Evaluation of Pd-Pt alloy on Alumina for the Hydrogen Isotopes Separation

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1. Introduction

Pd-Pt (Palladium-platinum) alloys have been reported as more effective column materials than pure Pd for a hydrogen isotope separation. 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. The reason for this is that 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 [1, 2].

B. Pawelec et al. reported that a simultaneous reduction of palladium and gold precursors by ethanol in the presence of PVP (polyvinylpyrrolidone) was useful for creating a Au-Pd cluster on an alumina support and the sample prepared by the reduction method showed an enhanced activity and relatively large alloy particles in a comparison with the classical incipient wetness co-impregnation method [3].

On the basis of the above reports, the manufacturing of Pd-Pt alloy on alumina has been attempted by using an impregnation method in the presence of ethanol and PVP. The produced materials were packed into a GC column and tested for their separation behavior of the hydrogen isotopes in this work.

2. Experiment

The Pd-Pt alloy (PPA) on alumina, which was prepared by impregnation and simultaneous reduction method, was subjected to test for their separation behavior of the hydrogen isotopes

2.1 Gas chromatography of hydrogen isotopes

To evaluate the performance of the PPA for the separation of hydrogen isotopes, a gas chromatographic column was prepared. The column used was a stainless steel tube of 3m in length and 3mm in inner diameter which was filled with a mixture of PPA and Cu powder. The net weight of the loaded Pd was about 1.5 g. The Cu powder used had a 40-100 mesh size and its purity was 99.5%. The PPA particles were dispersed by Cu powder which reduced the amount of expensive noble metal alloys and enhanced the thermal conduction of the packing materials.

The chromatographic system used is illustrated in Figure 1. The effluent gas from an outlet line was introduced into an orifice nozzle which is part of a sampling line for a quadruple mass spectrometer (QMS).

The prepared column was placed in the GC system, and then a thermal treatment was performed at 523 K for 2 hr in a flow of Ar gas to remove the adsorbed volatile impurities from the packing materials. Next, the column was cooled down to the required test temperature and Ar gas as a carrier gas was passed through the column line at a flow rate of 10 cc/min. The sample gases used were H_2, D_2, and a 29.2% D_2-H_2 gas mixture. The chromatograms for H_2, D_2, and the mixed gas were observed under given conditions. The amount of sample gas was about 2.01 mmol at an atmospheric pressure. After a test run, the column was reactivated by heating it at 523 K for 2hr in an Ar flow of 10 cc/min.

The effluent gas from the GC system was directed into a quadruple mass spectrometer to analyze the composition of the effluent gas. The H_2, HD, and D_2 fractions in effluent gas were determined from the QMS information of the molar mass.
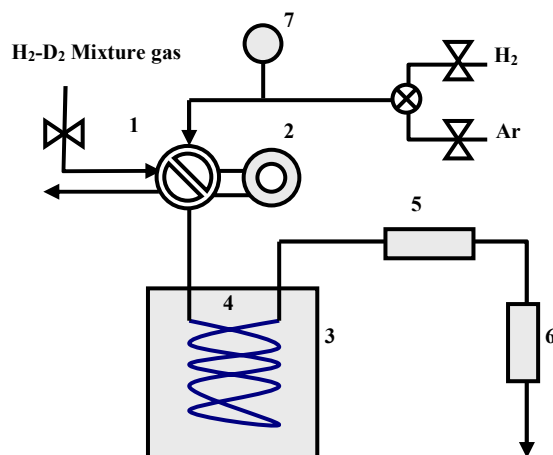

Figure 1. Schematic diagram of the gas chromatograph system for the hydrogen isotope separation; 1. Automated six valve, 2. Sample loop, 3. Electric chamber, 4. GC column, 5. TCD, 6. Flow meter, 7. Pressure gauge.

3. Results and Conclusion

3.1 Chromatograms of the Isotopes Separation

The chromatographic system shown in Figure 2 was equipped with a 17 wt% Pd-PPA packed column. Also the separation of the 29.2% D_2-H_2 gas mixture was investigated by using the column. Typical example of the chromatograms from the TCD detector is shown in Figure 2. The vertical axis is the intensity of the TCD signal which is proportional to the amount of hydrogen gas, and the horizontal axis is the retention time from an

injection of the D_2-H_2 gas mixture. The first peak (Peak I) appeared at about 12 min. Peak I increased sharply and then dropped rapidly during a period of 15 min. The second peak (Peak II) was developed before Peak I dropped to a ground intensity at about 30 min. Peak II was not sharp like Peak I, but showed a very broad band shape which lasted for about 200 min. Peak II dropped rapidly at about 240 min. This chromatographic appearance was reproducible in the repeated test. A small peak before Peak I was detected which was an unintended air peak that was introduced into the chromatographic system during the operation of an automated six-valve. It seems that Peaks I and II were due to the D_2 and H_2 gas respectively by considering the size of their peak areas.
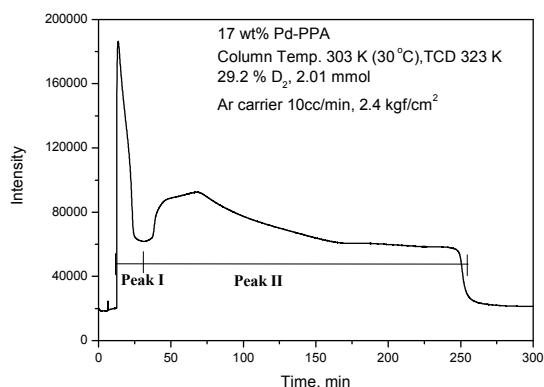

Figure 2. Gas chromatogram for the H2-D2 gas Mixture using 17 wt% Pd- PPA at 303 K, read from the TCD.

3.2 QMS Analysis of the Chromatograms

The TCD could not resolve the signal of the effluent gas into the D_2, HD, and H_2 components. But it was possible when the effluent gas was introduced into the QMS system. Thus the effluent gas from the GC system was analyzed in the QMS system. Figure 3 shows the output of the chromatogram from the QMS in which the effluent gas was divided into the H_2, HD, and D_2 components. The superposition of each peak in Figure 3 was almost the same in appearance with the TCD result in Figure 2. The D_2 peak appeared at first and then the H_2 peak followed. The D_2 peak was intensive and sharp in comparison with the H_2 peak, and it did not drop directly to a ground intensity from the top of the peak. The D_2 peak was sustained at a constant intensity for some time, and then it dropped to a ground intensity simultaneously with a development of the H_2 and HD peaks. The HD peak appeared twice when the D_2 and H_2 peaks occurred. The HD peak below the D_2 peak seemed to be due to the residual hydrogen atoms in the GC column because the HD peak area was decreased with an increase of the activation temperature and the treatment time of the GC column before a test run. The development of a HD peak below the H_2 peak was inevitable in the repeated tests even though a sufficient

activation was performed. The development of the second HD peak was reasoned from the fact that the D_2 may proceed more rapidly with regards to the H_2 in the column at the initial stage and so some part of the D_2 may be absorbed into the latter part of the column material during the initial stages. Then the latter H_2 arrives at the latter part, and the absorbed Deuterium may be exchanged with some part of the H_2 and thus HD was developed and flowed out together with the H_2.
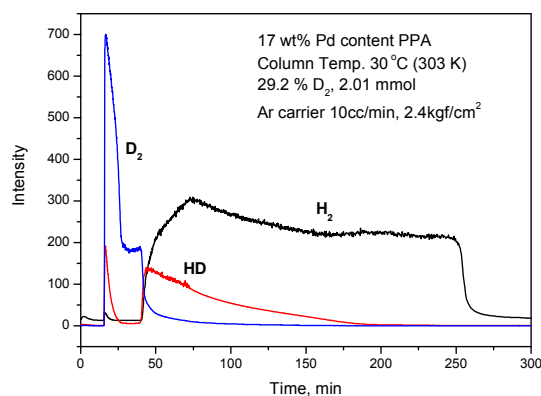

Figure 3. QMS chromatogram for the 29.2% D2-H2 gas Mixture using a 17 wt% Pd-PPA at 303 K..

Consequently, it was concluded that PPA could be made by an impregnation and alcohol reduction method, and successfully applied to the separation of mixed hydrogen isotopes. The separation performance of the PPA was in good agreement with a previously reported Pd-Pt alloy by an arc melting or barrel sputtering method. This process seems to be a promising technique for a mass production of Pd-Pt alloy on alumina.

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