



A comparative study of the catalytic activity of Nd (III) and Sm (III) Schiff base complexes towards the hydroxylation reaction of catechol

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ABSTRACT

Zeolite encapsulated Nd (III) and Sm (III) complexes of Schiff bases derived from salicylaldehyde and o-aminophenol have been synthesized and characterized by elemental, FT IR, thermogravimetric, SEM and XRD analyses. The catalytic behavior of the synthesized complexes against hydroxylation reaction of catechol was studied. Initial rate study reveals that Nd (III) Schiff base complexes are more active.

Keywords- zeolite encapsulated complexes, Nd (III), Sm (III), Schiff base, catechol oxidation, and catalysis.

INTRODUCTION

Co-ordination chemistry of lanthanides is of special significance to a wide variety of chemical, biological and applied Problems (Lund & Catal, 1975 and Romanovsky et. al, 1998). Neodymium (III) and Samarium (III) Schiff base complexes find varied applications in agricultural and industrial fields (Konar, 1998). Complexes of Nd (III) ions with macrocyclic ligands containing pyridine were prepared in which Nd (III) ions act as templates for the cyclic condensation of organic carbonyl compounds with primary diamines (Vardy et al, 1998 and Kowalak et. al, 1991). Review of literature reveals that the lanthanide cations are excellent NMR probes of their immediate environment in enzymes (Henrici et. al, 1975 and Bhadravathi et al, 2007). Maurya and coworkers synthesized seven co-ordinate $[NdL_2(NO_3)_3]$ with ligands formed by the condensation of 4-antipyrene carboxaldehyde with aromatic amines, which reveals the importance of chelate effect in the stability of lanthanide complexes (Tschudisteiner et. al, 1958 and Moeller et. al, 1965). Di and trivalent dinuclear Samarium(III) complexes supported by pyrrol based tetradentate Schiff bases were found to be catalytically active towards oxidation reactions (Gupta et. al, 2009). Metal complexes formed in zeolite cages can act as biomimetic catalyst (Rafelt G.S.; Clark J.H.; Catal.Today; 3 2000, Itchings G.S.; chem. Commun.301, 1999). Considering the high applicability's and desirable attributes of zeolite encapsulated complexes, present study aims at encapsulating complexes of Nd (III) and Sm(III) in zeolite cages. The comparison of their catalytic properties towards catechol oxidation reaction was also investigated.

MATERIALS AND METHODS

Synthetic Y - zeolite in Na^+ form was exchanged with Na^+ ions to remove any unexchanged hydrogen ions in the zeolite matrix, Salicylaldehyde (Merck), 2- amino phenol (Merck) Neodymium nitrate, samarium nitrate, catechol (Lobachemie) and 30 % H_2O_2 (Merck) were used as obtained. Solvents employed were either of 99% purity or purified by known laboratory procedures.

Physical Methods and Analysis

CHN analyses of the ligands and complexes were done using an elemental analyzer (Elementar model vario EL III). The metal percentage present in the complexes was determined using ICP -AES Spectrometer (Thermo Electron, IRIS Intrepid II XSP DUO). IR Spectra were recorded as KBr pellets (Schimadzu, 8000). Thermogravimetric analyses were done at a heating rate of $10^\circ C$ min⁻¹ in nitrogen atmosphere from ambient temperature up to $1200^\circ C$ (Perkin Elmer, Diamond TG/DTA). X-ray diffraction pattern of the parent zeolite and zeolite encapsulated complexes were recorded by Bruker AXSD8 Advance diffractometer. The morphology of the samples was examined by scanning electron microscopy (JEOL, JSM – 840A).

Synthesis

Synthesis of the ligand was done according to the reported procedures (Chittilappilly et. al, 2008 and Sailaja et. al, 1999).

Preparation of Metal Exchanged Zeolite (Nd Y and Sm Y)

NaY (2.5gm) was stirred with each of Neodymium (III) nitrate and Samarium (III)

nitrate Solutions (0.001M, 250 ml) at 70°C for 4h. The slurry was filtered and washed with deionized water to make it free from anions. It was then dried at 130°C for 1h and then at 450°C for 4h.

Synthesis of Nd (III) and Sm (III) Zeolite encapsulated complexes of salap

NdY and SmY (2.5gm each) was added to a solution of the ligand in methanol (0.5 gm in 25 ml), the mixture was refluxed for 4h to ensure complexation. The resultant mass was filtered and soxhlet extracted with methanol until the extracting solvent become colourless. The uncomplexed metal ions in the zeolite and ionisable portions of the ligand were removed by ion exchange with NaCl solution (0.1M, 250ml) for 24h. It was filtered, washed free of chloride ions and finally dried at 100°C for 2h and stored in vacuum over anhydrous calcium chloride.

Catalytic Hydroxylation of Catechol Preparation of substrate solution

A standard solution of catechol ($1 \times 10^{-2} \text{ mol dm}^{-3}$) was prepared by dissolving a definite amount ($2.75 \times 10^{-2} \text{ gm}$) of catechol in 25 ml of methanol. The resultant solution was used as the stock solution. The solution was prepared afresh before each set of kinetic runs.

Preparation of Stock Solution of H₂O₂

H₂O₂ (30% w/v; 1 ml) was diluted to 100 ml in a standard flask and was used as such for the catalytic studies.

Screening Studies

A preliminary screening study of the catalytic activity was conducted towards catechol hydroxylation reaction using

H₂O₂. The product of the reaction was monitored spectrophotometrically.

Kinetic Procedure

Catechol solution in methanol was treated with H₂O₂ (1 ml) and monitored spectrophotometrically. The maximum obtained were due to catechol. Hence it was understood that no reaction takes place in the absence of catalyst.

For following the reaction kinetically, catechol solution (9 ml) was mixed with the catalyst (0.01 gm) and the reaction was initiated by adding H₂O₂ solution (1 ml). The reaction products were monitored spectrophotometrically at an interval of 30 seconds by measuring the absorbance at 380 nm. The blank used was a mixture of catechol solution (2.5 ml) and H₂O₂ (0.8 ml). The reaction was monitored also at a third wavelength at which products of the reaction do not absorb. The absorbance (N.R. Suja. N. Sridevi, K.K.M.Yusuff, Kinet. Catal 45, 2004) measured at the later wavelength corresponds to the scattering due to the catalyst particles. To get the actual absorbance of the product at a particular wavelength, the absorbance due to the scattering was deducted. The initial rate of the reaction was determined from concentration – time plot.

RESULTS AND DISCUSSION

Characterization

Elemental analysis (Table-1) of NaY revealed a Si/Al ratio of 2.6 that corresponds to a unit cell formula Na₅₄(AlO₂)₅₄(SiO₂)₁₃₈ nH₂O for NaY. Almost constant value of Si/Al ratio was found even after the metal exchange and formation of complexes confirming the retention of the zeolite frame work during complexation. The unit cell formula of

Neodymium and Samarium exchanged zeolites were derived to be Na_{48.7} Nd_{2.4} (AlO₂)₅₄ (SiO₂)₁₃₈• nH₂O and Na_{39.6} Sm_{4.8} (AlO₂)₅₄ (SiO₂)₁₃₈. nH₂O from the metal percentages of NdY and SmY. The elemental analysis confirms the presence of metal complexes in the zeolite matrix.

Table- 1. Analytical Data

Sample	%C	%H	%N	%Metal	%Si	%Al	%Na
NaY	-	-	-	-	20.9	7.9	9.6
NdY	-	-	-	2.6	20.7	7.9	1.8
SmY	-	-	-	2.9	20.6	7.9	1.7
NdY Salap	9.14	0.42	1.02	2.3	20.1	7.6	2.0
SmY Salap	10.10	0.42	1.21	2.6	20.0	7.7	1.9

TG curves shows that the pattern of decomposition is the same for all encapsulated complexes. It provides a useful tool to study about the stability of complexes. The data is given in Table-2.

Table-2. TG Data of encapsulated complexes

Compound	Decomposition temperature	Weight loss (%)
NdYSalap	170	13.376
SmYSalap	120.5	20.5

IR band around 1639cm⁻¹ in the ligand is shifted to lower frequencies in both zeolite encapsulated complexes, which confirms complexation at nitrogen of the azomethine group (Table-3). The stretching vibrations of water molecules present in the zeolite lattice

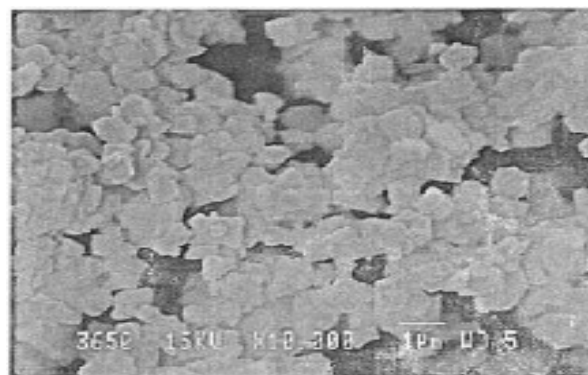
can be seen around 3448 - 3466 cm⁻¹. IR band of free ligand occur in the region 1141cm⁻¹ due to co of phenolic group. However, this is absent in encapsulated complexes. This might be due to the complexes between 1022 and 1024 cm⁻¹ which is absent in corresponding ligands (T.A. Egerton, A. Hagan, F.S. Stone, J.C. Vickerman, J.Chem.soc.Faraday Trans. 1-68,1972). Hence it can be assigned to the zeolite frame work vibrations. Other major zeolite frame work bands appear around 577 and 578 cm⁻¹.

Table- 3. IR Spectral Data

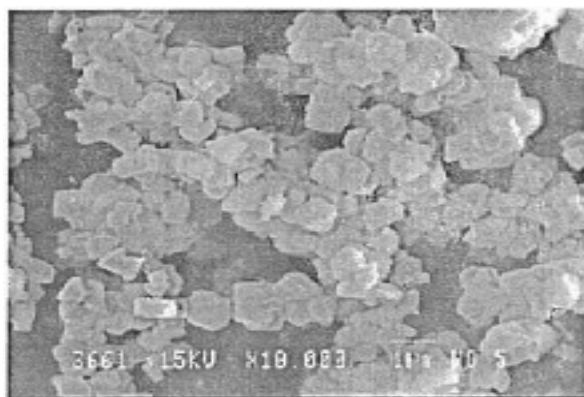
Compound	ν_{O-H}	ν_{C-O} phenolic gp	ν_{C-N} azomethine group	$\nu_{zeolite}$ peaks	$\nu_{zeolite}$ peaks	$\nu_{co-ordinated H_2O}$
Salap		1141	1639			
NdY Salap	3448		1633	1024	577	788
SmY Salap	3465		1632	1022	578	788

Scanning electron micrographs of encapsulated complexes before and after soxhlet extraction were taken which shows that surface species formed during complexation were completely removed by soxhlet extraction (Thomas et. al, 1988).

Scanning Electron Micrographs



Before Extraction



After Extraction

Zeolite frame work retains its crystallinity even after encapsulation (W.W. Holloway Jr. M. Kestigian. Spectrochim. Acta 22 1966), which is evidenced by the similar x-ray diffraction patterns of the NdY, and SmY corresponding encapsulated zeolite complexes.

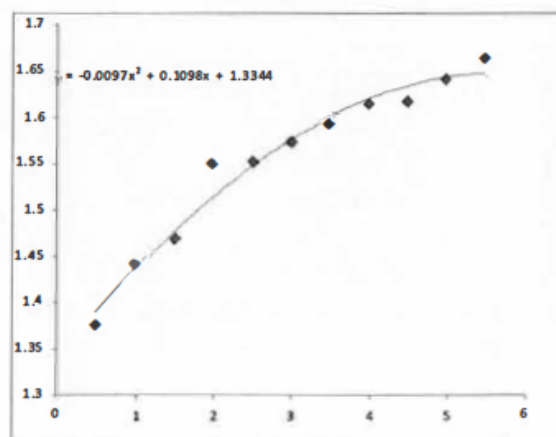
Comparison of catalytic activity of the encapsulated complexes of Neodymium and Samarium

The reaction was found to be selective towards the formation of 1, 2, 4-trihydroxy benzene in the presence of encapsulated complexes of Nd (III) and Sm (III). The initial rates obtained during the catalytic activity studies of the synthesized complexes are presented in Table -4. Out of these two complexes, Nd (III) Salap is more active and shows higher initial rates during catalysis.

Table-4. Initial rates and percent conversion of catechol-H₂O₂ reaction using encapsulated complexes of Nd(III) and Sm(III) as catalyst

Catalyst	Initial rate/unit weight of metal 10 ⁴ (mol dm ⁻³ s ⁻¹)
NdYSalap	119.14
SmYSalap	84.13

Kinetic plot of Absorbance versus Time for Catechol – H₂O₂ reaction



X axis: Time
 Y axis: Absorbance

CONCLUSION

Zeolite encapsulated Nd (III) and Sm (III) complexes of Schiff bases have been synthesized and characterized. The integrity of encapsulation was confirmed by spectroscopic studies as well as chemical and thermal analysis. The similarity in XRD patterns of NaY, NdY, SmY and encapsulated complexes revealed that the frame work retains its crystal structure even after complexation. The removal of surface species was ascertained by SEM analyses. The co-ordination of ligands with metal ion was ascertained in all cases by IR spectra. Both NdY salap and SmY salap catalyse

catechol hydroxylation by H_2O_2 selectively to 1, 2, 4-trihydroxy benzene. A comparative study of the initial rates of the reaction was done in all cases. The catalytic activity of NdY salap is found to be greater than that of SmY salap.

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