observed from the ethoxy precursors.

^{29}Si CP/MAS NMR of **3z** prepared under acidic hydrolysis conditions of **3a** followed by solvent replacement[10] and vacuum drying shows three resonances at −59, −68, and −76 ppm, respectively. The peaks correspond to branched silicates that correlate with the substructures PhSi-(OH)$_2$(SiO) (T$_1$^{Ph}), PhSi(OH)(OSi)$_2$ (T$_2$^{Ph}), and PhSi(OSi)$_3$ (T$_3$^{Ph}).[19,20] The ^{29}Si resonances were deconvoluted, and the areas, after correction for contact times, were integrated. Xerogels prepared by acid-catalyzed hydrolysis/condensation of **3a**, **4a**, and **5a** indicate the degree of condensation to be approximately 60–70%. Base-catalyzed hydrolysis[18] and solvent gradient processing produce materials with a higher degree of condensation (75–85%). The absence of a ^{29}Si resonance corresponding to Q$_4$ (silicate, −110 ppm) indicates the monomers retain their integrity during hydrolysis and do not suffer aryl group cleavage. Although quantitative conclusions regarding the calculated degree of condensation must be interpreted with caution,[20c] the materials reveal an extent of condensation similar to that found in pure silicate xerogels.

In conclusion, it is shown that organic spacers can be inserted at regular intervals into the Si–O–Si silicate structure. Sol–gel processing allows for the preparation of aryl-bridged polysilsesquioxanes, high surface area materials that have certain morphological properties in common with silicates but with added opportunities for systematic modification. Applications of these and related materials to chromatography, optics, and molecular level control of morphology will be presented in forthcoming articles.

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Electrocatalytic Reduction of CO$_2$ by Thin Polymeric Films Containing Metallic Rhodium

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Direct reduction of carbon dioxide at most common electrode surfaces (e.g., Pt or C) occurs with large overpotentials[1–3] and, typically, stops at the stage of two-
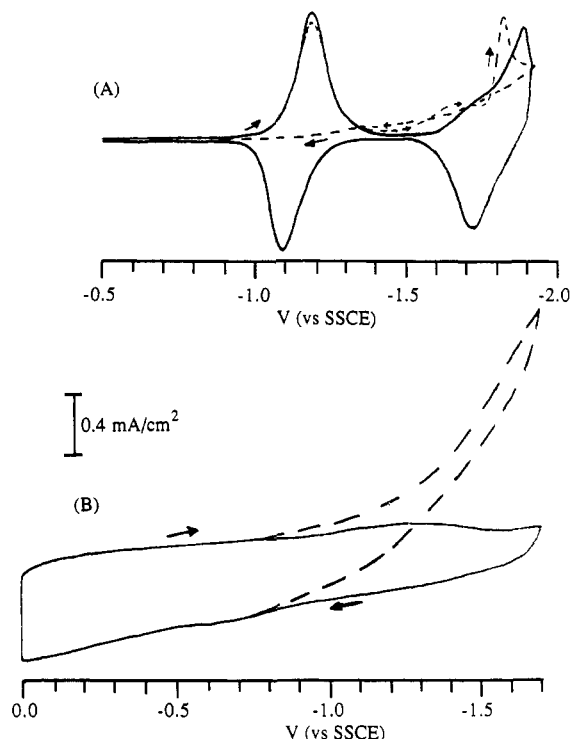

Figure 1. (A) Cyclic voltammetry of a 2.2 × 10^{-8} mol/cm^2 poly[Rh(vbpy)(COD)]Br film at 50 mV/s in 0.1 M TBABr/CH$_3$CN solution under N$_2$ (solid line) and CO$_2$ (broken line) atmospheres. (B) Cyclic voltammetry of the poly[Rh(vbpy)-(COD)]Br film at 100 mV/s after a 20-min electrolysis in 0.1 M TBABr/CH$_3$CN in the presence of CO$_2$ and [Rh(COD)Cl]$_2$. The solid line was recorded under N$_2$, and the broken line under CO$_2$ atmospheres.

electron, single carbon reduction products such as formic acid or carbon monoxide. Recently, metal electrodes such as Ru,[4] Cu,[5] Mo,[6] and Au[7] and semiconductor electrodes, for example, GaAs,[8] have been successfully employed to produce methanol, methane, and/or ethylene. During our studies on the electrocatalytic reduction of CO$_2$ by transition-metal complexes in homogeneous solution[9] and in some related preparative studies of thin polymeric films on electrode surfaces,[10] we have found that metallic Rh can

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Table I. CO₂ Reduction Products from Bulk Electrolyses on poly[Rh(vbpy)(COD)]/Rh(0)[a]

entry	[H₂O], M	total coulombs[b]	Faradaic efficiencies[d] of formation,[d] %				
			H₂	CH₄	CH₃OH	CH₂=CH₂	CH₃CH=CH₂
1	0	16.5	1.5	18.4	<1	<1	<1
2	0	7.8	0.5	5.1	38	<1	<1
3	0	10	1	8.1	18.1	<1	<1
3	0.1	40	17	2.0	40	<1	<1
4	0.1	20	27	1.4	28	<1	<1
5	0.1	50	20	7.2	12	10	<1
6	0.01 M HCl	50	0.5	13	<1	4.5	1.0

[a] In CH₃CN solutions of 0.1 M TBAH at −1.60 V vs SSCE. Films grown on vitreous carbon electrodes, original surface coverage of poly[Rh(vbpy)(COD)]Br ∼ 10⁻⁷ mol before Rh(0) deposition. No CO₂ reduction is observed at bare vitreous carbon. [b] Not exhaustive—catalytic current in all cases was at least one-third of original and fairly stable (although most show slow degradation) when electrolysis was stopped. [c] Defined as {100nF(moles of product)}/(coulombs of charge passed), where n is the number of moles of electrons delivered per mole of product and F is Faraday's constant, 96 500 C/mol of electrons. In all cases the Faradaic efficiency for CO, formate and oxalate was <1.0%. [d] Not all of the products have been identified, so the values do not add up to 100%.

be deposited in polymeric films of poly[4-vinyl-4′-methyl-2,2′-bipyridine] (poly[vbpy]). This new material is a very active catalyst for CO₂ reduction. In this communication we describe the preparation and electrocatalytic properties of this supported-metal electrocatalyst, and our initial success in producing multiple-electron reduction products from CO₂ past the two-electron stage.

Films of poly[Rh(vbpy)(COD)]Br (COD is 2,5-cyclooctadiene) were prepared on platinum, glassy carbon, or vitreous carbon electrodes as described previously.[10] The electrochemistry of the resulting gold-orange film in fresh 0.1 M (n-C₄H₉)₄NBr (TBABr)/CH₃CN under an atmosphere of N₂ is shown in Figure 1A (solid line). In the presence of CO₂ (Figure 1A, broken line) the first reduction is partially reversible if the potential is switched at −1.3 V (versus SSCE), but scanning through the second wave leads to both loss of electroactivity and the characteristic orange coloration of the film. These observations are consistent with earlier observations that Rh(I) could be removed easily from poly[Rh(vbpy)(COD)]Br films by chemical means to leave only a film of optically transparent poly(vbpy). In the same studies it was found that rhodium could be quantitatively reincorporated by soaking the poly(vbpy) films in CH₃CN solutions containing the reactive dimer, [Rh(COD)Cl]₂.[10]

In this work, when a modified electrode that had been reduced in the presence of CO₂ as described above was treated with [Rh(COD)Cl]₂, the cyclic voltammetry of the original poly[Rh(vbpy)(COD)]Br film was regenerated. This demonstrates that the polymer network was left intact during exposure to CO₂ and that an interaction between CO₂ and the reduced complex leads to Rh removal from the poly(vbpy) film.

Controlled potential electrolysis of poly[Rh(vbpy)-(COD)]Br films at −1.55 V (vs. SCE) in 0.1 M TBABr/CH₃CN in the presence of CO₂ *and* 0.5 mM [Rh(COD)Cl]₂ resulted in suprising current vs time curves. During the initial phase of the electrolysis there was a relatively small catalytic current density (j_{cat} ∼ 0.15 mA/cm²), but after an induction period of ∼1 min the current started to *increase*. After 5 min, j_{cat} = 0.80 mA/cm² and at 20 min j_{cat} = 1.5 mA/cm². At this point, the smooth, initially orange modified- electrode surface had become jet-black. Only very small constant currents (<0.1 mA/cm²) were observed at bare electrodes (Pt, Rh, or C) in the presence of both CO₂ and [Rh(COD)Cl]₂ or, at the modified electrodes, in the presence of [Rh(COD)Cl]₂ and the absence of CO₂.

In one electrode preparation, after a 20-min electrolysis period, XPS spectral analysis of the new film showed intense Rh 3d transitions at 311.8 and 307.1 eV (Figure 2A, broken line). These are shifted to lower binding energies
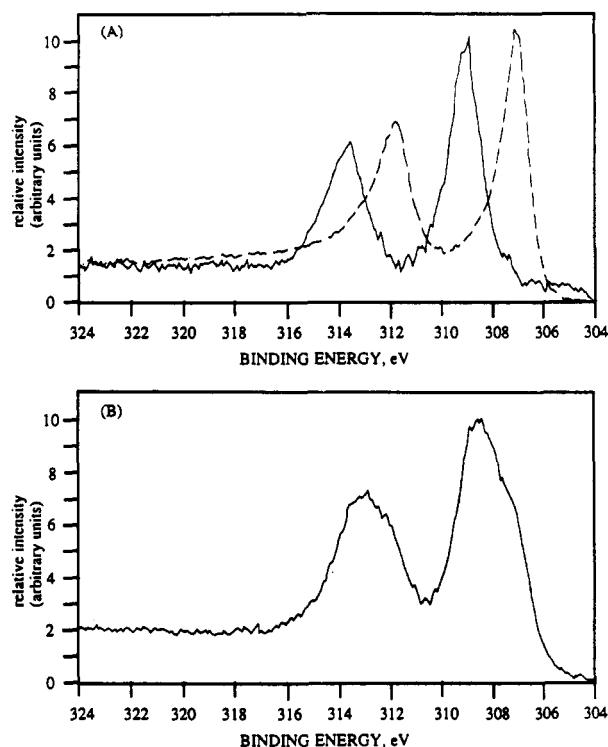

Figure 2. (A) Solid line: ESCA of a poly[Rh(vbpy)(COD)]Br film showing Rh₃d peaks at 313.6 and 309.0 eV. Broken line: ESCA of a poly[Rh(vbpy)(COD)]Br film after a 20-min electrolysis (as in Figure 1B), illustrating the shift in Rh₃d peaks to 311.8 and 307.1 eV. (B) ESCA of a poly[Rh(vbpy)(COD)]Br film after only 1-min electrolysis, showing a mixture of Rh compounds.

by almost 2 eV from those of the parent polymer poly-[Rh¹(vbpy)(COD)]Br, which occur at 313.6 and 309.0 eV (Figure 2A, solid line). The shifts are consistent with a change in oxidation state from Rh(I) to Rh(0) following the electrolysis.[11] The Rh:N ratio has also changed dramatically, from 0.4:1 for the parent polymer to 3.4:1 following this electrolysis.

In an experiment designed to show the composition of the electrode at short preparations times, a 1-min electrolysis of [Rh(COD)Cl]₂/CO₂ under conditions similar to those given above resulted in the XPS spectral data shown in Figure 2B. Although their individual peaks are not resolved because of their large band width, the spectrum is reminiscent of either overlapping Rh(I) and Rh(0) or an

(11) Infrared spectral analysis of the black material shows *no* absorptions in the CO stretching region (between 1600 and 2100 cm⁻¹), which demonstrates that the new material does not contain rhodium carbonyl compounds.

intermediate oxidation state material. The Rh:N ratio in this case was 0.74:1.

The cyclic voltammetry of the Rh-impregnated films immersed in fresh electrolyte/solvent (Figure 1B, solid line) displays a background current ascribable to a substantial non-Faradaic current component, with no reproducible, distinguishing peaks. In the presence of CO_2 a current enhancement is seen to begin near −1.0 V and continue to increase in current until past −1.6 V (Figure 1B, dashed line). By contrast, pure Rh wire shows no current enhancement in the presence of CO_2 under identical experimental conditions.

Controlled potential electrolyses at −1.60 V (vs SSCE) of the Rh-impregnated films prepared in the manner described above were performed in the presence of CO_2 using large vitreous carbon electrodes and employing a number of different water concentrations.[12] The results are shown in Table I. The electrolyses were not exhaustive, and in each case, the electrodes were catalytically active when the electrolyses were stopped.[13] Although reproducibility of the product yield is less than desirable, a number of important observations can be made. First, less than 1% CO, formate, or oxalate is observed under any electrolysis condition. Second, electrolyses in fresh 0.1 M TBAH/CH_3CN produces hydrocarbons and CH_3OH even without added H_2O, although with 0.1 M H_2O added, the catalytic currents increase dramatically to form significant amounts of CH_3OH, in addition to H_2. Last, in all cases, CH_4 is also produced in significant yield. Even when 0.01 M HCl is used as the proton source instead of water, CH_4 and other hydrocarbons are obtained but little H_2 is observed.

The distribution of hydrocarbon products is reminiscent of a low molecular weight Fischer–Tropsch reaction product distribution.[14] For example, in experiment no. 6 the current yields of hydrocarbons were methane, 13.0%; ethane, 0.3%; ethylene, 4.5%; propene, 0.9%; propane, 0.4%; and total butenes, 0.3%.[15] Rh metal has been shown to be an active Fischer–Tropsch catalyst for the reduction of CO (and CO_2) with H_2;[16-18] however, in our case, the reactivity is brought about electrochemically at ambient temperature and low pressure by using CO_2, a proton source, and electrons, instead of more extreme conditions with CO and H_2.

To our knowledge, this is the first report of successful CO_2 reduction by a supported rhodium metal electrocatalyst. A significant aspect of the results is that an otherwise low-reactivity metal, in an electrochemical sense, has been converted into an active electrocatalyst for CO_2 reduction by its deposition into a polymer that is attached to an electrode surface.

(12) The nominal water content in our "dry" CH_3CN is ~0.5–1 mM.

(13) During the synthesis of a Rh metal modified electrode 6–10 C of charge is consumed. In one of our best runs, ca. 30 C of charge can be accounted for as products at which point the catalytic current is still >50% of the initial current.

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Metal Complexes in Inorganic Matrices. 4.[1] Small Metal Particles in Pd–SiO2 Composites by Sol–Gel Processing of Metal Complexes

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By the sol–gel technique, a variety of solid materials with interesting properties can be made, among them composites containing small metal or metal oxide particles dispersed in a ceramic matrix.[2,3] One of the problems connected with this method is the control of the average metal particle size and the metal distribution. Ueno et al.[4a] reported that hydrolysis of a mixed solution of metal glycolates and Si(OEt)₄ (TEOS) supplies silica-supported metals (Ni,[4] Fe,[5] Rh[6]) with particularly small and homogeneous particle sizes. The glycolates are formed in situ from the corresponding metal nitrates in an ethylene glycol solution. Environments of the metal atoms were probed by EXAFS spectroscopy at all steps of the Ni–SiO2 preparation.[4b] According to these results, dissolving nickel nitrate in ethylene glycol results in a metal glycolate, in which the metal atom is octahedrally surrounded by six oxygen atoms. Octahedral coordination of nickel is retained on addition of TEOS and subsequently on hydrolysis, but ^{1}H NMR spectroscopic detection of 1,2-diethoxyethane indicates that some of the glycolate ligands are replaced by OSi(OEt)₃ groups. Even in the dried gels, discrete Ni–O–Si species exist. Only on calcination do tiny NiO clusters develop, which on reduction by H_2 give small and uniform metal particles. The key to control the metal particle size is the high dispersion of the metal compound prior to calcination and reduction, due to bonding between the metal and the supporting matrix.

Although the ethylene glycol modification of the sol–gel method gives striking results, it may not be equally successful, if less oxophilic metal ions (or metal ions forming no glycolates) are employed. Therefore, a more general approach to dispersing metal complexes would be the use of a chemically adjustable link between the metal ion and the support, for instance, molecules of the type AxxxxSi(OR)₃. In these bifunctional compounds, a group A, capable of binding to the particular metal ion, is connected with the hydrolyzable Si(OR)₃ group via an inert spacer,

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