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Solid-State NMR of ^{13}C in Ethylene Adsorbed on Silica-Supported Ruthenium

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Abstract: A variety of experimental nuclear spin dynamics on ^{13}C, including standard cross-polarization (CP), CP with magic angle spinning (CP/MAS), CP/MAS with dipolar dephasing, and single-pulse experiments with and without proton decoupling have been applied to the study of adsorption and reaction of ethylene on silica-supported ruthenium. NMR of ^{13}C using CP/MAS allowed us to simultaneously observe the transformations of chemisorbed and weakly adsorbed molecules during reaction of ethylene to form products. Direct ^{13}C excitation allowed quantitative measurements of the various species present. From these experiments it was determined that the decomposition of ethylene at room temperature formed strongly adsorbed species such as acetylide and alkyl groups. Recombination of adsorbed species and hydrogenation of ethylene occurred rapidly at room temperature, forming weakly adsorbed ethane and *cis*- and *trans*-2-butene that subsequently hydrogenated to butane. The strongly adsorbed species identified as acetylide was not appreciably consumed in the formation of products, although it most likely served as a source of hydrogen for other reactions. Spin counting revealed that there was one carbon in the strongly adsorbed layer for each surface ruthenium atom.

I. Introduction

Understanding the adsorption and reaction of simple molecules on metal surfaces is of great importance in the study of adhesion, corrosion, lubrication, and catalysis. Considerable progress has been made in determining the orientation and molecular structure of chemisorbed hydrocarbon species on metal surfaces by using a variety of techniques such as infrared spectroscopy (IR) and electron energy loss spectroscopy (EELS).

The adsorption, rearrangement, and decomposition of ethylene on single-crystal surfaces of group VIII transition metals has been studied extensively.[1-30] Adsorption and subsequent rearrangement of ethylene have been observed to depend on the specific metal and the crystallographic orientation of the surface. At low temperatures, (e.g., <150 K) ethylene typically adsorbs in either a π-bonded or di-σ-bonded mode. When a sample is heated, a variety of intermediate products are observed, including ethylidyne ($\equiv C-CH_3$), ethylidene ($=CH-CH_3$), acetylide ($-C\equiv CH$), vinylidene ($=C=CH_2$), and vinyl species ($-CH=CH_2$). Further heating causes continued dehydrogenation of these species and, under certain conditions, carbon–carbon bond scission. The higher temperature decomposition products in most cases are graphitic carbon and hydrogen.

Of particular interest for the present study are the results reported for ethylene adsorption and decomposition on ruthenium single crystals. Recently Hills et al.[1] reported EELS and temperature-programmed desorption (TPD) results that describe the adsorption and subsequent decomposition of ethylene on Ru(0001) over a temperature range from 110 to 700 K. They interpreted their results to mean that ethylene rehybridized from sp^2 to sp^3 and formed a di-σ-bonded adsorbed species at 110 K. Heating the sample from 150 to 280 K resulted in some desorption of molecular ethylene and dehydrogenation of ethylene to form both ethylidyne and acetylide. The acetylide was stable up to 380 K, while the ethylidyne began to decompose around 330–355 K. Further increases in temperature led to the eventual formation of surface carbon and the desorption of molecular hydrogen. Activation energies for the formation and decomposition of ethylidyne on Ru(0001) were given by Greenlief et al.[2] as 5.0 ± 1 and 12 ± 2 kcal/mol, respectively.

Earlier studies of Ru(0001) using HREELS and TPD[3] and ultraviolet photoelectron spectroscopy (UPS) with TPD[4] also indicated that ethylene adsorbed in a di-σ-molecular orientation. Ethylidyne formation was noted at temperatures greater than 300 K, but in these two studies the formation of acetylide was either not reported[3] or questioned.[4]

When ethylene was adsorbed on a stepped Ru(1,1,10) surface, however, no ethylidyne was observed.[4] Instead, C–H bond cleavage occurred at 110 K to form acetylide and vinylidene species. This type of structure-sensitive behavior for ethylene adsorption and decomposition has also been noted on platinum surfaces.[5]

The validity of comparing results from single crystals with results from studies using supported catalysts, where the catalyst surface is not so well defined, has been a matter of debate. Many of the surface science techniques available under ultrahigh vacuum conditions are not amenable to the study of supported metal catalysts. Infrared spectroscopy[28-30] and more recently nuclear

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magnetic resonance (NMR)[31-36] have been used to characterize the orientation and structure of molecules adsorbed on the small metal particles in supported catalyst systems.

Beebe et al.[28] used IR to make a detailed characterization of ethylene adsorbed onto an aluminum-supported palladium catalyst. At room temperature an immediate irreversible conversion of ethylene to ethylidyne occurred. The ethylidyne was found to be stable up to 400 K. Later studies of alumina-supported Pt, Rh, and Ru[29] also showed that ethylene was converted to a surface species exhibiting the characteristic vibrational modes of ethylidyne.

By using IR spectroscopy, Cruz and Sheppard[30] observed the conversion of ethylene to ethylidyne on silica-supported platinum similar to what has been noted previously on Pt(111) single-crystal surfaces.[7,8] They concluded that the di-σ-bonded ethylene was adsorbed at two distinct sites on the surface. On only one of these sites was ethylidyne formed, once again suggesting inherent differences between adsorption sites for the adsorption of ethylene and the subsequent converstion to ethylidyne.

As previously mentioned, NMR is emerging as a powerful technique for the study of real catalyst systems. Duncan and Dybowski,[31] Slichter,[32] and Wang et al.[33] have reviewed much of the previous work and advances that have made NMR a valuable method for studying species adsorbed on metal surfaces. For example, Wang and Slichter[34] reported results describing the adsorbed structures and subsequent reactions of ethylene on Pt/Al_2O_3 catalysts. Spin-echo methods enabled them to observe C–C and C–H dipolar couplings in the double-labeled ^{13}C ethylene. At room temperature all of the C–C bonds were found to be intact with an internuclear distance of 1.49 Å. Half of the carbon was found to have directly bonded hydrogen and a C–H dipolar coupling consistent with a rotating $-CH_3$ group. On the basis of this information, they proposed that ethylidyne is the sole species present at room temperature.

On the other hand, in a recent study of ethylene on alumina- and silica-supported platinum catalysts, Gay[35] saw no evidence for the presence of a surface ethylidyne species. Gay employed delayed decoupling experiments that are designed to eliminate signals from carbons with directly bonded hydrogen, leaving only the signal from unprotonated carbons and highly mobile protonated carbons. No signal from unprotonated surface carbons, such as in a $\equiv C-CH_3$ species, was observed. A species identified as a π-bonded olefin was observed on all samples. Part of the discrepancy between the results of Wang and Slichter[34] and Gay[35] may be due to adsorbed species on the alumina support in the former. Chin and Ellis[36] used ^{13}C NMR to study the adsorption of acetylene on alumina and on alumina-supported platinum. They found evidence that alumina provided adsorption sites independent of the metal.

In this paper we report results of a solid-state NMR study of ^{13}C in ethylene adsorbed on silica-supported ruthenium catalysts. A variety of experimental spin dynamics including standard cross-polarization (CP), CP with magic angle spinning (CP/MAS), CP/MAS with dipolar dephasing or variable contact time, and single pulse experiments with and without proton decoupling have been employed. The goal of this work was to probe the chemical and structural properties of adsorbed species and decomposition products on a supported ruthenium catalyst at pressures much higher than possible in ultrahigh vacuum experiments.

II. Experimental Procedures

Materials and Preparation Procedures. Catalyst samples used in this study were prepared by using an ion exchange technique described by Gay[37] with two modifications. First $Ru(NO)(NO_3)_3$ not $RuCl_3$ was used as the metal salt; second, instead of simply washing the catalyst with ammonia, ammonia was added to the solution to bring the pH to approximately 9–10. The catalyst was allowed to soak in that solution. The above technique allowed us to attain high metal dispersions (0.37) with a high ruthenium loading (12% by weight). All catalysts were supported on Cab-O-Sil HS-5 amorphous, fumed silica (with a BET surface area of 300 m^2/g). Additional samples containing only amorphous, fumed silica were also prepared by adding water to the silica (2 mL per g SiO_2). All samples were dried overnight at 383 K. Reduction was performed either during the dispersion measurements or when the NMR sample was prepared. In either case the sample (80–100 mg) was reduced for 2 h in 15 sccm hydrogen at 573 K.

Ruthenium dispersions were measured by using strong hydrogen chemisorption.[38] Reduced and evacuated samples were exposed to hydrogen (0–60 Torr) and allowed to equilibrate in order to generate a total hydrogen adsorption isotherm. The reversible hydrogen adsorption isotherm was collected under the same conditions after a 10-min evacuation period (to 10^{-6} Torr) following the first adsorption step. The amount of strong hydrogen adsorption was found by taking the difference between the values of the total and reversible isotherms extrapolated to zero pressure.

NMR sample preparation was done on a home-built adsorption apparatus consisting of a multiport glass manifold connected to a high-vacuum system[38] with a flow-through capability for catalyst reduction. The samples (80–100 mg of catalyst in 5.0 mm OD Norell XR-55 NMR sample tubes) were reduced, evacuated to a pressure of less than 10^{-5} Torr, and then cooled to room temperature. Samples were then dosed with ethylene (single ^{13}C-labeled, double ^{13}C-labeled, or natural abundance) at either liquid nitrogen or room temperature and then sealed. Prior to sealing, some samples were evacuated or given additional treatments (see below).

NMR Equipment and Experimental Techniques. The species adsorbed on the catalysts were studied by NMR of ^{13}C. Transient techniques included CP and direct excitation, both of which were done with and without MAS and proton decoupling. The details of the NMR experiments are given below.

The CP/MAS experiments were carried out on a home-built spectrometer operating at 100.06 MHz for ^1H and 25.16 MHz for ^{13}C.[39] A double-tuned, single coil probe was constructed which allows for MAS of sealed samples at rates exceeding 5 kHz (with air drive). A spinning speed of 5 kHz avoids the problems associated with spinning sidebands of ^{13}C at the resonant frequency of 25 MHz. The spinning assembly is a modified version of the design by Shoemaker and Apple[40] with macor and torlon used as stator and rotor materials, respectively.

All spectra were acquired with a dwell time of 10 μs by using 2K quadrature detection and Fourier transformed after zero filling to 8K. To attenuate base line distortion associated with pulse breakthrough and receiver recovery, we used the proton spin temperature inversion with an add–subtract of ^{13}C free-induction decays.[41] A proton B_1 field of 50 kHz was used for cross-polarization and decoupling. To minimize the effect of possible Hartmann–Hahn mismatch, we monitored the ^{13}C CP intensities versus ^{13}C rf field with a static adamantane sample. No measurable effect on the impedance of the probe because of the presence of samples was detected. In addition to standard CP/MAS experiments, "selective polarization" techniques were applied. These include variable contact time and dipolar dephasing measurements.

Throughout the work, all resonance line positions were determined in ppm with respect to tetramethylsilane (TMS). The δ scale is used, with positive numbers being downfield (deshielded). Only the range from 400 to −300 ppm is usually shown because no features were observed outside of this region.

As will be shown later, the species identified on the surfaces by using the CP/MAS technique display a wide variety of chemical and physical

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properties. Some species exhibit rigid structures that are strongly adsorbed on the surface, and others appear to be mobile, weakly adsorbed molecules. Although high mobility does not preclude the cross-polarization and ^1H–^{13}C cross-polarization can be observed in organic liquids,[42,43] the Hartmann–Hahn matching condition becomes very critical in this case. For mobile species the kinetics of polarization are different than that found in solids, and intensity distortions in the spectra may occur when both types of species are present. Thus, despite increased sensitivity offered by the cross-polarization technique, direct pulsed FT NMR detection (Bloch decay) is advantageous for quantitative analysis of the adsorbed species providing ^{13}C spin–lattice relaxation times (T_1) are known and providing sufficient sensitivity can be achieved. In this study the T_1 relaxation times for different carbons observed on the surface were determined from the results of a progressive saturation experiment on a 100 MHz spectrometer. Subsequently, ^{13}C spectra were taken with the delays of $5T_{1L}$, where T_{1L} is the longest carbon spin–lattice time constant detected in a sample. Also, ^{13}C spin counting was performed in order to determine the amounts of different types of carbon present on and over the catalyst surfaces by comparing the integrated intensity of the ^{13}C absorption peaks with that of a reference sample.

For highly mobile molecules, the line narrowing techniques of strong proton decoupling and magic angle spinning did not lead to markedly increased resolution. For those species, the application of methods used in NMR of liquids proved helpful in identifying different types of carbon deposited on the surface of the catalysts via the observation of J splittings. These measurements were carried out on a Bruker 300 WM spectrometer, operating at the ^{13}C frequency of 75.41 MHz.

III. Results

C_2H_4 on SiO_2. The initial CP/MAS experiment was performed with single-labeled C_2H_4 adsorbed on pure silica to determine whether any adsorption of ethylene on the support might be detected. The experimental conditions used were similar to those used later in the presence of ruthenium: 2 ms cross-polarization, 4.5 kHz sample spinning, and 1 s delay between scans. The only feature that was clearly distinguished after 100 000 scans was a narrow peak located at 123 ± 1 ppm. The position of this line and the observation that its line width (<20 Hz) was only slightly affected by MAS suggested this resonance represents ethylene either weakly adsorbed on the silica surface or experiencing restricted motion in the micropores. In subsequent experiments, the narrow peak at 123 ppm was never observed in the presence of ruthenium.

On the basis of this experiment, we concluded that the silica surface does not play a significant role in the conversion of ethylene, and all of the species and catalytic transformations identified on surfaces of the catalysts studied are due to the presence of ruthenium.

C_2H_4 on Ru/SiO_2. Subsequently, a series of ^{13}C NMR experiments were performed on singly labeled (90% ^{13}C) ethylene adsorbed on a catalyst sample. The catalyst had a 12% (by weight) ruthenium loading with a dispersion of 0.37. The singly labeled ethylene was adsorbed, with the solid catalyst at ~80 K during the adsorption process. At this temperature, ethylene condensed into the sample tube. On the basis of the pressure change in the adsorption apparatus manifold (at room temperature), the amount of ethylene introduced into the tube was calculated to be about 1–1.5 molecules per surface ruthenium atom.

In Figure 1a–c, the CP/MAS proton decoupled spectra taken under the same experimental conditions for 1 day, 7 days, and 30 days after preparation are presented. Each spectrum is the result of 150 000 cross-polarizations taken with a contact time of 2 ms and a recycle time of 0.5 s between the scans (proton T_1 relaxation time was determined to be less than 100 ms). Two types of resonance lines can be clearly distinguished: a group of narrow, Lorentzian peaks and a pair of broad features located between 160 and −50 ppm.

The narrow peaks are located at 126 ± 1 ppm (a), 26 ± 1 ppm (b), 18 ± 1 ppm (c), 14 ± 1 ppm (d), and 6 ± 1 ppm (e). Their line widths of 50–100 Hz are primarily associated with the time constant of the apodization function. The measured line widths in the absence of apodization vary from less than 25 Hz (peaks d and e) to 75 Hz (peak a). It immediately became clear that these resonances represented species of high mobility that are not rigidly attached to the surface of ruthenium. This inference was confirmed by two experiments performed without line-narrowing techniques. These experiments were performed 8 and 9 days after preparation of the sample, and their results, presented in Figure 2 (parts a and b), are to be compared with the spectrum of Figure 1b. In the static experiment (Figure 2a), where only strong proton decoupling was applied (no MAS), the line widths of the sharp resonances remained almost unaffected. Only the width of peak (a) increased slightly to 150 Hz. In figure 2b, a spectrum taken without either magic angle spinning or proton decoupling is shown. Although the broad features underlying the high-resolution spectra were broadened almost beyong observation, the narrow peaks could still be seen. The width of peak (a) increased to about 500 Hz, and overlapping multiplets due to J splittings were found for peaks (b)–(e).

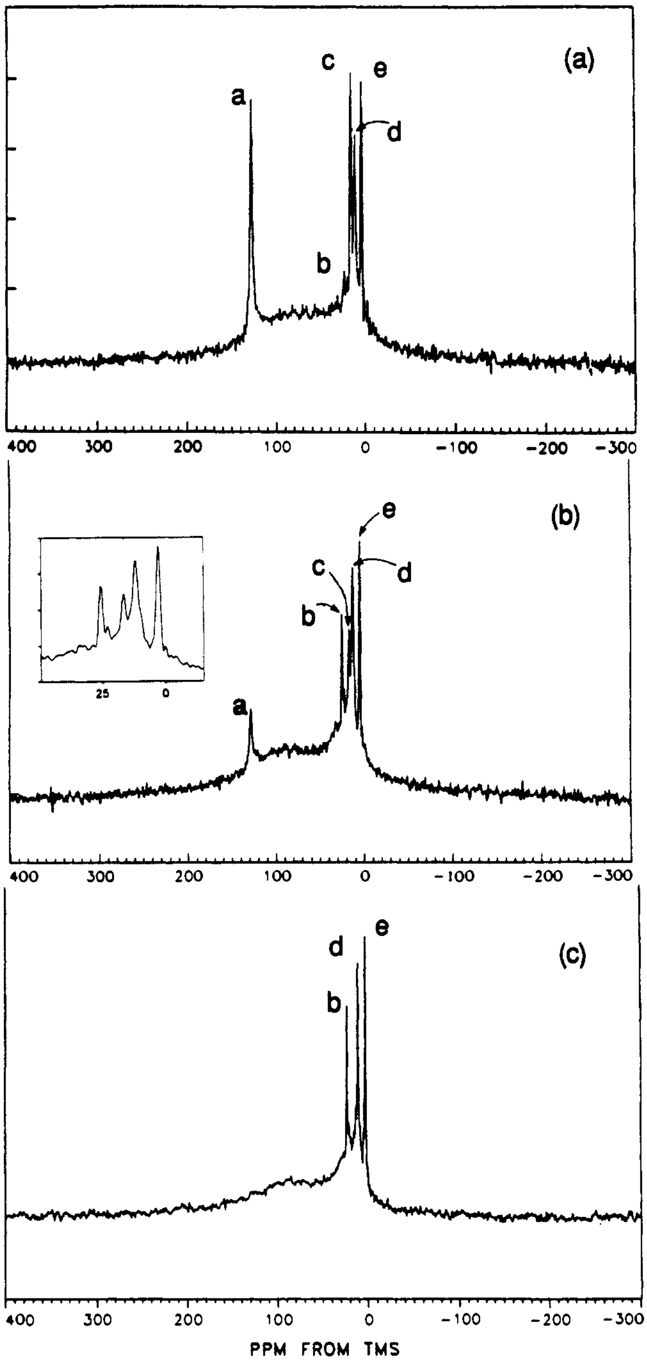

Figure 1. ^{13}C CP/MAS spectra of species on ruthenium surface as a result of adsorption of ethylene at room temperature: (a) 1 day, (b) 7 days, and (c) 30 days after sample preparation, respectively.

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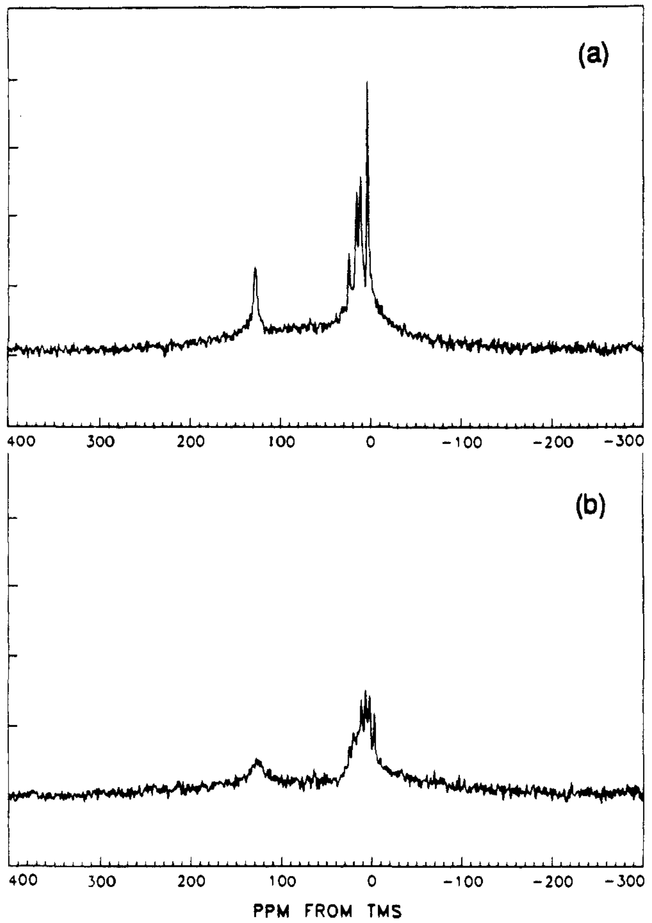

Figure 2. ^{13}C CP spectra of species on a ruthenium catalyst as a result of adsorption of ethylene at room temperature: (a) static and (b) static and no decoupling. Both spectra were taken approximately 1 week after adsorption of ethylene.

By performing ^{13}C NMR on the same sample at a higher magnetic field, further information on the nature of the *J* multiplets was achieved. In this experiment, a direct carbon excitation at a frequency of 75.4 MHz was applied. The upfield portions of high-resolution ^{13}C spectra of the catalyst, taken with and without scalar decoupling, respectively, are shown in Figure 3 (parts a and b). The results of these experiments indicate that the line at 26 ppm represents CH_2 carbons, while the resonances at 14 and 6 ppm correspond to carbons in methyl groups. Note that line (c) is missing from the high field spectra. As will be discussed later, this peak represents an intermediate of the catalytic reaction. The high field measurements presented in Figure 3 were performed more than a month after sample preparation when the intermediate had already been transformed to a product. Subsequent high field measurements with a fresh sample revealed peak (c) to be due to the presence of a methyl group.

At this point, it may be concluded that the narrow features in Figure 1 represent weakly adsorbed hydrocarbon molecules that reorient fast enough to reduce line-broadening interactions (at room temperature). For lines (b)–(e) the ^{1}H–^{13}C dipolar interactions were averaged out to nearly zero, which implies a frequency of rotation of at least 10^5 Hz. The idea that lines (a)–(e) represent liquid-like, weakly adsorbed species was further supported by the result of a CP/MAS experiment with a sample that was saturated with labeled ethylene for about 15 min at room temperature and then evacuated to a pressure of 10^{-5} Torr. The narrow resonances were essentially eliminated after the evacuation (see Figure 4), indicating they arose from weakly adsorbed species.

Those species that are rigid (strongly chemisorbed) on the surface of ruthenium exhibit NMR spectra not narrowed by molecular motion. The chemisorbed species, under conditions of high-resolution, solid-state NMR, are represented by the broad features in the ^{13}C NMR spectra that do not disappear upon evacuation. Although MAS and strong proton decoupling led to a considerable reduction of the observed line widths (compare Figures 2 (parts a and b) and 1), a severe broadening (about 3 kHz) remained even under high-resolution conditions. Homonuclear ^{13}C–^{13}C dipolar interactions between neighboring ^{13}C spins were excluded as the broadening mechanism under MAS at 5 kHz. For example, in ethylene where the magnitude of the interaction between the pair of ^{13}C nuclei (1.34 Å internuclear distance) is about 3.1 kHz, the contribution of dipolar broadening would be eliminated by MAS as 5 kHz. (Indeed, the NMR of double ^{13}C-labeled ethylene on the same catalyst was found to exhibit the same line shape as the singly labeled sample.) Thus the broadening observed was inhomogeneous in nature and was associated with the distribution of the local environments on the metal particles.

Before the assignments of the ^{13}C spectral lines are discussed, the validity of the observed chemical shifts merits some consideration. From high-resolution NMR studies carried out on weakly adsorbed molecules, it is known that their chemical shifts deviate

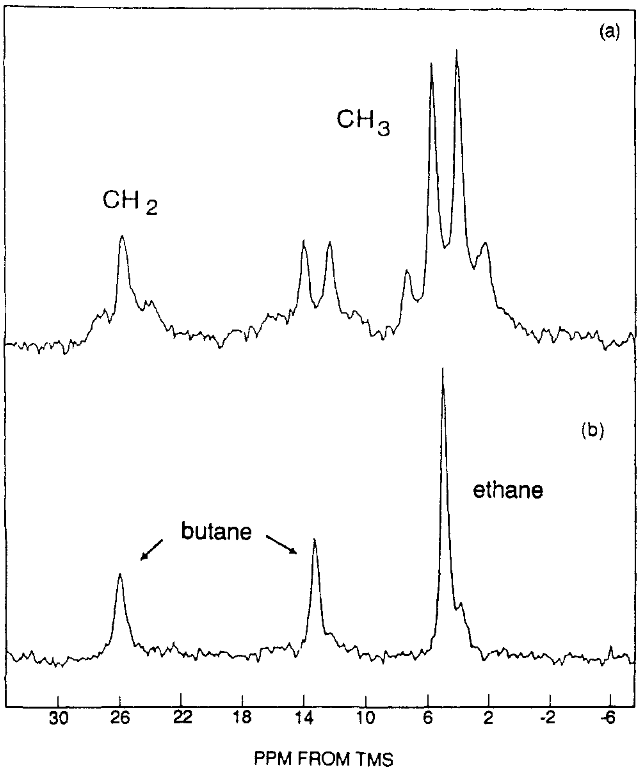

Figure 3. High-resolution ^{13}C spectra of weakly adsorbed species (at a frequency for ^{13}C of 75.4 MHz): (a) without proton decoupling and (b) with proton decoupling.

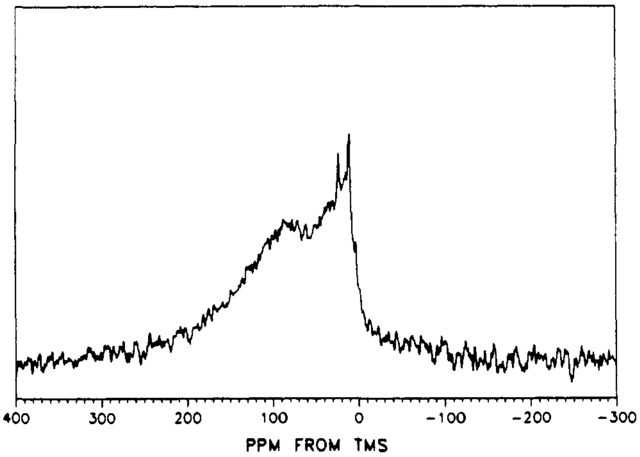

Figure 4. ^{13}C CP/MAS spectrum of a sample that had been exposed to 100 Torr of ethylene at room temperature for 15 min and then evacuated for 10 min.

Table I. ^{13}C Chemical Shifts in ppm[46]

		C^a	C^b
ethane	C^aH_3–C^aH_3	5.7	
butane	C^aH_3–C^bH_2–C^bH_2–C^aH_3	13.4	25.2
trans-butene	C^aH_3–$C^b(H)$=$C^b(H)$–C^aH_3	17.6	126.0
cis-butene	C^aH_3–$C^b(H)$=$C^b(H)$-C^aH_3	12.1	124.6

from the values determined in the liquid state.[44] In the absence of paramagnetic adsorption sites, the deviations may be primarily due to bulk susceptibility and van der Waals interactions. As has been demonstrated by Duncan et al.,[45] in the ^{13}C NMR spectrum of a sample of ruthenium powder saturated with TMS a downfield shift of only 1.1 ± 1 ppm was observed. The influence of van der Waals interactions can be evaluated experimentally by comparing ^{13}C NMR shifts observed for adsorbed molecules relative to respective liquids. For typical molecules, upfield shifts of the ^{13}C NMR lines of 1–2 ppm due to van der Waals interactions have been observed.[44] Only for methane have upfield shifts of up to 10 ppm been reported. In the present work the combined effects of bulk susceptibility and van der Waals interactions on liquid-like, weakly adsorbed species are inferred to result in relatively small ($<$2 ppm) shifts relative to liquid-state spectra.

On the basis of the information from the ^{13}C NMR experiment, the following assignments for the narrow resonances were made: peak (a) is a superposition of CH carbons of *trans*- and *cis*-2-butene; peak (b) represents a CH_2 carbon of butane; peak (c) corresponds to a CH_3 group of *trans*-2-butene; peak (d) represents methyl groups in butane and *cis*-2-butane; and peak (e) corresponds to CH_3 groups of ethane. The identification of peaks was based on observed chemical shifts as compared with the data from liquid state ^{13}C NMR (Table I),[46] from multiplicities of J splittings, and from intensities corresponding to different peaks (as obtained via direct ^{13}C NMR measurements).

Although the identification of the peak representing ethane was straightforward, the identification of the other resonances requires additional explanation. The assignment of peaks (b) and (d) in Figures 1c and 3 was based not only on the observed chemical shifts but also on the 1:1 ratio of the corresponding CH_2 and CH_3 intensities obtained from Bloch decays with no signal enhancement. Note that the intensity of peak (b), I_b, increases slowly as the sample gets "older" and that the intensity ratio of 1:1 between I_b and I_d is observed only on aged samples after peaks (a) and (c) disappear.

It appears that in a fresh sample, where $I_b \ll I_d$ (see Figure 1a), peak (d) is a superposition of two lines. This feature is still seen in Figure 1b (see inset). The upfield component of peak (d) was identified as CH_3 groups of *cis*-2-butene. In solution, the CH carbon in *cis*-2-butene resonates at ~125 ppm, which matches well with the position of line (a). Subsequently, peak (c), which could be found only in the presence of peak (a) in the spectra, was identified as a methyl group of *trans*-2-butene. The CH carbon in *trans*-2-butene resonates at 126 ppm. This leads us to conclude that peak (a) represents CH carbons of both *cis*- and *trans*-2-butene that resonate 1 ppm from each other and are indistinguishable in our experiments. These assignments are also supported by the fact that in all spectra studied, the relation $I_a + I_b \approx I_c + I_d$ holds.

In summary, several weakly adsorbed species have been found on the Ru/SiO_2 catalyst surface at room temperature: on the fresh sample ethane, an approximate 3:1 mixture of *trans*- and *cis*-2-butene and a small amount of butane were observed (Figure 1a). Only ethane and butane could be seen 30 days after the sample was prepared (Figure 1c). No evidence was found for the presence of weakly adsorbed ethylene in the sample.

Next we focus on the broad ^{13}C lines underlying the sharp peaks (Figures 1 and 4). These broad features represent species chemically bound to the metal. As indicated earlier, the broadening is inhomogeneous and cannot be eliminated. In spite of this broadening two different features can be distinguished: a downfield peak centered at ~85 ppm and a narrower peak centered at ~20 ppm.

Some species may be excluded as possible candidates by examining available chemical shift data. The lack of a resonance near 400 ppm, characteristic of carbidic carbons observed by Duncan et al.[45] on ruthenium during CO hydrogenation, eliminates the possibility of carbidic species. At temperatures above 280 K, the presence of ethylidyne has been observed as one of the intermediates in the interaction of ethylene on a Ru(0001) surface.[1-4] Carbynes typically exhibit a low field resonance between 200 and 400 ppm. The quaternary carbon of the ethylidyne ligand in $Ru(CO)_9(\mu\text{-}H)_3(\mu_3\text{-}CMe)$ complex was found to resonate at 219.3 ppm.[47] If it is assumed that Knight shifts of ^{13}C are not dominant in the species reported herein, then carbynes can be excluded. The presence of carbenes ($M{=}C{=}CH_2$) has also been excluded on the same basis; carbenes exhibit a low field resonance at $>$200 ppm.[47]

The broad resonances centered at about 85 ppm could represent two species: π-bonded ethylene and acetylide. Stephenson and Mawby[48] have presented ^{13}C NMR results on ethylene complexes of ruthenium showing ethylene π-bonded to ruthenium complexes resonating around 55–60 ppm. Acetylide formation is documented on both Ru(0001)[1,2] and Ru(1,1,10).[4] The assignment of the broad base from 50–100 ppm as acetylide is suggested by chemical shift data of organometallic species.[47,49] Carty et al.[49] reported shifts for a series of polynuclear acetylide complexes with varying alkynyl groups present. On the basis of the shifts given, a μ_2-η^2-acetylide species best fits our data. In this orientation, a σ-bond is formed by the α-carbon ($-C_\alpha{\equiv}C_\beta H$) with ruthenium, while a π-bond is formed with a second ruthenium atom.

On the basis of the chemical shift alone, we cannot unambiguously distinguish between the acetylide and π-bonded ethylene species. However, two facts suggest that the peak centered at about 85 ppm is acetylide. First, acetylide is known to be stable on ruthenium single-crystal surfaces at room temperature and higher.[1,2,4] The π-bonded species either decomposes or molecularly desorbs in the 150–280 K temperature range.[1] Hence, it is unlikely that π-bonded ethylene is stable on supported ruthenium particles at room temperature. Second, two different kinds of CP/MAS experiments were performed in an attempt to discriminate between quaternary and protonated carbons. The dipolar dephasing experiment is similar to a standard CP experiment except for the delay T_{DD} which precedes the decouling pulse and acquisition of data. A plot of the intensity of ^{13}C adsorption versus T_{DD} indicated that a fraction (about 20%) of carbons contributing to the broad peak centered at 85 ppm has no directly bonded hydrogen. Similar results (about 30%) could be inferred from a plot of this peak intensity versus CP contact time (variable contact time experiment). Of the possible species that have unprotonated carbon (acetylide, ethylidyne, and vinylidene), only acetylide has the correct chemical shift. Note that because of the low intensity of the signal the above experiments are very time consuming and are not accurate. Also, it is likely that intermolecular interactions (dephasing and polarization transfer) among adsorbed species take place. Thus, the determination of the relative mount of unprotonated carbons is only semiquantitative. A possibility that there is a small contribution to the broad peak at about 130 ppm due to vinyl group cannot be totally excluded, however.

The resonances at 0–40 ppm were assigned to various surface-attached alkyl groups. This was indicated not only by the chemical shift but also by the fact that the distribution of resonances was narrower, probably because of their weaker, single-

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Table II. ^{13}C T_1's and Amounts[a] on the Surface

species	T_1 (s)	^{13}C ($\times 10^{18}$)[b]	C/Ru^{surface}
ethane	0.28 ± 0.02	6.2	
butane		5.8	
(14 ppm)	1.0 ± 0.10		
(26 ppm)	0.75 ± 0.10		
total weakly adsorbed		12.0	1.1
strongly adsorbed	0.35 ± 0.10	13.4	1.2

[a] Error margin is ~20%. [b] Note that singly labeled ethylene was used in this experiment, and ^{13}C represents half of the total carbon.

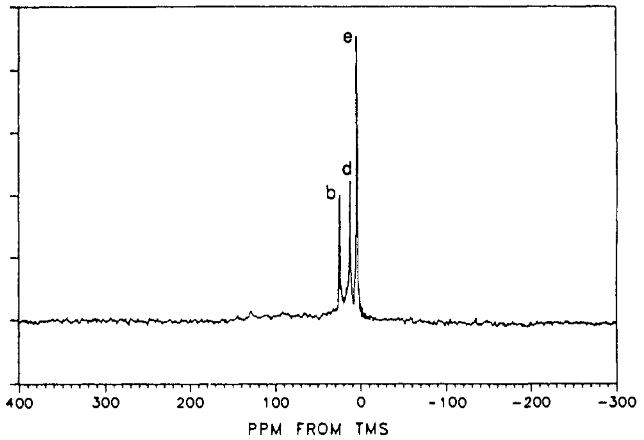

Figure 5. ^{13}C Bloch decay spectrum (with MAS and strong proton decoupling).

bond attachment to the metal. The above conclusion was further supported by the results of a dipolar dephasing experiment. At a dephasing time of 100 μs there was not a complete elimination of the intensity in the 0–40 ppm range. In particular, a clearly distinguished feature located at about 15 ppm was concluded to represent the resonance of CH_3 in an ethyl group.

Quantitative Measurements. Direct excitation of ^{13}C nuclei was used in spin counting experiments. The intensities of all observed resonances were separated and analyzed as a function of a delay between the scans. The data were fit with a computer in order to infer the relaxation times, T_1, and to extrapolate the intensities to an infinite delay for all types of carbon. The relaxation measurements for carbon were time consuming; hence, the values reported were estimated from 4 to 5 spectra. The experiments were performed under high-resolution conditions (MAS and proton decoupling), so that T_1's (^{13}C) could be determined for different types of chemisorbed and weakly adsorbed carbon-containing species (Table II). The experiment was performed with a sample 2 months after it was prepared when all the species present on the surface were assumed to have reached their final room-temperature concentrations.

A spectrum taken with a delay of 2 s and 125 000 scans is shown in Figure 5. The contrast of this spectrum with that from CP/MAS presented earlier is clearly visible. For the reasons given previously, the technique of cross-polarization enhanced the signals from rigid species relative to signals from mobile species. A detailed examination of the spectrum revealed that in spite of the change of the relative intensities of weakly adsorbed and chemisorbed species, the corresponding line shapes remain virtually the same.

The intensities extrapolated to infinite delay time were compared with the intensity of a standard measured under the same conditions to calculate the number of carbon nuclei of different types on the studied surface. The results of the intensity measurements are presented in Table II. On the basis of dispersion and weight loading, the number of surface ruthenium atoms in the sample was estimated to be 2.2×10^{19}, which indicated that there was one chemisorbed carbon atom (2.7×10^{19}) for each surface ruthenium atom. Also, within the error of our measurement, the concentrations of weakly adsorbed species was about the same (2.4×10^{19}). The weakly adsorbed species were an approximately 2:1 molar mixture of ethane and butane.

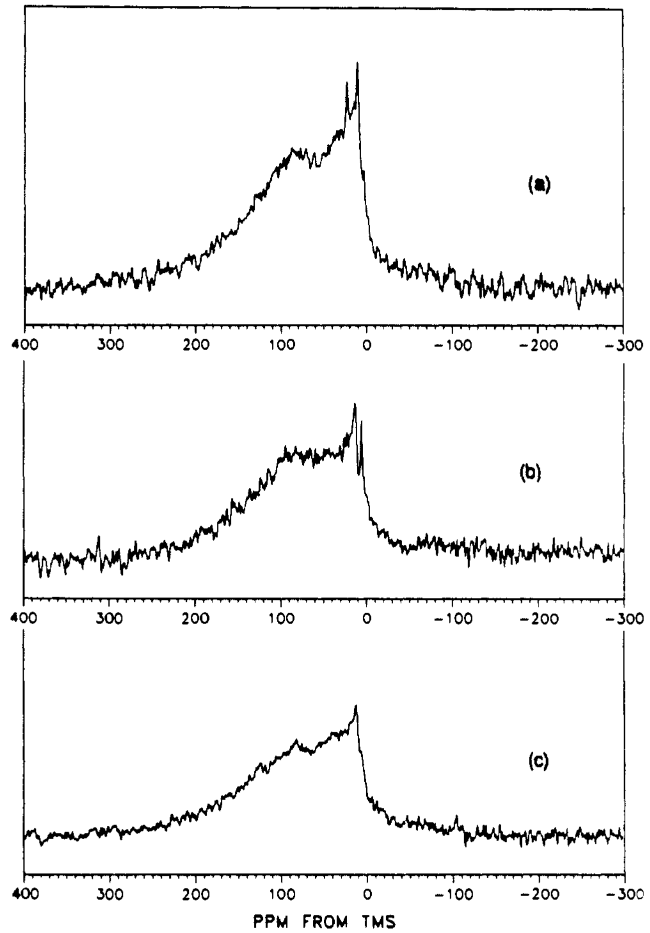

Figure 6. Sequential-dose experiments in which all samples were first exposed to labeled ethylene at room temperature for 15 min followed by evacuation. The sample in (a) had no additional treatment. The sample in (b) was then exposed to unlabeled ethylene for 15 min followed by evacuation. The sample in (c) was treated the same as above and was also given an additional exposure to unlabeled ethylene for 12 h before evacuation.

Sequential-Dose Experiment. In order to probe the relationships and possible interactions among the weakly adsorbed and chemisorbed species, two additional sets of CP/MAS experiments were performed by using a sequential-dose procedure. In one set of experiments, a sample containing 12% ruthenium was first saturated (at room temperature) with ^{13}C labeled ethylene for ~15 min and then evacuated to 10^{-5} Torr so that only the strongly adsorbed layer remained. (The ^{13}C NMR on previous samples prepared under similar conditions proved this time period to be long enough to form all observed species.) The CP/MAS spectrum of this sample is presented in Figure 6a. An identical sample was then exposed to unlabeled ethylene (40 Torr) for a period of 15 min after which it was evacuated to 10^{-5} Torr. The spectrum for this second sample is shown in Figure 6b. The third sample was the same as the second except after evacuation it was again exposed to unlabeled ethylene at about 40 Torr for an additional 12 h before evacuation and sealing. The spectrum for the third sample is presented in Figure 6c. Examination of the spectra, which were taken under the same conditions (15000 accumulations with 0.5 s delay between scans), indicated that the chemisorbed species centered at ~85 ppm was not significantly depleted with repeated adsorptions of unlabeled ethylene. If the chemisorbed species was consumed in further reactions, one would expect to see a substantial decline in intensity at 85 ppm because unlabeled ethylene, with a natural abundance of ^{13}C (1.1%), was used in the second and subsequent steps. Whatever the role this species plays in the formation of products, once it forms it remains relatively inert at room temperature.

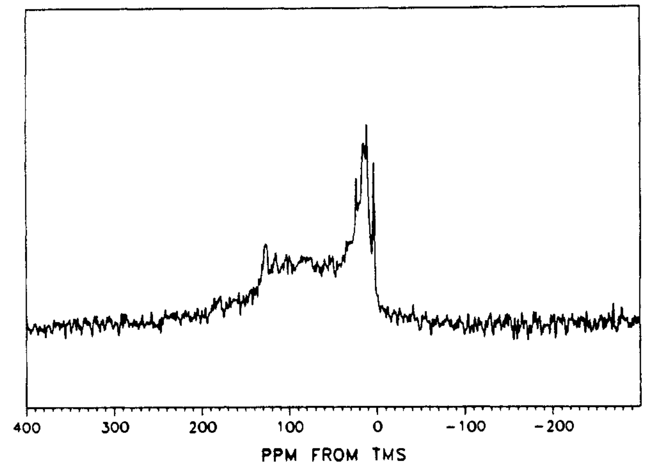

Figure 7. Sequential-dose experiment in which unlabeled ethylene was first adsorbed on the catalyst followed by evacuation and then exposure to labeled ethylene.

On the other hand, the intensity associated with the strongly adsorbed alkyl groups (0–40 ppm) did decrease, especially during the first adsorption of unlabeled ethylene. Some ^{13}C remained in this adsorption state, but a sizable amount of this species participated in subsequent reactions to form weakly adsorbed products that were evacuated from the sample tube.

A similar sequential-dose experiment was performed in which unlabeled ethylene (and, hence, not observable by NMR) was first used to saturate the surface with a chemisorbed layer. After the sample was evacuated, ^{13}C-labeled ethylene was admitted to the sample, and a CP/MAS spectrum was taken by using the same parameters mentioned above. The results of this second sequential-dose experiment are presented in Figure 7. If the labeled ethylene had been incorporated into the strongly chemisorbed layer, a peak similar to that in Figure 6a would be expected. The spectrum in Figure 7 indicates some intensity around the 85-ppm region, but most of the broad-line intensity appears in the strongly adsorbed alkyl region and in the weakly adsorbed product peaks. Note that the sample was not evacuated, and weakly adsorbed, labeled species appeared in the spectrum.

Ethane Experiments. A second set of experiments using Bloch decay was performed to ascertain the location of the product molecules ethane and butane on the catalyst. On the basis of results of spin counting, equal amounts of carbon in the narrow peaks (weakly adsorbed) and the broad base (strongly chemisorbed layer) were found. This result suggested that perhaps the weakly adsorbed product molecules were in a liquid-like layer over the strongly chemisorbed species. Another possibility is that the weakly adsorbing species were associated with the high surface-area support material. To test this idea, we performed experiments in which ~50 Torr of singly labeled (90%) ethane was introduced to three samples at 295 K. The samples consisted of the following materials: (1) pure SiO_2, (2) 12% Ru/SiO_2, and (3) 12% Ru/SiO_2 that had been exposed to unlabeled ethylene and evacuated. All samples were then exposed to ethane. Results are presented in Figure 8 (parts a–c). A resonance for ethane (5 ± 1 ppm) was seen in all cases. This resonance corresponds to what was observed for the formation of ethane resulting from the adsorption of ethylene. In addition, a resonance assigned to methane, at −3 ppm, is seen in Figure 8b.

An interesting feature indicated by Figure 8b is that ethane experiences self-hydrogenolysis on a clean ruthenium surface even at room temperature. The additional hydrogen that must be supplied to form the methane probably comes from dehydrogenated, strongly adsorbed species that are present in quantities too small to be adequately observed.

It is also interesting to note that the ethane peak is about twice as broad on the clean Ru/SiO_2 sample (Figure 8b) as it is on either the pure silica sample (Figure 8a) or the Ru/SiO_2 sample that has first been exposed to unlabeled ethylene (Figure 8c). The increased width is most likely due to interactions with the ruthenium metal. The peak width observed for the ethane resulting from ethylene adsorption (Figure 1) is comparable to the ethane peak in Figure 8 (parts a and c). This result suggests that the ethane product formed upon ethylene adsorption was either weakly adsorbed on (or weakly interacting with) the silica support or weakly adsorbed on the chemisorbed layer rather than directly interacting with the metal.

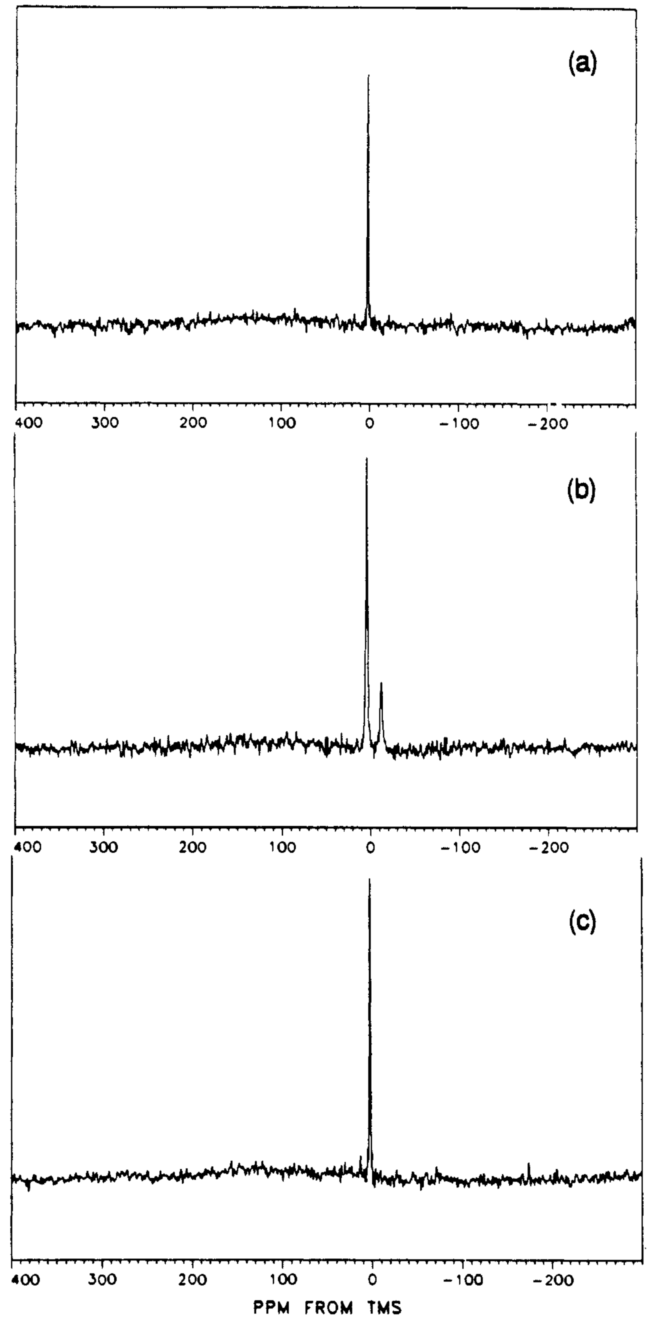

Figure 8. ^{13}C spectra of ethane adsorbed on (a) pure silica, (b) freshly reduced 12% Ru/SiO_2, and (c) 12% Ru/SiO_2 with an unlabeled chemisorbed layer.

IV. Discussion

By using pressures high enough to produce more than monolayer coverage, we observed the formation of C–C bonds, hydrogenation of π-bonds forming normal paraffins, and the dehydrogenation of ethylene to form rigid, chemisorbed species. In the following section, the various species observed in this work are discussed and compared with those previously documented.

Chemisorbed Layer. The first step in the adsorption of ethylene is the formation of a rigid chemisorbed layer, identified as alkyl and acetylide species. Spin-counting experiments revealed that there was about one carbon atom in the strongly adsorbed layer for each surface ruthenium atom.

In our study, adsorption could be performed at low temperatures <100 K, but spectra were taken at room temperature. Data accummulation times were typically between 12 and 24 h. Because of these two constraints, it was not possible to monitor the transformations occurring from 110–300 K, but one can speculate on possible reaction pathways. On the basis of our data, we see no evidence for the formation of a surface ethylidyne. It is possible, however, that an ethylidyne intermediate was formed along with acetylide and that upon warming to room temperature this species decomposed or hydrogenated to form products.

The formation of acetylide releases three hydrogen atoms that are available for hydrogenation reactions. The other rigid surface species have chemical shifts in the range from 0–40 ppm, typical of sp^3-hybridized carbon. Ethyl group formation is possible either through the direct hydrogenation of an ethylene molecule or through the hydrogenation of a surface species.

Another possible alkyl species, one that may account for the observed products butene and butane, is a metallocycle species. Metallocycle pentane can be formed from ethylene via organometallic synthesis.[50-52] In fact, it has been shown that the bis(ethylene)-to-transition-metal metallocycle pentane conversion is a reversible process.[51] The presence of a metallocycle surface species has been postulated to be an intermediate in butane hydrogenolysis on iridium single crystals.[53] In addition, Basu and Yates[54] observed a C_4 metallocycle species on alumina-supported rhodium by using IR spectroscopy.

The formation of a metallocycle pentane on the ruthenium surface could occur through a pathway similar to olefin metathesis.[55] An ethylene molecule could react with a surface carbene species to form a cyclic butane intermediate that could subsequently rearrange to a metallocycle pentane or desorb directly to form a 2-butene. In any event, if the C_4 adsorbed species is formed directly[50-54] or is formed through the mechanism described above, carbon–carbon bonds are formed, and the subsequent production of butenes as a primary product is possible.

Jordan and Bell[56] have studied the interaction of ethylene and hydrogen over a silica-supported ruthenium catalyst. They observed that ethylene underwent hydrogenation to ethane, hydrogenolysis to methane, and reaction to form C_3^+ olefins and paraffins. Hydrogenation was the predominate pathway, accounting for 90% of the ethylene conversion. Oligomerization of ethylene or surface species occurred through a chain growth mechanism involving the insertion of one and two carbon-containing units into chains producing an array of C_3^+ products. The formation of odd carbon-number-containing species or products larger than C_4 was not observed in our study. Hydropolymerization does not appear to be the operable mechanism in the samples studied in our investigation.

Weakly Adsorbed Layer. We have observed the catalytic transformation of ethylene on the surface of a ruthenium catalyst involving the formation of C–C bonds at room temperature. Three different product molecules of the catalytic reaction were identified: ethane, *cis*- and *trans*-butene, and butane. Ethane and *cis*- and *trans*-butene are formed rapidly. We were able to generate a spectrum in which both species were near the maximum observed concentrations approximately 20 h after preparation. The butene slowly hydrogenated to form butane. After approximately 10 days the butene was completely converted to butane. (A first-order rate constant of 0.3 $days^{-1}$ was estimated.)

Both ethane and butane were very weakly bound to the catalyst surface, while the *cis*- and *trans*-butene intermediates in the formation of butane were somewhat more rigidly bound. The evidence for this conclusion is the fact that the peak at 125 ppm was broadened in the absence of MAS and strong proton decoupling.

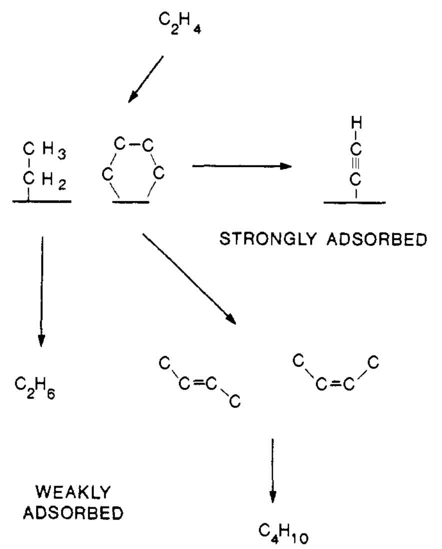

Figure 9. Postulated pathways for ethylene decomposition and adsorption on silica-supported ruthenium at room temperature.

cis- and *trans*-2-butene adsorption on Pt(111) has been studied by Avery and Sheppard.[57] At low temperatures both species were adsorbed in a di-σ-bonded fashion, but when they were heated to 250–300 K, C–H bond scission occurred, and the two forms were indistinguishable. Under the conditions of their study, Avery and Sheppard found that further heating of the sample led to total decomposition of the adsorbate to surface carbon. Under the conditions of our study, we were able to differentiate the two forms of 2-butene at room temperature, and we were able to observe the transformation of butene to butane.

Ethane formation probably occurred through direct hydrogenation of ethylene or the hydrogenation of surface alkyl groups. Gupta et al.[58] observed self-hydrogenation of ethylene to ethane on supported ruthenium catalysts. They used a sequential pulse injection method and studied samples in the temperature range of 296 to 650 K. In the absence of coadsorbed hydrogen, self-hydrogenation of ethylene with an activation energy of 18 kcal/mol was reported on Pt(111).[6] The activation energy for hydrogenation in the presence of coadsorbed hydrogen, however, was found to be 6 kcal/mol. A similar study on Ru(0001) reported that hydrogenation of ethylene occurred in the presence of hydrogen, while no self-hydrogenation was seen.[22] In the present study, no additional hydrogen was added, yet significant hydrogenation of ethylene to ethane was observed. For supported catalysts with a metal dispersion of 37%, approximately 25% of all surface atoms are in defect-like edge and corner lattice positions. It is not surprising that the hydrogenation behavior of supported catalysts is different from that of the close-packed, low-index-plane, single-crystal surfaces. Note that the formation of acetylide resulted in the release of enough hydrogen to account for all the hydrogen needed to form the hydrogenated products.

The overall picture of the adsorption, decomposition, and reaction of ethylene on silica-supported ruthenium inferred from the results of the present work is summarized in Figure 9. At room temperature the ethylene adsorbed and rapidly formed strongly adsorbed acetylide and alkyl species that probably consisted of ethyl and metallocycle groups. In addition, ethane and a mixture of 2-butenes were rapidly formed and were weakly adsorbed (most likely on the support) or were experiencing restricted motion in the pores of the support. The butenes were then slowly hydrogenated to form butane. The sequential dosing experiments indicated that once formed, the rigid species identified as acetylide was not significantly consumed in subsequent catalytic

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conversions. The strongly adsorbed alkyl species, however, did appear to participate in the formation of products. The extension of the various NMR techniques to allow data accumulation at low temperatures will help uncover the operable mechanism in the adsorption and reaction of ethylene on silica-supported ruthenium.

V. Conclusions

NMR allows detection of chemisorbed species and also weakly adsorbed molecules at coverages higher than those used in spectroscopies employing ultrahigh vacuum conditions. The application of ^{13}C high-resolution NMR techniques allows the formation of a coherent picture of the chemistry of a relatively complex system by determining the structure and abundance of molecular species adsorbed on the catalyst surface. The ^{13}C CP/MAS technique allows simultaneous observation of the transformations of chemisorbed and weakly adsorbed molecules. Direct ^{13}C excitation allows quantitative measurements of the various species present.

From these experiments we observed the decomposition of ethylene at room temperature to form strongly adsorbed species identified as acetylide and alkyl groups. Recombination of the adsorbed alkyl species and hydrogenation of ethylene occurred rapidly at room temperature and formed weakly adsorbed ethane and *cis*- and *trans*-2-butene that subsequently hydrogenated to butane. The formation of C–C bonds is postulated to take place through a metallocycle adsorbed species.

The strongly adsorbed species identified as acetylide was not appreciably consumed in the formation of products, although it may have served as a host for other reactions. Finally, spin counting revealed that there was one carbon in the strongly adsorbed layer for each surface ruthenium atom.

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Registry No. $H_2C{=}CH_2$, 74-85-1; Ru, 7440-18-8; CH_3CH_3, 74-84-0; $CH_3(CH_2)_2CH_3$, 106-97-8; *trans*-butene, 624-64-6; *cis*-butene, 590-18-1.

Light Noble Gas Chemistry: Structures, Stabilities, and Bonding of Helium, Neon and Argon Compounds

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Abstract: Theoretically determined geometries are reported for the light noble gas ions Ng_2C^{2+}, Ng_2N^{2+}, Ng_2O^{2+}, $NgCCNg^{2+}$, $NgCCH^+$, $NgCN^+$, and $NgNC^+$ (Ng = He, Ne, Ar) at the MP2/6-31G(d,p) level of theory. In a few cases, optimizations were carried out at CASSCF/6-31G(d,p). The thermodynamic stability of the Ng compounds is investigated at MP4(SDTQ)/6-311G(2df,2pd) for Ng = He, Ne and at MP4(SDTQ)/6-311G(d,p) for Ng = Ar. The structures and stabilities of the molecules are discussed in terms of donor–acceptor interactions between Ng and the respective fragment cation, by using molecular orbital arguments and utilizing the analysis of the electron density distribution and its associated Laplace field. Generally, there is an increase in Ng,X binding interactions of a noble gas molecule NgX with increasing atomic size of Ng. In some cases the Ne,X stabilization energies are slightly smaller than the corresponding He,X values because of repulsive p–π interactions in the neon compounds. The argon molecules are in all cases significantly stronger bound.

1. Introduction

In a recent theoretical study of compounds containing the most inert chemical element helium, we found[2] that He can form strong chemical bonds in ions and may even be bound in the ground state of a neutral molecule, i.e., HeBeO. The most important criterion for a potential binding partner of helium is its electronic structure, rather than its electronegativity or positive charge. The structures and stabilities of He compounds could be rationalized by using the model of a donor–acceptor complex.[2] Helium bonds can be very strong with a dissociation energy of up to 90 kcal/mol, if the binding partner provides low-lying empty σ orbitals. The electronic structure of the molecules has been investigated with the aid of an electron density analysis. This revealed covalent He,C bonds in several cations and dications.[2] The neutral compound HeBeO was found, however, to be an unusually stable (D_0 = 3 kcal/mol) van der Waals complex where the attractive interactions are dominated by charge-induced dipole interactions.[2,3]

There are two other noble gas elements, neon and argon, which have resisted so far all attempts to force them into binding with other atoms to form a stable compound.[4] Little is known about neon and argon chemistry.[5] In two recent papers we have investigated the electronic structure and bonding in diatomic cations HeX^+,[6] NeX^+, and ArX^+[7] with X being a first-row element

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[†] Part of this work was performed at the Molecular Research Institute, Palo Alto, CA.

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