論　文

水素同位分離用ガスクロマトグラフのカラム材の担体と重水素との相互作用

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Deuterium Interactions with Supports of Functional Materials of an Advance Gas Chromatographic Column for Hydrogen Isotope Separation

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Abstract

Adsorption and desorption characterristics of deuterium were studied for kieselguhr, alumina and silicon carbide by means of thermal desorption spectroscopy. They are expected to be the supports of the advanced gas chromatography for the separation of hydrogen isotopes around room temperature. Kieselguhr and alumina showed considerable interactions with deuterium. The interactions were attributed to the presence of hydroxyl groups on their surfaces. They act as a sink of hydrogen and a release source of deutrated water, suggesting substantial impairment regarding separation efficiency. The alumina on which Pd was supported confirmed the role of surface hydroxyl groups as a sink for hydrogen atoms spilling over from the Pd particles. However, silicon carbide showed no evidence of any interaction with deuterium, suggesting that it is a promising material as a support for functional metals or alloys for the columns of the advanced gas chromatography for hydrogen isotope separation.

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1. Introduction

The separation of hydrogen isotopes is one of the most important tritium processings for thermonuclear fusion reactors as well as ITER (International Thermonuclear Experimental Reactor), where a burning fraction of the fuel is expected to be around several percents. The fuel particles exhausted from the reactor core should be purified and separated to tritium and deuterium of high purity for re-fueling. Several methods have been proposed for the isotope separation in fuel processing and waste handling [1]. Among those, liquid hydrogen distillation has been considered to be the first candidate for the isotope separation for fuel processing [2]. Cryogenic-wall thermal diffusion attracts attention recent years as well [3, 4].

Gas chromatographic separation is also promising for the isotope separation because of its simple operation principle and construction, high separation efficiency and so on. Two types of gas chromatographic techniques have been developed so far. One is based on the isotope effect on physical adsorption by inert materials at low temperature around 78 K. The other utilizes the isotope effect on hydrogen absorption by metals like Pd at higher temperatures [5]. The former requires a large amount of liquid nitrogen as coolant. The latter needs rather complicated operation procedures because of its feature of replacement chromatography, where tritium inventory in the column becomes large [6].

The present authors have studied to improve those features and showed that it is possible to separate hydrogen and deuterium around 100℃ with Pd-column and around room temperature with use of a Pd-Pt alloy without any replacement gas as well as coolant [7, 8, 9]. In our previous studies, however, a separation column was prepared with a mixture of a functional meterial, Pd or Pd-Pt alloy, and inert material like Cu, which were in powder forms of relatively large particle sizes [8]. Our previous works strongly suggest that much improvement would be expected for this advanced gas chromatography for hydrogen isotope separation, if fine particles can be dispersed on a support material. This paper describes preliminary examinations of the potentiality of three different materials such as kieselguhr, alumina and silicon carbide as support.

2. Experimental

Three kinds of meterials, kiselguhr, γ-Al_2O_3 and SiC, were selected as candidates for a support of functional metals of separation columns. The powder of kieselguhr

was below 300 mesh, which was purchased from Kanto Chemicals. The silicon carbide powder was about 300 mesh, purchased from Furuuchi Chemicals, and the γ-alumina was in pellet form with about 1.6 mm diameter sintered from powder, which was delivered from Nikki Universal. Its density and surface area were 0.47g/cm³ and 190m² /g, respectively. The alumina pellets on which fine Pd-particles (this will be denoted as Pd/Al₂O₃ below) were supported were also as a model of working materials of separation columns. Its size, density and surface area were the same as the γ-almina mentioned above. Deuterium of 99.6% purchased from Nihon Sanso was used to examine adsorption and desorption of hydrogen isotopes by/from the above materials.

Figure 1 shows the block diagram of the experimental apparatus used in the present study. It was a high vacuum system made of stainless steel. The vacuum system was equipped with a pressure gauge, an ionization gauge and a quadruple mass spectrometer. It could be evacuated to 1.3×10^{-7} Pa with a sputter ion pump and a turbomolecular pump backed with an oil-sealed rotary pump. The samples could be heated up above 1200 K with an electric furnace, where the temperature was measured with a chromel-alumel thermocouple fixed to the outer surface of the sample tube.

Each of the samples was weighed to about 16 mg to put into the sample tube made of quartz. It was evacuated below 1.5×10^{-6} Pa at room temperature before each experimental run. Outgassing from the samples was measured by means of

Fig.1. Experimental apparatus used for adsorption and TDS measurements.

thermal desorption spectroscopy. Subsequently after the evacuation, the sample was heated linearly with time at a rate of 20 K/min from room temperature to 1073 K, while desorbing gases were measured with the mass spectrometer. Adsorption and/or desorption of deuterium was measured by exposing the sample to deuterium gas of a given pressure around 850 Pa at room temperature for several hours. The amount of deu-
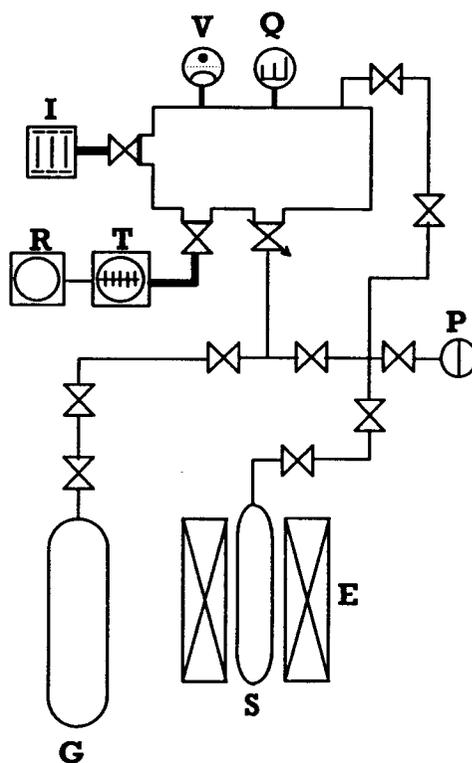
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terium absorption was evaluated from the pressure decrease in a constant volume. After deuterium gas being pumped out from system, desorption of deuterium was measured by means of thermal desorption spectroscopy, where the conditions were the same as the above degassing measurements.

3. Results

3. 1. Desorptin spectra for kieselguhr

Figure 2 shows an example of the out-gassing properties of kieselguhr observed with thermal desorption spectroscopy. The principal desorption species was H_2O. Less intense signals were also observed for H_2, CO, CO_2 and others. In the figure, the desorption spectrum of hydrogen is shown as well because hydrogen behavior is much concerned with separation character-
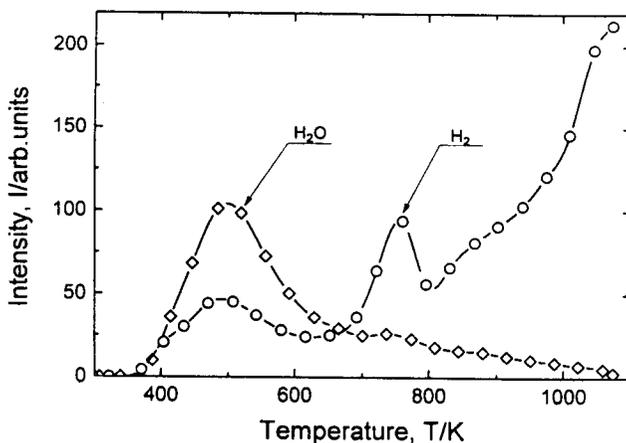

Fig.2. Out-gassing from as-received kieselguhr ; sample weight $=15.8mg$: H_2 signal being multiplied by 100.

istics of hydrogen isotopes by the advanced gas chromatograph [8] . Water formed a desorption peak at 500 K and decreased its signal intensity with increasing temperature. The decrease, however, was gradual and a shoulder or peak appeared around 750 K. A desorption peak of hydrogen was observed at the temperature of the first peak of water. Afterward, the spectrum showed a sharp intense peak at 750 K, where the shoulder was observed in the water spectrum, and then increased further with temperature. It should be noticed that the signal intensity of hydrogen was about two orders of magnitude smaller than that of water.

To examine interactions with hydrogen isotope gases, the as-received samples were exposed to D_2 and desorption characteristics of hydrogen isotopes were measured. The as-received samples was exposed to D_2 under the conditions appeared in the figure caption. Subsequently, the system was evacuated to 1×10^{-6} Pa and the sample was heated linearly with time at 20K/min.

Figure 3 shows the desorption spectra observed for the as-received kieselguhr exposed to D_2. Light water, H_2O, gave a similar desorption spectrum to that shown in Fig.2. Namely, the first predominant peak was observed at the same temperature as the predominant peak of water in the preced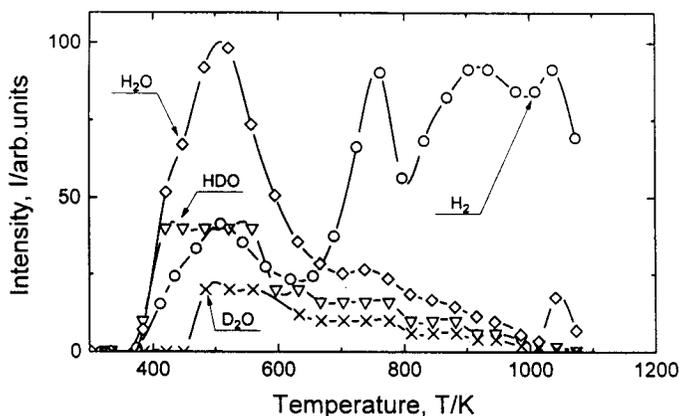ing spectrum, and the second peak was at 750 K, where the shoulder appeared in Fig.2. Hydrogen made desorption peaks at 500, 750, 900 and 1050 K. The first and second peaks correspond to those of water, and the third peak was observed at the temperature where the shoulder ·was observed in the H_2O spectrum. It is also noticeable that the first two peaks agree well with those observed in the degassing spectrum.

Fig.3. Desorption of deuterium after exposing as-received kieselguhr to D_2 ; sample weight=15.8 mg, exposure pres. =6.43 Torr, temp. =296 K, time=90min.: signals from H_2, HDO and D_2O begin multiplied by 100, 200 and 200, respectively.

The deuterium exposure gave rise to the desorption of HDO and D_2O, although their signal intensities were considerably weaker than that of H_2O ; the signal intensities plotted in this figure was multiplied by 200. The desorption of D_2O started at a little higher temperature than light water and made a broader peak around 550 K. HDO formed a flat-top peak ranging from 420 to 580 K. These observations indicate that isotope exchange reactions take place on the surface.

The sample degassed at 1073 K were also examined to look at effects of rigorous out-gassing. Nmely, the sample was exposed to deuterium at room temperature and then its desorption behavior was measured. The observed desorption spectra shown in Fig.4 were different from those observed for the as-received kieselguhr exposed to D_2 On the other hand, they resembled the degassing spectra shown in Fig.2. A desorption peak and a shoulder appeared around 450K for H_2O, although the extent of desorption was about $1/400$ of the degassing spectrum. This temperature was quite near to that of water in the degassing spectrum, suggesting that the desorption of light water was due to the same adsorbed species and/or mechanisms. On the other hand, the desorption of hydrogen was not observed below 600 K. It was only observable at higher

temperatures, although the signal intensity was very weak ; about $1/1500$ of that in Fig. 2. This should be also due to the reduced amount of adsorbed water on the surface.

In addition to the light water desorption, the out-gassed sample also showed a desorption peak of HDO, whereas there appeared no desorp-

Fig.4. Desorption of deuterium after exposing degassed to D_2 ; sample weight = 15.8 mg, exposure pres. = 6.45 Torr, temp. = 298 K, time = 90 min.

tion peak of D_2O. The principal change owing to the out-gassing at 1073 K from the as-received kieselguhr exposed to D_2 was the reduction of the amount of desorbed H_2O, whereas the amount of HDO desorption did not decrease much. These observations indicate that the species or mechanisms responsible for HDO desorption was not affected much by the out-gassing at high temperature.

3. 2. Desorption spectra for alumina

Figure 5 shows out-gassing spectra observed for the alumina. Water formed the predominant peak at 480 K. The peak was accompanied by a tail with a shoulder around 600 K and then a dull peak appeared around 900 K. Hydrogen made a peak at the temperature where the first peak of water was observed, and then kept an almost constant level at higher temperatures.
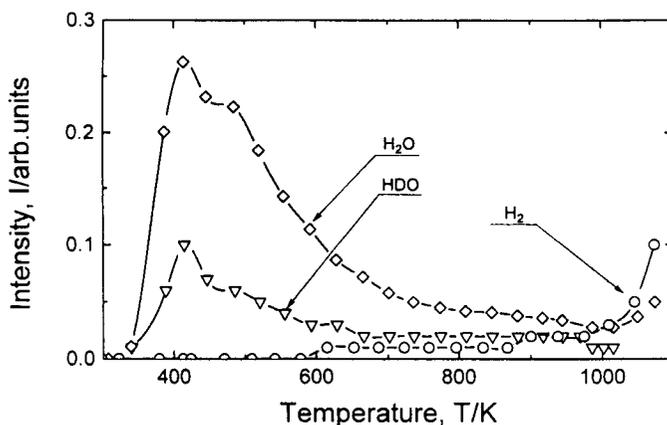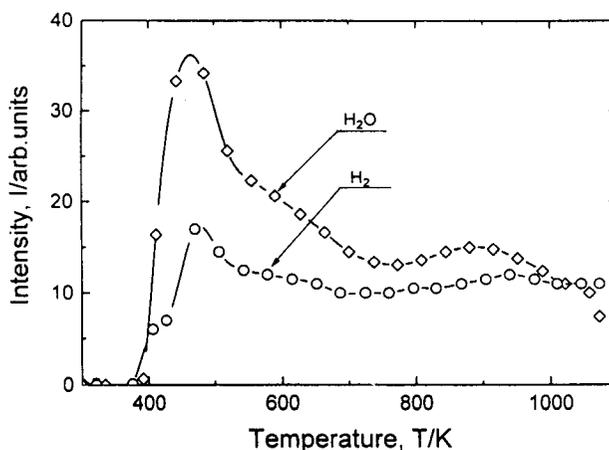

Fig.5. Out-gassing from as-received γ-alumina ; sample weight = 16.6 mg : H_2 signal being multiplied by 100.

Figure 6 shows the de-sorption spectra for the as-received alumina exposed to D_2. They resembled the degassing spectra of H_2O and H_2 in Fig.5, except the H_2 peaks at 820 and 980 K, whereas a broad peak app-eared in Fig.5.

It was also observed that deuterium desorbed as HDO and D_2O. They form-ed the desorption peaks at 480 K, which is the same temperature as that of H_2O, although the intensi-ties of the former two were considerably smaller than H_2O. These observations also indicate the occurrence of exchange reactions between D_2 and adsorbed water or hydroxyl groups on the sur-face of as-received alumina.

Fig 7 shows the desorp-tion spectra observed for the out-gassed alumina ex-posed to D_2. There was no desorption peak of water

Fig.6. Desorption of deuterium after exposing as-receiv-ed γ-alumina to D_2 ; sample weight = 16.8 mg, exposure pres. = 6.33 Torr, temp. = 298 K, time = 90 min.: signals from H_2, HDO and D_2O being multiplied by 100.

Fig.7. Desorption of deuterium after exposing degassed γ-alumina to D_2 ; sample weight = 16.6 mg, ex-posure pres. = 6.32 Torr, temp. = 297 K, time = 90 min.: signals from H_2, HD and D_2 being mul-tiplied by 5.

observed at 500 K for the as-received sample with and without D_2 exposure. The signal intensity of water increased gradually with temperature from 500 to 900 K and then steeply rose. It should be mentioned, however, that the scale of the ordinate is $1/200$ of Fig.5 and 6. This indicates that water desorbable at low temperature had been re-moved by the degassing at 1073 K, whereas a trace amount of adsorbed water was still present on the surface. The peak of H_2 observed at 500 K for the as-received alu-
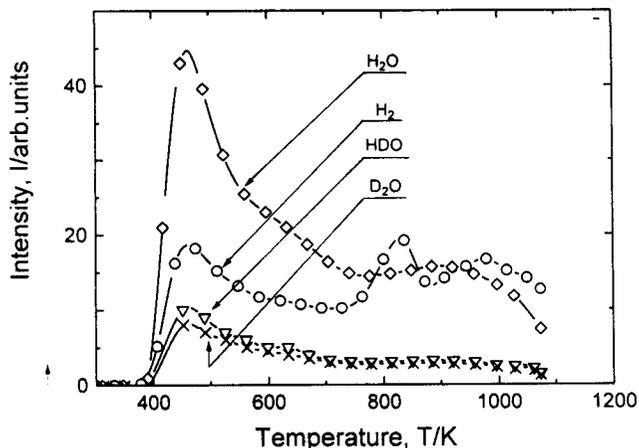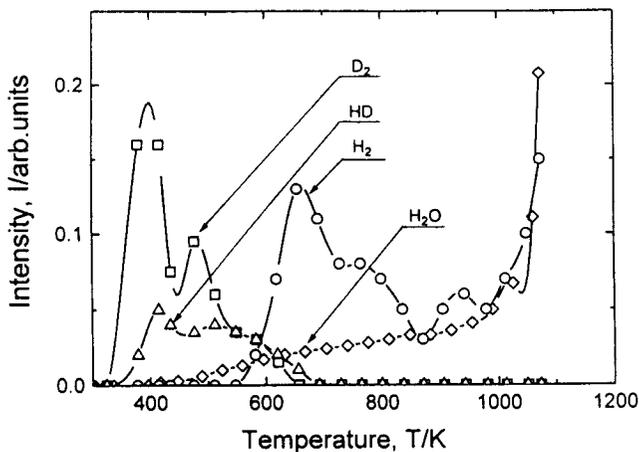
mina exposed to D_2 disappeared from the spectrum and the most intense peak appeared at 650 K, and the secondary and tertiary peaks at 800 and 920 K, respectively, which were hidden in Fig.5 and 6. The characteristic features of this sample lies in the fact that there was no desorption of HDO, but deuterium desorbed as D_2 and HD. The spectrum of D_2 appears to have two desorption peaks in the temperature range from 400 to 500 K. That of HD showed a similar feature, although the peaks shifted a little higher temperatures.

3. 3. Desorption spectra for silicon carbide

Silicon carbide showed different out-gassing spectra from the other two as seen in Fig.8. The predominant desorption peak of water appeared at 620 K, which is a little higher than the peaks observed for kieselguhr and alumina. The signal intensity decreased very slowly, in comparison with the other two, with temperature rise and shoulders appeared around
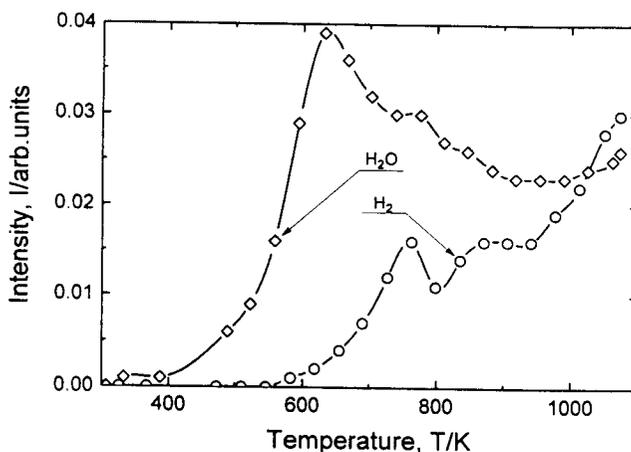

Fig.8. Out-gassing from as-received silicon carbide; sample weight = 15.9 mg.

750 and 850 K. There was no hydrogen peak around the first peak of water, but a peak of water appeared at 750 K, where the second minor peak of water was observed. The signal intensity increased with temperature above 800 K by forming a shoulder around 900 K. It is mentioned that the signal intensities of these spectra were a few orders of magnitude smaller than those for the kieselguhr and alumina, although the quantitative comparison is hard because of the lack of knowledge of their surface areas.

The as-received silicon carbide exposed to D_2 showed considerably different desorption spectra of water and hydrogen from the other two and from the degassing spectra of silicon carbide as seen in Fig.9. The signal intensity of H_2O began to increase at almost the same temperature as that in the degassing spectrum, but the spectrum did not show apparent desorption peaks. After the stepwise increase, the signal intensity

was kept at a level almost invariant with the temperature. In addition, the first H_2 peak observed in Fig.8 disappeared. It should be noticed, however, that the signal intensities decreased to below a few ten percents of those for the degassing spectra. The difference between Fig.8 and 9 is ascribed to the presence of a smaller amount of adsorbed water on the sample surface used for this measurement. The decrease of the adsorption amount for the sample exposed to D_2 appears due to the exposure procedures, where the sample was more rigorously pumped than the degassing ex-
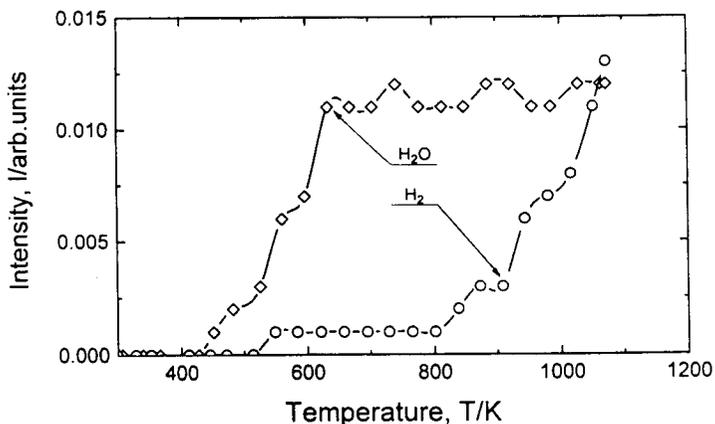

Fig.9. Desorption of deuterium after exposing as-received silicon carbide to D_2 ; sample weight = 16.8 mg, exposure pres. = 6.33 Torr, temp. = 298 K, time = 90 min.
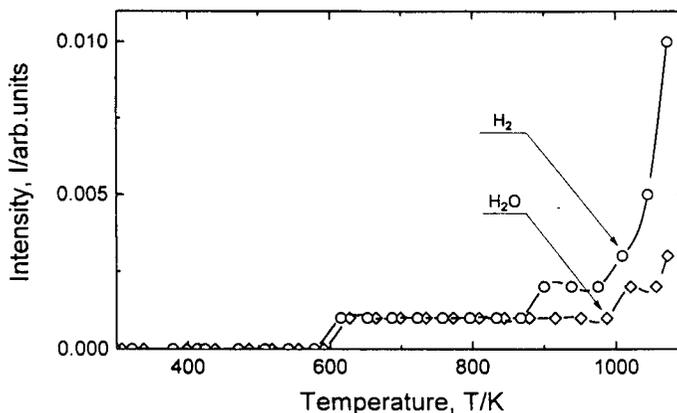

Fig.10. Desorption of deuterium after exposing degassed silicon carbide to D_2 ; sample weight = 15.4 mg, exposure pres. = 6.33 Torr, temp. = 297 K, time = 90 min.

periments. The characteristics of silicon carbide, however, is apparent from these observations that there was no desorption of deuterium. Namely, this meterial is inactive to hydrogen isotopes.

Fig 10 shows the desorption spectra observed for the out-gassed silicon carbide exposed to D_2. There were no desorption peaks of H_2O and H_2 at 620 and 760 K, respectively, observed for the as-received silicon carbide. Only weak signals began to appear above 600 K and increased with temperature. There was no desorption of deuterium, indicating that the out-gassed surface of silicon carbide has no activity to interact with hydrogen isotope gases.

3. 4. Desorption of deuterium from Pd／Al$_2$O$_3$ exposed to D$_2$

A functional material for gas chromatography is required to be supported by an inert material from the view points of separation efficiency and economy. However, some support materials are expected to effect the adsorption and desorption characteristics of functional material. To examine the effect, the Pd／Al$_2$O$_3$ powder was exposed to D$_2$ under the similar conditions as the above experiments. The powder was first degassed at room temperature and then at 523 K. The desorption spectra observed after the deuterium exposure are shown in Fig.11. There were no desorption peaks around 500 K observed for the as-received alumina exposed to D$_2$. On the other hand, the desorption peaks of H$_2$O appeared at 640 and 900 K. They corespond to the shoulder and the broad peak in Fig.6. The appearance of these peaks should be due to the reduced amount of adsorbed species.

The point of important concern with the isotope separation is that significant amount of deuterium desorbed as HDO in addition to D$_2$O, HD and D$_2$. A minor amount of deuterium desorbed as HD and D$_2$, which formed peaks at 340 and 370 K, respectively. These temperatures are much lower than those of H$_2$ observed in Figs. 5-6. In addition, the desorption amount of HD and D$_2$ was considerably larger than that observed in Fig.6.
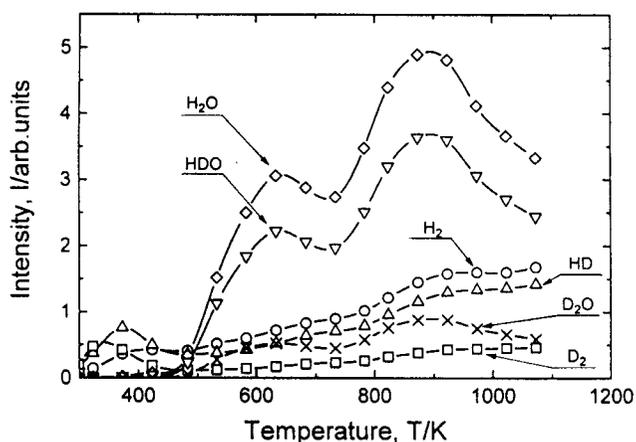

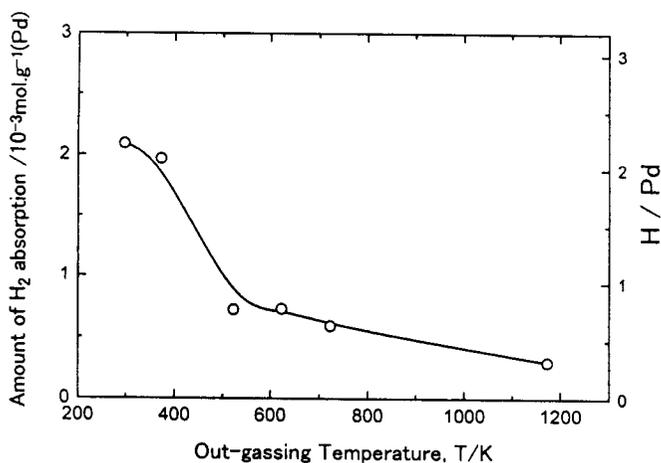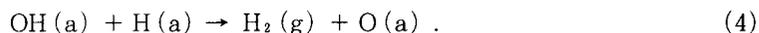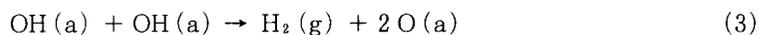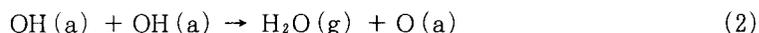Fig.11. Desorption of deuterium after exposing Pd／Al$_2$O$_3$ degassed at 523 K.

Fig.12. Variation of absorption amount of H$_2$ at 298 K on Pd／Al$_2$O$_3$ degassed at diffrent temperatures.

Figure 12 summarizes the measurements of hydrogen absorption by the Pd/Al$_2$O$_3$ sample degassed at varying temperature. It shows that the amount of adsorption decreased with increasing degassing temperature. The sample degassed at temperatures below 400 K showed the absorption amounting to [H]/[Pd] ~ 2.2. On the other hand, the out-gassing at 1173 K gave the ratio about 0.3. It should be noted that the ratio below 0.1 has been reported for the equilibrium hydrogen absorption by Pd under the similar conditions to the present study [10] . Namely, the present data exceed the equilibrium absorption, suggesting that excess hydrogen was absorbed by the support material. This point was confirmed by thermal desorption spectroscopy for the deuterium exposed sample out-gassed at defferent temperatures, which showed that the lower the out-gassing temperature was, the larger the amount of HDO and D$_2$O desorption.

4. Discussion

4. 1. Degassing properties

Three samples showed a similar degassing property ; that is, the first desorption peak of water appeared in a temperature region from 500 to 600 K. The desorption peak of water in this region is commonly observed for a variety of materials, for example, metals, alloys and ceramics [11, 12, 13] . It has been attributed to adsorbed water molecules or hydroxyl groups. Accordingly, the first desorption peaks of water observed in Figs.2, 5 and 8 should be also ascribed to water molecules or hydroxyl groups on the surfaces. Since the first H$_2$O peaks for each of the samples were accompanied with H$_2$ peaks, these peaks should be attributed to the decomposition of adsorbed water and/or hydroxyl groups, presumably through side reactions of water desorption. Namely, the desorption of water in the temperature range from 500 to 600 K is accompanied with decomposition reactions on the surfaces as

$$H_2O(a) \rightarrow H_2O(g) \qquad (1)$$

$$OH(a) + OH(a) \rightarrow H_2O(g) + O(a) \qquad (2)$$

$$OH(a) + OH(a) \rightarrow H_2(g) + 2O(a) \qquad (3)$$

$$OH(a) + H(a) \rightarrow H_2(g) + O(a) . \qquad (4)$$

At higher temperatures, it is not plausible to assume the presence of water molecules adosorbed as they stand [14] . Desorption of water should take place through a surface reaction between adsorbed hydroxyl groups as Eq.2. In addition, the release of hydrogen is also expected by Eqs.3 and 4
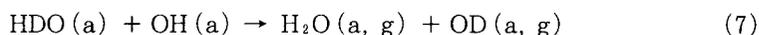
The gradual decrease of water signals toward higher temperature and the appear-

ance of shoulders and／or small peaks suggest that there are different kinds of adsorption sites or desorption mechanisms on the surfaces of these materials [14] .

On account of the above observations, it can be concluded that a considerable amount of water was adsorbed on the sample surfaces as H_2O (a) and／or OH (a) . A part of adsorbed water desorbs as hydrogen through side reactions of water desorption, although the amount was significantly smaller than that of water. The behavior of adsorbed water is likely to impair the isotope separation by the advanced gas chromatography using those materials as the support of functional metals or alloys.
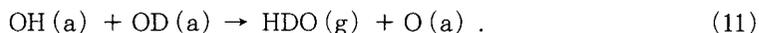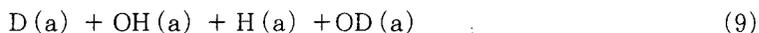
4. 2. Interactions between the support materials and D_2

A typical feature for the as-received kieselguhr and alumina exposed to deuterium was the deuterium desorption as HDO and D_2O. On the other hand, silicon carbide did not show any evidence of deuterium release. Namely, the release of deuterium was material dependent, suggesting the contribution of surface reactions such as adsorption and isotope exchange reactions, since gaseous exchange reactions should hardly proceed in the present experimental conditions. It is plausible to assume that the exchange reactions take place through the adsorption of deuterium as

$$D_2 (g) \rightarrow 2D (a) \tag{5}$$

$$D (a) + H_2O (a) \rightarrow H (a) + HDO (a, g) \tag{6}$$

$$HDO (a) + OH (a) \rightarrow H_2O (a, g) + OD (a, g) \tag{7}$$

$$D (a) + OH (a) \rightarrow H (a) + OD (a) . \tag{8}$$

The adosorbed deuterated water and hydroxyl groups will desorb as deuterated water. No evidence of D_2 and HD desorption appears due to an excessively small population of adsorbed deuterium to associate each other on the surface.

With respect to the degassed samples, the kieselguhr should still hold on appreciable quantity of hydroxyl groups on the surface even after the vacuum heating at 1073 K. Consequently, the deuterium adsorbed on the surface desorbs as deuterated water through the isotope exchange reactions as

$$D (a) + OH (a) + H (a) + OD (a) \tag{9}$$

$$OH (a) + OH (a) \rightarrow H_2O (g) + O (a) \tag{10}$$

$$OH (a) + OD (a) \rightarrow HDO (g) + O (a) . \tag{11}$$

The larger amount of H_2O desorption than HDO suggests that there was a greater number of OH (a) than D (a) . Because of the small amount of adsorbed deuterium,

the desorption of D_2 could not be observable in the present experimental conditions.

On the other hand, it appears that there was not enough hydroxyl groups on the surface of the degassed alumina to release adsorbed deuterium as HDO. Accordingly, the isotope exchange reaction, Eq.9, proceeded in only a small extent and the association reaction between adsorbed deuterium atoms dominates the formation and release of HDO. Namely, the adsorbed deuterium is released as D_2 and HD through

$$D(a) + D(a) \rightarrow D_2(g) \tag{12}$$

$$D(a) + OH(a) \rightarrow HD(g) + O(a) . \tag{11}$$

The appearance of two peaks of D_2 and HD indicates the presence of two different adsorption sites of OH(a) or D(a), or desorption mechanisms. The formation of H_2 peaks at higher temperature indicates different mechanisms from those of D_2 and HD and the presence of distinct adsorption sites of OH(a).

4. 3. Interactions between Pd／Al₂O₃ and D₂

The desorption peaks of hydrogen around 500 K appeared in Fig.11 is not due to the reactions described by Eqs. 4 and 12, but the association reaction of hydrogen isotopes ad／absorbed by Pd. It should be mentioned here, however, that most of deuterium desorbed as HDO. Apparently, Pd supported by Al_2O_3 is not responsible for the desorption of HDO as well as D_2O and H_2O. They should arise from the hydroxyl groups on the support surface. Separate measurements for the Pd／Al₂O₃ samples showed only desorption peaks of D_2, HD and H_2 around 500 K for the sample degassed rigorously at 1073 K. There were only negligibly minor desorption of H_2O, HDO and D_2O. In addition, the amount of hydrogen absorption by the Pd／Al₂O₃ sample was greater than the reported equilibrium values; the excess absorption increased with less intense out-gassing, which leaves a greater number of adsorbed water molecules and hydroxyl groups on the surface.

These observations clearly indicate that the hydroxyl groups act as sinks for hydrogen isotope atoms absorbed by Pd through the spill-over phenomenon. From this view point, the observations described above clearly indicates that kieselguhr and alumina are not appropriate as supports of functional materials for the advanced gas chromatography for the separation of hydrogen isotopes, because the removal of the hydroxyl groups from them is considerably hard. In addision, even rigorously degassed powders will be easily poisoned by humidity in the air during the preparation of separation columns. On the other hand, hydrophilic materials like silicon carbide are

highly promising because they have no sink of hydrogen isotope atoms and hence inactive to the hydrogen spill-over as well as humidity.

Although it is premature to discuss details of the adsorption sites on the surfaces of kieselguhr and γ-alumina, it is noteworthy to mention that the inactivity of silicon carbide to deuterium exposure appears due to its filled covalent bond between Si and C.

4. Conclusions

Deuterium-material interactions were studies for kieselguhr, γ-alumina and silicon carbide to find appropriate carrier to support functional materials for the advanced gas chromatographic columns to separate hydrogen isotopes around room temperature without any replacement gas.

It was found by means of thermal desorption spectroscopy for the non-treated and well degassed samples exposed to D_2 gas at 800 Pa and room temperature for several hours that the kieselguhr and the γ-alumina release adsorbed deuterium as HDO, D_2O and HD, This is due to the fact that they retained considerably large amounts of adsorbed water as molecules and hydroxyl groups on their surfaces. They act as sinks for deuterium adsorbed and release it at elevated temperatures. This effect was more enhanced by the presence of Pd on γ-alumina. Those observations strongly suggest that hydrophilic supports significantly impair the functionality of selected metals or alloys.

Silicon carbide with and without degassing, on the other hand, showed no noticeable interactions with deuterium gas. It is expected to be a promising material as the support of functional meterials for the advanced gas chromatography for hydrogen isotope separation.

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