

## **Effect of Concentration of Hydrogen Chloride Gas on Chlorination Treatment of Waste Containing Antimony-Uranium Composite Oxide Catalyst - 11274**

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### **ABSTRACT**

To clarify the effect of the concentration of hydrogen chloride gas on chlorination treatment for the volatilization of antimony from antimony-uranium composite oxide catalyst, which was used in the acrylonitrile synthesis, chlorination experiments were carried out by changing the concentration of hydrogen chloride gas from 0.6 to 6 vol%. There was remarkable difference in chemical composition of the remaining uranium oxide;  $\text{UO}_2$  was detected in the sample treated with 6 vol% hydrogen chloride gas for 40 min by XRD analysis while  $\text{U}_3\text{O}_8$  was examined in that treated with 0.6 vol% hydrogen chloride gas. Addition of oxygen gas was effective to prevent decrease in the valence of uranium. By the treatment with 6 vol% hydrogen chloride gas and 0.1 vol% oxygen for 40 min, 92 % of antimony volatilized from the waste although uranium remained as  $\text{U}_3\text{O}_8$  on silica support.

### **INTRODUCTION**

An antimony-uranium composite oxide catalyst was created by a team who developed a famous acrylonitrile synthesis process, Sohio Process, in USA in 1960s [1-4]. In practice, the catalyst was supported on silica to give it attrition resistance in fluidized bed for the synthesis [5]. Several Japanese chemical companies imported the catalyst from USA and employed to synthesis acrylonitrile until the early 1980s. Then, they changed the catalyst to more hazardless one, such as a molybdenum-bismuth-iron composite oxide, etc., and they stocked the waste containing antimony-uranium composite oxide catalyst without any treatment. The composite oxide is so stable chemically that it was difficult to dissolve in nitric acid or hydrochloric acid. The contents of antimony and uranium in the waste were approximately 30 and 15 wt%, respectively. In Japan today, 200 tons as metallic uranium estimated as the waste stored in the several companies with the rigid managements under legislation.

In order to remove uranium from the waste containing composite oxide catalyst, we proposed the chlorination treatment of the composite oxide catalyst [6]. It is known that antimony (III) chloride has relatively low boiling point at 497 K. If antimony converted into its chloride destroying the composite oxide, it would volatilize from the waste remaining uranium oxide on silica support. Because uranium oxide is soluble in nitric acid, uranium could be removed from the waste by nitric acid leaching after the chlorination treatment. In the previous study, we could volatilize antimony from the waste and converted uranium composite oxide into uranium oxide ( $\text{U}_3\text{O}_8$ ), which was soluble with nitric acid, by contacting 30 mg of the catalyst with 1 vol% hydrogen chloride gas at a flow rate of  $50 \text{ cm}^3 \text{ min}^{-1}$  in a flow-type reactor at 1173 K for 1 h [6]. In addition, we could demonstrate that more than 90 % uranium in the waste was dissolved with 3

mol dm<sup>-3</sup> nitric acid at 353 K for 10 min, following the chlorination treatment [6]. For the practical use of this method, further discussions for the treatment conditions, such as concentration of the gas, type of reactor, *etc.*, are necessary. In the present study, we aimed to clarify the effect of the concentration of hydrogen chloride gas on the chlorination of the waste containing the composite oxide catalyst.

## EXPERIMENTAL

The waste containing the catalyst employed in this study was a real waste sample obtained from 3R Corporation, Japan. Its uranium, antimony and silicon contents were 13, 15 and 30 wt%, respectively.

Figure 1 illustrates the experimental apparatus. Approximately 30 mg waste was loaded in a platinum cell whose diameter was 1.5 cm and volume was 0.7 cm<sup>3</sup> and hung in a quartz tube reactor equipped in an electric furnace (ARF 30K, Asahi Rika Seisakusho, Japan). The reactor was heated with purging with argon gas up to 1173 K. After it achieved the temperature of 1173 K, 0.6-6 vol% hydrogen chloride gas diluted with argon (Japan Fine Products Co. Ltd., Japan) was introduced into the reactor at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>. A line of oxygen gas was also connected to the lines hydrogen chloride and argon gas in order to control the gas condition in the reactor.

After the reaction, the sample was conducted to the analyses; the weight change of the sample by using a balance (GR-202, A&D Co. Ltd., Japan), the identification of compounds by X-ray diffraction (XRD) (MiniFlex, Rigaku Co., Japan) and the chemical composition analysis by using ICP-AES (ICPE-9000, Shimadzu, Japan) following the dissolution of the sample with alkali fusion.

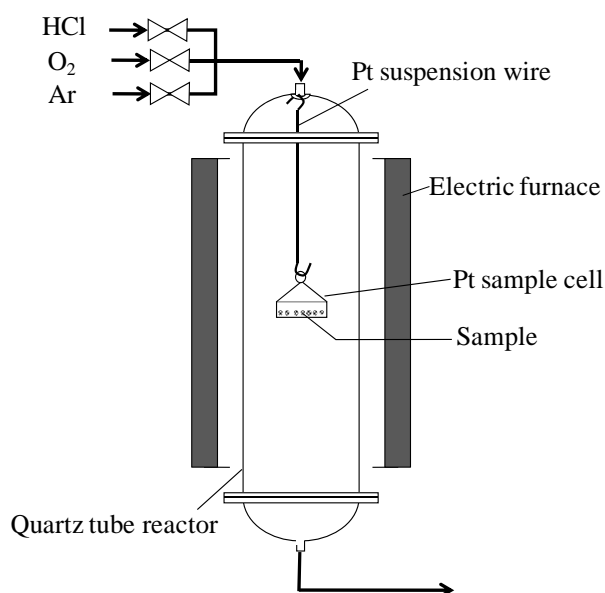


Fig. 1 Experimental apparatus.

## RESULTS AND DISCUSSION

The weight changes of the waste containing the composite oxide catalyst treated with 0.6, 1 and 6 vol% hydrogen chloride gas were shown in Fig. 2. Although the different concentrations of hydrogen chloride gas were employed, the weight loss of the waste treated for 10 min were almost same at 87wt%. Then, the rates of the loss changed with the hydrogen chloride concentrations, *i.e.*, the higher concentration of hydrogen chloride gas made it faster.

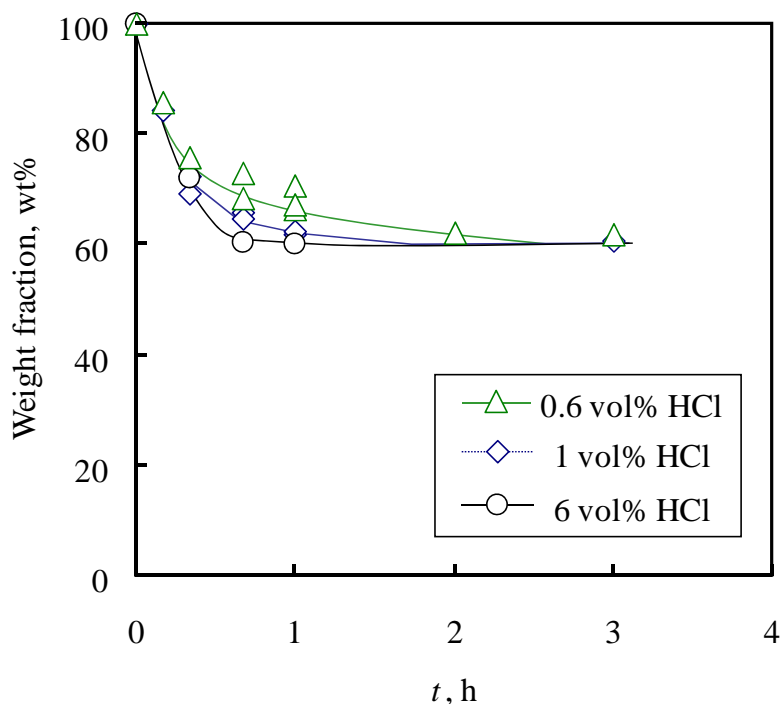


Fig. 2 Weight changes of the waste treated with 0.6, 1 and 6 vol% hydrogen chloride gas at 1173 K.

Figure 3 shows the XRD patterns of non-treated waste, the waste treated with 0.6 vol% hydrogen chloride gas for 20, 40 min, 1 and 3 h and reference data of  $USb_3O_{10}$ ,  $USb_3O_5$  and  $U_3O_8$ . Compared with the reference data of  $USb_3O_{10}$  (Fig.3 (f)), it was confirmed that the composite oxide in the waste (Fig.3 (a)) was  $USb_3O_{10}$  initially. With the treatment, it changed to  $USbO_5$ , and then  $U_3O_8$  (Fig.3 (b-e)). After 3 h, there were no peaks showing the composite oxide but uranium oxide,  $U_3O_8$  (Fig.3 (e)).

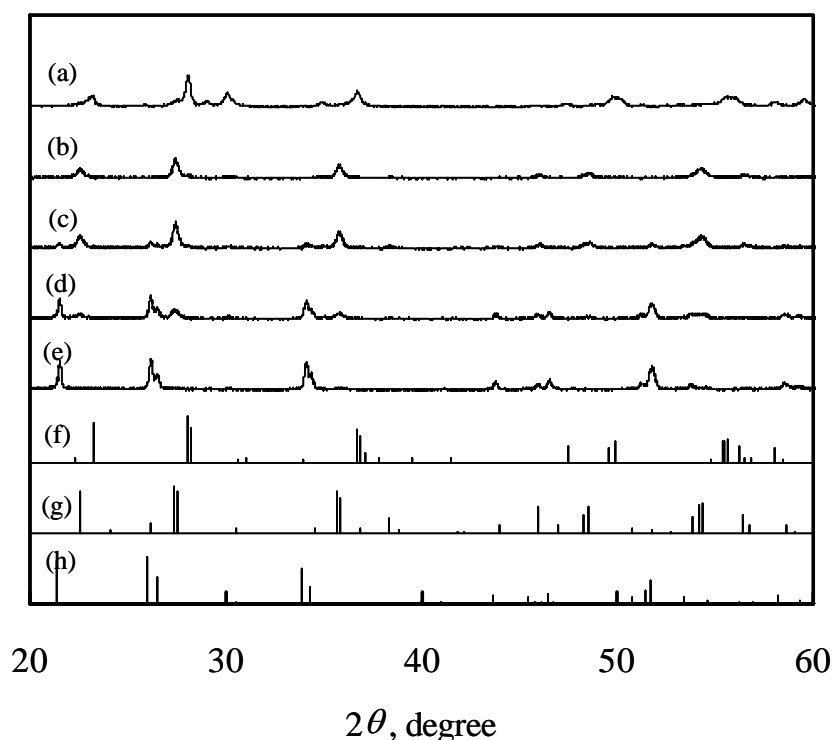


Fig. 3 XRD patterns of (a) non-treated waste, the waste treated with 1 vol% HCl for (b) 20 min, (c) 40 min, (d) 1 h and (e) 3 h, and reference data of (f)  $USb_3O_{10}$ , (g)  $USb_3O_5$  and (h)  $U_3O_8$ .

The XRD patterns of the waste treated with 6 vol% hydrogen chloride gas for 20 and 40 min were shown in Fig. 4. The peaks of uranium oxide,  $U_3O_8$ , were appeared with those of the composite oxide,  $USbO_5$ , in the XRD pattern of the catalyst treated with 6 vol% hydrogen chloride gas for 20 min. On the contrary, the peaks appeared in the pattern of that treated for 40 min were representing only uranium dioxide,  $UO_2$ . It is known that compounds containing tetravalent uranium are insoluble mildly acidic condition [7]. As for the uranium removal by acid leaching following the chlorination treatment,  $U_3O_8$  is preferred than  $UO_2$  as remaining uranium oxide form in the waste. To prevent decrease in the valence of uranium, an addition of oxygen gas was examined. The result of the XRD analysis obtained from the sample treated with 6 vol% hydrogen chloride and 0.1 vol% oxygen gas for 40 min was also shown in Fig. 4. By adding 0.1 vol% oxygen gas, the product uranium oxide changed to  $U_3O_8$  successfully.

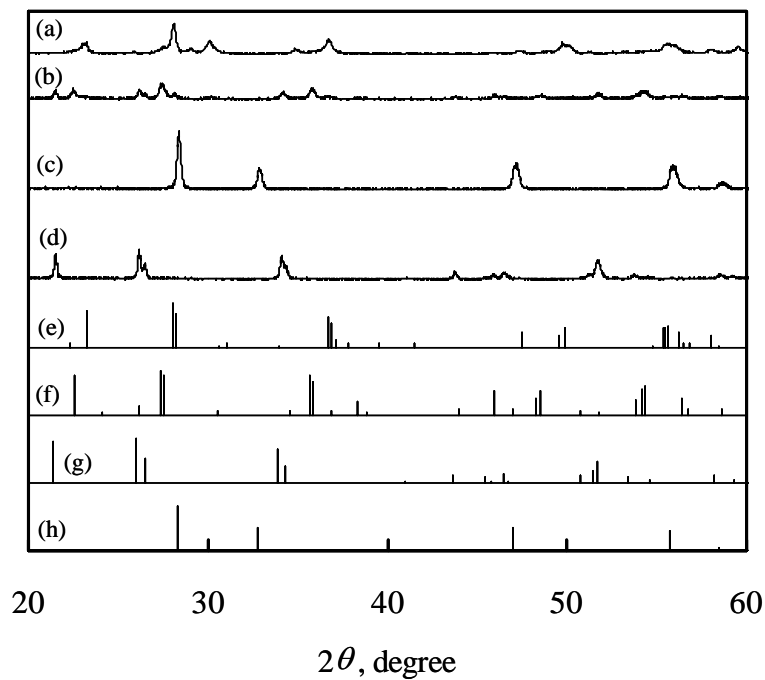


Fig. 4 XRD patterns of (a) non-treated waste, the waste treated with 6 vol% HCl for (b) 20 min, (c) 40 min, (d) 6 vol% HCl and 0.1 vol%  $O_2$  for 40 min, and reference data of (e)  $USb_3O_{10}$ , (f)  $USb_3O_5$ , (g)  $U_3O_8$  and (h)  $UO_2$ .

Figure 5 shows the  $\log p_{O_2}$ - $\log p_{Cl_2}$  potential diagram of the U-Cl-O system at 1173 K, which was drawn by the aid of a commercially available software (HSC Chemistry ver.5.1, Outotec Research, Finland). This figure shows that  $U_3O_8$  exists stably when oxygen partial pressure is greater than  $2.5 \times 10^{-6}$  atm. At the beginning of the reaction, the oxygen partial pressure was high because of oxygen existed as the composite oxide. As the reaction proceeded, the oxygen partial pressure seemed to decrease, and it resulted in the formation of uranium dioxide. However, it could remain in the region of  $U_3O_8$  when 0.1 vol% oxygen gas was added, as shown with a circle in Fig. 5.

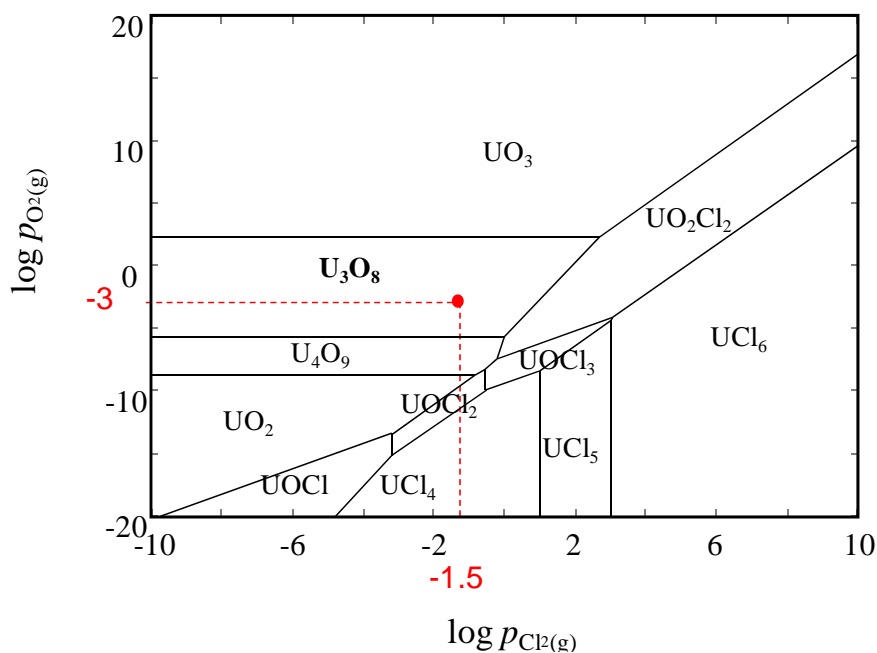


Fig. 5 Log  $p_{O_2}$ -log  $p_{Cl_2}$  potential diagram of the U-Cl-O system at 1173 K.

Table 1 shows the contents of antimony, uranium and silicon in the samples. By the treatment with 6 vol% hydrogen chloride gas and 0.1 vol% oxygen for 40 min, 92 % of antimony volatilized from the waste although all uranium remained as  $U_3O_8$  on silica support.

Table 1 Contents of antimony, uranium and silicon in the samples

	Content, wt% (Removal fraction, %)		
	Sb	U	Si
Non-treated sample	30	13	15
Sample treated with 6 vol% HCl and 0.1 vol% $O_2$ for 40 min	4 (92)	21 (0)	24 (0)

### CONCLUSION

From experiments changing the concentration of hydrogen chloride gas from 0.6 to 6 vol%, the initial reaction rate based on the sample weight loss was not improved significantly. On the other hand, there was

remarkable difference in chemical composition of the remaining uranium oxide;  $\text{UO}_2$  was detected in the sample treated with 6 vol% hydrogen chloride gas for 40 min by XRD analysis while  $\text{U}_3\text{O}_8$  was examined in that treated with 0.6 vol% hydrogen chloride gas. In the XRD pattern of the sample treated with 6 vol% hydrogen chloride gas for 20 min, the peaks of  $\text{U}_3\text{O}_8$  existed as well as those of unreacted antimony-uranium composite oxide. It was considered that the valence of uranium decrease after the chlorination of antimony. The  $\log p_{\text{O}_2}$ - $\log p_{\text{Cl}_2}$  potential diagram of the U-Cl-O system at 1173 K shows that  $\text{U}_3\text{O}_8$  exists stably when oxygen partial pressure is greater than  $2.5 \times 10^{-6}$  atm. By the treatment with 6 vol% hydrogen chloride gas and 0.1 vol% oxygen for 40 min, 92 % of antimony volatilized from the waste containing the composite oxide catalyst although uranium remained as  $\text{U}_3\text{O}_8$  on silica support.

#### ACNOWLEDGMENT

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