Effect of temperature on the separation of hydrogen isotopes using Pd-Pt alloy on α-alumina

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1. Introduction

The separation of hydrogen isotopes in heavy water-cooled reactors and nuclear fusion plants has been an important topic. K. Watanabe et al. studied a chromatographic separation of hydrogen isotopes for a Pd-Pt alloy made by an argon arc melting and showed that a simple chromatographic process could be possible without any replacement gas when using a Pd-Pt alloy. This method was called a 'self-developing gas chromatography', SDGC [1]. The advantages of a Pd-Pt alloy are that it does not need any replacement gas and the operation condition is milder than when pure Pd metal is used. Because the equilibrium pressures of the hydrogen isotopes increase with an increasing Pt content due to a decrease of the heat of absorption in the alloys.

The effect of an operating condition during the process was studied systematically [2], in which a moderate operation temperature, a high carrier gas pressure and a slow flow rate may be necessary to achieve a good separation. There was an attempt to reduce precious Pd-Pt alloy during the process by the deposition of Pd-Pt alloy on α-alumina powder without a decrease of the separation efficiency. According to the results, only 0.35g of Pd-Pt alloy on α-alumina powder was needed to give a good separation efficiency which result could be attainable in the case of 1.5g of Pd-Pt alloy powder. Recently the practical application of Pd-Pt alloy to a self developing gas chromatography process was studied for the purpose of a tritium extraction.

The preparation of Pd-Pt alloy on α-alumina powder was accomplished by a barrel sputtering system. But the loading of Pd-Pt alloy onto α-alumina was so low in this method that only 0.04 g of Pd-Pt alloy was included in the 5g sample. A high loading of a Pd-Pt alloy onto α-alumina powder was attempted in our study. For the purpose, an impregnation and a simultaneous alcohol reduction method was selected, which was successfully applied in the formation of Au-Pd alloy on an alumina support. And then samples of 6 wt%, 17wt%, and 29wt% Pd-Pt alloy on α-alumina were manufactured in our study [3]. This paper deals with the characteristics of the hydrogen isotope separation using the produced materials. Especially, the separation behavior for a H_2-D_2 mixture gas during the SDGC process is discussed in terms of an operating temperature.

2. Experiment

2.1 Materials

The gases used were H_2, D_2, a 29.2% D_2-H_2 mixture gas as a sample gas, and Ar as a carrier gas. The α-alumina used as a support for the Pd-Pt alloy was purchased from Aldrich, and the particle size was a 100 mesh. Three loadings (6wt%, 17wt%, and 29wt%) of a Pd-Pt alloy (5wt% Pt content) onto α-alumina (denotes as PPA) were used as column materials, which were prepared by using a simultaneous alcohol reduction method. A precise preparation method and its characterization have been described in a previous paper [3]. The chromatographic column was not only filled with PPA but also with Cu powder. The PPA particles were dispersed by Cu powder which reduced the amount of expensive noble metal alloy and enhanced the thermal conduction of the packing materials. The Cu powder used had a 40-100 mesh size and its purity was 99.5%.

The chromatographic column used was a stainless steel tube of 3m in length and 3mm in diameter. A column named PPA1 was made. PPA1 was packed with 8.82g of 17wt% PPA and 13.49g of Cu. The net weight of the Pd-Pt alloy loaded was about 1.5 g.

2.2 Apparatus and Procedures

The hydrogen isotope separation system used was illustrated in a previous paper [3]. The system was composed of a chromatographic column, an electric chamber, a sample loop, an automated six-valve, a thermal conductivity detector (TCD), a sample gas inlet, and some gas reservoirs. A sample gas was introduced into the sample loop. A carrier gas was flowing through the chromatographic column, which was in the electric chamber to sustain a constant temperature. The sample gas in the loop could be injected into the column by a reaction of the automated six-valve. The thermal conductivity of an exit gas was measured by TCD.

After setting up a PPA column, the column was first activated by a heating at 523 K for 2 hr in a flow of Ar gas to remove volatile impurities such as adsorbed water. Next, the column was cooled down to the required test temperature. The Ar gas as a carrier gas was passed through the column at a constant flow rate, 10 cc/min. The sample gas used was a 29.2% D_2-H_2 mixture gas. The sample loop was sustained at an atmospheric pressure. The volume of the sample loop was 45.1 cc. The equivalent molar mass was about 2.01 mmol at an atmospheric pressure in the sample loop of 45.1 cc.

After a run, the column was reactivated by heating it at 523 K for 2hr in an Ar flow of 10 cc/min.

The outlet line of the chromatographic system was connected to a sampling line of a quadruple mass spectrometer (QMS). The pressure of the QMS chamber was set at 1×10^{-7} torr. The relative sensitivities of the mass spectrometer for H_2, HD, and D_2 had already been determined.

3. Results and Discussion

3.1 TCD chromatograms

Figure 2 shows the effects of the temperature on the TCD chromatograms for the 29.2% D_2-H_2 mixture using the PPA1 column. The flow-rate of the carrier gas and the amount of sample gas were adjusted to 10 cc/min and 2.01 mmol respectively. The Y-axis shows the TCD intensity and the X-axis shows the retention time in a logarithmic scale. The retention time of the sample gas was considerably decreased with an increase of the operating temperature. But the shape of the TCD chromatogram was almost unchanged with the temperature.
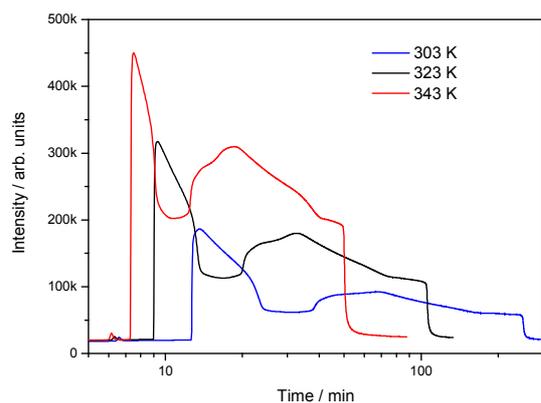
Figure 1. Effects of a temperature on the TCD Chromatograms for the 29.2% D_2-H_2 mixture using the PPA1 column: flow rate = 10 cc/min, sample gas = 2.01 mmol.

3.2 QMS Chromatograms

The QMS chromatograms were re-plotted into H and D intensities. Figure 2 shows the hydrogen and deuterium recovery chromatograms of the PPA1 column for the 29.2% D_2-H_2 mixture with different column temperatures. The chromatograms in Figure 2 correspond to the TCD chromatograms in Figure 1. It was easier to understand the hydrogen and deuterium separation behaviors in this modified QMS chromatograms.
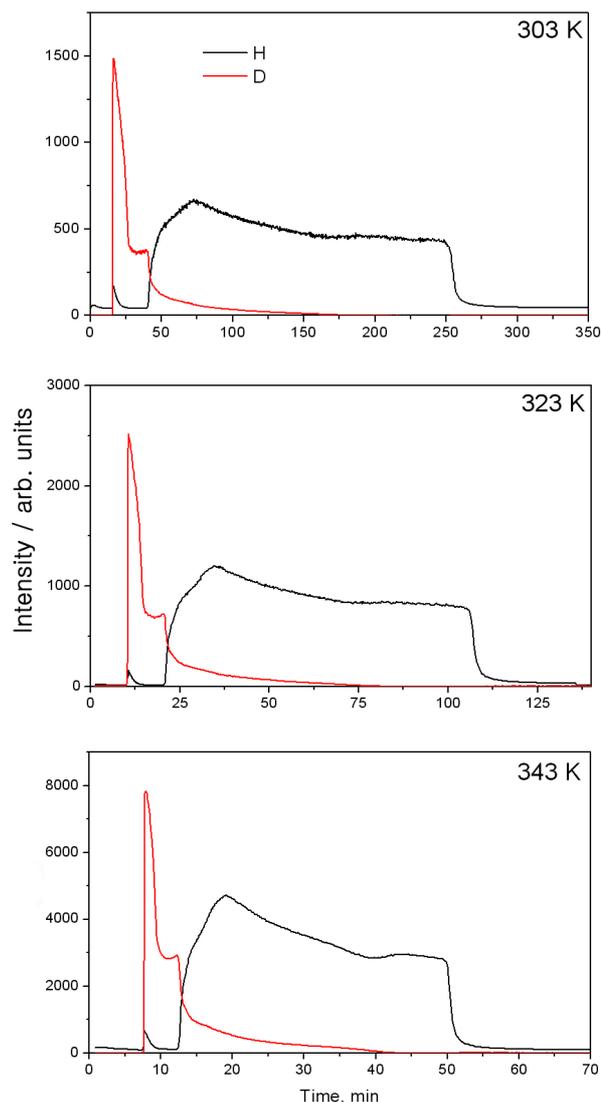
Figure 2. Hydrogen and deuterium recovery chromatograms of the PPA1 column for the 29.2% D_2-H_2 mixture with different column temperatures: flow rate = 10 cc/min, sample gas = 2.01 mmol.

In Figure 2, only the retention time was reduced with an increase of the operating temperature, and no other clear differences were observed. Therefore precise analysis was needed for the results.

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