Applied Catalysis B: Environmental 202 (2017) 21–32

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Remarkable catalytic properties of rare-earth doped nickel ferrites synthesized by sol-gel auto-combustion with maleic acid as fuel for CWPO of dyes

Petrisor Samoila[a,*], Corneliu Cojocaru[a], Liviu Sacarescu[a], Petronela Pascariu Dorneanu[a], Andrei-Adrian Domocos[b], Aurelian Rotaru[c]

[a] "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41 A 700487 Iasi, Romania
[b] "Alexandru Ioan Cuza" University, Departament of Physics, 11, Carol I Boulevard, 700506 Iasi, Romania
[c] "Stefan Cel Mare" University, Faculty of Electrical Engineering & Computer Science, 13Universitatii Street, 720229 Suceava, Romania

ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form 16 August 2016
Accepted 3 September 2016
Available online 5 September 2016

Keywords:
CWPO
Rare earth doped spinel ferrites
Maleic acid
Kinetic modeling of catalytic reaction
Desirability function approach

ABSTRACT

$NiFe_{1.98}RE_{0.02}O_4$ (where RE = La, Sm, Gd and Dy) spinel ferrites were synthesized by sol–gel autocombustion method using maleic acid as fuel. The effect of rare-earth cations (RE) doping on structural, magnetic and catalytic properties of nickel ferrite is reported. XRD and FT-IR analysis revealed the successful insertion of the rare-earth cations into the spinel matrix in all samples. We observed a decreasing of crystallite and particle sizes (estimated from XRD patterns and TEM micrographs, respectively) as well as the magnetization value in the presence of lanthanide ions into the spinel structure. Additionally, these ferrites were employed as heterogeneous catalysts for catalytic wet hydrogen peroxide oxidation (CWPO) of Orange II azo-dye. The color removal efficiency was boosted from 30.6% for undoped nickel ferrite to 90.6% for the lanthanum doped nickel ferrite, after only 15 min of reaction. The decolorization of Orange II solution followed the pseudo-first-order kinetics and was achieved via decay reaction as demonstrated by Langmuir-Hinshelwood model. The remarkable increase in catalytic performance of doped nickel ferrites with a very small amount of rare-earth cations was correlated with the size factor, expressed as the ratio between particle and crystallite size. The desirability function approach enabled to identify the optimal material ($NiFe_{1.98}La_{0.02}O_4$) with the best catalytic performance; the smallest size factor and appropriate magnetic properties.

1. Introduction

The pollution of water resources by large quantities of aqueous organic effluents, especially phenolic compounds and azo-dyes, generated from diverse industries such as petrochemical, pharmaceutical, chemical, textile, cosmetics or agro-alimentary has a negative environmental impact, affecting the quality of drinking water for the next generation [1,2]. The increasing strict regulations for the protection of environment are imposing lower discharge limits of toxic and potentially hazardous pollutants that are difficult to satisfy with the conventional technologies [1]. The current wastewater treatment methods based on biological, thermal, and physicochemical processes have limitations in terms of applicability, effectiveness and costs [3]. Therefore, the development of new and more efficient systems for wastewater treatment represents a great challenge for the researchers.

In this context, the Advanced Oxidation Processes (AOPs) are postulated as an attractive alternative for treating wastewater containing organic pollutants [4,5]. Usually, the AOPs procedures involve the generation of nonselective and extremely reactive hydroxyl radical ($HO^{\bullet}$) in the reaction medium, which is one of the most powerful oxidation agents due to its high oxidation potential ($E^0 = 2.8$ V) [4,6]. The classification of advanced oxidation processes in Fenton, photo-Fenton, ozonation, photocatalysis, catalytic wet oxidation, etc. is based on the ways in which HO• radicals are generated from different sources (H_2O, O_2, H_2O_2, O_3) [7–9]. The most common sources of hydroxyl radicals are the reactions of hydrogen peroxide with the Fenton or Fenton-like reagents at room temperature [4,10]. Note that, when Fenton systems are used at

* Corresponding author.
E-mail addresses: samoila.petrisor@icmpp.ro, samoila.petrisor@yahoo.com (P. Samoila).

http://dx.doi.org/10.1016/j.apcatb.2016.09.012

temperature higher than the room temperature, the processes are called catalytic wet hydrogen peroxide oxidation (CWPO) [4].

Heterogeneous CWPO is extremely attractive, among various AOPs techniques, enabling the complete mineralization of refractory organic pollutants into carbon dioxide, water and other innocuous inorganic compounds [3]. Usually, iron oxides such as magnetite (Fe_3O_4), maghemite (γFe_2O_3) and hematite (αFe_2O_3) are successfully used as heterogeneous WPO catalysts [11]. However, the development of new iron containing poly-metallic oxides with enhanced activity in CWHPO technologies is of great interest [3,4,10,12,13].

The use of other iron-based materials, such as spinel ferrites, for the catalytic degradation of organic pollutants, represents a promising alternative to achieve catalytic performances more interesting then the single metal oxide component [5,11–14]. In these cases, catalysts might be easily recovered from the reaction environment because of their magnetic properties and reused for several runs [8,13]. Despite encouraging results achieved, further systematic research work is required in order to improve the catalytic activity of the spinel ferrites. Catalytic performances of spinel ferrites are strongly influenced by various factors like chemical composition; crystallite and particle size; as well as microstructural characteristics [15]. These factors could be fine-tuned by selecting a particular route of material synthesis or an appropriate chemical composition.

Recent studies reveal a good potential of the use of rare-earth oxides and rare-earth containing polymetallic oxides for organic pollutants degradation [16–23]. In this respect, the investigation of the influence of rare-earth doping on spinel ferrites characteristics deserves special attention. It was observed that structural parameters, the perturbation occurring in the Fe^{3+}—O^{2-}—Fe^{3+} bonds (the rare earth cations are bulky), particle sizes, magnetic and catalytic properties are strongly influenced by the presence of very small amounts of Dy and Gd cations in the structure of the Ni—Zn and Ni—Mn—Cr ferrites, respectively, making these kind of materials potential candidates for CWPO applications [15,24]. Nevertheless, careful survey of the literature reveals only one study reporting the enhanced catalytic activity of ferrite nanoparticles doped with rare-earth ions in CWPO of organic pollutants [25]. Note that, the insertion of rare-earth cations into the spinel matrix is difficult because of their larger ionic radii [24]. Among the synthesis methods usually employed for the rare-earth doped spinel ferrites (solid-state reaction, coprecipitation or hydrothermal) the sol-gel autocombustion is an attractive way to obtain nanocrystalline mixed oxides. This method is extensively used because of its specific characteristics like: use the chemical energy instead of the electric energy, simple synthesis setup, easy component adjustment, rapid synthesis, and ease of scale up. The sol-gel autocombustion became a reference synthesis procedure for preparation of catalytic materials [26]. The selection of the fuel agent for this kind of synthesis is essential. Thus, in a previous study we showed that from four different fuels (urea, cellulose, citric and tartaric acids) used for the synthesis of Dy substituted Ni-Zn ferrite, only cellulose, citric acid and tartaric acid led to the dissolution of dysprosium cations into spinel structure and only citric acid and cellulose lead to pure spinel phase [15].

In this work, at the first time, we used maleic acid as the combustion agent to dope the nickel ferrite with bulky cations like La^{3+}, Sm^{3+}, Gd^{3+} and Dy^{3+}. It is important to note that, only two papers discussing this carboxylic acid as a combustion agent were reported, and both presenting the preparation of some hexagonal ferrites [27,28]. To the best of our knowledge, so far, no study was reported dealing with maleic acid as fuel agent for the synthesis of any spinel ferrites. Likewise, for the first time, we used rare-earth doped spinel ferrites as catalysts for CWPO of the Orange II azo-dye, which was chosen as the model pollutant.

2. Experimental

2.1. Catalysts preparation

Nanoparticles of Ni ferrite doped with rare earth (RE) cations like La, Sm, Gd and Dy with formula $NiFe_{1.98}RE_{0.02}O_4$ were obtained by sol-gel autocombustion method using maleic acid as fuel. Likewise, the undoped $NiFe_2O_4$ ferrite was prepared for comparison purposes. Analytical reagent graded nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$], lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$], samarium nitrate [$Sm(NO_3)_3 \cdot 6H_2O$], gadolinium nitrate [$Gd(NO_3)_3 \cdot 6H_2O$], and maleic anhydride [$C_4H_2O_3$] were used to prepare the ferrite samples, as purchased from Sigma-Aldrich. Dysprosium nitrate solution 1 M was obtained in situ from Dy_2O_3 and nitric acid 20% solution. First, the metal nitrate solutions were mixed in stoichiometric proportions. Second, a solution of maleic acid was mixed with each sample of metal nitrates mixture into 1:1 molar ratio of fuel agent to cations. The mixed solutions were heated at 80 °C on a water bath, under continuous stirring, until a viscous gel was formed. Consequently, the gel was gradually heated at 350 °C on a sand bath, until the self-ignition was clearly observed and a dark powder was formed. The obtained powders were thermal treated in three steps: pre-sinterization at 500 °C/5 h, and sinterization at 700 °C/5 h and at 900 °C/7 h, respectively.

The obtained materials were denoted N700, NL700, NS700, NG700, ND700 and N900, NL900, NS900, NG900, ND900, respectively, indicating the rare-earth cation employed and the annealing temperature (i.e. L = La, S = Sm, G = Gd, D = Dy, 700 = 700 °C and 900 = 900 °C).

2.2. Catalysts characterization

Structural characterization of the spinel ferrite powder heated at 700 °C and at 900 °C was performed by recording the powder X-ray diffraction (XRD) patterns using a Shimadzu LabX 6000 diffractometer equipped with graphite monochromator and CuKα (λ = 0.15406 nm) radiation. The powders were scanned in the range 20–80° (2θ) with a scanning rate of 0.02°/s.

The formation of spinel-type phase at 700 °C and at 900 °C was monitored by means of infrared spectroscopy using a Bruker Vertex 70 FTIR spectrometer at room temperature with a resolution of 2 cm^{-1} (KBr pellets technique). The spectra were registered in transmission mode in the range of 350–900 cm^{-1}.

The morphology, microstructure and chemical composition of ferrite samples annealed at 900 °C were investigated using Hitachi High-Tech HT7700 Transmission Electron Microscope (TEM) equipped with a Bruker XFlash 6 energy dispersive X-ray (EDS) detector, operated in high contrast mode at 120 kV accelerating voltage. Samples were prepared by dispersion of the nanoparticles in ethanol, ultrasonication for 1 min, drop casting on carbon coated copper grids (300 mesh, Ted Pella) and drying in vacuum at 50 °C. The particle size distribution and the average particle sizes were determined using ImageJ software, by measuring at least 100 grains for each studied material from at least six different micrographs.

Magnetic measurements for the materials sintered at 900 °C were performed using an MPMS3 (7T) SQUID magnetometer, at room temperature (300 K), in DC mode, under an applied magnetic field of 4000 Oe. Before each measurement, the sample was demagnetized in AF (alternating field).