

Synthesis and Characterization of Functionalized MCM-41 with Copper– and Manganese–Phenanthroline Complexes

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The modification of the internal pore surface of mesoporous MCM-41 with 3-aminopropyl yielded amine group functionalized MCM-41. Copper(II) and manganese(II) phenanthroline complexes were grafted onto the functional MCM-41 via the coordination of the respective metal ion with the amine group. The metal ion complex functionalized mesoporous materials were characterized by powder X-ray diffraction (XRD), nitrogen adsorption/desorption at 77 K, solid state diffuse reflectance UV spectroscopy, and electron spin resonance (ESR) at 293 K as well as cyclic voltammetry. Preliminary studies suggested that the nature and electroactivity of metal ion complex functionalized MCM-41 differed significantly from those of metal ion complex impregnated MCM-41. © 2000 Academic Press

INTRODUCTION

The development of mesoporous silicates such as MCM-41 has generated interest due to the potential applications of mesoporous materials as catalysts, catalyst supports, separation media, and host materials for inclusion compounds (1, 2). The narrow pore size distribution, tailorable pore size ranging from 1.5 to 10.0 nm, and high inner surface area have added a new dimension to intrapore chemistry that had previously focused on zeolites as hosts (3). In MCM-41, an estimated 8–27% of silicon atoms are siloxy groups, which have been utilized to covalently anchor functional groups onto the inner surface walls (1, 4). D. Brunel (5) grafted functional 3-chloropropyl onto the internal walls of MCM-41 through Si–O–Si bonds, and Jacobs (6) reported the modification of 3-mercaptopropyl on the walls of MCM-41. Sulfonic acid functionalized mesoporous silicates performed well in typical strong-acid catalyzed reactions (6).

Transition-metal ions grafted into zeolites were conventionally used as heterogeneous catalysts for the transformation of small organic molecules (7, 8). The mesopore

channels of tubular MCM-41 were satisfied to immobilize large organometallic complexes. Manganese(II) 2,2'-bipyridine complex incorporated into MCM-41 by an impregnation method exhibited higher catalytic activity for the oxidation of styrene than the corresponding homogeneous catalyst (9). It has been found that chromium acetylacetonate complex functionalized MCM-41 exhibits more activity for polymerization of ethylene (10).

In the present work, the copper(II) and manganese(II) phenanthroline complex functionalized MCM-41 were synthesized. They were characterized by XRD, nitrogen sorption at 77 K, solid state UV spectroscopy, and ESR spectra at 293 K; cyclic voltammetry experiments were carried out to investigate their electroactivity.

EXPERIMENTAL PROCEDURES

Synthesis of Mesoporous MCM-41

MCM-41 (Si/Al = 35) was synthesized by mixing cetyltrimethylammonium bromide (CTAB, 98%), NaOH (Analytical reagent), NaAlO₂ (Analytical reagent), fumed SiO₂ (99%), and distilled water. The molar composition of the gel was CTAB/SiO₂/NaAlO₂/NaOH/H₂O = 1.0:4.0:0.1:1.9:200. The gel was heated to 373 K for 4–5 days in a steel autoclave under autogenous pressures after stirring for 2 h at room temperature. The product was filtered, washed with distilled water, and then dried at ambient conditions. The as-synthesized MCM-41 was calcined in air at 873 K for 6 h to remove the surfactant CTAB.

Modification of MCM-41 with 3-Aminopropyl

A 1.0g amount of calcined MCM-41 was placed in a 100-ml round-bottom flask with 50 ml of dry hexane (Analytical reagent) and 5.0 ml of 3-aminopropyltriethoxysilane. The mixture was stirred and refluxed at 343 K for 12 h under the protection of nitrogen. The white 3-aminopropyl functional MCM-41 (MCM-ap) was washed repeatedly with ethanol and then dried at 353 K for more than 12 h. There is about

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10.9 wt% 3-aminopropyl group in MCM-ap by C, N, H organic elemental analysis (Elementar Varioel: C, 6.99%; N, 2.44%; H, 1.48%).

Complexes Grafted onto Functional MCM-ap

Copper and manganese ion complex: $[\text{Cu}(\text{phen})_2\text{Cl}]\text{OH} \cdot 3\text{H}_2\text{O}$ and $[\text{Mn}(\text{phen})_2\text{Cl}]\text{OH} \cdot 3\text{H}_2\text{O}$ were previously synthesized according to published procedures (11). A 0.02 M solution of the copper(II) or manganese(II) complex was prepared by dissolving the appropriate amount of complex into 50 ml of distilled water. A 1.0-g amount of MCM-ap was added, and the mixture was then stirred for 6 h at room temperature. The solid products were washed with distilled water and ethanol by filtration. At last, the solids were dried in a vacuum oven at 353 K overnight. The copper functionalized MCM-41, MCM-ap-Cu(phen)₂, appeared blue, while the manganese complex, MCM-ap-Mn(phen)₂ appeared pale brown.

Complexes Impregnated in MCM-41

The impregnation of copper(II) or manganese(II) complexes in MCM-41 was carried out under the same experimental conditions: 1.0 g of MCM-41 was added in 50 ml of 0.02 M copper(II) or manganese(II) complex solution, and then the mixture was stirred for 6 h at room temperature.

Cyclic Voltammetry (CV) of Copper- and Manganese-Phenanthroline Functionalized MCM-41

A standard three-electrode cell was used for the electrochemical experiments. The working electrode was prepared by pressing (2 tons/cm², 5 min) sample (0.2 g) and graphite (0.2 g) to a hard tablet, in which graphite was used as electronic conductor. The reference electrode was an aqueous saturated calomel electrode (SCE), and a platinum slice was used as counter electrode. The electrolyte consisted of a solution of 0.1 M H₂SO₄ or 0.1 M KNO₃ dissolved in refined dimethyl sulfoxide (DMSO). The electrochemical experiments were controlled by ZF-3 potentiostat and ZF-4 potential scanner.

RESULTS AND DISCUSSION

The scheme in Fig. 1 summarizes the reactions between calcined MCM-41 and the metal ion complex. Firstly, 3-aminopropyl modifies the inner walls of mesoporous MCM-41 and yields amine ligands by using (EtO)₃Si(CH₂)₃NH₂ as precursor. No water is involved in the synthesis system to prevent (EtO)₃Si(CH₂)₃NH₂ from hydrolyzing in advance and thus influencing the condensation. Then, $[\text{M}(\text{II})(\text{phen})_2\text{Cl}]\text{OH}$ ($\text{M}(\text{II}) = \text{Cu}(\text{II})$ or $\text{Mn}(\text{II})$) goes

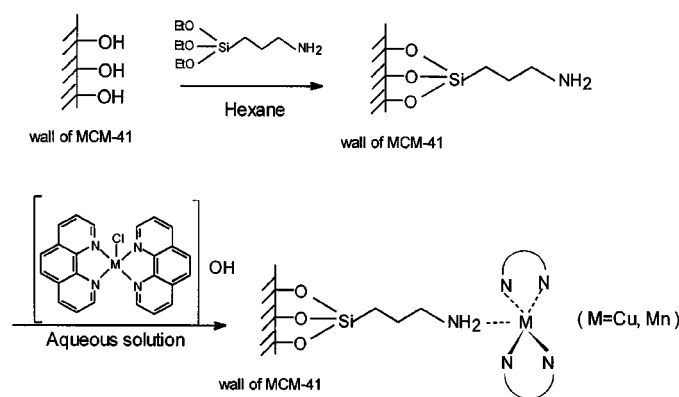


FIG. 1. Schematic of reactions between mesoporous MCM-41 and metal ion complexes.

into the pores of functional MCM-41 and $\text{M}(\text{II})$ is coordinated by grafted amine ligands displacing of Cl. Thus, mesoporous silicate MCM-41 and metal ion complex are linked with 3-aminopropyl. Table 1 gives the results of elemental analysis (AA 6401 atomic absorption spectrometer) of functional MCM-41.

X-ray powder diffraction patterns (Rigaku D/max rb, $\text{CuK}\alpha$) of the samples are shown in Fig. 2. The patterns show Bragg peaks at low reflection angles between 1.8 and 10.0°, which are typical of mesoporous MCM-41 materials. The XRD patterns of b, c, and d suggest that a long-range order are still kept in the hexagonal phase, though they indicate a slightly lower crystallinity in functionalized MCM-41 than the unmodified MCM-41 (a) because the other Bragg peaks cannot be achieved clearly. Especially, the intensity of (100) reflection is decreased sharply with the addition of 3-aminopropyl and metal ion complexes grafted. In addition, the loss of other Bragg peaks and the decrease in (100) intensity could be due to contrast matching between the silica walls and the content of the channels after functionalization.

N₂ sorption isotherm is an efficient way for providing information about the pore system of mesoporous materials (1, 12). Figure 3 shows the nitrogen adsorption/desorption isotherms (Micromeritics ASAP 2010; the samples were outgassed under 3 μmHg vacuum at 433 K for 6 h) at 77 K

TABLE 1
Elemental Analysis Results

Samples	M (wt%)	M/Si molar ratio	M/NH ₂ molar ratio
MCM-ap-Cu(phen) ₂	2.15	0.027	0.200
MCM-ap-Mn(phen) ₂	1.81	0.026	0.193

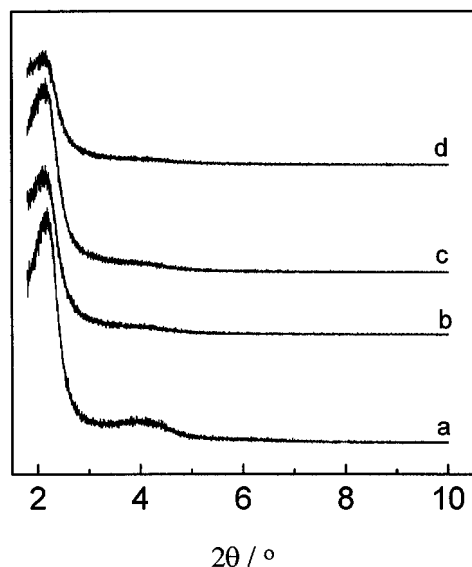


FIG. 2. XRD of (a) calcined MCM-41, (b) MCM-ap, (c) MCM-ap-Cu(phen)₂, and (d) MCM-ap-Mn(phen)₂.

and the pore distribution of the Cu(II), Mn(II) complex functionalized MCM-41. The isotherms can be classified as type IV according to IUPAC. The Brunauer–Emmett–Teller (BET) surface area and specific pore volume of Cu(II) and Mn(II) ion complex functionalized MCM-41 reduce remarkably compared to calcined MCM-41. The sorption experiment yields a BET surface area for calcined MCM-41 of 1128 m²/g and pore volume of 1.45 cm³/g. When MCM-41 was modified with 3-aminopropyl on the inner surface, its BET surface area and pore volume reduce to 738 m²/g and 0.97 cm³/g, respectively. Introducing either Cu(II)- or Mn(II)-phenanthroline complex into 3-aminopropyl functional MCM-41 leads to a further decrease of the BET surface area and pore volume. For MCM-ap-Cu(phen)₂, they decrease to 636 m²/g and 0.68 cm³/g, while for MCM-ap-Mn(phen)₂, they are 668 m²/g and 0.70 cm³/g. Correspondingly, the metal ion complexes have influence on the Barrett–Joyner–Halender (BJH) pore diameter distribution of the materials.

Solid state UV spectroscopy (Perkin–Elmer Lambda 20) of samples is illustrated in Fig. 4. There are three peaks in the range of 190–500 nm. The former two ($\lambda = 200$ nm, 230 nm) assigned to π - π charge-transfer bands of phenanthroline, and the latter ($\lambda = 264$ nm) is the characteristic band of metal-to-ligand charge transfer (12). In UV spectra of both MCM-ap-Cu(phen)₂ and MCM-ap-Mn(phen)₂, the absorption band edges have a slight red shift compared to impregnated MCM-Cu(phen)₂ and MCM-Mn(phen)₂, respectively, because of the coordination of metal ion with amine ligands.

Copper and manganese ion are highly sensitive to ESR spectroscopy (13, 14). Figure 5 shows room-temperature ESR spectra of copper and manganese complex functionalized MCM-41 (Bruker ER-200D ESR spectrometer). There is no signal difference between the metal ion complex precursors and metal ion complex functionalized MCM-41. Thus the coordination states of Cu(II) and Mn(II) are unaffected by the process of grafting. The three small peaks with $g_{\parallel} = 2.290$ and the strong singlet with $g_{\perp} = 2.065$ in Fig. 5A are attributed to copper ion. In contrast to simple manganese ion, different spectroscopic features are observed (Fig. 5B): in addition to the sextet lines, a broad singlet at $g_{\perp} = 2.010$ of MCM-ap-Mn(phen)₂ is observed, which is typical for a manganese(II) complex.

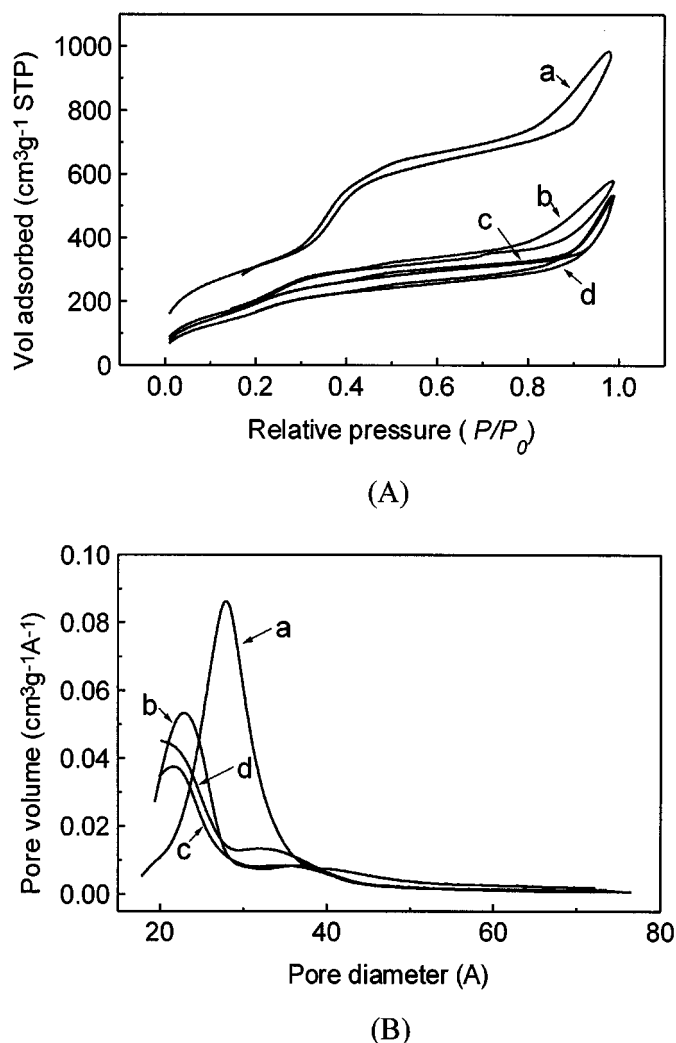


FIG. 3. (A) N₂ adsorption/desorption isotherms at 77 K of (a) calcined MCM-41, (b) MCM-ap, (c) MCM-ap-Cu(phen)₂, and (d) MCM-ap-Mn(phen)₂. (B) Pore diameter distribution of samples.

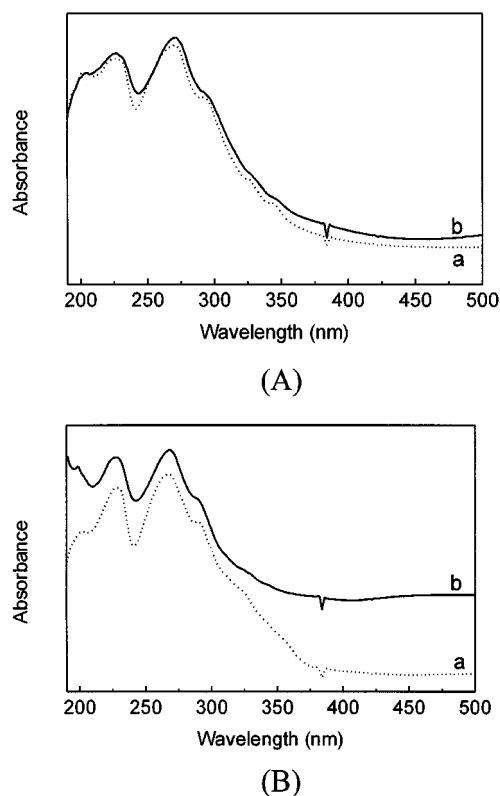


FIG. 4. (A) Solid state UV spectra of (a) MCM-Cu(phen)₂ and (b) MCM-ap-Cu(phen)₂. (B) Solid state UV spectra of (a) MCM-Mn(phen)₂ and (b) MCM-ap-Mn(phen)₂.

Cyclic voltammetry (CV) was performed to test the electroactivity of the grafted metal ion complexes onto MCM-41, and these were compared to the complexes impregnated into MCM-41 under the same experimental conditions. The observed redox processes probably reflect the electroactivity of metal ion complexes located in the inner pore of MCM-41 (15).

In Fig. 6, the voltammograms recorded during the applied cyclic voltammetric scans on the copper complex grafted electrode are shown. The voltammograms of MCM-Cu(phen)₂ in 0.1 M H₂SO₄ or in 0.1 M KNO₃ have very similarly shaped CV curves, and no clear electroactivity could be observed in potential ranges from -1.5 V (SCE) to $+1.5$ V (SCE). The electroactivity of MCM-ap-Cu(phen)₂ in DMSO is noticeably different from impregnated MCM-Cu(phen)₂. It shows a well-defined anodic peak near $+1.0$ V (SCE) in 0.1 M H₂SO₄ DMSO solution; however, the reverse sweep shows no reduction of MCM-ap-Cu(phen)₂. In 0.1 M KNO₃ DMSO solution, the anodic peak appears near 0.58 V (SCE), which suggests that MCM-ap-Cu(phen)₂ is relatively active in neutral solution compared to acid solution. Additionally, the intensity of cyclic voltammograms of both MCM-ap-Cu(phen)₂ and

MCM-Cu(phen)₂ do not decay with redox cycles performed.

Figure 7 illustrates the cyclic voltammograms of manganese complex grafted onto mesoporous MCM-41. In acid 0.1 M H₂SO₄ DMSO solution, both functionalized MCM-ap-Mn(phen)₂ and MCM-Mn(phen)₂ have similarly shaped CV curves. In the forward scan, the current is observed slight increase up to $+0.85$ V (SCE) followed by a nearly exponential increase. In the reverse scan, the quickly increase is occurred at -0.85 V (SCE). In neutral 0.1 M KNO₃ DMSO solution, impregnated MCM-Mn(phen)₂ is more electroactive than functionalized MCM-ap-Mn(phen)₂. From the voltammogram of MCM-Mn(phen)₂, we could find a well-defined anodic peak at -0.1 V (SCE) and a cathodic peak at -0.8 V (SCE) are attributed to Mn⁴⁺/Mn²⁺ process. However, in the CV curve of MCM-ap-Mn(phen)₂, only a cathodic peak at -0.8 V (SCE) can be observed.

In summary, from the results of CV experiments, MCM-ap-Cu(phen)₂ is more electroactive than MCM-Cu(phen)₂, while MCM-ap-Mn(phen)₂ is more electrochemically stable than MCM-Mn(phen)₂.

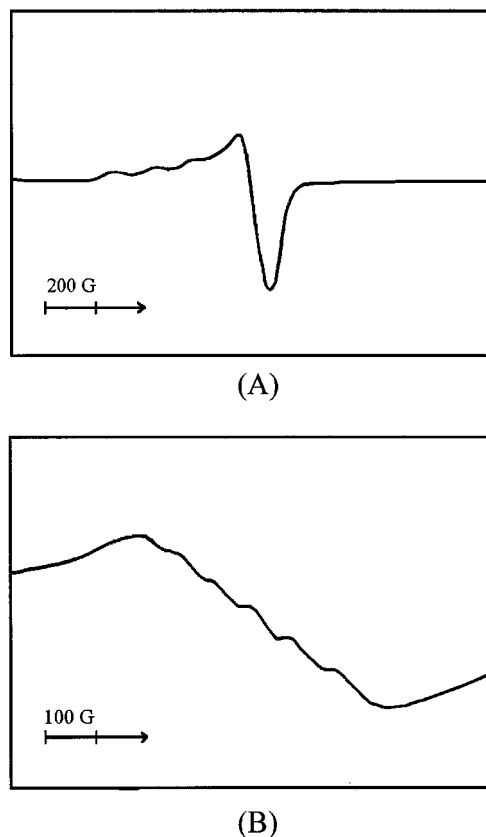
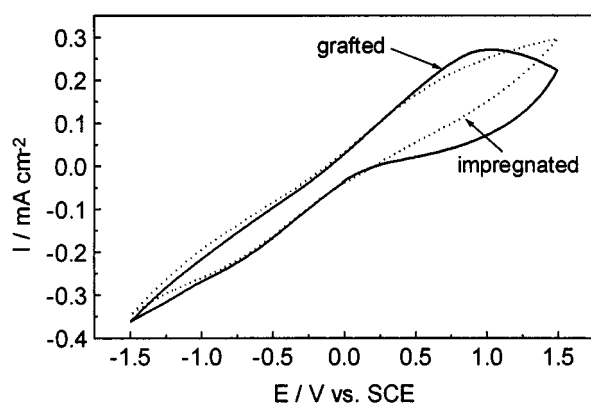
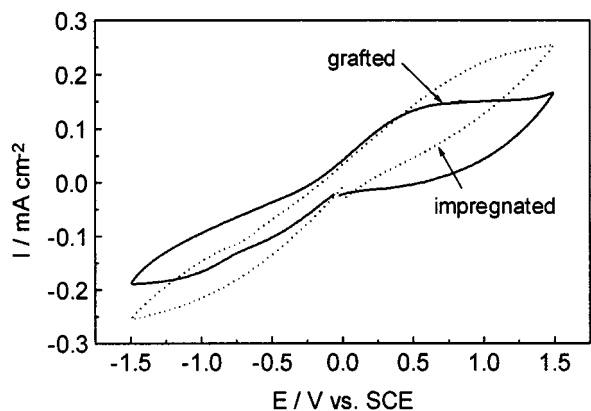


FIG. 5. (A) ESR spectrum of MCM-ap-Cu(phen)₂ at 293 K. (B) ESR spectrum of MCM-ap-Mn(phen)₂ at 293 K.



(A)

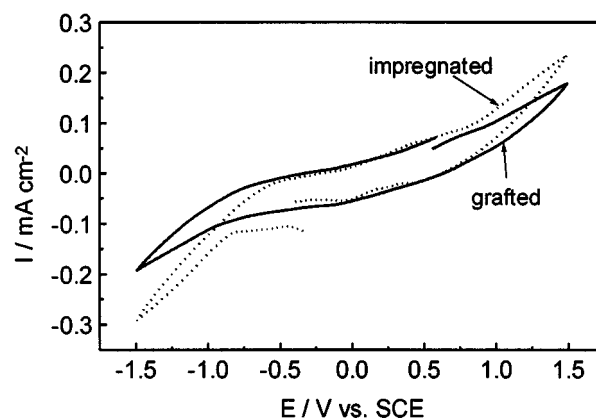


(B)

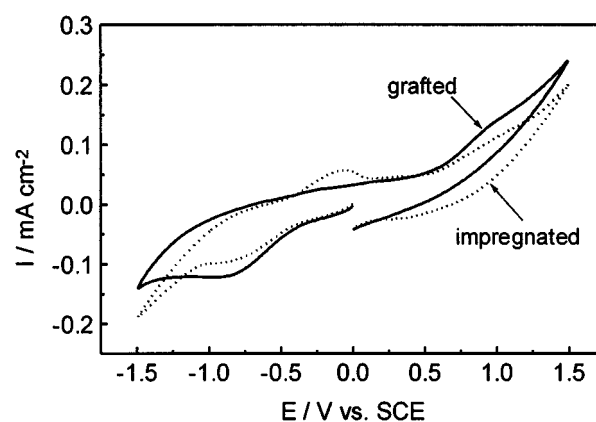
FIG. 6. Cyclic voltammograms of (—) copper complex grafted onto functionalized MCM-41 (MCM-ap-Cu(phen)₂) and (···) copper complex impregnated into MCM-41 (MCM-Cu(phen)₂), (A) in DMSO solution of 0.1 M H₂SO₄ and (B) in DMSO solution of 0.1 M KNO₃. Potential scan rate = 50 mV/s.

CONCLUSION

The functionalization of the pore walls of mesoporous MCM-41 has been achieved by the treatment of amine functional MCM-41 with [Cu(phen)₂Cl]⁻ and [Mn(phen)₂Cl]⁻, respectively. The BET surface area and specific pore volume of MCM-ap-Cu(phen)₂ or MCM-ap-Mn(phen)₂ decrease sharply, and absorption band edge of functionalized MCM-41 has a slight red shift in solid state UV spectroscopy. In ESR spectra, the copper and manganese complex functionalized MCM-41 show a strong singlet at $g_{\perp} = 2.065$ and a broad singlet with sextet lines centered at $g_{\perp} = 2.010$, respectively. The results of cyclic voltammetry experiments suggest that MCM-ap-Cu(phen)₂ is more electroactive than MCM-Cu(phen)₂, while MCM-ap-Mn(phen)₂ is more electrochemically stable than MCM-Mn(phen)₂.



(A)



(B)

FIG. 7. Cyclic voltammograms of (—) manganese complex grafted onto functionalized MCM-41 (MCM-ap-Mn(phen)₂) and (···) manganese complex impregnated into MCM-41 (MCM-Mn(phen)₂), (A) in DMSO solution of 0.1 M H₂SO₄. (B) in DMSO solution of 0.1 M KNO₃. Potential scan rate = 50 mV/s.

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