USE OF DERIVED DERIVATIVE THERMOGRAVIMETRIC CURVES IN THE COMPOSITIONAL STUDY OF TWO-COMPONENT OXIDE SYSTEMS

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Reaction between two oxides leading to the formation of a new compound through a change in weight can be studied by TG methods. However, for catalyst preparations, in most of the cases the starting materials are not oxides. The more common methods of coprecipitation or kneading of the precipitated oxides are employed. In such cases the TG and DTG curve of the composites are of a complex nature for several possible reasons including the formation of new compounds. The interpretation of the conventional DTG curve of such a sample and identification of temperature regions for any new thermal activity thus presents problems. For such studies the use of a derived derivative thermogravimetric curve is suggested as described in this paper. This curve indicates the differences between the experimental thermal behaviour of the composite vis-a-vis theoretical thermal behaviour of the composite computed from the thermal behaviour of its constituents. The regions of a new thermal activity can be readily located and interpreted. Two systems are described, $MgO-Cr_2O_3$ and $MgO-Fe_2O_3$.

Many of the industrial catalysts are binary oxide compositions. A problem which is often encountered in the preparation of these type of catalysts is the uncertainty of obtaining a desired composition by the usual methods of coprecipitation or kneading of the hydrated oxides. The composites obtained in most of the cases are not simple mixtures of the two components. Their characterization from TG or DTG curves is not easier. The difficulties are due to several factors such as deviation in the expected stoichiometry of the precipitates and formation of new compounds by interaction between the precipitates.

For a complete description of two-component precipitate systems the problem can be simplified by making use of TG data obtained for the individual precipitates (single component) and the composite precipitate under the identical condition of precipitation. A plot which compares the real decomposition behaviour of the composite precipitate with the expected decomposition pattern can be constructed, which will indicate all the regions of new thermal activity due to the formation of new compounds or any such changes in the composite. We propose to call this plot as a derived derivative thermogravimetric curve. This method has been found to be very useful and simple for describing the composite precipitate. It has specific application in the study of two-component precipitates. Two systems, $MgO-Cr_2O_3$ and $MgO-Fe_2O_3$ are described as examples.

Basic principle

The plotting of a derived derivative thermogravimetric curve for a composite requires the following data.

1. Chemical analysis (% of oxides) of the composite (% AO + % B_2O_3 for example) and its TG data (W_{ex})

2. TG data of the constituent precipitates when precipitated individually. e.g. AO. xH_2O (precipitate I: TG data W_I) and $B_2O_3 \cdot yH_2O$ (precipitate II: TG data W_{II}).

The percentages of oxides determined in the composite are converted to corresponding hydrated forms e.g. a.AO.xH_2O and b.B_2O_3.yH_2O for which TG data are available. For the derived derivative curve $\Delta[W_{ex} - (W_I' + W_{II}')]$ is plotted as a function of temperature where,

W_{ex} = experimental weight loss(%) in the composite at a certain temperature (T)

W_I', W_{II}' = weight loss in the constituent precipitates (e.g. in a.AO.xH_2O and b.$B_2O_3 \cdot yH_2O$) calculated from W_I and W_{II} at the same temperature (T).

In the above plot, ($W_I' + W_{II}'$) represents the total weight loss based on the assumption that the composite is a simple mixture of the constituent precipitates and that the decomposition of either of the precipitates is not affected in presence of the other. In most of the instances this may not be the case and the theoretical data, ($W_I' + W_{II}'$) will differ from the experimental TG data of the composite (W_{ex}). The derivative of these differences, $\Delta[W_{ex} - (W_I' + W_{II}')]$ will be characteristic of the composite and thus indicative of the true state of the two components in the composite. If the composite behaves as a simple mixture of the precipitate of the two components, without any change whatsoever in the decomposition behaviour of the either of the precipitate, the derived derivative curve will be merely a horizontal. The presence of additional thermal activities and absence of an expected thermal activity will be indicated by positive and negative peaks respectively. The quantities involved may be computed from the area under the peaks.

Experimental

Sample preparation

All the samples were prepared from 'Analar' grade reagents.

The individual hydrated oxides of magnesium, chromium and iron were precipitated by adding $4N$ ammonia solution to a molar solution of corresponding nitrate salts at room temperature. The precipitates were washed till free from nitrate ions and dried at 110° for 16 hrs.

The coprecipitated samples were similarly precipitated with ammonia solution from a solution mixture containing requisite quantities of respective nitrates [1]. The MgO, Cr_2O_3 and Fe_2O_3 content of the samples were determined by standard volumetric methods [2].

Thermal analysis

The TG data for the samples were obtained in a Stanton Massflow Thermo-balance with a sensitivity of 0.2 mg per division, under following conditions,
    Sample weight: 100 – 150 mg, heating rate: 6.5°C/min, atmosphere: air.

Applications

MgO-Cr$_2$O$_3$ system

Formation by the reaction between the hydrated oxides, in the solid state

When precipitated separately the hydrated forms of MgO and Cr$_2$O$_3$ are Mg(OH)$_2$ and Cr$_2$O$_3$ · 4H$_2$O respectively. The DTG curves of these two compounds are shown in Fig. 1 (I and II).
    The decomposition of Mg(OH)$_2$ occurs between 300 – 380° (peak 350°), which is in agreement with the published TG data for this compound [3 – 4].
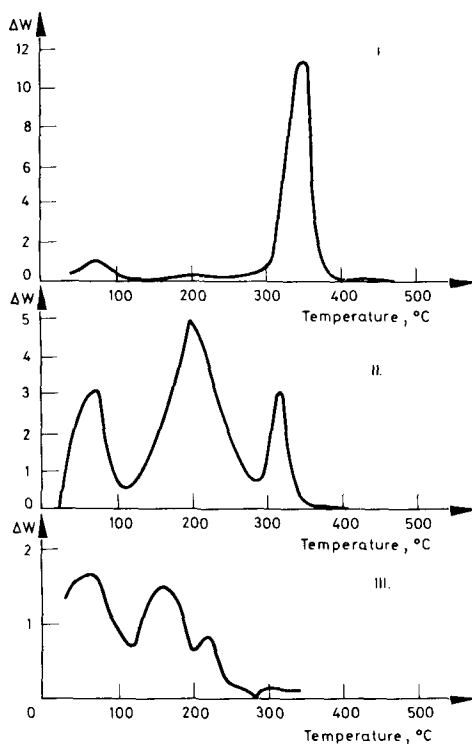

Fig. 1. DTG curves of Mg(OH)$_2$ (I), Cr$_2$O$_3$ · 4 H$_2$O (II) and FeOOH (III)

The precipitation of chromium hydroxide with varying water molecules, $Cr(OH)_3 \cdot xH_2O$, where x may vary from 3.0 to 1.0 has been reported [5]. In the present work the composition of the chromium hydroxide is found to be $Cr(OH)_3 \cdot$

Table

Description of the samples

Sample No.	Description	TG wt. loss, %	Chemical analysis, %		
			MgO	Cr_2O_3	Fe_2O_3
1.	Mixture of hydrated MgO and Cr_2O_3	33.5	13.1	51.82	—
2.	Coprecipitated MgO and Cr_2O_3	34.3	6.49	59.78	—
3.	Mixture of hydrated MgO and Fe_2O_3	18.8	16.25	—	64.45
4.	Coprecipitated MgO and Fe_2O_3	23.7	2.53	—	73.65
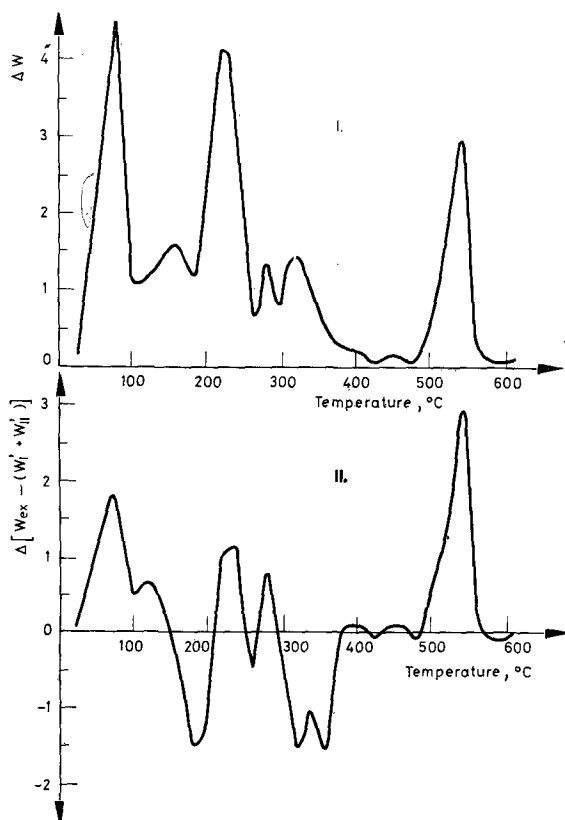
Fig. 2. DTG(I) and derived derivative (II) plots for mixture of $Mg(OH_2)$ and $Cr_2O_3 \cdot 4\,H_2O$

· H_2O which may be written as $Cr_2O_3 \cdot 4H_2O$. This compound more or less continuously dehydrates but with three well defined peaks at 75, 200 and 320°.

A composite was prepared by mixing and grinding together the two precipitates *viz.* $Mg(OH)_2$ and $Cr_2O_3 \cdot 4H_2O$. The analysis of this sample (sample No. 1) is given in the table. The DTG curve is shown in Fig.2(I), which shows three prominent peaks at 75, 220 and 540° and three small peaks at 160, 280 and 320°. The absence of the peak due to dehydration of $Mg(OH)_2$ (350°) and presence of a new peak (540°) are the noticeable features of the DTG curve of the composite. This indicates that some changes or reaction have occurred in the system, $Mg(OH)_2$ + + $Cr_2O_3 \cdot 4H_2O$ during grinding process. A complete description of these changes and assignation of DTG peaks to the corresponding reactions may not be possible without prior knowledge of the system.

The derived derivative curve for the same sample is shown in Fig. 2(II). Positive peaks at 75, 120, 240, 280, 540° and two large negative peaks at 180° and 320° are observed. While the positive peaks represent the additional thermal activities at these temperatures the negative peaks signify the absence of expected thermal activities. The temperature region of the second negative peak corresponds to the temperature of dehydration of $Mg(OH)_2$. Obviously either whole or part of the $Mg(OH)_2$ is no longer present as $Mg(OH)_2$. A reasonable assumption would be that it is present as MgO which is formed from $Mg(OH)_2$ during the grinding process. Similarly another negative peak at 180° indicates the absence of some of the $Cr_2O_3 \cdot 4H_2O$ or the presence of this as Cr_2O_3. The amount of MgO and Cr_2O_3 corresponding to those negative peaks can be calculated. Similarly the positive peak at 540° representing the additional thermal activity indicates the presence of an intermediate compound formed during grinding and which is likely to be $MgCrO_4$, decomposing at 540° to $MgCr_2O_4$. Computing the quantities involved following composition for this composite is arrived at $Mg(OH)_2$ = 6.04%; $Cr_2O_3 \cdot$ · $4H_2O$ = 51.96%; $MgCrO_4 \cdot 3H_2O$ = 42.09%.

The probable mode of formation of $MgCrO_4$ during grinding process would be,

$$Cr_2O_3 \cdot 4H_2O + 2Mg(OH)_2 + 3O \rightarrow 2MgCrO_4 + 6H_2O.$$
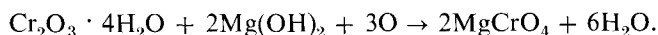
The several positive peaks in the derived derivative curve i.e. at 75, 120, 240, and 280° are due to the dehydration of the remaining $Mg(OH)_2$ and $Cr_2O_3 \cdot 4H_2O$ at these temperatures and also the water associated with the precursor $MgCrO_4 \cdot$ · $3H_2O$. At 540° the precursor $MgCrO_4$ decomposes to $MgCr_2O_4$ releasing oxygen which appears in the form of a positive peak in the derived derivative curve.

$$2MgCrO_4 \rightarrow MgCr_2O_4 + MgO + 3O.$$
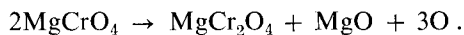
Similar conclusions were drawn in our earlier investigation [1] and by other authors [6, 7].

Thus it may be seen that derived derivative curve provides data for the complete description of the processes occurring during the grinding together of the two precipitates, and helps in formulating the composite precipitate.

Formation by the reaction between the hydrated oxides during coprecipitation

The result of chemical analysis of the coprecipitated sample is given in the table. Several peaks are indicated in the DTG curve of this sample (Fig. 3. I) from which it may be very difficult to draw inferences regarding the composite. The derived derivative curve of this sample is shown in Fig. 3. II. Two large negative peaks at 200° and 320° identical to the negative peaks observed in sample 1 point out the similarity in the basic nature of the two samples. A comparatively smaller peak at 540°, however, shows that the quantity of $MgCrO_4$ present is much less due to the smaller percentage of $Mg(OH)_2$ in sample 2. From the derived derivative curve the percentages of various components of the coprecipitated mass can be computed and composition is obtained which is $Cr_2O_3 \cdot 4H_2O = 62.68\%$; $Cr_2O_3 = 5.08\%$; $MgCrO_4 = 22.54\%$ and $H_2O = 9.7\%$. The $MgCrO_4$ (precursor) may be in the hydrated state ($MgCrO_4 \cdot 3H_2O$) to account for the H_2O indicated in the above composition.
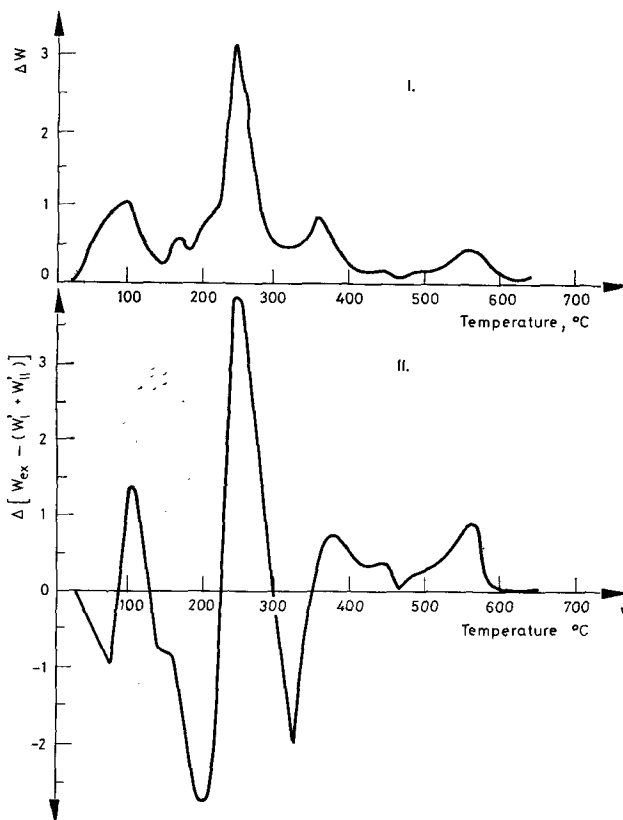

Fig. 3. DTG(I) and derived derivative (II) plots for coprecipitated $Mg(OH_2)$ and $Cr_2O_3 \cdot 4 H_2O$

MgO - Fe_2O_3 system
Formation by reaction between the hydrated oxides in solid state

While the hydrated form of MgO is $Mg(OH)_2$, the Fe_2O_3 in the hydrated state was obtained in its topochemical form having composition FeOOH [8]. The precipitation of iron hydroxide may result in the formation of $Fe(OH)_3$ or FeOOH depending upon the reagents and conditions employed. Initially the precipitate is often amorphous $Fe(OH)_3$ which gradually changes to crystalline FeOOH [9]. The DTG curve of FeOOH is shown in Fig. 1 (III).
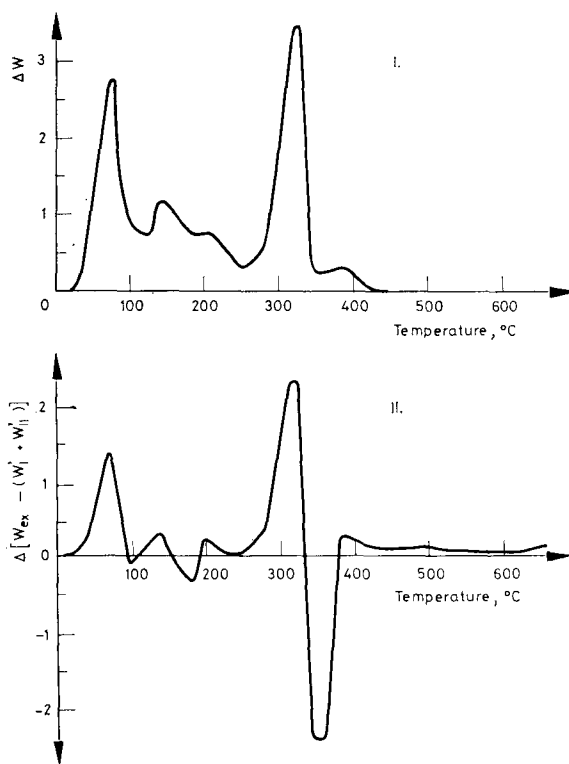

Fig. 4. DTG(I) and derived derivative (II) plots for mixture: $Mg(OH_2)$ and FeOOH

A mixture of $Mg(OH)_2$ and FeOOH in appropriate proportions was subjected to grinding. The results of chemical analysis and thermal analysis (DTG curve) of the composite thus obtained (sample 3) are given in Table and Fig. 4(I) respectively. The derived derivative curve (Fig. 4II) shows a negative peak between 340 – 360° indicating the disappearance of a certain amount of $Mg(OH)_2$. Two prominent positive peaks at 75° and 300° represent the addition of some new species dehydrating at these temperatures. A systematic calculation revealed the following composi-

tions; $Mg(OH)_2 = 8.26\%$; $FeOOH = 1.67\%$; $Fe(OH)_3 = 28.37\%$; $Fe_2O_3 = 41.75$ %; $MgO = 10.54\%$ and $H_2O = 9.41\%$. Thus the changes which occur during grinding of $Mg(OH)_2$ and $FeOOH$ are the formation of $Fe(OH)_3$, Fe_2O_3 and MgO by reaction in the solid state. The Fe_2O_3 and MgO thus formed may be associated as a precursor to the spinel, $MgFe_2O_4$. The water (9.41 %) may be present as water of hydration of $MgFe_2O_4$ (precursor) as $MgFe_2O_4 \cdot 2H_2O$. Now the DTG curve (Fig. 4.I) can be explained on the basis of the above composition. The peak at $75 - 100°$ is due to dehydration of $Fe(OH)_3$ which continues up to $250°$. At $300 - 320°$ a large peak represents the dehydration of residual $Mg(OH)_2$ as well as probably the precursor, $MgFe_2O_4 \cdot 2H_2O$. These results are similar to those obtained by Ermolenko and Karataeva [10] for mechanical mixture of iron hydroxide and magnesium hydroxide.

Formation by reaction between the hydrated oxides during coprecipitation

The DTG and derived derivative curves for the coprecipitated sample are shown in Fig. 5 I; II. A large positive area in the derived derivative curve suggests the addition of water in the sample over and above of that associated with the expected
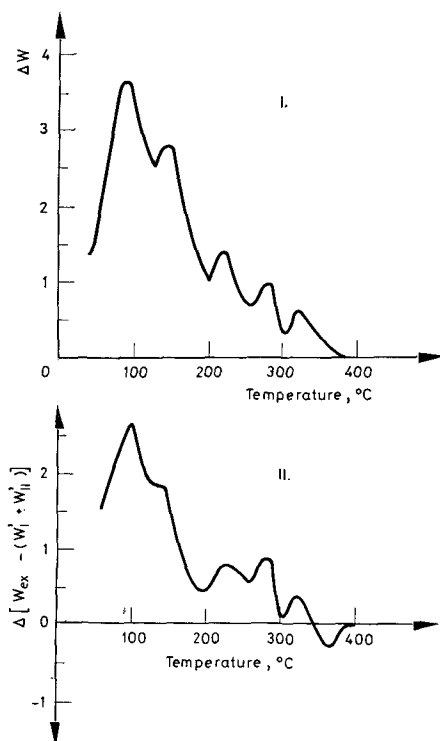

Fig. 5. DTG(I) and derived derivative (II) plots for coprecipitated $Mg(OH_2)$ and $FeOOH$

amounts of $Mg(OH)_2$ and FeOOH in the sample. The absence of whatever small quantity of $Mg(OH)_2$ might be present is indicated by a small negative peak at $360°$. The composition of the precipitate which emerges from the derived derivative data is $Fe(OH)_3 = 85.17\%$; $MgO = 2.52\%$; $Fe_2O_3 = 9.99\%$ and $H_2O = 2.25\%$. The MgO and Fe_2O_3 represents the precursor composition.

Thus in the coprecipitated sample also, we obtain the precursor $MgFe_2O_4 \cdot 2H_2O$ and large quantity of $Fe(OH)_3$ is precipitated instead of expected FeOOH. Another feature is the absence of any magnesium as $Mg(OH)_2$. The absence of $Mg(OH)_2$ and the formation of $MgFe_2O_4$ spinel at $400-500°$ from probably a precursor in coprecipitated samples has been reported earlier [10−12].

In all the above cases the TG loss agrees with the composition arrived at, with the help of the derived derivative curve. Thus the derived derivative curve has been found to be very useful in elucidating the nature of the two-component systems and studying the reactions occurring between two hydrated oxides leading to the formation of new intermediate compounds particularly during catalyst preparations.

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RÉSUMÉ − Les méthodes thermogravimétriques (TG) permettent de suivre les réactions entre deux oxydes lorsque celles-ci s'accompagnent d'une variation pondérale et conduisent à la formation de composés nouveaux. Cependant, lors de la préparation des catalyseurs, les matériaux de départ ne sont pas, en général, des oxydes. Les méthodes les plus couramment employées sont la coprécipitation ou le malaxage des oxydes précipités. Les courbes TG et TGD des mélanges sont alors de nature complexe, pour diverses raisons, parmi celles-ci la formation de composés nouveaux. L'interprétation de la courbe TGD conventionnelle d'un tel prélèvement et l'identification des domaines de température correspondant à une activité thermique nouvelle quelconque, présentent des problèmes. On propose dans cet article d'utiliser la dérivée de la courbe thermogravimétrique dérivée pour de telles études. Cette courbe indique les différences entre le comportement thermique expérimental du composite et son comportement théorique calculé à partir de celui de ses constituants. Les régions où une activité thermique nouvelle se manifeste sont faciles à déceler et à interpréter. Les deux systèmes suivants sont décrits: $MgO-Cr_2O_3$ et $MgO-Fe_2O_3$.

ZUSAMMENFASSUNG — Reaktionen zwischen zwei Oxiden, welche unter Gewichtsänderungen zur Bildung neuer Verbindungen führen, können durch TG-Methoden untersucht werden. Jedoch sind bei der Herstellung von Katalysatoren die Ausgangsstoffe in den meisten Fällen keine Oxide. Die üblichen Methoden der Mitfällung oder des Knetens der gefällten Oxide werden eingesetzt. In solchen Fällen sind die TG- und DTG-Kurven der Zusammensetzungen aus verschiedenen Gründen von komplexer Art, eingeschlossen die Bildung neuer Verbindungen. Die Deutung der konventionellen DTG-Kurve einer solchen Probe und die Identifizierung der Temperatubereiche neuer thermischer Effekte stellt in diesem Falle Probleme dar. Für solche Untersuchungen wird der Einsatz einer derivierten DTG-Kurve, wie im Artikel beschrieben, vorgeschlagen. Diese Kurve zeigt die Differenzen zwischen dem experimentellen thermischen Verhalten der Zusammensetzungen gegenüber dem theoretischen thermischen Verhalten, das aus seinen Bestandteilen errechnet worden ist. Die Bereiche einer neuen thermischen Aktivität können leicht entdeckt und gedeutet werden. Zwei Systeme, $MgO-Cr_2O_3$ und $MgO-Fe_2O_3$ werden beschrieben.

Резюме — Реакция между двумя окисями, приводящая к образованию нового соединения путем изменения веса, может быть изучена ТГ методами. Однако при получении катализаторов, в большинстве случаев, начальные материалы не являются окислами. Наиболее общими применяемыми методами является соосаждение или перемешивание осадков окислов. В таких случаях кривые ТГ и ДТГ этих составов очень сложны по природе из-за некоторых возможных причин, включая и образование нового соединения. Интерпретация обычной ДТГ кривой такого образца и идентификация температурных областей для какой-либо новой термической активности представляет собой проблему. Для таких исследований, как описано в настоящей работе, предлагается использовать выведенную производную термогравиметрической кривой. Такая кривая показывает различия между экспериментальными термическим поведением соединения по отношению к теоретическомй термическомй поведению состава, вычисленному из термического поведения его составных частей. Области новой термической активности могут быть легко локализованы и интерпретированы. Описаны две системы $M_8O-Cr_2O_3$ и $MgO-Fe_2O_3$.