April 2008 Volume 3 Issue 2

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 3(2), 2008 [123-127]

Thermal behavior of β-PbO_2, a study of thermogravimetry and differential scanning calorimetry

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Received: 2nd December, 2007 ; Accepted: 7th December, 2007

ABSTRACT

The compound lead (IV) oxide β-PbO_2 was prepared in our laboratory. The Thermal behavior of this compound was studied using both techniques of Thermogravimetery and Differential Scanning Calorimetery under O_2 gas atmosphere from 25 to 600°C. The identityof products at different stages were confirmed by XRD technique. Results obtained using both techniques support same decomposition stages for this compound. Three distinct energy changes takes place, two endothermic and one exothermic in DSC results. The amount of ΔH for each peak is reported.

KEYWORDS

Lead (IV) oxide;
XRD;
Thermal analysis;
Thermogravimetry;
TGA;
Differential scanning calorimetry;
DSC.

INTRODUCTION

Lead compounds are used in different industries world-wide due to their chemical and physical characteristics[1-6]. One of the most important characteristics of the lead is its reactions with acids and bases as well as with air, which are well-known as oxidation. In consequence of these kind of reactions compounds like "lead (II) oxide, lead (IV) oxide, sulfate, lead carbonate, lead nitrate as well as alkaline lead acetate" have been produced. Some are the end product of a desired process but most of them are undesired byproducts and are known as disturb compounds[8,9].

Lead (IV) oxide is one of the most important compounds used in lead-acid batteries, which are produced daily all over the world[5,7].

Two morphology α and β are known for lead(IV) and lead(II) oxide[3,7]. The goal of this work was to investigate the thermal properties of β-lead (IV) oxide in different temperature conditions. Pure lead (II) oxide has been reported to be the final product of thermal decomposition process of number of different lead compounds[10-12]. The Morphology of these compounds were also reported[13-15].

EXPERIMENTAL

Materials and equipment

β-Lead (IV) oxide was prepared in this labortory as described in this paper.

TGA: Thermogravimeter, Mettler TG50, coupled with a TA processor.

DSC: Differential Scanning Calorimeter, Mettler DSC25, coupled with a TA processor.

XRD: X-Ray diffractometer D 5000, Siemens, Kristalloflex.

Preparation of β-PbO_2

50g $Pb(CH_3COO)_4$ was poured into a beaker with about 460ml of distilled water and all crystals were crushed until all $Pb(CH_3COO)_4$ decomposed hydrolytically to β-PbO_2. The precipitate was separated in a centrifuge after 10 minutes, filtered and washed with 460ml of double distilled water four times. This product was washed with 50ml water twice and collected on a glass frit after complete mixing. It was washed slowly four times with 25ml acetone to remove any remaining water. It was dried immediately in vaccum desicator over blue gel[16]. The dried product has a coffee-brown color.

X-ray diffraction of β-PbO_2

The lead (IV) oxide sample was prepared for X-ray using Bedacryl and exposed with CuKα1 radiation for two hours. Figure 1 shows the XRD diagram of the compound β-PbO_2.

TGA analysis of β-PbO_2

30.801mg of β-PbO_2 were weighted in a standard container from corundum. This sample was heated (1°C/min) from 25 to 600°C under O_2 gas atmosphere (15ml/min) (figure 2).

DSC analysis of β-PbO_2

A sample of β-PbO_2 were placed in a standard crucibles from aluminium and weighed accurately (30.967 mg) using a microbalance. The sample was sealed with special equipment. The sealed crucible was placed in the DSC equipment and the sample was heated from 25 to 600°C, with aheating rate of 5°C/min, under O_2 gas atmosphere. DSC curve of this sample is shown in figure 3.

RESULTS AND DISCUSSION

Thermal investigations of β-PbO_2

TGA and DTG results

Both TGA and DTG curves of thermal decomposition of β-PbO_2 is shown in figure 2 . The curve in the upper part shows the weight loss (vertical axis) versus increase in temperature (horizontal axis) and in the lower section of the same figure, first derivative of weight loss is shown in vertical axis versus temperature increase in horizontal axis.

So one can differentiate better between the stages of the thermal decomposition. The results indicate thermal decomposition consists of four separate stages in the temperature range of 25-600°C and summarized in

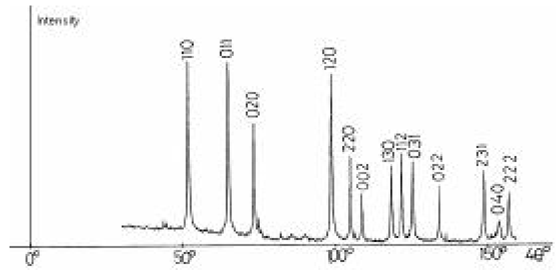

Figure 1: XRD diagram of β-PbO2

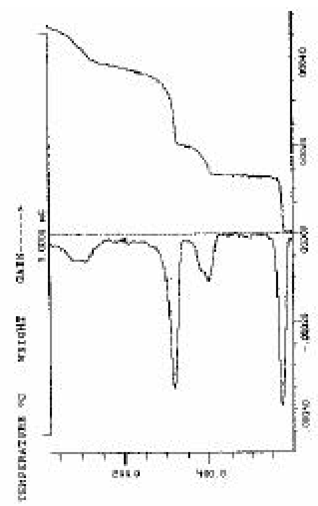

Figure 2 : TGA diagram of β-PbO2

TABLE 1: results from the thermal investigations of β-PbO_2 in range 25-600°C in O_2 atmosphere (15ml/min), 1°/mim

Phase no.	Start temp. [°C]	Turning-point [°C]	End temp. [°C]	Weight decrease [mg]	Weight decrease [%]
1	25	100	200	0.527	1.711
2	250	318	350	0.890	2.89
3	350	390	450	0.370	1.20
4	500	574	600	0.693	2.25

TABLE 1.

The first stage takes place between 25-200°C. The Calculations of weight loss shows that small quantities of water is present at the end of this region and it corresponds to a chemical formula of β-$PbO_2 \cdot 0.06H_2O$. The DTG curve shows that the first stage in TGA curve actually consists of two different phenomena. First phenomenon is the loss of absorbed water and the second one is decomposition of the starting compound.

Spectroscopic quantitative analysis in this study also corroborates this finding as well.

The computed stoichiometry of decomposition products are in good agreement with experimental results (quantitative and percent decrease in weight).

1. First stage of decomposition (25-200°C)

A low heating rate of 1°C/min was chosen to determine the real value of adsorbed quantity of water as well as finding out more information on what is taking place in this temperature range. The experiment was acomplished in the O_2 atmosphere with a constant gas flow of 15ml/min.

As is to be inferred from the results of the figures 2 & 3, the first phase of (decomposition) pyrolysis reaction of β-PbO_2 occurs in the range of 25-200°C. As in the Case of β-PbO_2 we observed here also the O_2 and H_2O separation Comparison of TGA & DTG curve for this stage suggests two processes i.e. loss of adsorbed water followed by loss of O_2.

By subtraction of the experiment-tally determined quantity of water (by spectrometric quantitative analysis) from the entire amount of weight loss one can approximately compute the separated O_2-quantity and reach to the following formula β-PbO_2.0.06H_2O. X-ray investigation supplied an identical XRD diagram to β-PbO_2. now we wanted to compute the separated O_2-quantity for the range 25-200°C by subtraction of the experimentally determined quantity of water from the entire decrease in weight approach. The kind of crystal of the product belonges therefore to the nonstoechiometric compound on (with broad homogeity range). The XRD analysis supplied a similar XRD diagram asβ-PbO_2. The evaluation of the results as well as spectrophotometric analysis the formula $PbO_{1.823}$.

2. Second stage of decomposition (250-350°C)

From the experimentally results is to be used, that the product lost within the range 250-350°C about 3% of its weight. The experiment was acoomplished in the O_2 atmosphere with a constant gas flow of 15ml/min. The X-ray analysis supplied a similar XRD diagram as $Pb_{12}O_{19}$. The evaluation of the results as well as spectrometric analysis the brutto formula: $PbO_{1.425}$.

3. Third stage of decomposition(350-450°C)

The third weight loss equals to about 1.2% starting material and occurs in the temperature range of 350-450°C. The X-ray analysis of the product confirms presence of Pb_3O_4. This was checked by spectrometric analysis and the calculated brutto formula of $PbO_{1.22}$ is reached .

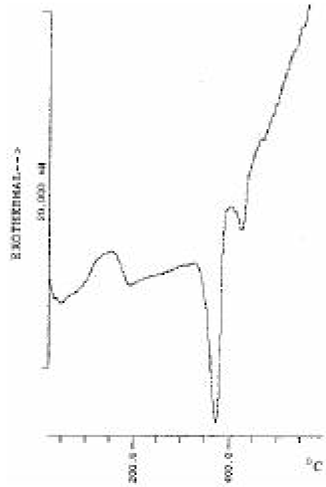

Figure 3 : DSC diagram of β-PbO2

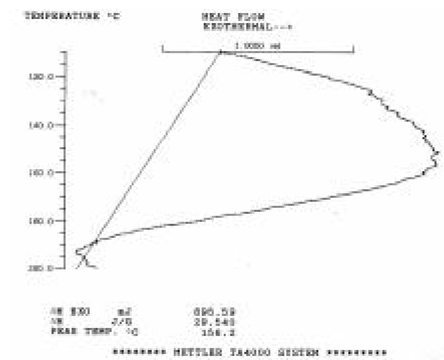

Figure 4 : The first stage of DSC diagram of β-PbO2

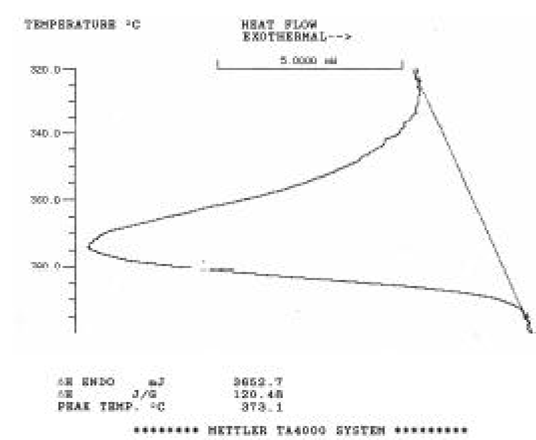

Figure 5 : The second stage of DSC diagram of β-PbO2

4. Fourth stage of decomposition(500-6200°C)

The fourth phase of thermal decomposition of β-PbO_2 is completed with loss of about 2.3% in weight and PbO is identified as the chemical entity of the product.

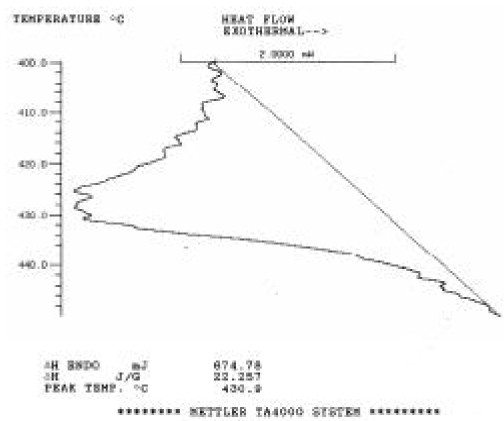

Figure 6 : The third stage of DSC diagram of β-PbO2

We want to point out again that the pyrolysis of β-PbO_2 within the range 25-600°C in the O_2-atmosphere led to PbO, i.e. the reaction β-PbO_2→PbO ran off completely with approximately 600°C. From the above TG diagram it is evident that the pyrolysis reaction of β-PbO_2 in the range 25-600°C consists of four stages. The final decomposition product is PbO.

Therefore, study of thermal Behavior of β-PbO_2, by Thermogravimetry suggests four different stages as discussed above. At first the compound losses water followed by loss of oxygen in separate stages and change of Pb (IV) to Pb (II). These changes occur at different temperatures and separate steps of thermal decomposition. These steps could be studied by using another technique (DSC) and energy of each step could be determined.

DSC results

Both exothermic or endothermic reactions are shown in figure 3. This heat flow can be either exothermic or endothermic. The energy is shown on vertical axis in mW and temperature is recorded on horizontal axis in °C. The TA processor was used to compute the enthalpy of an exothermic or endothermic reaction by entering the begining and the termination point of each deflection. A straight or a sigmoide base line can be selected which shows the change in C_p of a sample due to change in temperature. The surface area under each peak is computed automatically by the TA processor. As results we receive ΔH_{exe} or ΔH_{end} in J/g.

If we compare the TGA & DSC results as figures 2 and 3 with each other we see that they confirmed each other. DSC results of thermal decomposition of β-PbO_2 are shown in figures 3-6. The first reaction shown in figure 3 is an exotherm and it starts at 110°C and ends at 195°C. The area under the peak was computed by TA processor. This reaction is represented more largely and more exactly in the figure 4. The maximum point of this reaction occurs at 156°C. The ΔH was 29.54J/g, or 7.07 kJ/mol. A second reaction occurs between 330 and 390°C. This reaction is an endotherm. This part of the curve is shown more largely and more exactly in the figure 5. The area under the curve is computed. The maximum of this reaction is at 373°C. The ΔH for this peak is 120.48J/g or 28.82kJ/mol. The third peak (endothermic) starts at 400°C and ends at 450°C as shown in figure 3. which is enlarged and shown in figure 6. The maximum of this reaction is at 431°C. The value of ΔH was computed to be 22.26J/g or 5.32kJ/mol. These results confirms that the pyrolysis of βPbO_2 between 25-450°C occurs in three separate steps (one exotherms and two endotherms).

CONCLUSION

Thermal behavior of β-PbO_2 was examined using TGA, DSC techniques and following pathway was obsereved for the thermal decomposition of β-PbO_2 after XRD experiments confirms presence of $Pb_{12}O_{19}$ and Pb_3O_4 as compounds produced in the process of decomposition as well as identity of the final product PbO (mixed α & β) at 600°C.

β-PbO_2→Pb12O_{19}→Pb_3O_4→PbO

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