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THERMOCHEMICAL STUDIES ON THE FORMATION AND CONSTITUTION OF THE ZINC OXIDE–ALUMINIUM OXIDE SYSTEM

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ABSTRACT

This study is based on thermogravimetric (TG), differential thermal analysis (DTA) and chemical analysis of the $ZnO–Al_2O_3$ system. The coprecipitation from mixed nitrate salt solutions of zinc and aluminium results in the formation of zinc basic carbonate and aluminium hydroxide, and is also a precursor to aluminate spinel ($2ZnO \cdot 3Al_2O_3$) only in the samples in which aluminium is present in near or above stoichiometric quantities. Grinding of the mixtures of individual precipitates maintains the similarity with coprecipitates in forming a "precursor", but to a lesser extent. The endothermic peak in DTA at 275°C in some coprecipitated and mixed samples hints at the formation of a precursor since the individual precipitate does not have a peak at this temperature. The "precursor" to spinel obtained in the precipitation stage in some coprecipitated samples is freely soluble in 1 *M* HCl, and that obtained at 450°C is partially soluble which cannot be detected by the usual X-ray technique due to its highly disordered structure in amorphous state. The "precursor" is converted around 800°C to an actual spinel structure, which is almost insoluble in *M* HCl and is detectable by X-rays.

INTRODUCTION

The method of preparation of a mixed oxide system intended to be used as a catalyst uniquely affects its catalytic properties. The chemistry of precipitation and the identification of compounds formed in mixed oxide systems of catalytic importance, particularly for the $ZnO–Al_2O_3$ system, have not been well studied.

The interest generated in the $ZnO–Al_2O_3$ system is due to its catalytic properties in dehydrogenation and dehydration reactions. Even ZnO alone, though it mainly affects dehydrogenation, finds application due to its high absorptive efficiency for removing H_2S from naphtha feed stocks in the fertilizer and petrochemical industries. The life of the ZnO is limited by the allowable H_2S slip from the bed which generally occurs when about 16–18% of the sulphur is built up, and at this stage more than 45% of the free ZnO remains unutilized. The use of ZnO finely dispersed over Al_2O_3 appears to provide an absorptive surface without affecting its capacity and activity[1] with additional advantages of reducing the cost of the finished product and increasing the mechanical strength.

Uma and Kuriacose[2] have studied different preparations of ZnO–Al_2O_3 for the dehydrogenation and dehydration of isopropanol. These authors found that Al_2O_3 interacts with ZnO above 500°C to give rise to a new species having higher dehydrogenation activities. They suggested that this new species may be a spinel ($ZnAl_2O_4$) or a "precursor" to spinel. Chemical composition of "precursor" is similar to that of spinel but, due to the highly disordered structure of the former, X-rays fail to detect it. The spinel formation generally occurs at elevated temperatures, and for $ZnAl_2O_4$ from zinc oxide and aluminium oxide, a temperature of 1200°C has been employed[3]. The formation of this type of compounds, *e.g.*, zinc aluminate and zinc ferrites etc., has also been reported at a lower temperature[4]. The precursor method employed by Whipple and Wold[5] and Wickham[6] for the preparation of spinels consists of coprecipitating the relevant compounds in a finely dispersed form which, on heating at a much lower temperature, results in the formation of spinels.

In the present paper thermochemical studies on the ZnO–Al_2O_3 system are presented and an attempt has been made to identify both the compounds formed at the precipitation stage and the resulting products of decomposition. In subsequent publications on this subject we propose to present the decomposition kinetics of mixed precipitates, their physico-chemical properties and their correlations with catalytic activity.

EXPERIMENTAL

Preparation

Coprecipitated samples. From a solution containing requisite amounts of $Zn(NO_3)_2$ and $Al(NO_3)_3$ precipitation was carried out by the addition of ammonium carbonate. The precipitates obtained were washed free of ammonium nitrate and oven dried at 110°C. All the reagents used were of BDH Analar grade.

Mechanically mixed samples. — The oven dried precipitates separately obtained from $Zn(NO_3)_2$ and $Al(NO_3)_3$ solutions with ammonium carbonate, were mixed in different ratios and ground for 30 minutes in a mortar and pestle.

Measurements

TG. About 50 mg of sample was non-isothermally decomposed at a heating rate of 6.5° C/min in a Stanton Mass Flow Thermobalance with a sensitivity of 0.2 mg/division.

DTA. Curves were taken at a heating rate of 10°C/min using ignited alumina as reference material in an assembled DTA unit consisting of a GallenKamp furnace, a Bausch & Lamb recorder and an Ether Transistrol Programmer.

Chemical analysis. The estimations of zinc and aluminium were carried out by conventional EDTA method using Erochrome T. indicator. The separation procedure for zinc and aluminium was the same as that given by Vogel[7].

RESULTS AND DISCUSSION

Chemical analysis, DTA and TG of pure zinc and aluminium precipitates

Chemical analysis of the precipitate (Table 1, sample 1A) obtained from zinc nitrate solution with ammonium carbonate indicates the compound to be zinc basic

TABLE 1

CHEMICAL ANALYSES OF SAMPLES 1A-1G

Sample	*% ZnO in oven dried precipitate*	*% Al_2O_3 in oven dried precipitate*	*% ZnO in the decomposed product* (500 °C)	*% Al_2O_3 in decomposed product* (500 °C)
1A	73.89	—	99.2	—
1B	—	58.12	—	98.9
1C	61.89	7.38	89.38	10.67
1D	53.64	11.78	81.97	18.03
1E	36.17	22.94	64.18	38.82
1F	25.03	31.81	44.02	55.98
1G	11.09	53.90	17.07	82.93

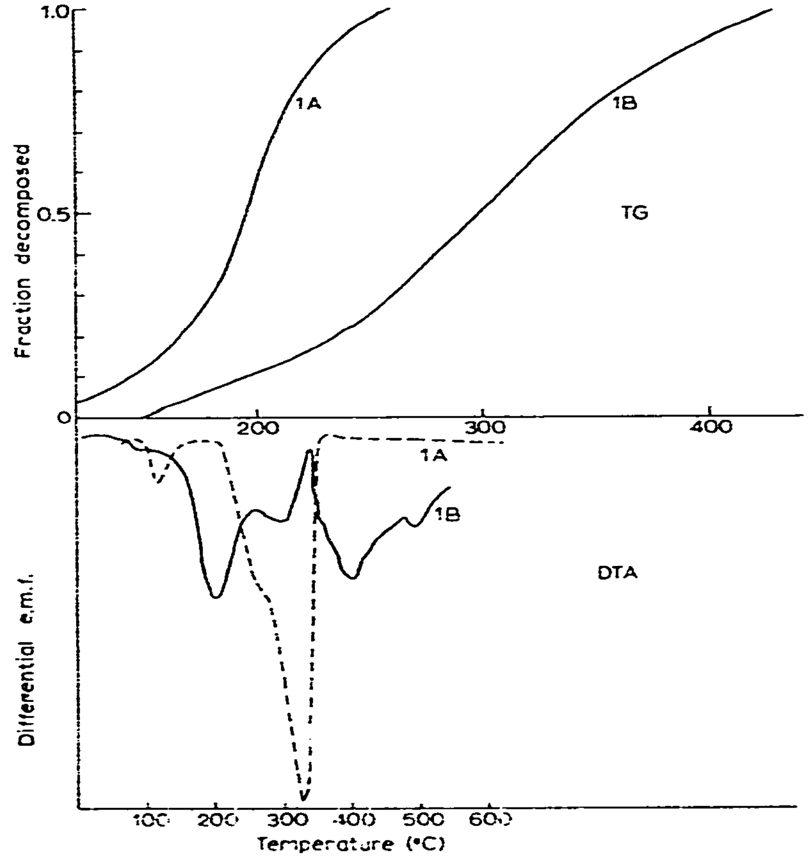

Fig. 1. DTA and TG curves for pure precipitates.

carbonate having the composition, $2ZnCO_3 \cdot 3Zn(OH)_2$, similar to hydrozincite. The initiation of decomposition of the precipitate is indicated at 150°C by TG and 200° C by DTA (Fig. 1). The difference may be due to the different heating rates employed. Thermal decomposition of zinc basic carbonate appears to be controversial. According to Duval[8], the precipitate gradually loses retained water up to 370° C at which temperature a horizontal in the TG curve corresponding to the formula, $5ZnO \cdot 2CO_2$, begins. This compound, according to Duval, maintains its stability up to 879°C and then dissociates with the elimination of CO_2, and towards 1000°C the oxide is formed quantitatively. Beck[9] and Mellor[10], on the other hand, indicate that hydrozincite or zinc basic carbonate decomposes completely between 300–400°C, the end product being ZnO. We have observed that in sample 1A the decomposition is complete around 370°C, and a total weight loss of 23.0% (Table 2) approximates the following reaction:

TABLE 2

EXPERIMENTAL AND THEORETICAL WEIGHT LOSSES FOR SAMPLES 1A–1G

Sample	*Experimental wt. loss %* *1*	*Theoretical*[a] *wt. loss %* *2*	*Theoretical*[b] *wt. loss %* *3*	*Theoretical*[c] *wt. loss %* *4*
1A	23.0	25.8	—	—
1B	39.9	41.3	—	—
1C	24.0	24.2	19.5	18.7
1D	26.8	27.0	15.5	16.4
1E	26.8	26.9	7.1	9.3
1F	25.8	29.48	0.48	3.5
1G	24.7	37.69	29.2	25.5

[a] Assuming no compound formation. [b] Assuming formation of $ZnO \cdot Al_2O_3$. [c] Assuming formation of $2ZnO \cdot 3Al_2O_3$.

$$2ZnCO_3 \cdot 3Zn(OH)_2 \rightarrow 5ZnO + 2CO_2 + 3H_2O$$

In confirmation of the proposed formula and mode of decomposition of the sample 1A, a Carbon–Hydrogen Analyzer was used to estimate CO_2 and H_2O, and the results obtained were 14.0% and 8.6%, respectively. This decomposition appears in the form of a single large endothermic peak at 325°C in DTA curve. The chemical analysis of the solid residue after decomposition at 400°C is very nearly ZnO (99.2%) and not $5ZnO \cdot 2CO_2$ as postulated by Duval[8].

Precipitation from aluminium nitrate solution with ammonium carbonate results in the formation of $Al(OH)_3$ which is normally associated with some waters of crystallization[8,10]. On the basis of chemical analysis and experimental weight loss (Sample 1B, Tables 1 and 2), the probable formula appears to be $2Al(OH)_3 \cdot H_2O$. In the DTA curve (Fig. 1), two large peaks at 200°C and 400°C and two small peaks at 300°C and 500° C indicate the stepwise dehydration. Chemical analysis of the decomposition product at 500°C is 98.7% Al_2O_3 with 1.3% combined water which is expelled between 500–1000°C. Based on DTA and TG data, the dehydration scheme for this compound may be outlined as follows:

$$2Al(OH)_3 \cdot H_2O \xrightarrow[200\,^\circ C]{-H_2O} Al_2O_3 \cdot 3H_2O \xrightarrow[300\,^\circ C]{-\frac{1}{2}H_2O} Al_2O_3 \cdot 2\tfrac{1}{2}H_2O \xrightarrow[400\,^\circ C]{-2H_2O}$$

$$Al_2O_3 \cdot \tfrac{1}{2}H_2O \xrightarrow[500\,^\circ C]{-\frac{1}{2}H_2O} Al_2O_3$$

Mixed precipitate system

Coprecipitation of two components may result in the formation of some intermediate species, about which useful information can be obtained from TG and DTA along with the chemical analysis data.

The TG curves (Fig. 2) for all such samples (1C to 1G) are fairly smooth and without any breaks. The DTA curves (Fig. 3) indicate remarkable variations in the number of peaks and corresponding temperature as compared with the respective

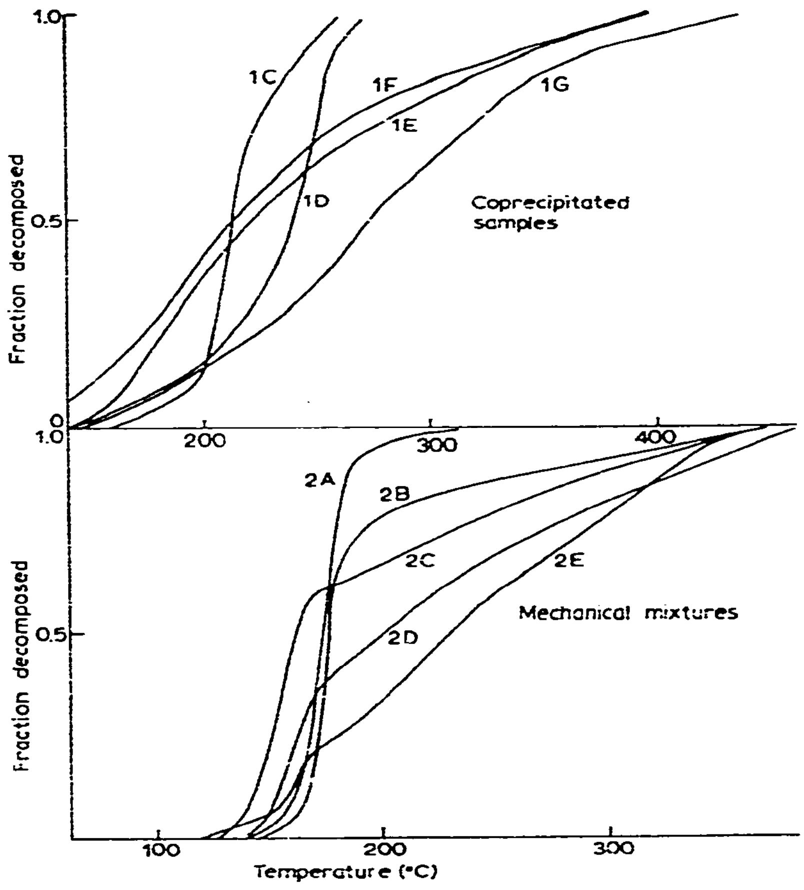

Fig. 2. TG curves for coprecipitated and mechanically mixed samples.

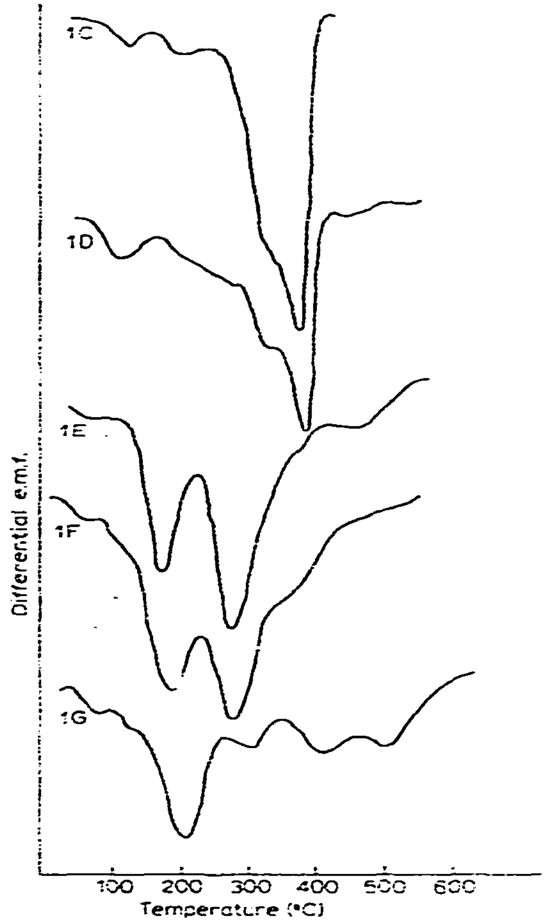

Fig. 3. DTA curves for coprecipitated samples.

single components. Most interesting feature is the appearance of a peak at 275°C in samples 1E and 1F, when in pure components it is absent.

In Table 2 experimental weight losses as observed in TG (column 1) are compared with the theoretical value which have been calculated assuming thermal decomposition of $2ZnCO_3 \cdot 3Zn(OH)_2$ and $2Al(OH)_3 \cdot H_2O$ present as such in the samples as determined by chemical analysis (Table 1). It can be seen that experimental values compare well with these theoretical values (Table 2, column 2) for samples 1C, 1D and 1E. This indicates that there is no interaction during precipitation between zinc and aluminium compounds which retain their identities in these samples. In sample 1F a 14% deviation is observed from the theoretical value which increases to 52% in sample 1G. This suggests that, at least in these two cases, the samples are not a simple mixture of zinc basic carbonate and aluminium hydroxide. The only other possibility which can account for the lower experimental values is probably the interaction of the precipitates leading to formation of new species which could be the precursor to zinc aluminate spinel.

In the literature[2] two different formulae for zinc aluminate have been reported, *viz.* $ZnO \cdot Al_2O_3$ and $2ZnO \cdot 3Al_2O_3$. The reaction between zinc basic carbonate and aluminium hydroxide may be written either as eqn. (1) or (2):

$$2ZnCO_3 \cdot 3Zn(OH)_2 + 5[2Al(OH)_3 \cdot H_2O] \rightarrow 5[ZnO \cdot Al_2O_3] + 2CO_2 + 23H_2O \quad (1)$$

$$2[2ZnCO_3 \cdot 3Zn(OH)_2] + 15[2Al(OH)_3 \cdot H_2O] \rightarrow 2[2ZnO \cdot 3Al_2O_3] + 4CO_2 + 66H_2O \quad (2)$$

Assuming that one of the above reactions occurs during coprecipitation, the loss corresponding to excess unreacted component according to both of the above schemes has been calculated and given in columns 3 and 4 of Table 2 which hints that the most probable compound is formed in sample 1G and is $2ZnO \cdot 3Al_2O_3$, *i.e.* by process (2). Incidentally, only in this sample is the Al_2O_3 present (82.9%) above the stoichiometric quantity (65.2%) according to the above formula. In sample 1F (Al_2O_3, 55.98%), comparison of experimental weight loss with different calculated values does not indicate cent percent formation of any precursor to a spinel. However, a partial reaction (approx. 15% of zinc basic carbonate reacting) may account for the small difference between the experimental (Table 2, column 1) and calculated values (Table 2, column 2). On the basis of the above results three obvious conclusions can now be drawn:

1. Formation of a precursor having the formula, $ZnO \cdot Al_2O_3$, is not favoured.
2. For complete interaction between zinc basic carbonate and aluminium hydroxide during coprecipitation to form precursor, $2ZnO \cdot 3Al_2O_3$, the percentage of Al_2O_3 should be equal or above the stoichiometric ratio (as in sample 1G).
3. Partial interaction may take place to form a precursor when the percentage of Al_2O_3 present in the system is appreciably high, but not in stoichiometric quantity (as in sample 1F).

The DTA curves (Fig. 3) further support the formation of a precursor to spinel during coprecipitation in sample 1G and also indicate a solid state reaction in samples 1E and 1F. Comparing the DTA curves of samples 1C and 1D (Fig. 3) with its individual constituents (Fig. 1) it appears that the decomposition peak of zinc basic carbonate is merely shifted to 385 °C, and small peaks at 200 °C and 300 °C correspond to the dehydration of aluminium hydroxide. The samples 1E and 1F are characterized by the appearance of a new peak at 275 °C as well as the small dehydration peaks. This may be due to a solid state reaction during decomposition. The peak again disappears in sample 1G, and the peak corresponding to zinc basic carbonate is also markedly absent which is similar to the curve of pure aluminium hydroxide except in peak areas. This supports our earlier conclusion that the zinc basic carbonate present in this sample has been reacted with the requisite amount of aluminium hydroxide to form the aluminate precursor during coprecipitation.

Relating the above observations with alumina concentrations in the sample it may be concluded that the concentration of Al_2O_3 determines the extent to which aluminate precursor will be formed either at the coprecipitation stage or during the decomposition. In samples 1C and 1D containing 10% and 18% Al_2O_3 respectively the precursor is not formed at any stage while in samples 1E and 1F containing 38.8% and 56% Al_2O_3 respectively, precursor formation occurs mainly during decomposition and only partially at the later coprecipitation stage. The precursor formation takes place in the sample 1G containing 82.9% Al_2O_3 mainly during coprecipitation.

Attempt for the estimation of precursor

X-ray analysis failed to indicate any spinel in either the oven dried precipitates or the samples decomposed at 500°C. Solubility characteristics in dilute acids have been utilized for the qualitative estimation of the precursor. From the literature it is known that actual spinels are mostly insoluble in dilute acids. All the oven dried precipitates were found to be completely soluble in *M* HCl while the decomposed product of the precipitates obtained by heating at 500°C have a different solubility in *M* HCl on boiling for 5 minutes (Table 3). Solubility of ZnO abruptly declines in samples 1F and 1G which only qualitatively support our previous conclusions.

TABLE 3

Sample no.	*% ZnO extracted*
1C	76.1
1D	76.7
1E	72.6
1F	44.9
1G	27.9

Quantitative estimation of the precursor by this method, it appears, is not possible. As mentioned earlier, oven dried sample 1G is completely soluble in dilute acid inspite of the fact that it contains the precursor (formed during coprecipitation). This sample on heating at 500°C becomes partially insoluble and only 27.9% of the total ZnO is extractable, indicating that while the precursor of the oven dried sample is soluble, it is transformed probably through some ordering of the crystal structure into a less soluble form on heating, but still remains undetectable by X-ray analysis. The sample 1G obtained at 500°C was further heated at 800°C (2 hours) and now only 1.3% of the ZnO was soluble. X-ray analysis of this sample indicated the presence of the spinel, $2ZnO \cdot 3Al_2O_3$. It is to be concluded that transformation of soluble precursors to the actual spinel is a gradual process depending on the temperatures. While a temperature of 1200°C is required for a solid state reaction[3] between the oxide mixtures to form zinc aluminate spinel, a temperature around 800°C appears to be sufficient for the formation of spinels by coprecipitation methods.

TABLE 4

CHEMICAL ANALYSES OF SAMPLES 2A–2E FORMED BY MECHANICAL MIXING

Sample	*% ZnO in decomposed product*	*% Al_2O_3 in decomposed product*	*% experimental wt. loss*	*% theoretical wt. loss*[a]	*% zinc basic carbonate reacted*[b]
2A	91.9	8.1	24.4	24.7	—
2B	83.4	16.6	26.0	26.4	—
2C	65.4	34.6	29.0	29.8	—
2D	45.7	54.3	30.4	33.2	7
2E	24.0	76.0	32.0	36.6	20

[a] Assuming no compound formation. [b] Calculated on the basis of formation of $2ZnO \cdot 3Al_2O_3$.

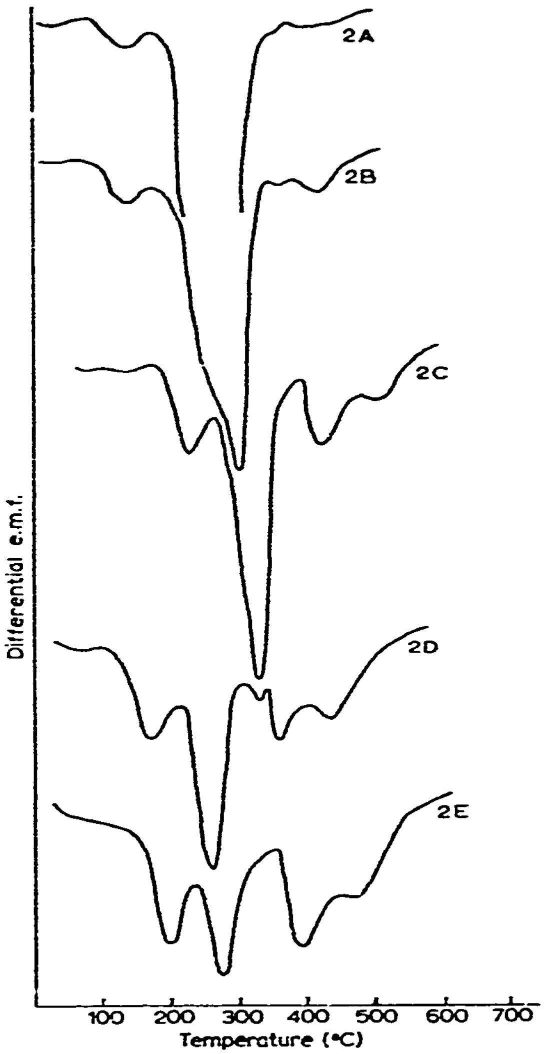

Fig. 4. DTA curves for mechanically mixed samples.

Mechanical mixtures of zinc basic carbonate and aluminium hydroxide

The idea of incorporating the study of mechanical mixtures is to compare the results with the coprecipitated samples and get more insight into the mode of formation of precursor during the decomposition process. The TG curves (Fig. 2) indicate sharp breaks which approximately correspond to the concentration of the respective components present in the samples. Chemical analysis and TG data (Table 4) indicate a similar interaction as in coprecipitated samples. The extent of reaction is however much less since in sample 2E, where Al_2O_3 is above stoichiometric quantity, only 20% of zinc basic carbonate seems to react to form $2ZnO \cdot 3Al_2O_3$, as compared to complete interaction in a similar coprecipitated sample 1G.

The DTA curves (Fig. 4) further support the fact that interaction takes place at 275°C to form the precursor in the samples containing higher percentages of alumina, *e.g.*, 2C, 2D and 2E. The samples containing a lower percentage of alumina, *e.g.* 2A and 2B, do not indicate any interaction and only the peaks corresponding to a decomposition or dehydration reaction of the individual components are observed, as in the similar coprecipitated samples.

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