JOURNAL OF CATALYSIS **83**, 238–241 (1983)

Characterization of Pd-on-Alumina and Pd-Si Glasses by Isomerization and Hydrogenation of (+)-Apopinene

In our study of the catalytic properties of metallic glasses, we examined the hydrogenation and isomerization of *cis*-cyclododecene over Pd–Si and Pd–Ge metallic glasses and crystalline materials (*1*). We found different results over the crystalline materials as compared to the glassy materials; however, the use of *cis*-cyclododecene to characterize such surfaces has the drawback of producing an isomer (*trans*-cyclododecene) in the reaction which has a rate of hydrogenation different from the parent compound. These differences in rates of hydrogenation mask the actual amounts of isomerization that are occurring and, therefore, conceal the kinds of catalytic sites available on the surface. Therefore, we have tested the molecule (+)-apopinene as a surface probe to distinguish the relative percentages of terraces, ledges, and kinks available on metallic surfaces. This probe molecule is more useful than *cis*-cyclododecene because its isomerization product, (−)-apopinene, has the identical rate of hydrogenation on a symmetrical surface. Moreover, because of the *gem*-dimethyl group on the bridge, the molecule is hindered from adsorbing with the *gem*-dimethyl group pointing toward the surface, so it is forced to approach the surface with only one side of the double bond. Previously we showed that the isomerization of (+)-apopinene is much faster than isomerization of other alkenes (*2*). This high rate of isomerization is attributed to an extra isomerization pathway, a 1,3-sigmatropic hydrogen shift (*3, 4*), which occurs on terrace sites (*5*). Therefore, isomerization will reflect the total number of ledge, kink, and terrace sites, whereas, addition will reflect only the number of kink sites. In this paper we report the first results of the use of (+)-apopinene as a probe molecule on metallic glasses, as well as on a set of palladium–alumina catalysts with differing crystallite size.

EXPERIMENTAL

(+)-Apopinene was prepared by oxidation of α-pinene $[\alpha]_D^{22}$ +47.1° (neat) to myrtenal followed by decarbonylation (*6*).

The crude apopinene obtained by a fast distillation (*2*) from the decarbonylation was collected in a temperature range of 140–150°C. Pure (+)-apopinene was obtained by preparative gas chromatography (25 ft. by 3/8 in. 35% Apiezon-L on chromosorb-W, at 180°C and 92 ml/min He flow rate).

The highest optical rotation $[\alpha]_D^{25}$ +47.4° (neat) was observed for (+)-apopinene collected at the beginning of the distillation and the lowest, $[\alpha]_D^{25}$ +40.2° (neat), for that collected at the end.

A series of Pd–Al_2O_3 catalysts were prepared on 80–200 mesh gamma-alumina donated by the Katalco Company. This alumina has a surface area of 260 m^2/g as measured by BET nitrogen adsorption. It was heated at 140°C at 10^{-5} Torr for 24 h, cooled, and impregnated with a solution prepared by dissolving the required amount of $PdCl_2$ (MCB) in a suitable volume of 0.01 *M* HCl. The resulting slurry was stirred vigorously for about 15 min and dried in a rotary evaporator under reduced pressure at 65°C. The impregnate was further dried in air at 110°C for 18 h, calcined in air at 160°C for 12 h, and finally reduced at 300°C under a 10-ml/min stream of ultrahigh purity grade hydrogen (Air Products) for 24 h.

Pd–Si splats were prepared according to

0021-9517/83 $3.00

the procedures previously reported (*1*). One-tenth-gram pieces of a $Pd_{80}Si_{20}$ master alloy were remelted to 1600°C and rapidly solidified in a shock tube splat cooler to form metastable glassy flakes. These flakes are 5- to 20-μm thick with a surface area of 0.055 m^2/g as measured by Kr BET adsorption. Portions of the Pd–Si splats were crystallized by 1-h isothermal aging in 10^{-5} Torr vacuum at 500 and 700°C. One catalyst, 5% palladium-on-alumina, was supplied by Engelhard Industries and was used directly from the bottle.

TABLE 1

Results of Hydrogenation of (+)-Apopinene over Different Pd Catalysts

Catalyst	No.[a]	% Addition	% Isomerization
0.03% Pd/Al_2O_3	1	5.3	25.4
	2	10.5	44.7
	3	15.4	60.8
	4	20.2	72.0
0.05% Pd/Al_2O_3	5	5.0	44.8
	6	8.3	55.1
	7[b]	15.0	55.2
	8	15.4	82.1
	9	19.0	96.5
1.0% Pd/Al_2O_3	10	4.2	44.8
	11	7.4	63.8
	12	12.3	94.8
	13	14.4	96.6
	14[b]	15.6	96.6
5.0% Pd/Al_2O_3 (Engelhard)	15	5.0	48.5
	16	10.4	68.6
	17	15.5	81.8
	18	20.0	100.0
Pd–Si Splats 151	19	15.9	20.7
151[c]	20	2.0	10.0
151[c]	21	22.5	55.2
152	22	15.1	20.7

[a] Not sequence of experiments, but sequence in Table.

[b] Catalysts in Nos. 5–6 and 8–13 were heated at 300°C in H_2 for 12 h; all other catalysts were not.

[c] Splats in Nos. 20 and 21 were crystallized samples of splat 151.

The hydrogenation and isomerization of (+)-apopinene were carried out with deuterium gas in an apparatus similar to that previously described (*7*). In a typical experiment, a 500-μl sample of (+)-apopinene was injected onto a palladium catalyst which had been pretreated with deuterium for several hours. Shaking the reaction vessel at 2200 rpm resulted in hydrogenation. After the desired percentage hydrogenation was accomplished, as determined by deuterium uptake, the reaction mixture was analyzed by gas chromatography (GC). Good agreement was obtained between the amount of deuterium taken up and the gas chromatographic analysis of the percentage of apopinane. The GC column was also used to separate the remaining apopinene from the reaction mixture for optical analysis. The optical rotation of the apopinene was measured using a Bendix automatic polarimeter series 1100. This polarimeter was adjusted before each measurement using (−)-2-octanol of known optical rotation.

RESULTS

The results of the hydrogenation and isomerization of (+)-apopinene are shown in Table 1. In this table the percentage of addition is also the percentage of the saturated apopinane which was produced in the reaction. The percentage of isomerization (racemization) was calculated as the percentage of optical rotation lost by the apopinene which was recovered from the reaction mixture. Although the absolute rate of uptake of deuterium varied from reaction to reaction, the ratio of the isomerization (or racemization) to addition was consistent.

In experiments 5 through 13, excluding 7, the catalysts were further reduced in hydrogen at 300°C for 18 h. Dramatic changes occurred on the 0.05% catalyst; however, on the 1% catalyst very little effect was detected. These changes, we believe, are due to sintering. The 0.05% catalyst contains many tiny crystallites which coalesce upon sintering, whereas the 1% catalyst contains only large crystallites to start with and, therefore, is not influenced by sintering. Compared to our 1% catalyst, isomerization is relatively slower over the 5% Engelhard catalyst. This suggests that the Engelhard catalyst has more small crystallites than our 1% catalyst. The results in Table 1 are plotted in Fig. 1 and discussed in the following section.

Apopinene isomerization occurs exclusively on Pd and not on the alumina support under reaction conditions. This was shown in two ways. First, no isomerization occurs when (+)-apopinene is subjected to hydrogenation conditions for 24 h over the alumina support which had been pretreated in the same manner as the Pd-on-alumina catalyst. Second, even more isomerization relative to addition occurs over palladium-black (not shown in Table 1) than over the Pd-on-alumina catalysts.

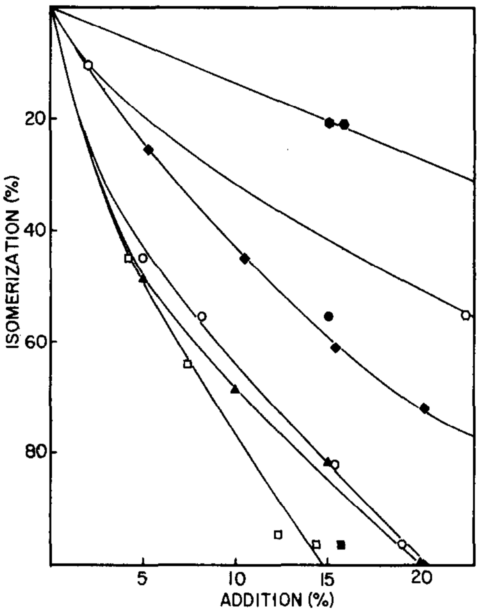

FIG. 1. Plot of (+)-apopinene isomerization vs addition over catalysts of different surface characteristics. Pd–Si Glass (●), Pd–Si glass crystallized (○), 0.03% Pd-Al_2O_3 (♦), 0.05% Pd-Al_2O_3 (●), 0.05% Pd-Al_2O_3 sintered (○), 1.0% Pd-Al_2O_3 (■), 1.0% Pd-Al_2O_3 sintered (□), 5.0% Pd-Al_2O_3 (Englehard) (▲).

DISCUSSION

The results correlated in Fig. 1 produce a family of curves representing different surface characteristics. Those catalysts which produce a higher ratio of isomerization to addition are the ones with rather large crystallites (5 and 1% Pd) and, therefore, high percentages of terraces. On the other hand, the catalysts with small crystallites (0.03% and unsintered 0.05% Pd), produce a lower ratio of isomerization to addition and have relatively high percentages of ledges and kinks. Likewise, the glasses, which have no long-range order and, therefore, are devoid of terraces, catalyze an even lower ratio of isomerization to addition.

Of particular interest are the experiments on the crystallized glass (Nos. 20 and 21) which showed a higher ratio of isomerization to addition than the parent glass. This is similar to the results of Yokoyama *et al.* (*8*) on Fe and Ni base amorphous alloys, who observed a decrease in the rate of hydrogenation of CO as a result of crystallization of initially glassy ribbons. This high ratio of isomerization to addition on the crystallized Pd–Si glass suggests a higher percentage of ledges and kinks than the 0.03% Pd.

Initially we expected the crystallized glasses to have many terraces and to produce results similar to the 1% palladium. However, the glasses may not have flat surfaces which crystallize into terraces. Rather, they may have substantial protuberances which crystallize into staircases of steps and kinks. Staircases would be expected from crystallized protuberances since formation of lower surface energy, low Miller index terraces on the crystallized glasses would require considerable solid state diffusion. Although such extensive diffusion can occur in supported metal particles it may be difficult on splats. For example, several workers have shown that Pd rearranges under mild conditions (*9*). Also the persistence of the ledges and kinks on the crystallized Pd–Si glass may be due to the suppression of surface diffusion by the presence of surface segregated silicon. Therefore we believe the data favor a glassy surface structure which is not twodimensionally random (flat), but is three-dimensionally random (hilly or rolling).

In summary, we believe we have shown that (+)-apopinene has considerable promise for the characterization of catalytic surfaces. It reveals surface features that are not readily available to physical techniques and heretofore have not been characterized by chemical means.

ACKNOWLEDGMENTS

We acknowledge the help of S. Megli, who prepared the splats, and W. Kowbel, who crystallized one of them. We are grateful for the support of this work by the U.S. Department of Energy, Division of Material Sciences, Office of Energy Research through Contract DE-AC02-81ER 10897.

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Received November 9, 1982