



Some Thermochemical Properties of High Calorific Mixture of Fe-KClO₄

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Abstract: The paper presents physicochemical characterization of components of the reaction mixture of iron powder and polycrystalline KClO₄. Reactivity of the studied substrates was tested in the solid-state reaction. Research has been done to determine the effect of the grain shape and degree of crystallisation of substrates on their selected thermochemical properties. Taking into regard amount of the generated heat and the amount of oxygen not involved in the reaction with iron, the mixtures containing 13, and 17 wt.% of KClO₄ were found the most effective among those studied.

Keywords: solid-state interaction in the Fe-KClO₄ system, granulometric, SEM and X-ray methods

Introduction

Heat generating mixture is a high calorific material for specific applications in technology. A heating mixture is composed of a reducer, usually an appropriate metal in a powder form, and a strong oxidant such as, for instance, KClO₄, KBrO₄,

KMnO₄, BaCrO₄ or CaCrO₄. Potassium chlorate(VII) was chosen for the present research from among 23 various chlorates broadly described in the literature of the subject [1], which had been taken into consideration as oxidising agents. It was noted that graining of the preparation serving as an oxidizing agent plays an important role in its reactivity in a high energy mixture [2].

Numerous papers concerning research on thermal decomposition of the potassium chlorate(VII) described the influence of many simple [3, 4] and complex oxides of metallic elements with a defined structure, such as example perovskite and spinel [5], non-metallic elements [6] and metals [7, 8] on the course of this process. Among the studied substances, oxides of transition elements, such as example NiO [9], MnO₂ [10], Cr₂O₃ [11] and also iron oxides [12-14] were discovered to have had the greatest influence.

Present research aimed at determining the influence of the method of preparing the potassium chlorate(VII) applied in the high energy heating mixture along with commercial iron powders. Moreover, the influence of graining and presence of the phase of iron oxides functioning as activators upon thermo-chemical properties of the heating mixture in the system Fe-KClO₄ was determined.

Materials and Methods

Three potassium chlorate(VII) preparations and two commercial iron powders were studied. They were used for preparing appropriate mixtures of which tablets were then made and subjected to a study of reactivity in the solid state in the temperature range 20-800 °C.

Samples

The commercial potassium chlorate(VII) by Fluka was subjected to preliminary crystallisation from aqueous solution [15]. The obtained preparation was then subjected to further crystallisation with the distilled water (A), 40% aqueous solution of ethanol (B) and 96% ethanol (C) used as crystallization media. Later on in the present paper these preparations are denoted as: KClO₄ (A), KClO₄ (B) and KClO₄ (C) respectively. The iron powders used in the research were commercial samples obtained from POCH – Gliwice, Poland (Fe-1) and Merck (Fe-2).

In thermochemical investigations and measurements of specific density samples in the form of tablets, ca 0.88 mm thick and with a diameter of 6 mm, obtained by mixing a proper ratio of substrates and applying a pressure of 4 MPa, were used. The studied mixture was composed of iron powders and potassium chlorate(VII) powders: 9, 13, 17, 21 and 25 wt.%.

Granulometric analysis

The grain sizes of the investigated samples were measured by laser light scattering 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 preparation studied were mixed with a few drops of ethanol until a homogenous paste was obtained which was then introduced into 96% ethanol and stirred in the granulometer attachment until a homogenous suspension was formed.

Because of the susceptibility of polycrystalline potassium chlorate(VII) to agglomeration, granulometric measurements were made after subjecting the studied sample to ultrasounds for 1 min, and after 3 min its grain size distribution was determined.

Technique of preparing and carrying out the granulometric measurements of iron powders is described in detail in the paper [16].

Results of measurements are presented in the form of volumetric and numerical distribution as a function of particle diameter and particle size concentration expressed in %.

Scanning electron microscopy (SEM)

SEM analysis was performed using an electron microscope SEM 515 (Philips) with working distance of 14 mm, accelerating voltage 15 kV and digital image recording DISS.

X-ray diffractometry

X-ray analysis was performed on a Philips powder diffractometer model PW 1070 controlled by an IBM PC unit, using CoK α radiation and an iron filter. The patterns were recorded for $10^\circ < 2\Theta < 100^\circ$ for the gaps of $1^\circ/1^\circ$ at a counter step 0.04° and for the time of pulse counting of 2 seconds. The reflexes were identified with the help of the APD (automatic powder diffraction) provided by Philips.

For precise determination of the profile of potassium chlorate(VII) the reflexes were analysed at a counter step of 0.02° in the 2Θ range $28.0\text{--}35.5^\circ$.

Specific volume

Specific volume of appropriate mixtures composed of the iron powder (7.82 g cm^{-3}) and KClO₄ (2.52 g cm^{-3}), in the form of tablets, was determined on the basis of measurements of their weight, with accuracy of 0.0001 g, and diameter and height, with accuracy of 0.01 mm. The results obtained were compared with those calculated after assuming some determined chemical composition.

Reactivity in the solid state between KClO_4 and Fe

Reactivity of the applied commercial iron powders was tested in the solid-state reaction with potassium chlorate(VII) using mixtures of both containing – respectively – 9, 13, 17, 21 and 25% wt. KClO_4 .

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 with mass, of about 0.12 g were heated at the rate of $40\text{ }^\circ\text{C min}^{-1}$ from room temperature to $800\text{ }^\circ\text{C}$ in the dynamic atmosphere of inert gas (Ar) at the flow rate of $150\text{ cm}^3\text{ min}^{-1}$.

Results and discussion

Samples

Commercial KClO_4 used in the research was subjected to preliminary crystallization in order to eliminate detectable quantities of the majority of impurities, e.g. chlorates.

Elaboration of proper crystallization conditions using various crystallisation media aimed at obtaining preparations of polycrystalline potassium chlorate(VII) with varying crystallite sizes. Obtained samples of KClO_4 were labelled as (A), (B) and (C), and used without additional mechanical treatment.

Granulometric analysis

Figure 1a presents volumetric distribution of grains of potassium chlorate(VII) preparations and their suspensions in the granulometer attachment. In all cases, two maxima on the volumetric distribution curve were observed: the first maximum corresponded to single crystallites and the second one – to conglomerates.

Application of ultrasounds during measurements permitted breaking these conglomerates as demonstrated by the shape of curves presented in Figure 1b. For KClO_4 (A) (solid line) as many as three maxima were noted at about 10, 100 and $400\text{ }\mu\text{m}$ respectively. This suggests that there is still diversification of the crystallite sizes with domination of crystallites with diameter of ca $100\text{ }\mu\text{m}$. Crystallization of potassium chlorate(VII) from the aqueous ethanol solution (KClO_4 (B) (dash line) leads to formation of crystallites with dominating size of 10 and $40\text{ }\mu\text{m}$. Using ethanol as the crystallization medium results in obtaining smallest crystallites – the maximum is observed at ca $25\text{ }\mu\text{m}$ (dotted line).

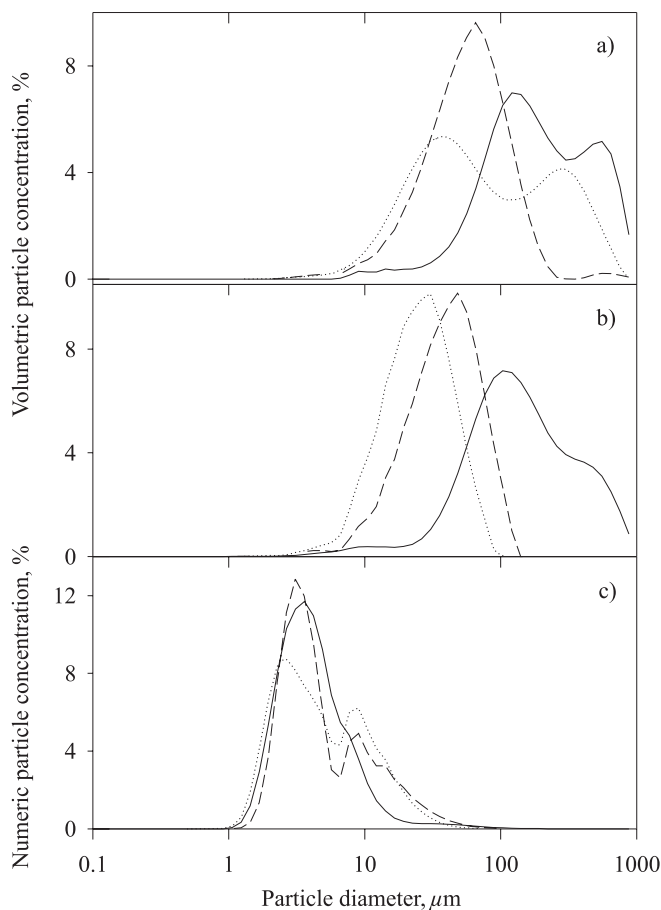


Figure 1. Particle size concentration as a function of their size: a) volumetric distribution without ultrasounds; b) volumetric distribution with ultrasounds; c) numerical distribution with ultrasounds (KClO₄ (A) – solid line; KClO₄ (B) – dash line; KClO₄ (C) – dotted line).

Numerical distribution of grains of the studied preparations of KClO₄ presented in Figure 1c indicates that application of ultrasounds leads to formation of crystallites characterized by bidispersive nature of the distribution of grain diameters in all studied preparations. This proves that grains of the size of about 2-3 μm and 10 μm dominate in the studied polycrystalline samples of KClO₄. It follows from the shape of curves presented in Figure 1c that there exists considerable size similarity between crystallites revealed by preparations of KClO₄

(B) and those shown by KClO_4 (C).

Relatively high residual value for KClO_4 (C) amounting to ca 6%, in volumetric as well as numerical grain distribution, points to the existence of considerable differences between values obtained experimentally and those calculated. Residual value indicates that the shape of grains in this preparation is far from spherical.

Results of granulometric measurements made for iron powder preparations used in this research are discussed in detail in the paper [16]. Preparations labelled as Fe-1 and Fe-2 in the volumetric distribution of grains display presence of maxima at diameters of 48, 56 μm and 8, 10 μm respectively. Numerical distribution of grains of these preparations is characterized by the monodispersive nature with maximum at 0.3 and 2.6 μm respectively.

Scanning electron microscopy (SEM)

In order to establish real shape of grains in potassium chlorate(VII) polycrystalline powder samples, the preparations studied were subjected to the scanning electron microscopy (SEM) observations. The SEM micrograph images are shown in Figure 2 revealing the presence of three types of grain shapes. KClO_4 (A) is composed of grains of varying size without any visible defects on their surfaces as shown on the micrograph in Figure 2a.

In KClO_4 (B), the photograph of which is presented in Figure 2b, grains of the shape similar to those in Figure 2a can be seen but much smaller (10-30 μm). Besides, small concavities can be noticed on their surfaces, which can be traces of detachment of smaller grains from earlier existing conglomerates (Figure 2b). The shape of grains of KClO_4 (C) visible in Figure 2c is different when compared to the remaining preparations studied (see Figures 2a and 2b). They are relatively big, flat grains with frayed edges. Smaller grains that can be seen on the micrograph are probably fragments of big and irregular in shape ones.

Our earlier SEM studies of the iron powders used in the research revealed that they were composed of spherical grains (sample F-2) or flat grains with sharp edges (sample Fe-1) [16].

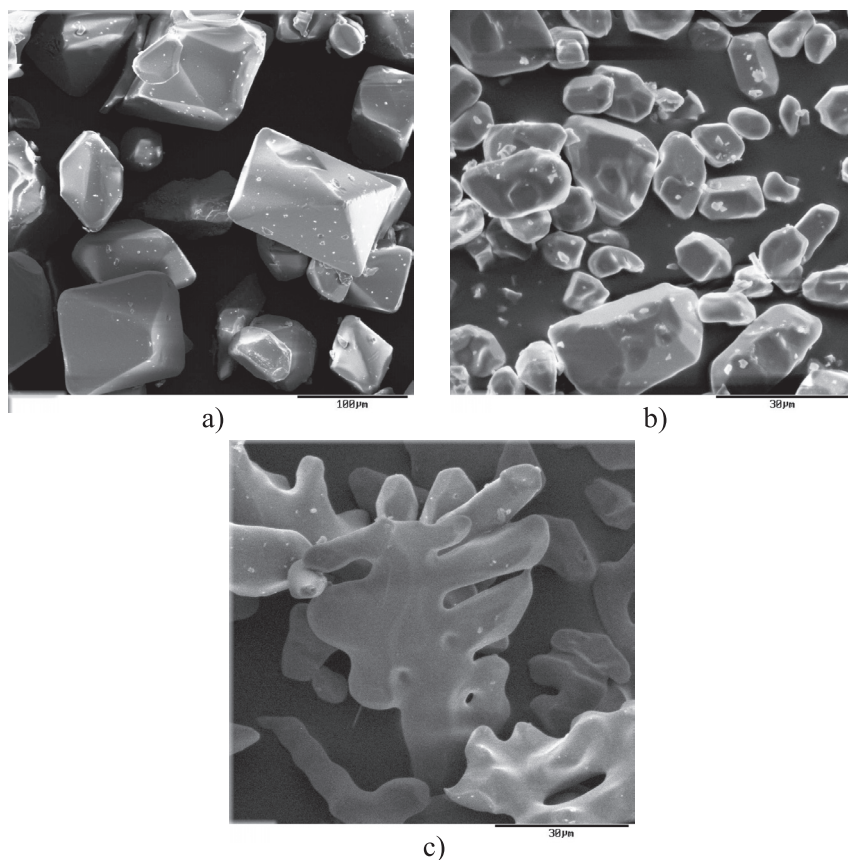


Figure 2. SEM micrographs of the polycrystalline KClO₄ samples: a) KClO₄ (A); b) KClO₄ (B); c) KClO₄ (C).

X-ray diffractometry

Presence of the KCl phase was noted in the initial commercial KClO₄, and it was eliminated by preliminary crystallisation of this preparation from aqueous solution. The X-ray diffraction patterns of the investigated KClO₄ samples (A), (B) and (C) are shown in Figure 3.

As follows from the intensity and FWHM of the reflexes, there is only the phase of potassium chlorate(VII) with different degree of ordering of the internal crystalline structure. KClO₄ (A) reveals diffraction lines of greatest intensity but a low value of FWHM, which points to the presence of big crystallites forming a mosaic structure. In KClO₄ (B) the reflex lines are less intense but they show

slightly greater FWHM value when compared to KClO_4 (A), which suggests presence of slightly smaller crystallites in this preparation. The smallest crystallites are present in KClO_4 (C), as shown by smaller intensity of the demonstrated reflexes (see Figure 3c).

Earlier analysis of commercial iron powders revealed the presence of the phase $\alpha\text{-Fe}$ only [16].

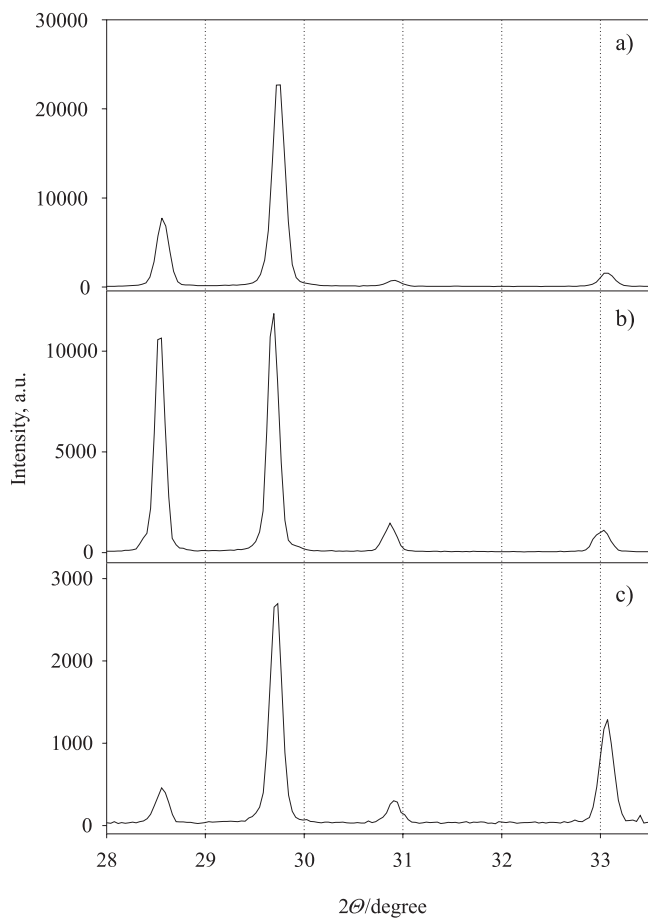


Figure 3. X-ray diffraction patterns of the samples:
a) KClO_4 (A); b) KClO_4 (B); c) KClO_4 (C).

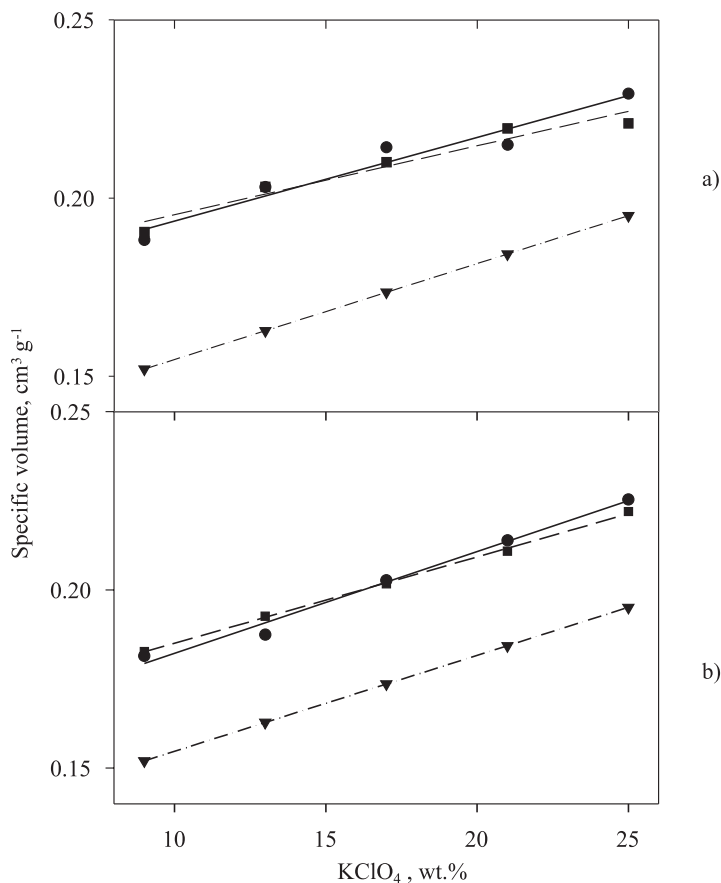


Figure 4. Specific volume of the Fe-KClO₄ mixture in the function of concentration of KClO₄; a) KClO₄ (A); b) KClO₄ (C); specific volume calculated (dash-dot line), Fe-1 (solid line), Fe-2 (dash line).

Specific volume

Specific volume of the mixtures of the KClO₄ preparations and commercial iron powders was measured after pressing them. Figure 4a and 4b show dependence of the value of specific volume for selected mixtures in the function of the KClO₄ concentration. The diagrams presented indicate that different shapes and grain sizes revealed by KClO₄ (A) and KClO₄ (B) are not reflected in the determined values of the specific volume of the relevant mixtures.

Therefore, difference in the determined volume values result from different

shape and size of the iron powders' grains.

Spherical grains characteristics of Fe-2 give tablets with lower specific volume values in the whole range of concentrations of KClO_4 (A) as well as (B). Differences are much smaller when it comes to greater content of potassium chlorate(VII).

Reactivity in the solid state between KClO_4 and Fe

Results of the thermochemical studies of selected mixtures of potassium chlorate(VII) and iron powder are given in Figure 5. The parameters observed for evaluation of the suitability of heating mixtures were: temperature in which reaction between potassium chlorate(VII) and iron is being initiated, degree of conversion of KClO_4 which reacted with iron, and total heat effect accompanying this conversion.

During heating, at 299.5 °C pure potassium chlorate(VII) undergoes a reversible phase conversion, which is related to transformation of its structure from orthorhombic to the regular one; at 574 °C - it melts, and at 620 °C it undergoes rapid decomposition [17]. Besides, during the experiment, an additional energetic effect was observed, which could be attributed to the process of melting at 770.6 °C of the product of decomposition of KClO_4 i.e. KCl. It follows from the presented in Figure 5a relationship of the decomposition temperature of the mixture of potassium chlorate(VII) and iron (Fe-1) as function of the KClO_4 (A) contained that, at the content of 9% wt. KClO_4 , the temperature of its decomposition is decreased by ca 155 °C in comparison to the pure preparation. Further increase of the concentration of KClO_4 in the mixture led to further decrease of the temperature of its decomposition, which, at 25% wt., reached 235 °C. In the system KClO_4 (C) – Fe-1, similar dependence was noted, only the decomposition temperature of KClO_4 was by 42 °C higher.

In mixtures composed of the Fe-2 powder and KClO_4 (A) and KClO_4 (C), respectively, one can note also the decrease of the temperature of decomposition of KClO_4 , but to a slightly smaller extent (see Figure 5b).

Relationships presented in Figures 5a and 5b suggest that it is the form of the iron powder used (spheres, scales) which determines the value of the temperature of decomposition of KClO_4 in the mixture.

Another characteristics determining practical suitability of the high energetic mixture is a degree of conversion of KClO_4 expressed in %. In the calculation, only the amount of oxygen liberated after decomposition of KClO_4 , which reacted with the iron powder, was taken into consideration. The remaining amount of oxygen, which did not react with the Fe powder, was released to the atmosphere surrounding the tablet, and it was not considered while evaluating the degree

of KClO₄ conversion. The data presented in Figure 5c and Figure 5d imply that with a small content of potassium chlorate(VII) in the heating mixture almost total conversion of oxygen released after its decomposition to the corresponding iron oxides was observed. Increased amount of KClO₄ in the mixture results in the decreased degree of its conversion, however, with KClO₄ (A) this effect was more pronounced than with KClO₄ (C).

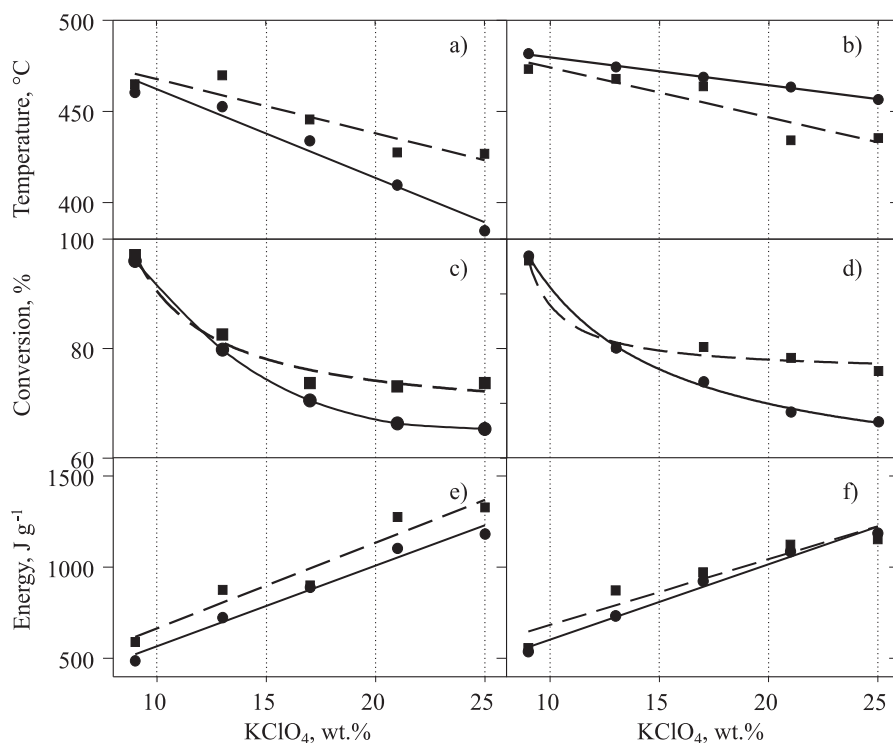


Figure 5. Parameters reactivity (temperature of the initial decomposition; conversion of KClO₄; amount of energy evolved during the interaction) in the solid state reaction of the KClO₄-Fe mixture for the selected samples as a function of the potassium chlorate(VII) concentration: a), c) and e) KClO₄ (A)-Fe-1 – solid line, KClO₄ (C)-Fe-1 – dash line; b), d) and f), KClO₄ (A)-Fe-2 – solid line, KClO₄ (C)-Fe-1 – dash line.

It was noted that the iron powder used as a reducer in the heating mixture also significantly affects the degree of conversion of KClO_4 . Smaller degree of conversion of KClO_4 – both (A) and (C) – was observed when the Fe-1 powder had been used as a reducer. This effect cannot be explained by diversification of the specific surfaces of iron powders used in the experiment, because for the Fe-1 and Fe-2 samples they were $0.84 \text{ m}^2 \text{ g}^{-1}$ and $0.50 \text{ m}^2 \text{ g}^{-1}$, respectively.

Similar values of the specific density of the studied heating mixtures in the form of tablets suggest that this parameter should not influence on the degree of conversion of KClO_4 . So, the observed differences in the reactivity of the applied iron powders may result from the size of grains as well as from the presence of relevant oxides on their surface. The process of reduction by hydrogen a sample Fe-1 takes place in three steps. The first reduction peak (weak) appears at 245°C , corresponding to the transition of Fe_2O_3 to Fe_3O_4 . The second peak is at 342°C and can be assigned to the transition of Fe_3O_4 to FeO . The final peak at 407°C corresponds to the transition of FeO to Fe . A comparison of the peaks area implies that the dominant phase is Fe_3O_4 . In sample Fe-1 there are also trace amounts of the Fe_2O_3 phase. In Fe-1, it was noted that considerable quantities of iron oxides (Fe_3O_4 , Fe_2O_3 and FeO) covered its surface, while in the sample of Fe-2 much smaller quantities of oxide phases (Fe_3O_4 and FeO) were present with a dominating phase of Fe_3O_4 [16].

Moreover, in the numerical grain distribution, a sample of Fe-2 revealed greatest population of grains with diameter of $10 \mu\text{m}$, while in the sample of Fe1 – the diameter of $30 \mu\text{m}$ prevailed. Figures 5c and 5d illustrate the influence of the grain size in the studied preparations of KClO_4 upon the reactivity of the heating mixture in the system Fe- KClO_4 . KClO_4 (A), characterised by a relatively big size of grains, is a much weaker oxidant of iron grains than KClO_4 (C) whose grains are small and have a very large surface.

Figures 5e and 5f show the extent of the energetic effect accompanying reactions occurring in the mixture Fe- KClO_4 . The observed energetic effect is related not only to the process of the exothermic reaction of decomposition of KClO_4 , but also to oxidation of the surface of the iron powder by oxygen released after its decomposition.

It follows from the above-described relationships that along with the increase of the amount of KClO_4 in the heating mixture increases the amount of heat generated as a result of the reactions of oxidation of the iron powder as well as decomposition of KClO_4 .

Conclusions

- Physical properties of KClO₄ and the iron powder samples studied, especially the shape of the grains and their internal structure, differ depending on the methods of their preparation, which is manifested by the character of the solid-state reaction Fe-KClO₄.
- Smaller grains of KClO₄ cause greater decrease in the decomposition temperature in the presence of the iron powder; this effect is more pronounced for higher concentrations of KClO₄.
- KClO₄ samples of smaller grains and low crystallinity are responsible for greater conversion of iron and reduce the amount of oxygen not participating in the reaction.
- The surface of the powders is covered with a thin layer of iron oxides with the dominant phase of Fe₃O₄, which is an important factor in solid-state reaction Fe-KClO₄.
- The presence of iron +2 in the dominant phase Fe₃O₄ causes decrease of the decomposition temperature of potassium chlorate(VII).
- The parameter determining the applicability of iron powders in mixtures of high calorific value is the thickness of the iron oxide layer on the surface of the metal.

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