J. Am. Chem. Soc. **1995,** *117,* 5523−5530 5523

Oxygen-Activated Combustion of Alkenes on the Pd(100) Surface

Xing-Cai Guo and Robert J. Madix*

Contribution from the Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025

Received August 22, 1994⊗

Abstract: Reactions of ethylene, propene, 1-butene, and 1,3-butadiene have been investigated on atomic oxygen-covered Pd(100)-p(2 × 2)-O surface using temperature-programmed reaction spectroscopy. All four alkenes undergo combustion yielding H_2O, CO, and CO_2. No partial oxidation products were observed. H_2 is evolved after the oxygen is consumed. Compared to dehydrogenation reactions on the clean Pd(100) surface, O(a) inhibits both adsorption and reaction of ethylene. For propene, 1-butene, and 1,3-butadiene, in contrast, O(a) does not inhibit adsorption and also activates reactions—all C−H bonds react facilely with O(a) forming H_2O below the dehydrogenation temperature on the clean surface. Isotope experiments show that initial reactions occur predominantly with the vinylic C−H bonds of 1-alkenes. Low-temperature CO_2 evolution and desorption-limited CO evolution provide evidence for oxygen addition to the carbon atoms of dehydrogenated alkene intermediates. Indirect reactions resulting from dehydrogenation at clean sites and oxidation of H(a) and C(a) lead to high-temperature H_2O evolution above 300 K and CO and CO_2 evolution above 400 K.

Introduction

Catalytic combustion of hydrocarbons is one of the three ways to diminish automobile emissions in the three-way catalytic converter,[1] the other two being oxidation of carbon monoxide and reduction of nitrogen oxides. Palladium is one of prime ingredients in the three-way catalysts, together with platinum and rhodium. Recently Pd has gained much attention in automotive catalysis as a possible substitute for Rh and/or Pt because of its lower cost.[2] On the other hand, little fundamental work has been done toward understanding the processes of hydrocarbon combustion on Pd surfaces. In the present work we have investigated alkene combustion on the Pd(100) surface at an oxygen coverage of 0.25 O/Pd under ultrahigh vacuum conditions, using temperature-programmed reaction spectroscopy (TPRS). The alkenes studied include ethylene, propylene, 1-butene, and 1,3-butadiene. A report on the combustion of aromatic hydrocarbons will soon be published.

There are two possible pathways through which alkenes may catalytically combust: (1) *indirect combustion*, in which alkene first adsorbs and dehydrogenates by interaction with the surface to adsorbed H(a) and C(a), which are then oxidized by coadsorbed O(a) to H_2O and CO or CO_2; and (2) *oxygen-activated combustion*, in which preadsorbed O(a) abstracts H from alkene (or its fragments) breaking a C−H bond to form OH(a) which leads to H_2O formation, or O(a) attacks C on alkene (or its fragments) forming a C−O bond, which leads to CO or CO_2 formation well below the temperatures characteristic of reaction of C(a) and O(a). In order to separate these two possibilities as much as possible, we have first studied the dehydrogenation of alkenes on the clean Pd(100) surface and then investigated their reactions on the O(a)-precovered Pd(100)-p(2 × 2)-O surface.

We will show that on the clean Pd(100) surface all alkenes dehydrogenate through a series of intermediates in a temperature range from 200 to 900 K. On the Pd(100)-p(2 × 2)-O surface, while atomic oxygen inhibits ethylene dehydrogenation, the dehydrogenation of higher alkenes is activated by the presence of O(a), yielding H_2O and CO_2 below the dehydrogenation temperature on clean Pd(100). The total dehydrogenation yields for higher alkenes on Pd(100)-p(2 × 2)-O are similar to that on the clean surface. At low alkene coverages all molecules are dehydrogenated to form H_2O below 450 K. The vinylic C−H bonds are preferentially broken in the initial reaction. Low-temperature evolution of CO_2 and the desorption-limited CO evolution indicate that O(a) directly attacks the C atoms of the alkene fragments—a distinctly different mechanism from the indirect scavenging reactions.

Experimental Section

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 μA, 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.[3,4]

High-purity alkenes from lecture bottles were used without further purification: ethylene (Matheson, CP grade), propene, 1-butene, and 1,3-butadiene (Aldrich, 99+%). Deuterated isotopes were also used: propene-*3,3,3*-d_3 (MSD Isotopes, 98% D), propene-d_6 (MSD Isotopes, 99.3% D), and butene-*1,1*-d_2 (CDN Isotopes, 99.6% D). 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 oxygen was adsorbed on Pd(100) at 300 K via a capillary array doser with an O_2 exposure of 6 langmuirs (1 langmuir = 10^{-6} Torr s), yielding a p(2 × 2)-O LEED pattern corresponding to an oxygen coverage of 0.25 O/Pd.[5]

All TPRS measurements were taken with a UTI mass spectrometer interfaced to a desk top computer which was capable of multiplexing

---

⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1995.

(1) Hegedus, L. L.; Gumbleton, J. J. *CHEMTECH* **1980**, *10*, 630.

(2) Taylor, K. C. *Catal. Rev.—Sci. Eng.* **1993**, *35*, 457.

(3) Klier, K.; Wang, Y.-N.; Simmons, G. W. *J. Phys. Chem.* **1993**,*97*,633.

(4) Behm, R. J.; Christmann, K.; Ertl, G.; Van Hove, M. A. *J. Chem. Phys.* **1980**, *73*, 2984.

(5) Stuve, E. M.; Madix, R. J. *Surf. Sci.* **1984**,*146*, 155.

0002-7863/95/1517-5523$09.00/0

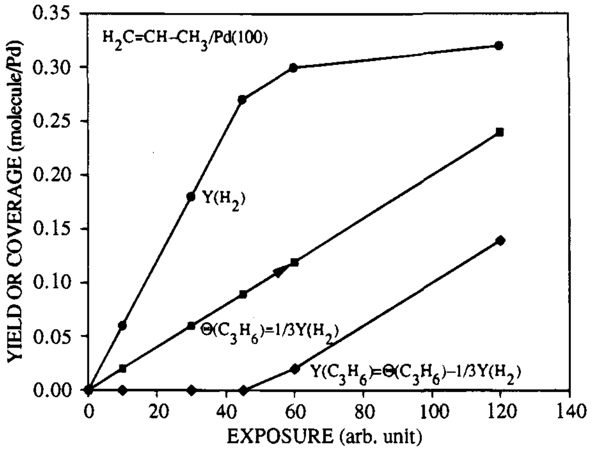

Figure 1. Calibration of adsorption coverage and desorption yield for alkenes on Pd(100) as illustrated here for propene. See text for detail.

up to 200 masses. Usually less than 10 masses were monitored to increase the signal-to-noise level. Digitized data are displayed below in joined straight lines. When necessary, spectrum deconvolution was performed to subtract contributions from higher mass fragments, such as CO^+ from CO_2 or fragments from the parent alkene molecule. A nearly linear heating rate of 4 K/s was used for all the spectra presented below.

Product yields were expressed as equivalent molecules per Pd atom on the surface. The TPRS peak areas for H_2 and CO were calibrated to their saturation TPD areas which correspond to 0.5 H_2/Pd[6] and 0.80 CO/Pd,[5] respectively. The TPRS areas for H_2O and CO_2 were calibrated from the remaining O(a) coverage following reactions with H(a) and CO(a), respectively. Even under 5×10^{-11} Torr vacuum, adsorption from background gases was not negligible. On the clean Pd(100) surface, background adsorption of H_2 and CO was estimated to be 0.06 H_2/Pd and 0.008 CO/Pd, respectively. The background H_2 contribution was subtracted from the dehydrogenation TPRS spectra. On Pd(100)-p(2 × 2)-O, background H_2 and CO adsorption led to the formation of 0.008 H_2O/Pd and 0.008 CO_2/Pd, respectively. No desorption of H_2 or CO was observed.

Alkene coverages were calibrated by comparing the H_2 evolution at low alkene coverage to the H_2 saturation coverage. As illustrated in Figure 1 for propene adsorption on clean Pd(100), at low coverages all C_3H_6(a) molecules dehydrogenate with no molecular propene desorption. Thus the coverage of C_3H_6(a) can be calculated from the H_2 yield, which has been calibrated based on H_2 saturation TPD. At high coverages, molecular propene desorption also occurs. The initial C_3H_6(a) coverage is now the sum of one-third the H_2 yield and the C_3H_6(desorbed) yield, i.e., $\Theta(C_3H_6) = (1/3)\ Y(H_2) + Y(C_3H_6)$. The initially linear increase of the H_2 yield versus exposure means that the sticking probability of propene on Pd(100) is constant over this exposure range. Further, the mass spectrometer sensitivity factor for C_3H_6 is independent of exposure, and the integrated TPD areas divided by the yield of propene desorbing must be independent of exposure. The linear extension of the initial C_3H_6(a) coverage from low to high exposures shown in Figure 1 satisfies these criteria. Once the C_3H_6(a) coverage and H_2 yield is known for a certain exposure, the C_3H_6(desorbed) yield can be calibrated from $Y(C_3H_6) = \Theta(C_3H_6) - (1/3)\ Y(H_2)$. The sensitivity factors obtained from the yield and TPD areas at exposures of 60 and 120 shown in Figure 1 are the same, confirming the validity of the method. The linearity of the initial propene coverage with exposure signifies a constant adsorption probability. Furthermore, the calibration factor may then be used for even higher exposures where the adsorption probability is no longer constant with increasing coverage. The same procedure was carried out for each alkene, avoiding calibration of relative mass spectrometer sensitivities which usually have vary large errors. The major error of our procedure comes from the value of the saturation coverage of H_2, which is estimated to be approximately 10%.

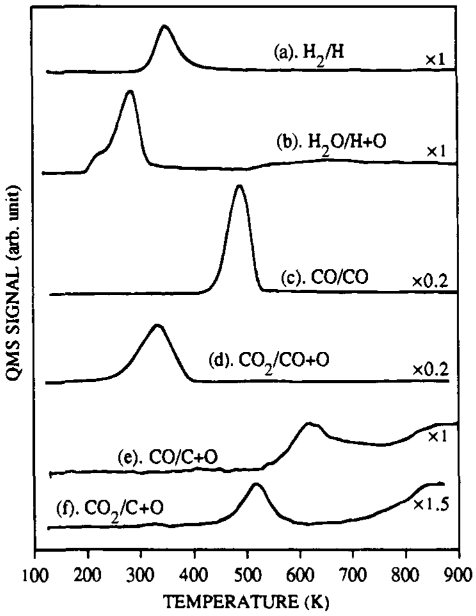

Figure 2. Evolution of product molecules H_2, H_2O, CO, and CO_2 from Pd(100) or Pd(100)-p(2 × 2)-O: (a) H_2/H/Pd(100), $\Theta(H) = 0.26$ H/Pd; (b) H_2O/H/Pd(100)-p(2 × 2)-O; (c) CO/CO/Pd(100), $\Theta(CO) = 0.15$ CO/Pd; (d) CO_2/CO/Pd(100)-p(2 × 2)-O, $Y(CO_2) = 0.21$ CO_2/Pd; (e) CO/C + O/Pd(100), $\Theta(O) = 0.03$ O/Pd; (f) CO_2/C + O/Pd(100), $\Theta(O) = 0.14$ O/Pd.

Results and Interpretation

A. Evolution of Product Molecules H_2, H_2O, CO, and CO_2 from Pd(100) or Pd(100)-p(2 × 2)-O. For the purpose of calibration we first determined the temperature-programmed desorption (TPD) or TPR spectra of the product molecules H_2, H_2O, CO, and CO_2 (Figure 2). The H_2 desorption spectra (Figure 2a) are from hydrogen adsorbed on clean Pd(100) at 120 K with a coverage of 0.26 H/Pd. Desorption of H_2 starts at 300 K and reaches maximum at 355 K. This experiment sets a reference temperature for desorption-limited H_2 evolution.

H_2O evolution from H(a) adsorbed on Pd(100)-p(2 × 2)-O (Figure 2b) starts at 195 K, showing a desorption maximum at 285 K with a shoulder at 235 K. For lower O(a) coverages H_2O evolves in the same temperature range (data not shown). H_2O evolution in this temperature range is rate-limited by OH disproportionation, since desorption-limited H_2O evolves below 200 K from Pd(100).[7] The broad feature between 500 and 1000 K in Figure 2b is from the sample holder.

Desorption-limited CO evolution from CO(a) on clean Pd(100) at a coverage of 0.15 CO/Pd is shown in Figure 2c. The desorption peak temperature is around 500 K. CO adsorption on Pd(100)-p(2 × 2)-O leads to CO_2 evolution at 335 K (Figure 2d) for a yield of 0.21 CO_2/Pd. CO_2 evolution is rate-limited by CO(a) + O(a) reaction, because CO_2 rapidly desorbs at this surface temperature.

Reaction-limited CO and CO_2 evolution from reactions of O(a) and C(a) on Pd(100) occurs at 625 and 500 K, respectively (Figure 2, e and f). In these experiments C(a) was deposited on the surface by ethylene adsorption at 120 K and annealing to 550 K to desorb hydrogen (see next section). O_2 was exposed at 300 K and the crystal was then cooled to 120 K. Small O_2 exposure leads to CO evolution at 625 K (Figure 2e, 0.03 O/Pd), while large O_2 exposure gives CO_2 at 500 K (Figure 2f, 0.14 O/Pd). In both cases the high-temperature features around 900 K may be due to O(a) reaction with subsurface carbon which has diffused beneath the surface during temperature ramping.

---

[6] Nyberg, C.; Tengstål, C. G. *Phys. Rev. Lett.* **1983**, *50*, 1680.

[7] Stuve, E. M.; Jorgensen, S. W.; Madix, R. J. *Surf. Sci.* **1984**, *146*, 179.

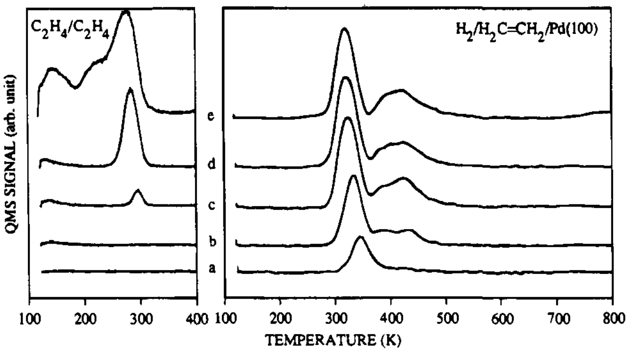

Figure 3. Desorption and dehydrogenation of ethylene on Pd(100) at variable adsorption coverages: (a) 0.03; (b) 0.06; (c) 0.11; (d) 0.14; (e) 0.25 C_2H_4/Pd.

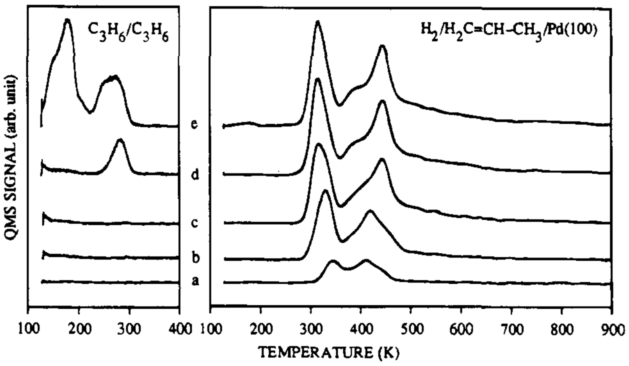

Figure 4. Desorption and dehydrogenation of propene on Pd(100) at variable adsorption coverages: (a) 0.02; (b) 0.06; (c) 0.09; (d) 0.12; (e) 0.24 C_3H_6/Pd.

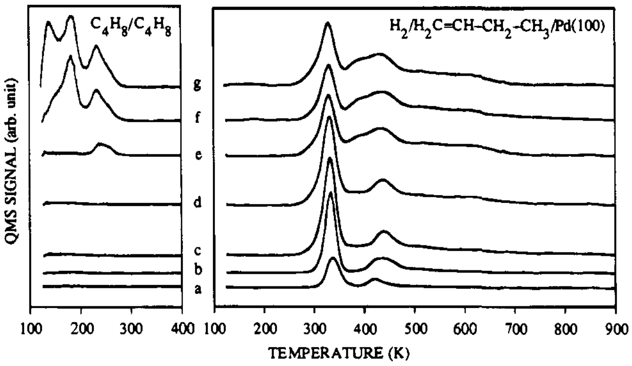

Figure 5. Desorption and dehydrogenation of 1-butene on Pd(100) at variable adsorption coverages: (a) 0.02; (b) 0.04; (c) 0.06; (d) 0.08; (e) 0.09; (f) 0.13; (g) 0.21 C_4H_8/Pd.

B. Dehydrogenation of Ethylene, Propene, 1-Butene, and 1,3-Butadiene on Clean Pd(100). Alkenes were adsorbed on clean Pd(100) at a surface temperature of 120 K with variable exposures. Dehydrogenation of alkenes yields adsorbed hydrogen H(a) on the surface, which desorbs associatively as H_2. H_2 evolution may be either desorption-limited or reaction-limited, depending on whether dehydrogenation occurs below or above 300 K (cf. Figure 2a).

Figures 3−6 display the TPR spectra of ethylene, propene, 1-butene, and 1,3-butadiene on clean Pd(100). H_2 desorption (0.06 H_2/Pd) due to background adsorption during sample cooling has been subtracted from all the H_2 spectra. At low exposures no molecular alkene desorbs. All alkenes on the surface dehydrogenate, yielding H(a) and C(a). Even at very low coverages all four alkenes exhibit two H_2 evolution peaks; one is desorption-limited at 350 K, and the other is reaction-limited above 400 K. These results indicate that each alkene dehydrogenates in two major steps, one occurring below 300 K and the other above 400 K. Both the desorption-limited and reaction-limited H_2 evolution peaks increase in magnitude as alkene coverage increases. The fraction attributable to the desorption-limited H_2 peak decreases with increasing coverage. A high-temperature tail develops for propene, butene, and butadiene above 500 K. As coverage increases further, a fraction of the adsorbed alkene molecules start to desorb, as shown in the left panels of Figures 3−6. At this point the amount of desorption-limited H_2 starts to decrease for butene and butadiene, and the high-temperature tail becomes a broad peak. Desorption-limited H_2 evolution disappears for butadiene at saturation coverage, because surface hydrogen is consumed by butadiene to form 0.02 butene/Pd as shown in the left panel of Figure 6. No hydrogenation was detected for ethylene, propene, and butene, although these 1-alkenes can undergo efficient H−D exchanges, as reported elsewhere.[8]

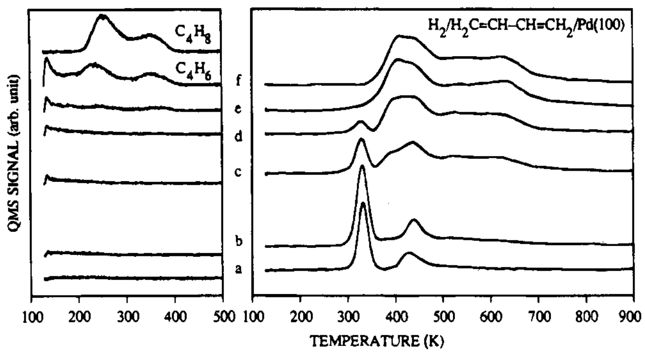

Figure 6. Desorption and dehydrogenation of 1,3-butadiene on Pd(100) at variable adsorption coverages: (a) 0.04; (b) 0.06; (c) 0.13; (d) 0.17; (e) 0.20; (f) 0.27 C_4H_6/Pd.

Table 1. Total Adsorption Coverage, Molecular Desorption Yield, and Dehydrogenation Yield of Alkenes on the Clean Pd(100) Surface for Saturation Exposures at 120 K

alkene molecule	desorption yield (alkene/Pd)	dehydrogenation yield (H_2/Pd)	dehydrogenation yield (alkene/Pd)	adsorption coverage[a] (alkene/Pd)
ethylene	0.15	0.19	0.10	0.25
propene	0.13	0.32	0.11	0.24
butene	0.12	0.36	0.09	0.21
butadiene	0.12	0.38	0.13	0.27

[a] It should be noted that the saturation coverage varies with adsorption temperature.

Table 1 lists the total adsorption coverages and the dehydrogenation yields for saturation alkene exposure at 120 K. The saturation coverage for simple alkenes is in the range from 0.25 to 0.21 alkene/Pd, decreasing as the molecular chain increases from ethylene to propene to butene. From butene to butadiene there is an increase of 8 kcal/mol in adsorption energy as estimated from the high-temperature desorption peak (225 K for butene and 350 K for butadiene). The dehydrogenation yields are similar for simple alkenes (0.10 alkene/Pd), but slightly more dehydrogenation occurs for butadiene (0.13 butadiene/Pd).

C. Combustion of Ethylene, Propene, 1-Butene, and 1,3-Butadiene on Pd(100)-p(2 × 2)-O. Adsorption of ethylene, propene, 1-butene, and 1,3-butadiene was studied on the atomic oxygen covered Pd(100)-p(2 × 2)-O surface at 120 K with a variable alkene exposure. Under these conditions TPR spectra (Figures 7−10) heating up to 1070 K yielded no partial oxidation products; only total oxidation (combustion) products H_2O and CO_2 (and CO when alkene is in excess) were found.

---

(8) Guo, X.-C.; Madix, R. J. *J. Catal.*, in press.

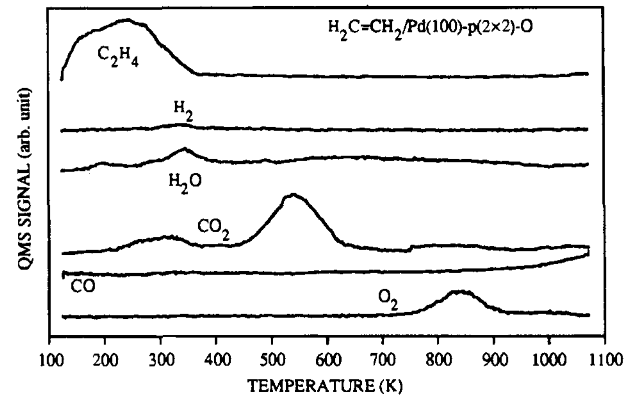

Figure 7. Temperature-programmed reaction spectra of ethylene adsorbed on Pd(100)-p(2 x 2)-O at saturation ethylene exposure. The product yields are listed in Table 2.

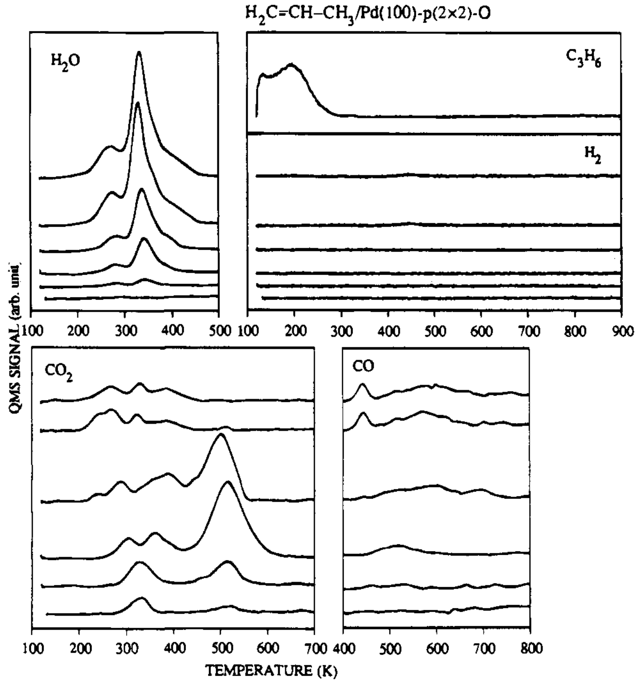

Figure 8. Temperature-programmed reaction spectra of propene adsorbed on Pd(100)-p(2 x 2)-O at variable propene exposure. The bottom spectrum for each product is from a blank experiment without propene exposure. Exposures for other spectra were 0.05, 0.10, 0.20, 0.30, and 0.60 langmuir. The product yields for the saturation exposure are listed in Table 2.

Even at higher O(a) coverages (up to 1 O/Pd) combustion was the only reaction detected (data not shown). The product yields for the saturation alkene exposure are listed in Table 2. The reacted alkene coverages were derived from the sum of H_2O and H_2 yields. The C(a) coverage including C diffused into the bulk was calculated from carbon mass balance between reacted alkenes and the sum of CO and CO_2. Desorbed alkene yields were calibrated by using the calibration factor for each alkene obtained from experiments on the clean surface (cf. Experimental Section). Adsorbed alkene coverage was the sum of reacted and desorbed alkene yields.

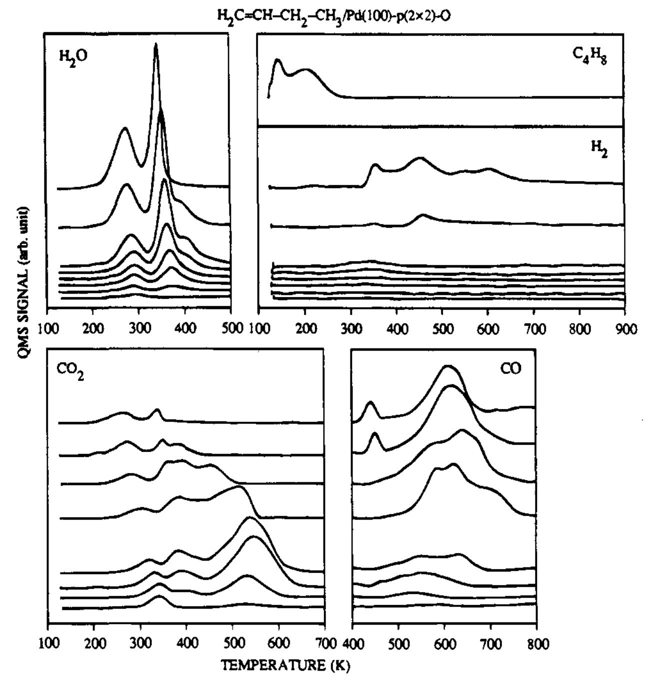

Figure 9. Temperature-programmed reaction spectra of 1-butene adsorbed on Pd(100)-p(2 x 2)-O at variable 1-butene exposure. The bottom spectrum for each product is from a blank experiment without 1-butene exposure. Exposures for other spectra were 0.01, 0.03, 0.04, 0.08, 0.10, 0.15, and 0.25 langmuir. The product yields for the saturation exposure are listed in Table 2.

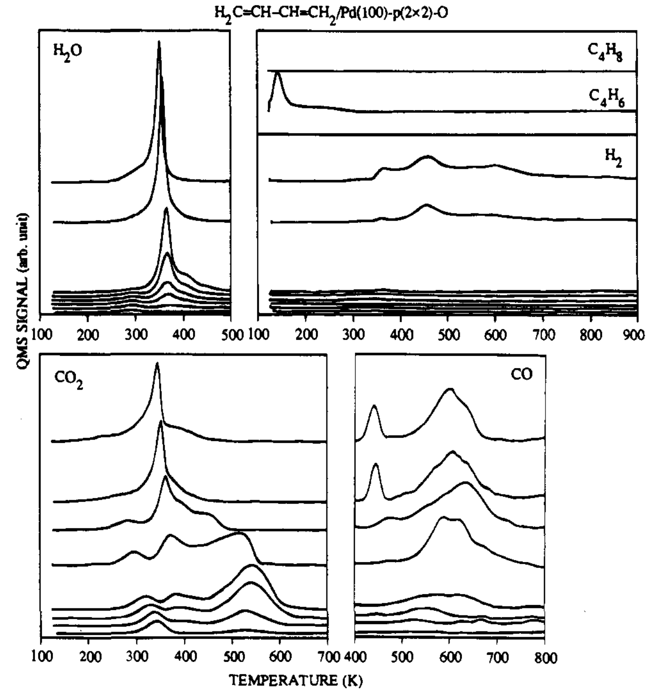

Figure 10. Temperature-programmed reaction spectra of 1,3-butadiene adsorbed on Pd(100)-p(2 x 2)-O at variable 1,3-butadiene exposure. The bottom spectrum for each product is from a blank experiment without 1,3-butadiene exposure. Exposures for other spectra were 0.001, 0.003, 0.005, 0.01, 0.02, 006, and 0.30 langmuir. The product yields for the saturation exposure are listed in Table 2.

Very little ethylene reacts with O(a) on Pd(100)-p(2 x 2)-O, and there is no indication of direct reactions (Table 2 and Figure 7). H_2O evolution near 350 K is rate-limited by ethylene dehydrogenation on Pd sites unaffected by adsorbed O and subsequent reactions between H(a) and O(a), as the peak temperature for water evolution is well above that from H(a) + O(a) reaction on the clean surface (cf. Figure 2b). The low-temperature CO_2 around 300 K is due to O(a) reaction with coadsorbed CO from the background. The CO_2 evolution at 530 K is apparently due to O(a) reacting with totally dehydrogenated C(a) atoms, as it closely resembles that from O(a) + C(a) reaction (cf. Figure 2f). No CO is formed from ethylene on Pd(100)-p(2 x 2)-O, since O(a) is in excess by 0.13 O/Pd. Of 0.16 ethylene/Pd adsorbed at saturation, which is consider-

Table 2. Yield (Molecules/Pd or Atoms/Pd) of Alkene Combustion on the Pd(100)-p(2 × 2)-O Surface for Saturation Exposures at 120 K

	reaction products								
alkene molecule	H_2O	H_2	CO_2	CO	O(a)	C(a)[a]	reacted alkene	desorbed alkene	adsorbed alkene
ethylene	0.02	0.02	0.04	0.00	0.13	0.00	0.02	0.14	0.16
propene	0.20	0.07	0.01	0.03	0.00	0.23	0.09	0.14	0.23
butene	0.19	0.20	0.01	0.04	0.00	0.36	0.10	0.14	0.24
butadiene	0.12	0.19	0.03	0.07	0.00	0.30	0.10	0.13	0.23

[a] The carbon coverage includes C diffused into the bulk.

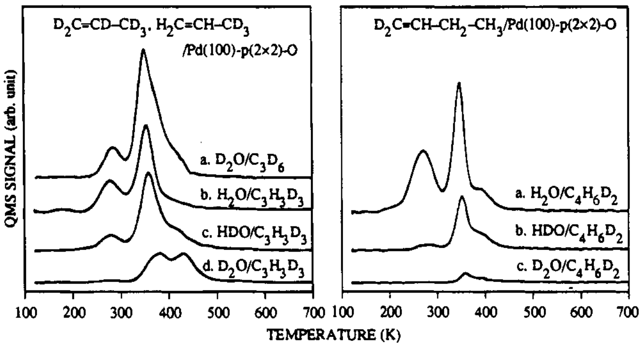

Figure 11. Evolution of water isotopes from deuterated propene (propene-d_6 and propene-*3,3,3*-d_3) and butene-*1,1*-d_2-1 on Pd(100)-p(2 × 2)-O at a low exposure.

ably smaller than on clean Pd(100), 0.14 ethylene/Pd desorbs molecularly in a broad peak below 370 K. O(a) on Pd(100) seems to block ethylene adsorption *and* inhibit ethylene dehydrogenation.

Propene, butene, and butadiene have very similar reacted coverages (0.10 molecule/Pd) and adsorbed coverages (0.23 molecule/Pd) for saturation exposures at 120 K (Table 2). In fact, these quantities on Pd(100)-p(2 × 2)-O are comparable to those on clean Pd(100) (cf. Table 1). Clearly O(a) does not block adsorption or inhibit reactions of propene, butene, and butadiene, unlike the case of ethylene. The TPRS features on Pd(100)-p(2 × 2)-O are also similar for propene, butene, and butadiene (Figures 8−10). At low coverages *all* H atoms of the alkene molecule react with O(a) to form H_2O below 400 K; no H_2 evolves from the surface. This result is in sharp contrast to the behavior on clean Pd(100), where reaction-limited H_2 evolves above 400 K in the second stage of dehydrogenation (cf. Figures 4−6). Apparently, O(a) facilitates the C−H bond scission of higher alkenes on Pd(100), at least subsequent to the first dehydrogenation step.

For propene and butene (Figures 8 and 9) there are two H_2O peaks which develop simultaneously as coverage increases, indicating that there are two stages in O(a) + alkene reactions. The low-temperature H_2O peak at 280 K coincides with that from H(a) + O(a) reaction on Pd(100) (cf. Figure 2b), suggesting that the H_2O evolution is not rate-limited by C−H bond scission, but by recombination. However, the high-temperature H_2O peak above 300 K (340 K for propene and 350 K for butene) is clearly rate-limited by C−H bond scission. As coverage increases, both H_2O peaks shift down in temperature and a shoulder appears above 400 K.

To further distinguish the two water evolution processes within the alkene, experiments were performed using deuterated alkenes (Figure 11). In these experiments alkene exposures were low enough so that there was no evolution of hydrogen or its isotopes. All alkene molecules reacted with O(a) to form water. Experiment with $D_2C{=}CD{-}CD_3$ shows that deuterated propene reacts similarly as non-deuterated propene (Figure 11). Unlike the results for Ag(110),[9a] there is no significant deuterium kinetic isotope effect. Qualitatively, in the low-temperature peak there is little C−D bond breaking for $H_2C{=}CH{-}CD_3$ and $D_2C{=}CH{-}CH_2{-}CH_3$. This result implies that the low-temperature H_2O originates mainly from the vinylic 2-H atoms of the 1-alkene. Quantitative distributions of H (or D) in the two pathways to water are listed in Table 3. Differences in mass spectrometer sensitivity between H_2O and D_2O were taken into account and estimated from the ratio of their total areas and the H/D ratio in the molecule. In calculating the relative contribution of HDO to H and D, half the HDO peak was added to H_2O and D_2O. Contribution from the mass fragment OD^+ (18 amu) to H_2O was subtracted; it was assumed to have the same fraction of D_2O as OH^+ from H_2O.

Table 3. Distributions of H or D in Water Evolution in the Low-Temperature Range and in the High-Temperature Range for Propene and 1-Butene on Pd(100)-p(2 × 2)-O[a]

	hydrogen (H)			deuterium (D)		
	low	high	total	low	high	total
$H_2C{=}CH{-}CH_3$	$1_{(1.2)}$	$5_{(4.8)}$	6	$0_{(0.0)}$	$0_{(0.0)}$	0
$D_2C{=}CD{-}CD_3$	$0_{(0.1)}$	$0_{(0.0)}$	0	$1_{(1.2)}$	$5_{(4.8)}$	6
$H_2C{=}CH{-}CD_3$	$1_{(0.8)}$	$2_{(2.2)}$	3	$0_{(0.2)}$	$3_{(2.8)}$	3
$H_2C{=}CH{-}CH_2{-}CH_3$	$2_{(2.1)}$	$6_{(5.9)}$	8	$0_{(0.0)}$	$0_{(0.0)}$	0
$D_2C{=}CH{-}CH_2{-}CH_3$	$2_{(2.2)}$	$4_{(3.8)}$	6	$0_{(0.1)}$	$2_{(1.9)}$	2

[a] The numbers shown are rounded from those in the parentheses.

The product distributions for $H_2C{=}CH{-}CH_3$ and $H_2C{=}CH{-}CH_2{-}CH_3$ were calculated from the H_2O TPR spectra in Figures 8 and 9, respectively. The distribution remains approximately constant as the coverage varies. As Table 3 shows, of six H atoms in $H_2C{=}CH{-}CH_3$ one H goes to low-temperature H_2O, suggesting cleavage of one C−H bond, while the remaining five appear in the high-temperature H_2O. This ratio also holds for the corresponding routes of $D_2C{=}CD{-}CD_3$. For $H_2C{=}CH{-}CD_3$ one C−H bond reacts at low-temperature, while the two C−H bonds and three C−D bonds react at high-temperature. For $H_2C{=}CH{-}CH_2{-}CH_3$ and $D_2C{=}CH{-}CH_2{-}CH_3$ low-temperature reaction occurs with two C−H bonds. The two C−D bonds in $D_2C{=}CH{-}CH_2{-}CH_3$ all react at high-temperature. Taking these together, it is clear that the vinylic C−H bond in propylene is predominantly cleaved at low-temperature while the allylic or methylenic C−H bonds react at high-temperature. The exact origin of the two hydrogens in 1-butene cannot be specified, however.

For butadiene (Figure 10), the low-temperature H_2O peak is much smaller and shifts up to 320 K at saturation coverage, indicating that O(a) also has some inhibiting effect for butadiene dehydrogenation compared to the clean surface. The high-temperature H_2O evolution occurs at 370 K, similar to that for butene. At high butene and butadiene coverages, H_2 evolution occurs as soon as H_2O evolution terminates when O(a) becomes depleted. The H_2 evolution is similar to that from dehydrogenation on clean Pd(100).

Formation of CO and CO_2 from propene, butene, and butadiene on Pd(100)-p(2 × 2)-O represents a minor reaction channel compared to H_2O formation (Table 2). Consequently, a large amount of C(a) is left on the surface. The TPR spectra

---

(9) (a) Roberts, J. T.; Madix, R. J.; Crew, W. W. *J. Catal.* **1993**, *141*, 300. (b) Redhead, P. A. *Vacuum*, **1962**, *12*, 203.

Table 4. Activation Energies (kcal/mol) for the Evolution of Reaction Products at *Saturation* Alkene Coverages Estimated from the Evolution Peak Temperatures with the Assumption of a Constant Preexponential Factor of 10^{13} s^{-1} and a Constant Order of 1

	E_a (kcal/mol) (T_p (K))								
	Pd(100)		Pd(100)-p(2 × 2)-O						
	H_2		H_2O		CO_2			CO	
ethylene	25.4 (415)			20.7 (340)		18.5 (305)	33.3 (540)		
propene	27.0 (440)		16.3 (270)	19.4 (320)	15.7 (260)	19.4 (320)	23.2 (380)	27.0 (440)	35.6 (575)
butene	26.0 (425)	37.2 (600)	16.3 (270)	19.4 (320)	15.7 (260)	20.1 (330)		27.0 (440)	37.2 (600)
butadiene	24.8 (405)	38.5 (620)		20.7 (340)		21.0 (345)		27.0 (440)	36.9 (595)

for CO and CO_2 are shown in Figures 8−10 at various alkene coverages. The bottom spectrum in each case was a blank experiment without alkene exposure. It shows small CO_2 peaks from reactions of O(a) with coadsorbed CO from the background (335 K) and with surface C(a) impurities (520 K) (cf. Figure 2, d and f). As alkene coverage increases, the 335 K CO_2 peak due to reaction of CO(a) with O(a) shifts downward. Its intensity remains the same since exposing alkene does not introduce more CO onto the surface. With increasing alkene coverage the 520 K CO_2 peak increases initially, then decreases, and finally diminishes. This is caused by the changing ratio of C(a) to O(a). In between these two CO_2 peaks two other CO_2 peaks emerge as coverage increases, which appear to coincide with the high-temperature H_2O peaks. They develop more distinctly for butadiene than for propene and butene. As proven by isotope coadsorption experiments, these CO_2 evolution peaks are from neither CO(a) + O(a) reaction nor C(a) + O(a) reaction. They must be due to direct O(a) reactions with alkene intermediates following C−H bond scission, forming C−O bonds with an activation energy lower than that of C(a) + O(a) reaction but higher than that of CO(a) + O(a) reaction. This suggestion is further supported by the appearance of desorption-limited CO at 450 K. Although it occurs at 500 K on clean Pd(100) (Figure 2c), desorption-limited CO evolution is shifted down by 50 K with coadsorbed alkenes as shown by CO^{18} coadsorption experiments. The desorption-limited CO evolution at 450 K also indicates that the C−O bond forms below 400 K. The high-temperature CO peak around 600 K is from O(a) reaction with C(a) on the surface (cf. Figure 2e).

Apparent activation energies for the surface reaction rate-limited processes can be approximated from the peak temperatures by the Redhead method,[9b] assuming a value for the preexponential factor. The activation energies are summarized in Table 4 for the evolution of all products. These values were estimated for a heating rate of 4 K/s, a constant preexponential factor ($\nu = 10^{13}$ s^{-1}) and a constant order ($n = 1$). Peak temperatures are given in Table 4 for identification of the reactions involved (see above).

Discussion

A. Alkene Dehydrogenation. Ethylene adsorption and dehydrogenation on Pd(100) have been studied previously with high-resolution electron energy loss spectroscopy (HREELS).[10] It has been shown that at saturation coverage $H_2C{=}CH_2$ adsorbs on Pd(100) in both di-σ and π-bonded forms. Upon heating, the π-bonded form desorbs molecularly, while the di-σ bonded form undergoes progressive dehydrogenation. Initial dehydrogenation occurs at 250−300 K, yielding a surface vinyl species ($HC{=}CH_2$) which decomposes into CH_2(a) and CH(a). CH_2(a) further dehydrogenates to CH(a) around 300 K and CH(a) finally dehydrogenates at 360−525 K. These observations are consistent with the coverage-dependent TPRS results obtained in the present work.

Little work has been done previously for higher alkenes on the Pd(100) surface. Many studies have been concentrated on the Pt(111) surface.[11] Both propene and butene are found to bond to Pt(111) in a di-σ form for the vinyl group, with the alkyl group pointing away from the surface.[12] Dehydrogenation commences from the di-σ-bonded vinyl group at 250−300 K, forming alkylidyne species. Similar di-σ bonding is expected for propene and butene on Pd(100). However, alkylidyne formation is not likely to occur on Pd(100) since no ethylidyne species was observed for ethylene on Pd(100).[10a] Ethylidyne was found to form for ethylene on Pd(111),[10b] indicating the importance of surface crystallography.

Butadiene was studied also on Pt(111) with TPRS and HREELS for saturation coverage at 170 K.[13] From 170 to 300 K HREELS spectra showed di-σ adsorption across both C=C bonds without any loss of hydrogen as shown by TPRS. It was concluded that butadiene dehydrogenation occurs above 300 K. However, the behavior at saturation coverage can be misleading as shown by our variable coverage experiments on Pd(100) (Figure 6). At low coverages butadiene dehydrogenates in a manner similar to butene; dehydrogenation begins below 300 K. At high coverages self-poisoning suppresses the low-temperature dehydrogenation and self-hydrogenation consumes surface hydrogen. These two effects produce an illusive TPR spectrum at saturation which falsely suggests that butadiene dehydrogenates only above 300 K. *The results at low coverages reflect more closely the behavior of individual molecules on the surface.*

B. Alkene Combustion. Combustion mechanisms on Pd(100)-p(2 × 2)-O. The previous HREELS study of ethylene on O(a) covered Pd(100) surface has shown that ethylene dehydrogenation is inhibited by limiting the formation of di-σ-bonds.[10] On Pd(100)-p(2 × 2)-O only the π-bonded form of ethylene was observed, which desorbed molecularly upon heating. Presumably, only the π-bonded form exists also for propene, 1-butene, and 1,3-butadiene on Pd(100)-p(2 × 2)-O. Why then does so little reaction occur for ethylene, while the higher alkenes react facilely with O(a)? The difference is not entirely because ethylene desorbs before it reacts. Molecular ethylene desorption from Pd(100)-p(2 × 2)-O is similar to other alkenes and covers a wide temperature range extending to 370 K (Figure 7), which is above that of the low-temperature H_2O evolution from propene and butene. The reason may lie in the structural differences between ethylene and the higher alkene molecules. As we have demonstrated with isotopic butene (Figure 11b and Table 3), the methylenic C−H bonds do not react during low-temperature H_2O evolution. All four C−H bonds in ethylene are of this type and do not react below 370

---

(10) (a) Stuve, E. M.; Madix, R. J. *J. Phys. Chem.* **1985**, *89*, 105; *Surf. Sci.* **1985**, *152/153*, 532; **1985**, *160*, 293. (b) Gates, J. A; Kesmodel, L. L. *Surf. Sci.* **1982**, *120*, L461; *124*, 68.

(11) See review e.g.: Sheppard, N. *Annu. Rev. Phys. Chem.* **1988**, *39*, 589.

(12) Avery, N. R.; Sheppard, N. *Proc. R. Soc. London.* **1986**, *A405*, 1.

(13) Avery, N. R.; Sheppard, N. *Proc. R. Soc. London.* **1986**, *A405*, 26.

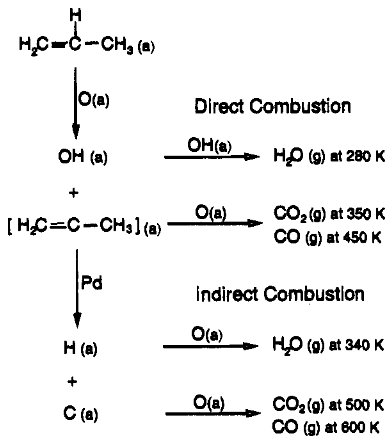

Figure 12. Schematic summary of the proposed combustion mechanisms of propene on Pd(100)-p(2 × 2)-O.

K. Above 370 K all adsorbed ethylene molecules have already desorbed.

We have also shown that the vinylic C−H bond of propene and (by analogy) butene reacts readily with O(a) on Pd(100)-p(2 × 2)-O, leading to low-temperature H_2O production. We suggest that these reactions are due to direct O(a) reactions with H atom of the C−H bond, instead of the C−H bond breaking first, followed by O(a) + H(a) reaction, although H_2O evolution is similar to that from O(a) + H(a) reaction on Pd(100). First, π-bonded alkene molecules do not dehydrogenate on clean Pd(100).[10] It is unlikely that the π-bonded form would dehydrogenate on Pd(100)-p(2 × 2)-O, since O(a) inhibits the dehydrogenation of ethylene and butadiene compared to that on the clean surface. Second, the low-temperature H_2O cannot be solely due to dehydrogenation on the clean sites present as defects or boundaries of the p(2 × 2)-O structure. If it were the case, the low-temperature H_2O peak would not increase simultaneously as the high-temperature H_2O peak (Figures 8 and 9), and hydrogen distributions between the two H_2O peaks would not remain constant as the coverage increases (Table 3). It should be noted that the reaction between O(a) and the C−H bond may occur at even lower temperature, forming OH(a) on the surface, since H_2O evolution is rate-limited by OH(a) disproportionation.[7]

Dehydrogenation on this surface appears to be inhibited by the presence of adsorbed oxygen. The release of low-temperature H_2O opens up sites for adsorbed alkene molecules to migrate to and dehydrogenate on, yielding the high-temperature H_2O which is limited by C−H bond scission. Evidence for this conclusion comes from the observations that H_2 evolves as soon as H_2O evolution is terminated due to depletion of reactive O(a). Accompanying the high-temperature H_2O evolution is the reaction of O(a) with intermediates to form a C−O bond, which leads to low-temperature CO_2 evolution and desorption-limited CO evolution. However, the high-temperature H_2O evolution cannot be the result of O(a) attack on C atoms of an alkene intermediate in any stage of dehydrogenation, because the CO_2 yield is too low to fully account for the H_2O yield (cf. Table 2). Actually, the C−O bond formation may be initiated by the breaking of C−H bonds, since at low alkene coverages the CO_2 evolution evolves at a higher temperature than H_2O. It is interesting to note that at high alkene coverages the O(a) which forms CO is not reactive with H(a) to form H_2O; instead H_2 evolution occurs while CO forms and evolves. This may be because either O(a) is trapped by C(a) adatoms making it unavailable to H(a) or O(a) is actually bound to C(a). The combustion mechanisms are summarized schematically in Figure 12 for propene.

For butadiene, the low-temperature H_2O peak is smaller than that of propene and butene and shifted upward to 320 K. The difference of butadiene from butene is conjugation of C═C double bonds and absence of allylic C−H bonds. Conjugation stabilizes the vinylic C−H bond making it less reactive toward O(a). In support of this argument, styrene (also conjugated) exhibits the same behavior as butadiene in reacting with O(a) on Pd(100)-p(2 × 2)-O.[8]

C. Comparison to Ag(110) and Rh(111). Combustion of alkenes is always involved (though purposely avoided) in the selective oxidation of alkenes. Selective alkene oxidation has been investigated extensively on Ag(110)[14] and Rh(111),[15] respectively to the right and the left of Pd in the periodic table. Atomic oxygen on Ag(110) reacts facilely with alkenes through an acid−base reaction (proton abstraction from the acidic C−H bonds) or epoxidation (oxygen cyclic addition to the C═C double bonds).[14] Ethylene does not react with O(a) under UHV because it desorbs before it can react,[17] although ethylene epoxidation occurs at high pressures. Propene combusts only, which is initiated by acid−base reaction of the acidic allylic H.[9,17] Partial oxidation occurs for 1-butene forming 1,3-butadiene via acid−base reaction; oxygen addition to butadiene yields 2,5-dihydrofuran which can be further converted to furan and maleic anhydride.[18]

On Rh(111)-p(2 × 1)-O (0.50 O/Rh) alkenes with a vinylic C−H bond can be oxidized to ketone, e.g. propene to acetone, butene, and butadiene to the corresponding methyl ketones.[15] Although no surface intermediates have been spectroscopically identified, it has been proposed that direct oxygen addition to C_2 occurs forming an oxametallacycle, and subsequent β-H elimination and 1-C hydrogenation form ketone. During these reactions allylic C−H bonds are not broken and no acid−base reaction occurs. Inhibition of dehydrogenation by O(a) is thought to be the key for partial oxidation, because at lower O(a) coverages only combustion takes place.

In our experiments on Pd(100), no partial oxidation products were detected for O(a) coverages up to 1 O/Pd for any of the alkenes studied. The high atomic oxygen coverage has been achieved in this experiment using NO_2 on Pd(100) following the prescription of Banse and Koel on Pd(111);[19] NO_2 works on Pd(100) (this work) as on Pd(111). Inhibition of dehydrogenation by O(a) occurs for ethylene and, to certain extent, for butadiene. For propene and 1-butene the vinylic C−H bonds react preferentially with O(a). O(a) reacts with alkene intermediates, forming C−O bonds facilely.

Reactivity of the vinylic C−H bond on Pd(100)-p(2 × 2)-O seems not to be governed by the gas-phase acidity, which applies well on Ag(110). The allylic C−H bond of propene is the most acidic (ΔH_{acid} = 391 kcal/mol), but it is less reactive than the vinylic C−H bond. We also found that norbornene (bicyclo-[2.2.1]-2-heptene) combusts easily, despite the fact that its gas-phase acidity (ΔH_{acid} = 402 kcal/mol) is similar to that of ethylene (ΔH_{acid} = 406 kcal/mol).[8] On the other hand, initial C−H bond scission is not induced by O addition to the C atom of alkene as it is proposed to occur on Rh(100)-p(2 × 1)-O.

Oxygen addition to C atoms does occur on Pd(100)-p(2 × 2)-O, but apparently only to the C atoms of alkene intermediates after the C−H bond reaction with O(a). In addition, efficient H_2O formation and evolution on Pd(100)

---

(14) Madix, R. J.; Roberts, J. T. In *Surface Reactions*, Madix, R. J., Ed.; Springer: Berlin, 1994, Chapter 1.

(15) Xu, X.; Friend, C. M. *J. Am. Chem. Soc.* **1991**, *113*, 6779.

(16) Barteau, M. A.; Madix, R. J. *Surf. Sci.* **1981**, *103*, L171.

(17) Barteau, M. A.; Madix, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 344.

(18) Roberts, J. T.; Capote, A. J.; Madix, R. J. *Surf. Sci.* **1991**, *253*, 13.

(19) Banse, B. A.; Koel, B. E. *Surf. Sci.* **1990**, *232*, 275.

make hydrogenation impossible, as no self-hydrogenation of butadiene occurs on Pd(100)-p(2 × 2)-O, although it occurs on clean Pd(100) (cf. Figure 10). Hydrogenation is an essential step in the proposed mechanism of ketone formation from alkene on Rh(100)-p(2 × 1)-O,[15] where H_2O evolves at a higher temperature than ketone evolution. In conclusion, efficient reactions between O(a) and the C−H bonds may prevent ketone formation on Pd, while strong bonding of alkene to the surface prevents the application of gas-phase acidity concepts to alkene oxidation on Pd. This makes Pd a good catalyst for alkene combustion rather than selective oxidation.

Summary

The adsorption and reaction of ethylene, propene, 1-butene, and 1,3-butadiene have been studied on the clean Pd(100) and atomic oxygen-covered Pd(100)-p(2 × 2)-O surfaces. The following conclusions can be drawn from the results.

On Clean Pd(100). (1) All four alkenes dehydrogenate progressively in the temperature range from 200 to 900 K. Saturation adsorption coverage at 120 K is in the range from 0.21 to 0.27 alkene/Pd. About 0.10 alkene/Pd dehydrogenates, and the rest desorbs molecularly below 400 K.

(2) Self-hydrogenation occurs for butadiene at high coverages, whereas, at low coverages, butadiene dehydrogenates in a similar manner as butene. No self-hydrogenation was observed for 1-alkenes.

On Pd(100)-p(2 × 2)-O. (3) All four alkenes undergo combustion yielding H_2O, CO, and CO_2. No partial oxidation products were detected even for O(a) coverage up to 1 O/Pd. The saturation alkene coverage is similar to that on the clean surface except for ethylene. O(a) inhibits adsorption and reaction of ethylene.

(4) At low alkene coverages, *all* C−H bonds react facilely with O(a), forming H_2O below 450 K, well below the temperature of complete dehydrogenation on the clean surface. Thus, O(a) activates the reactions of propene, butene, and butadiene.

(5) Isotope experiments show that the low-temperature H_2O evolution at 280 K results predominantly from O(a) reactions with the vinylic C−H bonds of 1-alkenes.

(6) Low-temperature CO_2 evolution and desorption-limited CO evolution give evidence for O(a) addition to the C atoms of dehydrogenated alkene intermediates. However, efficient H_2O formation prevents O-containing intermediates from hydrogenating and producing partial oxidation products such as ketones.

(7) Indirect reactions resulting from dehydrogenation at clean sites and oxidation of H(a) and C(a) lead to high-temperature H_2O evolution above 300 K and CO and CO_2 evolution above 400 K.

Acknowledgment. The authors gratefully acknowledge the support of the National Science Foundation (NSF CTS-9300188-001) without which this work would not have been completed.

JA942814J