Synthesis, characterization and catalytic activity of μ-oxo bridged dinuclear iron 1,10 phenanthroline complex encapsulated in MCM-41

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Abstract

This paper describes the encapsulation of μ-oxo bridged dinuclear iron 1,10 phenanthroline (Fe-phen) complex in MCM-41. These systems have been characterized by thermogravimetric analysis (TGA), UV–Vis, FT-IR, EPR and cyclic voltammetry. On encapsulation reduction potential of Fe-phen is shifted by 275 mV more positive due to perturbation of molecular energy levels. Because of antiferromagnetic coupling a decrease in EPR signal intensity is observed as temperature is lowered from 300 to 77 K. By comparing the performance of the heterogeneous system with the free complex in the oxidation of benzyl alcohol using *t*-butyl hydroperoxide (TBHP), a protection effect of the matrix over the active center was evidenced by high turnover and yield of product. UV–VIS spectrum shows in neat complex Fe–O–Fe bridge is cleaved during the oxidation of benzyl alcohol while in encapsulated system, it is stable. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic properties of transition metal complexes encapsulated inside the zeolite matrix have received considerable attention in recent times. The well defined and ordered structure of zeolites provides an ideal environment to entrap active metal complexes or metal clusters. These modified systems can be exploited as catalysts [1]. Inorganic complexes encapsulated in such porous systems can even mimic natural enzymes and can therefore be termed as zeozymes [2]. In biological systems, there are some enzymes which have Fe–O–Fe bridge as active centers. Methane mono-oxygenase catalyses the formation of methanol from methane. Ribonucleotide reductase catalyses the formation of deoxyribonucleotide precursors for DNA bio-synthesis. Recent studies [3] have shown that well designed binuclear iron complexes can act as a model for these enzymes and function as efficient catalysts for the oxidation of various organic substrates. But they lose their catalytic activity due to cleavage of Fe–O–Fe bridge [4]. Can one stabilize this Fe–O–Fe bridge like in biological enzymes by encapsulating in porous media? This paper describes the encapsulation of μ-oxo bridged dinuclear iron 1,10 phenanthroline complex ($Fe_2O(phen)_4Cl_4.6H_2O$) in MCM-41 materials. The stability of Fe–O–Fe bridge was studied using oxidation of benzyl alcohol as a probe reaction.

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2. Experimental

2.1. Preparation of catalyst

Si–MCM-41 and $Fe_2O(Phen)_4Cl_4.6H_2O$ (Fe-phen) complex were prepared according to the methods reported in literature [5,6]. The impregnation was done by taking stoichiometric amount of $FeCl_3.6H_2O$ (Loba Chemie, 99%) and 1,10 phenanthroline (CDH, 99.5%) in 100 ml of water. MCM-41 was suspended in this solution and stirred for 36 h. The resulting red colored solid (Fe-phen–MCM-41) was filtered and dried at room temperature. In another experiment, 0.1 g of the Fe-phen complex was dissolved in 50 ml of methanol and MCM-41 was suspended in that solution and stirred for 3 h. After 3 h, methanol was evaporated to dryness. This catalyst was designated as Fe-phen–MCM-41(sads).

2.2. Characterization

To study the thermal property of both neat (Fe-phen) and encapsulated complexes (Fe-phen–MCM-41), the thermogravimetric and differential thermal analyses (TGA/DTA) were performed on an Perkin Elmer TGA (Delta Series TGA 7) instrument at a heating rate of $20 \, \text{K} \, \text{min}^{-1}$ in air. UV–Vis spectra were recorded with Perkin Elmer Lamda17 Spectrophotometer. For neat (Fe-phen) and encapsulated complexes (Fe-phen–MCM-41), the spectra were carried out in methanol using 1 cm quartz cell and in nujol mull at room temperature respectively. The FT-IR (Perkin Elmer 1760 FT-IR controlled by Perkin Elmer professional computer using Idris software) spectra for the samples were recorded in the range $400–4000 \, \text{cm}^{-1}$ at room temperature using KBr diluted pellet. EPR (varian E-112 EPR spectrophotometer) spectra were recorded at room temperature as well as at liquid nitrogen temperature. The cyclic voltammogram (Wenking potentioscan (POS73) with digital 2000 X-Y recorder) of neat and encapsulated complexes were recorded in 0.1 M KCl. The measurements were done using grains of MCM-41 adhered to carbon block ($1 \, \text{cm}^2$) as working electrode, Pt foil ($1.5 \, \text{cm}^2$) as counter electrode and Ag/AgCl as reference electrode. The cyclic voltammaogram of neat complex was taken by dissolving 0.01 M Fe-phen in 0.1 M KCl using Pt as working electrode.

2.3. Catalytic activity

The catalytic experiments were carried out at 303 K in a 100 ml double necked round bottom flask, attached to a reflux condenser. Benzyl alcohol (3.9 mmol), acetonitrile (solvent, 10 ml), tertiarybutylhydroperoxide (12.4 mmol) and the catalyst (0.05 g) were stirred for 20 h. The products were analyzed by gas chromatography (Nucon 5600, FID, SE 30 column).

3. Results and discussion

3.1. Thermal analysis

Fig. 1 shows the thermogram of the neat and encapsulated complexes. Neat complexes showed multiple weight losses due to the removal of water, chloro- and phenanthroline-ligands. The total weight loss observed (85%) is comparable to that of theoretical value (85.55%). On encapsulation, one observed a single stage decomposition of various ligands at 423 K. This may be due to the adsorption of decomposed ligands on the MCM-41 matrix. The concentration of the metal complex inside the MCM-41 matrix is calculated from data of weight loss obtained from TGA which corresponds to 2.6×10^{-5} mol/g.

3.2. Electronic spectroscopy

UV–Vis spectra (Fig. 2) of neat (Fe-phen) and encapsulated complexes (Fe-phen–MCM-41) showed bands between 220 and 350 nm. The band positions and the corresponding transitions (shown in parenthesis) are given in Table 1. The transitions $p_{z(O)} \rightarrow d_{z^2(Fe)}$ and $p_{z(O)} \rightarrow d_{xz(Fe)}$ are overlapping with ligand transitions [3]. The characteristic band observed at 320 nm for both neat and encapsulated complexes corresponds to charge transfer from the oxygen to Fe orbital which is absent in the monomeric complexes. No significant shift in the peak positions of neat and encapsulated complexes were observed.

3.3. FT-IR spectroscopy

The neat iron 1,10 phenanthroline (Fe-phen) complex shows bands between 400 and $1600 \, \text{cm}^{-1}$ (Fig. 3). Fe–O–Fe asymmetric stretching band was
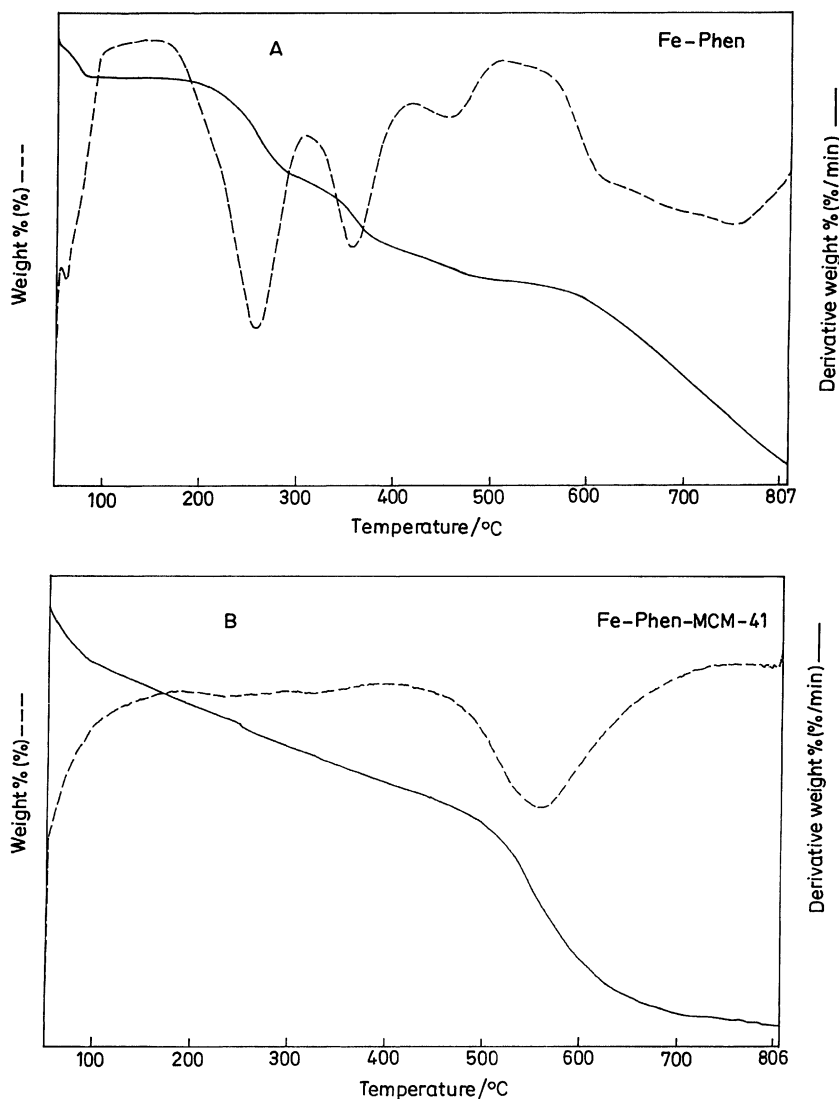
Fig. 1. TGA(——) and DTG(------) profiles of (A): Fe-phen, (B): Fe-phen–MCM-41.

observed at $841\,cm^{-1}$ for neat complex. But MCM-41 bands are predominant in this region. Due to lower concentrations of complex inside the MCM-41 matrix, no intense peaks between 1200 and $1600\,cm^{-1}$ were observed.

3.4. EPR spectroscopy

In binuclear iron 1:1 complexes, the two spins of iron (III) are antiferromagnetically-coupled [3].

A decrease in EPR (Fig. 4) signal intensity is observed when temperature was lowered from 300 to 77 K for both neat (Fe-phen) and encapsulated (Fe-phen–MCM-41) complexes. It indicates that complexes are binuclear and antiferromagnetically coupled. The signal observed at $g = 2.099$ (Table 1) corresponds to antiferromagnetically coupled binuclear iron species. The signal at $g = 4.13$ is due to magnetically non-interacting iron (III) species which is an impurity normally encountered in binuclear
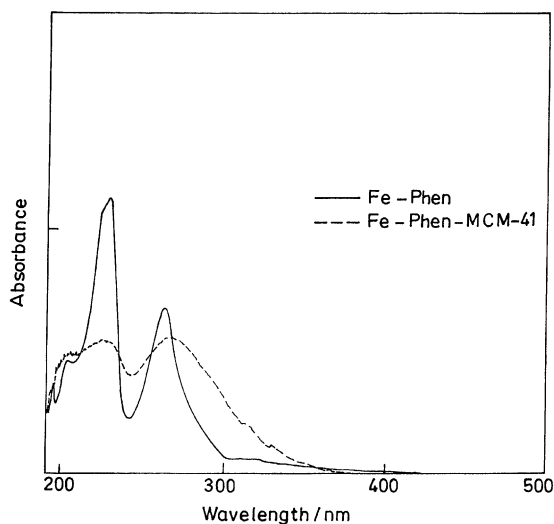
Fig. 2. UV–VIS spectrum of Fe-phen (—); Fe-phen–MCM-41(--------).

Table 2
Catalytic activity towards benzyl alcohol oxidation[a]

Catalyst	Benzyl alcohol conversion (mol%)	TON
Fe-phen–MCM-41	34.9	1041
Fe-phen–MCM-41(first reuse)	23.3	989
Fe-phen	7.1	80

[a] Reaction conditions: temperature: 303 K; time: 20 h; acetonitrile: 10 ml; benzyl alcohol: 3.9 mmol; TBHP: 2.4 mmol; catalyst: 0.05 g.

ferric complexes. There is no significant shift in the *g* values upon encapsulation.

3.5. Cyclic voltammetry

In order to understand the redox potential of metal complex inside the MCM-41 matrix, cyclic voltammograms for both neat and encapsulated complexes were recorded. The voltammogram obtained for neat complex (Fig. 5A) shows two peaks. The first one (I) corresponds to irreversible reduction of $[Fe_2O(phen)_4(H_2O)_2]^{4+}$ to $Fe(phen)_3^{2+}$ and the second peak (II) corresponds to the redox process of $Fe(phen)_3^{2+}/Fe(phen)_3^{3+}$ [7]. On encapsulation (Fig. 5B), the first peak is shifted by 0.275 V (Table 1) more positive and second peak is unaffected. This shift indicates that the oxidizing capacity of the complex is altered in the encapsulated state. In order to differentiate complex present on the external surface from that of encapsulated one, cyclic voltommogram was recorded for Fe-phen–MCM-41(sads). Three peaks were observed (Fig. 5C). Peaks I and II were similar to that of peaks observed for Fe-phen–MCM-41. Peak I(*S*) corresponds to the reduction of the complex present on the external surface. It is also reported in literature that the complex present on the external surface is having different redox potential compared to that of complex present inside the zeolite matrix

Table 1
Physiochemical characterization of neat and encapsulated Fe-phen complexes

Techniques	Fe-phen	Fe-phen–MCM-41	Fe-phen–MCM-41 (sads)
UV–VIS[a]	228[b] ($p_{z(O)} \rightarrow d^2_{z(Fe)}$)	228[c] ($p_{z(O)} \rightarrow d^2_{z(Fe)}$)	
	265[b] ($p_{z(O)} \rightarrow d_{xz(Fe)}$)	269[c] ($p_{z(O)} \rightarrow d_{xz(Fe)}$)	–
	320[b] ($p_{x(O)} \rightarrow d_{xz(Fe)}$)	320[c] ($p_{x(O)} \rightarrow d_{xz(Fe)}$)	
EPR[d]	2.099	2.099	–
	4.197	4.198	
Cyclic voltammetry[e]			0.09 I (*S*)
	0.025 (I)	0.3 (I)	0.29 (I)
	0.915 (II, E_{pc})	0.9 (II, E_{pc})	0.9 (II, E_{pc})
	0.885 (II, E_{pa})	0.88 (II, E_{pa})	0.75 (II, E_{pa})

[a] λ_{max} (nm).

[b] Measured in methanol.

[c] Measured as nujol mull.

[d] At liquid nitrogen temperature.

[e] Cathodic (E_{pc}) and anodic (E_{pa}) peak potentials in volts versus Ag/AgCl.
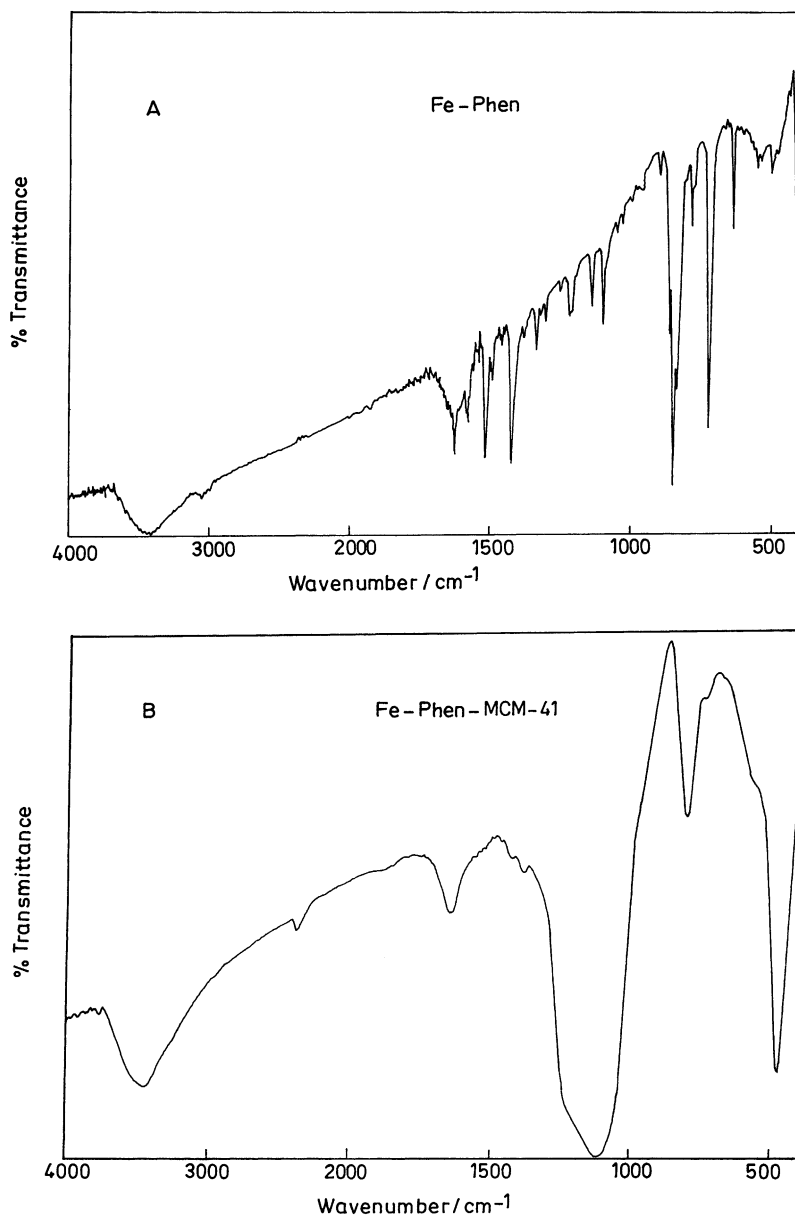
Fig. 3. FT-IR spectrum of (A): Fe-phen; (B): Fe-phen–MCM-41.

[8]. The cages, channels, side pockets of zeolites and MCM-41 can provide constrained environment to the complexes [9,10] and this can activate them [10]. Because of the field gradient, the complex molecule is having different redox potentials at different places of the MCM-41 matrix.

3.6. Catalytic activity

The results of the catalytic activity studies carried out in the oxidation of benzyl alcohol over the encapsulated and neat Fe-phen complexes are presented in Table 2. Benzaldehyde is the only product observed
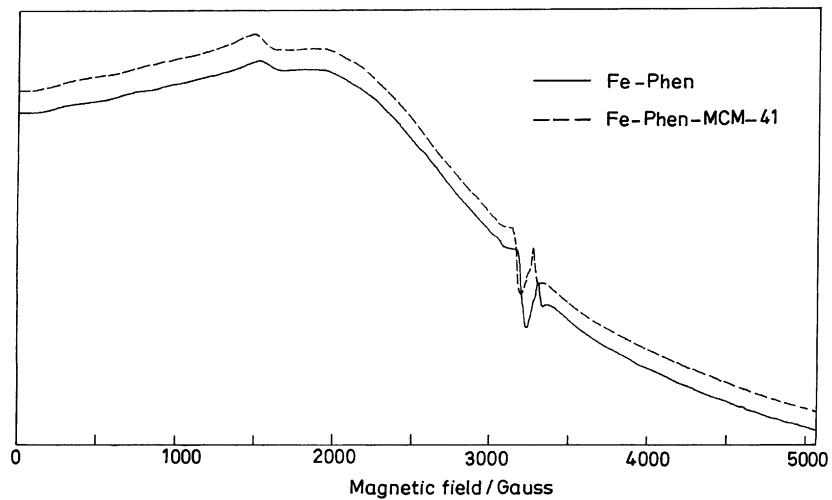
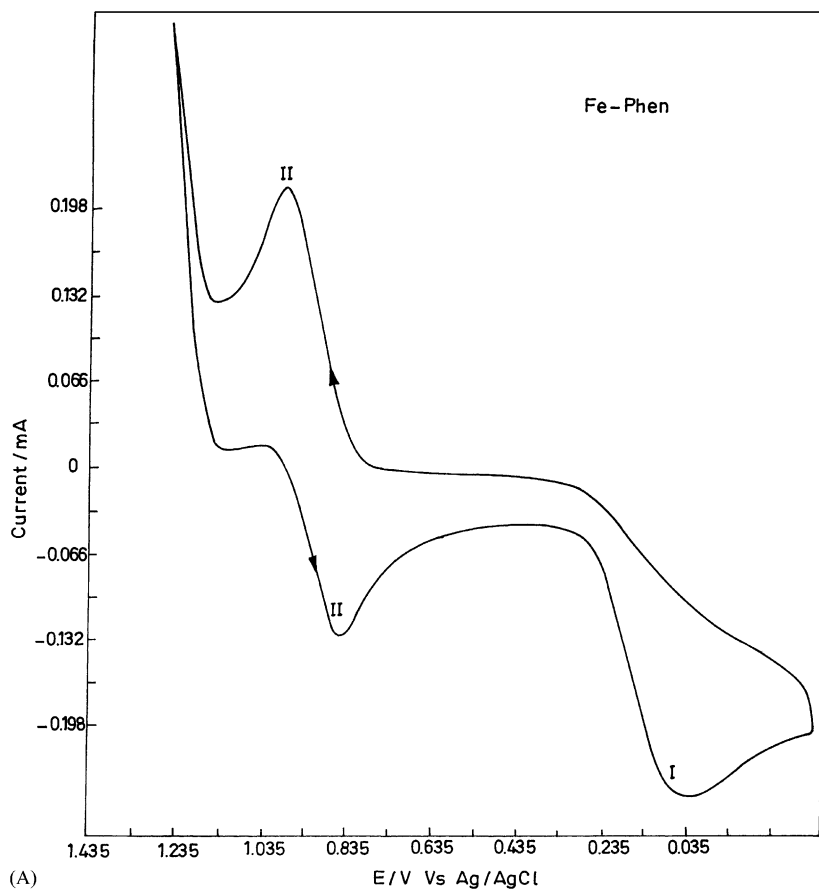Fig. 4. EPR spectrum of Fe-phen (——); Fe-phen–MCM-41 (--------).

Fig. 5. Cyclic voltommogram of (A): Fe-phen; (B): Fe-phen–MCM-41; (C): Fe-phen–MCM-41(sads).
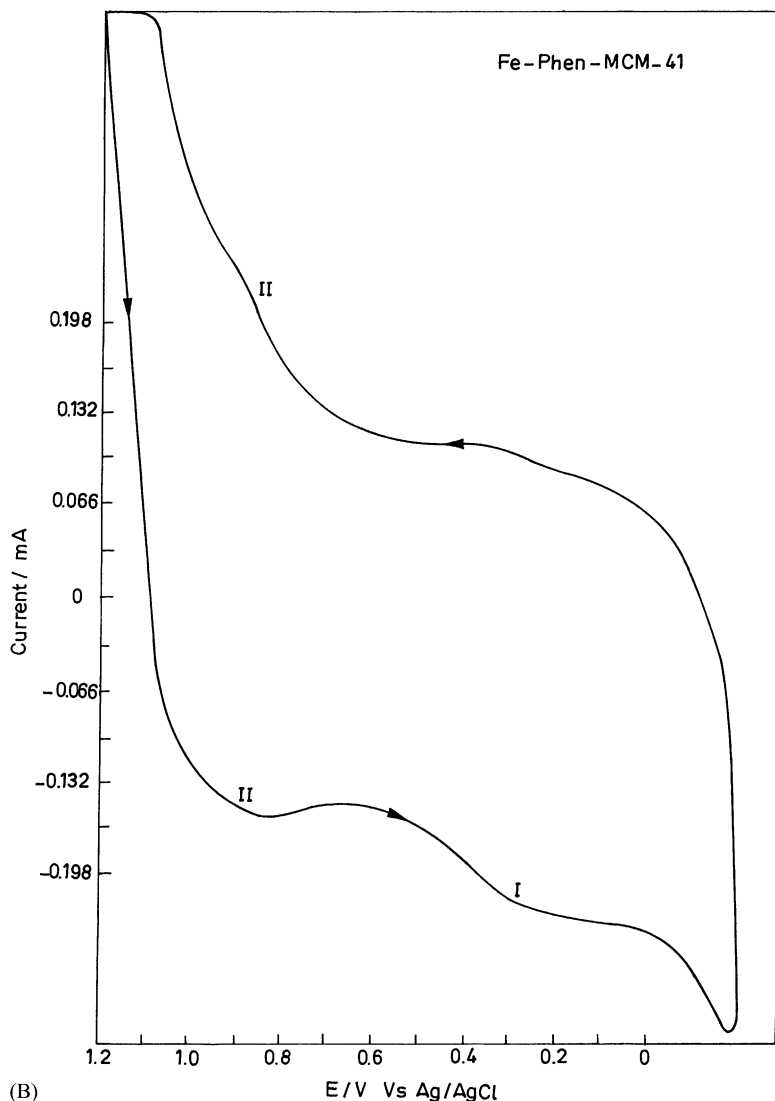
Fe–Phen–MCM–41

(B)

E / V Vs Ag/AgCl

Fig. 5. (*Continued*).

both in neat and encapsulated complexes. It is noticed that the Fe-phen complex in the encapsulated state is more active than the neat complex. Turnover number (TON) increased 13 times upon encapsulation. UV–VIS spectra (Fig. 6) is taken for neat Fe-phen complex in benzyl alcohol. The characteristic band observed at 380 nm corresponds to charge transfer from the oxygen to Fe orbital ($p_{x(O)} \rightarrow d_{xz(Fe)}$), which is absent in the monomeric complexes. After addition of TBHP, the band at 380 nm decreases and a new broad band was observed at 520 nm, whose intensity increased with respect to time, indicates the formation of mononuclear $Fe(phen)_3^{2+}$ complex [11]. During the activation of TBHP the Fe–O–Fe bridge is cleaved and forms mononuclear complex, which is inactive for benzyl alcohol oxidation. Fe-phen–MCM-41 was reused and it gives TON of 989. The slight decrease in turnover number may be due to blockage of pores
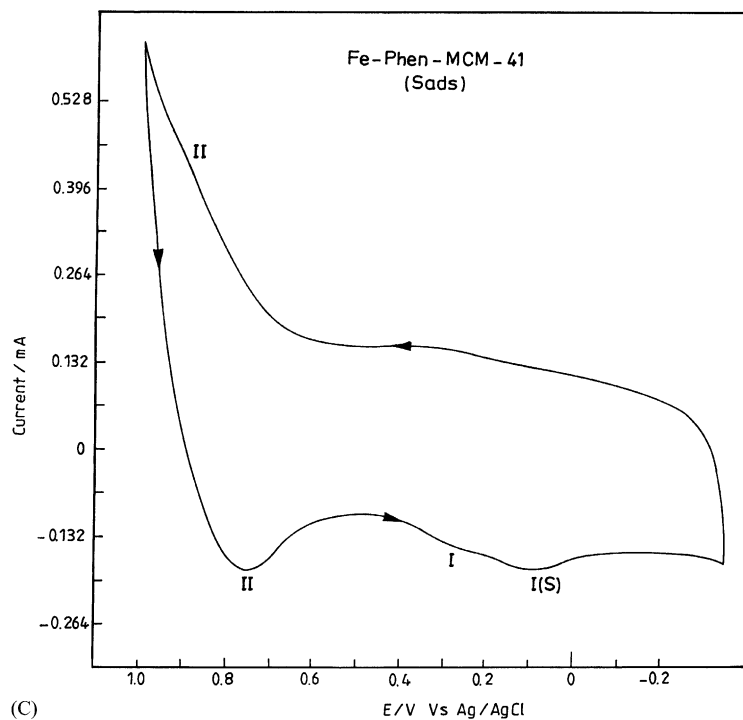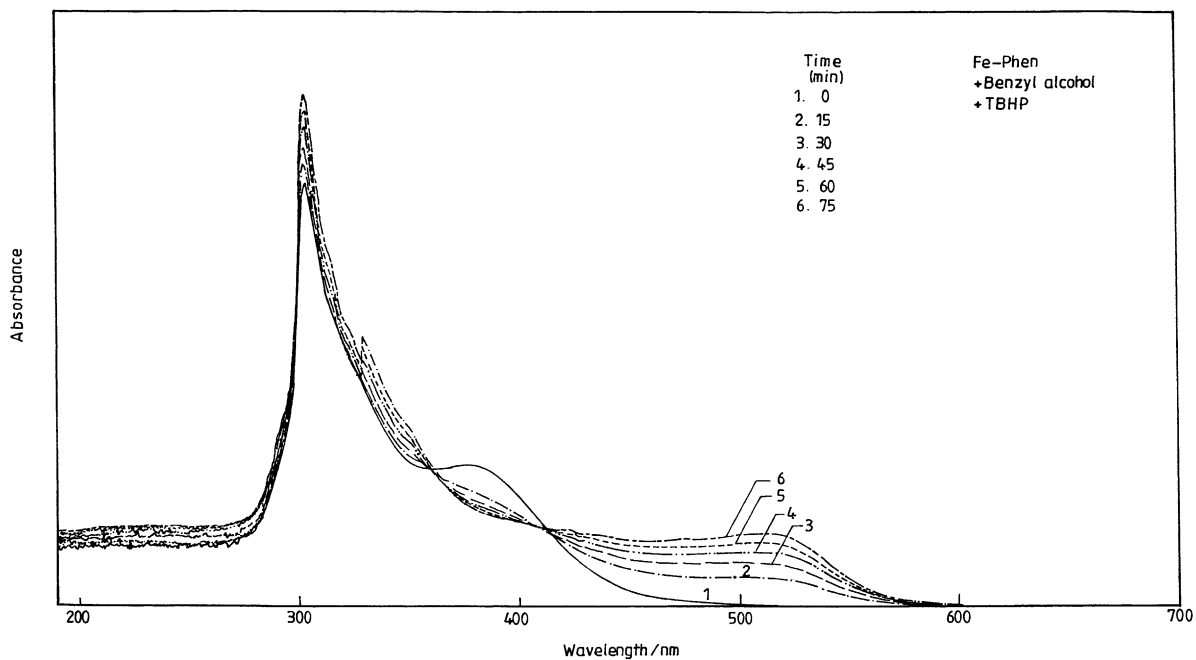
Fig. 5. (*Continued*).

Fig. 6. UV–VIS spectrum of Fe-phen in benzyl alcohol and TBHP.

by organic substrates. This provides an evidence that Fe-phen complex in the encapsulated state is quite stable and it is not undergoing any molecular degradation.

4. Conclusions

Binuclear Fe-Phen complex was encapsulated inside the mesoporous channels of the MCM-41. The neat and encapsulated complexes were characterized by TGA, FTIR, UV–VIS, EPR and cyclic voltammetry. The oxidation of benzyl alcohol was studied in both neat and encapsulated complexes. TON increased 13 times upon encapsulation. UV–VIS spectrum shows that Fe–O–Fe bridge is cleaved during the oxidation of benzyl alcohol. In the encapsulated state, the TON is maintained upon recycling and molecular degradation of the complex does not occur. These are only in a limited sense attempt to replicate the features of the processes that are occurring in nature in facile manner, but they can provide vital clues for generating systems in future which can at least generate systems which can mimic natural processes though not efficiently as it takes place in nature.

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