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Characterization of Palladium Surfaces with (+)-Apopinene: Correlation of Reaction Paths with Surface Features

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The molecular probe (+)-apopinene is chosen for the characterization of metal surface sites because of its unique structural features. These features allow clear distinctions of adsorption side and double bond position. By measuring the relative rates of double bond migration and addition, k_i/k_a, it is shown that (+)-apopinene is sensitive to 17 different Pd catalyst preparations. Among these, a set of alumina-supported Pd catalysts ranging in dispersions from 0.055 to 1.00 (131 to 8.4 Å by EM) yielded results consistent with the notions that ^{3}M-type sites (highly coordinatively unsaturated) catalyze principally addition and ^{2}M-type sites catalyze principally isomerization. (+)-Apopinene distinguishes between reduced PdO_2 samples which have undergone different extents of surface reconstruction.

INTRODUCTION

Correlations of metal surface structure with catalytic reactivity have made great progress in recent years. This progress has occurred for two principal reasons. First, the development of sophisticated instrumentation has made possible the examination of crystalline surfaces in unprecedented detail (*1*), and second, the development of an understanding of organometallic complexes has furnished specific systems after which surface complexes can be modeled (*2*).

Growing out of this understanding is a picture of metal surfaces which includes a variety of sites on which specific chemical reactions are thought to occur. It is the possibility of correlating these well-known surface sites with a well-understood family of interrelated reactions that has stimulated this study.

Critical to such a study is the development of a variety of sophisticated molecular probes which will undergo unambiguous transformations on specific surface sites. To start with we have chosen the transformations associated with the hydrogenation and exchange of alkenes because of our experience in that field and because of the relatively high level of mechanistic understanding which now exists in it. These transformations are addition, exchange, *cis–trans* isomerization, double bond migration, and hydrogen shifts. These and other reactions have been identified and correlated with possible surface sites by Ledoux (*3*). Similarly, but approaching from the organometallic model side, some of these reactions have been correlated with possible surface sites by Siegel *et al.* (*2*) and elaborated on by Augustine (*4*).

Together they present the following picture. Metal surfaces contain three principal kinds of sites, planes (faces or terraces), edges (or steps), and corners (vertices or kinks or isolated atoms) (*3*). These sites appear to be related to three kinds of organometallic coordination sites (^{1}M, ^{2}M, and ^{3}M, respectively) (*2, 4*). Coordination sites similar to those on faces possess one coordinative unsaturation (one empty site), those

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similar to edges, two, and corners, three. So a surface possessing many highly coordinatively unsaturated sites will have many sites similar to corners, and the two terminologies are almost interchangeable for crystalline surfaces. However, for glassy surfaces the terminology using the degree of coordinative unsaturation is more convenient.

Each type of site is believed to catalyze certain reactions. For example, addition is thought to occur on ^{3}M sites (*2, 3*) but ^{2}M sites have also been suggested (*4*). ^{1}M sites are thought to catalyze only 1,3-intramolecular hydrogen shifts (*3*) and ^{2}M sites are proposed to catalyze isomerizations and exchange (*2–4*). In principle, each of the more highly coordinatively unsaturated sites can also catalyze the reactions of the less unsaturated sites. For example, ^{3}M can also catalyze isomerizations, exchange, and 1,3-intramolecular hydrogen shifts, and ^{2}M can also catalyze 1,3-intramolecular hydrogen shifts.

In fact, this picture is probably too simple for an actual working catalyst because an array of nine surface sites ranging from atoms with coordination numbers of 4, C_4 (vertex of an octahedron), to 11, C_{11} [(110) plane], can be easily identified on fcc crystals (*5*). There are nine instead of eight because there are two different types of C_7 (steps at (111) plane). In addition, if an adatom on a (111) plane is considered (coordination number 3) then a total of ten different kinds of sites are identifiable. And, finally, if multiple atom sites (e.g., three atoms) of various possible arrangements are considered, more possibilities exist. Some of these other possibilities have already been recognized and discussed, for example, C_{10} and C_{11} (*6*), and subdivisions of the ^{3}M, ^{2}M, and ^{1}M sites (*4*). Of course, several of these sites may catalyze the same reaction step with different activation energies so caution must be exercised in the interpretation of data.

Because of difficulties in reproducing absolute rates, especially in liquid-phase hydrogenations (*7*), it is important to use a molecular probe which will undergo as many as possible of the above reactions at the same time on the same surface. In that way the relative rates of each reaction can be compared one to the other.

Particularly difficult reactions to study are the two kinds of isomerizations of the C–C double bond, *cis–trans* isomerization, and migration (positional) isomerization. Difficulties occur because each isomer usually interacts differently with the surface sites and therefore exhibits different strengths of adsorption, different rates of exchange, and different rates of addition. Moreover, if many exchangeable hydrogens are available, the resulting extensive exchange reaction is likely to dilute the surface deuterium and obscure pristine exchange information (*8*). Finally, the possibility of a molecule flipping from one of its sides to another (in the case of rings) (*9*) can limit its usefulness by obscuring 1,3-intramolecular hydrogen shifts as well as exchange processes.

We have eliminated the above problems by constructing the molecular probe (+)-apopinene. Because of its peculiar geometry, it can present only one side of its double bond to the surface. Therefore, double bond migration leads to its enantiomer which has reactivities identical to the starting enantiomer for a symmetrical surface. Only four positions in the molecules are potentially available for exchange.

The molecule undergoes an extremely rapid double bond migration which is approximately ten times as fast as that in cy-

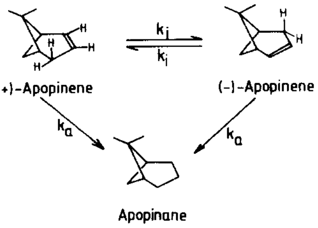

FIG. 1. Reaction scheme for apopinene hydrogenation and isomerization.

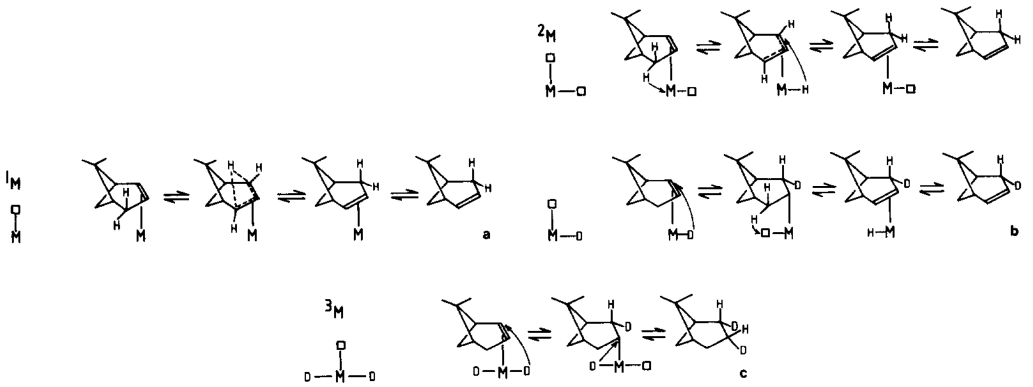

FIG. 2. Proposed mechanism of hydrogenation and isomerization of (+)-apopinene on: (a) ¹M (plane) sites, (b) ²M (ledge) sites, and (c) ³M (vertex and kink) sites.

clohexene (*10*). This facile double bond migration, we have suggested, may be due to the peculiar geometry which stereodirects a 1,3-intramolecular hydrogen shift (*3, 10–14*). [However, others have not found this shift (*13b, 14*).] Therefore, (+)-apopinene undergoes virtually all of the reactions thought to be catalyzed by each type of surface site (Fig. 2) and avoids many of the problems inherent in other molecules. Our choice of palladium as a catalyst for the initial study was made because of the availability of rapidly cooled (splat cooled) palladium alloys of silicon and germanium, some of which were glassy. These alloys exhibit abilities different from those of supported palladium when catalyzing the various hydrogenation reactions of *cis*-cyclododecene (*15*) and (+)-apopinene (*16*). Therefore, we decided to prepare a group of standard palladium catalysts to which we could compare the rapidly cooled alloys. Our reasoning was to prepare a range of crystallite sizes on alumina (*17–19*), some with very tiny crystallites of palladium, which should have few ¹M sites and many ³M sites, and others with larger and larger crystallites which should have more and more ¹M sites and fewer and fewer ³M sites.

Initially, we prepared a series of Pd/Al_2O_3 catalysts by the incipient wetness technique (*16*). These catalysts, indeed, catalyzed a range of relative rates, but we strove for a larger range (smaller crystallites) and have now prepared a series of Pd/Al_2O_3 catalysts by the ion exchange technique. These we have characterized by electron microscopy and by hydrogen and carbon monoxide chemisorptions. We assumed that the smallest crystallites would catalyze more addition relative to isomerization in comparison to larger crystallites because the smallest crystallites should have more ³M sites relative to either ²M or ¹M sites than the large crystallites.

METHODS

Materials

(+)-Apopinene was prepared as previously described (*8, 10*) with the following modifications. After preparation of myrtenal from α-pinene a fast steam distillation was used to separate myrtenal from the reaction mixture. Then, instead of 10 g myrtenal and 1 g 5% Pd/$BaSO_4$ (*16*), the yield from the decarbonylation was improved by using 40 g myrtenal and 2 g 5% Pd/$BaSO_4$. The yield was further improved by running the decarbonylation and the distillation of the (+)-apopinene rapidly (20–25 min). Yields from this last reaction were 75–80% and the highest optical rotation obtained for (+)-apopinene was $[\alpha]_D^{25} = +54.2°$.

The gases were all high purity. For hydrogenation and deuteriumation experi-

TABLE 1

Pretreatment for the Pd/Al_2O_3 Catalyst

% Pd/Al_2O_3[a]	Reduction[b]		Purging time[c] (min)
	Temp (K)	Time (min)	
0.01	473	20	60
0.05	473	90	50
0.18	473	120	60
0.40	573	120	100
1.0	623	240	60

[a] All Pd/Al_2O_3 catalysts were made by the ion exchange technique.

[b] Flowing hydrogen, 20 ml/min.

[c] After reduction the catalyst was purged with flowing argon, 20 ml/min, at the reduction temperature prior to cooling.

ments the hydrogen was Air Products ultrahigh purity grade and the deuterium was Linde CP grade (99.5%). It was further purified before entering the reaction system by passing first through a 12-cm column of 0.5% Pd on Linde SK 300 zeolite (65 g) and then through a 23-cm column of Linde 3A molecular seive (150 g). Gases used for the chemisorption measurements were argon (Linde, <0.5 ppm oxygen), helium (Linde, <0.5 ppm oxygen), hydrogen (Linde, ultrahigh purity), and carbon monoxide (Linde, research grade). The carrier gases, Ar and He, were further purified by flowing through a deoxygenating column (BTS) regenerated before every experiment.

The catalysts were a mixture of commercial preparations and our special preparations. The commercial catalysts were a Pd powder purchased from Ventron (60 mesh, 99.9%) (*15*), Pd black donated by Engelhard Industries, 5% $Pd/BaSO_4$ purchased from Aldrich, three 1% Pd/Al_2O_3 catalysts (49, 22, and 5.5% dispersion) donated by Engelhard Industries, PdO_2 donated by Engelhard (reduced at 400°C for 5 h before use), 5% Pd/C purchased from Matheson, Coleman and Bell, and a Pd foil purchased from Ventron (0.05 mm thick, 99.9%). The special preparations included three splat cooled samples: a $Pd_{80}Si_{20}$ splat, a $Pd_{77}Ge_{23}$ splat, and a pure Pd splat which were prepared by the shock tube technique previously described (*15*).

Finally, a series of Pd/Al_2O_3 catalysts were specially prepared as standards. These catalysts were prepared by incorporating Pd^{2+} ions into neutral γ-Al_2O_3 (Katalco, 378 m^2/g) using the following ion exchange technique.

A quantity (12–14 g) of dry, wet-sieved alumina was stirred very gently in 200 ml of 1.0 *F* NH_4^+ ions. Excess ammonia was removed by washing until a pH of 7.0 was reached in the wash. The slurry was then treated with a requisite amount of $PdCl_2$ dissolved in 0.01 *F* HCl. The mixture was then gently stirred for 14–18 h to obtain a maximum of NH_4^+ ion substitution by the dissolved Pd^{2+} ions. The slurry was washed again with water and then with ACS reagent grade methanol (Fisher).

The Pd^{2+}–Al_2O_3 catalyst precursors were dried under flowing argon at 393 to 403 K for 2 h, heated in argon to the reduction temperature, and then reduced under flowing hydrogen. The reduction times and temperatures for each catalyst are shown in Table 1. Following the reduction, the catalyst was kept under flowing argon at the same temperature for 1 to 2 h before it was finally cooled to room temperature at a rate no greater than 8 K/min. The final weight of catalyst was measured as quickly as possible. The catalyst was stored under vacuum for at least 72 h and then kept in a desiccator under an argon atmosphere.

Apparatus and Procedures

Catalyst characterization by chemisorption and electron microscopy. A dynamic chemisorption method, originally developed by Gruber (*20*), was adapted to a pulse chromatographic technique for the chemisorption measurements of the 5% Pd/C, 0.01% Pd/Al_2O_3, 0.05% Pd/Al_2O_3, and 0.18% Pd/Al_2O_3 catalysts. Small pulses (usually 25 μl) of the adsorbate, H_2 or CO, were introduced into the carrier gas through an eight-port sampling valve. For maximum detector sensitivity argon was used as the carrier gas for H_2 chemisorption, while helium was used as the carrier

TABLE 2

Chemisorption Data for the Supported Pd Catalysts

Catalyst	$\%D_H$[a]			$\%D_{CO}$[b]	Average $\%D$	Method[c]
	Trial 1	Trial 2	Trial 3			
0.01% Pd/Al_2O_3[d]	105	101	104	—	103 ± 1.7	Impulse
0.05% Pd/Al_2O_3	87.0	84.3	87.7	87.5	86.6 ± 1.2	Impulse
0.18% Pd/Al_2O_3	78.8	84.9	85.6	80.8	82.5 ± 3.1	Impulse
0.40% Pd/Al_2O_3	78.2	74.4	79.9	—	77.5 ± 2.1	Static
1.0% Pd/Al_2O_3	40.2	39.6	43.1	—	41.0 ± 1.4	Static
5% Pd/C[e]	14.5	13.3	—	9.7	12.5 ± 1.9	Impulse
5% Pd/$BaSO_4$[f]	73.1	73.2	73.0	—	73.1 ± 0.1 ±0.1	Static

[a] Dispersion as calculated from hydrogen chemisorption data.

[b] Dispersion as calculated from carbon monoxide chemisorption data.

[c] The chemisorptions were done by either a dynamic impulse technique or a static technique (see Methods for details).

[d] All Pd/Al_2O_3 catalysts were made by the ion exchange technique.

[e] The 5% Pd/C catalyst was purchased from Matheson, Coleman, and Bell.

[f] The 5% Pd/$BaSO_4$ catalyst was purchased from Aldrich.

for CO chemisorptions. Adsorbate pulses at 3- to 5-min intervals were continued until successive peak sizes increased and converged to a steady value. The reference peak area, totally eluted areas, was verified by sending adsorbate pulses through a blank cell containing an equivalent amount of the catalyst support (Al_2O_3).

Catalyst samples of 0.5 to 2.0 g were used for chemisorption measurements. The chemisorption pretreatment consisted of heating in argon to 300°C, reducing in hydrogen for 2 h at 300°C, purging in argon for 1 h at 300°C, and cooling in argon to room temperature. The chemisorption was then done in the previously stated manner, after which the sample was heated to 300°C in argon for 1 h and cooled to room temperature. This was done to sweep off the chemisorbed hydrogen for another measurement. This adsorption–desorption cycle was repeated for three to four trials, and for the 0.18% Pd/Al_2O_3, 0.05% Pd/Al_2O_3, the 5% Pd/C the last trial was a carbon monoxide chemisorption.

The chemisorptions for the 1.0% Pd/Al_2O_3, 0.4% Pd/Al_2O_3, and 5% Pd/$BaSO_4$ were done on a static chemisorption instrument. Prior to the measurement, these catalysts were put under a vacuum (1×10^{-5} Torr) for $\frac{1}{2}$ h at room temperature, heated to 300°C in flowing hydrogen, reduced in hydrogen for 2 h at 300°C, put under vacuum for $\frac{1}{2}$ h at 300°C, and cooled to room temperature while under the vacuum. At this point, a known volume of hydrogen was introduced into the sample chamber and its pressure was monitored by a Setra digital pressure gauge. Because the volume of the sample chamber had been calibrated with known volumes of helium, it was possible to calculate the amount of hydrogen absorbed on the catalyst. The pretreatment was repeated before each trial. Chemisorption data for these catalysts are shown in Table 2. The stoichiometries used for these processes were the same as those used by Benson *et al.* (*21*) for the estimation of the fraction of exposed palladium atoms (dispersion).

The link between the dispersion as measured by the above procedure and the average metal crystallite size on the support was established by assuming model geometries such as fcc cubic, octahedral, and fcc cubooctahedral shapes for the crystallites. Based on a statistical treatment (*5, 22, 23*) of geometries the number of the various kinds of atoms, such as vertices, planes, edges, and bulk, can be expressed in polynomial form with the number of metal atoms along an edge as the variable. By modifying the calculations to take into account the unexposed crystallite face in contact with the support, the following equations are derived, in which D represents the fraction of metal atoms exposed; n, the number of unit cells along the length across the crystallites; a, the lattice parameter; and d, the crystallite size:

for an fcc cubooctahedral crystallite,

$$D = \frac{27n^2 + 6n + 4}{8n^3 + 15n^2 + 12n + 4}$$

for an fcc octahedral crystallite,

$$D = \frac{(3)(7n^2 + 3n + 2)}{(2)(2n^3 + 6n^2 + 7n + 3)}$$

For both fcc octahedral and fcc cubooctahedral models,

$$d = n \times a/2.$$

All of the supported catalysts were examined in a Hitachi H500H electron microscope (EM). These data are summarized in Table 3.

The hydrogenation/deuteriumation apparatus. The same design previously reported (*16*) was used with *improvements* in the shaking mechanism. Shaking was done by an adjustable speed drive system with a matched SCR control. Very effective gas–liquid mixing could be achieved at a shaking speed of 1800—2000 rpm, as monitored by a digital stroboscope. The Pyrex reactor has a 15 × 100-mm cylindrical reaction chamber with double helical Vigreux indentations. It was jacketed for temperature control by water circulation. Liquid samples could be introduced through a septum injection port.

The amount of catalyst used varied from 5 to 80 mg. The Pd/Al_2O_3 catalysts were stored under argon in a vacuum desiccator connected to a vacuum manifold. Weighing of the catalyst was done in air. Pretreatment of the catalyst in the reactor turned out to be important for certain catalysts. For the Pd/Al_2O_3, Pd powder, reduced PdO_2, Pd black, and 5% $Pd/BaSO_4$ catalysts the procedure of purging air from the reactor with D_2 was sufficient to obtain highly reproducible activity. However, the Pd foil and splat cooled materials required special pretreatment. This special pretreatment was developed so that the splat cooled materials could be reused because only very small quantities were available to us. The procedure consisted of a cycle of deuterium treatment at 423 K, outgassing under vacuum at 373 K, and deuterium treatment at room temperature. The shaking speed of 1850 rpm for apopinene was found to eliminate gas–liquid boundary diffusion by a series of experiments in which shaking rate was systematically increased until the hydrogenation rate reached a constant value. The (+)-apopinene reactions were stopped at various extents of saturation, as determined by the amount of gas uptake. The amount of saturation, determined by GC, was in close agreement with the gas uptake. The unreacted apopinene was separated from the reaction mixture, its optical rotation was measured, and the extent of its isomerization (racemization) was calculated.

Analytical

Gas chromatography. GC separations of (+)-apopinene reaction mixtures were accomplished with a Varian Aerograph Model 1864-4 gas chromatograph with a thermal conductivity detector and 25 ft × $\frac{3}{8}$ in. column of 35% Apiezon-L on 60–80 mesh Chromosorb-W at 453 K and 90 ml/min helium flow.

Optical rotations. Optical rotations of neat apopinene (70 to 100 μl) were mea-

TABLE 3

The Comparison of Electron Microscopy Data and Chemisorption Data

Catalyst	Chemisorption data			Electron microscopy data			$\%D_{\text{em-oct}}$[d]
	$\%D_{\text{avg}}$	Particle size (Å)		Avg particle size (Å)	Range (Å)	$\%D_{\text{em-Cu-oct}}$[c]	
		Cu-oct[a]	Oct[b]				
0.01% Pd/Al_2O_3	103 ± 1.7	2	3	8.4	4.0– 15.0	68	83
0.05% Pd/Al_2O_3	86.6 ± 1.2	4	8	9.7	6.0– 18.0	62	78
0.18% Pd/Al_2O_3	82.5 ± 3.1	5	9	18.7	9.0– 47.0	39	54
0.40% Pd/Al_2O_3	77.5 ± 2.1	6	10	23.0	8.0– 68.0	33	55
1.0% Pd/Al_2O_3	41.0 ± 1.4	18	27	46.1	10.0–140.0	18	27
5% Pd/C	12.5 ± 1.9	75	167	86.7	15.0–265.0	11	20
5% Pd/$BaSO_4$	73.1 ± 0.1	7	12	118.2	22.0–206.0	7	17
1.0% Pd/Al_2O_3 Engelhard	49.0[e]	14	22	25.8	6.0– 71.0	30	43
1.04% Pd/Al_2O_3 Engelhard	22.0[e]	36	65	32.3	12.0– 71.0	25	36
1.11% Pd/Al_2O_3 Engelhard	5.5[e]	130	240	131.1	45.0–438.0	6	16

[a] Particle size as calculated from chemisorption data assuming that the crystals are fcc cubooctahedra (*5*, *22*).

[b] Particle size as calculated from chemisorption data assuming that the crystals are fcc octahedra (*5*, *22*).

[c] The dispersion as calculated from electron microscopy data assuming that the crystals are fcc cubooctahedra (*5*, *22*).

[d] The dispersion as calculated from electron microscopy data assuming that the crystals are fcc octahedra (*5*, *22*).

[e] These dispersions were furnished by Engelhard industries.

sured with a Bendix NPL automatic polarimeter, Series 1100, in a bubble trap Pyrex cell of 1-mm optical path length. The instrument was calibrated with (−)-2 octanol, $[\alpha]_D^{25} = -9.00°$.

RESULTS

The optical rotations of recovered apopinene at various percentages deuteriumation are shown in Table 4.

The results are influenced by the purity of the (+)-apopinene. Although purified twice by gas chromatography, it was still necessary to pass (+)-apopinene through freshly activated basic Al_2O_3 (Camag) under inert atmosphere [900 μl (+)-apopinene, 0.5 g Al_2O_3, 2.5-cm column, He] to prevent poisoning of some of the catalysts. We found that no isomerization occurred during the GC and alumina purifications. In fact, (+)-apopinene retained its original optical rotation during three GC purifications. Moreover, when the Al_2O_3 used for the Pd/Al_2O_3 preparation was treated identically as in the catalyst preparations, it caused no isomerization under deuteriumation conditions. Finally, we found that no isomerization occurred at room temperature when (+)-apopinene was allowed to contact the Camag Al_2O_3 for 24 h.

Our preliminary report (*16*) did not use the last purification (Al_2O_3) and for some of the catalysts (the splats) an induction period and slightly faster isomerizations were observed. Table 5 compares some results with and without the last purification step.

TABLE 4

Results from Hydrogenation of Pd catalysts

	% Optical rotation	% Addition	k_i/k_a
Pd/Al_2O_3			
0.01%	77.0	3.9	2.5
	60.7	9.8	
	51.9	12.2	
0.05%	73.4	5.3	2.6
	55.5	10.4	
	41.1	15.7	
	31.8	19.3	
0.18%	77.3	3.2	4.0
	61.5	6.5	
	38.9	11.6	
	24.5	15.6	
0.40%	62.7	4.3	5.7
	61.0	5.2	
	51.2	5.8	
	23.6	12.5	
	9.7	18.1	
1.00%	78.5	2.4	6.2
	57.6	5.2	
	33.4	10.1	
	36.8	10.2	
	35.6	10.3	
	32.7	10.5	
	17.4	13.8	
	3.1	22.2	
1.11%	66.0	6.7	3.3
	47.3	11.1	
	29.3	16.5	
1.04%	39.8	7.4	8.7
	27.3	9.7	
	2.0	19.4	
1.0%	38.3	7.0	10.7
	8.8	13.2	
	0.75	19.3	
$Pd/BaSO_4$ 5%	45.3	8.3	4.9
	28.0	12.6	
	10.4	20.4	
Pd black	77.5	1.5	10.1
	53.7	3.8	
	27.5	5.4	
	34.8	5.6	
	36.1	5.8	
	14.8	8.9	
	11.5	10.8	
	12.2	13.1	
	2.8	16.4	
	0.4	22.4	
Reduced PdO_2	68.4	7.3	1.9
	52.7	14.0	
	46.6	18.5	
	43.8	19.5	
	44.1	19.6	
+ 6 cycles[a]	72.5	5.4	2.5
	51.5	12.5	
	36.3	18.5	
+ 12 cycles	64.2	6.4	3.4
	42.7	11.8	
	21.2	20.2	
+ 18 cycles	41.1	10.9	4.0
	19.1	18.7	
Pd/C 5%	64.7	5.0	3.3
	25.4	18.6	
Pd powder	64.5	5.8	3.4
	42.5	11.7	
	27.5	17.5	
Pd foil	84.3	9.2	0.96
	70.9	16.3	
$Pd_{80}Si_{20}$ 1.60	92.0	5.3	0.68
	85.5	11.0	
	84.4	11.5	
	81.4	14.1	
	77.9	17.0	
	73.5	20.2	
$Pd_{77}Ge_{23}$ 1.01	90.0	8.5	0.59
	84.0	13.5	
	81.6	16.8	
	76.5	19.8	
Pure Pd splat 10.1	89.1	8.6	0.57
	78.1	19.7	

[a] During one cycle the catalyst was kept in flowing hydrogen at 373 K for 45 min, then in Ar for 60 min.

Although differences were observed for the splats, no significant differences were found for the Pd/Al_2O_3 catalysts. We assume that the concentration of the poison is small and, therefore, has a small effect on the higher surface area catalysts but has a large affect on the low surface area splats. In this study all experiments except those on Pd/Al_2O_3 used fully purified (+)-apopinene.

For the Pd/Al_2O_3 catalysts prepared in this lab the particle sizes obtained from electron micrographs are somewhat higher than the particle sizes that were calculated from chemisorption data (see data Table 3). This could be caused by the possible loss of small particles during the preparation of the EM samples (*24*) and/or the inability to see the smaller particles (about 4 Å or smaller) in the electron microscope. Also, the chemisorption data for our catalyst with the smallest Pd loadings are the least reliable, because of the problems involved in detecting the small volumes of gas that these catalysts adsorb. Most of the commercial catalysts had good correlations between the electron microscopy data and the chemisorption calculations based on cubooctahe-

TABLE 5

Results with (+)-Apopinene Purified in Different Ways (Catalysts: Heat-Treated $Pd_{80}Si_{20}$ splat, 1.53)

	% Optical rotation	% Addition	k_i/k_a
(+)-Apopinene, purified by GC	83.9	5.3	1.7
	65.4	10.2	
	53.7	16.8	
(+)-Apopinene, purified by GC and Al_2O_3	88.7	6.1	0.81
	81.7	9.4	
	73.9	17.7	

dral crystals. However, the EM data on the Engelhard 1.0% Pd/Al_2O_3 correlated best with the calculations based on fcc octahedra while the EM data on the $Pd/BaSO_4$ did not fit at all with the chemisorption calculations. We suspect that the Pd does not form normal crystal shapes on $BaSO_4$.

For the ion exchanged Pd/Al_2O_3 catalyst the EM results confirm the presence of very small particles for low loadings and large particles for higher loadings. This correlation is about as good as previously reported (*16*). In one case, 1.11% Pd/Al_2O_3, the EM showed particles composed of large carpets (approx 131 Å) with dense regions resembling fuzzy balls. These contrasted with the large particles observed in our 1.00% Pd/Al_2O_3 which exhibited smooth crystalline shape (approx 46 Å).

DISCUSSION

A simple plot of isomerization vs addition produces curves which are not readily evaluated quantitatively (*16*). Therefore, a straight line relationship was derived as shown in Fig. 3. In this figure, the terms in parentheses represent mole fractions of the respective species at any time t. Thus, the fraction of hydrogen addition (Add) would be y, while the fraction of isomerization (Iso) would be $x/(1 - y)$. To establish a correlation between Add and Iso, solutions for x and y must be obtained.

The differential equation for y is

$$dy/dt = k(1 - y) \qquad (1)$$

where $k = k_a P_H$ = constant at a given hydrogen pressure. The solution for the above is

$$y = 1 - e^{-kt}. \qquad (2)$$

Similarly, the differential equation for x is

$$-dx/dt = (k + 2k_i) - k_i(1 - y) \qquad (3)$$

which, by combining with Eq. (2), becomes

$$dx/dt + (k + 2k_i)x = k_i e^{-kt}. \qquad (4)$$

The above can be solved for x as follows:

$$x = \tfrac{1}{2}(e^{2k_i t} - 1)/e^{(k+2k_i)t}. \qquad (5)$$

From Eqs. (2) and (5), and from the previous definitions for Add and Iso

$$\ln(1 - 2\ \text{Iso}) = \frac{2k_i}{k_a P_H} \ln(1 - \text{Add}). \qquad (6)$$

Plots of the data according to Eq. (6) produce straight lines as shown in Figs. 4 and 5. The slopes of these lines give the ratios of the pseudo-rate constants (they also contain the concentrations of the active sites) of isomerization and addition for the different catalysts. As can be seen from Figs. 4 and 5, these slopes are extremely sensitive to the method of preparation. And, consequently, the ratios of k_i/k_a exhibit a wide range of values, from 11 (1.0% Pd/Al_2O_3) to 0.57 (pure Pd splat). Each catalyst can be distinguished from the others.

At this stage it is not clear which catalytic features correlate with k_i/k_a. Mechanistically speaking, those catalysts with high concentrations of ^3M type sites should exhibit high rates of addition, i.e., low k_i/k_a. Indeed, for the chemisorption and EM characterized Pd/Al_2O_3 catalysts this is gen-

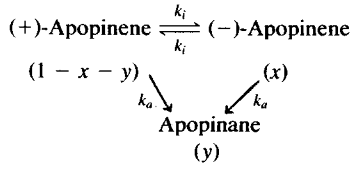

FIGURE 3

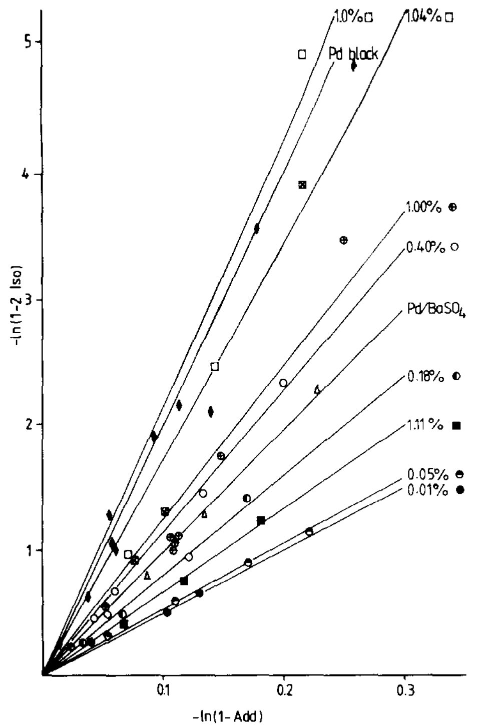

FIG. 4. Plots ln(1 − 2 Iso) vs ln(1 − 2 Add) for Pd/Al_2O_3, Pd/$BaSO_4$, and Pd black catalysts. Slopes of the lines are $2k_i/k_aP_H$ for the catalysts.

erally true. The lower loaded catalysts with the smaller particles give low k_i/k_a and the higher loaded catalyst give high k_i/k_a. The exception, 1.11% Pd, may contain considerable nonuniformity, as suggested by EM, and, therefore, may contain high concentrations of ^{3}M type sites. That k_i/k_a correlates better with loading than with either chemisorption or EM data may reflect the large uncertainties in these techniques.

In the region of low relative isomerization activity are the foil and the splat cooled materials. We have suggested that these possess few sites of low coordinative unsaturation (^{1}M and ^{2}M) and many sites of high coordinative unsaturation (^{3}M). For the glassy alloys we suggest these highly coordinatively unsaturated sites occur on protuberances (*16*). These protuberances may crystallize into staircases which contain many sites of medium coordinative unsaturation. The splat cooling processes seem to produce such a high ^{3}M surface even when the product is crystalline, for example, pure Pd. Similarly, the process used in preparing the foil must introduce many such sites.

In the region of high relative isomerization activity are the more heavily loaded Pd/Al_2O_3 catalysts, with the exception of 1.11% Pd as noted, and Pd black. This activity seems to be characteristic of the larger regular crystalline Pd particles and may indicate a high percentage of ^{2}M type sites.

One of the most interesting observations is the ability of (+)-apopinene to distinguish between different preparations of reduced PdO_2. Following the technique of Palczewska and co-workers (*25*) we sequentially prepared and destroyed the β-hydride phase several times. After several cycles we measured k_i/k_a. More cycles lead to increased k_i/k_a, which suggests that surface reconstruction occurs with concomitant production of ^{2}M sites form ^{3}M sites.

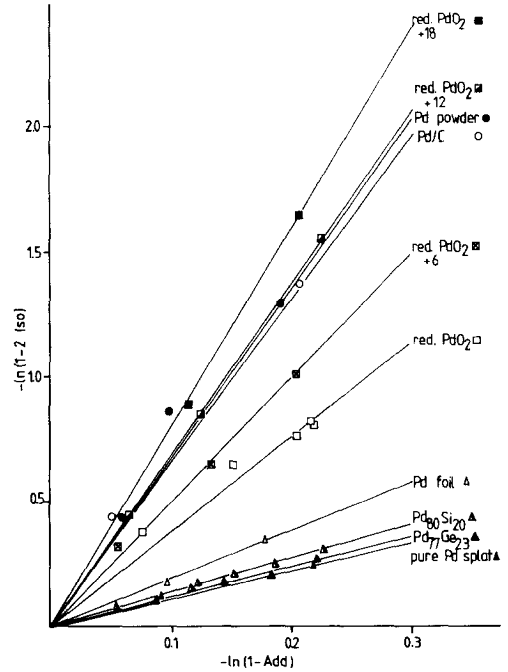

FIG. 5. Plots of ln(1 − 2 Iso) vs. ln(1 − Add) for reduced and surface reconstructed Pd/O_2; Pd/C; the pure Pd powder; foil and splats; and the Pd–Si and Pd–Ge splats. Slopes of the lines are $2k_i/k_aP_H$ for the catalysts.

In conclusion we propose that (+)-apopinene can differentiate between the many different types of palladium surfaces. This differentiation identifies similar surfaces which are not obvious from chemisorption and/or electron microscopy information.

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