relatively flat, but low, barrier heights as shown in Figure 3F. The surface was now completely oxidized, and the exposed surface, after removal from the solution, appeared covered with a grayish film. This film has previously been associated with surface oxidation.[26]

The STM images presented above suggest that the formation of a graphitic oxide overlay occurs according to a nucleation and growth mechanism. The irreversible breaking of C–C bonds and the formation of graphitic oxide overlayer in the dilute acid environment studied here probably occur initially at step and defect sites (such as seen in Figure 2A) on the otherwise flat HOPG surface. The oxidation proceeds most rapidly along step and ridge sites and at a somewhat slower rate into the basal plane. The basal plane is unaffected by the cycling until the oxide grows in from initial defect sites. The oxide overlayer formed through this anodic procedure exhibits a barrier height that is substantially lower than that found for the bare HOPG surface, which is consistent with

its more insulating nature. This overlayer is also amorphous and loses the layer structure present in unoxidized HOPG.

This study illustrates the utility of the STM for following in situ progress of electrochemical reactions. We have demonstrated that atomic resolution is obtainable under potential control. Simultaneous barrier height measurements have proven useful in following the appearance of an overlayer structure and should, in general, have utility in following the progress of electrochemical reactions on electrode surfaces. With slightly improved resolution, images of atoms on metal surfaces[27] might be possible, enabling study of a wide variety of electrochemical processes with the STM.

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Electrogenerated Chemiluminescent Emission from an Organized (L–B) Monolayer of a Ru(bpy)3²⁺-Based Surfactant on Semiconductor and Metal Electrodes

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Electrogenerated chemiluminescence (ECL) from an organized monomolecular layer of a surfactant derivative of Ru(bpy)3²⁺ consisting of a single stearamidomethylene chain linked to one bipyridine unit at the 4-position and abbreviated Ru(bpy)2(bpy-C19)²⁺ has been observed at the surfaces of In-doped tin oxide, Pt, and Au electrodes. The surfactant monolayer was coated on the substrate electrodes by the Langmuir–Blodgett method. ECL was generated in an electrochemical cell containing an aqueous oxalate solution by applying a positive potential to the electrode modified by the monolayer of Ru(bpy)2(bpy-C19)²⁺. The ECL of the emitter monolayer deposited on an In-doped SnO2 electrode was quite intense with an emission maximum at ca. 680 nm. The ECL of the monolayer deposited on Pt and Au electrodes was generally 10²–10³ times weaker than that on SnO2, but still easily detectable.

We report here the first observation of the electrogenerated chemiluminescence (ECL)[1] from a monomolecular layer of emitter molecules confined to the surface of a solid electrode. The emitter employed was a surfactant derivative of tris(bipyridine)ruthenium complex, which was deposited on smooth metal or semiconductor electrodes as an organized assembly by the Langmuir–Blodgett (L–B) method

Ru(bpy)2(bpy-C19)²⁺   (I)
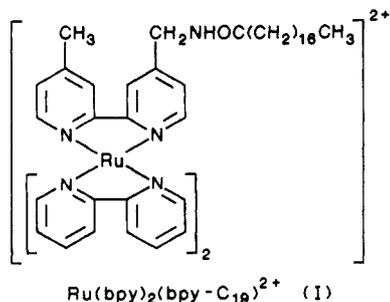
The observed luminescent emission was generated from the coated electrodes placed in aqueous oxalate solutions and biased to positive potentials. ECL has been generated in a variety of electrochemical systems, including polymer films on electrode surfaces.[2] The ECL of the Ru(bpy)3²⁺/C2O4²⁻ in aqueous media arises from the oxidation of Ru(bpy)3²⁺ at an electrode in the presence of oxalate by the following proposed reaction sequence:[3]

$$Ru(bpy)_3^{2+} \rightarrow Ru(bpy)_3^{3+} + e \qquad (1)$$

$$Ru(bpy)_3^{3+} + C_2O_4^{2-} \rightarrow Ru(bpy)_3^{2+} + C_2O_4^{-} \qquad (2)$$

$$C_2O_4^{-} \rightarrow CO_2 + CO_2^{-} \qquad (3)$$

$$Ru(bpy)_3^{2+} + CO_2^{-} \rightarrow Ru(bpy)_3^{+} + CO_2 \qquad (4)$$

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{+} \rightarrow Ru(bpy)_3^{2+*} + Ru(bpy)_3^{2+} \qquad (5)$$

$$Ru(bpy)_3^{3+} + CO_2^{-} \rightarrow Ru(bpy)_3^{2+*} + CO_2 \qquad (6)$$
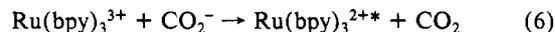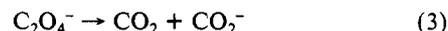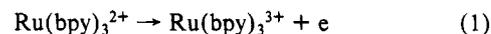
This ECL system was found useful in the determinations of both Ru(bpy)3²⁺ and oxalate at low concentration levels.[4]

There have also been studies of the synthesis of surfactant derivatives of Ru(bpy)3²⁺ and their photochemical properties in solution and as organized monolayer assemblies.[5,6] The reported luminescent emission of such surfactant monolayers, however,

(1) See, for example: (a) Bard, A. J.; Faulkner, L. R. In Electroanalytical Chemistry; Bard, A. J., Ed.; Dekker: New York, 1977, Vol. 10, and references therein. (b) Faulkner, L. R. In MTP International Review of Science: Physical Chemistry Series Two; Herschbach, D. R., Ed.; Butterworths: London, 1976, Vol. 9, p 213, and references therein. (c) Bard, A. J.; Faulkner, L. R. Electrochemical Methods; Wiley: New York, 1980; pp 621–629.

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(4) (a) Ege, D.; Becker, W. G.; Bard, A. J. Anal. Chem. 1984, 56, 2413. (b) Rubinstein, I.; Martin, C. R.; Bard, A. J. Ibid. 1983, 54, 1580.

(5) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, P. P.; Whitten, D. G. J. Am. Chem. Soc. (a) 1976, 98, 2337; (b) 1977, 99, 4947.

(6) Kalyanasundaram, K. Coord. Chem. Rev. 1982, 46; 218–224 and references therein (ref 257–265).

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always involved films coated on the surface of an insulator and generated by photoexcitation. The present monolayer ECL experiment with conductive and semiconductive substrates was motivated by our interest in electrochemical, electron-transfer, and energy-transfer processes at electrified interfaces. We also hope to use such organized layers for analytical applications and in imaging of surfaces, as described below.

Experimental Section

Preparation and Purification of the Surfactant $Ru(bpy)_3^{2+}$. Ruthenium(II) bis(2,2'-bipyridine)(4-methyl-4'-aminomethyl-2,2'-bipyridine) perchlorate,[7] 20 mg, and ca. 100 mg of stearoyl chloride (Nu-Check Prep) were dissolved in 10 mL of dichloromethane (Baker, spectrophotometric grade) and held at ca. 5 °C under an N_2 atmosphere. Pyridine (Mallinckrodt, spectrophotometric grade) was then added dropwise and the reaction was allowed to occur for several hours with magnetic stirring. The inorganic precipitate and the solvent were removed by filtration and distillation under reduced pressure, respectively. The desired product, I, left in the flask was identified by silica gel thin-layer chromatography from the fluorescence induced by UV irradiation. The purification of the product was carried out by open-column liquid chromatography with an activated silica particle column (20 cm × 1 cm, 100 mesh) and CH_2Cl_2 and MeOH (Baker, spectrophotometric grade) eluants. I was crystallized from the final MeOH solution in the refrigerator. The resulting solid was washed several times with Milli-Q water and dried in a vacuum desiccator. It was finally recrystallized twice from chloroform (Fisher, spectrophotometric grade) at -20 °C. The $Ru(bpy)_2$-$(bpy-C_{19})^{2+}$, collected as the perchlorate salt, was a red solid and weighed ca. 10 mg. Its purity was assessed by high-resolution proton NMR in CD_3Cl. Its resistance against hydrolysis in neutral aqueous medium was also checked by NMR after extracting the solution with D_2O.[8]

Preparation of Electrodes. In-doped SnO_2 on glass and platinum on glass and mica, as well as Pt and Au foils, were used as substrates for coating with monolayers of I. Pt/mica and Pt/glass electrodes were prepared by sputtering Pt (ca. 200 nm thick) on freshly peeled mica sheets and clean glass slides in an Ar plasma with a MRC (Material Research Co., Orangeburg, NY) Model 8620 sputtering system. All substrates were cleaned prior to use. The SnO_2/glass slides were cleaned by soaking in a KOH/EtOH bath, sonicating in PrOH, and rinsing with water. The metal electrodes were cleaned by sonicating in acetone followed by rinsing with 0.5 M H_2SO_4 and water. A monolayer of I was deposited on the substrate by the Langmuir–Blodgett method with a Lauda film balance (Brinkmann, Westbury, NY). Thirty microliters of a 2.00 mM chloroform solution of I (equiv 3.6 × 10^{16} molecules) was spread on the surface of a subphase solution, 1.0 mM $NaClO_4$ (Fisher) in water. The subphase solution was cleaned by filtration through a Nylon-66 filter, pore size 0.2 μm (Rainin, Woburn, MA) and adjusted to pH 7. The transfer of the monolayer film to the electrode substrates was done at a lifting rate of 0.5 cm/min and a controlled constant surface pressure of 30 dyn/cm. The surface pressure–area isotherms were recorded with the film balance apparatus.

Electrochemical and ECL Measurements. The electrochemical measurements were made with a PAR (Princeton Applied Research, Princeton, NJ) Model 175 potential programmer and a PAR Model 173 potentiostat. The ECL experiments were performed in a Pyrex cell containing an aq. 0.4 M Na_2SO_4 (MCB) and 0.02 M $Na_2C_2O_4$ (MCB) solution, with the substrate electrode modified by a monolayer of I as the working electrode, and a Pt gauze counter electrode and a saturated calomel reference electrode (SCE). The ECL emission was detected with a Hamamatsu
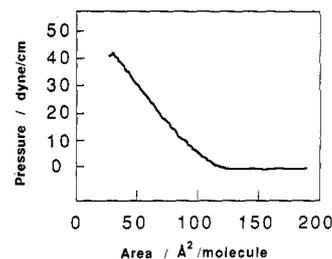
Figure 1. Surface pressure–area isotherm of I at 22 ± 1 °C. Subphase: 1.0 mM $NaClO_4$ aqueous solution (pH 6.7).
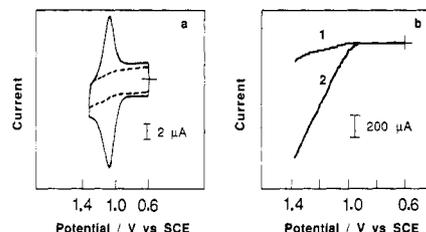
Figure 2. (a) Cyclic voltammogram of monolayer of I coated on an In-doped SnO_2 electrode (ca. 0.8 cm²) obtained in 0.5 M Na_2SO_4 aqueous solution (pH 5) at a scan rate of 200 mV/s. Dotted line indicates background current. (b) Current–potential curves for the oxidation of oxalate at a bare In-doped SnO_2 electrode (1) and at the same SnO_2 electrode coated with a monolayer of I (2), obtained in 0.02 M $Na_2C_2O_4$, 0.4 M Na_2SO_4 aqueous solution (pH 5.5) at 200 mV/s. Electrode area: ca. 0.35 cm².

(Middlesex, NJ) Model R928 photomultiplier tube (PMT) and a Model C1230 photon counter. The PMT was sealed in a cooling chamber at ca. -25 °C. The ECL emission spectra were taken with an Oriel (Stamford, CT) Model 77250 monochromator that was placed between the optical cell and the PMT and driven by an electric motor at a speed of ca. 1.2 nm/s. All experiments were carried out at room temperature (22 ± 1 °C).

Results and Discussion

Monolayer Deposition. A monolayer of I, formed by spreading a small quantity of the surfactant dissolved in chloroform on the surface of a neutral 1.0 mM $NaClO_4$ aqueous solution, showed the surface pressure–area isotherm given in Figure 1. The pressure started to rise at ca. 125 Å/molecule and then increased almost linearly with a decrease in area until ca. 42 dyn/cm, when the monolayer film broke. This monolayer film of I with a single hydrocarbon chain was more compressible than most of the other surfactant derivatives of $Ru(bpy)_3^{2+}$ with two attached hydrocarbon chains.[5,6] The pressure–area isotherm was reproducible in both the compression and expansion modes over time periods of several minutes (typical of cyclic voltammetric and ECL measurements), indicating that hydrolysis was negligible in neutral aqueous solution. The composition of the subphase solution can affect the pressure–area isotherms of the surfactant derivatives of $Ru(bpy)_3^{2+}$ and the molecular packing structures in organized monolayers.[5,6] In our preparations, a dilute solution of $NaClO_4$ was used as the subphase, because perchlorate ion was the counter ion in I. The same subphase was used with all electrode substrates. Since all of the electrode substrates have hydrophilic surfaces, the transfer of the monolayer to the electrodes was made by lifting the electrodes out of the subphase solution. The surfactant monolayer was thus coated on the electrodes with the hydrophilic site, the $Ru(bpy)_3^{2+}$ head group, against the electrode surface, and the hydrophobic hydrocarbon chain sticking out toward the solution. The coated electrode was then transferred in air to a deaerated solution in the electrochemical cell. Previous studies[9]

(7) This compound was prepared and purified by Dr. Walter Dressick. We are indebted to Dr. Dressick for providing us with this compound.

(8) ¹H NMR (CD₃Cl) δ 0.083 (t, 3, $-CH_2CH_3$), 1.10–1.35 (br, 28, $-CH_2(CH_2)_{14}CH_3$), 1.45–1.65 (br, 7, $-COCH_2CH_2(CH_2)_{14}CH_3$, $-NH-$, $2H_2O$), 2.26 (t, 2, $-COCH_2CH_2-$), 2.49 (S, 3, bpy-CH_3), 4.55 (d, 2, phy-CH_2NH-), 7.30–8.50 (comp, 22, pby-H). For details, see Xun Zhang, Ph.D. Dissertation, University of Texas at Austin, 1989.

(9) For example, see: (a) Lee, C.-W.; Bard, A. J. *J. Electroanal. Chem.* **1988**, *239*, 441. (b) Daifuku, H.; Aoki, K.; Tokuda, K.; Matsuda, H. *J. Electroanal. Chem.* **1985**, *183*, 1. (c) Fujihira, M.; Araki, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2379. (d) Facci, J. S.; Falcigno, P. A.; Gold, J. M. *Langmuir* **1986**, *2*, 732. (e) Yokota, T.; Itoh, K.; Fujishima, A. *J. Electroanal. Chem.* **1987**, *216*, 287. (f) Matsuda, H.; Aoki, K.; Tokuda, K. *J. Electroanal. Chem.* **1987**, *217*, 1, 15.
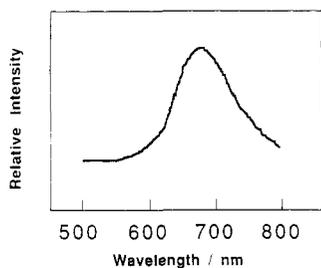
Figure 3. ECL emission spectrum of monolayer of I coated on an In-doped SnO_2 electrode, in 0.02 M $Na_2C_2O_4$, 0.4 M Na_2SO_4 aqueous solution (pH 5.5) with the electrode at +1.25 V vs SCE.

of electrodes coated with organized monolayers prepared on the L–B film balance suggest that reorganization of the film does not occur during such a transfer.

Cyclic Voltammetry. The cyclic voltammogram (CV) for a monolayer of I coated on SnO_2 electrode at a scan rate, v, of 200 mV/s in 0.5 M Na_2SO_4 solution (pH 5) is shown in Figure 2a. The background current at a clean SnO_2 electrode in supporting electrolyte is shown as the dotted line in Figure 2a. The CV showed an anodic peak at +1.06 V vs SCE and had the charac-teristics of a redox system confined to an electrode surface.[10] The oxidation and reduction peaks were almost symmetrical and showed no diffusional tails. The peak current, i_p, was proportional to v, from 50 to 500 mV/s. The difference between the anodic and cathodic peak potentials, ΔE, was ca. 30 mV and the potential width at the half-height of the peaks was slightly greater than the ideal value of 91 mV. Note that the anodic current after the peak did not drop to the background level but attained a higher steady-state value, similar to what has been seen previously in acidic solution.[9b] This additional anodic current may be the indication of a catalytic component, e.g., the oxidation of water, by the surfactant derivative of $Ru(bpy)_3^{3+}$, regenerating the $Ru(bpy)_2(bpy-C_{19})^{2+}$.[9b] The CV response remained essentially the same for scans at 200 mV/s over a period of at least 5 min. The integrated CV response was equivalent to coverage of about 130 Å^2/molecule.

Figure 2b shows a CV for the oxidation of oxalate at a bare SnO_2 electrode (curve 1) and the SnO_2 electrode coated with a monolayer of I (curve 2), in 0.02 M $Na_2C_2O_4$ and 0.4 M Na_2SO_4 (pH 5.5), at v = 200 mV/s. At a bare SnO_2 electrode the oxi-dation of oxalate is quite sluggish. The oxidation of oxalate at the SnO_2 electrode modified by a monolayer of I was fast, in agreement with past results with $Ru(bpy)_3^{2+}$ solutions and films,[2,3] where $Ru(bpy)_3^{2+}$ oxidation catalyzes that of oxalate. The ob-served increase in the anodic current was more pronounced here than in the previous cases involving dissolved $Ru(bpy)_3^{2+}$, indi-cating the monolayer system is a better catalyst for the oxidation of oxalate. At the I-monolayer-covered electrode surface, the oxidation of most of the oxalate ions probably proceeds through the mediation of the oxidized surfactant, $Ru(bpy)_2(bpy-C_{19})^{3+}$, which would be regenerated very rapidly at the electrode at the applied potential.

Electrogenerated Chemiluminescence. ECL from a monolayer of I was observed with both SnO_2 and metal electrodes. When the potential of the working electrode with a monolayer of I was stepped to +1.25 V vs SCE to oxidize $Ru(bpy)_2(bpy-C_{19})^{2+}$ to the +3 form, emission was observed. The rather intense ECL emission found with a SnO_2 electrode produced the spectrum shown in Figure 3, generally characteristic of the luminescent emission of $Ru(bpy)_3^{2+}$ species. The emission peak at 680 nm is at a longer wavelength than that found for solution phase $Ru(bpy)_3^{2+}$ (ca. 610 nm). The shift is caused by interactions among the surfactant molecules and between the surfactants and solid electrode surface. The emission maximum following pho-toexcitation of $Ru(bpy)_2(bpy-C_{19})^{2+}$ dissolved in MeCN was at about 600 nm. Previous studies of surfactant $Ru(bpy)_3^{2+}$ species
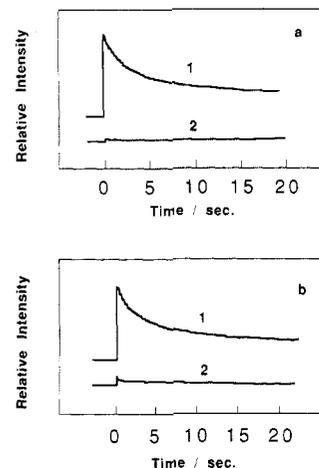
Figure 4. ECL emission from monolayer of I coated on metal electrodes (1) and background emissions of the same electrodes after washing off the monolayer with chloroform (2), in 0.02 M $Na_2C_2O_4$, 0.4 M Na_2SO_4 aqueous solution (pH 5.5) with a potential step of +1.25 vs SCE applied to the electrode at time 0. (a) Pt/mica electrode; (b) Au foil electrode.

have shown similar red shifts in emission curves compared to $Ru(bpy)_3^{2+}$ upon coating the surfactant on an insulating surface.[5,6]

ECL of the monolayer of I deposited on metal electrodes (i.e., Pt/mica, Pt/glass, Pt and Au foils) was also detected, although these emission intensities were generally 100–1000 times lower than those on a SnO_2 electrode of similar area. Pt sputtered on mica was shown by scanning tunneling microscopy (STM) to be atomically smooth.[11] The ECL emission from a monolayer of I coated on such a Pt/mica electrode has been recorded and is shown in Figure 4a (curve 1). The emission was greatest im-mediately after the potential step and then decayed with the square root of time during the initial several seconds, suggesting that the intensity is limited by the rate of diffusion of oxalate ions from solution bulk to the electrode surface. To assure that the observed emission was not from impurities or a hydrolysis product of I in solution, the experiment was repeated with the same electrode and solution after wiping off the surfactant monolayer from the Pt/mica surface with chloroform. The result is shown in Figure 4a (curve 2); essentially no emission was detected following the potential step at the same sensitivity setting of the photon counter. In Figure 4b ECL emission from an Au foil electrode coated with a monolayer of I (curve 1) is compared to that from the same electrode after rinsing in chloroform (curve 2). The results for other metal electrodes (Pt/glass and Pt foil) were essentially identical with the ones presented in Figure 4.

ECL of the $Ru(bpy)_3^{2+}$-based system in a monolayer differs in several ways from that of similar system in solution. One would expect the excited-state $Ru(bpy)_3^{2+}$ centers (R*) in the monolayer to be quenched much more effectively by the conductive substrate by both energy- and electron-transfer routes.[12] The fact that the intensity of emission is much greater at SnO_2 than the metal films suggests that this type of quenching occurs. Nevertheless, emission is seen from R* that are very near (several angstroms) the metal surface, showing that emission from the relatively long-lived em-itter (radiative lifetime ca. 1 μs) can compete with the quenching process. One might also expect second-order quenching processes among $Ru(bpy)_3^{2+}$ centers, e.g.,

$$Ru(bpy)_3^{3+} + Ru(bpy)_3^{2+*} \rightarrow Ru(bpy)_3^{2+} + Ru(bpy)_3^{3+} \quad (7)$$
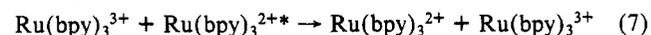
to be more important in the monolayer, because the species are held in close proximity (ca. 13 Å from center to center according to the CV molecular area estimation) (i.e., the effective concen-trations are high). On the other hand, the monolayer species are

(10) See, for example: (a) Laviron, E. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1982; Vol. 12. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 519.

(11) Liu, H.-Y.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1985**, *132*, 2666.

(12) See, for example: (a) Kuhn, H.; Mobius, D.; Bucher, H. In *Physical Methods of Chemistry*; Weissberger, A., Rossiter, B. W., Eds.; Wiley-In-terscience: New York, 1970; Vol. I, Part IIIB, Chapter VII. (b) Chandross, E. A.; Visco, R. E. *J. Phys. Chem.* **1968**, *72*, 378.

less mobile on the electrode surface and perhaps cannot orient for most effective electron and energy transfer between the species.

The rates of the reactions leading to R*, eq 1–6, may also differ in the monolayer. For example, production of the critical intermediate, CO_2^-, may be more effective in the monolayer, if the direct oxidation at the electrode surface of it and $C_2O_4^{2-}$ are effectively blocked by the monolayer. In this case any CO_2^- at the monolayer will produce either R* directly via eq 6, or indirectly via (4) and (5); other processes leading to loss of this very reducing species, e.g., reduction of protons or dimerization, must also be occurring in both monolayer and solution reactions.

While a fuller elucidation of the processes described above requires further studies, the availability of an excitable monolayer assembly on conductive substrates should allow a number of novel experiments to be carried out. For example, the study on the effect of electrode material and potential on the quenching of R* following photoexcitation should be possible. ECL has been used as a highly sensitive analytical method;[4] the monolayer approach

may provide for even higher sensitivity, with a lesser amount of material concentrated on an electrode surface. It may also be useful in the fabrication of a fixed probe for ECL. When combined with the techniques of STM or scanning electrochemical microscopy,[13] with video detection and imaging,[14] it should be possible to detect optically the distribution of small numbers of molecules or the arrival of suitable reactant molecules at the monolayer/solution interface. Experiments of this type are under way in our laboratory.

(13) Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *J. Am. Chem. Soc.*, submitted for publication.
(14) See, for example: (a) Bilhorn, R. B.; Sweedler, J. V.; Epperson, P. M.; Denton, M. B. *Appl. Spectrosc.* **1987,** *41,* 1114; (b) **1987,** *41,* 1125. (c) Hiraoka, Y.; Sedat, J. W.; Agard, D. A. *Science* **1987,** *238,* 36.

Silicon-29 Cross-Polarization/Magic Angle Spinning NMR Evidence for Geminal Silanols on Vacuum-Activated Aerosil Silica

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Silicon-29 CPMAS NMR spectroscopy has been used to study aerosil silica which has been activated under vacuum up to 1000 °C and where spectra have been recorded with samples still under vacuum. For all temperatures up to 800 °C activation, a signal due to geminal [$Si(OH)_2$] silanol groups was detected, thus clearly demonstrating for the first time that these species exist on aerosil silicas which have been vacuum activated in this temperature range. Line broadening occurs for 1000 °C activation, and the geminal signal cannot be distinctly resolved.

Part of the infrared spectrum of an aerosil silica which has been activated at 450, 600, 800, or 1000 °C is shown in Figure 1. This spectral region is associated with the OH stretching vibrations of surface silanol groups, and the sharp peak near 3747 cm^{-1} was attributed years ago[1] to this vibrational mode of isolated (that is, not hydrogen-bonded) single SiOH groups in which the surface Si atom is attached to three other Si atoms via SiOSi siloxane bonds. Several groups[2–5] have attempted to show that this sharp band, which is also in the spectra of silica gels, could be resolved into more than one component and that the various components could be assigned to single and geminal, $Si(OH)_2$, silanol groups, where in the latter case, the surface Si atom would have two SiOSi bonds. In most cases, it was shown[6,7] that the apparent resolution could be attributed to improper balancing of the two beams of a double-beam infrared spectrometer due to the presence of water vapor which is strongly absorbing in this spectral region. Exceptionally, Fink and Plotzki[5] reported a shoulder near 3742 cm^{-1} for an aerosil activated at 650 °C which they attributed to geminal silanols, but this finding cannot be duplicated by others.[6–11]

Theoretical calculations[12,13] have shown that the OH stretching frequencies of isolated single and geminal silanols should be very close, having a 1–2-cm^{-1} separation, and for this reason one rationalizes the failure of infrared spectroscopy to "resolve" distinct components. However, Hoffmann and Knözinger[8] were the first to show that, following activation near 900 °C, the peak becomes relatively symmetrical and its maximum shifts to 3747 cm^{-1}, as is shown in Figure 1 (a lower resolution was used to obtain our spectra). They speculated that the peak at 3749 cm^{-1} was due to single SiOH species and that part of the intensity at 3747 cm^{-1} was due to geminal silanol species. However, other interpretations could be advanced for these experimental observations because the surface of silica changes considerably as dehydroxylation proceeds[14,15] (see Discussion). Therefore, infrared spectroscopy has not provided conclusive evidence that geminal silanol groups exist on vacuum-activated aerosil silica and this controversy remains unresolved.

By contrast, silicon-29 MAS and CPMAS NMR have been very successfully used to study the SiOH structure of silica gels[16–19]

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(2) Hair, M. L.; Hertl, W. *J. Phys. Chem.* **1969,** *73,* 2372.
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(9) Ryason, P. R.; Russell, B. G. *J. Phys. Chem.* **1975,** *79,* 1276.
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