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Synthesis of ferrite grade g-Fe_2O_3

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Abstract. Iron(II) carboxylato–hydrazinates: Ferrous fumarato–hydrazinate (FFH), $FeC_4H_2O_4{\cdot}2N_2H_4$; ferrous succinato–hydrazinate (FSH), $FeC_4H_4O_4{\cdot}2N_2H_4$; ferrous maleato–hydrazinate (FEH), $FeC_4H_2O_4{\cdot}2N_2H_4$; ferrous malato–hydrazinate (FLH), $FeC_4H_4O_5{\cdot}2N_2H_4$; ferrous malonato–hydrazinate (FMH), $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$; and ferrous tartrato–hydrazinate (FTH), $FeC_4H_4O_6{\cdot}N_2H_4{\cdot}H_2O$ are being synthesized for the first time. These decompose (autocatalytically) in an ordinary atmosphere to mainly g-Fe_2O_3, while the unhydrazinated iron(II) carboxylates in air yield a-Fe_2O_3, but the controlled atmosphere of moisture requires for the oxalates to stabilize the metastable g-Fe_2O_3. The hydrazine released during heating reacts with atmospheric oxygen liberating enormous energy,

$$N_2H_4 + O_2 \rightarrow N_2 + H_2O;\ \Delta H_2O = -621\ kJ/mol,$$

which enables to oxidatively decompose the dehydrazinated complex to g-Fe_2O_3. The reaction products $N_2 + H_2O$ provide the necessary atmosphere of moisture needed for the stabilization of the metastable oxide.

The synthesis, characterization and thermal decomposition (DTA/TG) of the iron(II) carboxylato–hydrazinates are discussed to explain the suitability of g-Fe_2O_3 in the ferrite synthesis.

Keywords. Carboxylate; hydrazine; metastable oxide; ferrite.

1. Introduction

Technologically important ferrites of general formula, MFe_2O_4 (M = divalent metal) are generally synthesized by a solid state reaction between Fe_2O_3 and MO. The solid state reactions are normally sluggish in nature, and hence, in ceramic technique granulations are done to get reactive fine particles of the starting materials, compacted and then heat treated to very high temperatures, > 1000°C. Many a times the repeated grinding and heat treatments are given to achieve a single phase ferrite of desired composition. Reactivity of sluggish solid state reactions are enhanced by choosing defective starting materials by intentionally adding foreign impurities called as doping. Structural compatibility also plays an important role. In ferrites synthesis the iron oxide in hexagonal corundum structure form, a-Fe_2O_3, is made to react with the cubic divalent metal oxides, MO, to get cubic spinel, MFe_2O_4. Here, at high temperatures the a-Fe_2O_3 transforms into cubic spinel magnetite, Fe_3O_4, which then reacts easily with the cubic MO resulting into cubic spinel. However, it has been observed (Huhn 1987; Tuan *et al* 1992; Shrotri *et al* 1992) that the iron oxide in cubic spinel form, g-Fe_2O_3, as a starting material in ferrites synthesis enhances the solid state reaction and a better quality material could be obtained. The cubic spinel, g-Fe_2O_3, is a defective oxide with vacancy ordered structure of unit cell structure, $(Fe^{3+})_8\ [Fe^{3+}_{40/3}\ \square_{8/3}]O_{32}$, where ( ), [ ] and □ represent tetrahedral, octahedral and vacant sites, respectively. This defective cubic oxide reacts easily with the cubic MO giving cubic spinel easily. And, such enhanced reactivity of g-Fe_2O_3 in ferrite, $MgFe_2O_4$ synthesis has been realized by us (Verenkar 1997; Sawant 1998; Rane *et al* 1999) that confirms the fact that cubic defective iron oxide, g-Fe_2O_3, is a better starting material in ferrites manufacture. This is also in conformity with certain solid state reactions which are favoured if they are carried out at the phase transformation temperature of one of the reactants (Hedvaall effect); formation of $CoAl_2O_4$ is easier at the $g \rightarrow a$ transformation of Al_2O_3. Thus, the enhanced reactivity of cubic g-Fe_2O_3 is the combined effect of its structural compatibility, defective structure and its transformation to a-Fe_2O_3 during the heat treatment with cubic MO. In the synthesis of LiMn ferrite it was observed (Sano and Tamaura 1999) that g-Fe_2O_3 is more suitable than even other cubic spinel oxide, magnetite, Fe_3O_4, $(Fe^{3+})_8\ [Fe^{3+}_8\ Fe^{2+}_8]O_{32}$, may be because it is not defective.

Considering the importance of g-Fe_2O_3 in the synthesis of ferrites, we (Rane *et al* 1981; Moye *et al* 1993; Verenkar 1997; Sawant 1998) have been investigating an easier method of preparation of this oxide from various precursors such as iron(II) oxalate, formate, iron hydroxides and iron oxyhydroxides and their hydrazinates. Especially the iron(II) carboxylate, ferrous oxalate dihydrate, $FeC_2O_4{\cdot}2H_2O$, is a widely studied precursor in the synthe-

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sis of Fe_2O_3. In air the ferrous oxalate decomposes to *a*-Fe_2O_3, while in a controlled atmosphere of a known partial pressure of moisture the decomposed product is mainly *g*-Fe_2O_3. However, the ferrous oxalate on hydrazination yields complexes of known composition such as $FeC_2O_4{\cdot}2N_2H_4$, $FeC_2O_4{\cdot}N_2H_4{\cdot}2H_2O$ and these decompose autocatalytically at an ordinary temperature and pressure into mainly *g*-Fe_2O_3. This easy formation of the *g*-Fe_2O_3 has also been observed (Sawant 1998) in iron(II) formates.

Hydrazine method has opened up a new area of coordination chemistry involving metals ranging from transition, lanthanides to actinides (Athavale and Padmanabh Iyer 1967; Ferrari *et al* 1966; Braibanti *et al* 1968; Sharov 1977; Sharov *et al* 1977; Ravindranathan and Patil 1987; Kikkawa *et al* 1995; Goto *et al* 1996; Patil *et al* 1997; Yasodhai and Govindarajan 1999). The thermal products of hydrazinated complexes produce high reactivity metal/mixed metal oxides due to explosive decomposition.

The metal carboxylates are in general pyrophoric in nature and the decomposition at low temperatures involves the release of enormous amount of volatile gas products leading them to very fine oxide products of high surface area. The hydrazination of the oxalates further makes them to explosively decompose giving still finer oxide products. Since we observed the easy formation of *g*-Fe_2O_3 from the hydrazinated iron(II) oxalate as compared to the rigorous temperature and atmosphere control need for the formation of the oxide from the unhydrazinated carboxylate, we have been studying hydrazine method to prepare the oxide from other iron(II) carboxylates: ferrous fumarate, ferrous succinate, ferrous malonate, ferrous tartrate, ferrous malate and ferrous maleate.

The ferrous-fumarate, -succinate, -malonate and tartrate are found to decompose to mainly *a*-Fe_2O_3 in air (Venkataraman *et al* 1987, 1989; Rahman *et al* 1988; Venkataraman and Mukhedkar 1990; Nikumbh *et al* 1993) and like ferrous oxalate (Rane *et al* 1981) they too decompose to *g*-Fe_2O_3 in a controlled atmosphere of moisture. We present here preparation and decomposition of hydrazine complexes of these and two other (ferrous malate and maleate complexes), prepared for the first time.

2. Preparation and characterization

2.1 *Preparation: Solution and equilibration method*

A requisite quantity of sodium salts of fumaric, succinic, maleic and malic acid was added to a known amount of hydrazine hydrate (95–99%) in an inert atmosphere of nitrogen and stirred well for 2–3 h and then a freshly prepared ferrous chloride was run down till the precipitation was complete. The contents were further stirred for another 60 min in the N_2 atmosphere. The precipitate was then filtered, washed with alcohol and then dried. Malonic acid was used in the preparation instead of its sodium salt. Ferrous tartrate was prepared from ferrous ammonium sulphate and sodium tartrate and the dry ferrous tartrate was then equilibrated over hydrazine atmosphere by storing in a petri dish in a desiccator containing hydrazine hydrate. (Caution: hydrazine and hydrazine derivatives were carcinogenic. They were handled carefully in a fume cupboard.)

2.2 *Characterization*

Hydrazine content of all the complexes and the intermediate thermal products was analyzed titrimetrically using KIO_3. The percentage of iron, carbon and hydrogen was estimated by standard analytical techniques. Infrared band regions were detected using a FTIR spectrometer (Shimadzu FTIR, model 8101A) of complexes and their thermal intermediate products. Pyknometric density of the complexes was also determined.

2.3 *Thermal decomposition: isothermal, DTA/TG*

Simultaneous differential thermal analysis (DTA) and thermogravimetric (TG) analysis were done on STA 1500 instrument from room temperature (*RT*) to 700°C. Isothermal weight loss studies were carried out at various temperatures established based on DTA/TG traces. All hydrazinate complexes decomposed autocatalytically when the samples were spread in a petri dish and a burning splinter brought near to it. Initially a glow was formed which then spread throughout the bulk, thereby, completing the decomposition in an ordinary atmosphere. Weight loss studies of these were also done.

2.4 *Phase identification, microstructure (SEM) and magnetic characteristics*

X-ray powder diffraction (XRD) studies of all the thermal products were carried out on Rigaku D MAX II diffractometer using Cu and Fe targets. Phase identification was done by comparing the observed d_{hkl} values with the JCPDS file Nos 24–81 and 25–1402. Scanning electron micrographs (SEM) of all the thermal products were taken on Cambridge Stereoscan S 250 MK III. Saturation magnetization values, J_S, in emu/g of the thermal products were measured on a high field hysteresis loop trace described by Likhite *et al* (1965) and supplied by M/s Arun Electronics, Mumbai.

3. Results and discussion

3.1 *Chemical formula*

Important infrared band positions, chemical contents of hydrazine, iron, carbon, hydrogen and isothermal weight

losses of all the complexes are shown in table 1 and from these chemical formulas are fixed as

(i) ferrous fumarato–hydrazinate (FFH), $FeC_4H_2O_4{\cdot}2N_2H_4$, (ii) ferrous succinato–hydrazinate (FSH), $FeC_4H_4O_4{\cdot}2N_2H_4$, (iii) ferrous maleato–hydrazinate (FEH), $FeC_4H_2O_4{\cdot}2N_2H_4$, (iv) ferrous malato–hydrazinate (FLH), $FeC_4H_4O_5{\cdot}2N_2H_4$, (v) ferrous malonato–hydrazinate (FMH), $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$ and (vi) ferrous tartrato–hydrazinate (FTH) $FeC_4H_4O_6{\cdot}N_2H_4{\cdot}H_2O$.

There are distinctly two categories of complexes: FMH and FTH which have water of crystallization, while the others without any water of crystallization.

3.2 *Thermal analysis*

DTA/TG traces of all complexes are shown in figure 1. (FFH) $FeC_4H_2O_4{\cdot}2N_2H_4$, (FSH) $FeC_4H_4O_4{\cdot}2N_2H_4$, (FEH) $FeC_4H_2O_4{\cdot}2N_2H_4$, (FLH) $FeC_4H_4O_5{\cdot}2N_2H_4$ all with no water of crystallization show multistep exothermic peaks with corresponding weight loss steps. The samples with water of crystallization, (FMH) $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$ and (FTH) $FeC_4H_4O_6{\cdot}N_2H_4{\cdot}H_2O$, however, indicate mainly one intense exothermic peak with corresponding weight loss.

The intermediate thermal products obtained at different fixed temperatures in the range *RT*–350°C were analyzed for the hydrazine contents in them (table 2). All dihydrazinate complexes indicated loss of hydrazine at ~ 150°C in steps, but then it was difficult to monitor such reactions, as the removal of the second hydrazine molecule immediately sets in an intense oxidative decomposition of the dehydrazinated complex. In fact, the exothermic reaction releases so much energy due to explosive oxidation of the liberated hydrazine, N_2H_4, with the atmospheric oxygen (Schmidt 1984),

$$N_2H_4 + O_2 \rightarrow N_2 + H_2O; \quad \Delta H = -621 \text{ kJ/mol},$$

that the heat is sufficient to oxidatively decompose the dehydrazinated complex into metal oxide.

The hydrazinate complexes with water of crystallization, however, showed one step reaction with intense exothermic peak. Majority contents of hydrazine and water were lost (table 2) below 100°C and then there occurred further decomposition due to dehydrazinated complex. A total decomposition occurred at 180–200°C in (FMH) $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$. The FMH has 20·43(%) N_2H_4 which on heating to 50°C lost 7·85% weight and at 70° the loss was 9·5%, but the hydrazine content in these two temperatures remained, respectively, at 16·42 and 16·18%. Our calculation indicates that at ~ 70°C the complex releases one molecule of H_2O and half a molecule of N_2H_4 and the product at this stage must have 16·85(%) N_2H_4 which is close to the observed value of 16·18%. Then the complete removal of the remaining N_2H_4 takes place at ~ 170°C and a major weight loss occurs at ~ 180°C. These results indicate that the decomposition of FMH has a sequence: dehydrazination → dehydration → dehydrazination followed by oxidative decomposition.

Table 1. Chemical analysis, density, IR, and total weight loss of iron(II) carboxylato–hydrazinates.

	Chemical analysis (%)			Density	Infrared data (cm^{-1})							Total weight loss (%)	
Hydrazinates		Obsd.	Calcd.	(g cm^{-3})	*d*(o–c–o)	ν(N–N)	$\nu_c(NH_2)$	ν_c(o–c–o)	ν_{asy}(o–c–o)	ν(NH)	ν(H_2O)	Obsd.	Calcd.
$FeC_4H_2O_4$	N_2H_4	27·16	27·35	1·38	800	960	1130	1377	1650	3237	–	65·86	65·81
$2N_2H_4$	Fe	24·00	23·88										
(FFH)	C	19·30	20·52										
	H	3·96	4·27										
$FeC_4H_4O_4$	N_2H_4	27·52	27·11	1·18	800	964	1126	1350	1624	3262	–	65·94	66·10
$2N_2H_4$	Fe	23·87	23·68										
(FSH)	C	20·30	20·35				1176			3310			
	H	3·67	5·00							3350			
$FeC_3H_2O_4$	N_2H_4	20·43	21·46	1·51	795	962	1132	1370	1620	3306	3170	64·30	64·35
$1{\cdot}5N_2H_4{\cdot}H_2O$	Fe	24·25	24·95										
(FMH)	C	17·90	16·08			936							
	H	3·73	4·46										
$FeC_4H_4O_6$	N_2H_4	12·41	12·61	1·22	820	931	1184	1320	1600		3150	68·54	68·56
$N_2H_4{\cdot}H_2O$	Fe	25·50	25·17										
(FTH)	C	17·22	18·90										
	H	3·53	3·94										
$FeC_4H_2O_4$	N_2H_4	26·74	27·37	1·9	835	970	1130	1305	1620	3330		65·85	65·85
$2N_2H_4$	Fe	24·67	23·88										
(FEH)							1150	1395		3260			
							1175						
$FeC_4H_4O_5$	N_2H_4	25·12	25·43	1·86	828	970	1128	1300	1611	3397		68·5	68·32
$2N_2H_4$	Fe	22·80	22·16										
(FLH)							1150	1390		3252			
							1175						

The ferrous tartrato–hydrazinate (FTH) $FeC_4H_4O_6 \cdot N_2H_4 \cdot H_2O$, on the other hand, shows (table 2) water loss at ~ 60°C as the *RT* hydrazine content of 12·41% of the complex remains same at this temperature. Further heating leads to the removal of hydrazine. The sequence of reaction here is dehydration → dehydrazination followed immediately by oxidative decomposition. Thus, these two complexes with water of crystallization decompose exothermally in one step, while the complexes with no crystallization of water show multistep decompositions. Hence, the dehydrazination and dehydration together make the total decomposition process reactive as revealed by the single step exothermic reaction. The *bis*-hydrazine maleate and *bis*-hydrazine fumarate complexes of Co, Ni and Zn were also found (Govindrajan *et al* 1995) to show single and multistep decompositions and they have suggested reactive and less reactive reactions in these systems yielding metal oxide products.

3.3 *Phase identification, microstructure (SEM) and magnetic characterization*

The X-ray analysis of the thermal and autocatalytic decomposition products of all the complexes were found to be *g*-Fe_2O_3. The *d* values observed and the reported ones of the *g*-Fe_2O_3 are shown in table 3. Saturation magnetization values, J_S, in the range 18–43 emu/g are observed (Verenkar 1997) for all these oxide samples. The values found in the present investigation are low, however, J_S in the range 50–74 emu/g are also observed in the literature (Khalafalla and Morrish 1972; Coey and Khalafalla 1972).

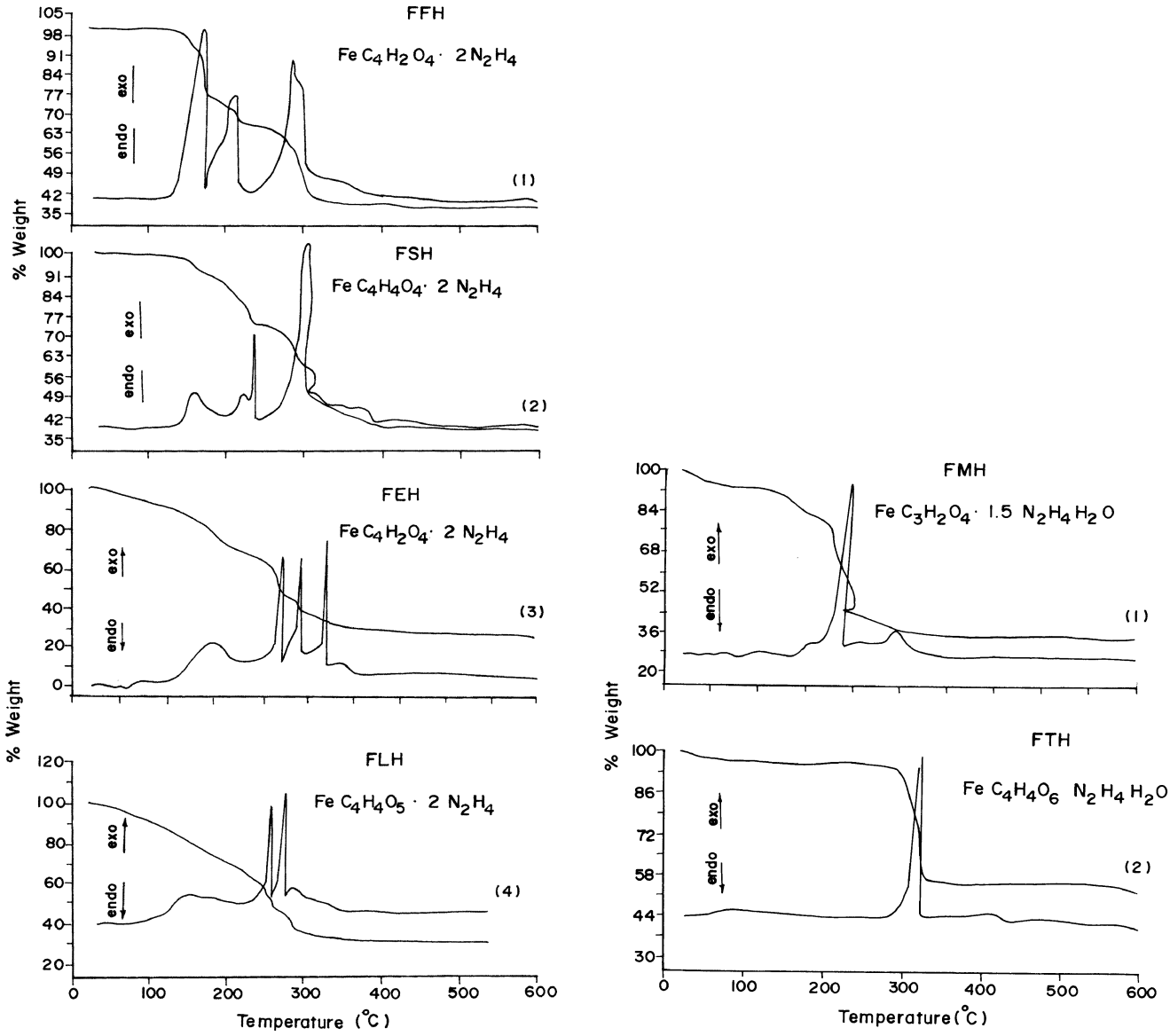

Figure 1. DTA/TG traces of iron(II) carboxylato–hydrazinates.

One explanation for such low values in our studies may be due to some admixture of *a*-Fe_2O_3 as found in our XRD patterns. This is expected in our method of preparation where explosive decomposition of the hydrazinated complexes release so much heat which eventually convert few *g*-Fe_2O_3 particles into *a*-Fe_2O_3. However, under the controlled atmosphere of moisture the unhydrazinated complexes did yield pure *g*-Fe_2O_3 with J_S of 74 emu/g. Although the autocatalytically decomposed hydrazine complexes did not yield *g*-Fe_2O_3 of better magnetic characteristics, they are good enough for the purpose of ferrite preparation as revealed by our studies on $MgFe_2O_4$ (Rane *et al* 1999) as compared to the ferrite prepared from commercial grade *a*-Fe_2O_3. Iron oxides consisting of large

Table 2. Isothermal weight loss and hydrazine analysis of iron(II) caboxylato–hydrazinates.

		Isothermal/chemical analysis		
Sr. No.	Hydrazinates	Temp.(°C)	Wt. Loss (%)	% N_2H_4
1.	Ferrous fumarato–hydrazinates	RT	–	27·16
	(FFH) $FeC_4H_2O_4{\cdot}2N_2H_4$	70	3·20	22·35
		90	15·35	5·44
		110	19·50	2·40
		200	37·65	–
		310	64·15	
2.	Ferrous succinato–hydrazinate	RT	–	27·52
	(FSH) $FeC_4H_4O_4{\cdot}2N_2H_4$	50	1·2	27·52
		90	21·02	3·36
		140	25·20	–
		176	29·50	
		193	56·65	
		248	66·25	
		310	67·10	
3.	Ferrous maleato–hydrazinate	RT	–	26·74
	(FEH) $FeC_4H_2O_4{\cdot}2N_2H_4$	58	2·5	25·44
		96	12·05	17·66
		156	30·05	3·73
		172	34·00	–
		182	55·55	
		225	64·40	
4.	Ferrous maleato–hydrazinate	RT	–	25·12
	(FLH) $FeC_4H_4O_5{\cdot}2N_2H_4$	50	6·4	21·95
		100	17·05	10·17
		150	30·45	2·40
		175	31·65	–
		200	35·70	
		225	55·15	
		250	64·05	
		300	66·55	
5.	Ferrous malonato–hydrazinate	RT	–	20·43
	(FMH) $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$	50	7·85	16·42
		70	9·50	16·18
		95	12·25	17·38
		120	18·00	13·62
		140	21·40	9·77
		150	24·90	9·61
		170	32·00	5·68
		182	63·10	–
6.	Ferrous tartrato–hydrazinate	RT	–	12·41
	(FTH) $FeC_4H_4O_6{\cdot}N_2H_4{\cdot}H_2O$	62	6·00	12·41
		80	12·35	10·73
		102	16·00	7·13
		140	19·85	4·85
		160	22·50	2·40
		225	68·20	–

Table 3. X-ray data of iron oxides obtained by autocatalytic decomposition of iron(II) carboxylato–hydrazinate.

g-Fe_2O_3 (reported) tetragonal	*d*	–	2·95	2·78	–	2·514	2·086	–	1·701	1·604	1·474	1·272
g-Fe_2O_3 (reported) cubic	*d*	–	2·95	2·78	–	2·52	2·08	–	1·70	1·61	1·48	1·27
Fe_3O_4 (reported)	*d*	–	2·967	–	–	2·532	2·099	–	1·715	1·616	1·485	1·281
a-Fe_2O_3 (reported) rhombohedral	*d*	3·66	–	–	2·69	2·51	2·20	1·838	1·69	–	1·452	–
FFH (autocatalytic)	*d*	–	2·97	2·777	2·70	2·519	2·08	1·84	1·69	1·603	–	–
FSH (autocatalytic)	*d*	–	2·95	2·771	–	2·53	2·09	–	1·718	1·61	–	–
FMH (autocatalytic)	*d*	–	2·97	2·78	2·70	2·524	2·09	1·84	1·69	1·607	–	–
FTH (autocatalytic)	*d*	–	2·95	2·78	2·70	2·524	2·09	1·84	1·696	1·607	–	–
FEH (autocatalytic)	*d*	–	–	–	2·70	2·526	–	1·84	1·697	1·604	1·484	–
FLH (autocatalytic)	*d* (*I*/*Io*)	–	2·96	–	2·70	2·519	–	1·839	1·695	1·608	1·48	–

percentage of g-Fe_2O_3 enhanced reactivity (Huhn 1987) to produce $ZnFe_2O_4$. In fact, the SEM studies on these synthetic cubic spinel g-Fe_2O_3 particles in nano-metre size of high surface (BET) area of 50–90 $m^2\ g^{-1}$ reacted easily with the cubic MgO resulting in well densified cubic $MgFe_2O_4$ ferrite of better quality.

4. Conclusions

(I) Iron(II) carboxylato–hydrazinates: ferrous fumarato–hydrazinate (FFH), $FeC_4H_2O_4{\cdot}2N_2H_4$; ferrous succinato–hydrazinate (FSH), $FeC_4H_4O_4{\cdot}2N_2H_4$; ferrous maleato–hydrazinate (FEH), $FeC_4H_2O_4{\cdot}2N_2H_4$; ferrous malato–hydrazinate (FLH), $FeC_4H_4O_5{\cdot}2N_2H_4$; ferrous malonato–hydrazinate (FMH), $FeC_3H_2O_4{\cdot}1{\cdot}5N_2H_4{\cdot}H_2O$; ferrous tartrato–hydrazinate (FTH), $FeC_4H_4O_6{\cdot}N_2H_4{\cdot}H_2O$; are being easily synthesized.
(II) The iron(II) carboxylato–hydrazinates decompose (autocatalytically) in an ordinary atmosphere mainly to g-Fe_2O_3, while the unhydrazinated iron(II) carboxylates in air yield a-Fe_2O_3, but the controlled atmosphere of moisture requires for the oxalates to stabilize the metastable g-Fe_2O_3.
(III) Hydrazine method enables the synthesis of g-Fe_2O_3 easily from the iron(II) carboxylates.
(IV) Uniform, nano-metre size, high surface area defect cubic spinel g-Fe_2O_3 from iron(II) carboxylato–hydrazinates reacts easily with cubic MgO yielding high quality cubic spinel $MgFe_2O_4$, while with the commercial 0–2 μm size particles of a-Fe_2O_3 one ends up with low performance ferrite due to the presence of unreacted a-Fe_2O_3 as an admixture.

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