October, 1983] © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 3129—3133 (1983) 3129

The Formation and Thermal Decomposition of Hydrous Lead(II) Oxide Prepared by the Alkoxide Method

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(Received December 7, 1982)

Lead(II) isopropoxide was hydrolyzed by addition to water in order to investigate the effects of temperature, rate of hydrolysis, seeds and anions added in aqueous phase on the formation of hydrous lead(II) oxide. Thermal decomposition of the resulting hydrous lead(II) oxide was also investigated using TG and DTA techniques. It was found that the metastable phase of lead(II) oxide, $3PbO \cdot H_2O$ (tetragonal), was formed only under certain strict conditions, *i.e.*, at higher rate of hydrolysis and at temperatures below 40 °C, whereas the anhydrous lead(II) oxides such as massicot (orthorhombic), litharge (tetragonal), or a mixture of the two were formed under conditions other than those described above. In the presence of massicot seed in aqueous phase, massicot was predominantly formed under the formation conditions of $3PbO \cdot H_2O$. It was also found that the presence of anions such as citrate and EDTA ions, which have higher complexing ability with Pb^{II} ion, facilitated the formation of $3PbO \cdot H_2O$ even under the formation conditions of massicot. In the heating process, $3PbO \cdot H_2O$ was changed to litharge at 168 °C with the release of its water of crystallization and then transformed to massicot at 650 °C. The reaction order and activation energy for the dehydration were 0.9 and 112.6 kJ mol^{-1}, respectively.

Although many hydrous lead(II) oxides such as $5PbO \cdot 2H_2O$,[1,2] $8PbO \cdot 3H_2O$,[2] $3PbO \cdot H_2O$,[3–5] and $2PbO \cdot H_2O$[3,4] have been prepared by the hydrolysis of $Pb(NO_3)_2$ and $Pb(CH_3COO)_2$ solutions, these contents of the water of crystallization have been thought to be ambiguous. This is because of this small amounts compared with the total weights of these hydrous lead(II) oxides and of the strong affinities for carbon dioxide in air.[5] Therefore, an investigation to clarify the relationship between the formation conditions and the chemical composition and other properties of the hydrous lead(II) oxides is desirable.

The authors have previously proposed a new industrial method for the production of lead(II) oxide ("Oxygen Pressurized Wet Milling Method"[6,7]), in which many spherical granules of metallic lead (3—5 mm in diameter) are oxidized with pressurized oxygen in the presence of water at temperatures below about 60 °C in a rotating mill. In the course of this developments further information about the formation of the hydrous lead(II) oxides was also necessary, since the hydrous lead(II) oxide ($3PbO \cdot H_2O$) was formed together with massicot and litharge according to the conditions. $3PbO \cdot H_2O$ is characterized by its very small particle size and higher activity for chemical reactions; which properties seem to be advantageous for a variety of industrial uses.

On the other hand, it is well known that the products obtained by the hydrolysis of lead(II) salts tend to be affected by the presence of anions such as CH_3COO^-, NO_3^-, and Cl^-, and anhydrous lead(II) oxides or basic lead(II) compounds are often formed instead of the hydrous lead(II) oxides.[8,9] As a starting material for the hydrolysis of $lead^{II}$ ion without the effect of anions, lead(II) isopropoxide can be used conveniently.[10]

This study will deal with the formation of hydrous lead(II) oxide by the hydrolysis of lead(II) isopropoxide, especially with the effects of changes in temperature, rate of hydrolysis, and additions of seeds and anions. The thermal decomposition of the resulting hydrous lead(II) oxide was also studied by TG and DTA techniques.

Experimental

Reagents. All the reagents used were of extra pure grade. The isopropyl alcohol was purified by fractional distillation. Anhydrous lead(II) acetate was used after drying overnight at 110 °C. The water used was obtained by double distillation of dilute potassium manganate(VII) aqueous solution.

Procedure. An alcoholic solution containing 3.0 wt% lead(II) isopropoxide was prepared according to the method reported by Yamaguchi *et al.*[10] Sodium isopropoxide was first prepared by the reaction of 0.68 g metallic sodium with a 200 cm^3 of isopropyl alcohol (Eq. 1). Then, 4.8 g of anhydrous lead(II) acetate was

$$Na + C_3H_7OH \longrightarrow Na(OC_3H_7) + 1/2H_2, \qquad (1)$$

added to the alcoholic solution and the mixture refluxed for 6 h (Eq. 2). After centrifuging to remove sodium acetate, 3.0 wt%

$$Pb(CH_3COO)_2 + 2NaOC_3H_7 \xrightarrow[C_3H_7OH]{83\,^{\circ}C,\ 6\,h} Pb(OC_3H_7)_2 + 2CH_3COONa\downarrow \qquad (2)$$

lead(II) isopropoxide solution was obtained.

The hydrolysis of the alkoxide was carried out as follows: A 400 cm^3 of the distilled water was transferred to a 1 dm^3 three-necked glass flask equipped with a reflux condenser, a dropping funnel, a thermometer, and a magnetic stirrer, and heated to the desired temperature under nitrogen atmosphere. Subsequently, a 200 cm^3 portion of alcoholic solution of the alkoxide in the dropping funnel was added to the distilled water with vigorous stirring (Eq. 3). The resulting suspension was stirred for further 30 min.

$$Pb(OC_3H_7)_2 + H_2O \longrightarrow PbO\downarrow + 2C_3H_7OH \qquad (3)$$

After measuring the pH of the suspension, the product was filtered off, washed with acetone and diethyl ether, and dried over P_2O_5 under reduced pressure.

Analysis. The X-ray diffraction patterns were obtained using a Rigaku Denki Geigerflex D-2F with Ni filtered Cu *Kα* radiation, with 30 kV and 15 mA. The observation of the product was carried out with a Hitachi-Akashi Scanning

Electron Microscope MSM 4C-102. The IR absorption spectra were obtained on a Nippon Bunko IR-E spectrometer with the KBr pellet technique. DTA and TG were performed using a Rigaku Denki Thermoflex over the range from room temperature to 700 °C. α-Al_2O_3 was used as a standard substance and the rate of temperature rise was 10 °C/min.

Results and Discussion

Effects of Temperature and Hydrolysis Rate. The effects of temperature and hydrolysis rate on the crystal form of the product are given in Table 1. In these experiments, the hydrolysis rate was changed by controlling the rate of addition of the alkoxide solution to the aqueous phase. Figure 1 also shows the X-ray diffraction patterns of these typical products shown in Table 1. According to the conditions, three kinds of lead(II) oxides, *i.e.*, $3PbO\cdot H_2O$,[11] massicot,[12] and litharge[13] were formed as single phases or as binary mixtures. A product consisting of only $3PbO\cdot H_2O$ was obtained under the conditions of low temperatures (<40 °C) and high hydrolysis rate. With decreasing hydrolysis rate, the amount of massicot in addition $3PbO\cdot H_2O$ was gradually increased. One other noticeable result was that the formation of $3PbO\cdot H_2O$ was independent of the pH of the resulting suspension in the range of 9—12. On the other hand, a product consisting of only litharge was obtained under the conditions of high temperatures and hydrolysis rate. Similarly the amount of massicot in addition to litharge increased with decreasing hydrolysis rate, and a product consisting of only massicot was obtained at low hydrolysis rate. Thus formation of massicot and litharge is identical

Table 1. Effects of temperature and hydrolysis rate on the crystal form of the lead(II) oxide prepared by the alkoxide method

No.	Temp °C	Addition speed of alkoxide s/200 cm^3	Product$^{a)}$
1	25	2	H
2	40	2	H
3	50	2	L
4	60	2	L
5	80	2	L
6	25	5	H
7	25	3×10^2	M+H
8	25	1.2×10^3	M+H
9	25	6×10^3	M
10	60	5	L+M
11	80	5	L+M

a) H: $3PbO\cdot H_2O$, L: litharge, M: massicot.

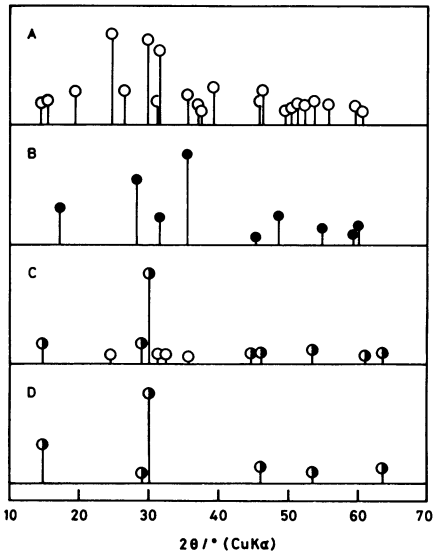

Fig. 1. X-Ray diffraction patterns of the lead(II) oxides prepared by the alkoxide method.
○: $3PbO\cdot H_2O$, ◑: massicot, ●: litharge, (A): sample No. 1, (B): sample No. 4, (C): sample No. 7, (D): sample No. 9 in Table 1.

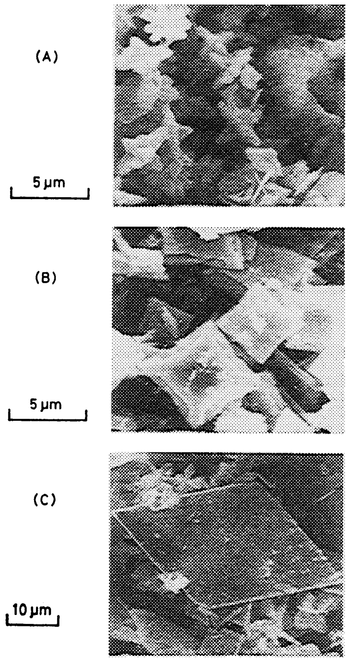

Fig. 2. Scanning electron micrographs of the lead(II) oxides prepared by the alkoxide method.
(A): $3PbO\cdot H_2O$, (B): litharge, (C): massicot.

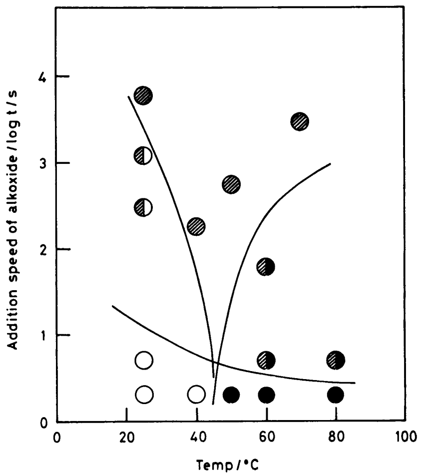

Fig. 3. Formation region of three kinds of the lead(II) oxides prepared by the alkoxide method.
○: $3PbO\cdot H_2O$, ▨: massicot, ●: litharge, ◑▨: mixture.

Table 2. Free energies of formation of lead(II) oxide

Lead(II) oxide	ΔG_f° / kJ mol^{-1}	
	Latimer[14]	Spencer *et al.*[15]
$3PbO \cdot H_2O$	—	−187.7
Massicot	−188.5	−188.1
Litharge	−189.4	−188.7

with that reported by Yamaguchi *et al.*[10] As shown in Fig. 2, the precipitated $3PbO \cdot H_2O$ was a petal shaped crystal of 2—5 μm in size, which were smaller than those of massicot and litharge. Figure 3 demonstrates the formation regions of these three lead(II) oxides. It was found that the formation of pure $3PbO \cdot H_2O$ was limited to a sharply defined region of low temperature and high hydrolysis rate.

In general, a crystal nuclei generated from a homogeneous phase during a reaction (Eq. 3) does not always correspond with that of the thermodynamically stable phase. A crystal nuclei of a metastable phase is often formed under nonequilibrium states of supersaturation. The standard free energies of formation of these three lead(II) oxides are given in Table 2.[14,15] The thermodynamical stability is found to be litharge>massicot> $3PbO \cdot H_2O$ in that order. Thus, $3PbO \cdot H_2O$ is a metastable phase.

Effect of Seed. A series of experiments was carried out in which three kinds of lead(II) oxides prepared by the alkoxide method were previously added in an aqueous phase and the results of the effect of various seeds on the crystal form of the product are given in Table 3. When 0.2 g (corresponding 20 wt% amount for the product yield) of massicot seed was added, the product, consisting only of massicot, was obtained even under the formation conditions of $3PbO \cdot H_2O$, whereas the addition of 0.1 g of massicot seed had no affect because its amount was not enough against the supersaturation. The same results in the presence of massicot seed was also observed under the formation conditions of litharge. This result means that massicot is apparently more stable than litharge in this experiment, contrary to the thermodynamical stability order. It is generally known that the crystal form of lead(II) oxide is affected by a small amount of impurities (especially Si^{IV} ion) and massicot is predominantly formed.[16] Following the addition of $3PbO \cdot H_2O$ and litharge seeds under the formation conditions of massicot, the crystal form of the product was always massicot, as expected from the apparent stability order.

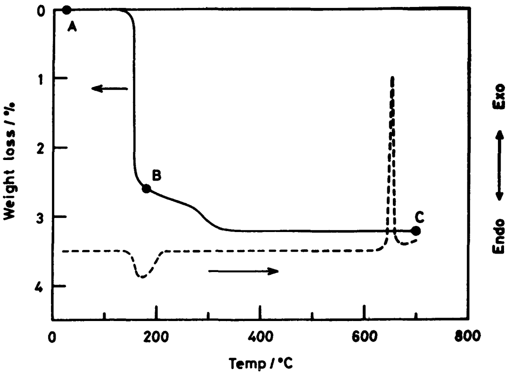

Fig. 4. TG and DTA curves of the hydrous lead(II) oxide ($3PbO \cdot H_2O$) under an air atmosphere.
Heating rate of furnace: 10 deg/min, amount of sample: 37.4 mg.

Effect of Anions. A series of experiments was carried out under the formation conditions of massicot in which several anions were previously dissolved in aqueous phase in a concentration range of 1×10^{-4}—1×10^{-3} mol dm^{-3}. The results of the effect of these anions on the formation of $3PbO \cdot H_2O$ are given in Table 4. A product consisting only of $3PbO \cdot H_2O$ was obtained instead of massicot following the addition of citrate ion or EDTA ion. A minor amount of $3PbO \cdot H_2O$ was also obtained, together with massicot, following the addition of sulfate ion. However, the coexisting acetate and chloride ions did not affected the crystal form of the product. The complexing ability of these anions with lead^{II} ion is decreased in the order: EDTA>citrate> sulfate>acetate>chloride.[17] Therefore, it was concluded that the presence of the anions having higher formation ability of the lead^{II} complex facilitated the selective formation of $3PbO \cdot H_2O$.

Lead^{II} ion forms an octahedron configuration coordinating H_2O molecule or OH^- ion in aqueous solution. If certain anions having high complexing ability with lead^{II} ion are presented in the solution, H_2O molecule or OH^- ion is rapidly substituted for these anions according to these complexing abilities and concentrations. It is generally known that the crystal form of the nuclei is affected by the coordinating anions when metal ions such as iron and titanium are precipitated by the hydrolysis.[18,19] In these studies, the polymorphism has been interpreted by a mechanism in which the order of the formation energy of the critical nuclei is

Table 3. Effect of seed on the crystal form of the lead(II) oxide prepared by the alkoxide method

No.	Seed (Amount / g)$^{a)}$	Temp / °C	Addition speed of alkoxide / s/200 cm^3	Product$^{a)}$	
				Without seed	With seed
1	M (0.1)	25	2	H	H+M
2	M (0.2)	25	2	H	M
3	M (0.2)	60	2	L	M
4	L (0.2)	25	2	H	M+H
5	L (0.2)	60	6×10^3	M	M
6	H (0.2)	25	3×10^2	M	M

a) H: $3PbO \cdot H_2O$, L: litharge, M: massicot.

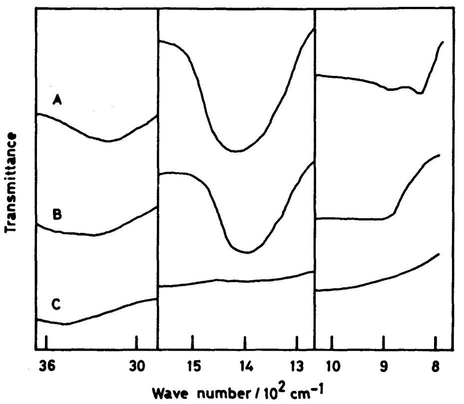

Fig. 5. Infrared spectra of the heating products of the hydrous lead(II) oxide ($3PbO\cdot H_2O$).
(A): Room temperature, (B): 180 °C, (C): 720 °C.

Table 4. Effect of additives on the crystal form of the lead(II) oxide prepared by the alkoxide method[a)]

No.	Additive	Concentration of additive mol dm^{-3}	Product[b)]
1	None	—	M
2	Citric acid	1×10^{-4}	H
3	Citric acid	1×10^{-3}	H
4	Acetic acid	1×10^{-4}	M
5	Sulfuric acid	1×10^{-4}	M(+H)
6	Hydrochloric acid	1×10^{-4}	M+BS(+H)
7	EDTA	1×10^{-4}	M
8	EDTA	1×10^{-3}	H

a) All experiments were conducted under the conditions as follows: temperature, 25 °C; adding speed of alkoxide, 50 min/200 cm; pH of suspension, 9.5—9.8. b) H: $3PbO\cdot H_2O$, L: litharge, M: massicot, BS: basic salt.

reversed by the adsorption of the coordinating anions. The results obtained here are also consistant with the mechanism reported by earlier investigators.

Thermal Decomposition of $3PbO\cdot H_2O$. TG and DTA curves, in air, for $3PbO\cdot H_2O$ obtained by the alkoxide method are shown in Fig. 4. The weight loss on heating was indicated on the TG curve at 160—170 °C. This was due to the release of the water of crystallization, corresponded with the sharp endothermic peak of the DTA curve at 168 °C. A second weight loss was also indicated on the TG curve in the temperature range of 180—350 °C. The X-ray diffraction patterns of three samples obtained at A (before heating), B (180 C°), and C (720 °C) in Fig. 4 indicated that they were $3PbO\cdot H_2O$, litharge and massicot, respectively. That is, $3PbO\cdot H_2O$ was first changed to litharge with the release of the water of crystallization and then transferred to massicot in the heating process. Although

$$3PbO\cdot H_2O \xrightarrow{160\,^\circ C} PbO(\text{litharge}) \xrightarrow{650\,^\circ C} PbO(\text{massicot})$$

the weight loss calculated from the formula of $3PbO\cdot H_2O$ should be 2.5 wt%, the total weight loss obtained from the TG curve in Fig. 4 was 3.2 wt%. Therefore, it would seem that only the first weight loss (2.5 wt%) is due to the release of the water of crystallization and the second to the release of other impurities. Figure 5 shows the IR spectra for the three samples A, B, and C. The spectrum of sample A ($3PbO\cdot H_2O$) displays four distinct bands at 860, 1420, 1630, and 3200 cm^{-1}. The bands at 1630 and 3200 cm^{-1} are the OH stretching band and the OH bending band, respectively. The bands of 860 and 1420 cm^{-1} can be assigned to CO_3^{2-}. As described previously, $3PbO\cdot H_2O$ has strong affinity for CO_2 gas in air, which being responsible for the ambiguous amount of the water of crystallization of hydrous lead(II) oxides. Doi *et al.*[20)] proposed the following thermal decomposition scheme for lead(II) carbonate:

$$3PbCO_3 \longrightarrow 2PbCO_3\cdot PbO + CO_2\uparrow(316\,^\circ C), \qquad (4)$$

$$2(2PbCO_3\cdot PbO) \longrightarrow 3(PbCO_3\cdot PbO) + CO_2\uparrow(339\,^\circ C), \qquad (5)$$

$$3(PbCO_3\cdot PbO) \longrightarrow 2(PbCO_3\cdot 2PbO) + CO_2\uparrow(373\,^\circ C), \qquad (6)$$

$$PbCO_3\cdot 2PbO \longrightarrow 3PbO + CO_2\uparrow(\text{about } 435^\circ C). \qquad (7)$$

From this result, it was concluded that the second weight loss at 180—350 °C in Fig. 4 was due to this decomposition of $PbCO_3$ in the precipitate.

The methods of Freeman-Carroll[21)] and Coats-Redfern[22)] were used to study the kinetics of the dehydration. These methods can only be used for a single elementary reaction. The formura of the Freeman-Carroll method is written as

$$\Delta \log(dW/dt)/\Delta \log W_r = n - \Delta(1/T)/2.303\,RT(\Delta \log W_r), \qquad (8)$$

where dW/dt is the weight change in mg per minute, n the order of the reaction, T the absolute temperature, and $W_r = W - W_c$, where W is the weight (mg) at time t, and W_c the weight (mg) of the sample at the end of the reaction. E is the energy of activation. If the plot of the ratio $\Delta\log(dW/dt)/\Delta\log W_r$ values *vs.* $\Delta(1/T)/\Delta\log W_r$ is linear, the activation energy and the reaction order will be given by its slope and intercept, respectively. This is illustrated in Fig. 6, where the linear relationship is observed. The results are given in Table 5.

When the reaction order is other than unity, the formula of the Coats-Redfern method is written as

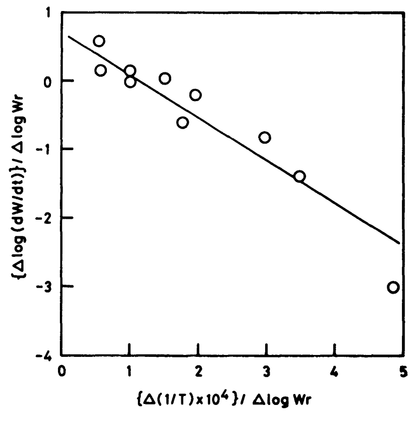

Fig. 6. Freeman-Carroll straight line for the dehydration step of the hydrous lead(II) oxide ($3PbO\cdot H_2O$).

TABLE 5. REACTION ORDER AND ACTIVATION ENERGY OF THE THERMAL DEHYDRATION OF THE HYDROUS LEAD(II) OXIDE

Method	Activation energy kJ mol^{-1}	Reaction order
Freeman-Carroll	112.8	0.7
Coats-Redfern	112.4	1.0
Average	112.6	0.9

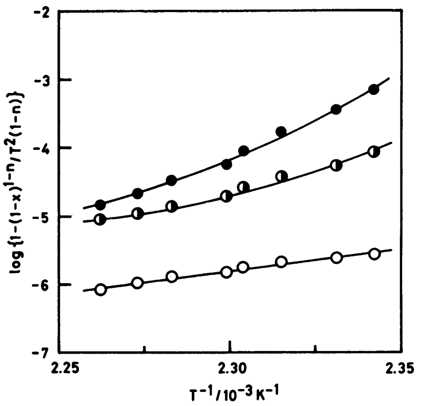

Fig. 7. Coats–Redfern straight line for the dehydration step of the hydrous lead(III) oxide ($3PbO \cdot H_2O$). order n —●: 1.0, ◑: 2.0, ○: 3.0.

$$\log\{1-(1-x)^{1-n}/(1-n)T^2\} = \log(AR/\phi E)(1-2RT/E) - E/2.303RT, \qquad (9)$$

where x is the fraction of reaction, ϕ the heating rate of furnace and A the frequency factor. Graphic representation of the log $\{1-(1-x)^{1-n}/(1-n)T^2\}$ values as a function of $1/T$ gives a straight line of slope $-E/2.303R$ for the correct value of n. This is illustrated in Fig. 7 and the results are given in Table 5. No difference between the results obtained by either method was observed and the average apparent activation energy and reaction order were 112.6 kJ mol^{-1} and 0.9, respectively.

The authors wish to thank Prof. Taijiro Okabe of the Department of Applied Chemistry, Tohoku University for his helpful discussion.

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