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Thermal decomposition of barium ferrate(VI): Mechanism and formation of Fe^{IV} intermediate and nanocrystalline Fe_2O_3 and ferrite[☆]

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ABSTRACT

Simple high-valent iron-oxo species, ferrate(VI) ($Fe^{VI}O_4^{2-}$, Fe(VI)) has applications in energy storage, organic synthesis, and water purification. Of the various salts of Fe(VI), barium ferrate(VI) ($BaFeO_4$) has also a great potential as a battery material. This paper presents the thermal decomposition of $BaFeO_4$ in static air and nitrogen atmosphere, monitored by combination of thermal analysis, Mössbauer spectroscopy, X-ray powder diffraction, and electron-microscopic techniques. The formation of Fe^{IV} species in the form of $BaFeO_3$ was found to be the primary decomposition product of $BaFeO_4$ at temperature around 190 °C under both studied atmospheres. $BaFeO_3$ was unstable in air reacting with CO_2 to form barium carbonate and speromagnetic amorphous iron(III) oxide nanoparticles (<5 nm). Above 600 °C, a solid state reaction between $BaCO_3$ and Fe_2O_3 occurred, leading to the formation of barium ferrite nanoparticles, $BaFe_2O_4$ (20–100 nm).

1. Introduction

Oxidized iron usually exists in ferrous (Fe(II)) and ferric (Fe(III)) forms, but high-valent iron compounds of Fe(IV), Fe(V), and Fe(VI) have also been intensively studied in the last decade [1–4]. For example, several oxoiron(IV) ($Fe^{IV}{=}O$) and oxoiron(V) ($Fe^{V}{=}O$) complexes containing model organic ligands have been synthesized to understand the biological imperative of oxidative transformation in biological environment [5–11]. Another class of high-valent iron species are simple tetraoxy high-valent iron anions such as $Fe^{IV}O_4^{2-}$ (Fe(IV)), $Fe^{V}O_4^{3-}$ (Fe(V)), and $Fe^{VI}O_4^{2-}$ (Fe(VI)), commonly called ferrates. These have also been of great interest due to their potential in homogeneous water oxidation catalyst, energy storage, green chemistry oxidations, and detoxification of contaminants and toxins [12,13]. Examples of the application of Fe(VI) include generation of oxygen from water, production of super-iron batteries, selective conversion of alcohol to aldehyde, and oxidative transformation of cyanotoxins and antibiotics [12,14–19].

In the past few years, we have been interested in mechanistic studies on the reduction of Fe(VI) to answer whether the reactions go through either $1{-}e^-$ or $2{-}e^-$ transfer steps with the formation of Fe(V) and Fe(IV) intermediates, respectively, where Fe(III) and Fe(II) are final iron reduced species [13,19,20]. Some progress has been made by understanding relationships between reaction rates and thermodynamic potentials [21]. A handful studies on experimental evidences suggest both kinds of electron transfer mechanistic pathways [14,20,22]. The recent advancement in oxidative mechanism was possible due to improvement in analytical techniques.

A previous study on the thermal decomposition of potassium ferrate(VI) (K_2FeO_4) did not observe any intermediate iron species (i.e. Fe(V) and Fe(IV)), which are highly unstable [23]. However, recent work with synchrotron radiation using a nuclear forward scattering experimental technique clearly showed these unstable intermediate iron species [24]. The present paper focuses on barium ferrate(VI), $BaFeO_4$, which exhibited a high discharge performance at high current when applied as a battery material [25]. This performance may be related to the formation of a relatively stable intermediate with perovskite-like structure during decomposition of $BaFeO_4$. In contrast, the discharge intermediate of

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[☆] ESI available: additional Mössbauer and XRD spectra.
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K_2FeO_4 was very unstable and immediately converted to Fe(III) oxides [26,27]. Significantly, comprehending the decomposition mechanism of salts of Fe(VI) is of utmost importance to advancing the fundamental chemistry of ferrates, which may lead to simple synthesis of these compounds and an efficient performance of a super iron discharged battery. The aim of the current paper is the mechanistic understanding of the thermal decomposition of $BaFeO_4$.

A few reports on the decomposition of $BaFeO_4$ under thermal and humid conditions have conflicting findings in terms of intermediate iron oxidation state(s) and final iron oxide phases [26–32]. Our results in the current paper unequivocally demonstrate the formation of Fe(IV) as intermediate species and final nanoscale-iron oxide and -ferrite phases. The objectives of the article are to: (i) provide evidence of the electron transfer steps of decomposition of $BaFeO_4$ by using thermogravimetry (TG), differential scanning calorimetry (DSC), and Mössbauer spectroscopy techniques, (ii) distinguish decomposition of $BaFeO_4$ under static air and inert atmosphere, and (iii) learn the nature of reduced iron(III) oxide phases by applying low temperature (5 K)/in-field (5 T) Mössbauer spectroscopy, variable temperature X-ray diffraction (VT-XRD), and imaging (scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) techniques.

2. Experimental details

2.1. Sample preparation

Barium ferrate(VI) was prepared by using a method reported earlier [33]. Briefly, a basic solution of the barium chloride was allowed reacting with a solution of K_2FeO_4 at 0 °C. Solutions used in this procedure were purged with nitrogen in order to minimize the presence of atmospheric CO_2. A rapid filtration of the barium ferrate(VI) obtained was carried out in order to increase the purity of product.

2.2. Techniques

Thermal analysis was carried out simultaneously in the thermogravimetric (TG) and calorimetric (DSC) analysis device (STA 449 °C, Netzsch). The samples were dynamically heated from 25 °C to 1000 °C in the dynamic atmospheres of argon and air (both with the flow of 30 ml/min) with a heating rate of 10 °C/min. Evolved gasses were analyzed using a mass spectrometry device (QMS 403 C, Aëolos).

X-ray powder diffraction (XRD) experiments were performed with a PANalytical X'Pert PRO instrument (CoK_α radiation) equipped with an X'Celerator detector and programmable divergence and anti-scatter slits. Standard samples were placed on a zero-background Si slides, gently pressed in order to obtain sample thickness of about 0.5 mm and scanned in the 2θ range of 10–90° in steps of 0.017°. The *in-situ* variable-temperature XRD measurement was performed in an X-ray reaction chamber XRK 900 (Anton Paar GmbH) under constant nitrogen flow (20 ml/min) and temperature range from 100 °C to 600 °C. The heating slope was 40 °C/min and XRD patterns were collected in steps of every 20 °C (2θ range of 20–60°; 10 min each scan). Therefore, the resulting slope was approximately 2 °C/min. In the reaction chamber, the powder sample was placed into the sample holder made of glass ceramics (Macor).

The transmission ^{57}Fe Mössbauer spectra were measured using a Mössbauer spectrometer in a constant acceleration mode with a ^{57}Co(Rh) source. The isomer shift values were related to metallic alpha iron at room temperature (RT). The measurements were carried out at 25 and 300 K in a zero external magnetic field as well as at 5 K in an external magnetic field of 5 T, applied parallel to the direction of the gamma ray propagation. Low temperature and in-field measurements were conducted using a cryomagnetic system of Oxford Instruments. TEM images were obtained on JEOL 2010 instrument with LaB_6 cathode at accelerating voltage of 160 kV. SEM images were obtained on the field-emission scanning electron microscope (SU6600, Hitachi) working at 6 kV.

3. Results and discussion

3.1. Characterization of synthesized $BaFeO_4$

Initially, the as-prepared $BaFeO_4$ sample, labeled as BF, was analyzed by Mössbauer spectroscopy. A Mössbauer spectrum recorded at room temperature (RT), shown in Fig. S1a of the 'ESI', had a doublet (84.1% of spectral area) with hyperfine interaction parameters $\delta_{Fe} = -0.90$ mm/s, $\Delta E_Q = 0.17$ mm/s; typical for a hexavalent iron atom [34]. The minor doublet (15.9% of spectral area) with hyperfine interaction parameters $\delta_{Fe} = 0.31$ mm/s, $\Delta E_Q = 0.61$ mm/s was ascribed to (super)paramagnetic iron(III) oxides or oxyhydroxides.

Next, the XRD pattern of a BF sample was examined (Fig. S1b of the 'ESI'), which showed diffraction lines corresponding to only two crystalline phases, orthorhombic $BaCO_3$ and orthorhombic $BaFeO_4$. The observed weight ratio between $BaFeO_4$ and $BaCO_3$ is 85:15. Since no additional phase was observed in the XRD pattern, the Fe(III) phase identified in the Mössbauer spectroscopy measurement is therefore X-ray amorphous. The presence of $BaCO_3$ and Fe(III) were considered as impurities present in the initial BF sample.

3.2. Thermal decomposition study

3.2.1. Thermal analysis

In this study, thermal decomposition of $BaFeO_4$ was first monitored in air by TG and DSC techniques. Fig. 1a shows three main decomposition steps. The first step was within a temperature range from 25 to 230 °C, which was ascribed to a dehydration of the sample. The second step started at 230 °C and was related to the decomposition of $BaFeO_4$. The second step was completed at 310 °C. It was accompanied by an endothermic effect, and mass loss was 3.0 wt%. The third step occurred within a broad temperature range from 600 °C to 920 °C; it exhibited two thermal effects on the DSC curve and overall mass loss was 4.25 wt%. The chemical transformation of barium carbonate describes the third step [35].

The results of thermal analysis of decomposition of the BF sample under an inert environment (i.e. Ar) are shown in Fig. 1b. Both the TG and DSC curves of the BF sample were very similar to those seen under air (Fig. 1b vs. Fig. 1a). The only significant difference was a slightly higher mass loss (4.0 wt%) observed in an inert atmosphere during the second decomposition step, which could be explained by the absence of carbon dioxide. As expected, the evolution of oxygen was detected within the second decomposition step (230–300 °C) by mass spectrometry of evolved gasses (Fig. 1c). The evolution of carbon dioxide, from $BaCO_3$, was observed in the temperature range from 550 to 1000 °C (Fig. 1d).

3.3. Mössbauer spectroscopy measurements

In the following parts, thermodynamic decomposition was examined by isothermal heating of the BF sample at different temperatures in air, followed by characterization of selected samples by Mössbauer spectroscopy. The BF sample was heated at 190 °C for 2 h, at 300 °C for 1 h, and at 600 °C for 1 h (each heat treatment started from the initial BF sample) and labeled as BF190,