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INFLUENCE OF PREPARATION ATMOSPHERES AND DOPING OF METAL IONS ON THE CATALYTIC ACTIVITY OF α-Fe_2O_3 ON THE THERMAL DECOMPOSITION OF $KClO_4$

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ABSTRACT

The influence of preparation atmospheres and doping of metal ions on the catalytic activity of α-Fe_2O_3 on the thermal decomposition of $KClO_4$ was investigated by means of DTA and X-ray techniques. Oxygen, air and nitrogen were used as preparation atmospheres, and Li^+, Mg^{2+}, Cu^{2+}, Ti^{3+}, B^{3+}, Al^{3+} and Si^{4+} were doping agents. The catalytic activity, which was indicated with the initial decomposition temperature (T_i) of $KClO_4$–α-Fe_2O_3 mixture (1 : 1 by wt), was increased by preparing the oxide in oxygen atmosphere rather than in air or nitrogen and by doping of Li^+, Mg^{2+} and Cu^{2+}. The tri-valent ions showed no effect and Si^{4+} showed the inhibition effect on the activity. The specific surface area and the crystalline size of α-Fe_2O_3 were found to have no relation to T_i value. It was considered that the enhanced activity results from the p-type semiconductivity of the oxides prepared by calcination in oxygen atmosphere and by doping of lower valent ions.

INTRODUCTION

It had previously been reported[1, 2] by the present authors that the catalytic activity of α-Fe_2O_3 for the thermal decomposition of $KClO_4$ mainly depended on the preparation temperature of the oxide rather than the starting material; the low preparation temperature resulted in the high catalytic activity, the large specific surface area, and the small crystalline size of the oxide. From these results, α-Fe_2O_3 prepared in air at low temperatures was presumed to have a low crystallinity and a high concentration of Fe^{2+}-donor center with the low ionization energy. The catalytic effect was discussed, therefore, on the basis of the electron transfer and the oxygen abstraction models.

On the other hand, it has been reported[3, 4] that the catalytic activity of MgO[3] and Mn_2O_3[4] on the decomposition is enhanced by being doped with lower valent metal ion(Li^+). The enhanced activity was interpreted on the basis of the positive hole theory. However, the influence of doping on the catalytic activity of α-Fe_2O_3 has not been reported.

TABLE 1

PREPARATION METHODS OF α-Fe_2O_3

α-Fe_2O_3 samples	*Starting materials*	*Atmosph. (ϕ = 100 ml min^{-1})*	*Temp. (°C)*	*Doping materials (1 mol%)*
Group 1	α-Fe_2O_3[a]	oxygen	500–900	—
		air	500–900	—
		nitrogen	500–900	—
Group 2	$Fe(OH)(CH_3COO)_2$	oxygen	500–1200	—
		air	500–1200	—
		nitrogen	500–800	—
Group 3	$FeSO_4 \cdot 7H_2O$	air	700–900	—
		air	700–900	$LiOH \cdot H_2O$
		air	700–900	$Mg(OH)_2$
Group 4	α-Fe_2O_3[b]	air	600–900	—
		air	600–900	$Mg(OH)_2$
		air	600–900	$Al(OH)_3$
		air	600–900	SiO_2
Group 5	Fe_3O_4[c]	air	600	—
		air	600	Li^+
		air	600	Cu^{2+}
		air	600	Ti^{3+}
		air	600	B^{3+}

[a] Prepared by calcination of $FeC_2O_4 \cdot 2H_2O$ in a stream of oxygen (100 ml min^{-1}) at 450°C for 1 h.
[b] Prepared by calcination of $FeC_2O_4 \cdot 2H_2O$ in a stream of air (100 ml min^{-1}) at 500°C for 1 h.
[c] Prepared by precipitation from the equimolar aqueous solution of $FeSO_4$ and $Fe_2(SO_4)_3$ containing various metal ions.

In this work, α-Fe_2O_3 samples were prepared in different atmospheres and different metal ions were doped in the oxides, in order to investigate the influence of preparing histories on the catalytic activity of the oxides.

EXPERIMENTAL

Materials

Five groups of α-Fe_2O_3 samples shown in Table 1 were prepared by the calcination of various iron compounds to compare the influence of preparation atmospheres (Group 1 and 2 samples) and of doping of metallic ions (Group 3, 4 and 5 samples).

Group 1 samples were obtained by the preliminary decomposition of $FeC_2O_4 \cdot 2H_2O$ in a stream of oxygen (100 ml min^{-1}) at 450°C for 1 h, and the subsequent calcination in a stream of oxygen, air or nitrogen (100 ml min^{-1}), respectively, at temperatures of 500–900°C for 1 h. Group 2 samples were prepared by the decomposition of $Fe(OH)(CH_3COO)_2$ in a stream of oxygen, air or nitrogen (100 ml min^{-1}), respectively, at temperatures of 500–1200°C for 1 h.

Group 3 samples were obtained from the mixtures of $FeSO_4 \cdot 7H_2O$ and

$LiOH \cdot H_2O$ or $Mg(OH)_2$ (M/Fe = 1 mol%; M = Li, Mg) by the decomposition in a stream of air (100 ml min^{-1}) at temperatures of 700–900°C for 1 h. The mixing was carried out in an agate mortal for 90 min. In order to remove residual sulfate ion in α-Fe_2O_3, the samples were washed with hot water until no $BaSO_4$ precipitate was observed in the filtrate, and then dried in air at 110°C for 8 h. Group 4 samples were obtained from the mixtures of α-Fe_2O_3 and $Mg(OH)_2$, $Al(OH)_3$ or SiO_2(amorphous) (M/Fe = 1 mol%) by the calcination in a stream of air (100 ml min^{-1}) at temperatures of 600–900°C for 1 h. α-Fe_2O_3 employed for making the mixture was prepared by decomposition of $FeC_2O_4 \cdot 2H_2O$ in a stream of air (100 ml min^{-1}) at 500°C for 1 h. Group 5 samples were obtained from Fe_3O_4 samples[5] which were precipitated from the equimolar aqueous solution of $FeSO_4$ and $Fe_2(SO_4)_3$ containing $LiNO_3$, $Cu(NO_3)_2$, $Ti_2(SO_4)_3 \cdot 8H_2O$ or $Na_2B_4O_7 \cdot 10H_2O$ (M/Fe = 1 mol%) by use of 6M NaOH. Fe_3O_4 samples were oxidized to give α-Fe_2O_3 in a stream of air (100 ml min^{-1}) at 600°C for 1 h.

All samples were ground to pass 200 mesh sieve. $KClO_4$ and other materials used were GR reagents from Kanto Chemical Co. $KClO_4$ and α-Fe_2O_3 (weight ratio = 1 : 1) were mixed in an agate mortal for 20 min.

DTA and X-ray diffraction

DTA apparatus and X-ray diffractometer employed were the same as those previously described[1, 2]. DTA experiments were carried out at a heating rate of 5°C min^{-1} in air atmosphere, and a chromel–alumel thermocouple was used for the temperature measurement. The reference material was α-Al_2O_3 prepared by calcining of Al_2O_3(Merck) in air at 1330°C for 3 h. The weights of the sample and reference material were 1 g.

The initial decomposition temperature (T_i)

The value of T_i of the $KClO_4$-α-Fe_2O_3 mixture was determined by measuring the onset temperature of exothermic deflection of the DTA curve, and confirming the existence of the decomposition product (KCl) in the X-ray diffraction pattern of DTA sample heated up to the onset temperature. The accuracy of T_i was ± 5°C.

Specific surface area and crystalline size

The specific surface area and the crystalline size of α-Fe_2O_3 were estimated by the BET method[6] and the X-ray diffraction method[7], respectively.

RESULTS

The thermal decomposition of $KClO_4$ and $KClO_4$–α-Fe_2O_3 systems

Figure 1 shows the typical DTA curves of $KClO_4$ with α-Fe_2O_3 of Group 1 prepared in a stream of oxygen. The arrow in the figure indicates the initial decomposition temperature (T_i). Curve(a) of $KClO_4$ alone shows two endothermic peaks at 310 and 570°C and an exothermic peak at 600°C. These three peaks correspond to

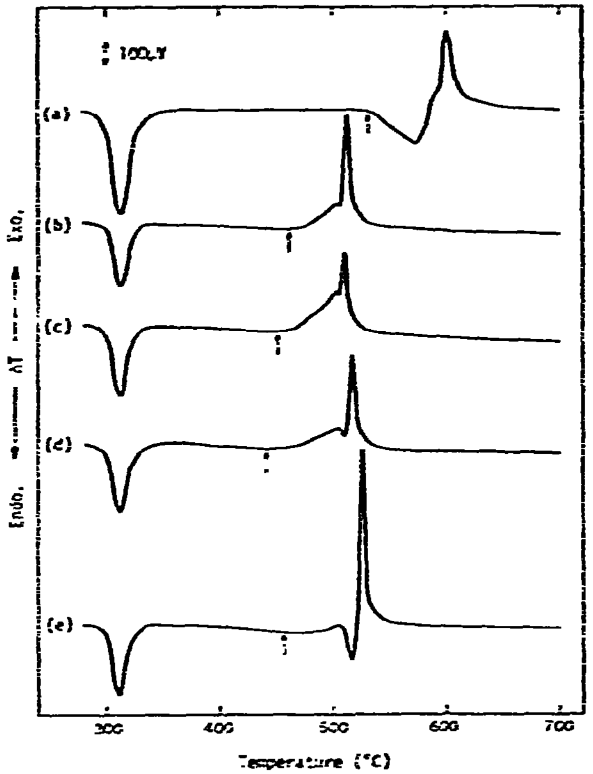


Fig. 1. DTA curves of $KClO_4$ with α-Fe_2O_3 of Group I prepared by calcination of α-Fe_2O_3[a] in a stream of oxygen. (a) $KClO_4$ (b) $KClO_4$ + α-Fe_2O_3 (prepared at 500°C); (c) $KClO_4$ + α-Fe_2O_3 (prepared at 650°C); (d) $KClO_4$ + α-Fe_2O_3 (prepared at 700°C); (e) $KClO_4$ + α-Fe_2O_3 (prepared at 800°C). ↑: Initial decomposition temperature (T_i).

the solid-phase transition from the rhombic to the cubic form, the fusion of solid $KClO_4$ and the exothermic decomposition in the liquid phase, respectively[8]. Curves (b)–(e) correspond to $KClO_4$ with α-Fe_2O_3 prepared at 500, 650, 700 and 800°C, respectively. In curve(b), the exothermic reaction starts at about 460°C before the beginning of the fusion of $KClO_4$. The X-ray diffraction patterns of the sample heated to 460°C indicated the presence of KCl. Accordingly, the exothermic peak of curve(b) is considered to be due to the solid-phase thermal decomposition before the fusion. The endothermic fusion peak and subsequent liquid-phase decomposition peak are relatively smaller than those of $KClO_4$ alone(Curve(a)). It is presumed, therefore, that the addition of the oxide leads to a considerable extent of the solid-phase thermal decomposition of $KClO_4$. Curves (c)–(e) show that the thermal decomposition also takes place in the solid-phase, and T_i and the shape of the peaks of fusion and decomposition depend on the preparation temperature of α-Fe_2O_3.

The influence of preparation atmospheres of α-Fe_2O_3 on the thermal decomposition of $KClO_4$

Figure 2 indicates the relation between T_i and the preparation temperature of

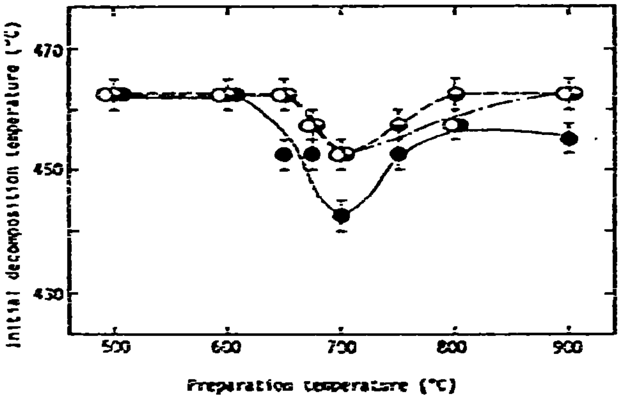
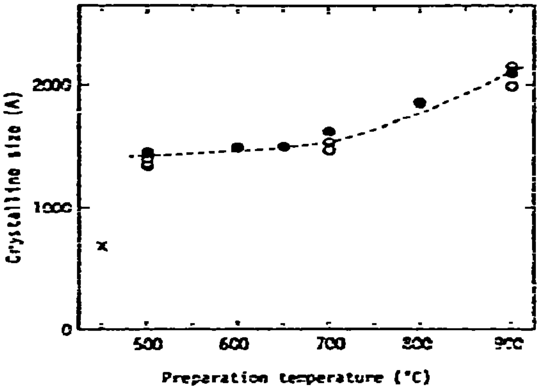


Fig. 2. Relation between initial decomposition temperature (T_i) of $KClO_4$ and preparation temperature of α-Fe_2O_3 (Group 1). ●, α-Fe_2O_3 (prepared in oxygen); ⊖, α-Fe_2O_3 (prepared in air); ○, α-Fe_2O_3 (prepared in nitrogen).



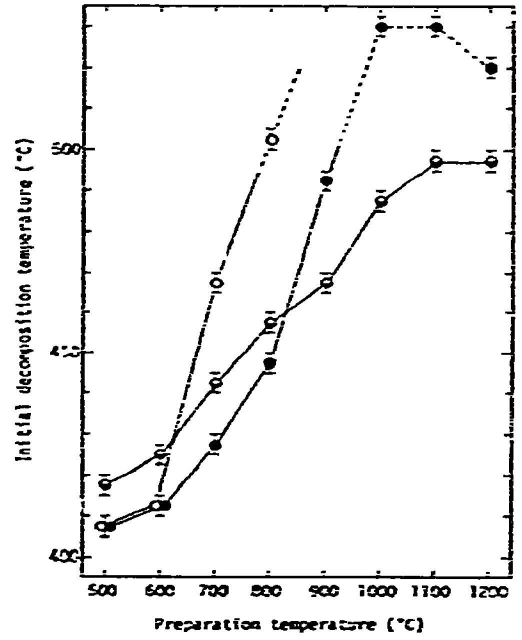


Fig. 3. Relation between crystalline size and preparation temperature of α-Fe_2O_3 (Group 1). ●, α-Fe_2O_3 (prepared in oxygen); ⊖, α-Fe_2O_3 (prepared in air); ○, α-Fe_2O_3 (prepared in nitrogen); ×, α-Fe_2O_3*.

Fig. 4. Relation between initial decomposition temperature (T_i) of $KClO_4$ and preparation temperature of α-Fe_2O_3 (Group 2). ●, α-Fe_2O_3 (prepared in oxygen); ⊖, α-Fe_2O_3 (prepared in air); ○, α-Fe_2O_3 (prepared in nitrogen). ——, Solid-phase decomposition; – – –, molten-phase decomposition.

three series of α-Fe_2O_3 of Group 1. All α-Fe_2O_3 prepared at 500 and 600°C show the same T_i value in spite of the differences in the preparation atmospheres. In the temperature range above 650°C, a prominent decrease in T_i can be observed for all α-Fe_2O_3 prepared at 700°C and the oxides prepared in oxygen have a lower T_i than those prepared in air and nitrogen. Both α-Fe_2O_3 prepared in air and in nitrogen show the same catalytic activity on T_i. Figure 3 shows the relation between the crystalline size and the preparation temperature of three series of α-Fe_2O_3. The crystalline size slightly increases above 700°C, however, it is not influenced by the preparation atmosphere. There is no correlation between the crystalline size and T_i value shown in Fig. 2.

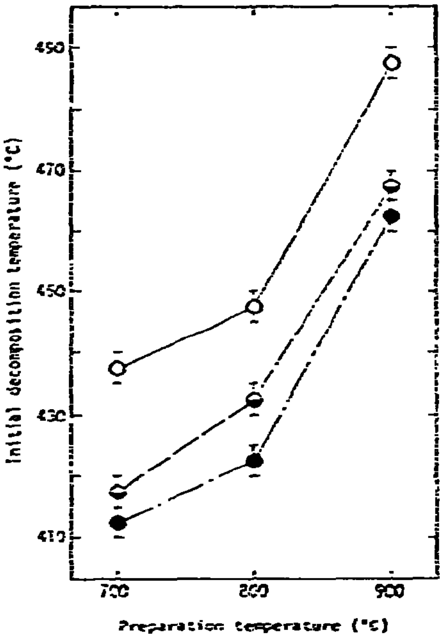
Several investigators have reported[9, 10] the change in the reactivity of α-Fe_2O_3 prepared at about 700°C on the formation reaction of $CdFe_2O_4$, the catalytic decomposition of H_2O_2 and the solubility in HCl[9], and the change in electrical conductivity of α-Fe_2O_3[10]. It may be considered that these phenomena are the Hedvall effect since both the Curie temperature and the Tammann temperature are near 700°C.

Figure 4 shows the relation between T_i value and the preparation temperature of α-Fe_2O_3 of Group 2. In the case of α-Fe_2O_3 prepared in air (◒), T_i increases almost linearly with increasing of the preparation temperature of α-Fe_2O_3 up to 1100°C, and then shows a similar value at 1100 and 1200°C. All α-Fe_2O_3 prepared in air resulted in a solid-phase decomposition. In the case of α-Fe_2O_3 prepared in oxygen (●), T_i of α-Fe_2O_3 prepared at temperatures below 800°C is slightly lower than those in air. However, T_i increases steeply from 450 to 490°C at preparation temperatures between 800 and 900°C. Above 1000°C, the solid-phase decomposition has disappeared and T_i has similar value to that for $KClO_4$ alone (530°C). On the other hand, the oxides prepared in a stream of nitrogen (○) were found by X-ray diffraction to be a mixture of α-Fe_2O_3 and Fe_3O_4. The oxides prepared in nitrogen indicate low T_i values at 500 and 600°C in a similar manner to the oxide prepared in oxygen atmosphere, but T_i increases suddenly at 600–800°C and the solid-phase decomposition disappeared at 800°C. Table 2 shows the specific surface area and the crystalline size of α-Fe_2O_3 prepared in oxygen and air. The surface area of two series of α-Fe_2O_3 decreases with increasing preparation temperature, but the values are little affected by the differences in the preparation atmosphere. The crystalline size is also little affected by the differences in the preparation atmosphere, and it increases with an increase in the preparation temperature. From the results mentioned above, the

TABLE 2

CHANGE IN SPECIFIC SURFACE AREA (S) AND CRYSTALLINE SIZE (*d*) OF α-Fe_2O_3 OF GROUP 2

		Preparation temp. (°C)							
		500	*600*	*700*	*800*	*900*	*1000*	*1100*	*1200*
α-Fe_2O_3 (prepared in air)	S(m²/g)	13.5	11.6	9.9	8.0	3.5	1.5	1.9	2.0
	d (A)	710	880	1110	1420	1750	3360	3950	4110
α-Fe_2O_3 (prepared in O_2)	S(m²/g)	15.8	13.1	10.3	6.7	4.8	1.9	1.7	0.6
	d (A)	730	850	1100	1600	2100	3010	2910	3770



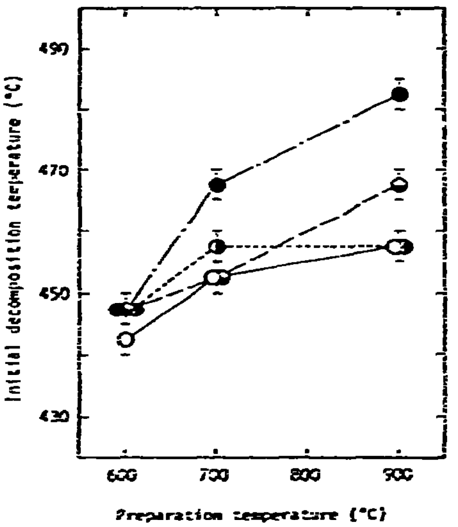


Fig. 5. Relation between initial decomposition temperature (T_i) of $KClO_4$ and preparation temperature of α-Fe_2O_3 (Group 3). ○, pure α-Fe_2O_3; ◒, α-Fe_2O_3 + Li^+ (1 mol%); ●, α-Fe_2O_3 + Mg^{2+} (1 mol%).

Fig. 6. Relation between initial decomposition temperature (T_i) of $KClO_4$and preparation temperature of α-Fe_2O_3 (Group 4). ○, pure α-Fe_2O_3; ◑, α-Fe_2O_3 + Mg^{2+} (1 mol%); ◒, α-Fe_2O_3 + Al^{3+} (1 mol%); ●, α-Fe_2O_3 + Si^{4+} (1 mol%).

differences of the catalytic activity caused by the change in preparation atmospheres and temperatures are not explicable from the differences in the specific surface area and the crystalline size of the catalysts.

The influence of doping of various metal ions on the catalytic activity of α-Fe_2O_3 on the thermal decomposition of $KClO_4$

Figure 5 shows the relation between T_i and the preparation temperature of α-Fe_2O_3 of Group 3, which were prepared by the decomposition of mixtures of $FeSO_4 \cdot 7H_2O$ and metal hydroxides. The presence of 1 mole per cent of lower valent metal ions, such as Li^+ and Mg^{2+}, leads to an increase in the catalytic activity of α-Fe_2O_3; T_i of the doped oxides are 15–25°C lower than that of undoped oxide.

Figure 6 shows the relation between T_i and the preparation temperature of α-Fe_2O_3 (Group 4) doped with $Mg(OH)_2$, $Al(OH)_3$ and SiO_2. Only SiO_2 shows a considerable increase in T_i compared with that of undoped oxide. On the other hand, $Mg(OH)_2$ and $Al(OH)_3$ give slight influence on T_i.

Figure 7 shows DTA curves of $KClO_4$ with α-Fe_2O_3 (Group 5) prepared in air by the calcination of coprecipitated Fe_3O_4. The shape of the decomposition peak of $KClO_4$ and its T_i value depend on the kind of doping metal ions. Comparison with Fig. 1 shows that the fusion peak of $KClO_4$ shown at about 500°C disappears except

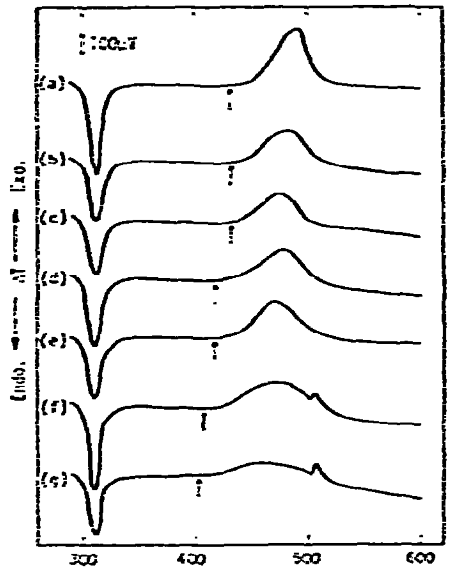


Fig. 7. DTA curves of $KClO_4$ with α-Fe_2O_3 (Group 5) containing various metal ions. (a) $KClO_4$ + pure α-Fe_2O_3; (b) $KClO_4$ + α-Fe_2O_3 (Ti^{3+}; 1 mol%); (c) $KClO_4$ + α-Fe_2O_3 (B^{3+}; 1 mol%); (d) $KClO_4$ + α-Fe_2O_3 (Cu^{2+}; 1 mol%); (e) $KClO_4$ + α-Fe_2O_3 (Li^+; 1 mol%); (f) $KClO_4$ + α-Fe_2O_3 (Li^+; 5 mol%); (g) $KClO_4$ + α-Fe_2O_3 (Li^+; 10 mol%). ↑: Initial decomposition temperature (T_i).

TABLE 3

INFLUENCE OF DOPING OF VARIOUS METAL IONS ON INITIAL DECOMPOSITION TEMPERATURE (T_i) OF $KClO_4$ AND CRYSTALLINE SIZE (d) OF α-Fe_2O_3

α-Fe_2O_3 prepared by calcination of Fe_3O_4 containing various metal ions in air at 600°C for 1 h.

Doping ion	*T_i (°C)*	*d (Å)*
Fe^{3+} (pure α-Fe_2O_3)	430–435	960
Ti^{3+} : 1 mol%	430–435	630
B^{3+} : 1 mol%	430–435	760
Cu^{2+} : 1 mol%	415–420	900
Li^+ : 1 mol%	415–420	920
Li^+ : 5 mol%	405–410	890
Li^+ : 10 mol%	400–405	1040

for the cases of doping of 5 and 10 mole per cent of Li^+ (Curve(f) and (g)). Table 3 summarizes the crystalline size of α-Fe_2O_3 (Group 5) and T_i, in which the relationship between crystalline size and T_i is not observed. Doping of lower valent metal ions, such as Li^+ and Cu^{2+}, resulted in a lowering of 15°C of T_i in comparison with undoped α-Fe_2O_3. Furthermore, T_i was lowered with an increase in amounts of Li^+ ion doped. On the other hand, the tri-valent metal ions such as Ti^{3+} and B^{3+} do not affect the T_i value.

DISCUSSION

The influence of the preparation atmospheres on the catalytic activity of α-Fe_2O_3

In previous papers[2, 11], the promoting action of the oxide on the thermal decomposition of $KClO_4$ was considered according to the following scheme;

For n-type semiconductive oxides,

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

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

For p-type semiconductive oxides,

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

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

α-Fe_2O_3 is usually classified as an n-type semiconductor[12] with Fe^{2+} ion in slight excess, but some authors have reported the oxide being an intrinsic type[13, 14], and others being n- or p-type conductor[15, 16]. Solymosi et al.[9] measured the electric conductivity of α-Fe_2O_3 under various partial pressures of oxygen and found that the conductivity showed the n-type character in partial pressure of oxygen below 10^{-1} torr and the p-type character in higher oxygen pressure. They concluded that the p-type conductivity was a consequence of oxygen excess in oxide and the conductivity could be ascribed to the following reaction;

$$3/4O_2 \rightarrow Fe\square'' + 3\oplus + 1/2Fe_2O_3 \qquad (3)$$

where, $Fe\square''$: vacancy. $\oplus$: positive hole.

Consequently, it is considered that α-Fe_2O_3 prepared in oxygen, in this study, will probably be p-type semiconductive oxide and eqn (2) may, therefore, be applicable. On the other hand, α-Fe_2O_3 prepared in air or nitrogen is n-type and eqn (1) may be applicable.

It is found from Fig. 2 that the catalytic activity of α-Fe_2O_3 with p-type character is higher than that of the oxide with n-type character. This result agrees with an earlier investigation by Rudloff et al.[17] that p-type semiconductive oxides generally show the higher catalytic activity on the decomposition than n-type oxides. The reason for the superiority of p-type character may be considered as follows.

Gardner et al.[16] reported that the positive hole in α-Fe_2O_3 is less mobile than the electron at the temperatures below 330°C, and reversely at higher temperatures the hole becomes more mobile than the electron. Therefore, in the temperature range where the catalytic thermal decomposition of $KClO_4$ occurs, the mobility of hole is presumed to be higher than that of electron. Accordingly, the differences in catalytic activity shown in α-Fe_2O_3 samples prepared in oxygen and air or nitrogen may probably be interpreted on the basis of the mobility of charge carrier.

On the other hand, α-Fe_2O_3 of Group 2 showed a very complex behavior

(Fig. 4). In the case of α-Fe_2O_3 (Group 2) prepared directly from $Fe(OH)(CH_3COO)_2$ by its thermal decomposition, it is considered that the mechanism of catalysis is really complicated because the concentration of holes or electrons, their ionization energy, etc., may vary with the preparation temperature and the preparation atmosphere.

The influence of doping of various metal ions on the catalytic activity of α-Fe_2O_3

It is found from Figs. 5 and 7 that the catalytic activity of α-Fe_2O_3 increases by doping of 1 mole per cent of Li^+, Mg^{2+} and Cu^{2+} ions. In the preceding section, it is presumed that the enhanced catalytic activity caused by calcining in oxygen may be attributed to the role of positive holes with higher mobility than electrons. Similarly, the influence of doping of metal ions with a lower valency than the Fe^{3+} ion is also anticipated to be due to the action of positive holes in the oxide.

On the basis of the principle of controlled valency[12], it can be assumed that the positive holes may be generated by doping of the lower valent ions in the oxide. For example, the case of doping of Mg^{2+} ion could be considered as follows;

$$2MgO + 1/2O_2(g) \rightarrow 2Mg_{(Fe)}^{-} + 2\oplus + Fe_2O_3 \qquad (4)$$

where, $Mg_{(Fe)}^{-}$: Mg^{2+} ion situated in the lattice point of Fe^{3+} ion. $\oplus$: positive hole.

Gardner et al.[16] and Lessoff et al.[18] have reported that the Seebeck voltage of α-Fe_2O_3 doped with di-valent metal ions such as Mg^{2+}, Ni^{2+}, etc. showed the p-type semiconductive character. Consequently, it can be considered that positive holes introduced by doping of lower valent metal ions contribute to the increase of catalytic activity of α-Fe_2O_3 in a similar manner as in the case of α-Fe_2O_3 prepared in oxygen. This assumption is supported by the fact that the catalytic activity of α-Fe_2O_3 of Group 5 is increased with an increase in amounts of Li^+ ion doped, and reversely unaffected by doping of tri-valent metal ions.

On the other hand, it is found from Fig. 6 that the catalytic decomposition was inhibited by α-Fe_2O_3 doped with SiO_2. This is not explicable on the basis of the principle of controlled valency[12], since if Si^{4+} ions are introduced in the oxide lattice, the concentration of Fe^{2+} ion, i.e., electron, would increase and thus the catalytic activity would be increased in terms of the mechanism shown in eqn (1). In the previous paper[11], it was found that DTA of $KClO_4$–SiO_2 mixture showed the liquid-phase decomposition and T_i of 550°C. Consequently, the inhibition by doping of SiO_2 is presumed to be due to the coating effect of SiO_2 on the surface of α-Fe_2O_3.

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