Nuclear-Magnetic-Resonance Study of the Bonding and Diffusion of CO Chemisorbed on Pd

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The authors report use of ^{17}O and ^{13}C NMR to study the bonding of CO on Pd particles. By ^{17}O-^{13}C double resonance, they measure the CO bond length to be 1.20 ± 0.03 Å. The ^{13}C resonance frequency is exceptionally high, 310 ppm above values typical for metal carbonyls. Evidence that the shift arises from electron-spin polarization is given from studies of the magnitude and the dependence on temperature and frequency of the ^{13}C spin-lattice relaxation time. A diffusion energy of 6 ± 2 kcal/mol, half that of CO on Pt, is deduced from motional narrowing of the ^{13}C NMR line.

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We report NMR studies of CO chemisorbed on Pd metal for samples consisting of small metal particles supported on alumina. We have determined the C—O bond length in an experiment which directly measures the magnetic dipolar coupling between ^{17}O and ^{13}C nuclei in isotopically enriched ^{13}C^{17}O molecules. Since the dipolar coupling depends strongly on the internuclear distance, this experiment is a sensitive probe of the bond length. The C—O bond length is expected to be strongly influenced by bonding to the metal surface, so that measurement of the bond length provides an important test of theories of the bonding of CO to the metal.

To our knowledge, the only other measurement of the bond length of CO chemisorbed on metals is that of Behm and co-workers.[1] They measured the bond length of CO chemisorbed on a Pd(100) single-crystal surface using low-energy electron diffraction (LEED), and found 1.15 ± 0.10 Å. Our result represents a threefold increase in the accuracy of the measurement, and allows comparisons with the bond length of CO in other cases.

We use an ^{17}O-^{13}C spin-echo double resonance (SEDOR) experiment in which we observe the effect on the ^{17}O NMR of flipping the spins of the ^{13}C nuclei. This is the first reported use of ^{17}O NMR to study chemisorption on metal surfaces. We discuss how we have solved the problems posed by the particularly weak ^{17}O signal and the complications arising from the quadrupole coupling of the ^{17}O nuclei.

The ^{13}C NMR of the chemisorbed CO has some unusual features which give further information about the bonding of the CO to the Pd surface. The center of the ^{13}C resonance line is 540-ppm higher in frequency than the ^{13}C resonance of tetramethylsilane (TMS), which is commonly used as a reference. This is the largest reported shift for ^{13}C in molecules that do not contain paramagnetic centers, and falls far outside the range of known ^{13}C chemical shifts. We show that the shift arises from electron spin polarization (a Knight shift) which results from the mixing of the Pd conduction band with the CO molecular orbitals. The resonance narrows at higher temperatures because of the diffusion of the CO on the Pd surface, but the details of the narrowing differ strongly from conventional cases. We show that this difference results from the distribution in the size of our Pd particles. From the narrowing, we deduce an activation energy for diffusion of 6 ± 2 kcal/mol, only half that of CO on Pt,[2,3] the element directly below Pd in the periodic table.

Our samples are small Pd particles supported on η-alumina. They are 5% Pd by weight. The fraction of Pd atoms at the surface of the particles has been measured by chemisorption and is 19%. The surface is saturated with CO. We have used two types of CO gas: CO enriched to 90% in ^{13}C for the ^{13}C line shape and relaxation measurements, and CO enriched to 36% in ^{17}O and 99% in ^{13}C for the measurements involving ^{17}O NMR. The adsorption is done at room temperature. Our sample preparation procedure has been previously described.[4]

To measure the C—O bond distance, we have used a SEDOR pulse sequence introduced by Wang, Slichter, and Sinfelt.[5] We observe the ^{17}O spin echo that follows an ^{17}O 90°-180° pulse sequence, with and without a ^{13}C 180° pulse applied a time τ after the ^{17}O 90° pulse. The ^{13}C pulse reduces the ^{17}O signal. We measure the reduction as the difference in the amplitude of the ^{17}O spin echo with and without the ^{13}C pulse, normalized to the amplitude without the ^{13}C pulse, and call it the SEDOR fraction f.

In contrast to our previous studies of surfaces, which involved NMR of ^{13}C and ^{1}H, both nuclei with spin $\frac{1}{2}$, ^{17}O has spin $\frac{5}{2}$ with consequent complications arising

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from electric quadrupole coupling. Indeed, we observe only the ^{17}O transition in which the component of the ^{17}O spin parallel to the magnetic field (typically 80 kG) changes between $+\frac{1}{2}$ and $-\frac{1}{2}$. The limitation to only one of the five transitions, combined with the low gyromagnetic ratio of ^{17}O and the modest isotopic enrichment, makes the ^{17}O signal difficult to observe.

By our previous methods, it would have taken three weeks to collect each data point. Two modifications reduce this time to three hours. First, we increase the magnetization by performing the experiment at 4 K instead of 77 K. Second, we replace the normal 90°-180° spin-echo sequence with a Carr-Purcell[6] sequence. In the standard sequence we generate one echo in each repetition of the experiment. The time between repetitions must be comparable to the spin-lattice relaxation time. In the Carr-Purcell sequence, we repeatedly refocus the magnetization with 180° pulses to generate trains of eight echoes within a single repetition. By adding the echoes together we improve the signal-to-noise ratio per cycle by $\sqrt{8}$, and increase the speed of data collection eightfold.

The SEDOR fraction is given by[7]

$$f = \alpha \langle 1 - \cos A\tau \rangle_{\text{average over all angles}}, \tag{1}$$

where α is an overall scaling factor to account for the efficiency at flipping ^{13}C spins and for background ^{17}O in the Al_2O_3 of the sample, τ is the time between the ^{17}O 90° pulse and the ^{13}O 180° pulse, and A is the C-O dipolar coupling,

$$A = (\gamma_O \gamma_C \hbar / r^3)(1 - 3\cos^2\theta). \tag{2}$$

Here γ_O and γ_C are the gyromagnetic ratios of the ^{17}O and the ^{13}C, respectively, $\hbar$ is Planck's constant divided by 2π, r is the C-O internuclear distance, and θ is the angle between the CO bond axis and the external magnetic field. Because A is inversely proportional to the cube of the internuclear distance, the τ dependence of the SEDOR fraction is a sensitive probe of the bond length.

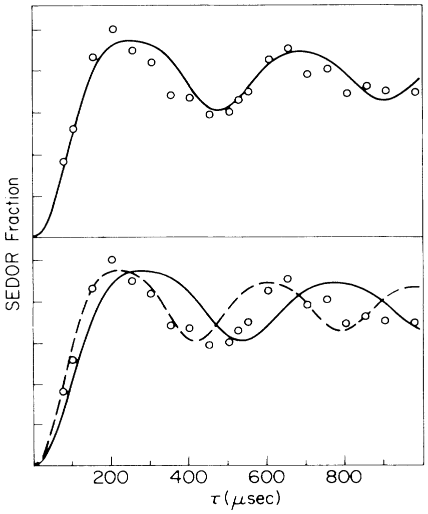

FIG. 1. SEDOR fraction vs τ for CO chemisorbed on Pd. (a) The data fitted by a bond length of 1.20 Å. (b) Predictions for bond lengths 1.15 Å (dashed line) and 1.25 Å (solid line). Each data point represents the sum of approximately 10000 spin echoes.

Our experimental results are shown in Fig. 1(a) with the theoretical prediction for a bond length of 1.20 Å. The only parameters of the fit are the bond length, which determines the frequency of the oscillations, and the scaling factor α which has no effect on the frequency. Shown in Fig. 1(b) are predictions for bond lengths of 1.15 and 1.25 Å. They clearly do not fit the data. We therefore assign a bond length of 1.20 ± 0.03 Å.

CO bonds to metal surfaces in both bridge and linear configurations, but for CO adsorbed at saturation on Pd(100) and Pd(111) surfaces, only bridge configurations are found.[1,8] Our measured bond length is somewhat longer than the 1.12 to 1.16 Å found in linear carbonyls, and is typical of that in bridging carbonyls.[9]

Figure 2 shows the ^{13}C resonance line for CO chemisorbed on Pd measured from 198 to 298 K. Zilm[10] has observed a ^{13}CO line shape at room temperature that agrees with our room-temperature result. The narrowing of the line between 198 and 298 K and the frequency shift upon narrowing, both seen in Fig. 2, are discussed below.

The breadth of the low-temperature line is due to anisotropy in the chemical shift tensor and to the inhomogeneous field induced by the susceptibility of the Pd particles, $4\pi\chi/3 = 268$ ppm. The center of the line is 540 ± 30 ppm downfield from the ^{13}C resonance of TMS, often used as a reference. This 540-ppm shift is much larger than those in metal carbonyl molecules, which are generally in the range 180–270 ppm.[11] The

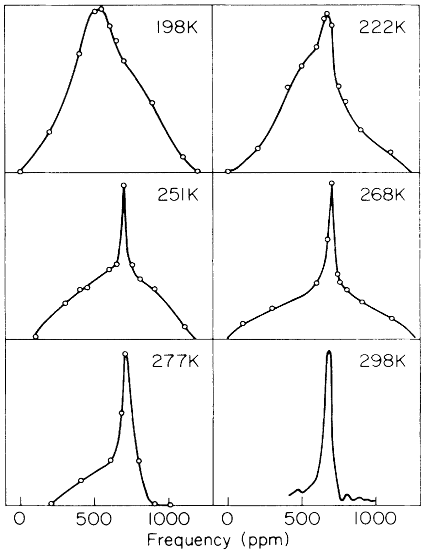

FIG. 2. The ^{13}C line shape as a function of temperature.

chemical shift for bridge bonded CO in metal carbonyls is typically 230 ppm.[11]

Thus we take the ^{13}C chemical shift of CO chemisorbed on Pd to be 230 ppm. Our previous studies of CO chemisorbed on Pt[4] suggest that the additional shift of 310 ppm might be a Knight shift, arising from polarization of conduction-electron spins. If there is a Knight shift K, then there must be a corresponding relaxation time T_1 given by the Korringa relation[12]

$$T_1 T K^2 = (\hbar/4\pi k_B)(\gamma_e^2/\gamma_n^2)B. \tag{3}$$

Here T is the temperature in degrees Kelvin, $\hbar$ Planck's constant, k_B Boltzmann's constant, γ_e and γ_n the gyromagnetic ratios of the electron and the nucleus, respectively, and B a constant of the order of unity. There may be additional relaxation mechanisms present that are associated with the conduction electrons but do not give rise to a net shift of the NMR line.[3] For all such mechanisms, T_1 is inversely proportional to the temperature. Therefore the relaxation time must be at least as short as that predicted by the Korringa relation. We take $B=1$ and calculate $T_1 T = 43 \pm 7$ s K for a Knight shift of 310 ± 30 ppm. The data in Fig. 3 show that, below 200 K, $T_1 T = 29$ s K. We conclude that below 200 K the temperature dependence of the spin-lattice relaxation clearly reflects the presence of conduction electrons at the ^{13}C nucleus, a result of the mixing of the Pd conduction band with the CO molecular orbitals, and that the observed shift is a Knight shift.

The decrease of the product $T_1 T$ in the range 200–400 K can be accounted for if the frequency shift upon narrowing seen in Fig. 2 is a Knight shift. We postulate that an increase in the Knight shift occurs because we observe the NMR associated with sites on the Pd surface that we do not detect at lower temperatures. Fast diffusion can also produce a decrease in the product $T_1 T$ which should be dependent on the NMR frequency.[13] We find no such frequency dependence (Fig. 3). This result is expected from our measurement of the diffusion rate, which is described below.

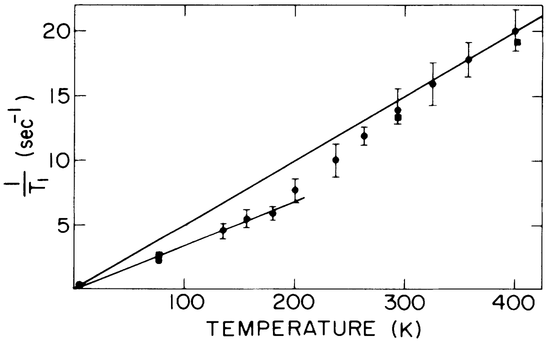

FIG. 3. The dependence of the ^{13}C spin-lattice relaxation rate $1/T_1$ on temperature at magnetic fields of 80 kG (circles) and 58 kG (squares).

As the temperature is increased from 198 to 298 K, the NMR adsorption lines appear as a superposition of a narrow and a broad line (Fig. 2). Line narrowing is a familiar phenomenon in NMR, and results from the averaging of the local magnetic fields seen by each nucleus as it diffuses. These peculiar line shapes suggest the presence of two diffusion energies, but we find that we can explain our result with a single diffusion energy, if we simply take into account the distribution in the sizes of the Pd particles in our sample. We also note that the line narrows to 50 ppm. This incomplete narrowing has been previously observed and explained for C atoms on Pt particles.[13]

Motional narrowing occurs when the correlation time τ for diffusion is less than the inverse of the rigid lattice linewidth $\delta\omega_0$. Then the narrowed linewidth $\delta\omega$ is given by

$$\delta\omega = (\delta\omega_0)^2 \tau. \tag{4}$$

τ is the average time for a CO molecule to explore an area large enough to sample all values of the local fields. We assume that on the particle surface the number of jumps required to sample all local fields is $(\pi d/4a)^2$, where d is the particle diameter and a the jump distance. We take a as the Pd-Pd nearest-neighbor distance. If the mean time between jumps follows an Arrhenius behavior, we can relate the diffusion energy E, particle size d, and temperature T by

$$\tau = (\pi d/4a)^2 \nu^{-1} \exp(E/k_B T), \tag{5}$$

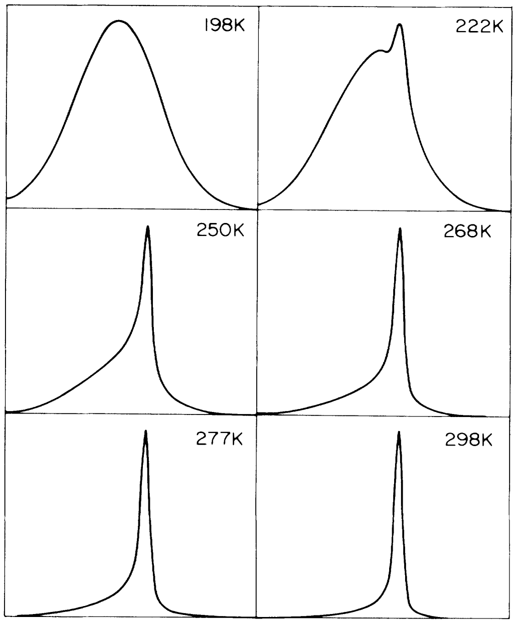

FIG. 4. The results of a computer simulation of the line narrowing. The simulation assumes a diffusion energy of 6 kcal/mol and a particle-size distribution reasonable for our sample.

where v is a frequency prefactor we take to be $10^{13}\ \mathrm{s}^{-1}$.

This model can account for the details of the narrowing if we assume a particle-size distribution consistent with surface area measurements and electron microscope studies of our sample. The onset of narrowing corresponds to motion on the smallest Pd particles. Narrowing is complete when motion is fast enough to satisfy the criterion for narrowing, $\tau \ll 1/\delta\omega_0$, on the largest particles. From the temperature range over which the narrowing occurs, and with our particel-size distribution, we deduce a diffusion energy for CO on the Pd surface, $E = 6 \pm 2$ kcal/mol. The accuracy is determined by uncertainties in the parameters of the model rather than scatter in the data.

The results of a computer simulation of the narrowing are shown in Fig. 4. We have assumed a diffusion energy of 6 kcal/mol and the particle-size distribution deduced for our sample. The simulation starts with a Gaussian line 600 ppm broad and allows narrowing to a Gaussian line 50 ppm broad shifted 200 ppm downfield. The simulation shows that the unusual shapes of the partially narrowed lines are due to the particle-size distribution.

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