Iodine Gas Trapping using Granular Porous Bismuth

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1. Introduction

Volatile fission products such as ^{3}H, ^{14}C, ^{85}Kr, and ^{129}I are emitted as off-gases during high-temperature voloxidation of spent fuel reprocessing [1]. ^{129}I is a radionuclide with a very long half-life of 1.57×10^{7} years and has negative health effects to the human body. Therefore, the emission of ^{129}I into the air is closely regulated by the Environmental Protection Agency (EPA) [2].

Many methods for trapping gaseous ^{129}I have been developed thus far, including wet scrubbing and adsorption using silver loaded zeolites [3]. Although wet scrubbing can effectively remove iodine, it suffers from corrosion of the vessel due to high concentration of the scrubbing solution [3]. Silver loaded zeolites also show effectiveness in capturing ^{129}I gas, yet weak thermal stability of physisorbed iodine remains a challenge [4].

We studied a novel and facile method to trap iodine gas using bismuth. Granular bismuth having many pores was synthesized using bismuth nitrate and polyvinyl alcohol as a bismuth precursor and pore forming agent, respectively. Reaction of iodine and our samples resulted in an iodine capturing capacity of more than 2 times that of the commercial grade silver exchanged zeolite (AgX).

2. Methods and Results

In this section, we describe the summary of synthetic process of the adsorbent material and its performance results . Detailed discussions of the results are found elsewhere [5].

2.1 Synthesis of Granular Porous Bismuth

For the synthesis of granular porous bismuth, we purchased bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot5H_2O$, 98%, Sigma-Aldrich, MO, USA) and polyvinyl alcohol (PVA, Junsei, Tokyo, Japan) as a bismuth precursor and pore forming agent, respectively. A typical process is followed: aqueous solutions of $Bi(NO_3)_3\cdot5H_2O$ and PVA were mixed and stirred, resulting in a transparent solution with a yellowish color. It was dried in oven and then calcined in a thermal furnace at 400 ℃ for 3 hrs in air to remove PVA. To examine the reduction effect, further heat-treatment was carried out in another set of samples. The samples were thermally treated at 310 ℃ for 12 hrs in a 4% H_2/Ar atmosphere.

2.2 Iodine Capture Test

The most important parameter for evaluating the adsorbents is the pollutant adsorbing capacity. We designed a simple system to investigate the reaction tendency of our granular porous bismuths with iodine gas. Nonradioactive iodine crystal was put into an alumina crucible, followed by a stacking of the testing samples. The crucible containing sample was covered with a lid and moved to a furnace, where the temperature was elevated to 200 ℃ and maintained for 24 hrs. Because iodine is a very volatile element and its boiling point is 182.8 ℃, the gas-solid reaction between iodine and our samples is easily achieved. For comparison, iodine capture tests using bismuth powder (Bi, 100 mesh, 99%, Sigma-Aldrich, MO, USA) and AgX (granular, 20 mesh, Sigma-Aldrich, MO, USA) were also conducted using the same experimental condition.

2.3 Results and Discussion

Fig. 1 shows as-synthesized granular porous bismuths treated with hydrogen and those not treated with hydrogen. The color difference between two sample sets is believed to be attributed to the difference of the oxidation state of bismuth: samples thermally treated in air have more oxidized bismuth than samples thermally treated in hydrogen.

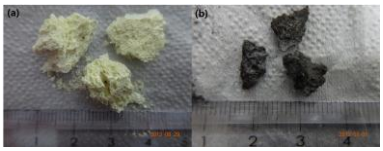

Fig. 1. As synthesized granular porous bismuth (a) not treated with hydrogen and (b) treated with hydrogen.

Fig. 2 shows images of samples after an iodine capture test. The reddish color in the surfaces of the samples indicates that a chemical reaction occurred between iodine and bismuth, forming bismuth iodine compounds.

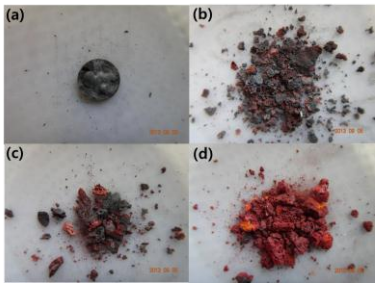

Fig. 2. Samples of granular porous bismuth after iodine capture test ((a) Bi powder, (b) BP1, (c) BP2, and (d) BP3).

The newly formed phases on the samples were identified using an X-Ray Diffraction (XRD) method. As shown in Fig. 3, most of the peaks were assigned to BiI_3 or BiOI. Interestingly, the intensity of the main peaks in BiI_3 gradually decreased, whereas that in BiOI gradually increased as the sample number increased. Herein, the sample indexed with a high number had a higher surface area and pore volume than that indexed with a low number. In other words, the formation of reaction products was closely connected to the internal structure of the samples.

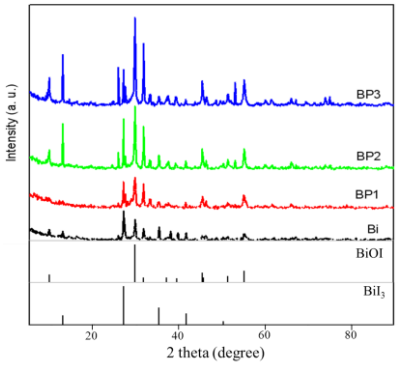

Fig. 3. XRD result of samples of granular porous bismuth and bismuth powder after iodine capture test.

The difference of the reaction products is attributed to the difference in governing reactions dependent upon the internal structure of the samples. As schematically explained in Fig. 4, most of the reaction occurs on the surface of samples with a low pore volume. In this case, the governing reaction is one that makes BiI_3 due to the high pressure of iodine gas. In contrast, a significant portion of the reaction occurs inside of pores for the samples with a high pore volume. In this case, BiOI is easily formed due to the relatively high pressure of oxygen. Due to the difference of atomic masses between oxygen and iodine, diffusion of oxygen gas into pores is relatively easy compared to diffusion of iodine gas.

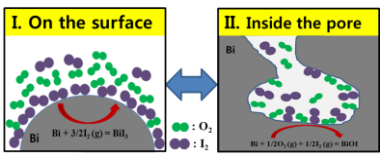

Fig. 4. Schematic diagram explaining difference of governing reaction between surface and pore.

Fig. 5 shows iodine capture capacity of various samples. The result tells us that samples treated with hydrogen have iodine trapping capacity of more than 0.7 g per unit mass of sample at the maximum. When the deviation of data in repetitive experiments was considered, the average iodine trapping capacity was 0.55 g per unit mass of sample. This result is very encouraging considering that iodine trapping capacity of AgX is merely 0.25 g per unit mass of AgX. Interestingly, samples not treated with hydrogen does not react with iodine gas at all, suggesting that reaction tendency of Bi_2O_3 and Bi with iodine gas is remarkably different.

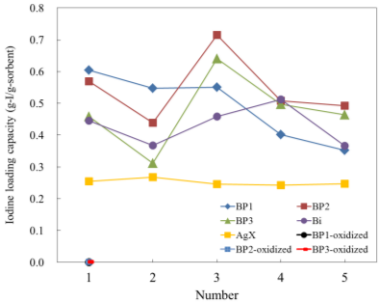

Fig. 5. Iodine capture capacity of various samples.

3. Conclusions

Granular porous bismuths synthesized using bismuth nitrate and PVA show a promising performance in capturing iodine gas. The use of bismuth in trapping ^{129}I gas can reduce the process cost as bismuth is cheap. Further study is going on to improve the mechanical property of granular porous bismuths for their easy handling.

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