# Thermal behaviour of iron(II) oxalate dihydrate in the atmosphere of its conversion gases

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Using a device for thermogravimetric analysis, a dynamic study of thermally induced solid-state transformations of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O in the atmosphere allowing full participation of gaseous products (CO, CO<sub>2</sub>, H<sub>2</sub>O) in the reaction system was carried out. Solid phases formed at various temperatures between 25 and 640 °C were identified and characterized using <sup>57</sup>Fe Mössbauer spectroscopy, TG and XRD. Up to 230 °C, evolution of two molecules of the water of crystallization takes place. Superparamagnetic nanoparticles of magnetite (Fe<sub>3</sub>O<sub>4</sub>) are formed as the primary product of the decomposition of FeC<sub>2</sub>O<sub>4</sub>, together with gaseous CO and CO<sub>2</sub>. In the next stage above 380 °C, the crystallization of magnetite is accompanied by a reduction of the remaining ferrous oxalate to iron carbide (Fe<sub>3</sub>C) by carbon monoxide. Thermally induced conversion of iron carbide into  $\alpha$ -Fe and carbon is expected between 400 and 535 °C as the major chemical process. In the last reaction step, above 535 °C, magnetite is reduced to wüstite (FeO) by carbon monoxide evolved at lower temperatures. On the grounds of quantitative Mössbauer data possible competitive reactions are discussed and a temperature dependent reaction model is suggested.

### 1. Introduction

Metal oxalates represent an important group of compounds employed in solid-state chemistry as precursors for thermally induced syntheses of various nanocrystalline metal oxides.<sup>1–15</sup>

In recent years many studies have been published on the thermal behaviour of ferrous oxalate dihydrate (FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) in various reaction atmospheres.<sup>16–30</sup> Depending on the experimental conditions, a diversified scale of reactions resulting in solid products varying in composition and valence state of iron has been reported. From the point of view of the basic research, the mechanism of these solid-state reactions is the key experimental issue as the published data are very controversial. The practical reason of interest in FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O is its easy thermal decomposability yielding various nanocrystalline phases of iron including oxides with great application potential.<sup>31–33</sup>

Obviously one can easily come across many experimental conditions that influence transformation routes, their intermediates and the final products, but the reaction atmosphere represents the most important one. With respect to the reaction atmosphere, the decomposition process seems to be the most straightforward under *oxidative conditions* (air, O<sub>2</sub>). It is generally agreed that the transformation process occurs in two steps including dehydration followed immediately by

oxidative decomposition resulting in  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) as the final decomposition product.<sup>16–21</sup> There are however some uncertainties concerning possible intermediates. Thus, FeO<sup>16–18</sup> and Fe<sub>3</sub>O<sub>4</sub><sup>19</sup> were suggested to be the primary decomposition products in oxygen or dry air, while  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) was stabilized when a significant amount of water vapour was present in the reaction atmosphere.<sup>16,18,22,23</sup> In our previous work we observed simultaneous formation of both  $\gamma$ - and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> polymorphs in the superparamagnetic state emerging at the very beginning of the decomposition in air.<sup>21</sup>

The conversion process in an inert atmosphere (N2, Ar) or vacuum proceeds in two steps too but, unlike in oxidative conditions, the individual steps are much better separated and the composition of the reaction products seems to be more controversial. Most authors identify FeO as the primary conversion phase that subsequently decomposes to  $Fe_3O_4$  and  $\alpha$ -Fe due to its instability below 570 °C.<sup>17,24,25</sup> The uncertainties however concern the following conversion steps and the composition of the final transformation products. Thus,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> along with FeO and Fe<sub>3</sub>O<sub>4</sub> were identified in the XRD pattern of a sample isothermally treated in dry nitrogen at 440 °C.<sup>26</sup> Primary creation of FeO in dry nitrogen was also observed by Rane et al.,<sup>18</sup> who suggest the subsequent reaction of FeO with FeC<sub>2</sub>O<sub>4</sub> yielding Fe<sub>3</sub>O<sub>4</sub> as the final decomposition product. In the case of a nitrogen atmosphere containing water vapour, Fe<sub>3</sub>O<sub>4</sub> as a single phase was detected,<sup>16</sup> similarly as in argon atmosphere.<sup>26,27</sup> Despite the same reaction atmosphere (Ar), a completely different phase composition of the samples including Fe<sub>4</sub>C, Fe<sub>3</sub>O<sub>4</sub> and Fe is reported,<sup>28</sup> evidently due to the participation of the conversion gas in the reaction system.

Thermal decomposition of  $FeC_2O_4 \cdot 2H_2O$  carried out in a *reducing atmosphere* of  $H_2$  proceeds again in two steps taking place at quite separate temperatures, attributed to primary dehydration followed by reductive decomposition. Among the

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solid reaction products, FeO, Fe<sub>3</sub>O<sub>4</sub>,  $\alpha$ -Fe and Fe<sub>3</sub>C were detected depending on the temperature conditions. As expected, FeO as the primary product consequently decomposed into Fe<sub>3</sub>O<sub>4</sub> and  $\alpha$ -Fe.<sup>27,29</sup> In the next reaction steps magnetite and iron carbide were transformed to  $\alpha$ -Fe, although the intermediate formation of Fe<sub>3</sub>C is marginally discussed. In addition to pure hydrogen, its mixture with NH<sub>3</sub> in a ratio of 1 : 1 was used as a reduction atmosphere to monitor the decomposition mechanism of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O. Mössbauer spectra revealed a mixture of FeO with superparamagnetic Fe<sub>3</sub>O<sub>4</sub> at the very beginning of the conversion. At higher temperatures reduction of Fe<sub>3</sub>O<sub>4</sub> to  $\alpha$ -Fe and its nitridation towards various iron nitrides took place simultaneously.<sup>30</sup>

Being aware of the literature discrepancies concerning the mechanism of the decomposition process, especially in inert and reducing atmospheres, it seems to be highly probable that gaseous conversion products more or less participated in the formation of the solid phases through solid–gas reactions. This can be related to the experimental arrangement, especially to insufficient draining of the decomposition gases by passing through the used atmosphere. Surprisingly, there are no literature data on the thermal decomposition of ferrous oxalate dihydrate in the atmosphere of the conversion gases.

The presented work is the first attempt to describe the decomposition mechanism of  $FeC_2O_4 \cdot 2H_2O$  under conditions in which gaseous phases have the full possibility of participation in the reaction process.

### 2. Experimental

Before the thermal treatment, FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O powder (Sigma Aldrich) was finely homogenized in an agate mortar. A certain amount of material (5.7 mg) was encased inside an aluminium capsule with an interior diameter of 5.45 mm (depth 1.6 mm) and sealed by an aluminium cover. Dynamic calcinations were carried out in the furnace of a thermogravimetric analysis (TGA) device (TGA XP-10, THASS GmbH). The samples were dynamically heated up to chosen temperatures (max. 640 °C) with a heating rate of 5 °C min<sup>-1</sup> and then quickly  $(-20\text{--}25~^\circ\text{C}~\text{min}^{-1})$  cooled down. To prevent the access of oxygen from the air into the reaction system the furnace was permanently (during both heating and cooling processes) supplied with a continuous flow of nitrogen (50 ml min<sup>-1</sup>). The dynamics of the decomposition process were also checked by differential scanning calorimetry (DSC) measurements (DSC XP-10, THASS GmbH) within the range of 25-400 °C with a heating rate of 1  $^{\circ}$ C min<sup>-1</sup>.

Solid decomposition products were identified *ex situ* by Mössbauer spectroscopy and X-ray powder diffraction (XRD). Transmission <sup>57</sup>Fe Mössbauer spectra of 512 channels were collected using a Mössbauer spectrometer in constant acceleration mode with a <sup>57</sup>Co(Rh) source. Measurements were carried out at 300 and 5 K using a cryomagnetic system from Oxford Instruments. XRD patterns were recorded using a Philips X'Pert MPD device with CoK<sub> $\alpha$ </sub> radiation and equipped with primary monochromator and X'Celerator detector. Powdered samples were spread on silicon slides and step-scanned within the angular range of 10–120° (in conventional 2 $\theta$  geometry) with a step of 0.008°.

#### 3. Phase composition of the conversion products

#### 3.1 TG and DSC analyses

The TG curve of the  $FeC_2O_4 \cdot 2H_2O$  powder (Fig. 1a) can be divided into three main temperature intervals related to the weight loss. The first weight decrease of about 20.1% within the range of 170-230 °C can be assigned to the process of dehydration (theoretical value 20.0%) resulting in complete loss of two water molecules. Afterwards, there is a long part of the curve up to 330 °C characterized by a slow weight decrease (1.2%) followed immediately by a steep fall in weight (39.2%)finishing at 415 °C. Let's notice that the total weight loss at 415 °C does not correspond to the formation of any of the expected compounds (Fe, Fe<sub>3</sub>O<sub>4</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, iron carbides) as a single phase. The last temperature interval above 415 °C is accompanied by a slow decrease in weight with apparent inflection in the TG curve at 535 °C. The total mass loss of 62.3% detected at 640 °C again cannot be assigned to any single phase and indicates rather the formation of a mixture of conversion products. The letters (A-G) in the TG curve indicate the temperatures at which the dynamic heating was stopped and the phase composition of samples consequently analysed by Mössbauer spectroscopy (see Section 3.2) and XRD (see Section 3.3).

DSC analysis (Fig. 1b) was performed with a slower heating rate allowing better resolution of the overlapped processes as indicated in the TG curve. Generally, the curve shows two endothermic effects. The first one, narrower and more intensive, with a minimum at 168 °C stands obviously for the process of dehydration. The second one, much broader, irregular in its shape, and apparently weaker in intensity with a local minimum at 376 °C, reflects a more complex process



**Fig. 1** TGA (a) and DSC (b) curves of  $FeC_2O_4 \cdot 2H_2O$  dynamically heated in the atmosphere of its own decomposition gaseous products. Heating rates: 5 °C min<sup>-1</sup> (TG), 1 °C min<sup>-1</sup> (DSC).

embodying several steps proceeding either simultaneously and/ or consecutively within a relatively short temperature range (285–395 °C). The slight temperature shift between the heat effects observed in DSC and the corresponding weight losses in TG have obviously been caused by the different heating rates.

#### 3.2 Mössbauer spectroscopy

The spectrum of initial FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O measured at room temperature (RT) displays one symmetrical doublet with hyperfine parameters of  $\delta = 1.18$  mm s<sup>-1</sup> and  $\Delta E_Q =$ 1.70 mm s<sup>-1</sup> (Fig. 2a) typical for divalent high-spin iron. After heating up to 210 °C, the hyperfine parameters of the RT Mössbauer spectrum (Fig. 2b) gradually change towards  $\delta = 1.2$  mm s<sup>-1</sup> and  $\Delta E_Q = 2.2$  mm s<sup>-1</sup>, evidently due to the dehydration process and the formation of anhydrous ferrous oxalate. Along with the dominant FeC<sub>2</sub>O<sub>4</sub> phase there is still a small amount of undecomposed precursor in the sample; however no other Fe-phase is detected. RT Mössbauer spectra of the samples heated up to higher temperatures are demonstrated in Fig. 3 and their parameters summarized in Table 1.

The initial stage of decomposition of anhydrous FeC<sub>2</sub>O<sub>4</sub> (up to 363 °C) is well characterized by the RT Mössbauer spectrum of sample A, which can be fitted with two doublets. Following the hyperfine parameters (see Table 1), the first one can be attributed to remaining FeC<sub>2</sub>O<sub>4</sub>. Isomer shift of the second broad component ( $\delta = 0.36 \text{ mm s}^{-1}$ ) is typical for superparamagnetic iron(III) oxides,<sup>21,34–36</sup> however it also corresponds well to more or less stoichiometric superparamagnetic Fe<sub>3</sub>O<sub>4</sub>.<sup>37–40</sup> In the RT spectrum of sample B (dynamic treatment up to 395 °C) there remain only traces of the FeC<sub>2</sub>O<sub>4</sub> doublet (RA = 4.3%). Compared to sample A, the



Fig. 2 RT Mössbauer spectra of non-treated  $FeC_2O_4{\cdot}2H_2O$  (a) and of the sample heated up to 210  $^\circ C$  (b).

dramatic increase of the superparamagnetic component is evident. Furthermore, we observe three magnetically split components. Hyperfine parameters of two of them,  $\delta =$  $0.26 \text{ mm s}^{-1}$ ,  $\varepsilon_Q = 0.03 \text{ mm s}^{-1}$ , H = 49.0 T and  $\delta =$  $0.66 \text{ mm s}^{-1}$ ,  $\varepsilon_Q = 0.02 \text{ mm s}^{-1}$ , H = 45.3 T, are in full agreement with those reported for Fe<sup>3+</sup> and Fe<sup>3+/2+</sup> in tetrahedral (A) and octahedral (B) sites of the Fe<sub>3</sub>O<sub>4</sub> structure, respectively.<sup>41–43</sup> The third magnetic component with lower values of isomer shift (0.16 mm s<sup>-1</sup>) and hyperfine magnetic field (20 T) can be clearly assigned to Fe<sub>3</sub>C.<sup>36,44</sup>

One can readily visualise that the content of the superparamagnetic component is highest in sample B (see Table 1). To identify its origin we measured a Mössbauer spectrum of an as-prepared sample at 5 K (sample B<sub>1</sub>). Compared to the room temperature spectrum, the  $Fe^{2+}$  doublet assigned to  $FeC_2O_4$ and the sextet attributed to Fe<sub>3</sub>C slightly shifted in hyperfine parameters due to the decreased temperature of measurement, their relative spectrum areas however remained almost unchanged. Instead of the original superparamagnetic doublet and the small broadened Fe<sub>3</sub>O<sub>4</sub> sextet observed in the room temperature spectrum (B), a new intensive broad magnetically split component fitted by means of four sextets appears in the spectrum recorded at 5 K (B<sub>1</sub>). Such drastic change of the shape of the spectrum is in agreement with magnetite behaviour below the Verwey transition temperature  $(T_{\rm V})$ where the crystal structure remains no longer cubic. Although the fitting procedures of the magnetite spectrum below  $T_{\rm V}$  differ depending on the used theoretical model<sup>45</sup> and stoichiometry, the observed isomer shift parameters are consistent with those reported in the literature.42,46 On the grounds of the low temperature measurement we can conclude that the above discussed superparamagnetic doublet component can be dominantly ascribed to magnetite nanoparticles, although a negligible fraction of Fe<sub>2</sub>O<sub>3</sub> cannot be excluded.

Compared to sample B, the RT Mössbauer spectrum of sample C (thermal treatment up to 415 °C) reveals a decrease of the spectrum area of the superparamagnetic component accompanied by a simultaneous increase of the ferrimagnetic Fe<sub>3</sub>O<sub>4</sub> fractions, obviously as a result of the thermally induced crystallization process of magnetite. Hyperfine parameters of Fe<sub>3</sub>C evidence better crystallinity and a more ordered structure as demonstrated by a slight change of the hyperfine magnetic field (H = 20.5 T). As the last phase a tiny amount (1.6% of the total spectrum area) of  $\alpha$ -Fe represented by a magnetically split component with a zero value of isomer shift and a hyperfine magnetic field of 33 T was identified in the spectrum of sample C.

The qualitative phase composition found in the Mössbauer spectrum of sample D is identical to that observed in the previous case (sample C). From the quantitative point of view, there is a significant increase of the spectrum area of  $\alpha$ -Fe (13.9 *vs.* 1.6%) while the area of the Fe<sub>3</sub>C sextet is clearly reduced (10.1 *vs.* 20.5%). Such comparison therefore indicates the progressive decomposition of iron carbide to alpha-iron at temperatures between 415 and 475 °C. The Mössbauer spectrum of the sample dynamically heated up to 535 °C (E) does not reveal any presence of Fe<sub>3</sub>C. The total content of magnetite including superparamagnetic and ferrimagnetic fractions (*ca.* 77%) remains almost the same as in samples C



Fig. 3 Mössbauer spectra of samples A, B, C, D, E, F, G obtained by dynamic thermal treatment of  $FeC_2O_4$ ·2H<sub>2</sub>O in the atmosphere of the gaseous decomposition products up to temperatures 363, 395, 415, 475, 535, 590 and 640 °C respectively. B<sub>1</sub>—LT Mössbauer spectrum (5 K) of sample B.

and D. This fact reflects the thermal stability of the magnetite phase up to 535 °C. The Mössbauer spectra of samples F and G (thermal treatment up to 590 and 640 °C respectively) are very similar and exhibit the presence of magnetite,  $\alpha$ -Fe and new Fe<sup>2+</sup> doublets with parameters of  $\delta = 1.02-1.05$  mm s<sup>-1</sup>,  $\Delta E_Q = 0.41-0.44$  mm s<sup>-1</sup> and  $\delta = 0.83-0.84$  mm s<sup>-1</sup>,  $\Delta E_Q =$ 0.70-0.71 mm s<sup>-1</sup>. The hyperfine parameters of the Fe<sup>2+</sup> doublets match well with those reported for FeO (wüstite).<sup>47,48</sup> The spectrum area of the Fe<sup>2+</sup> doublets in sample F (*ca.* 52%) corresponds to the decrease of the magnetite content between 535 °C and 590 °C (77 vs. 24%), evidently due to the proceeding reduction of Fe<sub>3</sub>O<sub>4</sub> to FeO within this temperature range. Above 590 °C, no final conversion products including Fe<sub>3</sub>O<sub>4</sub>, FeO and  $\alpha$ -Fe undergo any other thermally induced reactions as evidenced by the constant phase composition of samples F and G.

#### 3.3 XRD data

Generally, the results obtained by X-ray powder diffraction agree well with the phase composition of the heated samples determined by Mössbauer spectroscopy. The representative

Table 1 Mössbauer parameters of samples A, B, B<sub>1</sub>, C, D, E, F, G

Sample	$T_{\rm max}/{^{\circ}{\rm C}^a}$	$T_{\rm meas}/{ m K}^b$	$\delta/\mathrm{mm~s}^{-1 d}$	$\Delta E_{\rm Q}/{\rm mm~s}^{-1~e}$	$\epsilon_{\rm Q}/{\rm mm~s}^{-1f}$	$H/T^g$	$RA (\%)^h$	Site assignment
А	363	$RT^{c}$	1.21	2.23			70.1	Ferrous oxalate
			0.36	0.49			29.9	SP magnetite
В	395	RT	1.15	2.22	_		4.3	Ferrous oxalate
			0.35	0.21	_		73.7	SP magnetite
			0.26	_	0.03	49.0	2.5	Magnetite (site A)
			0.66	_	0.02	45.3	5.2	Magnetite (site B)
			0.16		0.07	20.0	14.3	Cementite
B <sub>1</sub>	395	5	1.24	1.98			3.7	Ferrous oxalate
			0.28		0.09	25.0	13.3	Cementite
			0.53		-0.02	52.7	16.1	Magnetite below $T_{\rm V}$
			0.46		-0.02	50.7	50.7	8
			0.54		-0.02	48.0	12.1	
			0.68		0.17	44.3	4.0	
С	415	RT	0.32	0.05			22.7	SP magnetite
			0.29		0.02	48.8	22.5	Magnetite (site A)
			0.66		0.02	45.6	32.7	Magnetite (site B)
			0.15		0.09	20.5	20.5	Cementite
			0.01		0	33.0	1.6	Alpha-iron
D	475	RT	0.32	0.08			9.9	SP magnetite
			0.29		0.01	48.8	24.9	Magnetite (site A)
			0.66		0.02	45.6	41.2	Magnetite (site B)
			0.14		0.08	20.4	10.1	Cementite
			0.02		-0.01	32.9	13.9	Alpha-iron
Ε	535	RT	0.32	0			12.5	SP magnetite
			0.28	_	0.03	49.0	25.8	Magnetite (site A)
			0.66		0.02	45.7	38.8	Magnetite (site B)
			0.01		0	33.0	22.9	Alpha-iron
F	590	RT	0.28		0.02	49.0	7.6	Magnetite (site A)
			0.66		0.01	45.8	16.3	Magnetite (site B)
			0.02		0.01	33.1	23.2	Alpha-iron
			1.02	0.41	_		13.0	Wüstite
			0.84	0.71			39.9	,, doute
G	640	RТ	0.27		0.02	48.9	7.5	Magnetite (site A)
	0.0		0.63		0.01	45.5	20.0	Magnetite (site B)
			0.01		0.01	33.0	22.6	Alpha-iron
			1.05	0 44			99	Wüstite
			0.83	0.70			40.0	abtite

 ${}^{a}T_{\text{max}}$  = temperature up to which the decomposition proceeded (see text).  ${}^{b}T_{\text{meas}}$  = temperature at which the Mössbauer spectrum was recorded.  ${}^{c}$  RT = room temperature.  ${}^{d}\delta$  = isomer shift (with respect to metallic iron, ±0.01).  ${}^{e}\Delta E_{\text{Q}}$  = quadrupole splitting (±0.01).  ${}^{f}\varepsilon_{\text{Q}}$  = quadrupole shift (±0.01).  ${}^{g}H$  = hyperfine magnetic field (±0.1).  ${}^{h}$  RA = relative spectrum area (±0.2).

diffraction patterns well demonstrating the decomposition process are shown in Fig. 4.

The XRD pattern of sample A (not shown) reveals the diffraction lines corresponding to anhydrous ferrous oxalate as the only crystalline phase in the system. Moreover, slight indications of diffraction peaks, which can be ascribed to the nanocrystalline spinel structure either of maghemite or magnetite, were detected.

Sample B (Fig. 4B) represents a mixture of ferrous oxalate, iron carbide and magnetite, as the presence of maghemite, which has the spinel structure of the same type and therefore an almost identical diffraction pattern, was excluded on the grounds of the Mössbauer measurement. Following the XRD pattern of sample B, magnetite is a prevailing component in the primary stage of the decomposition of ferrous oxalate; the broad diffraction lines however reflect its nanocrystalline character, which matches well with the Mössbauer data.

In sample C (Fig. 4C) there is no longer evidence of ferrous oxalate. Its absence indicates that the oxalate transformation finished after heating up to 415 °C. The diffraction lines of magnetite are much narrower and more intensive than in sample B, clearly due to its progressive crystallization above 395 °C. The fact that Mössbauer spectroscopy shows a fraction

of superparamagnetic nanoparticles at temperatures above 400 °C, while the quite narrow XRD lines indicate rather larger particles, is well explainable. The intensive and narrow diffraction lines observed in XRD reflect the contribution of the larger particles with higher coherent length, while the contribution of the smaller (superparamagnetic) particles is suppressed. In accordance with the Mössbauer spectrum of sample C, a trace admixture of  $\alpha$ -Fe was identified.

The qualitative phase composition found from the XRD pattern of sample D (not shown) is the same as that in sample C, however the line intensities indicate the increasing content of iron at the expense of iron carbide. The XRD pattern of sample E (Fig. 4E) exhibits a mixture of only two phases—magnetite and metallic iron. While the lines belonging to Fe<sub>3</sub>C completely disappeared, more intensive diffraction lines of  $\alpha$ -Fe evidence that its content in the sample increases with temperature. It is worth pointing out that the line intensities belonging to magnetite remain almost unchanged in the XRD patterns of samples C, D and E. The constant content of the magnetite phase supports the quantitative Mössbauer analysis and reflects its thermal stability up to 535 °C.

Above 535  $^{\circ}$ C, a distinct fall of the magnetite content accompanied by new diffraction peaks belonging to



Fig. 4 XRD patterns of representative samples B, C, E and G. Assignment of individual phases: O = ferrous oxalate, FeC<sub>2</sub>O<sub>4</sub>; C = cementite, Fe<sub>3</sub>C; M = magnetite, Fe<sub>3</sub>O<sub>4</sub>; I = iron,  $\alpha$ -Fe; W = wüstite, FeO.

non-stoichiometric FeO was recorded in the XRD patterns of samples F (not shown) and G (Fig. 4G).

## 4. Discussion of the reactions occurring at various temperatures

Apparently, the first step of the decomposition process includes the loss of two molecules of water of crystallization (eqn (1)) as proved by the thermogravimetry results (see Section 3.1) and confirmed by the Mössbauer spectrum of the sample dynamically heated up to 210 °C (see Fig. 2b), where the anhydrous ferrous oxalate appears to be the dominant phase. FeC<sub>2</sub>O<sub>4</sub> is thermally stable up to *ca.* 350 °C as clearly seen from the TG curve.

$$FeC_2O_4 \cdot 2H_2O \rightarrow FeC_2O_4 + 2H_2O$$
 (1)

The mechanism and kinetics of the processes taking place during the further thermal treatment are reflected in Fig. 5 showing the temperature dependence of relative areas of the Mössbauer spectra corresponding to individual compounds. The experimental points have been mathematically fitted by error functions and as expected, curves typical for consecutive reactions have been obtained. Following these curves, FeO and  $\alpha$ -Fe clearly represent the final decomposition products, while Fe<sub>3</sub>C and Fe<sub>3</sub>O<sub>4</sub> behave as conversion intermediates.

As transparently demonstrated in Fig. 5, the primary decrease of  $Fe^{2+}$  ions of the  $FeC_2O_4$  structure is accompanied by the corresponding increase of the spectrum areas corresponding to iron atoms in the magnetite structure. This reciprocal relation confirms that magnetite is the primary product of ferrous oxalate decomposition finishing at 415 °C, in accordance with eqn (2).

$$3 \text{FeC}_2 \text{O}_4 \rightarrow \text{Fe}_3 \text{O}_4 + 4 \text{CO} + 2 \text{CO}_2$$
 (2)

At the very beginning of the decomposition process,  $Fe_3O_4$  forms superparamagnetic nanoparticles as discussed in Section 3.2. It is interesting to note that at temperatures around 360 °C, only superparamagnetic magnetite nanoparticles along with the precursor occur in the sample (see Fig. 3A). The different solubility of ferrous oxalate and magnetite in water allows easy separation of the nanoparticles from the reaction mixture. The optimization of the reaction conditions leading to the simple synthesis of nanomagnetite is now being investigated by our research team.

The third decomposition step, following the primary dehydration and secondary conversion of  $FeC_2O_4$  into



Fig. 5 Temperature dependence of the relative spectrum areas as obtained from Mössbauer spectra of the samples heated between 363 and 640  $^\circ$ C.

magnetite, includes the formation of  $Fe_3C$  at temperatures above 363 °C. Generally, there are two possible routes of its formation: either by the reduction of ferrous oxalate (eqn (3a)) or of magnetite (eqn (3b)) by carbon monoxide evolved during the previous step (eqn (2)):

$$3\text{FeC}_2\text{O}_4 + 2\text{CO} \rightarrow \text{Fe}_3\text{C} + 7\text{CO}_2$$
 (3a)

$$Fe_3O_4 + 6CO \rightarrow Fe_3C + 5CO_2$$
 (3b)

With respect to the amount of carbon monoxide necessary for the reduction of one mole of the solid reactant, the reaction (3b) is evidently less probable as the yield of CO by reaction (2) is much lower than theoretically required. Moreover, based on the quantitative Mössbauer data in Fig. 5, there is no evidence to suggest that there has been a link between magnetite and iron carbide. Hence, it is obvious, that iron carbide is formed in the third decomposition step (at temperatures above *ca.*  $360 \,^{\circ}$ C) as a result of the reduction of FeC<sub>2</sub>O<sub>4</sub> by gaseous CO (eqn (3a)), whereas the reaction mechanism (3b) can be almost excluded.

Taking into account reactions 1, 2 and 3a and following the quantitative phase composition of sample C determined by Mössbauer spectroscopy, the overall decomposition process proceeding up to 415  $^{\circ}$ C can be expressed by the general equation:

$$FeC_{2}O_{4} \cdot 2H_{2}O + 2b/3CO \rightarrow a/3Fe_{3}O_{4} + 4a/3CO + 2a/3CO_{2} + b/3Fe_{3}C + 7b/3CO_{2} + 2H_{2}O$$
(4)

The letters *a* and *b* in the stoichiometry coefficients represent the relative spectrum areas in the Mössbauer spectrum of sample C. For the sake of simplicity, the negligible contribution of  $\alpha$ -Fe has been ascribed to Fe<sub>3</sub>C as alpha-iron is formed exclusively at the expense of iron carbide.

After insertion of the variables *a* and *b*, the equation can be evaluated:

The theoretical mass loss accompanying this reaction can be easily calculated as 59.2%, which correlates with the mass loss obtained experimentally from the TG measurement (59.7%).

Within the temperature region of 475–535 °C (samples D, E), iron carbide is gradually decomposed as manifested by its decreasing spectrum area from 20.5% to zero, while magnetite, as the second decomposition intermediate, remains stable (Fig. 5). This fall in the iron carbide content is accompanied by a corresponding increase of the content of metallic iron (1.6–23% of the spectrum area). As no other compounds were observed either by Mössbauer spectroscopy or XRD, we can conclude that  $\alpha$ -Fe is formed from iron carbide by its thermal conversion at temperatures 415–535 °C, in accordance with eqn (6):

$$Fe_3C \rightarrow 3Fe + C$$
 (6)

The fact that carbon was not detected in any of the samples C-E by XRD can be easily explained by its very low weight

contribution (less than 1.5 wt% following the Mössbauer data) and probable XRD amorphous character. Within the temperature region of 535–590 °C (samples E, F) a massive decrease in magnetite content compensated by a simultaneous increase of the wüstite content was registered. These trends reflect that there is a direct reaction relation between Fe<sub>3</sub>O<sub>4</sub> and FeO in the system. The reach of a sufficiently high temperature (535 °C) acts as a trigger for the reduction of magnetite to wüstite as Fe<sub>3</sub>O<sub>4</sub> remained stable in a broad temperature interval below it. Concerning the reduction mechanism, there are two possible routes with participation of either carbon monoxide (eqn (7a)) or solid carbon (eqn (7b)) as reducing agents formed in previous reaction steps:

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$
 (7a)

$$Fe_3O_4 + C \rightarrow 3FeO + CO$$
 (7b)

Nevertheless, the reduction route (7b) seems to be very improbable or negligible because of the very low content of carbon in the system as mentioned above. On the other hand, the initial molar ratio of carbon monoxide to magnetite (4:1), which are the products of reaction (2) at low temperatures, is much higher than that (1 : 1) necessary for the hightemperature reduction route (7a). Thus, the amount of CO should be sufficient for the initiation and the course of reaction (7a), although a certain fraction was consumed during the reduction of ferrous oxalate to iron carbide (eqn (3a)). Moreover, it is highly probable that a certain amount of carbon monoxide is oxidized to carbon dioxide (eqn (8)) by air-oxygen trapped inside the capsule during the sample preparation. This hypothesis is supported by the fact that magnetite reduction is not fully completed up to the final temperature of 640 °C, evidently due to the absence of a reducing agent.

$$CO + 1/2O_2 \Leftrightarrow CO_2$$
 (8)

It is also worth mentioning that there are no indications of the disproportionation of FeO (eqn (9)) as would be expected due to the well-known instability of wüstite below 570  $^{\circ}$ C.<sup>49,50</sup>

$$4\text{FeO} \Leftrightarrow \text{Fe}_3\text{O}_4 + \alpha \text{-Fe} \tag{9}$$

This should be accompanied by a change of the  $\alpha$ -Fe content above 535 °C, which has not been observed (see Fig. 5). The reasons behind the presence of FeO in the samples at room temperature could be related to its stabilization by CO<sub>2</sub> that was evolved during the reaction (eqn (7a)).

# 5. Conclusion—temperature dependent reaction model

Following the experimental results presented in this study, we suggest a unique five-step decomposition mechanism of  $FeC_2O_4 \cdot 2H_2O$  in the atmosphere of its conversion gases:

I. Release of crystal water proceeding within the temperature range of 170–230  $^\circ\mathrm{C}$ :

$$FeC_2O_4 \cdot 2H_2O \rightarrow FeC_2O_4 + 2H_2O$$

II. Thermally induced conversion of  $FeC_2O_4$  to  $Fe_3O_4$  and carbon oxides at temperatures above 230 °C:

$$3\text{FeC}_2\text{O}_4 \rightarrow \text{Fe}_3\text{O}_4 + 4\text{CO} + 2\text{CO}_2$$

III. Reduction of ferrous oxalate by carbon monoxide to Fe<sub>3</sub>C (above 360  $^{\circ}$ C):

$$3FeC_2O_4 + 2CO \rightarrow Fe_3C + 7CO_2$$

IV. Thermal conversion of Fe<sub>3</sub>C (415–535 °C):

$$Fe_3C \rightarrow 3Fe + C$$

V. Thermally induced reduction of magnetite to FeO by carbon monoxide (above 535  $^{\circ}$ C):

$$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$$

It should be emphasized that reactions II, III and IV could serve as the guides for thermally induced solid-state syntheses of magnetic Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>C and  $\alpha$ -Fe nanoparticles.

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#### References

- 1 C. J. Cong, L. Liao, J. C. Li, L. X. Fan and K. L. Zhang, *Nanotechnology*, 2005, 16, 6, 981.
- 2 M. E. Mendoza, F. Donado, R. Silva, M. A. Pérez and J. L. Carrillo, *J. Phys. Chem. Solids*, 2005, **66**, 6, 927.
- 3 K. F. Zhang, X. Z. Sun, G. W. Lou, X. Liu, H. L. Li and Z. X. Su, Mater. Lett., 2005, 59, 22, 2729.
- 4 N. Audebrand, S. Raite and D. Louer, *Solid State Sci.*, 2003, **5**, 5, 783.
- 5 E. Jeanneau, N. Audebrand and D. Louer, J. Solid State Chem., 2003, **173**, 2, 387.
- 6 C. Drouet and P. Alphonse, J. Mater. Chem., 2002, 12, 10, 3058.
  7 E. Jeanneau, N. Audebrand and D. Louer, J. Mater. Chem., 2002,
- 8 C. Boudaren, J. P. Auffredic, P. Benard-Rocherulle and D. Louer, *Solid State Sci.*, 2001, 3, 8, 847.
- 9 S. Dash, R. Krishnan, M. Kamruddin, A. K. Tyagi and B. Raj, J. Nucl. Mater., 2001, 295, 2–3, 281.
- 10 V. Carles, C. Laurent, M. Brieu and A. Rousset, J. Mater. Chem., 1999, 9, 4, 1003.
- 11 N. Audebrand, J. P. Auffredic and D. Louer, *Chem. Mater.*, 1998, 10, 9, 2450.
- 12 J. H. Choy, Y. S. Han and S. J. Kim, J. Mater. Chem., 1997, 7, 9, 1807.
- 13 X. S. Li, L. Y. Chen, C. Y. Xie, Y. F. Miao, D. M. Li and Q. Xin, *Thermochim. Acta*, 1995, 260, 115.
- 14 M. Insausti, M. K. Urtiaga, R. Cortes, J. L. Mesa, M. I. Arriortua and T. Rojo, J. Mater. Chem., 1994, 4, 12, 1867.
- 15 P. K. Dutta, P. K. Gallagher and J. Twu, Chem. Mater., 1993, 5, 12, 1739.
- 16 V. Rao, A. L. Shashimohan and A. B. Biswas, J. Mater. Sci., 1974, 9, 430.
- 17 B. Boyanov, D. Khadzhiev and V. Vasilev, *Thermochim. Acta*, 1985, **93**, 89.

- 18 K. S. Rane, A. K. Nikumbh and A. J. Mukhedkar, J. Mater. Sci., 1981, 16, 2387.
- 19 M. Popa, J. M. Calderon-Moreno, D. Crisan and M. Zaharescu, J. Therm. Anal. Calorim., 2000, 62, 633.
- 20 A. S. Brar and K. S. Khabre, *Indian J. Chem., Sect. A*, 1982, 21, 920.
- 21 R. Zboril, L. Machala, M. Mashlan, M. Hermanek, M. Miglierini and A. Fojtik, *Phys. Status Solidi C*, 2004, 1, 3583.
- 22 V. Chhabra, M. Lal, A. N. Maitra and P. Ayyub, *Colloid Polym. Sci.*, 1995, **273**, 939.
- 23 V. Borker, K. S. Rane and V. N. Kamat Dalal, J. Mater. Sci.: Mater. Electron., 1993, 4, 241.
- 24 R. A. Brown and S. C. Bevan, J. Inorg. Nucl. Chem., 1966, 28, 387.
- 25 M. A. Mohamed and A. K. Galwey, *Thermochim. Acta*, 1993, 213, 269.
- 26 M. R. Anantharaman, S. S. Shewale, V. S. Rao, K. Seshan and H. V. Keer, *Indian J. Chem., Sect. A*, 1982, 21, 990.
- 27 V. Carles, P. Alphonse, P. Tailhades and A. Rousset, *Thermochim.* Acta, 1999, 334, 107.
- 28 Y. Kong, D. Xue and F. Li, Phys. Status Solidi A, 1996, 154, 553.
- 29 F. Li, Y. Kong and D. Xue, Phys. Status Solidi A, 1995, 148, 129.
- 30 N. N. Mallikarjuna, B. Govindaraj, A. Lagashetty and A. Venkataraman, J. Therm. Anal. Calorim., 2003, 71, 915.
- 31 R. Zboril, L. Machala, M. Mashlan and V. Sharma, *Cryst. Growth Des.*, 2004, 4, 6, 1317.
- 32 A. B. Bourlinos, R. Zboril and D. Petridis, *Microporous Mesoporous Mater.*, 2003, 58, 155.
- 33 R. Zboril, M. Mashlan and D. Petridis, *Chem. Mater.*, 2002, 14, 969.
- 34 Ll. Casas, A. Roig, E. Molins, J. M. Greneche, J. Asenjo and J. Tejada, *Appl. Phys. A*, 2002, **74**, 591.
- 35 A. Peigney, P. Coquay, E. Flahaut, R. E. Vandenberghe, E. De Grave and C. Laurent, J. Phys. Chem. B, 2001, 105, 40, 9699.
- 36 S. Herreyre, P. Gadelle, P. Moral and J. M. M. Millet, J. Phys. Chem. Solids, 1997, 58, 10, 1539.
- 37 S. Si, A. Kotal, T. K. Mandal, S. Giri, H. Nakamura and T. Kohara, *Chem. Mater.*, 2004, **16**, 18, 3489.
- 38 D. K. Kim, M. Mikhaylova, Y. Zhang and M. Muhammed, *Chem. Mater.*, 2003, **15**, 8, 1617.
- 39 A. A. Novakova, V. Y. Lanchinskaya, A. V. Volkov, T. S. Gendler, T. Y. Kiseleva, M. A. Moskvina and S. B. Zezin, J. Magn. Magn. Mater., 2003, 258, 354.
- 40 V. S. Zaitsev, D. S. Filimonov, I. A. Presnyakov, R. J. Gambino and B. Chu, J. Colloid Interface Sci., 1999, 212, 1, 49.
- 41 M. A. Karakassides, D. Gournis, A. B. Bourlinos, P. N. Trikalitis and T. Bakas, J. Mater. Chem., 2003, 13, 4, 871.
- 42 A. C. Doriguetto, N. G. Fernandes, A. I. C. Persiano, E. Nunes Filho, J. M. Greneche and J. D. Fabris, *Phys. Chem. Miner.*, 2003, **30**, 5, 249.
- 43 R. E. Vandenberghe, C. A. Barrero, G. M. da Costa, E. Van San and E. De Grave, *Hyperfine Interact.*, 2000, **126**, 1–4, 247.
- 44 P. Coquay, E. De Grave, R. E. Vandenberghe, C. Dauwe, E. Flahaut, C. Laurent, A. Peigney and A. Rousset, *Acta Mater.*, 2000, **48**, 3015.
- 45 E. Murad and J. Cashion, Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilization, Kluwer Academic Publishers, Boston, U. S. A., 2004.
- 46 F. J. Berry, S. Skinner and M. F. Thomas, J. Phys.: Condens. Matter, 1998, 10, 1, 215.
- 47 I. V. Murin, V. M. Smirnov, G. P. Voronkov, V. G. Semenov, V. G. Povarov and B. M. Sinelnikov, *Solid State Ionics*, 2000, 133, 3–4, 203.
- 48 G. M. da Costa, E. De Grave, P. M. A. de Bakker and R. E. Vandenberghe, J. Solid State Chem., 1994, 113, 2, 405.
- 49 F. X. Redl, C. T. Black, G. C. Papaefthymiou, R. L. Sandstrom, M. Yin, H. Zeng, C. B. Murray and S. P. O'Brien, *J. Am. Chem. Soc.*, 2004, **126**, 44, 14583.
- 50 R. M. Cornell and U. Schwertmann, *The Iron Oxides*, VCH, Weinheim, Germany, 1996.