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Research Note

An Investigation into the Structure and Thermal Properties of Lead Hydroxide

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The compound, lead hydroxide $Pb_6O_4(OH)_4$, was prepared by a method used for the first time in the authors laboratory. The compound was identified by XRD and it's purity was determined by analytical methods (100%). The thermal characteristics of this compound were investigated by using a thermogravimetry (TGA). This compound was found to be stable at room temperature and at 160°C will decompose completely to produce lead (II) oxide.

INTRODUCTION

Lead is used in different industries world-wide [1-3]. Nowadays, lead is widely used because of its chemical and physical characteristics [4-6] and the manufacturing of batteries (lead-acid-batteries), which are produced daily all over the world [5,7], is one of its most important uses. Also, many alloys are manufactured with lead. One of the most important characteristics of lead is its reaction with acids and bases, as well as with air, which is well-known as oxidation. In consequence of these kinds of reactions, important compounds have been developed, such as lead sulfate, lead carbonate, lead nitrate and lead hydroxide, most of which are known as disturb compounds. One of the well-known tasks of industry is to keep energy consumption as low as possible [8,9].

The goal of this work is to investigate the properties of lead hydroxide and find a suitable and economical procedure to recover lead in a useful form, when it can be reused by industry as metallic lead or its compounds [8-11]. The recovery of lead from lead hydroxide or waste materials in industry is presently done using a reduction method, i.e., using coke and heating it up to 1300 degrees. A lot of energy is required to reach this temperature in order to complete this process. To produce lead (II) oxide from lead, one must use energy again. However, this work suggests an economical procedure by which lead hydroxide can be converted into lead (II) oxide directly using much less energy.

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EXPERIMENTAL

Preparation

Lead (II) acetate (20 g) was dissolved in 50 ml of water. Then, 100 ml of a 10% caustic soda solution (10 g NaOH solved in 90 ml water) was added under constant stirring, which rapidly formed a white precipitate. Subsequently, the suspension was filtered and the white precipitate was washed with ample amounts of CO_2-free water. The product was dried in a vaccum desiccator over blue silica gel.

X-ray Diffraction of Lead Hydroxide

The lead hydroxide sample was prepared in Bedacryl and exposed over a period of two hours with CuKα1 radiation. The densitometer curve of Guinier's diagram was obtained (Figure 1). This curve helps to differentiate the XRD peaks as separately and as best as possible.

Electron Microscopic Investigation of Lead Hydroxide

The first series of the morphologic investigation of lead hydroxide was accomplished with a SEM electron microscope (REM-JEOL-JSM-840). The preparation of the sample was also accomplished by a coating of the surface with gold (3-4 min). The reasonable enlargements were 5000 times. The second series of electron microscopic investigation with TEM equipment was

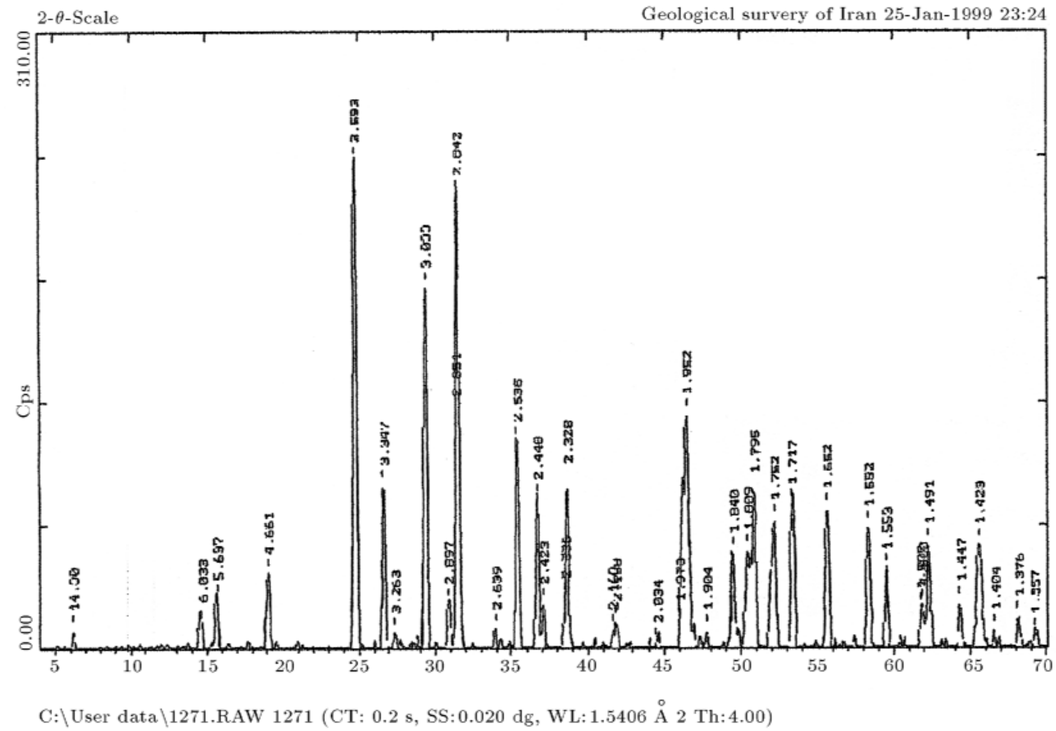

Figure 1. XRD diagram of lead hydroxide.

accomplished (EM-Hitachi, H-600). The sample was prepared as follows. The white powdery sample was coated, first, with carbon. This carbon film was then treated with HF acid from the surface and investigated using the TEM equipment.

Thermal Investigation of Lead Hydroxide

The thermal investigation was accomplished using a thermogravimeter (Mettler- TG 50), with a TA processor attached.

TG analysis in an oxygen atmosphere: A standard crucible (from corundum) was filled with 28.308 mg lead hydroxide and placed into the TG balance. Then, the sample was heated under the following specifications: Starting temperature: 25°C, final temperature: 600°C, heating rate: 5°C/min and stream gas: O_2.

TG analysis in a nitrogen atmosphere: About the same quantity of lead hydroxide as above was put into a standard crucible and placed into the TG balance. Then, the sample was heated under the following specifications: starting temperature: 25°C, final temperature: 600°C, heating rate: 5°C/min, stream gas: N_2 entered to the TA-processor.

RESULTS AND DISCUSSION

A white precipitate, $Pb_6O_4(OH)_4$, is produced by addition of a lead (II) acetate solution to an alkaline solution. It is sparingly soluble in water. Lead hydroxide as a base is easily soluble in an acidic solution. Its acidic character is more weakly pronounced. It is soluble only in a concentrated caustic solution under formation of the Plumbate. Lead hydroxide as simple $Pb(OH)_2$ is not well-known. X-ray analysis shows that the structure contains a pseudocubic Pb_6O_8-cluster, similar to the structure of $MoCl_8^{4+}$, with an 8 O atom center over the surface of a PbO octahedron and in an infinite row by H-bonding. One finds the same type of structure with tin hydroxide [7]. When adding $Pb(Ac)_2$ to ammonia or a caustic soda solution, with the exclusion of CO_2, a green shining substance is produced.

The XRD results show good agreement with the standard diagram of lead hydroxide (Figure 1) (ASTM 21-474). The analysis of the product showed that the sample is stable. By this method, lead hydroxide was produced for the first time in pure form. Other researchers have reported the preparation of PbO by this method, under different conditions. They have reported that, by adding lead nitrate to an alkaline solution, lead hydroxide [12,13] is produced. The mentioned method was used by the present authors but no pure product was obtained.

An SEM photograph of the produced lead hydroxide is shown in Figure 2. The crystals are round, with a diameter of 1 μm and are arranged well next to each other forming large round crystals.

A TEM photograph of the produced lead hydroxide is shown in Figure 3. The crystals are somewhat

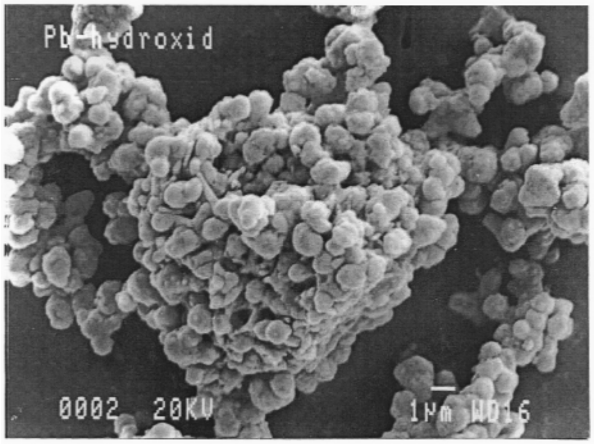

Figure 2. SEM electron microscopic photograph of lead hydroxide; enlargement is 5000 X.

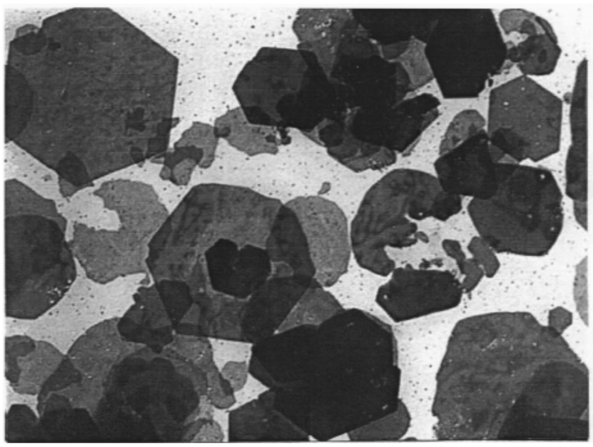

Figure 3. TEM electron microscopic photograph of lead hydroxide; enlargement is 30000 X.

larger and form round crystals. Individual particles look hexagonal and can be observed in small and large dimensions. Apart from broken crystals, they are mainly arranged crystals. The TEM photograph was reasonably enlarged 30000 times.

Specific Surface, Particle Size and Crystal Size of the Lead Hydroxide

Electron micrographs were used for the estimation of the particle size of the lead hydroxide. The specific surface of 1.9 m^2/g was determined by BET. From this information, the crystal size was computed to be 2397 Å. The adsorbed quantity of water was calculated from TG experiments to be 1.7. Therefore, this formula of $Pb_6O_4(OH)_4 1.7H_2O$ was determined.

Thermal Investigation

The top of the illustration in Figure 4 represents the weight loss of the sample as a function of the temperature. The DTG curve is shown in the lower part. The gradual weight loss of the compound is recorded on the right side of the illustration. From a comparison of the numbers shown in Figure 4 with the DTG curve shown in the same figure, it is evident that the TA processor divided this whole series of decomposition reactions into five large sections. The TG curve has several small stages and it is required that they should be examined in sequence here. It is important to point out that this pyrolysis reaction was accomplished in the O_2 stream. The flow meter showed a constant value of 15 ml/min with the measurement. Interestingly enough, a reaction stage is observed here, at which the oxidation of the sample takes place. This stage is in the temperature range 340-480°C and the sample lost a total of 6% of its weight. In connection with this important result, the above attempt was repeated, under a N_2 stream (see Figure 5), with the expectation that the decomposition reaction of the lead hydroxide done in the N_2 atmosphere would be in good agreement with the final products of α- and β-PbO. In the last case over-oxidation reaction did not occur. The sample lost a total of 5% in weight. From these results, the same thermal behavior of the lead hydroxide in different atmospheres was observed. In the first stage, the sample loses about 3% of its weight and in the second stage 1-1.5%. For identification of the compounds, the temperature was increased during the completion of each stage and the sample was examined using an XRD method. It was clearly stated that the final product consisted only of α- and β-PbO, which was a good result. The chemical analysis showed no impurities.

As shown in Figure 4, this curve consists of five stages. In the first stage, i.e., temperature range 25-170°C, the pyrolysis reaction of lead hydroxide takes place and PbO is produced. It develops a mixture of α- and β-PbO. In the second stage, i.e., temperature range of 170-280°C, the last weight loss is observed. The XRD analysis confirms the products α- and β-PbO. In the third stage, i.e., temperature range of 280-430°C, the product absorbs O_2 from the atmosphere, i.e., causing over oxidation. The weight of the substance increases and the PbO is converted to a mixture of $Pb_{12}O_{19}$ and Pb_2O_3. In the fourth stage, i.e., temperature range of 430-480°C, the O_2 absorption reaction takes place again. The weight of the substance increased again and Pb_3O_4 was developed. The products of the third and fourth stages were confirmed by the XRD method. The fifth stage converted Pb_3O_4 to PbO so that the weight decreased. This took place in the temperature range of 480-600°C. A comparison between Figures 4 and 5 shows that, in a N_2 atmosphere, only two stages are to be observed. After these two stages, a mixture of α- and β-PbO was received. Because no O_2 was present, no over-oxidation took place.

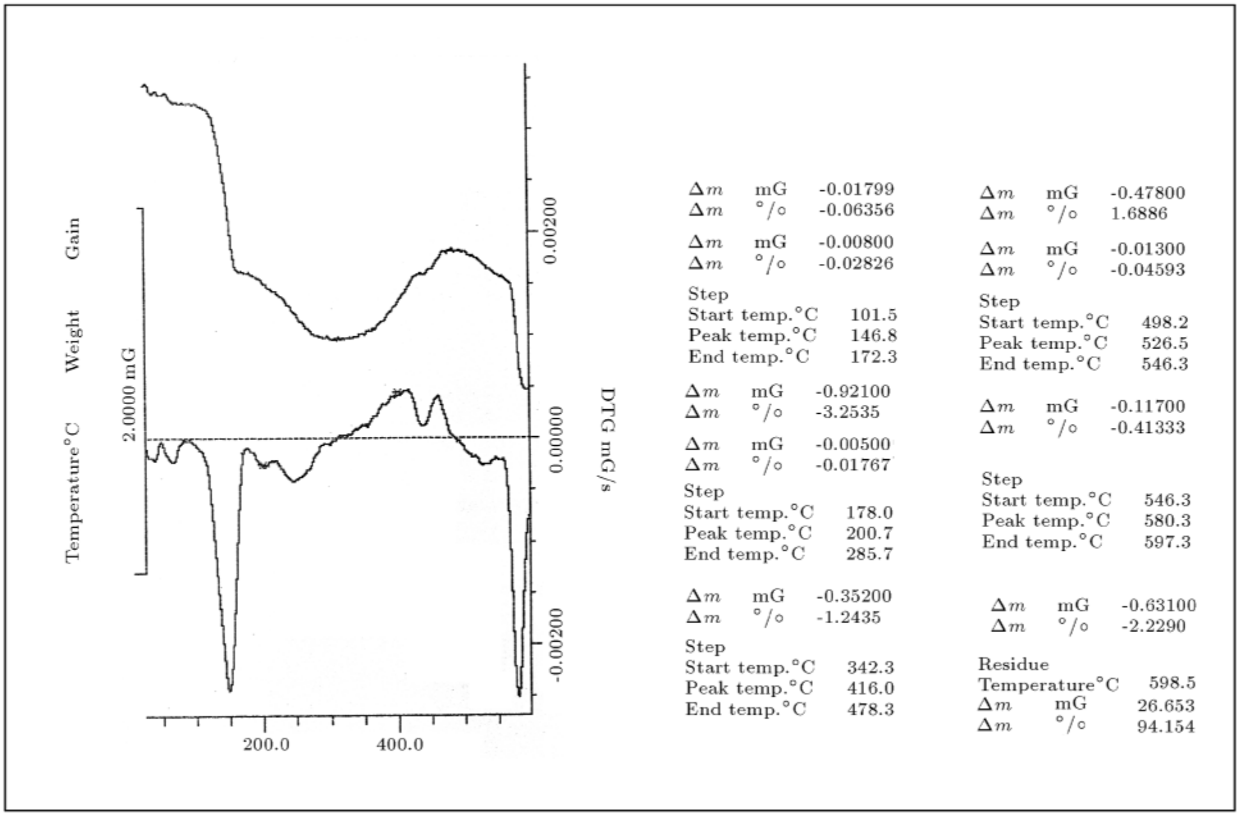

Figure 4. Thermogram of lead hydroxide with temperature range of 25-600°C, under the O_2 stream.

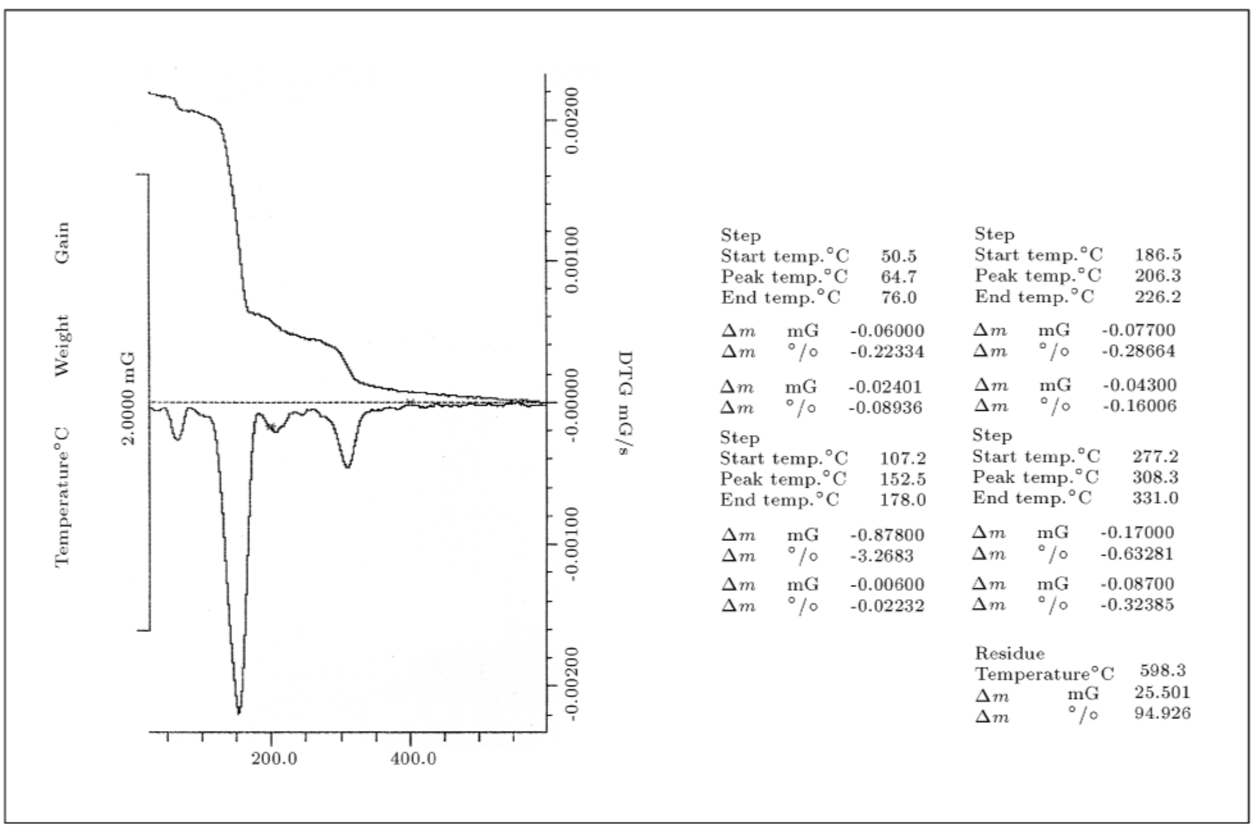

Figure 5. Thermogram of lead hydroxide with temperature range of 25-600°C, under the N_2 stream.

These results suggest that the method described by the authors is successful for the synthesis of lead hydroxide and the product exists as pure lead hydroxide. The thermal investigations of lead hydroxide by the TG method showed that under an O_2 or N_2 atmosphere, the compound decomposes to α- and β-PbO. Since PbO does not contain impurities, it can be reused in industry. Thus, lead hydroxide can be converted to PbO, which is an economical procedure for industry. For this reason, if a constant temperature of 160°C could be achieved, then, lead hydroxide could be converted to PbO (instead of a reduction of Pb compounds at 1300°C in industry). With application of the exact conditions reported in this work, industry could receive a useful lead compound from waste materials using less energy.

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