (glycine, see Figure 5) system. Thus, by adjusting the fuel composition, one may synthesize monophase α - and γ - Fe_2O_3 powders with high surface area.

Citric Acid–Nitrate System. Citric acid is a colorless, crystalline organic compound with melting point $\sim 153\text{ }^\circ\text{C}$ and belongs to the family of carboxylic acids. This fuel gives a well-crystalline α - Fe_2O_3 product with high surface area for $\phi < 1.5$ compositions in air (see Table 4). This effect can be explained by the fact that relatively low temperatures (up to $450\text{ }^\circ\text{C}$) were observed during combustion in this system (see Figure 9), and simultaneously, the amount of gas formation is higher than that with glycine fuel (see Discussion for details). For these reasons, as shown below, citric acid appears to be the best fuel for synthesis of pure Fe_3O_4 phase powder with high surface area.

Different Fuels–Iron Nitrate in Argon. As discussed above, by adjusting the fuel/oxidizer composition, one may synthesize monophase α - and γ - Fe_2O_3 with high surface area. Experiments with the same fuels but in an *inert* atmosphere allowed us to synthesize a *magnetite* (Fe_3O_4) phase of iron oxide. This result suggests that the fuel–oxidizer interactions in the solution first lead to the formation of Fe_3O_4 that reacts further with the atmospheric O_2 to yield Fe_2O_3 phases. As seen from Table 5, the highest surface areas up to $50\text{ m}^2/\text{g}$ were obtained using citric acid. The typical microstructure of synthesized magnetite is shown in Figure 10. While flakelike morphology powder (Figure 10a) is similar to that of α - Fe_2O_3 (compare with Figure

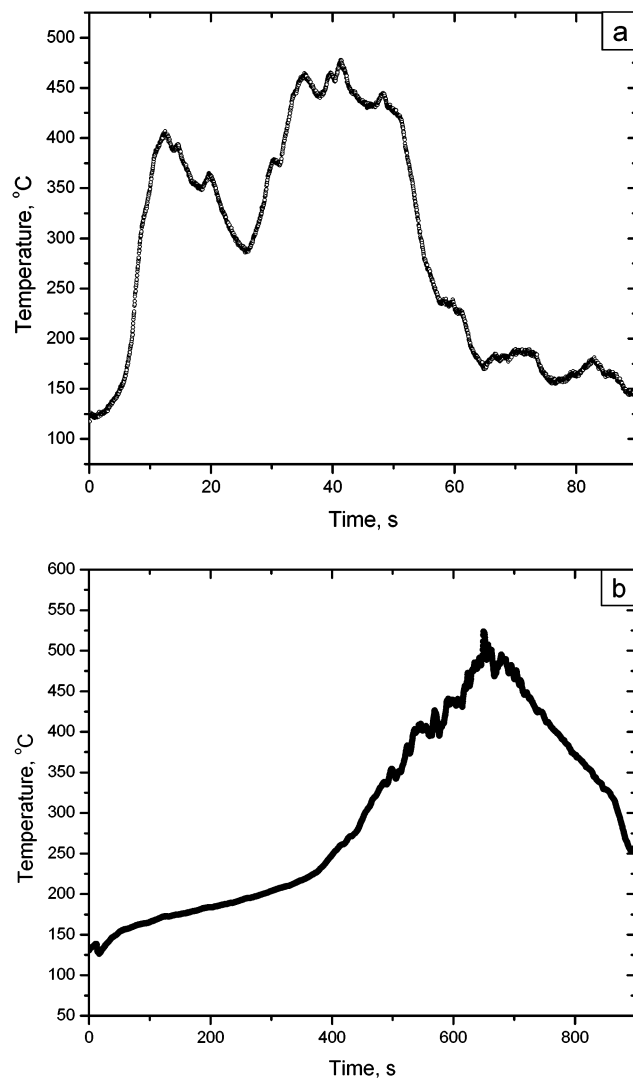
Table 3. Phase Composition and Surface Area for the Hydrazine/Glycine–Iron Nitrate System

glycine ϕ_1	hydrazine ϕ_2	mol of O ₂ required		total ϕ	phase composition	surface area, m ² /g
		glycine	hydrazine			
0	0.4	0	0.025	0.4	amorphous	85
0.3	0.7	0.01386	0.011	0.55	α -Fe ₂ O ₃	65
0	1	0	0.0164	1	(α + γ)-Fe ₂ O ₃	52
0.5	0.5	0.0231	0.008	1	(α + γ)-Fe ₂ O ₃	50
0.6	0.4	0.0277	0.0065	0.74	(α + γ)-Fe ₂ O ₃	23
0.8	0.2	0.0369	0.003	0.86	(α + γ)-Fe ₂ O ₃	10
1	0	0.0462	0	1	(α + γ)-Fe ₂ O ₃	4

**Figure 8.** Characteristic microstructures (SEI) of synthesized γ -Fe₂O₃: (a) $\times 60K$; (b) $\times 130K$; (c) $\times 500K$.

6a), the surface nanostructure (Figure 10c) is closer to that of γ -Fe₂O₃ (compare with Figure 8c).

All the above results were obtained using the same oxidizer (i.e., iron nitrate) but different fuels, including

**Figure 9.** Temperature–time profile for the citric acid–iron nitrate system in air for different ϕ : (a) $\phi = 1$; (b) $\phi = 3$.**Table 4. Phase Composition and Surface Area for the Citric Acid–Iron Nitrate System**

ϕ	phase composition	surface area, m ² /g
1	α -Fe ₂ O ₃	35
1.2	α -Fe ₂ O ₃	45
1.4	α -Fe ₂ O ₃	42
3	α -Fe ₂ O ₃	30

mixtures. In addition, we investigated the idea of utilizing *both* complex iron content precursors and fuel, as discussed next.

Glycine/Hydrazine–Iron Oxalate/Iron Nitrate System. Iron oxalate (FeC₂O₄) is not an oxidizer because it decomposes to pure FeO and CO₂.²² Since a

Table 5. Phase Composition and Surface Area for Different Fuels and Iron Nitrate in Argon

fuel	surface area, m ² /g	composition
glycine	4	Fe ₃ O ₄
hydrazine	42	(α + γ)-Fe ₂ O ₃
citric acid	45	Fe ₃ O ₄

Table 6. Phase Composition and Surface Area for the Glycine/Hydrazine–Iron Nitrate/Oxalate System

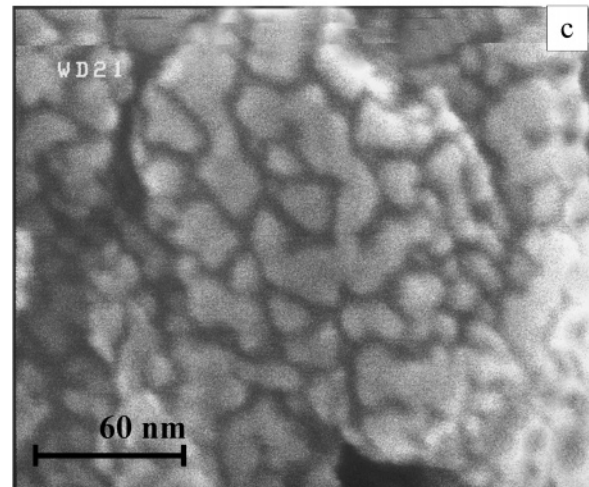
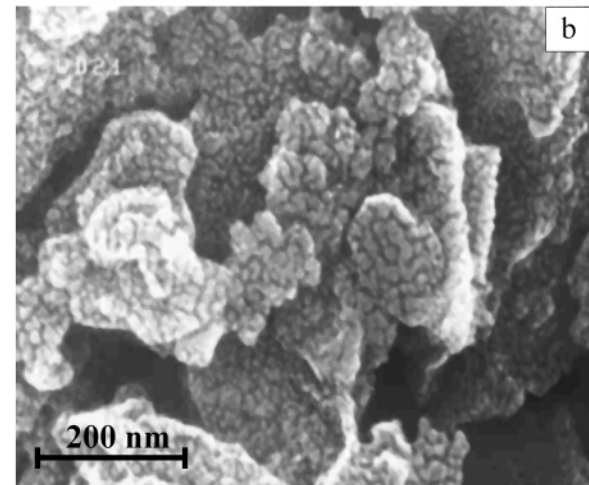
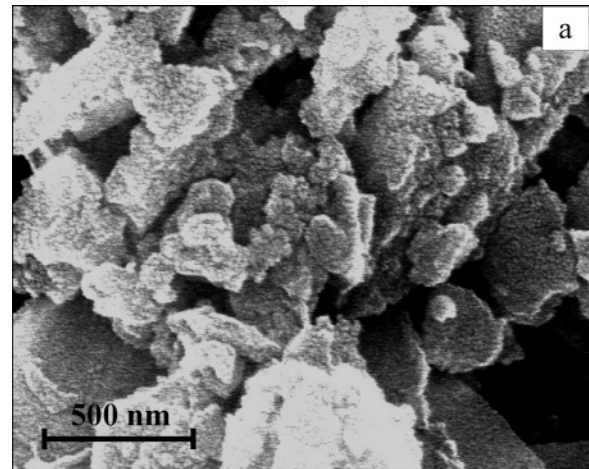
iron nitrate	iron oxalate	phase composition	surface area, m ² /g
1	0	α -Fe ₂ O ₃	60
0.7	0.3	(α + γ)-Fe ₂ O ₃	75
0.5	0.5	(γ + α)-Fe ₂ O ₃	175
0.3	0.7	γ -Fe ₂ O ₃	120
0	1	amorphous	168

significant amount of gas phase is formed, a mixture of iron nitrate (as oxidizer) and oxalate was used in an attempt to produce high surface area γ -Fe₂O₃. Experiments were conducted in air with complex glycine/hydrazine fuel of constant composition (1/9 by weight ratio). Table 6 presents data on obtained product phase composition and specific surface area. It may be seen that use of oxalate, in general, leads to the formation of powders with higher surface area and larger γ -phase fraction than with nitrate alone. At an optimum composition, the pure maghemite was synthesized with surface area \sim 120 m²/g. Also, this complex iron-containing precursor allowed the synthesis of $\gamma + \alpha$ product with surface area up to 175 m²/g, which appears to be the highest reported value for powders produced by using the combustion approach.

Hydrazine–Iron Oxalate/Ammonium Nitrate System. Finally, to further investigate the idea of gas evolution influence on the process of microstructure formation, we used an inert iron-containing precursor (i.e., oxalate) and non-iron-containing ammonium nitrate oxidizer along with hydrazine as a fuel. As expected, an increasing amount of NH₄(NO₃) increases reaction temperature as well as gas evolution. The former favors a decrease of product surface area, while the latter promotes its increase. It is clear from the results presented in Table 7 that, for this system, the latter effect predominates.

Discussion

Glycine–Iron Nitrate System. To clarify the mechanism of interaction, some additional experiments were conducted in an inert (argon) ambient atmosphere. Figure 11 represents typical temperature profiles for combustion of mixtures at $\phi = 1$ and 3. In a comparison of Figures 2 and 11, three important observations may be outlined: (i) T_{ig} does not depend on composition of ambient gas; (ii) for both cases, detected maximum temperatures were lower in argon than in air; (iii) there is an essential absence of the second stage of interaction for the fuel-rich compositions in argon. These results clearly indicate that a two-step reaction mechanism is

**Figure 10.** Characteristic microstructures (SEI) of synthesized Fe₃O₄: (a) \times 60K; (b) \times 130K; (c) \times 500 K.

in general responsible for the final product formation. First, relatively rapid reaction initiates in the temperature range 125–150 °C and proceeds primarily due to glycine oxidation by oxygen-containing species formed

Table 7. Phase Composition and Surface Area for the Hydrazine–Iron Oxalate/Ammonium Nitrate System

iron oxalate	ammonium nitrate	surface area, m ² /g	phase composition
0.6	0.4	53	γ -Fe ₂ O ₃
0.4	0.6	100	γ -Fe ₂ O ₃
0.3	0.7	124	(α + γ)-Fe ₂ O ₃

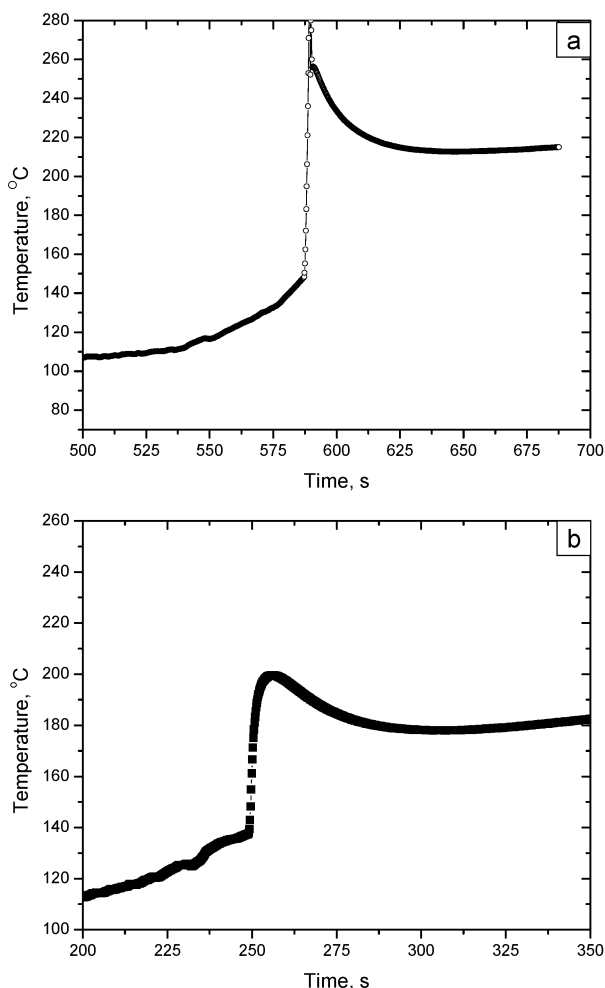


Figure 11. Temperature–time profile for the glycine–iron nitrate system in argon for different ϕ : (a) $\phi = 1$; (b) $\phi = 3$.

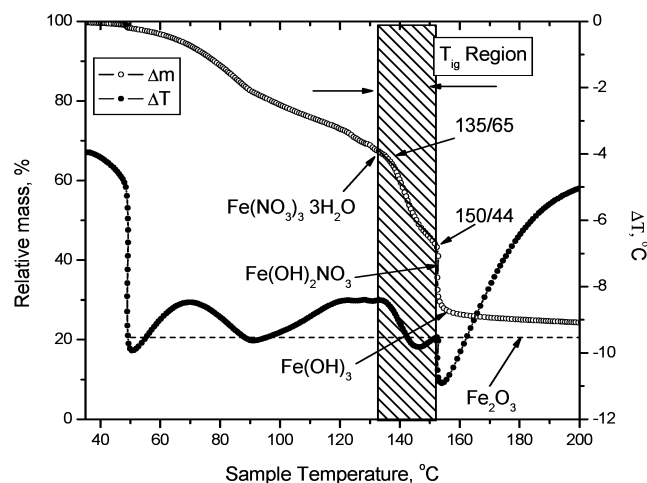


Figure 12. TGA/DTA data analysis for iron nitrate in air and its combustion characteristics with glycine.

in solution. Some ambient oxygen also participates during this stage, defining maximum temperature, T_m . For fuel-rich compositions, this rapid stage is followed by a slower burning process utilizing oxygen from air.

Let us consider the reaction during the first stage in more details. Figure 12 shows data for TGA/DTA analysis of iron nitrate in air. It can be seen that the measured temperature region for system ignition (125–150 °C; see Figure 4) fits well with the temperature

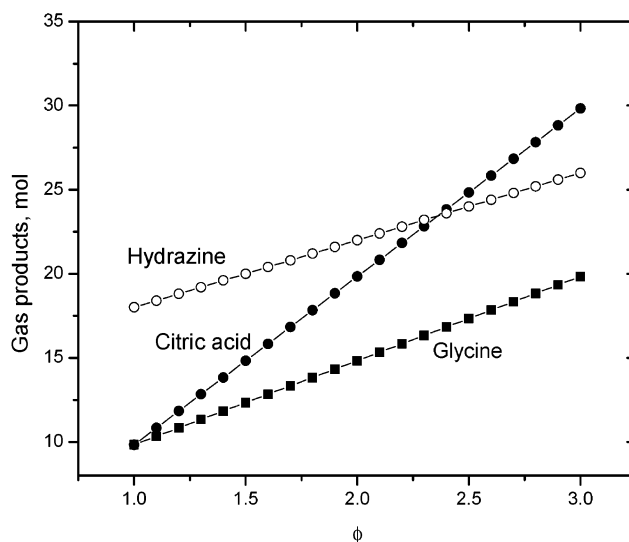


Figure 13. Stoichiometrically calculated gas evolution as a function of ϕ for different fuels.

interval for rapid nitrate decomposition. As shown recently,²³ this decomposition leads to the formation of HNO_3 species which, at this relatively high temperature, immediately (either directly or with preliminary oxygen formation) reacts with glycine. Thus, ignition in the glycine–nitrate system is related to a specific phase transformation (i.e., oxidizer decomposition) and not to the “classical” relation between rates of heat release and loss.²⁴ In this sense, the nature of the ignition process in the solution–type system is similar to that observed for the heterogeneous solid mixtures.²⁵

The second stage of oxidation is slower because oxygen derives not from ideally mixed (on the molecular level) solution, but from air. This gas–solid combustion is controlled by oxygen diffusion through the “inert” air component, i.e., nitrogen. Further, this combustion stage involves substantial gas evolution, which increases with increasing ϕ ratio following reaction stoichiometry (see Figure 13). Note that the latter effect was not measured quantitatively but was confirmed by visual observation.

It appears that the gases evolved play an important role in the formation of product microstructure. Indeed, while the maximum reached temperature remains relatively high (>500 °C), the surface area of synthesized oxides increases dramatically for $\phi > 1.6$ (see Figure 5). For this system, the change occurs at the transition from the rapid SHS to slower VCS combustion mode. In the latter case, the large amount of gas-phase product inhibits agglomeration (sintering) of formed oxide powder and together with lower temperature leads to increased product surface area.

Hydrazine–Iron Nitrate System. The reaction proceeds differently when using hydrazine as the fuel. As shown above, the ignition temperature for this system is lower and in the range 105–115 °C. This observation can be explained by super-positioning the

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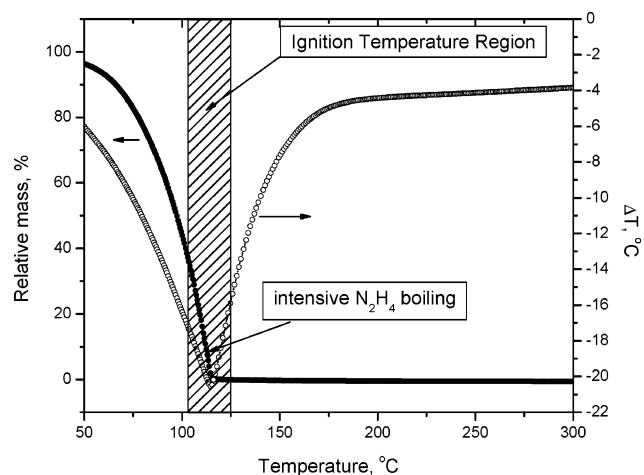


Figure 14. TGA/DTA data analysis for hydrazine in air and its combustion characteristics with iron nitrate.

experimental TGA/DTA data for hydrazine decomposition and the ignition temperature range (Figure 14). It is clear that rapid interaction in this system is related to the N_2H_4 boiling and not to iron nitrate decomposition, which occurs at higher temperature, as in the glycine-based case. Another evidence for this conclusion is the existence of temperature drop, owing to endothermic boiling, just prior to ignition (see Figure 7).

Additional experiments conducted in argon for a fuel-rich mixture ($\phi = 3$) showed that, instead of an “explosion” type reaction, a relatively slow oscillation type synthesis process occurs. In light of all the above observations, the mechanism of interaction in this system can be suggested as follows. Again, two oxygen-containing species, one in solution and the other in air, should be considered. In this system, owing to the relatively low temperature of hydrazine evaporation, its interaction with oxygen in air becomes significant. Increasing ϕ increases the availability of fuel in the gas phase, which explains why reaction is more vigorous for larger ϕ (see Figure 7) and also why interaction in an inert atmosphere is significantly slower than that in oxidizing environments. These gas-phase contributions also explain higher product surface area than with glycine (see Table 2 and Figure 5), although synthesized under similar temperature conditions.

Further, as shown experimentally, while the solution is boiling in air, ignition of pure hydrazine does not occur. Thus, initiation of the reaction in solution at lower (than for the glycine case) temperature means that gas-phase molecules of hydrazine are sufficiently active to reduce iron nitrate before its decomposition. Following this trigger, fuel evaporation intensifies and its gas-phase reaction with oxygen in air becomes predominant. Note that, again in this case, rapid reaction initiation is related to a characteristic temperature, viz. boiling of fuel.

Citric Acid–Iron Nitrate System. Citric acid has a melting/decomposition temperature higher than the observed ignition temperature (Figure 15), which corresponds to nitrate decomposition. This may indicate that reactions in this case should proceed similar to the glycine-based system. However, the temperature–time profiles (see Figure 9) show that the interactions are slower and do not depend as strongly on ϕ as for glycine. While the two systems have comparable ΔH_{rxn} ,^{26,27}

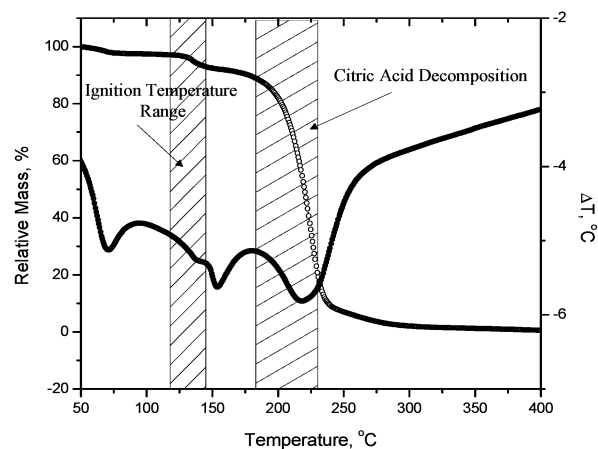


Figure 15. TGA/DTA data analysis for citric acid in air and its combustion characteristics with iron nitrate.

hence close adiabatic combustion temperatures, differences in their behavior can be explained by reactivities of the two precursors. Indeed, as shown elsewhere,²⁸ based on studies of iron nitrate with model fuels, the activity of a $-\text{NH}_2$ type ligand appears to be higher as compared to the $-\text{OH}$ group, which in turn is more active than $-\text{COOH}$. This explains why, containing a $-\text{NH}_2$ group, glycine is a more reactive fuel than citric acid, which involves only $-\text{OH}$ and $-\text{COOH}$.

Concluding Remarks

In the present work, three iron oxide powders, viz., $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, and Fe_3O_4 , that are important for different applications were synthesized by using the combustion synthesis (CS) method. The mechanisms of solution ignition and combustion were addressed in details never reported previously. It was shown that the characteristic *phase transformations* taking place in the investigated systems are responsible for the observed rapid chemical reactions.

Based on the obtained fundamental knowledge, for the first time in the literature, the above powders with well-crystalline structures and surface areas in the range 50–175 m^2/g were produced using a *single* approach while simultaneously avoiding additional calcination procedures. It was also shown that utilizing *complex* fuels and *complex* oxidizers is an attractive methodology to control product composition and properties.

Thus, it was illustrated that aqueous CS is a flexible technique where precursors are mixed on the molecular level and, under the unique conditions of rapid high-temperature reactions, nanoscale iron oxide powders of desired compositions can be synthesized in one step. These features suggest that the described combustion method is promising for the synthesis of a variety of nanopowders with desired phase compositions and properties.

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