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Spectroscopic Studies of the Thermal Decomposition Products of Hydrated Cerous Oxalate

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Abstract

The thermal decomposition of hydrated cerous oxalate has been studied by means of thermogravimetry, differential scanning calorimetry, infrared spectroscopy, powder X-ray diffraction, magnetochemistry, and X-ray photoelectron spectroscopy. Materials were isothermally calcined at appropriate temperatures and then subjected to a series of spectroscopic investigations. It was found that the dehydration and oxalate decomposition steps were effectively merged into a concerted decomposition when isothermal heating conditions were used. The only product identifiable by powder X-ray diffraction in the calcination products was ceric oxide, CeO_2. Magnetochemical data demonstrated that one could not form analytically pure ceric oxide in the temperature range studied and that substantial amounts of amorphous cerium(III) products were also obtained. These observations were corroborated by detailed X-ray photoelectron spectroscopic studies of the materials.

Introduction

Due to the extreme insolubility of the lanthanide oxalates, they have been used historically as gravimetric reagents for the determination of lanthanide ions. Since the final step in the analytical procedure normally consists of calcination to constant weight as the oxide, studies of thermal decomposition have been of importance [1–3]. Recently, a systematic investigation of the thermal decomposition of all lanthanide oxalates was conducted employing both thermogravimetry (TG) and differential thermal analysis (DTA) approaches with the intention of categorizing the systematic trends [4]. For most lanthanide oxalate compounds, the decomposition proceeds in two stages. The first stage involves loss of water, while the second stage involves oxalate decomposition. The formation of oxycarbonate species may also occur during the calcination.

The thermal decomposition of hydrated cerium(III) oxalate is somewhat complicated, since during the calcination, cerium(III) is oxidized to cerium(IV). All workers have inferred that the oxidation takes place upon oxalate decomposition [4, 5]; however, conventional methods of thermal analysis cannot totally elucidate this process. X-ray photoelectron spectroscopy (XPS) has been used to study the oxidation of cerium(III) in hydrated cerous carbonate during its calcination [6], since the spectra due to cerium(III) and cerium(IV) are quite different. When combined with conventional thermal analytical procedures, the XPS approach can be used to more exactly describe the details of the decomposition pathways.

A detailed understanding of the oxidation/decomposition processes of hydrated cerium(III) oxalate is important also as an attempt to use the system as an experimental model. The cerium(III) cerium(IV) reaction is the most commonly studied III → IV transition for either the 4f or 5f series of elements. Since the cerium(III) compound studied here is both hydrated and surrounded by carboxylic-type ligands, it makes an excellent model for studying the formation of thermally induced intermediate and mixed species of lanthanides and actinides. This is extremely important in the development of models for determining the reaction chemistries in applied research areas such as nuclear waste.

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In the present work, the thermal decomposition of hydrated cerous oxalate was examined in detail. Conventional TG and differential scanning calorimetry DSC studies were conducted to confirm the details provided by earlier workers. Materials were fired under isothermal conditions at a series of temperatures, and each sample was studied by X-ray photoelectron and infrared spectroscopy, magnetochemistry, and X-ray diffraction. It was established that under isothermal heating conditions, the dehydration and oxalate decomposition steps cannot be distinguished. The oxidation of cerium(III) to cerium(IV) is only partial when these reactions are complete, however, since the calcination products maintain a degree of paramagnetism.

Experimental

Hydrated cerous oxalate was prepared according to the conventional method. Stock cerium(III) solutions were prepared by dissolving reagent grade cerous nitrate in double-distilled water. The compound was precipitated in quantitative yield through the addition of excess oxalic acid. The compound was suction filtered, washed extensively with distilled water, and allowed to air-dry. Elemental analyses were consistent with the existence of the decahydrate, $Ce_2(C_2O_4)_3 \cdot 10H_2O$. *Anal.* found (calc.) Ce, 38.61 (38.68); C, 9.88 (9.95); H, 2.70 (2.78)%. The percentage of oxygen was determined by difference, obtaining 48.81% (found) against 48.59% (calc.). No nitrogen was detected in the final product, indicating the absence of any possibly occluded nitrate.

Thermogravimetric measurements were obtained on a Perkin-Elmer TGS-2 system, while differential scanning calorimetric determinations were obtained on a DuPont 9900 system. In both cases, a heating rate of 5 K/min was used, and the samples were heated in flowing air. The measurements of isothermal gravimetry were obtained by determining the percent weight loss associated with fresh samples of hydrated cerous oxalate when they were heated for three hours in a tube furnace.

Infrared spectra of the calcination products were taken as KBr pellets, using a 1% dispersion in KBr of the cerium products. All data were obtained on a Perkin-Elmer Model 1330 spectrometer. The spectra were calibrated against a polystyrene standard.

Magnetic susceptibility measurements were made using a SHE 905 SQUID magnetometer. The samples were run as powders in previously calibrated containers, with sample sizes ranging between 0.1 to 0.9 g. The applied magnetic fields were 5 and 40 kG, and the sample temperature was varied between 5 and 300 K. The magnetic susceptibilities of the samples were not found to exhibit a significant dependence on field strength.

X-ray photoelectron measurements were performed on a Physical Electronics Model 555 spectrometer, using a 300 W magnesium (Mg $K\alpha$ = 1253.6 eV) anode source and a 50 eV bandpass for the high resolution studies. The specimens were mounted in the spectrometer by pressing the powder into indium foil. Measurement of the adventitious carbon 1s binding energy was hampered by the presence of three overlapping transitions, and thus deconvolution of the spectra was required. The data handling system and the deconvolution procedure have been previously described [7]. Charge referencing was then made to the adventitious carbon 1s transition at 285.0 eV.

Results and Discussion

A variety of decomposition mechanisms have been advanced to explain the thermal reactions associated with cerous oxalate. In the conventional TG experiment, water loss to either a trihydrate [8] or hemihydrate [4] is observed first. Continued heating leads to rapid decomposition of the coordinated oxalates; in air, one obtains CeO_2 as the final product. Heating in inert atmospheres greatly increases the temperatures required for the oxalate decomposition [5] and even can lead to the formation of Ce_2O_3 rather than CeO_2 [3].

Since the spectroscopic characterization of partially decomposed samples requires material calcined under isothermal conditions, the relationship between conventional thermal methods and isothermal techniques was established. To do this, samples of hydrated cerous oxalate were heated in open crucibles for four hours and the weight loss associated with each sample was determined. This procedure yielded an isothermal thermogravimetry (ITG) profile of the compound, and an example is shown in Fig. 1. For comparative purposes, the corresponding conventional TG and DSC heating curves (obtained at heating rates of 5 K/min) are also included in the figure.

One immediately notes in Fig. 1 that the dehydration and oxalate decomposition steps were effectively merged in a single reaction when one employed isothermal heating conditions. One could not determine from the ITG curve whether oxalate decomposition accompanied the dehydration. It is most probable that the dehydration reactions occurred within the same temperature range as indicated by the DSC and TG, but the oxalate decomposition occurred at significantly lower temperatures in the isothermal experiments. The isothermal decomposition appeared to be totally complete by 573 K, since no further weight loss could be detected in material heated

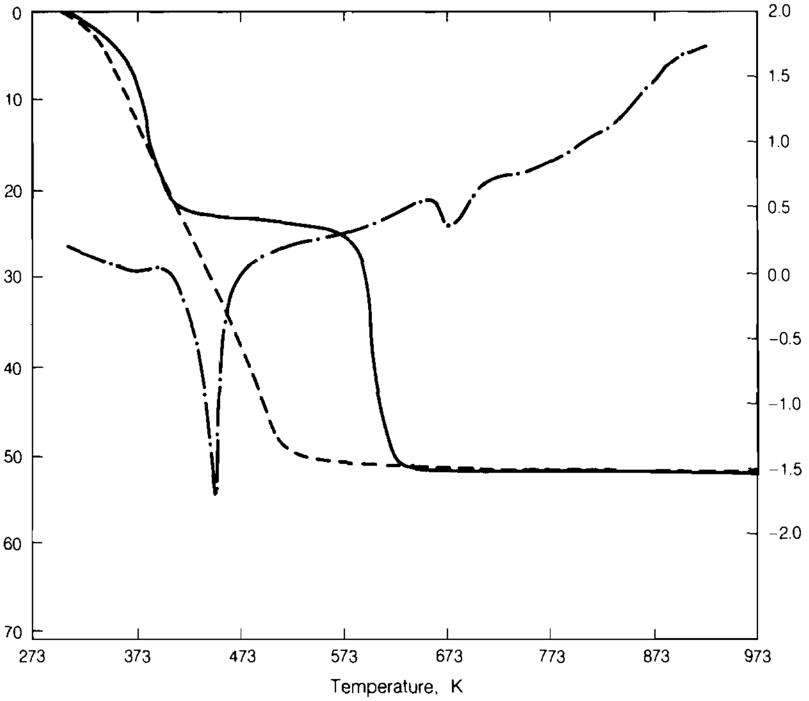

Fig. 1. Conventional thermogravimetric (———) and isothermal thermogravimetric (------) analysis curves for hydrated cerous oxalate. The differential scanning calorimetric trace (—•—•—) is also shown for comparison.

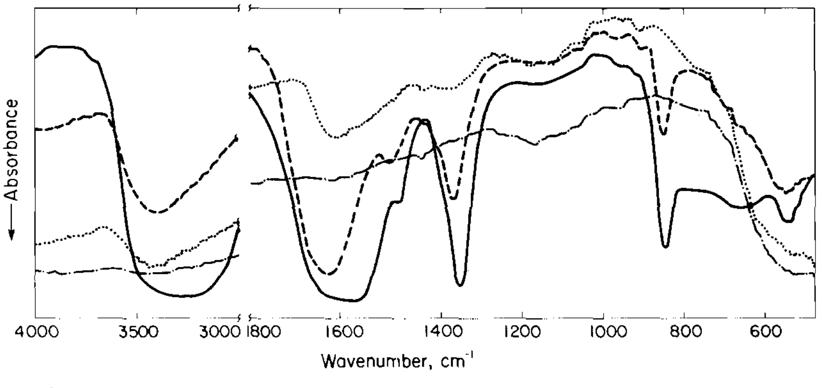

Fig. 2. Infrared spectra of the thermal decomposition products of hydrated cerous oxalate, corresponding to calcination temperatures of 298 K (———), 475 K (------), 810 K (•••••), and reagent grade ceric oxide, CeO_2, (— — —).

at temperature values ranging up to 1073 K. The same limiting weight loss was reached in both the TG and ITG experiments (51%) and corresponded to the formation of CeO_2.

Infrared (IR) spectra were obtained on the materials decomposed under isothermal conditions to initiate studies of the decomposition mechanisms. Spectra of representative examples are shown in Fig. 2. The 3400 cm^{-1} region reflected the water content of the compounds, with extremely strong absorption being noted in the hydrated starting material. A large fraction of the water absorption was lost after heating at 475 K, and essentially none remained in the 810 K material. The vibrational bands observed in the 1430–1450 and 1280–1300 cm^{-1} regions have been documented for oxalate compounds [9] as being related to the carbonyl functional group, while the 1600 cm^{-1} band arises from both the hydroxyl and carbonyl group. Upon calcination of the hydrated cerous oxalate, all oxalate IR absorptions decreased in magnitude. At calcination temperatures equal to 523 K and higher, the only feature attributable to the carbonyl group was a weak band at 1300 cm^{-1}. This feature was probably due to small amounts of chemisorbed carbon dioxide or some type of carbonate species.

The IR spectrum of reagent grade ceric oxide showed no bands uniquely attributable to carbonyl groups, and the intensities of both –OH bands were attenuated by a factor of 1/6. These results suggest that the material obtained in the high temperature calcinations was ceric oxide containing a surface coverage of hydroxyl groups. No evidence was seen in the IR spectra implicating the existence of new species during the decomposition process.

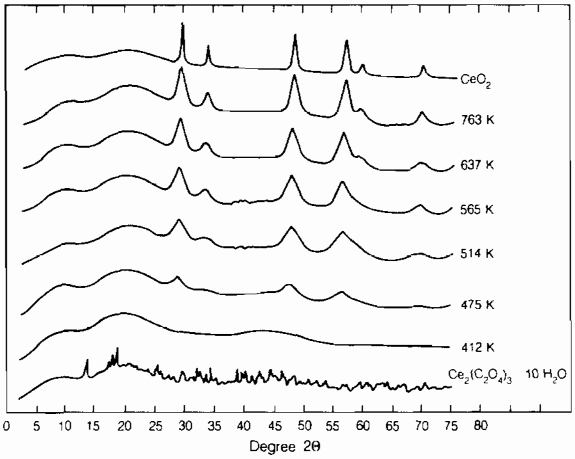

Fig. 3. X-ray powder diffraction patterns of hydrated cerous oxalate and its calcination products at various temperatures.

Further characterization of the samples heated under isothermal conditions was obtained by powder X-ray diffraction studies. The results of these investigations are shown in Fig. 3. The initial cerous oxalate material was found to be highly crystalline, and 58 peaks were observed in the XRD between 2-theta angles of 2 and 75 degrees. Simple drying of the compound at 412 K totally destroyed all crystallinity, and one observed a powder pattern characteristic of a purely amorphous sample. The broad curves in the powder patterns were due to contributions from the adhesive tape used to mount the compounds. Peaks indicative of the first crystalline material were observed at 475 K. Comparison with reagent grade CeO_2 revealed that these new peaks were due to the presence of ceric oxide. In fact, no XRD pattern other than that of CeO_2 was observed in any of the calcined samples. This was further evidence that when heated under isothermal conditions, hydrated cerous oxalate decomposed in essentially one step to ceric oxide.

Besides the dehydration and oxalate decomposition steps, the thermal decomposition process also resulted in the oxidation of cerium(III) to cerium(IV). This oxidation transformed the cerium(III) from a paramagnetic f^1 configuration to an f^0 configuration for diamagnetic cerium(IV). Magnetochemical studies represented an ideal manner in which to study the oxidation process and to place the cerium oxidation in context with the other thermal decomposition steps. The temperature dependence of the bulk magnetic susceptibility was obtained for each calcined sample, and those data are presented in Fig. 4.

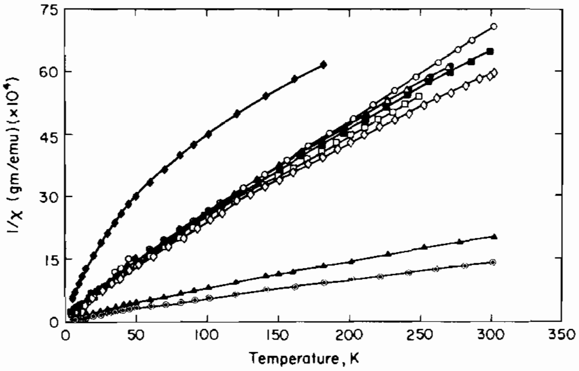

Fig. 4. Temperature dependence of the magnetic susceptibility of the various calcination products. Curves are shown for material heated at 412 K (⊙), 475 K (▲), 515 K (□), 563 K (■), 585 K (△), 613 K (○), 637 K (●), and 810 K (◇). Data obtained for reagent grade ceric oxide (◆) are also included for comparison purposes.

As shown in Fig. 1, the ITG data indicated that the isothermal decomposition was complete by 523 K. The magnetochemical data of Fig. 4 indicated that the oxidation process was complete at the same temperature value. However, it is extremely significant to note that the complete oxidation of cerium(III) to cerium(IV) did not occur and that only a limiting value was reached. The magnetic susceptibility curve for reagent grade CeO_2 was significantly different than any of the calcination samples, thus reflecting its diamagnetic properties. This result was not completely surprising, since it is known that the high temperature portions of the cerium/oxygen phase diagrams are exceedingly complex and characterized by variability in composition [10]. Similar observations were made when studying the isothermal decomposition of hydrated cerous carbonate [6].

A far more definitive probing of the decomposition chemistry was obtained through the performance of X-ray photoelectron spectroscopic studies on the calcined cerium oxalate samples. Figures 5 through 7 show the C 1s, O 1s, and Ce 3d spectra for cerous oxalate samples calcined at various temperatures. Binding energies extracted from these studies are summarized in Table I.

The XPS spectrum of the parent compound showed three transitions in the C 1s region (Fig. 5) and two transitions in the O 1s region (Fig. 6). The high binding energy peak (288.8–289.1 eV) observed in the C 1s region of all samples was consistent

TABLE I. X-ray Photoelectron Data for $Ce_2(C_2O_4)_3 \cdot 10H_2O$ and its Thermal Decomposition Products

Heating temperature	Binding energies[a,b] and Relative peak areas[c]													
	Cerium 3d region			Oxygen 1s region				Carbon 1s region						
	3/2	5/2												
298 K	903.9	885.0	*1.00*	531.8	*6.39*	529.1	*0.69*	288.8	*1.26*	285.0	*0.53*	282.0	*0.29*
412 K	904.1	885.5	*1.00*	531.9	*6.50*	529.1	*0.68*	288.8	*1.36*	285.0	*0.56*	281.2	*0.16*
475 K	898.0	882.0	*1.00*	531.7	*1.53*	529.2	*2.34*	289.1	*0.32*	285.0	*0.34*	281.8	*0.14*
810 K	898.0	882.0	*1.00*	532.1	*1.00*	529.1	*3.19*	289.1	*0.06*	285.0	*0.47*	283.7	*0.21*

[a] In electron volts (eV). [b] Charge referenced using the 1s = 285.0 photoelectron line of adventitious carbon. [c] Relative to the total area of the Ce 3d transitions; all areas have been adjusted for the atomic sensitivity factors from ref. 15 using the values Ce = 12.5; O = 0.63; C = 0.205; the relative peak areas are shown in italics.

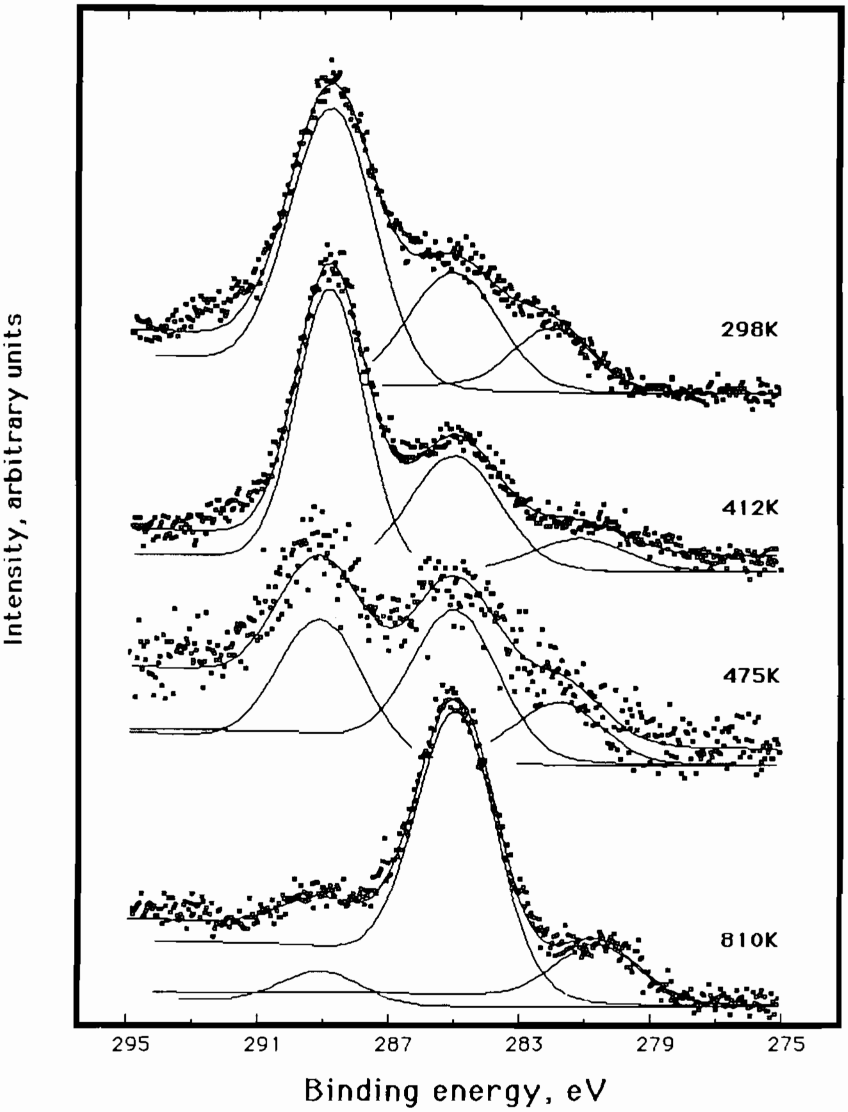

Fig. 5. Carbon 1s X-ray photoelectron spectra of hydrated cerous oxalate and its decomposition products formed at various temperatures.

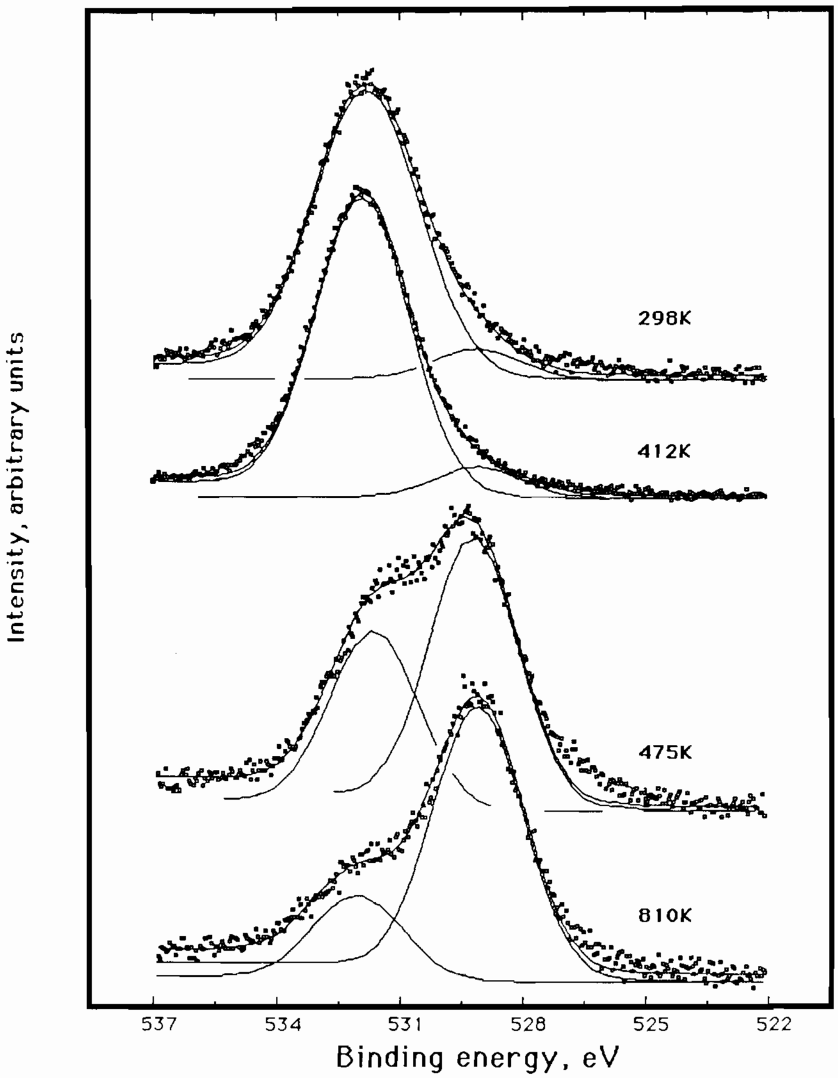

Fig. 6. Oxygen 1s X-ray photoelectron spectra of hydrated cerous oxalate and its decomposition products formed at various temperatures.

with binding energies observed for the carbon in other carbonate and oxalate compounds [11]. Since this peak was observed in materials fired at high temperatures, it is highly likely that re-adsorption of carbon dioxide onto the ceric oxide surfaces occurred. Such processes would be consistent with the results of the IR studies. The lower binding energy peak was not highly reproducible in either position or intensity, and it was probably due to a carbide impurity introduced during the processing of the cerium metal* before conversion to the oxalate. The peak at 285.0 eV was attributed to adventitious carbon and was used as the energy reference for all other binding energy values.

A single transition was observed at 531.8 eV in the O 1s region (Fig. 6) of the initial compound. This binding energy value was consistent with that which would be expected for either water, a carbonate, or an oxalate [6, 11]. In this case, the 531.8 eV line could be viewed as an 'averaged' line containing both the water and the oxalate ion in the parent molecule. The O 1s of oxygen in the sample calcined at 810 K appeared at 529.1 eV, and this value was quite close to the O 1s peak observed in reagent grade CeO_2 (529.5 eV).

The O 1s line of the parent compound was observed to be broadened toward lower binding energies. Burroughs *et al.* [12] demonstrated that similar broadening was associated with the hydration of the

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*Several possibilities were considered for this impurity but were rejected on the basis of either the intensity of other characteristic lines or the implausibility of a particular element being associated with a cerium salt. Terbium, for example, exhibited a weak $4p_{3/2}$ photoelectron line in this region, but could be ruled out on the basis of a total absence of the terbium 4d line at 150 eV.

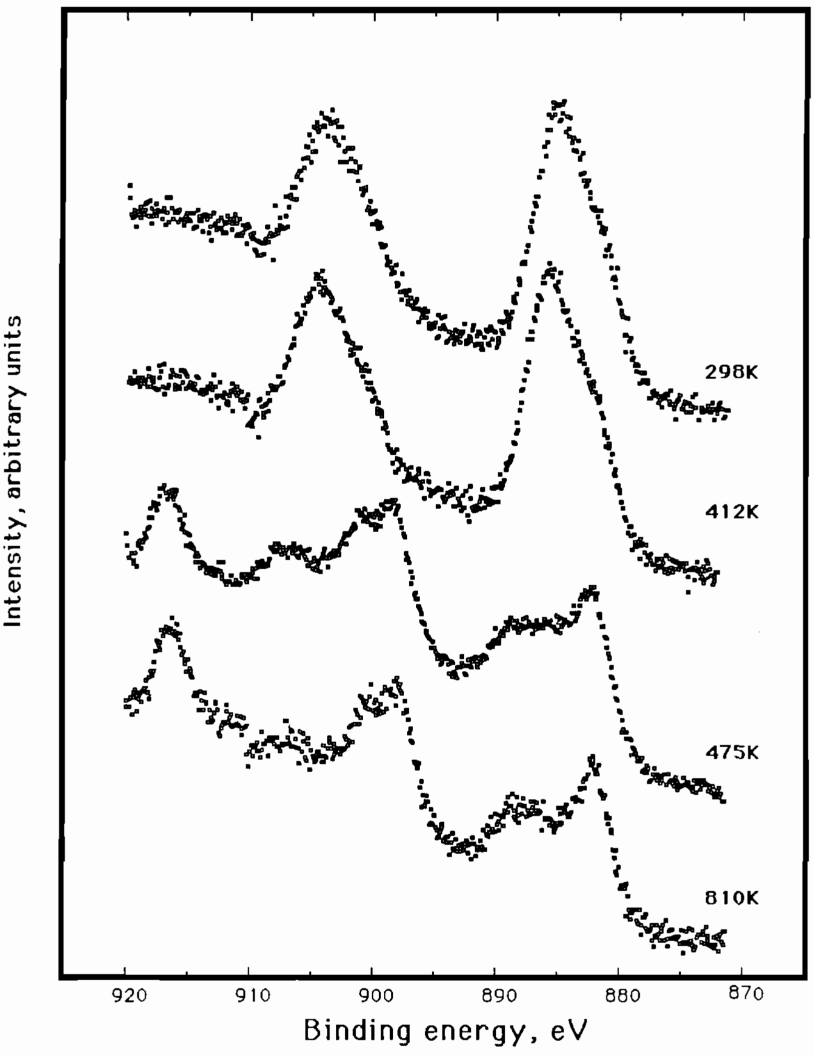

Fig. 7. Cerium $3d_{5/2,3/2}$ X-ray photoelectron spectra of hydrated cerous oxalate and its decomposition products formed at various temperatures.

cerium salts, and such asymmetric lines have been reported for metal oxides containing either bulk or adsorbed water [13]. The material heated at 412 K exhibited a narrowed O 1s line, indicating the existence of partial sample dehydration. These spectra could be deconvoluted into two peaks (Fig. 6) showing the maximum contribution of an oxide component to the broadened O 1s peak, even though the X-ray powder pattern did not yet indicate that an appreciable amount of CeO_2 had formed. Samples heated at temperatures exceeding 473 K contained a true oxide component, as indicated by the shifting of the band centroid to lower binding energies.

The relative peak areas for the O 1s line did not differ significantly between the parent compound and the sample annealed at 412 K, despite the fact that some bulk dehydration occurred during the annealing process at 412 K. This result, combined with the low oxygen/cerium ratio given in Table I, indicated that the surface lost H_2O when introduced to the vacuum system.

All data obtained during the course of the present work suggest that under isothermal heating conditions, the cerium(IV) oxidation occurred simultaneously with the dehydration and oxalate decomposition reactions. For the parent cerous oxalate, peaks at 885.0 and 903.9 eV were observed. These values were in excellent agreement with previously reported cerium(III) $3d_{5/2}$ and $3d_{3/2}$ transitions in hydrated cerous carbonate [6] after correcting for differences in the assumed reference position of the C 1s line of adventitious carbon. Likewise, an analysis of five cerium(III) salts has demonstrated that the uppermost two spectra of Fig. 7 are characteristic of trivalent cerium compounds [14]. One usually observes a spin-orbit splitting of 18.4 eV together with two shakedown satellites. The complex spectrum observed in the 810 K calcination sample was characteristic of the cerium(IV) oxidation state and has been the subject of extensive study [13, 11]. The line around 917 eV was well separated from the cerium(III) transitions and could be used to identify small amounts of cerium(IV) in the presence of cerium(III). Unfortunately, no single cerium(III) line could be isolated from the cerium(IV) lines, and hence the XPS data could not be used to verify the presence of cerium(III) in the materials calcined at elevated temperatures (as was indicated by the magnetic data). The cerium 3d spectrum of the 475 K sample contained lines from both cerium(III) and cerium(IV) compounds, in agreement with both the magnetic and thermal data. In the same material, the O 1s spectrum indicated the presence of oxide, hydroxyl, and carbonyl oxygens, while the C 1s spectrum featured carbonyl type carbon species.

The majority of the 532.1 eV O 1s transition was due to the hydroxyl species, since the 289.1 eV C 1s transition was a factor of twenty less intense, This would preclude the possibility of a carbonate-type species being the main contributor to this line. It also agrees with the infrared data discussed above.

Conclusions

Through the use of a broad range of spectroscopic techniques, a considerable amount of new information has been gathered regarding the thermal decomposition of hydrated cerous oxalate. The thermal decomposition pathways were found to be exceedingly simple when the material was heated under isothermal conditions. The dehydration and oxalate decomposition steps effectively merged into a concerted decomposition. The situation was quite different under dynamic heating conditions, since there were two separate reaction steps. The only identifiable product in the calcination products by powder X-ray diffraction was ceric oxide, CeO_2. Moreover, magnetochemical studies demonstrated that one could not form analytically pure cerium(IV) oxide and that substantial amounts of amorphous cerium(III) products were also obtained. These observations were corroborated by detailed X-ray photoelectron spectroscopic studies of the same materials.

Acknowledgements

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