

NANOSTRUCTURED IRON OXIDE POWDERS BY MICROWAVE ASSISTED SYNTHESIS

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Abstract. A range of nanostructured oxides with excellent properties is used in technology and science for applications in several fields: catalysis, gas detection, biomedical applications. The most studied forms of oxides are hematite, maghemite and magnetite. In this study, microwave-assisted hydrolytic synthesis and microwave-assisted coprecipitation synthesis are described for the preparation of undoped and doped iron oxide powders using iron (III) chloride (FeCl_3), potassium chloride (KCl) as precursors and sodium hydroxide (NaOH) solution as a hydrolysis agent. Microwave-assisted hydrolysis was performed at different concentrations of FeCl_3 precursor: 0.1 M, 0.4 M, 0.7 M to which a constant concentration of hydrolysis agent was added, and the synthesis to obtain potassium-doped powders consisted of co-precipitation of 0.1M FeCl_3 and 0.025M KCl precursor solutions in the presence of 2M NaOH hydrolysis agent. The developed powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The novelty is the use of potassium as a doping element for iron oxide, for potential application as catalyst. Hematite doped with 5% K was obtained by microwave-assisted coprecipitation synthesis. The presence of K was evidenced by EDS, while XRD spectra indicate successful doping of iron oxide with potassium, either interstitially or by substitution. By microwave synthesis, an increase in particle size was observed with increasing calcination temperature. The formation of the crystalline hematite phase was not obtained in the microwave heating process but following calcination of the powders.

Keywords: iron oxide; potassium-doped iron oxide; microwave-assisted hydrolysis; microwave-assisted coprecipitation.

1. INTRODUCTION

Nanostructured oxides are an important class of nanomaterials with many uses in science and technology. In recent decades, nanostructured metal oxides have gained considerable attention due to their excellent properties and potential applications in many areas of catalysis, biomedical, gas sensing, materials chemistry, and electrochemistry [1]. The most widespread element on earth is iron. The iron oxide form is found in sixteen different phases. Among the most widespread and oxide forms being studied are hematite ($\alpha\text{-Fe}_2\text{O}_3$), maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4). The most stable oxide form is hematite, which

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can be used as a precursor to obtain Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$. Additionally, hematite is often applied in catalysis and gas sensors due to its low toxicity, high sensitivity/activity, and high corrosion resistance [2].

Different methods of synthesis of nanostructured metal oxides have been described in the literature, such as sol-gel, hydrolysis, thermal decomposition, sonochemistry, microwave, hydrothermal [3-5]. Various methods for synthesizing nanostructured metal oxides use various experimental parameters such as pH of the synthesis solution, surfactant, reaction temperature, precursor concentrations and pressure to control the morphology and size of the nanostructure, almost all methods [6].

Compared to the syntheses listed above, the microwave-assisted hydrolytic method is an efficient and simple method and, which has a relatively low time process. The most popular method for synthesizing Fe_xO_y is co-precipitation. The method consists of mixing precursors that comprise $\text{Fe}^{2+}/\text{Fe}^{3+}=1:2$ in basic solutions at room temperature or at elevated temperatures. The type of precursors used, such as (sulfates, nitrates, chlorides, perchlorates), synthesis temperature, pH value and other parameters, such as stirring speed, iron ion concentration ratio, greatly influence the morphology and size of the iron oxide nanoparticles. Superparamagnetic iron oxide nanoparticles with controlled dimensions by precipitation in basic FeCl_3 and FeCl_2 salts were obtained by Massart et al.[7]. in 1981. They studied the influence of the base used (ammonia, methylamine and sodium hydroxide), pH value, $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio on the reaction yield, diameter and polydispersity of the nanoparticles formed. Nanoparticles ranging in size from 4.2 nm to 16.6 nm were obtained by varying these parameters. XRD results showed a rhombohedral (hexagonal) structure with the R-3c space group in all samples. The spherical morphology of iron oxide nanoparticles resulting from hydrolysis was demonstrated by TEM and SEM [8].

Kirillov et al. [9] elaborated magnetite nanoparticles by co-precipitation of iron(II) sulfate and iron(III) chloride in the presence of citrate ions at room temperature and in argon medium. The different nanoparticle sizes observed by SEM (from 10.5 nm to 4.4 nm) were obtained by changing the molar concentration of citrate.

Magnetic magnetite nanoparticles ranging from 3 nm to 20 nm in diameter were synthesized by Zeng and Sun [10] by co-precipitation of a stoichiometric mixture of Fe(II) and Fe(III) salts in a basic medium using sodium hydroxide or ammonium hydroxide. To obtain information on the structure of the nanoparticles (Fe_3O_4), high-resolution TEM and XRD HRTEM were performed. A spherical morphology with a size of about 20 nm of iron oxide nanoparticles was confirmed by SEM.

Abdelmajid et al [11] described the preparation of $\alpha\text{-Fe}_2\text{O}_3$ hematite nanoparticles using a simple chemical co-precipitation method based on the iron chloride hexahydrate precursor. They followed the impact of varying the precursor concentration on $\alpha\text{-Fe}_2\text{O}_3$ crystal phase, size and morphology in experiments. The characteristics of the fabricated hematite nanoparticles were investigated by XRD, TEM, SEM. XRD data showed a rhombohedral (hexagonal) structure with the R-3c space group in all samples. TEM and SEM were confirmed by uniform spherical morphology. The obtained data showed that the particle sizes varied from 21 nm to 82 nm, and with increasing precursor concentration ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) the particle sizes increased from 21 nm for pure $\alpha\text{-Fe}_2\text{O}_3$ synthesized with $[\text{Fe}^{3+}] = 0.05 \text{ M}$ to 82 nm for pure $\alpha\text{-Fe}_2\text{O}_3$ elaborated with $[\text{Fe}^{3+}] = 0.4\text{M}$.

Risbud et al [12] obtained monodisperse, uniform, small-sized Fe_3O_4 nanoparticles by surfactant-free co-precipitation method using iron chlorides with a molar ratio $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$ at pH = 11-12. XRD data showed a cubic structure. By SEM, the morphology of iron oxide nanoparticles with a size of about 8.5 nm was determined.

Mutasim I. Khalil [13], starting from an aqueous Fe^{3+} salt solution, instead of using two iron precursors. The procedure involved the addition of iron chloride to an aqueous

solution of potassium iodide in a molar ratio of 3:1. Potassium iodide reduced the iron salt. The mixture was hydrolyzed with 25% ammonia to yield black magnetite precipitate. Spherical magnetite nanocrystals with a diameter of 7.84 nm, rods with a diameter of 6.3 nm and a length of 46.2 nm were obtained. The morphology of Fe₃O₄ nanocrystals was analysed using a scanning electron microscope and a transmission electron microscope with an accelerating voltage of 200 kV.

Using this method, Kim et al [14] synthesized magnetite and showed that they could obtain different compositions of oxyhydroxides. Depending on the Fe²⁺/Fe³⁺ molar ratio depends to a large extent, the composition, respectively, the size of the magnetite. Goetite [FeO(OH)] was formed for $x = 0.1$, and for values of $x = 0.2$, respectively $x = 0.3$, a distinct oxyhydroxide phase and variable sizes of non-stoichiometric magnetite were obtained. Nanoparticles homogeneous in size and composition were obtained at a molar ratio of 0.5. However, the best-established molar ratio used is $x = 0.5$. Morpho-structural characterization of the elaborated iron oxyhydroxide nanoparticles was performed by XRD, TEM, SEM. The XRD data revealed an orthorhombic structure. SEM has been used to determine the morphology of iron oxide nanoparticles with a size of 40 nm [15].

For example, M. Farahmandjou et al [16] developed α -Fe₂O₃ nanoparticles by co-precipitation synthesis using iron chloride hexahydrate (FeCl₃·6H₂O) precursor and ammonia solution as a hydrolysis agent. The probes were analyzed by high-resolution transmission electron microscopy (HRTEM), field scanning electron microscopy (FESEM), X-ray diffraction (XRD) and electron scattering spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectrophotometry. The XRD results revealed that the iron oxide nanoparticles exhibited a single phase, hematite, in the powders calcined at 500°C, and the crystallite size was 30 nm, a size also confirmed by HRTEM. The SEM surface morphological studies described sphere-shaped particles with cluster formation. EDS spectra indicated impurity-free iron and oxygen peaks with minor elements. Narrow peaks in the FTIR spectra showed the purity of Fe₂O₃ nanoparticles, and the absorption peak in the UV-Vis spectra showed low band energy of 2.58 eV.

Aivazoglou et al [17] elaborated a simple microwave-assisted synthesis of iron oxide nanoparticles using solutions of polyethylene glycol (PEG) or PEG and β -cyclodextrin (β -CD)/water iron chloride salts in the presence of an ammonia solution. Heating time, microwave power and the presence of PEG are key factors shaping the dimensional properties of the nanoparticles. The developed nanopowders were characterized by X-ray diffraction (XRD), transition electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, vibrational sample magnetometer (VSM), X-ray photoelectron spectroscopy (XPS) and thermal analysis (TG/DSC).

Niederberger and coworkers [18] elaborated by microwave-assisted method iron oxide nanoparticles and analyzed the effect of the precursors on the size of the synthesized powders. For the preparation of iron oxide nanoparticles, the precursors iron(II) acetyl acetonate, iron acetate and iron(III) acetyl acetonate were used. The obtained nanoparticles have the following sizes: 11 nm, 7 nm, and 5 nm. Mitar et al [19] synthesized hematite by microwave-assisted hydrothermal synthesis using 0.1 M FeCl₃ solution as a precursor in alkaline medium with heating in a microwave oven at 800 W with a temperature variation: 150°C, 200°C, and 250°C for 20 min.

This research highlights the preparation by microwave-assisted hydrolytic synthesis of iron oxide powders and potassium-doped iron oxide using iron (III) chloride (FeCl₃), potassium chloride (KCl) as precursors and sodium hydroxide (NaOH) solution as a hydrolysis agent. Microwave-assisted hydrolysis was achieved at different concentrations of FeCl₃ precursor: 0.1 M, 0.4 M, 0.7 M and constant concentration of hydrolysis agent added.

Morphostructural characterization was performed by scanning electron microscopy (SEM), X-ray diffraction technique (XRD) and FTIR spectroscopy.

2. MATERIALS AND METHODS

2.1. MATERIALS

For this study, all reagents used for iron oxide synthesis were of analytical grade with no additional purification. Ferric chloride (FeCl_3), potassium chloride (KCl), sodium hydroxide (NaOH) was purchased from Merck (Germany). Distilled water and ethanol were used to remove impurities and avoid agglomeration.

2.2. SYNTHESIS

2.2.1. Synthesis of iron oxide by microwave-assisted hydrolysis

Microwaves are used to heat a solution quickly and homogeneously by applying electromagnetic radiation at wavelengths between 1 m and 1 cm. Most commercially used microwaves work at a frequency of 2.45 GHz. Microwave-assisted hydrolytic synthesis of iron oxide consists of hydrolysis of precursor solutions (0.1M; 0.4M; 0.7M FeCl_3) in the presence of the hydrolyzing agent 2M NaOH, which was subjected to dielectric heating generated by interactions between molecular dipole moments and high-frequency electromagnetic radiation ferric chloride solutions of different concentrations (0.1M, 0.4M, 0.7M) by dissolving FeCl_3 in distilled water. The acidic ferric chloride solutions were magnetically homogenized at 600 rpm for 10 min. The precipitation of Fe(III) chloride solutions of different concentrations (0.1M, 0.4M, 0.7M) was carried out by drip addition of 2M NaOH solution. A brown suspension was formed after the NaOH solution was homogenized with the FeCl_3 solution. The mixture was placed in a microwave reactor and heated for 12 min at 200 W, 300 W, and 400 W, resulting in a red suspension. All samples were dried for 12 h in air at room temperature and calcined at 300°C and 800°C.

The equipment used in the synthesis are: hydrolysis recipient, magnetic stirrer with temperature sensor, pH meter, microwave furnace, Neos GR and heat treatment furnace, Nabartherm. Experimental parameters for microwave-assisted hydrolytic synthesis are summarized in Table 1.

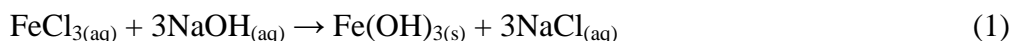
Table 1. Parameters for microwave-assisted hydrolytic synthesis.

Lot/Code	Precursor	Precursor concentration	Hydrolysis agent	Heating time [min]	Reaction parameters		Calcination Temperature [°C]
					W	pH	
7P/P _{20s}	FeCl ₃	0.1M	2M NaOH	12	200	11	300
7P/P _{21s}							800
7P/P _{23s}		0.4M			300		300
8P/P _{24s}					800		
9P/P _{26s}		0.7 M			400		300
9P/P _{27s}							800

The particle formation involves nucleation and crystal growth. There are two types of crystal growth mechanisms, diffusion-based crystal growth, or Ostwald ripening (O-R), and

oriented attachment (O-A) crystal growth. Ostwald ripening refers to the particle growth mechanism based on dissolution-precipitation in solution [20]. This mechanism is explained by the decrease in free energy of particles that tend to the thermodynamic steady-state and coalesce to form a larger particle [21, 22]. In oriented attachment, the particle growth mechanism is based on aggregation along with preferential crystallographic directions [20]. In this method, there are three main stages of iron oxide processing: the process of mixing the precursors under magnetic stirring; microwave heating, and calcination. The first stage is the process of mixing the precursors under magnetic stirring. In this stage, nucleation occurs - it is obtained when the amount of FeCl₃ and the NaOH solution reach stoichiometric conditions.

The equations (1-3) of hematite synthesis reactions are as follow:



From equations (1) and (2), the precipitates obtained in the first stage of hematite particle synthesis are FeO(OH), or goethite. The second stage is the microwave heating process. In this stage, the crystal growth occurs. The crystal growth mechanism can be a combination of O-R and O-A mechanisms. By heating the solution in the microwave field, an increase in the size of the solid particles proportional to the increase in heating time was observed. The last step in the microwave-assisted synthesis of iron oxide particles is calcination. In this stage, the powder obtained from precipitation is crystallized.

2.2.2. Synthesis of potassium-doped iron oxide by microwave-assisted coprecipitation

The preparation of potassium-doped iron oxide consisted of the co-precipitation of 0.1M FeCl₃ and 0.025M KCl precursor solutions in the presence of 2M NaOH-hydrolyzing agent. The elaboration of potassium-doped iron oxide by microwave-assisted coprecipitation was realized using the parameters presented in Table 2.

Table 2. Parameters for microwave-assisted coprecipitation synthesis.

Code	Precursor	Precursor concentration	Hydrolysis agent concentration, NaOH	Reaction parameters		Calcination Temperature [°C]
				W	pH	
PK8	FeCl ₃	0.1M	2M	350 W	11	300
PK9	KCl	0.025M				800

2.2.3. Analytical techniques

The powders obtained by microwave-assisted hydrolytic synthesis have been characterized with the most up-to-date techniques in use such as scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS), X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR).

Morphological characterization of oxide particles is determined by Hitachi SU8230 high-resolution electron microscope (Hitachi High-Technologies Corporation, Tokyo, Japan) at 20 KV, equipped with specialised detectors for secondary electrons, back-scattered electrons, transmitted electrons as well as an EDS detector for analysis by energy dispersive X-ray fluorescence spectrometry.

X-ray diffraction analysis for iron oxide developed by microwave-assisted hydrolytic synthesis were performed using the Rigaku Ultima IV X-ray diffractometer (Rigaku, Wilmington, MA, USA) equipped with a D/teX Ultradetector, graphite monochromator for $k\beta$ radiation and a vertical goniometer in Bragg-Brentano focusing. X-ray patterns were recorded using $\text{CuK}\alpha$ radiation the 2θ range between 18° and 100° , with a step size of 0.05° , scanning speed $3^\circ/\text{min}$. XRD spectrum analysis was performed using PDXL 2 software and crystalline compounds were identified using the PDF 4+ 2021 database.

A vibrational study was conducted using Fourier transform infrared spectroscopy (FTIR). IR spectra were recorded using a Jasco 6300 FTIR spectrometer (Jasco Inc., ABL&E-JASCO Romania S.R.L., Cluj-Napoca, Romania) in the $4000\text{-}400\text{ cm}^{-1}$ region at 25°C with a TGS detector, Spectra Manager II software. ATR spectra were obtained using a Gladi ATR attenuated total reflectance device, Cosinus apodization. The instrument had a spectral resolution of 4 cm^{-1} , for all spectral determination.

3. RESULTS AND DISCUSSION

3.1. RESULTS

Micrographs of iron oxide powders prepared by microwave-assisted hydrolytic synthesis are indicated in Figs. 1-6. In this respect, Figs. 1, 3, and 5 illustrate SEM micrographs of the powder calcined at 300°C for 3h; Figs. 2, 4, and 6 illustrate SEM micrographs of the powder calcined at 800°C for 3h.

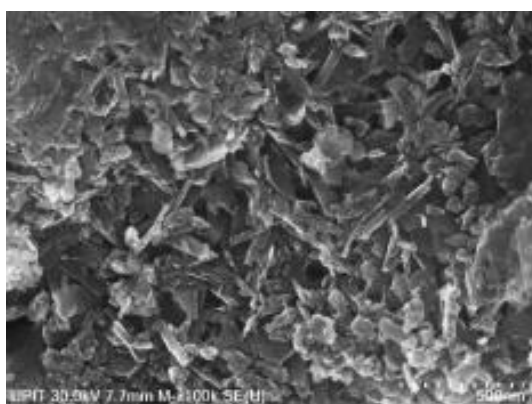


Figure 1. SEM image for P_{20s} sample (powder calcined at 300°C for 3h)

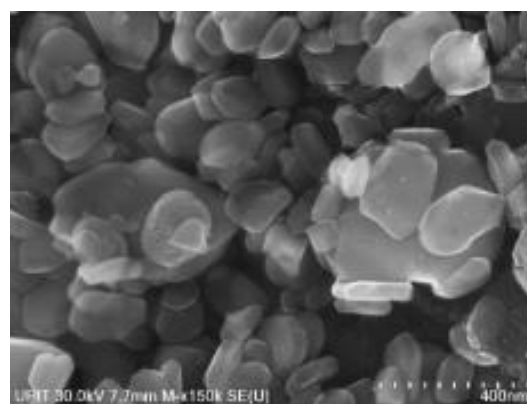


Figure 2. SEM image for P_{21s} sample (powder calcined at 800°C for 3h)

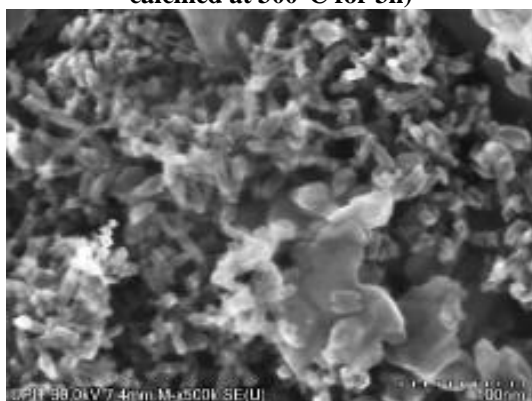


Figure 3. SEM image for P_{23s} sample (powder calcined at 300°C for 3h)

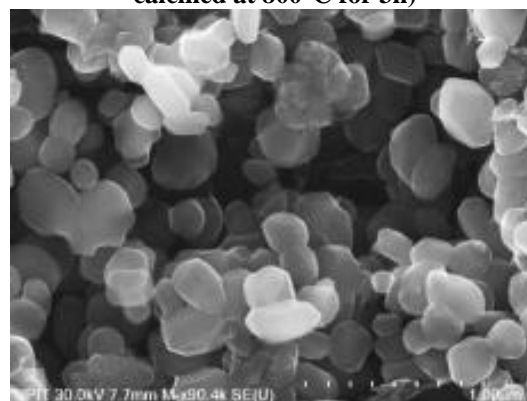


Figure 4. SEM image for P_{24s} sample (powder calcined at 800°C for 3h)

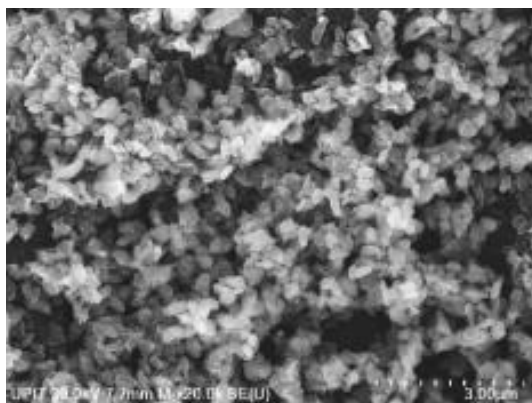


Figure 5. SEM image for P_{26s} sample (powder calcined at 300°C for 3h)

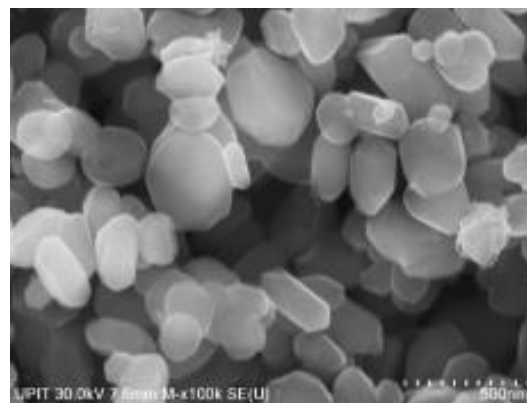


Figure 6. SEM image for P_{27s} sample (powder calcined at 800°C for 3h)

From the analysis of the SEM images, it can be seen that the particles agglomerate and with increasing calcination temperature, the morphology of the particle changes from platelets (Figs. 1, 3, and 5) to spherical shape and irregularly shaped polyhedral (Figs. 2, 4, and 6). Using ImageJ image analysis software on batches 7P, 8P, and 9P, ten measurements were performed to estimate the particle size as accurately as possible.

The measured values were used to calculate an average value for each powder from different lots. Thus, for the P_{20s} powder in batch 7P, platelets with lengths between 60 and 156 nm were identified. For the P_{21s} powder, spherical particles with diameters of approximately 71-133 nm were identified. Morphological analysis shows the change of shape from platelets to spheres. Thus, for the P₂₃ powder, the particles identified as platelets have lengths between 154-327 nm and spherical particles with diameters approximately 79-161 nm were identified for the P_{24s} powder of batch 8P and polyhedral with irregular shapes. For P_{26s} and P_{27s} powders, respectively, the particle morphology was analyzed after the calcination process at different temperatures, 300°C and 800°C. For sample P₂₆, platelets with lengths ranging from 248-600 nm can be identified and, for the P_{27s} powder, polyhedral particles with irregular shapes and spherical particles with diameters of approximately 72-217 nm were identified. The results are presented in Table 3.

Table 3. Average particle size for synthesized Fe₂O₃.

Lot/ code	Conditions for obtaining/Microwave assisted hydrolytic synthesis/ Temperature /Calcination [°C]	Average particle size [nm]	Shape
7P/P _{20s}	0,1M Fe ³⁺ , pH=11/300°C	110	pellet
7P/P _{21s}	0,1M Fe ³⁺ , pH=11/ 800°C	98	sphere
8P/P _{23s}	0,4M Fe ³⁺ , pH=11/ 300°C	252	pellet
8P/P _{24s}	0,4M Fe ³⁺ , pH=11/800°C	126	sphere
		176	polyhedron
9P/P _{26s}	0,7M Fe ³⁺ , pH=11/ 300°C	395	pellet
8P/P _{27s}	0,7M Fe ³⁺ , pH=11/ 800°C	131	sphere

The chemical elemental compositions of iron oxide powders produced by microwave-assisted hydrolytic synthesis are described by energy dispersive spectroscopy (EDS) analysis method. Fig. 7 illustrates the overlapping EDS spectra of the powders from lots 7P, 8P, and 9P.

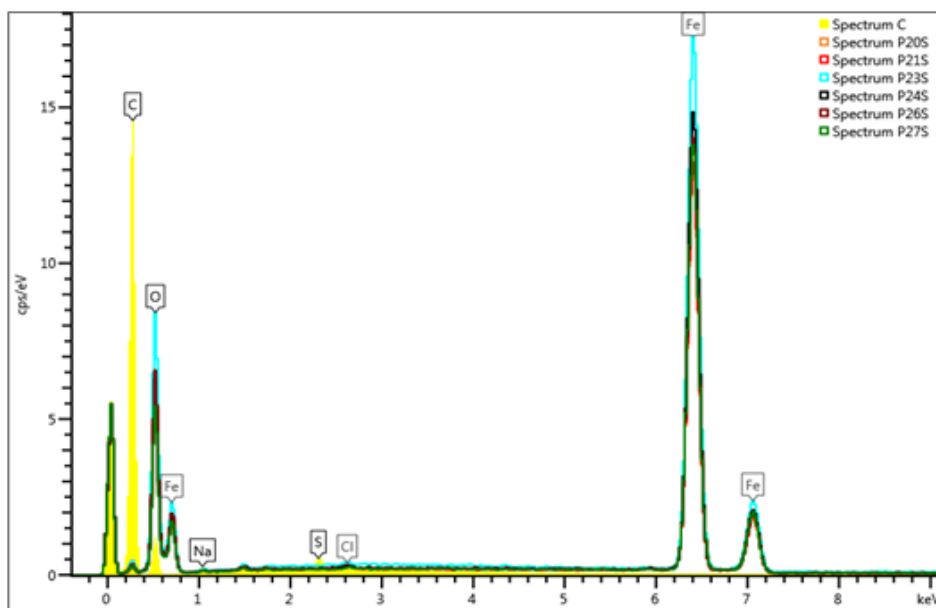


Figure 7. EDS overlapping spectra of carbon tape support and lots 7P, 8P, and 9P.

The spectra indicate the following mass percentage values concise in Table 4.

Table 4. Quantitative EDS analysis.

Element	Wt [%] P _{20s}	Wt [%] P _{21s}	Wt [%] P _{23s}	Wt [%] P _{24s}	Wt [%] P _{26s}	Wt [%] P _{27s}
Fe	74.32	76.23	75.87	76.28	74.83	77.65
O	25.68	23.43	25.96	23.56	25.17	22.35
Na	-	-	-	-	-	-
Cl	-	0.34	0.16	0.16	-	-
Total	100	100	100	100	100	100

EDS investigation highlighted the presence of Fe and O elements in samples P_{20s}, P_{26s}, P_{27s} powders. The presence of chlorine ion (Cl⁻) traces in powders P_{21s}, P_{23s}, P_{24s} can be explained by the fact that it (Cl⁻) was not removed by repeated washing with distilled water and ethyl alcohol.

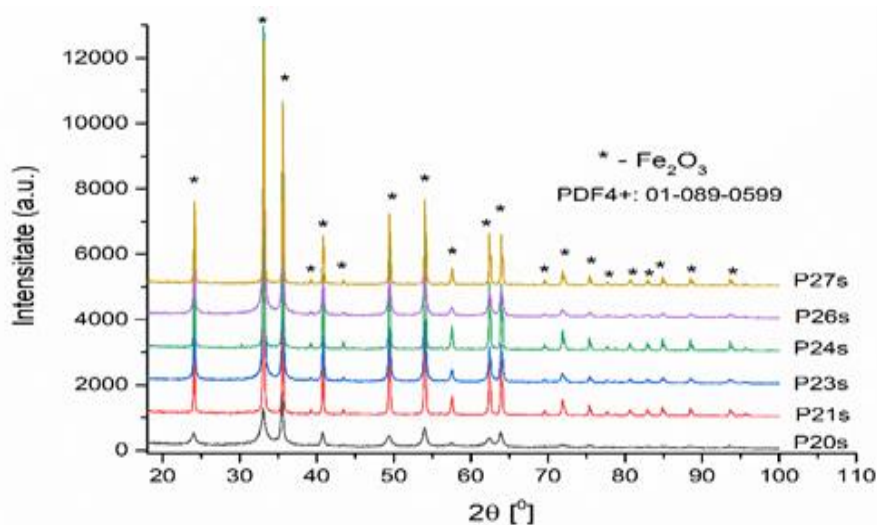


Figure 8. XRD patterns for batches 7P, 8P, 9P.

Fig. 8 represents the overlapping X-ray spectra for powders of batches 7P, 8P, 9P, prepared by microwave-assisted hydrolytic synthesis. The X-ray spectra show the formation

of a single-phase characteristic of hematite with a hexagonal structure in agreement with ICDD-PDF-01-089-0599. Starting from the fact that the most nanoparticles have a spherical shape according to Lian et al. [19] the crystallite size values of the lattice planes of family (104) were calculated using the Scherrer formula, and the results are shown in Table 5.

$$D_{\text{hkl}} = k\lambda/\beta\cos\theta_{\text{hkl}},$$

where k is the shape factor (0.9), λ is the wavelength (0.15418 nm, $\text{CuK}\alpha$), β is the full width at half maximum (FWHM), and θ are the diffraction angle.

Table 5. The crystallite size on the 104 planes for Fe_2O_3 .

Lot/Code	Conditions for obtaining/Microwave assisted hydrolytic synthesis/ Temperature /Calcination [$^{\circ}\text{C}$]	Crystallite size [nm]
7P/P _{20s}	0.1M Fe^{3+} , pH=11/300 $^{\circ}\text{C}$	10
7P/P _{21s}	0.1M Fe^{3+} , pH=11/ 800 $^{\circ}\text{C}$	49
8P/P _{23s}	0.4M Fe^{3+} , pH=11/ 300 $^{\circ}\text{C}$	31
8P/P _{24s}	0.4M Fe^{3+} , pH=11/ 800 $^{\circ}\text{C}$	60
9P/P _{26s}	0.7M Fe^{3+} , pH=11/ 300 $^{\circ}\text{C}$	33
9P/P _{27s}	0.7M Fe^{3+} , pH=11/ 800 $^{\circ}\text{C}$	62

In Figs. 9 and 10 infrared spectra (FTIR) of Fe_2O_3 powders obtained by microwave-assisted hydrolytic synthesis are shown. The interior spectrum shows the 450-700 cm^{-1} range, while the large spectrum shows the 400-4000 cm^{-1} range. Table 5 reveals the tentative assignments of chemical bonds, as well as the functional groups in the compounds.

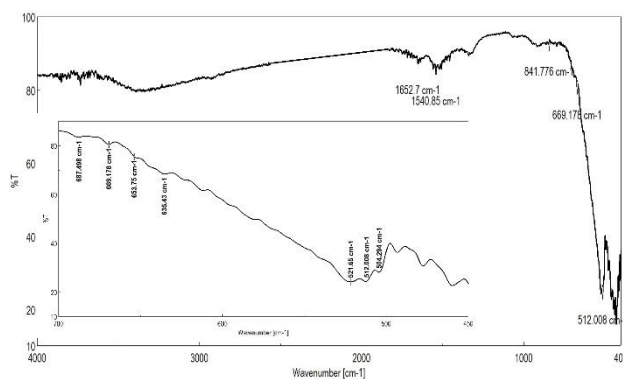


Figure 9. Fourier transform infrared (FT-IR) spectra of Fe_2O_3 sample P_{23s} (powder calcined at 300 $^{\circ}\text{C}$ for 3h, $[\text{Fe}^{3+}] = 0.4 \text{ M}$)

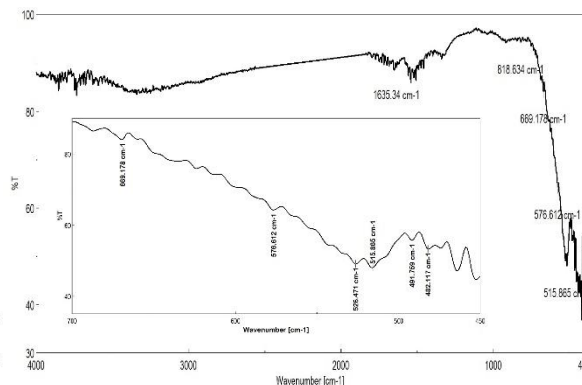


Figure 10. Fourier transform infrared (FT-IR) spectra of Fe_2O_3 sample P_{26s} (powder calcined at 300 $^{\circ}\text{C}$ for 3h, $[\text{Fe}^{3+}] = 0.7 \text{ M}$)

Table 6. IR peaks and assignments of Fe_2O_3 nanostructured particles.

Tentative assignment	Frequency [cm^{-1}]	
	P _{23s}	P _{26s}
stretching vibrations C=O	1652	1635
stretching vibrations Fe-O	841	818
	669	669
	653	576
	521	526
	512	515

Strong bands below 700 cm^{-1} are characteristic features Fe_2O_3 and are attributed to the Fe-O stretching mode [23]. In the region below 700 cm^{-1} four absorption peaks were found at 669 , 653 , 521 , and 512 cm^{-1} corresponding to metal-oxygen (Fe-O) vibrational modes in a hematite lattice for sample $\text{P}_{23\text{s}}$ and 669 , 576 , 526 and 515 cm^{-1} for sample $\text{P}_{26\text{s}}$.

SEM micrographs of iron oxide powders doped with 5% at. K doped powders prepared by microwave-assisted coprecipitation are presented in Figs. 11 and 12. Fig. 11 exemplifies the SEM micrograph of the powder doped and calcined at 300°C for 3h and Fig. 12 explains the SEM micrograph of the powder doped and calcined at 800°C for 3h.

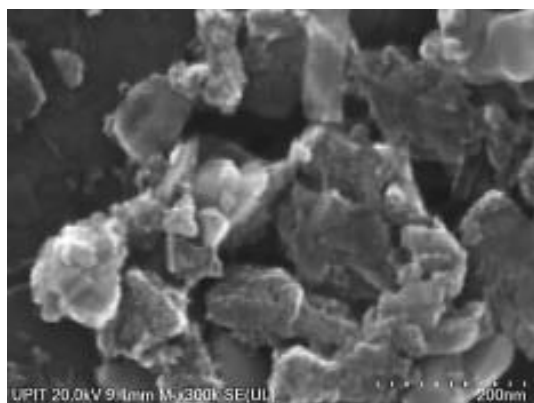


Figure 11. SEM image for PK8 sample (powder calcined at 300°C for 3h)

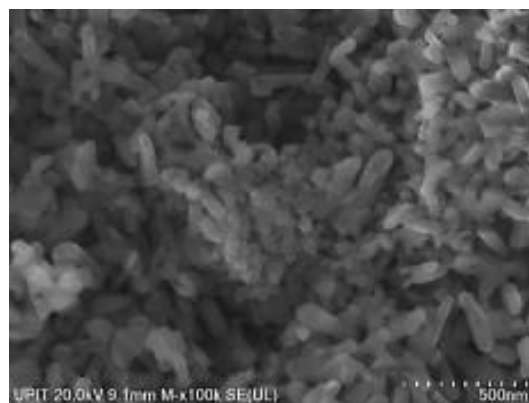


Figure 12. SEM image for PK9 sample (powder calcined at 800°C for 3h)

SEM images show particle agglomeration, and with increasing calcination temperature different particle morphologies change from platelets (Fig. 11) to irregularly shaped polyhedral (Fig. 12). For the PK8 powder, plates with diagonals ranging from 83 - 189 nm were identified, and for the PK9 powder, irregularly shaped polyhedron with diagonals ranging from 49 - 111 nm and plates with diagonals ranging from 86 - 258 nm were identified.

The results are presented in Table 7.

Table 7. Average particle size for synthesized potassium-doped Fe_2O_3

Samples	Conditions for obtaining/Microwave assisted hydrolytic synthesis/ Temperature /Calcination [$^\circ\text{C}$]	Size [nm]	Shape
PK8	0.1M Fe^{3+} ; 0.025 M K^+ pH=11/ 300°C	117	pellet
PK9	0.1M Fe^{3+} ; 0.025 M K^+ pH=11/ 800°C	75	polyhedron
		174	pellet

EDS for 5% K- Fe_2O_3 from Fig. 13 confirms the presence of the elements Fe, O and K.

X-ray spectra of potassium-doped powders produced by microwave-assisted hydrolytic synthesis present the diffraction maxima characteristic of the hexagonal structure of hematite and can be observed for PK8 and PK9 powders.

Fig. 14 evidence the presence of a single phase, hematite, also confirmed for potassium-doped and undoped powders produced by microwave-assisted hydrolytic synthesis, by presenting the overlapped the X-ray spectra of non-doped $\text{P}_{20\text{s}}$, $\text{P}_{21\text{s}}$ and doped PK8, PK9 powders. In the experimental diffraction pattern, no additional diffraction lines related to potassium (dopant) are observed, which indicates a successful doping of iron oxide with potassium either interstitial or substitutional.

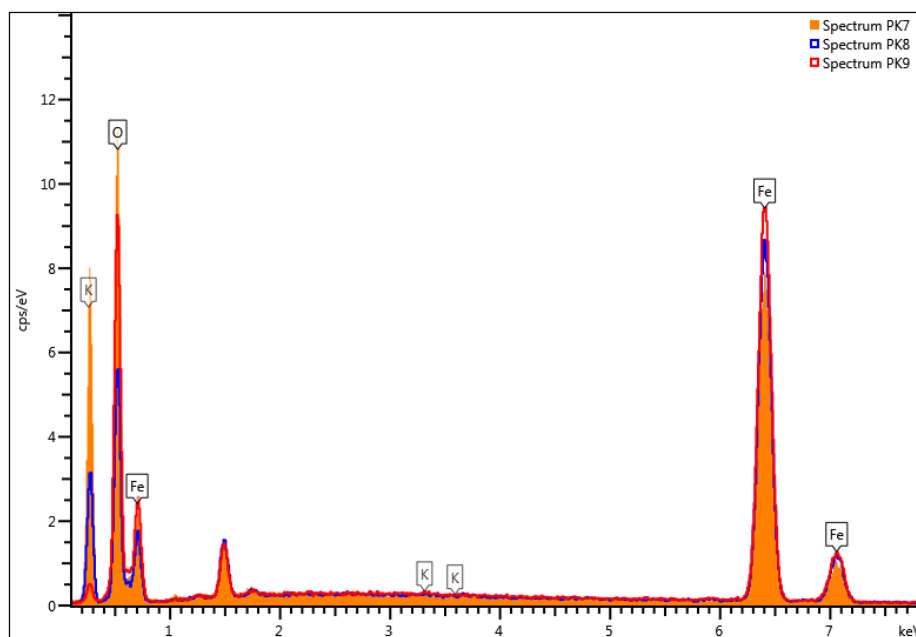


Figure 13. EDS overlapping of 5%K-Fe₂O₃.

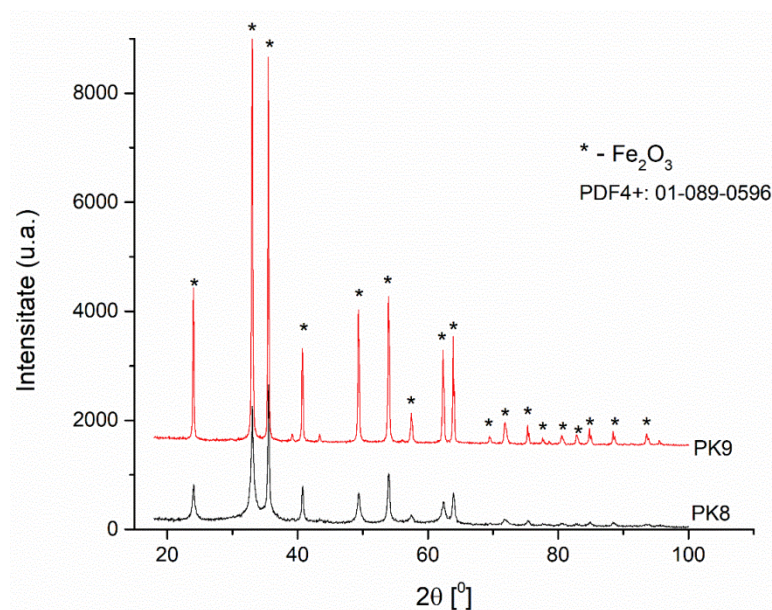


Figure 14. Overlapping XRD patterns of doped powders PK8 and PK9.

Fig. 14 evidence the presence of a single phase, hematite, also confirmed for potassium-doped and undoped powders produced by microwave-assisted hydrolytic synthesis, by presenting the overlapped the X-ray spectra of non-doped P_{20s}, P_{21s} and doped PK8, PK9 powders. In the experimental diffraction pattern, no additional diffraction lines related to potassium (dopant) are observed, which indicates a successful doping of iron oxide with potassium either interstitial or substitutional. The results of the qualitative and quantitative phase analyses that were identified using the PDF 4+ database and the Scherrer relationship on the selected plane (104) are shown in Table 8.

Table 8. The crystallite size on the 104 plane for potassium-doped Fe₂O₃.

Samples	Conditions for obtaining/Microwave assisted hydrolytic synthesis/ Temperature /Calcination [°C]	Crystallite size [nm]
PK8	0,1M Fe ³⁺ ; 0,025 M K ⁺ pH=11/ 300 ⁰ C	15
PK9	0,1M Fe ³⁺ ; 0,025 M K ⁺ pH=11/ 800 ⁰ C	40

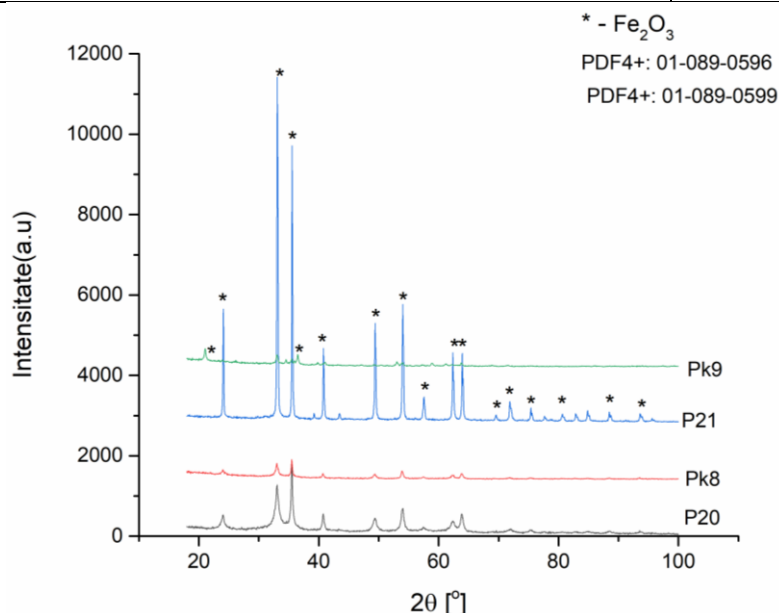
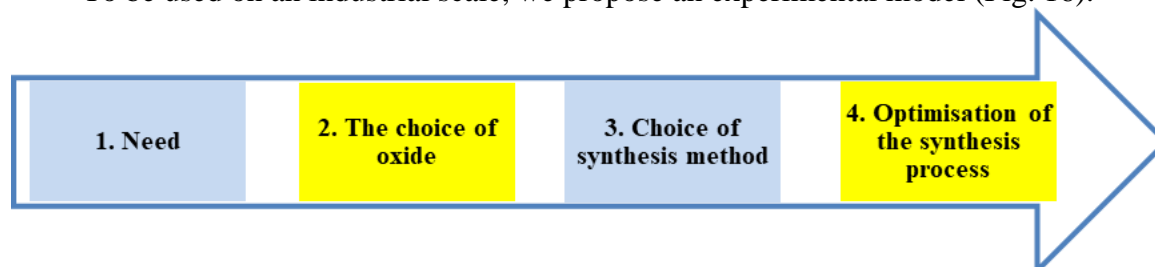
**Figure 15. Overlapping XRD patterns of non-doped P_{20s}, P_{21s} and doped PK8, PK9 powders**

Table 9 shows the lattice parameters for potassium-doped and undoped iron oxide elaborated by microwave-assisted hydrolytic synthesis.

Table 9. Lattice parameters for potassium-doped and undoped iron oxide

Samples	Lattice parameters	
	a=b	c
P20	5.038	13.743
PK8	5.040	13.768
P21	5.035	13.747
PK9	5.037	13.755

To be used on an industrial scale, we propose an experimental model (Fig. 16).

**Figure 16. Experimental model diagram for nanostructured iron oxide developed by microwave-assisted synthesis.**

1. Need - Obtaining nanomaterials by microwave-assisted hydrolytic synthesis with catalytic applications especially for selective catalytic reduction (SCR) of NO_x with NH₃ in diesel exhaust gas due to the low cost and accessibility of the precursors, as well as the reproducibility on an industrial scale.

2. The choice of oxide - Iron oxide is based on nanoscale structural diversity coupled with magnetic properties and wide range of catalytic applications.

3. The choice of the synthesis method - Microwave-assisted hydrolytic synthesis of nanostructured iron oxide and potassium-doped iron oxide.

4. The optimization of the synthesis process - Removal of chlorine ions by repeatedly washing with distilled water and ethyl alcohol. Because of the processing, it was necessary to wash the powders with distilled water and ethyl alcohol to remove the chlorine residue.

4. CONCLUSIONS

Microwaves-assisted hydrolytic synthesis has been successfully performed for the preparation of undoped and potassium-doped iron oxide nanoparticles. By microwave synthesis, an increase in particle size was observed with increasing calcination temperature. The formation of the crystalline hematite phase was not obtained in the microwave heating process. The calcination temperature must convert the prepared sample from the microwave heating process into hematite particles. At the calcination temperature of 800°C a high rate of transformation of the powder into hematite was obtained. Increasing the concentration of the precursor causes the particle size to increase as follows: the platelet size of powders calcined at 300°C after washing varies from 110 to 395 nm; the spherical particle size of powders calcined at 800°C after washing varies from 98 nm to 131 nm. The morphology of the particle changes from platelets to spheres and irregularly shaped polyhedra. EDS analysis indicates Fe, O elements for P_{20s}, P_{26s}, P_{27s} powders; the presence of traces of the chlorine ion (Cl⁻) in the powders P_{21s}, P_{23s}, P_{24s} can be explained by the fact that it (Cl⁻) was not removed by repeated washing with distilled water and ethyl alcohol. XRD spectra reveal qualitative information consisting of the determination of a single-phase, hexagonal hematite structure according to ICDD-PDF-01-089-0599. The crystallite dimensions were calculated with the Scherrer relation on the selected plane (104). Increasing the precursor concentration causes the crystallite size to increase from 10 nm to 33 nm for powders calcined at 300°C. Increasing the precursor concentration increases the crystallite size from 49 nm to 62 nm for powders calcined at 800°C. Increasing the calcination temperature increases the crystallite size. FTIR data showed the Fe-O stretching mode of Fe₂O₃ for powders P_{23s} and P_{26s}. The presence of the doping element was evidenced by EDS analysis. For PK8 and PK9 powders processed by microwave-assisted coprecipitation, calcined at 300°C and 800°C respectively, SEM identified morphologies that changed as a function of calcination temperature, from pellets to irregularly shaped polyhedra, and XRD spectra showed the formation of a single hematite phase with a hexagonal structure, consistent with PDF4+2021- DB:01-085-0596. By doping iron oxide with 5% potassium, no significant changes in lattice parameters were observed.

Powders developed by microwave-assisted hydrolytic synthesis can be used as precursor materials in potential future catalytic applications e.g., for selective catalytic reduction (SCR) of NO_x with NH₃ in diesel exhaust gas due to the low cost and accessibility of the precursors, as well as reproducibility on an industrial scale.

The experimental research performed opens up new development opportunities in the field of nanomaterials with catalytic applications, in particular based on iron oxide, due to uses for the production of catalysts, the dehydrogenation of organic compounds, rechargeable batteries in the cathode composition, reduction of nitrogen oxides in the flue gas mixture.

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