Journal of Alloys and Compounds 643 (2015) S287–S296

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Theoretical and experimental influence of aerosol assisted CVD parameters on the microstructural properties of magnetite nanoparticles and their response on the removal efficiency of arsenic

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ARTICLE INFO

Article history:
Available online 8 January 2015

Keywords:
MNPs
AACVD
Hollow magnetite nanoparticles
Vapor deposition
Nanostructured materials

ABSTRACT

The development and optimization of methodologies to generate magnetite nanoparticles is currently an innovation topic. For a desired application such as arsenic removal from waste water, the generation of these nanostructures with specific microstructural properties is determinant. Therefore, it is necessary to understand the phenomenon during the nanoparticles formation process. Thus, in this work it is reported the influence of synthesis parameters of AACVD technique on the formation of magnetite nanoparticles. Parameters were according to: (1) synthesis temperature, (2) tubular reactor diameter, (3) concentration of the precursor solution and type of solvent, (4) carrier gas flow and (5) solvent type in the collection process. The effect of these synthesis parameters on the morphology, size and microstructure are discussed in detail and related with the mechanism of formation of the particles. Theoretical simulations were performed on two of these parameters (1 and 4). The microstructure and surface morphology of the different nanostructures obtained were characterized by field emission scanning electron and transmission electron microscopy. Subsequently two materials, were selected for further microstructural analysis. Finally, to determine the removal efficiency in the two materials the arsenic adsorption was evaluated. A major contribution of this work was the calculation of the number of spherical particles formed from a single drop of precursor solution. This calculation matched with the value found experimentally.

1. Introduction

Currently, solid, hollow or porous magnetite nanoparticles (MNPs) are being extensively studied due to their magnetic properties, porosity, crystallinity and surface area. These properties make particles suitable for biomedical and environmental applications [1–11]. In order to properly employ MNPs on those fields, the nanoparticles must achieve several properties such as size, high magnetization, high surface area and crystallinity. All these properties depend on the final morphology, size and structure developed by the MNPs during the synthesis [4,8,9,12–14]. One of the main topics in nanotechnology is the tailoring of the properties from the synthesis process [10,15,18]. However, it is very important that nanoparticles may be synthesized by low cost methodologies with potential for industrial scale application. In this sense, aerosol assisted chemical vapor deposition (AACVD) is a simple technique for one-step synthesis of hollow and porous MNPs. AACVD technique consists of three stages: (1) the formation of the cloud of the precursor solution, (2) transportation of the cloud by the carrier gas into the furnace where both, the chemical reaction and the solid particle transformation are carried out and, (3) the particle recovery process. The basics of the technique have been reported elsewhere [13,16–18]. The final morphology and structure of the MNPs by AACVD method greatly depend on the synthesis parameters such as furnace temperature, carrier gas flow, concentration and type of precursor and the tubular reactor diameter. In literature there are few works describing the phenomenon occurring inside the tubular reactor and the process of particle formation [18]; other works reported the numerical simulation of the drop–particle transformation process in the spray pyrolysis system [19,20]. Hence, it is necessary to study the effect of the processing parameters on the final properties of the MNPs. The aim of the present work is to study the effect of the synthesis parameters of the AACVD method on the final microstructure and adsorption

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http://dx.doi.org/10.1016/j.jallcom.2014.12.064
0925-8388/

properties of MNPs. Besides the detailed characterization provided, other contributions of the work include the calculation of the number of particles formed from one drop of precursor at two different temperatures of synthesis, and the removal efficiency of MNPs on water containing As^{+3} and As^{+5} ions.

2. Materials and methods

2.1. Theoretical simulation

The actual geometry of the furnace employed in the AACVD experiments was first simulated by SolidWorks-Fluidworks® software. The distribution of temperature, carrier gas velocity and heat transfer from the furnace into the tubular reactor, were calculated in this way. More simulation details were reported in references [13,18].

2.2. Synthesis of the MNPs at different conditions

MNPs were synthesized by AACVD technique according to the details previously reported [13,18], employing Iron (II) chloride (99.9%, Sigma–Aldrich) as the precursor. The parameters varied during the synthesis of the MNPs were: the concentration and type of solvent used in the precursor solution, temperature of the furnace, the diameter of the tubular reactor and the type of solvent used during the recovering process. The level of variation on each of the parameters is presented in Table 1. Carrier gas mixture flow rate (Ar:Air) was set at 250:4 $cm^3\ min^{-1}$. A total of 11 materials were synthesized, producing different types of MNPs; each experiment was identified with a capital letter from A to K.

2.3. MNPs microstructural characterization

The microstructure of the MNPs was analyzed in two field emission microscopes. The surface morphology was observed in a scanning electron microscope (SEM) JEOL JSM-7401F, while the microstructure was analyzed in a high resolution transmission electron microscope (HRTEM) JEOL JEM-2200FS. After analyzing the 11 materials by these techniques, two materials were selected (D and E) for further microstructural characterization such as particle size distribution, percentage of porosity and arsenic removal tests. Crystalline phases were identified by X-ray diffraction (XRD) in a Panalytical X-Pert system using Cu Kα radiation at 40 kV and 35 mA. Raman spectroscopy was employed for identifying the magnetite phase in the powders. The specific surface area was determined by the BET method using liquid nitrogen. Magnetic properties were evaluated with a vibrating sample magnetometer. All these tests allowed to properly determining the differences in microstructure, elemental composition, morphology, porosity and particle size, to correlate all these changes with the influence of the synthesis parameters [13,14].

2.4. Arsenic ions removal tests

Sodium arsenite (III) (>99%) and sodium arsenate heptahydrate (>98%) (both from Sigma–Aldrich) were dissolved separately in tridistilled water (JT Baker) to obtain stock solutions of As^{+3} and As^{+5}, respectively. Stock solutions were prepared a concentration of 0.05 ppm in a fixed volume of 100 mL. A sample of 10 mg of MNPs was added to each arsenic solution and thoroughly mixed with a mechanical stirrer during times of 1, 5, 10 and 15 min (this first part of the experiment is called contact time). After elapsing the contact time, mechanical agitation was stopped, and begins the second part of the experiment, which is the time of separation. In this time, MNPs were left to sediment by placing the beaker on a magnet of 1 T. Solution was maintained undisturbed by a recovery time of 30 min. To determine the real time of adsorption efficiency of nanoparticles, experiments were made by eliminating the separation time, the experiment was made under the same conditions described considering two contact times 1 and 10 min, after the contact time, samples were centrifuged immediately at 3500 rpm by 5 min. Then, the supernatant solution was removed and stored in a flask for further analysis. Each test was done in duplicate, together with a solution free of arsenic ions (blank solution). The remaining concentration of As^{+3}, As^{+5} and Fe in the solutions was quantified by atomic absorption spectroscopy (AAS GBC, model Avanta Sigma). After the removal tests, MNPs were dried and analyzed by both SEM and HRTEM. The relative concentration of the adsorbed arsenic was determined by energy dispersive spectroscopy (EDS) analysis.

Table 1
Variation of synthesis parameters in the AACVD method to obtain different materials.

Material	Temperature (K)	Precursor concentration (mol L^{-1})	Tubular reactor inner diameter (mm)	Solvent used in precursor solution- and the recovering process
A	773	0.01	9	Methanol–methanol
B	873	0.01	9	Methanol–methanol
C	973	0.01	9	Methanol–methanol
D [14]	723	0.05	15	Methanol–methanol
E [14]	773	0.05	15	Methanol–methanol
F	873	0.05	15	Methanol–methanol
G	773	0.05	6	Methanol–water
H	773	0.05	9	Methanol–water
I	773	0.05	15	Methanol–water
J	723	0.05	15	Methanol–water
K	723	0.05	15	Water–water

3. Results and discussion

3.1. Theoretical simulation of the temperature distribution inside the furnace and the carrier gas flow

The actual geometry of the furnace employed in the AACVD experiments, the distribution of temperature, carrier gas velocity and heat transfer from the furnace into the tubular reactor, were simulated by SolidWorks – FluidWorks®. New calculations were performed employing the following starting data: nominal temperature 773 K, diameter of the tubular reactor of 15 mm and carrier gas flow ratio of 1:0.015. Fig. 1a shows the temperature distribution inside the furnace for a nominal temperature of 773 K and Fig. 1(b and c) shows the carrier gas flow behavior inside the tubular reactor. Along the tubular reactor at approximately 23 cm from the entrance, the temperature reached 703 K. According to thermogravimetric analysis (TGA), this value is the minimal temperature required for the chemical decomposition of the iron precursor and the subsequent formation of iron oxide into the magnetite phase. In the middle zone of the furnace, about 25–70 cm after the entrance, the temperature inside the tubular reactor is close to the nominal temperature (Fig. 1a). Low temperatures at the entrance and exit of the tubular reactor were observed. This low temperature was reached in these zones because both ends of the tubular reactor are open and exposed to room temperature. Fig. 1b shows the temperature distribution in the carrier gas. The carrier gas enters at room temperature into the tubular reactor and starts to warm up as it travels through the reactor. This behavior is similar to that simulated with a nominal temperature of 723 K [14]. Fig. 1c shows the carrier gas velocity profile. Velocity is low near the wall of the tube, while the maximum velocity is achieved at the center of the reactor. This is a typical behavior provoked by the friction of gas molecules on the walls of the tubular reactor.

3.2. Influence of each parameter varied in the characteristics of the MNPs

Fig. 2 shows SEM and TEM images of the MNPs synthesized at the different conditions (materials A–K in Table 1). As observed in the figure, small variations in the parameters produce changes in morphology, microstructure and particle size.

3.2.1. The effect of temperature

This parameter was studied at three different temperatures: 773, 873 and 973 K. For the tubular reactor of 9 mm in diameter, these variations in temperature correspond to images A–C in Fig. 2, respectively. At 773 K, the material A is conformed of well-defined nanostructured hollow spheres with a porous surface formed of crystallites. The average spherical particle size was 250 nm. The fact of obtaining this material with these characteristics by the AACVD technique can be described by the following mechanism: the first step is the production of a cloud of droplets or aerosol, which is generated by the ultrasonic nebulizer. This cloud is transported into the tubular reactor by the carrier gas.