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Metallic Nature and Surface Diffusion of CO Adsorbed on Ru Nanoparticles in Aqueous Media: A ^{13}C NMR Study

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We report the first observation of the ^{13}C nuclear magnetic resonance spectroscopy (NMR) of ^{13}CO, adsorbed from ^{13}CO saturated 0.5 M sulfuric acid solutions, onto the surfaces of commercial Ru-black nanoparticles. The ^{13}C NMR spectra consist of a symmetrically broadened peak having a large isotropic shift as compared to CO adsorbed onto supported Ru catalysts. The variation of the spin−lattice relaxation rate follows Korringa behavior, indicating the metallic nature of adsorbed CO, in addition to varying across the spectrum in a Korringa-like manner. Motional narrowing of the NMR spectrum at higher temperatures, together with an additional contribution to the spin−lattice relaxation rate, indicate that adsorbed CO undergoes rapid diffusion on the particle surfaces. A two-band model analysis of the NMR results indicates that the CO adsorption bond is weaker on Ru as compared to either Pt or Pd. This is also supported by a reduction in the activation energy for CO diffusion on Ru vs either Pt or Pd nanoparticles.

Introduction

Study of metal surfaces is one of the most active areas of research that addresses a broad range of fundamental questions in surface science,[1] and research on the role played by transition metal nanoparticles in fuel cell catalysis is of particular interest, because the emerging technologies involve alternate and renewable sources of energy.[2] Solid-state nuclear magnetic resonance (NMR) spectroscopy has emerged as one useful probe with which to investigate the surface electronic properties of catalyst nanoparticles.[3,4] NMR experiments can be carried out by using either a metal catalyst nucleus (e.g., ^{195}Pt)[5,6] or an NMR-active adsorbate (e.g., ^{13}C of adsorbed CO).[7,8] ^{13}C NMR of adsorbed CO is particularly informative because it can be used to deduce both the electronic properties of the nanoparticle surfaces, as well as the nature of CO bonding with the transition metal.[8−11] CO adsorbed onto platinum surfaces acquires a metallic nature, due to mixing of the molecular orbitals of CO with the conduction electron states of the metal catalyst. In one model, this mixing is described in terms of an electron donation from the 5σ orbital of CO to the metal, together with a back-donation of charge from the metal d-band to the $2\pi^*$molecular orbital.[12] The "renormalized" molecular orbitals of CO acquire a finite local density of states at the Fermi energy (E_f-LDOS) and this imparts metallic behavior to the adsorbed CO.[13] ^{13}C NMR is a highly sensitive technique with which to investigate the metallic nature of such adsorbed species on metal surfaces because, in addition to the commonly observed chemical shift (which arises due to the orbital moment of electrons interacting with the nuclear magnetic moment), there will be a Knight shift in the NMR frequency, due to the Fermi contact interaction between the conduction electrons with the adsorbate nuclei. This Knight shift interaction then leads to more efficient nuclear spin−lattice relaxation, which follows the well-known Korringa behavior.[14]

In fuel cells, reactions frequently occur at relatively low temperatures, and catalyst poisoning due to CO adsorption is often a problem, so high surface area Pt nanoparticles are generally combined with one or more other transition metals to obtain CO-tolerant catalysts.[15,16] Addition of Ru to Pt has been found to be particularly effective in the generation of CO-tolerant catalysts for direct methanol oxidation fuel cells (DMFC), so understanding the nature of CO bonding on Ru is of interest to help decipher the promotional role played by Ru in such bimetallic catalysts. We have therefore carried out a ^{13}C NMR investigation of CO adsorbed onto a commercial Ru-black catalyst, because it seemed likely that studying this interaction might help us understand the role of Ru in the bimetallic catalysts. Unlike CO adsorbed onto supported Ru nanoparticles, we find a large isotropic shift and a symmetric broadening of the NMR spectrum of CO adsorbed on Ru-black. T_1 generally follows Korringa behavior, but a detailed study of the temperature dependence of T_1 also reflects the occurrence of surface diffusion of adsorbed CO. A two-band model analysis of the NMR shift and relaxation parameters shows that CO is adsorbed only weakly onto Ru-black, when compared to CO adsorbed on pure Pt nanoparticles.

Experimental Section

About 300 mg of Ru-black (Alfa-Aesar) was used for this NMR study. Ruthenium oxide(s) present on the surface of the as-received material were reduced by passing a continuous stream of hydrogen gas for 20 h at room temperature, and the nanoparticles were then transferred into an electrolyte (0.5 M

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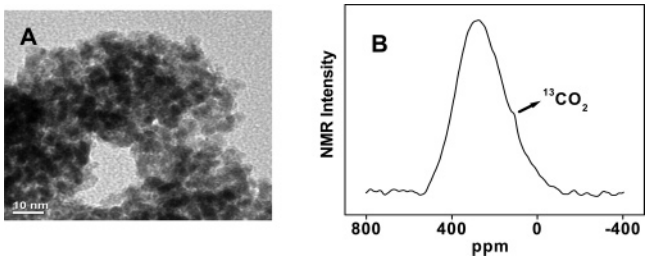

Figure 1. (A) Transmission electron micrograph of Ru-black. (B) ^{13}C NMR spectrum of CO adsorbed on Ru-black, obtained at room temperature. The spectrum is reconstructed by adding three individual spectra recorded at different carrier frequencies.

D_2SO_4). CO was adsorbed onto the nanoparticle surfaces by bubbling ^{13}C[99%] enriched CO gas (Cambridge Isotopes) through the electrolyte. Excess CO was then removed by bubbling with high purity Ar (S. J. Smith Welding Co.) and the sample plus electrolyte transferred to an NMR ampule and then flame sealed. NMR experiments were carried out by using a "home-built" 8.45 T NMR spectrometer. A spin−echo sequence ($\pi/2-\tau-\pi$) with 16-step phase cycling was used to acquire the NMR signals. Typical 90° pulse widths were ∼5 μs and the τ values were 30 μs. Averaging 400 spin−echoes yielded a signal-to-noise ratio of about 40. NMR spectra were constructed by adding Fourier transformed spectra recorded at three different carrier frequencies. Chemical shifts are reported with respect to tetramethylsilane (TMS) using the IUPAC δ-scale. Spin−lattice relaxation times between 80 and 300 K were measured with an inversion−recovery sequence using a home-built NMR probe housed in a continuous flow cryostat (Oxford CF1200, Concord, MA).

Results and Discussion

The Ru nanoparticles used for this study have diameters in the 2−5 nm range, as can be seen from the transmission electron micrograph (TEM) of the as-received material shown in Figure 1A. Although there is some agglomeration, the highly porous nature of the sample helps preserve a large surface area, which was measured to be about 50 m^2/g, from CO adsorption. The ^{13}C NMR spectrum obtained at room temperature (Figure 1B) consists of a broad, rather symmetric Gaussian whose center of gravity is at 253 ± 6 ppm, from TMS. The narrow feature at 128 ppm arises from $^{13}CO_2$ present in the electrolyte, produced from surface desorbed CO which got oxidized.[17] In previous work, the static NMR spectrum of CO adsorbed on silica-supported Ru nanoparticles had an asymmetric line shape in which the line-broadening seen was attributed to a chemical shift anisotropy, rather than to susceptibility effects arising from the interaction with the metal particles.[17−19] This was confirmed in this earlier work via "magic-angle" spinning (MAS), which produced narrow NMR lines in the range 177−195 ppm,[18,20,21] from which it was concluded that CO was adsorbed primarily in a linear or end-on configuration.[18] Preliminary results on the infrared absorption of CO adsorbed on Ru-black show that there is very little bridge-bonded CO on our samples and most molecules bind end-on.[22] However, in the present case, we find a significantly larger isotropic shift (253 ± 6 ppm) for CO adsorbed on Ru-black than for the supported catalysts, and the similarity of the line shape with that of CO adsorbed onto Pt nanoparticles[8] suggests that there may be a substantial Knight shift experienced by CO in this system. This question can be pursued further because in metallic systems the hyperfine interaction which gives rise to the Knight shift also leads to the Korringa behavior for spin−lattice relaxation. Here, the temperature dependence of T_1 for a typical metallic system is given by[14]

$$T_1T = \frac{\hbar}{4\pi k_B K^2}\left(\frac{\gamma_e}{\gamma_n}\right)^2 B \tag{1}$$

where K is the Knight shift, γ_e and γ_n are the electron and the nuclear gyromagnetic ratios, respectively, and B is a constant that measures electron−electron interaction effects. Korringa relaxation is the NMR fingerprint of metallic state and for simple metals, and eq 1 implies that the relaxation rate (T_1^{-1}) at a given spectral position should vary linearly with temperature. On the other hand, at a given temperature, the relaxation rate when measured at different positions across a broad NMR spectrum should be proportional to the square of the Knight shift, in which case eq 1 can be rewritten as

$$T_1^{-1} = \frac{T}{S}(\delta - \delta_{orb})^2 \tag{2}$$

where S is the Korringa constant given by the constant terms on the right-hand side of eq 1, B is taken to be equal to 1, and the Knight shift (K) is given by the difference between the total NMR shift (δ) and the orbital part (δ_{orb}). We show in Figure 2A the relaxation rate measured across the spectrum at $T = 80$ K. The solid line is a fit to eq 2 from which we obtain $S = 5.0$ (± 1.5) $\times 10^{-6}$ s·K, which agrees well with the theoretical S value of 4.16×10^{-6} s·K. The fit also gives the orbital shift: $\delta_{orb} = 159 \pm 32$ ppm, in the range of the orbital shifts found for linear CO on various supported Ru catalysts reported previously.[18]

At higher temperatures, however, there are major deviations from the type of (static) behavior seen in Figure 2A, due to the onset of molecular motion, i.e., diffusion of CO over the catalyst surface, as shown in Figure 2B. Evidence for this motional effect can be seen as a line narrowing effect on the NMR spectra (Figure 2C,D), in which the fwhm decreases from 250 to 205 ppm, when the temperature is increased from 80 to 280 K. And, in addition, the temperature dependence of T_1 in the range $T =$ 80−300 K has an unusual feature at higher temperatures. As can be seen in Figure 2B, the relaxation rate follows typical Korringa behavior at low temperatures, then deviates at ∼200 K and becomes Korringa again in the high-temperature region. Such a deviation in T_1 from pure Korringa behavior is clearly another manifestation of the surface diffusion of adsorbed CO. However, this additional contribution to spin−lattice relaxation is only significant over a narrow range of temperatures. In this region, the total relaxation rate can be written as[23]

$$T_1^{-1} = aT + \frac{2(\Delta\omega)^2\tau}{(1 + \omega_0^2\tau^2)} \tag{3}$$

where the first term represents the Korringa contribution and the second term describes the surface diffusion contribution. $\Delta\omega$ is the local field inhomogeneity seen by the ^{13}C spins, 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_a, through the Arrhenius relation:

$$\tau = \tau_0 \exp(E_a/k_BT) \tag{4}$$

The solid line in Figure 2B is a fit to eq 3 by assuming the preexponential term to be equal to 1×10^{-13} s and the activation energy (E_a) determined for surface diffusion obtained from this fit is 4.1 ± 0.3 kcal/mol. The correlation time τ calculated from

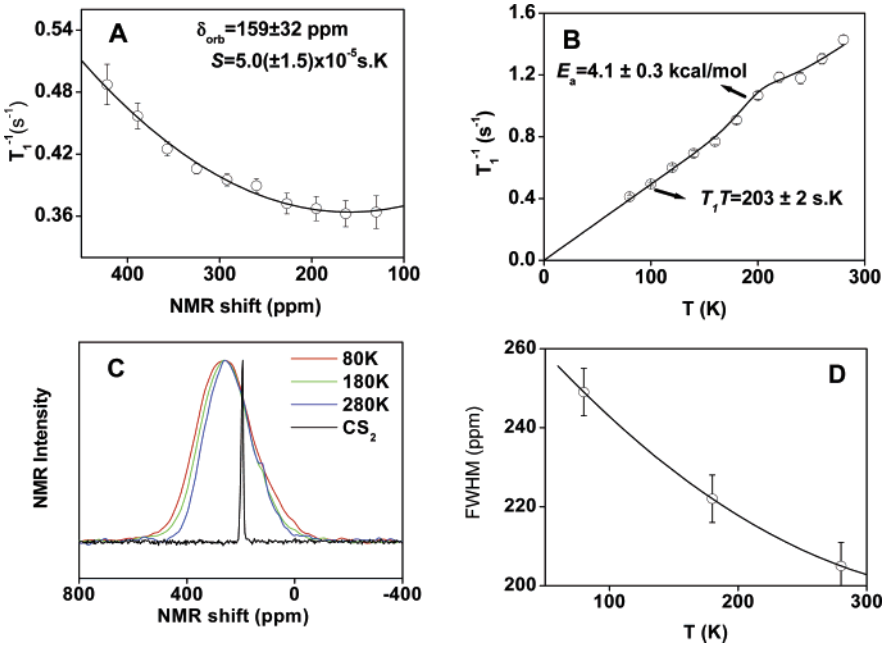

Figure 2. (A) Variation of the spin−lattice relaxation rate of ^{13}CO on Ru-black across the spectrum, at $T = 80$ K. The solid line is a fit to the Korringa behavior given by eq 2. (B) Temperature dependence of the spin−lattice relaxation rate measured at the peak maximum position. T_1^{-1} follows Korringa behavior at low temperatures; the deviation above 200 K is attributed to the surface diffusion effect. The solid line is the fit to eq 3. (C) Line narrowing effect on the ^{13}CO NMR spectra. The ^{13}C NMR spectrum of CS_2, recorded under identical conditions, is also shown as a reference for the chemical shift and instrument line broadening. (D) Variation of fwhm with temperature. The solid line is a "guide for the eye".

TABLE 1: E_f-LDOS for the Two Orbitals of CO, Obtained from a Two-Band Model Analysis[26] of the NMR Parameters

CO chemisorbed on	$D_{2\pi^*}(E_f)$ (Ry-atom)$^{-1}$	$D_{5\sigma}(E_f)$ (Ry-atom)$^{-1}$
Pt-black[a]	7.3 ± 0.3	0.5 ± 0.1
Pd on alumina[b]	9.2 ± 0.4	3.5 ± 0.2
Ru-black	3.9 ± 0.2	0.1 ± 0.1

[a] Data from ref 8. [b] Data from ref 9.

the maximum of T_1^{-1} using eq 3 is 1.8×10^{-9} s, which lies in the range of correlation times usually observed for the spin−lattice relaxation of small molecules in solutions, for example, glycerol in water.[24] Such short correlation times strongly suggest that the adsorbed CO undergoes rapid surface diffusion. The activation energy obtained here is much less than that found for isolated carbon atoms on Pt clusters, or for CO adsorbed onto either Pt or Pd nanoparticles,[25] which are in the range 6−10 kcal/mol. If we assume that the E_a value obtained from the analysis of the NMR data is a measure of the strength of CO adsorption bond, then we can conclude that CO adsorption is weaker on pure Ru nanoparticles than it is on either Pt-black or Pd. Further evidence in support of this conclusion is given by a two-band model[26,27] analysis of these NMR results given in Table 1. Here, we show the computed E_f-LDOS of the molecular orbitals of CO adsorbed on Pt, Pd, and Ru-black. These results clearly indicate a much smaller $D_{2\pi^*}$ as well as a smaller $D_{5\sigma}$ E_f-LDOS for CO on Ru than on Pd or Pt, consistent with the low activation barrier to diffusion.

Conclusions

The variation of the relaxation rate across the spectrum at low temperatures and its temperature dependence indicate that CO adsorbed on Ru-black has a metallic nature, unlike the CO adsorbed on supported Ru nanoparticles which are more akin to diamagnetic metal carbonyls. The temperature dependence of the ^{13}CO NMR line shape, as well as the deviation of the relaxation rate from Korringa behavior, show that CO undergoes rapid diffusion on the Ru surface. The activation energy E_a estimated from the analysis of T_1 measurements shows that there is a significant reduction in the barrier to diffusion as compared to CO adsorbed on Pt-black. And, the reduction in the E_f-LDOS for CO on Ru as compared to CO on Pt (or Pd), is another indication that CO adsorption onto Ru is weak when compared to that found in Pt nanoparticles. This weakening of the surface adsorption bond is likely to make a substantial contribution to the improved catalytic activity of Pt−Ru bimetallic catalysts in DMFC.

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