Journal of Thermal Analysis, Vol. 18 (1980) 329—339

THERMOGRAVIMETRIC AND EPR STUDY OF THE SOLID-STATE REACTIONS BETWEEN ZINC CHROMATE AND ZINC OXALATE

Z. GABELICA, E. G. DEROUANE and *R. HUBIN

*Facultés Universitaires de Namur, Département de Chimie, Laboratoire de Catalyse, 61, rue de Bruxelles, B-5000 — Namur, Belgium; *Université de Liège, Département de Chimie Générale et de Chimie Physique, B-4000 — Sart Tilman par Liège 1, Belgium*

(Received April 17, 1979)

The formation of some catalytically active Cr(V) and Cr(III) species is studied when the progressive thermal reduction of zinc chromate is enhanced by the addition of solid zinc oxalate, the reducing agent CO being formed in situ, during thermal analysis. When compared with the decomposition of pure $ZnCrO_4$, Cr(VI) reduction, as followed by EPR, is similar concerning the nature of the intermediate Cr species formed: Cr(V), Cr(III) in a Cr_2O_3-like bulk phase and Cr(III) dispersed in ZnO. However, the temperature range of "Cr_2O_3" formation, as well as the magnitude of the Cr(III)—Cr(III) interaction in such a phase is found to be strongly dependent on the amount of ZnO formed. On the other hand, after the Cr(V) species resulting from progressive oxygen release have disappeared, some other stable Cr(V) species are formed again at higher temperatures. Their formation may be related to a further reduction of the remaining Cr(VI) species by CO stemming from the oxalate.

In a previous paper [1] we have shown how the electron paramagnetic resonance (EPR) technique can be successfully combined with thermogravimetric analysis (TG) for the elucidation of complex decomposition mechanisms of some pure copper(II) and zinc chromate phases. The progressive formation and stabilization of intermediate Cr(V) and Cr(III) species was evidenced by EPR.

The present work is intended as a more detailed investigation of the progressive vacuum decomposition of solid-state mixtures of zinc chromate and zinc oxalate. We have shown previously [2] that the thermal decomposition of $ZnC_2O_4 \cdot 2\,H_2O$ leads to the formation of gaseous and superficially adsorbed CO species. In this paper, we examine how the in situ production of strong reducing species such as CO will influence the Cr(VI) reduction and hence the intermediate formation and stabilization of different chromium(V) and chromium(III) species.

Experimental

$ZnCrO_4$ and $ZnC_2O_4 \cdot 2\,H_2O$ were prepared as described previously [1, 2]. Mixtures of the two solids were obtained by grinding a moles of $ZnCrO_4$ with b moles of $ZnC_2O_4 \cdot 2\,H_2O$, with $a : b = 2 : 1$, corresponding to the hypothetical Cr(VI) — Cr(V) reduction by CO, and with $a : b = 2 : 3$ corresponding to the hypothetical Cr(VI) — Cr(III) reduction by CO. TG and EPR operating conditions are described in [1].

Results and discussion

TG data

The thermal analyses of the mixtures *a* $ZnCrO_4$ + *b* $ZnC_2O_4 \cdot 2\,H_2O$, as followed by TG are schematically shown and interpreted in Fig. 1. They are compared in the same Figure to the curves obtained under the same conditions for pure $ZnCrO_4$ and $ZnC_2O_4 \cdot 2\,H_2O$.

The successive reaction intervals and plateaus clearly suggest a multi-stage reaction, and from the quantitative interpretation of the weight losses it is possible to identify all the intermediate phases and to conclude that each compound under-

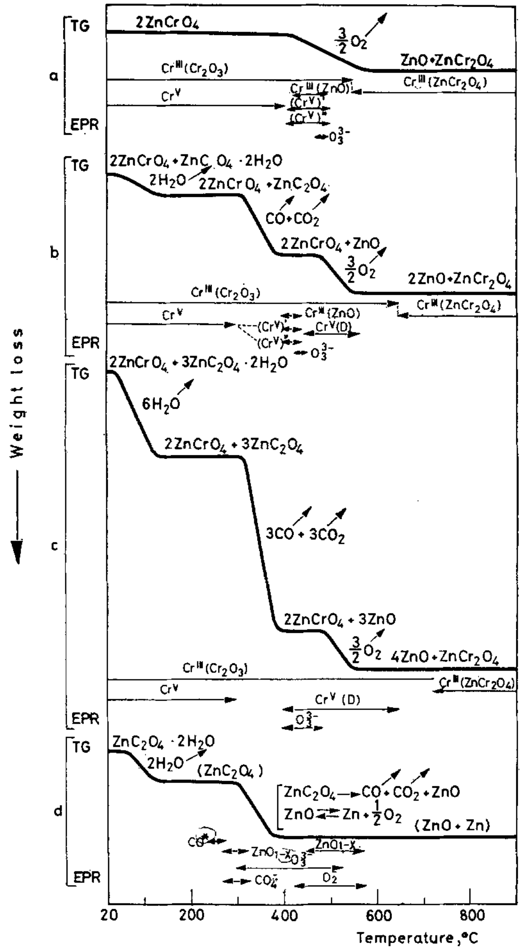

Fig. 1. TG and EPR data for the vacuum thermal decomposition of a) $ZnCrO_4$; b) $2\,ZnCrO_4$ + + $ZnC_2O_4 \cdot 2\,H_2O$; c) $2\,ZnCrO_4 + 3\,ZnC_2O_4 \cdot 2\,H_2O$; d) $ZnC_2O_4 \cdot 2\,H_2O$. EPR signals as indicated

goes its own decomposition more or less independently in the mixture. Nevertheless, the following differences are observed.

a) After the ZnO phase has been formed, no further weight loss is observed. The oxidative character of chromium(VI) ions prevents any further reduction of ZnO, yielding a non-stoichiometric ZnO_{1-x} phase. Such a reaction does occur when pure zinc oxalate is calcined under vacuum [2].

b) The decompositions of both CrO_4^{2-} and $C_2O_4^{2-}$ ions seem to begin at somewhat higher temperatures that in the case of the pure compounds, as shown in Table 1.

Table 1

Reaction	Initial decomposition temperature, °C		
	pure compound	2 : 1 mixture	2 : 3 mixture
$ZnC_2O_{4(s)} \rightarrow ZnO_{(s)} + CO_{(g)} + CO_{2(g)}$ (1)	290	330	340
$ZnCrO_{4(s)} \rightarrow (ZnO + 1/2\, Cr_2O_3)_{(s)} + 3/2 O_{2(g)}$ (2)	400	470	490

EPR data

EPR turned out to be sufficiently sensitive to reveal several solid–solid, gas–solid and/or gas-surface interactions between the different intermediate species stemming from the progressively decomposed chromate–oxalate mixtures. These data also provide detailed information on the decomposition mechanisms, which are not readily obtained by TG. Eight distinct EPR signals are successively and/or simultaneously detected, most of them being stable over a wide range of temperature. Their assignments are given in Table 2 and their characteristics (g values and temperature ranges of stability) are compared.

Radicals stemming from the oxalate ions

The successive reactions occurring during the vacuum thermal decomposition of $ZnC_2O_4 \cdot 2\,H_2O$ involve the formation of five different paramagnetic species which are characterized by EPR. They are referred to here as signals E to I in Table 2.

In particular, the formation of $V_I\,(O_3^{3-})$ radicals supposes a mechanism involving reaction of oxygen from the ZnO lattice:

$$O_{2\,(\text{lattice})}^{-} + CO_{4\,(\text{ads. on ZnO})}^{-} \rightarrow CO_{2\,(g)} + O_{3\,(\text{ads})}^{3-} \quad (\text{mechanism A}) \qquad (1)$$

On the other hand, only the O_3^{3-} species (signal E) are detected when both $ZnCrO_4$ and the chromate/oxalate mixtures are calcined. Their characteristics (temperature ranges of stability, g values and intensities) are slightly different from those of O_3^{3-} ions stemming from the vacuum treatment of pure zinc oxalate (Table 2), and this suggests that the mechanism of their generation may be somewhat different from mechanism A. As confirmation, neither CO_{ads}^{x} species stemming from the $C_2O_4^{2-}$

Table 2

EPR signals observed during the thermal decomposition

Signals and their assignments	$ZnCrO_4$		$2\ ZnCrO_4 + ZnC_2O_4 \cdot 2\ H_2O$	
	T °C	g factors	T °C	g factors
$[A] = Cr(III)/Cr_2O_3$ ↓ $[A'] = Cr(III)/ZnCr_2O_4$	25→>520 ↓ 900	$g_{iso} = 1.975$ $g_{iso} = 1.978$	25→>520 ↓ 900	$g_{iso} = 1.975$ $g_{iso} = 1.977$
$[B] = Cr(III)/ZnO$	440–480	$g_\perp = 1.9894$ $g_\parallel = 1.9653$ $g_{iso} = 1.9813$	400–440	$g_\perp = 1.9884$ $g_\parallel = 1.9653$ $g_{iso} = 1.9813$
$[C] = Cr(V)$	25	$g_\perp = 1.9804$ $g_\parallel = 1.9487$ $g_{iso} = 1.9698$	25	$g_\perp = 1.9804$ $g_\parallel = 1.9487$ $g_{iso} = 1.9698$
	perturbed between 200–250°		perturbed between 200–250°	
	↓ 400	$g_\perp = 1.9798$ $g_\parallel = 1.9478$ $g_{iso} = 1.9691$	↓ 300	$g_\perp = 1.9798$ $g_\parallel = 1.9476$ $g_{iso} = 1.9683$
$[C'] = Cr(V)'$	440–480	$g_\perp = 1.9817$ $g_\parallel = 1.9352$ $g_{iso} = 1.9692$	400–440	$g_\perp = 1.9800$ $g_\parallel = 1.9408$ $g_{iso} = 1.9669$
$[C''] = Cr(V)''$		$g_\perp = 1.9792$ $g_\parallel = 1.9450$ $g_{iso} = 1.9678$		$g_\perp = 1.9790$ $g_\parallel = 1.9439$ $g_{iso} = 1.9671$
$[D] = Cr(V)$	not observed		450–560 ↓ 650	$g_\perp = 1.9828$ $g_\parallel = 1.9410$ $g_{iso} = 1.9599$
$[E] = O_3^{3-}$	480	$g_{iso} = 2.0077$	440	$g_{iso} = 2.0065$
$[F] = CO^x_{ads}$ $[G] = ZnO_{1-x}$ $[H] = CO_4^-$ $[I] = O_2^-$				

entities nor ZnO_{1-x} phases are detected in EPR. This is easily explained when we consider that the former may react with superficial Cr(V) species already formed at low temperature (referred to as signals C, C' and C'' – Table 2) in the following way:

$$CO^x_{(ads)} + Cr(V)_{(ads\ or\ in\ bulk)} \rightarrow CO_{2(g)} + Cr(III) \qquad (2)$$

while ZnO_{1-x} cannot exist under strong oxidation conditions. We believe that CO_4^- formation is not possible in the present case, so the O_3^{3-} species must be formed *via* of zinc chromate, zinc oxalate and their mixtures

Signals and their assignments	$2\,ZnCrO_4 + 3\,ZnC_2O_4 \cdot 2\,H_2O$ T °C	$2\,ZnCrO_4 + 3\,ZnC_2O_4 \cdot 2\,H_2O$ g factors	$ZnC_2O_4 \cdot 2\,H_2O$ T °C	$ZnC_2O_4 \cdot 2\,H_2O$ g factors
[A] = $Cr(III)/Cr_2O_3$ ↓ [A'] = $Cr(III)/ZnCr_2O_4$	25→>520 ↓ 900	$g_{iso} = 1.976$ ↓ $g_{iso} = 1.979$		
[B] = $Cr(III)/ZnO$	only traces			—
[C] = Cr(V)	25 perturbed between 150–200° ↓ 300	$g_{\perp} = 1.9804$ $g_{\parallel} = 1.9487$ $g_{iso} = 1.9698$ $g_{\perp} = 1.9813$ $g_{\parallel} = 1.9510$ $g_{iso} = 1.9712$		—
[C′] = Cr(V)′	not observed			
[C″] = Cr(V)″				
[D] = Cr(V)	400–600 ↓ 700	$g_{\perp} = 1.9828 \rightarrow 30$ $g_{\parallel} = 1.9176 \rightarrow 37$ $g_{iso} = 1.9611 \rightarrow 59$		—
[E] = O_3^{3-}	400–480	$g_{iso} = 2.0040$	300–525	$g_{iso} = 2.0033$
[F] = CO^{x}_{ads}			240–260	($g_{iso} = 2.0043$)
[G] = ZnO_{1-x}			275–325 475–575	($g_{iso} = 1.96$)
[H] = CO_4^-			275–325	($g_{iso} = 2.0182$)
[I] = O_2^-			475–575	($g_{iso} = 2.0185$)

a different mechanism when chromate(VI) ions are present. Wong *et al.* [3] have detected a weak isotropic EPR signal ($g = 2.008$), similar to *E*, upon ZnO activation at 450° followed by reaction with molecular oxygen and further re-evacuation. They attributed it to "spin-exchanged clusters of O^- ions" (V-type center), whose shape, linewidth and g_{iso} value proved to be equivalent to those of the O_3^{3-} radical (triangular array of three superficial O^- ions), detected on MgO [4] and more recently on TiO_2 [5].

Comparable operating conditions are achieved when $ZnCrO_4$ is calcined, and O_3^{3-} formation may involve a similar mechanism: both ZnO and O_2 species formed upon $ZnCrO_4$ decomposition are activated in vacuum at high temperature and can react (Mechanism B). The same mechanism can also account for O_3^{3-} formation in the calcined chromate/oxalate mixtures, as supported by our EPR data (Table 2).

Paramagnetic ions stemming from the chromate(VI) ions

When compared with the decomposition process of pure $ZnCrO_4$, the Cr(VI) reduction sequence in the chromate/oxalate mixtures is similar as regards the nature of the intermediate Cr species formed. EPR shows that Cr(V) ions, Cr(III) ions dissolved in ZnO, and Cr(III) ions incorporated in a Cr_2O_3-like phase are present. Figure 2a – e gives typical examples of EPR spectra recorded during the thermal decomposition of the 2:1 mixture. The successive growth and decay of most of the resonances can be related to a reduction sequence of Cr(VI) ions [1]. However, the gaseous CO reducing species, as well as their relative amount and the total amount of the residual ZnO formed upon the oxalate decomposition (Table 3), are found to influence to a large extent the initial mechanisms of the chromate(VI) ion decomposition.

On proceeding from a non-reducing system yielding low ZnO residual concentrations (pure $ZnCrO_4$) to a strong reducing system yielding a high ZnO residual concentration (2 : 3 mixture) (see Table 3), the following differences are observed:

Table 3

$$2\,ZnCrO_4 + b\,Zn_2C_2O_4 \left\{ \begin{array}{l} T^\circ \rightarrow [2\,ZnO + Cr_2O_3] \rightarrow ZnCr_2O_4 + ZnO \text{ for } b = 0 \\ T^\circ \rightarrow [3\,ZnO + Cr_2O_3] \rightarrow ZnCr_2O_4 + 2\,ZnO\,(+\ 1\,CO\uparrow) \\ \hfill \text{for } b = 1 \\ T^\circ \rightarrow [5\,ZnO + Cr_2O_3] \rightarrow ZnCr_2O_4 + 4\,ZnO\,(+\ 3\,CO\uparrow) \\ \hfill \text{for } b = 3 \end{array} \right.$$

Cr(III) *ions*

The changes in the Cr(III) ions concentration (some being initially present in $ZnCrO_4$, formed by a partial reduction of Cr(VI) ions during the hydrothermal synthesis at 200° are strongly dependent on the amount of ZnO formed. Figure 3 shows the comparative variation of the linewidth of signal A as a function of temperature for the three systems. EPR results indicate that:

– Between 200 and 520° the total amounts of Cr(III) ions formed are comparable. This indicates that CO has little or no influence upon Cr(VI) reduction.

– The Cr(III) ions formed are incorporated into a phase of which the Cr(III) concentration increases up to 520°, and this incorporation must be progressive.

– The increasing linewidth results from an increasing interaction between neighbouring ions. This means that the Cr(III) ions initially formed are progressively transferred into another Cr_2O_3-like phase where ZnO seems to play an important role.

– The more ZnO is formed, the more Cr(III) ions are incorporated into such a phase.

– The maximum Cr(III) incorporation does not depend on the calcination temperature of the precursor (mixture).

– Above 520°, a progressive decrease of the linewidth assumes a reordering of the material, finally resulting in the crystallization of spinel zinc chromite. The latter begins to form above 600°, when additional Cr(III) ions resulting from the spontaneous thermal reduction of the remaining Cr(VI) ions are formed, as seen by TG.

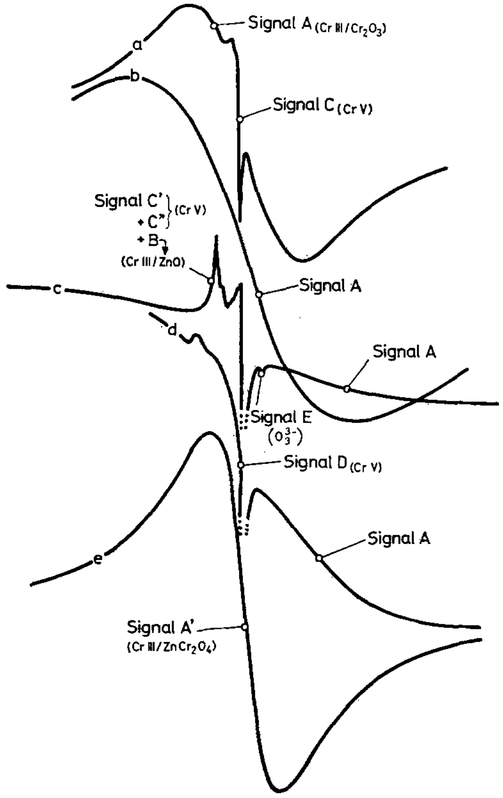

Fig. 2. EPR spectra of the mixture $2\,ZnCrO_4 + ZnC_2O_4 \cdot H_2O$ after vacuum activation. a) at room temperature; b) at 335°; c) at 440°; d) at 520°; e) at 850°. EPR signals identified and assigned as indicated

– $ZnCr_2O_4$ resulting from the Cr(III)-rich Cr_2O_3-like phase seems to be well ordered and to crystallize at lower temperatures, as suggested by the narrow linewidth of the Cr(III)/$ZnCr_2O_4$ EPR signal at 850° (Fig. 3 and Table 4).

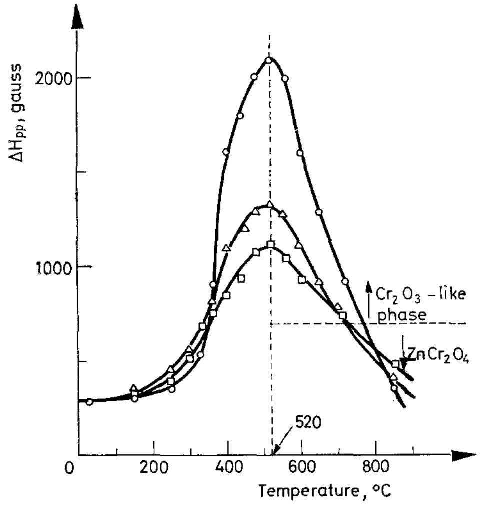

Fig. 3. Variation of the linewidth of EPR signal *A* (Cr(III)/Cr_2O_3) as a function of activation temperature; ○ = $ZnCrO_4$; △ = 2 $ZnCrO_4$ + ZnC_2O_4 · 2 H_2O; □ = 2 $ZnCrO_4$ + 3 ZnC_2O_4, · 2 H_2O

Table 4

2 $ZnCrO_4$ + *b* ZnC_2O_4

	b = 0	*b* = 1	*b* = 3	Remarks
Z_nO/Cr_2O_3 ratio	2	3	5	
ΔH_{pp}(Cr(III)/Cr_2O_3) at 520° (gauss)	1120	1330	2100	Influence of [ZnO] No influence of [CO]
ΔH_{pp}(Cr(III)/$ZnCr_2O_4$) at 850° (gauss)	470	400	370	(Spontaneous Cr(VI) → Cr(III) reduction)
Cr(III)/ZnO (signal *B*) stable between	440–480°	400–440°	traces	Influence of [ZnO]
Cr(V) (signal *C*) changes at	250°	250°	200°	Some [H_2O] influence?
disappears at	400°	300°	300°	(Spontaneous Cr(VI)→ Cr(V) reduction)
Cr(V) (signals *C*' + *C*'') stable between	440–480°	420–440°	not observed	Influence of [CO]
Cr(V) (signal *D*) intensity	not obs.	medium	strong	
stable between	—	450–500°	400–650°	Influence of [CO]

Finally, the amount of Cr(III) ions dissolved in ZnO, forming a solid solution (signal *B*), decreases as the ZnO concentration in the residue increases. When compared to the decomposition of pure $ZnCrO_4$, signal *B* is weak and appears and disappears at lower temperatures in the case of the 2 : 1 mixture, while only traces of such a signal can be detected in the case of the 2 : 3 mixture. This suggests that Cr(III) ions incorporated into a ZnO-rich Cr_2O_3-like phase are more stable than a solid solution of Cr(III) ions in ZnO.

Further studies are now being carried out to elucidate the stabilizing role of ZnO towards the Cr_2O_3-like phase.

Cr(V) *ions*

In $ZnCrO_4$, some chromium(V) ions (EPR signal *C*) are detected at room temperature and found to be stable up to 400°. They are formed during the hydrothermal synthesis and could be due either to a partial thermal reduction with oxygen release and/or to a possible influence of the reducing character of water on Cr(VI) ions around 200°. These Cr(V) species undergo some structural rearrangement near 250°, as supported by the slight change in the g value of the corresponding EPR signal.

When oxalate is added to the chromate, signal *C* appears earlier and a similar structural rearrangement occurs, but at a lower temperature (Table 4). We conclude that the reduction of such Cr(V) species leading to Cr(III) ions is enhanced either by some H_2O resulting from the oxalate dehydration occurring at this temperature, or by the affinity of the Cr(III) ions so formed for a ZnO-rich Cr_2O_3-like phase.

When pure $ZnCrO_4$ is heated between 440 and 480°, two other different Cr(V) intermediate species appear (referred to as signals C' and C''). Similar signals are observed during the thermal treatment of the mixtures. In the 2 : 1 system they appear and disappear at lower temperatures (400 – 440°), while they have completely vanished in the case of the 2 : 3 system. Their genesis is therefore supposed to be independent on the former Cr(V) ions (signal *C*). We suggest that their reduction to Cr(III) is favoured by the release of CO from the oxalate.

Finally, a narrow and asymmetric EPR signal (signal *D*) is observed at higher temperature only in the case of thermal analysis of the chromate/oxalate mixtures. Its g values ($g_{\perp} = 1.98$ and $g_{\parallel} = 1.915$) compare favourably with the g values characterizing Cr(V) (Table 2). Both the concentrations and the stabilities of these new Cr(V) species increase with the amount of oxalate in the mixture: they appear at 450° in the case of the 2 : 1 mixture (400° for the 2 : 3 mixture) and remain remarkably stable over a wide range of temperature. The intensity of signal *D* begins to decrease only above 500° for the 2 : 1 system and some traces of it are still detected at 650° (650 and 700°, respectively, for the 2 : 3 system). As these Cr(V) ions are generated at a temperature at which some Cr(VI) still remains unreduced, and at which CO begins to be released, we can assume that the latter must be responsible for this Cr(VI) reduction to the intermediate oxydation state (V). The great stability of these Cr(V) species accounts for the fact that they are not reduced further by CO to the oxidation state (III). The role of CO as selective reductor is supported by the fact that no *D* type Cr(V) ions are observed in the thermal analysis of pure $ZnCrO_4$.

The influence of ZnC_2O_4 on the successive formation and disappearance of different Cr(V) and Cr(III) ions stemming from zinc chromate is summarized in Table 4.

Conclusions

As general conclusions, this work shows that:

a) The thermal behaviours of the various chromate/oxalate mixtures can be elucidated by the use of combined TG/EPR techniques.

b) EPR yields important and detailed information about the formation of intermediate Cr(V) and Cr(III) paramagnetic species and of some radicals such as O_3^{3-} ions.

c) The most important findings concerning the role of oxalate ions in the reduction process of Cr(VI) are the following:

– Cr(III) ions can be stabilized in large concentrations in a Cr_2O_3-like bulk phase when the amount of ZnO in the residual solid mixture is important;

– the ZnO concentration in such a phase can indirectly influence the formation of some other species, such as Cr(III) ions dissolved in ZnO, or Cr(V) ions resulting from the spontaneous Cr(VI) reduction;

– CO released during the decomposition of the oxalate ions plays a major role in reducing some Cr(V) ions preliminarily formed, and in reducing some of the remaining Cr(VI) ions, leading to the formation of large amounts of other Cr(V) species which remain stable over a wide range of temperature.

References

1. Z. Gabelica, E. G. Derouane and R. Hubin, J. Thermal Anal., 18 (1980) 315.
2. Z. Gabelica, R. Hubin and E. G. Derouane, Thermochim. Acta, 24 (1978) 315.
3. N. B. Wong, Y. Ben Taarit and J. H. Lunsford, J. Chem. Phys., 60 (1974) 2148.
4. M. Boudart, A. Delbouille, E. G. Derouane, V. Indovina and A. B. Walters, J. Am. Chem. Soc., 94 (1972) 6622.
5. P. Meriaudeau and J. C. Védrine, J. Chem. Soc. Faraday, 72 (1976) 472.

Zusammenfassung — Die Bildung einiger katalytisch aktiver Cr(V) und Cr(III) Species wird für den Fall untersucht, bei dem die progressive thermische Reduktion von Zinkchromat durch Zugabe von festem Zinkoxalat gefördert wird, wobei das Reduktionsmittel CO in situ, während der Thermoanalyse gebildet wird.

Ein Vergleich mit der Zersetzung der reinen $ZnCrO_4$ ergibt die Ähnlichkeit der durch EPR verfolgten Cr(VI)-Reduktion hinsichtlich der Beschaffenheit der gebildeten Cr Intermediärspecies: Cr(V), Cr(III) in einer Cr_2O_3-artigen Hauptphase und Cr(III) in ZnO dispergiert. Jedoch sind Temperaturbereich der »Cr_2O_3«-Bildung sowie der Umfang der Cr(III)—Cr(III) Wechselwirkung in einer solchen Phase stark von der Menge des gebildeten ZnO abhängig. Andererseits werden nach dem Verschwinden der durch die progressive Sauerstoff-Freisetzung entstandenen Cr(V)-Species wider einige andere stabile Cr(V)-Species bei höheren Temperaturen gebildet. Ihre Bildung mag mit einer weiteren Reduktion der noch vorhandenen Cr(VI)-Species durch aus dem Oxalat stammendes CO verbunden sein.

Резюме — Изучено образование некоторых каталогически активных частиц Cr(V) и Cr(III) при термическом восстановлении хромата цинка, ускоряемого добавлением твердого оксалата цинка, вследствие образования CO, как восстановителя, во время термолиза. Из данных ЭПР следует, что восстановление Cr(VI), так же как и в случае разложения $ZnCrO_4$ без добавки оксалата цинка, является подобным относительно природы образующихся промежуточных Cr частиц: Cr(V) и Cr(III) в объёме фазы, подобной Cr_2O_3, а Cr(III) диспергирован в ZnO. Установлено, что как температурная область образования «Cr_2O_3», так и значение Cr(III)—Cr(III) взаимодействия в такой фазе сильно зависит от количества образующейся окиси цинка. С другой стороны, установлено, что после распада образующихся на этой стадии Cr(V) частиц, некоторые другие стабильные Cr(V) частицы вновь образовывались при высоких температурах. Образование этих новых частиц может быть обусловлено дальнейшим восстановлением оставшихся Cr(VI) частиц моноокисью углерода, выделяющейся из оксалатов.