Off-line experiments of isothermal gas chromatography for Zr and Hf tetrachlorides

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The periodic table today contains 118 elements, and elements with $Z \geq 104$ are called superheavy elements. Gas-phase chemical separation is one of the most utilized techniques to study chemical properties of the superheavy elements. Gas-phase chromatography is a method for determining the adsorption enthalpy (ΔH_{ads}) of an element of interest in a volatile compound based on its adsorption-desorption processes on a column surface. To clarify chemical properties of element 104, Rf, gas chromatographic behaviors of chlorides of Rf and its homologs, Zr and Hf, have been studied. The reported sequence of volatility was Zr ≳ Rf > Hf,[1,2] but the relation between Zr and Hf chlorides differs from the sequence of sublimation expected from their vapor pressure curves in macro-scale.[3] In this study, we investigated gas chromatographic behaviors of Zr and Hf chlorides at off-line to clarify this contradiction.

Radiotracers of ^{88}Zr ($T_{1/2}$=83.4 d) and ^{175}Hf ($T_{1/2}$=70 d) were produced via ^{89}Y(d, $3n$) and ^{175}Lu(d, X) reactions, respectively, using a 24-MeV deuteron beam supplied by the RIKEN K70 AVF cyclotron. These tracers were chemically separated from the target materials by means of anion exchange chromatography and stored in 1 M HCl solution. The solution of radiotracers of ^{88}Zr and ^{175}Hf in tracer-scale, or $MOCl_2 \cdot 8H_2O$ (M=Zr, Hf) water solution mixed the tracer solution in the macro-scale, was infiltrated into a carbon filter plugged into the chlorination part (see Fig. 1). Oxychlorides of Zr and Hf were converted tooxide flushing air at 650℃, and then the oxides were converted to tetrachlorides with carbon tetrachloride at 500－600℃ in He gas. The formed tetrachlorides of Zr and Hf were collected on a carbon filter at the MCl_4 part. Then, $ZrCl_4$ and $HfCl_4$ evaporated at 400℃ and passed through an isothermal column (φ4.0 mm i.d. and 30 cm long) at various temperatures (macro-scale: 80, 100, 125, and 140℃, tracer-scale: 140, 150, 160, and 170℃). Cumulative yields of the volatile species passing through the column and collecting at the cooling part were obtained through γ-ray measurement.

Figure 2 shows the dependence of the yields of Zr and Hf on the temperature of the isothermal column for 4.5 min of collection time in the macro- and tracer-scale. In the macro-scale (ca.10^{18} molecules) the adsorption enthalpies of $ZrCl_4$ and $HfCl_4$ were considerd to be –82.8 and –78.4 kJ mol^{-1}, respectively. The relationship between these adsorption enthalpies is in agreement with the relationship expected from the vapor pressure curves.

On the other hand, the adsorption enthalpies of Zr and Hf tracer-scale (ca.10^{10} molecules) were –93.0 and –93.1 kJ mol^{-1}, respectively, which differ from those at the macro-scale. In the macro-scale, $ZrCl_4$ and $HfCl_4$ cover the column surface, and interact with the same chemical species. In contrast, in the tracer-scale, the volatile compounds adsorbed on the quartz surface, and the strengths of interaction were almost the same for Zr and Hf. Because the retention time of chlorides of Zr and Hf chloride in the tracer-scale are smaller than those in the macro-scale, tetrachloride is subjected to strong interactions by the quartz surface.

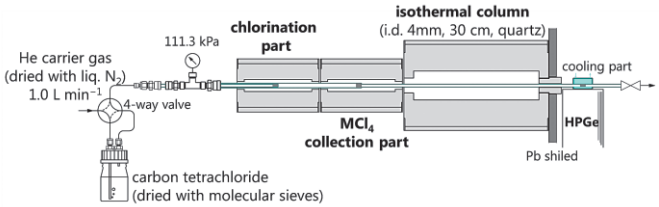

Fig. 1. Schematic view of the experimental set-up for off-line isothermal gas-chromatography of $ZrCl_4$ and $HfCl_4$.

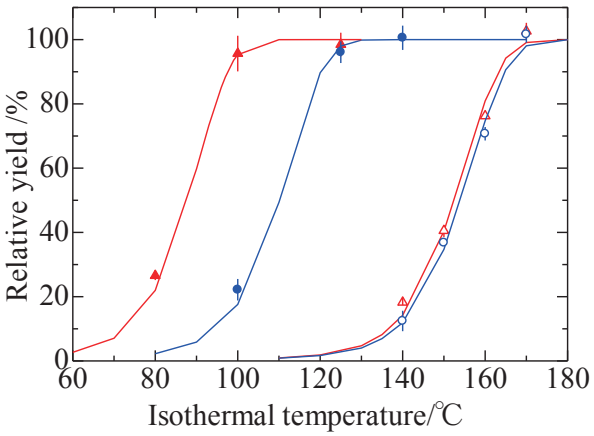

Fig. 2. Yields of Zr and Hf as a function of isothermal temperature. Circles and triangles show Zr and Hf, respectively. Close and open symbols show macro- and tracer-scale, respectively. Curves indicate results of Monte Carlo simulation.[4]

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References

1) B. Kadkhodayan et al., Radiochim. Acta **72**, 169 (1996).
2) A. Türler et al., J. Alloys Compd. **271**, 287 (1998).
3) R. P. Tangri, D. K. Bose., Thermochimica Acta **244**, 249 (1994).
4) I. Zvára., Radiochim. Acta **38**, 95 (1985).