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Formate as a Surface Probe for Ruthenium Nanoparticles in Solution ^{13}C NMR Spectroscopy

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Catalysis using colloidal nanoparticles in the solution phase is an active research area.[1] There is also considerable interest in tailor-made preformed nanoparticles as catalyst precursors in solution by nanoscience and nanotechnology, which are known to offer excellent control over particle structure and morphology.[2] It is generally accepted that catalysis can take place differently on different crystallographic faces and locations of a transition-metal crystallite; hence many reactions are sensitive to the structure of the nanoparticle catalyst.[3] Thus, the use of small adsorbate molecules to probe surface sites on metal particles by spectroscopic techniques is an interesting, topical area. There are extensive and continuing studies using solid-state techniques, such as magic-angle spinning (MAS) NMR and surface vibrational spectroscopy, applied to supported metal particles.[4] However, there is a limited number of studies aiming to characterize the surface of colloidal metal particles in the solution phase. In the early 1990s, Bradley et al. reported the use of low-resolution solution ^{13}C NMR spectroscopy at 1.76 T (equivalent to 75 MHz ^{1}H NMR spectroscopy) for the characterization of PVP-stabilized palladium nanoparticles with pre-adsorbed CO (PVP = poly(vinylpyrrolidone)).[5] They noticed enormous chemical shifts for the adsorbed CO molecules as well as large broadening of line widths owing to the Knight shift effect (the ^{13}C nucleus couples to the conduction electrons of metal particles larger than the quantum size, where the metallic properties begin when the size of the particle is above a critical dimension, causing typically a few hundred ppm shift in both peak maxima and peak width). This large perturbation of the adsorbed-CO resonance essentially masks analytically valuable chemical shift data, which invalidates the application of NMR spectroscopy for metal-site diagnosis. To our knowledge, no follow-up work after that of Bradley et al. has been reported, despite the fact that solution NMR spectroscopy is commonly applied to molecular species in solution and can be a very useful technique to investigate the surface chemistry of colloidal metallic particles without the need for ultra-high-vacuum (UHV) conditions. Herein, we demonstrate that formate species bind to metal surfaces in a manner similar to adsorbed CO molecules, but their carbon nucleus is isolated from the mobile electrons of the metallic structure by an oxygen-atom spacer, which allows for the first time the interrogation of surface features of the particles in solution by high-field solution ^{13}C NMR spectroscopy without the undesirable Knight shift problem, hence facilitating site differentiation and quantification at high resolution.

Ruthenium nanoparticles in the catalytically relevant size range of 1.8–4.0 nm were prepared using a PVP stabilizer and a polyol reducing agent. The nanoparticles were nearly monodisperse, with standard deviation less than 0.3 nm. The attenuated total reflectance (ATR) IR spectrum of CO adsorption was recorded for different sizes of colloidal ruthenium particles (Figure 1). Three adsorption bands can be seen: 2050 cm^{-1} is assigned to linearly bonded CO (monodentate) on Ru surface atoms, 1945 cm^{-1} to bridging carbonyls, and 1975 cm^{-1} to multiple individual CO molecules adsorbed on low-coordinate Ru atoms (multicarbonyl mode). Similar observation of the three adsorption modes and assignments were also reported for supported Ru particles with preadsorbed CO.[4c,d,6]

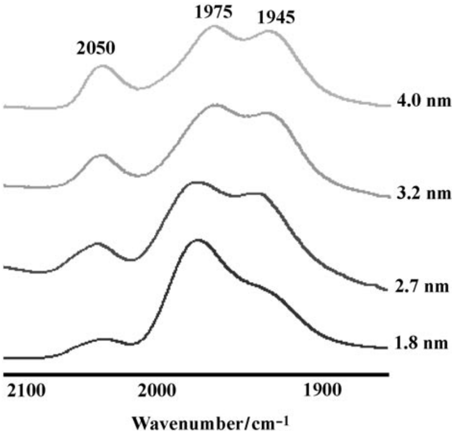

Figure 1. ATR-IR spectra of adsorbed CO on different sizes of PVP-Ru nanoparticles

This result supports the general view that although a rigid polymer such as PVP is coordinated to individual metal particles as stabilizer, representative metal sites on the particle are still available for small-molecule adsorption and catalysis.[1a,5b] However, our colloidal Ru particles showed a higher proportion of multicarbonyl vs. bridging mode than did supported Ru catalysts (in this case without heat treatment), which reflects the rough Ru surface prepared by stabilizer without annealing. According to the IR spectrum, the bridging and linear modes grew at the expense of the multicarbonyl mode with increasing particle size. The multi-

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carbonyl was the major mode for the smallest size (1.8 nm), while larger nanoparticles (3.2 and 4.0 nm) gave higher bridging-to-multicarbonyl and bridging-to-linear ratios.

Formate species are able to bind to metal centers in a variety of ways through formic acid adsorption.[7] Thus, formic acid adsorption over PVP-Ru nanoparticles was studied by ATR-IR spectroscopy. Apart from the PVP peaks, we observed new peaks arising from symmetric υ_s(OCO) and asymmetric υ_{as}(OCO) stretching of monodentate formate at 1330 and 1618 cm^{-1}, respectively (Figure 2). The symmetric and asymmetric modes of O-C-O stretching at 1362 and 1585 cm^{-1} of bridging formate were also evident, but no bidentate formate was observed. Not all of the adsorbed bridging formate species were completely in C_{2v} orientation, indicative of a rough surface causing tilting. It is clearly evident that the adsorption of formate species on PVP-Ru nanoparticles is size-dependent (Figure 2). The bridging species becomes the main mode of adsorption at the expense of the monodentate species as the size of the nanoparticle increases. Thus, the results for formate adsorption are in line with the CO adsorption experiments. However, this technique is unable to reveal the existence of a multi-monodentate mode (that is, multiple formate ions bound to the same Ru atom) at highly unsaturated Ru sites; presumably the adsorption peak (or peaks) of such a mode would be indistinguishable from other modes owing to the closely congested and broad features of the spectrum. As a result, CO appears to be a better surface probe than formate in the case of IR spectroscopy.

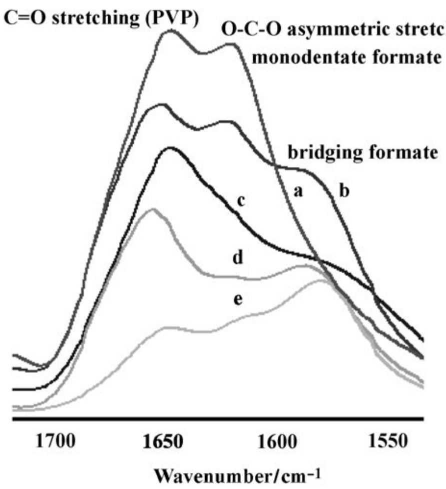

Figure 2. ATR-IR spectra of formate species on different sizes of PVP-Ru nanoparticles: a) 1.8, b) 2.3, c) 2.7, d) 3.2, e) 4.0 nm at room temperature.

The adsorption of formic acid on PVP-Ru nanoparticles was also investigated by high-resolution solution ^{13}C NMR spectroscopy at 11.7 T (equivalent to 500 MHz 1H NMR spectroscopy). Figure 3 shows a resonance peak of chemisorbed formic acid at 165.68 ppm (a slight shift compared to the molecular form at $\delta = 165.58$ ppm) as well as a small sharp peak corresponding to dissolved CO_2 at $\delta = 124.68$ ppm with a peak width of less than 0.02 ppm (rapid exchange with gaseous CO_2), indicative of a small degree of surface decomposition of formate to CO_2 and H_2. However, three additional but distinctive sharp peaks at $\delta = 165.22$, 165.49, and 165.75 ppm are clearly visible. Their typical peak widths are about 0.02–0.04 ppm, which is slightly larger than those of dissolved gas and molecular species, reflecting the surface-bound state of the formate species (longer T_1). This slower relaxation could be due to a slow restricted tumbling of the sterically hindered polymer-stabilized colloidal particles in solution, accounting for the anisotropic peak broadening. The sizes of the formate peaks were significantly enhanced when a high concentration of formic acid was used. Thus, the resonances at $\delta = 165.75$, 165.49, and 165.22 ppm are assigned to the bridging, multi-monodentate, and monodentate modes, respectively, which are consistent with the general order in the observed values of corresponding molecular formates, thus showing clearly the absence of a Knight shift effect.[8] It would be interesting to use higher field NMR spectroscopy to further resolve the individual modes into subpeaks arising from closely related sites. But the differences in chemical shift are expected to be very small, which poses a challenge as the introduction of the oxygen-atom spacer in the adsorbate renders this probe molecule less surface-sensitive. Nevertheless, an increase in particle size from 1.8 to 4.0 nm results in an increase in the ratio of bridging to multi-monodentate and bridging to monodentate species (Figure 4). Again, the progression we observe is consistent with the fact that for a hexagonal close-packed ruthenium particle of 1.8 nm, most atoms lie on edges or at vertices of the particle, where monodentate formate is thought to be present (although the

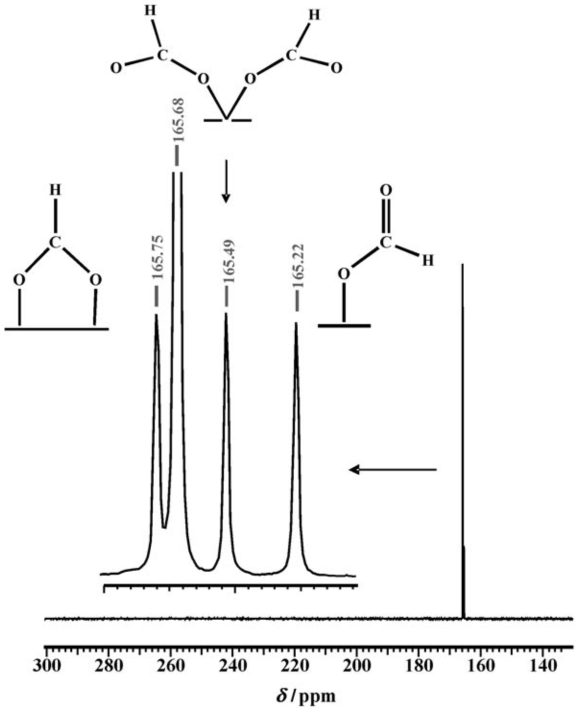

Figure 3. Three adsorbed formate species on PVP-Ru nanoparticles together with chemisorbed formic acid observed by ^{13}C NMR spectroscopy at room temperature (1:1 molar ratio of formic acid to ruthenium)

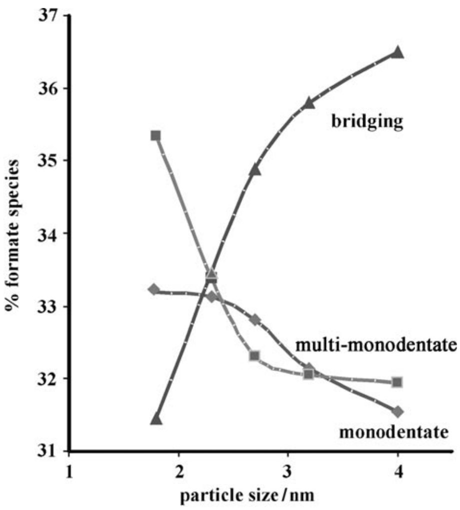

Figure 4. Variation of adsorbed formate species over five different sizes of PVP-Ru nanoparticles.

binding mode is also coverage-dependent). For highly coordination-unsaturated sites on vertices, defects, steps, or adatoms on the corrugated surface, the multi-monodentate mode is most prevalent. On the other hand, for large particles the surface of crystallites will consist of many terrace sites, which give rise to the bridging mode. The relative populations of the various formate species thus match well with the results of the ATR-IR spectra for CO and formic acid adsorption experiments, but this time the sharp peaks are clearly separated from each other. This result is also directionally consistent with the early model based on geometric analysis of the progressive change in terrace, edge, and corner sites on different sizes of close-packed crystallites.[9] However, the peaks in the NMR spectrum are more precise and quantifiable.

It is also interesting that the change in site population with decreasing size seems more abrupt than predicted from the model based on geometric analysis. Particularly, the sudden switch of site population from 2.3 to 1.8 nm towards multi-monodentate from the bridging mode reflects a drastic structural or topographical change in particles reaching the critical size regime. Interestingly, the Knight shift effect observed in the case of colloidal palladium with preadsorbed CO was also dramatically diminished at or below a size of 2 nm, indicative of the quantum size effect (switch to non-metallic character).[10] Peculiar catalytic properties of metals at such small sizes have recently been noted.[11] On the other hand, a particle of 2 nm would contain a few hundred atoms, which could be sufficient to allow the formation of a metallic lattice and well-defined band structure. As a result, one other possibility is that such a small quasi-spherical particle may create structural alteration in surface-atom packing, which may account for the deviations from the close-packed structure.[5b] It would be interesting to probe the surface structure and topography at this size.

Carbon monoxide is a conventional probe molecule for metal particles, and it has well-documented vibrational absorption modes. However, its degree of coverage, its surface distribution, and the presence of co-adsorbates are known to have significant effects on the peak position and peak width, which make it difficult to clearly identify and quantify metal sites. ^{13}C NMR spectroscopy could offer higher peak resolution and quantification. However, Bradley et al. noted the insurmountable Knight shift problems in colloidal transition metals above their quantum sizes in solution NMR spectroscopy.[5a] Duncan et al. also reported the missing peak from bridging CO using MAS NMR spectroscopy of silica-supported ruthenium, even though ruthenium gave a smaller Knight shift than other metals.[12] Clearly, the bridging mode experiences a much larger Knight shift than CO bound linearly on the faces of crystallites (the ^{13}C nucleus is even closer to the surface), thus causing severe downshifting and broadening of this mode beyond the detection limit.[13] Thus, in all these early studies, the Knight shift problems were clearly encountered if the probed nucleus was being placed directly on a metal surface through chemisorption. In contrast, we show that formate, with the OCO group, binds to surface metal atoms in a manner very similar to CO, but for formate the carbon nucleus is separated from the metal by oxygen as a spacer. This greater separation eliminates the Knight shift in NMR spectroscopy. We do not yet know whether there is any preferable orientation of this probe molecule on the surface, nor have we investigated coverage effects. But it is reasonable to assume that the surface concentration of each mode may be deduced at good resolution with calibration supported by other techniques.

In conclusion, formic acid adsorption combined with solution ^{13}C NMR spectroscopy allows different metal sites on colloidal metallic nanoparticles to be probed without using UHV techniques. Herein, we have collected the first ^{13}C NMR spectrum of PVP-stabilized Ru, which can reflect surface features of the metal without suffering from Knight shift problems. We believe this new characterization technique is valuable as a fist step in guiding the tailoring of metal sites for catalytic reactions through site maximization or site blockage and poisoning in solution, thus leading to ultra-selective metal nanocatalysts.

Experimental Section

Poly(vinylpyrrolidone) (PVP)-protected ruthenium nanoparticles were synthesized by the reduction of ruthenium salt ($RuCl_3$) with polyol solvent (diethylene or triethylene glycol) in the presence of PVP according to a modified literature procedure.[14] Both $RuCl_3$ (0.0500 g, 0.2023 mmol Ru) and PVP (0.120 g) were dissolved in the polyol (30 mL) under stirring and heated to 160 °C in an inert (N_2) atmosphere. After 3 h, a transparent dark brown solution of colloidal Ru nanoparticles was obtained. The Ru nanoparticles were precipitated in acetone, washed twice with acetone, and dried at room temperature under N_2. The size and distribution of the nanoparticles were characterized by transmission electron microscopy (TEM). TEM samples were prepared by placing a drop of colloidal dispersion of PVP-Ru nanoparticles in methanol onto a carbon-coated copper grid and subsequently allowing the solvent to evaporate. TEM images were taken using a FEI/Philips CM 20 microscope. Adsorption of formic acid and CO on the surface of colloidal PVP-Ru nanoparticles was investigated by ATR-IR spectroscopy. The spectra were acquired using a Nicolet 6700 ATR-IR spectrometer with a liquid-nitrogen-cooled MCT detector. A small drop of test sample was placed on smart golden gate-ZeSe (zinc selenide)/diamond crystal surface and evaporated at room temperature. The test sample for the formic acid adsorption study was composed of PVP-Ru nanoparticles in aqueous formic acid (1.00 mL, 0.5 M) in the molar ratio 2.5:1 (formic acid/Ru metal). For the CO adsorption study, the test sample was prepared by purging 1% CO in He into a sample of colloidal PVP-Ru (0.2023 mmol of Ru) in distilled water (1.00 mL) for 3 h. The ^{13}C NMR spectra were recorded on a 500 MHz Bruker AVII NMR spectrometer. The test samples were prepared by mixing PVP-Ru nanoparticles in deuterium oxide (0.5 mL) and H^{13}COOH in deuterium oxide (0.20 mL, 1 M, molar ratio formic acid/Ru metal 1:1). All spectra were the result of 3075 scans taken with a 2 s recycle delay.

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[1] a) A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757; b) J. D. Aiken, R. G. Finke, *J. Mol. Catal. A* **1999**, *145*, 1.

[2] a) S. E. Habas, H. Lee, V. Radmilovic, G. A. Somorjai, P. Yang, *Nat. Mater.* **2007**, *6*, 692; b) Y. J. Xiong, J. M. McLellan, J. Y. Chen, Y. D. Yin, Z. Y. Li, Y. N. Xia, *J. Am. Chem. Soc.* **2005**, *127*, 17118.

[3] R. Narayanan, M. A. El-Sayed, *J. Phys. Chem. B* **2005**, *109*, 12663.

[4] a) R. K. Shoemaker, T. M. Apple, *J. Phys Chem.* **1985**, *89*, 3185; b) K. W. Zilm, L. Bonneviot, D. M. Hamilton, G. G. Webb, G. L. Haller, *J. Phys. Chem.* **1990**, *94*, 1463; c) S. Y. Chin, C. T. Williams, M. D. Amiridis, *J. Phys. Chem. B* **2006**, *110*, 871; d) M. Kantcheva, S. Sayan, *Catal. Lett.* **1999**, *60*, 27.

[5] a) J. S. Bradley, J. M. Millar, E. W. Hill, *J. Am. Chem. Soc.* **1991**, *113*, 4016; b) J. S. Bradley, J. M. Millar, E. W. Hill, S. Behal, B. Chaudret, A. Duteil, *Faraday Discuss.* **1991**, *92*, 255.

[6] E. Guglielminotti, G. C. Bond, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 979.

[7] T. M. Duncan, R. W. Vaughan, *J. Catal.* **1981**, *67*, 49.

[8] a) Y. Gao, J. Kuncheria, G. P. A. Yap, R. J. Puddephatt, *Chem. Commun.* **1998**, 2365; b) M. K. Whittlesey, R. N. Perutz, M. H. Moore, *Organometallics* **1996**, *15*, 5166.

[9] R. Vanharde. F. Hartog, *Surf. Sci.* **1969**, *15*, 189.

[10] G. Schmid, L. F. Chi, *Adv. Mater.* **1998**, *10*, 515.

[11] Y. Sun, L. Zhuang, J. Lu, X. Hong, P. Liu, *J. Am. Chem. Soc.* **2007**, *129*, 15465.

[12] T. M. Duncan, K. W. Zilm, D. M. Hamilton, T. W. Root, *J. Phys. Chem.* **1989**, *93*, 2583.

[13] A. M. Thayer, T. M. Duncan, D. C. Douglass, *J. Phys. Chem.* **1990**, *94*, 2014.

[14] X. P. Yan, H. F. Liu, K. Y. Liew, *J. Mater. Chem.* **2001**, *11*, 3387–3391.