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^{13}C NMR Study of Acetylene Cyclotrimerization on Platinum/Alumina Catalysts

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Abstract: The reactions of acetylene on supported 10% Pt/alumina catalysts have been studied using variable temperature solid-state ^{13}C NMR with magic-angle spinning. In the vicinity of room temperature, high loadings of acetylene cyclotrimerize to form benzene. No obvious differences were observed between catalysts prepared from η- or γ-alumina. Benzene also forms from dehydrogenation of cyclohexane on these catalysts. At 123 K the motionally averaged ^{13}C shielding tensor is accounted for by a model involving rapid rotation about the C_6 axis and libration of that axis with a root mean square angle of 33°. This motion is independent of whether it is directly adsorbed or prepared from acetylene in situ. Quantitative adsorption of acetylene and spin-counting measurements revealed that an amount of ^{13}C corresponding to ca. 0.3-monolayer coverage of the platinum particles *is invisible in ^{13}C MAS spectra*, presumably due to susceptibility broadening. This observation extends the work of Slichter et al. to higher pressures and reconciles the conflicting conclusions of two previous NMR investigations of the system. The present report underscores the need to apply complementary NMR techniques to the study of adsorbates on metals with large susceptibility anisotropies and the need to control adsorbate loadings.

Introduction

The reactions of hydrocarbons on supported-metal catalysts are of considerable academic and practical interest. For example, small platinum particles supported on alumina or other oxides are used as catalysts in a variety of important industrial processes such as hydroisomerization, selective re-forming, and hydrocracking.[1,2] In spite of the importance of these reactions, detailed mechanistic information, in particular on the structures of surface-bound intermediate species, is generally lacking. Much of what we know about the structure and reactivity of surface species on the actual supported-metal catalysts is based on assumed analogies to the exhaustive literature of spectroscopy on single-crystal surfaces.[3-5] That area has now matured to the point where detailed studies of the interactions of selected hydrocarbons with low-index-plane surfaces over pressure ranges of ca. 13 orders of magnitude are available.[6] In spite of the success of conventional surface spectroscopy there remains a need for detailed investigations of the surface chemistry of the actual supported catalysts. For example, the surfaces of nanometer-size particles are not well modeled by low-index planes, and various roles of the support are known or suspected in a number of catalytic transformations.

At first glance, solid-state NMR techniques would seem to be well suited for characterizing the structures of adsorbed species on supported-metal catalysts. Indeed, NMR in a variable temperature mode is proving capable of elucidating reaction mechanisms on zeolite catalysts *without a metal component*.[7-9] Unfortunately, even nonferrous metal particles have several properties which contribute to the shielding observed by a nucleus in close contact with that particle. Most metal particles have a large anisotropic bulk magnetic susceptibility, which distorts the applied magnetic field in their vicinity in such a fashion that a large inhomogeneous line-broadening mechanism is introduced.[10] This effect is only partially reduced with magic-angle spinning (MAS).[11] Furthermore, the ^{13}C resonance of CO on supported Pt is known to exhibit a large Knight shift due to the conduction electrons in the metal.[12-14] Finally, chemical shift data on appropriate organometallic model compounds are not always available. The above problems suggest that even in favorable cases when the chemical shifts of adsorbates on metal particles can be resolved, the assignment of such values to chemical structures will be difficult.

Slichter and co-workers have sought to avoid the above difficulty by eschewing the chemical shift interaction in favor of information on dipolar coupling and multiple-quantum coherences.[15-17] These can be measured in the presence of large inhomogeneous broadening, but at the expense of chemical shift information. In their studies of low levels of acetylene adsorption on Pt/η-alumina,[15] Slichter and co-workers concluded that the majority species formed at room temperature was similar to $>C{=}CH_2$ with a bond length of 1.44 Å: a value consistent with a C–C bond order of ca. 1.5. Slichter et al. also provided for a minority (23 ± 7%) species, described as HCCH, in order to fit their spin echo double resonance data and account for their multiquantum coherence result.[15] Similar species are known to form on Pt(111). A di-σ,π-bonded acetylene (presumably Slichter's minority species) is known to convert to a vinylidene (presumably the majority species in Slichter's work) near room temperature.[18] Vinylidene is also known to react with coordinated hydrogen to form ethylidyne ($>CCH_3$) on Pt(111) at room temperature and above.[18] Slichter's ^{13}C NMR results for supported Pt are, therefore, quite consistent with the surface science literature with the exception that no ethylidyne was observed in the NMR work. In more recent work using ^{2}H spectroscopy, Slichter resolved this remaining discrepancy by showing the formation of ethylidyne from acetylene and hydrogen adsorbed on supported Pt.[19,20]

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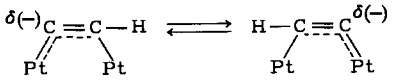
Slichter's ^{13}C spin echo experiments are very elegant, but they tend to integrate over all of the chemical species present on a catalyst. Thus, the interpretation of the result is model-dependent, and erroneous conclusions could be possible if there were significant quantities of any species not included in the model. This was the view of a recent commentary on the work of Slichter et al., by Chin and Ellis.[21] The latter workers used the ^{13}C chemical shift interaction to probe a very similar system: acetylene on Pt/γ-alumina. ^{13}C chemical shifts for adsorbates were measured in that work using the more familiar solid-state NMR techniques of cross polarization, magic-angle spinning, and ^{1}H dipolar decoupling.[22] Chin and Ellis came to two important conclusions.[21] The first was that high loadings of acetylene can react directly with the support to form surface-bound species such as $AlOCH{=}CH_2$ and $AlOCH_2(CH_2)_2CH_3$. A major conclusion of the Chin and Ellis paper was that if reactions also occurred with the support in Slichter's experiments, their interpretation could be incorrect.[21] Recently, Slichter and co-workers reported that ^{13}C spin echo measurements detected no residual carbon on bare alumina from acetylene adsorption, after the support was evacuated to 10^{-6} Torr.[20] Chin and Ellis's second observation was that on *catalysts containing Pt* an intense ^{13}C signal was observed at 129 ppm after adsorption of a higher loading of acetylene. The chemical shift of this signal and its behavior in the momentary absence of proton decoupling are clearly inconsistent with the vinylidene and di-σ,π-bonded species proposed by Slichter.[15] Chin and Ellis assigned the 129-ppm peak to a rapidly tautomerizing surface-bound monoanion of acetylene:



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The above species lacks precedent in the surface science literature, but it satisfactorily accounts for all of Chin and Ellis's spectroscopic observations.

The above differences in conclusions, from two studies using very different NMR methods to study very similar systems, are reminiscent of the earlier debate in the UHV surface science community[18,23-26] that culminated in the elucidation of the structure of ethylidyne.[24] We have followed the present debate with interest. In 1991 we published a study on the reactions of high loadings of acetylene on zeolite supports[27] and verified the first claim of Chin and Ellis for alumina heated with an overpressure of acetylene. The present investigation considers the role of the platinum. We duplicate Chin and Ellis's observation that a species with a ^{13}C chemical shift of ca. 129 ppm forms when high loadings of acetylene are adsorbed on supported Pt. However, we show that this species is not a surface-bound monoanion of acetylene, but rather benzene. The cyclotrimerization of acetylene to benzene on Pd is a known reaction from single-crystal work and has recently been observed for the first time on supported Pd,[6,28,29] but this is apparently the first report of its occurrence on supported platinum. Using quantitative adsorption of acetylene and spin-counting techniques, we find that an amount of ^{13}C equivalent to ca. 0.3-monolayer coverage of the metal particles *is unobservable in a standard ^{13}C MAS chemical shift spectrum.* This latter result raises the possibility that both Slichter et al. and Chin and Ellis made valid observations concerning the chemistry of acetylene on supported Pt but reached what appeared to be incompatible conclusions because of the large differences in sample loadings and because susceptibility effects make it very difficult to observe the species described by Slichter in a standard magic-angle spinning experiment.

Experimental Section

Sample Preparation. Acetylene-$^{13}C_2$ (99% ^{13}C), benzene-$^{13}C_6$, and cyclohexane-$^{13}C_1$ (99% ^{13}C) were obtained from Cambridge Isotopes. Purity of the acetylene was confirmed by NMR, mass spectrometry, and gas chromatography. Versal B (Bayerite), the precursor for η-alumina, was donated by LaRoche Chemicals. γ-Alumina was obtained from Strem. Platinum catalyst samples were prepared by impregnating the γ- or η-alumina supports. Appropriate amounts of chloroplatinic acid necessary to achieve a 10% Pt loading were stirred with the support and heated until dry. Catalyst samples were calcined in flowing air for 16 h at 393 K, then reduced in flowing hydrogen from 393 to 843 K over the course of 4 h, and held at 843 K for 1 h. Catalyst samples were cooled to room temperature in flowing hydrogen. The catalyst was then stored in a dry nitrogen glovebox until needed. Prior to use, catalyst samples were cleaned at 623 K in alternating flows of hydrogen and oxygen, evacuated for 10 h to $<10^{-5}$ Torr, and cooled to room temperature. Platinum dispersions were measured by hydrogen chemisorption and were 0.45–0.55 for all of the catalysts used in this investigation.

Samples were prepared for NMR study by loading freshly cleaned catalyst into 7-mm MAS rotors or glass ampules in a dry nitrogen glovebox. In the first method, the rotors were loaded with approximately 0.4 g of catalyst and then placed into the CAVERN vessel described in ref 7 (or an improved version of that apparatus). The glass ampules, which were designed to fit inside Chemagnetics 7-mm rotors, were obtained from Wilmad Glass Company. Glass ampules were loaded with approximately 0.2 g of catalyst and attached via a Cajon ultratorr fitting to a stopcock. These samples were attached to a vacuum line and evacuated for approximately 1 h via liquid nitrogen trap and diffusion pump to a pressure of $<10^{-5}$ Torr. With the exception of the low-temperature adsorption, the acetylene was allowed to contact the catalyst for 40 min prior to evacuation or capping. Either of two methods were followed at this point: the sample was evacuated for 30 min and then capped[30] or sealed using a liquid nitrogen bath and torch (a method similar to that used by Chin and Ellis),[21] or the sample was capped or sealed with a known overpressure of acetylene. The first method was intended to remove excess acetylene or any other physisorbed species, whereas the overpressure method was used in this investigation to force the cyclotrimerization reaction. Both of these procedures give loadings significantly higher than those used by Slichter and co-workers. In spin-counting experiments, the loading of acetylene was quantified by measuring the pressure of gas in a known volume before and after contact, using a Baratron pressure transducer.

A low-temperature adsorption experiment was performed that followed the above steps prior to acetylene adsorption. Immediately prior to adsorption the CAVERN vessel was cooled to approximately 223 K. Simultaneously the NMR probe was also cooled to 223 K. Loading of the gas then took place, and the rotor was capped. The rotor was transferred to the probe without appreciable heating, and spectra acquisition commenced while the sample temperature was slowly raised.

NMR Spectroscopy. All ^{13}C MAS NMR spectra were obtained at either of two resonance frequencies: at 50.06 MHz on a Chemagnetics CMC-200 spectrometer or at 75.47 MHz on a CMX-300 instrument. Typical values for the ^{13}C and ^{1}H 90° flips were 4.5 μs, and a 2-ms contact time was used for cross-polarization spectra. Interrupted decoupling[31] spectra were obtained using a 50-μs delay. Proton decoupling (γB_1 = ca. 50 kHz) was used for all spectra. MAS spinning speeds were 3–5 kHz unless stated otherwise.

Mass Spectrometry. The mass spectral data were obtained using a Fourier transform ion cyclotron resonance mass spectrometer (FT-MS) equipped with a differentially pumped two-section ion cell, an Extrel 2001 data system, and a 3-T Oxford superconducting magnet.[32,33] Samples were introduced into the cell by a variable leak valve (at a sample pressure of 4×10^{-7} Torr). Ionization was performed by electron impact at an electron beam energy of 70 ev and a 2 ± 0.02 μA emission current. Spectra were acquired in the single-cell mode.

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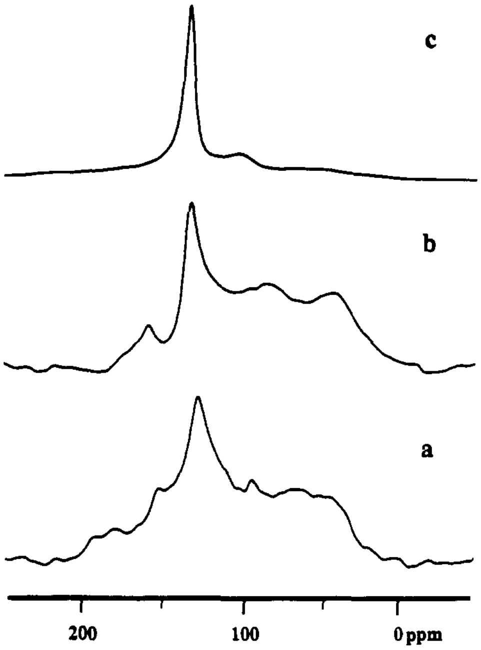

Figure 1. 50-MHz ^{13}C CP/MAS NMR spectra of adsorbates on supported Pt catalysts. For each sample 20 000 transients were taken at room temperature, and 400 Hz of line broadening was used: (a) acetylene-$^{13}C_2$ on 10% Pt/γ-alumina; (b) acetylene-$^{13}C_2$ on 10% Pt/η-alumina; (c) benzene-$^{13}C_6$ on 10% Pt/η-alumina.

Results and Discussion

A number of samples of acetylene on 10% supported Pt catalysts were prepared using the methods described by Chin and Ellis.[21] Figure 1 shows ^{13}C MAS spectra obtained with cross polarization of representative samples of C_2H_2-$^{13}C_2$ on 10% Pt/γ-alumina (Figure 1a) and 10% Pt/η-alumina (Figure 1b). Although there were minor variations in the appearance of spectra obtained for different samples, the overall impression was that the results were comparable for the two supports. This conclusion is significant because it rules out the form of alumina in the support as the source of the discrepancy in the two previous investigations.[15,21] The spectra in Figure 1 are qualitatively very similar to those reported by Chin and Ellis. The dominant feature is a ^{13}C resonance at ca. 130–131 ppm. Control experiments demonstrated that the peak did not form on the support alone, i.e., the metal component was necessary for its formation. The broad spectral features in Figure 1 include sidebands from the 130-ppm peak, signals from species bound to the support, and signals possibly from minority species associated with the metal. The reader is referred to ref 21 for the details of these assignments.

Figure 1c shows a ^{13}C CP/MAS spectrum of a sample prepared by the direct adsorption of benzene-$^{13}C_6$ on Pt/η-alumina. Comparing the spectra in Figure 1, one notes a strong similarity in the appearance of the 130-ppm resonance in the sample prepared by benzene adsorption with those prepared from acetylene. The higher signal to noise and narrower line widths in Figure 1c reflect the higher loading of benzene achieved by direct adsorption. Our rationale for making the above comparison will become apparent later in this paper.

Chin and Ellis assigned their 129-ppm peak to the equilibrating structure **1** to account for the observation that ca. $^1/_2$ of the signal intensity was lost after 50 μs of interrupted decoupling.[31] In rigid solids, such an experiment would be expected to eliminate the signal from a static CH carbon but only modestly attenuate that from a carbon without directly attached protons. In the presence of molecular motion of amplitudes and frequencies intermediate between the rigid lattice and isotropic, extreme narrowing limits, the interpretation of an interrupted decoupling experiment becomes tenuous. All of the samples described in Figure 1 exhibited the response to interrupted decoupling reported in ref 21; i.e., the 130-ppm peak narrowed somewhat and was reduced in intensity by a factor of ca. $^1/_2$. Furthermore, the same behavior was observed for a sample prepared by adsorbing benzene on η-alumina without a metal component. Clearly, at low loading levels and room temperature, benzene has sufficient mobility on the catalyst studied in this investigation that the interrupted decoupling experiment is unreliable as an assignment tool.

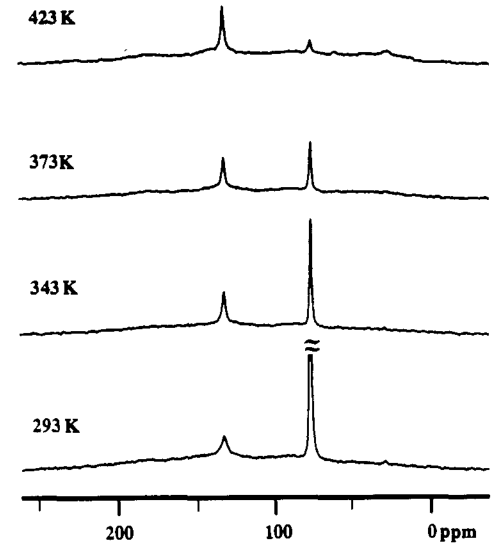

Figure 2. Variable temperature ^{13}C CP/MAS NMR spectra of an overpressure of acetylene-$^{13}C_2$ on 10% Pt/η-alumina. At a resonance frequency of 75 MHz 400 transients per spectrum were obtained, and 25 Hz of line broadening was used.

The rationale for considering the possibility that the 130-ppm resonance was due to benzene was the result of the experiment depicted in Figure 2. In that experiment, the MAS rotor was capped with a 13-Torr overpressure of acetylene, and the ^{13}C CP/MAS spectrum at 298 K in Figure 2 was obtained. That spectrum shows a large peak due to unreacted acetylene, as well as a 130-ppm resonance *substantially larger than that obtained when the sample was evacuated prior to sealing* (cf. Figure 1b). In making the comparison, note that Figure 1b required 20 000 scans (as in ref 21) whereas the spectra in Figure 2 required only 400 scans each. Heating the sample in the MAS rotor while acquiring spectra (Figure 2) resulted in the near complete conversion of the acetylene to the 130-ppm resonance and smaller amounts of other species similar to those reported previously. The 130-ppm peak was narrower at the high loading in Figure 2 (cf. Figure 1) and narrowed further upon heating.

Although the signal intensities of the spectra in Figure 1 are low enough to possibly be consistent with monolayer coverage on the Pt particles, the much larger signals in Figure 2 clearly are not. Thus we were motivated to reassign the 130-ppm resonance to a free molecular species, which is assumed to be present at multilayer coverage on the metal and/or spilled over onto the support. From chemical shift considerations, the most reasonable candidate was benzene, which has an isotropic ^{13}C chemical shift of 129–130 ppm in solution.

Three experiments were performed to confirm this assignment. Figure 3 shows slow-speed ^{13}C CP/MAS spectra which were obtained at 123 K and near identical spinning speeds. The sideband patterns are clearly identical for the two samples. The spectrum in Figure 3a is of the sample of acetylene on Pt/η-alumina whose room temperature spectrum is shown in Figure 1b. The spectrum in Figure 3b is of a second sample of the same catalyst to which benzene-$^{13}C_6$ had been directly adsorbed. The sideband patterns in Figure 3 were analyzed using the method of Herzfeld and Berger,[34] and almost identical principal components characteristic of effective axial symmetry were obtained for the two spectra: Figure 3a, δ_{11} = 173 ppm, δ_{22} = 174 ppm, δ_{33} = 43 ppm; Figure 3b, δ_{11} = 172 ppm, δ_{22} = 172 ppm, δ_{33} = 43 ppm. Solid benzene in the high-temperature phase, for which rapid

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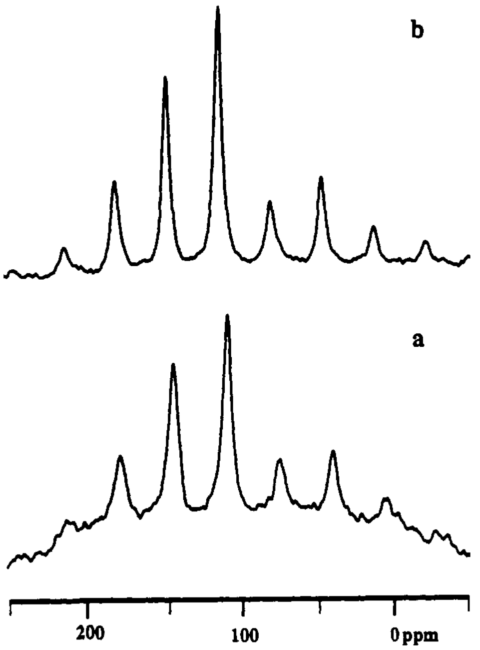

Figure 3. ^{13}C CP/MAS NMR spectra showing acetylene or benzene adsorbed on 10% Pt/η-alumina and subsequently evacuated. At a resonance frequency of 50 MHz and a temperature of 123 K 400 transients were collected for each sample, and 25 Hz of line broadening was used: (a) acetylene-$^{13}C_2$ at a spinning speed of 1785 Hz; (b) benzene-$^{13}C_6$ at a spinning speed of 1770 Hz.

motion about the C_6 axis leads to effective axial symmetry, has the following principal components: $\delta_\perp = 192$ ppm; $\delta_\parallel = 14$ ppm.[35] We assumed that the difference between the ^{13}C principal components of the adsorbed benzene and benzene in the solid phase was due to libration about the C_6 axis of the surface species. A number of spectral simulations were performed, and excellent agreement was obtained with a root mean square librational angle of 33°. ^{13}C–^{13}C dipolar coupling was ignored in the above treatment, because the spinning speeds used were significantly larger than the motionally averaged coupling.

Further evidence for the assignment of the 130-ppm resonance to benzene was the observation that this signal formed when cyclohexane-$^{13}C_1$ was heated on Pt/η-alumina (Figure 4). Dehydrogenation of cyclohexane to benzene on supported Pt is a well-known reaction.[36,37]

The third, and perhaps most conclusive, piece of evidence for the reassignment of the 130-ppm NMR signal is afforded by the Fourier transform mass spectral data in Figure 5. Acetylene-$^{13}C_2$ was adsorbed on Pt/η-alumina using the conditions described in ref 21. First, the sample was heated in the vacuum line to 323 K, and a small amount of desorbed gas was collected in a cold trap. FT-MS analysis of that sample (Figure 5a) revealed a large signal for acetylene-$^{13}C_2$ and a smaller signal at *m/e* 84 due to benzene-$^{13}C_6$. The catalyst sample was introduced directly into the FT-MS instrument without exposure to the atmosphere. The catalyst sample was then heated in the mass spectrometer, and large signals were observed for labeled benzene (Figure 5b).

The cyclotrimerization of acetylene to benzene on various forms of Pd is a well-studied reaction.[6,28,29] On Pd(111) it is the only detectable process *at high pressure*, and it occurs at temperatures as low as 140 K without C–H bond scission.[6,28,29] Acetylene cyclotrimerization on supported Pd has also recently been observed.[38] To investigate the low-temperature reactivity of the acetylene–Pt/η-alumina system, we performed an overpressure

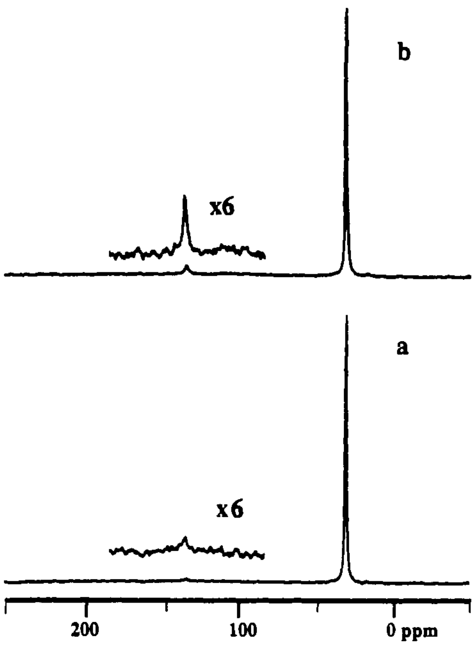

Figure 4. ^{13}C Bloch decay/MAS NMR spectra of cyclohexane-$^{13}C_1$ adsorbed onto 10% Pt/η-alumina. At a resonance frequency of 50 MHz 100 transients were taken, and 25 Hz of line broadening was used: (a) room temperature prior to heating; (b) room temperature after heating to 423 K.

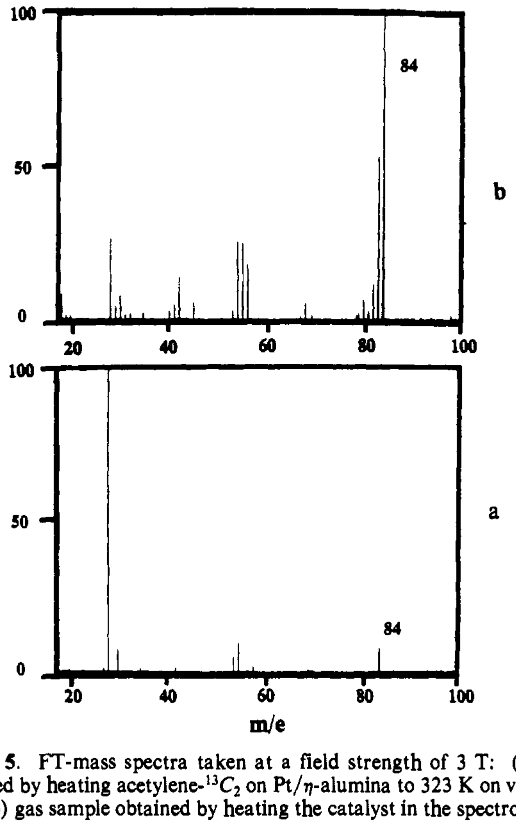

Figure 5. FT-mass spectra taken at a field strength of 3 T: (a) gas obtained by heating acetylene-$^{13}C_2$ on Pt/η-alumina to 323 K on vacuum line; (b) gas sample obtained by heating the catalyst in the spectrometer.

adsorption at 173 K and transferred the sealed MAS rotor to the precooled NMR probe. This experiment was performed using the CAVERN technique described elsewhere.[7] ^{13}C spectra (not shown) were acquired as the sample temperature was slowly raised to 303 K. Formation of the 130-ppm resonance did not commence until ca. 290 K, and no other species were observed. We conclude that supported Pt is apparently less active for acetylene cyclotrimerization than single-crystal Pd.

Using overpressure adsorption conditions, therefore, acetylene cyclotrimerizes on supported Pt to form a significant amount of

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benzene, and this process accounts for the observation of a ^{13}C resonance at 129–131 ppm. But what of the species proposed by Slichter et al.?[15] As stated in the Introduction, nuclear spins closely associated with Pt particles may be difficult to detect in chemical shift spectra, even with the application of magic-angle spinning. It is reasonable that there are indeed carbon-containing species bound to the metal surface, but they are unobservable in standard ^{13}C MAS spectra. Spin-counting experiments were performed to check the plausibility of the above argument. Duplicate measurements were performed to quantify the observed ^{13}C signals in comparison with the known acetylene-$^{13}C_2$ uptake measured using vacuum line techniques. The polymer Delrin was selected as an integration standard because of its inertness, the location of its ^{13}C signal (89 ppm) in an open spectral region, and its ease of weighing and handling. In each experiment ca. 0.1 g of Delrin was mixed with Pt/η-alumina catalyst, and an overpressure adsorption of acetylene-$^{13}C_2$ was performed. ^{13}C MAS spectra were then acquired at room temperature using direct excitation (90° pulse) of the carbon spins to facilitate quantitation (cross polarization was not used in these experiments, because of the possibility of additional sources of quantitation error with that mode of excitation). A pulse delay of 75 s was used in this experiment because of the long ^{13}C T_1 of Delrin (15 s). Of the 0.34 mmol of acetylene adsorbed per gram of catalyst, integrations of the resulting spectra accounted for only an average of 86%. In other words, ca. 0.095 mmol of the adsorbed ^{13}C per gram of catalyst was undetectable in these samples. Using the known surface area of the Pt in these catalysts and the measured gas uptakes, and assuming an average of one C per surface Pt atom, the "missing" label is consistent with 0.3-monolayer coverage of the metal. This carbon is probably associated with metal-bound species of the type described by Slichter.[15] Apparently these species are not readily observed in standard ^{13}C MAS experiments. In a ^{13}C NMR study of the reactions of CO on Ru/SiO$_2$ catalyst, Duncan observed a 300-ppm-wide resonance at 350 ppm due to the formation of a ruthenium carbide phase.[39] The magnetic susceptibility of platinum is substantially larger than that of ruthenium, and it is apparent that the observation of well-resolved ^{13}C MAS signals from rigid species closely associated with Pt particles might be an exception rather than the rule. The only evidence that we have seen of ^{13}C signal intensity in MAS spectra that might be due to the "missing" species is in low-temperature spectra such as Figure 3a. Inspecting that figure, one notes a very broad background that is not seen in otherwise identical experiments prepared with direct adsorption of benzene. We have not investigated this feature any further, but ca. 200-ppm width suggests species experiencing susceptibility broadening.

In conclusion, this study has extended the work of Slichter and co-workers to higher pressures of acetylene on supported Pt. Conventional ^{13}C chemical shift spectra obtained with magic-angle spinning are shown to reveal a previously unknown reaction of this system: cyclotrimerization of acetylene at high pressure to form benzene. This result explains an earlier observation of Chin and Ellis that had been reported as a possible criticism of the Slichter study. However, a standard ^{13}C MAS experiment is unable to detect the immobile carbons closely associated with the Pt particles previously characterized by Slichter et al. This study underscores the need to apply several types of NMR experiments to the same sample to avoid weaknesses inherent in individual experiments. This study also suggests a need to control adsorbate loadings very carefully in NMR studies of supported metal catalysts.

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Registry No. CH≡CH, 74-86-2; C_6H_6, 71-43-2; Pt, 7440-06-4.

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