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Iron Oxalate Decomposition Process by Means of Mössbauer Spectroscopy and Nuclear Forward Scattering

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Abstract. This study reports the transformation kinetics of the thermal decomposition of the iron(II) oxalate dihydrate studied in detail by two different techniques: the transmission Mössbauer spectroscopy and the nuclear forward scattering of synchrotron radiation. Both methods were applied to observe three steps of the decomposition process when the iron oxalate transforms to the amorphous iron oxide. The hematite/maghemite ratio was determined from the transmission Mössbauer spectra using an evaluation procedure based on a subtraction of two opposite sides of spectra. The results obtained indicate that the amount of hematite increases with an annealing time prolongation.

INTRODUCTION

Recently, iron oxides in magnetic form, i.e., maghemite, hematite and magnetite, have been intensely investigated due to a great number of their possible applications including solar water decomposition, drug transport, hyperthermia and magnetic separation. The thermal decomposition of iron(II) oxalate dihydrate, $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is one of the easily accessible methods to obtain Fe_2O_3 nanoparticles. The behavior of the decomposition process was reported in many studies [1–8].

It was observed by applying TG and DTA that during the heating of iron oxalate dihydrate there is firstly observed an endothermic reaction at temperatures between 150 to 200 °C, which is attributed to dehydration of iron oxalate, thus only FeC_2O_4 remains [1,6]. With an increase of temperature the dehydrated iron oxalate transforms on air into superparamagnetic amorphous Fe_2O_3 and finally to a combination of maghemite and hematite whose ratio is dependent on many factors such as thickness of the sample [3] or temperature [4]. On the other hand, when heated up in an atmosphere of its gaseous products, the composition is different due to low concentration of oxygen [1,8]. Such samples demonstrate the presence of magnetite and wüstite.

The nuclear forward scattering (NFS) is a method that utilizes Mössbauer effect in combination with a synchrotron radiation. In comparison with the conventional Mössbauer spectroscopy NFS has much shorter time of data acquisition. Actually, it shortens the acquisition time to only one minute. This makes NFS an excellent tool for the *in-situ* investigation of chemical transformations. In our research it was applied to observe early stages of transformation during heating of the iron(II) oxalate dihydrate.

In this paper we studied the transformation kinetics during the heat treatment based on the preparation method described in [4]. In order to characterize the composition of resulting samples and the transformation kinetics, the transmission Mössbauer spectroscopy (TMS) was used.

EXPERIMENTAL DETAILS

Iron oxalate with unit formula $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ from Sigma-Aldrich company was homogenized in the mortar for 10 minutes. 1 g of prepared powder was placed into a ceramic cup with a bottom diameter of 2 cm and inserted into

the muffle furnace at room temperature (RT). The samples were then heated up to the 350 °C with a heating rate of 40 °C per minute. This took approximately 8 minutes. After reaching the required temperature the samples were isothermally treated. During the isothermal heating the samples were withdrawn from the furnace after being isothermally annealed for specific time. The prepared samples and time of their isothermal annealing are listed in the Table 1. They were characterized by transmission Mössbauer spectroscopy at room temperature. All the TMS spectra were fitted using CONUSS software [9] which is mainly used to analyze NFS interferograms but it is also capable of analysis of the TMS spectra.

TABLE 1. List of prepared samples and their hyperfine parameters.

Sample	Duration of isothermal annealing (min)	Isomer shift (mm/s)	Quadrupole splitting (mm/s)	Hyperfine field (T)	Relative area (%)	Composition
S1	precursor	1.125	1.726	-----	100	FeC ₂ O ₄
S2	8	1.145	2.180	-----	6.1	FeC ₂ O ₄
		0.263	0.773	-----	73.8	am-Fe ₂ O ₃
		0.320	- 0.172	48.211	11.8	hematite
		0.199	-----	41.201	8.3	maghemite
S3	12	0.263	0.757	-----	77.7	am-Fe ₂ O ₃
		0.308	- 0.208	49.377	10.7	hematite
		0.295	-----	46.208	11.6	maghemite
S4	16	0.296	0.755	-----	78.4	am-Fe ₂ O ₃
		0.343	- 0.195	49.424	11.4	hematite
		0.331	-----	45.485	10.2	maghemite
S5	20	0.261	0.745	-----	75.5	am-Fe ₂ O ₃
		0.304	- 0.196	49.425	11.6	hematite
		0.296	-----	46.081	12.9	maghemite
S6	40	0.259	0.755	-----	62	am-Fe ₂ O ₃
		0.303	- 0.213	49.884	18.7	hematite
		0.279	-----	47.397	19.3	maghemite
S7	60	0.253	0.788	-----	46.1	am-Fe ₂ O ₃
		0.306	- 0.213	50.076	27.7	hematite
		0.276	-----	48.089	26.2	maghemite
S8	80	0.218	0.900	-----	23.1	am-Fe ₂ O ₃
		0.303	- 0.218	50.616	40.8	hematite
		0.285	-----	48.959	36.1	maghemite
S9	100	0.218	0.900	-----	8.6	am-Fe ₂ O ₃
		0.303	- 0.218	50.783	48.2	hematite
		0.298	-----	49.296	43.2	maghemite
S10	120	0.218	0.900	-----	9.7	am-Fe ₂ O ₃
		0.302	- 0.219	50.501	48.4	hematite
		0.292	-----	49.156	41.9	maghemite
S11	140	0.218	0.900	-----	8	am-Fe ₂ O ₃
		0.303	- 0.220	50.806	49.4	hematite
		0.291	-----	49.603	42.6	maghemite
S12	160	0.218	0.900	-----	6.5	am-Fe ₂ O ₃
		0.304	- 0.221	50.859	50.2	hematite
		0.294	-----	49.612	43.3	maghemite
S13	180	0.218	0.900	-----	5.1	am-Fe ₂ O ₃
		0.315	- 0.222	50.657	49.7	hematite
		0.313	-----	49.535	45.2	maghemite

Samples isothermally heated for 1 hour, 2 hours and for 3 hours were investigated also by powder diffraction in Bragg-Brentano configuration using PANalytical X'Pert PRO diffractometer equipped with Co anode source. Diffraction patterns were accumulated in the 2 θ range of 5-115 degrees.

Nuclear forward scattering experiments were performed at the P01 station at PETRA III. Homogenized iron oxalate was placed into a sample holder with two mica windows. After that the sample was placed in the furnace and heated up to the temperature of 450 °C in two steps. First step was from 70 °C up to 300 °C with heating rate of

30 °C/minute. In the second step, after reaching the 300 °C, the heating was slowed down to 10 °C per minute. Finally, at the temperature of 450 °C the sample was isothermally annealed for 22 minutes. NFS time spectra were accumulated after each minute during the heat treatment.

RESULTS AND DISCUSSION

The transformation kinetics of the thermal decomposition of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ can be followed by transmission Mössbauer spectra plotted in Fig. 1. Apart from the samples obtained after isothermal heating the transmission spectrum of the precursor has been also measured (Fig. 1a).

FIGURE 1. TMS spectra of iron oxalate before heat treatment (a) and selected samples isothermally heated for 8 min (b), 12 min (c), 60 min (d), 120 min (e) and 180 min (f).

The model used to fit the transmission spectrum of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is represented by a doublet with quadrupole splitting $Q = 1.726$ mm/s and isomer shift $IS = 1.125$ mm/s, shown in Fig. 1a. These values are in a good agreement with the previous studies [1]. After the heating starts the oxalate dries out and the structure decomposes to the amorphous Fe_2O_3 which exhibits superparamagnetic behavior at room temperature [5]. After 8 minutes of isothermal heating (Fig. 1b) all the iron oxalate has not been yet decomposed as there is still visible peak at the right side of the amorphous Fe_2O_3 doublet. As it can be seen in the Fig. 1b, the iron oxalate contribution is small compared to the intensity of the superparamagnetic amorphous Fe_2O_3 doublet which is the product of dehydration of the iron oxalate dihydrate. Also there is already a clearly visible formation of hematite/maghemite mixture which is pronounced by a sextet component.

During the following heating no iron oxalate component is present in the spectra and the formation of magnetically ordered grains of Fe_2O_3 can be followed in the Fig. 1c-f. Even after the 3 hours of isothermal heating there are still remnants of the superparamagnetic amorphous Fe_2O_3 .

Hematite and maghemite transmission Mössbauer spectra differ in magnitude of the hyperfine magnetic field and the quadrupole splitting where hematite usually exhibits $B_{\text{hf}} = 51.8$ T, $Q = -0.197$ mm/s and $IS = 0.37$ mm/s [10] and typical maghemite hyperfine parameters are $B_{\text{hf}} = 50$ T, $Q = 0$ mm/s and $IS = 0.35$ mm/s [10]. However, in case of small nanograins the magnetic hyperfine field is smaller with a large distribution which complicates the differentiation of maghemite and hematite in RT Mössbauer spectra.

The transmission Mössbauer spectra of samples S3-S13 were fitted using three component model where the first component, a doublet with a quadrupole splitting around 0.7 mm/s, corresponds to an amorphous Fe_2O_3 . The other two components are represented by two sextets describing maghemite and hematite. The hematite sextet exhibits quadrupole splitting of -0.19 mm/s while maghemite quadrupole splitting is zero due to the cubic symmetry. Isomer shift, quadrupole splitting and hyperfine magnetic field with its distribution were fitted for all three components and also Debye temperature. Only for the samples annealed for 80 minutes and longer the isomer shift and the quadrupole splitting of the amorphous Fe_2O_3 component were fixed at 0.218 mm/s and 0.9 mm/s due to low intensity of the doublet.

The obtained amounts of amorphous Fe_2O_3 and magnetically ordered phase represented by two sextets are plotted in Fig. 2. It is clearly visible that the amount of amorphous Fe_2O_3 decreases at the expense of the magnetic components. However, the amounts of maghemite and hematite are strongly correlated with their widths of magnetic hyperfine field distribution. Therefore, in order to obtain information about the presence of maghemite/hematite ratio in the samples, different method of analysis of the Mössbauer spectra was devised.

This evaluation procedure only provides the information about the ratio of hematite to maghemite. It is based on the fact that zero quadrupole splitting in maghemite makes the spectrum symmetrical around its center. On the contrary, hematite exhibits nonzero quadrupole splitting producing asymmetrical sextet where first and sixth peak move in different direction in comparison with the remaining four peaks.

FIGURE 2. Relative amounts of components during isothermal heating.

Firstly, the center between second and fifth line in the spectrum is to be found. Then the left and right side of the spectrum, with respect to determined center, are folded. The area A_S as the summed areas of first (A_L) and sixth (A_R) line is calculated (Fig. 3a). In the next step, area A_R is computed as absolute value of the difference of areas A_L and A_R (Fig. 3b). The ratio R_A of hematite to maghemite is proportional to the ratio of A_S and A_d according to the equation

$$R_A = \frac{A_S}{A_d} = \frac{A_L + A_R}{|A_L - A_R|}, \quad (1)$$

as the part of the spectrum which belongs to the symmetric sextet of maghemite is removed by subtraction while the asymmetric hematite peaks remain.

The results show an increase of hematite in the sample with prolongation of the annealing time. Based on the results, we can identify three steps of the iron oxalate decomposition process. First is a formation of amorphous Fe_2O_3 , next is a growth of small grains of maghemite and the final step is a structural transformation from

maghemite to hematite. This procedure was applied to all the spectra and obtained hematite/maghemite ratio R_A is plotted in the Fig. 4.

FIGURE 3. Example of the TMS spectra folding: (a) Area of outer peaks of sextet after folding and (b) absolute value of area after their subtraction.

FIGURE 4. Ratio of hematite in comparison to maghemite in the isothermally heated samples.

Three samples, S7, S10, S13, heated for one, two and three hours, were analyzed using the powder XRD. Their XRD patterns are shown in Fig. 5. The XRD patterns were analyzed using Rietveld analysis and determined amounts of maghemite and hematite are shown in the Table 2.

TABLE 2. Presence of hematite/maghemite based on analysis in XRD.

Sample	Ratio (%)	Component
S7	92.8	hematite
	7.2	maghemite
S10	98.7	hematite
	1.3	maghemite
S13	100	hematite

The results obtained from XRD are in contradiction with the results from the Mössbauer spectroscopy where we observed the hematite/maghemite ratio reaching 1 after three hours of annealing. However, the results from XRD pattern exhibit only 7% of maghemite for the sample S7 (Fig. 5a) annealed for one hour. Moreover, XRD pattern for sample S10 (Fig. 5b) exhibits maghemite amount below 1% and in the sample S13 (Fig. 5c) there is only hematite

present according to the XRD pattern. This disagreement could be caused by a formation of very small and not well developed maghemite particles which do not exhibit a long range ordering but only a short range ordering connected with a development of magnetism. The amount of hematite and maghemite in the sample obtained from the diffraction pattern could be also influenced by a texture in the sample when several diffraction peaks of maghemite have strong overlap with hematite diffractions.

The second method used to study transformation kinetics in the iron oxalate dihydrate was the nuclear forward scattering.

FIGURE 5. XRD patterns of the samples isothermally heated for (a) 1 hour, (b) 2 hours and (c) 3 hours.

From the shape of the interferograms we can emphasize that the iron oxalate transformed to amorphous Fe_2O_3 during the annealing up to the temperature of 375 °C (Fig. 6a-e). Then it is fully amorphous (Fig. 6f-h) and in the next step the maghemite and hematite grains start to develop during isothermal annealing at 450 °C approximately after 30 minutes of annealing (Fig. 6i-n). It is visible from the first two quantum beats that lay in the range between 20 and 40 nanoseconds. From their development the formation of hematite/maghemite grains can be followed. The evaluation of the hematite/maghemite ratio is not possible due to poor statistics. Nevertheless, the results appear to confirm the presence of the first two steps of the decomposition process.

CONCLUSIONS

The decomposition process of the iron oxalate has been investigated by transmission Mössbauer spectroscopy, X-ray powder diffraction and by nuclear forward scattering. The hematite/maghemite ratio was determined from the

Mössbauer spectra using specifically developed analytical method utilizing the symmetry of a maghemite sextet. The results obtained from this method were not confirmed by X-ray diffraction which demonstrates the difficulty of evaluating the Mössbauer spectra comprising a mixture of hematite and maghemite nanoparticles. Three steps of the decomposition process were observed by Mössbauer spectroscopy. The early stages of the decomposition were followed by NFS. The results from NFS experiment are in an agreement with the ones obtained using conventional Mössbauer spectroscopy confirming the presence of the first two steps in the decomposition process.

FIGURE 6. NFS interferograms accumulated during annealing.

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REFERENCES

1. M. Hermanek, R. Zboril, M. Mashlan, L. Machala, and O. Schneeweiss, *J. Mater. Chem.* **16**, 1273 (2006).
2. M. Hermanek, R. Zboril, I. Medrik, J. Pechousek, and C. Gregor, *J. Am. Chem. Soc.* **129**, 10929 (2007).
3. M. Hermanek and R. Zboril, *Chem. Mater.* **20**, 5284 (2008).
4. C. Gregor, "The Effect of Synthesis Conditions on the Catalytic Activity of Iron Oxides, Prepared by the Solid-State Reaction", Ph.D. thesis, Palacký University, 2012. (*in Czech*)

5. R. Zboril, L. Machala, M. Mashlan, and M. Hermanek, “Nanocrystalline Iron(III) Oxides Formed under Dynamic Heating of Ferrous Oxalate Dihydrate in Air”, in *Industrial Applications of the Mössbauer Effect, AIP Conference Proceedings*, edited by M. Gracia, J. F. Marco, and F. Plazaola (American Institute of Physics, Melville, New York, 2005), Vol. 765, pp. 257–262.
6. Y. Feng, T. Hu, Z. Pu, M. Wu, and J. Mi, *J. Therm. Anal. Calorim.* **122**, 947 (2015).
7. M. A. Mohamed and A. K. Galwey, *Thermochim. Acta* **213**, 269 (1993).
8. V. Rao, A. L. Shashimohan, and A. B. Biswas, *J. Mater. Sci.* **9**, 430 (1974).
9. W. Sturhahn, *Hyperfine Interact.* **125**, 149 (2000).
10. R. M. Cornell and U. Schwertmann, *The Iron Oxides: Structure, Properties, Reactions, Occurences and Uses* (Wiley-VCH, Weinheim, 2003), pp. 156–159.