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Chemisorption of Ethylene on Supported Platinum Studied by High-Resolution Solid-State NMR

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The adsorption of ethylene on a series of supported platinum catalysts has been studied by high-resolution solid-state ^{13}C NMR. Catalysts have been prepared with SiO_2 or Al_2O_3 supports, of high and low dispersion, and with or without the use of Cl-containing precursors. All catalysts show a species which is identified as a π-bonded olefin. On catalysts containing Al_2O_3 or Cl^-, this species reacts to form other species. The main reaction products are probably σ-adsorbed species with an intact C=C double bond, and possibly surface alkyls. Delayed decoupling experiments have been used to identify nonprotonated carbon, which in general is not found. The presence of $M{\equiv}C{-}CH_3$ and $M{=}C{=}CH_2$ species is excluded on all of the catalysts studied.

INTRODUCTION

The mode of adsorption of olefins on metals is one of the archetypal problems of surface chemistry. The type of bonding and the degree of surface reaction are topics of continuing interest. In the particular case of ethylene on Pt, studies have been carried out on single-crystal surfaces by LEED (*1–7*), UPS (*4, 8–10*), and EELS (*11, 12*). On supported Pt and Pt black there are studies by infrared (*13–15, 32*), ultraviolet (*16*), and NMR (*17, 18*) spectroscopy.

The most studied C_2H_4–Pt system is certainly the (111) single-crystal surface (*1, 2, 4, 8–12*). Most workers find a low-temperature state whose structure is not yet firmly established, together with a state forming near room temperature. The room temperature form of ethylene on Pt(111) is widely accepted to be ethylidyne, in a (2 × 2) structure, although there is some dissent (*19*). It should be noted that if a recent (*20*) determination of the absolute coverage is correct, the conventional view is in severe difficulty, due to packing constraints. Unfortunately, the other crystal faces have been much less studied, and the relevance of the Pt(111) studies to dispersed catalysts is not obvious, in view of the observation (*21*) that these expose mainly (100) surfaces after treatment in H_2. Beebe and Yates (*33*) point out that ethylidyne has never been observed on a well-characterized surface of other than threefold symmetry. Taken with the result of (*21*), this suggests that we should not expect ethylidyne on supported Pt catalysts.

Infrared spectroscopy of supported Pt catalysts shows a variety of species resulting from the chemisorption of ethylene. Morrow and Sheppard (*13*) observe three different species, depending on temperature, for a Pt–SiO_2 catalyst prepared by impregnation with H_2PtCl_6. They attribute these, on the basis of C–H stretching frequencies, to associatively σ-diadsorbed species with differing C—C bond orders and numbers of hydrogens. They also infer indirectly the presence of surface C not bound to H. Prentice *et al.* (*14*) claimed to find a π-complexed form of ethylene, based on the C=C stretching band near 1500 cm^{-1}. Soma (*15*), using an impregnated Pt–Al_2O_3 catalyst, also found a π-complex, particularly at low temperatures, together with a σ-diadsorbed species. Beebe and Yates (*32*) have found ethylidyne on a Pt–

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Al_2O_3 catalyst, together with other species which were not identified. This would suggest that under some conditions, (111) surfaces can form on supported Pt.

Wang *et al.* (*17*) have carried out an NMR study of ethylene on a Pt–Al_2O_3 catalyst. These workers used spin-echo methods to observe the C–C and C–H dipolar couplings, using doubly ^{13}C-enriched ethylene. They find that essentially all of the C–C bonds are intact at room temperature, with a bond length of about 1.49 Å. Half of the carbon is found to have directly bonded H and a C–H dipolar coupling consistent with a freely rotating CH_3 group. Thus these workers propose the ethylidyne group as essentially the sole species on their catalyst at room temperature.

Shibanuma and Matsui (*18*) have also studied ethylene on unsupported Pt, using broadline ^1H spectroscopy. From an analysis of the dipolar lineshapes, these workers conclude that the LEED-derived ethylidyne species cannot be present, and propose instead a $—CH_2—CH=$ species for the room-temperature adsorbed phase. This appears to be directly contradictory to the results of Wang *et al.* and suggests the possibility of fundamental differences between supported and unsupported polycrystalline Pt.

EXPERIMENTAL

In view of the discrepancy between the NMR results of (*17*) and (*18*), neither of which agreed with our preliminary results, it was decided to study several catalyst preparations, to determine whether ethylene reactivity was affected by any of the common variables of catalyst preparation. For supported Pt catalysts, these variables comprise mainly metal particle size, nature of support, and the presence or absence of chlorine in the catalyst. We have therefore prepared Pt–SiO_2 and Pt–Al_2O_3 catalysts by adsorption from $Pt(NH_3)_4(NO_3)_2$ solution (catalysts 1 and 2) and by impregnation with H_2PtCl_6 solution (catalysts 3 and 4). Catalyst 2 is a sample of catalyst 1 heat-treated in air to yield a chlorine-free catalyst of somewhat lower dispersion. Catalysts 5 and 6 were prepared by impregnation with $Pt(NH_3)_4(NO_3)_2$ at pH 7, to yield Cl-free catalysts of much lower dispersion. All catalysts were reduced in flowing H_2 at 450°C.

The characteristics of the catalysts studied are listed in Table 1. Dispersions were measured by hydrogen chemisorption with extrapolation to zero pressure, assuming a surface stoichiometry of Pt–H. Ethylene coverages are saturation coverages, calculated using the measured dispersion value. In all cases the saturation ethylene coverage was reached at a pressure below 0.1 Torr, and samples saturated at such a low pressure were used for the NMR studies.

Samples were prepared on a vacuum line in NMR tubes, with a sample depth of about 2 cm. After reduction of the catalyst with H_2 at 450°C and overnight pumping at the same temperature, adsorption of singly ^{13}C-enriched ethylene was carried out at room temperature. When adsorption had ceased, typically in about 30 min, the sample was frozen with liquid N_2, to prevent any possible thermal damage during sealing, and sealed off.

High-resolution ^{13}C spectra were recorded on a home-built spectrometer operating at a field of 1.4 T. Single-contact Hartmann–Hahn cross-polarization was employed, with a field strength of 50 kHz for both polarization and decoupling. A cross-polarization time of 2 ms was used,

TABLE I

Catalyst Characteristics

Catalyst No.	Weight percent	Support	Cl^-	Dispersion	C_2H_4 coverage[a]
1	5	SiO_2	No	1.3	0.26
2	5	SiO_2	No	1.1	0.22
3	10	SiO_2	Yes	0.36	0.26
4	10	Al_2O_3	Yes	0.61	0.25
5	10	SiO_2	No	0.24	0.27
6	10	Al_2O_3	No	0.23	0.27

[a] Adsorbed ethylene molecules per surface Pt atom, based on the measured dispersion.

unless otherwise stated. Sealed 5-mm samples were spun in a magic-angle spinner which has previously been described (*22*), typically at a speed of 2.5 kHz. The proton spin–lattice relaxation times were found to be fairly short, permitting recycle rates of 1 to 3 Hz.

Intensity and relaxation measurements were performed on the same instrument, using static samples in 12-mm tubes. The larger sample size and better filling factor permit an order-of-magnitude decrease in the time required for these measurements. Cross-polarization rates were observed by variation of the contact time. Rotating-frame relaxation of protons was assessed by spin-locking the protons for a variable length of time before the ^{13}C cross-polarization pulse was applied. Intensity measurements using excitation by 90° pulses were performed using the pulse sequence of Duncan *et al.* (*34*) to avoid the accumulation of artefacts due to pulse feed-through and acoustic resonance. Proton decoupling (50 kHz) was applied only during data acquisition in these experiments.

For intensity measurements a standard of natural ammonium bicarbonate was used. This was found to give a cross-polarization intensity enhancement of 4.1 ± 0.2 relative to 90° pulse excitation, in good agreement with the theoretical value. It was also verified to give the correct ^{13}C intensity relative to an adamantane sample, within a relative uncertainty of ±5%. Standard and unknown samples were of the same size and placed at the same position in the probe. The probe proton and carbon channels were tuned by minimizing reflected power with the sample in place, thus ensuring the same tuning for standard and unknowns.

RESULTS AND DISCUSSION

As can be seen from Table 1, the total amounts of adsorbed ethylene are similar for all catalysts, amounting to approximately one adsorbed ethylene per four surface platinum atoms. The ^{13}C spectra for all catalysts are displayed in Fig. 1. These spectra were recorded using a sweep width that encompassed the range of chemical shifts from 900 to −700 ppm with respect to TMS. Only the central region of the spectra is displayed in Fig. 1, since in no case were any features observed outside of this region.

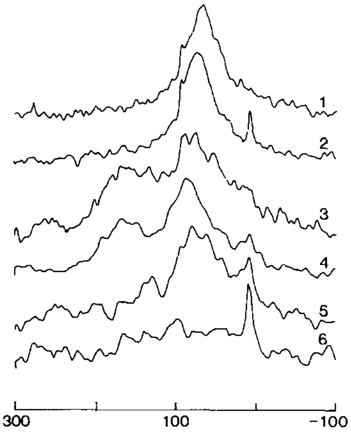

FIG. 1. ^{13}C spectra for monolayer coverage of ethylene on all catalysts. Spectrum numbers correspond to catalyst numbers in Table 1. Each spectrum results from 1 to 8 × 10^5 single contact cross-polarizations. Scale is in parts per million with respect to TMS.

It is immediately apparent that substantial differences in the spectra of ethylene adsorbed on different catalysts exist. The one feature common to all spectra is a line in the region of 70–90 ppm with respect to TMS. In addition some of the catalysts show rather broader features in the vicinity of 130–170 and 30–50 ppm. Catalyst 4 had a fairly strong peak in the 30- to 50-ppm region initially, but its intensity decreased over a period of several days, as illustrated in Fig. 2. This is the only catalyst for which changes were observed on a time scale of days to months. Since at least 10 h is required to record one of these spectra, changes on a shorter time scale could not be observed. In some cases a narrow line is observed at 5 to 6 ppm. This arises from a gaseous or physisorbed species, as shown by an increase in its relative size when spectra are excited by 90° pulses instead of

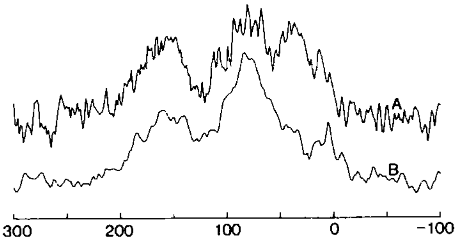

FIG. 2. (A) Spectrum of ethylene on catalyst 4 recorded during the day after sample preparation. (B) Recorded 3 months after preparation.

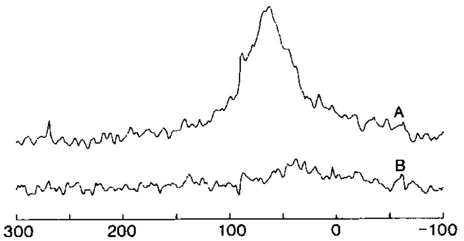

FIG. 3. (A) Spectrum 1 of Fig. 1. (B) Same sample run with a 50-μs decoupler delay.

by cross-polarization. Given the value of the chemical shift, this is clearly C_2H_6, formed by self-hydrogenation.

Further information on the state of the adsorbed carbon can be obtained by a delayed decoupling experiment (*23*, *24*). In such an experiment, the decoupler is turned off for a short period following cross-polarization, and before acquisition of the free induction decay. During this period, the C–H dipolar interaction causes dephasing of ^{13}C magnetization, which is not reversed when the decoupler is switched back on during the FID. Thus a high-resolution spectrum is observed, but with reduced intensity for those carbons having dipolar couplings to protons. By adjusting the delay time, selectivity with respect to the C–H dipolar coupling strength, and hence with respect to the C–H distance, is obtained.

We have used this experiment with a delay of 50 μs, which has been shown (*24*) to cause virtually complete destruction of signals from carbons with a directly bonded hydrogen, and only small effects on C more distant from H. (The exception to this generalization is CH_3 groups (*24*) where rapid rotation partially attenuates the dipolar coupling. Signals from rotating methyl groups should be reduced, but not eliminated, with this length of delay.) We have applied this experiment to all samples, and typical results are shown in Figs. 3 and 4. In all cases the carbon signal is essentially destroyed. The largest residual peak observed for any sample is the small low-field peak shown in Fig. 4 for catalyst 3. From these results, it is concluded that essentially all of the observed surface carbon has directly bonded protons, on all catalysts.

Since the carbon is observed by cross-polarization from protons, it is of course possible that there exists on the surface nonprotonated carbon which is so remote from protons that it is never observed. This could occur if there were complete dissociation of ethylene to surface carbon, with loss of hydrogen to the gas phase as H_2 or as C_2H_6. This may have occurred with catalyst 6, which can be seen to give a spectrum of low intensity in comparison with catalyst 5, although it has essentially the same concentration of adsorbed ethylene. However, the nonprotonated carbon in species such as $M{\equiv}C{-}CH_3$ and $M{=}C{=}CH_2$ would certainly be observed under the present cross-polarization conditions, so the presence of substantial amounts of any such species in these experiments is excluded. It is probable that there is also no fully deprotonated carbon in the

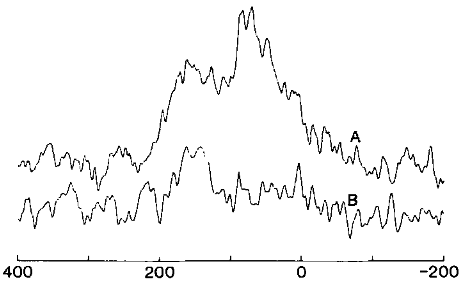

FIG. 4. (A) Spectrum 3 of Fig. 1 (B) Same sample run with a 50-μs decoupler delay.

immediate vicinity of chemisorbed H, since intermolecular cross-polarization should lead to a signal. We have easily observed H–C cross-polarization in CO/H_2 coadsorbed layers on Ru, under conditions where the position and anisotropy of the CO resonance demonstrate the absence of any chemical reaction (*25*).

To further investigate the above points, it is of interest to determine whether the observed NMR signals account for all of the ^{13}C present in the samples. To do this in the case of signals from cross-polarization requires fairly extensive experimentation. Correct intensity measurements require that the cross-polarization be complete, and that there be no significant decay of magnetization during the cross-polarization period, as a result of rotating-frame relaxation. Thus we must measure cross-polarization rates, and $T_{1\rho}$. The latter must be measured from the ^{13}C spectrum rather than ^1H, since the samples contain many protons (on the support) which are of no relevance to ^{13}C spectroscopy. This is a rather time-consuming program of experimentation on dilute samples, even using 12-mm samples as noted above. It has therefore been carried out only for samples of catalysts 1 and 4, which are representative of the two main varieties of spectroscopic behaviour.

In principle, complete cross-polarization can be achieved by a sufficiently long contact time. In practice this is limited by rotating-frame relaxation and by instrumental effects. The latter comprise mainly deviation from the Hartmann–Hahn matching condition due to pulse amplitude droop and thermal effects. Thermal effects can range from further mismatching due to detuning, up to total destruction of the probe and sample if high power is applied for a sufficiently long time. None of these effects is important in our apparatus for contact times of less than 5 ms.

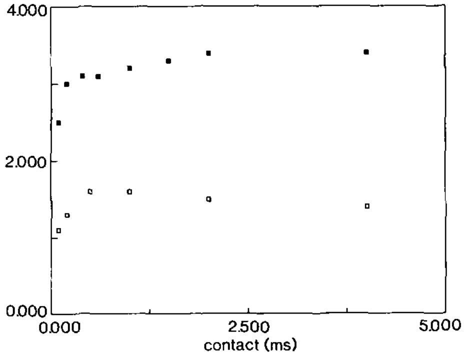

FIG. 5. Intensity (arbitrary units) vs contact time (ms). (■) Sample 1; (□) sample 4.

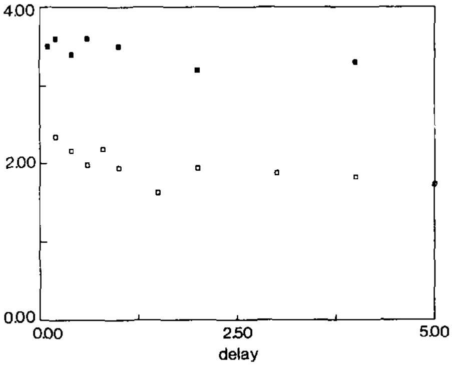

FIG. 6. Intensity (arbitrary units) vs delay (ms) between spin-locking and cross-polarization. (■) Sample 1; (□) sample 4.

The effects of varying contact time for samples 1 and 4 are shown in Fig. 5. It can be seen that both samples cross-polarize rapidly on the time scale of 1 ms. For sample 1, the signal is essentially constant for contact times of 2 to 5 ms. Sample 4, on the other hand, shows a decay, indicating rotating-frame relaxation.

Figure 6 shows the effect of a variable delay between spin-locking and cross-polarization time, for a constant contact time of 200 μs. Both samples show some decay of magnetization, which is relatively greater for sample 4. The data of Fig. 6 were used to correct the intensity measurements for decay during the 2-ms contact time employed.

In addition to cross-polarization measurements, intensities were also measured with 90° pulse excitation. The NMR measurements appear to reveal a certain amount of ethane in the samples. This cannot be assayed by NMR, since it will be partitioned in an unknown ratio between the gas phase, which extends outside the coil, and a physisorbed phase on the support. To determine this material, the sample tubes were reattached to the vacuum system after NMR measurements, and the ethane was collected by room temperature desorption into a liquid nitrogen trap. The trap was then warmed and the amount of gas was determined volumetrically. The collected gas sample was then analyzed mass spectroscopically and found to consist only of ethane, within experimental uncertainty.

The results of all of these intensity measurements are displayed in Table 2. This shows the fraction of the original ^{13}C measurable by NMR with the two types of excitation, and the fraction recovered from the gas phase. Ideally, the sum of the 90° NMR and gas phase results should equal 1 if all carbon is accounted for. As can be seen, the mass balance is reasonably satisfactory for both samples, given an uncertainty of about ±10% in the NMR intensity measurements. Clearly a large fraction of the adsorbed carbon is not missing, although the data are consistent with a small deficit. The 90° and cross-polarization results agree for sample 1 within experimental error. For sample 4 there is definitely missing intensity in the cross-polarization measurement. This must mean either carbon on the surface which is remote from any protons, or a population with extremely short rotating-frame relaxation time, undetected by the measurements of Fig. 6.

TABLE 2

Detected Fraction of Originally Adsorbed Carbon

Catalyst No.	90° pulses[a]	Cross-polarization[a]	Gas phase
1	0.88	0.92	0.05
4	0.79	0.55	0.07

[a] From integral of spectrum excluding area of ethane peak.

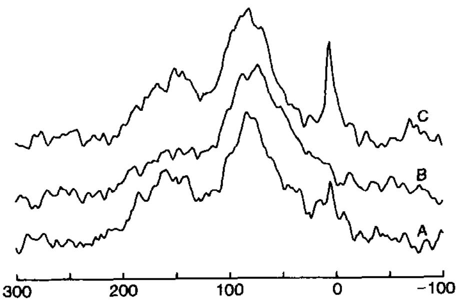

FIG. 7. Spectra of ethylene on sample 4 with different excitation conditions: (A) 2-ms cross-polarization, (B) 200-μs cross-polarization, (C) 90° pulses.

Since sample 4 shows decreasing intensity with increasing contact time, together with increased intensity upon 90° pulse excitation, it is of interest to determine whether there are any spectroscopic differences. Figure 7 shows high-resolution (MAS) spectra of sample 4 with 90° pulse excitation, and with 200-μs cross-polarization time, together with the 2-ms cross-polarization spectrum from Fig. 1. As can be seen, there are no major spectroscopic changes. Not surprisingly, the ethane peak at 6 ppm is bigger for 90° pulse excitation. The most noticeable difference is that the peak at 140–160 ppm is smaller, relative to the peak at 80–90 ppm for the 200-μs cross-polarization. This can indicate either longer average C–H distances, leading to a slower cross-polarization rate for this peak, or a loss of intensity in the 80 ppm peak due to rotating-frame relaxation at the longer contact time.

Interestingly, there is little spectral difference between the 2-ms cross-polarization and the 90° pulse excitation. In view of the results of Table 2, showing greater absolute intensity for the latter, the carbon not found by cross-polarization must be distributed throughout both spectral regions.

Interpretation of the observed chemical shifts can be attempted by reference to the shifts of metal complex compounds of known structure. There is a large body of relevant experimental data (*26*). Ethylene might adsorb nondissociatively forming a π-complex. Alternatively, dissociation might lead to σ-vinyl species or a carbene. Further dissociation could lead to acetylenes, either σ- or π-bonded, to carbynes, or to σ-diadsorbed species. Self-hydrogenation might lead to surface alkyl groups. Examining the data (*26*) for Pt complexes, one finds that small π-complexed olefins have ^{13}C shifts of 30 to 90 ppm, depending on the nature of the other ligands. π-bonded acetylenes, for which there are less data, fall in the range of 60 to 120 ppm. σ-vinyl species are found to resonate at 120 to 180 ppm, with the carbon bound to the metal being at a lower field. σ-acetylenes, for which there are again less data, have the bound carbon at 60–100 ppm, and the other acetylenic carbon at 95–120 ppm. Carbenes typically have a low-field resonance in the 200 to 300 ppm range. No data are given in (*26*) for Pt carbynes. In view of the occurrence of $M{\equiv}C{-}CH_3$ on Pt(111) it would be interesting to have data for a Pt complex with this fragment. The best one can do is to observe that the $\equiv C{-}CH_3$ group in Cr (*27*), W (*28*), and Co (*29*) complexes has a carbyne resonance in the region of 230–360 ppm, and a methyl resonance at 35–45 ppm. Finally small alkyl groups bound to Pt typically have the bound carbon resonance in the range of -10 to 10 ppm.

Taking these data as transferable to the surface-adsorbed case, we can place some limits on what species are present in the adsorbed layer. This type of interpretation must be regarded as somewhat uncertain, since the possibility exists of Knight shifts arising from interaction with electron spins in the Pt metal. There is no a priori way to know how big these shifts might be. For the well-studied case of hydrogen adsorption on Pt (*35, 36*) these shifts range from 0 to about 50 ppm, depending on the particle size and adsorbate coverage. The Knight shifts are smaller for more disperse catalysts and for higher coverages. A catalyst such as sample 1 of the present paper shows a zero Knight shift when saturated with hydrogen. It seems likely that the Knight shift would be similarly small in the present work, since the carbons will be more distant from Pt than adsorbed H and will have considerable *p*-orbital participation in their bonding. Since we reproducibly see a peak at 70–90 ppm independent of dispersion, it appears likely that Knight shifts are small for all of the present samples. Due to the large chemical-shift range of ^{13}C, an uncertainty of 10–20 ppm arising from possible Knight shifts would not invalidate qualitative arguments regarding the broad spectral regions in which peaks are observed, but would preclude detailed discussion of small effects.

We note, first, that there are no peaks found in the extreme low-field region characteristic of carbenes and carbynes. This is consistent with the argument made above from delayed decoupling data. Such species are apparently not formed on supported Pt under the present conditions.

The ubiquitous species at 70–90 ppm could reasonably be a π-complex or an acetylene. A σ-bonded acetylene is unlikely, as the delayed decoupling experiment shows no nonprotonated carbon in this region; this eliminates the $M{-}C{\equiv}C{-}H$ structure. For the high-dispersion SiO_2-supported catalysts where this is the only species, the static spectrum gives some information. In the spectrum of a static sample, the line broadens to 1600 Hz and remains symmetric about its midpoint. This places an upper limit of about 100 ppm on the chemical-shift anisotropy of this species. In addition, we fail to observe spinning sidebands of as much as 10% of the centreband intensity, when the spinning rate is reduced to 800 Hz. This places about the same upper limit on the anisotropy (*30*). This anisotropy is much too small for a static acetylene (*31*), but could be consistent with a π-complexed olefin, or possibly a π-complexed acetylene rotating about the normal to the $C \equiv C$ bond. The former suggestion seems preferable, since the latter should lead to an asymmetric lineshape in the static spectrum, due to the axial symmetry of the acetylenic shift tensor.

CONCLUSION

For the reasons given above, we reject the general presence of $\equiv C-CH_3$ groups on any of the present catalysts. The only feature observed that might correspond to such a species is the transient peak (Fig. 2) at about 40 ppm, observed on catalyst 4. This might reasonably be the CH_3 resonance of such a species. Unfortunately a corresponding carbyne resonance is lacking, although given the poor signal-to-noise ratio of Fig. 2A, this is not conclusive.

The simplest view of the results is that the species resonating at 70–90 ppm is indeed a π-bonded olefin. Since this is found on all catalysts, it is probably the first species formed. On Cl-free SiO_2-supported catalysts, nothing further occurs. In the presence of Cl^- or Al_2O_3, the adsorbed layer is more reactive and a variety of other species is formed. The large peak at 130–170 ppm (catalysts 3 and 4) could be accounted for as σ-vinyl groups, or σ-diadsorbed species with a $C=C$ double bond. There is a suggestion of some intensity in this region for catalyst 5, which suggests that larger metal particle sizes may also lead to increased reactivity. Finally the intensity in the 30 to 50 ppm region can result from any type of alkyl group. As shown in Fig. 2, these tend to disappear slowly at room temperature.

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REFERENCES

1. Stair, P. C., and Somorjai, G. A., J. *Chem. Phys.* **66,** 573 (1977).
2. Kesmodel, L. L., Dubois, L. H., and Somorjai, G. A., *J. Chem. Phys.* **70,** 2180 (1979).
3. Firment, L. E., and Somorjai, G. A., *Surf. Sci.* **55,** 413 (1976).
4. Fischer, T. E., and Kelemen, S. R., *Surf. Sci.* **69,** 485 (1977).
5. Fischer, T. E., and Kelemen, S. R., *J. Vac. Sci. Technol.* **15,** 607 (1978).
6. Lang, B., Joyner, R. W., and Somorjai, G. A., *Surf. Sci.* **30,** 454 (1972).
7. Baron, K., Blakeley, D. W., and Somorjai, G. A., *Surf. Sci.* **41,** 45 (1974).
8. Lo, W. J., Chung, Y. W., Kesmodel, L. L., Stair, P. C., and Somorjai, G. A., *Solid State Commun.* **22,** 335 (1977).
9. Demuth, J. E., *Surf. Sci.* **80,** 367 (1979).
10. Albert, M. R., Sneddon L. G., Eberhardt, W., Greuter, F., Gustafsson, T., and Plummer, E. W., *Surf. Sci.* **120,** 19 (1982).
11. Ibach, H., Hopster, H., and Sexton, B., *Appl. Surf. Sci.* **1,** 1 (1977).
12. Ibach, H., and Lehwald, S., *J. Vac. Sci. Technol.* **15,** 407 (1978).
13. Morrow, B. A., and Sheppard, N., *Proc. R. Soc. London Ser. A* **311,** 391 (1969).
14. Prentice, J. D., Lesiunas, A., and Sheppard, N., *J. Chem. Soc. Chem. Commun.*, 76 (1976).
15. Soma, Y., *J. Catal.* **59,** 239 (1979).
16. Soma, Y., *Bull. Chem. Soc. Japan* **44,** 3233 (1971).
17. Wang, P.-K., Slichter, C. P., and Sinfelt, J. H., *J. Phys. Chem.* **89,** 3060 (1985).
18. Shibanuma, T., and Matsui, T., *Surf. Sci.* **154,** L215 (1985).
19. Demuth, J. E., *Surf. Sci.* **93,** L82 (1980).
20. Freyer, N., Pirug, G., and Bonzel, H. P., *Surf. Sci.* **125,** 327 (1983).
21. Wang, T., Lee, C., and Schmidt, L. D., *Surf. Sci.* **163,** 181 (1985).
22. Gay, I. D., *J. Magn. Reson.* **58,** 413 (1984).
23. Opella, S. J., and Frey, M. H., *J. Amer. Chem. Soc.* **101,** 5854 (1979).
24. Alemany, L. B., Grant, D. M., Alger, T. D., and Pugmire, R. J., *J. Amer. Chem. Soc.* **105,** 6697 (1983).
25. Gay, I. D., unpublished results.
26. Mann, B. E., and Taylor, B. F., "^{13}C NMR Data for Organometallic Compounds." Academic Press, New York, 1981.
27. Fischer, E. O., and Richter, K., *Chem. Ber.* **109,** 2547 (1976).
28. Fischer, E. O., and Kreis, G., *Chem. Ber.* **109,** 1673 (1976).
29. Aime, S., Milone, L., and Valle, M., *Inorg. Chim. Acta* **18,** 9 (1976).
30. Herzfeld, J., and Berger, A. E., *J. Chem. Phys.* **73,** 6021 (1980).

31. Zilm, K. W., and Grant, D. M., *J. Amer. Chem. Soc.* **103,** 2913 (1981).

32. Beebe, T. P., and Yates, J. T., Jr., *J. Phys. Chem.* **91,** 254 (1987).

33. Beebe, T. P., and Yates, J. T., Jr., *Surf. Sci.* **173,** L606 (1986).

34. Duncan, T. M., Yates, J. T., Jr., and Vaughan, R. W., *J. Chem. Phys.* **73,** 975 (1980).

35. Sheng, T.-C., and Gay, I. D., *J. Catal.* **71,** 119 (1981).

36. De Menorval, L. C., and Fraissard, J. P., *Chem. Phys. Lett.* **77,** 309 (1981).