

SYNTHESIS AND CATALYTIC PROPERTIES OF $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ FERRITE

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Abstract

Copper-zinc spinel oxide nanoparticles have been prepared by method of precipitation with following thermal treatment. DTA, X-ray powder diffraction, IR Spectroscopy and ^{57}Fe Mössbauer spectroscopy were used for the samples characterization. The formation of ferrite phase with cubic structure was observed for the materials treated at 400°C, 500°C, 700°C. A significant change in the average crystallite size from 19.3 to 42.8 nm and slight increase in the lattice parameters with the annealing temperature increase were detected. The highest catalytic activity in methanol decomposition with about 70% selectivity to CO and hydrogen was observed for the sample obtained at 400°C.

Key words: nanocrystalline ferrite materials, Mössbauer spectroscopy, methanol decomposition

1. INTRODUCTION

Nanostructured ferrite materials are topics of many scientific investigations due to their potential application in biology, electronics and catalysis. The spinel ferrite materials can be denoted with general formula $\text{M}^{2+}\text{Fe}_2^{3+}\text{O}_4$, where M could be Co, Cu, Zn, Ni, etc. Mixed Ni-, Zn- and Cu- ferrites are of great interest and many investigations have been done for their application such as multilayer chip inductors, electronic devices, computer devices, communication (Tangcharoena T.) (Lin C.-H., 2009), (Hashim M., 2013). $\text{Zn}_x\text{Ni}_{1-x}\text{Fe}_2\text{O}_4$ spinel ferrite has been used at large scale to produce all kinds of broadband elements (Ajmal M., 2008). According to (Lee M., 2012) the inverse spinels are known to have catalytic activity that originates from a change in the oxidation state of the [B] site metal ion (2+ and 3+). In our previous work (Velinov N., 2012) we demonstrated synthesis of bi-component Ni-Zn ferrites with different composition and their catalytic behaviour in methanol decomposition was tested. The formation of defect spinel structure was confirmed by the calculated degree of lattice microstrain and the complex relation between the catalytic activity and samples composition was assumed as a result of ions environment changes in this defective structure. The aim of current investigation is to study the effect of the annealing temperature on the formation of mixed multi-component $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ spinel ferrites from hydroxide carbonate precursor. Their catalytic properties in methanol decomposition to CO and hydrogen and the changes with the spinel phase under the reaction medium are also in the focus of the investigation. Recently, methanol decomposition has received a considerable interest as a potential source of ecological fuel for fuel cells, gas turbines and vehicles due to its relatively low reforming temperature, high energy density, safe to handle and low cost (Wilson M., 2009). Despite copper catalysts are typically used for methanol decomposition (Yong S., 2008), (Lin S., 2009), (Velinov N., 2013), to the best of our

knowledge, there are no reports in the literature regarding the catalytic behavior of mixed Zn-Cu ferrites in reaction of methanol decomposition.

2. EXPERIMENTAL

2.1. Synthesis

$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ has been prepared by thermal synthesis from hydroxide carbonate precursor. As starting materials were used $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in corresponding ratio. The mixed Cu, Zn, Fe nitrate solution was precipitated with drop wise addition of 1M Na_2CO_3 with continuous stirring up to pH=9. The precipitate was wash with distilled water and dried at room temperature to form hydroxide precursor powders. The thermal treatment (TS) was carried out in air at temperature at 300°C, 400°C, 500°C, 700°C with duration of four hours. The samples were denoted as $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4 \text{ TS}_x$, where x is the annealed temperature in °C.

2.2. Methods of characterization

The dried hydroxide carbonate precursor (HC) was analysed by Thermogravimetry-Differential Thermal Analysis (TG-DTA) using “Stanton Redcroft” (England) in static air at 10 K/min heating rate. The powder XRD patterns were recorded by use of a TUR M62 diffractometer with $\text{Co K}\alpha$ radiation. The observed patterns were cross-matched with those in the JCPDS database. The average crystallites size (D), the degree of microstrain (ϵ) and the lattice parameters (a) of the studied ferrites were determined from the experimental XRD profiles by using the PowderCell-2.4 software (Kraus W., 2000). The instrumental broadening of diffraction peaks is equal to 0.020° Bragg angle. It was determined by Al standard and was excluded at calculation of crystallites size and the degree of microstrain. The Mössbauer spectra were obtained at room temperature (RT) with a Wissel (Wissenschaftliche Elektronik GmbH, Germany) electromechanical spectrometer working in a constant acceleration mode. $^{57}\text{Co/Rh}$ source (activity $\cong 50$ mCi) and $\alpha\text{-Fe}$ standard were used. The experimentally obtained spectra were fitted using CONFIT2000 software (Žák T., 2006). The parameters of hyperfine interaction such as isomer shift (IS), quadrupole splitting (QS), effective internal magnetic field (H_{eff}), line widths (FWHM), and relative weight (G) of the partial components in the spectra were determined. The infrared (IR) spectra were recorded using a Nicolet 20SXC IR spectrometer, on samples pelletized with KBr.

2.3. Catalytic experiments

Methanol conversion was carried out in a flow reactor (0.055 g of catalyst, three times diluted with grounded glass), argon being used as a carrier gas (50 ml/min). The methanol partial pressure was 1.57 kPa. The catalysts were tested under conditions of a temperature-programmed regime within the range of 350-770 K with heating rate of 1 K/min. On-line gas chromatographic analyses were performed on HP apparatus equipped with flame ionization and thermo-conductivity detectors, on a PLOT Q column, using an absolute calibration method and a carbon based material balance. The products selectivity was calculated as $X_i/X \cdot 100$, where X_i is the current yield of the product i and X is methanol conversion.

3. RESULTS AND DISCUSSION

TG-DTA measurements were carried out to investigate the thermal evolution of hydroxide carbonate precursor and formation of spinel ferrite phase. The TG curve describes weight loss of 17 % at low temperatures as can be seen in Fig. 1. The weight loss corresponds to endothermal effect due to the dehydration and decarbonisation of the hydroxide carbonate precursor.

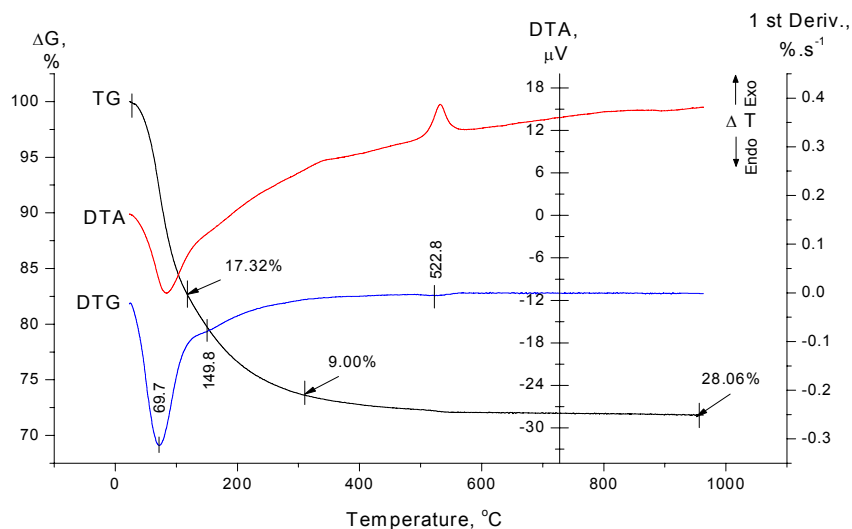


Fig. 1 DTA analysis of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\text{-HC}$ sample

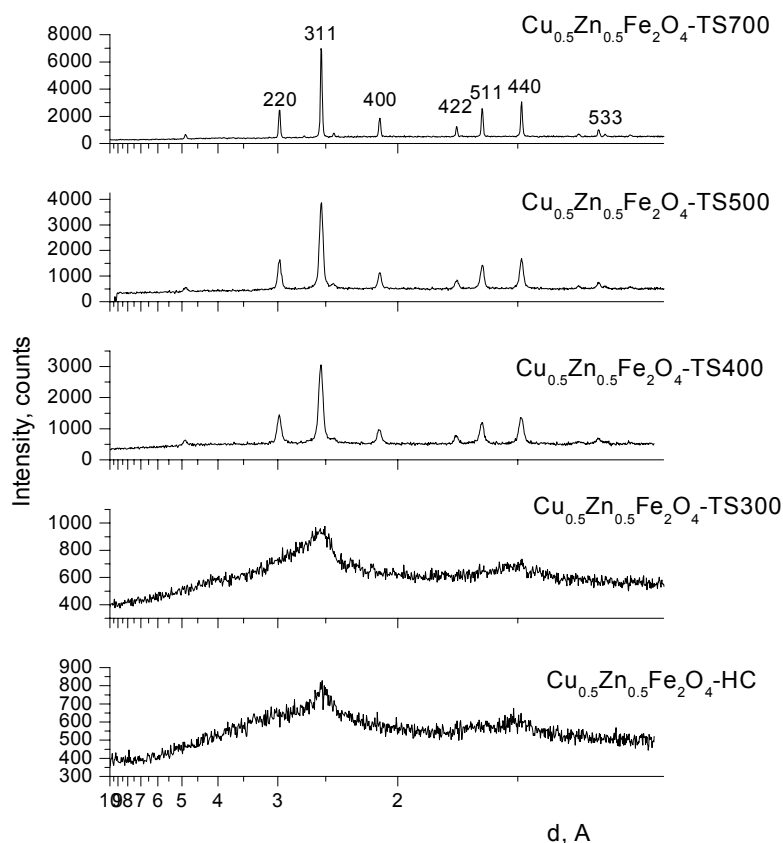


Fig. 2 XRD analysis of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples HC, TS300, TS400, TS500 and TS700

The observed exothermal effect in higher temperature is not accompanied with mass loss and could be associated with formation of crystalline Cu-Zn ferrite phase.

Powder XRD patterns of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ HC precursor and the samples obtained after HC thermal treatment at 300, 400, 500 and 700°C are presented in Fig. 2. As can be seen the sample treated at the lowest temperature shows still amorphous behavior. The Bragg reflections for the samples synthesized above 300°C at (220), (311), (400), (422), (511), (400), (533) are conspicuous and correspond to spinel crystal structure (PDF 770012).

Average crystallites size (D), degree of microstrain (ϵ) and lattice parameters determined from XRD patterns of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS 400, 500, 700 are given in Table 1. The reflections became narrower with annealing temperature increase in the range 400-700°C (Fig.2). This effect was also confirmed by calculation approach using Williamson-Hall method, where an increase of crystallites size from 19.30 nm to 42.80 nm was observed. Similar dependence has been reported by (Hua P., 2010), (Hua P., 2011), (Sujatha C., 2012). The appearance of small quantities of secondary phase of Fe_2O_3 in the sample $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS 700 was also detected, that can be effect of annealed treatment (Tsoncheva T., 2010).

Table 1. Average crystallites size (D), degree of microstrain (ϵ) and lattice parameters determined from XRD patterns of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS400, TS500 and TS700

Sample	Phases	D, nm	$\epsilon 10^3$, a.u	a, Å	%
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS400	Fd3m(227)-cubic	19.30	3.65	8.40	100
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS500	Fd3m(227)-cubic	21.79	2.80	8.41	100
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS700	Fd3m(227)-cubic	42.80	0.35	8.41	98
	Fe_2O_3				2

The IR transmittance spectra of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -HC and $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -(TS) are shown in Fig 3. The absorption broad band in the range from 1250 to 1750 cm^{-1} consisting of three separately maxima at 1382 cm^{-1} , 1469 cm^{-1} and 1629 cm^{-1} was detected in the spectrum of HC. They can be attributed to vibration of HCO_3^- and CO_3^{2-} groups. The band at about 3400 cm^{-1} is typical for OH-groups vibrations. The IR spectra of the samples obtained at 400, 500, 700 °C reveal two absorption bands at about 400 cm^{-1} and 563 cm^{-1} . These bands are a common feature of all ferrites and the variations in their wavenumbers can be attributed to the changes in the Fe^{3+} - O^{2-} bond length at octahedral (Fe-O-B) and tetrahedral (Fe-O-A) site of unit cell, respectively (Mahmoud M., 2012).

Mössbauer spectra of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples treated at 300, 400, 500, 700 °C are presented in Fig. 4. The calculated parameters of Mössbauer analyses are listed in Table 2. The Mössbauer spectra of hydroxide carbonate precursor powder and $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS300 consist of quadrupole doublet component, indicating that the samples are paramagnetic. The spectrum of the sample $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS400 was fitted with doublet due to the super-paramagnetic behavior with relative weight $G=22\%$ and sextet with ferrimagnetic behavior with $G=78\%$. The secondary phase of $\alpha\text{-Fe}_2\text{O}_3$ in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS 700 sample detected by XRD analysis was confirmed also by Mössbauer spectra as a sextet % with parameters of $IS=0.37$ mm/s, $QS=-0.20$ mm/s, $H_{\text{eff}}=51.4$ T and relative weight $G=4\%$. The best fitting of the data for $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ -TS 500 is defined as one sextet of Fe^{3+} ions in tetrahedral position and with more than one sextet of Fe^{3+} ions in octahedral position.

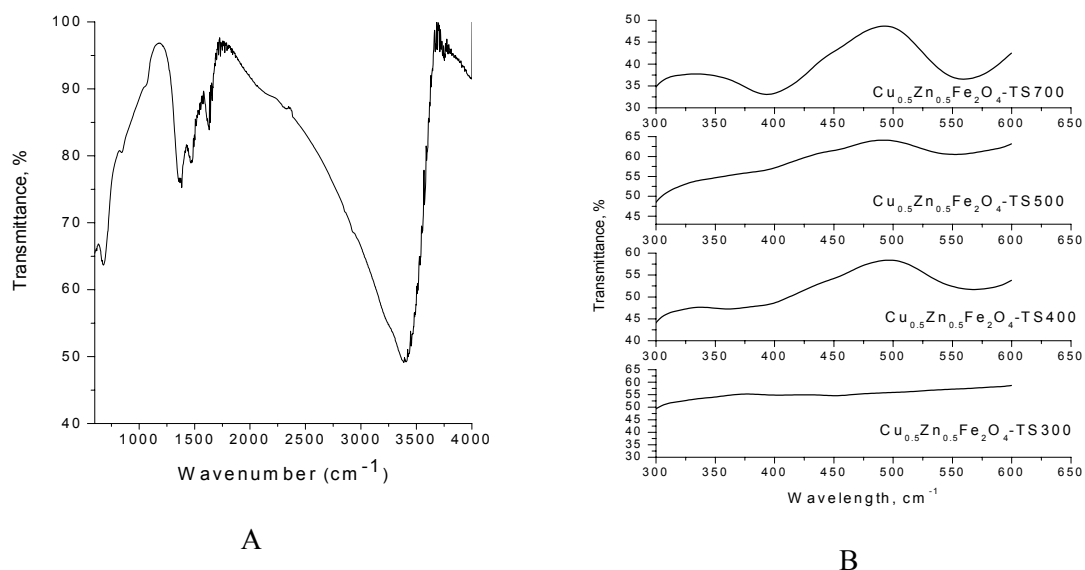


Fig. 3 IR transmittance spectra of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\text{-HC}$ (A) and $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS}$ (B)

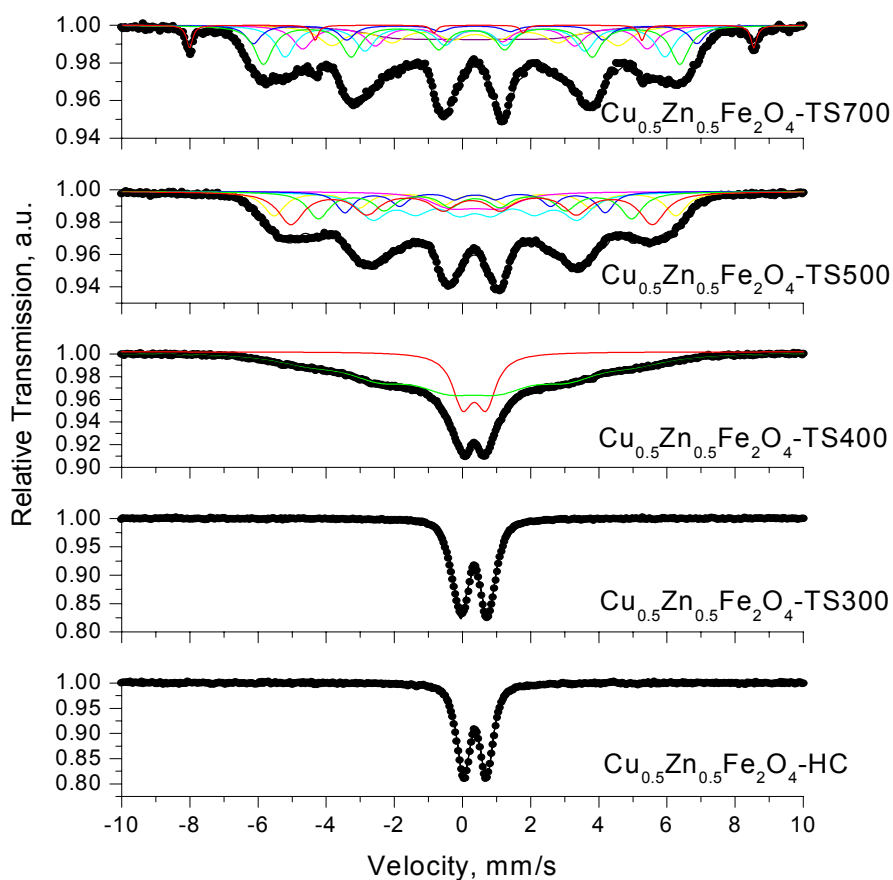


Fig. 4 Mössbauer spectra of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ samples

Table 2 Parameters of Mössbauer spectra of the investigated samples

Sample	Components	IS, mm/s	QS, mm/s	H _{eff} , T	FWHM, mm/s	G, %
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -HC	Db	0.37	0.68	-	0.43	100
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS300	Db	0.34	0.81	-	0.52	100
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS400	Sx1	0.30	-0.03	29.6	2.44	78
	Db	0.35	0.69	-	0.71	22
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS500	Sx1-Fe ³⁺ tetra	0.27	0.46	32.0	0.91	25
	Sx2- Fe ³⁺ octa	0.37	0.00	28.5	0.77	18
	Sx3- Fe ³⁺ octa	0.37	0.00	23.7	0.60	10
	Sx4- Fe ³⁺ octa	0.37	0.00	18.7	1.02	24
	Sx5- Fe ³⁺ octa	0.37	0.00	5.6	1.23	8
	Sx6- Fe ³⁺ octa	0.37	0.00	34.6	0.75	15
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS700	Sx1- Fe ³⁺ Fe ₂ O ₃	0.37	-0.20	51.4	0.22	4
	Sx2- Fe ³⁺ tetra	0.27	0.00	37.0	0.65	23
	Sx3- Fe ³⁺ octa	0.37	0.00	40.4	0.55	8
	Sx4- Fe ³⁺ octa	0.37	0.00	34.6	0.68	19
	Sx5- Fe ³⁺ octa	0.37	0.00	31.4	0.70	15
	Sx6- Fe ³⁺ octa	0.37	0.00	26.1	0.93	16
	Sx7- Fe ³⁺ octa	0.37	0.00	15.4	0.02	14

Temperature dependencies of methanol conversion and the changes with the CO selectivity for all ferrite materials are presented in Fig. 5. Methane (up to 5-10 %) and CO₂ (up to 25-30 %) were also detected as by-products. The samples differed significantly in their activity depending on the annealing temperature and superior catalytic activity even at relatively low temperatures (430-450 K) was observed for Cu_{0.5}Zn_{0.5}Fe₂O₄ -TS400. The catalytic activity was lower for the sample with low degree of crystallization of spinel phase (Cu_{0.5}Zn_{0.5}Fe₂O₄ -TS300). It also significantly decreased for the samples obtained at higher annealing temperature, and according to the XRD and Mössbauer spectra, it could be due to the growth of the ferrite particles and partial destruction of ferrite phase with the formation of Fe₂O₃ as well.

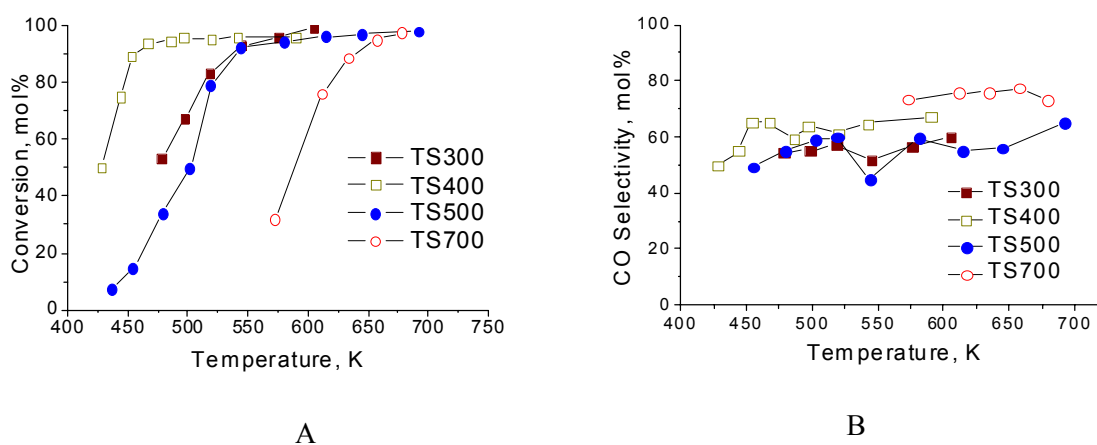


Fig. 5 Methanol conversion (A) and CO selectivity (B) vs. temperature of Cu_{0.5}Zn_{0.5}Fe₂O₄ ferrites

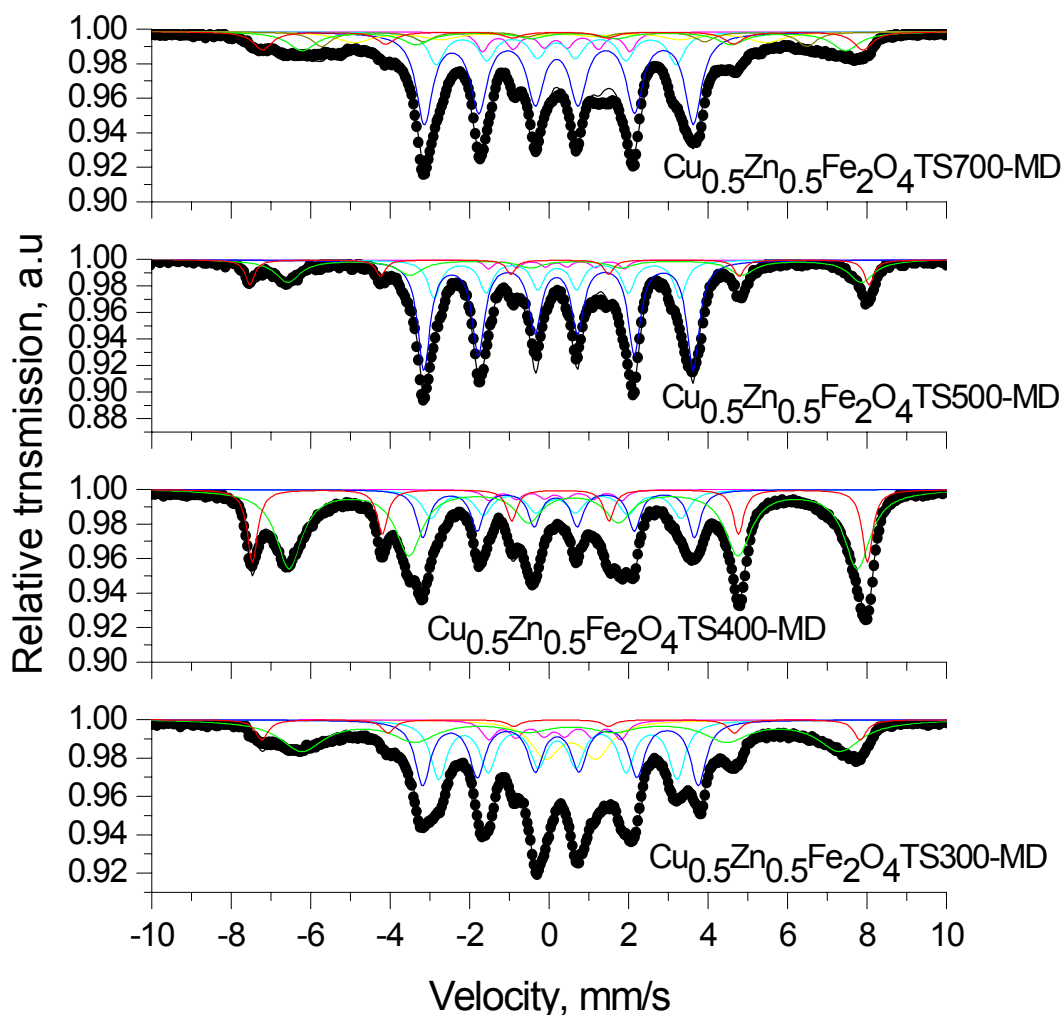


Fig. 6 Mössbauer spectra of samples after catalytic test

Phase transformation of catalysts after the catalytic test was detected by XRD (not shown) and Mössbauer spectroscopy (Fig. 6 and Table 3). The XRD analysis revealed reflections of ZnO, Fe_5C_2 and metallic Cu in all investigated samples. A spinel structure, which could be attributed to Zn-substituted magnetite, was also registered. This assumption is illustrated by Mössbauer spectra of the materials, which calculated parameters of superfine interaction correspond to $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$. Zn-substituted magnetite can be denoted with the formula $(\text{Zn}^{2+}_x\text{Fe}^{3+}_{1-x})_{\text{tetra}}[\text{Fe}^{3+}_{1+x}\text{Fe}^{2+}_{1-x}]_{\text{octa}}\text{O}_4$. Mössbauer spectrum of magnetite (Fe_3O_4) i.e. $x=0$ consist of two Zeeman sextets (for Fe^{3+} tetra and Fe^{3+} octahedral coordination) with $\text{Fe}_{\text{tetra}}\text{-Fe}_{\text{octa}}$ relative weight ratio of 1:2. However, the calculated ratio of Sx1 and Sx2 of samples after catalytic reaction is higher than 1:2, which could be attributed to the substitution of Fe^{3+} in tetrahedral position in magnetite lattice with zinc ions. The estimated degree of Zn-ions is given in Table 3 by formula: $x=1-2A/B$, where A and B are the relative weight of Sx1 and Sx2, respectively. It was observed a clear tendency of formation of the same phases in

investigated samples in different proportion. About 14 % non-reduced ferrite phase is registered by Mössbauer spectra for Cu_{0.5}Zn_{0.5}Fe₂O₄-TS700-MD.

Table 3 Parameters of Mössbauer spectra of the investigated samples after catalytic reaction of methanol decomposition

Sample	Components	IS, mm/s	QS, mm/s	Heff, T	FWHM, mm/s	G, %
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS300-MD	Sx1- Zn _x Fe _{3-x} O ₄ , Fe ³⁺ _{tetra}	0.30	0.00	46.8	0.38	5
	Sx2- Zn _x Fe _{3-x} O ₄ , Fe ^{2,5+} _{octa} (x=0.62)	0.54	0.01	42.0	1.33	27
	Sx3- χ -Fe ₅ C ₂	0.24	0.09	21.5	0.47	26
	Sx4- χ -Fe ₅ C ₂	0.21	0.01	18.6	0.49	25
	Sx5- χ -Fe ₅ C ₂	0.14	0.01	10.3	0.41	7
	Db	0.54	1.27	-	0.87	10
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS400-MD	Sx1- Zn _x Fe _{3-x} O ₄ , Fe ³⁺ _{tetra}	0.28	-0.01	48.0	0.31	17
	Sx2- Zn _x Fe _{3-x} O ₄ , Fe ^{2,5+} _{octa} (x=0.32)	0.61	0.00	44.4	0.80	50
	Sx3- χ -Fe ₅ C ₂	0.20	0.07	21.2	0.37	17
	Sx4- χ -Fe ₅ C ₂	0.17	0.01	19.4	0.51	13
	Sx5- χ -Fe ₅ C ₂	0.15	0.01	10.3	0.35	3
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS500-MD	Sx1- Zn _x Fe _{3-x} O ₄ , Fe ³⁺ _{tetra}	0.26	0.00	48.4	0.28	8
	Sx2- Zn _x Fe _{3-x} O ₄ , Fe ^{2,5+} _{octa} (x=0.06)	0.66	-0.03	44.8	0.75	17
	Sx3- χ -Fe ₅ C ₂	0.21	0.05	21.0	0.37	52
	Sx4- χ -Fe ₅ C ₂	0.20	0.00	19	0.38	19
	Sx5- χ -Fe ₅ C ₂	0.18	0.00	10	0.27	3
Cu _{0.5} Zn _{0.5} Fe ₂ O ₄ -TS700-MD	Sx1- Zn _x Fe _{3-x} O ₄ , Fe ³⁺ _{tetra}	0.30	0.07	46.9	0.56	8
	Sx2- Zn _x Fe _{3-x} O ₄ , Fe ^{2,5+} _{octa}	0.62	0.00	42.5	0.85	12
	Sx3- χ -Fe ₅ C ₂	0.21	0.05	21.03	0.50	44
	Sx4- χ -Fe ₅ C ₂	0.18	0.00	18.77	0.49	15
	Sx5- χ -Fe ₅ C ₂	0.17	0.01	11.53	0.36	7
	Sx6-Cu _{0.5} Zn _{0.5} Fe ₂ O ₄	0.38	0.00	37.93	0.59	6
	Sx7-Cu _{0.5} Zn _{0.5} Fe ₂ O ₄	0.28	0.00	32.24	1.06	8

4. CONCLUSION

Nanocrystalline $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ ferrite materials were successfully synthesized by method of coprecipitation with following thermal treatment in the range 300-700 °C. A significant change in the average crystallite size from 19.30 to 42.80 nm with increase of annealing temperature was observed. The sample obtained at 400 °C reveal the highest catalytic activity with about 70% selectivity in methanol decomposition to CO and hydrogen. XRD and Mössbauer analysis of the samples after the catalytic test reveal decomposition/reduction transformations with the ferrite spinel structure by the influence of the reaction medium with the formation of a mixture of $\text{Zn}_x\text{Fe}_{3-x}\text{O}_4$ and Fe_3C_2 .

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REFERENCES

- Ajmal M., Maqsood A. (2008) Structural, electrical and magnetic properties of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites ($0 \leq x \leq 1$), Volume 460, *Journal of Alloys and Compounds* Issues 1-2 54–59.
- Hu P., Yang Hai-bo, Pan De-an, Wang Hua, Tian Jian-jun, Zhang Shen-gen, Wang Xin-feng, Volinsky Alex A. (2010) Heat treatment effects on microstructure and magnetic properties of Mn–Zn ferrite powders, *Journal of Magnetism and Magnetic Materials* 322 173–177.
- Hu P., Pan D., Wang X., Tian J., Wang J., Zhang S., Volinsky A. A. (2011) Fuel additives and heat treatment effects on nanocrystalline zinc ferrite phase composition, *Journal of Magnetism and Magnetic Materials* 323 569–573.
- Hashim M., Alimuiddin, Shirsath S. E., Kumar S., Kumar R., Roy A. S., Shah J., Kotnala R.K. (2013) Preparation and characterization chemistry of nano-crystalline Ni–Cu–Zn ferrite, *Journal of Alloys and Compounds* 549 348–357.
- Kraus W., Nolze G. (2000) PowderCell for Windows, Federal Institute for Materials Research and Testing, Berlin.
- Lee M. S., Lee J. Y., Lee W., Moon D. J., Lee K. (2012) The effect of Zn addition into NiFe_2O_4 catalyst for high-temperature shift reaction of natural gas reformat assuming no external steam addition, *International Journal of Hydrogen energy* 37 11218-11226.
- Lin S. D., Ting C. H., Chen L. (2009) The steady state methanol decomposition reaction over Cu/Zn and Cu/Cr catalysts: Pretreatment, operando EXAFS and activity study, *Applied Catalysis A: General* 360 226–231
- Lin C., Wang C., Fu Y. (2009) Characterization of Ni–Cu–Zn ferrite prepared from industrial wastes, *Ceramics International* Volume 35, Issue 6, August, Pages 2325–2328.
- Mahmoud M.H., Abd-Elrahman M.I. (2012) Infrared investigations of Cu–Zn ferrite substituted with rare earth ions, *Materials Letters* 73 226–228.

Sujatha Ch., Reddy V. K., Babu S. K., Reddy R. A., Rao K.H. (2012) Effects of heat treatment conditions on the structural and magnetic properties of MgCuZn nano ferrite, *Ceramics International* 38 5813–5820.

Tangcharoena T., Ruangphanit A., Pecharapa W. (2013) Structural and magnetic properties of nanocrystalline zinc-doped metal ferrites (metal=Ni; Mn; Cu) prepared by sol–gel combustion method, *Ceramics International* 39 S239–S243.

Tsoncheva T., Manova E., Velinov N., Paneva D., Popova M., Kunev B., Tenchev K., Mitov I. (2010) Thermally synthesized nanosized copper ferrites as catalysts for environment protection, *Catalysis Communication* 12 105-109.

Velinov N., Manova E., Tsoncheva T., Estournès C., Paneva D., Tenchev K., Petkova V., Koleva K., Kunev B., Mitov I./ (2012) Spark plasma sintering synthesis of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferrites: Mössbauer and catalytic study *Solid State Sciences* 14 1092-1099.

Velinov N., Koleva K., Tsoncheva T., Manova E., Paneva D., Tenchev K., Kunev B., Mitov I. (2013) Nanosized $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite as catalyst for methanol decomposition: Effect of preparation procedure, *Catalysis Communications* 32 41–46.

Wilson M.S. (2009) Methanol decomposition fuel processor for portable power applications, *International Journal of Hydrogen energy* 34 2955-2964.

Yong S.T., Hidajat K., Kawi S. (2008) The roles of Cu, Zn and Mn in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Mn}_2\text{O}_4$ spinel-lattice catalyst for methanol decomposition, *Catalysis Today* 131 188–196.

Žák T., Jirásková Y. (2006) CONFIT: Mössbauer spectra fitting program, *Surface and Interface Analysis* 38 710.