Reproducibility of the Synthesis of Iron Oxide Nanoparticles Produced by Laser Pyrolysis

R. Alexandrescu a, V. Bouzas b, R. Costo c, F. Dumitrache a, M. A. García b, M. P. Morales. c, I. Morjan a, C. J. Serna c and S. Veintemillas-Verdaguer c

c Inst. Ciencia de Materiales de Madrid CSIC, Madrid, Spain

Abstract. During the development of the BONSAI Project, the need for high quantities of iron oxide nanoparticles with some specific characteristics intensified the problem of the reproducibility in the nanoparticle production. Given the fact that the reaction yield for the production of the smallest and more homogeneous nanoparticles (BONFEX4) was very low (in the range of 1g/day), the process had to be repeated several times. These repetitions involved the use of three different CO₂ lasers (two of monomodal gaussian beams TEM₀₀ mode with spot sizes of 4 and 3.5 mm and one multimodal of 4 mm spot size). Keeping constant the rest of the experiment parameters (including the laser density) we obtained similar powders in nature as revealed by X-ray diffraction, and similar particle size distributions, but with different magnetic properties. When the same laser was used the reproducibility of the magnetic properties increased significantly.

Keywords: Laser Pyrolysis, Nanoparticles, Superparamagnetism, Iron Oxide

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INTRODUCTION

The application of the laser pyrolysis to the preparation of magnetic colloids for biomedical applications demands homogeneous samples of e.g. 10 g of magnetic iron oxide. Even when the productivity of the preparation of iron oxide by this technique using ethylene as sensitizer is of 1g/hr in average, the productivity of the iron oxide nanoparticles below 5 nm of particle size is about to 20 mg/hr. The dispersion of these powders could generate the finest magnetic colloids and are demanded by the BONSAI consortium (sample BONFEX4). The obvious approach is to mix up different batches obtained with the same experimental parameters, but in order to do this safely, the experiment must be reproducible. In this work we tested this important issue using different lasers and repeating the same process in the same equipment.
EXPERIMENTAL DETAILS

The equipment for the production of iron oxide nanoparticles by laser pyrolysis has been previously described \(^2\). The main experimental parameters are the laser power density and the input rate of the iron pentacarbonyl. In the preparation of BONFEX4 the laser density was reasonably well controlled to 159 W/cm\(^2\) (standard deviation of 25 experiments 5.6 W/cm\(^2\)), but the evaporation rate of the iron pentacarbonyl ranged from 0.02 to 0.12 g/hr. The rest of the parameters (C\(_2\)H\(_4\) flux 9.0 sccm, coaxial N\(_2\) flux 22.0 sccm, windows N\(_2\) flux 720 sccm, air flux 40 sccm, pressure 400 mbar) are precisely controlled. In order to check the effect of the laser beam shape, we tested three laser beams: (B1) 4 mm diameter Gaussian shape (mode TEM\(_{00}\)), (B2) 3.5 mm diameter Gaussian shape (mode TEM\(_{00}\)) and (B3) 4 mm diameter multimode with a more even distribution of energy across the beam profile. Using the beam B2 we repeated the same experiment 13 times in order to evaluate the variability of the process when the same apparatus is employed.

The powder parameters employed for the comparison were: The Sherrer crystallite size (x) and unit cell (a) parameter obtained by X-Ray diffraction (XRD), the particle size (D) obtained by counting particles using the SCION Image ® computer program on the Transmission Electron Microscopy (TEM) images taken at 200K magnification, the carbon content obtained by elemental analysis and in selected cases the hysteresis cycle measured at room temperature using a VSM magnetometer.

RESULTS AND DISCUSSION

Plotting of the productivity (p [g/hr]) in front of the consumption rate (c [g/hr]) using the three laser beams, we obtained a straight line (p = 0.29 ± 0.02 c). This indicates that the chemical process is not dependent on the precursor input rate, probably due to the low proportion (2%) of the iron pentacarbonyl in the carrier gas/sensitizer ethylene.

The use of different laser beams at constant laser density had little effect on the particle and crystallite sizes, and impurity content (see Table 1), but affected the magnetic properties significantly (see Figure 1A). The results suggest that the more uniform distribution of energy of multimode beam B3, is more favorable for the production of magnetic nanoparticles than the commercial Gaussian beams.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>CELL PARAMETER</th>
<th>SHERRE S SIZE</th>
<th>TEM SIZE</th>
<th>C% w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>BONFEX4</td>
<td>(B1) 8.40 Å</td>
<td>2.4 nm</td>
<td>2.6 nm</td>
<td>2.45</td>
</tr>
<tr>
<td>BFX4R</td>
<td>(B2) 8.38 Å</td>
<td>2.9 nm</td>
<td>2.6 nm</td>
<td>3.02</td>
</tr>
<tr>
<td>RBONFEX4</td>
<td>(B3) 8.38 Å</td>
<td>2.6 nm</td>
<td>2.7 nm</td>
<td>2.22</td>
</tr>
</tbody>
</table>
Repetition of the same experiment in the same equipment showed Scherrer sizes of $3.5 \pm 0.5$ nm, TEM particle sizes $3.1 \pm 0.5$ nm (the standard deviation (0.5 nm) of the set of samples measured was much less than the standard deviation of the individual measure (2 nm) itself) and the carbon content $2.82 \pm 0.2$ % w/w. The magnetic measurements show good reproducibility in this case (Figure 1B), with saturation magnetization values of 11.86 and 11.19 emu/g sample respectively for the batches 4G and 4F.

CONCLUSION

The different batches produced using the same experimental setting are similar enough to be considered the same sample, and consequently they could be mixed. But when different laser systems are employed, the different distribution of energy in the laser beam profile strongly influences the magnetic properties of the samples, even under constant laser density.

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REFERENCES