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Dedicated to Professor Eugen Segal
on the occasion of his 80th anniversary

STRUCTURAL CHARACTERIZATION OF NICKEL OXIDE OBTAINED BY THERMAL DECOMPOSITION OF POLYNUCLEAR COORDINATION COMPOUND $[Ni_2(OH)_2(H_3CCH(OH)COO^-)_2(H_2O)_2 \cdot 0.5H_2O]_n$

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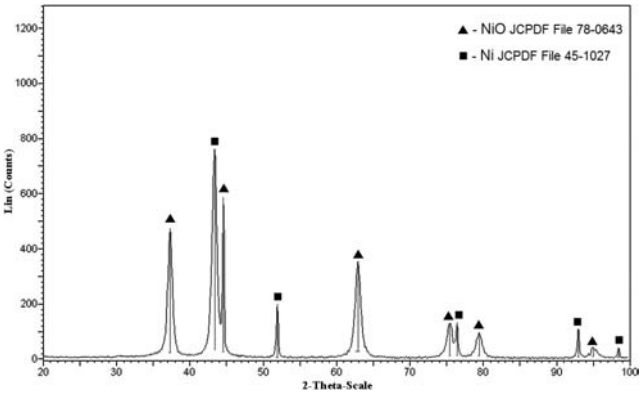
The crystalline structure, composition and surface morphology of nickel oxide obtained at relatively low temperature by thermal decomposition of the polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$, where L is lactate anion (2-hydroxypropionate), were determined by the following methods: powder XRD (X-ray diffraction), EDX (energy dispersive X-ray) and SEM (scanning electron microscopy).
The analysis of X-ray diffraction data show that the nickel oxide is relatively well cristalliyed and can be indexed on the basis of a cubic symetry.
The quantitative elemental analysis by EDX revealed that the product of thermal decomposition of the coordination compound is oxygen-deficient non-stoichiometric nickel oxide.
According to SEM images, the particles of nickel oxide exhibit irregular forms and their size is widely distributed between 10 nm and 5 μm.



INTRODUCTION

Several studies about the properties of nickel oxide and its applicability as catalysts have been performed by different authors.[1-6] In its reduced form, nickel oxide has been mainly used for reactions such as the hydrogenation of nitriles.[7-9]

The use of different preparative methods allows to obtaining nickel oxides with different properties. In the literature, there are described nickel oxides which have been prepared with different degrees of crystallinity, particle sizes (from nanophases to millimeters),[10] morphologies and with specific surface areas.[11]

Several papers presents the decomposition of nickel nitrate hexahydrate to nickel oxide.[12-14] The study of the samples obtained at several temperatures and residual pressure conditions suggests the presence of intermediate compounds with different characteristics, which give place to NiO samples with different surface properties.

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Nanosized materials have attracted many research workers because of their unusual properties based on size-quantization effect and large surface area.[15-19] Nanosized nickel oxide is of great interest because it exhibits anomalous electronic[20-22] and magnetic[23-26] properties. The characteristic properties of nanosized NiO particles also enable one to tailor materials for a variety of applications including catalysis,[27-29] electrochromic windows[30] and sensors.[31] These properties can be enhanced with decreasing the particle size and are highly dependent on particle size. That is why the precise control of the size and distribution in nanometer regime is required. In addition, a facile preparation process that allows convenient production of these particles is necessary for miscellaneous news applications. So far, many different methods have been attempted to synthesize nanosized NiO, such as thermal decomposition,[32,33] microemulsion,[34] precipitation,[35,36] electrochemical deposition,[37] sol–gel technique[38,39] and surfactant-mediated method.[40] The thermal conversion of homo- and hetero-polynuclear complexes with anions of carboxylic acids as ligands have been carried out to oxide systems with irreductible structure and properties, required by the modern technology in various fields.[41-51] These compounds decompose at relatively low temperatures, forming simple or mixed oxides and volatile products (CO, CO_2, H_2O).

The present paper is from a series devotet to the research of the oxyde systems obtained by thermal decomposition of some polynuclear coordination compounds. The main objective of such research is to put in evidence the importance of the precursors in the obtaining of simple and mixed metallic oxydes with different properties and applications.

The present paper has been focused on the characterization of nickel oxide obtained by thermal decomposition of new polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ (L - lactate anion). It will be shown that this coordination compound could be a precursor for non-stoichiometric nickel oxide obtaining at relatively low temperature. The structure, composition and surface morphology of the so obtained nickel oxide will be determined.

RESULTS AND DISCUSSION

X-Ray diffraction

XRD analysis, which is the most useful technique for identification of crystalline structure, was employed to investigate the crystallinity and purity of the solid product obtained by thermal conversion in air of the polynuclear coordination compound. The XRD pattern of the NiO sample (Fig. 1) shows the presence of the characteristic peaks for NiO, in the range of 35 – 100^0 2θ, in accordance with JCPDF File 78-0643. Also, characteristic peaks for Ni are observed (JCPDF File 45-1027). The formation of Ni is due to the reductive character of ligand ($H_3CCH(OH)COO^-$). The important peaks for NiO and Ni are presented in Table 1.

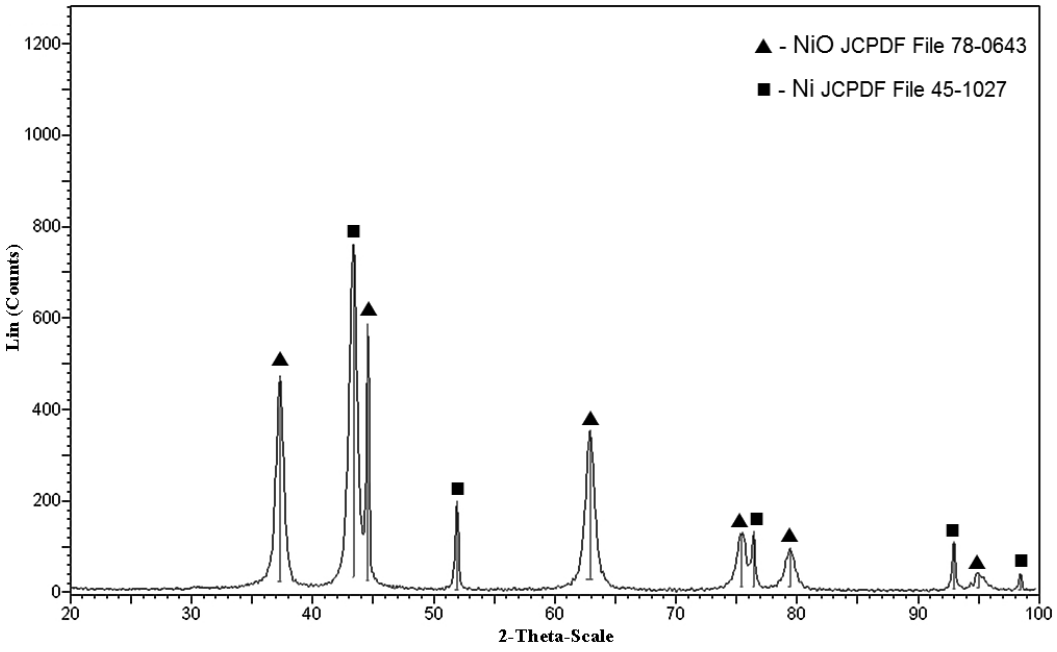


Fig. 1 – The XRD of the solid product obtained by thermal conversion in air of the polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$.

Table 1

X-ray diffraction data

d-spacing (Å)	Relative Intensity (%)	Angle (°2 Theta)	Peak Height (counts)	Background (counts)	Tip Width (°2 Theta)	Significance
2,4094*	61,59	37,2893	448,34	23,63	0,4000	6,22
2,0845	100,00	43,3729	727,95	33,29	0,1000	100,00
2,0316	**77,16**	**44,5627**	**561,65**	**22,17**	**0,2500**	**8,18**
1,7598	**26,48**	**51,9142**	**192,74**	**6,64**	**0,3000**	**6,32**
1,4763	44,83	62,9016	326,31	28,46	0,6500	13,27
1,2594	15,48	75,4161	112,67	12,70	0,2500	0,62
1,2453	**16,59**	**76,4213**	**120,80**	**11,81**	**0,2000**	**1,72**
1,2057	11,53	79,4158	83,94	12,49	0,2500	0,60
1,0622	**14,12**	**92,9634**	**102,81**	**7,33**	**0,2500**	**2,95**
1,0448	4,33	94,9991	31,53	10,33	0,2500	0,67
1,0171	**4,91**	**98,4594**	**35,77**	**5,26**	**0,2500**	**1,68**

* - NiO; - **Ni**

Table 2

Crystallographic data for NiO

d (Å)	Int. (%)	2θ	$\sin^2\theta$	$(h^2 + k^2 + l^2)$	C	(hkl)	a (Å)	ā (Å)	V (Å^3)
2,4094	61,59	37,2893	0,1022	3	0,0340	(111)	4,1772		
2,0845	100,00	43,3729	0,1365	4	0,0341	(200)	4,1727		
1,4763	44,83	62,9016	0,2722	8	0,0340	(220)	4,1772	4,1775	72,9037
1,2594	15,48	75,4161	0,3741	11	0,0340	(311)	4,1772		

As can be seen, the sample is relatively well crystallized and can be indexed on the basis of a cubic symmetry.

The lattice parameters were obtained from the following relationship[52,53]:

$$\sin^2\theta = C(h^2 + k^2 + l^2), \text{ where } C = \lambda^2/4a^2$$

The results of the X-ray structural analysis are given in Table 2.

This indicates a good agreement between the data and the structural model.[53] Also, the XRD pattern of the NiO sample obtained by thermal conversion in air of the polynuclear coordination compound reveals that the diffractogram can be determined as NiO with face-centered cubic phase, also known as the bunsenite structure (lattice constant *a* of cubic unit cell: 0.4177 nm) owing to diffraction peaks at 37.28, 43.37, 62.90, 75.41 and 79.41°, which can be perfectly filed to (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystal planes, respectively (JCPDS 47 – 1049). The crystallite size of the NiO sample can be calculated using Sherrer formula:[54]

$$L = \frac{k\lambda}{\beta \cos\theta},$$

where L is the crystallite size, k is the Sherrer constant usually taken as 0.89, λ is the wavelength of the X-ray radiation (0.154056 nm for Cu Kα), and β is the full width half maximum (FWHM) of diffraction peak measured at 2θ. The estimated crystallite size of the analyzed NiO from line broadening of (2 0 0) diffraction peak at 43.37°, which is the most preferentially oriented crystal plane, is approximately 21.1 nm. Peaks of Ni were found in the XRD pattern, indicating that the nanocrystalline NiO obtained via this method consists of impurified phase.

Energy dispersive X-ray (EDX) microanalysis

A quantitative elemental analysis by EDX of very small areas revealed that the product of thermal decomposition of the complex is a non-stoichiometric oxide.

In Fig. 2 is presented the EDX profile in an area of the surface. It will be noted that the area analyzed by EDX was smaller than 50 nm in diameter.

Table 3 shows the stoichiometry and composition of the nickel oxide analyzed by EDX in an area of the surface.

This indicates that the product of thermal decomposition of the coordination compound is oxygen-deficient non-stoichiometric nickel oxide impurified with Ni.

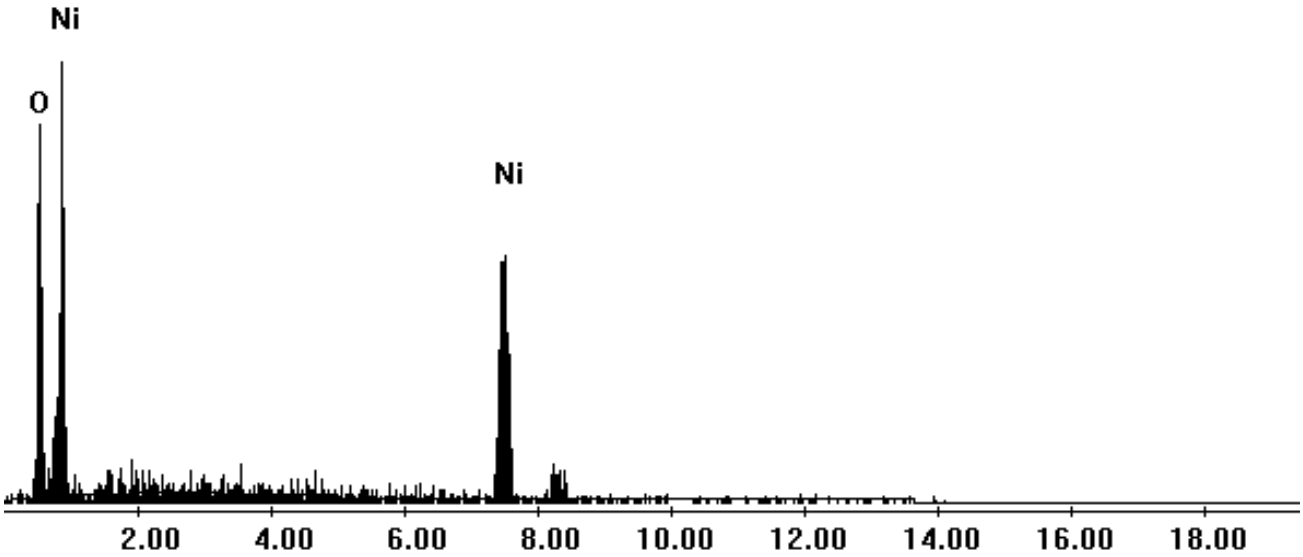


Fig. 2 – EDX profile in an area of the surface.

Table 3

Composition and stoichiometry of NiO obtained from EDX

Composition	(Wt %)	(At %)
Ni	81.50	54.56
O	18.50	45.44
Ni:O (At. ratio)		1.2

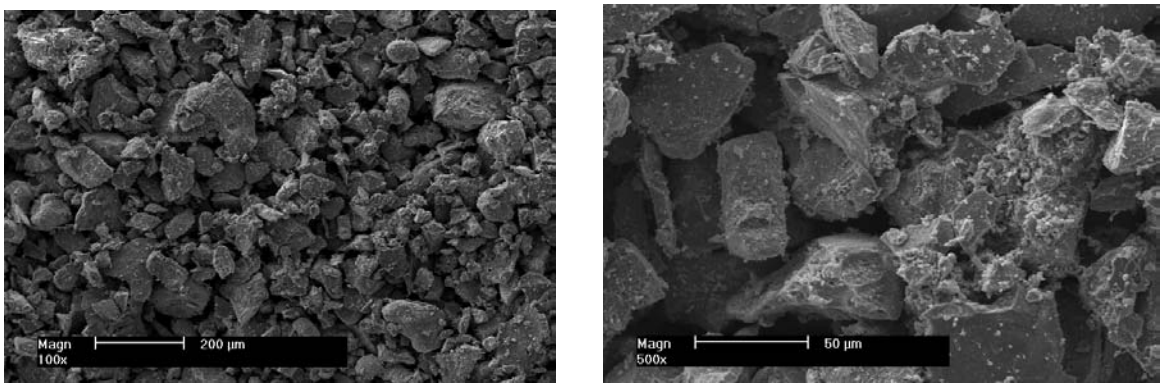
SEM micrography

In order to obtain the useful information about the surface morphology and particle size of the nickel oxide obtained by thermal decomposition of the complex, SEM analysis was performed.

The SEM micrographs (Fig. 3) at different magnification values show that the thermal decomposition product has a microporous structure with a large specific area and are no well-defined particles.

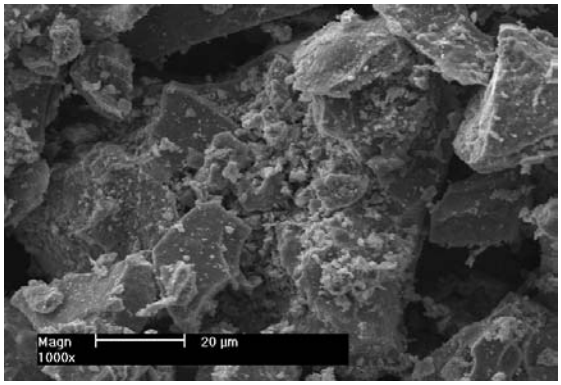
The particles seem parallelepiped with some defined edges but with faces which seem to be formed by small and conglomerated particles (Fig. 3a) that remind cubic crystallites. Other faces can be seen as a group of well-differentiated particles but without defined forms. The increase in the magnification (Fig. 3b-3e) did not allow for better differentiation of the particles.

The formation of NiO aggregates comprising very tiny three-dimensional disordered primary nanoparticles was visibly observed.

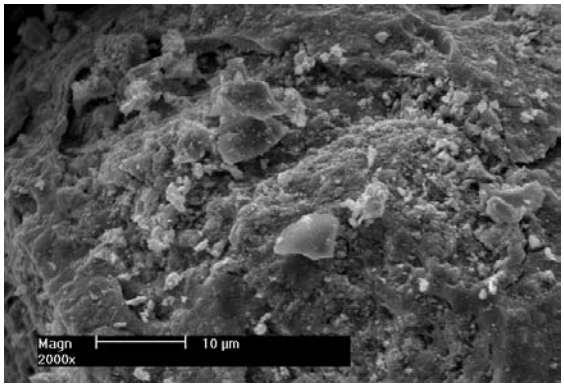


(a) (b)

Fig. 3 – SEM micrographs at different magnification of NiO.



(c)



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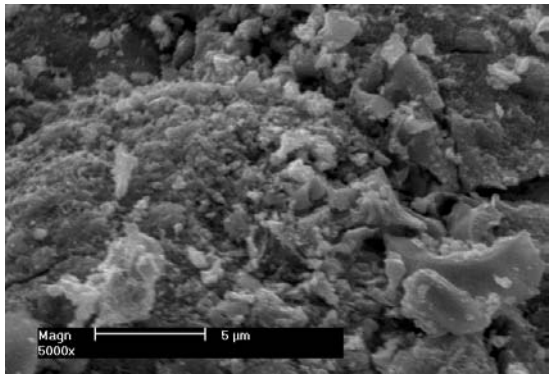

(e)

Fig. 3 – SEM micrographs
at different magnification of NiO.

Nickel oxide obtained by thermal conversion in air of the novel synthesized coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ is a product with very different crystalline morphology. The particles exhibit irregular forms and their size is widely distributed between 10 nm and 5 µm.

EXPERIMENTAL

The obtaining of nickel oxide

The synthesis, by an original method (based on the oxidation reaction of 1,2-propanediol in an alcohol-water system by nickel nitrate and the simultaneous isolation of the coordination compound from the reaction system), and the characterization of the polynuclear coordination compound, $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ were reported in our previous paper.[45]

The results of thermal analysis (TG/DTG, DTA) shown[45] that the following steps occur at the progressive heating of the coordination compond in air atmosphere:

$$Ni_2(OH)_2(H_3CCH(OH)COO^-)_2(H_2O)_2 \cdot 0.5H_2O \xrightarrow{I(50-150^\circ C)-2.5H_2O}$$

$$Ni_2(OH)_2(H_3CCH(OH)COO^-)_2 \xrightarrow{II(150-250^\circ C)-2H_2O} Ni_2O(C_4H_8O(COO^-)_2$$

$$\xrightarrow{III(250-355^\circ C)+6O_2-4H_2O-6CO_2} 2\ NiO$$

(Temperature ranges correspond to the heating of the investigated compound with a heating rate of 5 $K.min^{-1}$.)

According to these results, nickel oxide was obtained by heating, in static air atmosphere at a temperature range of 355 ^0C, of the mentioned coordination compound.

Methods of characterization of nickel oxide

The crystal structure of the nickel oxide obtained by thermal decomposition of polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ was evaluated by X-ray diffraction (XRD), and his microstructure was examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) microanalysis.

Powder X-Ray diffraction patterns of the samples were obtained with a Philips X'PERT diffractometer using Cu K_α radiation (λ = 1,54056Å). The X-Ray power was 40 KV and 50 mA.

The powder samples were grounded in order to reduce the granulation (when necessary) and then pressed in the specimen holder using acetone. The patterns were recorded over a range of 2Θ angles from 20^0 to 100^0 and crystalline phases were identified using the Joint Committee on Powder Diffraction Standards-International Centre for Diffraction Data (JCPDS-ICDD) files. The data were collected with the Philips X'PERT Data Collector programm and processed with Philips X'PERT Graphics & Identify. The insignificant peaks (with an importance less than 0.4) were neglected.

Energy dispersive X-ray microanalysis (EDX) and scanning electron microscopy (SEM) images were recorded on a XL 30 ESEM scanning electron microscope with wolfram cathode (Philips – 2000), operating at accelerating voltage 15 kV, magnification values in the range 100-5000x.

CONCLUSIONS

NiO obtained by thermal decomposition of polynuclear coordination compound $[Ni_2(OH)_2L_2(H_2O)_2 \cdot 0.5H_2O]_n$ is a non-stoichiometric oxide impurified with Ni. The XRD results validate that the synthesized NiO possesses crystallinity of cubic phase. The SEM images show that the NiO nanoparticles were formed with aggregations.

The particles exhibit irregular shapes and their size is widely distributed between 10 nm and 5 μm.

In the future work the results obtained in the investigation of the electrocatalytic properties of the nickel oxide synthetized by the method described in the present paper will be presented.

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