JOURNAL OF CATALYSIS **104**, 17–30 (1987)

Calorimetric Heat of Adsorption Measurements on Palladium

II. Influence of Crystallite Size and Support on CO Adsorption

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Received July 9, 1986; revised September 30, 1986

Integral heats of adsorption of CO, Q_{ad}, have been measured at 300 K on unsupported Pd powder and on a family of Pd catalysts prepared from SiO_2, η-Al_2O_3, SiO_2–Al_2O_3, and TiO_2 using a modified differential scanning calorimeter. For the samples studied, there was no evidence that Q_{ad} was noticeably affected by the supports used to prepare the catalysts, and although high-temperature reduction of Pd/TiO_2 catalysts sharply decreased the CO chemisorption, the Q_{ad} values for these samples were comparable to those for the other catalysts. On the other hand, Pd crystallite size was found to have a significant effect on Q_{ad}. For poorly dispersed samples, which contained average crystallite sizes up to 1000 nm, the Q_{ad} values were usually close to 22 kcal $mole^{-1}$; however, they increased sharply when the average Pd crystallite size dropped below 3 nm. The highest value, 35 kcal $mole^{-1}$, was measured on the most highly dispersed samples. Although changes in either surface geometry or electronic properties as Pd crystallites sizes decrease below 5 nm could affect Q_{ad}, the 13 kcal $mole^{-1}$ increase on very small crystallites was larger than expected from ultrahigh-vacuum studies of CO chemisorption on Pd single-crystal surfaces. Consequently, changes in the electronic properties as Pd crystallite size decreases appear to be the major factor causing the stronger CO–Pd bond strengths, in agreement with recent model calculations.

INTRODUCTION

The heat of adsorption of a gas adsorbed on a metal surface is an important parameter because it not only represents a characteristic property related to the structure of that surface but also is intricately involved in rate equations which describe reactions involving that species. Langmuir–Hinshelwood rate expressions provide straightforward examples of the effect of heats of adsorption on reaction kinetics, and more complicated rate equations assuming nonuniform surfaces frequently utilize the heat of adsorption to represent surface nonuniformity (*1, 2*). In addition, recent studies have shown that the use of particular supports to disperse a metal component, such as TiO_2, can markedly decrease the chemisorption capacity after high-temperature reduction (HTR) (*3, 4*). Many subsequent studies have verified this behavior and numerous explanations have been proposed; however, the two general possibilities to account for this behavior are either a physical blockage of metal surface sites due to the migration of a TiO_x species over the metal surface, first proposed by Naccache and co-workers (*5*) or a chemical modification of the adsorbate–metal bond strength caused by a metal–support interaction, for example, direct bonding between the dispersed metal and support cations or atoms, as initially proposed by Tauster and coworkers (*3, 6*). A combination of both effects obviously can occur, and different types of chemical interactions have been proposed.

In regard to other considerations, certain reactions have been found to be structure sensitive for which a variation in turnover frequency occurs as the metal crystallite size decreases (*7*), and various models describing the geometric and electronic prop-

0021-9517/87 $3.00

erties of crystallites predict that the transition to bulk-like behavior should be most marked as the particles grow from <1 nm to 5 nm (*8, 9*). Also, should interactions occur between the metal particles and the support, they would be expected to be maximized for states of high dispersion, i.e., small crystallites. Both of these influences could be reflected by changes in heats of adsorption, Q_{ad}.

Although Q_{ad} values have been obtained for unsupported Pd in ultrahigh vacuum (UHV) systems, there has been no systematic study of heats of adsorption on dispersed Pd catalysts to determine the influence of crystallite size and the support on this parameter. Such an investigation is inherently more complicated because of the importance of eliminating artifacts due to pore diffusion and readsorption in these porous materials. We have circumvented this problem by modifying a differential scanning calorimeter (DSC) to obtain integral, isothermal heats of adsorption (*10*), and this technique has been used to characterize adsorption over a wide range of Pd crystallite size using SiO_2, η-Al_2O_3, SiO_2–Al_2O_3, and TiO_2 as supports. This paper reports the direct calorimetric measurement of Q_{ad} values for CO; the studies of H_2 and O_2 adsorption are reported separately (*11, 12*).

EXPERIMENTAL

Catalyst Preparation

The supports used in this study were SiO_2 (Davison Grade 57), SiO_2–Al_2O_3 (Davison Grade 979, 13% alumina—abbreviated Si–Al in the tables), η-Al_2O_3 (Exxon Research & Engineering Co.), and TiO_2 (Degussa P25, 80% anatase, 20% rutile). All support materials were calcined at 773 K in flowing air for 4 h prior to metal loading. Catalysts were prepared by incipient wetness impregnation using an aqueous solution of $PdCl_2$ (Ventron Corp.) or palladium actylacetonate (Aldrich) dissolved in excess benzene (Baker Analyzed) (*13*). Several catalysts were prepared by ion exchange using $Pd(NH_3)_4(NO_3)_2 \cdot 2H_2O$ (Spex) or $PdCl_2$ dissolved in deionized, distilled (D, D) water. The unsupported Pd sample was Pd powder (Johnson Matthey, Puratronic Grade—99.999%). The Pd weight loadings of the supported catalysts were determined by plasma emission spectroscopy and neutron activation analysis. Pure support blanks were prepared by impregnating calcined support materials with (D, D) water and then drying overnight in air at 393 K. Additional details and descriptions of the catalysts have been provided in the first paper in the series (*11*).

Chemisorption

The chemisorption uptakes were measured in a volumetric adsorption system equipped with an Edwards Model E02 oil diffusion pump backed by a GCA Vac-Torr Model 150 mechanical pump, which produced an ultimate vacuum near 5×10^{-7} Torr (10^{-4} Pa). A Texas Instruments precision pressure gauge and a Granville–Phillips Model 260-002 ionization gauge were used to measure the pressures. Further details are given elsewhere (*14*).

Catalyst samples (~0.4 g) prepared by the impregnation method were heated either in 50 $cm^3\ min^{-1}$ of He from room temperature to 448, 533, 673, or 723 K prior to a 1-h reduction in 50 $cm^3\ min^{-1}$ of H_2, or in a mixture of 15 $cm^3\ min^{-1}$ of H_2 and 60 $cm^3\ min^{-1}$ of He at 448, 673, 723, or 773 K (see Table 1). The catalysts prepared by ion exchange were treated in 50 $cm^3\ min^{-1}$ of He at 573 K for 1 h, cooled to room temperature, and then reduced in a flowing gas mixture of H_2 and He as stated above.

All the samples were given one of the above pretreatments and stored in a desiccator before chemisorption measurements. The method described by Benson *et al.* (*15*) was used to determine both chemisorption uptakes of H_2 at 300 K on each sample as well as the uptake of H_2 due to bulk Pd hydride formation. The measurement of H_2 uptakes was repeated at least once to ensure that the Pd dispersion was stabilized. Chemisorption uptakes of CO on two of the

TABLE 1

Uptakes of H_2 and CO on Pd Catalysts

Catalyst (sample)	Pretreatment[a] (K)			Gas uptake (μmole/g cat)			Fraction exposed	
	T_c	T_i	T_r	Chemisorption		Reversible CO	H/Pd	CO/Pd
				H_2	CO			
1.71% Pd/SiO_2								
(I)	—	533	673	8.5	15.5	5	0.11	0.10
(II)	—	533	673	9.0	15	6	0.11	0.09
0.48% Pd/SiO_2	573	300	573	10.5	21.5	7.5	0.45	0.48
2.10% Pd/SiO_2								
(I)	—	300	573	67	127.5	24	0.68	0.65
(II)	—	533	673	65.5	119.5	22	0.66	0.61
1.23% Pd/SiO_2								
(I)	573	300	573	40	77	14.5	0.69	0.67
(II)	573	533	673	36.5	77.5	17.5	0.63	0.67
0.39% Pd/SiO_2	573	300	573	9	20	6.5	0.49	0.55
1.95% Pd/Si–Al								
(I)	—	448	448	32.5	69.5	20	0.35	0.38
(II)	—	448	673	26	55	22.5	0.28	0.30
(II)	—	533	673	18	33	19	0.21	0.18
(IV)	—	673	673	16	34	18	0.17	0.19
(V)	—	723[b]	673	9	20	15.5	0.10	0.11
1.16% Pd/Si–Al	573	300	573	32	59	12.5	0.59	0.54
0.98% Pd/Si–Al								
(I)	573	300	573	28.5	57	13.5	0.62	0.62
(II)	573	533	673	21	34	26	0.46	0.37
1.80% Pd/Al_2O_3	—	533	673[c]	28.5	45	23.5	0.34	0.27
0.32% Pd/Al_2O_3	573	300	573	7.5	15.5	9	0.50	0.52
0.36% Pd/Al_2O_3								
(I)	—	448	448	10	19.5	5	0.59	0.58
(II)	—	300	573	9.5	16	9	0.56	0.47
0.54% Pd/Al_2O_3	573	300	573	13.5	30	10	0.53	0.59
2.33% Pd/Al_2O_3								
(I)	—	300	573	52	75.5	27	0.48	0.34
(II)	—	533	673	41	65	31.5	0.37	0.30
2.03% Pd/TiO_2								
(LTR)	—	448	448[c]	30	64.5	34.5	0.31	0.34
(HTR-I)	—	448	773	0.8	3.2	—	—	—
(HTR-II)	—	448	773	1.7	4.4[d]	—	—	—
(HTR-III)	—	448	773	1.3	3.3[d]	—	—	—
1.88% Pd/TiO_2								
(LTR)	773	448	448	14.5	22	35	0.16	0.13
Pd powder	773	300	573	6[d]	4.5[d]	—	~0	~0

[a] T_c, calcination temperature; T_i, Temperature at which H_2 was introduced; T_r, reduction temperature.

[b] Sample treated in 20% O_2 at 673 K after an initial reduction at 723 K.

[c] Sample exposed to CO and treated in 20% O_2 at 573 K.

[d] Uptakes at 10 Torr.

samples (noted in Table 1) were also determined at this stage by the dual-isotherm method of Yates and Sinfelt (*16*). In these cases, the samples were treated in a flowing gas mixture of 20% O_2 and 80% He at 573 K for 30 min after each CO uptake measurement to facilitate complete removal of CO. A portion of each of these samples was then taken and used for measurement of heats of adsorption and Pd weight loadings. The portion remaining was used for additional measurements of H_2, O_2, and CO uptakes after subsequent pretreatments paralleling those in the calorimeter. Equilibrium pressures during adsorption measurements were routinely recorded 30 min after the first dose of gas was introduced to the samples and 5 min after each of the subsequent doses.

Calorimetric Measurements

Energy changes during chemisorption at 300 K were measured by a modified Perkin–Elmer DSC-2C differential scanning calorimeter which has been described elsewhere (*10, 11*). Between 30 and 100 mg of the catalyst was placed in the sample holder and an equal amount of pure support was placed in the reference holder to balance energy changes due to physical adsorption of the gas on the support. When heats of adsorption on unsupported Pd powder or the pure supports were measured, a piece of stainless steel or aluminum of equal mass was placed in the reference holder. The same pretreatment procedures used for the chemisorption measurements were repeated before each heat of adsorption measurement; however, all reductions were carried out in a gas mixture of 8 $cm^3\ min^{-1}$ H_2 and 32 $cm^3\ min^{-1}$ Ar, and removal of adsorbed H_2 from the catalyst was accomplished by purging the sample with 40 $cm^3\ min^{-1}$ Ar for 1 h either at the reduction temperature or at 20–50 K below the reduction temperature if the sample was reduced at 673 K or higher. Purging for more than 1 h did not affect the energy change measured for H_2 chemisorption, which indicated that complete removal of H_2 was achieved after 1 h with no subsequent O_2 contamination (*12*). After the pretreatment, the sample was cooled to 300 K; a step change to a constant CO pressure (typically 75 Torr) in the carrier gas was made via a switching valve, the energy change during adsorption of CO was recorded as a function of time, and then it was integrated to give the total energy change. After the initial CO exposure, the sample was purged with pure Ar at 300 K for 60 min to remove physisorbed CO and CO was then reintroduced. The second CO exposure typically resulted in a negligible energy change because of cancellation of changes due to physical adsorption by the pure reference support.

RESULTS

Chemisorption

The final chemisorption uptakes of H_2 at 150 Torr and CO at 75 Torr, obtained after a number of pretreatment cycles, are listed in Table 1, and three sets of CO isotherms are shown in Fig. 1. The dispersion, *D* (or fraction exposed), represented as the H_{ad}/Pd_{total} ratio, was usually stabilized after one pretreatment, and exposure to air at room temperature had no significant effect on the dis-

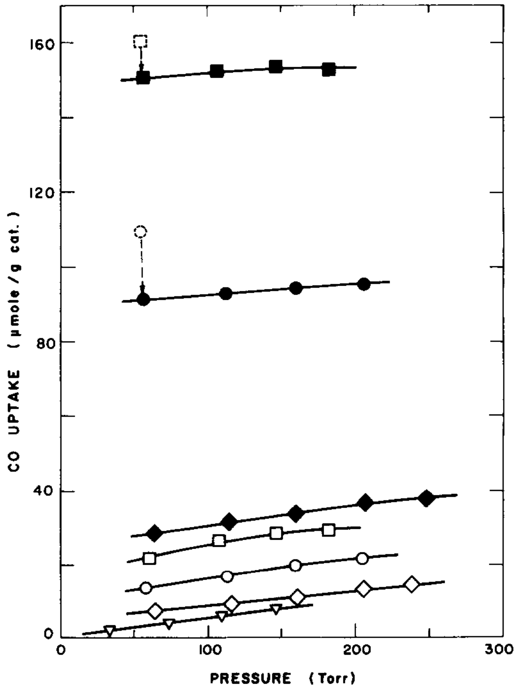

FIG. 1. CO adsorption isotherms at 300 K on pure SiO_2 and Pd/SiO_2 catalysts: 2.10% Pd/SiO_2 (I) (■, □), 1.23% Pd/SiO_2 (I) (●, ○), 0.48% Pd/SiO_2 (◆, ◇), pure SiO_2 (▽). Solid symbols: total CO uptakes; open symbols: reversible CO uptakes; dashed symbols: uptakes based on the lowest pressures recorded after introduction of the first dose of CO to the samples.

persion. Treatment in O_2 at 573 K for certain samples also did not change the fraction exposed; however, gas uptakes tended to drop after the catalysts had been exposed to CO at 300 K, and this effect of CO was particularly noticeable for the more highly dispersed Pd catalysts, as shown in Table 2. The uptakes on the highly dispersed Pd catalysts did not recover to the original values even after treatments in a flowing O_2/He mixture at 573, 673, or 773 K. It was also observed that during the first adsorption measurement on the most highly dispersed catalysts, the CO pressure decreased for the first 2 min and then started to increase slowly, as indicated in Fig. 1. A special experiment was conducted which found that this continuous increase in CO pressure lasted for more than 1 h. A sample of the gas was withdrawn from the adsorption cell and analyzed with a quadrupole mass spectrometer, but the only gas detected was CO. Any CO_2 formed from the disproportionation reaction could be measured if present because CO_2 was detected after briefly heating a Pd/Al_2O_3 sample in CO to 573 K. This phenomenon of increasing pressure was observed only during the first exposure, i.e., the very first isotherm measurement, and never occurred in any subsequent exposure to CO.

TABLE 2

Effect of CO Exposure on Chemisorption Uptakes

Catalyst (sample)	Cycle No.	Pretreatment[a]		Chemisorption[b] (μmole/g cat)		
		T_c (K) O_2/He	T_r (K) H_2/He	H_2	O_2	CO
2.10% Pd/SiO_2	1	—	573	68.5	77.5	—
(I)	2	—	573	67	74.5	127.5
	3	—	573	47	51.5	95
(II)	1	—	673	70.5	—	—
	2	—	673	65.5	68	119.5
	3	—	673	48.5	—	90.5
	4	573	673	48	—	—
1.23% Pd/SiO_2						
(I)	1	—	573	40	49.5	—
	2	—	573	41.5	—	—
	3	—	573	41.5	—	77
(II)	1	—	673	40	47	—
	2	—	673	36.5	49	77.5
	3	—	673	24.5	32.5	55
(III)	1	—	573	42	50.5	—
	2	573	573	42	47.5	74
	3	573	573	26.5	30	49
	4	673	573	28	—	—
	5	773	573	26	—	—
2.33% Pd/Al_2O_3	1	—	673	42.5	—	—
	2	—	673	41	33	65
	3	—	673	—	—	60
2.03% Pd/TiO_2						
(LTR)	1	—	448	32	20	[c]
	2	573	448	34.5	20	74
	3	573	448	32	23	67
	4	—	448	—	—	64
	5	573	448	—	—	64.5
	6	573	448	30	24.5	—

[a] Calcination in O_2/He was applied only once to the cycle indicated, and samples were reduced for 1 h before each chemisorption measurement.

[b] CO uptake was measured last in each cycle.

[c] Sample exposed to CO but uptake not measured.

Heats of Adsorption of CO

A typical DSC run is shown in Fig. 2a. Chemisorption of CO on Pd proceeded rapidly, and the energy change due to adsorption was typically completed in less than 2 min when 10% CO (75 Torr) was introduced

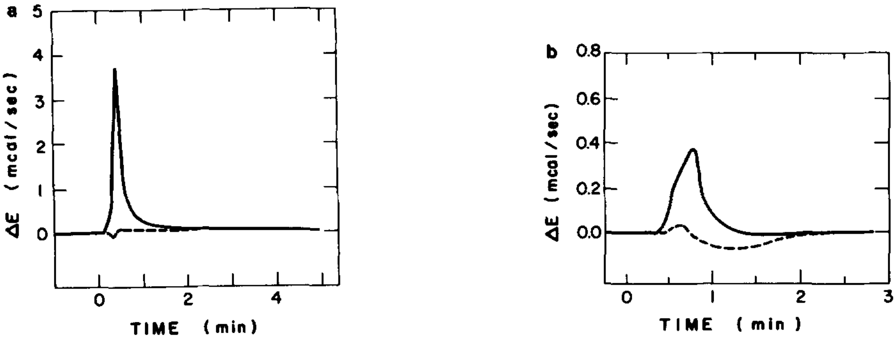

FIG. 2. Energy changes, ΔE, measured during CO adsorption on Pd catalysts at 300 K: (a) 1.95% Pd/SiO_2–Al_2O_3 (II), (b) 2.03% Pd/TiO_2 (HTR-II). Solid line: first CO uptake; dashed line: readsorption of CO after a 1-h purge at 300 K.

to the DSC. As mentioned previously, readsorption of CO after purging with Ar at 300 K for 5 min or 1 h usually resulted in only a small energy change because of cancellation of changes by the pure reference support. The energy change during readsorption, however, became more noticeable for samples with a large CO chemisorption uptake, and the reason for this is discussed later. A close balance of physical adsorption between the sample and the pure reference support became critical for samples with a small CO chemisorption uptake, such as high-temperature reduced Pd/TiO_2. This problem could be minimized by using a CO/Ar mixture with low CO concentrations for the DSC measurements. In Fig. 2b, a CO/Ar mixture of 1.4% CO was used for the 2.03% Pd/TiO_2 (HTR) sample II, and the variation caused by physical adsorption was greatly reduced. Most samples were completely reduced in 1 h in the DSC, as indicated by an essentially constant H_2 heat of adsorption (*11*). However, the Pd/TiO_2 samples reduced at 773 K required a longer reduction time to reach a stable condition because in the DSC the reducing gas contacts the sample by diffusing to it rather than flowing through it as in the chemisorption cell, and hence reduction of the TiO_2 was less efficient in the DSC. The measured energy changes, ΔE, and calculated integral heats of adsorption, Q_{ad}, for CO at 300 K on each sample are listed in Table 3, and Q_{ad} values are plotted versus Pd crystallite size in Fig. 3 using the relationship d (nm) = $1.13/D$ (*17*).

TABLE 3

Heats of Adsorption of CO on Palladium Catalysts and Pure Supports

Catalyst (sample)	Reduction temperature (K)	d^a (nm)		Energy change	
			CO_{ad}^b (μmole/g cat)	ΔE (mcal/g cat)	ΔH_{ad} (kcal/mole)
1.71% Pd/SiO_2					
(I)	673	11.3	15.5	385	24.9
(II)	673	10.7	15	427	28.5
0.48% Pd/SiO_2	573	2.5	21.5	637	29.5
2.10% Pd/SiO_2					
(I)	573	1.7	127.5	4,145	32.5
(II)	673	2.3	119.5	3,430	28.7
1.23% Pd/SiO_2					
(I)	573	1.6	77	2,715	35.3
(II)	673	1.7	77.5	2,498	32.2
0.39% Pd/SiO_2	573	2.3	20	712	35.6
1.95% Pd/Si–Al					
(I)	448	3.2	69.5	1,594	22.3
(II)	673	3.9	55	1,209	22.0
(III)	673	5.9	33	676	20.5
(IV)	673	6.5	34	578	17.0
(V)	673	11.5	20	446	22.3
1.16% Pd/Si–Al	573	1.9	59	1,716	29.1
0.98% Pd/Si–Al					
(I)	573	1.8	57	1,573	27.6
(II)	673	2.5	34	1,086	31.9
1.80% Pd/Al_2O_3	673	3.4	45	914	20.3
0.32% Pd/Al_2O_3	573	2.3	15.5	503	32.5
0.36% Pd/Al_2O_3					
(I)	448	1.9	19.5	458	23.5
(II)	573	2.0	16	573	35.8
0.54% Pd/Al_2O_3	573	2.1	30	1,011	33.7
2.33% Pd/Al_2O_3					
(I)	573	2.4	75.5	1,760	23.3
(II)	673	3.0	65	1,271	19.6
2.03% Pd/TiO_2					
(LTR)	448	3.6	64.5	1,533	23.8
(HTR–I)	773	—	3.2	55	17
(HTR–II)	773	—	4.4	115	26
(HTR–III)	773	—	3.3	103	31.2
1.88% Pd/TiO_2	448	6.9	22	669	30.4
Pd powder	573	—	4.5	108	24.0
SiO_2	673		4.5	21	4.7
SiO_2–Al_2O_3	673		27	272	10
Al_2O_3	673		13.5	126	9.4
TiO_2 (I)	448		43	391	9.1
(II)	773		54	640	11.8

[a] Based on H_2 chemisorption uptakes.

[b] From Table 2 except for pure supports.

It is recognized that dispersions calculated from chemisorption uptakes represent an average of all Pd particle sizes; consequently, if a catalyst has a broad size distribution, a significant fraction of the gas will be adsorbed on particles much smaller than suggested by the mean crystallite size. A wide range of metal particle size may be produced from the solution trapped in micropores and macropores during impregnation, unless the surface chemistry is favorable for the precursor to anchor onto the support by chemical bonding. Although the same method was used for impregnation with the H_2PdCl_2 solution, the final pH of the solution after contact with the support surface would be expected to be favorable for $PdCl_4^{2-}$ ions to adsorb on oxides such as Al_2O_3 or TiO_2, but not on SiO_2 (*18*). Consequently, the 1.71% Pd/SiO_2 catalyst may

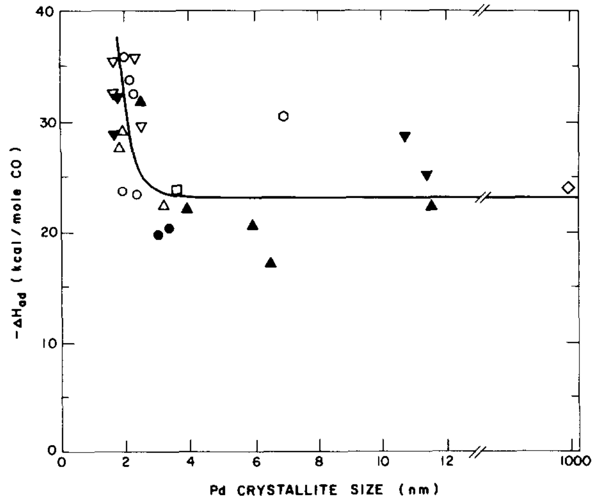

FIG. 3. Heats of adsorption ($Q_{ad} = -\Delta H_{ad}$) of CO on supported and unsupported palladium: Pd/SiO_2 (▼, ▽), Pd/SiO_2–Al_2O_3 (▲, △), Pd/Al_2O_3 (●, ○), Pd/TiO_2 (□, ○), Pd powder (◇). Solid symbols: samples reduced at 673 K; open symbols: samples reduced at 573 or 448 K.

well have a broad Pd crystallite size distribution, and this may have contributed to the relatively high Q_{ad} measured on this catalyst. A similar situation may also have existed for the 1.88% Pd/TiO_2 because of its lower surface area and higher Pd loading. The 1.88% Pd/TiO_2 sample is also the only one that had been calcined at 773 K and reduced at only 448 K. The high Q_{ad} measured on this catalyst may have been caused by these complications. The cause of the exceptionally low Q_{ad} on one sample of 0.36% Pd/η-Al_2O_3 is not known, but may be due to contamination which occurred during placement in the DSC and was not fully removed by the subsequent low-temperature reduction (LTR) at only 448 K. Most of the Q_{ad} data were based on a single measurement per sample because of the concern about residual carbon contamination; consequently, the Q_{ad} values for the family of Pd catalysts reflect all the uncertainties contained in the measurements of energy, adsorption, and weight loading.

DISCUSSION

Chemisorption

The chemisorption of H_2, O_2, and CO has been used in the past to calculate Pd crystallite size, but O_2 or CO chemisorption has been assumed to be less reliable because the adsorption stoichiometries for oxygen and CO may vary with the exposed crystallographic planes (*19*). Although CO uptakes on supported Pd are routinely measured using dual isotherms (*16, 19*), a close look at our results indicates that a small amount of weakly adsorbed CO may be removed from the Pd surface during the 5-min evacuation at 300 K. For example, the amount of CO physisorbed on pure SiO_2 at 75 Torr is about 4.5 μmole/g and is rather insensitive to the pretreatment (extent of dehydration); however, our data for the Pd/SiO_2 catalysts clearly show that uptakes of CO measured with the readsorption isotherm always exceeded 4.5 μmole/g, as shown in Table 1 and Fig. 1. In addition, this extra uptake was proportional to the amount of chemisorbed CO. Based on these results, about 10–12% of the total adsorbed CO appears to desorb during this evacuation at 300 K. In fact, Conrad *et al.* have reported a weakly adsorbed CO species on Pd (110) which can be pumped off slowly at room temperature (*20*). This weakly adsorbed CO was also detected by the DSC as a small energy change during readsorption of CO on some samples. Because the same adsorption–readsorption procedures were followed in the DSC for the heat of adsorption measurements, this behavior caused no problem as the results in Table 3 represent values for irreversibly adsorbed CO. However, it does imply that the integral heats of adsorption reported here may correspond more closely to near monolayer, rather than complete, coverage of CO.

Although hydrogen chemisorption is frequently used to measure Pd dispersion, it is complicated by bulk Pd hydride formation at pressures typically used to achieve saturation coverages. The adsorption–backsorption method of Boudart and co-workers (*15*) circumvent this difficulty by first measuring the total hydrogen uptake due to both adsorption and absorption, decomposing the hydride by evacuating at 300 K for 20–30 min, leaving only chemisorbed hydrogen on the Pd surface, and then measuring the backsorption of hydrogen which is typically attributed to the reformation of bulk hydride. However, a study of this family of Pd catalysts has indicated that about 15% of the hydrogen adsorbed on the surface can be removed on the more highly dispersed samples, and the same percentage is very likely desorbed from all Pd surfaces, but is more difficult to distinguish on large crystallites because of the large degree of bulk hydride decomposition (*11*). This trend is consistent with the CO adsorption and indicates that the actual Pd dispersion may be underestimated by H_2 chemisorption, particularly for very small Pd crystallites. This possibility is further supported by the fact that O_2 uptakes on the highly dispersed samples typically exceeded both H_2 and CO uptakes, and none of this chemisorbed oxygen was removed by evacuation (*12*).

The enhanced formation of subcarbonyls on very small metal crystallites has been previously reported for Rh, Fe, Ru, and Ni (*21–25*), and the formation and decomposition of such Pd species may account for the increasing CO pressure during initial isotherm measurements and the subsequent loss of Pd surface area (Table 2). Although Pd carbonyls are much less stable than most other metal carbonyls, formation of $Pd(CO)_4$ from Pd atoms and clusters has been reported (*26, 27*). Extremely small Pd clusters could easily exist in these well-dispersed Pd/SiO_2 catalysts and could form Pd carbonyl species which migrate, collide, and decompose into larger Pd aggregates at 300 K. The last step would increase the CO pressure. A similar mechanism has been proposed for changes in Rh crystallite morphology (*28, 29*). Changes in this range of crystallite size (0.3–2 nm) would be difficult to detect by TEM (*30*). Other possible explanations for this behavior have been considered, such as CO disproportionation and CO dissociation. The former reaction to form CO_2 has been reported during thermal desorption studies of Pd catalysts (*30, 31*), and it is conceivable that local heating during chemisorption of CO might induce CO disproportionation, especially on highly dispersed Pd, but no gas phase CO_2 was detected by mass spectroscopy after CO was introduced to a 1.23% Pd/SiO_2 sample ($D = 0.69$). Furthermore, disproportionation of CO would not produce a pressure increase if each carbon atom simply replaced a chemisorbed CO molecule on the Pd surface. CO dissociation to produce C and O atoms coadsorbed with CO on the Pd surface could explain the pressure increase if a CO molecule were forced to desorb, but a subsequent exposure of a sample with CO chemisorbed on it to H_2 in the DSC showed no large energy change attributable to the presence of adsorbed oxygen, as the H_2–O_2 titration reaction is very exothermic. The uptakes of all three gases, H_2, O_2, and CO, consistently dropped by 30% after the first set of CO isotherms, even after a treatment in H_2 or O_2 at 573 K or higher. This absence of regenerability strongly implies a decrease in dispersion and eliminates carbon contamination as an explanation because Ichikawa *et al.* found that the carbon deposited on their Pd catalysts was very reactive with H_2 (*30*).

The slow increase in CO pressure during adsorption measurements on the most highly dispersed catalysts makes a precise determination of CO uptake difficult. DSC runs indicated that energy changes associated with CO adsorption were completed in 2 min, but the uptakes listed in Table 3 are based on pressures recorded 30 min after the adsorption started. Therefore, the heats of adsorption calculated for the most highly dispersed catalysts may be somewhat overestimated; however, even if uptakes were based on the lowest pressures recorded, Q_{ad} would be lowered by no more than 3 kcal mole^{-1} for the most highly dispersed catalysts, except for the 1.23% Pd/SiO_2 (I) sample.

Heats of Adsorption

Heats of adsorption of CO on unsupported Pd surfaces are available in the literature (*20, 32–37*), and Q_{ad} values obtained in UHV systems for the low index planes of Pd are listed in Table 4. Isosteric heats of adsorption of CO on these surfaces were determined from adsorption isotherms using the Clausius–Clapeyron equation. As shown in Table 4, the initial Q_{ad} values for CO are not markedly dependent on the different planes, and they vary between 34 and 40 kcal mole^{-1}. Explanations for this relative insensitivity have been proposed in model calculations (*38, 39*). Doyen and Ertl suggest that a large number of metal atoms contribute significantly to the chemisorption bond, and therefore the number of metal atoms in direct contact with CO is not crucial to the bonding strength (*38*). Isosteric heats of adsorption of CO on single-crystal surfaces generally remain fairly constant up to one-half monolayer coverage. At higher coverages the surface structure of adsorbed CO starts to compress, and Q_{ad} values decrease sharply due to direct CO–CO interactions (*34*) or indirect electronic interactions through metal atoms (*39*). Consequently, the integral Q_{ad} values for CO measured here are expected to be less than the initial heats of adsorption in Table 4. Since most isosteric heats of adsorption were measured over limited ranges of CO coverage, the integral heats of adsorption were estimated in two ways: first, Q_{ad} was extrapolated to zero to obtain a coverage θ', then by integrating from $\theta = 0$ to $\theta = \theta'$ an upper limit for the integral Q_{ad} value was obtained, whereas integration from $\theta = 0$ to $\theta = 1$ provided a lower limit. The coverages of CO on some of the planes were not determined directly, and estimations of the limits were then based on the work function changes given in the original papers. These estimated values for integral heats of adsorption are also listed in Table 4. As shown in Table 3, all our measured Q_{ad} values fall within the expected ranges except for the most highly dispersed samples.

TABLE 4

Initial Heats of Adsorption and Estimated Integral Heats of Adsorption of CO on Pd

Surface	Initial Q_{ad}[a] (kcal/mole CO)	Estimated integral Q_{ad} (kcal/mole CO)			Ref.
		Upper limit	θ'	Lower limit	
Pd(111)	34	31	0.5	16	(*33*)
Pd(100)	35.7	27	0.8	22	(*34*)
Pd(100)	38.5	33	0.7	23	(*35*)
Pd(110)	40	32	(max. θ)[b]	—	(*20*)
Pd(210)	35	29	(max. θ)[b]	—	(*20*)
Pd(310)	35	29	(max. θ)[b]	—	(*20*)
Pd(111)/step	34	30	0.5	16	(*20*)
Pd(110)	(55, 45, 9, 5)[c]	—	—	—	(*36*)
Pd film	43	—	—	—	(*37*)

[a] Taken from Ref. (*32*).

[b] Based on work function change.

[c] Thermal desorption results.

Both adsorption and calorimetric measurements indicate that CO is weakly adsorbed on the pure supports used in this study. Uptakes of CO on the supports increase with the pretreatment temperatures, except for SiO_2. The adsorbed CO can be removed from the supports by a 5-min evacuation at 300 K, but the complete removal of a very small fraction of CO adsorbed on SiO_2–Al_2O_3 requires a longer evacuation time. Heats of adsorption of CO on these oxide supports ranged from 5 to 12 kcal mole^{-1} (Table 4). Della Gatta *et al.* reported a value of 14 kcal mole^{-1} at low coverages of CO on an η-Al_2O_3 sample dehydrated at 1013 K, but this value dropped to 2 kcal mole^{-1} at high coverages (*40*).

Crystallite Size Effect

The integral CO heat of adsorption remains essentially constant at 23 ± 3 kcal mole^{-1} over a range of crystallite size from 1000 to about 3 nm, as shown in Fig. 3, and then increases sharply on crystallites smaller than 3 nm to a maximum near 36 kcal mole^{-1}. This trend appears to be essentially independent of the support, within experimental accuracy. Crystallite size is a parameter that is known to affect the catalytic properties of dispersed metals for certain structure-sensitive reactions (*7*). This effect is sometimes attributed to changes in surface geometry and coordination number (*8*) or to changes in electronic properties (*9*); however, the two parameters are not readily separated as they both vary with crystallite size, especially when particle size drops below 4 nm. Such a size effect has been reported in IR and UPS spectra of CO adsorbed on Pd (*13, 41, 42*), although interpretation of UPS spectra is complicated by various factors. In the IR study, the CO stretching frequency decreased as the Pd crystallite size decreased (*13*). Although an excellent correlation exists between heats of adsorption and IR data for CO adsorbed on Pd (*43*), model calculations indicate that the shift in CO stretching frequency may primarily reflect changes in the coordination number of the chemisorption site and may bear no definite relation to the strength of the chemisorption bond (*39*). In a thermal desorption study, Ichikawa *et al.* observed an additional low temperature CO peak along with a concurrent CO_2 peak during CO desorption from a highly dispersed Pd catalyst, whereas only a high temperature CO peak was observed for a Pd catalyst with low dispersion (*44*). However, it has been shown that carbon deposition on Pd can shift CO TPD peaks to lower temperatures (*35*), and it is possible that the low-temperature peak observed by Ichikawa *et al.* was a consequence of carbon deposition occurring during thermal desorption runs.

As mentioned earlier in this section, the CO heat of adsorption on single-crystal surfaces has been shown to be rather insensitive to Pd surface geometry (*20, 33–35*), and since the increase in Q_{ad} on small Pd particles is larger than the variation reported on different crystal planes, the variation in electronic properties is presumed to be the more dominant factor in the increase of Q_{ad} on small crystallites although the effect of surface defects cannot be completely discounted. Model calculations and XPS studies strongly suggest that electronic behavior and other properties of metal clusters become bulk-like for crystallite sizes greater than 2–3 nm (*9, 45, 46*). The Q_{ad} values measured in this study become constant and equal to those for bulk Pd, within experimental accuracy, when average particle sizes reach 3 nm, in excellent agreement with predictions based on model calculations (*9*) and XPS results (*45, 46*). Therefore, these results provide evidence that the bonding strength between adsorbate and metal can be significantly affected by changes in the electronic properties of metal crystallites.

Using X-ray absorption spectroscopy, Mason (*47*) has shown that the number of *d*-orbital vacancies increases with the Pd dispersion and that these additional *d* vacancies in small Pd crystallites can enhance the bonding between CO and Pd. The *d*-vacancy concentration, however, is not the only property changing with crystallite size as the work function, band width, and details in the density of states can also change (*48*). Differences between bulk metal and small metal crystallites are also manifested by changes in the lattice parameter (*49*). Adsorption of CO on semi-infinite surfaces (*50*) is an approach employed in model calculations that have used changes in band structure to explain trends in heat of adsorption across the periodic table, but these calculations do not consider the effect of crystallite size. A theoretical calculation of a Ni_2CO cluster suggests that CO bonds much more strongly with the Ni atoms in this cluster than with a Ni(111) surface (*51*); however, the ligand–cluster bonding strength predicted by cluster calculations is sensitive to the assumptions made to simplify the calculations (39). Presently it appears that a more detailed model is needed to elucidate how changes in these various properties affect the bonding strength between a specific adsorbate and a metal crystallite.

Although Pt and Pd are in the same column and are neighbors in the periodic table, a similar trend of Q_{ad} with dispersions above 0.65 was not obvious for Pt (*52*); however, many of the samples with crystallite sizes below 3 nm were TiO_2-supported and had somewhat lower Q_{ad} values than the typical Pt catalysts. In addition, we have found that the support noticeably alters Q_{ad} for CO on Pt (*53*). Finally, a difference in catalytic properties between Pt and Pd is not uncommon; for example, it has been reported that Pt and Pd exhibit a completely different crystallite size effect on methylcyclopropane hydrogenolysis (*54*). Also, some unique characteristics of Pt are observed in work function changes upon chemisorption of CO and H_2 (*55, 56*), in IR spectra of adsorbed CO (*55*), and in band structures (*57*). The different chemisorption properties of Pt may be due, at least partially, to the spin–orbit effects that give Pt surfaces a rather unique local density of states (*58*), because the bond strength between adsorbate and metal particle can be quite dependent upon the distribution of the local density of states for surface metal atoms (*59*).

Support Effects

Because crystallite size appears to have a significant effect on the CO heat of adsorption, one must compare only those samples with comparable dispersions to search for any support effect on Q_{ad}. For the samples shown in Fig. 3, a single trend appears to exist for the variation of Q_{ad} with crystallite size, and different supports with comparable dispersions show no significant differences in Q_{ad}. The three most notable exceptions, 1.71% Pd/SiO_2, 1.88% Pd/TiO_2 (LTR), and 0.36% Pd/Al_2O_3 (I), were discussed under Results. The behavior of the Pd/TiO_2 sample could be further complicated if the creation of new adsorption sites on the support surface or at the Pd–titania interface is facilitated by the Pd because their influence would not be canceled by the pure TiO_2 support.

The actual dispersion of the 2.03% Pd/TiO_2 (HTR) sample cannot be determined by chemisorption because of its abnormal chemisorption properties, and therefore the Q_{ad} measured on this sample is not shown in Fig. 2. However, since these low uptakes cannot be explained by sintering, and redispersion has not been observed for TiO_2-supported Pd (*60*), we expect the 2.03% Pd/TiO_2 (HTR) sample to have a dispersion similar to, or slightly less than, that of the LTR sample. Based on this estimated dispersion, the CO heats of adsorption on the Pd/TiO_2 (HTR) samples were not markedly different from values on the other catalysts of comparable dispersion even though the chemisorption of H_2 and CO was greatly suppressed. It has been proposed that suppressed chemisorption of H_2 and CO on TiO_2-supported group VIII metals after HTR is due to an electronic interaction between the metal and partially reduced TiO_2 that results in a weakened metal–adsorbate bond (*6*). A number of studies have used XPS to probe for such electronic interactions in Pt/TiO_2 and Rh/TiO_2 systems, and conflicting results have been reported (*61–63*). At least in one case XPS results showed no difference between Pt/TiO_2 (HTR) and Pt/TiO_2 (LTR) regarding the core-level binding energies of Pt (*61*). However, Fleisch *et al.* have shown that the Pd $3d_{5/2}$ binding energies for Pd on SiO_2 were the same as metallic Pd and independent of crystallite size, but a negative shift occurred for reduced Pd on La_2O_3, with the largest crystallites being the most electronegative (*64*).

Another explanation attributes the suppression of chemisorption to blockage of metal surface sites by the migrating support, such as TiO_x species, during high temperature reduction (*5*). This latter explanation would not necessarily cause a change in the heat of adsorption. Recently Bell and co-workers conducted TPD studies of Pd/SiO_2 and Pd/La_2O_3 catalysts and have attributed reduced chemisorption capacity to LaO_x moieties on the Pd surface and changes in the TPD spectra to both morphological changes in the Pd crystallites and charge transfer from these partially reduced LaO_x species (*65, 66*). The results in Table 3 imply that the principal reason for decreased CO chemisorption is physical blockage of Pd surface sites by TiO_x species because the CO that does chemisorb, whether on the Pd only or also on newly created sites involving the titania support, retains a high Q_{ad} value.

Although electronic interactions between metals and conventional supports such as SiO_2–Al_2O_3, Al_2O_3, and zeolites have been suggested to explain reported support effects on catalytic properties (*67, 68*), the results in this study do not indicate a significant support effect on CO bond strengths on Pd, at least on crystallites that are 3 nm or larger. Similar results have been obtained for H_2 and O_2 chemisorption on Pd (*11, 12*). Consequently, we tend to discount simple arguments invoking electron transfer between the metal and support as an explanation for large variations in catalytic activity because noticeable changes in Q_{ad} values would also be anticipated. However, for extremely small metal clusters such interactions may be more likely.

SUMMARY

Heats of adsorption of CO on supported Pd appear to be relatively insensitive to the support used. High-temperature reduction in H_2 suppressed chemisorption of CO and H_2 on a Pd/TiO_2 catalyst, but the Q_{ad} value for CO on this sample was comparable to those measured on regular Pd catalysts. These findings suggest that support effects on the catalytic properties of Pd involving reactions with CO, such as CO hydrogenation, may be due to direct involvement of the support in the catalytic sequence, but are unlikely to be a consequence of changes in electronic properties of Pd due to electronic interactions between it and the support. The suppression of chemisorption that routinely occurs for TiO_2-supported Pd after high-temperature reduction appears to be primarily due to blockage of the metal surface by TiO_x species rather than to a decrease in surface bond strength. However, a significant crystallite size effect exists and the CO heat of adsorption increases noticeably from about 23 kcal $mole^{-1}$ to near 36 kcal $mole^{-1}$ as the Pd crystallite size decreases below 3 nm. The variation of Q_{ad} with Pd particle size is much larger than anticipated by assuming only changes in crystallographic structure on the particle surface are responsible; consequently, the changes in electronic properties that are predicted for very small Pd particles appear to be the dominant factor.

ACKNOWLEDGMENT

This research was supported by the U.S. DOE, Division of Basic Energy Sciences, under Grant DD-FG02-84ER13276.

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