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Zero-valent iron nanoparticles preparation

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ABSTRACT

Zero-valent iron nanoparticles were synthesized by hydrogenating $[Fe[N(Si(CH_3)_3)_2]_2]$ at room temperature and a pressure of 3 atm. To monitor the reaction, a stainless steel pressure reactor lined with PTFE and mechanically stirred was designed. This design allowed the extraction of samples at different times, minimizing the perturbation in the system. In this way, the shape and the diameter of the nanoparticles produced during the reaction were also monitored. The results showed the production of zero-valent iron nanoparticles that were approximately 5 nm in diameter arranged in agglomerates. The agglomerates grew to 900 nm when the reaction time increased up to 12 h; however, the diameter of the individual nanoparticles remained almost the same. During the reaction, some byproducts constituted by amino species acted as surfactants; therefore, no other surfactants were necessary.

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1. Introduction

Nanoparticles can be made up from most of elements of the periodic table, and they can be classified based on their components as organics [1,2], inorganics [3,4], metallic [5,6], semiconductors [7], ionics [8] and moleculars [9].

Metallic nanoparticles are of particular interest the because of their quantum size effects and their large surface areas. Nanoparticles with magnetic properties, superparamagnetism and quantum tunneling of magnetization, have received considerable attention [10–12] because they have a wide variety of biomedical applications [13], such as their uses as contrast enhancement agents for magnetic resonance imaging (MRI) [14,15], bioprobes [16] and cell sorters [17]. Most of these types of nanoparticles can enter the cell, and even the nucleus, and interact with DNA and cellular proteins [18]. They have the potential to improve therapies such as cancer drug delivery [19,20]. Monodisperse nanoparticles of zero-valent iron are ideal for these kinds of applications because they have a high saturation magnetization at room temperature and a high reactivity [21].

Metallic nanoparticles can be obtained by "top-down" methods that include the mechanical grinding of bulk metals and subsequent stabilization of the resulting nanosize metal particles; however, it is difficult to obtain narrow particle size distributions in this way [22]. The "bottom-up" methods form nanoparticles by starting from either atomic or molecular precursors in gas or solution, but these techniques are often unable to yield simultaneous control over nanoparticle structure, surface chemistry, monodispersity, crystal structure and assembly [23–25].

Among "bottom-up" methods, there are a great variety of chemical methods for the synthesis of metallic nanoparticles in which it is possible to control the shape, size distribution and properties of nanoparticles with kinetics parameters such as the temperature and, the concentration of stabilizing agents. These methods include the thermolysis [26], hydrolysis [27] or reduction [28] of precursors of organometallic and coordination compounds [29–32]. Recently, several colloidal chemical synthetic procedures have been developed to produce monodisperse nanoparticles; these methods have a series of stages that take place in the liquid phase [33] in the presence of a surfactant. First, metallic atoms can be obtained by reducing precursors using chemical redactors in solution [34,35]. In a second stage, the atoms begin to nucleate, and these nuclei begin to grow slowly until they form nanoparticles [36–38]. The composition and the size of the formed particles depend on parameters such as the reaction time, the temperature and the surfactant molecule length [39].

Recently, several colloidal chemical synthetic procedures have been developed to produce zero-valent iron nanoparticles. One of the most common procedures involves the decomposition of iron pentacarbonyl, Fe(CO)₅, to generate metallic iron atoms [40–43].

Other important organometallic precursors include the amido complexes. These are easily accessible precursors used obtain zero-valent iron nanoparticles; they decompose under hydrogen pressure, and the resulting residue can serve as a surfactant that surround the nanoparticles. An example of this type complex is bis [bis(trimethylsylil)amido] iron (II), Fe[N(SiMe₃)₂]₂. The decomposition of this complex has been reported in solution at 150 °C under

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Fig. 1. Scheme of the stainless steel reactor used during the reaction.

a hydrogen atmosphere at 3 bars of pressure over 48 h in the presence of hexadecylamine and long chain acids. The results showed zero-valent nanoparticles with a cubic shape and an average diameter of 7 nm [44]. Moreover, the synthesis of Rh and Fe nanoparticles has also been reported from the hydrogenation of $Rh(C_3H_3)_3$ and $[Fe[N(Si(CH_3)_3)_2]_2]$, which produced core-shell nanoparticles with an Rh core and a Fe shell. The average particles size was 2.1 nm [45].

In this work, zero-valent iron nanoparticles were synthesized by hydrogenating $[Fe[N(Si(CH_3)_3)_2]_2]$ at room temperature and a



Fig. 2. Progress of the synthesis reaction of zero-valent iron nanoparticles as a function of time.

pressure of 3 atm. A stainless steel pressure reactor lined with PTFE was adapted for the synthesis. Several samples were taken at different times during the reaction to study the progress of the reaction and the shape and the diameter of the nanoparticles, during the entire process. The progress of the reaction was determined by gravimetric methods. The results of the dynamic light scattering of pure nanoparticles established that the average diameter of the particles increased with the reaction time because of the formation of aggregates of nanoparticles. The transmission electron microscopy analysis confirmed a spherical shape and a



Fig. 3. Images of samples taken at (a) 0.5 and 1.5 h, (b) 3 h, (c) 8 h and (d) 12 h of reaction.

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Fig. 4. Z-average diameter as a function of reaction time for unpurified nanoparticles.

diameter less than 5 nm for the zero-valent iron nanoparticles during all reaction times.

2. Experimental

2.1. Reagents

The hexamethyldisilazane (HN[Si(CH₃)₃]₂) and the iron bromine (II) (FeBr₂) (from Aldrich) were reagent grade, and they were used as received. The n-butyl lithium (C₄H₉Li) was placed in 2.5 M hexane (from Aldrich). The THF (>99.0%), diethyl ether (99.9% anhydrous) and pentane (98%) (from Aldrich) were distilled, dried in the presence of CaH₂, degassed and stored in an anaerobic chamber [46]. The precursor of the iron particles, bis[bis(trimethylsilyl)amido]iron(II) [Fe[N(Si(CH₃)₃)₂]₂], was used as received [47].

2.2. Synthesis of nanoparticles

The reactions for the synthesis of nanoparticles were carried out as a batch process. Bis[bis(trimethylsilyl)amido]iron(II) $[Fe[N(Si(CH_3)_3)_2]_2]$ was obtained by means of the following reaction [47]:

$$\begin{aligned} & FeBr_2(THF)_2 + 2LiN[Si(CH_3)_3]_2 \xrightarrow{Et_2O} Fe[N(Si(CH_3)_s)_2]_2 + 2LiBr \\ & + 2THF \end{aligned}$$

 $Fe[N(Si(CH_3)_3)_2]_2$ was extracted and purified in pentane. In this reaction, approximately 1.4 g (0.27 mmol) of compound was obtained. The efficiency of the reaction was approximately 55%.

The Fe[N(Si(CH₃)₃)₂]₂ obtained was dissolved in 200 mL of pentane. The solution was loaded into a stainless steel pressure reactor. The reactor was pressurized to 3 atm of H₂ at room temperature, and the reaction time was 12 h. The iron nanoparticles were produced by means of the following reaction:

$$Fe[N(SiMe_3)_2]_2 + H_2 \xrightarrow{pentene} Fe^0 + 2HN(SiMe_3)_2$$

An austenitic 230 mL stainless steel reactor (Parr Instruments Company model 452HC2-T316) was used to synthesize the iron nanoparticles. The reactor was lined with PTFE, and it was equipped with a mechanical stirrer connected to a Pitched Blade Impeller, which was also lined with PTFE. For the feeding of the reactants and the sample collection, the reactor was adapted according to the scheme in Fig. 1.

With this system, 9 samples of 9 mL were taken at different reaction times to observe the growth of the nanoparticles. In all cases, a black precipitate was produced. The particles formed were transferred to a Schlenk flask and dried with a vacuum. The samples were put in a vacuum chamber where they were stored in glass ampoules and sealed at the temperature of liquid nitrogen to prevent oxidation before characterization.

2.3. Gravimetry

The progress of the zero-valent iron nanoparticles synthesis reaction was calculated by gravimetric techniques. From each sample, 3.5 mL of reaction solution was extracted. The extraction was made with a syringe that had a filter on the needle so that the iron nanoparticles were not extracted. Five samples (0.2, 0.4, 0.6, 0.8 and 1 mL) from each resulting solution were placed in a 1 mL vials with rubber caps and aluminum seals saturated with nitrogen. The vials had been weighed previously. The precursor was then separated from the reaction solution by evaporating the pentane. The precursor was quantified to determine the conversion as a function of the reaction time.



Fig. 5. (a) Transmission electron micrograph and (b) EDX spectra for the sample taken at 1.25 h.



Fig. 6. Particle size distribution of the sample of purified iron nanoparticles taken at 12 h measured at intervals of (a) 3 min, (b) 6 min, (c) 9 min and (d) 12 min.

2.4. Dynamic light scattering (DLS)

The hydrodynamic diameter of the iron nanoparticles was determined using dynamic light scattering (DLS). Samples of unpurified and purified nanoparticles were measured at 25 °C, using a Malvern Zetasizer Nano ZS instrument. To prevent the oxidation of nanoparticles, a glass cell with a Shclenk valve type was used, which was designed and made for this propose. The nanoparticles were purified with pentane washes. The purified particles were re-dispersed in pentane with Auto Science model AS5150B ultrasound equipment. The particle size distribution was calculated using the software provided by Malvern in the light scattering equipment.

2.5. Electron diffraction (ED), transmission electronic microscopy (TEM), X-ray energy dispersive (EDX) spectroscopy

The size and morphology of zero-valent iron particles were determined using a JEOL JEM 1230 microscope at 100 kV, which was coupled to an EDX model EDS7215, SPEC:143 eV with an INCA model ATW2 window. The sample was purified with pentane washes and placed onto carbon-coated copper grids inside a vacuum chamber. The samples were added to glass ampoules saturated with nitrogen to prevent oxidation. The presence of Fe⁰ and the qualitative analysis characteristic of the nanoparticles were determined by means of X-ray energy dispersive spectroscopy at 100 kV and in the energy range



Fig. 7. Particle size distribution by DLS for samples taken at (a) 2 h, (b) 5 h and (c) 8 h of reaction in the synthesis of zero-valent iron nanoparticles.

emitted by the Fe is 6.403 eV for the K-alpha emission and 0.776 eV for the L-alpha emission.

3. Results and discussion

The preparation process for the zero-valent iron nanoparticles was modified from the previously reported methods [44,48,49]. The first modification was that the reaction was carried out in a PTFE-lined stainless steel reactor and that had a mechanical stirrer. This system allowed to take samples at different reaction times; samples were taken at 0.5, 1.25, 2, 3, 4, 5, 6, 8, 10 and 12 h to follow the conversion, growth and shape change of the nanoparticles. A second modification of the commonly reported process entailed pressurizing the reaction system to 3 atm with hydrogen at room temperature. Finally, during the reaction, some amino ligands were produced as byproducts, and these amino ligands stabilized the system [45] hence, it was not necessary to use a surfactant, which influences the formation of small nanoparticles.

The percentage of the conversion of nanoparticles, N_p , in each sample was calculated using Eq. (1):

$$N_{\rm p} = 1 - \frac{m_{\rm p}}{m_{\rm s}} \times 100 \tag{1}$$

where $N_{\rm p}$ is the conversion of nanoparticles, $m_{\rm p}$, is the precursor mass and $m_{\rm s}$, is the solution mass without nanoparticles.

The conversion of zero-valent iron nanoparticles was obtained by taking into account that the formation of nanoparticles had a 1:1 stoichiometry. In this way, the results of the conversion of zerovalent iron nanoparticles as a function of time are presented in



Fig. 8. Z-average size of purified nanoparticles as a function of reaction time.

Fig. 2. The conversion of nanoparticles increased with the reaction time and reached 100% conversion at 12 h.

Images of the samples taken at different reaction times are shown in Fig. 3. After 30 min it was possible to observe that a portion of the coordination compound had reacted with hydrogen, and the color of the solution changed from green to black, indicating that the decomposition of the Fe precursor and the formation of zero-valent iron nanoparticles had occurred.



Fig. 9. Transmission electron micrographs of zero-valent iron nanoparticles for (a) 2 h, (b) 5 h and (c) 12 h of reaction time.

500 nm

From the results of the measurements of dynamic light scattering (DLS) of the unpurified and purified samples of nanoparticles taken at different reaction times, different particle diameter moments (number average diameter, D_n ; weight average diameter, D_W ; and Z-average diameter, D_Z) were calculated using Eqs. (2)–(4), and the polydispersity index (PDI) was determined using Eq. (5) [50]:

$$D_{\rm n} = \frac{\sum n_i D_i}{\sum n_i} \tag{2}$$

$$D_{\rm W} = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \tag{3}$$

$$D_{\rm Z} = \frac{\sum n_i D_i^5}{\sum n_i D_i^4} \tag{4}$$

$$PDI = \frac{D_n}{D_W}$$
(5)

where n_i is the number of nanoparticles with diameter D_i .

The results of the Z-average diameters as a function of the reaction time the unpurified nanoparticles are shown in Fig. 4. The iron nanoparticles produced had an average diameter smaller than 10 nm, except for the samples taken at 1.25 h and 12 h. This discrepancy can be explained by the observation that the byproduct produced during the reaction forms micelles that are swollen with the precursor.

20 nm

These results were confirmed by means of transmission electron microscopy. Fig. 5 shows a micrograph and the EDX spectra of the sample taken 1.25 h after the reaction was initiated. A micelle aggregate swollen with $Fe[N(Si(CH_3)_3)_2]_2$ can be observed, and the spectra confirm the presence of Si. This figure demonstrates that, at this reaction time, the conversion to nanoparticles was less frequent.

The samples of iron nanoparticles were purified and redispersed in pentane. The re-dispersed particles were measured by dynamic light scattering at intervals of 3, 6, 9 and 12 min. The results of the particle size distribution at these intervals for the sample taken at 12 h are shown in Fig. 6.

The particle size distributions obtained by DLS for purified samples of zero-valent iron nanoparticles at 2, 5 and 12 h of reaction are shown in Fig. 7 as examples of the samples taken during all reaction times for which the average size was 239, 324 and 850 nm, respectively. All the nanoparticles samples presented high polydispersity because the polydispersity value was larger than 1.

The results of the Z-average size as a function of the reaction time for the purified zero-valent iron nanoparticles are shown in Fig. 8. The volume taken from each sample was always the same. As the reaction time increases, the average size also increases up to values of approximately 900 nm; however, these large entities consisted of aggregates because the sample was purified. These results suggest that, as the reaction progressed, more and more particles were produced, and causing the aggregate to become enlarged. This hypothesis was confirmed with transmission electron microscopy images, which are shown in Fig. 9.



Fig. 10. Transmission electronic micrographs of zero-valent iron nanoparticles after (a) 2 h, (b) 5 h and (c) 12 h of reaction time.



Fig. 11. The EDX spectrum and the ED pattern for zero-valent iron nanoparticles.

The typical images obtained by transmission electron microscopy of pure nanoparticles collected after 2, 5 and 12 h of reaction are presented in Fig. 8 to illustrate the formation of zero-valent iron nanoparticles.

The nanoparticles began to aggregate as the reaction progressed. The images show that the aggregates are formed by nanoparticles with spherical shapes.

The spherical shape is confirmed in Fig. 10, which presents images of samples taken at 2 h, 5 h and 12 h of reaction time on a smaller scale than in Fig. 8. The figure reveals that the zero-valent iron nanoparticles have a diameter smaller than 5 nm in all cases. The size and morphology remained constant during the entire reaction. This can be explained due to that the formation of a nanoparticle requires the accumulation of precursors in a single nanodomain and by the deformability of the precursor ligands, which acted as a surfactant layer that controlled the material exchange process among nanodomains [44,51]. In this case, the precursor had a low concentration, and, consequently there was a lower material exchange rate, resulting in the formation of a greater number of nuclei and smaller nanoparticles with spherical shapes [52].

A bright field images of nanoparticles along with the corresponding EDX analysis and electron diffraction pattern are presented in Fig. 11. These images confirm that the particles are actually constituted by Fe⁰. The unlabeled peaks shown in the EDX pattern belong to Cu from the grid.

4. Conclusions

It was possible to synthesize zero-valent iron nanoparticles by hydrogenating of bis[bis(trimethylsilyl)amido]iron(II) [Fe[N(-Si(CH₃)₃)₂]₂] at room temperature and a pressure of 3 atm in a stainless steel reactor. The design of the reactor employed in the synthesis allowed samples to be taken at different times during the reaction. It was possible to determine that 100% conversion of the zero-valent iron nanoparticles was reached after 12 h of reaction. The results of the DLS and TEM analysis demonstrated the existence of nanoparticles with spherical shapes and diameters smaller than 5 nm, which formed aggregates as large as 900 nm. The results of the EDX and electron diffraction techniques confirmed the presence of zero-valent iron in the nanoparticles. The microanalysis results revealed the presence of 100% zero-valent iron.

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