Chlorination of antimony and its volatilization treatment of waste antimony-uranium composite oxide catalyst

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Summary. For the waste antimony-uranium composite oxide catalyst, the chlorination of antimony and its volatilization treatment were proposed, and evaluated using hydrogen chloride gas at 873–1173 K. During the treatment, the weight loss of the composite oxide sample, which resulted from the volatilization of antimony, was confirmed. An X-ray diffraction analysis showed that uranium oxide, U_3O_8 , was formed during the reaction. After the treatment at 1173 K for 1 h, almost all the uranium contained in the waste catalyst was dissolved by a 3 M nitric acid solution at 353 K within 10 min, although that of the non-treated catalyst was less than 0.1%. It was found that the chlorination and volatilization treatment was effective to separate antimony from the composite oxide catalyst and change uranium into its removable form.

1. Introduction

In the 1960s, an antimony-uranium composite oxide catalyst was created by a team who developed the famous acrylonitrile synthesis process, the Sohio Process, in the USA [1–4]. The catalyst was a composite oxide of antimony and uranium supported on porous silica beads. The contents of the antimony and uranium in the catalyst were approximately 30 and 15 wt %, respectively. Several Japanese chemical companies employed the catalyst to synthesize acrylonitrile until the 1980s. They then changed the catalyst to the less hazardous one, such as a molybdenum-bismuth-iron composite oxide, *etc.* [5–7], and they stored the catalyst waste without any treatment. In Japan today, 200 tons of metallic uranium are estimated as stored waste by several companies due to the strict management under Japanese legislation.

For the removal of uranium from the waste catalyst, the acid leaching of the catalyst seemed to be effective since it is widely used in many refining processes [8–10]. Prior to the present study, the catalyst dissolution in nitric acid and hydrochloric acid was tried. However, it was not dissolved. Uranium oxide seemed to remain undissolved by forming a composite oxide with antimony oxide. If antimony was separated from the catalyst destroying the composite oxide,

uranium could be more easily removed than from the raw catalyst waste. In order to separate the antimony, we proposed the chlorination and volatilization treatment of the catalyst. It is known that antimony (III) chloride has the relatively low boiling point at 493 K [11].

In this study, the feasibility of the proposed treatment was confirmed using an antimony-uranium composite oxide bulk sample, a simulated catalyst sample of the composite oxide supported on silica beads, and a real waste catalyst sample. The samples were treated with hydrogen chloride gas employed as the chlorination reactant at 837–1173 K, and then they underwent to chemical analyses and a leaching test with 3 mol dm⁻³ (M) nitric acid.

2. Experimental

2.1 Materials

The preparation of the sample was based on Grasselli's paper [3]. The antimony-uranium composite oxide bulk sample was prepared by combining 0.635 g Sb_2O_3 (Wako Pure Chemical Ind., Ltd., Japan), a 50 cm³ $\text{UO}_2(\text{NO}_3)_2$ aqueous solution with the uranium content of 11.4 g dm⁻³, and 110 cm³ of 70% HNO_3 (Wako Pure Chemical Ind., Ltd., Japan) for 1 h. The solution was brought to a pH of 8 by addition of 28% HN_4OH (Wako Pure Chemical Ind., Ltd., Japan), filtered, dried in a muffle furnace (KDF S-80, Denken Co. Ltd., Japan) at 393 K for 2 h, heated at 700 K for 3 h and then at 1200 K for 30 h. For the simulated catalyst sample, 0.317 g Sb_2O_3 , 25 cm³ of the $\text{UO}_2(\text{NO}_3)_2$ aqueous solution and 55 cm³ of 70% HNO_3 were mixed for 1 h. In the solution, porous silica beads whose particle diameter ranged from 0.15–0.18 mm (Unibeads 3S, GL Science, Inc., Japan) were added and well-mixed. The beads had pores of 10 nm in mean diameter. The pH of the solution was adjusted to 8 with 28% HN_4OH . The resulting slurry was filtered, dried at 393 K for 2 h, heated at 700 K for 3 h, and then at 1200 K for 30 h. The product was sieved using sieves with the mesh sizes of 0.125 and 0.212 mm. The real waste sample was obtained from the 3R Corporation, Japan.

Fig. 1 shows XRD patterns of the three samples employed in this study along with comparison to the Powder Diffraction Data of the composite oxides of uranium and antimony. In the XRD pattern of the real waste sample, peaks of $\text{USb}_3\text{O}_{10}$ were confirmed, while those of $\text{USb}_3\text{O}_{10}$ and

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Fig. 1. XRD patterns of samples: (a) composite oxide, (b) simulated catalyst, and (c) waste catalyst.

Table 1. Elemental contents in samples.

Sample	U, wt%	Sb, wt%	Si, wt%
Composite oxide	39	36	—
Simulated catalyst	12	12	21
Waste catalyst	13	30	15

USbO_5 existed in the patterns of the composite oxide sample and the simulated catalyst sample.

Table 1 shows the elemental contents in the samples. The contents were obtained by measuring the element concentration in the solution by inductively-coupled plasma atomic emission spectrometry (ICP-AES) (ICPE-9000, Shimadzu, Japan) following the dissolution of the sample by alkali fusion.

2.2 Chlorination procedure

Fig. 2 illustrates the experimental apparatus. Approximately 30 mg of each sample was placed in a platinum sample cell whose diameter was 1.5 cm and volume was 0.7 cm^3 . The cell was hung in a quartz tube reactor placed in an electric furnace (ARF 30 K, Asahi Rika Seisakusho, Japan). After purging the air inside the reactor with argon gas, the reactor was heated to a given temperature, *i.e.*, 873, 973, 1073 or 1173 K. After the temperature of the reactor became stable, 1 vol % hydrogen chloride gas diluted with argon (Japan Fine Products Co., Ltd., Japan) was introduced into the re-

Fig. 2. Experimental apparatus.

actor at the flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. After the reaction, the sample was analyzed; the weight change of the sample using a balance (GR-202, A&D Co., Ltd., Japan), the identification of the compounds by X-ray diffraction (XRD) (MiniFlex, Rigaku Co., Japan) and the chemical composition analysis by ICP-AES following the dissolution of the sample with alkali fusion.

2.3 Leaching test

To examine the leachability of uranium, leaching tests were conducted on the samples as follows: approximately 10 mg of each sample was mixed with 5 cm^3 3 M HNO_3 in a vessel, which was placed in a water bath kept at 353 K using a magnetic stirrer for 10 min. The uranium concentration in the leaching solution was measured by ICP-AES.

3. Results and discussion

3.1 Chlorination of Sb-U composite oxide

Without the flow of hydrogen chloride gas into the reactor, the weight of the composite oxide sample did not change even at 1173 K, while a decrease in weight was observed during the flow of hydrogen chloride gas. The weight changes of the sample at different chlorination temperatures

Fig. 3. Weight change of the Sb-U composite oxide.

Fig. 4. Sb and U content change of the Sb-U composite oxide.

are shown in Fig. 3. At 873 K, the weight slowly decreased; the weight fraction remained 68 wt % after 6 h of the chlorination treatment. The higher the reaction temperature, the faster the weight decreased. However, there seemed to be a limit in the weight fraction decrease up to 50 wt %.

The contents of antimony and uranium in the sample changed with the chlorination temperature and time as shown in Fig. 4. The antimony content decreased with time, and it became approximately 1 wt % after 3 h and 1 h at 1073 and 1173 K, respectively. In contrast, the uranium content increased up to 77 wt %.

The amount of uranium contained in the treated sample was calculated using the weight fraction shown in Fig. 3 as follows:

$$\begin{aligned} (\text{U amount, g}) &= (\text{Initial sample amount, g}) \\ &\times (\text{Weight fraction after treatment, wt\%})/100 \\ &\times (\text{U content after treatment, wt\%})/100 \end{aligned} \quad (1)$$

If there was no volatilization of the uranium, the amount of uranium should not change; *i.e.*, the following equation was derived from Eq. (1).

$$\begin{aligned} (\text{U content in initial sample, wt\%}) &= \\ (\text{Weight fraction after treatment, wt\%})/100 \\ &\times (\text{U content after treatment, wt\%})/100 \end{aligned} \quad (2)$$

When the uranium content was 77 wt %, and the limit weight fraction was 50 wt %, the uranium content was calculated to be approximately 39 wt %, which was same as that shown in Table 1. Therefore, it was found that the uranium was not volatilized, but the antimony was volatilized by the chlorination treatment.

Fig. 5 shows the change in the XRD patterns with the chlorination treatment at 1173 K. In the non-treated composite oxide sample, two composite oxides, $\text{USb}_3\text{O}_{10}$ and USbO_5 , existed. After a 0.5 h treatment, the peaks of one of the composite oxides, $\text{USb}_3\text{O}_{10}$, disappeared; on the other hand, the peaks of uranium oxide, U_3O_8 , appeared as shown in Fig. 5(b). The peaks of the composite oxide finally disappeared and those of the uranium oxide were found in the patterns of the sample treated at 1173 K for 1 h. From the

Fig. 5. XRD patterns of the Sb-U composite oxide (a) without treatment, and with treatment at 1173 K for (b) 0.5 h and (c) 1 h.

uranium content in the oxide shown in Table 1, the weight fraction was estimated to be 46 wt % based on the assumption that all the antimony was removed from the composite oxide and the uranium oxide, U_3O_8 , was formed. The limit to the decrease in the weight fraction, 50 wt %, in Fig. 3 was close to this value.

3.2 Chlorination of the catalysts and leaching tests

Fig. 6 shows the results obtained using the simulated catalyst for which the composite oxides were supported on silica beads. At 1173 K, there was no change in the weight fraction over 1 h. For this sample, the limit in the weight fraction remained at 87 wt %. Based on the assumption that the remainder was only U_3O_8 and SiO_2 , the weight fraction was calculated to be 60 wt %. In the sample treated at 1173 K for 3 h, a certain amount of antimony still remained, and its contents of antimony and uranium were 3 and 15 wt %, respectively.

From the XRD analysis, it was confirmed that the uranium composite oxide contained in both samples of the simulated catalyst and the real waste sample were converted into uranium oxide, U_3O_8 , with the treatment at 1173 K for 1 h. Table 2 shows the results of the leaching tests with

Fig. 6. Weight change in the simulated catalyst treated at 1173 K.

Table 2. Removed fraction of uranium dissolved with 3 M nitric acid at 353 K.

Sample	Chlorination treatment ^a	U, %
Simulated catalyst	Non-treated	< 0.1 ^b
	Treated	85 ± 7
Waste catalyst	Non-treated	< 0.1 ^b
	Treated	100 ± 7

a: Chlorination treatment with 1 vol % HCl gas at 1173 K for 1 h;

b: Lower than the detection limit of ICP-AES.

3 M nitric acid. Uranium leaching from both samples of the simulated catalyst and the real waste catalyst were lower than 0.1 wt %. With the treatment at 1173 K for 1 h, the uranium contained in both samples dissolved in 3 M nitric acid, and the uranium leaching fractions, 85 ± 7 and 100 ± 7%, were obtained for the simulated catalyst sample and the real waste sample, respectively. Although it was considered that a certain amount of antimony remained in both samples, the leachability of uranium has significantly increased using the proposed method.

4. Conclusion

The volatilization of antimony by chlorination was proposed to convert the uranium contained in the waste antimony-uranium composite oxide catalyst, which was used in the acrylonitrile synthesis process, into an acid leachable form. The results of the chlorination experiments employing the antimony-uranium composite oxide, a mixture of $\text{USb}_3\text{O}_{10}$ and USbO_5 , as a sample with hydrogen chloride gas at

873–1173 K showed that antimony in the composite oxide was volatilized, while the uranium was converted into uranium oxide, U_3O_8 . By chlorination treatment of 30 mg samples (a simulated catalyst sample, which was composed of silica beads supporting the composite oxide, and a real catalyst waste sample) with 1 vol % hydrogen chloride gas at 1173 K for 1 h, more than 85% of the uranium contained in the waste catalyst dissolved in the 3 M nitric acid solution at 353 K within 10 min, although that of the non-treated catalyst was lower than 0.1%. The proposed chlorination treatment was confirmed to be effective to separate antimony from the composite oxide catalyst and change uranium into its removable form.

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