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Microcalorimetric Studies of H_2, C_2H_4, and C_2H_2 Adsorption on Pt Powder

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Microcalorimetric measurements of C_2H_4 adsorption on Pt powder at 303 and 173 K gave initial heats of 160 and 120 kJ/mol, which correspond to formation of ethylidyne species plus atomic hydrogen and to molecularly bonded C_2H_4 species, respectively. Microcalorimetric measurements of C_2H_2 adsorption on Pt powder at 303 and 173 K gave initial heats of 220 and 210 kJ/mol, respectively. Initial heats of H_2 adsorption on Pt powder at 403 and 173 K were 90 kJ/mol. Exposure of Pt samples to C_2H_4 hydrogenation at 298 K under conditions for which ethylidyne species form, results in decreases in the saturation coverages of H_2 and C_2H_4 adsorption, as well as decreases in the strengths of interaction of these species with the surface (by 20–30 kJ/mol) at 173 K. Exposure of Pt to C_2H_4 hydrogenation at conditions for which ethylidyne species do not form, results in a decrease in the saturation uptake and the adsorption strength of H_2 at 173 K. These surfaces contain significant amounts of adsorbed hydrogen, since they show formation of C_2H_6 upon C_2H_4 adsorption at 173 K. © 1998 Academic Press

Key Words: **microcalorimetry; hydrogen; ethylene; acetylene; adsorption; platinum; ethylene hydrogenation.**

INTRODUCTION

The interactions of ethylene with both single crystal platinum surfaces and supported platinum catalysts have been widely studied, and the results of these investigations reveal the presence of distinct surface species depending on temperature. For example, ultrahigh vacuum studies of ethylene adsorption on Pt(111) have identified π-bonded ethylene species at temperatures below 52 K (1), di-σ-bonded ethylene species from 100–250 K (2–8), and ethylidyne species from 280–450 K (3, 5–15). Adsorption studies have also identified the presence of π-bonded and/or di-σ-bonded ethylene species at low temperatures (<170 K), as well as dehydrogenated ethylene species (e.g., ethylidyne, ethylylidyne, vinylidene, etc.) near room temperature on Pt(100), Pt(110), and Pt(210) surfaces (16–23), on supported platinum films (24, 25), and on supported platinum catalysts (26–28). Importantly, Sheppard and De La Cruz have shown in a recent review (29) that comparable results are obtained when ethylene is dosed onto supported platinum catalysts and onto platinum single crystal surfaces. For example, infrared spectra show the presence of π-bonded and di-σ-bonded species when ethylene is dosed onto silica- and alumina-supported platinum at low temperatures (<195 K), whereas ethylidyne species form at room temperature. Figure 1 illustrates schematically the abovementioned species.

The strengths with which the aforementioned species interact with platinum have been probed primarily with temperature-programmed desorption. For example, the activation energy for desorption of molecular ethylene from Pt(111) has been reported to range from 29–75 kJ/mol (7, 30–32). More recently, Dumesic and co-workers (33, 34) have used heat-flux microcalorimetry to measure the heat of ethylene adsorption on supported platinum catalysts, and King and co-workers (35–37) have used ultrahigh vacuum microcalorimetry to measure the heat of ethylene adsorption on platinum single crystals. These studies were performed on platinum surfaces at temperatures near 300 K, where ethylene dehydrogenates to form ethylidyne species and surface hydrogen, and the results will be discussed later in this paper.

Similar to ethylene on platinum at low temperatures (<250 K), acetylene has been shown to adsorb associatively with its C–C axis parallel to the platinum surface (2, 3, 6, 7, 38–40). Vibrational spectroscopy (41) and molecular orbital theory (40) have shown that two types of molecular bonding can occur depending on the platinum surface. On a Pt(111) surface, acetylene is thought to form two σ-bonds and one π-bond to three platinum atoms (di-σ/π-bonded acetylene as shown in Fig. 1) (2, 39–41) in threefold hollow sites (40, 42). On Pt(100), acetylene adsorbs into fourfold hollows, possibly forming four σ-bonds to platinum atoms (tetra-σ-bonded acetylene as shown in Fig. 1) (16, 40, 41).

At higher temperatures, a number of different species have been suggested to form during the adsorption of acetylene on platinum. Acetylene has been shown to adsorb associatively at higher temperatures (>280 K) with its C–C axis normal to the platinum surface (2, 3, 6, 9, 38, 41, 43). Vinylidene species have been suggested to be responsible

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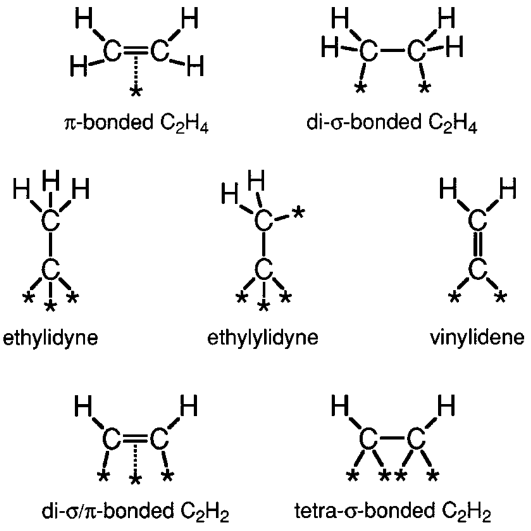

FIG. 1. Schematic diagram of C_2 species identified spectroscopically on platinum surfaces (29, 41) (* represents a surface platinum atom).

for this type of adsorption (3, 4, 7, 38, 43, 44); however, ethylidyne species (6, 9), which form in the presence of surface hydrogen (2, 3, 9, 39, 41, 43, 45–47), and ethylylidyne species (2, 45) have also been proposed to form.

The present microcalorimetric study was undertaken at various temperatures (173 to 403 K) to probe the adsorption strengths of hydrogen, ethylene, and acetylene on platinum powder. The spectroscopic literature discussed above suggests that both ethylene and acetylene adsorb associatively at 173 K, but ethylene should dissociate at 303 K to form ethylidyne species and atomic hydrogen. In this investigation, we employed a novel microcalorimetric technique (48) that allows the exposure of samples to adsorbate gases without excessive surface contamination. Additionally, we have applied this method to study platinum surfaces that have undergone ethylene hydrogenation at different reaction conditions.

EXPERIMENTAL

Microcalorimetric measurements were performed at 173, 303, and 403 K using a Setaram BT2.15D heat-flux microcalorimeter. The calorimeter was connected to a gas handling system and a volumetric system employing Baratron capacitance manometers for precision pressure measurement ($\pm 0.5 \times 10^{-4}$ Torr). The maximum apparent leak-rate of the volumetric system (including the calorimetric cells) was 10^{-6} Torr/min in a system volume of approximately 70 cm^3 (i.e., 10^{-6} μmol/min). The ultimate dynamic vacuum of the system was ca 10^{-7} Torr.

The calorimetric procedures used in this study have been described in detail elsewhere (48, 49). Briefly, each sample was treated *ex situ* in ultra-pure flowing gases and subsequently sealed in a Pyrex capsule. This capsule containing the sample was then broken in a special set of calorimetric cells (48) after the sample had attained thermal equilibrium with the calorimeter. In this manner, it was possible to expose the sample to the adsorbate gas without significant surface contamination, as outlined below. After the capsule had been broken, the microcalorimetric data were collected by sequentially introducing small doses (1–10 μmol) of hydrogen, ethylene, or acetylene onto the platinum sample (~1.0 g) until it became saturated. The resulting heat response for each dose was recorded as a function of time and integrated to determine the energy released (mJ). The amount of gas adsorbed (μmol) was determined volumetrically from the dose and equilibrium pressures and the system volumes and temperatures. The differential heat (kJ/mol), defined as the negative of the enthalpy change of adsorption per mole of gas adsorbed, was then calculated for each dose by dividing the heat released by the amount adsorbed.

Sample treatments for the microcalorimetric experiments were performed in a downflow Pyrex treatment cell (48). A 5 mm OD × 18-cm long Pyrex NMR tube (Wilmad Glass) was sealed to the side of the treatment cell and served as both the fill port and a capsule in which to seal the samples. Ultrahigh purity hydrogen (99.999%, Liquid Carbonic), used for sample treatments and for adsorption studies, was purified by passage through a palladium-alloy thimble. Ultrahigh purity helium (99.999%, Liquid Carbonic), also used for sample treatments, was purified by passage over heated (473 K) copper turnings and activated molecular sieves (13X) cooled to 77 K. These gases further purified by passage through a bed of reduced Oxy-Trap (Alltech Association, Inc.) and a bed of reduced iron catalyst to remove oxygenates. Ethylene (99.9%, Matheson) and acetylene (99.6%, Liquid Carbonic), used for adsorption studies, were purified by successive freeze/pump/thaw cycles with liquid nitrogen. Oxygen (Liquid Carbonic), used for calcinations, was dried by passage over activated molecular sieves (13X) at room temperature.

Platinum powder (99.9%, Aldrich) for microcalorimetric studies was calcined in flowing oxygen for 3 h at 623 K, treated in flowing hydrogen for 1 h at 298 K and for 2 h at 373 K, and then purged with flowing helium for 0.5 h at 373 K and for 2 h at 473 K to remove adsorbed hydrogen. The reduced platinum powder was then isolated in 350 Torr of helium at room temperature and sealed in the Pyrex tube attached to the side of the treatment cell.

It should be noted that the underlying rationale for the above experimental method is to use ultra-high purity gases for sample treatments (impurities <1 ppm), to work in cells with low leak-rates (~10^{-6} μmol/min), and to use high surface area samples (~50 μmol sites in the cells). For example, after a sample had been treated in H_2, we removed the adsorbed hydrogen by flowing He over the sample at 473 K for 2 h. During this period of time, we introduced at most

0.3 μmol of impurities on a sample with 50 μmol of surface sites. Similarly, after the sample capsule was broken in the microcalorimeter, we waited about 0.5 h before beginning microcalorimetric adsorption measurements. During this time, we introduced only 10^{-5}–10^{-4} μmol of impurities onto 50 μmol of surface sites. In addition, the surface area of active metal in the microcalorimeter (10^4 cm^2) was much higher than the surface area of the cell walls ($\sim$10 cm^2), and contamination of the sample from outgassing of species from the cell walls was negligible.

Platinum surfaces that are more characteristic of those found under reaction conditions for ethylene hydrogenation were prepared on a kinetics apparatus equipped with mass-flow controllers and an EAI Quad 250B residual gas analyzer. The kinetics apparatus was configured such that the ethylene and hydrogen flows were mixed in a gas manifold and then directed to the sample treatment cell. The reactor effluent was subsequently routed to the residual gas analyzer. Hydrogen (Liquid Carbonic) used in these studies was purified by passage through a Deoxo unit (Engelhard) and activated molecular sieves (13X) at 77 K, while ethylene (99.9%, Matheson) was purified by passage through reduced Oxy-Trap (Alltech Association, Inc.) and activated molecular sieves (13X) at room temperature. Helium (Liquid Carbonic), used to purge unreacted gases from the treatment cell after ethylene hydrogenation, was purified by passage through a reduced Oxy-Trap and activated molecular sieves (13X) at 77 K. In these studies, the platinum powder was first treated in flowing oxygen for 3 h at 623 K. The platinum powder was then reduced in flowing hydrogen for 1 h at 298 K and for 2 h at 373 K, followed by cooling to room temperature in flowing hydrogen prior to ethylene hydrogenation. The ethylene hydrogenation reaction was started in flowing hydrogen (10–50 sccm) at 298 K and 760 Torr pressure by initiating a step change in the ethylene flowrate (0–50 sccm) to achieve C_2H_4/H_2 ratios of 5.0, 0.5, and 0.0 (no C_2H_4). The concentrations of hydrogen, ethylene, and ethane leaving the reactor were monitored with the residual gas analyzer. After the reaction reached steady (ca 10 min), the ethylene and hydrogen flows were stopped and the sample was purged with flowing helium at 298 K (until the reactor effluent concentrations of hydrogen, ethylene, and ethane became negligible, ca 1 h) to remove unreacted gases from the sample cell. These platinum samples having undergone ethylene hydrogenation were sealed with 350 Torr helium in the attached Pyrex tube for calorimetry. The rate of ethylene hydrogenation was negligible when an empty reactor (treatment cell) was tested in the kinetic apparatus.

RESULTS

Clean Platinum Powder

Microcalorimetric measurements of hydrogen, ethylene, and acetylene adsorption were performed on reduced platinum powders to establish the adsorption strengths of these molecules on platinum. The differential heats of adsorption were measured at room temperature (403 K for hydrogen) for comparison with heats of adsorption reported in the literature, and also at 173 K, where ethylene and acetylene adsorb associatively (2, 3, 29, 39, 41).

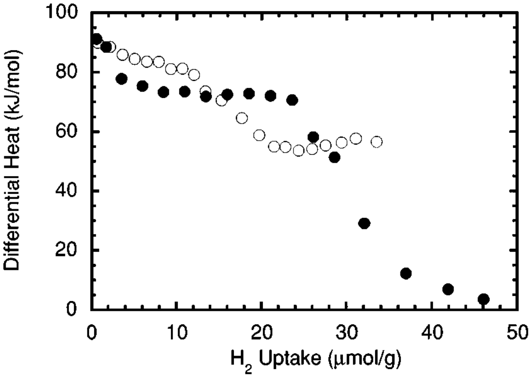

FIG. 2. Differential heat of hydrogen adsorption on platinum powder at 303 K (○) and 173 K (●).

Figure 2 shows the microcalorimetric results for hydrogen adsorption on platinum powder at 403 and 173 K. At 403 K, hydrogen adsorbs dissociatively on platinum with an initial heat of 90 kJ/mol, in agreement with the heats of 90 ± 5 kJ/mol reported for hydrogen adsorption on silica- and zeolite-supported platinum catalysts (33, 50, 51). The differential heat decreases slowly as the first 12 μmol/g of hydrogen adsorb. At higher hydrogen coverages the differential heat decreases to ca 55 kJ/mol and remains constant at this value until the surface becomes saturated with hydrogen at a coverage of ca 30 μmol/g.

At 173 K hydrogen adsorbs on platinum with an initial heat of 90 kJ/mol. Within the first 5 μmol/g of hydrogen coverage, the differential heat decreases to value of ca 75 kJ/mol and remains constant at this value for the next 20 μmol/g of hydrogen uptake. Further increases in the hydrogen coverage cause the differential heat to decrease until a saturation uptake of ca 40 μmol/g is reached.

Microcalorimetric measurements of ethylene adsorption on platinum powder at 303 and 173 K are shown in Fig. 3a, and the corresponding adsorption isotherms are shown in Fig. 3b. At 303 K, ethylene adsorbs on platinum with an initial heat of 160 kJ/mol. This value is in general agreement with results of microcalorimetric measurements on single crystal surfaces, which gave heats of 174 ± 4 and 170–205 kJ/mol for ethylene adsorption on Pt(111) (37) and Pt(110) (35), respectively. Our value also agrees with heats of 150 ± 5 kJ/mol reported for ethylene adsorption on Pt/SiO_2 (33, 34). The differential heat decreases to a value of ca 150 kJ/mol as the first 10 μmol/g of ethylene adsorb. At higher coverages, however, the differential heat *apparently* increases and then decreases at higher coverages until the surface becomes saturated with a total ethylene uptake of

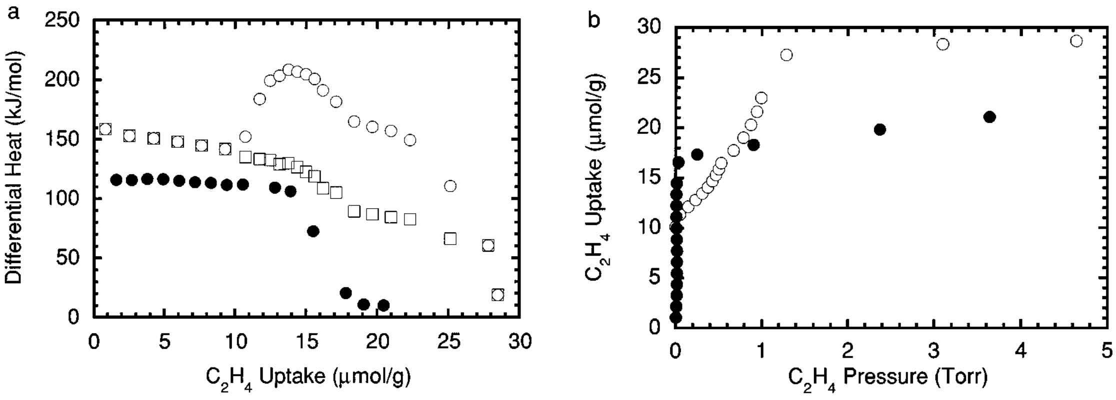

FIG. 3. Ethylene adsorption on platinum powder at 303 K (○) and 173 K (●), and 303 K corrected for ethane formation (□): (a) differential heat plot and (b) adsorption isotherm.

ca 30 μmol/g. A similar change occurs in the corresponding adsorption isotherm (Fig. 3b) in which the pressure begins to increase with coverage after only 10 μmol/g of ethylene have adsorbed.

The apparent increases in the differential heat and in the pressure with coverage observed for ethylene adsorption at 303 K are the result of ethane formation, as confirmed in a separate experiment, which introduces errors in the volumetric measurements of adsorbate uptake. Ethylene was dosed onto platinum powder at 303 K until the residual pressure in the sample cell reached ca 1 Torr (the pressure where the gaseous ethane concentration would be significant according to Fig. 3b). The sample was then isolated in the sample cell and the composition of the remaining gas phase was analyzed with the residual gas analyzer. The mass spectrum obtained showed that ethane was the primary gas phase component and indicates that ethane forms (self-hydrogenation) when ethylene is dosed onto clean platinum powder at 303 K. Similar results have been reported by Godbey and co-workers (31) who observed ethylene self-hydrogenation when a Pt(111) surface saturated with ethylene at 150 K was heated in vacuum to 300 K. Figure 3a also shows the differential heat of ethylene adsorption at 303 K versus coverage, corrected for the effects of ethane formation as presented in the discussion. The apparent maximum in this curve has vanished, and the heat decreases monotonically with coverage.

At 173 K, ethylene adsorbs on platinum with an initial heat of 120 kJ/mol, in agreement with differential heats of 120–136 kJ/mol reported for the adsorption of molecular ethylene on Pt(110) (35). The differential heat remains constant at the value of 120 kJ/mol for the first 15 μmol/g of ethylene uptake. At higher coverages, the differential heat decreases with increasing ethylene coverage until a saturation value of ca 20 μmol/g is reached. The ethylene adsorption isotherm obtained at 173 K (Fig. 3b) shows a steady increase in ethylene coverage with successive ethylene doses until the surface becomes saturated (ca 20 μmol/g), at which point ethylene no longer chemisorbs and the ethylene pressure increases.

Microcalorimetric measurements of acetylene adsorption on platinum powder at 303 and 173 K are shown in Fig. 4. At 303 K, acetylene adsorbs on platinum with an initial heat of 220 kJ/mol, which is comparable to the values of 178–192 kJ/mol measured in an isoperibol calorimeter for acetylene adsorption on an evaporated platinum film (52). The differential heat remains constant at ca 220 kJ/mol for the first 20 μmol/g of acetylene uptake. At higher coverages, the differential heat apparently increases slightly and then decreases until a saturation coverage of ca 32 μmol/g is reached. The apparent increase in the differential heat with coverage at ca 20 μmol/g likely is an artifact caused from ethylene formation (43, 46).

At 173 K, acetylene adsorbs on clean platinum with an initial heat of ca 210 kJ/mol. The differential heat subsequently decreases to ca 200 kJ/mol and remains constant at this value until ca 15 μmol/g of acetylene have adsorbed. Further increases in the acetylene coverage cause the differential heat to decrease until a saturation coverage of ca 20 μmol/g is reached. The highly covered platinum surface

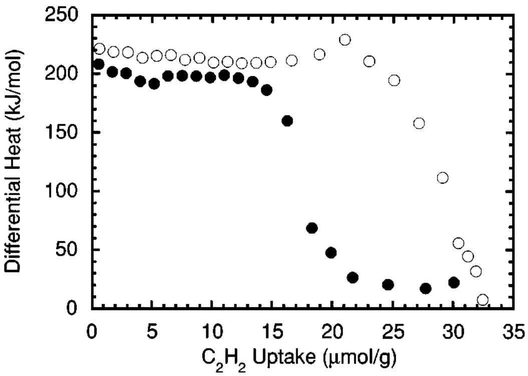

FIG. 4. Differential heats of acetylene adsorption on platinum powder at 303 K (○) and 173 K (●).

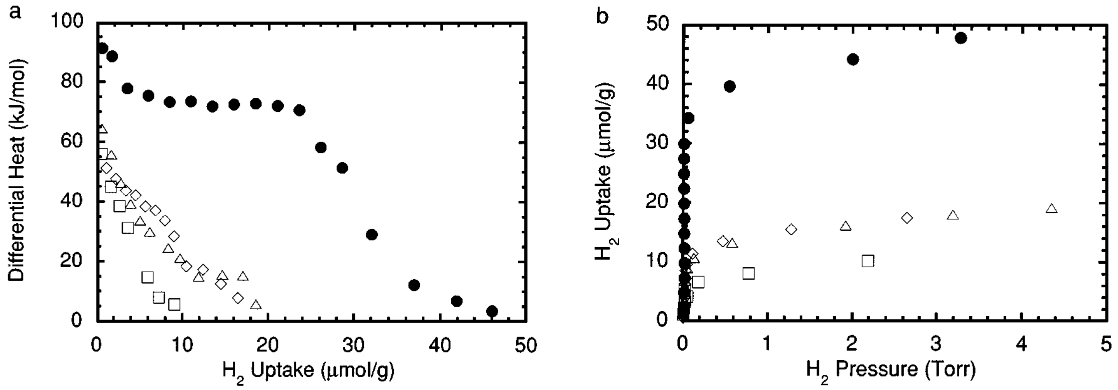

FIG. 5. Hydrogen adsorption at 173 K on platinum powder (●) and platinum powders after ethylene hydrogenation at 298 K and 760 Torr with C_2H_4/H_2 ratios of 5.0 (□), 0.5 (△), and 0.0 (◇) (no C_2H_4): (a) differential heat plot and (b) adsorption isotherm.

continues to adsorb acetylene weakly (20 kJ/mol) until the surface coverage reaches ca 30 μmol/g.

Platinum Powder after Ethylene Hydrogenation/Adsorption

Microcalorimetric measurements of hydrogen and ethylene adsorption were also performed on platinum powders which had been exposed to reaction conditions for ethylene hydrogenation. The reaction conditions chosen were those used by Rekoske *et al.* (28) for ethylene hydrogenation over Pt/SiO_2 at 298 K and 760 Torr. These authors showed via *in situ* FTIR that ethylidyne species formed on Pt/SiO_2 when the C_2H_4/H_2 ratio was equal to 5.0, but these species did not form for $C_2H_4/H_2 = 0.5$. Experiments were also conducted to examine how adsorbed hydrogen affects the adsorption of both hydrogen and ethylene. The microcalorimetric experiments were performed at 173 K to ensure that ethylene adsorbed molecularly, since molecularly adsorbed ethylene is believed to be the active species for ethylene hydrogenation (53).

Figure 5a shows the microcalorimetric results for hydrogen adsorption at 173 K on platinum powders which have undergone ethylene hydrogenation at 298 K and 760 Torr, and Fig. 5b shows the corresponding adsorption isotherms. Also shown for comparison are the microcalorimetric results for hydrogen adsorption at 173 K on clean platinum powder. Under reaction conditions where ethylidyne species are present on platinum ($C_2H_4/H_2 = 5.0$), the initial heat of hydrogen adsorption is reduced significantly from 90 kJ/mol for the clean platinum surface to ca 55 kJ/mol. Moreover, the hydrogen uptake is reduced to a value of ca 5–10 μmol/g (Fig. 5b) from the value of 40 μmol/g obtained for the clean platinum surface. Under reaction conditions, where ethylidyne species are not observed on platinum ($C_2H_4/H_2 = 0.5$ or $C_2H_4/H_2 = 0.0$), the initial heats of hydrogen adsorption are also decreased to values of 65 and 55 kJ/mol, respectively. The hydrogen uptakes are also reduced; however, more sites (ca 15–20 μmol/g, Fig. 5b) are available for hydrogen adsorption on these samples, compared to the platinum sample which contains ethylidyne species.

Figure 6a shows microcalorimetric results for ethylene adsorption at 173 K on platinum powders which have undergone ethylene hydrogenation, and Fig. 6b shows the

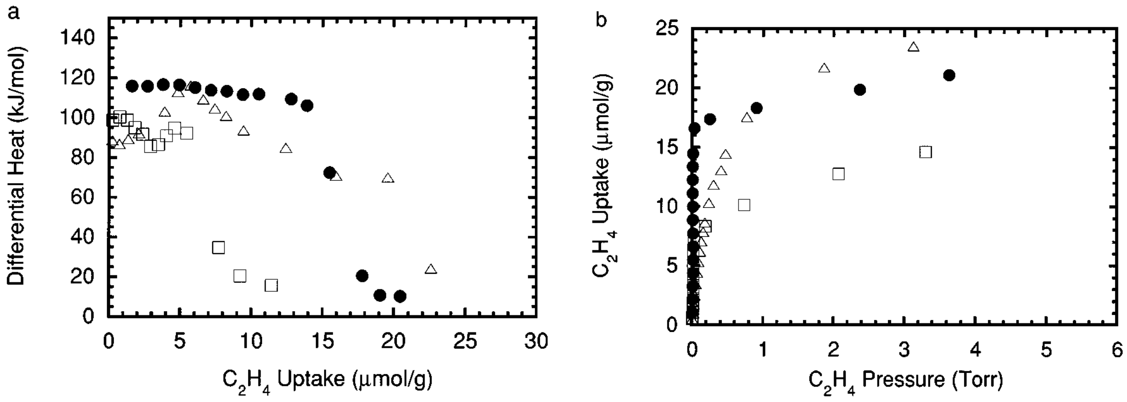

FIG. 6. Ethylene adsorption at 173 K on platinum powder (●) and platinum powders after ethylene hydrogenation at 298 K and 760 Torr with C_2H_4/H_2 ratios of 5.0 (□) and 0.5 (△): (a) differential heat plot and (b) adsorption isotherm.

corresponding adsorption isotherms. Also shown for comparison are the microcalorimetric results for ethylene adsorption at 173 K on clean platinum powder. Under reaction conditions where ethylidyne species are present on platinum ($C_2H_4/H_2 = 5.0$), the differential heat of ethylene adsorption is reduced from 120 kJ/mol for the clean platinum surface to ca 100 kJ/mol. Moreover, the ethylene uptake is reduced to a value of ca 10 μmol/g from the value of 20 μmol/g obtained for the clean platinum surface. Under conditions where ethylidyne species are not observed on platinum ($C_2H_4/H_2 = 0.5$), the initial heat of ethylene adsorption is reduced to ca 90 kJ/mol from the value of 120 kJ/mol on clean platinum. Within the first few micromoles of ethylene uptake, the differential heat increases to ca 115 kJ/mol and then decreases with further increases in the ethylene coverage until a saturation coverage of ca 23 μmol/g is reached. The corresponding adsorption isotherm (Fig. 6b) shows an increase in pressure with increasing ethylene coverage prior to saturation, indicating formation of ethane.

DISCUSSION

Clean Platinum Powder

The microcalorimetric results of the present study show that hydrogen adsorbs on platinum powder with a strength of 90 kJ/mol (Fig. 2). Since hydrogen atoms adsorb primarily in threefold fcc hollows on platinum (54), the decrease at 403 K in the heat of hydrogen adsorption at approximately 50% of the saturation coverage suggests the onset of adsorbate interactions, i.e., hydrogen atoms populating threefold fcc hollows adjacent to filled sites. A similar decrease in isosteric heats of adsorption has been reported for hydrogen adsorption on Rh(110) (55).

The microcalorimetric results obtained at 173 K show only one plateau of differential heats versus coverage, which is located between the two heat plateaus obtained at 403 K (Fig. 2). This behavior results because the rate of hydrogen desorption is negligible at 173 K (e.g., a desorption rate constant of 10^{-12} s^{-1} at 173 K for a desorption activation energy of 80 kJ/mol); therefore, each gas dose does not equilibrate with the powder at 173 K, and the adsorption takes place chromatographically through the sample bed. These results show, however, that platinum powders prepared for the present study have ca 80 μmol/g of surface platinum atoms, assuming a surface stoichiometry of one H atom per surface Pt atom at saturation coverage. The observed heat of non-equilibrated hydrogen adsorption of ca 75 kJ/mol shown in Fig. 2 is in general agreement with the integral heat of hydrogen adsorption of 83 kJ/mol on Pt powder reported by Sen and Vannice (56).

The microcalorimetric results for ethylene adsorption show that ethylene adsorbs on platinum powder with heats of 120 kJ/mol at 173 K and 160 kJ/mol at 303 K (Fig. 3), indicating that different surface species are formed at these temperatures. Over oxide-supported platinum catalysts, infrared spectroscopy (29) has shown that ethylene adsorbs molecularly at 173 K and dissociates to form ethylidyne species and surface hydrogen at 303 K. Studies of ethylene adsorbed on Pt(111) at temperatures between 100 and 250 K have shown that ethylene adsorbs associatively with its C–C axis parallel to the platinum surface (2–8) in threefold hollows (57). In contrast, studies of ethylene adsorbed on Pt(111) at temperatures above 280 K (3, 5–15) indicate that ethylene adsorbs dissociatively, losing one hydrogen atom per ethylene molecule, and rearranges such that its C–C axis is normal to the surface. The resulting ethylidyne species forms bonds to three surface platinum atoms in a threefold fcc hollow (58, 59). Thus, the initial heats of 120 and 160 kJ/mol measured in the present work represent the formation of molecularly adsorbed ethylene and ethylidyne species plus atomic hydrogen on platinum, respectively. These heats are in agreement with microcalorimetric measurements on platinum single crystal surfaces (35, 37), where the heats of ethylene adsorption to form di-σ-bonded and π-bonded species were reported to be 136 and 120 kJ/mol, respectively, and the heat of formation of ethylidyne species plus adsorbed hydrogen was reported to be 170–174 kJ/mol. Recent quantum mechanical calculations for ethylene adsorbed on platinum clusters (60) predict that the heats of ethylene adsorption to form di-σ-bonded and π-bonded ethylene species are 135 and 95 kJ/mol, respectively, and the heat of ethylene dissociation to form ethylidyne species and adsorbed hydrogen atoms is 155 kJ/mol; both of these values are in general agreement with the present results and the surface science literature.

Another result from this work is that the saturation coverage of ethylene adsorbed on platinum powder at 173 K is ca 20 μmol/g (Fig. 3), which corresponds to one-fourth the number of accessible platinum sites (80 μmol/g). This result is in agreement with the saturation coverage of 0.23–0.25 monolayers determined for the adsorption of di-σ-bonded ethylene on Pt(111) at 100 K (61, 62). In contrast, it appears that the saturation uptake of ethylene on Pt at 303 K is ca 30 μmol/g (0.37 monolayers; see Fig. 3), which disagrees with the saturation coverage of 0.21–0.25 monolayers reported for ethylidyne species on Pt(111) at 300 K (61, 62). The formation of ethane, however, complicates this comparison, as explained below.

The apparent increases in the differential heat of ethylene adsorption (Fig. 3a) and in the pressure (Fig. 3b) with coverage observed for ethylene adsorption at 303 K were shown to result from ethane formation, in which ethylene molecules react with surface hydrogen atoms as a result of ethylidyne formation (self-hydrogenation). Since ethane is the predominant gas phase species present, it is possible to correct the data based on the assumption that ethylene adsorption at 303 K involves two reactions: (1) formation of ethylidyne species and adsorbed hydrogen and (2) reaction of ethylene with surface hydrogen to form ethane (self-hydrogenation). The heat of ethane formation via reaction (2) is -45 kJ/mol, since the gas phase heat of ethylene hydrogenation is -135 kJ/mol (63) and the measured heat of dissociative hydrogen adsorption is -90 kJ/mol.

The corrected plot of differential heat versus coverage for ethylene adsorption on platinum powder at 303 K is shown Fig. 3a. The corrected differential heat data show two regions of differential heat beginning with heats of 160 kJ/mol at zero coverage and 90 kJ/mol after 20 μmol/g of ethylene have adsorbed. The first region of differential heat (160 kJ/mol) corresponds to the formation of ethylidyne species and atomic hydrogen. A significant decrease in the differential heat occurs as the ethylene uptake nears 20 μmol/g, suggesting that the saturation coverage by ethylidyne species is 0.25 monolayers, as reported in the literature (61, 62). The second region of differential heat (90 kJ/mol) suggests that a different form of ethylene adsorption (e.g., molecular adsorption) takes place at coverages exceeding 0.25 monolayers.

The microcalorimetric results for acetylene show that this molecule adsorbs on platinum with a heat of 210 kJ/mol at 173 K and 220 kJ/mol at 303 K (Fig. 4). At low temperatures ($<$250 K), acetylene has been shown to adsorb associatively on platinum surfaces (41) on a Pt(111) surface to form two σ-bonds and one π-bond to three platinum atoms (di-σ/π-bonded acetylene). The low surface area Pt powder used in this study is probably composed primarily of (111) planes (64) with threefold hollows; therefore, the heat of 210 kJ/mol measured at 173 K for associatively adsorbed acetylene likely corresponds to formation of a di-σ/π-bonded acetylene species. Importantly, recent quantum mechanical calculations for acetylene adsorbed on platinum clusters containing threefold hollows predict that acetylene bonds to the three platinum atoms at these sites with a strength near 200 kJ/mol (60), in agreement with the present results.

While acetylene has been shown to adsorb associatively at higher temperatures ($>$280 K) (2, 3, 6, 9, 38, 41, 43). It has also been proposed that ethylidyne species (6, 9), may form in the presence of surface hydrogen (2, 3, 9, 39, 41, 43, 45–47), and ethylylidyne species (2, 45) may also form at these higher temperatures. Recent quantum mechanical calculations for CCH_2 species adsorbed on platinum clusters (60) favor a species with its C–C axis aligned at an angle to the surface, corresponding to a heat of acetylene adsorption equal to 270 kJ/mol. Moreover, King and co-workers (35) report that the heat of ethylene adsorption to form ethylylidyne plus adsorbed hydrogen on Pt(110) is equal to 205 kJ/mol. This value corresponds to a heat of 290 kJ/mol for the formation of this species from acetylene (assuming that the heat of hydrogen adsorption is 90 kJ/mol and the enthalpy of formation of gaseous acetylene and hydrogen from ethylene is 175 kJ/mol (63)). The fact that we do not measure an initial heat near 270 kJ/mol is probably caused by the lack of equilibration of acetylene with the platinum powder at 303 K. Accordingly, the initial heat of 220 kJ/mol measured for acetylene adsorption on platinum at 303 K cannot be attributed to the formation of a single species. Instead the observed heat may be attributed to formation of several species including di-σ/π-bonded acetylene species and adsorbed CCH_2 species.

Another result from the present work is that the saturation coverage for molecularly adsorbed acetylene (173 K) on platinum is 0.25 monolayers (20 μmol/g), in agreement with the (2×2) LEED pattern observed for acetylene chemisorbed on Pt(111) (42, 65), and also with molecular orbital theory (40). This result is also expected given that both ethylene and acetylene adsorb molecularly with their C–C axes parallel to the platinum surface at this temperature and both species have the same saturation coverages (i.e., 0.25 monolayers). The additional acetylene uptake at coverages exceeding 0.25 monolayers is likely due to multilayer formation, as suggested by the weak adsorption strength (20 kJ/mol) measured at these coverages.

Importantly, it should be noted that at the low adsorption temperatures (173–303 K) employed in this study, strongly adsorbed ($\Delta H_{ads} > 90$ kJ/mol) ethylene and acetylene species do not equilibrate with the platinum surface, as evidenced for hydrogen adsorption at 173 K ($\Delta H_{ads} =$ 75 kJ/mol). Thus, the differential heats measured for ethylene and acetylene (120 and 210 kJ/mol, respectively) represent average heats of adsorption over a range of surface coverages.

Platinum Powder after Ethylene Hydrogenation/Adsorption

The microcalorimetric data from this study provide qualitative information about surface species and their relative coverages on platinum samples that have been used for ethylene hydrogenation and then purged with helium for 1 h at 298 K. A saturation uptake of 15 μmol/g was obtained for hydrogen adsorption at 173 K on the platinum sample exposed only to hydrogen ($C_2H_4/H_2 = 0.0$) (Fig. 5b). This result indicates that after purging with helium at 298 K, 50 μmol/g of surface platinum sites are covered with irreversibly adsorbed atomic hydrogen. A saturation coverage of 15 μmol/g was also obtained for hydrogen adsorption at 173 K on the platinum sample which had undergone ethylene hydrogenation in excess hydrogen ($C_2H_4/H_2 = 0.5$). Since this sample was exposed to ethylene, the surface could contain adsorbed hydrocarbon species. Infrared spectroscopy (26, 28), however, has shown that ethylidyne species are not formed on platinum during ethylene hydrogenation in excess hydrogen. Moreover, molecularly adsorbed ethylene species would have likely reacted in excess hydrogen to form ethane. Thus, this surface contains primarily adsorbed hydrogen and behaves in a similar manner to the sample that had been exposed only to hydrogen.

In contrast, a saturation coverage of only ~5 μmol/g was obtained for hydrogen adsorption on the platinum sample which had undergone ethylene hydrogenation in excess ethylene ($C_2H_4/H_2 = 5.0$), indicating that 70 μmol/g of surface sites are blocked by adsorbates. Ethylidyne species are the predominant hydrocarbon species formed on platinum under these conditions, as shown by FTIR (28). Also, significant amounts of molecularly adsorbed ethylene are apparently not present on this platinum surface, as the formation of ethane was not observed during hydrogen exposure. For the purpose of the present discussion, platinum surfaces having undergone ethylene hydrogenation in excess ethylene ($C_2H_4/H_4 = 5.0$) and excess hydrogen ($C_2H_4/H_2 = 0.5$) (and then purged with helium at 298 K) are thus presumed to be covered primarily with ethylidyne species and atomic hydrogen, respectively.

The microcalorimetric results for hydrogen adsorption at 173 K on platinum powders which have undergone ethylene hydrogenation (Fig. 5) show that the presence of ethylidyne species and atomic hydrogen reduces the number of accessible adsorption sites and weakens the strength of the remaining hydrogen adsorption sites. Importantly, these results suggests that the heat of hydrogen adsorption on the working platinum surface during ethylene hydrogenation is lower than that value characteristic of the clean surface, i.e., <60 kJ/mol in contrast to 90 kJ/mol.

The microcalorimetric results for ethylene adsorption at 173 K on platinum powders which have undergone ethylene hydrogenation (Fig. 6), show that the presence of ethylidyne species decreases the number of platinum sites available for ethylene adsorption and weakens the adsorption of ethylene on the remaining sites. Figure 6 shows that ethylene adsorbs with an initial heat of 100 kJ/mol and a saturation uptake of 10 μmol/g (compared to 5 μmol/g for dihydrogen adsorption) on platinum surfaces containing ethylidyne species ($C_2H_4/H_2 = 5.0$). This result suggests that the adsorbed ethylene is π-bonded to platinum on a surface containing ethylidyne species. The 100 kJ/mol heat of adsorption for π-bonded ethylene on platinum powders containing ethylidyne species is consistent with recent quantum mechanical predictions for π-bonded ethylene on platinum clusters (60) of 95 kJ/mol. These calculations suggest that π-bonded ethylene adsorbs at atop sites in agreement with the literature (53). Further evidence for the presence of π-bonded ethylene on platinum surfaces containing hydrocarbon species has been reported in the literature. Mohsin and co-workers (26, 27) have shown, using FTIR spectroscopy, that π-bonded ethylene co-exists with di-σ-bonded ethylene at 180 K and with ethylidyne species at 300 K on the surface of a Pt/Al_2O_3 catalyst. Hensley and Kesmodel (25) have shown via HREELS that both π-bonded ethylene and di-σ-bonded ethylene are present on a Pt/Al_2O_3 film at 165 K. Masel and co-workers have shown via HREELS that π-bonded ethylene coexists with hydrocarbon species (17, 18, 20, 22) and adsorbed hydrogen (21, 23) on the (110) and (210) surfaces of platinum. More recently, Cremer and co-workers (53) have observed that π-bonded ethylene species form on a Pt(111) surface containing both ethylidyne and di-σ-bonded ethylene species during ethylene hydrogenation at 298 K.

It should be noted that the adsorption isotherms obtained at 173 K for hydrogen and ethylene adsorption on platinum powders containing ethylidyne species and for hydrogen adsorption on platinum powders containing adsorbed hydrogen do not show an increase in the hydrogen or ethylene pressures with coverage prior to saturation. These results indicate that ethylidyne species are neither displaced by hydrogen and ethylene nor hydrogenated to ethane in the presence of hydrogen at 173 K. In contrast, the microcalorimetric results for ethylene adsorption at 173 K on platinum powders containing adsorbed hydrogen (Fig. 6) show that ethylene is hydrogenated to ethane by adsorbed hydrogen, as indicated by the apparent increase in the pressure with increasing ethylene uptake prior to saturation (Fig. 6b). Evidence for the formation of ethane for adsorbed hydrogen was given previously for ethylene adsorption on clean platinum powder at 303 K. Also, Berlowitz *et al.* (30) have shown that ethane forms at temperatures as low as 150 K when a Pt(111) surface containing co-adsorbed ethylene and hydrogen is heated from 100 K.

The decrease in the initial heat of ethylene adsorption observed for the platinum sample having undergone ethylene hydrogenation in excess hydrogen ($C_2H_4/H_2 = 0.5$) suggests that ethylene is bound more weakly on platinum in the presence of adsorbed hydrogen. Similar conclusions were reached by Berlowitz *et al.* (30) who showed that ethylene desorbs at lower temperatures on Pt(111) in the presence of pre-adsorbed hydrogen, and by Masel *et al.* (21, 23) who observed a more weakly bound form of π-bonded ethylene in the presence of co-adsorbed hydrogen on Pt(110) and Pt(210). In addition, the ethylene saturation coverage obtained for this sample (23 μmol/g) suggests that all of the adsorbed hydrogen is removed from the surface during subsequent dosing with ethylene, exposing all the platinum sites for subsequent ethylene adsorption.

CONCLUSIONS

Differential heats of adsorption for hydrogen, ethylene, and acetylene on platinum powder were determined at 173 K. Hydrogen adsorbs dissociatively on platinum powder with a heat of 90 kJ/mol and a saturation coverage of 40 μmol/g, corresponding to 80 μmol/g of surface platinum sites. Ethylene and acetylene adsorb associatively at 173 K with heats of 120 and 210 kJ/mol, respectively, and saturation coverages of 0.25 monolayers. At 173 K, ethylene appears to be both di-σ-bonded and π-bonded to the platinum surface, while acetylene most likely becomes di-σ/π-bonded to the platinum surface. At 303 K, ethylene adsorbs dissociatively to form ethylidyne species and atomic hydrogen with a heat of 160 kJ/mol. Acetylene adsorbs at 303 K with a strength of 220 k/mol which may be attributed to the formation of di-σ/π-bonded acetylene as well as the formation of adsorbed CCH_2 species.

Microcalorimetric results for platinum powders having undergone ethylene hydrogenation under reaction conditions where ethylidyne species are present show that the saturation uptakes and the strengths of interaction of ethylene and hydrogen with the surface at 173 K are significantly reduced. The adsorbed ethylene species formed under these conditions are presumably π-bonded to the platinum surface with an adsorption strength of 100 kJ/mol. Under reaction conditions where ethylidyne species are not formed, a significant amount of reactive hydrogen is present on the platinum surface, and this hydrogen reacts to form ethane upon the adsorption of ethylene.

We suggest that the microcalorimetric methods employed in this study provide an effective means of measuring the strengths of adsorbate-surface interactions, not only on clean metal surfaces, but also on metal surfaces which have been exposed to reaction conditions. These techniques can also provide information for both clean and working (catalytic) metal surfaces at low temperatures, where hydrocarbons adsorb associatively.

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