Overcoming the Inhibition Effects of Citrate: Precipitation of Ferromagnetic Magnetite Nanoparticles with Tunable Morphology, Magnetic Properties, and Surface Charge via Ferrous Citrate Oxidation

Tim Granath, Karl Mandel,* and Peer Löbmann

This study demonstrates how the method of thermally assisted oxidative precipitation in water can be opened for—the so far neglected—metal organic iron(II) complexes (herein: citrate) in order to obtain, in one step, ferromagnetic magnetite nanoparticles, possessing essential ligand properties. Based on a dedicated analysis of the specific precursor in combination with the consideration of known properties of the ligand, it is possible to identify existing inhibition-attributes of the iron organyl such that these can be overcome. Moreover, they can be exploited in a targeted manner; thus, simply by changing concentrations, a variety of magnetite nanoparticle morphologies with distinct properties can be obtained. In the case of the herein investigated ferrous citrate, three major inhibition effects are identified. While two of them efficiently prevent the formation of magnetite and need to be addressed to be overcome, the third can be exploited to selectively synthesize, for example, relatively stable carboxyl group-bearing nuclei clusters, exhibiting the properties of magnetically responsive photonic crystals, or relatively large mesocrystals, whose intraparticular magnetic interactions are apparently disturbed.

1. Introduction

Abundance, low-cost, non-toxicity, and plethora of applications are the reasons why iron oxides have been and remain to be compounds of great relevance.[1,2] Probably most prominent among the family of iron oxides is magnetite (Fe₃O₄), owing its recognition to its magnetic properties.[1–4]

In the recent decades, a lot of effort was put into achieving nanoscale magnetite. The reason for this extraordinary interest in the nano form of magnetite is its applicability in, for example, ferrofluids,[5,6] as inductively heatable objects,[3,7] for magnetically supported identification and authentification,[8,9–11] for wastewater treatment and separation applications,[12–15] for catalysis,[12,14–17] as pigment,[1,18] for sensors,[12,19] as well as in theranostic and biomedical applications.[20–23]

Although recent research has focused on superparamagnetic nanoparticles,[21,24,25] the larger ferromagnetic variants are more relevant for most applications, as, due to the reduced ratio of chemically active surface area to volume of the relatively inert core, they are overall much more stable toward oxidation processes, thus retain their desired properties longer.[17,23,26]

Among the reported methods that yield ferromagnetic magnetite nanoparticles, solvothermal synthesis most likely offers the widest range of possible particle variations that can be achieved.[17,27,28] The price of this variety, however, is the relatively high technical and energetic effort that is needed to conduct the synthesis. In addition, the conditions often require the use of solvents or additives that are not entirely harmless, and, moreover, may not always be completely removed from the surfaces of the particles that are obtained.

An alternative synthesis method, which is significantly less demanding in terms of equipment and energy, is the thermally assisted oxidative precipitation, which is based on a two-step process: The first step involves the formation of a sparingly soluble hydroxide (Equation (1)), which, in the second step, (partially) oxidizes and finally yields the desired iron oxide Fe₃O₄ (Equation (2)).[29,30]
In a previous publication, we demonstrated that a simple variation of the concentration of the fundamental reagents, which are involved, can provide access to a variety of morphologically and magnetically distinct ferromagnetic nanoparticle.

Although the basic principle of the approach has been known for a long time and, due to a detailed systematic description by Sugimoto and Matijević, has experienced a revival since the 1980s, its potential hardly seems to have been exploited so far. Almost no literature exists, in which iron-containing species other than the simple iron(II) salts, such as ferrous sulfate or the ferrous halides, were reported to yield magnetite nanoparticles. Moreover, surprisingly, relatively little literature can be found, dealing with subsequent modification of particles prepared by the thermally assisted oxidative precipitation route. The reason for this could be that the subsequent modification is associated with the following difficulties, which result from the nature of those ferromagnetic particles:

- The nanoparticles are relatively large, entailing an increased sedimentation tendency, which makes homogenization nearly impossible—the system undergoes sedimentation and sedimented particles are poorly accessible for modifications and moreover inclined to form aggregates more easily.
- From our own findings, we can state that anions, which are present in the synthesis, not only significantly affect the magnetic and morphological particle-properties, but very likely also occupy the particle surface, thus making subsequent modification more challenging or perhaps even impossible.

While the anions might—on the one hand—hinder modification, it might be—on the other hand—exactly this anion-ligand-influence that could be the starting point for an in situ modification of ferromagnetic particles, using this method of thermally assisted oxidative precipitation, thus circumventing the difficulties. Previously described attempts of a respective in situ modification are largely limited to the admixture of relevant molecules, such as citrate. Associated discussions usually describe that, depending on the concentration, the desired particle formation was inhibited, completely prevented or, due to ligand competition, product mixtures emerged. This is probably also the reason why the direct use of ferrous organic complexes has hardly been reported to date. In fact, to best of our knowledge, we only found one experiment reported in literature in this regard by Sugimoto and Matijević who mention that they washed several times with water and ethanol, and finally dried.

To make progress in this regard and additionally open up the pathway for using metal organic iron(II) precursors for nanoparticle formation, we consider it as highly crucial to carefully take into account the very specific properties of the introduced organic ligands. Complexing properties of introduced organic ligands might inhibit particle formation significantly, as it is commonly accepted to date. For example, carboxylates are much stronger complexing agents than the anions of the simple ferrous salts, with the result that the latter readily dissociate and “expose” the iron(II) for hydroxide formation, whereas the former do not. Furthermore, it must be taken into account that, depending on the type of molecule used, side reactions have to be expected, possibly additionally catalyzed by the metal center.

In this work herein, we demonstrate, by using ferrous citrate as an example, a methodological approach to successfully obtain carboxyl-group-bearing ferromagnetic nanoparticles by oxidative precipitation in water from metal organic precursors in one step. This is achieved by taking the specific properties and behavior of the ligand(s) into account. In addition, we also highlight how the relationships that were found could be used to specifically influence the morphology, magnetic properties, and surface charges of the resulting nanoparticles.

The metal organic precursor ferrous citrate was chosen, as the ligand citrate represents a molecule that is relatively commonly used in the colloidal field. Probably the most important role of citrate, which adsorbs relatively easily to metal surfaces, is its function as an electrostatic stabilizer, useful for numerous nanoparticulate materials. Usually, the adsorption proceeds in such a way that not all carboxyl groups coordinate to the surface. On the one hand, this causes the stabilizing effect, but on the other hand, it also allows the free carboxyl groups to be used as basis for further modifications, which might otherwise not be possible on bare particle surfaces. Thus, citrate can be considered as a small but highly adhesive molecule that is capable to act as an anchor in order to modify different particles in the same way. Ideally, the use of ferrous citrate as an iron(II) source enables the synthesis of ferromagnetic particles directly modified in-situ upon their evolution, which would otherwise require a tedious, subsequent further citrate modification step.

2. Results and Discussion

As stated, in order to achieve any nanoparticles via precipitation in an aqueous environment, starting with metal organic precursors, it is crucial to understand the ligand of choice in detail before performing the synthesis. Therefore, Section 2.1 initially deals in some detail with the precursor ferrous citrate, in order to be able to make reliable predictions regarding the expectable behavior that may influence the nanoparticle formation.

Based on the findings, a systematic and stepwise approach is conducted in Section 2.2 to overcome any inhibiting attributes of the metal organic iron(II) source to achieve the targeted ferromagnetic magnetite nanoparticles.

2.1. Analysis of the Ferrous Citrate Precursor

The iron(II) precursor used herein was synthesized as described in patent number US 3091626. In brief, ferrous chloride and citric acid were dissolved in water in a 1:1 molar ratio and two molar equivalents of ammonia were added. The solution was then boiled under reflux for 2 h, yielding a white precipitate, which was filtered, washed several times with water and ethanol, and finally dried.

Although approved as a food additive and also used as a source of iron in the medical field, there is no definitive consensus on the complex structure of ferrous citrate(s). This may be as they oxidize easily and are therefore difficult to analyze, or as there may be variances due to the different preparation routes.
Since no further information was available for the as prepared precursor, an attempt, using rudimentary analyses, was made to derive the properties that were considered to be relevant for the objective to ultimately achieve the magnetite precipitation (see Section S1, Supporting Information).

The analyses revealed that the synthesized ferrous citrate is most likely identical to the iron (II) citrate coordination polymer \([\text{Fe(HCitH)(H}_2\text{O)}]_n\).\(^{[53]}\)

In order to emphasize that citric acid in principle has four acidic groups, we use the abbreviation HCitH\(_3\), where the leading H addresses the proton of the alcohol group and the subsequent H’s the protons of the carboxyl groups. Cit stands for the entirely deprotonated species citrate. Furthermore, for simplification and since it can in principle be transferred equivalently, only the monomeric form \([\text{Fe(HCitH)(H}_2\text{O)}]\) is referred to in the following.

It was also found that the iron citrate salt, which is basically a monoaacid, presumably due to an intramolecular proton transfer, behaves like a dicarboxylic acid, once dissolved in water (Equation (3)).

\[
\text{[Fe(HCitH)(H}_2\text{O)}] \rightarrow \text{[Fe(HCitH)(OH)]}
\] (3)

From the analytical data, and largely independent of the true structure, certain assumptions regarding expected inhibition effects can be derived and combined with the known properties of citric acid.

For instance, due to the remaining carboxylic acid groups, it must be expected that a higher amount of base is required to achieve the preliminary hydroxide stage of iron(II) and thus final precipitation of iron oxide in the first place. Ideally, this buffer effect can be addressed stoichiometrically.

From citric acid it is known that it can be oxidized. However, the oxidation path, the oxidation level and thus the final oxidation product depends on the oxidizing agent, the temperature and the presence of catalysts.\(^{[54–56]}\) Although there are no iron(II) specific studies on the oxidation behavior of citrate with nitrogen, it is assumed that a new molecule emerges, but also that both, electrostatic and steric repulsion effects are reduced. Transferred to the citrate ligand, it can then be expected that such a molecular change will primarily affect the particle-forming processes. Beyond that, surface groups, other than those predicted for citrate, occur.

The above discussion shows that one needs to be aware of all potential transformations of the organic part of the metal organic precursor when employing it in the aqueous thermally assisted oxidative precipitation of magnetite.

2.2. Achieving Precipitation of Ferromagnetic Magnetite from Ferrous Citrate

For a typical attempt to precipitate ferromagnetic magnetite, the ferrous citrate precursor \([\text{Fe(HCitH)(H}_2\text{O)}]\) is mixed with deionized water and allowed to boil under reflux, while constantly bubbling in nitrogen. The concentration of iron(II) for the entire mixture was set to 20 mm. After complete dissolution and reaching boiling temperature, an already mixed alkaline oxidation solution, consisting of varying amounts of KOH as base and KNO\(_3\) as oxidant, is added all at once. Under precipitation conditions, the previously clear, slightly greenish ferrous citrate solution immediately turns dark green. Within the subsequent 4 h reaction period, throughout which nitrogen is still continuously introduced, complete oxidation takes place, giving rise to a black, magnetic product.

To understand the mutually interlinked dependencies of the obtained precipitation result from the ferrous citrate precursor on concentration variations of the base KOH and the oxidant KNO\(_3\), it is helpful to express the latter two as iron-based ratios \(R_{\text{OII}}\) (Equation (4)) and \(R_{\text{OX}}\) (Equation (5)), respectively.

\[
R_{\text{OII}} = \frac{[\text{OH}^-]}{[\text{H}^+] - 2 \cdot [\text{Fe}^{3+}]} \quad (4)
\]

\[
R_{\text{OX}} = \frac{[\text{NO}_3^-]}{[\text{Fe}^{3+}]} \quad (5)
\]

Although no extra acid is added, Equation (3) suggested that a value according to Equation (6) should be considered for the proton concentration used in Equation (4).

\[
[\text{H}^+] = -[\text{COOH}] = 2 \cdot [\text{Fe}^{3+}] \quad (6)
\]

In order to specifically resolve the presumed effects of the citrate ligand on the product formation, a methodological approach was followed, which is reflected in the subsequent chapters. Initially, Section 2.2.1 addresses the expected buffer
effect. Section 2.2.2 deals with the oxidation behavior. Finally, Section 2.2.3 provides an analysis of the $R_{OH}$-dependent ligand influences with respect to the resulting product properties.

2.2.1. Citrate Ligand Buffering Effect

Figure 1a summarizes the measured pH values (from Figure 1g), according to a stepwise addition of an equivalent amount of base to a 20 mM ferrous citrate solution. These pH values are compared with the pH-dependent forms of citric acid and Fe$^{2+}$ in Figure 1b–d. Based on this comparison, by combining the dominant forms at the points, assumptions are made for plausible states of the precursor, allowing to relate the chemical conversion according to Figure 1f and, consequently, the precipitation behavior.

Assuming that even when ferrous citrate is used, the general process proceeds via two steps and the formation of the iron hydroxide Fe(OH)$_2$ is considered a necessary step, the base titration was first carried out under non-oxidative conditions.

For the pristine solution, that is, with zero equivalent portions of base, a pH of 3.9 was measured. Following the path, this corresponds rather exact to the points at which citric acid is predominantly singly deprotonated and iron(II) remains completely dissociated. Combined, this results in the already proposed precursor state [Fe(HCitH$_2$)$_2$(OH)]$^+$. According to Equation (4), and considering two acidic groups, the initial value of $R_{OH}$ is $-4.0$. Even after a long period of reaction, no precipitation takes place from this solution. It always remains unchanged, namely light-green and clear.

After addition of one equivalent of base, the pH was measured to be 5.6, which coincides with the specific point where citric acid has its maximum concentration for the doubly deprotonated form. Iron(II) continues to exist completely dissociated. With respect to the precursor, it can be assumed that one of its two carboxylic acid groups has also been deprotonated, thus giving [Fe(HCitH)$_2$(OH)]$^+$. $R_{OH}$ at this point is $-3.0$. Again, no precipitate forms, although a color change does occur: The solution still appears clear, but now turned yellow instead of remaining light-green as before.

Further base addition causes an increasing darkening until finally, soon before reaching the second base equivalent, a relatively fine, dark-green product begins to precipitate, which turns brown when exposed to air. The pH value at the second base equivalence point was found to be 8.9. Compared to the individual species, this is the point at which citric acid is almost exclusively completely deprotonated and iron(II) begins to form the monohydroxide. Thus, with regard to the precursor, we conclude that the two suspected carboxylic acid groups are completely deprotonated, yielding [Fe(HCit)(OH)$_2$]$_2$+, leaving the metal center now free for additional hydroxide coordination. $R_{OH}$ at this point, has a value of $-2.0$, which is identical to the value at which precipitation occurs when ferrous sulfate is used as the iron(II) source.

Up to this point, it can be concluded that one major part of the precursor-inhibition-function is due to the additional amount of base, which is required to completely deprotonate the carboxylic acid groups that shield the iron(II) center and thus prevents formation of the necessary hydroxide intermediate Fe(OH)$_2$.

After the addition of three base equivalents, a pH of 10.8 was measured. Citric acid is still completely deprotonated at this pH, whereas Fe$^{2+}$ mainly forms the dihydroxide, that is, the decisive preliminary stage (Figure 1c illustrates only the soluble dihydroxide form, drawn as a surrogate for the insoluble one, which precipitates almost quantitatively at this point).[58]

Accordingly, it can also be assumed for the state of the ferrous citrate precursor that it has formed an equivalent dihydroxide [Fe(HCit)(OH)$_2$]$_3^2$; as a result of the OH$^-$ replacing the remaining ionically coordinating carboxyl group from the iron(II) center. Already at this point, that is, at $R_{OH} = -1.0$, precipitation proceeds quantitatively. This is consistent with the hypothesis that the dissolved species already possesses a hydroxide group, so that once the precipitation zone is reached, the amount of base, necessary to give rise to the precipitating dihydroxide species, is reduced accordingly. However, a more detailed analysis of the conversion progress in the range between $-2.0 < R_{OH} < -1.0$ reveals that instead of the originally expected linear correlation (Figure 1f dark gray curve), a quadratic one seems to exist (Figure 1f light gray curve).

This indicates that at least three species are competing with each other, which is also supported by the fact that, according to Figure 1c, between the second and third base-equivalent, the “omitted” monohydroxide maximum of Fe$^{2+}$ is located. It can be assumed that there would be an inflection point at the corresponding pH value of about 10.2, which, however, cannot be clearly resolved from the experimental data. Considering this “species gap”, the quadratic behavior is quite reasonable, even if no detailed processes can be derived on the basis of the available data. However, the results are fairly clear: As the base content increases, the equilibrium shifts toward the precipitation product, thus causing some kind of “precipitation-catalyzing-effect” in this narrowed equivalence range.

Further base addition exhibits no more significant changes, except that much larger flocs are formed and that the supernatant finally appears colorless and clear after sedimentation. However, it seems likely that additional base-dependent effects will be revealed when other properties are considered, since with increasing pH the ligand equilibrium between OH$^-$ and citrate is shifted in favor of OH$^-$. If the titration is finally carried out under oxidative conditions, there are initially no differences observed with regard to the precipitation behavior. Precipitation starts at about $R_{OH} = -2.0$ and was quantitative at about $R_{OH} = -1.0$. However, the product obtained, after a certain reaction time (typically 4 h) and with a sufficient amount of oxidizing agent (typically a quantity corresponding to $R_{Ox} = 5.0$), appears as a black, magnetic solid. Considering the pH curve in comparison with the non-oxidative titration (Figure 1g), it is noticeable that between $-2.0 < R_{OH} < -1.0$ the pH value “falls back” to 8.9, that is, to the precipitation limit, revealing that the transformation is a self-limiting process. Very likely, the reason for the difference is the base consumption and the proton release associated with the oxidation process, respectively. This difference is no longer noticeable in the higher $R_{OH}$ range, due to the small net quantity of released protons.

In summary, focusing on the inhibition effect, it can be stated that, compared to a readily dissociating species such as ferrous sulfate, the use of ferrous citrate requires two
additional base equivalents to achieve hydroxide precipitation. Below this level, there is a buffer zone in which the precursor remains dissolved. Thus, it can be stated that assuming water-dissolved ferrous citrate as a diacid is suitable to establish a stoichiometric relationship with respect to the precipitation behavior.

2.2.2. Citrate Ligand Oxidation Effect

Once the hydroxide precipitation behavior was understood, the oxidation behavior was investigated. The syntheses were carried out according to the standard procedure, using different amounts of oxidant. Initially, experiments were carried out.
in the quantitative precipitation zone $-1.0 < ROH < 0.0$, since it was assumed that under these conditions any suspected pH-dependent influences on oxidation behavior would have only a reduced effect. Stoichiometrically, and taking into account the experience with ferrous sulfate,[31] it was assumed that already an oxidant concentration corresponding to $ROx = 0.7$ would be sufficient to quantitatively convert the used iron(II) into magnetite. However, Figure 2 illustrates that this oxidant quantity is not appropriate when ferrous citrate is used as a precursor.

In fact, at $ROx = 0.7$ (Figure 2a1), almost only an amorphous to poorly crystalline product was found. The corresponding Fourier transform infrared (FTIR) spectrum (Figure 2b) from this product, after drying, also exhibits a specific band around 1000 cm$^{-1}$, which cannot be associated to the targeted magnetite. However, when the amount of oxidant was increased ($ROx = 3.1$), spherical particles were found in high proportions as well (Figure 2a2). Accordingly, the infrared band at 1000 cm$^{-1}$ decreases, while a second band at about 570 cm$^{-1}$ appears, which can be associated to magnetite.[1,2,59]

When the amount of oxidant was increased even further ($ROx = 4.1$), the amorphous product can no longer be identified microscopically (Figure 2a3). Also, infrared spectroscopic analysis reveals no more indications. Thus, only the IR band at 570 cm$^{-1}$ is still present, while the band at 1000 cm$^{-1}$ has completely disappeared. Accordingly, it can be assumed that the reaction at this oxidant concentration exclusively yields the particulate product. A further increase then shows no subsequent changes (Figure 2a4).

However, depending on $ROH$, differences become apparent: Around $ROH = 0.0$, the previously satisfying oxidant concentration was no longer sufficient to obtain one product exclusively (Figure 2c1,d1). The amorphous product was additionally found again, whose formation, however, could again be prevented by further increasing the amount of oxidant to $ROx = 5.0$ (Figure 2c2,d2).

At very high base concentrations, which is, for example, at $ROx = 11.0$, the reduced amount of oxidant ($ROx = 4.1$) seems

![Figure 2. SEM images (row a) and FTIR spectra (b) revealing the $ROx$-dependent existence of an apparently amorphous by-product, distinguishable in the infrared spectra by the band at about 1000 cm$^{-1}$ (highlighted in red) from the target product, exhibiting a band at 570 cm$^{-1}$ (highlighted in green). SEM images (c–e) as well as the corresponding FTIR spectra (f) exemplarily show this also for products obtained at different $ROH$ values. Scale bars are 200 nm.](image)
to be sufficient once again, since neither scanning electron microscopy (Figure 2e1)) nor infrared spectroscopy show any evidence of the amorphous product. However, the particles differ in terms of size and morphology, indicating the influence of the base concentration, which will be considered in more detail in the following chapter.

Additional analysis of the powders using X-ray diffraction (XRD) (Figure S5b, Supporting Information) indicates that the amorphous product, associated with the IR band at 1000 cm\(^{-1}\), could be ferrihydrite. The particulate product, associated with the IR band at 570 cm\(^{-1}\), appears relatively clearly to be magnetite Fe\(_3\)O\(_4\) or maghemite \(\gamma\)Fe\(_2\)O\(_3\), both of which are nearly impossible to distinguish via X-ray diffraction or infrared spectroscopy.\(^{[5,28,60]}\) However, taking into account its black appearance and that it also leaves a black streak when dragged over a white surface, in combination with its magnetic properties (especially the high saturation magnetization; see Section 2.2.3), we assume that the particulate product is mainly magnetite.

Thus, the \(R_{OH}\) values that are provided should not be regarded as absolute limits. Nevertheless, they are capable of showing very clearly that the use of ferrous citrate as a precursor requires an additional amount of oxidant.

### 2.2.3. Citrate Ligand Repulsion Effects

Once, both, the precipitation and oxidation behavior were investigated and understood with regard to favorable particle formation conditions, the properties of the obtained magnetite particles were investigated. For this purpose, the oxidation concentration was kept constant and \(R_{OH}\) was varied, while the synthesis procedure was otherwise kept unchanged. \(R_{OH} = 5.0\) was chosen as the constant value for the amount of oxidant, which corresponds to the minimum concentration that reliably generated only magnetite over the entire \(R_{OH}\) range tested. Merely in the range of \(-2.0 < R_{OH} < -1.5\), product mixtures were obtained more frequently, which is why this range is not considered in detail within the following discussion.

**Figure 3** presents a comparison of properties (non-magnetic ones; magnetic ones will be discussed later) of exemplarily selected particulate magnetite products as a function of \(R_{OH}\).

The scanning electron microscopy (SEM) images (row a) in Figure 3 show, once again, very clearly what was already evident when analyzing the oxidation behavior: There are significant \(R_{OH}\)-dependent differences with respect to particle morphology. Additional transmission electron microscopy (TEM) images (row b) in Figure 3 further elucidate these differences.

The magnetite nanoparticles obtained in the low \(R_{OH}\) range \((-1.5 < R_{OH} < -1.0)\) are almost spherical, highly clustered, and relatively small with diameters of about 50 nm. Up to about \(R_{OH} = 4.0\), they remain largely round, but their size increases significantly and they become more compact. When \(R_{OH}\) was increased even more, the resulting particles also became larger and more compact. Beyond that, however, they deviate more and more from their spherical shape. Finally, at very high \(R_{OH}\) they similarly form facets as their ferrous sulfate analogs obtained under similar conditions.

Although, as confirmed by X-ray diffractograms (Figure 3c), all products appear to be the same material, the infrared spectromgs show clear differences (Figure 3d).

Thus, with increasing \(R_{OH}\), the intensities of the carboxyl bands at 1570 cm\(^{-1}\) and 1390 cm\(^{-1}\) decrease. Vice versa, the intensities of the OH bands at 880 cm\(^{-1}\) and 820 cm\(^{-1}\) increase.

This behavior is also reflected by the isoelectric point IEP of the particles (Figure 3e): The IEP is clearly in the acidic region where \(R_{OH}\) is low and carboxyl bands are present. With increasing \(R_{OH}\) and correspondingly decreasing carboxyl band intensities, the IEP shifts more and more toward higher pH values. Finally, at high \(R_{OH}\), that is, when even hardly any more carboxyl bands are apparent, the IEP is at a pH of about 6.0, which corresponds to that found for particle-analogues, using ferrous sulfate as the precursor.\(^{[31]}\)

Both, IEP and infrared analysis, show relatively clearly that, up to a certain \(R_{OH}\), the ligand or a residue of it is still present on the particle surface after conversion. This behavior has already been observed in an earlier work when ferrous sulfate was used: The iron(II) ligand resides in the product under certain conditions and thus it can be specifically exploited and
transferred to other ligands. Both analytical results also support the hypothesis that the citrate ligand undergoes changes presumably due to self-oxidation, which is dependent on ROH.

These oxidation-induced structural changes can be used to also explain the morphological differences.

- At low ROH values, the ligand remains largely intact. In the case of citrate, this implies that both, a high electrostatic and a certain steric repulsion are present, preventing the initially generated magnetite nuclei from fusing into larger entities. Rather, they remain isolated as clusters.[61]

- At increased ROH (intermediate values of ROH), the citrate ligand oxidizes correspondingly more, which is primarily accompanied by the irreversible loss of the carboxyl groups. Thus, the citrate ligand loses both, acidity and size. As a consequence, the repulsion is weakened and the nuclei can converge more closely. Accordingly, the obtained particles appear more compact, exhibit less intense carboxyl bands and have an IEP shifted toward higher pH values.[61]

- Finally, at very high ROH, the primordial citrate ligand no longer possesses any acidic groups or has even been completely exchanged. Fusion processes are then hardly impeded any more, thus, the known faceted mesocrystals emerge.[31,61]

A closer comparison of the IEP from particles obtained at ROH = −1.5 (pH$_{\text{IEP}}$ = 3.9) suggests a relatively low citrate concentration, respectively, a surface loading that may originate rather from a dicarboxylic than from a tricarboxylic molecule such as citrate, which typically causes IEP values that are even lower.[44,45,49,62] Taking the oxidation behavior of citrate into account, along with assuming that the central carboxyl group oxidizes relatively easily, it can be conjectured that the remaining surface molecule is not citrate itself but, for example, an oxidation product such as acetone dicarboxylic acid. This assumption can be reconciled very well with the observed oxidant scavenger effect, which already plays a decisive role even at low ROH values.

Besides the non-magnetic properties of the particle products, also a study of their magnetic properties helps to understand the formation process and the role of citrate better. Figure 4 depicts the ROH-dependent magnetic properties together with the particle sizes and photographs of suspensions containing a specific type of obtainable particles.

The graphs in a) and b) in Figure 4 show that both, saturation magnetization $M_S$ and coercivity $H_C$ follow the same trend. Initially, both values are, with $M_S \approx 60$ emu g$^{-1}$ and $H_C \approx 20$ Oe, respectively, relatively low but they increase relatively quickly with increasing ROH and finally gradually converge toward a more or less constant plateau. This behavior is largely independent of ROX.

The saturation magnetization bulk value for magnetite is reported to be about 92–100 emu g$^{-1}$.[2] This value is attained at about ROH = 4.0, providing further evidence that the product is mainly magnetite. The fact that the values in the lower ROH range are below this can be explained comprehensively on the basis of the previous observations:
Since the saturation magnetization is given as a mass-related value, non-magnetic fractions will cause a reduction in this respect. The foregoing analyses showed that the citrate ligand, or part of it, is still a product constituent after conversion and thus contributes significantly to the total mass. This ratio is greater the larger the residual molecule. At low $R_{OH}$ values, the molecule seems to be largest, making the mass-related saturation magnetization values appear small. With increasing $R_{OH}$, the molecule becomes smaller due to the associated oxidation processes. Accordingly, it subsequently contributes less to the total mass, thus resulting in higher saturation magnetization values. Finally, from about $R_{OH} = 4.0$, the molecule becomes so small, or presumably even completely replaced at even higher $R_{OH}$ values, that the corresponding saturation magnetization value is no longer significantly different from the bulk value.

The trend of the mass-independent coercivity cannot be explained by this. This appears to be largely related to the crystal lattice sizes (Figure 4c). Thus, the crystallites become larger with increasing $R_{OH}$. Since the smallest crystallite size, at $R_{OH} = -1.5$, is already above the size assumed as the limit for superparamagnetic properties at room temperature,$^{[63,64]}$ all particles are ferromagnetic and exhibit a coercivity correlating with the domain size ($\approx$ crystallite size).

However, it is noticeable that the particles whose infrared spectra show intense OH bands (see Figure 2d) also follow this trend. For the particle-analogues obtained from ferrous sulfate, there is a significant jump in coercivity values to above 300 Oe, which was justified by admitting an intraparticle magnetic interaction.$^{[31]}$ This no longer seems to be the case with the particles obtained from ferrous citrate. A possible cause would be that growth, even at high $R_{OH}$, does not originate entirely from pure Fe(OH)$_2$, but from a preliminary stage to which an oxidation residue of the ligand is still attached, which does not hinder hydroxide preferential growth, but very much prevents intraparticle interactions.

Finally, Figure 4d displays a distinctive feature of the products obtained at $-1.5 < R_{OH} < -1.0$: Particles obtained in this range behave, in a concentration dependent manner, in dispersion like the magnetic-responsive photonic crystals known from various solvothermal syntheses.$^{[9-11,64-69]}$ Thus, they are capable to diffract light in dependence of the strength of an applied magnetic field which counteracts their mutual steric and electrostatic repulsion, leading to a precise balance, which is crucial to obtain the observed effect.$^{[9,11,66-69]}$

This further demonstrates the potential of thermally assisted oxidative precipitation, as much more than just “simple” magnetite particles are accessible, thereby.

2.3. Summary

Figure 5 schematically summarizes the identified influences of the ferrous citrate precursor [Fe(HCitH)(H$_2$O)] on the formation of magnetite, Fe$_3$O$_4$, via thermally assisted oxidative precipitation.

Analyzing the precursor in detail revealed that the ferrous citrate complex increases its acidity when dissolved in water. This is probably facilitated due to a proton being shared between the coordinated water molecule and a carboxyl group of the citrate ligand. Because of the stabilizing effect of the solvent water, the coordinating water molecule dissociates and transfers the shared proton to the carboxyl group. At the same time, the resulting hydroxide takes over the charge-balancing role of the former carboxylate. This gives rise to a species which—on the one hand—shields the iron(II) center more strongly due to the increase in acidity, but which—on the other hand—also already possesses a hydroxide group. As a result, in an aqueous environment, a higher amount of base is required to neutralize the complex and expose the iron(II) center than indicated by the powder analysis. However, once the acidic groups are deprotonated, the shielding effect is inverted, since the intramolecular proton transfer also induced a hydroxide group. Accordingly, less base is required for the formation of the dihydroxide species. Practically, this implies that experiments that stoichiometrically assume a monoaacid will not be successful, even if twice the amount of base is used.

Nevertheless, even if this amount is exceeded, another effect must be overcome that strongly inhibits subsequent iron
oxidation. Thus, when [Fe(HCitH)(H2O)] is used, the minimum amount of oxidant required for a complete conversion to Fe3O4 is—compared to FeSO4—increased by a factor of 5 to 6. This is probably caused by the citrate ligand, which somehow acts as an oxidant scavenger to be preferentially oxidized itself. Only when enough oxidant is available to “satisfy the scavenger”, also magnetite formation starts.

If this takes place at still relatively low base concentrations, only rugged clustered, spherical nuclei-assemblies are formed, which exhibit a negative surface charge. This can be explained as the citrate ligand remains relatively intact, that is, it still possesses carboxyl groups that cause both, steric and electrostatic repulsion between the nuclei, thus preventing further fusion.

However, if the base and oxidant concentrations are increased even more, it causes the citrate ligand(residue) to oxidize further, which is accompanied by the loss of its carboxyl groups. Accordingly, the ligand increasingly loses its repulsive effects and the nuclei can fuse much more densely. The resulting products still appear spherical, but are much more compact and also hardly exhibit any negative charge.

Finally, when the amount of base is increased even further, the citrate ligand seems to be completely expelled or oxidized to such an extent that it no longer has any influence on the fusion process. In this case, the obtained products are very similar to those resulting from a likewise precipitation with ferrous sulfate, that is, tightly fused, faceted mesocrystals with a surface charge typical for unmodified magnetite. However, there are still differences: The iron citrate products exhibit a similarly high saturation magnetization but a significantly lower coercivity. A possible reason for this is that a minimal ligand residue is still present, which hardly affects the fusion process but inhibits intraparticle magnetic coupling.

3. Conclusion

In this work, a methodological approach was proved, using iron(II) citrate as an example, to demonstrate how the method of thermally assisted oxidative precipitation can be opened up for the use of metal organic iron(II) complexes in order to obtain, in one step, ferromagnetic magnetite nanoparticles, which possess essential properties of the ligand. Due to a dedicated analysis of the chosen precursor ferrous citrate, it was possible to identify three characteristics of the complex that inhibit the generation of magnetite. The 1st inhibition effect results from the acidity of the complex, which is—presumably due to an intramolecular proton transfer—greater in solution than analyses of the powder would suggest. However, it was found that—on the one hand—this acidity-increasing effect initially protects the metal center from hydroxide attack more effectively, but—on the other hand—apparently induces an already coordinated hydroxide, which, after overcoming the acid groups, accelerates the precipitation process similarly. The 2nd inhibition effect arises from the ligand citrate, which acts as an oxidant scavenger that “devours” the oxidant for self-oxidation, even before it reaches the metal center. It was found that this is a pH-dependent effect, most likely related to the availability of the catalytic iron(II) center and thus also directly related to the citrate-to-hydroxide ligand exchange process. The 3rd inhibition effect is due to the pH-dependent coordination affinity of the ligand, combined with its steric and electrostatic repulsive properties, which affect the fusion behavior of the nuclei. While the first two inhibiting properties have to be overcome, and therefore define to some extent the minimum amount of base and oxidant to be used in order to synthesize ferromagnetic magnetite nanoparticles, it was found that the third effect can be utilized selectively to enable the preparation of product variations that differ notably in morphology and size, but moreover in surface characteristics and magnetic properties. By demonstrating that ferromagnetic magnetite nanoparticles can also be obtained from ferrous organic precursors using thermally assisted oxidative precipitation, this method may experience a renaissance, since it apparently has a similarly high potential as, for example, the solvothermal route, but in contrast requires less effort and also permits temperature-dependent access to iron oxides other than magnetite.

Figure 5. Schematic summary illustrating the effect of the amount of base (red) and oxidant (green) on the inhibition functions of the ferrous citrate [Fe(HCitH)(H2O)], used herein, as a precursor for thermally assisted oxidative precipitation of magnetite Fe3O4 with different nano forms.
4. Experimental Section

Materials: Iron(II) chloride tetrahydrate (FeCl₂·4H₂O, 99.3%), citric acid monohydrate (H₃Cit·H₂O, ≥99%), sodium dihydrogen citrate (Na₂HCit·H₂O, ≥99%), and potassium dihydrogen citrate sesquihydrate (Na₂HCit·1.5H₂O, ≥99%) were all obtained from Sigma-Aldrich. Potassium nitrate (KNO₃, 99%), disodium hydrogen citrate sesquihydrate (Na₂HCit·1.5H₂O, ≥99%) and trisodium citrate dihydrate (Na₃Cit·2H₂O, ≥99%) were obtained from Acros Organics. Potassium hydroxide (KOH, 90%, flakes) was obtained from VWR International. Ammonia (NH₃, 30% in water) was obtained from Roth.

Precursor Synthesis: The synthesis of the organometallic iron(II) citrate precursor is based on the experimental description given in patent number US 3091626.[iii] Accordingly, ferrous chloride and citric acid were dissolved in water in a 1:1 molar ratio and two molar equivalents of ammonia were added. The solution was then boiled under reflux for 2 h. Subsequently, the white precipitate was filtered, washed several times with water and ethanol, and finally dried.

Nanoparticle Synthesis: The synthesis is performed according to the approach already described.[iii] Accordingly, assuming a monomeric species, 20 mm of the as prepared ferrous citrate precursor were dissolved in deionized (135 mL) water and allowed to boil while introducing nitrogen. In parallel, KOH and KNO₃, according to the desired ratios in deionized (135 mL) water and allowed to boil while introducing nitrogen. After about 20 min of conditioning (equal time given to reach boiling), the basic oxidation solution was added to the ferrous salt solution. A typical reaction was then allowed to proceed for 2 h. Subsequently, the white precipitate was filtered, washed several times with water and ethanol, and finally dried.

Elementary Analysis: Elemental analysis was performed using Euro EA 3000 (Euro Vector).

Thermal Analysis: Coupled thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) thermal analysis were carried out using a Netzsch STA 449C Jupiter system combined with a Netzsch QMS 403C Aeolos Quadrupole Mass Spectrometer. The sample holders were made of Al₂O₃. Ar gas was chosen as inert atmosphere. Heating was conducted from room temperature to 600 °C with a heating rate of 10 K per minute.

Qualitative Methods: Non-converted iron, which was still dissolved in the supernatant after the reaction, was quantified colorimetrically using 2,2’-bipyridine as chelator.

Scanning Electron Microscopy (SEM): Scanning electron micrographs were taken on a Zeiss Supra 25 SEM at 2 kV (field emission) and 2.9 mm working distance, usually using the in-lens detector. Samples were prepared from suspensions on a thin gold plate, which were placed on an SEM sample holder after drying.

Transmission Electron Microscopy (TEM): Transmission electron micrographs were taken with a JEM-2010 TEM from JEOL at 200 kV acceleration voltage. Samples were prepared on carbon film supported copper mesh grids obtained from Quantifoil Micro Tools GmbH.

Zeta Potential Measurements: To determine the isoelectric points, zeta potential measurements were performed with a Zetasizer Nano ZS from Malvern Instruments. Therefore the respective particles were dispersed in a 1 mM NaCl solution. HCl, respectively, NaOH was used to adjust different pH values.

Magnetic Measurements: Magnetic properties were studied with a vibrating-sample magnetometer (VSM, VersaLabTM 3T cryogen-free VSM), cycling the applied field from –30 to +30 kOe with a step rate of 50 Oe s⁻¹. Detailed analyses were carried out by cycling the applied field from –3 to +3 kOe with 5 Oe s⁻¹. The temperature was set to 300 K. It should be noted that magnetization values within this work are given in emu g⁻¹ (cgs units) which can be set equal to A m² kg⁻¹ (SI units).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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colloidal nanostructures, nanoparticle aggregation, non-classical crystallization, oriented attachments, oxidant scavenger, photonic crystals

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