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TG AND DTA STUDIES ON THE THERMAL DECOMPOSITION OF $KClO_4$–α-Fe_2O_3 MIXTURES

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ABSTRACT

The catalytic effect of α-Fe_2O_3 on the thermal decomposition of $KClO_4$ was studied by TG and DTA methods. The ferric oxide was prepared from $FeC_2O_4 \cdot 2H_2O$ by its thermal decomposition in air. DTA and TG curves showed that the addition of α-Fe_2O_3 led to an acceleration effect on the solid-state decomposition of $KClO_4$. The acceleration effect increased with a decrease in the preparation temperature and an increase in the mixing ratio of α-Fe_2O_3. From TG curves, the rate constant, k, was estimated by assuming a first-order rate law. An Arrhenius plot of k showed a straight line, which had a sharp bend at the temperature, T_B, characteristic of the respective α-Fe_2O_3 sample. It was suggested that the solid-state decomposition proceeded below T_B and the liquid-state decomposition above T_B. The fraction of $KClO_4$ decomposed in the solid state, α_B, was estimated to be 0.03 for pure $KClO_4$. The α_B value for the sample mixed with α-Fe_2O_3 prepared at 1000, 750 and 500°C was 0.065, 0.07 and 0.39, respectively. The increase in mixing ratio resulted in an increase in α_B: $\alpha_B = 0.06$ for 1% α-Fe_2O_3, 0.16 for 10%, 0.26 for 30% and 0.39 for 50%. The activation energy of the solid-state decomposition, E_s, of pure $KClO_4$ was 78.4 kcal mol^{-1} and those of $KClO_4 + \alpha$-Fe_2O_3 mixtures were 53.6, 60.2 and 60.8 kcal mol^{-1} for the oxide prepared at 500, 750 and 1000°C, respectively. The change in mixing ratio of the oxide did not show any effect on E_s. The activation energy of the liquid-state decomposition, E_l, for pure $KClO_4$ was 151.4 kcal mol^{-1} and those of $KClO_4 + \alpha$-Fe_2O_3 mixtures were in the range 147.8–155.4 kcal mol^{-1}. Changes in the preparation temperature and the mixing ratio of α-Fe_2O_3 did not give a systematic influence on E_l.

INTRODUCTION

It has been known that various foreign substances, in particular, the metallic oxides, can catalytically accelerate the thermal decomposition of $KClO_4$ [1]. In previous papers [2–7], the authors have reported the results of DTA and SEM experiments on the catalytic effect in the $KClO_4 + \alpha$-Fe_2O_3 system. The results have shown that the ferric oxide leads to a large decrease in the initial decomposition temperature of the perchlorate and the oxide promotes the solid-state decomposition occurring before melting. In the

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present experiments, the TG technique was used in addition to DTA and the influence of preparation temperature and mixing ratio of α-Fe_2O_3 prepared from $FeC_2O_4 \cdot 2H_2O$ was examined for the decomposition of $KClO_4 + \alpha$-Fe_2O_3 mixtures.

EXPERIMENTAL

Materials

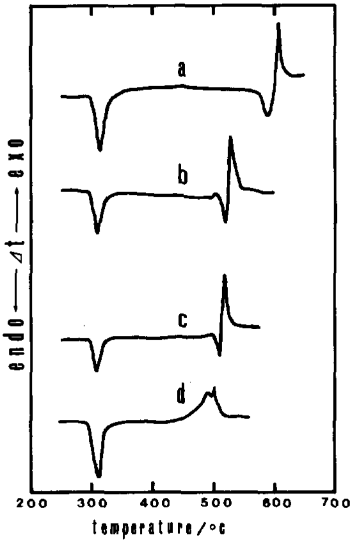
A commercial $KClO_4$ reagent (Wako Pure Chemicals Ltd.) was used after grinding it below 200 mesh size. Ferric oxide, α-Fe_2O_3, was prepared from $FeC_2O_4 \cdot 2H_2O$ (Wako) by calcining in flowing air (100 ml min^{-1}) for 1 h at 500, 750 and 1000°C. The calcination was carried out in an electric furnace with a quartz tube and an alumina boat. The oxide obtained was ground to pass through a 200 mesh sieve. The mixing of $KClO_4$ with α-Fe_2O_3 was carried out in an agate mortar. The mixing ratios of the oxide were 1, 10, 30 and 50 wt%. The mixing time was 20 min in the cases of 10, 30 and 50 wt% and was 60 min for 1 wt%. The time was selected on the basis of reproducibility of the DTA curve.

DTA

Apparatus and procedures have previously been described in detail [2]. The apparatus consisted of two quartz tubes (10 mm ID) placed vertically in a tubular furnace. The sample powder was packed on the quartz wool layer fixed in the quartz tube which could be quenched with cold water to stop the reaction. Reference material was packed in another tube. The experimental conditions were: weight of sample and reference material (α-Al_2O_3, > 200 mesh), 1 g; heating rate, 4.2°C min^{-1}; chromel–alumel thermocouple (0.3 mm diameter); atmosphere, static air.

TG

The apparatus used was a Cahn electrobalance (Model RG) with a quartz hang-down tube (35 mm ID). The sample was placed in a quartz basket (10 × 10 mm) suspended from the arm of the balance by means of a quartz wire (0.3 mm diameter). The sample temperature was measured with a thermocouple by putting its tip at 5 mm below the bottom of a basket. The sample in the basket was covered with quartz wool to prevent it from flying out by the explosive decomposition of $KClO_4$. The experimental conditions were: sample weight, 20 mg; heating rate, 4.2°C min^{-1}; chromel–alumel thermocouple (0.5 mm diameter); atmosphere, static air of 150 mmHg. At 150 mmHg, the buoyancy effect was observed to be constant up to 1000°C.



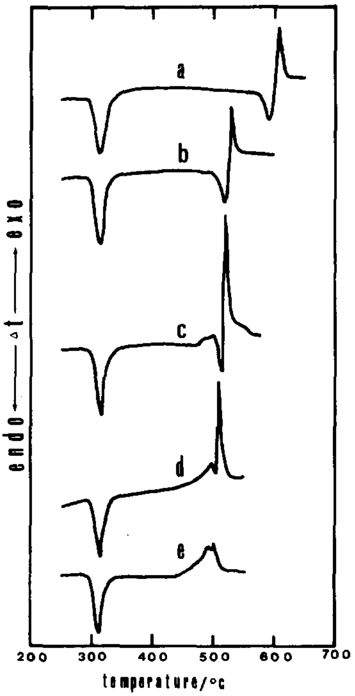


Fig. 1. Effect of preparation temperature of α-Fe_2O_3 on DTA curve of $KClO_4$ + α-Fe_2O_3 mixtures. (a) Pure $KClO_4$, (b) $KClO_4$ + α-Fe_2O_3 prepared at 1000°C, (c) $KClO_4$ + α-Fe_2O_3 at 750°C, (d) $KClO_4$ + α-Fe_2O_3 at 500°C. Heating rate, 4.2°C min^{-1}; atmosphere, static air; mixing ratio of α-Fe_2O_3, 50 wt%.

Fig. 2. Effect of mixing ratio of α-Fe_2O_3 on DTA curve of $KClO_4$ + α-Fe_2O_3 mixtures. (a) Pure $KClO_4$, (b) $KClO_4$ + 1 wt% α-Fe_2O_3, (c) $KClO_4$ + 10 wt% α-Fe_2O_3, (d) $KClO_4$ + 30 wt% α-Fe_2O_3, (e) $KClO_4$ + 50 wt% α-Fe_2O_3. Preparation temperature of α-Fe_2O_3, 500°C; heating rate, 4.2°C min^{-1}; atmosphere, static air.

XRD

A Geigerflex (type 2001) diffractometer (Rigaku Denki Co.) was used for the powder XRD of the samples. The diffraction conditions were: target, Co; voltage, 35 kV; current, 10 mA; scanning speed, 1° min^{-1}.

RESULTS AND DISCUSSION

Figure 1 shows DTA curves of pure $KClO_4$ and $KClO_4$ containing 50 wt% of α-Fe_2O_3 prepared at 500, 750 and 1000°C. The endothermic peak at 310°C in curve (a) of pure $KClO_4$ corresponds to crystallographic transformation of solid $KClO_4$ from rhombic to cubic form ($\Delta H = 3.29$ kcal mol^{-1} [8]). As found from curves (b), (c) and (d), this peak is not affected by mixing of α-Fe_2O_3. The endothermic peak at 590°C in curve (a) is due to melting of solid $KClO_4$ ($\Delta H = 2.3$ kcal mol^{-1} [8]) and the sharp exothermic peak at 608°C results from the liquid-state decomposition of the perchlorate ($\Delta H = -6.8$ kcal mol^{-1} [8]). Thus, as reported previously [2–7], DTA curve (a) suggests that the decomposition reaction of pure $KClO_4$ occurs in the liquid phase after melting. Curves (b), (c) and (d) show that the mixing of α-Fe_2O_3 (50 wt%) results in a lowering of the exothermic peak temperature. The peak pattern of melting and decomposition observed for samples containing α-Fe_2O_3 prepared at 1000 and 750°C (curves b and c) is similar to that for pure $KClO_4$ (curve a). However, the peak temperatures of endothermic melting are 520 and 510°C, and the peak temperatures of exothermic decomposition are 528 and 519°C, respectively; i.e., 70–80°C lower than the peak temperatures observed for pure $KClO_4$. Furthermore, the slight exothermic deflection can be detected just before the endothermic peak of the melting in curves (b) and (c). In the case of the sample mixed with α-Fe_2O_3 prepared at 500°C (curve d), it is apparent that the exothermic deflection mentioned above is much pronounced, starting at ~ 420°C, and the endothermic peak (495°C) due to the melting of solid $KClO_4$ becomes very small. The facts lead to the conclusion that the addition of α-Fe_2O_3 to $KClO_4$ results in the acceleration of the solid-state decomposition of the perchlorate before melting, the extent of the acceleration increasing with decreasing preparation temperature of the oxide. The crystallite sizes of α-Fe_2O_3 prepared at 500, 750 and 1000°C were 1.0×10^3, 2.9×10^3 and 3.3×10^3 Å, respectively, which were estimated according to the line broadening method by using the XRD peak of the (104) face at $2\theta = 38.6°$. This change in the crystallite size will correspond to an increase in crystallinity or a decrease of imperfection in the oxide with an increase in preparation temperature. Accordingly, the change in the acceleration effect is assumed to be due to a change in the crystallinity of the oxide. XRD of the samples obtained after DTA experiments showed the diffraction lines corresponding to only KCl and α-Fe_2O_3, which indicate that no reaction occurred between $KClO_4$ and α-Fe_2O_3.

Figure 2 shows the effect of mixing ratio of α-Fe_2O_3 prepared at 500°C on the DTA curves of $KClO_4$ + α-Fe_2O_3 mixtures. The addition of 1 wt% of α-Fe_2O_3 leads to a decrease in the exothermic peak temperature by 83°C, from 609°C for pure $KClO_4$ (curve a) to 526°C (curve b). The lowering of the peak temperature by further addition of the oxide from 1 to 50 wt% occurs to a lesser extent, i.e., 26°C, from 526°C (curve b) to 500°C (curve e). On the other hand, the increase in mixing ratio of α-Fe_2O_3 results in the following facts: a decrease in the area of the endothermic peak due to melting of $KClO_4$; a decrease in the onset temperature of exothermic deflection appearing before the endothermic peak of melting, which may correspond to the onset temperature of solid-state decomposition of the perchlorate; and an increase in the area of this exothermic deflection. These

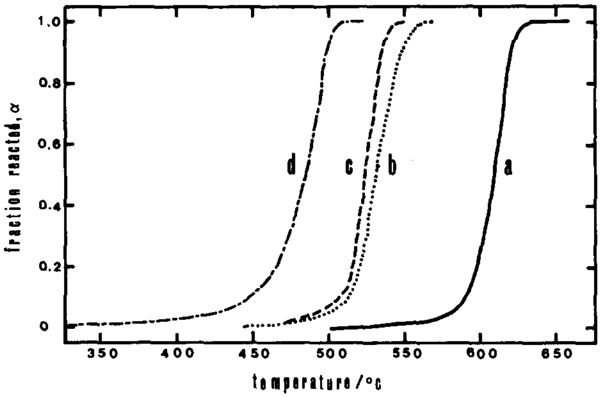


Fig. 3. Effect of preparation temperature of α-Fe_2O_3 on TG curve of $KClO_4$ + α-Fe_2O_3 mixtures. (a) Pure $KClO_4$, (b) $KClO_4$ + α-Fe_2O_3 prepared at 1000°C, (c) $KClO_4$ + α-Fe_2O_3 at 750°C, (d) $KClO_4$ + α-Fe_2O_3 at 500°C. Heating rate, 4.2°C min^{-1}; atmosphere, 150 mmHg air; mixing ratio of α-Fe_2O_3, 50 wt%.

facts indicate that the amount of solid-state decomposition of $KClO_4$ increases with an increase in mixing ratio of α-Fe_2O_3. It is considered that an increase in the mixing ratio of α-Fe_2O_3 results in an increase in the area of contact between $KClO_4$ and α-Fe_2O_3 particles. Thus, the accelerating action of the oxide for the decomposition is suggested to occur at the point of contact.

Figure 3 shows the TG curves of the decomposition of $KClO_4$ containing 50 wt% of α-Fe_2O_3 prepared at different temperatures. Figure 4 shows those containing different amounts of α-Fe_2O_3 prepared at 500°C. The TG results in these figures are consistent with DTA results in Figs. 1 and 2; a decrease in the preparation temperature and an increase in mixing ratio of the oxide

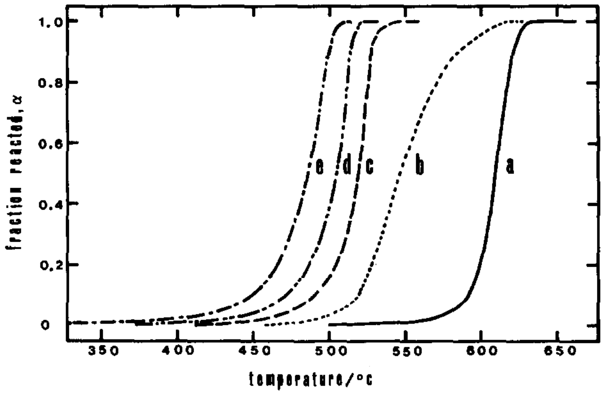


Fig. 4. Effect of mixing ratio of α-Fe_2O_3 on TG curve of $KClO_4$ + α-Fe_2O_3 mixtures. (a) Pure $KClO_4$, (b) $KClO_4$ + 1 wt% α-Fe_2O_3, (c) $KClO_4$ + 10 wt% α-Fe_2O_3, (d) $KClO_4$ + 30 wt% α-Fe_2O_3, (e) $KClO_4$ + 50 wt% α-Fe_2O_3. Preparation temperature of α-Fe_2O_3, 500°C; heating rate, 4.2°C min^{-1}; atmosphere, 150 mmHg air.

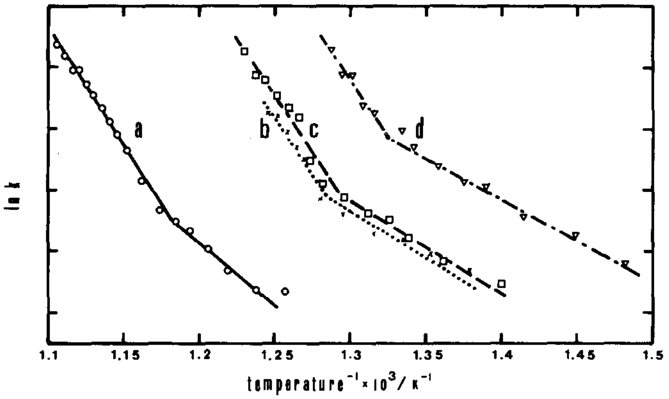


Fig. 5. The Arrhenius plots of the rate constant, *k*, for decomposition of pure $KClO_4$ and $KClO_4$ mixed with α-Fe_2O_3 prepared at different temperatures. (a) Pure $KClO_4$, (b) $KClO_4$ + α-Fe_2O_3 prepared at 1000°C, (c) $KClO_4$ + α-Fe_2O_3 at 750°C, (d) $KClO_4$ + α-Fe_2O_3 at 500°C. The value of *k* was estimated from TG curves in Fig. 3 by assuming a first-order rate law.

result in a shift of the TG curve towards the lower temperature range. The TG curve of the $KClO_4$ + 1 wt% α-Fe_2O_3 mixture (curve b in Fig. 4) shows a slower increase in α value above $\alpha = 0.5$ than that observed for other mixtures. The reason for this different mode of the TG curve of 1 wt% α-Fe_2O_3 is unknown at present.

Figures 5 and 6 are the Arrhenius plots of the rate constant, *k*, for the decomposition. The rate constant was estimated on the basis of the assumption of a first-order rate law $[d\alpha/dt = k(1 - \alpha)]$ and the $d\alpha/dt$ value measured from the tangent graphically drawn to the TG curve in Figs. 3 and

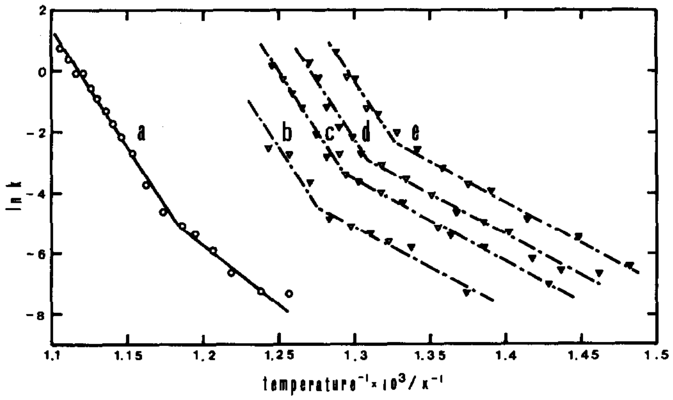


Fig. 6. The Arrhenius plots of the rate constant, *k*, for decomposition of pure $KClO_4$ and $KClO_4$ mixed with α-Fe_2O_3 at different mixing ratios. (a) pure $KClO_4$, (b) $KClO_4$ + 1 wt% α-Fe_2O_3, (c) $KClO_4$ + 10 wt% α-Fe_2O_3, (d) $KClO_4$ + 30 wt% α-Fe_2O_3, (e) $KClO_4$ + 50 wt% α-Fe_2O_3. The value of *k* was estimated from TG curves in Fig. 4 by assuming a first-order rate law.

TABLE 1

The temperature, T_B, of the sharp bend in the Arrhenius plot of the rate constant (Figs. 5 and 6), the onset temperature, T_D, of melting of $KClO_4$ estimated from DTA curves (Figs. 1 and 2), the fraction decomposed, α_B, up to T_B estimated from TG curves (Figs. 3 and 4), and the activation energies, E_s and E_l, of the decomposition of $KClO_4$ in the solid and liquid states

	T_B (°C)	T_D (°C)	α_B	E_s (kcal mol^{-1})	E_l (kcal mol^{-1})
pure $KClO_4$	573	570	0.03	78.4	151.4
$KClO_4 + \alpha$-Fe_2O_3					
(1000°C, 50%) [a]	506	510	0.065	60.8	147.8
(750°C, 50%)	500	498	0.07	60.2	145.4
(500°C, 50%)	481	490	0.39	53.6	148.6
(500°C, 30%)	492	495	0.26	53.4	155.4
(500°C, 10%)	500	500	0.16	54.2	152.8
(500°C, 1%)	511	500	0.06	52.7	152.9

[a] Temperature is the preparation temperature of α-Fe_2O_3 and percentage is the mixing ratio of α-Fe_2O_3 to $KClO_4$.

4. It is found from Figs. 5 and 6 that both pure $KClO_4$ and the $KClO_4 + \alpha$-Fe_2O_3 mixture result in a straight line and there is a sharp bend in the line at a temperature characteristic of each sample. As found in tables 3–5 of ref. 1, the majority of kinetic analyses reported have been based on a first-order rate equation, though a few authors have reported that the decomposition rate obeyed Prout–Tompkins and contracting-cube equations.

The fact that, in Figs. 5 and 6, the Arrhenius plot has a sharp bend for each sample implies that the decomposition behavior is changed in the temperature ranges before and after the sharp bend. Table 1 contains values of T_B, temperature of the bend in the lines in Figs. 5 and 6, and T_D, onset temperature of the endothermic DTA peak corresponding to melting of $KClO_4$ shown in Figs. 1 and 2. The temperatures T_B and T_D are found to be in fairly good agreement with each other. Accordingly, it is reasonable to assume that the solid-state decomposition proceeds at temperatures below T_B in contrast to the liquid-state decomposition above T_B. The value of T_B is observed to decrease with a decrease in the preparation temperature and with an increase in the mixing ratio of α-Fe_2O_3. In Table 1, α_B is shown, which was defined as the fraction decomposed up to T_B and was estimated from the TG curves in Figs. 3 and 4. The value of α_B is a measure of the amount of $KClO_4$ decomposition proceeding in the solid phase. Since α_B of pure $KClO_4$ is 0.03, the solid-state decomposition is indicated to occur even without α-Fe_2O_3. As mentioned previously, however, the DTA result of pure $KClO_4$ (Figs. 1 and 2, curve a) gave no indication of the solid-state decomposition. This discrepancy is considered to arise since $\alpha_B = 0.03$ is so small that the exothermic DTA deflection could not be detected before melting, within the sensitivity of the apparatus. Table 1 shows α_B increasing with a decrease in the preparation temperature and an increase in the mixing ratio of α-Fe_2O_3. These changes in α_B suggest that the acceleration of the solid-state decomposition of $KClO_4$ by α-Fe_2O_3 operates at the interface between $KClO_4$ and α-Fe_2O_3 particles, and the oxide of smaller crystallite size, which is thought to have lower crystallinity or higher reactivity, greatly accelerates the decomposition. As has been indicated by Harvey et al. [9], the $KClO_4$–KCl system gives the eutectic melting. Thus, the acceleration of the solid-state decomposition forming KCl by α-Fe_2O_3 will lead to the lowering of T_B and T_D as shown in Table 1.

The activation energy was calculated from the slope of the lines in Figs. 5 and 6. The activation energies, E_s and E_l, in Table 1 correspond to the values for solid-state decomposition below T_B and for the liquid-state decomposition above T_B, respectively. The values of E_l are scattered between 145 and 153 kcal mol^{-1}, but no systematic change in E_l can be observed for the changes in the preparation temperature and the mixing ratio of α-Fe_2O_3. Furthermore, pure $KClO_4$ shows 151.4 kcal mol^{-1} which is comparable to the values for $KClO_4 + \alpha$-Fe_2O_3 mixtures. Accordingly, α-Fe_2O_3 is regarded as having no catalytic effect on the liquid-state decomposition of $KClO_4$ occurring after melting. The value of E_l is about twice that estimated by Kissinger's method [2]. The activation energy for solid-state decomposition, E_s, is observed to decrease from 78.4 kcal mol^{-1} for pure $KClO_4$ to 60, 61 and 54 kcal mol^{-1} for $KClO_4$ containing α-Fe_2O_3 prepared at 1000, 750 and 500°C, respectively. However, the mixing ratio of α-Fe_2O_3 prepared at 500°C has no influence on E_s as seen in Table 1. From these facts, it is concluded that α-Fe_2O_3 leads to a decrease in the activation energy for the solid-state decomposition of $KClO_4$ and the magnitude of the decrease depends on the preparation temperature of the oxide. The increase in α_B with the mixing ratio is considered to be due to an increase in the frequency factor in the Arrhenius relation which is caused by the increase in the contact area between $KClO_4$ and α-Fe_2O_3 particles with an increase in the mixing ratio.

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