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Modified Activities and Selectivities of Silated–Oxidized–Reduced Pd and Pt Catalysts

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Supported nanoscale Pd and Pt particles lose their ability to catalyze hydrogenation and to hydrogenolyze triethylsilane when silated with either trimethyl silane or silane. Subsequently exposing these silated catalysts to oxygen restores their hydrogenation activities to various extents depending on their metal particle sizes. Large particles (<50%D) experience partial restoration, whereas small particles (>50%D) experience virtually complete restoration (85–111%) of their original alkene hydrogenation activity. Benzene hydrogenation activity on Pt and triethyl silane hydrogenolysis activities on Pd are restored less than alkene hydrogenation activities on Pt and Pd. Additional data from XPS, FTIR, DSC, TGA, and hydrogen chemisorption measurements point to a mechanism in which silation produces surface silicon, some of which migrates into the metal particle and some of which remains on the surface and poisons hydrogenation and hydrogenolysis activities. Oxidation produces PdO_2 (or PtO_2) and SiO_2 at the surface, and because the surface Si concentration has been reduced, interior Si migrates back to the surface where it is also oxidized. Hydrogen does not reduce SiO_2 but does reduce PdO_2 to Pd metal, which now presents a new reconstructed surface for hydrogenation. Thereby, Si alloyed to nanoscale Pd particles imparts not only new chemical characteristics, but also new physical characteristics. The reconstructed larger Pd–Si particles are not able to form as many favorable hydrogenation sites as before silation–oxidation–reduction, whereas the reconstructed smaller Pd–Si particles are able to form more hydrogenation sites than before. Likely the smallest Pd particles experience instabilities, rendering them incapable of maintaining many active hydrogenation sites; however, alloying with Si enlarges and stabilizes them such that they are capable of maintaining more active sites than before. © 1996 Academic Press, Inc.

INTRODUCTION

Over metal catalysts triethylsilane (Et_3SiH) hydrogenolyzes in stages, losing one ethyl group at a time until only strongly adsorbed Si remains on the metal surface (1). This strongly adsorbed Si is difficult to remove and poisons catalytic activity. Whereas earlier attempts to reactivate the poisoned catalyst by heat treatment were only partially successful, we have discovered that these silicon-poisoned catalysts can be reactivated by an oxidation–reduction treatment.

This discovery arose from our continued examination of the hydrogenolysis of triethylsilane, Et_3SiH, and the decomposition of silane, SiH_4, as sources of Si for poisoning (modifying) supported palladium and platinum catalysts. Not only do triethylsilane and silane poison Pd and Pt catalysts for both the hydrogenolysis of triethylsilane and the hydrogenation of cyclohexene, cyclopentene, and benzene, but also fully poisoned catalysts can be reactivated by oxidation and reduction. Reactivation is structure sensitive; smaller metal crystallites achieve greater reactivation, in some cases more than 100% reactivation of the original hydrogenation activity.

METHODS

Catalysts. Catalysts were either prepared in this laboratory or provided by others. The Pd black and the three 1% Pd/Al_2O_3 catalysts (5.5, 22, and 49% dispersion) were donated by Engelhard Industries. The 1.48 and 0.825% Pt/SiO_2, and 1.45% Pd/SiO_2 catalysts were obtained from the laboratories of Burwell and Butt (2). All of the remaining catalysts, 0.65, 0.34, 0.083, 0.46, and 3% Pd/SiO_2, were prepared in this laboratory by Daniel Ostgard, who characterized them by hydrogen chemisorption and electron microscopy (3). The silica was 120–140 mesh, wide pore, grade 62 Davison gel with a surface area of 285 m^2/g, a pore volume of 1.2 ml/g, and an average pore diameter of 14 nm (2).

Substrates. Cyclohexene, ACS reagent grade (99%), Fisher Scientific Co., was purified by distillation in an argon atmosphere and filtered through activated alumina under argon to remove traces of oxygen and peroxides (4).

The alumina (80–200 mesh) used for gas chromatography (GC) analysis was activated by heating at 400°C for

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3 h in flowing argon. Cyclopentene, 99.5% by GC, was obtained from Fluka. Cyclohexane, Aldrich Chemical Co., was 99.9+% HPLC grade. Both cyclopentene and cyclohexane were purified in the same manner as described above for cyclohexene. Certified ACS spectroanalyzed benzene (Fisher Scientific Co.) was used without further purification. Triethylsilane (99%) was purchased from Aldrich and used as received.

Gases. Zero grades argon and helium were obtained from MG Industries Gas Products and purified immediately before entering the reaction system by passing first through a purifier containing molecular sieves and activated carbon and then through an Altech Oxytrap, which lowered the oxygen concentration to less than 0.1 ppm. Ultrahigh purity hydrogen (MG Industries, minimum purity 99.999%) was used for chemisorption characterizations and for liquid-phase hydrogenations. Hydrogen used in poisoning experiments and in gas phase hydrogenations was purchased from Air Products. All of the hydrogen was purified by passage through the two purifiers described above. Additionally, all gases except oxygen and silane were further purified by passage through a MnO/SiO_2 trap (remove traces of oxygen) before passing into the reactor. Oxygen (Linde Specialty Gas, ultrahigh purity grade) and silane (Aldrich Chemical Co., 99.9%) were used without further purification.

Apparatuses. The apparatus for poisoning and hydrogenation has been previously described (5). Catalysts, 0.5–8.0 mg, were placed in reactor and, in some cases, 60.0–75.0 mg of silica gel was mixed thoroughly with the catalyst such that a small amount of catalyst was dispersed over a 2- to 3-cm length of the reactor.

Before each experiment the catalyst was treated with hydrogen at 300°C for 2 h. For the poisoning experiments, triethylsilane was injected at 250°C into flowing hydrogen (25 ml/min) and passed over the catalyst at 250°C. hydrogenations were carried out at 100°C and 420 ml/min. The exiting hydrogen stream was split before entering the GC and only 45–46 ml/min of hydrogen was passed through the GC where the reaction mixtures (cyclohexene–cyclohexane and cyclopentene–cyclopentane) were analyzed at 190°C on a 200 × 0.3-cm column filled with silica gel (60–80 mesh).

In a typical gas phase experiment, pulses of cyclohexene or cyclopentene were injected into the hydrogen stream to determine the initial catalytic activity. After experimental conditions were adjusted, successive injections of triethylsilane and alkene were made and the percentage hydrogenation of alkene was measured until catalytic activity ceased. Oxidation of the Si-poisoned catalysts was accomplished by simply exposing the catalyst to air or by passing pure oxygen over it at room temperature for 2 h.

Liquid-phase hydrogenations were carried out at 1 atm in the following manner. After poisoning the catalyst with Et_3SiH in a reactor attached to a gas-phase apparatus, the reactor containing the catalyst was transferred to the liquid-phase constant pressure hydrogenation apparatus previously described (6, 7). Special precautions were taken to prevent oxygen contact during reactor transfer. The reactor was connected to each apparatus by special quick connectors which seal automatically when disconnected. In this way the poisoned catalyst inside the reaction vessel could be transferred to the hydrogenation apparatus in the absence of air.

A small number of special analytical experiments were performed to learn more about the silation–oxidation–reduction process. These experiments included photoacoustic Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Additionally, X-ray photoelectron spectroscopy (XPS) data were reported earlier (8, 9).

The XPS and TGA apparatuses have been described in our earlier publications (5, 8–12). The DSC apparatus was a DuPont 990 thermal analyzer with a 910 DSC cell base, and the photoacoustic FTIR apparatus consisted of an Mtech Model 100 phtoacoustic cell fitted with a KBr optical flat. The photoacoustic infrared spectra were collected on a Nicolet 740 FTIR spectrometer. The background for the FTIR spectrum was obtained utilizing dry carbon black. Helium gas was used to purge the photoacoustic cell because of its superior thermocoupling properties. One-hundred twenty-eight scans were collected at 8 cm^{-1} resolution to produce the FTIR spectra.

RESULTS

Initially, we were examining the effect of silation on hydrogenation of Pd catalysts. We decomposed triethylsilane, Et_3SiH, over a Pd/SiO_2 catalyst in flowing H_2 at 200°C and transferred it to the liquid-phase hydrogenation apparatus. To our surprise the hydrogenation rate was faster than before silation. Several careful repeat experiments convinced us that exposure of the catalyst to oxygen was increasing

TABLE 1

Hydrogenations in the Liquid Phase without Exposure to Air

Expt.	Weight (mg) of catalyst[a]	E_3SiH (μl)	Reactant	Rate (ml/min/mg)
1a	11.3	0	0.1 ml cyclohexene	0.23
1b	11.3	0	0.1 ml cyclopentene	0.25
2a	10.3	1	0.1 ml cyclohexene	0.092
2b	10.3	1	0.1 ml cyclopentene	0.099
3a	10.4	3	0.1 ml cyclohexene	0.058
4a	11.0	5	0.03 ml cyclohexene	0.022
4b	11.0	5	0.03 ml cyclopentene	0.042
4c	11.0	5	0.03 ml cyclohexene	0.020
5a	10.7	8	0.1 ml cyclohexene	0.0
6a	10.4	8	0.1 ml cyclohexene	0.0

[a] Catalyst, 0.46% Pd/SiO_2; dispersion, 61.6%.

TABLE 2

Correlation of Rate of Cyclohexene Hydrogenation (Liquid Phase) with Amount of Ethane from Et_3SiH Hydrogenolysis over Pd/SiO_2[a]

Expt.	Et_3SiH injected	Volume of ethane (μl)	Rate of hydrogenation cyclohexene (ml/min/mg)
32	0	—	0.066 (fresh catalyst)
33	0.5 μl @ 150°C	7.5	0.065
34	0.5 μl @ 200°C	8.1	0.052
35	0.5 μl @ 250°C	9.6	0.046
36	2 × 0.5 μl @ 250°C	12.8	0.019
37	4 × 0.5 μl @ 250°C	16.1	0.000

[a] Catalyst, 0.083% Pd/SiO_2; %D = 83.2.

its hydrogenation activity. Therefore, we installed quick-connect couplers to the reaction vessel, silated the catalyst, transferred the silated Pd/SiO_2 to the liquid-phase hydrogenation apparatus in the absence of air, and obtained lower hydrogenation activities. The six studies in Table 1 show that rates of hydrogenation for cyclohexene and cyclopentene (experiments 1a and 1b) on the fresh, unpoisoned 0.46% Pd/SiO_2 catalyst are 0.23 and 0.25 ml/min/mg, respectively, but decrease as silation occurs. This decrease continues as Et_3SiH is injected (experiments 2–6) and the catalyst is inactive after injection of only 8 μl of triethylsilane. Additionally, treating each of several catalysts with increasing amounts of Et_3SiH produces increasing amounts of ethane which correlate with decreasing rates of hydrogenation (Table 2). Repeatedly silating the same catalyst not only poisons hydrogenation, but also poisons Et_3SiH hydrogenolysis over Pd/Al_2O_3 (Table 3). Clearly, silation poisons hydrogenation in an ordinary way in the absence of oxygen.

To understand the effect of oxidation on silated Pd, we carried out several liquid-phase hydrogenations with silated (Et_3SiH, 250°C), deliberately oxidized (24°C, 2 h), and reduced (H_2, 250°C, 2 h) Pd/SiO_2. Results of hydrogenations on this catalyst (Table 4) show an average rate increase of 18% for cyclohexene and 14% for cyclopentene (compare experiments 7 and 8 in Table 4 to experiments 1a and 1b in Table 1). In fact, all rates are higher than those on fresh catalyst (0.23–0.25) ml/min/mg. During liquid-phase hydrogenations silation–oxidation increases hydrogenation rates.

TABLE 3

Correlation of Rate of Cyclohexene Hydrogenation (Liquid Phase) with Amount of Ethane from Et_3SiH Hydrogenolysis over Pd/Al_2O_3[a]

Expt.	Et_3SiH injected	Volume of ethane (total) formed (in μl)	%Conversion of cyclohexene
38	0	—	100.0 (Fresh catalyst)
39	1 μl @ 250°C	8.83 (8.83)	38.7
40	2 × 1 μl @ 250°C	0.12 (8.95)	15.2
41	3 × 1 μl @ 250°C	0.05 (9.00)	2.2
42	4 × 1 μl @ 250°C	0.05 (9.05)	0.0
43	5 × 1 μl @ 250°C	0.00 (9.05)	0.0

[a] Catalyst, 1% Pd/Al_2O_3; %D = 5.5.

TABLE 4

Hydrogenation in the Liquid Phase on the Silated–Oxidized Catalyst[a]

Expt.	Weight (mg) of catalyst	Et_3SiH (μl)	Substrate	Rate (ml/min/mg)
7a	10.8	7	0.07 ml cyclohexene	0.28
7b	10.8	7	0.08 ml cyclopentene	0.29
7c	10.8	7	0.07 ml cyclohexene	0.27
8a	10.6	2	0.07 ml cyclohexene	0.27
8b	10.6	2	0.07 ml cyclopentene	0.29
8c	10.6	2	0.07 ml cyclohexene	0.25

[a] Catalyst, 0.46% Pd/SiO_2; dispersion, 61.6%.

Similar rate increases occur with gas-phase hydrogenations after silation with silane, SiH_4, then oxidation. This gas-phase procedure allowed us to silate the catalyst, subject it to various treatments, *in situ*, and carry out gas-phase hydrogenations without removing the catalyst from the reactor (Table 5). During these gas-phase experiments, we noticed that one catalyst (0.34% Pd/SiO_2) with 85.9%D attained a slightly larger rate increase than another catalyst (0.46% Pd/SiO_2) with lower dispersion, 61.6%D, had attained during the liquid-phase hydrogenation–oxidation experiments. Therefore, we looked for structure sensitivity.

Catalysts with a range of dispersions (0.6–85.9%) were available for structure sensitivity studies. So poisoning experiments were conducted and gas-phase hydrogenations

TABLE 5

Hydrogenation of Cyclohexene in the Gas Phase on Pd/SiO_2[a] Treated with SiH_4 and CS_2

		%Conversion of 2 μl cyclohexene			
Expt.	SiH_4 (μl)	Initial	After poisoning	After oxidation	%Reactivation
23a	0	48.7	—	—	—
23b	100		1.4	57.8	118.7
23c	100		0	43.7	89.7
23d	2 × 90		0	35.8	73.5
23e	90		0	42.9	88.0
23f	2 × 90		0	34.3	70.4
23g	90		0	39.4	80.9
23h	2 × 1 CS_2[b]		0	26.4	54.2
23i	90		0	30.2	62.0

[a] 0.6 mg 0.34% Pd/SiO_2 (%D = 85.9).
[b] CS_2 was injected instead of SiH_4.

TABLE 6

Influence of Silation–Oxidation on Highly Dispersed Catalyst Activities in Gas-Phase Hydrogenations

Expt.	Catalyst (mg)	Dispersion (%)	Et_3SiH (μl)	Ethane (μl)	%Conversion of 2 μl cyclohexene			%Reactivation
					Initial	After silation	After oxidation	
9a	0.65% Pd/SiO_2 (0.8 mg)	75.9	0.0	0.0	79.1 (420)[a]	—	—	—
9b	0.65% Pd/SiO_2	75.9	1.0	2.2		21.5	82.5	104.0
9c	0.65% Pd/SiO_2	75.9	1.0 × 2	1.9 and 0.5		—	—	—
10a	0.34% Pd/SiO_2 (0.7 mg)	85.9	0.0	0.0	68.0 (690)[a]	—	—	—
10b	0.34% Pd/SiO_2	85.9	1.0	1.8		58.6	70.0	103.0
11a	0.083% Pd/SiO_2 (2.3 mg)	83.2	0.0	0.0	12.8 (170)[a]	—	—	—
11b	0.083% Pd/SiO_2	83.2	1.0	0.45		7.9	14.2	111.0
12a	0.46% Pd/SiO_2 (2.6 mg)	61.6	0.0	0.0	85.8 (240)[a]	—	—	—
12b	0.46% Pd/SiO_2	61.6	1.0 × 5	5.9, 1.0, 0.9, 0.8, and 0.6		9.9	84.5	98.5
12c[b]	0.46% Pd/SiO_2	61.6	10.0	3.1, 1.2, 1.0, 0.8, 0.6, 1.0, 0.33, and 0.3		2.7	94.8	110.5
12d	0.46% Pd/SiO_2	61.6	1.0	3.2		25.0	92.5	108.0
13a	1.45% Pd/SiO_2 (0.4 mg)	51.6	0.0	0.0	17.3 (120)[a]	—	—	—
13b	1.45% Pd/SiO_2	51.6	1.0	1.0		6.6	18.8	109.0
13c	1.45% Pd/SiO_2	51.6	1.0	0.23		5.2	18.3	106.0
14a	1% Pd/Al_2O_3 (1.0 mg)	49.0	0.0	0.0	41.9 (180)[a]	—	—	—
14b	1% Pd/Al_2O_3	49.0	1.0	3.4		11.9	59.5	142.0
14c	1% Pd/Al_2O_3	49.0	1.0	2.1		7.0	34.2	81.6
14d	1% Pd/Al_2O_3	49.0	1.0	0.83		6.6	43.6	104.0

[a] Number of cyclohexene molecules converted per surface Pd atom (turnover number).

[b] In experiment 12c, 10 μl of Et_3SiH was injected as follows: 1, 1, 1, 1, 1, 3, 1, and 1.

of cyclohexene were used to monitor the effects of poisoning. The results in Table 6 show that catalysts with high dispersion, such as the 0.65% Pd/SiO_2 (75.9%D), exhibit an initial percentage conversion of 79.1 for 2 μl of cyclohexene (experiment 9a). The first injection of 1 μl of triethylsilane resulted in the formation of 2.2 μl of ethane and decreased the percentage conversion of cyclohexene to 21.5% (experiment 9b). Oxidation of the poisoned catalyst in flowing oxygen, followed by reduction, reactivated the catalyst to a higher activity, 82.5% conversion (experiment 9b). The percentage reactivation with respect to the fresh catalyst was 104% ($82.5/79.1 \times 100 = 104\%$). Unlike hydrogenation activity, however, the amount of ethane formed (hydrogenolysis activity) over the oxidized Si-poisoned catalyst was less than that formed over the fresh catalyst (experiment 9c), 1.9 and 0.5 ml of ethane, respectively, for the next two injections of 1 μl of Et_3SiH compared to 2.2 ml from 1 μl (experiment 9b). Oxygen treatment of the silicon poisoned 0.34% Pd/SiO_2, 0.083% Pd/SiO_2, 0.46% Pd/SiO_2, 1.45% Pd/SiO_2, and 1% Pd/Al_2O_3 (49%D) catalysts also increased their hydrogenation activities above those of the original unpoisoned catalyst (experiments 10–14). Moreover, experiments 12c and 12d, 13c, and 14c and 14d show that the reactivated catalyst can be repeatedly repoisoned by injecting more Et_3SiH and subsequently reactivated by oxidation and reduction.

In contrast to the highly dispersed catalysts, those with low dispersion, 1% Pd/Al_2O_3 (%D = 22), 1.1% Pd/SiO_2, 1% Pd/Al_2O_3 (%D = 5.5), 3% Pd/SiO_2, and Pd black, exhibited only partial recovery of their hydrogenation activity after oxidation (Table 7, experiments 15–21). At low dispersion, oxygen restores less than the original activity, but at high dispersion, oxygen restores more than the original activity.

Because carbonaceous residues from Et_3SiH decomposition might cause these activity decreases, we silated 0.34% Pd/SiO_2 (%D = 85.9) with silane, SiH_4. Data in Table 5 show that, after silane poisoning and before oxidation, essentially no hydrogenation activity occurs. However, after first oxidation, it exhibits 118.7% of its original hydrogenation activity, after two cycles, 89.7% of its original activity, and after three cycles, 73.5%. With succeeding cycles the activity

TABLE 7

Influence of Silation–Oxidation on Low Dispersed Catalyst Activities in Gas-Phase Hydrogenations

					%Conversion of 2 μl cyclohexene			
Expt.	Catalyst (mg)	Dispersion (%)	Et_3SiH (μl)	Ethane (μl)	Initial	After silation	After oxidation	%Reactivation
15a	1% Pd/Al_2O_3 (1.0 mg)	22	0	0	58.9 (560)[a]	—	—	—
15b	1% Pd/Al_2O_3	22	2 × 1	3 and 0		0	29.4	49.9
15c	1% Pd/Al_2O_3	22	1	0.6		0	24.4	41.4
16a	1.1% Pd/SiO_2 (1.0 mg)	7	0	0	40.5 (1100)[a]		—	—
16b	1.1% Pd/SiO_2	7	1	2.0		0	1.0	2.3
17a	1% Pd/Al_2O_3 (2.1 mg)	5.5	0	0	70 (1260)[a]	—	—	—
17b	1% Pd/Al_2O_3	5.5	1	4.4		0.75	20.7	29.6
18a	3% Pd/SiO_2 (0.9 mg)	10	0	0	58.9 (450)[a]	—	—	—
18b	3% Pd/SiO_2	10	2 × 1	3.7 and 0		0	7.0	11.9
19a	Pd black (0.4 mg)	0.6	0	0	82.5 (720)[a]	—	—	—
19b	Pd black	0.6	1	13.7		4.1	5.2	6.0
19c	Pd black	0.6	1	0.41		0	19.6	23.7
20a	Pd black (0.5 mg)	0.6	0	0	82.9 (580)[a]	—	—	—
20b	Pd black	0.6	3 × 1	13.2, 0.6, and 0		0.71	6.7	8.1
21a	Pd black (0.4 mg)	0.6	0	0	61.4 (530)[a]	—	—	—
21b	Pd black	0.6	1	19.6		1.0	6.8	11.0

[a] Number of cyclohexene molecules converted per surface Pd atom (turnover number).

went up and down slightly. Clearly, the oxidation effect is related to Si and not C.

On the other hand, the effect could occur in the absence of Si, so experiments were conducted to evaluate the effect of oxidation in the absence of Si on the fresh supported catalyst at room temperature (Table 8). Within experimental error, conversions percentages are the same before and after oxygen treatment. Likewise, silica gel used for catalyst preparation (experiment 27) exhibits no catalytic activity either for decomposing triethylsilane or for hydrogenating cyclohexene.

TABLE 8

Standard Experiments

			%Conversion of 2 μl cyclohexene	
Expt.	Catalyst	Et_3SiH (μl)	Before oxidation	After oxidation
24	0.65%Pd/SiO_2	0	53.8	53.4
25	1.45%Pd/SiO_2	0	17.3	17.4
26	Pd black	0	82.9	82.3
27	Silica gel[a]	10	0	0

[a] 10 μl of Et_3SiH was injected and no ethane was formed.

Since the effects could be due to Si or a thin overlayer of SiO_2 covering the Pd (13), we introduced a typical Pd poison, CS_2 (14). The injection of carbon disulfide (CS_2) should lower the percentage conversion of cyclohexene if Pd metal is exposed. Experiment 23h (Table 5) reveals that injection of 2 × 1 μl of CS_2 lowers the conversion from 80.9 to 0% and subsequent oxidation restores part of the activity (67%). We conclude that the hydrogenations are occurring on a Pd surface rather than a SiO_2 overlayer. The possibility remains, however, that hydrogen is dissociating on Pd then spilling over onto SiO_2 where hydrogenation is occurring.

Not surprisingly, SiO_2 forms on the surface during oxidation as shown by FTIR spectroscopy. Bands appear at 1061 (Si–O–Si antisymmetric stretch), 768 (Si–O–Si symmetric stretch), and 423 cm^{-1} (Si–O–Si, O–Si–O symmetric bending). Each of these is decreased to frequencies lower than those that occur in bulk silica, suggesting that bonds to Pd may exist. Additionally, migration of Si between the bulk and surface of the Pd particles is shown by XPS measurements which reveal that the concentration of SiO_2 increases on the surface after oxidation (9).

At saturation, small Pd particles contain more than three Si atoms for every Pd atom. In a microbalance (TGA) experiment the 0.34% Pd/SiO_2 (86%D) catalyst was cleaned by repeated oxidation–reduction cycles at 200°C to constant weight and then silated with SiH_4 at 200°C to constant weight. The initial weight of 2.9318×10^{-3} g increased to 2.9408×10^{-3} g or 3.4 Si atoms for every Pd atom.

A similar microbalance experiment with Et_3SiH yielded ambiguous results, presumably because Et_3SiH decomposition deposits Et_xSi- residues and carbonaceous residues on the surface. In fact, silation resulted in a much larger weight increase than could be accounted for by Si alone. However, after oxidation at 25°C for 10 h and reduction at 200°C for 4 h, the weight decreased until the final weight corresponded to approximately the ratio of Si/Pd found for the SiH_4 silated catalyst in the previous paragraph. Likely, the oxidation at 25°C was too mild to remove residues; rather, reduction at 200°C removed residues. Existence of such residues was consistent with CO and H_2 chemisorption experiments.

CO adsorption decreases with increasing decomposition of Et_3SiH (Table 9). When several different samples of the 0.46% Pd/SiO_2 (62%D) were subjected to different amounts of Et_3SiH at 250°C, their CO adsorption capacities decreased with increased amounts of Et_3SiH decomposed. This suggests that CO adsorption is blocked at the surface by Si, Et_xSi- residues, or carbonaceous residues. H_2 chemisorption supports the latter two suggestions.

Dynamic H_2 and CO chemisorption measurements, performed like the CO chemisorptions described above, showed similar results for the Et_3SiH silated 1% Pd/Al_2O_3 (22%D) catalyst. Initial silation decreased H_2 chemisorption capacity and oxidation restored some, but not total, capacity. The CO chemisorption capacity of the same sample was measured before silation but not before oxidation; however, after oxidation, the CO capacity was also reduced. Following these, more careful static H_2 chemisorption measurements were performed on catalysts silated with both Et_3SiH and SiH_4 to differentiate between Si alone and surface residues from Et_3SiH decomposition.

In the static chemisorption apparatus previously described (15), samples of the 0.46% Pd/SiO_2 (62%D) and Pd black (0.51%D) catalysts were subjected first to cleaning (H_2, 10^{-5} Torr, 2 h), then, to three H_2 chemisorption measurements (68°C), next, to silation with SiH_4 (2 h, 25°C, to constant pressure), and finally, to three more H_2 chemisorption measurements. These measurements are shown in Table 10 along with similar measurements for Et_3SiH silation, which were accomplished in a separate U-tube reactor by injecting 500 mg Et_3SiH (during 10 min) into H_2 flowing over the cleaned (H_2, 2 h, 300°C) catalyst at 250°C, cooling to 25°C, purging with He, and oxidizing with O_2. These Et_3SiH silated–oxidized samples were transferred to the chemisorption apparatus where the %D measurements were performed. Comparisons of the %D's for the differently silated catalysts reveal no change in %D when silated with SiH_4, but lower %D when silated with Et_3SiH. Thus Si does not interfere with H_2 chemisorption but residues from Et_3SiH decomposition do.

Although Si does not interfere with the quantity of H_2 chemisorbed, it does interfere with the nature of the chemisorption. DSC measurements (Table 12) of the heats of adsorption of H_2 at 100°C on both the unsilated and silated–oxidized (SiH_4 at 250°C air at ambient) 0.34% Pd/SiO_2 (86%D) catalysts result in only 58% of the heat of adsorption on the silated–oxidized catalyst as on the unsilated catalyst. The surface has changed. This change in the nature of the surface is again reflected in the catalytic activities for hydrogenation of alkenes (already described), the hydrogenation of benzene, and the hydrogenolysis of Et_3SiH.

Hydrogenations were also performed in the gas phase with both cyclohexene and benzene over a Pt/SiO_2 cata-

TABLE 9

CO Chemisorption Capacity as a Function of Et_3SiH Hydrogenolyzed over Pd/SiO_2[a]

Expt.	Weight	μl Et_3SiH after oxidation	μl of CO	μl CO/mg of catalyst
28	145.7	0	53.9	0.37
29	127.0	3	34.3	0.27
30	140.9	5	31.0	0.22
31	157.2	10	14.2	0.09

[a] Catalyst, 0.46%, $PdSiO_2$; %D = 60.

TABLE 10

Hydrogen Chemisorption Data[a] for 0.46% Pd/SiO_2 (60%D) and Pd Black (0.51%D) before and after Treatment with Et_3SiH_4/O_2

Catalyst	Treatment	%Exposed atoms
0.46% Pd/SiO_2	Untreated; fresh; several months prior to treatments	61.6 ± 1.0[b]
0.46% Pd/SiO_2	Untreated; just prior to Et_3SiH/O_2 treatments	59.7 ± 1.1[b]
0.46% Pd/SiO_2	Treated with Et_3SiH/O_2	39.0 ± 1.3[b]
0.46% Pd/SiO_2	Untreated; just prior to SiH_4/O_2 treatments	59.7 ± 1.1[b]
0.46% Pd/SiO_2	Treated with SiH_4/O_2	61.3 ± 1.0[c]
Pd black	Untreated; fresh; several months prior to treatments	0.511 ± 0.005[b]
Pd black	Untreated; just prior to Et_3SiH/O_2 treatments	0.526 0.512[d] 0.519 ± 0.007[e]
Pd black	Treated with Et_3SiH/O_2	0.316 ± 0.003[b]
Pd black	Treated with SiH_4/O_2	0.578[f]

[a] Isotherms carried out at 68°C at H_2 pressures from 5 to 30 Torr.

[b] Average deviation of three measurements.

[c] Average deviation of four measurements.

[d] D_2 instead of H_2 used for isotherms; demonstrates absence of β-hydride phase during H_2 chemisorption at 68°C.

[e] Average deviation of above two measurements.

[f] Only one measurement.

TABLE 11

Pt/SiO_2[a] Activity and Selectivity as Functions of Et_3SiH Hydrogenolyzed

		%Conversion of 2 μl cyclohexene				%Conversion of 2 μl benzene			
Expt.	Et_3SiH (μl)	Initial	After poisoning	After oxidation	%Reactivation	Initial	After poisoning	After oxidation	%Reactivation
22a	0	88	—	—	—	57.9	—	—	—
22b	2 × 1		0.64	96.6	110		0	18.4	32
22c	2 × 1		0.75	98.8	112		0	4.9	8.5
22d	2 × 1		6.2	93.6	106.4		0	2.4	4.1
22e	2 × 1		6.7	66.1	75.1		0	0.6	1.0
22f	1		4.8	76.4	86.8		0	0.9	1.5
22g	1		3.8	51.7	58.7		0	0.7	1.2

[a] Catalyst, 0.825% Pt/SiO_2; dispersion, 81%.

lyst (0.825%Pt/SiO_2, 81%D). Hydrogenations were carried out first with cyclohexene and then with benzene as shown in Table 11. When only 2 μl of Et_3SiH was injected, benzene hydrogenation activity was completely poisoned and cyclohexene hydrogenation activity was almost completely poisoned. After oxidation, however, activities were very different.

Whereas 110% of the activity was restored for cyclohexene hydrogenation, only 32% was restored for benzene hydrogenation. Even after three cycles of poisoning–oxidation–reduction (experiments 22b–22d), the percentage conversion of cyclohexene was still about 6% higher than its original value, whereas benzene conversion was only 1% of original and never restored to its initial value. The percentage reactivation for benzene drops sharply after introducing several microliters of triethylsilane followed by oxidation.

DISCUSSION

The complete sequence of modification involves silation, oxidation, and reduction. Each of these has an effect on the catalyst and, therefore, on the catalytic reactions conducted on them.

TABLE 12

Calorimetric Measurements (J/g cat) of Hydrogen Adsorption on Pd Black and 0.34% Pd/SiO_2

		Pd black treated with		0.34% Pd/SiO_2	
Temp.	Pd black	Et_3SiH[a]	SiH_4[b]	Untreated	SiH_4 treated[b]
Ambient	5200	8.3	6.6	—	—
100°C	6100	24.8	172	15430	9000

[a] Pd black was treated in another apparatus with Et_3SiH (20, 4, 4, and 4 μl)) at 250°C followed by oxidation (O_2, 2 h, ambient) after each Et_3SiH treatment.

[b] Catalysts were treated with an indeterminate amount of SiH_4 in the DSC cell by passing SiH_4 over the catalyst on the sample pan.

Silation. Although silation is common in the semiconductor industry (16) and silation builds materials resembling metallic glass catalysts (17), deliberate modification of noble metal catalysts by silation is rare and its effects on catalytic activities have been only slightly explored (1, 18). Some explorations of catalytic activities have been made with similar materials prepared from high-temperature reduction of Pd/SiO_2 catalysts (19). The information generated in this present work shows that silation alone modifies Pd in several ways.

Modifications with SiH_4 and Et_3SiH produce different catalysts because the latter deposits carbonaceous residues on the surface. Principle evidence for carbonaceous residues rests with the hydrogen chemisorption measurements. Table 10 reveals that less hydrogen is chemisorbed (lower %D) on the Et_3SiH-treated Pd/SiO_2 than on the SiH_4-treated Pd/SiO_2. The same is true for Pd black. Nevertheless, the dominant effect of silation is not deposition of C but deposition of Si.

Several measurements show that Si deposition lowers surface Pd concentration. For example, CO chemisorption decreases after silation with Et_3SiH followed by oxidation (Table 9), and the heat of hydrogen chemisorption decreases after silation with both Et_3SiH and SiH_4 (Table 12), but the important results are that silation decreases catalytic activity.

Et_3SiH decomposition activity decreases with exposure (Table 3). Repeated injections of Et_3SiH generate smaller and smaller amounts of ethane until the catalyst ceases to decompose Et_3SiH. This decrease in Et_3SiH decomposition activity coincides with a decrease in hydrogenation activity (Tables 2 and 3). A decrease in hydrogenation activity also results from silation with SiH_4 (Table 5). In both cases, the decrease in hydrogenation activity is structure sensitive.

For low dispersed catalysts, hydrogenation activity decreases substantially with only a small amount of silation (Table 7, experiments 15b, 16b, 18, 19b, 20b, 21b, and 22b). In contrast, for highly dispersed catalysts, hydrogenation activity decreases slowly with even large amounts of silation (Tables 1 and 6, experiments 2a, 2b, 3a, 5a, 5b, and 9b–14b).

This difference between low and highly dispersed catalysts must reflect fundamental differences in the kind and/or distribution of active sites. For example, the larger particles should expose higher percentages of plane sites than the smaller particles. So one could conclude that silation poisons plane sites more than edge or corner sites. Poisoning planes should lower hydrogenation activity if addition occurs predominantly on planes, as we have proposed (3), rather than on corners (20, 21). Such a poisoning contrasts with deposition of metals such as gold on Pt and Pt particles. There, the preferred sites for depositions are edges and corners (22). On the other hand, one could conclude that corners and edges are indeed silated first, but because so few sites exist on the larger particles, poisoning is rapid. In contrast, on the smaller particles many such sites exist and poisoning requires more silation. Nevertheless, evidence from silation does not differentiate between these possibilities; additional evidence from oxidation and reduction helps differentiate.

Oxidation. Oxidation of unsilated catalysts causes no changes in hydrogenation activities (Table 8). But oxidation of silated catalysts causes substantial changes in hydrogenation activities and these changes correlate with particle size. However, since hydrogenation activities are the only reactions tested, little can be said about catalytic activities in the absence of hydrogen. Nevertheless, physical measurements (XPS and FTIR) reveal movement of Si and Pd.

XPS shows that oxidation draws Si to the surface of silated Pd (9). The surface ratio of Si to Pd (3.97) is higher on the Et_3SiH silated–oxidized Pd black than it is on the silated–unoxidized Pd black (2.35). Therefore, poisoning with Et_3SiH gradually coats the Pd surface with Si, which diffuses into its interior. Finally, the Si coat kills hydrogenation activity. However, oxidation converts Si to SiO_2 at the surface. Since the Si concentration at the surface is lowered by conversion into SiO_2, more Si diffuses from the bulk to the surface where it is oxidized too. This process increases the ratio of Si : Pd at the surface. Additionally, XPS shows that deliberate oxidation (exposure to O_2 in addition to air) of silated Pd decreases the surface ratio of $Si^0 : Si^{IV}$ from 0.480 to 0.225. The low initial value of 0.480 results from exposure to air during transport to the XPS apparatus. Deliberate oxidation with oxygen at room temperature produces more SiO_2 at the surface. SiO_2 at the surface is also confirmed by FTIR spectroscopy, in which Si–O bonds appear at the surface of silated–oxidized Pd. These IR bands are not typical of bulk silica.

Although SiO_2 covers part of the Pd surface, it does not seem to interfere with hydrogenation. In fact, small Pd particles exhibit high activity (in some cases higher activity) for hydrogenation than before silation–oxidation–reduction. Likely, oxidation also converts Pd^0 to PdO_2, but H_2 reduces PdO_2 back to Pd^0 during hydrogenation (9).

Reduction. Reduction seems to accomplish several things. First, reduction converts PdO_2 to Pd^0, a fact supported by poisoning with CS_2 (Table 5, experiment 23h). Also, reduction restores some Et_3SiH hydrogenolysis activity, and reduction cleans the surface by removing residues from Et_3SiH decomposition. Finally, reduction changes hydrogenation activity.

Silation diminishes and oxidation–reduction restores cyclohexene and cyclopentene hydrogenation activities. This restoration is structure sensitive. Large particles exhibit less than 50% restoration (Table 7) and small particles exhibit 100% restoration (Table 6). Indeed, some catalysts exhibit greater than 100% restoration. However, this is not the case for benzene hydrogenation activity. Benzene hydrogenation activity is never fully restored, a phenomenon also observed for high-temperature reduced Pd/SiO_2 (23).

Partial restoration of benzene hydrogenation activity compared to complete restoration of cyclohexene hydrogenation activity signals different sites for the two hydrogenations. Over the same catalyst with the same silation–oxidation–reduction sequence, hydrogenation activity is never restored as completely for benzene as for cyclohexene. This implies a larger cluster (24), multiplet (25), or ensemble (26) requirement for benzene than for cyclohexene hydrogenation and further signals the presence of a new and reconstructed surface resulting from the silation–oxidation–reduction sequence.

Reconstructed surface. Several results point to the existence of a reconstructed Pd surface after silation–oxidation–reduction. In addition to changes in hydrogenation activities for cyclohexene, cyclopentene, and benzene is the change in hydrogenolysis activity for Et_3SiH. Also, surface compositions of Pd, Si, and SiO_2 show changes. These, coupled with the decreased heat of H_2 adsorption revealed by DSC, decreased CO chemisorptive capacity, and changed surface compositions revealed by XPS, all point to a reconstructed Pd surface. But the question remains: why does the reconstructed Pd surface have different catalytic activity? What is the mechanism?

Possible mechanism(s). Two processes occur simultaneously with Et_3SiH treatment of Pd catalysts: (i) carbonaceous residues accumulate on the surface and (ii) silicon coats the surface and diffuses into the bulk of the Pd particle. Since SiH_4 produces similar catalytic results, the carbonaceous residues seem to be insignificant and, additionally, they appear to be removed by hydrogen. So the significant process is silicon deposition (silation) and the resulting surface modification.

The simplest mechanism for this process we stated before: "During poisoning the silicon atoms dissolve into Pd or Pt crystallites forming a Pd–Si (or Pt–Si) alloy which gradually loses its activity at higher Si concentrations. Upon oxidation, Si returns to the surface and is oxidized to SiO_2. Metal is also oxidized at the surface but reduction with H_2 reduces only the metal particles which now present a new and different surface" (7–9). [A similar proposal, but from a different starting point, has been advanced to explain catalytic results obtained from high-temperature reduced and oxidized Pd/SiO_2 (16).] However, what kind of new surface forms, where is the SiO_2 located, and why is hydrogenation activity restored more for small than for large particles?

Likely, the new Pd surface is different; otherwise, it would not exhibit different catalytic activity. The new active surface could be composed of Pd only, Pd–Si alloy, Pd with patches of SiO_2, or some combination of all of these. Since SiO_2 as well as Si^0 are on the surface of the silated–oxidized Pd, the surface must be composed of Pd and/or Pd–Si alloy with patches of SiO_2. A Pd-like surface is favored because CS_2 poisons its hydrogenation activity. Since Pd–Si alloys are catalytically similar to Pd (15), we conclude that the new active surface is a Pd–Si alloy (areas of pure Pd cannot be excluded) with patches of SiO_2. Dilution of surface Pd by Si in a Pd–Si alloy would reduce the Pd cluster (multiplet or ensemble) size and possibly account for reduced benzene hydrogenation activity. However, alkene hydrogenation activities are more difficult to explain.

Alkene hydrogenation activities over these unsilated Pd catalysts typically exhibit mild structure sensitivity. As particle sizes decrease, activities increase through a maximum near 60%D and then fall (3, 27). Similar behavior occurs for other reactions (28, 29). Because edge populations of regular octahedra and cubooctahedra also rise through maxima, we believe edges are important components of the active sites for these reactions. Therefore, the increasing restoration of hydrogenation activities with increasing dispersions on these silated Pd catalysts agrees with our belief that edges are important. However, after reaching a maximum around 50%D, the activities remain high even for the smallest particle, so this explanation is incomplete. If predicted populations of edges on regular crystallites were the only factor involved, catalytic activities should decrease above approximately 70%D. But they remain relatively constant. So, the chaotic topography of SiO_2 islands in a Pd–Si ocean is different from the ordered topography of a uniform Pd sea.

The difference could result from the islands of SiO_2, the Pd–Si surface, or the interaction of the two. Indeed, SiO_2 has been implicated in hydrogen spillover and hydrogen penetration of overlayers of silica have been demonstrated (11). But these explanations seem inadequate because CS_2 poisons hydrogenation. We conclude, therefore, that the principle difference must reside with the Pd–Si surface, which presents a favorable surface for hydrogenation, even though its surface area is smaller than before silation–oxidation–reduction and even though it is partly covered by SiO_2. The Pd–Si surface must possess a unique property favorable for hydrogenation. This property may be a dominance of edges resulting from some unique shape, for example, a cigar shape, as suggested by Masel's calculations (30). Or it may be a dominance of edges resulting from increased size and stability imparted by Si to the tiny Pd particles.

We have proposed that the rate maxima at approximately 60%D for several reactions (alkene hydrogenation, double-bond migration, aldehyde decarbonylation, and oxirane hydrogenolysis) result from edge maxima (31). Thus, particles larger than 60%D are too inflexible to reconstruct into many steps while particles smaller than 60%D are too small to accommodate steps and too flexible to maintain stable structures. Optimum flexibility is important and Si likely alters flexibility.

Si alloyed to nanoscale Pd particles imparts not only new chemical characteristics, but also new physical characteristics. The particles are larger and probably less flexible than before silation. Because they are larger, they can accommodate ridges and steps and because they are less flexible, they retain them. Since the larger particles are not flexible enough to form many ridges before silation, they do not experience complete restoration after silation.

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