CHAPTER 5
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5. THERMAL DECOMPOSITION AND XRD STUDIES ON AUC PREPARED AT LOW TEMPERATURE

5.1. INTRODUCTION

The fabrication of uranium based nuclear fuels generally involves the preparation of uranium oxides (UO₃ or U₃O₈), which can be processed to ceramic nuclear fuel. ADU and AUC are the important intermediates for the preparation of uranium oxides. A number of publications on the preparation of ADU [1-3] and AUC [4-14] are reported. Uranium oxide powder obtained from AUC is more free-flowing, have a higher bulk density and are more suitable for the pellet fabrication without preliminary granulation or milling operations [15-20]. The AUC intermediate product is generally prepared from uranyl nitrate by adding mixture of NH₃ and CO₂ gases, NH₄OH and CO₂ gas, ammonium carbonate etc. as precipitants. Much larger quantity of chemicals (NH₃ and CO₂) as gases required for AUC process are a significant complication [17]. The depleted OH⁻ ion in the case of NH₄OH solution may affect the characteristic of AUC precipitate in terms of forming ADU by product [20]. Also the solubility of AUC in the filtrate is quite higher (>2000ppm of
uranium) by using above precipitants [16&20] and separate process step is required to recover the uranium in the filtrate.

It is reported in the literature [16] that precipitation temperature causes no drastic differences over particle distribution. So, in the present work, AUC is prepared by adding (NH₄)₂CO₃ at different temperature conditions in order to minimise the loss of uranium in the filtrate. Solubility as functions of temperature and feed uranium concentration are studied. Thermal decomposition of AUC prepared under cold condition (5-10°C) is characterised by TG/DTA and XRD. The intermediates and gases evolved during the decomposition of AUC are identified by EGA-MS. The oxide obtained from the calcination of AUC prepared at 5-10°C is also characterised by XRD.

5.2. EXPERIMENTAL

5.2.1. Reagents and chemicals

The chemicals used are nuclear grade U₃O₈ and nitric acid of AR/GR grade. Ammonium carbonate of E merk purified product.

5.2.2. Apparatus and Analytical methods

Visible digital spectrophotometer: U analysis
Systronic -166
Thermal analyzer, SETARAM Decomposition of AUC model Setsys 16/18 Spectra-MS
5.2.3. Procedure

5.2.3.1. Solubility of AUC as a function of temperature an feed uranium concentration

$U_3O_8$ is dissolved in nitric acid and prepared 400g/L uranium stock solution. A known volume of the above stock solution taken in a beaker and to this known volume of saturated ammonium carbonate solution is added with constant stirring at room temperature. It is allowed to settle and filtered by using whatmann filter paper No.541. The filtrate is analysed for uranium. The same experiment is repeated with different precipitation temperature conditions (5-20°C) by controlling the temperature using thermostate. The filtrations are carried out in cold and room temperature conditions. The filtrates are analysed for uranium.

A known volume of the solution containing 5-125 g/L of uranium is taken in a beaker and a known amount of ammonium carbonate salt is added with constant stirring at room temperature. This experiment is also carried out at low temperature conditions (5-
13°C). The precipitates are filtered and washed with 0.5 % ammonium carbonate solution. The filtrates are analysed for uranium. The AUC precipitated at 5-10°C is dried at room temperature and calcined to $\text{U}_3\text{O}_8$ at 850°C.

5.2.3.2. TG/DTA and EGA-MS studies

The TG/DTA of powder AUC sample precipitated at 5-10°C is carried out in a SETARAM model Setsys 16/18 Thermal Analyser at a heating rate of 5K/min over a temperature range of 300 to 1300K under flowing helium gas stream. 150 mg of the sample is taken in a platinum crucible and subjected to programmed heating in an Evolved Gas Analysis-Mass Spectrometry (EGA-MS) facility. The temperature-induced decomposition is followed by tracking the concentration of product gases like CO$_2$, NH$_3$ and H$_2$O by a quadrupole mass spectrometer (QMS). The ion intensities of various product gases are plotted as a function of specimen temperature to get the EGA-MS spectra.

5.2.3.3. X-Ray Diffraction study

X-Ray diffraction pattern on powder AUC and its oxide calcined at 850°C are obtained at room temperature with Philips Xpert pro analytical diffractometer using CuKα radiation
(λ=0.154056 nm, the data collection angle 2-theta ranges from 10-80°, scan size step 0.02 for AUC and 2-theta ranges from 20-80°, scan step 0.02 for U₃O₈).

5.3. RESULTS AND DISCUSSION

5.3.1. Solubility of AUC as a function of feed Uranium concentration and temperature

The solubility of AUC in excess saturated ammonium carbonate solution at different temperature is given in Table 5.1. It indicates that solubility decreases as temperature decrease. Uranium in the filtrate is reduced when decrease the operating temperature. Uranium in the filtrate is reduced from 2200 mg/L to 665 mg/L when the temperature is decreased from 32°C to 7°C. From the Table 5.1, it is also found that addition of low temperature (11°C) conditioned precipitant enhances the further reduction of uranium (105 mg/L) in the filtrate. Decrease of solubility with decreasing temperature may be attributed due to endothermic effect. No appreciable change is observed when filtration is carried out in cold conditions.

Complete precipitation of AUC in the feed containing uranium concentration less than 50g/L by the addition of saturated ammonium carbonate solution is difficult because of increase in solubility due to
Table 5.1. Effect of temperature on solubility of AUC

<table>
<thead>
<tr>
<th>S.No</th>
<th>Precipitation Temp. (°C)</th>
<th>(NH$_4$)$_2$CO$_3$ sol.Temp. (°C)</th>
<th>Uranium in filtrate (g/L)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>32</td>
<td>32</td>
<td>2.2080</td>
</tr>
<tr>
<td>2</td>
<td>19</td>
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<td>3</td>
<td>7</td>
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<td>0.6665</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>11</td>
<td>0.105</td>
</tr>
<tr>
<td>5</td>
<td>7</td>
<td>11</td>
<td>0.101*</td>
</tr>
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</table>

* Filtration carried out under cold conditions
increase in net volume. So solubility of AUC as a function of temperature in the solution containing 5-125 g/L uranium is carried out by adding ammonium carbonate salt. Solubility of AUC in excess ammonium carbonate salt at different temperature conditions is shown in Fig.5.1. It shows that solubility of AUC decreases steadily as feed uranium concentration increases. But in cold condition (5-13°C) solubility of AUC is decreased drastically.

Solubility of uranium in the filtrate during the precipitation of AUC by the addition of saturated ammonium carbonate solution is found to be higher than that of the AUC by the addition of ammonium carbonate salt in excess. This difference is more pronounced in the solution containing low uranium feed concentration. Addition of ammonium carbonate salt in excess during the precipitation of AUC maintains the optimum pH (>9.0) and CO$_3^{2-}$: UO$_2^{2+}$ required for AUC precipitation with minimum concentration of uranium in the filtrate. Also it keeps the C/U ratio >7.5 [15&16] so as to get exact greenish yellow colour of AUC product with the defined chemical formula of (NH$_4$)$_4$UO$_2$(CO$_3$)$_3$. AUC precipitate formed by the addition of (NH$_4$)$_2$CO$_3$ salt in excess settles very fast which facilitates simple and ease of filtration. This confined crystal is owning to the formation of free flowing oxide powder. 95-99.8% of
Fig. 5.1. Solubility of AUC as function of feed U concentration

Initial feed U concentration (gpl)

U in supernatant (gpl)
uranium recovery as AUC with minimum loss of uranium (250-10 mg/L) in the filtrate is achieved depending on feed uranium concentration.

Solubility data obtained in the present study reveals that solubility can be reduced when keeping the operating temperature low. In addition, the complication raised over the handling of NH₃ and CO₂ gases during the preparation of AUC product is effectively reduced by choosing (NH₄)₂CO₃ as precipitant.

5.3.2. Thermal decomposition studies

The TG/DTA plot is shown in Fig.5.2 (a). The DTA signal (Fig.5.2 (a)) shows two endothermic and one small exothermic peak. The TG weight change curve shows a major and sharp weight loss step in the temperature range 400 to 450K with a broad tail up to 620K. The weight change observed in this step is around 42% and accounts for most of the decomposition. After loss of ammonia and thermal disassembly of carbonate oxy-anion ligands, this hydrogen bonded monoclinic solid looses structural order and gets amorphosised. The product at the end of this step is an amorphous UO₃(H₂O)ₓ and its conversion to crystalline phase gives the exothermic signal at 530K.
Fig. 5.2. (a) TG/DTA of AUC (b) EGA-MS spectrum of AUC
The Fig. 5.2 (b) gives the EGA-MS spectra of the decomposition of AUC at 5K/min. Over this temperature range the EGA-MS spectra shows that the AUC decomposes by releasing NH₃, H₂O and CO₂. The CO and atomic oxygen signals are due to fragmentation of CO₂ under electron impact in QMS. Signal due to molecular oxygen was observed in this temperature range.

The small weight loss ~3% occurring at 830K matches with second CO₂ release peak and implies the decomposition of residual AUC. In addition to the product gases, there is a sharp release of oxygen suggesting a stoichiometric oxygen readjustment in the specimen. The product at this stage is UO₃.

There is a second molecular oxygen release in the temperature range of 1175 to 1250K, which is not observed in TG/DTA. This discrepancy may be due to difference in operating environment around the specimen in TG/DTA and EGA-MS. This high temperature oxygen release can be ascribed to conversion of UO₃ to U₃O₈.

In the reported literature [16] of the TG/DTA analysis of AUC, run at a heating rate of 5 deg/min, the DTA-curve indicates that an endothermic reaction with a minimum at 467K and the TGA-curve reveals a weight loss of 43.5%. The present study shows that the
weight loss is around 42% at 450K correspond to release of NH$_3$, CO$_2$ and H$_2$O, which is very much comparable with the published information. It is already reported [21] in the literature that the thermal decomposition of AUC occurs at 459K endothermically with the formation of NH$_3$, CO$_2$, UO$_3$ and water vapour accompanied with a theoretical weight loss of 45.22%. In our TGA curve shows that the thermal decomposition of AUC occurs endothermically with the formation of NH$_3$, CO$_2$, UO$_3$ and H$_2$O accompanied with total weight loss of around 45%, which is good agreement with the calculated value (45.2%) also.

It is reported in the literature [16] that the more than ten fold increase in surface area from AUC to UO$_2$, caused by the release of gases during calcination and reduction from the contents of NH$_4^+$ and CO$_3^{2-}$ that amount to more than 40% in AUC, assures good sinterability of UO$_2$ from AUC. In comparison, the fluffy nature of UO$_2$ from ADU implies high surface area and assures good sinterability, but makes additional powder treatments (e.g. preslugging and granulation) necessary for UO$_2$ from ADU to obtain reasonable pressing behavior.
5.3.3. X-Ray powder diffraction study

The monoclinic model system for AUC is taken from the literature [22] and AUC data is refined in the same system of space group C 2/c in the Le-Bail method using LHPM Software [23&24]. Rietveld Refinement plot of the AUC is shown in Fig.5.3. In this figure the calculated, observed, difference line of observed & calculated and the corresponding Bragg positions of AUC are shown. Comparative statement of cell constants is given in Table.5.2. Two theta and their d values of main peaks are also given in the Table.5.3. All data obtained for AUC of present study are in good agreement with reported values [20&21].

The XRD pattern of U₃O₈ ex- AUC is shown in Fig.5.4. Calculated, observed, difference line of observed & calculated and the corresponding Bragg positions of U₃O₈ are also shown in Fig.5.4. From the Intensity and the 2-theta values, the system is found to be orthorhombic and the space group is C 2mm. This is confirmed by the Rietveld Refinement pattern fit exactly. Comparative statement of cell constants is given in the Table 5.4. Data in Table 5.4 are resembled with reported values, which indicates that the system is very much comparable with reported values [21,25-27].
Table 5.2. Cell constants of (NH₄)₄UO₃(CO₃)₃

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present Work</th>
<th>Bachmann(21)</th>
<th>Malcic(21)</th>
<th>Graziani(21)</th>
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<tr>
<td>a(Å)</td>
<td>10.6524±0.0004</td>
<td>10.654±0.001</td>
<td>10.650±0.015</td>
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<td>b(Å)</td>
<td>9.3690±0.0003</td>
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<td>9.360±0.015</td>
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<td>c(Å)</td>
<td>12.841±0.0005</td>
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<td>β(°)</td>
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<td>V (Å³)</td>
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<td>Space Group</td>
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<td>Main Peak</td>
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<td>Reported value$^{(21)}$</td>
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<td>23.59</td>
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<td>23.5</td>
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Table 5.4. Cell constants of U₃O₈

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Present Work</th>
<th>B.O. Loopsta (^{(27)})</th>
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<tbody>
<tr>
<td>a(Å)</td>
<td>6.7184±0.0002</td>
<td>6.716(1)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>11.9590 ±0.0003</td>
<td>11.960(2)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>4.1470 ± 0.0001</td>
<td>4.147(1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>333.17</td>
<td>333.2</td>
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<td>Space Group</td>
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<td>C 2mm</td>
</tr>
<tr>
<td>Z</td>
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<td>2</td>
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</tbody>
</table>
Similarity of thermal decomposition behaviour of AUC prepared at low temperature when compared with the reported values and no evidence of phase transition in XRD patterns of AUC and its oxide show that the structural characteristics of AUC prepared at low temperature is resembling the AUC prepared using other conventional precipitants at room temperature.
REFERENCES


