

Elaboration of Copper Zinc Ferrite Nanoparticles: Application in Catalytic Wet H₂O₂ Oxidation of Phenol

E. Chater-Sari¹, C. Zegadi², A. Djelloul^{2,3,*}, S. Rodane¹, M. Sellami¹, M. Kameche², N. Bettahar²

¹ Laboratory of Physical Chemistry of Materials – Catalysis and Environment, Department of Chemistry, Faculty of Chemistry, University of Science and Technology of Oran (USTO) Mohammed Boudiaf, Algérie

² Département de Technologie des Matériaux, Faculté de Physique, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf USTO-MB, BP 1505, El M'naouer, 31000 Oran, Algérie

³ Centre de Recherche en Technologie des Semi-Conducteurs pour l'Energétique 'CRTSE' 02 Bd Frantz Fanon, BP: 140, 7 Merveilles, Alger, Algérie

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This work deals with the synthesis, characterization of mixed oxides of metals and their applications as catalysts. The synthesized ferrite solid solution of formula Fe₂Zn_{1-x}Cu_xO₄ has been prepared from ground frost. The purity of the samples has been verified by X-Ray Diffraction (XRD). The characterizations of samples have been carried out using Fourier Transform InfraRed Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). Refinement of lattice parameters of the solid solution has been elaborated from the basic compound NiFe₂O₄ indexing in a cubic unit cell of space group Fd3m. The trend of the diffraction lines shows that the structure was well crystallized, and there indeed a complete solid solution of cubic symmetry was formed. The SEM micrograph reveals that the samples are presented in the form of nanometer sized crystallites; the samples are in the form of fragments of different sizes in the Cu-Zn mixture. The results show the nanometric size of the grains varying between 90 and 130 nm. These newly elaborated materials have been applied as catalysts for heterogeneous reaction of oxidation of phenolic compounds; subject of investigations in the presence of hydrogen peroxide. The degradation products were analyzed by High Performance Liquid Phase Chromatography (HPLC). The obtained results showed powerful catalytic character of these oxides to completely degrade phenol.

Keywords: Sol-gel, Ferrites, Phenol, Oxidation.

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1. INTRODUCTION

Several transition metal oxides have been studied in recent years for various purposes due to their electrical properties and magnetic extraordinary [1]. The copper based oxides such as iron, cobalt or manganese and even noble metals palladium and platinum are very promising. Oxidation states of these elements and their electronic configurations are the origin of their remarkable structural properties, to great progress in the development of these materials for environmental applications [2]. Most of these mixed oxides were used in catalysis of oxidation in heterogeneous systems [3, 4]. They are made up of transition metals with variable oxidation states (Mo, Ni, Co, Fe, V, Nb).

Catalytic oxidation of organic compounds in aqueous solution is an important reaction for the purification of industrial effluents. In order to increase the yield of the reaction, an oxidizing agent such as hydrogen peroxide can be used advantageously [5]. This approach is part of a contribution in the field of catalysis for accessing a wide variety of catalysts. The goal of the present work was to test the capacity and efficiency of our oxides. It consists in the development of suitable catalysts in the laboratory, for the depollution of industrial waste sewage in polluting organic phenol. Within this framework, we have highlighted the solid solution of Fe₂Zn_{1-x}Cu_xO₄ ferrite prepared from ground freezing [6-7] with different fractions of $x = 0, 0.2, 0.4, 0.6, 0.8, 1$ and its use as a catalyst to degrade phenol [8]. After their synthesis,

these samples were characterized using the analysis techniques XRD, SEM and FTIR spectroscopy. Besides, the degraded products were analyzed by HPLC.

After spectra indexing and refinement of the lattice parameters, the results show the existence of a total solid solution of cubic symmetry of space group Fd3m. The substitution of zinc (RIV = 0.74 Å) by copper (RIV = 0.73 Å) was conducted for each measurement of fraction.

2. EXPERIMENTAL DETAILS

2.1 Materiel and Methods

The new sol-gel phase Fe₂Zn_{1-x}Cu_xO₄ [9] was prepared from a stoichiometric mixture of three salts: FeCl₃ (99 %), CuCl₂ (99.9 %) and ZnCl₂ (99.8 %) purchased from Prolabo and Rectapur respectively. Each salt was dissolved in an appropriate amount of distilled water or another solvent to obtain clear and limpid solutions before mixing in a beaker. After, an equivalent amount of citric acid was added as a ligand. The obtained mixture was then warmed up under agitation with temperatures ranging between 70 °C and 80 °C for 24 h until a freeze was attained. Then, the substance was dried inside an oven and crushed using an agate mortar. Next, it was put into aluminum pots for thermal treatment at a temperature of 650 °C for 24 h. As a first step, the content was heated up to 750 °C and then crushed. Finally, the product in the

* djelloulertse@gmail.com

form of very fine powder was synthesized. The products were compacted in the form of pellets in a press of 400 kgf/cm² and then heated to 800 °C during 24 h.

2.2 Characterization

After their synthesis, the catalysts were characterized using XRD, FTIR and SEM consequently. The XRD patterns were obtained using the diffractometer Bruker D8 Advance. The infrared spectra were performed using spectrophotometer Aircraft FT/IR-4200 type A in areas located between 4000 cm⁻¹ and 400 cm⁻¹. The SEM images were carried out using the optical apparatus Jeol JSM 6360LV.

3. RESULTS AND DISCUSSION

3.1 Structural and Morphological Properties

The XRD data was used to investigate the structural properties of copper zinc ferrite nanoparticles prepared by sol-gel method.

Fig. 1 illustrates the XRD spectra of Fe₂Zn_{1-x}Cu_xO₄ solid solution of all fractions. Refinement of lattice of the solid solution parameters was carried out from the basic compound NiFe₂O₄ indexing in a cubic unit cell of space group Fd3m [10].

Fig. 2 shows the variation of the mesh parameter a according to the fraction x of substitution of the solid solution Fe₂Zn_{1-x}Cu_xO₄ with $0 \leq x \leq 1$ prepared from the frost. The observed difference was due to the different ionic sizes of the two cations of substitution used throughout the synthesis.

The IR spectra of the material heated to 105 °C and 800 °C and prepared by sol-gel fraction 0.6 route are presented in Fig. 3 and Fig. 4, respectively. The IR spectra recorded for the samples heated to 105 °C show that the precursors are all common groups of citric acid as well as those of citrate salts. Indeed, citric acid first appears in wide bands 2500-3500 cm⁻¹ characteristic of carboxylic acids. The narrow strip located in the 1670-1760 cm⁻¹ band corresponds to the asymmetric stretching vibration C=O. The presence of citrate salts

(carboxylate ions) is distinguished by two strips located at about 1620-1540 cm⁻¹ corresponding to the asymmetric stretching vibrations of the respectively COO-monodentate complex and the bridged complex, and the band at about 1260-1300 cm⁻¹ for the symmetric vibrations COO. The absorption bands in the vicinity of 1406-1416 cm⁻¹ are due to metal chelating by citrate. Citrates common bands (acid and salt) are identified in the IR spectrum at frequencies of 3440, 3390 and 3380 cm⁻¹ due to the stretching vibrations OH and CH, respectively. Moreover, the broad bands at around 1030 and 1060 cm⁻¹ are used by the stretching vibration CO.

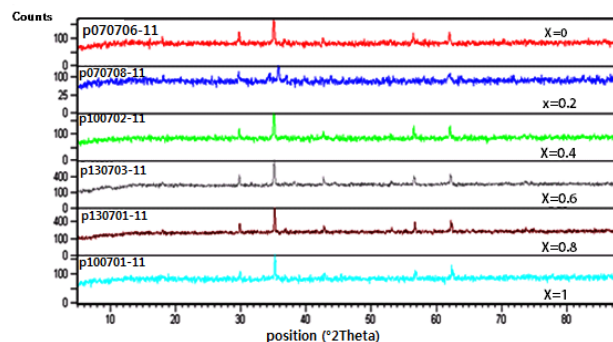


Fig. 1 – Diffraction pattern of the Fe₂Zn_{1-x}Cu_xO₄ solid solution prepared by sol-gel method

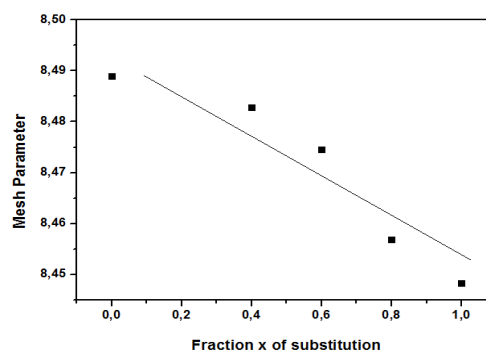


Fig. 2 – Variation of the lattice parameter a depending on the fraction x of the substitutional solid solution Fe₂Zn_{1-x}Cu_xO₄

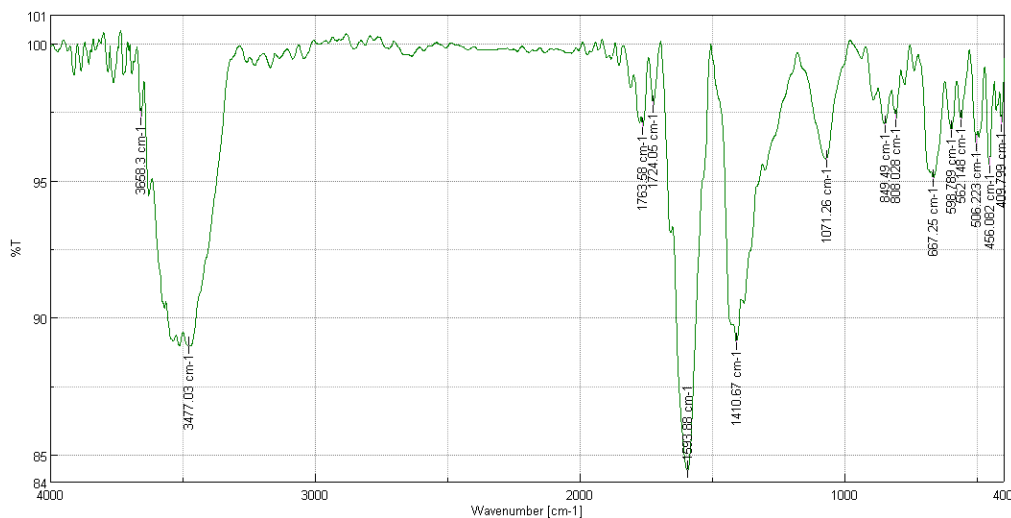


Fig. 3 – Infrared spectrum of the fraction $x = 0.6$ by the sol-gel developed before calcination

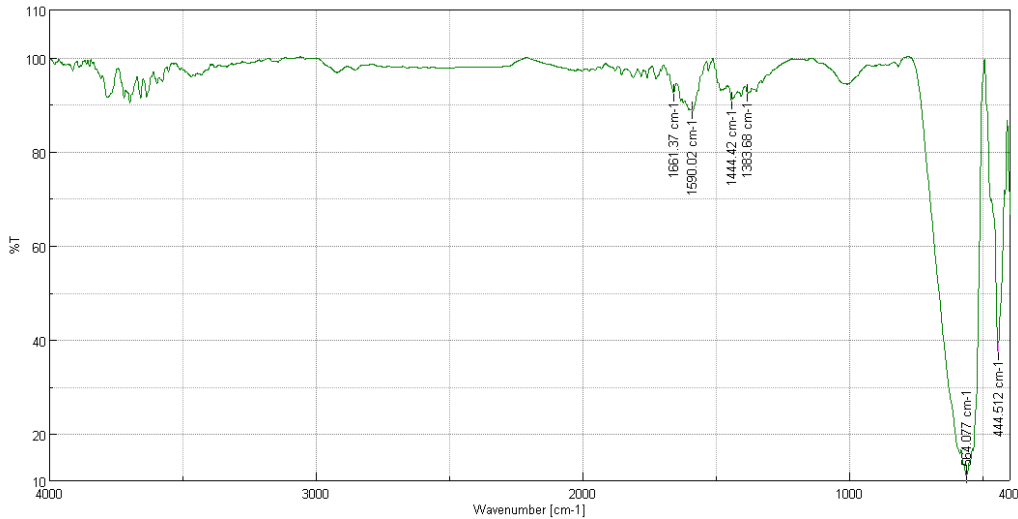


Fig. 4 – Infrared spectrum of the fraction $x = 0.6$ by the sol-gel developed after calcination

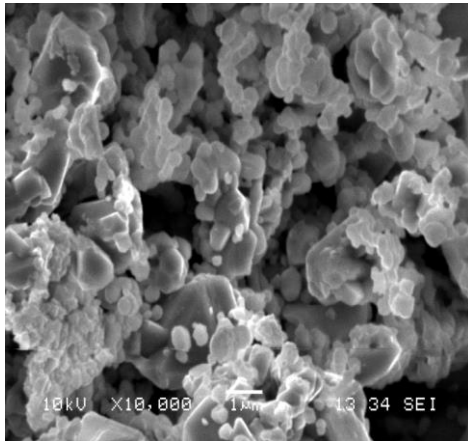


Fig. 5 – MEB photo of the compound Fe_2ZnO_4 ($x = 0$) synthesized by the sol-gel method

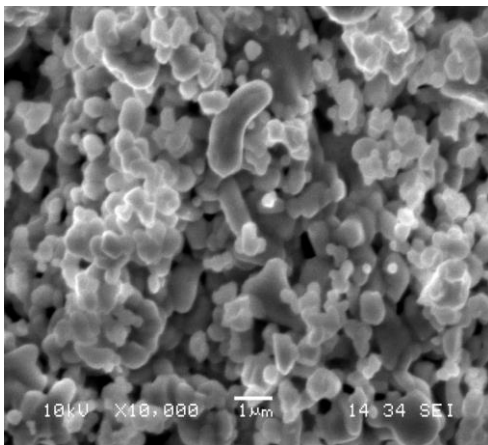


Fig. 6 – MEB photo of the compound $\text{Fe}_2\text{Zn}_{0.8}\text{Cu}_{0.2}\text{O}_4$ ($x = 0.2$) synthesized by the sol-gel method

Whilst, the symmetric vibration CO is illustrated by the intense and broad band at $1250\text{-}1260\text{ cm}^{-1}$. The stretching vibrations O-M and O-M-O are revealed by the bands located between 410 and 640 cm^{-1} .

Fig. 5, Fig. 6 and Fig. 7 give SEM images of solid solution $\text{Fe}_2\text{Zn}_{1-x}\text{Cu}_x\text{O}_4$ for fractions $x = 0, 0.2, 0.6$, re-

spectively. Samples are presented in the form of nanometer sized crystallites. The samples are in the form of fragments of different sizes in the Cu-Zn mixture. The average grain size D can be calculated using the Debye Scherrer's formula [11]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (1)$$

where β is the full width at half maximum (FWHM) of the diffraction peak. The results show the nanometric size of the grains varying between 90 and 130 nm .

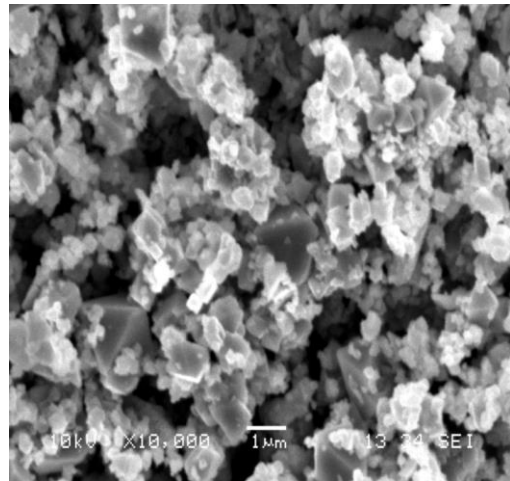


Fig. 7 – MEB photo of the compound $\text{Fe}_2\text{Zn}_{0.4}\text{Cu}_{0.6}\text{O}_4$ ($x = 0.6$) synthesized by the sol-gel method

The different catalysts to synthesize solid solutions of transition metal oxide are very solicited in the catalysis of oxidation in degradation of organic pollutants such as phenol [12].

The pH measurements show that it is acidic and becomes slightly more acidic [13].

The work shows the best results in acid and alkaline media in the presence of solid catalysts based on oxides of transition metals, whose active components pass easily in solution at low pH and can then contribute to activity [14]. The oxidation of phenol reaction

was made according to the procedure described in the literature [15]. In a tricol balloon equipped with a refrigeration system, 0.1 g of catalyst was introduced in the presence of 15 ml of a solution of phenol concentration 0.06 mol/l. After 15 min, hydrogen peroxide was added in molar phenol/H₂O₂ fraction equal to 3. It resulted in a high oxidizing power. In acid medium, there was a protonation of H₂O₂ oxonium ion [16], attributing electrophilicity to the peroxide. The whole was vigorously stirred at a constant temperature of 70 °C for 4 h. A thermometer was used to check and maintain the steady enclosure temperature, as well as a pH meter to measure the pH of the solution at the beginning and end of the reaction.

The first part of the experiment was devoted to the adsorption of compounds in solution on the surface of the catalyst. The phenomenon of adsorption caused a decrease of concentration of the compound in solution, variable according to the adsorbent/adsorbate ratio, i.e. the couple catalyst/compound in solution. There was transfer of the solution to the surface of the catalyst [17]. In practice, after 15 min, the concentration was almost stabilized inside the reactor, regardless of the adsorbent/adsorbate pair. The resulting mixture was filtered and then placed in a separator funnel. Then, a quantity of chloroform was added to extract the organic phase. The obtained samples were finally analyzed by HPLC.

Table 1 – Conversion and selectivity of various catalysts

	Phenol conversion rate	Products
Ferrite sol gel $x=0$	100%	Total selectivity
Ferrite sol gel $x=0.2$	100%	Total selectivity
Ferrite sol gel $x=0.4$	100%	Total selectivity
Ferrite sol gel $x=0.6$	100%	Total selectivity
Ferrite sol gel $x=0.8$	100%	Total selectivity
Ferrite sol gel $x=1$	100%	Total selectivity

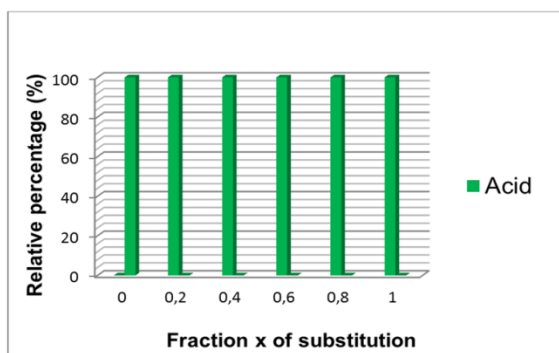


Fig. 8 – The relative percentages of the degradation products depending on the fraction x of substitution (sol-gel ferrite)

Table 1 summarizes the results of this analysis namely the conversion rates of oxidation of phenol for each substitution of the ferrite type Fe₂Zn_{1-x}Cu_xO₄ solution prepared through sol-gel as well as the selectivity of each catalyst. Besides, Fig. 8 shows the relative percentages of degradation products of fraction x of substitution. The results show that these catalysts are fully active in oxidation, since no trace of phenol was found in the results (Fig. 9, Fig. 10 and Fig. 11). In this way, we may notice that the degraded products were

acids for all substitutions with a percentage of 100 %. All the catalysts have thus a total selectivity.

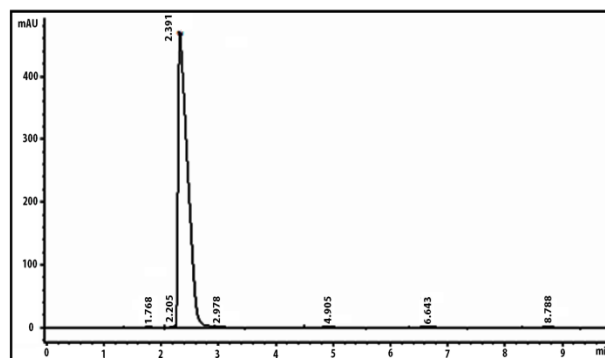


Fig. 9 – Phenol degradation in the presence of H₂O₂/ferrite catalyst type ($x = 0$)

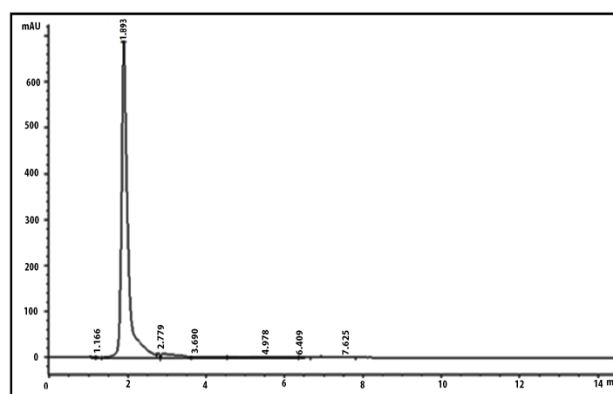


Fig. 10 – Phenol degradation in the presence of H₂O₂/ferrite catalyst type ($x = 0.2$)

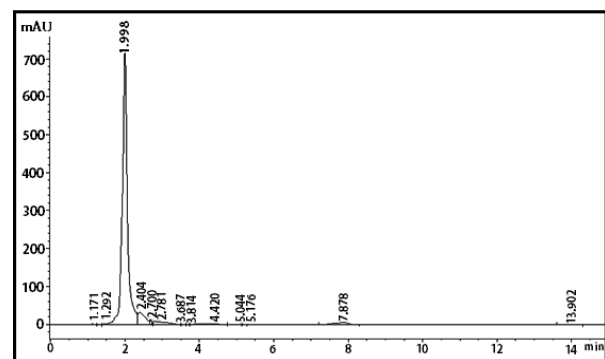


Fig. 11 – Phenol degradation in the presence of H₂O₂/ferrite catalyst type ($x = 0.6$)

4. CONCLUSIONS

The compound prepared by sol-gel process from ferrite solid solution of formula Fe₂Zn_{1-x}Cu_xO₄ with $0 \leq x \leq 1$ enabled to obtain a total solid solution of cubic symmetry of space group Fd3m with a decrease of the mesh parameter a from 8.49 Å down to 8.44 Å depending on the fraction x of substitution. This decrease may be due to the difference between the ionic radii of zinc (0.74 Å) and copper (0.73 Å). The spectra are fully similar to the spectrum of the starting compound NiFe₂O₄. The analysis of the samples by SEM allowed to see the state of the surface of our samples. We can conclude

that the grains forming the samples synthesized by the sol-gel method are in crystallite form of nanometric size in the presence of microcavities. Moreover, HPLC analysis revealed that the ferrite catalysts prepared according to sol-gel process were fully active in oxidation, since no trace of phenol was found.

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Розробка наночастинок фериту цинку міді: застосування в каталітичному вологому окисненні H_2O_2 фенолу

E. Chater-Sari¹, C. Zegadi², A. Djelloul^{2,3}, S. Rodane¹, M. Sellami¹, M. Kameche², N. Bettahar²

¹ *Laboratory of Physical Chemistry of Materials – Catalysis and Environment, Department of Chemistry, Faculty of Chemistry, University of Science and Technology of Oran (USTO) Mohammed Boudiaf, Algérie*

² *Département de Technologie des Matériaux, Faculté de Physique, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf USTO-MB, BP 1505, El M'naouer, 31000 Oran, Algérie*

³ *Centre de Recherche en Technologie des Semi-Conducteurs pour l'Energétique 'CRTSE' 02 Bd Frantz Fanon, BP: 140, 7 Merveilles, Alger, Algérie*

Ця робота стосується синтезу і характеристики змішаних оксидів металів та їх застосування як каталізаторів. Синтезований твердий розчин фериту $\text{Fe}_2\text{Zn}_{1-x}\text{Cu}_x\text{O}_4$. Чистота зразків була підтверджена рентгенівською дифракцією (XRD). Характеристики зразків отримували за допомогою інфрачервоної спектроскопії з використанням перетворення Фур'є (FTIR) та скануючої електронної мікроскопії (SEM). Уточнення параметрів решітки твердого розчину було розроблено з індексації основної сполуки NiFe_2O_4 у кубічній елементарній комірниці просторової групи $\text{Fd}\bar{3}m$. Тенденція ліній дифракції показує, що структура була добре кристалізована, і справді утворився повноцінний твердий розчин кубічної симетрії. Мікрофотографія SEM виявляє, що зразки представлені у вигляді кристалітів нанометрового розміру; зразки представлені у вигляді фрагментів різної величини в суміші Cu-Zn. Результати показують нанометровий розмір зерен, що змінюється між 90 і 130 нм. Ці нещодавно розроблені матеріали застосовуються як каталізатори для неоднорідної реакції окислення фенольних сполук; предмет дослідження за наявності перекису водню. Продукти деструкції аналізували високоефективною рідинною хроматографією. Отримані результати показали потужний каталітичний характер цих оксидів до повного розкладання фенолу.

Ключові слова: Золь-гель, Ферити, Фенол, Окислення.