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Calorimetric Heat of Adsorption Measurements on Palladium

III. Influence of Crystallite Size and Support on O_2 Adsorption

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Integral, isothermal heats of adsorption were measured for O_2 adsorption on a family of Pd catalysts at 300 K using a modified differential scanning calorimeter. On Pd crystallites between 3 and 1000 nm, Q_{ad} values exhibited no obvious trend and lay within 50 ± 6 kcal/mole O_2, regardless of the support. As the crystallite size decreased below 3 nm, Q_{ad} increased sharply to values near 80 kcal/mole O_2, which is equal to the maximum initial Q_{ad} values obtained in ultrahigh vacuum systems. Thus O_2 adsorption appears to parallel the behavior reported earlier for H_2 and CO although the trend is not so clear due to greater scatter in the data. No obvious influence of the support was observed for Pd dispersed on SiO_2, η-Al_2O_3, and SiO_2–Al_2O_3, but higher than expected values were obtained on TiO_2-supported Pd, which was attributed to oxygen adsorption on sites on the titania surface that were created during the reduction step. This change in the O_2 heat of adsorption is believed to be due primarily to an electronic effect, and the higher values on very small crystallites could be responsible for the enhanced CO dissociation recently reported on highly dispersed Pd.

INTRODUCTION

Heterogeneous catalysts facilitate reactions through a chemisorption process which significantly changes the potential energy surface of a reaction and typically creates a new reaction path with a reduced activation barrier. Therefore, chemisorption is an essential step in surface reactions, and the strength of the chemisorption bond, which has a large influence on the potential energy surface, is one of the most important parameters. Examples of correlations between catalytic activities and oxygen heats of adsorption have been included in a monograph by Golodets (*1*).

Although abundant data on heats of adsorption of gases on metals are available in the literature, almost all of the measurements have been carried out on bulk metals in the form of foils, filaments, or single-crystal surfaces (*2*). However, supported catalysts usually have metal particles with sizes ranging from around 10 nm to below 1 nm. As the surface-to-bulk ratio increases with decreasing particle size, metal particles are expected to have electronic properties different from those of bulk metals (*3*). Furthermore, it has been suggested that the electronic properties of metal particles can also be affected by the support (*4, 5*). The importance of measuring heats of adsorption of gases on small metal crystallites becomes quite obvious, but typical UHV techniques frequently cannot be used for particles distributed in a porous medium because of diffusion and readsorption effects (*6, 7*). However, the direct measurement by calorimetric techniques represents one method that can be applied to supported metal systems.

Both the support and Pd particle size have been reported to affect the activity of Pd for CO hydrogenation (*8–10*), but the origins of these effects are still not completely understood. Strong evidence suggests that CO dissociation is the rate-determining step in the methanation reaction

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over metals such as Pd and Pt, and because the bond strength between oxygen and the metal surface is an important driving force for CO dissociation, the heat of adsorption of oxygen on Pd may indirectly play a role in this reaction. The objective of this investigation was to study Pd crystallites dispersed on a variety of support materials, to determine if either crystallite size or the support altered the oxygen heat of adsorption and, if so, to see whether any catalytic effects could be explained by this variation in oxygen–Pd bond strength.

EXPERIMENTAL

Catalyst Preparation and Pretreatment

The support materials used in this study were SiO_2 (Davison grade 57), SiO_2–Al_2O_3 (Davison grade 979—13% alumina), η-Al_2O_3 (Exxon Research & Engineering Co.), and TiO_2 (Degussa P25). The supported catalysts were prepared by an incipient wetness method or an ion-exchange process using $PdCl_2$ (Ventron Corp.), tetraaminepalladium nitrate (Spex Ind., Inc.), or palladium acetylacetonate (Aldrich Chemical Corp.) as the Pd precursor. The sample of unsupported Pd consisted of high purity Pd power (Johnson Matthey Inc., Puratronic grade—99.999%). All catalysts except for those prepared from $PdCl_2$ were calcined in air or an O_2/He mixture at either 573 or 773 K before reduction. The final Pd weight loadings were determined by both neutron activation analysis and atomic emission spectroscopy. The preparation methods and further details are given in the first paper in this series (*11*).

Chemisorption

Gas uptakes of H_2 and O_2 were measured with a Texas Instruments Model 145 pressure gage in a volumetric adsorption system equipped with an Edwards Model E02 oil diffusion pump backed by a mechanical pump and liquid N_2 traps. An ultimate vacuum near 5×10^{-7} Torr (10^{-4} Pa) could be obtained, as measured by a Granville-Phillips Model 260-002 ionization gauge. H_2 and He (both 99.999% from Linde) were further purified by passage through Oxytraps (Alltech Associates), and the O_2 (99.99% from MG Scientific) was passed through a drying tube (Supelco). Details of the system are given elsewhere (*12*).

Both H_2 and O_2 uptakes were measured at room temperature. The sorption–readsorption method of Benson *et al.* was used to determine the irreversible hydrogen chemisorption (*13*), and the oxygen chemisorption was determined by extrapolating the adsorption isotherm to zero pressure to correct for physisorption on the support. The measurements of H_2 uptake were repeated for each sample to ensure that the adsorption capacity was stabilized. A portion of the sample was then used for heat of adsorption measurements while the remainder was placed back in the adsorption system so that additional uptake measurements to parallel those in the calorimeter could be made.

Calorimetric Measurements

Isothermal energy changes during oxygen adsorption at 300 K were measured using a modified Perkin–Elmer DSC-2C differential scanning calorimeter (DSC). The gas handling system incorporated mass flow controllers and a switching valve which regulated the carrier gas flow and allowed different gases to be introduced into the DSC for purging, reduction, and heat of adsorption measurements. Ultrahigh purity helium and argon (both 99.999% from MG Scientific) were further purified by passage through Oxytraps (Alltech Associates). Ultrapure hydrogen (10 ppb impurities) was produced by an Elhygen Mark V hydrogen generator and passed through an Oxytrap, while the oxygen was passed through a drying tube (Supelco). Details of the modifications required for the DSC and the calibrations for temperature and energy are described elsewhere (*14*).

Approximately 30–100 mg of catalyst was placed into the sample cavity, and an equal amount of pure support was loaded into the reference sample holder to compensate for physisorption on the support. When the Pd powder was studied, a piece of stainless steel was placed in the reference cavity. Pretreatments identical to those used for chemisorption measurements were followed except that all reductions in the DSC were carried out in a 20% H_2, 80% Ar mixture, and removal of hydrogen from samples after reduction was accomplished by purging the sample at or 20–50 K below the reduction temperature for 1 h in Ar. All energy changes were measured at 300 K by switching the 1 atm purge gas stream from pure Ar to 10% O_2 in Ar. Errors due to differences in thermal conductivity were minimal because of the similar values for O_2 and Ar (*14*).

RESULTS

Chemisorption

Chemisorption measurements indicated that most of the catalysts were stabilized after a 1-h reduction, and exposure of the samples to air had no significant effect on subsequent uptakes; therefore, only the final uptake measurements for each sample are listed in Table 1. Because it had been found that exposure to CO during the CO chemisorption studies caused appreciable loss of Pd surface area (*15*), all oxygen adsorption measurements were conducted prior to CO uptake measurements except for the 1.80% Pd/Al_2O_3 and the 2.03% Pd/TiO_2 (II) samples, which were treated in a flowing mixture of 20% O_2 in He at 573 K for 30 min after each CO exposure. Although oxygen chemisorption has been used to determine the dispersion (fraction exposed) of noble metals, some interesting discrepancies between hydrogen and oxygen chemisorption uptakes were apparent for some samples in Table 1. For samples with lower dispersions, the O_2 uptakes tended to be comparable to or lower than H_2 uptakes, as expected for immobile versus mobile monolayer coverage, but they were typically higher than the H_2 uptakes on the most highly dispersed samples. The variation in these adsorption ratios has been attributed to a fraction of the hydrogen monolayer coverage being weakly adsorbed and capable of being pumped off at 300 K (*11*).

Heats of Adsorption

A typical energy change during oxygen chemisorption as measured by the DSC is shown in Fig. 1. Readsorption of O_2 was conducted on every sample after purging it at 300 K for 1 h, but only negligible energy changes were observed which indicated strong oxygen chemisorption, no desorption, and minimal baseline disturbance due to switching of gases. The reproducibility of the calorimetric data for a given sample is indicated in Table 2 by the average deviation from the mean when more than one measurement was made on a given sample. Because of the excellent reproducibility, only one measurement of ΔE was made on many samples. Integral heats of adsorption of O_2 measured at 300 K, Q_{ad}, are listed in Table 2 and plotted versus the average Pd crystallite size in Fig. 2. To be consistent with previous studies, average crystallite diameters were calculated from the hydrogen chemisorption values using the equation, d (nm) = $1.13/D$, where D is the H_{ad}/Pd_t ratio and Pd_t is the total number of Pd atoms (*8*). However, using O_{ad}/Pd_t ratios instead gave an extremely similar plot (*16*).

Despite some uncertainties in the results

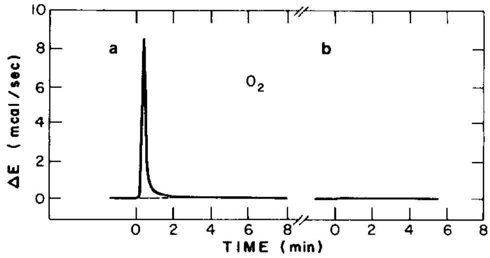

FIG. 1. (a) Energy change measured in DSC for O_2 adsorption on 1.95% $Pd/SiO_2–Al_2O_3$ (I); T = 300 K, P_{O_2} = 75 Torr, 0.0365 g. Dotted line represents baseline upon O_2 readsorption after purge. (b) Baseline for O_2 adsorption on pure $SiO_2–Al_2O_3$.

TABLE 1

Gas Uptakes of Chemisorbed Hydrogen and Oxygen

Catalyst (sample)	Pretreatment[a]			Gas uptake (μmole/g cat.) chemisorption		Fraction exposed	
	T_c (K)	T_i (K)	T_r (K)	O_2	H_2	O_{ad}/Pd_t	H_{ad}/Pd_t
1.71% Pd/SiO_2							
(I)	—	533	673	7.5	8.5	0.09	0.11
(II)		533	673	6.5	8.0	0.08	0.10
0.48% Pd/SiO_2	573	300	573	12.8	10	0.57	0.44
2.10% Pd/SiO_2	573						
(I)		300	573	74.5	67	0.75	0.68
(II)		533	673	68.0	65.5	0.69	0.66
1.23% Pd/SiO_2	573						
(I)		300	573	49.5	40	0.86	0.69
(II)		533	673	49.0	36.5	0.85	0.63
0.39% Pd/SiO_2	573	300	573	13.5	9	0.74	0.49
1.95% Pd/SiO_2–Al_2O_3	—						
(I)		448	448	24.0	32.5	0.26	0.35
(II)		448	673	29.5	26.5	0.32	0.29
(III)		533	673	19.0	18	0.21	0.21
(IV)		673	673	18.5	16	0.20	0.17
(V)		723[b]	673	12	9	0.13	0.10
1.16% Pd/SiO_2–Al_2O_3	573	300	573	27.5	32	0.50	0.59
0.98% Pd/SiO_2–Al_2O_3	573						
(I)		300	573	26.5	28.5	0.58	0.62
(II)		533	673	21.5	21	0.47	0.46
1.80% Pd/Al_2O_3	—	533	673[c]	19.0	28.5	0.22	0.34
0.32% Pd/Al_2O_3	573	300	573	10.5	7.5	0.70	0.50
0.36% Pd/Al_2O_3	—						
(I)		448	448	9.5	10	0.56	0.59
(II)		300	573	7.5	9.5	0.44	0.56
0.54% Pd/Al_2O_3	573	300	573	20.0	13.5	0.79	0.53
2.33% Pd/Al_2O_3	—						
(I)		300	573	28.5	52	0.26	0.48
(II)		533	673	33.0	41	0.30	0.37
2.03% Pd/TiO_2	—						
(I)		448	448	19.0	29.5	0.20	0.31
(II)		448	448[c]	23.0	30	0.24	0.31
1.88% Pd/TiO_2	773	448	448	14.0	14	0.16	0.16
Pd powder (I)	773	300	573	2.5	6[d]	0.0005	0.0013

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

[d] Uptakes at 6 Torr.

that could be introduced by a very broad or a biomodal Pd particle size distribution, a pattern emerges in Fig. 2—Q_{ad} for oxygen falls near 50 ± 6 kcal/mole on crystallites from 1 μm down to 3 nm, then it increases noticeably. Because we know of no reason to expect a minimum in Q_{ad}, a flat line has been drawn through the region of crystallite size above 40 nm. Despite some scatter among the data, this trend is essentially identical to that found for both H_2 and CO on these catalysts (*11*, *15*), and it strongly

TABLE 2

Integral Heats of Adsorption of Oxygen on Palladium Measured at 300 K

Catalyst (sample)	T_r (K)	d^a (nm)	O_2 uptake[b] (μmole/g cat.)	Energy change[b] (mcal/g cat.) ΔE_{ad}	Q_{ad}[c] (kcal/mole O_2)
1.71% Pd/SiO_2					
(I)	673	10.1	7.5	415	55.3
(II)	673	11.3	6.5	369	56.8
0.48% Pd/SiO_2	573	2.3	12.8 ± 0.1	770 ± 9	60.2 ± 1.2
2.10% Pd/SiO_2					
(I)	573	1.7	74.5 ± 1.5	4695	63
(II)	673	1.7	68.0 ± 1.5	4845	71.3
1.23% Pd/SiO_2					
(I)	573	1.6	49.5 ± 0.2	3110 ± 78	62.9 ± 1.8
(II)	673	1.7	49.0 ± 1.0	3101	63.3
0.39% Pd/SiO_2	573	2.5	13.5 ± 0.2	912	67.5
1.95% Pd/SiO_2–Al_2O_3					
(I)	448	3.2	24.0 ± 2.8	1330 ± 14.0	55.4 ± 7.1
(II)	673	3.9	29.5 ± 0.7	1459 ± 24.0	49.5 ± 2.0
(III)	673	5.9	19.0 ± 0.0	898	47.3
(IV)	673	6.5	18.5	808	43.7
(V)	673	11.9	12.0	669	55.8
1.16% Pd/SiO_2–Al_2O_3	573	1.9	27.5 ± 1.2	1661	60.4
0.98% Pd/SiO_2–Al_2O_3					
(I)	573	1.8	26.5 ± 0.2	1494	56.4
(II)	673	2.5	21.5 ± 1.2	1186	55.2
1.80% Pd/Al_2O_3	673	3.4	19.0 ± 1.0	1149 ± 5	60.5 ± 3.5
0.32% Pd/Al_2O_3	573	2.4	10.5 ± 0.2	639	60.9
0.36% Pd/Al_2O_3					
(I)	448	1.9	9.5 ± 0.2	490	51.6
(II)	573	2.0	7.5 ± 0.0	602	80.3
0.54% Pd/Al_2O_3	573	2.1	20.0 ± 0.3	1249	62.5
2.33% Pd/Al_2O_3					
(I)	573	2.4	28.5 ± 4.7	1357 ± 35	47.6 ± 9.1
(II)	673	3.0	33.0 ± 0.8	1321 ± 0	40.0 ± 1.0
2.03% Pd/TiO_2					
(I)	448	3.7	19.0 ± 1.0	1391 ± 17	73.2 ± 4.7
(II)	448	3.6	23.0 ± 1.9	1435	62.4
1.88% Pd/TiO_2	448	7.1	14.0 ± 0.5	1092	78
Pd powder	573	1000	2.5	133	53

[a] Based on H_2 chemisorption uptakes in Table 1.

[b] When more than one run was conducted, average values with their average deviation from the mean are listed.

[c] Values are listed with their absolute uncertainty (Ref. (*64*)).

suggests that O_2 heats of adsorption are higher on very small Pd crystallites. The maximum increase in the oxygen heat of adsorption on small crystallites appears to be over 20 kcal mole^{-1}, which is well outside the range of ΔH_{ad} values found on the larger crystallites. The Q_{ad} values for the Pd/TiO_2 (LTR) catalysts do not fit this trend as they are routinely too high. This is attributed to the partial reduction of the titania surface which can occur even during a low temperature reduction (LTR) in the presence of a metal such as Pd, which can activate H_2 and catalyze reduction of the

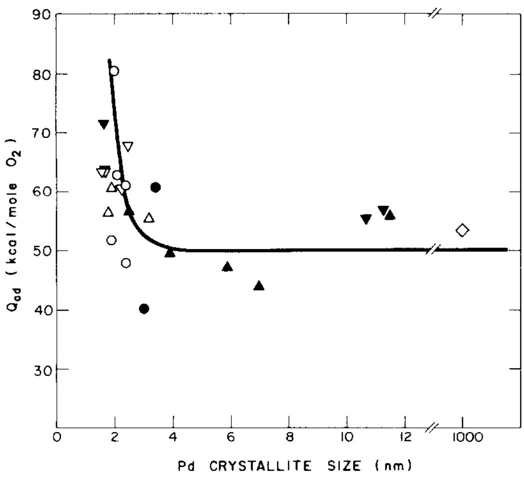

FIG. 2. Integral heat of adsorption of oxygen on Pd at 300 K versus crystallite size: Pd/SiO_2 (▼,▽); $Pd/SiO_2–Al_2O_3$ (▲,△); Pd/Al_2O_3 (●,○); Pd powder (◇); Solid symbols—T_r = 673 K, open symbols—T_r = 448 or 573 K.

titania. A portion of the irreversibly adsorbed oxygen would then be associated with reoxidation of the titania surface, which is very exothermic.

DISCUSSION

Chemisorption

In catalysis research chemisorption has become a standard characterization procedure for dispersed metal catalysts and dispersions of many metals estimated from chemisorption are often in good agreement with those determined by other methods. However, the difficulties involved in the use of oxygen chemisorption for dispersion measurements have been noted (*17*). These uncertainties can be associated with adsorption stoichiometries on different crystallographic planes (*18*), residual anions on the surface (*19*), and lower monolayer coverages due to immobile adsorption (*20*). In the study of this family of Pd catalysts, O_2 uptakes were usually similar to H_2 uptakes on the more poorly dispersed ($D \leqslant 0.4$) samples, in agreement with the study of Benson *et al.* (*13*), whereas they were frequently higher than the H_2 uptakes on the more highly dispersed catalysts. This variation did not correlate with the possible presence of residual anions, as proposed by Kravchuk *et al.* (*19*), and is more likely due to changes in surface structure associated with very small metal particles. The statistically favored increase of more open planes with lower average coordination numbers could allow a higher coverage than that anticipated for the close-packed (111) plane which should dominate large crystallites, and the results here imply that the O_{ad}/Pd_s ratio may well approach unity on very small crystallites. This conclusion agrees with the study of Lam and Boudart on oxygen adsorption on small Pd particles (*21*), and is further supported by the evidence that a small fraction (~0.15) of hydrogen adsorbed on Pd particles can be desorbed at 300 K (*11*). This consideration of reversible hydrogen adsorption would make the total H_2 uptakes much more consistent with the corresponding O_2 uptakes. The irreversibility of the oxygen adsorption is clearly an experimental advantage, and it provided very consistent isotherms and energy changes with minimal baseline correction (Fig. 1).

Heats of Adsorption

This study has shown that integral, isothermal O_2 heats of adsorption on metals can be rapidly and reproducibly measured in a modified, power-compensated DSC, provided that the thermal conductivity of the carrier gas is matched with the adsorbate (*14*). An additional advantage is the ease with which *in situ* pretreatments can be conducted. The Q_{ad} measurements, which were completed within 2–3 min, are listed in Table 2 and can be compared to those in Table 3, which represent initial Q_{ad} values reported in the literature for O_2 adsorption on Pd. With one exception, they were measured on unsupported bulk Pd (*22–28*), and values range between 40 and 80 kcal/mole O_2. The Q_{ad} results in this study are integral values and therefore are expected to be lower than the values in Ta-

TABLE 3

Previously Reported Heats of Adsorption of Oxygen on Pd

Surface	Q_{ad} (kcal/mole O_2)	Technique	Ref.
Pd(111)	55	TPD	22
Pd(100)	60	Isotherm	23
Pd(110)	80	Isotherm	24
Pd black	48	Isotherm	25
Pd film	67	Calorimetry	26
Pd wire	56	TPD	27
Pd/MgO	80–40	Calorimetry	28

ble 3. As an indication of this, as the oxygen surface coverage increased, these initial values decreased markedly to 48 kcal $mole^{-1}$ on the (110) surface (*24*) and to around 10 kcal $mole^{-1}$ for the MgO-supported Pd (*28*). Therefore, the integral heats of adsorption listed in Table 2 are consistent with these previous results. It is also worth noting that heats of formation of PdO ranging from 21 to 29 kcal/mole PdO (42–58 kcal $mole^{-1}$ O_2) have been reported (*1, 29*) which might provide estimates for further comparison of these integral values.

Support Effects

It has been shown in previous studies that the turnover frequency (TOF) for methanation from CO and H_2 over Pd decreases more than 100-fold in the order Pd/TiO_2 (HTR) > Pd/TiO_2 (LTR), Pd/Al_2O_3 $\geqq$ Pd/SiO_2-Al_2O_3, Pd/zeolite $\gg$ Pd/SiO_2, unsupported Pd (*8, 30*). The drastic change in chemisorption properties of Group VIII metals supported on TiO_2 after a high temperature reduction (HTR) in H_2 further suggested that support effects can be significant (*31*). Many explanations for this support effect have been proposed which include electronic interactions between metal and support (*4, 5, 31*), changes in morphology of metal particles (*32*), presence of metal cations stabilized by the support (*33*), creation of metal–support interfacial sites (*34–36*), and coverage of the metal surface by the support (*37, 38*). Although different techniques have been used to collect evidence for electronic interactions between Group VIII metals and support materials, conflicting results have been reported from X-ray photoelectron spectroscopy (XPS) studies and the issue of electron transfer to the metal particles still remains open (*39–43*).

Heat of adsorption measurements provide another approach to the investigation of electronic interactions between metals and supports, should they exist. As shown in Fig. 2, Q_{ad} for O_2 appears to increase noticeably as the Pd particle size decreases below 3 nm, but there is no clear evidence of a significant support effect as the trend is similar for all the supports in Fig. 2. Similar behavior was also observed for heats of adsorption of H_2 and CO on this same family of catalysts (*11, 15*). Unfortunately, we could not obtain unambiguous Q_{ad} values for O_2 on the TiO_2-supported catalysts because of the significant oxygen adsorption that can occur on the titania surface after reduction. Any additional surface reduction catalyzed by the Pd would not be compensated for by the pure support, and higher than expected Q_{ad} values were obtained (see Table 2). Consequently, we conclude at this time that support effects on the adsorption properties of Pd for O_2, if they exist at all, are small relative to crystallite size effects. This is consistent with the study of Gallezot *et al.*, who reported no electronic interactions between small metals particles and Lewis acid sites (*44*).

Crystallite Size Effects

Metal dispersion, i.e., crystallite size, is another important factor that can affect activity and selectivity of catalysts (*45*), and two major explanations for the origin of size effects have been proposed. The first invokes an ensemble effect and suggests that some reactions may proceed favorably on sites with a specific arrangement of surface atoms (*46*). The demand for special sites may be due to the requirement that multiple bonding of the reactant with the metal surface is necessary for these reactions (*47*). This geometric effect has also been interpreted in terms of conservation of orbital symmetry (*48*). The other explanation attributes the size effect to changes in bond strength between adsorbates and metal particles as a consequence of changes in the electronic properties. These changes in electronic properties can be a result of a localized effect created as the average coordination number of surface metal atoms changes with particle size or they can be due to changes in collective properties as the number of atoms in the crystallite varies (*49*). Because both geometric and electronic properties vary simultaneously as crystallites shrink from 5 nm to less than 1 nm, it is usually extremely difficult to separate the contributions of these two parameters.

Within the scatter of the data, the heat of adsorption of oxygen measured in this study appeared to be relatively invarient with crystallite size as it ranged from 1 μm to about 3 nm, then the Q_{ad} increased from an average value near 50 kcal $mole^{-1}$ to 70–80 kcal $mole^{-1}$ on the smallest Pd crystallites. Both model calculations (*50*) and experimental data (*51, 52*) have indicated that the electronic properties of Pd particles deviate from those of bulk Pd as particle size decreases below 3 nm. Model calculations have indicated that more than 100 metal atoms are needed in a cluster to develop bulk-like properties such as the bandwidth, the density of states profile, and the work function (*50*). Particularly, it has been shown by X-ray absorption spectroscopy that *d*-orbital vacancies increase as Pd dispersion increases, and hence stronger bonding on small crystallites has been predicted (*53*). In view of this and previous studies in which large changes in H_2 and CO heats of adsorption with particle size were found which could not be accounted for by considering changes in surface geometry only (*11, 15*), we again attribute this increase in Q_{ad} on very small crystallites primarily to changes in electronic properties. However, the limited initial Q_{ad} values measured on Pd single crystals admittedly make this conclusion less certain for O_2 adsorption because the highest value, near 80 kcal $mole^{-1}$, occurred on the more open (110) surface which is statistically more probable on small particles, and the lowest value, near 55 kcal $mole^{-1}$, occurred on the close-packed (111) plane which should dominate on large crystallites.

The difference between bulk Pd and small Pd crystallites may also be illustrated by their ability to dissociate CO (*54*). Dissociation of CO has not been reported in studies of CO chemisorption on a number of different Pd single-crystal planes (*55*), but the ability of Pd particles to dissociate CO has been shown to increase as dispersion increases (*54*). In one case, dissociation of CO on a highly dispersed Pd catalyst was reported as low as 373 K (*56*), which is far below the temperatures of normal thermal desorption peaks for CO on Pd single-crystal planes (*27*). These results suggest that geometric effects alone are not sufficient to facilitate CO dissociation, and this implies that the electronic properties of small Pd crystallites are the primary reason for their ability to dissociate CO.

Although symmetry (or geometric) effects can be an important factor in determining the activation energy for reactions on solid surfaces, as pointed out by Banholzer *et al.* (*48*), the heat of adsorption can also affect the activation energy as suggested by the Polanyi equation, $E_a = C + a(\Delta H)$, where C and a are empirical constants and ΔH is the enthalpy change of the reaction (*57*). A relation between E_a for the dissociation of molecularly adsorbed species and ΔH_{ad} ($Q_{ad} = -\Delta H_{ad}$) of the constituent atoms has also recently been derived from a bond energy–bond order approach (*58*). The successful application of symmetry effects to the dissociation of NO on Pt is possibly due to the exothermic nature of the reaction, as the bond energies (in kcal $mole^{-1}$) are E(N–O) = 151, E(Pt–N) = 127, and $E(\text{Pt–O}) = 83$ (*58*); therefore, the dissociation of molecularly adsorbed NO is exothermic by 59 kcal mole^{-1}. It has been suggested that in the Polanyi equation $a \cong 0.25$ for exothermic reactions whereas $a \cong 0.75$ for endothermic reactions (*59*); consequently, small changes in $E(\text{Pt–N})$ and $E(\text{Pt–O})$ on different crystal planes would have a minor effect on E_a, and symmetry effects may represent the dominant factor in dissociation of NO on Pt. In contrast, assuming $E(\text{C–O}) = 256$, $E(\text{Pd–C}) = \sim 140$ to 170, and $E(\text{Pd–O}) = 100$ kcal mole^{-1} (*58*), CO dissociation on bulk Pd may be an endothermic process because of the uncertainty of the Pd–C bond. Therefore, increases in $E(\text{Pd–O})$ and (very likely) $E(\text{Pd–C})$ with dispersion could have a much more significant effect on the activation energy for CO dissociation.

The effect of the O–metal bond strength on CO dissociation is of particular interest because breaking of the C–O bond is an important step in the methanation reaction. Since strong evidence exists that dissociation of CO is probably the rate-determining step for this reaction on metals such as Pd and Pt (*8*, *60*, *61*), effects that enhance the dissociation of CO would be expected to increase the activities of these metals. The increase in methanation activity of Pd with dispersion reported by Ichikawa *et al.* (*9*) is consistent with the trend of O_2 heats of adsorption found in this study. Although Rieck and Bell (*10*) have reported a trend contrary to the findings of Ichikawa *et al.*, they obtained variations in Pd dispersion by calcining some of the catalysts in oxygen at high temperatures which may have produced samples with bimodal size distributions (*62*). Consequently, further studies are needed to clarify this situation.

SUMMARY

The heat of adsorption of oxygen on a family of supported Pd catalysts has been measured calorimetrically to examine the influence of support and Pd crystallite size on this parameter. Although the support has been reported to affect the activities of Pd for certain reactions, the Q_{ad} values for oxygen on Pd appear to be relatively insensitive to typical supports. On the other hand, oxygen heats of adsorption increase noticeably as the Pd crystallite size drops below 3 nm. This is consistent with both model calculations and photoelectron spectroscopy data which suggest that small Pd crystallites have electronic properties different from those of bulk Pd. Although size effects on the adsorptive and catalytic properties of Pd (i.e., structure-sensitive reactions) can be due to changes in both electronic properties and surface geometry, these results imply that changes in the electronic properties of small Pd crystallites appear to be the major factor causing the observed increase in O–Pd bond strength.

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