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Journal of Nuclear Materials 288 (2001) 76–82

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Physical properties of thorium oxalate powders and their influence on the thermal decomposition

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Received 6 December 1999; accepted 12 October 2000

Abstract

Thorium oxalate dihydrate powders were obtained by precipitation from thorium nitrate solution using oxalic acid in the presence of ultrasound and mechanical agitation. Properties measured included particle morphology, particle size and particle size distribution, and specific surface area. The thermal decompositions of the powders were investigated by using thermogravimetry and differential thermal analysis techniques. The result showed that the thermal decomposition stages of the thorium oxalate dihydrate obtained by mechanical and ultrasonic agitation are same. The decomposition reactions of the oxalates precipitated in the presence of ultrasound proceed in a narrower temperature interval, within a shorter period of time. The kinetic parameters for each stage were calculated. © 2001 Elsevier Science B.V. All rights reserved.

PACS: 81.20.F; 43.35; 81.70.P; 21.65

1. Introduction

Thoria can be considered as a fuel for the nuclear breeder reactors since it gives birth to ^{233}U which is a fissile element by neutron bombardment. Thoria powders has been frequently prepared by the oxalate precipitation process followed by calcination. Properties obtained during precipitation persist through all the manufacturing stages and influence the properties of the final product. There are reports [1–3] that the use of ultrasound during the precipitation of solids from liquid solutions leads to different properties compared with solids prepared by chemically similar methods but using only mechanical agitation. Zeolites formed in ultrasonic field show reduced particle size and a narrower size distribution compared with those produced by conventional methodology [1]. Platinum blacks prepared by reduction of aqueous solutions of platinum metal salts with formaldehyde in the presence of ultrasound showed 62% increase in surface area. Similarly, sonication (25 kHz) during the precipitation of cobalt and nickel oxalates leads to a reduction in particle size, lower porosity, and increased specific surface area [2]. Ultrasound (90 kHz) when applied during the precipitation of silica gel led to reduction of 18% in surface area of the gel [3].

The aim of the present work, which is a part of wider study on sintering properties of thoria powders produced by calcining the thorium oxalates precipitated in the presence of ultrasonic fields, is to study physical properties of the thorium oxalate powders and their influence on the thermal decomposition behavior. Thorium nitrate and oxalic acid solutions were reacted to precipitate thorium oxalates. Two types of agitation were used, a mechanical stirrer and cleaning baths that impart ultrasonic agitation, during oxalate precipitation. The particle morphology, surface area, particle size and particle size distribution of thorium oxalates were determined. Thermal decompositions of the oxalates were investigated by using TGA and DTA techniques and the kinetic parameters for each step were calculated.

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PII: S0022-3115(00)00571-7

Table 1
Impurities in the thorium oxalate M, A, and B

Impurities	Thorium oxalate M (ppm)	Thorium oxalate A (ppm)	Thorium oxalate B (ppm)
Cd	16	15	15
Mn	9	9	9
Cr	8	8	7
Cu	47	46	48
Na	78	75	77
K	3	3	3
Ca	121	120	119
Mg	10	10	10
Fe	8	9	8
Zn	27	26	28

2. Experimental

Technical grade thorium nitrate (99.5 pct purity) (supplied by Rhone–Poulenc, France) and oxalic acid (obtained from Merck, Germany) were used in the experiments. A magnetic stirrer and cleaning baths that impart ultrasonic agitation, Bandelin–Sonorex (35 kHz) and Buehler (55 kHz), were separately used during thorium oxalate precipitation.

0.5 M thorium nitrate and 0.5 M oxalic acid solutions were prepared by dissolving respective salts in distilled water. A flat bottom reaction flask containing thorium nitrate solution placed on a stirrer. A magnetic stirrer was dropped in and a thermometer was inserted. The oxalic acid solution was added drop by drop (30 cm^3/min) to the thorium nitrate solution under stirring rate of 300 rpm. The temperature of the solution was 18°C. Other two flat bottom reaction flasks containing the thorium nitrate solutions were dipped into the cleaning baths containing water as sonicated liquid and the oxalic acid solutions were added drop by drop at the rate of 30 cm^3/min. The temperature of the solutions was maintained at about 18°C by cooling the reaction flasks with water. Digestion time was 360 min for both mechanical and ultrasonic agitation methods. The thorium oxalate precipitates were filtered through Whatmann 40 filter paper and washed with warm dilute oxalic acid-nitric acid solution followed by warm distilled water. The thorium oxalates were dried in an oven at 100°C for 24 h. For simplicity, these oxalates precipitated by mechanical, ultrasonic at 35 kHz and ultrasonic at 55 kHz agitation are denoted as M, A and B, respectively.

X-ray diffraction (XRD) analysis of the oxalates were done in a Jeol powder diffractometer using CuKα radiation. Particle morphologies of the oxalate powders were examined using a Joel-840 scanning electron microscope (SEM). Particle size distributions of the oxalates were determined by laser diffraction method which was performed in a Master-Sizer (Malvern, UK) instrument. Shimadzu Thermal Analysis System was used for TGA–DTA experiments. The starting sample amount was 34.5 mg. The heating rate was 10°C/min and the upper limit of the temperature was 600°C. All TGA–DTA experiments were performed in air atmosphere. Specific surface area measurements of the oxalates were performed using a micromeritic surface area analyzer with the BET method. The oxalate samples was degassed at 180°C for 1 h in air and 20 min in nitrogen atmosphere before the surface area measurements.

Impurities in the thorium oxalate dihydrate were determined by inductively coupled plasma–optical emission spectrometry (ICP–OES) and atomic absorption spectrometry (AAS) techniques and are given in Table 1.

3. Results and discussions

XRD peaks of the thorium oxalates obtained by mechanical and ultrasonic agitation are given in Figs. 1–3. The lattice constants of the oxalates obtained by mechanical and ultrasonic agitation are in accord with the ASTM card no: 18-1365.

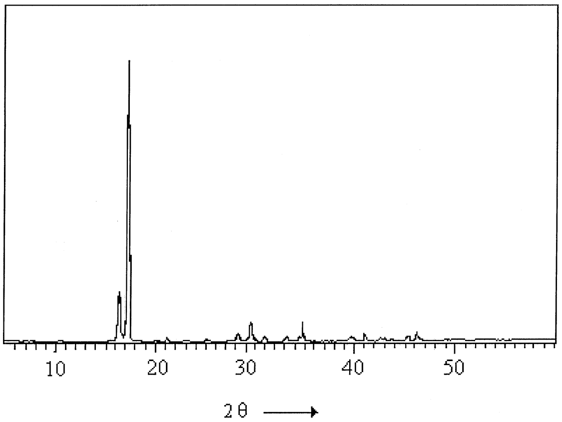

Fig. 1. X-ray diffractometer peaks of dihydrate thorium oxalate M.

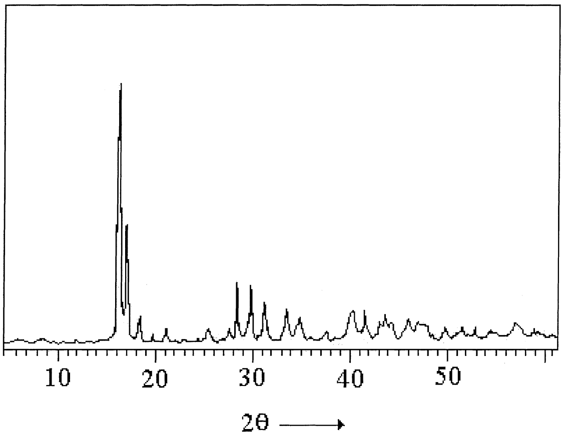

Fig. 2. X-ray diffractometer peaks of dihydrate thorium oxalate A.

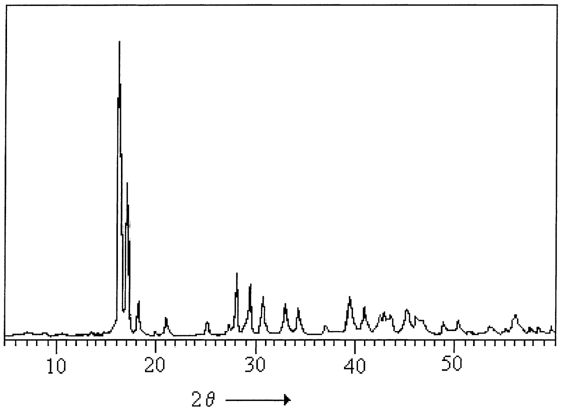

Fig. 3. X-ray diffractometer peaks of dihydrate thorium oxalate B.

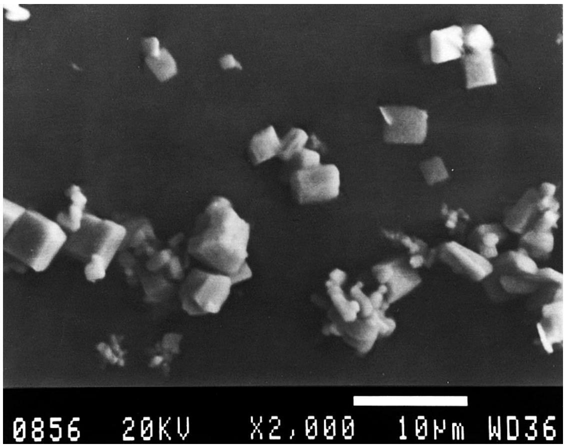

Fig. 4. Scanning electron microscopy micrograph of the thorium oxalate M.

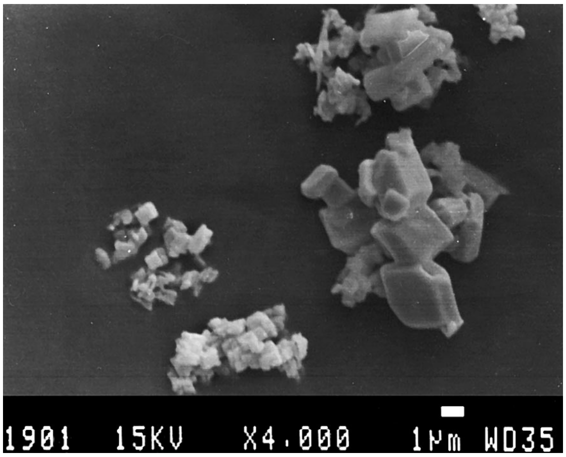

Fig. 5. Scanning electron microscopy micrograph of the thorium oxalate A.

The results indicate that the oxalates obtained by mechanical and ultrasonic agitation are in the same composition and contain two moles of crystal water.

Scanning electron microscopy micrographs of the oxalates are given in Figs. 4–6. SEM studies revealed that the particle morphology was largely unaffected by the acoustic field. The particles of the oxalates from precipitation with mechanical and ultrasonic agitation are in cubic shape but ultrasonic agitation caused reduction in particle size.

Particle size distributions of oxalate powders are shown in Fig. 7. A narrow particle size distribution was obtained for the oxalates precipitated in the presence of ultrasonic field. About 99% of the A oxalate particles were less than 19 μm, about 99% of the B oxalate particles were less than 26 μm and about 99% of the M oxalate particles were less than 30 μm. No particles less than 0.3 μm in size were observed. Median (50%) particle size of the oxalate M was about 8.1 μm whereas it was about 4.3 and 5.4 μm for the oxalate A and B, respectively.

Specific surface areas of the oxalates obtained by mechanical and ultrasonic agitation are given in Table 2. As seen from Table 2, the specific surface area of the oxalate produced by ultrasonic agitation is higher than that of the oxalate produced by mechanical agitation. These results correlate well with those found by SEM and particle size analyses. Namely, precipitation performed in ultrasonic fields gave reductions in particle size and particle size distribution.

TGA and DTA plots of the oxalates are given in Figs. 8 and 9, respectively. Thermogravimetry of the thorium oxalates in air atmosphere showed that the mass loss which occurred between the starting and

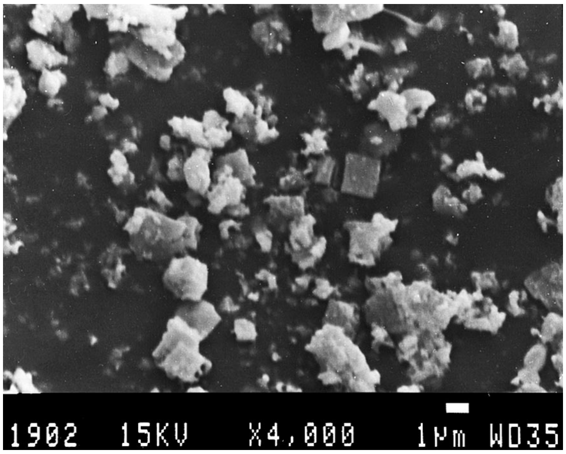

Fig. 6. Scanning electron microscopy micrograph of the thorium oxalate B.

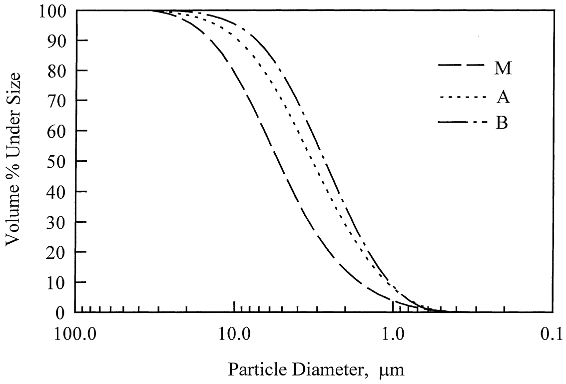

Fig. 7. Particle size distributions of thorium oxalate dihydrate powders.

ending material is about 41%. This also indicates the oxalates obtained by the both mechanical and ultrasonic agitation were $Th(C_2O_4)_2 \cdot 2H_2O$.

According to the TGA and DTA curves (Figs. 8 and 9) of this study decomposition of the oxalates produced ultrasonic and mechanical methods proceed in three stages:

$$\text{Stage 1}: Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$$
$$\text{Stage 2}: Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$$
$$\text{Stage 3}: Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2$$

The decomposition stages obtained from the present study agreed with those of Padmanabhan et al. [4]. D'Eye and Sellman [5] reported formation of carbonate as an intermediate product of oxalate decomposition and proposed that the decarbonization of thorium oxalate occurred as follows:

Table 2
Specific surface area of thorium oxalate M, A, and B

Thorium oxalate	Specific surface area (m^2/g)
M	1.86
A	3.85
B	4.71

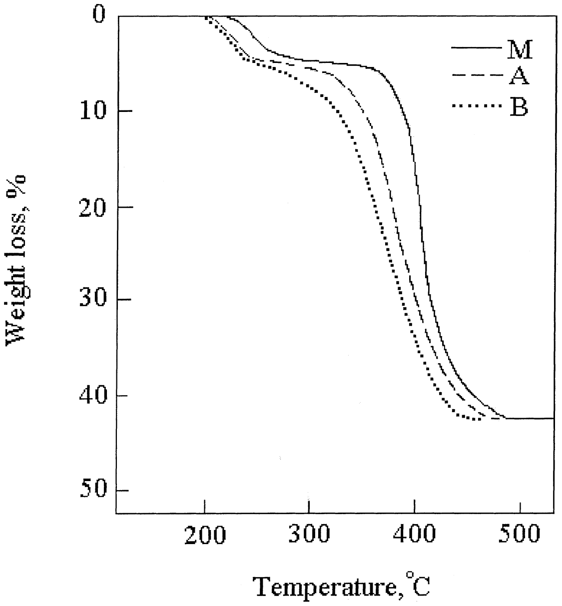

Fig. 8. TGA of thorium oxalate dihydrate powders in air atmosphere.

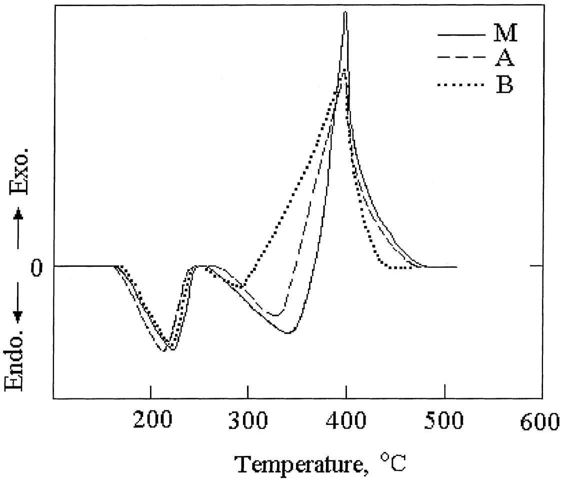

Fig. 9. DTA of thorium oxalate dihydrate powders.

$$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$$
$$Th(CO_3)_2 \rightarrow ThO_2 + 2CO_2$$

Recently, Aybers [6] has observed two endothermic and two exothermic peaks in his DTA curve obtained by the heating rate of 5°C/min. This difference between the present study and Aybers's work may be due to the differences in heating rates. The heating rate may influence the local atmosphere inside the sample and on its surface. An increase in the heating rate may give rise to an associated increase of the rate of thermal decomposition. Based on the surface area–temperature relationships obtained from the experimental work, Aybers [6] has claimed that an additional intermediate compound corresponding to $ThOCO_3$ forms during the thermal decomposition and suggested five decomposition steps:

$$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$$
$$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$$
$$Th(C_2O_4)_2 \rightarrow Th(CO_3)_2 + 2CO$$
$$Th(CO_3)_2 \rightarrow ThOCO_3 + CO_2$$
$$ThOCO_3 \rightarrow ThO_2 + CO_2$$

In order to substantiate the formation of intermediate products during the thermal decomposition, application of spectral techniques to thermal analysis is essential.

Although the thermal decomposition stages of the dihydrate thorium oxalates obtained by the two methods are the same the decomposition reactions proceed in a narrower temperature interval, within a shorter period of time for the oxalates A and B. The temperature at which thermal decomposition begins (T_i) and the temperature at which the decomposition reactions were completed (T_f) obtained from Fig. 8 for the oxalates M, A, and B are given in Table 3. As seen from Table 3, sonication during precipitation of thorium oxalate dihyrate leads to lower the temperature at which the thermal decomposition begins, as well as the temperature at which the thermal decomposition reactions are completed. In comparing the thermal decomposition curves of calcium carbonate and calcite, Richer and Vallet [7] found that the empirical decomposition temperatures obtained at the heating rate of 150°C/h in a stream of nitrogen gas were the following: powdered calcium carbonate, 783°C; powdered calcite, 802°C; cube of calcite weighing about 350 mg, 891°C. Likewise, for a chrysolite sample, Martinez [8] found that the decomposition temperature decreased with a decrease in sample particle size. For the ground material, there was a continuous loss in mass from about 50°C to 800°C, with the most rapid decomposition between 600°C and 700°C. For the massive material, there was little mass-loss until a temperature of about 600°C was attained. Similar results were obtained for serpentine and brucin–carbonate mixture. In general, a decrease in a particle size of the sample lowers the temperature at which thermal decomposition begins, as well as the temperature at which the decomposition reactions are completed. Various particle sizes will cause a change in diffusion of the product gases, which will alter the reaction rate and hence curve shape. The smaller the particle size, the greater the extent to which equilibrium is reached, and at any given temperature, the greater the extent of decomposition will be.

The DTA curves of the three oxalates (Fig. 9) indicate a change in the peak minimum temperatures. Effect of ultrasonic agitation on the peak minimum temperature (ΔT_{min}) of the three oxalates are given in Table 4. As seen from Table 4, a decrease in the par-

Table 3
Beginning and ending temperatures of the each stage

Decomposition reactions	Beginning (T_i) and ending temperature (T_f) of each stage, °C					
	M		A		B	
	T_i	T_f	T_i	T_f	T_i	T_f
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	210	260	200	242	203	238
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$	260	373	242	350	238	333
$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2$	373	498	350	470	333	450

Table 4
Effect of ultrasonic agitation on the peak minimum temperature (ΔT_{min}) of the thorium oxalate M, A and B

Decomposition reactions	M	A	B
	ΔT_{min} (°C)	ΔT_{min} (°C)	ΔT_{min} (°C)
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	223	212	220
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$	337	325	292
$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2$	397	396	396

Table 5
Kinetic parameters of decomposition reactions of thorium oxalate M, A, and B

Decomposition reactions	Apparent reaction order (n)			Activation energy (kcal/mol)		
	M	A	B	M	A	B
$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 \cdot H_2O + H_2O$	0.5	0.5	0.67	33.7	26.6	31.7
$Th(C_2O_4)_2 \cdot H_2O \rightarrow Th(C_2O_4)_2 + H_2O$	0.33	0.33	1	31.7	25.2	20.1
$Th(C_2O_4)_2 \rightarrow ThO_2 + 2CO + 2CO_2$	1	2	2	84.1	72.4	51.9

ticle size of the thorium oxalates that was caused by the ultrasonic effect during the precipitation produced a peak minimum temperature decrease for the dehydration reactions. There is no significant shift in the exothermic peak. There are conflicting studies concerning the effect of particle size and particle size distribution on the DTA curve in the literature. Langer and Kerr [9] found that an increase in the particle size of kaolinite produced a peak temperature increase for the dehydration reaction. There were no significant shifts in the phase-transition exothermic peak. Norton [10] found that the $\Delta T_{\min}$ values for kaolinite remained essentially constant, but that the temperature at which the dehydration reaction was completed varied from 610°C to 670°C over a particle-size range of <0.1 to 20–44 μm.

For a reaction in which the order is unknown, Coats and Redfern [11] derived the following expression:

$$\log\left\{\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right\} = \log\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.3RT}, \tag{1}$$

where n is the order of the reaction, α the fraction of the sample decomposed at time t, T the temperature in degrees Kelvin, A the frequency factor, a the heating rate in degrees per minute, R the gas constant and E is the activation energy.

A plot of either $\log\{[1-(1-\alpha)]^{1-n}/T^2(1-n)\}$ against $1/T$ or, where $n=1$, $\log\{[-\ln(1-\alpha)]/T^2\}$ against $1/T$, should result in a straight line of slope $-E/2.3R$ for the correct value of n. The quantity $\log(AR/aE)[1-(2RT)/E]$ appears to be reasonably constant for the most values of E and in the temperature range over which most reaction occur.

The kinetic parameters (apparent reaction order: n, and activation energy: E) for each step of the thermal decomposition of the oxalate M, A and B were calculated by Coats and Redfern method and are given in Table 5. Calculation are made for each decomposition step for the oxalates M, A, and B using n values: $n = 0$, $n = 0.33$, $n = 0.5$, $n = 0.67$, $n = 1$, $n = 2$ and the highest correlation coefficient is chosen for the determination of the apparent reaction order. The result shows that the activation energies of the thermal decomposition of the thorium oxalate A and B are lower than that of the thorium oxalate M.

4. Conclusions

The thorium oxalates obtained by mechanical and ultrasonic agitation are in the same composition and contain two moles of crystal water. Sonication (35 and 55 kHz) during the precipitation of thorium oxalate dihydrate leads to a reduction in particle size and particle size distribution, and increased specific surface area. The particle morphology was largely unaffected by the acoustic field. The particles of the oxalates from precipitation with mechanical and ultrasonic agitation are in cubic shape. Although the thermal decomposition steps of the dihydrate oxalates obtained by the two methods are the same; the decomposition reactions proceed in a narrower temperature interval, within a shorter period of time for the oxalates precipitated under the ultrasonic field. The activation energies of the thermal decomposition of the oxalates precipitated under the ultrasonic field are lower than that of the oxalate precipitated with mechanical agitation.

Acknowledgements

Support for this research by the Research Fund of the University of Istanbul under Project Number: T- 435/270697 is gratefully acknowledged.

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