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Sulfurization of rare-earth oxides with CS_2

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Abstract

In the scheme of spent fuel reprocessing by using sulfides, selective sulfurization of rare-earths in the fuel is considered followed by either magnetic separation or selective leaching of rare-earth sulfides from uranium oxides such as UO_2. In this paper, sulfurization behavior of rare-earth oxides was investigated by XRD and TG methods in the presence of CS_2. From the results of thermogravimetric study the sulfurization of europium proceeds as follows; sulfurization from Eu_2O_3 to Eu_3S_4 occurs at ca. 400 °C, then the Eu_3S_4 decomposes to EuS via non-stoichiometric sulfides at temperatures between 450 and 700 °C. From the results of thermogravimetry for Nd_2O_3, it was found that the weight curve showed monotonic increase from ca. 600 to 1000 °C. At 1000 °C, the value of weight increase was close to that for the formation of Nd_2S_3 from Nd_2O_3. The XRD result of the 1000 °C product showed a formation of a single phase of Nd_2S_3 which is compared with the thermogravimetric result as well as our previous results. The selective sulfurization of rare-earths in the mixture of rare-earth and uranium oxides was discussed by both experimental results and thermodynamical consideration.

Keywords: Europium; Neodymium; Sulfurization; Carbon disulfide; Thermogravimetry

1. Introduction

In the scheme of the reprocessing of spent nuclear fuel by sulfide process, selective sulfurization of rare-earths in the fuel is considered followed by the separation of $(U,Pu)O_2$ from selectively sulfurized rare-earths by either magnetic separation or selective leaching of rare-earth sulfides from uranium oxides such as UO_2 [1]. In the sulfurization step, sulfurization behavior of rare-earth oxides at low temperature is needed for understanding the reaction scheme. In our previous study for the sulfurization of $Nd_2(SO_4)_3$ with CS_2 [2,3], the sulfate changed to Nd_2S_3 via $Nd_2O_2SO_4$, Nd_2O_2S and NdS_2. Namely, the rare-earth sulfides could be formed from sulfate without forming the oxide. Some papers on the formation of rare-earth sulfides were reported but they did not discuss the sulfurization scheme at relatively low temperature [4–6]. On the other hand, it was reported that uranium sulfides could be formed from sulfate [7]. But, the UO_2 phase also appeared during the sulfurization of uranyl sulfate UO_2SO_4 by the use of CS_2 due to the wide area of UO_2 than rare-earth oxides, Ln_2O_3. These reaction passes were well-analyzed by both experimental and thermodynamical results.

In this paper, sulfurization behavior of rare-earth oxides was investigated by XRD and TG methods in the presence of CS_2.

2. Experimental

2.1. Sample preparation

Both Nd_2O_3 and Eu_2O_3 powders were obtained from Nippon Yttorium Co. Ltd., and used as received for raw samples. Then raw samples were heated in air at an intended temperature and the products were used as heat-treated samples. Analytical grade CS_2 with a boiling point of 46–47 °C and maximum water content of 0.02% (Wako Pure Chemicals Co. Ltd.) and nitrogen gas of 99.99% purity (Nippon Sanso Co. Ltd.) were used as received.

2.2. Thermogravimetric analysis

The apparatus for the thermogravimetric experiments was reported in elsewhere [4]. TG profiles were obtained in a vertical resistance tube furnace equipped with a quartz spring. A quartz basket containing the weighed sample, approximately 100 mg, was suspended from quartz spring at the center of the uniform (±1 °C) temperature zone of the furnace. The sample was heated at constant rates from room temperature to 1000 °C. Before heating, the reaction tube was evacuated to approximately 100 Pa for 30 min and then refilled with N_2 up to ambient pressure. After that, CS_2 and N_2 gas mixture was introduced. The change in length of the quartz spring caused by the weight change during heating was measured by a level meter (Mitsutoyo) with an accuracy of 0.001 mm. The change in length was calibrated by using a standard weight. The sensitivity of the spring was 7.04 mg/mm.

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2.3. *Sulfurization*

The sulfurization experiments were carried out at a heating rate of 1 °C min^{-1} with a CS_2/N_2 gas flow rate of 5/50 ml min^{-1}. The N_2 gas flow rate was measured using a digital mass flow meter (Kofloc Model DPM-2A).

2.4. *X-ray diffraction analysis*

For the phase analysis of the products, the X-ray powder diffraction was carried out with a Rigaku Type RAD-IC diffractometer using Cu Kα radiation (40 kV, 20 mA) monochromatized by curved pyrolytic graphite.

3. Results and discussions

3.1. *Thermogravimetry of Eu_2O_3*

Fig. 1 shows the thermogravimetric curves for the reaction of raw Eu_2O_3 with CS_2 with different heating rates of 2 and 5 °C min^{-1}. Since the final product at 1000 °C after the thermogravimetric measurement was found to be EuS, the TG curves were recalculated according to weight loss of the product at the end point of the curve. It is seen that the starting material, raw Eu_2O_3 could be the mixture of oxide and hydroxide. First, the weight decreases to oxysulfide, then it increase to the level of formation of sesqui sulfide, Eu_2S_3 at ca. 500 °C followed by the decomposition to EuS. The similar results were obtained for the different heating rate in these TG results.

Since the raw E_2O_3 was found to contain the other phase, the sample was heated in air at 600 °C and identified as the mono phase of Eu_2O_3 by XRD. The TG curves of the reaction of heat-treated Eu_2O_3 with CS_2 are given in Fig. 2. At a slow heating rate (2 °C min^{-1}), the weight sharply increased at ca. 400 °C to the theoretical weight increase level of Eu_3S_4 from Eu_2O_3. Then the weight decreased to the level of $EuS_{1.23}$ which corresponds to Eu_2S_3 by the decomposition. At 700 °C, the TG curve became flat suggesting that the EuS was formed by the decomposition and it was stable up to 1000 °C. In the case of 5 °C min^{-1}, similar TG curve to the 2 °C min^{-1} one was obtained but the formation of Eu_3S_4 was not observed. From the above results, Eu_2O_3 starts to react with CS_2 at $T \geq 400$ °C, and eventually $Eu(OH)_3$ present as impurity in the raw sample may react with CS_2 at lower temperature. This result was also compared with our previous result that TiO_2 powder contaminated with $Ti(OH)_4$ reacts with CS_2 at temperature lower than 500 °C [8].

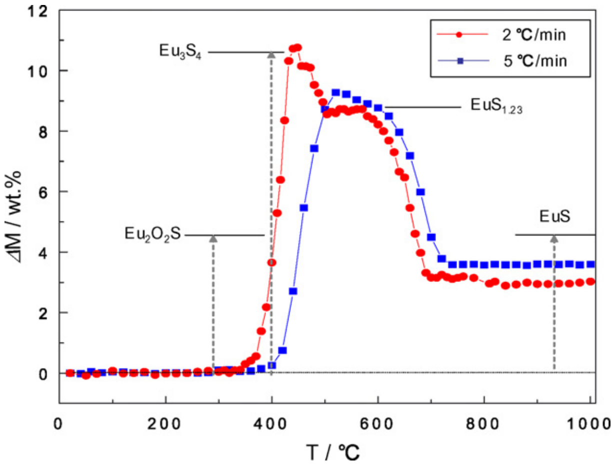

Fig. 2. TG curves of the reaction of heat-treated Eu_2O_3 with CS_2.

3.2. *Thermogravimetry of Nd_2O_3*

Fig. 3 shows the thermogravimetric curve for the reaction of raw Nd_2O_3 with CS_2 with different heating rates of 2 and 5 °C min^{-1}. Since the final product at 1000 °C after the thermogravimetry was found to be Nd_2S_3, the TG curves were recalculated according to weight loss of the product at the end point of the curve. It is seen that the starting material, raw Nd_2O_3, could also be the mixture of oxide and hydroxide. First, the weight decrease to oxysulfide appeared. Then the TG curve showed increase and decrease up to the level of formation of sesqui sulfide, Nd_2S_3 at ca. 1000 °C. The similar results were obtained for the different heating rate of 5 °C min^{-1} in this TG

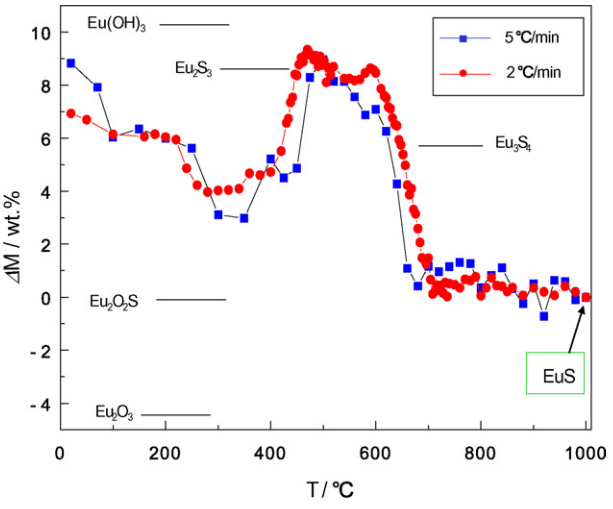

Fig. 1. TG curves of the reaction of raw Eu_2O_3 with CS_2.

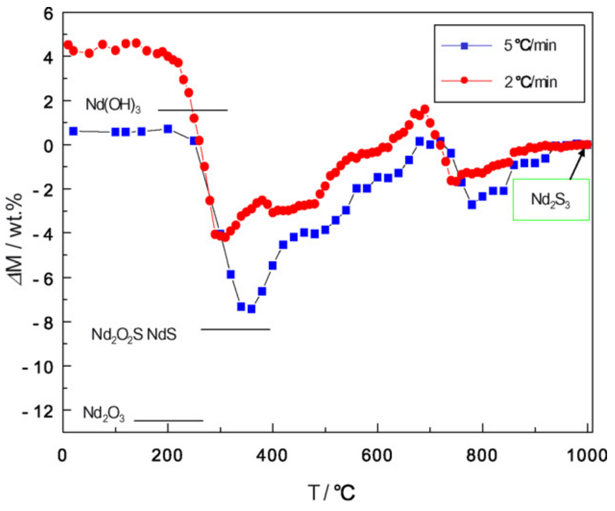

Fig. 3. TG curves of the reaction of raw Nd_2O_3 with CS_2.

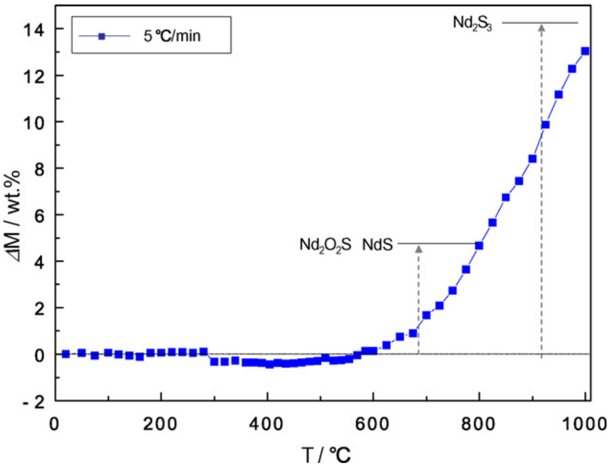

Fig. 4. TG curves of the reaction of heat-treated Nd_2O_3 with CS_2.

result. According to our previous report [2], the formation and decomposition of NdS_2 occurred showing the weight increase and decrease in TG curve. Actually, the formation of NdS_2 was observed between 400 and 600 °C with a heating rate of 1 °C min^{-1}.

As observed in the case of raw E_2O_3, the raw Nd_2O_3 was found to contain the hydroxide. The sample was heated in air at 600 °C and identified as the mono phase of Nd_2O_3 by XRD. The TG curve of the reaction of heat-treated Nd_2O_3 with CS_2 at 5 °C min^{-1} is given in Fig. 4. It is seen that no weight change up to 600 °C was observed and the weight monotonically increased from 600 to 1000 °C to the theoretical weight increase level of Nd_2S_3 from Nd_2O_3. Then the weight decreased to the level of $EuS_{1.23}$ which corresponds to Eu_2S_3 by the decomposition.

From the above results, the raw Ln_2O_3 could react with CS_2 even at low temperature due to the presence of hydroxide. On the other hand, UO_2 was found to react with CS_2 at temperature higher than 500 °C. These suggest the possibility of low temperature selective sulfurization of Ln_2O_3 by CS_2 in the presence of UO_2.

3.3. *Sulfurization of raw Ln_2O_3 at low temperatures*

Sulfurization of raw Ln_2O_3 samples by CS_2 at low temperatures was examined and the product was analyzed by XRD method. Fig. 5 shows the XRD patterns of the product obtained by sulfurization using CS_2 at 300, 400 and 500 °C for 1 h. Even at 300 °C, it was the mixture of Eu_3S_4 and Eu_2O_3. Then it became the mono phase of Eu_3S_4 at 400 °C followed by the formation of the mixture of Eu_3S_4 and EuS. In the case of raw Nd_2O_3, similar results were obtained as shown in Fig. 6; the mixture of Nd_2O_2S and unknown phases at 300 °C, then the mixture of Nd_2O_2S, unknown and NdS_2 at 400 °C, finally, the mixture of Nd_2O_2S and NdS_2 at 500 °C. The unknown phase should be the oxide form since it was disappeared with increasing temperature. Since uranium oxides, such as UO_2 and U_3O_8 is sulfurized with CS_2 at around 500 °C forming UOS, the selective sulfurization of rare-earths from the mixture of UO_2 and FP elements could be available.

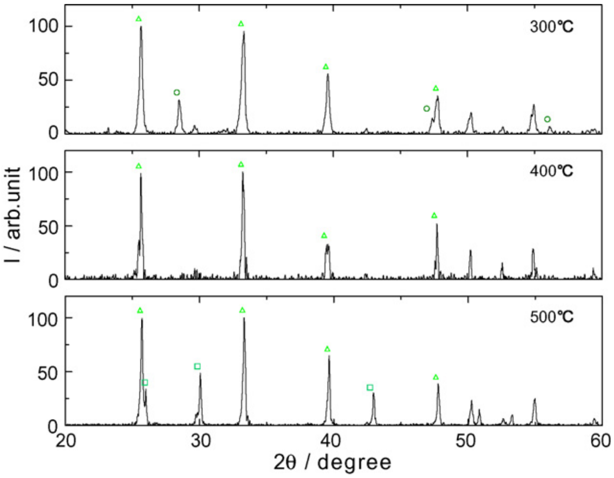

Fig. 5. XRD patterns of the products obtained by sulfurization of raw Eu_2O_3 using CS_2 at 300, 400 and 500 °C for 1 h: (◯) Eu_2O_3(JCPDS34-392); (△) Eu_3S_4(JCPDS32-382); (□) EuS(JCPDS26-1419).

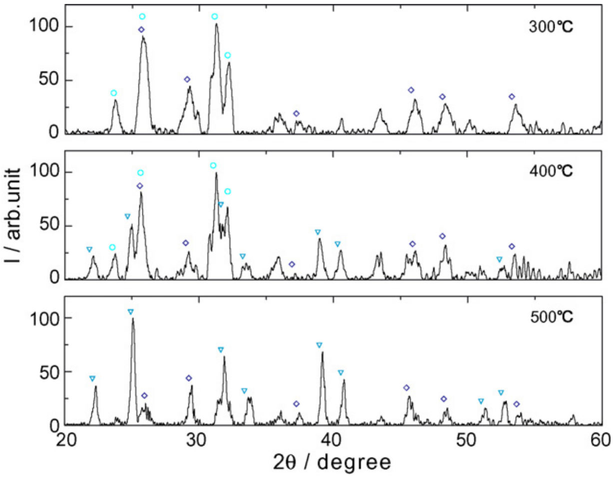

Fig. 6. XRD patterns of the products obtained by sulfurization of raw Nd_2O_3 using CS_2 at 300, 400 and 500 °C for 1 h: (◇) Nd_2O_2S(JCPDS27-321); (▽) NdS_2(JCPDS49-1602); (◯) unknown peaks.

4. Conclusion

For the selective sulfurization of rare-earth oxides from spent nuclear fuel by sulfide process, sulfurization behavior of rare-earth oxides with CS_2 was investigated by XRD and TG methods. The obtained results are as follows:

1) Hydroxide contained in raw Ln_2O_3 enabled the sulfurization by CS_2 even at low temperatures such as 300, 400 and 500 °C.
2) Sulfurization of Eu_2O_3 to EuS proceeds via formation of Eu_2O_2S and Eu_3S_4.
3) Nd_2O_3 was sulfurized to Nd_2S_3 via formation of Nd_2O_2S and NdS_2.

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