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Microwave flash synthesis of iron and magnetite particles by disproportionation of ferrous alcoholic solutions

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This paper reports the microwave-hydrothermal treatment of alcoholic solutions of ferrous chloride ($FeCl_2$) and sodium ethoxide (EtONa) solutions with a microwave autoclave designed by the authors (the RAMO system). Depending on the initial concentrations, hematite (α-Fe_2O_3), spinel phase ($Fe_{3-x}O_4$) or iron-magnetite (Fe^0-Fe_3O_4) nanocomposites are obtained with a lower grain size compared to conventional composites. Indeed, X-ray diffraction (XRD) analysis reveals grain sizes close to 20 nm for magnetite and 60 nm for metallic iron. However, the amount of metal is smaller (close to 11%). Furthermore, these particles are inert in the ambient atmosphere. Consequently, the RAMO (French acronym of Reacteur Autoclave MicroOnde) system appears to provide an efficient source of energy in rapidly producing inert powders of iron, magnetite and iron-magnetite composites.

1. Introduction

Microwave heating is an emerging technology which uses the ability of some liquids and solids to transform electromagnetic energy into heat. It is usually performed in domestic ovens or laboratory systems deriving from domestic ovens such as CEM or PROLABO microwave digesters. If the role played by microwave heating over collisionnal or mechanistic term remains unknown today, it is otherwise for its action on temperature [1, 2]. Indeed the specificity and the essential interest of microwave heating are the increase in the heating rate induced. Several degrees per second can be reached according to the microwave power used. Consequently reaction rate enhancements are usually close to two or three order of magnitude. The reaction rate enhancement is defined as the ratio between the conventional reaction time and the microwave reaction time.

Since the mid-80s, numerous works have been devoted to the synthesis of various compounds (organic, organometallic, coordination and intercalation) by using microwave heating [3]. Some papers have been published upon inorganic compounds produced by microwave heating of metallic salts solutions [4–19]. Among them, few papers deal with iron oxides or hydroxides [15–19]. They show that it is possible to produce hematite nanoparticles of various shapes. The main difference with the conventional heating is that it is possible to force hydrolysis of ferric solutions (Fe^{3+}) and obtain hematite without production of goethite [19]. Wang *et al.* have been interested in the formation of magnetite from ferrous (Fe^{2+}) and ferric solutions [15]. They have concluded that the electromagnetic field drives the reaction along a different pathway compared to conventional heating. Indeed, magnetite is produced as a result of Fe^{2+} ions diffusing into goethite. In order to bring new insights on the iron ions behavior under microwaves, we present here the study of the reactivity of Fe^{2+} alcoholic solutions. We report the use of an original microwave system for one step flash synthesis of iron-magnetite by disproportionation of ferrous alcoholic solutions. Microwave treatment of Fe^{2+} aqueous solutions give only magnetite. We hope to take advantage of reducing property of ethanol in order to produce metallic iron. The disproportionation of ferrous hydroxide ($Fe(OH)_2$) in potassium hydroxide aqueous solution has been previously observed by using conventional heating at atmospheric pressure or in hydrothermal pressure [20–22]. It leads to iron-magnetite composites when [KOH] = 14 M and Fe_3O_4 for lower KOH concentrations [22]. The powders are made of octahedrals of about 1 μm in size in which the metal is imbricate into the oxide. The association of a metal and an oxide in a composite structure leads to new properties. Indeed, it has been shown that composites made of a Fe-Co alloy and cobalt substituted magnetite allow to produce light olefins with a low CO_2 rate. Furthermore, they are more resistant than the classical iron based catalysts [23]. Thus, we present here the effect of the microwave process and the various phases that we have obtained depending on the Fe^{2+} and EtO^- concentrations used. Finally, we will compare the iron-magnetite composites with those prepared by conventional techniques.

2. Experimental procedure

2.1. The RAMO system

We started working on the design of an original microwave reactor the RAMO system (French acronym of Reacteur Autoclave MicroOnde) seven years ago. This experimental device is constituted of a microwave applicator associated with an autoclave. Compared to a domestic oven, our microwave oven allows a higher electric field strength for the heated sample. By varying the position of a plunger the resonant frequency of the cavity can be controlled and the effective cavity power can be increased by three orders of magnitude. The microwave generator used is a continuous wave system with a power up to 2 kW (2.45 GHz). The autoclave is made with polymer materials which are microwave transparent, chemically inert and sufficiently strong to accommodate the pressure induced. The reactants are placed in a Teflon flask inserted within a polyetherimide flask. A fiber-optic thermometry system, a pressure transducer and a manometer allow to measure simultaneously the temperature and the pressure within the reactor. Temperature measurements under microwave heating are very difficult. We must use a non-perturbing temperature sensor in order to avoid unwanted localized hot spots [24, 25]. The system is controlled by pressure. We adjust the microwave power in order to allow constant pressure within the vessel. A pressure release valve incorporated permits to use this experimental device routinely and safely. Furthermore, we can introduce an inert gas such as argon within the reactor to avoid sparking risk with flammable solvents.

This experimental device is able to raise the temperature from ambient to 200°C in less than 20 seconds (the pressure is close to 1.2 MPa and the heating rate is close to five degrees per second). Fig. 1 illustrates the relationship between temperature and pressure generated within the reactor for ethanol and the reactive medium used: ethanol reaches a temperature of 160°C and a pressure of 1.0 MPa in 40 seconds for a power of 1 kW. The reactive medium leads to a higher heating rate since metallic salt and sodium ethoxide increase the dielectric losses.

2.2. Operating conditions

All the chemical products : ferrous chloride ($FeCl_2.4H_2O$ Prolabo, Normapur, 24 127.237), sodium ethoxide (EtONa, Aldrich, 15.624-8, 96%), ethanol (Prolabo, Normapur, 20 821.296) were reagents grade used without further purification. Different concentrations of iron salt (from 0.2 M to 0.4 M) and sodium ethoxide (from 0 to 1 M) have been tested. The solution of sodium ethoxide in ethanol was prepared at room temperature and poured into the reactor. In order to avoid oxidation, ferrous chloride was dissolved in ethanol just before its use (orange solution). This solution was rapidly poured into the solution of sodium ethoxide. A green precipitate appears. The reactor was quickly sealed and an argon pressure introduced (0.4 MPa). Treatments were performed with RAMO. The treatment was decomposed in two steps. During the first step, the microwave power (1 kW) is applied until the pressure reaches a threshold value of 1 MPa. This pressure corresponds to a temperature close to 160°C (Fig. 1). During the second step, this pressure threshold was kept by adjusting the

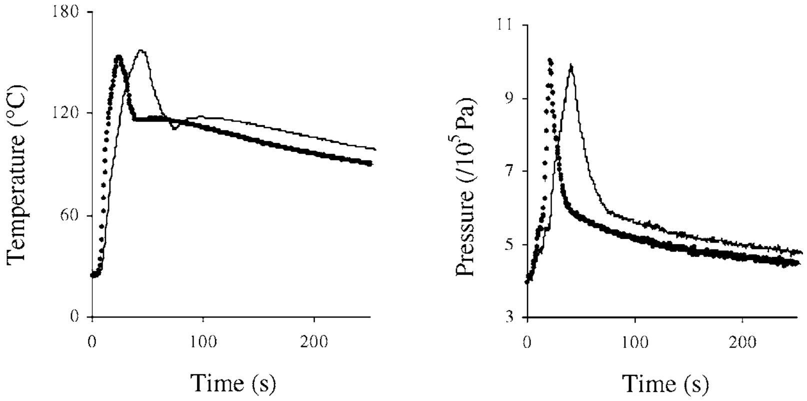

Figure 1 Temperature (a) and pressure (b) versus time for pure ethanol (- -) and reactive medium time (- -) for $[Fe^{2+}] = 0.3$ M, $[EtONa] = 0.7$ M and a microwave power equal to 1 kW.

microwave power. The heating rate is close to 10°C per second. Heating times were between 5 seconds and 30 minutes. After this treatment, powders were centrifuged and washed with distilled water in order to eliminate sodium and chloride ions. Finally, they were dried at room temperature.

2.3. Characterization methods

X-ray diffraction (XRD) measurements were performed at room temperature using a D5000 Siemens diffractometer to identify end-products and to determine the lattice parameters and the average grain sizes. X-ray diffraction data were collected with a monochromatic beam Copper Kβ ($\lambda = 0.139222$ nm) obtained with a secondary curved graphite monochromator. To obtain the parameters of the Bragg reflection, pattern decomposition was carried out by means of the profile-fitting program PROFILE. The program is part of the Socabim PC software package DIFFRACT-AT supplied by Siemens. A least-square refinement program (Celref) was used to determine the cell parameter and the Langford method or the Williamson et Hall method [26] were used to determine the average crystallite size of the spinel phase.

Transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDXS) were used to obtain microstructural information, to determine individual grain compositions and to identify phases. The samples were prepared by depositing the powder dispersed into ethanol onto a holey carbon coated 200 mesh copper grid. Some samples were also realized by embedding the powder into an Epon 812 resin. Thin slices were cut using an ultramicrotome equipped with a diamond knife. The 60–90 nm thick sections were then collected on a holey, carbon coated, 200 mesh copper grid. Samples were examined with a TOPCON 002B microscope operating at 200 kV (point to point resolution of 0.18 nm) and equipped with an ultrathin window KEVEX EDX spectrometer.

3. Results and discussion

The powders have been analyzed by X-ray diffraction. Five areas have been pointed out versus the ferrous chloride and sodium ethoxide concentrations. Fig. 2 exhibits precipitation domains for a treatment time equal to 10 min.

- For the smallest sodium ethoxide concentrations ($0 < [\text{EtO}^-] < 0.02$ M), the solution color is orange and no precipitate is observed (white circles on Fig. 2). After the microwave treatment, hematite (α-Fe_2O_3) is obtained in very little quantity. The color of the solution is the same after treatment as before. Hematite precipitation is assigned to the forced thermohydrolysis of ferric cations present in solution. On the contrary, thermohydrolysis of ferrous cations is impossible with our protocol.
- For sodium ethoxide concentrations between 0.02 M and 0.1 M (gray circles on Fig. 2), we obtain a green precipitate and hematite and magnetite are obtained simultaneously. The color of the solution after the microwave treatment is orange. Therefore major part of ferrous ions has not precipitated during the microwave heating.
- For sodium ethoxide concentrations between 0.1 M and 0.4 M, a spinel phase ($Fe_{3-x}O_4$) (black circles on Fig. 2) is obtained with a very small amount of akaganeite (β-FeOOH) and/or hematite (α-Fe_2O_3). The color of the solution after treatment is slightly orange showing that small amounts of ferrous ions are still in the solution. The cell parameter of this spinel phase is close to 0.8375 nm for all heating times. This value corresponds to an intermediate oxygen stoechiometry between maghemite ($a = 0.8346$ nm) and magnetite ($a = 0.8396$ nm). The grain size of this spinel phase is close to 8 nm for all heating times.
- For sodium ethoxide concentrations higher than 0.4 M (gray triangles and squares on Fig. 2), a metallic phase of bcc structure appears with a cell parameter of 0.2866 nm. This structure is

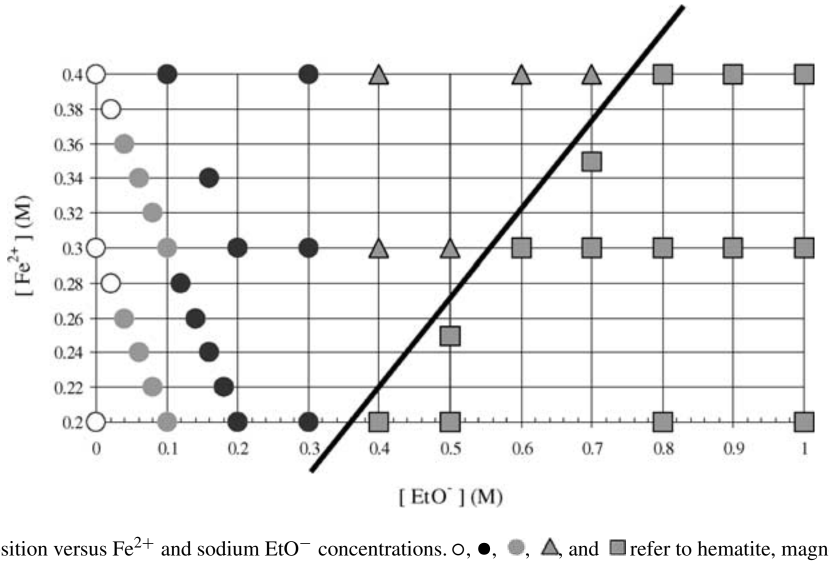

Figure 2 Powders composition versus Fe^{2+} and sodium EtO^- concentrations. ○, ●, ●, △, and ■ refer to hematite, magnetite, hematite-magnetite mixture, iron-magnetite mixture with impurities and pure iron-magnetite respectively.

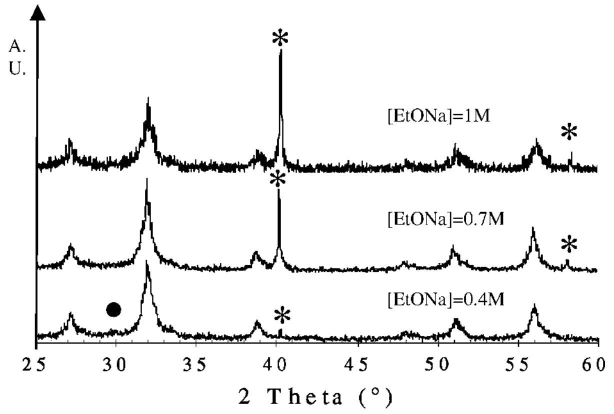

Figure 3 X-ray diffraction data versus sodium ethoxide concentration ($[Fe^{2+}] = 0.3$ M, heating time 10 minutes). The * correspond to α-Fe diffraction lines. The ● correspond to α-Fe_2O_3 principal line. The other diffraction lines correspond to the spinel phase.

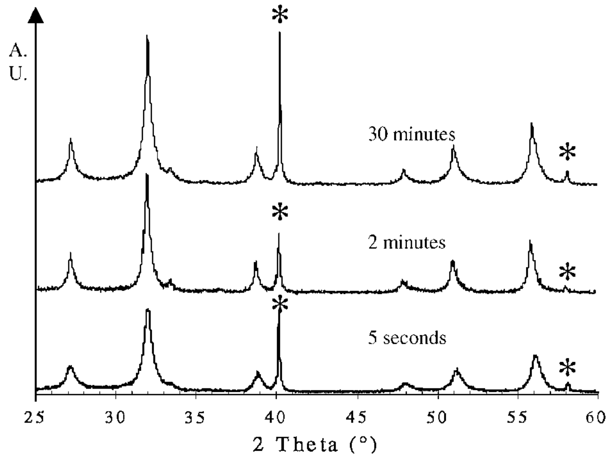

Figure 4 X-ray diffraction data versus heating time ($[Fe^{2+}] = 0.3$ M, $[EtONa] = 0.7$ M). The * correspond to α-Fe diffraction lines. The other diffraction lines correspond to the spinel phase.

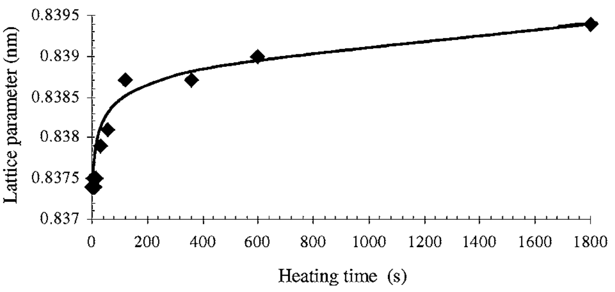

Figure 5 Lattice parameter of spinel phase versus heating time ($[Fe^{2+}] = 0.3$ M, $[EtONa] = 0.7$ M).

characteristic of α-Fe. The intensities of the Bragg reflections of α-Fe with respect to the magnetite ones, increase with the sodium ethoxide concentration as described by Fig. 3.

Nevertheless, in that area, two domains have been pointed out, separated by a straight line defined by a ratio between ferrous salt and sodium ethoxide ($[EtO^-] = 2\ [Fe^{2+}]$). On the left hand side i.e., for $[EtO^-] < 2\ [Fe^{2+}]$, small quantities of β-FeOOH or α-Fe_2O_3 occur in the powders and the spinel cell parameters are smaller. The colour of the solution after treatment is slightly orange, due to the incomplete precipitation of ferrous cations. On the right hand side of the line corresponding to $[EtO^-] > 2\ [Fe^{2+}]$, the spinel cell parameter is constant and close to that of magnetite with $a = 0.8390$ nm; no additional phase is detected and no ferrous cations are detected in the solution after centrifugation.

According to these data, it is possible to produce simultaneously iron and magnetite nanoparticles by microwave heating of alcoholic solutions of a ferrous salt. Moreover, it is necessary to overcome a critical value of sodium ethoxide concentration (0.4 M). If the solution is not microwave treated, no metallic iron is detected in the precipitate. It contains only the spinel phase with a lattice parameter of 0.8375 nm. In the literature, it is well known that the disproportionation of iron (II) is only observed in very basic aqueous solutions (ferrous hydroxide with excess of base) [20–22]. It seems that in alcoholic solution, we observe the same behavior with a ferrous ethoxide type complex $Fe(OEt)_2$. On the right hand size of the straight line, a study versus the heating time shows that the two phases (spinel and iron) are produced instantaneously. This result is described in Fig. 4. Longer heating times (up to 30 min) do not seem to change the composition. The lattice parameter of the spinel phase increases with the heating times and reaches a value close to the magnetite one, $a = 0.8390$ nm, for heating times greater or equal to 10 minutes (Fig. 5). The grain size of the spinel phase and metallic iron are respectively close to 15 nm and 60 nm. XRD patterns are the same after 10 months in air. Hence, metallic iron is not oxidized by ambient air.

The morphology and the texture of the powders have been observed by using transmission electron microscopy. EDSX analysis shows that no sodium nor chlorine are present in the powders. The powder deposited on a copper grid is arranged in rods as shown by Fig. 6a. An enlargement shows elementary grains with a size close to 10 nm (Fig. 6b). For heating times greater or equal to 4 minutes, some crystals with a size between 50 and 150 nm are also detected (Fig. 6c). A dissolution followed by a recrystallization can explain the formation of these crystals. Electron diffraction has been performed on thin slices obtained by the ultramicrotome technique. One easily observes the rings corresponding to magnetite and spots corresponding to the metal (Fig. 7). Despite the fact that the sample contains metallic iron with an average grain size of 60 nm, it was difficult to point it out by microscopy, because either it is in too small amounts, or it is difficult to cut it with the ultramichrotome technique and it is pulled off.

Comparing with similar composites obtained by using a conventional heating, we obtained much lower grain sizes (10–20 nm compared to 100 nm–2 μm) in a less basic medium: sodium ethoxide concentration (1 M) compared to aqueous potassium hydroxide (14 M) [22]. Nevertheless, the amount of metal is most probably smaller than the 40 mol% obtained with the conventional heating. In fact, it is not easy to estimate iron percentage because chemical analysis is

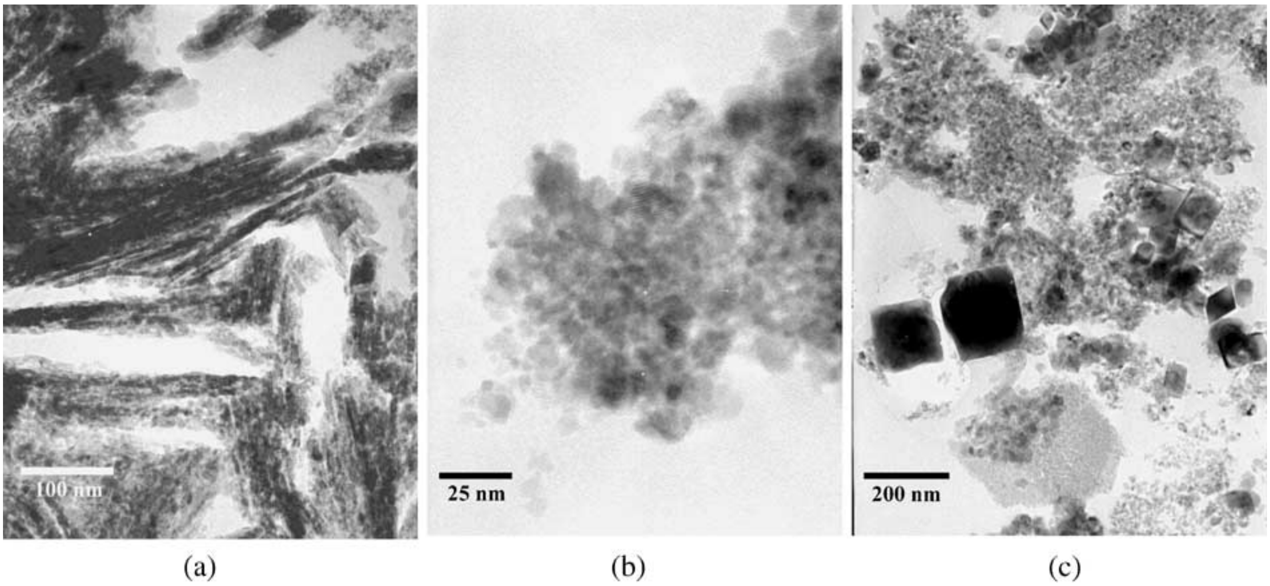

Figure 6 TEM micrographs for $[Fe^{2+}] = 0.3$ M and $[EtONa] = 0.7$ M treated 30 minutes.

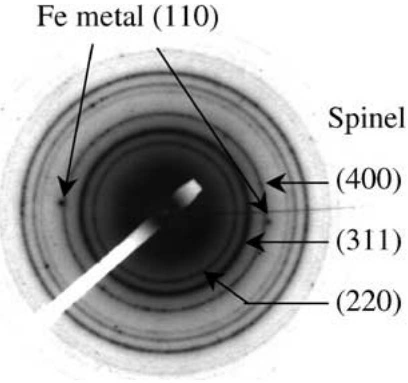

Figure 7 Electron diffraction pattern realized on thin slices of the sample obtained with $[Fe^{2+}] = 0.3$ M and $[EtONa] = 0.7$ M treated 4 minutes.

impossible. Results of the thermogravimetric analysis (TGA) are underestimated because of the presence of adsorbed water. The first estimation gives a percentage close to 11%.

4. Conclusion

In conclusion, the microwave-heating of alcoholic ferrous chloride solutions with sodium ethoxide can lead in a very short time (a few minutes) to several iron compounds. We have obtained hematite, spinel phase or an iron-magnetite mixture in relation to the precursor concentration. For specific operating conditions, we can produce iron-magnetite mixture inert to oxygen and very stable over time. Conventional hydrothermal treatments of alcoholic ferrous chloride solutions with sodium ethoxide cannot produce iron particles. The reason why the microwave heating drives the reaction along a different pathway compared to conventional heating is not clear. The time saving factor is close to ten comparing with similar composites obtained by using conventional heating of aqueous solutions (ten minutes by microwave heating corresponds to hundred minutes by conventional heating). Furthermore, microwave composites have a lower grain size but the amount of metal is likely smaller. Further work is required to improve the characterization of the nanocomposites produced and especially magnetic properties.

The RAMO system associates the iron (II) disproportionation with the advantages of microwave heating. Consequently, the microwave heating appears to provide an efficient source of energy in producing inert iron nanoparticles. The current interest in the use of microwaves is therefore associated with the attainment of new or improved properties as much as in purely economic benefit. This interest has occurred with the steadily growing applications of nanostructured materials. However, in many cases, applications of nanostructured materials cannot be fully exploited because of the restrictions imposed by the absence of suitable processing routes. The RAMO system is a batch system. It could be easily transposed to a continuous process with an industrial scale (several hundred kilograms by seconds).

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