Synthesis and Characterization of Cobalt−Complex Functionalized MCM-41

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Silanation of the internal pore surface of the mesoporous molecular sieve MCM-41 (40 Å) has yielded ethylenediamine (ED), diethylenetriamine (DET), and ethylenediaminetriacetic acid salt (EDT) functionalized sites. These grafted ligands were used for the preparation of cobalt(II) complexes covalently bound to the MCM-41 support. These materials were characterized by SEM, UV−vis, FTIR, ESR, and cyclic voltammetry as well as elemental analysis. Preliminary studies suggest the formation of a reversible cobalt−oxygen adduct with MCM-41 grafted ED and DET. The nature and reactivity of the MCM-41 bound complexes were found to differ significantly from functionalized amorphous silica.

Introduction

MCM-41, is a member of a family of mesoporous molecular sieves, recently reported by Mobil and designated as M41S.[1,2] The hexagonal form possesses an array of uniform mesopores that can be systematically tailored to pore sizes ranging from ∼15 to 100 Å. The nature of the MCM-41 pore structure can be adjusted by varying the type and concentration of surfactant template that is employed during synthesis.[3] These materials offer a distinct advantage over conventional supports such as silica, by providing a narrow pore size distribution in the mesopore size range which allows the use of substrates[4] too large for microporous materials. Beck et al.[1] estimated that approximately 14% of the silicon atoms in MCM-41(40) are siloxy groups, which play a charge-balancing role for the cetyltrimethylammonium template used in the synthesis.[5] Calcination of the MCM-41 to remove the organic template renders the pores accessible, and the resulting silanols can then be used to functionalize the support via reaction with alkoxysilyl compounds. Once anchored to the channel walls, the organosilane groups that possess donor amines can be used to prepare metal complexes grafted to the MCM-41. The objectives of our study were to modify the pore surface of MCM-41 type materials with potentially chelating ligands and then demonstrate the complexation of metal ions such as Co(II). The functionalization of mesoporous MCM-41,[6] as well as microporous materials such as zeolite Y,[7] using organosilanes has been recently reported. In this paper we have exploited this strategy for modifying the MCM-41 surface to produce several covalently bound cobalt−amine complexes.

Cobalt−amine complexes are of special interest for their ability to form reversible dioxygen adducts[8] which is an important characteristic of certain biologically relevant reactions. The potential for heterogeneous catalysis[9] has been recognized through the preparation of oxygen adducts of cobalt(II)−amine complexes bound to polymers,[10] ion-exchange resins,[11] and clays[12] as well as inside the supercages of Y type zeolites.[13] In the present study we successfully prepared and characterized a series of MCM-41 grafted metal−amine complexes, including ligands based on ethylenediamine (M41ED), diethylenetriamine (M41DET), and ethylenediaminetriacetic acid (M41EDT). Ethylenediamine

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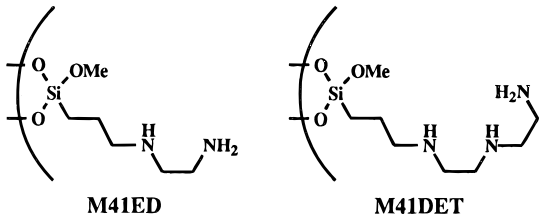

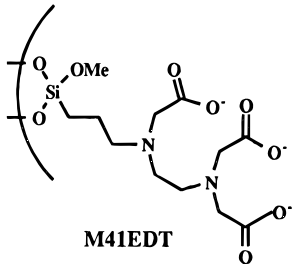

grafted to amorphous silica (SilED) was also prepared and used to compare with the MCM-41 grafted metal complexes. Preliminary experiments using ESR spectroscopy suggest that some of the supported cobalt(II) complexes of M41ED and M41DET may bind oxygen reversibly in contrast to the silica-supported complexes. The results below clearly demonstrate the uniform porosity of MCM-41 imparts properties to the support that are not observed with amorphous silica.

Experimental Section

General Techniques. Infrared spectra were recorded from KBr pellets using a Mattson 2025 FT-IR spectrophotometer. Electronic spectra were obtained from samples prepared as Nujol mulls between quartz plates using a Hitachi U-2000 UV−vis spectrophotometer. X-ray powder diffraction patterns were collected on a Scintag XDS 2000 diffractometer using Cu Kα monochromatic radiation. Scanning electron micrographs were obtained using a Philips XL30 SEM equipped with a Philips PV8500 EDAX spectrometer. Nitrogen desorption isotherms were collected with a Quantachrome Corp. NOVA-1000 physisorption instrument. ESR spectra were obtained using a Bruker ESP-300 X-band spectrometer. Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN).

Materials. Cetyltrimethylammonium chloride (C_{16}TMACl, 25% aqueous solution), trimethylammonium hydroxide pentahydrate (TMAOH), and fumed silica were used as received (Aldrich). Catapal alumina (73.3% Al_2O_3) as well as (trimethoxysilyl)propylethylenediamine, -diethylenetriamine, and -ethylenediaminetriacetic acid sodium salt (50%, Petrarch) were used as received. Ethylenediamine (Mallinckrodt) was vacuum distilled and stored under nitrogen.

Functionalization of MCM-41 (40 Å) with Organosilanes. MCM-41 was prepared from amorphous silica using a cetyltrimethylammonium template according to published procedures.[1,14] The 40 Å pore size was selected because of ease in preparation and characterization. The as-synthesized MCM-41 material was calcined in air at 540 °C for 10 h. The calcined MCM-41 product was characterized as similar to previously reported samples of the 40 Å mesopore hexagonal phase. X-ray diffraction (d_{100} = 39.8 Å) and nitrogen desorption isotherms (pore diameter = 32.6 Å, calculated using the Barrett−Joyner−Halenda method[15]).

Ethylenediamine Grafted MCM-41 (M41ED). MCM-41 (40 Å) (1.5 g) was placed in a 100 mL round-bottom flask containing 50 mL of dry toluene under a nitrogen flow. *N*-(2-aminoethyl)-3-(aminopropyl)trimethoxysilane (5 mL, 0.02 mol) was added to the stirred suspension. The mixture was then refluxed for 12 h under nitrogen. The functionalized M41ED was washed with dry toluene followed by methanol, deionized water, and a final methanol rinse using centrifugation. The M41ED sample was dried in a vacuum oven at 50 °C for 12 h.

Diethylenetriamine Grafted MCM-41 (M41DET). MCM-41 (40 Å) (1.5 g) was placed in a 100 mL round-bottom flask containing 50 mL of dry toluene under a nitrogen flow. (Trimethoxysilyl)propyldiethylenetriamine (5 mL, 0.02 mol) was added to the stirred suspension. The mixture was then refluxed for 12 h under nitrogen. The solid material was washed by centrifugation using dry toluene followed by methanol, deionized water, and a final methanol rinse. The M41DET sample was dried in a vacuum oven at 50 °C for 12 h.

Ethylenediaminetriacetic Acid Grafted MCM-41 (M41EDT). MCM-41 (40 Å) (1.5 g) was placed in a 100 mL round-bottom flask containing 30 mL of dry toluene under a nitrogen flow. (Trimethoxysilyl)propyldiethylenetriamine triacetic acid trisodium salt (3 mL, 0.003 mol) was added to the stirred suspension. The mixture was then refluxed for 12 h under nitrogen. A Dean−Stark trap was used to remove lower boiling components. The liquid phase was then decanted from the product mixture. The solid material was washed with dry toluene followed by methanol, deionized water, and a final methanol rinse using centrifugation. The M41EDT sample was dried in a vacuum oven at 50 °C for 12 h.

Ethylenediamine Grafted Silica (SilED). Silica gel (0.5 g, Aldrich) was placed in a 50 mL round-bottom flask containing 25 mL of dry toluene under a nitrogen flow. (Trimethoxysilyl)-propylethylenediamine (2.5 mL, 0.01 mol) was added with stirring. The mixture was then refluxed for 12 h under nitrogen. The solid materials were washed with dry toluene followed by methanol, deionized water, and a final methanol rinse using centrifugation. The SilED sample was dried in a vacuum oven at 50 °C for 12 h.

Complexation of Functionalized MCM-41 (40 Å). A 0.2 M solution of cobalt(II) was prepared in a 20 mL vial by dissolving the appropriate amount of chloride into 10 mL of freshly boiled deionized water. Functionalized MCM-41 (SilED, 0.5 g) was added and the solution purged with nitrogen. The mixture was then stirred for 12 h at room temperature. The solid products were washed with deionized water and methanol using centrifugation. The products were dried in a vacuum oven at 50 °C for 12 h.

Cyclic Voltammetry of Cobalt−Complex Functionalized MCM-41 (40 Å). Cobalt tetrafluoroborate ($Co(BF_4)_2$, Aldrich) and tris(ethylenediamine)cobalt(III) tetrafluoroborate ($Co(en)_3(BF_4)_2$, Aldrich), dry acetonitrile (ACN, Aldrich) and dimethyl sulfoxide (DMSO, Fisher), were used as received in the electrochemical experiments. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, Aldrich) electrolyte was dried in a vacuum oven at 50 °C for 24 h. Tetraethylammonium chloride (TEACl, Aldrich) was used as supplied. TEACl solutions were prepared in a nitrogen glovebox. Cyclic voltammetric measurements were conducted at room temperature using a Princeton Applied Research (PAR) 273A potentiostat, a PAR Versastat potentiostat, or a Tacussel PRG5 potentiostat. A standard three-electrode cell was used for the electrochemical experiments. Electrode potentials are referred to an aqueous saturated calomel electrode (SCE) placed in a separate cell compartment containing solvent and support electrolyte. A platinum gauze was used as counter electrode. The working electrode was prepared by pressing (3 tons/cm^2, 5 min) a sample/graphite mixture (1:1, w/w) onto a platinum grid (~20 mg of mixture/cm^2) according to a previously described procedure.[16] The $TBABF_4$ electrolytic solutions were purged with argon.

Results and Discussion

The reaction scheme in Figure 1 summarizes the sequence of events in the functionalization of MCM-41

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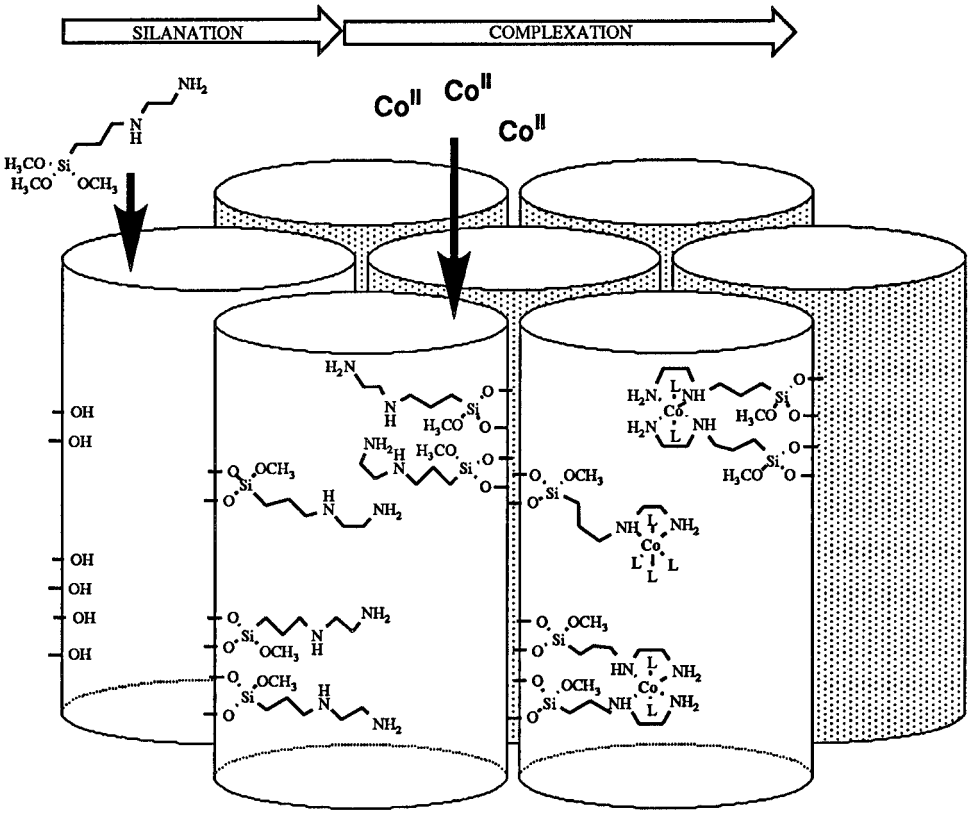

Figure 1. Schematic representation of the reaction sequence in the metal complex functionalization of MCM-41.

Table 1. Observed Frequencies of Liquid Organosilanes and Grafted MCM-41 and Silica Materials (cm^{-1})

R	trimethoxysilylpropyl−R (neat)	grafted M41-R (KBr pellet)	Co-M41-R (KBr pellet)	assignments[a]
ED	2937	2944	2956	$-CH_2-$ asym str
	2886	2886	∼2890	$-CH_2-$ sym str
	2840	∼2832		$-OCH_3$ sym str
	1598	∼1584	∼1660	$-NH_2$ def
	1462	1478	1470	$-CH_2-$ def
	1412	1410	1412	$Si-CH_2-$ def
DET	2933	2960	∼2960	$-CH_2-$ asym str
	2886	2894	∼2898	$-CH_2-$ sym str
	2840	∼2830		$-OCH_3$ sym str
	1605	∼1567	(∼1650)[b]	$-NH_2$ def
	1459	1474	1460	$-CH_2-$ def
	1412	1410		$Si-CH_2-$ def
EDT	2952	2960	2975	$-CH_2-$ asym str
		∼2890	∼2890	$-CH_2-$ sym str
	2844	∼2848		$-OCH_3$ sym
	1590	∼1605	∼1605	$-CO_2$ asym
	1408	1412	1412	$-CO_2-$ sym
	1331	1335	∼1335	$-CH_2-$ wag
		SilED	Co−SilED	
		2940	2956	$-CH_2-$ asym str
		2894	∼2890	$-CH_2-$ sym str
		∼2828		$-OCH_3$ sym
		∼1590	∼1663	$-NH_2$ def
		1482	1455	$-CH_2-$ def
		1412	∼1412	$Si-CH_2-$ def

[a] Assignments based on ref 13d and 25. [b] Unresolved from the H_2O deformation band.

with metal complexes. The first step involves treatment of the MCM-41 (40 Å) pore surface with the appropriate organosilane. The condensation of the (methoxysilyl)-propylamine with the accessible silanols on the supports pore surface yields MCM-41 grafted amine ligands. The condensation reaction modifies both external and inner channel silanols, however, since the high surface area in MCM-41 can be attributed to the pore system, internal functionalization of the channel walls should outnumber any external sites. Indeed, the decrease in pore size by virtue of silanization of the MCM-41 channels has been demonstrated by nitrogen adsorption.[1,7] Evidence of the successful silanization of the support can be obtained from the infrared spectra of all grafted materials, which showed characteristic $-CH_2-$ stretching bands at ∼2960 and ∼2890 cm^{-1}. Table 1 summarizes the band assignments for the CH stretching region and the 1800−1400 cm^{-1} region of the spectrum, where the support material is virtually transparent (except for the water absorption band at ∼1650 cm^{-1}).

The relative intensity of the 2840 cm^{-1} band, corresponding to the methoxy group of the organosilane grafting agents, decreases significantly in the functionalized MCM-41 samples as expected from the condensation reaction. Bands corresponding to $-NH_2$ and $-CH_2-$ deformation frequencies (scissoring) are also observed for M41ED, SilED, and M41DET. Carboxylate bands at ~1605 and 1412 cm^{-1} are clearly visible in the M41EDT spectra. The dry organosilane modified materials have shown no apparent degradation during several months of storage at room temperature.

The second step as shown in Figure 1 involves the complexation of Co(II) by the functionalized MCM-41 in aqueous solution, which yields strongly colored materials (light brown Co−M41ED and Co−M41DET, pink Co−M41EDT, and red Co−SilED). The change in color is by itself a good indication that the cobalt ions are coordinated by the grafted ligands, since no significant color change was observed when the calcined MCM-41 was treated with Co(II) under identical conditions. Although ion exchange with the support cannot be ruled out, it is considered a minor contribution to the total cobalt uptake by the grafted materials, as expected from the low aluminum loading of the parent MCM-41 (Si/Al ~ 40). The IR spectra of the cobalt−complex functionalized materials exhibit variation in the absorption bands rendering further evidence of the complexation of the ligands. For the Co−M41ED, Co−SilED, and Co−M41DET samples the $-NH_2$ band at ~1600 cm^{-1}, assigned to a scissoring mode, appears to shift toward higher frequencies. This band was also observed to shift to higher frequencies for intrazeolite ethylenediamine Co(II) complexes.[13] The $-CH_2-$ deformation band at 1480 cm^{-1} moves to lower wavenumbers, which is also not surprising. The shift of this $-CH_2-$ band was significantly greater for the Co−SilED sample compared to the Co−M41ED material, which may suggest a different coordination environment for the two samples which may also account for the differences in color. The shifts of such deformation bands associated with complexes of polyamine ligands such as ethylenediamine appear to vary depending upon electrostatic and covalent interactions as well as with conformational changes. Although these IR spectra have not provided structural information, they do indicate the cobalt has been complexed.

It can be estimated that the covalently attached ligands stretch over a length of approximately 10 Å, which would make it impossible for the Co(II) ions to be coordinated by ligands grafted to opposite walls of the 40 Å pore system in MCM-41, which restricts the coordination of the cobalt ions to adjacent ligands. In contrast, amorphous silica possesses a wide pore size distribution, which would enable many more coordination modes. This structural difference could be a determining factor for the mono-, bis-, or trisdiamine coordination of the grafted cobalt complexes, or even the mono-, bi-, or tridentate (i.e., DET) behavior of the ligands.

The cobalt concentrations from the elemental analysis of the cobalt−amine grafted MCM-41 materials shown in Table 2 indicate that M41EDT is the most effective material for the complexation of cobalt, with approximately one EDT group per cobalt. This is consistent with the known stability of EDTA cobalt(II) complexes

Table 2. Elemental Analysis Results

	wt % Co	wt % N	C/N	N/Co (expected)
cobalt−M41ED	1.94	3.66	2.8	7.9 (6.0)
cobalt−M41DET	1.30	4.02	2.7	13.0 (6.0)
cobalt−M41EDT	3.84	1.52	5.7	1.7 (2.0)
cobalt−SilED	1.58	5.52	2.4	14.7 (6.0)

($pK_f = 16.3$)[17] compared to the labile trisethylenediamine analogues ($pK_f = 5.9$) in aqueous solution. The N/Co ratios indicate that for Co-M41ED and Co-M41DET an excess of ligand is available for coordination. This excess is particularly high in the Co−SilED material. The C/N ratios suggest that the desired amine functions have been grafted intact to the aluminosilicate support. In fact, using the nitrogen concentration as an indicator of silylation coverage, it is estimated[18] that ~65% of accessible silanols in M41ED and ~50% in M41DET have been grafted, and only ~30% of the silanols in the case of the M41EDT. This would be consistent with a restricted migration into the channels of the mesoporous materials as the openings are constrained by the grafting process. This effect, as observed, is most profound for the bulkier EDT group.

The physical and spectroscopic properties described above for the functionalized MCM-41 materials offer evidence of the functionalization of the support and formation of cobalt complexes with very distinct characteristics depending on the ligand and the support used. However, no clear evidence regarding the nature of these complexes can be made with this information alone. In a related study using ED silane modified silica, Co(III) was complexed.[19] A red tris(ethylenediamine)cobalt(III) bound to silica was characterized to have an N_5O ligand field with one water molecule coordinated to the metal center and is prepared by reacting diamine-bonded silica with dichlorobis(ethylenediamine)cobalt(III) chloride. Dehydration resulted in a color change from red to yellow. The red Co−SilED sample may have tris(ethylenediamine)cobalt(II) complexes bonded to the silica where all three diamine ligands surrounding the metal are anchored to the support. There is no reason to suspect the Co(II) has been oxidized in Co−SilED, and heating the sample does not alter the color. The N/Co ratio would allow for as much as a 3:1 adduct with adjacent surface attached silanes. In contrast, the 40 Å pore structure of MCM-41 dictates a lower coordination number.

Electroactivity of Cobalt Complex Functionalized MCM-41. Cyclic voltammetry (CV) of the grafted cobalt complexes was performed using composite electrodes, which consist of a mixture of graphite and sample pressed against a platinum gauze (see Experimental Section).[16] This technique enables us to assess the electroactivity of the complexes grafted to the insulating MCM-41. It is necessary to note that since electron transfer can occur only if the electroactive species is in contact with the graphite particles, used as electronic conductors, the electroactivity observed would probably reflect the redox activity of metal

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complexes located at or near the pore openings of the MCM-41 support. Since most all the anchored complexes should be inside the pores, the observed CV should be representative of the bulk.

The CV of the ligand only modified MCM-41 materials showed no electroactivity in ACN over the +1.8 to −1.3 V vs SCE range. The CV of Co−M41ED, Co−M41DET, and Co−SilED samples exhibited a well-defined anodic peak accompanied by a substantially smaller cathodic signal, centered at +1.1 V vs SCE. The anodic and cathodic peak intensities decayed with consecutive oxidation cycles. A similar decay was obtained when the electrode was aged in solution for 30 min prior to collection of the first cycle followed by oxidation cycles acquired every 15 min. This observation indicates that the signal decays not by simple diffusion of the electroactive species into the bulk solution, but rather by a rapid chemical reaction that is either irreversible and/or causes loss of electroactive material into the bulk solution. This signal was assigned to the oxidation of chloride ion (with a reported potential of +1.15 V vs SCE),[19] which arises from the cobalt chloride used to prepare the complexes. Additionally the presence of chloride was confirmed by EDAX analysis of the samples. A Co−M41ED sample prepared using cobalt sulfate did not exhibit such a signal, and EDAX analysis of this sample did not reveal any chloride. The Co−M41EDT sample also prepared using cobalt chloride did not show any signals that could be assigned to chloride. The anionic EDT ligand precludes the need for coordination of chloride to the cobalt such that it is not retained on the MCM-41. These results suggest that the chloride detected in the MCM-41 samples modified with neutral ligands may be directly coordinated to the cobalt or present as an outer sphere charge balancing ion. Surprisingly, no signals that could be assigned to a Co^{3+}/Co^{2+} process were observed in ACN for these supported complexes. A sweep of the potential range between −2.0 to +0.5 V vs SCE in DMSO solution showed no conclusive electrochemical signals either. The electroactivity of tris(ethylenediamine)cobalt(II) in bulk solution has been reported.[20] In DMSO and ACN a reversible couple attributed to the Co^{3+}/Co^{2+} process is observed at −0.68 and −0.35 V vs SCE, respectively. However, the labile nature of $[Co(en)_3]^{2+}$ required the addition of 1,2-ethylenediamine (en) to prevent the irreversible reduction of the complex. The mono- and bis-en adducts have not been isolated in solution and therefore their electrochemical behavior is unknown.

Figures 2 and 3 show the CV of Co−M41ED and Co−M41DET in 0.1M $TBABF_4$ DMSO solution. No clear electroactivity is observed (curve a) until an excess (∼5 mM) of en ligand is added to the electrolyte solution (curve b). Indeed, curves 2b and 3b show a well-defined reversible couple of peaks centered at −0.62 V vs SCE. The potential of this redox process is similar to that corresponding to the Co^{3+}/Co^{2+} process observed for the $[Co(en)_3]^{2+}$ complex in bulk solution.[21] As noted above, the labile nature of this cobalt(II) species requires the addition of en to prevent irreversible reduction of the complex, hence, the redox process observed for Co−M41ED and Co−M41DET may be attributed to six amines coordinated to cobalt(II), grafted to the mineral support. Furthermore, the peak intensity did not decay with either immersion time or number of redox cycles performed, which suggests that the metal complex is indeed bound to the support. There is also no evidence that Co(II) can be ion exchanged under these conditions. If this were happening then we would see a signal decay as we did for chloride ion. We can also note that the observed redox signals shift toward negative potentials upon addition of chloride ion (0.05 M TEACl) to the electrolyte solution, as expected from the stabilization of the Co^{3+} form of the grafted complex. The Co−SilED sample showed similar electrochemical behavior.

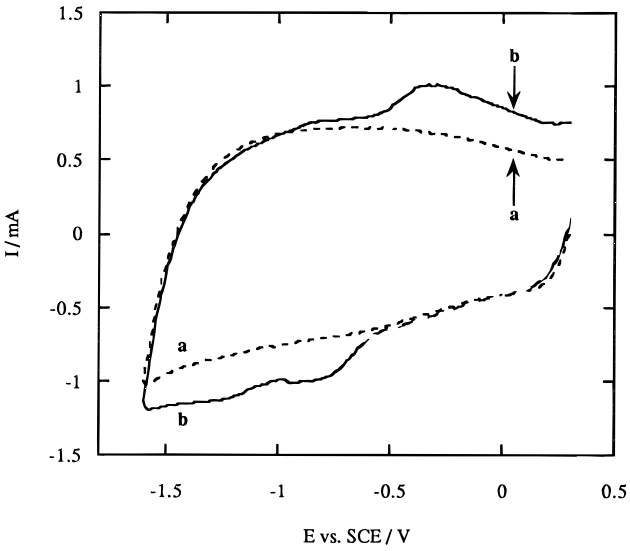

Figure 2. Cyclic voltammogram of a composite electrode containing Co-M41ED in DMSO (0.1 M $TBABF_4$): (a) before (---), and (b) after (—) addition of ethylenediamine. Potential scan rate = 100 mV/s.

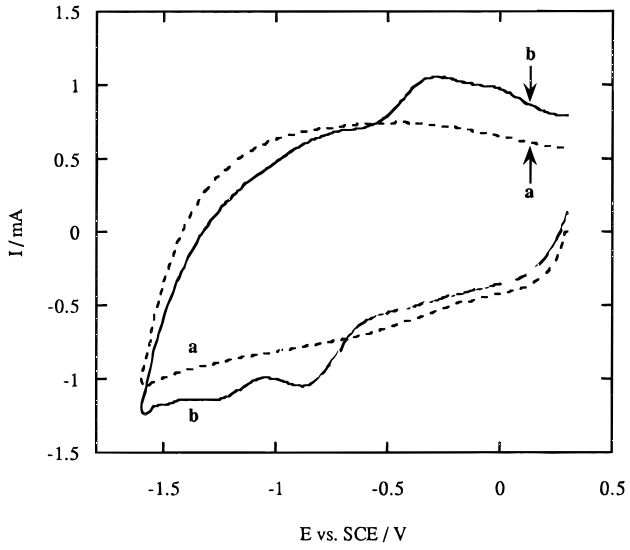

Figure 3. Cyclic voltammogram of a composite electrode containing Co-M41DET in DMSO (0.1 M $TBABF_4$): (a) before (---), and (b) after (—) addition of ethylenediamine. Potential scan rate = 100 mV/s.

The electroactivity of Co−M41EDT in DMSO is noticeably different from that of the other materials. The CV of this sample is shown in Figure 4. It displays a strong well-defined anodic peak at +0.1 V (labeled A) when the potential range was scanned at 100 mV/s. The

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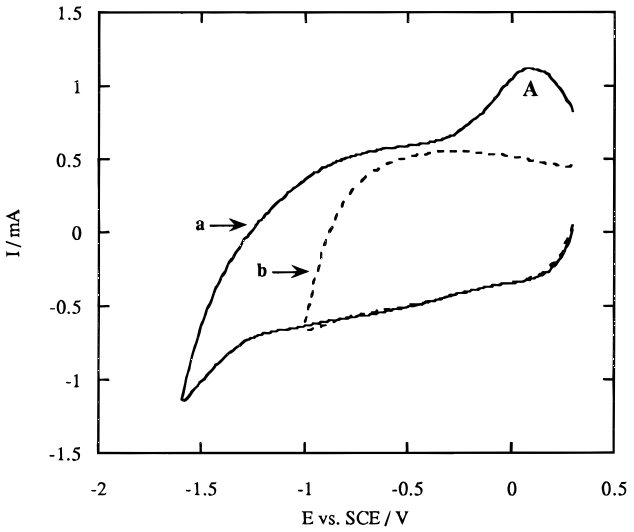

Figure 4. Cyclic voltammogram of a composite electrode containing Co-M41EDT in DMSO (0.1 M $TBABF_4$): (a) potential range from 0.2 to −1.6 V (—), and (b) restricted cathodic scan to −1.0 V (---). Potential scan rate = 100 mV/s.

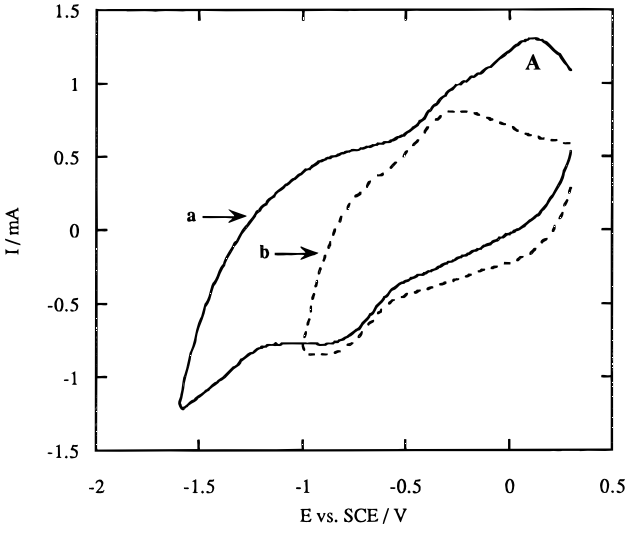

Figure 5. Cyclic voltammogram of a composite electrode containing Co-M41EDT in DMSO (0.1 M $TBABF_4$): (a) before (—), and (b) after (---) addition of ethylenediamine (restricted potential range). Potential scan rate = 100 mV/s.

peak disappears if the scan is switched positive of −1.0 V (see curve b, Figure 4). This indicates that the observation of the anodic process A requires reductive scan below −1.0 V. When the potential sweep is decreased to 25 mV/s, anodic and cathodic contributions to A are observed, centered at −0.55 V. The potential of this couple is consistent with the previously mentioned Co^{3+}/Co^{2+} process. Again, the peak intensity did not decay with either immersion time or redox cycles performed, which suggests that the metal complex is bound to the support. The significant difference between M41EDT and the other functionalized materials may be related to the relative stability of the complexes, where the diamine−cobalt(II) complexes are quite labile as noted above. Addition of ethylenediamine to the M41EDT-based electrodes yields a new redox couple centered around −0.5 V, at 100 mV/s, while peak A is still observed (curve a, Figure 5). When the electrode was allowed to age in solution for 1 h, peak A disappeared, while the redox couple at −0.5 V remained. The presence of this redox process may be explained by the formation of a mixed en-EDT complex, due to the displacement of the carboxylate groups by ethylenediamine ligands. In solution, the redox-catalyzed substitution of $edta^{4-}$ by en has been reported for $[Co(edta)]^-$.[22] The DMSO electrolyte solution used for our measurements would favor such a substitution.[23] The addition of chloride ions to the electrolyte solution shifts the anodic peak potential of the couple toward negative values. If chlorides are added prior to the addition of ethylenediamine, the formation of the reversible couple at the expense of A is immediate.

In summary, the electroactivity of the as-synthesized grafted metal complexes Co−M41ED, Co−SilED, and Co−M41DET is not clear prior to the addition of ethylenediamine because of complex stability. In contrast, for Co−M41EDT, a couple attributed to the Co^{3+}/Co^{2+} process is observed. When ethylenediamine is added to the electrolyte solution redox signals consistent with the Co^{3+}/Co^{2+} process for ethylenediamine−cobalt complexes are generated for all cobalt-containing functionalized samples. The signals attributed to this process do not decay with multiple redox cycles or aging of the immersed electrode, which suggests that the electroactive species are bound to the support. Our results tend to show that a mixed en (from solution) −ED, −DET, or −EDT (from the MCM-41 material) is formed upon addition of en to the electrolytic solution. In any case, the large capacitive current observed for the composite electrode voltammograms and the inherent difficulty to estimate the exact contribution of the faradaic component preclude any accurate calculations. It is clear, however, that the signals observed corresponds to only a small percentage of the cobalt determined by the elemental analysis.

Reactivity with Oxygen. The isolated Co−M41ED and Co−M41DET samples appear brown in color, while the Co−M41EDT and Co−SilED samples are pink and red, respectively. A reversible color change from brown to blue-gray was observed when the brown samples were heated to 80 °C (not high enough to thermally dissociate the amine ligands) under vacuum (10^{-2} Torr) and then later exposed to air or oxygen. The silica and Co−M41EDT supported complexes did not show this behavior. UV−vis spectra of Co−M41ED and Co−M41DET sample mulls show modification of the charge-transfer band at 265 nm upon evacuation and exposure to oxygen. However, the characteristic bands[10−13] at ∼340 nm associated with dioxygen adducts were not observed with this technique. The electronic spectra in the 400−600 nm range of the brown Co−M41ED and the red Co−SilED are displayed in Figure 6. This latter sample exhibits a band at 520 nm characteristic of Co(II) species. The Co−M41ED as well as the Co−M41DET samples showed significantly weaker or less-defined bands at this wavelength, which bears resemblance to the electronic spectra of oxygenated cobalt−en adducts.[13c]

Preliminary ESR studies were conducted to evaluate the nature of the supported cobalt species. Figure 7 displays the ESR spectrum at 13 K of the blue Co−M41ED after heating at 100 °C for 24 h. The large signal ($g = 5.361$) corresponds to high-spin Co(II), which

(22) Geselowitz, D. A.; Taube, H. *Inorg. Chem.* **1981**, *20*, 4036.

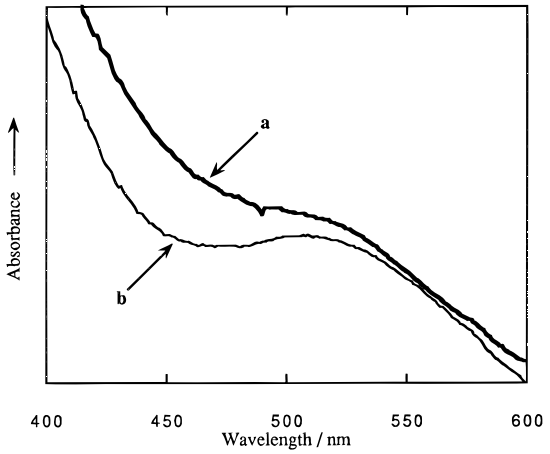

Figure 6. UV−visible spectra of as-synthesized (a) Co-M41ED and (b) Co−SilED.

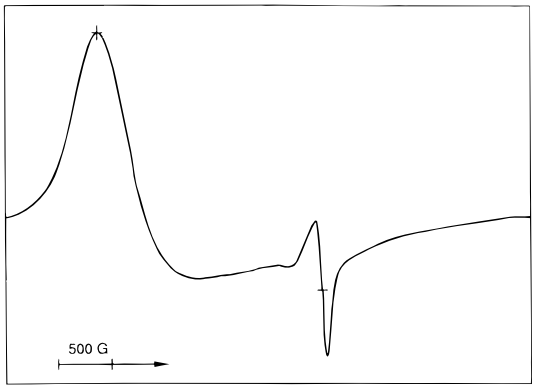

Figure 7. X-band ESR spectrum of Co-M41ED at 13 K evacuated for 24 h at 100 °C.

represents 98.5% of the ESR-detectable cobalt. The temperature dependence of the ESR signal intensity follows the Curie law.[24] The small signal ($g = 2.005$) may be assigned to a low-spin Co−O_2 adduct. However, this only reflects 1.5% of the ESR active cobalt. At 77 K the signal intensity does not change, and an expanded view is shown in Figure 8. The sharp band at $g = 2.005$ is assigned to an organic radical generated during thermal decomposition of the template. This band is superimposed on what appears to be a Co−O_2 ESR signal. The pattern associated with low spin cobalt appears to decrease only slightly after evacuation of the sample at 100 °C. Similar observations were found with Co−M41DET.

The formation of dioxygen adducts of thermally dissociated Co−ethylenediamine complexes has been reported inside zeolites.[13a,c,d] The signal in Figure 8 closely resembles that of the intrazeolite $Co(en)_2$−O_2 complex. $[Co(en)]^{2+}$, a high-spin pseudotetrahedral complex coordinated to the zeolite lattice, does not interact with oxygen. $[Co(en)_3]^{2+}$ reacts with oxygen irreversibly to produce cobalt(III) complexes, not characterized. Reversible dioxygen binding properties are

Figure 8. X-band ESR spectrum of Co-M41ED at 77 K.

only observed for $[Co(en)_2]^{2+}$, which forms a reversible oxygen adduct at room temperature. If we assume our supported complexes behave in a similar fashion, then it suggests that at least some cobalt ions inside the MCM-41 channels are coordinated by two diamine groups. Since the elemental analysis of the grafted cobalt complexes with M41ED, M41DET, and SilED suggest an excess of ligand that would favor at least six nitrogen donor groups per cobalt, it is reasonable to presume that the MCM-41 structure allows the formation of complexes with fewer ligands coordinated to cobalt in contrast to the grafted silica, which would favor higher or lower coordination depending upon the pore size. This would constitute a unique property of the mesoporous support where in our case the uniform 40 Å pores allow the formation of complexes not observed with silica. The question remains as to why there is such a significant color change in the Co−M41ED and Co−M41DET samples upon exposure to oxygen when only trace amounts of cobalt that could be ascribed to an O_2 adduct are detected by ESR.

Conclusions. The organosilane modified surface of MCM-41 can readily bind metals such as cobalt. The electroactivity of the as-synthesized materials was enhanced by the addition of ethylenediamine, resulting in electroactive species which show a redox couple consistent with the Co^{2+}/Co^{3+} process of an amine-coordinated complex. Preliminary studies suggest that the MCM-41 supported cobalt complexes M41ED and M41DET may exhibit oxygen binding properties. Further work is in progress to better define the nature of these reaction sites and the effect of the mesopore size. Functionalized MCM-41 type materials with chelate ligands and metal complexes may find applications in catalysis, and gas separations as well as in the sequestering of metal ions.

Supporting Information Available: Mid-FT-IR spectra for M41ED, M41DET, SilED, and M41EDT before and after complexation with cobalt(II) (5 pages). Ordering information is given on any current masthead page.

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