Electronic Alterations Caused by Ruthenium in Pt-Ru Alloy Nanoparticles as Revealed by Electrochemical NMR

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We have carried out a series of ¹⁹⁵Pt and ¹³C NMR spectroscopic and electrochemical experiments on commercial Pt-Ru alloy nanoparticles and compared the results with those on Pt-black samples having similar particle sizes. The Pt NMR spectrum of the alloy nanoparticles consists of a single Gaussian peak, completely different from the broad "multi-Gaussian" NMR spectra, which are generally observed for carbon-supported Pt catalysts. Spin-echo decay measurements show that the intrinsic spin-spin relaxation time (T_2) is much larger in the alloy compared to Pt-black. A "slow-beat" is observed in the spin-echo decay curve of the alloy, implying that the NMR frequencies of spin-spin coupled Pt nuclei in the alloy nanoparticles are quite similar, unlike the situation found with Pt-black. These ¹⁹⁵Pt NMR results strongly suggest that there is a surface enrichment of Pt atoms in the Pt-Ru alloy nanoparticles. The CO-stripping cyclic voltammogram (CV) of the Pt-Ru alloy nanoparticles is broader than that observed with platinum black and is shifted toward lower potential. The two-peak structure observed previously for the CO-stripping CV behavior of Pt-black containing spontaneously deposited Ru (Tong et al. J. Am. Chem. Soc. 2002, 124, 468-473) is absent in the alloy sample. The ¹³C NMR spectrum of CO adsorbed on the Pt-Ru alloy consists of a single peak, exhibiting only a small Knight shift. An analysis of the ¹³C spin-lattice relaxation results indicates that Ru addition causes a reduction in the Fermi level local density of states of the clean metal surface atoms and the $2\pi^*$ orbital of adsorbed CO. These NMR results suggest that alloving with Ru reduces the total density of states (DOS) at the Pt sites, in accord with conclusions drawn previously from synchrotron X-ray absorption studies of Pt-Ru electrocatalysts. This electronic alteration could be the basis for the ligand field contribution to the "Ru enhancement".

Introduction

Studying the effects of adsorbates on the electronic properties of metal surfaces is an important theme in contemporary surface science. Such investigations are directly relevant to many applications in heterogeneous catalysis, such as enhancing the CO-tolerance of the electrocatalysts used in fuel cells. The poisoning effect of chemisorbed CO considerably deteriorates the catalytic performance of Pt surfaces in direct methanol oxidation fuel cells, as well as in fuel cells using H₂ obtained by reformation. Alloying Pt with other transition metals is one of the best-known remedies for this poisoning effect,^{1,2} and among the transition metals, Ru appears to be one of the best promoters. The enhancement of the CO tolerance of Pt catalysts by Ru addition has been the subject of numerous investigations.³⁻⁶ For example, we have shown that electrocatalysts produced by adding Ru to Pt nanoparticles through the method of spontaneous deposition⁷⁻⁹ have significantly enhanced CO tolerance during methanol oxidation. There are two mechanisms which have been proposed for this "Ru enhancement" effect: (1) the bifunctional mechanism, which requires that the presence of Ru facilitates the creation of oxygen-containing species by activating water (The reaction of the Pt-CO surface complex with such oxygen-containing species then leads to rapid oxidation of the adsorbed CO.), and (2) the ligand field effect, which emphasizes the importance of electronic modifications on Pt due to Ru addition as being responsible for the enhanced catalytic activity. It is, however, difficult to disentangle these

two effects, and consequently, it is of interest to use additional, noninvasive, in situ spectroscopic probes of electronic structure, to investigate these interactions in more depth.

Electrochemical nuclear magnetic resonance (EC-NMR) has emerged as one powerful experimental technique that can help elucidate the electronic properties of metal surfaces, including, for example, how they may be modified by the presence of adsorbed species.^{10–12} Moreover, with EC-NMR, both sides of the electrochemical interface (the substrate and the adsorbate) can be probed. From an analysis of the metal and ligand Knight shifts and spin-lattice relaxation rates, one can derive quantitative estimates of the Fermi level local density of states (E_F-LDOS), together with their variations due to alloying, small molecule adsorption, and the surface diffusion of electrochemical adsorbates and putative poisoning intermediates. Here, we present the first report of the ¹⁹⁵Pt NMR of commercial Pt-Ru alloy nanoparticles (as opposed to spontaneously deposited Pt-Ru) and ¹³C EC-NMR results for CO chemisorbed on these catalysts, together with electrochemical CO-stripping measurements. We compare these Pt-Ru results with those obtained on unsupported Pt-black samples, and discuss their implications for improving our understanding of the structural and electronic alterations caused by Ru addition to Pt surfaces.

Experimental Section

Johnson-Matthey (Alfa Aesar, Ward Hill, MA) Pt-black and Pt-Ru nanoparticle catalysts (1:1 atomic ratio) were used for



Figure 1. Transmission electron micrograph of electrochemically cleaned, Pt-Ru alloy nanoparticles.

this study. The Pt–Ru particles have average sizes between 2 and 3 nm, as determined by transmission electron microscopy. 0.5 M H₂SO₄ was used as the electrolyte for the electrochemical measurements, and all electrode potentials in this report are referred to a reversible hydrogen electrode, RHE. The asreceived materials were electrochemically reduced by holding the electrode potential at 0.260 V in a three-electrode electrochemical cell under a continuous stream of ultrapure argon (S. J. Smith Welding Supply). An adlayer of CO was produced on some sample surfaces by chemisorption of [¹³C]-methanol (Cambridge Isotopes, Andover, MA) at this potential, and such samples were transferred to an NMR cell for the NMR study.⁷ The CO coverage was estimated from cyclic voltammetry (CV) using a slow scan rate (10 mV/min).

¹⁹⁵Pt NMR spectra were obtained "point-by-point" by recording spin-echo intensities as a function of applied radio frequency (from 74 to 78 MHz) using a "home-built" 8.45 T NMR spectrometer. A Hahn echo sequence $(\pi/2 - \tau - \pi)$ with 16-step phase cycling was used to acquire the spin-echoes. Typical 90° pulse widths of 5 μ s and a τ value of 30 μ s were used. ¹⁹⁵Pt spin-lattice relaxation time (T_1) measurements were made by using a saturation-comb sequence, while ${}^{13}CT_1$ values were obtained by using the inversion-recovery technique. Spin-spin relaxation time (T_2) measurements were carried out by observing the spin-echo intensity as a function of the pulse separation between the $\pi/2$ and π pulses in the Hahn echo sequence. Field/frequency ratios for ¹⁹⁵Pt are reported with respect to H₂PtCl₆; chemical shifts for ¹³C are reported with respect to TMS, using the convention that high-frequency, lowfield, paramagnetic or deshielded values are more positive (IUPAC δ -scale). All ¹⁹⁵Pt NMR measurements were made at 80 K, while ¹³C NMR experiments were performed as a function of temperature using an NMR probe housed in a continuous N₂-flow cryostat (Oxford CF1200, Concord, MA).

Results and Discussion

We show in Figure 1 a typical TEM photomicrograph of the as-received Pt-Ru material. The particles are clearly agglomer-



Figure 2. Point-by-point ¹⁹⁵Pt NMR spectra of Pt-Ru alloy nanoparticles obtained at 80 K. The solid symbols represent the NMR spectrum of electrochemically clean Pt-Ru, and the open symbols represent that of the CO adsorbed system.



Figure 3. ¹⁹⁵Pt NMR spectra of electrochemically cleaned Pt-black samples. Average particle sizes are (A, top) 2.8 nm and (B, bottom) 6 nm. Empty circles represent the experimentally obtained spin–echo intensities, and the solid line corresponds to the convolution pattern obtained from the Gaussian peaks (dotted lines). Both spectra have similar, multi-Gaussian appearances. The position of the "bulk" peak shows a slight variation as a result of the perturbation experienced by the interior atoms due to the particle's surface.

ated, a feature typical of unsupported Pt catalysts. Figure 2 shows two representative ¹⁹⁵Pt NMR spectra. The spectrum defined by the filled circles is for a "clean" Pt–Ru sample (reduced electrochemically) while the open squares are data points for such a clean sample covered with an adlayer of CO. Clearly, the Pt NMR spectrum shows little change due to the presence of adsorbed CO, although without the electrochemical reduction step, the "as-received" sample had a large feature at 1.089 G/kHz, due to oxidized platinum sites, basically as reported previously with other Pt catalysts.¹³

The ¹⁹⁵Pt NMR spectra of the two Pt-black samples (2.8 and 6 nm) are shown in Figure 3. Both spectra look quite similar, with the spin—echo intensities extending from a field/frequency ratio of 1.095 to 1.14 G/kHz. By way of reference, the ¹⁹⁵Pt NMR spectrum of bulk Pt (metal) appears at a field/frequency ratio of 1.138 G/kHz.¹³ Moving from bulk to nanoparticles has two major effects. First, there is a significant broadening of the spectrum, since Pt atoms on the surface and subsurface layers

resonate at different frequencies. On moving away from the interior of the nanoparticles, the d-electron local density of states shows a monotonic decrease, ¹⁴ causing a shift and broadening of the spectrum. Second, Pt atoms that are at the interior of the nanoparticles feel the perturbing effect of the particles' surfaces.¹⁵ As a consequence, the bulk peak itself shows a reduction in Knight shift. More specifically, the field/frequency ratio decreases from 1.138 to 1.1322 to 1.1306 G/kHz, when going from the bulk Pt to commercial Pt-black (6 nm as measured by TEM) to 2.8 nm Pt-black.

Conventionally, ¹⁹⁵Pt NMR spectra of carbon-supported, pure Pt nanoparticles have been analyzed using the layer model.¹⁶ In this model, Pt nanoparticles are assumed to be made up of various layers of a cubo-octahedron, in which atoms from a given layer give rise to a Gaussian peak with a given Knight shift and a width of the order of 1 MHz. The observed NMR spectrum is then attributed to the superposition of several such peaks, whose centers of gravity follow the "exponential healing theorem".16 The variation in the Knight shift of Pt atom layers is thought to arise from the variation in the d-like E_F-LDOS upon moving from the interior to the surface of the Pt nanoparticle.¹⁴ This deconvolution method has been very useful in interpreting the broad 195Pt NMR spectra observed with many supported Pt catalyst samples.¹⁰ But in the present case, the layer model deconvolution for unsupported platinum black is not successful, since it is not possible to obtain a sufficiently accurate particle size distribution, due to particle agglomeration. Nevertheless, it is possible to reproduce the experimentally observed NMR spectra via convolution of three or four Gaussian peaks, as shown in Figure 3. This is certainly suggestive of a layerlike structure for Pt-black nanoparticles, whose spectra encompass the range 1.095-1.14 G/kHz, consistent with Pt atoms on the surface, subsurface, and interior layers. However, in both samples, it is clear that the actual fraction of atoms that are in a macroscopic bulklike platinum environment is quite low.

Next, we consider the case of Pt-Ru alloy nanoparticles. For particles having an average diameter of 2-3 nm, the dispersion (defined as the ratio of the number of atoms on the surface to the total number of atoms) is about 40-50%, indicating that most of the atoms reside in the surface and subsurface layers. The average particle size of the Pt-Ru alloy nanoparticles is similar to that of the 2.8 nm Pt-black sample. However, the Pt NMR spectrum of Pt-Ru is completely different from that of Pt-black. It consists of a single symmetric Gaussian peak, centered at 1.104 G/kHz (Figure 2). For the Pt-black samples, the NMR spectrum extends from 1.095 to 1.14 G/kHz, while, for the Pt-Ru alloy nanoparticles, the NMR signal is clearly much narrower, extending only from 1.095 to 1.115 G/kHz. There are few if any Pt atoms resonating in the vicinity of 1.138 G/kHz (the ¹⁹⁵Pt NMR frequency of bulk Pt metal), and the whole spectrum is shifted toward lower Knight shifts, implying that there are no Pt atoms whose electronic properties resemble those of bulk Pt. In general, the NMR spectra of bimetallic catalysts can be expected to show broad, layerlike structures, so long as they retain a homogeneous composition within the nanoparticles. For example, for a Pt-Pd bimetallic catalyst having an average particle size of 2.4 nm, the ¹⁹⁵Pt NMR spectrum (Figure 4A) is found to extend from 1.09 to 1.13 G/kHz.¹⁷ On the other hand, if there is surface segregation of one of the components, then the NMR spectrum may consist of a relatively narrow peak, characteristic of the segregated surface film. Such a situation exists with Pt-Rh bimetallic clusters where the ¹⁹⁵Pt NMR spectra (Figure 4B) of samples



Figure 4. Schematic representation of three different Pt-alloy nanoparticle systems with their corresponding ¹⁹⁵Pt NMR spectra: (A) Pt– Pd (the spectrum is reprinted with permission from ref 17. Copyright 1996 American Chemical Society); (B) Pt–Rh (the spectrum is reprinted with permission from ref 18. Copyright 1988 Royal Society of Chemistry); (C) Pt–Ru (blue, Pt; green, Pd; red, Rh; brown, Ru).

having a low dispersion consist of a relatively narrow peak centered around 1.138 G/kHz.18 This corresponds to the NMR frequency of bulk Pt, which has led to the conclusion that the cores of these clusters are made up of pure Pt. In the case of the Pt-Ru alloy nanoparticles, the ¹⁹⁵Pt NMR spectrum is again relatively narrow, but it is now centered at about 1.104 G/kHz (Figure 4C). This strongly suggests that there is a major surface enrichment of Pt atoms in the Pt-Ru alloy nanoparticles. A schematic representation of the three alloy nanoparticle structures, together with their corresponding ¹⁹⁵Pt NMR spectra, is shown in Figure 4. In Figure 4C, we show some aggregation of surface Ru, consistent with recent infrared measurements¹⁹ on equivalent Pt-Ru alloy nanoparticle electrodes where vibrations corresponding to CO adsorbed not only to Pt but also to Ru surface domains were observed. Ru present on the surface of these nanoparticle electrodes leads to the formation of Pt/Ru boundaries, and the presence of such boundaries is necessary for the electrooxidation of CO via the bifunctional mechanism.¹⁹ Therefore, the combined EC-NMR and infrared data give evidence for participation of both electronic and bifunctional factors in the overall methanol electrooxidation mechanism.

Further evidence which supports surface enrichment of Pt comes from spin-spin relaxation time measurements. Figure 5A shows the spin-echo decay curve obtained at 1.1 G/kHz for the Pt-black sample. The decay can be fit to a single exponential (solid line) yielding a T_2 of $56 \pm 4 \,\mu$ s. The spin-spin relaxation data for the Pt-Ru alloy nanoparticles are very different, however, and are shown in Figure 5B. There is a clearly distinguishable "slow beat" pattern in the spin-echo decay curve. This "slow-beat" pattern in the spin-echo decay curve arises when it is possible to "flip" Pt nuclear spins which



Figure 5. (A) Spin-spin relaxation in Pt-black. The spin-echo decay experiment is performed at the peak position corresponding to the surface site. The solid line corresponds to a simple exponential fit which gave a T_2 value of $56 \pm 4 \,\mu$ s. (B) The "slow-beat" pattern observed for the spin-spin relaxation in a Pt-Ru catalyst. The indirect spin-spin coupling constant *J* value obtained from the five-parameter fit²⁰ (solid line) is in agreement with the value determined in ref 19.

are coupled via the pseudoexchange interaction, by a single rf pulse.²⁰ When the NMR frequencies of two neighboring Pt atoms differ very much, a given rf pulse cannot excite both of them simultaneously, due to radio frequency bandwidth limitations, and a beat structure is not seen. Since the NMR spectrum of the Pt-black sample extends over a wide frequency range, it is clear that the NMR frequencies of the Pt atoms in neighboring layers differ to such an extent that a given rf pulse cannot excite neighboring nuclear spins simultaneously. Consequently, one does not observe a "slow-beat" pattern for Pt-black (Figure 5A). When Ru is added to Pt, the ¹⁹⁵Pt NMR spectrum extends over a relatively narrow region and makes it possible to excite the indirectly coupled Pt nuclear spins by a single rf pulse, which results in the "slow-beat" pattern seen in the spin-spin relaxation results shown in Figure 5B. These measurements thus confirm a narrow dispersion of ¹⁹⁵Pt NMR frequencies in the Pt-Ru alloy nanoparticles and strongly support the idea that Pt atoms reside mainly on the surface of the nanoparticles.

The solid line shown in Figure 5B corresponds to a fiveparameter fit of the data, as described in detail previously,²⁰ which yields a *J*-coupling value of 3.8 ± 0.2 kHz and a $T_2 =$ $424 \pm 8 \ \mu$ s. The *J*-coupling value obtained for these Pt–Ru alloy nanoparticles agrees very well with the *J*-coupling value of 4 kHz reported earlier for Pt alloys by Froidevaux and Weger.²¹ The intrinsic spin–spin relaxation time is, however, longer in the alloy as compared to pure Pt-black. A possible explanation for this is that the spin–spin relaxation in Pt



Figure 6. Comparison of the CO-stripping CV from Pt-black and Pt-Ru alloy nanoparticles obtained after 12 h of methanol adsorption. The scan rate was 10 mV/min, and the surface areas are normalized. (Reprinted with permission from ref 12. Copyright 2003 Kluwer Academic/Plenum Publishers).

 TABLE 1: CO-Stripping CV and ¹³C NMR Parameters for CO Adsorbed on Pt-black and Pt-Ru

sample	Pt-black	Pt-Ru
peak of stripping CV (mV) fwhm of CV (mV) chemical shift δ (ppm) fwhm of NMR (ppm) T_1T (s•K)	519 ± 2 58 ± 1 370 ± 10 197 ± 15 59 ± 3	$276 \pm 4 \\ 108 \pm 2 \\ 244 \pm 10 \\ 239 \pm 15 \\ 158 \pm 6$

nanoparticles is strongly influenced by spin-lattice relaxation, which shows a variation due to the different $E_{\rm F}$ -LDOS values between the pure metal and the alloy.²⁰ In metallic systems, energy exchange between nuclear spins and conduction electron states lying very close to the Fermi energy is, primarily, responsible for spin-lattice relaxation, and it follows Korringa behavior ($T_1T = \text{constant}$). For surface sites on Pt-black (1.10 G/kHz), $T_1T = 52 \pm 3 \text{ ms}\cdot\text{K}$, but for the Pt-Ru alloy nanoparticles, T_1T becomes $109 \pm 5 \text{ ms}\cdot\text{K}$. This large increase in T_1T at the same spectral position is a clear indication of a significant reduction in the E_F-LDOS at the Pt sites, due to the presence of Ru in the Pt-Ru nanoparticle. This decreases the efficiency of the spin-lattice relaxation process and contributes, therefore, to the increase in T_2 .

In addition to ¹⁹⁵Pt NMR, ¹³C NMR of CO adsorbed on nanoparticle catalysts when combined with electrochemical measurements is another useful method with which to investigate surface electronic structure. We therefore carried out a series of ¹³CO NMR measurements on both Pt-black and Pt-Ru alloy nanoparticles, along with CO-stripping cyclic voltammetry. In the Pt-Ru alloy, the CO-stripping peak is shifted toward low potential (Figure 6 and Table 1), similar to the behavior shown previously by Pt-black samples having Ru deposited through spontaneous deposition.⁷ However, an important difference between the alloy and the Ru-deposited samples is the presence of two well-resolved CO-stripping peaks in the Ru-deposited system.⁷ As mentioned above, Ru spontaneously deposited onto Pt surfaces forms well-defined nanosized islands,²² and CO can be adsorbed onto both the Pt- and Ru-rich regions of these materials. This gives rise to two separate peaks in stripping voltammograms. The absence of the two-peak structure with the alloy electrode (Figure 6) indicates that the surface concentration of Ru islands is too low to manifest in the voltammetric experiment, but their presence is clearly established by the infrared measurements.¹⁹ Another interesting feature is the increase in peak width for the Pt-Ru alloy sample



Figure 7. Temperature dependence of the ¹³C spin–lattice relaxation of CO adsorbed on Pt-black. The inset shows the ¹³C NMR spectrum of CO adsorbed from a CO saturated medium.



Figure 8. Temperature dependence of the ${}^{13}C$ spin–lattice relaxation of CO adsorbed on Pt–Ru. The inset shows the ${}^{13}C$ NMR spectrum of the adsorbed CO.

(Table 1), which suggests that Ru induces a broad range of local electronic structural alterations, resulting in a broad distribution of Pt-CO adsorption bond strengths, although, unlike the situation with spontaneous deposition, the distribution is continuous rather than discontinuous.

In Figures 7 and 8, we show the temperature dependence of the spin-lattice relaxation for CO adsorbed on Pt-black and Pt-Ru alloy nanoparticles, respectively. Table 1 gives the NMR parameters for the two samples. For the alloy nanoparticles, the NMR spectrum has shifted to a much lower Knight shift (244 ppm) than that observed for CO on the Pt-black sample (370 ppm). In addition, there is an increase in the full-width at half-maximum height (from 207 to 249 ppm). These results are consistent with the CV results. That is, in Pt-black, the CV for CO-stripping is narrow, while that for the Pt-Ru alloy is somewhat broader, indicating a broader distribution of CO binding affinities in the alloy, due to slightly different local Pt-(Ru) bonding environments. Neither the CO-stripping CV nor the ¹³C NMR spectrum of Pt-Ru alloy show the two-peak structure observed for Pt-black samples decorated with Ru through spontaneous deposition⁷ in which CO may bind to both Pt and Ru domains.

In earlier work,²³ we established that there exists a linear correlation between the total E_F -LDOS at a metal surface and the ¹³C NMR chemical shift of adsorbed CO. This "¹³C shift versus clean metal E_F -LDOS" correlation has been found to apply to a variety of Pt nanoparticle electrode surfaces, as well as to Pd nanoparticles.²³ We therefore calculated the E_F -LDOS

TABLE 2: Fermi Level Local Densities of State for Clean Pt or Pt–Ru Metal Surfaces Obtained from the E_F-LDOS versus ¹³C Shift Correlation²³ and the E_F-LDOS for Adsorbed CO's $2\pi^*$ Orbital Obtained from the Two-Band Model¹⁶

sample	E_{F} -LDOS (clean metal surface) (Ry-atom) ⁻¹	$E_{\rm F}$ -LDOS of $2\pi^*$ orbital of CO (Ry-atom) ⁻¹
Pt-black Pt–Ru	$17.7 \pm 1.8 \\ 7.4 \pm 0.5$	7.0 ± 0.2 4.6 ± 0.1

for surface Pt atoms using this correlation. The results are given in Table 2, from which it can be seen that there is a significant reduction in the surface E_F-LDOS due to the presence of Ru, consistent with the ¹⁹⁵Pt NMR results. Specifically, the E_F-LDOS decreases from 17.7 (\pm 1.8) to 7.4 (\pm 0.5) (Ry-atom)⁻¹, when going from Pt to Pt–Ru.

Finally, yet another quantitative estimate of the electronic alterations produced by Ru can be obtained from the ¹³C NMR T_1 measurements. From the temperature dependence of the ¹³CO spin-lattice relaxation rates (Figures 7 and 8), it can be seen that CO molecule adsorbed on both Pt-black and Pt-Ru exhibits typical Korringa behavior. By analyzing the ¹³C NMR spinlattice relaxation rate data within the two-band model,¹⁶ we can directly deduce the $2\pi^*$ E_F-LDOS values shown in Table 2. Here, it can be seen that the presence of Ru causes a large reduction in the E_F-LDOS both at the surface Pt atoms and at the C atoms of adsorbed CO. 13C NMR investigations of CO chemisorbed on Pt-black nanoparticles decorated with Ru have also shown⁷ that the $2\pi^*$ E_F-LDOS of chemisorbed CO decreases with increasing Ru coverage. Thus, addition of Ru to Pt nanoparticle electrodes, whether by alloying or by surface deposition, has the same effect: a reduction in the $E_{\rm F}$ -LDOS at the Pt atoms and a concomitant reduction in the $2\pi^* E_F$ -LDOS of chemisorbed CO.7

Of course, it should also be pointed out that the local density of states (measured by NMR) is rather different from the total density of states (DOS), since the E_F-LDOS is the DOS projected onto the individual atoms.²⁴ In a recent paper, Mannstadt and Freeman²⁵ have illustrated this difference for clean Pt, Pd, and Rh. Therefore, the variation in the E_F-LDOS need not necessarily correlate with the variation in the total DOS. However, if we assume that d-electron effects are most important, it can be shown¹⁶ that faster relaxation at a constant spectral position implies a higher DOS. Therefore, it should be possible to correlate the increase/decrease in E_F-LDOS to the corresponding increase/decrease in the total DOS. It has also been shown that the calculated DOS at $E_{\rm F}$ for transition metals²⁶ decreases with a reduction in the d-band filling. Then, a reduction in the total DOS would correspond to an increase in electron vacancies. McBreen and Mukherjee²⁷ have carried out an X-ray absorption (XAS) study on a Pt-Ru alloy to try to understand the effects of Ru addition on the electronic properties of Pt.²⁷ They showed that when Pt is alloyed with Ru, it leads to an increase in Pt d-band vacancies, which would correspond to a reduction in the DOS at the Pt sites. Comparing our NMR results on Pt-black and the Pt-Ru alloy, we propose that when Ru is added to Pt, there is a decrease in the total DOS (as suggested by the decrease in E_F-LDOS), which arises from an increase in Pt d-electron vacancies. The d-band vacancies introduced by Ru addition would lead to a reduction in the electron density available for bond formation with adsorbed CO, consistent with the fact that there is a weakening of the CO chemisorption bond with increasing Ru coverage.7 This electronic alteration could be an important contribution to the "Ru enhancement" seen in Ru-modified Pt catalysts in methanol electrooxidation.

Conclusions

We have carried out a series of electrochemical ¹⁹⁵Pt and ¹³C NMR experiments on commercial Pt-Ru alloy nanoparticles and Pt-black. The 195Pt NMR spectrum of the alloy nanoparticles consists of a relatively narrow peak occurring near the surface peak position of Pt-black. The typical "layerlike" structure observed for the ¹⁹⁵Pt NMR spectra of Pt-black is absent in the Pt-Ru alloy. The spin-echo decay clearly shows the presence of a "slow-beat" pattern for the alloy, which is absent for Ptblack. From the Knight shift and spin-spin relaxation behavior of ¹⁹⁵Pt, we conclude that the surface of Pt-Ru alloy nanoparticles is enriched with Pt atoms. The CO-stripping CV and the ¹³C NMR spectrum of Pt-Ru alloy nanoparticles do not show the two-peak structure seen previously for Pt-black samples decorated with Ru.7 This suggets that Ru islands present at low coverage on the alloy surface¹⁹ are not manifested in the voltammetric experiment. The CO-stripping CV consists of a broad peak shifted toward lower potential with respect to that observed with Pt-black, and the 13C NMR spectrum of adsorbed CO consists of a single broad peak having a smaller Knight shift than that observed for CO on Pt-black. From spin-lattice relaxation measurements, we find that there is a significant reduction in E_F-LDOS at Pt sites, as well as on the C-sites of adsorbed CO, due to Ru addition, suggesting a decrease in the total DOS at $E_{\rm F}$ for the Pt atoms. These NMR results are consistent with previous synchrotron X-ray absorption studies, which have shown that the presence of Ru increases the Pt d-band vacancies in a Pt-Ru alloy. This could be the basis for the ligand field contribution to the "Ru enhancement" effect seen in MeOH electrooxidation, while infrared spectroscopy documents the contribution of the bifunctional mechanism to the enhancement. Apparently, both ligand and bifunctional contributions need to be considered, as suggested before.²⁸

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