THERMOANALYTICAL STUDY OF THE SOLID STATE REACTION BETWEEN HYDRATED ZnO AND Fe$_2$O$_3$

B. N. SINGH, R. K. BANERJEE and B. R. ARORA

*Catalyst Development and Production
Fertilizer (Planning and Development) India Ltd.
Sindri — 828122, Bihar, India*

The hydrated oxides which are formed by the addition of ammonium bi-carbonate to a solution of Zn(NO$_3$)$_2$ and Fe(NO$_3$)$_3$, and drying the precipitates at 110° are zinc hydroxy carbonate(I) and iron(III) oxide gel(II), respectively. A new, derived derivative thermogravimetric curve along with conventional DTA and DTG methods have been used to study the reaction between (I) and (II) in two components system.

A mixture of (I) and (II) subjected to grinding yields about 16% zinc ferrite 'precursor'. In a sample prepared by coprecipitation from the mixed nitrate solution and drying at 110°, nearly 70% 'precursor' is formed. The formation of zinc ferrite spinel reported to take place at low temperature in such cases appears to be related with the formation of the 'precursor', and reactivity and phase transformation temperature in Fe$_2$O$_3$.

Metal ferrites have many applications including their use as catalyst [1]. The reaction between ZnO and Fe$_2$O$_3$ in the solid state results in the formation of zinc ferrite spinel, ZnFe$_2$O$_4$. The lowest temperature [2] reported for this reaction to occur is 270° though generally the reaction is believed to occur [3—6] in the temperature range of 600—1000°. Such a large temperature range is explained on the basis of the reactivity of the oxides which include such factors as purity, surface area, intimate contact and cleanliness of the surface which favours the surface diffusion process through which the spinel formation is supposed to occur.

The formation of zinc ferrite has also been reported under entirely different conditions, such as impact compression [7] from equimolecular mixture of ZnO and Fe$_2$O$_3$ and by boiling the precipitates of Zn(OH)$_2$ and FeOOH gel with the matrix solution in aqueous medium [8]. The reported reaction between the hydrous oxides in aqueous medium might be taking place through some chemical reaction and formation of a 'spinel precursor'. The 'precursor' is converted to spinel at much lower temperature than the temperature of the formation of spinel from oxides.

The study of a reaction between hydrated oxides (hydroxides, basic carbonate etc.) under impact of grinding in the solid state or in aqueous medium poses problems. The identification and estimation of the reaction product (e.g. 'precursor' to spinel) in the composite becomes difficult because the reaction product is chemically similar to hydrated oxides and have poor crystalline structure and thus are undetectable by X-ray diffraction.

Thermochemical methods provide good scope for such studies. The reaction between the "hydrated ZnO" (in this case zinc basic carbonate) and hydrated Fe_2O_3 under impact grinding in the solid state as well as in solution during co-precipitation is studied by chemical and thermal analysis methods. The derived derivative thermogravimetric method [9] of plotting the data for two component system has been used to estimate the formation of zinc ferrite 'precursor' and study any other changes taking place in the chemical composition of the composites.

Experimental

Sample preparation

All the samples were prepared from Analar grade reagents. Studies were made with following four samples:

I. Precipitate obtained by adding a normal solution of NH_4HCO_3 to a normal solution of $Zn(NO_3)_2$ at $30-35°$, filtration, washing and drying in an air oven at $110°$.

II. Precipitate obtained by adding NH_4HCO_3 to a normal solution of $Fe(NO_3)_3$, filtration, washing and drying at $110°$.

III. Dried precipitates (I) and (II) mixed in 1 : 1 ratio by weight and ground together for 90 minutes in a Fischer Automatic grinder.

IV. Precipitate obtained by adding NH_4CO_3 to a mixed solution of $Fe(NO_3)_3$ and $Zn(NO_3)_2$, filtration, washing and drying at $110°$.

Chemical analysis

The dried samples were analyzed for Fe, Zn and CO_2 contents by standard volumetric methods described by Vogel [10]. The results are given in Table 1.

Thermal analysis

TG studies were carried out in a Stanton Massflow Thermobalance with a sensitivity of 0.2 mg per division, at a heating rate of 10 deg/min in air, with 100 mg of sample. DTA was carried out in a home-assembled unit.

Results and discussion

Composition and thermal properties of zinc precipitate (I) and iron precipitate (II)

The chemical analysis of sample I (Table 1) and thermal analysis (wt. loss upto $500° = 25.7$) relates the precipitate to a zinc basic carbonate of type $2 ZnCO_3 \cdot 3 Zn(OH)_2$; the exact formula being $ZnCO_3 \cdot 1.88 Zn(OH)_2 \cdot 0.19 H_2O$.

The basic reactions during precipitation leading to its formation are,

$$5\,Zn(NO_3)_2 + 10\,NH_4HCO_3 \rightarrow 2\,ZnCO_3 \cdot 3\,Zn(OH)_2 +$$
$$+ 10\,NH_4NO_3 + 8\,CO_2 + 2\,H_2O$$
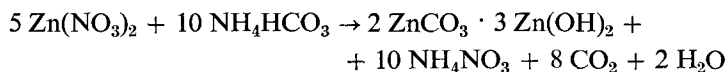
The decomposition (Fig. 1.1) starts at about 180° and a nearly constant weight corresponding to ZnO is obtained at 280°. This appears in the form of a single sharp endothermic effect in DTA curve (Fig. 1.2) in the temperature range of
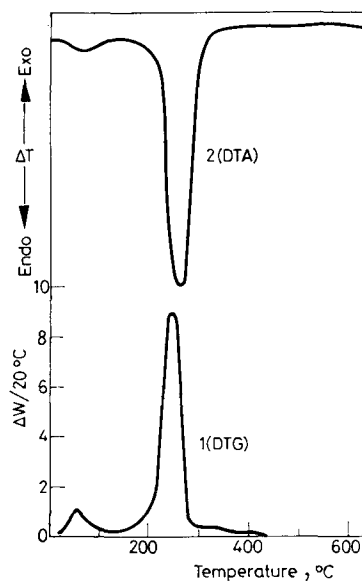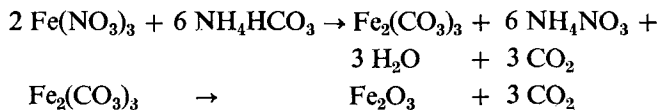

Fig. 1. DTA and DTG curves of zinc basis carbonate

200−300°. A small peak observed in both DTA and DTG curve at 65° is due to small amount of free water present in the sample.

The precipitate (Sample II) obtained by the addition of ammonium bi-carbonate to a solution of ferric nitrate is an iron(III)oxide gel, formed as follows,

$$2\,Fe(NO_3)_3 + 6\,NH_4HCO_3 \rightarrow Fe_2(CO_3)_3 + 6\,NH_4NO_3 +$$
$$3\,H_2O \quad + 3\,CO_2$$
$$Fe_2(CO_3)_3 \quad \rightarrow \quad Fe_2O_3 \quad + 3\,CO_2$$

The DTG curve (Fig. 2.1) shows its dehydration at 110° which appears as a large endothermic peak at 140° with a small break at 160° in the DTA curve (Fig. 2.2). While a low dehydration activity continues up to 400° and beyond as indicated in the DTG curve, a strong exothermic peak appears at about 500° in the DTA curve. These features of sample II correspond to that of an iron(III)oxide gel which has been well studied by Mackenzie [11] and Towe and Bradley [12].
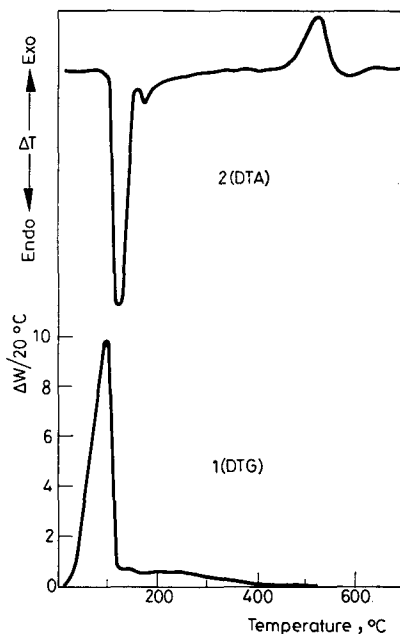
Fig. 2. DTA and DTG curves of iron oxide gel

Table 1

Analysis of the samples: Experimental values, and theoretical values based on the stated identities

Sample	Fe₂O₃, %		ZnO, %		CO₂, %		TG wt. loss	
	exptl.	theor.	exptl.	theor.	exptl.	theor.	exptl. 500°	theor.
I	—	—	74.27	74.26	13.90	13.94	25.7	25.7
II	77.53	77.55	—	—	0.0	0.0	20.4	22.4
III	40.45	40.45	38.70	38.74	6.21	6.25	20.4	20.2
IV	42.21	42.03	38.95	38.88	3.51	3.61	18.5	18.9

The exotherm at 500° represents the development of α-Fe₂O₃ structure from the 'proto hematite' state of the gel.

From TG data the composition of this sample is computed as, $Fe_2O_3 \cdot 2.57\ H_2O$.

Reaction between the zinc precipitate (I) and iron precipitate (II) in the solid state under impact grinding

The chemical analysis of the mixture (sample III) prepared by grinding together the precipitates I and II is given in Table 1.
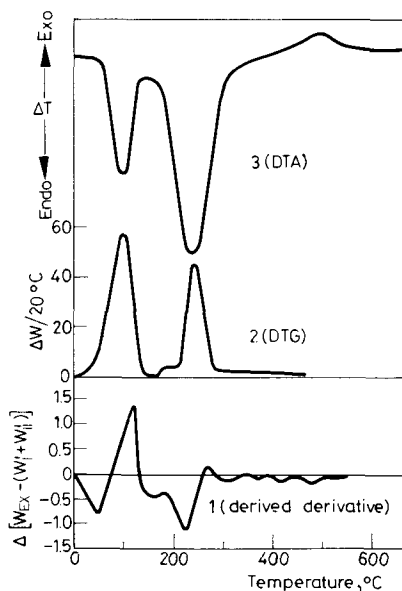
Fig. 3. Derived derivative, DTA and DTG curves of zinc—iron system (mechanical mixture)

The sample III decomposes, as shown in DTG curve in Fig. 3.2. If no interaction between the two precipitates occur during grinding, the peaks corresponding to decomposition of zinc basic carbonate and iron oxide gel are expected to appear proportionately in the DTG curve. The curve indicates two well defined peaks; one at $100°$ and another at $240°$ corresponding to dehydration of iron gel and decomposition of zinc basic carbonate, respectively. From the DTG curve, no conclusions can be drawn regarding the possible interaction between the two compounds during the grinding process, and is thus of little help in formulating the composite of a two component system.

The DTA curve shown in Fig. 3.3 also indicates the dehydration peak and decomposition peak of the two compounds at respective temperatures and furnishes no additional informations. However, a sharp well defined exothermic peak expected at about $500°$ corresponding to the development of α-F₂O₃ appears merely as a small hump at that temperature. According to Towe and Bradley [12] the exothermic peak in iron(III)oxide gel is due to nucleation of the dehydrated gel into α-Fe₂O₃. Its diminutive appearance in the mechanical mixture prepared by grinding indicates that either dehydrated iron oxide gel does not readily nucleate in presence of the zinc compound or the process is shifted to a higher temperature. Such an effect of the presence of other cations on DTA curves is well known [11]. Another explanation which stems from the variability in the DTA curves of iron (III)oxide gels obtained by different authors, would be that a perfection in cation

ordering might have taken place during the grinding process itself thus reducing or eliminating the exothermic process of transformation.

It is evident that both DTG and DTA curves are insufficient so far as the formulation of the composite in a two components system is concerned. For such instances, use of a derived derivative thermogravimetric curve [9] was suggested. In this curve the differences between the experimental behaviour and expected behaviour of a composite are plotted. If W_I and W_{II} are the respective experimental weight losses from component I and component II, as determined separately then W_I' and W_{II}', weight loss from the corresponding quantities of component I and II in the composite can be computed. If W_{ex} is the experimental weight loss in the composite under identical conditions, then a plot of $[W_{ex} - (W_I' + W_{II}')]$ against temperature would indicate the departure from the expected thermal behaviour of the composite. The inferences can be drawn from this regarding any interaction, mode of decomposition and changes in the composition of the composite.
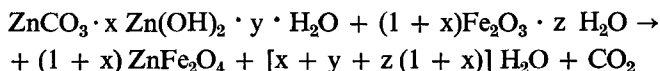
The derived derivative curve for sample III is shown in Fig. 3.1. A negative peak at 50° followed by a positive peak at 120° and again a negative peak at 220° are the features of this curve. The significance of the positive peak as representing an additional thermal activity and of negative peaks representing absence of an expected thermal activity has been discussed in our earlier paper [9]. Interpretation of the peaks in Fig. 3.1 therefore is (1) that a small quantity of iron oxide gel (negative peak below 100°) is reacting with a certain quantity of zinc basic carbonate (negative peak at 220°), possibly forming a new compound. (2) The dehydration temperature of the remaining iron oxide gel is shifted slightly to higher side while the remaining zinc basic carbonate decomposes at its normal temperature.

With these observations from the derived derivative curve and the quantities corresponding to positive and the negative peaks, the composition of the composite (sample III) has been arrived at which is,

Zinc precipitate,	$ZnCO_3 \cdot 1.88\,Zn(OH)_2$	$= 44.89\%$
Iron oxide gel,	$Fe_2O_3 \cdot 2.57\,H_2O$	$= 38.46\%$
Precursor spinel,	$ZnFe_2O_4$	$= 16.05\%$

All the experimental, thermal and chemical data, especially the percentage of CO_2 determined in the composite agrees with this composition (Table 1).

The general reaction leading to the formation of zinc ferrite 'precursor' during the grinding process may be written as,

$$ZnCO_3 \cdot x\,Zn(OH)_2 \cdot y \cdot H_2O + (1 + x)Fe_2O_3 \cdot z\,H_2O \rightarrow$$
$$+ (1 + x)\,ZnFe_2O_4 + [x + y + z\,(1 + x)]\,H_2O + CO_2$$

Thus, the reaction between the hydrated oxides of iron (iron(III)oxide gel) and zinc (hydroxy-carbonate) in the solid state under impact of grinding results in the formation of a small quantity (16.05%) of zinc ferrite 'precursor'.

The estimation of any additional quantity of the zinc ferrite possibly formed during the thermal decomposition process or beyond the temperatures of decomposition of the hydrated oxides requires other chemical and physical methods and is not considered here. The formation of zinc ferrite 'precursor' formed by the reaction between the corresponding hydrated oxides at room temperature and its estimation through a derived derivative thermogravimetric curve is only studied here.

Reaction between the hydrated oxides in the solution during coprecipitation

The technique of the derived derivative curve can as well be extended to the study of reaction between hydrated oxides during coprecipitation.

The DTG curve of coprecipitated sample IV, is shown in Fig. 4.2 The prominent peaks at about $60°$ and $220°$ represents possibly the dehydration of the ferric oxide gel and decomposition of zinc basic carbonate respectively. The DTA curve (Fig. 4.3) is in agreement with the DTG curve indicating both the processes as endotherms at nearly the same temperatures as observed in DTG curve. The DTA curve is further characterized by the presence of an exothermic peak at $520°$ similar to one observed in pure iron(III)oxide gel (Fig. 2.2). Thus, both DTG and DTA curves only suggest that the coprecipitated samples is probably a simple mixture of ferric oxide gel and zinc hydroxy carbonate which is not the case as will be shown by the derived derivative curve.
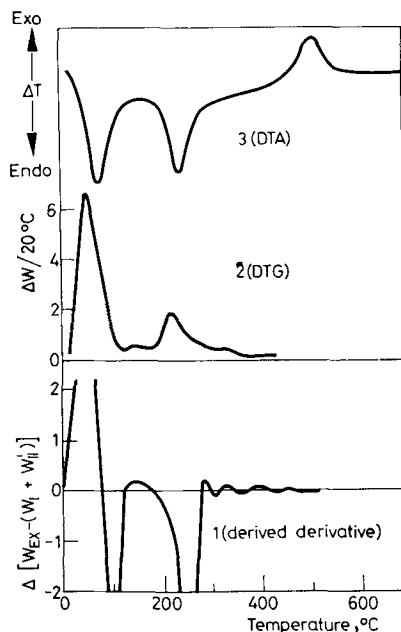

Fig. 4. Derived derivative, DTA and DGT curves of zinc—iron system (coprecipitated)

The derived derivative curve (Fig. 4.1) indicates a large positive peak at 50°, a large negative peak at 100° and 240°, respectively. Computing from the quantities associated with these peaks of this curve, we can arrive at following composition for this sample,

Zinc precipitate,	$ZnCO_3 \cdot 1.88\ Zn(OH)_2\ 0.19\ H_2O$	$= 25.94\%$
Iron precipitate,	$Fe_2O_3 \cdot 2.57\ H_2O$	$= 4.40\%$
Hydrated zinc		$(\%, 2+)$
ferrite 'precursor',	$ZnFe_2O_4 \cdot 2.58\ H_2O$	$= 69.52\%$

The above composition satisfies all the experimental data and is confirmed by the CO_2 analysis in the sample (Table 1). The nature of the derived derivative curve is now explicit, the first positive peak at 50° representing an additional thermal activity i.e. the dehydration of zinc ferrite 'precursor'; the negative peak at 100° signifying the absence of thermal activity due to dehydration of iron(III)oxide gel, which is present only in small quantity in this sample. The negative peak at 240° is again due to absence of certain quantity of zinc hydroxy carbonate in the precipitate.

The sharp exothermic peak in the DTA curve (Fig. 4.3) at 520° corresponding to the ordering of cationic structure and formation of hematite phase indicates that the gel structure is retained in the Fe_2O_3 part of zinc ferrite 'precursor'. It is probable, that at this temperature (520°) the actual zinc ferrite structure is formed from the 'precursor' zinc ferrite in the sample. The evidence for this has been obtained by Beretka [2] et al.

The reaction between zinc oxide and iron(III)oxide to form zinc ferrite at low temperature depends upon the relative reactivity of the oxides [2]. In case of mechanical mixture prepared by grinding of hydrated oxide in air, only a small quantity of 'precursor' zinc ferrite is formed through a chemical reaction at ambient temperature. Also, in this particular sample the exothermicity due to hematite phase formation at 500° is diminished. It would therefore appear that in this sample the formation of zinc ferrite structure will take place at a higher temperature. On the other hand, in a coprecipitated sample, a large quantity of 'precursor' is formed at ambient temperature during coprecipitation itself, and oxides formed in situ during thermal decomposition are more reactive. This will favour the formation of zinc ferrite at lower temperatures.

References

1. C. J. DEAN and M. P. COLLING, Chem. Abstr., 76 (1972) 50631 w.
2. J. BERETKA and M. J. RIDGE, Nature, 216 (1967) 473.
3. I. PORUBSZKY, G. BÉKÁSY, 3rd. Analytical Conference, 24—29 August, 1970, Budapest.
4. D. J. M. BEVAN, J. P. SHELTON and J. S. ANDERSON, J. Chem. Soc., (1948) 1729.
5. J. BERETKA and A. J. MARRIAGE, Austral. J. Appl. Sci., 15 (1964) 321.
6. D. W. HOPKINS, J. Electrochem. Soc., 96 (1949) 195.
7. G. A. ADADUROV, G. V., NOVIKOV, N. S. OVANESYAN, V. A. TRUKHTANOV and V. M. SHEKHTMAN, Fiz. Tverd. Tela, 11 (1969) 1988.

8. V. P. Chalyi and E. N. Lukachina, Izv. Akad. Nank. SSR, Neorg. Mater, 3 (1967) 1447.
9. B. R. Arora, R. K. Banerjee and B. N. Singh, J. Thermal Anal., 13 (1978) 499.
10. A. I. Vogel, Text Book of Quantitative Inorganic Analysis. Longmans Green, London 1964.
11. R. C. Mackenzie, Differential Thermal Analysis, Vol. 1, Academic Press. London. 1970.
12. K. M. Towe and W. F. Bradley, J. Colloid Interface Sci, 24 (1967) 384.

Résumé — Les oxydes hydratés formés lors de l'addition du bicarbonate d'ammonium à une solution de $Zn(NO_3)_2$ et de $Fe(NO_3)_2$ suivie du séchage du précipité à 110°, sont l'hydroxy-carbonate de zinc(I) et le gel de l'oxyde de fer(III) (II). On a utilisé une nouvelle technique de thermogravimétrie en dérivation, ainsi que les méthodes d'ATD et TGD conventionnelles, pour étudier la réaction entre (I) et (II) dans le système à deux composants.

Un mélange de (I) et de (II), soumis au broyage, donne environ 16 p.c. de ferrite de zinc «précurseur», tandis qu'un échantillon préparé par coprécipitation à partir de la solution des nitrates mixtes et séchage à 110°, en donne environ 70 p.c.

La formation du spinelle de ferrite de zinc décrite comme ayant lieu, dans des cas similaires, à des températures faibles, paraît être en rapport avec la formation du «précurseur» ainsi qu'avec la réactivité et la température de la transformation de phase de Fe_2O_3.

Zusammenfassung — Die durch Zugabe von Ammoniumbicarbonat zu einer Lösung von $Zn(NO_3)_2$ und $Fe(NO_3)_3$ und Trocknung des Niederschlags bei 110° gebildeten hydratisierten Oxide sind Zinkhydroxycarbonat (I) bzw. Eisen(III)oxidgel (II). Eine neue derivierte derivative thermogravimetrische Kurve wurde gemeinsam mit den konventionellen DTA und DTG Methoden zum Studium der Reaktion zwischen (I) und (II) in Zweikomponentensystemen eingesetzt.

Das Gemisch von (I) und (II) ergibt beim Mahlen etwa 16% Zinkferrit »Prekursor«. In einer durch Mitfällung der gemischten Nitrate und Trocknung bei 110° erhaltenen Probe wurde fast 70% »Prekursor« gebildet. Die Bildung von Zinkferritspinell, über dessen Entste-hung in solchen Fällen bei niedrigen Temperaturen berichtet wird, scheint mit der Bildung des »Prekursors« verbunden zu sein, sowie mit der Reaktivität und der Phasenübergangstempera-tur in Fe_2O_3.

Резюме — При добавлении бикарбоната аммония к раствору $Zn(NO_3)_2$ и $Fe(NO_3)_3$, обра-зуются гидроокиси, которые после высушивания при 110°, представляют собой, соответ-ственно, основной карбонат цикла (I) и гель окиси трехвалентного железа (II). Новая вы-веденная производная термогравиметрической кривой, наряду с обычными методами ДТА и ДТГ, была использована для изучения реакции между I и II в двухкомпонентных систе-мах. Смесь I и II, подверженная измельчению, содержит около 16% вещества, предшест-вующего образованию феррита цинка. В образце, полученном соосаждением смешанных растворов нитратов и высушенном при 110°, почти 70% образуется вещества, предшест-вующего образованию феррита цинка .Имеет место образование цинк ферритовой шпинели при низкой температуре и это может быть связано с образованием «предшественника» феррита цинка, реакционной способностью и температурой фазового превращения в Fe_2O_3.