Preparation of Uniform Colloidal Particles of Salts of Tungstophosphoric Acid[†]

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Uniform colloidal particles of thorium and cesium tungstophosphates of different morphologies have been prepared by controlled precipitation. The method consists of direct reaction of aqueous solutions of salts of the corresponding metals and tungstophosphoric acid, $H_3PW_{12}O_{40}$, at elevated temperatures (90 °C) under certain conditions of the reactant concentrations and the pH. The resulting Cs compound was stoichiometric, whereas the thorium heteropoly particles contained excess thorium due to the incorporation of its hydrolysis products, generated under the employed experimental conditions. The Cs compound showed a secondary structure similar to that of the parent acid, while the Th compound was amorphous to X-rays. Both samples exhibited different electrokinetic behavior, the isoelectric point of Cs−tungstophosphate being at pH 1.5, and that of the Th compound at pH 5.4.

Introduction

The salts of heteropoly acids have many applications, such as catalysts in oxidation, alkylation, or hydrosulfurization reactions, resulting in many cases in higher specific conversion rates than those obtained with their parent acids[1−6] and in higher thermal stability.[7,8]

Heteropoly compounds are composed of a polyoxoanion $XM_{12}O_{40}{}^{n-}$ where X = Si, P; M = Mo, W; and n = 3 or 4. The polyoxoanion crystallizes in the stable, so-called Keggin structure,[8−12] which is commonly described as the primary structure. These anions, accompanying cations, and other components, such as water, are arranged in secondary three-dimensional orders, the stability of which depends on different counterions and the amount of water.[13] Information on the Keggin structure can be obtained from the vibrational spectra, while the X-ray diffractometry patterns reflect the secondary structures.

The properties of the salts of heteropoly acids vary with the counterion. For example, compounds with small cations (e.g. Na^+) are water soluble, while those of larger cations, such as K^+, are insoluble.[13,14] These salts are usually prepared by neutralization of solutions of the free acids with stoichiometric quantities of metal carbonates, basic carbonates, or hydroxides,[15−17] or by mixing solutions of a salt of the desired cation and the free acid and evaporating to dryness.[12] These methods yield as a rule solids irregular in shape and size, often composed of aggregates and sometimes of nonstoichiometric products containing residual protons.[12] It also has been proposed that filtration, rather than evaporation to dryness, yields better products because the unreacted reagents are removed.[18]

In recent years particles uniform in size and shape of different inorganic compounds for various applications have been produced by controlled precipitation in homogeneous solutions.[19,20] Using the same process, it was demonstrated that monodispersed colloids of complex compositions, such as Zr and Th salts of tungstosilicic acid, $H_4SiW_{12}O_{40}$, could be obtained under certain experimental conditions.[21]

This article describes a method for the preparation of uniform sparingly soluble solids of tungstophosphoric

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acid, $H_3PW_{12}O_{40}$, by direct reaction of this acid with Cs or Th salts in aqueous solutions. The conditions for the precipitation of these solids as uniform particles have been established, and the products are characterized in terms of their composition, structure, and electrokinetic behavior.

Materials and Methods

Materials. 12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$, TPA, Baker analyzed reagent) was further purified by extraction with ether from a solution acidified with hydrochloric acid. The ether−acid complex was evaporated under vacuum and the free acid recrystallized twice. Thorium nitrate ($Th(NO_3)_4 \cdot 4H_2O$, Baker analyzed) and cesium chloride (CsCl, Aldrich) were used without further purification. All solutions were filtered through 0.22 μm pore size Nuclepore membranes to remove any possible particulate contaminants. The anionic surfactant AVANEL S-150 CG (PPG Ind.) was received as a 35 wt % aqueous solution.

Particle Preparation. Aqueous solutions containing thorium nitrate or cesium chloride were carefully introduced into the solutions containing 12-tungstophosphoric acid and AVANEL S-150 at room temperature. The resulting mixtures were immediately placed into a preheated water bath at 90 °C and kept there for 1 h. After aging, the dispersions were quenched to room temperature in an ice-cooled water bath. The particles were separated by filtration through 0.22 μm pore size membranes, and the solids were washed several times with distilled water and then dried in a desiccator before characterization.

Characterization. The resulting particles were examined by scanning electron microscopy (SEM). The electrophoretic mobilities were measured with a PenKem 3000 instrument at different pH values, adjusted with HNO_3 and KOH as needed.

The chemical composition of the samples was qualitatively assayed by energy-dispersive X-rays analysis (EDX). The weight content of P, W, and Th was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), while that of Cs was determined by flame atomic absorption (FAA)

The structures of the solids were evaluated by powder X-ray diffraction (XRD) and infrared (IR) spectroscopy. The crystallite size of the precipitated $Cs_3PW_{12}O_{40}$ was determined from the full-with of the half-maximum of the most intense X-ray peak using the Scherrer equation. Thermal gravimetric (TGA) and differential thermal (DTA) analyses were carried out at 20 °C min^{-1} heating rate in nitrogen flow.

Results

Table 1 summarizes the experimental conditions for the preparation of uniform cesium tungstophosphate, while electron micrographs in Figure 1a,b illustrate the resulting particles under the conditions given in the legend. The EDX analysis of these solid samples confirmed the presence of W, P, and Cs, while the quantitative chemical analysis gave 1.0% P, 66.0% W, and 11.3% Cs by weight.

The particle shape of the Cs compound was very much affected by the amount of surfactant used during precipitation. In the absence or at low concentrations of AVANEL S-150, spherical particles (as shown in Figure 1a) were obtained, while higher concentrations yielded octahedral particles (Figure 1b).

The molar ratio [CsCl]/[PTA] had an important effect on the rate of precipitation; at high ratios, i.e., 50−250, the particles were obtained in 1 h, while at the ratio of 6.25, much longer reaction times (∼12 h) were needed to produce the same kind of solids. At still smaller

Table 1. Conditions for the Preparation of Uniform Cesium Tungstophosphate Particles by Heating the Reacting Solutions at 90 °C for 1 h

PTA mol dm^{-3}	CsCl mol dm^{-3}	[CsCl]/ [PTA]	AVANEL g dm^{-3}	final pH	particle shape[a] and size (μm)
8×10^{-5}	2×10^{-2}	250		3.5	S (0.9)
8×10^{-5}	2×10^{-2}	250	0.03	3.5	S (0.9)
8×10^{-5}	2×10^{-2}	250	0.07	3.5	O (0.9)
8×10^{-5}	2×10^{-2}	250	0.15	3.5	O (0.9)
8×10^{-5}	2×10^{-2}	250	0.20	3.5	O (0.9)
8×10^{-5}	4×10^{-3}	50	0.15	3.5	O (0.9)
8×10^{-5}	5×10^{-4}	6.25	0.15	3.5	O (0.9)[b]
8×10^{-5}	2×10^{-4}	2.5	0.15	3.5	
8×10^{-5}	8×10^{-5}	1	0.15	3.5	
4×10^{-5}	1×10^{-2}	250	0.15	3.7	O (0.9)
8×10^{-4}	5×10^{-3}	6.25	0.15−0.5	2.7	A
8×10^{-4}	2×10^{-3}	250	0.15−0.5	2.8	A

[a] S, spherical; O, octahedral; A, aggregated. [b] 12 h reaction time.

ratios (<6.25) no precipitation was observed even after 24 h. Higher concentrations of the heteropoly acid (8×10^{-4} mol dm^{-3}) resulted in aggregates at any molar ratio of reactants or the amount of the surfactant.

Analogous data for the thorium tungstophosphate are described in Table 2 and the electron micrographs are pictured in Figure 1c,d, which show the particles to be spherical. The quantitative chemical analysis yielded 0.4% P, 30.0% W, and 42.8% Th by weight.

It is apparent from Table 2 that the surfactant concentration is a key factor in the precipitation of the Th compound as uniform particles; the latter are obtained only in the presence of AVANEL ranging between 0.15 and 0.3 g dm^{-3}, while at lower (<0.15 g dm^{-3}) or higher (>0.3 g dm^{-3}) amounts of the surfactant, aggregates were formed.

Table 2 also shows that the average diameter of uniform particles became larger with increasing the molar ratio [$Th(NO_3)_4$]/[PTA], ranging in size from 0.15 μm to 0.6 μm.

The bands at 700−1200 cm^{-1} in the FTIR spectra (Figure 2) of the Cs heteropoly compound shown in Figure 1a, are characteristic of the primary (Keggin) anion structure[22−24] as documented by the frequencies for the four bands listed in Table 3. The small differences in wavenumbers between the bands of the free acid and the salt can be attributed to the substitution of protons for Cs$^+$.[25,26] For the Th heteropoly compound the bands in the IR spectrum are not well defined, and they do not give enough evidence of the Keggin unit.

Figure 3 shows the XRD patterns of the original heteropoly acid and of both solids illustrated in Figure 1a,b. The Cs compounds display a pattern similar to that of the parent heteropoly acid, but the 2θ values are slightly shifted, probably due to the rearrangements in the spatial structure, when the protons are substituted by Cs$^+$. The pattern of the solid prepared in the presence of the surfactant indicates a somewhat less
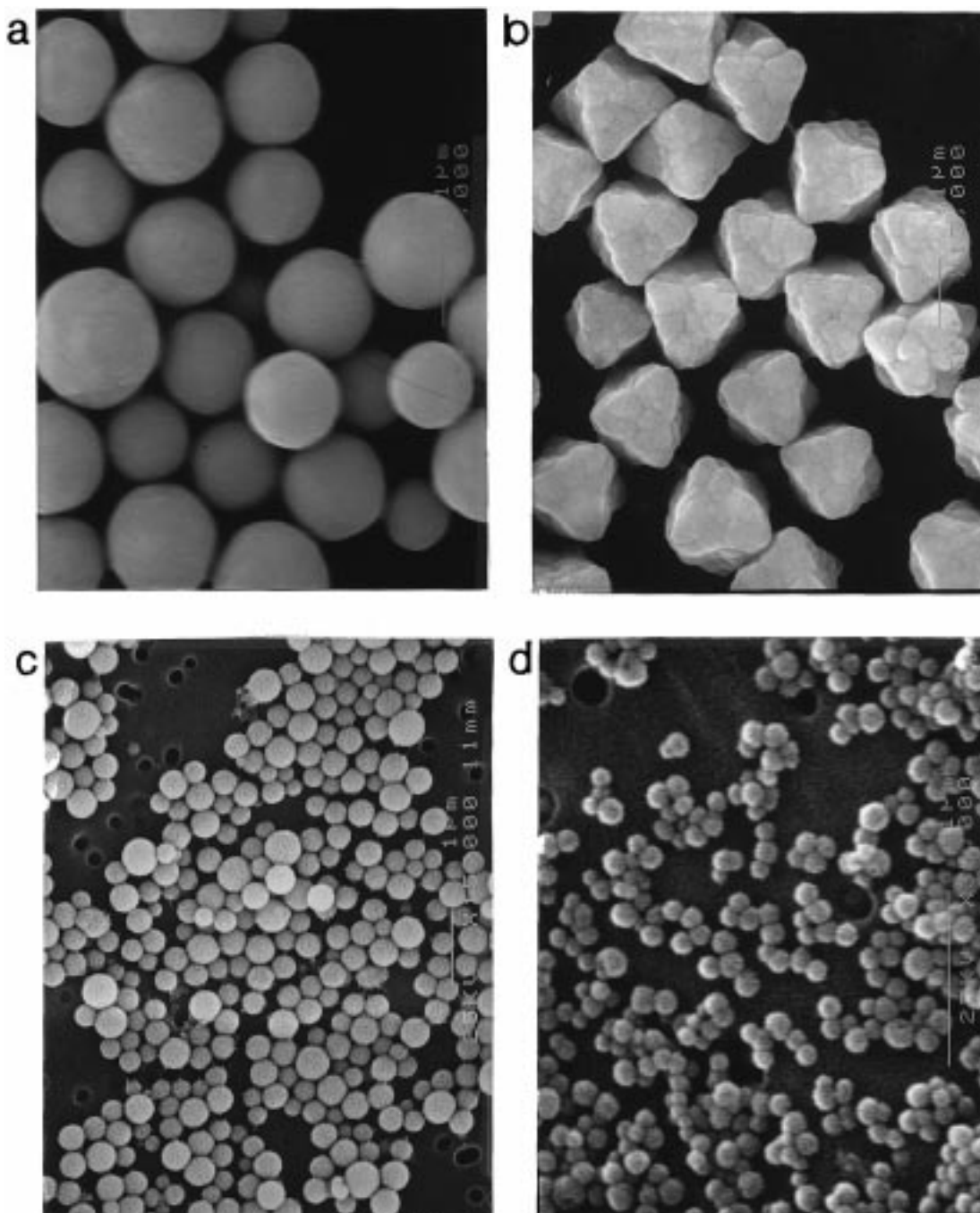
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Figure 1. (a) Scanning electron micrograph (SEM) of Cs-tunstophosphate particles prepared by aging at 90 °C for 1 h a solution containing 8×10^{-5} mol dm^{-3} tungstophosphoric acid (H$_3$PW$_{12}$O$_{40}$, TPA) and 2×10^{-2} mol dm^{-3} CsCl. (b) SEM of the same solid as in part a obtained in the presence of 0.2 g dm^{-3} surfactant AVANEL S-150. (c) SEM of Th-tungstophosphate particles prepared by aging at 90 °C for 1 h a solution containing 8×10^{-5} mol dm^{-3} TPA, 2.5×10^{-3} mol dm^{-3} Th(NO$_3$)$_4$, and 0.2 g dm^{-3} AVANEL S-150. (d) SEM of the same system as in part c obtained in solutions containing 4.6×10^{-4} mol dm^{-3} Th(NO$_3$)$_4$.

crystalline material than that of the particles obtained in its absence. The Th compound appeared amorphous to X-rays (Figure 4). Due to the big difference in charge between both Cs$^+$ and Th^{4+} cations, the secondary structure is expected to be affected. However, it is not clear if the XRD pattern is due to the amorphous nature of the Th compound (related to the spatial arrangement of the polyanions) or to the masking effect caused by the coprecipitated Th products.[23]

The isoelectric points (iep's) of the samples illustrated in Figure 1a,c, obtained from the plots of the electrokinetic mobilities as a function of the pH (Figure 5), were

at pH ~1.5 for the Cs compound and at pH ~5.4 for the Th compound.

The TGA plots of the Cs compounds illustrated in Figure 1a,b show only one step for the solid obtained in the absence of the surfactant (2.2% weight loss), while for the particles prepared in the presence of AVANEL two steps are seen (Figure 6). The first one over the range 100–400 °C (7.6% weight loss) is caused by dehydration, while the second from 400 to 600 °C (0.9% weight loss) is probably due to the decomposition of the remaining traces of the surfactant. The Th compound displays only one step weight loss of 6.9% over the range

Table 2. Conditions for the Preparation of Uniform Thorium Compound Particles by Heating the Reacting Solutions at 90 °C for 1 h

PTA mol dm^{-3}	Th(NO$_3$) mol dm^{-3}	[Th(NO$_3$)]/ [PTA]	AVANEL g dm^{-3}	final pH	particle shape^a and size (μm)
8×10^{-5}	3.5×10^{-3}	43.75	0.2	2.4	S (0.6)
8×10^{-5}	2.5×10^{-3}	31		2.4	A
8×10^{-5}	2.5×10^{-3}	31	0.07	2.4	A
8×10^{-5}	2.5×10^{-3}	31	0.15	2.4	S (0.5)
8×10^{-5}	2.5×10^{-3}	31	0.20	2.4	S (0.5)
8×10^{-5}	2.5×10^{-3}	31	0.30	2.4	S (0.5)
8×10^{-5}	2.5×10^{-3}	31	0.35	2.4	A
8×10^{-5}	1.5×10^{-3}	18.75	0.20	2.4	S (0.4)
8×10^{-5}	4.6×10^{-4}	5.75	0.20	2.5	S (0.15)
8×10^{-5}	8×10^{-5}	1	0.20	3.2	

^{a} S, spherical; A, aggregated.
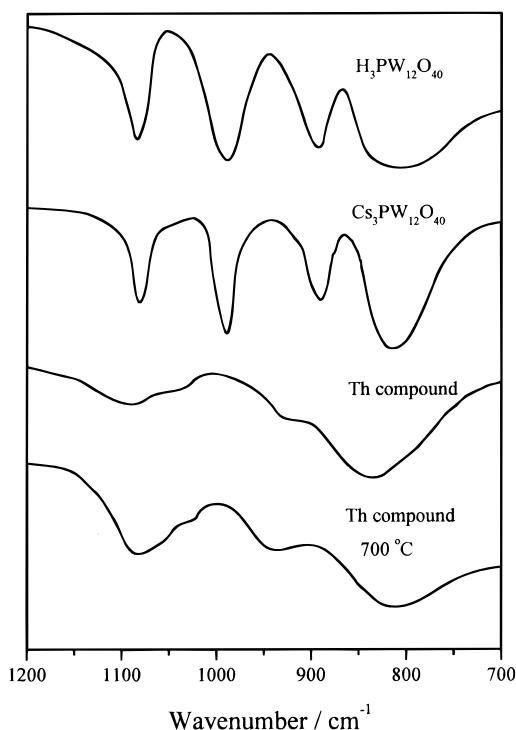
Figure 2. FTIR spectra of tungstophosphoric acid (H$_3$PW$_{12}$O$_{40}$), Cs$_3$PW$_{12}$O$_{40}$ (illustrated in Figure 1a), Th heteropoly compound (Figure 1c), and the same solid after calcination at 700 °C for 30 min.

Table 3. Frequencies Obtained from the FTIR Spectra for the Four Bands Corresponding to the Keggin Unit for the Parent Acid and Both Solids Shown in Figure 1a

| sample	ν_{as} (P−O)	ν_{as} (W−O)	ν_{as} (W−O−W)$_{inter}$	ν_{as} (W−O−W)$_{intra}$
H$_3$PW$_{12}$O$_{40}$	1080	983	889	801
Cs$_3$PW$_{12}$O$_{40}$^{a}	1080	985	887	812

^{a} Shown in Figure 1a.

50−400 °C. No further change at higher temperatures indicates a complete removal of the surfactant during the washing process.

The broad endothermic effect at low temperatures observed by the DTA for both Cs and Th compounds, illustrated in Figure 1a,c (Figure 7), coincides with the weight loss in the TGA, attributed to the dehydration of the samples. The exothermic peak in the DTA plot at 770 °C for the Th compound seems to correspond to a crystallization effect. The XRD pattern of this compound after its calcination at 700 °C for 30 min was
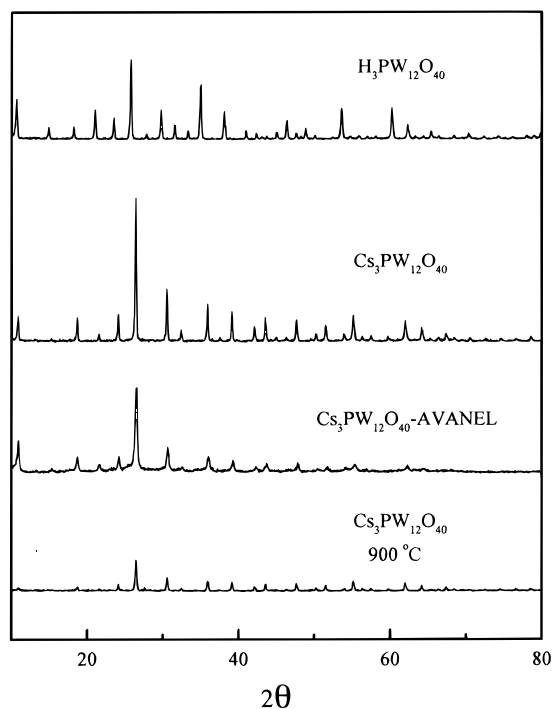

Figure 3. XRD pattern of: H$_3$PW$_{12}$O$_{40}$; Cs$_3$PW$_{12}$O$_{40}$ illustrated in Figure 1a; Cs$_3$PW$_{12}$O$_{40}$-AVANEL illustrated in Figure 1b; and Cs$_3$PW$_{12}$O$_{40}$ illustrated in Figure 1b after calcination at 900 °C for 30 min.
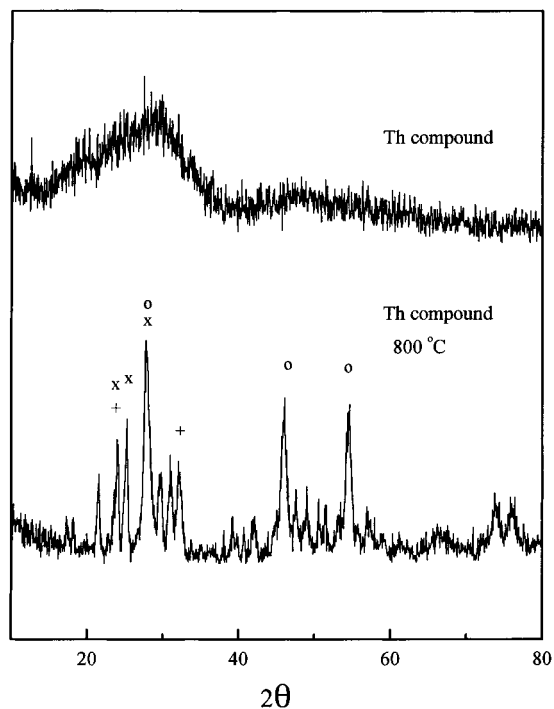

Figure 4. XRD pattern of the Th compound illustrated in Figure 1c before and after calcination at 800 °C for 30 min (x = ThW$_2$O$_8$, o = ThO$_2$, + = WO$_3$).

still characteristic of amorphous material, while the IR spectrum was very similar to that of the compound at room temperature (Figure 2). Further calcination at 800 °C for 30 min produced an XRD pattern with peaks characteristic of WO$_3$, ThO$_2$, and ThW$_2$O$_8$ (Figure 4). The decomposition of heteropoly compounds on heating into single and mixed oxides has been reported previously.[21,27]
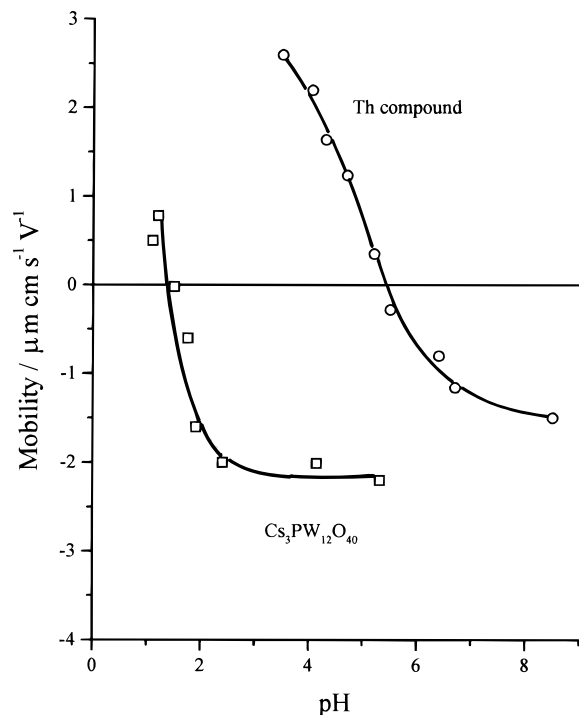
Figure 5. Electrokinetic mobilities as a function of the pH for the $Cs_3PW_{12}O_{40}$ particles shown in Figure 1a and for the Th compound particles shown in Figure 1c.
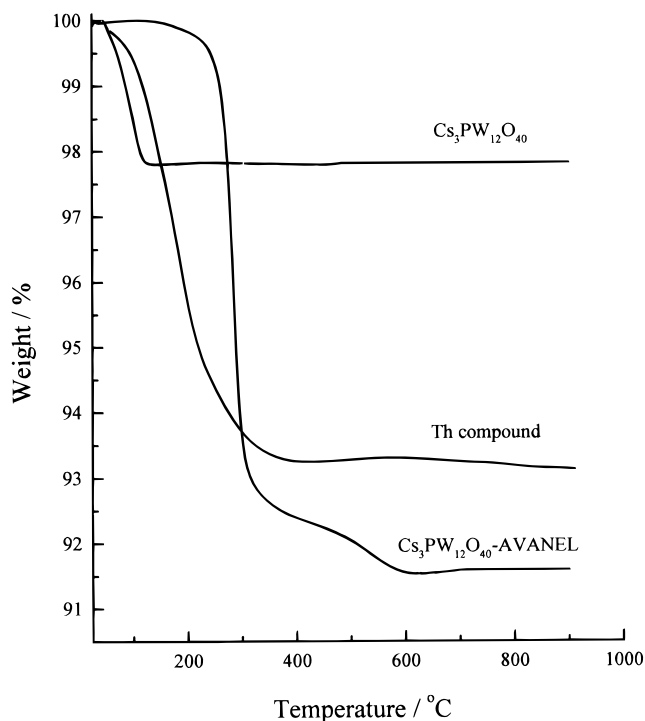
Figure 6. Thermogravimetric analysis for the $Cs_3PW_{12}O_{40}$ particles shown in Figure 1a, for the $Cs_3PW_{12}O_{40}$-AVANEL particles shown in Figure 1b, and for the Th heteropoly compound shown in Figure 1c.

No exothermic effect was observed in the DTA of the Cs compound, while the endothermic effect at 1000 °C is due to the melting of the solid.[28]

The shapes of the particles of both Cs compounds illustrated in Figure 1a,b are retained even after cal-
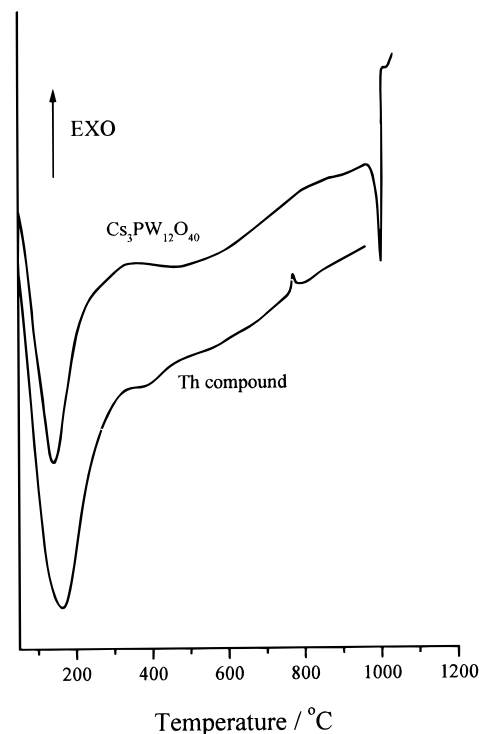
Figure 7. Differential thermal analysis (DTA) for the Cs_3-$PW_{12}O_{40}$ particles shown in Figure 1a and for the Th heteropoly compound shown in Figure 1c.

cination at 900 °C (Figure 8) for 30 min and so are their crystalline structures (Figure 3).

Discussion

The chemical analysis of the Cs compound yields the molar ratios [W]/[P] = 11.3 and [W]/[Cs] = 4.2, which is resonably close to the empirical formula $Cs_3PW_{12}O_{40}$·nH_2O (the amount of water depending on the preparation conditions, as observed by the thermal analysis). Additionally, the absence in the DTA trace of an exothermic effect at ∼600 °C, which would appear if some remaining acid sites were present, indicates the substitution of all protons with Cs during the precipitation process.[28]

The shape of $Cs_3PW_{12}O_{40}$ particles differed when prepared in the presence (octahedral, Figure 1b) or the absence (spherical, Figure 1a) of the surfactant. This finding is quite interesting, since inherently one would expect the opposite effect on the particle morphology. The spherical particles also showed smaller water content than the octahedral ones (Figure 6). The surface of the spheres appeared smooth (Figure 1a), and the solid was well crystallized with crystallites of ∼780 nm, close to the size of the final particles. Consequently, it would seem that these particles are formed by a nucleation and diffusion growth mechanism.

The octahedral particles produced in the presence of AVANEL S-150 contained ∼1% surfactant even after several washings, as well as a higher water content, which required higher temperatures for removal, as compared with the spherical particles. This solid appears to be composed of smaller subunits (SEM, Figure 1b), which is corroborated by the crystallite size of ∼57

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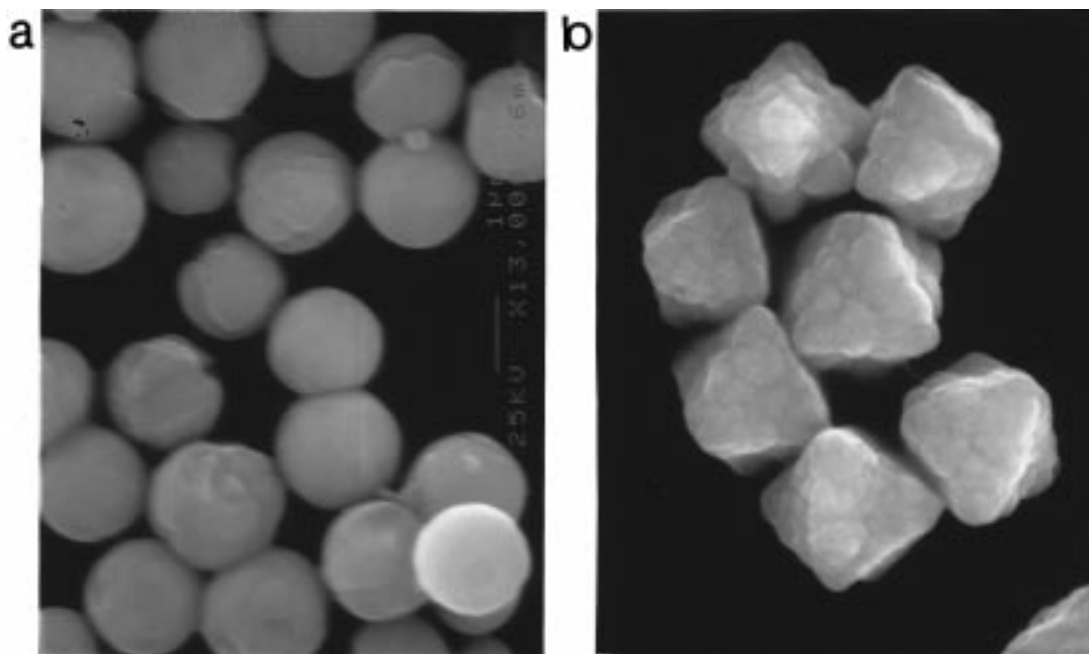
Figure 8. SEM of the samples illustrated in Figure 1a,b after calcination at 900 °C for 30 min.

nm, calculated from the broadening of the XRD peak. These experimental observations would indicate that the octahedral particles are produced by an aggregation mechanism. At first a nanometer size dispersion is formed, followed by the aggregation of these small crystals covered with the surfactant, which is difficult to completely remove by washing. Some water asociated with the hydrophilic group of the surfactant is also trapped, which would account for the TGA data obtained with this solid. The aggregation stage in the formation of uniform (sub)micrometer size colloids, which exhibit X-ray characteristics of crystalline solids, has been noted in a majority of dispersions produced by precipitation from homogeneous solutions.[20,29] Similarly, aggregation of Cs salts of 12-molybdophosphoric acid supported on silica has been established by XPS measurements.[30]

The chemical analysis of the solid formed with thorium ions yields molar ratios [W]/[P] = 12.3 and [W]/[Th] = 0.87, while a stoichiometric formula for $Th_3(PW_{12}O_{40})_4$ would give [W]/[Th] = 16, indicating a large excess of Th in the precipitate. The presence of hydrolyzed Th species in the reaction products is indicated by the decrease in the pH during the precipitation process; the pH of the original solution was 3.2, and after the precipitation it was 2.5. Separate experiments showed that aging a 2.5×10^{-3} mol dm^{-3} $Th(NO_3)_4$ solution at 90 °C for 2 h also caused the pH to drop from 3.1 to 2.6, while the system became turbid during this reaction time. These results make it difficult to ascertain if, indeed, a Th heteropoly compound is formed in this case. The XRD pattern does not offer any information, and the IR result does not show clearly the presence of the Keggin unit. It would, therefore, seem that one deals here with a mixed solid in which the heteropoly anion interacts with amorphous Th (hydrous)

oxide. However, it is noteworthy that one still can obtain reasonably uniform spherical particles.

The differences in the stoichiometry between both Cs and Th compounds also explain their electrophoretic behaviors. The iep of $Cs_3PW_{12}O_{40}$ is mainly due to the WO_6 octahedra of the Keggin unit because the Cs cation is located deep inside the secondary structure. A very low iep was reported for tungsten oxide (at pH < 1),[31] which is not far removed from the value obtained for Cs-tungstophosphate. The case of the Th compound is more involved because of the mixed composition of the solids. The iep reported for ThO_2 varies over a wide range, i.e. from pH 4.2 to 11.[31] The iep of 5.6 determined with the compound described in this study is within this range, and it may be due to the excess of thorium (hydrous) oxide in the particles.

It is interesting to compare the results of this study with dispersions of Th and Zr salts of tungstosilicic acid ($H_4PW_{12}O_{40}$) reported earlier.[21] In the latter case a stoichiometric Th compound was formed, while the solids with Zr had an excess of Zr (hydrous) oxide. Since these preparations were carried out at a temperature (70 °C) lower than in the present case, thorium did not hydrolyze to any significant extent, while the more easily hydrolyzable Zr ion did so. Consequently, a complete exchange of Th^{4+} for four protons took place, while solids of mixed composition resulted with the Zr salt.

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