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Hydrogenation of (+)-Apopinene over Pd–Si and Pd–Ge Glasses

INTRODUCTION

Metallic glasses are new materials which present the possibility of preparing new catalysts. From this point of view we have been studying the catalytic properties of glassy palladium alloys. Our approach has been to employ the molecular probe, (+)-apopinene (6,6-dimethyl-1R,5R-bicyclo [3.1.1] hept-2-ene), which is sensitive to catalytic sites of differing surface coordination. Although the mix of such sites on the glasses is unknown, it can be inferred from comparison of the apopinene results over glasses to the results over other standard palladium catalysts for which the mix can be estimated.

As the accumulation of physical characterization evidence from all palladium systems correlates with their chemical characterizations ((+)-apopinene reactivities) appropriate statements can be made about the nature of those catalytic surfaces which are difficult to characterize physically, such as metallic glasses.

Since our initial report of the catalytic properties of Pd-Si glasses (*1*), additional studies have appeared (*2–28*). Several of these studies are of hydrogenations but do not reveal differences between the glassy and crystalline structures (*8–10*). We believe this results from the lack of sensitivity for small differences in surface features of the molecular probes. In our studies (*1, 11, 12*) molecular probes have been carefully selected to be sensitive to these differences. In this present study we have examined a number of palladium materials, including splat cooled pure Pd as well as both glassy and crystalline Pd–Si and Pd–Ge prepared by both the shock tube and hammer-and-anvil techniques using the molecular probe (+)-apopinene. Because these materials produce much lower isomerizations than most Pd catalysts, a Pt foil is included as an example of a very low isomerization catalyst. These results can be compared to those obtained over a spectrum of supported and unsupported palladium catalysts for which percentages of exposed Pd atoms are available (*23*).

EXPERIMENTAL

(+)-Apopinene was prepared and purified in the manner previously described (*12*) with the exception that greater care in the procedures leads to materials with an optical rotation of $[\alpha]_D^{25} = 54.2°$ (*23*). The splat-cooled materials were prepared by two techniques. The first, the shock-tube (ST) technique, has been previously described (*1, 11, 12*); it involves blasting molten alloy through a nozzle onto a curved copper skid where it cools rapidly. The second, the hammer-and-anvil (HA) technique, is accomplished by arc-melting a small amount of the material on a water-cooled copper plate (anvil) above which is cocked a spring-loaded copper piston (hammer). Upon release the hammer smashes down on the anvil, interrupting the arc, splatting the molten material into a thin wafer, and rapidly cooling it. These wafers are thicker than those obtained by the shock-tube technique. The starting catalysts prepared and used in this study are identified in Table 1. Additionally, two materials purchased from Ventron Products were Pd foil, 0.025 mm thick, 99.9% purity, and Pt foil, 0.025 mm thick, 99.9% purity.

Hydrogenations with deuterium were carried out in the liquid phase as previously described (*12*) with the addition of a step in which (+)-apopinene was percolated

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TABLE 1

Material	I.D.	Prep.[a]	Structure[b]
$Pd_{80}Si_{20}$	Master alloy	—	Crystalline
	1.56	ST	Glassy
	1.60	ST	Partially glassy
	1.62	ST	Partially glassy
	50.0	HA	Partially glassy
	1	HA	Partially glassy
	2	HA	Partially glassy
	5	HA	Glassy
	7	HA	Metastable II
$Pd_{77}Ge_{23}$	1.01	ST	Partially glassy
	5.1	ST	Partially glassy
	5.2	ST	Partially glassy
Pd	10.1	ST	Crystalline
	10.1	HA	Crystalline
	100.00	HA	Crystalline

[a] ST is shock tube technique and HA is hammer-and-anvil technique.

[b] Typically, the ST and HA techniques produce structures which exhibit both glassy and crystalline X-ray patterns (*29*). When the X-ray pattern exhibits only minor or no evidence of crystallinity, the structure is termed glassy; when more than minor evidence of crystallinity is observed, the structure is termed partially glassy. In one case ($Pd_{80}Si_{20}$ 1, HA) a definite metastable II phase was identified (*30*).

through activated alumina immediately before hydrogenation (*23*). This pretreatment slightly decreased the ratio of isomerization to addition previously reported (*12*). Also, the catalysts were subjected to a pretreatment before injection of (+)-apopinene and the start of hydrogenation. This pretreatment was developed so 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. Reaction mixtures were analyzed and separated by gas chromatography.

RESULTS

The results of the hydrogenations are shown in Table 2. In this table the new value k_i/k_a is shown (*23*). The ratios k_i/k_a are determined from plots of ln(1-2Iso) vs ln(1-Add) according to the equation $\ln(1\text{-}2\text{Iso}) = \ln(1\text{-Add})2k_i/k_aP_H$ in which Iso is mole fraction of (+)-apopinene isomerized to (−)-apopinene and Add is mole fraction of apopinene hydrogenated. The maximum error in the ratios k_i/k_a is ±5% of the values except for the Pd–Si master alloy for which it is ±17%. In the case of the master alloy only a small amount was available and the rate was exceptionally slow. Each value was determined by at least two experiments. The 5% error is within the range typically obtained from many experiments with supported Pd and Pt catalysts.

TABLE 2

Experimental Data from Hydrogenation of (+)-Apopinene over Pure Pd and Pd–Si and Pd–Ge Alloys

Catalysts		Special treatment	k_i/k_a
Pd–Si	1.60	None	0.68 ± 0.03
		HT[a] (773 K, 2 h in Ar)	0.92 ± 0.04
		Above plus 12 cycles (45 min H_2/45 min Ar at 423 K)	0.84 ± 0.05
Pd–Si	1.62	None	0.91 ± 0.04
		HT (788 K, 24 h in Ar)	1.32 ± 0.09
		Second HT (895 K, 24 h in Ar)	1.29
Pd–Si	50.0	None	1.18 ± 0.03
		HT (795 K, 22 h in Ar)	1.44 ± 0.02
Pd–Si	1	None	1.00 ± 0.02
Pd–Si	2	None	1.41 ± 0.06
Pd–Si	5	None	0.92 ± 0.03
Pd–Si	7	None	1.06 ± 0.04
Pd–Si	1.56	None	0.77 ± 0.02
Pd–Si (Master alloy)		None	1.71 ± 0.29
Pure Pd (ST)	10.1	None	0.57 ± 0.03
Pure Pd (HA)	10.1	None	1.09 ± 0.05
Pure Pd	100.00	None	0.83 ± 0.04
		HT (873 K, 4 h in Ar)	0.85 ± 0.05
Pd–Ge	1.01	None	0.59 ± 0.02
Pd–Ge	5.1	None	0.64 ± 0.04
		HT (824 K, 20 h in Ar)	1.04 ± 0.03
Pd–Ge	5.2	None	0.96 ± 0.04
		HT (933 K, 12 h in Ar)	1.39 ± 0.04
Pd foil		None	0.96 ± 0.05
		HT (873 K, 2 h in Ar)	0.98 ± 0.005
		Above plus 10 cycles (45 min H_2/60 min vac. at 373 K)	0.97
Pt foil		None	0.09 ± 0.005

[a] Heat treatment.

Several catalysts were subjected to heat treatments in argon (1.60, 1.62, 50.0, 100.00, 5.1, 5.2, and Pd foil). Examination of the surface electronic structure via both Auger electron spectroscopy (AES) and UV photoelectron spectroscopy (UPS) show no difference in the spectra between the glassy splat flakes and the same flakes fully crystallized *in situ* (*31*). In two cases (1.60 and Pd foil) the β-hydride phase was made and destroyed several times in an effort to reconstruct the Pd surfaces (*32*). This seems not to have much affect on either the Pd–Si alloy or the Pd foil. Perhaps these structures were already stabilized by their heat treatments or perhaps their bulk structures hindered the β-hydride formation (*33*).

DISCUSSION

(+)-Apopinene is sensitive enough to detect small differences between catalysts. For example, catalyst HAPS 5 exhibits a glassy structure according to X-ray analysis and one major peak according to differential scanning calorimetry (indicates phase change), whereas catalyst HAPS 7 exhibits a metastable II structure according to X-ray analysis and one minor peak according to differential scanning calorimetry. These two materials are differentiated by (+)-apopinene hydrogenation. HAPS 7 shows a higher relative rate of isomerization than HAPS 5. Similarly, catalyst 1.56, which exhibits two major peaks according to differential scanning calorimetry, shows a lower relative rate of isomerization than HAPS 5.

In general, those catalysts prepared by the hammer-and-anvil technique show higher isomerization activity than those prepared by the shock-tube technique. We presume this results from a smaller amount of the glassy structure produced by the hammer-and-anvil technique.

Rapidly cooled pure Pd catalysts show catalytic activity similar to the alloys in spite of the absence of a metalloid. Pure Pd splats prepared by the two methods show the same differences as the alloys (for example, catalyst 10.1 (shock tube) catalyzes isomerization much less than catalyst 100.00). It seems clear that the principle difference in activities between these catalysts and supported Pd or Pd-blacks (*23*) is due to their method or preparation and not the presence of the metalloid.

Heat treatment of the alloys results in relative increases in isomerization activity over addition activity. In contrast, heat treatment of the pure Pd samples results in no changes in relative isomerization or addition activity.

Since surface analysis suggests no change in surface composition with heat treatment (*31*), we interpret these isomerization/addition results to indicate that the splat-cooled Pd–Si and Pd–Ge alloys are glassy and heat treatment causes surface structural changes which change the relative proportions of active sites that catalyze addition and/or isomerization. In contrast, splat-cooled pure Pd is already crystalline so heat treatment does not rearrange the active sites as much.

In absolute terms, however, addition activity (consumption of deuterium) changes with heat treatment. Heat treatment increases hydrogenation rates for Pd–Si but decreases them for Pd–Ge and pure Pd. These results over Pd–Si agree neither with those obtained in other systems (*2–4*, *8*) nor with our results over Pd–Ge. Typically the absolute activities decrease with heat treatment.

Although the absolute rates of hydrogenation in our reactions are subject to considerable variations, in every experiment with our heat treated Pd–Si we observed a rate increase. This suggests to us that the crystallized Pd–Si surface contains more active sites than the glassy Pd–Si surface, and, because isomerization increases more than addition, these new sites are better at isomerization than at addition. Such results might occur if the glassy surface contained many sites of high coordinative unsaturation with few nearest neighbors (e.g., Pd adatoms or atoms on protuberances (*12*)) which are better for addition than isomerization, and the crystalline surface made from heat treating the glass contained fewer sites of high coordinative unsaturation and more sites of lower coordinative unsaturation with more nearest neighbors (e.g., ledges, C_7, and kinks, C_6) (*34*) which are better for isomerization than for addition. Indeed the Pd–Si master alloy, which probably has few vertices, C_4, but many ledge sites or kinky ledge sites, catalyzes the highest ratio of k_i/k_a.

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