

Textural and catalytic properties of the $\text{Fe}_x\text{O}_y/\text{Fe}-\text{KClO}_4$ system

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Abstract

Selected properties of commercial iron powders, standardised in the atmosphere of hydrogen, have been studied. The reactivity of iron oxides in the thermal decomposition of KClO_4 in the solid-state mechanical mixture of Fe and KClO_4 containing 9, 13, 17, 21 and 25 wt.% of KClO_4 , respectively, has been tested by the differential thermal analysis (DTA) and thermogravimetric analysis (TG). It has been established that the Fe_3O_4 phase on the surface of the iron powder act as an effective catalysts in the thermal decomposition of KClO_4 .

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1. Introduction

The effect of different factors on thermal decomposition of potassium chlorate (VII) has been studied in many laboratories [1–3]. It has been established that in the presence of metal oxides, in particular those capable of different degree of oxidation, like Mn, Fe, Co and Ni, the temperature of KClO_4 decomposition is significantly lowered. For example, in the presence of Co_3O_4 this temperature decreases by 140 K [4,5]. From among the elements mentioned, the iron oxides in the form of pure phases such as $\alpha\text{-Fe}_2\text{O}_3$ [6,7] and FeO [8] have been applied as catalysts of the thermal decomposition of potassium chlorate (VII). The size of the KClO_4 grains [9] and the grains of the reductor has been shown to essentially affect the course of the reaction studied. The size of potassium chlorate (VII) grains can be changed by applying different conditions of crystallisation, while the size of reductor grains depends on the method and conditions of its obtaining. The most often used reductors are commercially available iron powder preparations [10]. They display a vari-

ety of surface properties following not only from the different way of preparation but depending mainly on the conditions of the final thermal treatment. On their surfaces there are many oxide phases occurring at different proportions, with the dominant phase Fe_3O_4 , and small contributions of the phases FeO and $\alpha\text{-Fe}_2\text{O}_3$ [11]. The iron oxide phases on the surface of the iron powders have been found to reveal catalytic activity in the reaction of potassium chloride (VII) decomposition by reducing the temperature of this reaction by about 180 K [12].

The aim of this study was to determine the effect of the textural properties of selected commercial iron powder preparations, after their standardisation, on their reactivity with potassium chloride (VII) in solid state

2. Experimental

2.1. Preparation of samples

The iron powders used in this study were samples of commercial products from POCH-Gliwice, Poland (Fe-1), MERCK (Fe-2), Riedel de Haen (Fe-3), KOCH Light Laboratories, (Fe-4). Prior to measurements, the preparations were

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standardised at 553 K, in air atmosphere for 1 h and then were kept in the dynamic atmosphere of 90% Ar + 10% H₂ at 563 K over a period of 2 h.

Commercial KClO₄ p.a. (Fluka) used in the study was subjected to preliminary crystallisation from H₂O and to the main crystallisation from EtOH–H₂O solution (1:1) in order to eliminate detectable quantities of the majority of impurities, e.g. Cl⁻, Na⁺. Moreover, the above procedure ensures obtaining sufficiently small grains without additional grinding.

Measurements were performed for mechanical mixtures of the commercial preparations of iron powders and potassium chlorate (VII), standardised prior to the measurements, in the form of tablets of about 0.8 mm thick and with a diameter of 6 mm, containing respectively 9, 13, 17, 21, and 25 wt.% KClO₄ and applying a pressure of 4 MPa.

2.2. X-ray diffractometry

X-ray analysis was performed for a mixture of iron powders and potassium chlorate (VII) in the form of tablets on a Philips powder diffractometer model PW 1070, using Co K α radiation and an iron filter. The patterns were recorded for $10^\circ < 2\Theta < 90^\circ$ at a counter step of 0.04° and for the time of pulse count of 2 s. The reflexes were identified with the APD (automatic powder diffraction) program provided by Philips. The measurements were performed for all iron samples studied in the form of powder and additionally for some samples in the form of tablets. Identification of various phases present in the mixture Fe–KClO₄ before as well as after the reaction of KClO₄ decomposition was carried out on the basis of a comparison of the XRD spectra with the data given by ASTM [13].

2.3. Surface area determination using BET method

Low temperature (77 K) krypton adsorption measurements were carried out using a sorption apparatus Micrometrics ASAP 2010. Prior to measurement, the samples were outgassed under vacuum 1.33×10^{-4} Pa at 403 K until constant weight, and then subjected to measurements of krypton adsorption and desorption. The BET equation was used to calculate the surface area.

2.4. Granulometric analysis

The grain size of the commercial iron powder preparations was measured by the laser light scattering method with the use of a granulometer made by Malvern Instruments model Mastersizer S in the range of particle diameters 0.04–900 μm . Samples of each of the preparations studied were mixed with a few drops (e.g. 2–3) of a surfactant (Nonidet P40 made by BDH) till getting a homogeneous paste, then it was introduced into distilled water and stirred in the granulometer attachment till getting a homogeneous suspension. The

concentration of the surfactant used was 0.02 wt.%. For the sample of pure KClO₄, making a relatively stable suspension with EtOH, no surfactant was added. The suspension was subjected to ultrasounds and after about 3 min the grain size distribution was measured. The results of measurements are presented in the form numerical distribution as a function of particle diameters and as a particle size concentration in percentage.

2.5. Temperature programmed reduction (TPR)

The temperature programmed reduction (TPR) experiments were carried out by means of a specially constructed instrument composed of a gas chromatograph with a thermal conductivity detector (TCD), electronic temperature controllers, a PC-818L card, allowing a collection of data from the conductivity detector and the furnace and sample thermocouples [14]. The conditions of the TPR measurements were as follows: temperature interval 298–1073 K, heating rate 40 K min^{-1} , specimen weight 10–120 mg, atmosphere 10% H₂ + 90% Ar (purity 99,999%), flow rate $50 \text{ cm}^3/\text{min}$. Taking into regard the complex character of the original TPR profiles they were subjected to smoothing and fitting procedure and the processed ones are shown in Fig. 3. The size of the peaks area was performed with the use of CuO as a reference material. All the TPR profiles were converted into mass equivalent.

2.6. Reactivity in the solid state between Fe and KClO₄

The reaction progress was followed by measuring the thermal effects in a differential thermo-analyser made by Netzsch model STA 409 C 3F in the measuring system differential thermal analysis/thermogravimetric analysis (DTA/TG) followed the reaction progress. The samples were heated at the rate of 40 K min^{-1} from room temperature to 1073 K in the dynamic atmosphere of inert gas (Ar) at the flow rate of $150 \text{ cm}^3 \text{ min}^{-1}$.

The reaction was carried out in a differential thermo-analyser made by Netzsch model STA 409 C 3F in the measuring system DTA/TG. The samples in the form of tablets were heated at the rate of 40 K min^{-1} from room temperature to 1073 K in the dynamic atmosphere of inert gas (Ar) at the flow rate of $150 \text{ cm}^3 \text{ min}^{-1}$. Reactivity of the commercial iron powder preparations subjected to standardisation in hydrogen atmosphere prior to the measurements, in mechanical mixtures with polycrystalline KClO₄ was assessed on the basis of the mass loss of the mixtures.

3. Results and discussion

3.1. Samples

The commercially available potassium chlorate (VII) preparation was analysed for the presence of main impurities:

Table 1
Contents of the main impurities contents in KClO_4 studied

Sample of KClO_4	Na^+	Cl^-
Initial	3.960	0.0088
After first step of crystallisation	0.248	<0.0005
After second step of crystallization	0.084	<0.0005

sodium and chloride ions, determined by the nephelometric analysis and atomic emission spectroscopy-inductively coupled plasma (AES-ICP).

The results given in Table 1 indicate that the crystallisation of KClO_4 from hot distilled water leads to a decrease in the concentration of chloride ions by one order of magnitude, e.g. to below the sensitivity of the analytical method used. In the case of sodium ions after the first step of crystallisation from aqueous solution their concentration decreases by about one order of magnitude as a result of the crystallisation from aqueous solution. After the second step of the crystallisation from EtOH–water (1:1) solution, a further decrease in the sodium ions concentration by about three times relative to the initial value was observed. The commercially available iron powders were standardised at 563 K in the atmosphere of 90% Ar + 10% H_2 , so at a temperature by 20 K lower than that at which hydrogen from the gas phase is built into the iron structure [15]. Moreover, hydrogen can react with iron forming FeH_x , whose presence has a significant effect on oxidation with KClO_4 [16].

3.2. X-ray diffractometry

Diffractograms of the KClO_4 sample studied revealed the presence of narrow diffraction lines assigned only to the potassium chlorate (VII) phase. Diffractograms of all iron powder preparations revealed the presence of the α -Fe phase but of a different degree of crystallisation as indicated by the FWHM of the reflexes [11].

Diffractogram of the tablet made of a mechanical mixture of the iron powder Fe-4 and potassium chlorate (VII) containing 17 wt.% of KClO_4 prior to the reaction of its decomposition revealed the presence of α -Fe and KClO_4 . Relative intensities of the reflexes obtained from the top and the bottom surface of the tablet were identical. The broadening of the reflexes assigned to the iron powder indicates the appearance of internal stress of II kind on tablet making. The diffractogram of the tablet after the decomposition of KClO_4 indicated a different phase composition at the top and bottom surface of the tablet, confirmed also by the difference in their colour. The phases identified on the top surface of the tablet were KCl, Fe_3O_4 , α - Fe_2O_3 and α -Fe (see Fig. 1A), while the phases identified on the bottom surface were a small amount of KCl and relatively great amounts of Fe_3O_4 , FeO and α -Fe (see Fig. 1 B). The differences in the amount of KCl are due to migration of the melted KCl towards the top surface of the tablet. The presence of α - Fe_2O_3 in the near-surface layer of

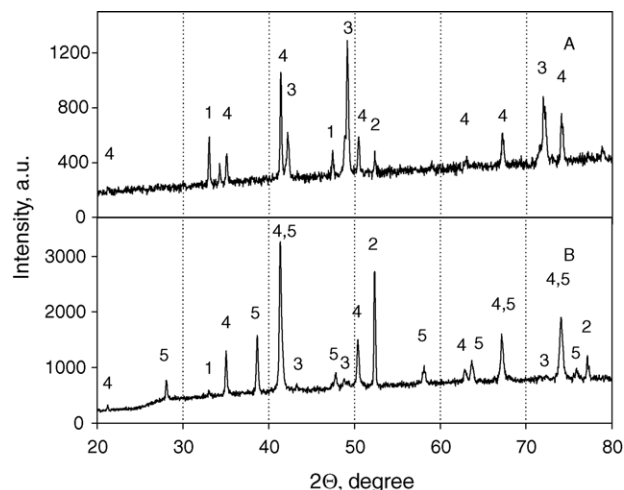


Fig. 1. X-ray diffraction patterns of the Fe-4- KClO_4 system in the form of a tablet containing 17 wt.% potassium chlorate (VII) KClO_4 , after the decomposition reaction: (A) upper side of the tablet and (B) bottom side of the tablet; identified phases: (1) KCl; (2) α -Fe; (3) FeO; (4) Fe_3O_4 ; and (5) α - Fe_2O_3 .

the tablet is caused by the oxidation of the iron powder surface with the oxygen released on the thermal decomposition of KClO_4 .

3.3. Surface area determination using BET method

The surface area of the commercially available iron powder preparations Fe-1, Fe-2, Fe-3 and Fe-4 takes relatively small values of 0.69, 0.31, 0.88 and $0.37 \text{ m}^2 \text{ g}^{-1}$, respectively. The shape of the isotherms of nitrogen adsorption/desorption for the samples without preliminary standardisation proves that their porous structure is very poor and mainly determined by the presence of slit pores at the grain borders [11]. The standardisation applied generated only small changes in the surface area of the preparations. The increase in the surface area of the sample Fe-1 was most probably caused by a reduction of the α - Fe_2O_3 phase whose presence was identified before the standardisation by the TPR method. The surface area of the preparations Fe-2 and Fe-4 decreased, while that of Fe-3 remained unchanged.

3.4. Granulometric analysis

Numerical distribution of grains of the KClO_4 preparations studied, presented in Fig. 2, indicates that application of ultrasounds leads to formation of crystallites characterised by bidispersive nature of the distribution of grain diameters. This proves that grains of the size of about 2–3 μm and 10 μm dominate in the polycrystalline samples of KClO_4 studied.

As has been observed for the curves of the volumetric distribution, the curves of the numerical distribution of the grain

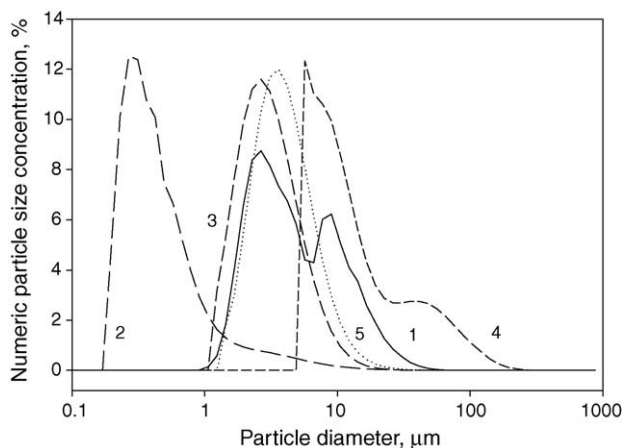


Fig. 2. Numerical particle size concentrations as a function of particle size for all samples studied: (1) KClO_4 ; (2) Fe-1; (3) Fe-2; (4) Fe-3; and (5) Fe-4.

sizes for samples Fe-2 and Fe-4 are similar. In these samples the grain diameter varies in the range 1.5–20 μm , with the maxima at 2.6 and 3.0 μm , respectively. The volumetric distribution shows that sample Fe-3 has grain sizes varying in the greatest range (5–250 μm) and the grains of the greatest size. The numerical distribution curve of grain size of this sample has three maxima: a strong one at about 8 μm , a broadened one at about 11 μm and another distinct one at about 45 μm .

The curve of numerical distribution of grain size for sample Fe-1 shown in Fig. 2 indicates the dominance of the grains in the range 0.2–10 μm , with those of the diameter close to 0.34 μm occurring in the greatest number. The above values are charged with some error because the shape of the grains differs from the spherical one. As has been reported earlier, the grains in this preparation have the shape of the scales [11,12].

3.5. Temperature programmed reduction (TPR)

The samples studied were subjected to the temperature-programmed reduction by hydrogen (TPR) to identify the iron oxides occurring on the surface of the iron powder preparations studied and to estimate the thickness of the layer they form on the surface of the grains. Fig. 3 presents the TPR profiles of all the samples studied. As follows from the profile obtained for sample Fe-1, the process of reduction takes place in two steps. The first reduction peak appears at 543 K, corresponding to the transition of Fe_3O_4 to FeO. The second peak is at 653 K [17,18] and corresponds to the transition of FeO to Fe. A comparison of the peaks area implies that the dominant phase is Fe_3O_4 , whose presence has not been revealed by the X-ray diffraction study. According to the analysis of the TPR profiles presented in Fig. 3, the dominant phase present on the surface of all samples studied is Fe_3O_4 accompanied by much smaller amounts

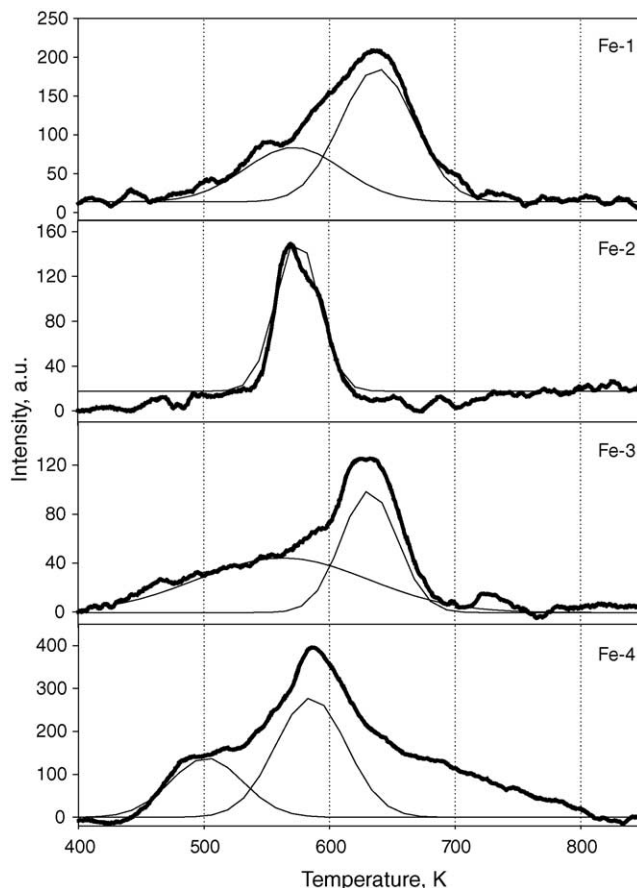


Fig. 3. Temperature-programmed reduction of the iron powder samples studied in the atmosphere of 90% Ar + 10% H_2 .

of FeO. No presence of the $\alpha\text{-Fe}_2\text{O}_3$ phase was detected, which follows from the standardisation conditions. Samples Fe-2 and Fe-4, characterised by similar parameters determined by granulometric studies and BET measurements, show significant differences in the amounts of iron oxides. In sample Fe-4 the amount of the oxides is almost three times greater than in Fe-2. The TPR curve of Fe-2 reveals only one maximum that can be assigned to the FeO phase. Interestingly, for sample Fe-3 characterised by the greatest surface area of 0.88 $\text{m}^2 \text{g}^{-1}$ the amount of oxide phases was not the greatest. The content of the dominant phase, which found to be Fe_3O_4 , changes in the following sequence Fe-4 > Fe-1 > Fe-3. It has been estimated the thickness of the iron oxides present on surface of iron powders on the basis of the size calibrated of the TPR profiles and BET surface area of the investigated samples. They were 1.5, 0.8, 0.5 and 3.0 nm for samples Fe-1, Fe-2, Fe-3 and Fe-4, respectively.

In the case of the TPR profiles samples of $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 strong broadening of peaks were observed. It may be explained different rates of the reduction of the oxide phases in the surface layer and in the bulk.

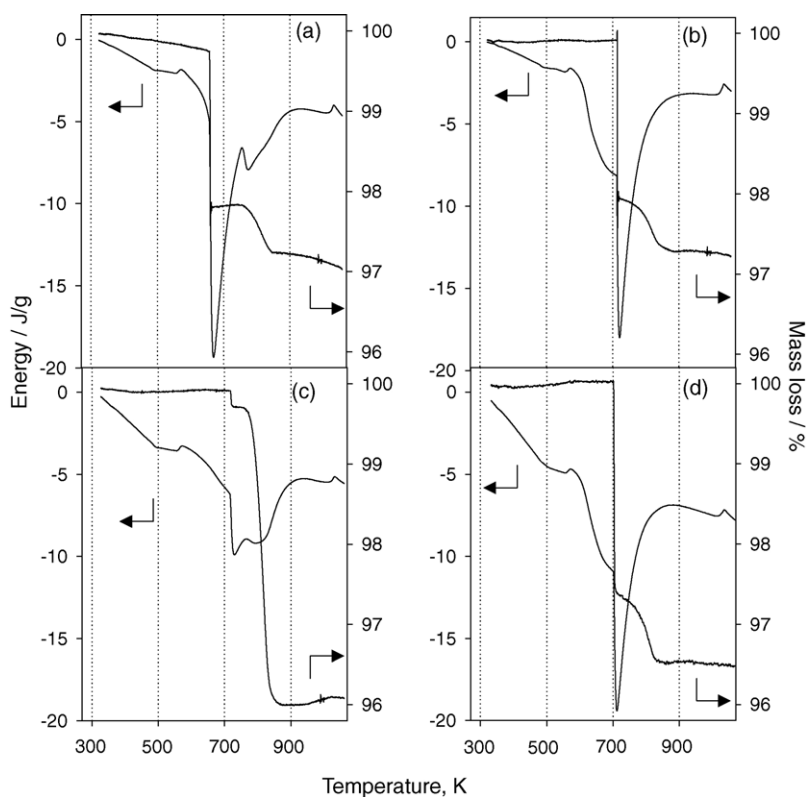


Fig. 4. TG-DTA curves of Fe–KClO₄ system containing 25 wt.% of potassium chlorate (VII) and samples of iron of different origin; (a) Fe-1; (b) Fe-2; (c) Fe-3; and (d) Fe-4.

3.6. Reactivity in the solid state between Fe and KClO₄

Fig. 4. presents the thermograms of mechanical mixtures composed of a given iron powder preparation Fe-1, Fe-2, Fe-3 or Fe-4 and KClO₄ in the amount of 25 wt.%. The DTA curves show an endothermic effect at 572.6 K that can be assigned to the reversible transition of KClO₄ from the rhombic into the regular phase, and an endothermic effect at 1043 K, assigned to the melting of KCl [19]. The temperatures of the above effects were used as internal standards for correction of the temperature of decomposition of potassium chlorate (initial decomposition temperature). For all samples the TG curves reveal two distinct stages related to the oxygen release during the process of KClO₄ decomposition. The first step of the thermal decomposition is related to the release of oxygen from the KClO₄ crystallites being in contact with the iron powder, while the second with the release of oxygen from the crystallites having no contact with the iron powder. The last stage may be also explained by a reduction of Fe₂O₃ produced in the first stage of decomposition of potassium chlorate (VII) to Fe₃O₄.

This process of reduction is not reflected in the DTA curves. A strong exothermic effect shown on DTA curves in Fig. 4 can be assigned to decomposition of KClO₄ and oxidation of the iron powder in which KClO₄ is in contact. The

temperatures at which mass loss is observed are different for different iron powder preparation. The lowest initial decomposition temperature of KClO₄ of 660 K, has been noted for Fe-1, while the highest of 720 K for Fe-3.

The energy effect corresponding to the first stage of decomposition is the lowest of 440 J/g, for Fe-3, while for the other iron powder preparations Fe-1, Fe-2 and Fe-4, it reaches 1200 J/g. Particularly interesting is the system Fe-3/KClO₄ with 25 wt.% of KClO₄, in which the majority of the oxidising agent is decomposed at 773–843 K, which is much different from the temperature of decomposition of pure KClO₄, equal 877 K [20]. Such a great difference in the temperatures of thermal decomposition of KClO₄ assigned to the effect of the reducing factor has not been observed yet (see Fig. 4 c). For this system a significant disproportion is observed in the mass loss at the first and at the second stages of KClO₄ decomposition. For the systems with Fe-2 and Fe-4, a similar character of the TG and DTA curves is observed. These systems differ in the temperatures of potassium chlorate (VII) decomposition and in the final mass loss due to the release of oxygen to the atmosphere (see Table 2).

As follows from the data given in Table 2, in all the Fe–KClO₄ systems studied, a decrease in the temperature of the thermal decomposition of KClO₄ and an increase in the heat released in the process are observed.

Table 2

Initial temperature of decomposition (K), heat of reaction (J/g) and conversion degree (%) of potassium chlorate (VII) in the system Fe–KClO₄

No.	Sample symbol	Content of KClO ₄ (wt.%)	Initial decomposition temperature (K)	Heat of reaction (J g ⁻¹)	Conversion of KClO ₄ (%)
1	Fe-1	9	728	516	0.7
2	Fe-1	13	720	862	8.3
3	Fe-1	17	706	1065	18.2
4	Fe-1	21	669	1354	22.2
5	Fe-1	25	660	1548	24.5
6	Fe-2	9	754	605	1.9
7	Fe-2	13	743	887	11.5
8	Fe-2	17	737	988	17.9
9	Fe-2	21	730	1160	25.0
10	Fe-2	25	714	1439	22.7
11	Fe-3	9	736	572	5.1
12	Fe-3	13	733	685	11.5
13	Fe-3	17	724	803	19.0
14	Fe-3	21	723	842	25.6
15	Fe-3	25	720	1201	34.0
16	Fe-4	9	755	613	4.8
17	Fe-4	13	744	781	13.7
18	Fe-4	17	737	952	16.1
19	Fe-4	21	731	1043	21.6
20	Fe-4	25	704	1132	30.4

4. Conclusions

On the basis of the above-discussed results it can be concluded that the textural parameters of the commercially available iron powder preparations have different effect on the thermal decomposition of KClO₄. The grain size and surface area of iron powders used have small effect on their reactivity, whereas the presence of iron oxide phases on their surface plays a substantial role.

In the presence of the Fe₃O₄ phase (Fe-2 and Fe-4) on the iron powder surface, the oxygen released on thermal decomposition of KClO₄ is used for their oxidation. This is reflected by a smaller mass loss and higher heat of the reaction. In the presence of the α-Fe₂O₃ phase on the iron powder surface (Fe-1 and Fe-3), the mass loss was greater and the heat of the reaction higher. The observed two-stage course of the thermal decomposition of KClO₄ in the presence of the iron powder as a reducing agent is a result of the presence of trace amounts of the Fe₂O₃ phase or any other iron oxide phase e.g. containing sulphur or nitrogen.

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