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STUDY OF THERMAL BEHAVIOR OF α-PbO_2, USING TG AND DSC

S. A. A. Sajadi[*]*, A. A. Alamolhoda and S. J. Hashemian*

Sharif University of Technology, Institute of Water & Energy, P.O.Box 11365-8639 Tehran, Iran

Using two techniques of thermogravimetry and differential scanning calorimetry under O_2 gas atmosphere from 25 to 600°C, the thermal behavior of laboratory-produced compound lead(IV) oxide α-PbO_2 was investigated. The identity of products at different stages were confirmed by XRD technique. Both techniques produced similar results supporting the same decomposition stages for the compound. Three distinct energy changes were observed, namely, two endothermic and one exothermic in DSC. The amount of ΔH for each peak is also reported.

Keywords: *DSC, lead(IV) oxide, TG, thermal analysis, XRD*

Introduction

Due to their chemical and physical characteristics, lead compounds are used in a wide variety of industries all over the world [1–6]. One of the most important characteristics of the lead concerns its reactions to acids and bases as well as to air, a process known as oxidation. Compounds like 'lead(II) oxide, lead(IV) oxide, sulfate, lead carbonate, lead nitrate as well as alkaline lead acetate' are the by-products of these reactions. Some are the end product of a desired process but most of them are undesired byproducts known as disturb compounds [7–9].

Lead(IV) oxide is one of the most significant compounds used in lead-acid batteries [8–13].

Lead(IV) and lead(II) oxide [3, 7] have two morphology known as α and β. The present research intended to investigate the thermal properties of α-lead(IV) oxide under different temperature conditions. It is said that pure lead(II) oxide is the final product of thermal decomposition process for a number of different lead compounds [14–17]. The morphology of these compounds was also studied [18–20].

Experimental

Materials and methods

α-Lead(IV) oxide was prepared in laboratory as described in this paper.

TG: 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 α-PbO_2

A $(NH_4)_2S_2O_8$ solution (25 g solved in 25 mL H_2O) was added to 100 mL saturated CH_3COONH_4 solution (solved in H_2O). Later on 32.5 g $Pb(CH_3COO)_2$ (solved in 30 mL H_2O) was slowly added to this mixture. Simultaneously 70 mL (25%) NH_3 solution was added as well. At first the solution turned yellow and then dark-brown and finally reddish. After 6 h stirring, 5 g $(NH_4)_2S_2O_8$ was added. This mixture was further-stirred about 38 h at 25°C. Then in order to remove excess of NH_3 and to bring unwanted lead compound in solution, it was heated up to 70°C. This mixture was cooled down and the supernatant (jut out) solution with white crystals of $PbAc_2$ was removed briefly. The black precipitation consisted of fine-grained and water insoluble of α-PbO_2. For the cleaning of the product it was transferred into some centrifuge container and was repeatedly washed with diluted CH_3COONH_4 solution. Afterwards it was dried in a desiccators over silica gel at 25°C.

X-ray diffraction of α-PbO_2

Using bedacryl, the lead(IV) oxide sample was prepared for X-ray and it was exposed to CuK_{α_1} radiation for 2 h. Figure 1 shows the XRD diagram of the compound α-PbO_2.

* Author for correspondence: sajadi@sharif.ac.ir

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Springer, Dordrecht, The Netherlands

TG analysis of α-PbO_2

33.346 mg of α-PbO_2 were weighted in a standard corundum container. This sample was heated (5°C min^{-1}) from 25 to 600°C under O_2 gas atmosphere (15 mL min^{-1}) (Fig. 2).

DSC analysis of α-PbO_2

A sample of α-PbO_2 was placed in a standard aluminum crucible and weighed accurately (15.834 mg) using a microbalance. A special equipment was used to seal the sample. The sealed crucible was placed in the DSC equipment and its temperature was raised from 25 to 600°C, with a heating rate of 5°C min^{-1}, under O_2 gas atmosphere. DSC curve of this sample is represented in Fig. 3.

Results and discussion

The XRD results obtained in this work is in a good agreement with standard diagram (ASTM 37-517) (Fig. 1).

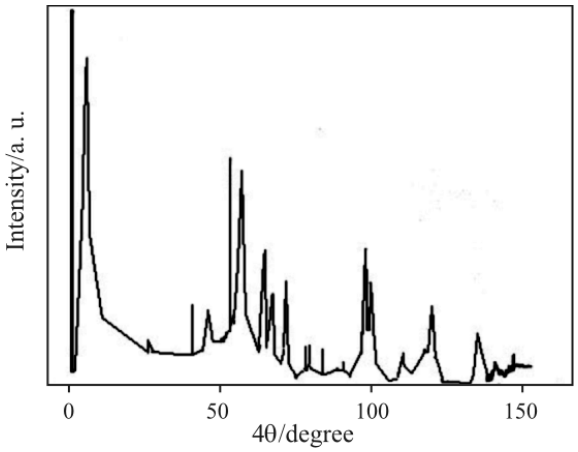

Fig. 1 XRD diagram of α-PbO_2

Thermal investigations of α-PbO_2

TG and DTG results

Both TG and DTG curves of thermal decomposition of α-PbO_2 are shown in Fig. 2. The curve in the upper part shows the mass loss (vertical axis) while horizontal axis and lower section show temperature increase, vertical axis shows the first derivative of mass loss while horizontal axis shows temperature increase.

So one can better differentiate between the stages of the thermal decomposition. The results indicate that thermal decomposition consists of three separate stages in the temperature range of 25–600°C, these results are summarized in Table 1.

Table 1 Results from the thermal investigations of α-PbO_2 in temperature range 25–600°C in O_2 atmosphere

Phase No.	Start temp./ °C	Turning point/ °C	End temp./ °C	Mass loss/ mg	Mass loss/ %
1	50.5	112.8	257.3	0.665	1.99
2	285.7	367.8	458.5	1.184	3.55
3	458.5	492.5	520.8	0.854	2.56

The first stage takes place between 50–257°C. The calculations of mass loss show that small quantities of water is present at the end of this region corresponding to a chemical formula of α-$PbO_2 \cdot 0.05H_2O$. The DTG curve shows that the first stage in TG curve actually consists of two different phenomena. First phenomenon is the loss of absorbed water and the second one is the decomposition of the starting compound.

Spectroscopic quantitative analysis in this study also corroborates this finding.

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

First stage of decomposition (50–257°C)

A heating rate of 5°C min^{-1} 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 accomplished in the O_2 atmosphere with a constant gas flow of 15 mL min^{-1}.

As can be inferred from the results of the Figs 2 and 3, the first phase of (decomposition) pyrolysis reaction of α-PbO_2 occurs in the range of 50–257°C. Concerning the case of α-PbO_2, the separation of O_2 and H_2O was also observed. Comparison of TG and DTG curve for this stage indicates the presence of two processes i.e. loss of adsorbed water followed by loss of O_2.

By subtracting the experimentally determined quantity of water (by spectrometric quantitative analysis) from the entire amount of mass loss (2%), one can approximately compute the separated O_2-quantity and obtain the following formula: α-$PbO_2 \cdot 0.05H_2O$. X-ray investigation supplied an identical XRD diagram to α-PbO_2. Now we wanted to compute the separated O_2-quantity for the range 50–257°C by subtracting the experimentally determined quantity of water from the entire decrease in mass approach. Therefore, the crystal of the product belongs to the stoichiometric compound (with broad homogeneity range). The XRD analysis supplied a similar XRD diagram as $Pb_{12}O_{19}$. The evaluation of the results as well as spectrophotometric analysis confirms presence of the formula $Pb_{12}O_{19}$.

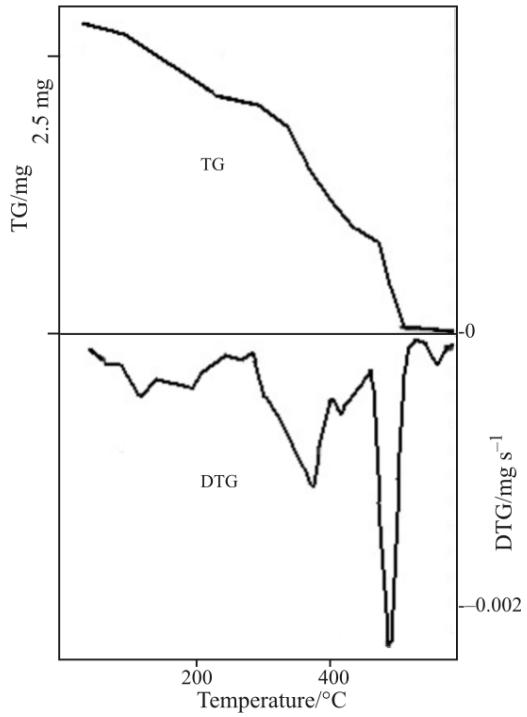

Fig. 2 Curve of α-PbO_2, temperature range 25–600°C

Second stage of decomposition (286–459°C)

The experiment results show that the product lost about 3.6% of its mass within the range 286–459°C. The experiment was accomplished in the O_2 atmosphere with a constant gas flow of 15 mL min^{-1}. The X-ray analysis supplied a similar XRD diagram as $Pb_{12}O_{17}$. The evaluation of the results as well as spectrometric analysis confirms the brutto formula: $Pb_{12}O_{17}$.

Third stage of decomposition (459–521°C)

The third mass loss equals to about 2.56% of the starting material and occurs in the temperature range of 459–521°C. The X-ray analysis of the product confirms presence of α- and β-PbO. This was checked by spectrometric analysis and the calculated brutto formula of PbO was obtained.

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

Therefore, the study of thermal behavior of α-PbO_2, by TG suggests four different stages as discussed above. At first the compound loses water followed by loss of oxygen in separate stages and changes into 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) to determine the energy of each step.

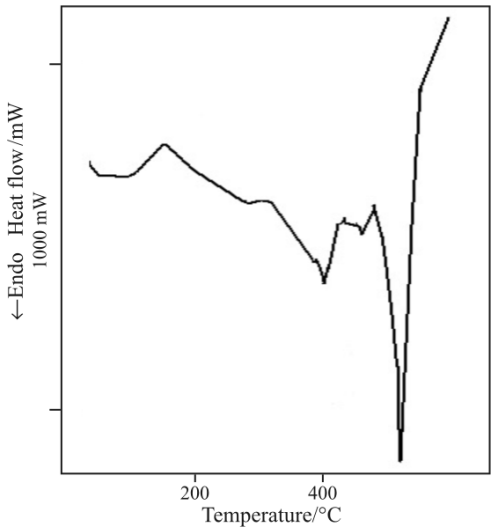

Fig. 3 DSC curve of α-PbO_2

DSC results

Both exothermic or endothermic reactions are shown in Fig. 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 beginning and the termination point of each deflection. A straight or a sigmoide baseline 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. The consequent results were ΔH_{exe} or ΔH_{end} in J g^{-1}.

If we compare the TG and DSC results as Figs 2 and 3 with each other we see that they confirmed each other. DSC results of thermal decomposition of α-PbO_2 are shown in Figs 3–6. The first reaction shown in Fig. 3 is an exotherm and it starts at 100 and ends at 200°C. The area under the peak was computed by TA processor. This reaction is represented more largely and more exactly in the Fig. 4. The maximum point of this reaction occurs at 145°C. The ΔH was 34.52 J g^{-1}, or 8.26 kJ mol^{-1}. A second reaction occurs between 350 and 430°C. This reaction is an endotherm. This part of the curve is shown more largely and more exactly in the Fig. 5. The area under the curve is computed. The maximum of this reaction is at 404°C. The ΔH for this peak is 49.57 J g^{-1} or 11.86 kJ mol^{-1}. The third peak (endothermic) starts at 480 and ends at 550°C as shown in Fig. 3 which is enlarged and shown in Fig. 6. The maximum of this reaction is at 527°C. The value of ΔH was computed to be 212.40 J g^{-1} or 50.81 kJ mol^{-1}. These results con-

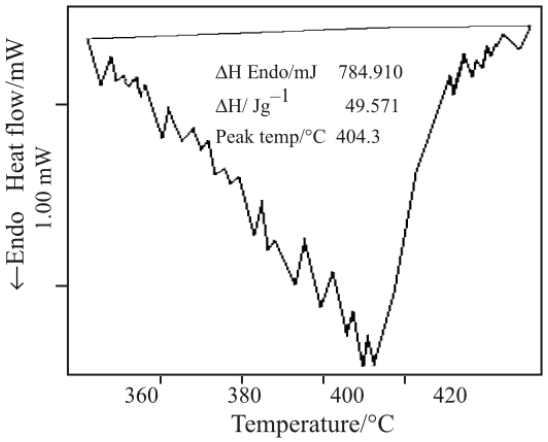

Fig. 4 The first stage of DSC curve of α-PbO_2

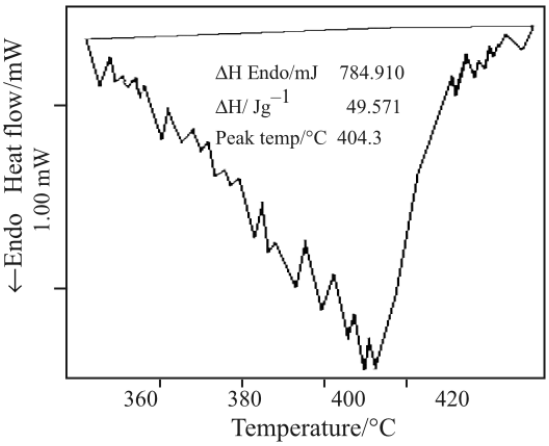

Fig. 5 The second stage of DSC curve of α-PbO_2

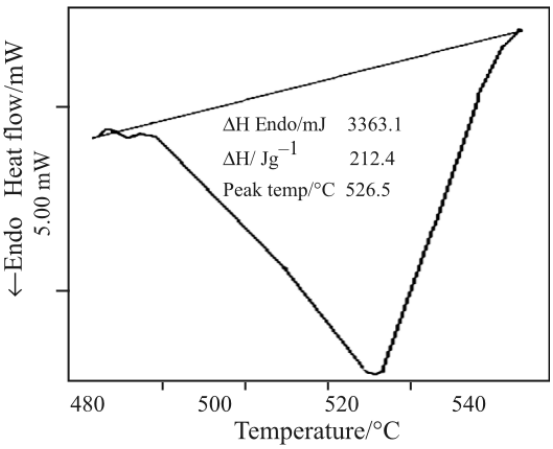

Fig. 6 The third stage of DSC curve of α-PbO_2

firms that the pyrolysis of α-PbO_2 between 50–550°C occurs in three separate steps (one exotherms and two endotherms).

If we use the entropy amount of the compound α-PbO_2 (76.6 J K^{-1} mol^{-1}), α-PbO (69.45 J K^{-1} mol^{-1}) [3], we received for the Δ*S* of the following reaction:

$$\alpha\text{-}PbO_2 \rightarrow PbO + 0.5O_2 \quad (1)$$

the value of 95.37 J K^{-1} mol^{-1}. Now we can use this value to calculate Δ*G* for the compound α-PbO_2 (218.99 kJ mol^{-1}), α-PbO (249.36 kJ mol^{-1}) and for the above reaction 30.37 kJ mol^{-1} [16]. The experimental received value for Δ*G* in this work is also 26 kJ mol^{-1}.

Conclusions

Thermal behavior of α-PbO_2 was examined using TG, DSC techniques and following pathway was observed for the thermal decomposition of α-PbO_2 after XRD experiments confirms presence of $Pb_{12}O_{19}$ and $Pb_{12}O_{17}$ as compounds produced in the process of decomposition as well as identity of the final product PbO (mixed α and β) at 600°C.

$$\alpha\text{-}PbO_2 \rightarrow Pb_{12}O_{19} \rightarrow Pb_{12}O_{17} \rightarrow PbO$$

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