Probe of the Surface of a Heterogeneous Catalyst: Double NMR of Carbon Monoxide Chemisorbed on Highly Dispersed Platinum

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The detailed NMR line of ^{195}Pt atoms in the surface layer of small particles of Pt metal on which CO has been chemisorbed has been observed. The surface ^{195}Pt are resolved from the ^{195}Pt resonances of atoms deeper in the particle by spin-echo double resonance between ^{195}Pt and ^{13}C. The ^{195}Pt resonance position and ^{13}C-^{195}Pt indirect spin coupling are found to be very similar to those in diamagnetic Pt-carbonyl molecules. The results show that CO bonds via the C atom and verify that concepts deduced from studies of large single crystals are valid for the small particles.

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Though NMR has been a powerful technique for studying solids and liquids, its use for studying surfaces has been more limited. In their recent article, Duncan and Dybowski[1] point out that "the systems in the past have consisted primarily of physically adsorbed species. Through analysis of relaxation times and changes in isotropic chemical shifts, these early studies provided information on . . . the transport mechanisms to and from the surface and the rate of exchange between the chemisorbed monolayer and the liquid-like overlayers." The studies to date have been on nuclei of adsorbed species, typically on material such as carbon or zeolites. Several years ago, we set out to detect the NMR of the surface layer of atoms in a metal, choosing Pt because of its significance in surface science and because of the NMR properties of ^{195}Pt. In this paper we report the successful measurement of the position and detailed NMR line shape of the surface ^{195}Pt for Pt coated with CO.

The first results of our group (Rhodes and coworkers)[2-5] showed by chemical means that the ^{195}Pt resonance of various coated samples was mainly in the vicinity of ^{195}Pt in diamagnetic compounds, but the surface NMR was not resolved from a nearby peak due to the NMR of deeper layers. Therefore the surface Pt line position was only approximately known and we could only guess at its width or shape. Using spin-echo double resonance (SEDOR) between ^{13}C and ^{195}Pt in samples of highly dispersed Pt catalysts with chemisorbed carbon monoxide (^{13}CO), we have now completely resolved the NMR of surface ^{195}Pt.[6] SEDOR is a pulse technique involving simultaneous excitation of the NMR of two different types of nuclei, e.g., ^{13}C and ^{195}Pt. Provided the nuclei are near enough to be coupled, the resonance of the ^{13}C affects the resonance of the ^{195}Pt, either directly through the nuclear dipolar interaction or indirectly through the electrons via the pseudoexchange and pseudodipolar interactions.[7] The strength of the coupling depends strongly on the proximity of the nuclei, so that observation of the size of the SEDOR effect can distinguish first neighbors from second neighbors, etc. Thus, for ^{13}CO on Pt, SEDOR gives a unique signature to the surface Pt atoms. Indeed, the coupling to deeper Pt layers is too weak for us to detect.

We obtain the line shape of the surface Pt nuclei, showing quantitatively that the position of the ^{195}Pt surface resonance and the strength of the ^{195}Pt-^{13}C spin-spin coupling are very similar to their values in diamagnetic Pt-carbonyl molecules. Such molecules are often used as models of the Pt surface. We find that the bonding of the CO to the Pt is through the carbon, demonstrate the absence of serious contamination of the surface, and provide an independent estimate of the CO coverage. While some of these results simply confirm the conventional wisdom and ultrahigh-vacuum (UHV) single-crystal studies, experimental support for bonding characteristics in high-dispersion samples has heretofore been inferred primarily from infrared vibration spectra. The

SEDOR results therefore supply a significant new perspective.

Our samples are 10% Pt by weight, supported on η-alumina, similar to those used by Rhodes and co-workers.[2-5] The samples are designated Pt-26-CO and Pt-76-CO, indicating the respective Pt dispersions, 26% and 76%, and the surface treatment. The dispersions were measured using hydrogen chemisorption. Approximately half a monolayer of CO enriched to 90% ^{13}CO was chemisorbed on the samples at room temperature following oxygen and hydrogen cleaning cycles at 300 °C. The NMR was observed at 77 K.

Line shapes were taken at the fixed frequency $\nu_0 = 73.1$ MHz, varying the applied static magnetic field H_0. Since the Pt signal is very weak, extensive signal averaging was required. Typically, about 10^6 repetitions were collected for each SEDOR point. SEDOR was observed by detecting the ^{195}Pt resonance while also exciting the ^{13}C resonance at the center of its line. When the magnetic field shift is measured relative to the standard ^{13}C reference compound tetramethylsilane (TMS), the ^{13}C line shapes are Gaussian, centered at -368 ppm with an rms width of 137 ppm for Pt-26-CO and centered at -316 ppm with an rms width of 178 ppm for Pt-76-CO. The total Pt NMR line shapes were measured by the pulse NMR method of spin echoes.[8]

Figure 1 shows the SEDOR and spin-echo lines for ^{195}Pt in samples Pt-26-CO and Pt-76-CO. The SEDOR signal is due only to ^{195}Pt nuclei that are at the surface (see below) while the spin-echo signal comes from all the ^{195}Pt nuclei in the sample. The areas under such lines are proportional to the number of nuclei contributing to the line. The line shapes have been corrected for the variation of the spin-spin and spin-lattice relaxation times across the ^{195}Pt line. The SEDOR signal has been scaled (to compensate for the inability of our alternating field to excite the whole ^{13}C line), the precise scaling being selected to emphasize the close match between the SEDOR and spin-echo line shapes on the low-field side.

The SEDOR data demonstrate the existence of a "surface peak" at the low-field end of the ^{195}Pt line for the small Pt particles. No SEDOR signal is observed for H_0/ν_0 above 1.115 kG/MHz in sample Pt-26-CO, but because of the poor signal-to-noise ratio in this part of the line we can only set an upper limit of about 15% of the total intensity at each H_0/ν_0 on the intensity due to surface nuclei. Comparing the areas of the SEDOR and spin-echo lines in Fig. 1, the fraction of nuclei giving a SEDOR signal is 40% for Pt-26-CO and 81% for Pt-76-CO, in fair agreement with the sample dispersions. The ease with which the intensity in the peak at $H_0/\nu_0 = 1.097$ kG/MHz can account for all the surface nuclei reinforces the conclusion that no surface nuclei are resonant at other parts of the line. We conclude that the SEDOR lines in Fig. 1 are a good representation of the contribution of the surface nuclei to the total line.

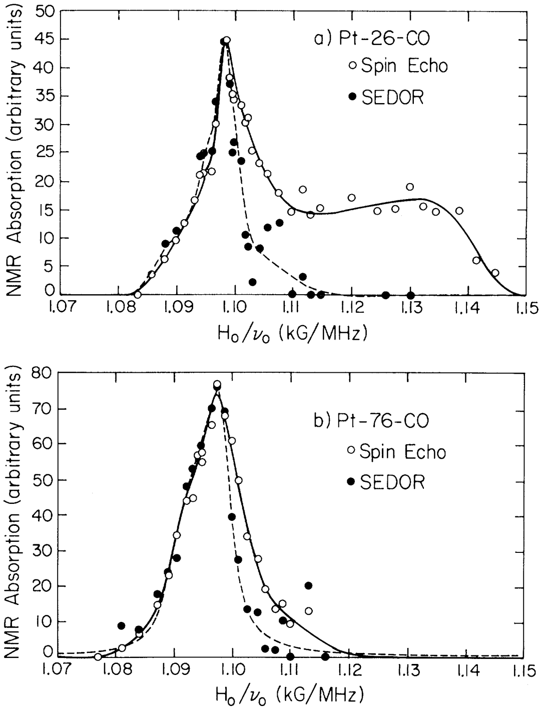

FIG. 1. SEDOR and spin-echo line shapes for (a) Pt-26-CO and (b) Pt-76-CO. The solid and dashed curves are shown only to guide the eye.

In contrast to the very different shapes of the total ^{195}Pt resonance line found in samples Pt-26-CO and Pt-76-CO, the SEDOR line shapes are almost the same for both samples. The centers of gravity of the lines are 1.0965 ± 0.0005 and 1.0954 ± 0.0005 kG/MHz for the 26% and 76% dispersions, respectively. Brown *et al.*[9] studied the ^{195}Pt resonance in carbonyls, finding $H_0/\nu_0 = 1.0975$ kG/MHz for ^{195}Pt in $[(\mathrm{Pt})_3(\mathrm{CO})_6]^{2-}$, $[\mathrm{Pt}_6(\mathrm{CO})_{12}]^{2-}$, and $[\mathrm{Pt}_9(\mathrm{CO})_{18}]^{2-}$ and another line at 1.0980 kG/MHz in the last molecule. Since the known range of Pt chemical shifts in diamagnetic compounds is from 1.0855 to 1.0995 kG/MHz, it is clear that the surface atoms in the metal coated with CO behave much like those in Pt carbonyls. The resonance is *far* from the

^{195}Pt resonance in bulk metal at 1.138 kG/MHz; however, the spin-lattice relaxation time of the surface ^{195}Pt is only 10 times slower than that in bulk metal. The width of the surface peak (330 G full width) is too big to arise from internuclear couplings. The asymmetric shape could result from variations in the chemical and Knight shifts[10] across the surface, from anisotropies in the chemical or Knight shifts, or from a superposition of lines of different widths with slightly different positions due to the inequivalent Pt bonding types. The latter hypothesis suggests that specific parts of the ^{195}Pt and ^{13}C lines might be correlated for SEDOR, but no correlation is observed. Study of SEDOR as a function of ^{13}C frequency enables one to plot the ^{13}CO line shape of CO adsorbed on the Pt, and in our case when this is compared with the ^{13}CO line shape observed directly it demonstrates that all the ^{13}CO in our sample is adsorbed on the Pt.

We measure the relative spin-echo intensity $S(\tau)$ observed with and without SEDOR using various pulse separations τ, shown in Fig. 2 for PT-76-CO. The data for sample PT-26-CO are similar. From this dependence we extract the value of the ^{195}Pt-^{13}C internuclear coupling.

A hypothesis as to the likely binding sites of CO on the Pt surface is needed to interpret the SEDOR data. We use a model based on the results of UHV studies of single-crystal Pt(111) surfaces, since small Pt particles expose mostly the (111) crystal face.[11] CO adsorption on Pt is molecular without any evidence for dissociation and forms half a monolayer at room temperature.[12,13] Below 270 K the CO overlayer orders into a $c(4\times 2)$ structure with a half-and-half mixture of on-top and bridge sites for the CO.[13,14] Three inequivalent Pt sites occur. Using this model and assumptions representative of the data, one can work out the theory of $S(\tau)$ as[6]

$$S(\tau)=\tfrac{1}{4}+\tfrac{1}{4}G(\tau,J_t,r_t)+\tfrac{1}{2}G(\tau,J_b,r_b), \qquad (1)$$

with

$$G(\tau,J,r)=1-\beta\{1-\exp[-(2\pi^2J^2+\alpha/r^6)\tau^2]\}, \quad (2)$$

where the first term in the exponential is from the indirect coupling J between the ^{195}Pt and ^{13}C, and the second term is from the dipolar interaction, with the internuclear separation r and

$$\alpha=\tfrac{2}{5}\gamma_{\mathrm{Pt}}^2\gamma_{\mathrm{C}}^2\hbar^2=6.615\times10^{-4}\ \text{Å}^6/\mu\text{sec}^2.$$

γ_{Pt} and γ_{C} are the respective gyromagnetic ratios. The subscripts b and t refer respectively to the bridge and on-top bonding sites for the CO. The parameter β gives the probability that an available site is occupied by a ^{13}C which has its spin flipped by the NMR. The solid curve in Fig. 2 is a least-squares fit of Eq. (1) to the data. While the fit shows that the model for the CO bonding site selected above is consistent with the data, other models are not ruled out. For example, a model for a $c(4\times 2)$ overlayer using only bridge sites, once also considered a possible structure,[12] gives the dashed line.

The indirect coupling J is relevant only if the C is directly bonded to the Pt. If this coupling is not included (by setting $J_b=J_t=0$) a Pt-C separation of about 1.5 Å follows from the fit to Eq. (1). Since this separation is less than the observed bond length in any Pt carbonyl, the data require that the CO be bonded to the surface Pt atoms through the C.

As in all measurements of ^{195}Pt-^{13}C internuclear couplings, the sum but not the relative sizes of the dipolar and indirect interactions are determined by NMR alone. Both couplings can be found from NMR if a measurement of the Pt-C bond distance is made, for example, by EXAFS (extended x-ray-absorption fine structure). In the current absence of such data, we estimate this bond length by the value observed in Pt carbonyls: $r_b=2.03$ Å for bridge bonds and $r_t=1.79$ Å for linear (on-top) bonds.[15] The least-squares fits to Eq. (1) then give $\beta=0.586$, $J_b=1294$ Hz, $J_t=1065$ Hz for Pt-26-CO, and $\beta=0.459$, $J_b=1646$ Hz, $J_t=1473$ Hz for Pt-76-CO. Given the observed ^{13}C lines, these values of β require the expected half monolayer coverage of CO. Also, notice that the values for J fall in the range of 1000 to 1800 Hz

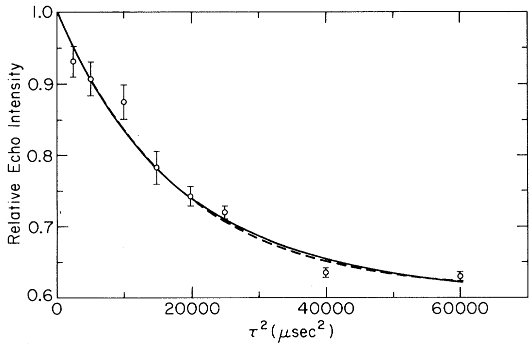

FIG. 2. Dependence of the relative spin-echo intensity with and without SEDOR on the pulse separation τ for Pt-76-CO. The solid curve is a least-squares fit to the data for a CO $c(4\times 2)$ overlayer with half bridge sites and half on-top sites. The dashed curve is for a fit assuming only bridge sites.

observed for Pt-CO complexes.[16] The SEDOR data therefore are consistent with the viewpoint that the bonding of CO to the Pt surface is very much like the bonding in carbonyls. The bond is thought to involve the Pt $5d$ orbitals and the CO 5σ and $2\pi^*$ orbitals.[12,17]

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Resonantly Stimulated Desorption of Pyridine from Silver Surfaces by Polarized Infrared Laser Radiation

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Resonantly excited desorption of pyridine molecules adsorbed on silver surfaces at 95 K has been observed. The strong dependence of the laser-induced desorption on the laser wavelength and the polarization of the incident radiation clearly show that molecular vibrational activation plays a major role in the observed desorption phenomenon. The desorption yields per laser pulse are also determined from the thermal desorption spectra and the x-ray photoemission-spectroscopy intensity analyses.

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The subject of laser-stimulated desorption has recently attracted considerable theoretical as well as experimental attention.[1-5] In the experiment reported by Heidberg *et al.*,[4] it was shown that CH_3F molecules adsorbed on a NaCl surface could be desorbed by resonant vibrational excitation of the molecules with an infrared laser. A similar experiment by Chuang[5] also showed that CO_2 laser pulses could excite the asymmetric ring-mode vibration of pyridine molecules and induce the adsorbed species to desorb from the surface of a KCl crystal which is optically transparent in the CO_2 laser wavelength region. In this Letter, we report the first study of resonantly stimulated desorption of pyridine from metallic silver surfaces excited by polarized CO_2 laser radiation. It is well known that the extent of infrared absorption by a molecular monolayer ad-