

論文

室温作動型水素同位体分離用 ガスクロマトグラフの開発(I) —パラジウムの利用と担体の影響—

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Development of Gas Chromatograph for Hydrogen
Isotope Separation Working at Room Temperature (I)

—Application of Palladium and Effects
of Supporting Materials—

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Abstract

Conventional gas chromatographic separation of hydrogen isotopes is based on the isotope effect on physical adsorption. It inevitably requires low working temperature, for example liquid nitrogen temperature. On the other hand, hydrogen isotopes are easily absorbed by palladium with considerable isotope effects at moderately high temperatures. This property is useful for gas chromatographic separation of hydrogen isotopes around room temperature. One problem of this application is the effects of supporting materials of Pd. The supporting materials often severely interfere with the isotope separation. In this study, Al_2O_3 was selected as a model of supporting materials. Its effect on the separation of hydrogen and deuterium from a 50% H_2 -50% D_2

mixture gas was examined and compared with support-free Pd.

Pd/Al₂O₃ packed columns showed very poor separation above room temperature, whereas considerably better results were obtained by the support-free Pd. Thermal desorption study on the adsorption and desorption of deuterium for those materials revealed that the Al₂O₃-support acts as a sink of deuterium atoms spilled from the Pd surface by forming adsorbed water, HDO(a), and hydroxyl group, OD(a) with exchange reactions of residual H₂O(a) and/or OH(a). As a consequence, the isotope effect on the adsorption or absorption of hydrogen isotopes by Pd was obscured by isotope effects of the exchange reactions, leading to the poor separation. This study revealed the importance of hydrophilic supporting materials for the development of gas chromatographs for hydrogen isotope separation work at room temperature or above.

1. Introduction

An increasing large amount of tritium has become to be used recently for a variety of chemical and physical studies as well as the research and development of safe handling techniques of a vast amount of tritium in thermonuclear fusion devices. One of the most important problems in those studies is tritium recovery, purification and isotope separation. A variety of isotope separation techniques has been developed so far for this purpose¹.

Gas chromatography is one of the promising methods because of its simple operation principle, simple construction of the device, considerably high separation factor, small tritium inventory and ease in operation. The conventional gas chromatographic separation of tritium, however, is based on the isotope effect on physical adsorption of hydrogen isotopes over porous adsorbents and hence requires low temperature around 78K². This gives rise to a problem for its use in small scale glove boxes because of evolution of a relatively large amount of nitrogen gas in a small volume.

Not only to improve this point but also to scale up those devices, the replacement chromatography with Pd has been studied first by Glueckauf and Kitt³, and developed in the last two decades^{4, 5, 6, 7}, because Pd shows large isotope effects on both the absorption and hydride formation at relatively high temperatures⁸. It is known, however, that the apparent separation factor depends very much on the surface conditions of Pd which is usually supported by various kinds of oxide powders. To examine effects of those supporting materials and mechanisms of reactions occurring on those surfaces, we have studied adsorption and/or desorption characteristics of deuterium on Pd supported by Al₂O₃. The characteristics were compared with support-free Pd-

powder, which was only mechanically mixed with Cu-powder.

2. Experimental

2. 1. Materials

Palladium supported by Al_2O_3 with 0.16 cm diameter was delivered from Nikki Universal Co. To prepare this material, $\text{Pd}(\text{NO}_3)_2$ was dissolved in water, in which Al_2O_3 powder was suspended. The absolute density and surface area of Al_2O_3 were 0.47 g/cm^3 and $190 \text{ m}^2/\text{g}$, respectively. Subsequently, the solution was heated at 423K for one hour to evaporate the water. After drying and sintering of the powder at 723 K for one hour in the air, it was reduced by hydrogen in a mixture gas of 30% H_2 -70% N_2 . The fraction of Pd on the Al_2O_3 powder was 2 wt%.

It was grounded with a mortar and a pestle, and the grains above 60 mesh were sieved for use. Powder of pure Pd was purchased from Furuchi Chemicals Co. Its size was below 100 mesh. The purity was guaranteed as 99.99%. It was used as a mixture with copper powder of 40-80 mesh. Those powders were used as samples in the present study and will be denoted below as Pd/ Al_2O_3 and Pd/Cu, respectively.

Deuterium, a mixture of 50% D_2 -50% H_2 and Ar gases were purchased from Nihon Sanso Co. Their purities were guaranteed above 99.6, 99.9 and 99.9995%, respectively. Argon was used as carrier gas for gas chromatography.

2. 2. Adsorption and desorption measurements

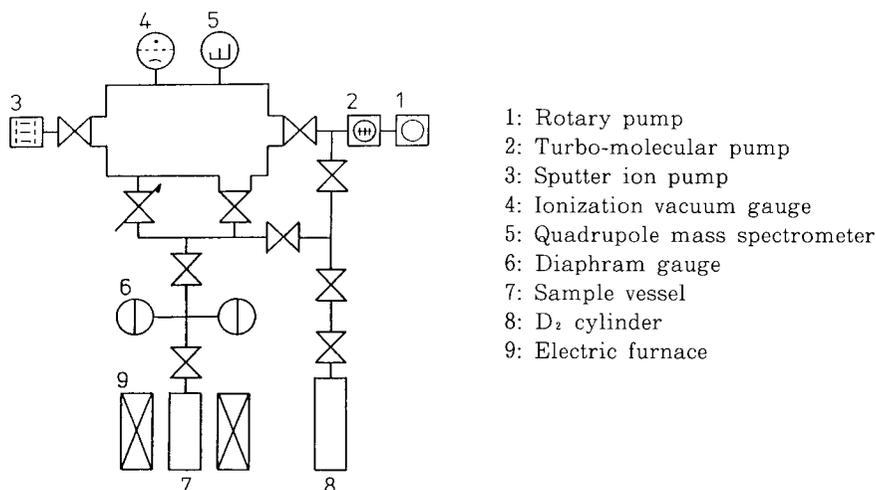


Fig. 1. Schematic diagram of the apparatus used for measuring adsorption and desorption of deuterium.

Figure 1 shows the schematic diagram of the apparatus used for measuring absorption and desorption of deuterium by Pd/Al₂O₃ and Pd/Cu. It was equipped with a vacuum gauge, a quadrupole mass spectrometer and two capacitance manometers (MKS Baratron of type 390HA-01000SP05 and 390HA-00001SP05). The system could be evacuated down to 1×10^{-7} Torr with a sputter-ion pump and a turbomolecular pump backed with an oil-sealed rotary pump.

The sample powder, Pd/Al₂O₃ or Pd/Cu, of 16 mg was set in the sample tube made of quartz glass and degassed to 5×10^{-7} Torr at given temperatures. It was exposed to D₂ of 6.95 Torr for 2 hours at room temperature. After pumping out of the gas, the sample was heated to 1123K to measure a thermal desorption spectrum. Desorbed gas species were measured with the quadrupole mass spectrometer.

2. 3. Gas chromatographic separation

Two chromatograph systems were used. Their schematic diagrams are shown in Figs. 2 and 3. They will be denoted below as GC-1 and GC-2, respectively. The main systems of them consisted of a separation column, a heat reservoir with heating or cooling devices, a sample gas inlet and a carrier gas reservoir. They were connected with stainless tubes. The main system was connected to an ultra-high vacuum system equipped with a quadrupole mass spectrometer. A part of the effluent gas from the end of the column was introduced into the vacuum system and analyzed with the mass spectrometer.

The sample powder packed in the column was first processed by heating at 523K in a flow of Ar-carrier gas at a rate of 10 cm³/min for 2 hours to remove adsorbed water and others. Subsequently, the column was cooled to a given operation temperature with flowing the carrier gas before each

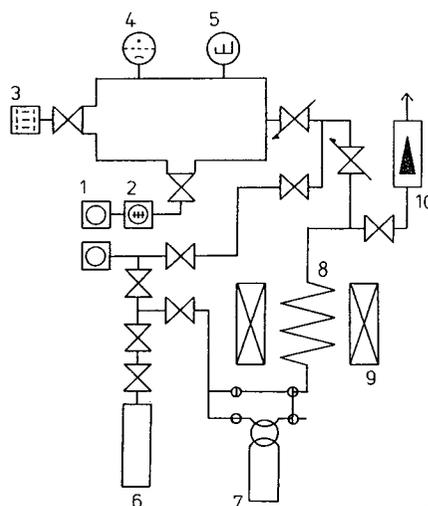


Fig. 2. Schematic diagram of gas chromatograph for hydrogen isotope separation.(GC-1)

- 1: Rotary pump
- 2: Turbo-molecular pump
- 3: Sputter ion pump
- 4: Ionization vacuum gauge
- 5: Quadrupole mass spectrometer
- 6: Ar cylinder
- 7: Sample vessel
- 8: Separation column
- 9: Electric furnace
- 10: Flow meter

Gas Chromatographic Hydrogen Isotope Separation

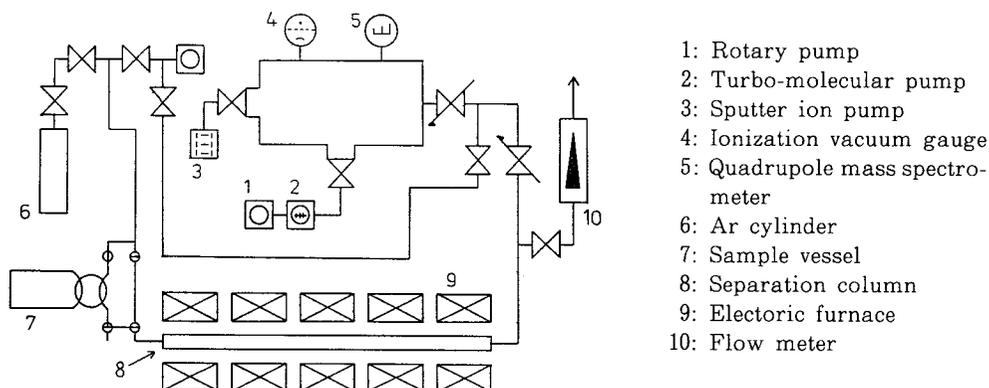


Fig. 3. Schematic diagram of gas chromatograph for hydrogen isotope separation.(GC-2)

run of the separation experiments. During this procedure, the variable leak valve was set to introduce a part of the effluent gas into the vacuum chamber at a pressure of 1.6×10^{-6} Torr. Lastly, the gas mixture of H_2 - D_2 was introduced into the column, where the amount of the sample gas was varied in a range from 0.26 to 2.35 mmol. The column temperature and the flow rate were 343K and $10 \text{ cm}^3/\text{min}$, respectively. The chromatogram was recorded using the mass spectrometer, whose relative sensitivities for H_2 , HD and D_2 were determined beforehand. On those measurements, GC-1 was used for Pd/ Al_2O_3 with a glass column of 0.34 cm inner diameter and 200 cm length packed with 8 g of the sample. Concerning GC-2, chromatograms were measured using a stainless steel column of 0.42 cm inner diameter and 200 cm length packed with the Pd/Cu powder, which is a mixture of 1.28 g of Pd and 75.4 g of Cu.

3. Results and discussion

3. 1. Absorption and desorption characteristics

Figure 4 shows an example of thermal desorption spectra observed for Pd/ Al_2O_3 after the exposure to D_2 at 6.95 Torr for 2 hours at room temperature. The sample had been degassed at 523K for 2 hours. It is seen in this figure that the desorbed gas species were isotopic hydrogen and water. However, no desorption of deuterium molecules took place. The amounts of desorbed waters were considerably greater than those of isotopic hydrogen molecules. One can also see that the number of desorbed hydrogen atoms was greater than that of desorbed deuterium atoms in both hydrogen isotope molecules and isotopic waters.

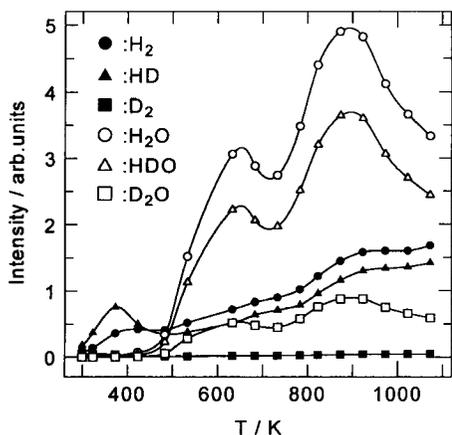


Fig. 4. Thermal desorption spectra for Pd /Al₂O₃ out-gassed at 523K and exposed to deuterium at room temperature.

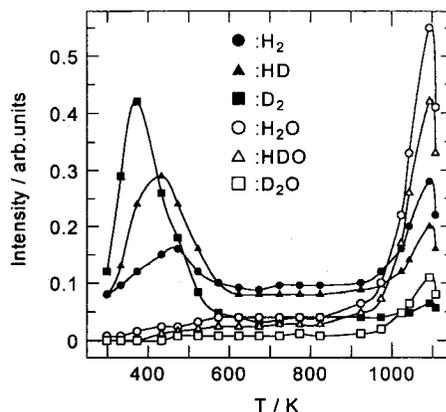


Fig. 5. Thermal desorption spectra for Pd /Al₂O₃ out-gassed at 1073K and exposed to deuterium at room temperature.

Concerning hydrogen isotope molecules, H₂ and HD showed a small peak at about 400K. They gradually increased their desorption rates to form dull peaks at about 900K. On the other hand, no desorption peak appeared for D₂. Most of hydrogen atoms, however, appeared in the form of water. Isotopic waters showed the first peak at about 600K and the second peak at about 900K. Those results indicate that a fairly large amount of hydrogen atoms was present on the surface. They desorbed from the sample during the temperature rise as H₂ and H₂O, or HD and HDO through isotope exchange reactions.

The desorption spectra shown in Fig. 5 were observed for the sample out-gassed at 1073K for 2 hours. The exposure conditions of deuterium were the same as those for the case of 523K out-gassing. Noticeable changes were observed by the out-gassing at the elevated temperature. One was the disappearance of the desorption peaks of isotopic waters at about 600 and 900K, which appeared in Fig. 4. Consequently, the amounts of desorption of water decreased to about 1/40 of the results shown in Fig. 4. The desorption peaks of isotopic waters appeared only above 1000K. On the other hand, isotopic hydrogen molecules did not show significant changes in the desorption amounts from the results shown in Fig. 4. The order of the desorption amounts, however, was reversed as D₂>HD>H₂. Namely, most of the adsorbed deuterium desorbed as D₂ and HD.

Figure 6 shows thermal desorption spectra for the Pd/Cu sample consisting of 16 mg and 26 mg of Pd and Cu powders, respectively. It was first degassed at 523K for

1 hour. After being cooled to room temperature, it was exposed to D_2 at 100.5 Torr for 40 min at room temperature. This figure remarkably differs from those shown in Figs. 5 and 6. Namely, desorbed gases were almost hydrogen isotopes. Only a trace amount of H_2O was desorbed around at 650 K. Among three hydrogen isotope molecules, the desorption of H_2 was most significant. It made three desorption peaks, at 350, 600, and 900K. The most intense peak was at 600K. The secondly intense peak was at 900K and the peak at 350K is the weakest.

A reason of the significant desorption of hydrogen is considered due that hydrogen had been absorbed by Pd during its preparation processes and the out gassing of it was insufficient in the gassing of it was insufficient in the present experimental conditions. A similar feature was also observed for D_2 , although the amount of desorption was considerably smaller than that of H_2 . This was because the absorbed amount of deuterium was fairly small in comparison with the amount of hydrogen which had been dissolved. Although details of the mechanisms of forming three desorption peaks are under investigation, above mentioned results clearly indicate that the desorption of water appeared in the previous two figures is due to Al_2O_3 in Pd/ Al_2O_3 samples.

It is well known that alumina absorbs water vapor and the adsorbed water exists as molecule, $H_2O(a)$, and/or hydroxyl group, $OH(a)$, on the surface⁹. Vacuum heating of this material causes to desorb those adsorbates. Suppose that the out-gassing of the Pd/ Al_2O_3 sample is insufficient and there remains a large number of $H_2O(a)$ and $OH(a)$ on the support surface. If deuterium molecules were adsorbed as atoms by Pd particles, they will spill over to the alumina surface. Furthermore, they will undergo isotope exchange reactions with $H_2O(a)$ to form $HDO(a)$. Adsorbed water molecules are usually mobile on the surface at room temperature. Hence, $HDO(a)$ can move to the sites of $OH(a)$ and undergoes an exchange reaction with $OH(a)$ to form $OD(a)$. Those reactions could be expressed as

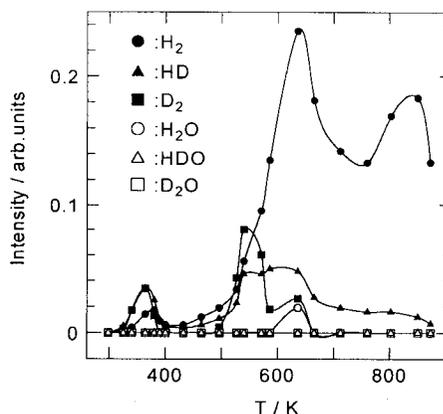
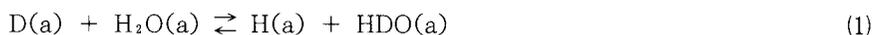


Fig. 6. Thermal desorption spectra for Pd/Cu out-gassed at 523K and exposed to deuterium at room temperature.

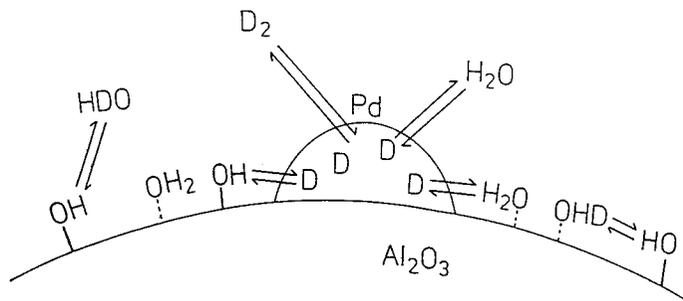
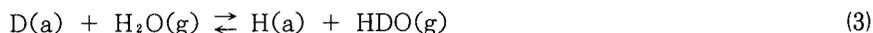


Fig.7. A model of isotope exchange reaction on the surface of Pd/Al₂O₃.

Those processes are schematically drawn in Fig. 7.

It is also plausible that the isotope exchange arises from reactions through gaseous water¹⁰. Namely, a deuterium atom on the Pd surface will be exchanged with a hydrogen atom of water molecule as



This deuterated water molecule will play a role of deuterium carrier as



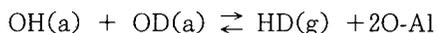
Subsequent heating of this material in vacuum to measure thermal desorption spectra could result in the desorption of water molecules from HDO(a) and OD(a) as



This appears to be a plausible mechanism of the desorption peaks of isotopic waters in Fig. 4.

The higher temperature out-gassing of the sample is expected to cause more complete desorption of H₂O(a) and OH(a)^{9, 10}. It is expected that there is no adsorbed water, H₂O(a), but could be a small number of OH(a)^{9, 10}. In this case, deuterium atoms formed on the Pd-particles hardly migrate to the support surface, because there is no deuterium carrier such as adsorbed water. Accordingly, diffusion of deuterium atoms is expected to be very slow. Consequently, adsorption of deuterium atoms by the support, Al₂O₃, should be very minor. This appears to be a plausible explanation of the disappearance of the desorption peaks of isotopic waters in the thermal desorption spectra shown in Fig. 6. On account of the above consideration, the desorption peaks of hydrogen isotope molecules around 400K arise from the hydrogen isotope

atoms absorbed or dissolved by Pd-particles. Therefore, the total desorption amounts of hydrogen isotope molecules were nearly equivalent between the samples out-gassed at 523K and 1073K. This is also consistent with the fairly weak bonding between hydrogen and palladium atoms. Concerning the desorption peaks of H₂ and HD at high temperatures observed in Fig.5, it appears that the reaction as



took place.

3. 2. Chromatographic separation

The sample of Pd/Al₂O₃ was out-gassed at 1073K and packed in the glass column. After processing the column as mentioned in the experimental section, 0.44 mmol of the sample gas, 50%H₂-50%D₂ mixture, was introduced as a pulse into the column at one time. The column temperature was 343K, and the flow rate of the carrier gas was 10 cm³/min. The introduction of the sample gas will be denoted below as a run. Initially, no efflux of hydrogen isotopes appeared in the effluent carrier gas. Hydrogen isotopes appeared only after repeating five runs. This indicates that the sample gas amounting to about 1.8 mmol was captured by the Pd/Al₂O₃ in those runs. As mentioned above, hydrogen isotope atoms could be spilled over to the Al₂O₃ area and captured by forming H₂O(a) as well as OH(a). They could not be easily desorbed from the surface. Consequently, no efflux of hydrogen isotopes took place in this case.

Chromatograms of hydrogen isotopes were observed only after this stage. At this stage, the support area is considered to be saturated with H₂O(a) and OH(a). Then, the excess of hydrogen atoms formed by Pd-particles could be desorbed from the material. Figure 8 shows the chromatograms by Pd/Al₂O₃ observed at the 18th run. Deuterium gas appeared first and hydrogen did last. The chromatograms of D₂ and HD showed rather sharp peaks, but they were accompanied by tails. Contrarily, H₂ gave a flat-top chromatogram. Those results suggest the existence of different mechanisms of forming a chromatogram of a given molecule species. The separation of three isotope molecules was poor.

On account of the relative sensitivity of the mass spectrometer for H₂, HD and D₂, the isotope ratio was evaluated as H₂: HD: D₂=1: 0.38: 0.25. Namely, the abundance ratio between H and D in the effluent was H: D=1: 0.37, which differed considerably from the 1: 1 ratio of the sample gas. It indicates that a part of deuterium still spilled over to the surface of Al₂O₃ and was captured there.

Considerably different behavior was observed for the support-free Pd/Cu sample. This column gave efflux of hydrogen isotopes introduced by the pulse of the sample gas from the first run. There was no evidence of capturing of the sample gas by the Pd and Cu powders. Figure 9 is an example of chromatograms by Pd/Cu. A pulse of the sample gas amounted to 2.35 mmol for this column. The column temperature was 343K, and the flow rate of the carrier gas was 10cm³/min. A deuterium rich gas flowed out first and then a hydrogen rich one appeared subsequently. The chromatogram of D₂ made a sharp peak. That of HD also showed a peak but was accompanied by a long tail. With respect to H₂, there appeared a shoulder and a peak, and they formed a broad chromatogram. This indicates that two different mechanisms play roles for the chromatogram of H₂. It is considered that those mechanisms are also valid for the formation of chrom for the formation of chromatograms of D₂ and HD.

There were some similarities on those characteristics to the results for Pd/Al₂O₃ as seen in Fig. 8, but the separation is much better in this case. In the elapsed time of 700 sec, in which 75% of D₂ flowed out, deuterium concentration in the effluent gas

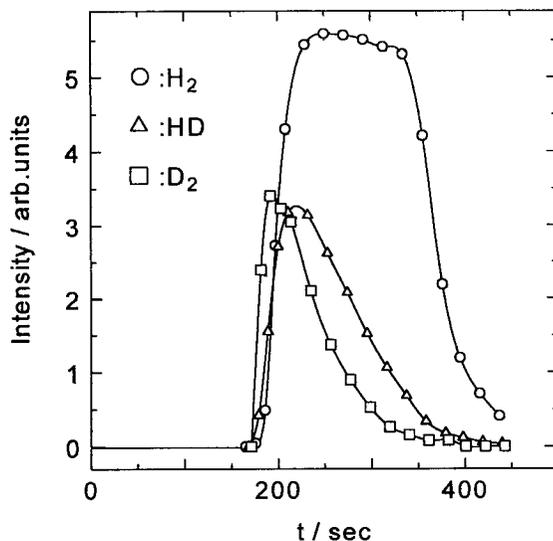


Fig. 8. Separation of hydrogen isotopes by Pd/Al₂O₃: column temperature=343K, flow rate=10 cm³/min, amount of the sample gas=0.44 mmol.

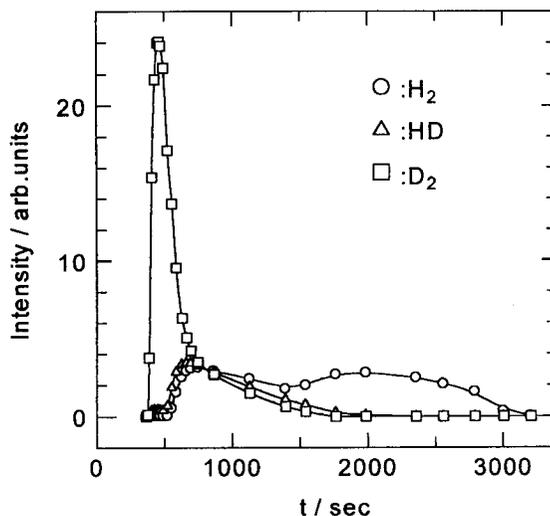


Fig. 9. Separation of hydrogen isotopes by Pd/Cu: The column temperature=343K, flow rate=10cm³/min, amount of the sample gas=2.35 mmol.

was 85.0%. The concentration of hydrogen was 81.5% after the elapsed time of 1100 sec, in which 75% of H_2 flowed out. In addition, the ratio among the effluent isotope molecules was $H_2 : HD : D_2 = 1 : 0.42 : 1.01$, which corresponds to the atomic ratio of $H : D = 1 : 1$.

The use or non-use of hydrophobic support, Al_2O_3 , is considered to play an important role for the different characteristics of the chromatograms between Pd/Al_2O_3 and Pd/Cu samples. As described above, the hydrophobic support acts as sink of deuterium and source of hydrogen atoms. It also provides sites for isotopic exchange reactions. When Pd/Al_2O_3 is packed in the separation column, hydrogen atoms produced by Pd -particles would migrate to the support area and undergo isotope exchange reactions or be captured. Those processes are schematically drawn in Fig. 7.

In the presence of $H_2O(a)$ or $OH(a)$ on the material packed in the separation column, chromatographic separation would arise from the isotope effects on not only H - Pd bonding but also H - O bonding. If the isotope exchange reaction between D_2 and $H_2O(a)$, or between D_2 and $OH(a)$ plays a predominant role, the separation should be poorer than the case that hydrogen absorption by Pd plays the role. This is because the isotope effects on H - O bonding is much smaller than H - Pd bonding^{1, 12}.

4. Conclusions

It is worthwhile to note that the present observations are not due to the usual replacement chromatography for hydrogen isotope separation by Pd packed columns. Namely, no hydrogen was introduced into the column as replacement gas after the sample gas charge. The absorbed hydrogen isotopes appear to develop themselves in the column. Details in mechanisms of the self-developed chromatography are under investigation and will be reported in near future.

The present study revealed that the support-free palladium could separate hydrogen and deuterium above room temperature, without introducing hydrogen into the column as replacement gas after sample gas charge. This suggests that the chromatographic hydrogen isotope separation could be possible with more simple system and operations than the conventional replacement chromatography developed so far. To improve this method, it appears important to develop palladium particles with large surface area. But, palladium supported by Al_2O_3 could hardly separate them. This is concluded to be due to the hydrophobic nature of Al_2O_3 , where molecular water and hydroxyl group can be easily formed by hydrogen isotope atoms spilled from Pd -particles. They act as a carrier and a sink of isotope atoms formed from dissociative adsorption or ab-

sorption of molecules by Pd. As a consequence, chromatographic separation is affected not only by the isotope effect on hydrogen absorption by Pd but also by the isotope effects on H₂O and OH formation, leading to poor overall separation of the chromatograms.

Therefore, It is required to develop hydrophilic supports of Pd to reduce the effects of adsorbed water and hydroxyl groups. It is also important to understand mechanisms of separation in view of thermodynamics and kinetic factors on one hand, and surface and bulk processes on the other.

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