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Comparative study of thermal decomposition of the sol–gel products of U and Ce by external and internal gelation processes

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Abstract

The synthesis of $U_{0.7}Ce_{0.3}O_{2+x}$ was carried out using external gelation (with urea/NH_3 solution) and internal gelation (with urea/hexamethylene tetramine). The compounds formed were characterized using thermal analytical techniques in Ar, vacuum and air, X-ray powder diffraction and effluent gas analysis by mass spectrometry. The compound formed through external gelation was found to form UO_3 as an intermediate product (identified by O_2 loss to form U_3O_8) whereas the compound formed through internal gelation resulted in single-phase UO_2, which could be sintered into homogeneous pellets with 97% th.d. in Ar + 2% H_2 atmosphere at temperatures as low as 1100 °C.

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1. Introduction

Incorporation of sol–gel synthesis of mixed-oxide fuel as the final part of the reprocessing would reduce some steps in the fast reactor fuel-cycle which in turn would decrease the turn-around-time of the fuel, Pu dust-hazard and wastage of Pu [1,2]. The studies on urania-ceria could help to simulate the high temperature phase behaviour of urania-plutonia [3]. Ganguly et al. [4–7] and Sood and his co-workers [8–11] had reported extensive work on micro-sphere pelletisation of urania and various mixed oxides of urania as well as urania-ceria by internal and external gelation. For achieving higher oxide densities, Ganguly et al. had developed a novel method of adding carbon-black as a pore former followed by burning it out thus generating highly porous materials which could be subsequently sintered to very high densities. They observed that the absence of carbon-black had resulted in the blackberry structure, which is considered as undesirable for nuclear fuels. According to King et al. [12] the internal gelation process for uranium yields the compound $(NH_4)_2(UO_2)_8O_4(OH)_{10} \cdot 8H_2O$. Nevertheless, some studies [10,13,14] had demonstrated that a careful choice of conditions for gelation and heat-treatment could yield very soft microspheres amenable for making high-density products.

A large volume of work on the thermal decomposition of ammonium diuranate (ADU) and related compounds have been reported reliably in the literature [15–26]. The thermal decomposition products of external gelation of ADU were characterized by a variety of techniques such as TG, DTA, IR, XRD and surface area measurements. Three significant studies on the products of internal gelation of ADU were made by Cordfunke [17], Lee [21] and King [26], who employed IR, EGA-MS and NMR respectively to discern the decomposition steps. On the contrary, the literature reports on analogous compounds of Pu or Ce as well as the phases

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bearing either U and Pu or U and Ce (which were prepared by external gelation) were found to be scanty if not incoherent. Even in the case of U compounds the literature on the thermal decomposition of internal gelation products are scarce. Therefore, a detailed investigation was made on the thermal decomposition behaviour of 70% UO_2–30% CeO_2 gel formed by either external or internal gelation in different atmospheres namely, Ar, vacuum and air. Besides TG–DTA, DSC studies and techniques such as evolved gas analysis by mass spectrometry (EGA-MS), a few more characterization techniques such as powder X-ray diffraction (XRD), carbon analysis, U, Ce and oxygen-to-metal ratio (O/M) analyses and density measurements were made use of. The results were analyzed and are presented here with a view to facilitating a better understanding of the decomposition process.

2. Experimental

2.1. Materials

Nuclear grade U_3O_8 (Nuclear Fuel Corp., India; purity better than 99.98%), cerous nitrate (K Chem, India; purity better than 99%), hexamethylene tetramine (HMTA) (Loba Chemie Pvt. Ltd., India; purity better than 99.5%), urea (Merck, India; purity better than 99.5%), ammonium nitrate (Praghathi Chemical Industries, India; purity better than 99%), reagent grade nitric acid and ammonia solution (Fischer Inorganic and Aromatics Ltd., India; and Merck, India) were made use of.

2.2. Procedure

2.2.1. Gelation methods

To a 100 cm^3 1 M solution of U and Ce nitrates corresponding to the composition $U_{0.7}Ce_{0.3}O_2$, 2.5 mol of ammonium nitrate and 4 mol of urea were added, boiled gently, followed by the addition to a 7 M ammonia solution. The bulk gel so formed by this external gelation process was filtered and washed with 1% ammonia solution and distilled water to neutral pH and dried at about 120 °C in air.

For internal gelation a 100 cm^3 chilled 1 M solution of U and Ce nitrates corresponding to the composition $U_{0.7}Ce_{0.3}O_2$, was mixed with a 10 cm^3 2 M solution of hexamethylene tetramine and urea. The resulting solution was gradually heated to 60–70 °C for completion of gel formation. Subsequent processing was identical with that of the external gelation process.

Compounds formed by external and internal gelation, designated as CFEG and CFIG respectively, were subjected to thermal decomposition at 600 °C in Ar atmosphere. The products of thermal decomposition were characterized essentially for the chemical composition by employing well established analytical procedures.

2.2.2. Characterization

The techniques used for the quantitative determination of uranium and cerium contents and O/M of the products were the same as reported elsewhere [3]. The technique developed by Ahmed et al. [27] was utilized for the determination of residual carbon. The products of thermal decomposition of CFEG and CFIG were homogenized by grinding using an agate mortar and pestle followed by compaction into cylindrical pellets of 10 mm diameter and 2–3 mm thickness in a hydraulic press at a pressure of 100 MPa. These pellets were subsequently sintered at 1100 °C in a dynamic stream of Ar + 2% H_2 gas mixture at a flow rate of 10^4 cm^3/h for 24 h. These pellets were also subjected to compositional analyses besides density and characterization by powder XRD. Pycnometric density measurements were carried out by employing dibutyl phthalate as the pycnometric liquid using a density kit (Precisa Instruments, AG). A horizontal thermal analysis system (Model Seiko 320) was employed for recording TG/DTA in Ar and static air. In vitro studies for the evolved gas were carried out by EGA-MS using a lab made set up [28,29]. The XRD patterns were obtained using a Rigaku (Model Miniflux) diffractometer as well as a Philips X-ray powder diffractometer within the 5 mass% threshold for the detection of impurity phases. High resolution electron microscopy (HREM) pictures were taken using a transmission electron microscope (Model JEOL 2000 EX II).

3. Results and discussion

The results of chemical analyses of the products of thermal decomposition (at 600 °C) of CFEG and CFIG are listed in Table 1. The results by chemical analysis, density measurements and structural analysis using XRD performed on the final products of sintering at 1100 °C/24 h in Ar + 2% H_2 atmosphere are summarized in Table 2.

It may be noted that the external gelation process for a solution of 69% U and 31% Ce nitrate mixture yielded

Table 1
Characterization of gelation products formed from equimolar U and Ce nitrate solution after decomposing at 600 °C in Ar atmosphere

Product	U (mol%)	Ce (mol%)	O/M	C (wt%)
CFEG	68.9	31.1	2.421	0.02
CFIG	68.7	31.3	2.187	0.60

CF: compound formed; EG: external gelation; IG: internal gelation.

Table 2
Characterization of thermal decomposition products of U, Ce gels after sintering at 1100 °C in Ar + 2% H_2 atmosphere

Product	U (mol%)	Ce (mol%)	O/M	C (wt%)	ρ (% th. density)	XRD characterization		
						d (pm)	*hkl*	Structure
CFEG	68.9	31.1	2.144	0.018	94	345.0 314.3 272.1 192.5	220 111 200 332	Orthorhombic + cubic
CFIG	68.7	31.3	2.07	0.020	97	314.3 272.1 192.9 164.2	111 200 220 311	Cubic

mixed oxide with O/M of 2.144, which is certainly not useful for fuel purposes. Hence, in order to achieve a low O/M ratio, sintering at much higher temperatures ($\simeq$1400 °C) in Ar + 2% H_2 mixture had to be resorted to, which route may be of marginal advantage over the conventional processing methods. Owing to the lower utility of external gelation method, estimation of the density was made assuming the validity of Vegard's law. The lower value of O/M achievable by internal gelation route was attributed to the formation of a uranyl trimer with HMTA as shown by NMR studies by King et al. [26] which provided a local reducing environment of nascent hydrogen on decomposition.

The characterization of CFEG and CFIG powders by HREM revealed them to be essentially made of submicron and nano-sized particles respectively (Fig. 1(a) and (b)). Fig. 1(b) shows a somewhat random distribution of small spherically shaped particles of a minor phase co-existing with a relatively large number of rod-shaped particles of a major phase. The average size of the nanocrystalline particles could be of the order of 2–3 nm, which value is only approximate owing to the dependence on statistics of collection. However, nano particles so produced by CFIG in this work are an order of magnitude smaller than those of pure UO_2 gel product reported by Suryanarayana et al. [10] employing IG. These authors observed the average UO_2 particle size to be 40–70 nm. The possible reason for the differences in the particle sizes could be attributed to different conditions of gelation. They further observed that the lower the U concentration in the feed solution compared to HMTA, the smaller was the size of the particles. They employed a large-volume system with mechanized stirring with gelation time of the order of 10–15 s, as compared to the much smaller scale (100 cm^3) solution with manual stirring and longer period (600–900 s) of gelation. Nevertheless, much smaller (2–3 nm) particles were found to result when the molar ratio of the cation concentration in the feed to that of HMTA as well as urea in the HMTA/urea mixture was optimized to 1:2.

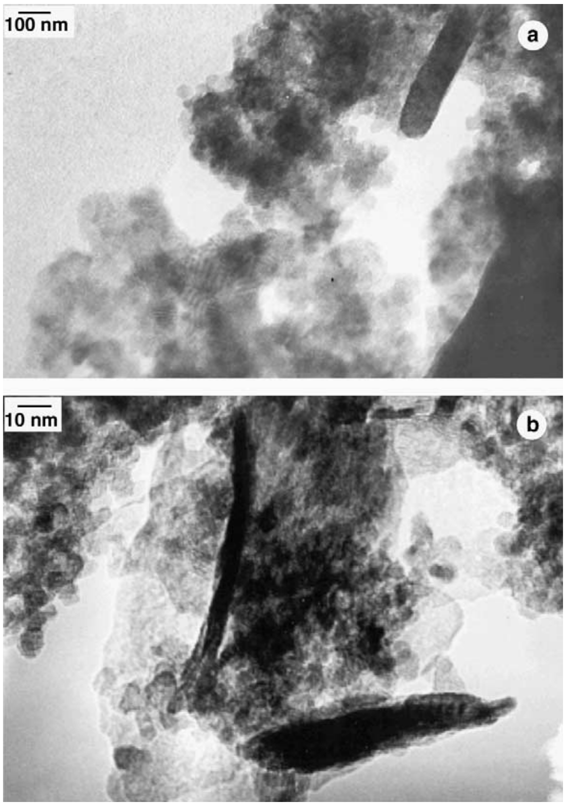

Fig. 1. High resolution electron micrographs of (a) externally gelated powder and (b) internally gelated powder.

The TG/DTA studies were mainly conducted for a preliminary understanding of the temperature ranges of the decomposition of the gel-products in various atmospheres (Ar, vacuum and air). The results of the TG/DTA studies on CFEG and CFIG are summarized in Table 3 and Figs. 2 and 3. The heating rate employed for TG/DTA in Ar and air environment was 10 °C/min while in the vacuum experiment it was 6 °C/min. The thermal decomposition of CFEG in Ar as well as in

Table 3
TG/DTA results on compounds formed by external and internal gelation in different decomposition environments

Product	Environment	Temperature ranges of weight-loss step (°C)	Exotherm (°C)	Endotherm (°C)	Inference/remarks
CFEG	Argon	1st weight loss: 50–270	272	76	Dehydration,
		2nd weight loss: 270–520	360	140	NH_3 loss,
		3rd weight loss: 520–550		550	$UO_3 \rightarrow U_3O_8$
CFEG	Vacuum	1st weight loss: 50–270	349	132	Dehydration,
		2nd weight loss: 270–500		545	NH_3 loss,
		3rd weight loss: 500–550			$UO_3 \rightarrow U_3O_8$
CFEG	Air	1st weight loss: 50–275	–	–	Dehydration,
		2nd weight loss: 275–550			NH_3 loss,
		3rd weight loss: 550–570			$UO_3 \rightarrow U_3O_8$
CFIG	Argon	1st weight loss: 50–220	279	84	Dehydration,
		2nd weight loss: 220–350	343	147	NH_3 loss
CFIG	Vacuum	1st weight loss: 50–270	275	89	Dehydration,
		2nd weight loss: 270–410	340		NH_3 loss
CFIG	Air	1st weight loss: 50–233	–	–	Dehydration,
		2nd weight loss: 233–270			NH_3 loss,
		3rd weight loss: 420–550			$UO_3 \rightarrow U_3O_8$

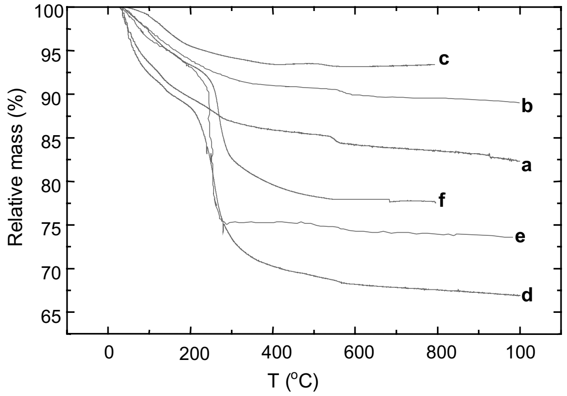

Fig. 2. TG curves of thermal decomposition of CFEG in (a) Ar, (b) air and (c) vacuum, and of CFIG in (d) Ar (e) air and (f) vacuum. The linear heating rate for the TG curves in Ar and air was 10 °C/min and in vacuum was 6 °C/min.

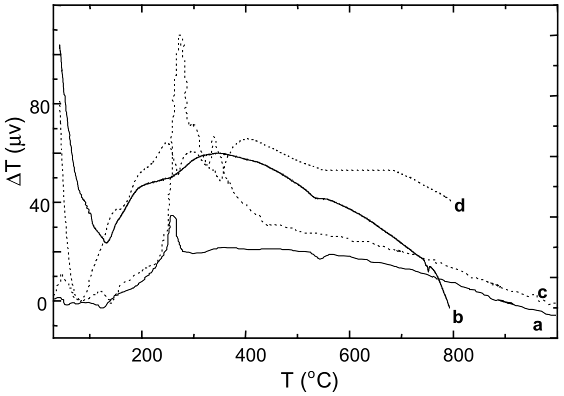

Fig. 3. DTA curves of thermal decomposition of CFEG in (a) Ar, (b) vacuum and of CFIG in (c) Ar and (d) vacuum.

vacuum proceeded with UO_3 as a major intermediate product as inferred from the results of TG/DTA (Fig. 2 (curve a and c), Fig. 3 (curve a and b)) in conjunction with those of EGA-MS (Fig. 4(a)). A similar comparison should be made between the results of TG/DTA and EGA-MS recorded on CFIG. Two steps of thermal decomposition of CFIG occurred over the ranges 50–220 °C and 250–350 °C in the TG/DTA curve (Fig. 2 (curve d and f), Fig. 3 (curve c and d)) encompassing the peak temperature of 80 and 250 °C observed in the EGA-MS spectra (Fig. 4(b)). The EGA-MS peaks corresponded to the evolution of NH_3 in the first step of decomposition and of NH_3 and CO_2 in the second step. These sets of figures differ significantly from those corresponding to the decomposition of CFEG by the absence of O_2 evolution. Thus, the product of thermal decomposition of CFIG was a UO_2 phase, which showed constancy in weight above 400 °C. This is in marked contrast to the weight loss occurring in the range 500–550 °C in CFEG under similar Ar and vacuum environments.

To conclude the investigation, the TG/DTA results on CFEG and CFIG recorded in ambient air atmosphere (Fig. 2 (curve b and e)) were analyzed in the light of the foregoing discussion. The presence of the third step is indicative of the formation of UO_3 as an inter-

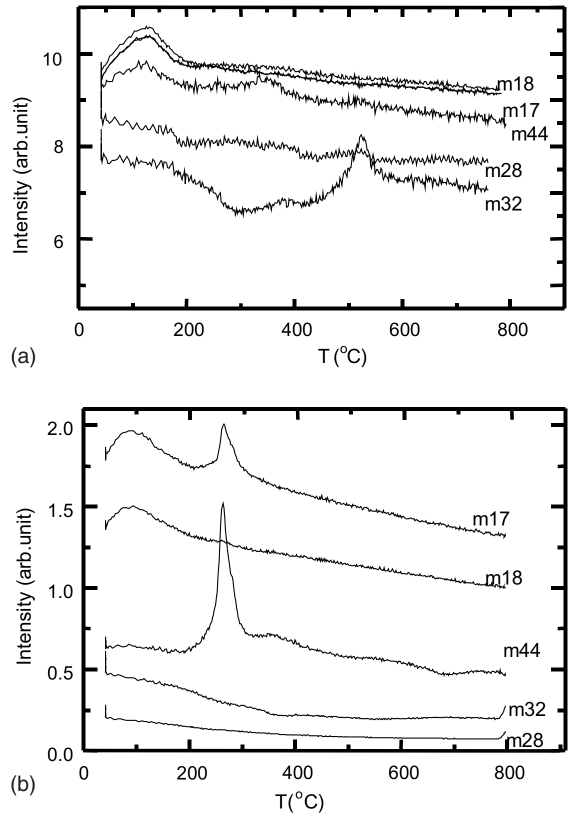

Fig. 4. EGA-MS spectra of (a) CFEG and (b) CFIG at linear heating rate of 6 °C/min in vacuum. The peaks were identified by mass numbers: (NH_3 (17), H_2O (18), CO_2 (44), CO or N_2 (28) and O_2 (32)).

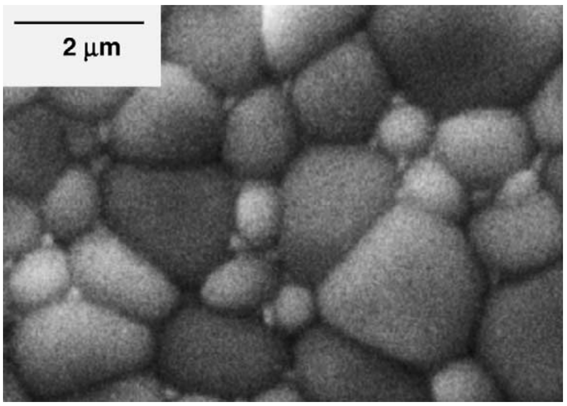

Fig. 5. Ceramograph of the internally gelated $(U_{0.69}Ce_{0.31})O_{2.07}$ sintered at 1100 °C/24 h in Ar + 2% H_2 atmosphere.

mediate from both CFEG and CFIG resulting in subsequent decomposition to the U_3O_8 phase. This significant observation has a bearing on the process formulation for the synthesis of mixed oxide fuels.

The conventional process of synthesis of mixed oxide fuels would invariably involve air calcination. This would in turn result in the formation of U_3O_8. Further, orthorhombic U_3O_8 was reported to exhibit limited solid solubility of ceria according to Nawada et al. [3], Markin et al. [30] and Tagawa et al. [31]. Likewise, Markin and Street [32] as well as Bret and Fox [33] reported the restricted solubility of PuO_2 in U_3O_8. Hence, the air calcination step if permitted as an intermediary in mixed oxide formation could result in the segregation of U and Ce in the case of $(U,Ce)O_2$ and U and Pu in the case of $(U,Pu)O_2$. To homogenize such a mixture higher temperatures of sintering have to be resorted to owing to the much lower rates of cationic diffusion. The advantages gained in achieving microhomogeneity in the IG process would be lost in resorting to air calcination.

Since the internal gelation technique involved a UO_2 type phase as an intermediate (not U_3O_8), sintering to required fuel densities could be achieved at a much lower temperature (1100 °C). A ceramograph of the sintered product is shown in Fig. 5. The occurrence of larger amounts of residual carbon (0.6%, Table 1) while calcining CFIG in Ar was observed. However, the level of residual carbon could be minimized to 0.02% by calcining in Ar, laden with moisture.

4. Conclusion

The formation of highly sintered $(U,Ce)O_{2+x}$ pellets (simulating $U_{0.7}Pu_{0.3}O_{2+x}$) was studied through two soft chemistry routes namely, external and internal gelation followed by decomposition in Ar, vacuum and air environments. By combining TG/DTA studies with EGA-MS spectra in vacuum, the formation of UO_3 as an intermediate product when synthesized via external gelation route was established whereas the synthesis via internal gelation resulted directly in the formation of a UO_2 phase. The disadvantage of the conventional air calcining was discussed in the light of UO_3 formation (identified by O_2 loss leading to U_3O_8 phase formation). To take advantage of the microhomogeneity of the product produced through the internal gelation route, thermal decomposition should be carried out in an inert (possibly moist Ar) atmosphere. This procedure would also facilitate sintering the mixed oxide to near theoretical density at temperatures as low as 1100 °C.

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