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THERMAL STUDIES ON AMMONIUM URANATES

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Abstract

Ammonium uranates are important intermediates in the preparation of nuclear fuel UO_2. These can generally be prepared through two different routes: heterogeneous (conventional) and homogeneous methods of precipitation. In the conventional method, ammonium hydroxide, gaseous ammonia and ammonium carbonate are the precipitating agents. In the homogeneous method, urea hydrolysis is used to generate in situ ammonia needed for precipitation. For the present studies, ammonium hydroxide is used for the conventional and urea for the homogeneous methods of precipitation. The uranates, thus prepared, are characterized by thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA). Thermally the numbers of decomposition steps are identical for both uranates but the temperatures of the decomposition and mass losses vary. The intermediate and final oxides are identified by X-ray diffractometry (XRD).

Keywords: calcining, digest, DTA, DTG, TG, uranates, XRD

Introduction

The fabrication of ceramic nuclear fuels generally involves preparation of inorganic hexavalent uranium compound, ammonium uranate, calcination to oxide and reduction to UO_2 followed by pressing and sintering to the pellet form [1]. It is essential to characterise the precursor, ammonium uranate, as the physico-chemical properties of the oxide, finally produced, depend on it [2–5]. A number of publications on the preparation and characterisation of ammonium uranates are reported [1–13]. Regarding the composition of ammonium uranates, conflicting views are seen in the literature. Some hold the view that the ammonium uranate system is heterogeneous with four different compounds existing together [9, 14]. Another view is that the ammonium uranate system is continuous, represented as $UO_2(OH)_{2-x}(ONH_4)_x \cdot y(H_2O)$ where the x and y values vary according to the preparative conditions [15–18].

In the present work, ammonium uranates are prepared through the conventional method using ammonium hydroxide and by the homogeneous method using urea. These are characterised by TG, DTG and DTA. The intermediate and final oxides obtained on heating are subjected to XRD. Also the powder characteristics of these uranates are reported.

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Experimental

Preparation of ammonium uranates

Conventional method

To 90 ml solution containing 200 mg of nuclear pure uranium, add 1.0 g of AR grade NH_4NO_3. Add 10 ml of 1:1 AR grade NH_4OH drop by drop over a period of 10 min, with constant stirring. Digest the precipitate for one h on the water bath. Filter, wash with 10 ml portion of 0.1% NH_4NO_3 five times and finally once with 5 ml of water. Dry at 105°C for one h.

Homogeneous method

To a solution of 100 ml containing 200 mg of nuclear pure uranium, add 1.0 g of AR grade NH_4NO_3 and 5.0 g of AR grade urea. Heat the solution, immersed in water bath for 2 h. Filter, wash and dry as given in the above procedure.

Thermal studies

TG, DTG and DTA are carried out using Thermal analyser model TGD 7000 RH. Accurately weighed 0.1 g of samples are taken for thermal analysis. For DTA, the samples are heated in an atmosphere of air up to 800°C at a rate of 10°C min^{-1}. Pre-heated alumina is used as reference material. TG, DTG and DTA curves are plotted at a chart speed of 120 mm h^{-1}.

X-ray diffraction studies

These are carried out on the intermediate and final oxides obtained from the uranates prepared by the two different routes, using Siemens D500 diffractometer with CuK_α X-ray radiation source.

Results and discussion

Physical characteristics of the ammonium uranates are given in Table 1. It is seen that the uranate prepared by the homogeneous route is free flowing, unlike the one obtained by the conventional method.

Table 1 Physical characteristics of ammonium uranates

Characteristics of ammonium uranate	Heterogeneous method	Homogeneous method
Nature	not free flowing	free flowing
Colour	reddish yellow	greenish yellow
Time of precipitation	immediate	precipitation starts after 15 to 20 min
Total filtration time including washing	90 min	30 min

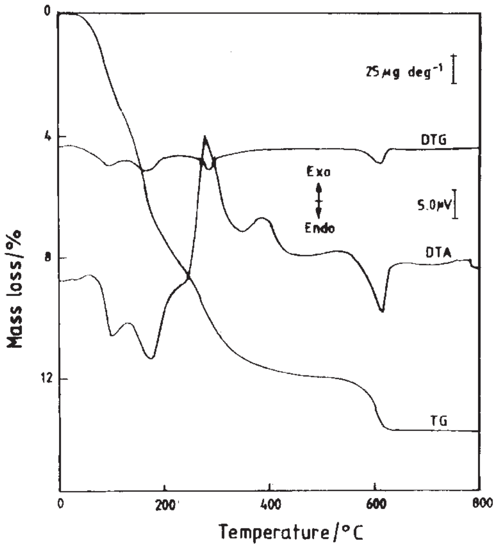

Fig. 1 TG-DTG-DTA curves of ammonium uranate (heterogeneous method)

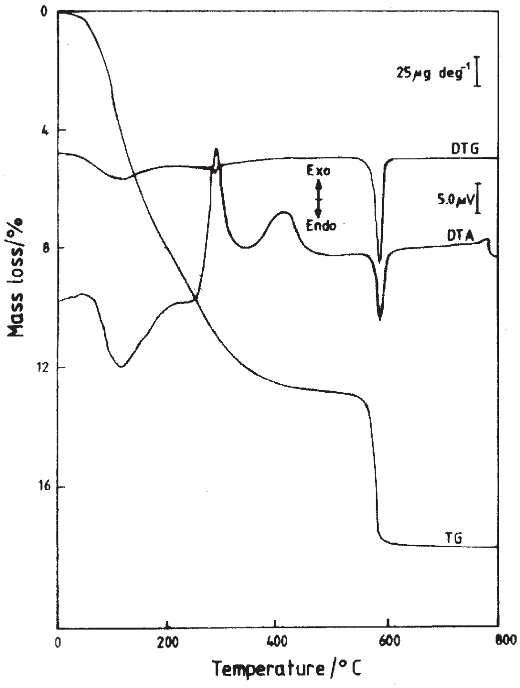

Fig. 2 TG-DTG-DTA curves of ammonium uranate (homogeneous method)

TG, DTG and DTA curves of ammonium uranate prepared through heterogeneous method are shown in Fig. 1. Figure 2 shows the TG, DTG and DTA of ammonium uranate prepared through homogeneous method. Mass losses at different temperatures are given in Table 2. Table 3 gives the nature of the DTA peaks and the temperatures at which they occur. TG shows that ammonium uranates, prepared by the two different routes, start decomposition immediately, on heating. In the DTA, one finds that there are two endothermic peaks, one at 105°C and another at 180°C for the uranate prepared by the conventional method. The first peak is assigned to the loss of moistüre and the second to that of coordinated water [13, 16, 19, 20]. DTA for the uranate prepared by the homogeneous method shows only a broad peak in the region, indicating that both moisture and coordinated water are released simultaneously. These are corroborated by the peaks seen in the DTG curves. This is also indicative that the coordinated water is not as strongly bound as in the uranate prepared by the conventional route.

Table 2 TG data of ammonium uranates

Precipitation method	Mass loss/% (Cumulative)			
	100°C	200°C	500°C	800°C
Heterogeneous	2.66	7.61	11.78	13.44
Homogeneous	3.60	8.60	12.00	17.00

Table 3 DTA data of ammonium uranates

Precipitation method	Temperature of DTA peaks/°C				
	I (Endo)	II (Endo)	III (Exo)	IV (Exo)	V (Endo)
Heterogeneous	105	180	295	390	620
Homogeneous		150	300	415	595

DTA further shows two exothermic peaks around 300 and 400°C for both the uranates. These are ascribed to the release of ammonia which is an exothermic process. There have been many different reasons given to the peaks observed in this region. Notz *et al.* have stated that the peak in the region of 250 to 300°C corresponds mainly to the loss of nitrate along with part of the ammonia [21]. Ippolitova *et al.* stated that the deflection in this region is associated with detachment of NH_4^+ ion which takes place in two stages [19]. According to El-Fekey *et al.* the deflection in the region is mainly due to the removal of nitrate impurities with some ammonia [22]. The presence of traces of nitrates in the ammonium uranate spilt up the peak in this range as reported by Price [23].

The stable region between 400–500°C is assigned to the oxide, UO_x which further undergoes self-reduction to give U_3O_8. TG curve shows that the mass loss beyond 500°C in the ammonium uranate prepared from homogeneous method is more indicating that the compound formed around 500°C has more mass than the one obtained through conventional method. It is pertinent to refer the work of Sato *et al.* [13]

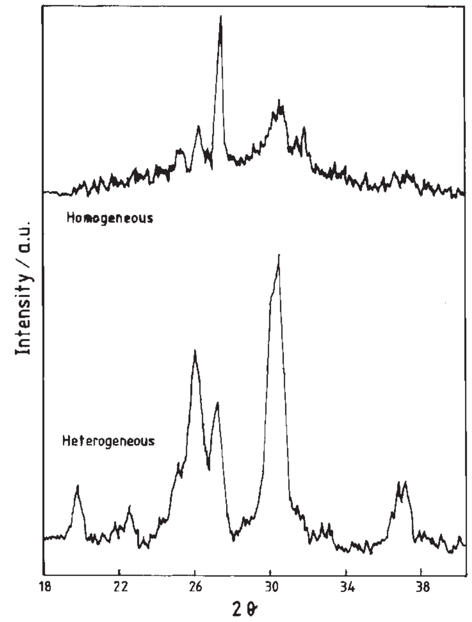

Fig. 3 XRD of intermediate oxide prepared by homogeneous and heterogeneous methods

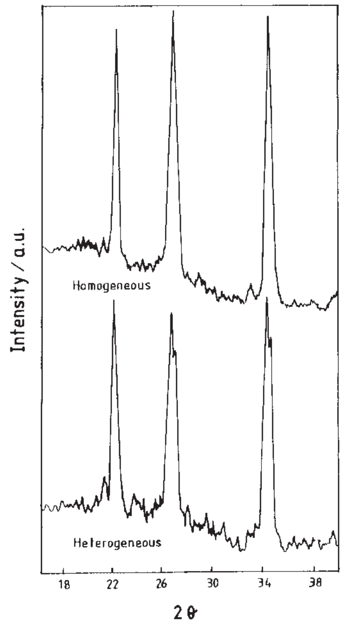

Fig. 4 XRD of U_3O_8 prepared by homogeneous and heterogeneous methods

in which they have reported that ammonium uranate decomposes to give UO_x, where $3 \leq x \leq 3.5$. In the present work ammonium uranate prepared through conventional method decomposes to give UO_x where $x = 3$, whereas in homogeneous method it decomposes to give UO_x, where $x = 3.6$.

From DTA the peak temperature at which the conversion of UO_x to U_3O_8 takes place is 620°C in conventional method. The decomposition starts at 560°C and ends at 640°C with a span of 80°C. In the homogeneous method, decomposition starts at 570°C and ends at 610°C with a span of 40°C. Samples were heated at 460°C to get the XRD patterns of the intermediate oxide, which is shown in Fig. 3. Figure 4 shows the XRD pattern of final product of decomposition. XRD patterns of intermediate oxide from conventional method resembles β-UO_3. In the case of homogeneous method, well defined XRD pattern is not observable. The final oxide in both cases is α-U_3O_8.

Conclusions

Physical characteristics of ammonium uranate prepared through the homogeneous method is better than the one prepared by the conventional method. The precipitate is easily filterable and washable. After drying it is free flowing. The thermal decomposition steps in both the cases are almost the same except that an intermediate oxide, $UO_{3.6}$, is formed in the homogeneous method of precipitation. The short span temperature for the conversion of this oxide to U_3O_8 indicates that this is more reactive than UO_3 prepared through conventional method. The final oxide obtained by calcining the ammonium uranates prepared by both the methods is α-U_3O_8.

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