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Short Report

Selective Oxidation of Amorphous Carbon by CO_2 to Produce Fe@C Nanoparticles from Bulky Fe/C Matrices

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In this work, a bulky Fe^0/carbon matrix obtained by a low cost and simple reduction/carbonization of Fe^{3+} salt with sucrose was treated with CO_2 to selectively oxidize the amorphous carbon to release the graphite like carbon coated magnetic Fe^0 particles. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman, X-ray diffraction (XRD), BET, thermogravimetric analysis (TG) (in CO_2) and particle size analyses showed that the treatment with CO_2 of the Fe/carbon bulky composite led to the selective oxidation of the more amorphous carbon with the formation of 125-132 nm Fe@C nanoparticles with surface areas of 217 $m^2\ g^{-1}$.

Keywords: Fe@C nanoparticles, activated carbon, CO_2 oxidation

Introduction

Magnetic nanoparticles have been extensively investigated in the last years for different applications such as catalyst support,[1-3] emulsion formation,[4] catalysts in biodiesel production,[5,6] photocatalysts[7,8] and waste water treatment.[9]

Magnetic particles can be composed of a magnetic nuclei coated with a protective layer of different materials to improve their stability and to introduce new surface properties and functionalities.[10] One of the most promising coatings is carbon due to its chemical stability, biocompatibility, possibility of surface modification and pore creation. Carbon coated magnetic nanoparticles can be produced by different methods such as arc discharge plasma,[11-13] pyrolysis of metallic complexes,[14] explosive reactions,[15] and continuous methods such as flame spray synthesis[16] and thermal plasma jet.[17] All the processes described above are relatively complex, expensive and demand special precursors. Different carbon coated magnetic nanoparticles have been also produced by chemical vapor deposition (CVD).[3,11,18] However, in general, these CVD procedures demand complex preparation of special nanostructured precursors.[19]

In this work, a versatile process to produce carbon coated magnetic nanoparticles based on the use of sucrose, iron salt and CO_2 is described. In this process, an aqueous solution of Fe^{3+} with sucrose is dried (equation 1) and thermally decomposed to form a solid amorphous carbon matrix containing Fe nuclei coated with a more organized graphitic carbon layer (equation 2). Sucrose can disperse Fe^{3+} very well and, by a simple thermal treatment, decomposes to form a carbon matrix which will reduce iron to form magnetic composite based on Fe^0, as described in previous work.[20] The Fe nanoparticles are coated with a more organized graphitic carbon layer whereas the rest of the matrix is composed mainly of amorphous carbon.[21] The isolation of these carbon coated Fe nanoparticles from the matrix was carried out by a simple selective oxidation of the amorphous carbon with CO_2 (equation 3). Figure 1 shows schematically this process. Carbon dioxide is a well-known selective oxidant of more defective carbon and it has been used to open carbon nanotubes[22] and to physically activate different types of coals.[23-25]

$$Fe^{3+}_{aq} + sucrose_{aq} \rightarrow Fe^{3+}/sucrose_{solid} \quad (1)$$
$$Fe^{3+}/sucrose_{solid} \rightarrow (Fe@C)/C_{matrix} \quad (2)$$
$$(Fe@C)/C_{matrix} + nCO_2 \rightarrow Fe@C_{free} + 2n\ CO \quad (3)$$

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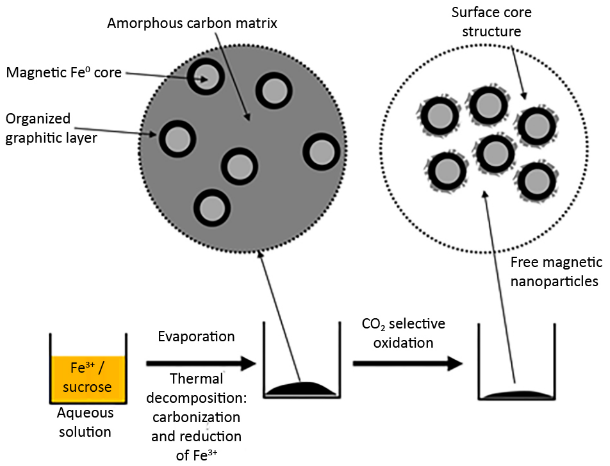

Figure 1. Schematic preparation of the Fe/carbon bulky composite followed by selective oxidation with CO_2 to produce the free Fe/C nanoparticles.

Experimental

Materials preparation

The magnetic material was obtained from a mixture of sucrose containing 8 wt.% of dispersed Fe^{3+} named as 8Fe. Initially, a $Fe(NO_3)_3.9H_2O$ solution containing 8 wt.% in iron was prepared at pH ca. 1. In a second step, the solution was heated and commercial sucrose was added slowly. The solution was evaporated to form a dark paste. This mixture was treated at 400, 600 and 800 °C under N_2 flow in a horizontal furnace (BLUE M. Lindberg) for 1 h. After this thermal treatment, the solid was extensively washed with water to eliminate organic contaminants and soluble Fe species. The preparation of these base bulky materials has been previously described.[20] The material containing 8 wt.% of iron and treated at 800 °C, named 8Fe800, was selectively oxidized in CO_2 atmosphere.

The selective oxidation with CO_2 was performed in a horizontal furnace (BLUE M.Lindberg) under a CO_2 flow of 50 mL min^{-1} and 250 mg of material heated at 10 °C min^{-1} up to 700 °C. The temperature was maintained at 700 °C to produce different burn-offs (carbon oxidation) of ca. 20, 40 and 50 wt.%.

Materials characterization

Transmission electron microscopy (TEM) analysis was done using a Tecnai G2-20 FEI equipment. TG analyses were carried out in a Shimadzu TGA-60, with a constant heating rate of 10 °C min^{-1} under a dynamic CO_2 flow (50 mL min^{-1}). Scanning electron microscopy (SEM) analysis was done using Quanta 200 ESEM FEG equipment. Raman spectra were obtained in a Senterra Bruker equipment, with excitation wavelength of 633 nm, a laser spot size of 20 µm with confocal imaging microscope, power of 2 mW and 30 scans with 2 seconds each at 10 different spots. The profile of light retention was recorded in a Shimadzu UV 2550 equipment, interfaced with a computer. The particle size tests were performed in a Zetasizer equipment using acetone as a dispersant in a glass container in 4 replicates for estimate the average size. The surface area was determined by nitrogen adsorption using the BET method with a 22 cycles of N_2 adsorption/desorption in an Autosorb 1 Quantachrome instrument. Magnetization measurements were carried out in a portable magnetometer with a fixed magnetic field of 0.3 T. Hysteresis loops were obtained at room temperature in a vibrating sample magnetometer (VSM) LakeShore 7404V.

Results and Discussion

The preparation of the Fe/C bulky composite from a Fe^{3+} salt and sucrose by a simple process has been described in a previous work.[20] Detailed analyses of one of the obtained composites (8Fe800: 8wt.% Fe treated at 800 °C) by TEM (Figure 2) showed the presence of a matrix composed of a more amorphous carbon with Fe particles (based on ca. 25% Fe^0 and ca. 54% Fe_3C).[20] The formation of a layer of more organized graphitic carbon coating is likely induced by the Fe surface or due to the heating on the particle surface during the reduction of the oxide. In order to produce free and isolated carbon coated Fe magnetic particles it is necessary to eliminate the amorphous carbon matrix.

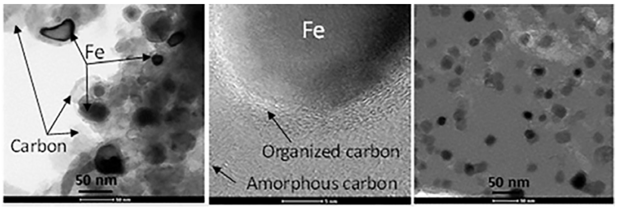

Figure 2. TEM images of the bulky sample 8Fe800.

As the amorphous carbon is much more reactive compared to more organized graphitic carbon,[26] it was investigated its selective oxidation using CO_2 (equation 4):

$$C_{amorphous} + CO_2 \rightarrow 2\,CO \quad (4)$$

In order to determine the temperature for selective oxidation, TG analysis in CO_2 has been carried out (Figure 3).

The TG curve for the sample 8Fe800 showed a continuous oxidation starting at 650 °C with three different processes as observed by derivative thermogravimetric analysis (DTG),

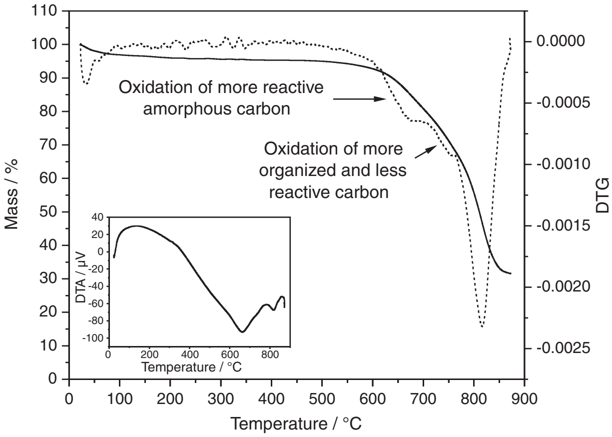

Figure 3. TG and DTG curves (in CO_2) for the sample 8Fe800 (detail: DTA curve).

i.e., two processes in the range 650-750 °C likely due to the oxidation of amorphous carbon and 750-900 °C due to the oxidation of more organized carbon. Based on these results, the composite 8Fe800 was treated with CO_2 at 700 °C for different times in order to remove the amorphous carbon and release the magnetic particles. The CO_2 reaction at 700 °C for 90, 150 and 200 min produced B.O. (burn-off, amount of carbon oxidized) of ca. 20, 40 and 50 wt.%.

SEM images (Figure 4) showed that the bulky particles are gradually oxidized converting bulky flat surface particles into agglomerates of well defined small particles after oxidation.

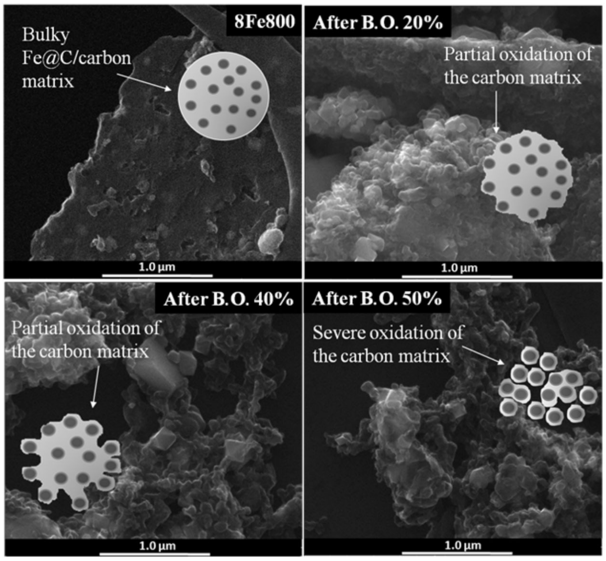

Figure 4. SEM images obtained of the sample 8Fe800 after selective oxidation with CO_2 to produce burn-offs of 20, 40 and 50 wt.%.

Raman spectra of the samples 8Fe800 after selective oxidation with CO_2 are shown in Figure 5. Raman spectrum of the sample 8Fe800 before oxidation is shown in the Supplementary Information (SI) section for comparison.

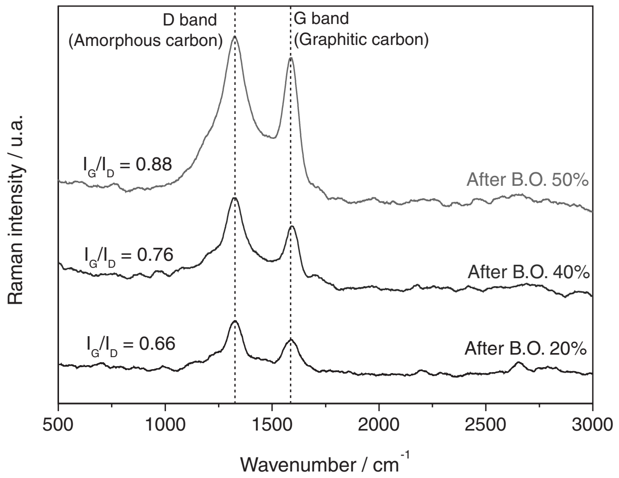

Figure 5. Raman spectra of the sample 8Fe800 after selective oxidation with CO_2 of 20, 40 and 50 wt.%.

It can be observed that the I_G/I_D of 0.66 after 20% B.O. increased after B.O. 40 and 50%, likely related to the consumption of the more amorphous defective carbon.

In order to separate different size fractions, the obtained particles of the sample 8Fe800 after 50% burn-off was dispersed in water. Figure 6 shows the suspension behavior by simple light scattering measurements at three different wavelengths (450, 600 and 750 cm^{-1}). It can be observed that immediately after dispersion, the light scattering is defined 100% due to the particles in suspension.

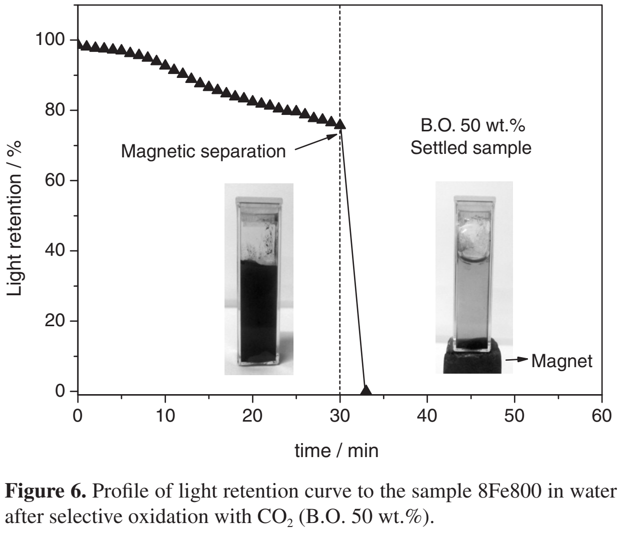

Figure 6. Profile of light retention curve to the sample 8Fe800 in water after selective oxidation with CO_2 (B.O. 50 wt.%).

After 30 min, the larger particles settled down, which can be clearly visualized. Separation, drying and weighting of the particles collected from the bottom of the UV-Vis cell suggested that approximately 20-30 wt.% of the particles settled in this initial period. The rest of the particles remained suspended in water with relative stability. Particle size estimation in a Zetasizer equipment suggested that after 15 min, the material obtained with burn-offs of 20,

Table 1. Carbon content, particles size, saturation magnetization and surface area of the samples

Sample	C content[a] / wt.%	Particles size[b] / nm	Saturation magnetization[c] / ($J\ T^{-1}\ kg^{-1}$)	BET surface area / ($m^2\ g^{-1}$)
8Fe800	61	–	22	138
8Fe800 after B.O. 20%	49	132	21	203
8Fe800 after B.O. 40%	37	128	–	–
8Fe800 after B.O. 50%	31	125	21	217

[a]Determined from TG results (see SI section) and burn offs values; [b]determined from zetasizer equipment; [c]obtained from VSM measurements.

40 and 50% showed average particle sizes of 132, 128 and 125 nm, respectively (Table 1). If a magnet was placed near to the test tube with the suspension, all the particles were attracted and removed from the aqueous media showing that all the particles are magnetic.

BET N_2 adsorption measurements showed that the composite precursor 8Fe800 (before CO_2 treatment) showed surface area of 138 $m^2\ g^{-1}$. On the other hand, the treatment of the 8Fe800 with CO_2 produced an increase of the surface area to 217 $m^2\ g^{-1}$ after selective oxidation of 50 wt.% with CO_2.

The suspended particles of the material 8Fe800 after 50% burn-off were analyzed by TEM (Figure 7). It can be observed the presence of isolated nanoparticles with sizes smaller than 50 nm. These nanoparticles are encapsulated by a carbon layer, which suggests that selective oxidation leads to removal of a more reactive carbon (amorphous carbon), remaining a more organized carbon as graphite, which encapsulates the nanoparticles forming a protective layer.

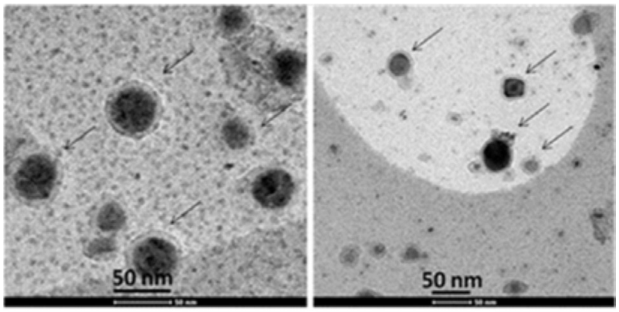

Figure 7. TEM images of the sample 8Fe800 after 50% burn-off.

Conclusions

A Fe/C bulky composite produced from Fe^{3+} and sucrose by a simple process can be treated with CO_2 at 700 °C for the selective oxidation of the more amorphous carbon to produce carbon coated magnetic Fe nanoparticles. The obtained material shows increased surface area (217 $m^2\ g^{-1}$) and is composed of particles with average size of ca. 130 nm formed by a Fe metal core coated with a more organized graphitic like carbon. This synthetic route is relatively simple and produces air/water stable versatile materials opening new and exciting application in catalysis and adsorption science. Preliminary results showed that Pd supported in these 8Fe800 materials produced excellent hydrogenation catalysts which can be easily recovered and reused for at least five times.

Supplementary Information

Supplementary information (Figures S1 and S2) is available free of charge at http://jbcs.org.br as PDF file.

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