December 2006 Volume 2 Issue 6

Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

MSAIJ, 2(6), 2006 [234-237]

Thermal Behavior Of Alkaline Lead Carbonate, A Study Of Thermogravimetry And Differential Scanning Calorimetry

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Received: 11th November, 2006
Accepted: 26th November, 2006

Web Publication Date : 27th December, 2006

ABSTRACT

The compound alkaline lead carbonate $3PbCO_3 \cdot 2Pb(OH)_2$ 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 identity of 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

Alkaline lead carbonate;
XRD;
Thermal analysis;
Thermogravimetry;
Differential scanning calorimetry.

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 kinds 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]. The goal of this work was to investigate the thermal properties of alkaline lead carbonate 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[8,13-15].

EXPERIMENTAL

Materials and equipment

Alkaline lead carbonate was prepared in this laboratory 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 alkaline lead carbonate

A lead (II) acetate solution (18.95 g solved in 225 ml H_2O) was prepared. To this solution was added slowly 25 ml freshly prepared 2 M NaOH solution. The pH value of this mixture amounted to 7.5. Through this clear solution led a weak air flow with help of a glas frite during two days. The formed white precipitation was filtered off with a filter paper and washed with hot CO_2-free water. Afterwards was dried in a desiccators over silica gel at 25°C.

X-ray diffraction of alkaline lead carbonate

The alkaline lead carbonate 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 alkaline lead carbonate.

TGA analysis of alkaline lead carbonate

28.838 mg of alkaline lead carbonate were weighted in a standard container from corundum.

Figure 1: XRD diagram of alkaline lead carbonate

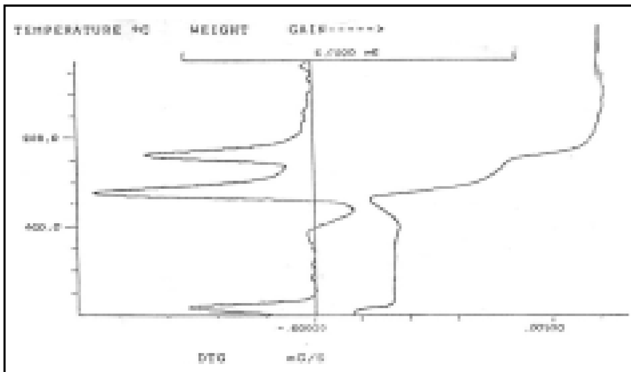

Figure 2: TGA diagram of alkaline lead carbonate

This sample was heated (5°C/min) from 25 to 600°C under O_2 gas atmosphere (15 ml/min) (Figure 2).

DSC analysis of alkaline lead carbonate

A sample of alkaline lead carbonate were placed in a standard crucibles from aluminium and weighed accurately (18.820 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 a heating rate of 1°C/min, under O_2 gas atmosphere. DSC curve of this sample is shown in figure 3.

RESULTS AND DISCUSSION

Thermal investigations of alkaline lead carbonate

TGA and DTG results

Both TGA and DTG curves of thermal decomposition of alkaline lead carbonate 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 three separate stages in the temperature range of 25-600°C and summarized in TABLE 1.

(1) First stage of decomposition (180-270°C)

A heating rate of 5°C/min was chosen to determine the real value of possibly 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.

As is to be inferred from the results of the figures 2 and 3, the first phase of (decomposition) pyrolysis reaction of alkaline lead carbonate occurs in the range of 180-270°C. As in the case of alkaline lead carbonate we observed here also the weight loss of 4.87%. Comparison of TGA and DTG curve for this stage suggests a decomposition process.

X-ray investigation supplied an identical XRD diagram to $3PbCO_3 \cdot 2PbO$. The evaluation of the results as well as spectrophotometric analysis the formula $3PbCO_3.2PbO$.

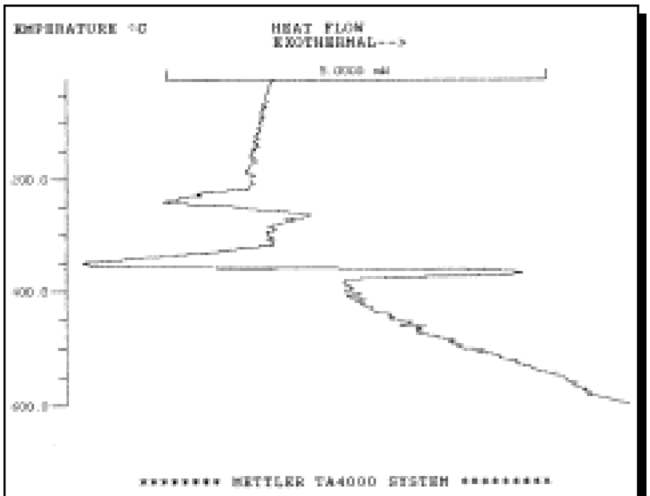

Figure 3: DSC diagram of alkaline lead carbonate

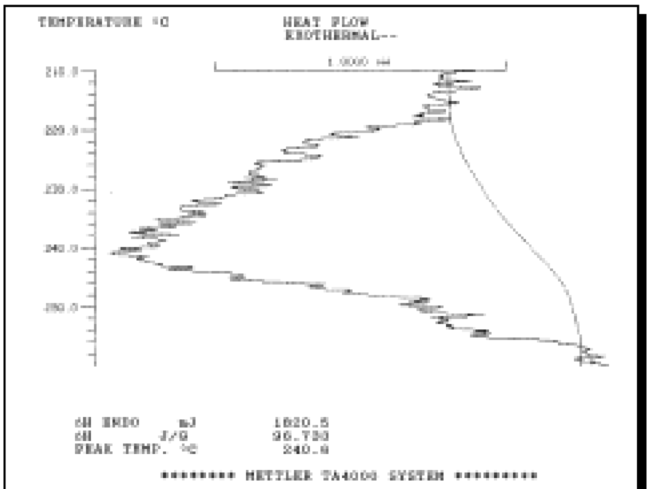

Figure 4: The first stage of DSC diagram of alkaline lead carbonate

(2) Second stage of decomposition (270-345°C)

From the experimentally results is to be used, that the product lost within the range 270-345°C about 6.75% of its weight. The experiment was accomplished in the O_2 atmosphere with a constant gas flow of 15 ml/min. The X-ray analysis supplied a similar XRD diagram as PbO. Some other lines have been observed, which could not be identify. The evaluation of the results as well as spectrometric analysis the brutto formula: PbO.

(3) Third stage of decomposition (345-420°C)

In the third stage, i.e. in the temperature range of 345-420°C, the product absorbs O_2 from the atmosphere, i.e. over oxidation. The weight of the substance increases 1.40% and PbO converted to Pb_3O_4. The X-ray analysis of the product confirms presence

TABLE 1: Results from the thermal investigations of alkaline lead carbonate in temperature range 25-600°C in O_2 atmosphere

Phase No.	Start temp. [°C]	Turningpoint [°C]	End temp. [°C]	Weight decrease [mg]	Weight decrease [%]
1	180	240	270	–1.40	–4.87
2	270	325	345	–1.95	–6.75
3	345	370	420	+0.40	+1.40
4	550	580	600	–0.58	–2.01

of Pb_3O_4. This was checked by spectrometric analysis and the calculated brutto formula of Pb_3O_4 is reached.

(4) Fourth stage of decomposition (550-600°C)

The third weight loss equals to about 2% starting material and occurs in the temperature range of 550-600°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 is reached .

We want to point out again that the pyrolysis of alkaline lead carbonate within the range 25-600C in the O_2-atmosphere led to PbO, i.e. the reaction $3PbCO_3{\cdot}2Pb(OH)_2 \rightarrow PbO$ ran off completely with approximately 600°C. From the above TG diagram it is evident that the pyrolysis reaction of alkaline lead carbonate in the range 25-600°C consists of three stages. The final decomposition product is PbO.

Therefore, study of thermal Behavior of alkaline lead carbonate, by Thermogravimetry suggests four different stages as discussed above. At first the compound losses water followed by loss of oxygen. 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 beginning and the termination point of each deflection. A straight or a sigmoid 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 figure 2 and 3 with each other we see that they confirmed each other. DSC results of thermal decomposition of alkaline lead carbonate are shown in figures 3-6. The first reaction shown in figure 3 is an endotherm and it starts at 210°C and ends at 260°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 240°C. The ΔH was 96.73 J/g, or 124.20 kJ/mol. The second peak (endothermic) starts at 310°C and ends at 364°C as shown in figure 3. which is enlarged and shown in figure 5. The maximum of this reaction is at 352°C. The value of DH was computed to be 331.43 J/g or 425.56 kJ/mol. The third peak (exothermic) starts at 355°C and ends at 384°C as shown in figure 3. Which is enlarged and shown in figure 6. The maximum of this reaction is at 363°C. The value of ΔH was computed to be 191.86 J/g or 246.35 kJ/mol. These results confirms that the pyrolysis of alkaline lead carbonate between 50-550°C occurs in three separate steps (one exotherms and two endotherms).

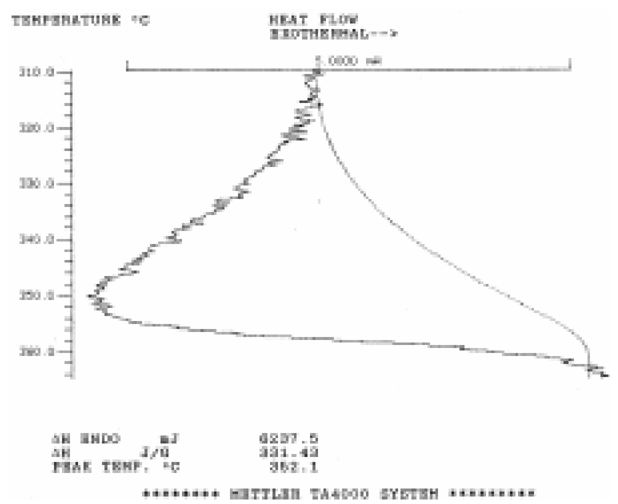

Figure 5: The second stage of DSC diagram of alkaline lead carbonate

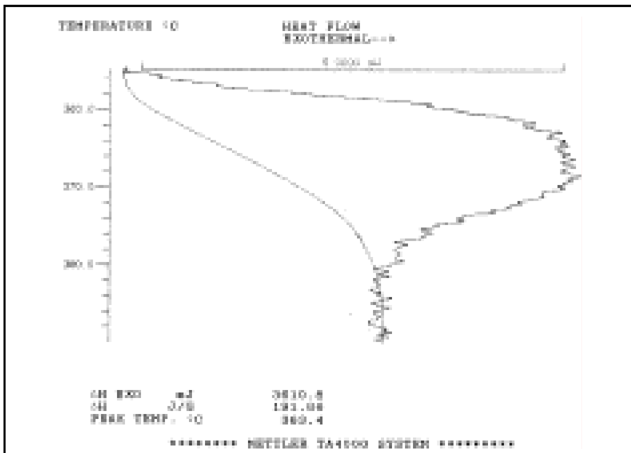

Figure 6: The third stage of DSC diagram of alkaline lead carbonate

CONCLUSION

Thermal behavior of alkaline lead carbonate was examined using TGA, DSC techniques and following pathway was obsereved for the thermal decomposition of alkaline lead carbonate after XRD experiments confirms presence of $3PbCO_3{\cdot}2PbO$ and Pb_3O_4 as compounds produced in the process of decomposition as well as identity of the final product PbO (mixed α and β) at 600°C.

$$2Pb(OH)_2 \rightarrow 3PbCO_3{\cdot}2Pb(OH)_2 \rightarrow 3PbCO_3{\cdot}\,2PbO \rightarrow PbO \rightarrow Pb_3O_4 \rightarrow PbO$$

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