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CATALYTIC EFFECT OF SOME CHROMITES ON THE THERMAL DECOMPOSITION OF $KClO_4$
Mechanistic and non-isothermal kinetic studies

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Abstract

The catalytic effect of two different groups of chromites on the non-isothermal decomposition of $KClO_4$ was studied. TG and DSC curves of the thermal behaviour obtained for $KClO_4$-alkaline earth chromites (Series 1) mixtures indicate the formation of $K_2Cr_2O_7$, through a solid-solid interaction, before accelerating the decomposition stage of $KClO_4$. Such an accelerating effect becomes more pronounced in the case of admixing $KClO_4$ with some transition metal chromites (Series 2). The results were discussed taking into consideration the electronic configuration of cations and the electrical properties of the chromite catalysts. The presence of coordinatively active cations, able to form surface complex with the oxygen of the perchlorate anion, was proved to be necessary for obtaining an active catalyst. The kinetic parameters and models describing the catalyzed thermal decomposition process of $KClO_4$ were evaluated by using a computer program that allows the analysis using five different methods. It was found that the adopted kinetic model for pure $KClO_4$ and that mixed with catalysts from Series 1 is one-dimensional movement of phase boundary. On the other hand, random nucleation mechanism was achieved in the presence of catalysts from Series 2. Finally, a tentative reaction mechanism consistent with the obtained results was suggested.

Keywords: catalyzed thermal decomposition, chromite catalysts, $KClO_4$

Introduction

It has been stated [1] that the mechanical addition of a foreign substance to metallic salts gives rise to significant changes in the thermochemical reaction behaviour of these salts. One of these reactions is the catalyzed thermal decomposition of perchlorates which has been investigated extensively [2–5] but inconsistent or even contradictory mechanisms have been proposed. Rudloff and Freeman [6] considered that only *p*-type semiconductors are the active catalysts for the decomposition of perchlorates. Moreover, others also shared the above view [7–9]. On the other hand, Morishima *et al.* [10] reported that the catalytic activity is related to electron hopping mechanism. Zengyuar *et al.* [11] suggested that the metal oxides containing metal cations with half-filled *d*-orbitals are likely to have high activities. Zhang *et al.* [12] indicated that the inconsistent results are probably caused by differences in the surface areas of the additives.

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In the present study we aim to investigate the catalytic effect of chromite catalysts on the thermal decomposition of $KClO_4$. The advantages of using chromite catalysts – in the thermal decomposition of $KClO_4$ – over the corresponding mixed oxides lie in both their geometric and electronic properties. Therefore, metal chromite catalysts represent the suitable catalysts for studying a catalytic process which involves a charge transfer mechanism [2, 13, 14]. In order to accomplish such a study, thermogravimetry (TG), differential scanning calorimetry (DSC), X-ray powder diffraction analysis and electrical conductivity measurements were performed. Finally, the kinetic parameters of the thermal decomposition process were evaluated using a computer program [15].

Experimental

Reagent grade chemicals were used, two groups of chromite catalysts were prepared in the present study. The first is the alkaline earth chromites (Series 1), namely $MgCr_2O_4$ (MgCr), $CaCr_2O_4$ (CaCr), $SrCr_2O_4$ (SrCr) and $BaCr_2O_4$ (BaCr); the second (Series 2) is the transition metal chromites, they are $CoCr_2O_4$ (CoCr), $NiCr_2O_4$ (NiCr), $CuCr_2O_4$ (CuCr) and $ZnCr_2O_4$ (ZnCr). All the above catalysts were prepared by impregnation method, stoichiometric amounts from the pre-prepared chromia gel sample [16] were mixed with the appropriate volume of the nitrate solutions of the different elements to form MCr_2O_4. Drying was conducted at 110°C for 48 h, then the mixtures were calcined at 850°C for 5 h. XRD patterns of the calcination products were recorded by using the powder diffraction technique at 2θ range between 2 and 80°, with the aid of a model PW2103/00 Philips diffractometer. The obtained diffraction patterns were matched with ASTM cards [17].

The electrical conductivity measurements were carried out using a conductivity cell described by Chapman *et al.* [18]. The temperature was controlled with the aid of a Cole-Parmer Digi-Sense temperature controller. The resistance measurements were carried out at 200–400°C in air using a Keithley 610-C solid state electrometer. The activation energy values (E_{elc}) of the prepared chromite catalysts were calculated applying Arrhenius equation and using the electrical conductivity measurements in the temperature range 200–400°C.

Catalytic thermal decomposition of $KClO_4$ (KP) was performed using homogeneous mixtures composed of KP with 20 wt% catalyst. Such a composition is suitable for tracing the reaction products by X-ray analysis. Thermogravimetry, differential thermogravimetry and differential scanning calorimetry, were obtained by using a 2000 DuPont thermal analyzer, with the heating rate 10°C min^{-1}.

Results and discussion

Effect of alkaline earth chromite catalysts (Series 1) on the catalytic thermal decomposition of $KClO_4$

Figure 1 (curve a) shows the TG curve of pure $KClO_4$. The curve indicates that the decomposition process of the salt takes place via one stage with a total mass loss amounts to 46.2% which is compatible with that theoretically anticipated one for the formation of KCl according to the suggested decomposition equation [13, 14]:

$$KClO_4 \rightarrow KCl + 2O_2 \tag{1}$$

It is also found from the TG curve that the pronounced decrease in mass begins at 510°C. At such temperature the DSC curve of pure $KClO_4$ (curve a in Fig. 2) indicates a broad endothermic peak which is related to the fusion process, this coincidence in temperature leads to the conclusion that both the fusion and decomposition process of $KClO_4$ takes place simultaneously [5]. Mixing the solid $KClO_4$ with the catalysts of Series 1, denoted as MgCr, CaCr, SrCr and BaCr, forced the decomposition process to proceed via two stages instead of one stage in case of pure $KClO_4$. In order to interpret this new behaviour, X-ray diffraction analysis was performed for the calcination products of $KClO_4$-catalyst mixtures at calcination temperature 415°C which is corresponding to the end of stage 1. The obtained diffractograms comprised the characteristic lines of both $KClO_4$ (dÅ=3.49 s, 3.15 s, 2.89 m) and the alkaline earth metal oxide (MO) corresponding to the metal chromites added [17]; where *MO*=MgO (dÅ=2.11 s, 1.49 m, 1.23 m), CaO (dÅ=2.78 m, 2.42 s, 1.7 m), SrO (dÅ=2.95 s, 2.57 s, 1.83 s) and BaO (dÅ=3.2 s, 2.7 s, 1.95 s). In addition, new lines at dÅ=3.66 m, 3.45 m, 3.28 s, 3.01 s and 2.84 s which are in excellent agreement with those reported [17] for $K_2Cr_2O_7$ were also detected. Accordingly, one can relate stage 1 to the solid state reaction between $KClO_4$ and the added chromite catalysts [4]. This solid state reaction can be expressed as follows:

$$yKClO_4 + xMCr_2O_4 \rightarrow xK_2Cr_2O_7 + (y-2x)KClO_4 + xMO + xCl_2 + 2xO_2 \tag{2}$$

where *M* is the cations of Mg, Ca, Sr and Ba; *y* and *x* are the number of moles of both $KClO_4$ and the catalyst added in each mixture, respectively.

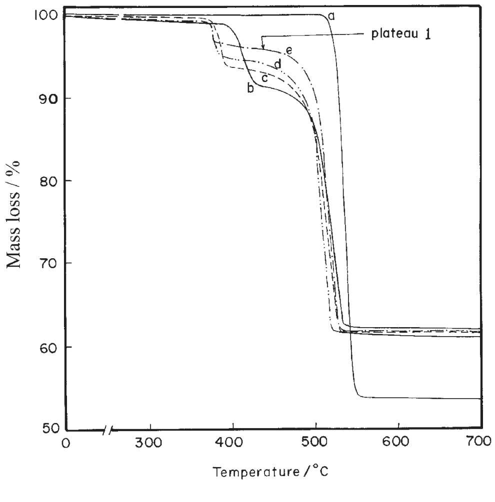

Fig. 1 TG curves of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with the chromites of Mg(II), Ca(II), Sr(II) and Ba(II) (b–e) respectively

The extent of stage 1 depends on the *x* value which is found to be increased as the atomic mass of the alkaline earth element decreased. Hence, the observed variation of the location of plateau 1 in the TG curves of the various mixtures (Fig. 1) can be referred to the increments of *x* value in the following sequence: MgCr>CaCr>SrCr>BaCr. The completion of stage 1 is followed by a second stage which is virtually related to the decomposition stage of $KClO_4$ – chromite mixtures leading to the final decomposition products KCl and O_2. The examination of the DTG curves in Fig. 3 shows that the decomposition stage of $KClO_4$ in its mixtures (curves b–e) is shifted to lower temperatures compared with that of pure $KClO_4$ (curve a). Such a situation confirms the existence of an accelerating effect arised from the catalytic action of the added catalysts. In this respect it is to remind that the chromite additives are actually converted to $K_2Cr_2O_7$ as well as the corresponding alkaline earth oxide at the end of stage 1 (according to Eq. (2)). Thus, it is plausible to ascribe the observed enhancement in the decomposition of $KClO_4$ to the formation of $K_2Cr_2O_7$ and/or the alkaline earth oxides. Since the TG curves of $KClO_4$ – chromite mixtures show almost the same behaviour in the temperature range corresponding to stage 2, one can suggest that only $K_2Cr_2O_7$; and not the alkaline earth oxides formed in stage 1, has a contributive effect on accelerating the decomposition process of $KClO_4$ [19].

Figure 2 shows the DSC results of $KClO_4$ (curve a) and $KClO_4$ – alkaline earth chromite mixtures (curves b–e) in the temperature range from ambient to 600°C. Two endothermic peaks can be distinguished for the pure salt, the first is a sharp one and maximized at 300°C where the second one is a broad peak starting at about 500°C, these two peaks are corresponding to the solid-phase transition from rhombic to the

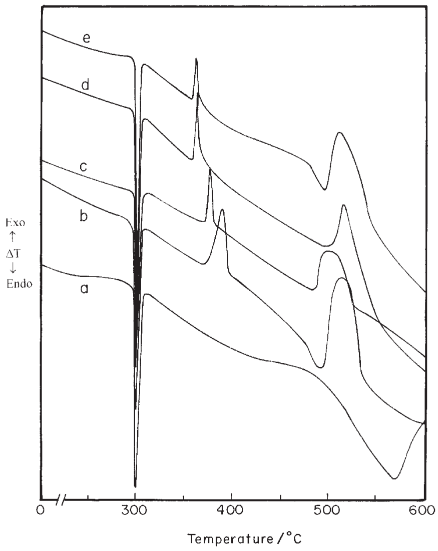

Fig. 2 DSC curves of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with chromites of Mg(II), Ca(II), Sr(II) and Ba(II) (b–e) respectively

cubic form and to the fusion of solid $KClO_4$ [13], respectively. The addition of the catalysts was found to have no effect on the phase transformation process of $KClO_4$, where the DSC pattern of all the mixtures (curves b–e) showed the same sharp endothermic effect at 300°C. On the other hand, three other peaks can be identified for each mixture. The first one is an exothermic peak in the temperature region before 400°C, the second one has an endothermic effect before 500°C followed by an exothermic peak. These three peaks are corresponding to the formation of $K_2Cr_2O_7$ through a solid-solid interaction between $KClO_4$ and the added chromite [4], fusion of $KClO_4$ and the decomposition of $KClO_4$, respectively. It must be noted that the DSC technique provides an excellent method for the determination of the extent of the solid-state reaction to form $K_2Cr_2O_7$, where the exothermicity of this reaction (expressed by the area of the exothermic peak before 400°C) was found to increase in the order of MgCr>CaCr>SrCr>BaCr, having the same sequence of x value increase.

Recently, it was assumed that the catalytic thermal decomposition of $KClO_4$ takes place via a mechanism which involves the formation of a surface complex between the perchlorate anion and the metal cation of the additives [20]. In this complex an oxygen atom of the perchlorate anion coordinates with the metal cation via the oxygen unshared electron pair, such interaction can weaken the oxygen-chlorine bond in the perchlorate anion and thus facilitates decomposition. Applying this concept, the activity of $K_2Cr_2O_7$ can be referred to the surface Cr(VI) cations. On the surface, especially on the edges, vertices, and structural defect sites of the $K_2Cr_2O_7$ crystallites, Cr(VI) may be coordinated by only three or even fewer oxygen ions. These unsaturated cations tend to attract ligand to form a stable tetrahedral coordination. Thus, the formation of coordination bond with the perchlorate anion becomes available leading eventually to the observed enhancement of the decomposition process [12]. On the other hand, the formation of a coordination bond with the alkaline earth cat-

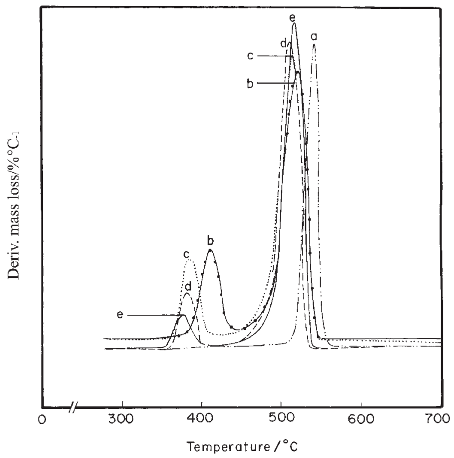

Fig. 3 DTG plots of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with the chromites of Mg(II), Ca(II), Sr(II) and Ba(II) (b–e) respectively

ions is less probable, this comes from the fact that these cations have noble gas configuration and are characterized by positive electrical fields which are effectively shielded by electrons. Consequently, the formation of such coordination bond by the unshared electron pair of the oxygen atom in the perchlorate anion must be expected to be very difficult because it requires to go into higher energy levels of these cations. These facts interpret the absence of any accelerating role in the presence of the alkaline earth oxides (formed in Eq. (2)).

On the basis of the above explanation, it can be assumed that the presence of coordinatively active sites plays a decisive role in evaluating the activity of catalysts. Aiming to support this assumption, the catalytic thermal decomposition of $KClO_4$ in the presence of some transition metal chromites, namely $CoCr_2O_4$, $NiCr_2O_4$, $CuCr_2O_4$ and $ZnCr_2O_4$ which have the electronic configurations d^7, d^8, d^9 and d^{10} for Co(II), Ni(II), Cu(II) and Zn(II) cations respectively, were studied.

Effect of transition metal chromite catalysts (Series 2) on the thermal decomposition of $KClO_4$

The TG curves and their differential plots (DTG) for the thermal decomposition of $KClO_4$ catalyzed by the transition metal chromites (Series 2) are seen in Figs 4 and 5 respectively. However, the general feature of the above TG curves indicates an accelerating effect in the decomposition process upon mixing $KClO_4$ with various catalysts. The following points can be easily detected on discussing the behaviour of each TG curve individually as presented straightforward. The TG curve together with DTG plot of $KClO_4$–CoCr mixture (curve b in Figs 4 and 5, respectively) indicate an interference between two different stages of the decomposition process. For $KClO_4$–NiCr mixture, two well separated stages are observed in both TG and DTG plots in a similar manner as that obtained previously for $KClO_4$ – alkaline earth chromite mixtures, this is again related to the formation of $K_2Cr_2O_7$. Evidence for this formation can also be attained from the DSC measurements (Fig. 6). The decomposition of $KClO_4$ is greatly influenced by the addition of CuCr catalyst compared with the resultant effect from addition any of the other catalysts. The TG curve of this mixture (curve d in Fig. 4) shows a noticeable lowering in the $KClO_4$ decomposition temperature by about 135°C. In case of mixing $KClO_4$ with ZnCr catalyst, a closely similar behaviour as in case of $KClO_4$–CoCr mixture was obtained.

The experimental evidence that the catalysts of Series 2 accelerate the thermal decomposition of $KClO_4$ more than the catalysts of Series 1 do, reflects the contributive role of the transition metal cations on accelerating the decomposition process of $KClO_4$. It is well known that such cations are coordinatively active having a higher tendency to accept extra electrons to form coordination bonds [20]. Accordingly, they can be considered to represent catalytically active sites able to accept electrons from the oxygen of the perchlorate anion leading eventually to the observed accelerating effect of the catalysts of Series 2. This explanation seems to be in agreement with the previous suggestion concerning the relationship between the catalytic activity and the electronic configuration of the metal cations.

In order to obtain further details concerning the role of the above catalysts on the decomposition process, X-ray analysis was performed on the decomposition products of $KClO_4$ – catalyst mixtures. Except for NiCr catalyst, there is no evidence for the formation of $K_2Cr_2O_7$ through a solid state reaction. The interference between the two stages appears in the decomposition process of both mixtures $KClO_4$–CoCr and $KClO_4$–ZnCr, is referred to the partial decomposition of $KClO_4$, in the first stage, to $KClO_3$ [21] which in turn, accelerates the subsequent decomposition stage to form KCl as a final solid product. The pronounced catalytic activity of CuCr catalyst is not accompanied by any detect-

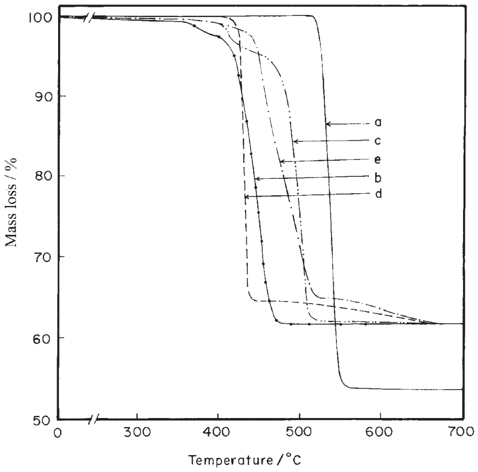

Fig. 4 TG curves of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with the chromites of Co(II), Ni(II), Cu(II) and Zn(II) (b–e) respectively

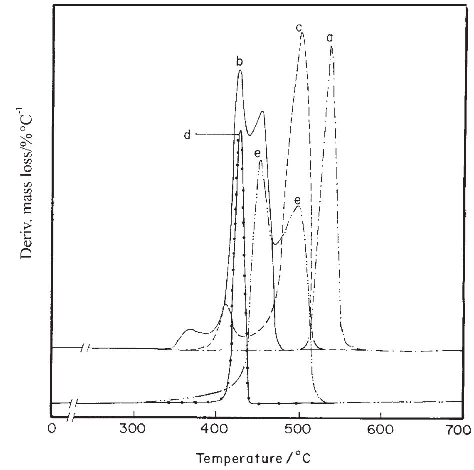

Fig. 5 DTG plots of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with the chromites of Co(II), Ni(II), Cu(II) and Zn(II) (b–e) respectively

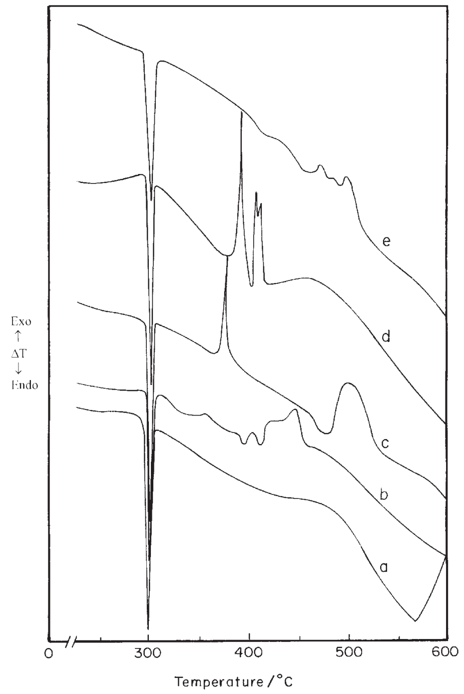

Fig. 6 DSC curves of pure $KClO_4$ (a) – and mixtures of $KClO_4$ with the chromites of Co(II), Ni(II), Cu(II) and Zn(II) (b–e) respectively

able structural changes, this result together with the fact that copper chromite represents a good example for the surface electron transfer cycle [22] between two different valency states $Cu^{2+}+e \Leftrightarrow Cu^{+}$, enables us to conclude that the electrical behaviour of the catalyst provides an additional factor (besides the electronic configuration of the cations) in determining the activity of various catalysts. Aiming at confirming this conclusion, the relationship between the activation energy values (E_{elc}) of the studied catalysts; as indicative parameter of the electrical conductivity process; and the accelerating role of these catalysts on the decomposition process of $KClO_4$ was followed. The E_{elc} values were calculated by using the electrical conductivity measurements in the temperature range 200–400°C and then applying Arrhenius equation. Results are depicted in Table 1.

Results of Table 1 clearly show that the higher accelerating effect on the thermal decomposition of $KClO_4$ (defined by the lowering in T_{m_2} value) is observed for $KClO_4$–CuCr mixture. A combination between the above finding together with the fact that copper chromite has the lowest E_{elc} value among all the investigated catalysts, leads to the conclusion that some kind of electron transfer process must be involved in the catalytic thermal decomposition of $KClO_4$ [13, 14]. Accordingly, it is noteworthy to mention that a catalyst characterized by an easier charge transfer process (i.e. lower E_{elc} value) is the most active one in catalyzing the decomposition reaction of $KClO_4$. On the other hand, the possibility of a solid-solid interaction to take place between $KClO_4$ and the added catalysts in the other mixtures, which involves the formation of the corresponding metal oxide (according to Eq. (2), makes if difficult to find a parallel relationship between the decrease of E_{elc} values of the catalysts and the expected increase in their accelerating effect towards the decomposition reaction of $KClO_4$.

Table 1 Activation energy values (E_{elc}) – from the electrical conductivity measurements – of the chromite catalysts together with the T_{m_1} and T_{m_2} values of the thermal decomposition of $KClO_4$

Catalyst	E_{elc}/eV	T_{m_1}/°C	T_{m_2}/°C
MgCr	1.25	413	524
CaCr	0.76	387	517
SrCr	1.01	382	513
BaCr	1.12	377	518
CoCr	1.53	427	452
NiCr	0.59	408	500
CuCr	0.55	–	426
ZnCr	0.99	453	499

T_{m_1} and T_{m_2} represent the temperatures (as detected from the DTG plots) corresponding the maximum rate of stage 1 and stage 2 in the decomposition process of $KClO_4$ – chromite mixtures respectively

Finally, the kinetic parameters and the kinetic models for the catalyzed thermal decomposition of $KClO_4$ were elucidated. In order to accomplish such a study a computer program [15] in BASIC has been applied by using the experimental TG/DTG non-isothermal thermogravimetric data. This program allows the Freeman-Carrol (FC), Horowitz-Metzger (HM), Dharwadkar and Karkhanavala (DK), Coats-Redfern (CR) and Doyle-modified by Zsakó-Zsakó treatments (ZZ)-methods to be performed for up to 14 different rate-controlling reactions, including n^{th}-order, Avrami-Erofeev, phase boundary movement and diffusional models. The obtained results from the computer program are summarized in Table 2.

An examination of the obtained E_a values of $KClO_4$ shows that only E_a value from (ZZ) method is in a good agreement with those reported in literature [23, 24], whereas those obtained from the other four methods showed much higher E_a values. Hence, in comparing the kinetic parameters of the studied $KClO_4$–chromite mixtures, we will only consider the results obtained from (ZZ) method.

The results of the kinetic analysis, applying ZZ method, show that the one-dimensional movement of phase boundary (F_0 function) [25] gives the best fitting data for the thermal decomposition stage of pure $KClO_4$. In addition there is no change in the decomposition mechanism upon mixing $KClO_4$ with the alkaline earth chromite catalysts. On the contrary to the above findings, it was found that the decomposition mechanism changes upon mixing $KClO_4$ with the transition metal chromite catalysts to be described by random nucleation Erofeev equation (A_3 function)

Table 2 The kinetic parameters and the kinetic models describing the thermal decomposition of $KClO_4$ (KP) pure and mixed with some chromite catalysts

Method		Sample								
		KP	KP–MgCr		KP–CaCr		KP–SrCr		KP–BaCr	
			St$_1$	St$_2$	St$_1$	St$_2$	St$_1$	St$_2$	St$_1$	St$_2$
FC	E_a	270.8	90.5	47.4	138.7	79.9	208.3	30.9	50.9	61.8
	log$A$	1.6	3.3	7.8	2.1	7.4	1.4	11.3	6.0	5.0
HM	E_a	312.3	58.7	82.6	181.6	145.3	120.7	66.2	152.5	72.5
	log$A$	36.8	16.7	20.8	36.8	36.5	36.6	16.4	36.7	18.1
	K.M.	Fn 2	Fn 0	Fn1/2	Fn 2	D_2	Fn 2	Fn 0	Fn 2	Fn 0
DK	E_a	131.0	21.5	58.4	51.7	91.7	55.5	53.5	29.7	43.7
	log$A$	33.7	4.4	14.0	15.1	23.5	16.5	12.8	7.7	9.9
	K.M.	Fn 2	Fn 0	Fn1/2	Fn 2	D_2	Fn 2	Fn 0	Fn 2	Fn 0
CR	E_a	307	54.3	71.2	177.6	60.5	117	56	150.5	65.2
	log$A$	38	8.6	9.7	27.3	8.4	18.6	7.8	23.6	8.9
	K.M.	Fn 2	Fn 0	Fn1/3	Fn 2	Fn 0	Fn 2	Fn 0	Fn 2	Fn 0
ZZ	E_a	60	56	60	31	60	27	56	25	60
	log$A$	16.5	18.5	17.2	11.0	17.4	9.7	16.2	9.1	17.2
	K.M.	Fn 0	Fn 0	Fn 0	A 4	Fn 0	A 4	Fn 0	A 4	Fn 0

Method		Sample						
		KP–CoCr		KP–NiCr		KP–CuCr	KP–ZnCr	
		St$_1$	St$_2$	St$_1$	St$_2$		St$_1$	St$_2$
FC	E_a	26.5	2.4	137.6	3.8	161.3	37.0	49.8
	log$A$	14.7	19.9	1.94	94.6	1.75	9.4	8.0
HM	E_a	45.4	180.0	76.8	87.0	199.4	46.4	141.9
	log$A$	12.0	36.7	22.7	22.7	36.8	11.7	36.5
	K.M.	Fn 0	Fn 2	Fn 1	Fn2/3	Fn 1	Fn 0	Fn2/3
DK	E_a	32.3	67.7	25.4	65.8	74	29.6	53.8
	log$A$	7.8	18.4	5.8	16.6	21.3	6.6	13.2
	K.M.	Fn 0	Fn 2	Fn 1	Fn2/3	Fn 1	Fn 0	Fn2/3
CR	E_a	38.4	176	74.3	155.2	345	40.9	139
	log$A$	6.1	24.8	11.5	20.3	38.2	6.2	18.7
	K.M.	Fn 0	Fn 2	Fn 1	D_3	D_3	Fn 0	Fn2/3
ZZ	E_a	39	29	24	25	52	44	25
	log$A$	12.7	9.4	8.3	7.7	17.1	13.8	7.7
	K.M.	Fn 0	A 4	A 3	A 3	A 4	Fn 0	A 3

St_1 and St_2 are the stage 1 and stage 2 of the decomposition process of $KClO_4$
E_a in kcal mol^{-1}, log$A$ in (s^{-1}) K.M. is the kinetic model

or random nucleation equation (A_4 function). The variation of the calculated E_{a_2} values (i.e. the activation energy of the decomposition stage of $KClO_4$) shows, in general, that the magnitude of E_a of pure $KClO_4$ (60 kcal mol^{-1}) does not alter for $KClO_4$ –alkaline earth chromite mixtures. Although the constancy in the activation energy values of the decomposition of $KClO_4$ seems to be in contradiction with the observed enhancement effect of these catalysts (a lowering in the E_a values must be expected in this case), it provides a further support for the suggestion that the accelerating effect of the catalysts is mainly electronic in nature rather than chemical. The same result can be achieved from the relatively higher value of E_a (52 kcal mol^{-1}) for the $KClO_4$–CuCr mixture compared with the pronounced accelerating activity of CuCr catalyst.

In conclusion, the catalytic thermal decomposition process of $KClO_4$–chromite mixtures involves a charge transfer mechanism. The accelerating role of the chromite catalysts depends on two reasons, the presence of metal cations on the surface of the catalyst which are electrically unsaturated and tend to attract electrons, as well as the electrical properties of the catalyst. The former acts as coordinatively active sites (CAS) able to accept pair of electrons from the oxygen atom of the perchlorate anion, this interaction can weaken the Cl–O bond (step I). The latter reason allows the oxygen to desorb through the availability of the charge movement (step II). Accordingly, the decomposition mechanism can be suggested as follows:

$$\mathrm{CAS} + \mathrm{ClO_4^-} \rightarrow \underset{\mathrm{I}}{\mathrm{CAS....O-ClO_3^-}} \rightarrow \underset{\mathrm{II}}{\mathrm{CAS....O^-} + \mathrm{Cl\dot{O}_3}} \rightarrow \mathrm{CAS} + 2\mathrm{O_2} + \mathrm{Cl^-}$$

where *CAS*, may be Cr(VI) or the transition metal cations Co(II), Ni(II), Cu(II) and Zn(II), $\mathrm{Cl\dot{O}_3}$=radical.

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