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Studies on supercritical hydrothermal syntheses of uranium and lanthanide oxide particles and their reaction mechanisms

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HIGHLIGHTS

- $Ln(NO_3)_3$ and $UO_2(NO_3)_2$ compounds are converted to their oxides (LnO_2, U_3O_8, or UO_3).
- $LnCl_3$ do not form their oxide compounds.
- HNO_3 or NO_3^- species act as the oxidizing agent.

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ABSTRACT

In order to develop preparation method of raw metal oxide particles for low decontaminated MOX fuels by supercritical hydrothermal (SH) treatments, we have investigated behavior of aqueous solutions dissolving U(VI), Ln(III) (Ln: lanthanide = Ce, Pr, Nd, Sm, Tb), Cs(I), and Sr(II) nitrate or chloride compounds under SH conditions (temperature = 400–500 °C, pressure = 30–40 MPa). As a result, it was found that $Ln(NO_3)_3$ (Ln = Ce, Pr, Tb) compounds produce LnO_2, that $Ln(NO_3)_3$ (Ln = Nd, Sm) compounds are hardly converted to their oxides, and that $LnCl_3$ (Ln = Ce, Pr, Nd, Sm, Tb), $CsNO_3$, and $Sr(NO_3)_2$ do not form their oxide compounds. Furthermore, HNO_2 species were detected in the liquid phase obtained after treating HNO_3 aqueous solutions containing $Ln(NO_3)_3$ (Ln = Ce, Pr, Tb) under SH conditions, and also NO_2 and NO compounds were found to be produced by decomposition of HNO_3. From these results, it was proposed that the Ln oxide (LnO_2) particles are directly formed with oxidation of Ln(III) to Ln(IV) by HNO_3 and HNO_2 species in the SH systems. Moreover, the uranyl ions were found to form U_3O_8 and UO_3 depending on the concentration of HNO_3. From these results, it is expected that the raw metal oxide particles for low decontaminated MOX fuels are efficiently prepared by the SH method.

1. Introduction

Mixed oxide (MOX) fuels of UO_2 and PuO_2 containing several percent minor actinide (MA) and fission products (FP) (so-called low decontaminated MOX fuels) have received much attention from viewpoints of enhancement of nuclear nonproliferation, establishment of closed fuel cycle, transmutation of long-life nuclides, fabrication cost, and so on [1–6]. The performances of MOX fuels such as thermal conductivity, reactivity, and mechanical strength depend strongly on physical-chemical characteristics of MOX raw powders [7–9]. Accordingly, control of particle sizes, density, structure, and composition should be quite essential for the preparation of MOX raw powders. Typical examples of the preparation methods include not only the milling-based processes such as the Micronized Master (MIMAS) blending, the Short Binderless Route (SBR), and Optimized Co-milling (OCOM), but also the chemical processes such as the Ammonium Uranyl Plutonyl Carbonate (AUPuC) precipitation and the Microwave Heating (MH) denitration [10–12]. However, the prepared powders are not necessarily homogeneous, because of their uneven thermal distribution and reaction efficiency.

Recently, various synthesis methods of individual oxides and mixed oxides consisting of homogeneous U, Pu, and lanthanide (Ln) particles have been investigated to fabricate the MOX raw powders. Sol–gel and thermal treatment processes have realized the syntheses of U–Ce and U–Th mixed oxides, (U, Ce)O_{2+x} and (U, Th) O_{2+x} [13,14]. In particular, CeO_2 is one of the most important

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materials, because of similarity of chemical and thermodynamic properties of CeO_2 to those of PuO_2 [15,16]. Uranium oxide powders doped with Ln oxides (Ln = La, Ce, Nd, etc.) have been synthesized using sol–gel and mechanochemical activation methods [17,18]. Syntheses of $(U, Th)O_{2+x}$ and $(U, La)O_{2+x}$ have been performed by using the co-precipitation of U and Th or La through the electrochemical reduction of U(VI) to U(IV) [19]. Preparation method of U, Th, and Ln mixed oxides using crystallized precursors has been also undertaken. After metal ions are precipitated as the precursors such as carbonate, oxalate, and hydroxide compounds, the resulting precursors can be converted to metal oxides due to thermal decomposition [20–26]. Although these methods make it possible to prepare homogeneous metal oxide particles with nanometer sizes, they require two-steps including chemical treatments such as precipitation or synthesis and thermal annealing treatments. Hence, the establishment of effective one-step preparation methods, in which actinide (Ac) and Ln particles can be directly generated from solutions, are quite essential to fabricate the sophisticated MOX raw powders.

On the other hand, supercritical water (SCW, critical temperature (T_c) = 374 °C, critical pressure (P_c) = 22.1 MPa) is expected as an adequate reaction medium for synthesizing multi-component and homogeneous metal oxide particles, because SCW has unique properties such as high diffusivity, low solubility of inorganic compounds, high solubility of organic compounds, and low dielectric constant, which are different from bulk water [27]. Since the nucleation and growth rates of metal oxide particles and their solubility in SCW are controlled with the slight variation of densities, objective metal oxide particles with versatile chemical components and crystalline structures can be formed by controlling the SCW reaction conditions. Previous studies on supercritical hydrothermal (SH) syntheses of various metal oxide particles have found out that micro-scale particles are obtained under sub-critical conditions owing to slow reaction rates, and that nano-scale particles are formed under supercritical conditions due to the higher reaction rates and lower solubility compared with sub-critical conditions [28–30]. Moreover, such SH reactions have been applied to the separation and recovery of Ln(III) and heavy metal species in simulated high-level liquid wastes as their oxides [31]. We have clarified that uranyl species in aqueous and ethanol solutions dissolving $UO_2(NO_3)_2 \cdot 6H_2O$ can be easily converted to U_3O_8 and UO_2 powders by the SH treatments, respectively [32,33]. This indicates that the uranium oxides are formed with changes of oxidation states of U. Similar metal oxide formation accompanied by the change of oxidation state is also observed in the SH treatment of $Ce(NO_3)_3$, i.e., the reaction product is Ce(IV) oxide (CeO_2) [34–38]. However, the reaction mechanisms for the formation of uranium oxides and CeO_2 have not been clarified yet. In order to produce well-defined U and Ln oxide particles for MOX fuels by utilizing the advantages of SH treatment method, it is essential to characterize the reaction products obtained under SH conditions and to understand their reaction mechanisms.

In the present study, hence, we performed SH treatments of aqueous solutions containing U(VI), Ln(III) (as simulants of MA), alkali-, and alkaline earth metal species in the ranges of 400–500 °C and 30–40 MPa. Based on data on the crystalline structures, morphologies, chemical compositions of the reaction products in solid and liquid phases, we elucidated the reaction mechanisms for SH syntheses.

2. Experimental

2.1. Materials

Metal nitrate compounds, $CsNO_3$ (99.99%), $Sr(NO_3)_2$ (98.0%), $Ce(NO_3)_3 \cdot 6H_2O$ (98.0%), $Pr(NO_3)_3 \cdot 6H_2O$ (99.95%), $Nd(NO_3)_3 \cdot 6H_2O$ (99.5%), $Sm(NO_3)_3 \cdot 6H_2O$ (99.5%), $Tb(NO_3)_3 \cdot 6H_2O$ (99.95%), and Ln(III) chloride compounds, $CeCl_3 \cdot 7H_2O$ (99.95%), $PrCl_3 \cdot 7H_2O$ (99.95%), $NdCl_3 \cdot 6H_2O$ (99.5%), $SmCl_3 \cdot 6H_2O$ (99.5%), $TbCl_3 \cdot 6H_2O$ (99.95%), were purchased from Wako Chemical Ind. Ltd. and Kanto Chemical Ind. Co., Ltd. These were used without further purification. Sample solutions for the SH experiments were prepared by dissolving appropriate amounts of metal nitrate or chloride compounds into distilled water (Autostill WG220, Yamato Co. Ltd.). Sample solutions containing uranium were prepared by dissolving known amount of $UO_2(NO_3)_2 \cdot 6H_2O$ into distilled water or HNO_3 aqueous solutions of various concentrations.

2.2. Apparatus and procedure for supercritical hydrothermal syntheses

The SH syntheses were performed using a system equipped with a high-pressure and -temperature cell (volume: 5 ml, Taiatsu Glass Co. Ltd.) made of Hastelloy, which is composed of Ni(55%), Mo(18–22 %), C(0.04–0.15 %), Fe(18–22 %), and Cr [33]. Fig. 1 shows a schematic illustration of the experimental setup for synthesizing metal oxide particles by the SH method. The sample solutions were introduced into the cell through the syringe pump (ISCO Model-

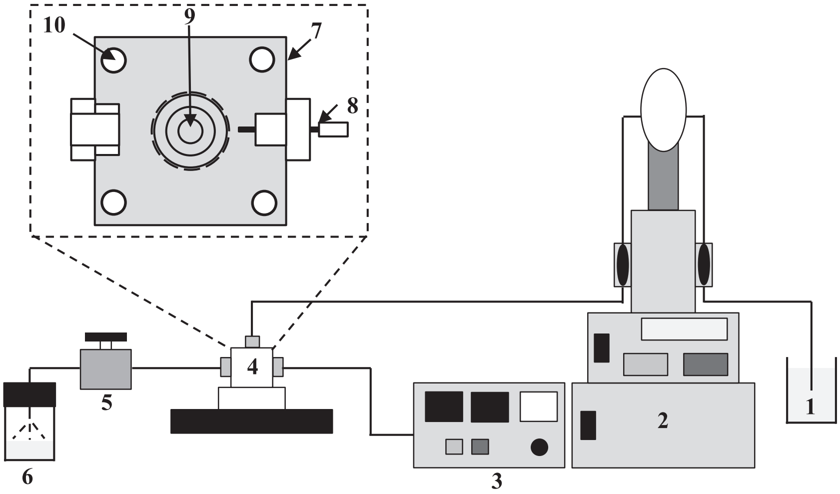

Fig. 1. Schematic illustrations of high-pressure and -temperature cell used in the present study. (1) sample solutions, (2) syringe pump, (3) temperature controller, (4) high-pressure cell, (5) leak valve, (6) collected products, (7) cell body, (8) thermocouple, (9) pipe for charging water, (10) electric heating rods.