Thermodynamic studies of studtite thermal decomposition pathways via amorphous intermediates UO_3, U_2O_7, and UO_4

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A B S T R A C T

The thermal decomposition of studtite $(UO_2)O_2(H_2O)_2 \cdot 2H_2O$ results in a series of intermediate X-ray amorphous materials with general composition UO_{3+x} ($x = 0, 0.5, 1$). As an extension of a structural study on U_2O_7, this work provides detailed calorimetric data on these amorphous oxygen-rich materials since their energetics and thermal stability are unknown. These were characterized in situ by thermogravimetry, and mass spectrometry. Ex situ X-ray diffraction and infrared spectroscopy characterized their chemical bonding and local structures. This detailed characterization formed the basis for obtaining formation enthalpies by high temperature oxide melt solution calorimetry. The thermodynamic data demonstrate the metastability of the amorphous UO_{3+x} materials, and explain their irreversible and spontaneous reactions to generate oxygen and form metaschoepite. Thus, formation of studtite in the nuclear fuel cycle, followed by heat treatment, can produce metastable amorphous UO_{3+x} materials that pose the risk of significant O_2 gas. Quantitative knowledge of the energy landscape of amorphous UO_{3+x} was provided for stability analysis and assessment of conditions for decomposition.

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1. Introduction

Studtite, $(UO_2)O_2(H_2O)_2 \cdot 2H_2O$, and metastudtite, $(UO_2)O_2(H_2O)_2$, form as alteration products on spent nuclear fuel (SNF) in aqueous environments [1–3]. They are important where spent fuel is altered during surface or geological storage, in nuclear accidents, and in the processing of uranium ores [1–12]. The formation of studtite in a nuclear waste repository is favorable where H_2O_2 is present under locally oxidative conditions [1,2,4,5], with the H_2O_2 generated and replenished by water radiolysis caused by high radiation dosage [13]. However, as shown by thermodynamic investigations by Kubatko et al. [4] and Guo et al. [11], both studtite and metastudtite have positive enthalpies of formation, 22.3 ± 3.9 and 15.8 ± 1.7 kJ/mol, from γ-UO_3, H_2O and O_2, respectively. This suggests that once studtite or metastudtite form, eventual decomposition may release soluble U(VI) [4,11]. Hence, understanding the decomposition pathway of studtite may help to clarify

aspects of UO_2 fuel degradation involving exposure to water. Studtite is often precipitated during production of uranium yellowcake from uranium ore processing, and decomposition of studtite or other uranium peroxides may release O_2 gas during transport and storage [14,15].

The decomposition of studtite upon heating under oxygen or argon atmospheres occurs in several steps [11,15–21]. Irreversible dehydration to metastudtite begins around 60 °C. Continued heating through 200 °C produces an X-ray amorphous material [11,18,21]. The amorphous phase can persist to 550–600 °C under heating rates of 10 °C per minute, beyond which α-$UO_{2.9}$ crystallizes, followed by U_3O_8 at higher temperature [11,17,18]. Among these intermediate decomposition products, the amorphous materials are interesting both because they appear to contain peroxide, and because their structures and reactivity with water are not fully understood [15,21]. Odoh et al. observed the reaction of amorphous uranyl-bearing material, obtained by heating studtite with water [15]: such a reaction may contribute to pressurization of drums containing yellowcake due to the generation of oxygen from the reaction [14,15].

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The amorphous nature of materials arising from the heating of studtite is challenging to characterization for structure, composition, and energetics. It has been proposed that amorphous material formed by heating studtite at 195 °C has composition U_2O_7 and contains uranyl and peroxide [15,16]. Other studies assumed this material is $UO_3 \cdot xH_2O$ [11,19,20], although the presence of water was not confirmed. In the most recent study, neutron scattering, spectroscopic measurements, and high-level computational studies demonstrated that heating studtite to 200 °C for 1 h results in a material close in composition to U_2O_7 that may consist of dimeric units of uranyl ions bridged through peroxide and oxo groups [15]. This study also found that the amorphous material continued to lose mass upon heating to higher temperatures, indicating a range of compositions.

In the present work, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) coupled with mass spectrometry (MS) have been used to study the thermal decomposition of studtite in detail. Correlating TGA and MS provides further compositional information for amorphous uranyl materials formed during heating. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to characterize uranyl and water in the materials. High temperature oxide melt solution calorimetry was employed to determine formation enthalpies of several amorphous materials with different well-characterized compositions. We also determined these enthalpies of reaction of the amorphous material with water on the basis of new and existing thermochemical data. Our results demonstrate that the reaction of amorphous uranyl materials with water that releases oxygen is exothermic in enthalpy, favorable in free energy, and spontaneous, confirming that these amorphous materials are unstable when exposed to water.

2. Experimental methods

2.1. Materials

All reagents, unless otherwise mentioned, were analytical grade and obtained from Merck KGaA Darmstadt. Studtite was synthesized from an acidic (HCl, pH ~ 3) aqueous UO_2 suspension by slowly adding (one drop per minute) a 30% (wt/wt) H_2O_2 solution to the mixture. After the desired amount had been added, the mixture was stirred for an additional 24 h at room temperature. The obtained light yellow precipitate was filtered, washed with deionized water, and dried at ambient temperature. Finally, metastudtite was obtained by dehydrating the prepared studtite at 90 °C for 48 h.

2.2. Thermal analysis

Differential thermal analysis and differential scanning calorimetry (TG-DSC) were performed simultaneously by heating the sample in a flowing argon atmosphere (40 mL/min) to 800 °C with a rate of 10 °C/min in a Netzsch 449 simultaneous thermal analyzer instrument. A mass spectrometer (Cirrus2) was connected to detect the released gases. The system was calibrated by decomposing CaC_2O_4. Acquired data were processed with the Calisto software package from AKTS. Detailed procedures have been described previously [11,22].

2.3. Infrared spectroscopy

The ATR-FTIR spectra of samples treated at 200 and 400 °C in argon, and their hydrated forms, were recorded in air from 700 to 4000 cm^{-1} employing a Bruker Vertex 70 FTIR spectrometer equipped with an ATR cell with diamond crystal.

2.4. High temperature oxide melt solution calorimetry

High temperature oxide melt solution calorimetry was conducted using a custom built Tian-Calvet twin microcalorimeter [23,24]. Powdered samples were hand pressed into small pellets (~5 mg) before heating in a furnace to the desired temperature. Subsequently, the pellets were quickly cooled and were dropped from room temperature into molten solvent (20 g of sodium molybdate ($3Na_2O \cdot 4MoO_3$)) in a Pt crucible at 702 °C. The calorimeter was calibrated using the heat content of ~5 mg α-Al_2O_3 pellets [23,24]. Oxygen gas was continuously bubbled through the melt at 5 mL/min to ensure an oxidizing environment and facilitate dissolution [25]. Flushing oxygen gas at ~50 mL/min through the calorimeter chamber assisted in maintaining a constant gas environment above the solvent [25]. Dissolution of uranium oxides and other uranium-containing compounds as U^{6+} species has been demonstrated in this solvent, and their drop solution enthalpy data were obtained previously [10,11,22,26–28]. Upon rapid and complete dissolution of the sample, the enthalpy of drop solution, ΔH_{ds}, was obtained. Finally, using appropriate thermochemical cycles (Table 2), enthalpies of formation of the amorphous materials from constituent oxides, $\Delta H_{f,ox}$ were calculated.

3. Results and discussion

Stepwise decomposition of studtite was observed during heating in the thermal analyzer: $(UO_2)O_2(H_2O)_2 \cdot 2H_2O \rightarrow (UO_2)O_2(H_2O)_2 \rightarrow$ amorphous uranyl phases $\rightarrow$ amorphous -$UO_3 \rightarrow \alpha$-$UO_{2.9} \rightarrow U_3O_8$ (Fig. 1). The mass loses are associated with release of oxygen and/or water, as shown by the MS peaks. Quenched samples from 210, 300, 400, 535, and 580 °C are labeled as sample A, B-1, B-2, C, and D, respectively. The resulting materials have different colors (Fig. 2). X-ray diffraction demonstrated that A is an incomplete decomposition product of metastudtite (Fig. 3). B-1 and B-2 were quenched after heating into the region of the TG that corresponds to a wide plateau (Fig. 1). Sample C was retrieved after heating to 535 °C and was identified as am-UO_3 by comparing TG data with calculated theoretical mass loss [11]. C is bright orange and is free of water (Fig. 2, Table 1), consistent with the previous study [11]. Samples B-1, B-2, and C are X-ray amorphous. Sample D is crystalline α-$UO_{2.9}$ [11]. Further heating leads to partial reduction of the uranium and transformation of α-$UO_{2.9}$ to U_3O_8 [11,19,20].

TGA and *in situ* MS revealed only two water peaks, associated with the decomposition of studtite and of metastudtite, both of which contain H_2O (Fig. 1), consistent with the amorphous uranyl compounds being anhydrous. Around 200 °C, the MS shows an oxygen peak accompanying decomposition of metastudtite, indicating that the initial X-ray amorphous decomposition product has less oxygen than metastudtite. The next oxygen signal in the MS was observed upon heating above 500 °C, where am-UO_3 (sample C) formed. Thus, samples B-1, B-2, and other amorphous uranyl materials formed below 500 °C are less oxygen-rich than metastudtite but more oxygen-rich than UO_3. Two small MS oxygen peaks occur from 535 to 580 °C and 610–660 °C, corresponding to the conversions am-$UO_3 \rightarrow \alpha$-$UO_{2.9}$, and α-$UO_{2.9} \rightarrow U_3O_8$, respectively.

The IR spectrum of B-2 in Fig. 4 contains strong broad peaks centered around 901 and 740 cm^{-1}, attributable to the stretching vibrations of uranyl in the amorphous uranium oxides, as reported by Sato et al. [21]. No peaks related to OH or H_2O stretching or bending modes were observed, confirming this amorphous material is free of structural water. The mass losses for forming B-1 and B-2 from studtite are 18.39 and 19.91%, respectively, indicating that these two samples have different compositions. Combining the results from TGA and IR analysis and considering charge neutrality,