The differences between the rate constants found in PhCN and ODCB could be attributed to differences in their dielectric properties and dynamics. A quantitative treatment is difficult because of the lack of the necessary data for ODCB in the literature.

Conclusions

We have determined the kinetic parameters and diffusion coefficients for the first reduction of C_{60} in two solvents, 1,2-dichlorobenzene and benzonitrile. The SECM/TLC technique employed combines the capability of quite fast heterogeneous kinetic measurements with the advantages of steady-state methods, i.e., it is free from problems caused by the ohmic drop and charging current and allows for a very simple treatment of the experimental data.

Acknowledgment. The support of this research by the National Science Foundation (CHE 9214480) is gratefully acknowledged. L. O. S. B. acknowledges the support of FAPESP (Fundação de Amparo a Pesquisa do Estado de São Paulo-Brazil). We appreciate the receipt of the paper by R. Fawcett and co-workers before publication.

Chemisorption of Ethylene onto Supported Pt/γ-Al_2O_3 and Ag/γ-Al_2O_3 As Followed by Solid-State Static and CP/MAS ^{13}C and Static ^{2}H NMR Spectroscopy

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Abstract: The adsorption of ethylene onto two metal-supported catalyst systems is reported. The first is Pt on γ-Al_2O_3. Here is it found that high-resolution solid-state ^{13}C CP/MAS methods *cannot* be utilized to investigate the structure of the adsorbed species. This arises due to the near ferromagnetic character of platinum metal. However, this problem can be circumvented by examining the solid-state ^{2}H NMR. From this investigations, it is clear that the dominant species on the surface is ethylidyne. These results are discussed in light of the previous work in the area. Ethylene adsorption was also examined for a supported silver system. In this system there are no problems with susceptibility of the metal surface. By utilizing a combination of mono- and dilabeled ^{13}C ethylene, the shielding tensor and the carbon-carbon bond distance of the adsorbed ethylene were deduced.

Introduction

In the past two decades, the adsorptions of alkenes and alkynes onto supported transition metals have been experimentally investigated by a number of high-resolution spectroscopic techniques, such as LEED,[1] infrared,[2] Auger,[3] and so on. In the particular case of ethylene onto supported Pt catalysts, the type of bonding and the associated reactions on the Pt surfaces are of continuing interest in the surface chemistry community. Unfortunately, the structures of these olefins on a Pt surface lead to archetypal problems and remain controversial to date. In the previous studies of ethylene on a Pt single crystal structure, Ibach et al.[4] showed, using EELS and TPDS, that the ethylidyne species formed upon the reaction of C_2H_4 with Pt(III). By utilizing infrared spectroscopy, Malik et al.[5] also concluded that the same species existed on Pt(III). The ethylidyne species on a 10% Pt/Al_2O_3 surface was proposed by Beebe et al.[6] and is consistent with the Bandy et al.[7] study of ethylene on a Pt/SiO_2 surface. However, on the basis of infrared spectroscopy, Prentice et al.[8] postulated a π-complexed form of ethylene on silica-supported Pt surfaces with the C═C stretching band near 1500 cm^{-1}, which was in agreement with Soma's[9] infrared study of adsorbed ethylene on 9% Pt/Al_2O_3 at 195 K. Alternatively, from an analysis of the dipolar line shapes on the ^{1}H NMR spectroscopy, Shibanuma et al.[10] ruled out the ethylidyne species and favored a multiply bonded species (—CH_2CH═) on unsupported platinum powder. In contrast to chemisorbed acetylene on a platinum catalyst, Slichter et al.[11a] explicitly deduced the structure of adsorbed ethylene by probing the dipolar interactions among the nuclei. They suggested an ethylidyne species (≡C—CH_3) with a C–C bond length of 1.49 ± 0.02 Å. The methyl group (–CH_3) on ethylidyne freely rotates about the C–C direction at 77 K. Carbon–carbon bond rupture occurs above 390 K, and the decomposition was completely finished at about 480 K. Later[11b] they confirmed a rotating methyl group by analyzing deuterium powder patterns at 77 K. Furthermore, in a high-resolution solid-state ^{13}C NMR study of the adsorbed ethylene on platinum catalysts, Gay[12] carried out the reaction of adsorbed ethylene on a series of catalyst preparations. In his report, Gay claimed that the adsorbed ethylene reactivity is correlated to the characteristics of Pt catalyst, e.g., the metal particle size, nature of support, and the dispersion of platinum atom. Gay had prepared 5% and 10% Pt on Al_2O_3 and SiO_2 support catalysts, with variable dispersions from 0.23 to 1.30, by adsorption and impregnation methods (with Cl$^-$ ions). He observed a π-bonded olefin species in all catalysts. The π-complexed olefin on Pt/γ-Al_2O_3 catalysts in the presence or absence of Cl$^-$ further reacts to form a σ-vinyl group or a species with a C═C double

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[†] Presented as partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry, University of South Carolina.

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bond and possibly other surface alkyls. From the results of delayed decoupling experiments, he also excluded the presence of $\equiv$C—CH_3 and $=$C$=$$CH_2$ on all of the catalysts studied. In a recent report, Gerstein and co-workers[13] summarize the reaction of ethylene on silica-supported Ru and Ru–Cu bimetallic catalysts as followed by ^{13}C NMR spectroscopy. They reported that at room temperature the adsorbed ethylene on ruthenium catalysts reacts rapidly and is converted to strongly adsorbed acetylides and alkyl species. Weakly adsorbed ethane, butane, and *cis*- and *trans*-2-butene were also observed.

In view of the differences reported by Slichter et al.,[11] Shibanuma,[10] Gerstein,[13] and Gay,[12] we decided to reinvestigate the structures on ethylene adsorbed at room temperature onto Pt/γ-Al by direct observation via high-resolution solid-state ^{13}C CP MAS, ^2H solid–echo NMR, and in situ FT infrared spectroscopies. As we will show subsequently, the Pt surface causes problems with the observation of select species adsorbed to the surface. In order to check the universality of this problem, we also examined the chemisorption of ethylene bound to silver. One of the motivating reasons for this portion of the investigation was the contrast between the electronic properties of platinum and silver metals, i.e., an open or closed d-block metal and its consequences on the local magnetic susceptibility. The chemisorption of ethylene onto silver catalyst supported on γ-alumina is investigated, including a determination of ethylene's carbon–carbon bond length, using high-resolution solid-state ^{13}C NMR.

Theoretical Background

By standard irreducible tensor methods,[14] one can derive expressions for the orientational dependence of the individual crystallites in a shielding powder line shape in the presence of homonuclear dipolar interactions, i.e.,

$$\omega(\theta,\phi,\alpha,\beta) = \omega^{D} + \omega^{CS}$$

where

$$\begin{aligned}\omega^{D} = \pm{}^{3}\!/\!_{2}\gamma_{I}^{2}\hbar r_{12}^{-3}[{}^{1}\!/\!_{2}(3\cos^2\theta - 1){}^{1}\!/\!_{2}(3\cos^2\beta - 1) - \\ {}^{3}\!/\!_{4}\sin 2\theta \sin 2\beta \cos(\alpha + \phi) + \\ {}^{3}\!/\!_{4}\sin^2\theta \sin^2\beta \cos(2\alpha + 2\phi)]\end{aligned}$$

$$\omega^{CS} = \omega_0\delta[{}^{1}\!/\!_{2}(3\cos^2\theta - 1) - {}^{1}\!/\!_{2}\eta \sin^2\theta \cos 2\phi]$$

Here α and β are the Euler angles which relate the dipole frame to the shielding PAS frame. Further, the Euler angles θ and ϕ relate the PAS frame of the shielding tensor to the LAB frame. The rest of the symbols have their usual meaning. In the case of ethylene, we will subsequently demonstrate that the dipole frame and the shielding frame are related via the α angle of 90° and the β angle of 90°, assuming that the C$=$C bond is along the y axis of the shielding PAS frame. In the absence of dipolar interaction, one can immediately determine σ_{xx}, σ_{yy}, and σ_{zz} or, alternatively, δ, η, and $<<$lvcσ. Therefore, the calculated dipolar powder spectrum is only a function of α, β, and $r_{C=C}$.

Experimental Section

Catalyst Sample Preparation. Platinum Samples. The 1% and 5% Pt supported on γ-alumina surface samples were purchased from Aldrich Chemical Company (surface area of γ-alumina > 250 m^2/g). The 10% Pt on γ-alumina support was purchased from AESAR Chemical Company. The 5% and 10% Pt catalysts were characterized by dispersion (percentage of available platinum atoms on the surface) on the Pulse ChemiSorb 2700 surface analyzer. The measurement of dispersion is based on the hydrogen chemisorption. Our typical samples have a dispersion of about 30–46%. The γ-alumina pellets were provided by Norton Chemical Process Product Division (No. SA6173; 220 m^2/g) and were ground into a fine powder. The high purity (>99% and 90%) of singly or doubly ^{13}C-enriched ethylene gas was purchased from MSD Isotope Co. and Cambridge Isotope Laboratory. The 99.3% deuterated ethylene, C_2D_4, was obtained from MSD Isotope Co.

A typical Pt catalyst on γ-Al_2O_3 of approximately 1.0 g was placed into the chamber of a glass tube (Pyrex) with a break-seal in the middle of the tube. Each sample was heated at 298 °C and evacuated to expel the adsorbed moisture and/or physisorbed organics on the catalyst surface for at least 3 h. The reduction–oxidation reaction was immediately carried out on the catalyst surface by alternating the flow of H_2 and O_2 at 298 °C. The surface cleaning procedure starts with a flow of H_2 over the catalyst for 5–10 min, followed by a pump cycle for about 3–5 min, followed by flow of O_2 over the surface for 3–5 min and then by another pump cycle of 3–5 min. This procedure is then repeated for a minimum of 10 times. The length of the various cycles was determined empirically by following the in situ FTIR of a sample which was comparable to our NMR samples. The catalyst sample was then pumped upon overnight at 298 °C. When the pressure reached approximately 10^{-6} Torr, the glass chamber with catalyst sample was flame-sealed under vacuum. After the other glass chamber was evacuated to about 10^{-6} Torr, an appropriate amount of a given adsorbate was condensed into the chamber. The chamber was sealed via a stopcock, and then the break-seal was shattered to introduce the measured amount of ethylene onto the catalyst surface at liquid nitrogen temperatures. This calibrated amount of adsorbate corresponds to approximately 50% saturation coverage for a monolayer of adsorbed gas on the catalyst surface, assuming the reaction stoichiometry of Pt–C and Al–C/Al–O–C. It is believed that the loaded ethylene on the catalyst surface still remains intact at 77 K. After the adsorbed ethylene was warmed to room temperature, this surface sample began undergoing a reaction at room temperature. After about 30 min, the catalyst sample was pumped upon again to remove any physisorbed gases. After being sealed, the chemisorbed surface sample was frozen and stored in liquid nitrogen to prevent any further possible thermal decomposition.

It has been shown by Steininger et al.[4] and in our studies that these samples are extremely unstable to air and O_2. Once these samples are briefly exposed to atmosphere, air oxidation will immediately occur to completely convert the surface species to carboxylic acids. This topic will be addressed in a subsequent paper.[15] Just prior to the performance of a given experiment, all NMR surface samples were packed in a 7-mm zirconia rotor with Kel-F end caps (Doty Scientific, Inc.) by carefully opening the sealed glass tube in a N_2 atmosphere dry box (Vacuum Atmospheric Company).

Silver Samples. Silver nitrate (ca. 99%) and potassium oxalate monohydrate (ca. 99%) were purchased from Aldrich Chemical Company. Ethanolamine (+99%) and ethylenediamine (+99%) were obtained from Aldrich Chemical Company. Calcium carbonate solution (1 mL = 1 mg of Ca^{2+}) was purchased from Fisher Scientific Company. Ethylene oxide (ca. 90%) was obtained from Eastman Kodak Company.

The preparation of Ag/Al_2O_3 catalyst was similar to the Nielsen and LaRochelle[16] method for the ethylene oxide process. A 0.01 M $K_2C_2O_4$ solution (50 mL) was mixed with 50 mL of 0.02 M $AgNO_3$ solution to form the precipitate of $Ag_2C_2O_4$. This white precipitate was filtered and rinsed several times with deionized water until the filtrate was free of potassium and oxalate ions. Two or three drops of calcium carbonate solution were added to the filtrate to ensure the absence of oxalate ions; otherwise the precipitate of calcium oxalate would be formed. Presumably, the potassium ion was also absent in the filtrate, implicitly indicated by the absence of precipitate of calcium oxalate. The washed precipitate of silver oxalate was immediately dissolved by rapid stirring in 25 mL of solubilizing/reducing aqueous solution. This reducing solution contained approximately 3.5 mL of ethylenediamine and 1.2 mL of ethanolamine (molar ratio of 5:2). The γ- and α-alumina powdered samples were heated at 120 °C under vacuum for 12 h to expel the adsorbed moisture and/or chemisorbed organics before being soaked in the silver solution. Partially dehydrated alumina (6.682 g) powder was soaked in the silver solution and stirred for about 10 min. The coated alumina support was separated from excess silver salt solution by decantation and filtration. This soaking procedure was repeated until the desired Ag percentage by weight was obtained. Approximately 3–8% Ag by weight on alumina support was typically produced in our sample preparation. The alumina-supported silver was placed into a Pyrex tube and heated in a furnace at 160 °C for 6 h. During this heating time, compressed air was admitted into the reaction tube to carry out the exhaust into a 2 M HCl aqueous solution. This aqueous acid solution was used to neutralize the exhaust vapor containing residual ethanolamine and ethylenediamine. The silver catalyst changed color from dark purple to

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black before elevating the temperature from 160 °C. The reduction reaction of supported silver/silver oxide was carried out for about 4 h at 360 °C to form metallic Ag deposited on alumina support. During this period of 4 h, the color changed from pale yellow to white-gray, indicating that the reduced silver was produced. All silver catalysts were stored in a desiccator to prevent any exposure to moisture and further feasible air oxidation.

The particle size of air-activated silver catalyst was measured by using a Hitachi S-2500 scanning electron microscope. Silver catalyst powder was first deposited onto a stainless steel die (12-mm diameter) by using a double-sided tape. This die with silver powder was then put into a glass chamber of a Techniques Hummer II gold sputter, and the chamber was evacuated for about 10 min. A gold thickness of about 300 Å was immediately sputtered onto the surface of die under vacuum. The silver catalyst powder firmly embedded in a thin layer of gold was examined under vacuum by scanning electron microscopy with a potential difference of 15 kV. All of our photomicrographs were obtained on a Polaroid photographic plates with a magnification of 15 × 10^3. Representative photomicrographs of 6% Ag/γ-Al_2O_3 and 3% Ag/α-Al_2O_3 catalysts (data not shown) indicated that the silver was present as substantially and uniformly spaced semispherical particles. The diamters of these well-dispersed particles are less than 10000 Å (1 μm).

A typical Ag catalyst on alumina powder of approximately 1.0 g was placed into the chamber of a glass tube (Pyrex) with a break-seal at the middle of the tube. Each sample was heated at 298 °C for at least 6 h with evacuation to expel the undesirable moisture and other physisorbed gases on the Ag surface. During the heating procedure, the whitish silver catalyst became gray. The glass chamber with the sample was sealed under vacuum at a final pressure of less than 10^{-5} Torr. The other chamber of the glass tube was evacuated to about 10^{-6} Torr to admit the measured amount of ethylene. The break-seal was shattered to condense the calibrated ethylene onto the catalyst surface at liquid nitrogen temperature. Assuming the reaction stoichiometry of Ag–C and Al–O–C, the calibrated amount corresponds to 50% saturation coverage to form a monolayer of adsorbed gas on the surface. The sample temperature was increased to room temperature. After 30 min, the residual physisorbed gases were removed by evacuation at room temperature. After being sealed, the NMR samples were stored in liquid nitrogen to prevent any possible thermal decomposition.

NMR Measurements. All high-resolution ^{13}C spectra were obtained on a Varian XL 300 NMR spectrometer operating at a field of 7.05 T. This corresponds to a ^{13}C resonance frequency of 75.429 MHz. The techniques of Hartmann–Hahn cross-polarization[17] magic angle spinning[18] (CP/MAS) and high-power ^1H decoupling were employed in our experiments by utilizing a 7-mm MAS probe (Doty Scientific, Inc.). The recycle delay of 3 s and $\pi/2$ pulse of 7 μs were used in all cases. In the particular case of ethylene, a compromise choice of a contact of 500 μs was generally used to observe a variety of surface species. The samples were typically spun at a speed of 3.5 kHz and 4.5 kHz, unless otherwise specified. A series of variable-temperature-temperature ^{13}C NMR experiments, ranging frmo −57 °C to room temperature, were performed using a Neslab CC-100 Cryocool.

The techniques of dipolar dephasing[19] was employed to identify the nonprotonated carbons in the sample. Basically, the method uses a spin–echo and a deliberate delay of interrupted decoupling. In all of our dephasing experiments, we employed a delay of 45 μs followed by a delay of (τ − 45 μs), which was followed by a π pulse of 14.5 μs. After the initial 45-μs delay, the decoupler was turned on. The resulting echo was acquired τ μs after the π pulse. The application of a π pulse is used to remove the linear phase distortions and also to give the proper signal intensity. The time interval τ is determined by the reciprocal of spinning speed.

The resonances in all of our solid-state ^{13}C spectra were referenced to the most shielded resonance in adamantane, which has a chemical shift at 29.5 ppm with respect to TMS. Only the region between 350 and −200 ppm is exhibited in all figures.

Solid-state ^2H powder spectra of chemisorbed C_2D_4 on 5% Pt/γ-Al_2O_3 were obtained at 100 K on a highly modified[20] Bruker WH-400 NMR spectrometer at a ^2H resonance frequency of 61.421 MHz. A single-resonance 5-mm NMR powder probe (Doty Scientific, Inc.) was used.

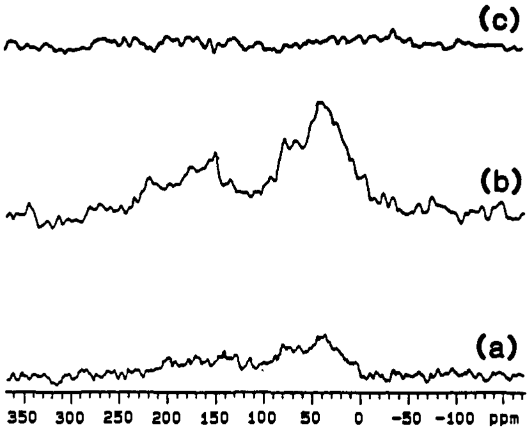

Figure 1. ^{13}C CP/MAS NMR spectra of (a) γ-alumina blank, (b) [1,2-^{13}C]ethylene adsorbed onto γ-alumina, and (c) same as b but with dipolar dephasing.

A quadrupole solid–echo[21] pulse sequence was employed for all spectra of static ^2H powder patterns. A perdeuterated polyethylene sample was utilized to measure the $\pi/2$ pulse. A pair of $\pi/2$ pulses of 2.4 μs were provided from an ENI LPI-10 linear amplifier at 950 W. In the experiment, a 30-μs τ value was used in obtaining a quadrupole echo signal. Three recycle delays of 50 ms, 1s, and 2s between scans were used to distinguish the signals among ^2H nuclei in methyl groups, π-complexed ethylene, and other possible alkyl groups on Pt surfaces at 100 K.

The analyses of the ^{13}C NMR spectra were facilitated by utilizing the NMR1 or VNMR programs, implemented in our lab on a Digital Equipment Corporation MicroVAX II computer system. The NMR1 program was obtained from New Methods Research, Inc. The VNMR program was provided by the Varian Instrument Division. In particular, the subtraction of one data set from another has been used the most in our structural analyses. These difference spectra will be presented subsequently. In the case of the dipolar powder spectra of ethylene on silver, the line shape calculations were performed on a Sun Microsystems 3/110 or a VAXStation 3540. The resulting calculated FID was then input into the Varian software to facilitate the comparison between theory and experiment.

FTIR Measurements. In our in situ FTIR experiments, a Nicolet Model 740 FTIR single-beam spectrometer was utilized to identify vibrational bands of the adsorbed ethylene on the Pt catalyst surface. All infrared spectra were acquired with 300 scans. A full aperture of 6.9-mm diameter was used to achieve a 0.125-cm^{-1} resolution for all FTIR spectra. In all of our FTIR experiments, pretreated samples for studying adsorbed species of ethylene on a catalyst surface were prepared similarly to the NMR samples, except that after the reduction–oxidation reaction the sample was pumped upon for approximately 3 h instead of overnight. In the in situ IR study of chemisorbed C_2H_4, a diffuse reflectance Collector & Controlled Environmental Chamber (purchased from Spectra-Tech Inc.) was used to replace the conventional quartz cell in the FTIR spectrometer. The Pt catalyst on alumina powder was directly placed in a micro sampling cup (13-mm diameter × 2 mm) within the reflectance chamber equipped with two KBr windows (13 mm × 2 mm, purchased from Spectra-Tech Inc.). This chamber can be heated up to 600 °C and also can be operated under vacuum. The advantage of a diffuse reflectance measurement is the elimination of the distortion caused by the specular components and light scattering on platinum wafers. The other advantage is the simplification of sample preparation, i.e., no wafers are needed. Both transmission infrared spectra of C_2H_2 and absorption infrared spectra of C_2H_4 on Pt/γ-Al_2O_3 or γ-Al_2O_3 in this paper have been ratioed with background in the mid-IR region of 4000–800 cm^{-1}. However, the study of adsorption for carbon-metal bonding (Pt–C) in the far-IR region is restricted. This is because of the transparency of the γ-alumina and the fact that γ-alumina-supported Pt wafers become ambiguous below 800 cm^{-1} due to the strong absorption of the Al–O vibration.[22]

Results and Discussion

A. Adsorption of Ethylene on γ-Al_2O_3 and Pt/γ-Al_2O_3.

The solid-state ^{13}C CP/MAS NMR spectra of [1,2-^{13}C]ethylene, 90%,

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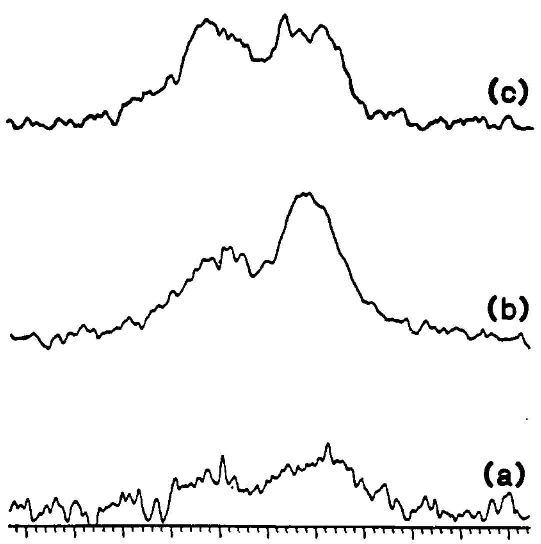

Figure 2. ^{13}C CP/MAS NMR spectra of [1,2-^{13}C]ethylene adsorbed onto (a) 1% Pt/γ-Al_2O_3, (b) 5% Pt/γ-Al_2O_3, and (c) 10% Pt/Al_2O_3.

adsorbed onto a γ-Al_2O_3 surface at room temperature is presented in Figure 1b. The low S/N ratio is reflective of the affinity of ethylene for the γ-alumina surface, and it is not as great as that demonstrated in our previous work[23] on acetylene. The existing sample background (Figure 1a) shows two weak, broad features in the regions of 0–90 ppm and 110–220 ppm. We attribute this existing background to residual carbon on the γ-alumina surface after the reduction–oxidation cleansing of the surface. In our FTIR study, a small absorption band at about 1400 cm^{-1} due to the adsorbed ethylene on γ-Al_2O_3 support at room temperature was also observed. Evidently, this weak 1400-cm^{-1} infrared band can be associated with NMR measurements in the region between 0 and 50 ppm. Earlier, the analogous weak absorption band at 1440 cm^{-1} was reported in Soma's[9] IR study of adsorbed ethylene on γ-Al_2O_3 support at −78 °C. In connection with our previous results of adsorbed acetylene on a γ-alumina surface,[23] we ascribed this observed broad band most likely to any type of alkyl groups on the γ-Al_2O_3 surface. Also, results from dipolar dephasing experiments, Figure 1c, show no nonprotonated carbon existing in this region. More details of structural elucidation for these possible surface alkyl species were precluded due to the broad low-intensity resonances.

The solid-state ^{13}C CP/MAS NMR spectra of [1,2-^{13}C]ethylene adsorbed on 1%, 5%, and 10% Pt/γ-Al_2O_3 are presented in Figures 2a, b, and c, respectively. Although the same measured amount of ethylene was employed as in our prevoius experiments[23] involving adsorption of acetylene onto the Pt/γ-Al_2O_3 catalyst, we observed much lower intensities and overlapping carbon resonances in all spectra. As a consequence of the low intensities in Figure 2 and the complexity of the spectra, several factors have to be taken into consideration. According to several studies of various gases chemisorbed onto transition metals, the strengths of chemisorption of a number of simple gases fall in the following sequence:[24]

$$O_2 > C_2H_2 > C_2H_4 > CO > H_2 > CO_2 > N_2$$

This simple qualitative indication shows that the concentration of chemisorbed ethylene on a platinum surface would be less than that of acetylene. However, considerations of the hydrogenation[12] reaction suggests that gaseous alkanes will be continuously formed by a considerable amount of chemisorbed ethylene and the variable source of hydrogen on the surface. In fact, a gas sample obtained by evacuation after the ethylene was adsorbed onto the surface for ca. 30 min was determined to be a mixture of a small fraction of ethane in a large amount of ethylene. Similar results have been observed by Gerstein and co-workers.[13]

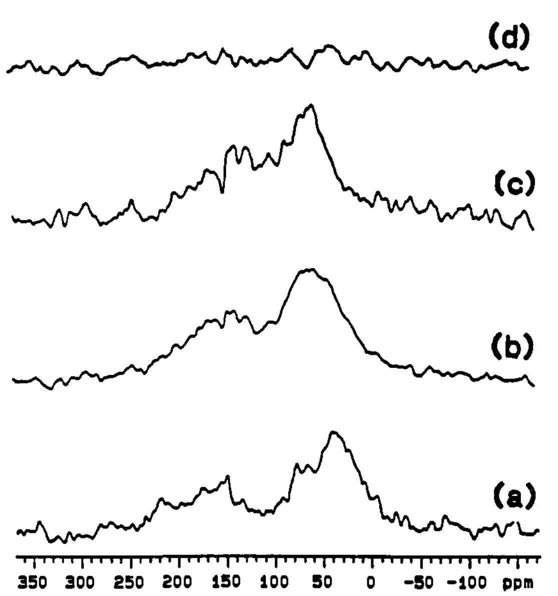

Figure 3. ^{13}C CP/MAS NMR spectra of [1,2-^{13}C]ethylene adsorbed onto (a) γ-alumina, (b) 5% Pt/γ-Al_2O_3, (c) the difference (b − a) spectrum, and (d) same as b but with dipolar dephasing.

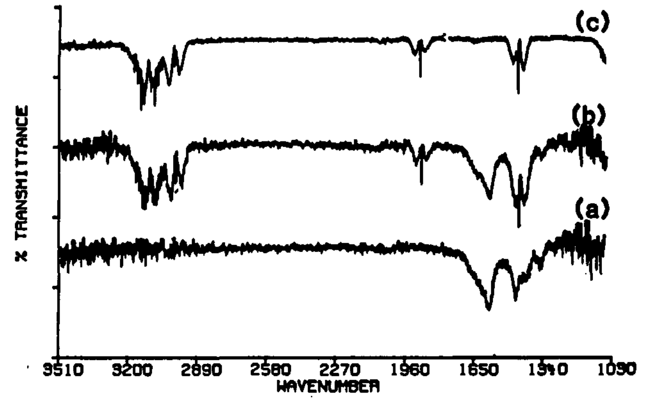

Figure 4. Infrared spectra of 5% Pt/γ-Al_2O_3 with (a) adsorbed C_2H_4 after evacuation, (b) excessively adsorbed C_2H_4 before evacuation, and (c) C_2H_4 in gas phase.

Although a fast rotating methyl group of ethylidyne species was reported by Slichter et al.,[11b] we did not observe any carbon resonances of this species in the CP dipolar-dephased spectrum in Figure 3d. Methyl groups and quaternary carbons are commonly observed under these conditions. Hence, the ^{13}C spectra do not support the presence of an ethylidyne species. However, such a conclusion makes certain assumptions concerning the efficiency of the CP process. As we shall discuss subsequently, these assumptions are no longer valid. Under these circumstances, we cannot eliminate the possible existence of the ethylidyne species $\equiv C-CH_3$ proposed in earlier Pt single crystal studies as well as those of Slichter et al.[11] As we will show subsequently, solid-state ^2H NMR affords a better perspective on the existence of the ethylidyne with these samples.

The IR spectra of chemisorbed ethylene on 5% Pt/γ-Al_2O_3 surface are presented in Figures 4a and b. Three broad features in Figure 4a at about 1550, 1440, and 1300 cm^{-1} were evident after evacuation. Examining the IR data of olefinic groups,[25] the strong broad peak at 1550 cm^{-1} was assigned to a double bond of chemisorbed ethylene on the Pt surface. This vibrational peak of a double bond most likely corresponds to the main resonance

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(23) Chin, Y. H.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 7653–7654.

(24) (a) Bond, G. C. *Heterogeneous Catalysis: Principles and Applications*; Oxford University Press: London, 1974.

(25) (a) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: Princeton, 1945; p 358. (b) Szymanski, H. A. *Interpreted Infrared Spectra*; Plenum Press Data Division: New York, 1966; Vol. 2, p 9.

at 58 ppm in Figure 3c. Although the complicated coupling between C–H and C–C bonds precludes our IR assignment in the region of 1400 cm^{-1}, certain characteristic features in Figure 4a, however, are still distinguishable. In light of the vibrational analysis of Zeise's salt,[26] the bands observed at 1440 and 1300 cm^{-1} were assigned to CH_2 scissor and CH deformation vibrations, respectively. Our IR results are consistent with Soma's[9] IR studies of adsorbed ethylene on alumina-supported Pt catalysts. In the study by Prentice et al.[8] of ethylene on silica-supported platinum, a strong vibration at about 1500 cm^{-1} due to the double bond was also reported, even though our preparation of NMR samples was different from theirs.

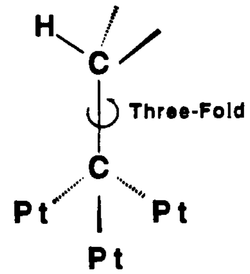
The details of the structural explanations may be somewhat precluded due to the overlapping and broad absorptions in Figure 3c. However, a reasonable hypothesis regarding the possible identity of the chemisorbed surface species is still obtainable from references to Pt complexes with known chemical shifts. A number of Pt complexes with π-bonded alkenes or σ-bonded vinyls as ligands have been reported.[27a] The ^{13}C isotropic shifts of π-bonded alkene complexes such as $Pt(C_2H_4)_3$[27b] range from 35 to 75 ppm, and the chemical shifts of σ-vinyl complexes vary from 120 to 160 ppm, depending on the character of the other bonded ligands. Hence, we ascribed the principal resonance at 58 ppm to the π-bonded ethylene species with a strong vibration band at 1550 cm^{-1}. The minor broad feature from 120 to 170 ppm most likely corresponded to a σ-vinyl species ($-CH{=}CH_2$). Since the relative intensity of π-bonded ethylene was much larger than that of the σ-vinyl species, the formation of σ-bonded species possibly resulted from the principal π-bonded ethylene via nondissociative conversion at room temperature. This unique nondissociative conversion was also reported by Demuth and Eastman[27] on the basis of ultraviolet photoelectron spectroscopy. They claimed that π-adsorbed ethylene on a Ni surface was converted into the σ-bonded form at room temperature under high-vacuum, hydrogen-free conditions.

We have seen that ^{13}C NMR and IR methods have proven to be useful in obtaining evidence that is consistent with the presence of both π- and σ-bonded ethylene species on the surface. However, it is not clear whether there are alkyl fragments as well on the surface. This ambiguity arises because of the broad lines observed in the ^{13}C NMR. However, we can unambiguously probe the existence of these alkyl fragments by exploiting their motional differences on the surfaces. First, consider the methyl group in an ethylidyne species ($\equiv C-CH_3$). Here the methyl group can jump about the three distinct states associated with its pseudo-three-fold axis. Now consider an ethyl group ($-CH_2CH_3$) attached to the surface. The methylene hydrogens are undergoing a similar motion to that of the methyl hydrogens in the ethylidyne species. However, the methyl hydrogens of the ethyl group are moving differently. Here the methyl hydrogens are experiencing two motional processes. That is, the methyl hydrogens are rotating about an axis which is itself rotating. These motional differences are all that is needed to differentiate between an ethylidyne or an ethyl fragment on a surface.

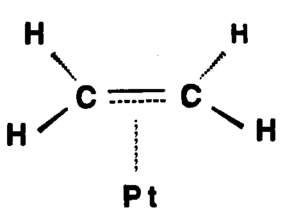
The spectroscopic vehicle used to exploit this motional differentiation is solid-state ^2H NMR. The quantitative details are provided in a paper by Greenfield et al.[28] However, only a schematic outline of the theory will be presented here. For a static deuteron, the frequency of a given isochromat is given by the expression

$$\omega(\alpha,\beta) = {}^1\!/_2\omega_Q[(3\cos^2\alpha - 1) - \eta\sin^2\alpha\cos 2\beta]$$

Here α and β refer to powder angles, which relate the orientation of a given isochromat with respect to the applied magnetic field.



Methyl of Surface Ethylidyne Species



Surface π-bonded Ethylene

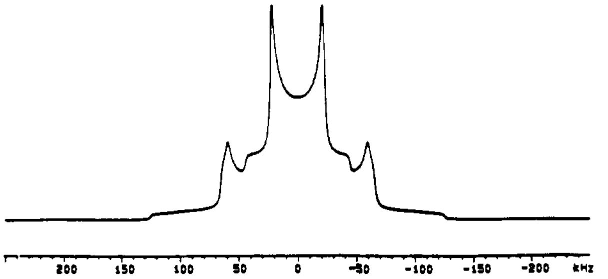


Figure 5. Simulated ^2H powder spectra of a π-bonded ethylene with rapidly rotating methyl group.

The term ω_Q is proportional to the quadrupole coupling constant for the deuteron, i.e.

$$\omega_Q = {}^3\!/_4(e^2q_{zz}Q/\hbar)$$

The asymmetry parameter $\eta = (q_{xx} - q_{yy})/q_{zz}$ is defined such that with $|q_{zz}|<|q_{yy}|<|q_{xx}|$, $0 \le \eta \le 1$. The factors q_{xx}, q_{yy}, and q_{zz} are the diagonal elements of the electric field gradient at the nucleus in question. The remaining terms have their usual meaning. Consider now the possibility that the deuteron (assume for simplicity that $\eta = 0$) jumps between N sites about an axis which makes Euler angles θ and ϕ with respect to the principle axis system (PAS) of the deuteron. The Euler angles θ and ϕ represent the transformation which must be applied to the PAS frame of the deuteron to bring it into coincidence with the jumping frame. The resulting expression for the deuteron frequency of a given isochromat now takes the form

$$\omega(\alpha,\beta,\theta,\phi) = {}^1\!/_4\omega_Q[(3\cos^2\alpha - 1)(3\cos^2\theta - 1) - 3\sin 2\alpha\cos\phi\sin 2\theta + 3\sin^2\alpha\cos 2\phi\sin^2\theta]$$

To be specific, for the case of a methyl group the angle θ is 70.528 779°, i.e., $180° - \theta_{tetra}$, and ϕ can take on the values 0°, 120°, and 240°, i.e., ϕ is the jump angle in this example. In the fast motion limit, we are allowed to average the expression for $\omega(\alpha,\beta,\theta,\phi)$ over the three jump angles

$$\omega(\alpha,\beta,70.528\,779°) = {}^1\!/_6\omega_Q[(3\cos^2\alpha - 1)]$$

Hence, the motionally averaged line shape is the time as in the static case (when η is 0), except that it has been scaled by a factor of $^1/_3$. Therefore, if the static quadrupole powder pattern exhibited a line shape characteristic of a 125-kHz value for $\omega_Q/2\pi$, then the motionally averaged line shape would be characteristic of a value for $\omega_Q/2\pi$ of 41.666... kHz. Parallel reasoning demonstrates that in the double axis case, i.e., a methyl group rotating about one axis which is itself rotating (assuming tetrahedral angles), the resulting value of $\omega_Q/2\pi$ will be reduced by another factor of $^1/_3$, i.e., the splitting will be reduced to 13.888... kHz.

Combining what we know from the ^{13}C NMR experiments and what we expect from the ^2H experiments, the following picture unfolds. At reduced temperature we would expect to see "rigid" lattice ^2H for the surface-bound π- and σ-ethylene. If these were the only sources of deuterons, then one would observe a line shape characteristic of a value of $\omega_Q/2\pi$ of 125–130 kHz. However,

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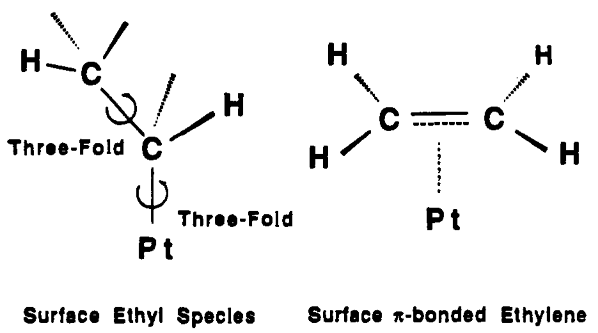
[26] (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press Inc.: New York, 1981, pp 89 and 192. (b) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1971**, 271.

[27] (a) Demuth, J. E.; Eastman, D. *Phys. Rev. Lett.* **1974**, *32*, 1123. (b) Demuth, J. E.; Eastman, D. *Jpn. J. Appl. Phys., Part 2* **1974**, Suppl. 2, 827.

[28] Greenfield, M. S.; Ronemus, A. D.; Vold, R. L.; Vold, R. R.; Ellis, P. D.; Raidy, T. E. *J. Magn. Reson.* **1987**, *72*, 89–107.



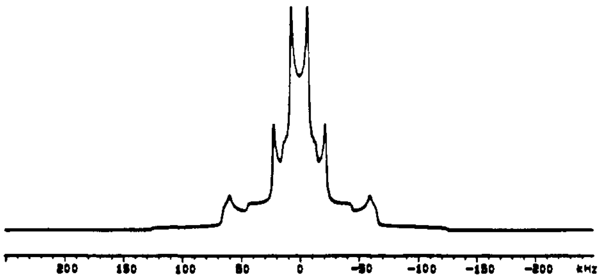


Figure 6. Simulated ^{2}H powder spectrum of a π-bonded ethylene and an ethyl fragment.

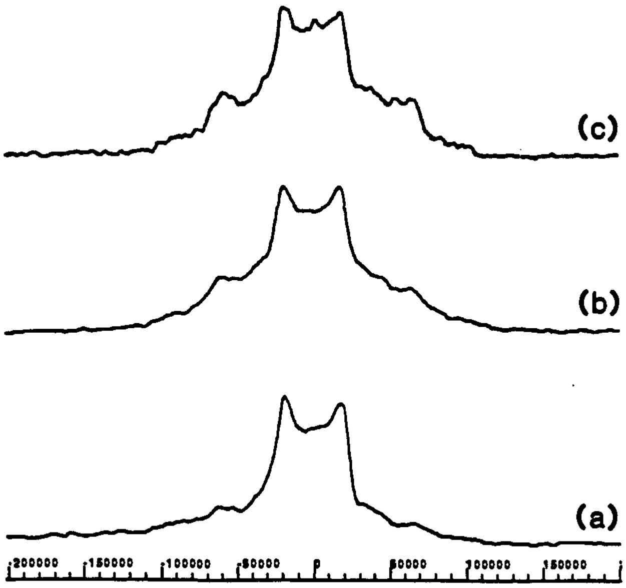


Figure 7. Solid-state 61.42-MHz ^{2}H NMR powder spectra of ethylene adsorbed onto 5% Pt/γ-Al$_2$O$_3$ with repetition rates of (a) 50 ms, (b) 1 s, and (c) 2 s. All spectra were recorded at 100 K after sample preparation.

we should observe motionally narrowed powder spectra for either the ethylidyne or the ethyl case. In the case of the ethylidyne species, we should observe a 41–42 kHz splitting for the methyl group superimposed on the 125–130 kHz line shape for the olefin. However, if we had, instead, an ethyl group on the surface, one would expect to see in addition to the "rigid" lattice spectrum a 41/42 kHz powder pattern for the methylene deuterons and a 13–14 kHz powder pattern for the methyl deuterons of the ethyl group. This situation is schematically represented in Figures 5 and 6, respectively. The experimental spectrum, Figure 7, is only consistent with the presence of the olefin and the ethylidyne species. Therefore, the *combination* of ^{13}C and ^{2}H NMR has clearly demonstrated the presence of π- and σ-ethylene on the surface in addition to the ethylidyne species.

In an attempt to further demonstrate the presence of molecular motion, we have collected the ^{2}H spectrum as a function of the recycle delay. The rationale for these experiments is based on the fact that rapidly moving groups (methyl groups) have a shorter spin lattice relaxation time (T_1) than other surface species which are immobile (π-complexed olefin). The ^{2}H NMR spectra of C_2D_4 on 5% Pt/γ-Al$_2$O$_3$ with repetition rates of 50 ms, 1 s, and 2 s are represented in Figures 7a, b, and c, respectively. All spectra were recorded at 100 K after sample preparation. As can be seen in Figure 7a, only the doublet with a splitting of approximately 40 kHz, characteristic of the methyl group, survived the 50-ms recycle delay. In Figures 8a and b, we present the ^{2}H NMR spectra of C_2D_4 with repetition rates of 50 ms and 1 s. Both spectra were recorded at 100 K, 1 day after sample preparation. Comparison between Figure 7b and Figure 8a showed the slight intensity increase of the methyl doublet. Hence, the sample is changing with respect to time, i.e., it is reacting with the surface as the experiment is progressing. These results are very different from those obtained by Slichter and co-workers.[11b] In their ^{2}H work, they noted that when the sample temperature was raised from 77 K to room temperature and back down to 77 K, the chemisorbed ethylene had *completely* reacted to form the ethylidyne species on the surface. This clearly demonstrates that their catalyst preparation is simply more reactive than the one employed here. This difference in catalyst reactivity is *one* of the keys to the differences experienced by the various NMR groups.

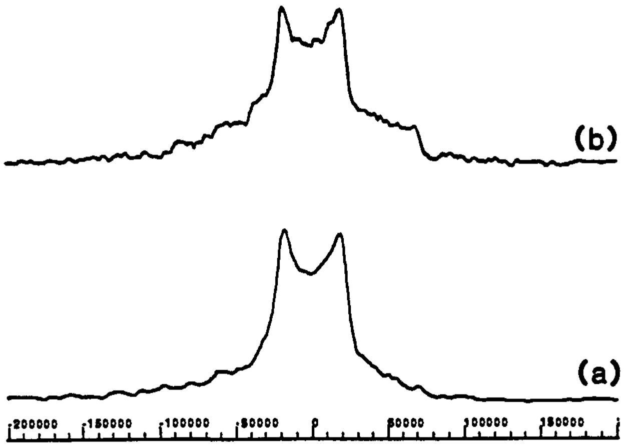


Figure 8. Solid-state 61.42-MHz ^{2}H NMR powder spectra of ethylene adsorbed onto 5% Pt/γ-Al$_2$O$_3$ with repetition rates of (a) 50 ms and (b) 1 s. Both spectra were recorded at 100 K, 1 day after sample preparation.

In view of this observation, comparisons of chemisorbed species between our NMR study and those of others should be made carefully by taking into consideration the Pt catalytic activities. The activity of a supported catalyst depends upon the weight percentage, size of Pt the particles, how "clean" the surface is, and the nature of the support. The dispersion is one of the most important factors in determining the activity of the catalyst. Therefore, the extent of ethylene reaction on a highly dispersed Pt catalyst should be different from that on a low-dispersion catalyst.

However, catalyst reactivity does not explain the *differences* between the structural observations made from the ^{13}C experiments and those deduced from the ^{2}H experiments. These differences arise from the nature of the platinum metal surface. Platinum is nearly a ferromagnet.[29] As a result, there are large anisotropic effects on the magnetic susceptibility of the surface. This results in significant shifts of the ^{1}H resonance frequency of a surface-bound residue. The consequence of this shifting is a large random resonance offset in the ^{1}H portion of the cross-polarization sequence. This, in turn, significantly reduces the efficiency of the CP experiment. That is, molecules which have their resonance frequencies shifted far off resonance cannot be observed. Hence, the CP/MAS experiment only allows for the observation of a subset of the surface species, i.e., those which are not shifted

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(29) Slichter, C. P., personnal communications. Bleaney, B. I.; Bleaney, B. *Electricity and Magnetism*, 3rd ed.; Oxford University Press: 1978; Chapter 15.

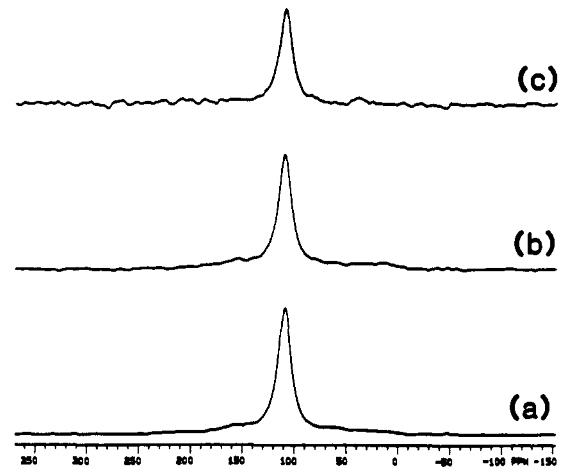

Figure 9. ^{13}C CP/MAS spectra of (a) [1,2-^{13}C]ethylene, 90%, (b) [1-^{13}C]ethylene adsorbed onto 6% Ag/γ-Al_2O_3, and (c) same as b but with dipolar dephasing. All spectra were recorded at room temperature.

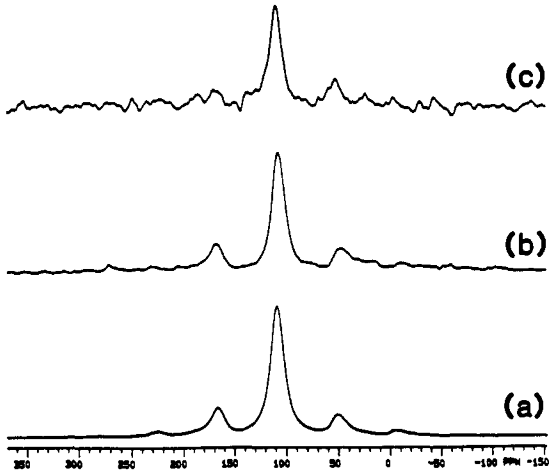

Figure 10. ^{13}C CP/MAS spectra of (a) [1,2-^{13}C]ethylene, 90%, (b) [1-^{13}C]ethylene adsorbed onto 6% Ag/γ-Al_2O_3, and (c) same as b but with dipolar dephasing. All spectra were recorded at 216 K.

significantly. This has been concluded by others, e.g., Zilm and co-workers[30] in their work with adsorbed CO on dispersed metals. Similar decoupling problems have also been observed by Pratum[31] in his work with materials of moderate susceptibility.

B. Adsorption of Ethylene on Ag/γ-Al_2O_3. Silver does have a completed d-level, and as a consequence it should not exhibit any of the difficulties observed using platinum. The ^{13}C NMR spectra of [1,2-^{13}C]ethylene and [1-^{13}C]ethylene chemisorbed onto 6% Ag/γ-Al_2O_3 recorded at 298 K are presented in Figures 9a a and b, respectively. In the presence of the silver metal, a resonance at 108 ppm was observed in both cases. An assignment of this resonance was achieved by comparing the literature values[32] for the ^{13}C chemical shifts of $[Ag(CH_2{=}CHMe)_2]^+$. One finds that the $=Ch_2$ of π-complexed propylene has a chemical shift of 109 ppm with respect to TMS. Consideration of the isotropic chemical shift at 108 ppm suggested that the carbon nuclei of the chemisorbed C_2H_4 have similar chemical environments. This observation leads to a reasonable hypothesis that the resonance at 108 ppm is that of a π-bonded ethylene where the C=C axis is parallel to the silver surface. Evidence for the presence of molecular motion was obtained by noting the absence of spinning sidebands at 298 K in Figures 9a and b. If this resonance does correspond to π-bonded ethylene, then one would expect to observe sidebands from the expected shielding anisotropy in the region between 0 and 200 ppm. By lowering the temperature to 216 K, the sidebands are clearly evident in Figures 10a and b. Hence, at room temperature the mobility of the ethylene is such as to render the shielding nearly isotropic.

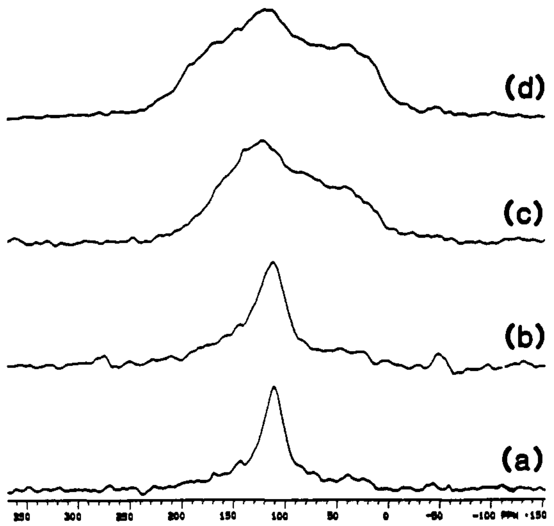

Figure 11. ^{13}C CP powder spectra of [1-^{13}C]ethylene adsorbed onto 6% Ag/γ-Al_2O_3, recorded at (a) 298 K, (b) 273 K, (c) 216 K, and (d) 100 K. All spectra were taken with 3600 transients and a pulse delay of 60 s.

In order to further probe motional details, we decided to examine the powder line shape as a function of temperature. Figures 11a, b, c, and d illustrate the chemical-shielding powder spectra of singly ^{13}C-enriched ethylene on 6% Ag/γ-Al_2O_3 obtained at 298, 273, 216, and 100 K, respectively. We observe a persistent increase of line broadening while the temperature is decreased. The development of a powder line shape (in going from higher to lower temperatures) is a consequence of the reduction in molecular motion. This reduction in motion leads to a decrease in the partial tensor averaging observed at the higher temperatures. Indeed, in Figure 11d at 100 K the molecular motion was nearly stopped. From these observations, one can make some comments about the potential motion of π-bonded ethylene on a silver surface. At room temperature the molecule is tumbling and rotating in the sense that the shielding tensor in Figure 11d is nearly averaged to its isotropic value in Figure 11a. Such a molecular motion cannot be a simple rotation about a particular axis. Rather, it would have to involve random rotations about several bonds. A detailed discussion of this motion is the subject of another publication.[33]

In general, a line shape of a static powder pattern in the presence and absence of a homonuclear dipolar interaction reveals a number of important parameters, such as a dipolar coupling and the anisotropy of the shielding tensor. The bond distance can be extracted from the dipolar coupling through its dependence upon $r_{C=C}^{-3}$. In order to successfully measure the bond length by probing the homonuclear dipolar interaction for a static powder sample, the molecular motion of ethylene has to be quenched by lowering the temperature. Otherwise, the line shape of the powder spectra will be narrowed and yield a partially averaged dipolar coupling. We assume that the dynamics present at 100 K is not sufficient to cause significant averaging of the dipolar coupling. The respective dipolar/shielding powder species of [1,2-^{13}C]-ethylene on 6% Ag/γ-Al_2O_3 at 100 K alone with its simulation are presented in Figures 12a and b, respectively. Clearly, the static powder spectrum in Figure 12a, with its distinct discontinuities at 100 K, is representative of the rigid lattice case for two coupled

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(30) Duncan, T. M.; Zilm, K. W.; Hamilton, D. M.; Root, T. W. *J. Phys. Chem.* **1989**, *93*, 2583–2590. Zilm, K. W.; Bonneviot, L.; Hamilton, D. M.; Webb, G. G.; Haller, G. L. *J. Phys. Chem.* **1990**, *94*, 1463–1472. Zilm, K. W.; Bonneviot, L.; Haller, G. L.; Han, O. H.; Kermare, M. *J. Phys. Chem.* **1990**, *94*, 8495–8498.

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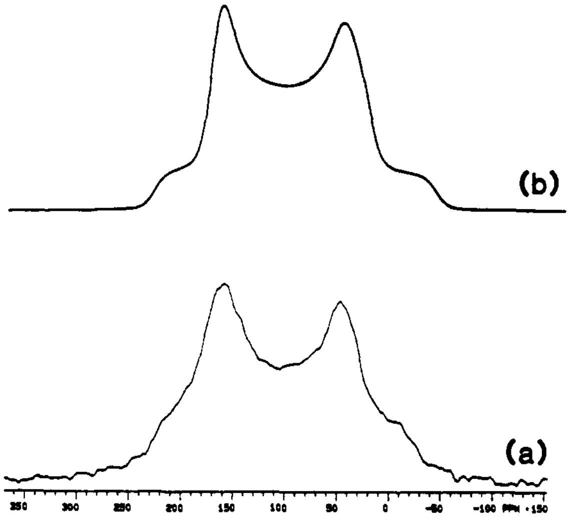

Figure 12. Comparison of (a) experimental and (b) calculated dipolar powder spectra of $^{13}C_2H_4$ on 6% Ag/γ-Al_2O_3 at 100 K. The bond distance used was 1.34 Å, $\Delta\sigma = -147.1 \pm 1.0$ ppm, $\eta = 0.9 \pm 0.1$, $\alpha = 90°$, and $\beta = 90°$.

spin-$^1/_2$ nuclei. Using Haeberlin's[14] tensor sign conventions, we deduced the principal tensor components of the shielding tensor in Figure 11d to be 192, 117, and 12 ppm for σ_{xx}, σ_{yy}, and σ_{zz}, respectively. These three principal components of the shielding tensor yield an isotropic chemical shift of 107 ppm (<<lvcσ). This value is in good agreement with the observed isotropic chemical shift extracted from the CP/MAS spectra, 108 ppm in Figures 8 and 9. In Figure 12b, we present the calculated spectrum in which the value of 1.34 ± 0.004 Å was used for the C=C bond distance ($r_{C=C}$) and the asymmetry parameter η was determined to be 0.79 ± 0.01. This calculated dipolar powder form is sensitive to the parameter of $r_{C=C}$. The calculated spectrum in Figure 12b was convolved with both Lorentzian and Gaussian broadening functions, which had line widths of 350 and 650 Hz, respectively. The line broadenings of Lorentzian and Gaussian functions were selected to broaden the base of the calculated spectrum without excessively altering the central feature of the line shape. The broadening of the experimental spectrum certainly must reflect, in part, the heterogeneity of the surface itself.

In earlier studies of ethylene,[34] bond lengths ranging from 1.335 to 1.34 Å have been reported. In alkene complexes, the C=C bond length can vary from a typical double bond to an analogous single bond in which the transition metal forms two σ-bonds to the terminal carbons.[35] This is due to the fact that the bond length of the olefinic group depends upon the extent of π-bonding interaction, usually accompanied by a π-backbonding effect.[36] The bond length determined from the present work is 1.34 ± 0.004 Å. Comparison of the bond length of ethylene (gas phase) with ours clearly demonstrates that the π-bonding between silver and ethylene is weak. Zilm and Grant[37] have used the homonuclear dipolar interaction to affix the shielding tensor elements to a molecule-fixed frame relative to the dipolar interaction. The same procedure was employed here, and the orientation was found to be identical to that reported by Zilm and Grant.[37] A more detailed analysis of these results and their implications with regard to consequences of promoters on silver surfaces will be presented in a subsequent publication.[38]

Conclusions

In the CP/MAS study of ethylene adsorbed on supported platinum, the principal species is denoted by a resonance at 58 ppm which corresponds to π-bonded ethylene with an associated strong IR stretching vibration at 1550 cm^{-1}. Likewise, the ^{13}C NMR indicated the presence of a σ-bonded ethylene species on the surface. However, the ^{13}C CP/MAS spectrum did not show evidence for the presence of the ethylidyne species. This comes about from the near-ferromagnetic nature of the platinum surface, which causes severe resonance offsets in the ^1H and ^{13}C spectrum. These offsets are large enough to prevent the CP experiment from working. Further, the random offsets in the ^{13}C spectrum would render the lines too broad to be observed. Hence, the CP/MAS spectrum observed in this study represents only a subset of the surface-bound species. The susceptibility problems observed here may also be the origin of some of the differences observed between our[23] group and those reported by Slichter and co-workers[39] for acetylene adsorbed onto supported platinum. The solid-state ^2H NMR of C_2D_4 is not as sensitive to these offsets. As a result, it provides a more accurate reflection of the species present on the surface. The solid-state ^2H powder patterns of ethylene distinctly exhibited the characteristics of a rapidly rotating methyl fragment, confirming the presence of the ethylidyne species. This species was proposed by Slichter but rejected by Gay[12] in his NMR studies. Gay's work suffered from the same problems encountered in the present investigation. It is clear that a multinuclear approach becomes important, e.g., ^2H in the present case. The ^2H experiments afford another advantage in this system: they are highly sensitive to the mode by which the quadrupole tensor is being *partially* averaged. As a result of this sensitivity, we were able to unambiguously deduce the presence of an ethylidyne species when ethylene chemisorbs onto Pt/Al_2O_3. Further, these experiments allow easy differentiation between ethyl groups and the ethylidyne species. In summary, the assignment of NMR resonances on surfaces is model dependent. To make such assignments as unambiguous as possible, the surface has to be examined by as many spectroscopic methods as is feasibly possible. Finally, the present work supports the conclusions drawn by Slichter and co-workers[11,39] concerning the structure of olefins adsorbed onto supported platinum catalyst.

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