



Copper(II) complexes of embelin and 2-aminobenzimidazole encapsulated in zeolite Y-potential as catalysts for reduction of dioxygen

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Abstract

Copper(II) complexes of two biologically important ligands, viz., embelin (2,5-dihydroxy-3-undecyl-2,5-cyclohexadiene 1,4-dione) and 2-aminobenzimidazole were entrapped in the cages of zeolite Y by the flexible ligand method. The capability of these compounds in catalyzing the reduction of oxygen (industrially known as deoxo reaction) was explored and the results indicate an enhancement of the catalytic properties from that of the simple copper ion exchanged zeolite. These point to the ability of the ligands in enhancing the oxygen binding capability of the metal ion. Elemental analyses, Fourier transform infrared (FTIR), diffuse reflectance and EPR spectral studies, magnetic susceptibility measurements, TG, surface area analyses and powder X-ray diffraction studies were used in understanding the presence, composition and structure of the complexes inside the cages. The study also reveals the increased thermal and mechanical stability of the complexes as a result of encapsulation.

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1. Introduction

Immobilization of transition metal complexes within the super cages of zeolites or mesoporous materials has been a topic of intense research in recent years, with the aim of producing materials that combine the activity of molecular catalyst with the sieving capability and ease of separation from the reaction mixture [1]. The reduction of dioxygen by hydrogen in presence of transition metal complexes is an area of

considerable interest with respect to gas separations. A primary application of this reaction, often known as the deoxo reaction is the removal of trace amounts of oxygen present as impurities in gas streams [2]. The catalysts used for this reaction are mainly Pt, Pd, Pd/alumina or their oxides [3–5], which are very costly. Moreover, these types of reactions involving small molecules are applied by numerous research workers as catalyst test reactions for characterization of various catalysts [6]. Though several transition metal complexes were found to be active in catalyzing the reaction, their application on an industrial scale is restricted either due to the decomposition of ligand by attack of oxygen or due to dimerization [7–10]. Zeolite encapsulation is known to safeguard the complexes from these usually encountered difficulties.

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In this paper we report the encapsulation of copper(II) complexes with two ligands, viz., embelin (2, 5-dihydroxy-3-undecyl-2,5-cyclohexadien-1,4-dione) and 2-amiobenzimidazole. The encapsulated complexes were characterized by several techniques. The ability of the complexes to function as catalysts for the reduction of oxygen was explored and the results indicate that (i) the complexes are catalytically active; (ii) the thermal and mechanical stability increases as a result of encapsulation; and (iii) copper complex of embelin, YCuEm is a better catalyst in terms of efficiency and stability which in turn indicates that embelin is a good ligand in modifying the oxygen binding ability of the metal ion.

2. Experimental

2.1. Syntheses of the encapsulated complexes

Encapsulation of the complexes was effected by the flexible ligand method [1]. The Cu^{2+} -exchanged zeolite Y (CuY), $\text{Cu}_x\text{Na}_{56-x}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}\cdot n\text{H}_2\text{O}$ was prepared from Na-zeolite Y (NaY from Süd Chemie, India) by ion exchange in an aqueous metal chloride solution CuY (~ 1 g) was refluxed with a solution of embelin (0.1 g) in methanol for 4–6 h whereby the ligand diffuses freely through the channels and coordinates with the metal ions. Once the complex is formed it becomes too large to exit the pore and becomes physically entrapped in the cages. It was also prepared by sealed heating of a mixture of embelin and CuY at 130°C for 2 h. The heterogeneous complexes thus obtained were filtered and subjected to soxhlet extraction with methanol and then with acetone for 48–72 h. The exhaustive extraction process is meant to remove the complexes and reactants adsorbed on the surface of the zeolite. Uncomplexed metal ions remaining in the zeolite were removed by back exchange of the zeolite with NaCl (0.01 M) solution for 12 h. It was then washed with hot deionized water to remove the chloride ions and dried in vacuum over anhydrous calcium chloride.

2.2. Characterization

Si, Al, Cu and Na ions in the sample were determined by ICP AAS and C, H, and N determined by

microanalyses. The crystallinity of the samples was ensured by a Rigaku D-Max C X-ray diffractometer (XRD) using Ni filtered Cu $\text{K}\alpha$ radiation. Surface area of the samples was measured by multipoint BET method using a micrometrics Gemini 2360 Surface area analyzer. Magnetic susceptibility measurements were done at room temperature on a simple Guoy balance. IR spectra were recorded on a Shimadzu 8000 Fourier transform infrared (FTIR) spectrophotometer. Diffuse reflectance spectra were recorded on a Cary Win spectrophotometer in the range 200–2000 nm using MgO as reference. Powder EPR spectra were recorded with a Varian E-109 X/Q band spectrophotometer. The spectra were calibrated with TCNE ($g = 2.0027$). The thermogravimetric analyses were done on a V5.1A Du Pont 2000 TGA at a heating rate of $20^\circ\text{C min}^{-1}$.

2.3. Catalytic testing

A micro catalytic reactor loaded with 0.2 g of catalyst was connected to a gas chromatograph through a gas-sampling valve. Hydrogen was passed through the reactor at a flow rate of 30 ml min^{-1} and oxygen gas was injected through the precalibrated loop of the auto gas-sampling valve. The hydrogen reduces the oxygen thus admitted into the reactor and the unreacted oxygen is carried into the thermal conductivity detector of the GC for analyses. The output signal is recorded and the concentration measured with reference to the calibration for a known quantity of oxygen. The percentage conversion was calculated from the concentration of the unreacted oxygen obtained from the chromatogram. Further, the product of the reaction was ascertained to be water from its peak observed in the chromatogram after reaction.

3. Results and discussion

3.1. Catalyst characterization

The results of the chemical elemental analyses are given in Table 1 and give a Si/Al ratio of 2.4 which corresponds to the unit cell formula [11] $\text{Na}_{56}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}\cdot n\text{H}_2\text{O}$ for NaY and $\text{Na}_{56}\text{Cu}_{15}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}\cdot n\text{H}_2\text{O}$ for CuY. The results from surface area analyses (Table 1) indicate that

Table 1
Analytical data

Sample	Elements (%)						Surface area	Magnetic moment
	Si	Al	Na	Metal	C	N		
NaY	22	8.7	7.4		–	–	507	–
CuY	20.85	8.24	3.26	5.2	–	–	492	1.9
YCuEm	22	8.7	3.96	4.7	1.95	–	370	1.9
YCuAb	20.3	8.02	3.9	3.92	2.4	1.2	403	1.9

there is a significant decrease in surface area after the encapsulation of the complexes, which could be interpreted as due to the formation of compounds in the cavities of zeolites [11–13]. Magnetic susceptibility measurements yielded values of ~ 1.9 B.M. for the zeolite encapsulated complexes as well as for the metal ion exchanged zeolite which is due to tetrahedral distortion from planar geometry [14].

A comparison of the IR spectra of the encapsulated complexes with that of the “free complex” and/or ligand indicates the presence of the complex inside the zeolite cavities. The strong absorption at 1610 cm^{-1} ($\nu_{\text{C=O}}$) in the spectrum of embelin (Fig. 1) is shifted to 1460 cm^{-1} in the case of the complex (YCuEm). Such a large shift has been reported for the free complex of embelin as well as for complexes of various dihydroxyquininoid ligands [15–17]. In the case of the encapsulated aminobenzimidazole complex (YCuAb) almost all the bands present in the ligand spectra are present in the spectra of the complex. The band at 1669 cm^{-1} in the ligand spectra (N–H bending of ring nitrogen) and that 1560 cm^{-1} (N–H bending of $-\text{NH}_2$ group) are shifted to lower frequencies in the spectra of the complexes indicating coordination of the amino as well as ring nitrogen,

Kubelka–Munk analysis was performed on the reflectance data and the results are represented in Fig. 2 as a plot of Kubelka–Munk factor ($F(R)$) versus wavelength. YCuEm exhibits bands at 12800 cm^{-1} with a shoulder at 17250 cm^{-1} . The position of the peaks compare well with that reported in literature for a penta-coordinated complex and the appearance of the shoulder as a greater intensity absorption to the higher energy side suggests a square pyramidal configuration [18]. Hence Cu(II) might be presumed to be in a five coordinated state with the fifth position being loosely bound by an H_2O molecule. In the case of YCuAb the bands observed at 14800 and 11200 cm^{-1} (Fig. 2)

point to a distorted octahedral geometry for the complex.

EPR spectra of the complexes (Fig. 3) and Cu(II) exchanged zeolite were recorded at LNT and the parameters are given in Table 2. On the basis of the parameters YCuEm can be assumed to have a square pyramidal structure [19] and YCuAb to have a square planar structure [20]. Further, hyperfine splitting observed in the spectra of YCuAb implies coordination of nitrogen to the metal ion.

Powder XRD patterns of the parent zeolite, metal ion exchanged-zeolite and the zeolite encapsulated complexes are shown in Fig. 4. No significant variation was observed in the diffraction pattern as a result of the metal exchange or encapsulation procedures which suggests that there is only little or negligible loss in crystallinity of the zeolite. Therefore, reduction in surface area is due to inclusion of the complex and not due to collapse of crystalline structure.

Thermal stability is an important criterion to be met by catalysts when it comes to high temperature applications. The thermal stability of our complexes was studied by TG in an inert atmosphere and in presence of air. There are three stages of water loss in the case of YCuEm. The first stage is due to loss of intra-zeolite and coordinated water molecules. Decomposition at this stage is ruled out since an IR spectrum taken at this stage reveals all the functional groups to be intact. The ligand portion decomposes only after $275\text{ }^\circ\text{C}$. The decomposition temperature is higher by $25\text{ }^\circ\text{C}$ than in

Table 2
EPR parameters

Sample	g_{\parallel}	g_{\perp}	A_{\parallel} (cm^{-1})	A_{\perp} (cm^{-1})
CuY	2.4	2.07	169.8×10^{-4}	40×10^{-4}
YCuEm	2.35	2.07	154×10^{-4}	110×10^{-4}
YCuAb	2.4	2.08	188×10^{-4}	58×10^{-4}

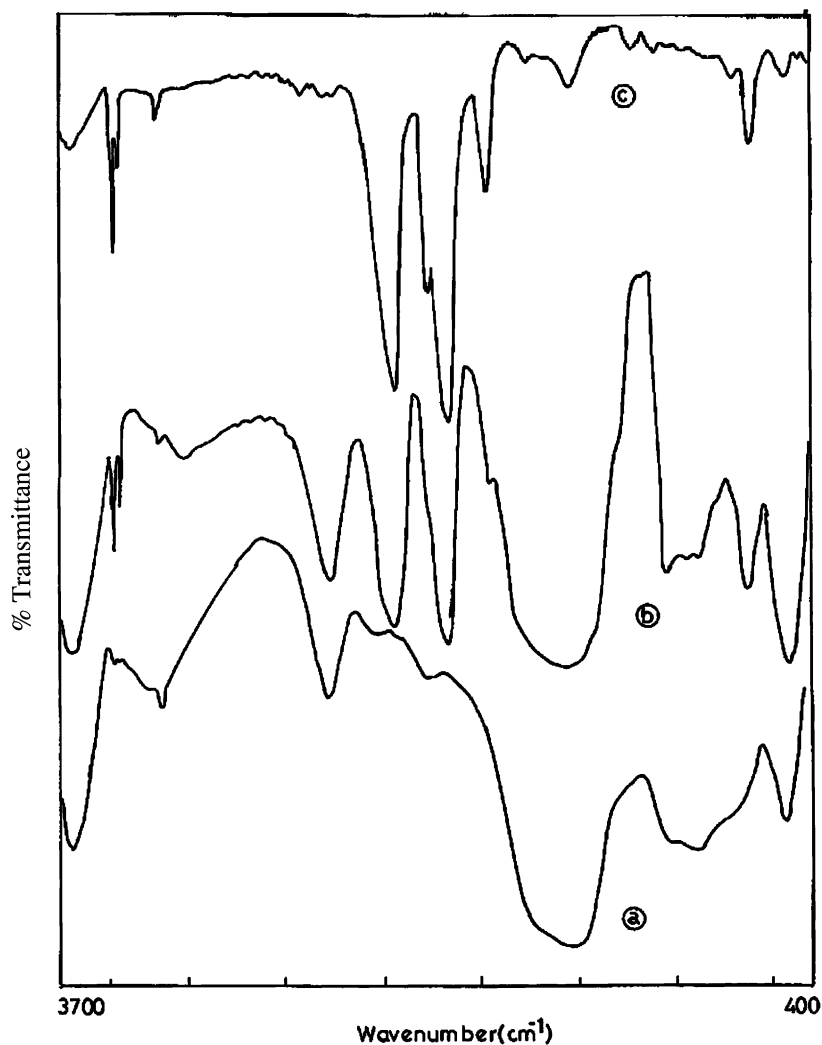


Fig. 1. IR spectra of: (a) CuY; (b) YCuEm; (c) CuEm.

the “free” complex indicating increased thermal stability as a result of encapsulation. In YCuAb also the ligand portion starts decomposing around 280 °C.

3.2. Activity of YCuEm and YCuAb

The encapsulated metal complexes exhibited an activity in the range 200–240 °C. It was observed that the complexes exhibited no activity at room temperature. On increasing the temperature the complexes start catalyzing the reduction. However, the conversion is

only 20–50% below 230 °C. At 230 °C, a sudden jump in the conversion (95% for 0.2 ml of oxygen injected into reactor containing 0.2 g of catalyst) was observed. In spite of effecting comparable conversions YCuEm turned out to be superior to YCuAb since the latter got deactivated after two runs. A plausible reason for the enhanced activity of YCuEm at this temperature could be due to the removal of coordinated water, which is substantiated by TG studies of the complex. The TG data of YCuEm shows that the first stage of decomposition starts at 60 °C and completes at 230 °C. The

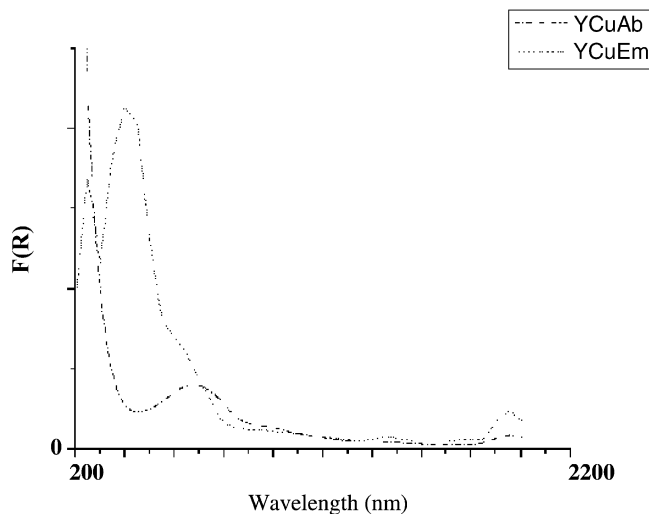


Fig. 2. Diffuse reflectance spectra of the encapsulated complexes.

decomposition at this stage is not due to the removal of the ligand. IR spectrum of the decomposition product at 230 °C exhibits the principal peaks in complex due to the ligand (Fig. 5) and therefore the mass loss up to this stage might be due to the loss of water. The loss of the coordinated water molecule could result in a different arrangement of ligands about the metal ion. This change in structure along with the tuning of the

redox potentials (benzoquinone are well known for their ability to tune the redox potentials of metal ions [21]) of the metal ion could be attributed to the sudden rise in catalytic activity of the complex at these temperatures.

From the FTIR spectrum of the catalyst pellets before and after the reaction it is seen that $\nu_{C=O}$ at 1460 cm^{-1} disappears and a new peak appears at 1555 cm^{-1} after the reaction (Fig. 6). This could be due to the strengthening of the C–O bond and consequent weakening of the M–O bond, when dioxygen molecule coordinates with the metal.

To ascertain the effect of the metal ion and zeolite cage structure on the activity the reactions were carried out in presence of CUY as well as NaY. No reaction was observed in presence of zeolite NaY. The ion exchanged zeolite, CuY exhibited a slight activity at lower temperatures. However, with increase in temperature the increase in activity was not that significant as that of the encapsulated complexes. The enhanced activity exhibited by the encapsulated complexes in comparison to the ion exchanged zeolite could only be due to the influence of the ligand. The ligand could induce changes in the structure as well as in the redox potential of the metal ions. In the case of the catalytic aziridination of styrene using transition metal exchanged zeolites [22], the by-product (benzaldehyde) formation was enhanced in the presence of bis(oxazoline) suggesting the role of ligands in increasing the

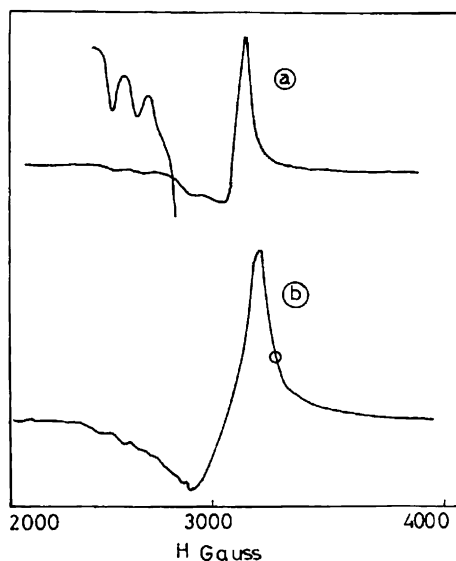


Fig. 3. EPR spectra of: (a) YCuEm; (b) YCuAb.

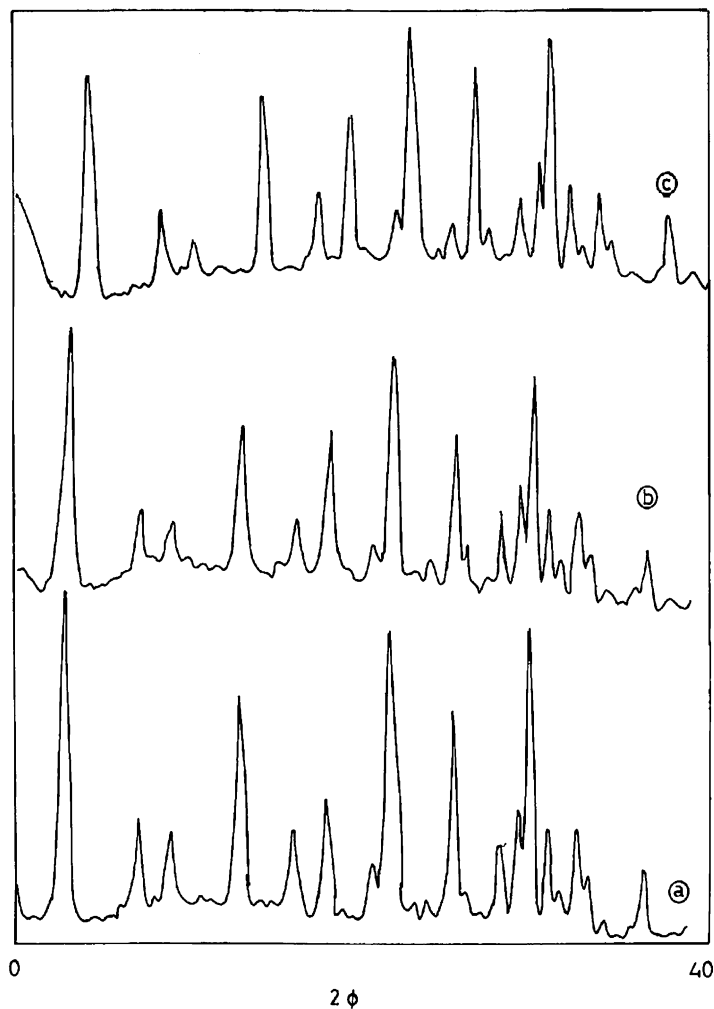


Fig. 4. XRD patterns of: (a) NaY; (b) YCuEm; (c) YCUAb.

oxidation activity. Therefore, in such reactions there can be problems due to the presence of molecular oxygen.

The percentage conversions of the two different volumes of oxygen indicate that the conversion is dependent on the concentration of oxygen gas. For 1.5 ml of oxygen injected into the reactor containing 0.2 g of catalyst, the percentage conversion was 59% which reduced to 10% when the amount of catalyst was reduced to 0.1 g suggesting a dependence of conversion on catalyst weight. However, the dependence seems to be complex as the conversion for 0.2 g of the catalyst is much greater than that for 0.1 g of the catalyst.

The effect of temperature on the percentage is given in Fig. 7. The results indicate maximum conversion at 230 °C.

3.3. Life cycle of the catalyst

One of the ways in which the zeolite encapsulated complex can lose its activity is by loss of the metal ions, which is brought about by leaching of the metal complex or reduction to free metal. In order to study the recycling efficiency of the catalyst, the experiment was carried out at 230 °C by injecting a known volume (1.5 ml) of oxygen gas at intervals of 2.5 min and

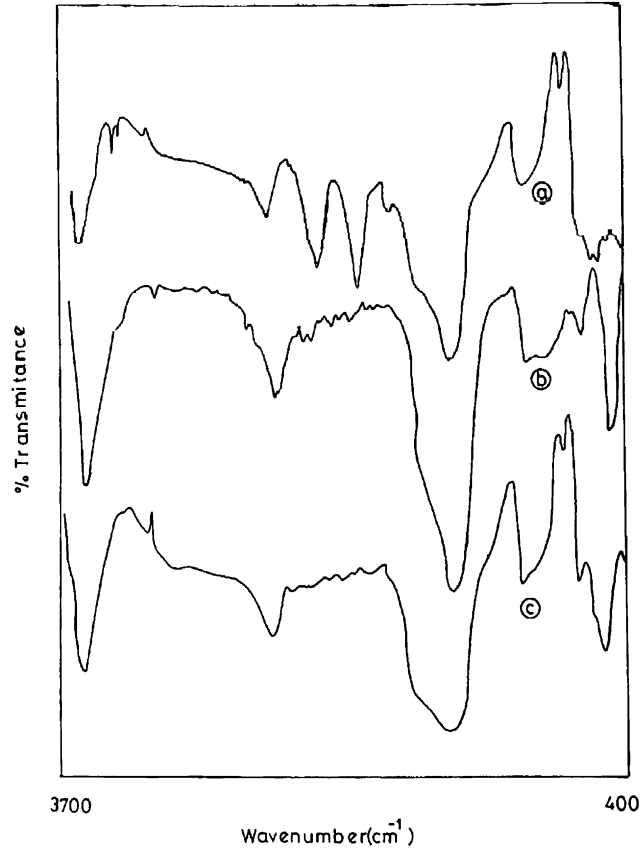


Fig. 5. FTIR spectrum of YCuEm isolated after TGA up to: (a) 270 °C; (b) 365 °C; (c) 470 °C.

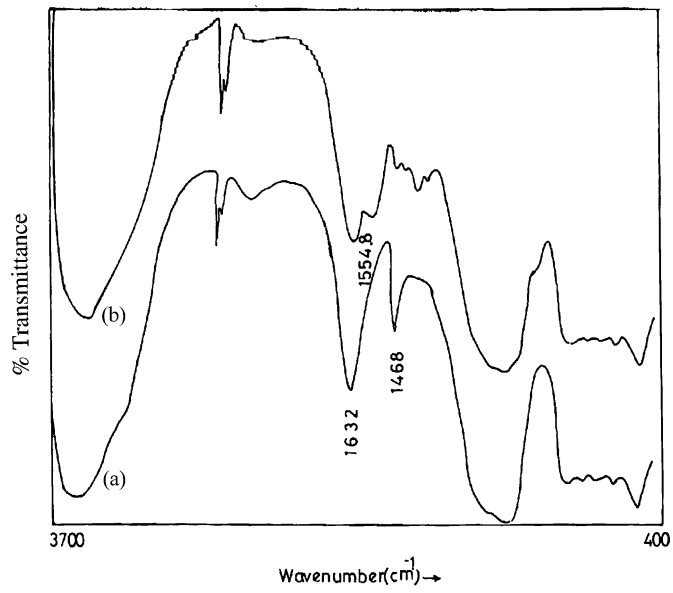


Fig. 6. FTIR spectra: (a) prior to reaction; (b) after reaction.

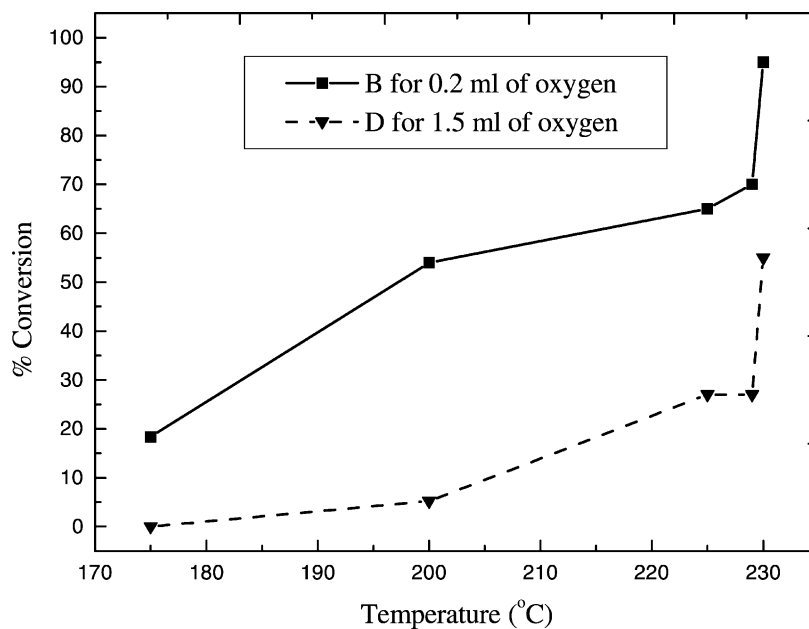


Fig. 7. Effect of temperature on the reduction of oxygen in presence of YCuEm.

monitoring the conversion. The results represented graphically in Fig. 8 show that the maximum conversion was maintained for 2.5 h, after which a slight decrease in activity was observed. An estimation of the catalyst at the end of the reaction revealed that

no metal leaching takes place during the reaction and the ligand to be intact. This also suggests the metal complexes are intact within the cavities and the structural features of the zeolite are not changed during the reaction.

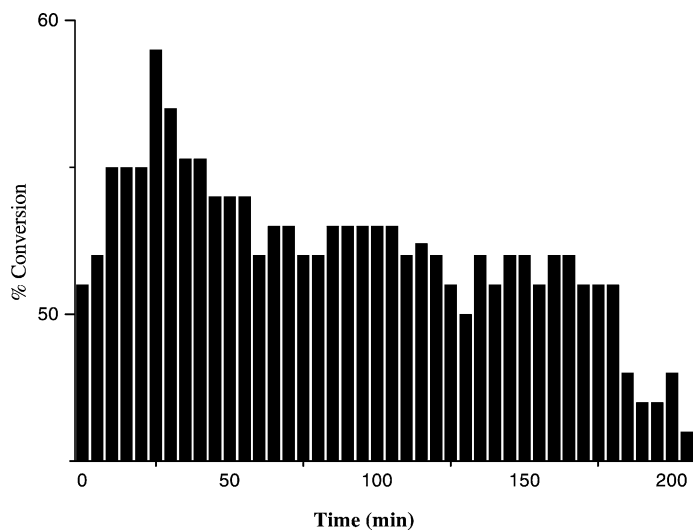


Fig. 8. Life cycle study of the catalyst, YCuEm.

4. Conclusion

In summary, dioxygen can be effectively reduced to water using YCuEm as catalyst. Though the YCuAb complex effects comparable conversion, it is not an efficient catalyst as it gets deactivated after two runs. The thermal stability of the copper embelin complex is increased as a result of encapsulation and the purpose of site isolation was also achieved. The finding that zeolite Y encapsulated Cu(II) embelin complex can act as a catalyst in the deoxo reaction is really interesting, as the classical catalysts used for this reaction are precious elements or their compounds. The optimization of the reaction conditions or modification of the complex could lead to far reaching applications in gas purification.

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