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NMR Characterization of the Hydrogen and Deuterium Phases Present in Pd/SiO_2 Catalysts

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Static and MAS (magic-angle-spinning) NMR spectroscopies were used to study D_2 (and H_2) interacting with large (1-μm) Pd crystallites as well as small (2- to 6-nm) Pd particles dispersed on SiO_2. Peaks were resolved for four different deuterium species—gas-phase D_2, β-phase Pd deuteride, weakly chemisorbed deuterium on Pd, and OD groups on the SiO_2 surface. Static experiments showed that the gas–deuteride exchange process was slow on the NMR time scale for larger Pd crystallites, and the two separate peaks remained resolved between 218 and 390 K with the 1-μm particles whereas they coalesced at 360 K with 6-nm particles. Above 230 K only a single peak representing the weighted average of these two phases was obtained with 2-nm particles. Strongly chemisorbed deuterium could not be detected, even by MAS, but the weakly chemisorbed species gave a single, pressure-dependent peak. It appears that it is only this latter species which is the intermediate in the rapid gas-phase/β-phase deuteride exchange process and which migrates to form the –OD groups on the silica. © 1989 Academic Press, Inc.

INTRODUCTION

Palladium catalysts enjoy widespread commercial use (*1*), possess unique adsorptive and catalytic behavior, and have been frequently studied. However, questions remain about the properties of very small Pd particles. For instance, evidence of structure sensitivity in hydrogenolysis reactions exists (*2*), and variations in activation energy in the H_2–D_2 exchange reaction have been reported (*3–5*). Also, it has been suggested that small Pd crystallites do not form bulk hydride phases (*6*), although this conclusion has been debated (*7, 8*). In addition, a recent calorimetric study has found that the integral heat of adsorption for H_2 on small Pd crystallites increases markedly from that on larger Pd crystallites and single-crystal surfaces (*9*). The identification of the various forms of hydrogen present in and on both large and small Pd crystallites could help explain these reported differences.

NMR spectroscopy has been successfully used in the past to study bulk Pd hydrides and deuterides (*10*), especially with respect to determining the diffusional properties of H and D through the metal lattice (*11–13*) and the low-temperature behavior of these hydrides (*14, 15*). More recently, ^1H NMR has been utilized in the study of H_2 on small supported particles of Pt (*16, 17*); however, apparently only two studies have been conducted on hydrogen associated with dispersed Pd particles. Sheng and Gay (*18*) studied H adsorbed on a silica-supported Pd catalyst at H_2 pressures of less than 1 Torr, while a more recent investigation (*19*) examined the adsorption and absorption properties of H_2 on alumina-supported Pd at different pressures and temperatures.

In this study, the properties of different sizes of silica-supported Pd crystallites were investigated using solid-state NMR spectroscopy of deuterium at temperatures from 218 to 388 K and pressures up to 500 Torr. The use of deuterium eliminates the background effects which can make proton

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spectra difficult to interpret. For example, the large peak usually detected for support hydroxyl protons in ^1H NMR does not appear in the deuterium spectrum. This is important because the resonances for adsorbed hydrogen have, in some cases, been found to overlap the hydroxyl resonances (*17*). The use of deuterium also assures that any detectable signals are from the sample itself, rather than the probe materials or the NMR tubes. This point is important because the signal from a given adsorbed species is often very weak, and even trace amounts of proton-containing substances in the probe itself can give rise to artifacts during repetitive scanning in the ^1H experiment.

In this study, we report both static and MAS NMR experiments which have provided evidence for the existence of four different deuterium species—gas-phase D_2, β-phase deuteride, weakly chemisorbed deuterium, and exchanged OD deuterons on the SiO_2 support. On small crystallites, a rapid exchange process that occurs above 250 K between the β-phase deuteride and the gas-phase D_2 appears to do so via the weakly chemisorbed form of deuterium. As the surface/volume ratio decreases on larger Pd crystallites, this rapid exchange is obtained only at much higher temperatures.

EXPERIMENTAL PROCEDURE

Catalyst Preparation

The two catalysts used in this study were prepared by different methods to vary dispersion. The support material in each case was Davison Grade 57 silica gel (BET surface area 200 m^2/g) which was crushed and sieved to 80–100 mesh and calcined at 773 K in air to remove adsorbed impurities. A low dispersion (ld) catalyst of 2.0 wt% Pd was prepared by incipient wetness impregnation using an aqueous solution of H_2PdCl_4 obtained by warming $PdCl_2$ (Alfa Ventron) in dilute hydrochloric acid. A high dispersion (hd) catalyst containing 2.48 wt% Pd was prepared by ion exchange with tetraamine palladium(II) nitrate as a precursor. The ion exchange was performed in a slurry phase using ammonium hydroxide for pH control as described previously (*9*). The catalysts were dried in air at 393 K for several hours before pretreatment. For reference purposes, a physical mixture of 2.3 wt% Pd powder (Puratronic Grade (99.999%), Alpha Products) and Davison 57 silica gel was prepared, and this sample will be referred to as (mx).

Adsorption Measurements

Sample pretreatment and chemisorption measurements were obtained using a stainless-steel adsorption system with a Balzers TSU-171 turbomolecular pump unit, which provided a vacuum of 1×10^{-7} Torr (1 Torr = 133 Pa) in the sample region. Chemisorption measurements were done volumetrically using a Baratron precision capacitance manometer for pressure readings. Deuterium gas (Cambridge Isotope Laboratories, 99.8% purity) was used with no additional purification, and all other gases were ultrahigh purity (99.999%) and were further purified by passing them through Oxytraps (Alltech Associates) prior to use.

The catalyst pretreatment consisted of evacuating the sample for 1 h at 300 K, heating to 393 K under vacuum and holding for 5 min, heating to 433 K and introducing H_2 at 1 atm (0.1 MPa), and then raising the temperature to 673 K and holding at that temperature for 1 h. For the pretreatments done in NMR tubes (see below), the H_2 atmosphere was evacuated and replaced with fresh H_2 four times during the 1-h reduction at 673 K. Following reduction, the samples were cooled to 653 K and evacuated at that temperature for 30 min, after which they were cooled to 300 K under vacuum. Prior to the NMR runs, deuterium was introduced into the evacuated samples in one dose, and adsorptions thus performed are hereafter referred to as "one-point" uptake measurements. For comparison, "multi-point" uptakes were also obtained using the dual-isotherm method described by Benson *et al.* (*20*).

NMR Spectroscopy

NMR spectroscopy was performed under both static and magic-angle-spinning (MAS) conditions. The static experiments were run on samples which were enclosed in re-sealable 5-mm-o.d. NMR sample tubes purchased from Wilmad Glass Co. (Part No. 507-JY-7). The original Teflon-glass seals on these tubes were found to leak, especially when the tubes were partially or totally evacuated; consequently, new stopper plugs with O-ring seals were fabricated from Delrin plastic. The final configuration had a single O-ring sealing surface and double O-ring seals in the valve body as well as at the attachment to the adsorption system. This design provided a sufficient seal for days. The tubes were readily attached to the adsorption system for *in situ* treatments and adsorption measurements via a glass adaptor.

The static deuterium NMR spectra were obtained on a Bruker WP-200 spectrometer equipped with a variable temperature (VT) controller. A broadband probe tuned to 30.72 MHz was used for all acquisitions. The deuterium lock channel was disconnected during acquisition, and all spectra were externally referenced relative to deuterated benzene (7.3 ppm) (*21*).

Two methods of acquisition were used to obtain the static spectra. Simple 90°x pulses of 11.3 μs were used for the earlier spectra; however, acoustic ringing resulted in a large spike at the beginning of the free-induction decay, and this had to be eliminated by left-shifting the spectra prior to the Fourier transform. The ringing problem was subsequently avoided by using a Hahn spin-echo pulse sequence (*22*), consisting of an 11.3-μs pulse followed by a 150-μs delay and a 22.6-μs refocusing pulse. Data collection commenced after a second delay of 150 μs to allow the spins to refocus. The appearance of the resonance lines remained the same using either acquisition method. For samples containing more than 20 Torr of D_2 pressure, 2000–6000 acquisitions were obtained, while 25,000–28,000 acquisitions were typically obtained for the samples containing lower pressures of D_2. All spectra were collected using quadrature phase cycling with quadrature phase detection and a 1-s pulse delay; 16,000 points were collected at a total sweep width of 20 kHz, and all spectra were line broadened by 40 Hz prior to the Fourier transform to improve the signal-to-noise ratio. These parameters and pulse sequences are more typical for liquid (or gaseous)-state ^{2}H NMR spectroscopy than for solid-state ^{2}H NMR spectroscopy. Quadrupolar powder pattern linewidths found in the latter case are on the order of 250 kHz; therefore, these spectra require sweep widths larger than 250 kHz and 90° pulse widths (usually used within the quadrupole echo sequence, $90x$–τ–$90y$–τ–acquire) less than about 2.7 μs for uniform excitation. The fact that assignable ^{2}H signals were obtained using liquid-state parameters immediately implies that the corresponding species are sufficiently mobile to average the quadrupole interaction to zero. Initial ^{1}H spectra of these samples were obtained on a Bruker WM-360 spectrometer using similar procedures.

In order to see all species, including those broadened by the quadrupole interaction, MAS spectra were obtained with simple 90° pulses on the (hd) catalyst using a Chemagnetics CMC-300A spectrometer operating at 45.72 MHz for deuterium. Following catalyst pretreatment and adsorption of D_2, the samples were sealed in glass capsules made from Wilmad 6.5-pp (6.5-mm-o.d.) ultrathin-wall NMR tubes using glassblowing techniques (*23*). The samples were sealed either under vacuum or with 500 Torr D_2 pressure, and all the pretreatment, adsorption, and seal-off procedures were done without air exposure. The sealed glass capsules were inserted into two-piece Delrin rotors supplied by Chemagnetics and spun at 2.6–3.2 kHz. A sweep width of 100 kHz was used with 90° pulses (4.0 μs) and a pulse delay of 1 s. These parameters, while not adequate for the standard nonspinning, quadrupole echo, solid-state experiment, are nevertheless sufficient to reveal solid-state ^2H resonances affected by the quadrupolar interaction, provided that the T_2 of the resonance is sufficiently long. The MAS spectra were externally referenced using a sealed sample of D_2 gas, which was defined to have a chemical shift of 10 ppm relative to TMS. MAS experiments were chosen rather than nonspinning quadrupole echo experiments because one obtains higher signal to noise with the narrow spinning sidebands provided that the T_2 is long enough to allow for instrumental "ringdown." This enables one to observe smaller quantities of D.

RESULTS

Adsorption

Prior to the NMR runs, each catalyst was pretreated as stated previously. Both the (ld) and the (hd) catalysts were put through two reduction/adsorption cycles before the first NMR experiments. Multipoint adsorption isotherms were determined between 40 and 260 Torr pressure and extrapolated to zero pressure, in accordance with the procedure of Benson *et al.* (*20*), to obtain both irreversible and reversible uptakes. For the one-point adsorptions, the uptake of D_2 on the support was determined by measuring the adsorption on pure silica using exactly the same procedure as that for the NMR samples and, assuming no irreversible adsorption, an isotherm slope was established and was used to determine the uptakes associated with the Pd by again extrapolating to zero pressure. For all the adsorption measurements, the reversible uptake was obtained after a 25-min evacuation at 300 K following the initial adsorption isotherm. The adsorption results for all of the samples are listed in Table 1. In most cases the uptakes were comparable and were affected little by repeated cycling. Using the irreversible D_2 uptakes obtained at 300 Torr with the one-point method, the catalyst weight, and estimates of the void volume, the relative amounts of deuterium in the gas phase, the bulk β-phase deuteride, and the chemisorbed phase were estimated. These results are shown in Table 2 for the (hd) and (ld) catalysts.

If all the reversibly adsorbed deuterium (D_{rev}) is assumed to be absorbed in the Pd

TABLE 1

Summary of D_2 Update Measurements[a]

Sample	Total uptake (μmole/g cat)		Reversible uptake (μmole/g cat)		Irreversible uptake (μmole/g cat)		Dispersion (%)	
	One point	Isotherm	One point	Isotherm	One point	Isotherm	One point	Isotherm
(mx)	77	66	77	59	0	7	0	7
(ld)	57	52	39	36	19	16	20	17
(hd)	96	85	27	36	69	49	59	42

	D_{rev}/Pd_b (300 K)		D_{rev}/Pd_b (363 K) One point	Particle diameter (nm)	
	One point	Isotherm		One point	Isotherm
(mx)	0.71	0.58	0.65	—	17
(ld)	0.51	0.46	0.41	6	7
(hd)	0.57	0.53	—	2	3

[a] Support uptake subtracted by extrapolation to 0 Torr.

TABLE 2

Calculated Deuterium Distribution Based on Uptake Measurements for (ld) and (hd) Catalysts at 300 Torr and 300 K

Sample	% Gas	% Adsorbed	% Deuteride
(ld)	40.3	19.3	40.4
(hd)	28.9	50.9	20.2
(hd)(14 Torr)[a]	2.5	95.8	1.7

[a] Extrapolated from D_2 isotherm; assuming D/Pd_b = 0.01 for α-phase.

lattice, the D_{rev}/Pd_b ratio (where $Pd_b = Pd_t - Pd_s$, i.e., $Pd_{bulk} = Pd_{total} - Pd_{surface}$) may be compared to previously reported values of the bulk deuteride ratio. For the (mx) sample, the values are comparable to the ratio of 0.65 at 300 Torr and 300 K predicted from phase diagrams (*24, 25*). The ratios for the smaller Pd crystallites are somewhat lower, but in agreement with the results of Boudart and Hwang, who found that the H_b/Pd_b ratio was constant at a value near 0.5 in Pd crystallites smaller than 10 nm (*26*). Previous work on H adsorption on Pd films (*27, 28*) and supported Pd crystallites (*2, 26, 29*) indicate that the transition region between α- and β-phases is reduced when the surface-to-volume ratio is large. This leads to lower values of the β-phase hydride ratio, and it appears that a similar effect is seen in this study.

Static NMR Spectra at 300 K

Initially, attempts were made to obtain the proton spectra of the (ld) and (hd) samples following H_2 adsorption; however, as previously found by Sheng and Gay (*17*), a strong resonance appeared near 0 ppm due to the hydroxyl protons of the SiO_2 support. An effort was made to remove this strong OH peak by subtracting the spectrum of each sample following re-reduction and evacuation from that obtained in the presence of H_2, but a peak, although less intense, remained near 0 ppm in both the (ld) and the (hd) samples, as shown in Fig. 1. At 115 Torr H_2, resonances attributable to the β-phase hydride were observed at 28 ppm for the (ld) sample and at 23 ppm for the (hd) sample, on the basis of previously reported shifts for this species (*18, 19*). In addition, a broad peak centered at approximately 12 ppm was observed for the (hd) sample, and a strong peak at approximately 7 ppm was observed for the (ld) sample. The peak at 7 ppm in the (ld) spectrum is attributable to gas-phase H_2, as discussed later; however, the species producing the broad peak at 12 ppm in the (hd) spectrum remains unknown. Further examination of the (ld) spectrum also shows that a broad peak may exist in the same region, since the

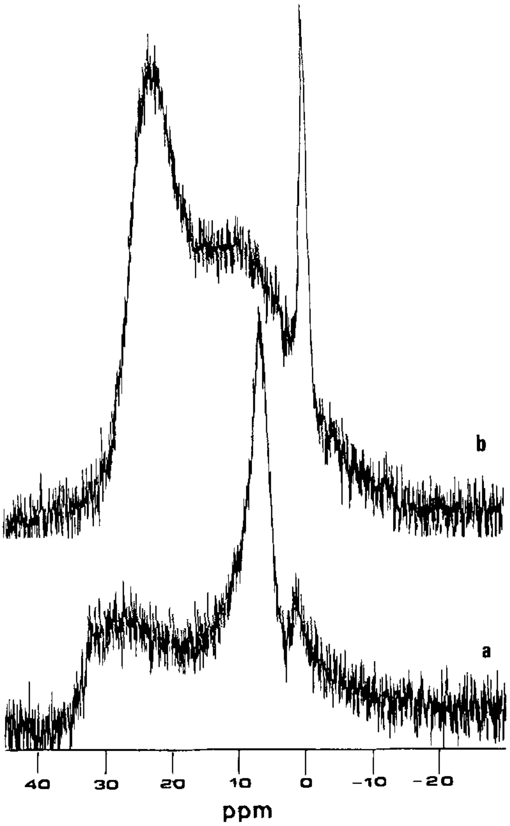

FIG. 1. Static proton NMR spectra at 360.13 MHz and 300 K for the (a) (ld) and (b) (hd) samples following reduction at 673 K and adsorption of H_2 at 115 Torr and 300 K. Spectra of the re-reduced, evacuated samples have been subtracted to yield these spectra.

signal between the gas and the hydride peaks does not return to the baseline. This broad signal and the peak for the OH groups complicate the interpretation of these spectra, especially since chemical shifts of adsorbed H can occur near the shift of the OH groups (*18*).

The difficulties with the OH resonances can be eliminated by using D_2 in place of H_2, as shown in Figs. 2 and 3. At 300 K and 300 Torr D_2, the (mx) and (ld) samples gave two peaks in the NMR spectrum, one for D_2 gas at approximately 10 ppm and another for the β-phase deuteride at 30–35 ppm (See Figs. 2 and 3). Under the same conditions, the (hd) catalyst gave only one peak at 24.4 ppm (Fig. 4). The assignment for the gas-phase peak was confirmed by collecting a spectrum of 500 Torr D_2 gas in an NMR tube. The chemical shift associated with the deuteride resonance compares well with that for the hydride in Fig. 1 and also with previously published values for the β-phase hydride (*18, 19*). The shifts of protons and deuterons in equivalent environments have been shown to be equal (*30*). These experiments yield chemical-shift information because the quadrupolar Hamiltonian has been averaged to zero by molecular motion. It is important to note that no peaks appeared in any other parts of the spectrum; thus, attention can be focused exclusively on the interaction between the deuterons and the Pd particles.

In addition to the spectra taken at 300 Torr D_2, several spectra were also taken at different pressures: for the (mx) sample, adsorption at 16 Torr was first performed to give a final D/Pd_b ratio of 0.05. No NMR signal was detected after approximately 27,000 scans under these conditions. For the (hd) catalyst, the pressure dependence of the peak shift was determined, and the results are shown in Fig. 5. In the pressure range from 40 to 600 Torr the shift increased with decreasing pressure. Addi-

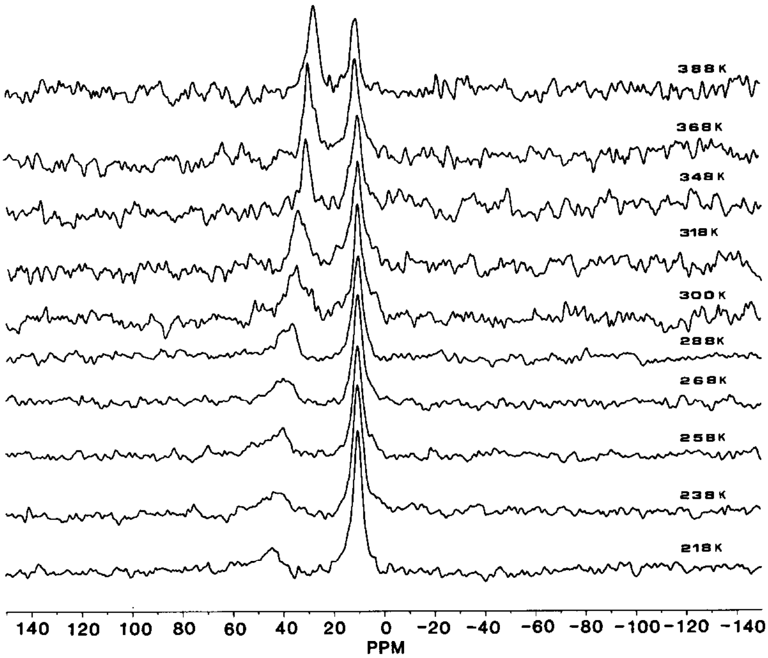

FIG. 2. Deuterium NMR spectra at 30.72 MHz for the (mx) sample at temperatures from 218 to 388 K. The sample was reduced at 673 K and D_2 gas adsorbed at 300 K and 300 Torr. The tubes were sealed with 300 Torr overpressure of D_2 at 300 K just prior to the collection of the NMR spectra.

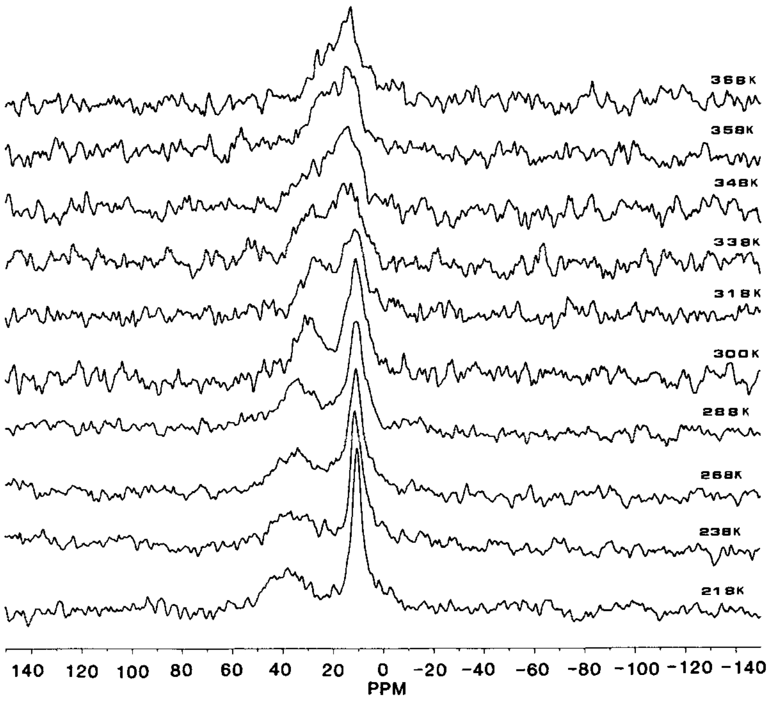

FIG. 3. Deuterium NMR spectra at 30.72 MHz for the (ld) sample at temperatures from 218 to 368 K. The sample was reduced at 673 K and D_2 gas adsorbed at 300 K and 300 Torr. The tubes were sealed with 300 Torr overpressure of D_2 at 300 K just prior to the collection of the NMR spectra.

tional experiments on the same sample showed that if D_2 was first adsorbed at 300 Torr and the sample was subsequently evacuated for 25 min prior to the NMR run, no signal could be detected after approximately 25,000 scans under static conditions. However, following adsorption at 300 Torr and evacuation to give residual pressures of 10 and 14 Torr, one negatively shifted peak was detected (Fig. 6). Figure 6 also shows a very weak signal that was obtained when the catalyst was outgassed for 5 min after D_2 adsorption at 300 Torr. This spectrum is denoted "0+ Torr" because some residual outgassing of the sample may have occurred following the seal-off, thus producing a low pressure in the tube. The NMR peaks in the low-pressure region were significantly broader than those observed at higher pressures, and they were also much further upfield. It is important to note that at any gas pressure only one peak appeared in these static experiments with the (hd) sample.

VT Static NMR Spectra

With the sealed sample tubes containing 300 Torr D_2 pressure at 300 K, NMR spectra were obtained over a range of temperatures for the (hd), (ld), and (mx) samples.

For the (mx) sample, the chemical shift of the deuteride peak decreased steadily as the temperature increased from 218 to 388 K, as shown in Fig. 2 and Table 3, and no coalescence between the gas-phase and the deuteride peaks was observed, even at high temperature. The gas-phase peak was stationary at approximately 10.6 ppm at all temperatures. At the lowest temperatures, the deuteride peak was quite broad, and the linewidth decreased steadily with increasing temperature up to 348 K, and at higher temperatures (368–388 K) the linewidth

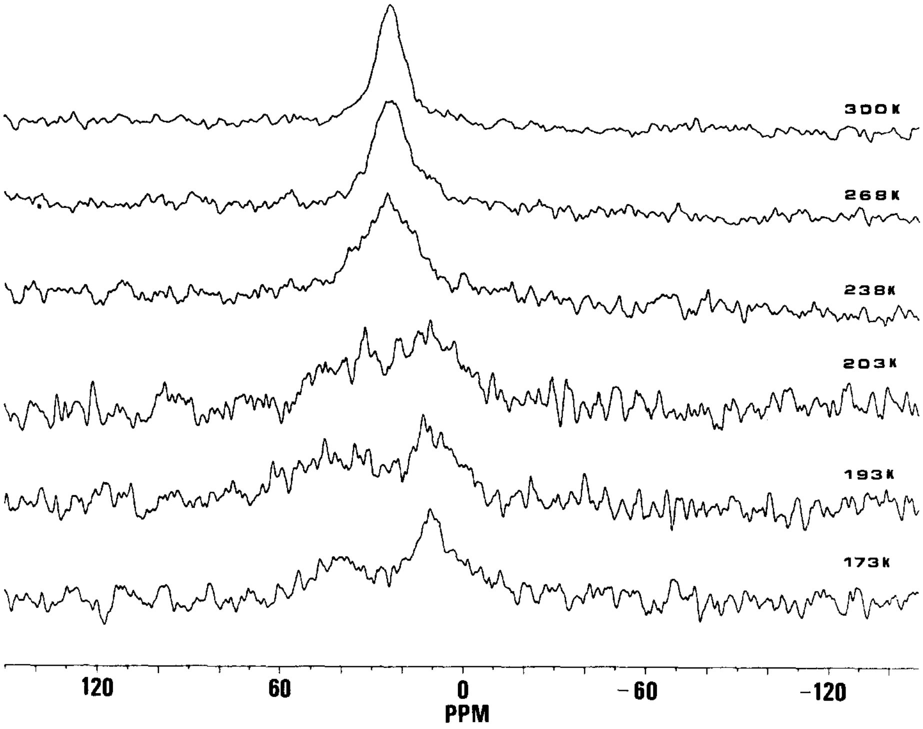

FIG. 4. Deuterium NMR spectra at 30.72 MHz for the (hd) sample at temperatures from 173 to 300 K. The sample was reduced at 673 K and D_2 gas adsorbed at 300 K and 300 Torr. The tubes were sealed with 300 Torr overpressure of D_2 at 300 K just prior to the collection of the NMR spectra.

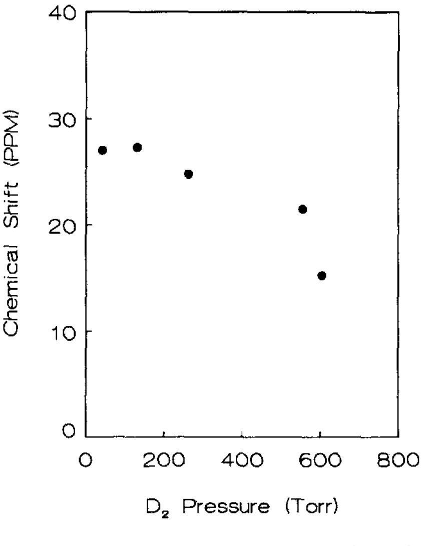

FIG. 5. D_2 pressure dependence of the chemical shift of the single peak observed in the (hd) catalyst at 300 K.

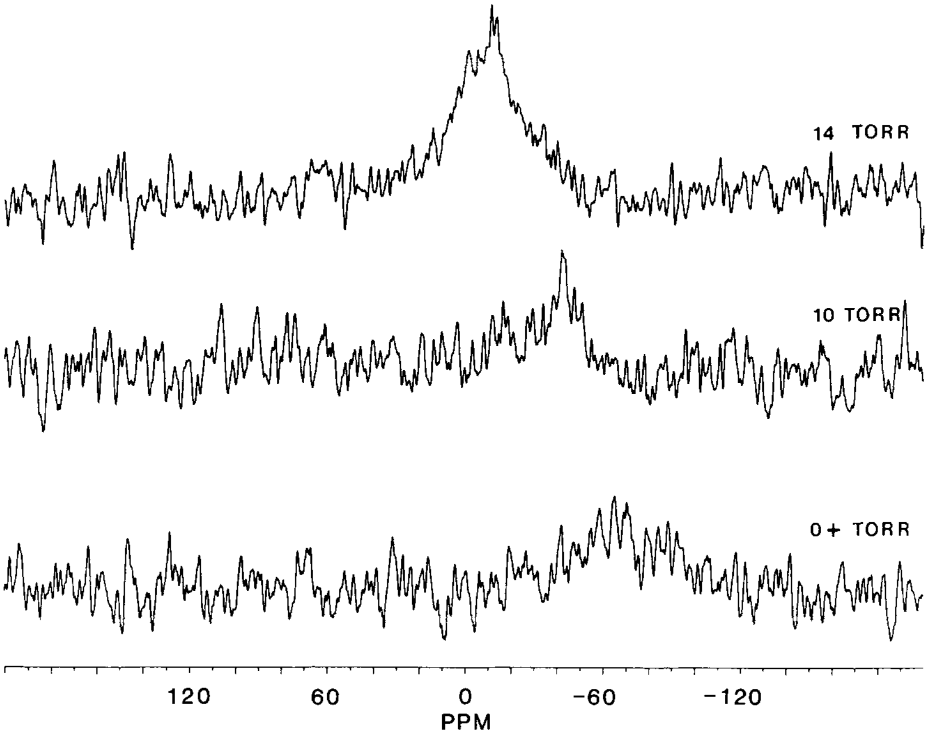

FIG. 6. Deuterium NMR spectra at 30.72 MHz for the (hd) sample at 300 K. The sample was reduced at 673 K, and D_2 gas adsorbed at 300 Torr at 300 K. Before spectrum collection the samples were evacuated to the indicated pressures and then sealed. The "0+" spectrum was taken after the catalyst was outgassed for 5 min prior to being sealed off.

fluctuated somewhat but remained fairly constant.

For both the (mx) and the (ld) samples, the D/Pd_t ratio at 363 K was estimated volumetrically to determine the extent of β-phase deuteride formation. This was done by returning the NMR samples to the adsorption system, performing a single-point adsorption at 300 K and 300 Torr, then sealing off the sample. The section of the sealed tube containing the catalyst was then heated to 363 K and the temperature was allowed to stabilize for 15 min. Care was taken to heat only the section of the NMR tube that would have been heated in the NMR probe. Following the stabilization period, the cell was opened to the vacuum manifold and the pressure increase was noted. Using temperature-corrected apparent dead volumes in the cell, the amount of β-deuteride was estimated from the change in the gas-phase molecules present. The results gave a D_{rev}/Pd_b ratio of 0.65 at 363 K for the (mx) sample, which is reasonably close to the ratio of 0.5 predicted at 353 K from phase diagrams (*31*). This ratio and the presence of the β-phase peak in the NMR spectra indicate that little decomposition of the deuteride had occurred during the high-temperature NMR runs.

For the (ld) catalyst, the chemical shift of the deuteride decreased from 39.7 ppm at 218 K to 28.6 ppm at 338 K, and the gas-phase shift gradually increased from approximately 9.9 to 12.6 ppm (Fig. 3, Table 3). Over this range of temperature, the deuteride peak linewidths fluctuated but showed no definite trend, while the gas-phase linewidth increased gradually with increasing temperature. At 348 K the gas

TABLE 3

Deuterium NMR Chemical Shifts and Linewidths at 300 Torr D_2

Sample	Temp (K)	β-phase deuteride		Gas phase		Coalesced peak	
		Shift (ppm)	Linewidth (Hz)	Shift (ppm)	Linewidth (Hz)	Shift (ppm)	Linewidth (Hz)
(mx)	218	44.4	281	10.6	133	—	—
	238	43.1	307	10.7	146	—	—
	258	40.9	267	10.6	133	—	—
	268	39.9	282	10.6	133	—	—
	288	37.4	230	10.7	136	—	—
	298	35.3	256	10.6	128	—	—
	318	34.1	218	10.7	151	—	—
	348	31.2	115	10.7	141	—	—
	368	29.2	133	10.5	141	—	—
	388	27.5	148	10.8	123	—	—
(ld)	218	39.7	512	10.7	141	—	—
	238	36.6	640	10.7	179	—	—
	268	34.5	512	10.6	218	—	—
	288	32.8	486	10.9	264	—	—
	298	29.5	525	11.7	235	—	—
	318	32.5	666	11.7	345	—	—
	325	30.2	538	13.1	371	—	—
	338	28.6	—	14.6	—	—	—
	345	—	—	—	—	15.5	666
	355	—	—	—	—	15.5	564
	368	—	—	—	—	13.4	353
(hd)	173	40.8	640	10.9	410	—	—
	193	40.8	1152	13.1	461	—	—
	203	—	—	—	—	22.0	1126
	218	—	—	—	—	26.2	922
	238	—	—	—	—	24.4	563
	268	—	—	—	—	24.5	410
	298	—	—	—	—	24.4	294

and deuteride peaks coalesced into a single broad peak (Fig. 3), and at higher temperatures up to 368 K, the coalesced peak decreased in linewidth. The last two observations imply that a rapid exchange process exists at the higher temperatures or, less likely, that the β-deuteride decomposed as the temperature was raised. To distinguish between these possibilities, the D/Pd_b ratio was estimated volumetrically, and a D/Pd_b ratio of 0.41 was found at 363 K and approximately 300 Torr. This ratio is still near the β-phase region (*31*). Considering this result and other observations to be discussed later, the single peak from the (ld) catalyst occurring at temperatures above 338 K arises from a rapid exchange process, rather than decomposition of the bulk deuteride phase.

The (hd) catalyst gave a single peak at 24.4 ppm at room temperature which broadened as the sample was cooled below 300 K (Fig. 4 and Table 3). Cooling to 203 K caused this peak to begin to split into two peaks, and further cooling to 173 K resulted in the resolution of two broad peaks, one with a shift of 40.3 ppm, indicative of the β-phase deuteride, and another at 10.9 ppm, representative of the gas phase. The trend exhibited in this series of spectra is again indicative of an exchange process, but in this case it is so rapid that coalescence occurred below 300 K. No spectra were collected above room temperature for this sample.

MAS NMR of the (hd) Sample

To elucidate the phases present in the (hd) catalyst, D_2 was adsorbed on a fresh, pretreated sample which was then sealed in a glass capsule with 500 Torr D_2. A MAS spectrum taken at 300 K and a spin rate of 3.2 kHz showed an extensive series of spinning sidebands and also a broad resonance at approximately 32 ppm, as shown in Fig. 7a. The presence of sidebands over a range of frequencies much larger than the deuterium chemical-shift range indicates the dominance of the quadrupolar Hamiltonian for some species. It also implies that molecular motion is insufficient to fully average the quadrupolar Hamiltonian for this species. The single peak at 32 ppm did not change in frequency as the spinning rate was changed, and it is tempting to assign it to the exchanging gas and β-deuteride; however, the rigorous assignment of the isotropic ^2H chemical shifts from MAS spectra requires sampling of the NMR signal in precise synchronism with the spinning rate, or the use of double-quantum methods (*32*). Rather than pursue these methods which are known to be difficult to implement, three additional (hd) samples were pretreated as before and then subjected to different conditions to eliminate certain species. In the first sample, D_2 was adsorbed at a maximum pressure of 10 Torr, and then the sample was outgassed at 300 K for 25 min prior to the seal-off. With this sample, no β-phase deuteride would have formed at the low adsorption pressure used, and any α-phase deuteride should have been removed by the evacuation prior to the seal-off. In this case, the spectrum in Fig. 7b was obtained under MAS conditions, and this spectrum is essentially identical to that shown in Fig. 7a, except that the β-phase deuteride peak is missing. This implies that the peak at 32 ppm is attributable to the β-phase deuteride. For the second sample, D_2 was again adsorbed at low pressure (maximum pressure, 9 Torr) and again outgassed at 300 K. This time, however, the sample temperature was subsequently raised to 673 K under continuous evacuation and outgassed at 673 K for 1 h prior to cooling to 300 K and sealing off. Although this treatment would have removed all of the adsorbed D from the Pd surface, a sideband pattern identical to that in Fig. 7b appeared. In the final sample, only enough D_2 was admitted to provide the irreversibly chemisorbed D (40 μmole D_2/g cat) on the Pd, and no MAS NMR signal was obtained.

For the samples where sidebands were obtained, spectra were collected at spinning rates of 2.6 and 3.2 kHz, and it was found that only the resonance near 7 ppm remained stationary. As seen in Figs. 7a and 7b, only a single series of sidebands occurs and spans almost all of the 100-kHz (>2000 ppm) sweep width covered in the spectrum. The origin of the spinning sidebands is discussed later.

DISCUSSION

In relating the data from this study to a pathway by which D_2 is first adsorbed and then dissociated and absorbed into the Pd lattice, the reasonable assumption is made that any bulk deuteride formed does so from an adsorbed surface species; consequently, there can be no direct exchange between the deuteride phase and the gas phase. From the adsorption results of this study, the concentration of adsorbed deuterium relative to that in the deuteride phase is quite large in the case of the (hd) catalyst, but extremely small in the (mx) sample. The fact that a coalesced NMR signal was observed for the (hd) catalyst at 300 K, whereas the (mx) and (ld) samples gave separate gas and β-deuteride peaks, indicates that a much more rapid exchange process exists in the (hd) sample than in the (mx) and (ld) samples. The rate of exchange

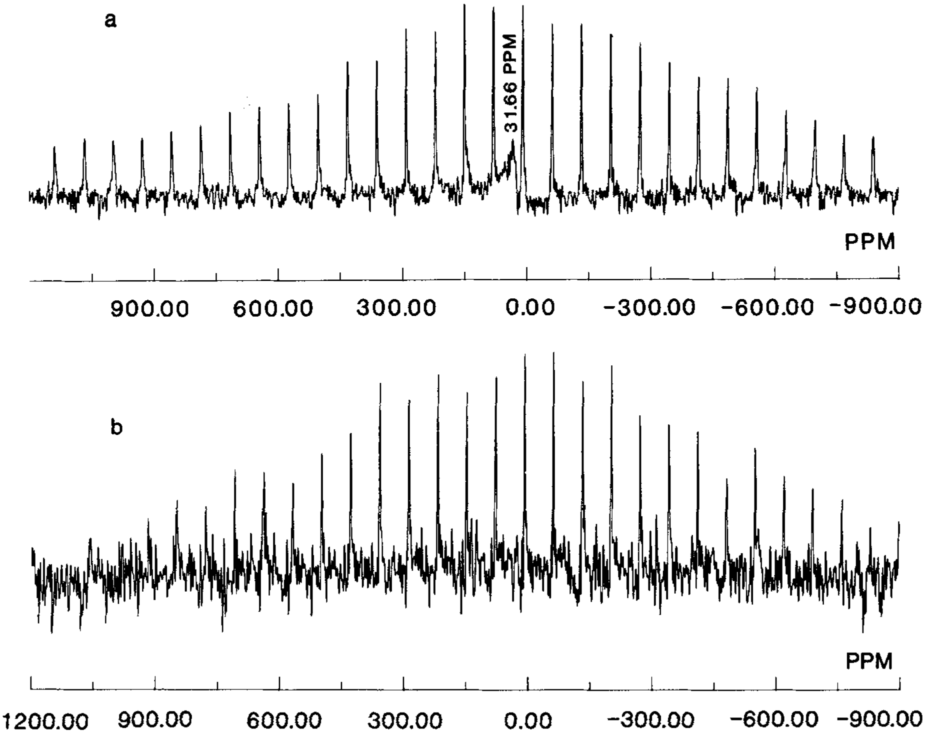

FIG. 7. MAS deuterium NMR spectra at 45.72 MHz of the (hd) sample at 300 K following sample reduction at 673 K and D_2 adsorption at 300 Torr. (a) Sample with D_2 adsorbed, then filled to 500 Torr D_2 prior to seal-off, spin rate = 3.2 kHz. (b) Sample with D_2 adsorbed at 10 Torr pressure, then evacuated for 25 min at 300 K prior to seal-off, spin rate = 3.2 kHz. The 100-kHz sweep width used in collecting these spectra was not quite sufficient to encompass all the sidebands, since a few folded-in peaks near the right edge of spectrum (b) appear.

is expected to be a strong function of the surface-to-volume ratio of the Pd crystallites, which would govern the amount of the adsorbed phase relative to the bulk deuteride and gas phases. For each of the samples in this study, the data obtained at 300 Torr D_2 are discussed with regard to exchange between the gas and the deuteride phases via an adsorbed species. Subsequently, the nature of the adsorbed D species is examined based on the low-pressure and MAS results obtained on the (hd) catalyst.

(*mx*) *Sample*

The (mx) sample is different from the impregnated catalysts in terms of both exchange behavior and linewidth variations with temperature. In this sample, the β-phase deuteride linewidth decreases with increasing temperatures from 218 to 348 K, whereas in the other samples the widths of the resolved deuteride peaks increased or remained about constant when the temperature was raised. The trend of decreasing linewidth with increasing temperature could be due to a number of factors, the most likely of which are quadrupolar/dipolar broadening, magnetic susceptibility broadening, and exchange effects. While all of these processes apply in general, the susceptibility broadening is not important in this case because previous studies have shown that at D/Pd_b or H/Pd_b ratios greater than 0.6 the magnetic susceptibility is nearly temperature independent (*24*, *33*).

It is very likely that quadrupolar and dipolar interactions are responsible for the lineshape variations. It is clear that there is a significant amount of deuteron motion within these samples since relatively narrow peaks were obtained, even in the static NMR measurements. While this motion is rapid enough to average most of the static quadrupolar and dipolar coupling, the extent of averaging would be less at the lower temperatures. The expected broadening at low temperatures has already been observed for bulk Pd hydrides (*34, 35*), and previous investigators have related this effect to the rate of proton diffusion in $PdH_{0.75}$. For both D and H, the influence of the static dipolar and quadrupolar interactions also results in decreased T_2 values at low temperatures (*36, 37*). For the β-phase hydride, the resonance linewidths were reported to decline most rapidly between 110 and 140 K, where activation energies of 2–3 kcal/mole have been estimated (*34, 35*). These values are about one-half that of 5.3 kcal/mole, measured for the proton self-diffusion coefficient determined from spin-echo techniques (*11*). For the (mx) sample, the lowest temperature attained was 218 K, and an Arrhenius plot of the linewidth data also shows a low activation energy of approximately 0.3 kcal/mole from 218 to 348 K. From the trends in linewidths and the chemical shifts observed, it appears that the (mx) particles are behaving as bulk Pd, which is consistent with the large (1-μm) crystallite size.

The observation that the linewidth decreases with increasing temperature also implies that interphase exchange effects are of minor importance in the (mx) sample. Models of classical, uncoupled exchange processes (*38*) predict that the peak widths of exchanging species will broaden significantly just prior to coalescence. While this behavior was observed in the (ld) and (hd) samples, the linewidths in the (mx) sample showed a trend opposite that expected if exchange was rapid. The proposal of a low deuteride–gas exchange rate in this sample is also consistent with the low surface area and large particle size of the Pd powder. The long diffusional distance in combination with the low surface/volume ratio would greatly decrease the net rate of exchange between the gas and the deuteride. In essence, the very small quantity of adsorbed species caused by the low surface-to-volume ratio acts as a "bottleneck" in the exchange process.

(ld) Sample

For the (ld) catalyst the surface-to-volume ratio is intermediate between the (hd) and the (mx) samples, but closer to the former, and the NMR spectra show that coalescence of the gas- and β-phase deuteride peaks takes place near 350 K. On the basis of the adsorption results, an average particle size near 6 nm was found in this sample, and it is of interest to compare the time it takes a deuteron to diffuse through this distance and the time resolution of the NMR. In order for the gas and deuteride phases to be resolved as separate peaks, the exchange frequency between these species must be lower than the difference between the limiting resonance frequencies of the individual species. Using the Einstein equation for diffusion (*39*),

$$X_{\mathrm{rms}} = (2Dt)^{1/2},$$

where D is the diffusion coefficient, t is the diffusion time, and X_{rms} is the particle radius in this case, it is estimated, on the basis of known values of D (*24*), that a deuteron may diffuse through a 6-nm particle in as little as 10^{-7} s at 300 K. In the NMR spectrum, the limiting separation between the deuteride and the gas-phase peaks on the basis of the data for the (mx) sample is approximately 30 ppm. At 30.72 MHz this separation is approximately 920 Hz, which implies that the average residence time a deuteron must spend in either the gas or the deuteride phase in order for the peaks to be separate is a millisecond or more. The diffusion time through the particle is nearly four orders of magnitude less than this, so it is not surprising that a coalesced peak is observed at the higher temperatures. At temperatures from 218 to 338

K, the net exchange rate between the gas and the β-deuteride is apparently limited by the lower surface/volume ratio of these particles and a slower exchange rate with the adsorbed phase on the Pd surface.

(hd) Sample

In the static NMR spectra, the presence of a single resonance line which was at the average chemical shift of the β-deuteride and the gas is strong evidence for the occurrence of a rapid exchange process in this sample. This was further confirmed by the split of this single peak into separate gas and deuteride peaks at low temperature due to a decreased exchange rate. The exchange process also manifests itself in the chemical-shift dependence on the D_2 pressure, as seen in Fig. 5. With a decreasing contribution from the gas phase at lower pressures, the expected shift, which is more weighted toward the deuteride, is observed.

In this sample, a rapid interphase exchange is facilitated by the small particle sizes giving a high surface/volume ratio and a large relative concentration of adsorbed surface species. Moreover, these small crystallites are likely to have a more "open" surface structure caused by larger fractions of high index planes (*9*). This type of surface morphology could further facilitate the passage of deuterons into and out of the interior of the crystallites.

A striking feature of the static NMR spectra acquired for this sample was that no separate peak for any chemisorbed phase was ever obtained at 300 Torr D_2, even after 25,800 scans, although 50% of the total deuterium in the sample was adsorbed on the Pd surface (Table 2). Sheng and Gay (*18*) also found only one peak for H adsorbed on a Pd/SiO_2 catalyst, and they attributed this to a rapid exchange between the adsorbed phase and the hydrogen dissolved in the Pd particles. In their study, however, the chemical shift of the resultant peak (28 ppm) was too high for such an explanation to be valid, especially if the shift of the adsorbed phase is negative, as they reported (*18*). In the present study, the adsorbed phase on the (hd) catalyst was characterized further by static and MAS experiments at low pressures or under vacuum to maximize the relative amount of adsorbed species in comparison to the gas and deuteride phases.

In the static NMR experiments at 300 K, a single upfield peak was observed following D_2 adsorption at 300 Torr and subsequent evacuation to a residual pressure of either 10 or 14 Torr D_2. In principle, this peak could be assigned to either adsorbed deuterium or the α-phase deuteride, on the basis of the previously reported chemical shifts of these species (*18, 40*) and phase diagrams which indicate that β-deuteride does not exist at these low pressures (*25*). There are, however, reasons for not assigning the resonance to the α-phase deuteride in the present case. First, the chemical shifts under 10–14 Torr D_2 are not as far upfield as reported for the α-phase deuteride in bulk Pd (*40*). Second, with the small Pd particles in this study, the fractions of bulk and surface atoms are comparable to each other. This, combined with the fact that the α-phase deuteride exists only at very low D/Pd_b ratios, means that the number of deuterons on the surface is far greater than that in the α-phase deuteride. Table 2 shows an estimate of the deuterium distribution at 14 Torr D_2 pressure and 300 K, where the uptakes were extrapolated from the D_2 isotherms at 300 K (the lowest measured pressure was 40 Torr). According to these estimates, the amount of deuterium in the adsorbed phase exceeds that in the α-phase deuteride by a factor of more than 50. In the ideal case, that is, disregarding dipolar and quadrupolar broadening and relaxation effects, this implies that the NMR signals from the adsorbed phase should be much stronger than those from the deuteride or the gas. A third point concerns the rate of deuteron movement within the α-phase. For the (mx) sample, no signal was detected after 27,000 scans following a

D_2 uptake to give a D/Pd ratio of 0.05, which is above, but near, the α-phase limit of 0.01 (*25*). This sample should have had the highest α-deuteride/adsorbed phase ratio because of its low Pd surface/volume ratio. It is likely that the lower mobility of D in the α-phase was insufficient to average the quadrupolar and dipolar broadening, thereby giving an extremely broad NMR signal. It can then be expected that the much lower concentration of the α-phase deuteride in the (hd) catalyst would not be detectable under static conditions at 300 K.

The negative shifts observed for this peak are consistent with previously reported shifts for H adsorbed on Pd (*18*) and Pt (*16, 17*). Previous work function measurements of H adsorption on Pd single crystals indicate that electron transfer occurs from Pd to H on the surface (*41*). Such a hydridic-type species would lead to increased shielding of the adsorbed deuterons and an upfield shift in the NMR spectrum. Considering the large percentage of the total deuterons in this phase as well as the chemical-shift information, it is reasonable to assign this upfield peak to adsorbed deuterium atoms.

The assignment of the deuterium species detected as spinning sidebands in the MAS experiments may be obtained by consideration of the species present following the previously described treatments. The presence of sidebands over more than 90 kHz immediately implies that the quadrupolar Hamiltonian has not been completely averaged by molecular motion, unlike the species observed in the static experiments. It is clear that the sidebands are not due to the α- or β-phase deuterides, since the bands appear after the catalyst is evacuated following low-pressure adsorption. In the case where D_2 was adsorbed and the catalyst was subsequently outgassed at 673 K, the sidebands still appear, implying that they do not originate from any D associated with the Pd crystallites. Therefore, the only reasonable assignment is that the sidebands originate from OD groups on the SiO_2 surface, since only this form of deuterium could remain following outgassing at 673 K. It was found that the peak at approximately 7 ppm remained stationary at spinning speeds of 3.2 and 2.6 kHz. If the position of this peak is taken as the isotropic shift of the powder pattern, then the assignment is also consistent with the previously reported shifts for OH (*42–49*) and OD (*50–51*) groups on various oxides. As mentioned previously, there is some uncertainty regarding the isotropic shift due to the quadrupole moment of D, and experiments are in progress to determine the true isotropic shift for these samples. These MAS NMR spectra also show that under a residual D_2 pressure, significant exchange between D adsorbed on the Pd and OH groups can occur, consistent with the results reported by Sheng and Gay (*17, 18*). With 500 Torr D_2, the signal-to-noise ratio of the sideband pattern is noticeably higher than in the case where the sample was evacuated (Fig. 7b), despite the fact that the latter spectrum had more scans. It is important to note that when just enough D_2 was admitted to give only the irreversibly chemisorbed phase with little or no reversible chemisorption, no NMR signal of any kind was observed. The lack of signal from the irreversibly chemisorbed D under MAS conditions implies that this species does not exchange with OH groups on the SiO_2.

While the Si–OD groups are detectable under MAS conditions, as mentioned before they are not mobile enough to give any signals in the static NMR experiments in this study. The sideband pattern appears as a result of incomplete averaging of the quadrupolar interactions of the adsorbed deuterons by magic angle spinning. Its width in this case clearly indicates that the motion of these groups is too slow to average these interactions such that the OD signals would be detectable at the sweep width of 20 kHz used in the static experiments. Maricq and Waugh (*52*) have described a procedure in which the quadrupole frequency and the quadrupolar asymmetry parameter may be evaluated by moment analysis of the spinning sidebands, assuming that the chemical-shift anisotropy is negligible compared to the quadrupolar interaction. By further assuming that the quadrupolar asymmetry parameter is negligible for deuterium in OD (*53*), a quadrupole frequency near 59 kHz was found, on the basis of the second moment of 13 sidebands around the central peak. This implies that the quadrupolar powder pattern would have a total width of approximately 89 kHz and would not be detectable in the static experiments run with a 20-kHz sweep width.

Considering the static and MAS NMR results obtained in this study, we conclude that, in addition to the β-phase deuteride, two different types of adsorbed deuterium have been observed: a mobile species associated with the Pd surface which leads to relatively narrow signals in the static NMR experiments, and a less mobile OD species which resides on the SiO_2 surface. The assignment of the D adsorbed on the Pd can be discussed further with regard to previous investigations, which have shown that adsorbed H can exist in both weakly and strongly held states on the Pd surface. The differences between these chemisorption states have been reported previously. For example, Lynch and Flanagan (*54*) showed that the weakly adsorbed state was in rapid equilibrium with H absorbed in the Pd lattice, and these H atoms were proposed to reside at the interstitial sites on the Pd surface. Furthermore, they suggested that strongly held H was not exchanging rapidly with either the protons in the Pd lattice or the weakly adsorbed species (*54*). More recent work on Pd single crystals indicate that a weakly held "subsurface" adsorption state exists (*54–59*), especially on the more open (110) plane, and Rieder and co-workers have also suggested that this weakly held species is equilibrated with gas-phase H_2 and H absorbed in the Pd lattice (*55, 56*). Our results also support this suggestion.

Finally, initial heats of adsorption (Q_{ad}) for H_2 on Pd single crystals are near 24 kcal/mole, and these Q_{ad} values decrease as surface coverage increases (*9*, and references therein). Behavior consistent with this has been observed for large, supported Pd crystallites, and measured integral Q_{ad} values of 15 kcal/mole were in good agreement with those estimated from UHV studies (14–20 kcal/mole) (*9*). However, on very small (<3-nm) Pd crystallites the Q_{ad} for H_2 increased noticeably to 24 kcal/mole, thus approaching initial Q_{ad} values and indicating that a large fraction of strongly adsorbed H (D) atoms should remain after evacuation (*9*). Chemisorption measurements in this previous study indeed showed that only about 15–20% of the chemisorbed hydrogen could be removed after a 25-min evacuation at 300 K (*9*). This more weakly chemisorbed species has a Q_{ad} value near 10 kcal/mole, which is close to the heat of formation of the β-phase hydride (9 kcal/mole). The similarity in H–Pd bond strengths between these two H species would facilitate exchange, consistent with our NMR results and the previous studies that were cited. The high Q_{ad} of the irreversibly adsorbed D supports the assumption that this is a rigidly bound phase on the Pd surface.

On the basis of these previous investigations, the upfield peak observed in the static NMR experiments at low D_2 pressures is assigned to the weakly chemisorbed species, and it is proposed that the interphase exchange pathway proceeds through this species rather than the more strongly adsorbed species, which could not be detected in our MAS experiments. This hypothesis is attractive for several reasons: First, a weakly adsorbed species would be more mobile than one which was strongly bound to the surface. Only a rapidly moving species could explain the relatively narrow (<2000-Hz) linewidths observed in the (hd) catalyst at low D_2 pressures. Second, it provides an explanation for the disappearance of the NMR signal after 25 min of outgassing, which would have removed the weakly adsorbed species but left the strongly adsorbed deuterium on the surface. The strongly adsorbed species remaining after evacuation was not detected in either the static or the MAS experiments, probably because it had a T_1 value much longer than 1 s. Third, the exchange pathway is consistent with previous reports that the weakly adsorbed species exchanges rapidly with both gas-phase and β-hydride hydrogen, while the strongly adsorbed state apparently does not. The similarity in H–Pd bond strengths in the β-hydride and weakly chemisorbed phases would also support this model. Finally, it is possible that the more open surface structure of the small (hd) particles facilitates the exchange process.

The OD groups identified in the MAS NMR experiments arise from D which dissociatively adsorbs on the Pd particles, then migrates onto the SiO_2 surface, and exchanges with hydroxyl protons. It is proposed that it is the weakly chemisorbed D species (Q_{ad} = 10–12 kcal/mole) on Pd that is responsible for the exchange with the OH groups. The low-pressure static NMR experiments showed that this weakly adsorbed mobile state of D can exist at 10–14 Torr, but it disappears rapidly as the pressure is lowered. Further support of this was provided by the absence of a sideband pattern in a sample where just enough D_2 was adsorbed to form only the irreversibly chemisorbed D species, leaving a very low residual pressure.

SUMMARY

Using a combination of static and MAS NMR spectroscopy, this study of D_2 (and H_2) interacting with both large and small Pd particles has resolved peaks representing four different deuterium species—gas-phase D_2, β-phase deuteride, mobile, weakly chemisorbed deuterium on Pd, and much less mobile OD groups on the SiO_2 support surface. No peaks representative of the strongly chemisorbed species could be detected; however, it is possible that broadline spectra with long pulse delays will give the quadrupolar powder pattern for this strongly adsorbed deuterium, and these experiments are underway. Static experiments showed that with large (1-μm) Pd crystallites, the exchange process is slow due to the low surface/volume ratio, and separate peaks for the gas-phase and β-phase deuteride are obtained between 218 and 390 K. For 6-nm Pd crystallites on SiO_2, the higher surface/volume ratio increases the rate of exchange and the two peaks coalesce at temperatures near 360 K. With highly dispersed Pd/SiO_2 catalysts (~2-nm crystallites), only a single peak, with a chemical shift equal to the weighted average of the gas-phase and β-phase deuteride, was obtained at temperatures as low as 230 K, and cooling to below 200 K was required to resolve two peaks. Static experiments with this catalyst under low D_2 pressures to prevent formation of the β-phase deuteride produced a single peak which broadened, became weaker, and shifted upfield as the gas-phase concentration decreased. This peak exhibits a pressure-dependent chemical shift similar to that reported by Sheng and Gay for hydrogen adsorbed on SiO_2-supported Pd (*18*), and we associate this peak with weakly chemisorbed deuterium that can be removed by evacuation at 300 K. These results are consistent with earlier proposals that it is only the weakly chemisorbed D species which exchanges rapidly with D_2 gas and the β-phase deuteride.

MAS NMR experiments conducted on the (hd) sample showed that a less mobile species of deuterium existed on the sample. On the basis of the fact that this species remains on the sample after high-temperature evacuation, and because it is absent in the presence of only strongly chemisorbed D, it was assigned to OD groups on the SiO_2 surface. Finally, it appears that these OD groups originate by exchange only with the weakly chemisorbed D atoms on the Pd surface, and not the strongly bound species.

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