Journal of Thermal Analysis, Vol. 18 (1980) 359–369

THE CATALYTIC EFFECTS OF METAL OXIDES ON THERMAL DECOMPOSITION REACTIONS, III.

THE INFLUENCE OF STRUCTURAL AND ELECTRONIC DEFECTS IN IRON OXIDES ON THEIR CATALYTIC EFFECTIVENESS WITH RESPECT TO THE THERMAL DECOMPOSITION OF POTASSIUM CHLORATE

W. K. RUDLOFF* and E. S. FREEMAN

(Received May 21, 1979)

The catalytic activity of a series of iron oxides on the thermal decomposition of potassium chlorate was investigated by methods of thermal analysis. Structural and electronic defects were introduced into the oxide by doping, heat treatment in different atmospheres, and irradiation with γ-rays. These induced defects changed in a systematic way the conductive properties of the iron oxides and correspondingly, their catalytic activity. The results are consistent with an *n*-type semiconductive behavior of the oxides.

The thermal decomposition of potassium chlorate and its intermediate disproportionation product, potassium perchlorate, is catalized by metal oxides [1–8]. While most of these authors treated this catalized reaction from a phenomenological point of view, Solymosi and coworkers [8–11] discussed it within the context of electronic defects in the oxide catalysts.

In a preceding investigation we found that the most catalytically active metal oxides are those of transition metals [12]. Oxides that are generally considered to possess *p*-type semi-conductive properties were observed to be very active catalysts, while, with the exception of Fe_2O_3, *n*-type oxides were less active.

The purpose of the present study was to define in more detail the relationship between the type and degree of semiconductivity of Fe_2O_3 and its catalytic activity in the thermal decomposition of potassium chlorate. The structural and/or electronic defect nature of the oxide was systematically changed by doping with foreign cations, by heat treatment in various gaseous environments, and by irradiation. The electrical properties were determined by resistance measurements and correlated to the catalytic activity as reflected in thermal analysis experiments.

Experimental

Preparation and standardization of iron(III) oxides having different defect structures

(Sample *a*): Fe_2O_3 was precipitated as hydroxide (or hydrous oxide) with ammonia buffered by NH_4Cl, washed with hot 2% NH_4NO_3 solution, dried, and ignited at 700°.

---

* Present address: University of Petroleum and Minerals Dhahran International Airport, P. O. Box 144 UPM Box 48 Dhahran, Saudi Arabia

(Sample *b*): One part of the oxide in Sample a was heated to 800°.
(Sample *c*): Another part of the same oxide was heated to 900°.

In order to systematically investigate the influence of the defect structure on its catalytic activity, a series of iron oxides was prepared under identical conditions by the following procedure. Reagent grade iron chloride was dissolved in a slightly acidic medium, and the solution standardized. Equal parts of the solution were then pipetted and mixed with solutions of 1/2 mole % of various foreign cations. All the mixtures were then precipitated with ammonia buffered by NH_4Cl. The precipitates were filtered directly and then ignited in a muffle furnace at 700°. The following oxides were prepared:

(Sample *d*): Iron(III) oxide, pure, ignition 700°.
(Sample *e*): Iron(III) oxide, $+Li_2O$, ignition 700°.
(Sample *f*): Iron(III) oxide, $+BeO$, ignition 700°.
(Sample *g*): Iron(III) oxide, $+ZrO_2$, ignition 700°.

Parts of the original Fe_2O_3 (d) were taken and heated in different atmospheres to create defects.

(Sample *h*): Iron(III) oxide, heated in oxygen at 800°.
(Sample *i*): Iron(III) oxide, heated in oxygen at 900°.
(Sample *j*): Iron(III) oxide, heated in oxygen at 1000°.
(Sample *k*): Iron(III) oxide, heated in argon at 800°.
(Sample *l*): Iron(III) oxide, heated in argon at 900°.
(Sample *m*): Iron(III) oxide, heated in argon at 1000°.

It was expected that heating in argon at very high temperature would create a slight oxygen deficiency on the surface of the oxide. No appreciable weight loss could, however, be observed after the heat treatment.

The influence of γ-irradiation defects on the catalytic activity of oxides was investigated in another series of oxides. To this end, reagent grade iron(III) oxide was irradiated for 65 hours.

(Sample *p*): Iron(III) oxide, B & A reagent grade, code 1741 assay (Fe_2O_3) min 99.0%, γ-irradiated, 5×10^6 rads.

(Sample *q*): Iron(III) oxide, B & A reagent grade, unirradiated.

All chlorate-catalyst mixtures were weighed in the proper ratios and then mixed for several hours on a shaker, dried and stored in a desiccator.

Determination of relative catalytic activity by means of thermal analysis

A modified version of a Chevenard thermobalance [12] was used for simultaneous differential thermal analysis and thermogravimetry in order to compare the catalytic activity of the different iron oxides.

Measurement of semiconductive properties

The electrical conductivity measuring device has also been described in the cited publication. Determination of the electrical conductivity in various atmospheres provided us with ideas on the type of defects introduced.

Magnetic susceptibility measurements

Magnetic susceptibilities were measured on the modified iron oxides at room temperatures with a view to elucidating the catalytic role played by the unpaired *d* electrons in the thermal decomposition of $KClO_3$.

The magnetic-susceptibility apparatus utilizes the standard technique of measuring, with a non uniform magnetic field, the force exerted on a sample; it is shown in Fig. 1.

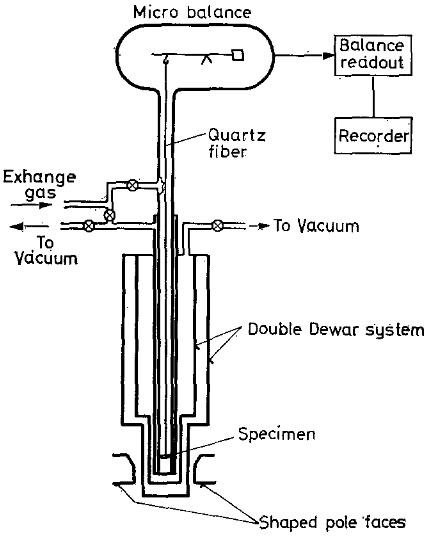

Fig. 1. Schematic representation of the magnetic susceptibility apparatus

For a sample of mass m in grams, in a magnetic field of H or with a vertical field gradient of $\mathrm{d}H/\mathrm{d}Z$, oe/cm at the sample, the vertical force F in dynes on the sample is given by

$$F = m\kappa H \frac{\mathrm{d}H}{\mathrm{d}Z} \tag{1}$$

where κ is the mass susceptibility. In our apparatus, a 4-inch electromagnet with shaped pole faces was used. This resulted in a $\left(H \frac{\mathrm{d}H}{\mathrm{d}Z}\right)$ of up to 3×10^7, $\mathrm{oe}^2/\mathrm{cm}$ calibration, using high-purity platinum metal of known susceptibility.

Vertical forces (showing up as weight changes in the sample) were measured by a Cahn electrobalance capable of weighing to parts of a microgram and having a graphic output.

All magnetic susceptibility measurements were made at ambient temperatures.

Results

Thermal analysis

The influence of foreign-cation doping on the catalytic activity of Fe_2O_3 with respect to the decomposition of $KClO_3$ is shown in Fig 2. It is seen that doping with Li^+ decelerates the reaction, while doping with Zr^{4+} accelerates it. Be^{++}-doped Fe_2O_3 decelerates at first, but the curve crosses the curve pertaining to the undoped oxide at around 400°.

The effect of heat treating Fe_2O_3 in argon and oxygen is seen in Fig. 3. If the oxide is preheated at 800 or 900° in oxygen, the decomposition of $KClO_3$ starts at higher temperatures than if preheated in argon. At higher temperatures (1000°) the difference between the oxygen- and argon-treated samples becomes negligible.

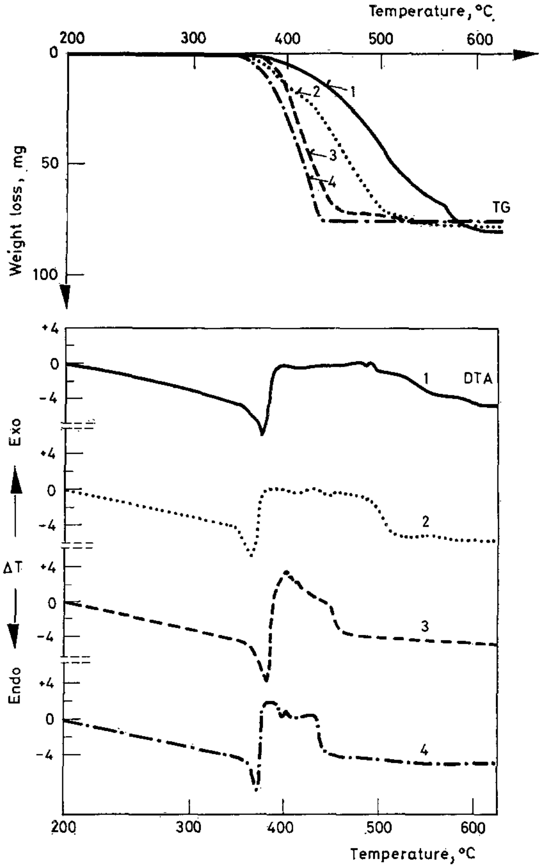

Fig. 2. The influence of doping on the catalytic activity of Fe_2O_3 with respect to thermal decomposition of $KClO_3$. 1 = Li doped Fe_2O_3; 2 = undoped Fe_2O_3; 3 = Be doped Fe_2O_3; 4 = Zr doped Fe_2O_3. Heating rate 10°/min; atmosphere, air; amount of $KClO_3$, 200 mg; ratio $Fe_2O_3/KClO_3 = 1/5$

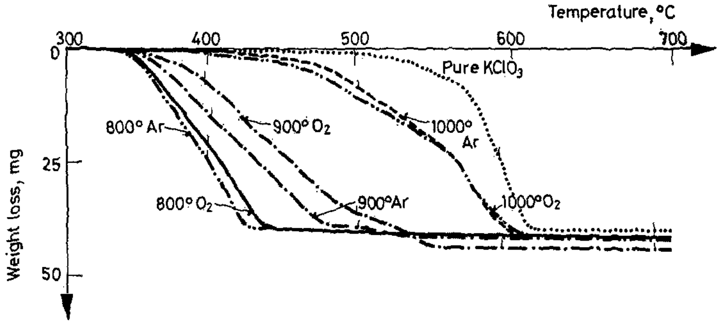

Fig. 3. TG curves of the catalytic activity of heat treated Fe_2O_3 on the decomposition of $KClO_3$ (oxides heated for 1 hr to the temperatures indicated)

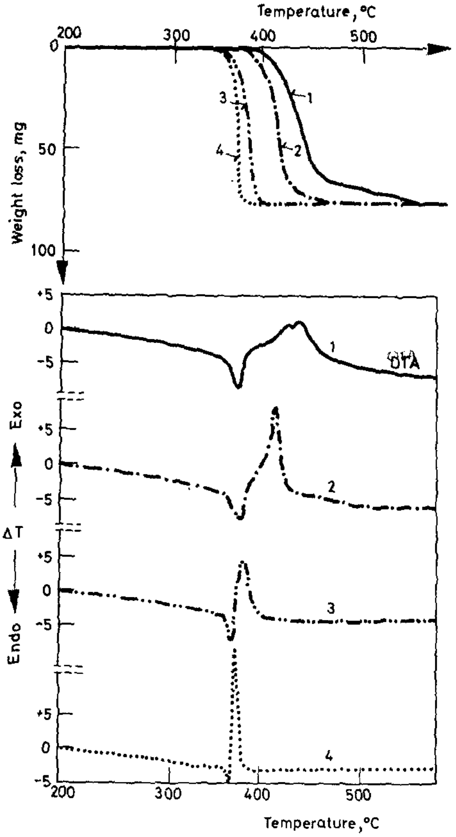

Fig. 4. Influence of irradiation on the catalytic activity of Fe_2O_3 with respect to decomposition of $KClO_3$. Mole ratio, Fe_2O_3: $KClO_3$. 1 = 1 : 20 unirradiated; 2 = 1 : 10 unirradiated; 3 = 1 : 20 irradiated; 4 = 1 : 10 irradiated. Weight of $KClO_3$, 200 mg; heating rate 10°/min; atmosphere, air

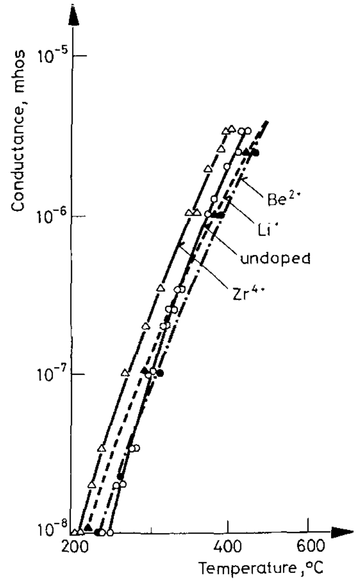

Fig. 5. Electrical conductance of doped Fe_2O_3 in air as a function of temperature

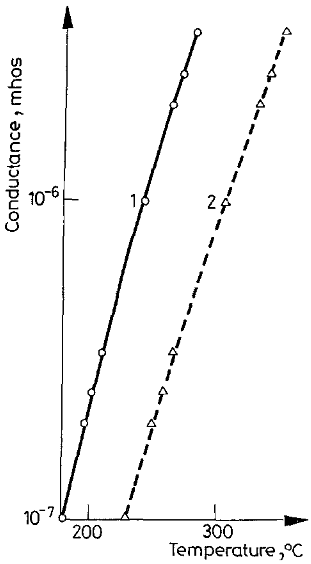

Fig. 6. Electrical conductance measured in air of Fe_2O_3 heat treated at 900° in (1) argon and (2) oxygen as a function of temperature

In Fig. 4 the thermal characteristics of irradiated Fe_2O_3 are compared with those of untreated reagent grade material. The decomposition of $KClO_3$ is initiated by the irradiated oxide at lower temperatures.

The electrical conductance of doped Fe_2O_3 is compared with that of the undoped oxide in Fig. 5. The order of conductance at above 350° is, Be^{2+}, Li^{+}, undoped, Zr^{4+}-doped Fe_2O_3.

The influence of heat treatment in oxygen and argon on the electrical conductance of Fe_2O_3 is shown in Figs 6 and 7, and it is observed that heat treatment in oxygen reduces the overall conductance as compared to heat treatment in argon.

Table 1 lists the analytical results of the dopant cation content in the oxides. It is seen that, except for Zr^{4+}, the dopant contents are less than 1 %. Tables 2 and 3 list the magnetic moments of heat-treated and -doped Fe_2O_3 samples, respectively. The magnetic moments decrease when the sample is heated in oxygen. The moments pertaining to the doped oxides decrease in the order Zr^{4+}, Be^{2+}, undoped, Li^{+}.

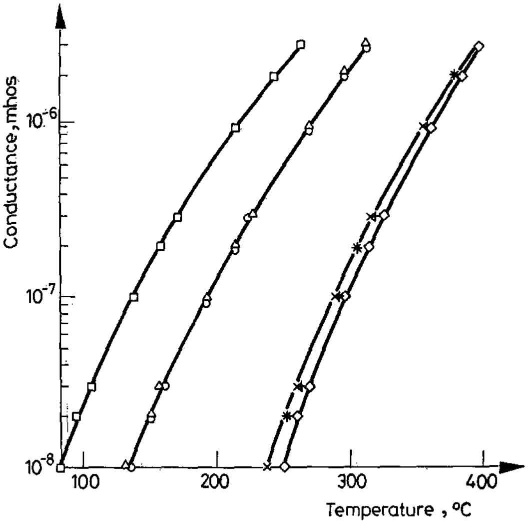

Fig. 7. Electrical conductance of a Fe_2O_3 pellet as a function of temperature. (Reversible treatment in different atmospheres on the same sample)

No	Heat, treatment		Heating duration above 500 °C in min	Atmosphere of conductivity experiments
	to temperature, °C	in atmosphere		
1	950	Ar	100	Ar
2	950	Ar	100	O_2
3	950	O_2	107	O_2
4	950	Ar	187	Ar
5	935	O_2	132	O_2
6	935	O_2	132	Ar

Table 1

Analysis of doped Fe_2O_3

Dopant	Weight, (%)	Precision, (%) estimate
Li	0.0050	±0.0003
Be	0.0170	±0.0006
Zr	1.3400	±0.0300

Table 2

Magnetic moments of Fe_2O_3 heat treated in different atmospheres

Sample treatment	Magnetic moment (Bohr magneton)
Prepared at 700° in air	3.81
Heated at 800° in Argon	3.75
Heated at 800° in Oxygen	3.65
Heated at 900° in Argon	3.75
Heated at 900° in Oxygen	3.69
Theoretical sample completely ionized as Fe^{+3}	5.90
Same, as Fe^{2++} or Fe^{4+}	4.90

Table 3

Magnetic moments of doped Fe_2O_3

Doping cation	Magnetic moment (Bohr magneton)
Zr^{4+}	4.27
Be^{2+}	4.15
Undoped	3.81
Li^{+}	3.76

Table 4*

Activation energies of the charge
Transport in heat-treated Fe_2O_3
(From conductance measurements on the same Fe_2O_3 pellet)

Consecutive run No.	Treatment at 955°	Activation energy (kJ/mole)
1	Heated in Ar	64
2, 3	Heated in O_2	110
4	Heated in Ar	50
5, 6	Heated in O_2	105

* Evaluated from Fig. 7

Discussion

Fe_2O_3 is classified as an *n*-semiconductor [13] and the trends observed in the electrical properties of our catalysts indicate the typical characteristics of such semiconductors. For one, oxygen depletion of the catalyst surface through heating to relatively high temperatures in an inert atmosphere increases the overall electrical conductance of the iron oxide, while the opposite is observed, when the oxide is heated in an oxygen atmosphere (Figs 6 and 7). Secondly, doping with cations of valences other than Fe^{3+} alters the electrical conductance in such a manner that the lower-valent cations such as Li^+ produces apparently a higher resistance of the oxide at temperatures, where the catalized decomposition of $KClO_3$ takes place, while the higher-valent Zr^{4+} induces decreased resistance. (Fig. 5).

These observations are consistent with the following notation of semiconductivity:

$$Fe_2O_{3(\mathrm{surface})} \rightleftharpoons 3/2\ O_{2(g)} + 6e_{\mathrm{cb}} + 2\ Fe^{3+}o \qquad (2)$$

where the number of electrons in the conduction band of the oxide, e_{cb}, is increased due to oxygen loss from the surface, while interstitial Fe^{3+}o-ions are formed. Consequently, the overall conductance of the oxide increases, after the sample has been heated in argon.

In an oxygen atmosphere the reverse of Eq. (2) takes place. The number of electrons in the conduction band is decreased leading to lower electrical conductance of the oxides (Figures 6 and 7).

Substitution of Fe^{3+} with small amounts of Zr^{4+} increases potentially the number of electrons in the conduction band of the iron oxide at elevated temperatures, while doping with Li^+ has the opposite effect.

Magnetic moments of the iron oxides are also affected by the thermal history and impurity content of the samples (Tables 2 and 3). Generally, higher-valent dopant cations such as Zr^{4+} tend to augment the magnetic moment of the oxide, while lower-valent cations such as Li^+ have the opposite effect. (Note: the magnetic moments were determined at room temperature.) Oxygen-treated iron oxides show lower magnetic moments than those heat-treated in argon.

As a general assumption, paramagnetism which is reflected in the magnetic moments, is associated with unpaired electrons in partially filled energy bands of transition metals and/or metal oxides [14, 15] Thus, the delocalized electrons in the conduction band of the iron oxides contribute apparently to both, the electrical conductivity, and the magnetic moments of these oxides.

Comparing the catalytic activity of the same oxides with their electronic effects, we observe similar trends. Higher overall electrical conductivity at the temperatures of chlorate decomposition and/or higher magnetic moments appear to be related to higher catalytic activity with respect to the thermal decomposition of potassium chlorate (Figs 2 and 3). Figure 8 summarizes this correlation: the initial weight loss at about 375° as it is catalized by the oxides, is plotted as a function of their electrical conductivity at the same temperature. (Note: the weight loss was averaged from three TG experiments each.) We observe that even the Be^{2+} doped oxide which is more reactive than the undoped catalyst as far as the overall reaction is concerned, falls in line, if only the initiation reaction at lower temperatures is taken into account (see also Fig. 2). As a rough approximation, the initial weight loss is, of course, proportional to the reaction rate, since in TG experiments the heating rate was kept constant, and the temperature increment is thus proportional to the time increment. Thus, in the final analysis, the reaction rate of the catalyzed thermal decomposition of potassium chlorate appears to be a function of the semi-conductive properties (or electronic defect content) of the iron oxide catalysts.

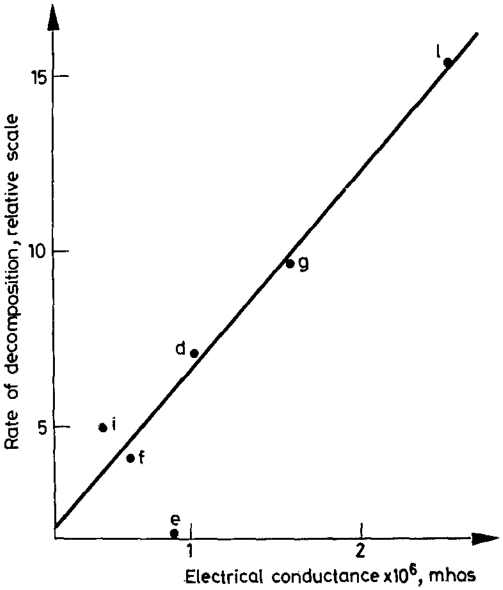

Fig. 8. Rate of initial $KClO_3$ decomposition as a function of the electrical conductance of iron oxide catalysts at 375°; d undoped and untreated; e Li^+ doped; f Be^{2+} doped; g Zr^{4+} doped; i heated at 900° in oxygen; l heated at 900° in argon

Iron oxides irradiated with gamma rays are also more reactive than untreated oxides emphasizing again that defect enhancement can significantly increase their catalytic activity (Fig. 4).

*

This work was supported by the U.S. Army Edgewood Arsenal under Project No. DA-18-035-AMC-341(A). The authors are grateful to Mr. B. Zeffert and Mr. Harry A. Brown for valuable discussions and useful suggestions.

The authors also wish to acknowledge Brent Boldt for the laboratory work which he conducted on this program.

References

1. H. A. NEVILLE, J. Am. Chem. Soc., 45 (1923) 2330.
2. F. E. BROWN, J. A. BURROUGHS and H. M. MCLAUGHLIN, ibid., 45 (1923) 1343.
3. J. A. BURROWS and F. E. BROWN, ibid., 48 (1926) 1790.
4. H. M. MCLAUGHLIN and F. E. BROWN, ibid., 50 (1928) 782.
5. S. S. BHATNAGAR, B. PRAKASH and J. SINGH, J. Ind. Chem. Soc., 17 (1939) 125.
6. F. E. BROWN and J. D. WOODS, Proc. Iowa Acad. Sci., 63 (1956) 410.
7. J. M. GAIDIS and E. G. ROCHOW, J. Chem. Educ., 40 (1963) 78.
8. F. SOLYMOSI and N. KRIX, Acta Chim. Acad. Sci. Hung., 34 (1962) 241.
9. F. SOLYMOSI and N. KRIX, J. Catal., 1 (1962) 468.
10. F. SOLYMOSI and K. JÁKY, J. Inorg. Nucl. Chem., 33 (1971) 2829.
11. F. SOLYMOSI and L. GERA, J. Phys. Chem., 75 (1971) 491.
12. W. K. RUDLOFF and E. S. FREEMAN, J. Phys. Chem., 74 (1970) 3317.
13. (a)W. E. GARNER, Chemistry of the Solid State, Butterworth Scientific Publications, London 1955; (b) O. KUBASCHEWSKI and B. E. HOPKINS, Oxidation of Metals and Alloys, Butterworth, Washington D. C. and London 1962, p. 24; (c) K. HAUFFE, Advan. Catalysis, 7 (1955) 213.
14. R. C. SAHNI, Symposium on the Chemical and Physical Effects of High-Energy Radiation on Inorganic Substances, Publ. by the American Society for Testing and Materials, 1964, p. 20.
15. G. C. BOND, Catalysis by Metals, Acad. Press, London and New York 1962. p. 20.

ZUSAMMENFASSUNG — Die katalytische Aktivität einer Reihe von Eisenoxiden gegenüber der thermischen Zersetzung von Kaliumchlorat wurde durch Methoden der Thermoanalyse untersucht. Strukturelle und elektronische Defekte wurden in das Oxid durch Dosierung, Wärmebehandlung in verschiedenen Atmosphären und Bestrahlung mit γ-Strahlen eingebaut. Diese induzierten Defekte änderten systematisch die Leitfähigkeitseigenschaften der Eisenoxide und dementsprechend ihre katalytische Aktivität. Die Ergebnisse stimmen mit dem Halbleiterverhalten des n-Typs der Oxide gut überein.

Резюме — Методами термического анализа была исследована каталитическая активность ряда окисей железа на процесс термического разложения хлората калия. Структурные и электронные дефекты были наведены в окиси путем легирования, тепловой обработки в различных атмосферах и облучением рентгеновскими лучами. Эти наведенные дефекты систематически изменяли проводимость окисей железа и, соответственно, их каталитическую активность. Результаты указывают на то, что окиси железа являются n-полупроводниками.