SHORT NOTE

Effect of Grain Size of AgNO₃ Loaded in Porous Material on Adsorption of CH₃I

Kenji TAKESHITA, Yoichi TAKASHIMA,
Nuclear Chemistry and Chemical Engineering Center, Institute of Research and Innovation*

Shiro MATSUMOTO,
Department of Applied Chemistry,
Saitama University**

Shin-ichi INAMI
Tokai Reprocessing Plant, Technical Service Division, Power Reactor and Nuclear Fuel Development Corporation***

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Radioactive iodine in dissolver off-gas (DOG) generated at reprocessing plants can be removed effectively by using solid adsorbents impregnated with AgNO₃(1)-(4). Both elemental iodine and organic iodide are bound to the solid adsorbents as silver-iodine compounds. The iodine adsorption proceeds through following three steps, the diffusion of iodine through the gas boundary layer, the pore diffusion of iodine and the reaction between iodine and AgNO₃ impregnant. The pore diffusion rate and the reaction rate are affected strongly by the pore size distribution and the dispersion of AgNO₃ impregnant, respectively.

We examined the effect of the pore size distribution on the adsorption behavior of iodine by a shallow bed reactor(5)-(6). Porous styrene-divinylbenzene copolymer (SDB) particles impregnated with metallic silver or AgNO₃ were prepared and the breakthrough curves of iodine were measured. It was clarified that the use of macroporous adsorbents is effective for increasing both the adsorption rate and capacity(6)-(8). In this paper, the solid adsorbents with different dispersion of AgNO₃ impregnant were prepared and the breakthrough curves of CH₃I were measured. The grain size of dispersed AgNO₃ impregnant was evaluated by means of X-ray diffraction analysis and the effects of the grain size on the adsorption rate and capacity of CH₃I were discussed.

1. Preparation of Solid Adsorbents

Porous SDB particles were prepared by the capsule polymerization technique(7). The crosslinking degree (the weight fraction of divinylbenzene in monomer solution) and the pore volume of prepared SDB particles were 20% and 1.9 cm³/g, respectively. The particles were sieved in the range of 1.0±0.1 mm.

The impregnation of SDB particles with AgNO₃ was carried out by the dioxane method and the newly proposed nitrate method. The dioxane method is a conventional technique(6), whose procedure consists of two steps, such as soaking the SDB particles in the mixture of dioxane and 50wt% AgNO₃ aqueous solution at 25°C and drying in vacuo at 70°C for 1d(6). The procedure of nitrate method consists of three steps, such as soaking the SDB particles in n-butylamine solution containing the silver-amine complex, [Ag(C₄H₉NH₂)₂]⁺NO₃⁻ at 25°C, decomposing thermally the complex to metallic silver in N₂ stream at 180°C and converting the metallic silver to AgNO₃ by reacting with a mixture of 1vol% NO₂ and 3vol% water vapor balanced with N₂ gas at 25°C.

2. Characterization of Solid Adsorbents

The X-ray diffraction pattern and the pore size distribution were measured for the prepared solid adsorbents. The diameter of AgNO₃ grains was evaluated by the Shirrer's equation using the half-width of X-ray diffraction peak (2θ=35.5°)(8). Figure 1 shows the relation between the AgNO₃ content and the grain diameter. The grain diameter for

* Takada, Kashiwa-shi 277.
** Shimo-okubo, Urawa-shi 338.
*** Tokai-mura, Ibaraki-ken 319-11.
the adsorbents by the nitrate method was reduced to about 60% of that by the dioxane method. The AgNO₃ impregnation by the nitrate method is useful for the formation of smaller AgNO₃ grains.

Figures 2(a) and (b) show the comparison between the pore size distributions for the adsorbents prepared by the dioxane- and the nitrate methods. These data were measured by a mercury porosimeter (Pore Sizer 9320, Shimadzu Co., Ltd.). The decrease of pore volume by the AgNO₃ impregnation may be attributable to the plugging of pores in SDB particles. For the adsorbents with the same AgNO₃ content, the pore volume in the adsorbents by the nitrate method is larger than that by the dioxane method. These results suggest that the decrease of the size of AgNO₃ grains is effective for avoiding the plugging of pores by the AgNO₃ impregnation.

3. Breakthrough Curves of CH₃I

The column tests of prepared adsorbents were carried out by an experimental apparatus which consists of a generator of CH₃I vapor, an adsorption bed and a FID (flame ionization detector) gas chromatography (GC). The dimensions of the adsorption bed were 1.5 cm I.D. and 1 cm long. The bed temperature was kept at 130°C. Dry air mixed with 9.15 × 10⁻⁶ mol/m³ CH₃I was used as a test gas. The gas flow rate was 2.3 cm/s CH₃I reacts with AgNO₃, which is converted to AgI. The
time-variation of the concentration of CH$_3$I in the effluent gas was measured by the FID gas chromatography.

Figure 3 shows the breakthrough curves of CH$_3$I for the adsorbents prepared by the dioxane method. The AgNO$_3$ contents of the used adsorbents were 0.10, 0.37 and 0.68 g-AgNO$_3$/g-SDB. The adsorption capacity of CH$_3$I increased with the AgNO$_3$ content. However, the conversions of AgNO$_3$ to AgI, which were calculated from the breakthrough curves, were 91, 85 and 73% for the AgNO$_3$ contents of 0.10, 0.37 and 0.68 g-AgNO$_3$/g-SDB, respectively. The shape of breakthrough curve became broader with increasing the AgNO$_3$ content. The adsorption rate tends to decrease with increasing the AgNO$_3$ content. This may be due to the decrease of the pore volume by the AgNO$_3$ impregnation, as shown in Fig. 2(a).

Figure 4 shows the breakthrough curves of CH$_3$I for the adsorbents prepared by the dioxane and nitrate methods. The breakthrough curves for the adsorbents prepared by the nitrate method were sharper than those by the dioxane method. For the adsorbents with the AgNO$_3$ content of 0.68 g-AgNO$_3$/g-SDB, the adsorption capacity of CH$_3$I was $2.94 \times 10^{-3}$ mol-CH$_3$I/g-SDB for those by the nitrate method. Thus, the conversion of AgNO$_3$ to AgI was increased to 91% by the application of the nitrate method. These results suggest that the decrease of the size of AgNO$_3$ grains is effective for increasing both the adsorption rate and capacity of CH$_3$I.

4. Conclusion
The diameters of AgNO$_3$ grains in the adsorbents prepared by the newly proposed nitrate method were reduced to about 60% of those by the dioxane method. The decrease of the size of AgNO$_3$ grains was effective for increasing both the adsorption rate and capacity of CH$_3$I.

REFERENCES