

The effect of anion treatment on the chemical stability of the coated Ag during iodine removal under strong alkaline medium

Myunggoo Kang^a, Seung-Kon Lee^a, Suseng Lee^a, and Jun Sig Lee^{b*}

^aDivision of Radioisotope Research, KAERI, 111 Daedok-daero 989beon-gil, Yseong-gu, Daejeon 34057, Republic of Korea

^bKorea Multi-purpose Accelerator Complex, KAERI, 181 Mirae-ro, Geoncheon-eup, Gyeongju-si, Gyeongbuk 38180, Republic of Korea

*Corresponding author: jlee15@kaeri.re.kr

1. Introduction

^{99m}Tc radioisotope, the daughter of ⁹⁹Mo, is the most widely used medical radioisotope.¹ ⁹⁹Mo can be produced in research reactors by neutron activation of ⁹⁸Mo or by fission of ²³⁵U. Former method is rather simple and inexpensive but gives low specific activity. So, the fission method with high specific activity has been widely used for the production of ⁹⁹Mo, called as Fission ⁹⁹Mo. Practically, fission ⁹⁹Mo is produced by alkaline digestion of irradiated ²³⁵U target and purification by adsorption column.² During the production, iodine isotopes with significant radioactivity co-exist with ⁹⁹Mo in the dissolved solution, in the form of iodide. It is essential to remove iodide from the solution to produce high purity ⁹⁹Mo product.

Materials containing Ag usually highest performance for iodine removal.³ In this regard, several studies have recently tried to introduce the silver coated alumina (AA) in the process of fission ⁹⁹Mo.^{2, 4} Herein, the chemical stability of the silver on the surface of alumina is one of important factors, to securely anchor iodine on surface of adsorbent. In previous report, the modification of Ag(s) to AgCl(s) significantly reduced Ag release from the sorbent material under weak acidic or natural media (pH 5~8).⁵ However, a study on the chemical stability of the coated Ag under strong alkaline solution has hardly been investigated.

To solve the abovementioned challenges, this study aimed to investigate and improve the chemical stability of AA in strong alkaline solutions. In order to prevent the release of Ag, we introduced counter anions on the surface of AA. To investigate the effect of anion's valence, both mono-valence (Cl⁻) and multi-valence (SO₄²⁻) anion was selected as counter ion.

2. Methods and Results

The silver coated alumina (AA) was synthesized by simply 'silver' mirror reaction (Fig. 1). Thereafter, the counter anion was attached to the surface of AA by using electrostatic interaction (Fig. 1).

2.1 Synthesis of AA

Commercial acidic alumina (200 ~ 300 μm) was sieved to remove fine particles under about 250 μm.

The sieved alumina was washed with distilled water and dried in an oven at 80 °C. The dried alumina (100.0 g) was added in the solution of the Tollens' reagent (25 wt% NH₄OH (25.0 mL), 2 M AgNO₃ (25.0 mL)). After stirring for 20 min, the pre-mixed solution of 1.0 M glucose (25.0 mL) and 3.2 M KOH (25.0 mL) was introduced into the stirred solution, followed by stirring for 10 min. After the color change of the solution was complete, the precipitate was washed several times with distilled water. The washed precipitate was calcined at 400 °C for 3 h. After cooling until room temperature, the calcined sample was stirred in 0.1M NaOH for 30 min to remove unattached Ag. The sample was washed with distilled water, re-annealed to 200 °C for 2 h. The finally obtained sample was called as AA.

2.2 Preparation of the anion treated AA (x-AA)

The as-prepared AA (50.0 g) was dispersed 0.1 M NaCl (100.0 mL) and stirring for 30 min. The treated sample was washed several times with distilled water to remove the remained salt after treatment. The washed sample was dried in an oven at 80 °C. The finally obtained sample was called as cl-AA. The treatment of sulfate substitute 0.1 M Na₂SO₄ for 0.1 M NaCl. This sample was named as s-AA.

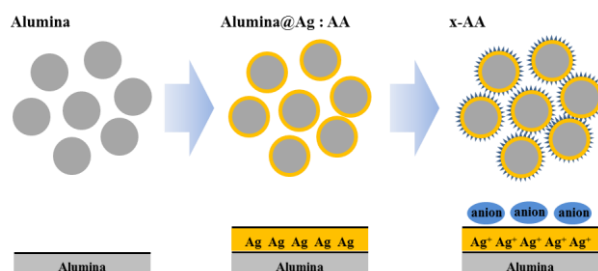


Fig. 1. Schematic diagram for preparing x-AA (x = cl and s).

2.3 Characterization of AA, cl-AA, and s-AA

The structure of sample was obtained by powder X-ray diffractometer. Fig. 2 shows the XRD pattern of the as-prepared AA. The XRD pattern represents the typical pattern of Ag metal and Al₂O₃. The component elements of x-AA samples were confirmed by energy dispersive spectroscopy (EDS) spectrum, as shown at Fig. 3. Each x-AA sample represents the peaks of chlorine and sulfur.

The result suggests that the surface of x-AA was treated to chloride and sulfate, respectively.

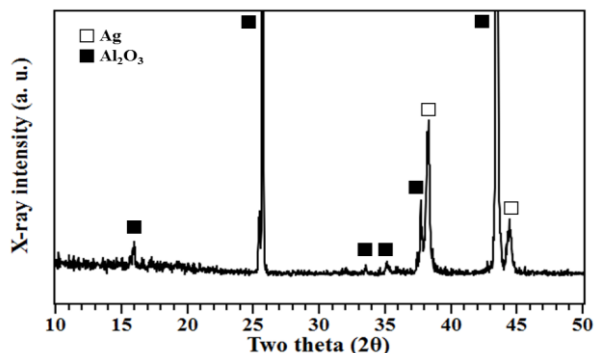


Fig. 2. XRD patterns of the synthesized AA sample.

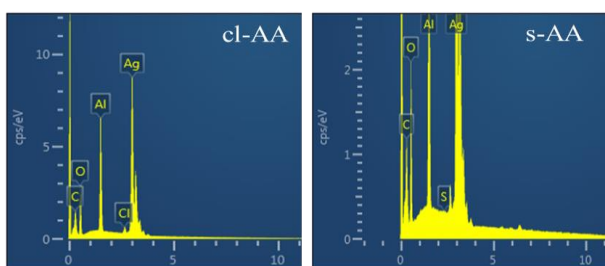


Fig. 3. EDS spectra cl-AA and s-AA.

2.5 Column test for the determination of iodine removal and the chemical stability of Ag

To determine the chemical stability during iodine removal, we perform the column test of each sample. The obtained samples were filled in a column with 15 cm height and 1.0 cm diameter. In this study three columns were prepared with AA, cl-AA, and s-AA. For each experiment, test solution of 5 ppm iodine solution (40.0 mL) based on 6.0 M NaOH. Prepared solution was loaded into the column at a rate of 10 mL/min. Fractions was sequentially collected by 5.0 mL.

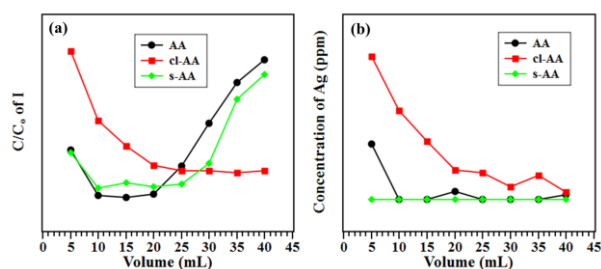


Fig. 4. (a) The Concentration ratio (C/C_0) of the remained iodine and (b) the concentration (ppm) of the released Ag versus filtration volume.

Fig. 4(a) shows the remained iodine concentration ratio (C/C_0) which calculated the absorbance of UV-vis spectrometer. The curve of cl-AA sample was gradually decreased in comparison with other samples. This result suggests that the treatment of Cl^- hinders to remove iodine quickly. On the other hands, AA and s-AA are

similar to curve shape. The total amount of the removed iodine was calculated to 0.21 (AA) and 0.23 (s-AA) mg by the UV absorbance, respectively. Herein, we believed that the attached sulfate never impede the adsorption of iodine on the surface of Ag.

From AAS measurement, Fig. 4(b) displays the concentration of the released Ag at each fraction. The quantities of the released Ag show the order of cl-AA, AA, and s-AA during iodine removal. This result suggests that surface treatment of multi-valent (SO_4^{2-}) anion has an effect on the chemical stability of the coated Ag. However, the sample of one-valent (Cl^-) anion continually released the Ag ion. Also, AA sample release Ag ion at three points. From these results we believed that the multi-valent anion potentially improve the chemical stability of the coated Ag under strong alkaline solution.

3. Conclusions

In conclusion, the Ag-coated alumina treated with counter anion (x-AA) was successfully synthesized by 'silver' mirror reaction and electrostatic interaction. We determined the structure and the counter anion of AA sample from the results of powder XRD and EDS measurements, respectively. The chemical stability test of the obtained AA, cl-AA, and s-AA samples were performed by using iodine removal test with adsorption column. The results of UV and AAS measurement at volume fractions show that sulfate improve the chemical stability of the coated Ag under strong alkaline medium without sacrificing the performance of iodine removal, such as quantity and rate. Based on this result, we found the effect of multi-valence anion for the synthesis of chemically robust Ag-coated alumina. This material can be potentially used for the elimination of iodine from the fission ^{99}Mo process.

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