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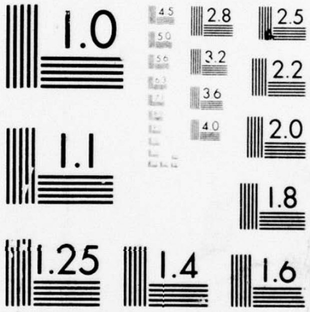

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^{13}C NMR spectrum of carbon monoxide chemisorbed on supported rhodium has been studied. Temperature dependent lineshape changes have been observed suggesting that anisotropic carbon monoxide motions occur in the chemisorbed layer.

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^{13}C NMR of CO Chemisorbed onto Dispersed Rhodium[#]

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[**] Deceased

The chemisorption of CO on transition metals has been extensively studied in attempts to characterize the adsorbed state of the molecule[1-5]. We wish to report here the first observation of a molecule chemisorbed on a dispersed metal catalyst by ^{13}C nuclear magnetic resonance (NMR). The preliminary spectra reported indicate that the adsorbed CO is undergoing anisotropic, or "fluxional," motion on the surface and strongly imply the presence of a species not observed by infrared techniques. To date, evidence for the surface intermediates for the catalytic methanation reaction of CO and H_2 over dispersed metal catalysts has been based on infrared studies [6]. Thus, the presence of a previously unobserved surface species is potentially important in understanding the reaction mechanism.

The sample was contained in a specially constructed infrared/NMR cell where both infrared and NMR measurements could be made. The infrared cell, a stainless steel body with single crystal CaF_2 windows, and the bakeable, all-metal 10^{-8} Torr vacuum system have been previously described[1]. The NMR measurements were made at 14.7 MHz in a 10 mm single-resonance probe using a previously described spectrometer[7]. A 10 mm pyrex tube fused to a copper tube and then welded to a ¼ inch stainless steel port of the infrared cell[1] served as the NMR sample holder. Since the low signal level of the NMR signals required signal averaging, an alternative pulse sequence, $90^o/180^o-\tau-90^o$, was used with free-induction decays taken after each 90^o pulse and alternately added and subtracted to eliminate instrumental artifacts. Approximately 400,000 such transients were accumulated for the room-temperature spectra and 100,000 for the lower temperature spectra. Transients were accumulated with $\tau = 500$ microseconds at intervals of 0.40 seconds to optimize the signal-to-noise.

The 2.2% Rh on Al_2O_3 sample was prepared as previously described[1,5], but with the addition of 100 ppm of Fe to the sample. The 2.2% Rh/Al_2O_3 sample was then reduced in H_2 at 150° C and degassed as previously described[1] and then exposed to 50 torr of 90% ^{13}C-enriched CO at room temperature. An infrared spectrum taken between 4000 and 1200 cm^{-1} confirmed that the surface was free of impurities observable by IR prior to adsorption. The infrared spectrum taken after adsorption was identical to the previously reported spectra taken at saturation coverages (see Figure 5d, reference 1). The corresponding ^{13}C NMR spectrum taken at 300 K is shown in Figure 1a. The CO gas pressure was reduced to 0.02 torr to prevent any extraneous signal from CO condensed on the alumina, and the ^{13}C NMR spectrum was taken again at 80 K and is illustrated in Figure 1b. Finally, the solid state ^{13}C spectra of a model compound, $Rh_2Cl_2(CO)_4$ was taken at room temperature (328 transients) and is shown for comparison in Figure 1c. The area of the ^{13}C spectra indicates that there is ~0.9 CO molecule adsorbed for each Rh atom, and this is consistent with an extrapolation of previously obtained adsorption isotherms at lower coverage.[1]

The center of mass, or isotropic chemical shift, of each spectrum is located near -191 ppm relative to tetramethylsilane (note σ values[8], not δ values are reported here). The constant center of mass together with a temperature-dependent lineshape that approaches that of the model compound at the lowest temperatures studied indicates that an activated anisotropic reorientational motion of the CO molecule on the surface is responsible for the partial collapse observed in the spectra of the surface-adsorbed CO. It is possible to rule out an activated exchange between the surface-adsorbed and gas phase carbon monoxide since the spectrum did not broaden after the CO gas pressure was reduced by 8 orders of magnitude. Fluxional, or ligand, exchange processes have been observed widely in organometallic molecules[9] and could be responsible for the observed motional averaging, as could a restricted diffusion over a small metal particle. Since the anisotropy of the ^{13}C chemical shift tensor of the carbonyl ligand is very large, ~400 ppm, it overlaps the spectra of other possible surface species and a clean separation of such spectra will require the application of more complex NMR techniques including the use of magic-angle sample spinning[10]. However, a simple observation of the lineshape changes as a function of surface treatment is already furnishing new information, and possibly most important, evidence for the existence of a previously unobserved species in high concentration on the surface. For example, previous infrared studies[1,5] have shown that the CO is slowly desorbed from the Rh sites at 300 K. By constantly evacuating with an ion pump for two months, the equilibrium pressure of the sample was reduced to 3×10^{-7} torr. The infrared signal decreased uniformly to 20% of its original area (for example, see Figure 4, reference 1). However, the ^{13}C NMR line retained 85% of its original area. Upon redosing to 50 torr of CO the infrared spectrum returns to 90% of its original intensity and the NMR spectrum returns completely. A naive argument assuming a concentration-independent extinction coefficient for the infrared spectra would suggest that only 20% of the surface species are observed with infrared techniques. Further experimental work confirms that the NMR techniques are observing other species not revealed by the infrared techniques; for example, heating the samples to 423 K for three hours in the presence of 20 torr of CO results in a new sharp feature at $\sigma \sim -176$ ppm in the NMR spectrum and increases the ^{13}C spectrum intensity by 30%, while the infrared spectrum exhibits a depletion of the doublet bond of the $Rh(CO)_2$ feature. Yet, isotopic exchange experiments (^{13}CO-^{12}CO) performed at room temperature demonstrate the rapid and complete exchange of all observed surface species for both the NMR and infrared spectra.

In summary, we have reported what we believe to be the first ^{13}C NMR spectra of molecules chemisorbed to a dispersed metal catalyst. We have demonstrated that even these preliminary spectra contain useful information for characterization of the surface species.

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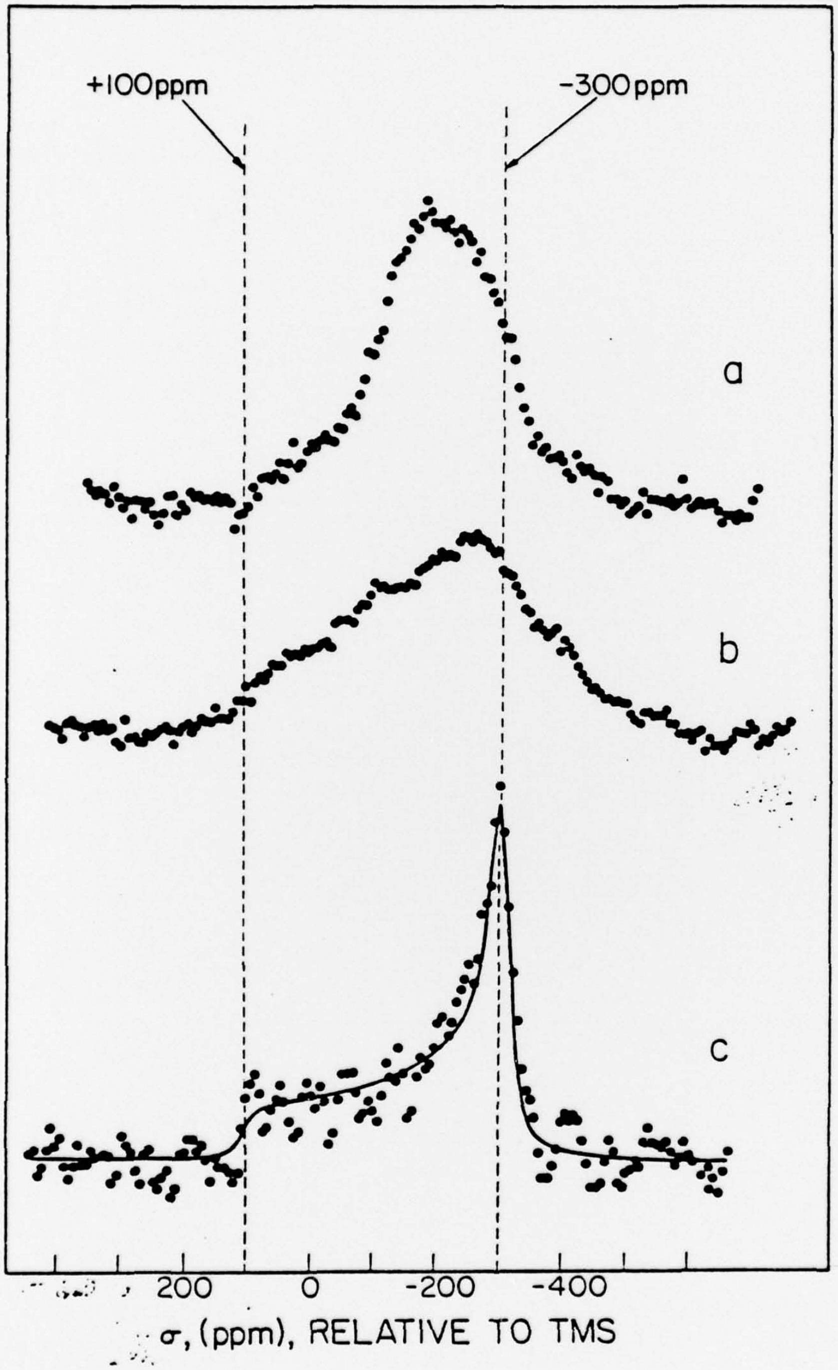
Figure Caption

Figure 1. ^{13}C NMR spectra of: (i) a 2.2% Rh/Al_2O_3 sample saturated with 50 torr of ^{13}CO at 300 K; (ii) the same sample, but pumped down to .02 torr ^{13}CO, and cooled to 80 K; and (iii) a solid compound, $Rh_2Cl_2(CO)_4$, at 300 K (enriched to 20% ^{13}C).


+100ppm
-300ppm
a
b
c
200
0
-200
-400
σ, (ppm), RELATIVE TO TMS