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Selective Hydrogenation of Alkynes over Metallic Glasses

Á. MOLNÁR,[1] G. V. SMITH, AND M. BARTÓK[1]

Department of Chemistry and The Molecular Science Program, Southern Illinois University, Carbondale, Illinois 62901

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The selectivities for half-hydrogenation of phenylacetylene, 1-octyne, and 4-octyne were examined over Pd–Si and Pd–Ge glassy (amorphous) and crystalline catalysts and, for comparison, over splat cooled pure Pd, reduced PdO_2, Pd foil, Pt foil, Pd/Al_2O_3, and Pd/C. Only the Pd/C and Pt foil gave less than 90% selectivities. Terminal alkynes comminute Pd structures and expose new active sites. These new sites are different on the rapidly cooled catalysts and the regularly crystallized catalysts. Although no significant changes are detected in alkyne hydrogenation selectivities after several hydrogenations, significant changes are revealed by (+)-apopinene (6,6-dimethyl-1*R*,5*R*-bicyclo[3.1.1]hept-2-ene). On the terminal acetylene-treated foils and on the reduced Pd oxide the rates of addition and isomerization of (+)-apopinene increase, but the ratio of the two rates remain almost the same. In contrast, the splat cooled catalysts show a higher rate increase for isomerization than for addition.

INTRODUCTION

Selective hydrogenation of acetylenic bonds to olefinic bonds is an industrially important transformation and a challenging task for both synthetic and catalytic chemists. The importance of the problem is illustrated by the numerous recent publications on particular aspects of the reaction (*1–10*).

As a continuation of our work on the catalytic activity of metallic glasses (*11–14*) we tested several glassy and crystalline palladium catalysts, and for comparison, palladium and platinum foils, as well as several supported palladium catalysts in the hydrogenation of acetylenic compounds. In some cases, (+)-apopinene was used to evaluate the effect of the prior hydrogenation of the acetylenic bond on the activity and selectivity of the catalysts for the hydrogenation and isomerization of the olefinic double bond.

EXPERIMENTAL

Materials. Phenylacetylene, 1-octyne, and 4-octyne (Aldrich) were distilled and percolated through freshly activated basic alumina (Camag) under helium before reaction (*15, 16*). Gas chromatographic analyses revealed no impurities. Heptane (Fischer, reagent grade) was kept on P_2O_5 for 48 h then distilled and percolated through a 30-cm-long $AgNO_3$–Al_2O_3 column (*17*). Deuterium (Linde, CP grade) and hydrogen (Linde, ultrahigh purity grade) were purified by passing through a 12-cm-long 0.5% Pd on zeolite (Linde SK 300) column then a 23-cm-long column of Linde 3A molecular sieve.

Catalysts. $Pd_{80}Si_{20}$ alloys: catalysts 1.60 and 1.62, were made by the shock tube technique, and catalysts HA 50.0, HAPS 1, and HAPS 2, were made by the hammer and anvil method. $Pd_{77}Ge_{23}$ alloys: catalysts 1.01 and 5.1 were made by the shock tube technique. Both the shock tube and hammer and anvil are rapidly cooling techniques. The shock tube technique blasts molten metal through a nozzle onto a curved copper plate and the hammer and anvil technique shoots a copper column (hammer) onto a molten slug of metal resting on a massive copper plate (anvil). Pure Pd: catalyst HAS 10.1 was made by the hammer and anvil technique. Reduced Pd oxide: $PdO_2 \cdot xH_2O$ (Engelhard Ind.) was

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[1] Permanent address: Department of Organic Chemistry, Jozsef Attila University, 6720 Szeged, Hungary.

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reduced in flowing hydrogen (8 ml/min) at 673 K for 5 h. Pd foil: 0.025 mm thick, 99.9% purity, was purchased from Ventron products as was Pt foil: 0.025 mm thick, 99.9% purity. The 1.0% Pd/Al_2O_3 (D = 0.49) and 1.11% Pd/Al_2O_3 (D = 0.055) were donated by Engelhard Ind. The 5% Pd/C was purchased from Matheson, Coleman and Bell. One glassy alloy (1.62) was crystallized by heat treatment (HT) at 788 K for 24 h under Ar.

Method. Hydrogenations were carried out in glass apparatus employing a small shaking vessel, manometer, and gas burette previously described (*18*) at atmospheric pressure and room temperature (298 K) in heptane as solvent. Phenylacetylene, 200 μl, and 250 μl of either 1- or 4-octyne were used, respectively. The total volume of the reaction mixture was 500 μl. The catalysts were kept under deuterium (or hydrogen) for 24 h at room temperature (298 K), then the solvent was injected into the reaction vessel and shaken for 30 min. Finally, the appropriate amount of reactant was injected. At certain intervals 10-μl samples were removed and analyzed by GC.

Analyses. The columns and GC conditions used for the analyses of samples were as follows: phenylacetylene, 20% DEGS on Chromosorb P (20 feet), 423 K, 20 ml/min He; 1-octyne, 20% ODPN on Chromosorb

TABLE 1

Hydrogenation of Phenylacetylene

Catalyst		No.	Selectivity[a]	Initial composition[b]			N_t[c]
				PhCCH	$PhCHCH_2$	$PhCH_2CH_3$	
$Pd_{80}Si_{20}$	1.62	(1)	97.7	94.3	5.6	0.1	13
	1.62 + HT	(2)	97.0	93.9	6.0	0.1	3
	HA 50	(3)	97.4	95.2	4.7	0.1	7
	HAPS 2	(4)	96.6	88.2	11.8	0	1
$Pd_{77}Ge_{23}$	1.01	(5)	96.9	97.2	2.8	0	8
	1.01	(6)	97.7[d]	96.5	3.5	0	7
	1.01	(7)	94.5(H)[e]	94.8	5.1	0.1	5
	5.1	(8)	95.7	96.4	3.6	0	9
Pure Pd	HAS 10.1	(9)	94.4	94.6	5.4	0	7
	HAS 10.1	(10)	94.4[f]	92.4	7.3	0.3	10
	HAS 10.1	(11)	95.2(H)	93.8	6.1	0.1	15
Pd foil		(12)	94.8	97.6	2.1	0.3	28
		(13)	96.3(H)	95.0	5.0	0	34
Red. Pd oxide		(14)	94.0	92.0	7.6	0.4	
1.0% Pd/Al_2O_3		(15)	94.5	95.7	4.3	0	1
		(16)	93.8(H)	95.2	4.2	0.6	2
1.11% Pd/Al_2O_3		(17)	96.3	95.5	4.5	0	7
		(18)	97.3(H)	95.1	4.9	0	12
5% Pd/C		(19)	89.8	95.4	4.2	0.4	
Pt foil		(20)	77.0	94.2	5.0	0.8	22

[a] Selectivity $= \frac{\%\ \text{ene}}{\%\ \text{ene} + \%\ \text{ane}} \times 100$ at 1.0 mol hydrogen uptake.

[b] Initial compositions were determined after low percentages of hydrogen uptake, which can be calculated from the data for each case.

[c] N_t = molecule sec^{-1} surface $atom^{-1}$. In the case of the splat cooled catalysts surface area of 0.055 $m^2\ g^{-1}$ were used (*11*). For Pd and Pt foils, the geometric surface areas were used. Values of 1.2×10^{19} surface Pd atoms m^{-2} (*20*) and 1.12×10^{19} surface Pt atoms m^{-2} (*21*) were used. Typical errors for these are ±10% of the value.

[d] The fifth consecutive hydrogenation on the same catalyst sample.

[e] Reactions in hydrogen instead of deuterium.

[f] After hydrogenations of 1-octyne and 4-octyne.

TABLE 2

Hydrogenations of 1-Octyne[a]

Catalyst		Selectivity	Initial composition			N_t
			1-Octyne	1-Octene	Octane	
$Pd_{80}Si_{20}$	1.60	93.9	95.7	4.3	0	1.5
	HAPS 2	95.3	94.9	5.1	0	10
$Pd_{77}Ge_{23}$	1.01	96.3(H)	95.4	4.6	0	7
	5.1	96.0	94.4	4.8	0.8	5
Pure Pd	HAS 10.1	92.0	94.5	5.5	0	45
	HAS 10.1	95.0(H)	96.6	3.4	0	9
Pd foil		95.3	91.8	7.2	1.0	15
Pt foil		57.5	95.5	3.0	1.5	20

[a] See footnotes in Table 1.

W (10 ft.), 333 K, 45 ml/min He (for separating 1-octyne from products) and 318 K, 15 ml/min He (for separating alkenes); 4-octyne, 25% $AgNO_3$–triethylene glycol on Chromosorb W (6 ft.), room temp., 15 ml/min He.

RESULTS

The only paper dealing with the semihydrogenation of phenylacetylene on amorphous and crystalline $Pd_{80}Si_{20}$ catalysts reports high selectivity (96% based on the Fig. 3 in the paper) (*19*). All splat cooled palladium catalysts and Pd foil used in our experiments exhibited similar high selectivity (94–98%) in the hydrogenation of all acetylenic compounds (Tables 1–3). Crystallization of the amorphous catalysts did not change selectivities or product compositions (Table 1, entries 1 and 2). Included, for comparison, are results over Pt foil.

During the hydrogenations of both phenylacetylene and 1-octyne on both the splat cooled catalysts and the foils the consumption of the first mole of hydrogen or deuterium resulted in the solution turning gray and turbid. This turbidity disappeared exactly at the complete consumption of the starting acetylene compounds, after

TABLE 3

Hydrogenations of 4-Octyne[a]

Catalyst		Selectivity	Initial composition				c/t[b]	N_t
			4-yne	c-4-ene	tr-4-ene	ane		
$Pd_{80}Si_{20}$	1.62 + HT	98.7	94.4	5.4	0.2	0	90/10	10
	HA 50	96.7	93.7	5.9	0.4	0	87/13	4
	HAPS 2	97.0	95.2	4.8	0	0	87/13	9
$Pd_{77}Ge_{23}$	1.01	97.9	94.9	5.1	0	0	87/13	16
	1.01	100.0(H)	95.6	4.4	0	0	93/7	16
Pure Pd	HAS 10.1	92.3	94.8	4.8	0.4	0	66/34	16
	HAS 10.1	96.0(H)	94.4	5.4	0.2	0	83/17	23
Pd foil		98.4	97.1	2.8	0.1	0	89/11	32
Pt foil		66.2	95.8	3.8	0.4	0	83/17	64

[a] See footnotes in Table 1.

[b] Ratio of *cis*-4-octene to *trans*-4-octene at 1.0 mol hydrogen uptake.

which a black deposit appeared on the walls of the reaction flask. The most remarkable example of this was observed in experiments using pure Pd HAS 10.1 during which observable fracturing of the sample also occurred. This phenomenon never occurred during hydrogenations of 4-octyne, so we suspected that part of the metal dissolved by complexation with terminal acetylenes. In support of this suspicion we found that some catalysts, which had been inactive for the hydrogenation of olefins, could be activated by first running the hydrogenation of a terminal acetylene. A similar phenomenon, the extraction of metal atoms by hydrocarbons, is believed to be connected to the hydrogenation of vinylacetylene (*5*). However, all our efforts to detect —C≡C—Pd compounds in the reaction mixture by IR failed.

Although no significant changes could be detected in acetylene hydrogenation selectivities after several consecutive hydrogenations on the same samples (Table 1, entries 5 and 6, 9 and 10), significant changes were revealed by (+)-apopinene, a molecular probe we have developed as a sensitive tool to trace minor alterations in the morphology of palladium catalysts (*13*, *22*).

On the terminal acetylene-treated foils and on the reduced Pd oxide the rates of both addition and isomerization of (+)-apopinene (6,6-dimethyl-1*R*,5*R*-bicyclo[3.1.1]hept-2-ene) increase, but the ratio of the two rates remain almost the same. In contrast, the splat cooled catalysts show a higher rate increase for isomerization than for addition (Table 4, k_i/k_a ratios).

TABLE 4

Changes of k_i/k_a Ratio[a] in (+)-Apopinene Hydrogenation

		k_i/k_a[b]		
		Original	After hydrogenation of terminal acetylene	
$Pd_{80}Si_{20}$	HAPS 1	1.00	1.30[c]	
$Pd_{77}Ge_{23}$	1.01	0.59	0.97[d]	1.00[e]
Pure Pd	HAS 10.1	1.09	1.39[d]	1.33[f]
Pd foil		0.96	0.84[d]	
Pt foil		0.09	0.09[d]	
Red. Pd oxide		1.91	1.92[d]	

[a] Calculated from $\ln(1\text{-}2\mathrm{Iso}) = \frac{2k_i}{k_a P_H} \ln(1\text{-}\mathrm{Add})$, where Iso = mole fraction of isomerization, Add = mole fraction of hydrogenation (*22*).

[b] Experimental error <5%.

[c] After hydrogenation of PhCCH and 1-octyne.

[d] After one hydrogenation of PhCCH.

[e] After 5 runs of hydrogenation of PhCCH.

[f] After additional hydrogenation of 1-octyne.

DISCUSSION

β-Hydride phase. Carturan *et al.* (*3*) found that Pd catalysts with 100% dispersion exhibited 100% selectivity in the semihydrogenation of phenylacetylene. They explained this high selectivity by the absence of the β-hydride phase in their highly dispersed catalysts (particle size < 1.9 nm). Also, Palczewska questions the easy formation of the β-hydride phase in bulk Pd (*23*). On the basis of these explanations we might presume that in our experiments on bulk catalysts (alloys and foil) the β-hydride phase does not form either. Additionally, the similarity of our results in both hydrogen and deuterium support this possibility.

On the other hand, the Pd on alumina catalysts exhibit the same high selectivities as the bulk catalysts, which suggests that it is not the β-hydride phase which causes decreased selectivities in Carturan's work (*3*). In support of this position is the work of Caga *et al.* (*4*) who detected the β-hydride phase in prereduced Pd oxide (100-nm particles) by X-ray diffraction studies, but, nevertheless, achieved high (94–98%) selectivities in the hydrogenation of 1-octyne. So, it appears that the presence or absence of the β-hydride phase is not the critical factor. Rather, the critical factor is a structure which incidentally allows or disallows the formation of the β-hydride phase. That is, certain active sites are responsible for the decreased selectivity in Carturan's work, and the population of these sites depends on the method of preparation and the presence of poisons and additives. For example, Kemball *et al.* (*24*) found that two types of active sites exist on Pd-on-alumina catalysts. One type can catalyze the hydrogenation of both acetylene and ethylene, the other can catalyze the hydrogenation of only ethylene. This latter can be easily poisoned by CO.

Another example which is in contrast to Carturan's work, is Boitiaux's report of decreasing selectivity for semihydrogenation of 1-butyne with increasing dispersion (*6*). Perhaps the different selectivities from the two laboratories reflect their different methods of preparation. The population of certain active sites responsible for the decreased selectivity is likely different on the different catalysts, especially those prepared from the Pd π-allyl (*3*). However, comparing these two sets of results may be misleading because different alkynes were used, and in one laboratory (*6*) all catalysts yielded rather low selectivities (73–90%), while in the other (*3*) for comparable conditions all selectivities were fairly high (91–100%).

In our previous paper (*13*) we suggested that the low isomerization ability of the glassy alloys is due to sites of very high coordinative unsaturation such as disordered Pd adatoms and isolated Pd atoms which are better for addition than isomerization. We suggest that these kinds of sites are also selective for high alkyne selectivity and may be the ^{3}**M** and/or ^{3}**MH** Siegel sites (*25*). Additionally, we suggest that they are produced by Pd π-allyl dissociation (*3*) which may deposit Pd in disordered Pd arrays in contrast to the Pd–AcAc dissociation (*6*) which, because of the higher reduction temperature, may deposit Pd in ordered arrays.

Also, in our previous paper (*13*) we suggested that heat treatment of the amorphous alloys converts the disordered arrays of atoms into ordered arrays of lower coordinative unsaturation, especially ledges and kinky ledges. Now, we suggest that the effect of the terminal alkynes is to expose such sites by comminution of the Pd structures. These newly exposed sites do not influence alkyne reactions. Likewise, the effect is not produced from fragmentation of the regularly crystallized Pd catalysts because the newly exposed surfaces are similar to the old. For them only the total exposed palladiums are increased and the rates of the different alkene reactions are increased accordingly.

However, for the splat cooled materials, fragmentation exposes new surfaces which are different from the old. These new surfaces exhibit greater order than the old because fractures occur at regions where disorder is greatest and, hence, the surfaces produced exhibit greater order. This is accentuated in the splat cooled pure Pd which, being crystalline, has many internal grain boundaries (disordered interfaces) between well ordered faces.

This suggestion is supported by the work of Kawashima and Hashimoto who cracked amorphous alloys by first diffusing Zn into the intersites of the alloys and then leaching out the Zn (*26*). Although their work did not look for the exposure of a different mix of sites, such a possibility exists.

We have also considered surface reconstruction (*8, 27*) as an explanation for the changes in k_i/k_a. Although this is a possibility, we believe it does not best explain our results.

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