Pd, Pd-4at%Pt 及び Pd-8at%Pt による水素吸収の 動力学的同位体効果

金 塋, 原 正憲, 渡辺国昭

富山大学 水素同位体科学研究センター

〒 930-8555 富山市五福 3190

Kinetic Isotope Effects on Hydrogen Absorption by Pd, Pd-4at%Pt and Pd-8at%Pt

Y. Jin, M. Hara and K. Watanabe

Hydrogen Isotope Research Center,

Toyama Univsersity, Gofuku 3190, Toyama 930-8555, Japan

ABSTRACT

Absorption of protium and deuterium by Pd, Pd-4at%Pt and Pd-8at%Pt powders under 200 mesh was measured in a dilute hydrogen concentration region at temperatures from 0 to 82 ℃ by recording the decline of hydrogen pressure in an experimental chamber due to hydrogen absorption. These measurements and data analyses gave the adsorption rate, desorption rate and diffusion constants of hydrogen isotopes for the alloys. The absorption was very fast, completed within a few tens of seconds, but there appeared a clear trend of decreases in the rate constants for adsorption, desorption and diffusion with increase in the Pt content in the sample. The activation energies for these rate processes increased with increase in the platinum content. Regarding isotope effects, protium showed a higher adsorption rate but lower desorption rate in the present temperature range. It was also found that protium diffused more slowly than did deuterium in all three samples.

1. Introduction

Palladium-platinum alloys have a great potential for application to an advanced gas chromatography for hydrogen isotope separation around room temperature without using any replacement gas[1, 2]. Our previous papers showed that the heat of hydrogen absorption as well as hydride formation decreases with increasing Pt-content in the alloy, whereas the thermodynamic isotope effect on hydrogen absorbability measured by the ratio of equilibrium pressures between protium and deuterium are almost constant irrespective of alloy composition, suggesting that one can select a proper alloy under a given operating condition of the chromatograph without changing the magnitude of the isotope effect[3, 4]. It is expected, however, that kinetic isotope effects should also affect the separation efficiency of a column under given conditions.

From this viewpoint, the present authors studied isotopic difference in the rates of absorption and desorption between protium and deuterium, by using a conventional vacuum microbalance[5, 6, 7]. According to the study, the absorption rate constant for protium was greater than that for deuterium and the desorption rate constant as well as the diffusion constant for protium were smaller than those for deuterium. The differences were, however, much smaller in comparison with the thermodynamic isotope effect. In addition, it was observed that these rate processes were slow and showed rather large activation energies. It was considered due to surface poisoning by residual gases in the experimental apparatus. Then the kinetic isotope effects as well as alloying effect are required to be confirmed by other conditions and/or systems.

Accordingly, an apparatus with much lower residual gas pressure was employed in the present study to reexamined the kinetic isotope effects on adsorption, desorption and diffusion between protium and deuterium.
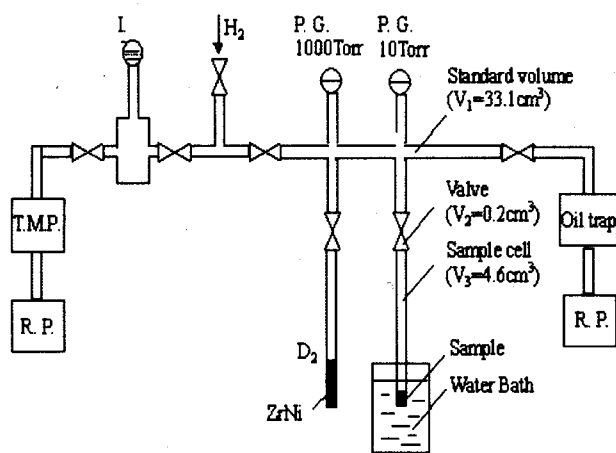
2. Experimental

Fig. 1. Block diagram of the experimental apparutus

Pure Pd, Pd-4 at% and Pd-8 at%Pt powders smaller than 200 mesh ($< 74\mu$m) were prepared from the corresponding plates purchased from Tanaka Noble Metal. The purities of these materials were guaranteed to be above 99.9%. The amounts of powder used for kinetic measurements were 0.3755g of Pd, 0.5107g of Pd-4at%Pt and 0.5213g of Pd-8at%Pt. Protium and deuterium gases were purchased from Nihon Sanso, whose purities were guaranteed as above 99.9999% and 99.6%, respectively. The protium gas was used without further purification, while deuterium was used after removing impurity gases by use of ZrNi alloy. A schematic diagram of the experimental apparatus is shown in Fig.1. The main part of the system including valves was made of a stainless steel, but the sample tube was prepared from quartz glass. The system was installed with an ionization gauge, two diaphragm pressure gauges, and a deuterium storage using ZrNi powder. It was evacuated by a turbomolecular pump backed with an oil-sealed rotary pump.

The residual pressure was routinely below 1.0×10^{-5} Pa. A rotary pump with an oil-trap was used for other purposes and not used in the present study. The standard volume had been determined to be 33.1 cm^3 and the volume of the sample tube as 4.6 cm^3.

Before each measurement, the sample was degassed at 300°C with the turbomolecular pump until the system was evacuated down to 1.0×10^{-5} Pa or below. Then the sample was stabilized at a given experimental temperature by a water (water/ice) bath for about 1 hour. Subsequently, the valve above the sample tube was closed and a prescribed amount of protium or deuterium was introduced into the standard volume. The measurement was started by opening the valve between the standard volume and the sample cell (Fig.1). The pressure change in the chamber and the average room temperature during the experiment were recorded. The hydrogen absorption was examined in the temperature range of from 0 to 82 °C, where the temperature could be controlled within ± 1°C. The initial protium and deuterium pressures were around 67 Pa.

3. Results and discussion

3.1. Data analysis

Since the present measurements were carried out by means of the constant volume method, the original experimental data were changes in hydrogen pressure with time as shown in Fig.2. In this case, a special attention is required for obtaining the initial absorption rate, because it is quite important for analyzing absorption kinetics. The initial hydrogen pressure in the experimental chamber was evaluated by accounting the sample volume as

$$V_{\text{exp}} = V_1 + V_2 + V_3 - V_{\text{s}}, \tag{1}$$

where V_1, V_2 and V_3 are the volumes of the standard volume, valve and sample tube in Fig.1, respectively; V_{s} is the sample volume evaluated from its weight and density. Then the initial point in pressure change data (t = 0) is $P_0 V_1 / V_{\text{exp}}$, where P_0 is the hydrogen pressure charged into the standard volume. The average hydrogen concentration in the sample in atomic fraction at time t is given as

$$C = \frac{2}{R T_{\text{r}} n_M} (P_0 V_1 - P_t V_{\text{exp}}), \tag{2}$$

where T_{r} is the average room temperature during the experiment and n_M the amount of sample in mole unit. Concerning the part of sample tube dipped into the water bath, the temperature deviation from the other part was neglected since the volume fraction of this part was so small.
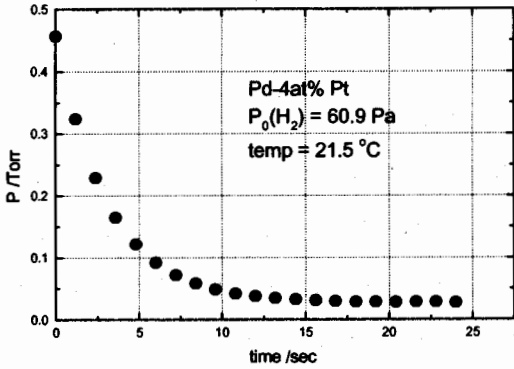
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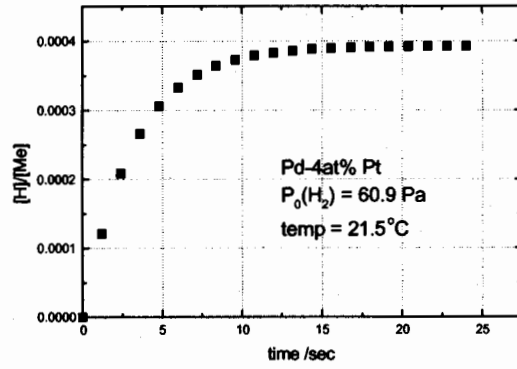**Fig. 2.** A typical pressure-time curve for protium absorption

Fig. 3. The corresponsind protium absorption curve

Figure 2 shows an example of pressure vs. time curves, which was observed for Pd-4at%Pt at 21.5 °C under the initial pressure of 60.9 Pa. Figure 3 is the absorption curve corresponding to the P-t curve in Fig.2. Both of the figures showed good smooth curves and then the initial rate of absorption could be determined precisely. This is especially important to analyze the reaction dynamics. As for the previous works, the absorption curves were measured by using a vacuum microbalance with a relatively larger chamber to keep the hydrogen pressure constant. Then an absorption curve was measured from weight gain of a sample under a constant pressure. However, the microbalance oscillated for a while by the pressure jump owing to hydrogen introduction into the chamber and then it was difficult to determine the initial rate of absorption. In the present study, on the other hand, hydrogen absorption curves were directly recorded with time during measurements.

Hydrogen absorption by metals in a solution range takes place via adsorption on the surface, diffusion into the bulk and dissolution. The processes are described as

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial r^2} + \frac{2}{r}\frac{\partial c}{\partial r}\right) \tag{3}$$

$$-D\left(\frac{\partial c}{\partial r}\right)_s = k_{ads}\, p\, (N_s^* - N_s)^2 - kN_s^2 \tag{4}$$

$$= k'_{ads}\, p\, (1 - C_s)^2 - k'_{des} C_s^2 \,, \tag{5}$$

where D is the diffusion constant of hydrogen, c the hydrogen concentration with respect to metal atoms, r the distance from the center of a powder particle which was assumed to be a sphere. As for the surface boundary condition, p, N_s^*, N_s and C_s are the hydrogen pressure, number of active sites for adsorption per unit area, that of adsorbed hydrogen atoms, and fractional hydrogen concentration on the surface, respectively. The surface hydrogen concentration, C_s, equals to N_s/N_s^*, and $k'_{ads}(= k_{ads}\,(N_s^*)^2)$ and $k'_{des}(= k_{des}(N_s^*)^2)$ are the apparent

rate constants for adsorption and desorption, respectively. Although the pressure changed with time, the programme for data analysis desribed in Ref[6] could be employed in simulating hydrogen absorption process in the present system only by replacing the constant pressure by varying pressure with time in the program.
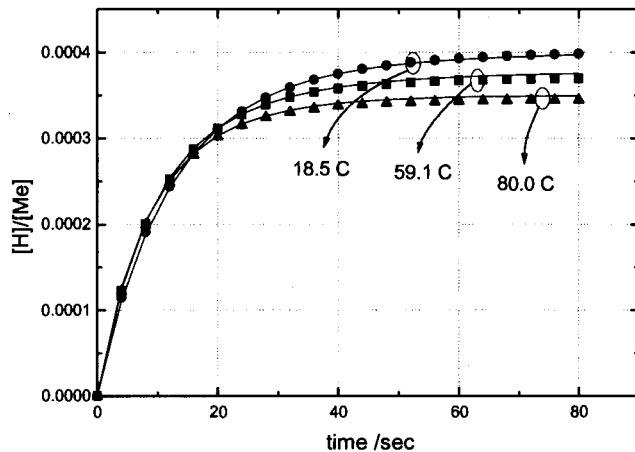

Fig. 4. Deuterium absorption data (dots) by Pd-4at%Pt at 18.9 C, 0.574 Torr; 59.1 C, 0.546 Torr and 80.0 C, 0.545 Torr, and simulation lines

Figure 4 shows the deuterium absorption curves at several different temperatures for Pd-4%Pt as an example. The dots are experimental data, which indicates that the adsorption reaches equilibrium within minutes under the present conditions, and the lines are simulation curves. It should be noted that the absorption was about one order of magnitude faster than the previous results observed by usin the micorbalance system, where the sample surfaces were much more poinsoned owing to the worse vacuum conditions[6, 7]. The simulation curves were obtained by solving numerically the set of equations described above. It is seen that the simulation curves agree quite well with the observations, indicating that kinetic parameters such as adsorption rate, desorption rate and diffusion constants could be determined well simultaneously. Other details of numerical simulation have been described elsewhere[6, 7].

3.2. Kinetic parameters and their temperature dependence

The temperature dependences of the adsorption rate, desorption rate and diffusion constants for hydrogen isotopes were determined from the analyses of hydrogen absorption curves. The Arrhenius plots are shown in Figs. 5, 7 and 9, where k'_{ads} and k'_{des} in the former two figures are the apparent rate constants. Each of the plot resulted in a fairly good straight line, from which the respective activation energies could be determined. The activation energies as well as the frequency factors are summarized in Table 1. The kinetic parameters for Pd-4%Pt alloy which had been determined with the microbalance apparatus are also listed in the table for comparison.
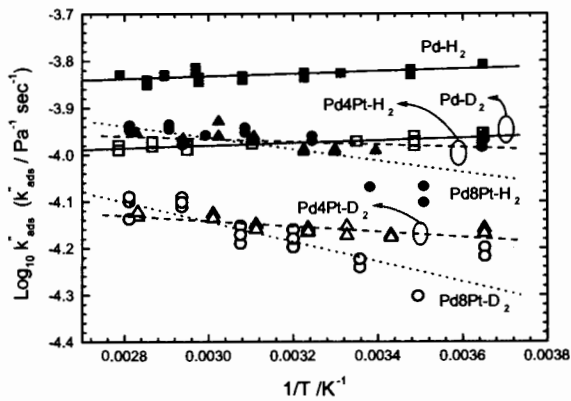
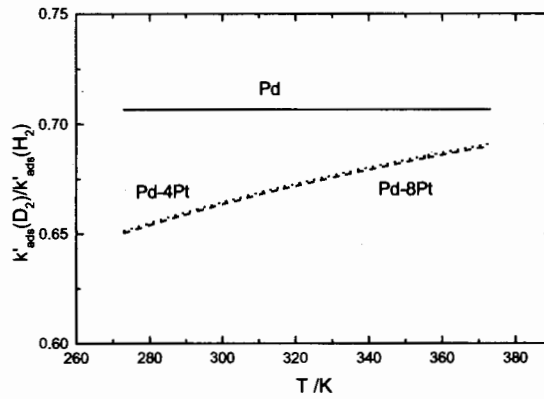**Fig. 5.** Arrhenius plots of adsorption rate constants

Fig. 6. Kinetic isotope effect on k'_{ads} evaluated from ν_{ads} and ΔE_{ads}

1) Isotope effects

Figures 5 and 6 show the temperature dependence of the apparent adsorption constants and the corresponding isotope effect on respective specimens. It is seen that the temperature dependence of the rate constants was very much weak as shown in the Table, and the activation energy for Pd appeared to be negative. It should be noted, however, that the measurements were carried out in a narrow temperature range and hence it was rather difficult to determine presicely the activation energies for such systems with weak temperature dependence. Although it is also true for the temperature dependece of the isotope effect as seen in Fig.6, it is apparent that the rate constant of protium is greater than that of deuterium for all the samples used in the present study, where the rate constant ratios were around 0.67 in the temperature studied here, although Pd appears to show the largest isotope effect.
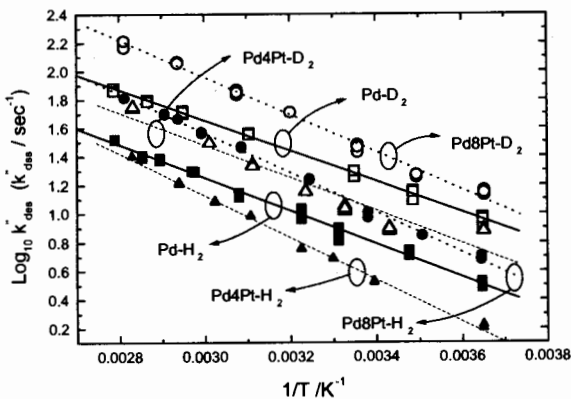

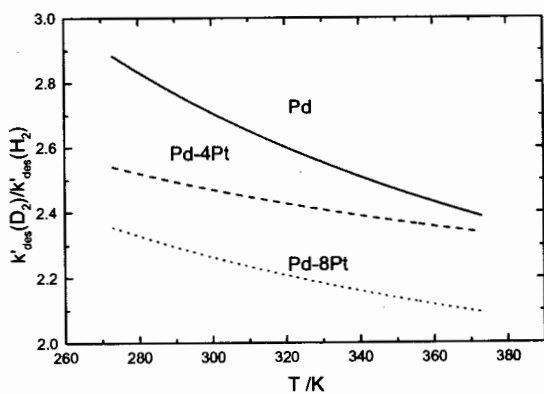**Fig. 7.** Arrhenius plots of desorption rate constants

Fig. 8. Kinetic isotope effect on k'_{des} evaluated from ν_{des} and ΔE_{ads}

With respect to the desorption process, Figures 7 and 8 show that the rate constant of deuterium was greater than that of protium for all the samples. Pd showed the largest isotope effect and Pd-8at%Pt gave the smallest ratio. The difference in the isotope effect decreased with temperature and this trend is in accordance with general expectation. Figures 9 and

10 show the temperature dependence of protium and deuterium diffusion constant, and the isotope effect. They indicate that the deuterium diffusion constant was greater than that of protium for all of the samples, and the largest isotope was observed for Pd and the smallest one was for Pd-8at%Pt. The size of the isotope effect decreases with temperature as expected for Pd and Pd-8at%Pt, but the opposite tendency is seen for Pd-4at%Pt: this is due to a negative small difference in the activation energies as $\Delta E_{dif}(H) - \Delta E_{dif}(D) = -0.4$, as seen in the Table, but the difference should be re-examined in future.
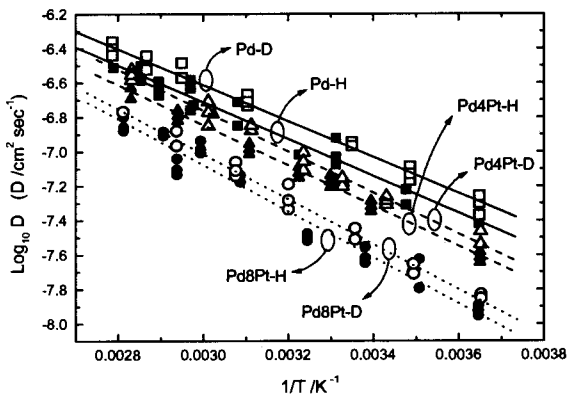

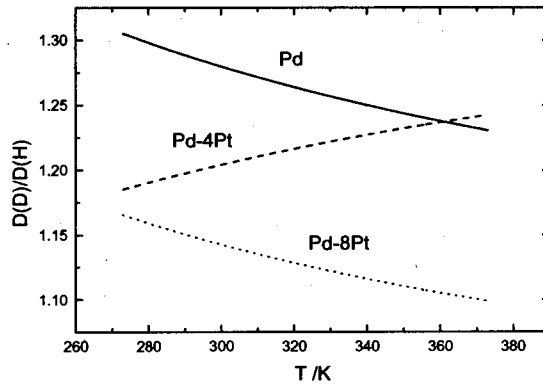**Fig. 9.** Arrhenius plots of diffusion constants

Fig. 10. Isotope effect on D evaluated from ν_{dif} and ΔE_{dif}

2) Alloyin effects

In Fig.5, it is seen that the adsorption rates of protium and deuterium decreased with increasing Pt-content in the alloy, as in the order of Pd > Pd-4at%Pt $\geq$ Pd-8at%Pt. According to Table 1, both the activation energies and frequency factors for protium and deuterium increase with increasing Pt-content in the alloy. The order of the adsorption activity,however, is principally determined by the difference in the frequency factors in the temperature range studied, as seen in Fig.5. Concerning the desorption, the rate was greatest for Pd-8at%Pt and smallest for Pd-4at%Pt as seen in Fig.7. This is reflected to the variation of frequency factor as well as activation energy with the Pt-content as Pd-8at%Pt > Pd > Pd-4at%Pt. As for diffusion, the diffusion constant decreases with increasing Pt-content in the alloy showing the order as Pd > Pd-4at%Pt > Pd-8at%Pt, where both the activation energies and frequency factors for protium and deuterium increase with the Pt-content.

Somewhat complex variations of the isotope and alloying effects with the Pt-content in the alloys were observed for both the activation energy and the frequency factor as mentioned above; although there appears a clear trend that the adsorption rate and diffusion constants of both protium and deuterium decrease with increasing Pt-content in the alloy, the desorption

7

Table 1. Kinetic parameters for hydrogen adsorption by Pd and Pd-Pt alloys

Material		Pd	Pd-4at%Pt			Pd-8at%Pt
Reference		this work	this work	Ref[5]	Ref[7]	this work
ν_{ads} /Pa^{-1} sec^{-1}	H$_2$	1.22×10^{-4}	1.32×10^{-4}	—	—	2.55×10^{-4}
	D$_2$	8.62×10^{-5}	1.07×10^{-4}	—	—	2.07×10^{-4}
ΔE_{ads} /kJ mol^{-1}	H$_2$	-0.5	0.6	19.2	29.1	2.4
	D$_2$	-0.5	1.1	—	32.8	2.9
ν_{des} /sec^{-1}	H$_2$	5.20×10^4	3.35×10^5	—	—	5.31×10^5
	D$_2$	7.41×10^4	6.25×10^5	—	—	8.05×10^5
ΔE_{des} /kJ mol^{-1}	H$_2$	22.1	28.1	37.2	48.1	26.5
	D$_2$	20.5	27.4	—	49.0	25.2
D_0 /cm^2 sec^{-1}	H	3.15×10^{-4}	4.56×10^{-4}	2.0×10^{-4}	2.0×10^{-4}	8.78×10^{-4}
	D	3.30×10^{-4}	6.45×10^{-4}	—	3.0×10^{-4}	8.21×10^{-4}
ΔE_{dif} /kJ mol^{-1}	H	20.5	22.4	29.7	28.7	25.6
	D	20.0	22.8	—	28.7	25.1

it should be mentioned that the residual pressure of the system used in the present study was still high, around 10^{-5} Pa, and the predominant component of the residual gas was water. Hence it is highly possible that the sample surface was poisoned in some extent before and during the experiments. In addition, the extent of surface poisoning was considered to be different among the samples used. These surface conditions are considered to play a role for the result that both the isotope and alloying effects did not show straight forward variation of the activation energy and frequency factor with the alloy composition. In spite of this ambiguity, it should be noted here that all of the absorption curves obtained in the present study can be reproduced quite well with the kinetic parameters listed in the table.

3) Comparison with Pd-4%Pt data from microbalance system

Comparing with the results for Pd-4%Pt obtained by using a vacuum microbalance system, the adsorption rate constants for protium and deuterium determined in this work are about 1 to 2 orders of magnitude greater. At the same time, the activation energies for the adsorption and the desorption determined here were much smaller than the previous values, especially for the case of adsorption as seen in the table. These observations indicate that the samples used in the present work had much more active for hydrogen adsorption as well as desorption. On account of the vacuum systems used in the present study and the previous work, the difference in the sample activity is due to the difference in the extent of surface poisoning by residual gases.

Nevertheless, the extents of kinetic isotope effects are not much different from each other. The kinetic isotope effects are rather small in comparison with the thermodynamic isotope effect. Namely, the separation efficiency of the gas chromatograph for hydrogen isotope separation is principally determined by the thermodynamic effect. But this comparison makes it clear that surface conditioning is very important for obtaining a column with good separation efficiency. Under conditions of poor surface cleanliness, the rates of adsorption and desorption are too slow and then the equilibrium between the gas and the column material is not established during the propagation of a flowing gas in the separation column. Incidentally, the separation efficiency becomes poor. In fact, this kind of phenomena has been observed in separation experiments. Sufficient separation efficiency has been only achieved after processing the column to activate material surfaces. According to the present and previous studies, the atmosphere for surface activation should be in high vacuum better than 1×10^{-5} Pa or in an inert gas containing oxygen-relating impurities like water below 1 ppb.

5. Conclusions

The kinetics of protium and deuterium absorption by Pd. Pd-4at%Pt and Pd-8at%Pt were studied by using a high vacuum system, providing much cleaner sample surface than previous microbalance apparatus. Hydrogen absorption in the present study took place much faster, one to two orders of magnitude, than the previous one. This was ascribed to the difference in the residual gas pressures of the systems. Nevertheless, it can be concluded that protium absorption is much faster than deuterium, whereas protium desorption and diffusion take place much slower than deuterium for each material. Concerning alloying effect, the rate of hydrogen absorption and diffusion decreases with increasing Pt-content in the material, whereas no clear dependence on Pt-composition was observed for the desorption rate constant. Comparison of the present and previous works makes it clear that surface conditioning of active material for the gas chromatograph is very important to obtain high separation efficiency. Under poor surface cleanliness, the absorption and desorption of hydrogen are to slow so that the equilibrium between the column material and flowing gas can not be established during the propagation of the gas in the column. A guideline for material processing is to activate the surface in vacuum under at least 1×10^{-5} Pa or in an inert gas atmosphere containing oxygen-relating impurity gases like water below 1ppb.

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