In Situ Infrared Study of Carbon Monoxide Adsorbed onto Commercial Fuel-Cell-Grade Carbon-Supported Platinum Nanoparticles: Correlation with ¹³C NMR Results

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Carbon monoxide chemisorbed via methanol dissociative chemisorption onto commercial fuel-cell-grade carbonsupported nanoscale platinum electrocatalysts has been investigated by in situ subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy (SNIFTIRS). The infrared stretching frequency and the Stark tuning rate (i.e., the slope of stretching frequency vs electrode potential) show a strong dependence on platinum particle size. Five platinum particle sizes were analyzed; with average diameters of 2.0, 2.5, 3.2, 3.9, and 8.8 nm. The infrared stretching frequency was found to increase with increasing particle size, while the Stark tuning rate was found to decrease. These results were correlated with those obtained by using solid-state ¹³C NMR (Tong, Y. Y.; et al. J. Am. Chem. Soc. **2000**, 122, 1123–29), showing that the particlesize-dependent variations in the infrared stretching frequency and the Stark tuning rate are due to the variation in the $2\pi^*$ back-donation from metal to CO caused by strong interactions between platinum nanoparticles and the conductive carbon support.

Introduction

The direct methanol oxidation fuel cell (DMFC) offers a highly desirable alternative energy source to the internal combustion engine for automotive applications.¹ A typical DMFC anode contains platinum nanoparticles, activated by suitable transition metal additives, and supported either on conductive carbon or directly onto a Nafion membrane.¹ Nanoparticles provide a sufficiently high surface area for efficient heterogeneous catalysis, while the carbon support maintains a high level of dispersion of the catalyst particles,² together with the necessary electrical conductivity. The poisoning of pure Pt electrodes by carbon monoxide (CO) is a significant problem, and ruthenium-modified Pt anodes have therefore been developed, which enhance catalytic activity by facilitating CO oxidation. However, poisoning is not completely eliminated, and the electrical energy output falls short of the theoretically attainable voltage difference of 1.2 V by at least $60\%^2$

In this paper, we probe CO bonding onto carbon-supported Pt nanoparticles of the type used as the anode material in DMFCs, by correlating the results from in situ infrared spectroscopy (subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy, SNIFTIRS) with those obtained by electrochemical ¹³C nuclear magnetic resonance (EC-NMR) spectroscopy.³ SNIFTIRS provides important qualitative information regarding the bond strengths of adsorbed CO but offers little insight into the origins of these bonding alterations (on, for example, changes in Pt particle size). On the other hand, ¹³C EC-NMR provides a quantitative description of metal-CO bonding interactions, via analysis of the Fermilevel local density of states ($E_{\rm F}$ -LDOS) at the carbon atom. Alterations in bond strength can therefore be directly linked

to changes in the $E_{\rm F}$ -LDOS. The combined SNIFTIRS/EC-NMR approach can thus in principle provide new information on the electronic structure of the metal/solution interface, relevant to the characterization of real world heterogeneous electrocatalysts,^{3–7} by combining qualitative bond strength and quantitative $E_{\rm F}$ -LDOS results.

Since the early 1980s, in situ FTIR has been used as a primary tool for elucidating the mechanism of the methanol electrooxidation reaction, both on bulk polycrystalline and on singlecrystal platinum electrodes, by providing molecular-level details on the species produced on the surface (e.g., bonding arrangements, types of chemical species present, relative percentages of such species, and reaction onset potentials, refs 8-14, and references contained therein). In the mid 1990s, Christensen et al. extended the in situ FTIR methodology to carbon-supported platinum nanoparticle electrodes,^{15,16} demonstrating that particle size alters the onset of methanol chemisorption.¹⁶ They proposed that the increased activity of carbon-supported platinum nanoparticles over bulk polycrystalline Pt was due either to increased availability of sites that facilitate methanol adsorption or to an interaction between the Pt nanoparticles and the carbon support. The latter can be expected to alter the electronic properties of the electrocatalyst and is commonly referred to as a "strong metal-support interaction".17-19 Another infrared observable of interest is the so-called Stark tuning rate, that is, the slope of the response of the CO's infrared vibrational stretch frequency to the electrode potential. The trend found experimentally here is that the more positive the electrode potential, the higher the stretching frequency.

While infrared spectroscopy provides qualitative information pertaining to the bond strength of adsorbed CO, ¹³C EC-NMR can now furnish additional, more quantitative insights into



Figure 1. Transmission electron micrograph (TEM) image of the 2.5 nm carbon-supported Pt sample. The inset shows the histogram of particle size distribution. The total number of particles counted was 400.

metal—CO bonding,³ which compliments the infrared observations by providing an electronic interpretation of CO chemisorption by determination of the Fermi-level local density of states ($E_{\rm F}$ -LDOS) at carbon. In this paper, we demonstrate the utility of a combined experimental approach, which provides new insights into problems such as the nature of the strong metal—support interaction and of the particle-size-dependent variation in Stark tuning rate.

Experimental Section

For the in situ IR measurements, the working electrode was constructed by depositing approximately 50-70 μ L of a Pt/ C-Nafion ink from a syringe onto a polished, glassy carbon electrode (1 cm in diameter). The Pt/C-Nafion ink was prepared by sonicating 50 mg of Vulcan/carbon-supported Pt nanoparticles (E-Tek Inc., Natrick, MA), 1000 mg of 5 wt % Nafion solution, 3 mL of Millipore (Millipore, Bedford, MA) water, and 100 μ L of tetraethyl phosphate (TEP). The carbon-supported Pt nanoparticles were directly obtained from E-TEK Inc. The average diameters were 2.0, 2.5, 3.2, 3.9, and 8.8 nm, provided by E-TEK, as determined from X-ray diffraction analysis. We have previously characterized in detail, by using ¹⁹⁵Pt NMR, transmission electron microscopy (TEM), and electrochemical cyclic voltammetry, three of the five samples: 2.0, 2.5, 8.8 nm.⁵ The results on particle size distribution obtained via these three independent methods were in excellent agreement with those provided by E-TEK. A typical TEM image is shown in Figure 1, depicting the distribution of sizes in the 2.5 nm sample. The inset shows the histogram obtained from 400 counts of particles, giving an average particle size of 2.7 nm with a standard deviation of 0.4 nm. Similar results were obtained for other samples. The infrared cell was constructed by using a CaF2 IRtransparent window at the bottom of the homemade cell,²⁰ with a working electrode connected to a glass rod fitted through the top of the cell, permitting it to be pressed down against the CaF₂ window. A Pt wire was used as the counter electrode, and a reversible hydrogen electrode (RHE) was used as the

reference. The electrolyte was 0.5 M HClO₄ and was prepared from concentrated analytical grade perchloric acid (from Merck Suprapur) diluted in pure water (from Millipore). The cell potential was controlled by using an LB 81 Wenking potentiostat and a Hi-tek waveform generator, connected to a BD90 X–Y recorder. A Bruker IFS 66v FTIR spectrometer was modified for beam reflectance at a 65° incident angle to the electrode surface. To remove interference from atmospheric water and CO₂, the beam path was evacuated. A N₂-cooled Infrared Associates HgCdTe detector was used. The reproducibility of the spectral acquisition was controlled by repeating each experiment at least three times, with freshly made electrodes, setting the spectrometer resolution to 4 cm⁻¹. To define the CO absorption band position further, selected data were also recorded at a resolution of 1 cm⁻¹.

Before the IR experiment, the Pt electrodes were characterized by cyclic voltammetry at 20 mV/s under an N₂ flow, limiting the upper potential limit to avoid the oxide region, which we previously found can induce sintering.⁵ CO was formed by dissociative chemisorption of 0.6 M methanol under open potential conditions for several minutes before the infrared measurements were begun. Spectra were obtained by using the SNIFTIRS method, which consists of recording the reflectivities of the electrodes at two potentials, at a frequency of 0.025 Hz for each scan. A total of 40 scans were co-added at each potential to form the spectra (128 interferograms being accumulated each scan) and were finally normalized as follows:

$$\Delta R/R = (R_{E_2} - R_{E_1})/R_{E_1}$$

with $\Delta E = E_2 - E_1 = 300 \text{ mV}$ ($E_2 > E_1$) being kept constant for each potential range. The sign of the adsorption band $\Delta A = -\Delta R/R$ depends on the relative surface concentration of species present at each potential limit.⁹

For NMR sample preparation, electrochemical characterization, and CO coverage determination, experiments were performed in a preparative three-electrode electrochemical cell. This consisted of a Pt gauze counter electrode, a 1 M NaCl Ag/AgCl reference electrode, and a working electrode made of smooth platinum foil holding about 500 mg of carbon-supported Pt nanoparticles. A PGP201 potentiostat/galvanostat manufactured by Radiometer (Villeurbanne, France) controlled the cell potential. The electrolyte was 0.5 M H₂SO₄, prepared from concentrated, analytical grade sulfuric acid from Mallinckrodt Baker Inc. (Paris, KY), diluted in Millipore water, deaerated with either ultrahigh purity oxygen-free N₂ or Ar.

NMR samples were prepared by dissociative chemisorption of ¹³C-labeled methanol (Cambridge Isotopes Laboratories, Cambridge, MA) onto the Pt surface at 250 mV vs RHE. Samples were then transferred into a 10 mm diameter × 25 mm length ampule and flame-sealed under vacuum. All NMR measurements were performed on "home-built" NMR spectrometers equipped with 3.5 in. bore 8.45 and 14.1 T superconducting magnets (Oxford Instruments, Osney Mead, Oxford, U.K.), Tecmag (Houston, TX) Aries data acquisition systems, and (at 8.47 T) an Oxford Instruments CF-1200 cryostat. Spin– lattice relaxation times were measured by using an inversion– recovery Hahn-echo data acquisition sequence.⁴

Results and Discussion

Figure 2 shows a collection of SNIFTIRS spectra of CO adsorbed on different size carbon-supported Pt nanoparticles, recorded at five potential step ranges. These results show that the CO peak position is dependent on the size of the carbon-



Figure 2. Collection of CO SNIFTIRS spectra for five different sized carbon-supported Pt nanoparticles. Spectra were acquired from the first five potential ranges for each particle size: 2.0 nm (---), 2.5 nm (---), 3.2 nm (---), 3.9 nm (---), and 8.8 nm (-).



Figure 3. Plot of CO IR peak position (left side, \bullet and \bigcirc) and the Stark tuning rate (right side, \blacksquare) vs particle size. The middle of the applied potential range for the data set was 450 mV vs RHE. Data obtained at 4 cm⁻¹ (\bullet) and 1 cm⁻¹ (\bigcirc) resolution.

supported Pt nanoparticles. In particular, CO adsorbed onto the smallest particles (2.0 nm in diameter) has the lowest vibrational frequency (Figure 2). Figure 3 depicts the behavior of the CO stretching frequency (left side) and Stark tuning rate (right side, vide infra, discussed in detail later in the text) as a function of platinum particle size for samples in which the middle of the applied potential range was 450 mV. The average CO stretching frequency values are presented in Table 1 for the five different Pt particle sizes. For the smallest Pt particle sizes studied, an increase of only 0.5 nm in particle diameter induces an 11 cm⁻¹ increase in the CO stretching frequency. Such a dramatic increase is only seen between the 2.0 and 2.5 nm Pt nanoparticles. The size effect appears to level out above 3.9 nm. The CO stretching frequency (Stark tuning rate) exhibits a local maximum (minimum) for the 3.2 nm Pt nanoparticles. This trend

 TABLE 1: Particle-Size Dependence of CO IR Frequency and the Stark Tuning Rate

Pt size, nm	IR frequency, cm ⁻¹	Stark tuning rate, cm ⁻¹ /V
2.0	2041.7 ± 2.3	61.5 ± 2.0
2.5	2053.3 ± 1.5	52.5 ± 1.0
3.2	2059.0 ± 1.0	42.5 ± 1.0
3.9	2056.3 ± 1.2	46.0 ± 1.0
8.8	2056.3 ± 1.2	46.0 ± 1.0

is confirmed by acquiring data with increased spectrometer resolution (1 cm⁻¹, Figure 3), but the origin of this effect is not understood at present.

The decrease in the infrared stretching frequency at a constant electrode potential as the particle size decreases could arise from a change in CO coverage, a change in coordination number, or changes in Pt-CO bond strength. The CO coverage was therefore analyzed independently, for all Pt particle sizes, from CO stripping peak currents determined via cyclic voltammetry. Following exactly the same CO adsorption procedure as that used during the infrared measurement, the average CO coverage for the different sample sizes was found to be $61 \pm 5\%$ of a monolayer. Therefore, CO coverage changes are not expected to have major effects on the spectra. Changes in Pt surface coordination number could also have an effect on the CO stretching frequency. Weaver et al. examined the CO vibrational frequency on the different Pt single-crystal surfaces in an electrochemical environment at 0.0 mV vs SCE (~250 mV vs RHE)²¹ and found that CO on the Pt(110) surface vibrates at 2071 cm^{-1} , while CO on Pt(111) vibrates at 2066 cm⁻¹ (at 60%) of a monolayer). CO on the Pt(100) surface vibrates at the lowest frequency, 2046 cm^{-1} (at 70% of a monolayer). The results we have obtained show a decrease in the $\nu_{\rm CO}$ of about 14 cm⁻¹ as the particle sizes decrease from 8.8 to 2.0 nm (Figure 3, left side). As the particle sizes decrease, the ratio of one type of surface plane to another may be altered, and the IR peak position might simply reflect a powder average over all of the crystallographic planes. However, the increased abundance of Pt(111) over Pt(110) surface sites could only shift the vibrational frequency by ≤ 5 cm⁻¹, much less than the range seen experimentally, Figure 3 (left side). Moreover, an increase in the prevalence of Pt(100) in smaller particles as being the sole origin for the decrease in ν_{CO} is clearly disproved by cyclic voltammetry, which shows a decrease in the intensity in the hydrogen adsorption/desorption region for the Pt(100) planes as the particle size decreases (cf. Figure 3 in ref 5). We are therefore left with an electronic mechanism as being the most plausible reason for the particle size dependence of $\nu_{\rm CO}$.

The size-dependent alteration of Pt electronic properties can be either due to the intrinsic size effect or to the strong metalsupport interaction, or both. However, three previously published observations lead us to exclude the possibility of intrinsic size effect. First, on unsupported platinum nanoparticles, no particle size effect on the CO stretching frequency was found.²² Second, it has previously been shown, for clean-surface Pt/oxide systems down to 1.0 nm, that the electronic properties of Pt surfaces are independent of Pt particle size, no matter what type of support materials (silica, alumina, titania) and what kind of preparation procedures (ion exchange, colloidal processes, impregnation) are used.²³ Third, for Pt particles encaged inside a zeolite matrix, the electronic properties of the Pt surfaces and the stretching frequency of chemisorbed CO are size independent, for a given matrix.²⁴ In view of these findings, and since all of our IR experiments were carried out under the same electrochemical conditions for each particle size, we conclude that the size dependence of the CO stretching frequency is most likely due to the strong metal support interaction. Such interactions can be probed in more detail by 13 C NMR, through the direct measurements of the *E*_F-LDOS.

As has been shown previously, the observation of the ${}^{13}C$ NMR Knight shifts and spin-lattice relaxation rates of ¹³CO on Pt enable a determination of the Fermi-level local density of states at ¹³C, an electronic property.^{3,25} On the basis of the Blyholder 5σ forward/ $2\pi^*$ backward metal-CO bonding mechanism,²⁶ a two-band model was proposed,³ permitting a determination of the 5σ and $2p^*$ Fermi-level local density of states, $D_{5\sigma}(E_{\rm F})$ and $D_{2\pi^*}(E_{\rm F})$. Notice that the Fermi-level local density of states calculations are based on a phenomenological model.³ Although systematic errors may exist (and it is difficult to estimate at this stage), the qualitative physical picture, i.e., the increase/decrease in $D(E_{\rm F})$ as chemical environment changes, should be correct. The change in $D(E_{\rm F})$ reflects a change in the experimentally measured Knight shift and the Korringa constant, which are independent of any theoretical model. The quality of the measurements and the uncertainty in the data analysis has been discussed in detail in refs 3 and 25. Specifically, it has been previously found³ that the $D_{5\sigma}(E_{\rm F})$ values are essentially independent of particle size, being 0.6, 0.7, and 0.6 Ry^{-1} ·molecule⁻¹ for the 2.0, 2.5, and 8.8 nm samples. However, for the $D_{2\pi^*}(E_F)$, there is a monotonic trend, with values of 7.4, 6.7, and 6.5 Ry⁻¹·molecule⁻¹ being obtained.³ Since in these cases, the change in $D_{2\pi^*}(E_F)$ can be correlated with the degree of $2\pi^*$ back-donation, i.e., the larger the $D_{2\pi^*}(E_F)$, the higher degree the back-donation, we predicted a decrease in CO stretching frequency as the $D_{2\pi^*}(E_{\rm F})$ increases. Indeed, a linear relationship was found³ between ν_{CO} and these $D_{2\pi^*}(E_{\rm F})$ results, with a slope of $-15 \pm 2 \,{\rm cm^{-1}/(Ry \cdot molecule)^{-1}}$ and an intercept of 2147 \pm 2 cm⁻¹ at zero $D_{2\pi^*}(E_{\rm F})$.

In addition to the CO infrared vibrational frequency, it is also possible to determine the response of the vibrational frequency to an applied potential (or electric field), i.e. the Stark tuning effect;^{10,11} see above. The Stark tuning effect is seen as an increase in the wavenumber with increasing applied potential, and the CO peak intensity follows the same general trend for all Pt nanoparticle sizes. Figure 4A (left side) shows a plot of a typical (2.5 nm sample) CO stretching frequency amplitude vs the middle value of the potential range. The first three (averaged) potentials show an increase in the CO amplitude, followed by a rounding off and decrease in the intensity of the subsequent points. At moderately low potentials, the CO surface coverage is constant, but once the potential is positive enough, the oxidation of CO is induced, and the CO coverage decreases.²⁷ Therefore, to determine the Stark tuning effect, only the first three potentials are used. Linear regression analyses were performed on the mean of all data points for the first three potentials for each size Pt nanoparticle, to determine the Stark tuning effect. Typical (2.5 nm sample) linear regression results are shown in Figure 4B, right side. The Stark tuning effect is directly proportional to the slope of the line and is particle sizedependent (Table 1 and Figure 3, right side). The potential dependence is most pronounced for the 2.0 nm carbon-supported Pt nanoparticles (61.5 cm^{-1}/V), while the value of the 8.8 nm particles is 46 cm^{-1}/V . These values are to be compared with the Stark tuning rate for a polycrystalline Pt electrode of 30 $cm^{-1}/V.^{28}$ A strong connection can be made between the SNIFTIRS observables when the Stark tuning rate is plotted against the CO stretching frequency (Figure 4B). That is, using the Pt particle size as an implicit parameter, an almost linear correlation is observed between $\partial \nu / \partial E$ and ν , which strongly



Figure 4. (A) Typical (2.5 nm sample) CO SNIFTIRS peak intensity vs applied potential range (left side, \bullet ; the solid curve is only for guiding eyes) for carbon-supported Pt nanoparticles and the corresponding linear regression for determining the Stark tuning rate (right side, \bigcirc). The potentials are represented as the middle of the applied range. (B) Correlation between the CO IR peak position and the corresponding Stark tuning rates for specific particle sizes. Note that the point for the 3.9 nm sample overlaps that for the 8.8 nm sample and the straight line is only used as a guide for comparison.

suggests that the variation in the Stark tuning rate observed here is due to the variation in $2\pi^*$ CO—metal back-donation bonding.

The present work demonstrates the complementary nature of in situ infrared spectroscopy and solid-state NMR in providing insights into the details of surface chemistry of electrochemisorbed CO on platinum. SNIFTIRS and ¹³C NMR results for CO adsorbed onto various size carbon-supported Pt nanoparticles show an alteration of the Pt electronic properties as the particle size changes, due, we believe, to strong metalsupport interactions. Smaller Pt nanoparticles feel a stronger overall electronic effect from the carbon support, because of an increasing fraction of metal-support interfacial surface area. Several Pt particle size-dependent trends are observed: there is a decrease in the CO IR stretching frequency, an increase in the Stark tuning rate, and enhanced $2\pi^*$ back-bonding as the particle sizes decrease. In particular, the Stark tuning effect for the 2.0 nm Pt particles is twice that of polycrystalline Pt. The 3.9 and 8.8 nm particles show essentially identical CO IR peak position and Stark tuning effect values, although both still exhibit Pt surface electronic structure alterations from polycrystalline

Pt. Our results also indicate that there is a linear relationship between IR peak position and $D_{2\pi^*}(E_F)$ and with Stark tuning rate for various size carbon-supported Pt nanoparticles.

On the basis of these results, we can therefore provide the following overall physical picture of carbon monoxide adsorbed onto a platinum electrode. Since the 5σ orbital of CO is essentially nonbonding, with the lone pair concentrated on carbon, and the $2\pi^*$ orbital is a much less polarized antibonding orbital, the change in CO stretching frequency is most effective through $2\pi^*$ back-donation: the higher the back-donation, the lower the CO stretching frequency. This is confirmed by the correlation of the infrared and ¹³C NMR data, the latter providing the degree of back-donation, i.e., the $2\pi^* E_{\rm F}$ -LDOS directly. Our results also indicate that the variation in Stark tuning rate is a function of the degree of the back-donation (smaller particles, higher $D_{2\pi^*}(E_{\rm F})$). That is, the higher the back-donation, the easier the C—O bond can be weakened at lower electrode potentials.

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