Reaction of Antimony-Uranium Composite Oxide in the Chlorination Treatment of Waste Catalyst – 13521

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ABSTRACT

The effect of oxygen gas concentration on the chlorination treatment of antimony-uranium composite oxide catalyst waste was investigated by adding different concentrations of oxygen at 0-6 vol% to its chlorination agent of 0.6 or 6 vol% hydrogen chloride gas at 1173 K.   The addition of oxygen tended to prevent the chlorination of antimony in the oxide.   When 6 vol% hydrogen chloride gas was used, the addition of oxygen up to 0.1 vol% could convert the uranium contained in the catalyst to U_3O_8 without any significant decrease in the reaction rate compared to that of the treatment without oxygen.

INTRODUCTION

The antimony-uranium composite oxide catalyst was created by a team who developed the famous acrylonitrile synthesis process, i.e., the Sohio Process, in the USA in the 1960s [1-4]. During actual use, the catalyst was supported on silica to give it an attrition resistance in a fluidized bed for the synthesis [5].   Several Japanese chemical companies imported the catalyst from the USA and employed it to synthesize acrylonitrile until the early 1980s.   They then changed the catalyst to a less hazard one, such as the molybdenum-bismuth-iron composite oxide, etc., and they stored the waste containing the antimony-uranium composite oxide catalyst without any treatment.   The composite oxide is so chemically stable that it was difficult to dissolve it in nitric acid or hydrochloric acid.   The contents of antimony and uranium in the waste were approximately 30 and 15 wt%, respectively.   Today, in Japan, it is estimated that 200 tons as metallic uranium is stored as waste by several companies with strict management rules under legislation.

We proposed chlorination treatment of the composite oxide catalyst in order to remove uranium from the waste [6-7].   A previous study examined treatment with 6 vol% hydrogen chloride gas and 0.1 vol% oxygen at a total flow rate of 50 cm^3 min^{-1} in a flow-type reactor held at 1173 K for 40 min [7]. Approximately 92 % of the antimony volatilized from 30 mg of the catalyst, although all the uranium remained as U_3O_8 on the silica support.   In the present study, we aimed to clarify the reaction of the antimony-uranium composite oxide during the chlorination treatment of the waste catalyst.

METHOD

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

The experimental procedure was same as in our previous study [7].   Figure 1 illustrates the experimental apparatus.   Approximately 30 mg of waste was loaded in a platinum cell whose diameter was 1.5 cm and volume was 0.7 cm^3.   The platinum cell was placed in a quartz tube reactor situated in an electric furnace (ARF 30K, Asahi Rika Seisakusho, Japan).   The reactor was heated while 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 the flow rate of 50 cm^3 min^{-1}.   An oxygen gas line was also connected to the hydrogen chloride and argon gas lines in order to control the gas condition in the reactor.

After the reaction, the sample underwent the floowing analyses; 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 (ICPE-9000, Shimadzu, Japan) following the dissolution of the sample by alkali fusion.
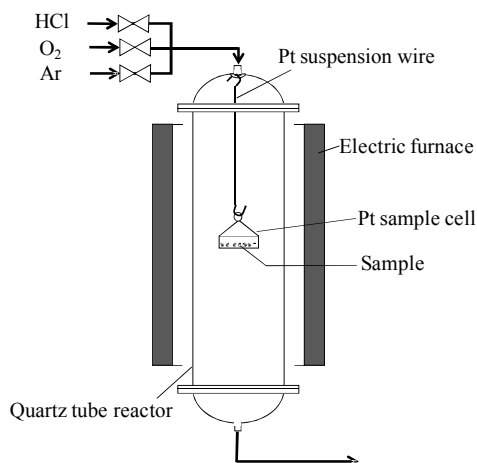

Fig. 1   Experimental apparatus.

RESULTS AND DISCUSSION

The XRD patterns of the samples treated with only 0.6 vol% hydrogen chloride gas are shown in Fig. 2.   The uranium-antimony composite oxide in the sample was found to change from

USb_3O_{10} to $USbO_5$, then to U_3O_8 with time.   The chlorination reaction was assumed to be the following two-step reactions:
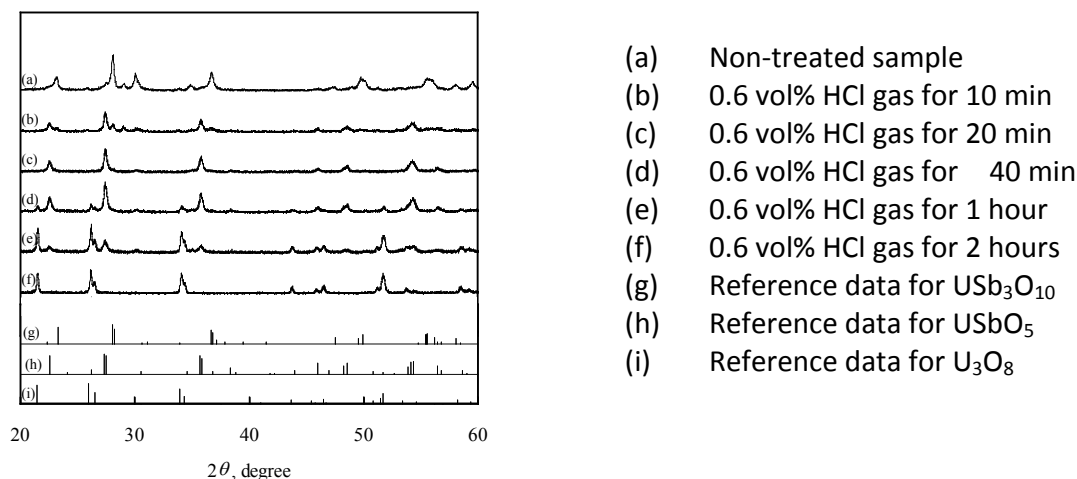
$$USb_3O_{10} + 10HCl \rightarrow USbO_5 + 2SbCl_5 + 5H_2O, \qquad (1)$$

$$USbO_5 + 5HCl \rightarrow 1/3U_3O_8 + SbCl_5 + 7/3H_2O + 1/6H_2. \qquad (2)$$

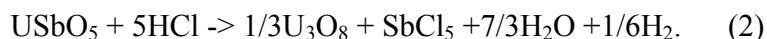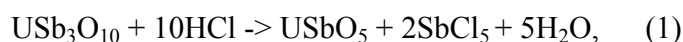|	
(a)	Non-treated sample
(b)	0.6 vol% HCl gas for 10 min
(c)	0.6 vol% HCl gas for 20 min
(d)	0.6 vol% HCl gas for 40 min
(e)	0.6 vol% HCl gas for 1 hour
(f)	0.6 vol% HCl gas for 2 hours
(g)	Reference data for USb_3O_{10}
(h)	Reference data for $USbO_5$
(i)	Reference data for U_3O_8

Fig. 2   XRD patterns.

When 6 vol% hydrogen chloride gas was used, UO_2 was detected in the sample treated for 40 min [7].   It was considered that a part of U_3O_8 was reduced as follows:
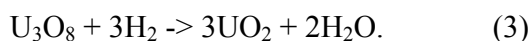
$$U_3O_8 + 3H_2 \rightarrow 3UO_2 + 2H_2O. \qquad (3)$$

Figure 3 shows the potential diagram of the U-H-O system at 1173 K, which was drawn using commercially available software [8].   From this figure, U_3O_8 seemed to stably exist when the oxygen partial pressure was greater than 0.001 vol%.
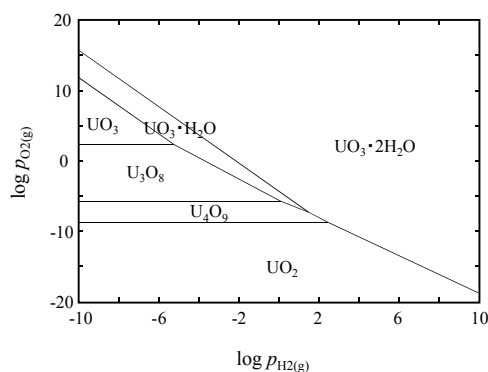

Fig. 3   Log p_{O2}-log p_{H2} potential diagram of the U-H-O system at 1173 K.

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The effect of the oxygen gas concentration on the chlorination treatment was investigated by adding different concentrations of oxygen from 0-6 vol% as shown in Fig. 4.   The vertical axis represents the weight fraction of the sample treated for 40 min.   Increasing the oxygen concentration lowered the fraction of waste converted.   The effect of oxygen increased with a decrease in the hydrogen chloride gas concentration.   When 6 vol% hydrogen chloride gas was used, the addition of oxygen up to 0.1 vol% could convert the uranium contained in the catalyst to U_3O_8 without any remarkable decrease in the reaction rate compared to that when treated without oxygen.
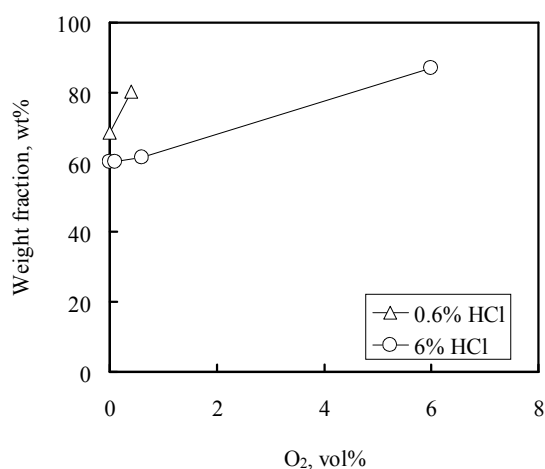
Fig. 4   Effect of oxygen gas concentration on the chlorination treatment

CONCLUSION

The effect of oxygen gas concentration on the chlorination treatment of antimony-uranium composite oxide catalyst waste was investigated by adding different concentrations of oxygen from 0-6 vol%. U_3O_8 seemed to stably exist when the oxygen partial pressure was greater than 0.001 vol% based on the potential diagram of the U-H-O system at 1173 K.   Increasing the oxygen concentration lowered the fraction of waste converted.   The effect of oxygen on the reaction rate increased with a decrease in the hydrogen chloride gas concentration.   When 6 vol% hydrogen chloride gas was used, the addition of oxygen up to 0.1 vol% could convert the uranium contained in the catalyst to U_3O_8 without any remarkable decrease in the reaction rate compared to that treated without oxygen.

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