Bonding and Motional Aspects of CO Adsorbed on the Surface of Pt Nanoparticles Decorated with Pd

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Spontaneous deposition of Pd onto catalytic grade Pt nanoparticles has been shown to yield Pt/Pd catalysts having enhanced catalytic activity toward formic acid oxidation, when compared to pure Pt- and Pd-black. Here, we report the results of electrochemical nuclear magnetic resonance (EC NMR) and electrochemical measurements of CO chemisorbed onto these Pt/Pd catalysts, to probe the nature of the CO chemisorption bond, as well as the motional behavior of adsorbed CO. The ¹³C NMR spectra are broad and can be deconvoluted into two peaks, assigned to CO adsorbed on Pt and Pd sites. From the temperature dependence of the spin–lattice relaxation rates, we conclude that CO chemisorbed on Pd undergoes fast diffusion. The activation energy (E_a) obtained from these results for CO on Pd is smaller than that found for CO adsorbed onto Pd nanoparticles supported on alumina. A two-band model analysis of the NMR data shows that the 5 σ orbital of CO makes a significant contribution to the chemisorption bond of CO on Pd, which agrees well with theoretical predictions. The interaction of Pd with Pt leads to a reduction in the Fermi level local density of states (E_f -LDOS) at the Pd sites, which reduces the strength of CO and, most likely, OH adsorption. This electronic modification is proposed to be responsible for the improved catalytic performance of Pt/Pd in formic acid oxidation.

Introduction

Fuel cell research plays a pivotal role in the development of alternate sources of energy for the future. Although hydrogen has become the fuel of choice for many applications, due to the risks involved in its handling, there have been numerous efforts directed toward the development of alternate, organic molecules for fuel cell use.¹ Methanol, ethanol, methyl formate, and formic acid are some of the more commonly used alternative fuels and recent work has shown that formic acid is a particularly attractive candidate.² Such fuel cells usually require a transition metal catalyst to carry out the oxidation reaction. Although Pt is the most well-known fuel cell catalyst, in its pure form it suffers from serious surface poisoning, due to adsorption of reaction intermediates. The catalytic activity of Pt surfaces toward formic acid oxidation has been studied in detail^{3,4} and many infrared spectroscopic studies^{5–7} of single crystal surfaces have established that CO adsorption is primarily responsible for surface poisoning. Pd surfaces have been found to possess far better catalytic activity toward formic acid oxidation,⁸⁻¹⁰ but a very slow deactivation is found to reduce the oxidation current. While the exact reason for this deactivation is still under investigation, the use of bimetallic catalysts largely circumvents this problem, and indeed, modifying a single component catalyst by adding one or more transition metals is well-known to enhance catalytic activity in many systems.¹¹

In recent work, we showed that modifying commercial Ptblack through spontaneous deposition of Ru is a very efficient method to produce fuel cell catalysts with excellent CO tolerance toward methanol oxidation.¹² Here, we report the results of an investigation of a Pt/Pd catalyst useful for the electrooxidation of formic acid, prepared by the spontaneous deposition¹³ of Pd onto commercial Pt-black. We study, in particular, the electronic and dynamic structure of CO on Pt/Pd using the techniques of cyclic voltammetry (CV) and electrochemical nuclear magnetic resonance (EC NMR). EC NMR has emerged as an excellent technique to elucidate the structural and electronic properties of catalytic nanoparticles.^{14,15} Several EC NMR investigations have been reported for Pt and its alloys, primarily since ¹⁹⁵Pt is a high NMR sensitivity nucleus.^{16,17} The spatial variation in the Fermi level local density of states (Ef-LDOS) of the Pt atoms in a nanoparticle leads to an unusually broad ¹⁹⁵Pt NMR spectra of nanoparticles.¹⁷ Pt atoms on the surface of the nanoparticle have very different electronic properties compared with those in the interior and they give rise to a distinct peak in the NMR spectrum, which is well separated from the response of the bulk atoms. Modifications of the nanoparticle surface, such as by chemisorption of a poisoning gas species, induce electronic alterations at the surface sites and these can be studied by observing the changes in the surface ¹⁹⁵Pt NMR peak. Such ¹⁹⁵Pt NMR studies have shown that there is a direct correlation between the Knight shift of the surface peak and the electronegativity of the adsorbate.16 In addition, Pt NMR studies of commercial Pt-Ru alloy nanoparticles have provided evidence for a surface enrichment of Pt atoms, and have yielded insights into the electronic alterations caused by the interactions between Ru and Pt atoms.¹⁷ When individual Pt nanoparticles are agglomerated, however, the surface peak in the ¹⁹⁵Pt NMR spectrum is not well separated from the response of atoms in the interior regions.¹⁷ In such cases, performing ¹³C NMR of adsorbed CO offers an alternative way of exploring the surface structural and electronic properties of the Pt nanoparticles. In addition, ¹³C NMR can also provide information on surface dynamics of adsorbed CO.

In earlier work using EC NMR, we showed that the addition of Ru to Pt reduces the CO adsorption bond strength and enhances CO surface mobility.^{17,18} To understand the electronic modifications caused by addition of Pd to Pt-black, we carried out ¹³C NMR investigations of CO adsorbed onto Pt/Pd, together with electrochemical measurements. The EC NMR results are compared with those obtained for pure Pt-black and Pd nanoparticles, revealing the nature of CO bonding to the Pd and Pt/Pd surfaces. We also discuss the relevance of these results to the electrooxidation of formic acid, and compare these results with those obtained previously with Pt/Ru catalysts.¹⁸

Experimental Section

Pt/Pd nanoparticle catalysts were prepared by the method of spontaneous deposition¹⁹ of Pd onto commercial, fuel cell grade platinum black (Johnson-Matthey, average diameter 6 nm). The Pt-black sample was cleaned at a constant potential of 0.46 V vs RHE and immersed in 5 mM $Pd(NO_3)_2 + 0.1 M H_2SO_4$ solution at open circuit potential. After 1 h of deposition, the sample was rinsed with Millipore water, followed by the reduction of adsorbed Pd precursors at 0.46 V, in 0.1 M H₂SO₄. Then, the spontaneous deposition and reduction process was repeated, to obtain a Pt/Pd sample with a surface Pd packing density (the ratio of the number of Pd atoms to the number of Pt surface atoms) of 0.5 ML, estimated via inductively coupled plasma (ICP) spectroscopy. Chronoamperometric measurements on formic acid oxidation were carried out at 0.4 V, using the Pt/Pd catalyst, and compared with results for pure Pt-black and Pd-black. For NMR measurements, about 500 mg of catalyst was used. ¹³CO was adsorbed onto the catalyst surfaces by bubbling [99%-13C] CO gas (Cambridge Isotopes Laboratories, Andover, Massachusetts) through the catalyst in 0.5 M D₂SO₄, at open circuit potential. After removing CO from the solution (by bubbling ultra-high-purity argon at 0.05 V), the catalyst was then transferred into a pre-cleaned NMR ampule, together with a portion (2-3 mL) of the electrolyte, and the sample flamesealed. A small amount of catalyst was left in the cell for further electrochemical measurements. All NMR measurements were carried out by using a "home-built" NMR spectrometer, equipped with an 8.47 T superconducting magnet (Oxford Instruments, Osney Mead, UK), and a Tecmag (Houston, Texas) Aries data acquisition system. A spin-echo pulse sequence $(\pi/2 - \tau - \pi - \tau - acquisition)$ with 16-step phase cycling to eliminate ring down was used for data acquisition. The typical $\pi/2$ pulse length was between 5 and 8 μ s, depending on the experimental conditions. Chemical (or frequency) shifts for ¹³C are given in ppm from tetramethylsilane (TMS), using the convention that high-frequency, low-field, paramagnetic or more deshielded values are positive (IUPAC δ -scale). Spin-lattice relaxation times were measured by using an inversion-recovery sequence followed by spin-echo data acquisition. The NMR experiments were performed as a function of temperature with use of a solenoidal coil probe housed in a continuous flow cryostat (Oxford CF1200).

Results and Discussion

Electrochemical Measurements. We show in Figure 1 typical results for the chronoamperometric (CA) measurements of formic acid oxidation. Both Pd-black and Pt/Pd show high activity when compared to Pt-black, which is essentially unreactive. The steady state current shows a 6-fold increase for the Pt/Pd catalyst when compared to Pt-black, indicating that Pt/Pd is a much better catalyst than Pt-black for the oxidation of formic acid. Pd-black initially has a much higher activity than Pt/Pd; however, the oxidation current shows a continuous decrease with time, indicating that the Pd atoms are slowly



Figure 1. Electrochemical chronoamperometric measurements of formic acid oxidation on Pt-black, Pd-black, and Pt/Pd catalysts.



Figure 2. Electrochemical CO stripping cyclic voltammogram of Ptblack, Pd-black, and Pt/Pd catalysts obtained under identical conditions at a scan rate of 5 mV/min. The dotted line represents the CO stripping CVs obtained for Pt-black and Pd-black.

getting deactivated. The oxidation current drops below that of Pt/Pd after 25 h, while the Pt/Pd catalyst shows a steady formic acid oxidation current. Thus, adding Pd to Pt-black reduces the deactivation of Pd atoms. In Figure 2, we show the CO stripping CV for pure Pt-black, Pt/Pd, and pure Pd-black samples. The CO stripping CV peak from the Pt/Pd catalyst is shifted toward higher potential compared with that of Pt-black, but to lower potentials when compared to that observed for Pd-black. Since the stripping potential is a measure of the CO tolerance on the nanoparticle surface, the shift in the stripping peak indicates that Pt/Pd still has a lower CO tolerance than Pt-black.5-7 Therefore, the data shown in Figure 2 confirm that the slow deactivation observed during formic acid oxidation on Pd surfaces is not due to CO adsorption, as discussed in more detail elsewhere.⁷ However, the interaction of Pd with the Pt substrate induces considerable electronic alterations on the surface Pt and Pd atoms, as can be seen from the shift in the CO stripping CV compared to pure Pt- and Pd-black.

NMR Spectroscopy. We show in Figure 3 the ¹³C NMR spectrum at 80 K of CO adsorbed onto Pt/Pd. The spectrum is broad but can be readily deconvoluted into a double Gaussian peak pattern, similar to the one obtained previously for ¹³CO



Figure 3. ¹³C NMR spectrum of CO adsorbed on Pt/Pd catalyst sample taken at 80 K.

 TABLE 1: Parameters Obtained from the Double-Gaussian

 Deconvolution of the ¹³C NMR Spectrum^a

catalyst	¹³ CO NMR shift (ppm)
Pt/Pd (peak 1)	627 ± 10
Pt/Pd (peak 2)	402 ± 10
Pd-black ²³	739
Pt-black ¹⁷	370 ± 10

 $^{\it a}$ The NMR shift values of CO adsorbed on Pt- and Pd-black samples are also given.

on Pt/Ru.¹⁸ The ratio of the areas of the two Gaussians is about 5:4, which is in reasonable agreement with the packing density obtained from the ICP analysis of Pt/Pd. The two peaks obtained from the deconvolution are at 627 and 402 ppm (Table 1). On pure Pt-black, adsorbed CO has a chemical shift of about 370 ppm,¹⁷ but on pure Pd nanoparticle surfaces, bridge-bonded CO shows a much larger shift (at ~739 ppm).^{20–23} Comparing our results with the earlier NMR investigations,^{17,20–23} we assign the peak at 627 ppm to bridge-bonded CO on Pd, while the 402-ppm peak is assigned to CO on Pt. The ¹³C NMR shift of CO adsorbed onto nanoparticle surfaces is directly proportional to the E_f-LDOS at the surface metal atoms. Thus, a larger shift for CO adsorbed onto Pd is ascribed to the larger E_f-LDOS at the Smaller shift of CO on Pd to a reduction in the E_f-LDOS on the Pd sites of Pt/Pd.

We next carried out a series of spin-lattice relaxation measurements, at both peak positions (402, 627 ppm) and as a function of temperature, and we show in Figure 4 the temperature dependence of the relaxation rate for CO adsorbed onto the Pt region (402 ppm). The Korringa behavior ($T_1T =$ constant) observed is characteristic of metallic systems. For such systems, the spin-lattice relaxation (T_1) and the Knight shift (K) are related by:²⁴

$$T_1 T = \frac{\hbar}{4\pi k_{\rm B} K^2} \left(\frac{\gamma_{\rm e}}{\gamma_{\rm n}}\right)^2 B \tag{1}$$

where γ_e and γ_n are the electron and nuclear gyromagnetic ratios, respectively, and *B* is a correction factor introduced to incorporate electron–electron interaction effects. Several previous investigations^{20,25} have shown that the NMR properties of CO adsorbed onto Pt and Pd nanoparticles follow Korringa behavior, indicating that CO becomes metallic. The temperature dependence of the relaxation rate for CO adsorbed onto the Pd sites is shown in Figure 5. Here, Korringa behavior is seen at low



Figure 4. Temperature dependence of ¹³C NMR spin–lattice relaxation rate measured at the peak position corresponding to CO adsorbed on Pt sites. The solid line corresponds to the Korringa behavior.



Figure 5. Temperature dependence of the ¹³C NMR spin–lattice relaxation rate for CO adsorbed on the Pd sites of Pt/Pd. The solid line corresponds to the fit to eq 2. The dotted line represents Korringa behavior at high temperatures. The peak in the relaxation rate seen at \sim 140 K is attributed to diffusional relaxation.

and at high temperatures, but near ~ 140 K, there is a peak in the relaxation rate, characteristic of a motional contribution to T_1 . This motional contribution can be attributed to the surface diffusion of CO on Pd. The net relaxation rate in this case can be written as:¹⁸

$$T_1^{-1} = aT + \frac{2(\Delta\omega)^2 \tau}{(1 + \omega_0^2 \tau^2)}$$
(2)

where the first term represents the Korringa contribution to the relaxation. The second term describes the surface diffusion contribution to the spin-lattice relaxation, where $\Delta \omega$ is the local field inhomogeneity seen by the ¹³C nucleus and ω_0 is the Larmor frequency. τ is the correlation time associated with the diffusional motion of CO and is related to the activation energy for diffusion, $E_{\rm a}$, through the Arrhenius relation:²⁶

$$\tau = \tau_0 \exp(E_{\rm a}/k_{\rm B}T) \tag{3}$$

Since τ is strongly temperature dependent, being very short at higher temperatures and very long at lower temperatures, the relaxation rate shows a peak at intermediate temperatures.

Analyzing the relaxation data with the help of eq 2, we obtained an activation energy for diffusion of 2 ± 0.5 kcal/ mol. From the temperature dependence of the ¹³C NMR line shape, Shore et al.²⁰ have determined the activation energy for the surface diffusion of CO adsorbed on Pd nanoparticles supported on alumina to be 6 ± 2 kcal/mol. Thus, there is a considerable reduction in E_a for CO adsorbed on Pd atoms deposited on Pt nanoparticles. This decrease in E_a can be attributed to the electronic alterations of Pd atoms due to their interactions with substrate Pt atoms, and it seems likely that this low barrier to diffusion may be related to the relatively high activity of the Pt/Pd catalyst in formic acid electrooxidation, and in its improved CO tolerance. The diffusion-enhanced relaxation behavior observed here is similar to that seen in a Pt/Ru catalyst,¹⁸ in which a peak in the relaxation rate was found near 270 K, corresponding to an Ea value obtained for Pt/Ru systems of \sim 5 kcal/mol.¹⁸ At higher temperatures, there is a slight change in the slope of the Korringa part as can be seen from the dotted lines in Figure 5. The exact reason for this change is not known; however, it is possible that it could be due to migration of CO onto Pd sites, which are not occupied at the lower temperatures. In any case, the temperatures at which the enhanced relaxation occurs are clearly correlated with $E_{\rm a}$ values. In Pt/Ru, E_a is ~5 kcal and the maximum is seen at \sim 270 K; in Pt/Pd, E_a is \sim 2 kcal and the maximum is seen at ~140 K, reflecting weaker CO bonding.

Bonding of CO onto Pt/Pd Surfaces. In the first approximation, the principal features of CO bonding to transition metal surfaces can be described by means of the Blyholder model.²⁷ According to this model, the CO 5σ and $2\pi^*$ molecular orbitals interact with the d band electrons of the transition metal. The 5σ orbital transfers electron density to the metal, while backdonation from the d band partially fills the $2\pi^*$ orbital in CO. Specific details of the adsorption bond, e.g., the amount of donation and back-donation, its correlation to the strength of the bond, and participation of other orbitals, depend on the electronic structure of the transition metal surface atoms. Chemisorption of CO onto single crystal surfaces of Pd has been intensively studied, both experimentally and theoretically. Cluster calculations²⁸ for CO chemisorbed onto the bridge sites of Pd(100) suggest that, in addition to the $2\pi^*$ back-bonding found for other transition metal surfaces, donation from the CO 5σ orbital to the partially occupied 4d-5sp metal hybrid orbitals contributes significantly to the chemisorption bond. An isolated Pd atom has a completely filled d band (4d¹⁰), but bonding in the metallic state implies a partial occupation of the 5sp band (formed from the hybridized s and p orbitals), with a lowering of the 4d population. Thus, the transition from a single Pd atom to a metallic Pd cluster is accompanied by significant changes in the average atomic configuration of the constituent atoms, and ab initio calculations²⁸ have shown that the Pd atomic configuration becomes more like 4d⁹5s¹ when the cluster size increases from Pd_2 to Pd_8 , with the presence of the partially occupied 5sp band in Pd metal being thought to be responsible for the increased 5σ donation from CO.

Here, we examine whether our NMR results provide additional information about the Pd–CO chemisorption bond. With the help of a two-band model,²⁹ we have shown previously that it is possible to analyze the ¹³C NMR spectra and relaxation behavior of CO adsorbed onto Pt and Pt/Ru surfaces.¹⁸ In this model, the ¹³C NMR observables (the Korringa product and

TABLE 2: ErLDOS Values for the Two Orbitals of CO, Obtained from the Two-Band Model Analysis of the NMR Parameters

CO chemisorbed on	$D_{2\pi^*}(E_f) (Ry-atom)^{-1}$	$D_{5\sigma}(E_{\rm f}) ({\rm Ry-atom})^{-1}$
Pt-black	7.3 ± 0.3	0.5 ± 0.1
Pt sites of Pt/Pd	9.0 ± 0.4	0.3 ± 0.1
Pd on alumina	9.2 ± 0.4	3.5 ± 0.2
Pd sites of Pt/Pd	6.9 ± 0.3	3.6 ± 0.2

the Knight shift) are expressed in terms of the Ef-LDOS of the $2\pi^*$ and 5σ orbitals of chemisorbed CO. For CO adsorbed on Pt, the orbital shift has been calculated³⁰ to be ~ 160 ppm, while for CO adsorbed on Pd, we take a Pd-carbonyl chemical shift of $\sim 230 \text{ ppm}^{22}$ to be the orbital shift. The E_f-LDOS values so derived for both 5σ and $2\pi^*$ orbitals of chemisorbed CO for Pt/Pd catalyst are shown in Table 2. Here, the two-band model analysis has also been applied to the T_1T and K values reported for the NMR of CO adsorbed onto the bridge sites of Pd nanoparticles (Becera et al.²²). The Pt-black¹⁸ E_f-LDOS values are also shown in Table 2, for comparison. From these results and those calculated for CO on Pt/Pd, it can be seen that for CO adsorbed on Pd nanoparticles and the Pd sites of the Pt/Pd catalyst, there is a considerably larger E_{f} -LDOS for the 5 σ orbital $(D_{5\sigma}(E_f))$ for Pd or Pt/Pd as compared to Pt-black or the Pt sites in Pt/Pd: \sim 3.5 vs \sim 0.4 states Ry⁻¹ atom⁻¹, respectively. This agrees well with the general picture of CO chemisorption on Pd, in which 5σ donation is expected to be significant. The effect of decorating Pd onto Pt-black is mainly reflected on the Ef-LDOS of the CO $2\pi^*$ orbital ($D_{2\pi^*}(E_f)$). For the Pt sites of Pt/ Pd, there is an increase in $D_{2\pi^*}(E_f)$ compared to Pt-black (9.0 vs 7.3 states Ry^{-1} atom⁻¹), while for the Pd sites of Pt/Pd, there is a reduction in the $D_{2\pi^*}(E_f)$ compared to Pd-black (6.9 vs 9.2 states Ry^{-1} atom⁻¹). Since $D_{2\pi^*}(E_f)$ is determined by the backdonation from the metal d band, a reduction in $D_{2\pi^*}(E_f)$ would imply that there is a decrease in the Ef-LDOS of the Pd d band, due to its interaction with Pt. Thus, according to the Blyholder model,²⁷ the CO adsorption bond becomes weaker on the Pd part of the surface. It should be noted that the description of transition metal-CO bonding in terms of the Ef-LDOS of the CO $2\pi^*$ orbital is model dependent. However, in the present case, the reduction in the activation energy for CO diffusion observed for CO adsorbed on the Pd sites is also a clear indication that the CO-Pd bond is weakened due to a reduction in the Ef-LDOS of Pd atoms, which we believe is also responsible for the improved catalytic activity of Pt/Pd toward formic acid oxidation vs that on pure Pd. Since the increase in the $D_{2\pi^*}(E_f)$ for CO adsorbed onto the Pt sites of Pt/Pd indicates that there is an increase in the Ef-LDOS of the Pt d band as a result of Pd deposition, CO is more strongly adsorbed onto these Pt sites. Apparently, the CO on the Pt part of the surface is strongly bonded and remains a spectator for formic acid oxidation, which occurs entirely on the Pd part of the surface.

These EC NMR results clearly show that there are large changes in the electronic structure experienced by Pt atoms as a result of their interactions with another transition metal, Pd. When these results are compared with our previous NMR results for the Pt/Ru systems,¹⁸ it can be seen that adding Ru (or Pd) to Pt affects the Pt d-band electrons, and that this effect is reflected in the $D_{2\pi^*}(E_f)$ values. The changes in the E_f -LDOS of Pt d electrons arise for a variety of reasons, including modifications in the Pt lattice (lattice strain effects), formation of new hybridized orbitals, and even a direct charge transfer between Pt and the other transition metal. Since the covalent radii of Pt (128pm), Pd (131 pm), and Ru (126 pm) are nearly equal,³¹ it seems reasonable to expect that the electronic alterations from lattice strain due to incorporating Pd or Ru to the Pt lattice would be rather minor. This strongly suggests, therefore, that it is a more direct electronic mechanism (either a charge transfer or a hybridization effect), which leads to the changes observed in the E_{f} -LDOS of Pt.

Finally, we briefly discuss the likely relevance of the present investigation to the question of formic acid oxidation on Pt/Pd catalysts. On Pt, formic acid oxidation occurs via a dual path mechanism.^{32–34} The direct dehydrogenation of HCOOH is given by:

$$\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2 \tag{4}$$

while the dehydration path involves the formation of CO as a poisoning intermediate:

$$\mathrm{HCOOH} \rightarrow \mathrm{CO} + \mathrm{H_2O} \tag{5}$$

The second reaction pathway (eq 5) is rather similar to that involved in methanol oxidation, since adsorbed CO is formed as a reaction intermediate. Although CO has been clearly identified⁵⁻⁷ as the poisoning adsorbate on Pt surfaces during formic acid oxidation, the slow deactivation of the Pd surface (Figure 1) is not actually thought to be due to CO adsorption since FTIR7 and infrared chemiluminescence35 studies of HCOOH oxidation have not detected the presence of adsorbed CO on Pd surfaces. Radiolabeling experiments³⁶ carried out with ¹⁴C]-HCOOH have also ruled out the presence of a carboncontaining species adsorbed on the surface of Pd-black during HCOOH oxidation. Arenz et al.7 suggest that formic acid oxidation on Pd surfaces takes place exclusively via the direct dehydrogenation path (eq 4) and that deactivation is due to the adsorption of OH on Pd. The present EC NMR results show that the interaction of Pd with Pt substrate atoms reduces the Ef-LDOS on Pd, and this could lead to a weakening of OH adsorption on Pd, making Pt/Pd a better catalyst for formic acid oxidation than pure Pd. The present investigation also shows that the spontaneous deposition of the catalytically active component (Pd) onto the transition metal that acts as a modifier (Pt) is indeed a successful method to produce very efficient bimetallic catalysts for fuel cell applications.

Conclusions

Electrochemical and EC NMR measurements have been carried out to investigate the bonding and dynamics of CO molecules adsorbed onto Pt/Pd catalysts. The results demonstrate that fast CO diffusion occurs on the Pd part of the Pt/Pd surface, with a reduced activation energy as compared to that found for CO adsorbed onto alumina-supported pure Pd nanoparticles. A two-band model analysis of the NMR parameters shows that CO adsorbs very strongly onto Pt, whereas the CO adsorption strength on Pd sites is much lower, compared to pure Pd. Consequently, CO chemisorption does not deactivate the Pd part of the Pt/Pd catalyst for formic acid oxidation. We also propose that the decrease in the E_f-LDOS of surface Pd atoms is responsible for preventing the deactivation of Pd atoms in Pt/ Pd catalysts by chemisorbed OH groups. When the current results are compared with those of previous ¹³CO NMR studies of the Pt/Ru system,¹⁸ we conclude that the effect of Pd on Pt is opposite to that seen with Ru, therefore a direct electronic mechanism (either a charge transfer or a hybridization effect) is responsible for the changes in E_f-LDOS of Pt atoms.

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