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Generation of active sites over Pt powder catalysts by UHV treatment
Temperature programmed desorption study

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Abstract

Temperature programmed desorption experiment of adsorbed hydrogen was carried out over UHV-treated Pt powder catalysts, that is Pt powder evacuated at high temperatures under ultrahigh vacuum ($\leqslant 10^{-7}$ Pa). Platinum powder evacuated at 673 K under conventional vacuum ($\approx 10^{-2}$ Pa) indicated two desorption peaks at 130 and 190 K. The peaks observed at 130 and 190 K were assigned to associatively and dissociatively adsorbed hydrogen species, respectively, by TPD experiment of co-adsorbed H_2–D_2. The Pt powder UHV-treated at 1073 K showed a new desorption peak which was assigned to dissociatively adsorbed hydrogen species at 160 K in addition to the peaks at 130 and 190 K observed on the Pt powder evacuated under 10^{-2} Pa. The fourth peak was observed at 250 K on Pt powder prepared by direct decomposition of hexachloroplatinic acid, which was a starting material of the Pt powder, at 673 and 1073 K under UHV. These new peaks at 160 and 250 K were also observed in the case of adsorption even at 77 K. Molecular hydrogen can be adsorbed dissociatively and activated on the Pt powder prepared by decomposition of hexachloroplatinic acid. The UHV-treated Pt powder catalysts at 1073 K indicated high activity for H_2–D_2 exchange reaction. Furthermore, the Pt powder prepared by the decomposition at 1073 K showed markedly high activity even at a reaction temperature of 77 K. These results clearly indicate that the UHV treatment generates new active sites for activation of hydrogen molecules.

Keywords: Platinum powder catalysts; Temperature programmed desorption; UHV treatment

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1. Introduction

Active sites on metallic catalysts have been studied widely [1]. Step and kink structures over well-defined single crystal surfaces of metals are possible active sites for some reactions [2–5]. Bernasek et al. have reported that the (997) stepped Pt surface was very active for H_2–D_2 exchange reaction in a molecular beam method [2,3]. Brundle, and Delouise and Winograd have reported that NO molecules have been dissociatively adsorbed easily over (331) step faces [6,7]. These results indicate that the much more unsaturated metal atoms which are located at the edge sites of step and kink structure or the bottom sites which are surrounded by number of metal atoms are expected to be more active for dissociation of H_2 or NO over the single crystal surfaces.

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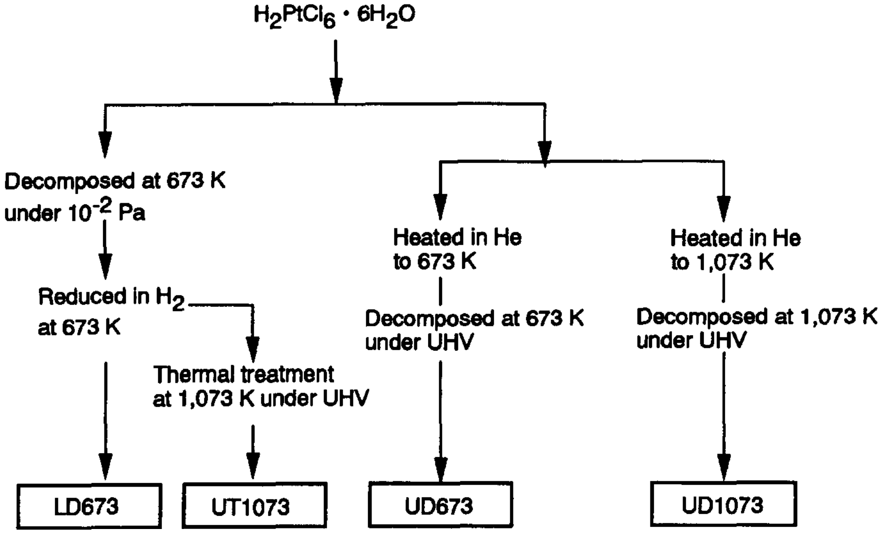
There are only few reports on the structure of active sites of polycrystalline metal surfaces, which are often observed on practical catalysts, because of their heterogeneity. Differences in activity and adsorption energy between single crystals and polycrystals are reported [8]. Our group has studied the surface roughening behavior and the enhanced activity [9–14].

An enhanced activity of Pd, Pt, and Rh metallic catalysts by thermal treatment under ultrahigh vacuum (UHV treatment) has been observed. Over Pd catalysts, the activity for H_2–D_2 exchange activity was enhanced by the UHV treatment at 673 K [9]. The enhanced activity was maintained after exposure of the Pd catalysts to atmosphere, if the catalyst was reduced in 13.3 kPa of H_2 at 473 K followed by evacuation under a conventional vacuum ($\approx 10^{-2}$ Pa) at the same temperature after air-exposure [9]. X-ray diffraction patterns of the Pt powders indicated that the enriched intensity of high-index faces of Pt was observed by the UHV treatment at 1073 K [9,10,12]. These results suggest that the enhanced activity was ascribed not only to the surface cleaning effect under UHV condition but to surface structural modification by the UHV treatment. A higher temperature was required to obtain the enhanced activity of Pt and Rh catalysts. The temperature at which the enhanced activity for H_2–D_2 exchange reaction was observed increased in the order of Pd < Pt < Rh [10,12]. This order was identical to that of melting point and/or sublimation temperature of these metals. These results strongly support the view that the UHV treatment brings about the surface structural modification that is surface roughening. A SEM study on surface roughening behavior of Pt foil model catalysts has been also reported [14]. The Pt foil surface was roughened by UHV treatment under the same condition as the enhanced activity was observed over Pt catalysts [14]. The presence of small amounts of chlorine impurity was essential for surface roughening. Liberation of the impurity of chlorine brought about surface roughening.

In this paper, details of generation behavior of these active sites is studied by temperature programmed desorption of H_2 and/or D_2 over the Pt powder catalysts. The relationship between the spectra and activity is also discussed. This paper will shed light on a possible model structure of active sites on practical metal catalysts.



Scheme 1. Preparation method of the Pt powder catalysis.

2. Experimental

2.1. Catalyst preparation and materials

Starting Pt powder was prepared by decomposing hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, Nakarai Tesque, Kyoto) under 10^{-2} Pa at 673 K followed by reduction in 13.3 kPa of H_2 at 673 K. This powder is referred to as LD673 in the following. The UHV treatment of the obtained Pt powder was carried out at 1073 K under 10^{-7} Pa. This Pt powder is referred to as UT1073. Direct decomposition of $H_2PtCl_6 \cdot 6H_2O$ under UHV was also carried out at 673 and 1073 K. The obtained samples are referred to as UD673 and UD1073, respectively. The Pt powder catalysts prepared here were summarized in Scheme 1. Hydrogen and deuterium were obtained from Kobe Oxygen and Takachiho Gas Chemicals, respectively, and were used without further purification.

2.2. Temperature programmed desorption

Temperature programmed desorption (TPD) of adsorbed hydrogen was carried out in a UHV pumping system installed with a mass spectrometer. The schematic setup of the TPD experiment is shown in Fig. 1. The Pt powder was charged in a quartz vessel directly linked with the UHV pumping system, and was reduced in 13.3 kPa of H_2 at 473 K for 1 h. The hydrogen in the vessel was evacuated to 10^{-2} Pa by a conventional pumping system, which was also equipped to the quartz vessel, then was evacuated to 10^{-7} Pa by the UHV pumping system followed by raising temperature to 673 or 1073 K. During the UHV treatment, desorbed gas was analyzed by the mass spectrometer. After the UHV treatment, the vessel was cooled to the prescribed temperature followed by adsorption in H_2 or an equimolar mixture of H_2 and D_2 for 10 min. The Pt powder catalysts in the vessel was cooled from the adsorption temperature to 77 K in the hydrogen atmosphere and then evacuated to 10^{-7} Pa. After the pressure in the vessel became constant, the temperature was raised in a constant rate. Before the TPD experiment warmed up to room temperature, the electric furnace and the reaction vessel were cooled in liquid N_2 as shown in Fig. 1. The liquid N_2 was evacuated from the vessel, then the program was started. Outputs from an ion gauge and a thermo couple attached to the quartz vessel were accumulated in a personal computer through a pre-amplifier and A–D converter. The

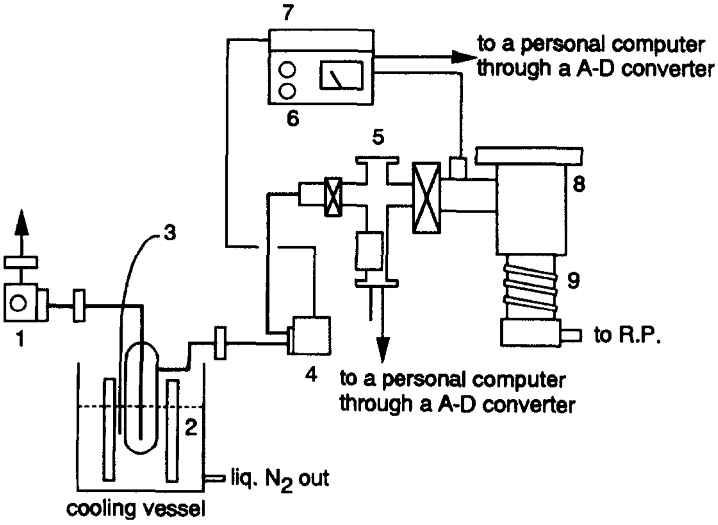


Fig. 1. Schematic setup of TPD experiment and UHV pumping system.

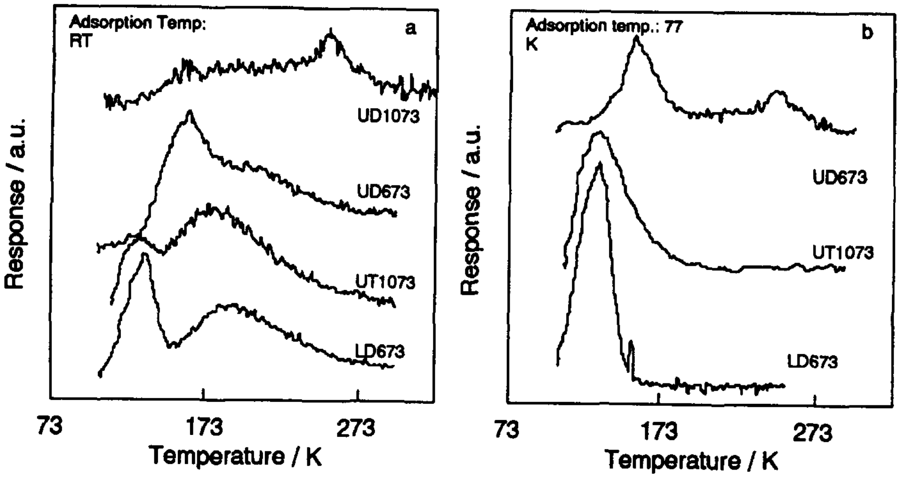


Fig. 2. TPD spectra of hydrogen adsorbed on the UHV-treated Pt catalysts adsorption temperature. (a) room temperature, (b) 77 K.

mass spectra of desorbed gases were also recorded in the case of TPD of H_2/D_2 co-adsorption. Deconvolution of the overlapped peaks was also carried out, providing that the overlapped peak consist of some single Gaussian peaks.

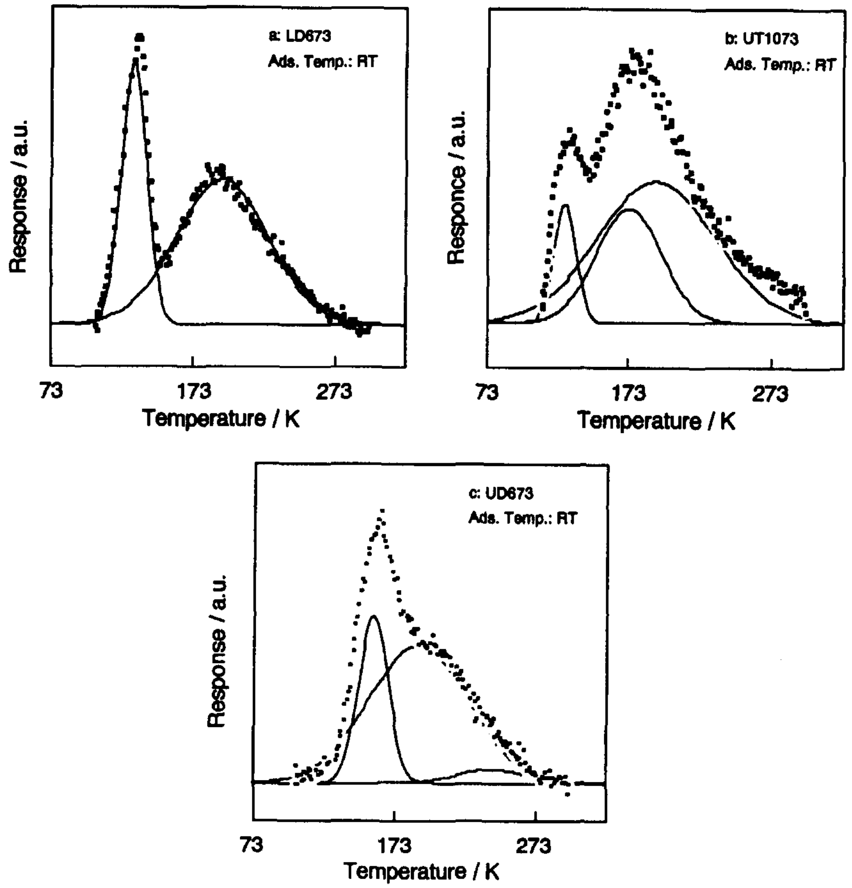


Fig. 3. Deconvolution of the TPD spectra of hydrogen adsorbed on the Pt powders. (a) LD673, (b) UT1073, (c) UD673.

3. Results and discussion

3.1. TPD spectra of adsorbed H_2

The morphology of the most active Pt powder catalyst, UD1073, was studied by SEM technic in the previous paper [14]. The wisker-like structure was observed over UD1073 as already reported [14]. The low active catalyst, LD673, indicated usual powder shape.

The TPD spectra of H_2 adsorbed on the Pt catalysts at room temperature and 77 K were shown in Fig. 2a and b, respectively. The figures indicate that the UHV treatment strongly affect the TPD spectra. Over the LD673 Pt powder catalyst, two desorption peaks were observed near 130 K (referred to α peak) and 190 K (referred to γ peak) as shown in Fig. 2a (adsorption temperature: room temperature) and 3a in which the spectrum was deconvoluted to two peaks. The Pt powder evacuated under UHV atmosphere at 1073 K (UT1073) indicated that some modification of the shape of the spectrum was observed as also shown in Fig. 2a. Fig. 3b shows the deconvolution of the overlapped peaks over UT1073. Three different peaks can be separated. The two peaks which were observed on LD673, α and γ peaks, were confirmed and an additional peak at 160 K (β peak) should be considered. Over UD673 catalyst, peak shape was markedly different from those of UT1073 and LD673. The result of deconvolution of the spectrum over UD673 was also indicated in Fig. 3c. Another new peak was observed at 250 K (δ peak) over UD673 in addition to β and γ peaks as shown in Fig. 3c. TPD spectra of H_2 ad-

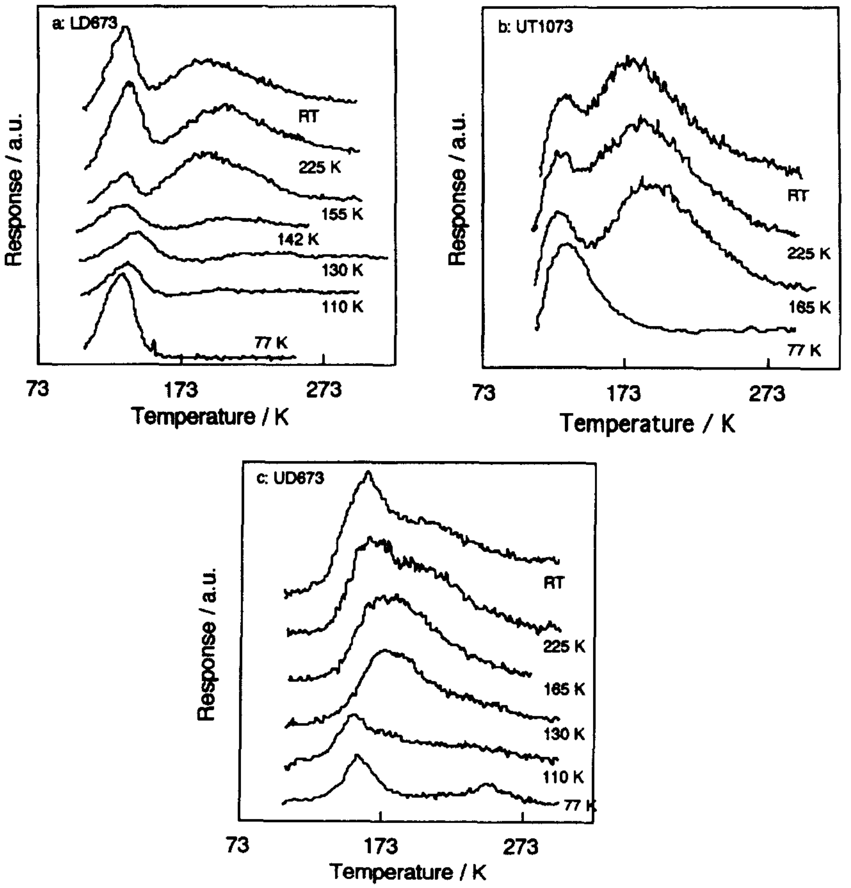


Fig. 4. TPD spectra of hydrogen adsorbed at various adsorption temperatures. (a) LD673, (b) UT1073, (c) UD673.

sorbed at 77 K are shown in Fig. 2b. The desorption peak on LD673 was observed at only 130 K and is referred to as α peak. On the spectrum over UT1073, broad β peak was overlapped to the α peak. Over UD673, significant β and δ peaks were observed, whereas no γ peak was observed as shown in Fig. 2b. The desorption peaks were somewhat broad and noisy, but the spectra was intimately reproducible. These results suggest that the adsorbed species corresponding to the γ peak required a high temperature to be formed. The peak at 130 K (α peak) was ascribable to desorption of associatively adsorbed H_2 because the peak was markedly sharp. A first order desorption peak would be expected sharp and asymmetrical, that is, the desorption rate (direct response) increases gradually and then decreases sharply with increasing temperature in the case of a linearly heating mode. A second order desorption peak would also be expected to be broad and symmetrical. The other peak at 193 K (γ peak) was considerably broad and also ascribed to desorption of H_2 dissociatively adsorbed on LD673. Fig. 2b shows that the new desorption peak (β peak) was observed at 160 K over UT1073. These results indicate that the UHV treatment of LD673 at 1073 K brought about generation of a new adsorption site for H_2. The isotope exchange reaction for H_2–D_2 over Pt powder catalysts has indicated that the activity was significantly enhanced by the UHV treatment of LD673 at 1073 K and that the activation energy was decreased from 27 to 7.4 kJ/mole as shown in our previous paper [12]. The generated adsorption site which was corre-

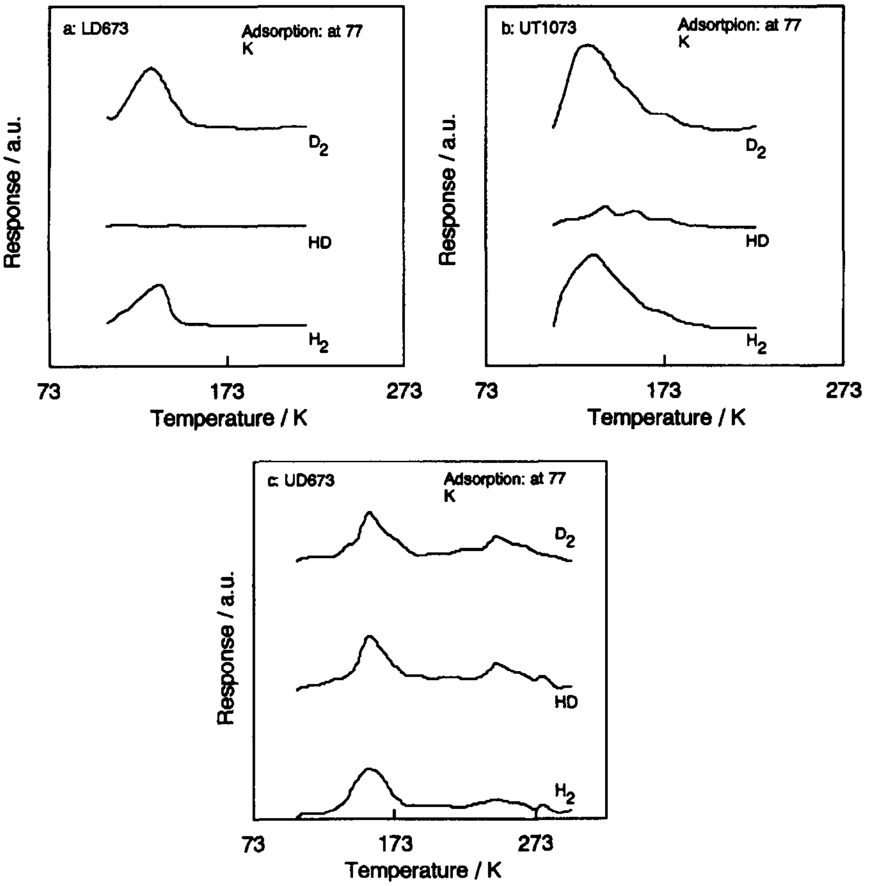


Fig. 5. TPD spectra of H_2–D_2 co-adsorbed on the Pt powders. (a) LD673, (b) UT1073, (c) UD673.

sponding to β peak seems to be very active for the H_2–D_2 exchange reaction. The direct decomposition of $H_2PtCl_6 \cdot 6H_2O$ at 673 and 1073 K also brought about a new desorption peak at 250 K (δ peak) as shown in Fig. 2. The H_2–D_2 exchange reaction over these UD673 and UD1073 showed markedly high activity even at 77 K as described in Ref. [12].

3.2. Effect of adsorption temperature

Temperature programmed desorption spectra of adsorbed H_2 at different temperatures are indicated in Fig. 4a to c. Over LD673, the intensity of the γ peak decreased drastically with decreasing adsorption temperature and below 130 K, no γ peak was observed as shown in Fig. 4a. Only an α peak was observed after adsorption carried out at 77 K. The γ peak also disappeared over UT1073 in the case that the adsorption was carried out at 77 K as shown in Fig. 4b. The β peak would be overlapped to an α peak. Fig. 4c shows that the β and δ peaks were clearly observed on UD673 at 77 K of adsorption temperature, whereas γ peak decreased considerably. These results indicate that the adsorption sites corresponding to γ peak requires high adsorption temperature for activation of molecular hydrogen and that the new adsorption sites corresponding β and δ peaks over UD673 indicated that high ability for dissociative adsorption of molecular hydrogen even at 77 K.

The adsorption temperature of 130 K was required to observe a γ peak at 190 K, whereas the β peak (160 K), of which the desorption temperature was lower than that of the γ peak, appeared even at 77 K. The strongly adsorbed species, which is desorbed at higher temperature, generally requires a lower adsorption temperature. The reason of this unique behavior is not well understood. One possibility is that the adsorption sites (entrance port of adsorbate) are different from the desorption sites (exit port of adsorbate). Another is that an preadsorption state is very important for the adsorption of molecular hydrogen of the β peak.

3.3. TPD spectra of co-adsorbed H_2 and D_2

Temperature programmed desorption over the surface on which H_2 and D_2 were co-adsorbed was carried out in order to determine whether each desorption peak came from dissociatively or associatively adsorbed hydrogen. Fig. 5a to c indicate TPD spectra of co-adsorbed H_2–D_2 over LD673, UT1073, and UD673 Pt powder catalysts at 77 K. Over LD673 catalyst, the α peak consisted of desorption of H_2 and D_2. This result clearly indicates that the α peak corresponds to associatively adsorbed hydrogen as also expected from the peak shape mentioned above. On the other hand, the β and δ peaks indicated significant HD desorption which is an evidence for dissociative adsorption even at 77 K as shown in Fig. 5c. Fig. 5b also shows significant amounts of HD desorption near 160 K over UT1073. These results indicate that the UHV treatment and the UHV decomposition generate new active sites for dissociation of molecular hydrogen [12,14].

3.4. Generation of active sites by UHV treatment and H_2–D_2 isotope exchange reaction

The temperature programmed desorption spectra over the Pt powder catalysts indicate that the four different adsorption species were confirmed. The feature of these species are summarized in Table 1. The peak which appeared at the lowest desorption temperature, α peak observed on LD673 and UT1073, was

Table 1
Feature of the desorption peaks over the UHV-treated Pt powders

	α peak (130 K)	β peak (160 K)	γ peak (190 K)	δ peak (250 K)
Temperature required for adsorption	$\geqslant 77$ K	$\geqslant 77$ K	$\geqslant 130$ K	$\geqslant 77$ K
Adsorption type	associative	dissociative	dissociative	dissociative

Table 2
Summary of TPD experiment and H_2–D_2 exchange activity

Pt catalyst	α (130 K)	β (160 K)	γ (190 K)	δ (250 K)	Activation energy for H_2–D_2 exchange/kJ/mole
LD673	○	–	○	–	27
UT1073	○	○	○	–	7.4
UD673	–	○	○	○	2.4
UD1073	–	○	○	○	1.2

assigned as an associatively adsorbed hydrogen as shown in Fig. 5a. The peak appearing at ca. 190 K, the γ peak, was a dissociatively adsorbed hydrogen as shown in Fig. 5b. This γ peak required at least and adsorption temperature of 130 K to appear. These results suggest that the γ peak is corresponding to activated adsorption sites. The β and δ peaks were assigned as hydrogen atoms adsorbed dissociatively as shown in Fig. 5c. It should be noted that these sites do not require high adsorption temperature as observed for the γ peak. Even at 77 K, hydrogen molecules can be readily adsorbed in β and δ states. Especially, the β peak indicated a unique fashion. The site or adsorption state corresponding to the β peak does not require high adsorption temperatures and also indicates low desorption temperatures summarized in Table 1. The adsorbed species which are readily formed at a lower temperature are expected to be tightly bound to the surface atoms. Unless the species can easily move to different kinds of adsorption sites, which have different adsorption configurations and/or adsorption energy, the tightly bound species will indicate a high desorption temperature or a high energy of desorption. The feature of the β peak suggests that the adsorption sites were not the same as the desorption sites of the β peak. The migration of adsorbed hydrogen from the adsorption sites to the desorption sites will be considered. The energy which was required for the migration will easily be compensated by the heat of adsorption.

Table 2 summarizes the relationship between TPD spectra and H_2–D_2 exchange activity. Over LD673, α and γ peaks were observed and LD673 indicated high activation energy as shown in Table 2. The sites or adsorption state corresponding to α peak do not efficiently participate in the H_2–D_2 exchange reaction. The adsorption state corresponding to the γ peak was effective for the reaction as observed on LD673. The peaks of β and/or δ were observed on UT1073, and UD673. The enhanced activity was observed on UT1073, which was evacuated under UHV at 1073 K; and markedly high activity even at 77 K was obtained over UD673 and UD1073 of Pt powder catalysts as summarized in Table 2. These results indicate that the sites corresponding to the β and δ peaks are markedly active sites for the hydrogenation reaction.

The surface composition and electronic state of the Pt powders were evaluated by XPS as shown in Table 3 [14]. The starting LD673, which was confirmed to be a Pt metal in bulk by XRD, indicated that a part of surface Pt was still in the oxidizing state. The binding energy of Pt4$f_{7/2}$ in the oxidized state was 73.2 eV, which was similar to the peak position over PtO

Table 3
Binding energy and amount of residual chlorine over the Pt powders

Catalysts	Binding energy (eV)			Cl/Pt
	Pt 4$f_{7/2}$	Pt 4$f_{5/2}$	Cl 2p	
UD1073	71.2	74.5	not detected	
UD673	71.3	74.6	199.0	0.23
UT1073	71.0	74.3	not detected	
LD673	71.5	74.7	199.4	2.8
	73.2	76.3		
Pt foil	71.1	74.5		

$PtCl_2$: 74.3 eV; PtO: 73.3 eV. Photoemission from 4$f_{7/2}$ orbital [19].

as shown in Table 3. The amount of chlorine in the Cl/Pt ratio remained at 2.8. The residual chlorine was observed only on UD673 among the other enhanced Pt powder catalysts, that is, UT1073, UD673, and UD1073. The reference binding energy of Pt 4f orbital of Pt metal was also shown in Table 3, and was similar to that over the enhanced Pt powder catalysts. The surface of the enhanced catalysts consisted of metallic Pt. Although the relationship between the amount of residual chlorine and the enhancement of the activity was not so clear, the residual chlorine over the Pt powder catalysts did not strongly affect the activity because of the high activity of UD673 which contained a significant amount of chlorine.

The atoms of oxygen and sulfur which were adsorbed strongly on Fe single crystals brought about surface reconstruction [15,16]. The driving force of the reconstruction is the bond formation between adsorbates and metal surface. The strong bond brought about the reconstruction easily. Leibsle et al. have been reported the surface reconstruction by oxygen adsorption over Rh(110) [17]. The adsorbed oxygen induced the reconstructed $p(2 \times 2)$, $c(2 \times 6)$ and $c(2 \times 8)$ structures were observed [17]. The reconstructed surface will be reformed to the original flat basal surface, because the reconstructed bare surface is not stable. This suggests that the surface reconstruction brought about by adsorption is a reversible phenomenon. The surface roughening behavior by the UHV treatment was brought about by desorption of the impurities involved in the near surface region of the Pt powder catalysts. The desorption resulted in restructuring not only of the surface but also of the near surface layer of the Pt powders. X-ray diffraction powder patterns indicated the change of the structure by the UHV treatment [12]. The obtained rough surface was stable at 1073 K even under low vacuum condition [12,14]. These results indicate that the roughening by the UHV treatment is different from the surface reconstruction by adsorption, and was caused by large scale restructuring.

A large amount of HCl and H_2O was desorbed from LD673 during the UHV treatment at 1073 K, which resulted in UT1073, whereas only slight desorption of H_2O was observed during the UHV treatment of LD673 at 673 K [12]. The enhanced activity of Pt powder was observed only after the UHV treatment at 1073 K [12]. These results indicate that the desorption of HCl was markedly important to obtain the enhanced activity. The desorption of HCl from the near surface of the LD673 Pt powder may roughen the surface as well as the structure of near surface bulk. The similar roughening behavior was observed over the Pt foil model catalysts [14,18]. The rough surface was observed by SEM study after the UHV treatment of the HCl-doped Pt foil at 1073 K [14].

Our previous results have indicated that the UHV treatment of Cl^--doped Pt foil model catalysts at 1073 K brought about a markedly rough surface. The condition, 1073 K of the treatment temperature, ultrahigh vacuum atmosphere, and presence of Cl^--impurity, were essential for the surface roughening. The removal of Cl^--impurity under UHV at 1073 K would bring about the surface roughening discussed previously. The rough surface of Pt was very active for H_2–D_2 exchange reaction as summarized in Table 2. Therefore, the generation of new active sites by the UHV treatment reported here strongly suggest that one of the highly active sites on Pt catalysts is located at the edge or corner structure which are well known as 'step' or 'kink' structures, respectively. It should be also noted that these results were obtained over polycrystalline Pt specimens. Our results significantly support this idea, that is, the step and/or kink structures are active sites on practical metallic catalysts.

4. Conclusions

The thermal treatment under ultrahigh vacuum at 1073 K generated two kinds of new desorption peaks over the Pt powders in temperature programmed desorption spectra of adsorbed hydrogen at 160 (β peak) and 250 K (δ peak). These new peaks were still observed in the case of adsorption at 77 K. It is considered that liberation of Cl^--impurity from the Pt powders brought about a rough surface. The Pt powder samples on which the peaks of β and δ were observed in TPD spectra indicated the marked activity for H_2–D_2 exchange reaction previously reported.

These results indicate that the thermal treatment under ultrahigh vacuum will generate new adsorption sites for molecular hydrogen. The new sites are considered to be located at edge and/or corner structures on the roughened surface. These structures are identical to the well known nano-scale structures, 'step' and 'kink' observed on single crystals.

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