Palladium-Hydrogen Interaction on Supported Palladium Catalysts of Different Metal Dispersions

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Abstract−Palladium-hydrogen interaction on supported Pd catalysts of different metal dispersions has been studied by hydrogen chemisorption and back-sorption, and by temperature-programmed desorption (TPD) of either deuterium or hydrogen from the Pd surface after different initial gas dosages. Pd interacts with three hydrogen species whose amounts vary with the metal dispersion and with the dosage pressure. The amount of hydrogen strongly adsorbed on the Pd surface increases with the metal dispersion but is unaffected by the hydrogen pressure. The amount of hydrogen absorbed in the bulk of Pd is significant with a poorly dispersed catalyst, particularly when the hydrogen pressure is higher than about 10 Torr, but decreases with the metal dispersion. Hydrogen weakly bound with Pd shows two characteristic TPD peaks, whose intensity depends on the metal dispersion and the initial gas dosage. The peak at 270-330 K, assigned to the recombination of absorbed hydrogen with surface hydrogen, is large with a poorly dispersed catalyst and grows with the initial hydrogen dosage. The intensity of the peak at 215-226 K is not affected by the metal dispersion or by the hydrogen dosage. It has been concluded that an analysis of the intrinsic properties of Pd catalysts should be based on an understanding of the hydrogen species associated with the catalysts.

Key words: Palladium, Hydrogen, Dispersion, Adsorption, Absorption, TPD

INTRODUCTION

The interaction of palladium with hydrogen has been studied extensively [Conrad et al., 1974; Behm et al., 1983; Ragaini et al., 1994] because the characteristic property of Pd to either adsorb or absorb hydrogen allows the metal to be used as an excellent hydrogenation catalyst [Thomas, 1970] as well as a hydrogen storage medium [Buchner, 1977]. The selective hydrogenation of acetylene is a typical example of hydrogenation process using palladium catalysts [Lee, 1990; Shin et al., 1998]. Palladium membrane is also used for hydrogen separation from gas mixture [Shu et al., 1991; Aoki et al., 1996]. Aldag and Schmidt [1971] reported in their study of hydrogen desorption from Pd filaments that hydrogen interacts with Pd in two modes: the α-state due to the dissolution of hydrogen in the Pd wire and the β-state corresponding to the adsorption of hydrogen on the Pd surface. According to Ragaini et al. [1994], surface-adsorbed β-state hydrogen may be classified again into two types representing either the weakly- or the strongly-adsorbed species. Therefore, hydrogen interacts with Pd in three basic modes: absorption in the bulk of Pd (H_{abs}), weak adsorption on the Pd surface (H_w), and strong chemisorption on the Pd surface (H_s). The H_{abs} species, corresponding to α-state hydrogen proposed by Aldag and Schmidt [1971], is frequently called dissolved hydrogen or Pd hydride to indicate its nature of interaction with the bulk of Pd. Konvalinka and Scholten [1977] proposed that the H_w species desorb from the Pd surface by the combination of surface hydrogen with hydrogen associated with the sub-surface sites, the latter species being verified by Behm et al. [1983] in their study of hydrogen TPD from Pd(110) single crystal.

In the case of supported Pd catalysts, the Pd-hydrogen interaction is affected by the metal dispersion. Aben [1968] reported that the amounts of absorbed hydrogen, H_{abs}, decreased as the metal dispersion increased, a trend confirmed by others [Boudart and Hwang, 1975; Borodzinski et al., 1976; Chou and Vannice, 1987]. In addition, Chou and Vannice [1987] reported that integral heats of adsorption of hydrogen (Q_{ad}) on Pd increased sharply as the Pd crystallite size dropped below 3 nm, which they attributed to changes in the electronic properties of small Pd crystallites. The same trend was observed by Zakumbaeva et al. [1983] with Pd/MgO catalysts.

In the work of Chou and Vannice [1987], they obtained heats of adsorption (Q_{ad}) or absorption (Q_{ab}) based on either the metal surface area measured by hydrogen chemisorption or the amount of absorbed hydrogen measured by hydrogen back-sorption. However, changes in the intrinsic heats with the metal dispersion should be analyzed considering the characteristic Pd-hydrogen interaction because the latter is affected by the metal dispersion as well as the hydrogen dosage condition. For this reason, we have studied the hydrogen adsorption/desorption properties of Pd/SiO₂ of different metal dispersions using hydrogen chemisorption, back-sorption and TPD methods. The results have been discussed related to previous explanations of the Pd-hydrogen interaction.

EXPERIMENTAL

Supported Pd catalysts were prepared by either the ion-ex-

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change (IE) or the incipient-wetness impregnation (IWI) method using $Pd(NH_3)_4(OH)_2$ or $Pd(NH_3)_4(NO_3)_2$ as the Pd precursor. The silica support was JRC-SIO6 (surface area=109 m^2/g) obtained from the Catalysis Society of Japan. The prepared catalysts were dried at 393 K for 12 h and calcined in O_2 at 573 K for 1 h before storage in a desiccator. The Pd loadings of the catalysts, pre-adjusted to be near 1 wt%, were determined by inductively coupled plasma-atomic emission spectroscopy (Perkin-Elmer, plasma 40). The sample catalysts are designated as Pd/SiO_2 (IE) and Pd/SiO_2 (IWI) respectively according to their preparation methods.

Hydrogen uptake by the catalysts was measured at room temperature in a volumetric adsorption system. Prior to the measurements, the sample was reduced in a H_2 flow at 573 K for 1 h, and then the cell was evacuated at the same temperature for 1 h. The amounts of hydrogen chemisorbed on the sample surface were determined by the back-sorption method described by Benson et al. [1973]. That is, the sample cell was evacuated at room temperature for 20 min after the initial isotherm measurements, and then a second isotherm was obtained by introducing hydrogen into the cell.

TPD experiments were made either in an ultrahigh vacuum (UHV) chamber with the base pressure below 5×10^{-11} Torr or in an atmospheric flow reactor. The UHV chamber was equipped with a quadrupole mass spectrometer (QMS, Balzers QMA 200 M) to monitor desorbed species from the sample surface. For vacuum TPD, the catalyst sample was reduced in a pretreatment chamber by flowing a 10% H_2/N_2 mixture at 623 K for 1 h. Gas near the sample surface was removed by pumping the chamber at the same temperature for 1 h, and then the sample was transferred to the UHV chamber. The sample was cooled to 120 K with liquid nitrogen, exposed to 10^{-6} Torr of deuterium at the same temperature for different periods, and finally heated to 710 K at 0.5 K/sec by a radiant, resistive tungsten-filament heater.

For the atmospheric TPD experiments, either pulses or a constant level of hydrogen were introduced into the N_2 stream flowing through a reactor containing sample catalysts. Then, the reactor was cooled to 200 K, flushed with flowing N_2 for 1 h, and

Fig. 1. Schematic diagram for vacuum TPD apparatus.

1. Sample holder	8. Rotary pump
2. Main chamber	9. Thermocouple
3. Pretreatment chamber	10. Leak valve
4. Mass spectrometer	11. Gate valve
5. D_2 cylinder	12. On-off valve
6. H_2/N_2 cylinder	13. Turbomolecular pump
7. Diaphragm pump	14. Ion pump

heated at 10 K/min for the desorption experiments. The effluent gas was analyzed with a mass spectrometer (QMS, VG Sensorlab 200).

Deuterium, instead of hydrogen, was used for the vacuum-TPD experiments because deuterium could be monitored more sensitively in the chamber than hydrogen. The base pressure of hydrogen in the vacuum chamber was as high as 10^{-6} Torr due to water desorbing from the chamber wall while that of deuterium was at low levels of 10^{-11} Torr. Deuterium is different from hydrogen only in the mass number and is expected to yield the same information as hydrogen. Fig. 1 shows a schematic diagram of the vacuum-TPD apparatus.

RESULTS AND DISCUSSION

1. Hydrogen Chemisorption and Back-sorption

Fig. 2(A) shows two isotherms obtained on Pd/SiO_2 (IWI): one due to the initial hydrogen uptake and the other obtained by the subsequent back-sorption after cell evacuation. The difference of the two isotherms gives the amount of strongly adsorbed hydrogen (H_s), which is commonly used for the estimation of the Pd surface area [Benson et al., 1973]. It is notable that the amount of hydrogen chemisorption remains almost constant over a wide range of the hydrogen pressure.

Two isotherms increase sharply near the hydrogen pressure of about 10 Torr eventually to reach the saturation level beyond 20 Torr. The sharp transition occurs because hydrogen dissolves in Pd to form Pd hydride (H_{abs}) at high pressures [Chou and Vannice, 1987]. In other words, hydrogen is initially "adsorbed on" the Pd surface when the pressure is low but is additionally "absorbed in"
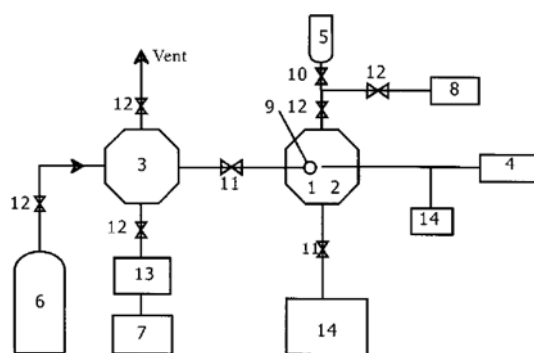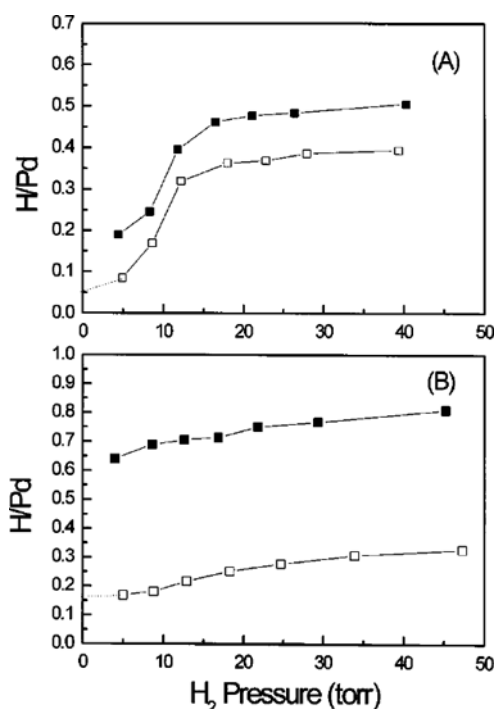

Fig. 2. Hydrogen isotherms on Pd samples.
(A) Pd/SiO_2 (IWI), (B) Pd/SiO_2 (IE) (Solid symbols: first isotherm, open symbols: second isotherm).

Table 1. Prepared catalysts and their chemisorption results

Sample	Precursor	Dispersion (Pd_s/Pd_{total})	d (nm)
1.05% Pd/SiO$_2$ (IWI)	Pd(NH$_3$)$_4$(NO$_3$)$_2$	0.1	11.3
1.23% Pd/SiO$_2$ (IE)	Pd(NH$_3$)$_4$(OH)$_2$	0.46	2.4

the bulk of Pd at high pressures. The hydrogen dissolution behavior is characteristic of Pd, which allows the metal to be used for a hydrogen storage medium [Buchner, 1977].

Fig. 2(B) shows that the amount of hydrogen chemisorbed on Pd/SiO$_2$ (IE) is larger than on Pd/SiO$_2$ (IWI), thus indicating that the former catalyst has a higher Pd surface area than the latter. Table 1 lists the metal dispersions (D) of the two sample catalysts estimated from the chemisorption results assuming that the H$_s$/Pd$_s$, hydrogen/surface Pd atom, ratio is 1. Table 1 also shows the average Pd crystallite sizes (d) obtained from the relationship, d (nm)=1.13/D [Wang et al., 1981]. The Pd particle size of 2.4 nm obtained with Pd/SiO$_2$ (IE) falls in the range that exhibited increased heats of hydrogen adsorption on and absorption in Pd according to Chou and Vannice [1987].

The sharp transition of isotherms near 10 Torr observed with Pd/SiO$_2$ (IWI) in Fig. 2(A) is not clearly shown in Fig. 2(B), indicating that hydrogen dissolution in the bulk of Pd is not significant with Pd/SiO$_2$ (IE). This result agrees with the previous reports that hydrogen absorption is suppressed when Pd crystallites are small [Aben, 1968; Boudart and Hwang, 1975].

Isotherms obtained by back-sorption represent both weakly-adsorbed (H$_w$) and absorbed (H$_{abs}$) hydrogen, one of which contributes to the isotherm at low pressures and the other beyond 10 Torr. Fig. 2 indicates that the amount of the low-pressure species estimated by the extrapolation of the back-sorption isotherm to zero pressure, presumably the H$_w$ species, is larger with Pd/SiO$_2$ (IE) than with Pd/SiO$_2$ (IWI). The result is not surprising because the former catalyst has a higher surface area than the latter.

2. Deuterium and Hydrogen TPD

Fig. 3 shows patterns of deuterium TPD from the two catalysts that have been exposed to 10^{-6} Torr of deuterium for different periods. In both cases, the peak intensity grows as the deuterium dosage increases up to about 1,600 L, beyond which the intensity levels off, indicating that the Pd surface is almost saturated with deuterium. The saturation pressure of about 1,600 L is higher than that for Pd single crystal or filament [Behm et al., 1983], whose surface is saturated with hydrogen at dosages as low as 50 L. We believe that the discrepancy between the two cases occurs because the sample catalysts of this study are supported on porous silica. Diffusion of deuterium in the catalysts must be severely limited under the conditions of this study because the mean free path of deuterium at 10^{-6} Torr is about 32.6 m, 6×10^7 times the average pore size of the catalyst.

The TPD curves of Figs. 3(A) and 3(B) may be resolved into three peaks centered at 228-240 K, 300-323 K and 410-412 K, which were attributed to H$_{abs}$, H$_w$ and H$_s$ respectively by Ragaini et al. [1994]. Symbols of H$_{abs}$, H$_w$ and H$_s$ have been used instead of D$_{abs}$, D$_w$ and D$_s$ because hydrogen and deuterium have the same properties although the atomic masses are different.

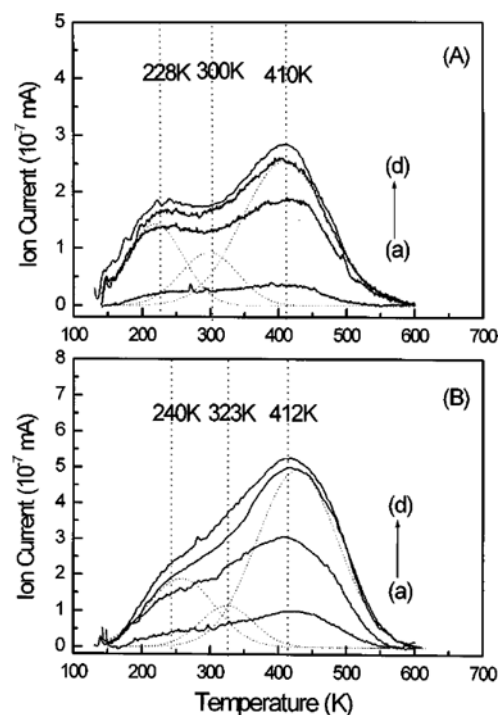It is worth noting in Fig. 3 that the peak positions are almost

Fig. 3. TPD patterns of D$_2$ from Pd samples in vacuum apparatus.
(A) Pd/SiO$_2$ (IWI); (a) 218 L, (b) 1,248 L, (c) 1,635 L, and (d) 2,132 L; (B) Pd/SiO$_2$ (IE); (a) 229 L, (b) 832 L, (c) 1,647 L, and (d) 1,898 L. Dotted lines are deconvolution results of the TPD pattern (c).

unaffected by the initial deuterium dosage, which contrasts with previous works reporting peak shifts [Aldag and Schmidt, 1971; Behm et al., 1983; Ragaini et al., 1994]. The difference arises because the deuterium dosage in this study is much higher than in the previous works and therefore the peaks have already reached the limiting positions. In fact, the location of the H$_s$ peak in this study, 410-412 K, is close to the limiting positions of the corresponding peaks reported in the previous studies [Aldag and Schmidt, 1971; Behm et al., 1983; Ragaini et al., 1994].

The major peak at 410-412 K assigned to H$_s$ is stronger with Pd/SiO$_2$ (IE) than with Pd/SiO$_2$ (IWI) so that the former catalyst shows almost one band with a shoulder while the latter shows two distinct bands. This agrees with the gas-uptake result that the former catalyst has a higher Pd surface area than the latter. Fig. 3 also shows the deconvolution results of the TPD patterns for the two catalysts obtained at 1,635 L and 1,647 L, respectively. The peak at 228-240 K appears with comparable intensity for the two catalysts. The peak near 300-323 K also shows almost the same intensity for the two catalysts although the conclusion is not definite due to possible errors in the deconvolution process. For both catalysts, the 300 K peak is the smallest among the three TPD peaks.

The TPD results obtained at atmospheric pressures after dosages of hydrogen either as pulses (Fig. 4) or as a stream of constant concentration (Fig. 5) show three peaks more clearly than in the case of the vacuum TPD. The peak at 415-445 K due to H$_s$ is stronger with Pd/SiO$_2$ (IE) than with Pd/SiO$_2$ (IWI), due to different Pd dispersions of the catalysts. Fig. 5 also shows that
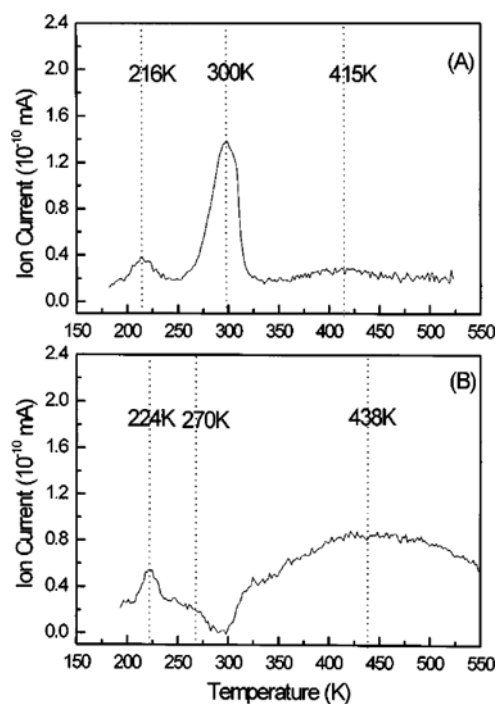
Fig. 4. TPD patterns from Pd samples in atmospheric system after pulse injection of H₂ at 200 K.
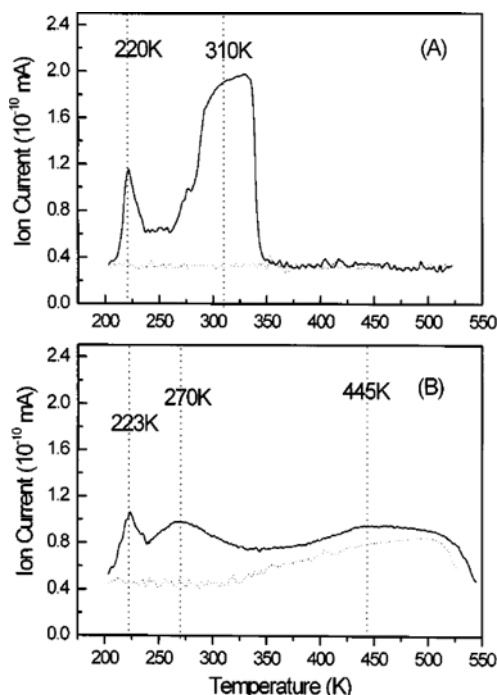(A) Pd/SiO₂ (IWI), (B) Pd/SiO₂ (IE).

Fig. 5. TPD patterns from Pd samples in atmospheric system after H₂ flowing at 300 K for 30 min.
(A) Pd/SiO₂ (IWI), (B) Pd/SiO₂ (IE). Solid lines are TPD patterns obtained after N₂ purging at 200 K for 1 hr. Dotted lines are TPD patterns obtained after N₂ purging at 300 K.

two peaks except for H_s are completely removed after the reactor has been purged with nitrogen at room temperature for 1 h. Therefore, the hydrogen species represented by the two peaks are bound

to Pd relatively weakly. Unlike in the case of vacuum TPD, the peak at 270-310 K appears distinctively, with a strong intensity particularly in the case of Pd/SiO₂ (IWI).

Two aspects are to be noted about the weakly bound hydrogen species in Figs. 4 and 5. One is that the peak at 270-310 K is much stronger with Pd/SiO₂ (IWI) than with Pd/SiO₂ (IE). The other is that the peak at 216-224 K, assigned to H_{abs} by Ragaini et al. [1994], appears with a comparable intensity for both catalysts. Following the assignment by Regaini et al. [1994], however, the intensity trend of the H_{abs} peak is contradictory to the gas-uptake result showing that the amount of absorbed hydrogen decreases with the Pd dispersion. On the other hand, the trend observed with the peak at 270-310 K, assigned to H_w by Ragaini et al. [1994], showing higher intensity with lower Pd dispersion seems to be better correlated with the gas-uptake result. Also of note is that by comparing the results of Figs. 3, 4 and 5 the peak intensity grows with the hydrogen dosage pressure following the order of vacuum<pulses<flow. Accordingly, it is obvious that the intensity of the peak at 270-310 K increases with the amount of absorbed hydrogen. The above complex and somewhat contradictory results clearly indicate that we need to understand the origin of the peaks associated with the weakly bound hydrogen species.

3. Origin of the Hydrogen Species

Konvalinka and Scholten [1977] observed a TPD peak at 293 K which they assigned to the recombination of "sub-surface" hydrogen with surface hydrogen. When Pd accommodating both dissolved and adsorbed hydrogen is subject to vacuum, hydrogen dissolved in the bulk of Pd diffuses to the surface where it combines with adsorbed hydrogen eventually to produce hydrogen desorbing from the Pd surface. This mechanism suggests that the intensity of the peak at 293 K depends on the amounts of both dissolved hydrogen (H_{abs}) and adsorbed hydrogen (H_s). According to the results in Figs. 4 and 5, the intensity of the peak at 293 K, 270-310 K in our study, seems to depend more on the amount of H_{abs} than on H_s. The mechanism also explains why the peak at 300-323 K in vacuum TPD (Fig. 3) is not so strong as in the case of atmospheric TPD (Figs. 4 and 5). Because the hydrogen dosage in vacuum TPD is much less than in atmospheric TPD, the amount of dissolved hydrogen is less and consequently the peak is weaker in the former case.

About the origin of the peak at 215-224 K, we do not yet have an unequivocal explanation. The result that the peak intensity is almost unaffected by the metal dispersion eliminates the possibility that the peak simply reflects the amounts of hydrogen dissolved in the bulk of Pd. Instead, it may be associated with specific Pd sites which accommodate a determined amount of hydrogen irrespective of the Pd crystallite size. The sites may either absorb or adsorb hydrogen, but they accommodate hydrogen weakly enough to lose it at relatively low temperatures.

Chou and Vannice [1987] reported that heats of hydrogen adsorption (Q_{ad}) and absorption (Q_{ab}) increased sharply as the crystallite size of Pd dropped below 3 nm, which they attributed to changes in the electronic properties of small Pd crystallites. They calculated the heat of adsorption (Q_{ad}) based on the Pd surface area estimated from the amount of hydrogen chemisorption (H_s), given by the difference between the initial hydrogen uptake and the back-sorption curves. The heat of absorption (Q_{ab}) was ob-

tained based on the amount of absorbed hydrogen estimated simply from the back-sorption data. However, it has been demonstrated in this study that hydrogen weakly associated with Pd in the back-sorption step consists of various species such as H_{abs} and H_w whose relative amounts change with the Pd dispersion as well as with the initial hydrogen dosage. Accordingly, the intrinsic value, Q_{ab}, should be estimated after full analyses of the hydrogen species.

CONCLUSIONS

From the results of hydrogen uptake and TPD experiments described above, we may conclude the following.

The amount of hydrogen strongly adsorbed on Pd increases with the metal dispersion and is independent of the initial hydrogen dosage, thus indicating that hydrogen chemisorption is a proper method to measure the Pd surface area. On the other hand, the amount of hydrogen weakly bound with Pd depends on both the metal dispersion and the initial hydrogen dosage. Weakly bound hydrogen is responsible for two characteristic peaks in the TPD experiments. The peak at 270-310 K, due to the recombination of absorbed hydrogen with adsorbed hydrogen, decreases with the metal dispersion but increases with the initial hydrogen dosage. The peak at 215-226 K is not affected by the metal dispersion or by the hydrogen dosage.

Accordingly, an analysis of the intrinsic properties of Pd crystallites, particularly as related to absorbed hydrogen, should be based on a full understanding of the weakly adsorbed hydrogen species in the catalysts.

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