

Decontamination of Uranium and Antimony from Spent Catalyst for Acrylonitrile Synthesis by Utilizing Phase Segregation of Borosilicate Glass

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ABSTRACT

Several decades ago, catalysts containing depleted uranium (U) and antimony (Sb) as a composite oxide were used for organic synthesis of acrylonitrile from propylene, ammonia and air, and the spent catalysts have been stored securely as uranium waste in drums of 200 liters in volume in Japan. Since these are categorized as radioactive waste containing naturally occurring radioactive materials, a safe and economical disposal should be performed in the future. Unfortunately, however, uranium isotopes have long half lives to decay, and the chemical and radioactive toxicity of several daughter nuclides are too significant to allow direct disposal in a shallow land burial site. We should take account of the chemical toxicity of antimony, too. We are proposing a method of decontaminating uranium and antimony and vitrifying the spent catalysts into a glass matrix by making use of the SiO₂ supports of the catalyst. The goals of our study are recovering uranium and antimony at high yields from the sub-micron pores of the SiO₂ supports of the catalysts, and conditioning into a proper waste form for shallow land disposal. In order to achieve these goals, treatment of the catalysts utilizing the phase segregation phenomena of borosilicate glass was proposed and experimentally tested in a laboratory scale using a real specimen of the catalyst. The recovery yields achieved by the experiments were greater than 99.30% for uranium and 97.0% for antimony, and the concentrations of uranium and antimony leached with de-ionized water for the final vitrified solids were below the detection limits of an inductively coupled plasma spectrometer, 0.1 mg dm⁻³.

INTRODUCTION

At one time the preferred catalyst for propylene ammoxidation to synthesize acrylonitrile from propylene, ammonia and air was a uranium-antimony oxide composition whose active phase was USb₃O₁₀.¹⁻³⁾ In the 1970's, the catalysts containing depleted uranium (U) and antimony (Sb) as the composite oxide,

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USb_3O_{10} , were used in Japan, and the spent catalysts have been stored securely as uranium waste in drums of 200 liters in volume. The number of the drums is around 10,500. Since these are categorized as radioactive waste containing naturally occurring radioactive materials, a proper disposal should be performed in the future. Unfortunately, however, uranium isotopes have long half lives to decay, and the chemical toxicity of antimony and the radioactive toxicity of several daughter nuclides from uranium may be too significant to allow direct disposal in a shallow land burial site. The best way to dispose of the spent catalyst in a shallow land site rationally is to follow the treatment of decontaminating both uranium and antimony. On the other hand, since the catalytic particles of the composite oxide are deposited in the tiny submicron cavities of the SiO_2 support, it is difficult to dissolve the particles by using an aqueous solution of mineral acid and extract uranium and antimony effectively. This is because water hardly enters the pores of submicron diameter due to its high surface tension and viscosity, and metallic species are stabilized by forming a composite oxide. This means the most usual treatment of aqueous dissolution and washing would not be applicable in this case. Recently, the authors have studied segregation of borosilicate glass, which was originally studied for HLW vitrification through thermal treatment into SiO_2 -rich and B_2O_3 -rich phases⁴⁻⁵⁾. During the process of the segregation, almost all of the metallic species contained in the borosilicate glass matrix will migrate and be enriched into the B_2O_3 -rich phase, which can be easily dissolved with aqueous mineral acid solutions. Therefore, it is highly expected that both uranium and antimony can be recovered by acid dissolution following the preparation and segregation of borosilicate glass matrix from the catalyst. In this case, a homogeneous borosilicate glass matrix including uranium and antimony is easily formed by adding only reagents of B_2O_3 and Na_3CO_2 , because the catalyst support is made of SiO_2 . Additionally the residue of the glass matrix is silica glass with low leachability and high chemical durability. The objectives of this technical paper are to show 1) the characteristics of the catalyst containing USb_3O_{10} on porous SiO_2 beads from the standpoint of waste treatment, the content of uranium and antimony, the leachability of uranium and antimony with aqueous acid solutions, and 2) the effectiveness of our proposed method of waste treatment in a laboratory scale, especially in the removing yields of uranium and antimony as well as the leaching rates of uranium and antimony from the final vitrified waste. Firstly, we prepared a composite oxide of U and Sb, USb_3O_{10} in bulk powder, and prepared a simulated catalyst by impregnating it on porous silica beads. In order to minimize the amount of uranium waste in our laboratory, we prepared $NdSbO_4$ as a simulated material for USb_3O_{10} , where U(V) is replaced by Nd(III) in the composite oxide with antimony. A real spent catalyst containing USb_3O_{10} was obtained from Three R Corporation, Japan and tested for the proposed method in the current study, too.

EXPERIMENTAL

Preparation of a composite oxide of U and Sb, USb_3O_{10}

A mixed nitrate solution containing uranium nitrate, which was prepared by dissolution of uranium

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nitrate hexahydrate in 70% HNO₃ (ACS reagent grade, Sigma-Aldrich Japan, Japan), and antimony nitrate, which was prepared by dissolving antimony oxide, Sb₂O₃, purchased from Wako Pure Chemicals Industries Ltd., Japan, in 70% HNO₃ (ibid.) was prepared and precipitated by adding 28% ammonium hydroxide of reagent grade (Wako Pure Chemical Industries Ltd., Japan). The concentrations of uranium and antimony in the acidic solution before the neutralization procedure were 0.0150 mol dm⁻³ and 0.0272 mol dm⁻³ respectively, which were determined by using an inductively coupled plasma atomic absorption spectrometer (ICP-AES) (SHIMAZDU ICPE9000). The ammonium nitrate and any other soluble salts were removed by filtration of the resulting slurry. Since it was reported that a catalytically active phase will appear and develop through heat treatment¹⁾, we kept the precipitates in an alumina crucible at 927 C for 30 hours in an electrical furnace (HPM-2, As One, Japan). During this heat treatment the phases of antimony oxides evaporated and were removed to a gaseous phase. By X-ray diffraction using an XRD device (Mini Flex, Rigaku Corp., Japan), we confirmed that the prepared powder was USb₃O₁₀.

Preparation of a composite oxide of Nd and Sb, NdSbO₄

A composite oxide of neodymium and antimony was prepared by a manner the same as that described in the previous subsection, but using Nd(NO₃)₃ for UO₂(NO₃)₂. X-ray diffraction of the prepared powder was performed.

Preparation of a simulated catalyst supporting particles of NdSbO₄ on SiO₂ support

Porous silica beads with pores of 10 nm in average diameter (Unibeads 3S, GL Science Inc., Japan) were added in the slurry of the hydrates of uranium or neodymium and antimony, which were prepared by the method described in the preceding subsections in EXPERIMENTAL. The same thermal treatment described in the subsection was applied to finish the composite oxides on the SiO₂ support.

Acid dissolution of USb₃O₁₀ and NdSbO₄

Acid leaching tests were performed for the prepared specimens of USb₃O₁₀ and NdSbO₄, and simulated catalysts supported on SiO₂ beads, as well as the real uranium catalyst for propylene ammoxidation to synthesize acrylonitrile. For the leaching tests, several milligrams of each specimen were placed in a container of 10 cm³ in volume made of tetrafluoroethylene with a 5 cm³ solution of 3 normal nitric acid, and was kept at 120 C for 6 hours. Elemental concentrations in the aqueous solution were determined with an ICP-AES (SHIMAZDU ICPE9000), and elemental leaching fractions were evaluated.

Analysis of elemental content for specimens

Alkali fusing with sodium carbonate (Wako Pure Chemical Industries Ltd., Japan, purity >99.5%) and boron oxide (Aldrich Japan, purity > 99.98%) was employed as a pretreatment to determine elemental contents for the specimens prepared in this study and the real spent catalyst. The fused chemicals were prepared and kept in a platinum crucible and dissolved with 5.0 normal hydrochloric

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acid into an aqueous solution for measurement with using an ICP-AES (SHIMAZDU ICPE9000).

Preparation of borosilicate glass from the simulated and real spent catalyst, phase segregation through heat treatment, and acid dissolution of the segregated samples

The preparation of a borosilicate glass matrix from the specimens we prepared and segregation through heat treatment were performed in a manner the same as that described in previously published papers.⁴⁻⁵⁾ The method of acid dissolution was also same as that described in the previous publications⁴⁻⁵⁾ and in the subsection of EXPERIMENTAL 4). A 5 g aliquot of each specimen was mixed with NaCO₃ and B₂O₃ in a platinum crucible, fused at 1400 C, and quenched on a metal plate of stainless steel at ambient temperature to form a borosilicate glass matrix. After forming a homogeneous glass matrix, the glass was heated and kept at 700 C for 12 hours so as to make the glass separate into two phases.

Measurement of leaching rates for the residual glass

The residual of glass materials after acid leaching was pulverized into sizes of 0.045 to 0.100 micrometers with a ball-mill (Pulverisette 7, FRITSCH Co. Ltd., Japan,) and leached with deionized water of 50 cm³ in a container of tetrafluoroethylen for 24 hours. The elemental concentrations of uranium and antimony in the aqueous solution were determined with an ICP-AES (SHIMAZDU ICPE9000E), and elemental leaching rates were evaluated.

RESULTS AND DISCUSSION

1) Preparation of composite oxides of uranium or neodymium with antimony

A typical results of X-ray diffraction analysis for the prepared oxide containing uranium and antimony is illustrated in Fig. 1. The pattern resulting from the prepared specimen agrees well with the referenced data, so the major constituent in the prepared specimen was confirmed as USb₃O₁₀. Similarly, the prepared specimen containing neodymium was confirmed to be Nd SbO₄, as is shown in Fig. 2.

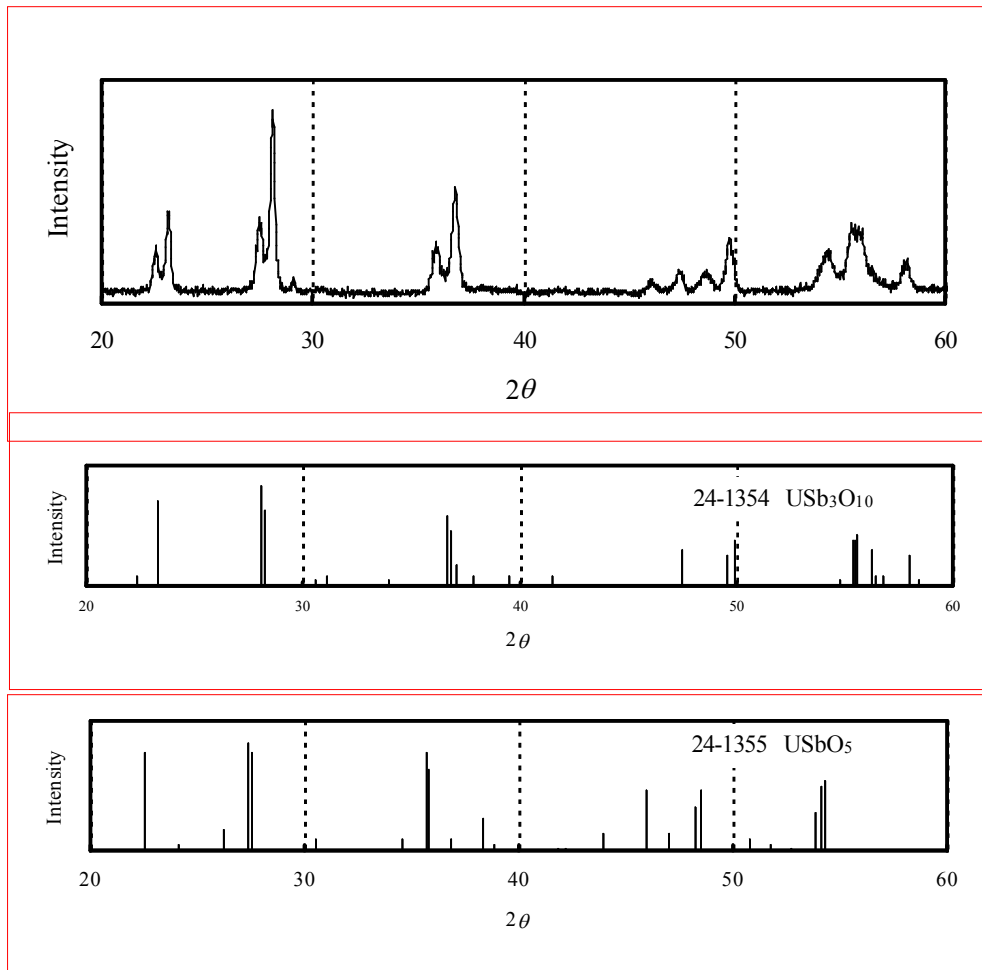


Fig. 1. An XRD pattern for the prepared specimen of a composite oxide containing uranium and antimony compared with a referenced one for $\text{USb}_3\text{O}_{10}$.

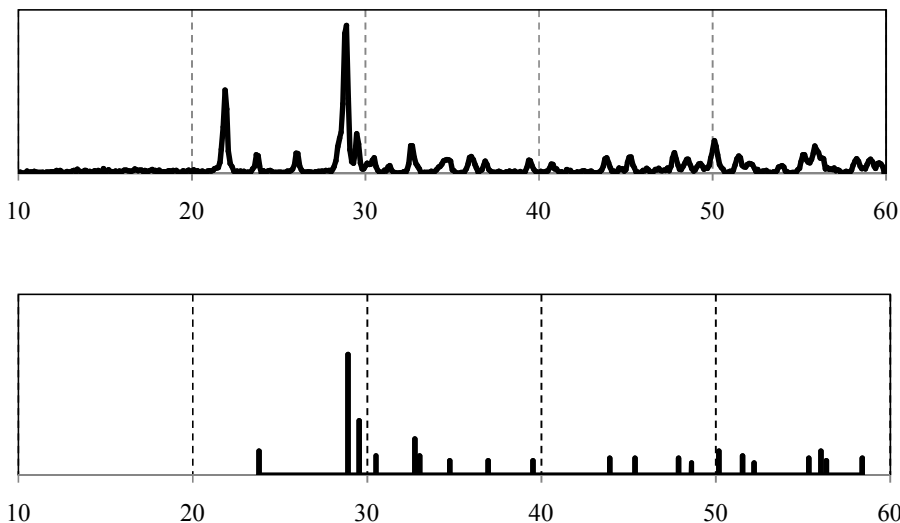


Fig. 2. An XRD pattern for the prepared specimen of a composite oxide containing neodymium and antimony compared with a referenced one for NdSbO₄.

2) Elemental contents of the prepared specimen and the real specimen

The analytically obtained elemental contents of the specimens are shown in Table I.

Table I. Elemental contents of the prepared specimens and the real spent catalyst

Specimen	#1	#2	#3	#4	#5
Element	(as powder)	(on SiO ₂ support)	(as powder)	(on SiO ₂ support)	(real sample)
U, %	39.3	12.1	--	--	15.4
Nd, %	--	--	25.7	13.7	--
Sb, %	35.7	20.6	59.3	31.5	33.8
Si, %	--	11.8	--	19.7	19.6

These data were used for calculation of fractions recovered by the proposed method or dissolved in nitric acid solutions.

3) Acid dissolution of prepared specimens

The dissolution test results are shown in Table II. As a result of the dissolution experiment using 3 mol dm⁻³ HNO₃, only 1% of the composite oxide was dissolved in aqueous solution, which was determined by an ICP-AES, whereas chemical reagents of Nd₂O₃ and U₃O₈ readily dissolved in nitric acid of 3 mol dm⁻³. The dissolution fraction of Sb₂O₃ in the same solution was 3.3% in the current

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study, which is in the same order of magnitude as the dissolution fraction observed for uranium in the composite oxide. This is a very important finding from the standpoint of waste management, and is a reasonable result from the fact that in a composite oxide, a metal is sometimes highly stabilized in a lattice of a composite oxide rather than in a single metal oxide. In addition to the fact that catalytic particles of a composite oxide are deposited in tiny pores of SiO₂, the stability of the composite oxide containing uranium and antimony makes it very difficult to dissolve in an aqueous acid solution. This is the reason why we need an alternative technique rather than the direct acid dissolution of catalytic particles on SiO₂ support.

Table II. Results of acid dissolution tests for specimens.

Specimen	#1	#2	#3	#4	#5
Dissolved fractions	(as powder)	(on SiO ₂ support)	(as powder)	(on SiO ₂ support)	(real sample)
U,%	1.0±0.2	0.7±0.3	--	--	1.2±0.1
Nd,%	--	--	39.8±0.2	31.9±0.2	--
Sb,%	0.52±0.02	4.0±0.1	1.5±0.2	3.7±0.2	1.1±0.1
Si,%	--	1.0±0.2	--	--	1.6±0.1

4) Vitrification of the specimen with NaCO₃ and B₂O₃, and segregation

Figures 3 and 4 respectively show images of prepared glass containing spent catalyst and segregated glass after heat treatment for 8 hours.

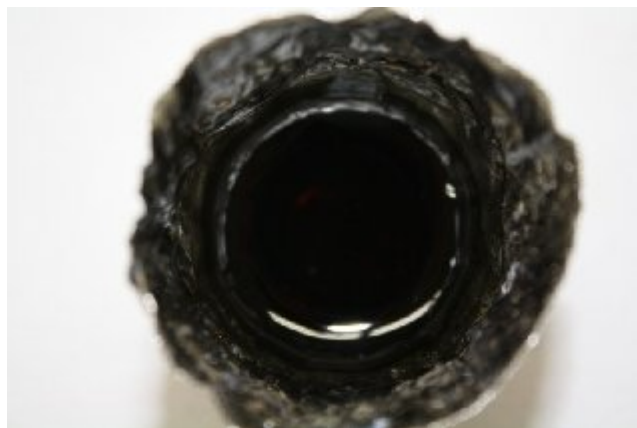


Fig. 3 Photograph of borosilicate glass matrix containing the spent catalyst formed in a platinum crucible



Fig. 4 Photograph of a phase segregated glass after heat treatment

5) Recovery fractions of uranium and antimony by acid leaching from the phase segregated glass

The total recovery fractions of uranium and antimony in this study are shown in Table III.

Table III. Total recovery fractions of uranium and antimony

	U content, mol kg ⁻¹	Sb content, mol kg ⁻¹
Spent catalyst (a)	6.49×10^{-1}	4.37×10^0
Residual glass (b)	4.55×10^{-3}	1.34×10^{-1}
Recovery fraction*, %	99.3	97.0

* Calculated as $1 - (b/a)$.

These results show that by applying the proposed method we can reduce the specific radioactivity of the spent catalyst from 2.7×10^4 Bqg⁻¹ to 1.9×10^2 Bqg⁻¹, which may meet the level allowable for a pit-type disposal site for uranium waste in Japan.

6) Leaching rate for the residual of the phase segregated glass

The concentrations of uranium and antimony were determined as below the detection limits (0.1 mg dm⁻³ for uranium and antimony) using an ICP-AES, which equivalently means less than 0.2 gm⁻² d⁻¹ in leaching rate. Since the current and tentatively allowed concentrations of uranium and antimony in drinking water in Japan are 0.002 mg dm⁻³ for both metals, further accumulation of data from leaching tests is necessary.

CONCLUSION

A novel decontamination method of uranium and antimony using the phase segregation of borosilicate glass has been proposed for spent catalysts containing UO_2 , which were once used for the organic synthesis of acrylonitrile from propylene, ammonia and air. The removal yields of this method were

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99.3% and 97.0% for uranium and antimony, respectively. The experimental results were obtained by using a real specimen in a laboratory-scale, and the concentrations of uranium and antimony leached with de-ionized water for the final vitrified solids were below the detection limits of an inductively coupled plasma spectrometer, 0.1 mg dm^{-3} .

References

1. J.L. Callahan, US Patent 3,198,750 (1965).
2. K. Grasselli and J. L. Callahan, Journal of catalysis, 14, 356-357 (1969).
3. J.B. Nagy, S. Maroie, H. Collette, A. Michel, Surface Science 163, L693-L701 (1985).
4. Y. Enokida, K. Sawada, and K. Uruga, The Proceedings of the International High Level Radioactive Waste Management Conference, CD-ROM (2008).
5. K. Uruga, K. Doka, K. Sawada, Y. Enokida, I. Yamamoto, Journal of Nuclear Science and Technol., 45, 9, 1-10 (2008).