Ethylene Adsorption on Al$_2$O$_3$-Supported Pt, Pt–Sn, and Pt–In Catalysts

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Ethylene adsorption on a family of Al$_2$O$_3$-supported Pt, Pt–Sn, and Pt–In catalysts was investigated at 300 K. The presence of Sn and In caused a decrease in ethylene uptake, similar to that observed in H$_2$ chemisorption measurements. Integral, isothermal heats of adsorption were measured and the heat of adsorption (Q_{ad}) values for C$_2$H$_4$ on small Pt crystallites were typically around 21 kcal/mol and not markedly altered by the presence of Sn or In. In contrast, higher Q_{ad} values of 30–31 kcal/mol were obtained for C$_2$H$_4$ adsorption on large Pt crystallites with no Sn or In. These results are best explained by recognizing that on large particles decomposition of ethylene to form species with a C–C single bond, such as ethylidyne (or ethylidene), is favored. These reactions are exothermic and provide the higher Q_{ad} values. This decomposition is suppressed on the smaller crystallites thus giving lower values consistent with those obtained from TPD of C$_2$H$_4$ from Pt single crystals which monitors only reversible desorption. This decomposition can also be suppressed by the addition of Sn or In, but it has little effect with highly dispersed Pt. The heat of irreversible adsorption of C$_2$H$_4$ on Al$_2$O$_3$, In/Al$_2$O$_3$, and Sn/Al$_2$O$_3$ without Pt was 4.9, 6.6, and 9.5 kcal/mol, respectively.   © 1996 Academic Press, Inc.

INTRODUCTION

The conversion of hydrocarbons on supported platinum bimetallic catalysts has been the subject of numerous studies in the literature (1–3). Compared to catalysts containing only Pt, improvement of selectivity and stability of Pt can be achieved with these latter systems. Both a change of bond strength between chemisorbed hydrocarbons and Pt surface atoms and a dilution of the surface Pt atoms to decrease ensemble size by the second metal have been proposed as reasons for the beneficial effect of the promoter. Olefins are usually associated with precursors to carbon formation in these hydrocarbon processes, such as catalytic reforming. Furthermore, the dehydrogenation of long-chain alkanes is inhibited by adsorbed olefins (4). Thus, an investigation of the influence of Sn and In—additives in a commercial de-

hydrogenation catalyst (5)—on the adsorption of a model olefin could shed some light on the mechanism of promotion. Heats of C$_2$H$_4$ adsorption on SiO$_2$-supported Pt catalysts have been reported in the literature only recently (6) and, in addition, there is a discrepancy between the values obtained from TPD measurements on single crystals (7–10) and those measured on platinum films by calorimetry (11). In this study, the adsorption of ethylene on a series of Al$_2$O$_3$-supported Pt, Pt–Sn, and Pt–In catalysts was investigated at 300 K by measuring adsorption isotherms and heats of adsorption of this probe molecule. This study complements our studies of H$_2$ and CO adsorption and of butane hydrogenolysis on this family of catalysts (12). An investigation of the effect of Pt particle size on the C$_2$H$_4$ heat of adsorption was also performed.

EXPERIMENTAL

In this study, γ-Al$_2$O$_3$ (Harshaw Al3996R, 200 m^2 g^{-1}) was used as the support material. Pt/Al$_2$O$_3$ catalysts were prepared by an incipient wetness technique using an aqueous solution of H$_2$PtCl$_6$ (0.7 cm^3/g) followed by drying at 393 K for 16 h and calcination in air at 773 K for 2 h. Bimetallic Pt–In/Al$_2$O$_3$ and Pt–Sn/Al$_2$O$_3$ catalysts were prepared with SnCl$_2$ or In(NO$_3$)$_3$ in three distinct ways: coimpregnation, (Pt + X)/Al$_2$O$_3$ (X = Sn or In); reimpregnation of Pt/Al$_2$O$_3$, X + (Pt/Al$_2$O$_3$); and reimpregnation of X/Al$_2$O$_3$, Pt + (X/Al$_2$O$_3$). The dried samples were ground and calcined in air at 773 K for 2 h. More details of the preparation and exact chemical compositions of the catalysts are described in Ref. (12). A Pt/SiO$_2$ catalyst prepared by ion exchange using Pt(NH$_3$)$_4$Cl$_2$ and SiO$_2$ (Davison Grade 57, 220 m^2 g^{-1}), as previously reported (13), was also investigated. A catalyst with large Pt crystallites was obtained by sintering 18.5% Pt/Al$_2$O$_3$ under a flow of 20% O$_2$/80% N$_2$ at 973 K for 2 h. The unsupported UHP Pt powder was obtained from Johnson Matthey (Puratronic Grade, 99.999%).

Ethylene uptakes were measured in a stainless-steel adsorption system equipped with a Balzers TSU-171 turbo-molecular pump that provided a vacuum below 10^{-6} Torr (1 Torr = 133.3 Pa) at the sample cell. Isotherm pressures

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were obtained using an MKS Baratron Model 310 capacitance manometer. The catalyst pretreatment consisted of drying at 393 K under He flow, followed by reduction in flowing 10% H_2/90% He at 723 K for 1 h, evacuation for 1 h at 698 K, and then cooling in vacuum to 300 K where all chemisorption measurements were made. The adsorption isotherms were obtained between 10 and 120 Torr. After the initial adsorption, the samples were evacuated for 1 h and a second isotherm was obtained to determine reversible adsorption.

The calorimetric measurements were performed in a modified Perkin–Elmer DSC-2C differential scanning calorimeter operated isothermally (13). All gas flows were controlled by mass flow controllers (Tylan Model FC260). Before the isothermal measurements in the DSC, the same pretreatment used in the chemisorption experiments was employed, except that the reduction was done under 10% H_2/90% Ar, and a 3-h purge was employed in lieu of the 1-h evacuation step. Ethylene exotherms were obtained at 58 Torr, with the base Ar carrier gas flowing at 35.0 cm^3 min^{-1}, while the makeup stream was switched from 3.0 cm^3 min^{-1} Ar to 3.0 cm^3 min^{-1} C_2H_4. A purge time of 1 h at 35.0 cm^3 min^{-1} Ar was used between the first and the second exotherm experiments. The energy changes were measured using nonporous glass beads in the reference side of the calorimeter. The gases used—H_2 (MG Ind., 99.999%), He (MG Indust., 99.999%), and Ar (MG Indust., 99.999%)—were further purified by passage through molecular sieves (5A, Supelco) and through Oxytraps (Alltech Assoc.), while C_2H_4 (MG Indust. 99.5%) was used without further purification.

RESULTS

The irreversible H_2 uptakes at 300 K, H/Pt ratios, and the concomitant Pt crystallite sizes calculated assuming equal proportions of the (100), (110), and (111) crystal planes are listed in Table 1. Crystallite sizes were calculated only for the monometallic catalysts, as it is known that the decrease in H/Pt ratios for bimetallic platinum catalysts is not due to a particle size increase (14). Table 1 also lists the C_2H_4 uptakes at 300 K and 58 Torr, the C_2H_4 partial pressure used in the calorimeter, while the energy changes measured in the DSC and the calculated heats of adsorption for these catalysts are listed in Table 2. The energy change during the initial uptake is listed under Total in Table 2, while that occurring during the second uptake after evacuation is given under Rev. Typical adsorption isotherms for ethylene on Pt/Al_2O_3, Pt–In/Al_2O_3, and Pt–Sn/Al_2O_3 catalysts are shown in Figs. 1–3. The calorimetric measurements for ethylene adsorption on these catalysts gave exotherms such as that presented in Fig. 4. The exotherms were well behaved and the integration was straightforward. Al_2O_3, Sn/Al_2O_3, and In/Al_2O_3 produced a small, but not negligible, amount of irreversibly adsorbed C_2H_4. In order to take this into account and obtain values associated with C_2H_4 adsorption only on the Pt, corrected values for the irreversible heat of C_2H_4 adsorption on Pt were calculated using the energy balance.

$$(\text{IrrevAds}_{Pt})(Q_{Pt,irrev}) + (\text{IrrevAds}_{Al_2O_3})(Q_{Al_2O_3,irrev})$$

$$= (\text{Total } \Delta E) - (\text{Rev } \Delta E).$$

TABLE 1

Hydrogen and Ethylene Uptakes on Pt at 300 K

Catalyst	Pt content (wt%)	Sn content (wt%)	In content (wt%)	Irrev H_2 uptake[a] (μmol/gcat)	Crystallite size (nm)	C_2H_4 uptake[b] (μmol/gcat)			C_2H_{4irr}/H_{2irr}
						Total	Rev.	Irrev.	
Al_2O_3	—	—	—	—	—	62	59	3	—
In/Al_2O_3	—	—	—	—	—	50.8	48.8	2	—
Sn/Al_2O_3	—	—	—	—	—	45.6	43.4	2.2	—
0.7% Pt/Al_2O_3	0.69	—	—	16.5	1.2	82.5	62.5	20	1.2
(Pt + In)Al_2O_3	0.66	—	0.81	7.4	—	68.3	56.3	12	1.6
In + (Pt/Al_2O_3)	0.71	—	0.78	10.7	—	72	58	14	1.3
Pt + (In/Al_2O_3)	0.68	—	0.80	11	—	69.9	54.9	15	14
(Pt + Sn)/Al_2O_3	0.92	0.73	—	11.3	—	62.1	49.1	13	11
Sn + (Pt/Al_2O_3)	0.95	0.87	—	10.3	—	62.9	50.9	12	1.2
Pt + (Sn/Al_2O_3)	0.89	0.82	—	12.1	—	65.2	52.9	12.3	1.0
18.5 Pt/Al_2O_3	18.5	—	—	233	2.2	278	72	206	0.88
18.5 Pt/Al_2O_3(S)[c]	18.5	—	—	15	35.3	54	36	18	1.2
Pt/SiO_2	0.96	—	—	23.6	1.2	47.9	26.4	21.5	0.91
Pt powder	100	—	—	2.0	1450	2.6	0.24	2.4	1.2

[a] Uptakes obtained by extrapolating the isotherms to zero pressure.
[b] Uptakes at 58 Torr.
[c] Sintered.

TABLE 2

Heats of Ethylene Adsorption on Supported Pt

Catalyst	Average energy change (mcal/g)		Q_{ad} (kcal/mol)		
	Total	Rev.	Total	Rev.	Irrev.[a]
Al_2O_3	221.5	206.8	3.5	3.5	4.9
In/Al_2O_3	168.0	154.9	3.3	3.2	6.6
Sn/Al_2O_3	169.6	148.7	3.7	3.4	9.5
0.7% Pt/Al_2O_3	645.8	282.8	7.8	4.5	20.5
$(Pt + In)Al_2O_3$	420.4	206.2	6.2	3.7	20.1
$In + (Pt/Al_2O_3)$	473.9	218.0	6.6	3.8	20.2
$Pt + (In/Al_2O_3)$	450.4	238.3	6.4	4.3	15.3
$(Pt + Sn)/Al_2O_3$	434.6	203.2	7.0	4.1	19.5
$Sn + (Pt/Al_2O_3)$	433.3	207	6.9	4.1	21.0
$Pt + (Sn/Al_2O_3)$	480.1	220	7.4	4.2	23.7
18.5 Pt/Al_2O_3	5821.7	423.0	20.9	5.9	26.5
18.5 $Pt/Al_2O_3(S)$	661.1	189.2	12.2	5.3	30.5
Pt/SiO_2	589.2	121.4	12.3	4.6	21.8
Pt powder	75.6	3.3	29.1	13.8	30.1

[a] Corrected for irreversible adsorption on the support; the uncertainty of these data is ±1.5 kcal/mol.
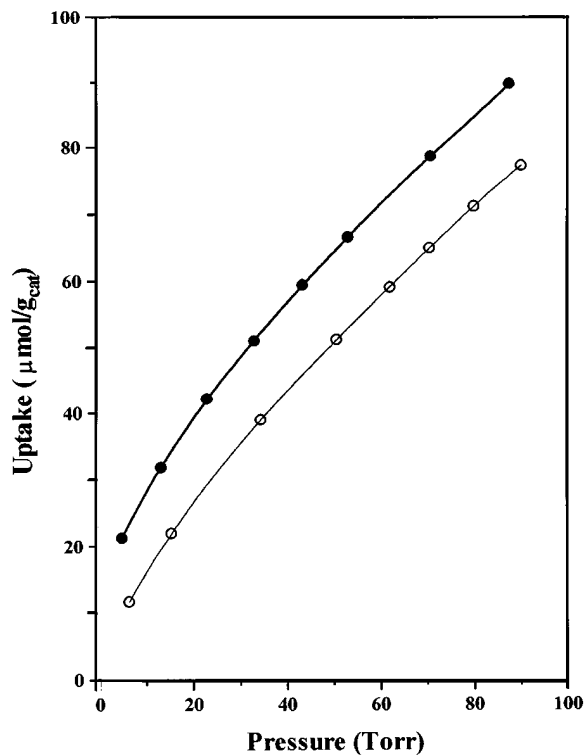

FIG. 2. Adsorption isotherms for ethylene on $(Pt + In)/Al_2O_3$. $T = 300$ K: total C_2H_4, closed circles; reversible C_2H_4, open circles.
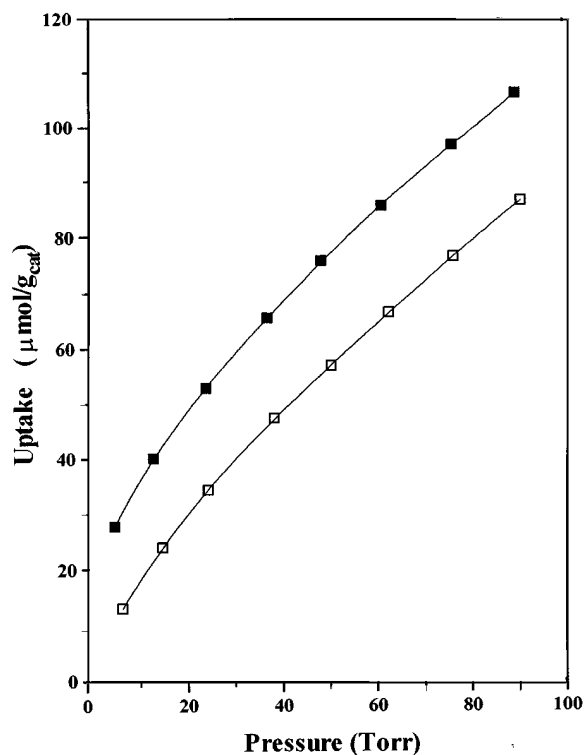

FIG. 1. Adsorption isotherms for ethylene on 0.7% Pt/Al_2O_3. $T = 300$ K: total C_2H_4, closed squares; reversible C_2H_4, open squares.
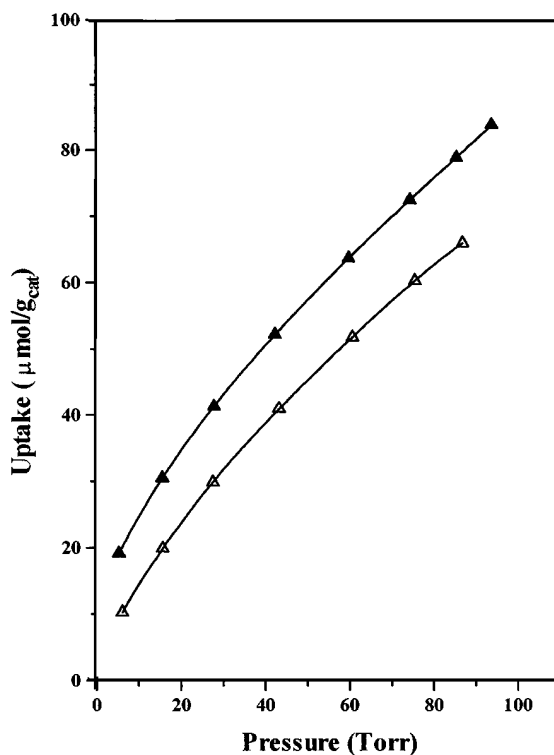

FIG. 3. Adsorption isotherms for ethylene on $(Pt + Sn)/Al_2O_3$. $T = 300$ K: total C_2H_4, closed triangles; reversible C_2H_4, open triangles.
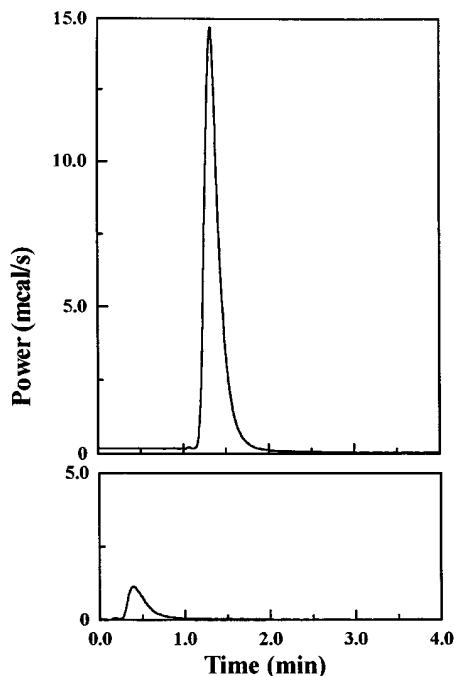
FIG. 4. Calorimeter exotherms for ethylene adsorption on 0.7% Pt/Al$_2$O$_3$. $T = 300$ K, $C_{C_2H_4} = 58$ Torr. Top, initial C$_2$H$_4$ adsorption; bottom, reversible C$_2$H$_4$ adsorption.

Here ΔE represents the energy change measured by integrating the exotherm, IrrevAds$_{Pt}$ is the amount of C$_2$H$_4$ irreversibly adsorbed on the Pt which is obtained by subtracting the irreversible adsorption on the Al$_2$O$_3$, IrrevAds$_{Al_2O_3}$, from that on the Pt/Al$_2$O$_3$ catalysts, and $Q_{Pt,\,irrev}$ and $Q_{Al_2O_3,\,irrev}$ represent the respective isothermal, integral heats of adsorption. In the case of the bimetallic catalysts, the irreversible heat of adsorption and the irreversible C$_2$H$_4$ uptake on Sn/Al$_2$O$_3$ and In/Al$_2$O$_3$ were substituted for the respective values of Al$_2$O$_3$ in the energy balance equation. The irreversible ethylene uptakes were quite similar to the irreversible H$_2$ uptakes, as shown by the C$_2$H$_{4irr}$/H$_{2irr}$ ratios in Table 1 that were near unity for most of the catalysts. The addition of the second metal caused a decrease in the platinum adsorption capacity for both H$_2$ and C$_2$H$_4$.

On the highly dispersed 0.7% Pt/Al$_2$O$_3$, an irreversible heat of adsorption (Q_{ad}) for C$_2$H$_4$ equal to 20.5 kcal/mol was measured. Although Pt + (In/Al$_2$O$_3$) showed a lower value (15.3 kcal/mol), and the Pt + (Sn/Al$_2$O$_3$) showed a higher value (23.7 kcal/mol), the irreversible heats of adsorption on the bimetallic catalysts were otherwise quite similar to that for the Pt/Al$_2$O$_3$ catalyst. However, all these values were distinctly lower than the one obtained with a high purity Pt powder (30.1 kcal/mol). To provide a basis for comparison and to determine if Pt crystallite size had any influence, measurements were also conducted with highly dispersed Pt/SiO$_2$, a high loading (18.5%) Pt/Al$_2$O$_3$, and a

poorly dispersed Pt/Al$_2$O$_3$ obtained by sintering the 18.5% Pt/Al$_2$O$_3$ at 973 K for 2 h under a flow of 20% O$_2$/80% N$_2$. After correction for adsorption on the support, the irreversible heat of adsorption for C$_2$H$_4$ on the sintered 18.5% Pt/Al$_2$O$_3$ was very similar to that obtained for the Pt powder, while the value obtained for C$_2$H$_4$ on small (1.2 nm) SiO$_2$-supported Pt crystallites was very similar to that obtained on the 1.2-nm Al$_2$O$_3$-supported Pt crystallites. The 18.5% Pt/Al$_2$O$_3$ sample with 2.2-nm crystallites exhibited an intermediate value. These results indicate that a crystallite size effect exists.

DISCUSSION

Reported values for the heat of adsorption of C$_2$H$_4$ on Pt have been restricted to unsupported Pt and SiO$_2$-supported samples and the results gathered from the literature are summarized in Table 3. From their TPD experiments, Salmeron and Somorjai (7) calculated an initial desorption energy for C$_2$H$_4$ on Pt(111) equal to 12 kcal/mol using a preexponential factor equal to 10^9 s^{-1}. However, Windham *et al.* (8) and Mohsin *et al.* (9) obtained desorption energies equal to 17 and 18 kcal/mol, respectively, when a preexponential factor equal to 10^{13} s^{-1} was used. Another limitation in the determination of heats of adsorption by these experiments (assuming adsorption is nonactivated) is that only about half of the ethylene is desorbed molecularly. The remaining molecules dehydrogenate during heating to either desorb decomposition products or deposit coke on the metal surface. Consequently, it is not possible to determine the heat of adsorption of the more strongly adsorbed ethylene by thermal desorption. Calorimetric measurements of ethylene adsorption on a well-dispersed Pt–SiO$_2$ catalyst provided an integral heat of adsorption of 23.3 kcal/mol (6), in excellent agreement with the value of 21.8 kcal/mol obtained in this work for 0.9% Pt/SiO$_2$. On the other hand, the measurement of heats of adsorption of C$_2$H$_4$ on Pt films by calorimetry gave an initial value of 35 kcal/mol which decreased moderately with coverage (11), and integration of

TABLE 3

Heats of Ethylene Adsorption on Pt Surfaces

Surface	Initial Q_{ad} (kcal/mol)	Integral Q_{ad} (kcal/mol)	Method	Reference
Pt/SiO$_2$	37	23.3	CAL	6
1 Pt–1.5 Sn/SiO$_2$	28.7	16.6	CAL	6
Pt(111)	12.0		TPD	7
Pt(111)	17.0		TPD	8
Pt(111)	18.0		TPD	9
p(2 × 2) Sn/Pt(111)	15.1		TPD	10
($\sqrt{3} \times \sqrt{3}$) Sn/Pt(111)	11.8		TPD	10
Pt film	35	31	CAL	11

the published data resulted in an integral heat of adsorption equal to 31 kcal/mol.

Our results show that a distinct difference exists between highly dispersed Pt and Pt existing as large crystallites. The integral heat of irreversible C_2H_4 adsorption at 300 K on small Pt particles on Al_2O_3 (after correction for adsorption on the support) is around 20 kcal/mol, while on larger particles the value is near 30 kcal/mol. These results indicate that on smaller particles most of the adsorbed ethylene has a lower heat of adsorption similar to that obtained from C_2H_4 desorption from TPD studies with single crystals; in contrast, larger supported Pt particles favor the formation of a more strongly adsorbed form of ethylene, which provides a higher Q_{ad} value but whose effect is not observed in the TPD studies because this C_2H_4 species dissociates or decomposes and does not desorb molecularly.

The identification of the species formed during the adsorption of C_2H_4 on supported or unsupported Pt has been the subject of numerous studies, due mainly to the importance of a fundamental understanding of the mechanism of ethylene hydrogenation. On Pt(111), it has been demonstrated that at 200 K, di-σ-bonded ethylene is the predominant adsorbed species, but upon warming to room temperature, this species rearranges with the loss of a hydrogen atom to form ethylidyne ($\equiv CCH_3$) (15–19). The rate of formation of ethylidyne on Pt(111) has been monitored by Mohsin *et al.* (9). Soma (20) investigated the adsorption of ethylene on 9% Pt/Al_2O_3 at 195 K using infrared spectroscopy and observed that π-adsorbed C_2H_4 was the main species present on the surface, but an additional band was assigned to a dehydrogenated adsorbed species ($=CHCH=$), which prevailed over the π-species at room temperature. The dehydrogenated species observed by Soma was later identified as ethylidyne by Beebe and Yates, who used transmission infrared spectroscopy to study the adsorption of C_2H_4 on 10% Pt/Al_2O_3 at 300 K (21). The presence of other hydrocarbon species in minor amounts was also reported. However, Mohsin *et al.* (22) reported the formation of three species upon adsorption of C_2H_4 at 180 K on 3% Pt/Al_2O_3: a π-bonded species, a di-σ-bonded species, and ethylidyne. At this low temperature they observed the conversion of the di-σ-adsorbed species to ethylidyne as a function of time. Upon increasing the temperature to 300 K, only the di-σ-adsorbed species was converted to ethylidyne and the π-bonded C_2H_4, which was also observed at room temperature, slowly desorbed during evacuation of the sample. The occurrence of all three species was also observed with Pt/SiO_2 at room temperature (23, 24).

NMR has also been used to examine the adsorption of C_2H_4 on Pt (25–29). The formation of a multiply bonded ($-CH_2CH=$) species on Pt powder has been suggested by Shibanuma and Matsui (25), while the presence of ethylidyne species on 2- to 4-nm Pt particles dispersed on Al_2O_3 has been proposed by Wang *et al.* (26) and Chin and Ellis

(27). In contrast, Gay has argued against the formation of ethylidyne species on SiO_2- and Al_2O_3-supported Pt and stated that π-bonded C_2H_4 is the predominant species; however, the data suggested that dissociation is favored on large Pt crystallites (28). Finally, on highly dispersed Pt/Al_2O_3 samples (ca. 1.0- to 1.4-nm Pt particles), Griffiths *et al.* reported that ethylidene ($=CHCH_3$) was the predominant species at 323 K (29).

Masel and co-workers have provided extensive information about the structure sensitivity of ethylene adsorption and decomposition. On the (1×1) Pt(100) surface the di-σ-ethylene was observed as on Pt(111); however, upon warming to room temperature, it decomposed to form di-σ-vinyledene ($=C=CH_2$) instead of ethylidyne (30). On (2×1) Pt(110) ethylene was adsorbed at 100 K as a mixture of π-bound ethylene and di-σ-ethylene, and some of these species desorbed upon heating to 300 K, while others decomposed to form a mixture of ethylidyne, ethylylidyne ($\equiv CCH_2-$), and hydrogen (31). The formation of an ethylylidyne intermediate was unique to (2×1) Pt(110). Another striking result was observed with (1×1) Pt(110). At 93 K the π-bound ethylene was the major adsorbed species and there was some desorption and some conversion to di-σ-ethylene upon heating to 220 K (32). Further heating to 300 K caused the formation of ethylylidyne, methane, ethane, and hydrogen, and the methane formation together with carbon formation at 400 K indicated that this face is especially active for coke formation. On Pt(210) much of the π-ethylene formed at 100 K remained adsorbed on the surface at 300 K, although there was some formation of ethane and methyl groups during the heating (33). The π-ethylene species was more stable on Pt(210) than on any other face of platinum.

These studies are important not only because they show that a variety of adsorbed ethylene species can exist on Pt surfaces, some of them involving dissociative adsorption, but also that most of the evidence indicates that ethylidene and other species that have lost hydrogen are favored on Pt single crystals and large crystallites and are much less likely to occur on very small Pt particles. The presence of π-bonded ethylene has also been observed on the supported samples, but not on Pt(111). In fact, single crystal studies showed that the relative presence of π-bonded or σ-bonded ethylene species depends strongly on the nature and geometry of the metal surface. In the case of clean surfaces, only π-adsorbed ethylene was observed on Pd(111) and Pd(110) (34–36). When appreciable amounts of carbon, oxygen, or alkali metal were also present on the metal surface, the π-adsorbed species seemed to be preferentially formed. This has been observed with carbon on Ni(110) (37), oxygen on Pt(111), Pd(100), Ag(110), Ir(111), Fe(111) (18, 38–41), and potassium on Pt(111) (7, 42, 43). The small crystallites in supported catalysts are in close contact with the oxygen atoms of the support; consequently, the

formation of the π-bonded form could be caused by a configuration similar to Pt(111)/O (22). It has been suggested that the preference for π-bonding on metal surfaces with coadsorbed O, C, or K is due to an electron transfer from Pt to those adsorbates. This would reduce the availability for back donation to the adsorbed ethylene (37). A geometric restriction was also suggested because the coadsorbed atom could reduce the number of two-atom metal ensembles that are needed for di-σ-adsorption.

The dependence of the heat of ethylene adsorption on Pt particle size observed here is consistent with the variety of species and decomposition pathways observed for the different Pt surfaces. Carter and Koel have calculated the heats of formation of several adsorbed species on Pt(111) thus making it possible to estimate the energetics of ethylene decomposition (44). The heat of adsorption of ethylene was chosen to be 17 kcal/mol based on a previous TPD study (8), and the enthalpy of reaction for the decomposition of adsorbed ethylene to ethylidyne was estimated as -12 kcal/mol; thus, the total heat evolved when ethylene is adsorbed and decomposed to ethylidyne would be 29 kcal/mol, which is very similar to the values obtained here for platinum powder and for the poorly dispersed 18.5% Pt/Al$_2$O$_3$(S). In similar fashion the total heat evolved for the formation of ethylidene would be equal to 33 kcal/mol (44). Consequently, the most obvious explanation for the higher heats of adsorption on large Pt particles is the conversion of the adsorbed ethylene molecule to a species with a C–C single bond, either with or without the loss of a hydrogen atom. These results strongly imply that the decomposition of adsorbed ethylene to species such as ethylidyne (or ethylidene) is suppressed on well-dispersed Pt samples. This is in accordance with the hypothesis that π-bonded ethylene, observed on the supported Pt samples, would not be decomposed to ethylidyne. So far we cannot determine whether this is due to geometric and/or electronic effects in these small Pt particles which stabilize π-bonded ethylene or whether it is due to the intimate contact of these small crystallites with the support.

A decrease in ethylene adsorption upon the addition of a second metal, similar to that which we have observed, was previously reported for Pt–Sn catalysts by Palazov *et al.* (45). A decrease in the heat of adsorption has been reported for both a Pt–Sn/SiO$_2$ catalyst with a Pt/Sn atomic ratio equal to 2/3 (6) and ordered Sn/Pt(111) alloys (10), and on the latter surfaces ethylene decomposition was completely suppressed. This behavior is very consistent with the postulate above and it was attributed to the removal of the larger Pt ensemble sizes needed for decomposition to occur (10). With the well-dispersed supported catalysts investigated in this study, the presence of the second metal did not cause much change in the heat of adsorption although ethylene uptakes were suppressed. However, this is not surprising because ethylene decomposition is already suppressed on these small Pt particles, and this implies that for Al$_2$O$_3$-supported catalysts, the major changes in ethylene adsorption occur when the Pt particle size is altered. As the particle size reaches some lower limit, the presence of the promoter does not appear to cause any significant additional change to the adsorption and decomposition behavior at room temperature and, consequently, the C$_2$H$_4$ bond strength on very small Pt particles is relatively insensitive to Sn and In promoters. The difference between SiO$_2$-supported and Al$_2$O$_3$-supported Pt–Sn catalysts suggests that the extent of interaction between metal and promoter can depend on the support and on the relative content of active metal and promoter in the catalyst.

SUMMARY

The adsorption of ethylene on Pt catalysts was investigated at room temperature. The presence of Sn and In caused a decrease in irreversible ethylene uptakes, consistent with H$_2$ chemisorption measurements. Integral, isothermal heats of adsorption were found to be around 20 kcal/mol on small (ca. 1.2 nm) Pt crystallites in either the presence or absence of the second metal, and these values are close to those obtained from TPD of C$_2$H$_4$ from single crystals. These results are consistent with previous calorimetric studies of H$_2$ and CO adsorption on these catalysts in which a geometric effect appeared to be the main mechanism of promotion (12). On the other hand, higher ethylene heats of adsorption near 30 kcal/mol were obtained on catalysts with large Pt crystallites, in agreement with previous calorimetric measurements of C$_2$H$_4$ adsorption on Pt films, and this difference is attributed to the extensive decomposition of ethylene that can occur on larger particles to form species such ethylidyne (or ethylidene) which have C–C single bonds. These reactions are exothermic and thus give a higher Q_{ad} value.

ACKNOWLEDGMENTS

REFERENCES

1. Sinfelt, J. H., "Bimetallic Catalysts: Discoveries, Concepts and Applications." Wiley, New York, 1983.
2. Dautzenberg, F. M., Helle, J. N., Biloen, P., and Sachtler, W. M. H., *J. Catal.* **63**, 119 (1980).
3. Burch, R., and Mitchel, J. A., *Appl. Catal.* **6**, 121 (1983).
4. Sadhykhova, Z. A., Nekrazov, N. V., Gurevich, V. R., and Kiperman, S. L., *Kinet. Katal.* **26**, 624 (1985).
5. Abrevaya, H., and Imai, T., U.S. Patent 4608360, 1986.
6. Cortright, R. D., and Dumesic, J. D., *J. Catal.* **148**, 771 (1994).
7. Salmeron, M., and Somorjai, G. A., *J. Phys. Chem.* **86**, 341 (1982).

8. Windham, R. G., Bartram, M. E., and Koel, B. E., *J. Phys. Chem.* **92**, 2862 (1988).

9. Mohsin, S. B., Trenary, M., Robota, H. J., *Chem. Phys. Lett.* **154**(6), 511 (1989).

10. Paffett, M. T., Gebhard, S. C., Windham, R. G., and Koel, B. E., *Surf. Sci.* **223**, 449 (1989).

11. Pálfi, S., Lisowski, W., Smutek, M., and Cerný, S., *J. Catal.* **88**, 300 (1984).

12. Passos, F. B., Schmal, M., and Vannice, M. A., *J. Catal.* **160**, 106–117.

13. Sen, B., and Vannice, M. A., *J. Catal.* **130**, 9 (1991).

14. Meitzner, G., Via, G. H., Lytle, F. W., Fung, S. C., and Sinfelt, J. H., *J. Phys. Chem.* **92**, 2925 (1988).

15. Kesmodel, L. L., Dubois, L. H., and Somorjai, G. A., *J. Chem. Phys.* **70**, 2180 (1979).

16. Demuth, J. E., *Surf. Sci.* **80**, 367 (1979).

17. Skinner, P., Howard, M. W., Oxton, I. A., Kettle, S. F. A., Powell, D. B., and Sheppard, N., *J. Chem. Soc. Faraday Trans. 2* **77**, 1203 (1981).

18. Steininger, H., Ibach, H., and Lehwald, S., *Surf. Sci.* **117**, 685 (1982).

19. Pettiette-Hall, C. L., Land, D. P., McIver Jr., R. T., and Hemminger, J. C., *J. Phys. Chem.* **94**, 1948 (1990).

20. Soma, Y., *J. Catal.* **59**, 239 (1979).

21. Beebe, T. P., Jr., and Yates, J. T., Jr., *Surf. Sci.* **91**, 254 (1987).

22. Mohsin, S. B., Trenary, M., and Robota, H. J., *J. Phys. Chem.* **92**, 5229 (1988); Mohsin, S. B., Trenary, M., and Robota, H. J., *J. Phys. Chem.* **95**, 6657 (1991).

23. de la Cruz, C., and Sheppard, N., *J. Chem. Soc. Chem. Commun.* 1954 (1987).

24. Rekoske, J. A., Cortright, R. D., Goddard, S. A., Sharma, S. B., and Dumesic, J. A., *J. Phys. Chem.* **96**, 1880 (1992).

25. Shibanuma, T., and Matsui, T., *Surf. Sci.* **154**, L215 (1985).

26. Wang, P. K., Slichter, C. P., and Sinfelt, J. H., *J. Phys. Chem.* **89**, 3606 (1985).

27. Chin, Y. H., and Ellis, P. D., *J. Am. Chem. Soc.* **115**, 204 (1993).

28. Gay, I. D., *J. Catal.* **108**, 15 (1987).

29. Griffiths, J. M., Bell, A. T., and Reimer, J. A., *J. Phys. Chem.* **97**, 9161 (1993).

30. Tysoe, W. L., Nyberg, G. L., and Lambert, R. M., *J. Phys. Chem.* **97**, 9161 (1993).

31. Gates, J. A., and Kesmodel, L. L., *J. Phys. Chem.* **76**, 4281 (1982).

32. Chesters, M. A., Mc Dougall, G. S., Pemble, M. E., and Sheppard, N., *Appl. Surf. Sci.* **22/23**, 369 (1985).

33. Sheppard, N., *Annu. Rev. Phys. Chem.* **39**, 589 (1988).

34. Stuve, E. M., and Madix, R. J., *J. Phys. Chem.* **89**, 105 (1985).

35. Backx, C., and de Groot, C. P. M., *Surf. Sci.* **115**, 382 (1982).

36. Kostov, K. L., and Marinova, T. S., *Surf. Sci.* **184**, 359 (1987).

37. Seip, U., Tsai, M-C., Küppers, J., and Ertl, G., *Surf. Sci.* **147**, 65 (1984).

38. Cassutto, A., Mane, M., Jupille, J., Tourillon, G., and Parent, Ph., *J. Phys. Chem.* **96**, 5987 (1992).

39. Zhou, X. L., Zhu, X-Y., and White, J. M., *Surf. Sci.* **193**, 387 (1988).

40. Hatzikos, G. H., and Masel, R. I., *in* "Catalysis 1987" (J. W. Ward, Ed.), p. 883. Elsevier, Amsterdam, 1988.

41. Yagasaki, E., Backman, A. L., and Masel, R. I., *J. Phys. Chem.* **94**, 1066 (1990).

42. Yagasaki, E., and Masel, R. I., *Surf. Sci.* **222**, 430 (1989).

43. Backman, A. L., and Masel, R. I., *J. Phys. Chem.* **94**, 5300 (1990).

44. Carter, E. A., and Koel, B. E., *Surf. Sci.* **226**, 339 (1990).

45. Palazov, A., Bonev, Ch., Shopov, D., Lietz, G., Sárkány, A., and Völter, J., *J. Catal.* **103**, 249 (1987).