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Textural and catalytic properties of the Fe_xO_y/Fe–$KClO_4$ 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 $KClO_4$.

Keywords: Iron powder texture; X-ray; TPR methods; Fe–$KClO_4$ mixtures

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 α-Fe_2O_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 variety 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 α-Fe_2O_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% H_2 at 563 K over a period of 2 h.

Commercial $KClO_4$ p.a. (Fluka) used in the study was subjected to preliminary crystallisation from H_2O and to the main crystallisation from EtOH–H_2O 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.% $KClO_4$ 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 Kα 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–$KClO_4$ before as well as after the reaction of $KClO_4$ 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 $KClO_4$, 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% H_2 + 90% Ar (purity 99,999%), flow rate 50 cm^3/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 $KClO_4$

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 cm^3 min^{-1}.

The reaction was carried out in a differential thermoanalyser 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 cm^3 min^{-1}. Reactivity of the commercial iron powder preparations subjected to standardisation in hydrogen atmosphere prior to the measurements, in mechanical mixtures with polycrystalline $KClO_4$ 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: