Lista celor 10 lucrari reprezentative care susţin conţinutul tezei

Conf. dr. ing. Stoia Marcela Elena

1 **Stoia M,** Barbu Tudoran L, Barvinschi P. Nanosized zinc and magnesium ferrites obtained from PVA-metal nitrates' solutions. J Therm Anal Calorim. 2013; 113(1): 11-19.

2 **Stoia M**, Barvinschi P, Barbu TL, Barbu M, Stefănescu M. Synthesis of nanocrystalline nickel ferrite by thermal decomposition of organic precursors, J Therm Anal Calorim. 2012; 108(3): 1033.

3 **Stoia M**, Pacurariu C, Istratie R, Barvinschi P, Locovei C. Thermoanalytical techniques: Excellent tools for the characterization of ferrite/SiO_2 nanocomposites and their precursors. J Therm Anal Calorim. 2016; 125: 1249.

4 **Stoia M**, Ștefănescu O, Vlase G, Barbu TL, Barbu M, Ștefănescu M. Silica matrices for embedding of magnetic nanoparticles. J Sol-Gel Sci Technol. 2012; 62(1): 31.

5 **Stoia M**, Barvinschi P, Barbu TL. Thermal decomposition of metal nitrates PVA-TEOS gels for obtaining M(II) ferrite/silica nanocomposites. J Therm Anal Calorim. 2013; 113(1): 21.

6 **Stoia M**, Barvinschi P, Barbu TL, Bunoiu M. Influence of polyols on the formation of nanocrystalline nickel ferrite inside silica matrices, J. Cryst. Growth. 2017; 457: 294.

7 **Stoia M**, Pacurariu C, Istratie R, Niznansky D. Solvothermal synthesis of magnetic Fe_xO_y/C nanocomposites used as adsorbents for the removal of methylene blue from wastewater. J Therm Anal Calorim. 2015; 121(3): 989.

8 **Stoia M**, Muntean E, Pacurariu C, Ciprian M. Thermal behavior of $MnFe_2O_4$ and $MnFe_2O_4$/C nanocomposite synthesized by a solvothermal method, Thermochim Acta. 2017; 652: 1.

9 **Stoia M**, Istratie R, Păcurariu C. Investigation of magnetite nanoparticles stability in air by thermal analysis and FTIR spectroscopy. J Therm Anal Calorim. 2016; 125: 1185.

10 **Stoia M**, Muntean C, Militaru B, $MnFe_2O_4$ nanoparticles as new catalyst for oxidative degradation of phenol by peroxydisulfate, J Environ Sci. 2017;53: 269.

J Therm Anal Calorim (2013) 113:11–19
DOI 10.1007/s10973-012-2888-z

Nanosized zinc and magnesium ferrites obtained from PVA–metal nitrates' solutions

Marcela Stoia · Lucian Barbu Tudoran · Paul Barvinschi

Received: 20 September 2012 / Accepted: 11 December 2012 / Published online: 10 January 2013

Abstract The paper presents a study regarding the possibility of obtaining zinc and magnesium ferrites starting from poly(vinyl alcohol)–metal nitrates solutions. By controlled heating of these solutions, a redox interaction takes place leading to the formation of some coordination compounds of the involved metal cations with the oxidation products of poly(vinyl alcohol) (PVA). FT-IR spectroscopy has evidenced the disappearance of the NO_3^- anions at 140 °C due to the redox interaction with PVA. Thermal analysis evidenced the difference in the interaction of the individual metal nitrates and PVA and thus the particularity of the preparation of each ferrite. The thermal decomposition of the synthesized precursors was finished below 400 °C as resulting from both thermal analysis and FT-IR spectroscopy. The obtained ferrites powders consist of fine nanoparticle with diameters ranging from 10 to 30 nm for the powders annealed at 500 °C, as resulting from the SEM images. The specific surface area of the powders obtained at 500 °C was 32.2 $m^2\ g^{-1}$ for $ZnFe_2O_4$ and 21.7 $m^2\ g^{-1}$ for $MgFe_2O_4$, characteristic of nanoscaled powders. The increasing of the annealing temperature at 1,000 °C leads to sintering of both ferrites, more advanced in the case of zinc ferrite.

M. Stoia (✉)
University Politehnica Timisoara, Piata Victoriei no. 2, 300006 Timisoara, Romania
e-mail: marcela.stoia@chim.upt.ro

L. B. Tudoran
Babes-Bolyai University, 5-7 Clinicilor Street, 400006 Cluj-Napoca, Romania

P. Barvinschi
West University of Timisoara, Bv. V. Parvan no. 4, 300223 Timisoara, Romania

Keywords Carboxylates · Ferrite · Nanoparticles · Poly(vinyl alcohol) · Thermal analysis

Abbreviations

PVA	Poly(vinyl alcohol)
FT-IR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

Introduction

Ferrites are well-known materials for their wide applications not only in the field of magnetic and electronic materials but also as catalysts and photo-catalysts [1]. Nanostructured ferrite exhibits unusual physical and chemical properties, which are significantly different from those of conventional bulk materials due to its extremely small grain size or large specific surface area. These properties make them interesting for biomedical applications [2]. Thus, the preparation and characterization of the nanocrystalline ferrite powders have attracted increasing attention in the last decade [3]. Lately, many investigations have been focused on the controlled synthesis of ferrite nanoparticles and also on the correlation between properties and the nanoparticle size/process parameters [4].

Many synthesis techniques such as sol–gel [5], coprecipitation [6], mechanochemical [7], microemulsion [8], hydrothermal [9], thermal decomposition of precursors [10], and others have been used to prepare ferrite nanoparticles.

PVA-based methods belong either to sol–gel or to precursor thermal decomposition methods [11, 12]. PVA acts as a metal chelating agent and thereby inhibits the segregation of metals during heating, but can also act as a fuel

J Therm Anal Calorim (2012) 108:1033–1039
DOI 10.1007/s10973-011-1903-0

Synthesis of nanocrystalline nickel ferrite by thermal decomposition of organic precursors

Marcela Stoia · Paul Barvinschi · Lucian Barbu Tudoran · Mirela Barbu · Mircea Stefanescu

ICMVTT2011 Conference Special Chapter

Abstract Nickel ferrite powders were synthesized by thermal decomposition of the precursors obtained in the redox reaction between the mixture of $Ni(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ with polyalcohol: 1,4-butanediol, polyvinyl alcohol and also with their mixture. During this reaction the primary C–OH groups were oxidized at –COOH, while secondary C–OH groups at C=O groups. The carboxylic groups formed coordinate to the present Ni(II) and Fe(III) cations leading to carboxylate type compounds, further used as precursors for $NiFe_2O_4$. These precursors were characterized by thermal analysis and FT-IR spectrometry. All precursors thermally decomposed up to 350 °C leading to nickel ferrite weakly crystallized. By annealing at higher temperatures, nanocrystalline nickel ferrite powders were obtained, as resulted from XRD. SEM images have evidenced the formation of nanoparticulate powders; these powders present magnetic properties characteristic to the oxidic system formed by magnetic nanoparticles.

Keywords Butanediol · Nickel ferrite · Nanoparticles · Polyvinyl alcohol · SEM

M. Stoia (✉) · M. Barbu · M. Stefanescu
Faculty of Chemistry and Chemical Engineering, University "Politehnica" Timisoara, P. Victoriei No. 2, 300006 Timisoara, Romania
e-mail: marcela.stoia@chim.upt.ro

P. Barvinschi
Faculty of Physics, West University of Timisoara, Bv. V. Parvan No. 4, 300223 Timisoara, Romania

L. B. Tudoran
Electron Microscopy Center, Faculty of Biology & Geology, Babes-Bolyai University, 5-7 Clinicilor Street, 400006 Cluj-Napoca, Romania

Abbreviations

1,4BG	1,4-butanediol
PVA	Polyvinyl alcohol

Introduction

Development of spinel ferrite nanoparticles has been intensively pursued because of their technological and fundamental scientific importance. Ferrites have received great attention as a result of their magnetic and electronic properties. It is well known that the chemical, structural, and magnetic properties of spinel ferrite nanoparticles are strongly influenced by their composition and microstructures, which are sensitive to the preparation methodologies [1]. Many ferrites with the spinel structure, MFe_2O_4 (where M: Ni, Zn, Mn, Co, Cd or their mixtures) are extensively used in a number of electronic devices. This is because of its high permeability at high frequencies, remarkably electrical resistivity, mechanical hardness, chemical stability, and reasonably low cost. Since the last decade, quite new and interesting magnetic properties have been reported for nanocrystalline spinel ferrites [2]. Spinel-type ferrite nanoparticles have gained great interest in the past few years because of their good electromagnetic performance and their applications in information storage, medical diagnosis technology, sensor technology, magnetic warming and cooling technology [3], efficient hyperthermia agents for cancer therapy [4], important catalysts for CO_2 and H_2O decomposition [5], and gas sensors for gases like liquefied petroleum gas, ethanol, CO, and CH_4 [6].

$NiFe_2O_4$ is one of the most important spinel ferrites which have attractive properties for the application as soft magnets and low loss materials at high frequencies.

J Therm Anal Calorim (2016) 125:1249–1263
DOI 10.1007/s10973-016-5394-x

Thermoanalytical techniques

Excellent tools for the characterization of ferrite/SiO_2 nanocomposites and their precursors

Marcela Stoia[1,2] · Cornelia Păcurariu[1] · Roxana Istratie[1] · Paul Barvinschi[3] · Cosmin Locovei[2]

Received: 13 November 2015 / Accepted: 7 March 2016 / Published online: 19 March 2016

Abstract Thermal analysis and FTIR spectroscopy were used to investigate the formation and thermal decomposition of several manganese ferrite precursors, obtained in the interaction between a mixture of manganese(II) nitrate and iron(III) nitrate (molar ratio 1:2) and different polyols/polyvinyl alcohol, 1,2-propanediol, and ethylene glycol, naked or embedded in silica gel. All prepared precursors consisted in mixture of Mn(II) and Fe(III) carboxylates, obtained through the polyol oxidation by nitrates ions. Similar manganese ferrite precursors were obtained in silica gel also. By the thermal decomposition of the naked precursors, manganese ferrite was obtained at 300 and 400 °C, as fine nanoparticles, with diameters up to 15 nm. Above 400 °C, the manganese ferrite has begun to decompose, due to the Mn(II) oxidation to Mn(III). At 700 °C, only crystalline phases containing Mn(III) were evidenced in the XRD patterns. In case of the precursors embedded in silica gel, their thermal decomposition took place at higher temperatures. Manganese ferrite was partially stabilized by the silica matrix. Thus, manganese ferrite was present in silica matrix, even at 1000 °C, with bixbyite ($FeMnO_3$) impurities. Pure manganese ferrite embedded in silica matrix was obtained in all cases, after annealing the powders obtained at 400 °C, in argon atmosphere, at 1000 °C. The magnetic behavior of the manganese ferrite/silica nanocomposites obtained at 1000 °C in air and in argon was superparamagnetic, with maximum magnetization values of 25 emu g^{-1}.

Keywords Thermal analysis · Carboxylates · Polyols · Silica · Manganese ferrite · Nanocomposites

Introduction

Over the past few years, magnetic nanoparticles have been explored for several biomedical applications such as facile gene delivery [1], MRI contrast agents [2], hyperthermia cancer treatment [3], and drug delivery applications [4]. In order to avoid aggregation, the nanoparticles can be dispersed in a matrix, leading to magnetic nanocomposite materials. Magnetic nanocomposites have peculiar and tunable properties, mainly depending on particle size and distribution of the nanocrystals, morphology and porosity of the matrix and interaction of the nanocrystals and the matrix [5]. The combination of mesoporous silica with magnetic nanoparticles and other functional molecules has gained increasing research interest among scientists in the last years [6]. Manganese ferrite nanoparticles ($MnFe_2O_4$) have received increasing attention for their remarkable magnetic properties, $MnFe_2O_4$ being a soft magnetic material with low coercivity, and moderate saturation magnetization, combined with a good mechanical hardness [5]. Magnetic manganese ferrite–silica nanocomposites and similar to them can be used as efficient adsorbents and catalysts [7, 8] and

Electronic supplementary material The online version of this article (doi:10.1007/s10973-016-5394-x) contains supplementary material, which is available to authorized users.

✉ Marcela Stoia
marcela.stoia@upt.ro

[1] Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timişoara, 6 Pârvan Blv., 300223 Timisoara, Romania

[2] Research Institute for Renewable Energy, Politehnica University Timişoara, P-ta Victoriei No. 2, 300006 Timisoara, Romania

[3] Faculty of Physics, West University of Timisoara, Bv. V. Pârvan, No. 4, 300223 Timisoara, Romania

J Sol-Gel Sci Technol (2012) 62:31–40
DOI 10.1007/s10971-012-2679-9

ORIGINAL PAPER

Silica matrices for embedding of magnetic nanoparticles

Marcela Stoia · Oana Ştefănescu · Gabriela Vlase · Lucian Barbu-Tudoran · Mirela Barbu · Mircea Ştefănescu

Received: 28 November 2011 / Accepted: 6 January 2012 / Published online: 24 January 2012

Abstract This paper presents a study regarding the formation of hybrid gels starting from tetraethyl orthosilicate (TEOS), polyvinyl alcohol (PVA) and 1,3-propanediol (PD) and their thermal evolution to mesoporous silica matrices. The possibility of obtaining homogenously dispersed cobalt ferrite inside the silica matrix starting from (TEOS–PVA–PD–Metal Nitrates) gels was also studied. The formation of the hybrid gels TEOS/PVA/PD with different compositions was studied by FT-IR spectrometry and thermal analysis, in order to evidence the interaction between the diol with the organic and the inorganic polymers. Both thermal analysis and FT-IR spectrometry have evidenced the formation of physical and chemical interaction between polyols and the siloxane network. Elemental mapping performed by SEM-EDX technique evidenced the formation of homogenous hybrids both in the presence of the absence of 1,3-propanediol. SEM images of the powders obtained by annealing the hybrid xerogels at 600 °C have evidenced the formation of mesoporous silica. By thermal treatment of the (TEOS–PVA–PD–Metal Nitrates) gels, 30%$CoFe_2O_4$/70%SiO_2 (mass percent) nanocomposites uniformly dispersed in silica matrix with characteristic magnetic properties, have been successfully synthesized.

Keywords Hybrid gels · PVA · 1,3-propanediol · Silica · Cobalt ferrite · Nanocomposite

1 Introduction

Polyvinyl alcohol (PVA) is a synthetic biocompatible polymer with a large number of hydroxyl groups that can reacts with several functional groups, which makes feasible a number of grafting modifications and cross-linking reactions of the polymer bone [1, 2]. Chemical cross-linking is a highly versatile method to create and modify polymers, where the mechanical, thermal and chemical stability can be improved. In the last decade PVA was intensively studied in order to be used in sensors and drug delivery system [2].

Polyvinyl alcohol hydrogels have been widely studied as water soluble polymers for numerous biomedical and pharmaceutical applications due to the advantages of nontoxic, non-carcinogenic and bioadhesive properties. Mostly water-soluble polymers have been used as reagents that will undergo physical or chemical cross-linking processes. They can also be blended with other water soluble polymers and undergo cross-linking process either physically or chemically [3]. Organic–inorganic hybrids that combine characteristics of organic and inorganic polymers lead to new high performance or high functional materials that will present advantages of the both components. Hybrids PVA/SiO_2 has been obtained from PVA/tetraethyl orthosilicate (TEOS) gels using cross-linking agents as glutaraldehyde [4] and sulfosuccinic acid [5]. Other studies

M. Stoia (✉) · O. Ştefănescu · M. Barbu · M. Ştefănescu
Faculty of Industrial Chemistry and Environmental Engineering, University "Politehnica", P-ta Victoriei no.2, 30006 Timisoara, Romania
e-mail: marcela.stoia@chim.upt.ro

G. Vlase
Research Centre "Thermal Analysis in the Environmental Field", West University of Timisoara, Str. Pestalozzi, no. 16, 300115 Timisoara, Romania

L. Barbu-Tudoran
Faculty of Biology and Geology, Electron Microscopy Center, Babes-Bolyai University, 5-7 Clinicilor Street, 400006 Cluj-Napoca, Romania

J Therm Anal Calorim (2013) 113:21–30
DOI 10.1007/s10973-012-2786-4

Thermal decomposition of metal nitrates

PVA–TEOS gels for obtaining M(II) ferrite/silica nanocomposites

Marcela Stoia · Paul Barvinschi · Lucian Barbu-Tudoran

Received: 20 September 2012 / Accepted: 16 October 2012 / Published online: 7 November 2012

Abstract The paper presents a study regarding the preparation of 40 %$M^{II}Fe_2O_4$/60 %SiO_2 nanocomposites (M = Ni, Zn, Cu) by thermal decomposition of metal nitrates—poly(vinyl alcohol)–tetraethyl orthosilicate gels. Thermal analysis and FT-IR spectroscopy have evidenced that a redox reaction takes place between PVA and NO_3^- ions in the pores of the formed hybrid gels. The result of this redox reaction is the formation of carboxylate-type coordination compounds that have the role of a precursor of the ferrite nanoparticles. By thermal decomposition of these precursors inside the silica matrix, the corresponding MFe_2O_4/SiO_2 nanocomposites are obtained starting with 600 °C, as resulting from XRD analysis. Elemental maps of the corresponding involved elements M (Ni, Zn, Cu), Fe, and Si have confirmed the homogenous distribution of the ferrite nanoparticles within the silica matrix. TEM images have shown that the nanocomposites were obtained as fine nanoparticles, with diameter up to 20 nm. All nanocomposites 40 %$M^{II}Fe_2O_4$/60 %SiO_2 obtained at 1000 °C presented magnetic properties characteristic to this type of nanocomposite.

M. Stoia
University Politehnica Timisoara, Piata Victoriei no.2, 300006 Timisoara, Romania

P. Barvinschi (✉)
West University of Timisoara, Bv. V. Parvan no. 4, 300223 Timisoara, Romania
e-mail: pc_barvi@yahoo.fr

L. Barbu-Tudoran
Babes-Bolyai University, 5-7 Clinicilor Street, 400006 Cluj-Napoca, Romania

Keywords Ferrite · Nanocomposites · Poly(vinyl alcohol) · Sol–gel · Silica

Abbreviations

PVA	polyvinyl alcohol
TEOS	tetraethyl orthosilicate
FTIR	Fourier transform infrared spectroscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction

Introduction

Nanosized particles exhibit unique chemical and physical properties compared to the corresponding bulk materials. Modern applications of different technologies ask for materials with better control on their size and on their properties. Composite materials are ideal from this point of view, combining among crystalline, amorphous, and polymer phases to enrich and enhance the properties. [1]. Nanocomposite materials composed from nanometric single or mixed metal oxide nanoparticles embedded in amorphous matrices reveal in particular more interesting magnetic, electric, and catalytic properties [2].

Nanocomposites constituted by particles dispersed in an inert matrix present unique properties, which significantly depend not only on the size and distribution of the particles, but also on the matrices' morphology and porosity. Sol–gel synthesis is a successful technique in nanocomposite synthesis due to the advanced control on the composition, purity, homogeneity, size, and properties of the dispersed nanoparticles [3]. There are though possibilities, due to the high surface of the interface between the

Journal of Crystal Growth 457 (2017) 294–301

Contents lists available at ScienceDirect

Journal of Crystal Growth

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

Influence of polyols on the formation of nanocrystalline nickel ferrite inside silica matrices

Marcela Stoia [a], Paul Barvinschi [b,*], Lucian Barbu-Tudoran [c], Mădălin Bunoiu [b]

[a] Research Institute for Renewable Energy, University Politehnica Timisoara, Victoriei Square No. 2, 300006 Timisoara, Romania
[b] Faculty of Physics, West University of Timisoara, Bv. V. Parvan No. 4, 300223 Timisoara, Romania
[c] Electron Microscopy Center, Faculty of Biology and Geology, "Babes-Bolyai" University, Clinicilor Street No. 5-7, 400006 Cluj-Napoca, Romania

ARTICLE INFO

Communicated by Falini Giuseppe
Available online 20 May 2016

Keywords:
A1. Characterization
A1. Crystallites
B1. Inorganic compounds
B2. Magnetic materials
B1. Nanomaterials

ABSTRACT

We have synthesized nickel ferrite/silica nanocomposites, using a modified sol–gel method that combines the sol–gel processing with the thermal decomposition of metal-organic precursors, leading to a homogenous dispersion of ferrite nanoparticles within the silica matrix and a narrow size distribution. We used as starting materials tetraethyl orthosilicate (TEOS) as source of silica, Fe(III) and Ni(II) nitrates as sources of metal cations, and polyols as reducing agent (polyvinyl alcohol, 1,4-butanediol and their mixture). TG/DTA coupled technique evidenced the redox interaction between the polyol and the mixture of metal nitrates during the heating of the gel, with formation of nickel ferrite precursors in the pores of the silica-gels. FT-IR spectroscopy confirmed the formation of metal carboxylates inside the silica-gels and the interaction of the polyols with the Si–OH groups of the polysiloxane network. X-ray diffractometry evidenced that in case of nanocomposites obtained by using a single polyol, nickel ferrite forms as single crystalline phase inside the amorphous silica matrix, while in case of using a mixture of polyols the nickel oxide appears as a secondary phase. TEM microscopy and elemental mapping evidenced the fine nature of the obtained nickel ferrite nanoparticles that are homogenously dispersed within the silica matrix. The obtained nanocomposites exhibit magnetic behavior very close to superparamagnetism slightly depending on the presence and nature of the organic compounds used in synthesis; the magnetization reached at ~5 kOe magnetic field was ~7 emu/g for all composites.

1. Introduction

Magnetic spinel ferrites MFe_2O_4, where M usually represents one or, in mixed ferrites, more than one of the divalent transition metals Mn, Fe, Co, Ni, Cu and Zn, or Mg and Cd, are an important class of magnetic materials. These spinel ferrites have remarkable magnetic properties, physical flexibility, high electrical resistivity, mechanical hardness and chemical stability [1]. Their properties remarkably change when the size of the particles reaches the nanometer range. Due to their unique magnetic properties which can be influenced by their shape, particle size and their composites with other materials, nickel ferrite ($NiFe_2O_4$) nanoparticles have been widely studied [2,3]. Nickel ferrite based nanomaterials have different practical applications in high frequency devices, power transformers, and gas sensors [4]. There are also potential applications of superparamagnetic nickel ferrite nanoparticles in medicine for local hyperthermia and targeted delivery of drugs in the body [5], as well as in some catalytic processes [6]. However, magnetic nanoparticles have a strong tendency to aggregate due to interparticle magnetic interactions and large nanoparticle surface reactivity. In order to avoid unwanted crystallite coarsening and particle aggregation, different routes like dispersion of the particles in various matrices (ion exchange resin [5], polymers [7,8] and silica [9,10]) or surface coating [11] were adopted. Composite materials formed by metallic or oxide particles dispersed in ceramic or vitreous matrices have important applications in areas such as catalysis and electronics [12]. Directional surface design and chemical engineering of nanocomposite layers opens enormous opportunities for creating unique magnetic adsorbents and next-generation drugs. Mesoporous materials formed by template synthesis have attracted increasing attention as potential materials for catalysis, separation and adsorption of molecules [6]. Chemical co-precipitation or microemulsion methods can be used to obtain ferrite nanoparticles well-encapsulated in silica shells and isolated from each other, while the ferrite nanoparticles prepared by sol–gel technique are confined in the silica matrix [13]. Generally, the sol–gel technique is considered as an

* Corresponding author.
E-mail address: pc_barvi@yahoo.fr (P. Barvinschi).

http://dx.doi.org/10.1016/j.jcrysgro.2016.05.034
0022-0248/

J Therm Anal Calorim (2015) 121:989–1001
DOI 10.1007/s10973-015-4641-x

Solvothermal synthesis of magnetic Fe_xO_y/C nanocomposites used as adsorbents for the removal of methylene blue from wastewater

Marcela Stoia[1,2] · Cornelia Păcurariu[1] · Roxana Istratie[1] · Daniel Nižňanský[3]

Received: 2 October 2014 / Accepted: 11 March 2015 / Published online: 26 March 2015

Abstract Magnetic iron oxides/carbon nanocomposites have been synthesized by a facile, one-step solvothermal method. XRD analysis evidenced the presence of a spinel phase in all samples, while FT-IR analysis suggested the presence of magnetite in the prepared samples. Mössbauer spectra, registered after 2 month, evidenced the complete transition of magnetite into maghemite. SEM images showed homogenous spherical nanoparticles with diameters up to 20 nm, smaller in case of the sample without carbon. The magnetic measurements showed that the saturation magnetization (Ms) value decreases with the increase in carbon content in composites. The values of Ms were higher than 30 emu g^{-1}, allowing the magnetic separation of the adsorbents. The Fe_xO_y/C and Fe_xO_y/2C nanocomposites were tested as adsorbents for methylene blue; the removal efficiency has increased with the carbon content of the adsorbents. The kinetic studies revealed that the adsorption process followed the pseudo-second-order model and the equilibrium data were correlated by the Redlich–Peterson isotherm.

Keywords Solvothermal · Iron oxides · Nanocomposites · Thermal analysis · Adsorbents · Methylene blue

✉ Marcela Stoia
marcela.stoia@upt.ro

[1] Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timişoara, 6 Pîrvan Blv., 300223 Timisoara, Romania

[2] Research Institute for Renewable Energy, Politehnica University Timişoara, P-ta Victoriei No.2, 300006 Timisoara, Romania

[3] Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Hlavova 8, 128 43 Prague 2, Czech Republic

Introduction

Magnetic nanoparticles have attracted much interest in the field of magnetic recording and in the areas of medical investigation and treatment and magnetic sensing. In particular, the nanoparticles of magnetic iron oxides such as Fe_3O_4 and γ-Fe_2O_3 are reported to be applicable for use in drug delivery systems, magnetic resonance imaging and cancer therapy [1–3]. Recently, magnetic materials have gained special attention in water purification, for their use as adsorbents, based on their numerous advantages such as high separation efficiency, simple manipulation process and soft operation conditions [4]. For such applications, the size, morphology, magnetic properties and surface properties of the magnetic nanoparticles are of great importance. These properties are reported to be significantly influenced by the employed synthesis method [1].

Many synthesis routes were developed for obtaining magnetic iron oxides such as: coprecipitation of Fe(II) and Fe(III) hydroxides [5], precipitation of Fe(II) hydroxide and oxidation [6], spray pyrolysis [7], sol–gel [8], thermal decomposition of different precursors [9], combustion [10] hydrothermal [11] and solvothermal [12]

The main advantage of the solvothermal method is the possibility to obtain iron oxides with tailored properties (shape and size of the nanoparticles) by tuning the reaction conditions. This method seems to be effective in avoiding the oxidation, hydrolysis and volatilization of the reactants, and also favorable for products crystallization due to the particular reaction condition inside the sealed autoclave [13].

Thermochimica Acta 652 (2017) 1–8

Contents lists available at ScienceDirect

Thermochimica Acta

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

Thermal behavior of $MnFe_2O_4$ and $MnFe_2O_4$/C nanocomposite synthesized by a solvothermal method

Marcela Stoia[a,b,*], Eliza Muntean[a], Cornelia Păcurariu[a], Ciprian Mihali[c]

[a] Politehnica University Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Pîrvan Blv., RO-300223, Timişoara, Romania
[b] Politehnica University Timişoara, Research Institute for Renewable Energy, P-ta Victoriei No.2, 300006, Timişoara, Romania
[c] "Vasile Goldis" Western University of Arad, The Institute of Life Sciences, No. 86, Liviu Rebreanu Street, 310414 Arad, Romania

ARTICLE INFO

Article history:
Received 28 October 2016
Received in revised form 24 January 2017
Accepted 11 March 2017
Available online 16 March 2017

Keywords:
Manganese ferrite
Activated carbon
Nanocomposite
Nanopowder
Thermal analysis

ABSTRACT

A new solvothermal method for $MnFe_2O_4$ nanoparticles and $MnFe_2O_4$/C nanocomposite synthesis is reported. Manganese ferrite nanoparticles thus sinthesized are not stable at thermal treatment in oxidizing atmosphere, due to Mn(II) oxidation to Mn(III), evidenced at 640 °C by thermal analysis. The FTIR spectroscopy also confirmed the oxidation of Mn(II) to Mn(III). XRD analysis has revealed the complete decomposition of manganese ferrite around 700 °C. The specific surface area of the composite with activated carbon was much higher (253 $m^2 g^{-1}$), in comparison with that of the naked ferrite (65 $m^2 g^{-1}$). Scanning electron microscopy and transmission electron microscopy images evidenced the obtaining of nearly spherical ferrite nanoparticles, with diameters within the range 10 nm – 30 nm, loaded on the surface of activated carbon in case of the composite. The magnetization of the synthesized composite (30 emu g^{-1}) was below the one of naked manganese ferrite (40 emu g^{-1}), but sufficient to insure a facile magnetic separation of the composite from aqueous solution, in case of its use as adsorbent for pollutant removal.

1. Introduction

$MnFe_2O_4$ is a magnetic ferrite with cubic spinel structure extensively used in various technological applications due to its magnetic properties (low coercivity and moderate saturation magnetization), combined with a good mechanical hardness [1]. Manganese ferrite nanoparticles are very important materials because they have proven to be useful in many magnetic applications, such as recording media devices [2], and for many biological applications such as controlled drug delivery, hyperthermia-based therapy [3], immuno-recognition and detection [4], biosensors [5], imaging [6], tissue engineering and regenerative medicine [7]. An interesting application which gained researchers interest is the use of manganese ferrite nanopowders as adsorbents and catalysts for wastewater treatment [8].

Various synthesis methods for the preparation of spinel manganese ferrite nanocrystals have been reported, including the sol–gel method [9], coprecipitation [10], thermal decomposition of precursors [11], reverse micelles [12], electro-crystallization method [13], the solvothermal and hydrothermal methods [14,15], mechanosynthesis [16], and high energy milling method [17].

The use of magnetic nanoparticles for the treatment of wastewater is limited due to their relative low surface area (up to 100 $m^2 g^{-1}$, depending on the synthesis method) [18,19]. In order to enhance the surface area and the adsorption properties of manganese ferrite nanoparticles, studies have been reported to synthesize activated carbon based nanocomposites using coprecipitation technique [20,21]. Hydrothermal method was used for the synthesis of zinc substituted manganese ferrite/activated carbon nanocomposites. It was established that manganese-zinc ferrite nanoparticles entered into the pores of activated carbon (AC) and blocked the pores, so that the total pores volume and BET surface area decreased. So, the higher the specific surface area of activated carbon and the lower the content of the manganese – zinc ferrite, the higher the specific surface area of the obtained nanocomposite was [22]. Still, the nanocomposites were contaminated with α-Fe_2O_3.

Our previous work on the synthesis of γ-Fe_2O_3/AC nanocomposites showed that the solvothermal method, using 1,2-propanediol as solvent is suitable for the obtaining of phases that require reducing environment [23,24]. For the synthesis of magnetite we have used two different precipitants: diethylamine and potassium hydroxide. The obtained magnetic iron oxides were formed from fine nanoparticles, smaller (5–10 nm) when potassium hydroxide was used as precipitant.

* Corresponding author at: Politehnica University Timişoara, Faculty of Industrial Chemistry and Environmental Engineering, 6 Pîrvan Blv., RO-300223, Timişoara, Romania.
E-mail address: marcela.stoia@gmail.com (M. Stoia)

http://dx.doi.org/10.1016/j.tca.2017.03.009
0040-6031/

J Therm Anal Calorim (2016) 125:1185–1198
DOI 10.1007/s10973-016-5393-y

Investigation of magnetite nanoparticles stability in air by thermal analysis and FTIR spectroscopy

Marcela Stoia[1,2] · Roxana Istratie[1] · Cornelia Păcurariu[1]

Received: 2 November 2015 / Accepted: 7 March 2016 / Published online: 24 March 2016

Abstract Magnetic iron oxides were prepared by precipitation of Fe(II) hydroxide using different precipitation agents: ammonia, benzylamine and sodium hydroxide, followed by oxidation with the oxygen dissolved in water. Thermal analysis, coupled with FTIR spectroscopy, has evidenced the formation of a mixture of magnetite and maghemite, with a higher content of magnetite in case of the powder synthesized with benzylamine. The stability of magnetite at oxidation by air during storage at room temperature and 60 °C was investigated by means of TG/DSC simultaneous thermal analysis, FTIR spectroscopy and X-ray diffractometry. Thermal analysis evidenced an exothermic process with mass gain in temperature range 100–190 °C, corresponding to magnetite oxidation process, but due to the superposition of other processes it could not offer quantitative information. FTIR spectroscopy has provided, especially through the first and second derivatives of FTIR spectra, the most valuable information regarding the evolution of magnetite to maghemite, due to their different characteristic bands. XRD technique has evidenced a slight shift of the main diffraction peaks at higher 2-theta values during the evolution of magnetite to maghemite. According to thermal analysis data, the powder synthesized with ammonia was completely oxidized after 15 days, while the other two powders, synthesized with benzylamine and sodium hydroxide, were completely oxidized after 110 days of keeping in air at room temperature. For a temperature of 60 °C, the oxidation was much faster; the oxidation process of the powder synthesized with benzylamine disappeared from TG/DSC curves after 1 day. All final powders were formed from nanoparticles with diameters up to 25 nm, with magnetic properties characteristic to nanometric maghemite.

Keywords Magnetite · Stability · Oxidation · Thermal analysis · FTIR spectroscopy

Introduction

Magnetic nanoparticles of iron oxides such as Fe_3O_4 and γ-Fe_2O_3 have attracted attention in biomedical applications such as drug delivery systems, magnetic resonance imaging (MRI) and cancer therapy [1–3] because of their biocompatibility and low toxicity in the human body [4]. Recently, magnetic materials have gained special attention as adsorbents in water purification due to their numerous advantages such as high separation efficiency, simple manipulation process and soft operation conditions [5, 6].

Many synthesis routes were developed for obtaining magnetite such as coprecipitation of Fe(II) and Fe(III) hydroxides [7], precipitation of Fe(II) hydroxide and oxidation [8], spray pyrolysis [9], sol–gel [10], thermal decomposition of different precursors [11], combustion [12], hydrothermal [13], solvothermal [6, 14] and ball milling [15]. However, magnetite nanoparticles are very much susceptible to air oxidation even at low temperatures [16]. The heating of magnetite nanoparticles in air at low temperatures leads to maghemite, while at higher temperatures maghemite is further oxidized to hematite [17].

✉ Marcela Stoia
marcela.stoia@chim.upt.ro; marcela.stoia@upt.ro

[1] Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timişoara, 6 Pîrvan Blv., 300223 Timisoara, Romania

[2] Research Institute for Renewable Energy, Politehnica University Timişoara, P-ta Victoriei No.2, 300006 Timisoara, Romania

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
JOURNAL OF ENVIRONMENTAL SCIENCES
www.jesc.ac.cn

$MnFe_2O_4$ nanoparticles as new catalyst for oxidative degradation of phenol by peroxydisulfate

Marcela Stoia[1,2], *Cornelia Muntean*[1,2,*], *Bogdan Militaru*[1]

1. *Faculty of Industrial Chemistry and Environmental Engineering, Politehnica University Timisoara, RO-300223 Timişoara, Romania. E-mail: marcela.stoia@upt.ro*
2. *Research Institute for Renewable Energy, Politehnica University Timisoara, RO-300006, Timisoara, Romania*

ARTICLE INFO

Article history:
Received 13 July 2015
Revised 26 September 2015
Accepted 12 October 2015
Available online 19 May 2016

Keywords:
Manganese ferrite
Nanoparticles
Phenol
Peroxydisulfate
Catalytic oxidation

ABSTRACT

Manganese ferrite nanopowder was prepared by thermal decomposition at 400°C of the gel synthesized from manganese and iron nitrates and polyvinyl alcohol. X-ray diffractometry evidenced that manganese ferrite was formed as single crystalline phase at this temperature. Scanning electron microscope images evidenced the formation of very fine spherical particles (d < 11 nm) of manganese ferrite, with specific surface area of 147 m^2/g. The powder obtained at 400°C was used as a catalyst for the oxidative degradation of phenol in aqueous solutions, in the presence of potassium peroxydisulfate as oxidant. High phenol removal efficiencies above 90% were reached at: pH 3–3.5, phenol initial concentration around 50 mg/L, peroxydisulfate:phenol mass ratio 10:1, and catalyst dose 3 g/L. Total organic carbon measurements showed that the degradation of phenol goes, under these conditions, to mineralization in an extent of 60%.

Introduction

In the last few years, nanoscale spinel ferrites have drawn a major attention because of their technological applications in magnetic recording, catalysts and ferrofluids. Nanoparticles of such magnetic materials have different characteristics in comparison with the bulk material, due to their small size and the effect of magnetic interactions between particles (Ahmed et al., 2011). Superparamagnetic spinel ferrites MFe_2O_4 (M = Mn, Fe, Co, Ni) are currently considered among the most successful magnetic nanoparticles for medical applications such as contrast enhancement in magnetic resonance imaging (MRI), magnetically guided drug delivery, and hyperthermia cancer therapy (Vamvakidis et al., 2013).

One of the magnetic ferrites applications extensively studied in the last decades is the removal of heavy metals from water bodies due to the abundant surface hydroxyl groups and magnetic properties, allowing their magnetic separation (Guan et al., 2013; Yao et al., 2014). The possibility to use magnetic materials to remove very toxic organic pollutants *e.g.*, phenol and its derivatives or organic dyes, has received a great attention in the last decades (Saputra et al., 2013a; Yao et al., 2014).

Phenol is an important pollutant in wastewater that can cause considerable damage and threat to the ecosystem and to the human health even at low concentrations. Phenol is a pollutant with high toxicity and poor biodegradability. It is also difficult to be degraded using primary and secondary treatment processes, needing a tertiary treatment of wastewater. These tertiary treatments can include advanced oxidation processes (AOPs) such as chemical oxidation, catalytic oxidation, thermal oxidation, wet air oxidation, *etc.* (Chen et al., 2014; Muhammad et al., 2012).

Advanced oxidation processes (AOPs) are the most promising method for degradation of organic pollutants in wastewater.

* *Corresponding author.* E-mail: cornelia.muntean@upt.ro (Cornelia Muntean).

http://dx.doi.org/10.1016/j.jes.2015.10.035