


Influence of gold presence and thermal treatment on recrystallization of copper-manganese ferrite catalysts

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Abstract The present work aims to evaluate the influence of synthesis conditions and gold addition on structural and functional characteristics of copper-manganese ferrites. Object of the investigation is spinel ferrite with composition $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$, thermally treated at different conditions. The influence of gold deposition on structure of ferrites and catalytic properties in water-gas shift reaction (WGSR) is studied on the ferrite sample obtained at 300 °C. Structural characteristics of samples are determined by Mössbauer spectroscopy and X-Ray diffraction. The Mössbauer spectra of treated at different temperature ferrite samples consist of sextet and doublet components. A comparative assessment of crystallite size of ferrite phase was accomplished from the calculated value of the hyperfine fields. It was established well expressed tendency of ferrite crystallite growth with increasing of thermal treatment temperature. Increasing of the ferrite crystallite size in presence of gold in the sample is established, too. The analysis of catalytic activity in WGSR shows unexpected result i.e. the activity of gold-modified ferrite sample is lower than that of the sample without gold. Probably this is due to complex factors, including recrystallization of the ferrite phase due to additional thermal treatment at higher temperature, addition of gold, changes of the structural features and phase composition during catalytic test.

Keywords Copper-manganese ferrites · Mössbauer spectroscopy · Water-gas shift reaction · Gold catalysts · Recrystallization

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2017), Saint-Petersburg, Russia, 3-8 September 2017*
Edited by Valentin Semenov

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1 Introduction

The ferrites with spinel structure can be divided to three groups according to occupation of divalent and trivalent cations of tetrahedral and octahedral positions – normal, inverse and partial inverse. Normal spinel is when all divalent cations occupy only tetrahedral sites, inverse – when all divalent cations occupy octahedral sites and partially inverse – when divalent cations are distributed in tetrahedral and octahedral sites. It is known, that different metal cations reveal different preferences to occupy tetrahedral and octahedral positions in the spinel structure [1].

The numerous studies of spinel ferrites are provoked by the interest to investigate the relation of structure and functional properties as magnetic, optical, catalytic etc. [2–5]. Typical example for catalyst with spinel structure is magnetite (Fe_3O_4). It is the main active phase of iron-containing catalysts in the high temperature stage of WGS, which performs at 350–450 °C [6]. It is known that in some cases multi-component ferrites have better catalytic behavior than single component ferrite [7–10]. Moreover, gold modified iron oxide shows high catalytic activity at low temperature [11]. It is known that the catalytic properties of ferrites strongly depend on the size of the particles, which are closely related to preparation conditions [12]. Mössbauer spectroscopy is suitable method for iron oxide nanoparticles investigation, by reason of its size sensitiveness [13].

The aim of the present work is to evaluate the influence of synthesis conditions and Au presence on structural and functional characteristics in WGS of copper-manganese ferrites. Object of the investigation is spinel ferrite with $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ composition, thermally treated at different conditions.

2 Experimental

Ferrite samples with $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ composition were synthesized by auto-combustion sol-gel method using the procedure of the lowest pH of the initial solution reported in [14] and followed by different thermal treatment. Shortly, following experimental procedure was used: $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in corresponding stoichiometric ratio was dissolved in distilled water at room temperature and constant stirring; citric acid was added to the solution in a molar ratio equal to the sum of the metal ions and stirring was continued at 60 °C; the water was evaporated partly from the solution by heating and continuous stirring on a magnetic stirrer; the auto-combustion process was performed by heating the samples in an oven at 150 °C for one hour. As-obtained sample was designated by $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-CA}$. Two samples were further thermally treated at 300 °C and 500 °C with a heating rate of 10 °C/min and holding at the reference temperature two hours, identified with $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300}$ and $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS500}$, respectively.

The modification of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300}$ by gold (2 wt.%) was carried out by deposition-precipitation method. The ferrite material was suspended in water, and the deposition was performed by simultaneous addition of an aqueous solution of HAuCl_4 and Na_2CO_3 at 60 °C and pH 7.0. The next steps included aging at 60 °C for 1 h, filtering and washing until complete removal of Cl^- ions, drying under vacuum at 80 °C and calcination in air at 400 °C for 2 h. The sample was denoted as $\text{Au/Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300+400}$. Additionally, one sample without gold was thermally treated at the same conditions ($\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300+400}$).

Powder X-ray diffraction (XRD) patterns were collected on a TUR M62 diffractometer with $\text{Co K}\alpha$ radiation. Phase identification was performed using ICDD-PDF2 Database.

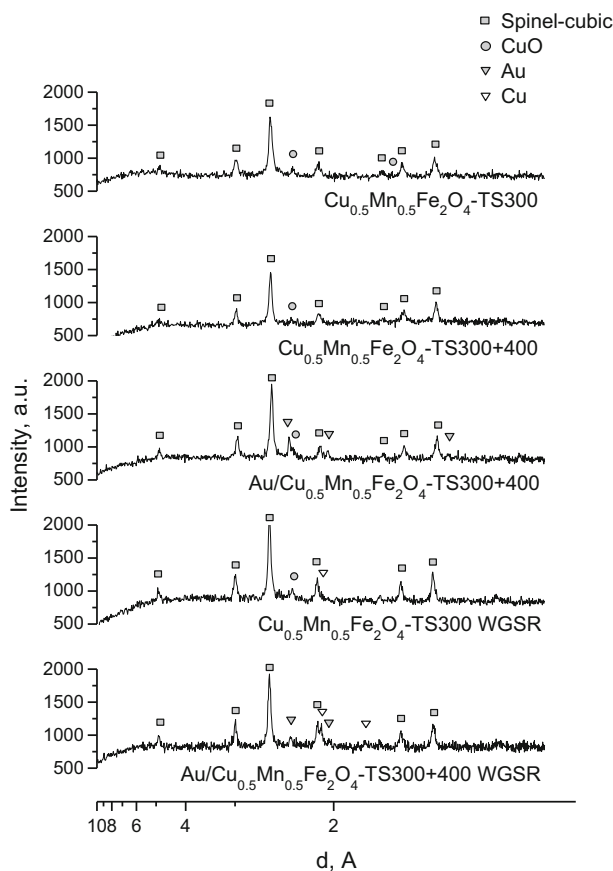


Fig. 1 XRD patterns of the investigated samples

The average crystallite size (D), the degree of microstrain (e) and the lattice parameters (a) of the studied ferrites were determined from the experimental XRD profiles by using the PowderCell-2.4 software and appropriate corrections for the instrumental broadening.

The Mössbauer spectra were recorded at room temperature (RT) using a Wissenschäftliche Elektronik GmbH, (Germany) electromechanical spectrometer working in a constant acceleration mode. A $^{57}\text{Co}/\text{Rh}$ (activity $\cong 10$ mCi) source and αFe standard were used. CONFIT2000 software [15] was used for fitting of the experimentally obtained spectra. The parameters of hyperfine interaction such as isomer shift (δ), quadrupole splitting (Δ), quadrupole shift (2ε), magnetic hyperfine field (B_{hf}), line widths (Γ_{exp}), and relative weight (G) of the partial components in the spectra were determined.

The water-gas shift activity tests were carried out in a flow reactor at atmospheric pressure. The catalytic measurements were conducted at the temperature range of 140–300 °C. The applied experimental conditions were as follows: catalyst bed volume – 0.5 cm³, space velocity – 4000 h⁻¹, partial pressure of water vapor 31.1 kPa and the reactant feed with model gas mixture (5.02 vol. % CO in argon). Before catalytic tests the samples were submitted to controlled mild reduction in a reaction mixture (CO/Ar and water vapor) up to

Table 1 Average crystallites size (D), degree of microstrain (ϵ) and lattice parameters of the ferrite phase in samples treated at different temperature determined from the experimental XRD profiles

Sample	Phase	D, nm	$\epsilon \cdot 10^3$, a.u.	Lattice parameters, Å	%
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -CA	Spinel, cubic	14.2	2.9	a=8.45	96.2
	CuO			a=4.75 b=3.38 c=5.09 beta=98.22	3.8
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300	Spinel, cubic	14.2	2.9	a=8.42	93.0
	CuO			a=4.68 b=3.44 c=5.18 beta=100.31	7.0
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS500	Spinel, cubic	20.3	2.7	a=8.38	76.8
	CuO	12.1	4.6	a=4.56 b=3.31 c=5.04 beta=98.89	1.4
	Fe ₂ O ₃	59.6	2.9	a=5.04 c=13.73	21.8
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300+400	Spinel, cubic	19.0	2.0	a=8.38	96.4
	CuO	12.5	4.8	a=4.67 b=3.35 c=5.16 beta=98.93	3.6
Au/Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300+400	Spinel, cubic	24.1	5.2	a=8.38	88.3
	Au	29.7	1.9	a=4.07	0.8
	CuO	13.0	4.7	a=4.68 b=3.43 c=5.07 beta=99.42	10.9
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300 WGSR	Spinel, cubic	28.2	3.2	a=8.47	83.7
	Cu	10.0	2.6	a=3.63	2.7
	CuO	12.7	6.0	a=4.66 b=3.50 c=5.07 beta=99.50	13.6
Au/Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300+400 WGSR	Spinel, cubic	37.3	5.1	a=8.47	91.2
	Au	11.9	4.6	a=4.03	1.0
	Cu	10.7	3.6	a=3.63	7.8

30 °C. The catalytic activity data were expressed by degree of CO conversion. The measurements were recorded after establishing of the steady-state conditions of conversion at corresponding temperatures.

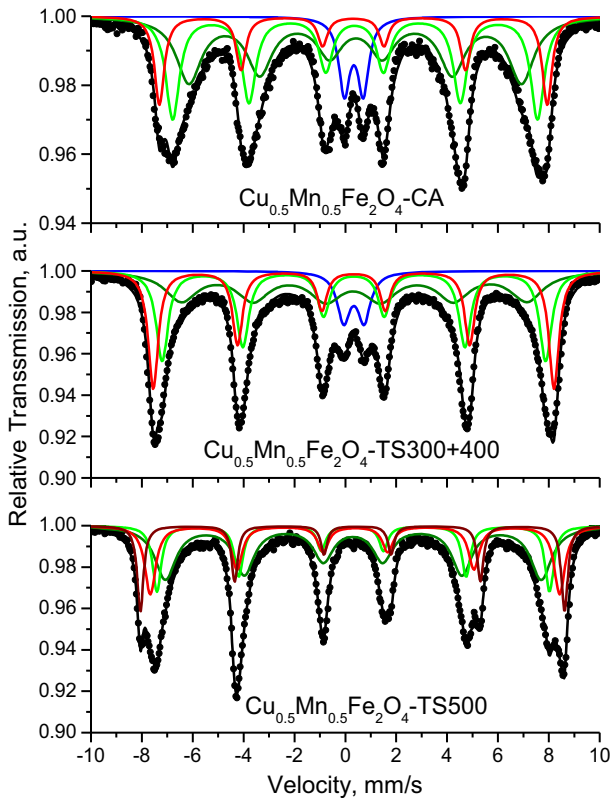


Fig. 2 Mössbauer spectra of samples thermally treated at different temperature

3 Results and discussion

The X-ray patterns of the samples are presented in Fig. 1. Calculated parameters from the experimental spectra are given in Table 1. Formation of cubic spinel phase (S.G. Fd3m, No. 227) was established in the sample after auto-combustion ($\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-CA}$). Presence of small quantity of additional CuO phase (4%) was also checked in this sample. Thermal treatment at 300 °C leads to slight increase of CuO content and decrease of unit cell parameter of the ferrite phase, while the ferrite crystallite size remains the same. A significant decomposition of the ferrite phase and hematite formation is established in the sample treated at 500 °C. As shown in Table 1, there is a strong correlation of ferrite crystal size and temperature of thermal treatment. Well defined reflections of Au are observed in gold modified ferrite sample, as the calculated average crystallite size is 29.7 nm. Comparison of diffraction data of gold modified sample with these of the ferrite sample treated at the same conditions shows, that presence of gold assist ferrite size increase at 400 °C, as well as CuO phase separation.

The Mössbauer spectra of the investigated samples are shown in Figs. 2 and 3. The fitted hyperfine parameters are presented in Table 2. All spectra of samples synthesized at different conditions, excluding $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS500}$, are consisting of sextets and doublets. The sextets with highest magnetic field (Sx1) in these spectra are related to tetrahedrally

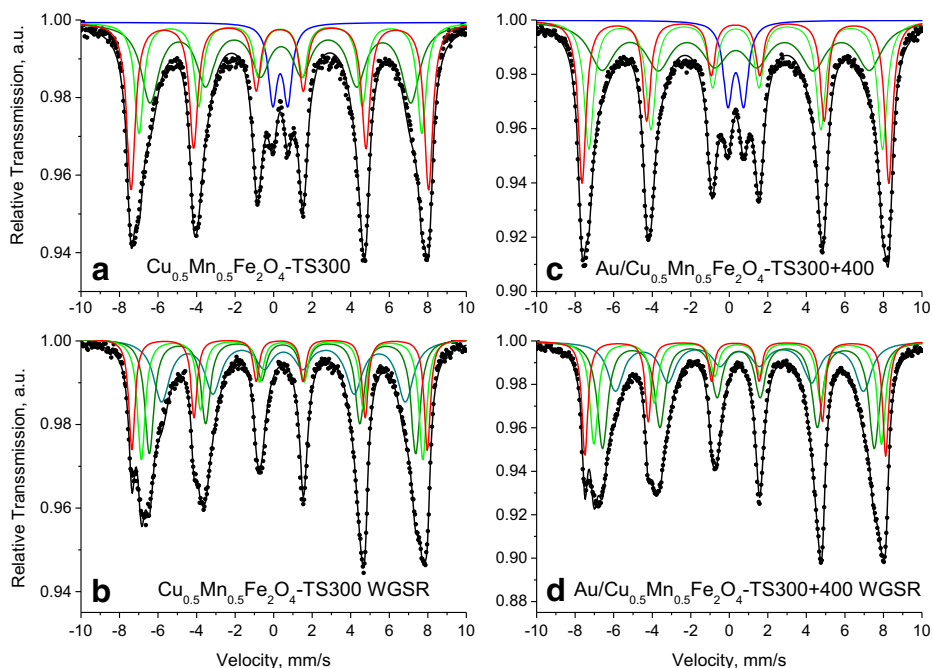


Fig. 3 Mössbauer spectra of samples $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300}$ before (a) and after catalytic test (b), $\text{Au/Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300+400}$ before (c) and after catalytic test (d)

coordinated Fe^{3+} ions. The sextets with higher isomer shift and lower Zeeman splitting (S_x2 and S_x3) than S_x1 can be related to Fe^{3+} ions in octahedral coordination and different non-iron near neighbors occupying tetrahedral positions. The doublet components in the spectra have relative weight 7–8 % and could be related to finely dispersed spinel particles with superparamagnetic behavior. Sextet with typical hyperfine parameters of $\alpha\text{-Fe}_2\text{O}_3$ is found in ferrite sample treated at 500°C which is in accordance with XRD results. An assessment for crystallite size of iron oxide phases could be accomplished from the calculated value of the magnetic hyperfine field of the sextet components [16]. In Table 2 are given the mean values of effective internal magnetic field (B_{mean}), where it is seen clear tendency for B_{mean} values increase with increasing of the treatment temperature. This observation is in accordance with the XRD results (Table 1) and proves ferrite recrystallization at higher temperatures. Additional effect of gold presence on recrystallization of ferrite phase is evident by comparing magnetic field of gold modified sample (46.4 T) with that of sample without gold treated at the same conditions (45.8 T).

The catalysts tested in WGS were analyzed by XRD and Mössbauer spectroscopy. The XRD results showed significant increasing of ferrite crystallite size (Table 1). The absence of superparamagnetic doublet in Mössbauer spectra after catalytic test confirmed also this phenomenon (Fig. 3, Table 2). Additionally, an increasing of isomer shift of the sextets of octahedral coordinated iron ions was observed in these spectra. Therefore a partial reduction of Fe^{3+} to Fe^{2+} has been occurred in reaction media. It can be noted that the final composition of the catalytic materials was formed in the reaction medium. The analysis of XRD results indicate, that copper in composition of the tested samples is separated as Cu and CuO phases consequently spinel ferrite phase in spent catalysts could be

Table 2 Mössbauer parameters of investigated samples (δ - isomer shift, Δ - quadrupole splitting, quadrupole shift (2ε), B_{hf} - magnetic hyperfine field, B_{mean} - mean effective internal magnetic field, Γ_{exp} - line widths, G - relative weight of the partial components in the spectra, LNT- spectra measured at liquid nitrogen temperature)

Sample	Components	δ , mm/s (error ± 0.01)	Δ , 2ε mm/s (error ± 0.02)	B_{hf} , T (error ± 0.2)	B_{mean} , T (error ± 0.2)	Γ_{exp} , mm/s (error ± 0.04)	G,%
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -CA	Sx1- Fe-tetra	0.31	0.00	47.4	43.3	0.46	17
	Sx2- Fe-octa	0.38	0.02	44.6			
	Sx3- Fe-octa	0.40	-0.03	40.6			
	Db-Fe ³⁺	0.33	0.74	-			
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300	Sx1- Fe-tetra	0.32	0.00	48.0	45.1	0.53	33
	Sx2- Fe-octa	0.35	0.00	45.6			
	Sx3- Fe-octa	0.37	-0.04	42.1			
	Db-Fe ³⁺	0.34	0.77	-			
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS500	Sx1- α -Fe ₂ O ₃	0.38	-0.20	51.8	-	0.30	16
	Sx2- Fe-tetra	0.29	0.03	47.9			
	Sx3- Fe-octa	0.39	-0.02	50.0			
	Sx4- Fe-octa	0.31	0.01	45.9			
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300+400	Sx1- Fe-tetra	0.33	0.00	48.9	45.8	0.47	28
	Sx2- Fe-octa	0.34	0.00	46.8			
	Sx3- Fe-octa	0.33	0.04	42.2			
	Db-Fe ³⁺	0.34	0.81	-			
Au/Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300+400	Sx1- Fe-tetra	0.32	0.00	49.4	46.4	0.49	27
	Sx2- Fe-octa	0.34	-0.01	47.3			
	Sx3- Fe-octa	0.33	-0.01	43.1			
	Db-Fe ³⁺	0.34	0.82	-			
Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ -TS300-WGSR	Sx1- Fe-tetra	0.31	0.00	47.6	43.3	0.38	19
	Sx2- Fe-octa	0.43	0.01	45.3			
	Sx3- Fe-octa	0.47	-0.01	42.9			
	Sx4- Fe-octa	0.51	-0.01	39.3			
Au/Cu _{0.5} Mn _{0.5} Fe ₂ O ₄ - TS300+400-WGSR	Sx1- Fe-tetra	0.31	0.00	48.5	44.4	0.37	19
	Sx2- Fe-octa	0.43	0.01	46.3			
	Sx3- Fe-octa	0.48	-0.01	43.8			
	Sx4- Fe-octa	0.54	-0.01	40.0			

defined as Mn-substituted magnetite. However, the XRD patterns of the sample modified by Au exhibited reflections typical for metallic copper and absence of reflections for copper oxides. This result is in agreement with recent results for the effect of Au deposition on alumina supported Cu-Mn mixed oxides [17]. The addition of gold improved reducibility and boosted the reduction of CuO and spinel phase to a lower temperature if compared to the Cu-Mn/Al₂O₃ sample.

The WGS catalytic activity results are presented in Fig. 4. Copper-manganese ferrite demonstrated higher catalytic activity than gold-copper manganese ferrite. This behavior

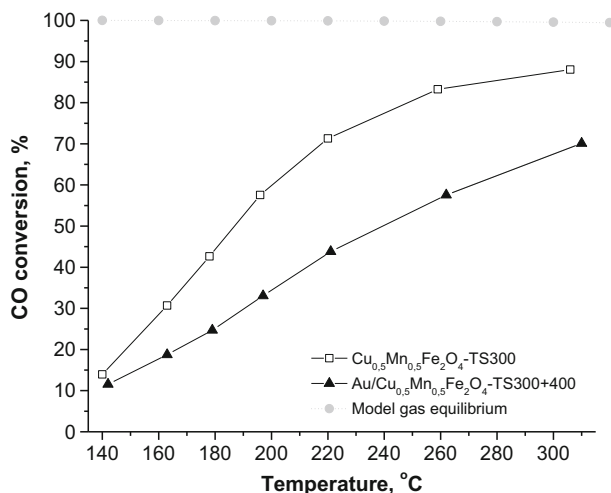


Fig. 4 WGSR catalytic activity data of $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300}$ and $\text{Au/Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300+400}$ samples

could be related to the facilitated recrystallization of the spinel ferrite in the presence of gold under WGS reaction conditions. The agglomeration leads to lack of catalytic active sites and lower activity. Another possible explanation could be associated with the presence of a separate phase of finely dispersed CuO in the sample $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4\text{-TS300}$ (Table 1). According to the literature, this phase is able to increase the mobility of lattice oxygen and hydroxyl groups participating in redox WGS mechanism and in this way to improve catalytic activity [18]. Moreover, considering the role played by different copper species in the WGS reaction, some studies proposed metallic Cu and either Cu^{1+} or Cu^{2+} cations as active sites [19, 20]. The total absence of positively charged copper ions due to the complete reduction to metallic Cu in Au-containing catalyst (Table 1) could be a reason of its lower catalytic activity.

4 Conclusions

It was established well expressed tendency of ferrite crystallite growth with increasing of thermal treatment temperature. Increasing of the ferrite crystallite size in presence of gold in the sample is established, too. The analysis of catalytic activity in WGSR shows that the activity of ferrite sample with gold deposition is lower than that of the sample without gold. Probably this is due to complex factors. One of them is the recrystallization of the ferrite phase due to both additional thermal treatment at higher temperature and gold presence.

Acknowledgments Financial support of project DFNI E02/2/2014 is greatly acknowledged.

References

1. Kovtunenکو, P.V.: Defect formation in spinels in oxygen nonstoichiometry (a review). *Glass Ceram.* **54**, 143–148 (1997)

2. Lang, L.L., Xu, J., Li, Z.Z., Qi, W.H., Tang, G.D., Shang, Z.F., Zhang, X.Y., Wu, L.Q., Xue, L.C.: Study of the magnetic structure and the cation distributions in MnCo spinel ferrites. *Physica B*. **462**, 47–53 (2015)
3. Wahba, A.M., Mohamed, M.B.: Structural and magnetic characterization and cation distribution of nanocrystalline $\text{Co}_x\text{Fe}_{3-x}\text{O}_4$ ferrites. *J. Magn. Magn. Mater.* **378**, 246–252 (2015)
4. Tholkappiyan, R., Vishista, K.: Combustion synthesis of Mg–Er ferrite nanoparticles: Cation distribution and structural, optical, and magnetic properties. *Mater. Sci. Semicond. Process.* **40**, 631–642 (2015)
5. Liu, K., Rykov, A.I., Wang, J., Zhang, T.: Chapter One -Recent advances in the application of Mössbauer spectroscopy in heterogeneous catalysis. *Adv. Catal.* **58**, 1–142 (2015)
6. Reddy, G.K., Smirniotis, P.G.: Water gas shift reaction - research developments and applications. Elsevier B.V, Amsterdam (2015)
7. Velinov, N., Koleva, K., Tsoncheva, T., Paneva, D., Manova, E., Tenchev, K., Kunev, B., Genova, I., Mitov, I.: Copper-cobalt ferrites as catalysts for methanol decomposition. *Cent. Eur. J. Chem.* **12**, 250–259 (2014)
8. Velinov, N., Koleva, K., Tsoncheva, T., Manova, E., Paneva, D., Tenchev, K., Kunev, B., Mitov, I.: Nano-sized $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$ ferrite as catalyst for methanol decomposition: Effect of preparation procedure. *Catal. Commun.* **32**, 41–46 (2013)
9. Tsoncheva, T., Manova, E., Velinov, N., Paneva, D., Popova, M., Kunev, B., Tenchev, K., Mitov, I.: Thermally synthesized nanosized copper ferrites as catalysts for environment protection. *Catal. Commun.* **12**, 105–109 (2010)
10. Koleva, K., Velinov, N., Tsoncheva, T., Mitov, I.: Mössbauer study of $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ catalytic materials. *Hyperfine Interact.* **226**, 89–97 (2014)
11. Andreeva, D., Idakiev, V., Tabakova, T., Andreev, A.: Low-temperature water–gas shift reaction over Au/ $\alpha\text{-Fe}_2\text{O}_3$. *J. Catal.* **158**, 354–355 (1996)
12. Hua, J., Zheng, K., Wei, X., Lin, Q.: Influence of calcination temperature on the structure and catalytic performance of Au/iron oxide catalysts for water–gas shift reaction. *Appl. Catal. A* **259**, 121–130 (2004)
13. Gabbasov, R.R., Cherepanov, V.M., Chuev, M.A., Polikarpov, M.A., Panchenko, V.Y.: Size effect of Mössbauer parameters in iron oxide nanoparticles. *Hyperfine Interact* **226**, 383–387 (2014)
14. Velinov, N., Petrova, T., Tsoncheva, T., Genova, I., Koleva, K., Kovacheva, D., Mitov, I.: Auto-combustion synthesis, Mössbauer study and catalytic properties of copper-manganese ferrites. *Hyperfine Interact* **237**, 1–11 (2016)
15. Žák, T., Jirásková, Y.: CONFIT: Mössbauer spectra fitting program. *Surf. Interface Anal.* **38**, 710–714 (2006)
16. Rangel, M.C., Querino, P.S., Borges, S.M.S., Marchetti, S.G., Assaf, J.M., Vásquez, D.P.R., Rodella, C.B., Silva, T.F., da Silva, A.H.M., Ramon, A.P.: Hydrogen purification over lanthanum-doped iron oxides by WGS. *Catal Today*(2017). <https://doi.org/10.1016/j.cattod.2017.05.058>
17. Tabakova, T., Kolentsova, E., Dimitrov, D., Ivanov, K., Manzoli, M., Venezia, A.M., Karakirova, Y., Petrova, P., Nihtianova, D., Avdeev, G.: CO and VOCs catalytic oxidation over alumina supported Cu–Mn catalysts: effect of Au or Ag deposition. *Top. Catal.* **60**, 11–122 (2017)
18. Khan, A., Smirniotis, P.G.: Relationship between temperature-programmed reduction profile and activity of modified ferrite-based catalysts for WGS reaction. *J. Mol. Catal. A* **280**, 43–51 (2008)
19. Edwards, M.A., Whittle, D.M., Rhodes, C., Ward, A.M., Rohan, D., Shannon, M.D., Hutchings, G.J., Kiely, C.J.: Microstructural studies of the copper promoted iron oxide/chromia water-gas shift catalyst. *Phys. Chem. Chem. Phys.* **4**, 3902–3908 (2002)
20. Kappen, P., Grunwaldt, J.-D., Hammershøi, B.S., Troger, L., Clausen, B.J.: The state of Cu promoter atoms in high-temperature shift catalysts—An in situ fluorescence XAFS study. *J. Catal.* **198**, 56–65 (2001)