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Selective Hydrogenation and H–D Exchange of Unsaturated Hydrocarbons on Pd(100)–p(1×1)–H(D)

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The adsorption and reactions of unsaturated hydrocarbons (ethylene, propene, 1-butene, acetylene, allene, 1,3-butadiene, 1,3,5-hexatriene, and 1,5-hexadiene) have been investigated on the Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D surfaces using temperature-programmed reaction spectroscopy (TPRS). It is found that 1-alkenes (ethylene, propene, and 1-butene) undergo efficient H–D exchange reactions below 300 K for all C–H bonds, whereas no hydrogenation products (alkanes) are observed. Conjugated polyenes (acetylene, allene, 1,3-butadiene, and 1,3,5-hexatriene) undergo selective hydrogenation to corresponding alkenes below or around 300 K, whereas no exchange reaction is observed to occur for the parent molecules. Nonconjugated polyene (1,5-hexadiene) undergoes both exchange and hydrogenation reactions, with its reactivity in between 1-alkenes and conjugated polyenes. The exchange reaction is proposed to occur via reversible hydrogenation to a half-hydrogenated intermediate. The relative quantities and evolution temperatures of successively H–D exchanged products are reproduced by kinetic simulations of competition between desorption and reaction. The absence of alkene hydrogenation may be due to stronger metal–hydrogen bonds on Pd(100) than on other metals such as Pt and Rh. Strong bonding of the half-hydrogenated intermediate to the surface may be the reason for the irreversible hydrogenation of conjugated polyenes to alkenes. Both exchange and hydrogenation reactions occur at all coverages, but at low coverages the reaction products dehydrogenate to C(a) and H(a) without product evolution. © 1995 Academic Press, Inc.

INTRODUCTION

The hydrogenation of unsaturated hydrocarbons on metal catalysts is an important process for industrial production and laboratory synthesis. One interesting case is the selective partial hydrogenation of multiply unsaturated hydrocarbons. The key issue here is to reach a high selectivity in the desired product.

For the reactions

$$\begin{tikzcd}
A(g) \arrow[d, shift right, "k_3"'] & B(g) \arrow[d, shift right, "k_4"'] & \\
A(a) \arrow[u, shift right, "k_{-3}"'] \arrow[r, "k_1"] & B(a) \arrow[u, shift right, "k_{-4}"'] \arrow[r, "k_2"] & C(g)
\end{tikzcd} \qquad [1]$$

selectivity for the intermediate product, B(g), can be defined as

$$S = \frac{\text{yield of B}}{\text{yield of B} + \text{C}}. \qquad [2]$$

Two kinds of selectivity have been recognized (1). First, if $k_1 > k_2$, selective formation of B will be obtained, this is called *mechanistic selectivity*. On the other hand, if $k_3/k_{-3} > k_4/k_{-4}$, adsorption of A will prevent the readsorption of B and hence the reaction cannot proceed to C. The selectivity here is termed *thermodynamic selectivity*.

An important example of selective hydrogenation is that of acetylene or polyenes to simple alkenes on palladium catalysts. This process is used industrially to remove acetylene and dienes from gas streams consisting mainly of alkenes (2). A selectivity of unity has been obtained in high-pressure studies on various Pd surfaces including supported catalysts (2) and single crystals (3). In contrast, other noble metals such as platinum show relatively poor selectivity for alkenes over alkenes (4). The difference in overall selectivity has been attributed to the difference in thermodynamic selectivity. For example, it was invoked that butadiene is more strongly adsorbed on Pd surfaces than butene, while their adsorption energies are similar on Pt surfaces (5, 6). Therefore, the adsorption of butadiene forces butene to desorb from Pd surfaces, whereas on Pt surface butene remains adsorbed and the reaction can proceed to butane (5). These arguments may be justifiable under high-pressure conditions, but the possible difference in mechanistic selectivity appears to have been ignored.

In the present work, we have investigated the selective hydrogenation of acetylene, allene, 1,3-butadiene, 1,3,5-hexadiene, and 1,5-hexatriene on the Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D surfaces under ultrahigh vacuum (UHV) conditions using temperature-programmed reaction spectroscopy (TPRS). For all these molecules facile hydrogenation to alkenes has been found to occur with unit selectivity. The adsorption and reaction of alkenes

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(ethylene, propene, and 1-butene) on Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D were also studied. For these molecules, facile H–D exchange occurs, but no hydrogenation to alkene was detected. These results demonstrate the importance of mechanistic selectivity in the selective hydrogenation on Pd catalysts.

EXPERIMENTAL

Experiments were performed in an ultrahigh vacuum chamber with a working base pressure less than 5×10^{-11} Torr. The Pd(100) crystal was prepared using standard metallographic techniques and polished down to 0.25 μm diamond paste. The Pd(100) surface was initially cleaned by cycles of Ar ion sputtering (600 eV, 10 mA, 300 K) and annealing (1300 K). This effectively removed sulfur impurities. Carbon impurities were removed by many hours of repetitive oxygen treatment (10^{-7} Torr, 1000 K) and annealing to 1300 K in vacuum. Routine cleaning consisted of oxygen treatment (10^{-8} Torr, 760 K) and annealing (1120 K). The clean Pd(100) surface yielded thermal desorption spectra for O_2 and CO in excellent agreement with the literature (7, 8).

The following high-purity alkenes were used without further purification: ethylene (Matheson, CP grade), propene, 1-butene, allene, and 1,3-butadiene (Aldrich, 99+%). Acetylene (Matheson, CP grade) was purified by passage through an ice-cold bath to remove traces of acetone impurities. 1,5-Hexadiene and 1,3,4-hexatriene (Aldrich, 99%) were purified with freeze–pump–thaw cycles. Gases were delivered to the surface through a stainless steel doser at a distance of about 5 mm from the doser exit to the surface. Atomic hydrogen (or deuterium) was adsorbed on Pd(100) at 125 K via a capillary array doser with an H_2 (D_2) exposure of ~20 L (1 L = 10^{-6} Torr s), yielding a p(1×1)–H(D) LEED pattern corresponding to a hydrogen coverage of 1 H/Pd (9).

All TPRS measurements were taken with a UTI mass spectrometer interfaced to a desktop computer which was capable of multiplexing up to 200 masses. Usually fewer than 10 masses were monitored to increase the signal-to-noise level in each channel. Digitized data are displayed below in joined straight line segments. When necessary, spectrum deconvolution was performed to subtract contributions from higher mass fragments. The cracking fractions used for the deconvolution were measured using the same mass spectrometer. A nearly linear heating rate of 4 K/s was used for all the spectra presented below.

RESULTS

a. Reactivity of 1-Alkenes on Pd(100)–p(1×1)–H(D)

The Pd(100) surface was exposed with H_2 before alkene exposure. The reaction of 1-alkenes (ethylene, propene, and 1-butene) on the Pd(100)–p(1×1)–H(D) surface yields no hydrogenation products (alkanes), but various H–D exchange products are formed. The TPR spectra for the masses of interest are displayed in Figs. 1a–1f for the adsorption of ethylene, propene, and 1-butene on the Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D surfaces, respectively. The results on the H(a)-covered surface (Figs. 1a, 1c, and 1e) show only the desorption of parent alkene molecules; no hydrogenated alkane products (ethane, propane, and butane) are formed. The TPRS measurements were performed over the temperature range from 120 to 1165 K, and no hydrogenation product was detected over the entire temperature range. The adsorption coverages of the alkenes of 0.25 molecules/Pd on H(a)-covered Pd(100) are similar to those on clean Pd(100) (10). About 0.15 molecules/Pd desorb molecularly from the surface, and the rest dehydrogenate. The dehydrogenation of alkene molecules on H(a)-covered Pd(100) yields extra H_2 evolution peaks (see below) and surface carbon, as it does on the clean Pd(100) surface (10). Surface carbon was removed with oxygen treatment after each measurement.

The temperature-programmed reaction spectra from D(a)-covered Pd(100) (Figs. 1b, 1d, and 1f) show the parent alkene as well as several higher masses. Because no hydrogenation occurs, the higher masses must be due to multiple H–D exchange reactions between adsorbed alkene molecules and D atoms.

All H atoms on each alkene molecule appear to be exchangeable with D adatoms. This is clear for ethylene shown in Fig. 1b, where H–D exchange proceeds to d_4 ethylene. For propene and 1-butene (Figs. 1d and 1f) the exchange yield decreases with increasing D atoms in the molecules, and it becomes undetectable before the exchange proceeds to the last H atom. Using partly deuterated 3,3,3-d_3-propene and 1,1-d_2-1-butene, however, it was demonstrated that the all H atoms can be exchanged with D adatoms, as shown in Figs. 2a and 2b.

b. Reactivity of Acetylene and Polyenes on Pd(100)–p(1×1)–H(D)

Figure 3 displays the TPR spectra of acetylene, allene, and 1,3-butadiene on the Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D surfaces. Masses are shown for the parent molecules, hydrogenation products, and H–D exchange products. The parent molecules desorb immediately upon heating. No more desorption occurs above 300 K. Partial hydrogenation products (+2H) evolve at 305, 220, and 235 K for acetylene (ethylene), allene (propene), and butadiene (butene), respectively. It is noted that no evolution of parent molecules accompanies these hydrogenation products after the spectrum is deconvoluted of higher mass fragmentation. Neither was alkane product (+4H) detected, as shown in Figs. 3a, 3c, and 3e in ex-

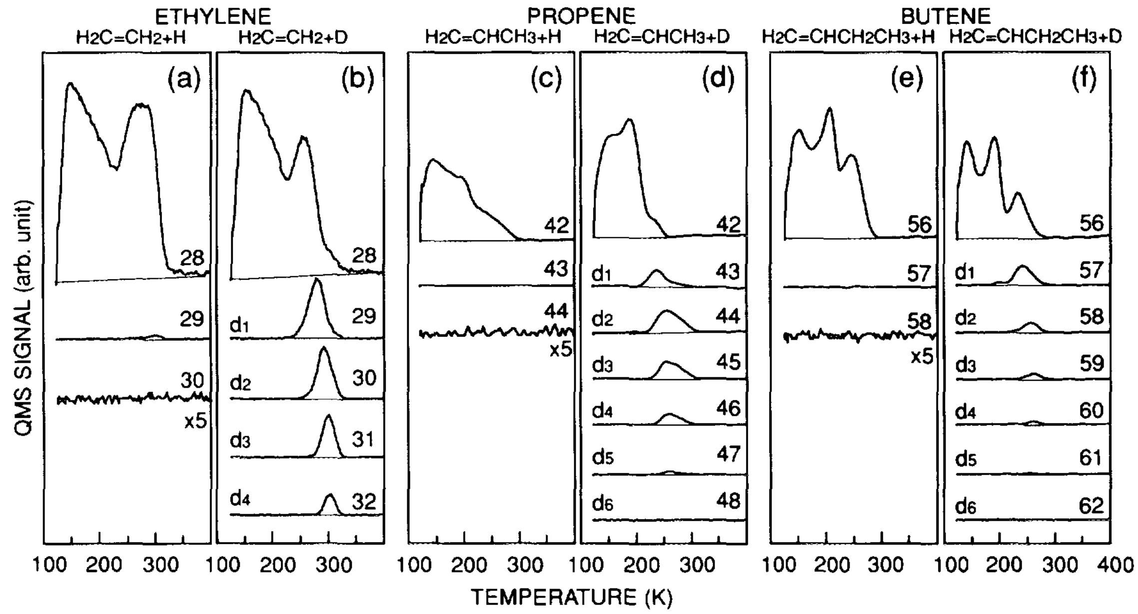


FIG. 1. Temperature-programmed reaction spectra of ethylene, propene, and 1-butene on Pd(100)-p(1×1)-H(D) with saturation exposure at 120 K. Mass fragments are deconvoluted. On Pd(100)-p(1×1)-H (a,c,e), the spectra reveal the absence of hydrogenation products. On Pd(100)-p(1×1)-D (b,d,f), the spectra show the evolution of various H-D exchange products.

panded scales. This indicates that a selectivity of unity for alkene (with respect to alkane) is achieved in the hydrogenation of acetylene, allene, and butadiene, which is consistent with the results of 1-alkene adsorption on Pd(100)-p(1×1)-H.

On the D(a)-covered Pd(100) surface, selective deuteration into d_2-alkenes was also observed as shown in Figs. 3b, 3d, and 3f. The d_2-alkenes undergo H-D exchange, leading to the evolution of higher masses at higher temperatures, with product distributions similar to the alkene H-D exchange shown in Figs. 1b, 1d, and 1f. No H-D exchange occurs for the parent molecules as indicated by the spectra of lower masses.

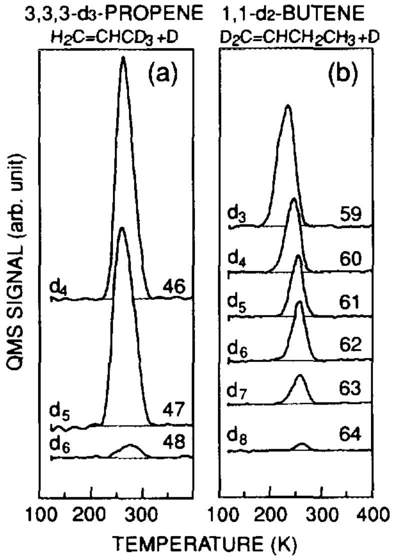


FIG. 2. Temperature-programmed reaction spectra of (a) 3,3,3-d_3-propene and (b) 1,1-d_2-1,1-butene on Pd(100)-p(1×1)-D with saturation exposure at 120 K. The spectra demonstrate that all H atoms of the alkene molecules can be exchanged with D adatoms.

Shown in Fig. 4 are TPR spectra of 1,3,5-hexatriene and 1,5-hexadiene on Pd(100)-p(1×1)-H(D). Hydrogenation of hexatriene proceeds in two stages yielding hexadiene (+2H) at 222 K and hexene (+4H) at 245 K. No further hydrogenation to hexane (+6H) was detected. On the D(a)-covered surface, no H-D exchange occurs for hexatriene as shown by the absence of mass 81-83 in Fig. 4b. 1,5-Hexadiene is hydrogenated to hexene (mass 84 in Fig. 4c). On the D(a)-covered surface, H-D exchange occurs for 1,5-hexadiene as shown by mass 83 and 84 in Fig. 5d. No hydrogenation to hexene (+4H) was detected.

c. Coverage Dependence

Selective hydrogenation of 1,3-butadiene was further investigated as a function of butadiene exposure on Pd(100)-p(1×1)-H. The TPR spectra are shown in Figs. 5a-5c for the parent molecule (butadiene, mass 54), hydrogenation product (butene, mass 56), and hydrogen (preadsorbed and dehydrogenated), respectively. It should be noted that no butane product was detected for any of the coverages studied, indicating a unity selectivity for butene. The bottom spectra for all three masses were

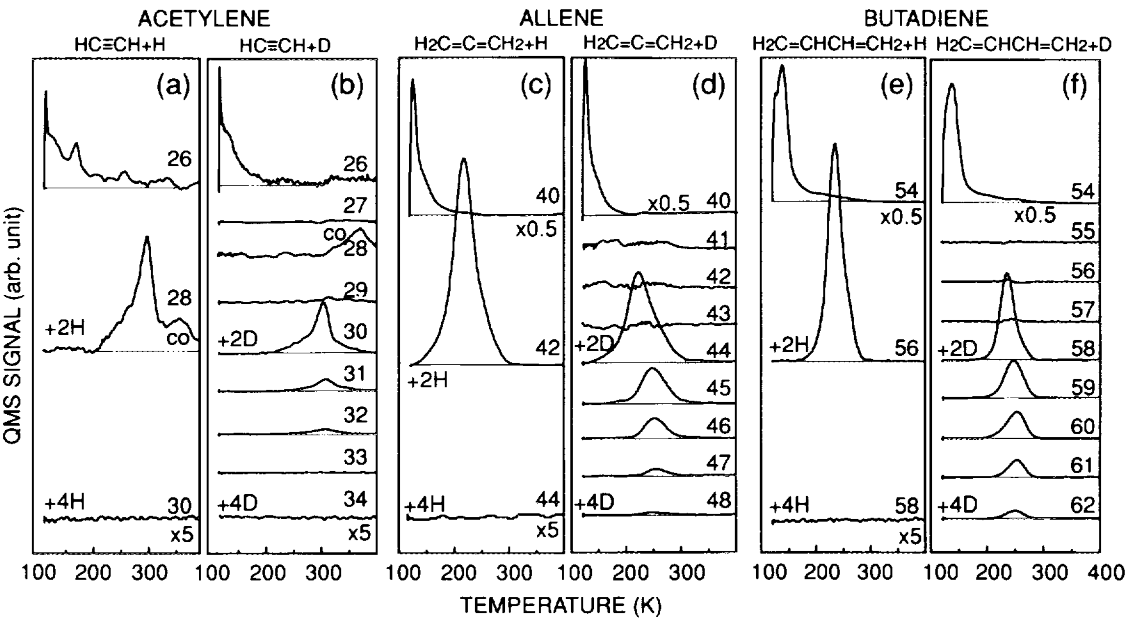


FIG. 3. Temperature-programmed reaction spectra of acetylene, allene, and 1,3-butadiene on Pd(100)-p(1 × 1)-H(D) with saturation exposure at 120 K. Mass fragments are deconvoluted. On Pd(100)-p(1 × 1)-H (a,c,e), selective hydrogenation to the corresponding alkene occurs for all three multiply unsaturated hydrocarbons. No alkanes are produced. For Pd(100)-p(1 × 1)-D (b,d,f) the alkene products undergo further H-D exchange. No H-D exchange occurs for the parent molecules. This indicates that the initial hydrogenation step is irreversible.

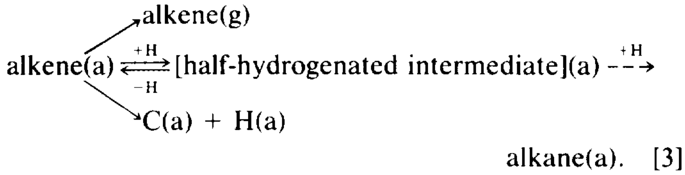
from a blank experiment without butadiene exposure. The H_2 spectrum shows the desorption-limited H_2 desorption at 335 K from Pd(100)-p(1 × 1)-H. Upon butadiene exposure on Pd(100)-p(1 × 1)-H, a reaction-limited H_2 evolution appears at 414 K, which increases in magnitude and shifts to higher temperature with increasing butadiene exposure. The development of H_2 evolution resembles that from butadiene dehydrogenation on the clean Pd(100) surface (10). At low exposures, no hydrogenation product evolves and little molecular butadiene desorbs. This suggests either that all adsorbed butadiene molecules dehydrogenate and no hydrogenation occurs, or that hydrogenation occurs, but all hydrogenation products reversibly dehydrogenate (see below). At higher exposures hydrogenation product (butene) evolves as does parent butadiene. The quantity of both butene and butadiene increases simultaneously until the butene yield saturates.

Figures 6a and 6b show TPR spectra of 1-butene and 1,3-butadiene adsorption on Pd(100)-p(1 × 1)-D, respectively. The exposure in each case was low so that no parent molecule desorbs and no reaction (H-D exchange or hydrogenation) product evolves. H_2, HD, and D_2 result from dehydrogenation and preadsorption. Preadsorbed D(a) desorbs at 335 K. Dehydrogenation and/or H-D exchange below 300 K leads also to desorption-limited H_2 and HD evolution at 335 K. The presence of D_2 and HD in the peak above 400 K indicates that the dehydrogenated fragments contain C-D bonds. This suggests that both H-D exchange and hydrogenation reactions occur at these low coverages, despite the fact that no reaction product evolves.

DISCUSSION

a. Exchange Reaction of Alkenes on Pd(100)-p(1 × 1)-H(D) without Hydrogenation

We have shown that on Pd(100)-p(1 × 1)-H(D) no alkene hydrogenation is observed, but the H-D exchange reaction occurs readily. Following the Horiuti-Polanyi scheme for ethylene hydrogenation (11), the exchange reaction for alkenes may occur through the dehydrogenation of a half-hydrogenated intermediate such as an alkyl species. Accompanying the exchange reaction are molecular alkene desorption and alkene dehydrogenation leading to C(a) and H(a), represented as follows:



$$\begin{tikzcd}[column sep=small] & \text{alkene(g)} & & \\ \text{alkene(a)} \arrow[ur] \arrow[dr] \arrow[r, shift left, "+\text{H}"] & {[\text{half-hydrogenated intermediate}](\text{a})} \arrow[l, shift left, "-\text{H}"] \arrow[r, dashed, "+\text{H}"] & \text{alkane(a)}. \quad [3] \\ & \text{C(a)} + \text{H(a)} & & \end{tikzcd}$$

The reason that the half-hydrogenated intermediate is not further hydrogenated to alkane on Pd(100) may lie in the strength of bonding of half-hydrogenated species or

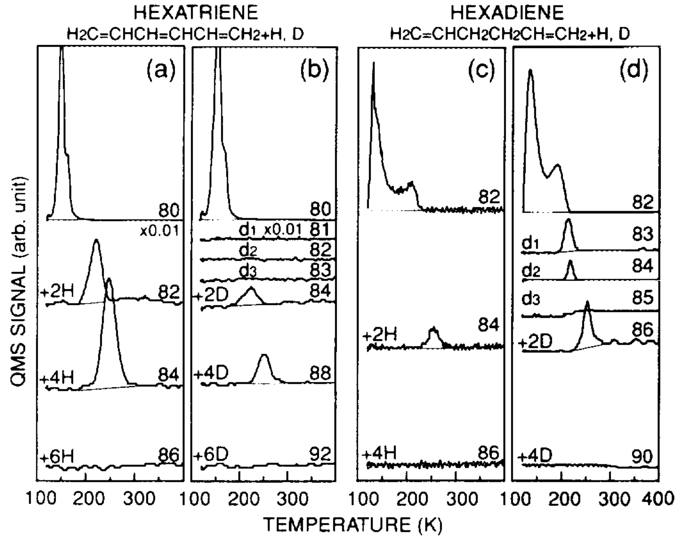


FIG. 4. Temperature-programmed reaction spectra of (a,b) 1,3,5-hexatriene and (c,d) 3,5-hexadiene on Pd(100)–p(1 × 1)–H,D with saturation exposure at 120 K. Mass fragments are deconvoluted. Selective hydrogenation occurs from hexatriene to hexadiene and to hexene, and from hexadiene to hexene. No hexane is detected. H–D exchange reaction occurs for 1,5-hexadiene.

hydrogen atom to the surface or both. Dehydrogenation of the half-hydrogenated species leads to desorption to exchanged alkene. This reaction competes with reductive elimination to form the alkane. Clearly reversible dehydrogenation of the half-hydrogenated species dominates on Pd(100). On Pt and Rh (4), however, both the H–D exchange reaction and hydrogenation to alkane occur. The differing behavior between Pd and these two metals may lie in the strength of the metal–hydrogen bond, since a distinctly different exchange mechanism on Pd is not likely. A stronger metal–hydrogen bond would inhibit further hydrogenation of the half-hydrogenated intermediate.

Values of the metal–hydrogen binding energy in the literature are listed in Table 1 for several metal surfaces. As can be seen, the value for Pd(100) is distinctly higher than for Pt(100), Rh(111), about the same as for Ni(100) and Fe(100), but lower than for W(100). This trend does indeed reflect the occurrence of hydrogenation reaction on these metal surfaces. Efficient hydrogenation of ethylene to ethane has been observed on Pt(111) (13) and Rh(111) (14). No ethane production was observed for ethylene adsorption on H-covered Ni(100) (15), Fe(100) (16), Pd(100) (this work), and W(100) (17), whereas the H–D exchange reaction occurs on all these surfaces. Furthermore, coadsorption of CO weakens Fe–H bonds (18) and induces ethane formation from ethylene on H-covered Fe(100) (19). On Pd(100); however, we did not observe ethane formation by coadsorbing CO with ethylene on H-

TABLE 1

Metal–Hydrogen Binding Energy (kJ/mol) for Adsorbed Atomic Hydrogen on Surfaces (12)

Metal	Surface	Binding energy
Pt	(100)-hex	247.5
	(111)	237
Rh	(110)	255
	(111)	255
Ni	(100)	264
	(110)	261
	(111)	264
Fe	(100)	265
	(110)	271
	(111)	260
Pd	(100)	266
	(110)	267
	(111)	260
W	(100)	284
	(110)	285
	(111)	294

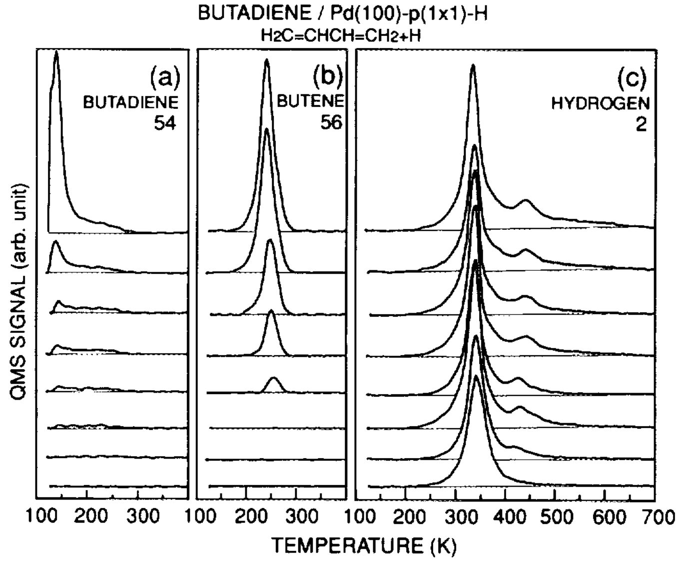


FIG. 5. Temperature-programmed reaction spectra of 1,3-butadiene on Pd(100)–p(1 × 1)–H at various initial coverages. (a) Parent molecule 1,3-butadiene; (b) hydrogenation product butene; and (c) preadsorbed and dehydrogenated H_2 at 334 K and 414–440 K, respectively. Butadiene exposures were 0.0, 0.2, 0.6, 0.8, 1.0, 1.2, 1.6, and 2.0 L, respectively.

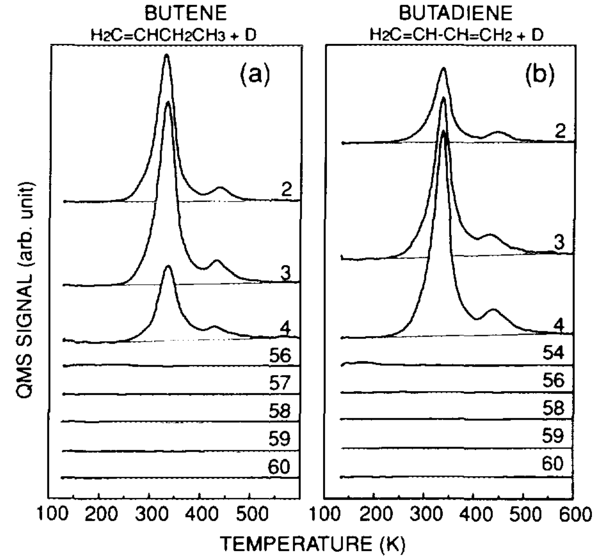


FIG. 6. Temperature-programmed reaction spectra of 1-butene and 1,3-butadiene on Pd(100)–p(1 × 1)–D at low coverages. Preadsorbed D(a) desorbs at 335 K. The presence of D_2 and HD in the peak above 400 K suggests that both H–D exchange and hydrogenation reactions occur at low coverages although there is no evolution of products. The exposures for both butene and butadiene were 0.15 L.

covered surface, and coadsorbed CO on Pd surfaces does not weaken the Pd–H bond (20).

The H–D exchange reactions compete with the desorption processes during TPR, and can be modeled as follows:

$$\begin{tikzcd}
C_nH_{2n}(g) & C_nH_{2n-1}D(g) & C_nH_{2n-2}D_2(g) \\
C_nH_{2n}(a) \arrow[u] \arrow[r, "+D,-H"] & C_nH_{2n-1}D(a) \arrow[u] \arrow[r, "+D,-H"] & C_nH_{2n-2}D_2(a) \arrow[u] \arrow[r, "+D,-H"] & \cdots
\end{tikzcd} \qquad [4]$$

To simulate the kinetics of these processes, we assumed that desorption and exchange are both first-order processes with a preexponential factor of 10^{13} s^{-1} (21) and that the deuterium kinetic isotope effect need not be included. The qualitative features of experimentally observed TPR spectra for the exchange products, in particular, the upward shifts in desorption temperatures (Fig. 7) and the relative yield distributions (Fig. 8), are reproduced with the activation energies given in Table 2. This confirms the limited validity of such a remarkably simple model. Qualitatively, the desorption activation energy decreases from ethylene to propene to butene. For ethylene, the rates of exchange and desorption are nearly the same. For propene, exchange seems faster than desorption, whereas the opposite is true for butene. However, since the rate constants for all exchange reactions have been assumed to be equal, we do not attempt to interpret the values of the activation energies further.

b. Selective Hydrogenation of Conjugated Polyenes on Pd(100)–p(1 × 1)–H(D) without Exchange Reaction

We have clearly shown that conjugated polyenes (acetylene, allene, 1,3-butadiene, and 1,3,5-hexatriene) can be selectively hydrogenated on Pd(100)–p(1 × 1)–H in ultrahigh vacuum into alkenes. This process can be represented for conjugated dienes as follows:

$$\begin{tikzcd}
 & \text{conjugated diene(g)} & \\
\text{conjugated diene(a)} \arrow[ur] \arrow[dr] \arrow[r, shift left, "+H"] & \text{[half-hydrogenated intermediate](a)} \arrow[l, shift left, dashed, "-H"] \arrow[r, "+H"] & \text{alkene(a)} \\
 & C(a) + H(a) &
\end{tikzcd} \qquad [5]$$

H–D exchange reactions of the product alkene occur as well. On the other hand, deuterium does not appear in the desorbing diene molecules. Such exchange is certainly expected from the behavior of the alkenes themselves. The absence of reversible dehydrogenation of the half-hydrogenated intermediate is consistent with its tendency for further hydrogenation to alkene; and a strong tendency for hydrogenation appears to overcome the barrier of Pd–H bond scission which limits complete hydrogenation of alkenes.

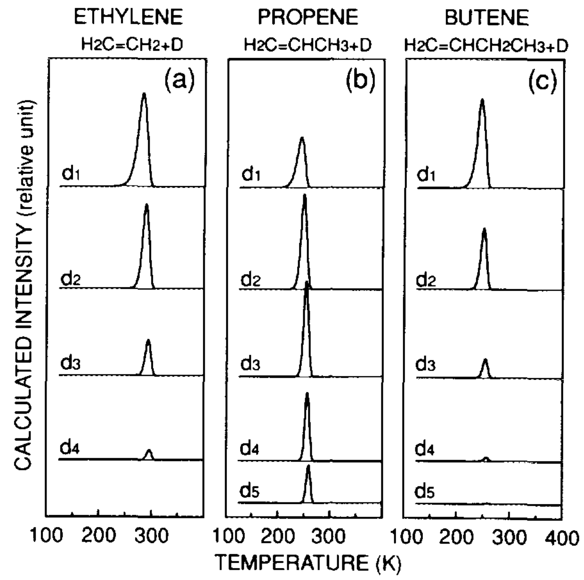


FIG. 7. Simulated temperature-programmed reaction spectra of ethylene, propene, and 1-butene on Pd(100)–p(1 × 1)–D using a kinetic model of H–D exchange as described in the text. These spectra reproduce experimentally measured ones shown in Fig. 1.

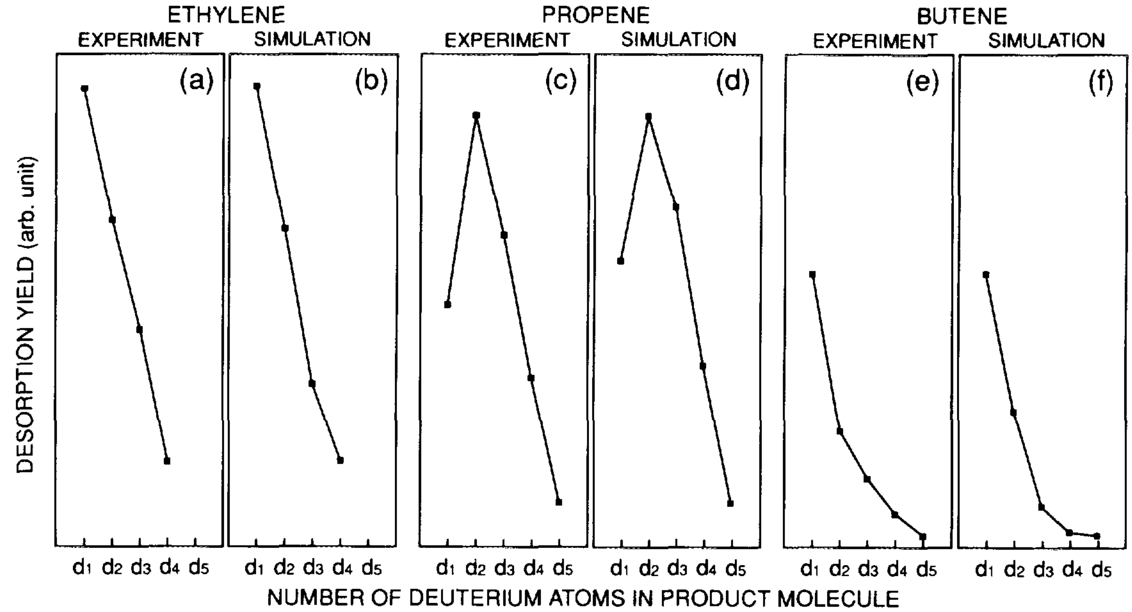


FIG. 8. Comparison of experimental and simulated product yield distributions of H–D exchange for ethylene, propene, and 1-butene on Pd(100)-p(1×1)-D. Relative yields are calculated from integration of TPR spectra shown in Figs. 1 and 7. Good qualitative agreements are achieved between experiments and kinetic simulations.

The high reactivity of conjugated dienes in hydrogenation may be related to the conjugation. Conjugated dienes such as butadiene may form a di-π bonded configuration on Pd using the two double bonds (6). Butadiene in the di-π bonded coordination is more strongly adsorbed than the single π-bonded butene. Similarly, the half-hydrogenated species of conjugated dienes may be more strongly bonded than that of alkene; the hydrogenation to the alkene need not proceed initially at one end of the molecule. Furthermore, in each case the half-hydrogenated species is stabilized at least by a C–Pd σ-bond in addition to possible di-σ bonding resulting from the unreacted π-bond. These factors would favor further hydrogenation of the half-hydrogenated intermediate over the reversal (i.e., exchange) of the intermediate. Hydrogenation of conjugated dienes leading to alkene formation consumes diene molecules which would otherwise undergo exchange and desorb molecularly. The absence of molecular diene desorption above 200 K is indeed seen for all the conjugated molecules which can be hydrogenated to alkenes (Figs. 4a–4f and Fig. 5a).

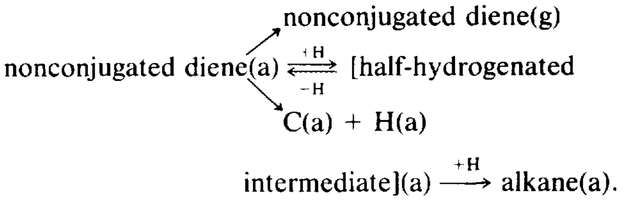
TABLE 2

Values of Activation Energies (kJ/mol) Used in the Kinetics Simulations of H–D Exchange and Desorption Processes (see Text for Detail)

	H–D exchange	Desorption
Ethylene	75.40	75.30
Propene	63.40	66.10
1-Butene	65.70	64.85

c. Exchange and Selective Hydrogenation of Nonconjugated Polyene on Pd(100)-p(1×1)-H(D)

As Fig. 5d shows, the desorption of mass 83 and 84 occurs at 213 and 218 K, respectively, for 1,5-hexadiene on Pd(100)-p(1×1)-D, and no desorption of higher masses appears at these temperatures. This indicates that the desorption of mass 83 and 84 is not due to fragmentation of higher mass products, but results from H–D exchange. The occurrence of H–D exchange suggests that 1,5-hexadiene is similar to 1-alkenes, unlike conjugated polyenes which do not undergo exchange. This difference implies that the half-hydrogenated intermediates produced from the conjugated species may retain some conjugation which stabilizes them toward dehydrogenation. On the other hand, 1,5-hexadiene can be hydrogenated to hexene (see Figs. 5c and 5d). In this aspect, it is similar to conjugated dienes, unlike 1-alkenes. The reactivity of nonconjugated diene is therefore somewhere between 1-alkenes and conjugated dienes: both exchange reaction and selective hydrogenation occur on Pd(100)-p(1×1)-H.



$$\text{nonconjugated diene(a)} \underset{-\text{H}}{\overset{+\text{H}}{\rightleftharpoons}} \text{[half-hydrogenated intermediate](a)} \xrightarrow{+\text{H}} \text{alkane(a)}; \quad \text{nonconjugated diene(a)} \nearrow \text{nonconjugated diene(g)}; \quad \text{nonconjugated diene(a)} \searrow \text{C(a)} + \text{H(a)} \qquad [6]$$

There may be two explanations for the behavior of nonconjugated dienes. First, the binding energy of the half-hydrogenated intermediate may be somewhere between those for 1-alkene and for conjugated diene, neither too weak to result in only exchange nor too strong to induce only hydrogenation. More specifically, one end function may bind the molecule to the surface while the other is hydrogenated. Second, exchange reactions often produce double bond migration (22) which may convert nonconjugated diene into conjugated diene. For 1,5-hexadiene, the exchange reaction needs to occur at least twice on the same molecule to form a conjugated diene. Although the exchange reaction is competing with other processes such as desorption, dehydrogenation, and hydrogenation, conversion to conjugated diene is not improbable.

d. Coverage Requirement for Product Evolution

As Fig. 8 shows, although no reaction products evolve, exchange reactions of 1-butene and selective hydrogenation of 1,3-butadiene do occur at low coverages on Pd(100)–p(1×1)–D. Figures 6 and 7 show that hydrogenation product (butene) evolves at the coverage where molecular butadiene desorbs. At lower coverages the reaction intermediate dehydrogenates, yielding C(a) and H(a). As discussed above, the desorbed product (alkene) molecules may be from weakly π-bonded surface species. These weakly bonded species are mobile on the surface. At low coverages they are able to find empty sites and becomes strongly σ-bonded to the surface leading to dehydrogenation. At coverages where the surface is saturated with strongly σ-bonded species, further adsorption will give weakly π-bonded species which may either desorb molecularly or undergo reactions (exchange or hydrogenation). The product molecules will evolve from the surface since there is no available empty sites to where they can migrate. This assertion is supported by the simultaneous development of butadiene and butene evolution as the coverage increases (Figs. 5 and 6). This is also consistent with the widely observed surface structure insensitivity of hydrogenation reactions on metal surfaces. On the other hand, dehydrogenation requires a large ensemble of surface sites, so that increasing coverage disfavors dehydrogenation. Thus even the σ-bonded hydrocarbons will desorb rather than dehydrogenate if there are not enough free sites to accept the H adatoms, as shown by Campbell *et al.* (23) for cyclic hydrocarbons on Pt(111) precovered with bismuth.

CONCLUSIONS

The adsorption and reactions of unsaturated hydrocarbons (ethylene, propene, 1-butene, acetylene, allene, 1,3-butadiene, 1,3,5-hexatriene, and 1,5-hexadiene) have been investigated on the Pd(100)–p(1×1)–H and Pd(100)–p(1×1)–D surfaces using temperature-programmed reaction spectroscopy. The following conclusions have been drawn from the results.

1. Alkenes (ethylene, propene, and 1-butene) undergo efficient H–D exchange reactions below 300 K for all C–H bonds, but no hydrogenation products (alkanes) are observed.
2. Following the Horiuti–Polanyi scheme for ethylene hydrogenation, the exchange reaction is proposed to occur through the reversal of a half-hydrogenated intermediate. The competition between molecular desorption and successive H–D exchange is demonstrated by kinetic simulations.
3. The absence of alkene hydrogenation is explained by stronger metal–hydrogen bonds on Pd(100) than on other metals such as Pt and Rh.
4. Conjugated polyenes (including acetylene, allene, 1,3-butadiene, and 1,3,5-hexatriene) undergo selective hydrogenation to corresponding alkenes below or around 300 K with a unit selectivity, whereas no exchange reaction is observed to occur for the reactant molecules, though the alkene products undergo exchange reactions.
5. Stronger bonding of the half-hydrogenated intermediate to the surface is invoked to account for the stronger tendency for irreversible hydrogenation of conjugated polyenes to alkenes.
6. Nonconjugated polyene (1,5-hexadiene) undergoes both exchange and hydrogenation reactions.

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