Thermochimica Acta, 20 (1977) 347–361
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EFFECT OF METAL OXIDE ADDITIVES ON THE THERMAL DECOMPOSITION OF PERCHLORATES, OXALATES AND HYDROXIDES

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(Received 4 October 1976)

ABSTRACT

The effects of α-Fe_2O_3 and α-Al_2O_3 additives on the thermal decomposition of perchlorates, oxalates and hydroxides were investigated by means of DTA, TG and X-ray techniques. It was found that the oxide additives catalytically promoted the decomposition of perchlorates ($NaClO_4$, $KClO_4$ and $Mg(ClO_4)_2$) and resulted in a lowering of the initial decomposition temperature (T_i). On the other hand, the oxides showed no significant effect on the decomposition of oxalates (FeC_2O_4 and CuC_2O_4) and hydroxides ($Mg(OH)_2$ and $Al(OH)_3$).

The thermal decomposition of $KClO_4$ was chosen to compare the catalytic effect of twelve metal oxides. The results indicated that the transition metal oxides such as Cr_2O_3, α-Fe_2O_3 and CuO markedly accelerated the decomposition; these oxides resulted in a solid-phase decomposition before fusion of $KClO_4$, and the initial decomposition temperature (T_i) of $KClO_4$ with oxides was about 100–200°C lower than that without catalyst. The oxides such as α-Al_2O_3 and MgO resulted in a slight lowering of the temperature of the fusion and promoted the molten-phase decomposition of $KClO_4$, but their effects were not so remarkable as those of the transition metal oxides. The modified catalytic mechanisms of transition metal oxides were proposed by considering the electron transfer and the oxygen-abstraction models.

INTRODUCTION

Recently, several investigators have studied the effect of metal oxide additives on the thermal decomposition of perchlorates, and observed that the oxides cause a lowering of the decomposition temperature[1–7] and an increase of the decomposition rate[7–13]. The tentative explanations have been made in terms of the charge transfer mechanism for the catalytic effect of metal oxides. Freeman et al.[2] have proposed that the rate controlling mechanism is the transfer of electron from the perchlorate ion to positive hole in the oxides. Rudloff and Freeman[3] employed thirteen metal oxides as catalyst for the decomposition of $KClO_3$ and $KClO_4$, and found that p-type semiconductive oxides show the remarkable effect on the decomposition, and the high electrical conductivity.

On the other hand, the effect of oxide additives on the thermal decomposition of oxalates and hydroxides has not been studied. The catalytic effect of oxides on the decomposition of these salts is expected to be different from that on perchlorates.

In this work, the effects of metal oxide additives such as α-Fe_2O_3 and α-Al_2O_3, on the thermal decomposition of perchlorates, oxalates and hydroxides were studied by means of DTA, TG and X-ray techniques. Furthermore, the catalytic decomposition of $KClO_4$ with ten kinds of oxides in addition to α-Fe_2O_3 and α-Al_2O_3 was investigated in some detail, and the electrical conductivity of oxides was measured to consider a relationship with catalytic activity.

EXPERIMENTAL

Materials

Perchlorates ($NaClO_4 \cdot H_2O$, $KClO_4$ and $Mg(ClO_4)_2 \cdot 6H_2O$), oxalates ($FeC_2O_4 \cdot 2H_2O$ and $CuC_2O_4 \cdot 1/2H_2O$) and hydroxides ($Mg(OH)_2$ and $Al(OH)_3$) used in the present experiments were GR reagent from Kanto Chemical Co.

Metal oxide additives

α-Fe_2O_3(S) was prepared by the dehydration of $FeSO_4 \cdot 7H_2O$ (Kanto) in air at 200°C for 30 min and the calcination in a stream of air (100 ml min^{-1}) at 700°C for 1 h. α-Fe_2O_3(A) was prepared by the calcination of $Fe(OH)(CH_3COO)_2$ in a stream of oxygen (100 ml min^{-1}) at 500°C for 1 h. α-Fe_2O_3(C) was GR reagent from Kanto Chemical Co. α-Al_2O_3 was prepared by the calcination of Al_2O_3 (Merck) in air at 1330°C for 3 h. Other metal oxide additives (B_2O_3, CaO, Cr_2O_3, CuO, Fe_3O_4, MgO, MnO_2, PbO_2, SiO_2 and ZnO) used were from Kanto Chemical Co. All samples were ground to pass a 200 mesh sieve. Samples for DTA and TG experiments were prepared by mixing the salts and oxides (weight ratio = 1 : 1) in an agate mortar for 20 min.

DTA

The gas-flow type DTA apparatus[4] was used for the DTA experiments. Two quartz tubes (i.d. = 10 mm) were used as the sample holder and the reference material holder, respectively. Since the quartz tube permits a rapid cooling of sample by the method of throwing water on the sample holder, an analysis of samples at a different stage of reaction was possible. The reference material was α-Al_2O_3. DTA experiments were carried out at a heating rate of 5°C min^{-1} in air atmosphere. Sample and reference material (1 g) were kept at a fixed position in a quartz tube by underlying loosely-packed quartz wool. Both ends of holders were open to give a convectional flow of air during the heating.

TG

The apparatus used consisted of a quartz spring (sensitivity; 32.5×10^{-6} g/0.01mm) and a quartz reaction tube (d = 40mm). The weight decrease of the sample was measured with a cathetometer as a function of temperature. A mixture of $KClO_4$ and additives (weight ratio = 1 : 1) of 100mg was placed in a cylindrical quartz dish (10 × 10mm). The measurements were carried out at a heating rate of 5°C min^{-1} in air atmosphere of 1 atm.

X-ray diffraction

The diffractometer used was of Geiger flex 2001 type (Rigaku Denki Co.), and was operated under the following conditions: Co-target, Fe-filter, 35kV and 10mA.

Electrical conductivity measurement

The electrical conductivity of oxides was measured at 50V d.c., in air atmosphere at temperatures up to 450°C. Oxide powders of 0.2g were pressed under 60–100 kg cm^{-2} into cylindrical pellets (10mm diam., 1mm thickness). Resistivity of pellets pressed between Pt-electrodes was measured by an ohmmeter (TOA Electronics, SM-9).

RESULTS

Effect of α-Fe_2O_3 and α-Al_2O_3 additives on the thermal decomposition of perchlorates, oxalates and hydroxides

Figure 1 shows DTA and TG curves of $KClO_4$ with additives, and an X-ray pattern of partially decomposed $KClO_4$. DTA curve(a) of pure $KClO_4$ shows two endothermic peaks at 310 and 570°C and an exothermic peak at 600°C. These three peaks correspond to solid-phase transition from rhombic to cubic form, fusion of solid $KClO_4$ and exothermic decomposition in the liquid state, respectively. X-ray diffraction patterns of the samples heated to 530 and 560°C showed the presence of KCl as the decomposition product of $KClO_4$. Therefore, it is found that the peak of fusion over the temperature range 530–590°C overlaps with that of the decomposition. In the DTA curve(b) of the $KClO_4$–α-Al_2O_3 system the peak temperatures of fusion and decomposition are 40 and 55°C lower than those in curve(a), respectively. The onset temperature of the fusion peak does not change. On the basis of these data, it may be speculated that α-Al_2O_3 promotes the molten-phase decomposition of $KClO_4$. In the DTA curve(c) of the $KClO_4$–α-Fe_2O_3(S) system a characteristic effect of α-Fe_2O_3 additive is found as compared with curves(a) and (b), i.e., the exothermic reaction is initiated at about 435°C before the beginning of fusion of $KClO_4$. The result of TG for the $KClO_4$–α-Fe_2O_3(S) system (Fig. 1-B) shows that the decrease in weight corresponding to eqn(1) also begins at 435°C.

$$KClO_4(s) \rightarrow KCl(s) + 2O_2(g) + 10.51(kcal/mol) \qquad (1)$$

Accordingly, the exothermic DTA peak of the $KClO_4$–α-Fe_2O_3(S) system is assumed to be due to the solid-phase thermal decomposition before the fusion. This assumption is reasonable because the sample heated to 440°C shown by an arrow on curve(c)

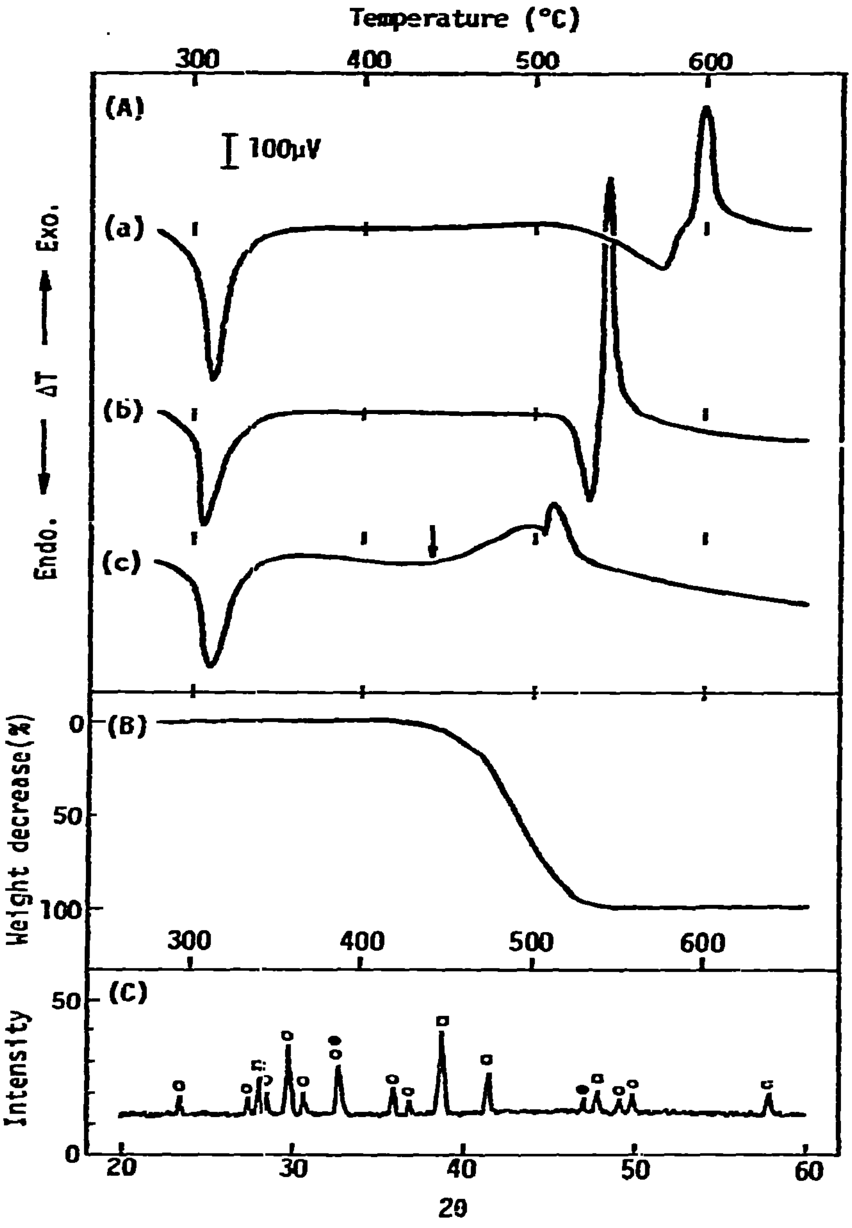

Fig. 1. Effect of additives on DTA and TG curves of $KClO_4$, and X-ray pattern of partially decomposed $KClO_4$. (A) DTA curves of $KClO_4$ with and without additives. (a) $KClO_4$ (b) $KClO_4$ + α-Al_2O_3 (c) $KClO_4$ + α-Fe_2O_3(S) (B) TG curves of $KClO_4$ with α-Fe_2O_3(S). (C) X-ray diffraction pattern of sample shown by arrow on DTA curve(c). ○, $KClO_4$; ●, KCl; □, α-Fe_2O_3.

indicated no symptom of fusion, and the X-ray diffraction pattern (Fig. 1-C) of this sample shows the presence of KCl. The solid-phase decomposition results in a decrease in the depth of fusion peak of $KClO_4$ and the height of succeeding liquid-phase decomposition peak in comparison with those for DTA curves(a) and (b).

Figure 2 shows the effect of additives on the DTA curves of $NaClO_4$ and

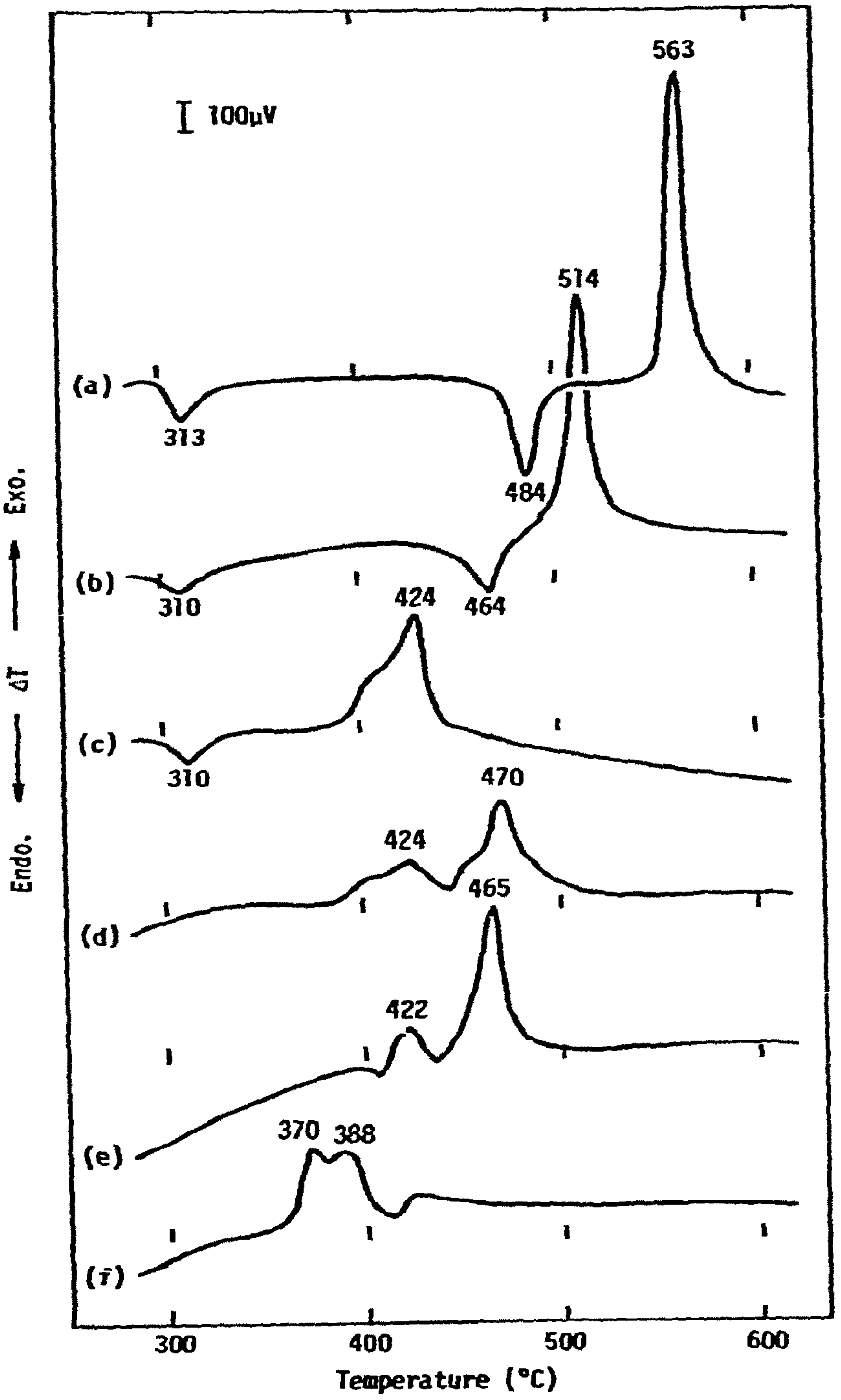

Fig. 2. Effect of additives on DTA curves of $NaClO_4$ and $Mg(ClO_4)_2$. (a) $NaClO_4$; (b) $NaClO_4$ + α-Al_2O_3; (c) $NaClO_4$ + α-Fe_2O_3(A); (d) $Mg(ClO_4)_2$; (e) $Mg(ClO_4)_2$ + α-Al_2O_3; (f) $Mg(ClO_4)_2$ + α-Fe_2O_3(A).

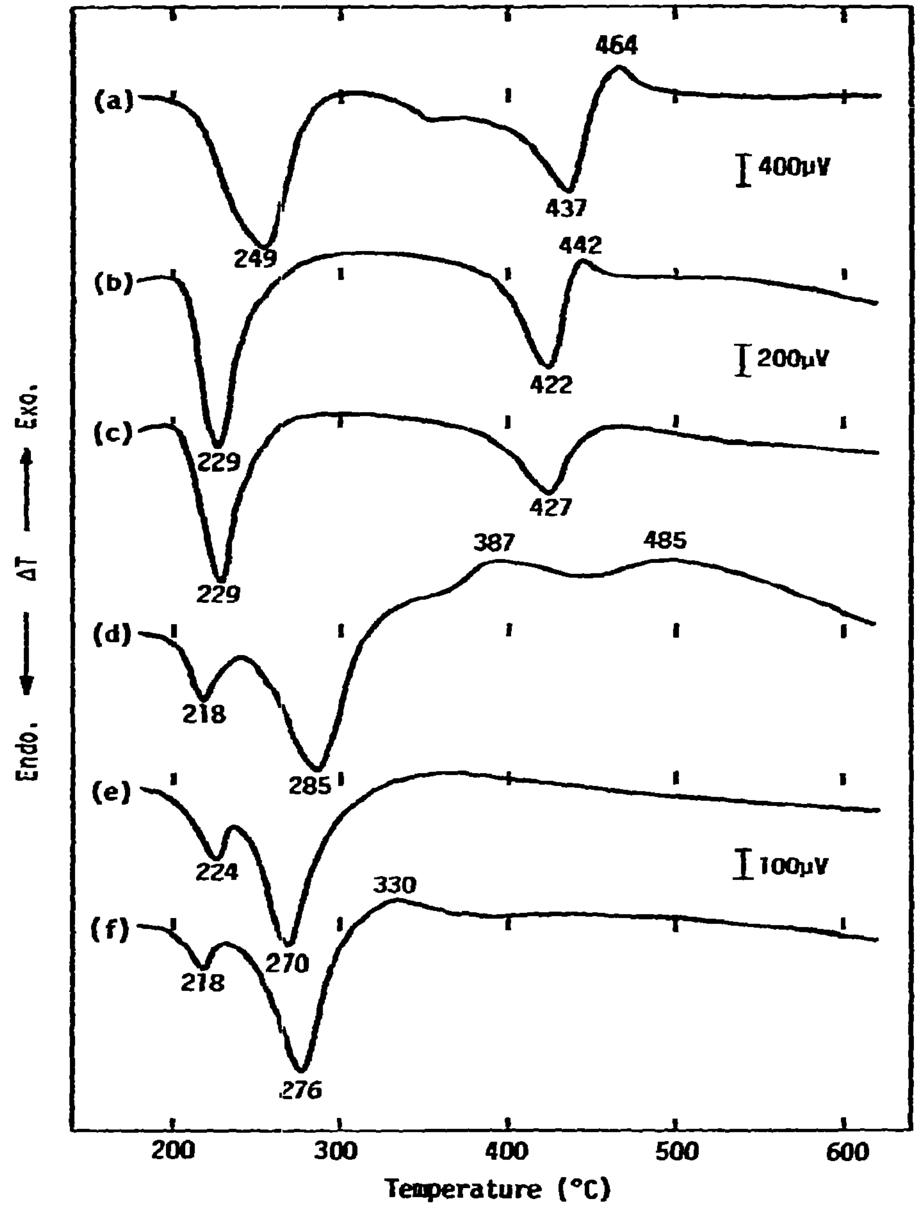

Fig. 3. Effect of additives on DTA curves of $FeC_2O_4 \cdot 2H_2O$ and $CuC_2O_4 \cdot 1/2H_2O$. (a) $FeC_2O_4 \cdot 2H_2O$; (b) $FeC_2O_4 \cdot 2H_2O + \alpha\text{-}Al_2O_3$; (c) $FeC_2O_4 \cdot 2H_2O + \alpha\text{-}Fe_2O_3$(A); (d) $CuC_2O_4 \cdot 1/2H_2O$; (e) $CuC_2O_4 \cdot 1/2H_2O + \alpha\text{-}Al_2O_3$; (f) $CuC_2O_4 \cdot 1/2H_2O + \alpha\text{-}Fe_2O_3$(A).

$Mg(ClO_4)_2 \cdot NaClO_4$ without additive (curve-a) gives three peaks in a similar manner to $KClO_4$. Two endothermic peaks correspond to solid-phase transition (313°C) and fusion (484°C) of $NaClO_4$, respectively[1]. One exothermic peak is due to the decomposition (563°C) of $NaClO_4$[1]. In the $NaClO_4$–α-Al_2O_3 system (curve-b), the peak temperatures of fusion and decomposition indicate the lowering of about 20°C and

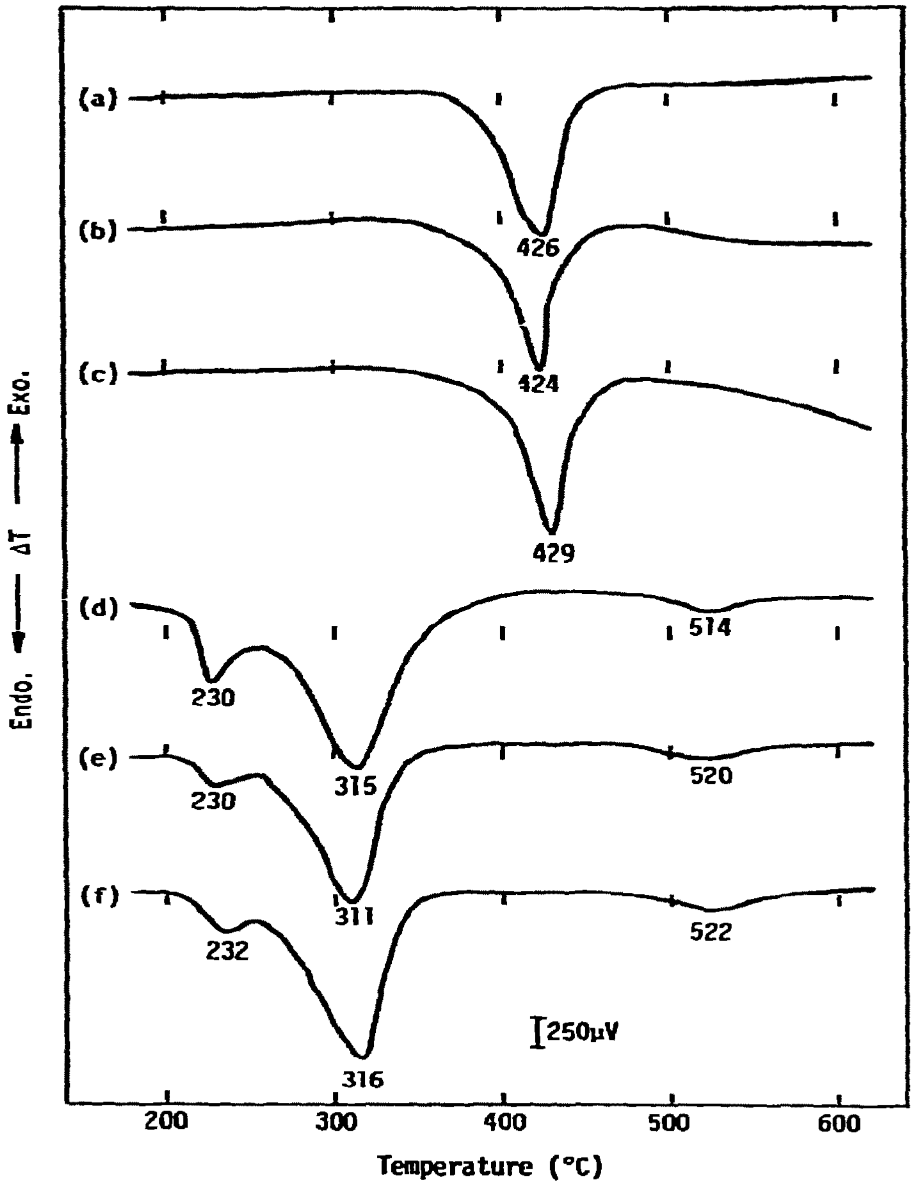

Fig. 4. Effect of additives on DTA curves of $Mg(OH)_2$ and $Al(OH)_3$. (a) $Mg(OH)_2$; (b) $Mg(OH)_2$ + α-Al_2O_3; (c) $Mg(OH)_2$ + α-Fe_2O_3(A); (d) $Al(OH)_3$; (e) $Al(OH)_3$ + α-Al_2O_3; (f) $Al(OH)_3$ + α-Fe_2O_3 (A).

50°C compared with those in curve(a). In the $NaClO_4$–α-Fe_2O_3 system (curve-c), the fusion peak disappears and the exothermic peak temperature lowers to 424°C. This means that the addition of α-Fe_2O_3 results in a solid-phase decomposition before the fusion of $NaClO_4$ and the marked lowering of the decomposition temperature in a similar manner as $KClO_4$. In the cases of $Mg(ClO_4)_2$, the thermal decomposition gives more complicated DTA curves (d, e, f). Acheson and Jacobs[14] showed that the decomposition products of $Mg(ClO_4)_2$ are mainly MgO, Cl_2 and O_2 in air atmosphere. In our samples heated to 600°C, only MgO was detected by X-ray diffraction as the solid product of the $Mg(ClO_4)_2$ decomposition. It was also found from TG experiments that these exothermic peaks on curves (d, e, f) correspond to the decomposition of $Mg(ClO_4)_2$. In the $Mg(ClO_4)_2$–α-Al_2O_3 system (curve-e), a sharpening of these peaks occurs. In the $Mg(ClO_4)_2$–α-Fe_2O_3 system (curve-f), a lowering of 50–70°C of the peak temperatures occurs.

Figure 3 shows the effect of additives on the DTA curves of $FeC_2O_4 \cdot 2H_2O$ and $CuC_2O_4 \cdot 1/2H_2O$. Curve(a) obtained for $FeC_2O_4 \cdot 2H_2O$ without oxide shows three peaks; first is the endothermic peak at 249°C due to the dehydration of the crystallization water, second is the endothermic peak at 437°C due to the decomposition, and third is the small exothermic peak at 464°C due to disproportionation[15, 16] of the decomposition product, $4FeO \rightarrow Fe_3O_4 + Fe$. Curve(d) for $CuC_2O_4 \cdot 1/2H_2O$ without additive shows two endothermic peaks at 218 and 285°C, which correspond to the dehydration and the decomposition, respectively, and a broad exothermic peak at about 390°C due to oxidation of Cu as the decomposition product[16]. In the cases of two oxalates with oxide additives (curves b, c, e and f), the effect of additives on the peak temperature is not so clear as in the case of perchlorates.

Figure 4 shows the effect of additives on the DTA curves for $Mg(OH)_2$ and $Al(OH)_3$. Curve(a) for $Mg(OH)_2$ without additive shows one endothermic peak (426°C) due to the dehydration of $Mg(OH)_2$ to MgO[17]. Curve(d) for $Al(OH)_3$ without oxide shows three endothermic peaks; the first is the transformation of $Al(OH)_3$ of large particle size to γ-AlOOH (230°C), the second is the dehydration of $Al(OH)_3$ of small particle size to η-Al_2O_3 (315°C) and the third is the dehydration of γ-AlOOH to γ-Al_2O_3 (514°C), respectively[19]. From DTA curves (b, c and e, f), it is found that each peak temperature of two hydroxides is not affected by addition of α-Al_2O_3 and α-Fe_2O_3.

Effect of twelve oxide additives on the thermal decomposition of $KClO_4$

In previous section, it was indicated that the catalytic effect of α-Fe_2O_3 and α-Al_2O_3 additives is most remarkable on the thermal decomposition of perchlorates and less on that of oxalates and hydroxides, and the different effects were observed between α-Fe_2O_3 and α-Al_2O_3. So, twelve oxides including α-Fe_2O_3 and α-Al_2O_3 were added to $KClO_4$ to test the differences of the catalytic effect of these oxides.

Figure 5 shows DTA results obtained for $KClO_4$ with twelve oxide additives. As shown in Table 1, oxide additives can be divided into two groups on the basis of the difference in the catalytic effects. Group I oxides are transition metal oxides. These oxides result in a solid-phase decomposition before fusion of $KClO_4$ and lowering of initial decomposition temperature (T_i) of $KClO_4$ by 100–200°C compared with that of pure $KClO_4$ (T_i = 530–550°C). T_i of the solid-phase decomposition was determined by measurement of the onset temperature of exothermic deflection of the DTA curve, and confirmed by the existence of the decomposition product (KCl) in the X-ray diffraction pattern of the DTA sample heated up to the onset temperature.

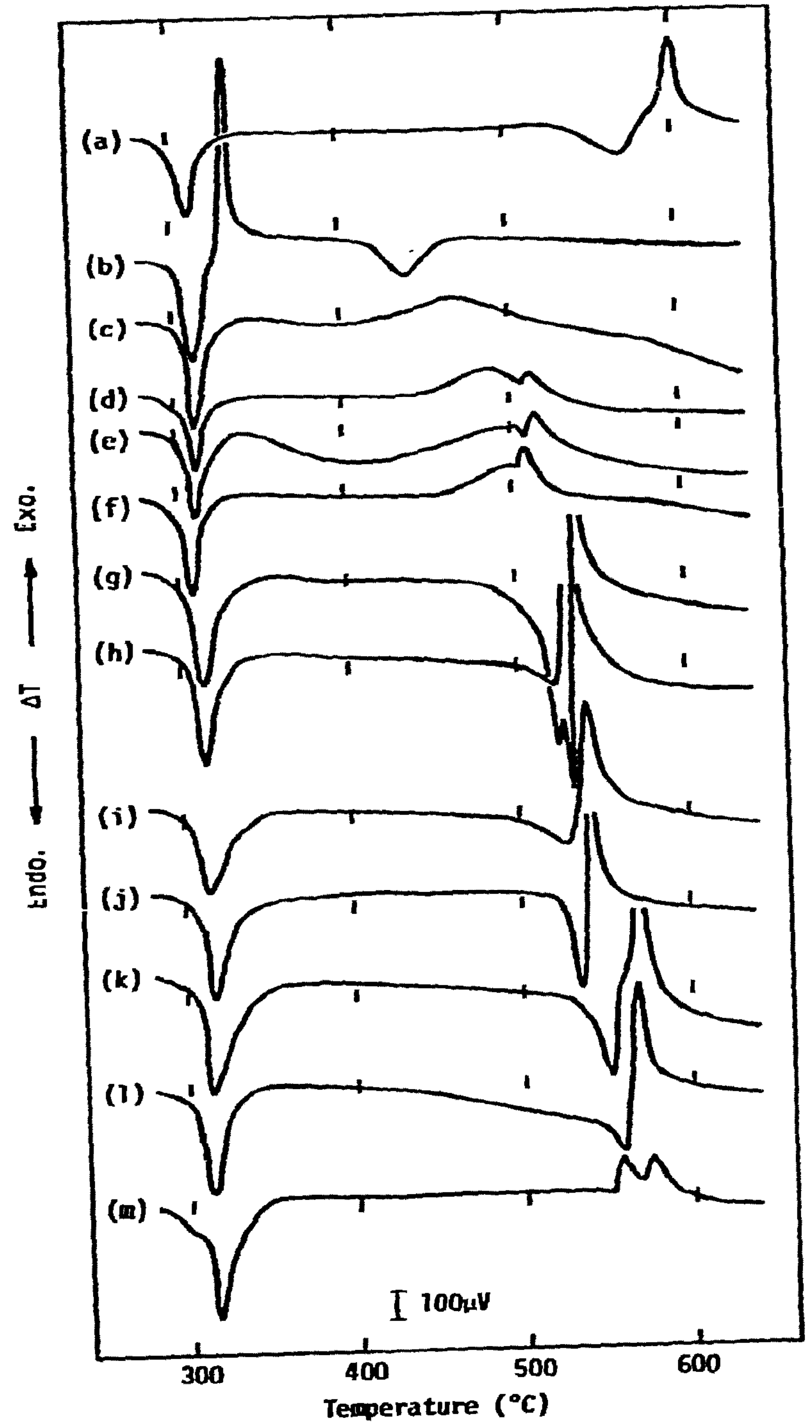

Fig. 5. DTA curves of $KClO_4$ with various oxides. (a) no oxide; (b) Cr_2O_3; (c) MnO_2; (d) α-Fe_2O_3(C); (e) Fe_3O_4; (f) CuO; (g) CaO; (h) PbO_2; (i) MgO; (j) α-Al_2O_3; (k) ZnO; (l) SiO_2; (m) B_2O_3.

TABLE I

EFFECT OF VARIOUS OXIDE ADDITIVES ON INITIAL DECOMPOSITION TEMPERATURE (T_i) OF $KClO_4$.

	Oxide	*T_i (°C)*
	pure $KClO_4$	*530–550*
Group 1[a]	Cr_2O_3	330–335
	MnO_2	400–410
	α-Fe_2O_3(C)	410–420
	Fe_3O_4	420–430
	CuO	420–430
Group 2[b]	CaO	480–500
	MgO	495–505
	PbO_2	510–515
	α-Al_2O_3	520–530
	ZnO	525–535
	SiO_2	545–550
	B_2O_3	545–550

[a] Group 1 oxides resulting in solid-phase decomposition of $KClO_4$.
[b] Group 2 oxides resulting in molten-phase decomposition of $KClO_4$.

The accuracy of T_i was ±5°C. Group 2 oxides are non-transition metal oxides. Temperatures of DTA peaks of fusion and decomposition of $KClO_4$ with the oxide additives are slightly lower than for pure $KClO_4$, and the molten-phase decomposition proceeds simultaneously with the fusion of $KClO_4$. The molten-phase decomposition temperature (T_i') is also lowered slightly compared with that for no additive, but the solid-phase decomposition did not occur by the addition of Group 2 oxides. T_i' was estimated as follows. Two temperatures were measured, the onset temperature (T_f) of endothermic peak of fusion and the temperature (T_p) of an intersection point of the baseline of the DTA curve with the line drawn along the left-hand arm of fusion peak. Then T_i' was defined to be in the ranges of T_f and T_p. None of the oxides have an influence on the peak temperature (310°C) for the solid-phase transition of $KClO_4$. Only Cr_2O_3 among twelve oxides shows a sharp exothermic peak immediately after the solid-phase transition. It is presumed that this peak is due to the overlapping of the catalytic decomposition of $KClO_4$ and the reaction between Cr_2O_3 and KCl formed, because KCr_3O_8 and $K_2Cr_2O_7$ were detected by X-ray diffraction of sample heated up to 355°C. At higher temperature (440°C), $K_2Cr_2O_7$ and Cr_2O_3 were revealed to exist.

DISCUSSION

Perchlorates

The thermal decomposition of perchlorates was remarkably affected by metal oxide additives. In particular, transition metal oxide additives, Group 1 in Table 1,

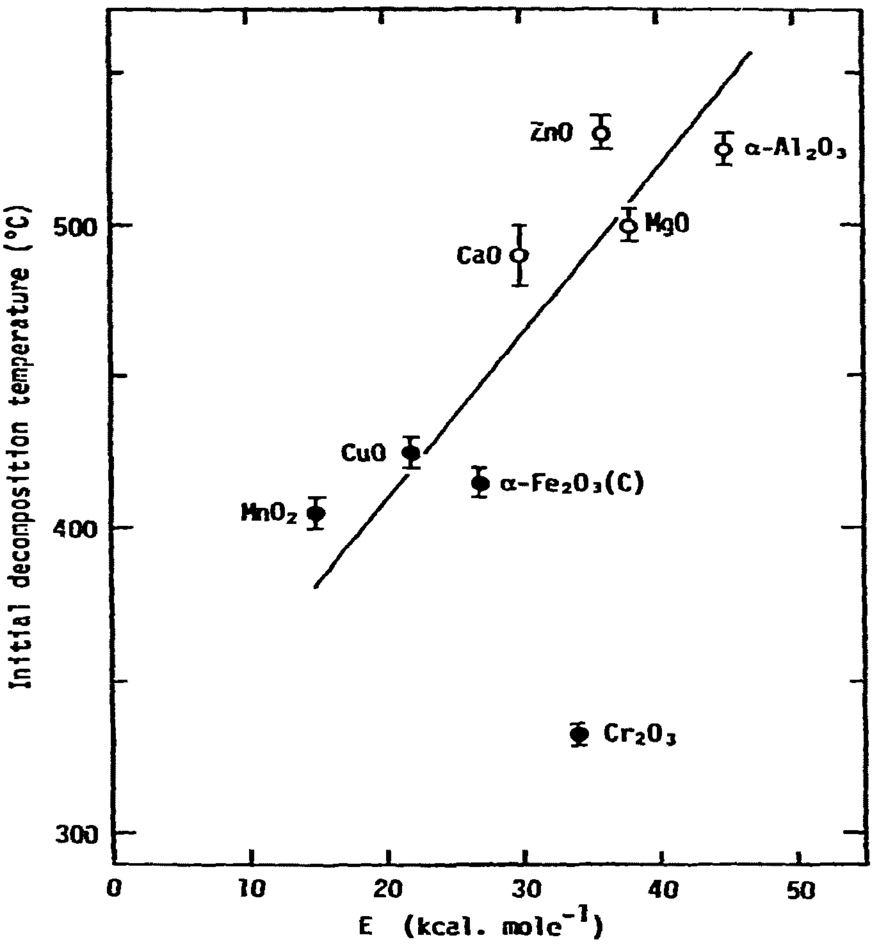

Fig. 6. Relation between activation energy for oxygen exchange reaction of oxide and initial decomposition temperature of $KClO_4$. ●, solid phase decomposition; ○, molten phase decomposition.

exerted the great effects resulting in a lowering of 50–200°C of initial decomposition temperature and solid-phase decomposition.

Markowitz et al.[1] concluded that the effect of metal oxide on the thermal decomposition of perchlorates is attributed to the abstraction of atomic oxygen from perchlorate ions. On the other hand, Freeman et al.[2] and Rudloff et al.[3] considered it to be due to the charge-transfer mechanism.

Figure 6 shows the relation between the activation energies (E)[26, 27] of the exchange reaction of oxygen-18 between the oxide surface and the surrounding gas, and the initial decomposition temperature (T_i) of $KClO_4$ measured in this experiment. E values correspond to the oxygen abstraction power of oxides. This figure shows that the higher the abstraction power of each oxide, the higher the catalytic effect on the thermal decomposition of $KClO_4$, and that the mechanisms proposed by Markowitz et al.[1] are reasonable.

On the other hand, it has been reported that the decomposition of $KClO_4$ proceeds as follows[20—24],

$$KClO_4 \rightarrow KClO_3 + 1/2O_2 \tag{2}$$

$$KClO_3 \rightarrow KCl + 3/2O_2 \tag{3}$$

In these processes, Cl^{7+} is reduced to Cl^{5+} and Cl^-, and O^{2-} is oxidized to O_2. In Fig. 7, the electrical conductivity of four metal oxide pellets (α-Fe_2O_3, Cr_2O_3, α-Al_2O_3 and MgO) measured in air are semilogarithmically plotted as a function of temperature. The electrical conductivities of α-Fe_2O_3 and Cr_2O_3 which show the remarkable effect on the thermal decomposition of $KClO_4$, are higher than those of α-Al_2O_3 and MgO by a factor of 10^2–10^5. This relationship between the electrical conductivity and the catalytic activity of oxides leads to the assumption that oxides

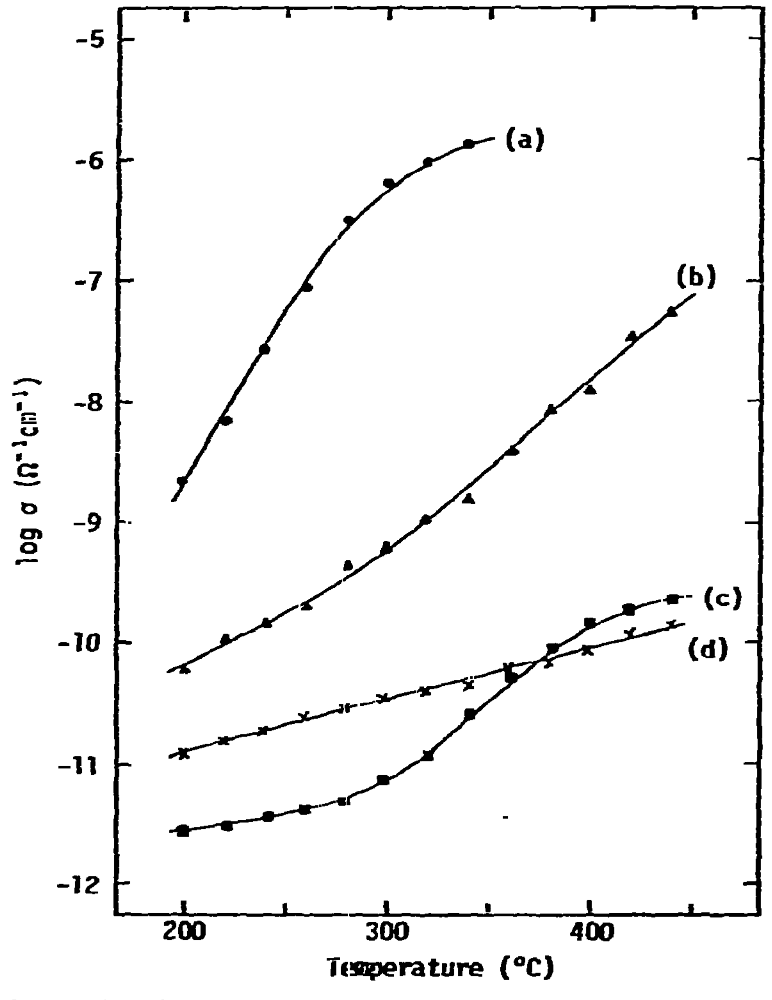

Fig. 7. Electrical conductivity of oxide pellets in air as a function of temperature. (a) Cr_2O_3; (b) α-Fe_2O_3; (c) MgO; (d) α-Al_2O_3.

act as a charge-transfer medium during the thermal decomposition of perchlorates. It has been considered that p-type semiconductive oxides are good catalysts on the thermal decomposition of perchlorates[2, 3, 6]. However, the results in our experiments indicated that n-type semiconductive oxides[25] such as α-Fe_2O_3 and MnO_2, and intrinsic type oxides[25] such as Fe_3O_4 and CuO also give great effects on the decomposition of perchlorates. Accordingly, it seems reasonable to assume that the effect of oxide additives on the thermal decomposition is closely related to the electrical conductivity of oxides rather than the type of semiconductor.

From these facts, the modified catalytic mechanisms were proposed by considering both the electron transfer between oxides and perchlorate ions and the abstraction of atomic oxygen from perchlorate ion by oxides.

For the case of n-type semiconductive oxides,

$$2e^-_{(oxide)} + ClO_4^- \rightarrow O^{2-}_{(oxide)} + ClO_3^- \rightarrow 1/2O_2 + ClO_3^- + 2e^-_{(oxide)} \qquad (4)$$

where, $e^-_{(oxide)}$ = electron of conduction band of oxide. $O^{2-}_{(oxide)}$ = oxygen ion abstracted by oxide.

For the case of p-type semiconductive oxides,

$$\oplus_{(oxide)} + ClO_4^- \rightarrow O_{(oxide)} + ClO_3 \rightarrow 1/2O_2 + ClO_3^- + \oplus_{(oxide)} \qquad (5)$$

where, $\oplus_{(oxide)}$ = positive hole of valence band of oxide. $O_{(oxide)}$ = oxygen atom abstracted by oxide. ClO_3 = radical.

Oxalates

The thermal decomposition of oxalates was little affected by α-Fe_2O_3 and α-Al_2O_3 additives as shown in Fig. 3.

It has been reported[28—32] that the thermal decomposition of oxalates proceeds according to eqn (6) in which the oxide (MO) and carbon oxides are formed,

$$FeC_2O_4 \rightarrow FeO + CO + CO_2 \qquad (6)$$

or eqn (7) in which the metal (M) and carbon dioxide are formed.

$$CuC_2O_4 \rightarrow Cu + 2CO_2 \qquad (7)$$

Dollimore et al.[30] assumed that the decomposition of bivalent metal oxalates to the oxide (MO) or the metal (M) would occur at a temperature at which the rupture of C–O bond or M–O bond is possible, respectively. In this assumption, the temperature of decomposition which produces the oxide (MO) depends on the dissociation energy required to break C–O bond, and the temperature of decomposition which produces the metal (M) depends on the size and the charge of the metal ion of oxalates since the rupture of the M–O bond is required. Thus, the oxide additives show little effect on the decomposition temperature of oxalates.

On the other hand, Jacobs et al.[31] considered the electron transfer mechanism for the decomposition of nickel oxalate, which was represented as follows:

$$C_2O_4^{2-} \rightarrow C_2O_4 + 2e \quad (8)$$

$$C_2O_4 \rightarrow 2CO_2 \quad (9)$$

$$Ni^{2+} + 2e \rightarrow Ni \quad (10)$$

Nagase et al.[32] also proposed that the decomposition of oxalates to the metal may occur by electron transfer from the oxalate ion to the metal ion. If the electron transfer may occur when oxalates decompose to give the metal, the decomposition of CuC_2O_4 in our experiments will probably be catalysed by α-Fe_2O_3 which promoted the decomposition of perchlorates by the electron transfer mechanism. Nevertheless, as shown in Fig. 3 the thermal decomposition of CuC_2O_4 was little affected by α-Fe_2O_3. This probably means that the decomposition of oxalate radicals to carbon dioxides shown in eqn (9) is the controlling step, so that the decomposition temperature may be governed only by the dissociation energy of the bonds.

Hydroxides

Anderson et al.[18] stated that the decomposition of magnesium hydroxide proceeds in the following three stages: first, some perturbation of the hydroxide lattice resulted from the interaction of adjacent hydroxyl ions; second, removal of water from the hydroxide; and third, crystallization of the dehydrated product to the formation of MgO crystallites.

α-Fe_2O_3 and α-Al_2O_3 additives had no effect on the thermal decomposition of hydroxides (Fig. 4). In a previous section, it was considered that the catalytic action of oxides on the decomposition reactions is the contribution to the electron transfer during the decomposition of materials. If the decomposition of hydroxides is initiated by the perturbation of the lattice[18], no effect of the oxide additives on the decomposition of hydroxides appears.

ACKNOWLEDGEMENTS

We thank Professor T. Matsushita and Dr. J. Fukushima, Hokkaido University, for their help in the electrical conductivity measurements of oxides.

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