Nuclear Magnetic Resonance Spectroscopic Study of the Electrochemical Oxidation Product of Methanol on Platinum Black

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Abstract: The adsorbate resulting from the potentiostatic, catalytic decomposition of methanol (0.1 M CH_3OH in 0.5 M H_2SO_4) on a platinum black electrode has been studied via ^{13}C nuclear magnetic resonance spectroscopy, at open cell potential. Cyclic voltammetry results indicate that coverage is a function of electrodecomposition time and potential. The spin−spin relaxation time T_2 is dependent on surface coverage and ranges from ~3 to ~1.8 ms at coverages ranging from 0.3 to 0.75 ML, due to the increased effectiveness of ^{13}C−^{13}C dipolar interactions at high coverage. At 0.5 ML, the temperature dependence of the ^{13}CO T_2 (in a ^2H_2O-exchanged electrolyte system) has been determined from 80 to 250 K. There is a well-defined peak in relaxation rate at ~170 K which can be modeled using a simple diffusional model having an activation energy of 7.9 ± 2.0 kcal/mol. Spin−lattice relaxation results from 10 to 250 K reveal Korringa behavior, with a T_1T product (and Knight shift) that is independent of surface coverage, and has the same value for the electrochemical adsorbate as gas phase CO adsorbed on Pt. The similarity in T_1T, T_2, Knight shift, and activation energy for surface diffusion are in general accord with values previously measured in gas phase heterogeneous catalyst systems and strongly support the idea of primarily on top CO with C-down, on one major type of surface site.

Introduction

NMR spectroscopy has become an important tool for the study of surface phenomena.[1,2] While NMR techniques enable investigation of both static and dynamic structural features, their poor sensitivity in surface studies requires samples of very high surface area. Hence, NMR studies have generally been carried out with small supported metal particles, as typically used in heterogeneous catalysis.[3] Recently, however, we have shown that unsupported metal electrocatalysts can also be investigated, even in an electrochemical environment, which opens up new possibilities for the study of electrode adsorption, surface diffusion of electrochemical adsorbates and poisoning reactions in fuel cells.[4] Such studies should also enable a comparison of results obtained from different types of spectroscopy[5] and, in the longer term, offer an exciting challenge for theoretical analyses of structure and bonding at the solid−liquid interface, including the effects of electrode potential on the electronic properties of the chemisorption bond.

Here, we are concerned with CO ex MeOH binding to platinum in an electrochemical environment. Earlier workers have indicated that the chemisorption of CO ex MeOH onto polycrystalline Pt can be generally characterized in terms of the presence of both bridge-bonded and linearly bonded CO.[6] At high MeOH concentrations (>0.1 M, in perchloric acid) both species appear to be present, whereas at lower concentrations, only bridge-bonded CO was found, using sum-frequency generation spectroscopy.[7] The presence of multiply-bonded CO was found to be much more pronounced on supported platinum particles than on bulk Pt metal.[8] We show (using variable temperature NMR experiments) that the electrochemical oxidation process used in this work produces CO which occupies only a single type of surface site, at high coverage. We deduced the activation energies for CO diffusion, the rates of CO motion, and make a comparison of results for CO on Pt at the gas/solid and solid/liquid interfaces. Our results on the electronic properties of the chemisorption bond, the surface diffusion rates, and the structure of the adsorbate suggest new avenues for the study of electrode adsorption and direct oxidation fuel cell (DMFC) catalysts, including in situ investigations.

Experimental Section

Sample Preparation. Fuel cell grade polycrystalline (PC) platinum black (~80 Å diameter) was obtained from Johnson & Matthey (Ward Hill, MA). The use of high surface area (24 m²/g) fuel cell grade platinum and 99.9% ^{13}C enriched methanol and CO (Cambridge Isotope Laboratories; Cambridge, MA) was necessary in order to obtain adequate sensitivity for the NMR measurements. All water used in the preparations was obtained from deionized water that had been further purified with a Millipore Milli-Q Plus 185 filtering system (Millipore, Redford, MA) to a resistivity of 18.2 MΩ/cm. D_2O

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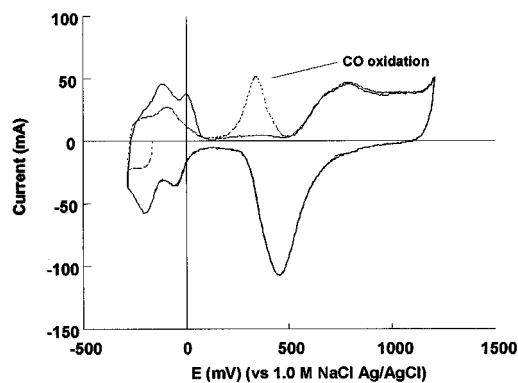
Figure 1. First cycle (dotted line) showing the amount of coverage from the CO oxidation peak. The second curve (solid line) is characteristic of the polycrystalline platinum voltammograms routinely obtained.

(SIGMA, St. Louis, MO) for T_2 measurements were distilled from potassium permanganate. All other reagents were reagent grade or better and were obtained from Aldrich (Milwaukee, WI), unless otherwise noted. All solutions were degassed by bubbling with ultrapure (99.9995%) N_2 for at least 30 min before use.

The preparation of CO from methanol decomposition on PC platinum black was accomplished in the following manner: First, the platinum powder was cleaned in hot (60 °C) chromic acid for at least 1 h. The platinum was then thoroughly rinsed with water and stored in 0.5 M sulfuric acid. The decomposition of methanol was performed in a specially designed three electrode electrochemical cell, which comprised a medium fritted funnel and a Teflon cap which supported the electrodes. The working electrode was a piece of perforated platinum foil fashioned into a square "boat", roughly 2 × 2 cm, placed on the frit of the funnel. The counter-electrode consisted of a piece of platinized platinum gauze roughly 6 cm². All potentials were referenced to a 1.0 M NaCl Ag/AgCl reference electrode. Between 300 and 400 mg of platinum powder was introduced into the boat via a pipet, and the potential cycled at 1.0 mV/s in 0.5 M sulfuric acid for approximately 12 h until a characteristic polycrystalline platinum voltammogram was obtained, as shown in Figure 1. The potential was then held at the desired value and the electrolyte drawn through the funnel by vacuum, leaving only enough (~5−10 mL) to maintain continuity between the electrodes. The potential was maintained in this manner for all steps requiring solution exchange. Finally, a solution of 0.1 M ^{13}C enriched methanol in 0.5 M sulfuric acid was introduced, and allowed to sit for a given length of time. The duration of the decomposition depended on the potential, and the amount of coverage desired. For direct ^{13}CO adsorption, ^{13}CO was simply sparged through the cell for the duration of the adsorption. At the end of the adsorption/decomposition, the ^{13}C-enriched MeOH/CO solution was removed by filtration. The cell was refilled with 0.5 M sulfuric acid and rinsing continued for a total of at least 6 complete volumes (50 mL each). Approximately 200 mg of the voluminous CO-platinum material was removed and mixed with roughly 300−400 mg (about 40−50% by volume) of glass beads (Sigma; 106 μm and smaller−cleaned identically to the platinum black) to reduce contacts between Pt particles and thus increase the radio-frequency field penetration during NMR measurements. At all times the CO-platinum was deep in the supporting electrolyte to minimize atmospheric exposure. The CO−Pt/glass mixture was transferred to a cylindrical Pyrex glass ampoule (1.0 cm diameter × 3.5 cm length) which was then attached to a vacuum apparatus fitted with a nitrogen purge line. Samples were subjected to reduced pressure (0.1 mmHg for about 10 s) and then purged with ultrapure nitrogen. The pump/purge cycle was repeated at least three times. The ampule was then chilled to 77 K and flame sealed under a slightly reduced pressure. The sample was stored at 77 K until NMR measurements were made. The remaining powder in the electrochemical cell was cycled from the holding potential to determine the amount of CO coverage, relative to active Pt surface sites, from the CO oxidation peak (Figure 1). During adsorption, the electrode potential was controlled by an Amel Model 550B potentiostat (ECO Incorporated, Cambridge, MA) or a Princeton Applied Research, Model 173 potentiostat (EG&G; Princeton, NJ) under computer control.
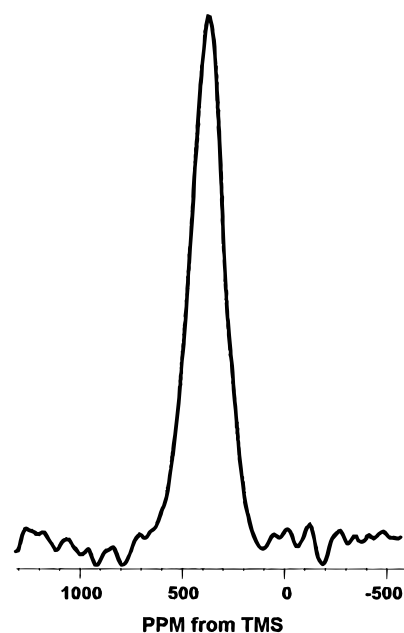

Figure 2. ^{13}C NMR line shape of +150 mV sample (4 h) at 80 K.

The deuterated samples were prepared as described above, except that the samples were rinsed with 0.5 M sulfuric acid in D_2O on the fifth and sixth rinses. The potential was maintained after the sixth rinse for 1 h, and then the sample was prepared and sealed in the above manner. The remaining powder was rinsed several times with 0.5 M sulfuric acid in normal water before coverage determination.

Nuclear Magnetic Resonance Spectroscopy. Carbon-13 NMR spectra were obtained on two "home-built" NMR spectrometers. The first consists of an Oxford Instruments (Osney Mead, UK) 8.45 Tesla 3.5-in. bore superconducting solenoid magnet, a Nicolet (Madison, WI) Model 1180 Explorer III-C/2090 transient recorder, and a variety of digital and radiofrequency circuitries. The sample probe was a conventional solenoid design and operated inside an Oxford Instruments CF-1200 cryostat, down to 10 K. The second instrument used a 7.0 Tesla Oxford magnet and a home made spectrometer. Spin-echo pulse excitation was used in all cases since the lines were broad. The 90° pulse widths were 5 μs at 8.45 T and 3 μs on the 7.0 T system at 80 K. Spin−lattice relaxation times were measured using a saturation-recovery method. A typical sample contained about 10^{19} ^{13}C spins. One measurement of a spin−lattice relaxation time required 12 to 18 h at 80 K and increasingly more scans at higher temperatures. Chemical shifts are reported in ppm from tetramethylsilane (TMS) and were set using external CS_2, taken as 192.8 ppm downfield from TMS, using the IUPAC δ-scale (high-frequency, low-field, paramagnetic or deshield-ed values are positive).

Results and Discussion

Type of Adsorbate and Adsorption Site. We show in Figure 1 the cyclic voltammogram of a typical sample produced by MeOH electrodecomposition on our polycrystalline fuel cell grade platinum electrode. The first cycle shows the amount of coverage, from the CO oxidation peak, while the second curve is characteristic of a clean platinum surface. Similar voltam-mograms were routinely obtained for all samples. Figure 2 shows a ^{13}C NMR spectrum of a +150 mV sample (4 h) at 80 K at a field of 8.45 T. The spectrum has a full width at half-height of 250 ppm, and the peak maximum occurs at 330 ppm downfield from TMS. These results are similar to those obtained for CO adsorbed from the gas phase onto small Pt particles[9] although the peak width is narrower due, we believe, to the presence of a smaller Knight shift distribution in the fuel cell Pt electrocatalyst sample.

The ^{13}C spin-lattice relaxation was found to follow a single exponential law of the form

$$M(t) = M_o(1 - e^{-t/T_1}) \qquad (1)$$

where $M(t)$, the magnetization at time t, recovers from 0 to M_o with a time constant T_1. Typical results are shown in Figure 3 and Table 1. Such single exponential relaxation behavior was found in all cases, independent of coverage or electro-oxidation potential. This is in sharp contrast to the results of previous studies of ^{13}CO chemisorbed from the gas phase onto supported Pt catalysts where multiple exponential behavior has been observed.[10] In both cases, spin-lattice relaxation can be attributed to the presence of conduction electrons on the CO adsorbate. Different adsorption sites can be expected to exhibit different relaxation rates, depending on the details of the Pt−CO chemisorption bond.

There are, however, two effects which could produce single exponential relaxation behavior even though the system actually has several sites with different intrinsic relaxation times: spin-diffusion and fast exchange between different binding sites. However, the following results lead us to rule out either of these mechanisms. First, we found that the T_1T was essentially constant from 10 to 250 K, so that motionally-averaged behavior from two or more sites of different T_1 values was unlikely given the temperatures below the onset of surface diffusion, which is discussed later. The other mechanism is spin-diffusion mediated by dipolar coupling amongst the ^{13}C spins. This process can only occur if the coupling is strong compared to the resonance frequency differences of neighboring spins. We have verified that this process does not occur by means of two experiments. First, we inverted half the line and observed that cross-relaxation or exchange between both lobes of the line did not occur in times short compared to T_1. Second, a sample with 10% ^{13}CO, prepared from 10% $^{13}CH_3OH$ mixed with 90% $^{12}CH_3OH$, was prepared, so that the average dipolar coupling among the ^{13}C spins became much weaker. Still, single exponential behavior with the same relaxation rate was observed, effectively ruling out spin-diffusion.

The surface coverage of many of our samples is known to be high from the CV measurements. In addition, an independent, microscopic characterization of surface coverage is provided by measurements of the spin−spin relaxation, T_2, as shown in Figure 4. We have actually obtained two sets of spin−spin relaxation data at 80 K. A rapid signal decay was obtained with H_2O in the electrolyte, while a slow decay was obtained with D_2O in the electrolyte. There are clearly major differences between the two relaxation plots, which must be attributed to the presence of nearby ^{1}H spins in the H_2O system. The decay of the echo-amplitude as a function of pulse spacing is the result of two mechanisms. First, the dipolar coupling among ^{13}C spins produces a so-called slow beat.[11] It can be approximated by a Gaussian having a time constant T_{2G}. Second, Pt spin-flips produce relaxation of Lorentzian character, with a characteristic time T_{2L}, as was shown previously by measurements with ^{13}CO diluted in ^{12}CO on small supported Pt particles.[11] Therefore, the spin−spin relaxation is expected to take the form

$$M(t) = M_o \exp[-(t/T_{2G})^2] \exp(-t/T_{2L}) \qquad (2)$$

Our relaxation curves are such that it is not possible to deduce from them both T_{2G} and T_{2L} at a signal-to-noise ratio which can be reasonably achieved. The Lorentzian process is in the strong collision limit in which the relaxation time is equal to

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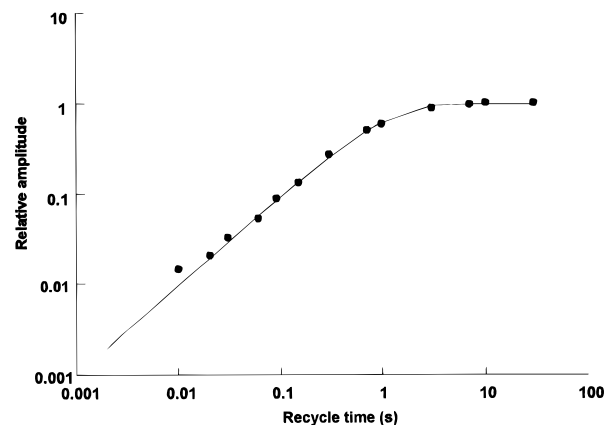(11) Ansermet, J. P.; Slichter, C. P.; Sinfelt, J. H. *J. Chem. Phys.* **1988**, *88*, 5963−5971.

Figure 3. ^{13}C spin−lattice relaxation at 80 K following open potential adsorption of methanol for 3 hours. Fit using a single exponential with a relaxation time T_1 of 1.0 s.
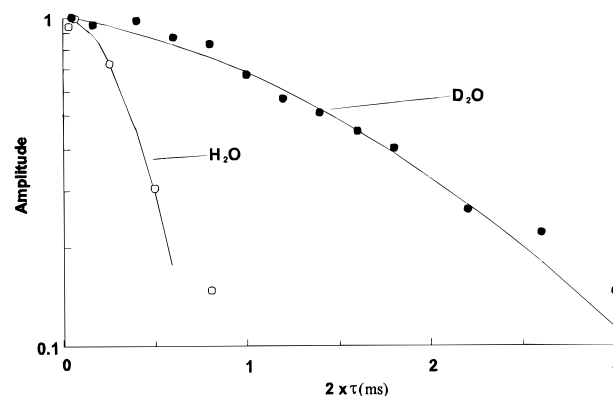

Figure 4. ^{13}C spin−spin relaxation at 80 K following methanol decomposition at −0.150 V for 3/4 hours. Sample in the presence of H_2O (○) and of D_2O (●).

Table 1. T_1T (s·K) for Several Samples

decomposition potential (V)	decomposition time (h)	surface coverage (%)	T_1T (s·K)
−0.200	5	25	78 ± 3
−0.150	24	70	96 ± 13
−0.150	4	55	88 ± 13
−0.150	3/4	30	80 ± 1
−0.150	1 (D₂O)	32	86 ± 3
0.0	3	72−79	82 ± 7
open	4	35	83 ± 10
+0.150	4 (D₂O)	48−41	84 ± 4
0.0	3−5 (D₂O)	50−76	77 ± 3
CO$_{(g)}$ adsorption in soln	3	18	88 ± 11

the correlation time and is independent of the strength of the coupling. However, we obtained an independent estimate of T_{2L} by measuring a sample in D_2O having a 9% ^{13}C isotopic abundance, and found approximately the same value as with samples of supported catalysts,[11] namely 2.7 ± 0.3 ms at 77 K. We used this T_{2L} value for all samples at 80 K. We next deduced T_{2G} from the spin−spin relaxation data obtained with samples at 77 K in D_2O, prepared under various conditions (Table 2). Again, CO coverage was deduced from CV measurements.

The relaxation data in Table 2 show the extent to which T_{2G} values are sensitive to coverage. The significance of these results becomes apparent when they are compared with theoretical estimates obtained from the slow beat behavior of simple ^{13}CO adlayer patterns on Pt single crystal surfaces.[12] For the three surface structures considered previously, T_{2G} is about 1.6 ms for c(4 × 2) at a coverage of 0.75 ML, 1.9 ms for c(2 × 2)

(12) Gaussian fits to the slow beats of ref 11.

Table 2. Coverage and T_{2G} of Samples in D_2O at 77 K

surface coverage (%)	T_{2G} (ms)
31[a]	2.9 ± 0.1
38[b]	2.1 ± 0.1
41[b]	2.1 ± 0.1
51[c]	1.9 ± 0.2
73[c]	1.8 ± 0.1

[a] Decomposition at −0.150 V. [b] Decomposition at +0.150 V. [c] Decomposition at 0.0 V.
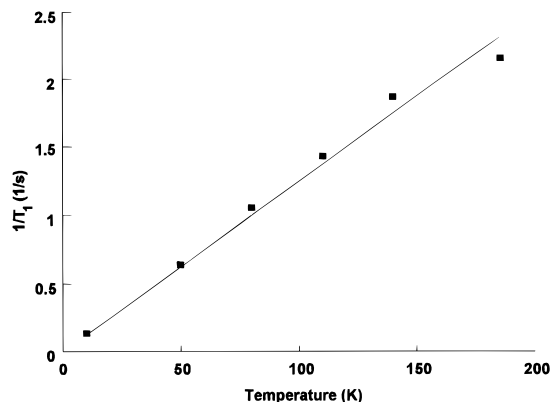
Figure 5. ^{13}C relaxation rate $(1/T_1)$ as a function of temperature. Methanol decomposition at −0.200 V for 5 hours. $T_1T = 78 \pm 3$ s·K.
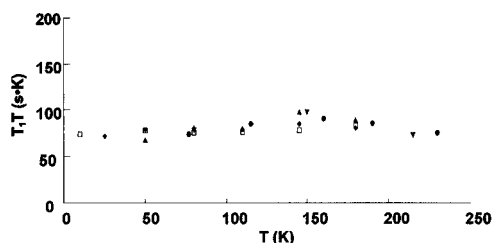
Figure 6. T_1T product as a function of temperature: ● 0.0 V 3 h; ▲ open 4 h; ▼ 0.0 V 3 h CO; ◆ −150 mV 3/4 h; □ −200 mV 5 h.

pattern on Pt(100) at 0.50 ML, and 3.2 ms for a ($\sqrt{3}$ × $\sqrt{3}$)R 30 pattern on Pt(111) at 0.33 ML. Apparently, the T_{2G} data for the electrochemical CO adsorbate on the polycrystalline platinum surface displays a similar T_{2G}-coverage relationship, consistent with increased homonuclear dipolar interactions at increased coverage.

Conduction Electrons at the C Atoms of the Adsorbate. The ^{13}C spin−lattice relaxation rate was found to be proportional to temperature for all samples, and a representative result is shown in Figure 5. That is, we find that

$$T_1T = \text{constant} \qquad (3)$$

This temperature dependence is unique to relaxation by conduction electrons. Furthermore, the magnitude of the relaxation rate is close to that of CO chemisorbed from the gas phase onto supported Pt particles, where it was shown to be due to conduction electrons at the ^{13}C nucleus.[10] We have also measured the T_1T product for several decomposition potentials and coverages as well as for CO(g) adsorbed onto Pt in this electrolyte system as shown in Table 1 and Figure 6.

The first column in Table 1 is the potential used for methanol decomposition/CO adsorption. One sample was prepared at open-cell potential, and three samples were exchanged with deuterated water in order to measure the spin−spin relaxation in the absence of protons in the electrolyte, and to verify that the protons of the electrolyte did not contribute significantly to T_1 relaxation of the ^{13}C. No definite trend in the T_1T product as a function of adsorption conditions, or temperature, could
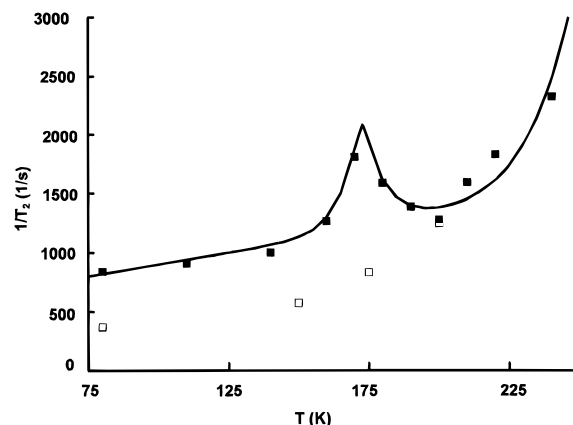
Figure 7. The temperature dependence of the ^{13}C transverse relaxation rate $(1/T_2)$ for deuterated samples. ^{13}C isotopic abundance: 99% (filled square), 9% (open square). Line: see text.

be identified, as shown for example in Figure 6, where the mean T_1T value is ∼80 ± 10 s·K. Interestingly, we find no evidence for multiple-T_1 components, unlike the situation observed previously with CO chemisorbed in vacuum.[10]

The T_1T product can also be used to make an estimate of the Knight shift, K, because both are related by the Korringa relation $T_1TK^2 = \hbar\gamma_e^2/4\pi\gamma_n^2$, to the extent that the relaxation is determined by the hyperfine contact term only and that many-body effects can be neglected.[13] For $T_1T = 80$ s·K, we predict a Knight shift of about 228 ppm. The purely orbital or chemical shift of CO on Pt can be expected to be about 165 ppm downfield from TMS, resulting in an overall frequency shift of about 390 ppm. The experimental shift is 330 ppm, Figure 2, in reasonable accord with prediction, but also possibly indicating the presence of electron orbital and hyperfine couplings, which contribute to T_1 but not to K. We believe that these spin−lattice relaxation and Knight shift measurements help characterize the chemisorption bond. For example, in contrast to the case of CO on Pt, the ^{13}C spin−lattice relaxation of CN on Pt is not at all accounted for by the Knight shift, indicating a weaker 5σ bond and a stronger 2π* bonding.[14] Moreover, the observation that the T_1T product for CO(g) adsorbed onto Pt from the electrolyte solution is the same as that obtained from methanol decomposition strongly supports the idea that both species have the same structure and that the adsorbate is hydrogen free.

Surface Diffusion of the Adsorbate. We next consider the surface diffusion of CO obtained by the electrocatalytic decomposition of MeOH. Here, we use the fact that the temperature dependence of T_2 can provide important information on the mobility of adsorbates.[15] We account for the temperature dependence of the relaxation rate, Figure 7, using a simple model. It involves three relaxation mechanisms: the fluctuations of the $^{13}C-^{13}C$ dipolar coupling by local motion of the adsorbate; the random motion over the entire surface of the particle in the field gradient produced by the particle itself, and a $1/T_2$ (other) term. Hence, we consider the following: (1) a $^{13}C-^{13}C$ dipolar coupling, with a splitting $\Delta\omega_1$; (2) diffusion through a local magnetic field gradient, ΔH_{loc}, due to the magnetic polarization of the paramagnetic particles, producing a frequency change $\Delta\omega_2$, and (3) $1/T_{2(other)}$, which represents all other relaxation mechanisms, for example, the relaxation by Pt spin flips (which is a term related to temperature, see, e.g., Figure 2 of ref 11).

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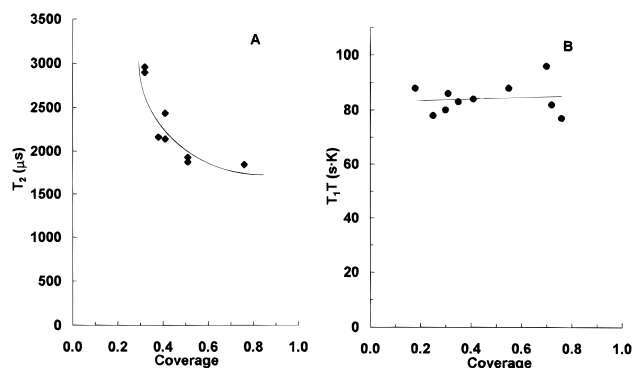(15) Ansermet, J.-P. Ph.D. Thesis, University of Illinois, 1985.

Figure 8. Spin−spin (T_{2G}) and spin−lattice (T_1) relaxation results for ^{13}CO on Pt as a function of surface coverage. A, T_{2G}; B, T_1T.

There are also two motional regimes, the strong collision limit, where $\tau_c \gg 1/\Delta\omega$, $1/T_2 = 1/\tau$, and the motional narrowing regime, where $\tau_c \ll 1/\Delta\omega$, $1/T_2 = \Delta\omega^2\tau$. For the dipolar interaction, the characteristic time τ_c is $\tau_c = \tau_{jump}$, while for diffusion over the Pt particle, $\tau_c = N^2\tau_{jump}$, where N is the number of jumps needed to travel over one quarter of the Pt surface circumference. The average jump time τ_{jump} is given by an Arrhenius relation

$$\tau_{jump} = \tau_o e^{E^*/k_BT}$$

where E^* is the activation energy.

We show in Figure 7 the ^{13}C T_2 relaxation results of our sample, for PtCO(ads) in D_2O, as a function of temperature. There is clearly a minimum in T_2 at about 170 K. This occurs when the correlation time for CO motion is on the order of the reciprocal of the $^{13}C-^{13}C$ dipolar coupling, that is at the crossover from the strong collision to the weak collision limit. This model accounts for the basic features of the temperature dependence of $1/T_2$ with $\Delta\omega_1 = 1$ kHz, $\Delta\omega_2 = 25$ kHz, $N = 25$, $\tau_o = 1 \times 10^{-13}$ s, $E^* = 7.9$ kcal/mol, and $1/T_{2(other)} = 400$ s^{-1} + 4 s^{-1} K^{-1} T.

These results obtained for CO on Pt in an electrochemical environment are quite close to those obtained previously for CO on a single crystal[16,17] and on supported Pt catalysts in vacuum,[18] where, in the latter case, an activation of energy of 6.5 ± 0.5 kcal/mol was deduced from the time evolution of a half-flipped line shape.

The Effects of Surface Coverage on Spin-Relaxation. Finally, we show directly in Figure 8 the effects of surface coverage on the relaxation times T_2 and T_1. For T_2, we find that T_{2G} decreases from ∼3 ms at low coverage to ∼1.8 ms at high coverage, Figure 8A, as noted briefly above. Moreover, these surface coverage results track very well the T_2 behavior computed previously for various well defined surface structures having from 0.33 to 0.75 ML coverage,[12] as shown in Figure 8A. In sharp contrast, there is essentially no change at all in T_1T as a function of coverage, as shown in Figure 8B. The fact that T_1T changes little if any with coverage indicates that there are not large changes in Pt−C bonding as a function of coverage, or at least that any changes do not affect T_1. The observation that T_{2G} decreases monotonically with coverage is

simply due to the fact that multiple C−C contacts increase as coverage increases, decreasing T_2. However, over the same range of coverage, neither the Knight shift, the lineshape nor the T_1T product change. This further supports the notion of a single type of site, with the T_{2G} versus coverage results simply being due to the increase in surface CO concentration—rather than a series of discrete structures, in which T_1T, the Knight shift and T_2 might all might reasonably be expected to change with coverage.

Conclusions

The results we have presented above give considerable information on the structure and bonding of the surface CO generated from methanol electrodecomposition on Pt-black fuel cell electrodes. Spin−lattice relaxation at low temperatures reveals the presence of a single type of site. The T_1T product is independent of the potential used for the electrodecomposition, and is also independent of surface coverage. The same T_1T product is obtained if CO is chemisorbed directly from a CO-saturated solution, implying that the product of methanol decomposition must be CO, not a reduced species such as COH or CHO. The observation that the T_1T product is independent of surface coverage indicates that the ^{13}C T_1 is dominated by a highly localized Pt−C interaction and is not influenced appreciably by the presence or absence of neighboring CO molecules. In contrast, the ^{13}C T_2 is strongly influenced by dipolar interactions with neighboring ^{13}C spins, with the experimental T_2 vs coverage results being in excellent agreement with previous calculations of T_2 for ^{13}CO on Pt at different coverage levels. This observation leads to an independent measure of surface coverage, and also provides strong evidence for the basic correctness of the homonuclear dipolar relaxation mechanism for T_{2G}.

The temperature dependence of the spin−spin relaxation reveals surface diffusion of the adsorbate, with an activation energy of 7.9 ± 2 kcal/mol, close to that found previously for gas phase heterogeneous catalyst systems. The spin−lattice relaxation time T_1 is inversely proportional to temperature in the range 10 to 250 K, indicating that carbon experiences the presence of conduction electron spins. The observation that the T_1T product, frequency shift, and line width for all electrochemically prepared adsorbates are independent of adsorption potential (or surface coverage) and have E^*, T_2, T_1T, and K values similar to those of gas phase CO on Pt implies that all have the same structure: linear, C-down, and nonprotonated. Since our surface is highly dispersed and clean (catalytically active) due to the oxidation−reduction cleaning cycles, it appears to represent an excellent model for the poisoning of fuel cell catalysts by CO as well as offering the opportunity to investigate systems not accessible from the gas phase, e.g., CN$^-$ on Pt.

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