

EFFECT OF PRELIMINARY MECHANICAL ACTIVATION ON THE BEHAVIOUR OF ORTHORHOMBIC LEAD DIOXIDE

C. Barriga, J. Morales and J. L. Tirado

DEPARTAMENTO DE QUÍMICA INORGÁNICA E INGENIERÍA QUÍMICA,
FACULTAD DE CIENCIAS, UNIVERSIDAD DE CÓRDOBA, SPAIN

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The thermal behaviour of mechanically activated α -PbO₂ was studied. Dry grinding led to the mechanochemical decomposition of this phase into a β -PbO₂ and Pb₃O₄ mixture. In contrast, wet grinding prior to the mechanochemical decomposition caused significant changes in the thermal decomposition temperature and an increase in the intensity of the exothermic effect at ca. 200 °C, which is associated with structural changes and a partial reduction of Pb(IV) to Pb(II). Throughout the exotherm, the crystallinity of α -PbO₂ increased and the cell dimension *b* decreased.

The thermal decompositions of the α -orthorhombic and β -tetragonal phases of lead dioxide have been extensively investigated [1–4]. The various intermediates between PbO₂ and PbO have been characterized, and the roles of the hydrogen and Pb(II) contents in the initial stages of decomposition have been pointed out [5–6].

The influence of the preparation method, chemical or electrochemical, on the thermal behaviour has also been studied [7]. Additionally, the mechanical activation of these polymorphs in simple laboratory grinders has been reported by Roy et al. [8–9].

In a previous paper [10], we examined the mechanically induced phase transition β -PbO₂ \rightarrow α -PbO₂, which is accompanied by significant increases in the Pb(II) and OH contents and by changes in the intermediates formed by thermal treatment of ground β -PbO₂. In the present work, the mechanochemical activation and decomposition of α -PbO₂ are studied, in order to acquire detailed knowledge on the effect of grinding on the thermal behaviour of lead dioxide.

Experimental

The starting material in this study was a chemically prepared sample of α -PbO₂. This sample was obtained by oxidation of a Pb(II) solution in a strongly ammoniacal solution of ammonium acetate [11]. Grinding was performed in a Retsch planetary ball-mill working at 80 rpm. The starting charge was 5 g and a 250 ml agate jar and five agate balls 10 mm in diameter were used.

The analytical procedure used for the determination of the chemical composition of lead dioxide was based on the method developed by Anderson and Stern [12]. Pb(IV) was reduced with As(III) in the presence of hydrochloric acid and the solution was back-titrated with KMnO₄.

Differential scanning calorimetry (DSC) was carried out in air and dynamic N₂ atmospheres with a Mettler TA 3000 apparatus calibrated with an indium metal sample.

Thermogravimetric (TG) traces were obtained in air with a Chan 2000 electrobalance and a heating rate of 8 deg/min. The sample weights were ca. 60 mg.

X-ray diffraction (XRD) patterns were recorded on a Siemens-D500 diffractometer, using Cu-K_α radiation.

Results and discussion

Figure 1 shows the DSC trace of the starting material, α -PbO₂. This curve reveals an initial exothermic effect at ca. 180°, which is accompanied by a simultaneous weight loss, and a complex association of endothermic effects corresponding to the decomposition steps α -PbO₂ → β -PbO_x → Pb₃O₄ → PbO [2].

In order to study the effect of the medium in which the mechanical activation was carried out, the preparation of the ground sample was performed both in dry and in wet media. It was found that dry grinding for 3 h led to the partial decomposition of lead dioxide. Complete loss of the X-ray diffraction lines of α -PbO₂ was reached after a grinding period of 6 h. When the treatment was carried out in wet medium (cyclohexane), the decomposition of α -PbO₂ did not occur below 21 h, as shown by the absence of extra reflections in the XRD patterns. This treatment allowed the activation of the dioxide, reflected by an increase in the content of structural imperfection as determined by XRD broadening analysis. Table 1 shows appreciable increases in the FWHM values relative to the original sample.

The DSC trace of this sample (Fig. 1) displayed a more pronounced exothermic peak at higher temperature (240°) and significant changes in the shapes of the various endothermic effects leading to the decomposition products.

Additionally, the decomposition product at 550° was Pb₃O₄ for the unground

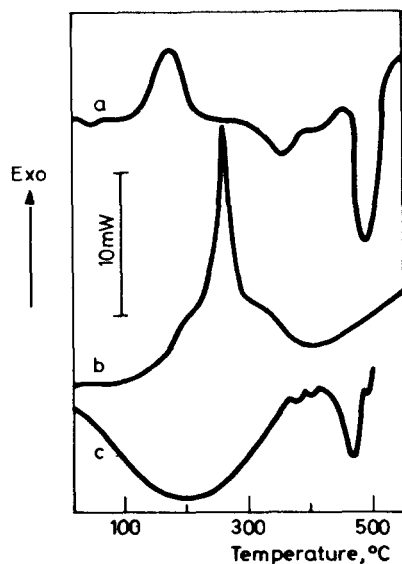


Fig. 1 DSC traces of a) original α - PbO_2 sample b) α - PbO_2 ground in cyclohexane for 6 h, c) α - PbO_2 ground in air for 21 h, this sample was partially decomposed during the grinding process

Table 1 Compositions and structural data for studied samples

	Pb(IV)/Pb _T	hkl	FWHM, rad. $\times 10^3$	a, Å	b, Å	c, Å	V ₃ , Å
α - PbO_2 original	0.960	002 021 200	8.02 13.26 5.93	4.96 ₉	6.00 ₇	5.50 ₂	164.22 ₈
α - PbO_2 (200 °C)	0.842	002 021 200	6.98 9.08 5.93	4.97 ₂	5.99 ₇	5.50 ₀	163.44 ₇
Wet-ground sample (6 h)	0.827	002 021 200	13.60 15.00 8.72	4.96 ₉	6.00 ₁	5.51 ₆	164.48 ₁
Dry-ground sample (21 h)	0.384	—	—	—	—	—	—

FWHM: full width at half maximum.

sample and PbO for the wet ground sample, probably as a consequence of the different crystallinity of the solid according to the XRD broadening data in Table 1. An analogous exothermic effect was detected in previous studies [7] in chemically prepared α - PbO_2 and was ascribed to the loss of OH and oxidation of the Pb(II)

content of the sample. However, this interpretation is difficult to correlate with the fact that the DSC curve of the original α -PbO₂ sample, recorded in dynamic N₂, showed an exothermic effect of similar intensity and at the same temperature. Additionally, a sample obtained by heating α -PbO₂ at temperatures higher than the exotherm showed no trace of decomposition in the XRD pattern.

The Pb(IV) contents of these samples are shown in Table 1. The total Pb content was determined from the TG data. In this way, the thermogravimetric curve was recorded until constant weight (complete decomposition to PbO).

If the Pb(IV)/Pb(II) ratio of the original α -PbO₂ and that of the same sample after thermal treatment above the exothermic effect are compared, the values observed cannot be used to explain the exotherm in terms of oxidation reactions.

On the other hand, determination of the unit cell dimensions of α -PbO₂ in this sample (Table 1), sheds new light on the nature of the exotherm. From these results and the FWHM values, it can be concluded that this effect is associated with structural changes involving a significant decrease in the parameter *b* of the α -PbO₂ lattice (Table 1) and a recovery of crystallinity, probably due to a partial reduction of Pb(IV) to Pb(II), as shown by the decrease in the Pb(IV)/Pb(II) ratio after the exotherm.

Finally, prolonged dry grinding caused the mechanochemical decomposition of α -PbO₂, leading to a mixture of β -phases with low O/Pb ratio. The Pb(IV)/Pb ratio for a sample ground for 21 h is 0.384 (Table 1) and is in accordance with a mechanochemical reduction process of Pb(IV) to Pb(II) [5–6]. The resulting composition is close to Pb₃O₄ (ratio = 0.333).

The DSC trace of this product (Fig. 1) exhibits a broad endotherm, followed by a sharp endothermic effect. The TG trace shows weight losses in the temperature intervals in which the two endotherms are observed. The first effect involves the loss of OH groups, while the second effect is associated with the decomposition of the oxide, finally to yield PbO, in a similar way to that found for the oxide intermediates described previously [6].

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Zusammenfassung — Es wurde das thermische Verhalten von mechanisch aktiviertem α -PbO₂ untersucht. Trockenmahlen führt bei der mechanochemischen Zersetzung dieser Phase zu einem Gemisch von Pb₃O₄ und β -Pb₃O₄. Im Gegensatz dazu führt ein der mechanochemischen Zersetzung vorangehendes Feuchtmahlen zu Veränderungen der Zersetzungstemperatur und zu einer Verstärkung der Intensität des exothermen Effektes bei ca. 200 °C, der von strukturellen Veränderungen und einer teilweisen Reduktion von Pb(IV) zu Pb(II) begleitet wird. Beim Anwachsen der Kristallinität von α -PbO₂ verringert sich die Gitterkonstante *b*.

Резюме — Изучено термическое поведение механически активированного α -PbO₂. При сухом размоле этой фазы происходит механикохимическое разложение ее до смеси β -PbO_x и Pb₃O₄. В противоположность этому, влажный размол, предшествующий механико-химическому разложению, вызывает значительные изменения температуры термического разложения и увеличивает интенсивность экзотермического эффекта при температуре около 200°, который вызван структурными изменениями и частичным восстановлением четырехвалентного свинца до двухвалентного. Во время всей экзотермы увеличивается кристалличность α -PbO₂ и уменьшается решеточный параметр *b*.