Characterization of Oxidation Behavior and Phase Transformation in Uranium Compounds via Integrated Structural Thermal Analysis

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1. Introduction

Uranium oxides are key materials in the nuclear fuel cycle, and their physical and chemical properties play a crucial role in fuel performance and processing [1]. These compounds exhibit non-stoichiometric compositions and multiple oxidation states, forming a series of phases between tetravalent uranium dioxide (UO_2) and hexavalent uranium trioxide (UO_3). Intermediate phases, such as U_4O_9, U_2O_5, U_3O_7, and U_3O_8, differ in oxygen-to-uranium ratios and structural stability [2]. Hyper-stoichiometric uranium dioxide (UO_{2+x}) retains a cubic fluorite structure for $0 \leq x \leq 0.25$, yet its thermodynamic and kinetic behavior under oxidation remains of particular interest for understanding phase transformations and stability limits [3]. In addition, uranyl nitrate hexahydrate ($UO_2(NO_3)_2{\cdot}6H_2O$) serves as an important uranium(VI) precursor in nuclear material processing, and its decomposition behavior provides insight into the transition from nitrate forms to stable oxide phases [4]. Investigating the oxidation and decomposition mechanisms of these uranium compounds is essential for advancing fuel fabrication, reprocessing, and waste management strategies in the nuclear industry.

In this study, the oxidation and decomposition behaviors of uranium compounds under various temperature conditions are systematically investigated to elucidate their phase transformation mechanisms and stability characteristics.

2. Methods and Results

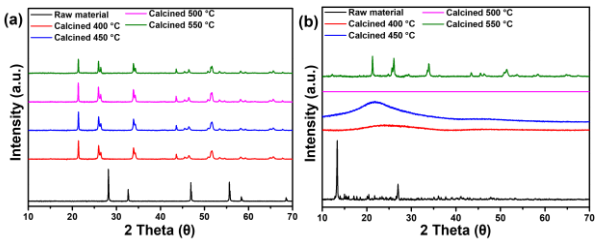

Fig. 1. The XRD patterns of (a) UO_2 and (b) $UO_2(NO_3)_2{\cdot}6H_2O$ after heat treatment at 400, 450, 500 and 550 °C in air.

For each experiment, 100 mg of UO_2 and $UO_2(NO_3)_2{\cdot}6H_2O$ were heat-treated at 400, 450, 500, and 550 °C in air with a heating rate of 10 ˚C min^{-1} and a holding time of 30 min at each target temperature.

The x-ray diffraction (XRD) patterns of the samples were measured using a MiniFlex 300/600 (Rigaku) over a 2θ range of 10–70˚ at a scan speed of 10˚ min^{-1} with a step width of 0.02˚, employing Cu Kα radiation (40 kV, 15 mA) and a D/teX Ultra2 detector.

At room temperature, the XRD pattern of UO_2 (Fig. 1a) exhibited sharp diffraction peaks consistent with crystalline UO_2 (PDF #00-067-0020). Upon heating between 400 and 550 ˚C, additional diffraction peaks

emerged, suggesting the formation of higher oxides such as α-U_3O_8 or α-UO_3. This observation is consistent with previous reports indicating that U_3O_8 is the predominant oxidation product of UO_2 under thermal treatment up to approximately 800 ˚C.

In contrast, the diffraction pattern of $UO_2(NO_3)_2 \cdot 6H_2O$ (Fig. 1b) at room temperature corresponded to crystalline uranyl nitrate hexahydrate (PDF #01-077-0121). Heating at 400–450 ˚C led to significant peak broadening, which indicated the formation of an amorphous UO_3 phase. At 500 °C, the onset of crystallization was observed with the emergence of peaks assignable to α-UO_3 and α-U_3O_8, although these phases could not be fully resolved due to peak overlap. After heating at 550 ˚C, well-defined peaks corresponding to α-UO_3 or α-U_3O_8 were detected, accompanied by a minor contribution from β-UO_3. These results are consistent with previous findings on the thermal decomposition of uranyl nitrate hydrates in air.

3. Conclusions

In this study, the oxidation and decomposition of $UO_2$and $UO_2(NO2)_2 \cdot 6H_2O$ were examined by heat treatment and XRD analysis. UO_2 retained its crystalline structure at room temperature and gradually oxidized to α-U_3O_8 in the range of 400–550 ˚C. $UO_2(NO_3)_2 \cdot 6H_2O$ showed a different behavior, where dehydration and denitration produced amorphous UO_3 at 400–450 ˚C, followed by crystallization into α-UO_3/α-U_3O_8 above 500 ˚C, with minor β-UO_3 detected at 550 ˚C. These results demonstrate the distinct oxidation and decomposition pathways of uranium oxides under controlled heating conditions.

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