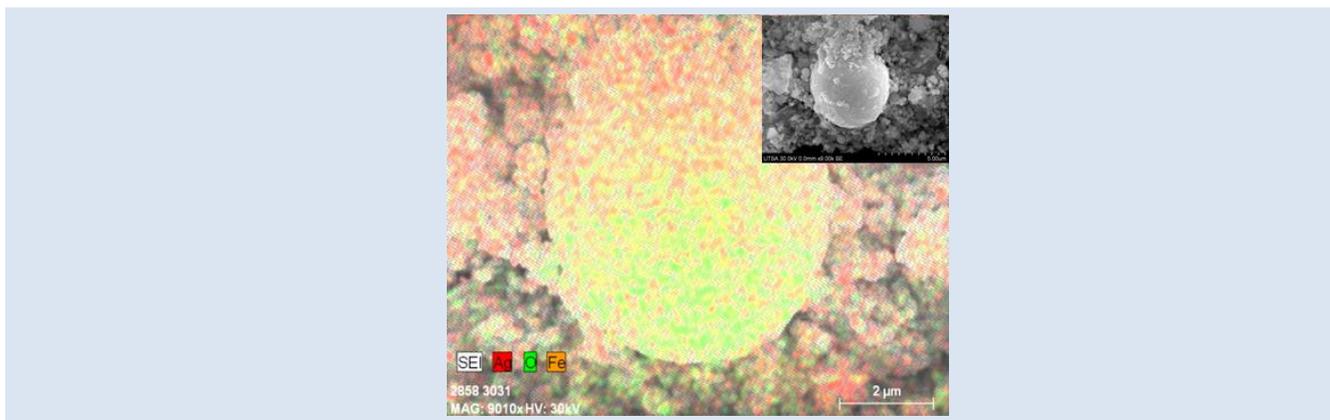


SYNTHESIS AND CHARACTERIZATION OF Ag NANOPARTICLES SUPPORTED IN BLAST FURNACE DUST MICROSPHERES

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ABSTRACT

We showed the feasibility to use blast furnace dust microspheres (BFDM), an industrial residue with magnetic properties, for the synthesis of silver nanoparticles (AgNP)/BFDM composites. A sol-gel Pechini modified method was used to synthesize AgNP/BFDM. AgNP formation was confirmed by SEM/EDS, which also showed a large Ag coverage on BFDM. Temperature-programmed reduction and oxidation (TPR/TPO) showed a strong interaction of AgNP with the surface iron species. The stability of reduced AgNP/BFDM, along with its magnetic properties, suggests that (AgNP)/BFDM composites may find application in catalysis and environmental remediation.

Keywords: silver nanoparticles; iron microspheres; sol-gel; Pechini method; steelmaking dust.

SÍNTESIS Y CARACTERIZACIÓN DE NANOPARTÍCULAS DE AG SOPORTADAS EN MICROESFERAS DE POLVO DE ALTO HORNO

RESUMEN

En este trabajo se presenta la factibilidad de emplear microesferas provenientes de polvo de Alto Horno (BFDM), el cual es un residuo industrial con propiedades magnéticas, para la síntesis de compósitos de nanopartículas de plata (AgNP)/BFDM. Para la síntesis de las (AgNP)/BFDM se usó el método sol-gel Pechini modificado. La formación de las nanopartículas de plata AgNP fue confirmada mediante MEB/EDS, observándose que la plata cubre las microesferas de polvo de Alto Horno. Se determinó que las nanopartículas de plata tienen una fuerte interacción en la superficie de las especies hierro del polvo de Alto Horno, a través de pruebas de oxidación y reducción a temperatura programada (TPR/TPO). La estabilidad de las nanopartículas soportadas en el polvo, (AgNP)/BFDM, y sus propiedades magnéticas, sugieren posibles aplicaciones en catálisis y remediación ambiental.

Palabras Claves: nanopartículas de plata; microesferas de hierro; método Pechini; polvos de acería.

1. INTRODUCTION

Functional nanomaterials made of magnetic iron oxide and silver nanoparticles (AgNPs) have unique properties and applications. Iron-based nanoparticles exhibit excellent magnetic properties, which make them very convenient in applications that require the separation of the material at a given stage of the process.

In the other hand, AgNPs find a myriad of applications because they are non-toxic, relatively inexpensive, and exhibit unique optical, catalytic and antibacterial properties [1]. In this way, recent reports show that magnetic iron oxide - silver core shell nanoparticles find widespread applications in imaging, drug delivery, catalysis and environmental remediation [2]. More specifically, such this kind of materials has been used as a new type of a broad temporal optical limiter for protecting light-sensitive objects [3]. In addition, the combination of magnetic and antibacterial features exhibited by these iron oxide-silver nanocomposites favored its application in medicine for the targeted transport of antimicrobials agents and its subsequent removal by an external magnetic field [1-3]. Recently, they have emerged as an alternative to conventional materials in catalysis because the adequate combination of magnetic and noble metal properties opens the possibilities to achieve desirable catalytic performance and effective separation by using external magnetic fields [4, 5]. In environmental remediation, they have recently used for the reduction of 4- nitrophenol and methylene blue in aqueous solutions [6]. Moreover, the coupling of silver electrical or thermal conductivity and the magnetic property of magnetite in a core-shell structure allows the design of novel materials with tunable electrical and magnetic properties.

Several synthetic methods have suggested for the preparation of magnetic core-silver shell nanoparticles including polyol or chemical reduction, impregnation, surface functionalization followed by deposition and solvothermal reduction [8]; few of these reports are related to the synthesis of AgNPs supported on magnetite particles [10, 11]. In the polyol reduction process, one of the more extended methods based on an alcohol-reduction reaction, silver ions (AgNO_3) are reduced to metallic silver (Ag^0) by reducing agents such as ethylene glycol and glucose. However, this method has two drawbacks because AgNPs is not stably

attached to the magnetite particles, and because it is difficult to obtain a uniform coating of AgNPs.

In this work, we propose to use furnace dust microspheres (BFDM), a residue of a steelmaking factory, as an inexpensive support to synthesize of AgNPs/BFDM composites. In this way, we also contribute to find applications for an industrial residue that otherwise may cause environmental issues. To avoid the drawbacks previously highlighted for the synthesis of magnetic core-silver shell nanoparticles, we used the sol-gel Pechini modified method to attach AgNPs on the surface of magnetite particles [11]. The Pechini method is based on an intensive mixing of positive ions in a solution, controlled transformation of the solution into a polymer gel, removal of the polymer matrix and development of an oxide precursor with a high degree of homogeneity. The advantages of Pechini method include a relatively low temperature of precursor treatment, and a high independence of the process conditions from the chemistry of positive ions contained in the final material [12-13]. From the practical point of view, the proposed method is simple and relatively inexpensive as to compare to other preparation methods. Thus, the objective of this work was to determine the feasibility to deposit AgNPs on an industrial residue to synthesize a composite with physicochemical properties suitable to find application in catalysis or environmental remediation.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

BFDM were obtained from a gas-dust cleaning system of a steelmaking industry. An average particle size of 80% $-44 \mu\text{m}$ was determined by dry analysis of meshes, using a Tyler sieve. Other chemical reagents used for the synthesis of the composites, i.e., silver nitrate (AgNO_3), citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), were chemical grade and they were purchased from Aldrich.

2.2 Composite synthesis

0.1 M AgNO_3 solution (50 mL) was mixed with 1 g of citric acid (CA). Then, BFDM residues (5 g) and ethylene glycol (EG) were added, in a molar ratio (CA:EG) of 1:4. Slurry was heated in a hot plate at constant agitation to evaporate the excess of water and then dried in air at 140°C by 24 h. The dry

mixture was finely ground in an agate mortar, and fired at temperature from 400 °C for 15 min in a tube furnace in air.

2.3 Characterization

2.3.1 Chemical

For chemical analysis, a representative sample of BFDM residue was dissolved and analyzed by atomic absorption spectroscopy (AAS) using a Thermo Electron Solar S4 spectrophotometer. The mineral phase composition of BFDM was determined by X-ray diffraction (XRD) using a Bruker D8 diffractometer and monochromatized CuK α radiation (generator tension = 40 kV, current = 30 mA). The XRD pattern was recorded from 5 to 70° (2 θ) with a step size of 0.02° and a counting time of 0.4s per step. In the other hand, the composite samples were analyzed by X-ray diffraction using a SIEMENS D-5000 diffractometer (25 mA and 35 kV), at scanning range of 20 to 55° (2 θ).

2.3.2 Physical

The textural characterization (i.e., surface area) of BFDM was performed using a physisorption analyzer Beckman Coulter model SA 3100; the corresponding N₂ adsorption isotherm was collected at 25 °C, after degasification at 110 °C. Additionally, BFDM morphological analysis was performed by scanning electron microscopy (SEM) using a Hitachi 5500 microscope at 10.2-10.5 A and 20 KV. In the other hand, the magnetic hysteresis properties of the composite samples were measured at room temperature using a vibrating sample magnetometer (VSM, Lakeshore 7400) with the inducing field sweeping from -15 to 15 kG.

2.3.3 Thermal

In addition, composite samples were subject to thermal treatments. First, 30 mg of the composite sample was subject to temperature programmed oxidation (TPO) using 30 ccm of 5% O₂/He and a heating rate of 10 °C/min. Then, a temperature programmed reduction (TPR) study was conducted by using 30 ccm of 5% H₂/Ar and a heating rate of 10 °C/min; a thermal conductivity detector was used to monitor the signal.

3. RESULTS AND DISCUSSION

3.1 Chemical and physical characterization

The chemical composition of BFDM obtained by AAS is shown in Table 1, where percentage of Fe corresponding to Fe total. However it is important to mention that the iron is in the form of Fe metallic and iron oxides (then, oxygen is the missing element not considered in Table 1). The chemical phases in the BFDM bulk were semi-quantitatively determined by XRD. Figure 1 shows the XRD pattern of a representative BFDM sample. Clearly, BFDM are formed by multiple compounds. The main phases found in the BF residue were a mix of metallic iron and iron oxides in the following proportionality: metallic Fe 40 %, wustite (FeO) 25%, magnetite (Fe₃O₄) 20% and hematite/franklinite (Fe₂O₃/ZnFe₂O₄) 15%. This composition agrees with the process of which BFDM comes from, where the powder was first in contact with a reductive atmosphere but then, as it was cooled with water, different oxidation conditions were formed. This is reflected in the diverse states of oxidation-reduction of Fe found in the samples. Therefore, partial oxidation of iron and iron oxides during heat treatment of BFDM is possible. Then, BFDM also will have Fe₂O₃ after heat treatment.

Table 1: BFDM chemical analysis (values in %).

SiO ₂	Al ₂ O ₃	CaO	MgO	Mn	Fe	Na ₂ O
3.10	0.45	12.94	3.36	0.70	41.55	0.984

The presence of Fe compounds made BFDM a magnetic material. The parameters of the HL at the field of 80 to 224 kOe were: remanent magnetization (Mr) of 7 memu (memu, a short of mili-emu = 10⁻³ emu/cm³ = A/m). These results indicated the low ability of the composites material to retain magnetism that has been induced. A magnetic saturation (Ms) of 69.93 to 78.99 memu and the coercive force (Hc) coercivity value of 120 to 128 Oe, and the HL shape obtained for BFDM are typical of ferromagnetism observed in magnetite mineral and soft ferrites. Based on these results, BFDM could be strongly attracted by a magnet. This feature is very important for the recovery of BFDM after use in any particular application. Results of N²

physisorption on BFDM showed a Type IV isotherm, corresponding to a mesoporous material. The specific surface area (SA) calculated by BET method was 21.7 m²/g. This SA was similar to those reported to magnetite synthesized by oxidative alkaline hydrolysis [10, 11].

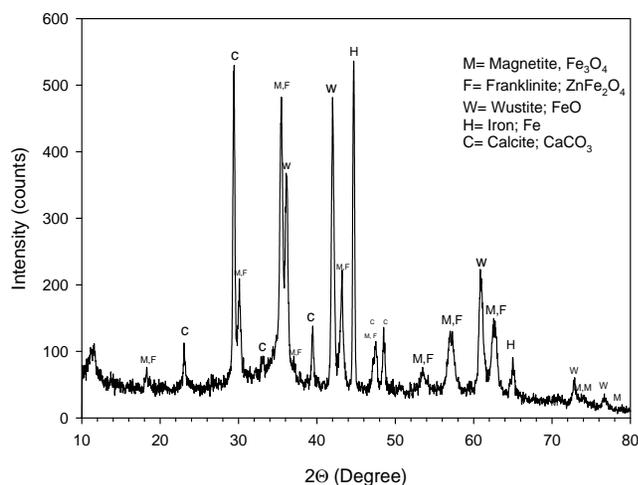


Figure 1. XRD pattern of a BFDM sample.

Figure 2 shows SEM micrographs of BFDM exemplifying the particles size and morphology. Microspheres (particle size less 10 μm) exhibited spherical-shaped particles and some side-striped eroded particles with octahedral shape; the shape variation is probably due to the intense erosion that occurs during the particles transport in the dust collection system. Figure 2b) shows SEM micrographs of AgNPs supported on BFDM microparticles. The shape of the iron oxides spheres in the BFDM was mostly spherical but size was very variable; some spheres were larger than 5 micron and some others were below 1 micron. In addition, in the left hand side micrograph several small bright particles (corresponding to silver) could be distinguished on the surface; many of these particles seemed to be attached to the surface. However, it was also possible to distinguish several bright particles that were not attached to the surface. In the right micrographs, an iron oxides particle of about 300 nm was shown. In the below right micrograph the size of the bright small silver particles was found between 35 and 55 nm.

Figure 3 shows a SEM micrograph and a chemical qualitative mapping of a BFDM particle. In the left micrograph, small bright spots were observed on the

microsphere surface as well as around it. The chemical microanalysis conducted using with SEM/Energy Dispersive X-Ray Spectrometer (EDS) showed that the small bright spots were metallic silver. The right micrograph indicate the chemical mapping, where the red color corresponding to silver, and green (oxygen) and orange (iron) color are combined to give the yellow color corresponding to BFDM particle, formed by iron metallic and iron oxides completely united or amalgamated (as if they were a single multicomponent phase), not as separate particles. This finding clearly confirmed that silver was supported in BFDM. SEM observations in different particles indicated that AgNPs nanoparticles were preferentially deposited on the smallest microspheres. This could be in agreement to that a bigger superficial area has better energetic conditions for the interaction or deposition of silver on the BFDM particles.

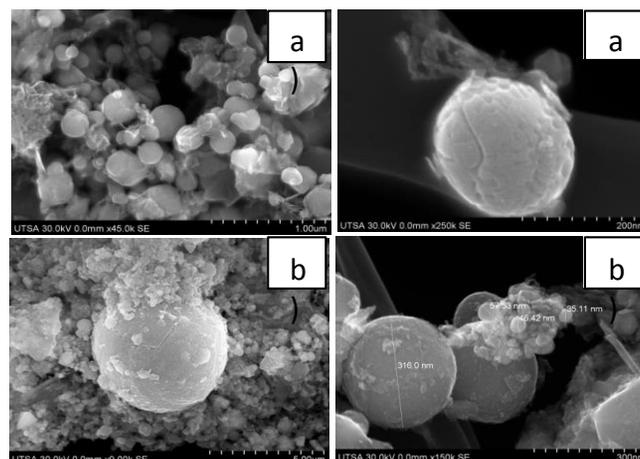


Figure 2. SEM micrographs of BFDM: a) without silver; b) with silver.

3.2 Thermal characterization

In a TPO/TPR analysis, a sample is placed in contact with a continuous stream of an oxidant/reducing gas mixture. Under this condition, the system temperature is linearly increased, at a specific heating rate. As a result, the chemical species on the surface might be oxidized/reduced. The variations in the concentration of the reducing/oxidant agent in the gas mixture are measured at the reactor outlet by using a thermal conductivity detector; the consumption reducing/oxidant agent are indicative that the sample has been oxidized/reduced. In this way, it is

possible to determine the oxidation/reduction temperature and, from the reducing/oxidant agent consumption, the stoichiometry of the process taking place on the surface. Results of TPO/TPR analysis are typically displayed as a graph of the O₂/H₂ consumption as function of temperature. In

several cases a cycle of TPO/TPR are suitable to, in the first treatment, fully oxidize the surface and then, in the last treatment, to characterize the reduction process taking place on the surface.

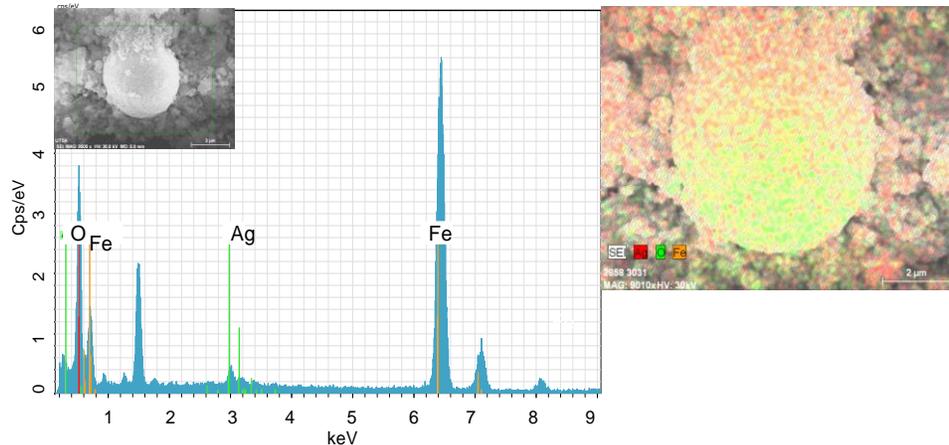


Figure 3. SEM/EDS micrograph (left) and chemical qualitative mapping (right) of Ag supported in BFDM.

Figure 4a) shows the TPO profile of an AgNP/BFDM sample. Clearly, there are at least three oxidation peaks at 297, 375 and 444 °C. In agreement with Free Energy ($\Delta G^{\circ}_{298^{\circ}\text{K}}$) data [14], the following oxidation process can be occurring in the following order:



Thermodynamically, the oxidation of Fe (Eq. 1) is the most favored. In this sense, the peak of 297 °C would indicate the oxidation of Fe⁰ to Fe²⁺; Due to the high Fe content in the sample, this peak is the most pronounced. The peak of 375 °C would indicate the oxidation of Fe²⁺ to Fe³⁺, mainly related to the oxidation of wustite (FeO) and magnetite (Fe₃O₄) according to Eqs. 2 and 4. Finally, the peak of 444 °C would indicate the oxidation of the magnetite (Eq. 3). Oxidation of the silver, if it is also thermodynamically possible (Eq. 5), would

only proceed at the end of the oxidation of the iron phases, in addition to considering that the intensity of the peak associated with the oxidation of the silver would be very short, due to the low content in the sample (<1% w/w). Then, it may be mentioned that the intensity of the oxidation peaks is related to the proportion or content of the oxidized species. The TPO profiles in Figure 4a) shows that in the presence of iron oxides, silver can stay in metallic state up to at high temperatures, since Fe goes through different oxidation states.

From Free Energy values the first reduction reaction corresponding to Eq. 6. This means that Ag₂O would be reduced first. As in oxidation, the low content of Ag₂O (in proportion to the sample) would show a small peak, probably with that observed at 250 °C. Then the reduction peak at 297 °C could be assigned to the reduction of Fe₂O₃ to Fe₃O₄ (Eq. 7). According Biabani et al. [12], the peak for pure Fe₂O₃ reduction is about 400 °C. Then, in the analyzed sample, the Fe₂O₃ reduction peak shifted from about 400 °C to 297 °C, which suggest that Fe₂O₃ is easier to be reduced in the presence of Ag. This is could be explained in terms of the affinity of oxygen by surface silver, which weakens the Fe–O bonds, and makes it easier to be reduced by

hydrogen. Then, a possible effect of silver was to activate oxygen where Fe₂O₃ acts as an effective oxygen donor [13].

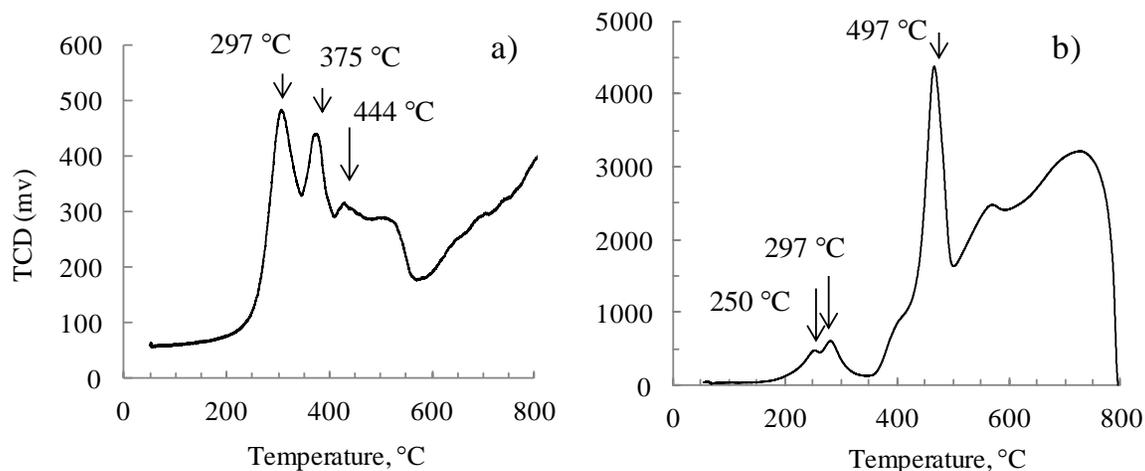
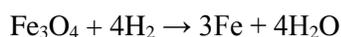
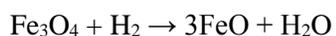
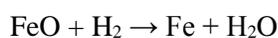
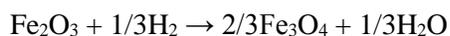
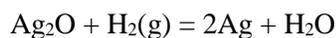


Figure 4. Thermal profile of AgNPs/BFDM: a) TPO; b) TPR.

Figure 4b) shows the TPR profile. According to



thermodynamic, the following reactions can occur:

$$\Delta G^\circ_{298^\circ\text{K}} = -54.007 \text{ kcal} \quad (6)$$

$$\Delta G^\circ_{298^\circ\text{K}} = -3.54 \text{ kcal} \quad (7)$$

$$\Delta G^\circ_{298^\circ\text{K}} = 2.051 \text{ kcal} \quad (8)$$

$$\Delta G^\circ_{298^\circ\text{K}} = 9.778 \text{ kcal} \quad (9)$$

$$\Delta G^\circ_{298^\circ\text{K}} = 15.93 \text{ kcal} \quad (10)$$

The same can be occurring to explain the reduction peak at 497°C, which could be associated to the reduction of magnetite Fe₃O₄ to FeO according to Eq. 9. However, it is important to consider that the magnetite is a metastable phase (Fe₃O₄ = Fe₂O₃·FeO) where the two states of oxidation of Fe coexist. Therefore, it is thermodynamically more feasible that the reduction of Fe⁺² a Fe⁰ occurs through the reaction described in Eq. 8, than directly by Eq. 9 and 10. Thus, silver would facilitate the donation of oxygen for the reduction to metallic Fe.

Relevantly, these results indicate that Ag would be active in a broad temperature range for catalytic applications. In summary, TPR and TPO results revealed that introducing AgNP to BFDM, coming from a residue of a steelmaking industry, enhanced the reduction of Fe₂O₃, indicating that a strong interaction between Ag and Fe₂O₃ occurred,

possible through the spillover of hydrogen from silver atoms.

4. CONCLUSIONS

AgNP were deposit on BFDM coming from a steelmaking industry by using the sol-gel Pechini modified method. The formation of AgNP was confirmed by SEM/EDS, which also showed that AgNP largely covered the BFDM particles. TPR/TPO analysis showed a Ag-Fe₂O₃ interaction. The stability of reduced AgNP supported on BFDM, along with magnetic properties characteristic of these microspheres, suggest they may have as a low-cost material for catalytic applications, including a best recovery of the material.

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