Radioactive Iodine (I-129) Gas Adsorption by Using Bismuth-Embedded SBA-15

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1. Introduction

Radioactive iodine (I-129) gas released as off-gas from spent nuclear fuel reprocessing affects negative health effects for a long time. Thus, many sorbents have been studied to capture I-129. Among them, the silver-exchanged mordenites (AgZ) are most commonly used for iodine capture, being considered as a benchmark sorbent [1]. However, high price and toxicity of silver are weak points of AgZ. In addition, a significant portion of iodine is physically captured in mordenite pores, which is fatal in disposal perspective. To overcome these problems, porous bismuth granule was studied to be used for iodine capture [2]. In this study, we made bismuth-embedded SBA-15 for iodine capture.

2. Methods and Results

2.1 Sorbent Synthesis

For a typical synthesis, micellar solution was prepared by dissolving 4 g of Pluronic P123 (EO70-PO20-EO70) into 125 g of 1.9 M HCl solution. Then, (41-x) mmol (x = 11.5, 14, or 20) of tetraethylorthosilicate (TEOS) was added and magnetically stirred at 40 ℃. After that, x mmol (x = 11.5, 14, or 20) of 3-mercaptopropyltrimethoxysilane (MPTMS) was added into the solution and stirred for 20 h at 40 ℃ to complete sol-gel reaction. The resultant mixture was poured into a PTFE bottle, which was tightly sealed and kept for 24 h at 100 ℃. In other case, the process was performed at 120 ℃ for 72 h to examine the effect of hydrothermal condition. The hydrothermally treated mixture was filtered to recover solid product and the solid was dried at 40 ℃ for 24 h. Surfactants within the solid product were removed by solvent extraction. Finally, the tihol-functionalized SBA-15 was obtained after drying at 40 ℃ for 24 h. Pristine SBA-15 as a reference was synthesized without MPTMS. For bismuth adsorption into the thiol-functionalized SBA-15, the sample was impregnated into bismuth solution at a ratio of 1 g: 100 mL for 6 h. After the impregnation was completed, the yellow-turned sample was separated from the solution, and dried at 40 ℃ for 24 h. Some portion of the bismuth-impregnated sample was thermally treated at 250 ℃ for 6 h in 4% H_2/Ar atmosphere. The samples at different synthesis stages and MPTMS molar ratios were named as shown in Table I.

Table I. Sample Names at Different Synthesis Stages and MPTMS Molar Ratios

[a]These samples were made with hydrothermal treatment at 120 ℃ for 3 days.

MPTMS/(MPTMS+TEOS) (molar ratio)	Synthesis stage		
	Thiol-functionalization	Bismuth-impregnation	Heat-treatment in 4%H_2/Ar
0.28	SBA-15-SH1	Bi-SBA-15-SH1	Bir-SBA-15-SH1
0.34	SBA-15-SH2	Bi-SBA-15-SH2	Bir-SBA-15-SH2
0.34	SBA-15-SH2A[a]	Bi-SBA-15-SH2A[a]	Bir-SBA-15-SH2A[a]
0.49	SBA-15-SH3	Bi-SBA-15-SH3	Bir-SBA-15-SH3

2.2 Morphological properties of sorbent

In this study, the bismuth-embedded SBA-15 was made through three phases. The optical images of the samples made at different phases are shown in Fig. 1. In the first phase, the thiol-functionalized SBA-15 (Fig. 1a) was synthesized by co-condensation process with MPTMS and TEOS as a thiol and silica precursor, respectively. The as-made thiol-functionalized SBA-15s were white granules with amorphous shape and size distributions of 2-5 mm. In the second phase, bismuth was adsorbed in the thiol-functionalized SBA-15. Upon immersing the granules in the prepared bismuth solution, these immediately turned yellow (Fig. 1b), suggesting bismuth was adsorbed in the granules. In the third phase, the specimens were thermally treated at 250 ℃ in 4%H_2/Ar flow, to turn to dark brown granules that were the final bismuth-embedded SBA-15 (Fig. 1c).

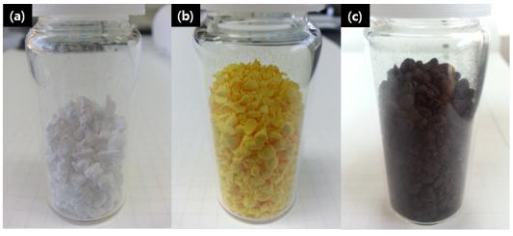

Fig. 1. Pictures of (a) thiol-functionalized SBA-15, (b) bismuth-embedded SBA-15 (before heat-treatment), and (c) bismuth-embedded SBA-15 (after heat-treatment).

2.3 Iodine Capturing Experiments

Fig. 2 exhibits the results of the iodine adsorption test for various samples conducted at 200 ℃ (or 150 ℃ for AgX) in steady air. The bismuth-embedded SBA-15s demonstrated the effective iodine capture with the highest capacity of 540 mg-I/g-sorbent. Compared to the results of AgX, our new sorbent accomplished 1.7 times higher capacity than that of the current baseline sorbent. It was also shown that the capacity was increased as the bismuth concentration in the samples increased. The pristine SBA-15 showed a substantially low capacity. The high data fluctuation is likely to be attributed to the removal of captured water within the SBA-15. The results strongly suggest that iodine capture is mostly dependent on bismuth, not SBA-15. However, the capacity was not directly proportional to the bismuth mass ratio. This is attributed to the noticeably reduced surface area due to the collapse of pore structure resulting in the lowered accessibility to iodine binding sites. The result indicates the accessible surface area is pivotal for iodine capture.

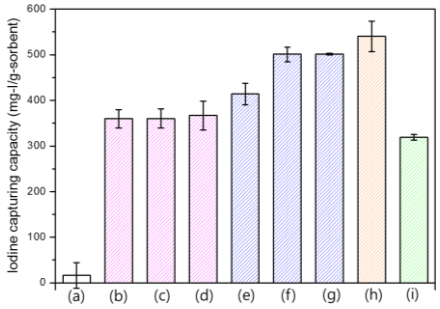

Fig. 2. Iodine capturing capacities in static air for (a) SBA-15, (b) Bi-SBA-15-SH1, (c) Bi-SBA-15-SH2, (d) Bi-SBA-15-SH3, (e) Bir-SBA-15-SH1, (f) Bir-SBA-15-SH2, (g) Bir-SBA-15-SH3, (h) Bir-SBA-15-SH2A, and (i) AgX (tested at 150 ℃).

2.4 Binding Mechanism

Yang et al. explained that the effective iodine adsorption with the bismuth-based sorbents was based on the bismuth affinity for iodine [2]. In other words, chemical adsorption (chemisorption) of iodine occurs since a chemical reaction between bismuth and iodine makes thermodynamically stable compounds. The thermodynamic accounts for iodine capture could also be applied in this study. It is different from the prior study that Bi_2S_3 instead of Bi was involved in the iodine capture. The XRD phase analysis (not shown here) revealed that BiI_3 was a primary compound that was made by iodine capture with the bismuth-embedded SBA-15s. Although the iodine capturing test was performed under static air, other compounds such as BiOI or Bi_2O_3 were not found unlike the previous study. In terms of thermodynamics, the formation of BiOI or Bi_2O_3 is also favorable at 473 K due to the negative values of $\Delta G_f°$ when Bi_2S_3 reacts with $I_2(g)$ in the presence of $O_2(g)$ (Table II). However, thermodynamic calculations showed a chemical reaction that involves Bi_2S_3, $I_2(g)$, and $O_2(g)$ to form BiI_3 and $SO_2(g)$ was most stable with $\Delta G_f° = -523.2$ kJ mol^{-1} at 473 K, which was significantly lower than that related with reactions to form BiOI or Bi_2O_3. It is worth noting that the small mass loss up to 100 ℃ shown in the TGA results suggests that physical adsorption (physisorption) of iodine also occurs, although chemisorption is a main process.

Table II. Chemical reactions related to iodine adsorption with Bi_2S_3 in static air, as well as Gibbs free energy of formation ($\Delta G_f°$) at 473 K.

chemical reaction	reaction product	$\Delta G_f°$[a] (kJ mol^{-1})
$0.5Bi_2S_3 + 1.5I_2(g) = BiI_3 + 1.5S$	BiI_3	-71.2
$0.5Bi_2S_3 + 0.5I_2(g) + 0.5O_2(g) = BiOI + 1.5S$	BiOI	-151.0
$0.5Bi_2S_3 + 1.5I_2(g) + 1.5O_2(g) = BiI_3 + 1.5SO_2(g)$	BiI_3	-523.2
$Bi_2S_3 + 1.5I_2(g) + 1.5O_2(g) = Bi_2O_3 + 3S + 1.5I_2(g)$	Bi_2O_3	-313.8

[a]These data were calculated with the HSC Chemistry 6.0 code.

3. Conclusions

The efficient capture of the long-lived I-129, released as off-gas from nuclear fuel reprocessing, have been of significant concern in the waste management field. In this study, bismuth-embedded SBA-15 mesoporous silica was firstly applied for iodine capture and storage. SBA-15 was functionalized with thiol (-SH) groups, followed by bismuth adsorption with Bi-S bonding, which was thermally treated to form Bi_2S_3 within SBA-15. The bismuth-embedded SBA-15s demonstrated high iodine loading capacities with 540 mg-I/g-sorbent maximally, which benefitted from the high surface area and porosity of SBA-15 as well as the formation of thermodynamically stable BiI_3 compound. Iodine physisorption could effectively be suppressed due to the large pores present in SBA-15, resulting in chemisorption as a main mechanism for iodine confinement.

REFERENCES

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