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.

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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–SiO$_2$ 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 Ax-xxxSi(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,

(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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(15) It is noteworthy that ~40–60% of the current is not accounted for as low molecular weight products. The missing current could be consumed in the formation of higher hydrocarbons as is often the case for Fischer–Tropsch reactions that use CO and H_2.

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symbolized as xxxx. It is well-known that, by use of such compounds as ligands, metal complexes, which are catalytically active in the homogeneous phase, can be heterogenized either by reaction with surface OH groups on supports such as silica and alumina[7] or by the sol-gel method.[1,8,9]

In this work, we report preliminary results showing that such ligands and derived metal complexes, LnM-Ax-xxxSi(OR)$_3$, can also be employed to control dispersion of the metal compound during the sol-gel process and to provide small metal oxide particles (and subsequently small metal particles), provided that the anchoring group A has a chemical composition that allows its removal during calcination.

Since a variety of stable transition-metal complexes with amine or ethylenediamine ligands are known, we used RHN(CH$_2$)$_3$Si(OR')$_3$ (for 1, R = H$_2$NCH$_2$CH$_2$, R' = Me; for 2, R = H, R' = Et) in this work to bind the metal ions. It turned out that isolation of the complexes containing these modified ethylenediamine or amine ligands is not necessary, because they are formed in situ, when solutions of nickel or palladium salts are mixed with 1 or 2. For instance, addition of 3 equiv of 1 to a concentrated aqueous solution of NiCl$_2$ results in an immediate change in color from green to violet blue and to initiation of gelation. Both the color and the UV spectrum of the gelating reaction mixture are identical with that of [Ni(en)$_3$]$^{2+}$ (en = H$_2$NCH$_2$CH$_2$NH$_2$) and indicate the presence of complexes [Ni(1)$_3$]$^{2+}$. Although we do not know the exact chemical composition of the intermediate complexes in every case, preliminary results indicate that the method for the preparation of small metal particles in SiO$_2$ by sol-gel processing of in situ formed metal complexes can be applied to a variety of metals.[10] In this communication, we restrict ourselves to demonstrating the utility of this method for Pd-SiO$_2$ composites.

Palladium(II) acetylacetonate is dissolved in ethanol or methanol (300 ml of alcohol/mmol of metal), and 3 equiv of 1 or 2 and a variable amount of TEOS (x mmol/mmol of metal) are added. The metal contents in the products is controlled by the relative amount of TEOS (x). In the present work, molar metal/TEOS ratios (1/x) between 1/8 and 1/150 were chosen. A 7.5-fold excess of water (relative to the amount of water necessary to hydrolyze all SiOR groups; i.e., 7.5(4x + 9) mmol of H$_2$O/mmol of metal) and NH$_3$ as the polycondensation catalyst are introduced into the system by adding the calculated amount of aqueous 0.2 N ammonia. The resulting homogeneous, light yellow mixture is heated for 3 days to 70 °C in a flask equipped with a reflux condenser and then allowed to stand at room temperature in an open beaker. While the solvent evaporates during several days, the polycondensation reaction is complete. The obtained solid, chemically homogeneous xerogel (3), is then heated to about 110 °C for 6 h, powdered, and dried at 70 °C and 10^{-3} Torr for 6 h. Washing of 3 with water and alcohol does not result in the elution of Pd^{2+} (checked by elemental analyses before and after washing), indicating that the metal ions are effectively fixed to the support by the ligands.

The metal complexes containing xerogel (3) are calcined by heating the very hygroscopic materials in a stream of
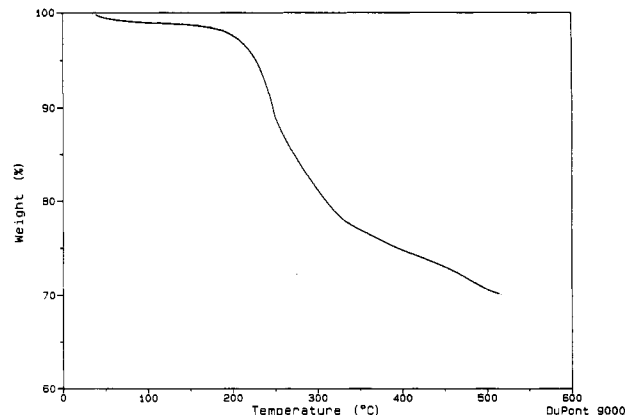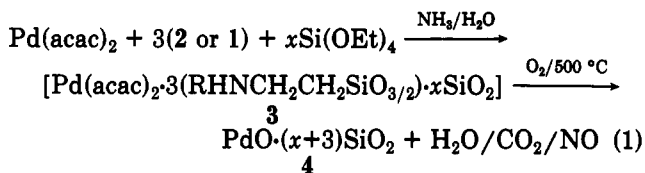
air at 500 °C for 2 h (when pure oxygen was used instead of air to oxidize gels containing nickel acetate, two minor explosions occurred for unknown reasons). During calcination, the color of the materials changes from that of the corresponding metal complex (yellow) to that of PdO (dark brown). Elemental analyses indicate nearly complete removal of C, H, and N from the materials, the composition of which is PdO·(x+3)SiO$_2$ (4) in this stage (eq 1). Figure

$$Pd(acac)_2 + 3(2 \text{ or } 1) + xSi(OEt)_4 \xrightarrow{NH_3/H_2O}$$

$$[Pd(acac)_2 \cdot 3(RHNCH_2CH_2SiO_{3/2}) \cdot xSiO_2] \xrightarrow{O_2/500 \,°C}$$
$$\underset{3}{}$$
$$\underset{4}{PdO \cdot (x+3)SiO_2} + H_2O/CO_2/NO \quad (1)$$

1 shows the thermogravimetric analysis of a sample of 3, prepared from Pd(acac)$_2$ (acac = acetylacetonate), 2, and TEOS (molar ratio 1:3:8), when heated in air. The initial weight loss (up to about 200 °C) is due to the removal of water. Oxidation and/or thermolysis of the organic components then occurs in several steps and is complete at 500 °C. At this point, the material contains only 0.18% carbon and no nitrogen. By mass spectrometry of the oxidation products, H$_2$O, CO$_2$, and NO are detected. If calcination is performed at lower temperatures, which would be preferable to restrict sintering of the metal compound, some organic moieties are retained, and the C and N values reach a nearly constant non-zero value after a certain period of time.

Reduction of the PdO particles in the SiO$_2$ matrix is achieved by heating 4 in a stream of hydrogen for several hours at 300 °C and results in a palladium metal-containing composite Pd·(x+3)SiO$_2$ (5). Figure 2 shows a typical scanning transition electron micrograph (STEM) of one of the Pd-SiO$_2$ composites (5 (x = 70), prepared from Pd(acac)$_2$, 2, and TEOS; metal content 2.38 wt % Pd). The metal is highly and homogeneously dispersed in the SiO$_2$ matrix, and the particle diameters are very small (average 2.2 nm) and uniform (0.75–3.75 nm) (Figure 3). Exactly the same result is obtained, if reduction with H$_2$ is carried out at 30 °C. Since temperatures for the reduction step are low, we assume that the PdO particle size in the PdO-SiO$_2$ composites (4) is about the same. In the range between x = 150 and x = 30, there is only a negligible effect of the metal contents of the composites on the dispersion of the metal: the average Pd particle diameter in 5 (x = 150) (1.1% Pd) is 2.1 nm and that in 5 (x = 30) (4.9% Pd) is 2.3 nm; the particle size distribu-

Figure 1. Thermogravimetric curve for a xerogel, prepared by sol-gel processing of Pd(acac)$_2$, 2, and Si(OEt)$_4$ (1:3:8). Heating rate 2.5 °C/min in a stream of air (54 mL/min) (Du Pont thermal analyzer 9000). Initial analytical values: C 22.1%, N 4.1%, H 2.5%.

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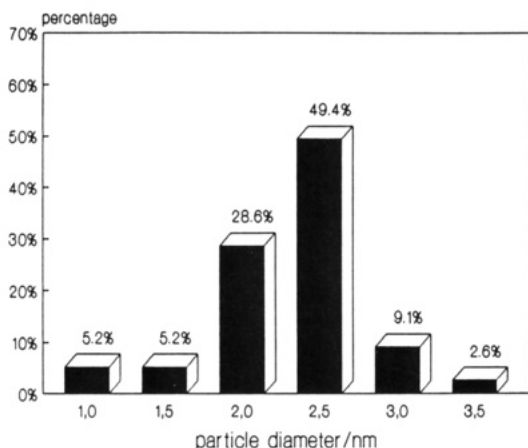
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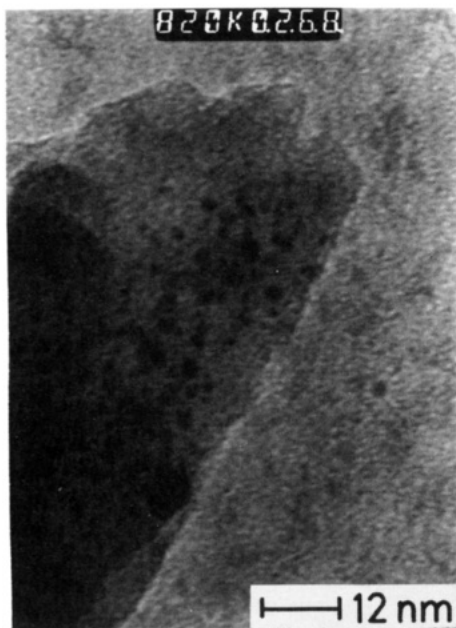
Figure 2. Scanning transmission electron micrograph of **5** (x = 70), prepared from $Pd(acac)_2$, **2**, and $Si(OEt)_4$ and containing 2.38 wt% Pd.

Figure 3. Pd particle size distribution of Pd–SiO$_2$ composite **5** (x = 70) (same as in Figure 2). Mean particle diameter 2.2 nm (calculated from 77 particles).

tions are very similar to those given in Figure 3.

To find out how anchoring of the metal complex via ligand **1** or **2** during polycondensation influences particle size and particle distribution of the resulting composites, we also prepared $PdO \cdot xSiO_2$ from $Pd(acac)_2$, ethylenediamine, and TEOS, without using **1** or **2**. Apart from this, the reaction conditions during polycondensation, calcination, and reduction were not altered, in order to avoid an influence of these parameters on the results. The Pd particle diameters in the thus-obtained composite $Pd \cdot 70SiO_2$ were between 2.25 and 9.75 nm (average 5.0 nm) and did not give an approximately Gaussian distribution curve.

Although preparation of the composites has not yet been optimized, these results show the soundness of our approach to prepare small metal particles in a ceramic matrix by sol–gel processing of metal complexes. Future efforts will be directed toward a generalization of this method.

A New Molecular Metal: (NHMe₃)₀.₅[Ni(dmit)₂] (dmit = 4,5-Dimercapto-1,3-dithia-2-thione)

$(NHMe_3)_{0.5}[Ni(dmit)_2]$ (dmit = 4,5-Dimercapto-1,3-dithia-2-thione)

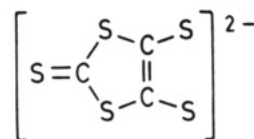Cristina Tejel, Brigitte Pomarède, Jean-Pierre Legros, Lydie Valade, and Patrick Cassoux*

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Transition-metal complexes of the dmit ligand (dmit = 4,5-dimercapto-1,3-dithia-2-thione) have been used as

$$\left[\begin{array}{c} S=C \underset{S}{\overset{S}{\diagup}} \underset{C}{\overset{C}{\Vert}} \underset{S}{\overset{S}{\diagdown}} \underset{S}{\overset{S}{\diagdown}} C \end{array} \right]^{2-}$$

precursors for the preparation of a number of conducting and superconducting π donor–acceptor or fractional oxidation state compounds.[1-6] Namely, four superconducting phases have been described: $TTF[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene, T_c = 1.7 K/7 kbar),[3] α- and α'-TTF-$[Pd(dmit)_2]_2$ (T_c = 1.7 K/20 kbar and 6.5 K/21 kbar, respectively),[4] and $(NMe_4)_{0.5}[Ni(dmit)_2]$ (T_c = 5 K/7 kbar).[5] Band structure calculations[6,7] and previous experimental studies[1-5] suggest that small modifications of the chemical environment in these systems could lead to new compounds exhibiting quite different transport properties.

We were thus tempted to check whether substitution of hydrogen atom(s) for methyl group(s) in the countercation of the $(NMe_4)_{0.5}[Ni(dmit)_2]$ superconductor would result in dramatic changes in the transport properties. We report here on the synthesis and electrochemical study of the $(NH_yMe_{4-y})_n[Ni(dmit)_2]$ series of precursor complexes (n = 2, 1; y = 1, 2, 3), the electrocrystallization of the $(NHMe_3)_{0.5}[Ni(dmit)_2]$ and $(NH_2Me_2)_x[Ni(dmit)_2]$ fractional oxidation state compounds, and the preliminary structural and conductivity studies of $(NHMe_3)_{0.5}[Ni(dmit)_2]$.

Due to the low stability of the $[NH_yMe_{4-y}]^+$ cations in the strong basic medium in which the dmit ligand generated from $dmit(COPh)_2$ is stable[1] and the high solubility of the $(NH_yMe_{4-y})_2[Ni(dmit)_2]$ complexes, the standard

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