



## Physicochemical Properties of Iron Powders Used as Reducing Agents in Materials of High Calorific Value

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**Abstract:** The paper reports physical and chemical characterisation of commercial preparations of iron powder and their solid-state reactivity with potassium chlorate(VII). The samples of the commercial products were subjected to: granulometric analysis, SEM observations, low-temperature adsorption and desorption of nitrogen, surface area determination by BET, XRD study of the phase composition and TPR. Iron(II) oxide present on the surface of iron powders acts as a catalyst in thermal decomposition of  $\text{KClO}_4$ . The iron powders were analysed in the aspect of their possible application as components of conducting heating mixtures in thermally activated primary batteries.

**Keywords:** iron powder, granulometric analysis, SEM, TPR, X-ray methods

### Introduction

In high-energy mixtures, the powders of such metals as Al, Mg, Zr, Fe, Ti and Mo are usually used as reducing agents. Their performance is determined by the size and shape of powder grains and by the chemi-

cal composition of their surface. Iron powders used as reducing agents are obtained as a result of reduction of pure magnetite by carbon, iron oxides by hydrogen and thermal decomposition of iron pentacarbonyl, diiron nonacarbonyl or iron(II) oxalate [1]. Moreover, the powders can be obtained by the electrolytic process, fluidized bed reduction and water gas atomization [2]. Full determination of the bulk and surface properties of iron powders is necessary for assessment of the usefulness of a given powder as a component of heating mixtures.

The aim of this study was to determine selected physicochemical properties of commercially available iron powders used as effective reducing agents of the heating mixtures.

## Materials and Methods

### Samples

The iron powders used in this research were samples of commercial products from POCH-Gliwce, Poland (**Fe-1**), KOCH Light Laboratories (**Fe-2**), Riedel de Haen (**Fe-3**). The preparations were not standardized prior to the measurements, except when studying the sorption properties with the use of nitrogen.

### Granulometric analysis

The grain sizes of the commercial iron powder preparations were 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  $\mu\text{m}$ .

Samples of each of the preparations studied were mixed with a few drops of the 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 suspension was subjected to ultrasounds and after about 3 min the grain size distribution was measured. The results are presented in the form of volumetric and numerical distribution as a function of the particles diameter and concentration of particles of a given size expressed in %.

### **Scanning electron microscopy (SEM)**

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

### **Adsorption/desorption isotherms**

Low-temperature (77 K) nitrogen adsorption measurements were carried out using a sorption apparatus Micrometrics ASAP 2010. Prior to the measurement, the samples were outgassed under vacuum  $1.33 \times 10^{-4}$  Pa at 400 K until a constant weight was reached. Nitrogen adsorption and desorption were carried out in the relative pressure range  $p/p_0 = 0-1$ . The BET equation was used to calculate the specific surface area.

### **X-ray diffractometry**

X-ray analysis was performed on a Philips powder diffractometer model PW 1070 controlled by IBM PC unit, using  $\text{CoK}_\alpha$  radiation and an iron filter. The patterns were recorded for  $10^\circ < 2\Theta < 90^\circ$  for the gaps of  $1^\circ/1^\circ$ , at a counter step of  $0.04^\circ$  and for the time of pulse counting of 2 seconds. The reflexes identified with the help of the program APD (automatic powder diffraction) provided by Philips. For precise determination of the profile of the iron diffraction lines (110), (200), (211) and (220), the reflexes were analysed at the counter step of  $0.02^\circ$ , in the  $2\Theta$  angle range of  $10-130^\circ$ , the other conditions remained unchanged. The measurements were performed for all iron samples studied in the form of powder and additionally for some samples in the form of tablets. The identification of various phases present on the surface of the samples was carried out on the basis of a comparison of the XRD spectra with the data given by ASTM.

### **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 [3]. The

conditions of the TPR measurements were as follows: temperature interval 330-1050 K, heating rate 10 K min<sup>-1</sup>, specimen weight 10-120 mg, atmosphere 10% H<sub>2</sub> + 90% Ar (purity 99,999%), flow rate 50 cm<sup>3</sup> min<sup>-1</sup>. All the TPR profiles were converted into mass equivalent.

### Study on the reactivity in the solid state between KClO<sub>4</sub> and Fe

Reactivity of the iron powder preparations studied was tested in the reaction with potassium chlorate(VII) in solid state, using each time a mixture of the molar ratio KClO<sub>4</sub>/Fe = 1/7.5 [4]. The reaction was carried out in a differential thermo-analyser, model STA 409 C 3F, made by Netzsch, in the measuring system of DTA/TG. The samples were heated at the rate 40 K min<sup>-1</sup> from room temperature to 1050 K in the dynamic atmosphere of inert gas (He) at flow rate 150 cm<sup>3</sup> min<sup>-1</sup>.

## Results and discussion

### Samples

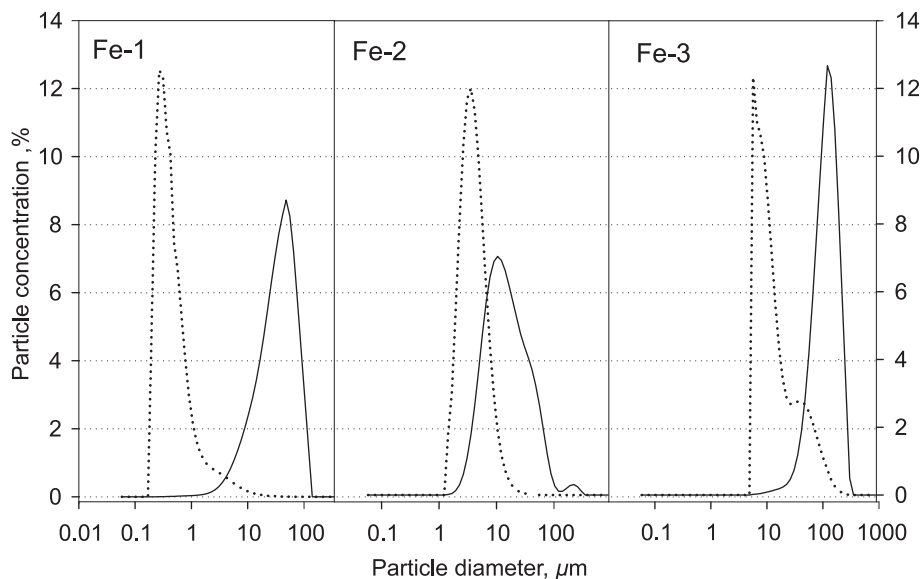
The symbols labelling the commercial iron powder preparations studied and their characterization in the aspect of their potential application as a component of heating mixtures are given in Table 1.

**Table 1.** Characterization of investigated samples

Sample-code	Specific surface area [m <sup>2</sup> g <sup>-1</sup> ]	Diffraction pattern					Solid state reaction Fe+KClO <sub>4</sub>		
		[200]			[211]		d)	e)	f)
		a)	b)	c)	a)	b)			
<b>Fe-1</b>	0.84 ± 0.05	0.504	788	312	0.551	1600	427	73.7	1328
<b>Fe-2</b>	1.12 ± 0.09	0.191	876	1788	0.214	1873	431	78.0	1607
<b>Fe-3</b>	0.67 ± 0.05	0.191	1190	1788	0.215	2655	440	71.5	821

- a) FWHM width of the peak in half of height, 2Θ/degree
- b) surface area of the diffraction pattern, a.u.
- c) crystallite size, Å
- d) decomposition temperature of KClO<sub>4</sub>, K
- e) degree of potassium chlorate conversion to iron oxides, %
- f) heat of reaction, J g<sup>-1</sup>

Figure 1 presents results of granulometric analysis of the samples Fe-1, Fe-2 and Fe-3 expressed as the relative volumetric and numerical distribution of grain concentration in % as a function of grain diameter.



**Figure 1.** Volumetric and numeric particle size concentration as a function of particle size for all samples studied: volumetric concentration (solid line), numeric concentration (dash line).

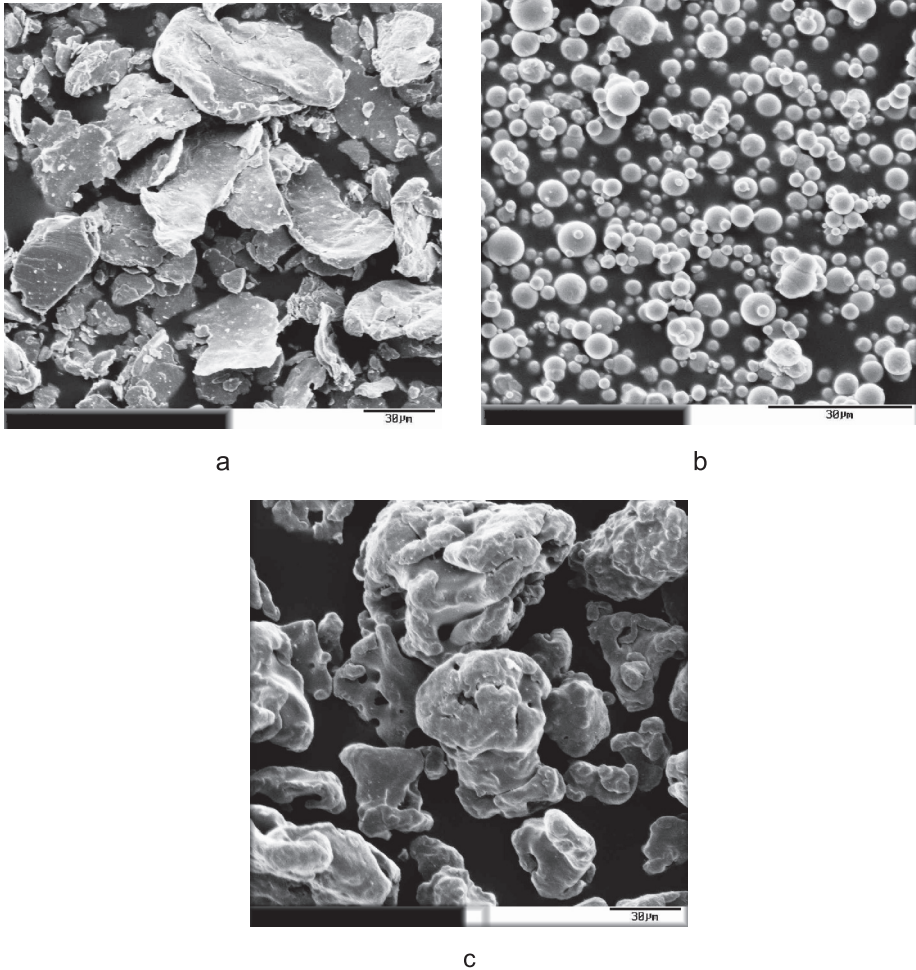
According to the above-presented curves, the preparations studied can be divided into two groups. The curve characterizing the first group, including sample Fe-3, indicate their monodisperse composition with the dominant grains of 120  $\mu\text{m}$ . The character of the curves illustrating the volumetric distribution of the grain size of the preparation indicates its polydispersion nature, which is implied by the maxima appearing at about 11, 30 and 200  $\mu\text{m}$  for sample Fe-2. The first is much pronounced, which means that the grains of 11  $\mu\text{m}$  in diameter have the greatest contribution in the total volume of this sample. The curves of the second group samples: Fe-1 and Fe-2 with stronger or weaker additional maxima proves their polydispersive

nature. As follows from the analysis of the curves presented, sample Fe-2 is composed of grains whose diameter varies from 2 to 300  $\mu\text{m}$ , with the dominant grains of the diameter of about 8 and 10  $\mu\text{m}$ , while sample Fe-3 has the dominant grains of the diameter of about 120  $\mu\text{m}$ . Similar volumetric distributions of grain size have been observed for samples Fe-1 for which two maxima are observed for the diameters 48 and 56  $\mu\text{m}$ . Figure 1 shows also the numerical particle size concentrations as a function of particle diameter for all iron powders samples investigated.

As has been observed for the curves of the volumetric distribution, the curves of the numerical distribution of the grain sizes for sample Fe-2 show that the grain diameter varies in the range 1.5-20  $\mu\text{m}$ , with the maxima at 3.5  $\mu\text{m}$ . As follows from the curve of the numerical distribution of iron grains, in this sample the dominant the iron grains are of about 3.5  $\mu\text{m}$  in diameter. The population of the grains of about 11  $\mu\text{m}$  in diameter is small, but these grains have the greatest contribution in the volume distribution. The weaker pronounced maxima on the volumetric particle size concentration dependence correspond to the particles of about 30 and 200  $\mu\text{m}$  in diameters. On the numerical particle size concentration curve at the points corresponding to the particles of the same size the function takes values close to zero. These results imply that the molecules of this size occur in small populations and are not representative for the sample.

Sample Fe-3 has been found to have grains of sizes varying in the greatest range (5-250  $\mu\text{m}$ ), 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  $\mu\text{m}$ , a broadened one at about 11  $\mu\text{m}$  and another distinct one at about 45  $\mu\text{m}$ . The sizes of the grains in sample Fe-1 vary in the range 0.2-40  $\mu\text{m}$ , and the largest population is made of the grains of the diameter close to 0.3  $\mu\text{m}$ .

Relatively low values of the residuals, not exceeding 0.6%, obtained for all samples indicate a good correlation between the experimental and calculated data.

**SEM studies**

**Figure 2.** SEM micrographs of the powder iron samples:  
a. Fe-1; b. Fe-2; c. Fe-3.

To determine a real shape of the grains in the iron powder samples, the preparations studied have been subjected to electron scanning microscopy (SEM) observations. The SEM images shown in Figure 2, reveal the presence of three types of the grain shapes. Sample Fe-1 is composed of the grains

in the shape of plates (Figure 2a), whose thickness was estimated as about 5-10  $\mu\text{m}$ . In sample Fe-2 the grains have spherical shape (Figure 2b) taken for Fe-2, but there are also aggregates made of two or three spheres. Moreover, on some spherical grains there are small nuclei also of spherical shape.

Figure 2c presents a photograph of sample Fe-3. The grains do not have sharp edges as those of sample Fe-1 (see Figure 2a), but the photographs reveal some pores in the grains of irregular shape being most probably a result of long time sintering. It should be mentioned that sample Fe-3 has grains of the greatest diameter.

### **Adsorption/ desorption isotherms and the surface area BET**

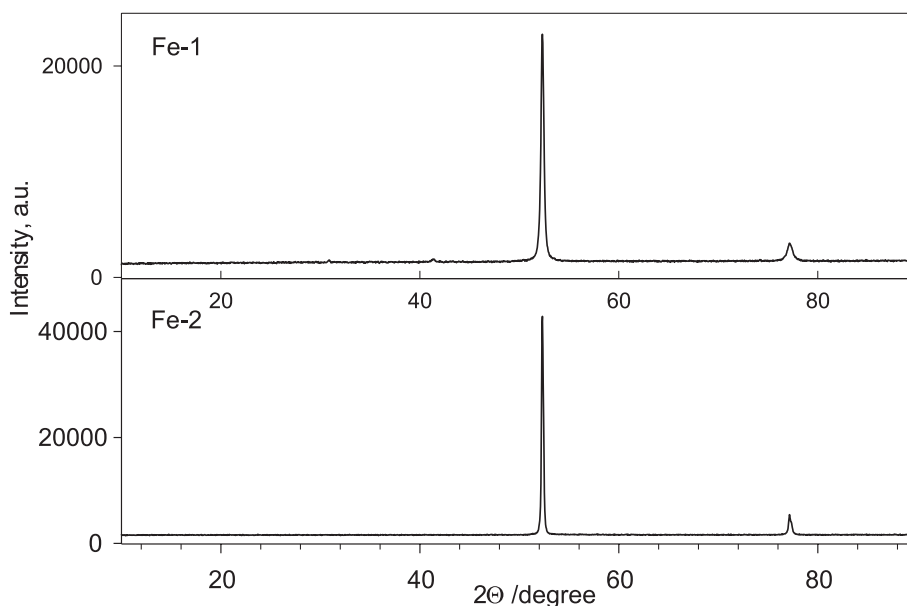
On the basis of the granulometric analysis and SEM photographs of the iron powder samples it was concluded that the samples did not have much developed surface area. In order to confirm this conclusion the nitrogen adsorption and desorption isotherms were determined for samples Fe-1, Fe-2 and Fe-3. The shape of the isotherms is typical of non-porous substances and the type of the hysteresis loop (long and narrow) testifies to a very poor porous structure that can be related to the presence of crevice pores between the grains of the iron powder [5].

Table 1 presents the surface areas of all samples studied. They are rather small and vary from 0.67 to 1.12  $\text{m}^2 \text{g}^{-1}$ .

### **X-ray analysis**

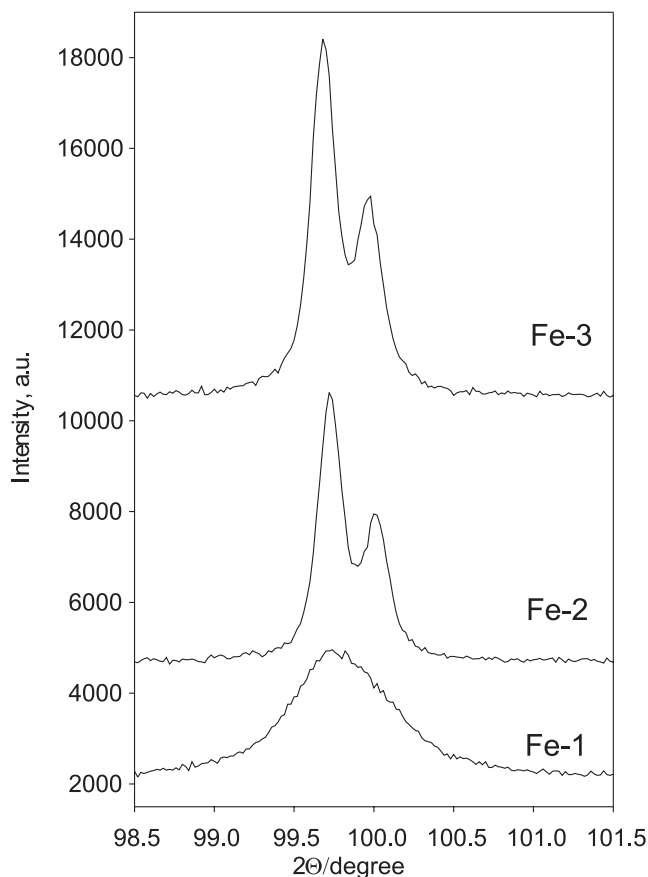
Figure 3 presents the X-ray diffraction patterns obtained for samples Fe-1, Fe-2. As expected, the diffraction lines are observed at the angle  $2\Theta$  of  $52.4^\circ$  and  $77.4^\circ$ , which corresponds to the values  $d = 2.0268$  and  $d = 1.4332$ , assigned to the reflections from the planes (110) and (200), respectively. Such diffraction patterns indicate the presence of the  $\alpha\text{-Fe}$  phase only [6]. The X-ray diffraction patterns do not show the diffraction lines that can be assigned to iron oxides, which are on the surface of the preparations studied, however, because of their low amounts they cannot be identified by this technique.





**Figure 3.** X-ray diffraction patterns of the samples Fe-1 and Fe-2.

Figure 4 presents the original shapes of the diffraction line profiles for the reflex (211) in the patterns of all samples studied. Table 1 gives the FWHM of the peaks and their total areas and the size of the crystallites calculated by the Hall method [7]. The shapes of the reflections profiles suggest that sample Fe-1 shows the least ordered structure of the surface and near-surface layers. High values of FWHM of the diffraction lines for this sample can be not only due to the presence of small size crystallites but also the inner stress of second order generated in the process of the iron sample production. Much more ordered inner structure have samples Fe-2 and Fe-3. As far as the size of the crystallites is concerned, the samples studied show great differences. The smallest crystallites occur in sample Fe-1 (of about 310 Å), while the crystallites in samples Fe-2 and Fe-3 have the size of 1800 Å.



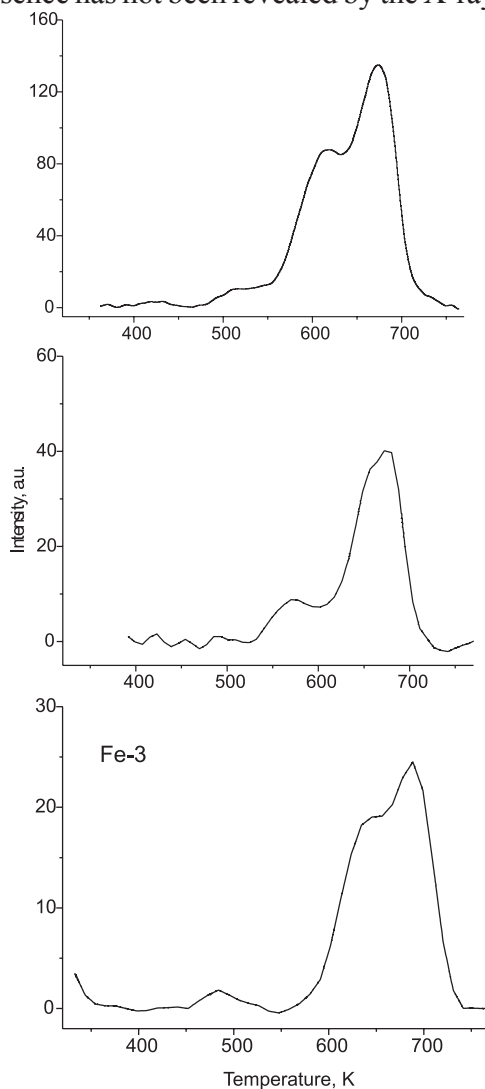
**Figure 4.** X-ray diffraction patterns of the samples investigated.

### TPR study

For qualitative determination of the iron oxides occurring on the surface of the commercial iron powder preparations studied and to estimate the thickness of the layer they form on the surface of the gains the measurements by the temperature-programmed reduction (TPR) by hydrogen were applied. Figure 5 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 three steps. The first reduction peak (weak) appears at 518 K, corresponding to the transition of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . The

second peak is at 615 K and can be assigned to the transition of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$ . The final peak at 680 K corresponds to the transition of  $\text{FeO}$  to  $\text{Fe}$  [8-10]. A comparison of the peaks area implies that the dominant phase is  $\text{Fe}_3\text{O}_4$ , whose presence has not been revealed by the X-ray diffraction study.



**Figure 5.** Temperature-programmed reduction of the iron powder samples by means hydrogen

As indicated by the analysis of the TPR profiles presented in Figure 5 the dominant phase present on the surface of all samples studied is  $\text{Fe}_3\text{O}_4$  accompanied by much smaller amounts of  $\text{FeO}$ . In sample Fe-1 there are also trace amounts of the  $\text{Fe}_2\text{O}_3$  phase. A comparison of the shapes and areas of the TPR profiles indicates that the greatest amount of oxides with the dominant phase  $\text{Fe}_3\text{O}_4$  occurs on the surface of Fe-1.

Sample Fe-3, characterized by similar parameters determined by granulometric studies and SEM images, show significant differences in the amounts of iron oxides in sample Fe-2 there are almost twice as much of them as in Fe-3.

Interestingly, for sample Fe-2 characterized by the greatest surface area of  $1.12 \text{ m}^2\text{g}^{-1}$  the amount of oxide phases was not the greatest. Sample Fe-3, whose surface area is almost two times smaller than that of Fe-2, is also characterized by small amounts of oxide phases with the dominant phase of  $\text{Fe}_3\text{O}_4$ .

### **Reactivity in the solid state between $\text{KClO}_4$ and Fe**

Results of the study on the reactivity between potassium chlorate(VII) and commercial iron powders in the solid state are given in Table 1. The reactivity of particular samples of iron powders was measured by the degree of potassium chlorate conversion. The remaining (unreacted) amount of  $\text{KClO}_4$  underwent decomposition but did not react with iron, and the oxygen liberated on the decomposition was released to the atmosphere. On the DTA curve besides the decomposition reaction of  $\text{KClO}_4$  two endothermic effects were observed [4]. The first peak corresponds to the phase transition from orthorhombic phase  $\text{KClO}_4$  into the regular one (at about 572 K). The second is associated with melting temperature of  $\text{KCl}$  (at about 1025 K). The temperatures of these thermal transformations were used as internal standards for correction of decomposition temperature of  $\text{KClO}_4$ .

As follows from the results obtained, the presence of iron powder leads to a decrease in the temperature of  $\text{KClO}_4$  decomposition by about 180 K. The applied pure  $\text{KClO}_4$  in the form of a tablet was shown to decompose at 886 K, by the thermogravimetric measurements (TG/DTA) [4].

The observed decrease in the decomposition temperature was explained by the catalytic activity of the phase FeO present on the surface of the commercial iron powders studied. The greatest amount of  $\text{Fe}_3\text{O}_4$  phase was found in Fe-1 sample, less in Fe-2 and in Fe-3 samples. The highest degree of potassium chlorate(VII) conversion was obtained for sample Fe-2, which was characterized by greater amount of the catalytic phase FeO and having a relatively high value surface area. For this sample the highest energetic effect corresponding to the decomposition reaction of  $\text{KClO}_4$  as well as oxidation reaction of iron powder to its oxides were observed. The surface area is proportional to the total heat of the reactions.

## Conclusion

The physical properties of the iron powder samples studied, especially the shape of the grains and their internal structure, differ depending on the methods of their preparation.

The surface of the powders is covered with a thin layer of iron oxides with the dominant phase of  $\text{Fe}_3\text{O}_4$ .

On the temperature-programmed reduction by hydrogen, for two of the iron powder samples (Fe-1, Fe-2), a process of low-temperature sintering was observed to occur at about 620 K. For sample Fe-3, such a process did not occur even at 925 K.

In the solid-state reaction between  $\text{KClO}_4$  and the iron powder samples studied, the temperature of potassium chlorate(VII) decomposition decreases by about 180 K.

The parameters determining the applicability of iron powders in mixtures of high calorific value are the thickness of the iron oxide layer on the surface of the metal and the surface specific area of the iron powder.

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