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The Effect of Pretreatment on Pd/C Catalysts

II. Catalytic Behavior

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Pd catalysts were anaerobically prepared using a Pd acetylacetonate precursor and a high surface area turbostratic carbon black which had been pretreated to change its surface functionalities and remove sulfur impurities. These Pd/C catalysts exhibited suppressed chemisorption and hydride formation, which was attributed to the presence of carbon atoms on the surface and in the bulk of Pd particles. The effect of these carbon atoms on three probe reactions—benzene hydrogenation, CO hydrogenation, and CO oxidation—was examined. If sulfur were not removed from the carbon, it contaminated the Pd surface and caused a drastic decrease in benzene hydrogenation activity and a decrease in both activity and activation energy in CO hydrogenation. Coverage of the Pd surface by carbon atoms had different effects on the three probe reactions. The turnover frequency (TOF) in benzene hydrogenation, a structure-insensitive reaction, was not affected for Pd supported on the clean carbon blacks, although specific activity was lower than expected based on crystallite size, and the apparent activation energies (8.5–10 kcal/mole) were slightly lower than anticipated. In contrast, the TOFs for methanation were substantially decreased, and the apparent activation energies varied over a wide range (5–30 kcal/mole). Under an oxidizing environment, these Pd/C catalysts had TOFs for CO oxidation similar to or higher than those for Pd/Al_2O_3 catalysts, and similar activation energies near 24 kcal/mole were obtained, thus indicating that the Pd surfaces present were alike.

INTRODUCTION

Carbon-supported palladium catalysts are widely used in industrial hydrogenation reactions (1), but the type of carbon and its pretreatment may affect Pd dispersion as can other parameters such as the metal precursor, the solvent, the method of preparation, and the catalyst pretreatment (2, 3). Suh *et al.* have recently reported that oxygen groups on activated carbon and carbon black increased Pd dispersion, but no corresponding increase in activity in the liquid-phase hydrogenation of dinitrotoluene was observed (4). Furthermore, carbon-supported Pd has exhibited lower specific activity compared to Pd on other supports for benzene hydrogenation (5) and 1,3-butadiene hydrogenation (6). Hydrogen spillover from Pd to carbon has been demonstrated by TPD experiments and H_2 titration measurements (3, 6, 7). A better understanding of the surface chemistry of carbon supports could reduce variations among batches of catalysts; however, few studies have tried to control the surface chemical properties of carbon support surfaces and determine their influence on catalytic behavior, and little emphasis has been placed on working with clean carbons free of contaminants such as sulfur.

In the present work, a carbon black with ppm metallic impurities but containing 1.3% sulfur was cleaned by a high temperature treatment (HTT) to remove reactive S and oxygen-containing functional groups from the carbon surface. However, certain types of surface groups can be replaced by appropriate procedures (8). Pd acetylacetonate dissolved in THF was used to avoid the presence of Cl and H_2O (9); thus the influence of pretreatment on the catalytic behavior of carbon-supported Pd in the absence of significant amounts of impurities like S, Cl, and trace metals was investigated, and the anaerobic conditions eliminated complications due to exposure to O_2 and H_2O. This family of Pd/C catalysts was thoroughly characterized by XRD, TEM, N_2 adsorption, H_2, O_2, and CO chemisorption, and calorimetry, as discussed in the preceding paper (9). The carbon pretreatment did not affect the dispersion of the Pd in these catalysts but carbon was present both on the Pd surface and in the bulk, which suppressed chemisorption and hydride formation (9). Benzene and CO hydrogenation were the two probe hydrogenation reactions and CO oxidation was the probe oxidation reaction chosen to study the effect of pretreatment as well as the influence of surface and bulk carbon atoms on the catalytic behavior of Pd.

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EXPERIMENTAL

Catalyst Preparation

Details have been given previously (9, 10), but a brief summary is as follows. Black Pearls 2000 (BP2000, Cabot Corp.), a carbon black with ppm metallic impurities and 1.3 wt% S designated C-AS IS (10), was given a high temperature treatment (HTT) under flowing H_2 or Ar for 16 h at 1223 K to remove reactive sulfur and oxygen from its surface (11). These two samples are labelled C-HTT-H_2 and C-HTT-Ar, respectively. The C-HNO_3 sample was prepared by boiling a portion of the C-HTT-Ar sample in 15.8 *N* HNO_3 for 6 h (8). An incipient wetness method using Pd acetylacetonate dissolved in dried, degassed tetrahydrofuran (THF) and standard Schlenk line techniques was employed to anaerobically prepare the catalysts, which were transferred without air exposure to reaction cells in a N_2-purged glove box. Two Pd/C-HTT-H_2 catalysts prepared by incipient wetness using $PdCl_2$ (2.1% Pd/C and 3.4% Pd/C), and a commercial 3.61% Pd/C catalyst (Johnson Matthey) were also investigated.

Benzene Hydrogenation

The kinetics of vapor-phase benzene hydrogenation were determined in a differential, fixed-bed reactor system described earlier (12). Ultrahigh purity H_2 and He (99.999%, MG Ind.) were further purified by passing them through Oxytraps (Alltech Assoc.) and molecular sieve traps, and O_2 (99.999%, MG Ind.) was purified by passage through a molecular sieve trap. Benzene (J.T. Baker Co., 99.994$^+$%) was degassed by freeze–thaw cycles under N_2, then introduced with a syringe pump into the preheated reactor inlet line where it was vaporized. The reaction was carried out after reduction of 0.15–0.20 g catalyst *in situ* at 573 K (9) under 50 Torr of benzene and 680 Torr of H_2 at a total flow rate of 47 sccm. Benzene conversion was kept below 10% to minimize heat and mass transfer effects. Arrhenius plots were obtained between 323 and 435 K for all Pd/C catalysts except the Pd/C-AS IS catalyst, which required a range 416–500 K. For each data point, a bracketing technique was used which consisted of a 25-min period under reaction conditions, a 10-min period for sample analysis, and a 25-min period under pure H_2 to minimize deactivation and adjust temperature for the next data point. An ascending temperature sequence was followed by a descending temperature sequence to check for deactivation. The reaction was also carried out over the 2.3% Pd/C-HNO_3 catalyst after an oxygen regeneration treatment using 2% O_2 and 98% He at 573 K for 30 min followed by the standard reduction procedure at 573 K.

CO Hydrogenation

All kinetic data were obtained at 1 atm using an H_2/CO ratio of 3:1 in a differential, plug-flow reactor system, described previously (11). Ultrahigh purity H_2 and He (99.999%, MG Ind.) were further purified by passing them through Oxytraps (Alltech Assoc.) and molecular sieve traps, and CO (99.99%, Matheson) and O_2 (99.999%, MG Ind.) were purified by passage through a molecular sieve trap. A 0.5 g sample was used for all Pd/C catalysts except the commercial 3.61% Pd/C catalyst (0.24 g). All the catalysts were given the standard *in situ* reduction pretreatment in 573 K described previously (9). Arrhenius plots were obtained over the temperature range 573–723 K using a bracketing technique and an ascending/descending temperature sequence to check for deactivation. This reaction was also carried out on 2.8% Pd/C-HTT-H_2 after a regeneration treatment using 10% O_2 and 90% He at 573 K for either 30 or 125 min followed by reduction at 573 K.

CO Oxidation

All kinetic data were obtained in a differential, plug-flow reactor using approximately 0.1 g catalyst which had been previously reduced in H_2 at 573 K. The reaction system has been described in detail elsewhere (13). Ultrahigh purity H_2 and He (99.999%, MG Ind.) were further purified by passage through Oxytraps (Alltech Assoc.) and molecular sieve traps, and CO (99.99%, Matheson) and O_2 (99.999%, MG Ind.) were purified by passage through molecular sieve traps. The CO oxidation reaction was conducted at 1 atm under 38 Torr O_2 and 38 Torr CO over the 2.8% Pd/C-HTT-H_2 catalyst, and under 132 Torr O_2 and 26 Torr CO over the 2.3% Pd/C-HNO_3 catalyst (balance He). A mixture of O_2 and He was passed over the catalyst for 5 min, followed by the appropriate CO, O_2, and He mixture for 25 min to attain steady state, and the product stream was then analyzed. The catalyst was purged in He for 30 min and heated or cooled to the next reaction temperature under He. Arrhenius plots were obtained over the temperature range 393–438 K using an ascending/descending temperature sequence to check for deactivation.

RESULTS

Benzene Hydrogenation

The activities and turnover frequencies (TOFs) at 413 K and activation energies in the benzene hydrogenation reaction are shown in Table 1, along with the chemisorption uptakes. The pretreatment of the carbon support had a significant effect on the activities of these Pd/C catalysts as it increased activities (per gram of Pd) up to 240-fold, i.e., the Pd/C-AS IS sample was always significantly less active than any of the Pd catalysts using a clean HTT carbon support. This is attributed to sulfur contamination of the Pd surface since sulfur is a well-known poison for hydrogenation reactions (14) and, in addition, S-containing gases were evolved from this catalyst during pretreatment

TABLE 1

Benzene Hydrogenation over Pd/C Catalysts; P_{Bz} = 50 Torr, P_{H_2} = 680 Torr

Catalyst	Activity[a] (μmole Bz/s·g cat)	Activity[a] (μmole Bz/s·g Pd)	TOF × 10^3 (s^{-1}) based on H_{ad}	TOF × 10^3 (s^{-1}) based on CO_{ad}	E_a (kcal/mole)	Irrev. uptake (μmole/g cat) H_2	Irrev. uptake (μmole/g cat) CO	Particle size[b], d_S (nm)
2.6% Pd/C-AS IS[c]	0.01	0.4	1.6	0.4	8.5	3	26	4.0[b]
2.1% Pd/C	1.99	94.8	62	27	8.5	16	75	20.7[b]
2.8% Pd/C-HTT-H_2	1.27	45.4	159	36	9	4	35	4.8[b]
2.8% Pd/C-HTT-H_2[d]	2.60	92.7	—	100	9.9	—	26	4.8[b]
3.1% Pd/C-HTT-Ar	0.88	28.4	73	33	9.2	6	27	5.6[b]
2.3% Pd/C-HNO_3	0.18	7.8	45	30	9.4	2	6	7.2[b]
2.3% Pd/C-HNO_3[e]	0.52	22.6	65	40	10.1	4	13	—
3.61% Pd/C (Commercial)	5.20	144.4	87	52	11.5	30	101	3.8[b]
1.36% Pd/C[c,f]	0.06	4.4	23	3.5	8.5	1.3	17	55.6[h]
2.48% Pd/SiO_2[g]	6.95	280	41	43	11.6	87	170	1.5[h]

[a] At 413 K.
[b] From TEM.
[c] After use in kinetic runs.
[d] After O_2 pretreatment at 573 K, cooling in O_2 to 300 K, purging in He, then heating in H_2 to a reaction temperature of 373 K.
[e] After O_2 pretreatment at 573 K prior to reduction.
[f] From Ref. 5.
[g] From Ref. 20.
[h] Based on H_2 chemisorption.

(9, 15). The highest activity (per gram of Pd) was attained with the 2.1% Pd/C and Pd/C-HTT-H_2 catalysts, followed by the Pd/C-HTT-Ar and Pd/C-HNO_3 samples; however, the catalysts made from $Pd(AcAc)_2$ and the HTT carbons had somewhat higher TOFs based on either H_2 or CO uptakes. The TOFs based on adsorbed H exhibited more than a threefold variation while those based on chemisorbed CO were quite consistent; consequently, CO chemisorption, which was less suppressed than H_2 chemisorption on these catalysts, appears to be a better measure of the active Pd surface. The TOFs, especially those based on CO, for Pd supported on the HTT carbons are quite consistent with those obtained previously for Pd/SiO_2 catalysts, particularly since the latter values were based on adsorption on the used catalysts, which gave lower uptakes. The TOFs for Pd/C-HNO_3 were very similar to those for the catalysts which had oxygen removed from the surface, thus indicating that introduction of oxygen groups on the carbon surface did not alter activity. After an oxygen treatment to clean the Pd crystallites, the activity of Pd/C-HNO_3 was increased threefold while the TOF increased only by a factor of 1.4; this is associated with C atoms present on the Pd surface after the pretreatment, as discussed later.

The Arrhenius plots for the different Pd/C catalysts are shown in Fig. 1. All the Pd/C catalysts had activation energies of 9.1 ± 1.0 kcal/mole, which are slightly lower than those observed for Pd on other supports but consistent with values previously obtained for C-supported Pd (5). After treating the Pd/C-HNO_3 sample in oxygen, the activation energy increased slightly from 9.4 to 10.1 kcal/mole. No temperature-dependent maximum in activity was observed because the temperature range was below 495 K, where the maximum occurs (5). The commercial Pd/C catalyst had the highest benzene hydrogenation activity and a somewhat higher activation energy of 11.5 kcal/mole, but the TOFs were similar to those for Pd supported on the HTT carbons. Some of this variation may be due to the presence of promoters (mainly Ca and Na) that exist in this commercial catalyst (15). No mass transfer limitations were evident upon applying the Weiss criterion to check for diffusional effects in this reaction (15). No significant deactivation was observed in these catalysts during the descending-temperature sequence except for the Pd/C-HTT-H_2 catalyst. The chemisorption uptakes on the Pd/C-AS IS catalyst after benzene hydrogenation were similar to those on the fresh catalyst, hence TOF values for the other catalysts were based on uptakes on the fresh samples (9).

CO Hydrogenation

The Pd dispersions, hydride ratios, activities, TOFs, and activation energies for the different catalysts in the CO

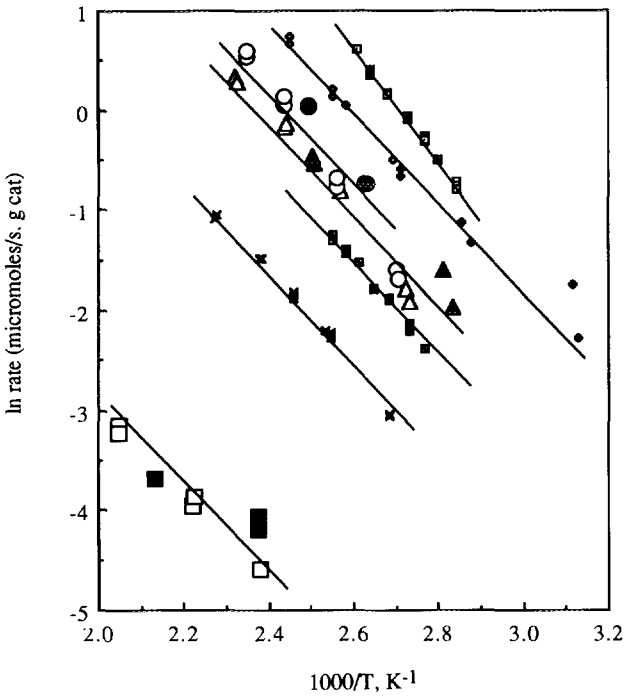

FIG. 1. Arrhenius plots for benzene hydrogenation over Pd/C catalysts reduced at 573 K: (◇, ◆) 2.1% Pd/C, (□, ■) Pd/C-AS IS, (○, ●) 2.8% Pd/C-HTT-H_2, (△, ▲) 3.1% Pd/C-HTT-Ar, (×, ×) 2.3% Pd/C-HNO_3, (⊡, ⊞) 3.61% commercial Pd/C, and (◰, ⊠) 2.8% Pd/C-HTT-H_2 after O_2 pretreatment for 30 min. Symbol pairs represent increasing T (second symbol) and decreasing T (first symbol).

hydrogenation reaction are shown in Table 2. Activities were extrapolated to 548 K from the Arrhenius plots to allow comparison with previous studies. Methane was the only hydrocarbon detected. No activity was detected below 633 K for 2.8% Pd/C-HTT-H_2, 2.6% Pd/C-AS IS, and 2.3% Pd/C-HNO_3, below 658 K for 3.1% Pd/C-HTT-Ar, or below 673 K for 2.1% Pd/C and 3.4% Pd/C, while the commercial 3.61% Pd/C catalyst showed no detectable activity up to 713 K. This is in contrast to the behavior of other Pd catalysts with comparable Pd surface area in which activities were detectable at temperatures as low as 523–573 K. The Arrhenius plots are shown in Fig. 2. Conversions were below 4%. During the CO hydrogenation reaction, only peaks corresponding to CO, H_2, CH_4, and H_2O were seen for the catalysts made from $PdCl_2$, Pd/C-HTT-H_2, and Pd/C-HTT-Ar, but a CO_2 peak was also observed with Pd/C-HNO_3 above 603 K, which can be attributed to the decomposition of oxygen-containing species on the carbon surface (8). Consistent with this explanation, no CO_2 peak was present when the reaction temperature was lowered, and a larger weight loss of 23% occurred for this catalyst compared to values of 6–9% for the other catalysts (15); the expected weight loss due to decomposition of the $Pd(AcAc)_2$ precursor is about 6%. No CH_4 was detected when only H_2 was flowing over the catalyst, thus showing the absence of any Pd-catalyzed gasification of the C support. This is consistent with a study of Pt dispersed on carbons with and without surface groups which found that no CH_4 was formed under 5% H_2 up to 1200 K (16).

The Arrhenius plots for these catalysts for methanation are shown in Fig. 2. The activation energies for these catalysts vary from 13 to 30 kcal/mole for Pd supported on the HTT carbons and fall within the range for Pd on other supports (17); however, it was only 5 kcal/mole for Pd supported on the untreated carbon. Severe deactivation was observed, even to the extent that no activity was detected with the 2.1% Pd/C, Pd/C-HTT-Ar, and Pd/C-HNO_3 catalysts during the descending temperature runs.

CO hydrogenation was also conducted on two 2.8% Pd/C-HTT-H_2 samples after either a 30 min or a 125 min regeneration in oxygen at 573 K. These two samples became active at lower temperatures after either oxygen pretreatment, although the activities at higher temperature were slightly lower than those for the catalyst without pretreatment. After the CO hydrogenation reaction, chemisorption was measured on the Pd/C-HTT-H_2 and Pd/C-HNO_3 catalysts. The hydrogen uptakes remained unchanged while the CO uptakes decreased slightly on one catalyst and increased slightly on another; however, the biggest change was in the hydride ratios, which doubled to 0.47 and 0.64, respectively, i.e., they moved closer to the expected ratio of 0.66 (9, 15).

CO Oxidation

The activities, TOFs, and activation energies for the two catalysts used in this reaction are listed in Table 3, along with the appropriate dispersions, and the Arrhenius plots for CO oxidation are shown in Fig. 3. The activities have been adjusted to standard conditions of 132 Torr O_2 and 26 Torr CO at 400 K to allow comparison with previous values using the appropriate rate equation, i.e., $r = kP_{O_2}^{0.3}P_{CO}^{-0.6}$ (18). The TOFs for the two Pd/C catalysts are comparable to or higher than those on Pd/δ-Al_2O_3, while the activation energies are similar to those reported previously (18). The Pd/C-HNO_3 catalyst, which chemisorbed a large amount of O_2 at 300 K but much less CO, had a very high TOF.

DISCUSSION

Industrial carbon-supported metal catalysts used for hydrogenation reactions can at times exhibit significant batch-to-batch variations in catalytic behavior (1, 2, 19). Pd/C catalysts have been found to have lower specific activities (i.e., turnover frequencies) than Pd on oxide supports for benzene and butadiene hydrogenation (5, 6). Thus the catalytic performance of Pd dispersed on a single carbon in three well-studied probe reactions—benzene hydroge-

TABLE 2

CO Hydrogenation over Pd/C Catalysts; $H_2/CO = 3$, $P = 1$ atm

Catalyst	Bulk hydride ratio (H_{ab}/Pd_b)	Dispersion (H/Pd)	Dispersion (CO/Pd)	Activity × 10^3 (μmole CH_4/s·g cat) at 548 K[a]	Activity × 10^3 (μmole CH_4/s·g cat) at 648 K	TOF × 10^3 @ 648 K (s^{-1}) H_2	TOF × 10^3 @ 648 K (s^{-1}) CO	E_a (kcal/mole)
2.6% Pd/C-AS IS	0.28	0.06	0.11	2.20	4.5	0.32	0.17	5
2.8% Pd/C-HTT-H_2	0.21	0.03	0.13	0.96	63.5	7.9	1.8	30
2.8% Pd/C-HTT-H_2[b]	0.38[c]	0.03	0.11	4.3	47.2	5.9	1.6	17
2.8% Pd/C-HTT-H_2[d]	0.38[c]	0.03	0.11	0.3	16.1	2.0	0.56	26
3.1% Pd/C-HTT-Ar	0.23	0.04	0.09	0.14	6.7	0.56	0.25	28
2.3% Pd/C-HTT-HNO_3	0.35	0.02	0.03	0.48	3.1	0.79	0.52	13
2.1% Pd/C	0.68	0.16	0.38	1.61	11.3	0.35	0.15	14
3.4% Pd/C	0.36	0.13	0.35	0.16	2.9	0.07	0.03	20
Pd powder[e]	—	—	0.05	0.5	45.4	—	10.8	32
2.48% Pd/SiO_2[f]	0.55[c]	0.26	0.27	7.1	413	6.9	6.5	29

[a] Extrapolated values.
[b] Pretreated in 10% O_2 at 573 K for 30 min prior to reduction.
[c] After kinetic runs.
[d] Pretreated in 10% O_2 at 573 K for 2 h prior to reduction.
[e] From Ref. (36).
[f] From Refs. (20, 37).

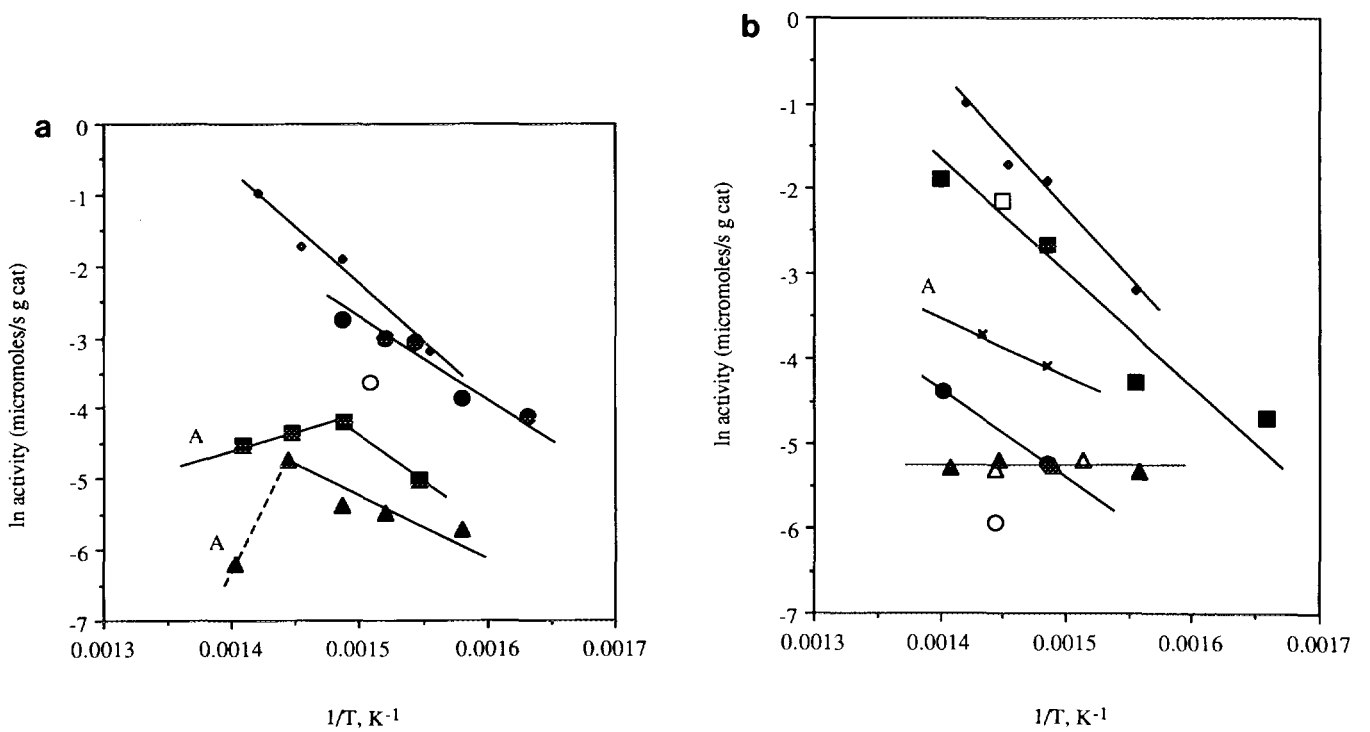

FIG. 2. (a) Arrhenius plots for CO hydrogenation (1 atm, $H_2/CO = 3$) over Pd/C catalysts reduced at 573 K: (◇, ◆) 2.8% Pd/C-HTT-H_2, (○, ●) 2.8% Pd/C-HTT-H_2 after O_2 pretreatment for 30 min, (□, ■) 3.1% Pd/C-HTT-Ar, and (△, ▲) 2.3% Pd/C-HNO_3. Closed symbols represent increasing T and open symbols represent decreasing T. The label A indicates no detectable activity during descending temperature run. (b) Arrhenius plots for CO hydrogenation (1 atm, $H_2/CO = 3$) over Pd/C catalysts reduced at 573 K: (◇, ◆) 2.8% Pd/C-HTT-H_2, (□, ■) 2.8% Pd/C-HTT-H_2 after O_2 pretreatment for 125 min, (○, ●) 3.4% Pd/C, (△, ▲) 2.6% Pd/C-AS IS, and (×) 2.1% Pd/C. Closed symbols represent increasing T and open symbols represent decreasing T. The label A indicates no detectable activity during descending temperature run.

TABLE 3

CO Oxidation over Pd/C Catalysts (T_{red} = 573 K); T = 400 K, P_{CO} = 26 Torr, P_{O_2} = 132 Torr

Catalyst	Activity[a] (μmole CO_2/s·g cat)	Specific activity (μmole CO_2/s·g Pd)	Dispersion[a] (CO/Pd)	TOF × 10^3 (s^{-1}) based on CO_{ad}	E_a (kcal/mole)
2.8% Pd/C-HTT-H_2	0.26	9.3	0.13	7.4	24.0
2.3% Pd/C-HNO_3	0.18	7.7	0.03	30.0	24.6
2.1% Pd/δ-Al_2O_3[b]	0.29	13.8	0.17	8.7	18.4[b]
2.19% Pd/δ-Al_2O_3[b]	0.12	5.47	0.29	2.0	23.4[b]

[a] Fresh catalyst.
[b] Average values (Ref. (18)).

nation, CO hydrogenation, and CO oxidation—after a specific pretreatment of the carbon support is of interest.

In the preceeding paper, strong evidence was provided to show that these Pd crystallites, formed from $Pd(AcAc)_2$ decomposition on a clean, high temperature treated (HTT) carbon black can contain interstitial C atoms as well as C atoms on the Pd surface (9). These carbon atoms interacted with the Pd during the reduction and evacuation steps at 573 K, and they suppressed chemisorption, reduced Pd β-hydride formation, expanded the Pd lattice, increased somewhat the H_2 heat of adsorption, but decreased slightly the Q_{ad} values for CO. Either a treatment in O_2 at 573 K or reducing conditions above 673 K partially or completely reversed these trends, presumably by removing C atoms from the Pd crystallites. The simplest model capable of explaining this behavior invokes Pd crystallites partially covered by C atoms which also contained bulk C atoms in interstitial, octahedral sites normally occupied by protons when the β-phase hydride forms (9).

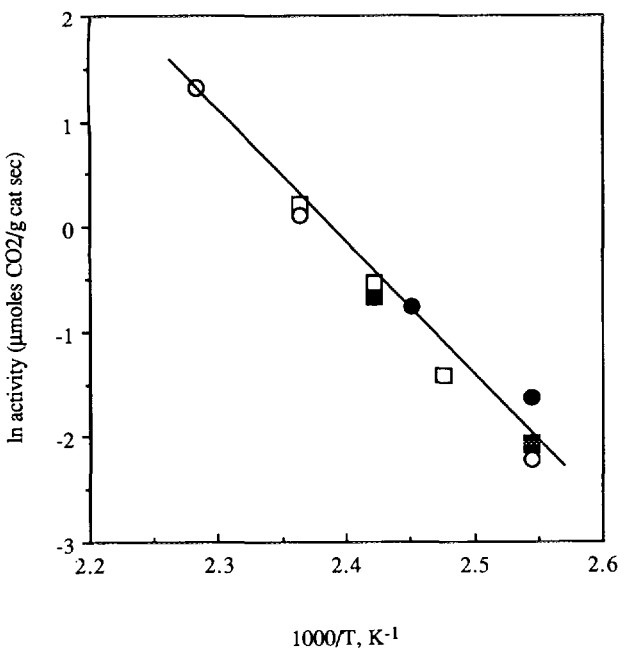

FIG. 3. Arrhenius plots for CO oxidation (1 atm, P_{CO} = 26 Torr and P_{O_2} = 132 Torr) over Pd/C catalysts reduced at 573 K: (○, ●) 2.8% Pd/C-HTT-H_2, (□, ■) 2.3% Pd/C-HNO_3. Closed symbols represent increasing T and open symbols represent decreasing T.

Benzene hydrogenation is usually considered to be a structure-insensitive reaction (5, 20, 21); if so, partial carbon overlayers would not be anticipated to have much effect on TOF values based on chemisorption to count Pd surface sites, presuming that bulk C atoms in the Pd lattice have no significant influence on the surface Pd atoms. This behavior is indeed observed, as indicated in Table 1. If the S-contaminated Pd/C-AS IS sample is excluded, TOF values are consistent, especially when based on CO chemisorption, and they are in excellent agreement with those measured on Pd/SiO_2 catalysts and a commercial Pd/C catalyst. This result strongly indicates an absence of any significant electronic effect due to C atoms in contact with surface Pd atoms. However, activities per gram of Pd are sometimes much lower than those for the Pd/SiO_2 and commercial Pd/C catalysts and, although lower Pd dispersions are partially responsible for this, this reason alone cannot account for the differences; thus, blockage of the Pd surface by carbon is implied by this comparison.

The apparent activation energies for benzene hydrogenation over these Pd/C catalysts were consistently 2–3 kcal/mole lower than the average E_a values for other Pd/oxide catalysts (5, 20). Although various explanations for this may exist, one is straightforward, based on a recent model developed by Lin and Vannice for benzene hydrogenation which proposes that the rate-determining step is the addition of the first H atom (22). The apparent rate constant in the numerator consists of the terms $kK_{Bz}K_{H_2}^n$, where the latter two parameters are equilibrium adsorption coefficients for benzene and hydrogen on the metal surface and n is dependent upon the coverage of the surface by H-deficient hydrocarbon species. Thus, a higher heat of adsorption (Q) for H_2 would result in a lower apparent activation energy, i.e., $E_{app} = E - Q_{Bz} - Q_{H_2}$. The Q_{ad} values for H_2 on these catalysts averaged

4–5 kcal/mole higher (9) than values for other Pd catalysts (23), and n, the observed reaction order on H_2, falls between 0.5 and 1 at this temperature (24); therefore, a decrease in E_a between 2 and 5 kcal/mole would be anticipated from these calorimetric results, which is precisely what was obtained. Despite this consistency, other effects of single carbon atoms on the overall mechanism, which could alter the assumptions involved, cannot be discounted (22).

The TOF of the Pd/C-AS IS sample is 100-fold lower than that of the best Pd/C catalyst and the activity per gram of Pd is 240-fold smaller despite this catalyst being the most well dispersed based on TEM (9). This clearly demonstrates the problem that can occur when an impurity like sulfur contained in carbon used as a support is not removed, and it may account for much of the variation in specific activities reported for carbon-supported metals. Unless removed by cleaning, this sulfur can migrate onto the Pd and poison it (9), as S can exert both electronic and geometric effects on reaction rates (14). Low TOFs have been reported by Barbier and co-workers and by Hoyos *et al.* for benzene hydrogenation over sulfur-contaminated Pt and for cyclohexane dehydrogenation over S-poisoned Pd (14, 25, 26). Consequently, based on our results, in the absence of sulfur Pd/C catalysts can have TOFs comparable to typical Pd catalysts—as represented by Pd/SiO_2 and commercial Pd/C catalysts—even if residual C atoms exist on the Pd surface and in the Pd lattice (9). The development of an appropriate cleaning procedure to remove these C atoms and prevent their return onto the Pd surface should provide more active Pd/C catalysts with activities comparable to their oxide-supported counterparts.

In contrast, the performance of these Pd/C catalysts for CO hydrogenation was markedly impaired relative to typical Pd catalysts, as demonstrated in Table 2, as some catalysts prepared from $Pd(AcAc)_2$ had a TOF 25 times lower than typical Pd/SiO_2 catalysts while the Pd/C catalysts containing Cl were as much as 200 times less active. The commercial Pd/C catalyst exhibited no detectable activity over the entire temperature range, and a similar catalyst from Johnson Matthey was previously found to be very inactive for CH_3OH synthesis at higher pressures, as was Pd dispersed on demineralized char (27). In addition, severe deactivation frequently occurred after a high temperature excursion (see Fig. 2) and apparent activation energies varied from 13 to 30 kcal/mole, a reflection, perhaps, of the deactivation process. In an earlier study, it was found that methanation activity decreased by only 50% in the presence of 2 ppm H_2S during CO hydrogenation (28), thus the similar TOF of the Pd/C-AS IS catalyst, which contains sulfur, compared to the least active, Cl-free Pd/C catalysts, is quite consistent with this earlier finding.

At the present time, this low specific activity is thought

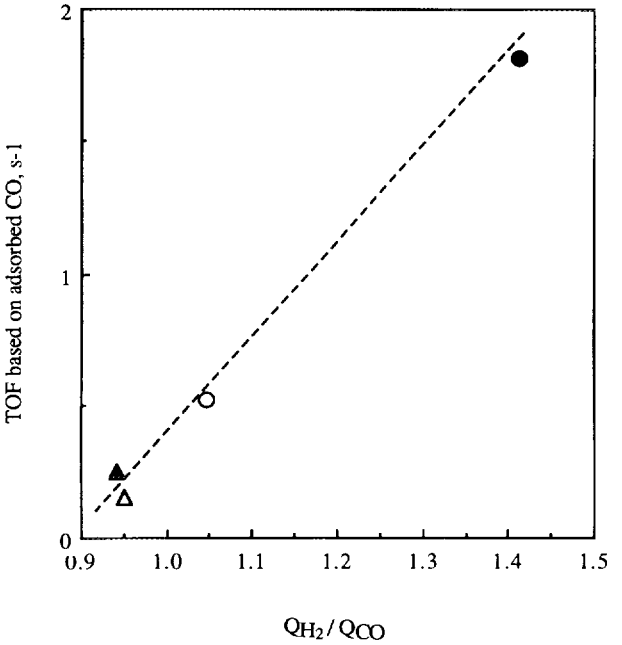

FIG. 4. Dependence of methanation TOF on the ratio of heats of adsorption for H_2 and CO on Pd/C catalysts: (△) 2.1% Pd/C, (●) 2.8% Pd/C-HTT-H_2, (▲) 3.1% Pd/C-HTT-Ar, (○) 2.3% Pd/C-HNO_3 (Q values from Ref. (9)).

to be due to the type of carbon on the Pd surface under reaction conditions. At higher temperatures, the carbon atoms in the Pd lattice could migrate to the Pd surface to be removed by H_2 (9). However, during gasification catalyzed by metal particles such as Pd, amorphous carbon can be converted to graphitic carbon (29). Recently, Lamber *et al.* have reported that Pd dispersed on amorphous carbon begins to form a graphitic overlayer around 700 K under vacuum (30). Consequently, both the low activity and the deactivation could be due to the formation of this unreactive overlayer of graphitic carbon. Evidence exists that the rate-determining step in CH_4 formation from CO and H_2 on Pd is the H-assisted dissociation of CO (17, 31); consequently, coverage of the Pd surface by either C atoms adsorbed in the threefold and fourfold hollow sites typically occupied by H atoms or a graphitic overlayer would decrease the rate of this important step and lower CO activity. Indeed, if all the C atoms in the Pd crystallites were assumed to migrate to the surface, initial coverages of C atoms would be close to a monolayer (9, 15). CO adsorption would be less affected because it occurs on Pd on-top sites. The formation of graphitic carbon at higher temperatures could further decrease activity and also cause deactivation. Sintering of Pd particles at these reaction temperatures is insufficient to explain the significant deactivation observed. An indication that surface hydrogen is important is provided by Fig. 4, which shows that the TOF

on these Pd/C catalysts increases as the heat of adsorption of H_2 increases relative to that of CO. The 2.8% Pd/C-HTT-H_2 catalyst, which had the highest TOF, also had the lowest H_{ad}/CO_{ad} ratio, which may indicate the highest concentration of singlet sites, assuming they cannot dissociatively adsorb H_2, relative to dual sites on this catalyst. However, an increase in Q_{ad} of H_2 compared to CO would facilitate more competitive coverage of hydrogen relative to CO on the PD surface, thus enhancing specific activity.

The reason for the very low TOF values with the Cl-containing Pd/C catalysts is not known at this time. SiO_2-supported Pd catalysts made from a $PdCl_2$ precursor had TOFs in the methanation reaction that were 2–4 times lower than TOFs for catalysts made from $Pd(NH_3)_4(NO_3)_2$ (32). It has been proposed that chloride poisons Ni when it is supported on carbon (33), and this may also occur with Pd. Cl–C complexes are known to exist (34), but their effect on the activity of supported metals has not been examined; however, Pd/C-HTT-H_2 catalysts made from $PdCl_2$ had suppressed H_2 uptakes, while CO and O_2 uptakes were higher than expected based on the average Pd particle sizes from TEM measurements (9). Thus part of the irreversible O_2 and CO uptake may be associated with the carbon support, which is consistent with the IR spectra of these Pd/C catalysts (15). It may also be that C atom migration to the Pd was facilitated by the presence of Cl; regardless, after a pretreatment which routinely provided very active Pd catalysts for methanation, these two catalysts possessed very low activities.

To examine the behavior of Pd/C catalysts under mild oxidizing conditions, especially when such conditions could facilitate the removal of C atoms from the Pd surface, CO oxidation was conducted over the Pd/C-HTT-H_2 and Pd/C-HNO_3 catalysts, and the results are given in Fig. 3 and Table 3. The activation energies were nearly identical and similar to those reported for Pd/Al_2O_3 catalysts in this temperature range (18). Furthermore, the TOF for Pd/C-HTT-H_2 was comparable to or higher than those for the Pd/Al_2O_3 catalysts while the Pd/C-HNO_3 catalyst was distinctly more active. As reported in the previous study, a treatment in O_2 at 573 K can remove some or all of the interstitial bulk carbon as well as some of the surface carbon (9). Thus it appears that carbon is removed during this reaction, and the Pd surfaces are similar to those in other Pd catalysts under these oxidizing conditions. Though the temperatures are too low for significant catalytic oxidation of the carbon support to occur, as verified by the absence of CO or CO_2 evolution in the presence of O_2 alone, CO can accelerate catalyzed gasification of carbon by O_2 (35). The weight loss of Pd/C-HTT-H_2 during CO oxidation was near that expected for $Pd(AcAc)_2$ decomposition, but the larger weight loss of Pd/C-HNO_3 indicated either that support gasification may be occurring, or many O-containing surface groups are being removed. The large concentration of O-containing surface groups on the C-HNO_3 sample may facilitate its gasification, which is consistent with the significant quantities of oxygen irreversibly adsorbed by both C-HNO_3 and Pd/C-HNO_3 at 300 K (9, 10). Alternatively, the higher TOF values may be partially due to the initially suppressed chemisorption on the surface, which did not include all the surface Pd atoms indicated by TEM. Regardless, the result to be emphasized here is that these Pd/C catalysts are comparable to or better than typical Pd catalysts for CO oxidation.

SUMMARY

The catalytic behavior of Pd dispersed on carbon can vary significantly compared to typical Pd/oxide catalysts, depending on the reaction involved. A previous study established that these Pd/C catalysts could contain C atoms in the Pd lattice and on the Pd surface. The TOFs for benzene hydrogenation over Pd dispersed on a clean, pretreated carbon black were very similar to those on Pd/SiO_2 catalysts, as expected for a structure-insensitive reaction, thus indicating the absence of any significant effects in this reaction due to the presence of C atoms. In contrast, the TOFs for CO hydrogenation to methane over these Pd/C catalysts were as much as 20 times lower than typical Pd catalysts and, in addition, significant deactivation occurred after operation at higher temperatures. Finally, for CO oxidation the Pd/C catalysts had activities and TOFs comparable to or even greater than Pd supported on alumina, indicating that similar Pd surfaces can be achieved and maintained under such an oxidizing environment. When reactive sulfur was present in the carbon support, it drastically decreased both activity and TOF for benzene hydrogenation and it lowered both activity and activation energy in the methanation reaction. Previously proposed reaction mechanisms are applicable for all three reactions over these Pd/C catalysts. Carbon atoms on the Pd surface and interstitial C atoms in the Pd lattice, which have been shown to exist (9), can explain the variations in catalytic behavior observed here. Benzene hydrogenation occurs at such a low temperature that surface carbon atoms remain to block a portion of the Pd surface; however, at higher temperatures such as those used for methanation, C atoms can form graphitic overlayers. In contrast, under mild oxidizing conditions, the surfaces of the C-supported Pd particles are cleaned of C atoms and are very active for CO oxidation. These results imply that it is during the reduction step in H_2 or, more likely, the subsequent evacuation step at 573 K that the Pd crystallites become contaminated by C atoms.

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