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# COMBINED EPR AND TG TECHNIQUES : COMPARISON OF THE THERMAL REDUCTION OF CHROMIUM (VI) IONS IN SOME ZINC CHROMATES AND CHROMATE-OXALATE MIXTURES (*)

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## ABSTRACT

Lower oxydation state chromium species which are successively formed and stabilized upon thermal reduction of chromate (VI) ions, are studied by combined EPR and TG-techniques.

The spontaneous oxygen release occuring during the vacuum thermal treatment of some zinc chromates leads to the formation of both Cr(V) and Cr(III) species, the latter being either dispersed in ZnO, clustered in a $Cr_2O_3$-like phase or ordered in a $ZnCr_2O_4$-spinel phase. The Cr/Zn ratio in the initial compound as well as the presence of some reducing $OH^-$ ions are critical for the stability of such intermediate Cr species.

When solid mixtures of $ZnCrO_4$ and $ZnC_2O_4$ are calcined, the $CrO_4^=$ reduction is enhanced by the in-situ genesis of reducing gaseous or adsorbed carbon monoxyde stemming from the oxalate. Surprisingly such a reducing system favours the high temperature formation of some other very stable Cr(V) species.

## INTRODUCTION

Mixed Cu(II)/Zn/Cr(III) oxydes appear either as intermediate or end products during the vacuum thermolysis of the corresponding copper and zinc chromates, oxalates, their mixture and/or their solid solutions. As the catalytic properties of such systems could be very sensitive to this method of preparation, it is important to better precise the thermal decomposition mechanisms of their precursors.

We have shown previously that while the whole decomposition process of many inorganic oxysalts could be elucidated by the simultaneous use of some classic

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The present approach consists in showing how EPR could proove indispensible to precise most of the complex interrelated and successive steps involving progressive formation and disappearance of lower oxydation state chromium species during the spontaneous thermal reduction of some zinc chromates.

Solid state reactions between zinc chromate and zinc oxalate were then investigated and compared. In such systems the simultaneous in situ genesis of both the support ($ZnO+Cr_2O_3$) and the reducing agent for Cr(VI) (carbon monoxyde) is expected to influence strongly the formation and stabilization of different Cr(V) and Cr(III) intermediate species.

Detailed experimental procedures, data, and discussion are presented elsewhere (ref. 2). In this paper, the main results and conclusions are summarized and compared.

## RESULTS AND DISCUSSION

The thermolyses of the following systems

I. $ZnCrO_4.3.5\ Zn(OH)_2.H_2O$
II. $ZnCrO_4$
III. $2ZnCrO_4 + ZnC_2O_4.2H_2O$
IV. $2ZnCrO_4 + 3ZnC_2O_4.2H_2O$

as followed by TG are schematically shown and interpreted on fig. 1.
The thermal decomposition of $ZnC_2O_4.2H_2O$ in similar conditions has been studied previously (ref. 3).

The TG data alone suggest that dehydration, oxalate decomposition and chromate decomposition are independant processes as supported by the successive plateaus and reaction intervals in the TG curves, and by the quantitative interpretation of the weight losses. Moreover, the chromate (VI) thermal reduction seems to occur in a very narrow range of temperature.

Our aim is to emphasize how the EPR technique proved to be sufficiently sensitive to reveal several other solid-solid, gas-solid and/or gas-surface interactions between the support and the different intermediate paramagnetic species formed during the calcination process. Such findings did account for quite different decomposition mechanisms and nevertheless complete the TG data.

In each system, several lower oxydation chromium species (Cr(V) and Cr(III) ions) are observed appearing at quite lower temperatures than suggested by the TG curves :

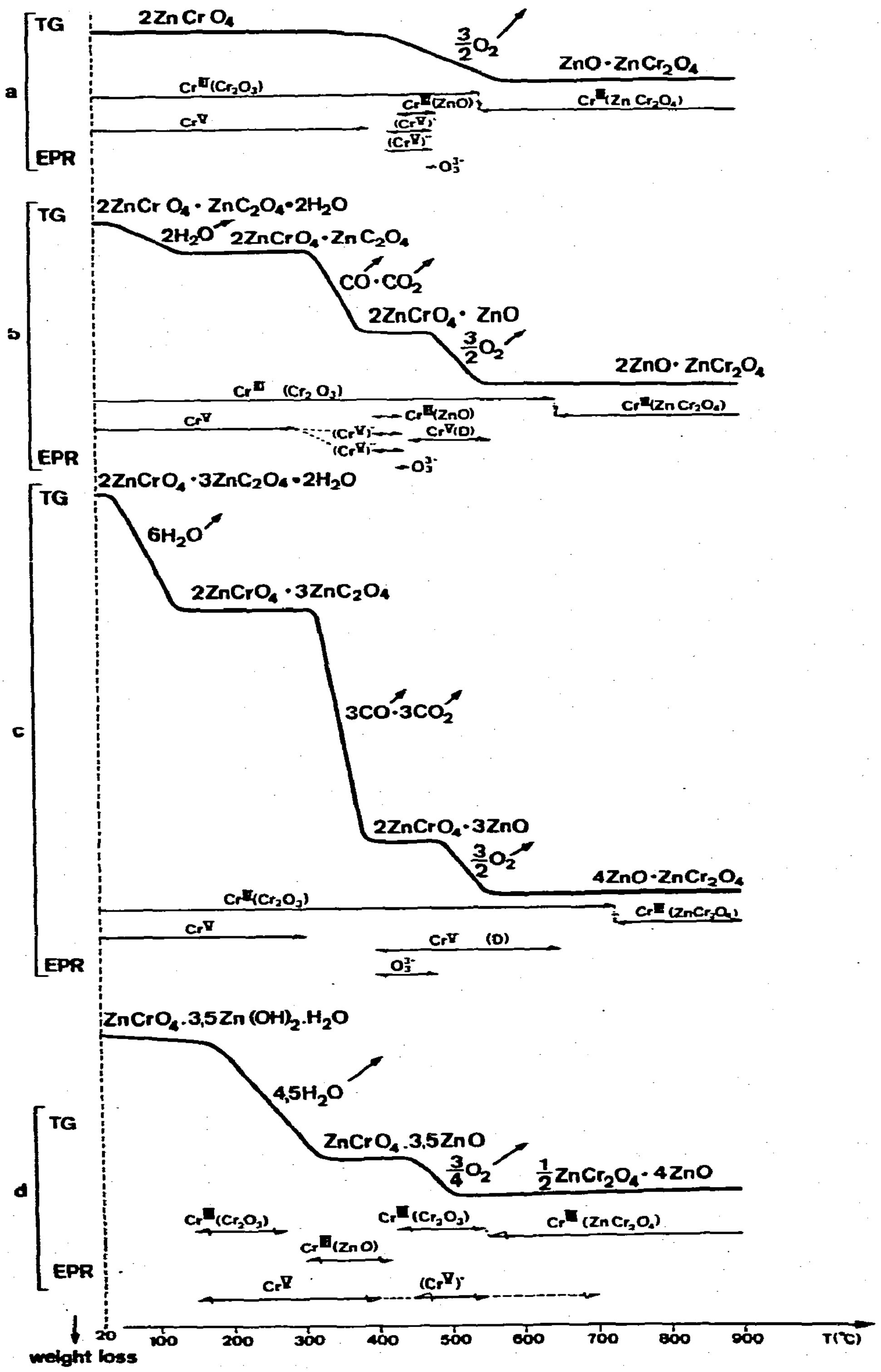


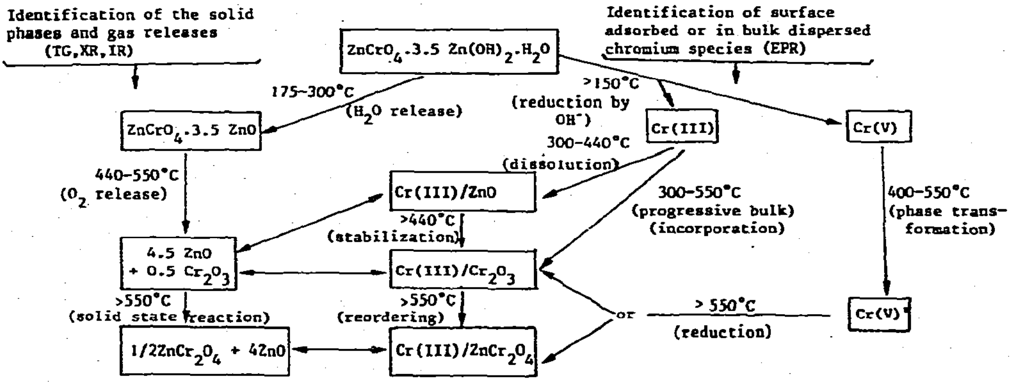
Figure 1 : TG and EPR data for the vacuum thermal decomposition of some zinc chromates and zinc chromate-oxalate mixtures.
EPR signals as indicated

a) Several different Cr(V) species resulting from a partial preliminary reduction of chromate (VI). The reducing agent is either $OH^-$ (system I) or the temperature provoking spontaneous $O_2$ release (system II) or both temperature and CO stemming from the oxalate (systems III and IV).

b) Cr(III) species preliminary formed by partial thermal reduction, which can either progressively enter a $Cr_2O_3$-like bulk phase or dissolve in ZnO as to form a solid solution. Then both phases disappear at higher temperatures due to a solid state reaction between ZnO and $Cr_2O_3$ resulting in the formation of zinc chromite and EPR confirms the presence of Cr(III) ions belonging to a well-ordered pure spinel phase.

All these intermediate species are closely interrelated and seem to be strongly dependant both on the reducing properties of the various species which are present ($OH^-$ ions, CO species) and on the nature of the solid matrix (amount of ZnO formed and $ZnO/Cr_2O_3$ ratio).

Typical interrelations between all the intermediate phases formed during the vacuum thermal decomposition of $ZnCrO_4.3.5\ Zn(OH)_2.H_2O$ are schematically smmarized as follows :



In the systems II, III and IV (i.e. $2ZnCrO_4$ + b $ZnC_2O_4.2H_2O$ with b respectively equal to 0, 1 and 3), the chromium intermediate species are similar although they appear and disappear at quite different temperatures. The total amount of ZnO in the residual solid phase (initially introduced in the form of $ZnC_2O_4.2H_2O$) as well as the amount of CO released upon oxalate decomposition seem to play the most important roles.

The influence of zinc oxalate on the successive formation and disappearance of different Cr(V) and Cr(III) ions stemming from $ZnCrO_4$, in the three systems, could be interestingly compared as follows :

| | b=0 | b=1 | b=3 | | | |
|---|---|---|---|---|---|---|
| mol ZnO/residue | 1 | 2 | 4 | | | |
| mol CO produced | 0 | 1 | 3 | | | |
| $ZnO/Cr_2O_3$ ratio | 2 | 3 | 5 | | | |
| EPR information | | | | Formed upon | Disappears upon | Remarks |
| EPR linewidth of $Cr(III)/Cr_2O_3$ signal at 520°C (gauss) | 1120 | 1330 | 2100 | T° ($O_2$ release) | transformation into $Cr(III)/ZnCr_2O_4$ | Influence of [ZnO] and/or $ZnO/Cr_2O_3$ ratio |
| T° range of formation of Cr(III)/ZnO species | 440-480 | 400-440 | traces | T° ($O_2$ release) | formation of $Cr(III)/Cr_2O_3$, more stable | |
| Cr(V) changes at | 250°C | 250°C | 200°C | $OH^-$ reduction, $O_2$ release | transformation into Cr(V)' | |
| Cr(V) disappears at | 400°C | 300°C | 300°C | | | |
| Cr(V)' stable between | 440-430 | 420-440 | not obs. | Cr(V) transf. | CO reduction | Influence of [CO] |
| Cr(V)" (new species formed when oxalate added) Intensity | not obs. | medium | strong | Cr(VI) reduction by CO | thermal reduction | |
| stable between | – | 450-500 | 400-650 | | | |

CONCLUSIONS

This work shows that :

1° When combined with TG, EPR can bring complementary and detailed informations on thermal reduction mechanisms of chromate (VI) ions.

2° In particular, EPR brings important and detailed informations about the formation and the stabilization, on the surface and in the bulk, of several Cr(V) and Cr(III) species.

3° The most important findings concerning the role of oxalate ions in the $CrO_4^=$ reduction process are the following :

a) Cr(III) ions can be stabilized in large concentrations in a $Cr_2O_3$-like phase where ZnO seems to play some important role.

b) Large concentrations of ZnO do stabilize such a phase leading to a relevant destabilization of other phases preliminary formed, such as Cr(III)/ZnO or some Cr(V) species.

c) CO released during the decomposition of oxalate ions is shown to play the most important role as selective reducing agent for both the preliminary formed Cr(V) ions and for some remaining Cr(VI) ions. In that case, large amounts of other different Cr(V) species appear and remain stable over a wide range of temparature.

## REFERENCES

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