

PHENOMENOLOGICAL STUDY OF THE CATALYTIC THERMAL DECOMPOSITION OF POTASSIUM PERCHLORATE BY IRON(II) OXIDES WITH DIFFERENT PREPARING HISTORIES

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The catalytic decomposition of KClO_4 by Fe_2O_3 , obtained by calcination of Fe(II) salts at different temperatures, was investigated by DTA, TG, X-ray and IR. A sample without catalyst was found to begin fusion and decomposition simultaneously, and to form an intermediate, KClO_3 . Addition of catalysts resulted in solid-phase decomposition before fusion of KClO_4 , and in a small amount of KClO_3 . The difference in catalytic effect observed for different catalysts was less in the molten-phase decomposition than in the solid phase. The initial decomposition temperature (T_1) increased with the temperature of preparation of the catalyst and showed a definitive relationship with the crystallite size of the catalyst. The change of T_1 is discussed on the basis of the n -type semiconductive properties of the catalyst.

Several investigators have studied the thermal decomposition of pure KClO_4 , and the decomposition catalyzed by metal oxides and halogenides [1–18]. Rudloff and Freeman [18] employed thirteen metal oxides in a systematic investigation of their catalytic effects on the decomposition, by means of DTA, TG and electrical conductivity methods, and concluded that (a) the catalytic activity increased with the p -type semiconductive character of the catalyst, (b) in some cases, for example Cr_2O_3 , the catalyst itself was oxidized irreversibly to a higher oxidation state during the decomposition, and (c) since the higher the electrical conductivity of the oxides, the higher the resultant catalytic activity, the decomposition might proceed through a charge-transfer mechanism, being at least in part ionic. Furthermore, they reported the interesting fact that Fe_2O_3 , although an n -type semiconductor, exhibited a catalytic activity comparable with that of p -type semiconductors.

Otto and Fry [1] described that the isothermal decomposition of KClO_4 containing Fe_2O_3 was unimolecular, that the rate constant was proportional to the amount of catalyst added, and that the sample in the course of decomposition was free from chlorate.

In a series of studies on the thermal decomposition of alkali metal perchlorates, Markowitz and Boryta [14] gave the heats of crystallographic transition, fusion and decompositions of KClO_4 , and also suggested that the role of MnO_2 as catalyst was the abstraction of atomic oxygen produced in the primary decomposition step.

The present paper is mainly phenomenological and introductory to the final objects, the elucidation of the mechanism of catalytic thermal decomposition of KClO_4 by Fe_2O_3 and the effect of the preparing history of the oxides on the catalytic activity; however, some discussion of the results is given on the basis of the *n*-type semiconductive properties of Fe_2O_3 .

Experimental

DTA. The gas-flow DTA apparatus (Fig. 1) consisted of two quartz tubes (i.d. = 10 mm) placed vertically in the furnace, one used as sample compartment and the other as reference compartment. The apparatus was designed to permit

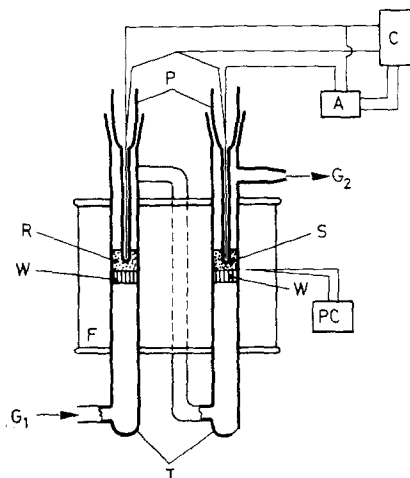


Fig. 1. Gas-flow type DTA apparatus. C: recorder, A: amplifier, PC: program temperature controller, G_1 , G_2 : gas inlet and outlet, F: furnace, W: quartz wool, S: sample, R: reference, T: quartz tube, P: inner quartz tube

any kind of gas flow through the sample layer. The pulverized sample and reference material were kept at a fixed position in the tube by underlying loosely-packed quartz wool. The sensor of the CA-thermocouple ($d = 0.3$ mm) in the inner tube was positioned at the center of the sample or reference material. The heating rate was controlled by an ECP-51B type program controller (Ohkura Electronic Ins.), and the differential temperature was recorded on a 25SB4-IR-6 type millivolt recorder (Ohkura) through an AM1001B type microvolt meter (Ohkura). The thermocouple was calibrated against the melting points of Sn, Pb and Zn. The reference material was 1 g of Al_2O_3 (-150 mesh) (Merck) calcined at 1290° for 3 hours. Samples of a total weight of 1 g were prepared by mixing KClO_4 (-200 mesh) and Fe_2O_3 (-300 mesh) with Al_2O_3 in an agate mortar. Al_2O_3

was used as the diluent to prevent the melt from falling in drops through the quartz wool layer.

TG. The apparatus used consisted of a quartz spring (sensitivity, 3.25×10^{-3} g/mm) and a quartz reaction tube ($d = 40$ mm) connected to a vacuum system. The sample of 0.1 g of a mixture of KClO_4 , Fe_2O_3 and Al_2O_3 (weight ratio = 4 : 1 : 5) was placed in a cylindrical quartz dish (10×10 mm) and evacuated at 10^{-3} mm Hg before heating. The weight decrease of the sample at constant volume and under the pressure of the evolved oxygen was measured with a cathetometer as a function of temperature, which was measured with a CA-thermocouple attached at the outer wall of the reaction tube.

X-ray diffraction. The diffractometer used was of Geigerflex 2141 type (Rigaku Denki Co.), and was operated under the following conditions; Cu-target, Ni-filter, 25 kV, 10 mA, $2^\circ/\text{min}$, and 1 sec-time constant. A Co-target and a Fe-filter were used for Fe_2O_3 . The crystallite size of Fe_2O_3 was evaluated from the breadth of the X-ray diffraction line in comparison with that of NaCl as standard [19].

Infrared spectra. IR absorption spectra were measured with an IR-E type spectrometer (Japan Spectroscopic Co.) in the range $700-4000 \text{ cm}^{-1}$, and an EPI-G2 type (Hitachi) in the range $400 \sim 4000 \text{ cm}^{-1}$. In all cases, the tablet for the IR spectra was prepared by mixing 2 mg of sample with 498 mg of KBr, followed by pressing the mass at 10 tons/cm^2 .

Specific surface area. The surface area of Fe_2O_3 was calculated by the BET method from the amount of Ar adsorbed at liquid nitrogen temperature. 14.6 \AA^2 [20] was employed as the cross-sectional area of Ar.

Density. Pycnometric density measurement for Fe_2O_3 was carried out at 20° using CCl_4 and taking its density as 1.5942 g/cm^3 [21]. Prior to measurements, Fe_2O_3 in a pycnometer half-filled with CCl_4 was evacuated for 30 minutes at a pressure of 20 mm Hg to expel included air.

Chemical analysis of ClO_3^- . Qualitative analysis was performed by observation of the white precipitates formed by Ag^+ with Cl^- resulting from the reduction of ClO_3^- by NaNO_2 in nitric acid solution.

Materials. KClO_4 (Kanto Chemical Co., Inc., GR grade) was recrystallized from distilled water. Thirteen Fe_2O_3 catalysts were prepared by 1-hour isothermal pyrolysis of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Kanto) in air at 700 , 800 and 900° , and of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Kanto) at 500 , 600 , 700 , 800 and 900° in air and in oxygen (see text).

Results and discussion

Influence of atmospheric conditions, recrystallization, particle size and amount of catalyst. There are essentially two endothermic peaks and an exothermic peak in the DTA curve of pure KClO_4 when measured in air. The solid-phase transition of the perchlorate from the rhombic to the cubic form results in the first endothermic peak (peak temperature designated as T_1) around 300° . The

second endothermic peak corresponds to the fusion of the solid perchlorate (T_f), followed by the exothermic peak of the decomposition (T_d). It has been found that the DTA profiles are influenced by factors such as the atmosphere, particle size and impurities [7, 22, 23]. The DTA curves of KClO_4 recrystallized zero, three and five times did not differ significantly. Fig. 2 shows DTA curves of KClO_4 (-200 mesh) measured in air at various flow rates. No significant change of the peak positions is observed in the Figure. Similar results were obtained for N_2 and O_2 . Rudloff and Freeman [17] also found the influences of N_2 and O_2 on the DTA curves of KClO_3 to be insignificant. Next, two sieve fractions of KClO_4 with particle sizes of 155~200 mesh and under 200 mesh did not give any change in the peak positions. Finally, the change of T_d was measured in air for KClO_4 (-200 mesh) containing different amounts of catalyst. As seen in Table 1, T_d decreases with the amount of catalyst and changes according to the preparing history of the catalyst.

Table 1
Effect of the amount of catalyst on the exothermic peak temperature (T_d) of the decomposition

Amount of catalyst (mol %)	T_d , °C			
	543	Fe ₂ O ₃ catalyst		
		A ^{a)}	B ^{b)}	C ^{c)}
0	543			
1.39		538	—	539
3.49		531	541	539
7.52		520	535	538
12.4		516	529	537
17.8		512	525	533
29.0		511	519	530

a) obtained from $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ calcined at 800° for 1 hr

b) obtained from $\text{Fe}(\text{OH})_3$ calcined at 300° for 1 hr

c) obtained from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ calcined at 800° for 1 hr

In subsequent experiments, all measurements were carried out by employing the recrystallized KClO_4 with a particle size of -200 mesh, Fe_2O_3 of -300 mesh, static air, and a fixed mixing ratio $\text{KClO}_4 : \text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3 = 4 : 1 : 5$ by weight.

Preparation of Fe₂O₃ catalysts. The results of DTA experiments in air showed that an endothermic deflection corresponding to the decomposition of FeSO_4 appeared between 650° and 780°, with the peak at 750°. Balek [24] showed by chemical analysis that $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ decomposed completely at 700° and that no anion traces were present. Thus, temperatures above 700° were taken for the preparation of Fe_2O_3 by isothermal decomposition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. After having been washed carefully with hot water, Fe_2O_3 obtained at 700° was found to be free

from SO_4^{2-} in tests with Ba^{2+} and by inspection for SO_4^{2-} IR absorption bands at 983 cm^{-1} and 1105 cm^{-1} . Brown and Bevan [25] have proposed a decomposition mechanism for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ on the basis of the results of DTA, TG and X-ray experiments. In the present experiment, DTA curves of the oxalate measured in air showed two exothermic peaks at 462° and 517° . From X-ray data, these

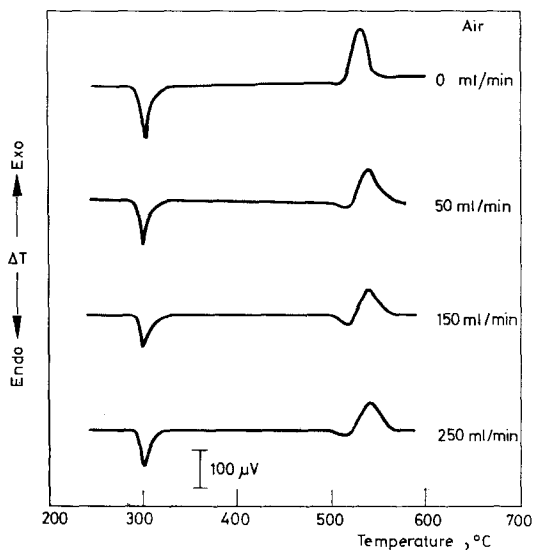
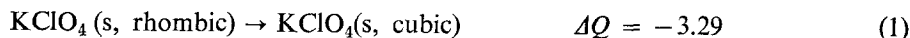


Fig. 2. DTA curves of KClO_4 in air at various flow rates. KClO_4 : -200 mesh, 100 mg; Al_2O_3 : -150 mesh, 800 mg; $\Phi = 4.4^\circ/\text{min}$

were found to correspond to the decomposition and the oxidation of FeC_2O_4 , respectively. The product of 1-hour pyrolysis of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at 500° gave the X-ray diffraction pattern of pure $\alpha\text{-Fe}_2\text{O}_3$, but the existence of a small amount of FeO was detected in the product obtained by 3-minute pyrolysis under the same conditions. On the basis of these results, Fe_2O_3 catalysts used in the present experiments were prepared by isothermal pyrolysis for 1 hour at temperatures above 700° for $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and above 500° for $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$.

Decomposition of KClO_4 . Markowitz and Boryta [14] give the heats of reactions (ΔQ , kcal/mole) as follows:

Transition of crystal structure:



Fusion:



Decomposition:





Fig. 3 shows typical DTA results of the catalytic decomposition. The endothermic peak around 300° arising from the solid-phase transition (Eq. 1) appears

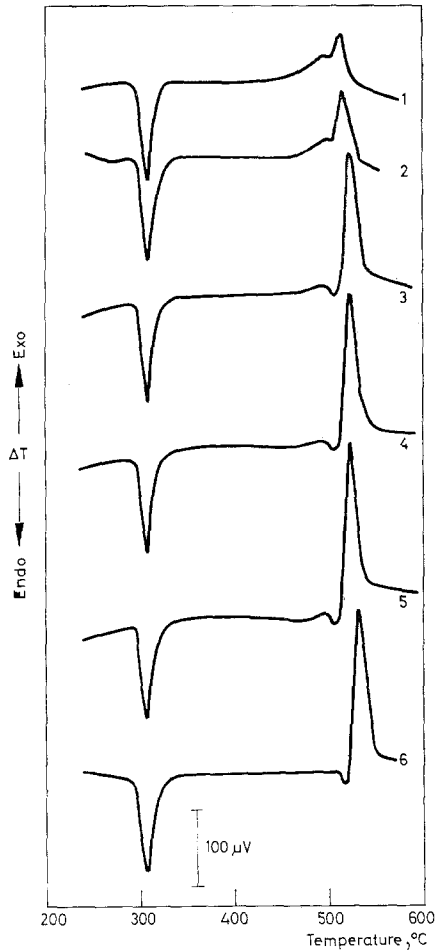


Fig. 3. DTA curves of KClO_4 containing Fe_2O_3 prepared from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by pyrolysis in air. Pyrolysis temperature: (1) 500° , (2) 600° , (3) 700° , (4) 800° , (5) 900° ; mixing ratio: $\text{KClO}_4 : \text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3 = 0.4 \text{ g} : 0.1 \text{ g} : 0.5 \text{ g}$; curve (6): $\text{KClO}_4 : \text{Al}_2\text{O}_3 = 0.4 \text{ g} : 0.6 \text{ g}$. $\Phi = 4.4^\circ/\text{min}$

in all the DTA curves, and its peak temperature (T_f) does not depend on the presence or the temperature of preparation of the catalyst. KClO_4 without catalyst but with Al_2O_3 shows the peaks of endothermic fusion (T_f) and exothermic decomposition (T_d) to be $60 \sim 100^\circ$ lower than the corresponding temperatures for pure KClO_4 reported in the literature [7, 12–14, 16, 18]. Rudloff and Freeman observed the lowering of T_f and T_d by about 60° by addition of Al_2O_3 to pure KClO_4 , although the catalytic activity of Al_2O_3 was found to be the least for the catalysts which they studied (Fig. 6, curves 13 and 14 in Ref. [18]). In the present experiments, Al_2O_3 was used as diluent to prevent the molten phase of KClO_4 from falling in drops, but the comparison of the catalytic activities of Fe_2O_3 samples with different preparing histories is possible, since the ratio $\text{KClO}_4 : \text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3$ was fixed in all experiments.

It is found in Fig. 3 that (a) both T_f and T_d increase in all cases with increase of the temperature of preparation of the Fe_2O_3 , (b) the addition of catalyst results in an exothermic deflection in the low-temperature range before the appearance of the endothermic peak of fusion, and (c) the area under this exothermic deflection seems to increase with decrease of the temperature of preparation of the Fe_2O_3 .

Fact (b) is considered to show that the addition of catalyst leads to the solid-phase decomposition before fusion [18]. Fig. 4 contains the DTA and X-ray diffraction patterns of partially decomposed samples. The samples for X-ray measurements were obtained by being cooled at room temperature, after having been heated up to the temperatures indicated in the Figure. The catalyst used was Fe_2O_3 prepared at 500° from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. In this Figure, the diffraction lines of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ are omitted, because no change was observed in them before and after the decomposition. It is seen in Fig. 4 that KCl is formed by decomposition of KClO_4 at stages 3 and 4, at which the endothermic fusion does not still appear in the DTA curve. This may confirm the solid-phase decomposition. The intensity of KCl lines increases and of KClO_4 lines decreases with temperature. In the case without catalysts, the X-ray data showed that the diffraction lines of KCl appear immediately after the beginning of the endothermic fusion of the KClO_4 , and the intensity then increases steeply with the progress of the decomposition in the molten phase. The existence of KClO_3 was not observed in the X-ray patterns of the samples with and without catalyst.

As seen in Fig. 3, the ratio of the area under the endothermic fusion peak to that under the endothermic solid-phase transition peak is evidently smaller than 0.7, which is the ratio between the ΔQ values of Eq. (2) and Eq. (1). This may be interpreted by assuming that the observed endothermic fusion peak represents the resultant of endothermic processes (Eqs (2) and/or (7)) and exothermic processes (Eqs (3), (4) and/or (5), (6), (8)) [14]. The lowering of T_f (fact (a)) may be attributed to KCl produced by solid-phase decomposition. Harvey et al. [5] presented a phase diagram for the system $\text{KClO}_4\text{--KCl}(\text{KClO}_3)$ and showed that the temperature range of phase change from solid to liquid decreased with the decrease of the ratio KClO_4/KCl . The DTA curves in Fig. 3 show that the initial exothermic deflection due to solid-phase decomposition starts at a lower

temperature as the temperature of preparation of the catalyst is lowered. This indicates that the lower temperature of preparation results in the formation of KCl at the lower temperature, and thus in the lowering of T_f . From these results, the catalytic thermal decomposition of KClO_4 may be conveniently divided into two categories, the decomposition in the solid phase and the decomposition in the liquid phase [5, 18].

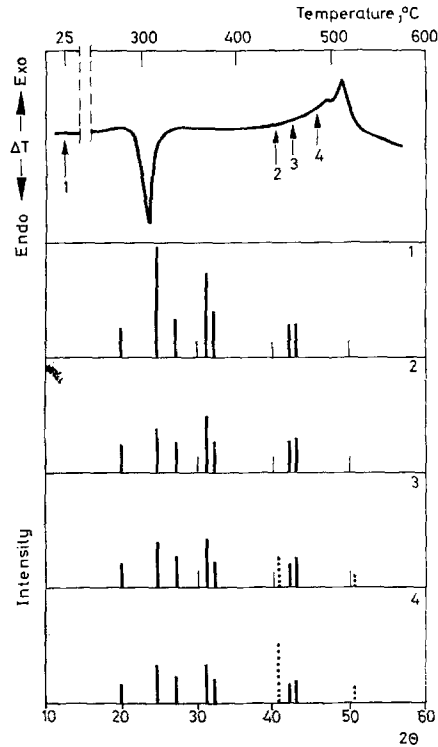


Fig. 4. DTA curves and X-ray patterns of partially decomposed KClO_4 containing Fe_2O_3 . Fe_2O_3 : from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ calcined at 500° in air. KCl , — KClO_4

Fig. 5 illustrates Kissinger plots [26] for the estimation of the activation energy of the liquid-phase decomposition from T_d at heating rates of 9.9, 7.1, 4.4 and $2.1^\circ\text{C}/\text{min}$. Open and full circles in the Figure indicate the data without and with catalyst (prepared from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at 800°), respectively. For the two cases, the reaction order estimated from the shape factor of DTA peak was 1.3 and 1.2, so that the liquid-phase decomposition may be approximated as a first-order reaction. Furthermore, the data in Fig. 5 are on a single line with a slope of 75 kcal/mole [5]. This shows that the catalytic effect of Fe_2O_3 is very small in the

liquid-phase decomposition. Another illustration is given in Fig. 6, which shows TG curves for samples with and without catalysts. In TG experiments, the temperature was measured with a thermocouple placed at the outer wall of the reaction tube, so that some temperature differences are seen in thermal profiles between the DTA curves in Fig. 3 and the TG curves in Fig. 6. The mutual com-

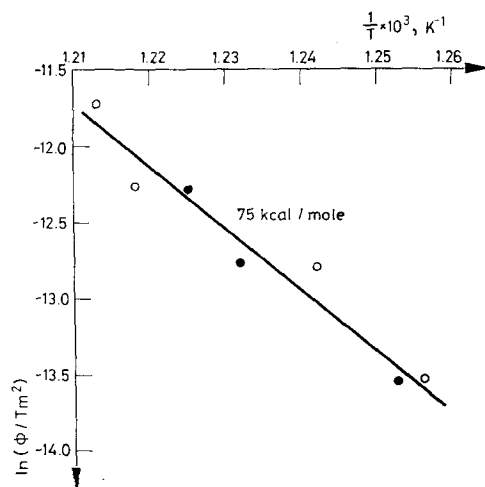


Fig. 5. Activation energy of the liquid-phase decomposition (Kissinger plot).
 ○ $\text{KClO}_4 + \text{Al}_2\text{O}_3$, ● $\text{KClO}_4 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ obtained from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at 800°

parison of the TG curves, however, is possible for differentiation of the catalytic effects of Fe_2O_3 with different preparing histories, since the TG measurements were carried out under the same experimental conditions. As seen in Fig. 6, the slopes of the TG curves in the region showing the steepest weight decrease are practically independent of the presence of catalyst and its preparation temperatures — the sample was liquefied in this region. This supports the conclusion of the small catalytic effect on the liquid-phase decomposition.

Fig. 7 contains DTA curves and IR spectra of partially decomposed samples. By referring to the IR spectra of pure KClO_4 and KClO_3 , it is found that the sample without catalyst (Fig. 7) simultaneously gives the weak absorption band of ClO_3^- and the beginning of the endothermic fusion (stage 2). The absorbancy increases thereafter with the progress of the decomposition, but it decreases after passing through the maximum value in stage 4 and becomes zero in the final stage. On the other hand, the sample containing catalyst showed a very weak band of ClO_3^- only at a temperature corresponding to T_d . From comparison of the absorbancies the amount of KClO_3 formed in the catalyzed decomposition was found to be smaller than in the uncatalyzed decomposition. Chemical analysis of ClO_3^- revealed the same results. If the decomposition of KClO_4 , as suggested

by Simchen [11], proceeds according to a successive reaction path, $\text{KClO}_4 \rightarrow \text{KClO}_3 \rightarrow \text{KCl}$ (Eq. (7) \rightarrow Eq. (8)), it is considered that the catalyst accelerates the latter step preferentially, so that the amount of ClO_3^- is small in the catalyzed decomposition. In addition to the successive reaction, if the direct decomposition from KClO_4 to KCl (Eqs (3) and (4)) occurs competitively, the catalytic decomposition is considered to proceed mainly through Eq. (3) or Eq. (4).

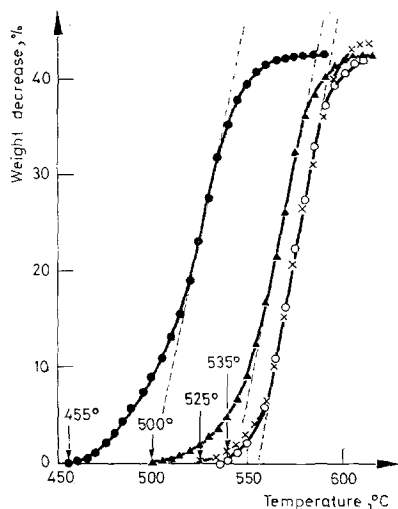


Fig. 6. TG curves of KClO_4 containing Fe_2O_3 prepared from $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ by pyrolysis in air. Pyrolysis temperature: \bullet — 500°, \blacktriangle — 700° and \circ — 900°; \times —: no catalyst; initial sample weight: 0.1 g, $\text{KClO}_4 : \text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3 = 0.4 \text{ g} : 0.1 \text{ g} : 0.5 \text{ g}$; $\Phi = 5^\circ\text{C}/\text{min}$

The pronounced catalytic effect seen in Fig. 6 is the change in the initial decomposition temperature (T_i), which increases with the temperature of preparation of the catalyst. This change in T_i is also observed in the corresponding DTA curves in Fig. 3; the lower the temperature of preparation of the catalyst, the lower the temperature of the initial exothermic deflection before the endothermic peak of fusion. The values of T_i determined from the TG curves are plotted in Fig. 8. Here we define T_i as the characteristic value indicating the catalytic activity of the Fe_2O_3 . From Fig. 8, it can be seen that the catalytic activity in the range of low preparation temperature decreases approximately in the order FeSO_4 in air $>$ FeC_2O_4 in O_2 $>$ FeC_2O_4 in air, and increases with decrease of the temperature.

Table 2 lists surface area, density and crystallite size of the catalysts. It is seen that the density increases with preparation temperature, except for Fe_2O_3 obtained by calcination of $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in O_2 , and that surface area decreases and crystallite size increases with the temperature. As found in Fig. 9, the plot

of the crystallite size as a function of the T_i determined from the TG curves (Fig. 6) shows a good relationship in that the latter increases with the increase of the value of the former. It can be presumed in general that Fe_2O_3 obtained

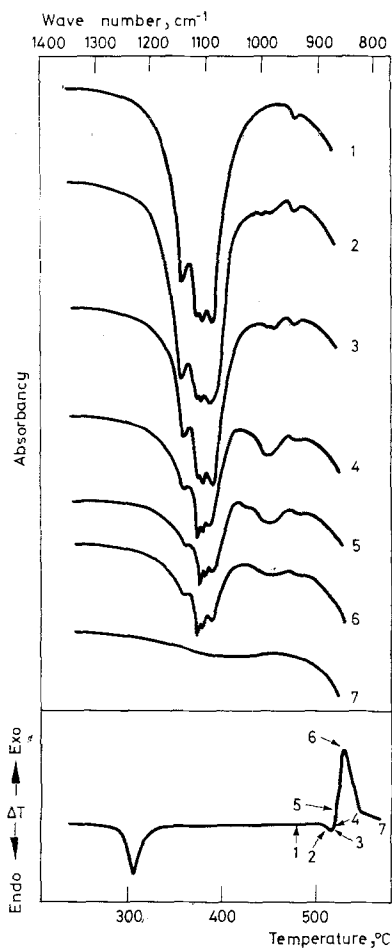


Fig. 7. DTA curve and IR spectra of partially decomposed KClO_4

by pyrolysis of iron salts grows at the higher calcination temperature into less distorted and less defective well-crystallized oxide. IR spectra of Fe_2O_3 catalysts showed that the absorbancy at 550 cm^{-1} and 450 cm^{-1} [27, 28] decreased, and their positions shifted to wavenumbers higher by $5 \sim 8\text{ cm}^{-1}$ with an increase in the temperature of preparation of the catalysts. Sato et al. [29] obtained a similar result for $\alpha\text{-FeOOH}$ with different ageing times, and concluded that this

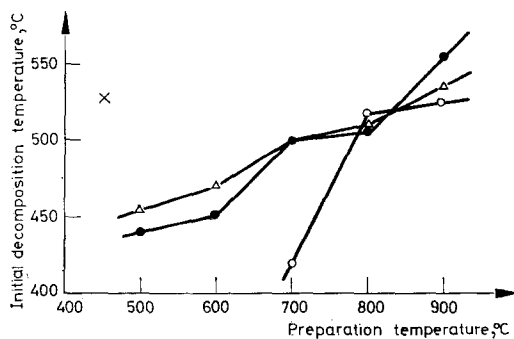


Fig. 8. Relation between initial decomposition temperature found by TG and temperature of preparation of catalysts.

Fe_2O_3 prepared from

- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, calcined in air
- $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in air
- △— $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in O_2
- × no catalyst

Table 2

Change in surface area, density and crystalline diameter of catalysts

Temperature of preparation of Fe_2O_3 , °C		500	600	700	800	900
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (calcined in air for 1 hr)	surface area (m^2/g)			31.0	9.9	3.7
	density (g/cm^3)			4.83	5.10	5.41
				4.78	4.89	5.49
	crystallite diameter (Å)			780	2510	2890
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (calcined in air for 1 hr)	surface area (m^2/g)	15.6	11.3	4.1	1.2	0.8
	density (g/cm^3)	5.00	5.09	5.04	5.23	5.23
			4.98	5.04	5.20	
			5.03	5.05		
crystallite diameter (Å)	810	1220	2070	2410	2880	
$\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (calcined in O_2 for 1 hr)	surface area (m^2/g)	20.6	8.5	7.2	6.2	3.0
	density (g/cm^3)	5.08	5.03	5.00	4.97	5.19
		5.08	5.17	5.09	4.97	4.95
			5.17	5.05	4.97	5.06
crystallite diameter (Å)	1280	1440	1860	1980	2600	

change in the IR spectra resulted from the increase in the crystallinity of the oxyhydroxide. The growth of crystallite of Fe_2O_3 can therefore presumably be used as a parameter of the increase of crystallinity.

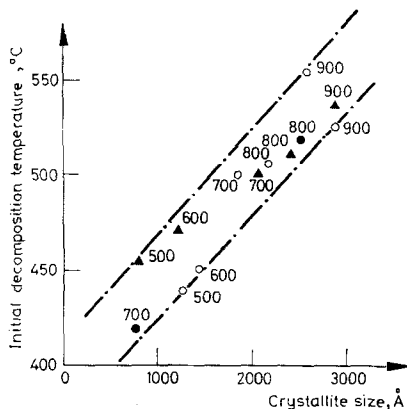
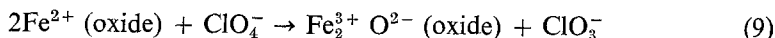


Fig. 9. Relation between crystallite size and initial decomposition temperature.

Fe_2O_3 prepared from {
 -●- $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, calcined in air
 -○- $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in O_2
 -▲- $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, in air
 Preparation temperatures are indicated in the Figure

$\alpha\text{-Fe}_2\text{O}_3$ is usually classified as an n -type semiconductor, with the metal ion in slight excess. According to Morin [30, 31], the donor center in the oxide is provided by the excess Fe^{2+} , which ionizes into Fe^{3+} to give the conduction electron. Pryor and Evans [32] have confirmed the existence of Fe^{2+} in $\alpha\text{-Fe}_2\text{O}_3$ calcined at fairly high temperature. It has been reported that oxygen did not chemisorb on $\alpha\text{-Fe}_2\text{O}_3$ at low temperature [33], but that the depletive chemisorption of oxygen at 100° resulted in a decrease of the electrical conductivity and the oxygen desorbed at same temperature under a pressure of 10^{-6} mm Hg, followed by the restoration of the conductivity [34]. On the other hand, the decomposition of KClO_4 can be regarded as a reduction of Cl^{7+} to Cl^{5+} or Cl^- . It may be speculated, therefore, that at around 400° , at which temperature the catalytic decomposition starts, the interaction between catalyst surface and chemisorbed oxygen of ClO_4^- promotes the ionization of the donor ion $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e$, and the electrons thus produced transfer to Cl^{7+} . Accordingly, the initiation of the decomposition of KClO_4 may probably be considered as follows:



The conductivity (σ) is expressed by

$$\sigma = \mu ne \quad (10)$$

where μ is the mobility, n is the concentration of conduction electrons and e is the charge of an electron. σ increases with n , which is a function of the concentra-

tion of donor centers (Eq. (11)). Rudloff and Freeman [18] concluded that the catalytic activity depended on the *p*-type semiconductive character, but they found that Fe_2O_3 , although of *n*-type, had a large conductivity, and an exceptionally high catalytic activity, i.e. a low T_i value. One of the possible explanations for this is that the Fe_2O_3 had a higher concentration of donor centers than the other *n*-type oxides (MgO , Al_2O_3 , TiO_2 and ZnO) which they used in the experiments, so that the reaction of Eq. (9) occurred more frequently even at low temperature (see below).

Mott and Gurney [35] have given an equation for n :

$$n = (N_D)^{1/2} \left(\frac{2m_e k_B T}{h^2} \right)^{3/4} \exp \left(\frac{-w_i}{2k_B T} \right) \quad (11)$$

where N_D is the number of donor center, m_e is the mass of an electron, w_i is the ionization energy of a donor center, and the others are well-known symbols. If the temperature-dependence of μ in Eq. (10) can be neglected, the slope of the plot of σ against $1/T$ gives the value of w_i . Okamoto et al. [36] found that hydrous ferric oxide aged in water for different periods had a decreased w_i and an increased surface area with a decrease in the crystallinity. Furthermore, according to Meyer's rule [37] the value of w_i is decreased by interaction between the donor centers, when their concentration is high. Since a small w_i means the ionization of the donor at low temperature, it is considered that the low crystallinity of Fe_2O_3 results in the low ionization energy and thus in the low initial decomposition temperature.

Conclusions

1. The decomposition of KClO_4 was not influenced by the atmospheric conditions.
2. $\alpha\text{-Fe}_2\text{O}_3$ acted as the catalyst mainly in the initial solid-phase decomposition. The liquid-phase decomposition was affected very slightly by the catalyst. The activation energy of the liquid-phase decomposition, estimated by Kissinger's method, was 75 kcal/mole both with and without catalyst.
3. KClO_4 containing no catalyst began to melt and to decompose simultaneously and KClO_3 formed as a reaction intermediate. Addition of catalyst resulted in the solid-phase decomposition and depressed the formation of the intermediate. The initial decomposition temperature increased with the temperature of preparation of the catalyst.
4. The change in initial decomposition temperature was correlated with the crystallinity of the Fe_2O_3 . The oxide with low crystallinity was presumed to have a high concentration of donor centers and a low ionization energy, which led to a low initial decomposition temperature.

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RÉSUMÉ — Etude par ADT, TG, RX et IR de la décomposition catalytique de KClO_4 par Fe_2O_3 obtenu par calcination de sels de Fe(II) à différentes températures. En l'absence de catalyseur l'échantillon commence par fondre tout en se décomposant et il se forme inter-

médiairement KClO_3 . En présence de catalyseur, la décomposition de la phase solide précède la fusion de KClO_4 et il n'apparaît que de faibles quantités de KClO_3 . Les différences de l'effet catalytique observées avec divers catalyseurs sont moins marquées dans la phase fondue que dans la solide. La température de décomposition initiale (T_i) augmente avec la température de préparation du catalyseur et est fixée par la granulométrie du catalyseur. Les variations de T_i sont discutées sur la base des propriétés de semi-conducteur type n , du catalyseur.

ZUSAMMENFASSUNG — Die katalytische Zersetzung von KClO_4 durch Fe_2O_3 , welches durch Kalzinierung von Fe(II)-Salzen bei verschiedenen Temperaturen erhalten wurde, wurde an Hand von DTA, TG, Röntgen und IR geprüft. Es wurde festgestellt, daß die Probe ohne Katalysator gleichzeitig zu schmelzen und sich zu zersetzen beginnt und ein Zwischenprodukt, KClO_3 , bildet. Die Zugabe von Katalysatoren ergab eine Zersetzung in der festen Phase, noch vor dem Schmelzen des KClO_4 und in kleinen Mengen des KClO_3 . Der Unterschied der katalytischen Wirkung verschiedener Katalysatoren war bei der Schmelzphasenzersetzung geringer als in der festen Phase. Die Anfangs-Zersetzungstemperatur (T_i) nahm mit steigender Herstellungstemperatur des Katalysators zu und zeigte einen ausgeprägten Zusammenhang mit der Kristallgröße des Katalysators. Die Änderungen von T_i wurden unter Erwägung der Halbleitereigenschaften vom Typ n des Katalysators erörtert.

Резюме — Исследован методами ДТА, ТГ, ИКС и рентгеноструктурного анализа каталитический распад KClO_4 под действием окиси железа Fe_2O_3 . погугленный кальцинированием солей Fe/II. J. Найдено, что без катализатора образец одновременно плавится и распадается, образуя промежуточный продукт KClO_3 . При добавлении катализатора до плавления KClO_4 происходит его твердофазное разложение и образуется в небольшом количестве KClO_3 . Установлено, что разница каталитического эффекта, наблюдаемого для различных катализаторов, была меньше при разложении в расплавленной фазе, по сравнению с твердой. Начальная температура распада (T_i) увеличивается с температурой приготовления катализатора и находится в определенной зависимости от размеров кристаллов катализатора. Обсуждается изменение T_i , исходя из n -тишных полупроводниковых свойств катализатора.